

DISSERTATION

CORE SUBSTITUTION OF DIHYDROPHENAZINE PHOTOREDOX CATALYSTS FOR
ORGANOCATALYZED ATOM TRANSFER RADICAL POLYMERIZATION

Submitted by

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ABSTRACT

CORE SUBSTITUTION OF DIHYDROPHENAZINE PHOTOREDOX CATALYSTS FOR ORGANOCATALYZED ATOM TRANSFER RADICAL POLYMERIZATION

Organocatalyzed atom transfer radical polymerization (O-ATRP) is a controlled radical polymerization method that uses organic photoredox catalysts (PCs) and visible light to produce polymers with well-defined structures. Organic PCs leverage an inherently sustainable resource, light, to drive chemical reactions under mild conditions and minimize dependency on rapidly depleting precious metals such as Ru and Ir, which are commonly used for catalysis. *N,N*-diaryl dihydrophenazine PCs in particular are notable for their success in mediating O-ATRP, producing polymers with low dispersities ($\mathcal{D} < 1.3$). However, the non-unity initiator efficiency ($I^* < 100\%$) observed using dihydrophenazines in prior work shows their limited ability to achieve targeted molecular weights. This low I^* has been attributed to a radical addition side reaction between the PC core and alkyl fragments generated during polymerization. In this work, core substitution (CS) is leveraged to modify PC structure as a route to block side reactivity and improve polymerization control. Exploration of alkyl CS revealed that the alkyl CS PC is the active catalyst during the majority of O-ATRP and can have improved catalytically relevant properties relative to the parent PC. Aryl and heteroatom CS PCs were also found to have improved PC properties, including longer excited state lifetimes and more highly reducing excited states. The new structure-property relationships revealed in this work were applied to improve polymerization outcomes and address current limitations of O-ATRP, such as expanding monomer scope and decreasing PC loadings. This work demonstrates the utility of CS as a versatile strategy to tune PC structure, properties,

and performance while enhancing the ability of organic PCs to produce advanced polymeric materials.

DEDICATION

To my family, friends, mentors, and River. I am incredibly grateful for your unwavering support along the way.

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INTRODUCTION AND CONTRIBUTIONS

This dissertation consists of four chapters, which are summarized below along with author contributions:

CHAPTER 1: Adapted from Corbin, D. A.; Puffer, K. O.; Chism, K. A.; Cole, J. P.; Theriot, J. C.; McCarthy, B. G.; Buss, B. L.; Lim, C. H.; Lincoln, S. R.; Newell, B. S.; Miyake, G. M. Radical addition to *N,N*-diaryl dihydrophenazine photoredox catalysts and implications in photoinduced organocatalyzed atom transfer radical polymerization. *Macromolecules* **2021**, *54*, 4507-4516. This chapter focuses on the development of alkyl core substituted phenazine photoredox catalysts (PCs) and their application in organocatalyzed atom transfer radical polymerization (O-ATRP). *Author contributed to polymerizations.*

CHAPTER 2: Adapted from Price, M. J.; Puffer, K. O.; Kudisch, M.; Knies, D.; Miyake, G. M. Structure-property relationships of core-substituted diaryl dihydrophenazine organic photoredox catalysts and their application in O-ATRP. *Polym. Chem.* **2021**, *12*, 6110-6122. This chapter includes the synthesis, characterization, and application of aryl core substituted phenazine PCs in O-ATRP. *Author contributed to polymerizations, catalyst synthesis, characterization, with a focus on transient absorption spectroscopy.*

CHAPTER 3: Adapted from Puffer, K.O.; Corbin, D.A; Miyake, G.M. Impact of Alkyl Core Substitution Kinetics in Diaryl Dihydrophenazine Photoredox Catalysts on Properties and Performance in O-ATRP. *ACS Catal.* **2023**, *13*, 14042-14051. This chapter focuses on exploration of the rate of alkyl core substitution and the implications of substitution rate in O-ATRP. *Author contributed to all experimental work.*

CHAPTER 4: Adapted from the submitted manuscript titled Influence of Dihydrophenazine Photoredox Catalyst Excited State Character and Reduction Potentials on

Control in Organocatalyzed Atom Transfer Radical Polymerization. This chapter explores the relationship between PC excited state character and redox properties and leverages the properties for improved polymerization control. *Author contributed to all experimental work.*

CHAPTER 1 – RADICAL ADDITION TO *N,N*-DIARYL DIHYDROPHENAZINE PHOTOREDOX CATALYSTS AND IMPLICATIONS IN PHOTOINDUCED ORGANOCATALYZED ATOM TRANSFER RADICAL POLYMERIZATION*

1.1 – OVERVIEW

Photoinduced organocatalyzed Atom Transfer Radical Polymerization (O-ATRP) is a controlled radical polymerization methodology catalyzed by organic photoredox catalysts (PCs). In an efficient O-ATRP system, good control over molecular weight with an initiator efficiency ($I^* = M_{n, \text{theo}} / M_{n, \text{exp}} \times 100\%$) near unity is achieved, and the synthesized polymers possess a low dispersity ($\mathcal{D}$). *N,N*-diaryl dihydrophenazine catalysts typically produce polymers with low dispersity ($\mathcal{D} < 1.3$), but with less than unity molecular weight control ($I^* \sim 60$ to 80%). This work explores the termination reactions that lead to decreased control over polymer molecular weight and identifies a reaction leading to radical addition to the phenazine core. This reaction can occur with radicals generated through reduction of the ATRP initiator or the polymer chain-end. In addition to causing a decrease in I^* , this reactivity modifies the properties of the PC, ultimately impacting polymerization control in O-ATRP. With this insight in mind, a new family of core substituted *N,N*-diaryl dihydrophenazines is synthesized from commercially available ATRP initiators and employed in O-ATRP. These new core substituted PCs improve both I^* and $\mathcal{D}$ in the O-ATRP of MMA, while minimizing undesired side reactions during the polymerization. Further, the ability of one core substituted PC to operate at low catalyst loadings is demonstrated, with minimal loss of polymerization control down to 100 ppm (weight average molecular weight [M_w]

* Corbin, D. A.; Puffer, K. O.; Chism, K. A.; Cole, J. P.; Theriot, J. C.; McCarthy, B. G.; Buss, B. L.; Lim, C. H.; Lincoln, S. R.; Newell, B. S.; Miyake, G. M. Radical addition to *N,N*-diaryl dihydrophenazine photoredox catalysts and implications in photoinduced organocatalyzed atom transfer radical polymerization. *Macromolecules* **2021**, *54*, 4507-4516.

= 10.8 kDa, $\bar{D} = 1.17$, $I^* = 104\%$ versus $M_w = 8.26$, $\bar{D} = 1.10$, $I^* = 107\%$ at 1000 ppm) and signs of a controlled polymerization down to 10 ppm of catalyst ($M_w = 12.1$ kDa, $\bar{D} = 1.36$, $I^* = 107\%$).

1.2 – INTRODUCTION

Photoredox catalysis has broadly impacted the synthesis of small molecules and polymers through enabling diverse and challenging reactions under mild reaction conditions.¹⁻⁵ Much of the progress in photoredox catalysis has leveraged well-established precious metal complexes based on ruthenium or iridium as photoredox catalysts (PCs).^{2, 6} While these PCs have certainly been effective in promoting a wide range of transformations, they also have raised concerns regarding the scarcity of these precious metals and the environmental impacts associated with their mining, use, and disposal.⁷ Our interest in photoredox catalysis has centered upon the development of strongly reducing organic photoredox catalysts as sustainable alternatives to precious metal-based PCs, especially for application in organocatalyzed atom transfer radical polymerization (O-ATRP).⁸⁻¹³

Since its introduction in 1995,^{14, 15} ATRP has blossomed into one of the most popular controlled radical polymerizations for the synthesis of polymers with targeted molecular weights and low dispersity ($\bar{D}$).¹⁶⁻²¹ Most commonly, traditional ATRP employs a transition metal catalyst – often copper or ruthenium – to mediate a reversible activation-deactivation mechanism. During this process, a polymer with a terminal C-X (X = halide) bond is activated to generate a reactive radical capable of chain propagation through reaction with a vinyl monomer. However, the radicals produced can also react with each other, leading to irreversible termination reactions that hinder polymerization control. As such, a key feature of ATRP is reversible deactivation, which regenerates the dormant C-X bond to lower the concentration of radicals in solution and kinetically limit undesirable termination reactions. While O-ATRP employs an organic catalyst instead, the same general mechanism is mediated during the polymerization (Figure 1.1).^{8, 22, 23}

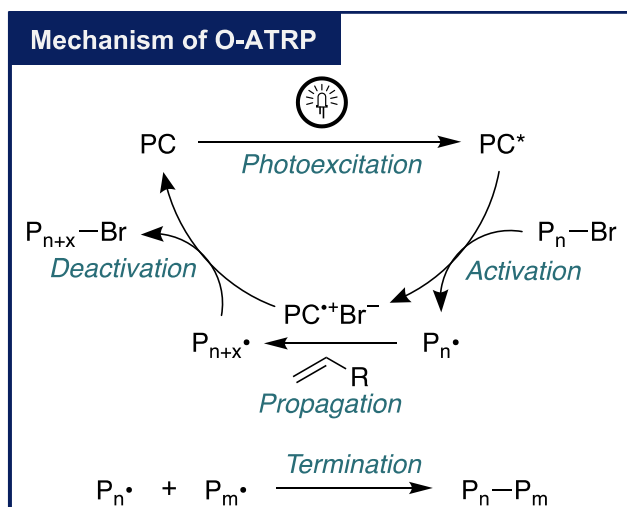


Figure 1.1. Proposed mechanism of organocatalyzed atom transfer radical polymerization proceeding through an oxidative quenching photoredox cycle.

Although traditional ATRP has been used to polymerize a wide variety of monomers and produce polymers with highly tunable structures and architectures,¹⁸⁻²⁰ its application in metal-sensitive systems has been limited by its dependence on metal-based catalysts. For example, in electronic applications, the presence of residual Cu catalyst trapped in the polymer matrix has been demonstrated to decrease the performance of the target polymer.²⁴ In addition, the polymerization of coordinating monomers can be challenging by metal-catalyzed ATRP, since coordination of the monomer to the catalyst can lead to a loss of desirable catalytic properties. By contrast, O-ATRP employs metal-free, organic catalysts, enabling its success in these metal-sensitive applications.²⁵⁻

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Previously, much of the work in this field has focused on the identification of novel PCs capable of mediating O-ATRP, including phenothiazines,^{22, 28-33} phenoxazines,^{10, 12, 34-36} dihydrophenazines,^{9, 37-39} dihydroacridines,^{13, 40} polyaromatic hydrocarbons,^{8, 41-43} and xanthene dyes^{44, 45}. While a number of these catalyst families have been demonstrated to produce polymers with a high degree of polymerization control, one of the most successful PC families has been the dihydrophenazines. Previous work with this catalyst family showed that the installation of *N*-aryl

groups with electron withdrawing functionalities or extended conjugation (eg. naphthalene) could produce highly controlled polymers with $\bar{D} < 1.1$,⁹ consistent with the standards of ATRP.¹⁶⁻²⁰ Through computational and experimental investigations, it was shown that these *N*-aryl functionalities promote intramolecular charge transfer in the excited state, leading to the formation of long-lived triplet excited state species capable of catalysis.⁹

However, one limitation of dihydrophenazines PCs in O-ATRP is that they consistently exhibit low initiator efficiency ($I^* = M_{n, \text{theo}} / M_{n, \text{exp}} \times 100\%$, $I^* \sim 60\%$ to 80%).⁹ Interestingly, when the dihydrophenazine core is further functionalized through installation of aryl substituents (Figure 1.2), this problem is alleviated and the resulting polymers from O-ATRP possess I^* near unity.³⁷ This observation led us to hypothesize that the low I^* seen with non-core substituted dihydrophenazines is a result of a side reaction between the initiator and the PC, which results in substitution of the PC core and consumption of the initiator prior to O-ATRP. In support of this hypothesis, recent work applying dihydrophenazines to the synthesis of poly(acrylates) showed evidence of this reactivity between diethyl-2-bromo-2-methylmalonate (DBMM) and 5,10-di(2-naphthyl)-5,10-dihydrophenazine.³⁹ Similar ligand substitution by radicals has also been observed with a polypyridal iridium complex, which altered the reactivity of the PC during the course of reaction.⁴⁶ However, the origin of this reactivity in dihydrophenazine PCs remains unknown, as does the impact of this core substitution on catalytic properties and successful O-ATRP.

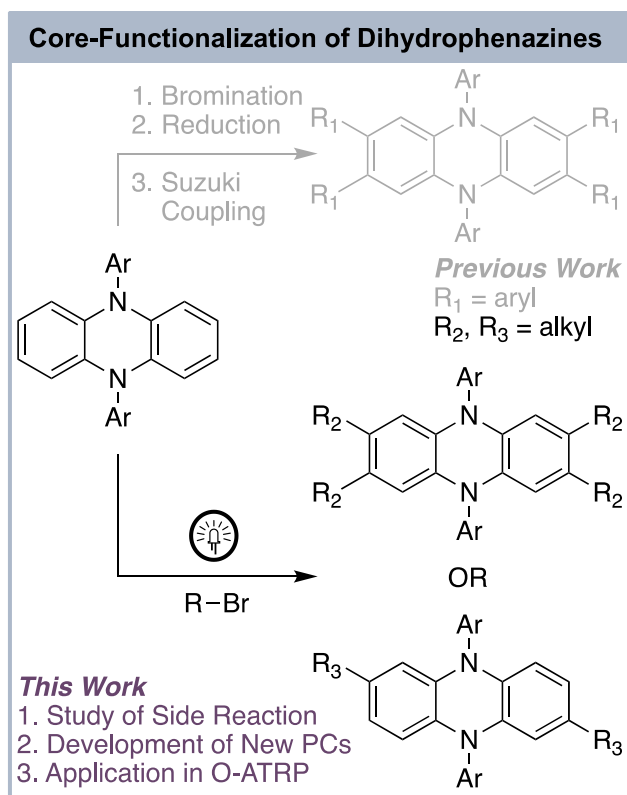


Figure 1.2. Previous work allowed for substitution of the dihydrophenazine core through bromination followed by aryl cross-coupling. This work exploits a side reaction between the PC and ATRP initiators to achieve core substitution.

In this work, we investigate the reaction of 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (**1**) with several common ATRP initiators to gain insight into this potential side reactivity in O-ATRP that can detract from I^* and produce PCs that are not necessarily expected from the onset of the reaction. These core substituted derivatives are isolatable and reveal that this substitution impacts catalytically relevant properties of these molecules. As such, when used as PCs in O-ATRP, these alkyl core substituted PCs achieve non-equivalent levels of success in producing polymers with low $\bar{D}$ and near unity I^* in comparison to using non-core substituted PCs. This work highlights the importance of continued mechanistic understanding of O-ATRP and catalyst evolution to realize improved catalyst systems. Furthermore, this insight is broadly relevant to small molecule transformations, introduces further considerations regarding PC side reactivity, and could lead to improved reaction systems by understanding the potential for the

catalyst to be altered during the course of reaction. Lastly, this radical addition to the core of *N,N*-diaryl dihydrophenazines could serve as an efficient and atom-economical means to access new PC derivatives with tailored photophysical properties.

1.3 – RESULTS AND DISCUSSION

PC **1** is one of the first visible-light absorbing PCs reported for O-ATRP. Although it was demonstrated to produce polymers with relatively low dispersity ($\bar{D} < 1.3$), I^* was typically less than 100% ($I^* \sim 60\%$ to 80%).⁹ To explore the possibility of radical addition to this catalyst during O-ATRP, PC **1** was irradiated with a variety of common ATRP initiators in *N,N*-dimethylacetamide (DMAc), essentially mimicking O-ATRP conditions but in the absence of monomer (Figure 1.3). When PC **1** was reacted with 10 equivalents of ethyl α -bromophenylacetate (EBP) in DMAc, the reaction mixture was irradiated for two hours and characterized by electrospray ionization mass spectrometry (ESI-MS) (Figure A1.30). The mass spectrum of the solution revealed peaks at m/z = 470.12, 632.19, 794.26, 956.33, and 1118.40,⁴⁷ consistent with zero to four equivalents of the ethyl phenylacetate fragment installed on the phenazine core.

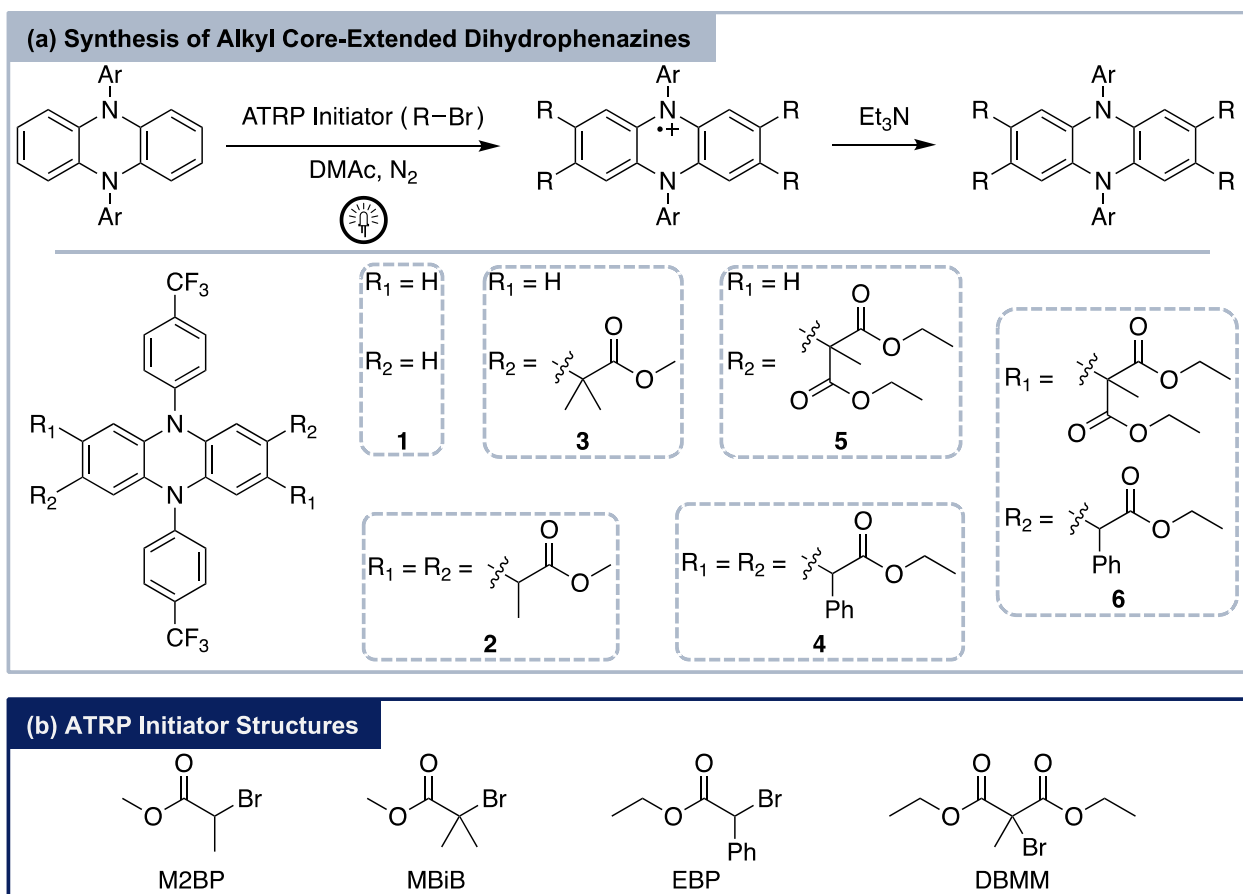


Figure 1.3. Scheme for the synthesis of core-extended dihydrophenazines through reaction with ATRP initiators (top) and structures (bottom) of the PCs investigated in this work (a). Structures of ATRP initiators used in this work (b).

In an effort to determine the positions of these new substituents by NMR, the irradiation time was increased to drive the reaction to higher conversion and reduce the number of products. After irradiating for 16 hours, the observed color of each solution was qualitatively different. In accord with the proposed single electron transfer reduction of the initiator, we hypothesized that the observed color change arose from formation of ${}^2\text{PC}^{\bullet+}\text{Br}^-$.⁴⁸ Supporting this hypothesis, the UV-visible absorption spectra of the reaction mixtures closely matched those of oxidized PCs generated electrochemically (Figure 1.4). Furthermore, electron paramagnetic resonance (EPR) spectroscopy confirmed the formation of a stable radical during the reaction of PC **1** with ATRP initiators. To convert these radical cation species to the neutral PCs, the reaction solutions were

quenched using triethylamine (TEA) as a sacrificial electron donor. The resulting yellow or orange compounds were purified by column chromatography and isolated in yields of 67% to 92%. The structures of core substituted PCs **2** – **6** were assigned based on NMR, as well as single-crystal X-ray diffractometry (SCXRD) in the case of **4** (see *Supporting Information – Photocatalyst Characterization*). Alternatively, **2** – **6** could also be isolated by precipitation of the reduced reaction solution in deionized water, followed by vacuum filtration, washing with cold methanol, and drying under high vacuum overnight.

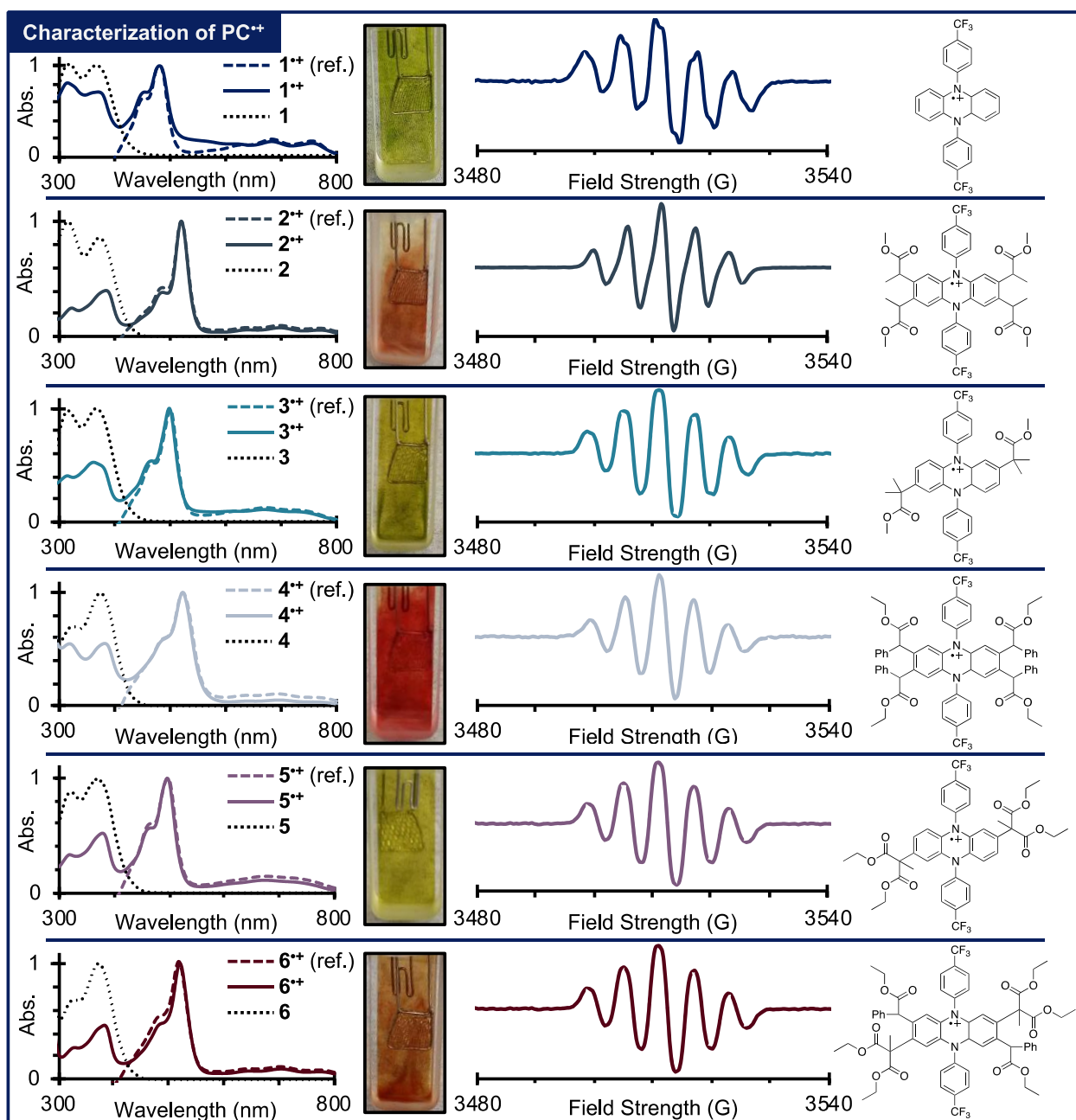


Figure 1.4. Characterization of the radical cations of PC 1 – 6 using UV-Visible spectroscopy coupled with spectro-electrochemistry (left), showing spectra of the PC (small dash), the isolated radical cations (solid), and the radical cations obtained by spectro-electrochemistry (large dash). Photographs of solutions after spectro-electrochemistry (middle), and electron paramagnetic resonance spectroscopy (right).

When ATRP initiators possessing a secondary bromide were employed (i.e. 2-methyl 2-bromopropionate [M2BP] and EBP), four substitutions at the 2-,3-,7-, and 8- positions of the dihydrophenazine core were observed. Instead, when ATRP initiators possessing a tertiary bromide were reacted with **1** (i.e. methyl α -bromoisobutyrate [MBiB] and DBMM), the resulting compounds exhibited only two core substituents (Figure 1.3). It should be noted that characterization of **3** and **5** revealed a mixture of regioisomers resulting from substitution at either the 2- and 7- positions or the 2- and 8- positions of the dihydrophenazine core (*see below*). However, these compounds could not be resolved by column chromatography, and figures in this report depict only one isomer for simplicity. We propose tetra- versus di-substitution is controlled by the sterics of the initiator (i.e. secondary versus tertiary bromide). In support of this hypothesis, when **5** was irradiated in the presence of EBP, further addition of the ethyl phenylacetyl radical ensued, resulting in the formation of **6** with four substituents on the dihydrophenazine core (Figure 1.3).

While these experiments support that radical addition to PC **1** is possible, they do not necessarily indicate that this reaction can occur during O-ATRP. To test this possibility, we performed O-ATRP using PC **1**, EBP, and methyl methacrylate (MMA). After 20 minutes, the reaction was stopped, the volatiles were removed, and the mixture was analyzed by ESI-MS (Figure A1.31). As expected, this analysis revealed that the ATRP initiator can in fact add to the PC core during O-ATRP, consistent with the observations made in the absence of MMA. What was unexpected, however, was the observation of core substitution with poly(methyl methacrylate (PMMA) oligomers as well.⁴⁷ As such, this experiment reveals that a major termination reaction in O-ATRP can be radical addition to the PC, especially at early reaction times. Ultimately, these

experiments provide important insight into why I^* often deviates from 100 %, since ATRP initiators and oligomers are consumed through addition to the catalyst.

With this new reaction pathway in mind, PCs **2** – **6** were characterized to understand how core substitution impacts their catalytically relevant electrochemical and photophysical properties (Table 1.1). Using density functional theory (DFT), the electrochemical properties of key catalytic states (^1PC , $^3\text{PC}^*$, and $^2\text{PC}^{*+}$) were computed to gain insight into the impact of core substitution on PC thermodynamics. In each case, the computationally predicted excited state reduction [$E^\circ(^2\text{PC}^{*+}/^3\text{PC}^*)$] and ground state oxidation [$E^\circ(^2\text{PC}^{*+}/^1\text{PC})$] potentials were similar to the parent compound. In addition, the photophysical and electrochemical properties of **1** – **6** were also experimentally determined. For **2** – **6**, the λ_{max} of absorption is redshifted 3–10 nm compared to the parent PC **1**. Interestingly, **4** and **6** both exhibit a significantly higher molar absorptivity (ϵ_{max}) than the parent PC **1**, possibly due to the added conjugation from the ethyl phenylacetate moiety. However, **2**, **3**, and **5** all possess a ϵ_{max} similar to that of **1**. With regard to the excited state properties of these compounds, core substitution generally leads to a shorter wavelength emission from the S_1 excited state, meaning that core substituted catalysts **2** – **6** have a higher energy singlet excited state ($E_{S1,\text{exp}}$) than **1**. Finally, core substitution also destabilized the radical cations of **4** and **5** relative to **1** [i.e. increased $E^\circ(^2\text{PC}^{*+}/^1\text{PC})$], while stabilizing those of **2**, **3**, and **6**.

Table 1.1. Electrochemical and photophysical characterization of PCs **1** – **6**.

PC	λ_{max} (nm) ^[a]	ϵ_{max} (M ⁻¹ cm ⁻¹) ^[b]	$\lambda_{\text{em, max}}$ (nm) ^[c]	$E_{S1, \text{exp}}$ (eV) ^[d]	$E_{1/2}$ ($^2\text{PC}^{*+}/^1\text{PC}$) (V vs. SCE) ^[e]	E°_{ox} ($^2\text{PC}^{*+}/^1\text{PC}$) (V vs. SCE) ^[f]	$E^{\circ*}_{S1, \text{exp}}$ ($^2\text{PC}^{*+}/^1\text{PC}^*$) (V vs. SCE) ^[g]	$E^{\circ*}_{T1, \text{calc}}$ ($^2\text{PC}^{*+}/^3\text{PC}^*$) (V vs. SCE) ^[h]
1	367	4600	611	2.02	0.28	0.21	-1.74	-2.17
2	373	5000	600	2.07	0.35	0.17	-1.72	-2.10
3	371	4300	611	2.02	0.30	0.15	-1.72	-2.10
4	377	7500	581	2.13	0.36	0.28	-1.77	-2.19
5	370	5000	602	2.06	0.36	0.23	-1.70	-1.99
6	372	6900	598	2.07	0.40	0.16	-1.67	-2.01

^[a]Measured in *N,N*-dimethylacetamide (DMAc). λ_{max} , maximum absorption wavelength; ^[b] ϵ_{max} , molar absorptivity at λ_{max} ; ^[c] $\lambda_{\text{em, max}}$, maximum emission wavelength; ^[d] $E_{\text{SI, exp}}^{0*}$, lowest singlet excited state energy determined from $\lambda_{\text{em, max}}$; ^[e]first oxidation potential determined in DMAc with NBu₄PF₆ as the electrolyte; ^[f]computationally predicted oxidation and reduction potentials (see *Supporting Information* for full computational details).

Given the previous observation of stable radical cations for **1** – **6** by EPR, we sought to synthesize the radical cation salt of the parent PC **1** so that we could probe the mechanism of radical addition. Adding Br₂ to a solution of PC **1** in benzene (Figure 1.5) resulted in an immediate color change and precipitation of a dark green powder from solution, which was isolated by filtration. This solid was recrystallized from methanol, and SCXRD of the resulting crystals indicated the formation of the radical cation tribromide salt (**1**^{•+}Br₃[−]). While this tribromide species was certainly an interesting discovery, it does not represent the proposed deactivator in O-ATRP (**1**^{•+}Br[−]). In order to convert the Br₃[−] anion to Br[−] and obtain the monobromide salt, **1**^{•+}Br₃[−] was refluxed in methanol for four hours. The choice of methanol in this step proved to be crucial, as using benzene instead led to bromination of the PC core.³⁷ The isolated material was then recrystallized from methanol, and SCXRD revealed the monobromide **1**^{•+}Br[−] radical cation salt.³⁷

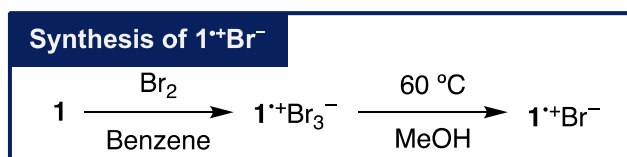


Figure 1.5. Scheme for the synthesis of **1**^{•+}Br[−].

To investigate the mechanism of core substitution with ATRP initiators, we explored the reactivity of **1** and **1**^{•+}Br[−] in the presence of free radicals generated by the thermal decomposition of azobisisobutyronitrile (AIBN) (Figure 1.6). Both **1** and **1**^{•+}Br[−] were each reacted with AIBN at 80 °C in DMAc in the dark to prevent unwanted photoexcitation of **1**. After one hour, ¹H NMR analysis revealed that the thermally generated isobutyronitrile radical had added to the dihydrophenazine core of **1**^{•+}Br[−] and generated the substituted neutral PC derivative. Instead, no

reaction was observed between PC **1** and AIBN, suggesting that core substitution occurs exclusively to $1^{+\bullet}\text{Br}^-$ and not **1**.

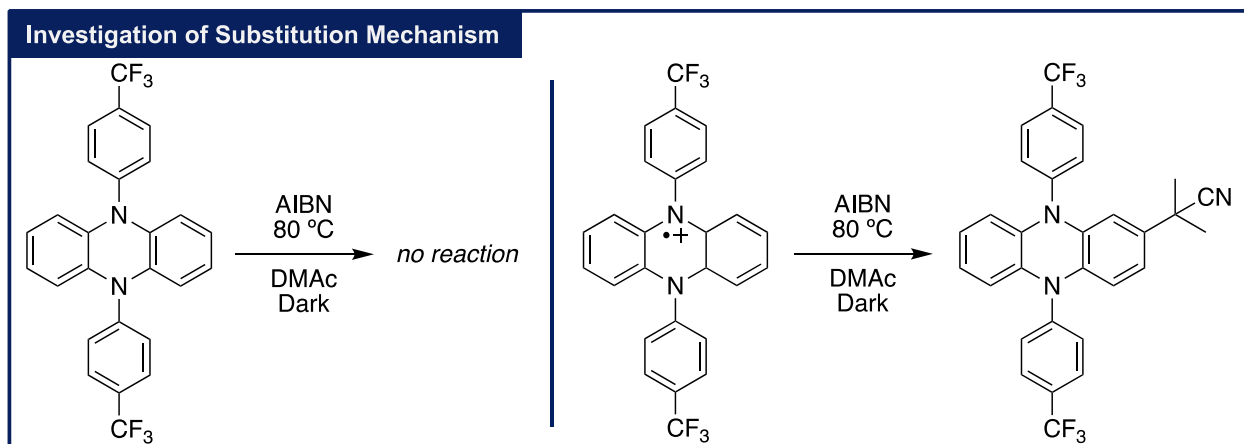


Figure 1.6. Model reactions reveal no reaction between thermally generated radicals with the ground state ^1PC (left), but radical addition occurs to $^2\text{PC}^{+\bullet}$ (right).

Based on these results, we propose the following mechanism for dihydrophenazine core substitution with ATRP initiators. Upon irradiation of **1**, 1^* activates the C-Br bond in the initiator to generate an alkyl radical and Br^- . After addition of the radical species to the 2- position of the PC core, the intermediate is deprotonated – possibly by Br^- – to restore aromaticity. The resulting species is a neutral, mono-substituted PC derivative that can likely re-enter the catalytic cycle, where this process is repeated for further substitution of the PC core. Depending on the sterics of the radical, the core can be substituted either two or four times. However regardless of the identity of the initiator, when the final substitution occurs, the di- or tetra- substituted PC undergoes photoexcitation and reaction with a final equivalent of initiator. Since core substitution is no longer feasible, this process results in the formation of a stable radical cation species, which is later reduced by addition of a sacrificial electron donor to the reaction solution.

To understand how core substitution impacts catalytic performance in O-ATRP, PCs **1** – **6** were employed in the O-ATRP of MMA under standard conditions – using DBMM as the initiator,

[MMA]:[DBMM]:[PC] = [1000]:[10]:[1], with 1 mL MMA, 1 mL DMAc as the solvent, and irradiated in a white LED beaker under N₂ atmosphere. In each case, all six PCs produced PMMA in a controlled fashion ($\bar{D} \leq 1.5$, $I^* \sim 100\%$), although with varying levels of polymerization control (Table 1.2). In particular, PC **4** exhibited excellent polymerization control, producing PMMA with a weight average molecular weight (M_w) = 10.2 kDa, $\bar{D}$ = 1.23, and I^* = 112% (entry 4). Interestingly, even PC **1** exhibited near unity I^* (I^* = 97%), although it should be noted that these polymerizations used DBMM as the initiator whereas previous work employed EBP.⁹ Nevertheless, PC **4** produced PMMA with lower $\bar{D}$ than PC **1** ($\bar{D}$ = 1.23 for **4** versus 1.32 for **1**), indicating superior performance in O-ATRP.

Table 1.2. Results of the O-ATRP of MMA using PCs **1-6**.

Entry	PC	Time (h)	Conversion (%) ^[a]	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa)	$M_{w, \text{exp}}$ (kDa) ^[b]	$\bar{D}$ ^[b]	I^* (%) ^[c]
1	1	8	78.3	8.09	8.38	11.1	1.32	97
2	2	8	73.0	7.57	7.35	10.1	1.37	103
3	3	8	88.6	9.12	8.47	12.0	1.42	108
4	4	8	89.9	9.25	8.26	10.2	1.23	112
5	5	8	83.3	8.59	8.40	11.0	1.31	102
6	6	8	96.1	9.88	8.02	9.94	1.24	123

Conditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc. Solutions prepared in the dark and then irradiated in a white LED beaker for specified time (see *Supporting Information – Supplemental Polymerization Data* for full details). ^[a]Determined by ¹H NMR. ^[b]Determined by GPC coupled with multi-angle light scattering. ^[c]Initiator efficiency (I^*) = ($M_{n, \text{theo}} / M_{n, \text{exp}}$) • 100%.

We next sought to improve upon these results by modification of the reaction solvent. Previously, several reports have shown that solvent choice in O-ATRP – especially using dihydrophenazine PCs – can have a significant impact on polymerization control.^{39, 49, 50} As such, solvents of varying polarity from DMSO to benzene were employed in the polymerization of MMA using **4** as the PC (Table 1.3). Consistent with previous findings,⁴⁹ this polymerization was most successful in less polar solvents such as ethyl acetate (EtAc: M_w = 5.16 kDa, $\bar{D}$ = 1.11, I^* = 100%) and benzene (M_w = 6.26 kDa, $\bar{D}$ = 1.12, I^* = 100%). Further, polymerizations in less polar

solvents (i.e. EtAc, benzene) were significantly slower than those in more polar solvents (i.e. dimethyl sulfoxide [DMSO], DMAc), reaching roughly half as much monomer conversion in the same amount of time. This detail might indicate improved deactivation in less polar solvents, though the impact of solvent on polymerization control will be discussed in greater detail later (*see below*). Regardless, since EtAc and benzene gave similar levels of polymerization control, EtAc was chosen for subsequent polymerizations since it is a “green” solvent and less toxic than benzene.

Table 1.3. Results from the O-ATRP of MMA using PC **4** in solvents of different polarity.

Entry	Solvent	Time (h)	Conversion (%) ^[a]	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa)	$M_{w, \text{exp}}$ (kDa) ^[b]	$\bar{D}$ ^[b]	I^* (%) ^[c]
(4)	DMAc	8	89.9	9.25	8.26	10.2	1.23	112
7	DMSO	8	68.6	7.12	12.6	24.3	1.93	56
8	MeCN	8	27.5	3.01	4.95	6.73	1.36	61
9	THF	8	21.3	2.38	5.53	6.25	1.13	43
10	EtAc	8	43.8	4.64	4.65	5.16	1.11	100
11	Benzene	8	53.5	5.61	5.59	6.26	1.12	100

Conditions: [MMA]:[DBMM]:[**4**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL solvent. Solutions prepared in the dark and then irradiated in a white LED beaker for specified time (*see Supporting Information – Supplemental Polymerization Data* for full details). ^[a]Determined by ¹H NMR. ^[b]Determined by GPC coupled with multi-angle light scattering. ^[c]Initiator efficiency (I^*) = ($M_{n, \text{theo}} / M_{n, \text{exp}}$)•100%.

Since dihydrophenazines with aryl core substituents were previously shown to operate effectively in O-ATRP at ppm-level catalyst loadings,³⁷ the ability of PC **4** to mediate O-ATRP under similar conditions was also investigated. In particular, we questioned whether core substitution alone would enable the PC to operate at low catalyst loadings – possibly through minimization of side reactions – or if another property unique to the aryl core substituted PCs is key to this ability. As such, polymerizations with **4** were performed with systematically reduced catalyst loadings – from 1000 ppm to 1 ppm. The resulting polymers were characterized by ¹H NMR (to determine monomer conversion) and gel permeation chromatography (GPC) coupled

with multi-angle light scattering (to determine the M_w , D , and I^*). Excitingly, polymerizations with as little as 100 ppm of **4** – an order of magnitude lower than standard conditions – showed almost no loss of polymerization control (Table 1.4), producing PMMA with low dispersity ($D = 1.17$ at 100 ppm versus 1.10 at 1000 ppm) and near-quantitative initiator efficiency ($I^* = 104\%$ at 100 ppm versus 107% at 1000 ppm). Moreover, polymerization control was maintained at loadings as low as 10 ppm of **4**, where $D = 1.36$ and $I^* = 107$.

Table 1.4. Results from the O-ATRP of MMA using PCs **1** and **4** at decreasing catalyst loadings.

Entry	[MMA]:[DBMM]:[PC]	[PC] (ppm)	Time (h)	Conv. (%) ^[a]	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa)	$M_{w, \text{exp}}$ (kDa) ^[b]	D ^[b]	I^* (%) ^[c]
<i>Polymerizations with PC 4</i>									
12	[1000]:[10]:[1]	1000	24	77.5	8.01	7.51	8.26	1.10	107
13	[1000]:[10]:[0.75]	750	24	81.9	8.45	7.60	8.66	1.14	111
14	[1000]:[10]:[0.5]	500	24	85.5	8.82	8.29	9.37	1.13	106
15	[1000]:[10]:[0.25]	250	24	90.5	9.31	8.71	10.0	1.15	107
16	[1000]:[10]:[0.1]	100	24	93.1	9.58	9.22	10.8	1.17	104
17	[1000]:[10]:[0.05]	50	24	94.1	9.68	8.94	11.1	1.24	108
18	[1000]:[10]:[0.025]	25	24	95.1	9.77	9.18	11.7	1.27	106
19	[1000]:[10]:[0.01]	10	24	92.0	9.47	8.89	12.1	1.36	107
20	[1000]:[10]:[0.005]	5	24	82.7	8.53	8.07	12.5	1.55	106
21	[1000]:[10]:[0.001]	1	24	56.1	5.87	9.92	17.2	1.73	59
<i>Polymerizations with PC 1</i>									
22	[1000]:[10]:[1]	1000	24	72.1	7.48	8.68	9.81	1.13	86
23	[1000]:[10]:[0.5]	500	24	82.2	8.48	8.86	10.2	1.15	96
24	[1000]:[10]:[0.1]	100	24	91.6	9.42	8.20	10.7	1.30	115
25	[1000]:[10]:[0.05]	50	24	95.5	9.81	8.85	12.6	1.42	111
26	[1000]:[10]:[0.025]	25	24	94.8	9.74	9.34	14.5	1.55	104
27	[1000]:[10]:[0.01]	10	24	79.6	8.23	8.20	14.5	1.77	100
28	[1000]:[10]:[0.005]	5	24	69.8	7.24	10.3	18.8	1.83	70
29	[1000]:[10]:[0.001]	1	24	34.6	3.72	18.3	32.8	1.79	20

Conditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[X]; 1 mL MMA, 1 mL solvent. Solutions prepared in the dark and then irradiated in a white LED beaker for specified time (see *Supporting Information – Supplemental Polymerization Data* for full details). ^[a]Determined by ¹H NMR. ^[b]Determined by GPC coupled with multi-angle light scattering. ^[c]Initiator efficiency (I^*) = ($M_{n, \text{theo}} / M_{n, \text{exp}}$) • 100%.

Since previous polymerizations with dihydrophenazines were often performed in DMAc,^{9, 37} we wondered whether the ability of **4** to mediate O-ATRP at such low catalyst loadings was due to core substitution or alternatively the choice of solvent. To test the influence of the solvent, similar polymerizations at reduced catalyst loadings were performed with **1**. Interestingly, this experiment revealed that **1** can also operate effectively at significantly reduced catalyst loadings, although not matching the performance of PC **4**. At 100 ppm, **1** still produced well controlled PMMA ($M_w = 10.7$ kDa, $\bar{D} = 1.30$, $I^* = 115\%$ versus $M_w = 9.81$ kDa, $\bar{D} = 1.13$, $I^* = 86\%$ at 1000 ppm), though **4** exhibited a higher degree of polymerization control at this concentration ($M_w = 10.8$ kDa, $\bar{D} = 1.17$, $I^* = 104\%$). In the case of **1**, the increase in I^* upon lowering [**1**] can likely be attributed to the fact that at lower catalyst loading (but with the same amount of initiator), less initiator is consumed through core substitution of the PC. At 100 ppm of **4**, the quantity of initiator consumed by core substitution is likely within the error for I^* . In addition, signs of a controlled polymerization are observed with catalyst loadings as low as 50 ppm of **1** ($M_w = 12.6$ kDa, $\bar{D} = 1.42$, $I^* = 111\%$), a significant improvement over previous results in DMAc³⁷.

To understand how changing the polymerization solvent enables such dramatic improvements in polymerization control, several previous reports have investigated the impact of different solvents in O-ATRP. For example, previous work with dihydrophenazine PCs showed that less polar solvents can alter the excited state energy, as observed through blue shifting of their fluorescence. In addition, computations showed that ion pairing in $PC^{++}Br^-$ should be stronger in less polar solvents, favoring the formation of this ion pair.⁵⁰ Since we hypothesize $PC^{++}Br^-$ is the deactivator in O-ATRP, the choice of less polar solvents may improve deactivation and thereby polymerization control. Macroscopically, this effect of solvent polarity on polymerization control has been observed on several occasions,^{39, 49, 50} as well as in this work.

In addition, solvent polarity can have drastic impacts on the photophysics and electrochemical properties of the PC, both of which can directly influence catalysis. In the case of 5,10-di(2-naphthyl)-5,10-dihydrophenazine, comprehensive investigation of these influences revealed that lowering the solvent polarity can: (1) decrease non-radiative decay of the singlet excited state; (2) increase intersystem crossing to the triplet excited state, which we propose is most catalytically active in O-ATRP; (3) increase the lifetime of both the singlet and triplet excited states; (4) increase the excited state energy; and (5) increase the oxidation potential of the radical cation $[E^{\circ}(^2\text{PC}^{+\bullet}/^1\text{PC})]$.³⁹ Each of these changes to the PC properties should ultimately improve catalysis in O-ATRP. In particular, decreasing non-radiative decay, increasing intersystem crossing, and increasing the excited state lifetimes should favor activation. In turn, the concentration of $\text{PC}^{+\bullet}$ during early reaction times should be greater, leading to effective deactivation sooner in the polymerization. In addition, increasing $E^{\circ}(^2\text{PC}^{+\bullet}/^1\text{PC})$ increases the driving force for deactivation, which in turn increases the rate of deactivation in O-ATRP.

Therefore, considering each of these reported solvent effects, the improvement in polymerization control and catalytic performance for both **1** and **4** in EtAc relative to DMAc can be rationalized. It should still be noted, though, that PC **4** did successfully mediate O-ATRP in a controlled fashion at lower catalyst loadings than PC **1**. This result, however, can likely be explained by the differences in photophysical and electrochemical properties of **1** and **4** outlined in Table 1. Most notably, **4** features stronger visible light absorption, observed as both a red shifted absorption ($\lambda_{\text{max}} = 377 \text{ nm}$ for **4** and 367 nm for **1**) and higher molar absorptivity ($\epsilon_{\text{max}} = 7,500 \text{ M}^{-1}\text{cm}^{-1}$ for **4** and $4,600 \text{ M}^{-1}\text{cm}^{-1}$ for **1**). Further, while the excited state reduction potentials $[E^{\circ}(^2\text{PC}^{+\bullet}/^3\text{PC}^*)$ and $E^{\circ}(^2\text{PC}^{+\bullet}/^1\text{PC}^*)]$ of **1** and **4** are similar, the radical cation of **4** is more oxidizing

[i.e. higher $E^\circ(2\text{PC}^{\bullet+}/1\text{PC})$] than that of **1**. As such, **4** should be more effective than **1** in both activation and deactivation, leading to overall better catalysis in O-ATRP as observed.

1.4 – CONCLUSIONS

This work investigated the possibility of radical addition to the organic photoredox catalyst 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (PC **1**) under conditions relevant to O-ATRP. Common ATRP initiators were reacted with **1** under irradiation, which revealed that fragments resulting from the reduction of the ATRP initiator by **1** could add to the PC core. Depending upon reaction time and the sterics of the ATRP initiator, up to four fragments could be installed on the PC core, and these derivatives could be isolated in good to excellent yields. If this reaction is performed in the presence of monomer, oligomeric species can also add to the PC core, revealing an important termination reaction in O-ATRP.

Through isolation of the radical cation of **1**, it was determined that radical addition occurs to $1^{\bullet+}$ and not **1**. Further, these substitutions generate compounds with different photophysical and electrochemical properties that can impact catalysis. As such, if these core substituted dihydrophenazines are employed as catalysts in the O-ATRP of MMA, they macroscopically perform non-equivalently in regard to control over the polymerization, as observed through the production of PMMA with varying molecular weights, $\bar{D}$, and I^* . In particular, PC **4** – formed through the reaction of **1** with EBP – showed excellent polymerization control, producing PMMA with $\bar{D}$ as low as 1.10 and $I^* = 100\%$. Through optimization of the reaction solvent, this PC could mediate a controlled polymerization of PMMA in EtAc down to 10 ppm of catalyst ($M_w = 12.1$ kDa, $\bar{D} = 1.36$, $I^* = 107\%$), whereas **1** operated effectively down to 50 ppm of catalyst ($M_w = 12.6$ kDa, $\bar{D} = 1.42$, $I^* = 111\%$).

Finally, the insight gained through this work has broad implications in the field of photoredox catalysis. First, a new route to functionalizing diaryl dihydrophenazines is presented

that enables the ability to not only further tailor the physical properties of this family of PCs but also minimize undesired side reactivity. Second, new catalyst design principles are introduced that emphasize designing PCs that minimize side-reactions. Lastly, this work highlights the importance of understanding potential side reactions that a catalyst may undergo during the course of a reaction, especially when they can alter the identity of the catalyst, modify the catalyst properties, and ultimately impact the success of the reaction.

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CHAPTER 2 – STRUCTURE–PROPERTY RELATIONSHIPS OF CORE-SUBSTITUTED DIARYL DIHYDROPHENAZINE ORGANIC PHOTOREDOX CATALYSTS AND THEIR APPLICATION IN O-ATRP[†]

2.1 – OVERVIEW

Photoinduced organocatalyzed atom-transfer radical polymerization (O-ATRP) is a controlled radical polymerization technique that can be driven using low-energy, visible light and makes use of organic photocatalysts. Limitations of O-ATRP have traditionally included the need for high catalyst loadings (1000 ppm) and the narrow scope of monomers that can be controllably polymerized. Recent advances have shown that *N,N*-diaryl dihydrophenazine (DHP) organic photoredox catalysts (PCs) are capable of controlling O-ATRP at PC loadings as low as 10 ppm, a significant advancement in the field. In this work we synthesized five new DHP PCs and examined their efficacy in controlling O-ATRP at low ppm catalyst loadings. We found that we were able to polymerize methyl methacrylate at PC loadings as low as 10 ppm (relative to monomer) while producing polymers with dispersities as low as $\bar{D} = 1.33$ and achieving initiator efficiencies (I^*) near unity (102%). In addition to applying these PCs in O-ATRP, we carried out a thorough investigation into the structure-property relationships of the new DHP PCs reported herein and report new photophysical characterization data for previously reported DHPs. The insight into the DHP structure–property relationships that we discuss herein will aid in the elucidation of their ability to catalyze O-ATRP at low catalyst loadings. Additionally, this work sheds light on how structural modifications affect certain PC properties with the goal of bolstering our understanding

[†]Price, M. J.; Puffer, K. O.; Kudisch, M.; Knies, D.; Miyake, G. M. Structure-property relationships of core-substituted diaryl dihydrophenazine organic photoredox catalysts and their application in O-ATRP. *Polym. Chem.* **2021**, *12*, 6110-6122.

of how to tune PC structures to overcome current limitations of O-ATRP such as the controlled polymerization of challenging monomers.

2.2 – INTRODUCTION

The development of organic photoredox catalysts (PCs) has revolutionized the way that chemists can approach both small molecule and macromolecular syntheses.¹⁻⁵ Establishing structure-property relationships of organic PCs is essential for guiding the development of new PCs with targeted properties and to increase their use and application in new chemical transformations. One specific application that knowledge of structure-property relationships in PCs has been leveraged for is organocatalyzed-atom transfer radical polymerization (O-ATRP). O-ATRP is a reversible-deactivation radical polymerization (RDRP) technique that employs the energy of visible light to synthesize polymers with controlled molecular weights and architectures (Figure 2.1). In RDRPs, successful control over the polymerization is typically assessed by the ability to produce polymers with low dispersity ($\bar{D}$) ($\bar{D} < 1.5$), targeted molecular weights, and retention of the polymer chain end group. O-ATRP was developed as an alternative to traditional metal catalyzed atom transfer radical polymerization (ATRP), one of the most widely used RDRP techniques. O-ATRP offers certain advantages over traditional metal catalyzed ATRP in that it enables the synthesis of polymers free of metal contaminants. Without metal contamination, polymers synthesized via O-ATRP can more readily be used for metal sensitive applications such as in electronics or biomedical technologies. From a sustainability perspective, O-ATRP utilizes a readily abundant source of energy (light) to drive a useful chemical reaction. Although non-organic catalysts have also been developed for visible light-driven ATRP,^{4,6,7} they necessitate the use of metals such as copper, ruthenium, or iridium which limits the potential applications of the polymers, as highlighted above. Furthermore, concerns about the sustainability of using precious metals such as iridium motivate use of organic PCs.⁸

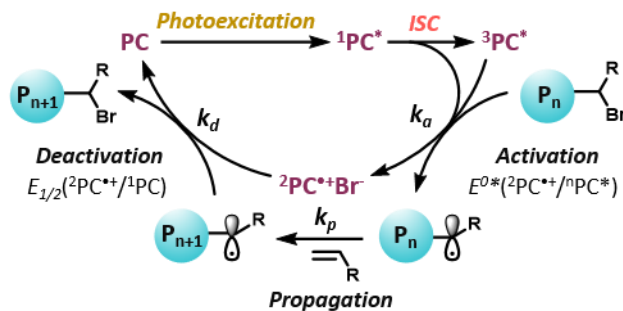


Figure 2.1. Proposed mechanism for O-ATRP.

Our research group has worked in the development of different families of highly reducing PCs originally tailored for O-ATRP, including *N*-aryl phenoxazines,⁹⁻¹¹ *N,N*-diaryl dihydrophenazines (DHPs),¹²⁻¹⁷ *N*-aryl phenothiazines,¹⁸ and *N*-aryl dimethyl dihydroacridines¹⁹ all of which are comprised solely of atoms with high natural abundance, further bolstering their prowess as sustainable catalysts.

Significant advances have been made toward increasing our understanding of the impact of certain PC properties on specific steps of the proposed O-ATRP mechanism.²⁰⁻²⁴ Simultaneous with the advancements in our understanding of relevant PC properties has been growth in our understanding of the intricacies of the proposed O-ATRP mechanism.²⁴ Here, we discuss a distilled version of the proposed mechanism for O-ATRP (Figure 2.1). In the first step of O-ATRP, a PC is photoexcited via irradiation. The excited state PC ($^n\text{PC}^*$) reduces either the alkyl halide initiator via a single electron transfer reaction to initiate polymerization or, once the polymerization has been initiated, reduces the halide-capped polymer chain end to re-activate polymerization. The rate of activation is defined as k_a . Reduction of the initiator/halide-capped polymer chain end yields a carbon-centered radical on the initiator/polymer chain end which can propagate through a reaction with monomer leading to polymerization. The rate of polymerization is defined as k_p . Reduction of the alkyl halide initiator or halide-capped polymer chain end also generates the oxidized PC species ($^2\text{PC}^{•+}$) and a halide anion (X^-) which we propose to form an ion pair.²⁵ This ion pair

(PC^{•+}X⁻) is proposed to deactivate the carbon centered radical on the chain end group of the growing polymer through reinstallation of the halide; the rate of deactivation is described as k_d . Deactivation yields both the halide-capped polymer and ground state PC. Key to the success of ATRP and O-ATRP is that k_d is faster than k_a . Rapid deactivation of the radical on the end group of the growing polymer chain helps minimize side reactions such as bimolecular radical termination and disproportionation, which are counterproductive to the synthesis of polymers with controlled molecular weights.

There are several thermodynamic requirements that PCs used to catalyze O-ATRP through an oxidative quenching cycle (Figure 2.1) must meet. The reduction potential of the excited state PC ($E^{\circ*}({}^2\text{PC}^{•+} / {}^1\text{PC}^*)$) must be reducing enough (~ -0.6 to -0.8 V vs. SCE) to reduce both the alkyl halide bond of the initiator and the polymer chain end alkyl halide bond.¹² Additionally, the ion pair of ${}^2\text{PC}^{•+}$ and X⁻ must be sufficiently oxidizing to deactivate the growing polymer chain (~ -0.8 V) to reinstall the halide. There are also several photophysical PC properties that are relevant to the O-ATRP mechanism (Figure 2.2). The absorption of visible light (400 nm–700 nm), and therefore a PC wavelength of maximum absorption ($\lambda_{\text{max,abs}}$) > 400 nm, enables the use of visible light to, selectively, stimulate photoexcitation of the PC. This attribute is desirable as use of ultraviolet (UV) light can cause unwanted side reactions due to the ability of many organic molecules, including those used in O-ATRP, to absorb UV light. PCs that possess a high molar extinction coefficient ($\epsilon_{\text{max,abs}}$) at the wavelength used for photoexcitation are preferred as having ${}^1\text{PC}^*$ in higher concentrations can lead to more efficient and uniform activation in O-ATRP and as the system is likely to be more resilient to differences in irradiation intensity. Upon photoexcitation, the PC is promoted to some singlet excited state (S_n) (Figure 2.2) from which it relaxes to the lowest S_1 energy state. From S_1 the PC, considered to be in the lowest energy singlet

excited state ($^1\text{PC}^*$) can relax back to the ground state either *via* a radiative pathway (fluorescence) or non-radiative pathway (Fig. 2.2), can react with a substrate via electron-transfer or energy transfer, or can undergo intersystem crossing to access the triplet excited state (T_1). The PC in the triplet excited state ($^3\text{PC}^*$) most commonly reacts with some substrate or via a radiative pathway (phosphorescence) or via non-radiative decay back to the ground state (S_0) (Fig. 2.2). Both $^1\text{PC}^*$ and $^3\text{PC}^*$ are highly reducing for the PCs discussed in this work and are likely responsible for activation in O-ATRP, though their individual contributions to activation has been speculated to be dependent on reactant concentrations.²⁰ As triplet excited state lifetimes (τ_{T1}) are longer than singlet excited states lifetimes (τ_{S1}) and are therefore more likely to engage in a bimolecular interaction, $^3\text{PC}^*$ is commonly attributed as the species responsible for activation. However, recent studies have shown that there are several factors that can influence the ratios of $^1\text{PC}^*$ and $^3\text{PC}^*$ responsible for activation in O-ATRP such as the concentration of initiator used,²⁰ the solvent that the polymerization is conducted in,²² and electron transfer rates influenced by the PC structure.²¹ As $^n\text{PC}^*$ is responsible for activation, it is important to understand how the structure of the PC influences the nature of $^n\text{PC}^*$. DHP PCs that access charge-transfer (CT) type excited states have been shown to be more effective PCs in controlling O-ATRP.¹³ In CT PCs, photoexcitation triggers a shift in electron density from one part of the molecule (the donor) to another part (the acceptor) generally resulting in a more-polar and stabilized excited state (Figure 2.2). The specific role of CT in improving PC control in O-ATRP is still debated.^{11, 23, 26, 27}

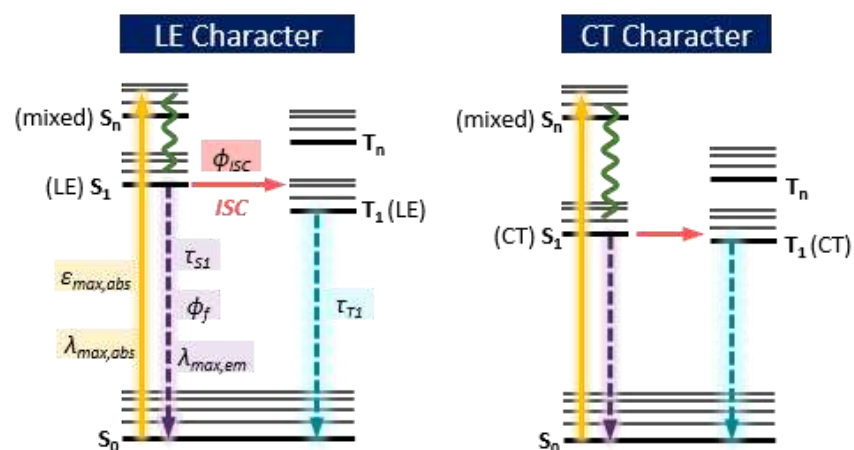


Figure 2.2. Jablonski diagrams representing PCs that form excited states with either local excitation (LE) character (left) or charge transfer (CT) character (right) in their lowest photoexcited states. Solid yellow arrow indicates photoexcitation from S_0 to S_n to form photocatalyst in the singlet excited state ($^1\text{PC}^*$). Purple and blue dashed arrows represent radiative decay from the lowest energy singlet excited state (S_1) and the lowest energy triplet excited state (T_1), or fluorescence and phosphorescence, respectively. Pink arrow represents inner system crossing (ISC) from S_1 to T_1 to form photocatalyst in the triplet excited state ($^3\text{PC}^*$). Green wavy line represents internal conversion (IC). PC properties associated with each type of aforementioned transition are labeled adjacent to those transitions in the Jablonski diagram on the left.

In previous work, core-extension of *N*-aryl phenoxazines, DHPs, and *N*-aryl dimethyl dihydroacridines has been shown to significantly impact PC properties and improve control in O-ATRP.^{11, 14, 15, 16, 17, 19} Prior work on aryl core-extended DHPs explored how core-extension of a particular DHP (which possessed an electron withdrawing 4-trifluoromethylphenyl *N*-aryl group) impacted PCs properties and control in O-ATRP (Figure 2.3).¹⁴ Importantly, the aryl-core extended DHPs were shown to control O-ATRP at catalyst loadings as low as 10 ppm, producing polymers with controlled molecular weights ($D < 1.42$) while achieving $I^* > 90\%$.¹⁴ The application of PCs at low ppm (<1000 ppm) was a significant advancement in the field of O-ATRP. The ability to control polymerizations at low PC loadings is beneficial both from a sustainability perspective and from a practical standpoint as low ppm PC loadings limits contamination of the polymers by the PC. In this work, we sought to further investigate structure-property relationships in core-extended

DHPs first, to gain insight into the properties that enable them to control O-ATRP at low ppm PC loadings and second, because deeper understanding of structure-property relationships in PCs can help direct the development of new PCs with properties that can help overcome current limitations in O-ATRP (Figure 2.3). Herein, we demonstrate the synthesis and characterization of five new core-extended DHP PCs, examine the structure-property relationships in those PCs, and investigate their ability to control the polymerization of acrylate and methacrylate monomers in O-ATRP. Furthermore, we provide new photophysical characterization data for previously reported DHPs and test their ability to control O-ATRP at low ppm PC loadings for the first time.

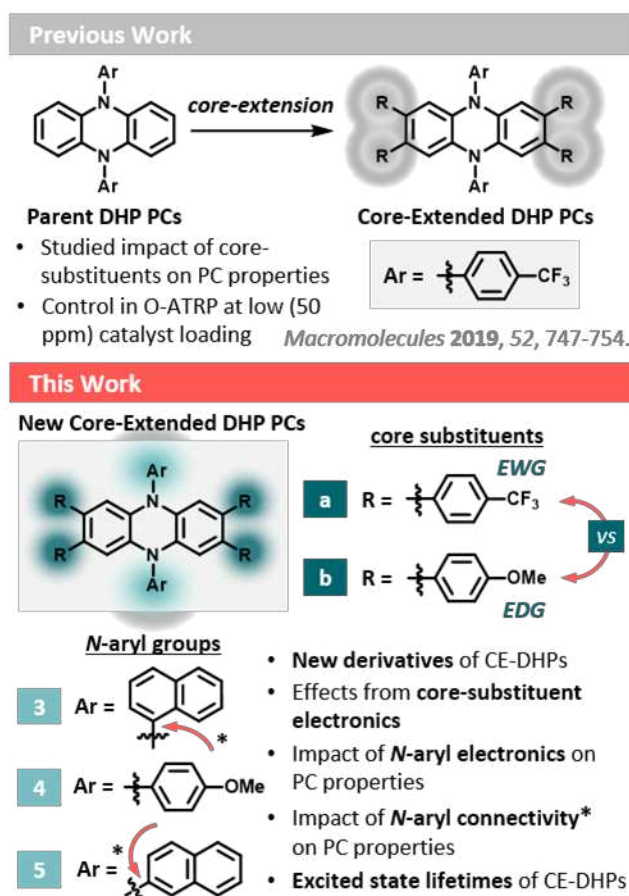


Figure 2.3. Previously reported work on core-extended DHPs (top). Focus of this work and structures for new core-extended DHPs developed in this work (bottom). *Different points of connectivity for naphthalene N-aryl group to DHP PC are indicated by red arrows.

2.3 – RESULTS AND DISCUSSION

Synthesis of PCs. The synthesis of core-extended DHPs involves several steps beginning with the reduction of phenazine (**1**) to dihydrophenazine (**2**) (Figure A2.3).²⁸ Following the synthesis of dihydrophenazine (**2**), Buchwald-Hartwig C-N cross coupling conditions are used to access the parent (non-core extended) DHP PCs **3**, **4**, and **5**. PC **5** was synthesized using C-N coupling conditions employed by our group for the synthesis of PCs **3**, **4**, and **5**, when we first reported the use of these PCs for O-ATRP in 2016.¹² Unfortunately, under these previous conditions the yield reported for PC **3** was only 3%.¹² In this work, we explored other C-N cross coupling conditions for the synthesis of PC **3** that were previously reported for the synthesis of 2-naphthyl-10-phenoxazine.¹¹ Using bis(dibenzylideneacetone) palladium(0) (Pd(dba)₂) and tri-tertbutyl phosphine (P(*t*Bu)₃) for the C-N cross coupling of dihydrophenazine (**2**) and 1-bromonaphthalene (instead of RuPhos and RuPhos precatalyst), we observed improved yields of PC **3** (57%). PC **4** was also synthesized using Pd(dba)₂ and P(*t*Bu)₃. Core-extension of PCs **3**, **4**, and **5** was accomplished by first brominating the DHP core (utilizing previously reported methods for the synthesis of core-extended DHPs)¹⁴ then through a Suzuki-Miyaura C-C cross-coupling reaction with the brominated DHP and the boronic acid of a phenyl substituent with either an electron withdrawing group (**a**) or an electron donating group (**b**) (Figure 2.3). Non-core-extended DHPs (or “parent DHPs”) discussed in this work include PCs **3**, **4**, and **5** which have *N*-aryl group **3**, **4**, or **5**, respectively (Figure 2.3). Core-extended DHPs discussed in this work include PCs **3a**, **4a**, and **5a** (which have electron withdrawing core substituent **a** and *N*-aryl group **3**, **4**, or **5**, respectively, as well as PCs **3b** and **5b** which have electron donating core substituent **b** and either *N*-aryl group **3** or **5**, respectively.

Photophysical characterization. To study the photophysical properties of the core-extended DHPs, we employed a combination of spectroscopic techniques and computational

approaches. First, we sought to probe how the *N*-aryl group and core substituents in core-extended DHPs impact photophysical PC properties (specifically the $\lambda_{\text{max,abs}}$, $\epsilon_{\text{max,abs}}$), the ability to access CT states, the excited state energies (E_{S1} & $E_{\text{T1,comp}}$), quantum yield of fluorescence (ϕ_f), and the excited state lifetimes (τ_{S1} & τ_{T1}).

Absorption. We hypothesized that core-extension would generally lead to a red-shift in the $\lambda_{\text{max,abs}}$ through stabilization of the π^* orbitals involved in photoexcitation, but were uncertain how the electron withdrawing or donating character of the core substituents might influence $\lambda_{\text{max,abs}}$. In previous studies where structure-property relationships of PCs with donor-acceptor structures similar to core-extended DHPs reported herein were examined (i.e., *N*-aryl phenoxazines¹¹, *N,N*-diaryl dihydrophenazines¹⁴, and *N*-aryl dimethyl dihydroacridines¹⁹), core-extension was shown to red-shift $\lambda_{\text{max,abs}}$. We observed that core-extension does lead to a red-shifted $\lambda_{\text{max,abs}}$ for these PCs (Table 2.1), however there appeared to be little to no notable effect on $\lambda_{\text{max,abs}}$ imparted by the electron withdrawing or electron donating character of the core-substituent. The $\lambda_{\text{max,abs}}$ for **3a** ($\lambda_{\text{max,abs}}$ = 385 nm) and **3b** ($\lambda_{\text{max,abs}}$ = 385 nm) were experimentally determined to be identical and that the $\lambda_{\text{max,abs}}$ of **5a** ($\lambda_{\text{max,abs}}$ = 373 nm) and **5b** ($\lambda_{\text{max,abs}}$ = 371 nm) are separated by only 2 nm. In contrast to the core substituents, the identity of the *N*-aryl group has a notable impact on $\lambda_{\text{max,abs}}$. The $\lambda_{\text{max,abs}}$ red-shifts by ~12 nm when the *N*-aryl group on CE-DHPs is changed from 2-naphthylene (PCs **5a** and **5b**) to 1-naphthalene (PCs **3a** and **3b**). Additionally, exchanging a naphthalene *N*-aryl group for an electron donating *N*-aryl group (4-methoxyphenol) results in a red-shift from 7 to 19 nm (PC **4a**: $\lambda_{\text{max,abs}}$ = 392 nm). Of the core-extended DHPs that have been reported, **4a** has the highest measured $\lambda_{\text{max,abs}}$ (392 nm).¹⁴

Table 2.1 Photophysical properties of PCs investigated in this study.

PC	$\lambda_{\text{max,abs}}$ (nm) ^[a]	$\epsilon_{\text{max,abs}}$ (M ⁻¹ cm ⁻¹) ^[b]	$\lambda_{\text{max,em}}$ (nm) ^[c]	Stokes Shift (nm)	$E_{\text{S1,exp}}$ (eV) ^[d]	$E_{\text{T1,comp}}$ (eV) ^[e]	Φ_f (%) ^[f]	τ_{S1} (ns) ^[g]	τ_{T1} (μ s) ^[h]
3	362	6,100	663	297	1.87	2.23	1.32	9	0.63
3a	385	22,200	586	201	2.12	1.91	9.00	17	144
3b	385	13,100	636	251	1.95	2.07	4.31	11	42
4	373	5,200	467	94	2.66	2.29	23.0	37	88
4a	392	20,900	599	207	2.07	1.82	36.0	13	— ^[i]
5	343	5,900	654	311	1.90	2.19	0.72	— ^[k]	3.5
5a	373	27,600	587	214	2.11	1.89	35.0	17	— ^[i]
5b	371	15,900	621	250	2.00	1.99	4.00	11	108

^[a]Maximum wavelength of absorption was measured using UV-Vis in DMAc. ^[b]Molar absorptivity calculated at λ_{max} in DMAc. ^[c]Maximum wavelength of emission was measured using steady-state fluorescence spectroscopy in DMAc. ^[d]Singlet energies were calculated using the maximum wavelength of emission ($E(\text{eV})=1239.8 / \lambda (\text{nm})$). ^[e]DFT calculations were performed at the uM06/6-311+G(d,p)//uM06/6-31+G(d,p) level of theory with CPCM-described solvation in DMAc. ^[f]Quantum yield of fluorescence was measured in DMAc using absolute methods. ^[g]Singlet excited state lifetime was determined by kinetic emission. ^[h]Triplet excited state lifetime was determined by kinetic absorption. ^[i]No triplet signal detected. ^[k]Singlet excited state lifetime was too short to measure as it was below the detection limit of the instrument.

Though the identity of the core substituents has little measurable effect on $\lambda_{\text{max,abs}}$, the molar absorptivity at $\lambda_{\text{max,abs}}$ ($\epsilon_{\text{max,abs}}$) is significantly impacted by the electronics of the core substituent (Figure 2.4). We hypothesized that, in accordance with previous work, $\epsilon_{\text{max,abs}}$ would increase with core-extension as a result of extended conjugation of the PC core. Indeed, the measured $\epsilon_{\text{max,abs}}$ values are between 7,000 and 21,700 M⁻¹cm⁻¹ larger for core-extended PCs than non-core-extended parent PCs. The measured increase in efficiency of photon absorption in core-extended PCs is corroborated by oscillator strength (f) values predicted using time-dependent density functional theory calculations (TD-DFT) (Figure 2.4B & Figures A2.61-A2.69). The predicted f values shown in Figures 3 and Figures A1.61-A1.69 approximate the strength of a certain electronic transition, in this case a π - π^* transition. Furthermore, we found that the $\epsilon_{\text{max,abs}}$ of PCs core-extended with the EWG **a** are significantly higher than the $\epsilon_{\text{max,abs}}$ for PCs core-extended with EDG **b**. Specifically, the $\epsilon_{\text{max,abs}}$ measured for **3a** ($\epsilon_{\text{max,abs}} = 22,200$) is 8,800 M⁻¹cm⁻¹ greater than the

$\epsilon_{\text{max,abs}}$ of **3b** ($\epsilon_{\text{max,abs}} = 13,100$) and the measured $\epsilon_{\text{max,abs}}$ of **5a** ($\epsilon_{\text{max,abs}} = 27,600$) is $11,400 \text{ M}^{-1}\text{cm}^{-1}$ higher than for **5b** ($\epsilon_{\text{max,abs}} = 15,900$). To explore potential factors that contribute to the significant difference in $\epsilon_{\text{max,abs}}$ between PCs **3a**, **4a**, and **5a** vs. PCs **3b** and **5b**, we used TD-DFT. The electronic transitions with the highest predicted oscillator strengths in PCs **3a**, **4a**, and **5a**, are predicted to occur between a π_{HOMO} centered on the PC core and a $\pi_{\text{LUMO}+n}$ spread across the PC core and all four core-substituents (Figure 2.4B & Figure A2.65-2.66). In contrast to PCs **3a**, **4a**, and **3b**, the electronic transitions with the highest predicted oscillator strengths for PCs **3b** and **5b** are forecasted to occur between a π_{HOMO} centered on the PC core and a $\pi_{\text{LUMO}+n}$ spread across the core and both *N*-aryl substituents (Figure 2.4B and Figure A2.69). Interestingly, the $\pi_{\text{LUMO}+n}$ is mixed excited state upon initial photoexcitation where charge transfer (CT) is not fully delocalized to the *N*-aryl group or the core-substituents, but nor is the nature of the excited state purely of predicted to have greater involvement in absorption resides more heavily on the core of **3b** than it does for **5b**. Our understanding is that all the core-extended DHPs are predicted to access a locally excited (LE) character. Considering the differences in where $\pi_{\text{LUMO}+n}$ is predicted the PC could influence the efficiency of photon absorption accounting for the difference in $\epsilon_{\text{max,abs}}$ reside for PCs **3a**, **4a**, and **5a** vs. for **3b** and **5b**, we postulate that the location of π^* orbitals on that we observed for core-extended DHPs with different core-substituents but the same *N*-aryl to group, although further investigations are necessary to further support this hypothesis.

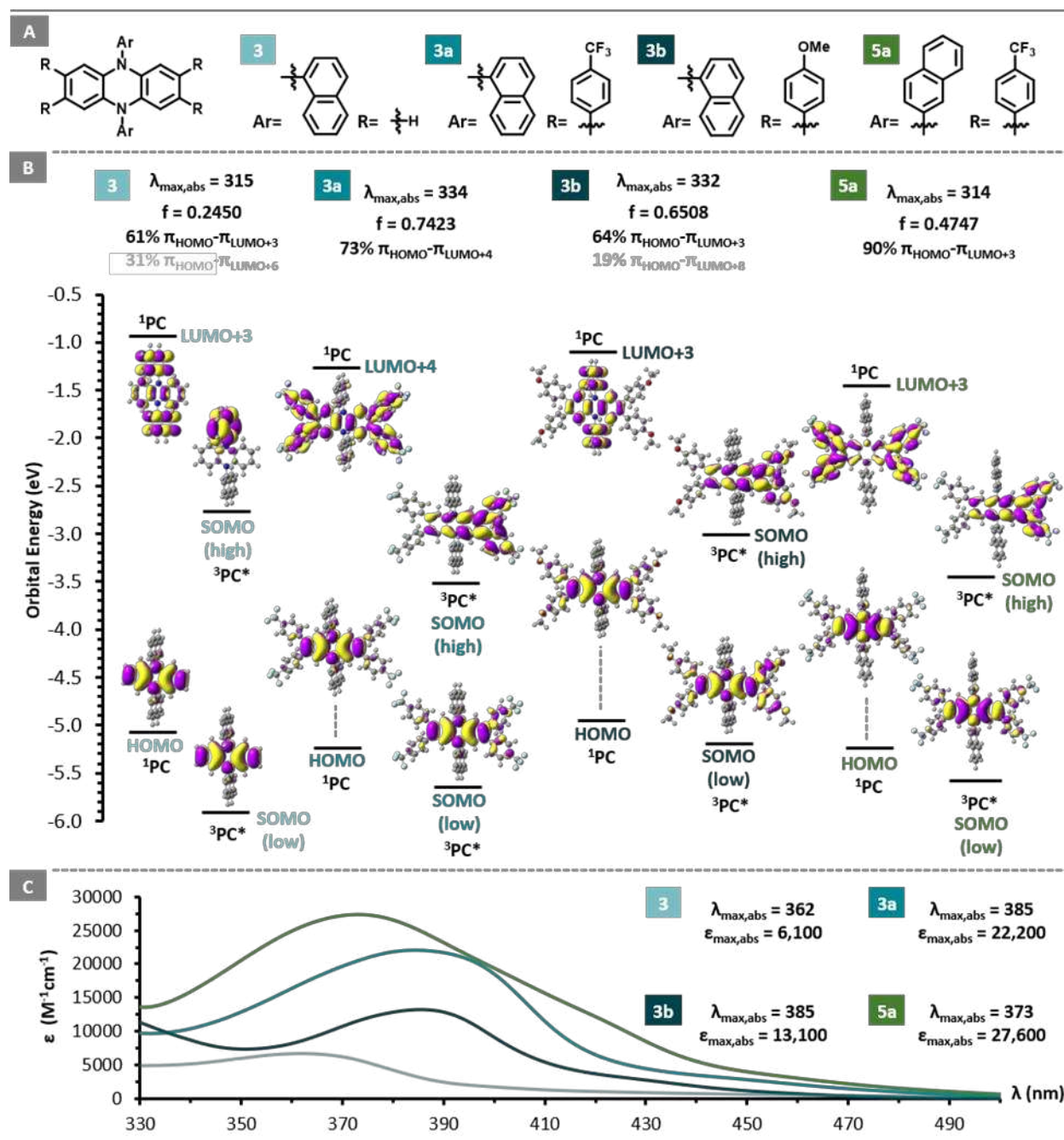


Figure 2.4. (A) Structures of PCs discussed in this figure. (B) Results from time-dependent density functional theory (TD-DFT) calculations of orbitals involved in excitation of PCs **3**, **3a**, **3b**, and **5a** at the predicted $\lambda_{\max, \text{abs}}$ (top) and visualized molecular orbitals predicted to be involved in photoexcitation (bottom). (C) UV-vis spectra of PC **3**, **3a**, **3b**, and **5a** acquired in *N,N*-dimethylacetamide (DMAc) with observed maximum wavelength of absorption ($\lambda_{\max, \text{abs}}$) in units of nm and molar extinction coefficient ($\epsilon_{\max, \text{abs}}$) in units of $\text{M}^{-1}\text{cm}^{-1}$ shown.

Though there is a measurable change in the $\epsilon_{\text{max,abs}}$ for CE-DHPs with different *N*-aryl groups, the shifts are of a lesser magnitude than for those observed from changing electron donating core substituents to electron withdrawing core substituents on PCs with the same *N*-aryl group. **4a** has the lowest $\epsilon_{\text{max,abs}}$ of **3a**, **4a**, and **5a**, but only $\sim 1,300 \text{ M}^{-1}\text{cm}^{-1}$ lower than **3a**. Of all the CE-DHPs investigated here, **5a** has the highest molar extinction coefficient at $\epsilon_{\text{max,abs}} \sim 27,600 \text{ M}^{-1}\text{cm}^{-1}$.^{Error! Bookmark not defined.} Despite the measured $\epsilon_{\text{max,abs}}$ of **5a** being $\sim 5,400 \text{ M}^{-1}\text{cm}^{-1}$ higher than **3a**, TD-DFT calculations predicted the $\epsilon_{\text{max,abs}}$ to be highest for **3a** and lowest for **5a** (Figure 2.4C).

Charge Transfer. A combination of DFT and experimental approaches were used to examine the nature of PC*. Studies of non-core extended DHPs support access to a CT excited state located primarily on the naphthalene *N*-aryl substituent for PCs **3** and **5**²⁵ and that the connectivity of the *N*-naphthalene group, specifically in *N*-aryl phenoxazines, does have an impact on CT.²⁶ In this work, we sought to investigate how core-extension and the *N*-aryl group impact CT in core-extended DHP PCs. First, we used fluorescence spectroscopy to measure the maximum emission wavelength ($\lambda_{\text{max,em}}$) and emission profile of parent and core-extended PCs (Table 2.1). For all the PCs, except PC **4**, we observed broad and featureless emission profiles suggesting that these PCs access a CT state for ¹PC*. We then used the measured $\lambda_{\text{max,em}}$ to calculate the Stokes shift ($\Delta\lambda$) for each PC [$\Delta\lambda = \lambda_{\text{max,em}} \text{ (nm)} - \lambda_{\text{max,abs}} \text{ (nm)}$]. We observed that $\Delta\lambda$ for PCs **3** and **5** decreases as a result of core-extension (Table 2.1). Interestingly, core-extension of PC **4** ($\Delta\lambda = 94 \text{ nm}$) to PC **4a** ($\Delta\lambda = 207 \text{ nm}$) results in a 113 nm increase in $\Delta\lambda$, suggesting that through specific core-modifications, parent DHPs that do not possess CT character can be modified to enable access to a CT state. As there is previous work supporting that core-extended *N*-aryl phenoxazines and core-extended DHPs can access a CT state located on the core substituents,^{11, 14} we hypothesized

that core-extension with EWG **a** would increase the $\Delta\lambda$ of PCs **3a** and **5a** relative to PCs with EDG **b** (**3b** and **5b**). To the contrary, we observed that the $\Delta\lambda$ of PCs **3a** ($\Delta\lambda = 201$ nm) and **5a** ($\Delta\lambda = 214$ nm) was significantly less than for PCs **3b** ($\Delta\lambda = 251$ nm) and **5b** ($\Delta\lambda = 250$ nm). In addition to examining the Stokes shift, CT character can be assessed for $^n\text{PC}^*$ by investigating solvatochromism, where the PC is dissolved in solvents of increasing polarity then photoexcitation via irradiation reveals how the energy of emission from polarized $^n\text{PC}^*$ is stabilized by solvents of increasing polarity resulting in a lower energy (red-shifted) emission (Figure 2.5B and Figures A2.46-A2.53). Solvatochromism of **3b** and **5b** appear more extensive than solvatochromism of **3a** and **5a** supporting our observation that the former have a larger $\Delta\lambda$.

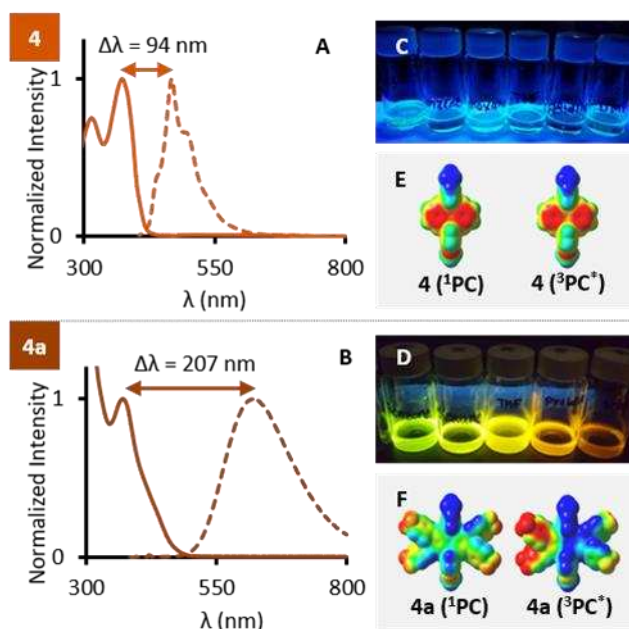


Figure 2.5. (A&B) Normalized absorption (solid) and emission (dashed) spectra of PCs **4** and **4a**, respectively, with Stokes shift shown in nm. (C&D) Photographs of PCs **4** and **4a** in solvents of increasing polarity from left to right while being irradiated with 365 nm light. (E&F) Electrostatic potential (ESP) maps (generated using DFT) showing areas of high electrostatic potential (red) and low electrostatic potential (blue) for the PC in the singlet ground state (left) and in the triplet excited state (right).

DFT calculations were also used to probe the CT character of PCs in the ground state and of $^3\text{PC}^*$. Generation and visualization of singly occupied molecular orbitals (SOMOs) of the parent

and core-extended $^3\text{PC}^*$ species show some degree of spatial separation between the low-lying SOMOs and high-lying SOMOs (Figure 2.5B & Figures A2.70-A2.72). For core-extended PCs, the high-lying SOMO of $^3\text{PC}^*$ is predicted to be distributed across the core and two of the core substituents whereas the low-lying SOMO is predicted to reside centered primarily on the core of $^3\text{PC}^*$ (Figure 2.5B and Figures A2.70-A2.72). Interestingly, there is minimal observable difference between the nature of the high lying SOMOs for **3b** and **3a** or between **5b** and **5a**.

Excited state absorption spectra of $^3\text{PC}^*$ for core-extended DHPs was measured using time-resolved absorption (TA) spectroscopy. The spectral signals were followed at a single wavelength over time to obtain kinetic data which was then used to determine triplet excited state lifetimes for the PCs. When comparing spectral absorption traces (Figure 2.6) of PCs with the same core substituent (i.e., **3b** and **5b**) and PCs with the same *N*-aryl group (i.e., **3**, **3a**, and **3b**) we observed similar features that support the SOMOs computationally predicted by DFT (Figure 2.4). For **3**, **3a**, and **3b**, a similar absorption feature of $^3\text{PC}^*$ is observed at ~333 nm. We propose that this absorption feature is representative of a high energy absorption from the low lying SOMO of $^3\text{PC}^*$ to some higher energy unoccupied molecular orbital (LUMO_{+n}). As the low lying SOMO of PCs **3**, **3a**, and **3b** are predicted to reside primarily on the core of the PC (Figure A2.70), it makes sense that the absorption features they have at ~333 nm would look similar. Furthermore, when comparing the spectral absorption traces of $^3\text{PC}^*$ for **3b** and **5b**, we note two similar features at ~590 nm and ~698 nm. We propose that these lower energy transitions are representative of excitation from the higher lying SOMO on the PC core substituent to some LUMO_{+n} . As these PCs share the same core substituent, it seems logical that these spectral absorption features at ~590 nm and ~698 nm would be similar.

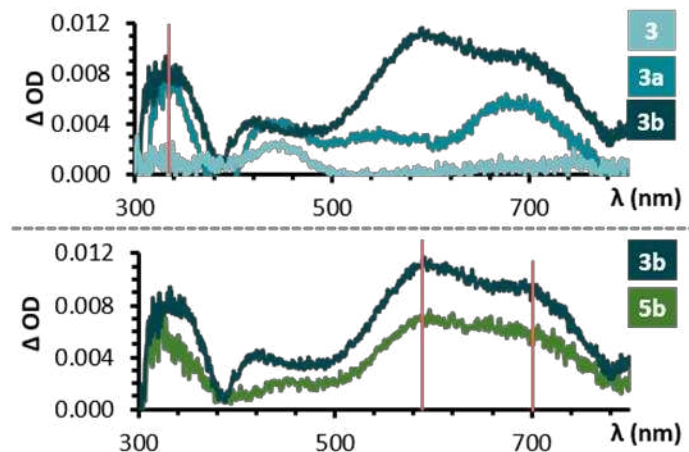


Figure 2.6. Overlapping spectral absorption traces of $^3\text{PC}^*$ for **3**, **3a**, and **3b** (top) as well as PCs **3b** and **5b** (bottom).

Interestingly, ESP maps of $^3\text{PC}^*$ generated using DFT suggest that the electrostatic potential of **3a**, **4a**, and **5a** is, largely, shifted away from the *N*-aryl group to one side of the molecule where for **3b**, **4b**, and **5b** electron density, though also shifted away from the *N*-aryl group, is shared between all four core substituents (Figures A2.73-A2.75). For PC **4**, a small $\Delta\lambda$ is observed (Figure 2.5A) as well as a lack of solvatochromism (Figure 2.5C) and there is no observable shift in electrostatic potential between the ground state singlet PC (^1PC) and $^3\text{PC}^*$ (Figure 2.5E). Interestingly, when PC **4** is core-extended with EWG **a**, there is a measurable increase in $\Delta\lambda$ (Figure 2.5B), in the extent of solvatochromism (Figure 2.5D), and electrostatic potential in $^3\text{PC}^*$ appears to shift from $^1\text{PC}^*$ so that electron density is heavily centered across two of the core substituents rather than on the PC core (Figure 2.5F). These observations suggest that core-extension can be used to modulate CT in PCs with a primary structure that does not possess CT character in the excited state.

Excited State Energies. Energies of PC singlet excited states ($E_{\text{S1,exp}}$) were experimentally determined from the $\lambda_{\text{max,em}}$ measured using fluorescence spectroscopy. $E_{\text{S1,exp}}$ for core-extended DHPs ranged from 1.95 eV to 2.12 eV and was determined to be higher for all core-extended DHPs

than for non-core-extended DHPs (with PC **4** vs. **4a** as an exception). Transitioning from EWG **a** to EDG **b** resulted in a decrease in E_{S1} by 0.17 eV for **3a** (2.12 eV) to **3b** (1.95 eV) and by 0.11 eV for **5a** (2.11 eV) to **5b** (2.00 eV). For core-extended DHPs the *N*-aryl group seems to have a smaller impact on E_{S1} than the electronics of the core substituent. $E_{S1,exp}$ for **3a** and **5a** are nearly isoenergetic and are higher than **4a** by <0.05 eV. Additionally, $E_{S1,exp}$ for **3b** and **5b** are only separated by 0.05 eV. Interestingly, core-extension of DHPs is predicted to lower the energy of the lowest energy triplet excited state ($E_{T1,comp}$) relative to the parent non-core-extended PCs. PCs **3a** ($E_{T1,comp} = 1.91$ eV) and **3b** ($E_{T1,comp} = 2.07$ eV) $E_{T1,comp}$ is predicted to be lower than that of the parent DHP PC (PC **3**: $E_{T1,comp} = 2.23$ eV). The same trend is observed between PCs **5** ($E_{T1,comp} = 2.19$ eV), **5a** ($E_{T1,comp} = 1.89$ eV) and **5b** ($E_{T1,comp} = 1.99$ eV) as well as for PCs **4** ($E_{T1,comp} = 2.29$ eV) and **4a** ($E_{T1,comp} = 1.82$ eV). For core-extended DHPs with the same core substituents, $E_{T1,comp}$ does not change by more than 0.08 eV which is within the margin of error for these calculations observed for a similar series of PCs.¹⁹ The same is true for the parent DHPs, where no more than a 0.10 eV shift in $E_{T1,comp}$ is predicted. Interestingly, the largest changes in $E_{T1,comp}$ are between core-extended DHPs with the same *N*-aryl group, but different core substituents. For example, for PC **3b** ($E_{T1,comp} = 2.07$ eV) core-extended with EDG **b** $E_{T1,comp}$ is predicted to be 0.16 eV higher in energy than $E_{T1,comp}$ for **3a** ($E_{T1,comp} = 1.91$ eV), the latter of which is core-extended with EWG **a**. Our observations suggest that the electronics of the core-substituent could have more impact on $E_{T1,comp}$ than the identity of the *N*-aryl group, however an expanded study of core-extended DHPs is necessary to confirm this.

Excited State Lifetimes. The excited state lifetimes (τ) of PCs are posited to have a significant role in PC reactivity as the lowest energy excited state must persist long enough to engage in a bimolecular reaction. Though there are exceptions, an excited state lifetime of >1 ns

is typically considered sufficient time for the excited state molecule to engage in a bimolecular reaction. Unfortunately, without measuring quantum yield of intersystem crossing (ϕ_{ISC}), we can currently only speculate on the relative concentrations of $^1PC^*$ and $^3PC^*$ in our system through measuring the quantum yield of fluorescence (ϕ_f ; *vide infra*), however we are able to investigate the impact of structural changes on the excited state lifetimes of core-extended and non-core-extended DHPs. Of the PCs for which we were able to measure excited state lifetimes, the singlet excited state lifetimes (τ_{S1}) ranged from 9 ns – 37 ns and triplet excited state lifetimes (τ_{T1}) ranged from 0.63 μ s – 144 μ s. For PC **3** (τ_{S1} = 9 ns; τ_{T1} = 0.63 μ s), both τ_{S1} and τ_{T1} are shorter than for core-extended derivatives **3a** (τ_{S1} = 17 ns; τ_{T1} = 144 μ s) and **3b** (τ_{S1} = 11 ns; τ_{T1} = 42 μ s). This trend could not be verified for PCs **5** due to insufficient data. In contrast to PC **3**, a decrease in τ_{S1} is observed after core-extension of PC **4** (τ_{S1} =37 ns) to **4a** (τ_{S1} =13 ns). When examining the effect of core substituent electronics on excited state lifetimes, we found that for PCs **3** and **5**, τ_{S1} is longer for derivatives that are core-extended with EWG **a** (PCs **3a** & **5a**: τ_{S1} =17 ns) than with EDG **b** (PCs **3b** & **5b**: τ_{S1} =11 ns). For PCs **3a** and **3b** the same trend is observed for $^3PC^*$ where for PC **3a** τ_{T1} =144 ns and for **3b** τ_{T1} =42 ns. The effect of the *N*-aryl group on the excited state lifetimes of core-extended DHPs is unclear. The experimentally determined τ_{S1} of **3a** (τ_{S1} = 17 ns) and **5a** (τ_{S1} = 17 ns) are equal as well as the τ_{S1} of **3b** (τ_{S1} = 11 ns) and **5b** (τ_{S1} = 11 ns), however there is a disparity in the triplet excited state lifetimes of core-extended PCs with different *N*-aryl groups (**3b**: τ_{T1} =42 ns; **5b**: τ_{T1} =108 ns). Interestingly, for non-core extended DHPs, PC **4** has a significantly longer τ_{S1} than PC **3**, and a longer τ_{T1} than PC **3** and PC **5**, suggesting that the *N*-aryl group does have a significant impact on the excited state lifetimes of non-core extended DHPs. We were unable to confidently measure and report the singlet excited state lifetime (τ_{S1}) of PC **5** as it was below the detection limit of our instrument. Furthermore, we were unable to detect a

triplet signal for PCs **4a** and **5a**, therefore a triplet excited state lifetime (τ_{T1}) is not reported for those PCs.

Quantum Yield of Fluorescence. There are several pathways known to compete with relaxation of a singlet excited state molecule via fluorescence including non-radiative decay pathways, quenching through energy transfer or electron transfer, and phosphorescence from T1. Though ϕ_f does not lend complete information regarding the contribution of the aforementioned pathways in relaxation of $^1\text{PC}^*$ to ^0PC , a low measured ϕ_f suggests that high quantum yield of intersystem crossing is possible for that PC.¹¹ We used fluorescence spectroscopy to experimentally determine the ϕ_f for both the core-extended and non-core extended PCs discussed in this study. On the whole, core-extension of DHPs appears to increase ϕ_f . The experimentally determined ϕ_f of PCs **3** ($\phi_f = 1.32\%$) and **5** ($\phi_f = 0.72\%$) were both lower than ϕ_f measured for the core-extended derivatives **3a** ($\phi_f = 9.00\%$) and **3b** ($\phi_f = 4.31\%$) as well as **5a** ($\phi_f = 35.0\%$) and **5b** ($\phi_f = 4.00\%$), respectively. We found that this trend also holds true for PCs **4** ($\phi_f = 23.0\%$) and **4a** ($\phi_f = 36.0\%$) which we noted have the highest ϕ_f out of the non-core-extended and core-extended DHPs, respectively. Though we did observe that ϕ_f for core-extended DHPs with EWG **a** is higher than that for core-extended PCs with EDG **b** (i.e., **3a** vs **3b**), the ϕ_f of PC **3a** is 26% lower than **5a**, so it seems there is significant variability between PCs that, though possessing the same core substituents, have different N-aryl groups.

Redox Properties. After assessing the photophysical properties of new core-extended DHPs, we sought to examine their electrochemical properties (Table 2.2). The experimental singlet excited state reduction potentials ($E^{0*}_{SL,exp}(^2\text{PC}^{*+}/^1\text{PC}^*)$) for core-extended DHPs in this study range from -1.62 to -1.78 V vs SCE. The $E^{0*}_{SL,exp}(^2\text{PC}^{*+}/^1\text{PC}^*)$ we measured for **3a**, **3b**, **5a**, and **5b** suggest that they are slightly more reducing than the parent non-core extended analogues; however

$E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$ does not vary by more than 0.14 V vs SCE. Contrary to this trend, $E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$ of PC **4a** ($E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*) = -1.73$ V vs SCE) is lower (more positive) than that of PC **4** ($E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*) = -2.5$ V vs SCE, respectively). The experimental oxidation potentials of $^2PC^{*+}$ were estimated from the $E_{1/2}(^2PC^{*+}/^1PC)$ which was determined using CV. $E_{1/2}(^2PC^{*+}/^1PC)$ for core-extended DHPs reported in this study range from 0.23 to 0.38 V vs SCE. Core-extension of PCs **3** and **5** resulted in no more than a 0.17 V vs SCE increase in $E_{1/2}(^2PC^{*+}/^1PC)$, however core-extension of **4** ($E_{1/2}(^2PC^{*+}/^1PC) = 0.16$ V vs SCE) with EWG **a** significantly decreased the stability of $^2PC^{*+}$ (PC **4a**: $E_{1/2}(^2PC^{*+}/^1PC) = 0.34$ V vs SCE). On the whole, core-extension of DHPs appears to destabilize $^2PC^{*+}$, rendering the core-extended derivatives more oxidizing than the parent DHPs while also destabilizing E_{S1} rendering **3a**, **3b**, **5a**, and **5b** more reducing from $^1PC^*$ than the parent derivatives.

Table 2.2 Measured and predicted electrochemical properties of PCs investigated in this study.

PC	$\lambda_{max,abs}$ (nm) ^[a]	$\epsilon_{max,abs}$ (M ⁻¹ cm ⁻¹) ^[b]	$\lambda_{max,em}$ (nm) ^[c]	Stokes Shift (nm)	$E_{S1,exp}$ (eV) ^[d]	$E_{T1,comp}$ (eV) ^[e]	Φ_f (%) ^[f]	τ_{S1} (ns) ^[g]	τ_{T1} (μ s) ^[h]
3	362	6,100	663	297	1.87	2.23	1.32	9	0.63
3a	385	22,200	586	201	2.12	1.91	9.00	17	144
3b	385	13,100	636	251	1.95	2.07	4.31	11	42
4	373	5,200	467	94	2.66	2.29	23.0	37	88
4a	392	20,900	599	207	2.07	1.82	36.0	13	— ^[i]
5	343	5,900	654	311	1.90	2.19	0.72	— ^[k]	3.5
5a	373	27,600	587	214	2.11	1.89	35.0	17	— ^[i]
5b	371	15,900	621	250	2.00	1.99	4.00	11	108

^{a]}All measurements were performed in a 3-compartment electrochemical cell with an Ag/AgNO₃ reference electrode in MeCN (0.01 M) and 0.1 M NBu₄PF₆ electrolyte solution. DMAc was used to solvate the PCs and in the working electrode compartment, while platinum was used as both the working and counter electrodes. E (V vs SCE) = E (V vs Ag/AgNO₃ [0.01 M]) + 0.298 V). ^[b]DFT calculations were performed at the uM06/6-311+G(d,p)//uM06/6-31+G(d,p) level of theory with CPCM-described solvation in DMAc. ^[c]Singlet excited state reduction potentials were calculated using the singlet energies (estimated from the maximum wavelength of emission) and the $E_{1/2}$. ^[d]Values were taken from ref. 11.

Taking a closer look at the effects of the core substituent electronics on the redox properties, we found that $E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$ is slightly more negative for **3a** and **5a** than for **3b** and **5b**, though only by 0.06 to 0.11 V vs SCE (Figure 2.7). Changing the *N*-aryl group on core extended DHPs appears to have even less impact than core-electronics on $E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$. Interestingly, computationally predicted triplet excited state reduction potentials ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*)$) have an opposite trend to what was observed for $E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$ excluding PCs **4** and **4a**. $E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*)$ is predicted to be lower for core-extended PCs (i.e., for **3** $E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -2.13$ V vs SCE and for PC **3a** $E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -1.67$ V vs SCE). When analyzing the effects of the core substituent electronics on $E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*)$, we found that $E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*)$ is slightly more negative for **3b** ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -2.06$ V vs SCE) and **5b** ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -2.00$ V vs SCE) than for **3a** ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -1.67$ V vs SCE) and **5a** ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*) = -1.75$ V vs SCE)). As was observed for $E^{0*}_{SI,exp}(^2PC^{*+}/^1PC^*)$ values, changing the *N*-aryl group in core-extended DHPs is predicted to have a smaller effect on ($E^{0*}_{T1,comp}(^2PC^{*+}/^3PC^*)$) than the changing the electronics of the core-substituent. Redox reversibility was observed for all core-extended DHPs to varying degrees suggesting that they can perform as catalysts in reactions dependent on repeated reduction and oxidation reactions such as O-ATRP (Figures A1.54-A1.60).

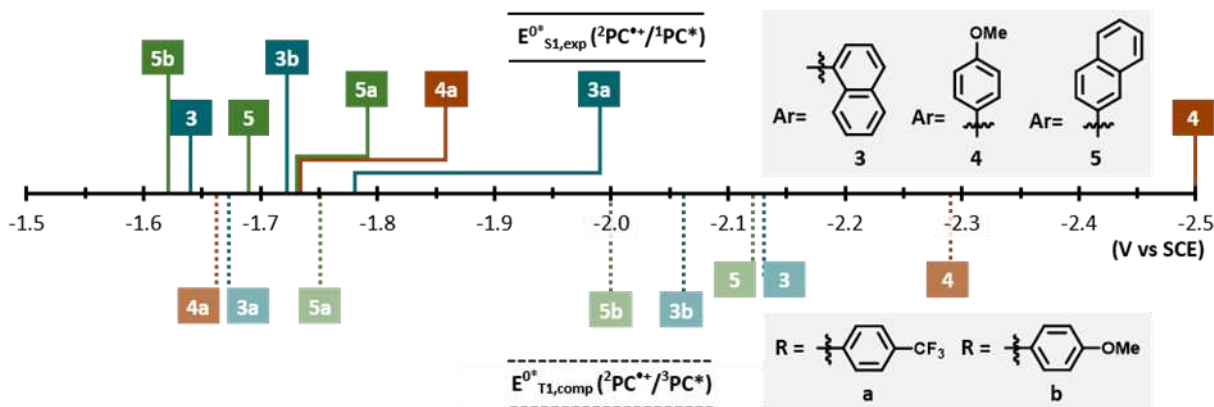


Figure 2.7. (Top) Electrochemical series of experimentally measured singlet excited state redox potentials (top) and computationally predicted triplet excited state reduction potentials (bottom) of PCs investigated in this study.

O-ATRP. After investigating the structure-property relationships for the core-extended DHPs presented in this work, we sought to understand how those properties ultimately impact PC performance in O-ATRP. First, PCs were applied in the O-ATRP of methyl methacrylate (MMA) using diethyl 2-bromo-2methylmalonate (DBMM) as the polymerization initiator and *N,N*-dimethylacetamide (DMAc) as the solvent (unless otherwise noted) so that [MMA]:[DMAc]:[DBMM] = [1000]:[1000]:[10] (Figure 2.8 & Table 2.3). PC loadings were varied between 500 ppm and 10 ppm with the ppm of PC being relative to mols of monomer. All polymerizations were irradiated in a white light LED beaker and carried out under N₂. PC performance was assessed based on the degree of control with which the polymerization proceeded. Polymerization control was evaluated by first analyzing initiator efficiency (I^*) and dispersity ($\bar{D}$). I^* is representative of the theoretical number average molecular weight ($M_{n,theo}$) divided by the observed number average molecular weight (M_n). If $I^* > 100\%$, this suggests that initiation was over efficient and that some of the polymer chains in the polymerization were initiated by means other than through reaction with the initiator (autoinitiation is one example). If $I^* < 100$, this suggests that initiation was inefficient due to undesirable side reactions or other processes that interfered with the polymerization of one polymer chain from one molecule of initiator. Herein, an $I^* > 90\%$ after 8h is considered good. PC control over polymer dispersity is considered moderate if $1.3 < \bar{D} < 1.5$, good if $1.1 < \bar{D} < 1.3$, and excellent if $\bar{D} < 1.1$. Additionally, PC control over the polymerization was evaluated based on the linearity of M_n growth with respect to monomer conversion throughout the polymerization and by the proximity of M_n to $M_{n,theo}$ at the same percent conversions. Polymerizations that proceeded with linear M_n growth and with M_n

characteristics.

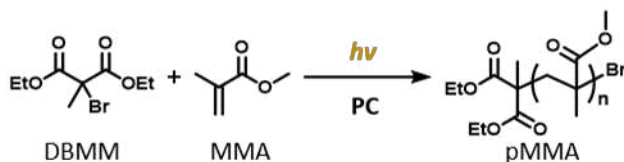


Figure 2.8: General reaction scheme for the light driven polymerization of methyl methacrylate (MMA) using a photocatalyst (PC) and diethyl 2-bromo-2-methylmalonate (DBMM) as the initiator.

Table 2.3. O-ATRP Results from Employing PCs for the Polymerization of MMA at Varied Catalyst Loadings.

Run	PC	[PC] (ppm) ^[b]	Conv. ^[c]	M_n (kDa) ^[d]	$\bar{D}$ (M_w/M_n) ^[d]	$I^*[e]$
2	3	100	68%	8.97	1.07	78%
3	3	50	85%	8.26	1.19	105%
5	3a	100	65%	7.71	1.10	87%
6	3a	50	86%	8.80	1.07	92%
7	3a	10	67%	7.17	1.49	97%
8	3b	100	51%	5.32	1.57	101%
9	4 ^[g]	1000	70%	24.7	1.57	29%
10	4a	100	65%	7.57	1.15	90%
11	4a	50	76%	7.53	1.27	104%
12	4a	10	67%	7.17	1.49	97%
14	5	100	77%	8.74	1.18	91%
15	5	50	87%	12.8	1.20	70%
16	5	10	62%	7.43	1.79	88%
18	5a	100	73%	8.08	1.09	93%
19	5a	50	80%	7.34	1.28	112%
20	5a	10	70%	7.54	1.42	96%
22	5b	100	73%	8.25	1.54	92%

^[a]All polymerizations were conducted using MMA (9.35 mmol at 4.63 M) as the monomer and DBMM (0.093 mmol) as the initiator in a ratio of [1000]:[100] with DMAc as the solvent. ^[b]PC loading is relative to mols of monomer. ^[c] Determined by ¹H-NMR spectroscopy. ^[d]Measured using GPC. ^[e]Initiator efficiency (I*) calculated by ((theoretical M_n / observed M_n)*100). ^[g]Data obtained from ref. 12.; polymerization was conducted using ethyl α-bromophenylacetate as the initiator rather than DBMM.

Previous work has demonstrated that DBMM can add to the core of parent DHP PC resulting in a decrease in I^* .^{15, 16} Based on the results of previous work, we hypothesized core-

extension of PCs **3**, **4**, and **5** would yield polymers with initiator efficiencies closer to unity due to the presence of core-extending substituents blocking sites on the PC core known to undergo radical addition of the initiator.¹⁴ Indeed, the I^* of polymers synthesized using core-extended DHPs was typically higher than for parent DHPs, however that increase varied largely (between 1% and 42% increase in I^*). Exceptions to this trend include PC **3a** employed at 50 ppm in DMAc (Table 2.3, Runs 6) and PC **5a** employed at 500 ppm (Table 2.3, Run 17) where polymers produced with the core-extended DHP did not have a higher I^* under the aforementioned conditions.

We also hypothesized that PCs **3a**, **3b**, **5a**, and **5b** would show increased control over the polymerization of MMA, in comparison to PCs **3** and **5**. Our reasoning stemmed from the fact that PCs **3a**, **3b**, **5a**, and **5b** have higher $\epsilon_{max,abs}$ at a $\lambda_{max,abs}$ closer to the emission of the LEDs than PCs **3** and **5** and are equally if not more oxidizing from $^2PC^{*+}$, have higher experimentally determined $E^{0*}_{S1,exp}$ ($^2PC^{*+}/^1PC^*$), and possess CT character. To the contrary, we observed no trends suggesting that core-extended PCs consistently produce polymer with lower $\bar{D}$ or closer to unity I^* than their analogous non-core-extended DHP. In fact, we observed that between PCs **3** and **3a** and between PCs **5** and **5a**, at the same PC loadings (50ppm and higher), $\bar{D}$ varied by less than 0.09, except for in run 6 (Table 2.3) where **3a** employed at 50 ppm loading yields polymer with $\bar{D}$ lower by 0.12 than polymer produced with **3** at 50 ppm PC loading. Overall, PCs core-extended with EDG **b** (PCs **3b** and **5b**) did not perform well in O-ATRP of MMA. For PCs **3b** and **5b**, M_n growth was not linear with respect to monomer conversion and $\bar{D}$ stayed above 1.5 at all conversions, indicating poor control throughout the duration of the polymerization (Figures A1.83, A1.95, & A1.96). As the properties of PCs **3b** and **5b** are comparable to other core-extended DHPs that performed well, we hypothesize that the relatively lower solubility of **3b** and **5b** may hinder their efficacy in controlling the polymerization. Neither **3b** nor **5b** dissolve completely during the

polymerization, thus the catalyst loading is uncertain. Furthermore, the insolubility could cause scattering of light, compromising maximum irradiation of the dissolved polymerization mixture and lowering the efficiency and uniformity of activation.

One of the most notable results we observed as a result of core-extension was that for PC **4**. Core-extension of PC **4** with EWG **a** to make PC **4a** enabled good control over the synthesis of poly(methyl methacrylate) (PMMA) ($D = 1.27$, $I^* = 104\%$) at 50 ppm PC loading. In comparison, the parent PC to PC **4a** (PC **4**) has shown poor control over the O-ATRP of MMA at a PC loadings as high as 1000 ppm ($D = 1.57$, $I^* = 29\%$).¹³ To explain this observation, we reviewed three notable differences in the photophysical and electrochemical properties of PCs **4** and **4a**. First, we have shown new data to support that **4a** can access a CT excited state due to core-extension whereas PC **4** is not predicted to access a CT excited state, the former of which has been attributed as an important PC property for success in O-ATRP.¹³ Second, the oxidation potential of PC **4a** ($E_{1/2} (^2PC^{+}/^1PC) = 0.34$ V vs SCE) provides more overpotential than PC **4** ($E_{1/2} (^2PC^{+}/^1PC) = 0.16$ V vs SCE) for driving deactivation in O-ATRP, the latter being essential to minimizing termination reactions during the polymerization which compromise control. Last, the $\epsilon_{\text{max,abs}}$ of PC **4a** ($\epsilon_{\text{max,abs}}=20,900 \text{ M}^{-1}\text{cm}^{-1}$) is significantly higher than for PC **4** ($\epsilon_{\text{max,abs}}=5,200 \text{ M}^{-1}\text{cm}^{-1}$). As noted earlier, a high $\epsilon_{\text{max,abs}}$ is posited to increase the population of $^nPC^*$ enabling uniform activation,²⁹ however results observed from the application of PCs **3** ($\epsilon_{\text{max,abs}}=5,500 \text{ M}^{-1}\text{cm}^{-1}$) and **5** ($\epsilon_{\text{max,abs}}=5,900 \text{ M}^{-1}\text{cm}^{-1}$) show that polymerization control was achieved at PC loadings as low as 50 ppm despite their comparable $\epsilon_{\text{max,abs}}$ values to PC **4**.

For PCs that yielded polymer with $D < 1.5$ after 8h of irradiation at 100 ppm PC loading (PCs **3**, **3a**, **4a**, **5**, **5a**), we proceeded to test their efficacy at even lower PC loadings (50 ppm and 10 ppm). Initially, we hypothesized that core-extended DHPs would give superior control at lower

PC loadings in comparison to parent DHPs due to their high molar extinction coefficients and the blockage of sites on the PC core noted to undergo side reaction with the initiator. At 100 ppm PC **5a** outperforms PCs **3**, **3a**, **4a**, and **5**; $\bar{D}$ remained below 1.5 at all conversions, M_n growth was linear with respect to conversion, at 8h the initiator efficiency was closest to unity ($I^* = 93\%$), and $\bar{D} = 1.09$ (Table 2.3, Run 18) (Figure A2.92). At 50 ppm, PC **3a** outperforms PCs **3**, **4a**, **5**, and **5a** (Table 2.3, Run 6). Although at 8 h, I^* is lower when using PC **3a** at 50 ppm ($I^* = 92\%$) than for runs with PC **3**, **4a**, and **5a**, the run using PC **3a** is unique in that $\bar{D}$ remained below 1.5 at all conversions and M_n growth remained linear with respect to conversion (Figure A2.81). Interestingly, for polymerizations shown in Table 2.3 that were run at 10 ppm PC loading, $\bar{D} > 1.5$ at all conversions, indicating poor control throughout the polymerization (Figures A1.82, A1.86, A1.90, & A1.94). Additionally, for the 10 ppm PC loading runs employing PCs **3a**, **4a**, and **5a**, pMMA only approaches the targeted M_n at high conversions—an indicator that initiation is slow. Initially, we posited that, the lack of control at 10 ppm PC loading was due to the concentration of PC being too low to afford a sufficient concentration of $^1PC^*$ upon photoexcitation. Interestingly, after doing a solvent screening using PC **3a** (see discussion below) we tried applying **4a** at 10 ppm in the same polymerization conditions noted above but using benzene as the solvent instead of DMAc (Table A1.4, run 33) and observed improved results in polymerization control ($\bar{D} = 1.33$ and $I^* = 102\%$) compared to the run using **4a** at 10 ppm in DMAc ($\bar{D} = 1.49$ and $I^* = 97\%$).

After determining that PC **3a** performed best at the lowest successful tested PC loading (50 ppm) for the polymerization of MMA in DMAc using DBMM as the initiator, we sought to assess the effect of solvent polarity on the polymerization results. Previously, several reports have shown that solvent can have a significant impact on polymerization control, especially for DHP PCs.^{13, 15,}
²⁵ PC **3a** was used to polymerize MMA at 50 ppm PC loading in tetrahydrofuran (THF), ethyl

acetate (EtOAc), benzene, and dichloromethane (DCM), in turn. Interestingly, we found that the performance of PC **3a** in the most polar solvent we tested (DMAc) ($\bar{D} = 1.07$, $I^* = 92\%$) yielded nearly identical results at 8h as the polymerization conducted in the least polar solvent we tested (benzene) ($\bar{D} = 1.06$, $I^* = 92\%$). For both of the aforementioned polymerizations (Table 2.4, Runs 6 & 25), M_n growth was linear with respect to monomer conversion and $\bar{D} < 1.5$ throughout the polymerization (Figures A1.81 & A1.99). As observed in previous studies,¹³ monomer conversion was slower in solvents of increasing polarity.

Table 2.4. Solvent screening with PC **3a** for O-ATRP of MMA.

Run	PC	Solvent	Conv. ^[b]	M_n (kDa) ^[c]	$\bar{D}$ (M_w/M_n) ^[c]	I^* ^[d]
6	3a	DMAc	86%	8.80	1.07	92%
23	3a	THF	78%	9.88	1.17	81%
24	3a	EtOAc	87%	8.79	1.23	102%
25	3a	Benz	89%	10.0	1.06	92%
26	3a	DCM	94%	8.88	1.24	109%

^[a]All polymerizations were conducted using MMA as the monomer, DBMM as the initiator, and PC **3a** as the catalyst in a ratio of [1000]:[100]:[0.05]. ^[b]Determined by ¹H-NMR spectroscopy.

^[d]Measured using GPC. ^[d]Initiator efficiency (I^*) calculated by ((theoretical M_n /observed M_n)*100).

Overall, the photophysical and electrochemical properties of core-extended PCs reported in Table 2.1 and Table 1.2 did not appear to significantly impact control over the polymerization of MMA through O-ATRP or their ability to control the polymerization at low ppm PC loadings > 50 ppm except for comparing results obtained using PC **4**¹³ vs PC **4a**.

To further probe the activity of core-extended DHPs, we investigated their ability to control the polymerization of an acrylate monomer: n-butyl acrylate (nBA). The polymerization of nBA by O-ATRP has been a persistent challenge in the field for several reasons. First, the high rate of propagation of acrylates necessitates highly efficient deactivation to achieve a controlled polymerization ($\bar{D} < 1.5$). Additionally, the increased bond strength of the carbon-bromine bond at the polymer chain end of poly(n-butyl acrylate) (pBA) relative to pMMA³⁰ necessitates a greater

driving force for activation relative to methacrylates. In combination, these properties of acrylate monomers and polymers require increased driving force for both activation and deactivation from PCs. Though the conditions and PCs applied for O-ATRP of nBA in this work did not yield polymer with $\bar{D} < 1.5$ (Table A1.4), recent work by McCarthy *et al.* and Buss *et al.* demonstrated controlled polymerization of nBA via O-ATRP using alkyl core-substituted DHPs and *N*-aryl dimethyl dihydroacridines, respectively.^{15, 19} We hypothesize that under the conditions investigated in this study core-extended DHPs do not have sufficient driving force for enabling efficient deactivation, and thus controlled polymerization, of acrylates and other monomers with high rates of propagation.

One of the more well-studied PCs for O-ATRP is 3,7-di(4-biphenyl) 1-naphthalene-10-phenoxazine (**PhenO**). However, to the best of our knowledge, **PhenO** has not been applied in O-ATRP at PC loadings lower than 1000 ppm. **PhenO** has a comparable $\epsilon_{\text{max,abs}}$ ($\epsilon_{\text{max,abs}} = 26,600$) to the PCs reported herein, absorbs at a comparable $\lambda_{\text{max,abs}}$ ($\lambda_{\text{max,abs}} = 388$ nm), has a higher oxidation potential ($E_{1/2} (^2\text{PC}^{*+}/^1\text{PC}) = 0.65\text{V}$ vs SCE), possesses CT character, has a longer triplet excited state lifetime ($\tau_{T1} = 480$ μs), has a high ϕ_{T1} ($\phi_{T1} = 90\%$), and is sufficiently reducing ($E^{0*}_{S1,\text{exp}} (^2\text{PC}^{*+}/^1\text{PC}^*) = -1.80$ V vs SCE; $E^{0*}_{T1,\text{comp}} (^2\text{PC}^{*+}/^3\text{PC}^*) = -1.70$ V vs SCE) compared to core-extended DHPs.³¹ To gain a better understanding of what properties might enable core-extended DHPs to work well at low ppm PC loadings, we decided to investigate **PhenO** in the O-ATRP of MMA at 50 ppm using DBMM as the initiator and DMAc as the solvent. As **PhenO** has comparable properties to core-extended DHPs, except for a higher oxidation potential (which could provide more driving force for efficient deactivation and improved polymerization control), we hypothesized that it would perform equally, if not better, in O-ATRP at a low PC loading. Interestingly, after 8 hours of polymerization, the dispersity reached using 50 ppm of **PhenO** ($\bar{D}$

= 1.81) was higher than the dispersity of any polymer sample at 8 hours synthesized with any of the core-extended or non core-extended DHP PCs that we investigated using the same polymerization conditions ([DMAc]:[MMA]:[DBMM] = [1000]:[1000]:[10]) (Table A1.4, run 34). Additionally, over the course of the polymerization M_n growth was not linear nor equivalent to $M_{n,theo}$. These data suggest that **PhenO** does not control O-ATRP of MMA under the aforementioned conditions (Fig. S105). We also investigated the activity of **PhenO** for O-ATRP of MMA at 100 ppm and 500 ppm PC loadings. After 8 hours of polymerization using 100 ppm of **PhenO**, the observed dispersity of the polymerization mixture was $\bar{D} = 1.78$ and the initiator efficiency was $I^* = 67\%$ (Table A1.4, run 35). After 8 hours of polymerization using 500 ppm of **PhenO**, the observed dispersity of the polymerization mixture was $\bar{D} = 1.39$ and the initiator efficiency was $I^* = 107\%$ (Table A1.4, run 36). Despite dispersity being less than 1.5 after 8 hours of polymerization using 500 ppm of **PhenO**, throughout the polymerization M_n growth is not linear with respect to conversion and M_n is consistently > 4kDa higher than $M_{n,theo}$. The results obtained using **PhenO** at 50, 100, and 500 ppm PC loadings for the polymerization of MMA demonstrate that **PhenO** is an inferior PC relative to DHPs for controlling the polymerization of MMA in O-ATRP at low ppm PC loadings under the conditions used in this work. One potential explanation for the inferior performance of **PhenO** relative to DHPs is that the overall yield of $^1PC^*$ vs $^3PC^*$ contributing to activation varies for different PCs at certain initiator concentrations.²⁰ If, at the concentration of DBMM used in our polymerizations, the concentration of the $^1PC^*$ species with a greater driving force for activation is higher for DHPs than it is for **PhenO**, activation with DHPs would be, comparatively, more efficient.

When considering the dispersity observed after 8 hours of polymerization and the linearity of M_n growth throughout the polymerization, PC **3a** performed the best out of the seven PCs

studied herein. At 50 ppm in DMAc PC **3a** produced pMMA with $\bar{D} = 1.07$ after 8 hours. PC **3** performed second best at 50 ppm in DMAc yielding PMMA with $\bar{D} = 1.19$ after 8 hours, followed by PC **5** ($\bar{D} = 1.19$ at 8 hours), then by PC **4a** ($\bar{D} = 1.27$ at 8 hours), then PC **5a** ($\bar{D} = 1.28$ at 8 hours). Importantly, after 8 hours $I^* > 90\%$ for all of these runs except the one using PC **5** ($I^* = 70\%$ after 8 hours). PCs **3b** and **5b** did not produce polymer with $\bar{D} < 1.5$ at 100 ppm PC loading and were, for that reason, not investigated in O-ATRP of MMA at 50 ppm. On the whole, further investigation into the PC properties and polymerization conditions that allow for polymerization control with PCs **3**, **5**, **3a**, **4a**, and, **5a** at low ppm PC loadings is needed.

2.4 – CONCLUSIONS

In this work, we were able to successfully synthesize five new highly reducing PCs, three of which proved to be excellent PCs for controlling the polymerization of MMA at PC loadings as low as 50 ppm and 10 ppm (under certain conditions). Furthermore, we demonstrated that non-core extended DHPs can achieve satisfactory polymerization results at PC loadings as low as 50ppm. The photophysical and electrochemical properties of the five new PCs reported here were investigated and the effect of core-extension, the electronics of the core substituents, as well as the identity and connectivity of the *N*-aryl group on PC properties were examined. We found that changing the *N*-aryl group in core-extended DHPs is predicted to have a smaller effect on predicted ($E^{0*}_{Tl,comp}(^2PC^{*+}/^3PC^*)$) values and experimentally determined $E^{0*}_{Sl,exp}(^2PC^{*+}/^1PC^*)$ than the changing the electronics of the core-substituent. Additionally, core-extension of DHPs appears to destabilize $^2PC^{*+}$, rendering the core-extended derivatives more oxidizing than the parent DHPs, but that overall neither changing the *N*-aryl group nor the core substituents has a significant impact on $E_{1/2}(^2PC^{*+}/^1PC)$. For PC properties relevant to photoexcitation, we found that core extension red-shifts $\lambda_{max,abs}$, and significantly increases $\epsilon_{max,abs}$. For $\lambda_{max,abs}$, the identity of the *N*-aryl group has a greater impact on $\lambda_{max,abs}$ than the electronics of core-substituents. To the contrary, we

observed that though there is a measurable change in the $\epsilon_{\text{max,abs}}$ for CE-DHPs with different *N*-aryl groups, the shifts are of a lesser magnitude than those observed when the core substituent is switched between EWG **a** and EDG **b** within PC families that have the same *N*-aryl group. In our analysis of the measured Stokes shifts for core-extended PCs, the identity of the *N*-aryl group was determined to have a smaller effect on $\Delta\lambda$ (and therefore an influence on CT) than altering the electronics of the core-substituent. We also reported experimentally determined excited state lifetimes for core-extended DHPs for the first time and found that core-extension appears to increase both τ_{S1} and τ_{T1} , that the electronics of the core have little effect on τ_{S1} , but do impact τ_{T1} for **3a** and **3b** and, additionally, we found that changing the connectivity of the *N*-aryl naphthalene group has no effect on τ_{S1} for core-extended DHPs **3a-b** and **5a-b**, but does impact τ_{S1} for the parent DHPs and τ_{T1} for both core-extended and non-core extended DHPs. Upon investigation ϕ_{f} for the PCs reported herein, we found that ϕ_{f} is relatively low (<9%) for all DHPs discussed in this work except for **4**, **4a**, and **5a** for which ϕ_{f} was still less than 40%.

After probing the ability of DHP PCs and **PhenO** to control O-ATRP at low PC loadings, we are still uncertain as to the PC properties and polymerization conditions that facilitate control at low ppm PC loadings for DHP PCs. Further investigation into PC properties such as ϕ_{ISC} and k_{a} at relevant concentrations of monomer and initiator may shed light on this.

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CHAPTER 3 – IMPACT OF ALKYL CORE SUBSTITUTION KINETICS IN DIARYL
DIHYDROPHENAZINE PHOTOREDOX CATALYSTS ON PROPERTIES AND
PERFORMANCE IN O-ATRP[‡]

3.1 – OVERVIEW

Organocatalyzed atom transfer radical polymerization (O-ATRP) is a controlled radical polymerization (CRP) method mediated by organic photoredox catalysts (PCs) for producing polymers with well-defined structures. While *N,N*-diaryl dihydrophenazine PCs have successfully produced polymers with low dispersity ($\mathcal{D} < 1.3$) in O-ATRP, low initiator efficiencies ($I^* \sim 60\text{--}80\%$) indicate an inability to achieve targeted molecular weights and have been attributed to the addition of radicals to the PC core. In this work, we measure the rates of alkyl core substitution (AkCS) to gain insight into why PCs differing in *N*-aryl group connectivity exhibit differences in polymerization control. Additionally, we evaluate how PC properties evolve during O-ATRP when a non-core-substituted PC is used. PC **1** with 1-naphthyl groups in the *N*-aryl position resulted in faster AkCS ($k_1 = 1.21 \pm 0.16 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 2.04 \pm 0.11 \times 10^{-3} \text{ s}^{-1}$) and better polymerization control at early reaction times as indicated by plots of molecular weight (number average molecular weight = M_n) vs. conversion compared to PC **2** with 2-naphthyl groups ($k_1 = 6.28 \pm 0.38 \times 10^{-4} \text{ s}^{-1}$; $k_2 = 1.15 \pm 0.07 \times 10^{-3} \text{ s}^{-1}$). The differences in rates indicate that *N*-aryl connectivity can influence polymerization control by changing the rate of AkCS PC formation. The rate of AkCS increased from the first to the second substitution, suggesting that PC properties are modified by AkCS. Increased PC radical cation (PC^{•+}) oxidation potentials ($E_{1/2} = 0.26\text{--}0.27 \text{ V vs. SCE}$) or longer triplet excited state lifetimes ($\tau_{T1} = 1.4\text{--}33 \text{ }\mu\text{s}$) for AkCS PCs **1b** and **2b** compared to parent

[‡]Puffer, K.O.; Corbin, D.A; Miyake, G.M. Impact of Alkyl Core Substitution Kinetics in Diaryl Dihydrophenazine Photoredox Catalysts on Properties and Performance in O-ATRP. *ACS Catal.* **2023**, *13*, 14042-14051.

PCs **1** and **2** ($E_{1/2} = 0.21\text{--}0.22$ V vs. SCE, $\tau_{T1} = 0.61\text{--}3.3$ μs) were observed and may explain changes to PC performance with AkCS. In O-ATRP, faster access to altered PC properties from AkCS results in better performance at early times for parent PCs. At later times when primarily AkCS PC is present, or when comparing AkCS PCs directly, PC properties determine control. Insight from evaluation of the formation, properties, and performance of AkCS PCs will facilitate their use in O-ATRP and in other PC-driven organic transformations.

3.2 – INTRODUCTION

Photoredox catalysis is an approach to chemical transformations that employs a catalyst activated by light to initiate redox chemistry and access unique chemical transformations under mild reaction conditions.¹⁻⁴ PC-mediated syntheses can be more energy efficient relative to typical thermally-driven methods, allow for spatial and temporal control, access unique reaction pathways, and can provide selective reactivity.⁵ In photoredox catalysis, photoexcitation results in an excited state PC (PC*) that is more reducing or oxidizing relative to the ground state PC and can engage in single electron transfer (SET) or energy transfer reactivities provided it is sufficiently long-lived for a bimolecular reaction to occur.⁶⁻⁸ Therefore, both the photophysical and redox properties of the PC are essential to performance.⁹ Substantial progress in photoredox catalysis has largely used Ru and Ir complexes, which are notable for strong visible light absorption, near unity triplet quantum yield (Φ_{ISC}), and redox stability.^{2,6} Despite their utility, Ru and Ir PCs are dependent on rare earth metals.¹⁰ If organic PCs can provide competitive photophysical and redox properties, they have the potential to serve as sustainable alternatives to precious-metal-based PCs.¹¹⁻¹⁴ Use of metal-based catalysts in polymerizations can present additional challenges, including incompatibility with certain reagents and contamination of the final polymer product. For example, atom transfer radical polymerization (ATRP) is a popular CRP method that employs transition metal catalysts such as Cu¹⁵ or Ru¹⁶ to produce well-defined

polymers. However, metal contamination of the polymer matrix can limit ATRP's use in certain metal-sensitive electronic or biomedical applications.¹⁷⁻¹⁹ Additionally, traditional ATRP may not be suitable for monomers that strongly interact with metal catalysts.^{17,20}

O-ATRP is a variant of ATRP that employs organic PCs and light to mediate a controlled polymerization. Consequently, O-ATRP eliminates metal contamination and can provide access to monomers that coordinate to metal catalysts while allowing for spatial and temporal control.^{12,18} As a CRP technique, O-ATRP allows for the synthesis of polymers with precisely tailored molecular weights, compositions, and architectures. Well-defined polymer structures are necessary for applications including drug delivery, surface functionalization, and more.²¹⁻²³ To achieve polymerization control, O-ATRP mediates an equilibrium between the activation and deactivation of a growing polymer chain (Figure 3.1). Activation by PC* is followed by rapid deactivation by the PC⁺⁺, resulting in a low concentration of radicals and minimizing undesirable bimolecular radical termination reactions which contribute to a high $\bar{D}$ (>1.5) and non-unity I^* . Adequate PC* reduction potentials [$E^\circ(^2\text{PC}^{++}/^n\text{PC}^*)$] and PC⁺⁺ oxidation potentials [$E^\circ(^2\text{PC}^{++}/^1\text{PC})$] are therefore critical aspects of PC design.^{24,25} For activation, the excited-state reduction potential [$E^\circ(^2\text{PC}^{++}/^n\text{PC}^*)$] of the PC must be sufficiently negative to reduce the C–Br bond of either an alkyl halide initiator or deactivated polymer chain-end ($[E^\circ(^2\text{PC}^{++}/^n\text{PC}^*)] < -0.6$ to -0.8 V vs. SCE). For deactivation, the PC⁺⁺ must have an oxidation potential positive enough to rapidly oxidize the propagating polymer radical, forming a halide-capped polymer ($E^\circ(^2\text{PC}^{++}/^1\text{PC}) > -0.8$ V vs. SCE) and regenerating the ground state PC. Photophysical properties including molar absorptivity ($\epsilon_{\text{max,abs}}$), wavelength of maximum absorption ($\lambda_{\text{max,abs}}$), charge transfer (CT) character, and excited state lifetimes (τ) have also been found to be catalytically relevant and influence polymerization control.^{6,18,26} Since the seminal reports of O-ATRP in 2014 with the use of perylene²⁷ and 10-

phenyl phenothiazine²⁰ as PCs for O-ATRP, several new families of highly reducing organic PCs have been used, including phenoxazines¹³, dihydrophenazines¹², dihydroacridines²⁸, and other phenochalcogenazines²⁹. This work focuses on dihydrophenazine PCs, which are notable for their highly reducing excited state and good polymerization control ($D < 1.3$).¹²

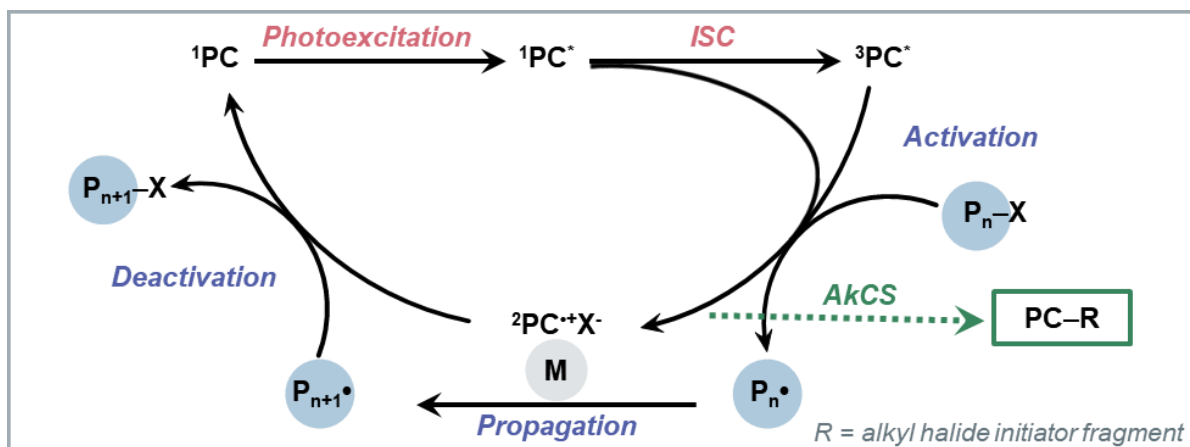


Figure 3.1. Proposed mechanism for O-ATRP, proceeding through an oxidative quenching photoredox pathway.

O-ATRP with dihydrophenazine PCs has proven to be a robust method for producing polymers with low D , but in early work I^* was typically 60–80%, which indicates an inability to achieve targeted molecular weights.¹² It was hypothesized that the observed low I^* is a result of initiator-derived alkyl radicals adding to the PC core, which prevents initiation and growth of the predicted number of polymer chains.³⁰ More recent work identified aryl core substitution (ArCS) as an approach to modify PC properties and improve I^* by blocking the positions available for addition of alkyl radicals to the PC core.^{31,32} In these studies, ArCS PCs were observed to have near unity I^* and facilitate control with low PC loadings in O-ATRP (5 – 50 ppm). Notably, low PC loadings simplify polymer purification and lower reagent costs, improving the overall utility of O-ATRP.^{31, 32} In other work, core substitution by radical addition of alkyl halide initiator fragments was investigated through the reaction of *N,N*-di(2-naphthyl)-5,10-dihydrophenazine (PC **2**) and diethyl 2-bromo-2-methylmalonate (DBMM) (Figure 3.2).³⁰ Through model reactions

and spectroscopic studies, it was found that alkyl radicals generated from the initiator add twice to the core of PC **2**, and that O-ATRP with an AkCS PC results in $I^* \sim 100\%$. Additionally, the AkCS side reaction was leveraged to create core-substituted PCs that mediated the polymerization of acrylate monomers via O-ATRP with moderate to good control ($\bar{D} = 1.15\text{--}1.45$, $I^* = 83\text{--}127\%$). In a following paper, AkCS was explored further through investigation of the reaction between 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine and four alkyl bromide O-ATRP initiators (Figure 3.2).³³ AkCS was found to alter PC photophysical and redox properties, and model reactions were used to improve mechanistic understanding of addition to the PC core by alkyl halide-derived radicals. Furthermore, AkCS combined with decreased solvent polarity was found to enable low PC loadings, with moderate control ($\bar{D} = 1.36$, $I^* = 107\%$) at 10 ppm. Similarly, Zhang et al. explored AkCS with 5,10-di(4-methoxyphenyl)-5,10-dihydrophenazine and several alkyl halide initiators and observed improved I^* for most AkCS PCs.³⁴

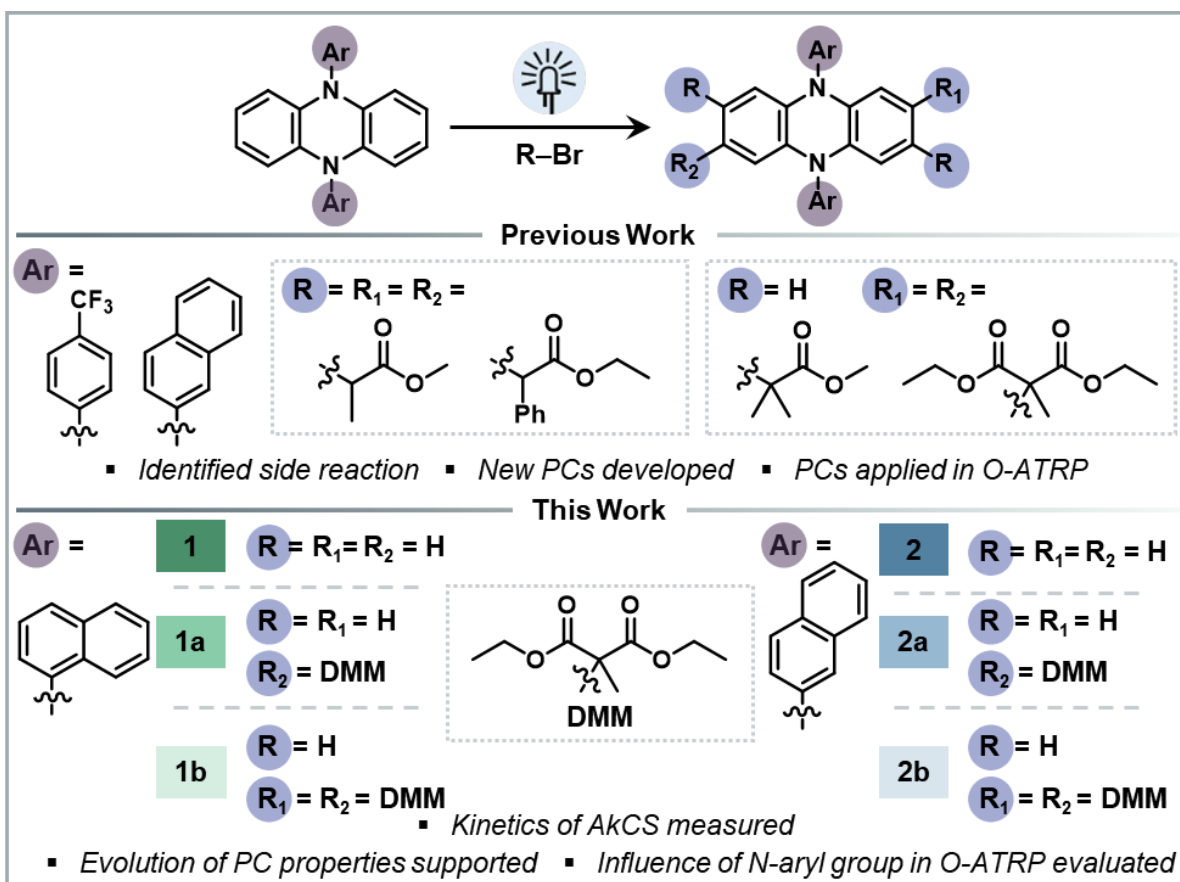


Figure 3.2. General schematic of the AkCS reaction (top), previous work on AkCS (middle) and PCs explored in this work (bottom). DMM = alkyl fragment of diethyl 2-bromo-2-methylmalonate, diethyl 2-methylmalonate. Note that while the PC 2-, 3-, 7-, and 8- positions can all undergo monosubstitution and disubstitution produces a mixture of 2- and 7- and 3- and 7- regioisomers, one isomer is depicted here for simplicity in both cases. See the SI for reaction conditions.

The changes to PC properties and polymerization outcomes observed with AkCS highlight the importance of evaluating the kinetics of AkCS. In the work described herein, we measured the rate at which core-substituted PC is formed and begins to mediate the polymerization in place of the parent PC (Figure 3.2). The rate of substitution was found to increase from the first to second substitution, indicating an evolution of PC properties that was supported through PC characterization. Additionally, PCs with *N*-aryl groups differing only in naphthyl connectivity had inequivalent rates of substitution, providing insight into why they perform differently in O-ATRP. Overall, this work provides fundamental understanding into how AkCS influences polymerization outcomes through the examination of the substitution rate and PC property evolution.

3.3 – RESULTS AND DISCUSSION

AkCS Kinetic Studies. While prior work demonstrated the impact of AkCS on PC properties and performance in O-ATRP and explored the mechanism of radical addition of alkyl halide initiator fragments to the core of *N,N*-diaryl dihydrophenazine PCs,^{30,33} the studies herein demonstrate the importance of the rate at which AkCS is occurring on reaction outcome. Previous studies on AkCS showed PC properties including molar absorptivity ($\epsilon_{\text{max,abs}}$), wavelength of maximum absorption ($\lambda_{\text{max,abs}}$), wavelength of maximum emission ($\lambda_{\text{max,em}}$), and redox potentials are altered by AkCS, as are polymerization outcomes (increased I^*).³³ Both observations suggest that PC properties are evolving over the course of the polymerization when parent PCs are used. We proposed that further understanding of the rate of AkCS and the properties of AkCS PCs would provide insight into why certain PCs impart superior polymerization control in O-ATRP despite similar structures. Specifically, we hypothesized that PC *N*-aryl group identity will impact rate of substitution and that differences in substitution rates can explain differences in PC performance. PCs **1** and **2**, differing only in the connectivity of their *N*-aryl groups, have been reported to perform inequivalently in O-ATRP.^{12,35} It is unclear from prior work which photophysical and redox properties account for the observed differences.³⁶ If the rates of AkCS for PCs **1** and **2** are inequivalent, PC properties will evolve more quickly for one PC, potentially explaining differences in polymerization outcomes. Alternatively, the final properties of the AkCS PC may determine polymerization control regardless of the speed with which they are accessed.

To explore the hypothesis above, we targeted the substitution of PCs **1** and **2** by the alkyl halide initiator DBMM. DBMM fragments ($R^\bullet$) were found to substitute the core of dihydrophenazine PCs twice to produce a disubstituted PC in prior work (combination of 2- and 7- and 3- and 7- regioisomers).³³ Tetra- versus disubstitution was determined by the sterics of the initiator, and with bulkier tertiary alkyl bromide initiators including DBMM resulting in

disubstitution. We hypothesized that for PC **1** and **2**, as sequential substitutions to the PC core by R[•] occurs, each substitution product and rate constant could be isolated. In preparation for the kinetic experiments, PCs **1**, **1a**, **1b**, **2**, **2a**, and **2b** were synthesized. Each derivative of the parent PC (monosubstituted PCs **1a** and **2a** and disubstituted PCs **1b** and **2b**) was isolated and found to have a distinct ¹H NMR spectra (Figures A3.8, A3.10, A3.12, and A3.14). The distinct spectra observed for the monosubstituted and disubstituted PCs indicated that the rate constants for substitution could be determined by following the reaction between the PCs **1** and **2** and R[•] via ¹H NMR.

The rate constants for the first substitution (k_1) were measured by irradiating PC **1** or **2** with DBMM in *N,N*-dimethylacetamide (DMAc) and monitoring the conversion to PCs **1a** and **2a** over time. The first substitution followed linear pseudo-first-order kinetics from which the rate constant k_1 was determined (Figure 3.3). By lowering the concentration of initiator relative to PC from excess to stoichiometric ([PC] = [DBMM] = 1.53 mM), the first substitution was promoted over the second. For determination of the rate constants for the second substitution (k_2), the same reaction conditions for the first substitution were applied with starting from monosubstituted PC **1a** or **2a** ([PC] = [DBMM] = 1.53 mM). The second substitution followed linear pseudo-first-order kinetics from which rate constant k_2 was determined (Figure 3.3). Notably, timepoints taken after ~50% conversion deviated from linear pseudo-first-order kinetics for both substitutions, suggesting that as DBMM concentration lowers, pseudo-first-order kinetics may no longer be a good approximation. For the AkCS reaction, activation was predicted to be rate-limiting and the concentration of DBMM was assumed to be very high relative to the concentration of PC*. However, as DBMM is consumed it may no longer be in large enough excess compared to PC* for this pseudo-first-order assumption to be accurate. To address this possibility, all timepoints

were taken before 50% conversion. A pseudo-first-order kinetic model was developed using the assumption that activation is the rate limiting step (Figure A3.29). The concentration of PC over time predicted by the model closely matched the experimentally measured concentrations, supporting this initial hypothesis of activation as the rate limiting step (Figure A3.30). Alternatively, radical addition of $R^\bullet$ to PC^{*+} could be the rate limiting step instead of SET, in which case second-order kinetics would apply (Figures A3.31 and A3.32). To support that AkCS of the PCs is a light-driven reaction, control reactions were performed under standard reaction conditions in the dark, and negligible AkCS was observed (Figures A3.25-A3.28).

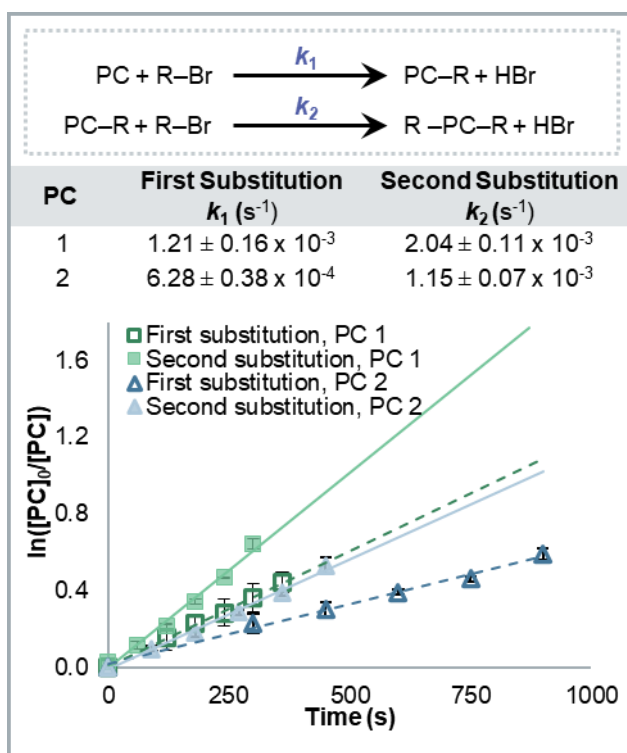


Figure 3.3. Pseudo-first-order kinetic plots from timepoints analyzed by 1H NMR for the first and second substitution of PC **1** and PC **2** by $R^\bullet$. Conditions: [DBMM]:[PC] = [1]:[1] in 7.50 mL DMAc. AkCS was run with a white LED beaker as the light source (see SI for more information). Rate constants for each substitution reaction were obtained from the slope of PC consumption ($\ln[PC]_0/[PC]$) vs. time.

Contrary to our initial prediction that the first substitution would be faster than the second due to the increased number of positions available for substitution, for PC **1** $k_2 = 2.04 \pm 0.11 \times 10^{-3}$

$^3 \text{ s}^{-1}$ and $k_I = 1.21 \pm 0.16 \times 10^{-3} \text{ s}^{-1}$. This same trend was observed for PC **2** ($k_I = 6.28 \pm 0.38 \times 10^{-4} \text{ s}^{-1}$; $k_2 = 1.15 \pm 0.07 \times 10^{-3} \text{ s}^{-1}$). The increase in AkCS rate after the first substitution suggests an evolution of PC properties occurs on this time scale during O-ATRP. In particular, the observed rate increases may indicate modification to properties that influence excited state reduction potential ($E^{\circ*}$) or PC^{•+} oxidation potential ($E_{1/2}$). Access to PC properties that facilitate either SET or radical addition, depending on which step is rate-limiting, would result in a faster second substitution of PC by R[•] due to the increased thermodynamic driving force for AkCS. Additionally, these results show changes to PC properties are happening at early reaction times relative to O-ATRP, which typically reaches high conversions between 8–24 hours depending on solvent polarity.^{30,35} The AkCS reactions reach ~50% conversion between 5–15 minutes, much shorter than the timescale of O-ATRP. The timescale of AkCS suggests that AkCS PCs mediate most of the polymerization. Importantly, AkCS PCs have different properties than non-AkCS PCs, so AkCS PC properties are overall more important for governing polymerization control.

Comparing PC **1** and PC **2**, PC **1** undergoes AkCS faster than PC **2** ($k_I = 1.21 \pm 0.16 \times 10^{-3} \text{ s}^{-1}$ for PC **1**; $k_I = 6.28 \pm 0.38 \times 10^{-4} \text{ s}^{-1}$ for PC **2**). Similarly, PC **1a** ($k_2 = 2.04 \pm 0.11 \times 10^{-3} \text{ s}^{-1}$) is substituted faster than **2a** ($k_2 = 1.15 \pm 0.07 \times 10^{-3} \text{ s}^{-1}$). We initially hypothesized that the increased sterics of PC **1** would inhibit core substitution and slow the rate of AkCS compared to PC **2**, but instead PC properties may determine the rate of core substitution. In previous work, it has been observed that PC **1** mediates O-ATRP with a faster polymerization rate than PC **2**, consistent with the trend observed here for AkCS.¹² Overall, the results from the kinetic experiments support the hypothesis that the *N*-aryl group will influence the rate of substitution, but further investigation is needed to determine why the 1-naphthyl group in PC **1** significantly increases the rate over 2-naphthyl in PC **2**. However, the increased rate of AkCS for PC **1** and faster access to improved PC

properties could explain why it has historically exhibited better polymerization control in O-ATRP than PC **2** (see below).³⁷

Photophysical and Redox Characterization of PCs. The observed increase in the rate between the first and second substitution led us to hypothesize that AkCS is modifying PC properties during the beginning of O-ATRP with PC **1** and **2**. To quantify the change in PC properties with AkCS, the photophysical and redox properties of the PCs were measured. Furthermore, in previous studies with dihydrophenazine PCs AkCS has been found to impact and often improve catalytically relevant properties including $\epsilon_{\text{max,abs}}$, $\text{PC}^{\bullet+} E_{1/2}$, and $E^{\circ*}$ which impact polymerization control in O-ATRP. We predicted that similar improvements to PC properties would be observed with AkCS of PC **1** and **2**.

Steady-state Absorption and Emission Spectroscopy. PC $\epsilon_{\text{max,abs}}$ and $\lambda_{\text{max,abs}}$ both are reported to influence PC performance in O-ATRP.^{13,26} Compared to PCs **1** and **2** ($\epsilon_{\text{max,abs}} = 4,300 \text{ M}^{-1}\text{cm}^{-1}$ for **1**; $7,100 \text{ M}^{-1}\text{cm}^{-1}$ for **2**), AkCS PCs **1b** and **2b** exhibit higher molar absorptivities ($\epsilon_{\text{max,abs}} = 6,800 \text{ M}^{-1}\text{cm}^{-1}$ for **1b**; $8,500 \text{ M}^{-1}\text{cm}^{-1}$ for **2b**) and have slightly red-shifted $\lambda_{\text{max,abs}}$ (Table 3.1). The high $\epsilon_{\text{max,abs}}$ observed for PC **2b** is notable because a higher $\epsilon_{\text{max,abs}}$ indicates an increase in the efficiency of photoexcitation and is typically correlated to better PC performance in O-ATRP due to increased excited state population. Examining the influence of AkCS on emission, it was found that the $\lambda_{\text{max,em}}$ is blue-shifted from parent PCs **1** and **2** ($\lambda_{\text{max,em}} = 645 \text{ nm}$ for **1**; $\lambda_{\text{max,em}} = 640 \text{ nm}$ for **2**) to AkCS PCs **1b** and **2b** ($\lambda_{\text{max,em}} = 629 \text{ nm}$ for **1b**; $\lambda_{\text{max,em}} = 623 \text{ nm}$ for **2b**) (Figure 3.4). The observed changes in $\lambda_{\text{max,abs}}$ and $\lambda_{\text{max,em}}$ indicate that AkCS of PC **1** and **2** by R' stabilizes the π^* orbitals involved in light absorption (S_n) or the ground state (S_0) while destabilizing the lowest energy (S_1) π^* orbitals involved in emission, which are likely CT states (see below for discussion on CT states). Consideration of the higher singlet excited state energies ($E_{S1,\text{exp}}$) observed for AkCS

PCs provides additional evidence for a slightly higher energy CT state. AkCS PC **1b** had a 0.05 eV increase in E_{S1} from PC **1** while AkCS PC **2b** had a 0.06 eV increase in E_{S1} from PC **2**. Overall, the change in absorption and emission of the PCs after AkCS supports that PC properties are modified with AkCS and therefore likely evolve during O-ATRP.

Table 3.1. Summary of photophysical properties for PCs.

PC	$\lambda_{\text{max,abs}}$ (nm) ^a	$\epsilon_{\text{max,abs}}$ (M ⁻¹ cm ⁻¹) ^a	$\lambda_{\text{max,em}}$ (nm) ^b	Stokes shift (nm) ^c	$E_{S1,\text{exp}}$ (eV) ^d	$E_{T1,\text{exp}}$ (eV) ^d	τ_{S1} (ns) ^e	τ_{T1} (μ s) ^e	Φ_f (%) ^f
1	362	4300	645	283	1.92	2.24	8.5	0.61	1.30
1b	365	6800	629	264	1.97	2.23	10	1.4	2.10
2	343	7100	640	297	1.93	2.34	4.0 ^g	3.3	0.56
2b	350	8500	623	273	1.99	2.30	7.9	33	1.74

^aMeasured by UV-vis spectroscopy in DMAc. ^bMeasured by steady-state fluorescence spectroscopy in DMAc. ^cStokes shift = $\lambda_{\text{max,em}} - \lambda_{\text{max,abs}}$. ^d E_{S1} and E_{T1} (eV) = 1239.8/ λ (nm); calculated from $\lambda_{\text{max,em}}$ from fluorescence (measured at room temperature) and phosphorescence (measured at 77 K), respectively. ^eDetermined by transient absorption spectroscopy. ^fMeasured in DMAc by absolute methods. ^gMeasured by time-correlated single photon counting in DMAc.

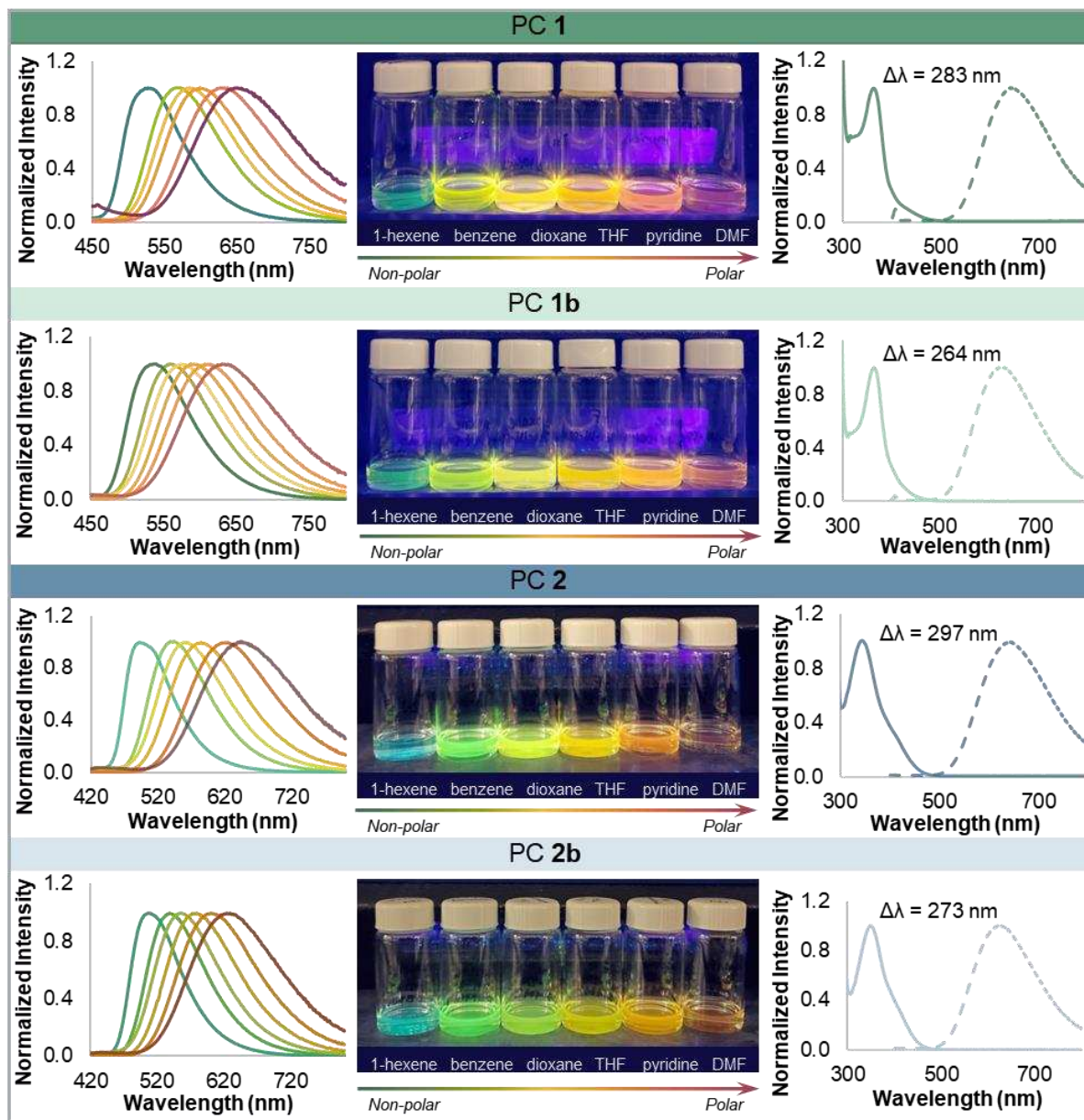


Figure 3.4. From left to right, overlaid emission profiles of PCs in different polarity solvents, photographs of the PCs dissolved in solvents of increasing polarities under UV light irradiation, overlaid normalized absorption (solid line) and emission (dotted line) spectra acquired in DMAc.

As a result of their blue-shifted $\lambda_{\text{max,em}}$ and red-shifted $\lambda_{\text{max,abs}}$, AkCS PCs display a smaller Stokes shift ($\Delta\lambda = \lambda_{\text{max,em}} - \lambda_{\text{max,abs}}$) than the corresponding parent PCs ($\Delta\lambda = 264$ nm for **1b**; 273 nm for **2b** $\Delta\lambda = 283$ nm for **1**; 297 nm for **2**). The Stokes shift provides insight into the CT character of the PC, with a large Stokes shift typically indicating CT character. PCs that access CT excited states have been found to perform better in O-ATRP than locally excited (LE) PCs, which we posit

is due to CT facilitating ISC to longer-lived triplet excited states³⁸ and enhanced electron transfer rates by consolidation of electron density.³⁷ While all the PCs herein exhibit broad and featureless emission profiles indicative of CT, the slight reduction of Stokes shift in AkCS PCs compared to the parent PCs suggests that AkCS is either altering the energy or character of the CT singlet state (Figure 3.4). To further evaluate the CT character of the PCs through solvatochromism, emission spectra were obtained in solvents of varied polarity. Consistent with the measured Stokes shifts, while the AkCS PCs displayed solvatochromism, the extent of solvatochromism was smaller than in the corresponding parent PC (Figure 3.4). Since solvatochromism in dihydrophenazine PCs arises from the stabilization of polar CT states by polar solvents and causes red-shifted emission,^{35,37} this data reinforces that AkCS PCs retain CT states, but the energetics of the CT state is altered by the core substituents.

Next we measured the PC triplet energies ($E_{T1,exp}$, determined from the $\lambda_{max,em}$ of phosphorescence measured at 77 K), which were all found to be higher than the E_{S1} measured at room temperature for each PC. While typically E_{S1} is higher or close to isoenergetic with the E_{T1} in dihydrophenazine PCs,³⁹ the observed increase from E_{S1} to E_{T1} is likely because E_{T1} was measured at 77 K, limiting internal conversion to a lower energy singlet state before ISC and within the triplet state after ISC. In the AkCS PCs, E_{T1} was higher for the PC **2** compared to PC **1** (E_{T1} = 2.24 eV for **1**; E_{T1} = 2.30 eV for **2**), and higher for PC **2b** compared to PC **1b** (E_{T1} = 2.23 eV for **1b**; E_{T1} = 2.30 eV for **2b**). Conclusions about the lowest energy triplet state (T_1) cannot be made based on these results, but they suggest that the initial states occupied after ISC (T_n) in the PC **2** family are higher than those in the PC **1** family. Additionally, while AkCS raises E_{S1} , it appears to lower the E_{T1} of the state accessed after ISC.

To evaluate decay pathways from the singlet excited state that compete with ISC or SET,

quantum yield of fluorescence (Φ_f) was measured. For all the PCs characterized, the Φ_f was low (0.56 – 2.10%), suggesting radiative decay through fluorescence is not a primary decay pathway. However, the AkCS PCs were found to have higher Φ_f than their respective parent PCs (ex. Φ_f = 1.30% for **1**, Φ_f = 2.10% for **1b**). Furthermore, the PC **1** family had higher Φ_f when compared to the PC **2** family (Φ_f = 0.56% for **2**, Φ_f = 1.74% for **2b**). While an increase in non-radiative decay pathways might be predicted from the addition of flexible, freely rotating alkyl core substituents, an increase in Φ_f is instead promoted.⁴⁰ The observed increase in Φ_f in the AkCS PCs is consistent with prior work demonstrating that CT states can minimize radiative decay.³⁸

Transient Absorption Spectroscopy. While the identity and duration of excited states have been found to be influential in determining PC performance in O-ATRP,²⁵ the excited-state lifetimes of AkCS dihydrophenazine PCs had not been evaluated prior to this work. The kinetic studies suggest that AkCS PCs are the dominant species after the beginning of the polymerization, and as such the excited-state lifetimes of the AkCS PCs were expected to have a significant influence on O-ATRP outcomes. The triplet excited state is proposed to be the most catalytically relevant in our system,^{25,41} and consequently the triplet excited-state lifetime (τ_{T1}) will impact polymerization control. However, the singlet excited-state lifetime (τ_{S1}) is still relevant at high substrate concentrations in dihydrophenazine PCs and is associated with a higher reaction driving force because of the higher $E^{\circ*}$ of singlet excited states relative to triplet.⁴¹ In comparison to the parent PCs, both AkCS PCs had longer τ_{S1} (τ_{S1} = 8.5 ns for **1**, τ_{S1} = 4.0 ns for **2**; τ_{S1} = 10 ns for **1b**, τ_{S1} = 7.9 for **2b**). Interestingly, PC **1** had a longer τ_{S1} than PC **2**, and PC **1b** had a longer τ_{S1} than PC **2b**. This suggests that both the alkyl substituents and the *N*-aryl group are influencing decay pathways from the singlet state, including but not limited to ISC.

Next considering the τ_{T1} , both AkCS PCs were found to have longer lifetimes than the

corresponding parent PCs, with the increase in τ_{T1} with AkCS much more pronounced for PC **2** and **2b** ($\tau_{T1} = 3.3 \mu\text{s}$ for **2**, $\tau_{T1} = 33 \mu\text{s}$ for **2b**) than for PC **1** and **1b** ($\tau_{T1} = 0.61 \mu\text{s}$ for **1**, $\tau_{T1} = 1.4 \mu\text{s}$ for **1b**). We initially hypothesized that AkCS would shorten τ_{T1} due to the freely rotating alkyl group, increasing access to non-radiative decay pathways. Based on increased τ_{T1} with AkCS, we instead propose that the addition of bulky alkyl groups to the core adds rigidity to the *N*-aryl group where the triplet excited state is most likely located due to steric constraints. Comparing the PCs with different *N*-aryl groups, the τ_{T1} of PC **2** was longer than PC **1**, and the τ_{T1} of PC **2b** was substantially longer than PC **1b**, opposite of the trend observed with τ_{S1} . Notably, the lifetime of PC **2b** is comparable to the lifetimes of ArCS PCs with CT to the core substituent.³² While currently there is no evidence to support CT to the alkyl core substituent, this result indicates that AkCS has a significant influence on the character and duration of excited states. Further exploration is needed to elucidate how AkCS is altering the population of excited states and leverage the effects for extended τ_{T1} and improved PC performance. Overall, the observed changes to PC excited states with AkCS support the evolution of PC properties.

Redox properties. Both $E^{\circ*}$ and $PC^{*+} E_{1/2}$ are critical to maintaining polymerization control in O-ATRP. Balancing these two intrinsically related properties to promote fast activation and maintain efficient deactivation is an essential part of PC design. Based on the increase in the rate of AkCS from the first to second substitution in both PCs, we hypothesized that $E^{\circ*}$ would increase with AkCS. Instead, the singlet excited state reduction potentials ($E_{S1}^{\circ*}$) for the AkCS PCs ($E_{S1}^{\circ*} = -1.70 \text{ V vs. SCE}$ for **1b**, $E_{S1}^{\circ*} = -1.73 \text{ V vs. SCE}$ for **2b**) were not significantly different from those of the parent PCs ($E_{S1}^{\circ*} = -1.70 \text{ V vs. SCE}$ for **1**, $E_{S1}^{\circ*} = -1.72 \text{ V vs. SCE}$ for **2**). This observation suggests that the driving force for activation is not responsible for the increase in rate between the first and second substitution – instead another catalytically relevant property

(ex. $PC^{*+} E_{1/2}$ or excited state lifetime) may be dominant. Further supporting that E_{S1}^{o*} does not determine rate of substitution, the E_{S1}^{o*} for PC **2** was higher than PC **1**, but PC **1** exhibited faster core substitution. PC **2b** had the highest E_{S1}^{o*} , which in combination with long τ_{T1} and high $\epsilon_{max,abs}$ indicates that this PC should be highest performing in O-ATRP. Recalling that the E_{T1} was measured at 77 K, which explains why the E_{T1}^{o*} is higher than E_{S1}^{o*} in these PCs, relative trends in E_{T1}^{o*} can still be evaluated. Similar to the trend observed in E_{S1}^{o*} , the E_{T1}^{o*} of the AkCS PCs ($E_{T1}^{o*} = -1.96$ V vs. SCE for **1b**, $E_{T1}^{o*} = -2.04$ V vs. SCE for **2b**) were lower than the E_{T1}^{o*} of the respective parent PCs ($E_{T1}^{o*} = -2.02$ V vs. SCE for **1**, $E_{T1}^{o*} = -2.13$ V vs. SCE for **2**) and the E_{T1}^{o*} of PC **2** was higher than PC **1**. Overall, the E^{o*} s were not improved significantly by AkCS and are not likely to be the source of differences in rates of AkCS or PC performance.

We then examined the $PC^{*+} E_{1/2}$, the driving force for deactivation in O-ATRP (Table 3.2). Comparing PC **1** and **2**, the $PC^{*+} E_{1/2}$ were comparable ($E_{1/2} = 0.22$ V vs. SCE for **1**, $E_{1/2} = 0.21$ V vs. SCE for **2**). With AkCS, $E_{1/2}$ increased from the parent PCs for both PC **1b** and **2b** ($E_{1/2} = 0.27$ V vs. SCE for **1b**, $E_{1/2} = 0.26$ V vs. SCE for **2b**). The increase with AkCS was surprising given the mildly electron-donating character of the alkyl groups, which is expected to stabilize the PC^{*+} and make it less oxidizing. However, the two esters on DBMM may be inductively withdrawing enough to destabilize the PC^{*+} . Just as the PC **1** and **2** $PC^{*+} E_{1/2}$ were very similar, the AkCS $PC^{*+} E_{1/2}$ are also within 0.01 V, indicating that the linkage of the *N*-naphthyl group in PC **1** vs. **2** does not have a strong influence on deactivation, while the core substituent has a moderate effect. A higher $PC^{*+} E_{1/2}$ promotes radical addition through the PC^{*+} after the activation step and may explain why the second substitution is faster than the first. This observation also suggests that the radical addition step in AkCS is more likely to be rate limiting than SET. However, the small differences observed between PC **1** and **2** suggest $PC^{*+} E_{1/2}$ is not strongly influential in

determining the faster rate of AkCS observed with PC **1** vs **2**. The increase in $PC^{*+} E_{1/2}$ with AkCS does support the hypothesis that PC properties are evolving and, in several cases, improving through AkCS.

Table 3.2. Summary of redox properties for PCs.

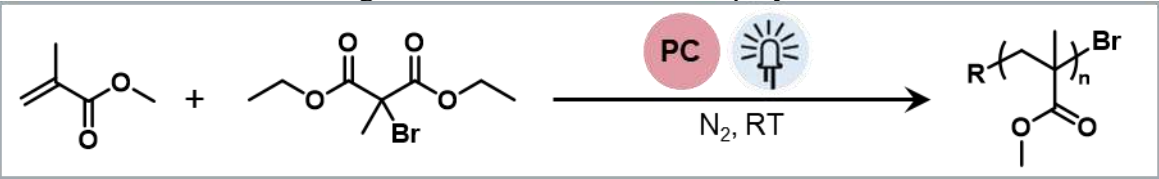
PC	$E_{1/2}$ ($^2PC^{*+}/^1PC$) (V vs. SCE) ^a	E_{S1}^{o*} ($^2PC^{*+}/^1PC^*$) (V vs. SCE) ^b	E_{T1}^{o*} ($^2PC^{*+}/^3PC^*$) (V vs. SCE) ^b
1	0.22	-1.70	-2.02
1b	0.27	-1.70	-1.96
2	0.21	-1.72	-2.13
2b	0.26	-1.73	-2.04

^aFirst oxidation potential measured in DMAc with NBu_4PF_6 as the electrolyte. ^bSinglet and triplet excited state reduction potentials were determined from the $E_{1/2}$ and singlet (E_{S1}) and triplet (E_{T1}) energies, respectively (see the SI for more details).

In summary, photophysical and redox characterization of the parent and AkCS PCs showed that most PC properties were modified through AkCS with $R^{\bullet}$. Several properties correlated with superior performance in O-ATRP improved with AkCS, including $\epsilon_{max,abs}$, excited state lifetimes, and $PC^{*+} E_{1/2}$. Observation of modified properties with PC **1b** and **2b** support the hypothesis that PC properties are evolving and demonstrate that the relevant properties for most of the polymerization are those of the core-substituted PCs. The higher $PC^{*+} E_{1/2}$ observed in the disubstituted PCs compared to parent PCs could explain the increase in AkCS rate if the radical addition step of AkCS is rate limiting rather than activation. To explore the possibility of radical addition as the rate-limiting step, second-order kinetic plots were examined for each PC substitution and were found to have reasonable fits, albeit worse than the fits for the pseudo-first-order plots in most cases (Figures A3.31 and A3.32). Overall, definitive correlation between changes in PC properties and the increase in substitution rate between the first and second substitution is still not fully elucidated and further investigation is needed to determine the rate-limiting step in AkCS. The reason for the increase in AkCS rate with 1-naphthyl versus 2-naphthyl also merits additional study. One possibility is that the longer donor-acceptor distance in PC **2** is

associated with a larger reorganization energy as observed for analogous phenothiazine PCs, which could slow electron transfer or radical addition.³⁶

Application of PCs in O-ATRP. After evaluating the influence of AkCS on PC properties, we wanted to assess if faster access to modified properties (as indicated by the rate of substitution) or the PC properties themselves are more important in determining polymerization control. We hypothesized that faster AkCS would result in better performance in O-ATRP. To explore this hypothesis, O-ATRP of methyl methacrylate (MMA) monomer was performed with each PC in DMAc with DBMM as the initiator (Table 3.3). Comparing the performance of parent PCs **1** and **2** in DMAc, **1** and **2** have similar $\bar{D}$ and I^* at 8 hours ($\bar{D} = 1.15$, $I^* = 89\%$ for **1**, $\bar{D} = 1.17$, $I^* = 90\%$ for **2**). However, PC **1** demonstrates significantly better control at early reaction times than PC **2** based on plots of M_n versus conversion, suggesting that faster core substitution promotes access to PC **1b** and consequently improved PC properties early on (Figures A3.86 and A3.88). Alternatively, the superior control of PC **1** at early times could be a result of faster PC^{*+} generation, which serves as a supplemental deactivator.^{30,42}

Table 3.3. O-ATRP results using PC **1**, **2**, **1b**, and **2b** for the polymerization of MMA^a


PC	Solvent	Conv. (%) ^b	$M_{n, \text{theo}}$ (kDa) ^b	$M_{n, \text{exp}}$ (kDa) ^c	$\bar{D}$ ^c	I^* (%) ^d
1	DMAc	87.1	8.97	10.1	1.15	89
1b	DMAc	91.3	9.39	10.2	1.12	92
2	DMAc	86.4	8.90	9.84	1.17	90
2b	DMAc	87.1	9.48	9.50	1.14	100
1	EtOAc	84.1	8.68	10.6	1.05	82
1b	EtOAc	87.5	9.01	8.79	1.07	102
2	EtOAc	79.5	8.21	8.22	1.04	100
2b	EtOAc	80.5	8.32	8.67	1.05	96

^aReaction scheme for the O-ATRP of MMA catalyzed by PCs **1**, **2**, **1b**, and **2b**. Conditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of solvent (DMAc or EtOAc), 1.00 mL MMA. O-ATRP was run with a white LED beaker as the light source (see the SI for more information).

^bConversion determined by ¹H NMR at 8 hours (DMAc) or 24 hours (EtOAc). ^cDetermined by GPC with multi-angle light scattering ^d $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

Polymerization control in O-ATRP was also evaluated with EtOAc as the solvent. Using a less polar solvent than DMAc (THF, EtOAc) has been found to improve O-ATRP outcomes in prior work.^{30,33} This effect is proposed to be the result of PC^{•+} destabilization in less polar solvents, which encourages ion pairing and increases PC^{•+} $E_{1/2}$, resulting in more efficient deactivation. Decreased solvent polarity also commonly improves properties related to activation by increasing Φ_{ISC} , decreasing non-radiative decay, and increasing excited state lifetimes.³⁰ As expected, O-ATRP in EtOAc resulted in a lower $\bar{D}$ for each PC compared to DMAc and lower I^* for all PCs except **1**. Comparing PC **1** and **2** in EtOAc, PC **1** exhibits lower I^* at 24 hours ($I^* = 82\%$, $\bar{D} = 1.05$) than PC **2** ($I^* = 100\%$, $\bar{D} = 1.04$). However, PC **1** shows better control at early reaction times in EtOAc compared to PC **2** based on plots of M_n versus conversion (Figure 3.5). Together these observations support the hypothesis that faster AkCS results in better control, but indicate the effect is most influential at early polymerization times. At later reaction times, PCs **1** and **2** have been

core-substituted to PCs **1b** and **2b** and the rate of AkCS no longer dominates polymerization control. This could explain why PC **2**, which evolves to PC **2b** with the best PC properties, has better control at high conversions than PC **1**. The consistent difference in PC performance between the PC **2** and PC **1** families suggests that the *N*-aryl group connectivity influences polymerization outcomes for both the parent and AkCS PCs.

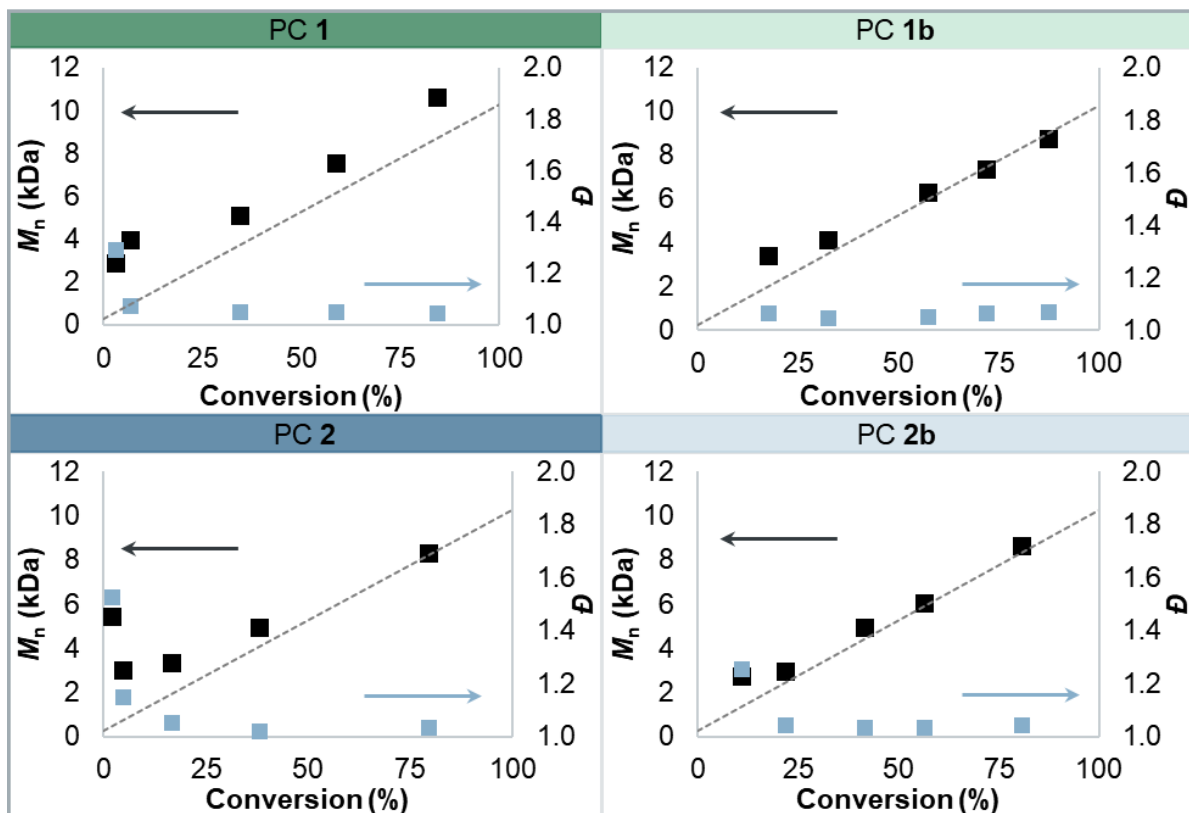


Figure 3.5. Plots of the growth of polymer M_n as a function of monomer (MMA) conversion to polymer (black squares) and $\bar{D}$ (blue squares, secondary y-axis) for each timepoint (2, 4, 8, 12, and 24 hours) in EtOAc. $M_{n, \text{theo}}$ values are represented by the gray dashed line.

Based on the improved $E_{1/2}$ and τ_{T1} observed in AkCS PCs, we hypothesized that AkCS would overall increase polymerization control in O-ATRP. Comparing the performance of PC **1** to **1b** in DMAc at 8 hours, AkCS resulted in comparable $\bar{D}$ and I^* ($\bar{D} = 1.15$, $I^* = 89\%$ for PC **1**; $\bar{D} = 1.12$, $I^* = 92\%$ for PC **1b**). Between PC **2** and **2b**, I^* improved with AkCS and $\bar{D}$ was similar ($\bar{D} = 1.17$, $I^* = 90\%$ for PC **2**; $\bar{D} = 1.14$, $I^* = 100\%$ for PC **2b**), indicating that AkCS can improve

polymerization control. However, the plots of M_n vs. conversion show that the AkCS PCs deviate from a linear trend at early timepoints in comparison to the parent PCs, indicating less control at the beginning of the polymerization (Figures A3.87 and A3.89). Loss of control at early times with PC **1b** and **2b** may result from eliminating the AkCS side reaction as a source of PC^{*+} buildup early in the polymerization, which helps drive deactivation to improve control.⁴² AkCS PCs also reached higher conversions than parent PCs, likely another effect from suppression of the AkCS side reaction (Table 3.3).

For the polymerizations in EtOAc, PC **1b** had a similar $\bar{D}$ to PC **1** ($\bar{D} = 1.05$ for PC **1**; $\bar{D} = 1.07$ for PC **1b**), but a higher I^* of 102% compared to 82% for PC **1** at 24 hours. PC **1b** also had better control at early times than PC **1** as shown by the plot of M_n versus conversion and maintained lower $\bar{D}$ throughout the polymerization (Figure 3.5). PC **2** and PC **2b** show nearly identical $\bar{D}$ and I^* in EtOAc at 24 hours ($\bar{D} = 1.04$, $I^* = 100\%$ for PC **2**; $\bar{D} = 1.05$, $I^* = 96\%$ for PC **2b**), indicating excellent control at high conversions for both PCs. At early reaction times, PC **2b** demonstrates a substantially more linear relationship between M_n and conversion than PC **2** as well as lower $\bar{D}$ (Figure 3.5). For both PC families, the AkCS PCs demonstrated better overall polymerization control than the parent PCs, supporting the hypothesis that AkCS improves PC performance in O-ATRP. Notably, in EtOAc PCs **1** and PC **1b** perform better at early times than PC **2** and PC **2b**, respectively. The observation that AkCS PCs show better control in the plots of M_n versus conversion over parent PCs in EtOAc while the opposite trend was observed in DMAc suggests that solvent polarity alters which effect dominates PC performance. We hypothesize that in the less polar solvent (EtOAc), AkCS PCs with improved PC properties exhibits overall better polymerization control, because solvent effects that bolster catalytically relevant properties will dominate (ex. extended τ_{T1}). In DMAc, the effect of additional PC^{*+} generated through AkCS seems

more influential and may explain the improved control of the parent PCs at early times, although the AkCS PCs still perform better at high conversions.

Since AkCS *N,N*-diaryl dihydrophenazine PCs have been shown to effectively mediate O-ATRP at low PC loadings in previous work,³¹⁻³³ the ability of AkCS PC **2b** to maintain polymerization control at PC loadings < 1000 ppm was evaluated (Table 3.4). O-ATRP down to 250 ppm PC showed minimal loss in polymerization control ($\bar{D} = 1.12$, $I^* = 96\%$), and moderate control was maintained at 50 ppm ($\bar{D} = 1.30$, $I^* = 96\%$). The ability of the AkCS PC to maintain polymerization control at low PC loadings indicates that **2b** is a robust, high-performing PC. To determine if AkCS PC **2b** can achieve higher molecular weights while maintaining control, polymerizations targeting DPs of 250, 500, and 1000 were performed. While polymerization control was maintained at a DP of 250 ($\bar{D} = 1.18$, $I^* = 96\%$), it was lost at DP = 500 and 1000, suggesting that the AkCS PCs are not suited for the controlled polymerization of high molecular weight polymers under these conditions (Table A3.1). Overall, the polymerization data shows that AkCS can be leveraged to achieve improved polymerization control even at low catalyst loadings, especially in low polarity solvents that enhance PC properties.

Table 3.4. O-ATRP results using PC **2b** for polymerization of MMA at varied PC loadings^a

PC Loading (ppm)	Conv. (%) ^b	$M_{n, \text{theo}}$ (kDa) ^b	$M_{n, \text{exp}}$ (kDa) ^c	$\bar{D}$ ^c	I^* (%) ^d
1000	80.5	8.32	8.67	1.05	96
500	78.6	8.13	8.11	1.08	100
250	88.2	9.08	9.47	1.12	96
100	92.9	9.56	9.46	1.21	101
50	94.6	9.72	10.11	1.30	96
25	91.2	9.38	9.44	1.55	99
10	77.0	7.96	18.91	1.49	42

^aConditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[1] 1.00 mL of EtOAc, 1.00 mL MMA. O-ATRP was run with a white LED beaker as the light source (see the SI for more information).

^bConversion determined by ¹H NMR at 24 hours. ^cDetermined by GPC with multi-angle light scattering ^d $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

3.4 – CONCLUSIONS

This work highlights an important consideration for O-ATRP mediated by unsubstituted dihydrophenazine PCs (ex. PC **1** and **2**), which are often utilized in O-ATRP – the parent PC and associated PC properties are only exclusively relevant at the beginning of the reaction. As the polymerization proceeds, AkCS PCs with distinct properties from the parent PCs were found to rapidly form. The rate of AkCS was influenced by *N*-aryl group connectivity, with PC **1** undergoing faster AkCS than PC **2**. Observation of faster AkCS for PC **1** improves our understanding of why PC **1** and **2** perform differently in O-ATRP, but further investigation is needed to determine the cause of the faster substitution rate in PC **1**.

Additionally, the second substitution of DBMM fragments to the PC core was found to be faster than the first, indicating evolution of PC properties upon AkCS. The evolution of PC properties was supported by PC characterization, which revealed that AkCS alters both photophysical and redox properties. Importantly, longer τ_{T1} and higher $PC^{*+} E_{1/2}$ was observed (τ_{T1} = 1.4–33 μ s, $E_{1/2}$ = 0.26–0.27 V vs. SCE), with the improved $E_{1/2}$ upon AkCS potentially explaining increases in rate after the first substitution if radical addition is rate limiting. The rate of AkCS was found to be more important in determining polymerization control at early reaction times, while at later reaction times the properties of the PCs accessed were more influential, especially in EtOAc. AkCS PCs were found to perform better in O-ATRP based on I^* (I^* = 92–102%) and plots of M_n vs. conversion when compared to parent PCs (I^* = 82–100%), again particularly in EtOAc, which has been found to enhance PC properties. Additionally, an AkCS PC was able to maintain polymerization control at PC loadings as low as 50 ppm.

Broadly, this work has improved the fundamental understanding of AkCS in dihydrophenazine PCs and advanced the development of PCs for O-ATRP. We envision radical addition to the core as a facile pathway to tune organic PC structure and properties while

simultaneously minimizing undesirable side reactivity. Insights from this work, including improved understanding of excited-state lifetimes and the influence of *N*-aryl connectivity, will direct future efforts in the design of organic PCs that are relevant to both O-ATRP and the wider field of photoredox catalysis.

3.5 – REFERENCES

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CHAPTER 4 – INFLUENCE OF DIHYDROPHENAZINE PHOTOREDOX CATALYST EXCITED STATE CHARACTER AND REDUCTION POTENTIALS ON CONTROL IN ORGANOCATALYZED ATOM TRANSFER RADICAL POLYMERIZATION[§]

4.1 – OVERVIEW

The development of *N,N*-diaryl dihydrophenazine organic photoredox catalysts (PCs) has enabled numerous examples of organocatalyzed atom transfer radical polymerization (O-ATRP) of methyl methacrylate (MMA) monomer for polymers with low dispersity ($D < 1.30$) and near-unity initiator efficiency ($I^* \sim 100\%$), as well as small molecule synthesis. In this work, we investigate the influence of core substitution (CS) by alkyl, aryl, and heteroatom groups on singlet excited state reduction potential ($E_{\text{SI}}^{\circ*}$). We observe that a highly reducing $E_{\text{SI}}^{\circ*}$ may be a result of a locally excited (LE)-dominated hybridized local and charge transfer (HLCT) excited state in CS PCs, which is influenced by the identity of the core substituent. Additionally, the LE-dominated HLCT character PCs maintain a relatively oxidizing PC radical cation oxidation potential ($E_{1/2}$) for deactivation compared to fully LE PCs reported in prior work. For example, a thiophenol core substituted (heteroatom CS, HetCS) PC shows the most negative $E_{\text{SI}}^{\circ*}$ (-2.07 V vs SCE), more LE character (Stokes shift = 124 nm), and has an oxidizing PC radical cation ($E_{1/2} = 0.30$ V vs SCE). The CS PCs with improved properties, including more negative $E_{\text{SI}}^{\circ*}$, perform best in O-ATRP of MMA with the HetCS PC showing the best control in both DMAc ($D = 1.08$, $I^* = 89\%$) and EtOAc ($D = 1.06$, $I^* = 97\%$). Additionally, the HetCS PC was found to mediate the controlled polymerization of *n*-butyl acrylate (*n*-BA) ($D = 1.24$, $I^* = 97\%$), which has remained challenging

[§] Puffer, K. O.; Olsen-Gwin, A. J.; Portela, B. S.; Chism, K. A.; Dworakowska, S.; Crace, E.; Paton, R. S.; Miyake, G. M. Influence of dihydrophenazine photoredox catalyst excited state character and reduction potentials on control in organocatalyzed atom transfer radical polymerization. *Submitted to ACS Catal.*

for phenazine-based PCs without supplemental deactivation, despite their highly reducing excited states. An aryl CS PC was found to have moderate control as low as 1 ppm PC, indicating facilitation of low PC loadings ($D = 1.33$, $I^* = 69\%$). The relationship between excited state character, E_{S1}^{o*} , and polymerization control observed in this work provides a foundation for increasing the utility of phenazine PCs that is broadly applicable to photoredox catalysis, as demonstrated through the controlled polymerization of *n*-BA and control at low PC loadings.

4.2 – INTRODUCTION

Using the excited state reactivity of a light-activated catalyst has unlocked an entire field of chemistry: photoredox catalysis.¹⁻⁵ Because photoredox catalysts (PCs) utilize the energy from light for single electron transfer chemistry, they can achieve difficult transformations under mild and energy-efficient conditions relative to traditional methods.⁶ Initially, much of catalyst design for photoredox catalysis stemmed from imitation of the properties of Ru and Ir metal-based PCs.^{7,8} An effective PC must absorb light to access an excited state (PC*), and PC* must be thermodynamically matched with the targeted transformation and be sufficiently long-lived to interact with the substrate and carry out the targeted chemistry. Consequently, the efficiency of light absorption (molar absorptivity, $\epsilon_{\text{max,abs}}$), excited state energy (E_{S1}), redox reversibility, excited state lifetime (τ), and quantum yield of intersystem crossing (Φ_{ISC}), are considered important PC design parameters.⁹ PCs that absorb visible light have the added benefit of reducing side reactions through selective excitation in the presence of other substrates that only absorb higher energy light.^{6,3,10}

More recently, the need to retain the PC properties necessary to carry out useful chemical transformations while minimizing the use of costly precious metals motivated the emergence of organic PCs.^{11,12} Diverse organic PCs have been developed to accommodate different chemical reactions, ranging from small molecule transformations to polymerizations.^{13,14} The application of

organic PCs has expanded the scope of controlled radical polymerizations (CRPs) including atom transfer radical polymerization (ATRP), a widely used polymerization strategy.¹⁵⁻¹⁷ In traditional ATRP, a thermally activated Cu or Ru catalyst is used to mediate a controlled polymerization.^{18,19} More recently, Ir and Ru PCs have been applied in ATRP, introducing several of the advantages of photoredox catalysis including spatial and temporal control.^{20,21} Organocatalyzed ATRP (O-ATRP) is a metal-free alternative that not only removes concerns over metal use and contamination^{16,15} but also enables the use of specific monomers that are incompatible with metal catalysts.²²⁻²⁴ For example, the polymer products from O-ATRP are compatible in biomedical applications like bioimaging²⁵ or in dielectric materials,²⁶ in part due to the lack of metal contaminants.

O-ATRP provides precise polymerization control due to the PC's ability to mediate the equilibrium between activation and deactivation of the propagating chain (Figure 4.1A). For activation, the PC must have a sufficient thermodynamic driving force, or PC* reduction potential ($E_{\text{red}} = E^{\circ*} = [E^{\circ}({}^2\text{PC}^{*+}/{}^n\text{PC}^*)]$) to reduce the halide chain-end ($E^{\circ*} < -0.6$ to -0.8 V vs SCE). Rapid deactivation follows activation and propagation, which results in a low concentration of radicals and minimizes irreversible bimolecular terminations that result in loss of polymerization control. Deactivation is governed by the PC radical cation (PC^{*+}) oxidation potential ($E_{\text{ox}} = E_{1/2} = [E^{\circ}({}^2\text{PC}^{*+}/{}^1\text{PC})]$) for reinstallation of the halide chain-end through oxidation of the propagating radical ($E_{1/2} > -0.8$ V vs. SCE). With O-ATRP, polymers with targeted molecular weights (near-unity initiator efficiency, $I^* \sim 100\%$), low variability in chain length ($D < 1.5$), and advanced architectures are accessible for applications including drug delivery,²⁵ electronics,²⁶ and surface functionalization.²⁷ Several families of organic PCs have been successfully applied to O-ATRP, starting with perylene and phenothiazine,^{22,28} and expanding to include phenazines (the focus of this work),²⁹ phenoxazines,³⁰ dihydroacridines,³¹ phenochalcogenazines,³² and more.

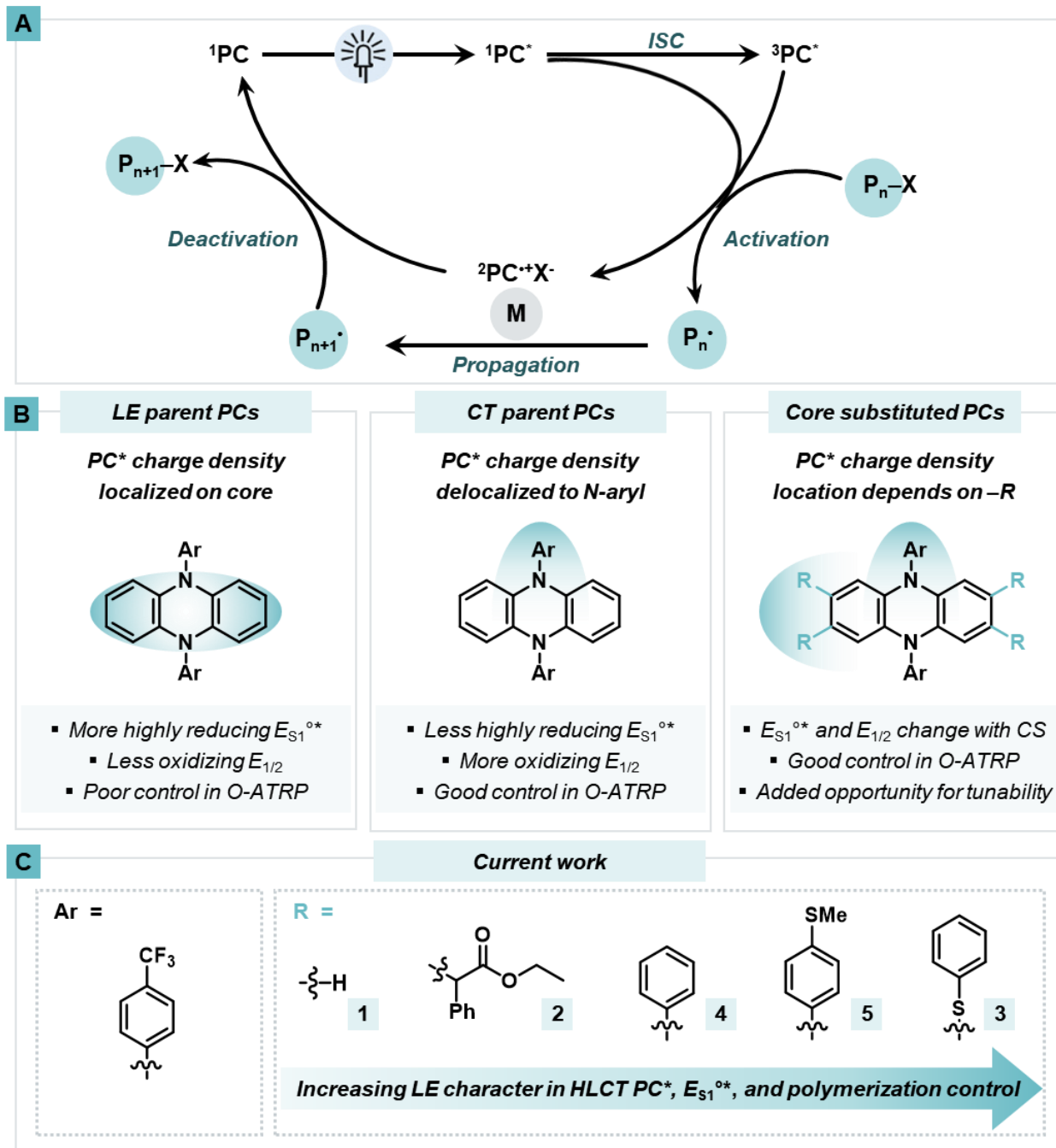


Figure 4.1. (A) Mechanism for O-ATRP proceeding through an oxidative quenching photoredox pathway. (B) Types of *N,N*-diaryl dihydrophenazine PCs explored in prior work. LE PCs typically have electron donating or neutral (phenyl) *N*-aryl groups while CT PCs have electron withdrawing or conjugated (naphthyl) *N*-aryl groups. Alkyl and aryl core groups have both been explored previously. (C) PCs explored in this work with a summary of the observed trends in excited state character, redox potential, and performance in O-ATRP.

The excited state character of the PC, which can be classified as either intramolecular charge transfer (CT) or locally excited (LE) in nature, also plays a major role in impacting

polymerization control for phenazine PCs (Figure 4.1B).³³ For CT PCs, in the excited state the electron density is relocated to a π^* molecular orbital (MO) that is lower in energy than the LE π^* MO, often on the *N*-aryl substituent. Both singlet and triplet CT character excited states can be accessed depending on the PC structure. In phenazine PCs, which typically have a shorter τ and lower Φ_{ISC} compared to similar PC families including phenoxazines and phenothiazines, the singlet excited state ($^1PC^*$) is expected to play an important role in catalysis at relevant concentrations of quencher (alkyl bromide initiator) due to the highly reducing $^1PC^*$ reduction potential (E_{S1}^{o*}).^{34,35} Even in PCs with near-unity Φ_{ISC} , the singlet state has been found to contribute to catalysis at the initiator and PC concentrations commonly used for O-ATRP, although high triplet yields allow for reactions to be performed at much lower catalyst concentrations.³⁴ Consequently, we expect the E_{S1}^{o*} to be a critical factor in PC performance for phenazine PCs 1-5 in this work. For LE PCs, electron density remains localized on the phenazine core in the excited state and a more negative E_{S1}^{o*} is observed compared to CT PCs. CT character PCs therefore fundamentally have a less reducing E_{S1}^{o*} due to the relocation of electron density to a lower energy excited state, which translates to a catalytically non-productive loss of energy. However, CT character PCs have been found to perform better than LE PCs, despite a less negative E_{S1}^{o*} .²⁹ Enhanced performance (in terms of polymerization control) is hypothesized to be the result of consolidation of electron density promoting faster electron transfer rates and changes to the location of electron density facilitating ISC, but is not fully understood.^{33,36} Alternatively, work by Orr-Ewing and coworkers concluded that CT PCs exhibit slower electron transfer rates than LE PCs, which they propose minimizes the concentration of radicals in solution and leads to improved control.^{35, 37-39} Improved control in CT character PCs could also be attributed to their typically more oxidizing $E_{1/2}$ compared to LE PCs, which would promote rapid deactivation.¹⁶ Another

consideration is that solvent polarity strongly influences CT character PCs due to their polar excited states, with more less polar solvents generally improving PC performance.⁴⁰

Recent investigation of the core substitution (CS) of phenazine PCs has introduced an additional scaffold for tunability. In works by Cole et al. and Price et al., aryl CS (ArCS) was investigated, and it was found that addition of electron-donating groups such as methoxyphenyl or *N,N*-dimethylaminophenyl on the core can increase E_{S1}^{0*} and introduce a new CT state onto the PC core substituents, although the increase in E_{S1}^{0*} is often accompanied by a decrease in $E_{1/2}$.^{41,42} Similarly, alkyl CS (AkCS) of phenazine PCs by alkyl halide initiator fragments in some cases resulted in a slightly more negative E_{S1}^{0*} while retaining or improving PC performance,⁴³⁻⁴⁵ but a decreased extent of CT character was observed.⁴⁶ These results demonstrate an important interplay between CS and E_{S1}^{0*} . In this work, we sought to investigate the relationship between CS and E_{S1}^{0*} , to design PCs that improve the performance of CT PCs by increasing E_{S1}^{0*} without eliminating the benefits of CT (Figure 4.1C). By exploring a series of alkyl, aryl, and heteroatom CS (HetCS) phenazine PCs, we found that CS can result in more highly reducing PCs with hybridized local and charge transfer (HLCT) character compared to the non-CS, fully CT character parent PC. Furthermore, the CS PCs maintain an oxidizing $E_{1/2}$ for effective deactivation in O-ATRP. Applying the PCs in O-ATRP, an improvement in control for both the polymerization of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BA) was observed for the most reducing and most LE character PC. This work establishes an improved understanding of the fundamental relationship between excited state character, E_{S1}^{0*} , and polymerization control.

4.3 – RESULTS

Photophysical characterization of PCs. While phenazine PCs with a highly negative E_{S1}^{0*} have been synthesized, in prior work the most reducing phenazine PCs have typically been restricted to those with LE character, which have been observed to perform poorly in O-ATRP

relative to PCs exhibiting CT character. Similarly, PCs with CT character have been designed and applied, but typically have a less negative E_{S1}^{0*} . Without a highly negative E_{S1}^{0*} , control in the polymerization of more challenging monomers like acrylates and acrylamides is limited in part due to secondary alkyl bromide chain-ends which are more difficult to reduce relative to monomers like MMA.^{29,33} Additionally, a highly oxidizing $E_{1/2}$ is necessary to overcome the faster propagation rates, which can also lead to a loss of polymerization control without rapid deactivation. In this work, we sought to design highly reducing PCs that retain the performance of CT character PCs by leveraging CS. To evaluate the relationship between the type of CS and E_{S1}^{0*} , a series of CS PCs were synthesized and characterized to determine photophysical and redox properties. The CS included AkCS by the alkyl fragments derived from the alkyl halide initiator ethyl α -bromophenylacetate (EBP), ArCS by phenyl and 4-(methylthio)phenyl, and HetCS by thiophenol. We hypothesized that HetCS would alter PC properties including $\lambda_{max,em}$ and E_{S1}^{0*} through strong π -donation of electron density into the core. Specifically, we predicted that because of the enhanced electron donation due to direct attachment of the sulfur to the core, PC properties would change more substantially relative to parent PC 1 in the HetCS PC than in the AkCS PC or ArCS PCs.

UV-Vis absorption measurements and time-dependent density functional theory (TD-DFT) computations were used to determine effects of CS on the absorption of the phenazine-derived PCs. Quantum chemical calculations were performed with Gaussian 16 rev C.01. Full computational details and references are given in the SI. PC 1 exhibits the most blue-shifted wavelength of maximum absorption ($\lambda_{max,abs} = 368$ nm) out of the PCs investigated in this work. TD-DFT calculations for PC 1 predict the $S_0 \rightarrow S_4$ excitation to be bright, with an oscillator strength (f) of 0.16 and with orbital contributions of 66% from the $\pi_{HOMO}-\pi_{LUMO+3}$ and 15% from

the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+6}$ (Figure 4.2). Both $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ and $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+6}$ transitions are characterized by the photoexcitation of an electron occupying the π orbital localized on the phenazine core (π_{core}) to the π^*_{core} and to the N -aryl substituent π^*_{aryl} orbital, resulting in HLCT initial excited states associated with absorption, $\pi_{\text{LUMO}+3}$ and $\pi_{\text{LUMO}+5}$ respectively HLCT states are characterized by having both LE and CT contributions, arising from the hybridization of LE and CT excited states.⁴⁷

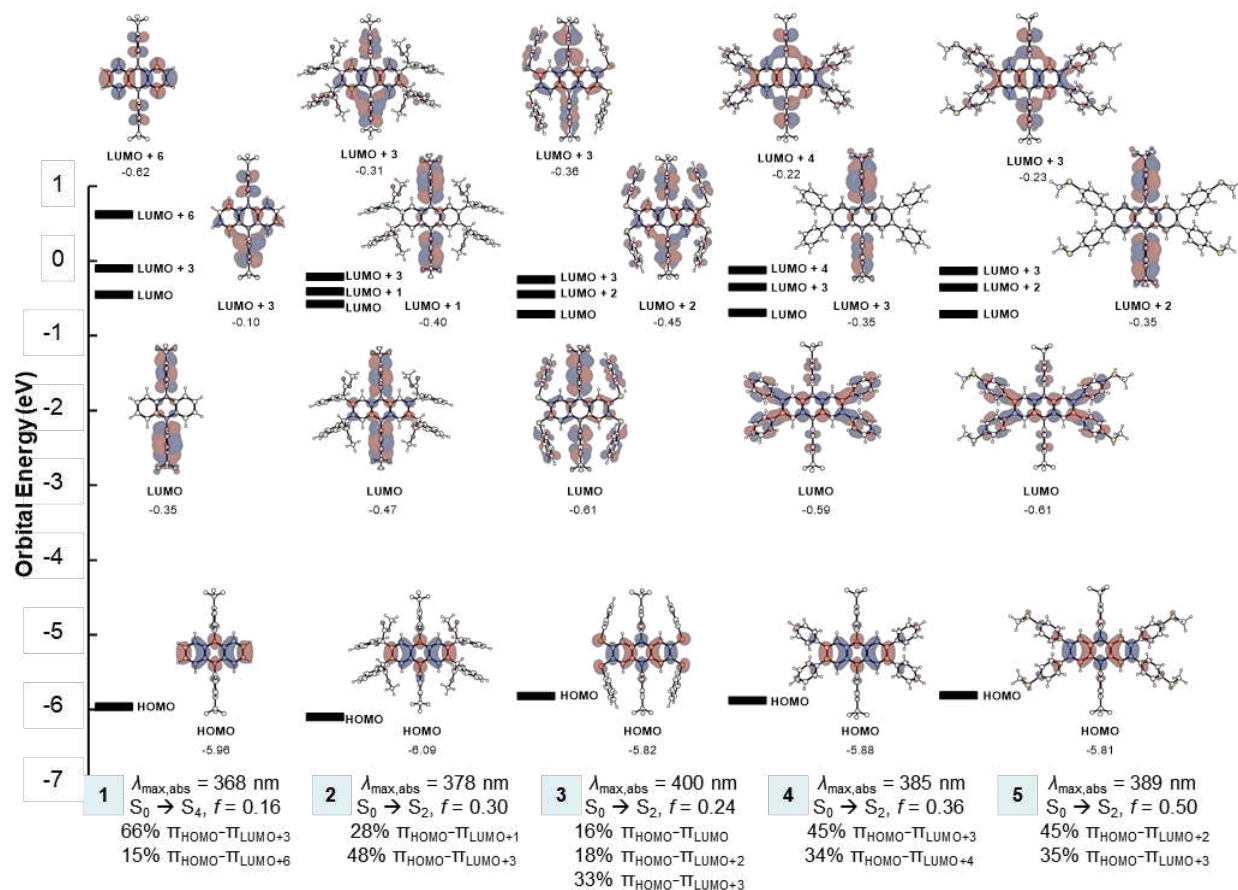


Figure 4.2. TD-DFT (M06-2X-D3/def2-SVPD[C,H],def2-TZVPD[N;O;S]-SMD^{DMAc}// ω B97X-D/6-31+G**-SMD^{DMAc}) computed percentage contributions of corresponding orbitals involved in the photoexcitation of PC **1**, **2**, **3**, **4** and **5** at their corresponding $\lambda_{\text{max,abs}}$ in N,N -dimethylacetamide (DMAc).

For the AkCS PC **2**, the $\lambda_{\text{max,abs}}$ (378 nm) corresponds to the $S_0 \rightarrow S_2$ excitation with $f = 0.30$ and orbital contributions of 28% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+1}$ transition and 48% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ transition. The $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+1}$ transition is of CT character, involving the π_{core} and π^*_{aryl}

orbitals while the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ transition is HLCT, involving the π_{core} , π_{aryl}^* and π_{core}^* orbitals. The HetCS PC 3 has a $\lambda_{\text{max,abs}}$ of 400 nm, which is assigned to be the $S_0 \rightarrow S_2$ excitation with $f=0.24$ and contributions of 16% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}}$ transition (HLCT character), 18% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+2}$ transition (HLCT character) and 33% for $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ transition (HLCT character). For the ArCS PC 4, the $\lambda_{\text{max,abs}}$ (385 nm) corresponds to the $S_0 \rightarrow S_2$ excitation with $f=0.36$ and orbital contributions of 45% $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ (CT character) and 34% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+4}$ (HLCT character). For the other ArCS PC 5, the $\lambda_{\text{max,abs}}$ (389 nm) corresponds to the $S_0 \rightarrow S_2$ excitation with $f=0.50$ and contributions of 45% for $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+2}$ transition (CT character) and 35% for the $\pi_{\text{HOMO}}-\pi_{\text{LUMO}+3}$ transition (HLCT character). All the CS PCs had red-shifted $\lambda_{\text{max,abs}}$ relative to PC 1, which is beneficial for visible-light driven catalysis as it indicates the most favorable absorptions lie further into the visible region (Table 4.1).⁷ Furthermore, CS PCs showed an increase in the $\epsilon_{\text{max,abs}}$ relative to parent PC 1 (4,600 M⁻¹cm⁻¹), indicating improved photoexcitation efficiency. Notably, PC 5 has the highest $\epsilon_{\text{max,abs}}$ (17,400 M⁻¹cm⁻¹) followed by PC 3 (13,100 M⁻¹cm⁻¹), which indicates that HetCS substitution and ArCS substitution with electron-donating groups lead to increased efficiency of photon absorption, which is further corroborated by their computed oscillator strengths.

Table 4.1. Summary of photophysical properties for PCs 1-5 in DMAc.

PC	$\lambda_{\text{max,abs}}$ (nm) ^a	$\epsilon_{\text{max,abs}}$ (M ⁻¹ cm ⁻¹) ^a	$\lambda_{\text{max,em}}$ (nm) ^b	E_{S1} (eV) ^d	$\Delta\lambda$ (nm) ^c	$\Delta\epsilon_{\text{em}}$ (nm) ^e
1	368	4,600 ^f	615	2.02	247	136
2	378	7,500 ^f	584	2.13	206	97
3	400	13,100	524	2.37	124	18
4	385	11,200	572	2.17	187	47
5	389	17,400	546	2.27	157	34

^aMeasured by UV-vis spectroscopy in DMAc. ^bMeasured by steady-state fluorescence spectroscopy in DMAc. ^c $\Delta\lambda = \lambda_{\text{max,em}} - \lambda_{\text{max,abs}}$. ^d $E_{\text{S1}} = 1239.8/\lambda$ (nm); calculated from $\lambda_{\text{max,em}}$ from fluorescence. ^eCalculated from $\lambda_{\text{max,em}}$ in dimethylformamide (DMF) - $\lambda_{\text{max,em}}$ in 1-hexene from fluorescence. ^fPreviously published in Corbin et al.⁴⁴ Additional characterization and details provided in SI.

For the wavelength of maximum emission ($\lambda_{\text{max,em}}$), which correlates with the $E_{\text{S}_1^{\circ*}}$, parent PC 1 has the most red-shifted $\lambda_{\text{max,em}}$ (615 nm) while HetCS PC 3 has the most blue-shifted $\lambda_{\text{max,em}}$ (524 nm) (Table 4.1). The observed difference in $\lambda_{\text{max,em}}$ between PCs 1 and 3 translates into a 0.35 eV difference in singlet excited state energy (E_{S_1}). The trend in $\lambda_{\text{max,em}}$ (blue-shifting with CS) is the inverse of the trend in $\lambda_{\text{max,abs}}$ (red-shifting with CS), suggesting that the core group is stabilizing the initial excited state associated with absorption (S_n) but destabilizing the lower energy excited state associated with emission (S_1). Comparing the energies of the S_n and S_1 states across PCs 1-5 shows that the changes to the energetics increase from parent to alkyl to aryl to heteroatom CS (Figure 4.3A). Furthermore, the trends in both the energy of S_1 and S_n suggest the type of CS has a consistent impact on $^1\text{PC}^*$. In support of our hypothesis that HetCS would alter PC properties more than AkCS and ArCS, PC 3 had the greatest impact on both $\lambda_{\text{max,abs}}$ and $\lambda_{\text{max,em}}$. However, it is unclear from the data above whether it is the heteroatom proximity to the core, the CS electronics, or another factor like substituent sterics that primarily determines the impact of the CS on the energies of the excited states. To gain further insight into core substituent electronics, we evaluated the PC redox properties.

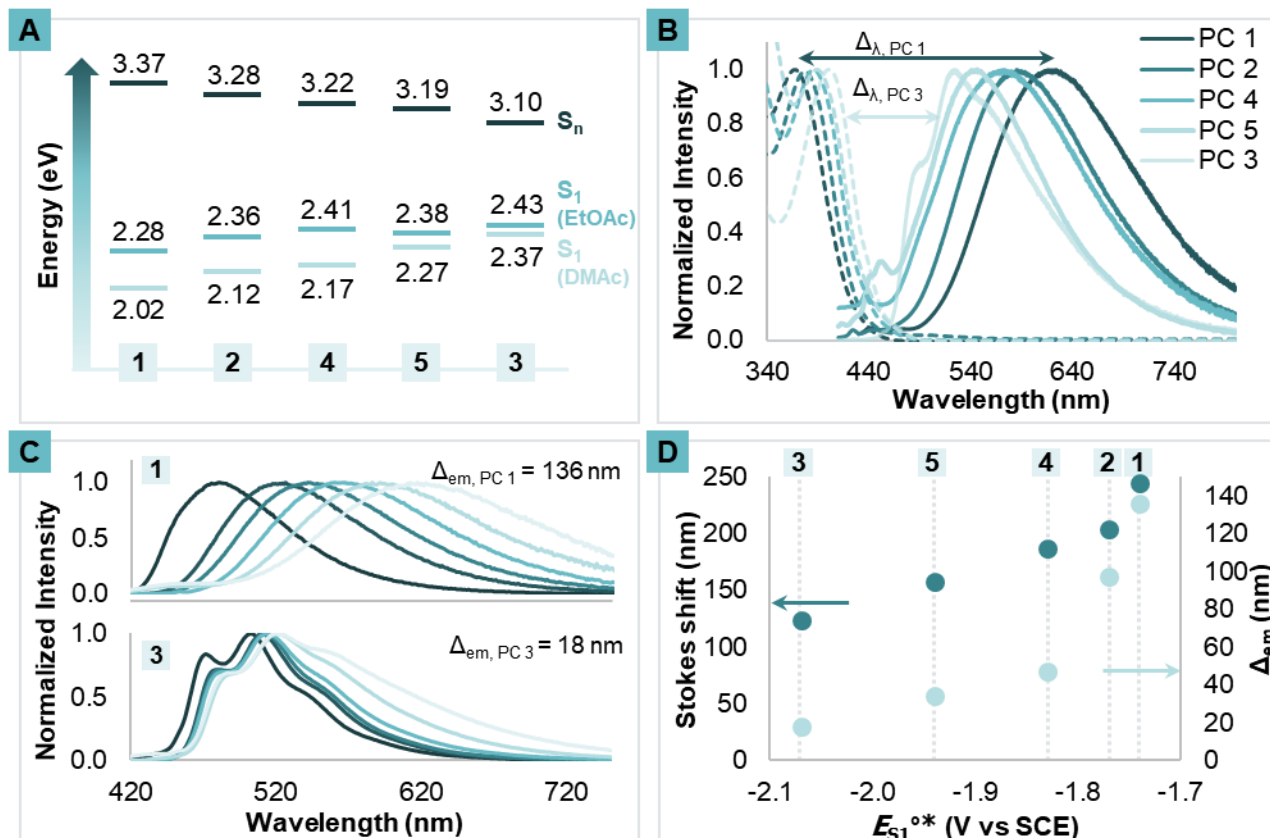


Figure 4.3. (A) Energy levels for S_1 (determined from $\lambda_{max,em}$ in DMAc and ethyl acetate (EtOAc)) and S_n states (determined from absorption; differences between S_n in DMAc and EtOAc are negligible) for PCs 1-5. (B) Overlaid normalized absorption (dotted line) and emission spectra (solid line) acquired in DMAc with the Stokes shift (Δ_λ) for PCs 1 and 3. (C) Overlaid emission profiles of PCs 1 and 3 in different polarity solvents (1-hexene, benzene, 1,4-dioxane, tetrahydrofuran (THF), pyridine, dimethylformamide (DMF)) with Δ_{em} (λ_{max} of most polar solvent, DMF - λ_{max} least polar solvent, 1-hexene), for PC 3 Δ_{em} was calculated from the highest intensity peak in the spectrum. (D) Trends in Δ_λ vs E_{S1}^{0*} and Δ_{em} vs E_{S1}^{0*} in DMAc. For comparison to PCs in prior work, see Figure A4.63.

Redox characterization of PCs. The increased E_{S1} observed in CS PCs suggests that CS PCs may have a more highly reducing E_{S1}^{0*} in comparison to the parent PCs. We hypothesized that HetCS will result in a more negative E_{S1}^{0*} due to the electron donating heteroatom groups (thiophenol) directly attached to the core. A more negative E_{S1}^{0*} is often accompanied by an $E_{1/2}$ decrease (less oxidizing) from PC^{*+} stabilization by the same electron donating group that destabilizes the $^1PC^*$ excited state ($E_{S1}^{0*} = E_{1/2} - E_{S1}$).^{41,42} Instead, we observed that CS increases the $E_{1/2}$ from parent PC 1 (0.21 V vs SCE), with the $E_{1/2}$ of the CS PCs only spanning 0.05 V vs

SCE (0.28 V vs SCE for PC 2; 0.34 V vs SCE for PC 4) (Table 4.2). Consequently, PC 3 had the most reducing E_{S1}^{0*} (-2.07 V vs SCE) out of the CS PCs, but the highly negative E_{S1}^{0*} was not accompanied by the expected $E_{1/2}$ decrease from PC^{++} stabilization. The increased $E_{1/2}$ compared to the parent suggests that the HetCS may instead be σ -withdrawing and destabilizing the PC^{++} , similar to observations from prior work on AkCS⁴⁶. This observation is supported by the crystal structure of PC 3, which shows that the thiophenol core groups are bent rather than in plane with the core, making π -donation less favorable (Figure A4.19). All the core substituents, including the phenyl group for PC 4, resulted in a more highly reducing E_{S1}^{0*} , further suggesting core group electronics alone may not explain the observed redox properties.

Table 4.2. Summary of redox properties for PCs 1-5.

PC	DMAc		EtOAc	
	$E_{1/2}(^2PC^{++}/^1PC^*)$ (V vs SCE) ^a	$E_{S1}^{0*}(^2PC^{++}/^1PC^*)$ (V vs SCE) ^b	$E_{1/2}(^2PC^{++}/^1PC^*)$ (V vs SCE) ^a	$E_{S1}^{0*}(^2PC^{++}/^1PC^*)$ (V vs SCE) ^b
1	0.21 ^c	-1.74 ^c	0.44	-1.84
2	0.28 ^c	-1.77 ^c	0.52	-1.84
3	0.30	-2.07	0.40	-2.03
4	0.34	-1.83	- ^d	- ^d
5	0.33	-1.94	0.43	-1.95

^aFirst oxidation potential measured in DMAc or EtOAc with tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as the electrolyte. ^bSinglet excited state reduction potentials were determined from the $E_{1/2}$ and singlet (E_{S1}) energies measured in DMAc or EtOAc (see the SI for more details). ^cPreviously published in Corbin et al.⁴⁴ ^dRedox properties for PC 4 were not measured due to poor solubility in EtOAc.

Evaluation of excited state (S_1) character. Based on the trends in redox properties observed in combination with the blue-shifted emission and the computed HLCT excited states in the CS PCs, we formulated the alternative hypothesis that the character of S_1 (LE, CT, or HLCT character) influences E_{S1}^{0*} . To evaluate the excited state character of the PCs, we first inspected the computed LUMOs of PCs 1-5 (Figure 4.2). Initial photoexcitation (absorption) for all PCs is either exclusively HLCT or contains a combination of CT and HLCT character. After the initial

photoexcitation, fast relaxation via internal conversion (IC) to the lowest singlet excited S_1 state occurs. For PC 1, the LUMO is exclusively the π^*_{aryl} orbital of the *N*-aryl substituent, which suggests that the lowest energy excited state (S_1) has CT character. For PC 2, the LUMO consists of π^*_{aryl} and π^*_{core} character, with more electron density localized on the π^*_{aryl} , which suggests the S_1 state has CT-dominated HLCT character. For PC 3, the LUMO has π^*_{aryl} , π^*_{core} and π^* of the core-substituents (π^*_{CS}) character, which indicates the S_1 has LE-dominated HLCT character (i.e. more LE character). Similar to PC 3, the LUMOs of PCs 4 and 5 have π^*_{aryl} , π^*_{core} and π^*_{CS} character, with more electron density localized on the phenazine core and substituents, which suggests the S_1 state for both catalysts are of HLCT nature.

Next, the Stokes shift ($\Delta\lambda$) for PCs 1-5 and the features of the emission spectra (Table 4.1, Figure 4.3B) were evaluated. A larger $\Delta\lambda$ and a broad, featureless emission spectrum is considered indicative of a CT character excited state.³³ The least reducing catalyst, PC 1, was found to have the largest $\Delta\lambda$ (247 nm) and a broad emission spectrum while the most reducing catalyst, PC 3, had the smallest $\Delta\lambda$ (124 nm) and three distinct features in the emission spectrum. Furthermore, the $\Delta\lambda$ decreases as $E_{S_1}^{0*}$ becomes more negative across the series of CS PCs, from parent to HetCS PC (1 $\rightarrow$ 2 $\rightarrow$ 4 $\rightarrow$ 5 $\rightarrow$ 3) (Figure 3D). To further explore the excited state character of PCs 1-5, emission spectra were obtained in solvents of varying polarities to determine the extent of solvatochromism (indicated by $\Delta\epsilon_m$) (Figure 3C, Figures A4.46- A4.50). In phenazine PCs with CT character, the polar excited state is stabilized by polar solvents and the $\lambda_{\text{max,em}}$ is red-shifted. Consistent with the trends observed in $\Delta\lambda$, PC 1 shows the largest $\Delta\epsilon_m$ (136 nm) and PC 3 shows the smallest (18 nm). The $\Delta\epsilon_m$ decreases as $E_{S_1}^{0*}$ becomes more negative from PC 1 $\rightarrow$ 2 $\rightarrow$ 4 $\rightarrow$ 5 $\rightarrow$ 3, indicating a decrease in CT character (Figure 3D). Next, the change in dipole moment ($\Delta\mu$) between the singlet excited state S_1 and S_0 was estimated for all PCs using the Lippert-Mataga equation (see SI for details). A

large $\Delta\mu$ is typically associated with more CT character, since it corresponds to a delocalization of electron density to a MO lower in energy than π^*_{core} , such as a π^*_{aryl} orbital. Introducing CS leads to a decrease in $\Delta\mu$, PC 1 $\rightarrow$ 2 $\rightarrow$ 4 $\rightarrow$ 5 $\rightarrow$ 3, with PC 1 showing the largest $\Delta\mu$ (23.0 D) and PC 3 showing the smallest $\Delta\mu$ (7.73 D).⁴⁷ Large $\Delta\mu$ for PCs 1 and 2 suggest that their excited states have more CT character, while the smaller $\Delta\mu$ in PCs 3 and 5 supports their increased LE character.³³ Overall, the trends in $\Delta\lambda$, $\Delta\epsilon_{\text{em}}$, and $\Delta\mu$ indicate that CS PCs show more LE character than parent PCs and support the alternative hypothesis that excited state character influences $E_{\text{S}_1}^{\circ*}$. The observed increase in LE character could be a result of changes to the energetics of the singlet LE state (S_{LE}) vs the singlet CT state (S_{CT}) due to CS, perhaps lowering the energy of S_{LE} so that more LE contributions to the HLCT state are favored. Altogether, LUMO electron density distribution, large $\Delta\mu$, high $\Delta\epsilon_{\text{em}}$ and their broad and featureless emission profiles suggest that their lowest excited states of PCs 1 and 2 are of CT and CT dominated HLCT character, respectively. However, PCs 3, 4, and 5 have S_1 states of HLCT character, with PC 3's HLCT excited state being the most LE-dominated, as indicated by experimental observations.

Characterization in EtOAc. With improved understanding of the PC properties that might be influencing $E_{\text{S}_1}^{\circ*}$, the photophysical and redox properties of PCs 1-5 were measured in a less polar solvent, EtOAc. We hypothesized that PCs with more LE-dominated HLCT character would show smaller changes in photophysical and redox properties (i.e. $\lambda_{\text{max,em}}$, E_{S_1} , $\Delta\lambda$, $E_{\text{S}_1}^{\circ*}$) related to solvent stabilization in EtOAc than the PCs with more CT character. As expected, a negligible change in $\lambda_{\text{max,abs}}$ was observed for all PCs (Table 4.3) but $\lambda_{\text{max,em}}$ is significantly more blue-shifted for CT character PC 1 in EtOAc ($\lambda_{\text{max,em}}$ = 544 nm) vs DMAc ($\lambda_{\text{max,em}}$ = 615 nm). In contrast, more LE character PC 3 is only slightly more blue-shifted in EtOAc ($\lambda_{\text{max,em}}$ = 510 nm) vs DMAc ($\lambda_{\text{max,em}}$ = 524 nm). The higher energy emission peak in PC 3 that was observed in DMAc was also present

in EtOAc and experienced a slightly smaller blue-shift in EtOAc (~10 nm), while the lower energy peak shifted even less (~4 nm). The same trend translates to E_{S1} , where a smaller change in E_{S1} from DMAc to EtOAc is observed with increasing LE character (1→2→4→5→3) (Figure 4.3A).

Table 4.3. Summary of photophysical properties for PCs 1-5 in EtOAc.

PC	$\lambda_{\max, \text{abs}}$ (nm) ^a	$\lambda_{\max, \text{em}}$ (nm) ^b	$\Delta\lambda$ (nm) ^c	$E_{S1, \text{exp}}$ (eV) ^d
1	367	544	177	2.28
2	380	525	145	2.36
3	400	510	110	2.43
4	386	514	128	2.41
5	389	521	132	2.38

^aMeasured by UV-vis spectroscopy in EtOAc. ^bMeasured by steady-state fluorescence spectroscopy in EtOAc. ^c $\Delta\lambda = \lambda_{\max, \text{em}} - \lambda_{\max, \text{abs}}$. ^d $E_{S1} = 1239.8 / \lambda$ (nm); calculated from $\lambda_{\max, \text{em}}$ from fluorescence.

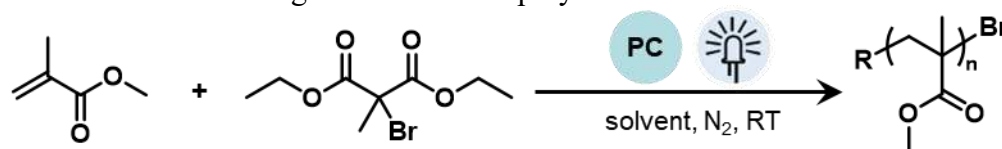
A more oxidizing $E_{1/2}$ was observed for all PCs in EtOAc compared to DMAc, likely due to decreased solvent stabilization of PC^{++} in EtOAc. PCs 1 and 2 have larger increases in $E_{1/2}$ in EtOAc (0.21 V vs SCE in DMAc, 0.44 V vs SCE in EtOAc for PC 1; 0.28 V vs SCE in DMAc, 0.52 V vs SCE in EtOAc for PC 2) while PCs 3 and 5 have smaller increases (0.30 V vs SCE in DMAc, 0.40 V vs SCE in EtOAc for PC 3; 0.34 V vs SCE in DMAc, 0.44 V vs SCE in EtOAc for PC 5) (Table 4.2). PCs 3 and 5 were also observed to have a second, reversible oxidation which likely corresponds to oxidation of the PC^{++} to a dication species (Figures A4.59 and A4.62). Combining the $E_{1/2}$ and E_{S1} to evaluate $E_{S1}^{\circ*}$, we found that PCs 1 and 2 have a more reducing $E_{S1}^{\circ*}$ in EtOAc (-1.84 V vs SCE for PCs 1 and 2) than in DMAc (-1.74 V vs SCE for PC 1; -1.77 V vs SCE for PC 2) while the $E_{S1}^{\circ*}$ for PC 3 and 5 changed negligibly. In contrast to prior work in which the $E_{S1}^{\circ*}$ did not change in a less polar solvent (THF) compared to DMAc because the E_{S1} and $E_{1/2}$ changed proportionally,⁴³ in this work we found that PCs with more CT character have a more reducing $E_{S1}^{\circ*}$ in EtOAc. Comparing PC properties in DMAc and EtOAc overall indicates that PCs with HLCT excited states, especially those with more LE contributions, are less affected by solvent polarity. The observation that the $E_{S1}^{\circ*}$ of PCs with more LE character is not altered as

much by solvent polarity as the more CT character PCs also supports the hypothesis that $E_{S1}^{\circ*}$ is influenced by excited state character.

O-ATRP of MMA with PCs 1-5. After gaining insight into the relationship between PC structure, excited state character, and $E_{S1}^{\circ*}$, we next sought to evaluate PC performance in O-ATRP. Despite CS leading to an increase in LE character in comparison to PC 1, we hypothesized that the CS PCs will result in better polymerization control due to their more highly reducing $E_{S1}^{\circ*}$, and oxidizing $E_{1/2}$. We propose that access to HLCT states may preserve the properties of CT PCs that are correlated with better O-ATRP performance of MMA. Based on this hypothesis, PCs 3 and 5 were expected to exhibit the most polymerization control in O-ATRP because they have the most negative $E_{S1}^{\circ*}$ and sufficiently oxidizing $E_{1/2}$ in this series of PCs, improving initiation and maintaining effective deactivation.

Examining the polymerization of MMA monomer in DMAc, PCs 2, 3, and 5 result in improved $\bar{D}$ ($\bar{D} = 1.18$ for PC 1; $\bar{D} = 1.08$ for PC 3; $\bar{D} = 1.10$ for PC 5) compared to PC 1 ($\bar{D} = 1.25$) despite increased LE character (Table 4.4). PC 4 was excluded from this trend due to its very poor solubility at 1000 ppm PC loading, leading to only moderate control ($\bar{D} = 1.36$). In terms of I^* , AkCS PC 2 exhibits the best molecular weight (MW) control ($I^* = 98\%$) while PCs 1 and 3 result in slightly higher MWs ($I^* = 93\%$ for PC 1; $I^* = 89\%$ for PC 3) than targeted and PCs 4 and 5 result in lower MWs ($I^* = 126\%$ for PC 4; $I^* = 118\%$ for PC 5) than targeted. All the PCs show a linear relationship between M_n and conversion, with PC 4 showing the least linear relationship (Figure 4.4). The control shown by PCs 3 and 5 in DMAc could be attributed to either the $E_{S1}^{\circ*}$ and $E_{1/2}$, both of which are improved relative to parent PC 1.

Table 4.4. O-ATRP results using PCs 1-5 for the polymerization of MMA in DMAc and EtOAc.^a



PC	Solvent	Conv. (%) ^b	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^c	$\bar{D}$ ^c	I^* (%) ^d
1	DMAc	97.0	9.96	10.7	1.25	93
1	EtOAc	81.2	8.38	10.2	1.07	82
2	DMAc	97.2	9.98	10.2	1.18	98
2	EtOAc	82.0	8.47	9.08	1.07	93
3	DMAc	88.2	9.08	10.2	1.08	89
3	EtOAc	78.3	8.09	8.37	1.06	97
4	DMAc	29.1	6.98	5.56	1.31	126
4	EtOAc	80.2	8.29	8.69	1.43	136
5	DMAc	79.5	6.97	6.97	1.10	118
5	EtOAc	74.6	7.72	7.02	1.10	110

^aReaction scheme for O-ATRP of MMA catalyzed by PCs 1-5. Conditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of solvent (DMAc or EtOAc), 1.00 mL of MMA. O-ATRP was run with a white LED beaker as the light source (see SI for more information). ^bConversion determined by ¹H NMR at 8 hours (DMAc) or 24 hours (EtOAc). ^cDetermined by gel permeation chromatography (GPC) with multi-angle light scattering, $\bar{D} = M_w / M_n$. ^d $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

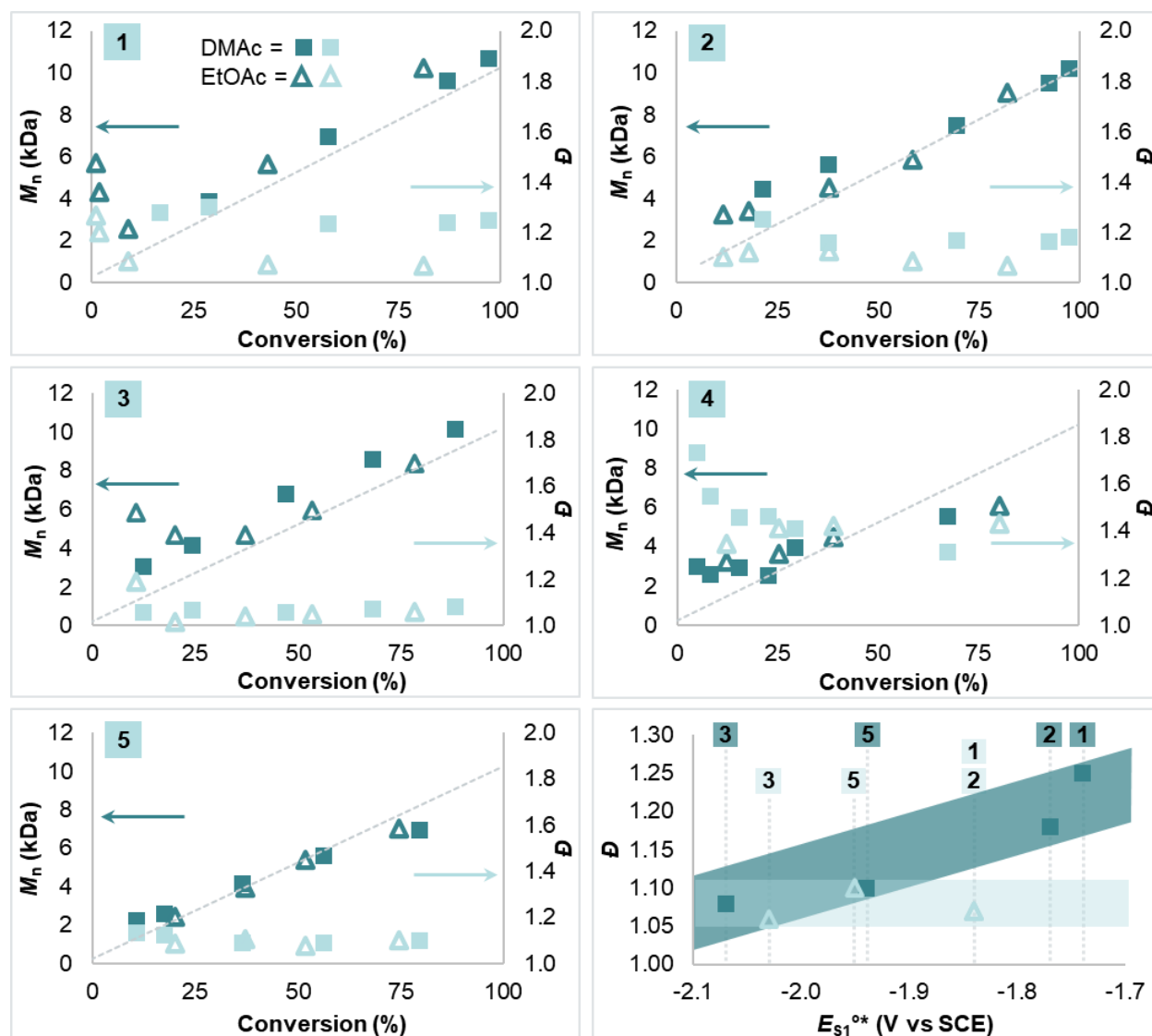


Figure 4.4. Plots of M_n vs monomer (MMA) conversion to polymer (PMMA) (dark turquoise) and D (light turquoise, secondary y-axis) for each time point in DMAc (squares) and EtOAc (triangles), PCs 1-5. See SI for more details on reaction conditions. $M_{n,theo}$ values are represented by the dashed grey line. The bottom right plot shows the trend observed between PC E_{S1}^{o*} and D in DMAc and EtOAc for PCs 1, 2, 3, and 5. PC 4 was excluded due to its limited solubility at 1000 pm PC.

Next, we ran O-ATRP in EtOAc to evaluate the impact of solvent polarity on PC performance. Based on trends observed in prior work,^{43,44} and our findings that solvent polarity alters PC properties (see previous sections), we hypothesized that EtOAc would improve PC performance in O-ATRP for PCs 1-5, especially because all PCs showed a more oxidizing $E_{1/2}$ in EtOAc. In EtOAc, all the PCs result in polymers with excellent D , with the exception again of PC

4 ($\bar{D} = 1.43$) due to poor solubility. PCs 1 and 2 with the greatest amount of CT character exhibit larger improvements in $\bar{D}$ from DMAc to EtOAc ($\bar{D} = 1.07$ in EtOAc for PCs 1 and 2), likely due to the increases in both $E_{S1}^{\circ*}$ and $E_{1/2}$ in EtOAc, while PCs 3 and 5 with the greatest amount of LE character produce a negligible change in $\bar{D}$ from DMAc to EtOAc ($\bar{D} = 1.06$ for PC 3; $\bar{D} = 1.10$ for PC 5 in EtOAc). Consequently, PCs 1-5 result in a narrower range of dispersities in EtOAc ($\bar{D} = 1.06 - 1.10$) in comparison to DMAc ($\bar{D} = 1.08 - 1.25$) (Figure 4.4, bottom right). Examining $\bar{D}$ in EtOAc and DMAc for each PC at timepoints throughout the polymerization also visually highlights the greater difference observed in polymerization control for the PCs with more CT character between solvents (Figure 4.4). These results suggest that solvent polarity influences $\bar{D}$ less in the more LE character HLCT PCs, potentially due to the smaller changes to $E_{S1}^{\circ*}$ between EtOAc and DMAc.

PCs 3 and 5 result in improved I^* in EtOAc, indicating that solvent effects still play a role in improving polymerization control in the more LE character HLCT PCs ($I^* = 97\%$ for PC 3; $I^* = 110\%$ for PC 5). It is possible that for PCs 3 and 5, the improved $E_{1/2}$ in EtOAc results in more efficient deactivation, which combined with already efficient activation encourages an I^* closer to 100%. However, this was not the case for PC 1 or 2 for which I^* decreases in comparison to DMAc ($E_{1/2} = 0.44$ V vs SCE, $I^* = 82\%$ for PC 1; $E_{1/2} = 0.52$ V vs SCE, $I^* = 93\%$ in EtOAc for PC 2). This may be because although the $E_{S1}^{\circ*}$ and $E_{1/2}$ increased in EtOAc for PCs 1 and 2, $E_{S1}^{\circ*}$ is still less reducing in comparison to the other PCs and activation may be inefficient. Overall, PC 3 in EtOAc shows the best polymerization control in terms of both $\bar{D}$ and I^* and showed a linear relationship between M_n at conversions above 25% (Figure 4.4). Other PC properties that are influenced by solvent polarity (i.e. triplet $\tau(\tau_{T1})$, Φ_{ISC} , non-radiative decay) may also play a role in

the observed improvements to polymerization control in EtOAc and will be explored in future work.

O-ATRP of MMA at low PC loadings and targeting higher MWs. The excellent performance of PC 3 in EtOAc led us to hypothesize that a more reducing $E_{S1}^{\circ*}$ and sufficiently oxidizing $E_{1/2}$ will result in improved performance in O-ATRP at low PC loadings (<1000 ppm) or targeting higher MWs. All PCs were found to maintain good control at 100 ppm, and PCs 3, 4, and 5 maintain moderate to good control at 10 ppm in terms of both I^* and $\bar{D}$ (at 10 ppm, $\bar{D} = 1.32$, $I^* = 97\%$ for PC 3; $\bar{D} = 1.26$, $I^* = 99\%$ for PC 4; $\bar{D} = 1.24$, $I^* = 96\%$ for PC 5) (Table A4.8). PC 5 shows moderate control as low as 1 ppm ($\bar{D} = 1.33$), the lowest phenazine PC loading for which control has been achieved in O-ATRP, although a non-unity I^* of 69% was observed. The superior performance of PC 5 over PC 3 indicates that a PC property other than $E_{S1}^{\circ*}$ or $E_{1/2}$ is potentially more important for determining polymerization control at low PC loadings. Performance at low PC loadings could be attributed to the slightly longer singlet excited state lifetimes (τ_{S1}) observed for PCs 3 ($\tau_{S1} = 2.40$ ns) and 5 ($\tau_{S1} = 2.22$ ns) compared to PCs 1, 2, and 4 (Figures A4.51-A4.55). However, τ_{S1} does not explain the better performance of PC 5 compared to PC 3 and at such low PC loadings, the triplet state is expected to contribute more significantly to catalysis.³⁴ The $\epsilon_{abs,max}$ may also be an important factor since highly efficient light absorption would be essential at low PC loadings ($\epsilon_{abs,max} = 17,400$ M⁻¹cm⁻¹ for PC 5; 13,100 M⁻¹cm⁻¹ for PC 3), or τ_{T1} , so that excited state is sufficiently long-lived at low concentrations. Comparison of the emission spectra of PC 3 under oxygen and under nitrogen shows that the lower energy feature is stronger under N₂ and quenched after exposure to oxygen, potentially indicating phosphorescence from an emissive triplet state (Figure A3.44). The performance of PCs 3 and 5 at low PC loadings, along with the quenching of a lower energy emissive feature in the presence of oxygen for PC 3, suggests that their triplet

properties could be influencing catalytic behavior. This merits further investigation into the triplet excited state properties of CS PCs in future work.

PCs 2, 3, and 5 were also evaluated for their ability to synthesize higher MW polymers (DP = 500) because they resulted in excellent polymerization control at 1000 ppm in EtOAc. Contrary to our hypothesis that a more reducing $E_{S1}^{\circ*}$ would result in improved performance, PC 2 shows the best control at DP = 500 ($M_n = 35.3$ kDa, $D = 1.27$, $I^* = 115\%$) while PCs 3 and 5 have poor control (Table A4.9). The observed control by PC 2 over the polymerization is better than in most prior work using O-ATRP to target higher MWs,^{46,48} however further investigation is needed to understand why. One possibility is that the PC 2, with the most oxidizing $E_{1/2}$ out of PCs 1-5 in EtOAc ($E_{1/2} = 0.52$), was able to deactivate the most effectively. Deactivation is critical to avoid irreversible termination, which is expected to increase at low initiator concentrations or high MWs.⁴⁹ Overall, these results indicate that while $E_{S1}^{\circ*}$ and $E_{1/2}$ play a critical role in determining polymerization control, other PC properties are important to consider and may outweigh redox properties in certain applications.

O-ATRP of *n*-BA with PCs 1-5. Based on the excellent performance of PC 3 in the polymerization of MMA, we hypothesized that PCs with a highly reducing $E_{S1}^{\circ*}$ and a relatively oxidizing $E_{1/2}$ will result in controlled polymerization of *n*-BA due to both more efficient activation of the harder to reduce polymer chain-end in *n*-BA and sufficient deactivation to accommodate the faster propagation rate. In prior work, control over the O-ATRP of *n*-BA by phenazine PCs has been difficult to achieve without addition or generation of supplemental deactivator.^{43,48} Improvements to control with supplemental deactivator as well as the success of dihydroacridine PCs in O-ATRP of *n*-BA led to the hypothesis that a highly oxidizing $E_{1/2}$ is the key determinant of control previously.³¹ For O-ATRP of *n*-BA in DMAc, we found that only PC 3 results in

moderate polymerization control ($\bar{D} = 1.38$, $I^* = 95\%$) (Figure 4.5C). In EtOAc, PCs 1, 3, and 5 promote control in terms of $\bar{D}$, but only PC 3 results in an $I^* \sim 100\%$ ($\bar{D} = 1.29$, $I^* = 74\%$ for PC 1; $\bar{D} = 1.24$, $I^* = 97\%$ for PC 3; $\bar{D} = 1.30$, $I^* = 69\%$ for PC 5). The good performance of PC 1 in EtOAc in terms of $\bar{D}$ was unexpected but can potentially be attributed to in situ generation of PC^{++} by the AkCS side reaction, which acts as supplemental deactivator.⁴³ The observed improvements in polymerization control in EtOAc were expected due to the enhancement of E_{S1}^{0*} and $E_{1/2}$ observed above, which should improve activation and deactivation, respectively.

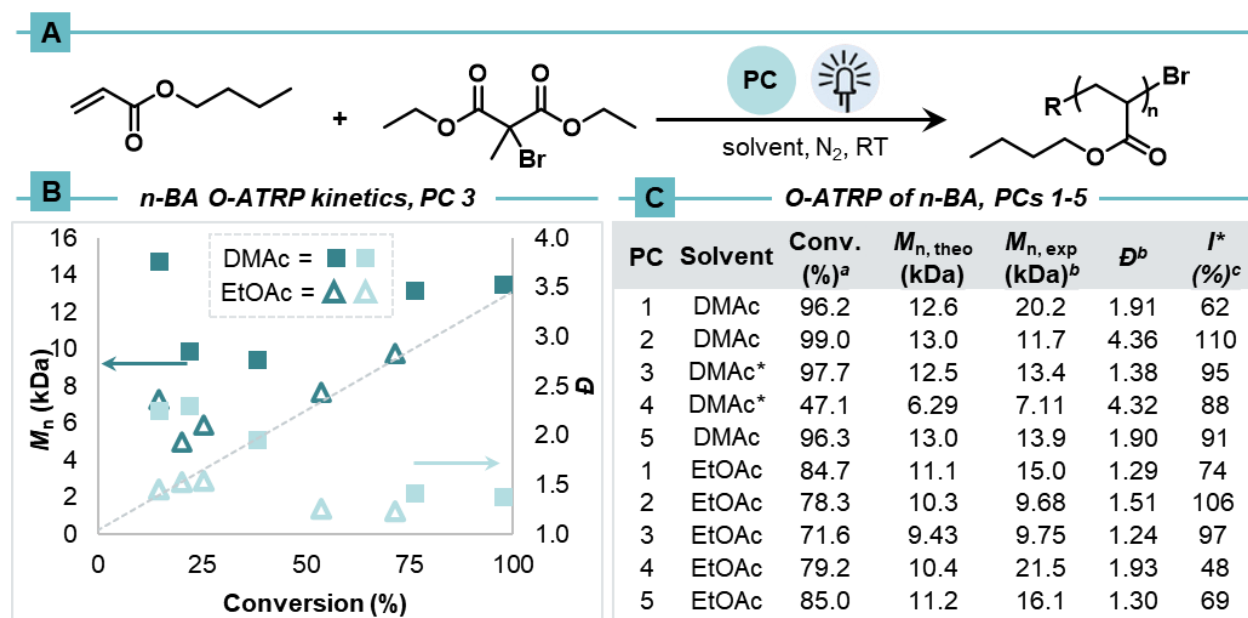


Figure 4.5. (A) Reaction scheme for O-ATRP of *n*-BA catalyzed by PCs 1-5. Conditions: [*n*-BA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of solvent (DMAC or EtOAc), 1.00 mL of *n*-BA. O-ATRP was run with a white LED beaker as the light source (see SI for more information). (B) Plot of M_n vs monomer (*n*-BA) conversion to polymer (P(*n*-BA)) (dark turquoise) and $\bar{D}$ (light turquoise, secondary y-axis) for each time point in DMAC (squares) and EtOAc (triangles), PC 3. See SI for more details on reaction conditions. $M_{n,theo}$ values are represented by the dashed grey line. (C) Table with: ^aConversion determined by ¹H NMR at 2 hours, *4 hours (DMAC) or 7 hours (EtOAc), ^bDetermined by GPC with multi-angle light scattering, $\bar{D} = M_w / M_n$. ^c $I^* = (M_{n,theo} / M_{n,exp}) \times 100$.

PC 3 also results in the most linear relationship between M_n and conversion, especially at conversions > 50% (Figure 4.5B). PCs 1, 2, 3, and 5 all result in some linearity between M_n and conversion in EtOAc (Figure A4.67). PC 2, with the most oxidizing $E_{1/2}$ in EtOAc, was found to

maintain poor control in terms of D (1.51) but a near-unity I^* of 106%. The poor D observed from PC 2 combined with the best overall performance of PC 3 and PC 5 suggests that for n -BA, the PCs with a highly reducing E_{S1}^{0*} and sufficiently oxidizing $E_{1/2}$ perform best. Overall, the results support the hypothesis that the PCs with most reducing E_{S1}^{0*} mediate the most controlled polymerization of n -BA, differing slightly from prior work which emphasized deactivation. Alternatively, another property such as the triplet τ , reorganization energy between PC redox states, or rates of electron transfer not examined in this work could be ultimately most influential in determining polymerization control in n -BA. While the data indicate that E_{S1}^{0*} as well as $E_{1/2}$ is crucial to polymerization outcomes for MMA and n -BA, and that the E_{S1}^{0*} is influenced by the excited state character of the PC, future work should further investigate why PCs with more LE character in this work perform well when in prior work PCs with CT character perform substantially better. We propose that because the PCs with more LE character in this work are HLCT with contributions from the π^*_{aryl} , π^*_{core} and π^*_{CS} orbitals, they may access the benefits of CT character PCs (ex. improved ISC, potentially to a CT character $^3\text{PC}^*$) while also achieving a highly negative E_{S1}^{0*} . Alternatively, the improved performance of the CS PCs could be a result of the combination of maintaining an oxidizing $E_{1/2}$ while accessing a highly negative E_{S1}^{0*} , whereas prior LE PCs typically had a much less oxidizing $E_{1/2}$.

4.4 – CONCLUSIONS

In this work, we investigated CS as an approach to designing PCs that are both highly reducing in the excited state and retain the excellent polymerization control reported for PCs with CT character. CS overall was found to improve several photophysical and redox properties ($\lambda_{\text{max,abs}}$, $\lambda_{\text{max,em}}$, $\epsilon_{\text{max,abs}}$, E_{S1}^{0*} , $E_{1/2}$) with HetCS notably resulting in a highly reducing E_{S1}^{0*} without an decrease in $E_{1/2}$. Exploration of CS also revealed that the excited state character of phenazine PCs

may play a role in determining $E_{S1}^{\circ*}$. While we initially hypothesized that HetCS would result in a high $E_{S1}^{\circ*}$ due to the electron donating heteroatom groups close to the core, lack of stabilization of the PC^{++} suggested that core group electronics alone do not explain redox properties in this PC series. Instead, CS PCs found to have more LE-dominated HLCT character, as supported by solvatochromism, Stokes shift, $\Delta\mu$, TD-DFT predicted LUMOs, and evaluation of solvent effects, were observed to have a more reducing $E_{S1}^{\circ*}$ (ex. -2.07 V vs SCE for PC 3).

Application of PCs 1-5 in O-ATRP of MMA showed that the PCs with more LE character and highly negative $E_{S1}^{\circ*}$ performed the best in DMAc, especially in regard to D ($D = 1.08$, $I^* = 89\%$ for PC 3). In EtOAc, PC 3 with the most LE-dominated HLCT character performed the best and showed a negligible change in D from DMAc but an improved I^* ($D = 1.06$, $I^* = 97\%$), indicating solvent effects still influence control in the more LE character HLCT PCs. Evaluation of PCs 1-5 in O-ATRP at low PC loadings, which resulted in moderate control as low as 1 ppm by PC 5 ($D = 1.33$, $I^* = 69\%$), suggests that while $E_{S1}^{\circ*}$ and $E_{1/2}$ affect polymerization control, other properties are still influential. For *n*-BA, HetCS PC 3 was able to mediate a controlled polymerization in both DMAc ($D = 1.38$, $I^* = 95\%$) and EtOAc ($D = 1.24$, $I^* = 97\%$) while PCs 1 and 5 showed moderate control only in EtOAc. The data suggest that a highly negative $E_{S1}^{\circ*}$ strongly influences control in O-ATRP of *n*-BA, though a sufficiently oxidizing $E_{1/2}$ also plays a role.

Overall, in this work we have leveraged CS to access controlled polymerization of MMA and *n*-BA by dihydrophenazine PCs. We envision that this work provides a foundation for tuning excited state character and $E_{S1}^{\circ*}$ while maintaining and oxidizing $E_{1/2}$ in order to develop organic PCs that will unlock new reactivity, ultimately advancing the field of photoredox catalysis.

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APPENDIX A – SUPPLEMENTARY INFORMATION FOR CHAPTER 1

MATERIALS AND METHODS

Purchased Chemicals

Phenazine Reduction. Phenazine and sodium hydrosulfite were purchased from Alfa Aesar. Reagent grade alcohol was purchased from Fisher.

For the synthesis of 1. Sodium tert-butoxide, 2-Dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos), RuPhos Pd G4, 4-bromobenzotrifluoride, and dioxane were all purchased from Sigma Aldrich.

For the synthesis of 2 – 6. Methyl 2-bromopropionate (M2BP), methyl α -bromoisobutyrate (MBiB), ethyl α -bromophenylacetate, diethyl-2-bromo-2-methylmalonate, triethylamine, and *N,N*-dimethylacetamide (DMAc) were purchased from Sigma Aldrich.

For the synthesis of 1^+Br^- . Molecular bromine, benzene, and methanol were purchased from Sigma Aldrich.

For electrochemistry. Tetra-*n*-butylammonium hexafluorophosphate (NBu_4PF_6), silver nitrate, acetonitrile, and DMAc were purchased from Sigma Aldrich.

For Polymerizations. Methyl methacrylate (MMA), DMAc, dimethyl sulfoxide (DMSO), acetonitrile (MeCN), tetrahydrofuran (THF), ethyl acetate (EtAc), M2BP, MBiB, EBP, DBMM, and ethyl α -chlorophenylacetate (ECIP) were purchased from Sigma Aldrich. Benzene was purchased from TCI America.

Chemical Preparation and Storage

For Polymerizations. All solvents were purchased anhydrous and degassed and used as received. MMA, M2BP, MBiB, EBP, ECIP, and DBMM were dried overnight using calcium hydride, distilled under reduced pressure, and freeze-pump-thawed three times. These chemicals

were stored at -40°C , in the dark, and under N_2 atmosphere when not in use. They were then warmed to room temperature prior to use each time.

Experimental Equipment

Electrochemistry. For all electrochemistry performed in this work, 0.1 M Bu_4NPF_6 was used as the supporting electrolyte. Cyclic voltammetry and spectro-electrochemistry were performed using a three-electrode cell. Cyclic voltammetry was performed with a glassy carbon working electrode, platinum counter electrode, and a silver/silver nitrate (0.01 M AgNO_3 in MeCN with 0.1 M Bu_4NPF_6) reference electrode. For spectro-electrochemistry, the working electrode was a platinum mesh. As appropriate, potentials were referenced to a saturated calomel electrode (SCE) by adding 0.29 V to the potential vs. AgNO_3 .

Light Reactors. The following LEDs were used in the construction of light reactors for this work. For light beakers, strips of white LEDs were purchased from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH). Reactors were constructed by wrapping a 400 mL beaker (10.0 cm tall, 8.5 cm diameter) with aluminum foil and wrapping LED strips (9 LED segments, 16" total) around the inside of the reactor (Figure A1.1). Figure A1.2 shows the qualitative emission spectrum of the LEDs used in this work.

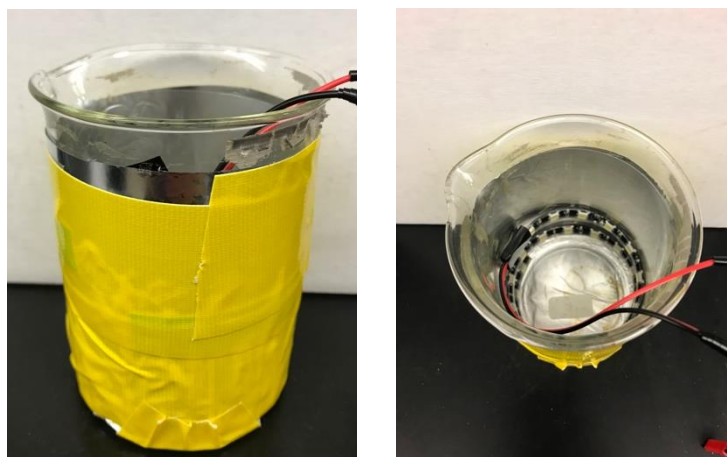


Figure A1.1 Photographs showing a side view (left) and top view (right) of the light beakers used in this work.

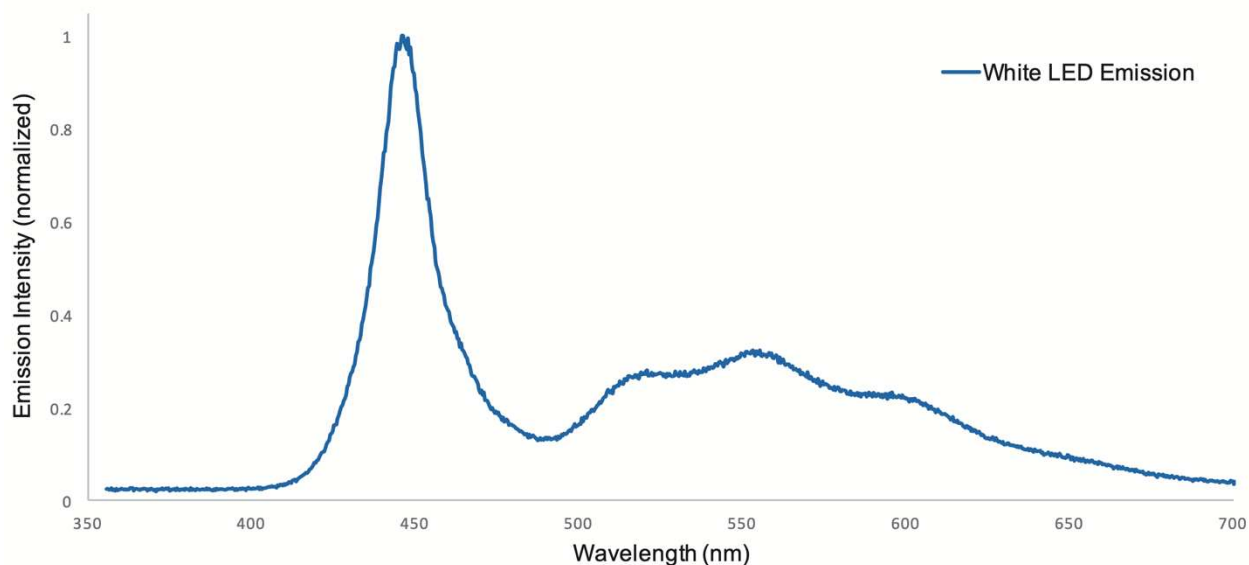


Figure A1.2. Emission spectrum of the LEDs used in this work.

Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy was performed using either a Bruker US 400 MHz spectrometer or a Bruker Ascend 400 MHz spectrometer. All ^1H NMR spectra are reported in δ units, parts per million (ppm), and are referenced to residual chloroform (7.26 ppm) or benzene (7.15 ppm) signals. Electron paramagnetic resonance (EPR) spectroscopy was performed using a Bruker ESR-300 spectrometer. EPR data for $\mathbf{1}^{+\bullet}\text{Br}^-$ was simulated using

EasySpin.¹ Analysis of polymer molecular weights were performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μm MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. For molecular weight analysis of PMMA, a dn/dc value of 0.084 was used. Electrochemical measurements were performed using either a Gamry Interface 1010B or 1010E potentiostat. UV-Visible spectroscopy was performed using an Agilent Cary 5000 UV-Vis-NIR spectrometer. Fluorescence spectroscopy was performed using an FS5 Spectrofluorometer from Edinburgh Instruments. Measurements of LED emission were made using an Olympus IX73 inverted microscope connected to a Horiba iHR 550 spectrometer with a Horiba Synapse back-illuminated CCD camera and a 1200 blaze/mm grating. For qualitative measurements of LED emission intensity, light sources were placed in the same configuration and the light directed into an opening in the microscope. Single crystal X-ray diffraction was performed using a Bruker D8 Quest ECO single-crystal X-ray diffractometer equipped with Mo K α ($\lambda = 0.71073 \text{ \AA}$). Data was collected and integrated using the Bruker APEX 3 software. Absorption correction were applied using SADABS.² Crystal structures were solved using SHELXT and refined with the aid of successive difference Fourier maps by SHELXL operated in conjunction with Bruker APEX 3.^{3,4} Hydrogen atoms were placed in ideal positions and refined using a riding model for all structures. Mass spectrometry was performed using a Thermo-Finnigan LTQ LC/MS-MS spectrometer equipped with a linear ion trap.

PROCEDURES

Synthesis of Photocatalysts

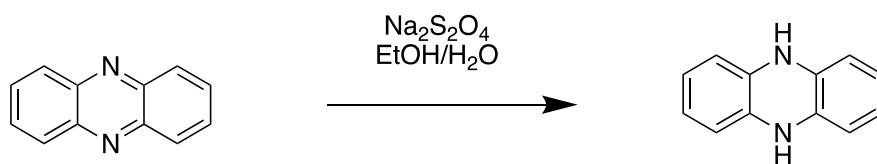


Figure A1.3. Scheme for the synthesis of dihydrophenazine.

Synthesis of 5,10-Dihydrophenazine. This synthesis was performed using a modified literature procedure.⁵ Phenazine (2.0 g, 0.011 mol) was dissolved in 70 mL of EtOH that had been sparged with N_2 for 30 min. This mixture was brought to reflux under N_2 and $\text{Na}_2\text{S}_2\text{O}_4$ dissolved in degassed water was added. The solution was then refluxed for 3 hrs and subsequently cooled to room temperature. The solid was collected using a swivel frit under N_2 and washed with sparged H_2O (3 x 100 mL). The solid was then dried overnight under vacuum before being brought into an N_2 filled glovebox. Yield: 1.90 g (95%). ^1H NMR (400 MHz, C_6D_6): δ 8.31-8.23 (m, 4H), 7.91-7.83 (m, 4H).

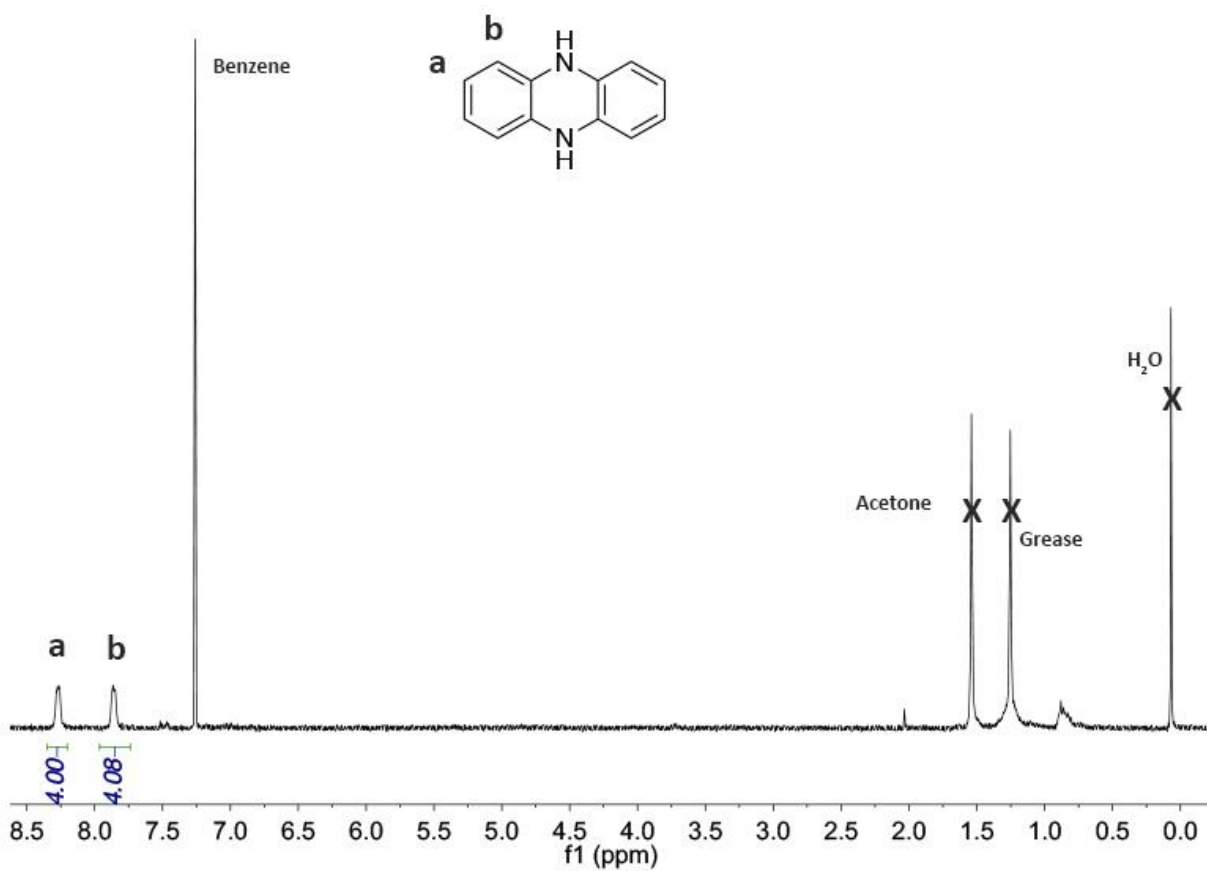


Figure A1.4. ^1H NMR spectrum of dihydrophenazine in C_6D_6 .

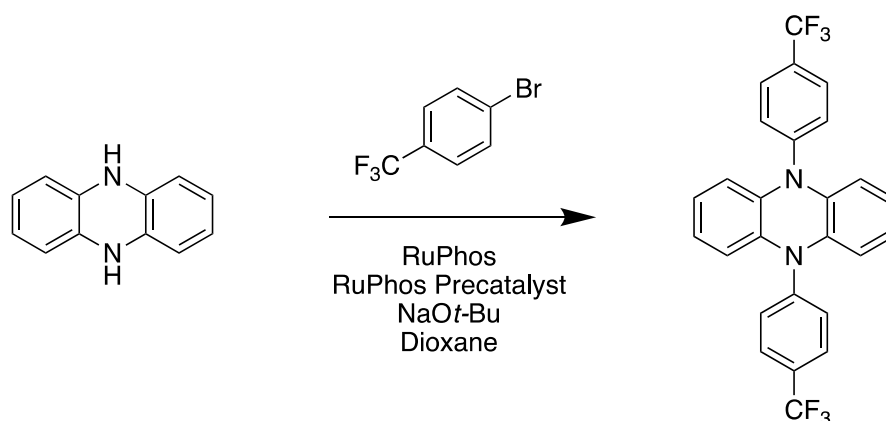


Figure A1.5. Scheme for the synthesis of **1**.

Synthesis of 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (1). This synthesis was performed using a modified literature procedure.⁶ Bromobenzotrifluoride was sparged with N₂ over ice for 15 minutes. 5,10-dihydrophenazine (2.00 g, 0.011 mol), RuPhos Pd G4 precatalyst (0.373 g, 0.000439 mol), and dioxane (16 mL) were added to an oven dried Schlenk flask in an N₂ filled glovebox. The flask was brought out of the glovebox and NaOt-Bu (4.22 g, 0.0439 mol), RuPhos (0.205 g, 0.000439 mol), and sparged bromobenzotrifluoride (6.15 mL, 0.0439 mol) were added under N₂. This mixture was refluxed overnight and subsequently cooled to room temperature. 600 mL of DCM and 300 mL of water were added. The product crashed out of solution over several minutes. Both layers were filtered and the solid was collected. The product was then recrystallized from boiling DCM/MeOH to yield yellow crystals. Yield: 4.2 g (81%). ¹H NMR (400 MHz, C₆D₆): δ 7.33-7.24 (m, 4H), 6.94-6.88 (m, 4H), 6.33-6.24 (m, 4H), 5.66-5.59 (m, 4H). ¹³C NMR (101 MHz, C₆D₆): δ 136.01, 131.32, 128.48-127.49 (unresolvable from solvent), 121.70, 113.39. ¹⁹F NMR (376 MHz): δ -62.26. Abs. λ_{max}: 367 nm. ε = 5200 M⁻¹·cm⁻¹. Em. λ_{max}: 611 nm.

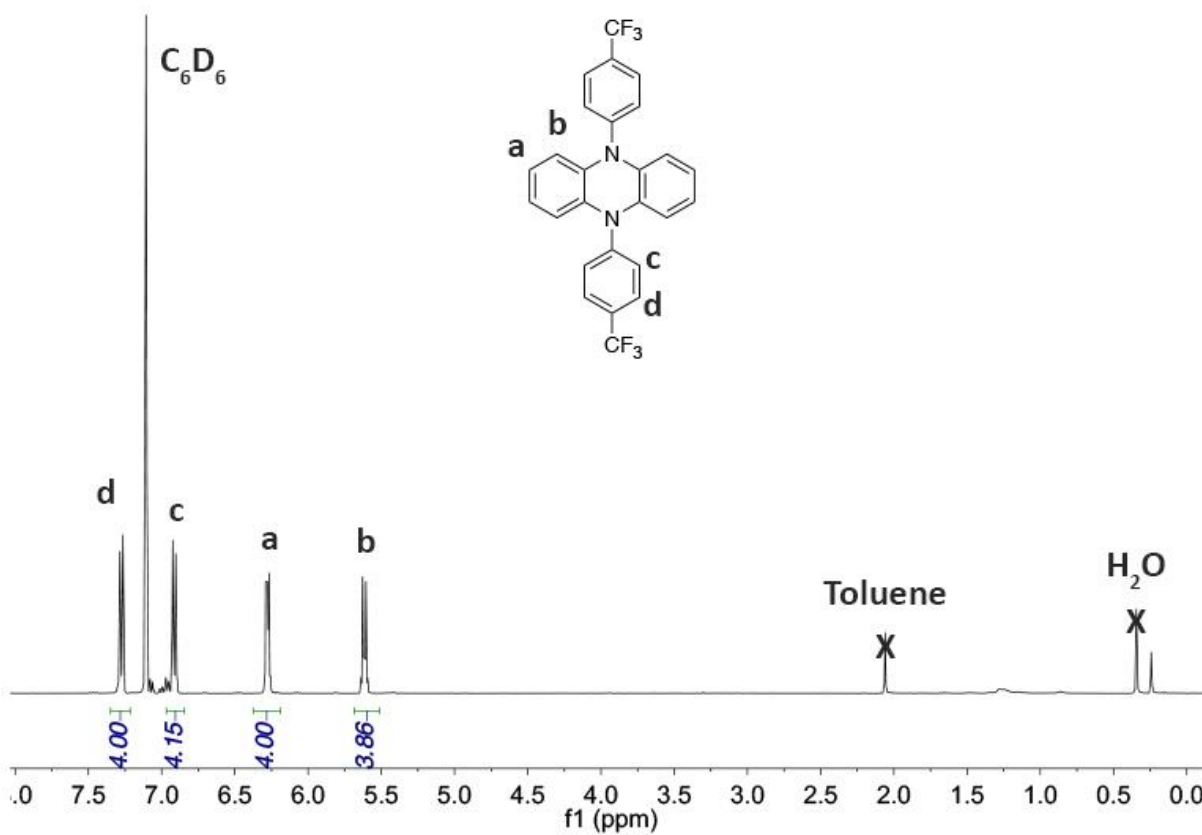


Figure A1.6. ^1H NMR spectrum of **1** in C_6D_6 .

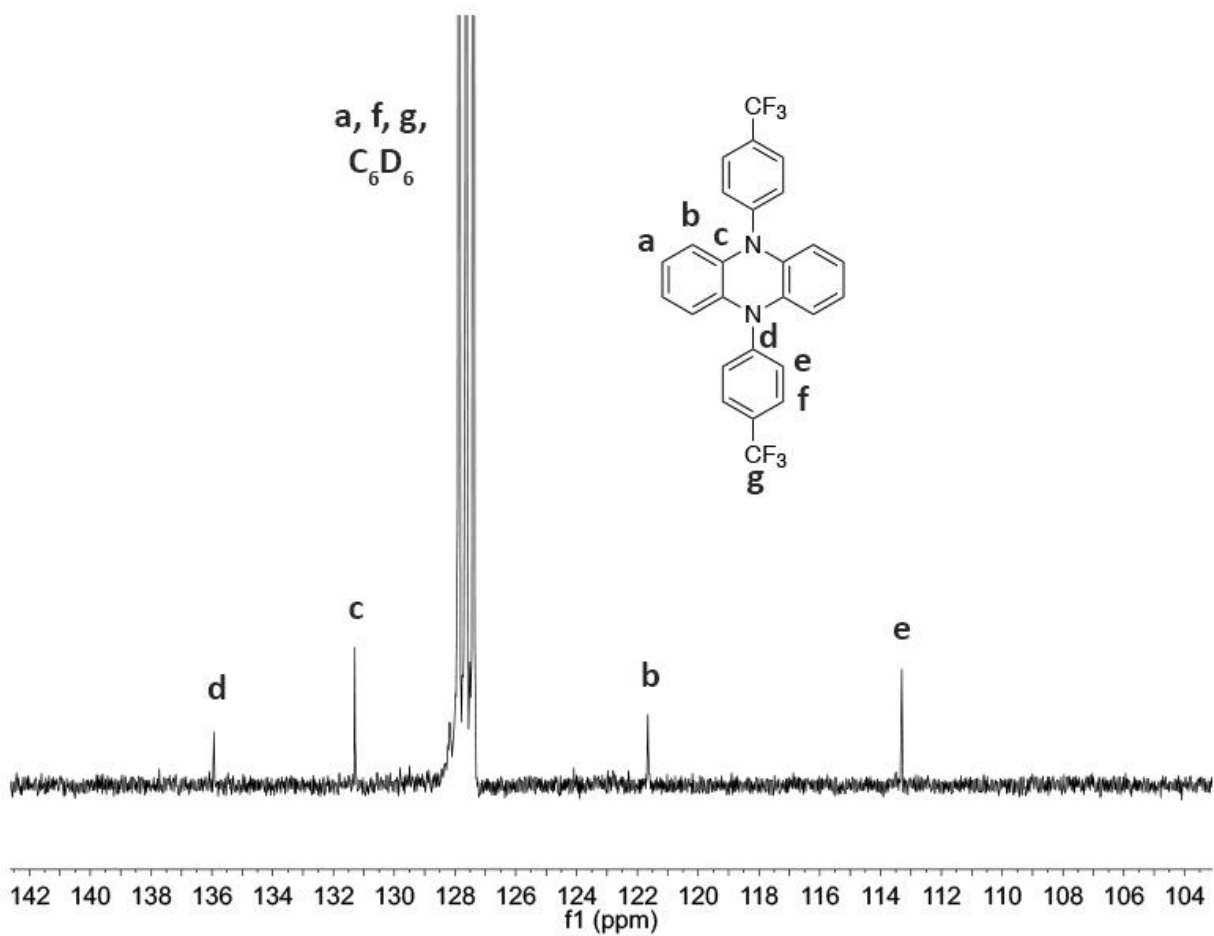


Figure A1.7. ^{13}C NMR spectrum of **1** in C_6D_6 .

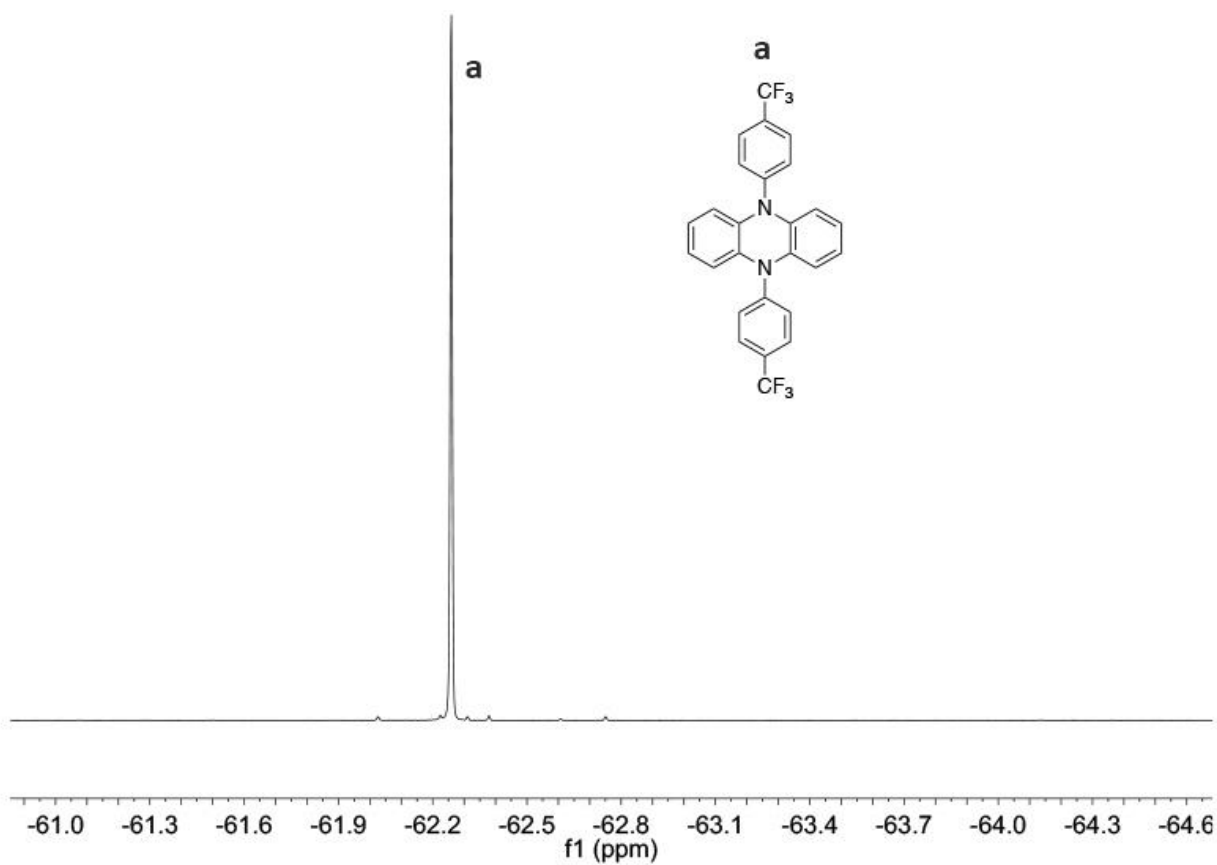


Figure A1.8. ^{19}F NMR spectrum of **1** in C_6D_6 .

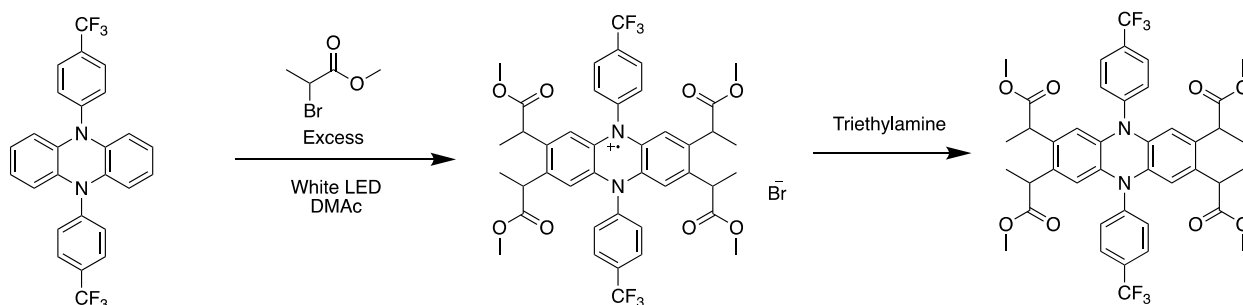


Figure A1.9. Scheme for the synthesis of **2**.

Synthesis of 2,3,7,8-tetra(methylpropionate-yl)-5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (2). 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (0.400 g, 0.000851 mol) was added to 40 mL of DMAc in a 100 mL vacuum flask in an N₂ filled glovebox. Methyl 2-bromopropionate (0.55 mL, 0.00425 mol) was added and the solution was stirred and irradiated with white LEDs overnight. Then the flask was removed from the box, opened to air and 20 mL of radical cation solution was removed for further study. To the remaining solution, 2 mL of triethylamine was added. This solution was then stirred for 5 minutes and the volatiles were subsequently removed by rotary evaporation and dry-loaded onto silica gel. The compound was purified by flash chromatography using a gradient of 0-30% EtOAc in hexanes with 5% triethylamine. Yield: 0.233 g (67.1%). ¹H NMR (400 MHz, C₆D₆): δ 7.42-7.32 (m, 4H), 7.10-7.04 (m, 4H (unresolvable from solvent)), 6.08-5.99 (m, 4H), 3.66 (q (*J* = 7.04 Hz), 2H), 3.58 (q (*J* = 7.07 Hz), 2H), 3.23-3.18 (m, 12H), 1.24-1.16 (m, 12H). ¹³C NMR (101 MHz, C₆D₆): δ 173.99, 144.44, 135.22, 132.42, 130.21, 113.71, 113.19, 51.22, 40.90, 40.67, 18.63. ¹⁹F NMR (376 MHz, C₆D₆): δ -62.21. Abs. λ_{max}: 373 nm. ε = 4600 M⁻¹·cm⁻¹. Em. λ_{max}: 600 nm.

Alternatively, the product could also be isolated after reduction with triethylamine by precipitation into DI water, resulting in the formation of a yellow solid. The solid was collected by vacuum filtration, washed with excess DI water and cold methanol (~20 mL), and then dried overnight under high vacuum. When 1.1 g of 5,10-di(4-trifluoromethylphenyl)-5,10-

dihydrophenazine starting material was used, 1.1 g (57%) of **2** was recovered using this method. Characterization matched that reported above.

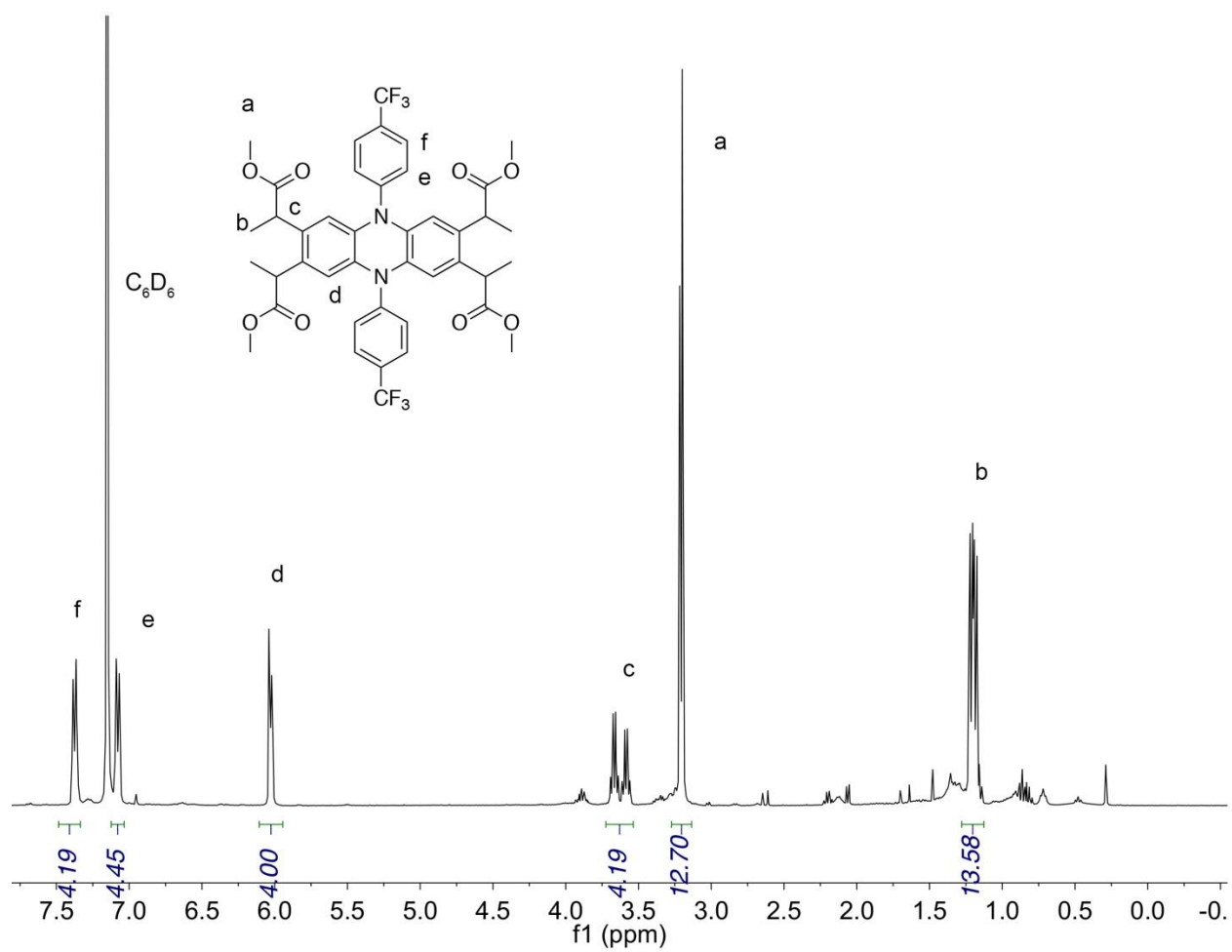


Figure A 1.10. ^1H NMR spectrum of **2** in C_6D_6 .

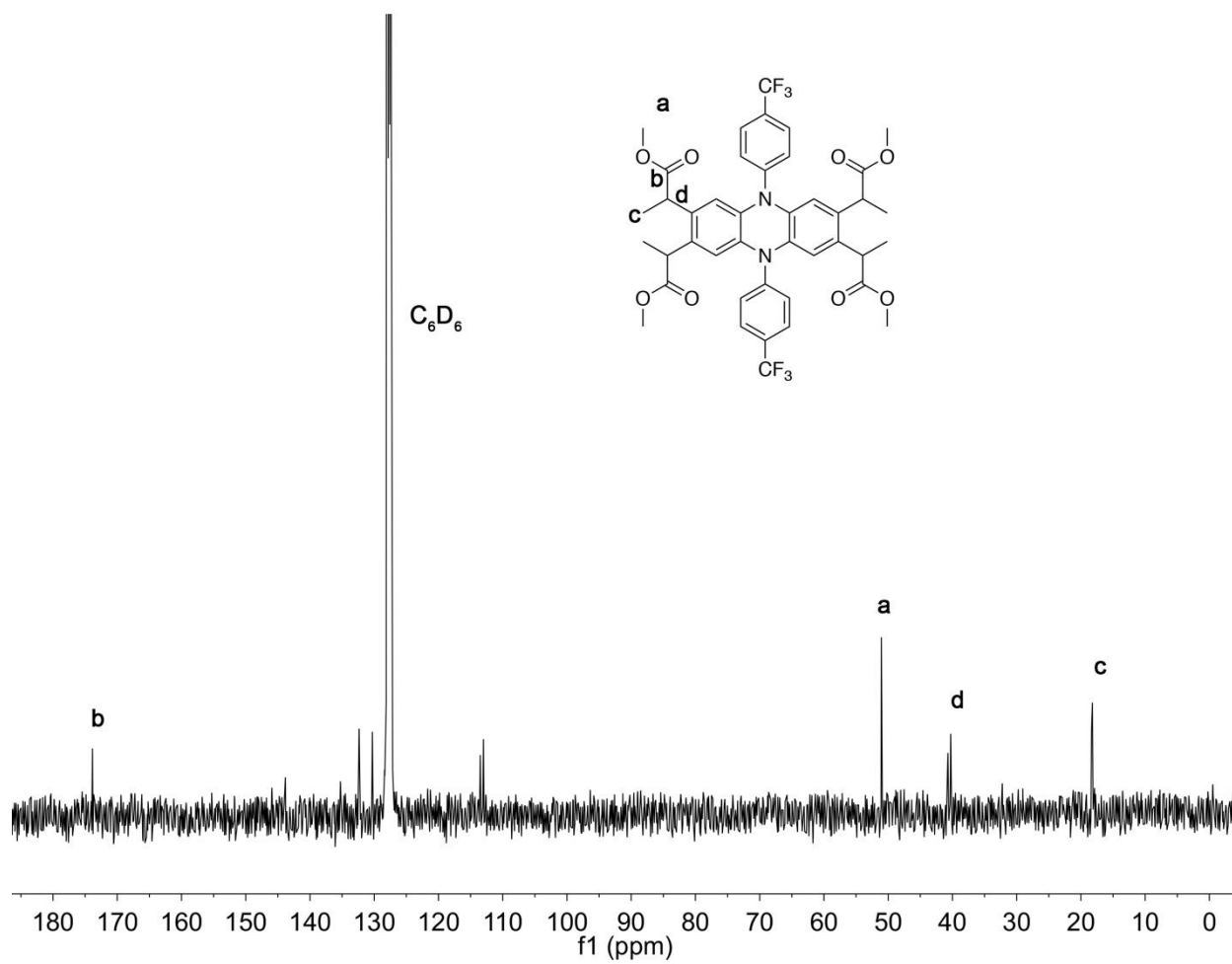


Figure A.11. ^{13}C NMR spectrum of **2** in C_6D_6 .

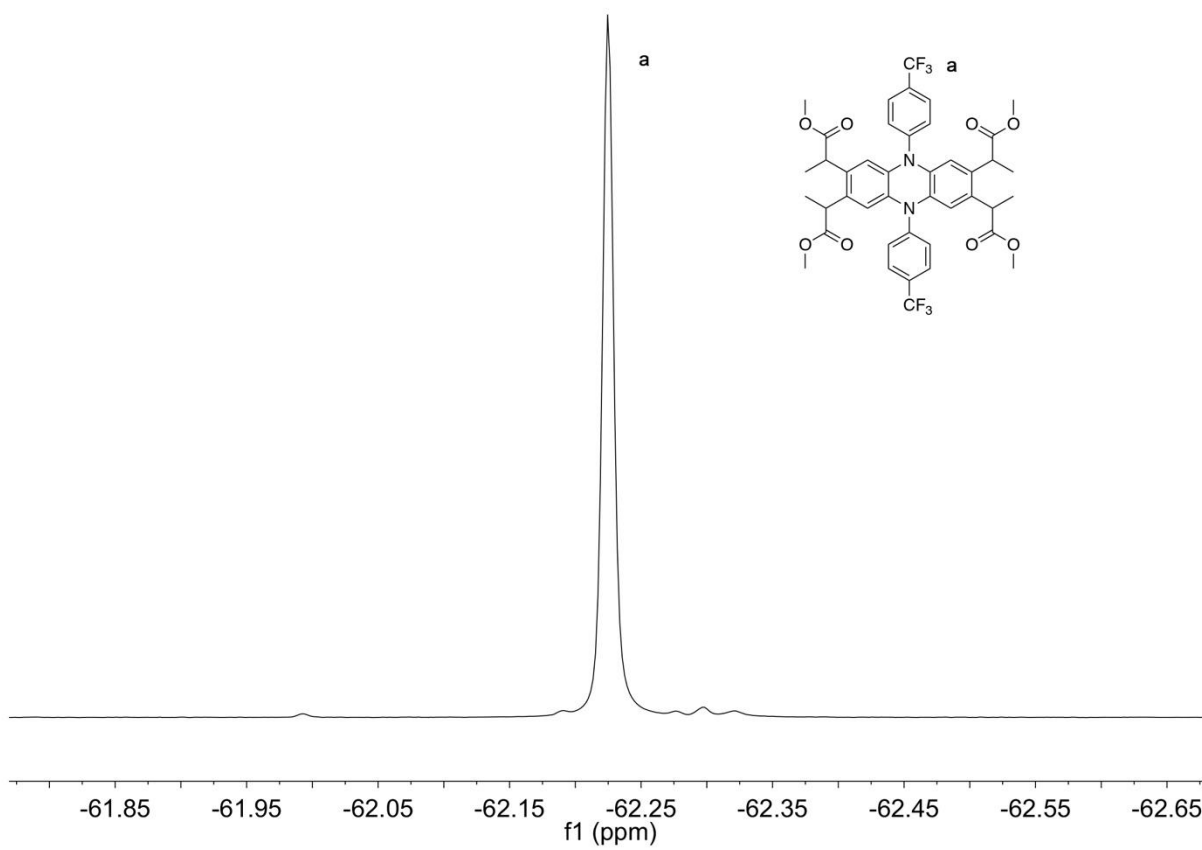


Figure A.12. ^{19}F NMR spectrum of **2** in C_6D_6 .

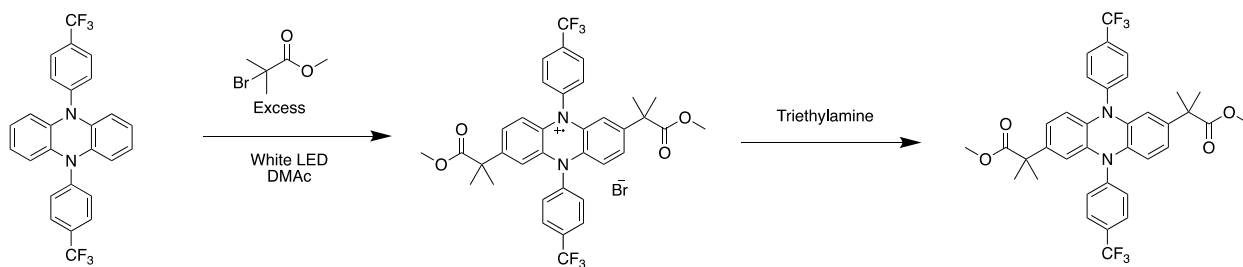


Figure A.13. Scheme for the synthesis of **3**.

Synthesis of 2,7-di(methylisobutyrate-yl)-5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (3). 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (0.200 g, 0.000425 mol) was added to 20 mL of DMAc in a scintillation vial in an N₂ filled glovebox. Methyl- α -bromoisobutyrate (0.55 mL, 0.00425 mol) was added and the solution was stirred and irradiated with white LEDs overnight. Then the scintillation vial was removed from the box, opened to air and 1 mL of triethylamine was added. The solution was then stirred for 5 minutes and the volatiles were subsequently removed by rotary evaporation. The residue was dissolved in EtOAc and dry-loaded onto silica gel. The compound was purified by flash chromatography using a gradient of 0-30% EtOAc in hexanes with 5% triethylamine. Yield: 0.218 g (76.5 %). ¹H NMR (400 MHz, C₆D₆): δ 7.22-7.14 (m, 4H), 6.87-6.76 (m, 4H), 6.29-6.20 (m, 2H), 5.85-5.75 (m, 2H), 5.52-5.40 (m, 2H), 3.03 (s, 6H), 1.15 (s, 12H). ¹³C NMR (101 MHz, C₆D₆): δ 175.86, 143.95, 138.62, 135.85, 135.40, 135.10, 134.61, 131.21, 130.86, 130.19, 119.05, 118.83, 113.75, 113.27, 112.33, 111.58, 51.16, 45.56, 26.01. ¹⁹F NMR (376 MHz, C₆D₆): δ -62.22. Abs. λ_{max} : 371 nm. ϵ = 4400 M⁻¹·cm⁻¹. Em. λ_{max} : 611 nm.

Alternatively, the product could also be isolated after reduction with triethylamine by precipitation into DI water, resulting in the formation of a yellow solid. The solid was collected by vacuum filtration, washed with excess DI water and cold methanol (~20 mL), and then dried overnight under high vacuum. When 1.1072 g of 5,10-di(4-trifluoromethylphenyl)-5,10-

dihydrophenazine starting material was used, 1.1466 g (72.6%) of **3** was recovered using this method. Characterization matched that reported above.

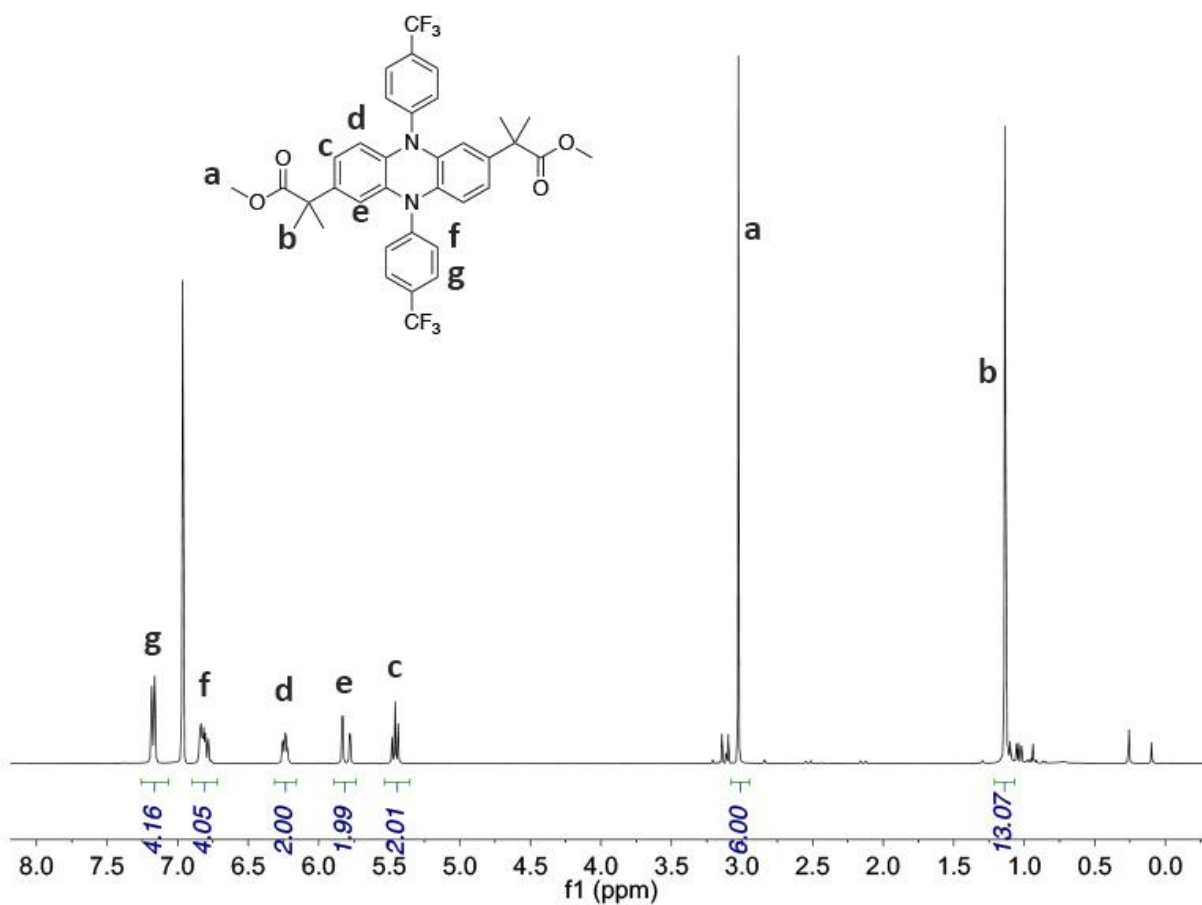


Figure A1.14. ^1H NMR spectrum of **3** in C_6D_6 .

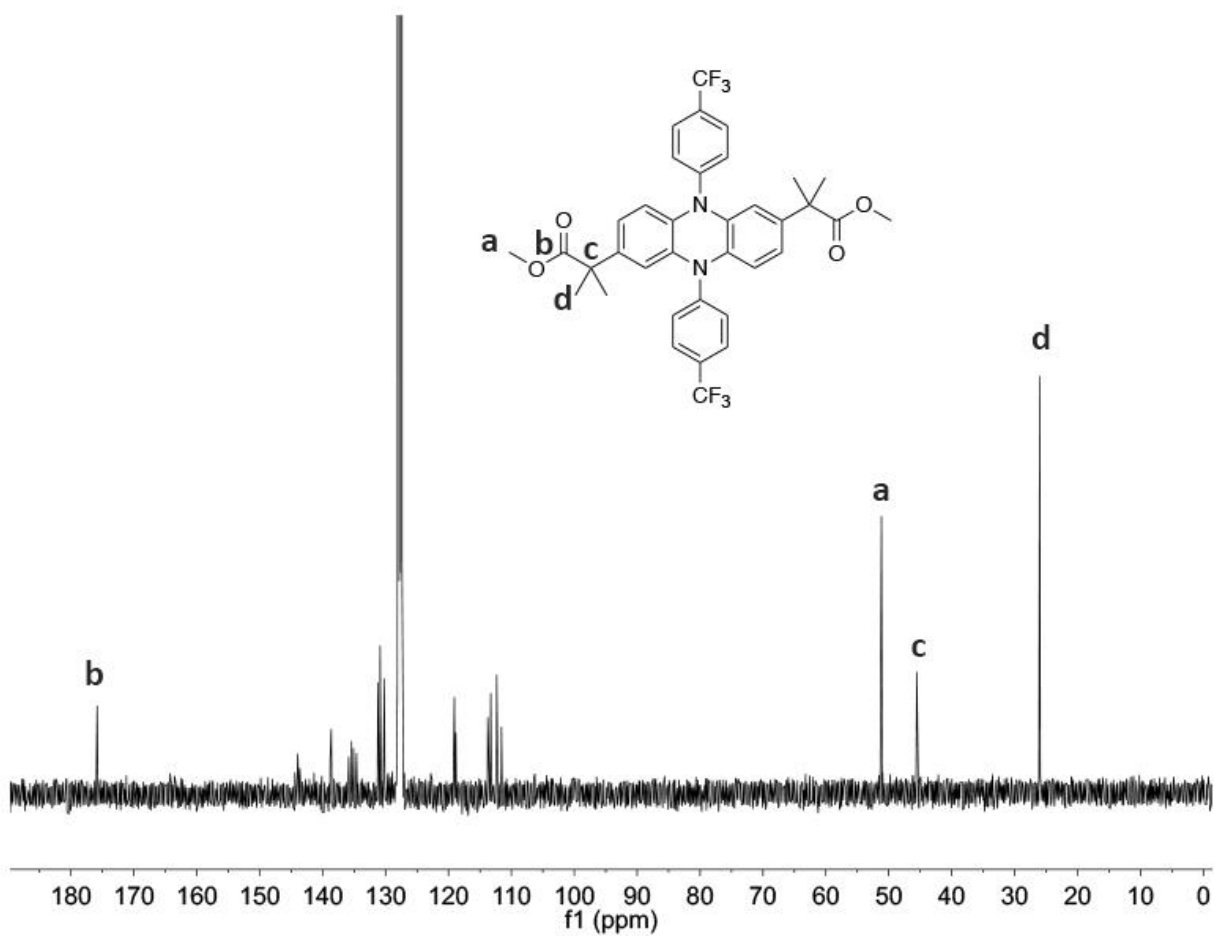


Figure A1.15. ^{13}C NMR spectrum of **3** in C_6D_6 .

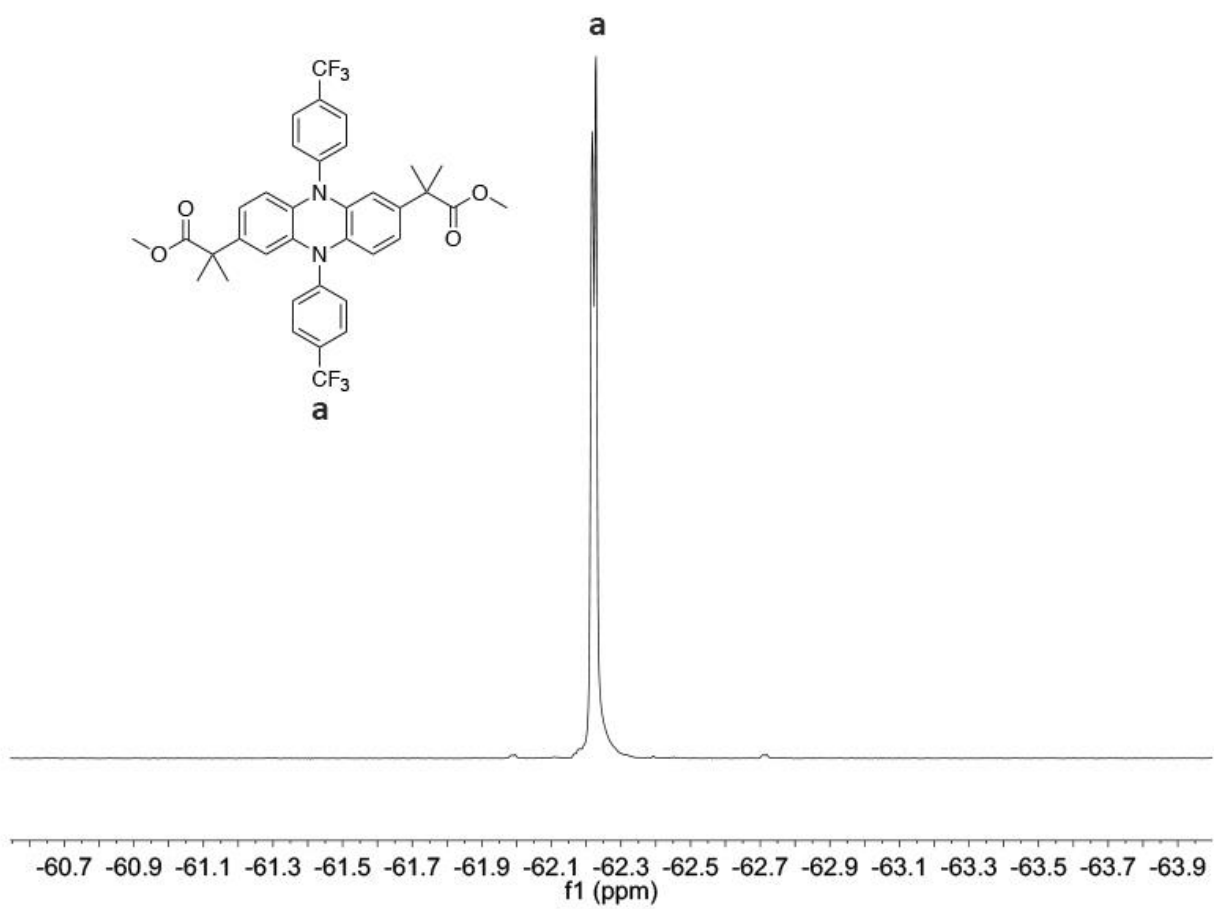


Figure A1.16. ^{19}F NMR spectrum of **3** in C_6D_6 .

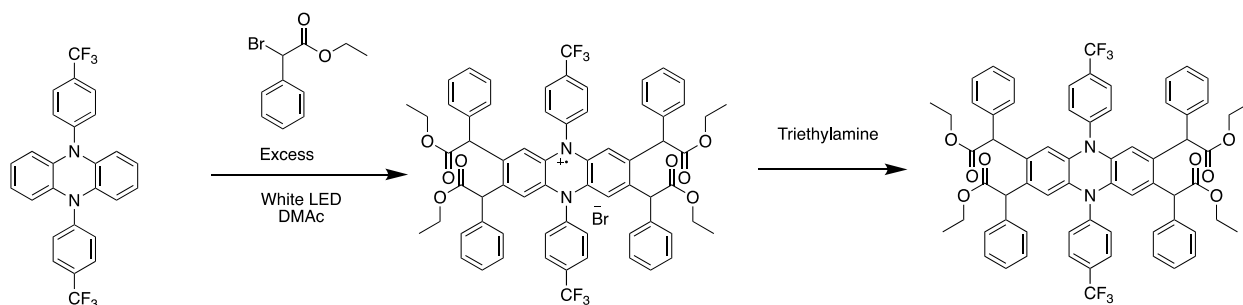


Figure A1.17. Scheme for the synthesis of **4**.

Synthesis of 2,3,7,8-tetra(ethylphenylacetate-yl)-5,10-di(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine (4). 5,10-di(4-(trifluoromethyl)phenyl)-5,10-dihydrophenazine (0.200 g, 0.000425 mol) was added to 20 mL of DMAc in a scintillation vial in an N₂ filled glovebox. Ethyl- α -bromophenylacetate (0.743 mL, 0.00425 mol) was added and the solution was stirred and irradiated with white LEDs overnight. Then the scintillation vial was removed from the box, opened to air and 2 mL of triethylamine were added. The solution was then stirred for 5 minutes and the volatiles were subsequently removed by rotary evaporation. The residue was dissolved in EtOAc and dry-loaded onto silica gel. The compound was purified by flash chromatography using a gradient of 0-50% EtOAc in hexanes with 5% triethylamine. The first yellow fraction was isolated as the compound named above. Yield: 0.423 g (88.7 %). ¹H NMR (400 MHz, C₆D₆): δ 7.07-6.94 (m, indistinguishable from solvent), 6.90-6.62 (m, 20H), 5.77-5.61 (m, 4H), 5.10-4.98 (m, 4H), 3.75-3.43 (m, 8H), 0.67-0.49 (m, 12H) ¹³C NMR (101 MHz, C₆D₆): δ 171.48, 171.30, 143.01, 138.57, 134.93, 130.87, 128.57, 128.27, 127.82, 127.56, 126.95, 125.56, 122.88, 114.80, 60.78, 52.50, 13.69. ¹⁹F NMR (376 MHz, C₆D₆): δ -62.33 Abs. λ_{max} : 377 nm. ϵ = 8500 M⁻¹·cm⁻¹. Em. λ_{max} : 581 nm.

Alternatively, the product could also be isolated after reduction with triethylamine by precipitation into DI water, resulting in the formation of an orange solid. The solid was collected by vacuum filtration, washed with excess DI water and cold methanol (~20 mL), and then dried

overnight under high vacuum. When 1.1167 g of 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine starting material was used, 1.4200 g (53.4%) of **4** was recovered using this method. Characterization matched that reported above.

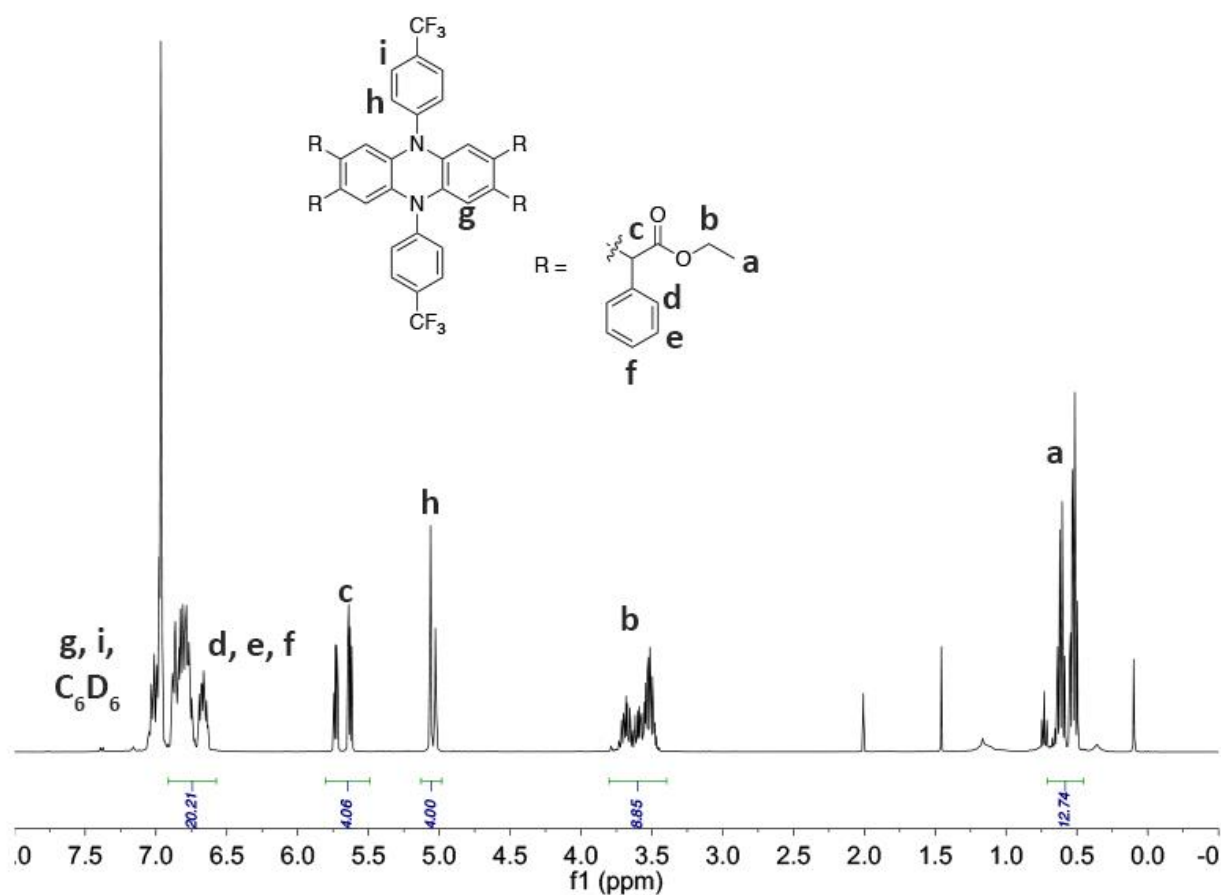


Figure A1.18. ¹H NMR spectrum of **4** in C₆D₆.

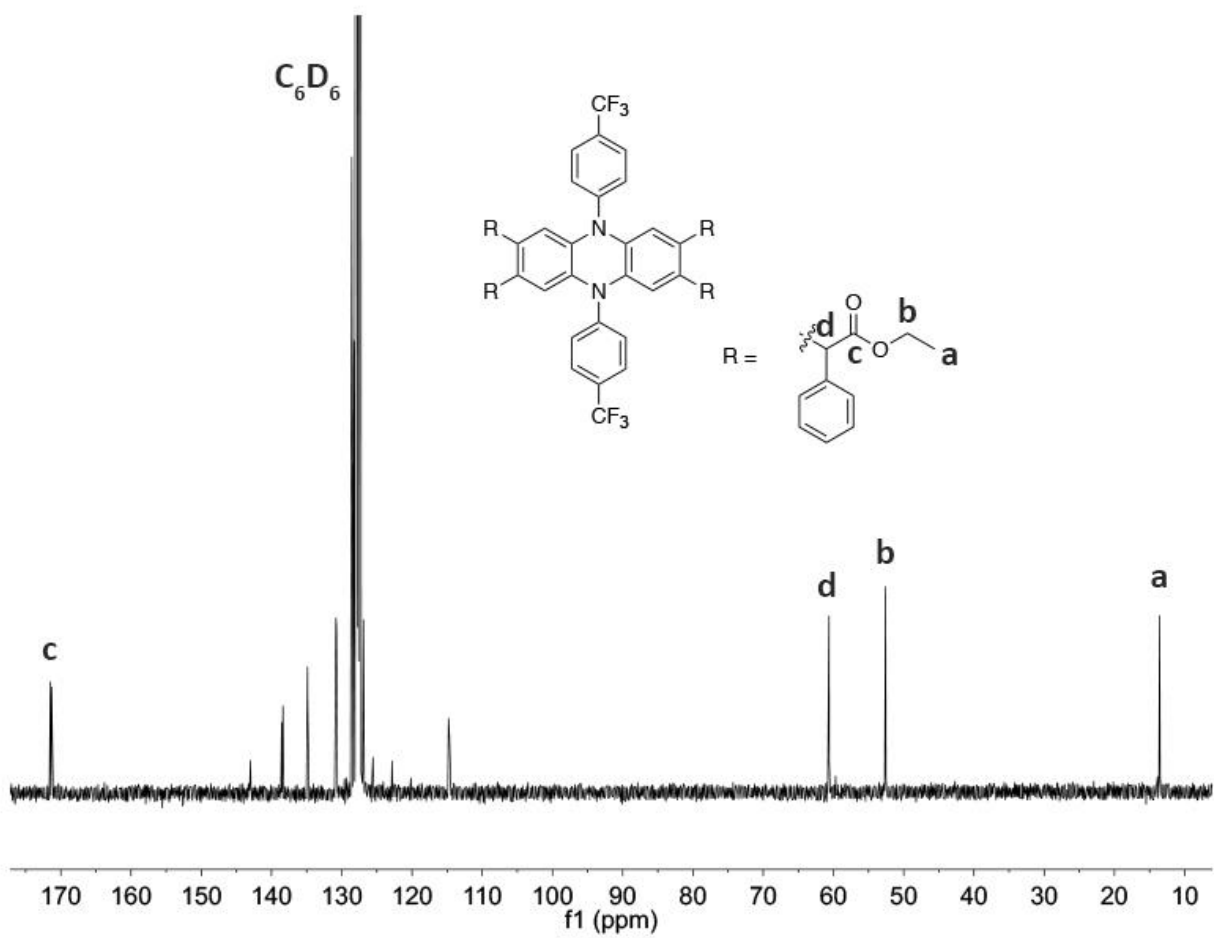


Figure A1.19. ^{13}C NMR spectrum of **4** in C_6D_6 .

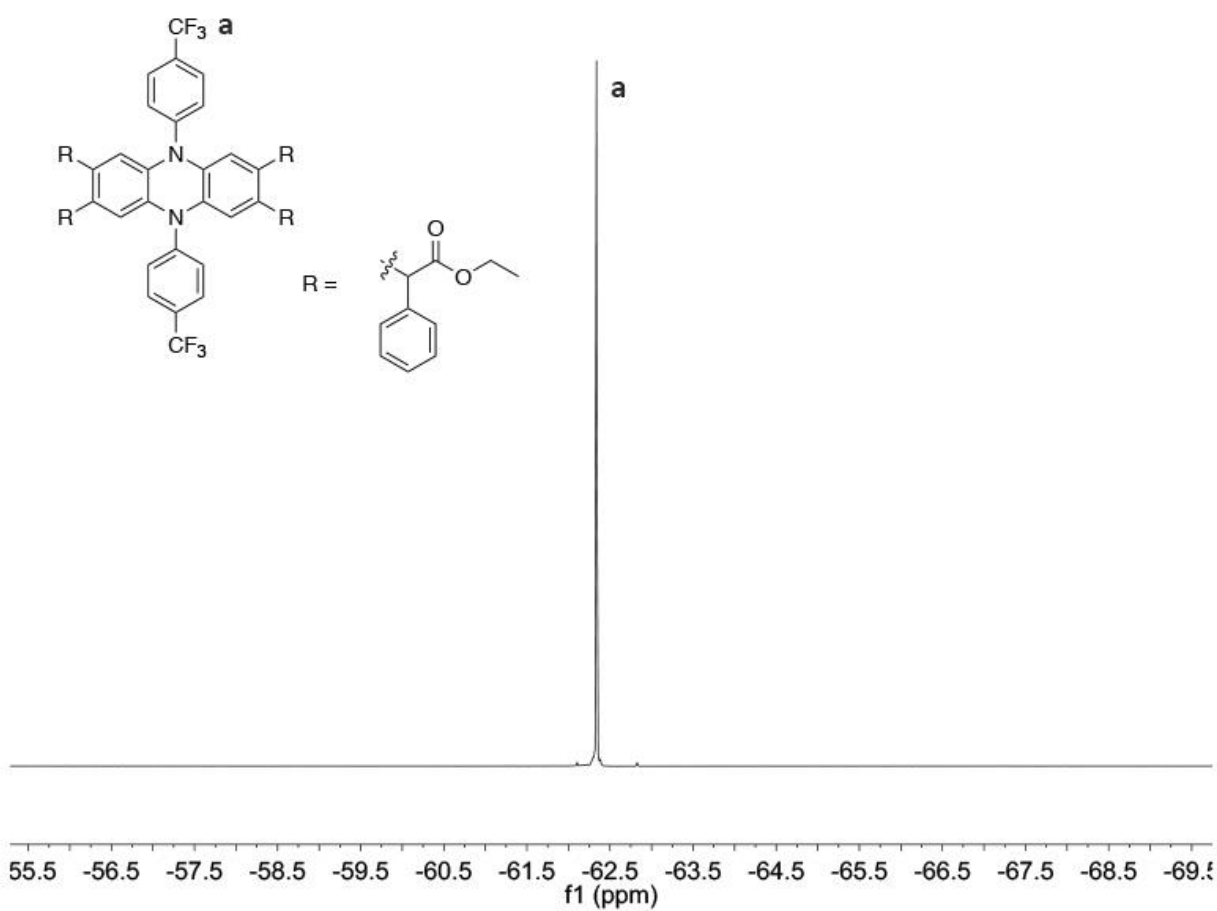


Figure A1.20. ^{19}F NMR spectrum of **4** in C_6D_6 .

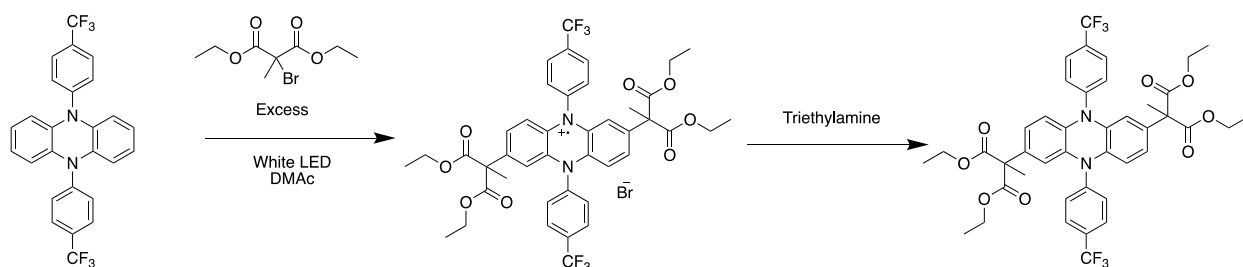


Figure A1.21. Scheme for the synthesis of **5**.

Synthesis of 2,7-di(diethyl-2-methylmalonate-yl)-5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (5). 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (0.400 g, 0.000851 mol) was added to 40 mL of DMAc in a 100 mL vacuum flask in an N₂ filled glovebox. Diethyl-2-bromo-2-methylmalonate (1.63 mL, 0.00851 mol) was added and the solution was stirred and irradiated with white LEDs overnight. Then the flask was removed from the box, opened to air and 20 mL of radical cation solution was removed for further study. To the remaining solution, 2 mL of triethylamine was added. This solution was then stirred for 5 minutes and the volatiles were subsequently removed by rotary evaporation and dry-loaded onto silica gel. The compound was purified by flash chromatography using a gradient of 0-30% EtOAc in hexanes with 5% triethylamine. Yield: 0.320 g (92.2%). ¹H NMR (400 MHz, C₆D₆): δ 7.41-7.30 (m, 4H), 7.13-6.90 (m, 4H (unresolvable from solvent)), 6.56-6.47 (m, 2H), 6.21-6.04 (m, 2H), 5.67-5.58 (m, 2H), 3.92-3.67 (m, 8H), 1.87-1.72 (s, 6H), 0.84-0.78 (m, 12H). ¹³C NMR (101 MHz, C₆D₆): δ 170.93, 143.76, 135.69, 135.36, 135.09, 132.30, 131.47, 131.32, 130.77, 120.81, 120.68, 114.54, 113.75, 113.00, 112.63, 61.15, 57.98, 21.90, 13.61. ¹⁹F NMR (376 MHz, C₆D₆): δ -62.23, -62.31, -62.35. Abs. λ_{max}: 373 nm. ε = 4600 M⁻¹·cm⁻¹. Em. λ_{max}: 602 nm.

Alternatively, the product could also be isolated after reduction with triethylamine by precipitation into DI water, resulting in the formation of a yellow solid. The solid was collected by vacuum filtration, washed with excess DI water and cold methanol (~20 mL), and then dried overnight under high vacuum. When 1.145 g of 5,10-di(4-trifluoromethylphenyl)-5,10-

dihydrophenazine starting material was used, 1.090 g (93.9%) of **5** was recovered using this method. Characterization matched that reported above.

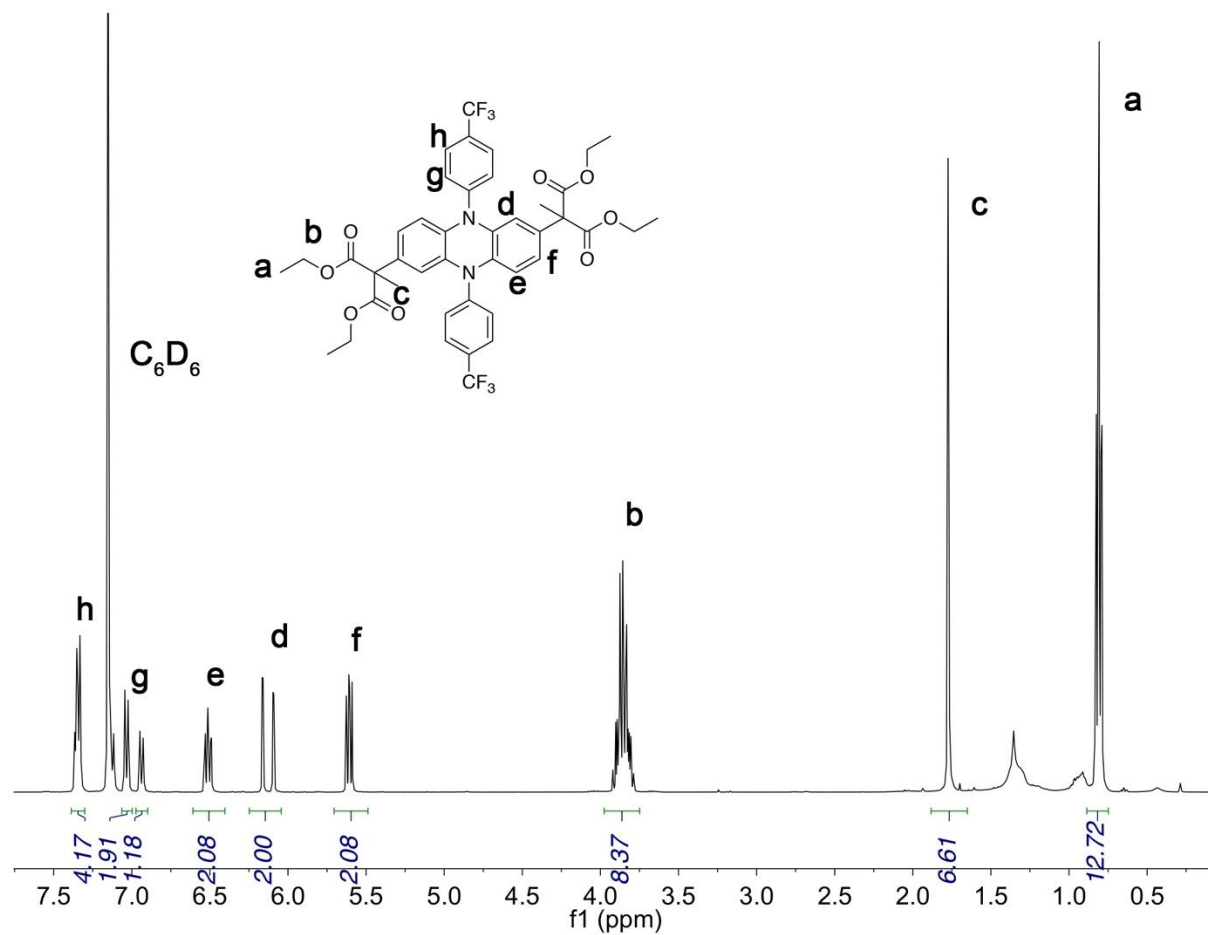


Figure A1.22. ¹H NMR spectrum of **5** in C₆D₆.

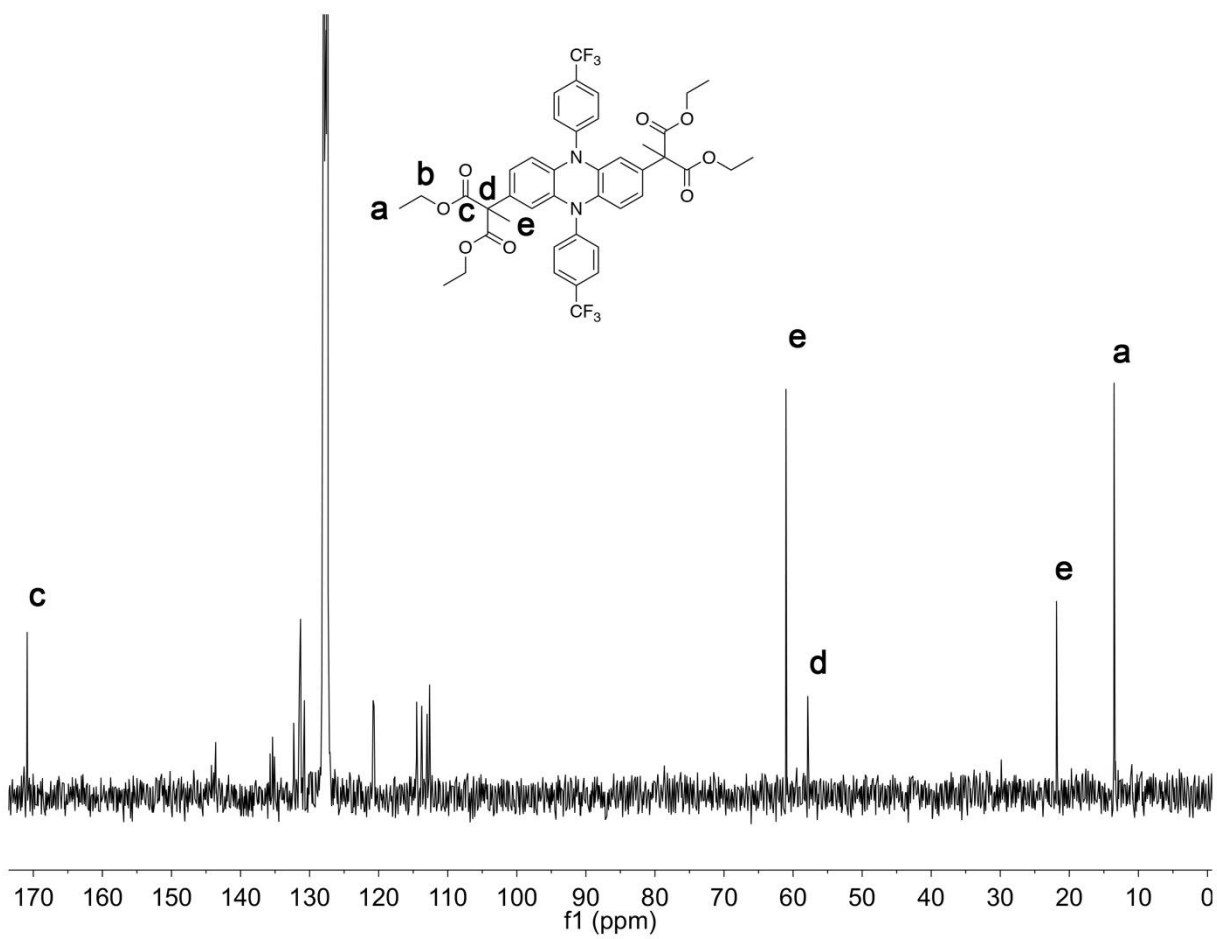


Figure A1.23. ^{13}C NMR spectrum of **5** in C_6D_6 .

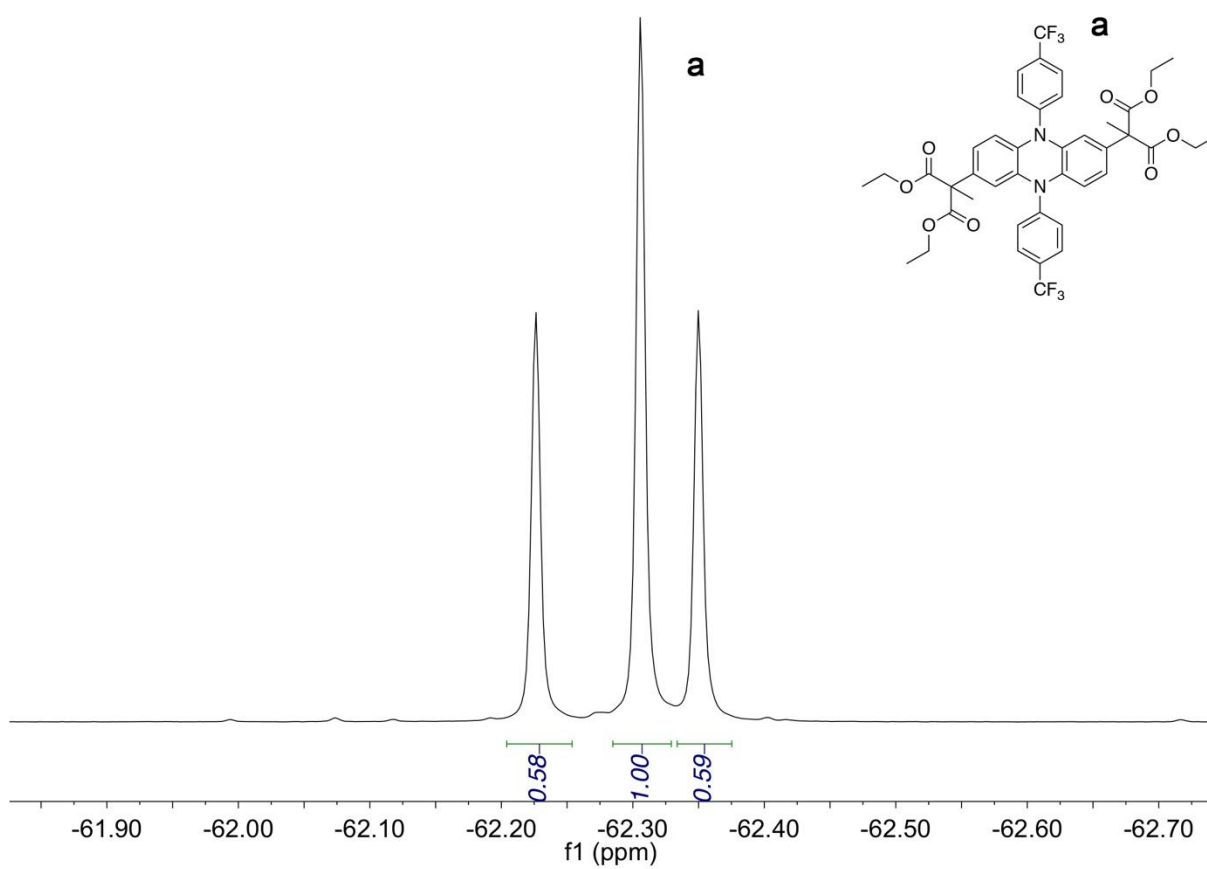


Figure A1.24. ^{19}F NMR spectrum of **5** in C_6D_6 .

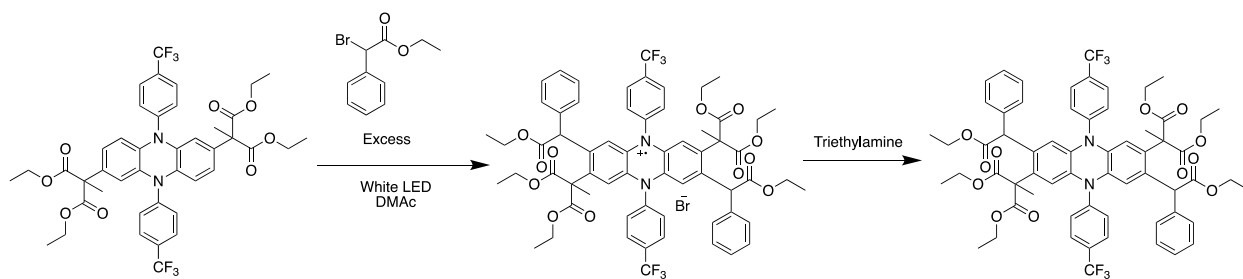


Figure A1.25. Scheme for the synthesis of **6**.

Synthesis of 2,7-di(diethyl-2-methylmalonate-yl)-3,8-di(ethyl phenylacetate-yl)-5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (6**).** 2,7-di(diethyl-2-methylmalonate-yl)-5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine (0.277 g, 0.00034 mol) was added to 20 mL of DMAc in a scintillation vial in an N₂ filled glovebox. Ethyl- α -bromophenylacetate (0.60 mL, 0.0034 mol) was added and the solution was stirred and irradiated with white LEDs overnight. Then the flask was removed from the box, opened to air. Then, 2 mL of triethylamine was added. This solution was then stirred for 5 minutes and the volatiles were subsequently removed by rotary evaporation and dry-loaded onto silica gel. The compound was purified by flash chromatography using a gradient of 0-50% EtOAc in hexanes with 5% triethylamine. Yield: 0.320 g (92.2%). ¹H NMR (400 MHz, C₆D₆): δ 7.38-7.20 (m, 8H), 7.08-6.83 (m, 10H), 6.27-6.04 (m, 2H), 5.77-5.60 (m, 2H), 5.23 (s, 2H), 3.97-3.64 (m, 12H), 2.00-1.90 (m, 6H), 0.90-0.71 (m, 18H). ¹³C NMR (101 MHz, C₆D₆): δ 171.38, 171.12, 139.99, 134.58, 132.19, 131.92, 131.23, 130.60, 130.09, 126.74, 118.84, 118.33, 112.36, 61.38, 60.63, 59.31, 52.87, 23.66, 13.54. ¹⁹F NMR (376 MHz, C₆D₆): δ -62.25, -62.35, -62.43. Abs. λ_{max} : 372 nm. ϵ = 7200 M⁻¹·cm⁻¹. Em. λ_{max} : 598 nm.

Alternatively, the product could also be isolated after reduction with triethylamine by precipitation into DI water, resulting in the formation of an orange solid. The solid was collected by vacuum filtration, washed with excess DI water and cold methanol (~20 mL), and then dried overnight under high vacuum. When 1.7978 g of **5** was used, 1.0895 g (38.9%) of **6** was recovered using this method. Characterization matched that reported above.

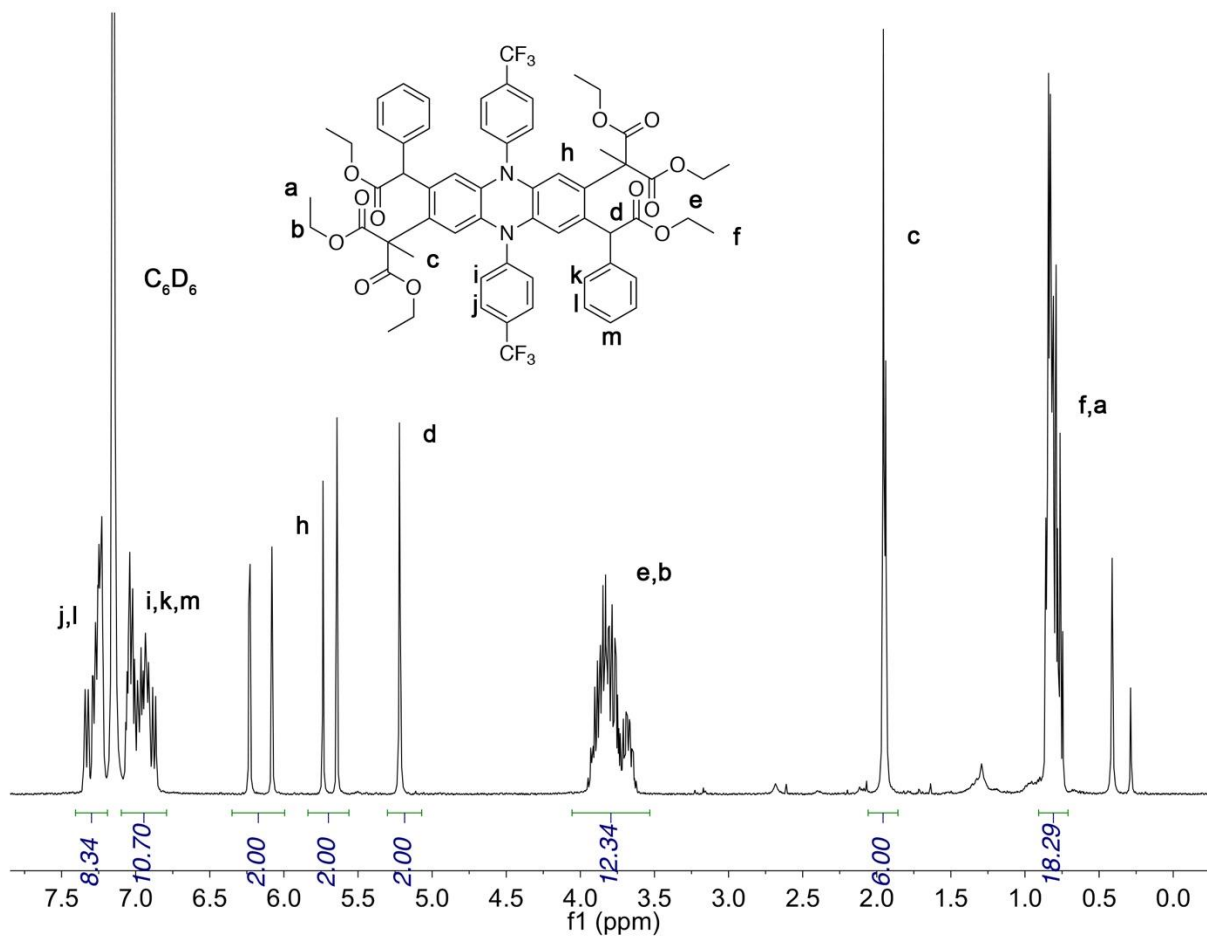


Figure A1.26. ^1H NMR spectrum of **6** in C_6D_6 .

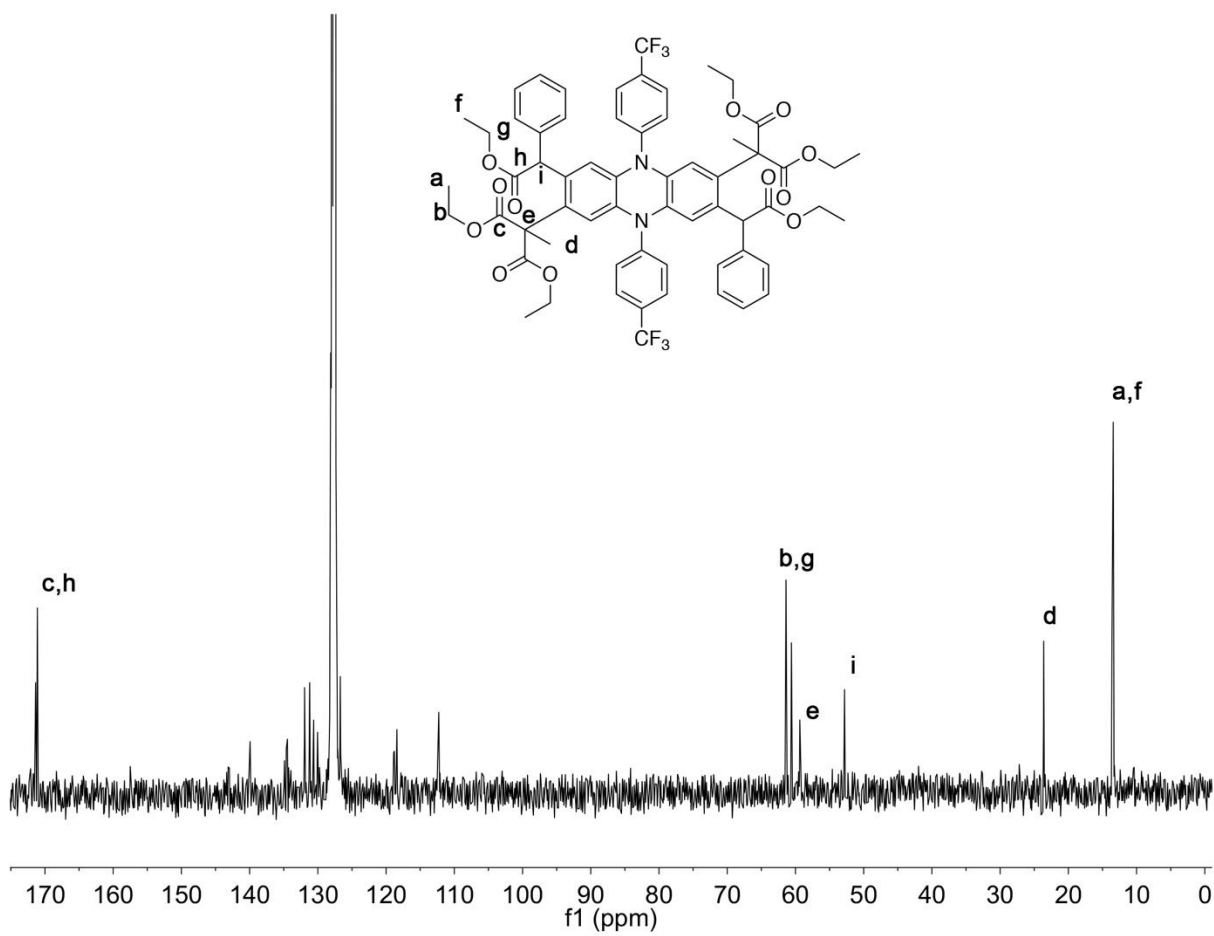


Figure A1.27. ^{13}C NMR spectrum of **6** in C_6D_6 .

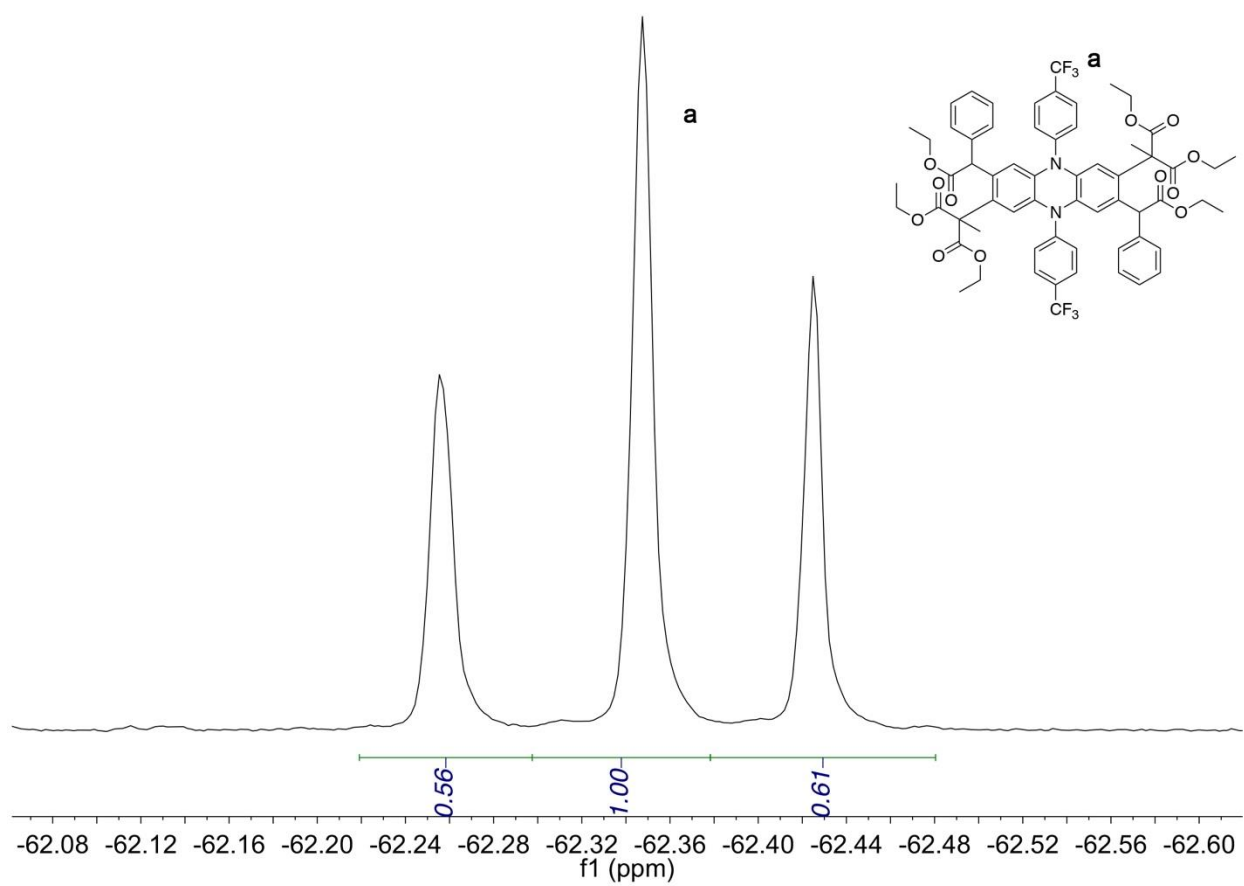


Figure A1.28. ^{19}F NMR spectrum of **6** in C_6D_6 .

Synthesis of Radical Cations

For UV-Vis, aliquots containing each radical cation were removed from the PC synthesis reaction mixture prior to the addition of triethyl amine.

For EPR spectroscopy of $1^{+\bullet} - 6^{+\bullet}$ as presented in the main text, radical cations of **1** – **6** were synthesized using 1 eq nitrosonium tetrafluoroborate. Oxidation of **1** – **6** was performed in DCM, after which the resulting radical cations were dissolved in DMAc and measured by EPR spectroscopy.

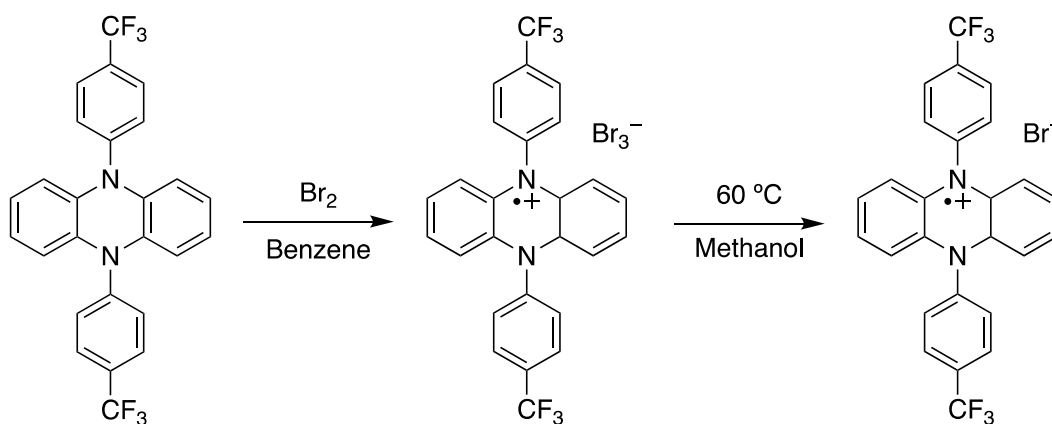


Figure A1.29. Scheme for the synthesis of $1^{+\bullet}\text{Br}^-$.

Synthesis of 5,10-di(4-trifluorobenzo)-5,10-dihydrophenazinium tribromide ($1^{+\bullet}\text{Br}_3^-$).

Alternatively, **1** (0.100 g, 0.213 mmol, 1 eq) was dissolved in 80 mL benzene and stirred vigorously. Molecular bromine (5.5 μL , 0.106 mmol, 0.5 eq) was added to the solution, which caused immediate precipitation of a dark green powder. The powder was collected by vacuum filtration and dried under high vacuum. The same product as above was obtained.

Synthesis of 5,10-di(4-trifluorobenzo)-5,10-dihydrophenazinium bromide ($1^{+\bullet}\text{Br}^-$). **1**

(0.200 g, 0.425 mmol, 1 eq) was dissolved in 80 mL benzene and stirred vigorously. Molecular bromine (43 μL , 0.851 mmol, 2 eq) was added to the solution, which caused immediate precipitation of a dark green powder. The powder was collected by vacuum filtration and recrystallized from methanol. Crystallography revealed the presence of a tribromide anion, so the

product was heated in methanol for 4 h, causing the solution to turn from green to red. The solution was placed in a freezer at -25 °C, which ultimately yielded green crystals of 1^{+}Br^{-} (characterized by crystallography in reference 7).

Investigation of Radical Addition to 1 and 1^{+}

Addition of EBP to 1 in the absence of MMA. A 20 mL vial was charged with 5 mg (0.01 mmol, 1.00 eq.) **1** and a stir-bar and brought into a nitrogen atmosphere glovebox. To this vial was added 1.00 mL DMAc and 10.0 eq. ATRP initiator EBP. The vial was then sealed and placed in a photoreactor on a stir-plate. After 2 hours, the vial was removed from the glovebox and the volatiles were removed under reduced pressure. The sample was then analyzed by ESI-MS.⁸

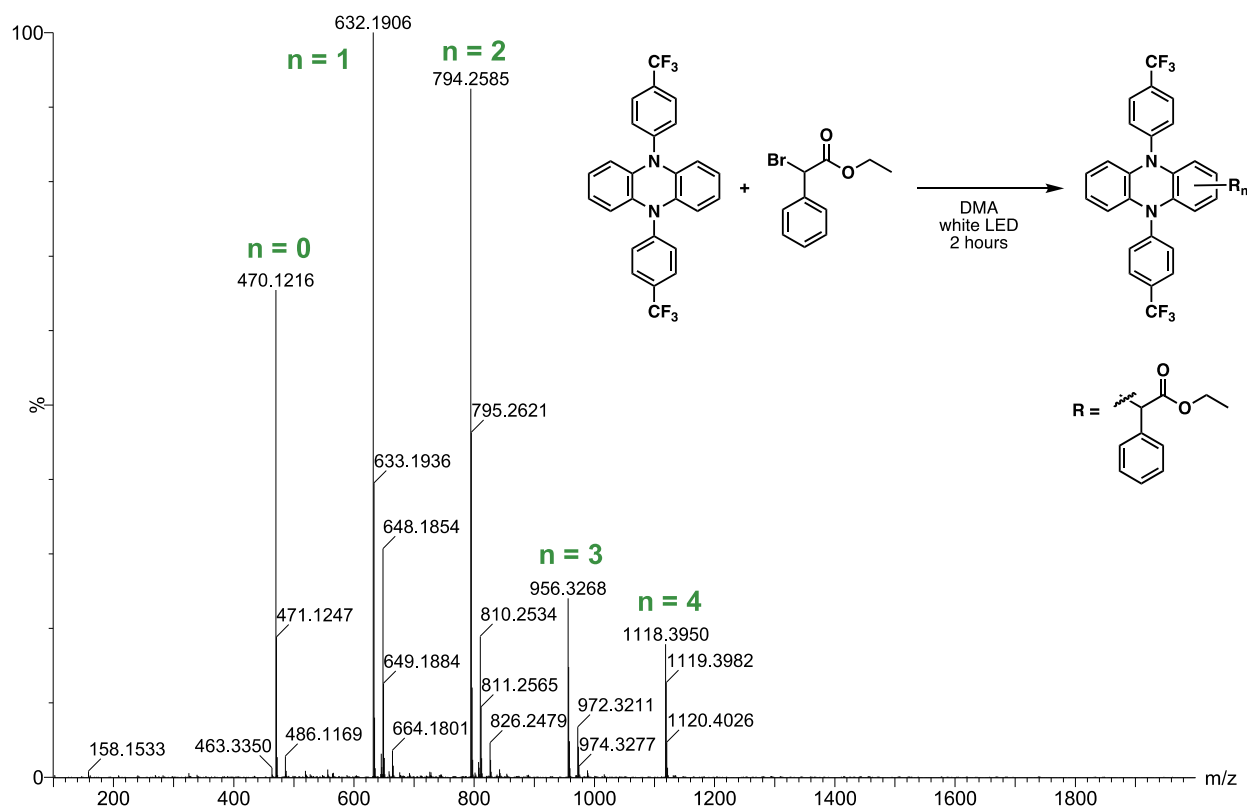


Figure A1.30. ESI mass spectrum of the residue of a core substitution reaction irradiated for 2h.⁸

Radical addition to 1 in the presence of MMA. A 20 mL vial was charged with 5 mg (0.01 mmol, 1.00 eq.) **1** and a stirbar and brought into a nitrogen atmosphere glovebox. To this vial was added 1.00 mL DMAc, 25.8 mg (0.106 mmol, 10.0 eq.) EBP, and 1.06 g MMA (10.6 mmol, 1000 eq.). The vial was then sealed and placed in a photoreactor on a stir-plate. After 20 minutes, the vial was removed from the glovebox and the volatiles were removed under reduced pressure. The sample was then analyzed by ESI-MS.⁸

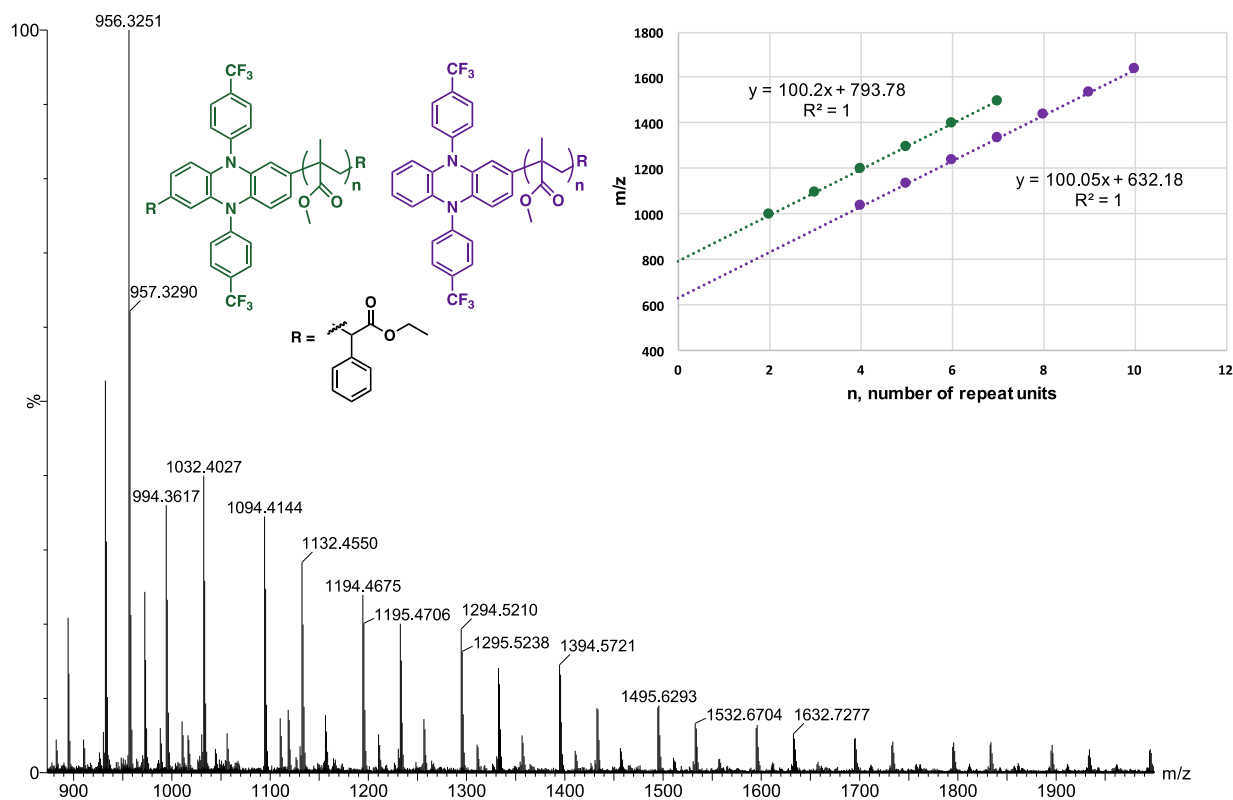


Figure A1.31. ESI mass spectrum of an O-ATRP reaction stopped after 20 min irradiation.⁸

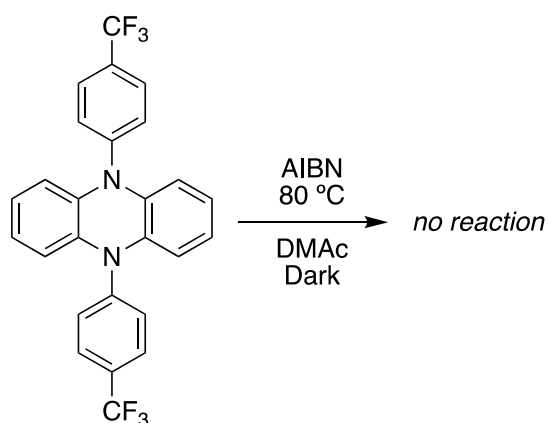


Figure A1.32. Scheme for the reaction of **1** with AIBN in deuterated DMAc.

Investigation of core substitution with AIBN and 1. **1** (20 mg, 0.0425 mmol, 1 eq) and AIBN (0.139 g, 0.851 mmol, 20 eq) were dissolved in deuterated (d_9) DMAc (1 mL). The ^1H NMR spectrum of the solution was acquired, and then the solution was heated to 80 °C for 1h. After heating, the ^1H NMR spectrum of the solution was once again taken to analyze the products of the reaction. No change to the PC spectrum was evident (Figure A1.34).

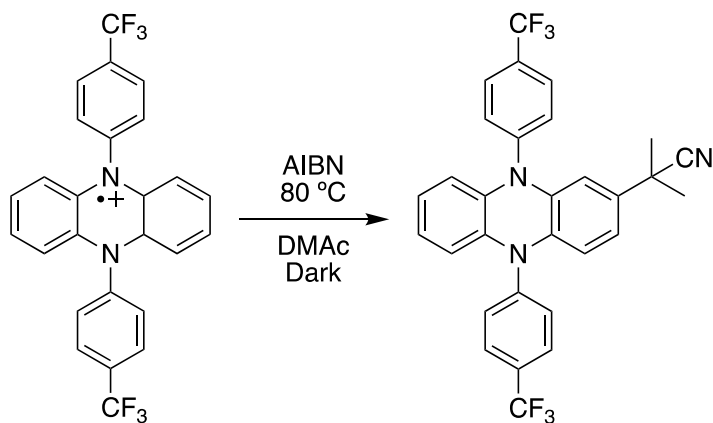


Figure A1.33. Scheme for the reaction of $\mathbf{1}^{+\bullet}\text{Br}^-$ with AIBN in deuterated DMAc.

Investigation of core substitution with AIBN and $\mathbf{1}^{+\bullet}$. $\mathbf{1}^{+\bullet}\text{Br}^-$ (20 mg, 0.0364 mmol, 1 eq) and AIBN (0.119 g, 0.729 mmol, 20 eq) were dissolved in deuterated (d_9) DMAc (1 mL). The ^1H NMR spectrum of the solution was acquired, and then the solution was heated to 80 °C for 1h. After heating, the ^1H NMR spectrum of the solution was once again taken to analyze the products of the reaction (Figure A1.34).

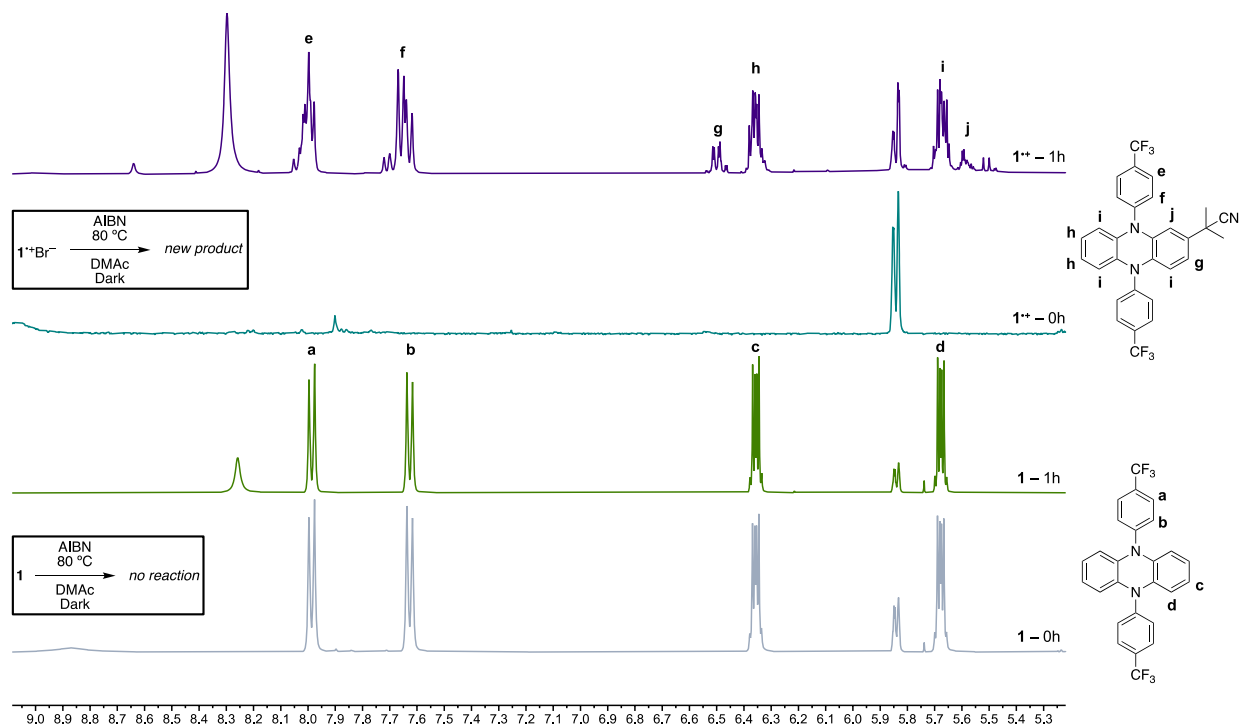


Figure A1.34. ^1H NMR spectra of **1** (bottom) and 1^{++}Br^- (top) reactions with AIBN at 0h and 1h.

General Polymerization Procedure

For polymerizations performed by O-ATRP with greater than 100 ppm PC, the PCs were weighted into scintillation vials and pumped into a nitrogen glovebox with a magnetic stir bar. Under a nitrogen atmosphere, solvent (1 mL), MMA (1 mL, 9.35 mmol, 1000 eq), and DBMM (17.9 μ L, 0.0935 mmol, 10 eq) were added to the vials. The vials were then sealed and irradiated in a white LED beaker with a fan blowing over the beaker for temperature control.

For polymerizations performed by O-ATRP with less than 100 ppm PC, the PCs were weighted into scintillation vials and pumped into a nitrogen glovebox. Under a nitrogen atmosphere, stock solutions of the PCs were made in EtAc and transferred to 20 mL scintillation vials with magnetic stir bars. Extra solvent (to reach a total of 1 mL solvent), MMA (1 mL, 9.35 mmol, 1000 eq), and DBMM (17.9 μ L, 0.0935 mmol, 10 eq) were then added to the vials. The vials were sealed and irradiated in a white LED beaker with a fan blowing over the beaker for temperature control.

To monitor polymerizations, 0.1 mL aliquots were removed periodically. Aliquots were quenched in a deuterated chloroform containing 250 ppm butylated hydroxytoluene (BHT). These solutions were then transferred to an NMR tube for ^1H NMR analysis to determine the extent of monomer conversion. Afterwards, solutions were dried and dissolved in unstabilized THF for GPC analysis to obtain number average molecular weight and dispersity.

PHOTOCATALYST CHARACTERIZATION

UV-Visible Absorption Spectroscopy

For determination of the molar absorptivity of **1** – **6**, a stock solution of **1** – **6** was prepared in DMAc. This stock solution was then diluted to form each of the measurement solutions prior to analysis by UV-Vis.

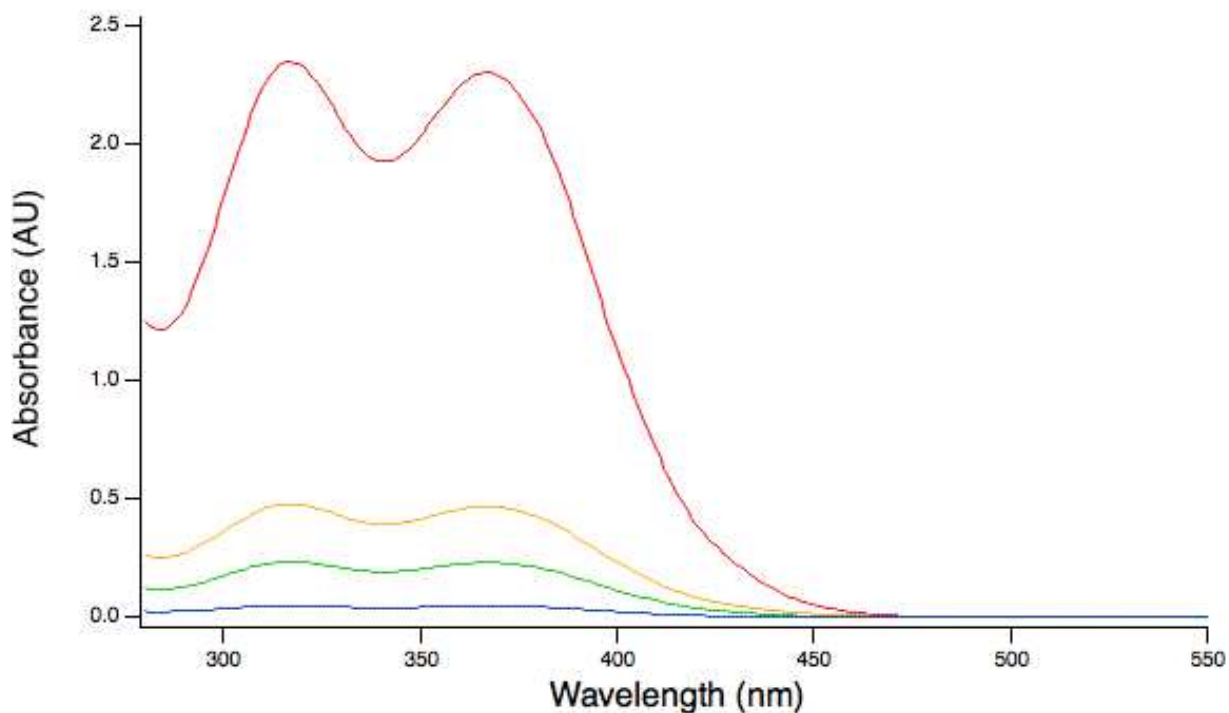


Figure A1.35. UV-Vis spectrum of **1** at four concentrations in DMAc.

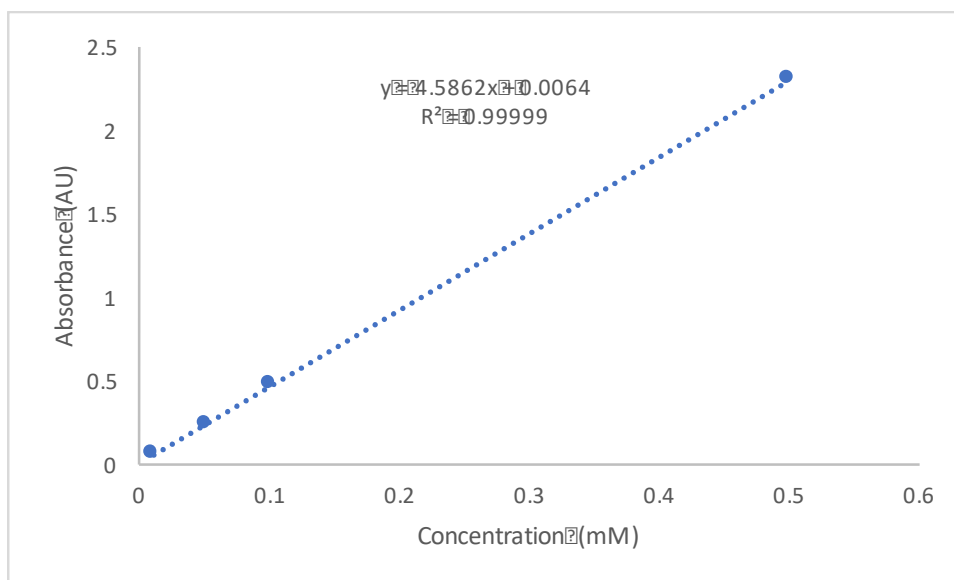


Figure A1.36. Beer's law plot for the determination of the molar absorptivity of **1** in DMAc at $\lambda_{\text{max}} = 367 \text{ nm}$.

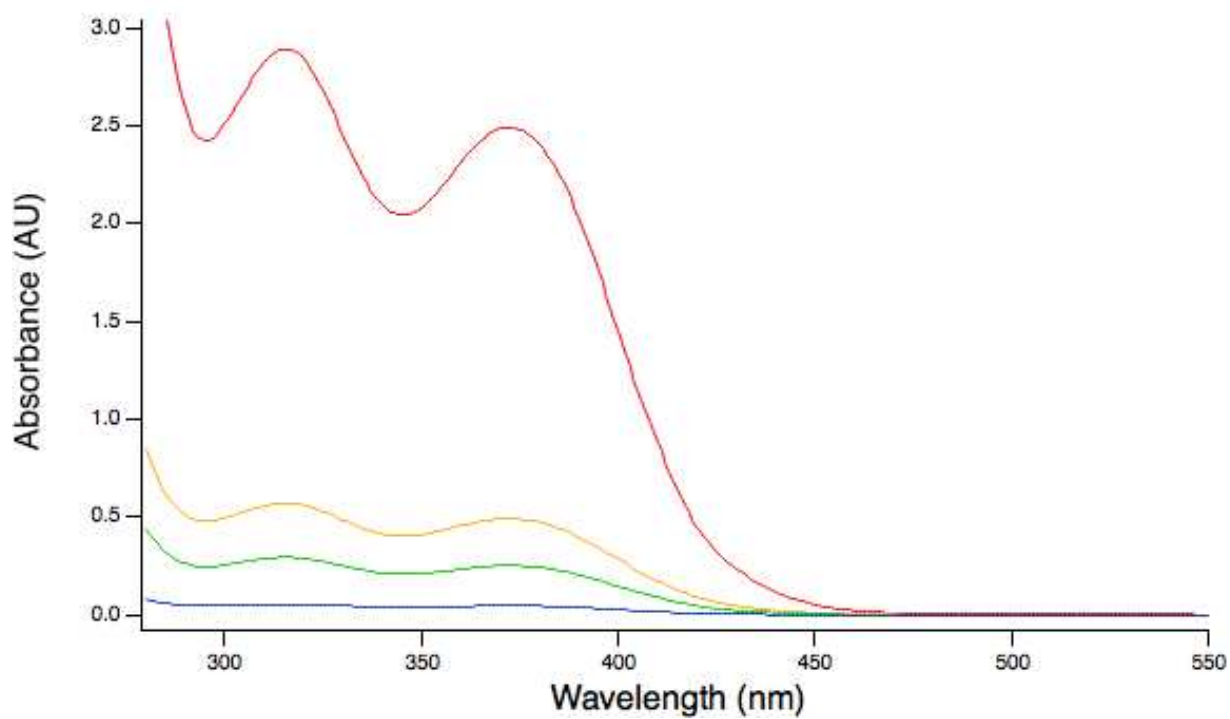


Figure A1.37. UV-Vis spectrum of **2** at four concentrations in DMAc.

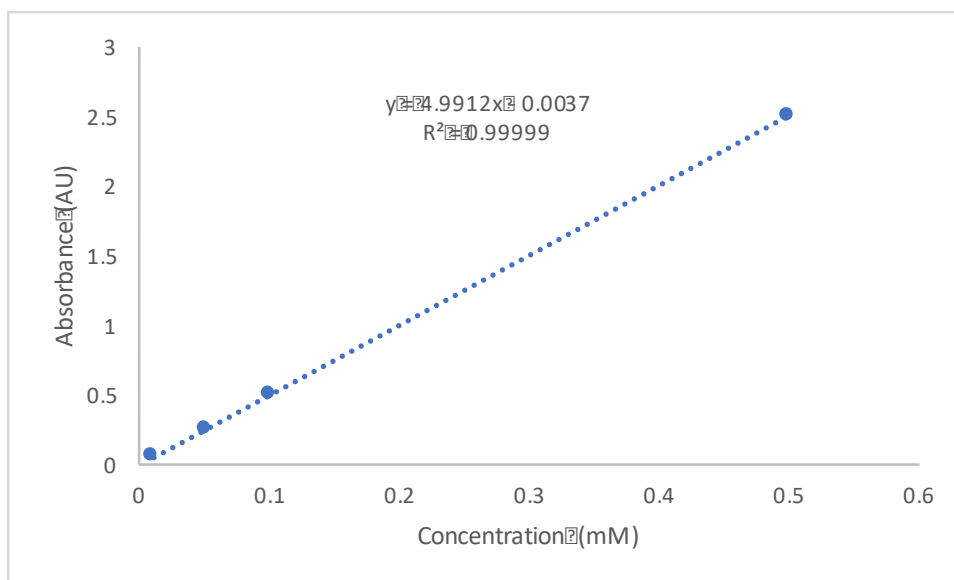


Figure A1.38. Beer's law plot for the determination of the molar absorptivity of **2** in DMAc at $\lambda_{\text{max}} = 373 \text{ nm}$.

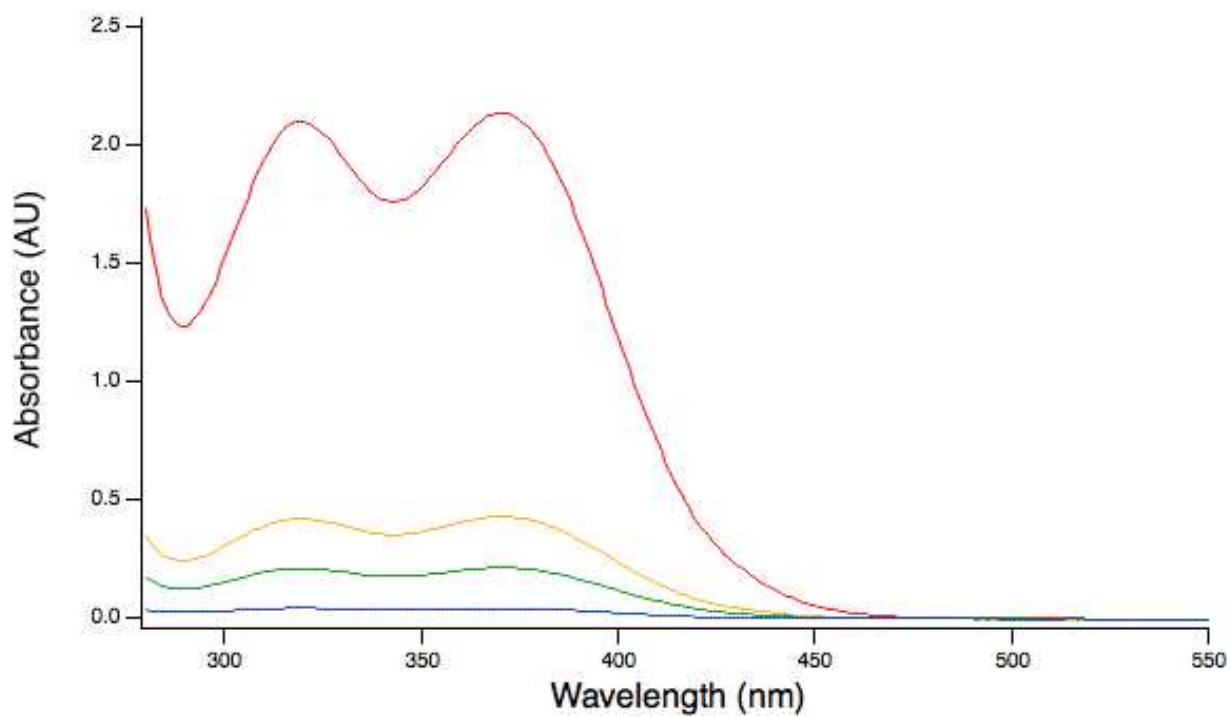


Figure A1.39. UV-Vis spectrum of **3** at four concentrations in DMAc.

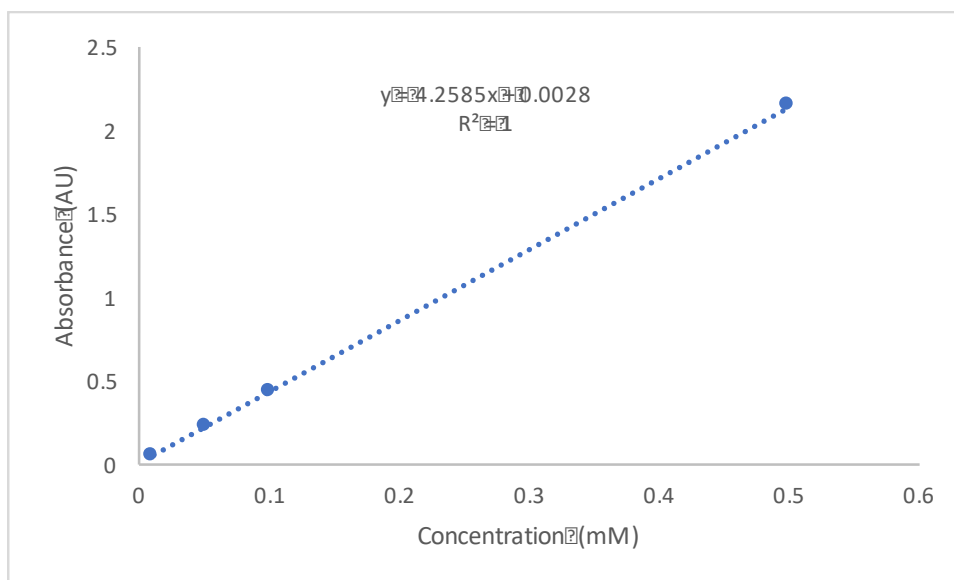


Figure A1.40. Beer's law plot for the determination of the molar absorptivity of **3** in DMAc at $\lambda_{\text{max}} = 371 \text{ nm}$.

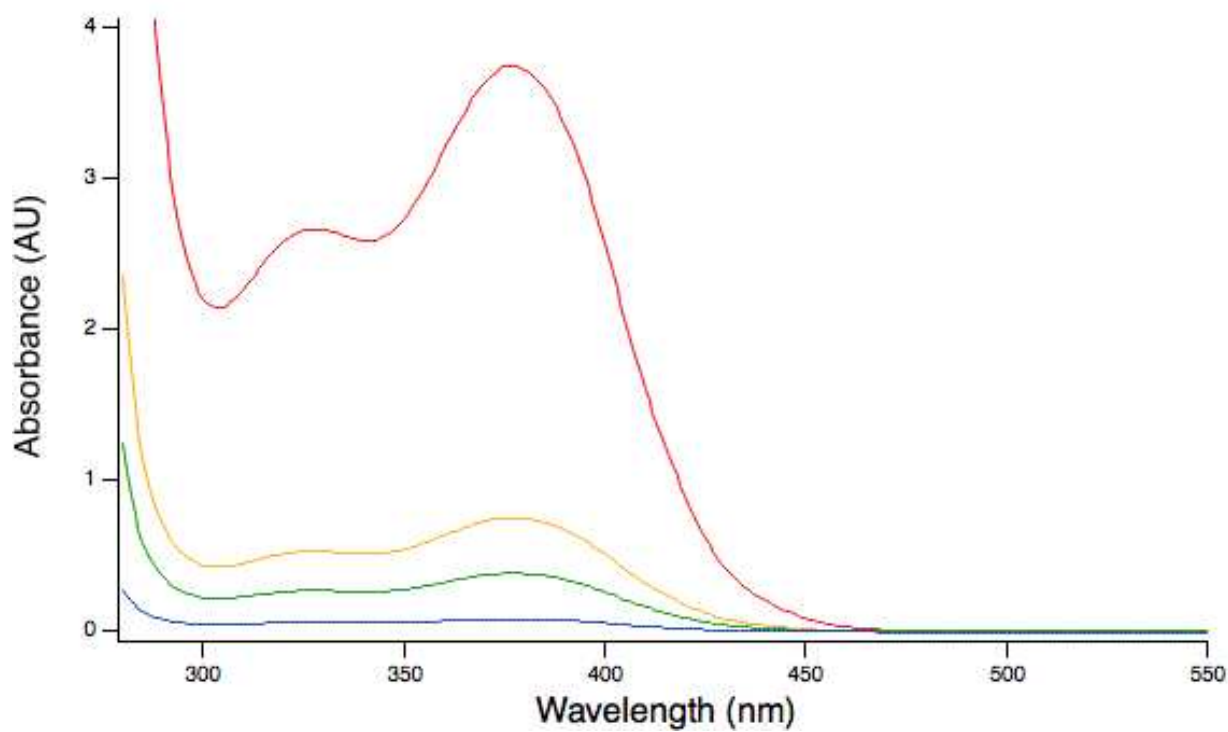


Figure A1.41. UV-Vis spectrum of **4** at four concentrations in DMAc.

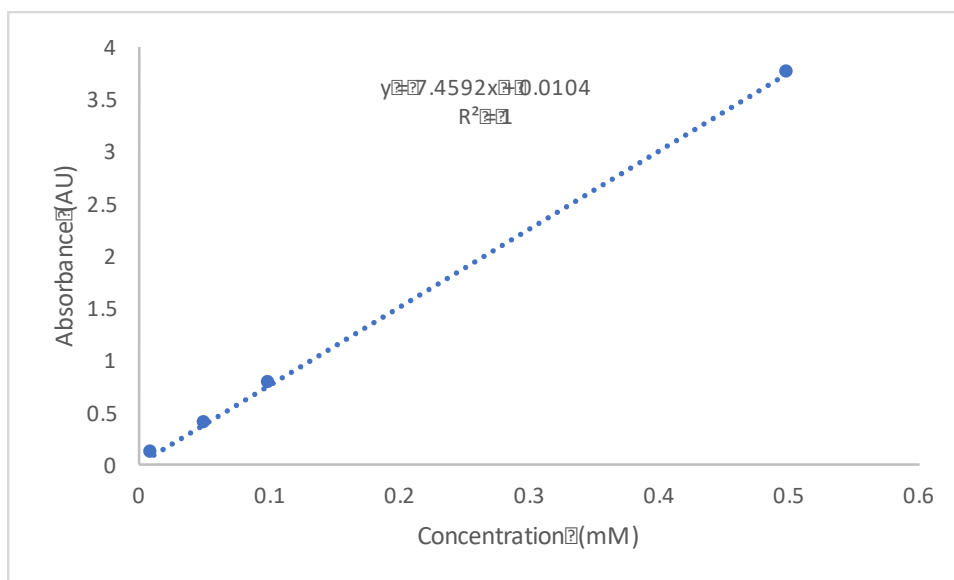


Figure A1.42. Beer's law plot for the determination of the molar absorptivity of **4** in DMAc at $\lambda_{\text{max}} = 377 \text{ nm}$.

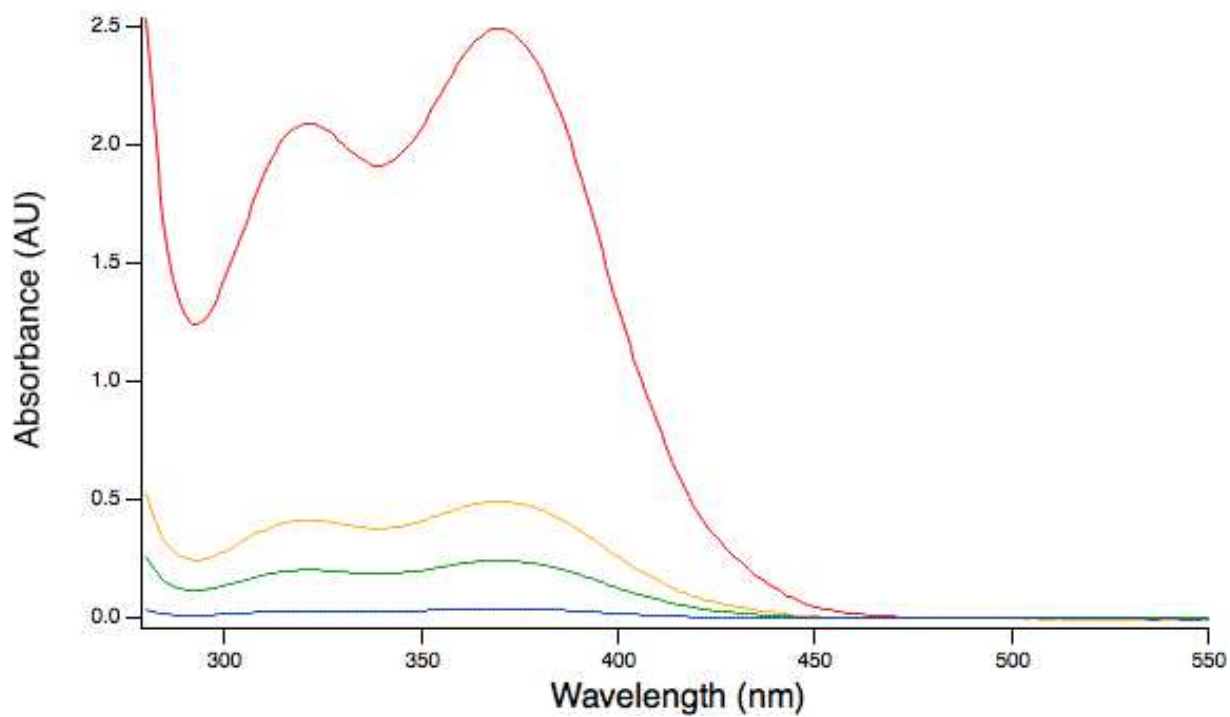


Figure A1.43. UV-Vis spectrum of **5** at four concentrations in DMAc.

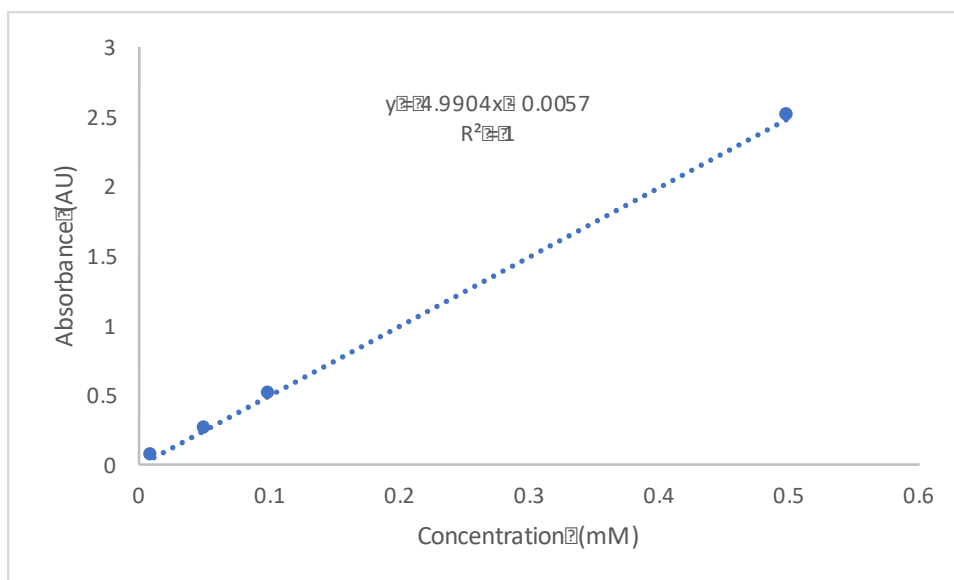


Figure A1.44. Beer's law plot for the determination of the molar absorptivity of **5** in DMAc at $\lambda_{\text{max}} = 370 \text{ nm}$.

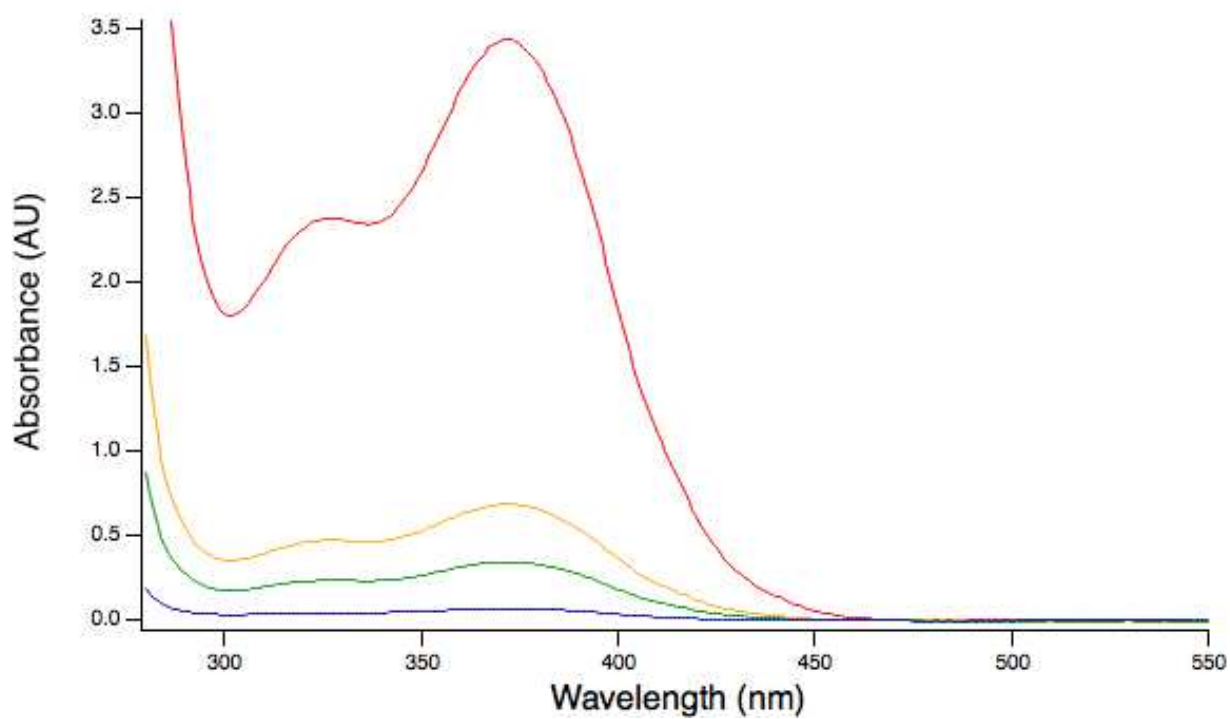


Figure A1.45. UV-Vis spectrum of **6** at four concentrations in DMAc.

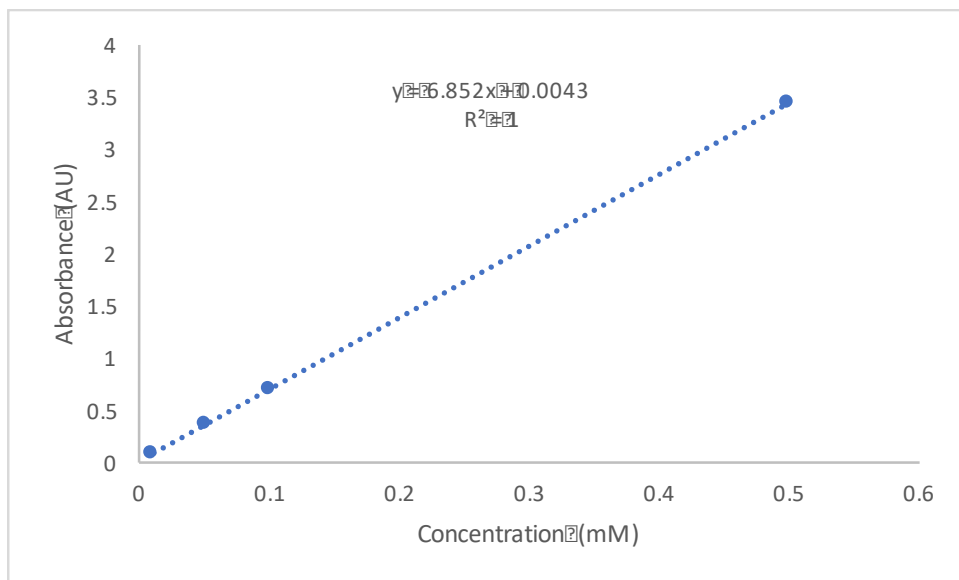


Figure A1.46. Beer's law plot for the determination of the molar absorptivity of **6** in DMAc at $\lambda_{\text{max}} = 372 \text{ nm}$.

Emission Spectroscopy

For measurement of the emission spectra of **1** – **6**, stock solutions of the PCs were prepared in DMAc. The stock solution was measured by emission spectroscopy and then diluted several times to prepare the other concentrations reported.

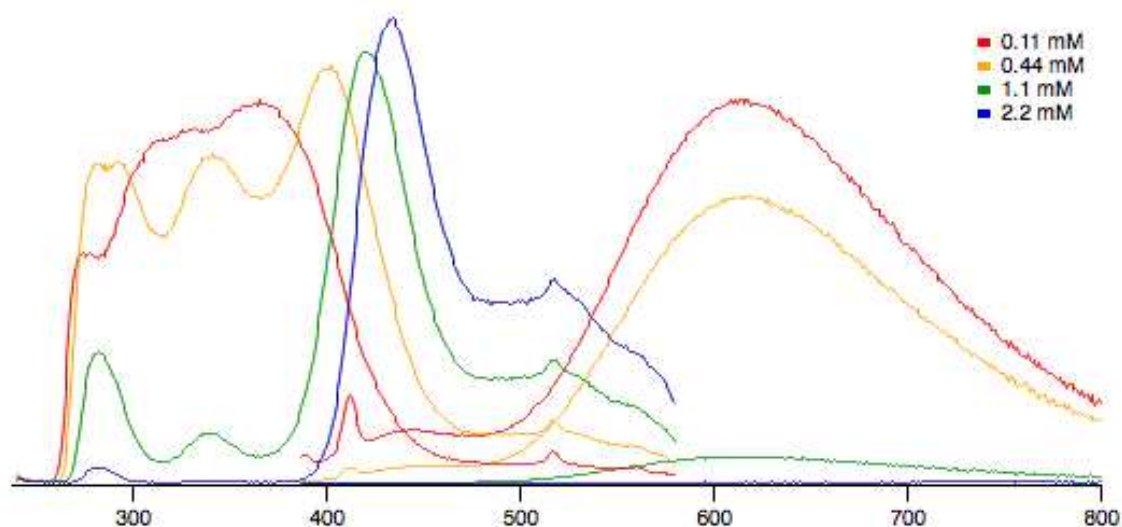


Figure A1.47. Emission (right) and excitation (left) spectra of **1** in DMAc at various concentrations.

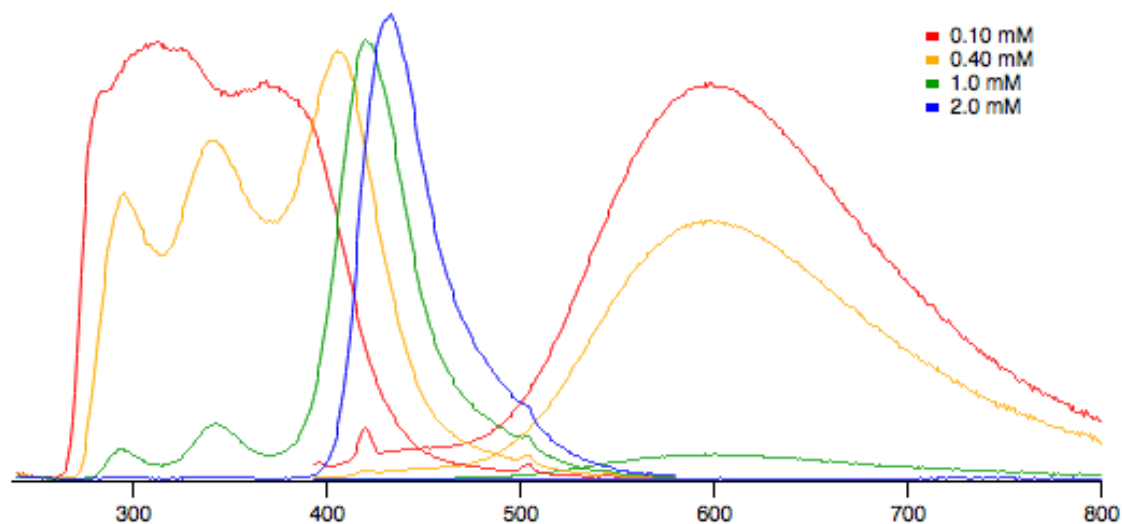


Figure A1.48. Emission (right) and excitation (left) spectra of **2** in DMAc at various concentrations.

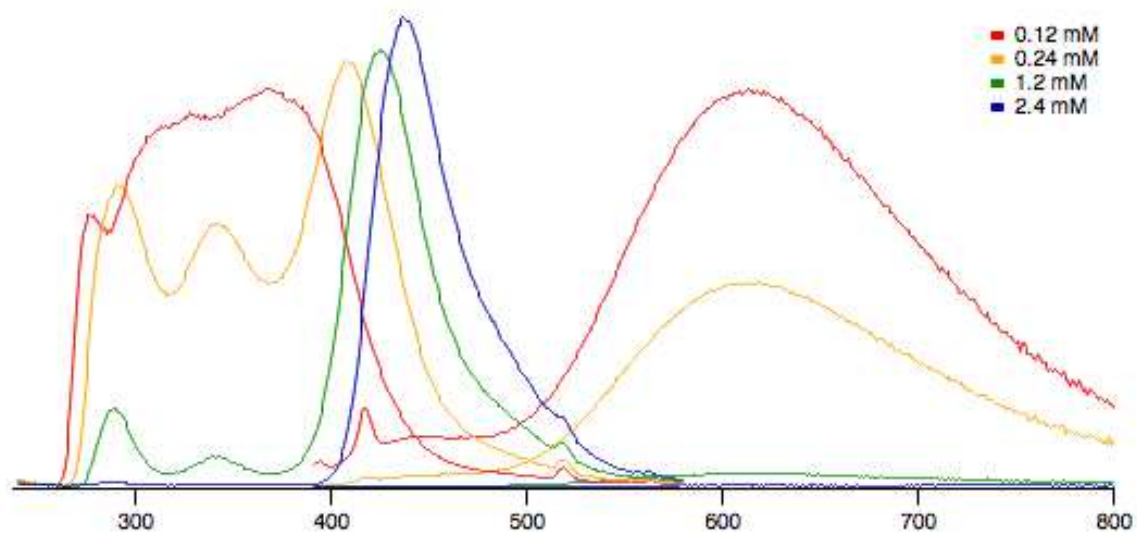


Figure A1.49. Emission (right) and excitation (left) spectra of **3** in DMAc at various concentrations.

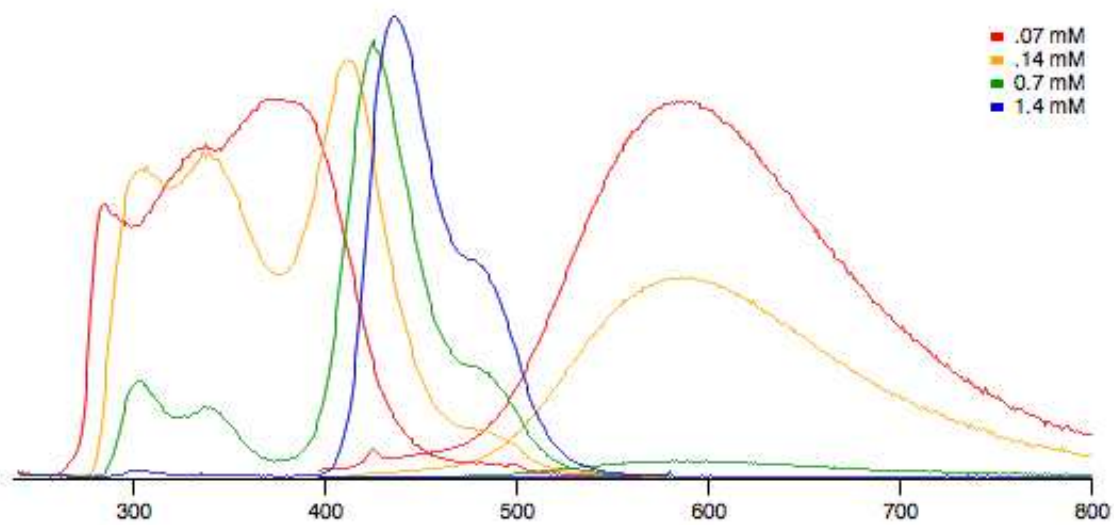


Figure A1.50. Emission (right) and excitation (left) spectra of **4** in DMAc at various concentrations.

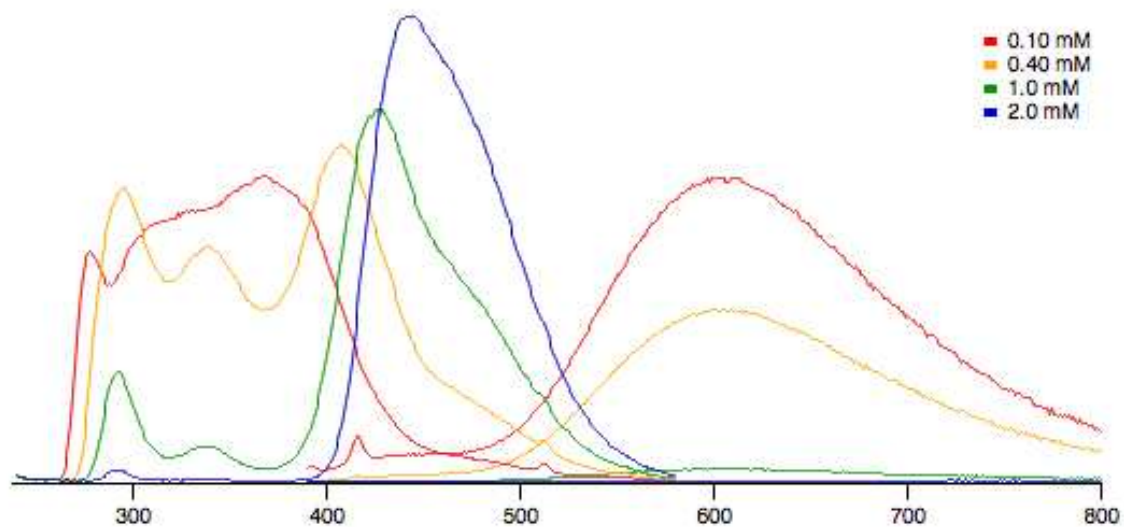


Figure A1.51. Emission (right) and excitation (left) spectra of **5** in DMAc at various concentrations.

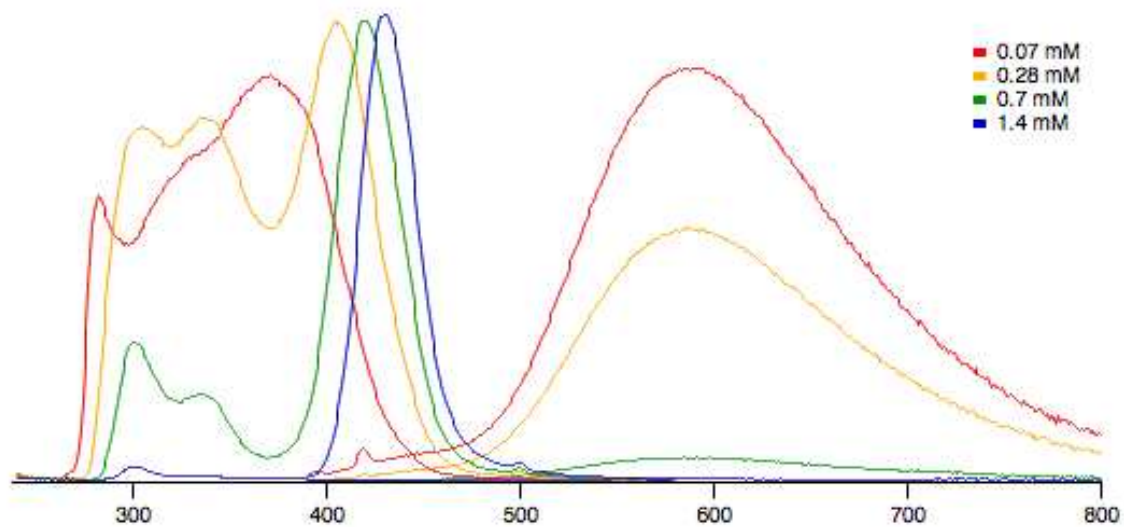


Figure A1.52. Emission (right) and excitation (left) spectra of **6** in DMAc at various concentrations.

Cyclic Voltammetry

See *Experimental Equipment* above for details regarding the reagents and electrodes used in these measurements. For each compound, solutions were prepared in DMAc with 0.1 M NBu₄PF₆ and degassed by nitrogen bubbling prior to measurement.

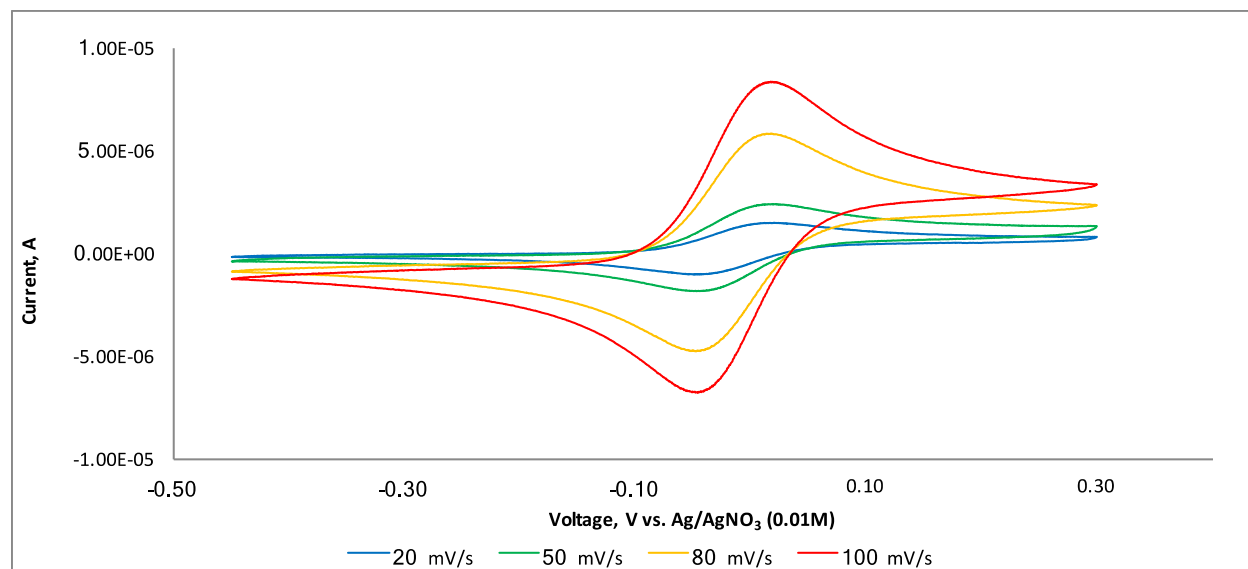


Figure A1.53. Cyclic voltammogram of **1** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

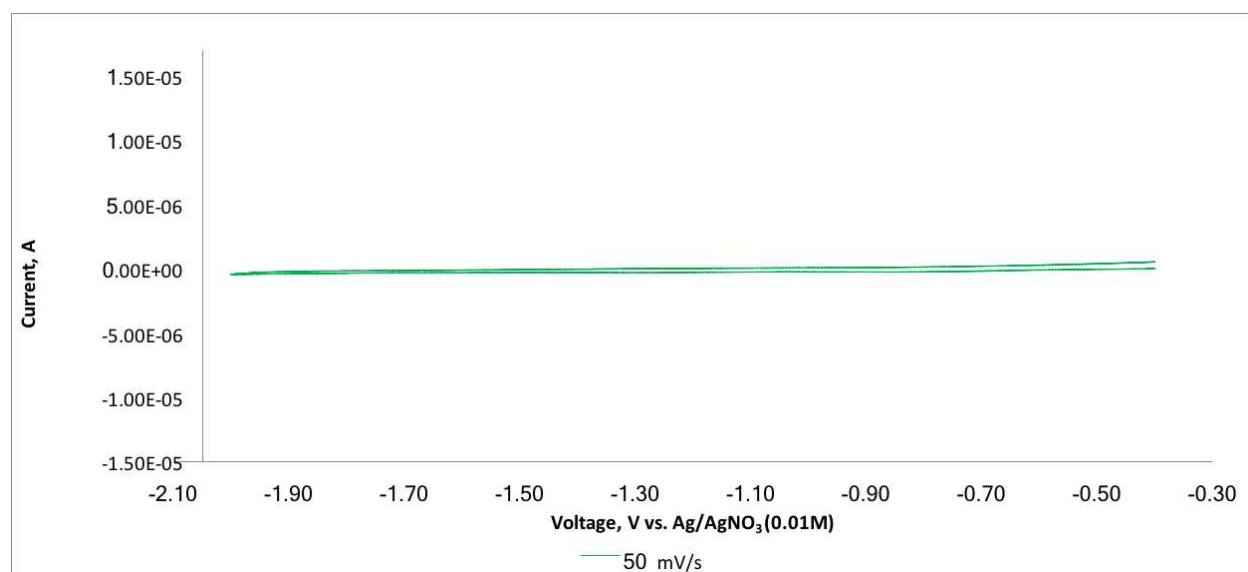


Figure A1.54. Cyclic voltammogram of **1** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

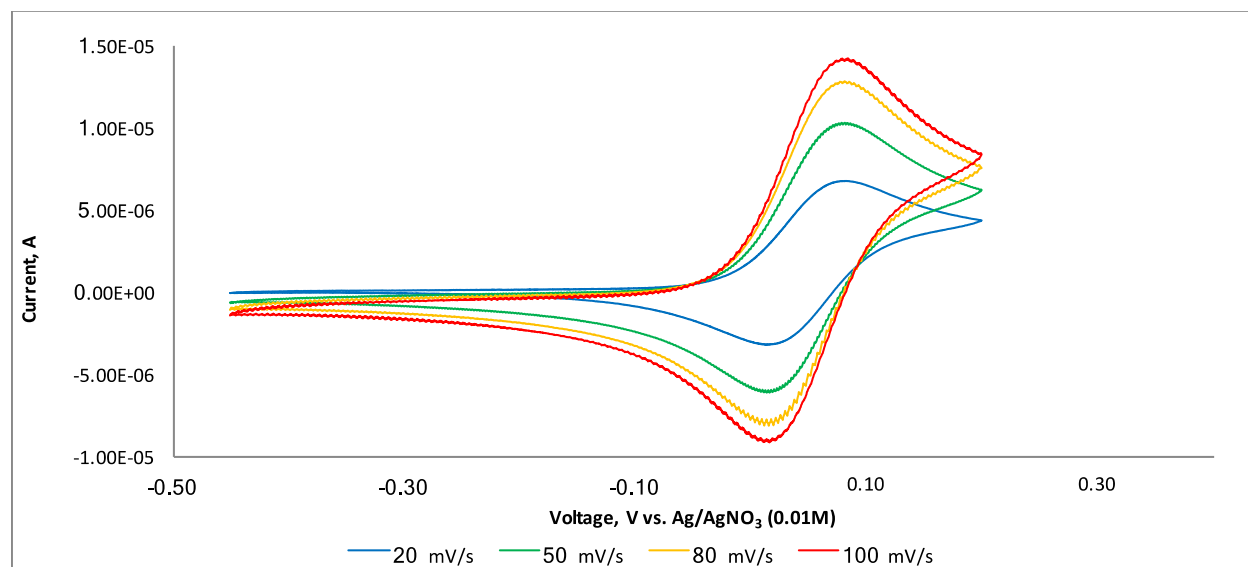


Figure A1.55. Cyclic voltammogram of **2** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

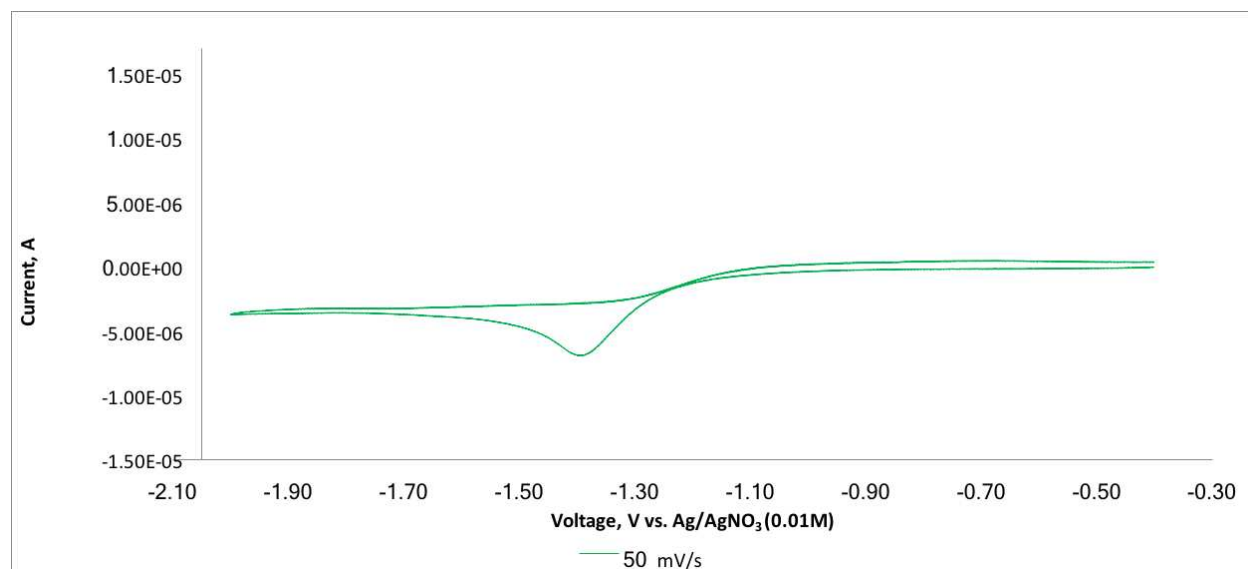


Figure A1.56. Cyclic voltammogram of **2** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

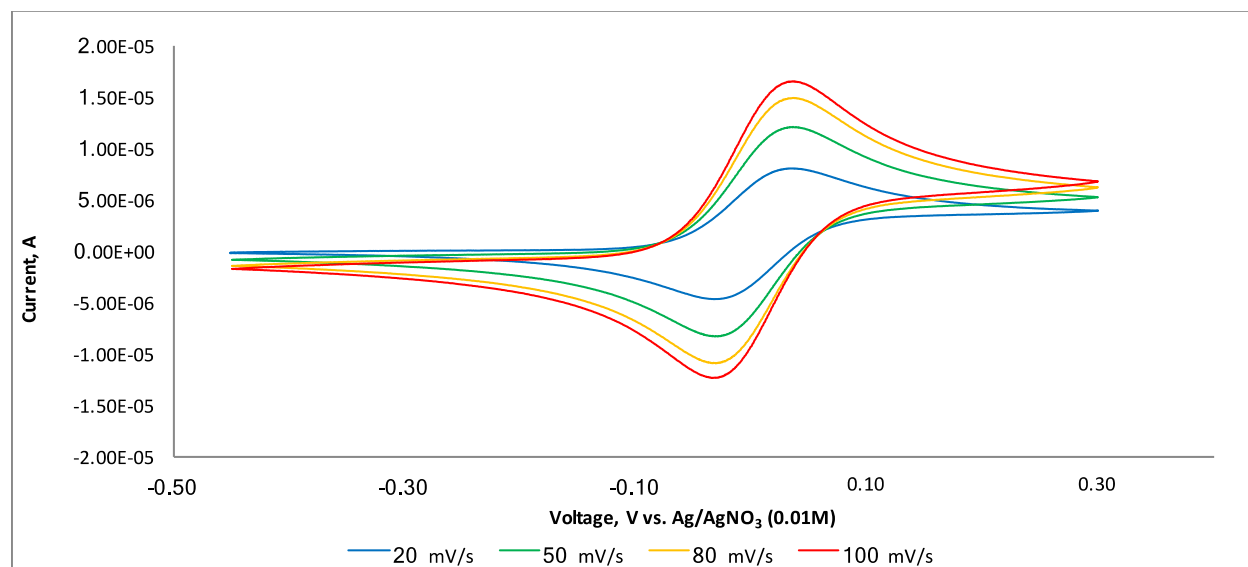


Figure A1.57. Cyclic voltammogram of **3** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

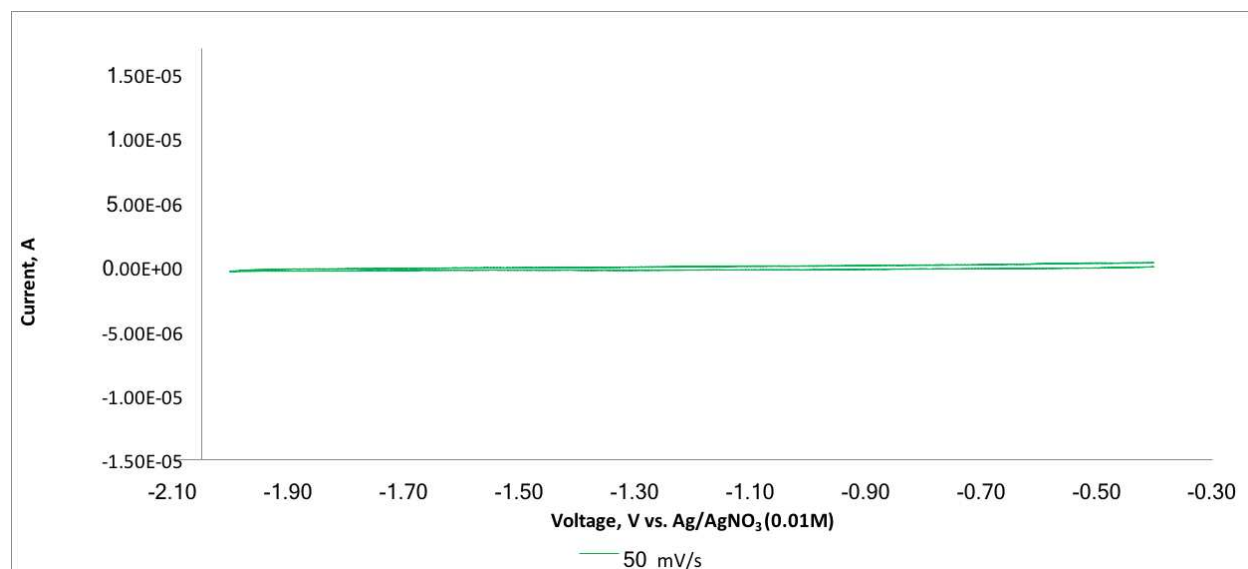


Figure A1.58. Cyclic voltammogram of **3** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

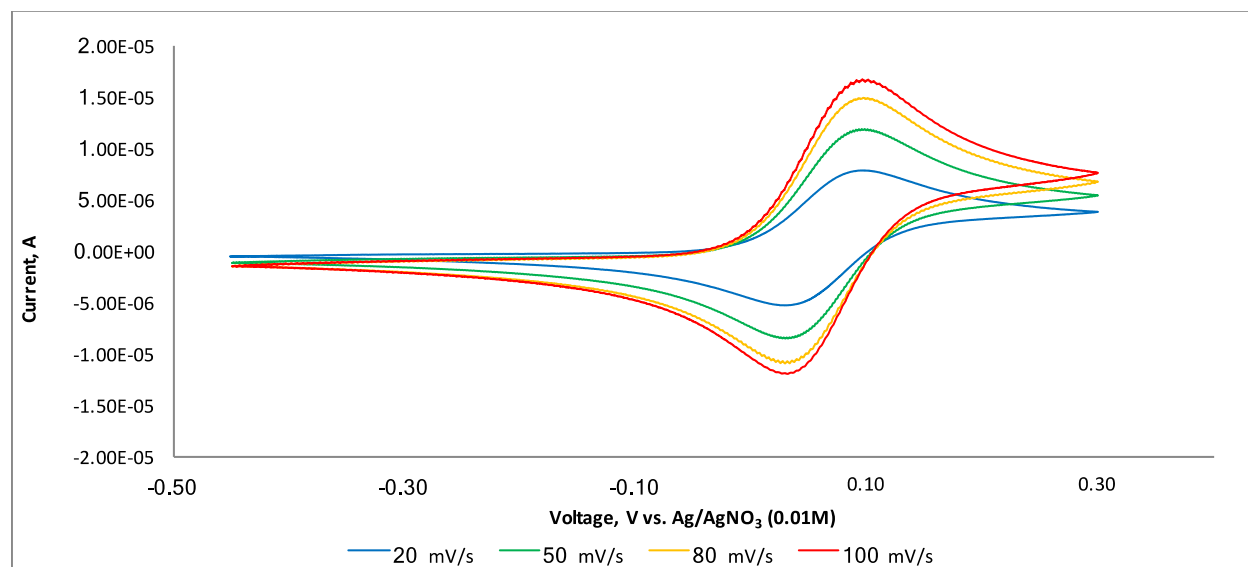


Figure A1.59. Cyclic voltammogram of **4** in DMAc with 0.1 M NBu_4PF_6 supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO_3 reference electrode in acetonitrile with 0.1 M NBu_4PF_6).

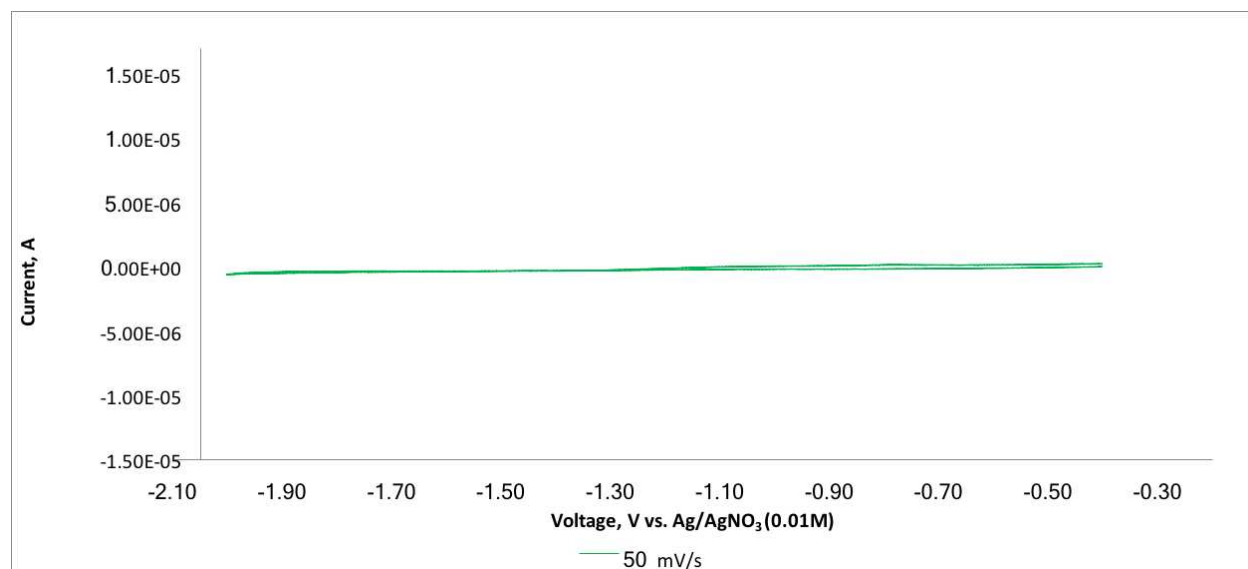


Figure A1.60. Cyclic voltammogram of **4** in DMAc with 0.1 M NBu_4PF_6 supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO_3 reference electrode in acetonitrile with 0.1 M NBu_4PF_6).

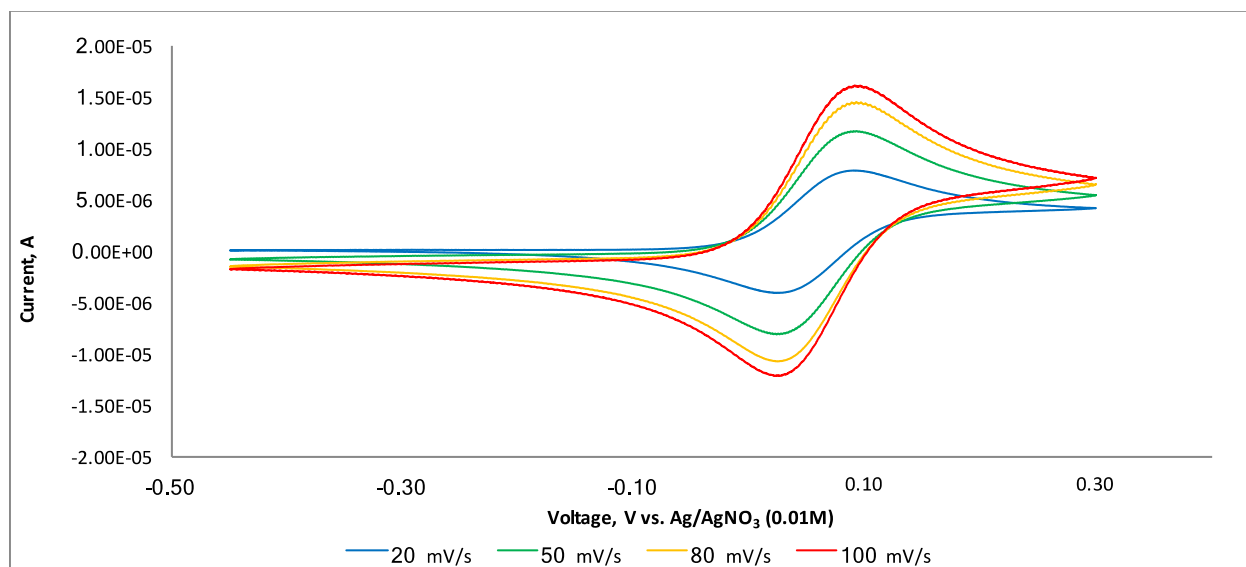


Figure A1.61. Cyclic voltammogram of **5** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

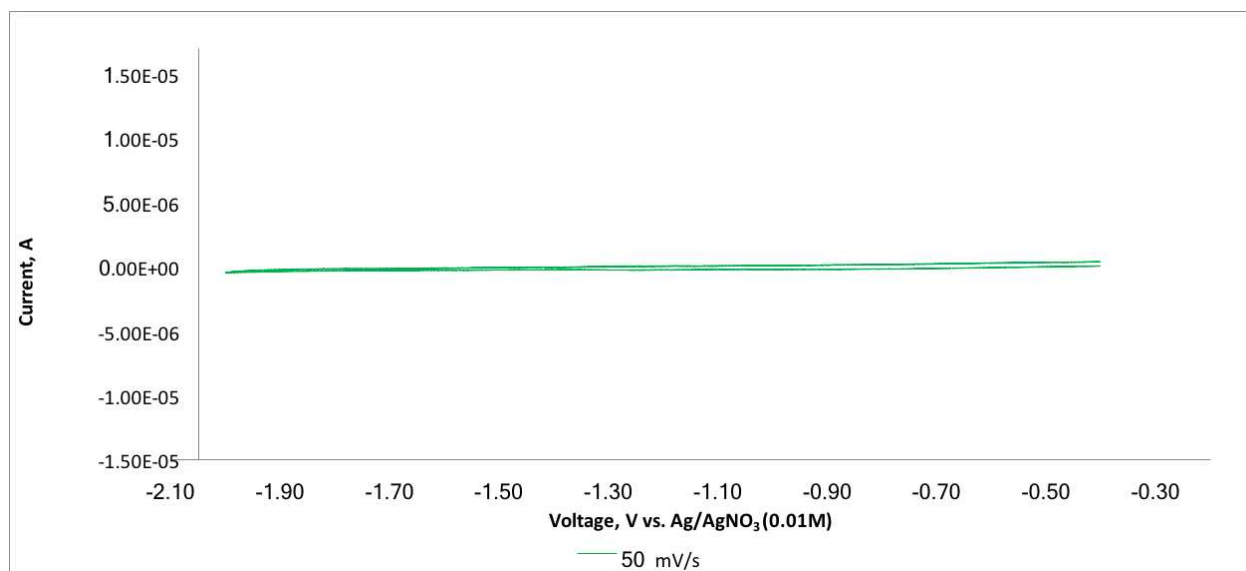


Figure A1.62. Cyclic voltammogram of **5** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

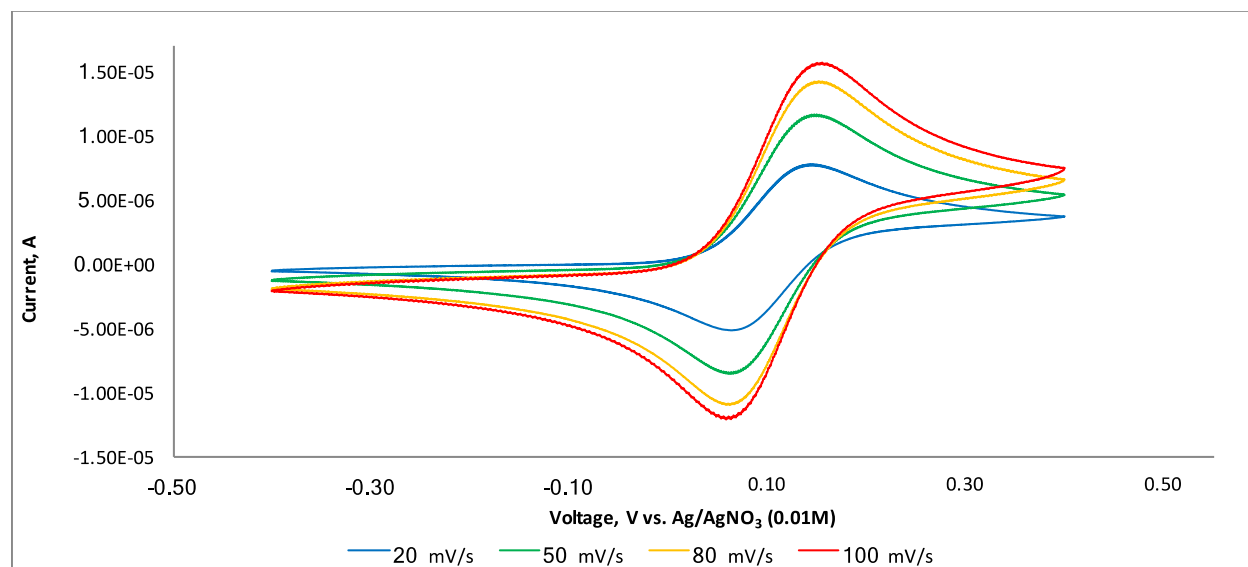


Figure A1.63. Cyclic voltammogram of **6** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the positive potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

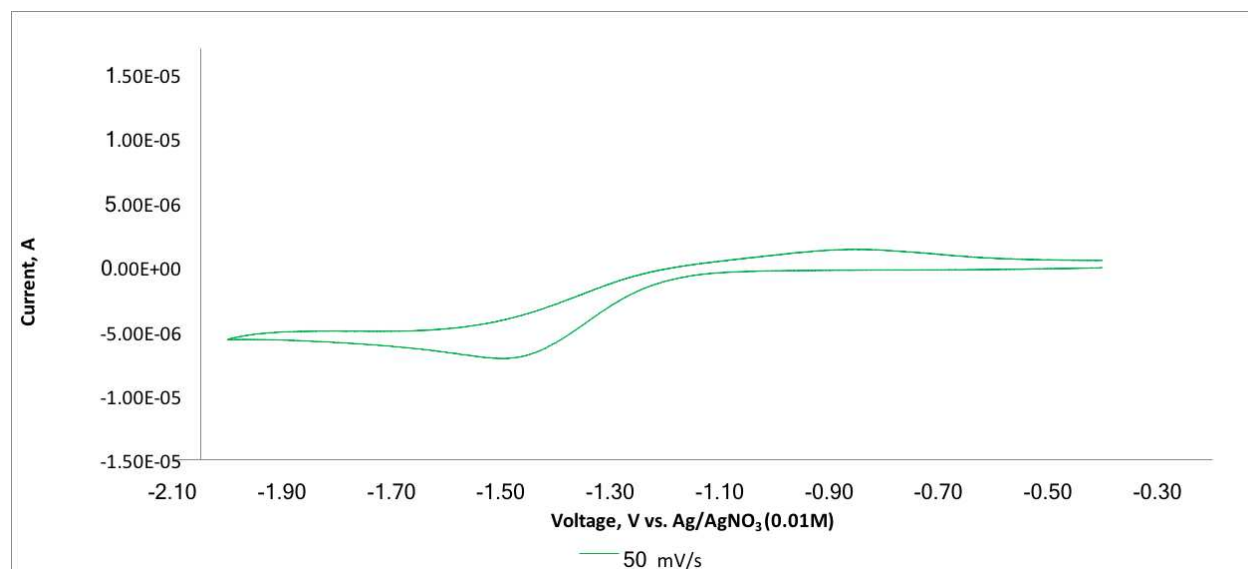


Figure A1.64. Cyclic voltammogram of **6** in DMAc with 0.1 M NBu₄PF₆ supporting electrolyte scanning in the negative potential direction (potentials versus 0.01 M Ag/AgNO₃ reference electrode in acetonitrile with 0.1 M NBu₄PF₆).

Crystallographic Information for 4

Crystals of **4** for X-ray diffraction were grown by diffusion of hexanes into benzene. The obtained crystal structure is shown below (hydrogens omitted for clarity).

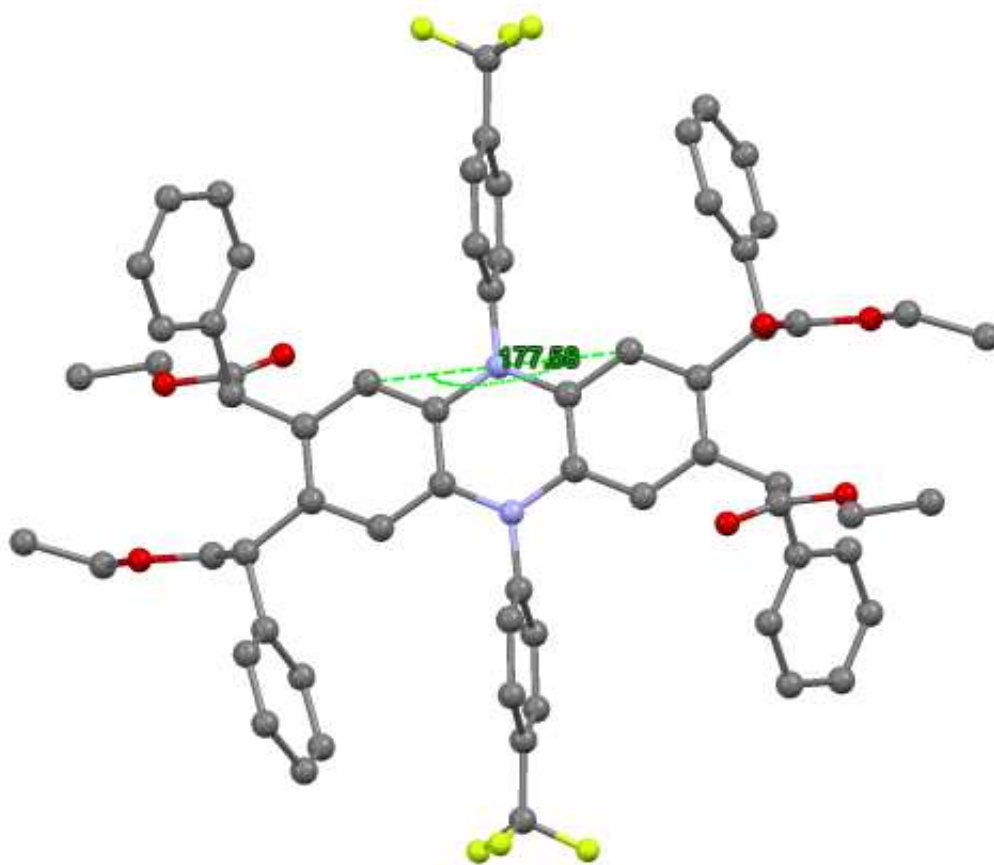


Figure A1.65. Crystal structure of PC **4** (hydrogens omitted for clarity).

Table A1.1. Crystallographic information for the structural refinement of **4**.

Identification code	gm15_PhenN-PhCF3-EBP4_report
Empirical formula	C ₆₆ H ₅₆ F ₆ N ₂ O ₈
Formula weight	1119.12
Temperature/K	104.(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.5181(6)
b/Å	14.7409(12)
c/Å	16.2314(13)
$\alpha/^\circ$	114.080(4)
$\beta/^\circ$	93.910(4)
$\gamma/^\circ$	102.462(4)
Volume/Å ³	1368.8(2)
Z	1
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.358
μ/mm^{-1}	0.102
F(000)	584.0
Crystal size/mm ³	0.108 × 0.049 × 0.026
Radiation	Mo K α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	5.02 to 50.06
Index ranges	-7 ≤ h ≤ 7, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	51869
Independent reflections	4844 [R_{int} = 0.1100, R_{sigma} = 0.0563]
Data/restraints/parameters	4844/0/372
Goodness-of-fit on F ²	1.014
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0568, wR_2 = 0.1310
Final R indexes [all data]	R_1 = 0.1041, wR_2 = 0.1563
Largest diff. peak/hole / e Å ⁻³	0.41/-0.23

RADICAL CATION CHARACTERIZATION

Electron Paramagnetic Resonance Spectroscopy

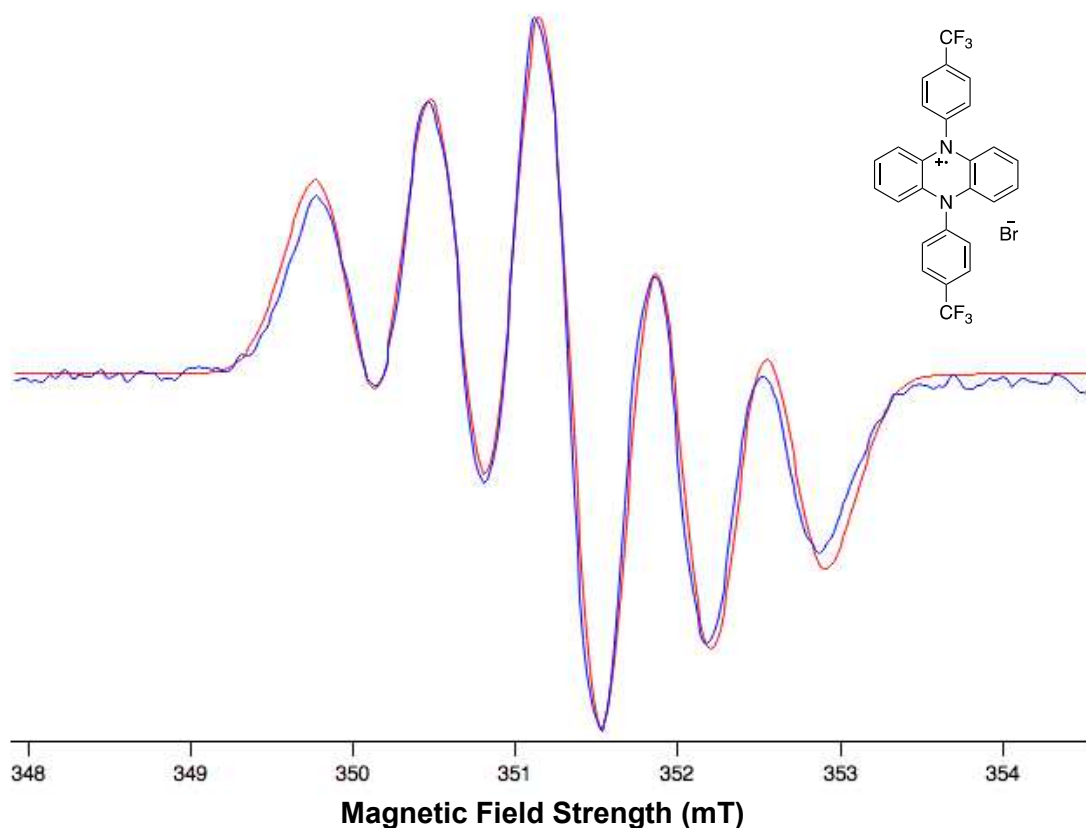


Figure A1.66. EPR spectrum of $1^{\bullet+}\text{Br}^-$ (blue) and simulated EPR spectrum (red).

Table A1.2. Parameters used in the simulation of the EPR spectrum of $1^{\bullet+}\text{Br}^-$.

Nuclei	n	g	A	Line width
^{14}N	2	2.00331	18.5657	
^1H	8	2.00092	1.59	.54367
C	12	1.9987	.031	

Spectro-Electrochemistry

Solutions for spectro-electrochemistry were prepared in the same manner as described for cyclic voltammetry. After degassing by nitrogen bubbling for 10 min, the cuvettes were placed in the UV-Vis spectrometer and a baseline spectrum collected. This spectrum was subtracted from subsequent spectra to subtract the PC signal and isolate that of the radical cation.

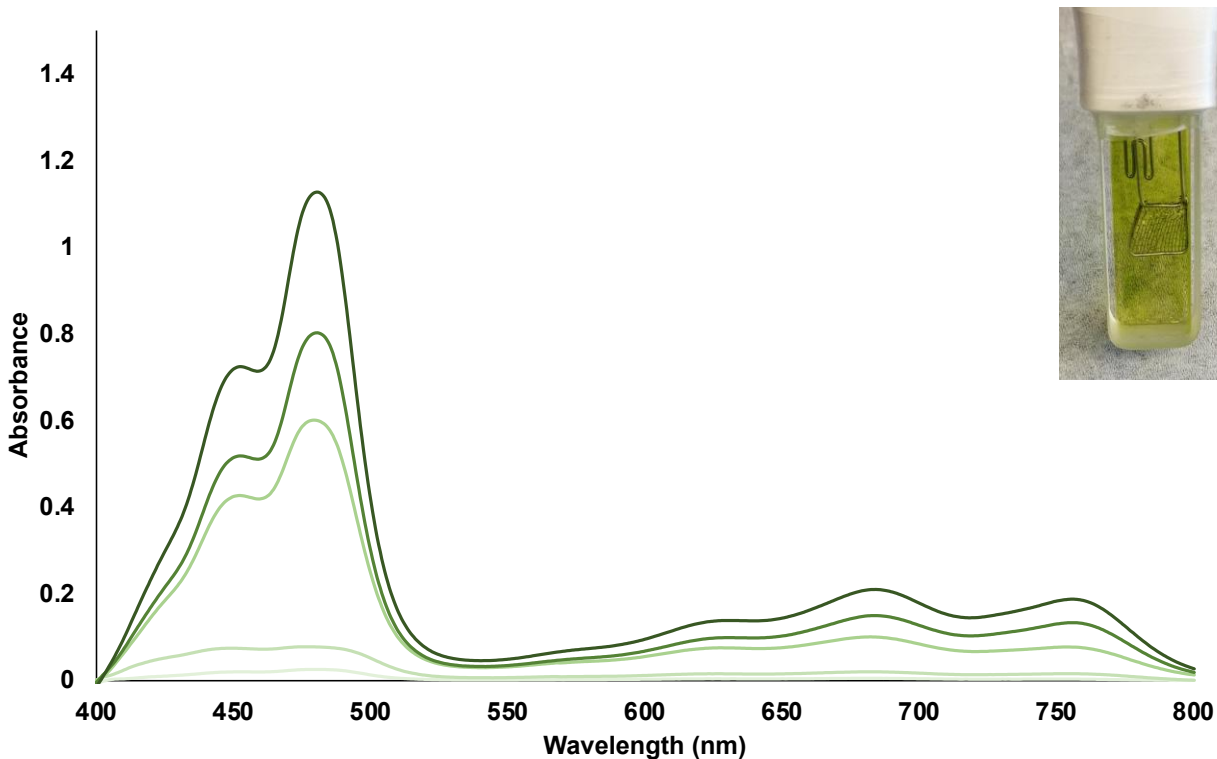


Figure A1.67. Spectro-electrochemistry of **1** to **1^{•+}** (spectrum of **1** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{app} = 0.09$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

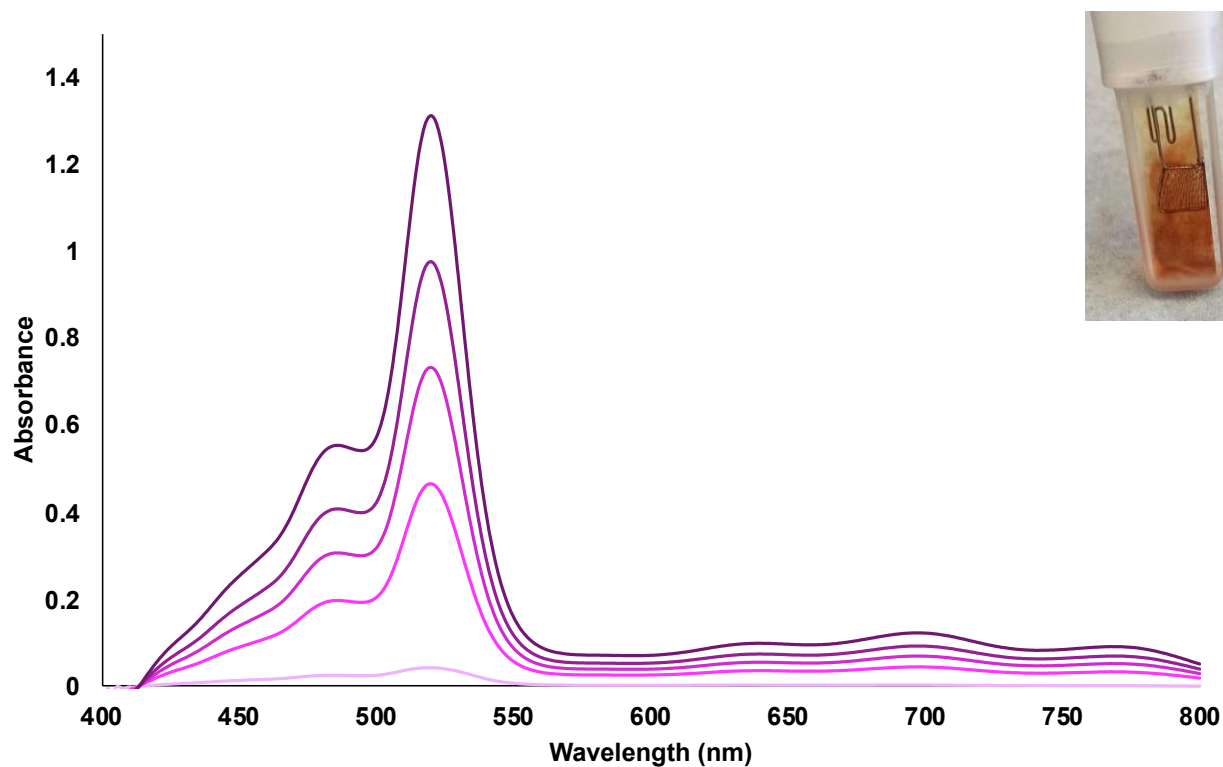


Figure A1.68. Spectro-electrochemistry of **2** to **2⁺⁺** (spectrum of **2** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{\text{app}} = 0.13$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

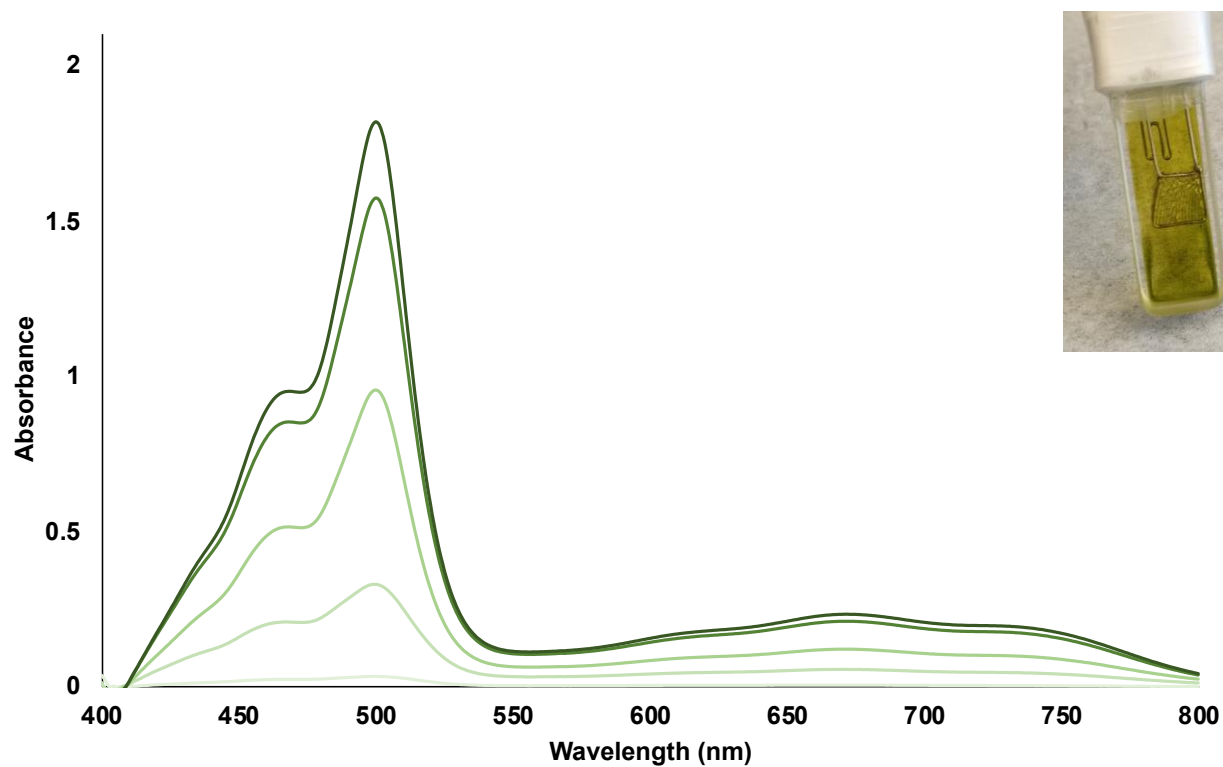


Figure A1.69. Spectro-electrochemistry of **3** to **3²⁺** (spectrum of **3** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{\text{app}} = 0.09$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

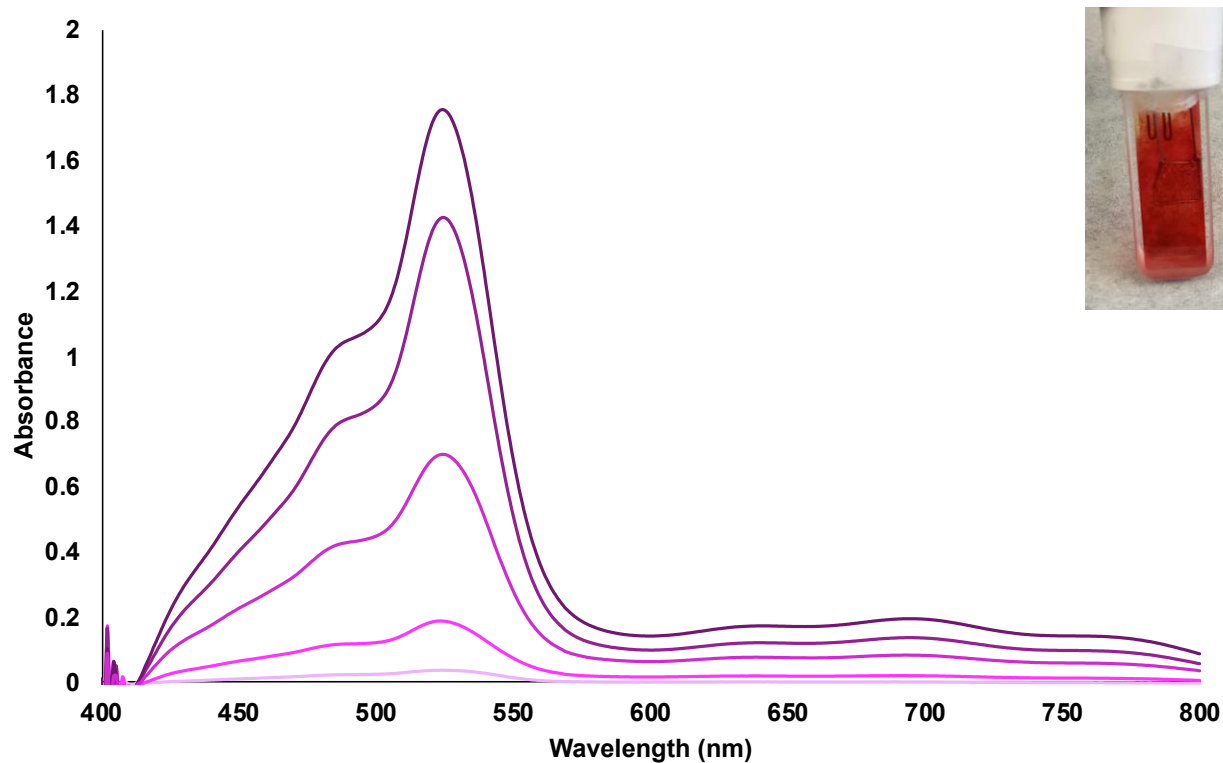


Figure A1.70. Spectro-electrochemistry of **4** to **4⁺⁺** (spectrum of **4** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{app} = 0.12$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

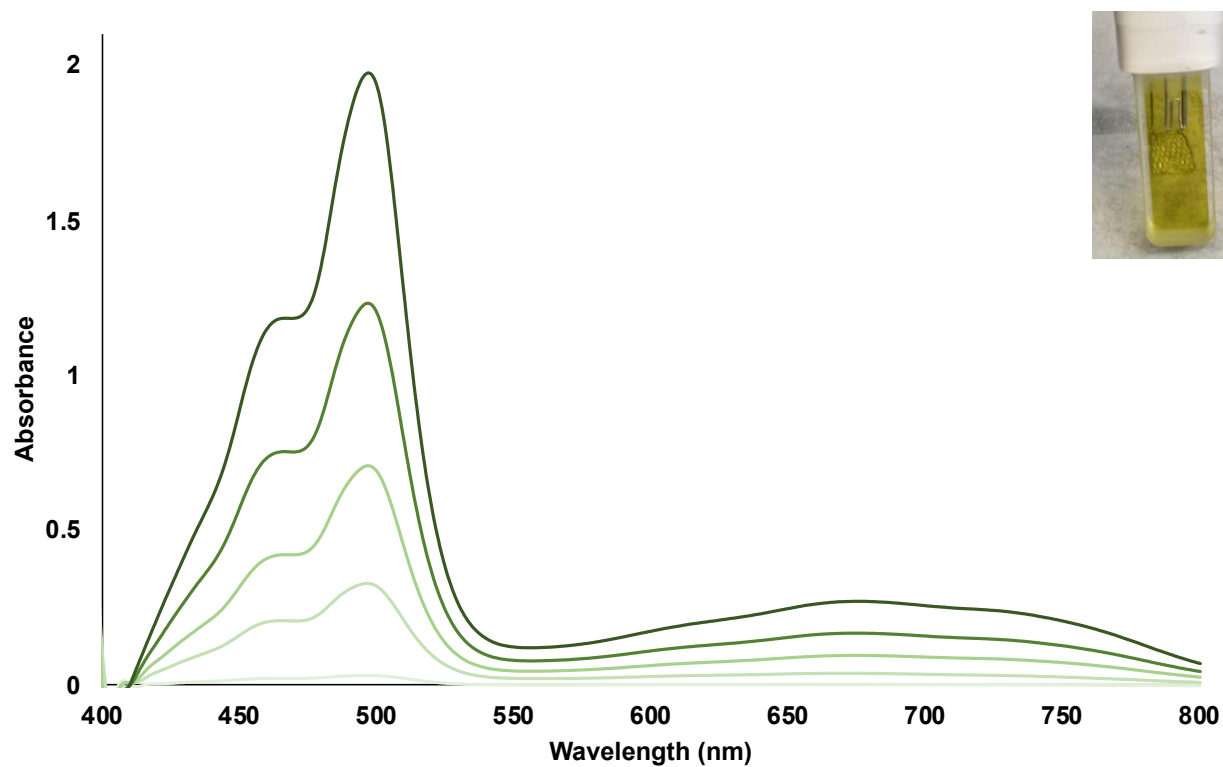


Figure A1.71. Spectro-electrochemistry of **5** to **5⁺⁺** (spectrum of **5** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{\text{app}} = 0.14$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

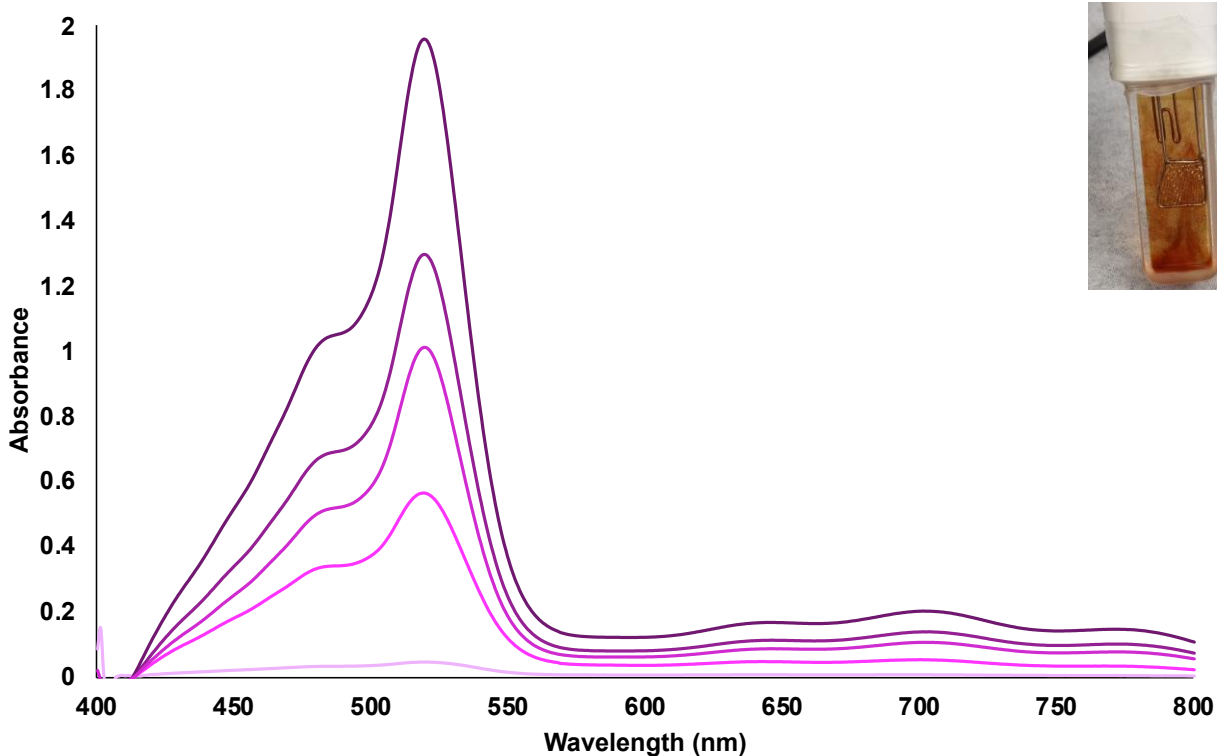


Figure A1.72. Spectro-electrochemistry of **6** to **6⁺⁺** (spectrum of **6** subtracted) in DMAc with 0.1 M NBu₄PF₆. $E_{\text{app}} = 0.17$ V vs. Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆). Figure inset shows the reaction solution after electrolysis.

UV-Visible Absorption Spectroscopy

UV-Vis spectra of the radical cations were obtained by removing an aliquot from the reaction solution after the synthesis of each PC but before addition of triethyl amine. Those spectra are shown below, along with the spectra of the neutral PCs and the radical cation spectra obtained by spectro-electrochemistry.

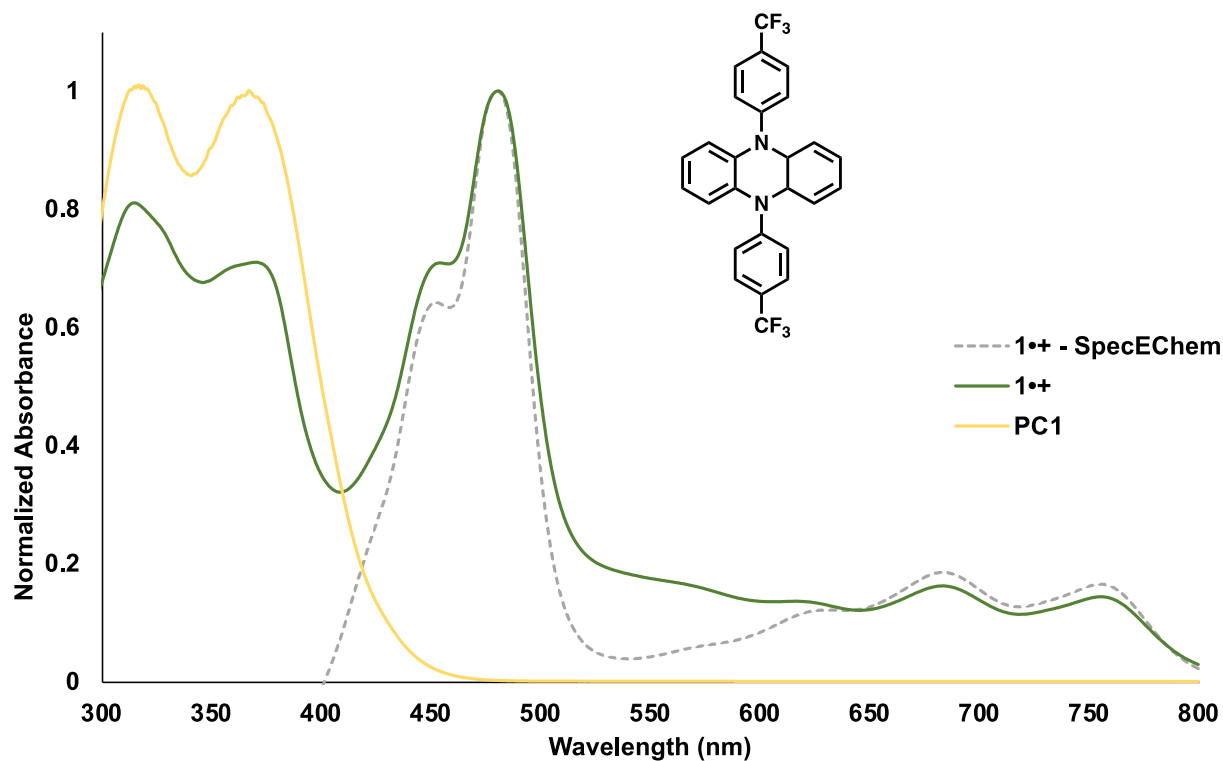


Figure A1.73. Overlapped UV-vis absorption spectra of **1** (solid yellow), **1**^{•+} generated during core substitution and removed after the reaction (solid green), and **1**^{•+} generated by spectro-electrochemistry (dashed grey).

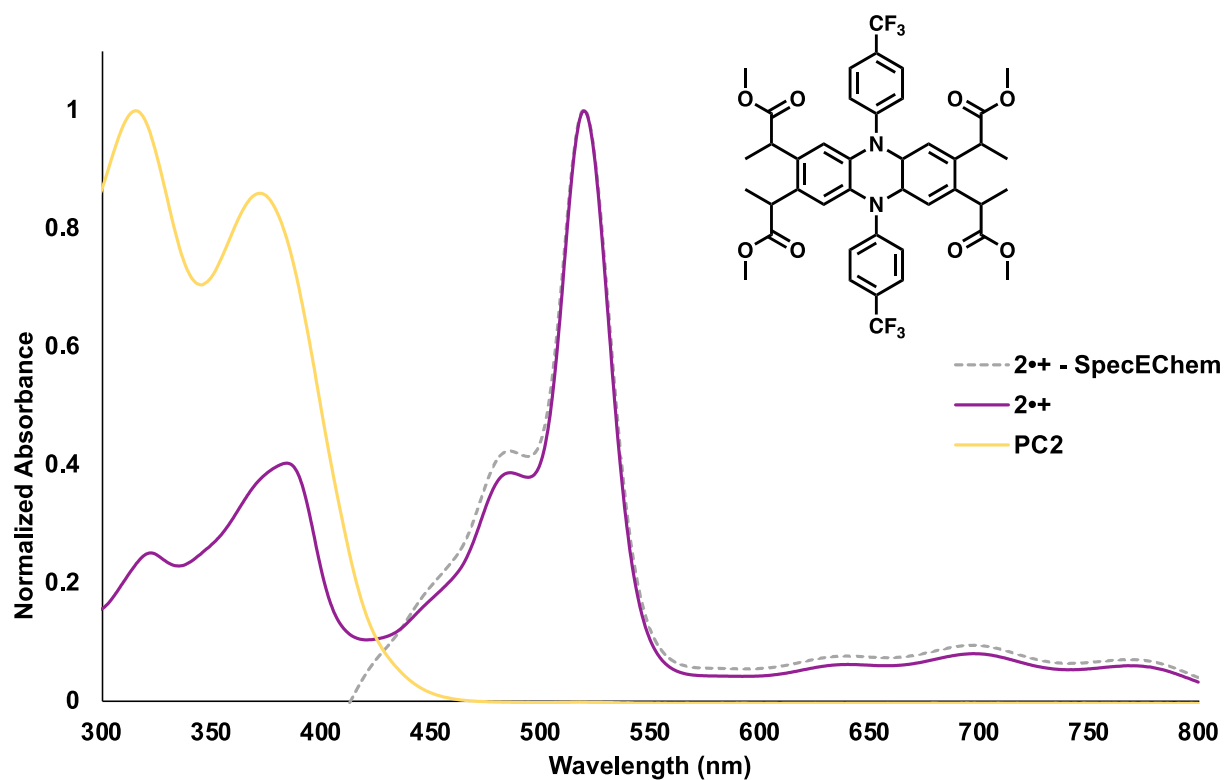


Figure A1.74. Overlapped UV-vis absorption spectra of **2** (solid yellow), **2^{•+}** generated during core substitution and removed after the reaction (solid purple), and **2^{•+}** generated by spectroelectrochemistry (dashed grey).

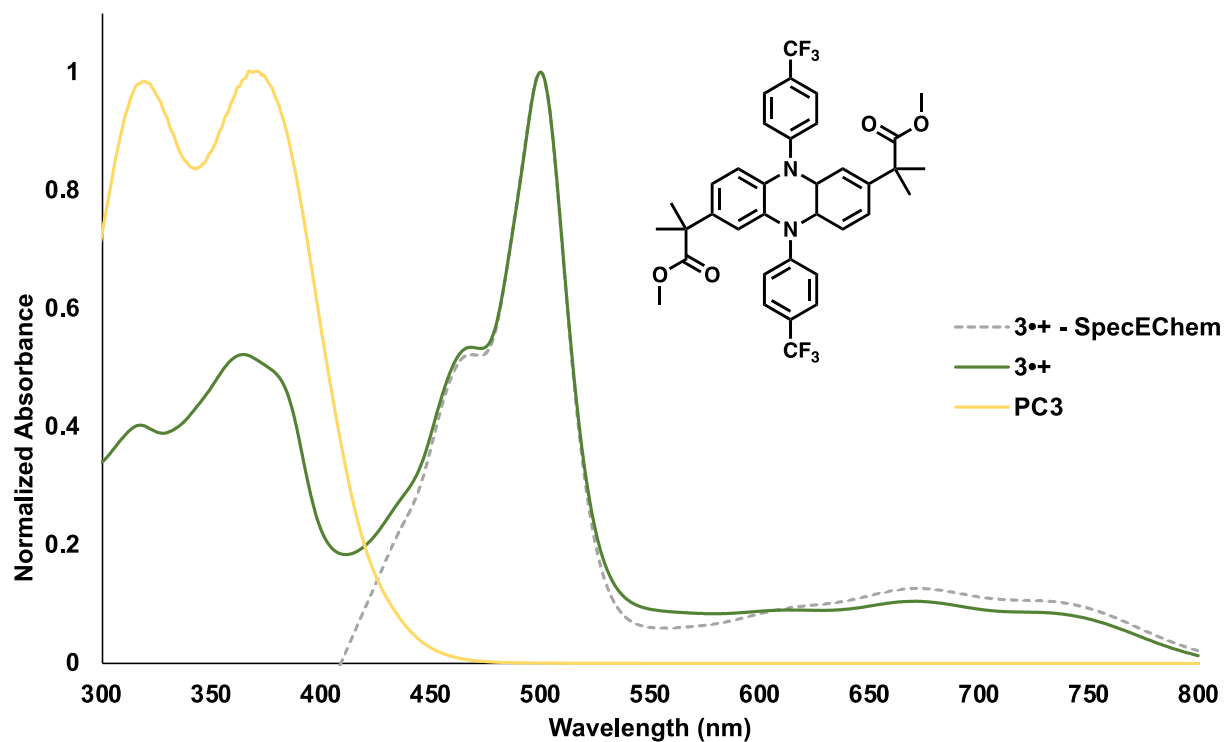


Figure A1.75. Overlapped UV-vis absorption spectra of **3** (solid yellow), **3^{•+}** generated during core substitution and removed after the reaction (solid green), and **3^{•+}** generated by spectroelectrochemistry (dashed grey).

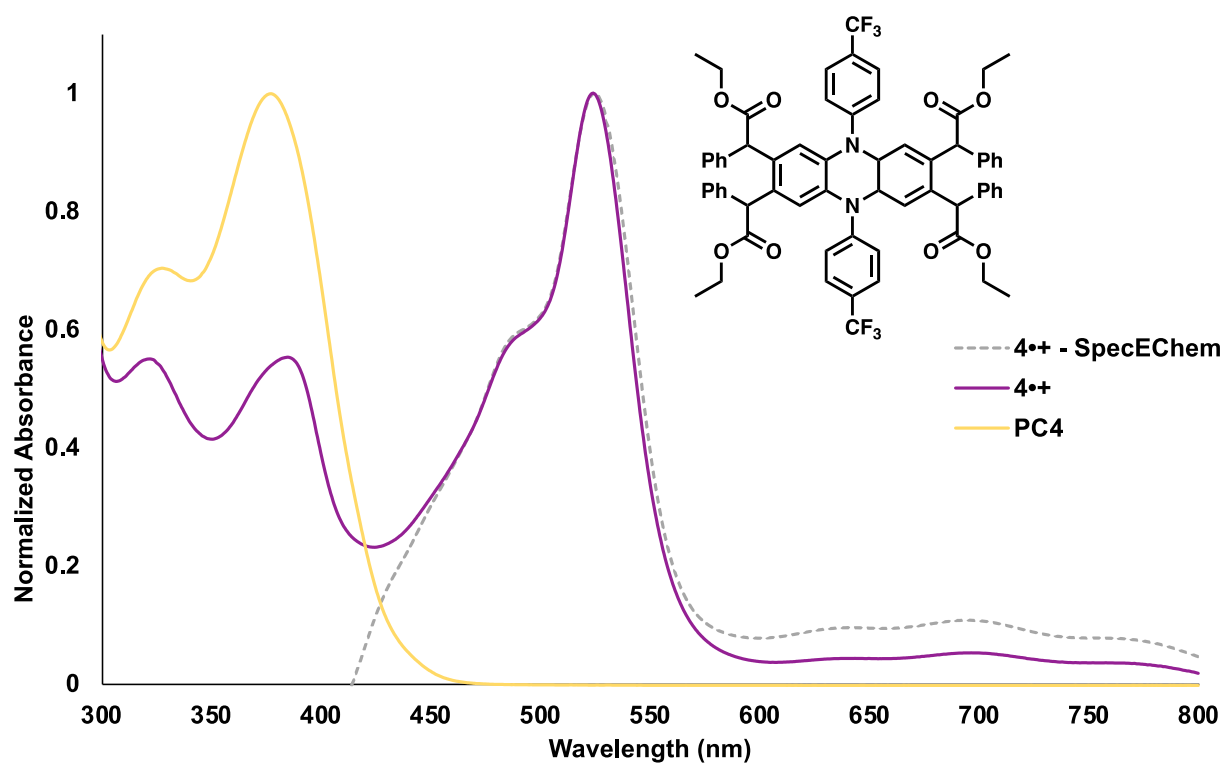


Figure A1.76. Overlapped UV-vis absorption spectra of **4** (solid yellow), **4^{•+}** generated during core substitution and removed after the reaction (solid purple), and **4^{•+}** generated by spectro-electrochemistry (dashed grey).

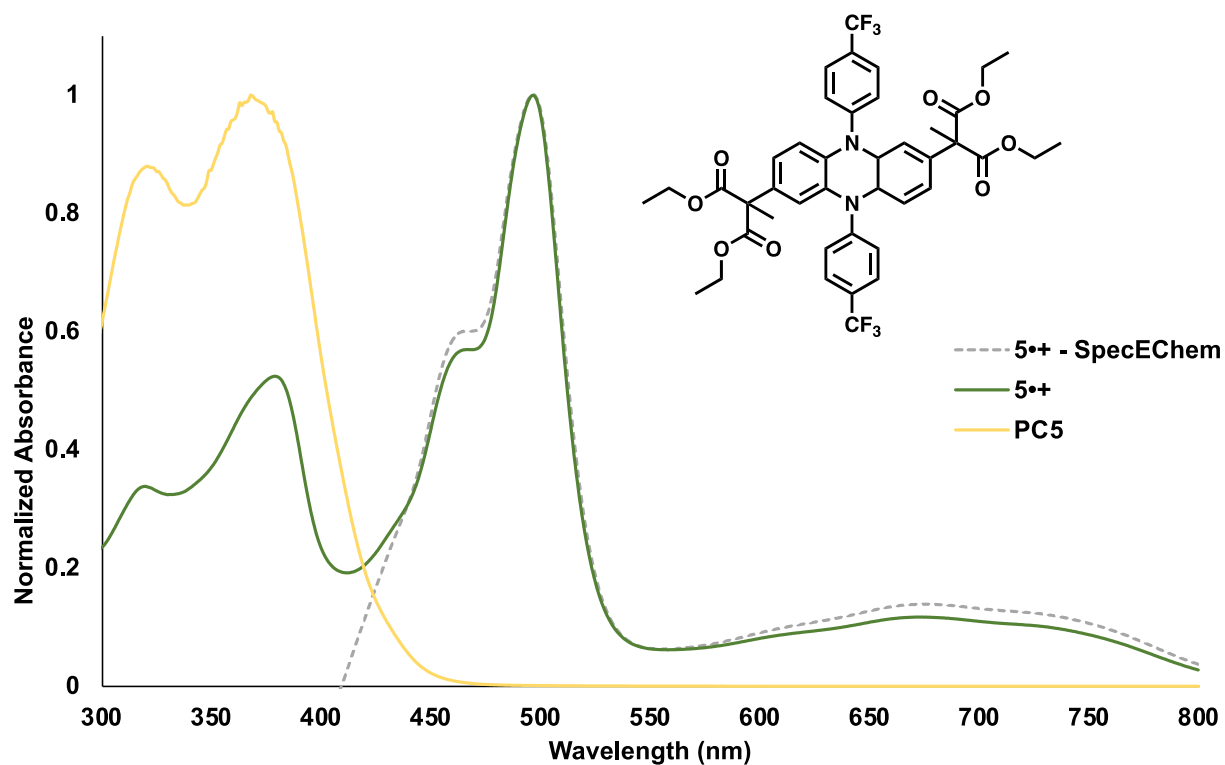


Figure A1.77. Overlapped UV-vis absorption spectra of **5** (solid yellow), **5•+** generated during core substitution and removed after the reaction (solid green), and **5•+** generated by spectro-electrochemistry (dashed grey).

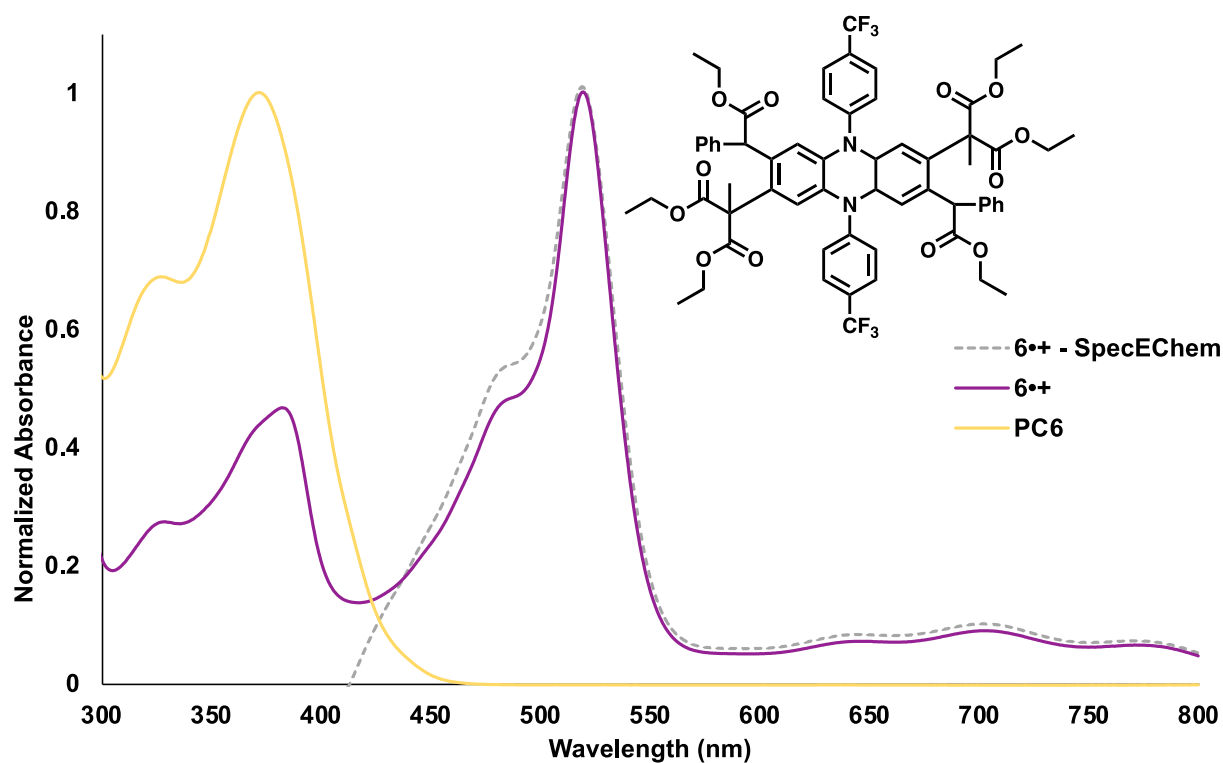


Figure A1.78. Overlapped UV-vis absorption spectra of **6** (solid yellow), **6**^{•+} generated during core substitution and removed after the reaction (solid purple), and **6**^{•+} generated by spectro-electrochemistry (dashed grey).

Crystallographic Information for $I^{\bullet+}Br_3^-$

Crystals of $I^{\bullet+}Br_3^-$ for X-ray diffraction were grown by dissolving the radical cation in methanol and layering with benzene. The obtained crystal structure is shown below (hydrogens omitted for clarity). It should be noted that while the quality of this crystal structure is poor and does not provide strong evidence for the structure of the radical cation, it does show formation of the tribromide ion, necessitating further treatment to obtain a monobromide anion. While the poor quality of this crystal structure would normally impede its publication, we emphasize its inclusion in this work simply to show evidence for the formation of the tribromide anion. In comparison to other tribromide compounds published in the Cambridge Structural Database (CSD), the bond lengths and bond angle of the tribromide shown here is consistent with previous data published for tribromides. As such, this crystal structure justifies further manipulation of this radical cation to obtain the desired anion, but it does not yield any reliable information regarding the structure of the radical cation itself. For this reason, and at the suggestion of the reviewers of this manuscript, this structure has been presented here but has not been deposited in the CSD.

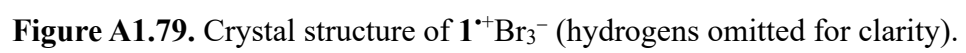


Table A1.3. Crystallographic information for the structural refinement of **1⁺Br₃⁻**.

Identification code	gm20_PhenN-PhCF3-BR3_report
Empirical formula	C ₂₆ H ₁₆ F ₆ Br ₃ N ₂
Formula weight	710.14
Temperature/K	100.(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.7300(6)
b/Å	10.3469(9)
c/Å	16.7221(14)
α/°	78.825(3)
β/°	77.881(3)
γ/°	83.304(3)
Volume/Å ³	1278.83(18)
Z	2
ρ _{calc} /g/cm ³	1.844
μ/mm ⁻¹	4.795
F(000)	690.0
Crystal size/mm ³	0.517 × 0.295 × 0.278
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.06 to 52.74
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	36270
Independent reflections	5214 [R _{int} = 0.0290, R _{sigma} = 0.0206]
Data/restraints/parameters	5214/0/329
Goodness-of-fit on F ²	1.049
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0712, wR ₂ = 0.1867
Final R indexes [all data]	R ₁ = 0.0834, wR ₂ = 0.1961
Largest diff. peak/hole / e Å ⁻³	8.23/-0.57

SUPPLEMENTAL POLYMERIZATION DATA

Initial Catalyst Screen in the O-ATRP of MMA

The following experiments were performed according to the *General Polymerization Procedure* outlined in the *Procedures* section of this document.

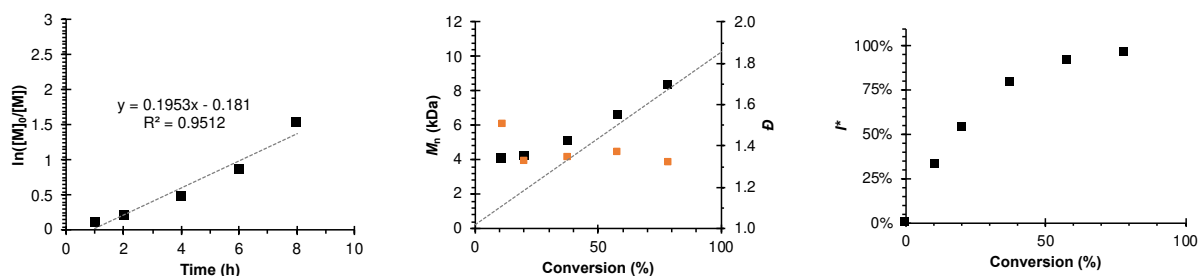


Figure A1.80. O-ATRP of MMA with **1**. [MMA]:[DBMM]:[**1**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and D (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

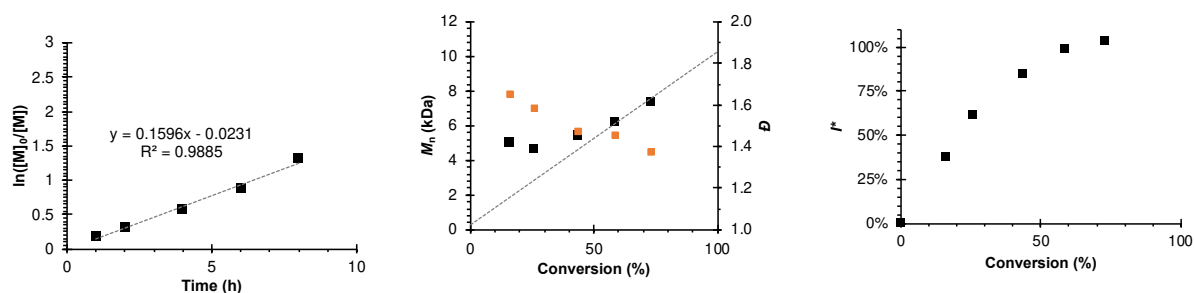


Figure A1.81. O-ATRP of MMA with **2**. [MMA]:[DBMM]:[**2**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and D (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

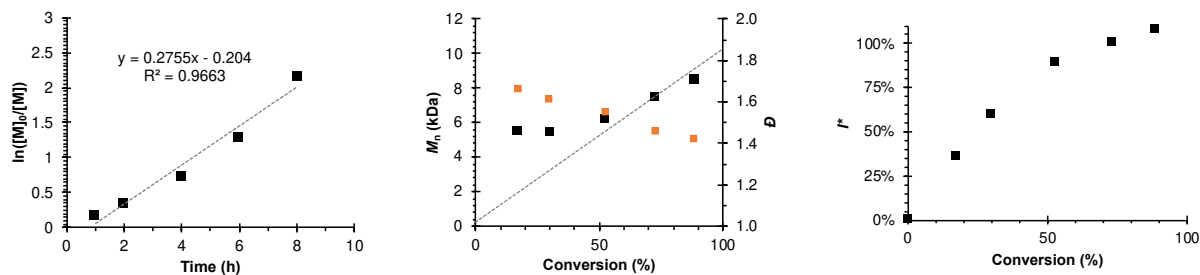


Figure A1.82. O-ATRP of MMA with **3**. [MMA]:[DBMM]:[**3**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and D (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

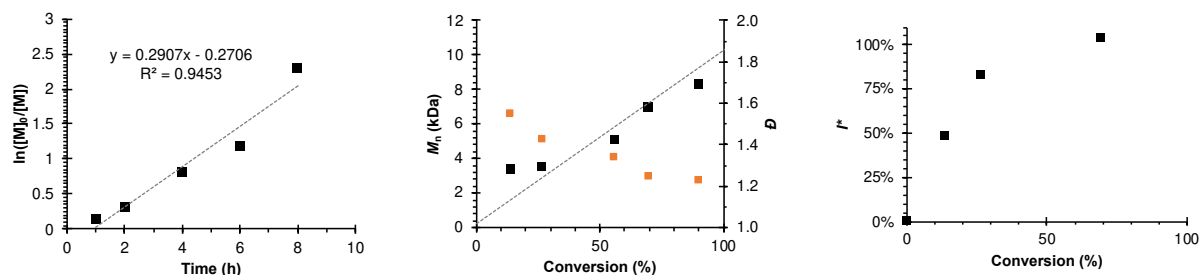


Figure A1.83. O-ATRP of MMA with **4**. [MMA]:[DBMM]:[**4**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and D (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

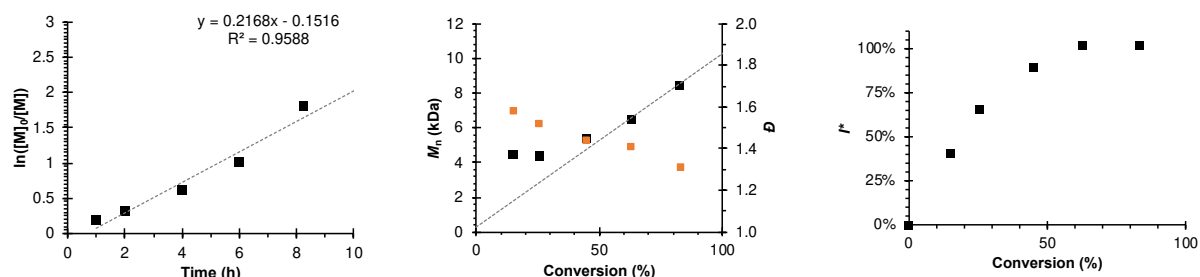


Figure A1.84. O-ATRP of MMA with **5**. [MMA]:[DBMM]:[**5**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and D (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

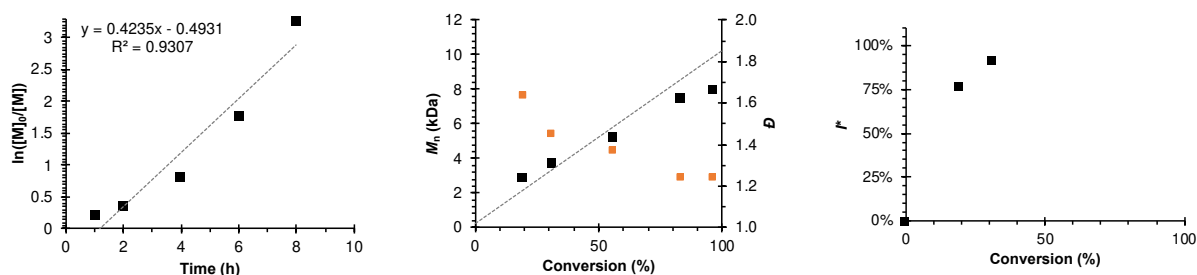


Figure A1.85. O-ATRP of MMA with **6**. [MMA]:[DBMM]:[**6**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. (Left) Pseudo-first order kinetics plot. (Middle) Evolution of polymer molecular weight (black) and $\bar{D}$ (orange) as a function of monomer conversion; grey dashed line represents the theoretical molecular weight growth. (Right) Initiator efficiency as a function of monomer conversion.

Solvent Screen

In an effort to improve upon the polymerization results above, polymerizations were performed in various solvents of different polarity. These polymerizations were performed according to the *General Polymerization Procedure* outlined in the *Procedures* section of this document. The results of these experiments are presented in Table 3 of the main text.

Initiator Screen

The ability of **4** to perform O-ATRP with different initiators was investigated. Polymerizations were setup and performed according to the *General Polymerization Procedure* outlined in the *Procedures* section of this document. In general, PC **4** showed excellent polymerization control with most alkyl bromide initiators investigated. When an alkyl chloride initiator was used instead (Table A1.4, entry S4), conversion was observed but with poor polymerization control, consistent with previous findings.⁹

Table A1.4. Results from the initiator screen using PC 4.

Entry	Initiator	Time (h)	Conv. (%) ^[a]	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^[b]	$\bar{D}$ ^[b]	I^* (%) ^[c]
S1	M2BP	24	79.6	8.14	7.15	1.11	114
S2	MBiB	24	89.6	9.15	5.12	1.10	179
S3	EBP	24	79.3	8.19	8.80	1.12	93
S4	ECIP	24	100	10.20	10.20	1.49	100
S5	DBMM	24	77.5	8.01	7.25	1.08	110

^[a]Determined by ¹H NMR. ^[b]Determined by GPC coupled with multi-angle light scattering.

^[c]Initiator efficiency (I^*) = ($M_{n, \text{theo}} / M_{n, \text{exp}}$) • 100%.

Gel Permeation Chromatography Traces

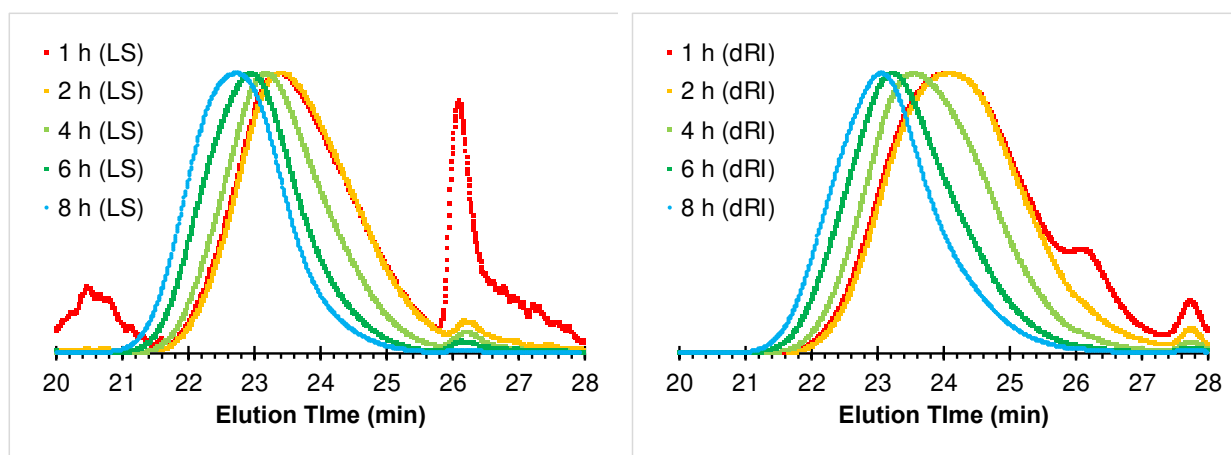


Figure A1.86. GPC traces for O-ATRP of MMA with **1**. [MMA]:[DBMM]:[**1**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

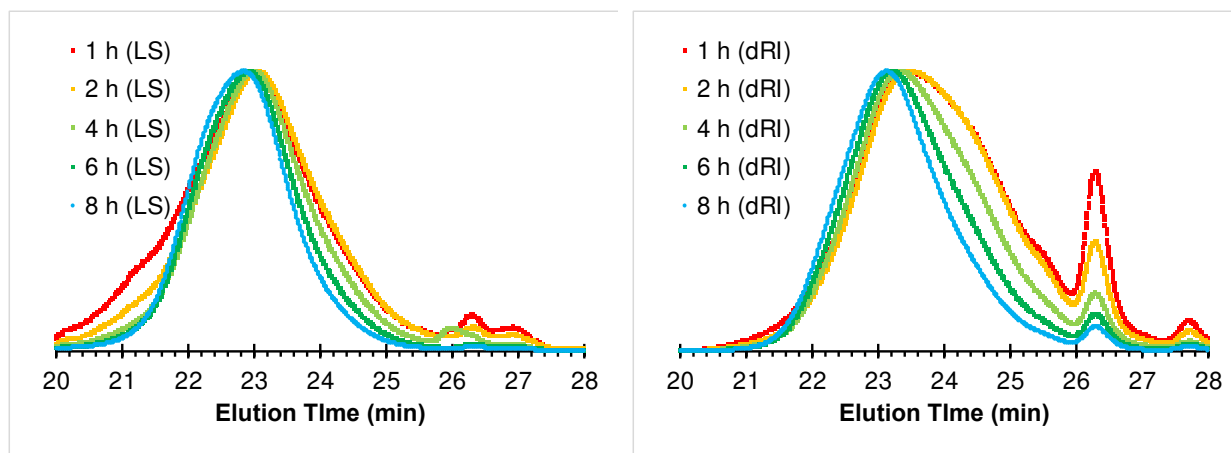


Figure A1.87. GPC traces for O-ATRP of MMA with **2**. [MMA]:[DBMM]:[**2**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

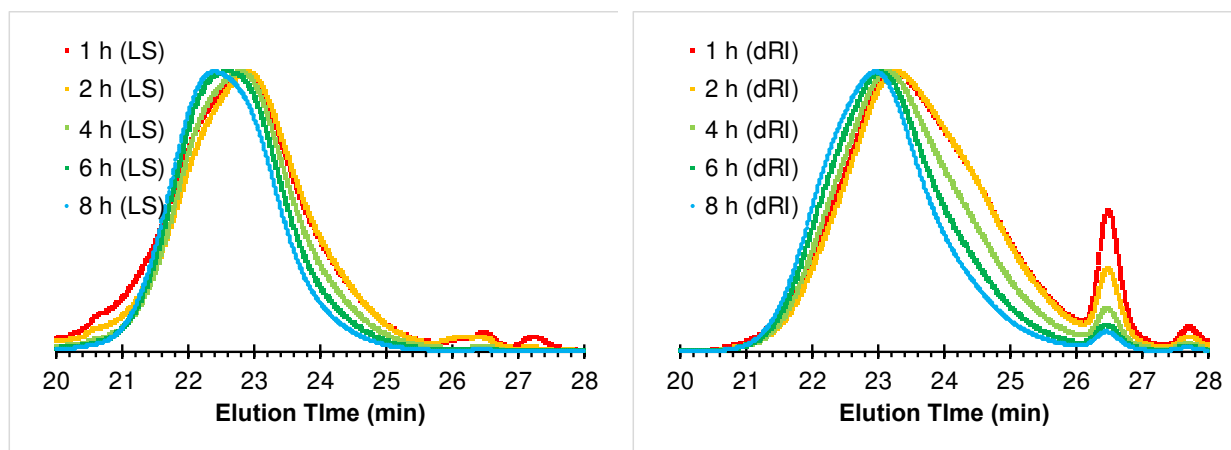


Figure A1.88. GPC traces for O-ATRP of MMA with **3**. [MMA]:[DBMM]:[**3**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

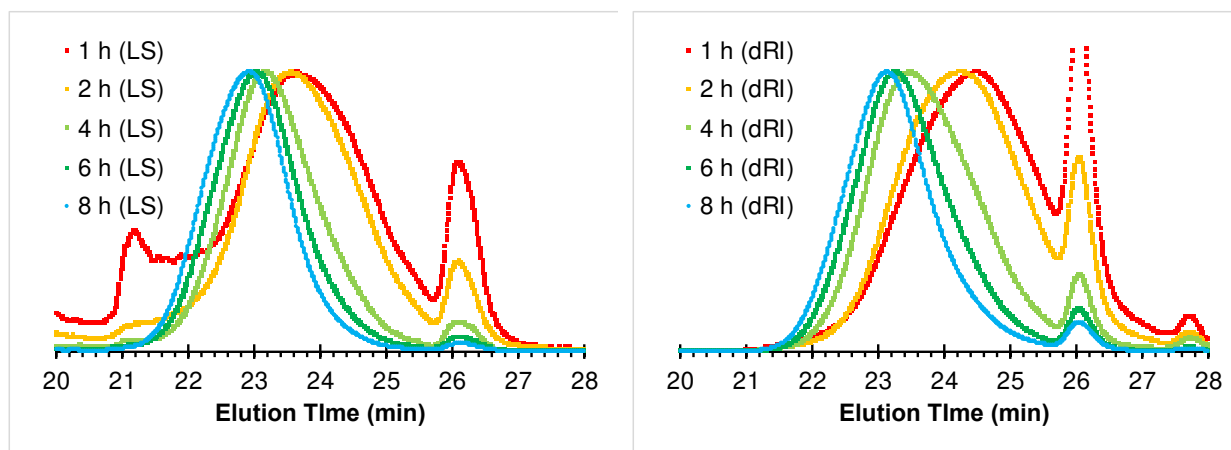


Figure A1.89. GPC traces for O-ATRP of MMA with **4**. [MMA]:[DBMM]:[**4**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

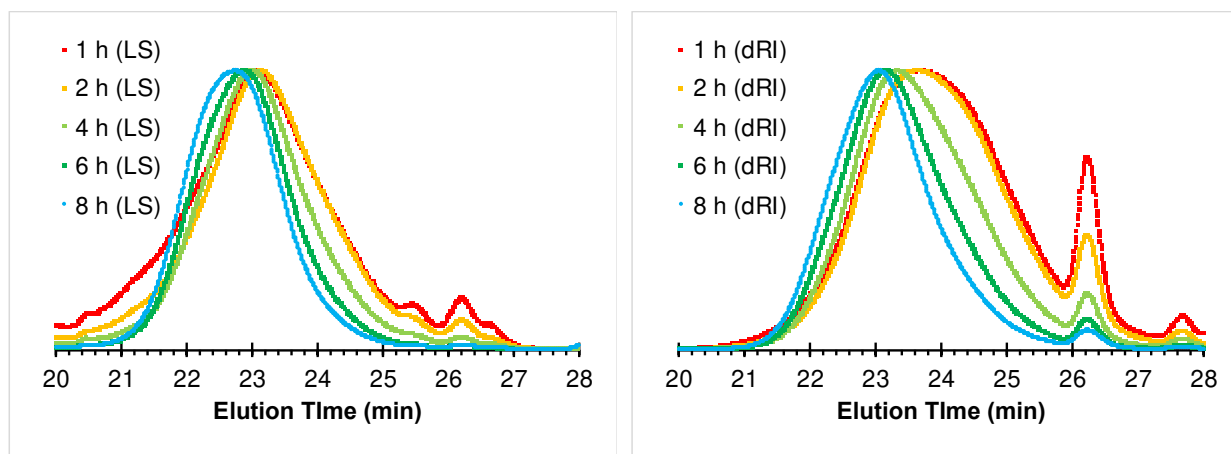


Figure A1.90. GPC traces for O-ATRP of MMA with **5**. [MMA]:[DBMM]:[**5**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

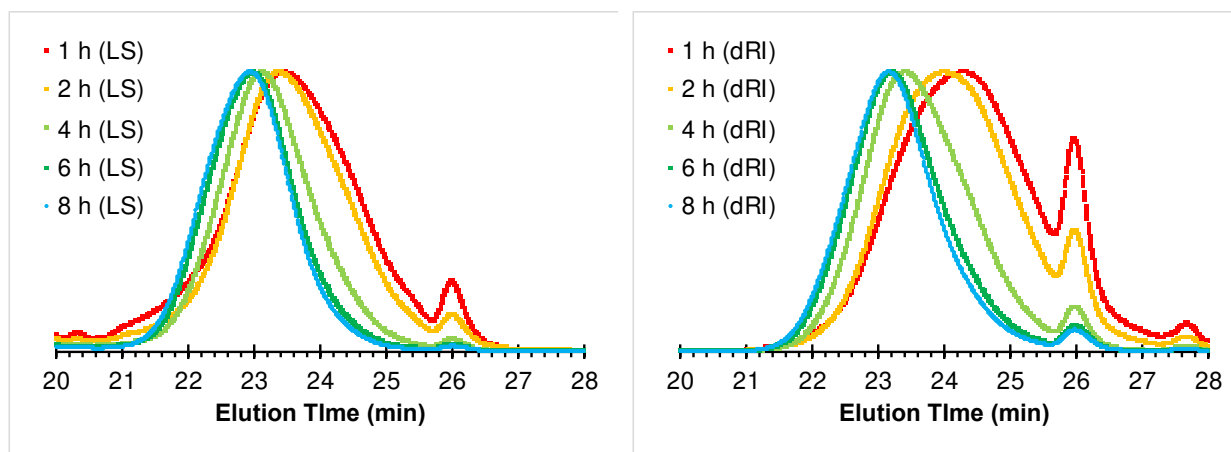


Figure A1.91. GPC traces for O-ATRP of MMA with **6**. [MMA]:[DBMM]:[**6**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL DMAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

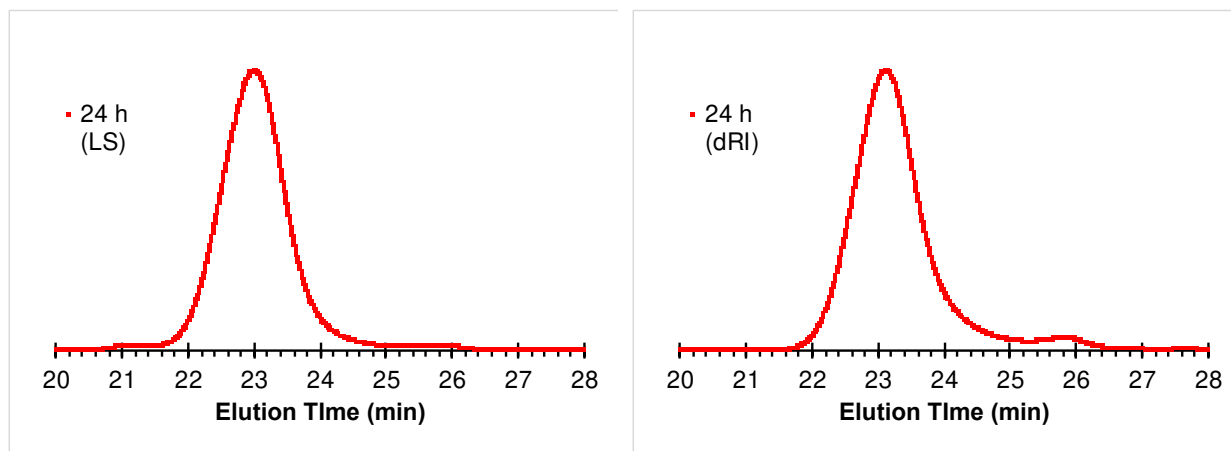


Figure A1.92. GPC traces for O-ATRP of MMA with **1**. [MMA]:[DBMM]:[**1**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL EtAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

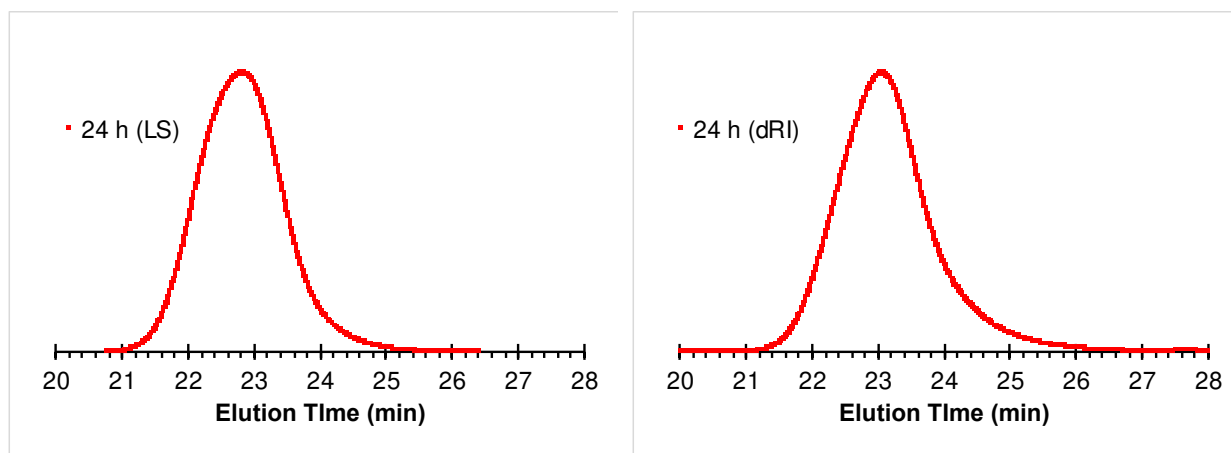


Figure A1.93. GPC traces for O-ATRP of MMA with **1**. [MMA]:[DBMM]:[**1**] = [1000]:[10]:[0.1]; 1 mL MMA, 1 mL EtAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

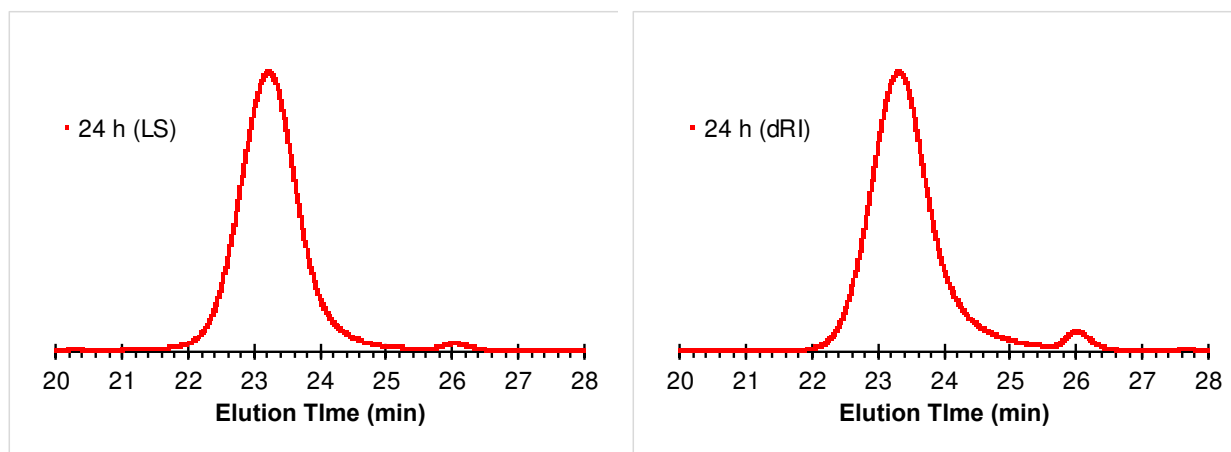


Figure A1.94. GPC traces for O-ATRP of MMA with **4**. [MMA]:[DBMM]:[**4**] = [1000]:[10]:[1]; 1 mL MMA, 1 mL EtAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

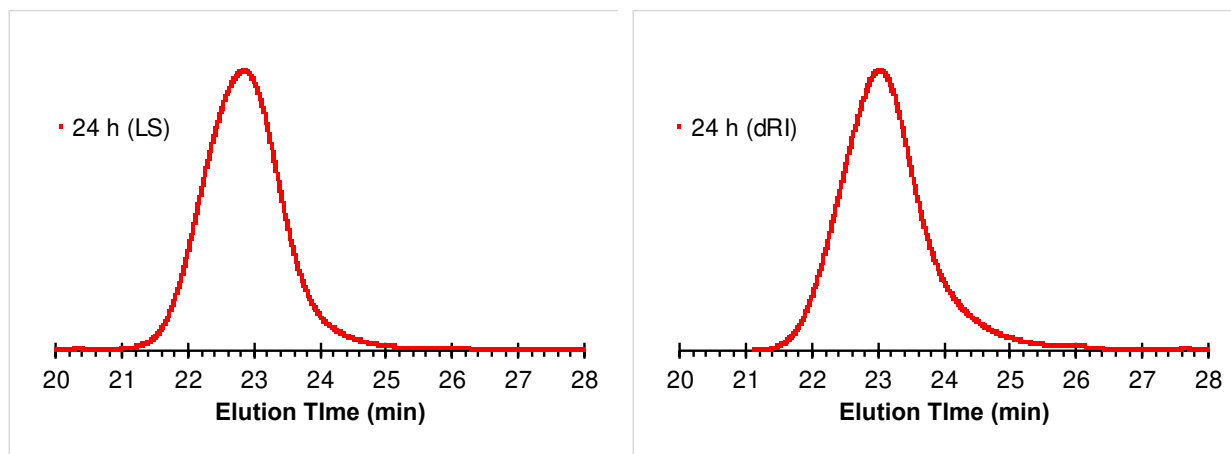


Figure A1.95. GPC traces for O-ATRP of MMA with **4**. [MMA]:[DBMM]:[**4**] = [1000]:[10]:[0.1]; 1 mL MMA, 1 mL EtAc; irradiated in a white LED beaker. Detectors: multi-angle light scattering (left) and differential refractive index (right).

COMPUTATIONAL DETAILS

Calculations were performed using the computational chemistry software package Gaussian 09 version D.01.¹⁰ We acknowledge the use of computational resources provided by the XSEDE – Comet Supercomputer.

Standard reduction potentials (E^0) were calculated following previously reported procedure.¹¹⁻¹⁴ A value of -100.5 kcal/mol was assumed for the reduction free energy of the standard hydrogen electrode (SHE). Thus, $E^0 = (-100.5 - \Delta G_{\text{red}})/23.06$ (V vs. SHE); for E^0 ($^2\text{PC}^{*+}/^3\text{PC}^*$), $\Delta G_{\text{red}} = G(^3\text{PC}^*) - G(^2\text{PC}^{*+})$ while for E^0 ($^2\text{PC}^{*+}/^1\text{PC}$), $\Delta G_{\text{red}} = G(^1\text{PC}) - G(^2\text{PC}^{*+})$. The Gibbs free energies of $^3\text{PC}^*$, $^2\text{PC}^{*+}$, and ^1PC were calculated at the unrestricted M06/6-311+G** level of theory in CPCM-H₂O solvent (single point energy) using geometries optimized at unrestricted M06/6-31+G** level of theory in CPCM-H₂O solvent. The triple zeta basis set (6-311+G**) generally improves the E^0 ($^2\text{PC}^{*+}/^1\text{PC}$) by ~0.1 V relative to 6-31+G**, while the triplet energy is invariant for these two basis sets.

For PCs **4** and **6**, the structural complexity of these PCs prevented convergence during the structure optimization step of these calculations. To simplify these calculations, they were performed at the same level of theory and using the same basis set, but in the gas phase rather than with a CPCM solvent model.

To reference to the Saturated Calomel Electrode (SCE), E^0 (vs. SHE) is converted to E^0 (vs. SCE) using E^0 (vs. SCE) = E^0 (vs. SHE) - 0.24 V. Triplet energies (in eV) of PCs were obtained by $[G(^3\text{PC}^*) - G(^1\text{PC})]$, in kcal/mol]/23.06.

Based on the comparison of our experimental and computational data set, the choice of CPCM solvation model is justified as the computed reduction potential closely approximates the experimental values. For example, the computed ground state oxidation potentials between the $^2\text{PC}^{*+}/^1\text{PC}$ redox couple is typically within ~0.15 to 0.25 V from the experimental values.

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MATERIALS AND METHODS

Purchased Chemicals and Materials

Phenazine Reduction (Figure A2.3-a): Phenazine was purchased from Sigma Aldrich, sodium dithionite was purchased from VWR, reagent alcohol was purchased from Sigma Aldrich. All chemicals were used as received.

Buchwald-Hartwig Coupling (Figure A2.3-b): (This method was used for the synthesis of PC 5): 2-bromonaphthalene, sodium t-butoxide, anhydrous Sure/Seal dioxane, dicyclohexylphosphino-2,6-diisopropoxybiphenyl (RuPhos), and RuPhos Pd G4, were purchased from Sigma Aldrich and used as received unless noted otherwise in “Chemical preparation and Storage.”

Buchwald-Hartwig Coupling (Figure A2.3-b): (This method was used for the synthesis of PCs 3 and 4): 4-bromoanisole, 2-bromonaphthalene, sodium t-butoxide, anhydrous Sure/Seal toluene, bis(dibenzylideneacetone) palladium(0) ($\text{Pd}(\text{dba})_2$), and tritertbutylphosphine were purchased from Sigma Aldrich and used as received unless noted otherwise in “Chemical preparation and Storage.”

Bromination Method I (Figure A2.3-c&e): Molecular bromine, benzene, and methanol purchased from Sigma Aldrich and used as received. Copper wire was purchased from Fisher and used as received.

Bromination Method II (Figure A2.3-c&d): Molecular bromine, benzene, and methanol purchased from Sigma Aldrich and used as received. Reagent grade Acetone was purchased from Fischer Scientific and used as received.

Suzuki Coupling (Figure A2.3-f): Tetrakis(triphenyl phosphine) palladium (0) ($\text{Pd(PPh}_3)_4$), 4- (trifluoromethyl)phenylboronic acid, 2-naphthylboronic acid, 4-methoxyphenylboronic acid, and Sure/Seal tetrahydrofuran (THF) were purchased from Sigma Aldrich. Potassium carbonate was purchased from VWR. All chemicals were used as received unless noted otherwise in “Chemical preparation and Storage.”

Polymerizations: Monomers: methyl methacrylate (MMA), styrene, n-butyl acrylate (nBA), vinyl acetate (VA), and *N,N*-dimethylacrylamide (DMA), as well as solvents: anhydrous Sure/seal *N,N*-dimethylacetamide (DMAc), ethyl acetate (EtOAc), benzene, dichloromethane (DCM) and tetrahydrofuran (THF) and diethyl 2-bromo-2-methyl malonate (DBMM) were purchased from Sigma Aldrich.

Deuterated solvents for NMR: All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used without further purification.

Chemical Preparation and Storage

Cross coupling reactions: Pd(dba)_2 and $\text{Pd(PPh}_3)_4$ were used as received, but were transferred to a nitrogen-filled glovebox before use. Tetrakis(triphenyl phosphine) palladium(0) was stored in the dark at -10 °C. 4-bromoanisole was sparged with nitrogen while stirring for 20 minutes before use.

Monomers and initiators for polymerizations (add other monomers): MMA, styrene, nBA, VA, DMA, and DBMM, were dried by stirring over calcium hydride for 12-16 hours, distilled under vacuum, then degassed via three freeze-pump-thaw cycles before being transferred to amber vials in a nitrogen filled glovebox. Monomers and initiators were stored under nitrogen, in the dark, at -10 °C, but were allowed to warm to room temperature before use.

Solvents for polymerizations: Dimethylacetamide (DMAc), tetrahydrofuran (THF), dichloromethane (DCM), and ethyl acetate (EtOAc) were obtained from Sigma Aldrich in Sure/Seal bottles, then used without further purification. Benzene was obtained and purified using an mBraun MB-SPS-800 solvent purification system, kept under nitrogen atmosphere, and stored over 3 Å molecular sieves.

Solvents for characterization: DMAc (99.8% anhydrous) was purchased from Sigma Aldrich in Sure/Seal bottles and used without further purification. HPLC grade acetonitrile (MeCN) for cyclic voltammetry was purchased from Fischer Scientific and used without further purification.

Instrumentation for Characterization

Nuclear magnetic resonance (NMR) spectroscopy: NMR spectra were obtained using a Bruker 400 MHz NMR Spectrometer. All ^1H NMR experiments are reported in parts per million (ppm) and were measured relative to the signals for residual dimethyl sulfoxide (2.5 ppm), benzene (7.16 ppm), or chloroform (7.26) in deuterated dimethyl sulfoxide, deuterated benzene, or deuterated chloroform, respectively.

Mass Spectroscopy of Photocatalysts: Electrospray Ionization Mass Spectroscopy (ESI-MS) was performed at the Colorado State University Central Instrumentation Facility.

Ultraviolet-visible (UV-Vis) spectroscopy: UV-Vis spectroscopy was performed on a Cary 5000 spectrophotometer. DMAc was used as the solvent for all data presented in this work. All samples were analyzed in 1 cm pathlength quartz cuvettes.

Fluorescence spectroscopy: Emission Spectra: Emission spectra were obtained using an Edinburgh Instruments FS5 spectrofluorometer. DMAc was used as the solvent for all sample data presented in this work and all samples were measured in quartz cuvettes with a 1 cm pathlength.

Absolute fluorescence quantum yields: Absolute fluorescence quantum yields (AFQY) were measured using an FS5 Spectrofluorometer from Edinburg Instruments with an SC-30 Integrating Sphere accessory using a direct excitation method. All samples were dissolved in DMAc at a concentration where the absorption intensity (A) was between A=0.09 and A=0.1, those samples were sparged with argon gas for 20 minutes, then transferred to 1 cm pathlength quartz cuvettes in a nitrogen filled glovebox before quantum yield analysis. Measurement was made over the photocatalyst samples (S) and reference solvents (R) scattering (R_s and S_s) and emission (R_e and S_e). The equation for the calculation of AFQY using the direct excitation method is:

$$AFQY = \frac{S_e - R_e}{R_s - S_s} \times 100$$

The scattering and emission spectral regions were measured separately. The AFQY values were calculated using the Fluoracle software via the equation above.

AFQY values were measured at the maximum wavelength of emission.

Cyclic voltammetry: Cyclic voltammograms were obtained using a Gamry electrochemical analyzer with an Ag/AgNO₃ (0.01 M in acetonitrile (MeCN)) reference electrode and tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M in DMAc) as the electrolyte for the working electrode. All samples were analyzed in DMAc at a concentration between 0.06 mM and 1 mM (depending on solubility) at a total volume of 25.0 mL and were sparged with nitrogen for 15 minutes before data collection. Platinum was used for the working and counter electrodes. Analysis was conducted at scan rates of 100 mV/s, 80 mV/s, 50 mV/s, and 20 mV/s with 7 cycles each. Data from the 6th cycle was analyzed unless otherwise noted. All voltammograms were corrected using the E_{1/2} of ferrocene as a reference.

Transient Absorption Spectroscopy: Transient absorption (TA) spectroscopy for determination of phenazine photocatalyst (PC) singlet and triplet excited state lifetimes was

performed on an Edinburgh Instruments LP980KS spectrometer with a Minilite Nd:YAG Q-switched laser (Continuum Lasers) configured to deliver a 355 excitation pulse. Spectral absorption data was acquired from 300-800 nm with time delays as indicated in the spectra shown below with an iStar ICCD camera (Andor) as the detector. Kinetic data was recorded utilizing a photomultiplier tube (included in the LP980) interfaced with an MD03022 mixed domain oscilloscope (Tektronix) as the detector. Time zero was set on the instrument using the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ to locate the pump pulse with a resolution of 1 ns. All kinetic traces shown were acquired with 50-75 averages and laser power between 3-15 mW/cm² at 1 Hz repetition rate. Time constants (excited state lifetimes) were calculated in the L900 software using an exponential tail fit. Spectral absorption data was offset corrected at all wavelengths using kinetic absorption data at the indicated wavelength to adjust ΔOD . Emission subtraction was done for spectra acquired at $t = 0$, while spectra acquired at $t = 200$ ns or $t = 400$ ns included a time delay to avoid emission signals and the emission subtraction step was omitted.

For each PC solution, the Beer-Lambert Law was used to calculate the concentration of PC needed for an absorbance intensity of 0.2 at the lambda max of absorbance. This resulted in solutions with an absorbance intensity of less than 0.2 at 355 nm (wavelength of the excitation pulse). To prepare the solutions, solid PC was weighed into a scintillation vial which was then brought into a N₂ filled glovebox. The appropriate amount of N,N-dimethylacetamide (DMAc) stored under N₂ was added to each vial, and 3 mL of the resulting solution was transferred to a quartz screw cap cuvette equipped with a Kontes valve and sidearm with a 1 cm path length. After completely sealing the cuvettes with caps, they were brought out of the glovebox. Each PC solution was analyzed by UV-vis on the instrument described herein both before and after TA spectroscopy to monitor if PC degradation occurred. None of the PC solutions analyzed in this work showed

evidence of degradation after TA, indicated by no observable change in the UV-vis spectra before and after TA spectroscopy was performed (Figure A1.45).

Polymer Characterization: Sample Prep for Analysis of Polymerization Kinetics and Molecular Weight Growth: To evaluate the kinetics and growth of molecular weight relative to the conversion of monomer (into polymer), an 0.1 mL aliquot of reaction mixture was taken after 1 hour, 2 hours, 4 hours, 6 hours, and 8 hours then immediately injected into a GC vial containing 0.5 mL of a solution of deuterated chloroform containing 250 ppm of a radical inhibitor (butylated hydroxyl toluene (BHT)). The aliquot was then analyzed using ^1H NMR spectroscopy. Through ^1H NMR spectroscopy the ratio of polymer to monomer (% conversion) was determined. After ^1H NMR analysis, the solvent was evaporated under air, then the sample was re-dissolved in HPCL-grade THF, filtered into a GPC vial using a 0.45 μm nylon filter, and finally analyzed by GPC with MALS. Characterization Instrumentation: Monomer conversion was determined using a Varian 400 MHz NMR Spectrometer. Molecular weights were determined by Gel Permeation Chromatography (GPC) coupled with multi-angle light scattering (MALS) using an Agilent HPLC fitted with one guard column, three PL-gel 5 μm MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector (MALS). The dn/dc value used for MMA in THF was 0.084, A dn/dc value of 0.063 in THF was used for poly(n-butyl) acrylate analysis.

Polymerization Batch Reactor Supplies and Design

Light Beakers for Polymerizations (Materials): One sixteen-inch strip of double-density white LEDs was purchased from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH). Emission spectra of LEDs used is shown in Figure A2.2.



Figure A2.1. 400 mL white light LED beaker photoreactor for polymerizations.

Light Beakers for Polymerizations (Setup): White light LED strip from Creative Lighting Solutions was wrapped inside a 400 mL beaker and used as the visible light source for the polymerizations described in this paper. The sides and bottom of the beaker were completely wrapped with tin foil and the led strips were coiled inside the bottommost portion of the beaker walls (Figure A2.1).

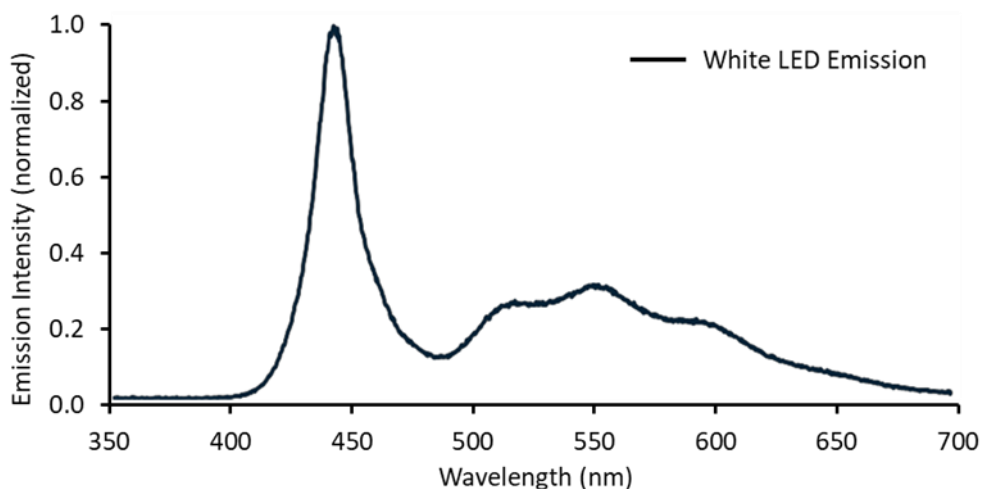


Figure A2.2. Normalized emission spectra of white light LEDs from creative lighting solutions.

PROCEDURES

Catalyst Synthesis

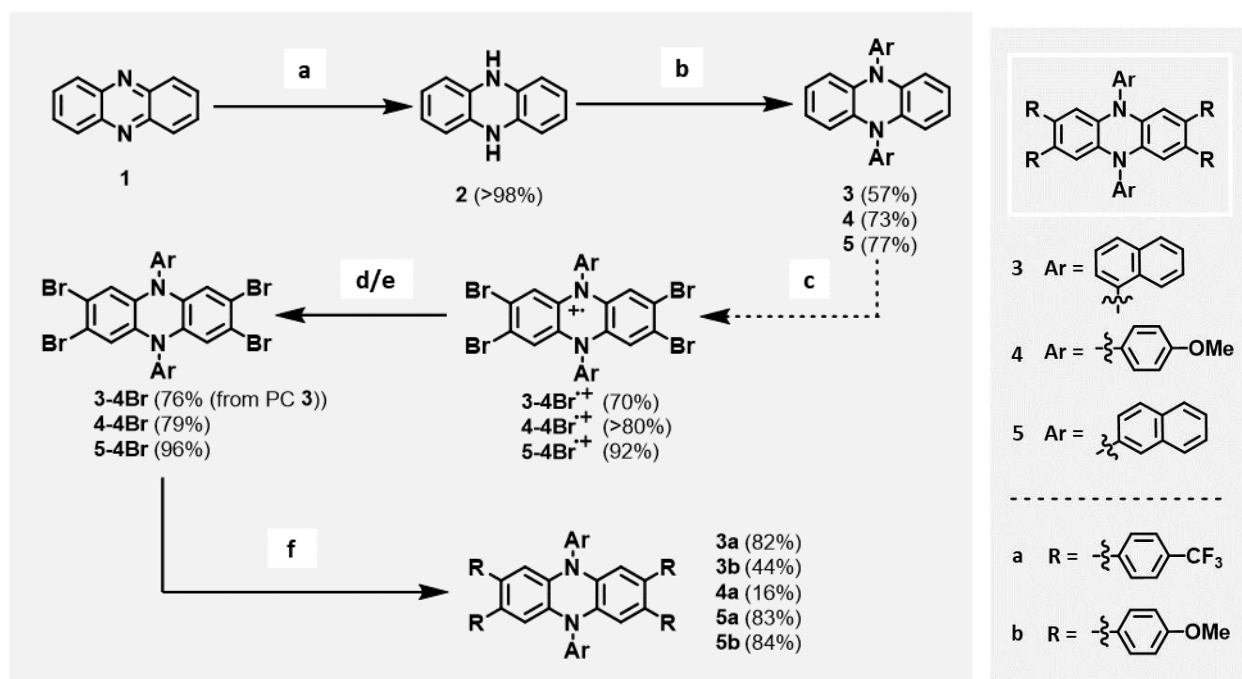


Figure A2.3. Synthetic scheme for synthesis of core-extended N,N-diaryl dihydrophenazines and structures. The mol percent yield from each step is noted adjacent to the labels of the final catalysts and catalyst intermediates.

Synthesis of N,N-diaryl dihydrophenazines (DHPs):

Synthesis of **2** (5,10-dihydrophenazine) (a)¹: Phenazine (27.6 mmol) was dissolved in reagent alcohol (EtOH) (150 mL) that had been sparged with N₂ for 30 min. This mixture was brought to reflux under N₂ and a solution of sodium dithionite (Na₂S₂O₄) (555 mmol) dissolved in degassed water (~700 mL) was added to the solution of phenazine under N₂ via a canula transfer. The reaction was solution was refluxed for 3.5 hours and subsequently cooled to room temperature. The solid was collected using a swivel frit under N₂ and washed with sparged H₂O (3 x 100 mL). The solid was then dried overnight under vacuum before being brought into an N₂ filled glovebox. (yield: 94%)

Synthesis of **3** (b)^{2,3}: 5,10-dihydrophenazine (1.098 mmol), NaOtBu (3.29 mmol), P(tBu)₃ (0.066 mmol), a stir bar, and 1-bromonaphthalene (4.39 mmol) were added to an oven dried

Schlenk flask which was then cycled under reduced pressure and backfilled with N₂ three times. The Schlenk flask was then brought into an N₂ filled glovebox and anhydrous 10 mL of Sure/Seal anhydrous toluene and Pd(dba)₂ (0.022 mmol) were added. The flask was then brought back out of the glovebox and the mixture was refluxed for 48 hours at 110°C then subsequently cooled to room temperature. The reaction mixture was then transferred to a separatory funnel and shaken in 100 mL of DI H₂O and 100 mL of DCM. The organic layer was recovered, washed with 100 mL of brine three times, then dried over Mg₂SO₄. After filtering off the Mg₂SO₄, the DCM was removed via rotary evaporation. The solids extracted from the crude reaction mixture were then dissolved in a minimal amount of DCM and recrystallized in the freezer after layering x3 volume of methanol on top of the DCM. Dark yellow solids were recovered. (Yield: 57%). ¹H NMR (400 MHz, C₆D₆) δ 8.68 – 8.54 (m, 2H), 7.75 – 7.66 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.46 (dd, *J* = 17.4, 7.1 Hz, 2H), 7.27 (dd, *J* = 15.5, 7.9 Hz, 7H), 6.07 (dd, *J* = 5.9, 3.4 Hz, 4H), 5.73 – 5.58 (m, 4H).

Synthesis of 4 (b) ^{2,3}: 5,10-dihydrophenazine (12.6 mmol), NaOtBu (37.9 mmol), P(tBu)₃ (0.756 mmol), and a stir bar were added to an oven dried Schlenk flask which was then cycled under reduced pressure and backfilled with N₂ three times. The Schlenk tube was then brought into an N₂ filled glovebox and anhydrous Sure/Seal toluene, Pd(dba)₂ (0.025 mmol), and 4-bromoanisole (21.1 mmol) (which was sparged under N₂ for 40 minutes) were added. The flask was then brought back out of the glovebox and the mixture was refluxed for 31 hours at 110°C then subsequently cooled to room temperature. The reaction mixture was dissolved in DCM (~100 mL) then washed twice with 400 mL of water, then with 100 mL of brine three times. The organic layer was dried using Mg₂SO₄ then filtered. Next, the solvent was removed via rotary evaporation. The solids obtained were dissolved in hot DCM, then x3 volume of warm hexanes was layered

onto of the DCM. Bright yellow crystals were recovered. (Yield: 73 %) ^1H NMR (400 MHz, DMSO) δ 7.34 – 7.27 (m, 4H), 7.24 – 7.17 (m, 4H), 6.24 (dd, J = 5.9, 3.4 Hz, 4H), 5.49 (dd, J = 5.8, 3.4 Hz, 4H), 3.84 (s, 6H).

Synthesis of **5 (b)**^{2,3}: 5,10-dihydrophenazine (27.4 mmol), NaOtBu (10.97 mmol), a stir bar, and 2-bromonaphthalene were added to an oven dried 250 mL Schlenk tube which was then cycled under reduced pressure and backfilled with N_2 three times. The Schlenk tube was then brought into in an N_2 filled glovebox and 50 mL of anhydrous Sure/Seal, RuPhos (1.09 mmol), and RuPhos Pd G4 (0.110 mmol) were added. The Schlenk tube was then brought back out of the glovebox and the mixture was refluxed for 48 hours at 110°C then subsequently cooled to room temperature. 600 mL of DCM and 300 mL of water were added to the crude reaction mixture. The product crashed out of solution over several minutes. Both aqueous and organic layers were filtered and the solid was collected. The product was then recrystallized from boiling DCM/MeOH in a 1:3 ratio to yield yellow crystals. (Yield: 77%) ^1H NMR (400 MHz, C_6D_6) δ 7.68 (dd, J = 5.3, 3.3 Hz, 4H), 7.64 – 7.57 (m, 2H), 7.57 – 7.49 (m, 2H), 7.32 (dd, J = 8.6, 2.0 Hz, 2H), 7.24 (dddd, J = 19.0, 8.2, 6.9, 1.4 Hz, 4H), 6.28 (dt, J = 7.5, 3.7 Hz, 4H), 5.86 (dd, J = 5.9, 3.4 Hz, 4H).

Synthesis of **3-4Br⁺** (c)⁴: PC **3** (0.460 mmol), benzene (200 mL), and bromine (9.20 mmol) were added to a round bottom flask containing a stir bar. The solution was refluxed at 60°C for 38.5 hours with a tube bubbling vapors from the reaction into a saturated aqueous solution of sodium dithionite. After 38.5 hours the reaction was cooled to room temperature and filtered. The reaction yielded 267 mg of dark blue solids. The filtrate (containing unreacted bromine) was neutralized using a solution of DI H_2O saturated with sodium thiosulfate. (Yield ~70%) (Not characterized by ^1H -NMR).

Synthesis of **4-4Br⁺⁺** (c)⁴: PC **4** (0.761 mmol), benzene (500 mL), and bromine (15.2 mmol) were added to a round bottom flask containing a stir bar. The solution was refluxed at 60°C for 24.5 hours with a tube bubbling vapors from the reaction into a saturated aqueous solution of sodium dithionite. After 24.5 hours the reaction was cooled to room temperature and filtered. The reaction yielded 267 mg of dark purple solids. The filtrate (containing unreacted bromine) was neutralized using a solution of DI H₂O saturated with sodium thiosulfate. (Yield >80%) (Not characterized by ¹H-NMR).

Synthesis of **5-4Br⁺⁺** (c)⁴: PC **5** (11.5 mmol), benzene (200 mL), and bromine (23.0 mmol) were added to a round bottom flask containing a stir bar. The solution was refluxed at 60°C for 12 hours with a tube bubbling vapors from the reaction into a saturated aqueous solution of sodium dithionite. After 12 hours the reaction was cooled to room temperature and filtered. The reaction yielded 882 mg of dark purple solids. The filtrate (containing unreacted bromine) was neutralized using a solution of DI H₂O saturated with sodium thiosulfate. (Yield ~92%) (Not characterized by ¹H-NMR).

Synthesis of **3-4Br** (d) (Method I)⁴: 160 mg of the solids obtained from the synthesis of **3-4Br⁺⁺** (~0.193 mmol) were added to a 1L round bottom flask. 500 mL of methanol was added along with a stir bar and 8g of copper wire cut into 1 inch pieces. The reaction mixture (a deep magenta color) was then stirred at ~60 °C for 30 minutes. After 30 minutes the reaction mixture had turned a creamy-orange color. The reaction mixture was subsequently cooled to room temperature and 86.4 mg of orange/yellow solids were collected via vacuum filtration and used without further purification. (Yield ~60%) (This sample was not used in synthesis, only the sample synthesized using Method II (see below) was used).

Synthesis of **3-4Br** (Method II) (c&e): Step 1): PC **3** (0.587 mmol), benzene (300 mL), and bromine (11.7 mmol) were added to a round bottom flask containing a stir bar. The solution was refluxed for 48.5 hours with a tube bubbling vapors from the reaction vessel into a saturated aqueous solution of sodium dithionite. After 48.5 hours the reaction was cooled to room temperature and filtered yielding shiny dark blue solids. The filtrate (containing unreacted bromine) was neutralized using a solution of DI H₂O saturated with sodium thiosulfate. Step 2): The recovered solids were dissolved in acetone (~500 mL) and allowed to stir for five hours at room temperature. The reaction mixture slowly changed from a deep magenta color to an opaque pale-yellow color. The reaction mixture was filtered and ~333 mg of solids were recovered. (Yield from **3** → **3-4Br**: ~76%) ¹H NMR (400 MHz, C₆D₆) δ 8.36 (dd, *J* = 17.1, 8.4 Hz, 2H), 7.51 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.45 (dd, *J* = 8.2, 4.5 Hz, 2H), 7.31 – 7.23 (m, 3H), 5.90 (d, *J* = 2.1 Hz, 4H).

Synthesis of **4-4Br** (d)⁴: 200 mg of the solids obtained from the synthesis of **4-4Br**⁺⁺ (~0.253 mmol) were added to a 1L round bottom flask. 500 mL of methanol was added along with a stir bar and 10g of copper wire cut into 1 inch pieces. The reaction mixture (a deep magenta color) was then stirred at ~80 °C for 3 hours. After 3 hours the reaction mixture had turned a light tan color. The reaction mixture was subsequently cooled to room temperature and 142 mg of light tan/yellow solids were collected via vacuum filtration. These solids were used without further purification. (Yield: 79%). ¹H NMR (400 MHz, C₆D₆) δ 6.78 (d, *J* = 8.5 Hz, 4H), 6.59 (d, *J* = 8.6 Hz, 4H), 6.06 (s, 4H), 3.15 (s, 6H).

Synthesis of **5-4Br** (d)⁴: 500 mL of methanol was added to **5-4Br**⁺⁺ solids in a round bottom flask with a stir bar. The solution was stirred at ~60 °C for 30 minutes. Then 7 ft of copper wire, cut into 1 inch pieces, was added to the round bottom flask. The solution was stirred at 60° C for 26 hours. The solution turned from a deep fusia color to a light orange color with a yellow solid

precipitated. After 26 hours, the reaction mixture was cooled to room temperature and the solid was collected via vacuum filtration. (Yield: ~96%). ^1H NMR (400 MHz, C_6D_6) δ 7.57 – 7.41 (m, 9H), 7.01 (dd, J = 8.6, 2.1 Hz, 2H), 6.08 (s, 4H).

Synthesis of **3a** (e)⁴: **3-4Br** (0.173 mmol), 4-trifluoromethylphenyl boronic acid (1.39 mmol) and a stir bar were added to a 100mL Schlenk tube. The Schlenk tube was then put under vacuum then backfilled with N_2 (three cycles) before transferring it to an N_2 filled glovebox. $\text{Pd}(\text{PPh}_3)_4$ (0.026 mmol) and 25.0 mL of anhydrous sure/seal THF was added. The storage tube was then taken out of the glove box and 4.50 mL of 2.00 M aqueous K_2CO_3 (that had been sparged with N_2 for >30 min) was added to the storage tube under N_2 . The mixture was heated to 110 °C and stirred for 45 hours. After allowing the reaction mixture to cool, the reaction mixture was transferred to a round bottom flask using THF, then 100 mL of water was added. The THF was removed via rotary evaporation and yellow/green solids crashed out into the water. The solution was then filtered to recover the solids. The recovered solids were then dissolved in DCM, and the solution was washed with equivolume of water three times then the organic layer was washed with brine. The solution was then dried with using Na_2SO_4 then filtered and concentrated via rotary evaporation. The recovered yellow solids were then dissolved in a minimal amount of warm toluene and any undissolved solids were filtered off. Small amounts of silver/grey solids were recovered from the solution during this step. Next, the toluene was removed by rotary evaporation then the recovered solids were redissolved in a minimal volume of DCM. Methanol (in three time the volume of DCM) was then layered on top of the DCM and the solution was put into the freezer to recrystallize. Bright yellow solids were recovered (Yield: 82%). ^1H NMR (400 MHz, C_6D_6) δ 8.85 (dd, J = 8.4, 4.5 Hz, 2H), 7.70 – 7.53 (m, 6H), 7.45 – 7.19 (m, 7H), 6.69 (dd, J = 8.5, 2.3 Hz,

9H), 6.57 (dd, $J = 8.1, 5.9$ Hz, 8H), 5.98 (d, $J = 1.5$ Hz, 4H). HRMS (ESI) calculated for (M^+) $C_{60}H_{34}F_{12}N_2$: 1010.2530; mass found: 1010.2480.

Synthesis of **4a** (e)⁴: **4-4Br** (0.446 mmol), 4-trifluoromethylphenyl boronic acid (3.57 mmol), and a stir bar were added to a 100mL Schlenk tube. The Schlenk tube was put under vacuum then backfilled with N_2 (three cycles) before transferring it to an N_2 filled glovebox. $Pd(PPh_3)_4$ (0.067 mmol) and 30.0 mL of THF were added. The storage tube was taken out of the glove box then 9.00 mL of 2.00 M aqueous K_2CO_3 that had been sparged with N_2 for >30 min was added to the storage tube under N_2 . The mixture was heated to 100 °C and stirred for 48 hours. After allowing the reaction mixture to cool, the reaction mixture was transferred to a round bottom flask using THF and 100 mL of water, the THF was then removed via rotary evaporation and dark green/yellow solids crashed out into the water. The solids were recovered by vacuum filtration, then hot DCM was added until the solids were almost entirely dissolved (~400 mL). The solution was then filtered and small amounts of silver/grey solids were recovered. The filtrate was then rotovapped down to yield bright yellow solids (Yield: 80%). Although the 1H -NMR looked relatively clean, we attempted to further recrystallize the yellow powder. The bright yellow powder was then redissolved in warm DCM which was layered with methanol (x2 volume relative to DCM) and yellow solids started to crash out. The yellow solids were recovered via vacuum filtration then dissolved in ~300 mL of toluene. Warm hexanes in three times the volume of toluene was then layered on top of the solution. The solution was transferred to the freezer and allowed to recrystallize. Bright yellow solids were then recovered via vacuum filtration (Yield: 16 %) 1H NMR (400 MHz, DMSO) δ 7.48 (dd, $J = 8.6, 3.5$ Hz, 13H), 7.20 (d, $J = 8.9$ Hz, 4H), 6.99 (d, $J = 8.0$ Hz, 8H), 5.57 (s, 4H), 3.80 (s, 6H). 1H NMR (400 MHz, C_6D_6) δ 7.29 (d, $J = 8.8$ Hz, 4H), 6.94

– 6.78 (m, 20H), 6.12 (s, 4H), 3.11 (s, 6H). HRMS (ESI) calculated for (M^+) $C_{54}H_{34}F_{12}N_2O_2$: 970.2428; mass found: Not detected.

Synthesis of **5a** (e)⁴: **5-4Br** (0.533 mmol) and 4-trifluoromethylphenyl boronic acid (4.27 mmol) were added to a 100mL storage tube. The storage tube was put under vacuum then backfilled with N_2 (3 cycles) before transferring it to an N_2 filled glovebox. $Pd(PPh_3)_4$ (0.080 mmol) and 40.0 mL of THF was added. The storage tube was then taken out of the glove box then 12.0 mL of 2.00 M aqueous K_2CO_3 that had been sparged with N_2 for >30 min was added to the storage tube under N_2 . The mixture was heated to 100 °C and refluxed for 24 hours. After allowing the reaction mixture to cool, the reaction mixture was transferred to a round bottom flask using THF, then THF was removed via rotary evaporation. DCM was added until the solids were almost entirely dissolved. The solution was then washed with equivolume of water three times then the organic layer was washed with an equivolume of brine two times. The solution was then dried with sodium sulfate and concentrated via rotary evaporation. The recovered yellow/green solids were then stirred in ~300 mL of hot toluene until almost everything had dissolved, then, after allowing it to cool, the solution was filtered. Small amounts of silver/grey solids were recovered from the product solution during this step. Warm hexanes in three times the volume of toluene was then layered on top of the solution. The solution was transferred to the freezer and allowed to recrystallize. Bright yellow solids were recovered via vacuum filtration. (Yield: 83 %) 1H NMR (400 MHz, C_6D_6) δ 7.97 (d, J = 2.0 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.58 (dt, J = 7.2, 3.6 Hz, 2H), 7.55 – 7.46 (m, 4H), 6.75 (q, J = 8.4 Hz, 16H), 6.18 (s, 4H). HRMS (ESI) calculated for (M^+) $C_{60}H_{34}F_{12}N_2$: 1010.2530; mass found: 1010.2517.

Synthesis of **3b** (e)⁴: **3-4Br** (0.175 mmol), 4-methoxyphenyl boronic acid (0.00140 mol), and a stir bar were added to a 100mL storage tube. The storage tube was put under vacuum then

backfilled with N₂ (three cycles) before transferring it to an N₂ filled glovebox. Pd(PPh₃)₄ (0.026 mol) and 10 mL of anhydrous Sure/seal THF was added. The storage tube was then taken out of the glove box then 6 mL of 2M aqueous K₂CO₃ that had been sparged with N₂ for >30 min was added to the storage tube under N₂. The mixture was heated to 110 °C and stirred for 48 hours. After allowing the reaction mixture to cool, THF was used to transfer the mixture to a round bottom flask. 100 mL of DI H₂O was added to the round bottom flask and then the THF was then removed via rotary evaporation—yellow solids precipitated into the water. The solids were recovered by vacuum filtration, rinsed with ~100 mL of methanol, then dissolved in hot DCM until the solids were almost entirely dissolved (~400 mL). The solution was then filtered and small amounts of silver/grey solids were recovered. The filtrate was then layered with x2 volume of methanol and placed in the freezer to recrystallize. (Yield: 44%). ¹H NMR (400 MHz, CDCl₃) δ 9.00 (dd, *J* = 8.8, 4.0 Hz, 2H), 7.76 (t, *J* = 6.7 Hz, 2H), 7.65 (dd, *J* = 13.4, 8.0 Hz, 3H), 7.59 (d, *J* = 8.3 Hz, 2H), 6.86 (dd, *J* = 8.4, 6.4 Hz, 9H), 6.37 – 6.24 (m, 9H), 6.19 (d, *J* = 1.7 Hz, 4H), 3.08 (s, 14H). HRMS (ESI) calculated for (M⁺) C₆₀H₄₆N₂O₄: 858.3458; mass found: 858.3441.

Synthesis of **5b** (e)⁴: **5-4Br** (0.667 mmol) and 4-methoxyphenyl boronic acid (5.33 mmol) were added to a 250 mL storage tube along with a stir bar. The storage tube was put under vacuum then backfilled with N₂ (x3) before transferring it to an N₂ filled glovebox. Pd(PPh₃)₄ (0.099 mmol) and 50.0 mL of THF were added. The storage tube was then taken out of the glove box then 15.0 mL of a 2.00 M aqueous K₂CO₃ that had been sparged with N₂ for >30 min was added to the storage tube under N₂. The mixture was heated to 100 °C and stirred for 24 h. After allowing the reaction mixture to cool, it was transferred to a round bottom flask using 100 mL of THF and 100 mL of water. The THF was then removed via rotary evaporation and yellow/green solids crashed out. The solids were then filtered off and the filtrate disposed of. Hot DCM was added to the until

the solids were almost entirely dissolved. The solution was then washed with equivolume of water three times then the organic layer was washed with brine. The solution was then dried with sodium sulfate, filtered, then concentrated via rotary evaporation. The solids were recrystallized by using hot dichloromethane to dissolve the solids, then adding three times that volume of methanol. The recovered yellow solids were then dissolved in warm toluene and filtered. Small amounts of silver/grey solids were recovered from the product solution during this step. The toluene was removed via rotary evaporation and the remaining solids were recrystallized again from hot DCM/MeOH in a ratio of 1:3 yielding bright yellow solids. (Yield: 84%) ^1H NMR (400 MHz, C_6D_6) δ 8.00 (s, 2H), 7.80 – 7.45 (m, 7H), 6.46 – 6.21 (m, 12H), 3.06 (d, J = 3.6 Hz, 12H). ^1H NMR (400 MHz, DMSO) δ 8.26 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 1.9 Hz, 2H), 8.05 (t, J = 7.6 Hz, 4H), 7.72 – 7.65 (m, 2H), 7.61 (q, J = 6.9 Hz, 4H), 6.66 – 6.53 (m, 18H), 5.54 (s, 4H). HRMS (ESI) calculated for (M^+) $\text{C}_{60}\text{H}_{46}\text{N}_2\text{O}_4$: 858.3458; mass found: 858.3435.

Polymer Synthesis

Approximately 15.0 mg of the catalyst was weighed into a 20 mL scintillation vial. Each catalyst was then dissolved in DMAc to a known concentration. A specific volume of the catalyst stock solution was then dispensed into a 20 mL scintillation vials such that when 1.00 mL of monomer was added to the reaction vial, the catalyst would either be at a 500 ppm, 100 ppm, 50 ppm, or 10 ppm catalyst loading relative to monomer. After the catalyst solutions were dispensed into scintillation vials, the DMAc was removed via rotary evaporation and the sample was dried on a high vac line for 24 hours. The scintillation vials containing catalyst were then equipped with a stir bar and brought into a nitrogen-filled glovebox. 1.00 mL of monomer and 1.00 mL of solvent was then added using Hamilton gas tight syringes and the solution stirred in the dark for 2 minutes. 17.8 μL of initiator (diethyl-2-bromo-2-methylmalonate) was then added using a Hamilton gas

tight syringe and the reaction vessel was immediately placed in the center of an LED beaker, the latter of which had been turned on for at least 5 minutes. The initial time for the start of the polymerization was noted at the moment the reaction vessel was transferred to the LED beaker and the polymerizations were allowed to proceed for eight hours. Polymerizations were run according to previously described methods.^{3,4}

CHARACTERIZATION OF CATALYST PROPERTIES

Table A2.2. Select experimentally determined and computationally predicted photophysical and electrochemical properties of PCs.

PC	$\lambda_{\text{max,abs}}$ (nm) ^[a]	ϵ_{max} (M ⁻¹ s ⁻¹) ^[b]	$\lambda_{\text{max,em}}$ (nm) ^[c]	$E_{\text{S1,exp}}$ (eV) ^[d]	$E_{\text{T1,comp}}$ (eV) ^[e]	Stokes Shift (nm)	Φ_f (%) ^[f]	$E_{1/2}$ (² PC ^{•+} / ¹ PC) (V vs SCE) ^[g]	$E_{\text{ox,comp}}^0$ (² PC ^{•+} / ¹ PC) (V vs SCE) ^[e]	$E_{\text{S1,exp}}^{0*}$ (² PC ^{•+} / ¹ PC*) (V vs SCE) ^[h]	$E_{\text{T1,comp}}^{0*}$ (² PC ^{•+} / ³ PC*) (V vs SCE) ^[e]
3	366	5,500	663	1.87	2.23	297	1.32	0.23	0.10	-1.64	-2.13
3a	385	21,900	586	2.12	1.91	201	9.00	0.34	0.24	-1.78	-1.67
3b	385	13,100	636	1.95	2.07	251	4.31	0.23	0.00	-1.72	-2.06
4	373	5,500	467	2.66	2.29	94.0	23.0	0.16	0.01	-2.50	-2.29
4a	392	21,000	599	2.07	1.82	207	36.0	0.34	0.16	-1.73	-1.66
5	343	5,900	654	1.90	2.19	311	0.72	0.21 ^[i]	0.06	-1.69	-2.12
5a	373	27,400	587	2.11	1.89	214	35.0	0.38	0.15	-1.73	-1.75
5b	371	16,000	621	2.00	1.99	250	4.00	0.38	0.00	-1.62	-2.00

^[a]Maximum wavelength of absorption was measured using UV-Vis in DMAc. ^[b]Molar absorptivity calculated at λ_{max} in DMAc. ^[c]Maximum wavelength of emission was measured using steady-state fluorescence spectroscopy in DMAc. ^[d]Singlet energies were calculated using the maximum wavelength of emission ($E(\text{eV})=1239.8 / \lambda (\text{nm})$). ^[e]DFT calculations were performed at the uM06/6-311+G(d,p)//uM06/6-31+G(d,p) level of theory with CPCM-described solvation in DMAc. ^[f]Quantum yield of fluorescence was measured in DMAc using absolute methods. ^[g]All measurements were performed in a 3-compartment electrochemical cell with an Ag/ AgNO₃ reference electrode in MeCN (0.01 M) and 0.1 M NBu₄PF₆ electrolyte solution. DMAc was used to solvate the PCs and in the working electrode compartment, while platinum was used as both the working and counter electrodes. $E (\text{V vs SCE}) = E (\text{V vs Ag/AgNO}_3 [0.01 \text{ M}]) + 0.298 \text{ V}$. ^[h]Singlet excited state reduction potentials were calculated using the singlet energies (estimated from the maximum wavelength of emission) and the $E_{1/2}$. ^[i]Values were taken from ref. 2.

Table A2.2. Experimentally determined singlet and triplet excited state lifetimes of PCs.

PC	τ_{S1} (ns) ^[a]	τ_{T1} (μ s) ^[b]	$\lambda_{\text{kinetic em}}$ (nm) ^[c]	$\lambda_{\text{kinetic abs}}$ (nm) ^[d]
3	9	0.63	617	445
3a	17	144	569	440
3b	11	42	608	593
4	37	88	466	450
4a	13	NA ^[e]	585	NA ^[e]
5	NA ^[f]	3.5	600	450
5a	17	NA ^[e]	575	NA ^[e]
5b	11	108	598	550

^[a]Singlet excited state lifetime determined by kinetic emission. ^[b]Triplet excited state lifetime determined by kinetic absorption. ^[c]Wavelength at which kinetic emission was measured. ^[d]Wavelength at which kinetic absorption was measured. ^[e]Excited state absorption signal was too weak to measure kinetic decay of excited state absorption, therefore a triplet excited state lifetime was not measured for this PC. ^[f]Kinetic emission measured at 600nm was determined to be 6.3 ns which is too close to the limit of detection for the instrument (6 ns) to be measured accurately, therefore this data is not included in the above table.

Ultraviolet-Visible Spectroscopy

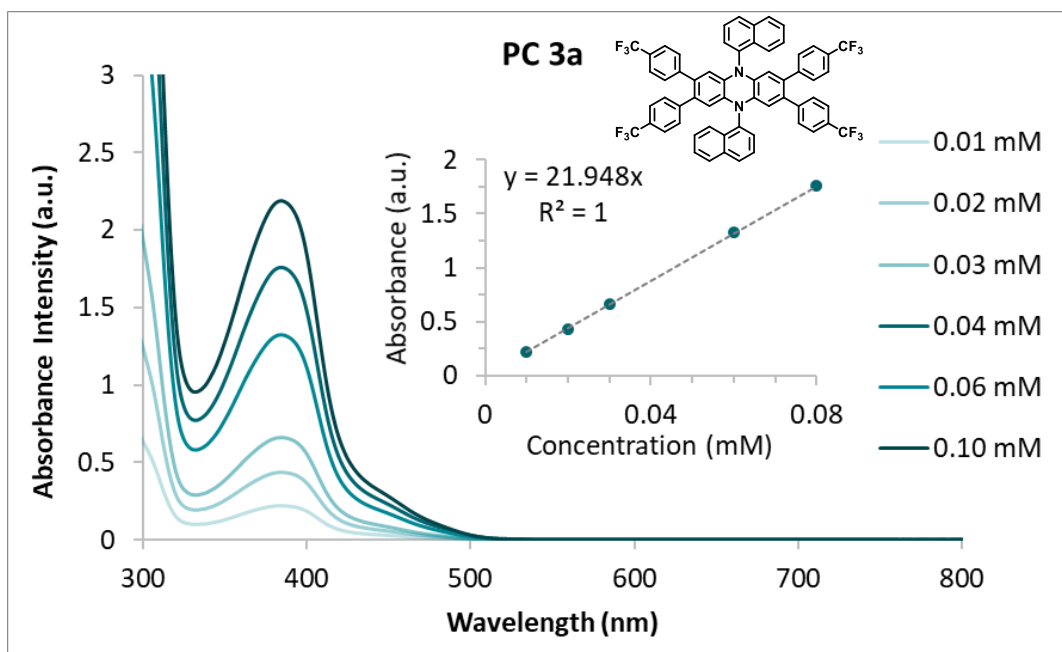


Figure A2.4. UV-Vis spectra of 3a at varied concentrations in DMAc in a quartz cuvette with a pathlength of 1cm. Secondary graph demonstrates the Beer-Lambert law relationship between concentration and absorbance at 385 nm.

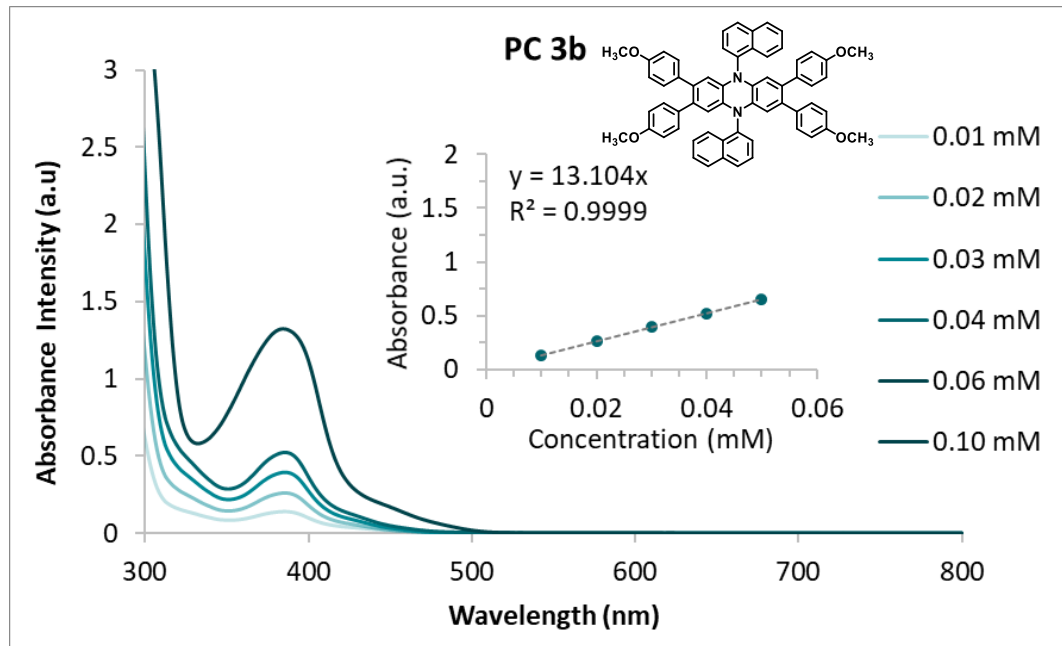


Figure A2.5. UV-Vis spectra of 3b at varied concentrations in DMAc in a quartz cuvette with a pathlength of 1cm. Secondary graph demonstrates the Beer-Lambert law relationship between concentration and absorbance at 385 nm.

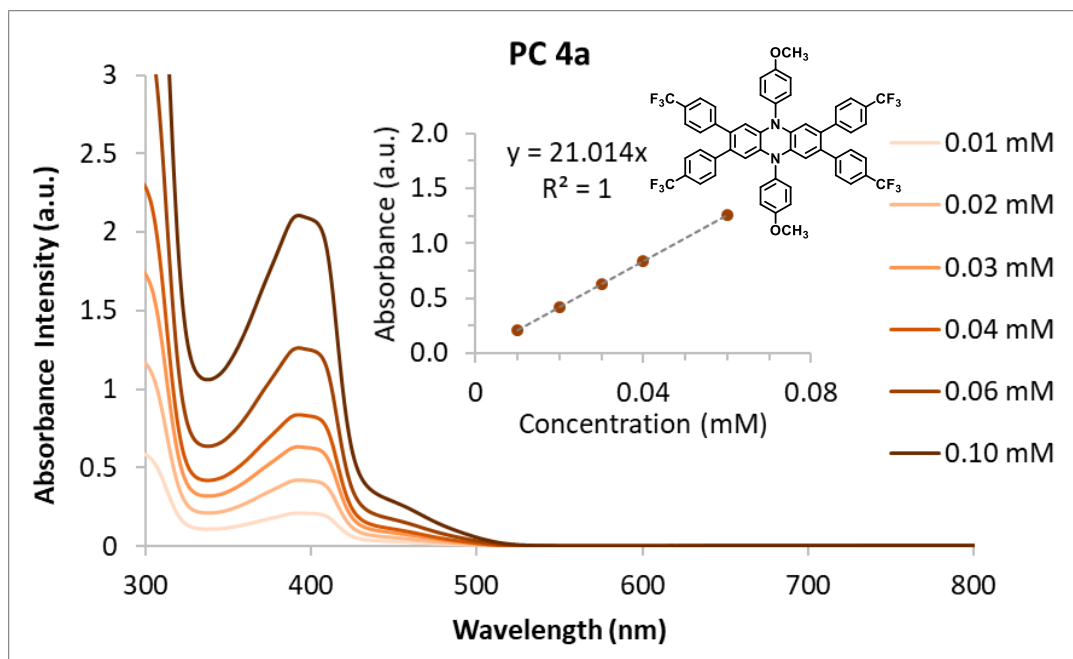


Figure A2.6. UV-Vis spectra of 4a at varied concentrations in DMAc in a quartz cuvette with a pathlength of 1cm. Secondary graph demonstrates the Beer-Lambert law relationship between concentration and absorbance at 392 nm.

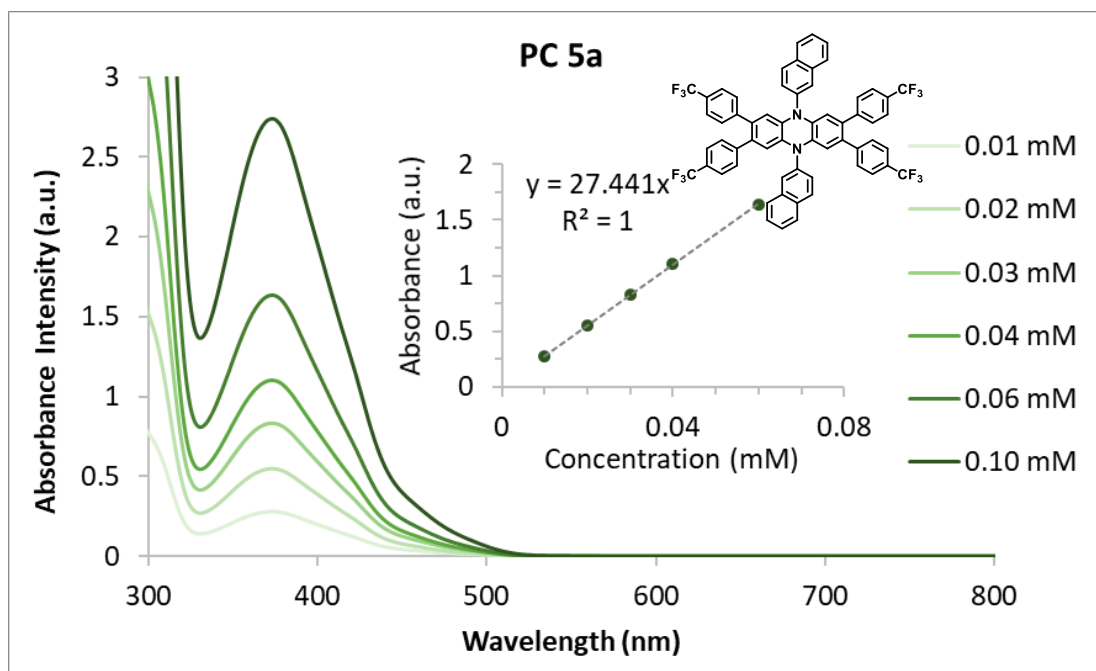


Figure A2.7. UV-Vis spectra of 5a at varied concentrations in DMAc in a quartz cuvette with a pathlength of 1cm. Secondary graph demonstrates the Beer-Lambert law relationship between concentration and absorbance at 373 nm.

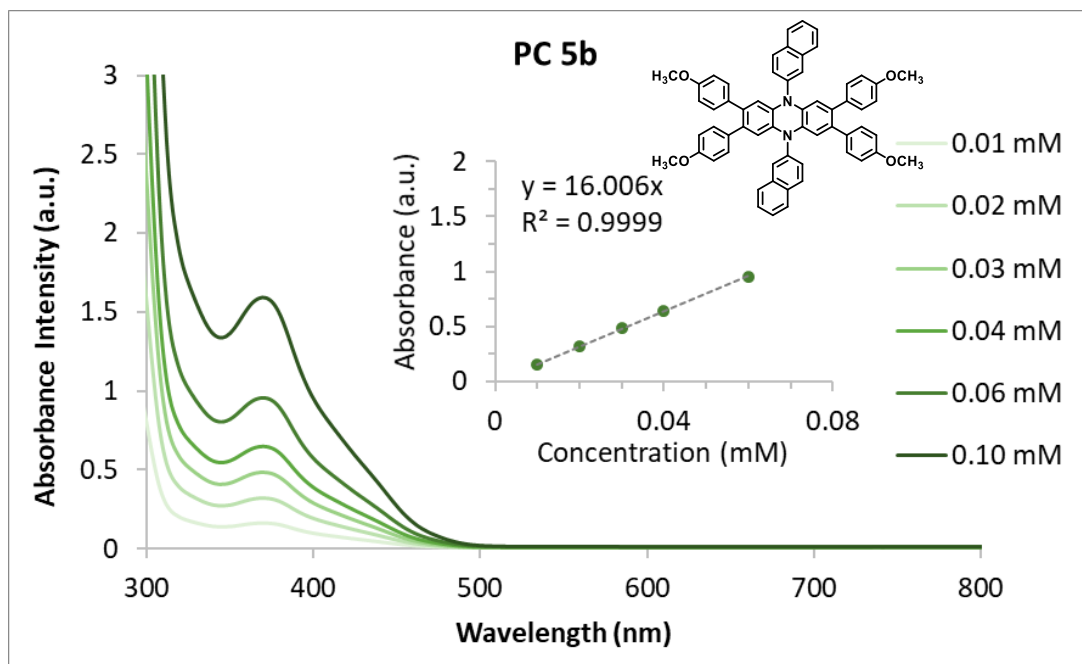


Figure A2.8. UV-Vis spectra of **5b** at varied concentrations in DMAc in a quartz cuvette with a pathlength of 1cm. Secondary graph demonstrates the Beer-Lambert law relationship between concentration and absorbance at 371 nm.

Fluorescence Spectroscopy

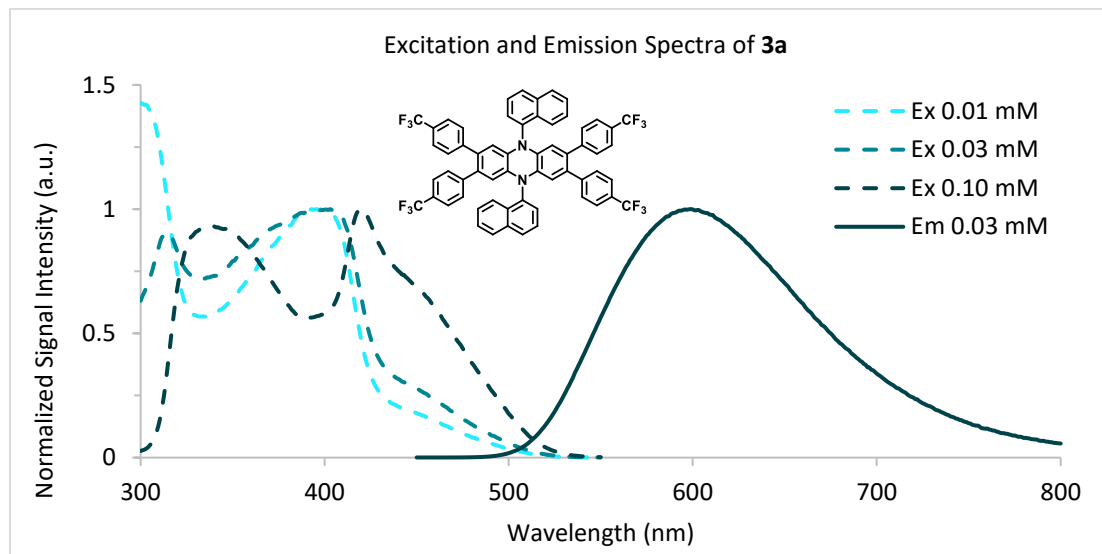


Figure A2.9. Fluorescence spectra of PC 3a. Dashed lines are the excitation spectra at varying concentrations in DMAc and the solid line is the emission spectrum at 0.03 mM in DMAc. Emission spectra was collected using an excitation wavelength of 385 nm and is representative of emission profiles at all concentrations between 0.01 mM and 0.10 mM. Excitation spectra were collected for emission at 586 nm.

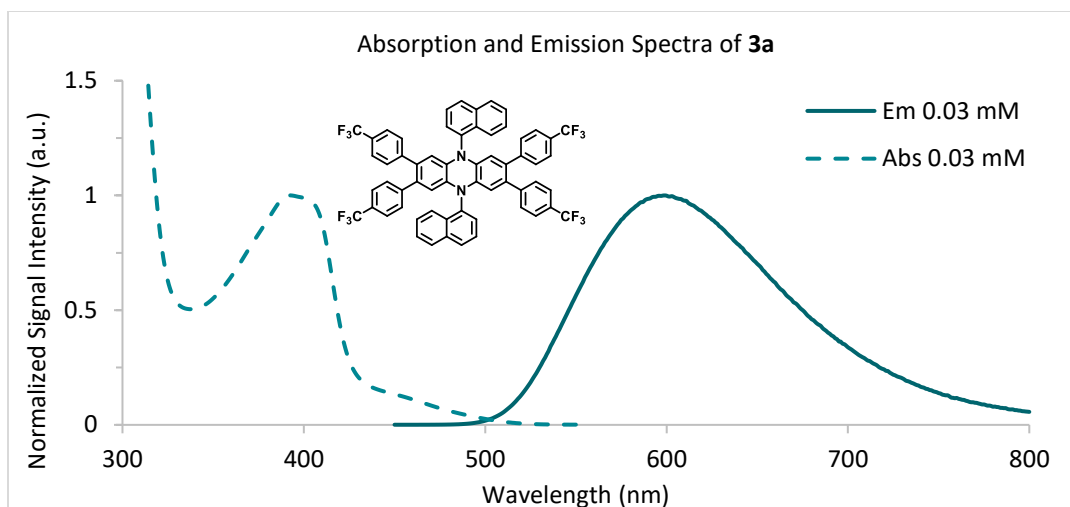


Figure A2.10. Emission spectra of PC **3a** (solid) and absorption spectra of **3a** (dashed) at 0.03 mM in DMAc. Absorption spectra was measured using UV-Vis and emission spectra was measured using fluorimetry. Emission spectra was collected using an excitation wavelength of 385 nm.

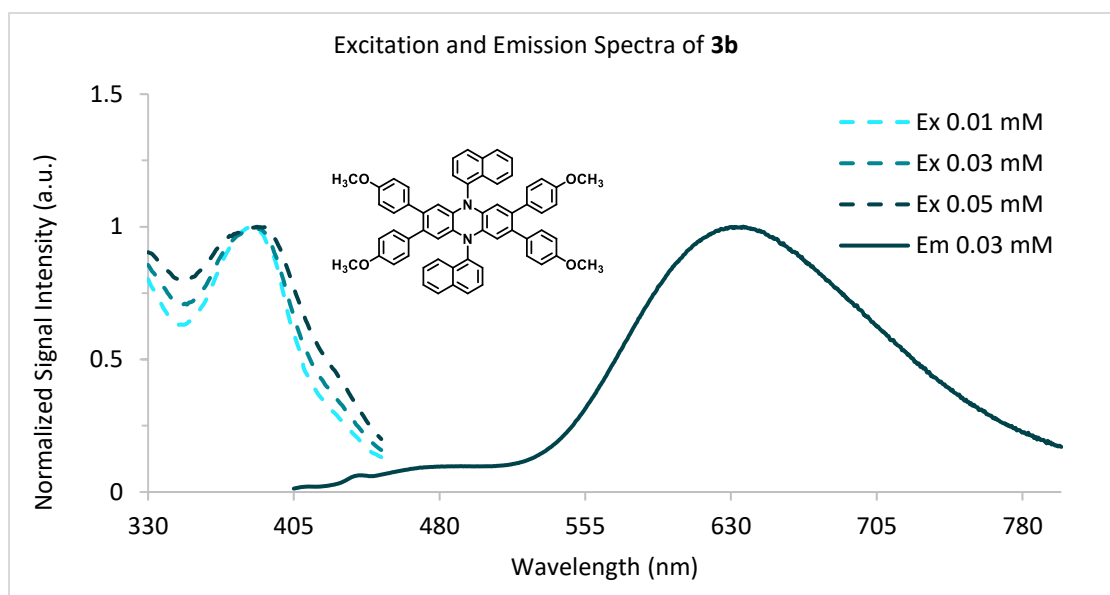


Figure A2.11. Fluorescence spectra of PC **3b**. Dashed lines are the excitation spectra at varying concentrations in DMAc and the solid line is the emission spectrum at 0.03 mM in DMAc. Emission spectra was collected using an excitation wavelength of 385 nm and is representative of emission profiles at all concentrations between 0.01 mM and 0.10 mM. Excitation spectra were collected for emission at 636 nm.

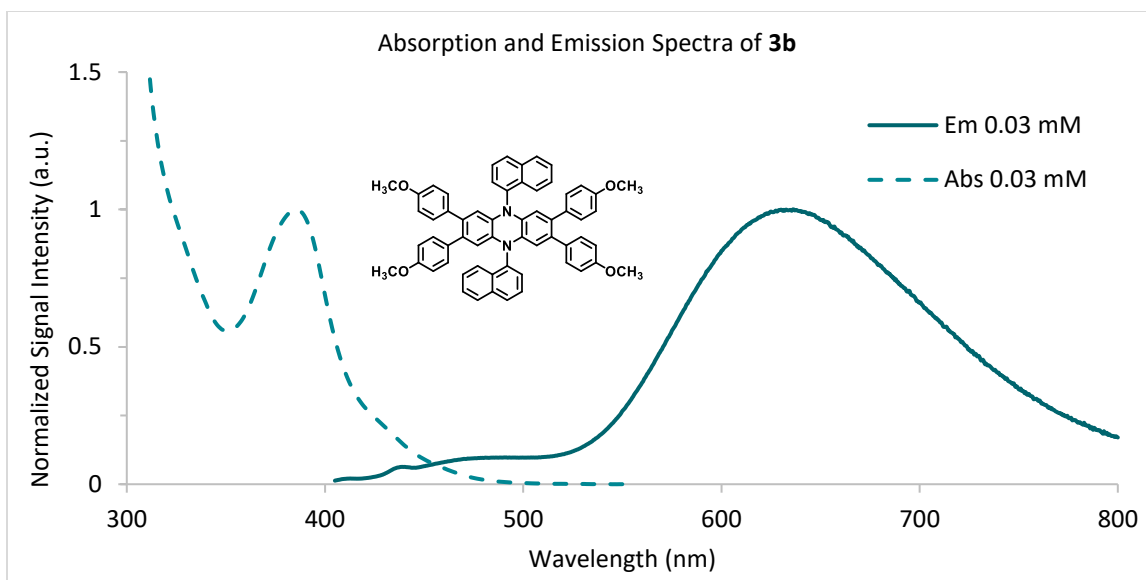


Figure A2.12. Emission spectra of PC **3b** (solid) and absorption spectra of **3b** (dashed) at 0.03 mM in DMAc. Absorption spectra was measured using UV-Vis and emission spectra was measured using fluorimetry. Emission spectra was collected using an excitation wavelength of 385 nm.

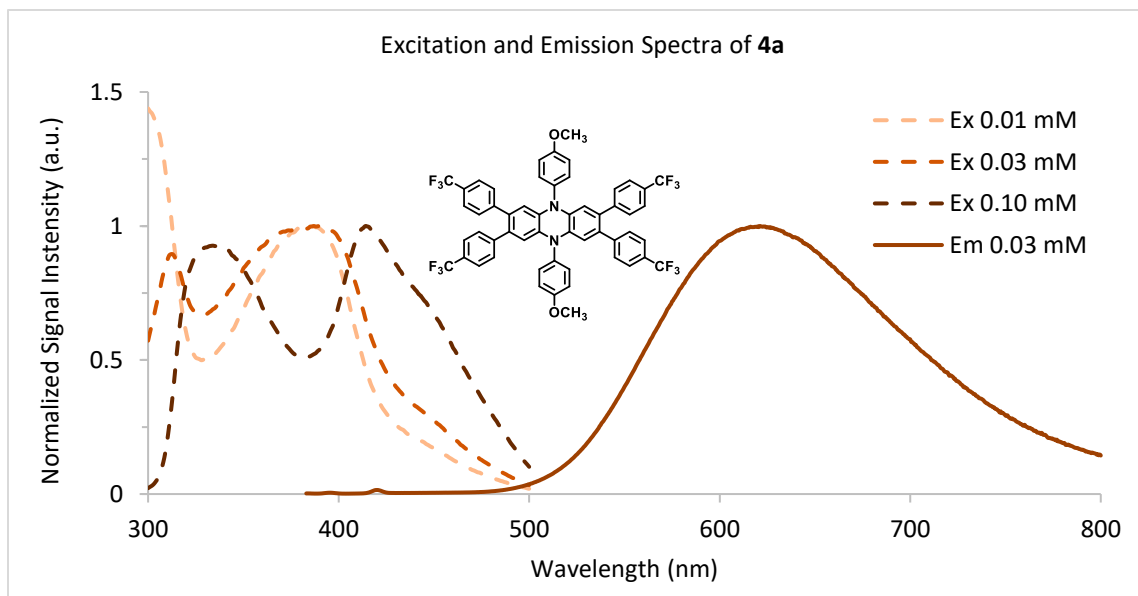


Figure A2.13. Fluorescence spectra of PC **4a**. Dashed lines are the excitation spectra at varying concentrations in DMAc and the solid line is the emission spectrum at 0.03 mM in DMAc. Emission spectra was collected using an excitation wavelength of 392 nm and is representative of emission profiles at all concentrations between 0.01 mM and 0.10 mM. Excitation spectra were collected for emission at 599 nm.

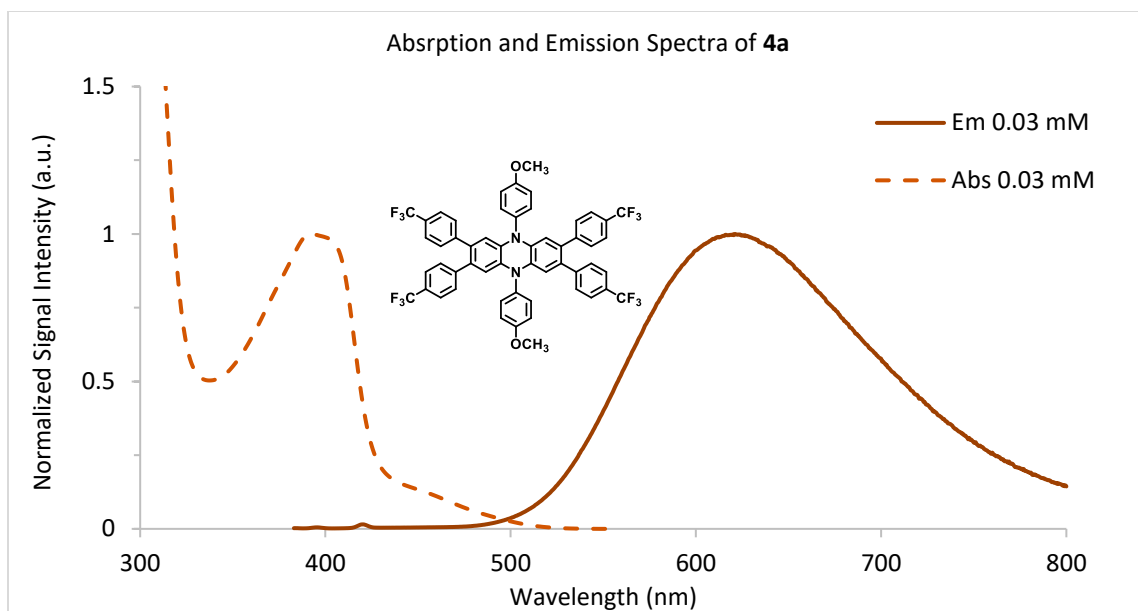


Figure A2.14. Emission spectra of PC **4a** (solid) and absorption spectra of **4a** (dashed) at 0.03 mM in DMAc. Absorption spectra was measured using UV-Vis and emission spectra was measured using fluorimetry. Emission spectra was collected using an excitation wavelength of 392 nm.

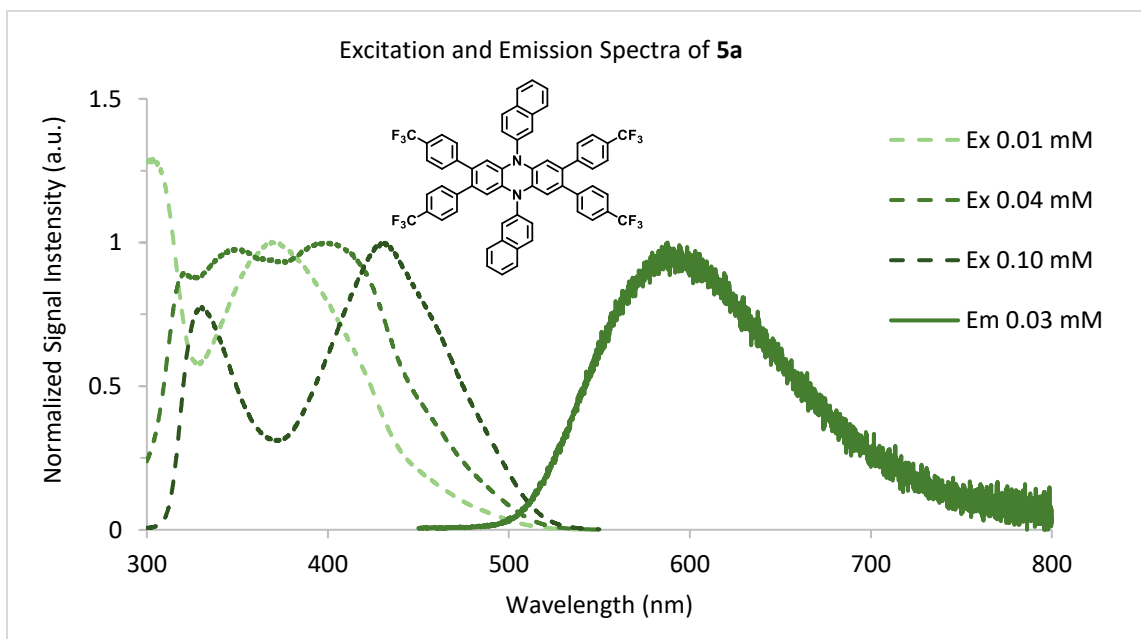


Figure A2.15. Fluorescence spectra of PC **5a**. Dashed lines are the excitation spectra at varying concentrations in DMAc and the solid line is the emission spectrum at 0.03 mM in DMAc. Emission spectra was collected using an excitation wavelength of 373 nm and is representative of emission profiles at all concentrations between 0.01 mM and 0.10 mM. Excitation spectra were collected for emission at 587 nm.

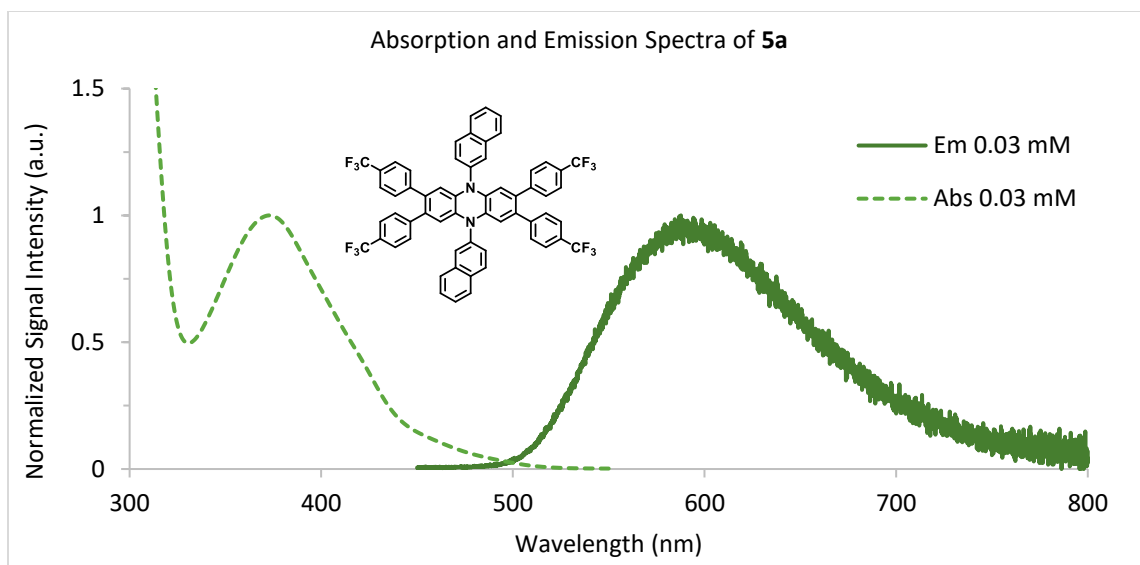


Figure A2.16. Emission spectra of PC **5a** (solid) and absorption spectra of **5a** (dashed) at 0.03 mM in DMAc. Absorption spectra was measured using UV-Vis and emission spectra was measured using fluorimetry. Emission spectra was collected using an excitation wavelength of 373 nm.

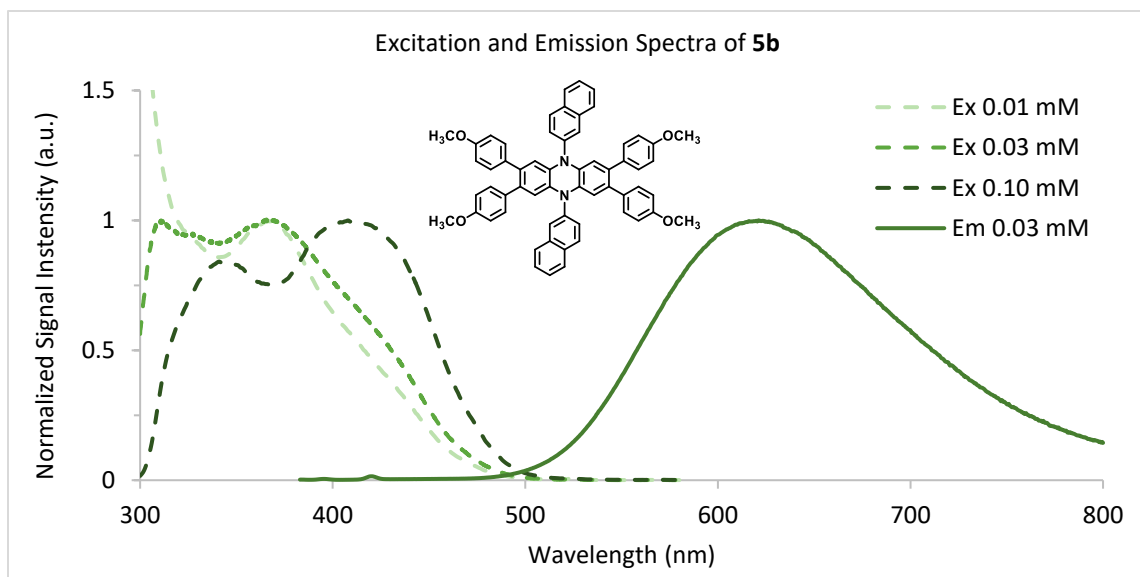


Figure A2.17. Fluorescence spectra of PC **5b**. Dashed lines are the excitation spectra at varying concentrations in DMAc and the solid line is the emission spectrum at 0.03 mM in DMAc. Emission spectra was collected using an excitation wavelength of 371 nm and is representative of emission profiles at all concentrations between 0.01 mM and 0.10 mM. Excitation spectra were collected for emission at 621 nm.

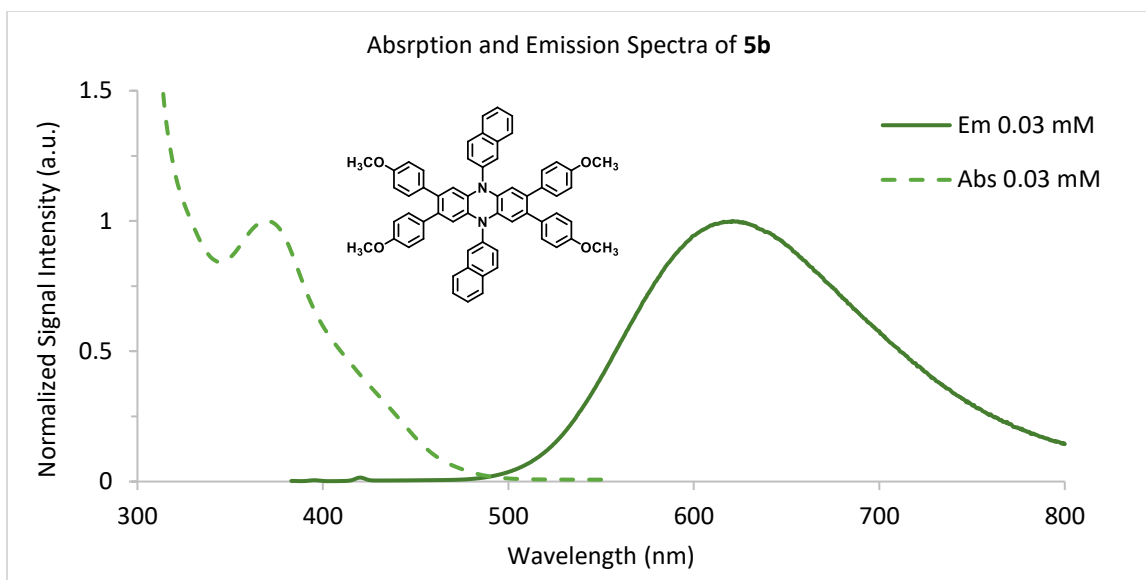


Figure A2.18. Emission spectra of PC **5b** (solid) and absorption spectra of **5b** (dashed) at 0.03 mM in DMAc. Absorption spectra was measured using UV-Vis and emission spectra was measured using fluorimetry. Emission spectra was collected using an excitation wavelength of 371 nm.

Transient Absorption Spectroscopy

Spectral Absorption Data

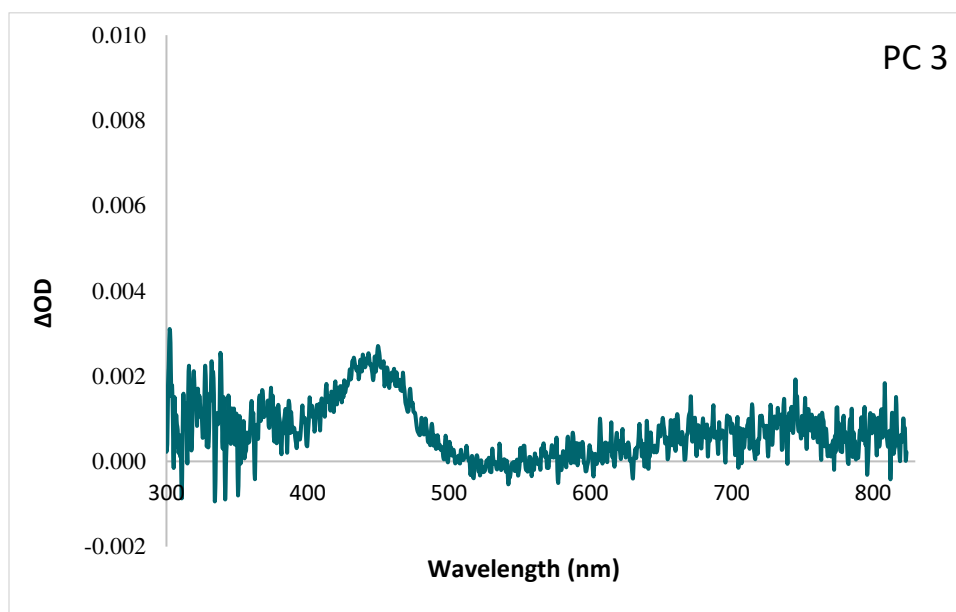


Figure A2.19. Spectral absorption of PC **3** in DMAc at a 200 ns time delay, with no emission subtraction. The excited state absorption (ESA) feature visible at $\lambda = 445$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 445$ nm.

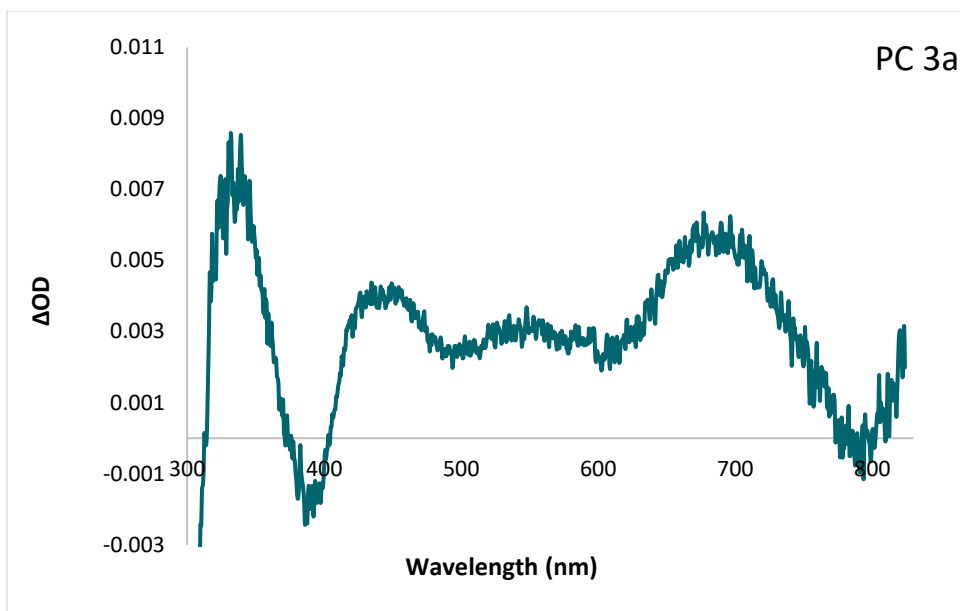


Figure A2.20. Spectral absorption of PC **3a** in DMAc with no time delay ($t = 0$ ns) and with emission subtraction. The ESA feature visible at $\lambda = 440$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 440$ nm.

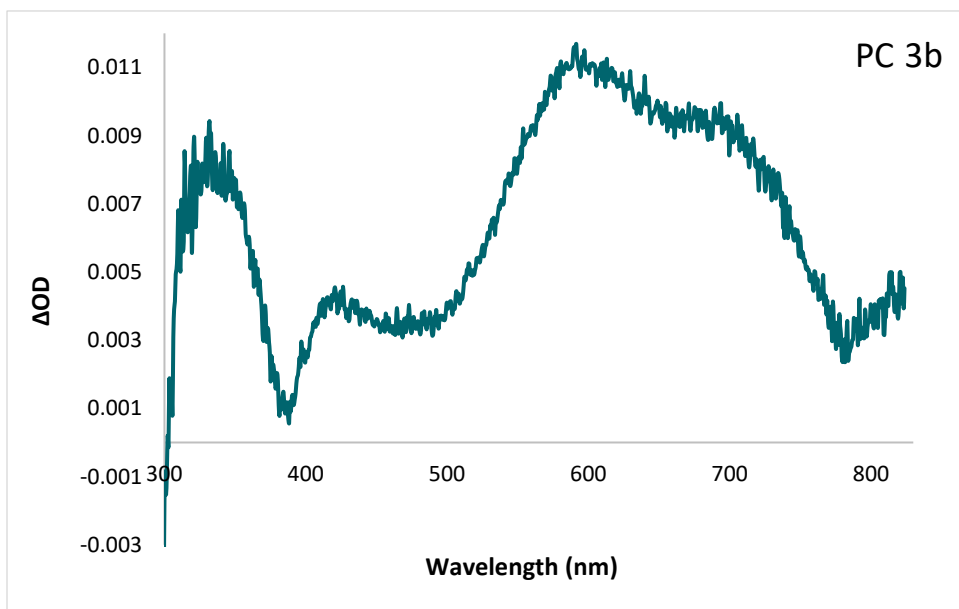


Figure A2.21. Spectral absorption of PC **3b** in DMAc at a 200 ns time delay, with no emission subtraction. The ESA feature visible at $\lambda = 593$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 593$ nm.

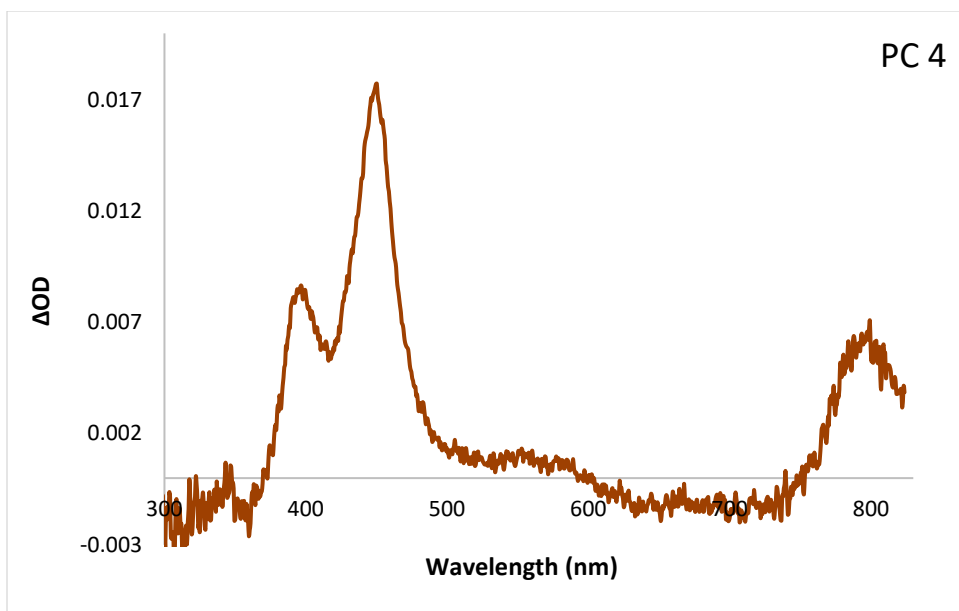


Figure A2.22. Spectral absorption of PC 4 in DMAc at a 400 ns time delay, with no emission subtraction. The ESA feature visible at $\lambda = 450$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 450$ nm.

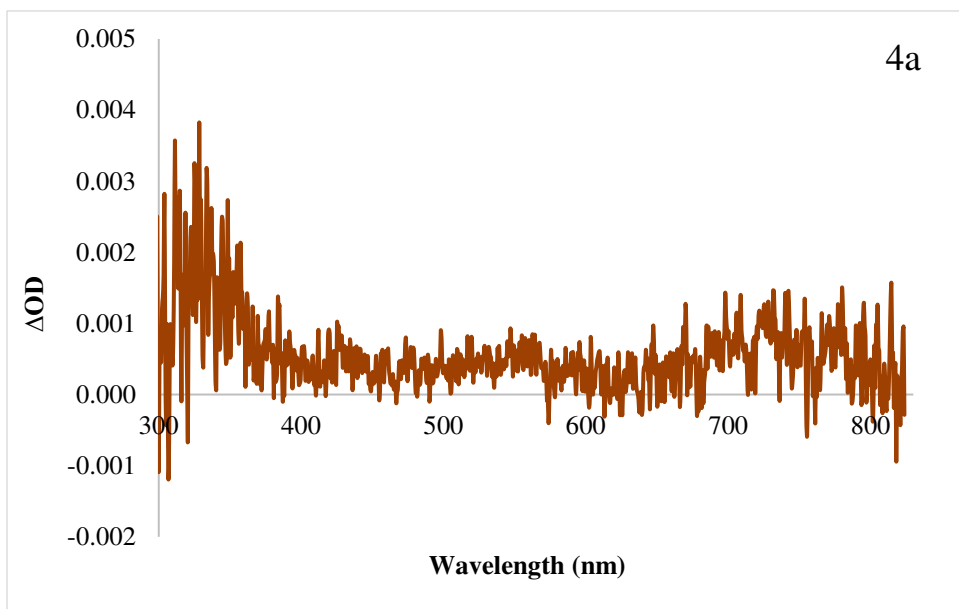


Figure A2.23. Spectral absorption of PC 4a in DMAc at a 200 ns time delay, with no emission subtraction. There are no distinguishable features that can be followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 450$ nm.

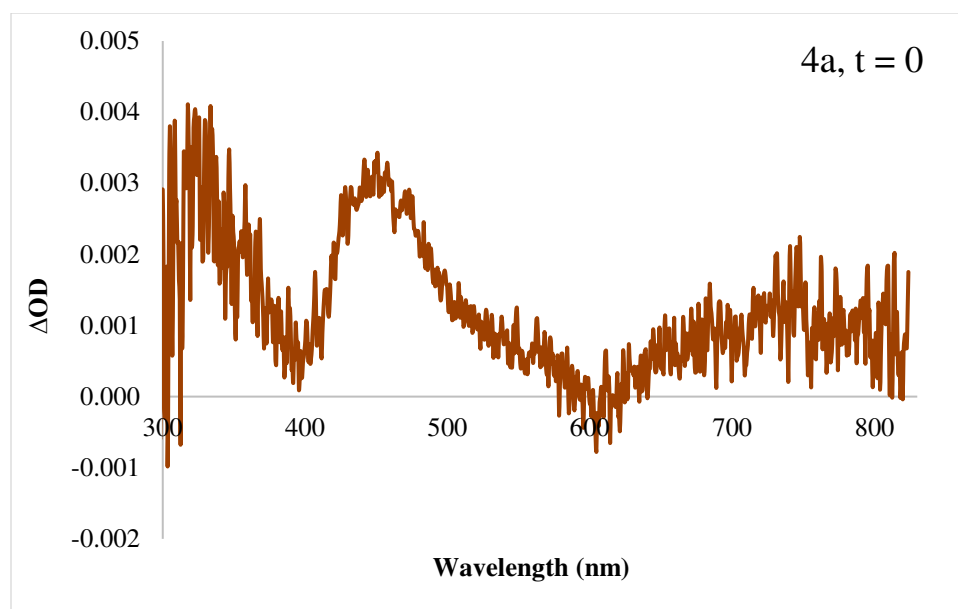


Figure A2.24. Spectral absorption of PC **4a** in DMAc with a 0 ns time delay and with emission subtraction. The ESA feature at $\lambda = 450$ nm was followed by kinetic absorption and fit with an exponential tail fit, resulting in determination of $\tau_{S1} = 14$ ns, in agreement with τ_{S1} determined by kinetic emission (13 ns). The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 450$ nm.

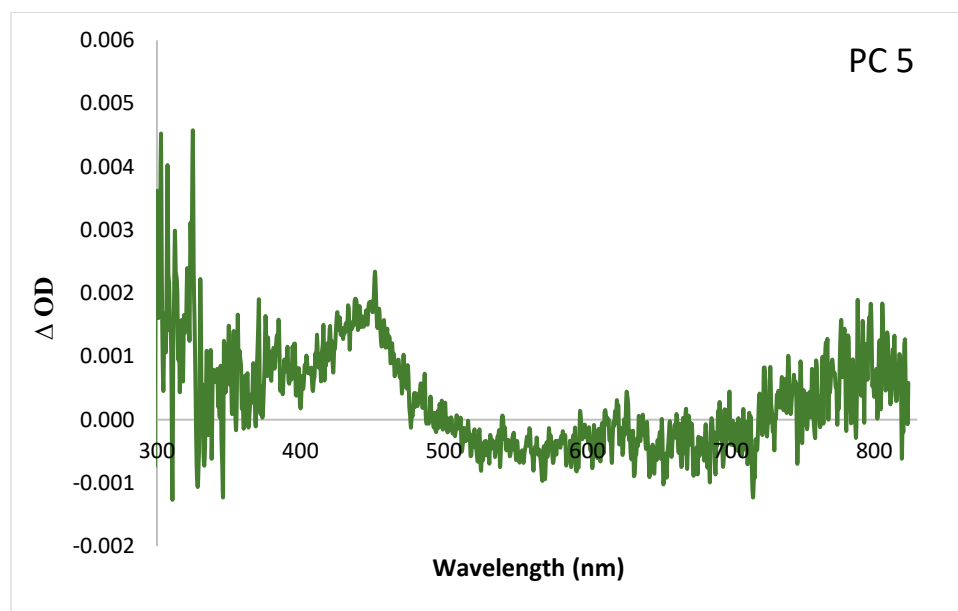


Figure A2.25. Spectral absorption of PC **5** in DMAc at a 200 ns time delay, with no emission subtraction. The ESA feature visible at $\lambda = 450$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 450$ nm.

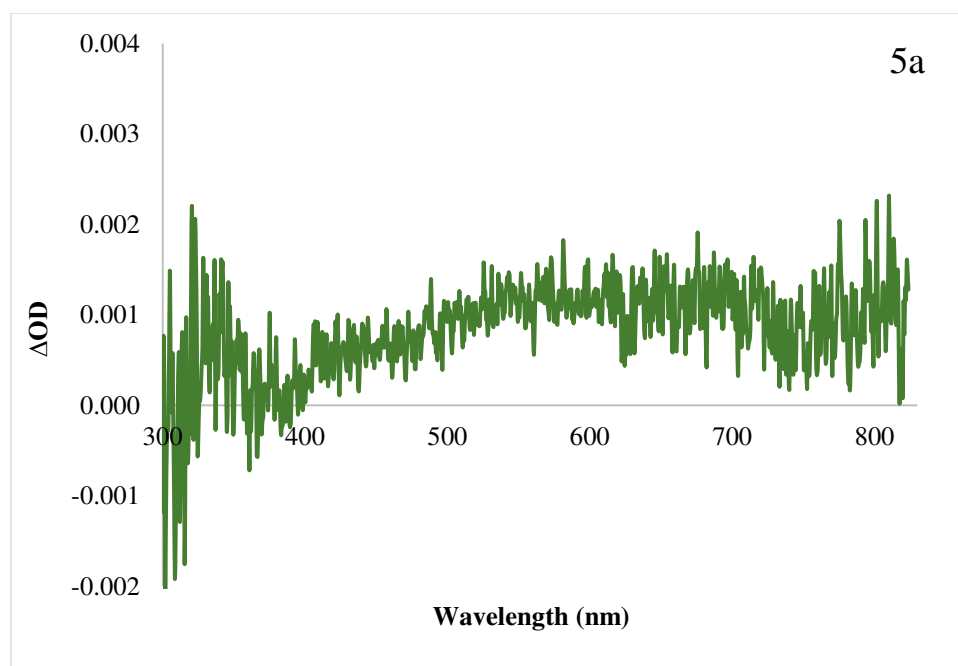


Figure A2.26. Spectral absorption of PC **5a** in DMAc at a 200 ns time delay, with no emission subtraction. There are no features that can be followed by kinetic absorption – the weak ESA at 570 nm was followed but no triplet single was detected. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 570$ nm.

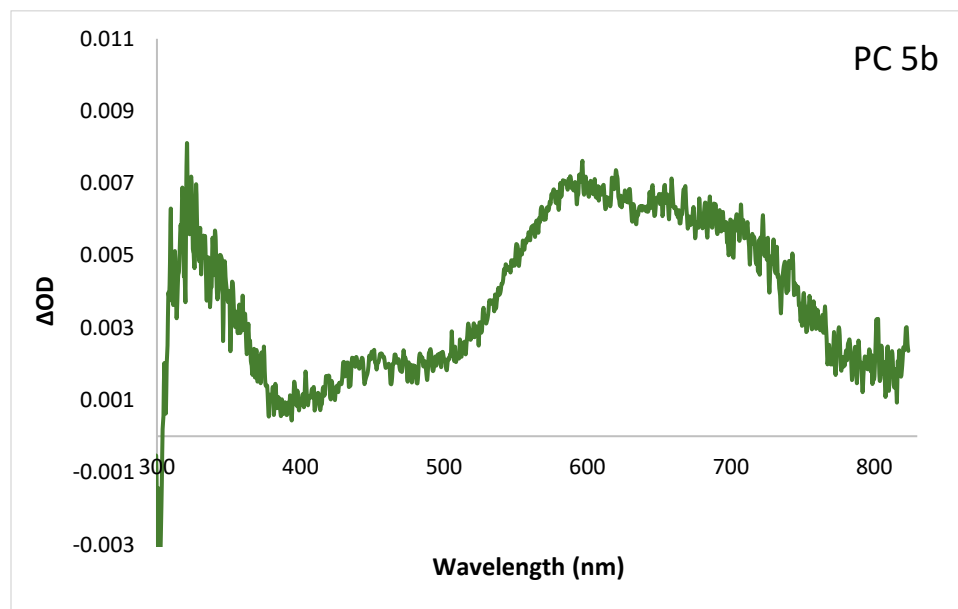


Figure A2.27. Spectral absorption of PC **5b** in DMAc at a 200 ns time delay, with no emission subtraction. The ESA feature visible at $\lambda = 550$ nm was followed by kinetic absorption. The spectral absorption data was offset corrected using kinetic data acquired at $\lambda = 550$ nm.

Kinetic Emission Data

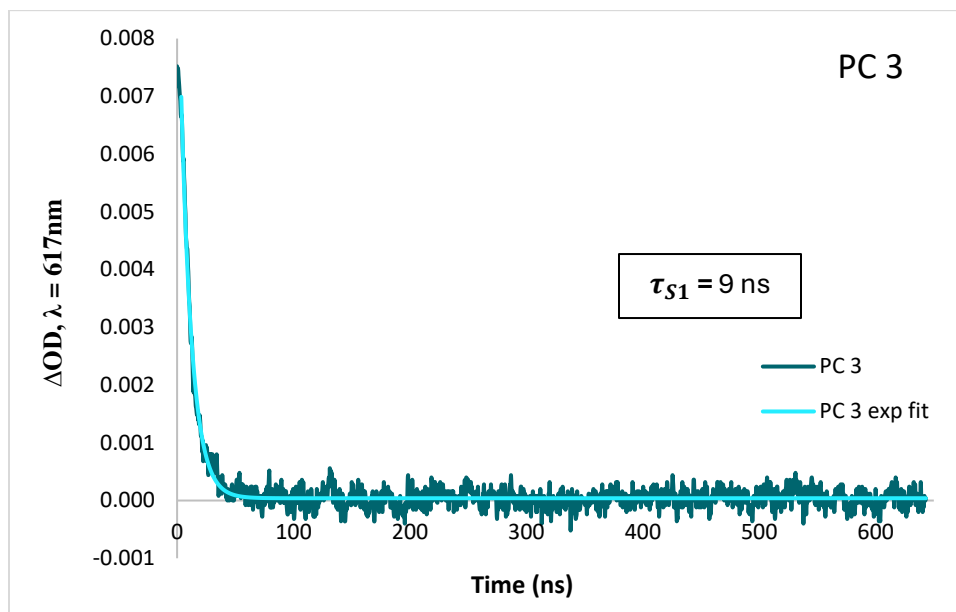


Figure A2.28. Kinetic emission trace for PC 3 in DMAc at 617 nm with an exponential tail fit for determination of τ_{S1} .

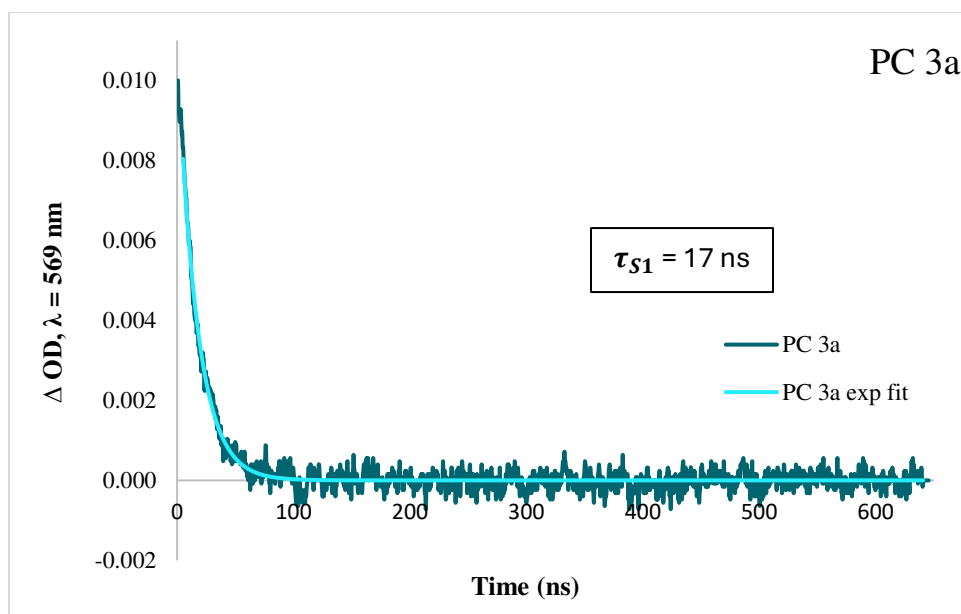


Figure A2.29. Kinetic emission trace for PC 3a in DMAc at 569 nm with an exponential tail fit for determination of τ_{S1} .

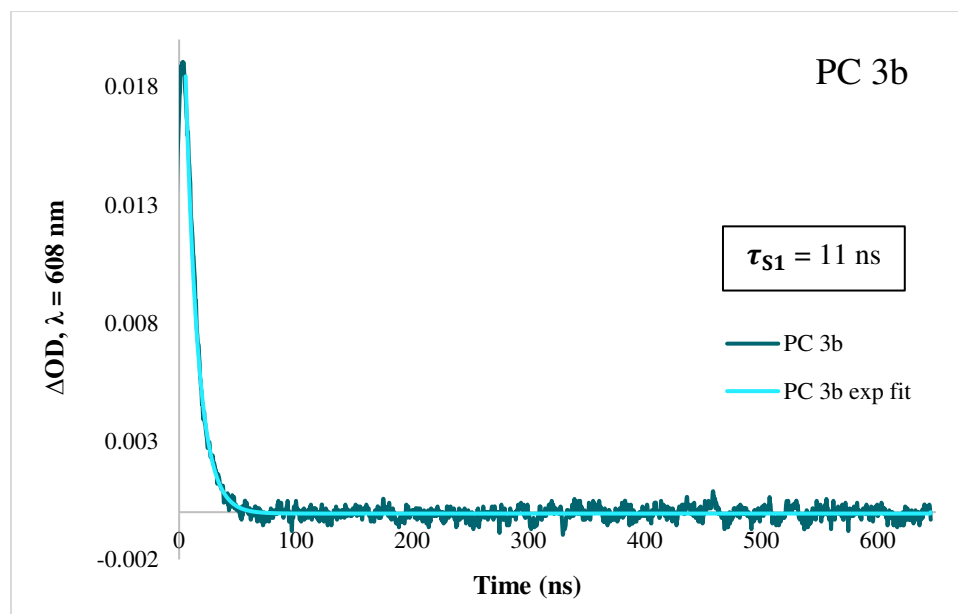


Figure A2.30. Kinetic emission trace for PC **3b** in DMAc at 608 nm with an exponential tail fit for determination of τ_{s1} . Kinetic emission was also measured at 462 nm, but τ_{s1} was found to be less than the 6 ns duration of the instrument laser pulse (below limit of detection).

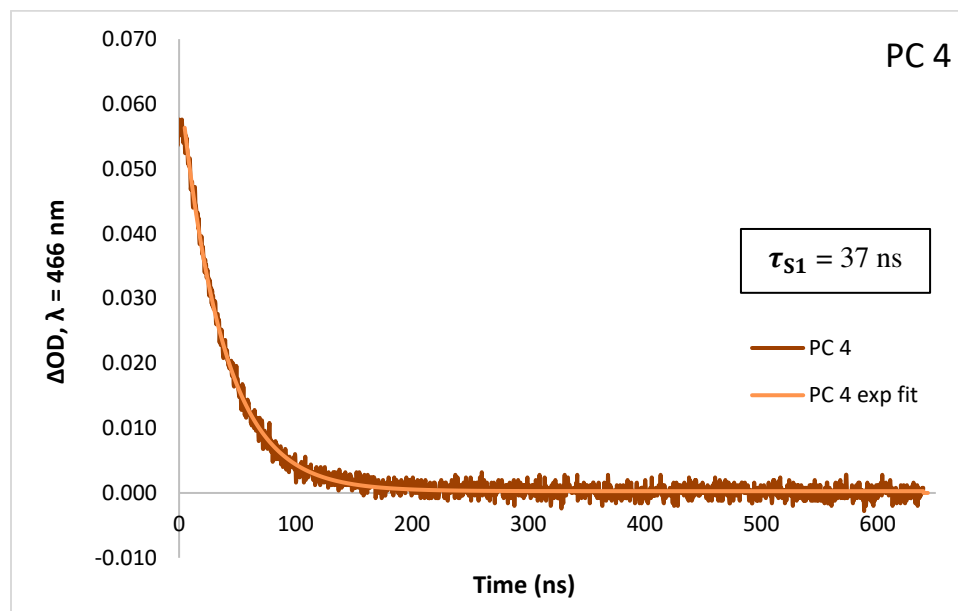


Figure A2.31. Kinetic emission trace for PC **4** in DMAc at 466 nm with an exponential tail fit for determination of τ_{s1} .

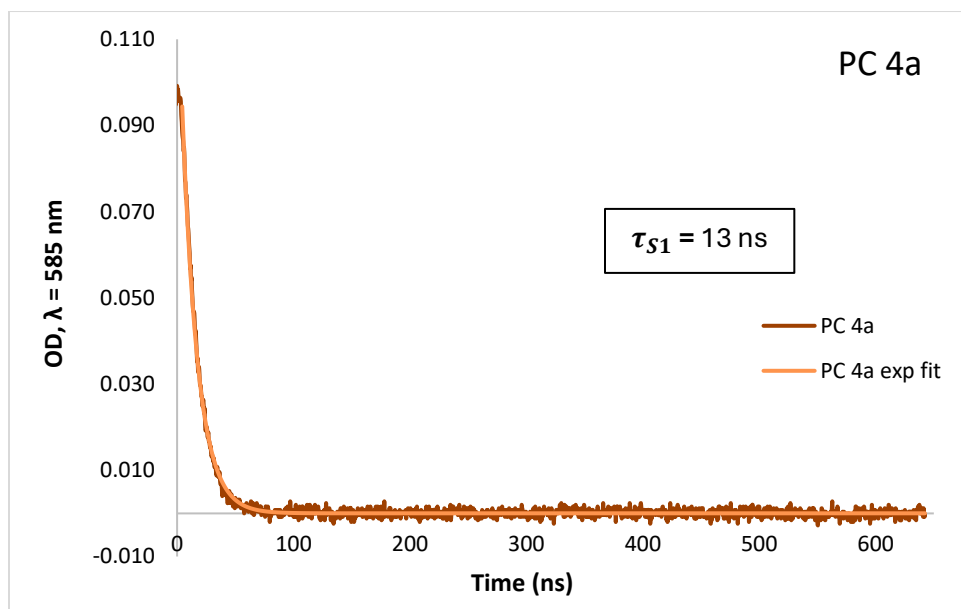


Figure A2.32. Kinetic emission trace for PC **4a** in DMAc at 585 nm with an exponential tail fit for determination of τ_{S1} .

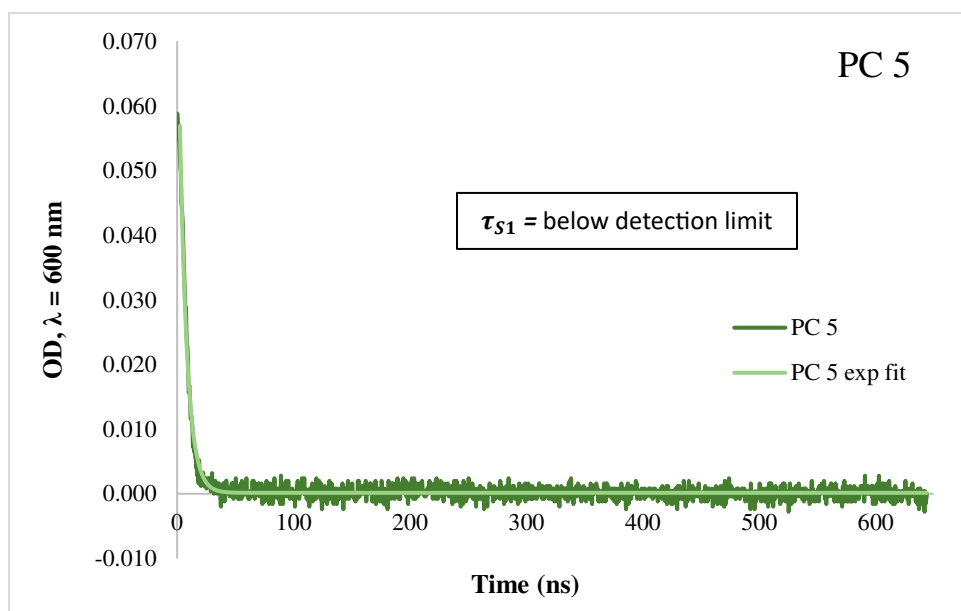


Figure A2.33. Kinetic emission trace for PC **5** in DMAc at 600 nm with an exponential tail fit for determination of τ_{S1} is shown above, however τ_{S1} was not reported because it was found to be less than the 6 ns duration of the instrument laser pulse (below limit of detection).

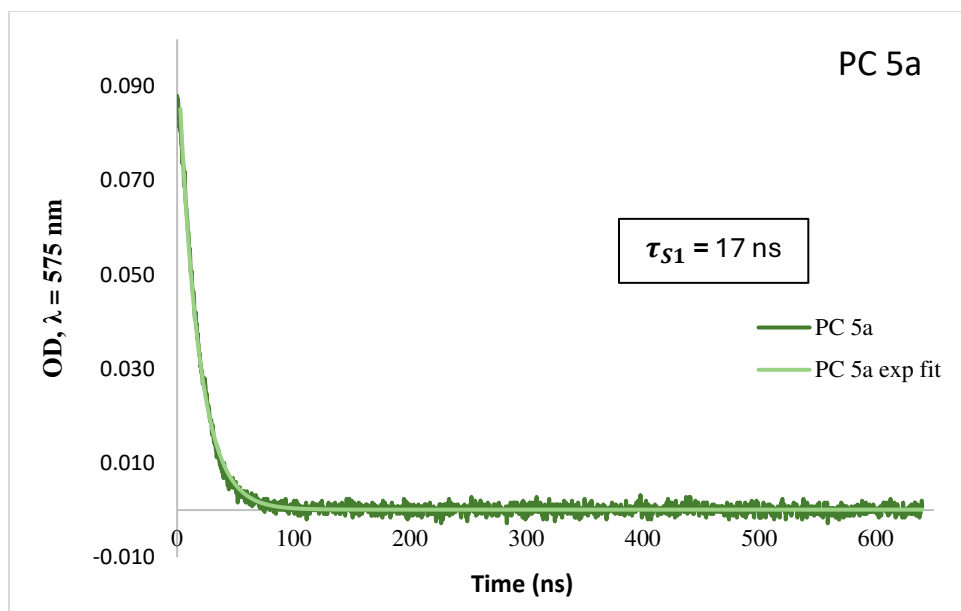


Figure A2.34. Kinetic emission trace for PC 5a in DMAc at 575 nm with an exponential tail fit for determination of τ_{S1} .

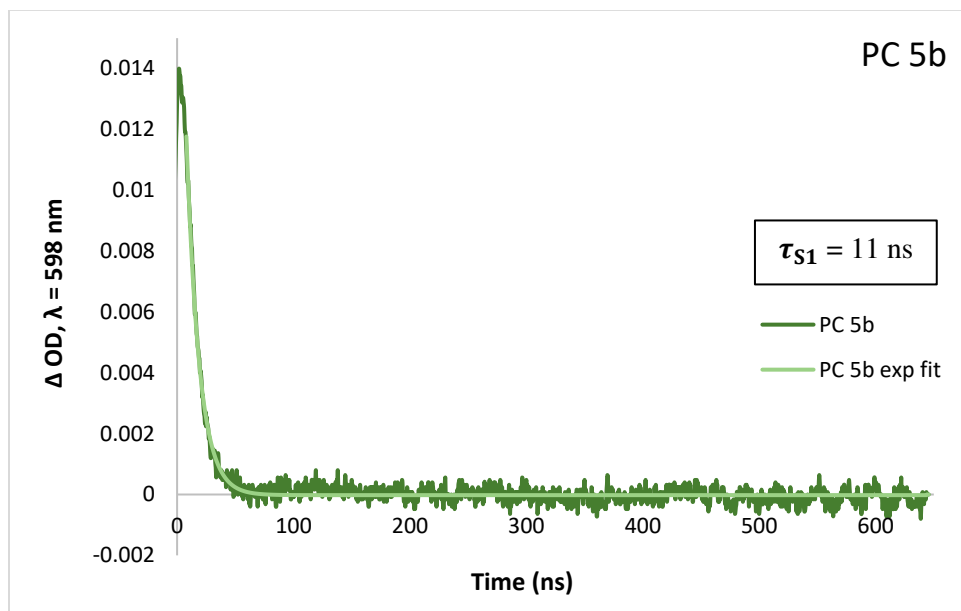


Figure A2.35. Kinetic emission trace for PC 5b in DMAc at 598 nm with an exponential tail fit for determination of τ_{S1} . Kinetic emission was also measured at 457 nm, but τ_{S1} was found to be less than the 6 ns duration of the instrument laser pulse (below limit of detection).

Kinetic Absorption Data

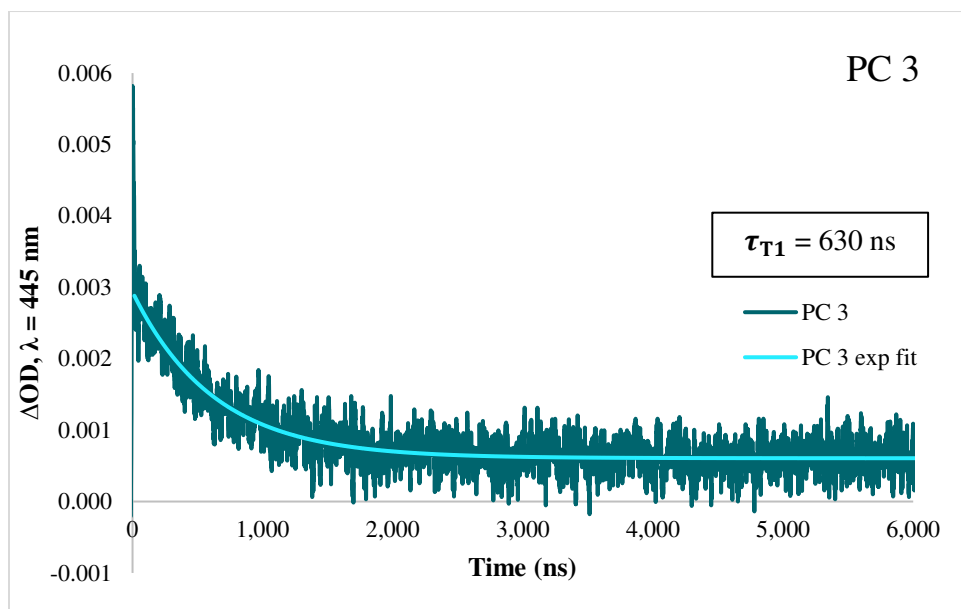


Figure A2.36. Kinetic absorption trace for PC 3 in DMAc at 445 nm with an exponential tail fit for determination of τ_{T1} .

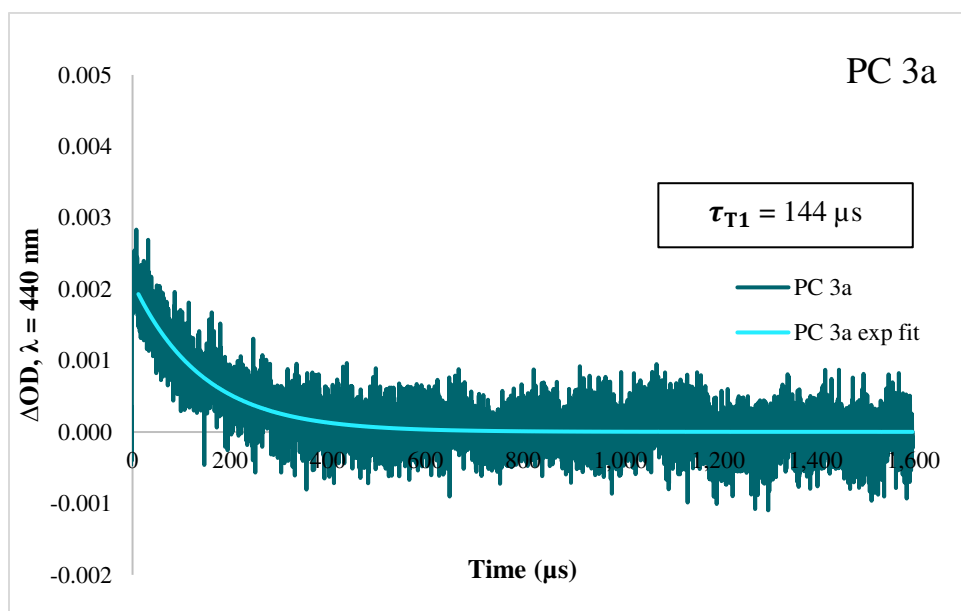


Figure A2.37. Kinetic absorption trace for PC 3a in DMAc at 440 nm with an exponential tail fit for determination of τ_{T1} .

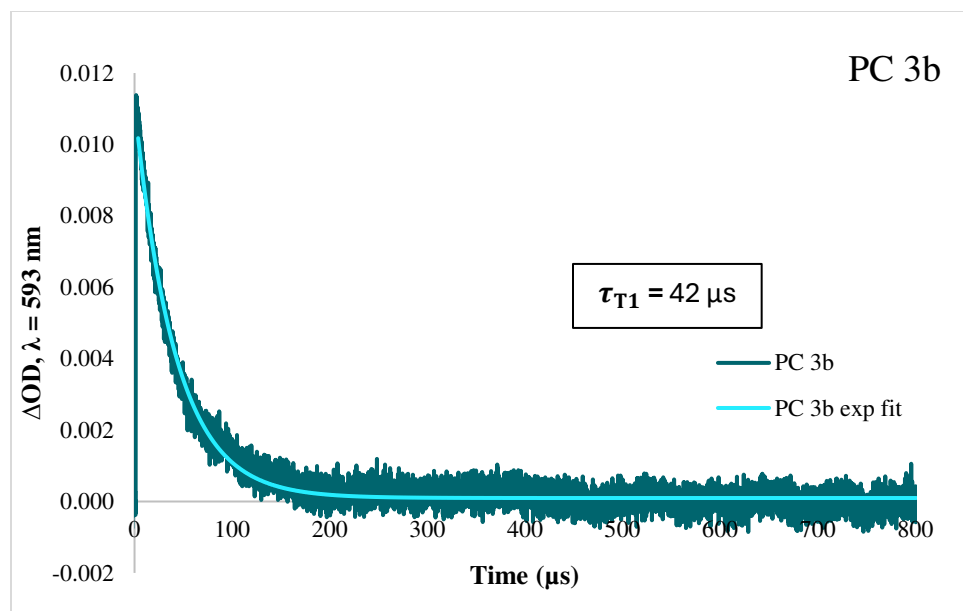


Figure A2.38. Kinetic absorption trace for PC **3b** in DMAc at 593 nm with an exponential tail fit for determination of τ_{T1} .

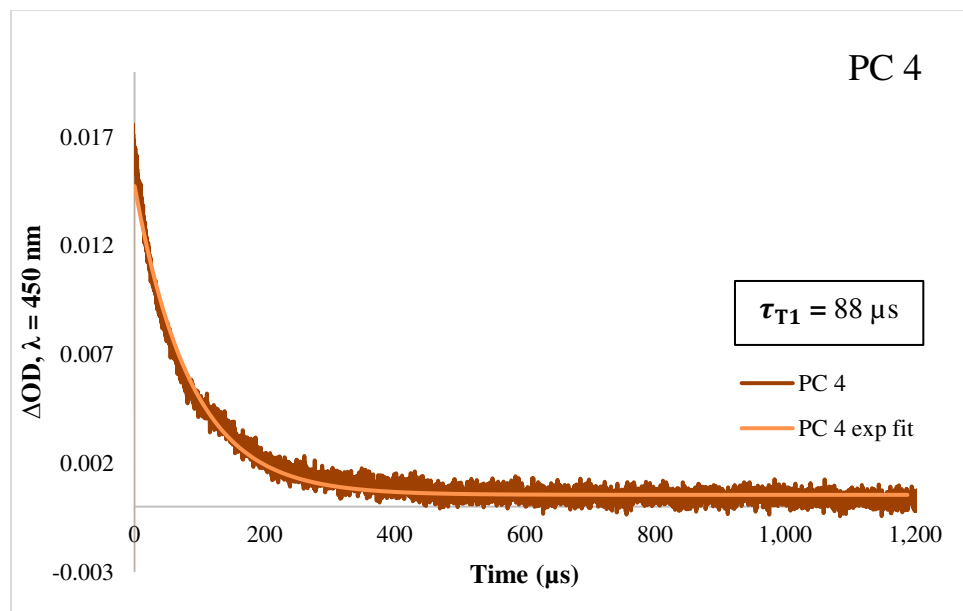


Figure A2.39. Kinetic absorption trace for PC **4** in DMAc at 450 nm with an exponential tail fit for determination of τ_{T1} .

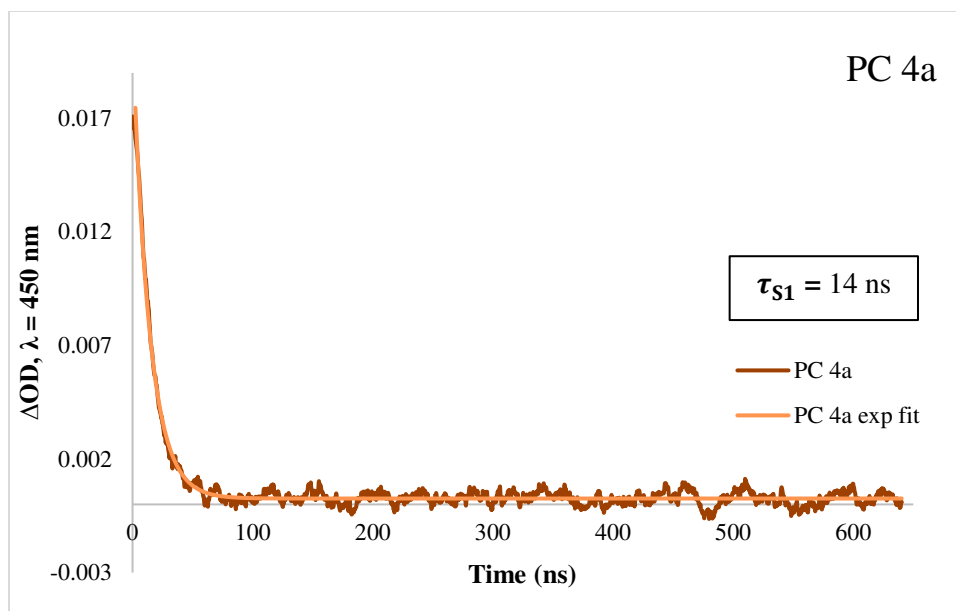


Figure A2.40. Kinetic absorption trace for PC **4a** in DMAc at 450 nm with an exponential tail fit for determination of τ_{S1} . By kinetic absorption $\tau_{S1} = 14 \text{ ns}$, in good agreement with τ_{S1} determined by kinetic emission ($\tau_{S1} = 13 \text{ ns}$).

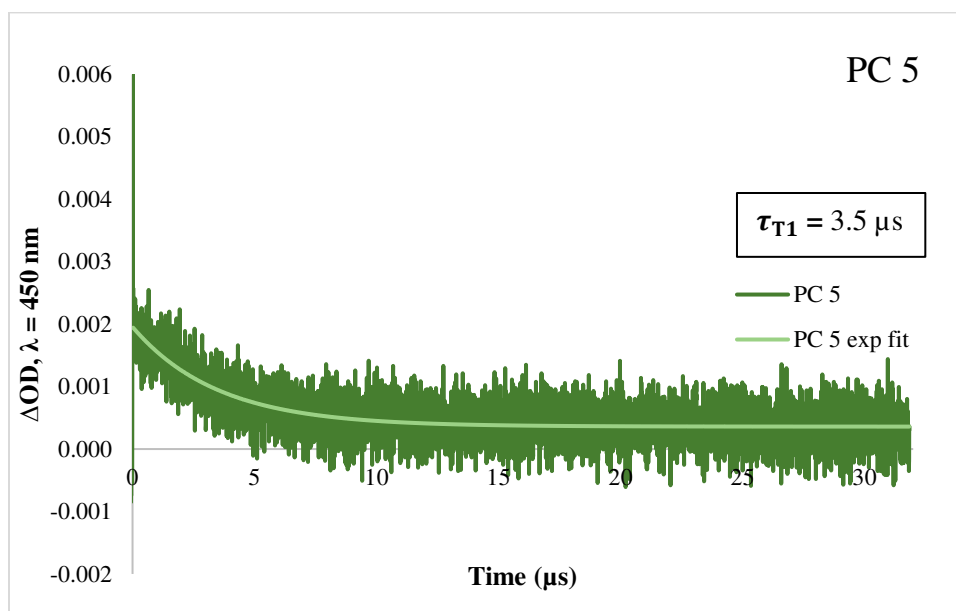


Figure A2.41. Kinetic absorption trace for PC **5** in DMAc at 450 nm with an exponential tail fit for determination of τ_{T1} .

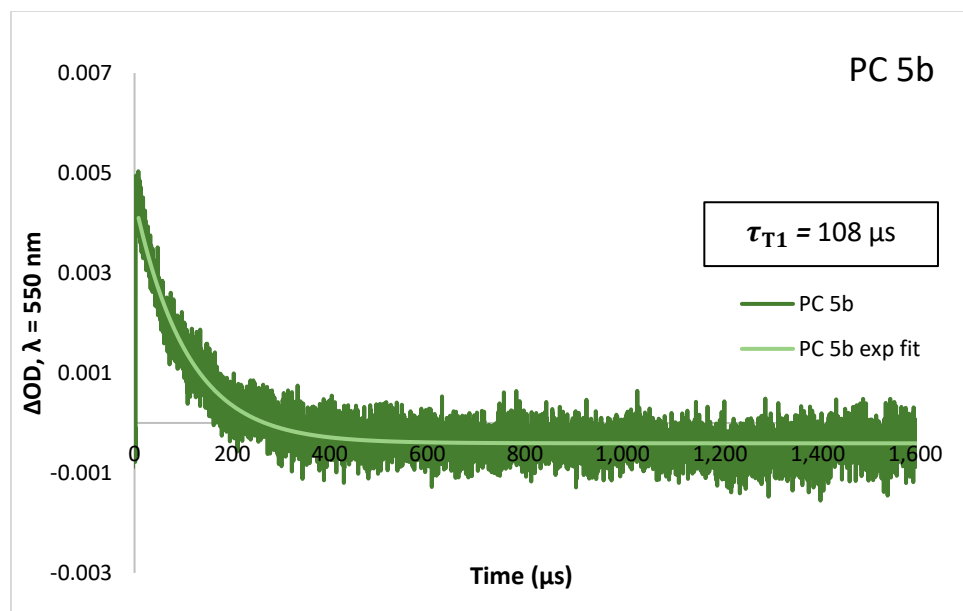


Figure A2.42. Kinetic absorption trace for PC **5b** in DMAc at 550 nm with an exponential tail fit for determination of τ_{T1} .

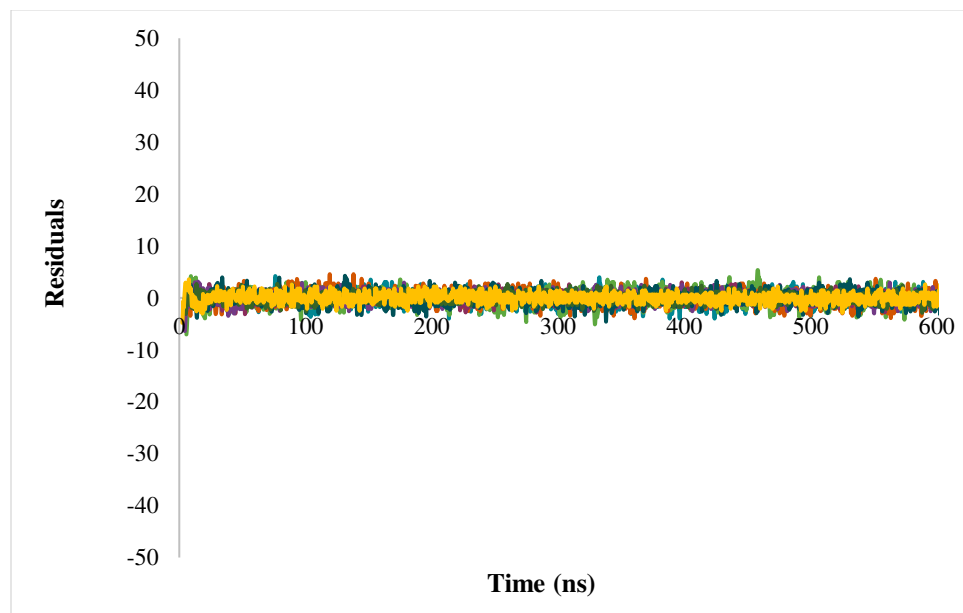


Figure A2.43. Overlaid residuals for exponential tail fits of the kinetic emission traces included in this work.

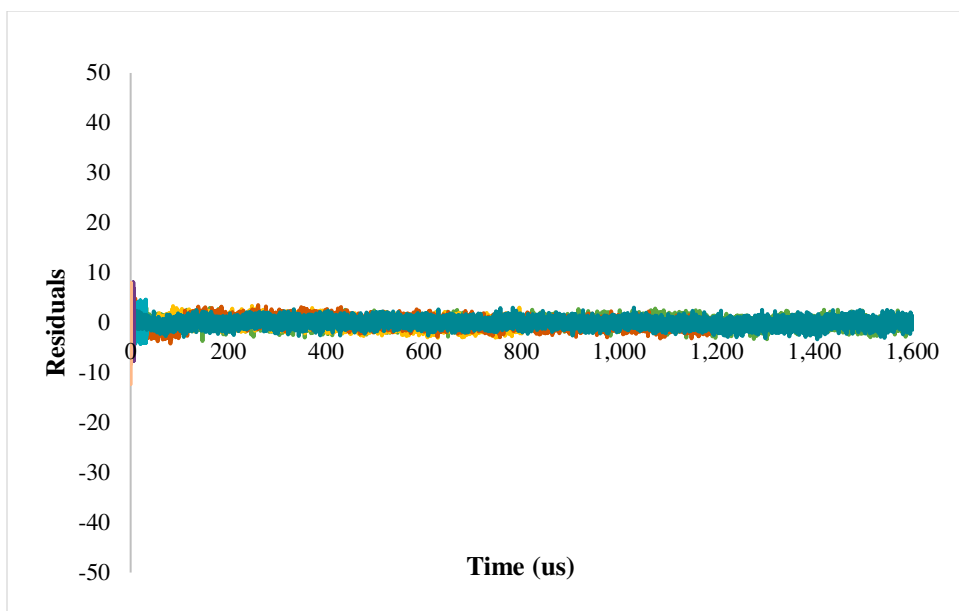


Figure A2.44. Overlaid residuals for exponential tail fits of the kinetic absorption traces included in this work.

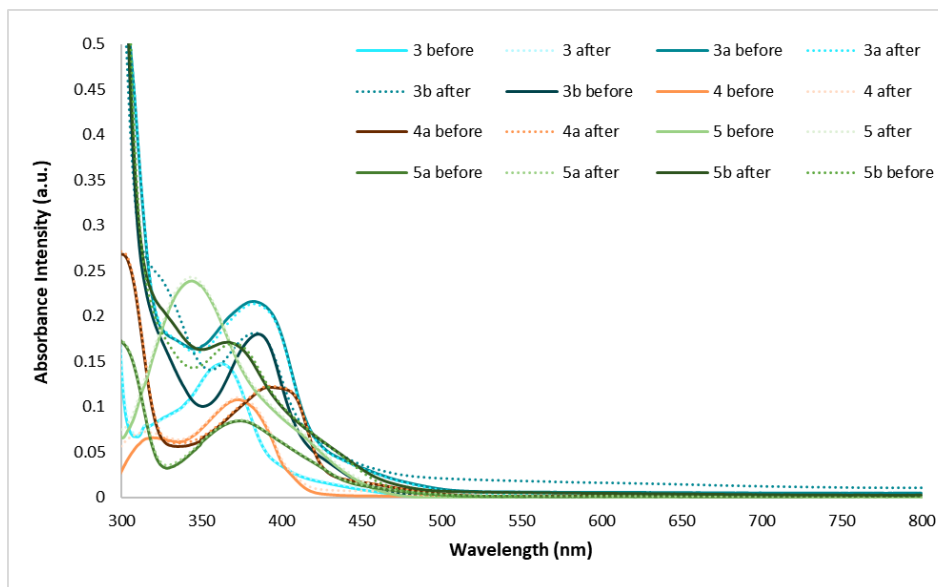


Figure A2.45. Overlaid UV-vis spectra of PC solutions used for TA spectroscopy, taken before and after TA spectroscopy was performed to monitor if PC degradation occurred. The PC solutions analyzed in this work did not show evidence of degradation after TA, indicated by no significant observable change in the UV-vis spectra before and after TA spectroscopy was performed.

Solvatochromism

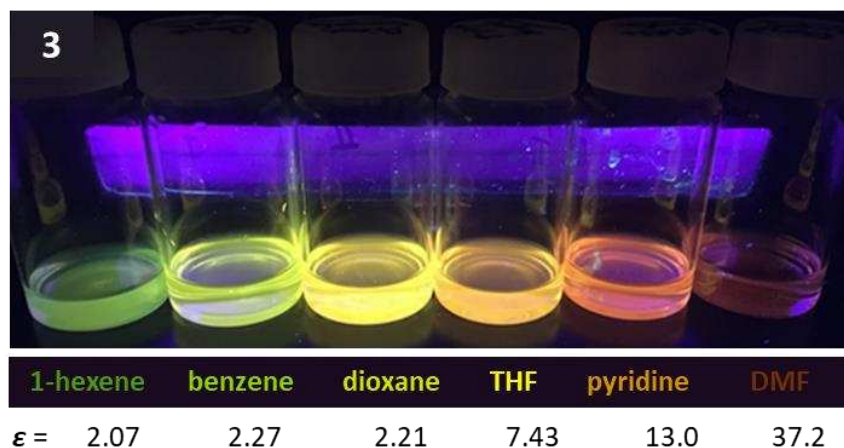


Figure A2.46. Previously reported photograph of PC **3** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light. (*J. Am. Chem. Soc.* **2017**, *139*, 348–355)

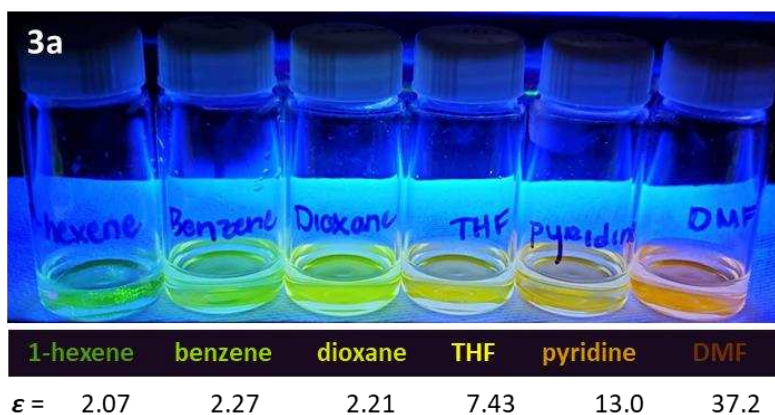


Figure A2.47. Photograph of PC **3a** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

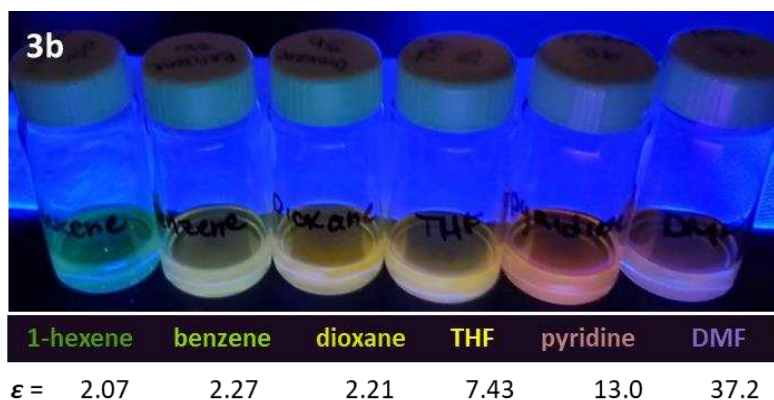


Figure A2.48. Photograph of PC **3b** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

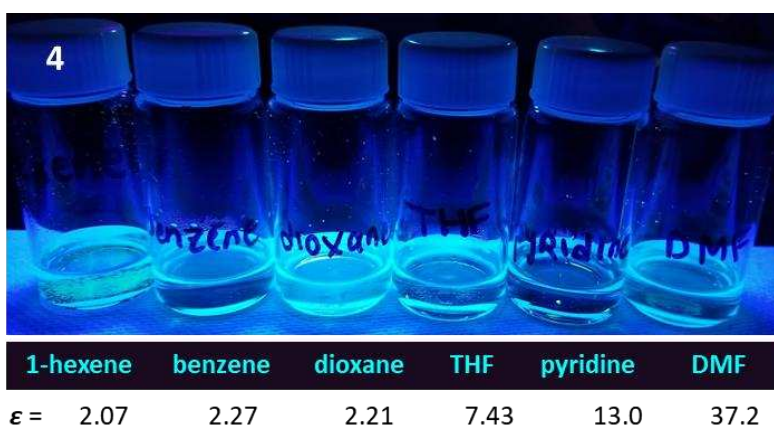


Figure A2.49. Photograph of PC **4** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

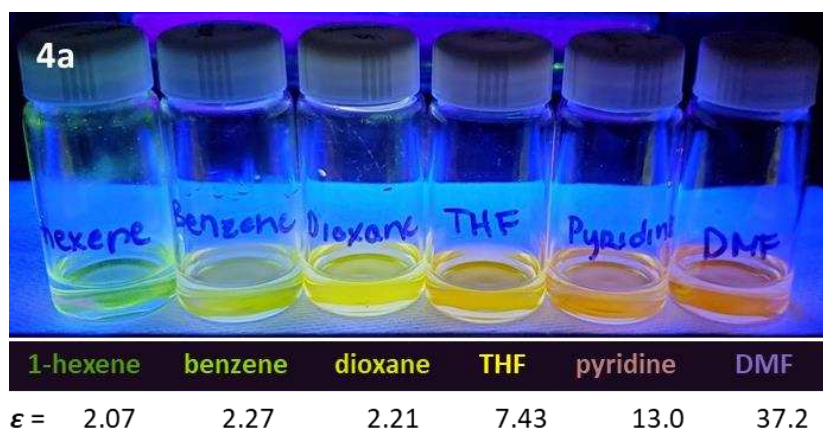


Figure A2.50. Photograph of PC **4a** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

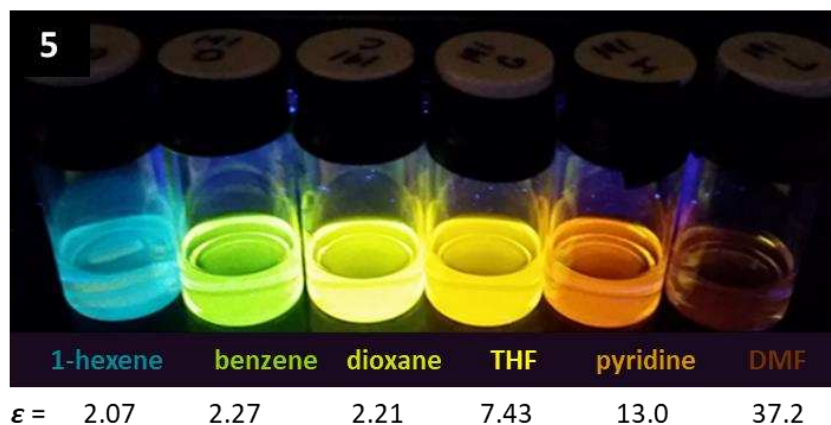


Figure A2.51. Previously reported Photograph of PC **5** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light. (*J. Am. Chem. Soc.* **2017**, *139*, 348–355).

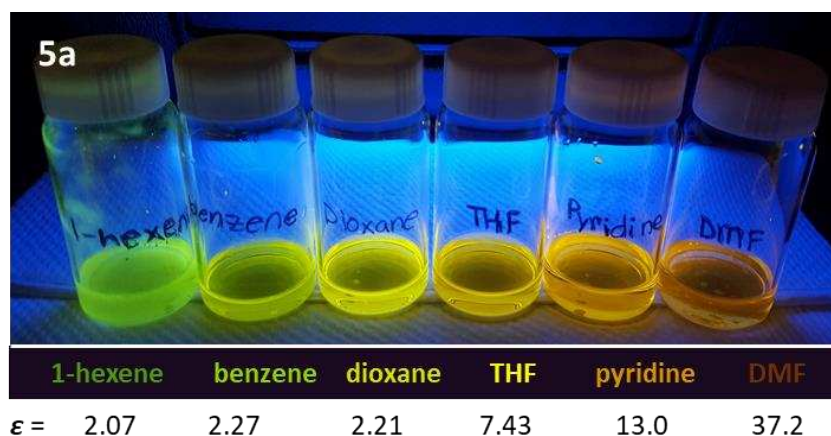


Figure A2.52. Photograph of PC **5a** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

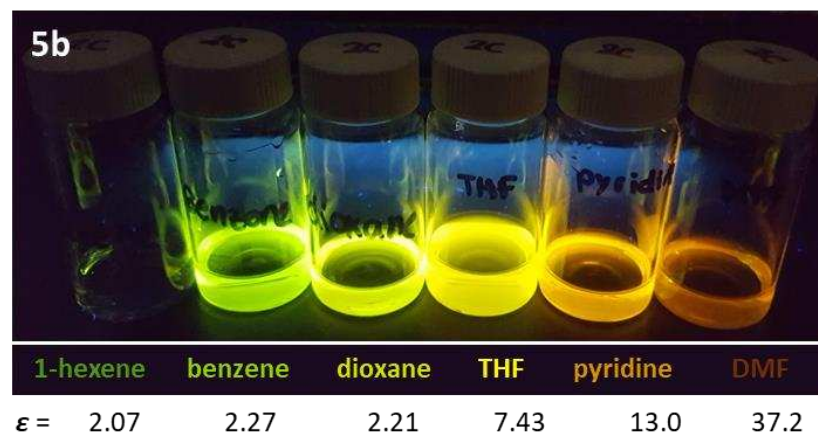


Figure A2.53. Photograph of PC **5b** dissolved in solvents of increasing polarity (from left to right) while under irradiation with 365 nm light.

Cyclic Voltammetry

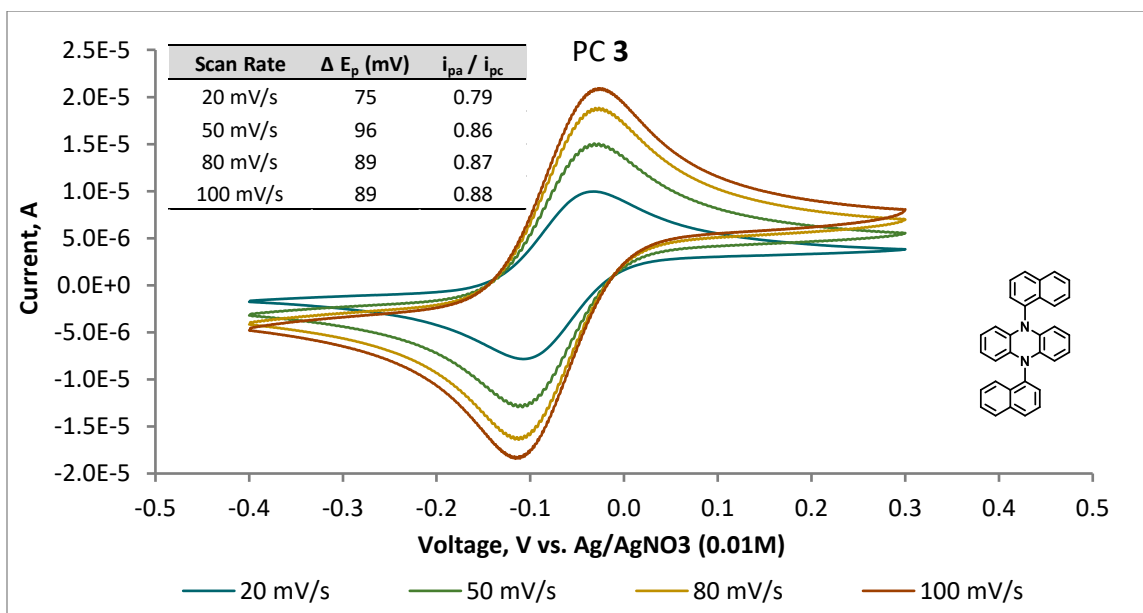


Figure A2.54. Cyclic voltammogram of PC 3 in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

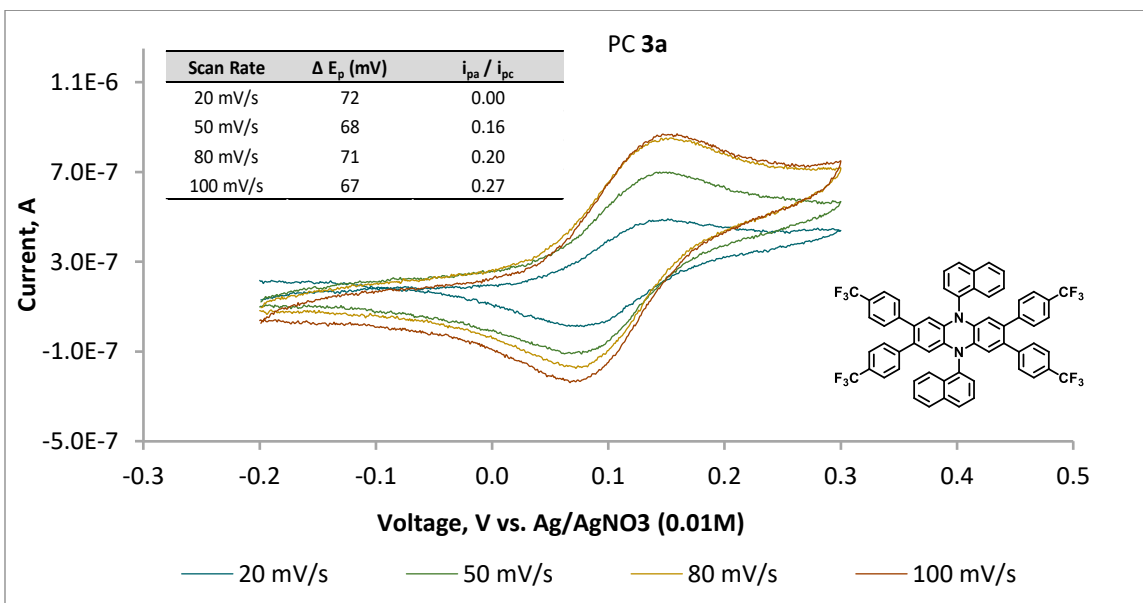


Figure A2.55. Cyclic voltammogram of PC 3a in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

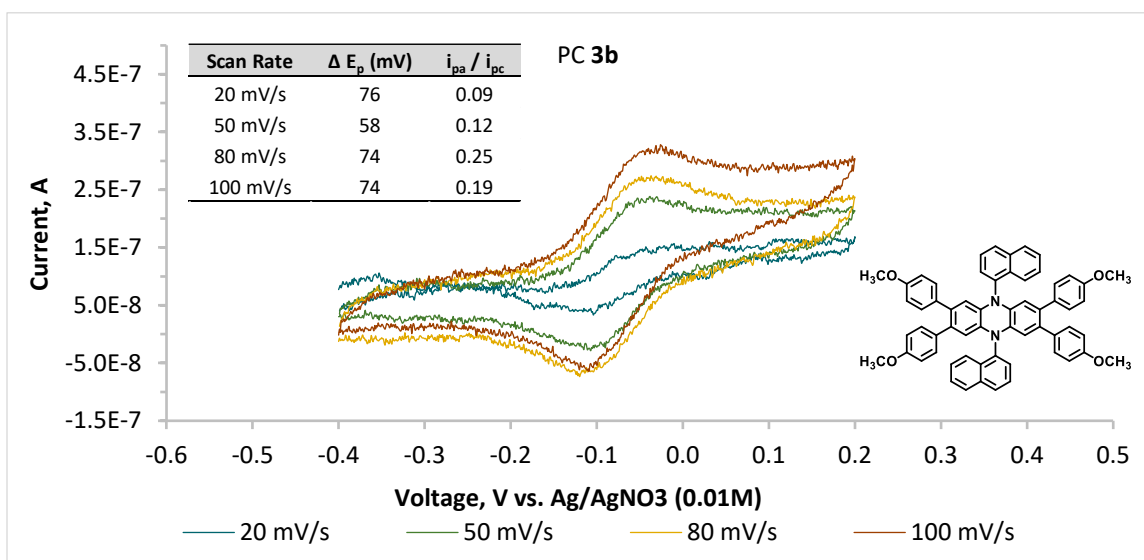


Figure A2.56. Cyclic voltammogram of PC 3b in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

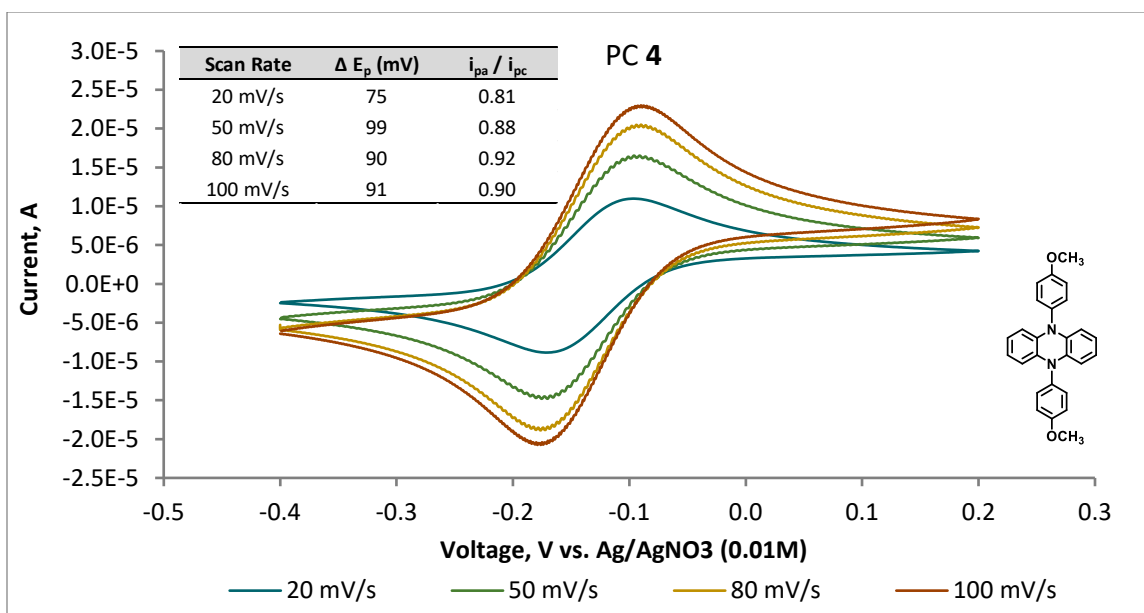


Figure A2.57. Cyclic voltammogram of PC 4 in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

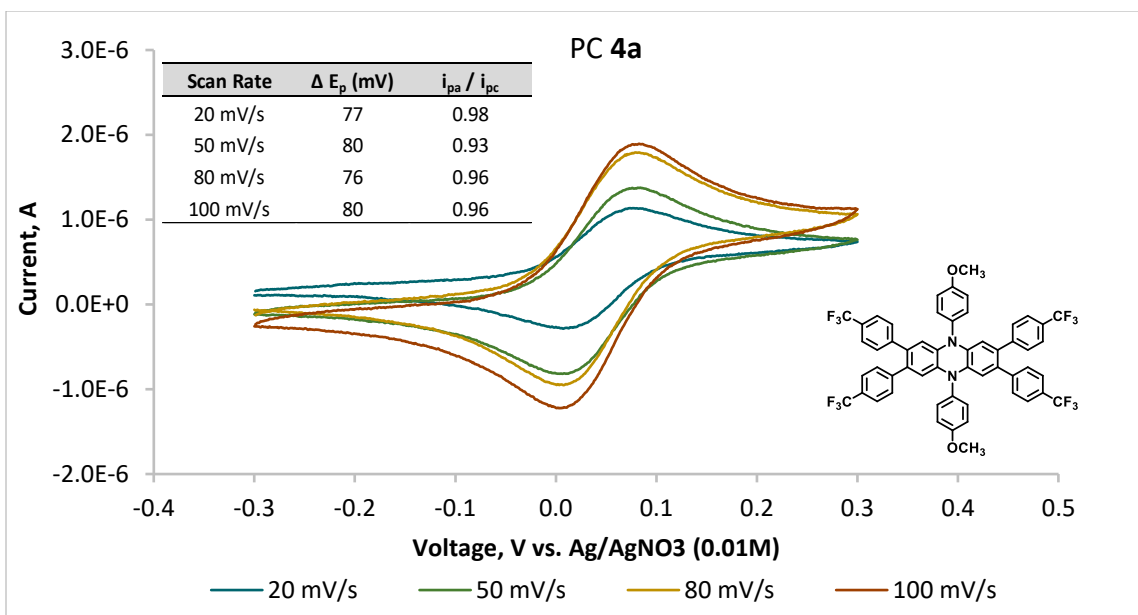


Figure A2.58. Cyclic voltammogram of PC 4a in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

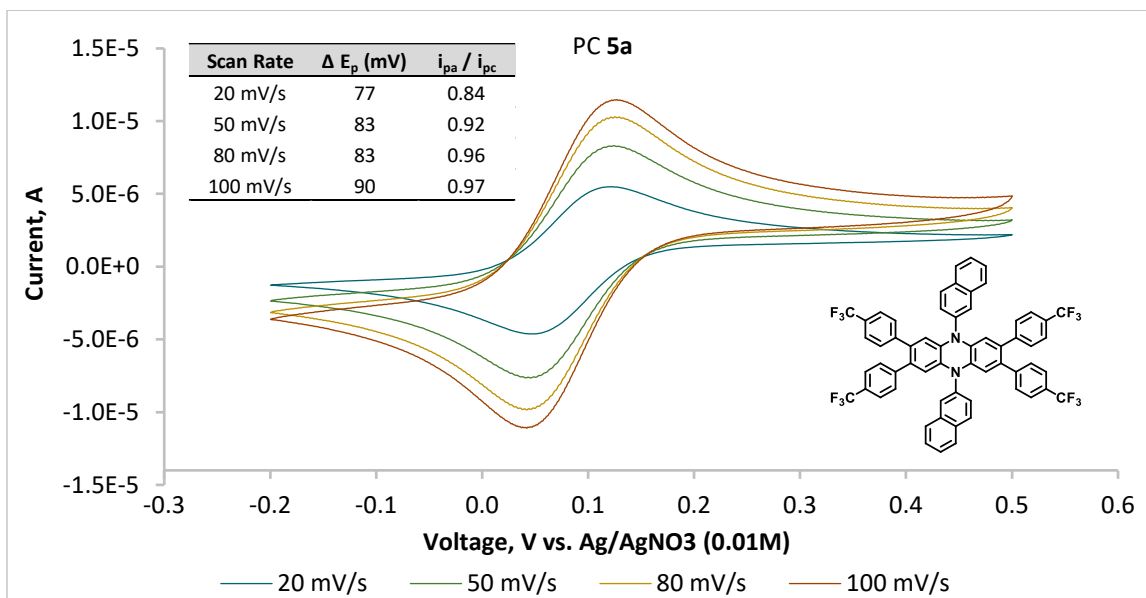


Figure A2.59. Cyclic voltammogram of PC 5a in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

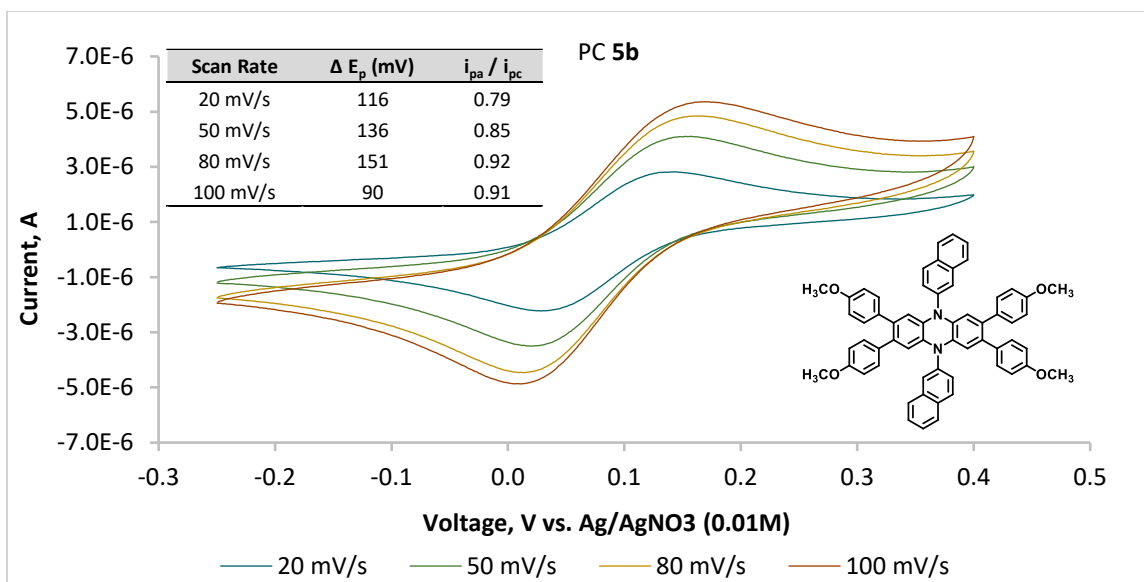


Figure A2.60. Cyclic voltammogram of PC 5b in DMAc at 20 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s scan rates. Inserted into the graph is a chart showing the ratios of peak anodic current to peak cathodic current (i_{pa}/i_{pc}) and the difference between peak anodic and peak cathodic current (ΔE_p) at each scan rate.

COMPUTATIONAL MODELING OF PCs

Excited State Calculations (TD-DFT)

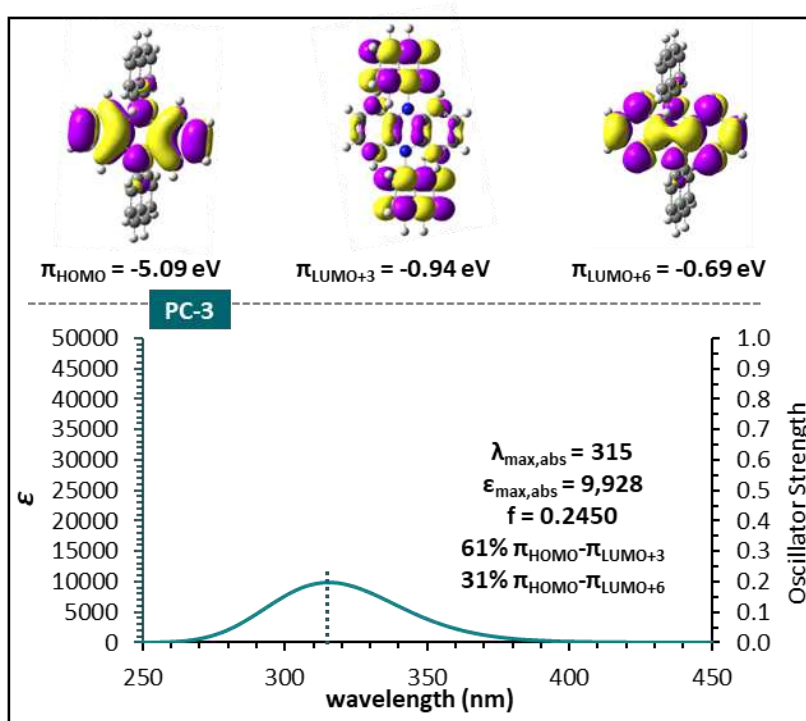


Figure A2.61. Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **3** detailed below (top). Computationally predicted UV–vis spectrum of PCs **3** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

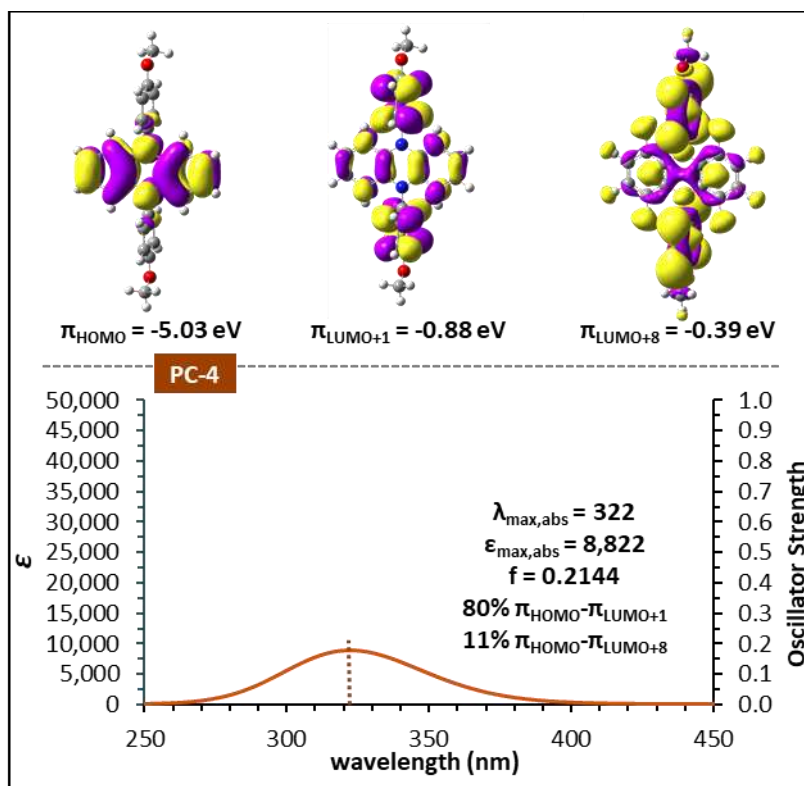


Figure A2.62: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC 4 detailed below (top). Computationally predicted UV-vis spectrum of PCs 4 along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{ cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

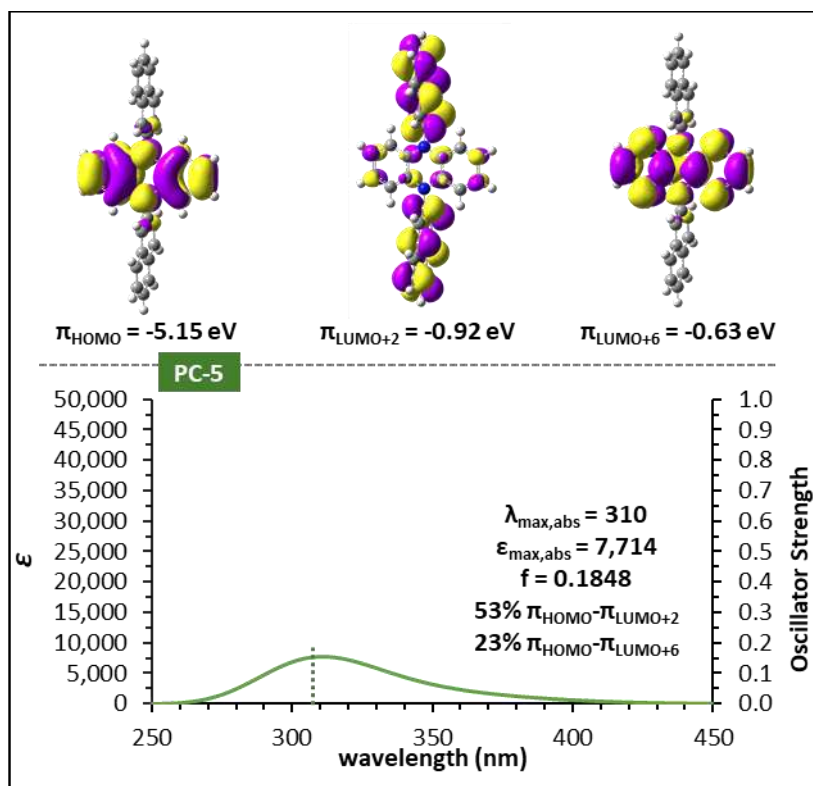


Figure A2.63: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **5** detailed below (top). Computationally predicted UV-vis spectrum of PCs **5** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{ cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

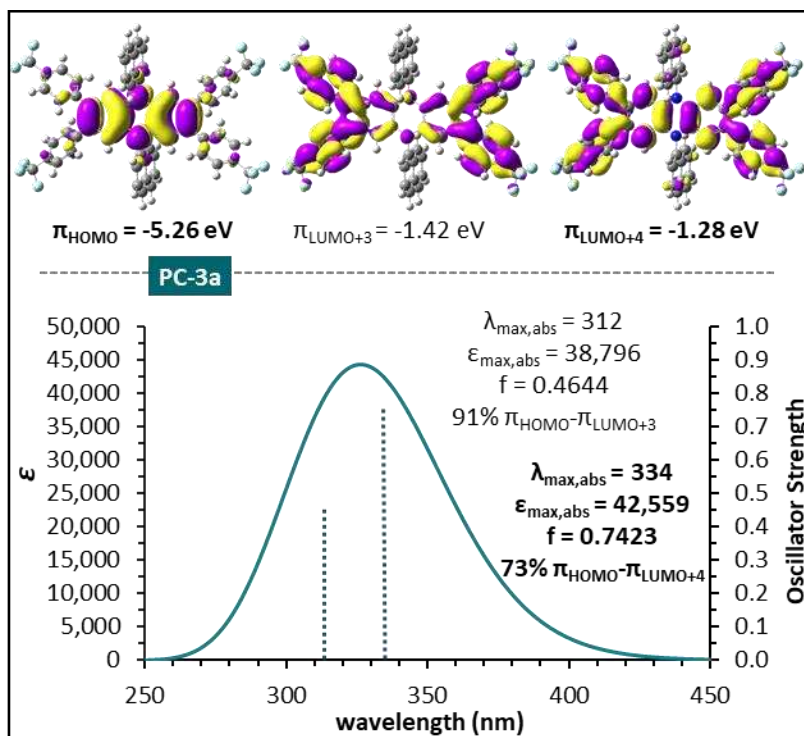


Figure A2.64: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **3a** detailed below (top). Computationally predicted UV-vis spectrum of PCs **3a** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

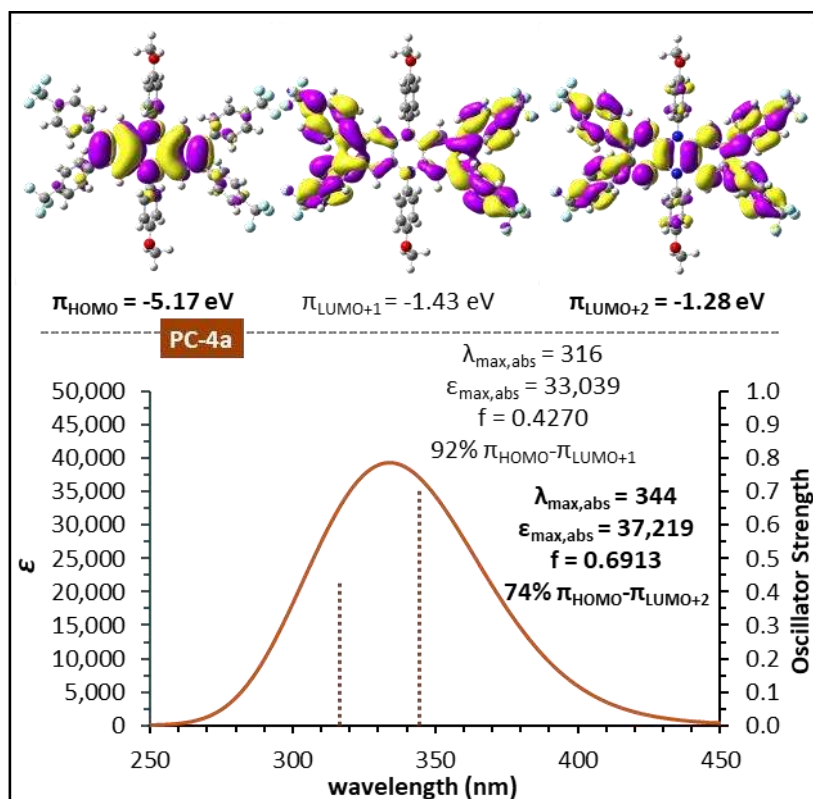


Figure A2.65: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **4a** detailed below (top). Computationally predicted UV–vis spectrum of PCs **4a** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

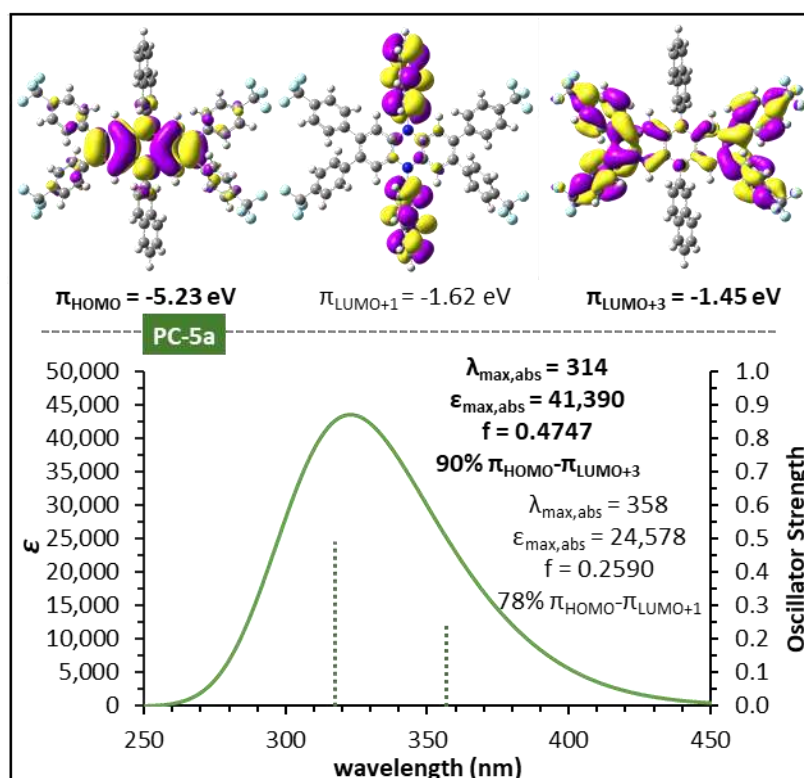


Figure A2.66: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **5a** detailed below (top). Computationally predicted UV–vis spectrum of PCs **5a** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

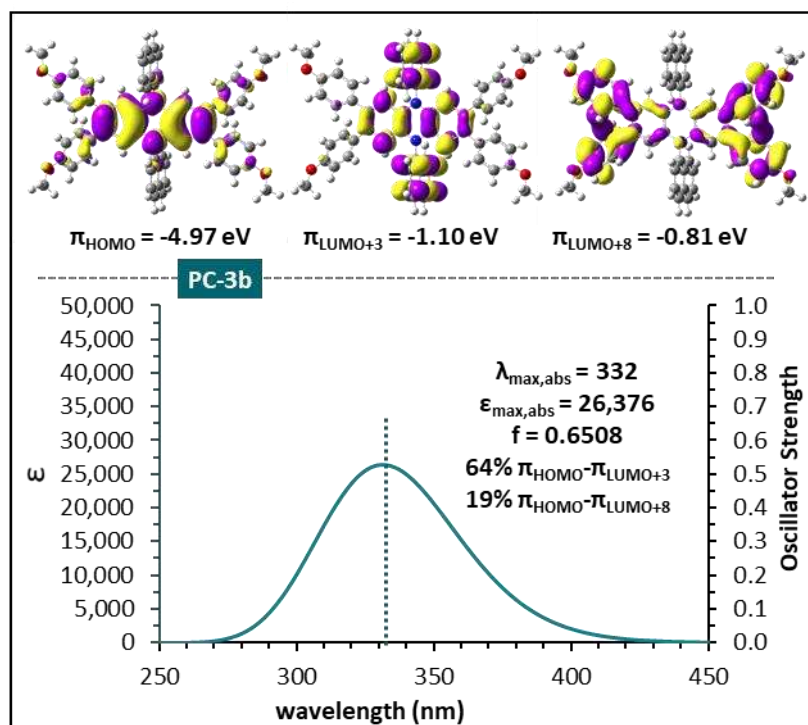


Figure A2.67: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **3b** detailed below (top). Computationally predicted UV–vis spectrum of PCs **3b** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

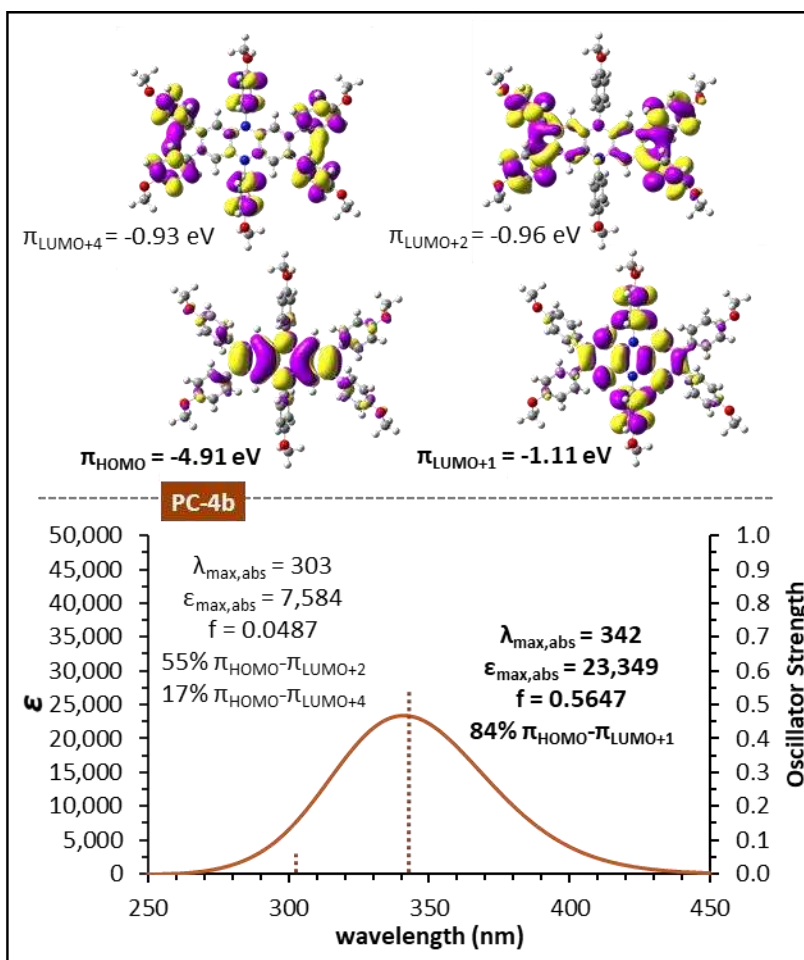


Figure A2.68: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **4b** detailed below (top). Computationally predicted UV–vis spectrum of PCs **4b** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

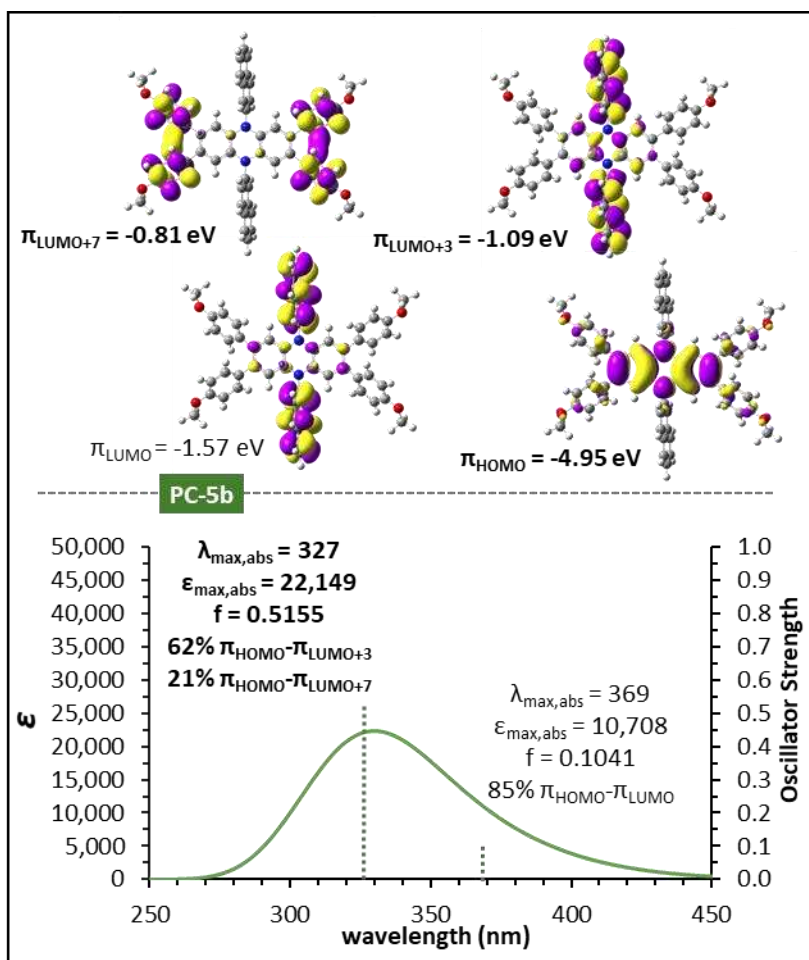


Figure A2.69: Computationally modeled molecular orbitals predicted to be involved in absorption transitions for PC **5b** detailed below (top). Computationally predicted UV–vis spectrum of PCs **5b** along with theoretically assigned percentage contributions (>15%) of various orbitals to the predicted absorption peaks. $\lambda_{\text{max,abs}}$ is the predicted absorption maximum wavelength and is reported in units of nm, $\epsilon_{\text{max,abs}}$ is the predicted molar extinction coefficient at the predicted $\lambda_{\text{max,abs}}$ and is reported in units of $\text{M}^{-1} \text{cm}^{-1}$, and f is the predicted oscillator strength; all of these values were predicted at the TD-DFT CAM-B3LYP/6-31+G(d,p)/CPCM-DMA level of theory (bottom).

Computationally Modeled Singly Occupied Molecular Orbitals (SOMOs) of PCs

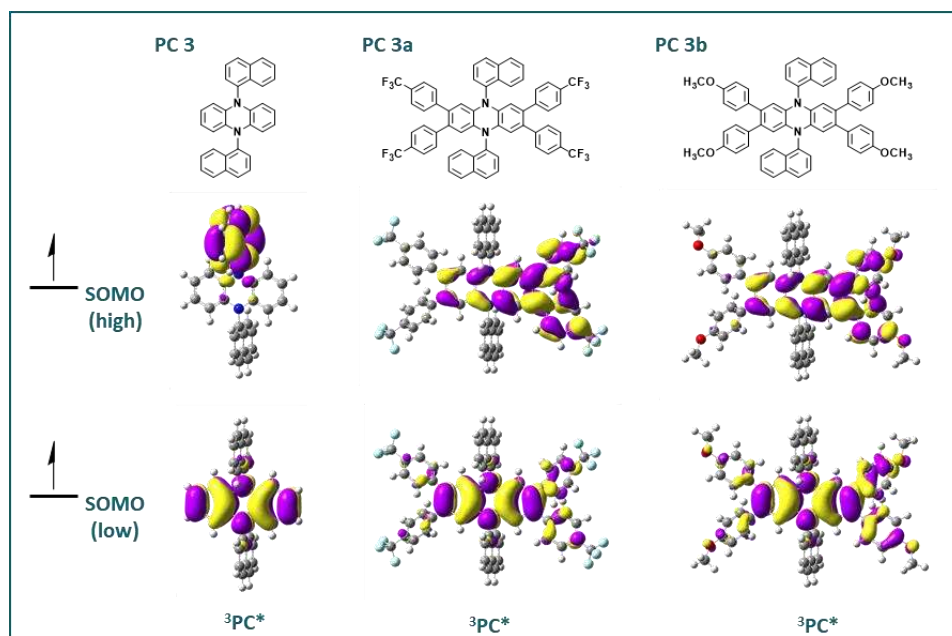


Figure A2.70. Computational modeling of the singularly occupied molecular orbitals (SOMOs) for PCs **3**, **3a**, and **3b** (from left to right); the lower lying SOMO (bottom row) and higher lying SOMO (top row) for each PC in the triplet excited state are shown.

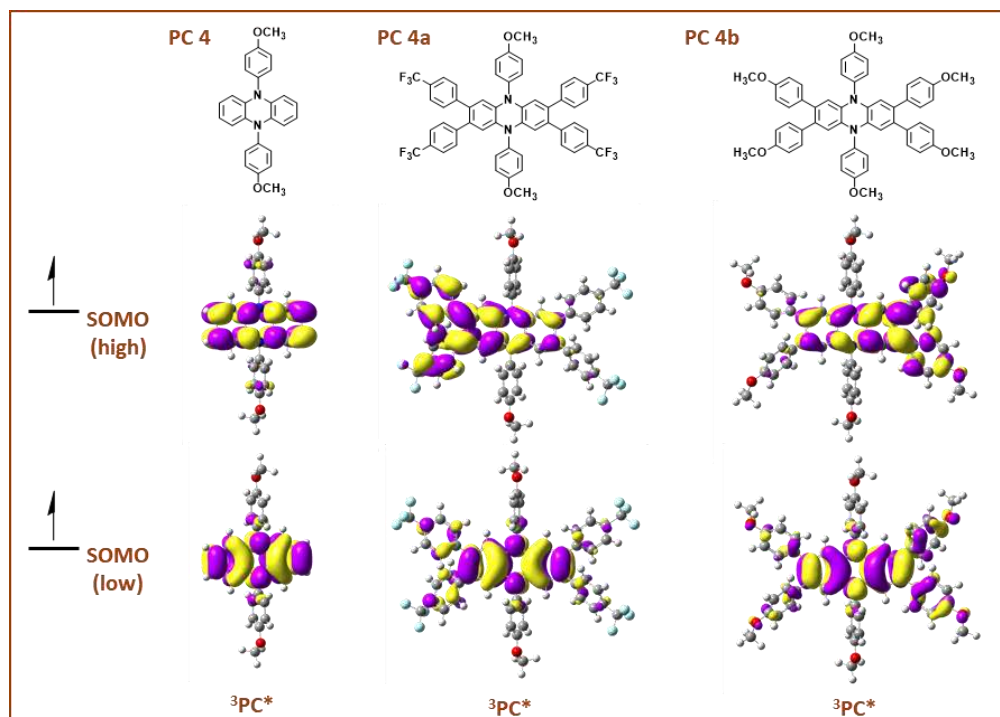


Figure A2.71. Computational modeling of the singularly occupied molecular orbitals (SOMOs) for PCs **4**, **4a**, and **4b** (from left to right); the lower lying SOMO (bottom row) and higher lying SOMO (top row) for each PC in the triplet excited state are shown.

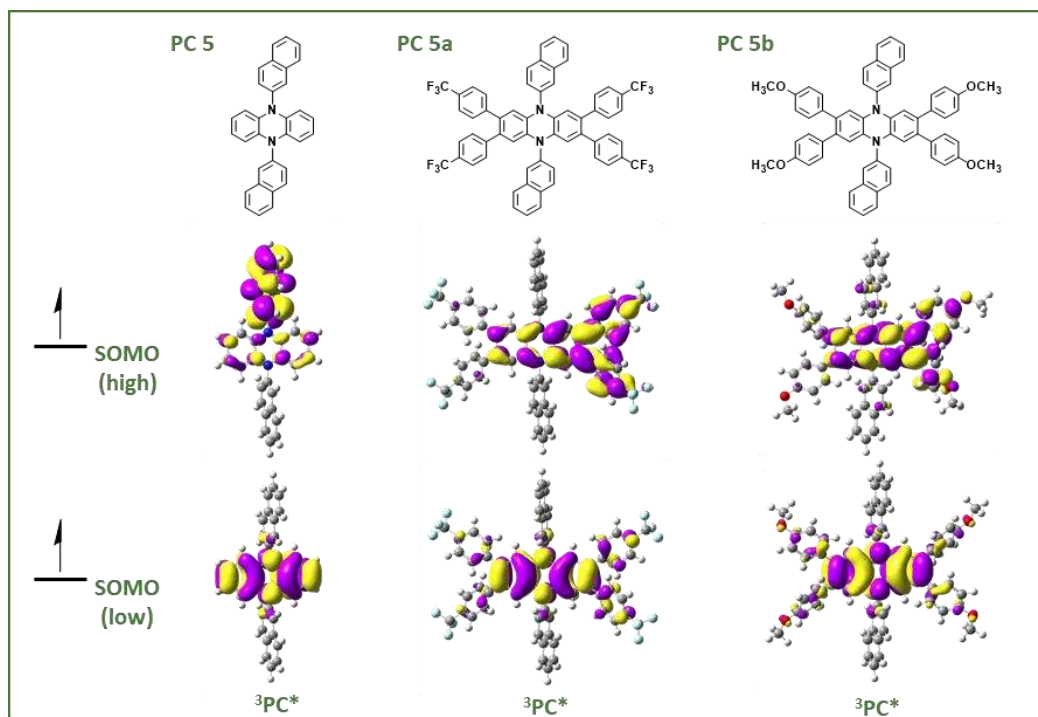


Figure A2.72. Computational modeling of the singularly occupied molecular orbitals (SOMOs) for PCs 5, 5a, and 5b (from left to right); the lower lying SOMO (bottom row) and higher lying SOMO (top row) for each PC in the triplet excited state are shown.

Computationally Modeled Electrostatic Potential (ESP) Maps of PCs

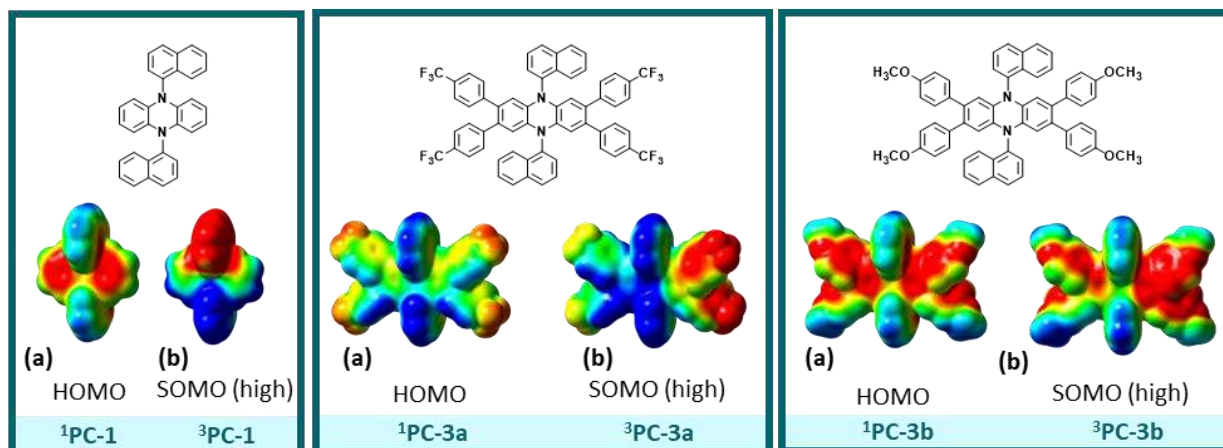


Figure A2.73. Electrostatic potential (ESP) mapped electron density for PCs 3, 3a, and 3b (from left to right) in the ground state (a) and triplet excited state (b) are shown. Red color represents electron rich regions and blue color represents electron deficient regions.

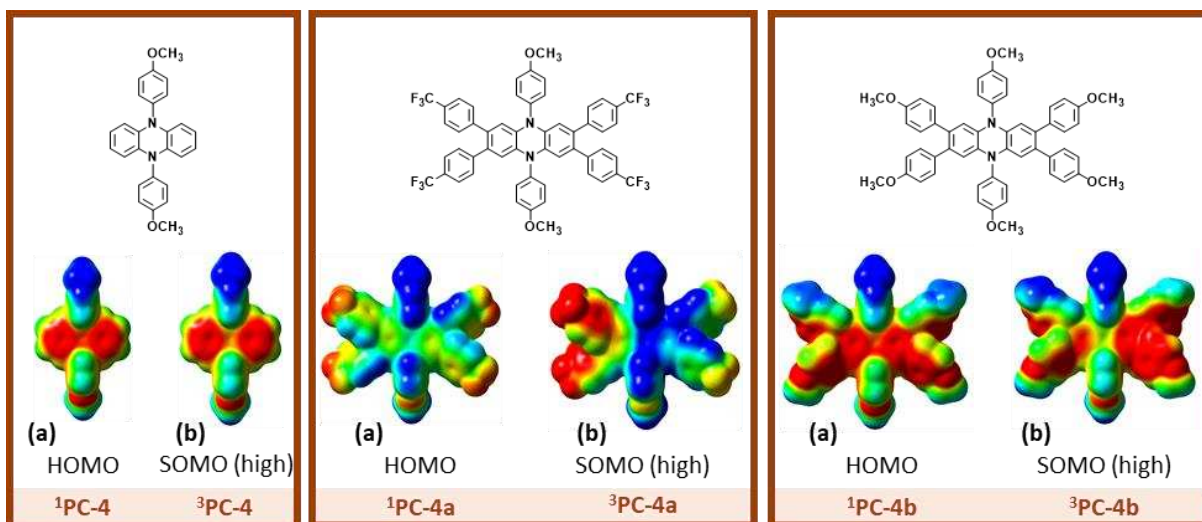


Figure A2.74. Electrostatic potential (ESP) mapped electron density for PCs 4, 4a, and 4b (from left to right) in the ground state (a) and triplet excited state (b) are shown. Red color represents electron rich regions and blue color represents electron deficient regions.

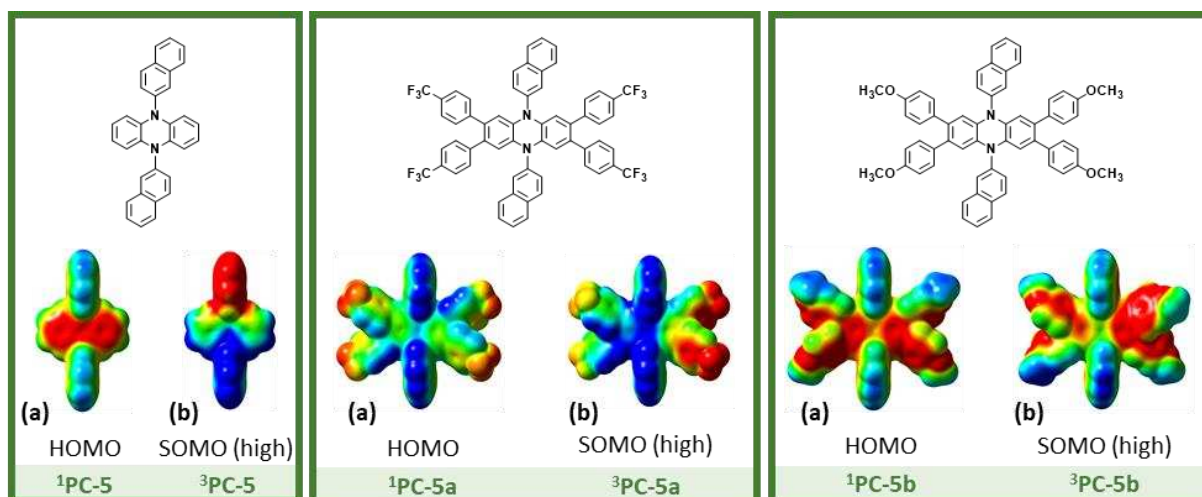


Figure A2.75. Electrostatic potential (ESP) mapped electron density for PCs 5, 5a, and 5b (from left to right) in the ground state (a) and triplet excited state (b) are shown. Red color represents electron rich regions and blue color represents electron deficient regions.

POLYMERIZATION DATA

Table A2.3. O-ATRP Results from Employing PCs for the Polymerization of MMA at Varied Catalyst Loadings^[a]

Run	PC	PC Loading (ppm) ^[b]	Conv. ^[c]	M_n (kDa) ^[d]	M_w (kDa) ^[d]	$\bar{D} (M_w/M_n)$ ^[d]	I^* ^[e]
1	3	500	42.9%	5.71	6.37	1.12	79.5%
2	3	100	67.5%	8.97	9.63	1.07	78.1%
3	3	50	84.6%	8.26	9.87	1.19	105%
4	3a	500	67.7%	7.53	7.76	1.07	93.4%
5	3a	100	64.5%	7.71	8.93	1.16	87.0%
6	3a	50	85.8%	8.80	9.46	1.07	91.9%
7	3a	10	66.8%	7.17	10.7	1.49	96.8%
8	3b	100	51.2%	5.32	8.33	1.57	101%
10	4a	100	65.4%	7.57	8.70	1.15	89.8%
11	4a	50	75.5%	7.53	9.55	1.27	104%
12	4a	10	66.8%	7.17	10.7	1.49	96.8%
13	5	500	84.3%	10.2	11.7	1.15	85.6%
14	5	100	77.1%	8.74	10.4	1.18	91.2%
15	5	50	86.6%	12.8	15.3	1.20	69.9%
16	5	10	62.4%	7.43	13.3	1.79	87.5%
17	5a	500	60.5%	9.00	9.76	1.08	70.1%
18	5a	100	72.7%	8.08	8.87	1.09	93.2%
19	5a	50	79.5%	7.34	9.42	1.28	112%
20	5a	10	69.9%	7.54	10.71	1.42	96.1%
21	5b	500	52.4%	5.45	9.20	1.69	101%
22	5b	100	73.3%	8.25	12.7	1.54	92.1%
34	PhenO ^[f]	50	56.3%	6.77	12.2	1.81	87.0%

^[a]All polymerizations were conducted using MMA as the monomer and DBMM as the initiator in a ratio of [1000]:[100] with DMAc as the solvent. ^[b]PC loading is relative to mols of monomer.

^[c]Conversion was determined by ¹H-NMR spectroscopy. ^[d]Measured using GPC. ^[e]Initiator efficiency (I^*) calculated by ((theoretical M_n /observed M_n)*100). ^[f]3,7-Di([1,1'-biphenyl]-4-yl)-10-(naphthalen-1-yl)-10H-phenoxazine

Table A2.4. Summary of results of O-ATRP of MMA in varied solvents using 50 ppm of 3b, O-ATRP of varied monomers in benzene using 50ppm of 3b, and O-ATRP with other PCs using optimized conditions. ^[a]

Run	PC	PC Loading (ppm) ^[b]	Monomer	Solvent	Conv. ^[c]	M_n (kDa) ^[d]	M_w (kDa) ^[d]	$\bar{D}$ (M_w/M_n) ^[d]	I^* ^[e]
6	3a	50	MMA	DMAc	85.8%	8.80	9.46	1.07	91.9%
23	3a	50	MMA	THF	77.7%	9.88	11.5	1.17	81.0%
24	3a	50	MMA	EtOAc	86.9%	8.79	10.8	1.23	102%
25	3a	50	MMA	Benz	89.2%	10.0	10.6	1.06	92.0%
26	3a	50	MMA	DCM	94.1%	8.88	11.0	1.24	109%
27	3a	10	MMA	Benz	83.2%	7.24	10.9	1.51	119%
28	3a	50	nBA	Benz	93.3%	14.4	24.4	1.69	85.0%
29 ^[f]	3a	50	DMA	Benz	85.8%	na	na	na	na
30 ^[g]	3a	50	VA	Benz	0.00%	na	na	na	na
31 ^[g]	3a	50	styrene	Benz	0.00%	na	na	na	na
32	4a	50	nBA	Benz	87.3%	11.9	28.8	2.41	96.0%
33	4a	10	MMA	Benz	51.9%	5.34	7.11	1.33	102%

^[a]All polymerizations were conducted using DBMM as the initiator in a ratio of [1000]:[100] for [monomer]:[DBMM]. ^[b]PC loading is relative to mols of monomer. ^[c]Conversion was determined by ¹H-NMR spectroscopy. ^[d]Measured using GPC. ^[e]Initiator efficiency (I^*) calculated by ((theoretical M_n /observed M_n)*100). ^[f]Molecular weight data was not obtained for this polymer. ^[g]Molecular weight data was not obtained as there was no conversion observed.

Polymerization Kinetics

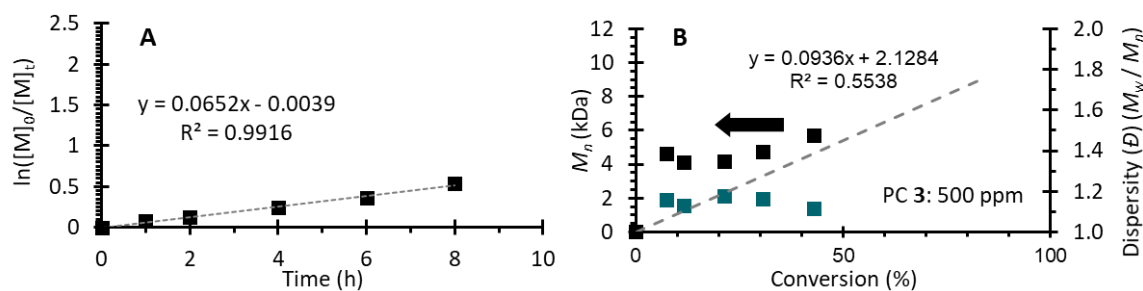


Figure A2.76. Polymerization data from Run 1 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[3] = [1000]:[1000]:[10]:[500]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

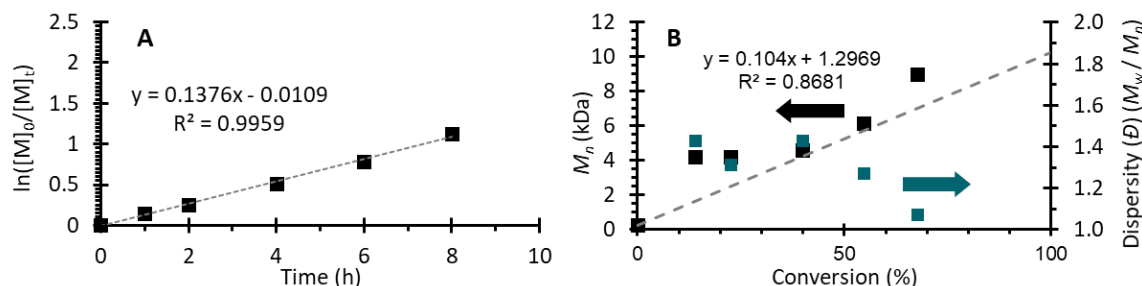


Figure A2.77. Polymerization data from Run 2 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[3] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

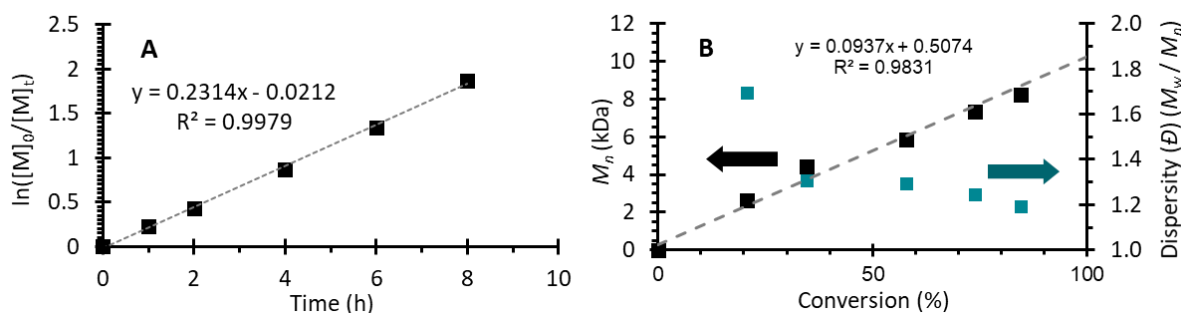


Figure A2.78. Polymerization data from Run 3 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[3] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

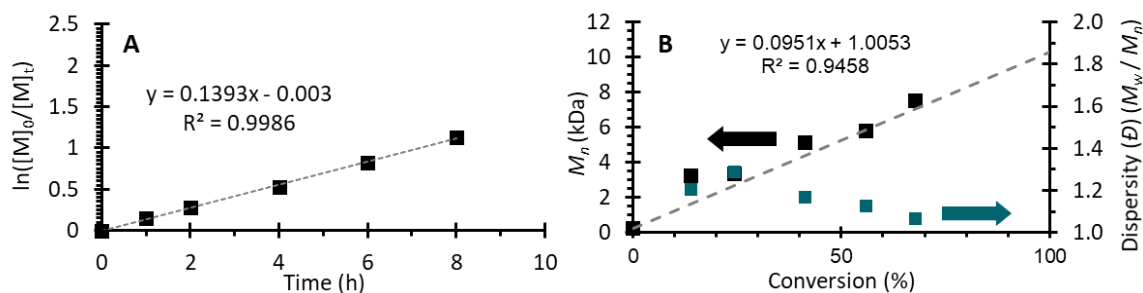


Figure A2.79. Polymerization data from Run 4 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[3a] = [1000]:[1000]:[10]:[500]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

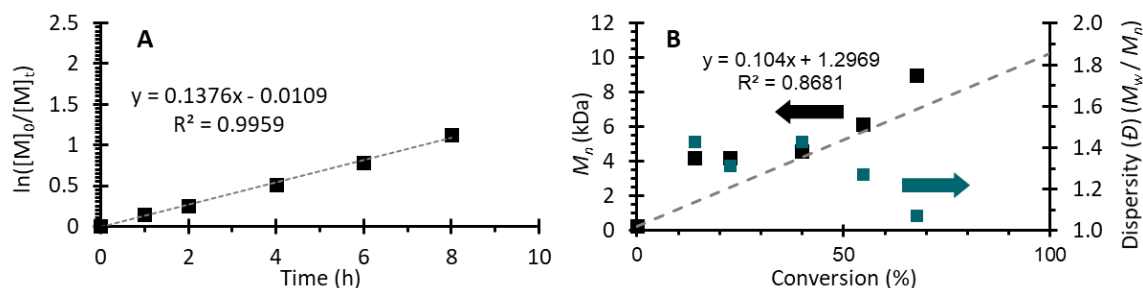


Figure A2.80. Polymerization data from Run 5 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[3a] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

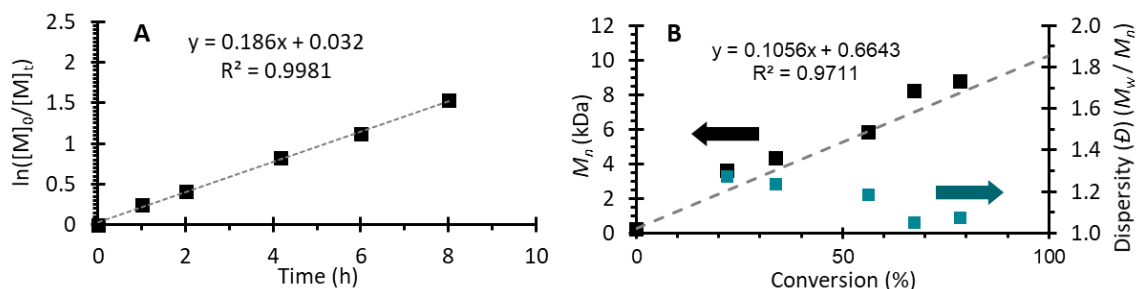


Figure A2.81. Polymerization data from Run 6 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[**3a**] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

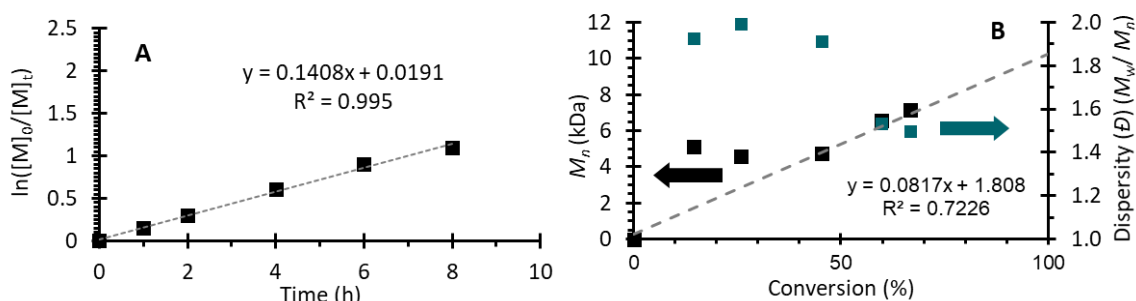


Figure A2.82. Polymerization data from Run 7 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[**3a**] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

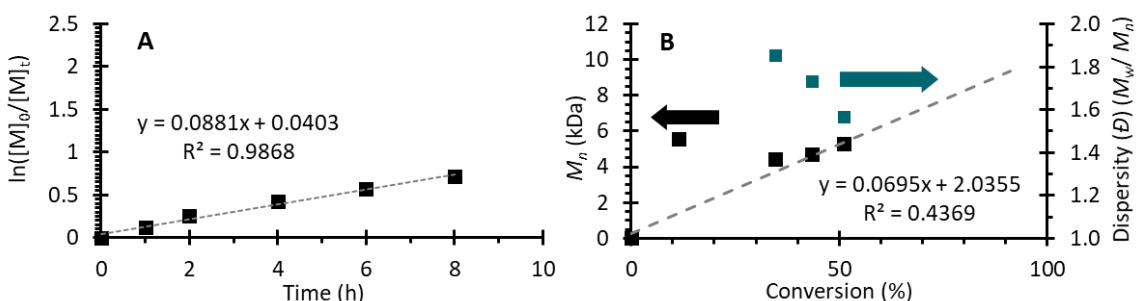


Figure A2.83. Polymerization data from Run 8 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[**3b**] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

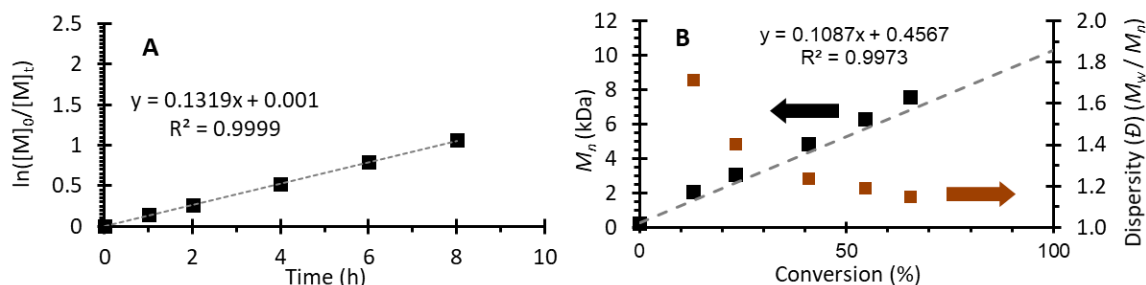


Figure A2.84. Polymerization data from Run 10 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[4a] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

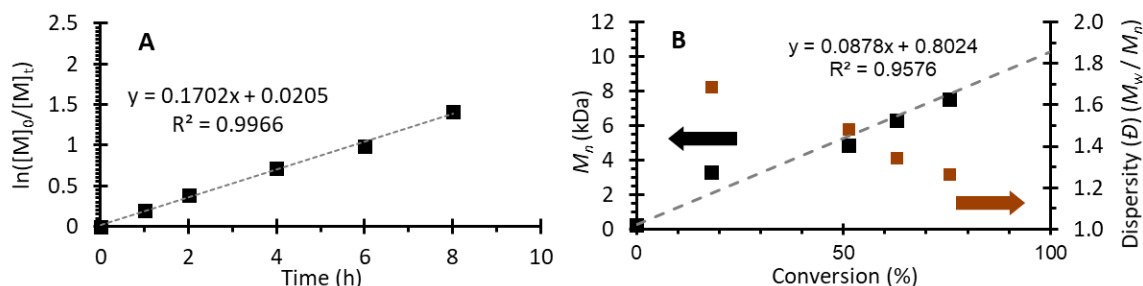


Figure A2.85. Polymerization data from Run 11 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[4a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

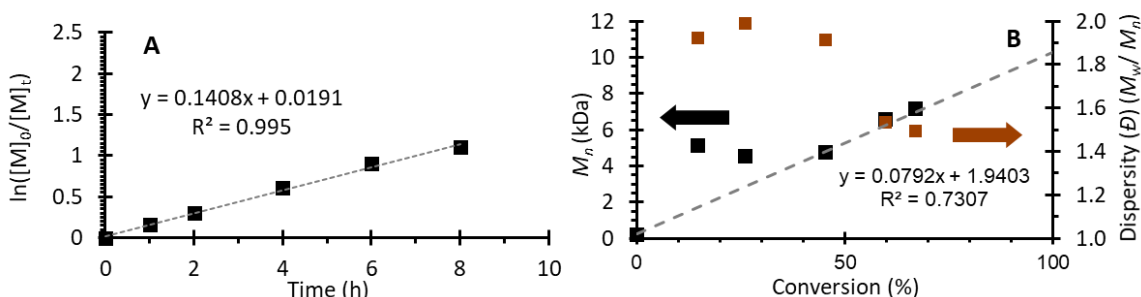


Figure A2.86. Polymerization data from Run 12 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[4a] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

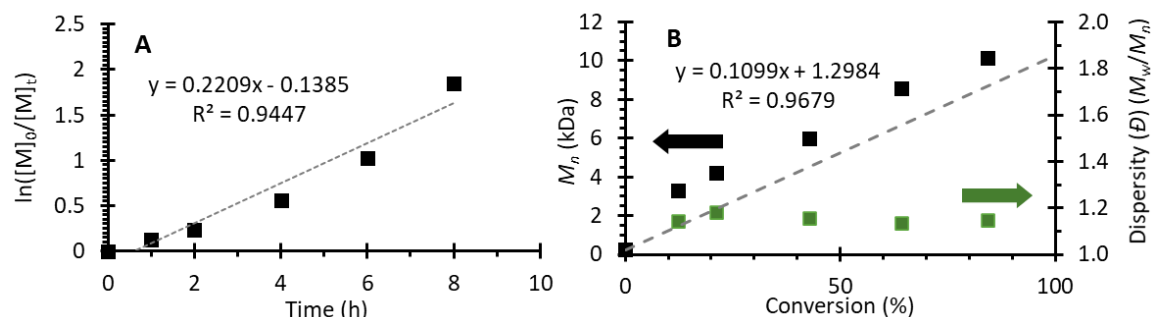


Figure A2.87. Polymerization data from Run 13 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5] = [1000]:[1000]:[10]:[500]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

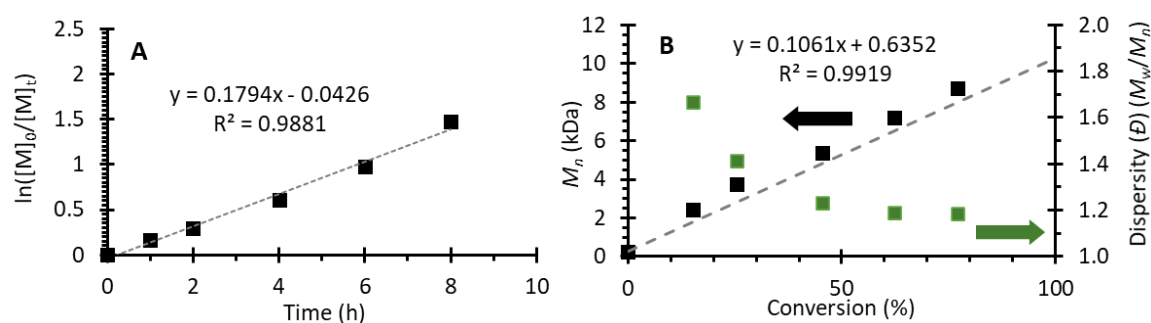


Figure A2.88. Polymerization data from Run 14 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

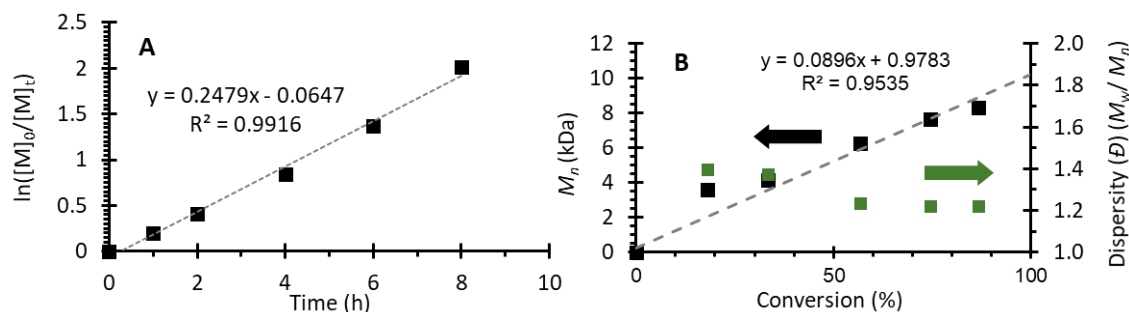


Figure A2.89. Polymerization data from Run 15 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

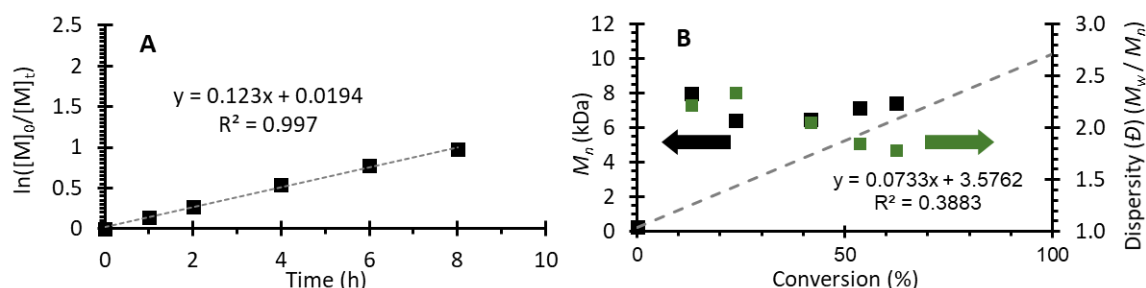


Figure A2.90. Polymerization data from Run 16 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

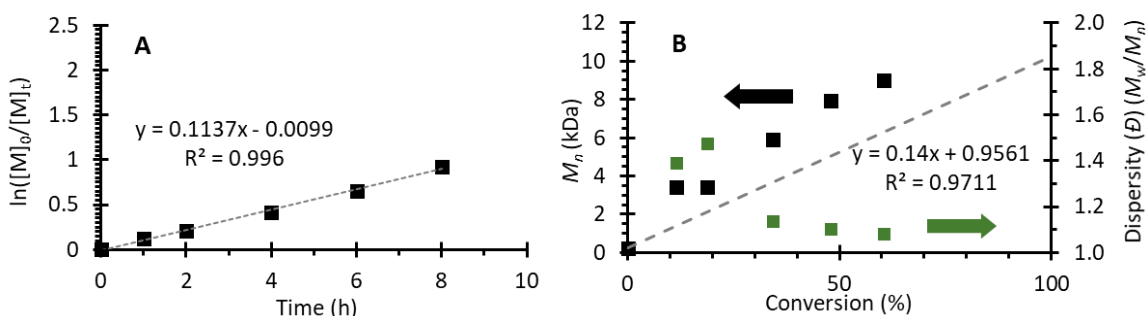


Figure A2.91. Polymerization data from Run 17 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5a] = [1000]:[1000]:[10]:[500]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

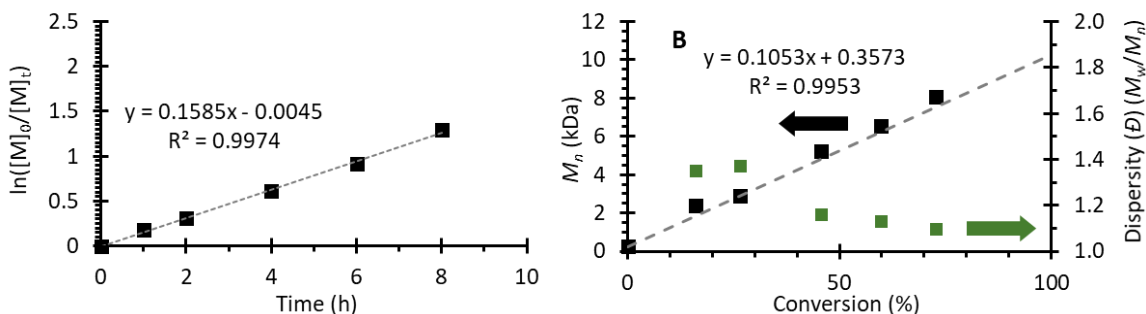


Figure A2.92. Polymerization data from Run 18 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5a] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

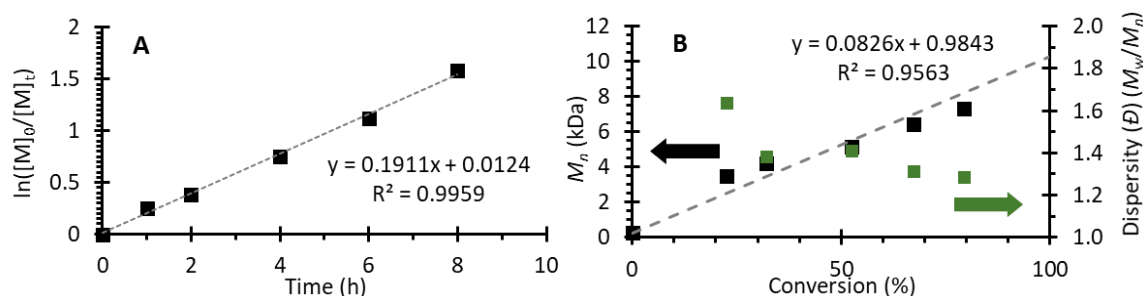


Figure A2.93. Polymerization data from Run 19 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

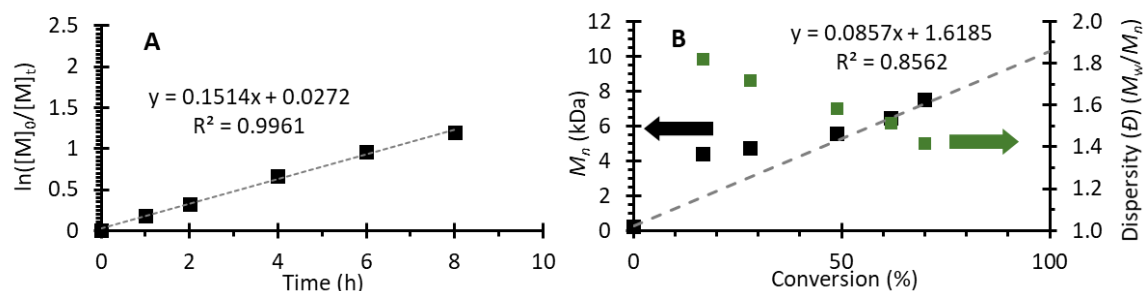


Figure A2.94. Polymerization data from Run 20 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5a] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

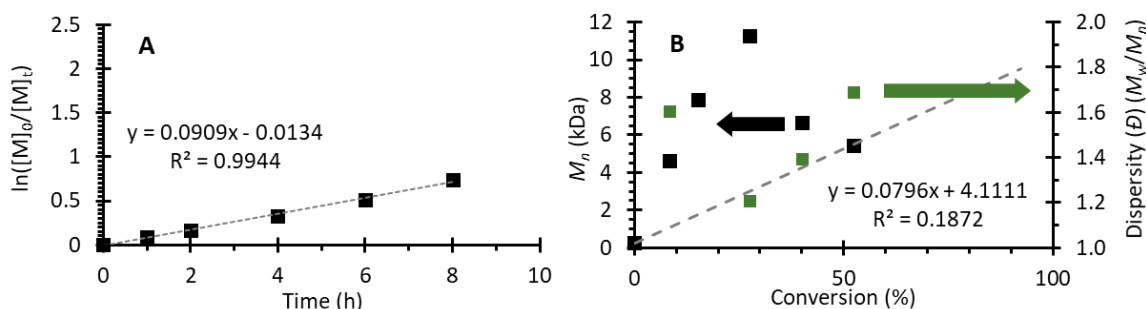


Figure A2.95. Polymerization data from Run 21 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[5b] = [1000]:[1000]:[10]:[500]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

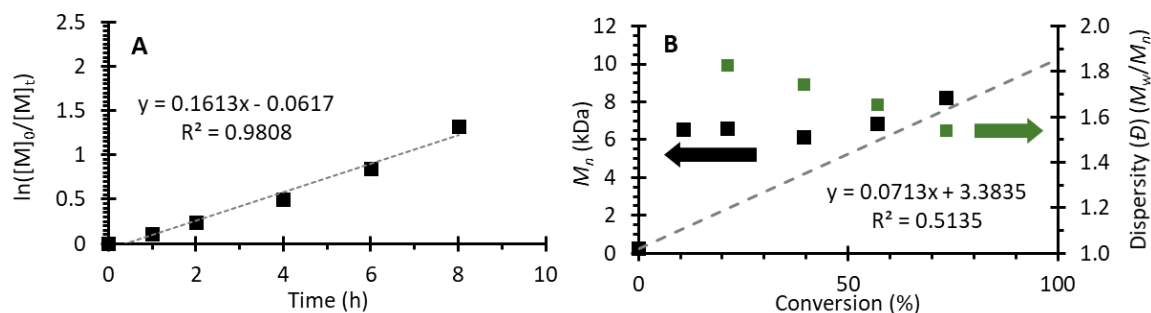


Figure A2.96. Polymerization data from Run 22 (Table A1.3). [MMA]:[DMAc]:[DBMM]:[**5b**] = [1000]:[1000]:[10]:[100]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (green squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

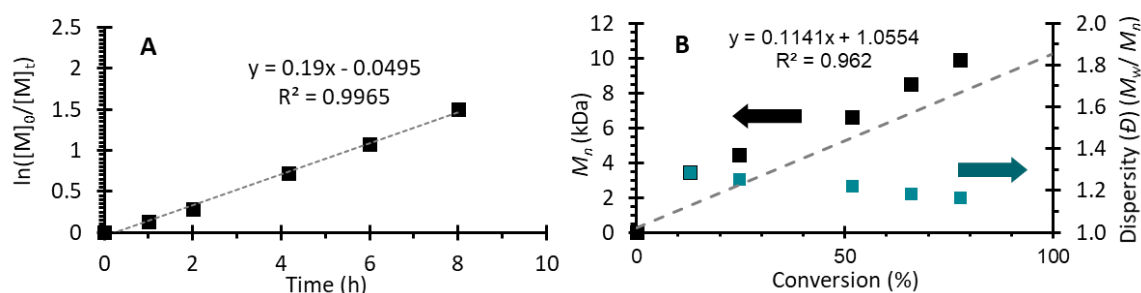


Figure A2.97. Polymerization data from Run 23 (Table A1.4). [MMA]:[THF]:[DBMM]:[**3a**] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

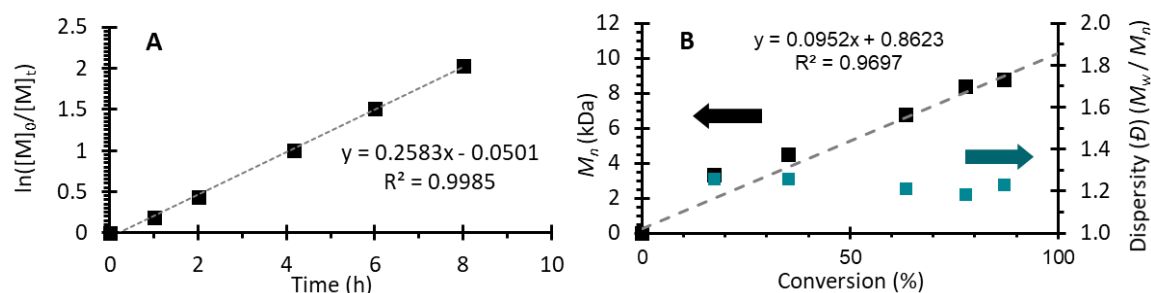


Figure A2.98. Polymerization data from Run 24 (Table A1.4). [MMA]:[EtOAc]:[DBMM]:[**3a**] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

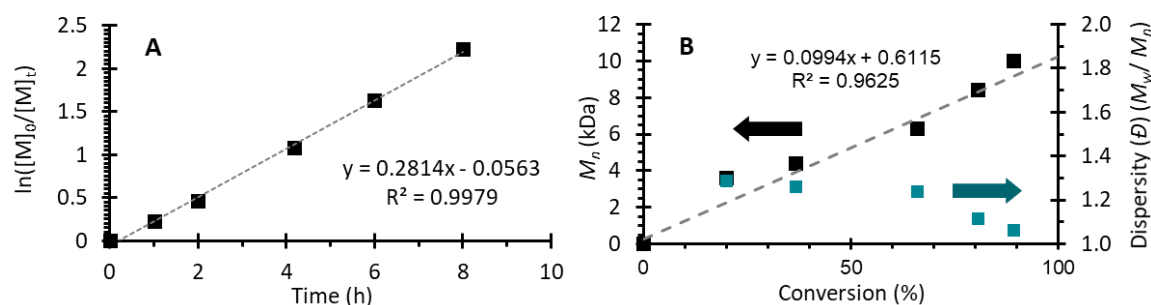


Figure A2.99. Polymerization data from Run 25 (Table A1.4). [MMA]:[Benz]:[DBMM]:[3a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

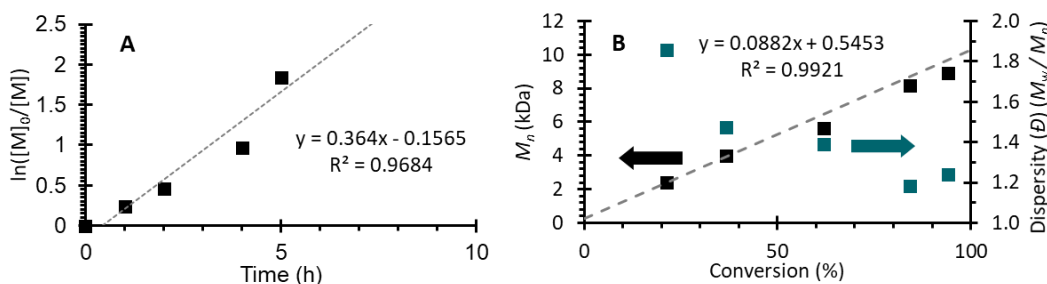


Figure A2.100. Polymerization data from Run 26 (Table A1.4). [MMA]:[DCM]:[DBMM]:[3a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

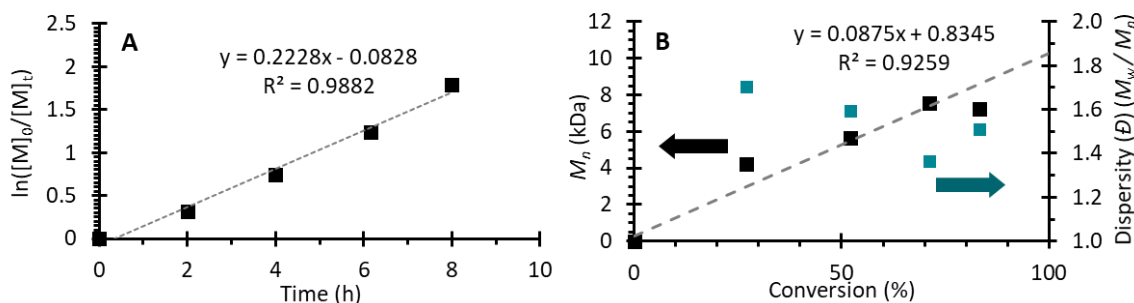


Figure A2.101. Polymerization data from Run 27 (Table A1.4). [MMA]:[Benz]:[DBMM]:[3a] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

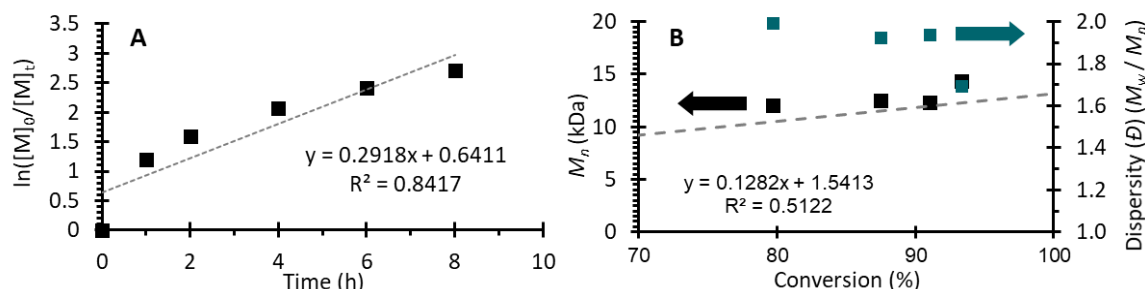


Figure A2.102. Polymerization data from Run 28 (Table A1.4). [nBA]:[Benz]:[DBMM]:[3a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (blue squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

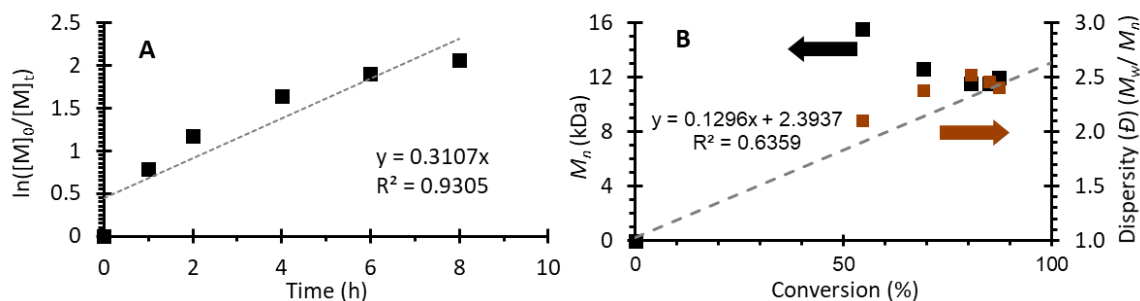


Figure A2.103. Polymerization data from Run 32 (Table A1.4). [nBA]:[Benz]:[DBMM]:[4a] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

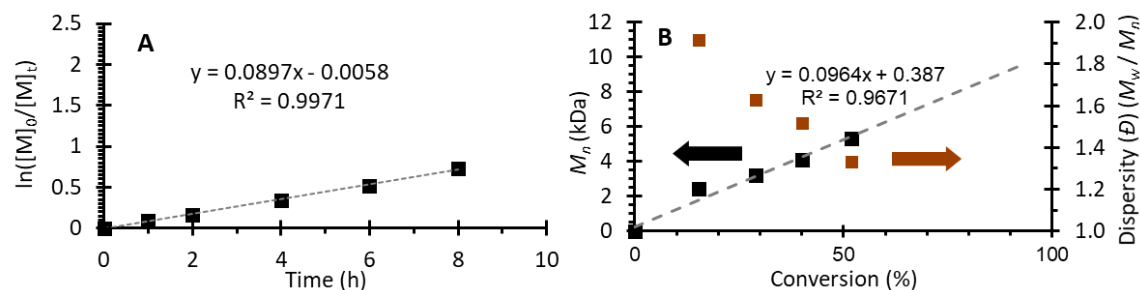


Figure A2.104. Polymerization data from Run 33 (Table A1.4). [MMA]:[Benz]:[DBMM]:[4a] = [1000]:[1000]:[10]:[10]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion.

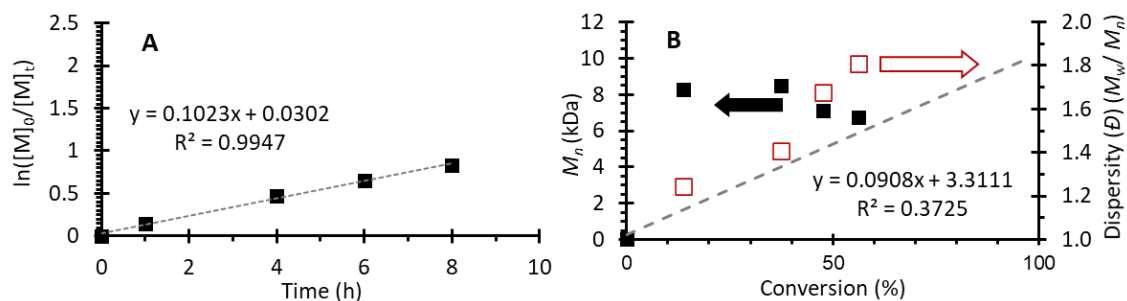


Figure A2.105. Polymerization data from Run 34 (Table A1.4). [MMA]:[DMAc]:[DBMM]:[PhenO*] = [1000]:[1000]:[10]:[50]. (A) First order kinetic plot of the natural log of monomer consumption as a function of time. (B) Plot of molecular weight (M_n) growth as a function of monomer conversion (black squares), theoretical M_n growth as a function of monomer conversion (dashed grey line), and dispersity as a function of monomer conversion (orange squares). Equation on chart (B) represents the trendline for the measured M_n growth as a function of conversion. *(PhenO: 3,7-Di([1,1'-biphenyl]-4-yl)-10-(naphthalen-1-yl)-10H-phenoxazine).

Chain Extension Experiment

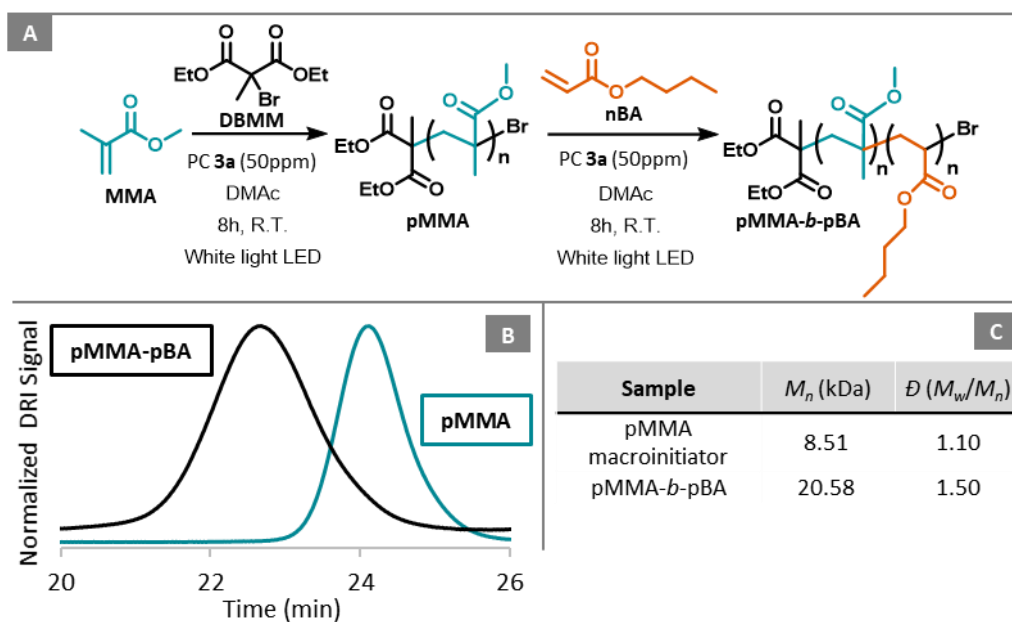


Figure A2.106. (A) Reaction scheme for chain extension of pMMA macroinitiator with nBA to form pMMA-*b*-pBA. The polymerization of the macromonomer was run in DMAc using DBMM as the initiator and MMA as the monomer in a ratio of [MMA]:[DBMM]:[3a] = [1000]:[10]:[0.05]. (B) Overlaid GPC traces of the isolated pMMA macroinitiator and the isolated pMMA-*b*-pBA block copolymer. (C) Molecular weight data (obtained using GPC) for the isolated pMMA macroinitiator and the isolated pMMA-*b*-nBA block copolymer.

¹H-NMR SPECTRA OF CATALYSTS & RELEVANT INTERMEDIATES

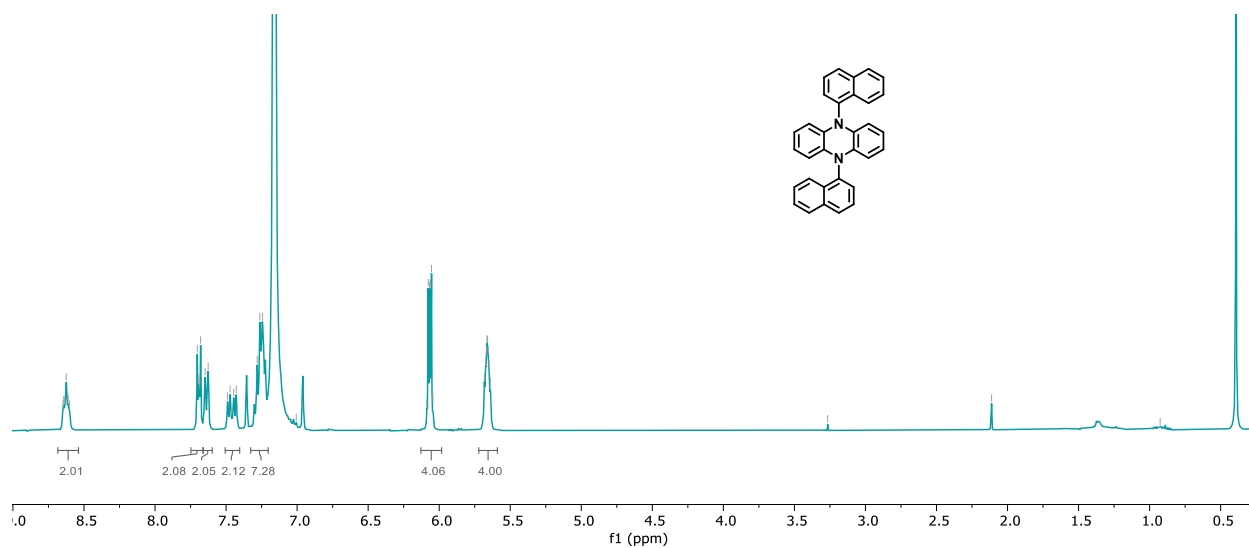


Figure A2.107. ¹H-NMR spectrum of **PC 3** in C₆D₆ after recrystallization.

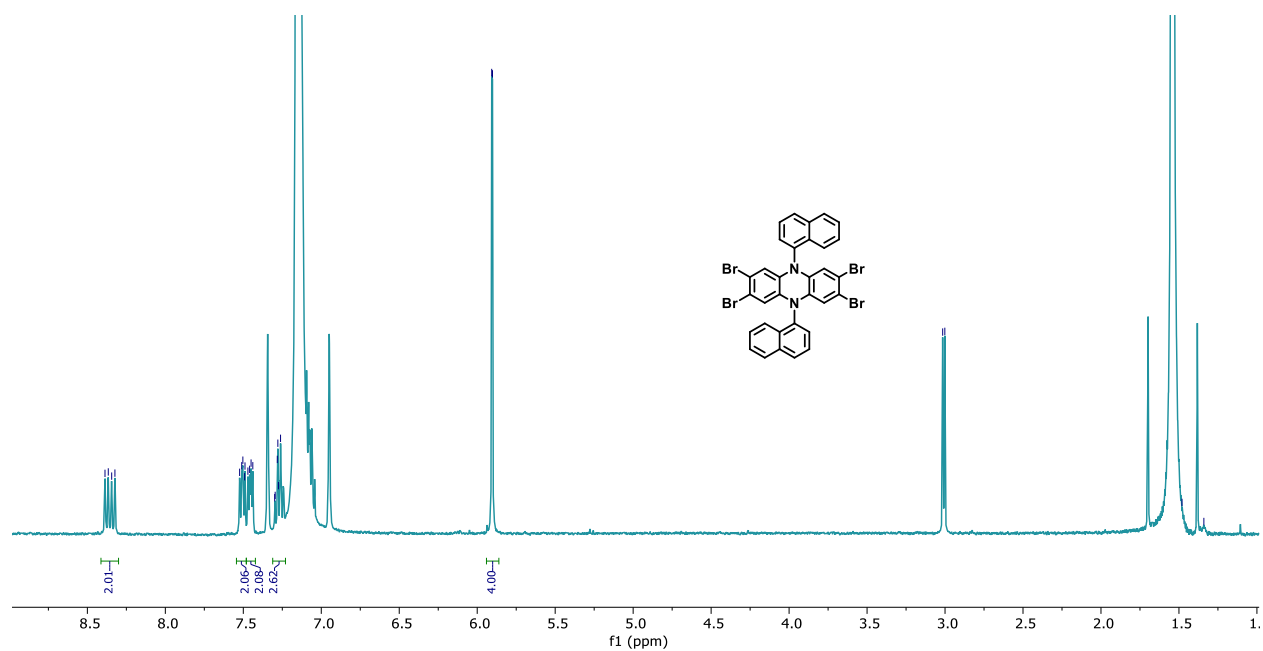


Figure A2.108. ¹H-NMR spectrum of unpurified **PC 3-4Br** in C₆D₆.

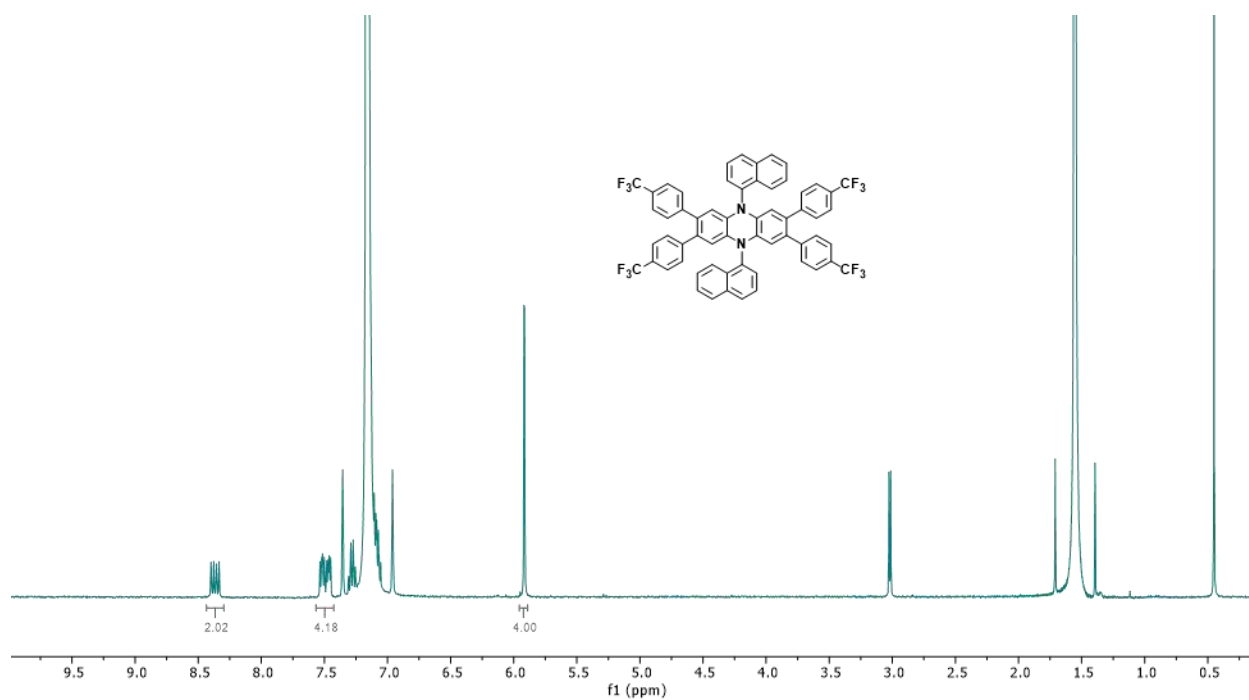


Figure A2.109. ^1H -NMR spectrum of PC 3a in C_6D_6 after recrystallization.

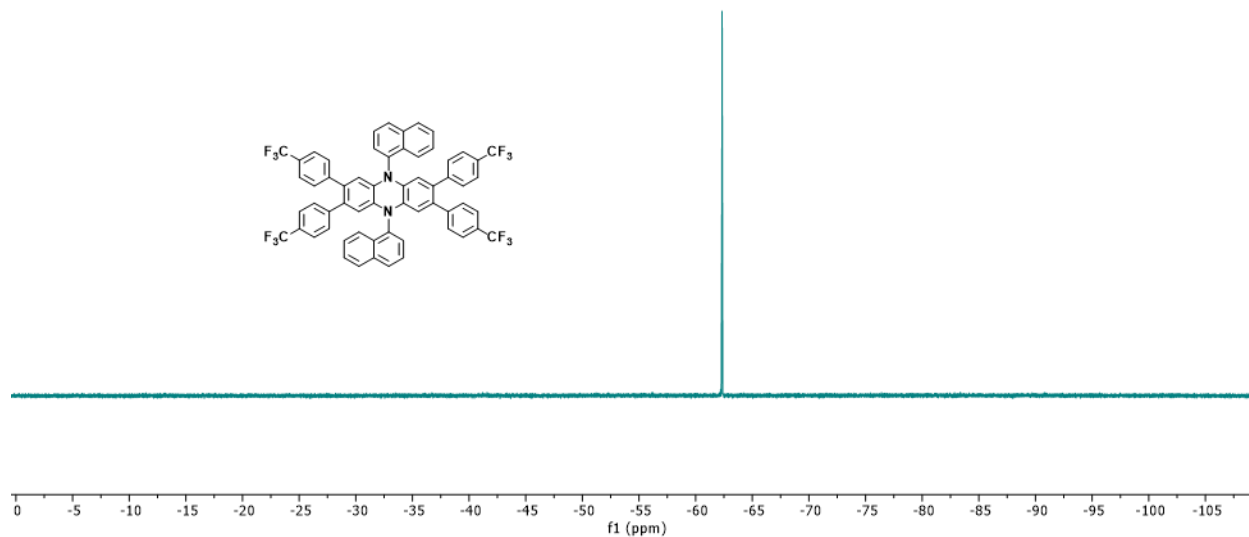


Figure A2.110. ^{19}F -NMR spectrum of PC 3a in C_6D_6 .

MP-3b_Benz.10.fid
Advisor miyake

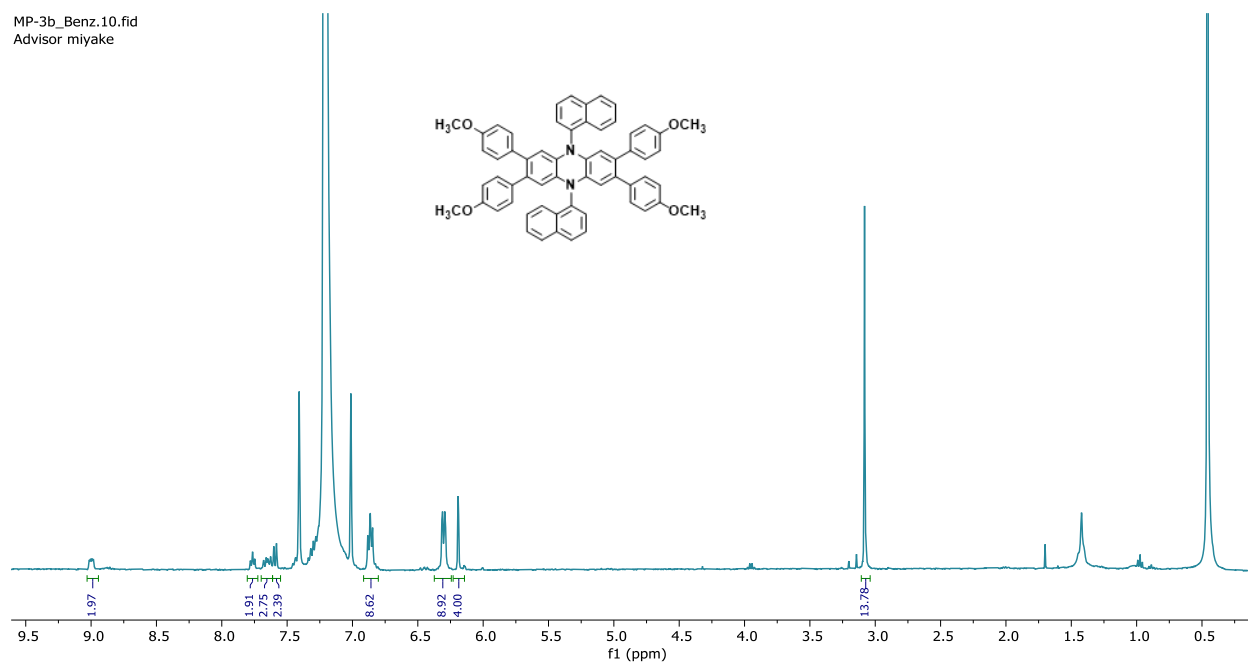


Figure A2.111. ¹H-NMR spectrum of PC 3b in C₆D₆.

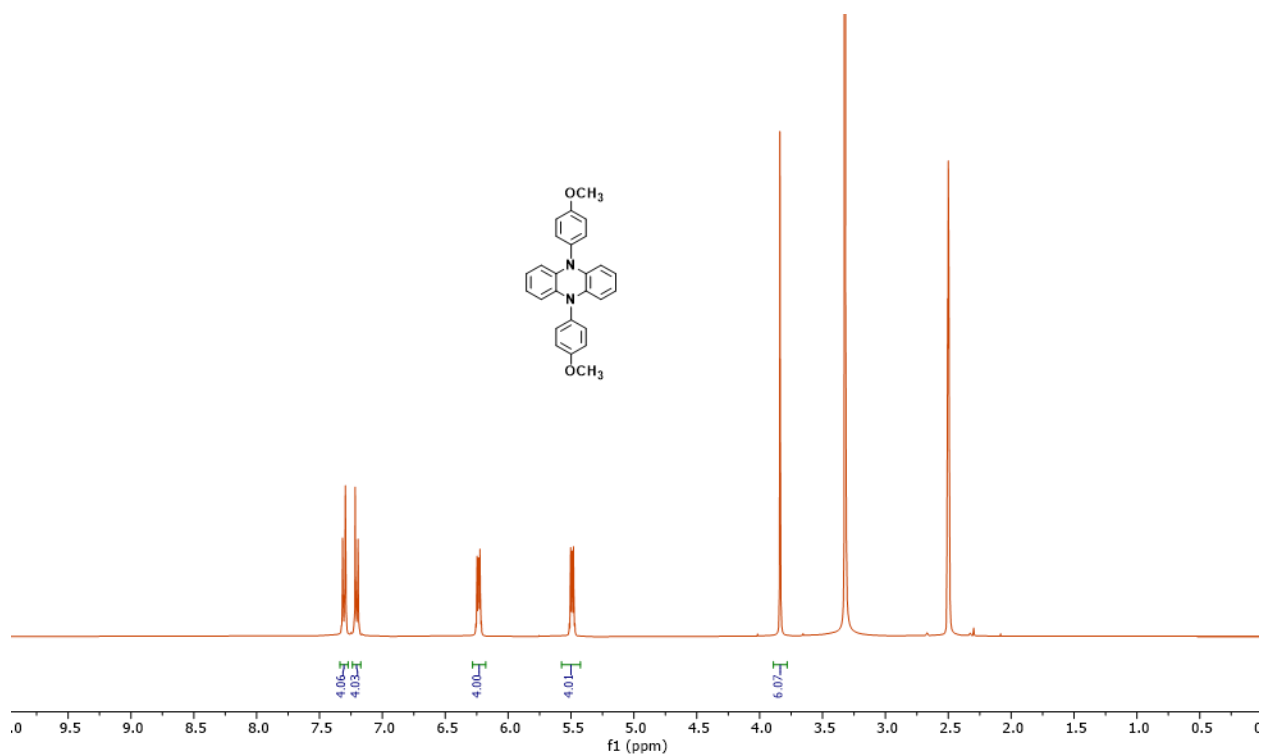


Figure A2.112. ¹H-NMR spectrum of PC 4 recrystallization from toluene-hexanes in DMSO-d₆.

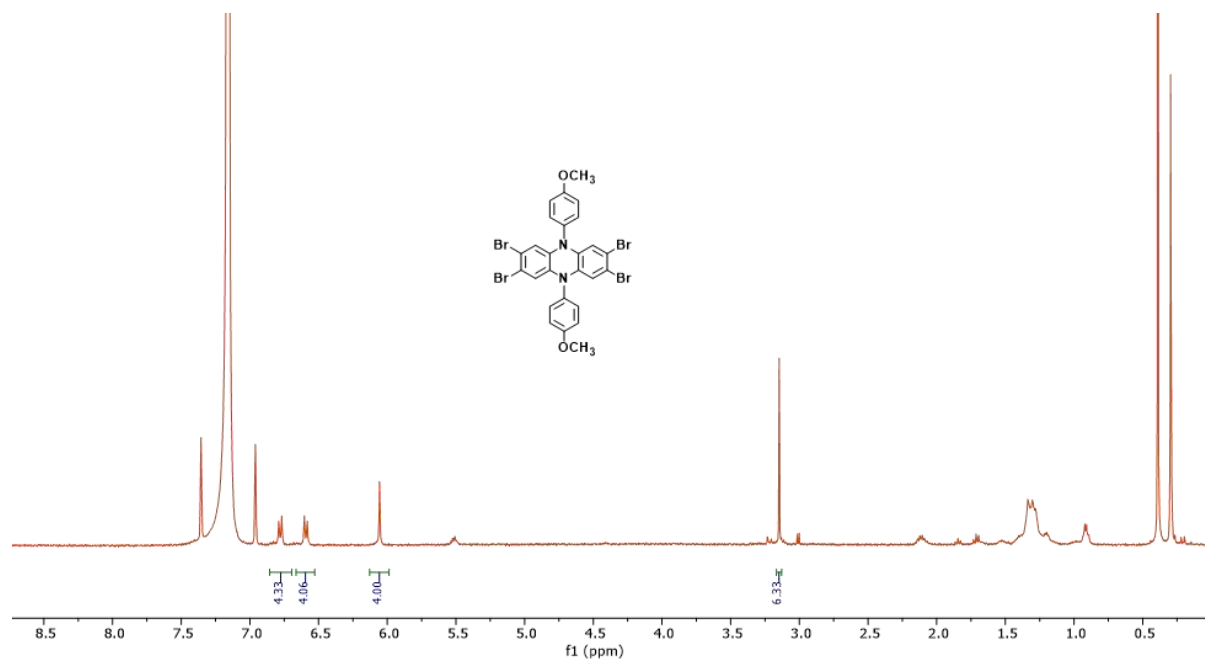


Figure A2.113. ^1H -NMR spectrum of unpurified **4-4Br** in C_6D_6 .

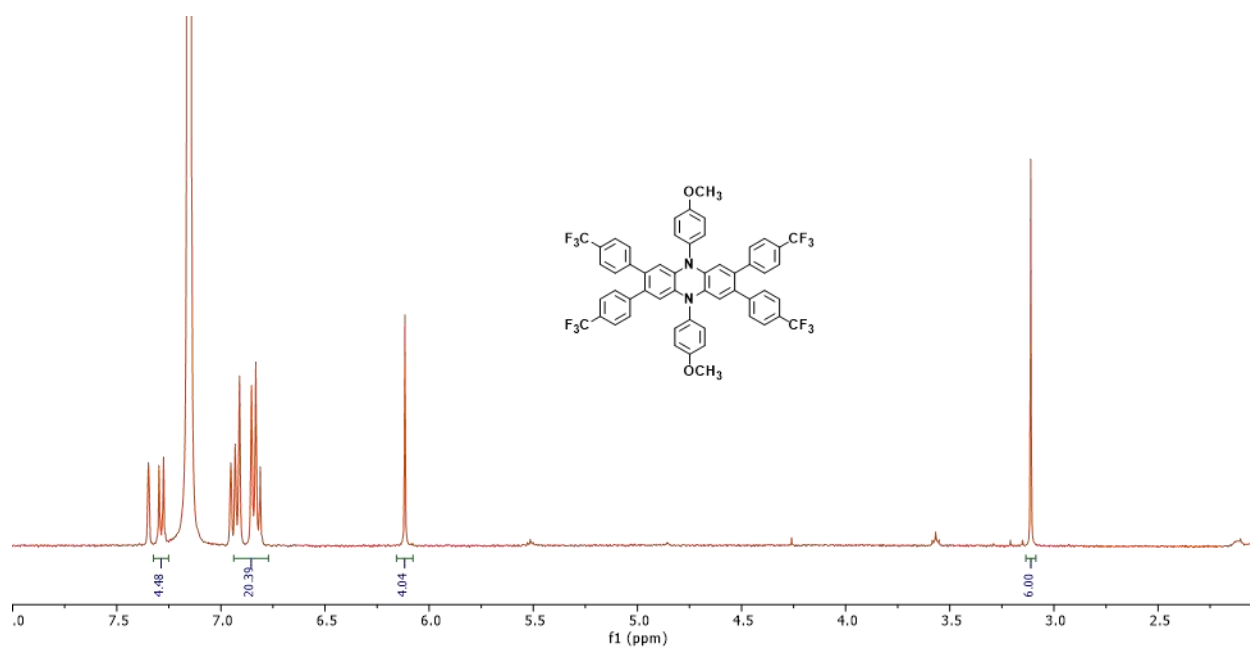


Figure A2.114. ^1H -NMR spectrum of **4a** in C_6D_6 after recrystallization.

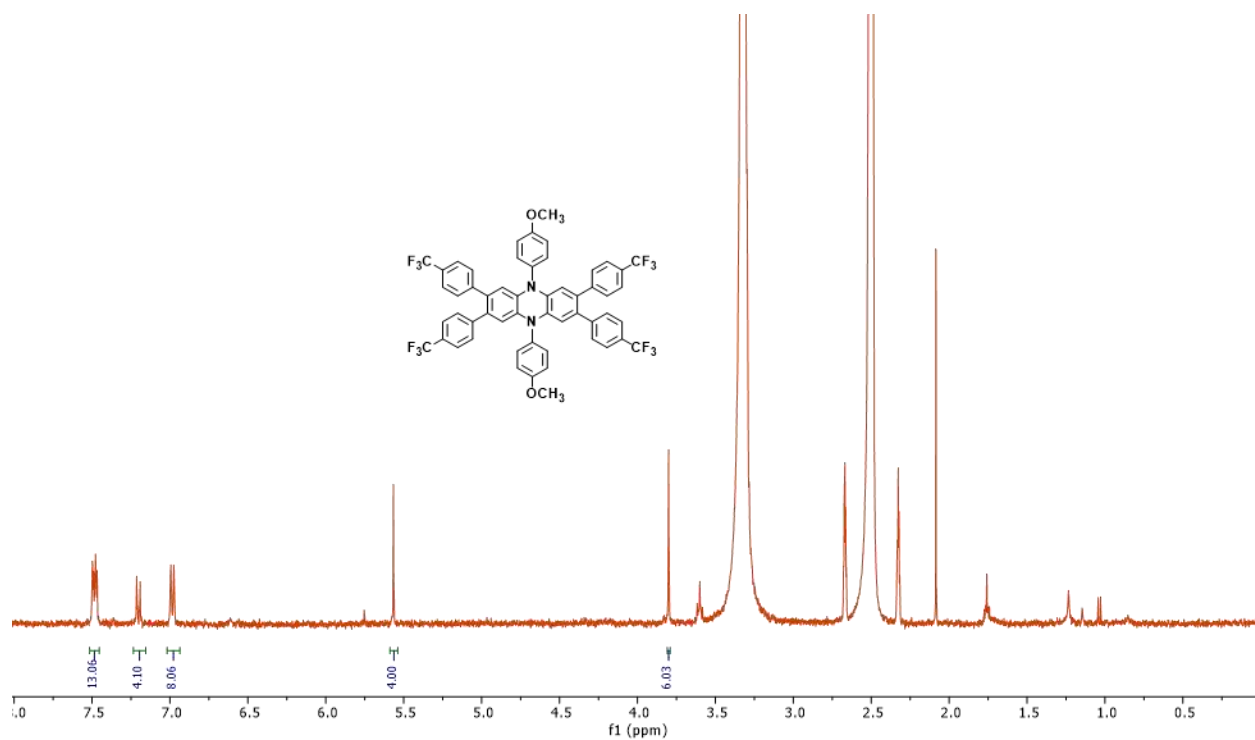


Figure A2.115. ¹H-NMR spectrum of **4a** in DMSO-d₆ after recrystallization.

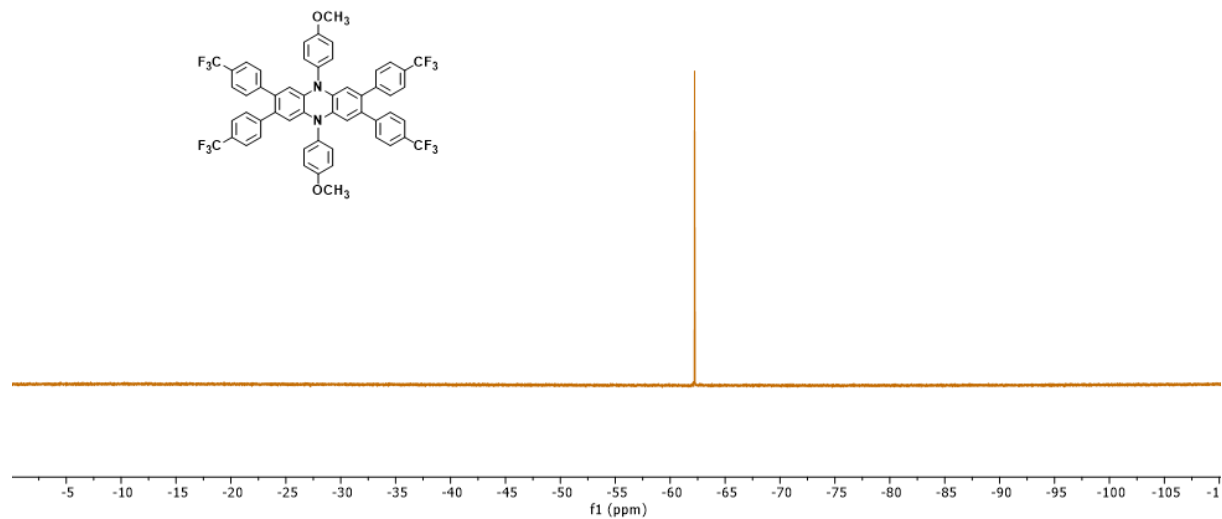


Figure A2.116. ¹⁹F-NMR spectrum of **PC 4a** in C₆D₆ after recrystallization.

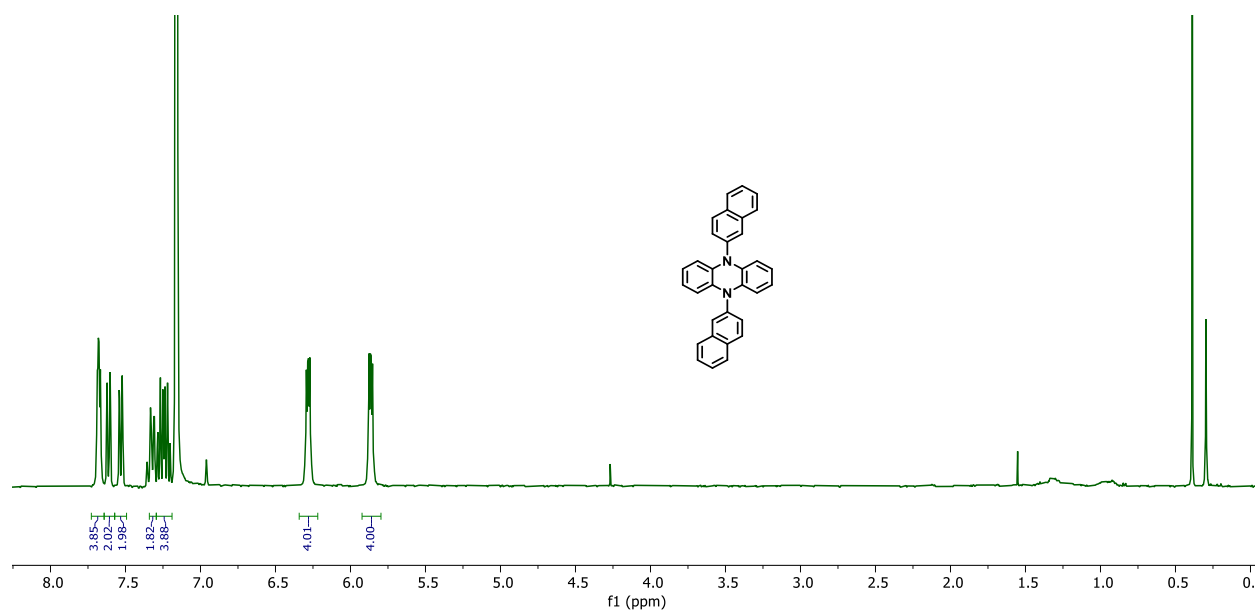


Figure A2.117. ^1H -NMR spectrum of PC **5** in C_6D_6 after recrystallization.

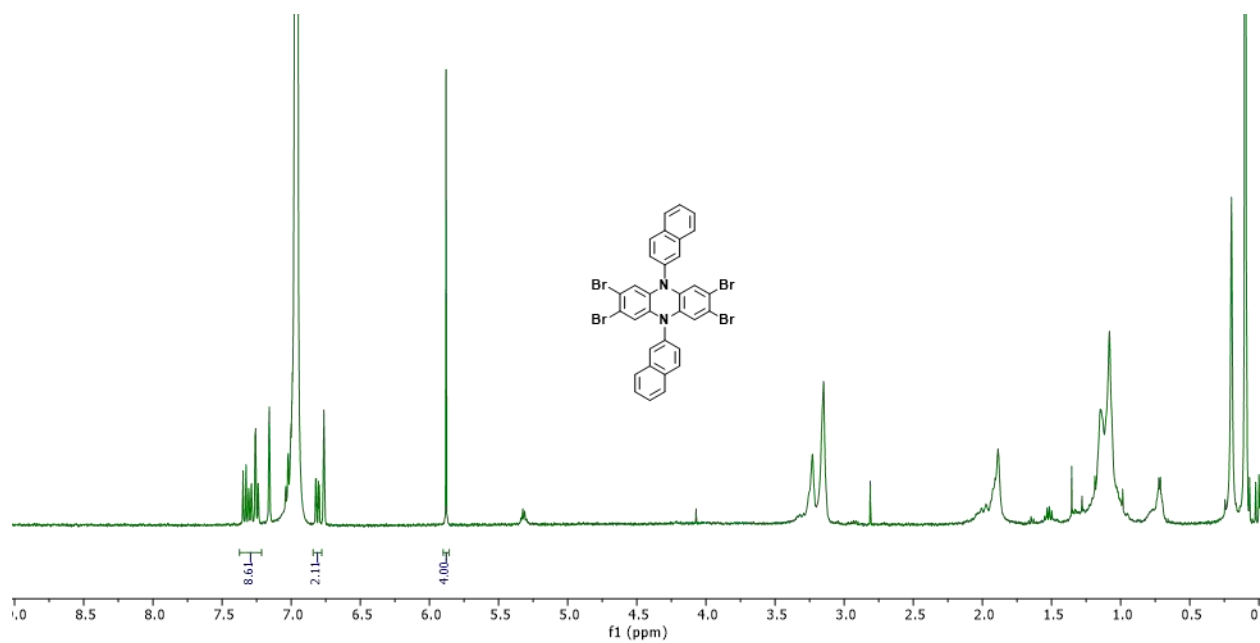


Figure A2.118. ^1H -NMR spectrum of unpurified **5-4Br** in C_6D_6 .

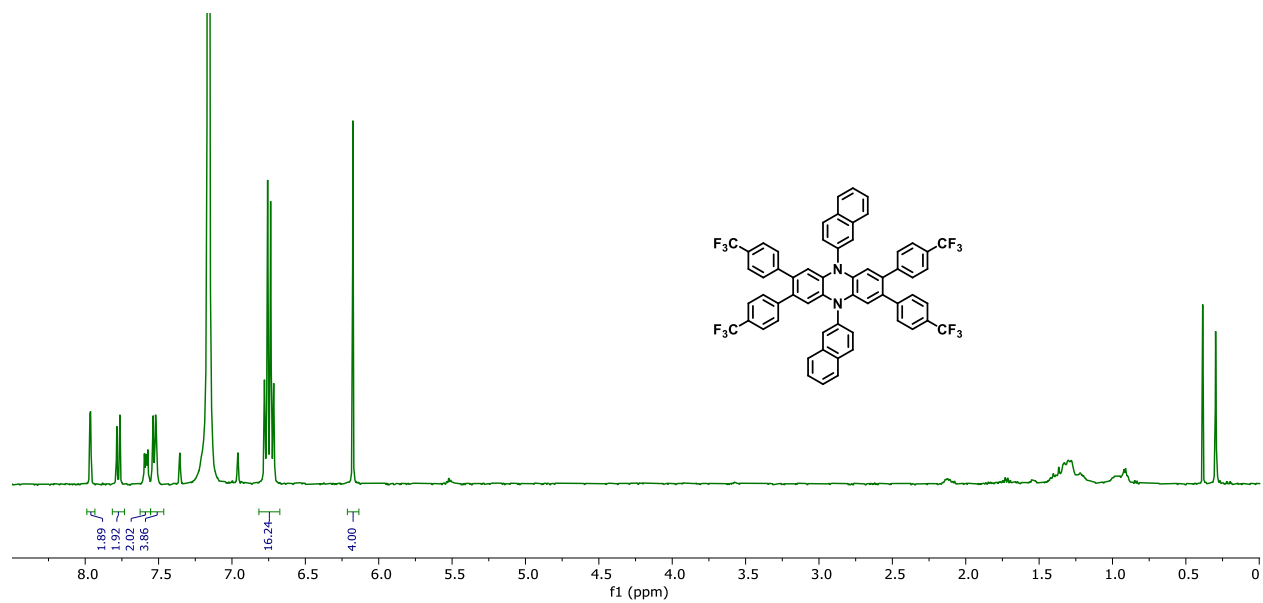


Figure A2.119. ¹H-NMR spectrum of PC 5a in C₆D₆ after recrystallization.

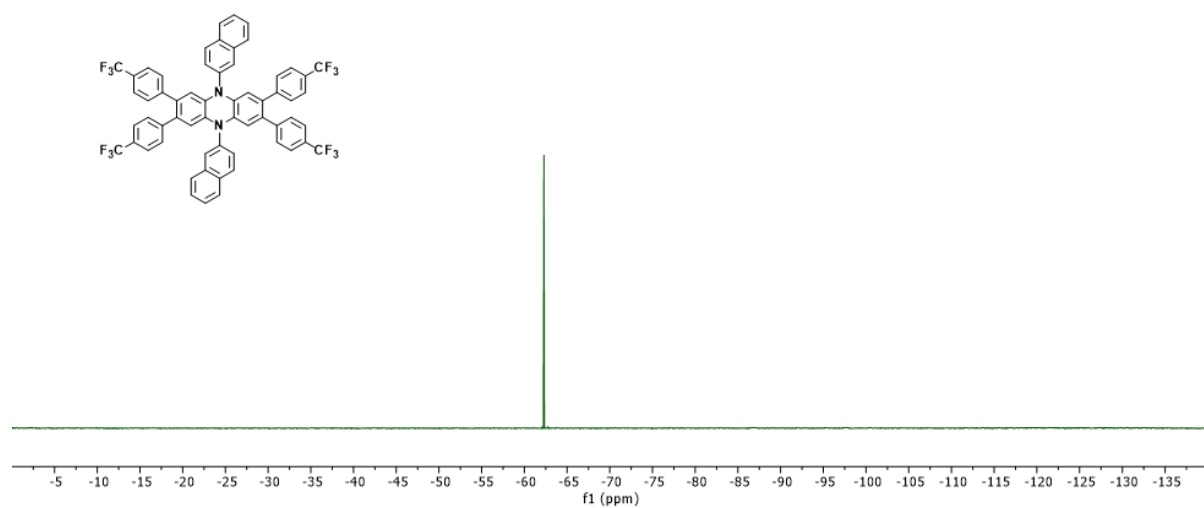


Figure A2.120. ¹⁹F-NMR spectrum of PC 5a in C₆D₆ after recrystallization.

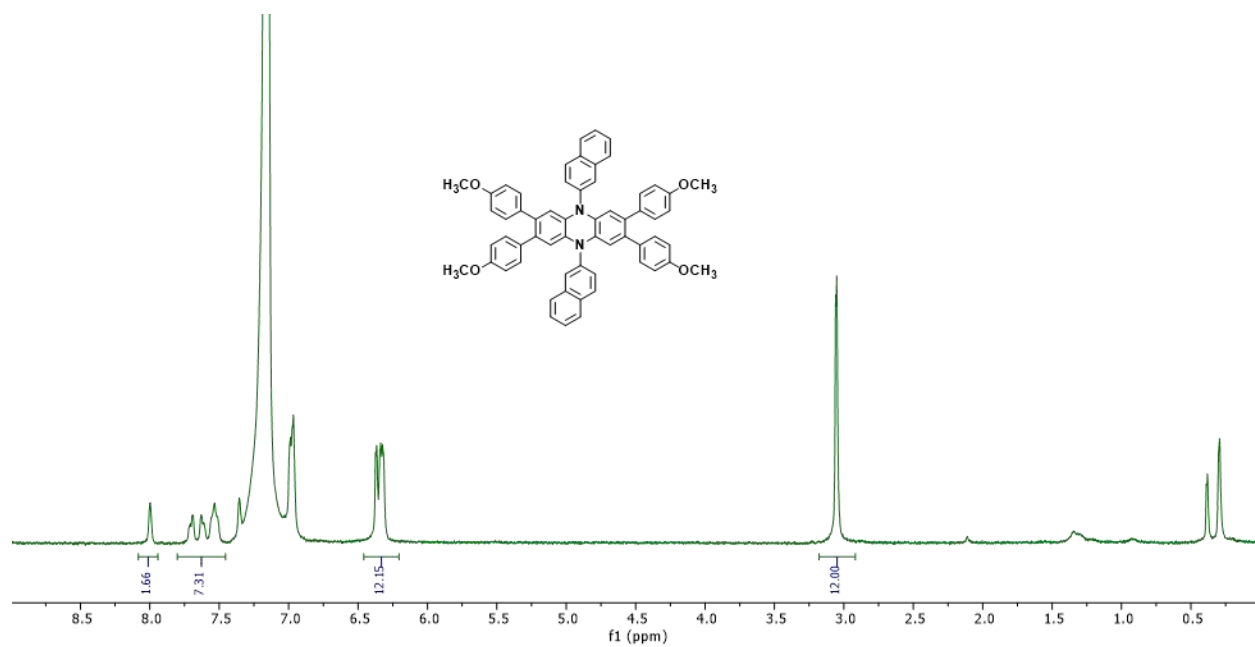


Figure A2.121. ¹H-NMR spectrum of PC 5b in C₆D₆ after recrystallization.

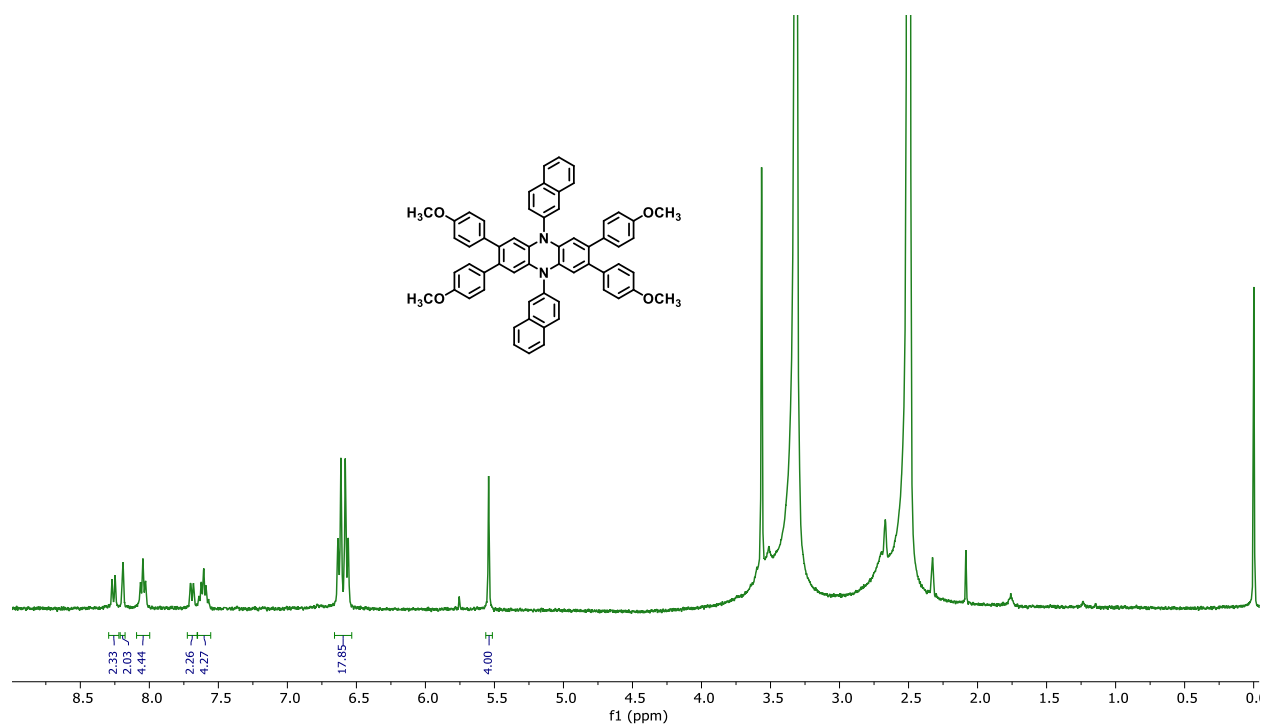


Figure A2.122. ¹H-NMR spectrum of PC 5b in DMSO-d₆ after recrystallization.

COMPUTATIONAL DETAILS

All calculations were performed using computational chemistry software package Gaussian 16. This work used the Extreme Science and Engineering Discovery Environment (XSEDE).

Reduction Potentials

Standard reduction potentials (E^0) of **3**, **4**, **5**, **3a**, **3b**, **4a**, **4b** and **5a**, **5b** were calculated following previously reported procedures.^{5,6,7,8} A value of -100.5 kcal/mol was assumed for the reduction free energy of the standard hydrogen electrode (SHE). Thus, $E_{T1,comp}^{0*} (^2PC^{*+}/^3PC^*)$ was calculated as $E_{T1,comp}^{0*} = (-100.5 - \Delta G_{red})/23.06$ (V vs. SHE) where $\Delta G_{red} = G(^3PC^*) - G(^2PC^{*+})$. $E_{ox,comp}^0 (^2PC^{*+}/^1PC)$ was calculated as $\Delta G_{red} = G(^1PC) - G(^2PC^{*+})$.

For **3**, **4**, **5**, **3a**, **3b**, **4a**, **4b** and **5a**, **5b** Gibbs free energies of $^3PC^*$, $^2PC^{*+}$, and 1PC were calculated at the unrestricted M06/6-311+G** level of theory in CPCM-H₂O solvent (single point energy) using geometries optimized at the unrestricted M06/6-31G** level of theory in CPCM-H₂O solvent. Values were converted from V vs. SHE to V vs. SCE by E^0 (V vs. SCE) = E^0 (V vs. SHE) – 0.24 V. The triplet energies ($E_{T1,comp}$) of DHPs and CE-DHPs were obtained by $E_{T1,comp}(\text{kcal/mol}) = [G(^3PC^*) - G(^1PC)]$ then converted from kcal/mol to eV by dividing $E_{T1,comp}(\text{kcal/mol})$ by 23.06. A CPCM-H₂O solvation model was chosen based on the results of previous work where the computed reduction potential approximates the experimental values within ~0.2 V to ~0.4 V.

Excited State Calculations (TD-DFT)

Using optimized ground state geometries, single point time dependent density functional theory (TD-DFT) calculations were performed using the rCAM-B3LYP/6-31+G(d,p)/CPCM-

DMA level of theory.⁹ rCAM-B3LYP was chosen because it gave better λ_{max} predictions that are closer to experimental values in comparison to rωB97xd level of theory.¹⁰

Electrostatic Potential (ESP) Calculations

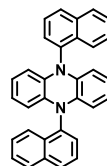
For geometries optimized using uM06/6-31G** (ground state singlets and excited state triplets), single point energy calculations with CHELPG¹¹ ESP population analyses were performed at uM06/6-31G** level of theory using a CPCM-DMAc solvation model. Total electron density of ¹PC and ³PC* were first plotted and then were mapped with ESP derived charges to show distribution of charges on the dihydrophenazine derivatives. Molecular orbitals of ¹PC (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) and molecular orbitals of ³PC* (high lying singly occupied molecular orbitals (SOMOs)) were mapped then visualized.

Molecular Coordinates

All coordinates are reported as XYZ Cartesian coordinates. Energies (E_{0K} (not ZPE and thermally corrected)) are computed at uM06/6-311+G**/CPCM-H2O level of theory and are reported in parentheses. Energies are reported in Hartrees units.

PC 3 – (ground state)

(-1341.480383)



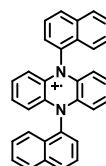
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C	-0.63151100	-9.10764700	-0.06859700
C	2.26948800	-6.87543500	3.15480600
C	2.28550900	-5.72529300	2.33831900
C	3.01109400	-4.61145600	2.74971300
H	3.02034300	-3.72623400	2.11958000
C	3.72686600	-4.61901300	3.94825100
C	3.71954300	-5.75049200	4.74412400
C	2.99120100	00 4.34468700	
H	0.11702900	-5.96660800	-1.09176600
H	0.07489800	- DC6014600	
H	2.97867700	-7.76018800	4.97123800
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N	1.52509800	-7.99878000	2.75210100
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H	4.28518800	-3.73422600	4.24246100
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PC 3 – (radical cation)

(-1341.309566)

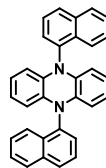
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C	-0.58833300	-9.10851200	-0.05389200
C	2.28701200	-6.89823400	3.12783900
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C	2.95469200	-4.58388100	2.76395600
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PC 3 – (neutral triplet)

(-1341.394364)



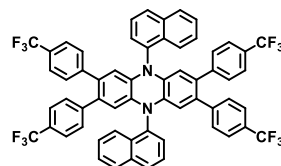
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PC 3a – (ground state)

(-3613.344380)

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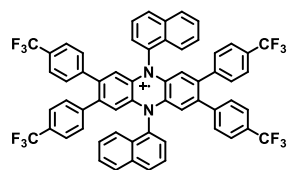
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C	6.45263600	-5.69637100	7.36805400
H	6.32795800	-5.26692400	5.27007600
C	4.39377200	-6.36988200	8.43252100
H	2.66075100	-6.44218900	7.17003800
C	5.75794100	-6.09486500	8.50526000
H	7.51799800	-5.49339600	7.42428700
H	3.85417300	-6.67781700	9.32561900
C	-1.42977800	-10.33645000	-0.37759300

C	-1.23902400	-10.99403400	-1.59764400
C	-2.31417700	-10.89642400	0.55360200
C	-1.91738400	-12.16991100	-1.88735400
H	-0.54266800	-10.58205900	-2.32463100
C	-2.99550800	-12.06950200	0.26978200
H	-2.47861200	-10.39178200	1.50329200
C	-2.79858400	-12.70596500	-0.95409200
H	-1.75685800	-12.67392500	-2.83578000
H	-3.68807400	-12.49099100	0.99518800
C	-1.31436900	-7.89385900	-2.18941200
C	-2.68521900	-8.15839300	-2.28062000
C	-0.63340600	-7.48535700	-3.34378200
C	-3.35737900	-8.03040200	-3.48840300
H	-3.23277500	-8.45987700	-1.39042700
C	-1.29851400	-7.35671100	-4.55275200
H	0.43444200	-7.28431300	-3.29018600
C	-2.66265900	-7.63182200	-4.62556400
H	-4.42272600	-8.23344400	-3.54469200
H	-0.75889800	-7.04869700	-5.44581300
C	6.43993900	-6.25001000	9.82476900
C	6.63810900	0.24633900	5.10014200
C	-3.54271600	-13.97308900	-1.22049300
C	-3.34457500	-7.47679700	-5.94512900
F	6.29997800	1.21036800	4.22787500
F	6.41583400	0.72796800	6.32717300
F	7.96394300	0.07585600	4.97269600
F	7.73692300	-5.92968300	9.77812000
F	5.87240200	-5.47900400	10.76658700
F	6.35823300	-7.51225800	10.27662500
F	-4.86855500	-13.80273800	-1.09295100
F	-3.32047000	-14.45461700	-2.44756900
F	-3.20443300	-14.93714600	-0.34831400
F	-4.64164300	-7.79676900	-5.89844500
F	-2.77722000	-8.24818400	-6.88674900
F	-3.26251300	-6.21467900	-6.39727900

PC 3a – radical cation

(-3613.167923)

C	-0.66910600	-7.99179700	-0.84901300
C	0.09092800	-6.90013500	-0.45864600
C	0.80099000	-6.88948000	0.74542000
C	0.72548400	-8.01732300	1.59726400
C	-0.02121600	-9.12640400	1.18982400
C	-0.70525300	-9.14374200	-0.01576800



C	2.16053100	-6.91404500	3.18500000
C	2.23610400	-5.78624800	2.33310200
C	2.98296000	-4.67724400	2.74046700
H	2.99646200	-3.79269200	2.11018300
C	3.66701600	-4.65992900	3.94604400
C	3.63065200	-5.81175900	4.77942800
C	2.87051300	-6.90336200	4.38911200
H	0.10683600	-6.01393600	-1.08650800
H	-0.03459300	-10.01100100	1.82004200
H	2.85446400	-7.78950300	5.01704200
N	1.55759200	-5.79692700	1.12826900
N	1.40390700	-8.00659300	2.80216400
C	1.64849600	-4.65569100	0.25085500
C	0.69458100	-3.61295800	0.38153600
C	2.65244700	-4.62232600	-0.68301800
C	-0.34766800	-3.62509800	1.33899200
C	0.81250800	-2.50656300	-0.51043600
C	2.75659500	-3.52043300	-1.55588700
H	3.35703300	-5.44868100	-0.74060400
C	-1.23639100	-2.58106700	1.40523100
H	-0.44183200	-4.46563400	2.02349300
C	-0.12306600	-1.44868600	-0.41197500
C	1.85507600	-2.49001100	-1.46866200
H	3.55244100	-3.49744300	-2.29420100
C	-1.12552000	-1.48392700	0.52351100
H	-2.03381300	-2.59802100	2.14337400
H	-0.02844700	-0.60720100	-1.09543700
H	1.92719100	-1.63654100	-2.13989200
H	-1.83877200	-0.66687000	0.59056100
C	1.31298500	-9.14784700	3.67954300
C	0.30897400	-9.18125800	4.61335400
C	2.26691500	-10.19055800	3.54886000
C	0.20478600	-10.28320300	5.48615700
H	-0.39562200	-8.35491300	4.67093500
C	2.14893500	-11.29701100	4.44075500
C	3.30921100	-10.17836300	2.59145700
C	1.10631100	-11.31362000	5.39891700
H	-0.59109100	-10.30623800	6.22443700
C	3.08451400	-12.35488200	4.34228000
C	4.19794300	-11.22238500	2.52521000
H	3.40340700	-9.33778800	1.90700900
H	1.03414200	-12.16713800	6.07008000
C	4.08702500	-12.31958000	3.40685700
H	2.98985200	-13.19641200	5.02568200
H	4.99541400	-11.20537700	1.78712100
H	4.80027600	-13.13663600	3.33978900

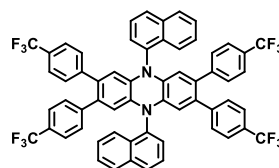
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C	5.22190100	-2.79062200	3.40099500
C	4.17663700	-2.82443600	5.57450600
C	5.86497200	-1.60711400	3.72691600
H	5.39169800	-3.24988000	2.42975700
C	4.81313600	-1.63518800	5.90138100
H	3.50842000	-3.29198200	6.29383800
C	5.65960500	-1.03080000	4.97840800
H	6.53174200	-1.13062700	3.01206100
H	4.64855300	-1.17672600	6.87163800
C	4.40586300	-5.91946900	6.03505400
C	5.76972200	-5.61290200	6.06768800
C	3.78401700	-6.37989100	7.20181500
C	6.49852600	-5.75972200	7.23960500
H	6.26812000	-5.26929600	5.16431900
C	4.50703700	-6.52014200	8.37579900
H	2.72093800	-6.60962300	7.18943800
C	5.86488900	-6.20943300	8.39280800
H	7.55912700	-5.52841300	7.25509500
H	4.01756700	-6.86729700	9.28282200
C	-1.41238000	-10.38757500	-0.39304600
C	-1.21470000	-10.97888600	-1.64464300
C	-2.25945200	-11.01369900	0.52909800
C	-1.85088100	-12.16825100	-1.97173000
H	-0.54680400	-10.51091600	-2.36399700
C	-2.90217600	-12.19733500	0.20298200
H	-2.42919200	-10.55477900	1.50050400
C	-2.69689400	-12.77321700	-1.04872700
H	-1.68636400	-12.62636400	-2.94216300
H	-3.56861300	-12.67428000	0.91784400
C	-1.44446200	-7.88408400	-2.10454800
C	-2.80824200	-8.19103800	-2.13701000
C	-0.82291600	-7.42332400	-3.27132200
C	-3.53726600	-8.04425300	-3.30879200
H	-3.30639400	-8.53493400	-1.23361600
C	-1.54616200	-7.28310300	-4.44517600
H	0.24009900	-7.19328300	-3.25906300
C	-2.90392600	-7.59419100	-4.46202600
H	-4.59780300	-8.27586500	-3.32415900
H	-1.05692800	-6.93567200	-5.35222200
C	6.61152200	-6.38072000	9.67728300
C	6.36528600	0.25062300	5.28913400
C	-3.40241500	-14.05465800	-1.35973300
C	-3.65079500	-7.42292700	-5.74636600
F	5.99617200	1.22896800	4.44804000
F	6.12715500	0.68200800	6.53074700

F	7.69409500	0.12123100	5.15727700
F	7.89629400	-6.02899000	9.57760000
F	6.06949500	-5.64522200	10.65982900
F	6.57662400	-7.65492100	10.09657200
F	-4.73131900	-13.92514000	-1.22888700
F	-3.16340300	-14.48629300	-2.60108700
F	-3.03400100	-15.03286000	-0.51817300
F	-4.93545300	-7.77504000	-5.64654400
F	-3.10870500	-8.15812700	-6.72910000
F	-3.61632300	-6.14865600	-6.16547400

PC 3a – neutral triplet

(-3613.271630)

C	-0.55555200	-7.96619300	-0.88116200
C	0.23542000	-6.89090500	-0.50166200
C	0.90766300	-6.85223700	0.72449100
C	0.76812400	-7.94716400	1.61328200
C	-0.02003000	-9.03482500	1.22268600
C	-0.67358300	-9.07648700	-0.00081600
C	2.21346300	-6.85301700	3.21652300
C	2.35131400	-5.72700900	2.30756000
C	3.09474900	-4.62990800	2.71119900
H	3.08645500	-3.74957100	2.07426000
C	3.73830600	-4.56098100	3.95063200
C	3.75246700	-5.78126900	4.78675000
C	2.92125200	-6.83954400	4.40794900
H	0.30668100	-6.03272100	-1.16468300
H	-0.09161500	-9.89331100	1.88535100
H	2.90571900	-7.73860100	5.01822000
N	1.68884200	-5.76961300	1.09241300
N	1.42279400	-7.92341900	2.83312800
C	1.79723900	-4.64853200	0.19953200
C	0.83893900	-3.60457600	0.29128200
C	2.81977700	-4.61653800	-0.71386900
C	-0.22045300	-3.60891800	1.23027700
C	0.96630900	-2.50905900	-0.61225300
C	2.93645700	-3.52617400	-1.60074200
H	3.53080800	-5.43902500	-0.74420700
C	-1.11671300	-2.57022700	1.26775400
H	-0.31643600	-4.44228800	1.92312300
C	0.02196300	-1.45571800	-0.54523300
C	2.02824200	-2.49910600	-1.54922000
H	3.74783400	-3.50893000	-2.32264000
C	-0.99697100	-1.48440000	0.37248400



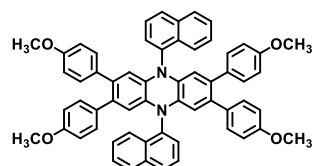
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H	-1.71620000	-0.67072100	0.41531700
C	1.30221400	-9.04931000	3.71836900
C	0.31189100	-9.05120600	4.66713400
C	2.22231900	-10.12348000	3.59070800
C	0.18504600	-10.14437100	5.54911500
H	-0.36676500	-8.20347900	4.72815700
C	2.08391000	-11.22242500	4.48841700
C	3.25649500	-10.14413500	2.62419700
C	1.05272400	-11.20330500	5.45897000
H	-0.60248400	-10.13901100	6.29711500
C	2.98848300	-12.30717500	4.38397400
C	4.11550700	-11.21207500	2.55203500
H	3.36477200	-9.30509900	1.94004700
H	0.96232700	-12.05047400	6.13621200
C	3.98183600	-12.30366400	3.43824500
H	2.87750800	-13.14337000	5.07182300
H	4.90695700	-11.21941700	1.80709600
H	4.67085000	-13.14114500	3.36703400
C	4.23287000	-3.27441700	4.40717000
C	4.72537500	-2.31176100	3.49326000
C	4.21183600	-2.90908900	5.77300000
C	5.15812100	-1.07151600	3.91462800
H	4.79920200	-2.56308000	2.43747400
C	4.63476600	-1.66055700	6.19468200
H	3.82220800	-3.60956100	6.50666400
C	5.11413200	-0.73163700	5.27213100
H	5.54580400	-0.35613600	3.19167900
H	4.58511200	-1.40087300	7.24867400
C	4.68064600	-5.98292400	5.88521600
C	5.96439800	-5.39071700	5.89131000
C	4.35168200	-6.81413800	6.98262300
C	6.86559800	-5.62792000	6.91423700
H	6.26592200	-4.76256600	5.05743300
C	5.24539400	-7.04097100	8.00908000
H	3.36046000	-7.25863600	7.04036700
C	6.51527500	-6.45223100	7.98296400
H	7.85371200	-5.17702700	6.87982700
H	4.96025500	-7.67242700	8.84840900
C	-1.41843900	-10.30740800	-0.34487700
C	-1.22307400	-10.95825900	-1.56820500
C	-2.30899400	-10.86836000	0.57983400
C	-1.89955900	-12.13328000	-1.86424200
H	-0.52390300	-10.54466300	-2.29143500

C	-2.98921500	-12.03994400	0.28795400
H	-2.48049200	-10.36551600	1.52911500
C	-2.78559100	-12.67204500	-0.93699600
H	-1.73466700	-12.63386700	-2.81363400
H	-3.68668200	-12.46278400	1.00768400
C	-1.27736600	-7.87382200	-2.16897600
C	-2.64837600	-8.14061200	-2.25643800
C	-0.59645300	-7.47100200	-3.32534900
C	-3.32172600	-8.01466500	-3.46339300
H	-3.19581400	-8.43904800	-1.36524500
C	-1.26363900	-7.34584900	-4.53342200
H	0.47194100	-7.27261900	-3.27469400
C	-2.62822400	-7.61905300	-4.60251900
H	-4.38731900	-8.21656700	-3.51751500
H	-0.72529800	-7.04038900	-5.42793800
C	7.43920800	-6.69443100	9.12206100
C	5.60827400	0.60715300	5.68817700
C	-3.52930900	-13.93802600	-1.21221800
C	-3.30849200	-7.48951100	-5.92615000
F	4.99449600	1.59996100	5.01775300
F	5.42879200	0.84432000	6.99338000
F	6.92338200	0.76062000	5.43944900
F	8.66769500	-6.20802800	8.90588200
F	6.99327700	-6.13448900	10.26365100
F	7.57403600	-8.00628000	9.38949400
F	-4.85505300	-13.76774100	-1.08681500
F	-3.30373600	-14.41242300	-2.44123200
F	-3.19247600	-14.90603000	-0.34428000
F	-4.62616800	-7.70083500	-5.85304000
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PC 3b – ground state

(-2723.174535)

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C	0.81039100	-8.05157100	1.54239900
C	0.11610300	-9.16664900	1.09497200
C	-0.62983900	-9.17060500	-0.09412600
C	2.26854300	-6.94326900	3.15627400
C	2.25040600	-5.77458000	2.37025400
C	2.94471100	-4.65951000	2.81767200
H	2.88289800	-3.73926600	2.24108500



C	3.69068100	-4.65556100	4.00675600
C	3.75337900	-5.83637000	4.76102700
C	3.02663200	-6.95289300	4.31866100
H	-0.02691500	-5.95320700	-0.98296100
H	0.17792100	-10.08689300	1.67155800
H	3.08770000	-7.87293400	4.89563200
N	1.51954100	-5.75635900	1.17195300
N	1.54113900	-8.06974100	2.74076500
C	1.60060700	-4.61759700	0.31556000
C	0.64638900	-3.57084600	0.44577000
C	2.59915700	-4.55004100	-0.62546800
C	-0.39546300	-3.60347800	1.40390100
C	0.75171000	-2.44969600	-0.42924900
C	2.69823200	-3.43725100	-1.48625800
H	3.31092100	-5.37007200	-0.69535300
C	-1.29427900	-2.56946500	1.48940700
H	-0.47000000	-4.46129200	2.06920300
C	-0.19305500	-1.40089800	-0.31318200
C	1.79269600	-2.41122900	-1.38879500
H	3.49409800	-3.40010300	-2.22515600
C	-1.19385600	-1.45793700	0.62338200
H	-2.09085200	-2.60360400	2.22848300
H	-0.10753700	-0.54789200	-0.98417300
H	1.85940700	-1.54836700	-2.04916700
H	-1.91372200	-0.64732900	0.70337200
C	1.46007800	-9.20851300	3.59714300
C	0.46146700	-9.27603500	4.53811000
C	2.41425900	-10.25530600	3.46698200
C	0.36226300	-10.38882000	5.39888500
H	-0.25026300	-8.45596900	4.60794300
C	2.30879600	-11.37646300	4.34198200
C	3.45618900	-10.22273200	2.50893400
C	1.26774300	-11.41489200	5.30145800
H	-0.43366100	-10.42592800	6.13772200
C	3.25349200	-12.42532600	4.22597000
C	4.35494000	-11.25681000	2.42348800
H	3.53084900	-9.36491700	1.84364600
H	1.20095000	-12.27776900	5.96180200
C	4.25436800	-12.36834400	3.28948300
H	3.16786300	-13.27834000	4.89693800
H	5.15157500	-11.22271400	1.68447600
H	4.97418200	-13.17900300	3.20953500
C	4.32462100	-3.38309400	4.42128200
C	5.05579200	-2.61676000	3.51265600
C	4.16804500	-2.87601000	5.72062800
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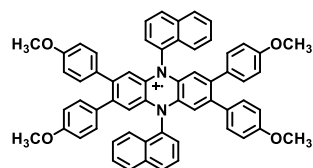
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C	5.45775600	-0.91394500	5.16582000
H	6.19171500	-0.83637700	3.12994700
H	4.59435500	-1.26828900	7.09464200
C	4.58691700	-5.98976300	5.97534400
C	5.93339600	-5.59414900	5.99505200
C	4.07145800	-6.58414700	7.12793000
C	6.71966200	-5.77953000	7.11705700
H	6.36877700	-5.14038700	5.10676500
C	4.84839200	-6.77740100	8.26857900
H	3.02776000	-6.89474500	7.14412300
C	6.18218700	-6.37199800	8.26536900
H	7.76521800	-5.48085200	7.12887700
H	4.40267400	-7.23687900	9.14559300
C	-1.26377000	-10.44306500	-0.50868900
C	-1.10705600	-10.95018200	-1.80799700
C	-1.99511400	-11.20932900	0.39986300
C	-1.66217000	-12.16118500	-2.17778300
H	-0.53045600	-10.38243300	-2.53584300
C	-2.56312500	-12.43133000	0.04454300
H	-2.13945600	-10.83763300	1.41330700
C	-2.39699700	-12.91213500	-1.25333500
H	-1.53332500	-12.55789100	-3.18204900
H	-3.13120100	-12.98963300	0.78245000
C	-1.52609400	-7.83640100	-2.06271800
C	-2.87254800	-8.23198700	-2.08242900
C	-1.01058600	-7.24200800	-3.21530200
C	-3.65879700	-8.04666000	-3.20448300
H	-3.30794800	-8.68569000	-1.19412200
C	-1.78747900	-7.04879500	-4.35596500
H	0.03310900	-6.93140200	-3.23142100
C	-3.12128700	-7.45423700	-4.35278400
H	-4.70436100	-8.34529700	-3.21626900
H	-1.34180300	-6.58925800	-5.23296900
O	5.96201000	0.25903700	5.62393400
O	7.03240100	-6.50920800	9.31336500
O	-2.90134700	-14.08505400	-1.71152200
O	-3.97147300	-7.31700000	-5.40080600
C	6.70143600	1.05318100	4.71965200
H	7.59421200	0.52680600	4.35671300
H	6.09216700	1.35716300	3.85806000
H	7.01125900	1.94334700	5.26941200
C	6.53301500	-7.11199700	10.48907600
H	5.70457800	-6.53351100	10.91909500

H	6.19141700	-8.13881200	10.30227800
H	7.35920700	-7.13494700	11.20148400
C	-3.64083900	-14.87922800	-0.80732900
H	-3.03160000	-15.18333700	0.05423700
H	-4.53359900	-14.35284700	-0.44436200
H	-3.95071100	-15.76932800	-1.35717400
C	-3.47209300	-6.71416100	-6.57649900
H	-2.64368400	-7.29268800	-7.00656000
H	-3.13047100	-5.68738500	-6.38965900
H	-4.29828600	-6.69123400	-7.28890500

PC 3b – radical cation

(-2723.007417)

C	-0.66955200	-7.96878000	-0.84112900
C	0.06362600	-6.86650100	-0.42172400
C	0.81542700	-6.87900600	0.75507200
C	0.80357200	-8.04094200	1.56294900
C	0.09663800	-9.16209200	1.12364500
C	-0.62134900	-9.16338900	-0.06505800
C	2.24528200	-6.94713700	3.15756600
C	2.25713700	-5.78520100	2.34968900
C	2.96407600	-4.66405400	2.78899000
H	2.91248600	-3.75017600	2.20401200
C	3.68206600	-4.66275700	3.97769100
C	3.73026900	-5.85736700	4.75376200
C	2.99708800	-6.95964400	4.33435900
H	0.01597600	-5.95023200	-1.00334200
H	0.14823000	-10.07597000	1.70862200
H	3.04473900	-7.87591400	4.91597500
N	1.54805500	-5.77617000	1.16045700
N	1.51265500	-8.04997400	2.75218000
C	1.61524200	-4.61884300	0.30521700
C	0.65285100	-3.58689400	0.45788400
C	2.61286500	-4.55630700	-0.63419800
C	-0.38466300	-3.62652500	1.42000600
C	0.75544600	-2.46283100	-0.41403100
C	2.70267300	-3.43829000	-1.48777400
H	3.32553900	-5.37433500	-0.71025900
C	-1.28311600	-2.59266100	1.51027800
H	-0.46520200	-4.48193500	2.08771000
C	-0.18961900	-1.41591200	-0.29096900
C	1.79255700	-2.41787700	-1.37725800
H	3.49447100	-3.39433700	-2.22965900
C	-1.18689000	-1.47810300	0.64860800



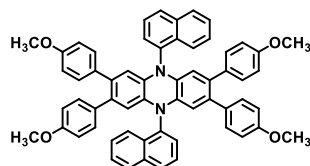
H	-2.07678700	-2.63092600	2.25176700
H	-0.10671800	-0.56076600	-0.95891500
H	1.85298200	-1.55117100	-2.03261300
H	-1.90745400	-0.66916900	0.73455600
C	1.44548100	-9.20730500	3.60741500
C	0.44786700	-9.26985500	4.54683700
C	2.40787900	-10.23924500	3.45473400
C	0.35807600	-10.38787900	5.40040800
H	-0.26481400	-8.45183400	4.62290900
C	2.30530300	-11.36331400	4.32664300
C	3.44538400	-10.19959700	2.49260200
C	1.26820100	-11.40828200	5.28987900
H	-0.43371500	-10.43184300	6.14230000
C	3.25037800	-12.41022200	4.20356700
C	4.34384600	-11.23345300	2.40231700
H	3.52590900	-9.34418300	1.82490300
H	1.20779000	-12.27499200	5.94522900
C	4.24763900	-12.34801600	3.26398100
H	3.16749100	-13.26537300	4.87150900
H	5.13751000	-11.19517500	1.66082100
H	4.96821100	-13.15694300	3.17802300
C	4.32254700	-3.40206900	4.40110900
C	5.04380400	-2.62906300	3.48902800
C	4.17564000	-2.91181200	5.70897400
C	5.61502800	-1.41329600	3.85172900
H	5.18381300	-2.99331300	2.47270900
C	4.72666100	-1.70171400	6.08082000
H	3.60635000	-3.48532000	6.43730800
C	5.45468400	-0.94287700	5.15556700
H	6.18050000	-0.84994400	3.11622400
H	4.60343700	-1.31169000	7.08792200
C	4.56242900	-5.99475600	5.96509000
C	5.90399400	-5.57978000	5.98017300
C	4.04990100	-6.59711800	7.11569900
C	6.69205800	-5.76245700	7.09905100
H	6.33494900	-5.12117400	5.09280400
C	4.82792300	-6.77735300	8.25508700
H	3.00892000	-6.91527500	7.13395700
C	6.15926000	-6.35955600	8.24864900
H	7.73476200	-5.45554300	7.11041600
H	4.38703200	-7.23671200	9.13413300
C	-1.26182500	-10.42407800	-0.48847900
C	-1.11491900	-10.91432800	-1.79634700
C	-1.98307800	-11.19709100	0.42359900
C	-1.66593500	-12.12442700	-2.16819800
H	-0.54563300	-10.34081400	-2.52467900

C	-2.55429700	-12.41285900	0.06089400
H	-2.12308700	-10.83284600	1.43992000
C	-2.39395300	-12.88327100	-1.24294600
H	-1.54271200	-12.51444600	-3.17530200
H	-3.11976600	-12.97621600	0.79639600
C	-1.50170600	-7.83139500	-2.05246200
C	-2.84326700	-8.24638300	-2.06755300
C	-0.98917600	-7.22902900	-3.20306700
C	-3.63132600	-8.06371100	-3.18643600
H	-3.27422400	-8.70499400	-1.18018700
C	-1.76719300	-7.04879900	-4.34245900
H	0.05180300	-6.91086400	-3.22131800
C	-3.09852600	-7.46660600	-4.33602900
H	-4.67402700	-8.37063300	-3.19780700
H	-1.32630000	-6.58943600	-5.22150200
O	5.95862500	0.22280600	5.61793900
O	7.00834600	-6.48664000	9.29242600
O	-2.89789000	-14.04895400	-1.70532300
O	-3.94760700	-7.33952800	-5.37981200
C	6.69267300	1.03023700	4.71771700
H	7.58476500	0.50936300	4.34685500
H	6.07696700	1.34116400	3.86389000
H	7.00138000	1.91423600	5.27727600
C	6.51981900	-7.09276300	10.47354100
H	5.68849400	-6.52026800	10.90468600
H	6.18918800	-8.12294300	10.28875000
H	7.35038600	-7.10473800	11.18058100
C	-3.63191800	-14.85639900	-0.80509700
H	-3.01620100	-15.16731700	0.04872500
H	-4.52401700	-14.33554200	-0.43422800
H	-3.94061400	-15.74040300	-1.36465500
C	-3.45907900	-6.73339300	-6.56092000
H	-2.62774800	-7.30587800	-6.99206600
H	-3.12845600	-5.70321200	-6.37611900
H	-4.28964400	-6.72141800	-7.26796300

PC 3b – neutral triplet

(-2723.094158)

C	-0.59033900	-7.99113900	-0.87037500
C	0.18686200	-6.91121900	-0.47051700
C	0.88822700	-6.89156000	0.73992100
C	0.78896000	-8.01495500	1.60045000
C	0.02287300	-9.10993400	1.18691600
C	-0.65817900	-9.13535100	-0.02372400



C	2.23980700	-6.93265700	3.21463400
C	2.32944700	-5.77004200	2.33592800
C	3.03873000	-4.66016700	2.77128800
H	2.98863500	-3.75644200	2.16826400
C	3.70084700	-4.61051700	3.99990400
C	3.77321100	-5.86405200	4.79666500
C	2.97410300	-6.93589900	4.39140600
H	0.21868600	-6.02972100	-1.10613300
H	-0.01001700	-9.99238700	1.82119600
H	3.00136500	-7.85587000	4.97071000
N	1.65589200	-5.80245000	1.12506000
N	1.46270400	-8.00764600	2.81260300
C	1.75228300	-4.67115300	0.24799400
C	0.78622800	-3.63490300	0.34809600
C	2.77406300	-4.61762800	-0.66575600
C	-0.27305000	-3.65876100	1.28713000
C	0.90313500	-2.52869100	-0.54399700
C	2.88188100	-3.51769400	-1.54170000
H	3.49236600	-5.43353200	-0.70459300
C	-1.17943500	-2.62924600	1.33606900
H	-0.35822800	-4.50181500	1.96963900
C	-0.05162800	-1.48512300	-0.46581200
C	1.96466700	-2.49885800	-1.48071900
H	3.69320800	-3.48601500	-2.26341500
C	-1.07004600	-1.53304100	0.45163900
H	-1.98910600	-2.65532800	2.06087800
H	0.04155700	-0.64377000	-1.15016100
H	2.03883400	-1.64713300	-2.15438900
H	-1.79708000	-0.72666500	0.50282500
C	1.35501900	-9.14434400	3.68132800
C	0.36726400	-9.16814800	4.63297700
C	2.28100700	-10.21191200	3.54063200
C	0.24888400	-10.27300800	5.50127800
H	-0.31743400	-8.32609700	4.70590400
C	2.15301500	-11.32353300	4.42446700
C	3.31342900	-10.21222000	2.57185000
C	1.12376000	-11.32504700	5.39693400
H	-0.53771100	-10.28288200	6.25046000
C	3.06621100	-12.39978100	4.30398200
C	4.18118000	-11.27199100	2.48389200
H	3.41066300	-9.36202000	1.89988900
H	1.04068500	-12.18162300	6.06336100
C	4.05770100	-12.37604700	3.35664200
H	2.96343000	-13.24596600	4.98095500
H	4.97133900	-11.26367800	1.73746400
H	4.75326100	-13.20713500	3.27342900

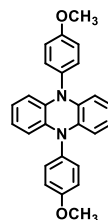
C	4.15894300	-3.32343400	4.50290800
C	4.62677000	-2.31527900	3.63816300
C	4.11942700	-3.00057200	5.87969200
C	5.01923600	-1.06369900	4.09544400
H	4.71353300	-2.52445300	2.57324900
C	4.50085900	-1.75726600	6.34523500
H	3.75062200	-3.73783700	6.58864000
C	4.95774100	-0.77402800	5.46065400
H	5.38330900	-0.32966600	3.38233500
H	4.44712100	-1.51572200	7.40465800
C	4.72738400	-6.06161500	5.87774900
C	5.99166700	-5.42615400	5.88698200
C	4.45709500	-6.92906900	6.95398100
C	6.91466100	-5.65974100	6.88764800
H	6.25765700	-4.75858700	5.07101300
C	5.37496500	-7.16667100	7.96897300
H	3.48454100	-7.41433700	7.01662200
C	6.61820100	-6.52999200	7.94245100
H	7.89021700	-5.17840500	6.87244900
H	5.10525900	-7.83662200	8.78030100
C	-1.37970000	-10.37357200	-0.38872900
C	-1.22665700	-10.97402600	-1.64900000
C	-2.20557700	-11.01469400	0.53664700
C	-1.87167300	-12.15556700	-1.96282200
H	-0.58055600	-10.50623400	-2.38925800
C	-2.86492100	-12.20429900	0.23647300
H	-2.35365500	-10.56485700	1.51717300
C	-2.69893200	-12.78040400	-1.02233200
H	-1.74550700	-12.62554100	-2.93525300
H	-3.50458600	-12.66284600	0.98443600
C	-1.34866000	-7.87166800	-2.13428600
C	-2.71500900	-8.18788700	-2.20775400
C	-0.73411200	-7.38793300	-3.29083300
C	-3.42536400	-8.02801000	-3.38259500
H	-3.22702100	-8.55635300	-1.32097800
C	-1.43410400	-7.22296500	-4.48368600
H	0.32755000	-7.14701400	-3.26703400
C	-2.78964400	-7.54566200	-4.53261600
H	-4.48558000	-8.26350300	-3.43671400
H	-0.91271900	-6.85206800	-5.36084000
O	5.31852800	0.41236700	6.01878900
O	7.58892400	-6.68366400	8.88232900
O	-3.28952000	-13.93202400	-1.42639400
O	-3.57015400	-7.42838500	-5.63504000
C	5.77836700	1.42749000	5.15337400
H	6.68791200	1.12253900	4.61811000

H	5.01272200	1.71011600	4.41803200
H	6.00704400	2.29176400	5.77937700
C	7.32287100	-7.55591500	9.95900500
H	6.46002000	-7.21924400	10.54968700
H	7.13669100	-8.58173400	9.61280200
H	8.21150600	-7.54994900	10.59261600
C	-4.12919200	-14.59733300	-0.50545400
H	-3.58056200	-14.89647300	0.39748100
H	-4.98306400	-13.97182500	-0.21331000
H	-4.49826200	-15.49093300	-1.01118500
C	-2.96861000	-6.93949500	-6.81611700
H	-2.15597500	-7.59512400	-7.15607400
H	-2.57344700	-5.92445700	-6.67710800
H	-3.75069100	-6.91701300	-7.57659600

PC 4 – ground state

(-1263.349137)

C	-0.41653400	-7.87943900	-0.76039800
C	0.31590200	-6.76128700	-0.35521000
C	1.07631300	-6.78310400	0.80979400
C	1.10762000	-7.96097600	1.58713100
C	0.38134900	-9.07135400	1.16805200
C	-0.38333000	-9.03411300	-0.00007200
C	2.73085600	-6.92276900	3.09362300
C	2.70180900	-5.74556700	2.31461600
C	3.55222600	-4.69392200	2.64127800
H	3.52490100	-3.78729400	2.04332600
C	4.42597300	-4.78311100	3.72733600
C	4.45375300	-5.93533900	4.49124300
C	3.60959100	-7.00051400	4.16989500
H	0.28732700	-5.85264400	-0.95011200
H	0.40708400	-9.97547100	1.77027200
H	3.62835200	-7.90372500	4.77325700
N	1.79362900	-5.65437900	1.24455100
N	1.85555800	-7.97627700	2.77738200
C	1.82028100	-9.13278100	3.61145500
C	2.73694200	-10.17092500	3.42768500
C	0.86751600	-9.23146000	4.61753900
C	2.69848100	-11.28741000	4.24397100
H	3.48256200	-10.08699700	2.63913300
C	0.81568100	-10.35079700	5.44404000
H	0.15576300	-8.41976900	4.75303400
C	1.73653000	-11.38340000	5.25741000
H	0.06238900	-10.40732300	6.22371500

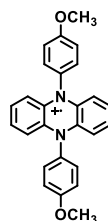


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C	0.80569000	-3.48091300	0.74945500
C	2.63975500	-4.27181500	-0.59430100
C	0.73632700	-2.31592100	-0.01056700
H	0.11499200	-3.63619100	1.57552700
C	2.58310800	-3.11839500	-1.35572700
H	3.37625100	-5.04340100	-0.81113100
C	1.62841100	-2.13451600	-1.06885800
H	3.26636300	-2.95227300	-2.18452300
H	-0.94744300	-9.91423100	-0.29772900
H	-1.00757100	-7.82921800	-1.67121200
H	5.07400500	-3.94266500	3.96193900
H	5.12503300	-6.02409900	5.34147100
H	3.40425200	-12.10446000	4.11895000
H	-0.00943200	-1.56344400	0.22663600
O	1.77901400	-12.51217600	6.00240100
O	1.64883600	-1.04602400	-1.87245700
C	0.83060300	-12.65101900	7.04167400
H	-0.19600800	-12.64298600	6.65318900
H	1.02653500	-13.61508100	7.51319500
H	0.93665100	-11.85547900	7.79066300
C	0.68868000	-0.03541900	-1.63650200
H	0.85545100	0.73320500	-2.39244100
H	-0.33362700	-0.42265900	-1.73642000
H	0.80827800	0.40833600	-0.63947300

PC 4 – radical cation

(-1263.181369)

C	-0.51661300	-7.80326800	-0.67567200
C	0.25298100	-6.71540100	-0.32235400
C	1.06441900	-6.76614800	0.82134500
C	1.07994500	-7.94511300	1.61085000
C	0.28973400	-9.04049200	1.23104900
C	-0.49743100	-8.96894800	0.10155700
C	2.66966400	-6.91893100	3.10925600
C	2.65790900	-5.74175700	2.31695700
C	3.46427600	-4.65413000	2.68494200
H	3.45490100	-3.75548900	2.07752100
C	4.26085100	-4.73026700	3.80751800
C	4.27058500	-5.89135600	4.59165300
C	3.48583400	-6.97190100	4.24948200
H	0.23781900	-5.81367500	-0.92505400
H	0.30524900	-9.94161400	1.83472200
H	3.49388300	-7.86979500	4.85793800

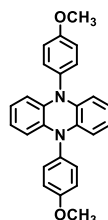


N	1.84613400	-5.68775300	1.19735800
N	1.87241900	-7.98991400	2.74456600
C	1.84843200	-9.16456200	3.57844300
C	2.78168200	-10.17890400	3.37255000
C	0.90049800	-9.26129200	4.58685500
C	2.75989400	-11.29502000	4.18816700
H	3.51871000	-10.08260200	2.57863600
C	0.87400200	-10.38225300	5.40868400
H	0.18195100	-8.45748500	4.73040500
C	1.80785300	-11.40318900	5.21110800
H	0.12876800	-10.44834900	6.19445500
C	1.80444500	-4.48120500	0.41107000
C	0.87764400	-3.49754300	0.72389100
C	2.68328700	-4.32467900	-0.65933200
C	0.81595200	-2.33580700	-0.03762700
H	0.20137900	-3.64213700	1.56321400
C	2.62566500	-3.17134900	-1.41922600
H	3.40131400	-5.10859300	-0.88860800
C	1.69161200	-2.17190000	-1.11457700
H	3.29440300	-3.01777300	-2.26131400
H	-1.10410200	-9.82343000	-0.18201800
H	-1.13961200	-7.75161400	-1.56324200
H	4.88129100	-3.88241800	4.08095900
H	4.89867400	-5.94552700	5.47546600
H	3.47436400	-12.10243000	4.05555200
H	0.08731200	-1.57158900	0.21235700
O	1.87160500	-12.52698500	5.95223800
O	1.71324600	-1.08969200	-1.91745000
C	0.93797000	-12.68239800	7.00586500
H	-0.09229400	-12.69336200	6.62897500
H	1.15893900	-13.64264500	7.47312800
H	1.04230200	-11.88491100	7.75221700
C	0.77579400	-0.05789400	-1.66765000
H	0.94610800	0.70356900	-2.42943900
H	-0.25427900	-0.42668800	-1.74990900
H	0.92365000	0.38518600	-0.67472200

PC 4 – neutral triplet

(-1263.259559)

C	-0.55131200	-7.80770100	-0.67516600
C	0.20972400	-6.72148600	-0.31762800
C	1.04470100	-6.75479600	0.81841200
C	1.07414900	-7.96304500	1.62548800
C	0.28756900	-9.06419100	1.22868000



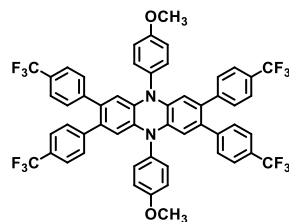
C	-0.50757000	-9.00552200	0.11027200
C	2.65229000	-6.91507900	3.13472200
C	2.64514900	-5.71737200	2.31141000
C	3.46353400	-4.63151300	2.68545000
H	3.46461600	-3.73895200	2.06509300
C	4.24936400	-4.68614400	3.81059800
C	4.24481300	-5.86103800	4.63099700
C	3.46309400	-6.93720800	4.28821200
H	0.17582200	-5.81580100	-0.91757400
H	0.31735900	-9.97089200	1.82750300
H	3.46540900	-7.82800700	4.91087900
N	1.83205400	-5.68543000	1.19605400
N	1.86646300	-7.98512200	2.75587800
C	1.85350300	-9.15618200	3.58416600
C	2.80301000	-10.15651600	3.38971900
C	0.89631200	-9.27797500	4.58017300
C	2.78977000	-11.28017500	4.19927500
H	3.54864200	-10.04271800	2.60588800
C	0.87452300	-10.40469000	5.39810400
H	0.16315900	-8.48571100	4.71560700
C	1.82622900	-11.40924900	5.20738500
H	0.11947200	-10.48688900	6.17321300
C	1.79384300	-4.49035000	0.40375700
C	0.90532200	-3.47841700	0.73410000
C	2.63953800	-4.35963700	-0.69535800
C	0.84941300	-2.31675400	-0.03220600
H	0.25381900	-3.60111700	1.59649600
C	2.58966800	-3.20901500	-1.46424100
H	3.32757900	-5.16567800	-0.94039100
C	1.69454100	-2.18306600	-1.13632500
H	3.23516200	-3.07823900	-2.32844900
H	-1.10336100	-9.86817000	-0.17477500
H	-1.18527200	-7.75568600	-1.55595900
H	4.87189200	-3.83633500	4.07634800
H	4.86087500	-5.90475300	5.52484400
H	3.51843600	-12.07615500	4.07193100
H	0.14982500	-1.53147200	0.23575100
O	1.89675900	-12.54048800	5.94502000
O	1.72097800	-1.10181700	-1.94813100
C	0.95057300	-12.71254900	6.98203700
H	-0.07449000	-12.73802400	6.59062700
H	1.17762600	-13.67046900	7.45194800
H	1.02909200	-11.91542400	7.73253100
C	0.82975900	-0.04100400	-1.66429500
H	0.99862600	0.71808400	-2.42926000
H	-0.21580700	-0.37180400	-1.71041400

H	1.02477100	0.39432200	-0.67564300
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PC 4a – ground state

(-3535.213942)

C	-9.32889400	-3.09819400	-0.97163000
C	-8.71760300	-2.89942300	0.27577600
C	-7.57698600	-3.58577600	0.66703400
C	-7.02175100	-4.53679100	-0.21412900
C	-7.61220500	-4.72103200	-1.45617500
C	-8.75288300	-4.01253600	-1.86312500
C	-5.29012000	-5.04302400	1.42458400
C	-5.83877400	-4.08401700	2.30120700
C	-5.21961000	-3.86527300	3.52338900
H	-5.61106900	-3.08888800	4.17594300
C	-4.07992200	-4.57493200	3.93147400
C	-3.55979600	-5.55682000	3.07833300
C	-4.17590400	-5.76141100	1.83420500
H	-9.17609000	-2.20552600	0.97591800
H	-7.15258600	-5.41481700	-2.15568800
H	-3.78425000	-6.53628100	1.17987900
C	-7.51340700	-2.36863000	2.78548500
C	-8.43065900	-2.71442500	3.76978400
C	-7.11497500	-1.03777200	2.64601900
C	-8.95625700	-1.74674400	4.62147000
H	-8.73400600	-3.75459100	3.87031300
C	-7.63350200	-0.06675700	3.48367300
H	-6.39706000	-0.77601600	1.87135500
C	-8.55683400	-0.41617600	4.47699000
H	-9.67049200	-2.03830000	5.38488800
H	-7.33921800	0.97548700	3.39252100
C	-5.31151600	-6.20884400	-0.72378900
C	-5.77669800	-7.52488600	-0.74199600
C	-4.28570400	-5.82796000	-1.57985900
C	-5.21806300	-8.44590300	-1.61037000
H	-6.58089000	-7.81434900	-0.06866100
C	-3.71342100	-6.74639100	-2.45522300
H	-3.93017000	-4.79973600	-1.55665800
C	-4.18206300	-8.06218700	-2.47082500
H	-2.91200300	-6.42772000	-3.11399500
H	-5.56411200	-9.47566300	-1.64247200
N	-6.97968200	-3.36781100	1.91579100
N	-5.88515500	-5.25801300	0.17424300
C	-3.46119300	-4.19672700	5.22177400
C	-4.25113300	-4.04788600	6.36593500



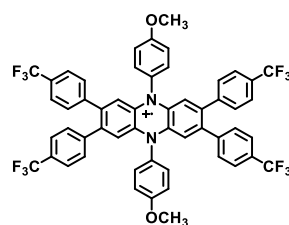
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C	-3.69268000	-3.65511500	7.57643800
H	-5.31714700	-4.25793500	6.30898000
C	-1.52548900	-3.53815100	6.52085900
H	-1.46110200	-4.02279700	4.43409100
C	-2.32886100	-3.40178000	7.65336500
H	-4.31722800	-3.55085600	8.45873500
H	-0.46029600	-3.32597400	6.58433600
C	-2.42329700	-6.43359100	3.43832100
C	-1.38081900	-6.64798200	2.52694000
C	-2.38128400	-7.09851900	4.66889000
C	-0.32436700	-7.48853400	2.84096000
H	-1.39538800	-6.13275500	1.56878600
C	-1.32636100	-7.94161500	4.98928200
H	-3.19213100	-6.95859600	5.38019900
C	-0.29533500	-8.13395400	4.07569900
H	0.48584100	-7.64027500	2.13095800
H	-1.30840500	-8.45468400	5.94626900
C	-9.24551500	-4.23363600	-3.24106900
C	-9.41046200	-5.53225200	-3.73265900
C	-9.51052700	-3.15549500	-4.09775500
C	-9.83806100	-5.75614100	-5.03589000
H	-9.21520100	-6.37892600	-3.07781600
C	-9.93552000	-3.37182600	-5.39724000
H	-9.36884300	-2.13891300	-3.73783600
C	-10.10164800	-4.67481300	-5.86752000
H	-9.96963300	-6.77020000	-5.40168500
H	-10.13092000	-2.52933200	-6.05726400
C	-10.58640100	-2.36851200	-1.24776700
C	-11.72181000	-3.03734900	-1.72782800
C	-10.67999500	-0.99757800	-0.98863100
C	-12.90499000	-2.35421700	-1.94998300
H	-11.67241900	-4.10735900	-1.91667000
C	-11.86470600	-0.30581200	-1.21055400
H	-9.80588600	-0.46294200	-0.62272000
C	-12.97667300	-0.98473300	-1.69312400
H	-13.78264000	-2.88311000	-2.31559200
H	-11.92065200	0.76063000	-1.01317900
C	-14.26985000	-0.28420500	-1.95083300
C	0.85654400	-9.03562100	4.37579500
C	-1.68226200	-2.97701800	8.93043100
C	-10.56993100	-4.86416000	-7.27271700
F	0.91265600	-10.06810500	3.51828400
F	2.02945300	-8.39182500	4.26170900
F	0.80396600	-9.54846400	5.60924600
F	-0.73228700	-3.84497600	9.31536000

F	-1.07108300	-1.78794900	8.80142400
F	-2.55162300	-2.86845700	9.94008400
F	-11.78621300	-4.32706900	-7.46391800
F	-9.75277400	-4.25966600	-8.15049200
F	-10.64669800	-6.15173800	-7.62379100
F	-14.63572400	-0.38172800	-3.23957900
F	-14.22177900	1.01751100	-1.65036300
F	-15.27266500	-0.82111600	-1.23663800
O	-3.70100900	-9.03459200	-3.27747000
O	-9.00380500	0.60255000	5.24520000
C	-9.94079700	0.30389000	6.26186700
H	-10.86468900	-0.11773100	5.84537300
H	-9.52557700	-0.39658700	6.99788500
H	-10.17025700	1.24837900	6.75699700
C	-2.65016200	-8.70124700	-4.16366600
H	-2.95558400	-7.92230400	-4.87410000
H	-1.75852700	-8.36283500	-3.62025400
H	-2.40963000	-9.61214000	-4.71345700

PC 4a – radical cation

(-3535.039672)

C	-8.37507200	-6.24385700	3.38951100
C	-7.94176600	-4.93899300	3.21394400
C	-7.11234400	-4.57302200	2.14957000
C	-6.67531800	-5.57165600	1.24526000
C	-7.14053900	-6.88009400	1.40606700
C	-7.98811600	-7.23383100	2.44419500
C	-5.40212700	-3.92349900	0.04087000
C	-5.86506200	-2.91934300	0.92582000
C	-5.48103300	-1.59322600	0.70463400
H	-5.89128600	-0.81468100	1.34072700
C	-4.63694300	-1.23905700	-0.33619400
C	-4.11261800	-2.25780200	-1.17933700
C	-4.51527600	-3.56913400	-0.98017300
H	-8.22532000	-4.18559900	3.94280000
H	-6.85968900	-7.63093800	0.67360900
H	-4.10278500	-4.35034100	-1.61151700
C	-7.14716600	-2.24916900	2.89023200
C	-6.33722200	-1.89198600	3.95858100
C	-8.38611800	-1.64109900	2.69389000
C	-6.75961000	-0.91311600	4.85076400
H	-5.37417700	-2.37948700	4.09202600
C	-8.81060800	-0.66860900	3.57942300
H	-9.00505800	-1.93493500	1.84931600



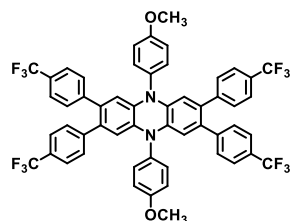
C	-8.00077900	-0.29816300	4.66201900
H	-6.12033300	-0.64213800	5.68449400
H	-9.77032700	-0.17512000	3.45525000
C	-5.37417000	-6.24375400	-0.70774900
C	-6.01146700	-6.37167400	-1.94140000
C	-4.31707800	-7.07258200	-0.36109300
C	-5.58002700	-7.33858500	-2.82944400
H	-6.83782900	-5.71159200	-2.19465500
C	-3.88234600	-8.04900500	-1.25016600
H	-3.83420500	-6.95458200	0.60629900
C	-4.51399500	-8.18313900	-2.48996300
H	-3.05371800	-8.68938800	-0.96806400
H	-6.05427100	-7.46528200	-3.79856600
N	-6.70014100	-3.26516600	1.97194600
N	-5.81844600	-5.23064700	0.21481100
C	-4.36357000	0.19966900	-0.54646700
C	-3.98786600	1.00753600	0.52937900
C	-4.52616800	0.78268100	-1.81020000
C	-3.76685700	2.36829500	0.35222100
H	-3.84857200	0.56232400	1.51213000
C	-4.31636600	2.13899200	-1.98836700
H	-4.83337000	0.16853700	-2.65335000
C	-3.93208000	2.93145900	-0.90655600
H	-3.46425600	2.98468800	1.19307300
H	-4.45454300	2.58877300	-2.96899100
C	-3.11639800	-1.99615800	-2.24098200
C	-3.28269900	-2.56395900	-3.51006200
C	-1.97479500	-1.22968100	-1.98586900
C	-2.33430900	-2.36511300	-4.50079200
H	-4.17285000	-3.15187800	-3.72302500
C	-1.01964000	-1.03397600	-2.97354100
H	-1.82416000	-0.79461700	-1.00058300
C	-1.20114800	-1.60075200	-4.23036800
H	-2.47424300	-2.80198600	-5.48694400
H	-0.13210700	-0.44607600	-2.76147800
C	-8.48445600	-8.62699400	2.48810300
C	-7.59010600	-9.69206200	2.35458700
C	-9.85263500	-8.90061400	2.61945200
C	-8.04391700	-11.00545000	2.36577800
H	-6.52509000	-9.49098400	2.26230900
C	-10.30874600	-10.20718100	2.62415200
H	-10.56226500	-8.08146300	2.70785500
C	-9.40230300	-11.26046800	2.50365200
H	-7.33928800	-11.82599500	2.27253100
H	-11.37196300	-10.41461300	2.71938500
C	-9.19604300	-6.54736400	4.58228800

C	-8.87494700	-7.61896000	5.42653900
C	-10.28751500	-5.73613600	4.90225800
C	-9.63194800	-7.87183800	6.55735400
H	-8.01944300	-8.24983600	5.19668900
C	-11.05498400	-5.99207200	6.03214800
H	-10.55174900	-4.90831100	4.24799500
C	-10.72665000	-7.06065100	6.85646100
H	-9.37314000	-8.70000300	7.21307800
H	-11.90931800	-5.36405300	6.26610600
C	-11.51444200	-7.36680300	8.09031200
C	-0.20235500	-1.40829500	-5.32725600
C	-3.71205900	4.39117400	-1.14791000
C	-9.94100300	-12.65555600	2.50733300
F	0.24201800	-2.58447300	-5.79538100
F	-0.74325400	-0.76535400	-6.37343500
F	0.86521500	-0.70600900	-4.93763100
F	-2.77520700	4.59486400	-2.08646500
F	-4.82890400	4.98666000	-1.59339900
F	-3.32425300	5.04493800	-0.04937700
F	-10.70290100	-12.88222400	3.58817700
F	-10.72448000	-12.87881300	1.44051300
F	-8.97880600	-13.58220000	2.49514500
F	-11.95522100	-8.63362600	8.08865900
F	-12.58033300	-6.57408400	8.23247700
F	-10.76408500	-7.22928200	9.19480500
O	-4.17087000	-9.09211400	-3.42276700
O	-8.50271200	0.66035200	5.46447300
C	-7.72024300	1.08343800	6.56700700
H	-7.54522300	0.26178800	7.27257900
H	-6.75631900	1.49134400	6.23819700
H	-8.29046600	1.86818300	7.06513500
C	-3.11053100	-9.98504400	-3.12936700
H	-2.16805500	-9.44747000	-2.96733800
H	-3.33672600	-10.59566600	-2.24634200
H	-3.00857200	-10.63504700	-3.99879600

PC 4a – neutral triplet

(-3535.141948)

C	-8.43126100	-6.25069400	3.39858300
C	-8.06817400	-4.92556500	3.14515600
C	-7.26102100	-4.55494500	2.07988000
C	-6.75122900	-5.59111200	1.19861800
C	-7.19446800	-6.89175600	1.37106800
C	-8.08249200	-7.26826000	2.38500300



C	-5.47235900	-3.92261300	0.00462400
C	-5.98752000	-2.90715400	0.85143500
C	-5.59992800	-1.58186000	0.62254200
H	-6.04710000	-0.79513800	1.22406200
C	-4.70197800	-1.23269500	-0.37551400
C	-4.13358500	-2.26014800	-1.18024700
C	-4.54384800	-3.57020100	-0.98071000
H	-8.33121300	-4.16213600	3.87218600
H	-6.90566500	-7.62533100	0.62395300
H	-4.09404600	-4.35742000	-1.57956600
C	-7.37486600	-2.21758800	2.72971100
C	-6.62136500	-1.80202500	3.81821300
C	-8.62670100	-1.65804500	2.47915000
C	-7.10914900	-0.81654200	4.67021100
H	-5.64714800	-2.25161700	3.99828400
C	-9.11901300	-0.67906200	3.32317600
H	-9.20507900	-1.99698700	1.62270800
C	-8.36369300	-0.25301800	4.42353300
H	-6.50821500	-0.50289600	5.51703500
H	-10.09083200	-0.22362400	3.15345000
C	-5.36011700	-6.25671900	-0.67780300
C	-5.95957900	-6.47691400	-1.91686400
C	-4.27959800	-7.02586700	-0.27002900
C	-5.46963000	-7.46925200	-2.74634700
H	-6.80722200	-5.86617900	-2.21983100
C	-3.78352300	-8.02816400	-1.09720900
H	-3.82712900	-6.84121500	0.70184300
C	-4.38080500	-8.25200300	-2.34055400
H	-2.93721600	-8.62199200	-0.76740800
H	-5.91571200	-7.66303700	-3.71794000
N	-6.86861000	-3.24482100	1.86299600
N	-5.87296100	-5.23401100	0.19027000
C	-4.42214400	0.20359800	-0.58798000
C	-4.11796800	1.03304800	0.49574000
C	-4.49136400	0.77113000	-1.86879700
C	-3.87548600	2.38913700	0.31194600
H	-4.04818600	0.60455100	1.49333500
C	-4.25522700	2.12167800	-2.05654800
H	-4.74590500	0.14573500	-2.72134800
C	-3.94008800	2.93209500	-0.96523600
H	-3.62684900	3.01834500	1.16117500
H	-4.32042900	2.55414900	-3.05254900
C	-3.06992400	-2.01527700	-2.17777500
C	-3.14646400	-2.59756800	-3.45010300
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C	-2.13232800	-2.41258400	-4.37643600

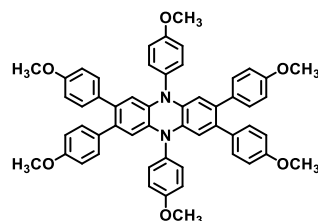
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C	-0.92590200	-1.05860800	-2.78323500
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C	-1.01968500	-1.64294500	-4.04230900
H	-2.20538200	-2.86282600	-5.36410300
H	-0.05420600	-0.46705800	-2.51961400
C	-8.69413200	-8.58264900	2.32230300
C	-8.01801600	-9.67891800	1.73436600
C	-9.99893200	-8.82903800	2.81564900
C	-8.60071000	-10.92710000	1.64078000
H	-6.99745000	-9.55267400	1.37967900
C	-10.58592700	-10.07592000	2.71382100
H	-10.56269600	-8.01483100	3.26297900
C	-9.89123300	-11.14171400	2.13554800
H	-8.04563700	-11.75190700	1.20097900
H	-11.59529600	-10.22822400	3.08958100
C	-8.99048700	-6.57509800	4.70071600
C	-8.68297700	-7.79188100	5.35551200
C	-9.82565600	-5.66822700	5.39057500
C	-9.15953700	-8.06636500	6.62151300
H	-8.02855500	-8.50905600	4.86744600
C	-10.31300300	-5.94780500	6.65492800
H	-10.11961500	-4.73853900	4.90781000
C	-9.98166000	-7.14863700	7.28355900
H	-8.88698000	-8.99898200	7.11263100
H	-10.96366100	-5.23680200	7.15663400
C	-10.48106600	-7.49083900	8.64173100
C	0.05007500	-1.46640400	-5.07005700
C	-3.69299100	4.38467600	-1.21282100
C	-10.54286900	-12.47022100	1.99240500
F	0.51244900	-2.64948100	-5.50511700
F	-0.40865500	-0.82200800	-6.15522100
F	1.09860100	-0.77427800	-4.61347500
F	-2.72973200	4.57022300	-2.12922100
F	-4.78861900	4.99635400	-1.69120000
F	-3.32331600	5.04303100	-0.10977300
F	-11.38442100	-12.73524200	3.00457400
F	-11.27575000	-12.56604900	0.86468400
F	-9.65127900	-13.47205300	1.94481400
F	-11.22594900	-8.61202000	8.63829400
F	-11.23412600	-6.52285800	9.17836100
F	-9.47336000	-7.72796400	9.50277600
O	-3.98104800	-9.19694600	-3.21756900
O	-8.92946500	0.70609000	5.18673500
C	-8.20603000	1.17568700	6.30938600
H	-8.02758500	0.37282200	7.03590500

H	-7.24475100	1.61322100	6.01142600
H	-8.82308700	1.94667500	6.77219500
C	-2.89438000	-10.02619700	-2.85060800
H	-1.97808000	-9.44279900	-2.69537500
H	-3.11680500	-10.59806400	-1.94074100
H	-2.74180000	-10.71855300	-3.67936300

PC 4b – ground state

(-2645.043127)

C	-3.32726200	-2.62009100	-2.39196800
C	-2.15348800	-2.55900600	-1.62343300
C	-1.83708900	-1.47626400	-0.81592900
C	-2.73907400	-0.39388700	-0.75291400
C	-3.89236700	-0.44362000	-1.52225600
C	-4.20980700	-1.53091700	-2.35345600
C	-1.31829200	0.69162900	0.90727500
C	-0.41875800	-0.39280400	0.84736600
C	0.67497000	-0.39840300	1.70128900
H	1.34114000	-1.25796300	1.69145600
C	0.93570300	0.63697600	2.61374200
C	0.06424100	1.73547200	2.64376500
C	-1.05064300	1.72828800	1.78957400
H	-1.48124800	-3.41359400	-1.63985400
H	-4.56309400	0.41217100	-1.51358400
H	-1.71143200	2.59160600	1.79872300
C	0.31013700	-2.47678000	-0.20463100
C	1.32287100	-2.35905900	-1.15817300
C	0.25371000	-3.60761800	0.60148000
C	2.26640700	-3.36130700	-1.29882300
H	1.35979700	-1.47091000	-1.78560700
C	1.19701500	-4.62299600	0.46998800
H	-0.53882200	-3.69070800	1.34279900
C	2.20891700	-4.49870600	-0.48454800
H	3.06374900	-3.28871800	-2.03385100
H	1.13696900	-5.49744100	1.11044100
C	-3.34598600	1.80826000	0.12462800
C	-3.20434300	2.87887400	-0.75963300
C	-4.36614100	1.82635300	1.06851000
C	-4.07253800	3.95433900	-0.69493400
H	-2.40390700	2.85559200	-1.49612700
C	-5.24429000	2.90366000	1.14622300
H	-4.46762700	0.98750000	1.75449900
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H	-6.03379200	2.90170400	1.89153800



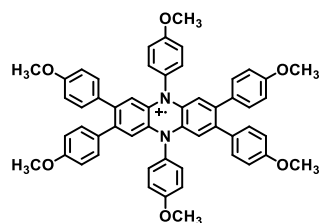
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N	-0.65508800	-1.43583200	-0.06112100
N	-2.43875300	0.70878300	0.06173800
C	-6.92026700	5.14844300	1.21146300
H	-7.41755000	6.10652700	1.05406900
H	-7.65035700	4.33870900	1.08393200
H	-6.52124600	5.11374800	2.23350600
C	3.15973500	-6.58806300	0.10220700
H	4.01034600	-7.19243800	-0.21587800
H	3.26730400	-6.34901600	1.16811100
H	2.23523700	-7.16110700	-0.04545600
C	2.08421800	0.47093900	3.53365400
C	1.94879100	0.66972900	4.91683100
C	3.32871500	0.05266600	3.06081500
C	3.01006700	0.46652400	5.77887800
H	0.98725300	0.98550200	5.31746800
C	4.41013300	-0.15620600	3.91469400
H	3.46478400	-0.10411600	1.99174100
C	4.25224300	0.05346100	5.28379000
H	2.90244800	0.61292700	6.85105400
H	5.36216900	-0.47582800	3.50181600
C	0.26871200	2.92906800	3.49552400
C	-0.79182200	3.47922500	4.21744300
C	1.51132200	3.57777900	3.57361200
C	-0.63874100	4.62276000	4.99882300
H	-1.76642700	2.99457500	4.18099700
C	1.68184400	4.71311400	4.34354100
H	2.35513400	3.18326900	3.01088000
C	0.60707800	5.24471300	5.06547500
H	-1.49020300	5.01090800	5.54975300
H	2.64305000	5.21884300	4.39784700
C	-5.43954100	-1.43496900	-3.17287100
C	-5.44384500	-1.74563700	-4.54209400
C	-6.63371600	-0.97837300	-2.61229400
C	-6.58853700	-1.61150300	-5.30551500
H	-4.52583100	-2.09491100	-5.01135600
C	-7.79687400	-0.83699500	-3.36592300
H	-6.66337900	-0.73682400	-1.55087500
C	-7.77672600	-1.15598100	-4.72279800
H	-6.58867000	-1.84597600	-6.36737700
H	-8.70515900	-0.48559600	-2.88566600
C	-3.57800000	-3.85996200	-3.16179000
C	-2.58018700	-4.40942100	-3.96775500
C	-4.79714100	-4.55018600	-3.07522000

C	-2.77294700	-5.59402800	-4.67565500
H	-1.62639900	-3.89144200	-4.05749000
C	-5.00548800	-5.72801900	-3.76881800
H	-5.59085400	-4.15371700	-2.44453600
C	-3.99439200	-6.25850600	-4.57808200
H	-1.97255000	-5.98226700	-5.29834600
H	-5.94729000	-6.26672300	-3.69565300
O	5.23150900	-0.11449000	6.20748800
O	0.87549600	6.35916300	5.79068300
O	-8.84438500	-1.05839600	-5.55392600
O	-4.29488600	-7.41525700	-5.22030400
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H	-0.57509000	6.23274400	7.28081600
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H	-1.00744500	7.24694600	5.87480600
C	6.49905300	-0.53599900	5.74867700
H	6.92749800	0.17958100	5.03429300
H	7.14434600	-0.59341300	6.62667000
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H	-3.72413700	-8.89668900	-6.46302100
H	-3.01268500	-7.31015100	-6.85944500
C	-10.05968400	-0.58927000	-5.00800600
H	-10.78123500	-0.57069100	-5.82620800
H	-10.43070700	-1.25507000	-4.21752100
H	-9.95386400	0.42450300	-4.59941300

PC 4b – radical cation

(-2644.878597)

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C	-2.77865500	-0.42871900	-0.67759000
C	-3.92439400	-0.45914500	-1.47488600
C	-4.20553000	-1.51605900	-2.33152300
C	-1.37380100	0.64676400	0.96005600
C	-0.45713000	-0.43067100	0.88231200
C	0.66990700	-0.41778100	1.70719300
H	1.33678500	-1.27493300	1.69542900
C	0.93033800	0.62137100	2.59116600
C	0.03984900	1.73398600	2.62505600
C	-1.09044600	1.71136300	1.81838200
H	-1.47416100	-3.42502500	-1.62736900



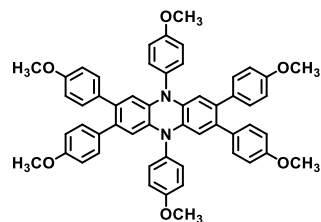
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C	0.25694800	-2.53434100	-0.12120200
C	1.27110900	-2.41408900	-1.06983200
C	0.17444300	-3.65362000	0.69449500
C	2.20611800	-3.42412900	-1.19648300
H	1.31787600	-1.52847900	-1.69934000
C	1.11263300	-4.67312100	0.57098500
H	-0.62435200	-3.72724200	1.42912300
C	2.13293800	-4.55841700	-0.37710500
H	3.00938000	-3.36007600	-1.92504200
H	1.04198400	-5.54454400	1.21375900
C	-3.42942500	1.73754600	0.23887300
C	-3.28557000	2.80032300	-0.65182300
C	-4.43485500	1.74054600	1.19462300
C	-4.15581500	3.87132800	-0.57698200
H	-2.49116700	2.77759900	-1.39425100
C	-5.31270400	2.81653800	1.27543100
H	-4.52808200	0.90132700	1.88019100
C	-5.17147200	3.88726300	0.38836400
H	-6.09639600	2.81246400	2.02615800
O	3.09263100	-5.48414200	-0.57606400
H	-4.07057900	4.71586100	-1.25494200
O	-5.96181000	4.97927500	0.38347300
N	-0.71001600	-1.47655000	0.01141200
N	-2.51111800	0.63144200	0.17113700
C	-6.99203100	5.05875000	1.35166700
H	-7.48785400	6.01727100	1.19472600
H	-7.72237800	4.24954200	1.22628000
H	-6.58601600	5.02492500	2.37048700
C	3.06499500	-6.65233200	0.22379100
H	3.91515600	-7.25951300	-0.08888800
H	3.16733900	-6.41023300	1.28906900
H	2.13892000	-7.22009100	0.06902800
C	2.09278200	0.48737300	3.49189300
C	1.97808500	0.72349100	4.87178800
C	3.32634000	0.05366400	3.00247500
C	3.05197000	0.53143600	5.71788600
H	1.02521100	1.04823800	5.28427300
C	4.42097100	-0.13398500	3.84069400
H	3.44416100	-0.12499200	1.93506800
C	4.28494800	0.10420900	5.20881200
H	2.96372800	0.69950700	6.78819700
H	5.36645000	-0.46048700	3.41913200
C	0.27230900	2.93474200	3.45200500
C	-0.77417900	3.50018900	4.18390900

C	1.52225500	3.57453200	3.49020000
C	-0.59825500	4.65410100	4.94075900
H	-1.74954200	3.01663000	4.18187100
C	1.71010900	4.72578500	4.22885500
H	2.35280800	3.16748000	2.91765000
C	0.65159200	5.27393300	4.96443100
H	-1.43325000	5.05520300	5.50676500
H	2.67238600	5.23093800	4.25056000
C	-5.41123800	-1.41686400	-3.17796800
C	-5.37545800	-1.70756100	-4.55188000
C	-6.61756500	-0.96713300	-2.63624100
C	-6.49735200	-1.55154000	-5.34129300
H	-4.44668500	-2.04749500	-5.00524700
C	-7.75892000	-0.81407600	-3.41627600
H	-6.67567600	-0.74852500	-1.57142500
C	-7.70054400	-1.10522600	-4.77964500
H	-6.47028200	-1.76314300	-6.40714400
H	-8.68088900	-0.47457600	-2.95468300
C	-3.54838500	-3.83371200	-3.18133300
C	-2.53000700	-4.37917100	-3.96517700
C	-4.78080400	-4.50602500	-3.14093800
C	-2.71785700	-5.54585600	-4.69967000
H	-1.56963800	-3.86963400	-4.02235400
C	-4.97888400	-5.67104800	-3.85516600
H	-5.58830000	-4.11190100	-2.52746300
C	-3.94951600	-6.19883000	-4.64498800
H	-1.90640000	-5.93147700	-5.30893900
H	-5.92666900	-6.20190700	-3.81646400
O	5.27560300	-0.04694900	6.11599600
O	0.93706600	6.39772300	5.65913800
O	-8.74159400	-0.98944200	-5.63374700
O	-4.24318100	-7.33779900	-5.31154700
C	-0.10449600	6.99119200	6.41001200
H	-0.48151300	6.30825100	7.18222200
H	0.32323300	7.87296200	6.88887800
H	-0.93835400	7.29888000	5.76599200
C	6.53755500	-0.48351900	5.64949600
H	6.96045500	0.21924300	4.92002300
H	7.19041600	-0.52949900	6.52214000
H	6.47370000	-1.47996100	5.19351800
C	-3.23039100	-7.91034500	-6.11591900
H	-2.35292200	-8.18914700	-5.51823100
H	-3.65996100	-8.80853800	-6.56157300
H	-2.91693500	-7.22582100	-6.91469400
C	-9.97388300	-0.52758100	-5.11494500
H	-10.66956100	-0.49532700	-5.95441800

H	-10.36641800	-1.20759500	-4.34798500
H	-9.87724900	0.47890200	-4.68779700

PC 4b – neutral triplet

(-2644.964206)



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C	-1.85965900	-1.49353300	-0.73020800
C	-2.81325100	-0.44709200	-0.59671100
C	-3.95861700	-0.48002900	-1.40029600
C	-4.21338800	-1.50085400	-2.30693800
C	-1.41872000	0.63587300	1.06333600
C	-0.42969500	-0.42660200	0.90974400
C	0.71407500	-0.38930600	1.69494200
H	1.38494200	-1.24398000	1.65761300
C	0.98084200	0.62590200	2.61615000
C	0.04951700	1.78053600	2.65699800
C	-1.13268600	1.68992900	1.92206000
H	-1.43919900	-3.37181000	-1.67455600
H	-4.65370100	0.35412300	-1.34886000
H	-1.81960200	2.53263400	1.94104500
C	0.26949100	-2.50394300	-0.12773900
C	1.29052100	-2.36079100	-1.06576600
C	0.19814300	-3.64001100	0.66519500
C	2.23742100	-3.35958100	-1.20649400
H	1.33260900	-1.46230600	-1.67762000
C	1.14623000	-4.65058100	0.52989600
H	-0.60351900	-3.73294400	1.39475200
C	2.17091300	-4.50887500	-0.40852600
H	3.04444500	-3.27482100	-1.92915900
H	1.07963600	-5.53409400	1.15668400
C	-3.56927800	1.59743500	0.47915700
C	-3.54636600	2.74515000	-0.31147800
C	-4.55217200	1.42909900	1.44361200
C	-4.51196900	3.72075200	-0.13281900
H	-2.76918000	2.86269500	-1.06357600
C	-5.52694900	2.40425000	1.62966700
H	-4.55483100	0.52679500	2.05138100
C	-5.50615500	3.55620600	0.83958200
H	-6.28991800	2.25618800	2.38666800
O	3.14361100	-5.42348300	-0.61766000
H	-4.51935100	4.62492300	-0.73545200
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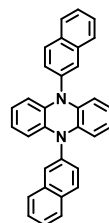
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H	-7.01063300	4.36331700	2.92361100
C	3.12227800	-6.60136900	0.16554400
H	3.98111900	-7.19642000	-0.14763100
H	3.21321900	-6.37358700	1.23530600
H	2.20355500	-7.17776100	-0.00278700
C	2.06511500	0.43813700	3.57075300
C	1.98705900	0.91098400	4.90227000
C	3.23295900	-0.27021500	3.22786300
C	2.99453800	0.67453100	5.81738200
H	1.10055300	1.45330200	5.22259200
C	4.25408400	-0.51082600	4.13844500
H	3.36144000	-0.62376400	2.20619700
C	4.14113700	-0.03682500	5.44739900
H	2.91399200	1.02979800	6.84257100
H	5.13742000	-1.05450900	3.81542900
C	0.37251200	3.04651200	3.30450300
C	-0.62623500	3.85671800	3.87569900
C	1.69281700	3.55021300	3.34899300
C	-0.34735100	5.09377500	4.44443800
H	-1.65363500	3.49718300	3.89939300
C	1.98189200	4.78048700	3.90704300
H	2.49853800	2.96947200	2.90622900
C	0.96635800	5.56647900	4.46340300
H	-1.15690500	5.67124200	4.88147800
H	2.99932600	5.16554100	3.91855500
C	-5.39773100	-1.37232500	-3.18212100
C	-5.31371700	-1.59304500	-4.56743100
C	-6.62990800	-0.96164100	-2.66850100
C	-6.40771600	-1.40868800	-5.39112700
H	-4.36577100	-1.90564300	-5.00142900
C	-7.74301900	-0.77207400	-3.48408000
H	-6.73028800	-0.79683000	-1.59686400
C	-7.63377200	-0.99642300	-4.85585400
H	-6.33857100	-1.56890300	-6.46444800
H	-8.68313800	-0.45820600	-3.04052200
C	-3.50644100	-3.77693800	-3.23821900
C	-2.47680300	-4.30015900	-4.02340800
C	-4.73551300	-4.45770000	-3.24260500
C	-2.64554800	-5.45119800	-4.78955400
H	-1.51747100	-3.78584400	-4.05254000
C	-4.91956000	-5.60187400	-3.99534700
H	-5.55581800	-4.08305100	-2.63334800

C	-3.87515200	-6.10814400	-4.77794400
H	-1.82001900	-5.81789000	-5.39222200
H	-5.86787400	-6.13397400	-3.99003700
O	5.08031600	-0.20635000	6.41672600
O	1.35475500	6.75573900	4.99700800
O	-8.64681300	-0.84573000	-5.74450600
O	-4.15507700	-7.23291200	-5.48175500
C	0.35405000	7.57604000	5.55938900
H	-0.15031200	7.08147400	6.40073900
H	0.85496000	8.47462700	5.92382200
H	-0.40015200	7.86340200	4.81419500
C	6.24962200	-0.91616600	6.07132300
H	6.80010500	-0.41877500	5.26114900
H	6.87604000	-0.94055100	6.96475300
H	6.02233700	-1.94615100	5.76403900
C	-3.12572600	-7.77901300	-6.28030600
H	-2.25707800	-8.07006000	-5.67477600
H	-3.54137400	-8.66714400	-6.75872300
H	-2.79832500	-7.07286000	-7.05491300
C	-9.89596200	-0.41293200	-5.24665700
H	-10.56852300	-0.35391000	-6.10375500
H	-10.30675800	-1.12254400	-4.51620200
H	-9.82124500	0.57765500	-4.77859600

PC 5 – ground state

(-1341.477327)

C	4.44053200	-5.39924000	2.62577000
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C	2.01768400	-5.33443700	2.75289700
C	2.02500400	-6.59653500	3.38405200
C	3.24113800	-7.23169100	3.61648400
C	4.44773700	-6.63729700	3.24280800
C	-0.41364200	-6.65121500	3.30261800
C	-0.42104400	-5.39051600	2.66878700
C	-1.62718300	-4.86696200	2.21322200
H	-1.63425400	-3.89395100	1.73025200
C	-2.82442700	-5.56564100	2.37797700
C	-2.81725400	-6.80142300	2.99946700
C	-1.61314500	-7.33966700	3.45672500
H	3.22170200	-3.78014900	1.90089500
H	3.24788100	-8.20128600	4.10663100
H	-1.60952300	-8.30765300	3.95003700
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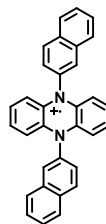


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C	0.75816000	-2.25679200	2.49973700
H	0.83855600	-4.43454800	-0.10032200
C	0.76030500	-1.02785700	1.79497100
H	0.73586500	-2.25640900	3.58840600
H	5.38238000	-7.15439300	3.44351100
H	5.36929200	-4.91891900	2.32927100
H	-3.75178600	-5.12911400	2.01652500
H	-3.73900900	-7.35998400	3.13930500
C	0.81773100	-2.29689000	-0.30034900
C	0.79037300	-1.04713400	0.36968200
C	0.79261900	0.18203400	-0.33350200
C	0.76693100	1.37557600	0.34366700
H	0.76920600	2.31360400	-0.20587400
C	0.73721700	1.39408400	1.75604600
H	0.71681500	2.34655000	2.27975100
C	0.73398500	0.21932900	2.46549700
H	0.81557100	0.16031400	-1.42169200
H	0.71108800	0.22716400	3.55373700
H	0.84096400	-2.30678800	-1.38853600
C	0.81427600	-8.49480500	4.31583400
C	0.77142100	-8.70693600	5.66940200
C	0.86758900	-9.58670900	3.41491200
C	0.77772900	-10.02466900	6.19127000
H	0.73104100	-7.85541400	6.34696100
C	0.87567200	-10.87010100	3.89213900
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H	0.91556600	-11.71498200	3.20692400
C	0.73675500	-11.56848500	8.05808000
H	0.69155800	-9.43590300	8.26881400
C	0.83517300	-12.44192500	5.80764000
C	0.78917800	-12.65948000	7.16194700
H	0.70059800	-11.75397800	9.12865300
H	0.87548200	-13.27818900	5.11173100
H	0.79292200	-13.67440400	7.55144500

PC 5 – radical cation

(-1341.307624)

C	4.42469300	-5.38246900	2.65938800
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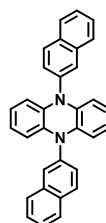
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C	-0.39346700	-6.73155100	3.14172100
C	-0.39782600	-5.45430700	2.52472000
C	-1.62007500	-4.86287400	2.17270400
H	-1.62305700	-3.88543500	1.70219500
C	-2.80535400	-5.52084400	2.42381400
C	-2.80107900	-6.78262300	3.03341600
C	-1.61151900	-7.38170000	3.38960900
H	3.23028700	-3.79176300	1.86182700
H	3.24521700	-8.26624900	4.01813700
H	-1.60778200	-8.35786200	3.86278900
N	0.80582900	-4.81564200	2.28525500
N	0.81436500	-7.30969700	3.48924300
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C	0.84971100	-3.44590700	0.25144700
C	0.75270000	-2.39426300	2.44474300
H	0.88799300	-4.36566200	-0.32719100
C	0.74939100	-1.11612600	1.83803600
H	0.71637200	-2.48402800	3.52918600
H	5.36946500	-7.12334100	3.52262900
H	5.36186900	-4.87944300	2.44229000
H	-3.74496500	-5.05352000	2.14587500
H	-3.73732300	-7.29603600	3.22914100
C	0.84719400	-2.21554700	-0.35295900
C	0.79749000	-1.02598300	0.41533700
C	0.79420600	0.25415100	-0.18947600
C	0.74567000	1.38941400	0.57949100
H	0.74365900	2.36758900	0.10562000
C	0.69815100	1.29813400	1.98871900
H	0.66015700	2.20657900	2.58412300
C	0.69987600	0.07268800	2.60534200
H	0.83091000	0.31854000	-1.27523600
H	0.66348400	-0.00553300	3.69015500
H	0.88372200	-2.13785900	-1.43750600
C	0.81783600	-8.60241600	4.12816200
C	0.77841400	-8.67266800	5.49588500
C	0.86102100	-9.75714300	3.31806300
C	0.78030500	-9.93629600	6.13178000
H	0.74556100	-7.76163800	6.09123300
C	0.86305000	-10.98988300	3.91806100
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C	0.74065300	-10.06064200	7.54144300
C	0.82297500	-11.11446700	5.32892700
H	0.89575600	-11.89320300	3.31267900

C	0.74321500	-11.29981700	8.13008300
H	0.70821200	-9.15660100	8.14627100
C	0.82411600	-12.37791800	5.96780400
C	0.78523500	-12.46816900	7.33639700
H	0.71272700	-11.38773500	9.21293000
H	0.85640700	-13.27465500	5.35192400
H	0.78652200	-13.44287500	7.81736700

PC 5 – neutral triplet

(-1341.391719)

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C	3.21044700	-4.62273400	2.63744300
C	1.99481700	-5.28654200	2.86959900
C	2.00679900	-6.57406400	3.46953700
C	3.23604800	-7.16905500	3.80136200
C	4.41580100	-6.49874700	3.56286300
C	-0.40678300	-6.62537500	3.38530100
C	-0.40746900	-5.33696300	2.78699400
C	-1.63109800	-4.72301600	2.47369900
H	-1.61361800	-3.73421600	2.02699900
C	-2.81966500	-5.36805200	2.73871400
C	-2.81753600	-6.65086700	3.31309700
C	-1.62988400	-7.27213400	3.63179500
H	3.18253600	-3.63599100	2.18681700
H	3.24616300	-8.15814500	4.24760900
H	-1.62927800	-8.26204000	4.07632200
N	0.79247600	-4.71888900	2.49860700
N	0.80371200	-7.21944400	3.69839800
C	0.79378400	-3.49817300	1.73038000
C	0.83133100	-3.58437500	0.34624700
C	0.75803900	-2.26944800	2.40860700
H	0.85798100	-4.56350200	-0.13008300
C	0.76168800	-1.05954400	1.66365600
H	0.72905600	-2.24582100	3.49737400
H	5.35901600	-6.96820500	3.82623100
H	5.33756800	-4.69235200	2.80744100
H	-3.76008900	-4.88096900	2.49910700
H	-3.75610300	-7.16009800	3.51088300
C	0.83452400	-2.40945600	-0.40673800
C	0.80111900	-1.12991700	0.22338300
C	0.80537300	0.07284300	-0.50866000
C	0.77284100	1.31926100	0.12786600
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C	0.73466500	1.38640100	1.51578600

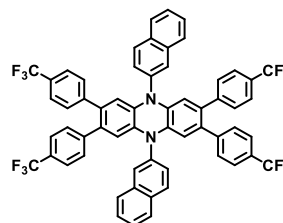


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H	0.83550000	0.01440100	-1.59737700
H	0.69922600	0.26282800	3.36401400
H	0.86442100	-2.45523000	-1.49451300
C	0.81432600	-8.56592700	4.20783400
C	0.77336700	-8.78376800	5.55995600
C	0.86687900	-9.62966400	3.28133500
C	0.78344700	-10.10872000	6.05768800
H	0.73329300	-7.94201000	6.24950700
C	0.87730000	-10.91951900	3.74438300
H	0.89796600	-9.40567300	2.21763200
C	0.74252200	-10.38482600	7.44569100
C	0.83621400	-11.19426100	5.13384600
H	0.91748400	-11.75319700	3.04637200
C	0.75333000	-11.68010800	7.89828700
H	0.70238300	-9.55100700	8.14397600
C	0.84600300	-12.51877500	5.63342600
C	0.80558500	-12.75631700	6.98426700
H	0.72169100	-11.88370200	8.96547800
H	0.88636500	-13.34343200	4.92424000
H	0.81358100	-13.77705000	7.35777900

PC 5a – ground state

(-3613.340800)

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C	-0.55755400	1.42664400	-1.63459900
C	0.60365200	1.85939200	-1.01216100
C	0.80613300	3.24399500	-0.83985400
C	-0.18105800	4.12000000	-1.26713100
C	-1.36953800	3.68343100	-1.87294200
H	-0.68645800	0.36294500	-1.81782900
H	-0.05082900	5.18489300	-1.09108000
N	1.58697000	0.95838300	-0.57831900
N	1.98751500	3.69813600	-0.23770000
C	2.68728500	1.40790600	0.16641800
C	3.57864700	0.52510500	0.75939000
C	2.89800300	2.79256400	0.32570100
C	4.69924300	0.95550000	1.48586700
H	3.38492900	-0.54233100	0.68797200
C	4.02060400	3.22140700	1.01851800
C	4.93896000	2.33206200	1.59676100
H	4.21500400	4.28848800	1.09081400
C	2.16952700	5.09945800	-0.02268500



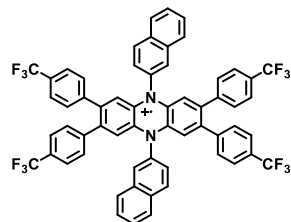
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C	2.79911100	5.87384400	-1.02387800
C	1.92459400	7.06006000	1.37372600
H	1.25494300	5.06306000	1.90603700
C	2.98848100	7.21819400	-0.82855000
H	3.12495000	5.38238700	-1.93788700
C	1.49683600	7.68661000	2.57006400
C	2.56214900	7.84595000	0.36797200
H	3.47357400	7.82265600	-1.59269800
C	1.69335200	9.03048200	2.76284300
H	1.01015700	7.08077800	3.33234500
C	2.74997100	9.23100700	0.59807500
C	2.32642200	9.80992500	1.76766900
H	1.36197800	9.50260000	3.68427900
H	3.23778800	9.82596400	-0.17208000
H	2.47618800	10.87370800	1.93420900
C	1.33255800	-0.44519300	-0.66555900
C	1.88637400	-1.18095400	-1.68165300
C	0.51449000	-1.05933300	0.31316600
C	1.65094900	-2.57484900	-1.76721900
H	2.51528000	-0.69063200	-2.42341600
C	0.26643200	-2.40530800	0.24918900
H	0.09278500	-0.44259600	1.10434100
C	2.21110400	-3.36673800	-2.79910600
C	0.82461300	-3.19803700	-0.78539300
H	-0.36145500	-2.88686900	0.99651200
C	1.96486900	-4.71543800	-2.85577400
H	2.84052500	-2.88452400	-3.54491200
C	0.58920000	-4.59166400	-0.87259200
C	1.14632200	-5.33352800	-1.88364600
H	2.40008600	-5.31530500	-3.65101100
H	-0.04212000	-5.06232100	-0.12092100
H	0.95997100	-6.40297000	-1.94094700
C	6.13556700	2.91110300	2.24673300
C	6.00597800	3.99412400	3.12239200
C	7.42254600	2.42825600	1.96816000
C	7.12080100	4.57774400	3.71156900
H	5.01390300	4.37569800	3.35484800
C	8.53693500	3.00477500	2.55293700
H	7.54665200	1.60156200	1.27258700
C	8.38692500	4.08171600	3.42705900
H	7.00290100	5.41359800	4.39461700
H	9.53184100	2.62827700	2.32501100
C	5.52553800	-0.07805600	2.14823400
C	5.86668000	0.02958100	3.50436000
C	5.94115200	-1.21208400	1.44409800

C	6.60327200	-0.96102600	4.13045200
H	5.53766100	0.89791400	4.07097600
C	6.68154500	-2.20981600	2.06683000
H	5.69224800	-1.30592000	0.38918300
C	7.01214300	-2.08399800	3.41029200
H	6.85502100	-0.87095800	5.18509600
H	7.00314600	-3.08286500	1.50675100
C	-2.72192900	1.72756800	-2.77569500
C	-3.18156700	2.25063400	-3.99300700
C	-3.36357100	0.60086600	-2.25097200
C	-4.25020700	1.67054900	-4.65535300
H	-2.68290200	3.11369400	-4.42833800
C	-4.43492800	0.01320200	-2.91174200
H	-3.02396000	0.18683300	-1.30371700
C	-4.87922300	0.54891400	-4.11435500
H	-4.59396900	2.08091900	-5.60254600
H	-4.92504600	-0.85839300	-2.48866800
C	-2.38556900	4.70964200	-2.19745500
C	-2.01883700	5.87056600	-2.88468900
C	-3.71722300	4.57068200	-1.78026700
C	-2.94916200	6.86710800	-3.15478900
H	-0.99142200	5.98719800	-3.22301900
C	-4.64763500	5.56141700	-2.04311700
H	-4.01592400	3.68119700	-1.22998600
C	-4.26364700	6.71168300	-2.73300700
H	-2.65344100	7.76128300	-3.69567500
H	-5.67519400	5.45015200	-1.70333800
C	-5.29515300	7.76289900	-2.98048200
C	-6.03081700	-0.04732700	-4.85555400
C	7.80297000	-3.13248200	4.12140800
C	9.61504500	4.66252300	4.04707000
F	-4.81651400	8.80837100	-3.66235800
F	-5.79923400	8.23649100	-1.82897100
F	-6.33852800	7.27914500	-3.67388700
F	-5.69111400	-0.38071000	-6.11115100
F	-7.05157900	0.81905700	-4.96189200
F	-6.50814000	-1.14939800	-4.26863100
F	8.09914400	-4.17639400	3.34052700
F	7.14093600	-3.60823200	5.18874300
F	8.96355600	-2.64415300	4.58882500
F	10.23390900	3.77113200	4.83900800
F	10.51443300	5.02255500	3.11700500
F	9.36003900	5.74271700	4.79252300

PC 5a – radical cation

(-3613.165563)

C	-1.51107100	2.21214000	-2.07937000
C	-0.57473800	1.35053300	-1.52936700
C	0.53765600	1.82107800	-0.82618700
C	0.72833500	3.21798700	-0.69658000
C	-0.22843200	4.08467600	-1.23352900
C	-1.34771300	3.61424000	-1.90318200
H	-0.68835500	0.28113500	-1.67997700
H	-0.11403200	5.15415600	-1.08272200
N	1.46000600	0.95475400	-0.27007500
N	1.83922400	3.69208900	-0.02399200
C	2.56627900	1.42877800	0.40913300
C	3.48508200	0.56003600	1.00519200
C	2.76631200	2.82593400	0.52513600
C	4.60217200	1.02742700	1.67963100
H	3.29643000	-0.50891900	0.97041100
C	3.90948900	3.29428500	1.18012000
C	4.83584300	2.42938300	1.74203200
H	4.09549300	4.36370100	1.21552000
C	2.04004700	5.11566800	0.09281500
C	1.58887000	5.76781800	1.21014100
C	2.69762800	5.78965100	-0.95816200
C	1.78073000	7.16483900	1.32828100
H	1.08438900	5.21730700	2.00261500
C	2.89149500	7.14303700	-0.85999600
H	3.03682000	5.22553900	-1.82355700
C	1.33237800	7.88521900	2.46205600
C	2.44268100	7.86339400	0.27494400
H	3.39654500	7.68313500	-1.65796000
C	1.53173300	9.23965100	2.54745100
H	0.82816500	7.34469400	3.26069400
C	2.63250200	9.26165300	0.39510800
C	2.18729200	9.93321300	1.50532700
H	1.18566500	9.78657900	3.42057300
H	3.13817000	9.79082500	-0.41029100
H	2.33737900	11.00646000	1.58843000
C	1.23916900	-0.46736200	-0.36201900
C	1.82256600	-1.17641200	-1.37881600
C	0.41964200	-1.08047600	0.61024700
C	1.60600100	-2.57190200	-1.47024100
H	2.44882100	-0.67087900	-2.11215600
C	0.19856500	-2.43088600	0.53597700
H	-0.01929800	-0.47264900	1.39773000



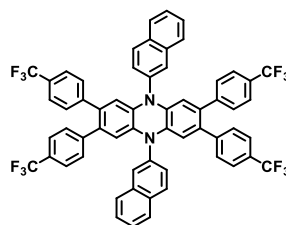
C	2.18651900	-3.35042000	-2.50069200
C	0.77944900	-3.20871400	-0.49639300
H	-0.42881000	-2.92491400	1.27469700
C	1.95837300	-4.70156000	-2.56271400
H	2.81503400	-2.85688800	-3.23925000
C	0.56400900	-4.60503000	-0.58992200
C	1.14022500	-5.33383600	-1.59916400
H	2.40788800	-5.29299200	-3.35599100
H	-0.06686600	-5.08708500	0.15430900
H	0.96942000	-6.40534100	-1.66233700
C	6.05553600	3.01346500	2.34242400
C	5.95407300	4.07076000	3.25007900
C	7.32655200	2.54979400	1.97748900
C	7.09403400	4.64904800	3.79528500
H	4.97203000	4.43095900	3.54848300
C	8.46413100	3.12931400	2.51207700
H	7.42182000	1.74027200	1.25776200
C	8.34670100	4.17773200	3.42425000
H	7.00571400	5.46306000	4.50811800
H	9.44944100	2.77539000	2.21805500
C	5.47517900	0.03399800	2.34272600
C	5.85012300	0.18896300	3.68426700
C	5.89604800	-1.10250200	1.64791200
C	6.62168000	-0.77353500	4.31210400
H	5.51978600	1.06340800	4.24014900
C	6.67773800	-2.06653300	2.27266200
H	5.62295300	-1.22469500	0.60220400
C	7.03584800	-1.90176500	3.60439800
H	6.89849100	-0.65481300	5.35718400
H	7.00779000	-2.94352500	1.72439800
C	-2.62096400	1.61807700	-2.85687000
C	-2.94090900	2.08748700	-4.13803500
C	-3.33877300	0.54088200	-2.33105900
C	-3.95628400	1.49378900	-4.86811000
H	-2.38021000	2.91403700	-4.56797900
C	-4.36267500	-0.05325000	-3.05845900
H	-3.10503600	0.17700900	-1.33299800
C	-4.67007200	0.42559400	-4.32549500
H	-4.19462000	1.85592100	-5.86548300
H	-4.92235800	-0.88372500	-2.63924300
C	-2.34882700	4.60309100	-2.36020300
C	-1.94296400	5.73630500	-3.06895300
C	-3.70670900	4.44333900	-2.05168500
C	-2.87045200	6.68761100	-3.47631200
H	-0.89278500	5.86372000	-3.32209500
C	-4.63202500	5.39252800	-2.44910400

H	-4.03290900	3.57303700	-1.48707800
C	-4.21313100	6.51324800	-3.16619300
H	-2.55005000	7.55949100	-4.03841200
H	-5.68365400	5.26746000	-2.20139800
C	-5.24709700	7.50626500	-3.59277800
C	-5.76122500	-0.18653300	-5.14505500
C	7.86371900	-2.92164900	4.31926300
C	9.60036600	4.75008800	4.00452900
F	-4.72627500	8.53780900	-4.26278800
F	-5.90985900	8.00705700	-2.53907100
F	-6.17000200	6.93963800	-4.38489900
F	-5.28742200	-0.68588800	-6.29682600
F	-6.68880300	0.72262700	-5.48183400
F	-6.38862900	-1.17882000	-4.50831500
F	8.17067800	-3.96833800	3.54797600
F	7.22621500	-3.39406800	5.40129800
F	9.01743600	-2.39702200	4.75960100
F	10.22960800	3.85432100	4.78128200
F	10.47199000	5.09581700	3.04545500
F	9.37551600	5.83446900	4.75208600

PC 5a – neutral triplet

(-3613.268850)

C	-1.52800800	2.30139700	-2.05097800
C	-0.57070900	1.42023400	-1.56912700
C	0.53957000	1.84639200	-0.83268800
C	0.70704600	3.23492800	-0.59453400
C	-0.27667400	4.11784700	-1.05227800
C	-1.39250000	3.68946100	-1.75789300
H	-0.65947000	0.36508400	-1.81327200
H	-0.18616700	5.17227800	-0.80595400
N	1.48227400	0.95497200	-0.35370700
N	1.81661000	3.67517300	0.10365900
C	2.61007500	1.37850400	0.32761500
C	3.54521800	0.49506200	0.84549200
C	2.78453300	2.80105500	0.56704900
C	4.66923900	0.91124500	1.56316600
H	3.33777200	-0.56871900	0.76919500
C	3.93804400	3.23379800	1.20397200
C	4.93661400	2.36151700	1.64374600
H	4.11404200	4.30414200	1.26663600
C	1.98951300	5.08379900	0.32944600
C	1.56304400	5.63591800	1.50882000
C	2.60956900	5.86118300	-0.67317600

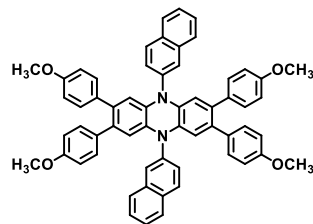


C	1.74145500	7.01980600	1.74475200
H	1.08947900	5.01057800	2.26411300
C	2.79174400	7.20399300	-0.46409800
H	2.93263000	5.37883900	-1.59290500
C	1.31679200	7.63300300	2.94837400
C	2.36816200	7.81719400	0.74121800
H	3.26856400	7.81837100	-1.22511500
C	1.50652800	8.97664600	3.15044200
H	0.83857000	7.01805900	3.70845700
C	2.54908100	9.20113100	0.98109800
C	2.12883200	9.76760600	2.15803900
H	1.17772100	9.43926800	4.07747000
H	3.02850000	9.80527500	0.21305700
H	2.27317700	10.83082200	2.33226100
C	1.24295200	-0.45477000	-0.49677700
C	1.81788500	-1.14640000	-1.53017000
C	0.41130000	-1.08968300	0.45187200
C	1.57952500	-2.53576000	-1.66617800
H	2.45662600	-0.62940200	-2.24461400
C	0.16477200	-2.43275700	0.33635700
H	-0.02004800	-0.49814100	1.25611200
C	2.15189500	-3.29322900	-2.71667800
C	0.73697500	-3.18860500	-0.71710900
H	-0.47458000	-2.93877000	1.05683100
C	1.90130200	-4.63807400	-2.82254600
H	2.79338600	-2.78819400	-3.43636800
C	0.49806100	-4.57750800	-0.85551200
C	1.06683800	-5.28563700	-1.88368900
H	2.34573400	-5.21205600	-3.63152500
H	-0.14534000	-5.07102700	-0.12944400
H	0.87774000	-6.35168800	-1.98057300
C	6.22450000	2.91915100	2.02269500
C	6.32200100	4.18569500	2.64117500
C	7.43736400	2.24257900	1.74933700
C	7.54583700	4.74730600	2.95885700
H	5.41406700	4.72376900	2.90563400
C	8.65911900	2.80777600	2.05501800
H	7.40914400	1.27396300	1.25725100
C	8.72668900	4.06346400	2.66792000
H	7.58664900	5.71717500	3.44698000
H	9.57702900	2.27575300	1.81119000
C	5.43671100	-0.08468200	2.29242100
C	6.03321000	0.20547500	3.54321500
C	5.58841800	-1.39982700	1.79862400
C	6.71921700	-0.75993100	4.25217500
H	5.92249100	1.19891300	3.97008700

C	6.28566000	-2.36449700	2.50347000
H	5.17942800	-1.65623600	0.82366600
C	6.85575800	-2.05358100	3.73881100
H	7.15011600	-0.51799100	5.22187600
H	6.40031500	-3.36273500	2.08963300
C	-2.60238900	1.74650000	-2.90164900
C	-2.93757100	2.33675600	-4.12963900
C	-3.27018000	0.57964800	-2.51578700
C	-3.90464200	1.77225100	-4.94332000
H	-2.41935400	3.23714800	-4.45165000
C	-4.24269200	0.01027600	-3.32788800
H	-3.03234200	0.12032900	-1.55874600
C	-4.55759800	0.60598500	-4.54304500
H	-4.14863300	2.22853100	-5.90016200
H	-4.75694900	-0.89329700	-3.01403700
C	-2.41294800	4.69852400	-2.11154400
C	-2.02742200	5.92883100	-2.65426300
C	-3.77609000	4.47084900	-1.86909000
C	-2.96912600	6.90585000	-2.95274100
H	-0.97570800	6.11590900	-2.86045800
C	-4.71795800	5.44113100	-2.16407000
H	-4.09478600	3.52775300	-1.43122700
C	-4.31472600	6.66075300	-2.70853700
H	-2.65715900	7.85423900	-3.38009100
H	-5.77161800	5.25804000	-1.96474100
C	-5.36589800	7.67183300	-3.03161800
C	-5.60018500	0.03200000	-5.44594600
C	7.65283800	-3.04473500	4.50872500
C	10.06484800	4.62516700	2.99236200
F	-4.85607300	8.82365000	-3.47950000
F	-6.12113800	7.95975200	-1.95973600
F	-6.20954800	7.21716900	-3.97236300
F	-5.12117000	-0.17068400	-6.68333300
F	-6.64865800	0.86028900	-5.58139000
F	-6.07592800	-1.13751600	-5.00716600
F	7.57926100	-4.28073700	4.00006400
F	7.25669500	-3.12011800	5.79210400
F	8.95904000	-2.71702600	4.55064700
F	10.76209800	3.82145500	3.81726800
F	10.82987600	4.76834100	1.89329500
F	9.99761300	5.82581000	3.58100000

PC 5b – ground state

(-2723.170996)



C	-2.05882500	2.16036100	1.14833300
C	-0.98940300	1.31691400	0.80511500
C	0.04107800	1.71122000	-0.03544400
C	0.00422700	3.00675300	-0.58944800
C	-1.04513000	3.84747200	-0.24725100
C	-2.07647800	3.46082400	0.62420600
H	-0.98660300	0.30129800	1.19337300
H	-1.05461800	4.86104300	-0.64171700
N	1.10438900	0.85275800	-0.35561700
N	1.02288500	3.41302200	-1.46460100
C	2.12364300	1.25942100	-1.22987200
C	3.17343800	0.41898000	-1.57139500
C	2.08681400	2.55496300	-1.78385800
C	4.20525000	0.80590200	-2.44217400
H	3.18286400	-0.59462300	-1.17701000
C	3.11781000	2.94958500	-2.62363900
C	4.18765900	2.10640500	-2.96620200
H	3.11506100	3.96522400	-3.01183500
C	1.01575800	4.74305300	-1.98134800
C	0.44326200	5.00616000	-3.20060500
C	1.61320800	5.77936800	-1.22517500
C	0.44659400	6.32049800	-3.72659400
H	-0.01191600	4.19611300	-3.76931000
C	1.62634200	7.06124200	-1.71008900
H	2.05557000	5.53429900	-0.26175500
C	-0.12866400	6.62537700	-4.98471300
C	1.04913700	7.36741600	-2.96811100
H	2.08479700	7.86421400	-1.13572500
C	-0.10631200	7.90826800	-5.47048100
H	-0.58783700	5.82159400	-5.55756400
C	1.05508200	8.68120600	-3.49698900
C	0.49138900	8.94596700	-4.71993500
H	-0.54955600	8.13178400	-6.43764300
H	1.51770100	9.47619600	-2.91457800
H	0.50221000	9.95786400	-5.11712400
C	1.11140900	-0.47735200	0.16091600
C	1.68399400	-0.74076000	1.38007300
C	0.51380600	-1.51343700	-0.59542000
C	1.68059200	-2.05520400	1.90579400
H	2.13930800	0.06913100	1.94890000
C	0.50061800	-2.79541600	-0.11077800
H	0.07136800	-1.26811200	-1.55873600

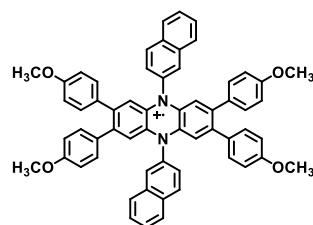
C	2.25590100	-2.36039100	3.16382100
C	1.07790000	-3.10190600	1.14713200
H	0.04204200	-3.59822700	-0.68527000
C	2.23346200	-3.64337800	3.64932200
H	2.71517900	-1.55676500	3.73680900
C	1.07188500	-4.41580800	1.67573800
C	1.63562800	-4.68086800	2.89859300
H	2.67672900	-3.86713800	4.61641800
H	0.60915500	-5.21063900	1.09319600
H	1.62475000	-5.69284700	3.29557000
C	-3.09891600	4.47196300	0.97843200
C	-3.75312600	5.20880100	-0.00947900
C	-3.41769200	4.75018200	2.31636200
C	-4.70384700	6.17902200	0.30307300
H	-3.52906700	5.00901600	-1.05642600
C	-4.35499400	5.71159700	2.64504400
H	-2.91288400	4.20230700	3.10995100
C	-5.00975900	6.43186600	1.63925500
H	-5.19707900	6.72018000	-0.49876200
H	-4.59745500	5.93271800	3.68186800
C	-3.12250000	1.60264700	2.01463500
C	-2.79653100	0.86651800	3.15482700
C	-4.48393900	1.74590400	1.70293800
C	-3.77155800	0.29290700	3.96789300
H	-1.74900300	0.74664000	3.42707300
C	-5.46513900	1.18291800	2.49765900
H	-4.77155100	2.30614700	0.81511700
C	-5.11692400	0.45116500	3.63874600
H	-3.47001700	-0.26559700	4.84887600
H	-6.51907800	1.28646300	2.25070300
C	5.22803600	-0.20506100	-2.79589700
C	5.54755900	-0.48323200	-4.13364100
C	5.88174300	-0.94190000	-1.80764200
C	6.48509100	-1.44459700	-4.46182300
H	5.04316700	0.06464800	-4.92749300
C	6.83268400	-1.91206100	-2.11967400
H	5.65706700	-0.74214700	-0.76082200
C	7.13933400	-2.16487500	-3.45570500
H	6.72812500	-1.66566800	-5.49852300
H	7.32544800	-2.45319600	-1.31754300
C	5.25178700	2.66446600	-3.83172700
C	4.92639400	3.40085000	-4.97192400
C	6.61305300	2.52147600	-3.51917600
C	5.90182300	3.97495800	-5.78416100
H	3.87902000	3.52055500	-5.24483300
C	7.59464800	3.08492700	-4.31308000

H	6.90023700	1.96109300	-2.63130900
C	7.24701400	3.81693900	-5.45417600
H	5.60072300	4.53366000	-6.66516700
H	8.64844200	2.98158400	-4.06542600
O	-5.91514400	7.34803400	2.06431400
O	-6.15086900	-0.06229700	4.35112600
O	8.28128000	4.33098300	-6.16565600
O	8.04492300	-3.08105300	-3.88032300
C	-6.61144000	8.08807600	1.08317900
H	-7.20365700	7.43411500	0.42933100
H	-7.28392400	8.75891800	1.62022000
H	-5.92766800	8.68508900	0.46532700
C	-5.84118900	-0.82021100	5.50200500
H	-5.30692600	-0.21932700	6.24979800
H	-6.79251500	-1.14987700	5.92260100
H	-5.23500500	-1.70161600	5.25363800
C	8.74099800	-3.82084800	-2.89883500
H	8.05712900	-4.41803500	-2.28125500
H	9.41392600	-4.49151100	-3.43553700
H	9.33272100	-3.16667600	-2.24475200
C	7.97216900	5.08918200	-7.31649600
H	7.36541000	5.97023500	-7.06827600
H	8.92367500	5.41941300	-7.73624200
H	7.43874300	4.48834200	-8.06492100

PC 5a – cation radical

(-2723.005097)

C	-2.04238400	2.13940300	1.12638900
C	-0.98891300	1.29813200	0.79242300
C	0.05084900	1.70353800	-0.04657600
C	0.01700800	3.00722600	-0.59801900
C	-1.03292000	3.86037000	-0.25063900
C	-2.04964200	3.46815200	0.61023000
H	-0.99391800	0.27760200	1.16366400
H	-1.02935000	4.87864100	-0.62896700
N	1.09808100	0.85713500	-0.36798300
N	1.03057500	3.40955900	-1.45003600
C	2.11164400	1.25946600	-1.22000700
C	3.16157200	0.40632000	-1.56738800
C	2.07780800	2.56315700	-1.77144300
C	4.17830200	0.79854800	-2.42824200
H	3.15800400	-0.61195100	-1.18905900
C	3.11757800	2.96856900	-2.61043300
C	4.17104500	2.12729500	-2.94439600



H	3.12258500	3.98909800	-2.98167300
C	1.00973100	4.74290400	-1.99396200
C	0.41908400	4.96676500	-3.21000900
C	1.61238000	5.78186800	-1.25212200
C	0.40849400	6.27320700	-3.75391200
H	-0.03766300	4.14373300	-3.75738600
C	1.60943100	7.05390900	-1.76202300
H	2.06779400	5.55440500	-0.29112700
C	-0.18368900	6.55353700	-5.00955000
C	1.01460600	7.33420400	-3.01764000
H	2.06968600	7.86840800	-1.20669500
C	-0.17363600	7.82918300	-5.51346700
H	-0.64482900	5.73889000	-5.56452100
C	1.00692900	8.63979800	-3.56586600
C	0.42690100	8.88112500	-4.78569300
H	-0.62917600	8.03599700	-6.47840800
H	1.47196700	9.44597600	-3.00170600
H	0.42686900	9.88653500	-5.19867500
C	1.11892600	-0.47620700	0.17594500
C	1.70958200	-0.70006600	1.39198800
C	0.51626700	-1.51517200	-0.56588600
C	1.72017200	-2.00650600	1.93589600
H	2.16633600	0.12296600	1.93935900
C	0.51921700	-2.78721200	-0.05598100
H	0.06084600	-1.28771100	-1.52687800
C	2.31236500	-2.28683300	3.19153000
C	1.11405100	-3.06750400	1.19963300
H	0.05895500	-3.60171100	-0.61130200
C	2.30231100	-3.56247800	3.69545200
H	2.77351100	-1.47218600	3.74649500
C	1.12172900	-4.37309700	1.74786300
C	1.70176500	-4.61442100	2.96768600
H	2.75785800	-3.76929000	4.66039000
H	0.65668400	-5.17927500	1.18371000
H	1.70179800	-5.61983000	3.38067200
C	-3.06873600	4.46892900	0.98470400
C	-3.69949400	5.24315100	0.00940300
C	-3.40090700	4.70085600	2.32914000
C	-4.64657100	6.20728100	0.34223700
H	-3.46615400	5.07321800	-1.04035800
C	-4.32696900	5.66421400	2.67591900
H	-2.91351600	4.12122100	3.11041400
C	-4.96325800	6.42153100	1.68399700
H	-5.12936300	6.77603100	-0.44632800
H	-4.57855100	5.85696500	3.71574100
C	-3.11858300	1.59258600	1.97647700

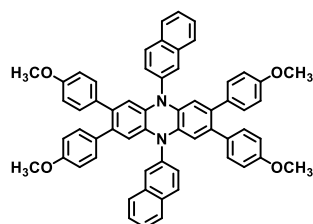
C	-2.80568900	0.83826700	3.10925600
C	-4.47496100	1.76127400	1.65287100
C	-3.79347500	0.27257500	3.90871900
H	-1.76228000	0.70510100	3.38964000
C	-5.46663900	1.19672300	2.43020700
H	-4.75084200	2.33265000	0.76910900
C	-5.13488100	0.44975500	3.56782600
H	-3.50644300	-0.29478800	4.78838000
H	-6.51695800	1.31298100	2.17558400
C	5.19743500	-0.20219700	-2.80269400
C	5.52974300	-0.43400200	-4.14711600
C	5.82811700	-0.97648300	-1.82739400
C	6.45585100	-1.39732000	-4.49388700
H	5.04242600	0.14569900	-4.92838800
C	6.77523500	-1.94057600	-2.16021800
H	5.59467900	-0.80663500	-0.77764100
C	7.09205000	-2.15471400	-3.50196600
H	6.70753900	-1.58997800	-5.53370000
H	7.25796100	-2.50938400	-1.37165400
C	5.24725600	2.67408700	-3.79448200
C	4.93439300	3.42851100	-4.92719900
C	6.60362700	2.50523800	-3.47093800
C	5.92220700	3.99417400	-5.72664900
H	3.89098600	3.56179200	-5.20753900
C	7.59533400	3.06975400	-4.24826300
H	6.87948000	1.93375200	-2.58723600
C	7.26360700	3.81684500	-5.38581000
H	5.63519900	4.56162800	-6.60625900
H	8.64565000	2.95337200	-3.99368700
O	-5.86196100	7.32943600	2.12567900
O	-6.17701700	-0.05609900	4.26419600
O	8.30576700	4.32265600	-6.08217600
O	7.99080700	-3.06257200	-3.94363600
C	-6.54985200	8.10366000	1.16222400
H	-7.14447600	7.47135100	0.49030300
H	-7.21797600	8.76335800	1.71757100
H	-5.85827600	8.71187200	0.56532600
C	-5.89101400	-0.82785100	5.41469400
H	-5.35982800	-0.23770200	6.17240200
H	-6.85217800	-1.14780000	5.81918000
H	-5.29336000	-1.71409000	5.16520600
C	8.67863400	-3.83684700	-2.98017700
H	7.98702500	-4.44513200	-2.38339300
H	9.34683500	-4.49647700	-3.53551400
H	9.27317200	-3.20457000	-2.30815000
C	8.01979800	5.09454000	-7.23259300

H	7.42224200	5.98081600	-6.98300300
H	8.98097800	5.41443000	-7.63708800
H	7.48852300	4.50451200	-7.99033400

PC 5b – neutral triplet

(-2723.092185)

C	-0.09037900	2.45918700	-2.82762800
C	0.11274100	1.23650400	-2.20184200
C	0.78753000	1.11417900	-0.98185100
C	1.27561600	2.29172400	-0.35356900
C	1.06417200	3.52336300	-0.98316000
C	0.38930800	3.64283900	-2.19071700
H	-0.22675000	0.33355600	-2.70264200
H	1.40341200	4.42796300	-0.48525900
N	1.00551000	-0.11579100	-0.38181300
N	1.93489800	2.18988400	0.86131900
C	1.66477800	-0.23674900	0.82886000
C	1.94185300	-1.46555800	1.41622100
C	2.13717200	0.97263300	1.48806700
C	2.61532500	-1.59781500	2.62948500
H	1.69904700	-2.36445900	0.85475300
C	2.73664800	0.86034000	2.73619400
C	2.94131600	-0.36072800	3.37916000
H	2.97186700	1.77797300	3.26989100
C	2.50512100	3.36483500	1.45430200
C	1.73187400	4.17534400	2.24475200
C	3.86647900	3.64982600	1.21273100
C	2.29361500	5.33491400	2.83274200
H	0.68497200	3.92954900	2.41698200
C	4.43208400	4.76548500	1.77458400
H	4.44177900	2.97547200	0.58253200
C	1.53131100	6.20266200	3.65094600
C	3.66800500	5.63406500	2.59426200
H	5.47946400	5.00101200	1.59605700
C	2.10387600	7.31865800	4.20905200
H	0.48336000	5.96732700	3.82799000
C	4.22804400	6.79271300	3.18413800
C	3.46407700	7.61630700	3.97333100
H	1.51034400	7.97918900	4.83602000
H	5.27704000	7.01718300	2.99874000
H	3.90483400	8.50350800	4.42100700
C	0.50459600	-1.30439200	-1.00938400
C	1.24626300	-1.91650300	-1.98656200
C	-0.74103800	-1.82266400	-0.59453000



C	0.76296500	-3.09110500	-2.61139000
H	2.20552800	-1.49601600	-2.28505000
C	-1.22682800	-2.96221100	-1.18377300
H	-1.29300200	-1.30626500	0.18746400
C	1.49403500	-3.75117400	-3.62790900
C	-0.49508400	-3.62418900	-2.20152000
H	-2.18657300	-3.37368500	-0.87731400
C	1.00149300	-4.89030900	-4.21435200
H	2.45308300	-3.33736800	-3.93433300
C	-0.97512000	-4.80047900	-2.82635900
C	-0.24424500	-5.41939200	-3.80993900
H	1.56973500	-5.39062400	-4.99436900
H	-1.93578800	-5.20371600	-2.51074800
H	-0.62292100	-6.32207900	-4.28271900
C	0.15455000	5.00121600	-2.72486100
C	1.18811400	5.93906600	-2.77002200
C	-1.11631400	5.41330400	-3.15800800
C	0.98510000	7.23828000	-3.22954700
H	2.18720300	5.64375400	-2.45321100
C	-1.33590400	6.69931900	-3.61431900
H	-1.94646400	4.71048900	-3.12447400
C	-0.28512000	7.62318900	-3.65650500
H	1.82097400	7.93077300	-3.25582100
H	-2.32210600	7.02116400	-3.94033500
C	-0.74278200	2.46200900	-4.15436500
C	-1.90376700	1.72027100	-4.38146900
C	-0.19652000	3.16335700	-5.24172900
C	-2.51399500	1.67093700	-5.63279200
H	-2.35707000	1.17687900	-3.55381800
C	-0.78742800	3.12321100	-6.49043000
H	0.71498300	3.74109200	-5.10176800
C	-1.95425400	2.37778700	-6.69626400
H	-3.42128800	1.08837200	-5.76088600
H	-0.35865000	3.65828300	-7.33438800
C	3.07355600	-2.92243900	3.03379300
C	4.30980800	-3.12137600	3.68932300
C	2.32120900	-4.07680500	2.75042100
C	4.76086800	-4.38530200	4.01789300
H	4.93630200	-2.26219800	3.91664800
C	2.76139800	-5.35272700	3.08034300
H	1.34505000	-3.97330300	2.27914400
C	3.99197900	-5.51584000	3.72040400
H	5.72241300	-4.52734700	4.50650200
H	2.13221000	-6.20703100	2.84786400
C	3.33610700	-0.35602700	4.78249400
C	2.86862600	-1.31690300	5.69946400

C	4.18297200	0.64882500	5.30256100
C	3.20423200	-1.27965800	7.04830300
H	2.19942300	-2.10083000	5.35340100
C	4.52721800	0.69365100	6.63865800
H	4.60201400	1.39508000	4.62956000
C	4.04030000	-0.27164700	7.52936000
H	2.80173800	-2.03781300	7.71411400
H	5.19149300	1.46517000	7.02164800
O	-0.60028400	8.85626300	-4.12424100
O	-2.45988700	2.40561800	-7.95409200
O	4.44021700	-0.14504800	8.82245700
O	4.51857200	-6.71222600	4.09384900
C	0.43065700	9.82049900	-4.18055900
H	1.24338500	9.50375000	-4.84754900
H	-0.01892500	10.73311700	-4.57493700
H	0.84577000	10.02589900	-3.18492000
C	-3.63443300	1.66213100	-8.20587800
H	-4.47465100	2.01556200	-7.59356500
H	-3.87484700	1.80881900	-9.26001100
H	-3.48186400	0.59106000	-8.01792400
C	3.77152800	-7.87367300	3.80348900
H	3.60701700	-7.98971700	2.72360400
H	4.35636800	-8.72014500	4.16753400
H	2.79770400	-7.86664800	4.31169400
C	3.97332700	-1.10377700	9.74657500
H	4.29988600	-2.11759300	9.47775100
H	4.39983500	-0.83737200	10.71518600
H	2.87752400	-1.09285400	9.82264500

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APPENDIX C – SUPPLEMENTARY INFORMATION FOR CHAPTER 3

MATERIALS AND METHODS

Unless otherwise stated, all chemicals were used as received without additional purification and stored per manufacturer specifications. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc.

Materials for Photocatalyst Synthesis

5,10-dihydrophenazine synthesis. Phenazine and sodium dithionite were purchased from Alfa Aesar. Reagent grade alcohol was purchased from Fisher Scientific.

***N,N*-di(2-naphthyl)-5,10-dihydrophenazine (PC 2) synthesis.** Sodium *tert*-butoxide, toluene, bis(dibenzylideneacetone) palladium(0), and tri-*tert*-butylphosphine were purchased from Sigma Aldrich. 2-bromonaphthalene was purchased from Alfa Aesar. Toluene was purified using an mBraun MB-SPS-800 solvent purification system and stored under nitrogen atmosphere. Dichloromethane and methanol were purchased from Fisher Scientific.

***N,N*-di(2-naphthyl)-5,10-dihydrophenazine (PC 1) synthesis.** 1-bromonaphthalene, sodium *tert*-butoxide, toluene, bis(dibenzylideneacetone) palladium(0), and tri-*tert*-butylphosphine were purchased from Sigma Aldrich. Toluene was purified using an mBraun MB-SPS-800 solvent purification system and stored under nitrogen atmosphere.

PC 1a, 2a, 1b, and 2b syntheses. Diethyl-2-bromo-2-methylmalonate (DBMM), triethylamine (TEA), *N,N*-dimethylacetamide (DMAc) and tetrahydrofuran (THF) were purchased from Sigma Aldrich. Dichloromethane and methanol were purchased from Fisher Scientific.

Materials for Kinetic Experiments

Diethyl-2-bromo-2-methylmalonate (DBMM), triethylamine (TEA), and anhydrous *N,N*-dimethylacetamide (DMAc) were purchased from Sigma Aldrich. Butylated hydroxy toluene (BHT) was purchased from Fisher Scientific. DBMM was dried over calcium hydride, distilled

under reduced pressure, degassed by freeze-pump-thaw, and stored in a nitrogen-filled glovebox freezer at -34 °C prior to use. DBMM was allowed to warm to room temperature before use.

Materials for PC Characterization

DMAc (99.8% anhydrous) was purchased from Sigma Aldrich in Sure/Seal bottles and HPLC grade acetonitrile (MeCN) for cyclic voltammetry was purchased from Fischer Scientific and used without further purification. 1-hexene, benzene, 1,4-dioxane, THF, pyridine, and DMF were purchased from Sigma Aldrich, Fisher Scientific, Alfa Aesar, or Oakwood Chemicals.

Materials for Polymerizations

DBMM and methyl methacrylate (MMA) were purchased from Sigma Aldrich and dried over calcium hydride, distilled under reduced pressure, degassed by freeze-pump-thaw, and stored in a nitrogen-filled glovebox freezer at -34 °C prior to use. *N,N*-dimethyl acetamide (DMAc), and ethyl acetate (EtOAc) were purchased from Sigma Aldrich (anhydrous, Sure/Seal bottles).

Experimental Equipment

Light reactors. Light beakers were composed of double-density white LED strips purchased from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH). The reactors were constructed by covering a 400 mL beaker (height = 10.0 cm, diameter = 8.5 cm) with aluminum foil and wrapping the white LED strips (9 LED segments, 16" total) around the inside of the beaker. For polymerizations, double the number of white LED segments were used (18 LED segments, 32" total).



Figure A3.1. Photographs of 400 mL white LED light beakers used for AkCS (left) and polymerizations (right).

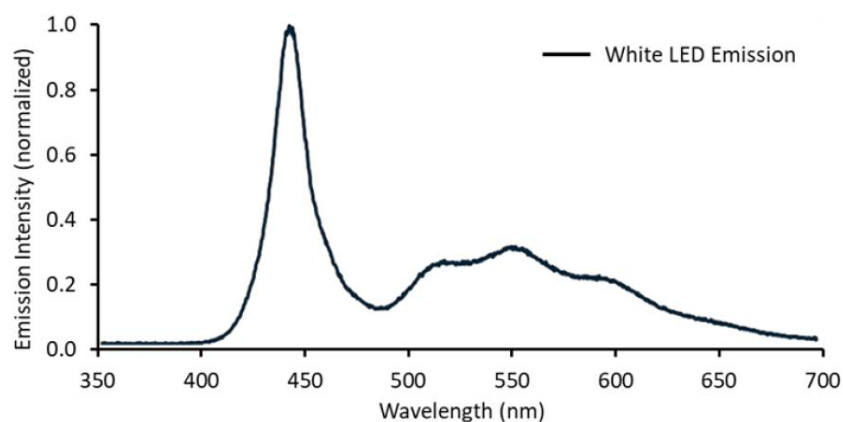


Figure A3.2. Normalized emission spectrum for the white LED lights used in AkCS reactions and polymerizations.

Instrumentation for Characterization

Nuclear magnetic resonance (NMR) spectroscopy. NMR was performed using either a Bruker US 400 MHZ spectrometer or a Bruker Ascend 400 MHZ spectrometer. All the ^1H NMR spectra are reported in δ units, parts per million (ppm), and are referenced to benzene (7.15 ppm) or chloroform (7.26 ppm) signals. All ^{13}C NMR spectra are reported in ppm relative to CDCl_3 (77.23 ppm) or C_6D_6 (128.62 ppm).

Matrix-assisted laser desorption/ionization (MALDI) Mass Spectrometry. High resolution mass spectrometry was performed using a Bruker ultrafleXtreme MALDI-TOF/TOF.

UV-Visible spectroscopy. UV-Visible spectroscopy was performed using an Agilent Cary 5000 UV-Vis-NIR spectrometer.

Fluorescence spectroscopy. Steady state fluorescence spectroscopy was performed using a FS5 Spectrofluorometer from Edinburgh Instruments. Fluorescence quantum yield measurements were performed using an FS5 Spectrofluorometer from Edinburgh Instruments equipped with an SC-30 integrating sphere via a direct excitation method.

Phosphorescence spectroscopy. Phosphorescence measurements were performed using an Edinburgh Instruments LP980KS spectrometer with a Minilite Nd-YAG Q-switched laser (Continuum Lasers) configured to deliver a 355 nm excitation pulse. Spectral emission data was obtained with the indicated time delays using an iStar ICCD camera (Andor) as the detector. Time zero was set on the instrument using the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ to locate the pump pulse with a resolution of 1 ns.

Time correlated single photon counting (TCSPC). TCSPC was performed using an FS5 Spectrofluorometer from Edinburgh Instruments with a TCSPC upgrade and a 365 nm EPLED from Edinburgh Instruments.

Transient absorption (TA) spectroscopy. Transient absorption (TA) spectroscopy was performed on an Edinburgh Instruments LP980KS spectrometer with a Minilite Nd:YAG Q-switched laser (Continuum Lasers) configured to deliver a 355 excitation pulse. Spectral absorption data was acquired with an iStar ICCD camera (Andor) as the detector. Kinetic data was recorded utilizing a photomultiplier tube (included in the LP980) interfaced with an MD03022 mixed domain oscilloscope (Tektronix) as the detector.

Cyclic voltammetry. Cyclic Voltammetry was conducted using a Gamry Interface 1010B potentiostat. A 5-port electrochemical cell (Gamry) was equipped with a glassy carbon working

electrode (Gamry), a Pt counter electrode, and an Ag/AgNO₃ reference electrode separated from the main compartment by a frit. The reference electrode was constructed by putting a silver wire into a fritted glass compartment containing a solution of 0.10 M NBu₄PF₆ and 0.01 M AgNO₃ in acetonitrile.

Gel permeation chromatography (GPC). Analysis of polymer molecular weights were performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μ m MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. A dn/dc value of 0.084 was used for PMMA molecular weight analysis.

SYNTHETIC PROCEDURES

Synthesis of Parent Photocatalysts

5,10-dihydrophenazine synthesis. This synthesis was performed using a literature procedure.¹ ^1H NMR (400 MHz, C_6D_6) δ (ppm): 3.93 (s, 2H), 5.57-5.79 (m, 4H), 6.31-6.61 (m, 4H).

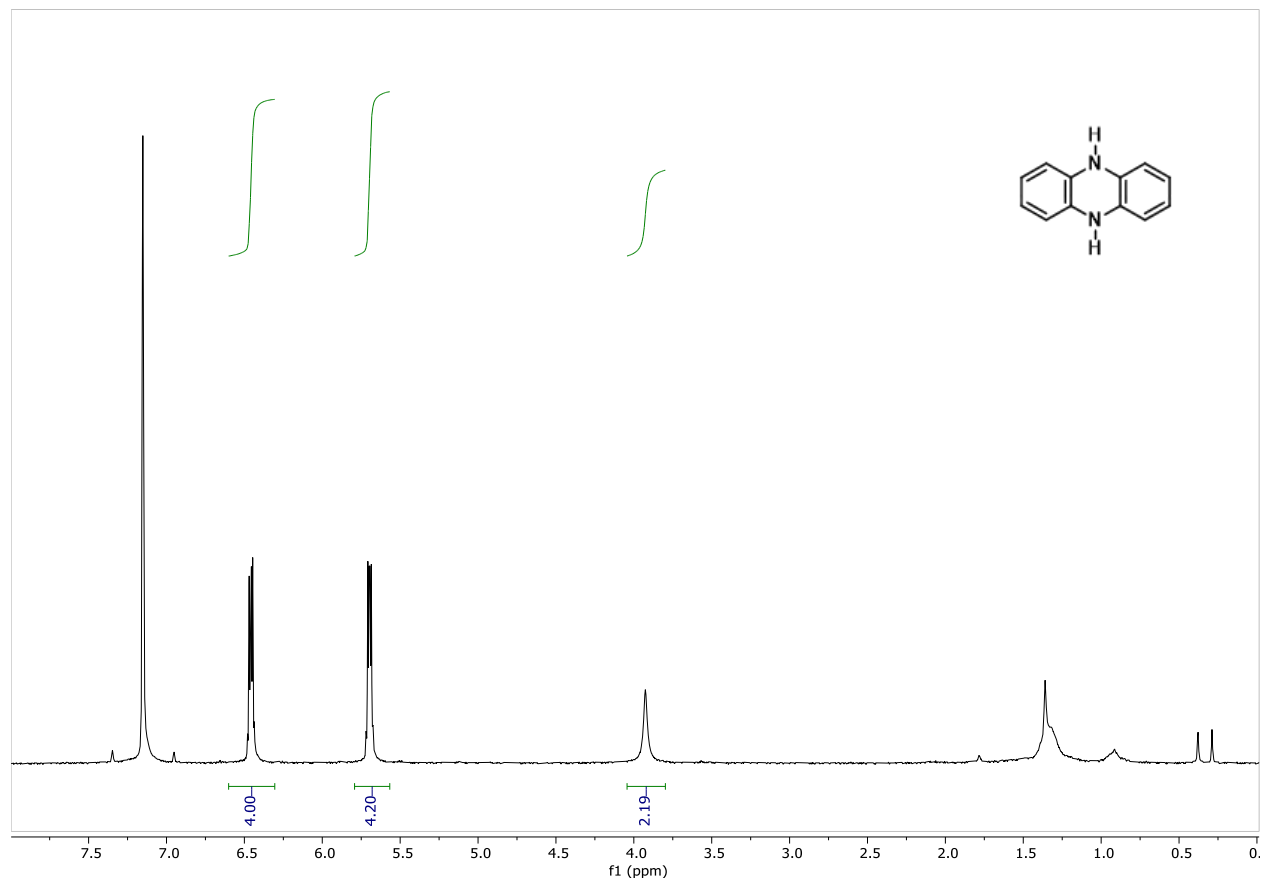


Figure A3.3. ^1H NMR spectrum of 5,10-dihydrophenazine in C_6D_6 .

5,10-di(1-naphthyl)-5,10-dihydrophenazine (PC 1) synthesis. This synthesis was performed using a modified literature procedure.² PC 1 was purified by dissolving it in toluene with heat, cooling to room temperature and running it through a silica plug deactivated with 3% TEA. The eluent was dried by rotary evaporation and then recrystallized in 1:3 DCM: MeOH at -18 °C, resulting in bright yellow solids obtained in a 31.6% yield. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 5.61-5.70 (dd, 4H), 6.03-6.10 (dd, 4H), 7.20-7.31 (m, 6H), 7.41-7.50 (m, 2H), 7.60 -7.72

(m, 4H), 8.56–8.66 (m, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 113.30, 121.69, 124.27, 124.38, 127.05, 128.91, 129.14, 129.53, 129.72, 132.29, 136.33, 136.96, 137.34.

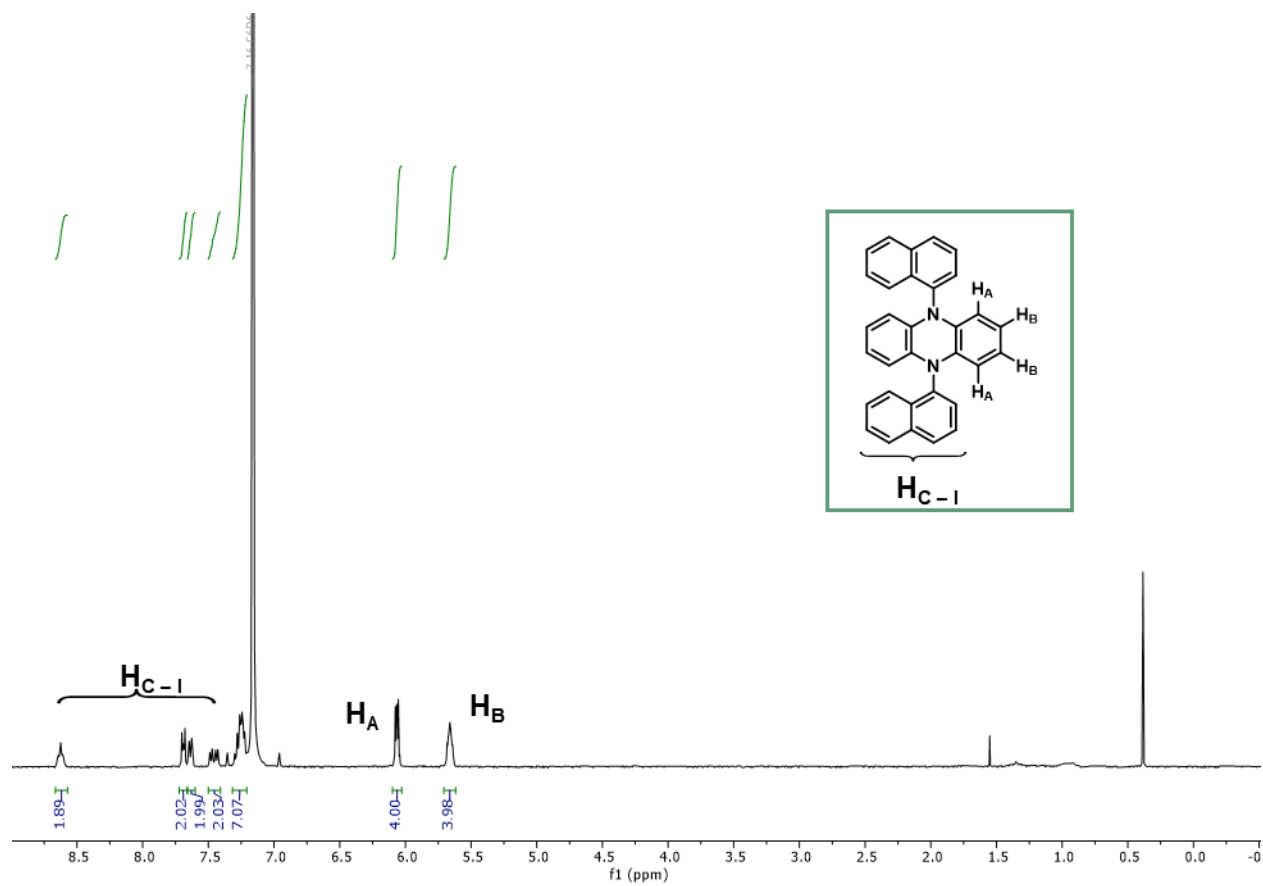


Figure A3.4. ^1H NMR spectrum of PC 1 in C_6D_6 .

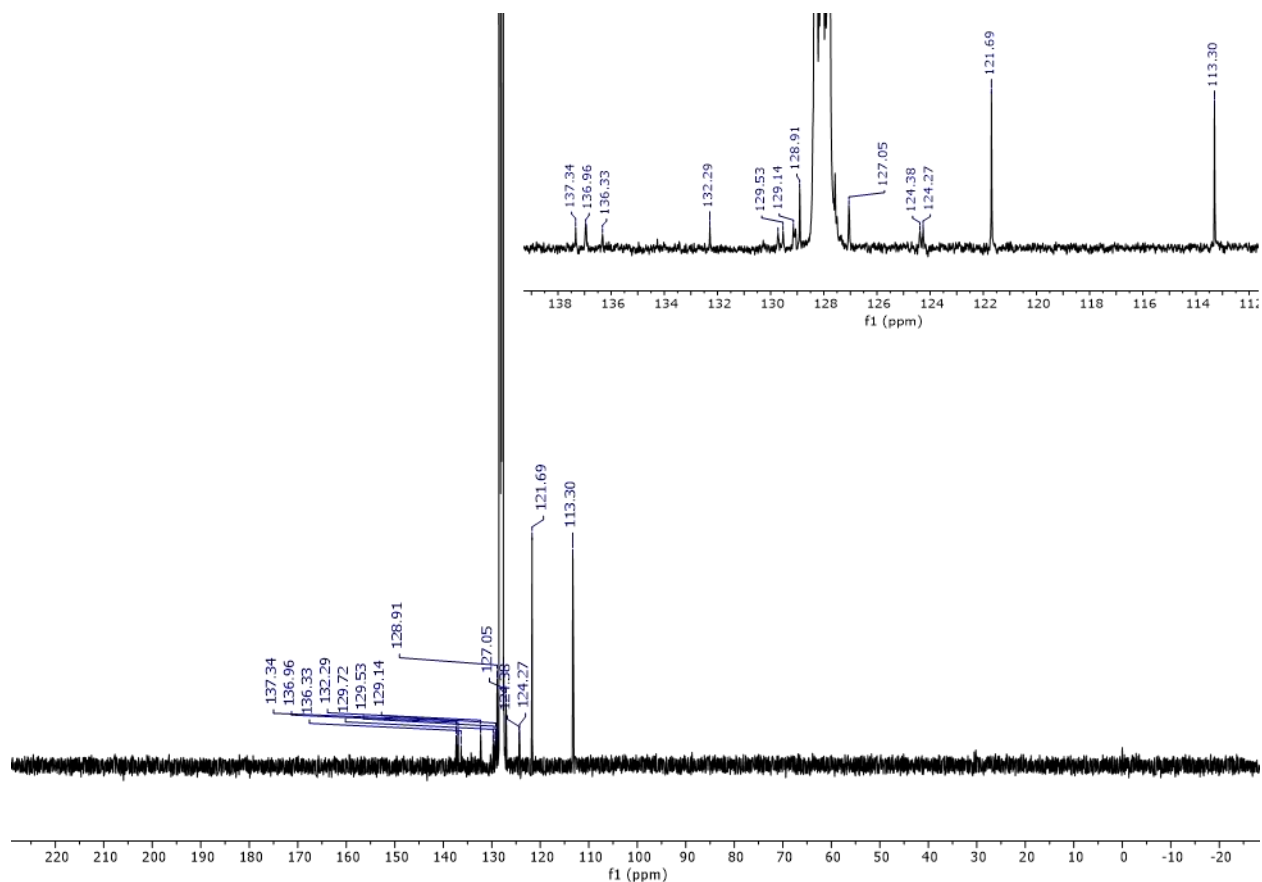


Figure A3.5. ^{13}C NMR spectrum of PC **1** in C_6D_6 .

5,10-di(2-naphthyl)-5,10-dihydrophenazine (PC 2) synthesis. This synthesis was performed using a modified literature procedure.² PC **2** was purified by dissolving it in toluene with heat, cooling to room temperature and running it through a silica plug deactivated with 3% TEA. The eluant was dried by rotary evaporation and then recrystallized in 1:3 dichloromethane: methanol at $-18\text{ }^{\circ}\text{C}$, resulting in bright yellow solids obtained in a 73.0% yield. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 5.82-5.90 (dd, 4H), 6.24-6.31 (dd, 4H), 7.19-7.34 (m, 6H), 7.50-7.62 (m, 4H), 7.60-7.72 (m, 4H), 7.65–7.70 (m, 4H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 113.40, 121.61, 126.47, 126.84, 129.11, 130.85, 131.94, 133.30, 135.60, 137.22, 138.08.

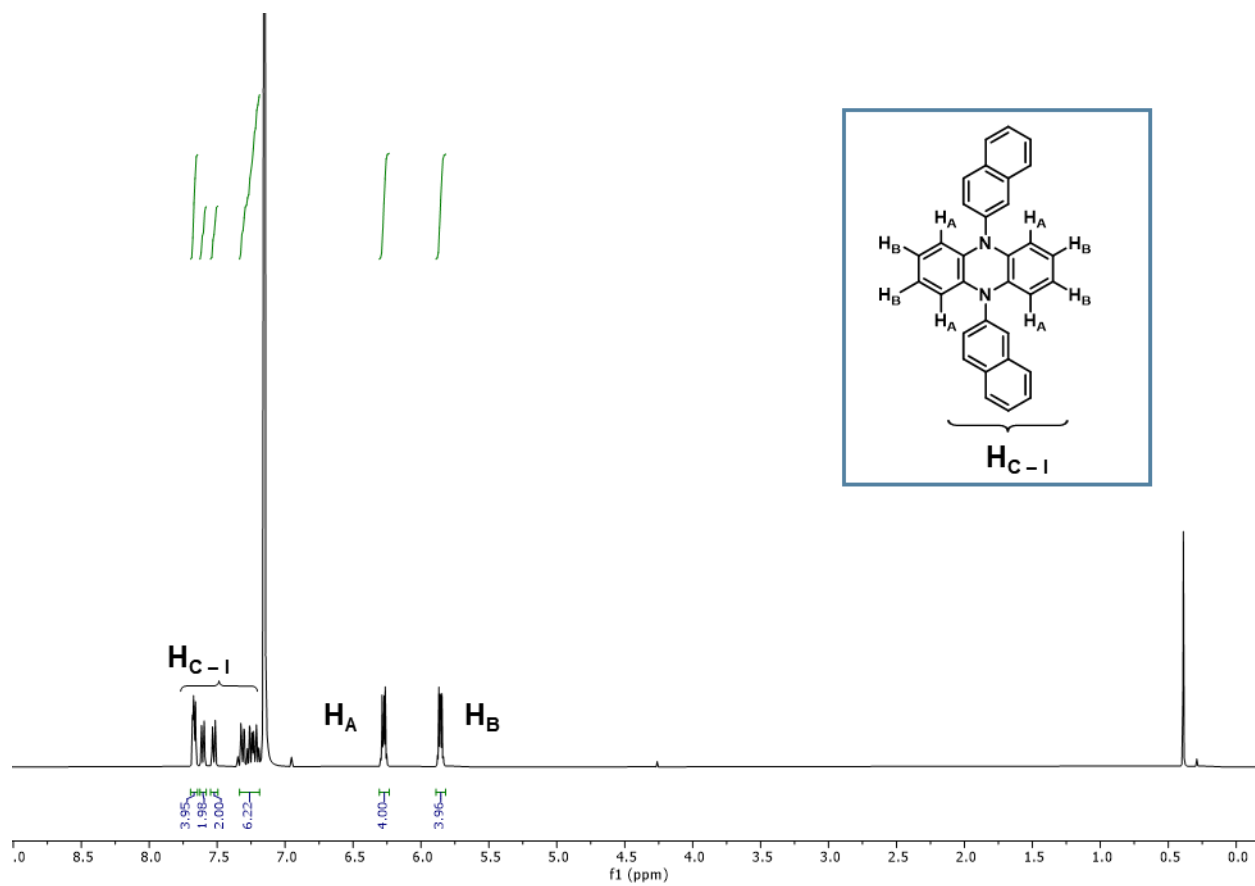


Figure A3.6. ^1H NMR spectrum of PC 2 in C_6D_6 .

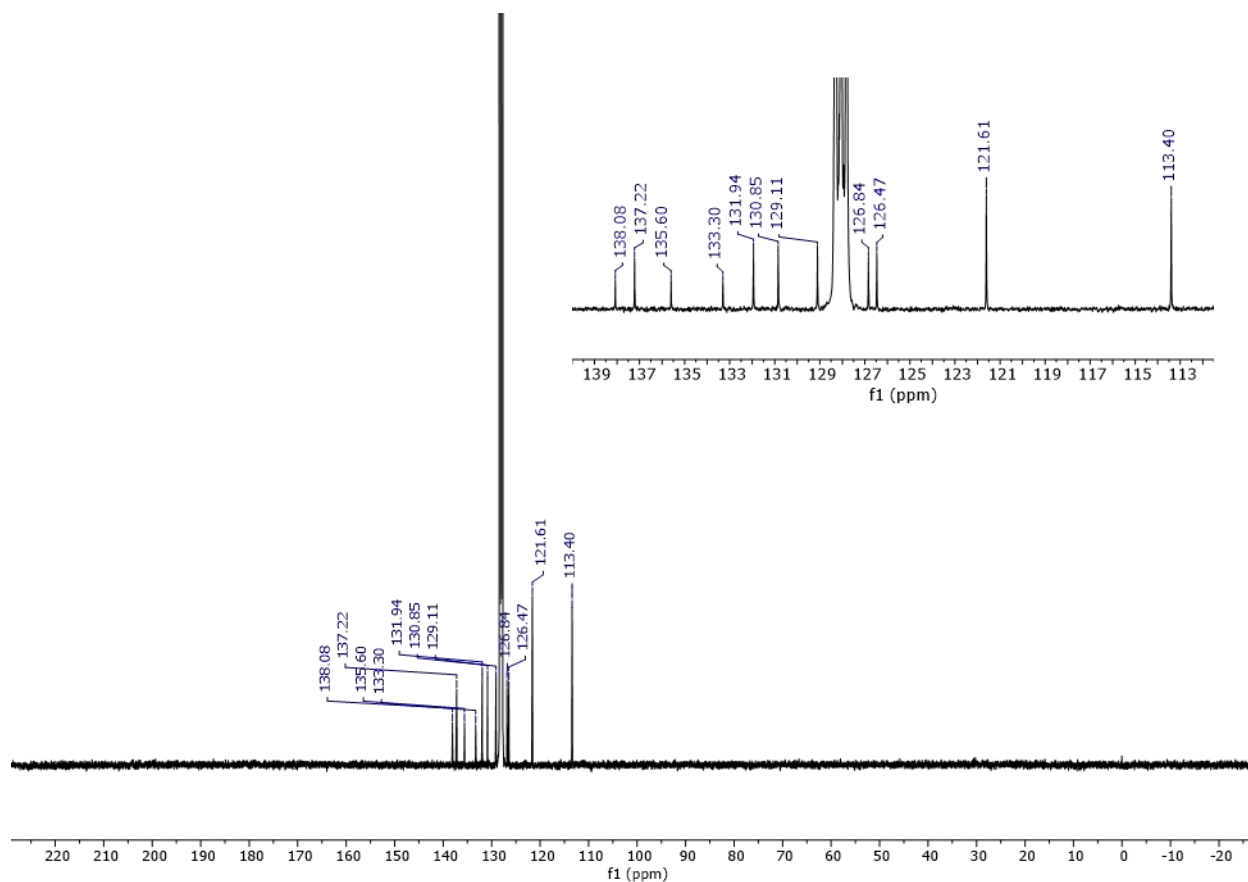


Figure A3.7. ^{13}C NMR spectrum of PC **2** in C_6D_6 .

Synthesis of AkCS Photocatalysts

2-(diethyl-2-methymalonate-yl)-5,10-di(1-naphthyl)-5,10 (PC 1a) dihydrophenazine synthesis. THF and DBMM were separately sparged with N_2 for approximately 30 minutes before addition to the reaction mixture. Under N_2 , PC **1** (0.288 mmol, 0.125 g, 1 eq.), THF (190 mL), and DBMM (0.0288 mmol, 55.0 μL , 1 eq.) were combined in a storage tube, then irradiated for 30 minutes in a white LED beaker. The reaction mixture was removed from the light source and opened to air, then 10 eq. TEA was added. The PC **1a** was purified using column chromatography prepared with a slurry of silica gel deactivated with 3% TEA/hexanes. The crude material was dissolved in a minimal amount of toluene and loaded onto the column. The components of the reaction mixture were eluted using 4:1 [3% TEA/hexanes: EtOAc]. Because PC **1** was visible by TLC in the PC **1a** fractions, a second gradient column from 100% [3% TEA/hexanes] to 8:1 [3%

TEA/hexanes: EtOAc] to 6:1 [3% TEA/hexanes: EtOAc] and third gradient column from 6:1 [3% TEA/hexanes: EtOAc] to 4:1 [3% TEA/hexanes: EtOAc] was run. Fractions were combined and dried down under reduced pressure. Samples were redissolved in a minimum of DCM and then precipitated in an excess of MeOH, filtered, and then dried under vacuum resulting in yellow solids in a 28.0% yield, which was determined the be PC **1a** by NMR. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 0.54 (m, 3H), 0.70 (m, 3H), 1.62 (s, 3H), 3.43–3.79 (m, 4H), 5.56 (m, 1H), 5.62–5.73 (m, 2H), 5.94 (d, 1H, $J = 11.6$), 6.02–6.11 (m, 2H), 6.21 (d, 1H $J = 9.20$), 7.20–7.71 (overlapping peaks, 12H), 8.46–8.69 (m, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 13.63, 13.84, 22.20, 58.22, 60.94, 61.04, 112.64, 113.34, 121.78, 127.07, 128.91, 128.96, 129.03, 131.87, 132.11, 136.36, 171.21.

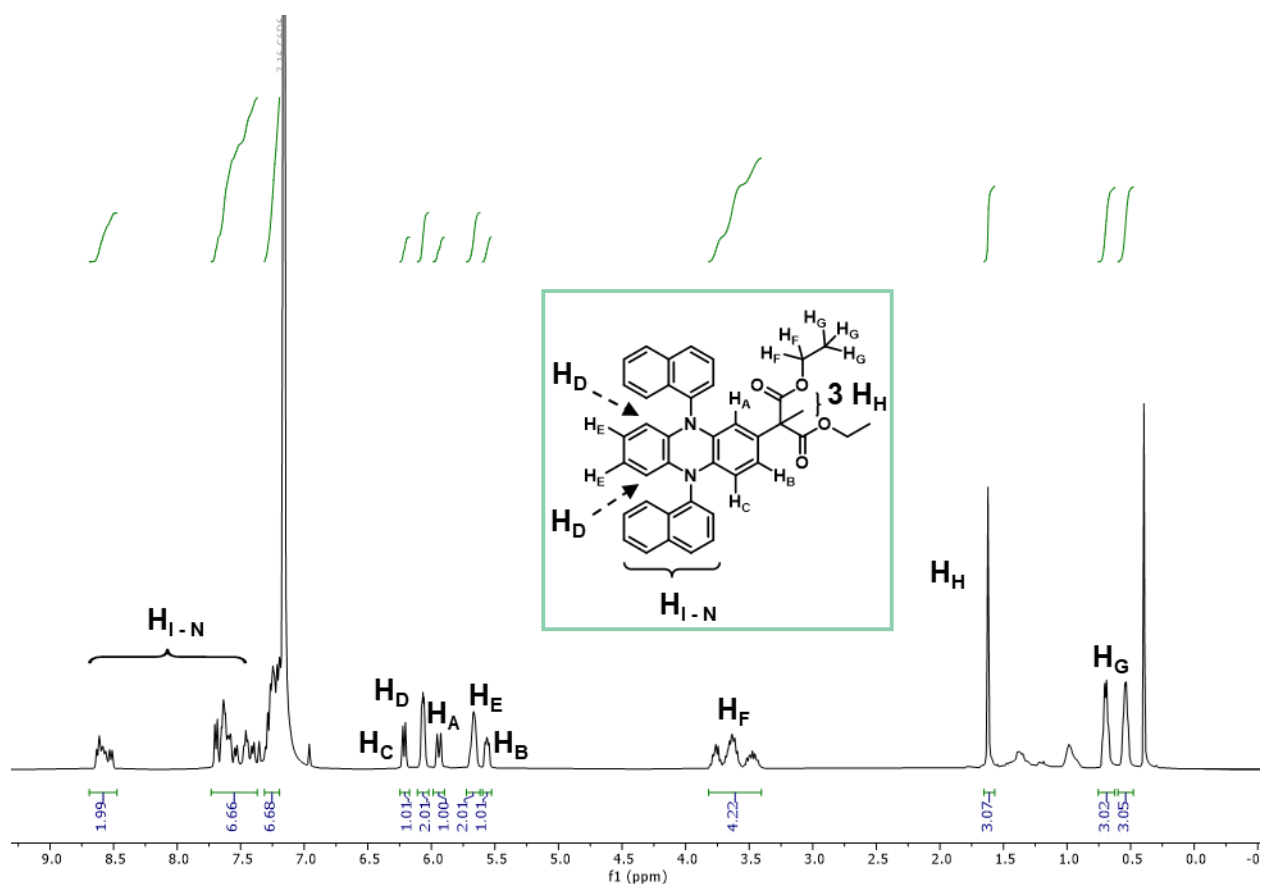


Figure A3.8. ^1H NMR spectrum of PC **1a** in C_6D_6 .

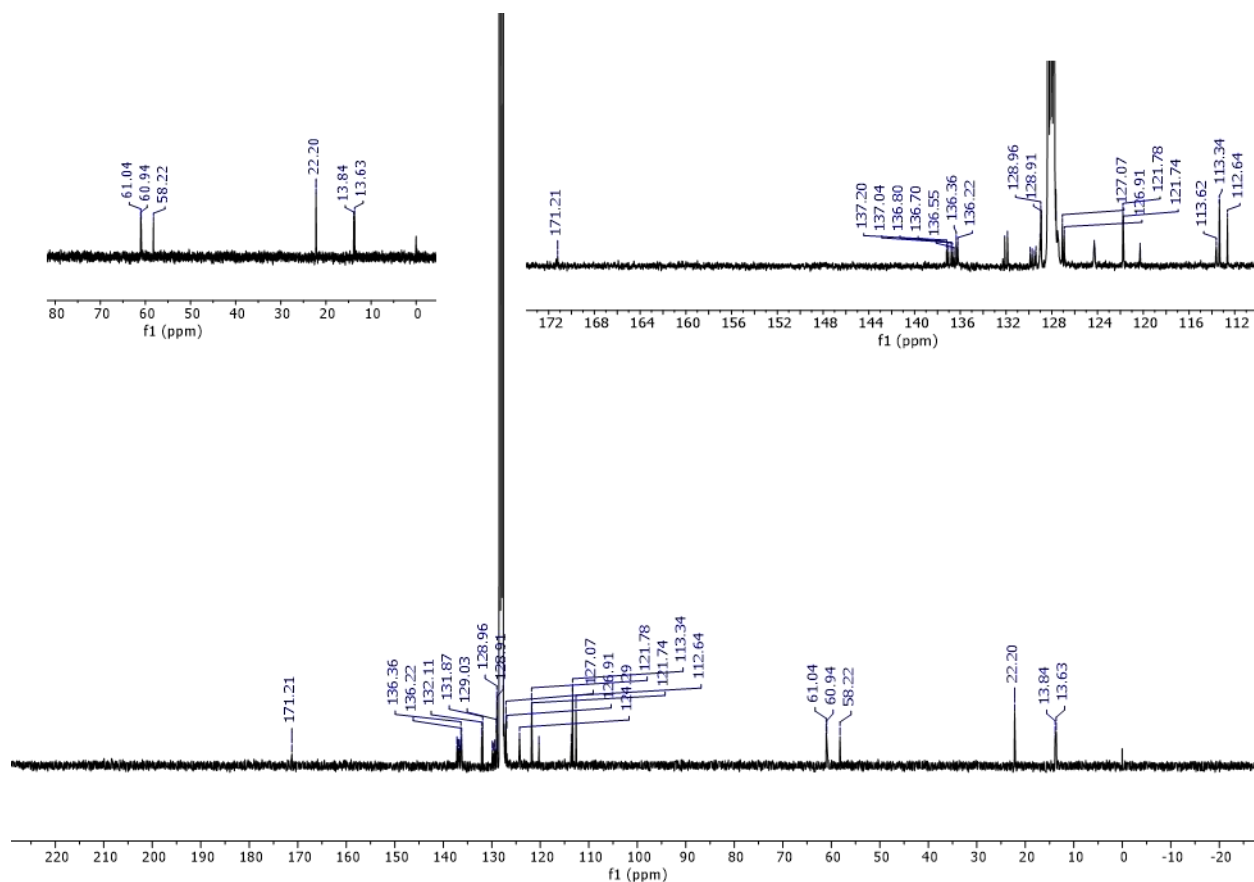


Figure A3.9. ^{13}C NMR spectrum of PC 1a in C_6D_6 .

2-(diethyl-2-methylmalonate-yl)-5,10-di(2-naphthyl)-5,10 (PC 2a) dihydrophenazine synthesis. THF and DBMM were separately sparged with N_2 for approximately 30 minutes before addition to the reaction. Under N_2 , PC 2 (0.288 mmol, 0.125 g, 1 eq.), THF (190 mL), and DBMM (0.288 mmol, 55.0 μL , 1 eq.) were combined in a storage tube, then irradiated for 24 hours in a white LED beaker. The reaction mixture was removed from the light source and opened to air, then 10 eq. of TEA was added. PC 2a was purified using column chromatography prepared with a slurry of silica gel deactivated with 3% TEA/hexanes. The crude material was dissolved in a minimal amount of toluene and loaded onto the column. The components of the reaction mixture were eluted using 4:1 [3% TEA/hexanes: EtOAc]. Because PC 2 was visible by TLC in the PC 2a fractions, a second gradient column from 100% [3% TEA/hexanes] to 8:1 [3% TEA/hexanes: EtOAc] to 6:1 [3% TEA/hexanes: EtOAc] was run. Fractions were combined and dried down

under reduced pressure. Samples were redissolved in a minimum of DCM and then precipitated in an excess of MeOH, filtered, and then dried under vacuum resulting in yellow solids in a 19.7% yield, which was determined the be PC **2a** by NMR. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 0.67 (t, 6H, $J = 7.20$), 1.73 (s, 3H), 3.66–3.81 (m, 4H), 5.77 (d, 1H, $J = 7.60$), 5.84–5.91 (m, 2H), 6.16 (d, 1H, $J = 2.00$), 6.25–6.31 (m, 2H), 6.38–6.44 (dd, 1H, $J_1 = 4.40$, $J_2 = 8.40$) 7.20–7.71 (overlapping peaks, 14H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 13.76, 22.29, 58.32, 61.14, 113.51, 113.53, 121.65, 121.70, 126.41, 126.51, 126.77, 126, 89, 129.01, 129.13, 130.75, 131.79, 131.91, 131.94, 133.33, 135.50, 135.58, 136.66, 136.77, 137.04, 137.09, 137.87, 138.02, 171.44.

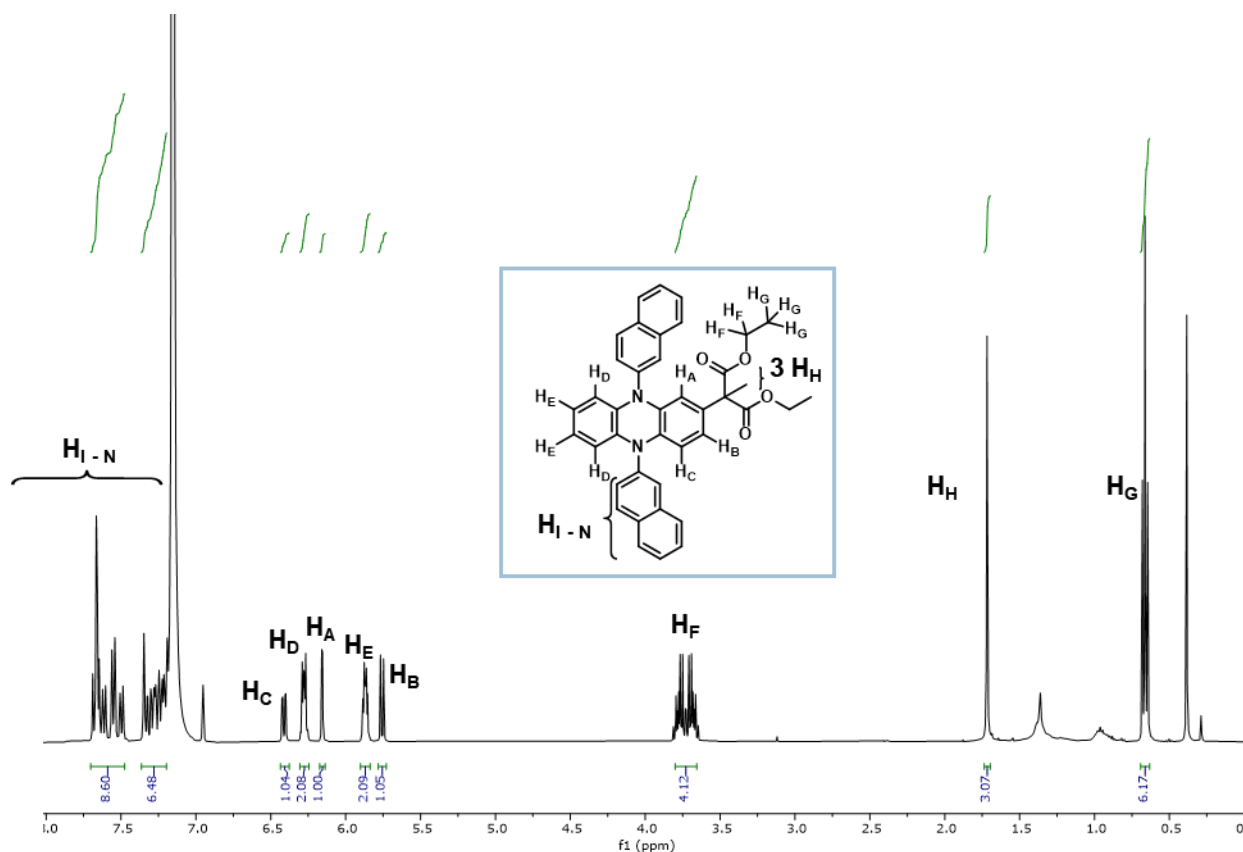


Figure A3.10. ^1H NMR spectrum of PC **2a** in C_6D_6 .

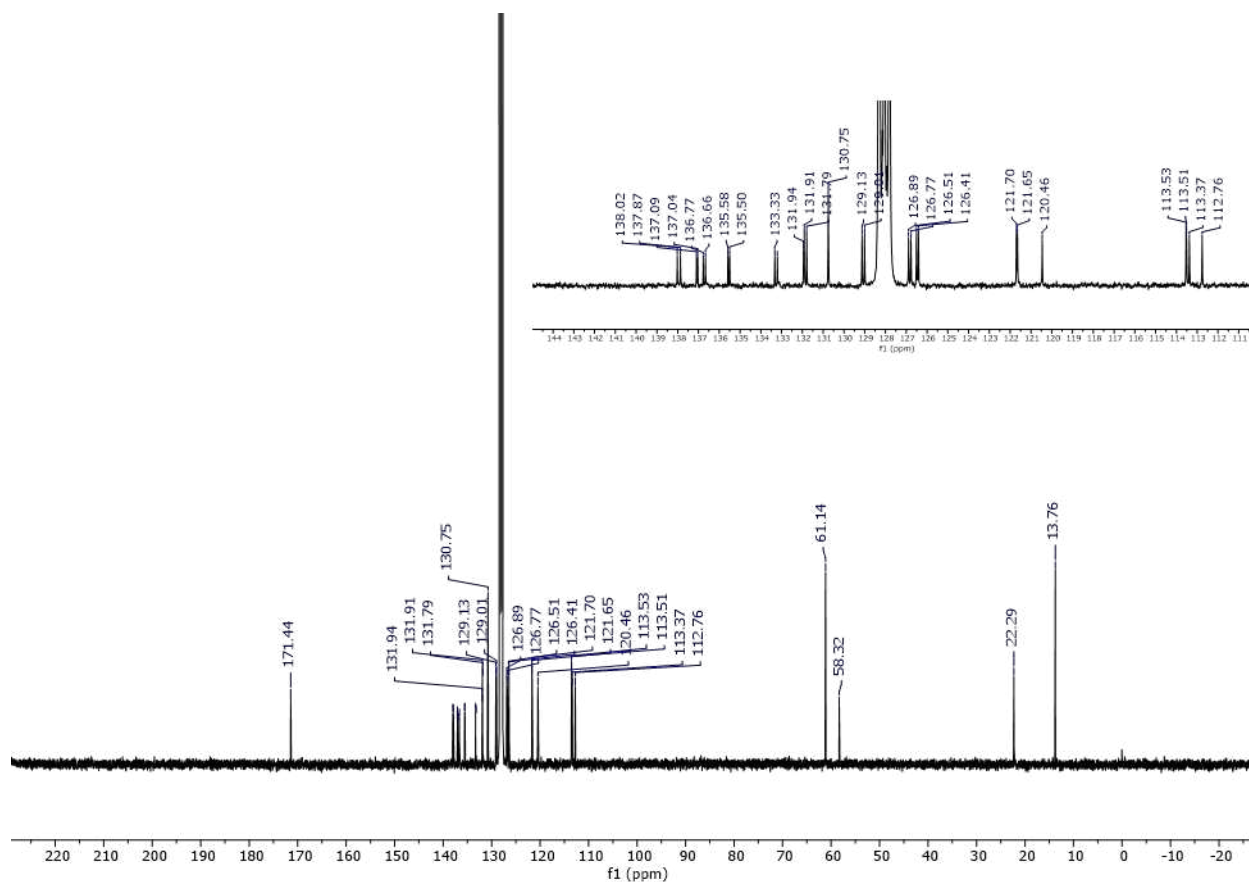


Figure A3.11. ^{13}C NMR spectrum of PC **2a** in C_6D_6 .

2,7-di(diethyl-2-methylmalonate-yl)-5,10-di(1-naphthyl)-5,10 (PC 1b)
dihydrophenazine synthesis. THF and DBMM were separately sparged with N_2 for approximately 30 minutes before addition to the reaction mixture. Under N_2 , PC **1** (0.575 mmol, 0.250 g, 1 eq.), THF (40 mL), and DBMM (2.87 mmol, 550 μL , 5 eq.) were combined in a storage tube, then irradiated for 24 hours in a white LED beaker. The reaction mixture was removed from the light source and opened to air, then 10 eq. TEA was added. PC **1b** was purified using column chromatography prepared with a slurry of silica gel deactivated with 3% TEA/hexanes. The crude material was dry loaded onto silica in 3% TEA in toluene. The components of the reaction mixture were eluted using 4:1 [3% TEA/hexanes: EtOAc]. Fractions were combined and dried down under reduced pressure. Samples were redissolved in a minimum of DCM and then precipitated in an excess of MeOH, filtered, and then dried under vacuum resulting in yellow solids in a 53.8% yield,

which was determined the be PC **1b** by NMR. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 0.47-0.59 (m, 6H), 0.65-0.74 (m, 6H), 1.62 (s, 6H), 3.39–3.84 (m, 8H), 5.53-5.63 (m, 2H), 5.91-6.02 (m, 2H), 6.18-6.26 (m, 2H), 7.20-7.71 (overlapping peaks, 12H), 8.38-8.66 (m, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 13.62, 13.84, 22.18, 58.22, 60.95, 61.05, 112.68, 112.70, 124.25, 126.93, 127.08, 128.89, 128.97, 136.13, 171.18, 171.33.

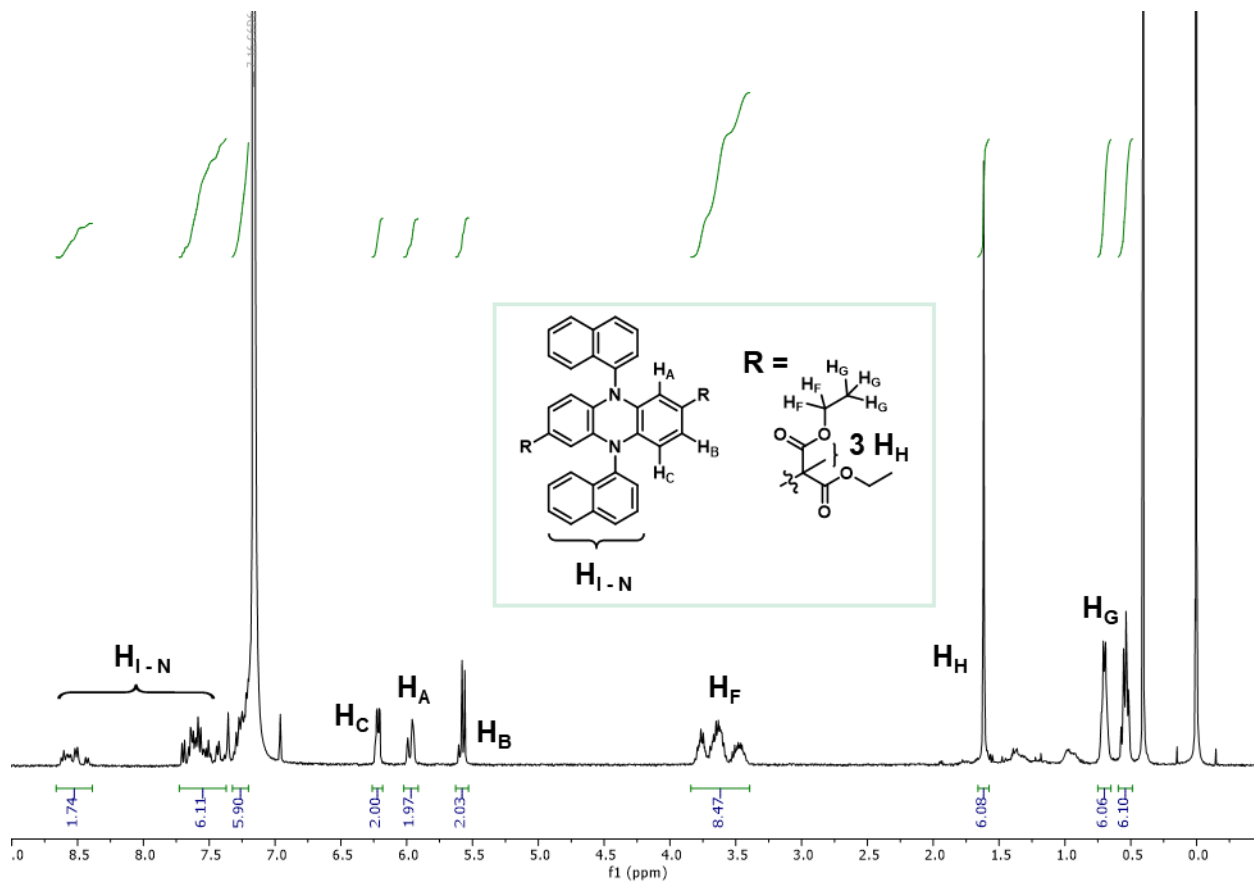


Figure A3.12. ^1H NMR spectrum of PC **1b** in C_6D_6 .

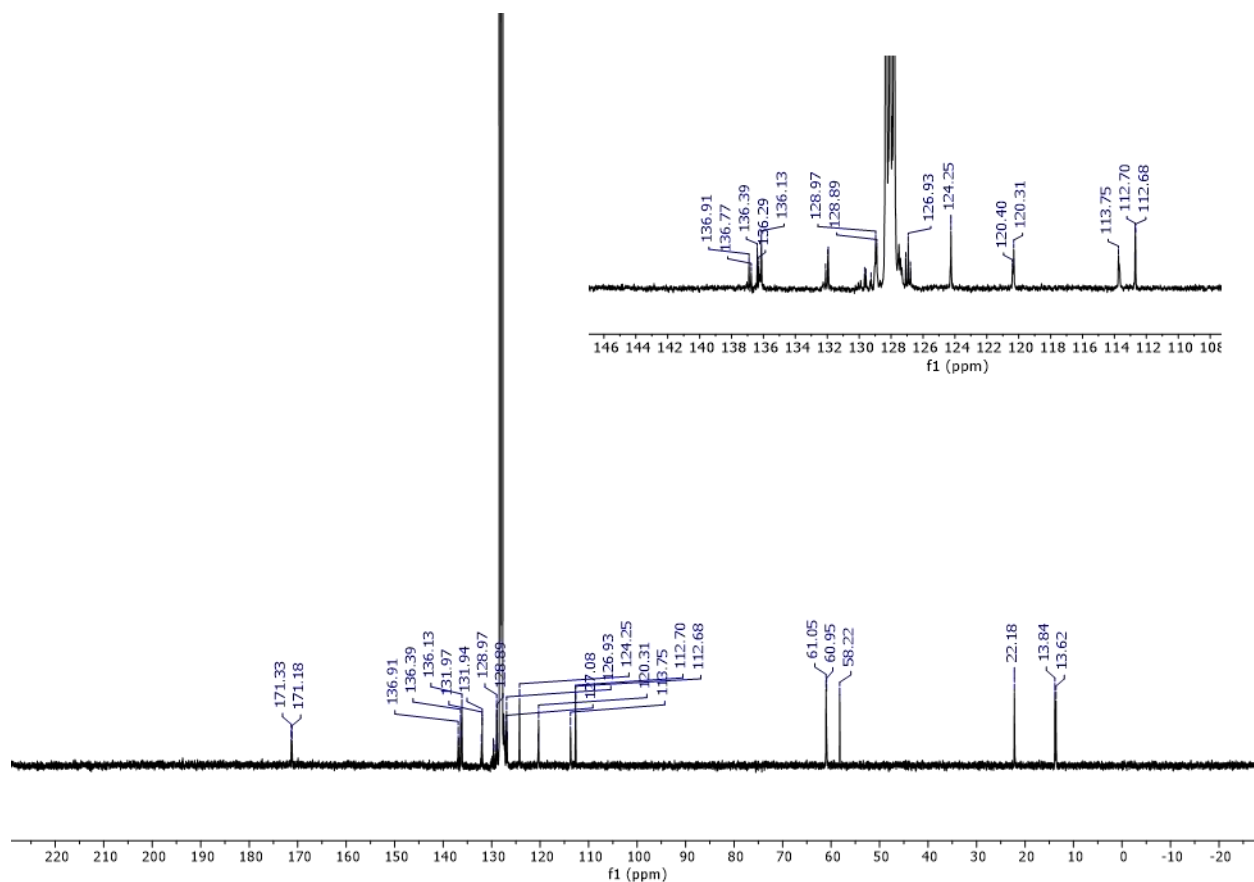


Figure A3.13. ^{13}C NMR spectrum of PC **1b** in C_6D_6 .

2,7-di(diethyl-2-methylmalonate-yl)-5,10-di(2-naphthyl)-5,10 (PC **2b**)
dihydrophenazine synthesis. THF and DBMM were separately sparged with N_2 for approximately 30 minutes before addition to the reaction mixture. Under N_2 , PC **2** (0.575 mmol, 0.250 g, 1 eq.), THF (40 mL), and DBMM (2.87 mmol, 55.0 μL , 5 eq.) were combined in a storage tube, then irradiated for 24 hours in a white LED beaker. The reaction mixture was removed from the light source and opened to air, then 10 eq. TEA was added. PC **2b** was purified using column chromatography prepared with a slurry of silica gel deactivated with 3% TEA/hexanes. The crude material was dry loaded onto silica in 3% TEA in toluene. The components of the reaction mixture were eluted using 4:1 [3% TEA/hexanes: EtOAc]. Fractions were combined and dried down under reduced pressure. Samples were redissolved in a minimum of DCM and then precipitated in an excess of MeOH, filtered, and then dried under vacuum resulting in yellow solids in a 53.3% yield,

which was determined the be PC **2b** by NMR. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 0.68 (t, 12H, $J = 7.20$), 1.73 (s, 6H), 3.64–3.84 (m, 8H), 5.78 (d, 2H, $J = 8.00$), 6.19 (d, 2H, $J = 2.80$), 6.42 (dd, 2H, $J_1 = 2.00$, $J_2 = 8.40$), 7.18–7.34 (overlapping peaks, 6H), 7.50–7.59 (m, 4H), 7.64–7.70 (m, 4H). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 13.76, 22.28, 58.32, 61.16, 112.86, 113.52, 120.54, 126.45, 126.82, 129.03, 130.66, 131.75, 135.48, 136.58, 136.61, 137.80, 171.43.

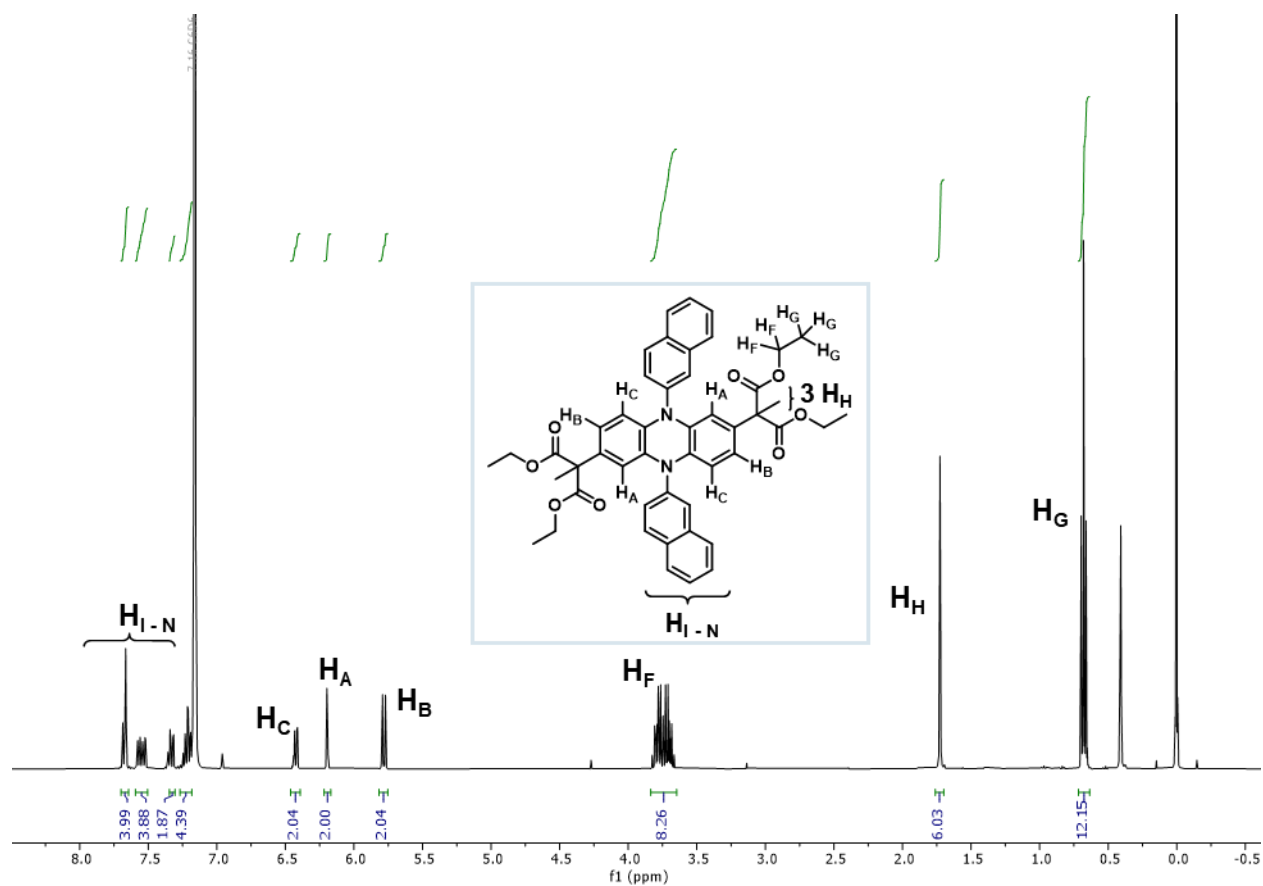


Figure A3.14. ^1H NMR spectrum of PC **2b** in C_6D_6 .

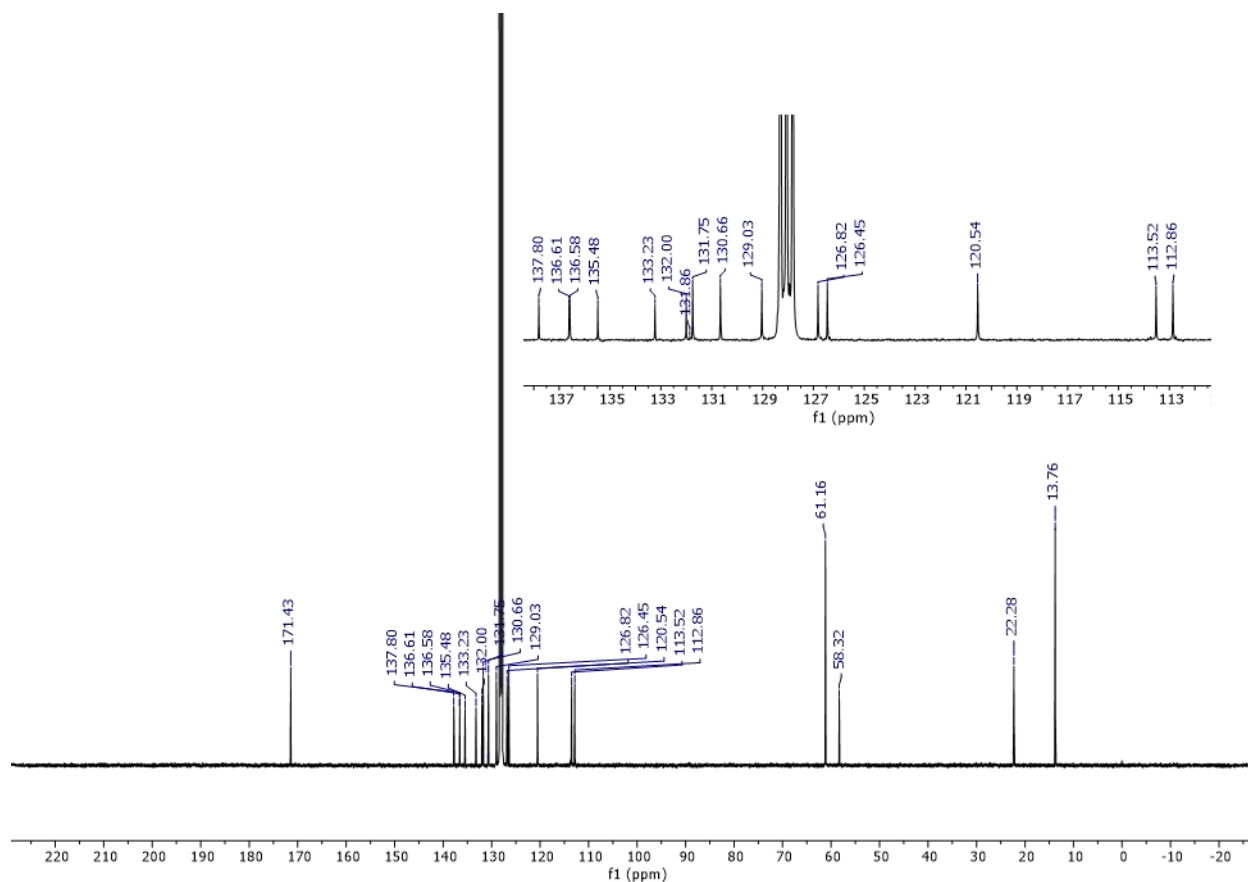


Figure A3.15. ^{13}C NMR spectrum of PC **2b** in C_6D_6 .

MALDI-TOF Mass Spectrometry of PCs

MALDI-TOF mass spectrometry analysis was performed in positive ion reflector mode. PC stock solutions were prepared at 5.0 mg/mL in THF. The solution prepared for spotting on the MALDI target plate contained 3 μL of 5.0 mg/mL PC stock solution and 20 μL THF (0.65 mg/mL). A 600 Da polyethylene glycol calibrant with trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix and a sodium trifluoroacetate additive was used.

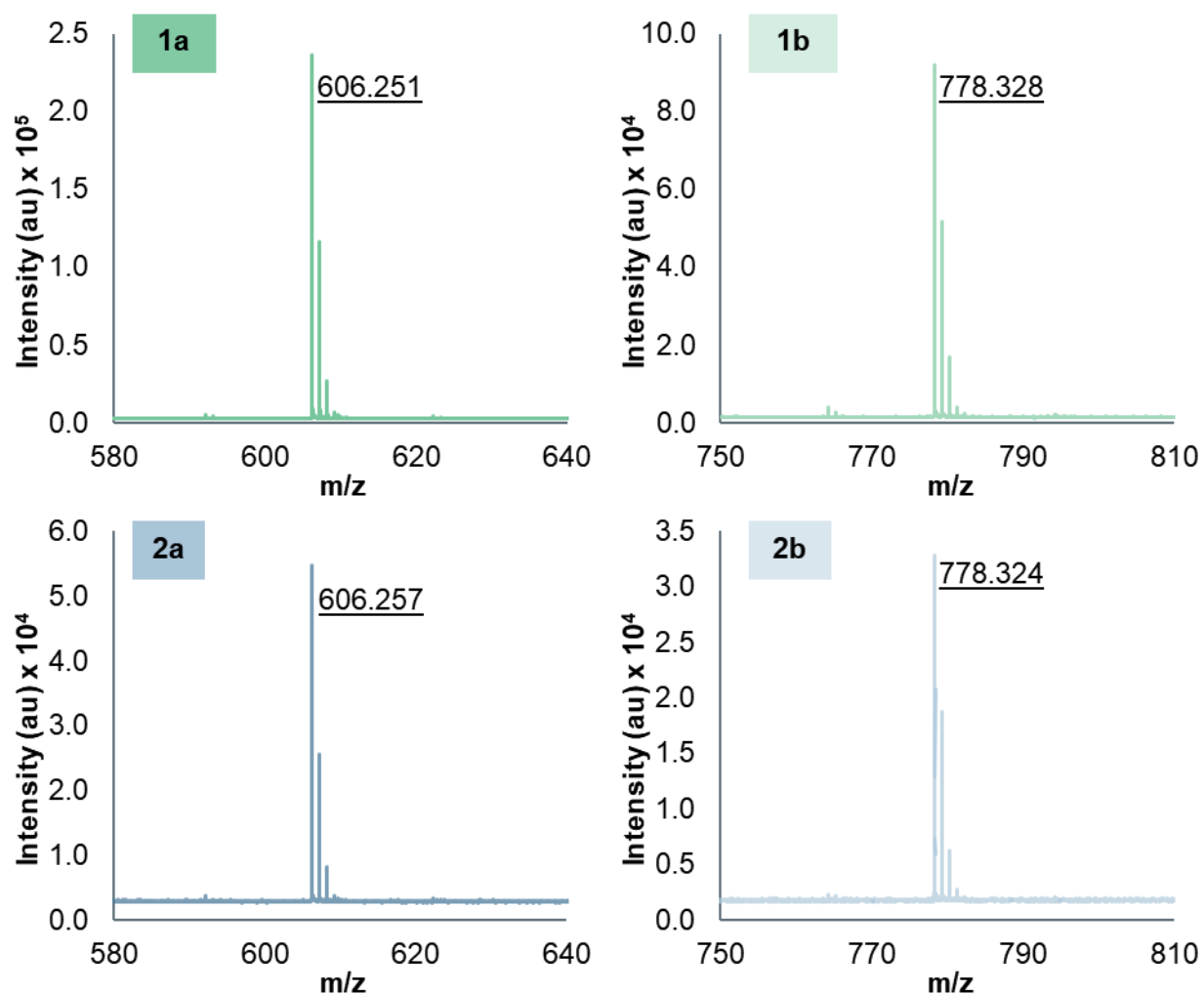


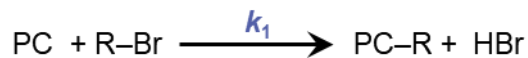
Figure A3.16. MALDI-TOF mass spectrum of PCs **1a**, **1b**, **2a**, and **2b**.

KINETIC EXPERIMENTS

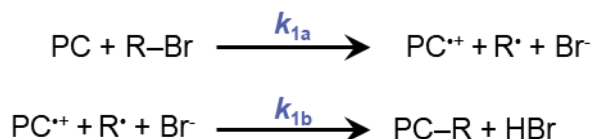
Pseudo-first-order Kinetic Equations

First Catalyst Substitution:

Chemical equation used for the first substitution, representing species monitored via ^1H NMR:



Detailed chemical equations representing proposed reaction steps:



Preliminary rate equation:

$$\frac{-d[\text{PC}]}{dt} = k_1[\text{PC}][\text{R-Br}]$$

Assume $[\text{PC}]$ is not equivalent to $[\text{PC}^*]$ because excited state concentration is lower:

$$\frac{-d[\text{PC}]}{dt} = k_1[\text{PC}^*][\text{R-Br}]$$

Apply pseudo-first-order assumption for rate law ($[\text{R-Br}] \gg [\text{PC}^*]$):

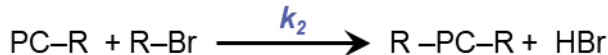
$$\frac{-d[\text{PC}]}{dt} = k_1[\text{PC}]$$

Integrated rate law:

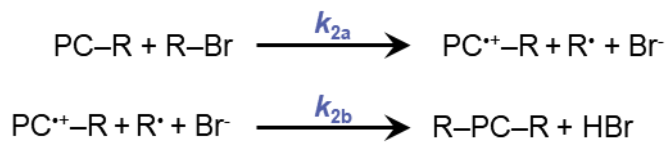
$$\ln \frac{[\text{PC}]_0}{[\text{PC}]_t} = k_1 t$$

Second Catalyst Substitution:

Chemical equation used for the second substitution, representing species monitored via ^1H NMR:



Detailed chemical equations representing proposed reaction steps:



Same approach as above for the rate equation (note that this derivation assumes the monosubstituted PC (PC-R) is used as a starting material. If the reaction is performed starting with unsubstituted PC, the rate law for the second substitution would be different):

$$\frac{-d[\text{PC-R}]}{dt} = k_2[\text{PC-R}]$$

Integrated rate law:

$$\ln \frac{[\text{PC-R}]_0}{[\text{PC-R}]_t} = k_2 t$$

First Catalyst Substitution

Kinetics of PC 1 substitution (first substitution). PC 1 (5.0 mg, 1 eq., 0.012 mmol) was weighed into a scintillation vial and brought into a N₂ filled glovebox. In the glovebox, 7.50 mL of DMAc was added to the reaction vial and left stirring in the glovebox overnight. In the dark, DBMM (2.2 μ L, 1 eq., 0.012 mmol) was added to the reaction vial, which was then irradiated under white LED lights for 6 minutes. 0.75 mL timepoints were taken between at 0, 2, 3, 4, 5, and 6 minutes into amber vials. The contents of the amber vials were dried down in the dark. 0.4 mL of a C₆D₆ solution with 250 ppm BHT and 5:1 [TEA]:[PC] was added to each timepoint and they were analyzed by ¹H NMR.

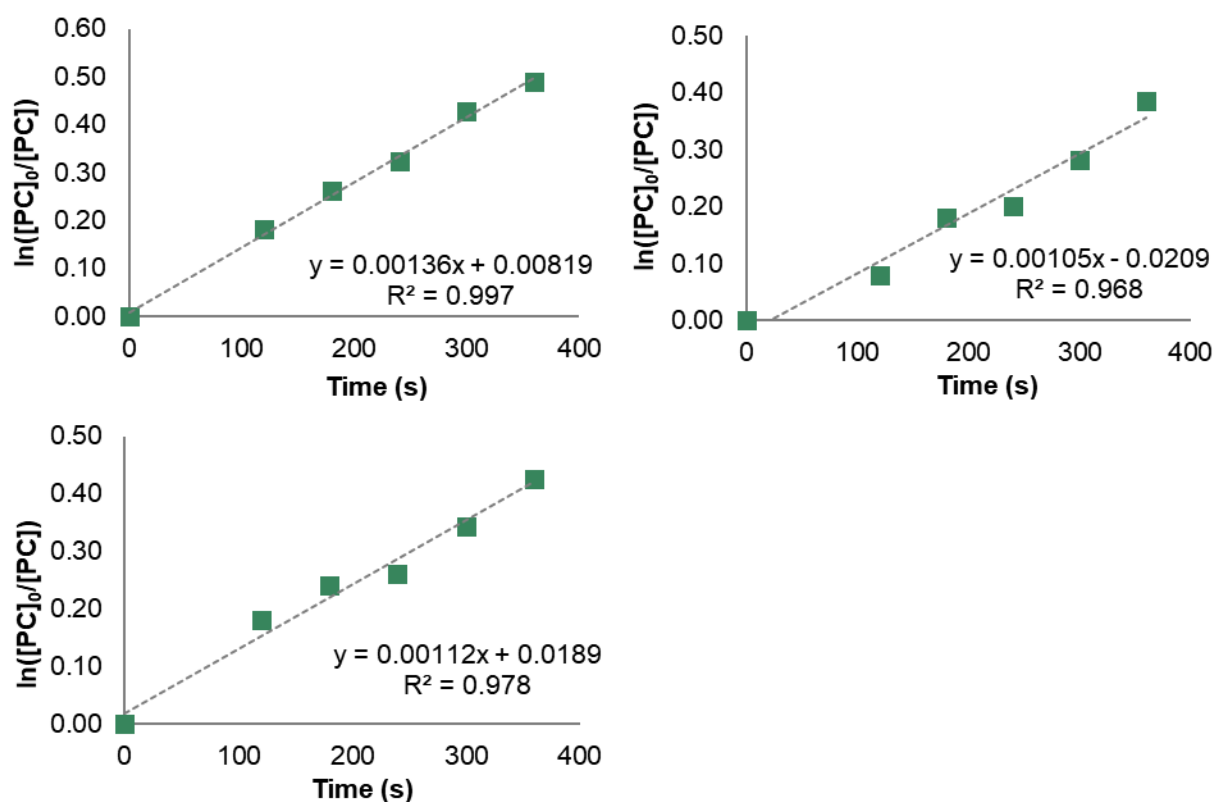


Figure A3.17. Pseudo-first-order kinetic plots from ¹H NMR of timepoints from the first substitution of PC 1, three trials. Rate constants (k) were determined from the slope of the line.

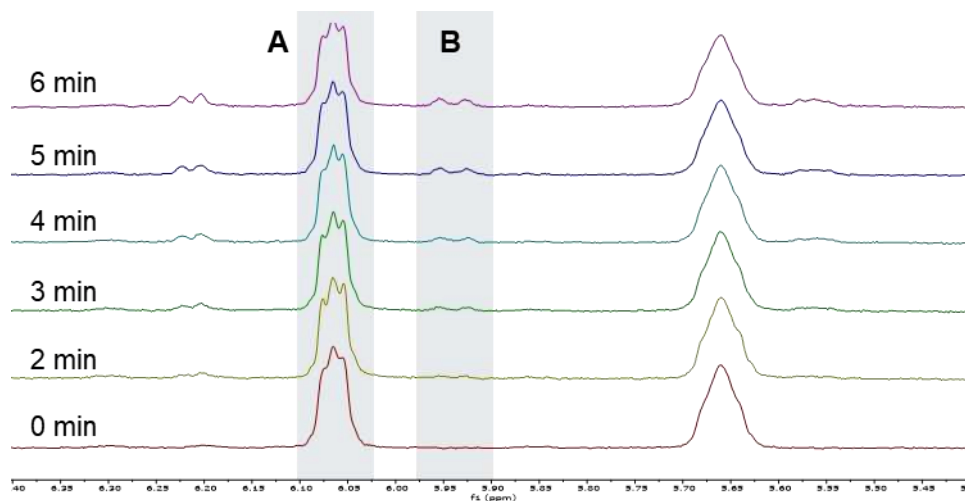


Figure A3.18. Overlaid ^1H NMR spectra of timepoints from the first substitution of PC **1**. Peaks **A** (reactant peak, PC **1**) and **B** (product peak, PC **1a**) were used to determine conversion and PC consumption (see below).

$$\% \text{ Conversion} = \frac{\int(B/1)}{\left[\int(B/1) + \left(\frac{\int A - (2 \cdot \int B/1)}{4} \right) \right]} \cdot 100$$

$$PC \text{ consumption} = \ln \frac{[PC]_0}{[PC]_t} = \ln \frac{100}{(100 - \text{conversion})}$$

Kinetics of PC 2 substitution (first substitution). PC **2** (5.0 mg, 1 eq., 0.012 mmol) was weighed into a scintillation vial and brought into a N_2 filled glovebox. In the glovebox, 7.50 mL of DMAc was added to the reaction vial and left stirring in the glovebox overnight. In the dark, DBMM (2.2 μL , 1 eq., 0.012 mmol) was added to the reaction vial, which was then irradiated under white LED lights for 15 minutes. 0.75 mL timepoints were taken between at 0, 5, 7.5, 10, 12.5, and 15 minutes into amber vials. The contents of the amber vials were dried down in the dark. 0.4 mL of a C_6D_6 solution with 250 ppm BHT and 5:1 [TEA]:[PC] was added to each timepoint and they were analyzed by ^1H NMR.

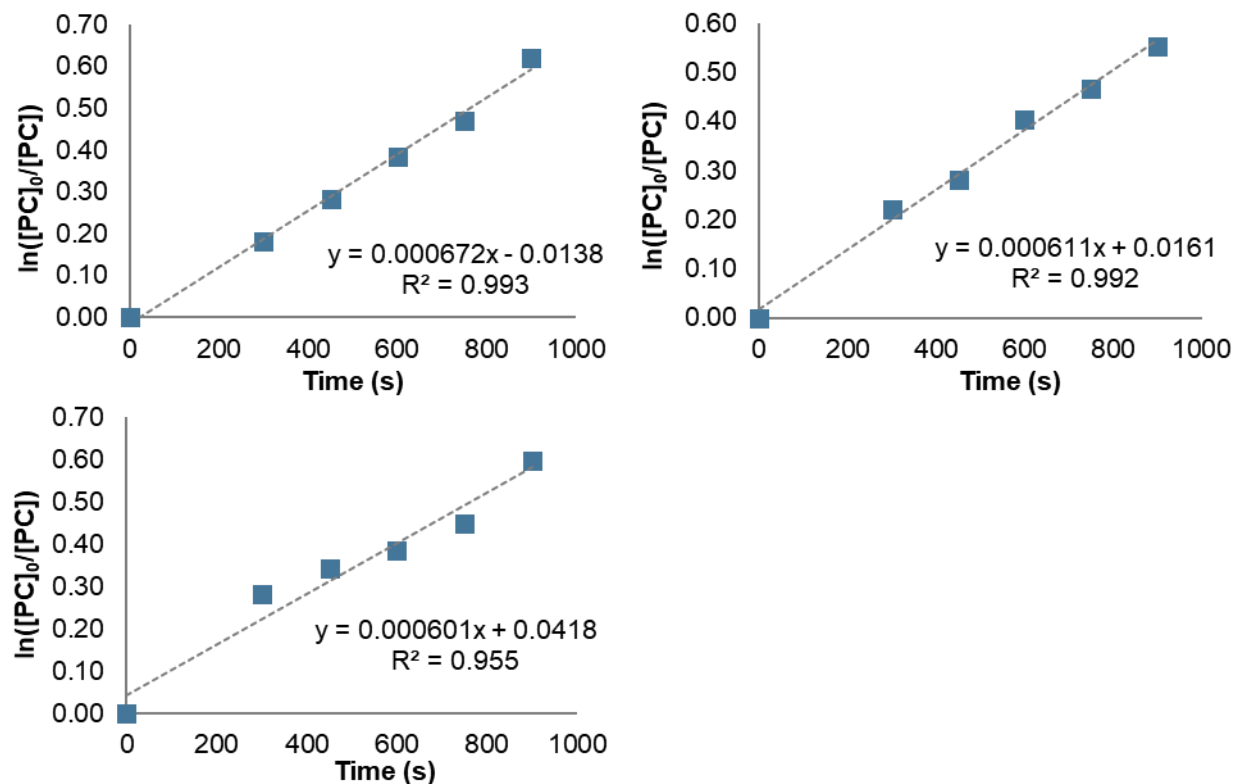


Figure A3.19. Pseudo-first-order kinetic plots from ^1H NMR of timepoints from the first substitution of PC **2**, three trials. Rate constants (k) were determined from the slope of the line.

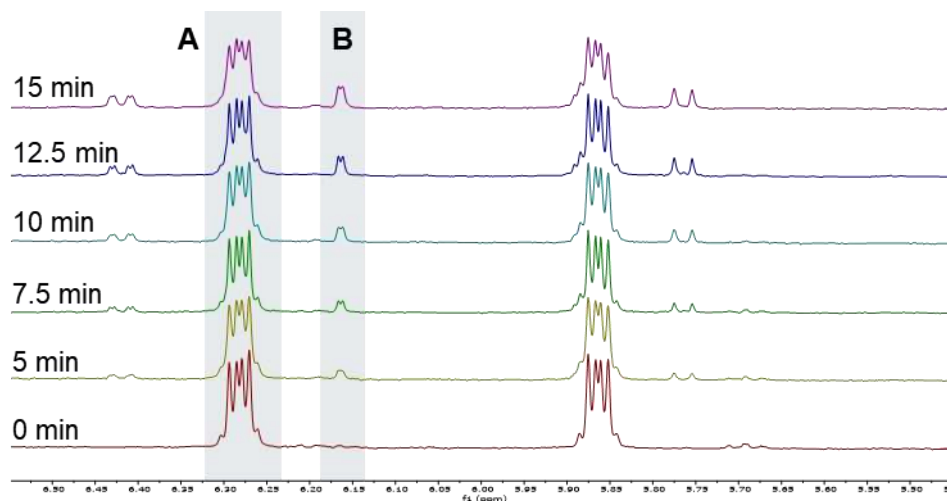


Figure A3.20. Overlaid ^1H NMR spectra of timepoints from the first substitution of PC **2**. Peaks A (reactant peak, PC **2**) and B (product peak, PC **2a**) were used to determine conversion and PC consumption (see below).

$$\% \text{ Conversion} = \frac{\int(B/1)}{\left[\int(B/1) + \left(\frac{\int A - (2 \cdot \int B/1)}{4} \right) \right]} \cdot 100$$

$$PC \text{ consumption} = \ln \frac{[PC]_0}{[PC]_t} = \ln \frac{100}{(100 - \text{conversion})}$$

Second Catalyst Substitution

Kinetics of PC 1a substitution (second substitution). PC 1a (7.0 mg, 1 eq., 0.012 mmol) was weighed into a scintillation vial and brought into a N₂ filled glovebox. In the glovebox, 7.50 mL of DMAc was added to the reaction vial and left stirring in the glovebox overnight. In the dark, DBMM (2.2 μL, 1 eq., 0.012 mmol) was added to the reaction vial, which was then irradiated under white LED lights for 5 minutes. 0.75 mL timepoints were taken between at 0, 1, 2, 3, 4, and 5 minutes into amber vials. The contents of the amber vials were dried down in the dark. 0.4 mL of a C₆D₆ solution with 250 ppm BHT and 5:1 [TEA]:[PC] was added to each timepoint and they were analyzed by ¹H NMR.

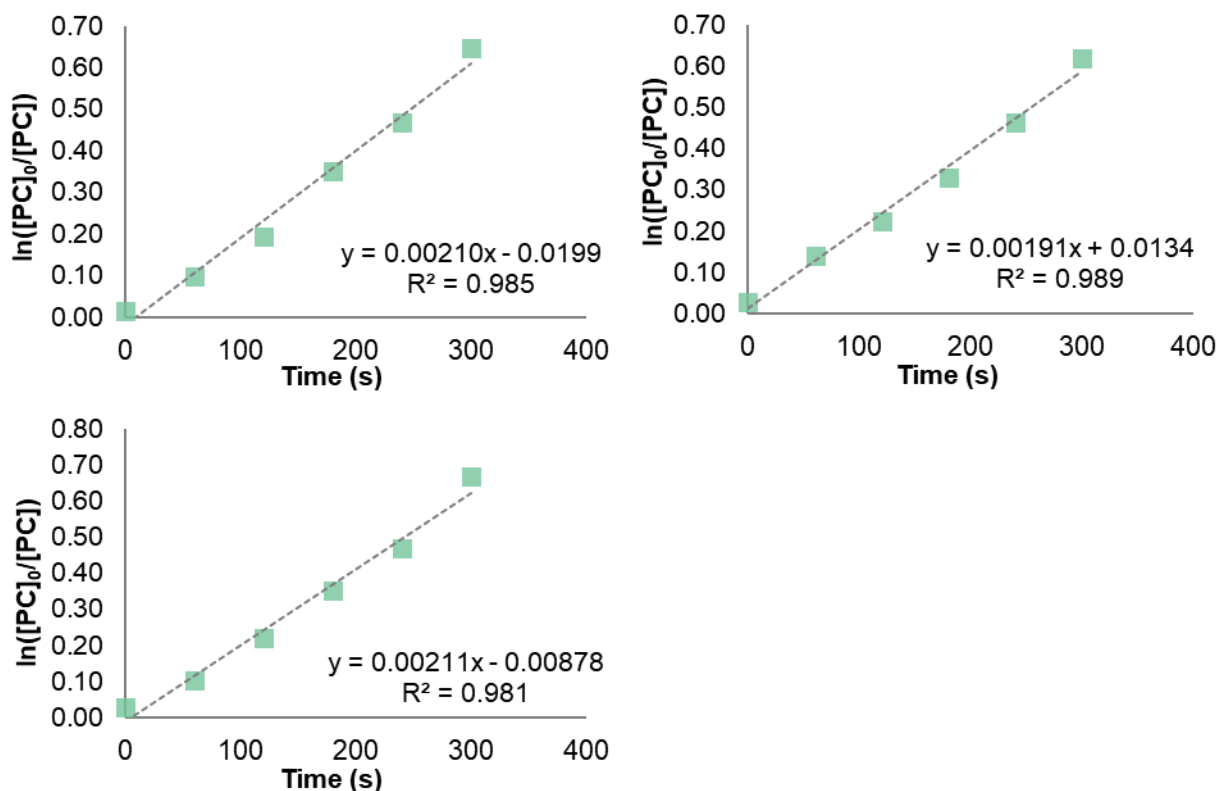


Figure A3.21. Pseudo-first-order kinetic plots from ^1H NMR of timepoints from the substitution of PC **1a**, (second substitution), three trials. Rate constants (k) were determined from the slope of the line.

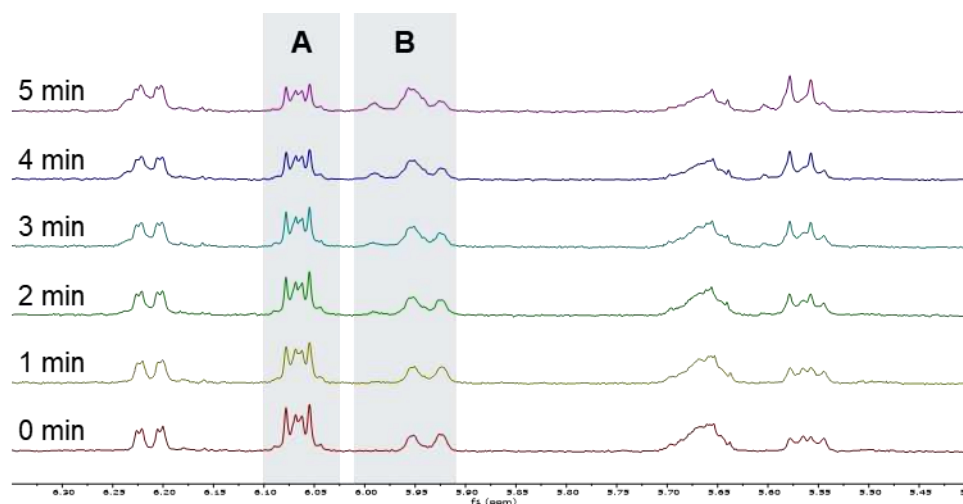


Figure A3.22. Overlaid ^1H NMR spectra of timepoints from the substitution of PC **1a** (second substitution). Peaks **A** (reactant peak, PC **1a**) and **B** (product peak, PC **1b**) were used to determine conversion and PC consumption (see below).

$$\% \text{ Conversion} = \frac{\left[\frac{\int B - (\int A/2)}{2} \right]}{\left[\frac{\int B - (\int A/2)}{2} \right] + \int A/2} \cdot 100$$

$$\text{PC consumption} = \ln \frac{[\text{PC}]_0}{[\text{PC}]_t} = \ln \frac{100}{(100 - \text{conversion})}$$

Kinetics of PC 2a substitution (second substitution). PC **2a** (7.0 mg, 1 eq., 0.012 mmol) was weighed into a scintillation vial and brought into a N_2 filled glovebox. In the glovebox, 7.50 mL of DMAc was added to the reaction vial and left stirring in the glovebox overnight. In the dark, DBMM (2.2 μL , 1 eq., 0.012 mmol) was added to the reaction vial, which was then irradiated under white LED lights for 7.5 minutes. 0.75 mL timepoints were taken between at 0, 1.5, 3, 4.5, 6, and 7.5 minutes into amber vials. The contents of the amber vials were dried down in the dark. 0.4 mL of a C_6D_6 solution with 250 ppm BHT and 5:1 [TEA]:[PC] was added to each timepoint and they were analyzed by ^1H NMR.

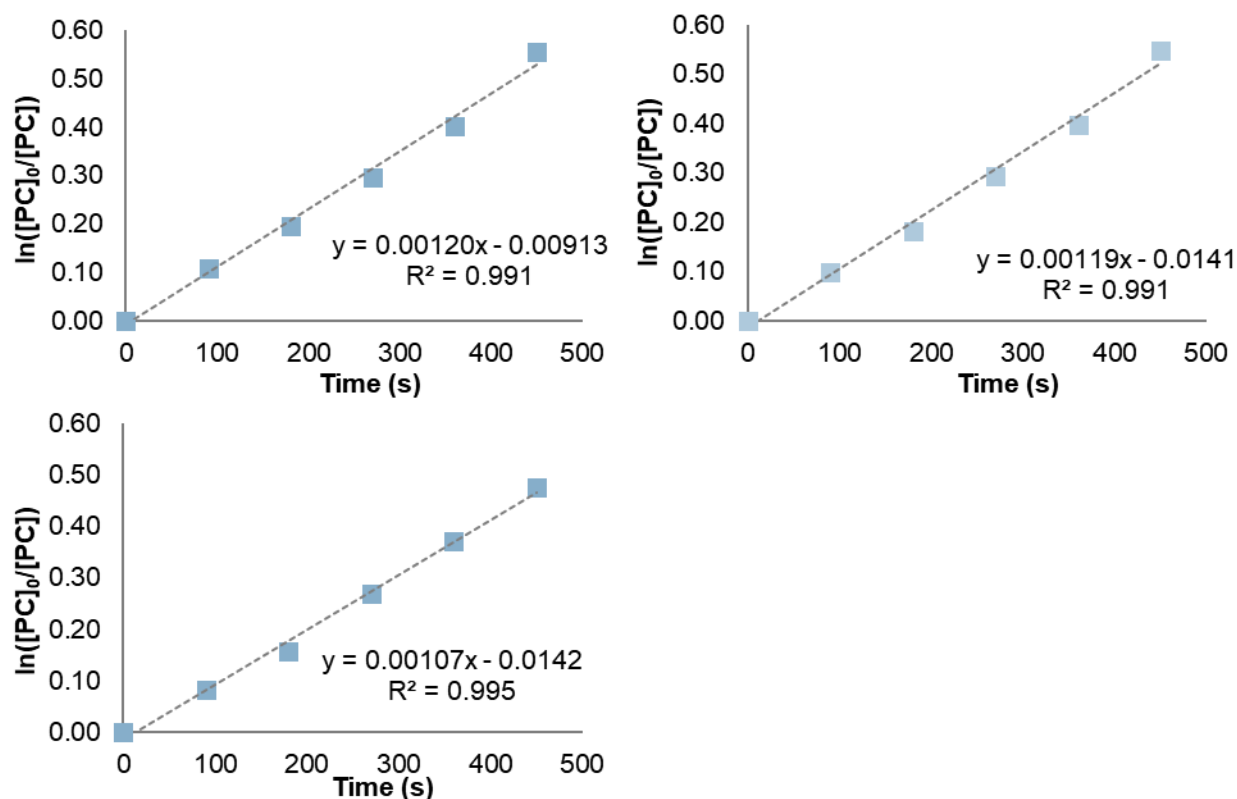


Figure A3.23. Pseudo-first-order kinetic plots from ^1H NMR of timepoints from the substitution of PC **2a**, (second substitution), three trials. Rate constants (k) were determined from the slope of the line.

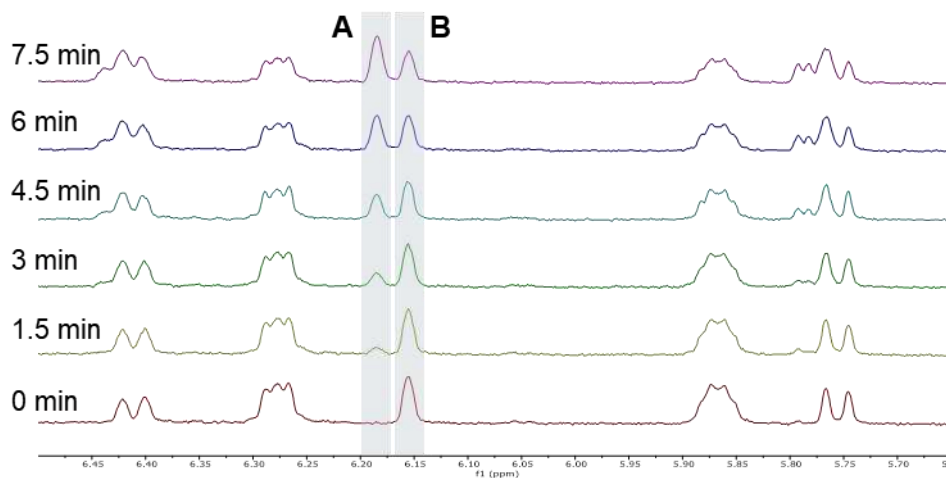


Figure A3.24. Overlaid ^1H NMR spectra of timepoints from the substitution of PC **2a** (second substitution). Peaks A (reactant peak, PC **2a**) and B (product peak, PC **2b**) were used to determine conversion and PC consumption (see below).

$$\% \text{ Conversion} = \frac{(\int B/2)}{(\int B/2) + (\int A/2)} \cdot 100$$

$$PC \text{ consumption} = \ln \frac{[PC]_0}{[PC]_t} = \ln \frac{100}{(100 - \text{conversion})}$$

AkCS Kinetics Control Reactions

For each control reaction, the same conditions described above in the *First Catalyst Substitution* and the *Second Catalyst Substitution* sections were used in the absence of light. All of the control reactions showed no AkCS without light.

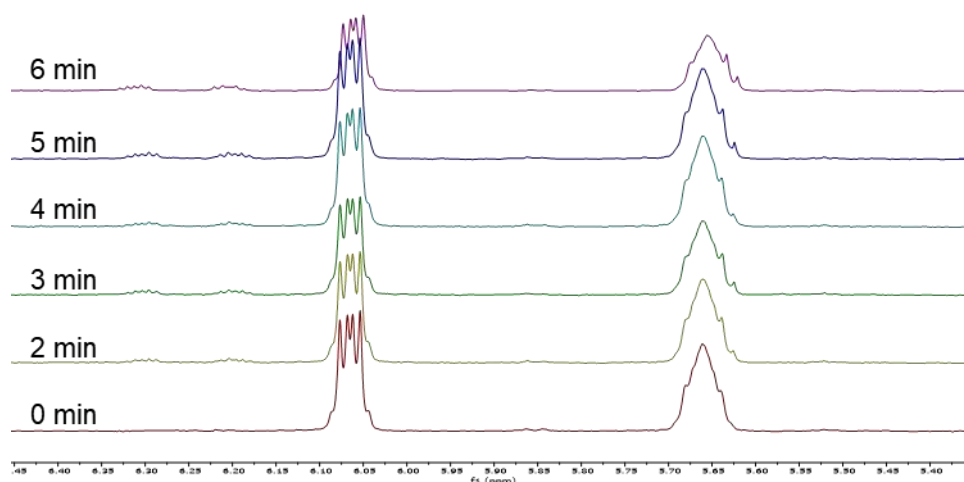


Figure A3.25. Overlaid ^1H NMR spectra of timepoints from the control reaction run in the dark for the first substitution of PC **1**. Negligible AkCS was observed.

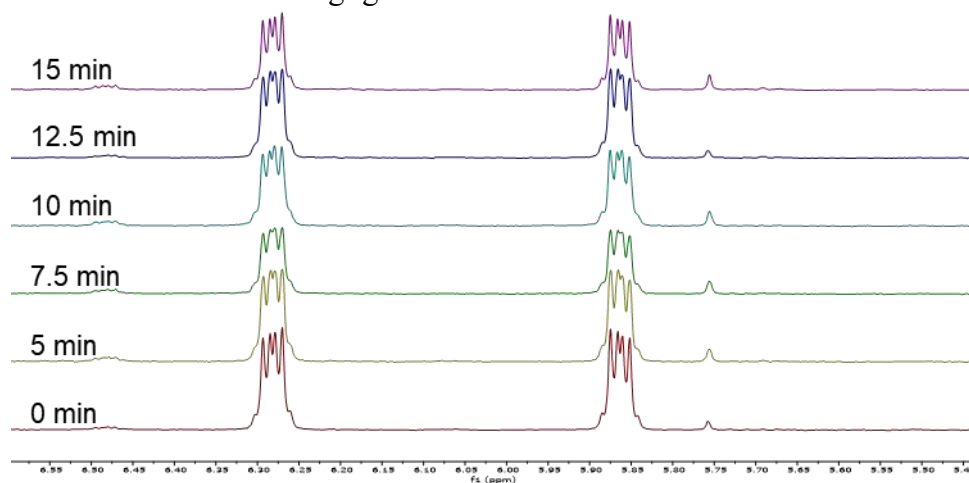


Figure A3.26. Overlaid ^1H NMR spectra of timepoints from the control reaction run in the dark for the first substitution of PC **2**. Negligible AkCS was observed.

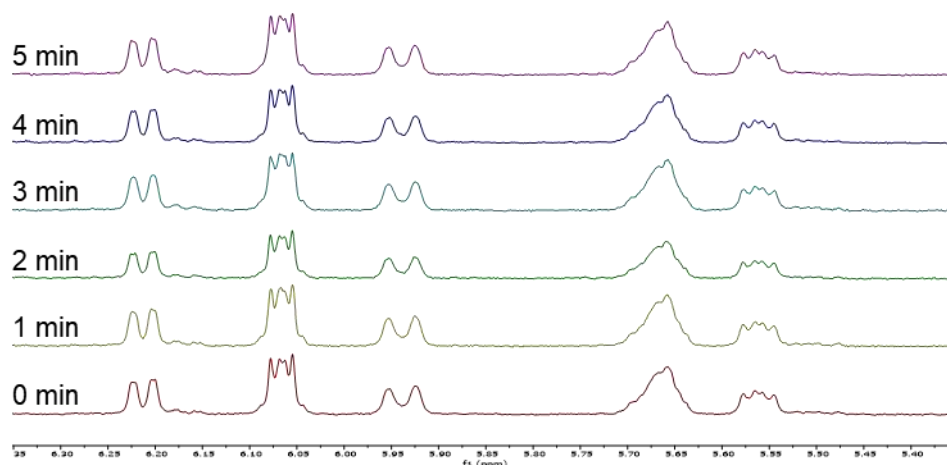


Figure A3.27. Overlaid ^1H NMR spectra of timepoints from the control reaction run in the dark for the first substitution of PC **1a** (second substitution). Negligible AkCS was observed.

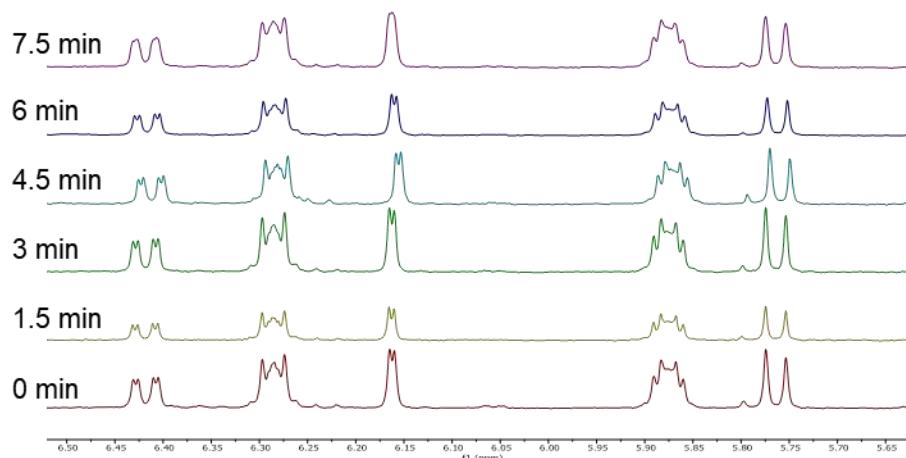


Figure A3.28. Overlaid ^1H NMR spectra of timepoints from the control reaction run in the dark for the first substitution of PC **2a** (second substitution). Negligible AkCS was observed.

Kinetic Modeling

The rate law for **PC** in the model below was derived as follows:

$$[PC]_t = [PC]_{t-1} + d[PC]$$

$$\frac{d[PC]}{dt} = -k_1[PC]_{t-1} [DBMM]_{t-1}$$

$$d[PC] = -k_1[PC]_{t-1} [DBMM]_{t-1} \cdot dt$$

$$[PC]_t = [PC]_{t-1} - k_1[PC]_{t-1} [DBMM]_{t-1} \cdot dt$$

The same derivation was applied for the other species in the model to obtain the following rate equations:

DBMM:

$$\frac{d[DBMM]}{dt} = -k_1[PC]_{t-1} [DBMM]_{t-1} - k_2[PC - R]_{t-1} [DBMM]_{t-1}$$

$$[DBMM]_t = [DBMM]_{t-1} - (k_1[PC]_{t-1} [DBMM]_{t-1} + k_2[PC - R]_{t-1} [DBMM]_{t-1}) \cdot dt$$

PC-R:

$$\frac{d[PC - R]}{dt} = k_1[PC]_{t-1} [DBMM]_{t-1} - k_2[PC - R]_{t-1} [DBMM]_{t-1}$$

$$[PC - R]_t = [PC - R]_{t-1} + (k_1[PC]_{t-1} [DBMM]_{t-1} - k_2[PC - R]_{t-1} [DBMM]_{t-1}) \cdot dt$$

PC-R₂:

$$\frac{d[PC - R_2]}{dt} = k_2[PC - R]_{t-1} [DBMM]_{t-1}$$

$$[PC - R_2]_t = [PC - R_2]_{t-1} + k_2[PC - R]_{t-1} [DBMM]_{t-1} \cdot dt$$

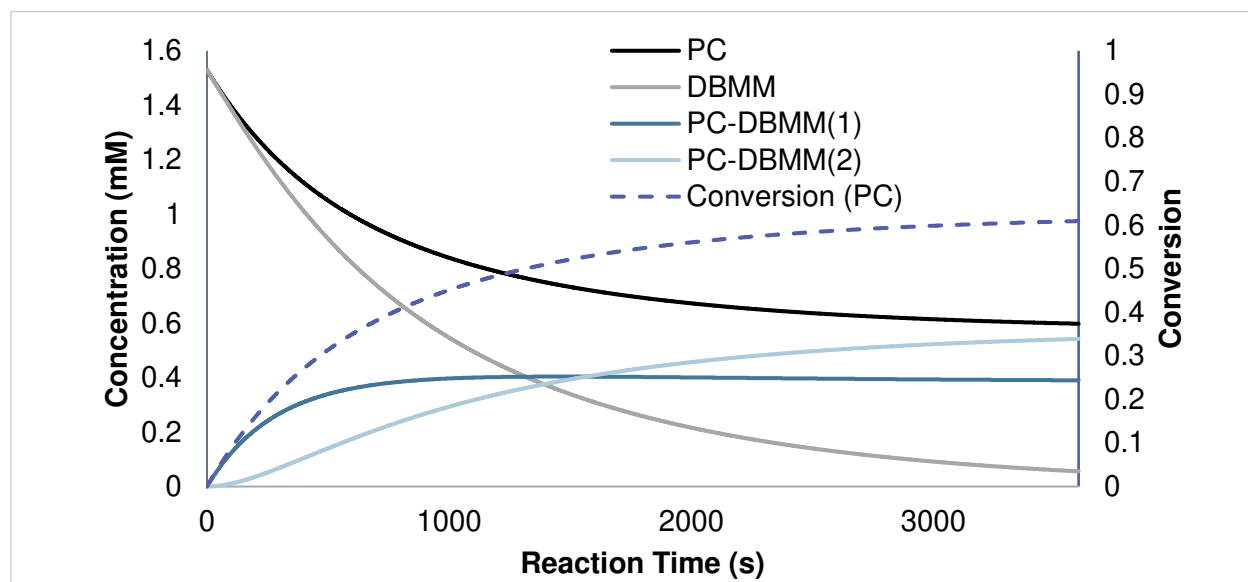


Figure A3.29. Kinetic modeling showing concentration (y-axis, left) and conversion (y₂-axis, right) of components (PC, PC-DBMM (1), PC-DBMM (2), and DBMM) in the AkCS reaction over time.

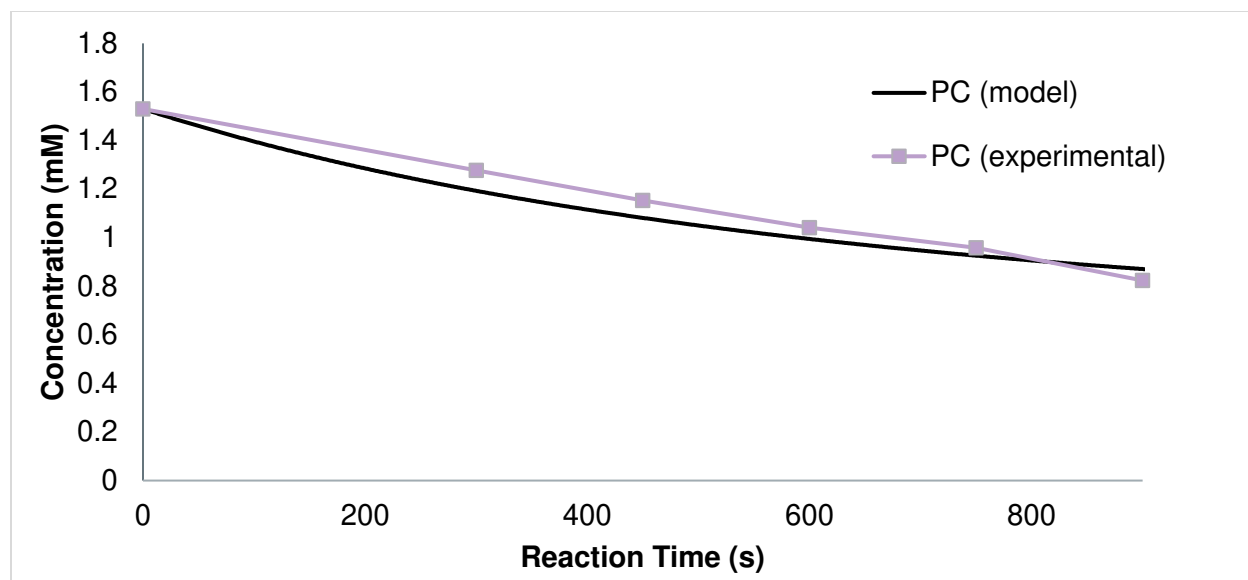
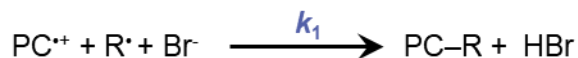


Figure A3.30. Comparison of the concentration of PC over time from the kinetic model (dark purple) to the experimental concentrations (light purple). The comparison shows that the model predicts the concentration of PC well on the AkCS reaction timescale.

Second-order Kinetics

First Catalyst Substitution:



Preliminary rate equation:

$$\frac{-d[\text{PC}^{\bullet+}]}{dt} = k_1[\text{PC}^{\bullet+}][\text{R}^{\bullet}]$$

Assume based on proposed reaction mechanism:¹

$$[\text{PC}^{\bullet+}]_0 = [\text{R}^{\bullet}]_0$$

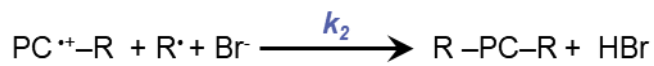
Therefore:

$$\frac{-d[\text{PC}^{\bullet+}]}{dt} = k_1[\text{PC}^{\bullet+}]^2$$

Integrated rate law:

$$\frac{1}{[\text{PC}^{\bullet+}]_t} = \frac{1}{[\text{PC}^{\bullet+}]_0} + k_1 t$$

Second Catalyst Substitution:



Same approach as above for the rate equation:

$$\frac{-d[\text{PC}^{\bullet+} - \text{R}]}{dt} = k_2[\text{PC}^{\bullet+} - \text{R}]^2$$

Integrated rate law:

$$\frac{1}{[\text{PC}^{\bullet+} - \text{R}]_t} = \frac{1}{[\text{PC}^{\bullet+} - \text{R}]_0} + k_2 t$$

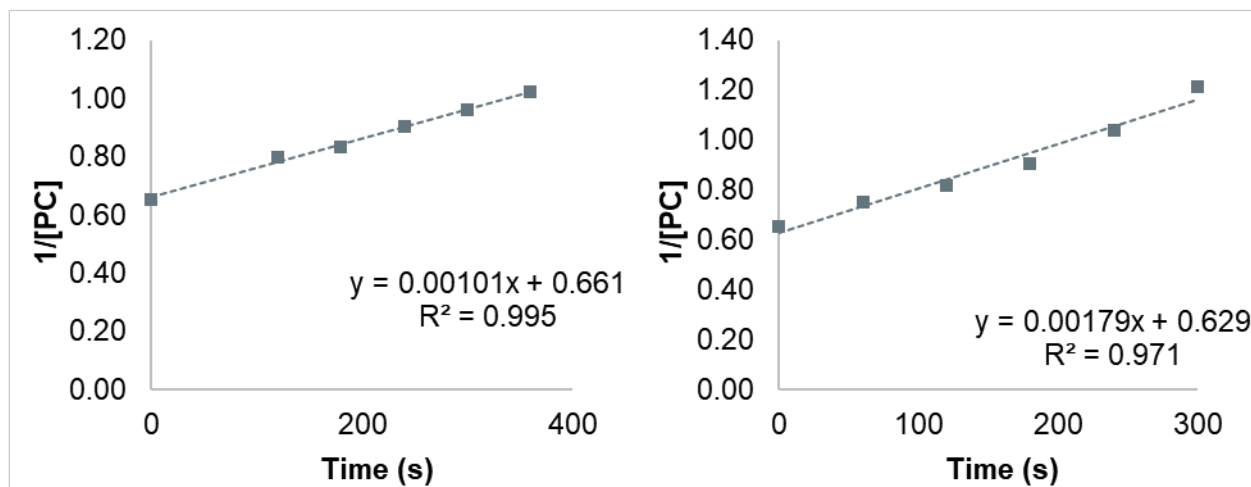


Figure A3.31. Second-order kinetic plots from ^1H NMR of timepoints from the substitution of PC 1, (first substitution, left) and the substitution of PC 1a (second substitution, right).

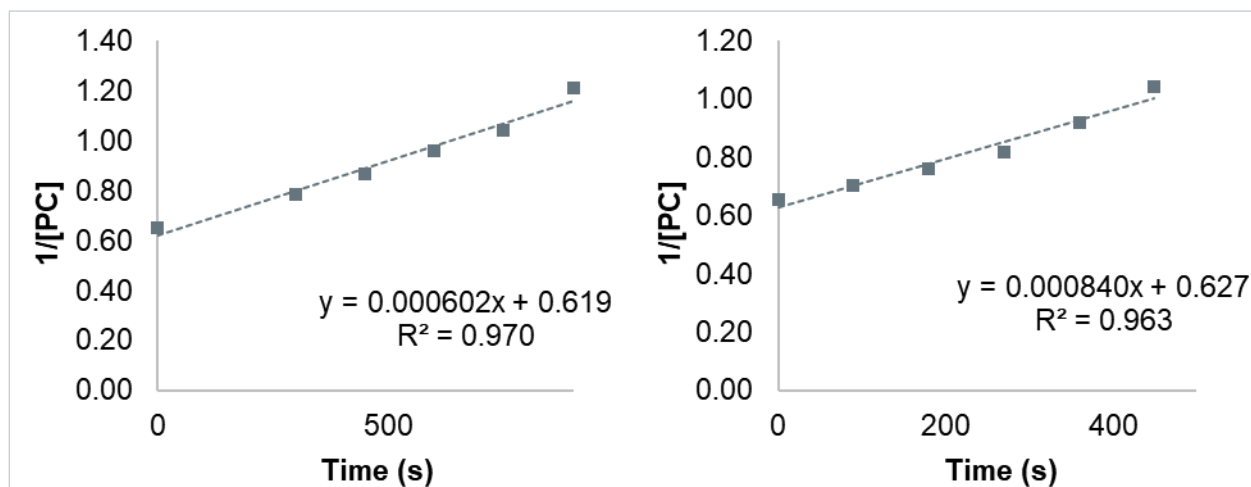


Figure A3.32. Second-order kinetic plots from ^1H NMR of timepoints from the substitution of PC 2, (first substitution, left) and the substitution of PC 2a (second substitution, right).

PHOTOCATALYST CHARACTERIZATION

UV-visible Spectroscopy

DMAc was used as the solvent for all UV-vis data presented in this work. All samples were analyzed in 1 cm pathlength quartz cuvettes. The molar absorptivity of each PC was determined using the following procedure: a stock solution of the PC was prepared in DMAc. This solution was then diluted to produce six solutions of different concentrations with a maximum absorbance roughly between 0 and 1.

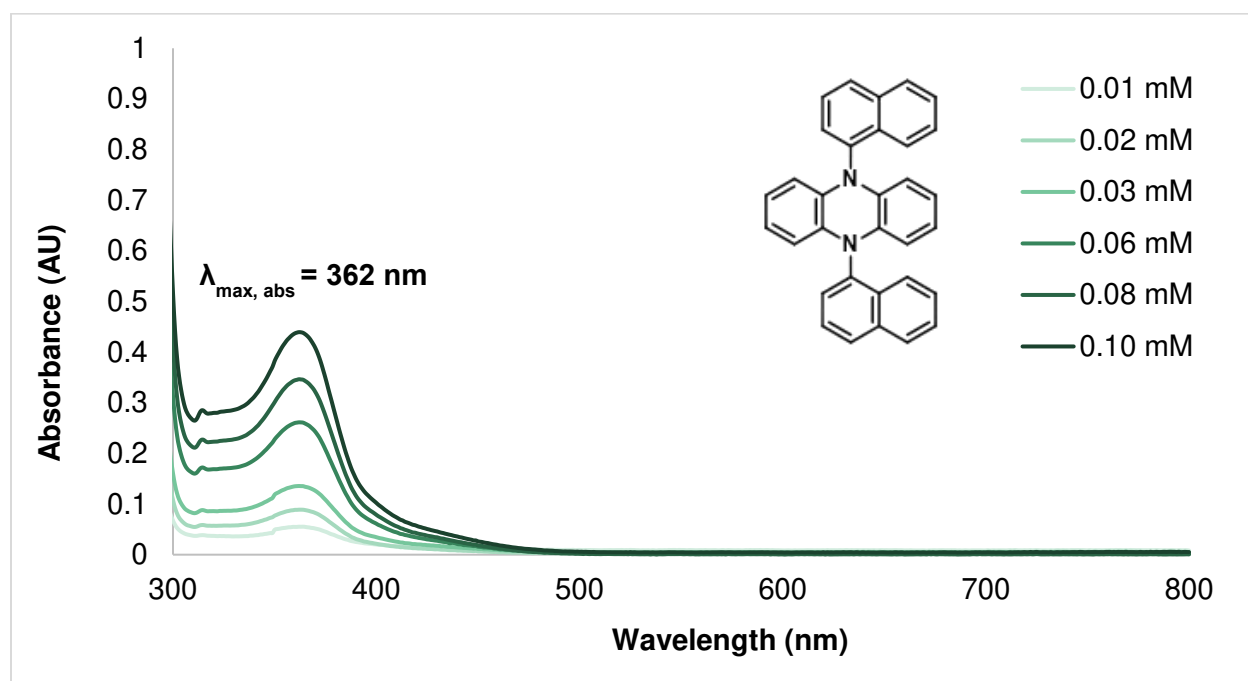


Figure A3.33. UV-visible absorption spectra for PC 1 in DMAc.

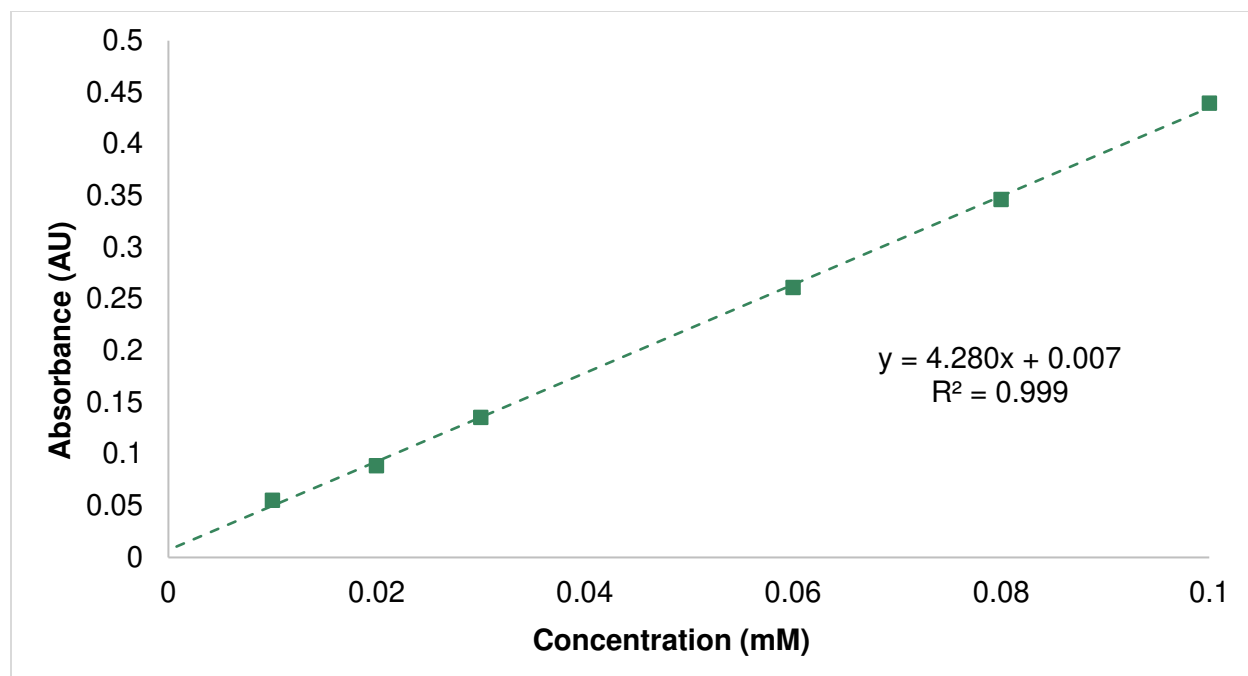


Figure A3.34. Beer's law curve used to determine the molar absorptivity of PC **1** in DMAc.

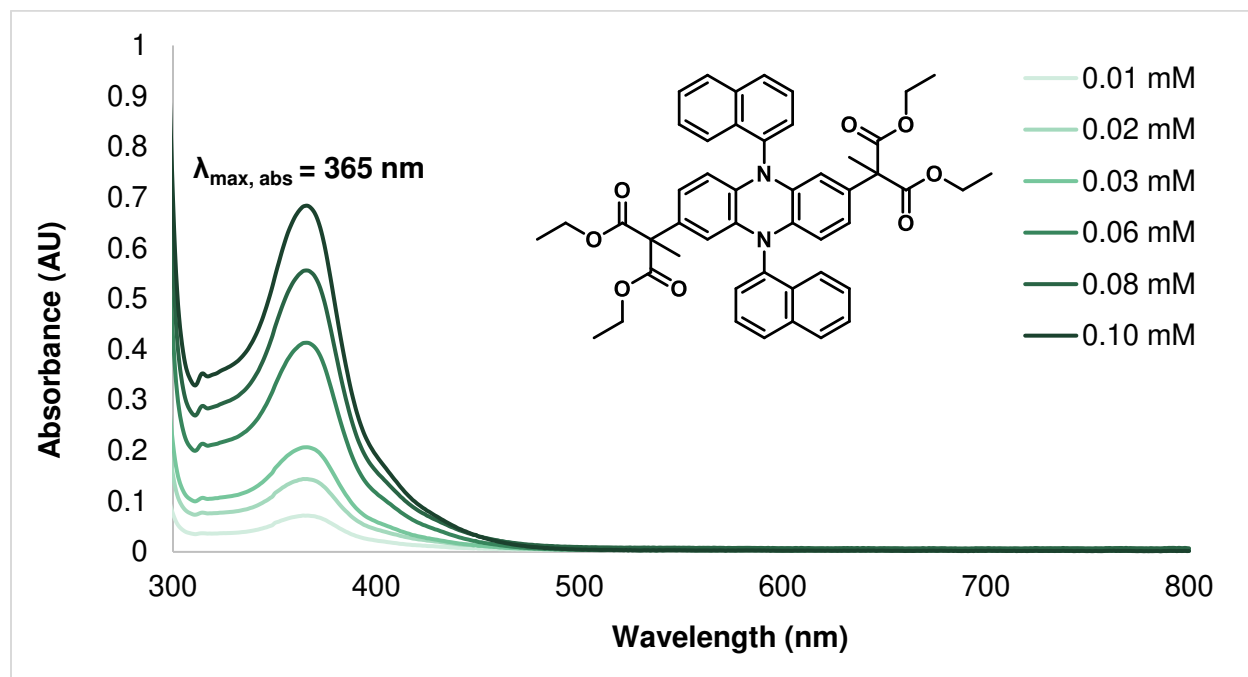


Figure A3.35. UV-visible absorption spectra for PC **1b** in DMAc.

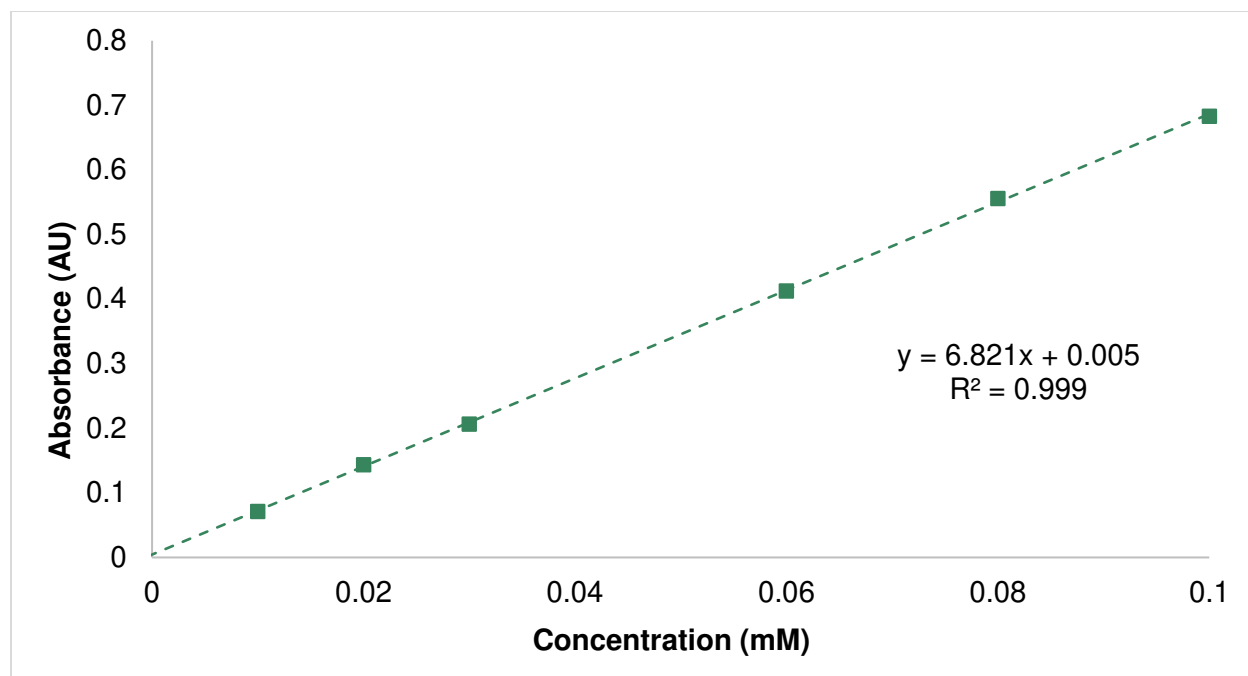


Figure A3.36. Beer's law curve used to determine the molar absorptivity of PC **1b** in DMAc.

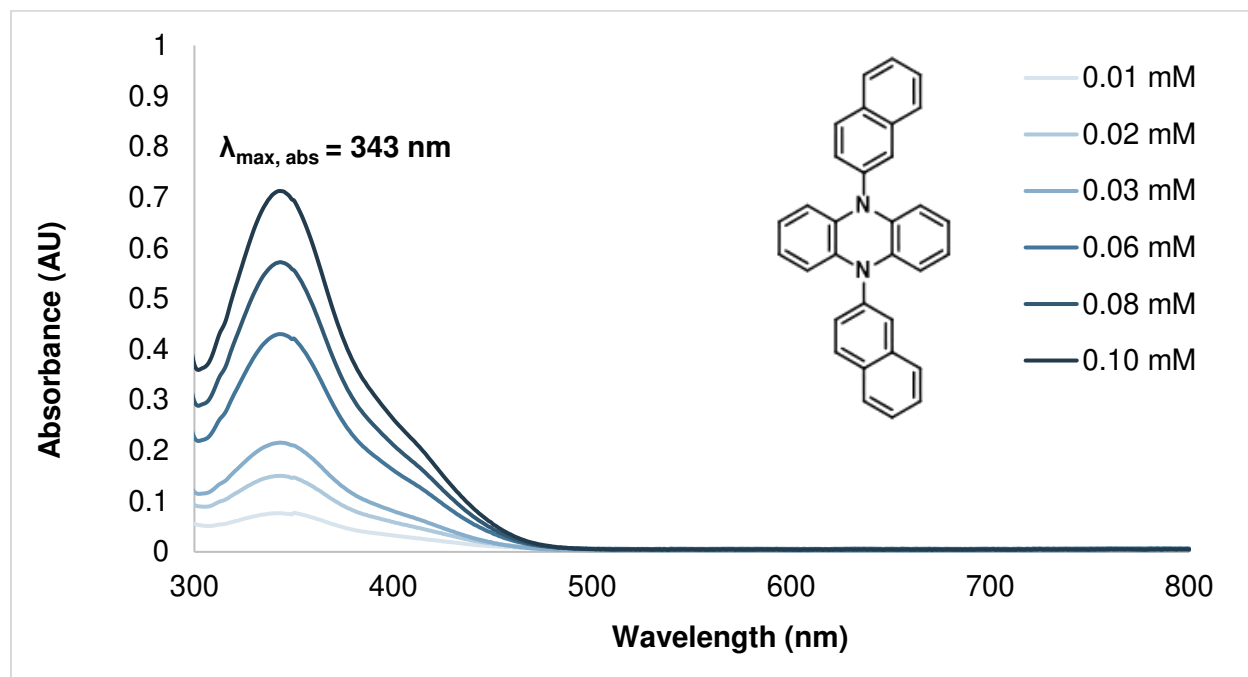


Figure A3.37. UV-visible absorption spectra for PC **2** in DMAc.

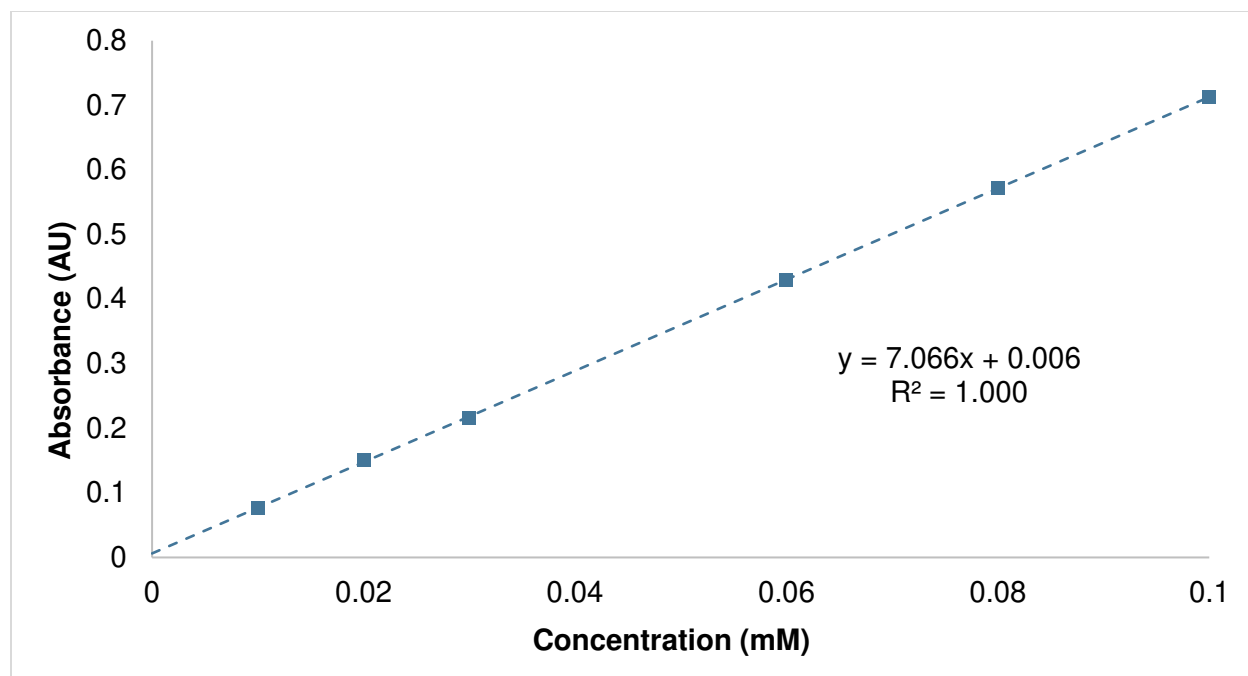


Figure A3.38. Beer's law curve used to determine the molar absorptivity of PC **2** in DMAc.

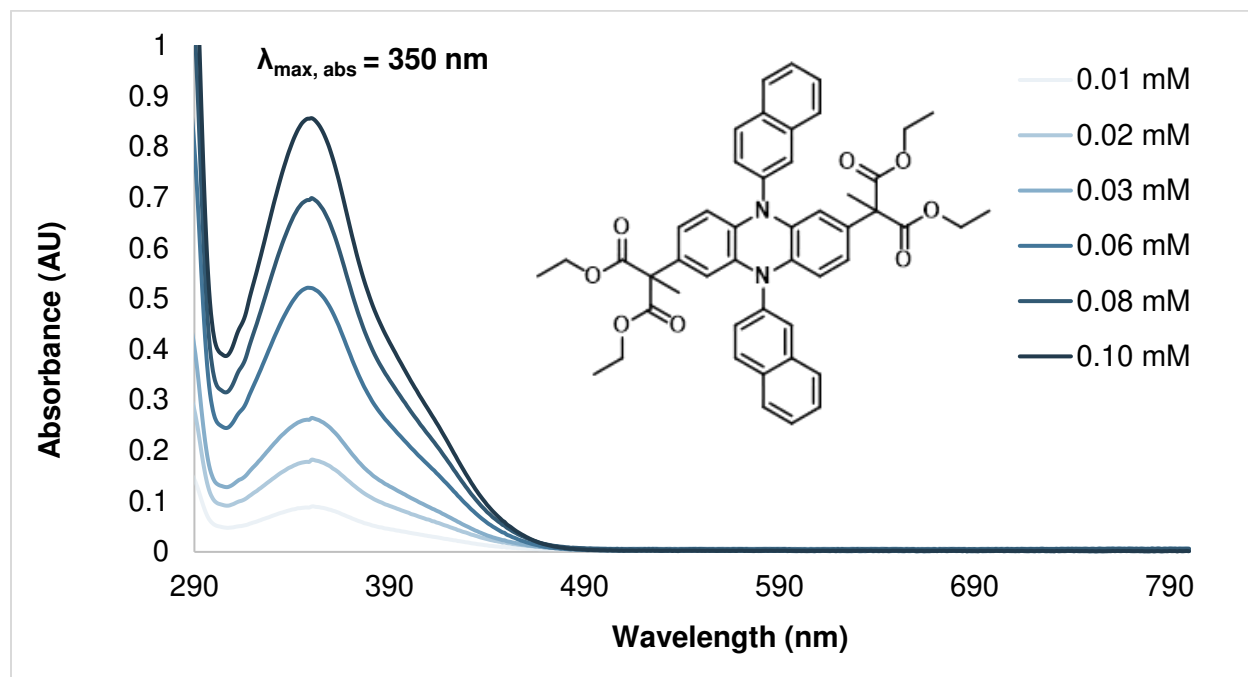


Figure A3.39. UV-visible absorption spectra for PC **2b** in DMAc.

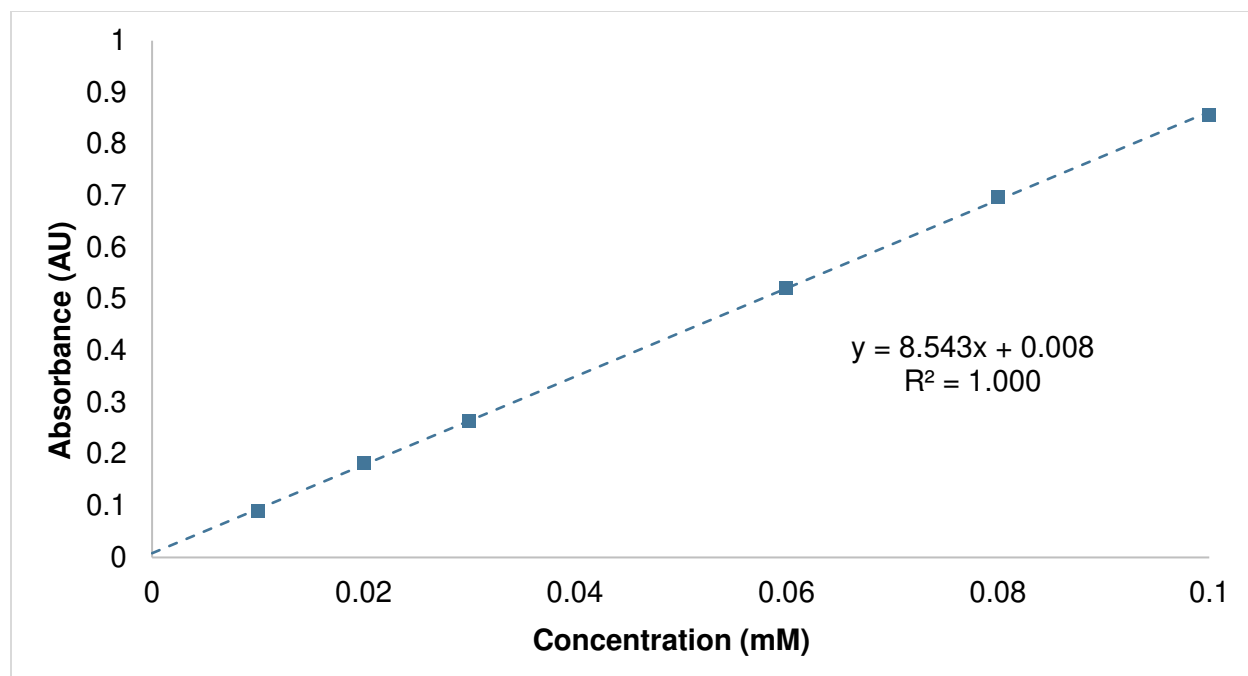


Figure A3.40. Beer's law curve used to determine the molar absorptivity of PC **2b** in DMAc.

Fluorescence Spectroscopy

Solutions of each PC were prepared in DMAc at an approximate concentration of 0.1 mM. All samples were analyzed in 1 cm pathlength quartz cuvettes. The emission spectra of each solution were measured using the wavelength of maximum absorption ($\lambda_{\text{max,abs}}$) as the excitation wavelength.

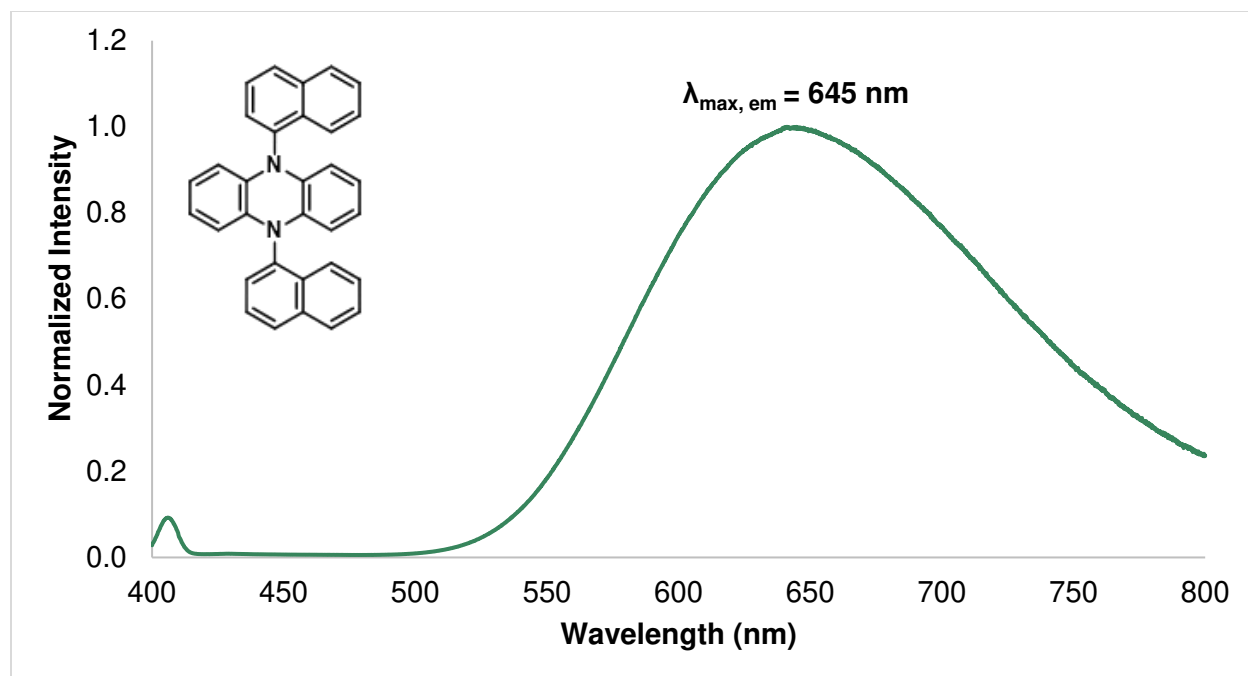


Figure A3.41. Fluorescence spectrum for PC **1** in DMAc.

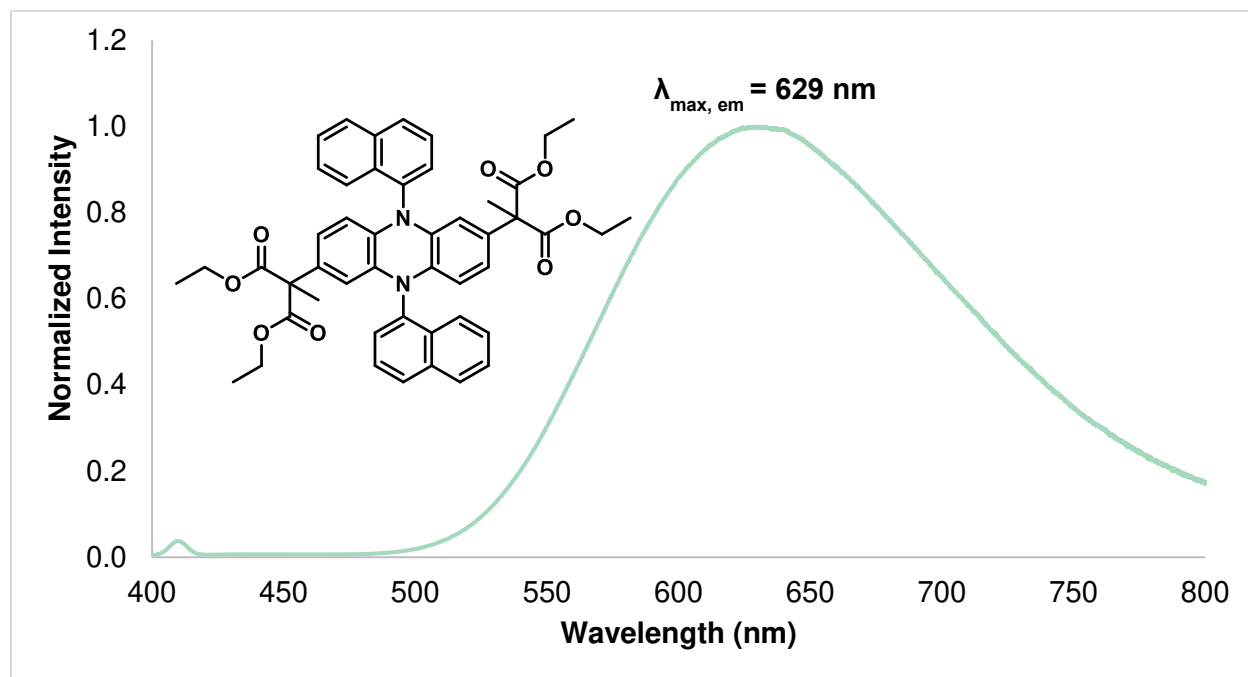


Figure A3.42. Fluorescence spectrum for PC **1b** in DMAc.

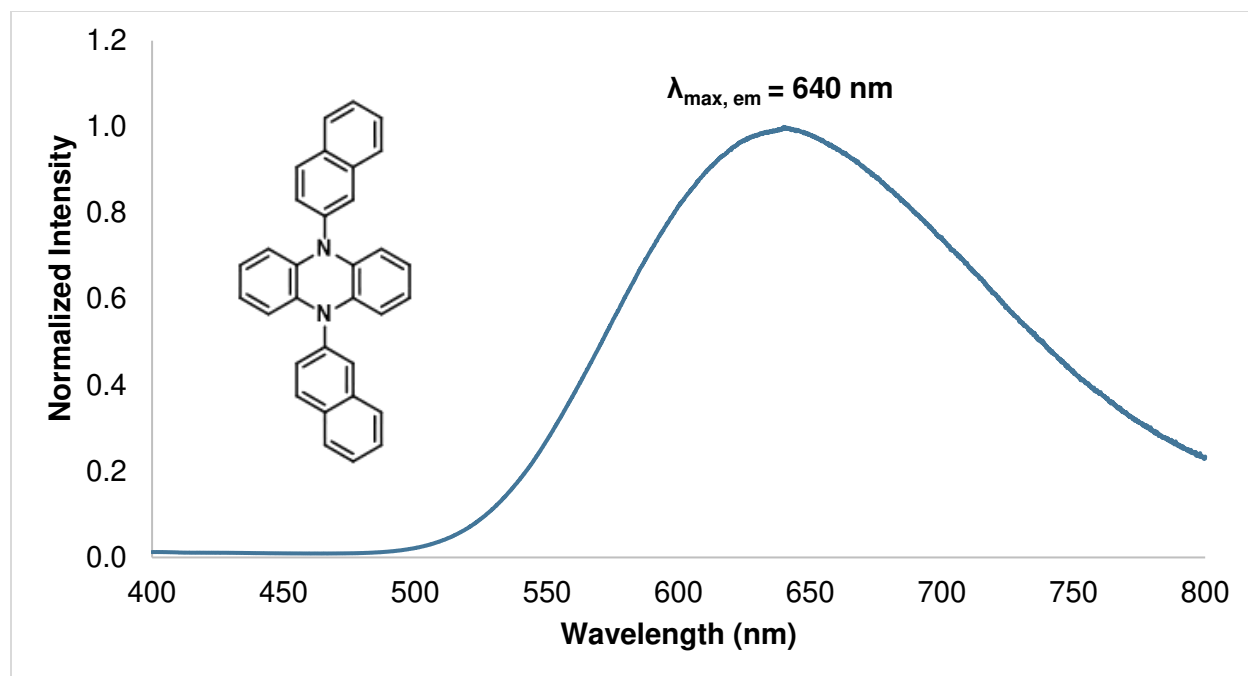


Figure A3.43. Fluorescence spectrum for PC **2** in DMAc.

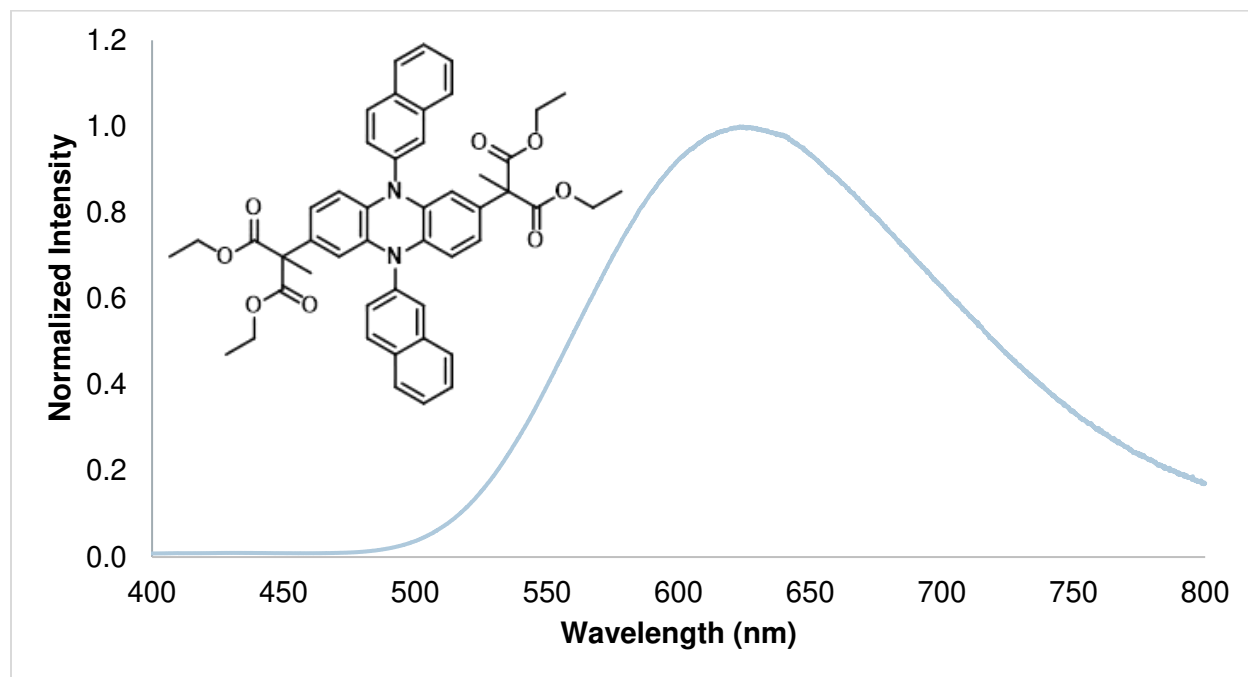


Figure A3.44. Fluorescence spectrum for PC **2b** in DMAc.

Quantum Yield of Fluorescence

Fluorescence quantum yield measurements were performed using the direct excitation method with an integrating sphere. In each case, solutions of PCs were prepared with $A < 0.2$. Both PC solutions and reference solvents were prepared in a nitrogen filled glovebox with DMAc as the solvent in 1 cm pathlength quartz cuvettes. Unless otherwise noted, the $\lambda_{\text{max,abs}}$ was used as the excitation wavelength. PC samples (S) and reference solvents (R) measurements were made to obtain scattering (R_s and S_s) and emission (R_e and S_e) data. The equation for calculation of absolute fluorescence quantum yield (AFQY) using the direct excitation method is:

$$AFQY = \frac{S_e - R_e}{R_s - S_s} \times 100$$

The scattering and emission spectral regions were measured separately. The AFQY values were calculated using the Fluoracle software via the equation above. AFQY values were measured at the maximum wavelength of emission ($\lambda_{\text{max,em}}$).

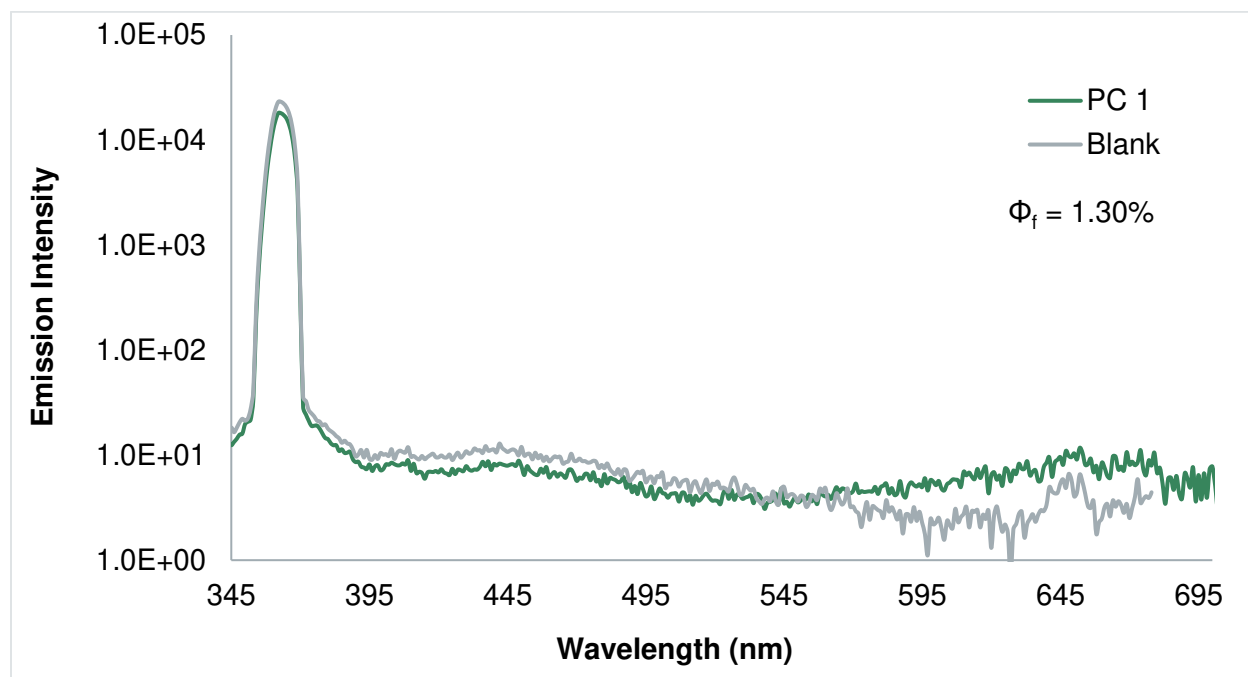


Figure A3.45. Emission spectrum of PC 1 with overlaid with the reference solvent spectrum used for measurement of fluorescence quantum yield.

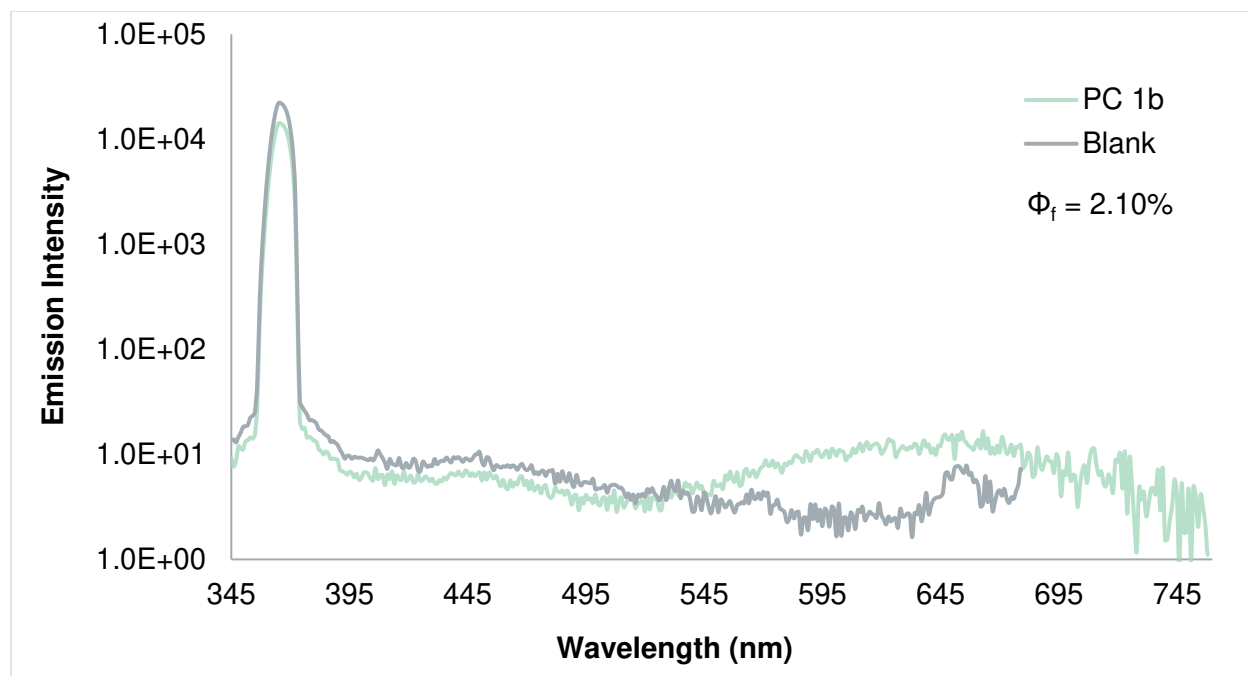


Figure A3.46. Emission spectrum of PC **1b** with overlaid with the reference solvent spectrum used for measurement of fluorescence quantum yield.

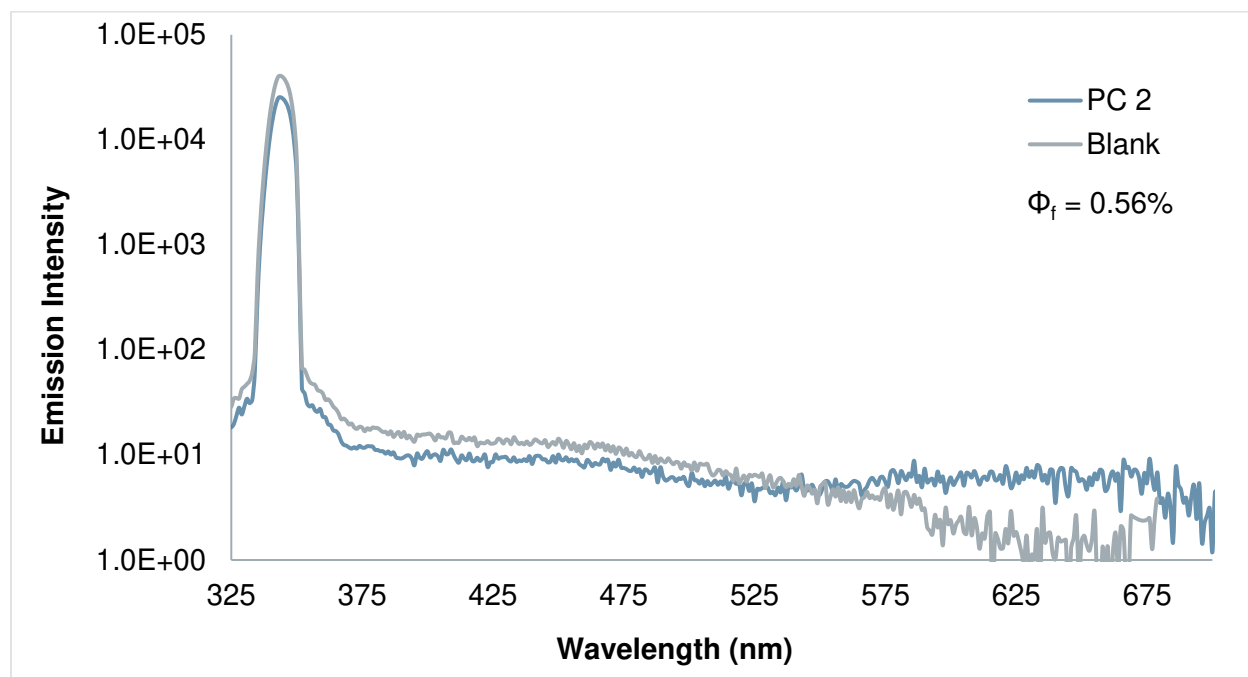


Figure A3.47. Emission spectrum of PC **2** with overlaid with the reference solvent spectrum used for measurement of fluorescence quantum yield.

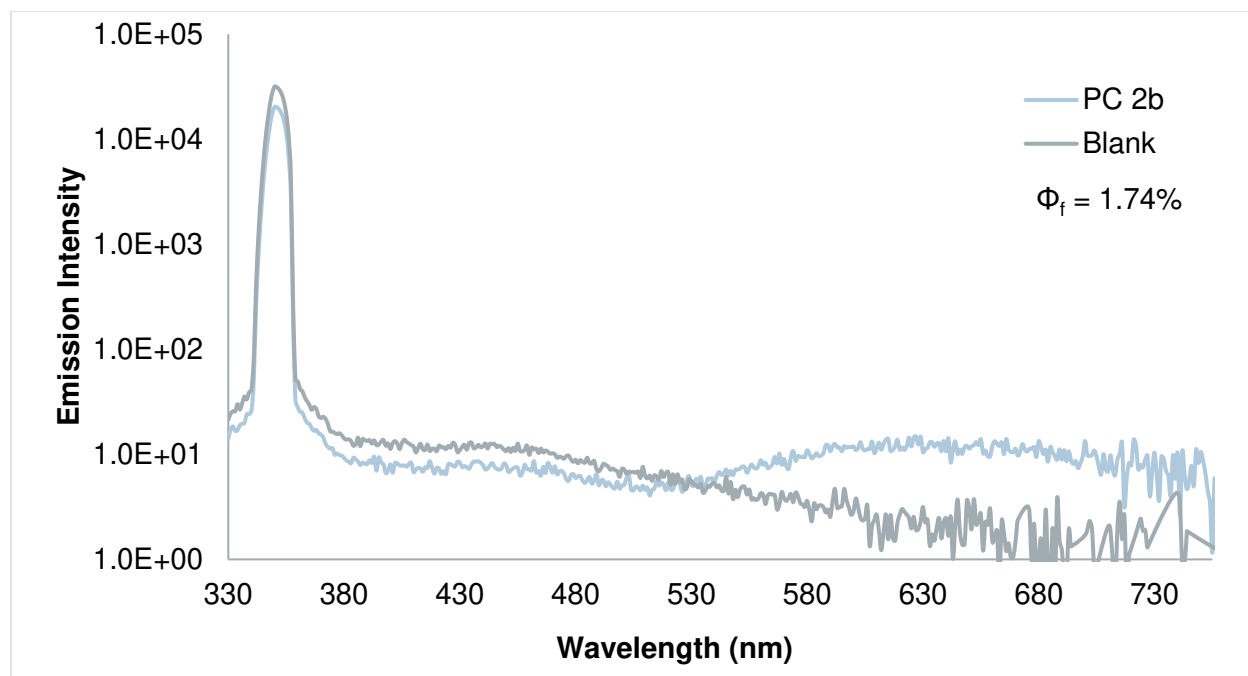


Figure A3.48. Emission spectrum of PC **2b** with overlaid with the reference solvent spectrum used for measurement of fluorescence quantum yield.

Phosphorescence Spectroscopy

The phosphorescence spectra of all PCs were collected in the following manner: a 0.1 mM solution of each PC was prepared in N,N-dimethylformamide (DMF) in a nitrogen filled glovebox and transferred to an NMR tube. The tube was then sealed, the cap wrapped with parafilm to minimize oxygen diffusion into the solution, and the sample was removed from the glovebox. The sample was excited with a 355 nm laser and its emission spectrum measured at room temperature with a 0 ns gate delay (100 ns gate width) or a 1 ms gate delay (30 ms gate width). In every case, measurements with a 1 ms gate delay at room temperature showed no emission signal, consistent with a lack of phosphorescence at room temperature. The samples were then cooled to 77 K and remeasured under the same conditions (with a 0 ns or 1 ms gate delay).

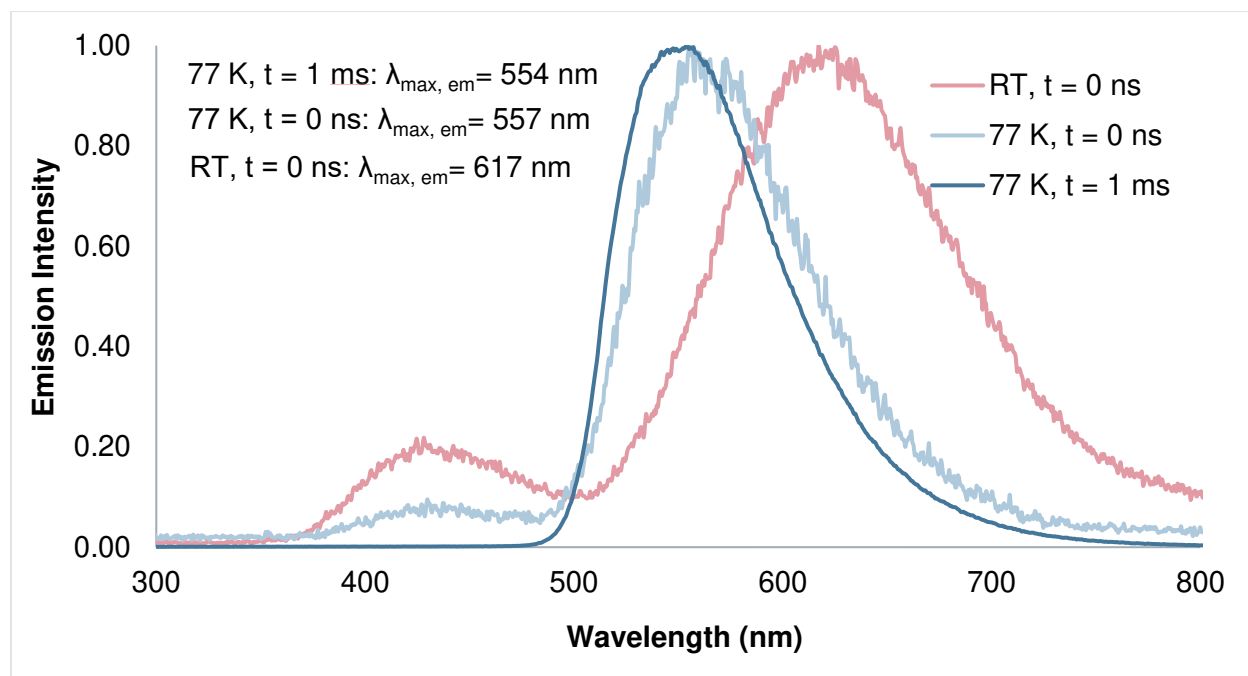


Figure A3.49. Room temperature fluorescence (red), low temperature fluorescence (light blue), and low temperature phosphorescence (dark blue) spectra of PC **1**.

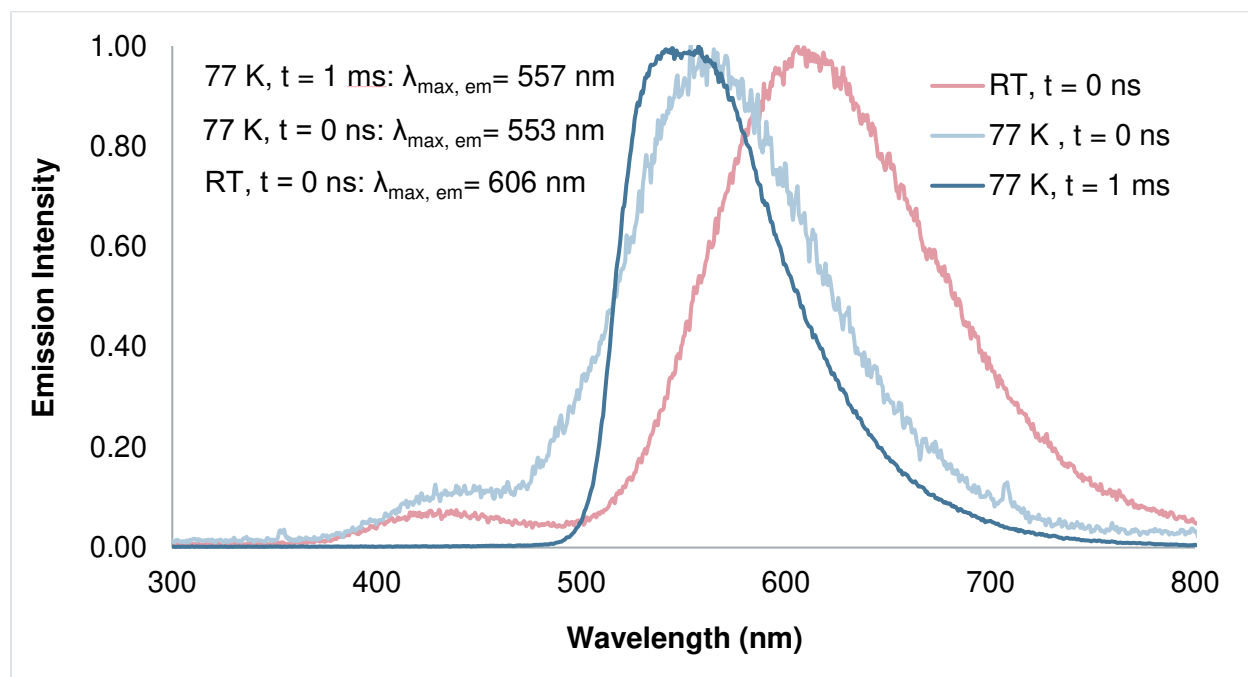


Figure A3.50. Room temperature fluorescence (red), low temperature fluorescence (light blue), and low temperature phosphorescence (dark blue) spectra of PC **1b**.

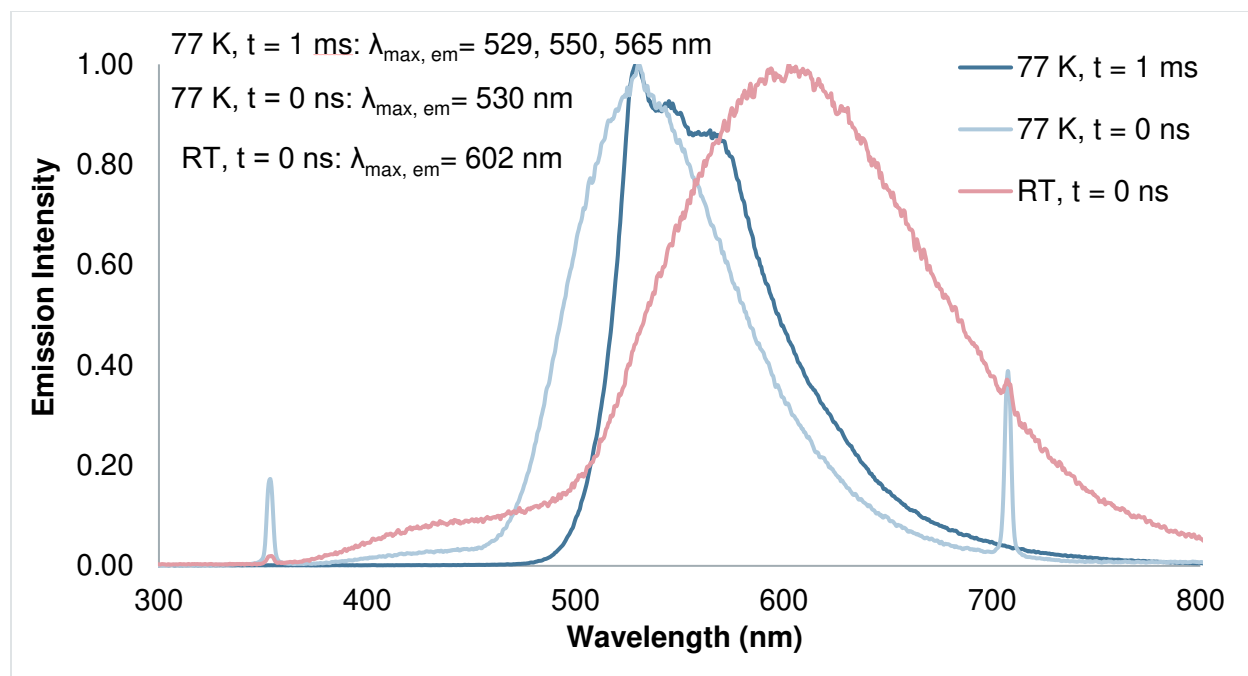


Figure A3.51. Room temperature fluorescence (red), low temperature fluorescence (light blue), and low temperature phosphorescence (dark blue) spectra of PC 2.

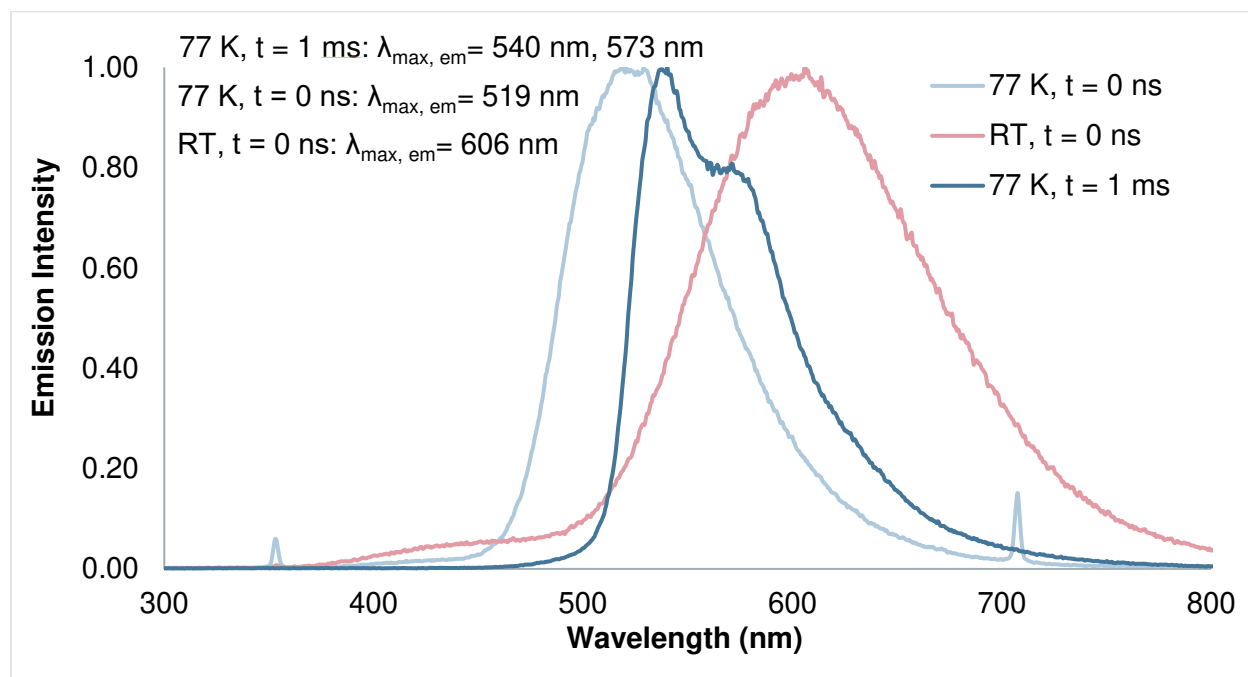


Figure A3.52. Room temperature fluorescence (red), low temperature fluorescence (light blue), and low temperature phosphorescence (dark blue) spectra of PC 2b.

Solvatochromism

Solutions of each PC were prepared in solvents of varying polarity (ϵ = dielectric constant): benzene, hexene, dioxane, THF, pyridine, and DMF at concentrations of 0.1 – 1.0 mM. All samples were analyzed in 1 cm pathlength quartz cuvettes via fluorescence spectroscopy to obtain the emission spectra.

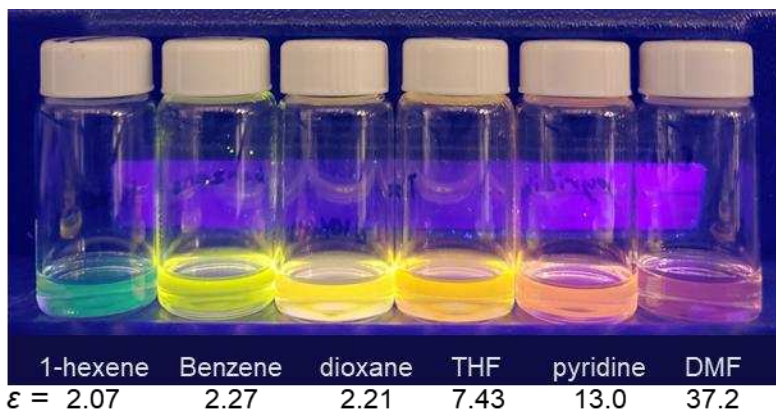
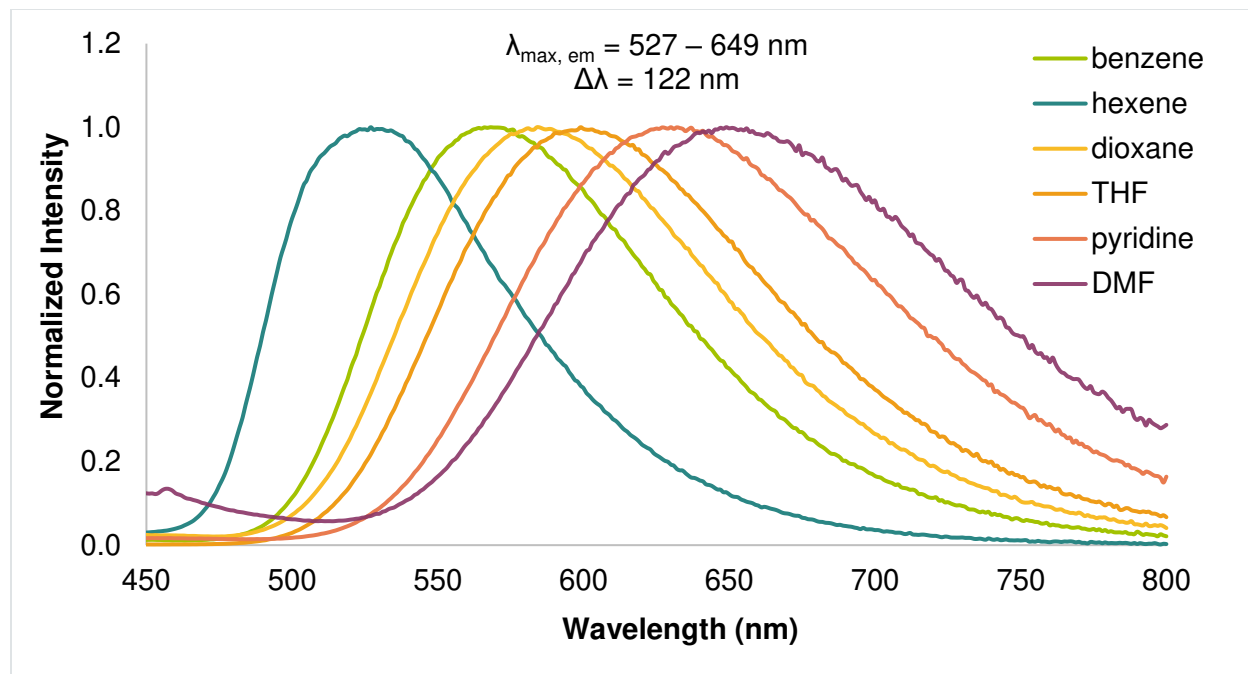


Figure A3.53. Overlaid emission profiles of PC 1 in different polarity solvents (top), photographs of PC 1 dissolved in solvents of increasing polarities under UV light irradiation (bottom).

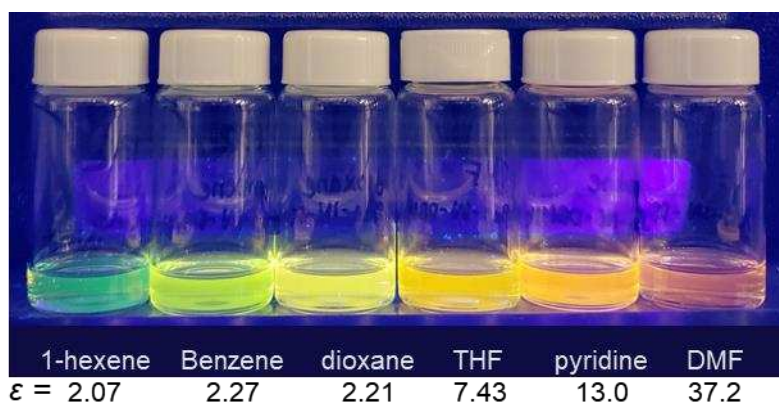
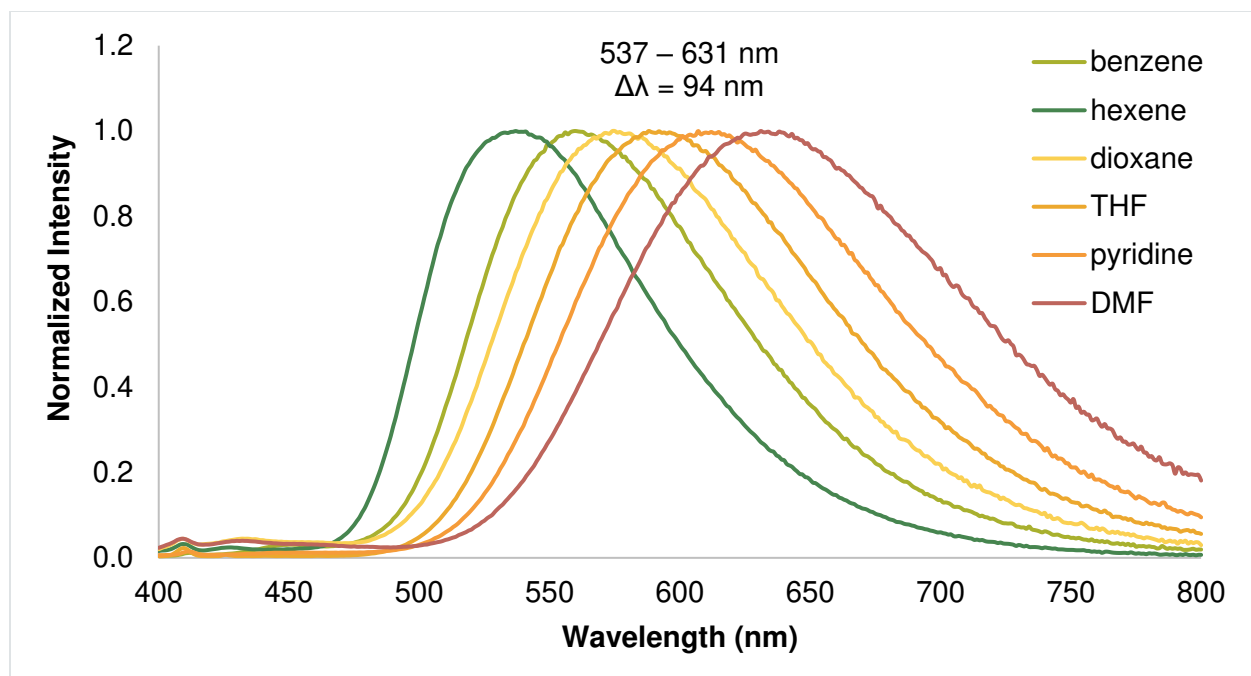


Figure A3.54. Overlaid emission profiles of PC **1b** in different polarity solvents (top), photographs of PC **1b** dissolved in solvents of increasing polarities under UV light irradiation (bottom).

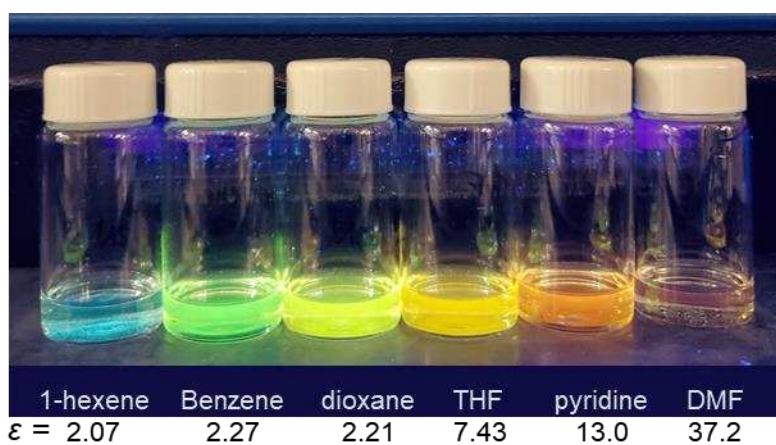
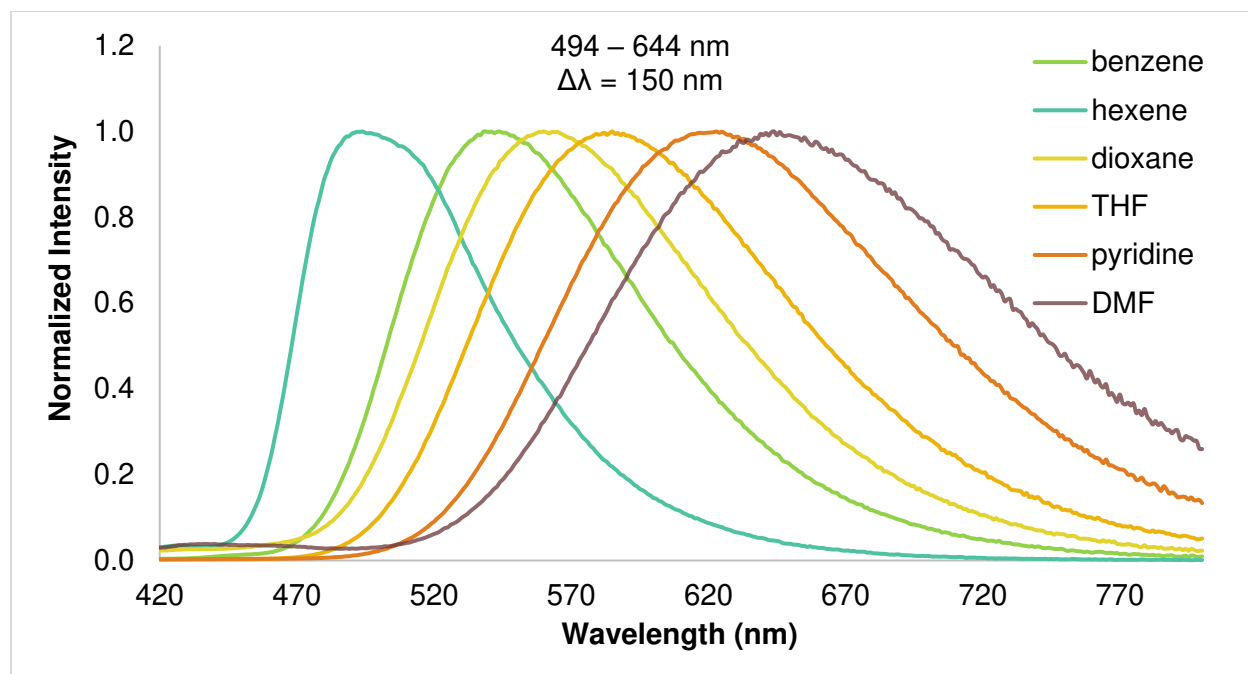


Figure A3.55. Overlaid emission profiles of PC **2** in different polarity solvents (top), photographs of PC **2** dissolved in solvents of increasing polarities under UV light irradiation (bottom).

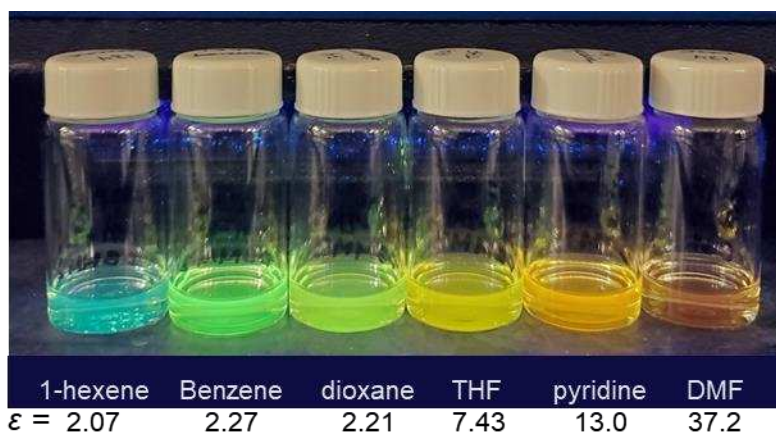
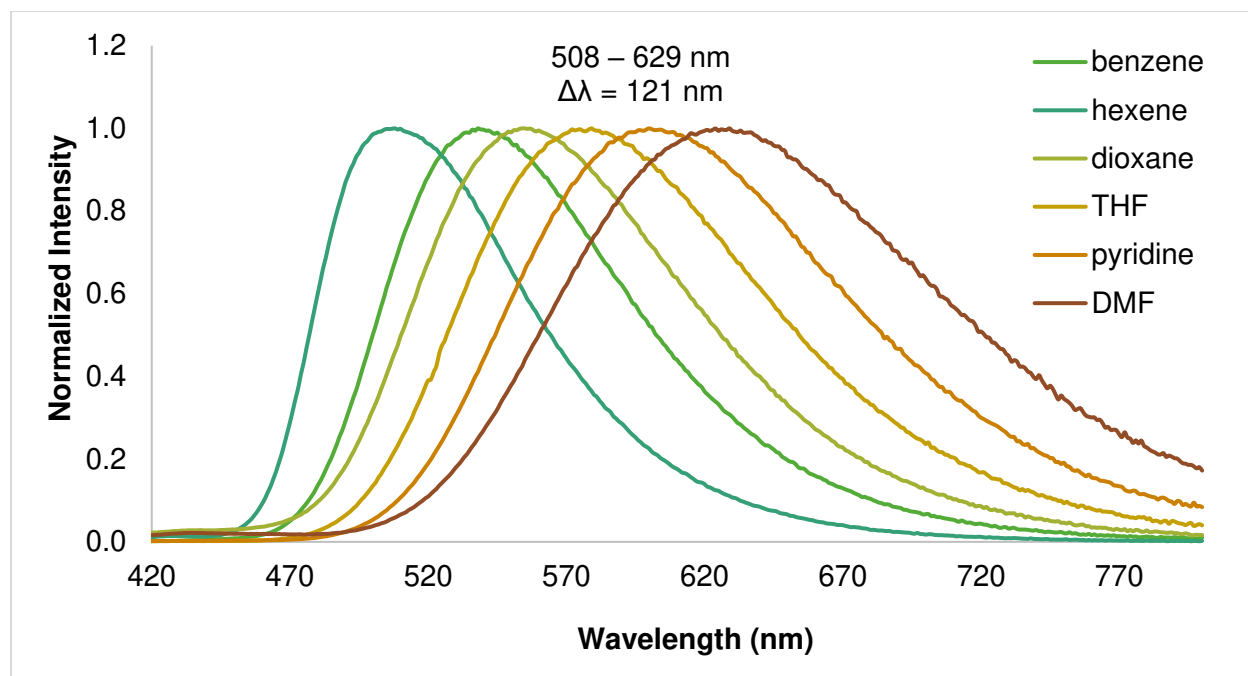


Figure A3.56. Overlaid emission profiles of PC **2b** in different polarity solvents (top), photographs of PC **2b** dissolved in solvents of increasing polarities under UV light irradiation (bottom).

Transient Absorption Spectroscopy

Time zero was determined and set using the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ to locate the pump pulse with a resolution of 1 ns. Kinetic traces were acquired with 50-75 averages and a laser power between $3\text{--}15 \text{ mW/cm}^2$ at a 1 Hz repetition rate. Time constants (excited state lifetimes) were calculated in the L900 software using an exponential tail fit. Spectral absorption data was offset corrected at all wavelengths using kinetic absorption data at the indicated wavelength to adjust

ΔOD . Spectra acquired at a $t > 0$ ns time delay avoided emission signals, so the emission subtraction step was omitted.

For each PC solution, the Beer-Lambert Law was used to calculate the concentration of PC needed for an absorbance intensity of 0.2 at the $\lambda_{\text{max,abs}}$. This approach resulted in solutions with an absorbance intensity of less than 0.2 at 355 nm (wavelength of the excitation pulse). Solutions were prepared in a N_2 filled glovebox in DMAc; 3.0 mL each solution was transferred to a quartz screw cap cuvette equipped with a Kontes valve and sidearm with a 1 cm path length. After completely sealing the cuvettes with caps, they were brought out of the glovebox. Each PC solution was analyzed by UV-vis on the instrument described herein both before and after TA spectroscopy to monitor if PC degradation occurred. None of the PC solutions analyzed in this work showed evidence of degradation after TA, indicated by no observable change in the UV-vis spectra before and after TA spectroscopy was performed.

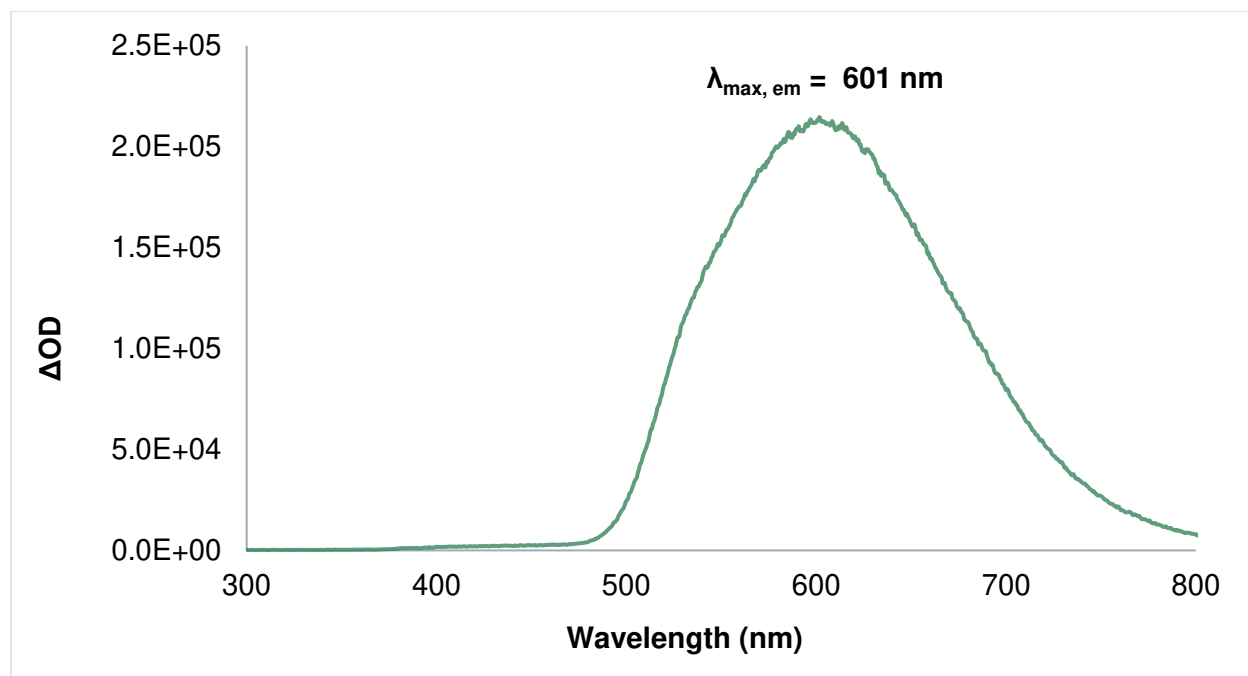


Figure A3.57. Spectral emission trace of PC 1 in DMAc.

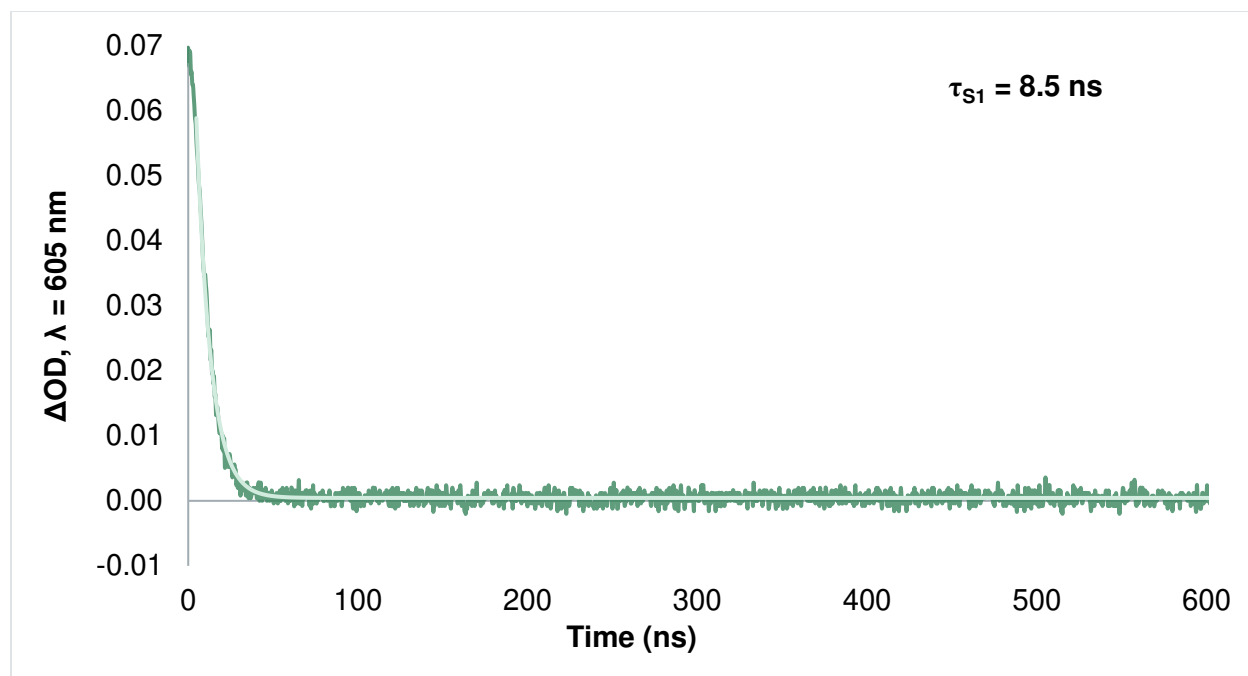


Figure A3.58. Kinetic emission trace for PC **1** in DMAc at 605 nm with an exponential tail fit for determination of τ_{S1} .

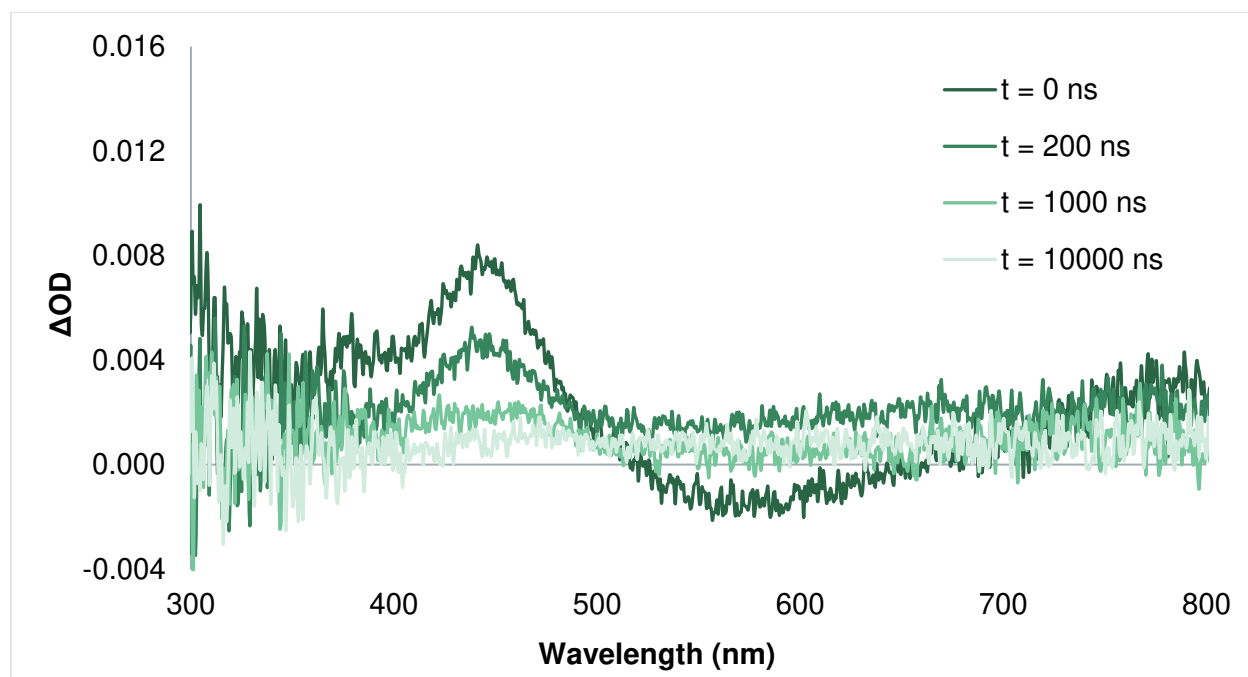


Figure A3.59. Spectral absorption traces of PC **1** in DMAc and various time delays, no emission subtraction. The spectral absorption data was offset corrected using kinetic absorption data acquired at $\lambda = 445$ nm.

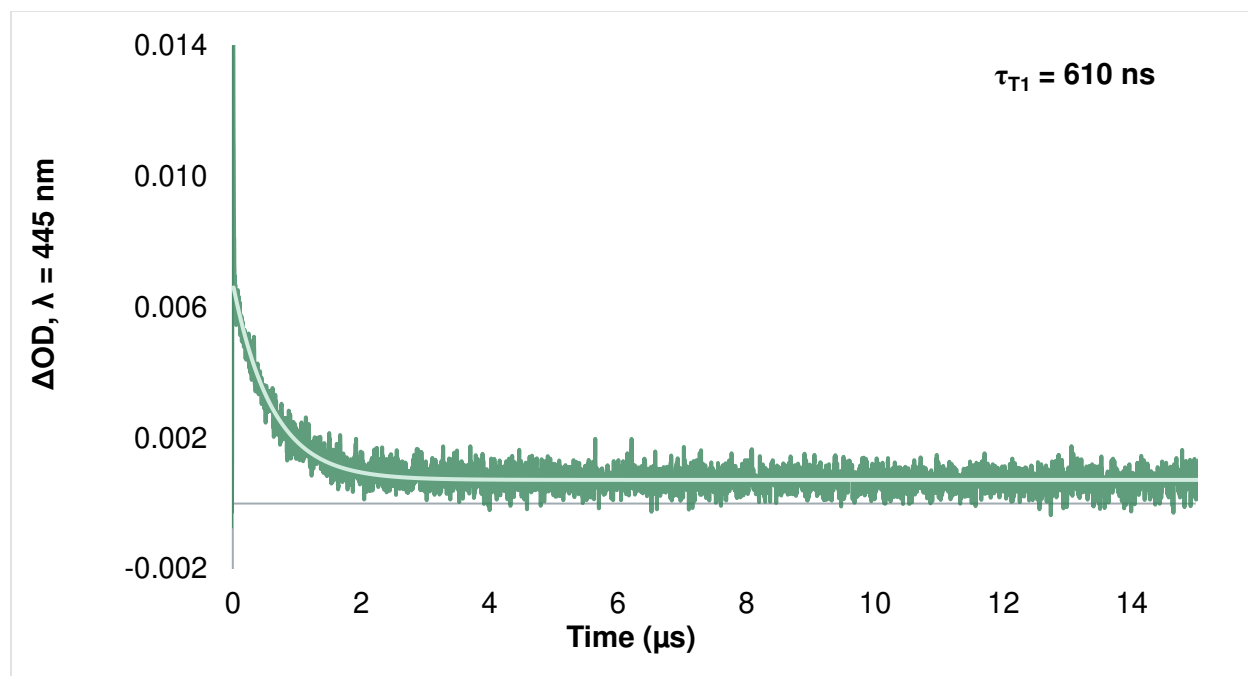


Figure A3.60. Kinetic absorption trace for PC **1** in DMAc at 445 nm with an exponential tail fit for determination of τ_{T1} .

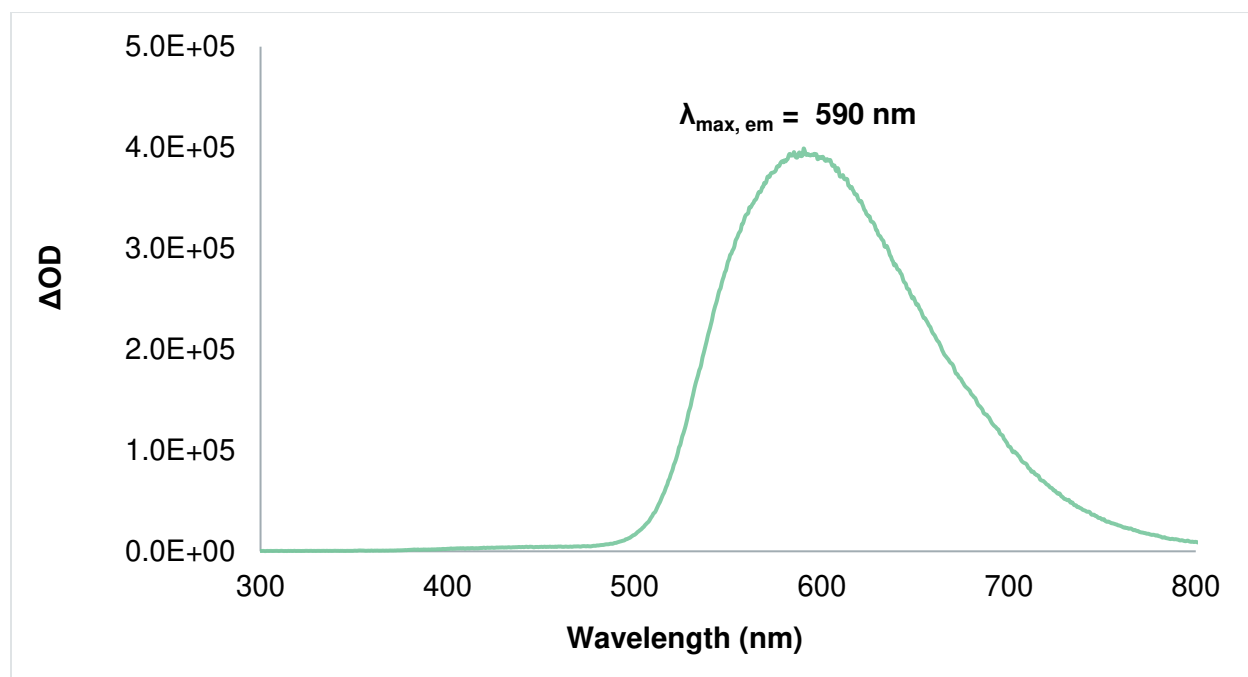


Figure A3.61. Spectral emission trace of PC **1b** in DMAc.

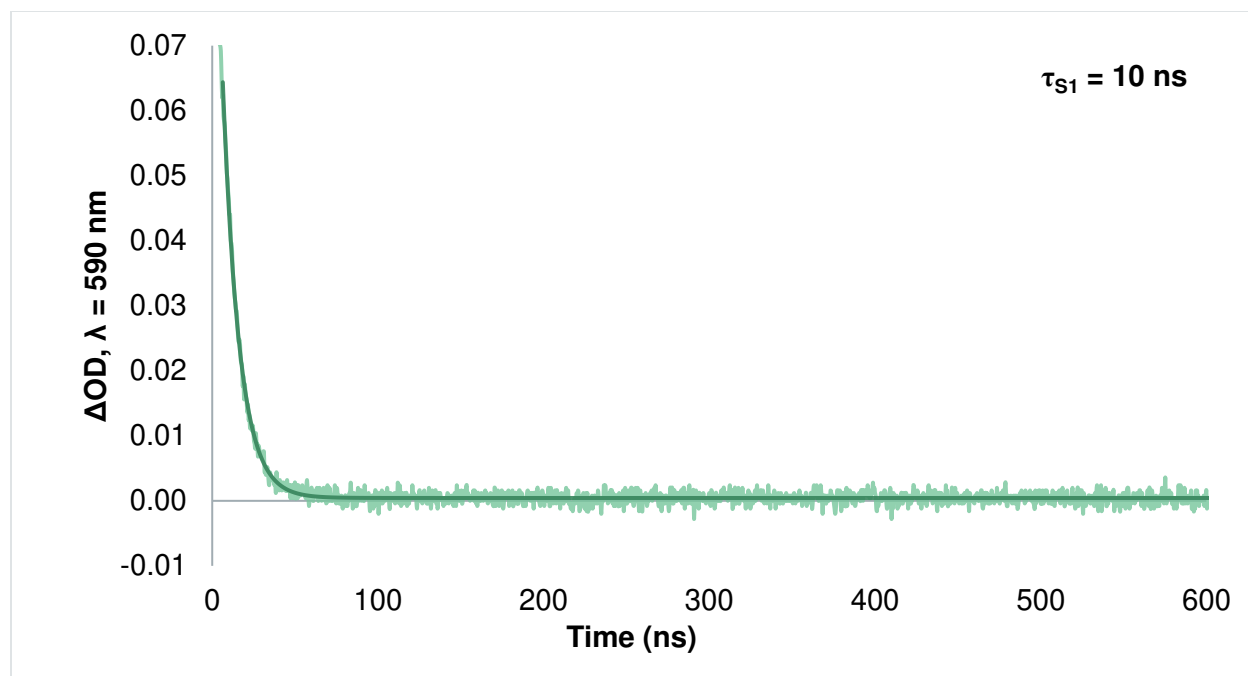


Figure A3.62. Kinetic emission trace for PC **1b** in DMAc at 590 nm with an exponential tail fit for determination of τ_{s1} .

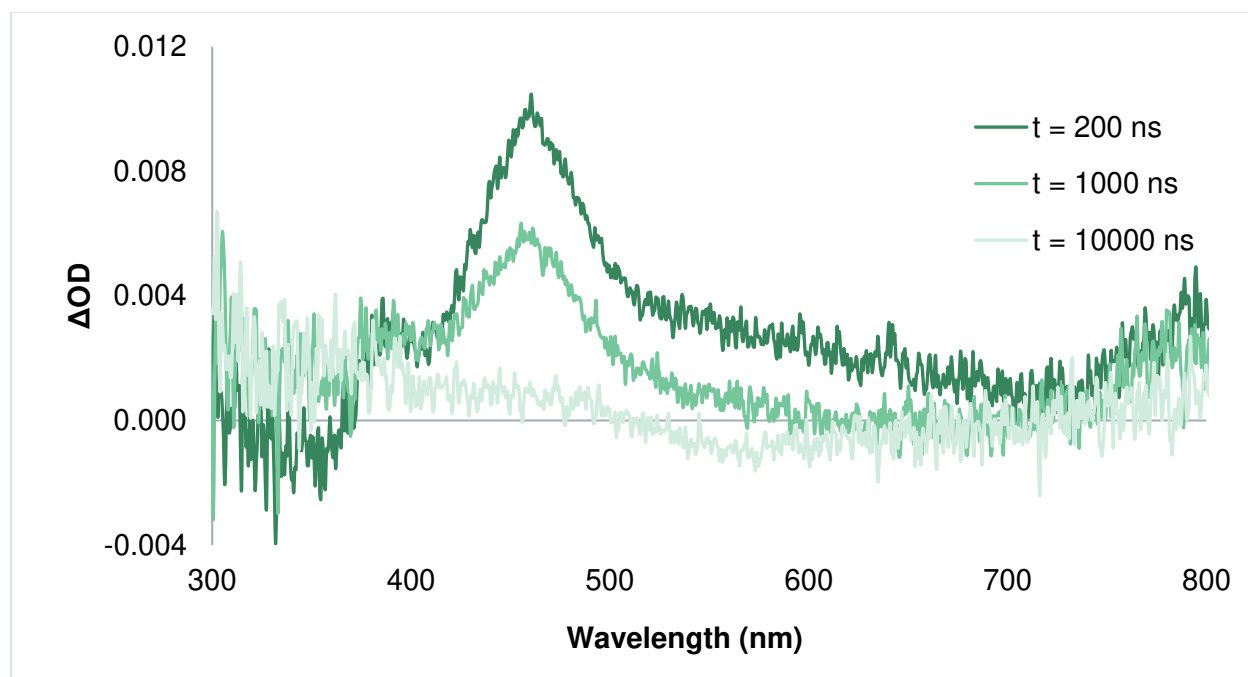


Figure A3.63. Spectral absorption traces of PC **1b** in DMAc and various time delays, no emission subtraction. The spectral absorption data was offset corrected using kinetic absorption data acquired at $\lambda = 460$ nm.

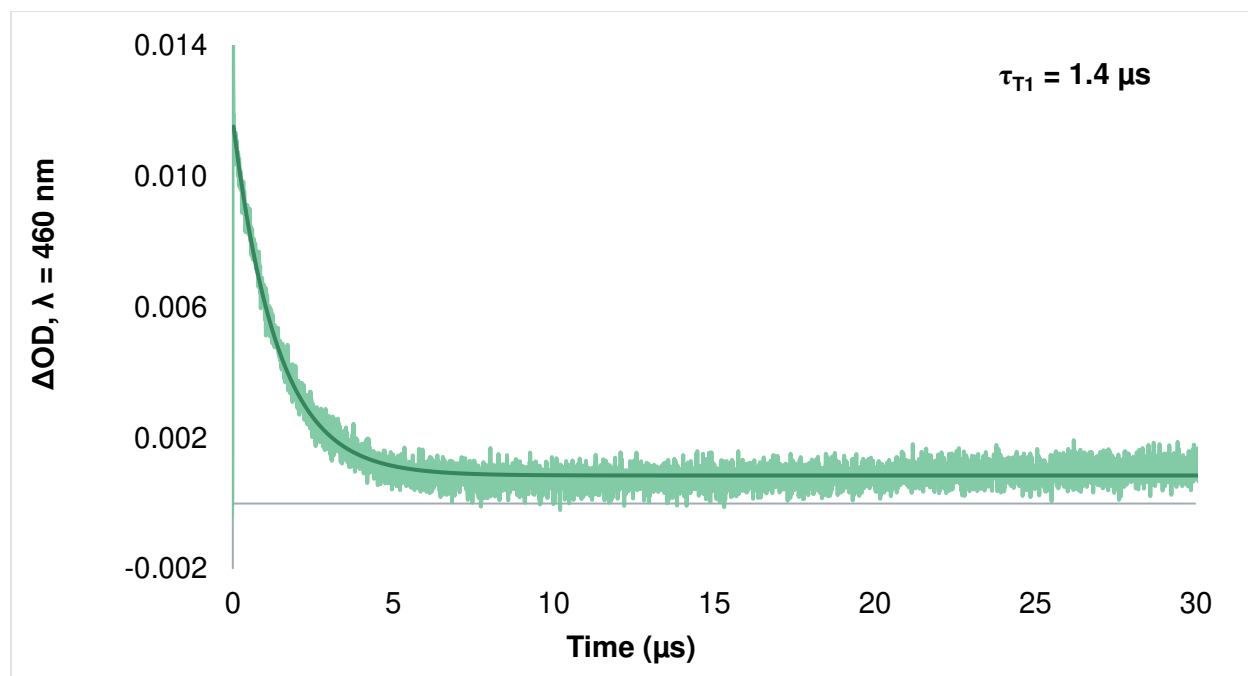


Figure A3.64. Kinetic absorption trace for PC **1b** in DMAc at 460 nm with an exponential tail fit for determination of τ_{T1} .

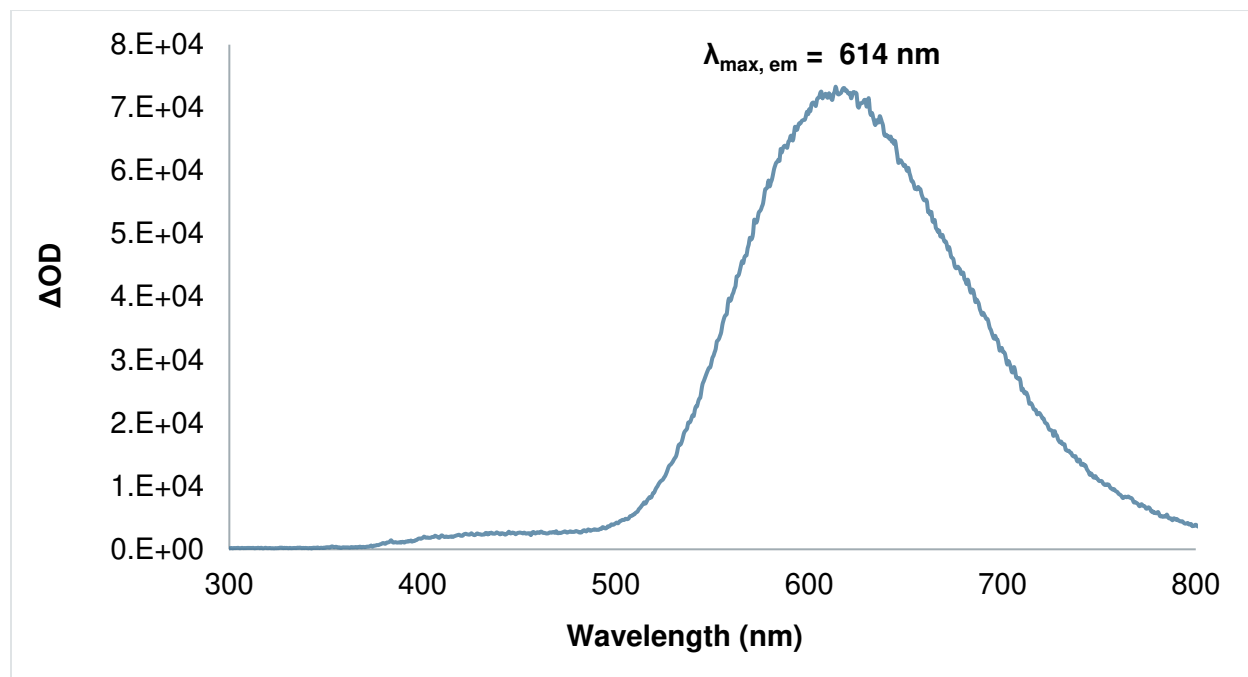


Figure A3.65. Spectral emission trace of PC **2** in DMAc.

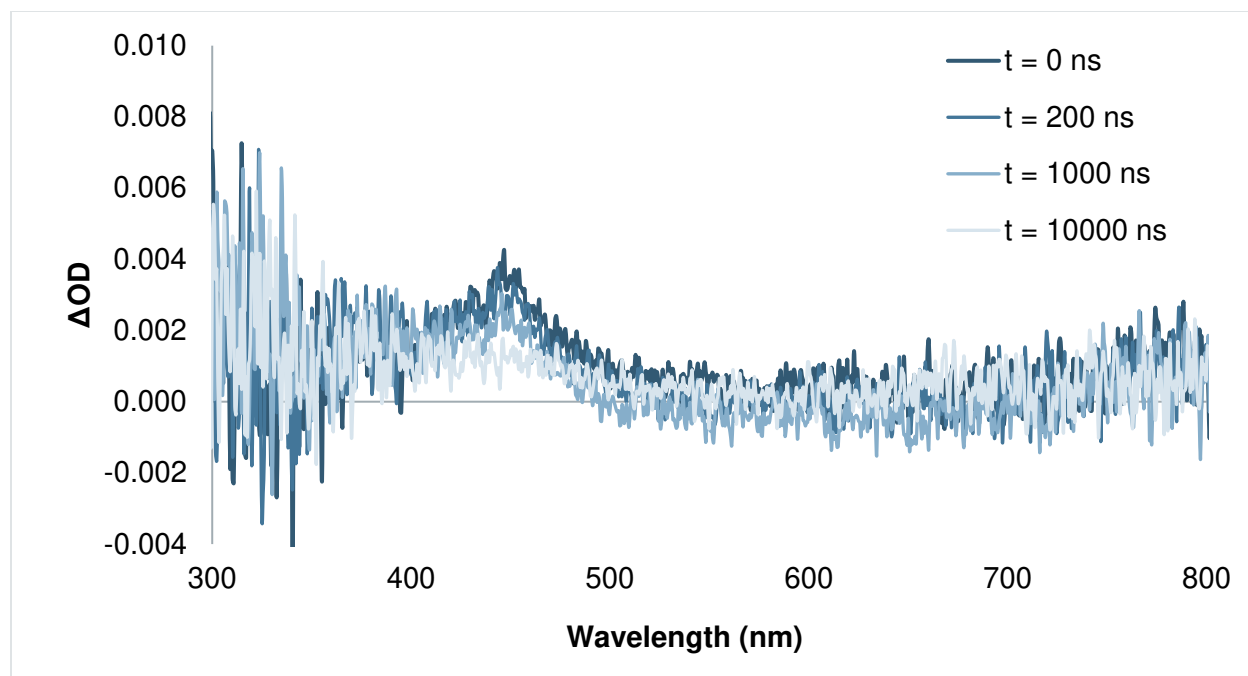


Figure A3.66. Spectral absorption traces of PC 2 in DMAc and various time delays, no emission subtraction. The spectral absorption data was offset corrected using kinetic absorption data acquired at $\lambda = 445$ nm.

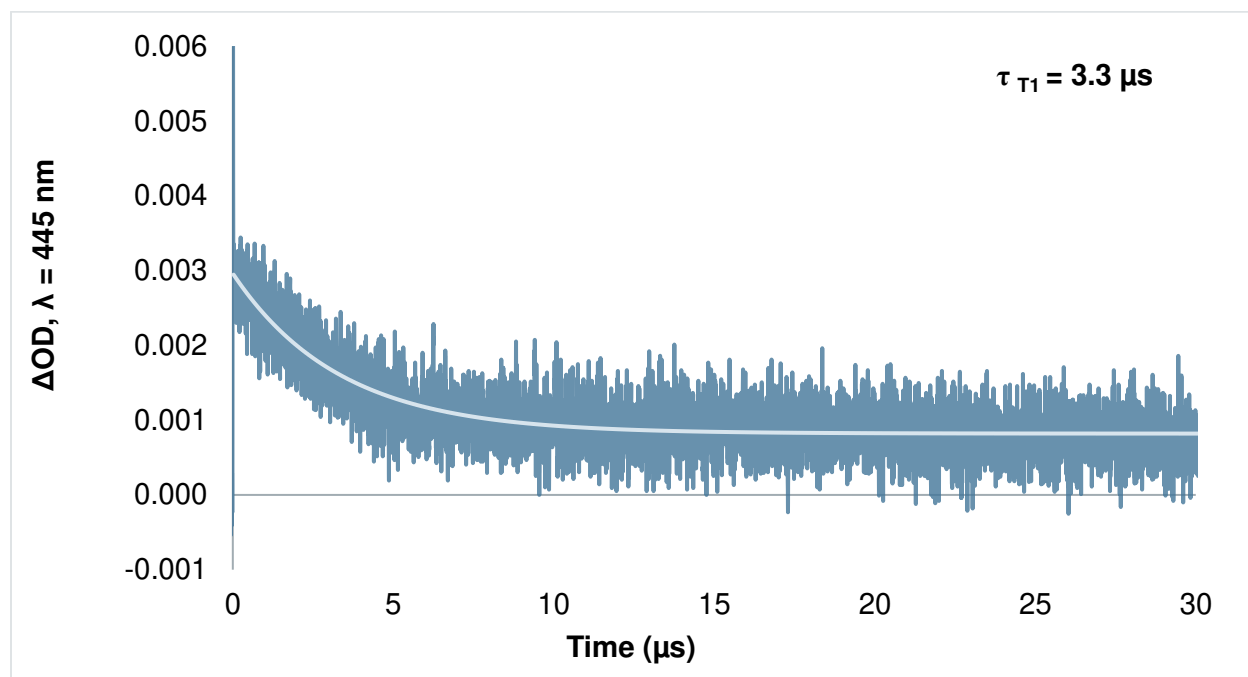


Figure A3.67. Kinetic absorption trace for PC 2 in DMAc at 445 nm with an exponential tail fit for determination of τ_{T1} .

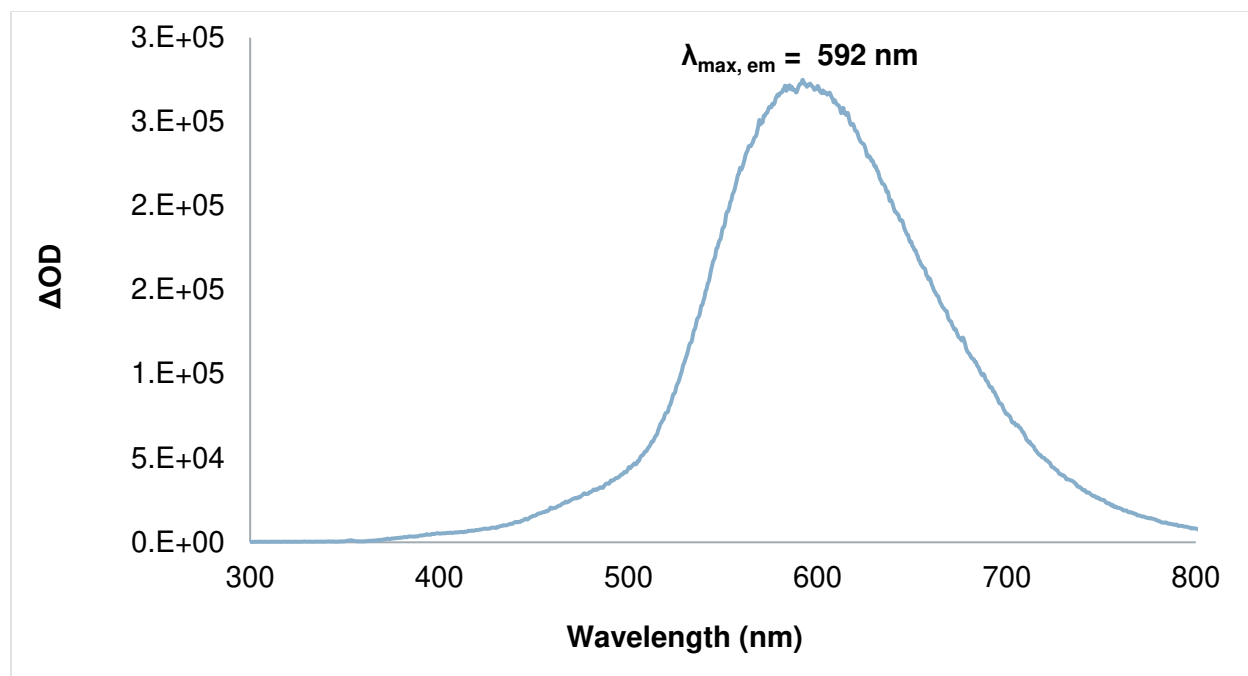


Figure A3.68. Spectral emission trace of PC **2b** in DMAc.

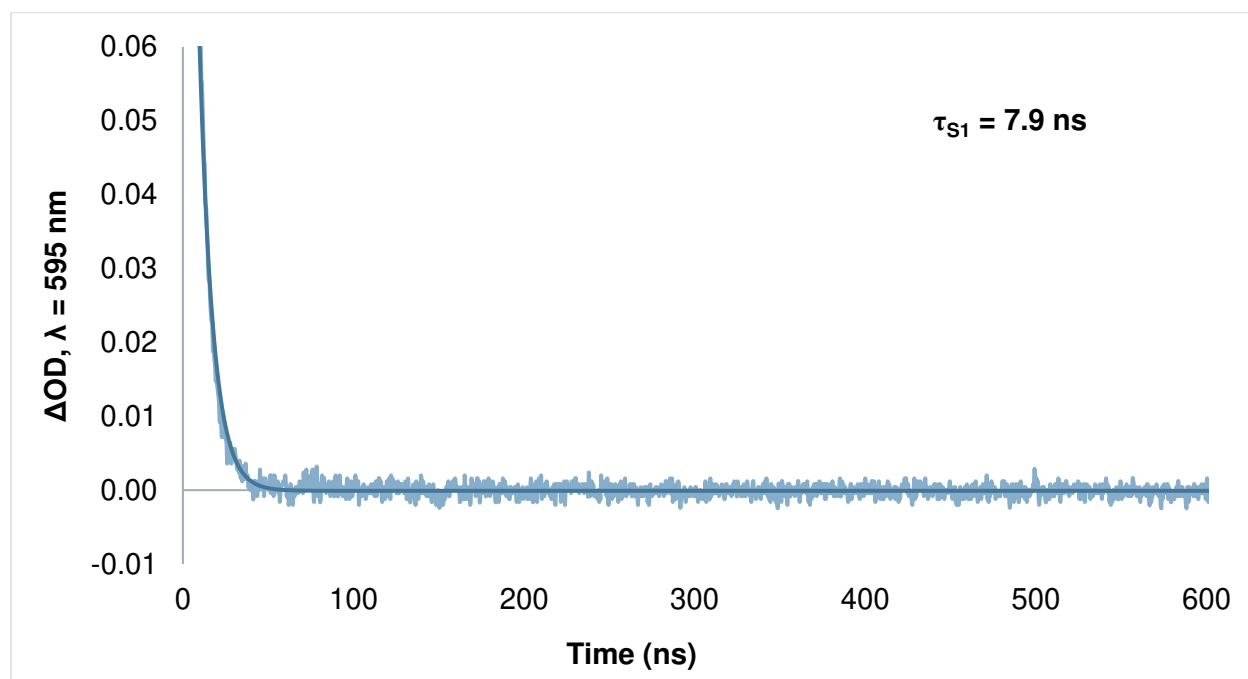


Figure A3.69. Kinetic emission trace for PC **2b** in DMAc at 595 nm with an exponential tail fit for determination of τ_{S1} .

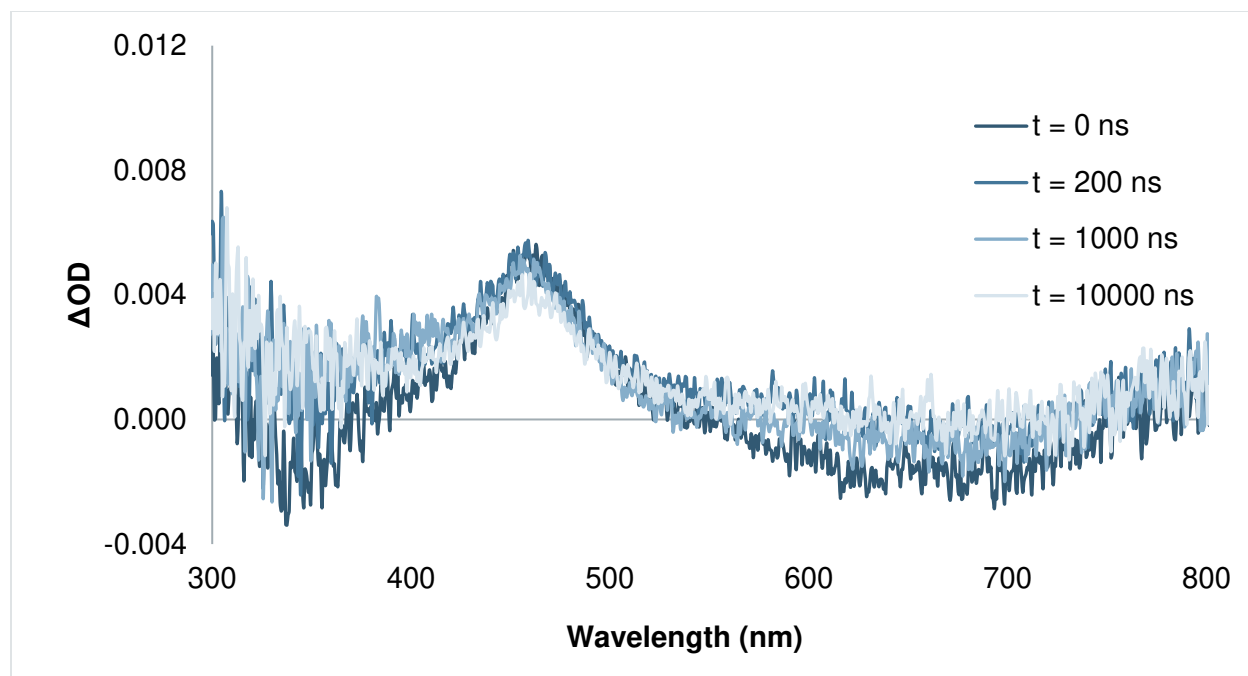


Figure A3.70. Spectral absorption traces of PC **2b** in DMAc and various time delays, no emission subtraction. The spectral absorption data was offset corrected using kinetic absorption data acquired at $\lambda = 460$ nm.

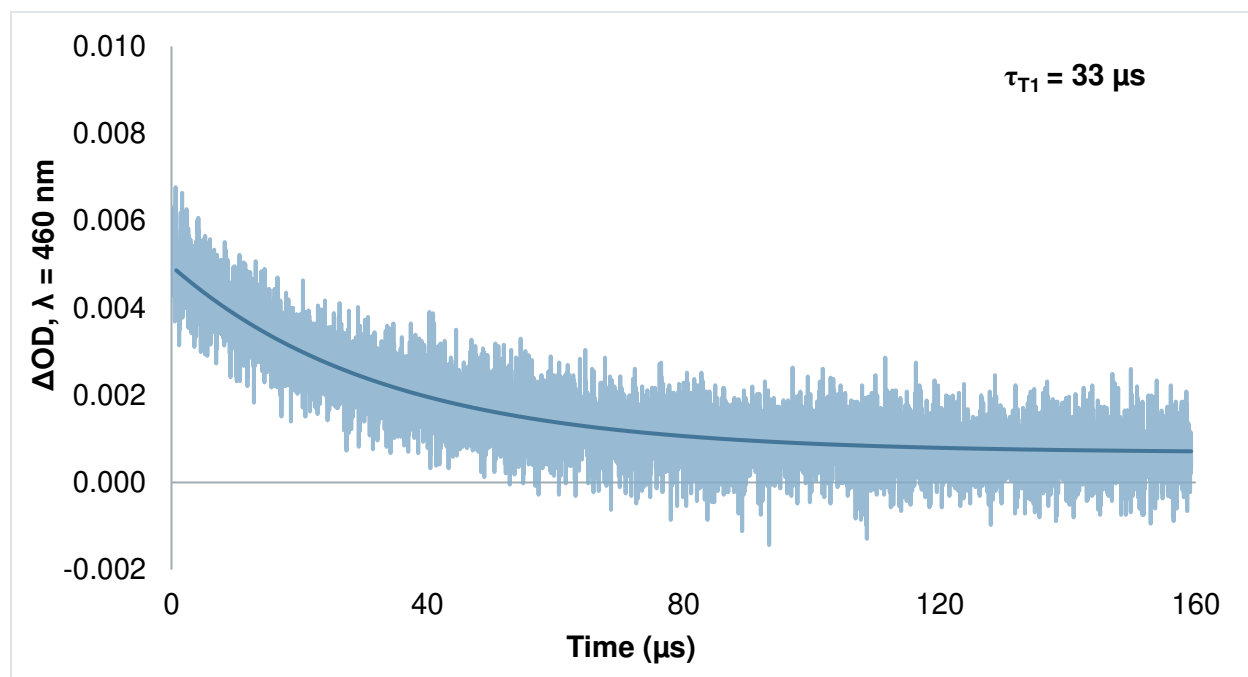


Figure A3.71. Kinetic absorption trace for PC **2b** in DMAc at 460 nm with an exponential tail fit for determination of τ_{T1} .

Time Correlated Single Photon Counting

The singlet excited state lifetime for PC **2** was measured by TCSPC. The PC **2** solution was prepared in DMAc in a nitrogen filled glovebox in air-free cuvettes equipped with Kontes valves as described for transient absorption spectroscopy. Measurements were performed until a maximum count value of 10,000 counts was achieved, and the data were fit with exponential tail fits excluding the instrument response region.

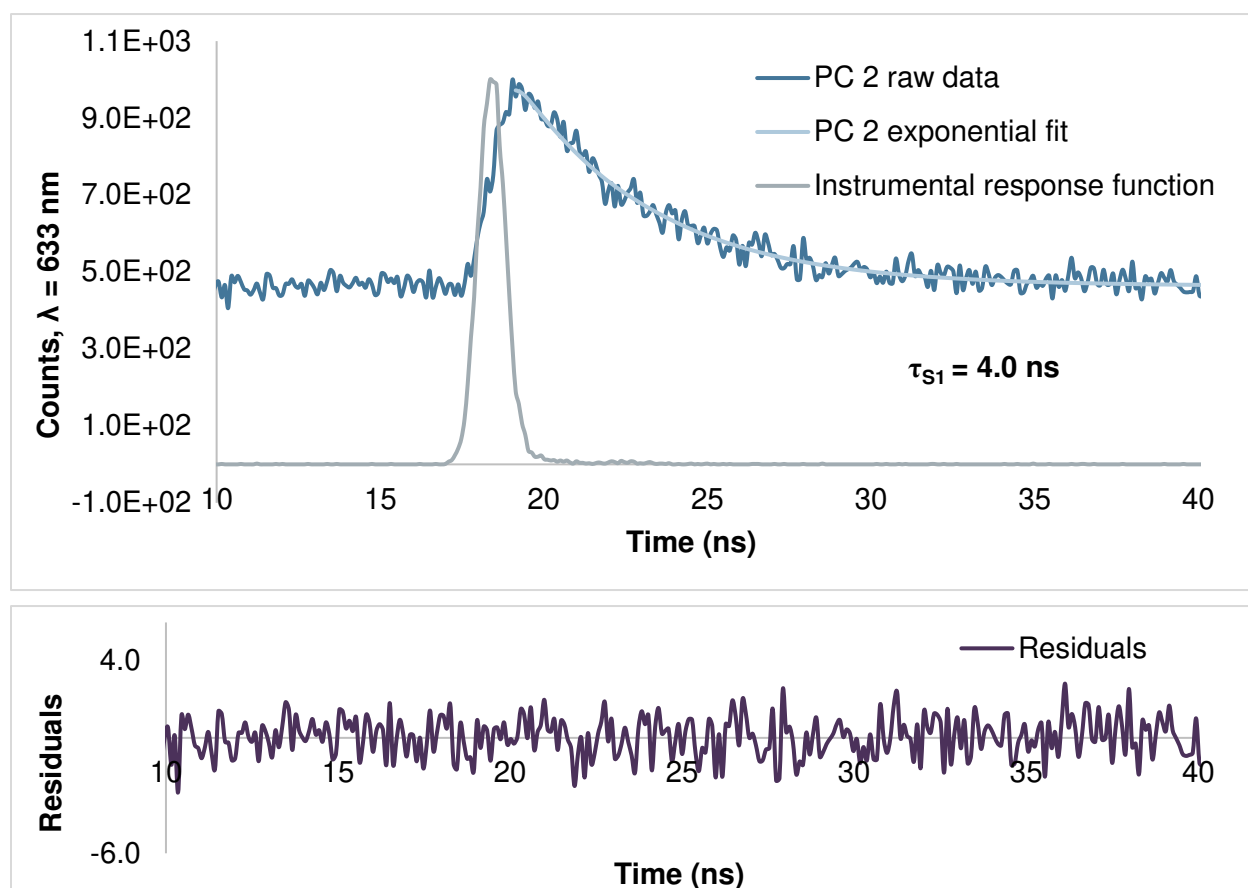


Figure A3.72. Fluorescence decay curve of PC **2** (dark blue) with instrument response function (light grey) and exponential fit of the decay data (light blue), $\lambda_{\text{ex}} = 343$ nm, $\lambda_{\text{em}} = 633$ nm. The data on the bottom (purple) shows the residuals from the exponential fit of the data.

Cyclic Voltammetry

Samples were characterized by cyclic voltammetry in DMAc. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate (NBu₄PF₆), the working electrode was a

glassy carbon disk, the counter electrode was a Pt disk, and the reference electrode was Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆ supporting electrolyte).

Potentials were converted versus the saturated calomel electrode (SCE) by adding 0.298 V to the potentials versus Ag/AgNO₃. Prior to measurement, the solutions were sparged with N₂ for 10-15 minutes, and measurements were performed under a positive pressure of N₂.

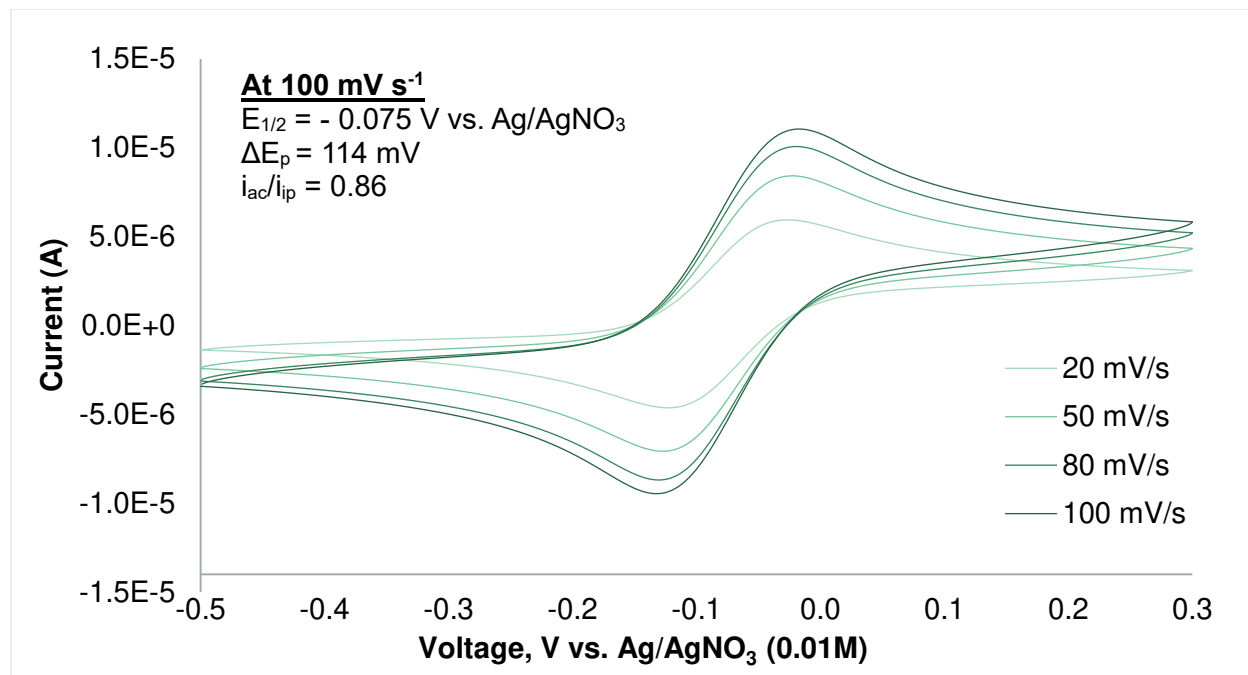


Figure A3.73. Cyclic voltammograms of PC 1 in DMAc at various scan rates.

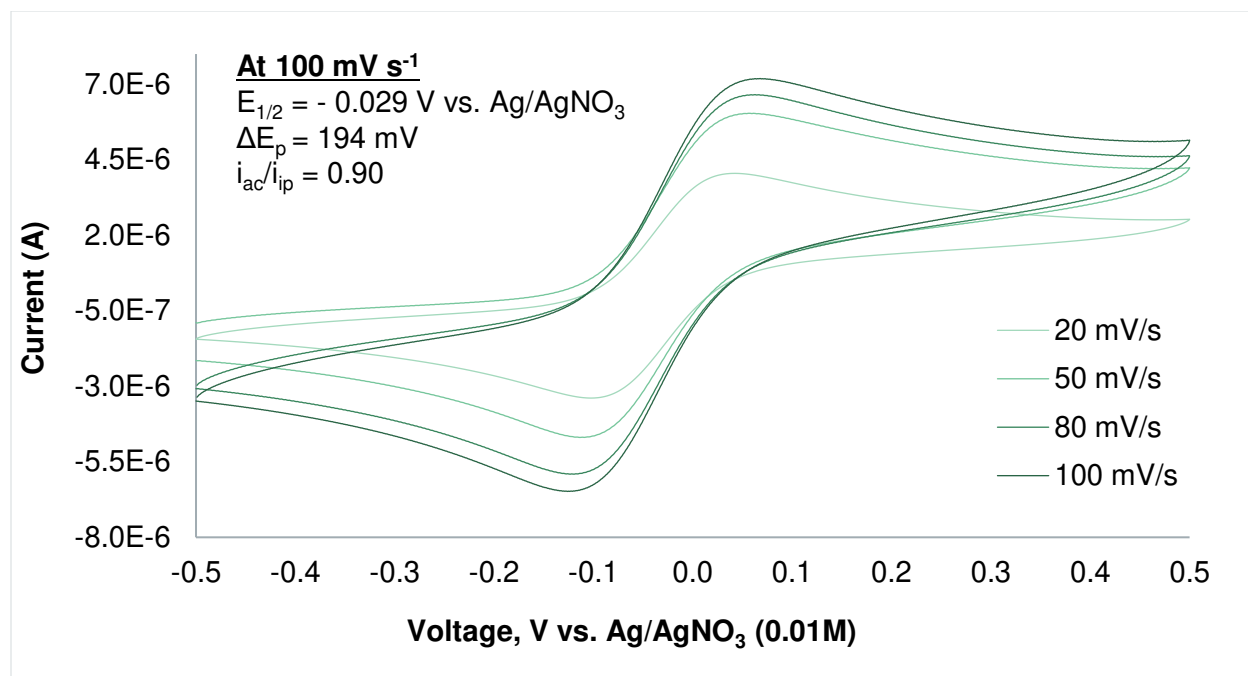


Figure A3.74. Cyclic voltammograms of PC **1b** in DMAc at various scan rates.

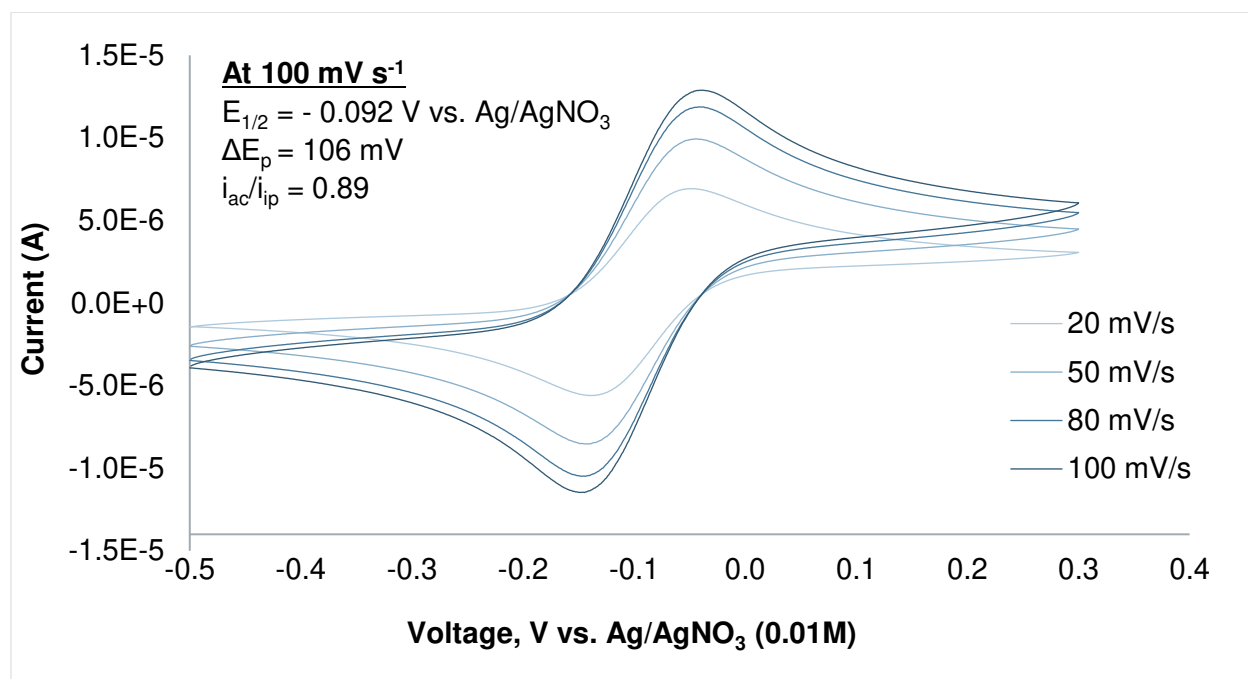


Figure A3.75. Cyclic voltammograms of PC **2** in DMAc at various scan rates.

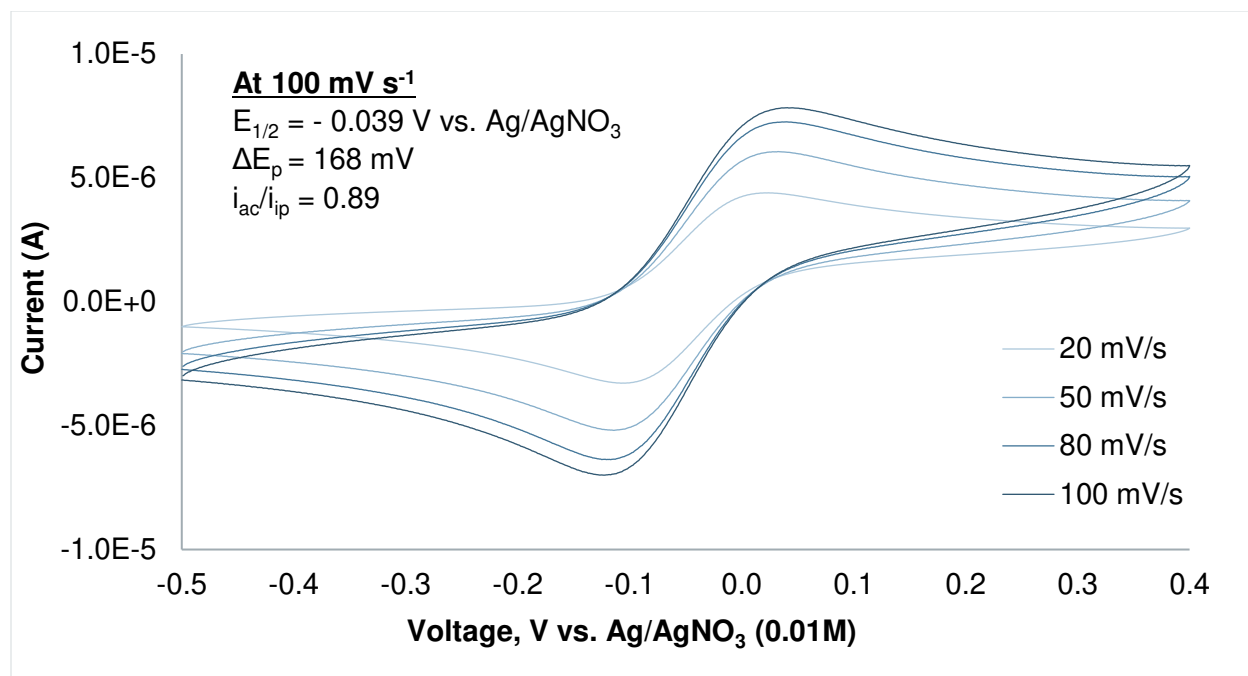


Figure A3.76. Cyclic voltammograms of PC **2b** in DMAc at various scan rates.

SUPPLEMENTAL POLYMERIZATION DATA

Reaction conditions unless stated otherwise were [MMA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of solvent (EtOAc or DMAc), 1.00 mL MMA in scintillation vials in a N₂ filled glovebox with stir bars. O-ATRP was run with a white LED beaker as the light source. To monitor polymerizations, 0.1 mL aliquots were removed periodically using a nitrogen purged syringe and needle. Aliquots were quenched in a deuterated chloroform containing 250 ppm butylated hydroxytoluene (BHT). These solutions were then transferred to an NMR tube for ¹H NMR analysis to determine the extent of monomer conversion. Afterwards, solutions were dried and dissolved in unstabilized THF for GPC analysis to obtain number average molecular weight and dispersity.

Analysis of polymer molecular weights were performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μm MIXED-C gel permeation columns, a Wyatt

Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. A dn/dc value of 0.084 was used for PMMA molecular weight analysis.

O-ATRP in DMAc

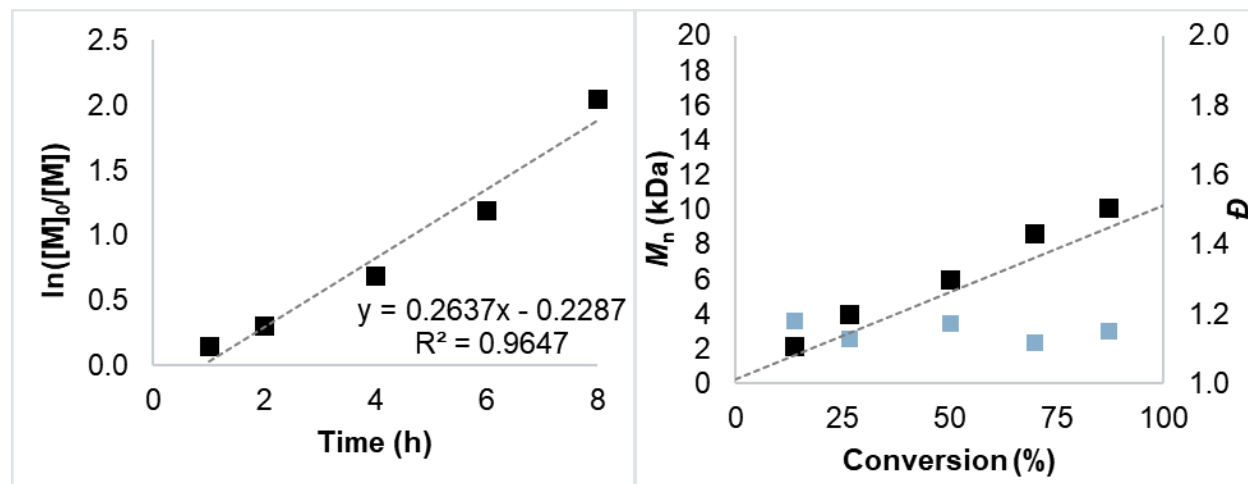


Figure A3.77. For O-ATRP of MMA run with PC 1: (Left) Pseudo-first-order kinetics plot. (Right) Plot of the growth of polymer M_n as a function of MMA conversion to polymer (black squares) and D (blue squares, secondary y-axis) for each timepoint (1, 2, 4, 6, and 8 hours). $M_{n,theo}$ values are represented by the gray dashed line.

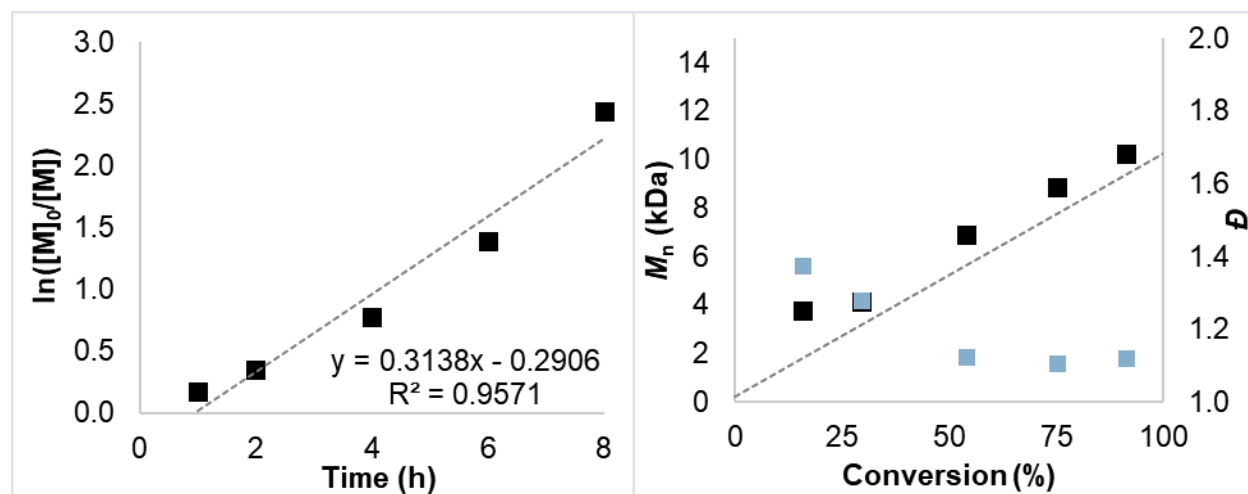


Figure A3.78. For O-ATRP of MMA run with PC 1b: (Left) Pseudo-first-order kinetics plot. (Right) Plot of the growth of polymer M_n as a function of MMA conversion to polymer (black squares) and D (blue squares, secondary y-axis) for each timepoint (1, 2, 4, 6, and 8 hours). $M_{n,theo}$ values are represented by the gray dashed line.

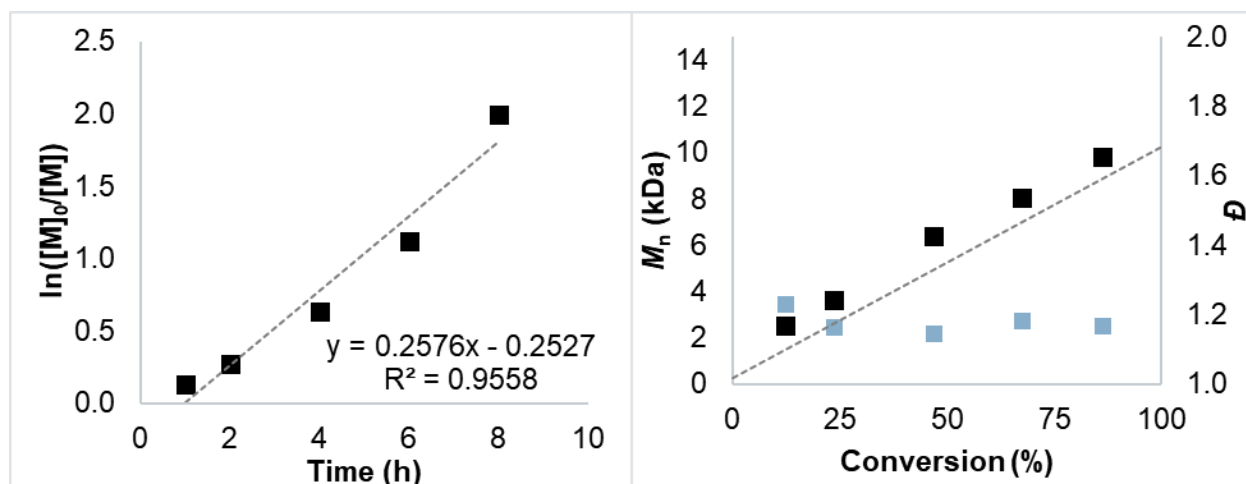


Figure A3.79. For O-ATRP of MMA run with PC 2: (Left) Pseudo-first-order kinetics plot. (Right) Plot of the growth of polymer M_n as a function of MMA conversion to polymer (black squares) and $\bar{D}$ (blue squares, secondary y-axis) for each timepoint (1, 2, 4, 6, and 8 hours). $M_{n,theo}$ values are represented by the gray dashed line.

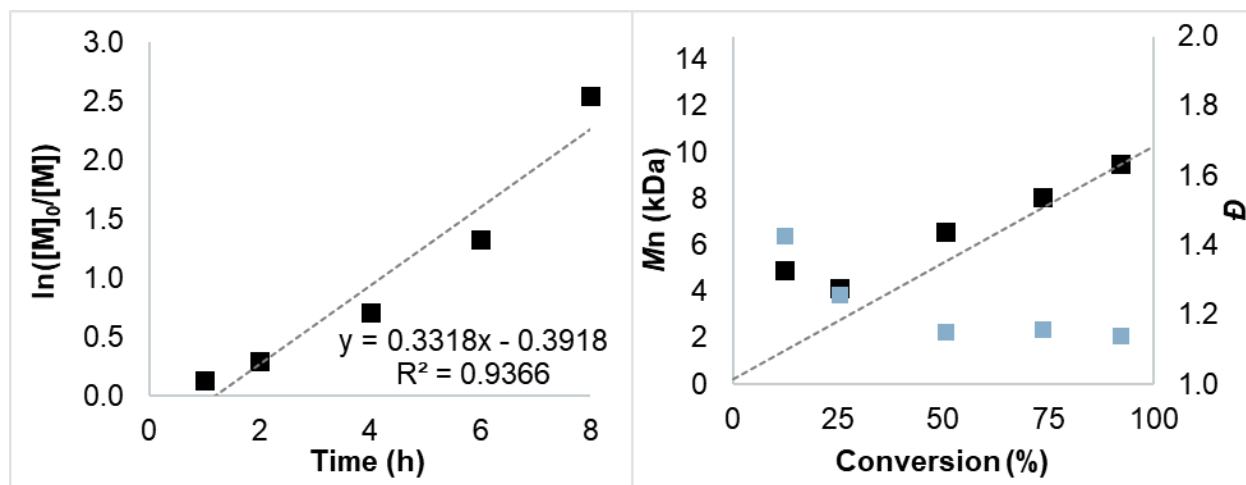


Figure A3.80. For O-ATRP of MMA run with PC 2b: (Left) Pseudo-first-order kinetics plot. (Right) Plot of the growth of polymer M_n as a function of MMA conversion to polymer (black squares) and $\bar{D}$ (blue squares, secondary y-axis) for each timepoint (1, 2, 4, 6, and 8 hours). $M_{n,theo}$ values are represented by the gray dashed line.

O-ATRP in EtOAc

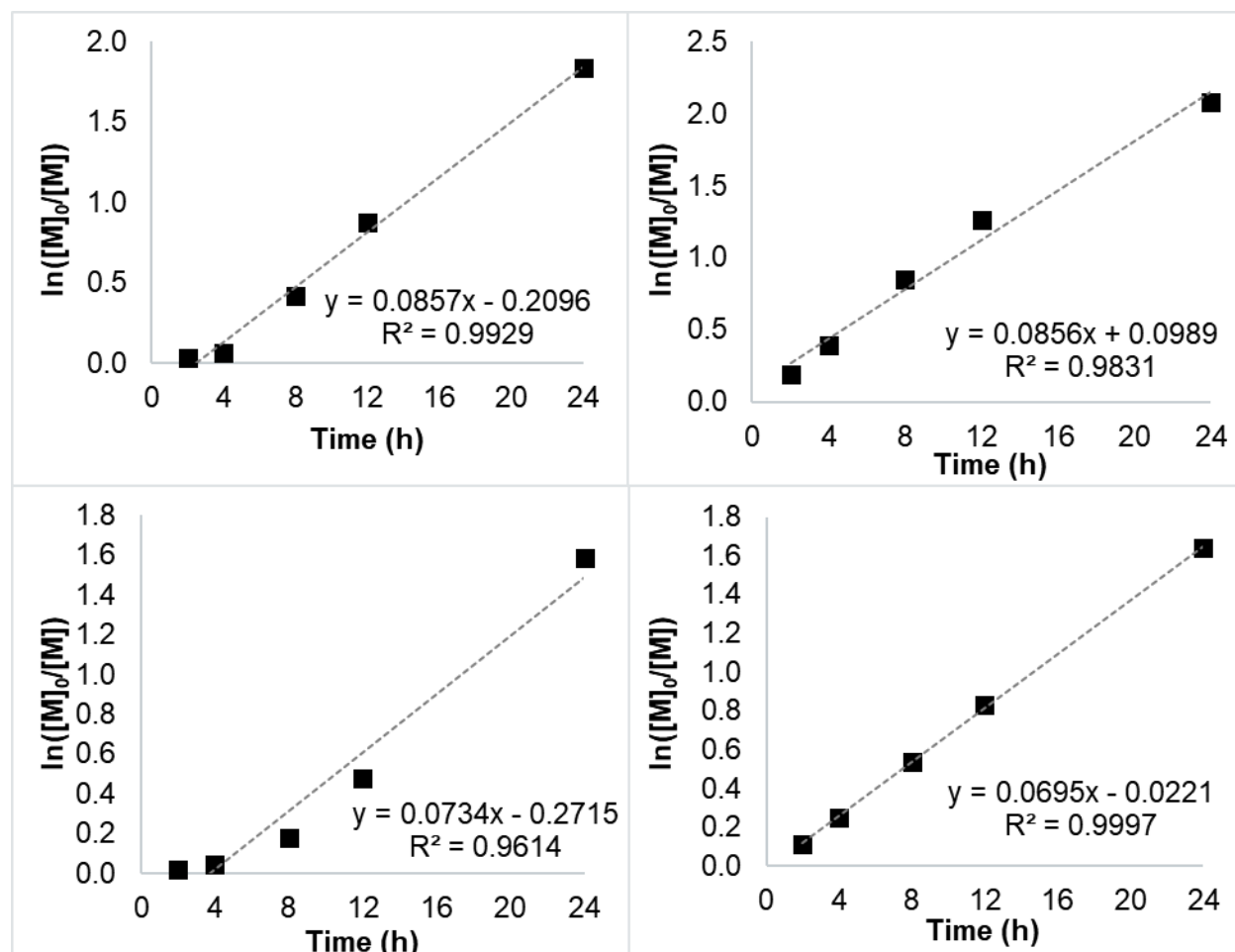


Figure A3.81. Pseudo-first-order kinetics plots for O-ATRP of MMA run in EtOAc with PC **1** (top left), PC **1b** (top right), PC **2** (bottom left), and PC **2b** (bottom right). Timepoints taken at 2, 4, 8, 12, and 24 hours.

Varied Degree of Polymerization Screen

Table A3.1. Results from O-ATRP using PC **2b** for the polymerization of MMA targeting different degrees of polymerization (DP).

Run	DP	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa) ^a	$M_{n, \text{GPC}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
S1	250	61.1	15.5	16.2	1.18	96
S2	500	59.8	30.2	24.1	1.84	125
S3	1000	61.8	62.2	26.3	2.06	236

Conditions: [MMA]:[DBMM]:[PC] = [1000]:[X]:[1], X = 4(S1); 2(S2); 1(S3), 2.00 mL EtOAc was used instead of 1.00 mL to avoid high viscosities, 1.00 mL MMA. ^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

Macroinitiator Synthesis

O-ATRP for synthesis of the macroinitiators was run as described at the beginning of the Supplemental Polymerization Data section. A separate polymerization was set up for each PC (**1**, **1b**, **2**, **2b**). The polymerizations were run for 24 hours in EtOAc. After 24 hours, the light beakers were turned off to stop the reaction. The reaction mixtures were precipitated into cold methanol and vacuum filtration was used to isolate the solid polymer. The polymer was redissolved into ~ 2 mL EtOAc and this isolation procedure was repeated 2 more times. The isolated polymer was dried under vacuum overnight before GPC analysis, which was performed as described earlier herein.

Table A3.2. Results from O-ATRP in EtOAc for macroinitiator synthesis, analysis done after polymer isolation.

Run	PC	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa) ^a	$M_{n, \text{GPC}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
S4	1	55.6	5.82	8.42	1.05	69
S5	1b	57.4	6.00	7.11	1.05	84
S6	2	32.4	3.50	5.81	1.05	60
S7	2b	47.6	5.02	6.07	1.04	83

^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

Chain Extensions

Polymerizations for the chain extension of poly(methyl methacrylate) macroinitiator with additional MMA monomer was set up with [MMA]:[macroinitiator]:[PC] = [1000]:[10]:[1], 1.00 mL of EtOAc, and 1.00 mL MMA. The mass of the macroinitiator synthesized by O-ATRP by each PC was set at 10 eq. and used to determine the concentration of PC and MMA. The PC was dissolved in EtOAc and MMA was added, then this solution was added to the macroinitiator vial and the mixture was stirred in the dark until the macroinitiator dissolved. A separate chain extension polymerization was set up for each PC (**1**, **1b**, **2**, **2b**). O-ATRP was run with a white LED beaker as the light source. The polymerizations were run for 24 hours after which the light beakers were turned off to stop the reaction. The reaction mixtures were precipitated into cold

methanol and vacuum filtration was used to isolate the solid polymer. The isolated polymer was dried under vacuum overnight before GPC analysis, which was performed as described earlier herein.

The resulting chain-extended polymers show increases in $\bar{D}$ and decreases in I^* compared to the macroinitiator, as well as low molecular weight shoulders. These results indicate a slight loss of polymerization control in the chain extensions, which has also been observed in prior work and is likely the result of inefficient initiation by the PC or increased solution viscosity. Overall, the chain extensions from isolated polymers (macroinitiators) support that the polymerizations occur through an O-ATRP mechanism with chain-end retention.

Table A3.3. Results from O-ATRP in EtOAc for chain extension, analysis done after polymer isolation.

Run	PC	$M_{n, \text{theo}}$ (kDa) ^a	$M_{n, \text{GPC}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
S8	1	8.63	19.2	1.30	45
S9	1b	8.26	15.0	1.13	55
S10	2	6.41	23.2	1.35	28
S11	2b	7.08	14.8	1.13	48

^aConversion determined by ^1H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

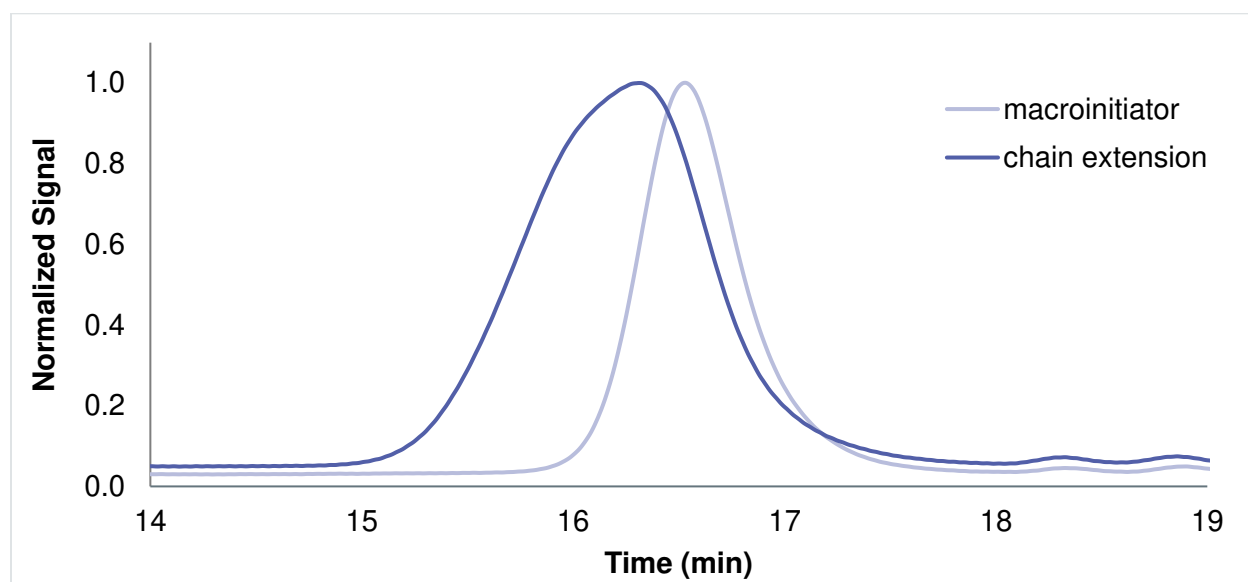


Figure A3.82. Overlaid GPC traces from dRI for isolated PMMA macroinitiator (light purple trace) that was used in O-ATRP mediated by PC 1 to produce chain-extended PMMA (dark purple trace).

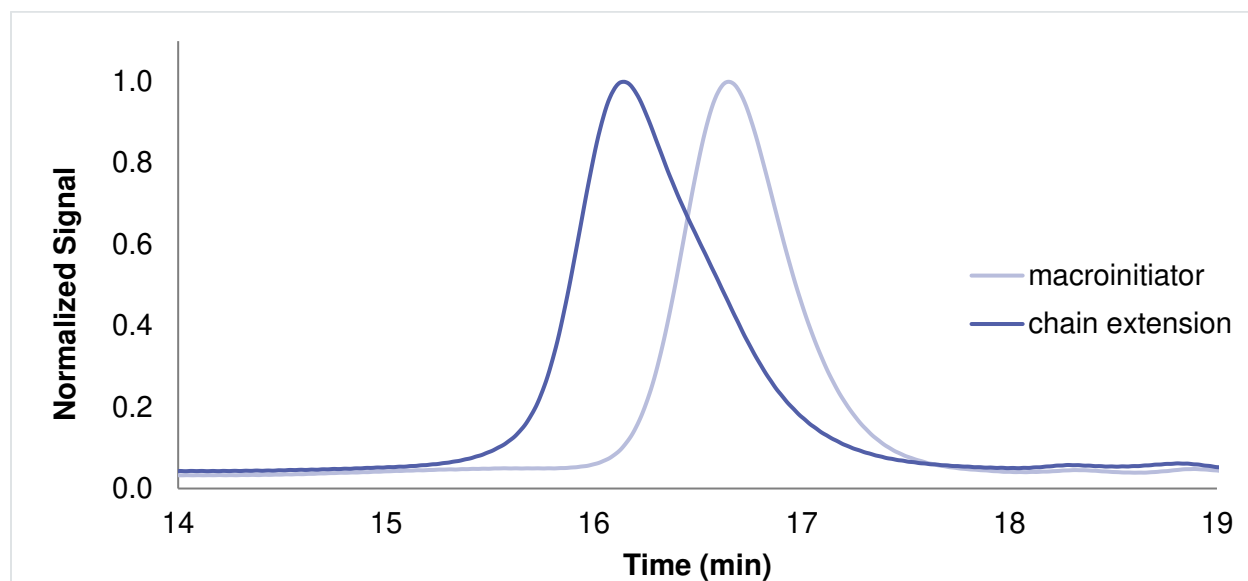


Figure A3.83. Overlaid GPC traces from dRI for isolated PMMA macroinitiator (light purple trace) that was used in O-ATRP mediated by PC **1b** to produce chain-extended PMMA (dark purple trace).

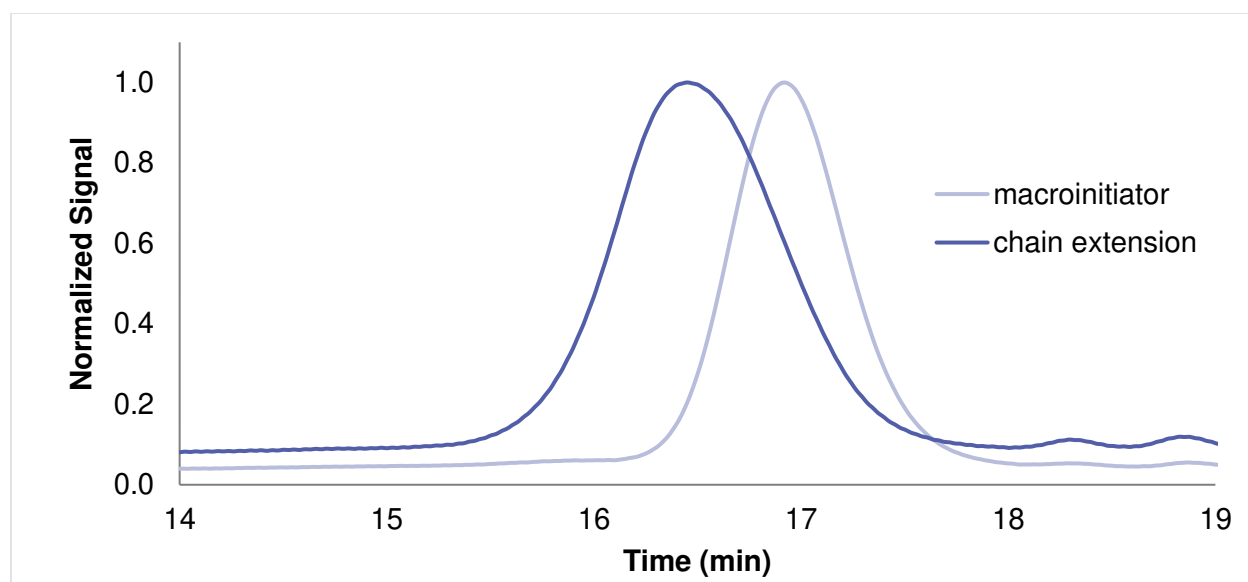


Figure A3.84. Overlaid GPC traces from dRI for isolated PMMA macroinitiator (light purple trace) that was used in O-ATRP mediated by PC **2** to produce chain-extended PMMA (dark purple trace).

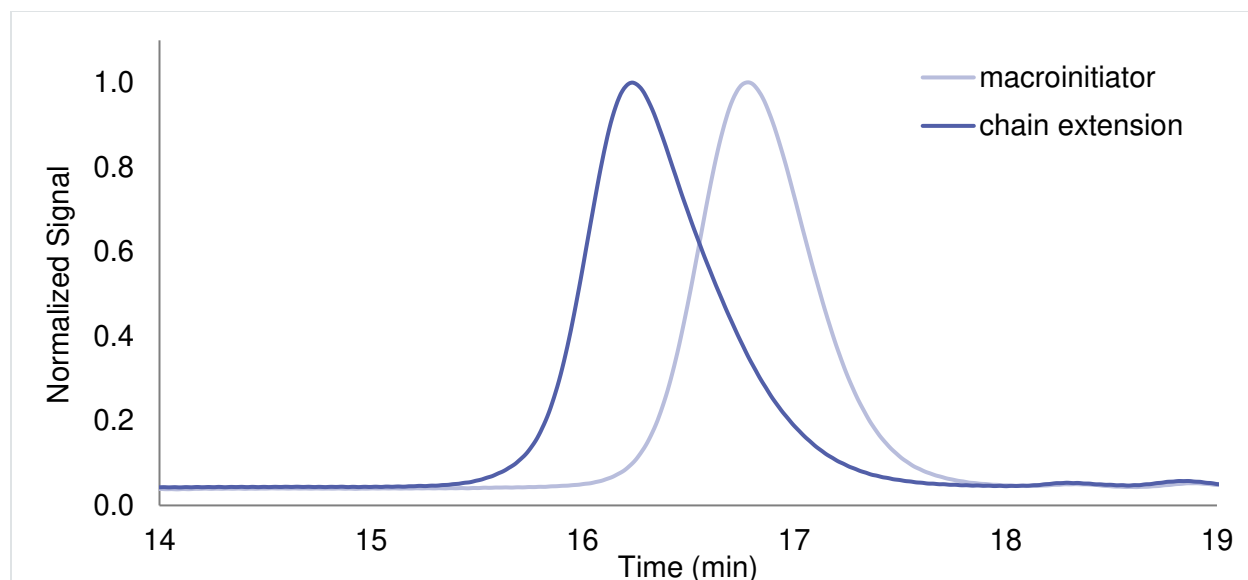


Figure A3.85. Overlaid GPC traces from dRI for isolated PMMA macroinitiator (light purple trace) that was used in O-ATRP mediated by PC **2b** to produce chain-extended PMMA (dark purple trace).

Control Reactions

O-ATRP control reactions were set up as described at the beginning of the Supplemental Polymerization Data section with the differences noted in Table A3.4 below. These control reactions indicate that catalyst **1b** is acting as a photoredox catalyst that mediates O-ATRP and allows for a controlled polymerization.

Table A3.4. O-ATRP controls with PC **1b** in EtOAc.

Run	Control	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa) ^a	$M_{n, \text{GPC}}$ (kDa) ^b	$\bar{D}$ ^b	I^* (%) ^c
S12	No PC	17.4	1.99	198.7	1.55	1.0
S13	No DBMM	48.5	5.10	153.1	1.87	3.3
S14	No PC and DBMM	6.5	0.91	1667	2.17	0.1
S15	No light	0	-	-	-	-
S16	No light, no PC	0	-	-	-	-

^aConversion determined by ^1H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$. S12 = no PC, S13 = no DBMM, S14 = no PC, no DBMM, S15 = no light, S16 = no light, no PC.

REFERENCES

- (1) Corbin, D. A.; Puffer, K. O.; Chism, K. A.; Cole, J. P.; Theriot, J. C.; McCarthy, B. G.; Buss, B. L.; Lim, C. H.; Lincoln, S. R.; Newell, B. S.; Miyake, G. M. Radical addition to *N,N*-diaryl dihydrophenazine photoredox catalysts and implications in photoinduced organocatalyzed atom transfer radical polymerization. *Macromolecules* **2021**, *54*, 4507-4516.
- (2) Price, M. J.; Puffer, K. O.; Kudisch, M.; Knies, D.; Miyake, G. M. Structure-property relationships of core-substituted diaryl dihydrophenazine organic photoredox catalysts and their application in O-ATRP. *Polym.Chem.* **2021**, *12*, 6110-6122.

APPENDIX D – SUPPLEMENTARY INFORMATION FOR CHAPTER 4

MATERIALS AND METHODS

Unless otherwise stated, all chemicals were used as received without additional purification and stored per manufacturer specifications. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc.

Materials for Photocatalyst Synthesis

Phenazine reduction and Buchwald coupling. Phenazine and sodium dithionite were purchased from Alfa Aesar and Sigma Aldrich. Reagent grade alcohol was purchased from Fisher Scientific. Sodium *tert*-butoxide, toluene, bis(dibenzylideneacetone) palladium(0), and tri-*tert*-butylphosphine were purchased from Sigma Aldrich. 4-bromobenzotrifluoride was purchased from Acros Organics. Toluene was purified using an mBraun MB-SPS-800 solvent purification system and stored under nitrogen atmosphere. Dichloromethane and methanol were purchased from Fisher Scientific.

Bromination and reduction. Molecular bromine, benzene, methanol, and TEA were purchased from Sigma Aldrich.

Alkyl core substitution. Ethyl α -bromophenylacetate (EBP), triethylamine (TEA), *N,N*-dimethylacetamide (DMAc) and tetrahydrofuran (THF) were purchased from Sigma Aldrich. Dichloromethane and methanol were purchased from Fisher Scientific.

Suzuki coupling. Tetrakis(triphenyl phosphine) palladium (0) and tetrahydrofuran were purchased from Sigma Aldrich. Potassium carbonate was purchased from VWR. 4-(methylthio)phenylboronic acid, and phenylboronic acid were purchased from Sigma Aldrich.

C-S coupling. Tris(dibenzylideneacetone)dipalladium(0), Xantphos, thiophenol, and DIPEA were purchased from Sigma Aldrich. Cesium carbonate was purchased from Fisher Scientific.

Materials for PC Characterization

DMAc (99.8% anhydrous) was purchased from Sigma Aldrich in SureSeal bottles and HPLC grade acetonitrile (MeCN) for cyclic voltammetry was purchased from Fischer Scientific and used without further purification. 1-hexene, benzene, 1,4-dioxane, THF, pyridine, and DMF were purchased from Sigma Aldrich, Fisher Scientific, Alfa Aesar, or Oakwood Chemicals.

Materials for Polymerizations

DBMM, methyl methacrylate (MMA), and *n*-butyl acrylate (*n*-BA) were purchased from Sigma Aldrich and dried over calcium hydride, distilled under reduced pressure, degassed by freeze-pump-thaw, and stored in a nitrogen-filled glovebox freezer at -34 °C prior to use. *N,N*-dimethyl acetamide (DMAc), and ethyl acetate (EtOAc) were purchased from Sigma Aldrich or Fisher Scientific (anhydrous, SureSeal bottles).

Experimental Equipment

Light reactors. Light beakers were composed of double-density white LED strips purchased from Creative Lighting Solutions (CL-FRS1210-5M-12V-WH). The reactors were made by wrapping a 400 mL beaker (height = 10.0 cm, diameter = 8.5 cm) with aluminum foil and wrapping the white LED strips (51 LED segments) around the inside of the beaker.

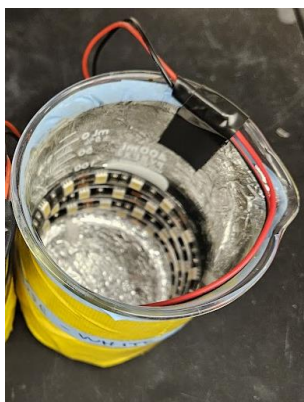


Figure A4.1. Photographs of 400 mL white LED light beakers used for polymerizations.

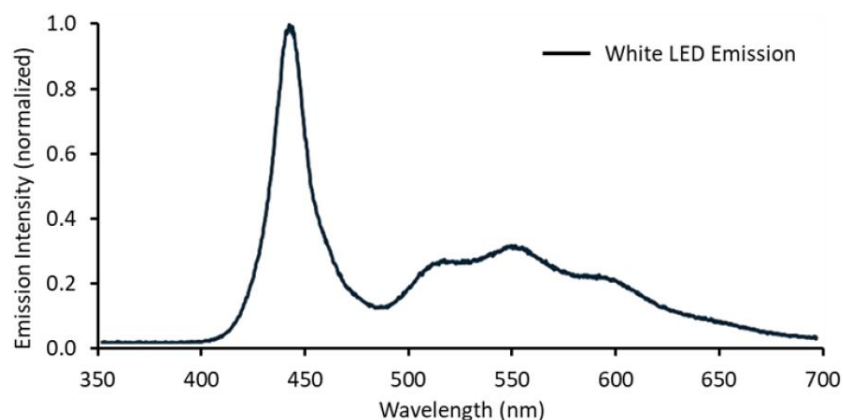


Figure A4.2. Normalized emission spectrum for the white LED lights used in polymerizations.

Instrumentation for Characterization

Nuclear magnetic resonance (NMR) spectroscopy. NMR was performed using either a Bruker US 400 MHz spectrometer or a Bruker Ascend 400 MHz spectrometer. All the ^1H NMR spectra are reported in δ units, parts per million (ppm), and are referenced to benzene (7.15 ppm) or chloroform (7.26 ppm) signals. All ^{13}C NMR spectra are reported in ppm relative to CDCl_3 (77.23 ppm) or C_6D_6 (128.62 ppm).

Matrix-assisted laser desorption/ionization (MALDI) Mass Spectrometry. High resolution mass spectrometry was performed using a Bruker ultrafleXtreme MALDI-TOF/TOF.

UV-Visible spectroscopy. UV-Visible spectroscopy was performed using an Agilent Cary 5000 UV-Vis-NIR spectrometer.

Fluorescence spectroscopy. Steady state fluorescence spectroscopy was performed using a FS5 Spectrofluorometer from Edinburgh Instruments.

Time correlated single photon counting (TCSPC). TCSPC was performed using an FS5 Spectrofluorometer from Edinburgh Instruments with a TCSPC upgrade and a 365 nm EPLED from Edinburgh Instruments.

Cyclic voltammetry. Cyclic Voltammetry was conducted using a Gamry Interface 1010B potentiostat. A 5-port electrochemical cell (Gamry) was equipped with a glassy carbon working electrode (Gamry), a Pt counter electrode, and an Ag/AgNO₃ reference electrode separated from the main compartment by a frit. The reference electrode was constructed by putting a silver wire into a fritted glass compartment containing a solution of 0.10 M NBu₄PF₆ and 0.01 M AgNO₃ in MeCN.

Gel permeation chromatography (GPC). Analysis of polymer molecular weights were performed via GPC coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μ m MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. A dn/dc value of 0.084 was used for PMMA molecular weight analysis and 0.065 was used for P(*n*-BA).

Single crystal X-ray diffraction (SCXRD). Data were acquired at Colorado State University's Analytical Resources Core (ARC) by Dr. Ethan Crace. See "Single Crystal X-ray Diffraction" for more details.

SYNTHETIC PROCEDURES

Synthesis of Photocatalysts

5,10-dihydrophenazine synthesis. This synthesis was performed according to a literature procedure.¹ ^1H NMR (400 MHz, C_6D_6) δ (ppm): 3.93 (s, 2H), 5.62-5.77 (m, 4H), 6.35-6.54 (m, 4H).

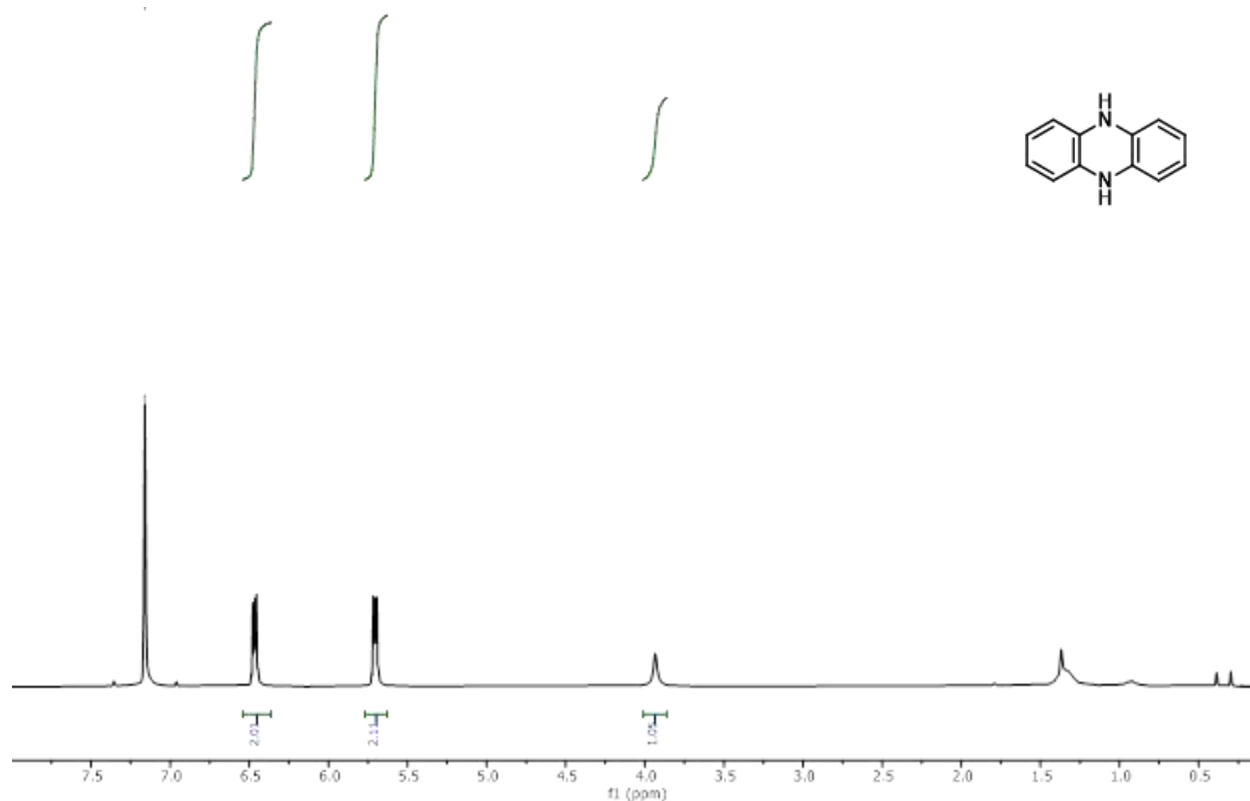


Figure A4.3. ^1H NMR spectrum of dihydrophenazine in C_6D_6 .

PC 1 synthesis. This synthesis was performed according to a literature procedure.² ¹H NMR (400 MHz, C₆D₆) δ (ppm): 5.60-5.71 (m, 4H), 6.28-6.36 (m, 4H), 6.93-6.99 (m, 4H), 7.29-7.34 (m, 4H).

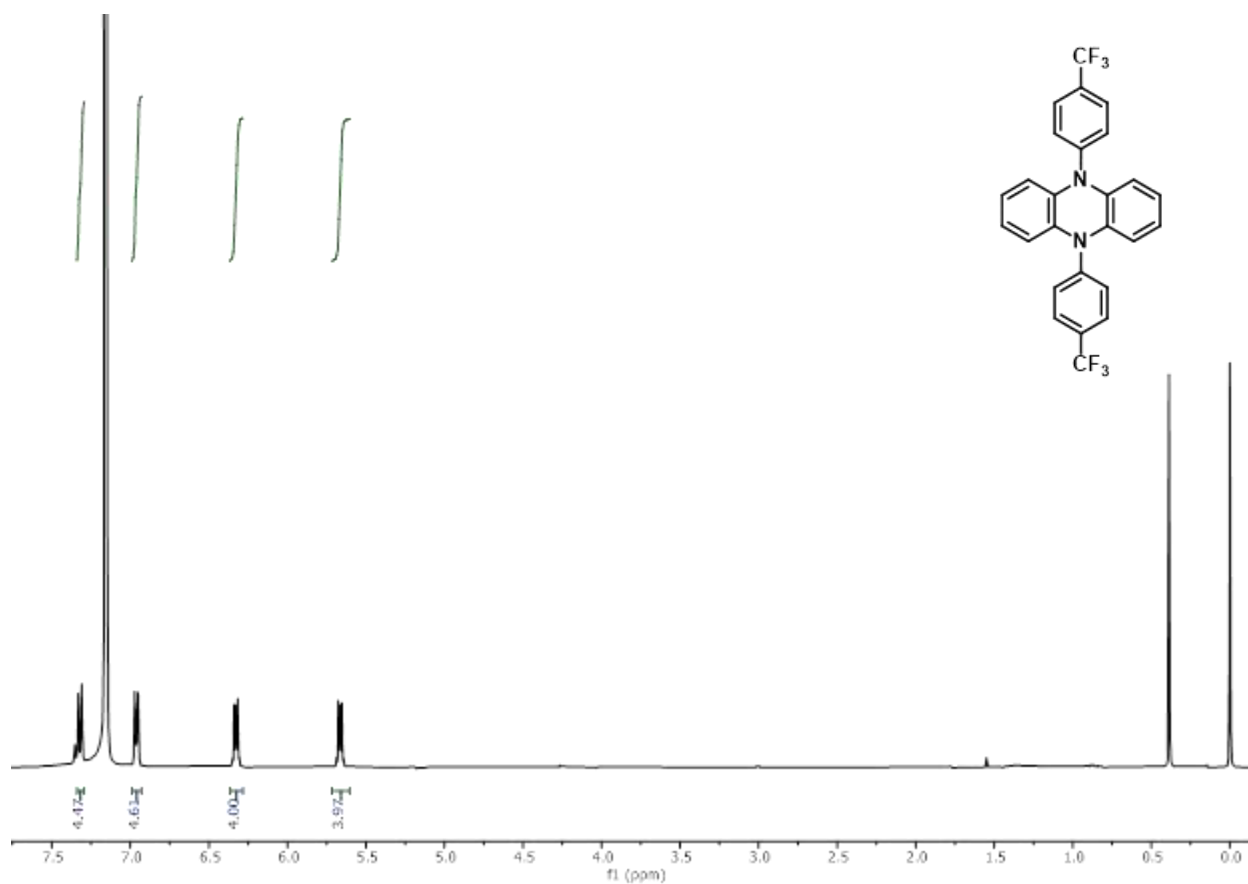


Figure A4.4. ¹H NMR spectrum of PC 1 in C₆D₆.

Bromination of PC 1. This synthesis was performed according to a modified literature procedure.² PC 1 (317 mg, 0.674 mmol, 1 eq.) was dissolved in 500 mL of benzene in a round bottom flask. Using a syringe, Br₂ was added (691 μ L, 13.5 mmol, 20 eq.). The reaction was refluxed at 80°C for 24 hours and then cooled to room temperature. The resulting purple solids were collected via vacuum filtration and dissolved in methanol (500 mL). 10 mL of TEA (53.4

mmol, 60 eq.) was added (a quick formation of yellow precipitate is observed) and the reaction mixture was stirred at room temperature for 18 hours. The yellow precipitate was collected via vacuum filtration and dried under vacuum. The precipitate was recrystallized in 1:3 DCM: MeOH for a 73% yield (0.610 mg). ^1H NMR (400 MHz, C_6D_6) δ (ppm): 5.80 (s, 4H), 6.66 (d, 4H, $J = 8.0$), 7.13 (d, 4H, unresolvable from solvent). ^{19}F NMR (376 MHz, C_6D_6) δ (ppm): -62.40 (s, 6F), -62.35, -62.37 (d, 6H, corresponding to tribrominated PC).

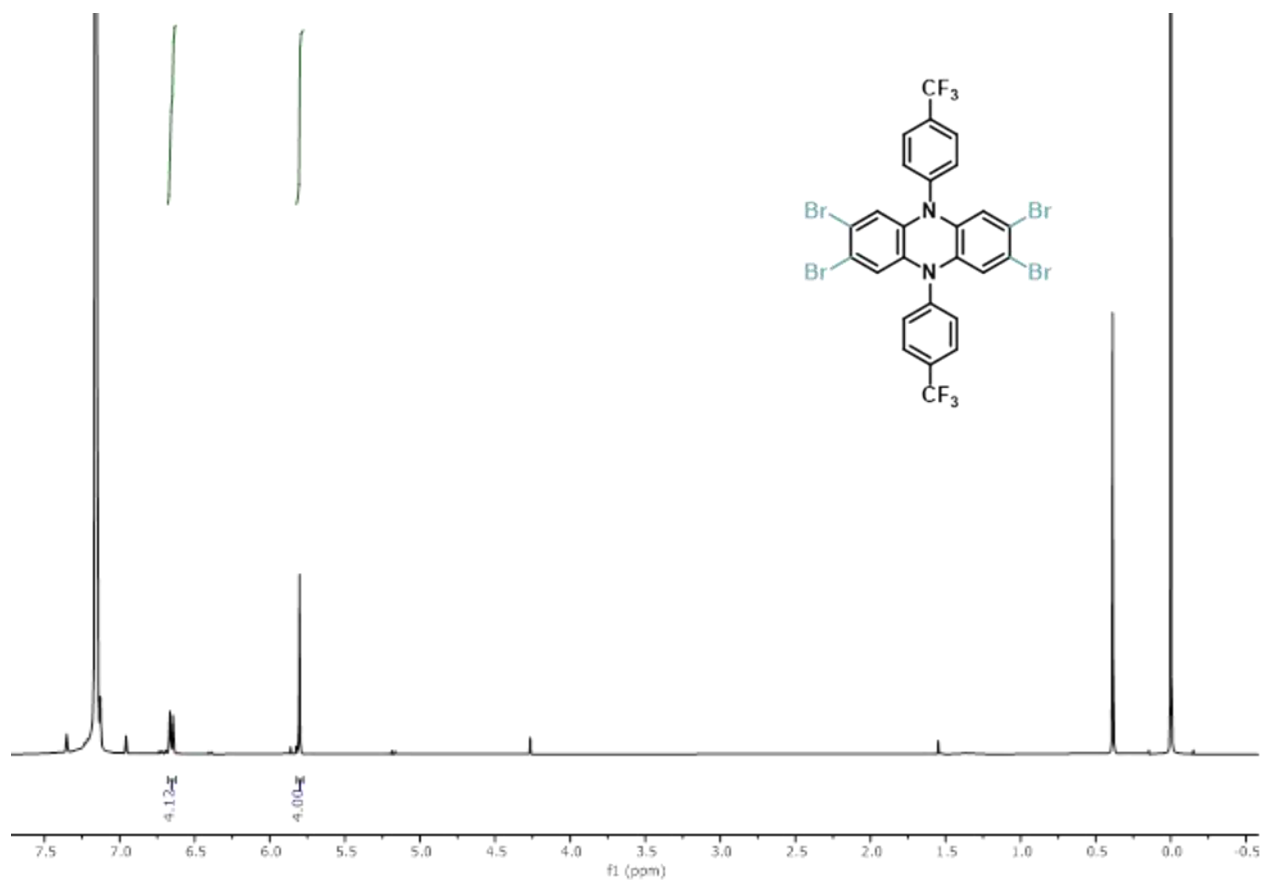


Figure A4.5. ^1H NMR spectrum of brominated PC 1 in C_6D_6 .

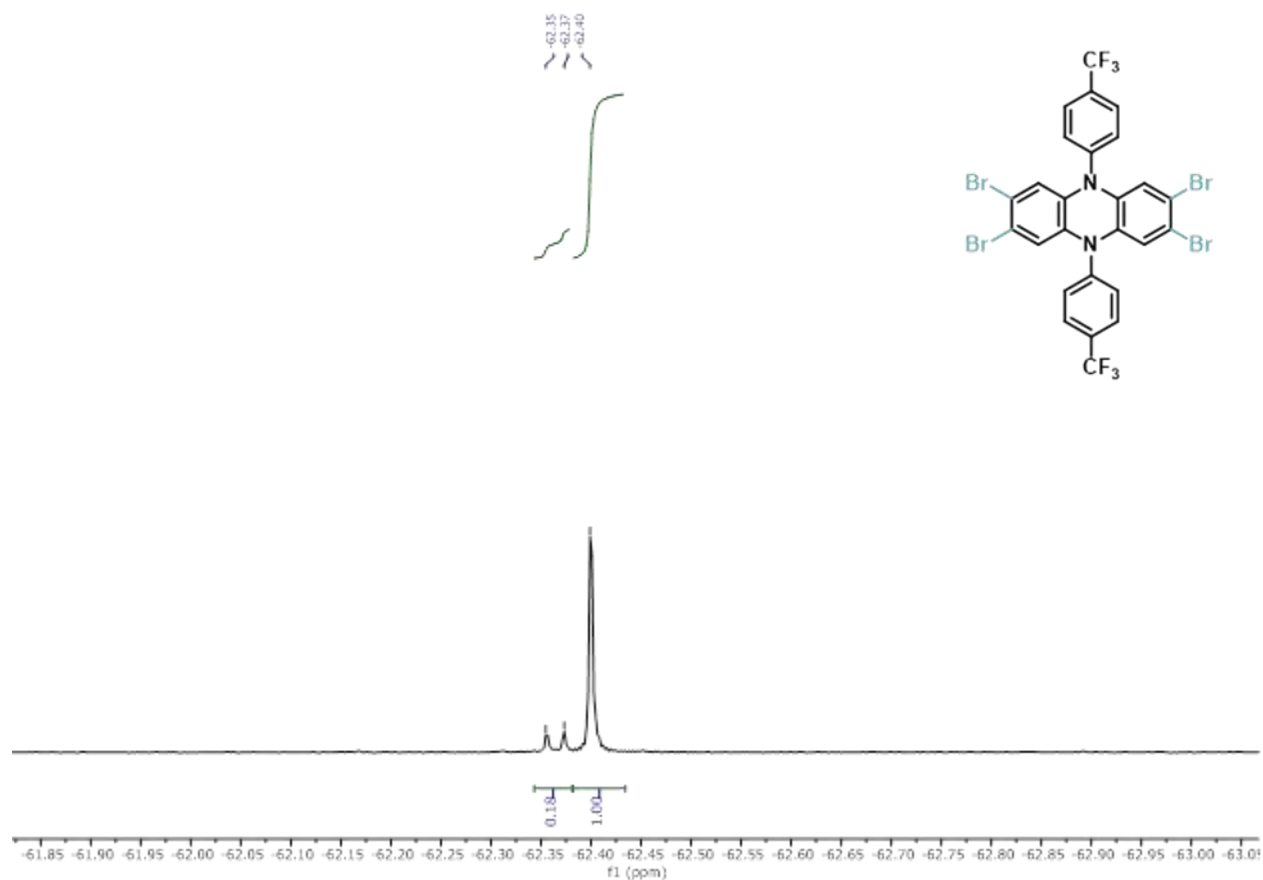


Figure A4.6. ^{19}F NMR spectrum of brominated PC 1 in C_6D_6 .

PC 2 synthesis. This synthesis was performed according to a literature procedure.¹ ^1H NMR (400 MHz, C_6D_6): δ 7.17-7.28 (m, 8H, indistinguishable from solvent), 6.81-7.10 (m, 20H), 5.78-5.96 (m, 4H), 5.24 (d, 4H, $J = 12.0$), 3.60-3.94 (m, 8H), 0.65-0.86 (m, 12H).

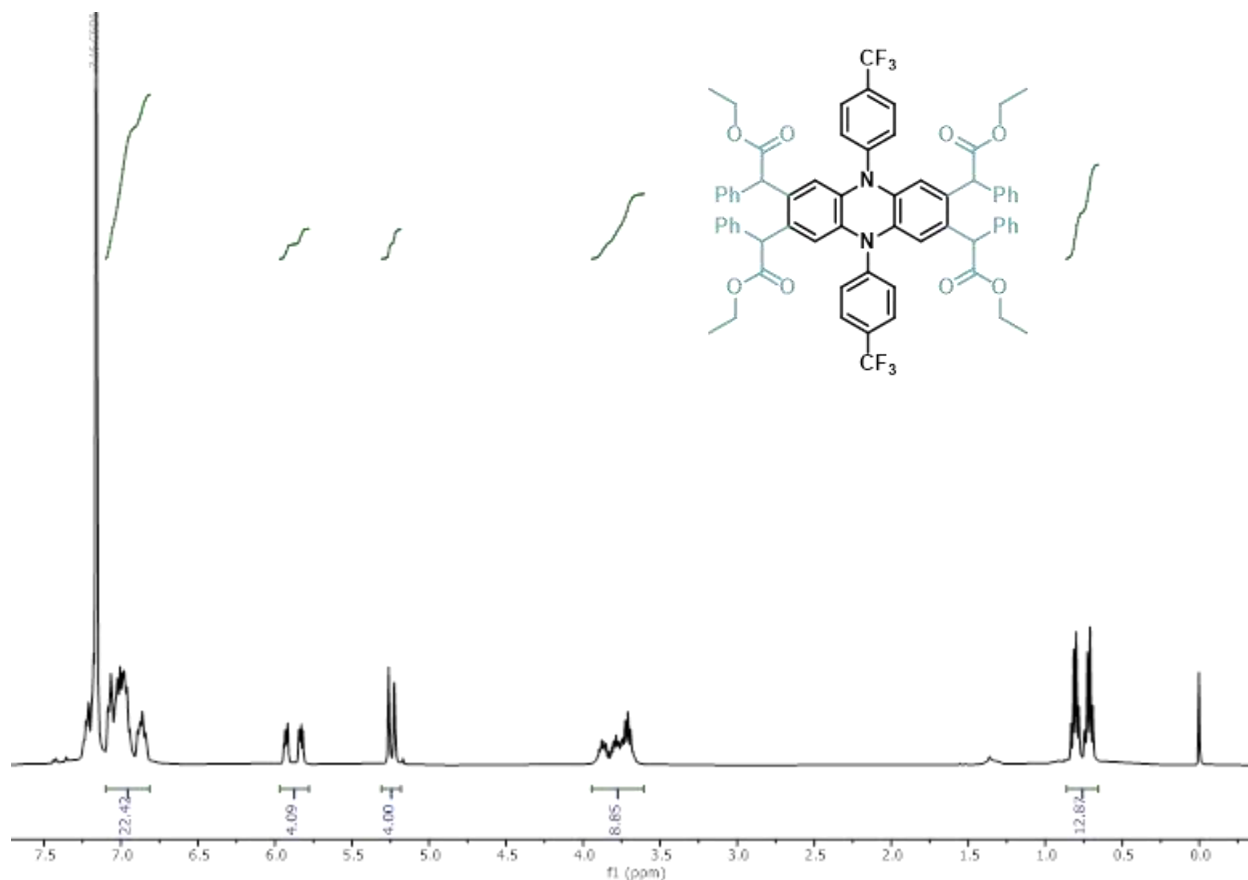


Figure A4.7. ^1H NMR spectrum of PC 2 in C_6D_6 .

PC 3 synthesis. To a storage tube, 205 mg of PC 1 (0.261 mmol, 1 eq.) and cesium carbonate 681 mg (2.09 mmol, 8 eq.) was added and brought into an N_2 filled glovebox. In the glovebox, 213 μL thiophenol (2.09 mmol, 8 eq.), 59.8 mg tris(dibenzylideneacetone)dipalladium(0) (0.065 mmol, 0.25 eq.), 75.6 mg of Xantphos (0.131 mmol, 0.5 eq) and 40 mL of 1,4-dioxane was added. The reaction was refluxed at 101°C for 48 hours and then cooled to room temperature. The reaction mixture was diluted with EtOAc and washed 1x with DI H_2O , 1x with saturated NaHCO_3 , and 1x with brine. Solvent was removed by rotary evaporation and the product was dry loaded onto silica. A gradient column from 20% EtOAc, 80% (3% TEA) in hexanes to 100% EtOAc was run. Fractions with $>15\%$ product were combined and dried down by rotary evaporation. An evaporative recrystallization in 1:4 EtOAc:hexanes resulted in yellow crystals, which were collected by vacuum filtration for a 43.9%

yield. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 5.58 (s, 4H), 6.62(d, 4H, $J = 8.0$), 6.82-6.89 (m, 12H, multiple peaks overlapping), 7.00 (d, 4H, $J = 8.0$), 7.14, (m, 8H, unresolvable from solvent peak). ^{13}C NMR (101 MHz, C_6D_6) δ (ppm): 115.68, 127.09, 128.96, 130.35, 131.46, 134.86, 134.97 ^{19}F NMR (376 MHz, C_6D_6) δ (ppm): -62.35 (s, 6H)

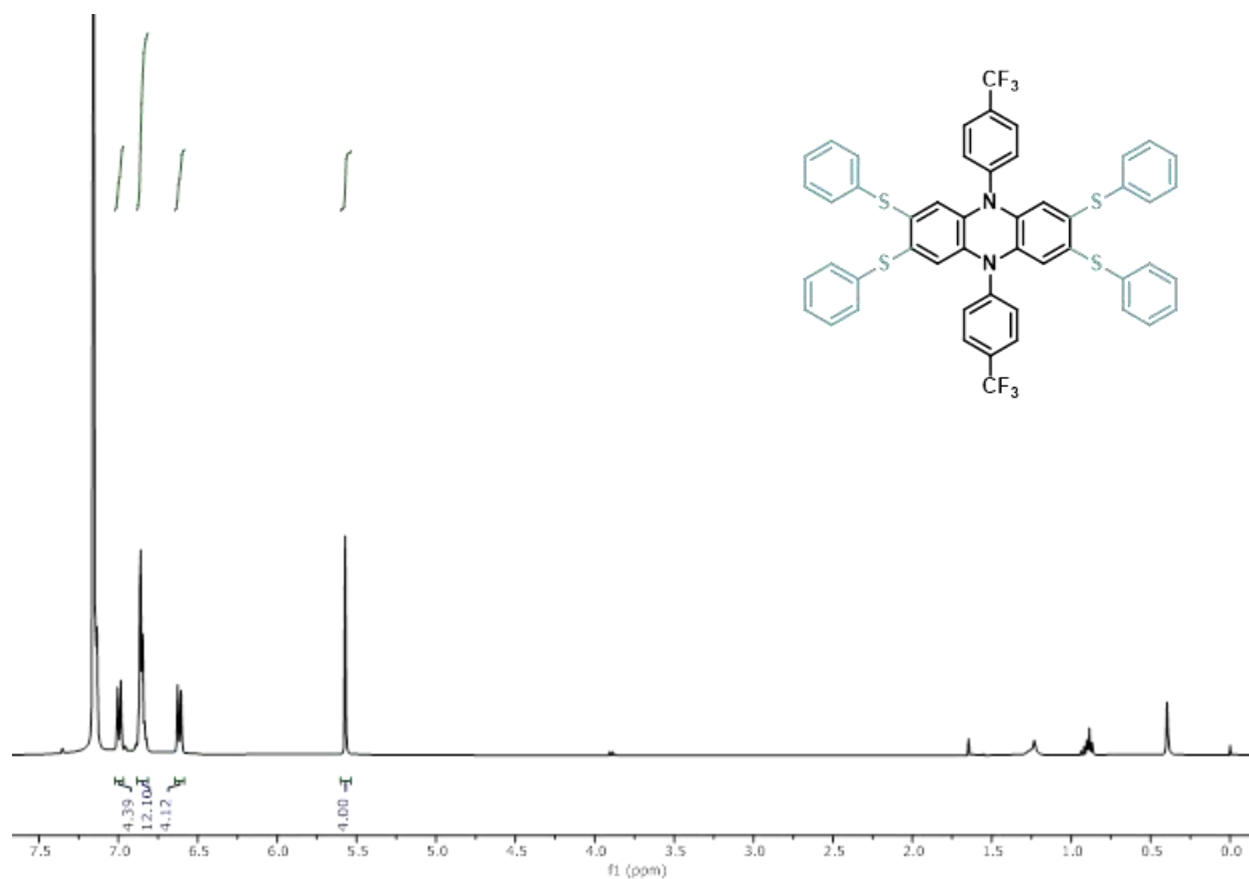


Figure A4.8. ^1H NMR spectrum PC 3 in C_6D_6 .

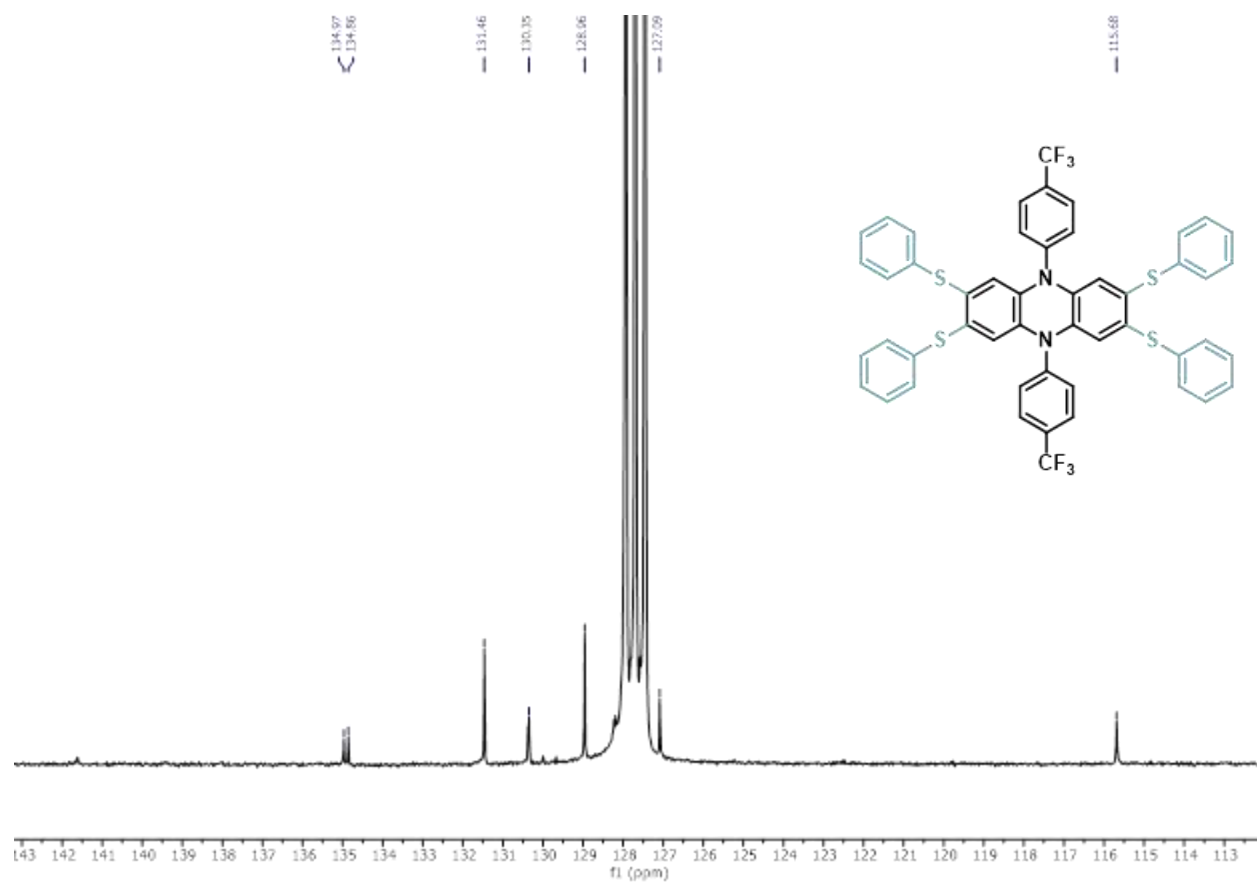


Figure A4.9. ^{13}C NMR spectrum PC 3 in C_6D_6 .

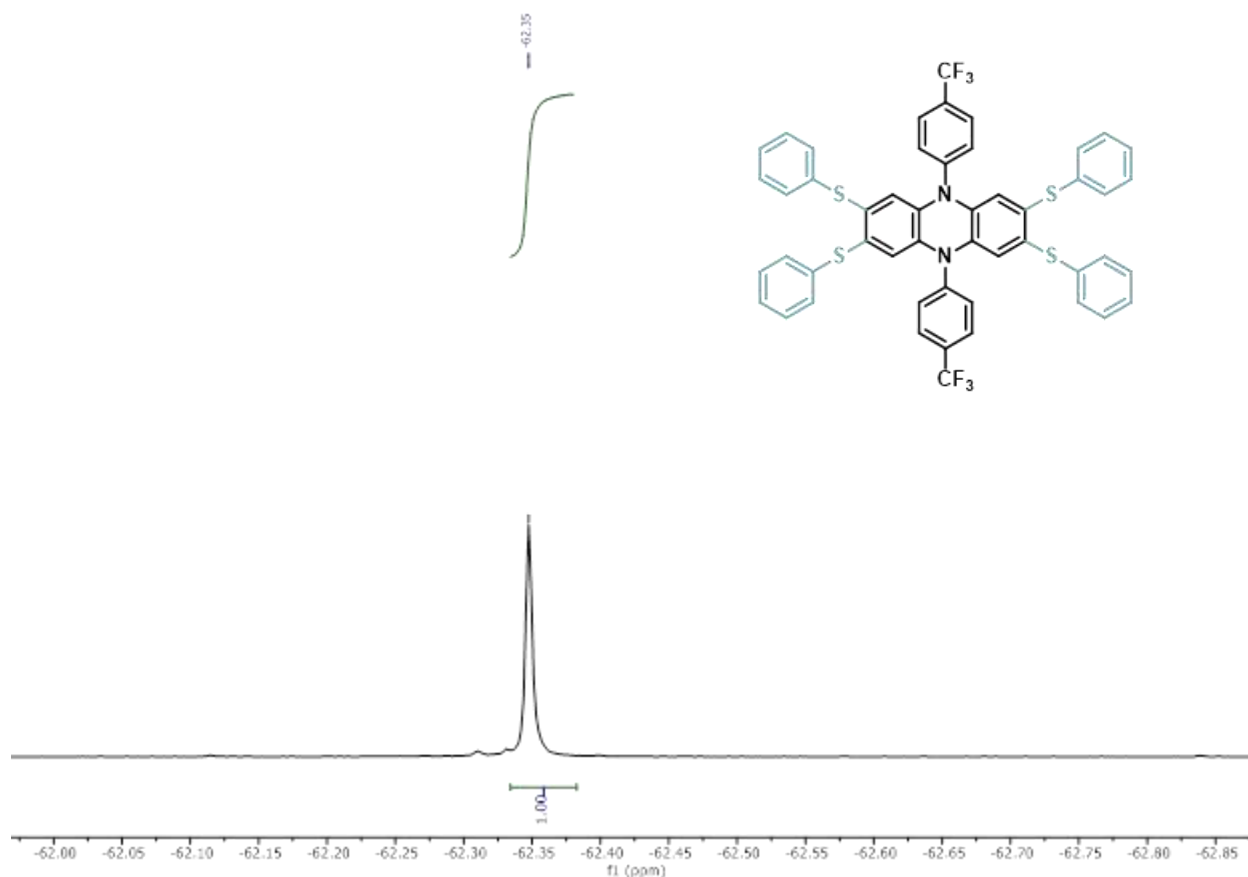


Figure A4.10. ^{19}F NMR spectrum PC 3 in C_6D_6 .

PC 4 synthesis. To a storage tube, 136 mg (0.173 mmol, 1 eq) of brominated PC 1 and 169 mg (1.38 mmol, 8 eq.) of phenylboronic acid was added. The storage tube was transferred into a N_2 filled glove box. In the glovebox, 30.0 mg (0.026 mmol, 0.15 eq) of $\text{Pd}(\text{PPh}_3)_4$ and 15 mL of THF were added to the storage tube. The storage tube was taken out of the glove box and 6 mL of 2M aqueous K_2CO_3 sparged with N_2 for ~30 min was added to the solution via syringe. The mixture was heated to 101 $^\circ\text{C}$ overnight, then cooled to room temperature. The reaction mixture was diluted with DCM then washed with water 2x and brine 1x. The solution was then dried with sodium sulfate. A solid crashed out of the solution and was collected by vacuum filtration and recrystallized in 1:4 DCM:MeOH for a yellow powder (46.2% yield). The liquid from the step before recrystallization was concentrated by rotary evaporation. The resulting solid was dry loaded onto silica and purified by a gradient column from 20% EtOAc, 80% (3% TEA) in hexanes to

100% EtOAc. Fractions were collected and dried down via rotary evaporation, then recrystallized in 1:4 DCM:MeOH for a yellow powder which was isolated by vacuum filtration (4.55% yield). The combined yield was 50.8%. ^1H NMR (400 MHz, C_6D_6): δ (ppm): 6.12 (s, 4H), 6.78-6.89 (m, 12H), 7.04-7.09(m, 8H, unresolvable from solvent), 7.22-7.27 (m, 8H, unresolvable from solvent). Due to the poor solubility of this catalyst in C_6D_6 and poor signal/noise, ^{13}C NMR spectrum was not obtained. ^{19}F NMR (376 MHz): δ (ppm): -62.23 (s, 6F).

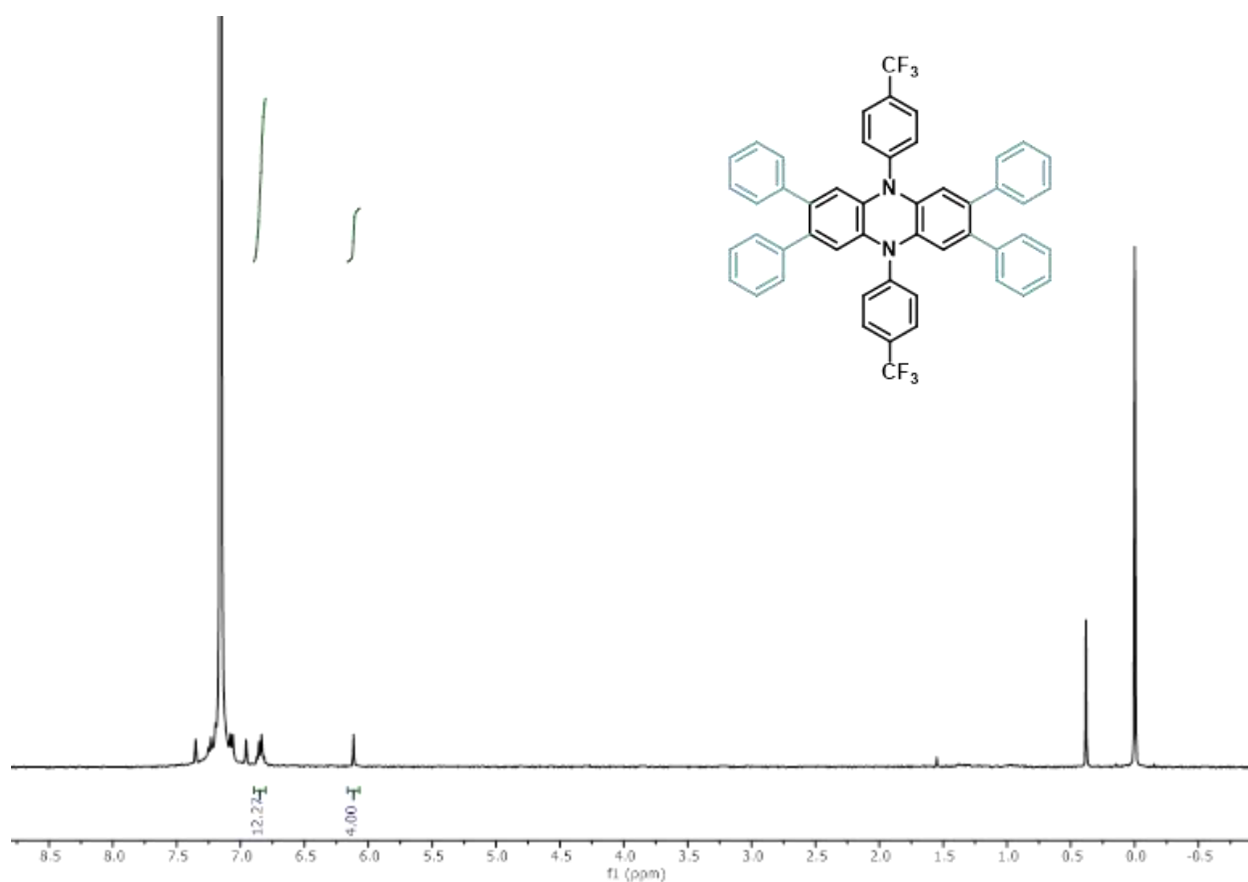


Figure A4.11. ^1H NMR spectrum PC 4 in C_6D_6 .

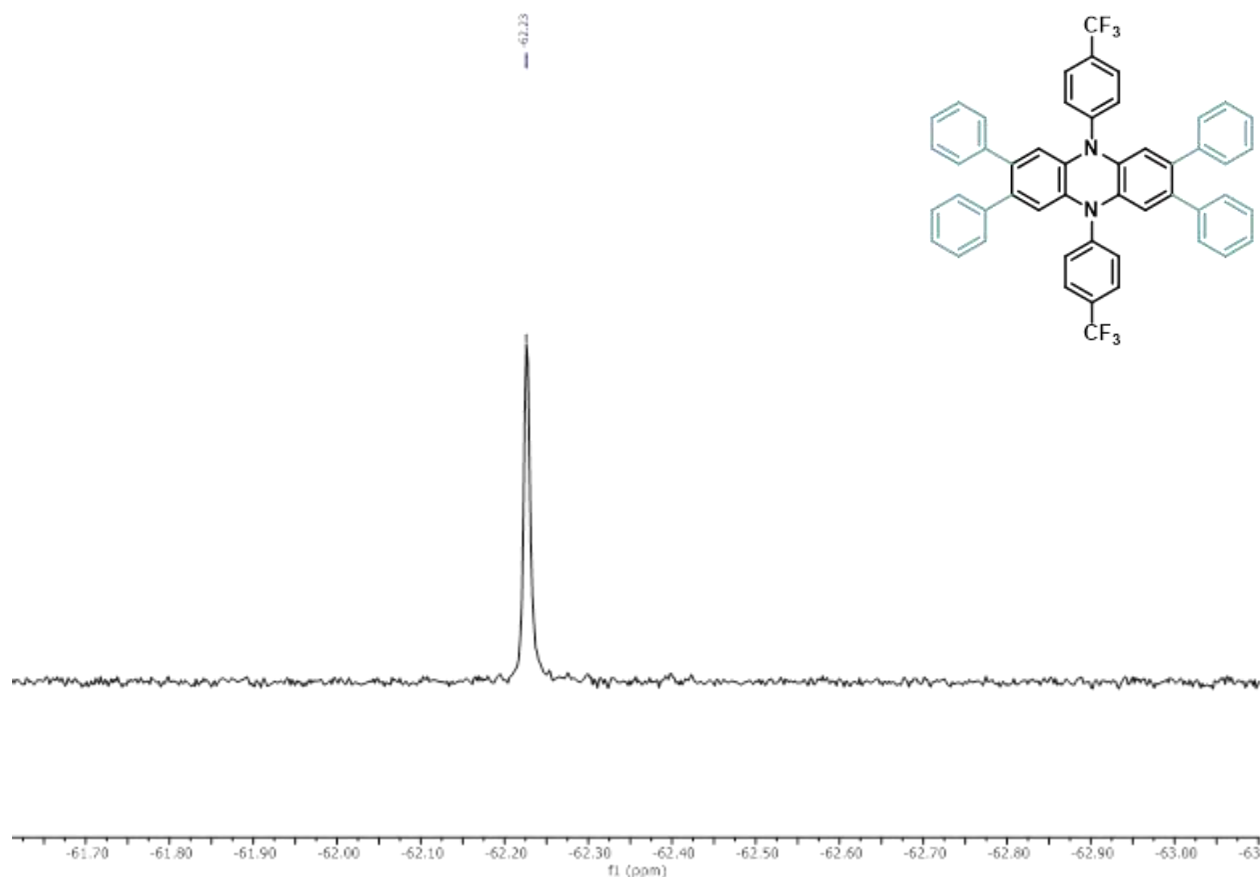


Figure A4.12. ^{19}F NMR spectrum PC 4 in C_6D_6 .

PC 5 synthesis. To a storage tube, 200 mg (0.254 mmol, 1 eq.) of brominated PC 1 and 342 mg (2.04 mmol, 8 eq.) of phenylboronic acid was added. The storage tube was transferred into a N_2 filled glove box. In the glovebox, 44.1 mg (0.038 mmol, 0.15 eq.) of $\text{Pd}(\text{PPh}_3)_4$ and 20 mL of THF were added to the storage tube. The storage tube was taken out of the glove box and 6 mL of 2M aqueous K_2CO_3 sparged with N_2 for ~30 min was added to the solution via syringe. The mixture was heated to 101 °C overnight, then cooled to room temperature. The reaction mixture was diluted with DCM then washed with water 2x and brine 1x. The solution was then dried with sodium sulfate and concentrated by rotary evaporation. The solid was dry loaded onto silica and purified by a gradient column from 20% EtOAc, 80% (3% TEA) in hexanes to 100% EtOAc. Fractions were collected and dried down via rotary evaporation, then recrystallized in 1:4 DCM:MeOH for a yellow powder which was isolated by vacuum filtration. The recrystallization was repeated for a

61.1% yield. ^1H NMR (400 MHz, C_6D_6): δ (ppm): 1.77 (s, 12H), 6.10 (s, 4H), 6.77 (d, 8H, $J = 8.0$), 6.96, (d, 8H, $J = 8.0$), 7.26 (d, 4H, $J = 12.0$), 7.35 (d, 4H, $J = 12.0$). ^{13}C NMR (101 MHz, C_6D_6): δ (ppm): 14.60, 115.74, 126.04, 129.69, 131.24, 133.73, 135.32, 137.44, 143.19. ^{19}F NMR (376 MHz): δ (ppm): -62.20 (s, 6F).

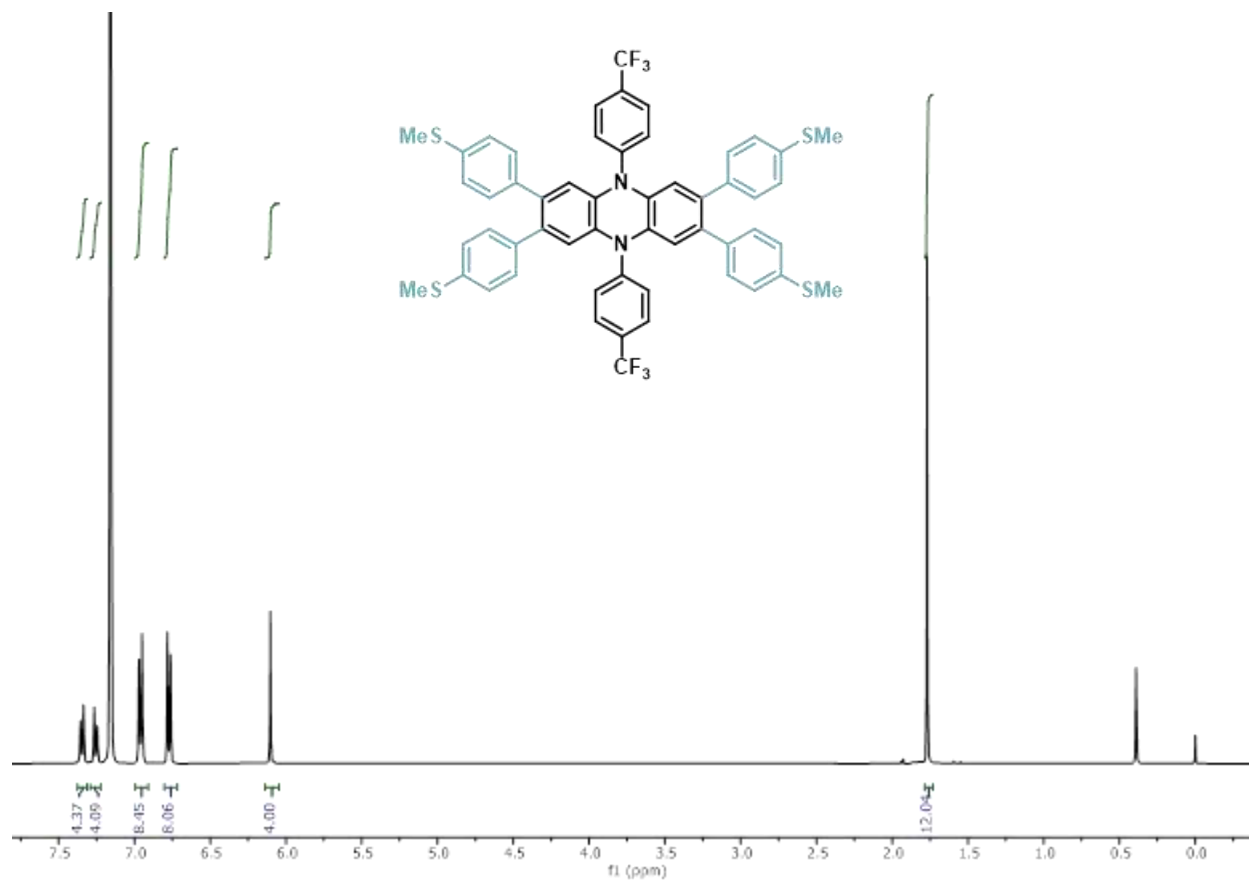


Figure A4.13. ^1H NMR spectrum PC 5 in C_6D_6 .

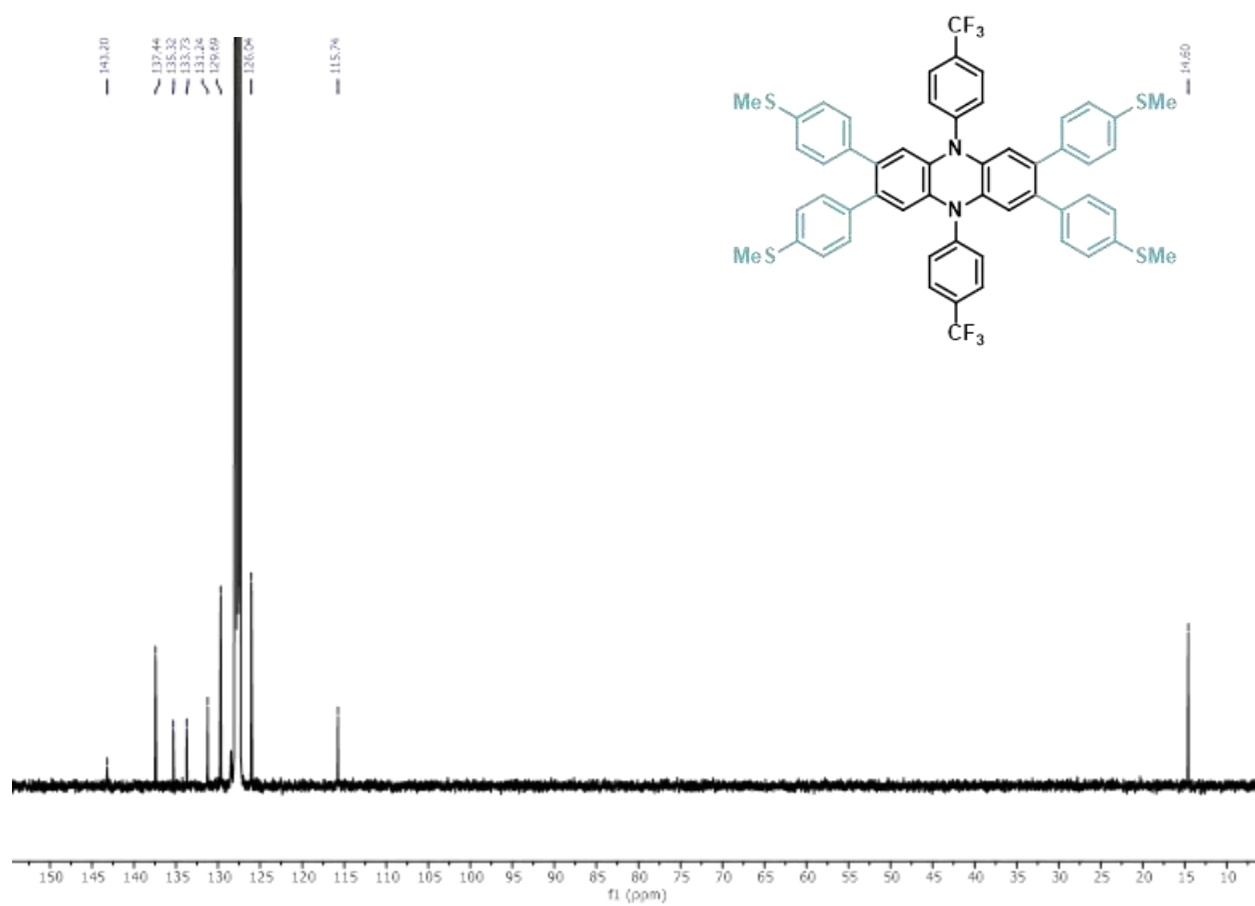


Figure A4.14. ¹³C NMR spectrum PC 5 in C₆D₆.

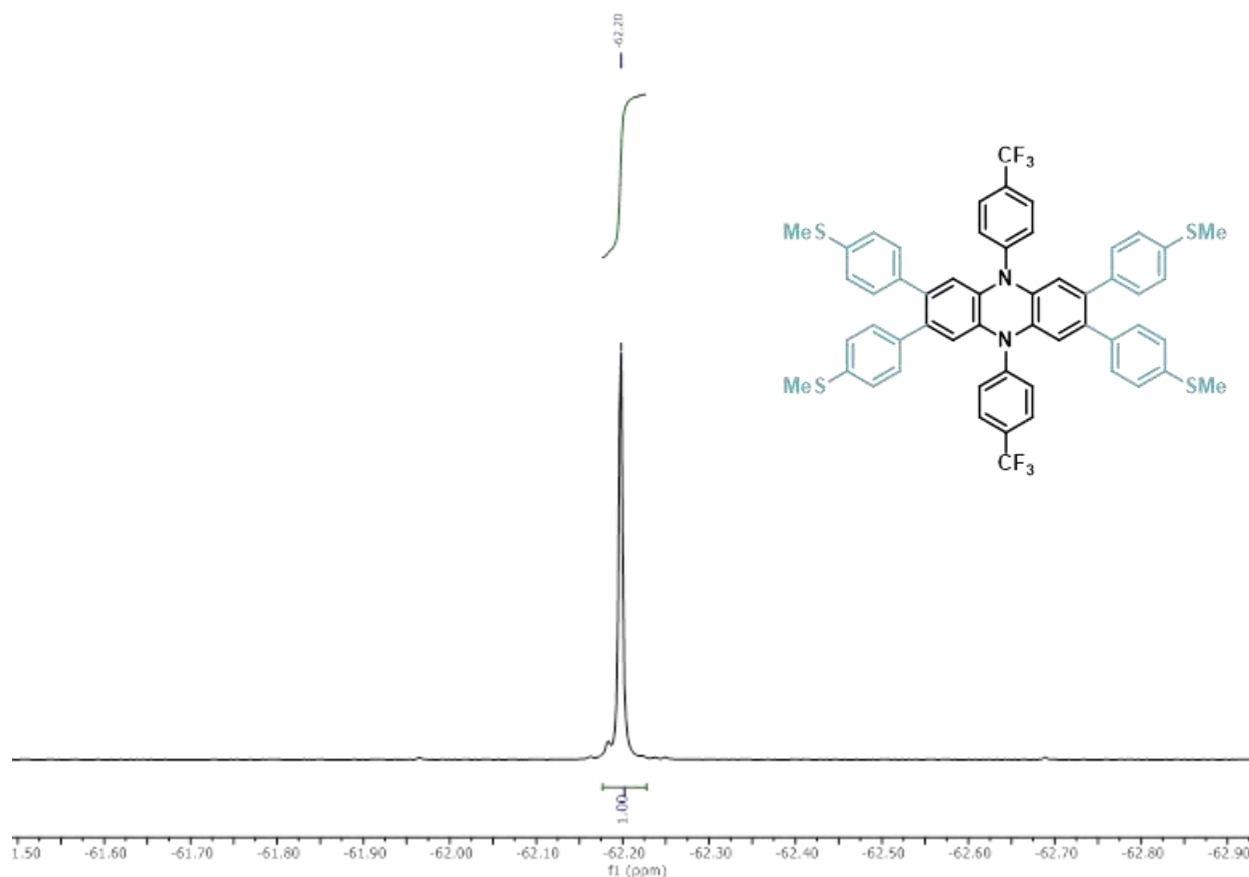


Figure A4.15. ^{19}F NMR spectrum PC 5 in C_6D_6 .

MALDI-TOF Mass Spectrometry of PCs

MALDI-TOF mass spectrometry analysis was performed in positive ion reflector mode. PC stock solutions were prepared at 5.0 mg/mL in THF. The solution prepared for spotting on the MALDI target plate contained 3 μL of 5.0 mg/mL PC stock solution and 20 μL THF (0.65 mg/mL). No calibrant or matrix was used.

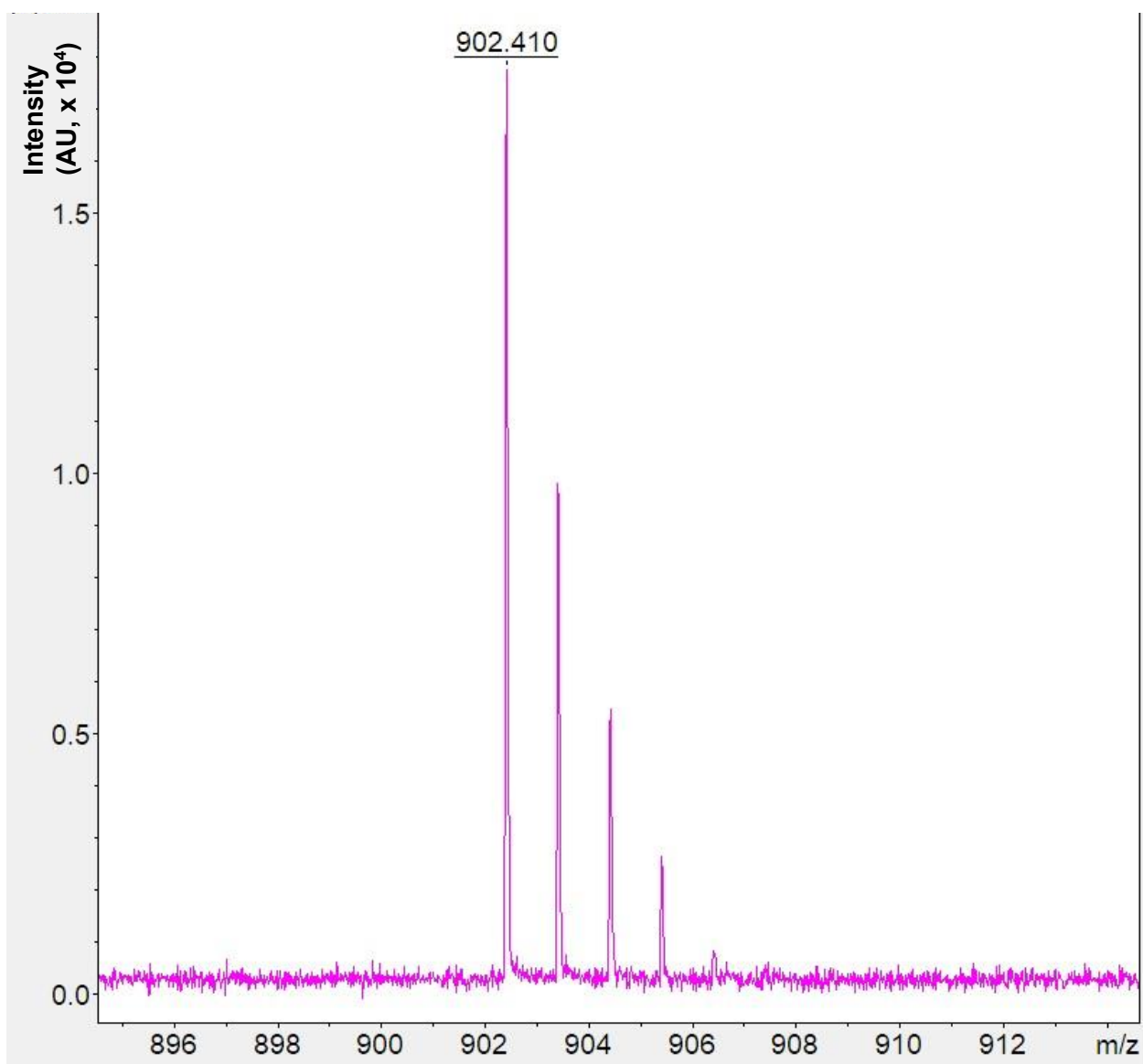


Figure A4.16. MALDI-TOF mass spectrum of PC 3.

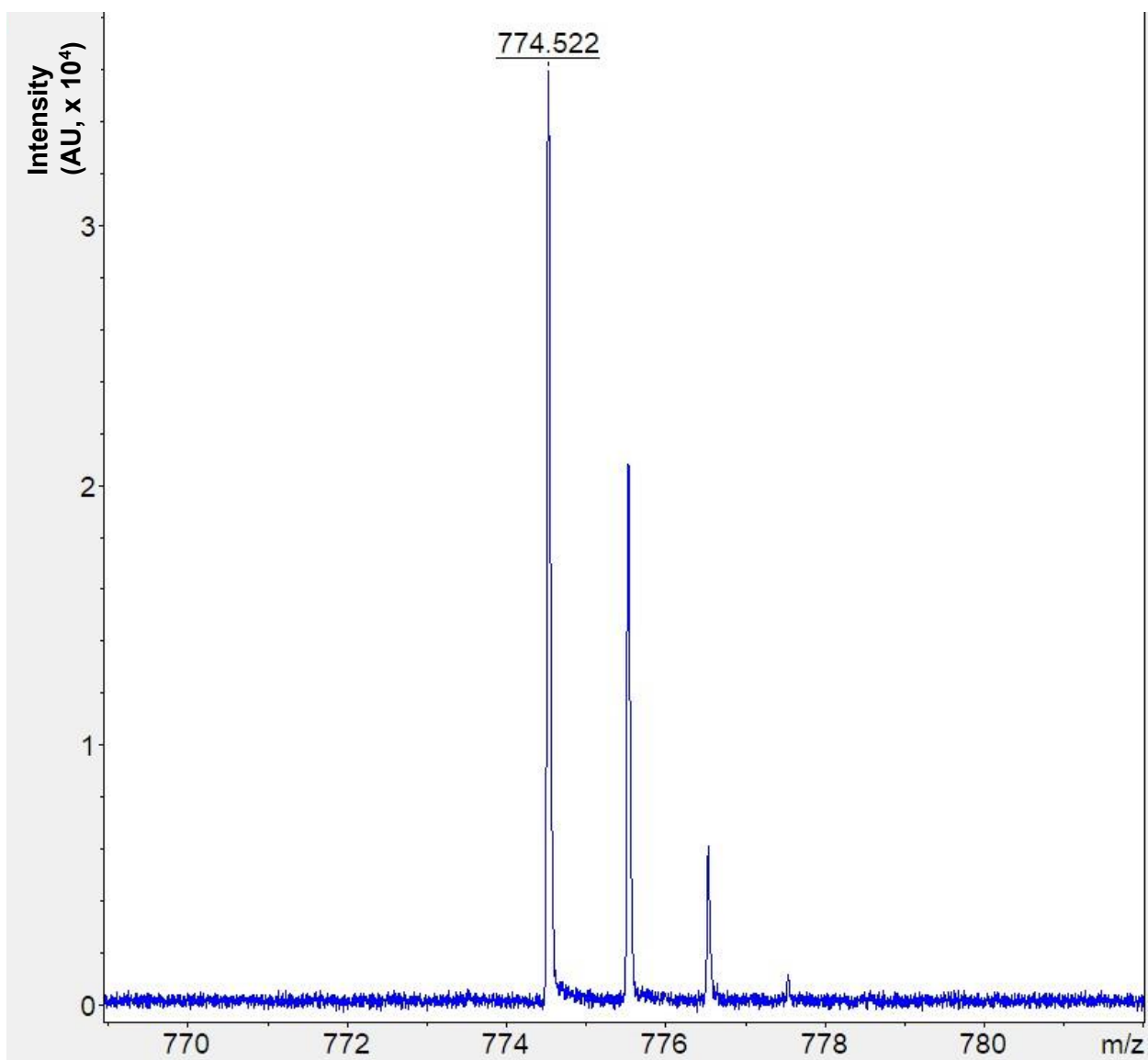


Figure A4.17. MALDI-TOF mass spectrum of PC 4.

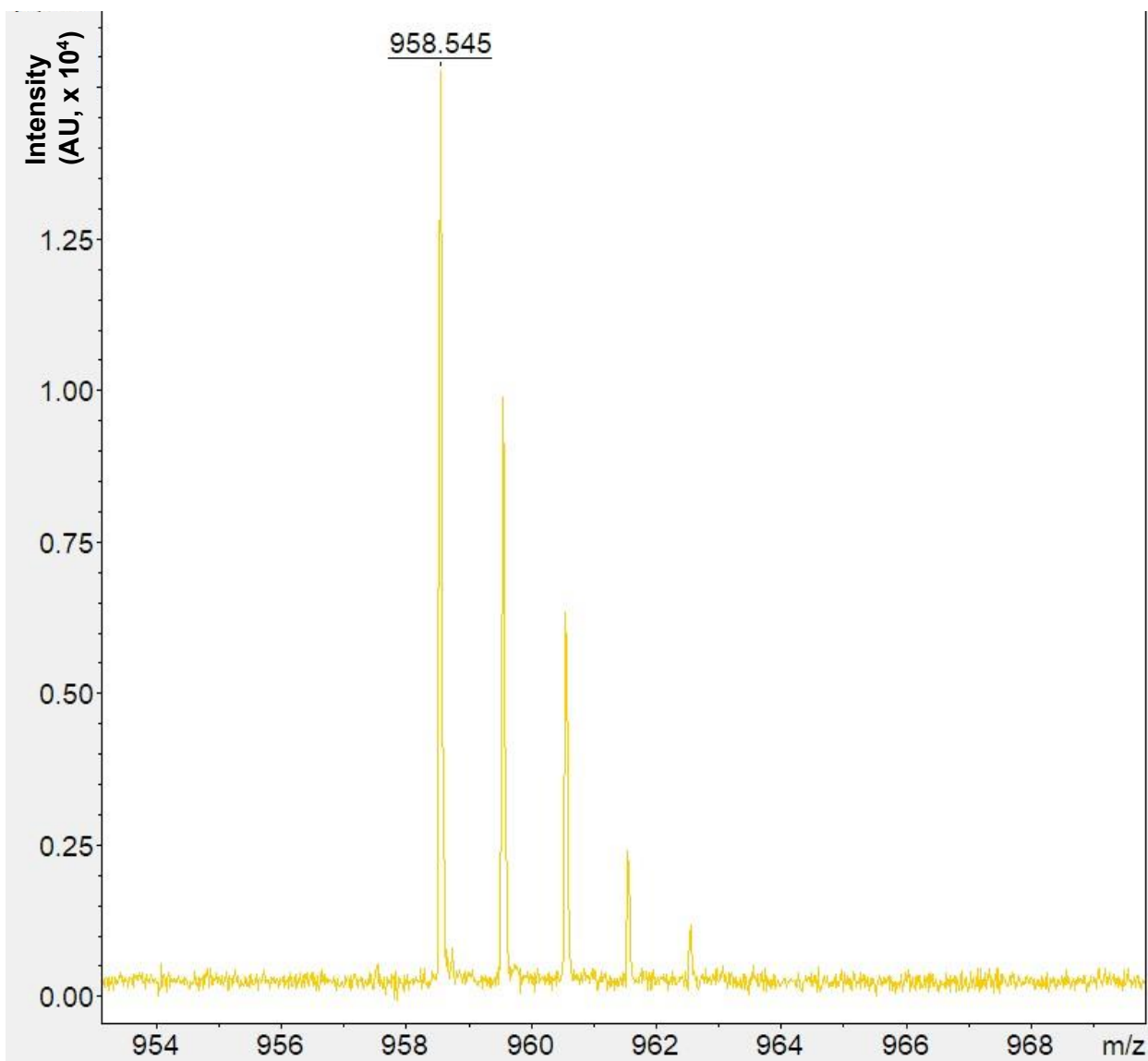


Figure A4.18. MALDI-TOF mass spectrum of PC 5.

Single Crystal X-Ray Diffraction

Crystals were grown by dissolving PC 3 in EtOAc and layering on hexanes (1:3 EtOAc: hexanes), then allowing solvent to evaporate until formation of crystals was observed. Crystals were coated in Paratone oil, mounted on a loop, and transferred to the Bruker D8 Quest diffractometer equipped with a Mo x-ray source and a CMOS Photon 50 detector. Frames were collected using ω and ϕ scans with a frame width of 1°. Frames were integrated with SAINT v8.40B and were corrected for absorption effects using SADABS v2016/2 implemented in APEX

5.³ Structures were solved using the intrinsic phasing method implemented in SHELXT v2018/2.⁴ The structure was refined against all data using SHELXL v2019/3 software package.⁵ Solution and refinement were performed using OLEX2 v1.5.⁶ Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at idealized positions and refined using a riding model with isotropic parameters. The CF₃ moiety is disordered over 3 positions due to competing weak interactions (F---F interaction for site with highest occupancy and aromatic C-H---F interactions on minor sites). The occupancies of these positions were refined using the SUMP 1 command for each disordered fluorine and then fixed at values to make each PART containing a CF₃ moiety make chemical sense (all fluorine atoms had matching occupancies). DFIX and SADI commands were required to enforce reasonable bond lengths for each C-F bond. SIMU, DELU, and EADP commands were used to limit the size of the atomic displacement parameters on the disordered fluorine atoms to reasonable values.

Table A4.1. Crystal data and structure refinement for PC 3.

Empirical formula	C ₅₆ H ₄₆ F ₆ N ₂ S ₄
Formula weight	989.19
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	7.4673(5)
b/Å	11.6217(8)
c/Å	14.4798(11)
α/°	90.462(3)
β/°	101.459(4)
γ/°	104.409(3)
Volume/Å ³	1190.62(15)
Z	1
ρ _{calc} /cm ³	1.380
μ/mm ⁻¹	0.264
F(000)	514.0
Crystal size/mm ³	0.102 × 0.022 × 0.016

Radiation	MoK α ($\lambda = 0.71076$)
2 Θ range for data collection/ $^{\circ}$	5.752 to 56.92
Index ranges	$-9 \leq h \leq 9, -15 \leq k \leq 15, -19 \leq l \leq 19$
Reflections collected	31891
Independent reflections	5967 [$R_{\text{int}} = 0.0897, R_{\text{sigma}} = 0.0662$]
Data/restraints/parameters	5967/198/326
Goodness-of-fit on F^2	1.022
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0614, wR_2 = 0.1335$
Final R indexes [all data]	$R_1 = 0.1111, wR_2 = 0.1554$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.22/-0.42

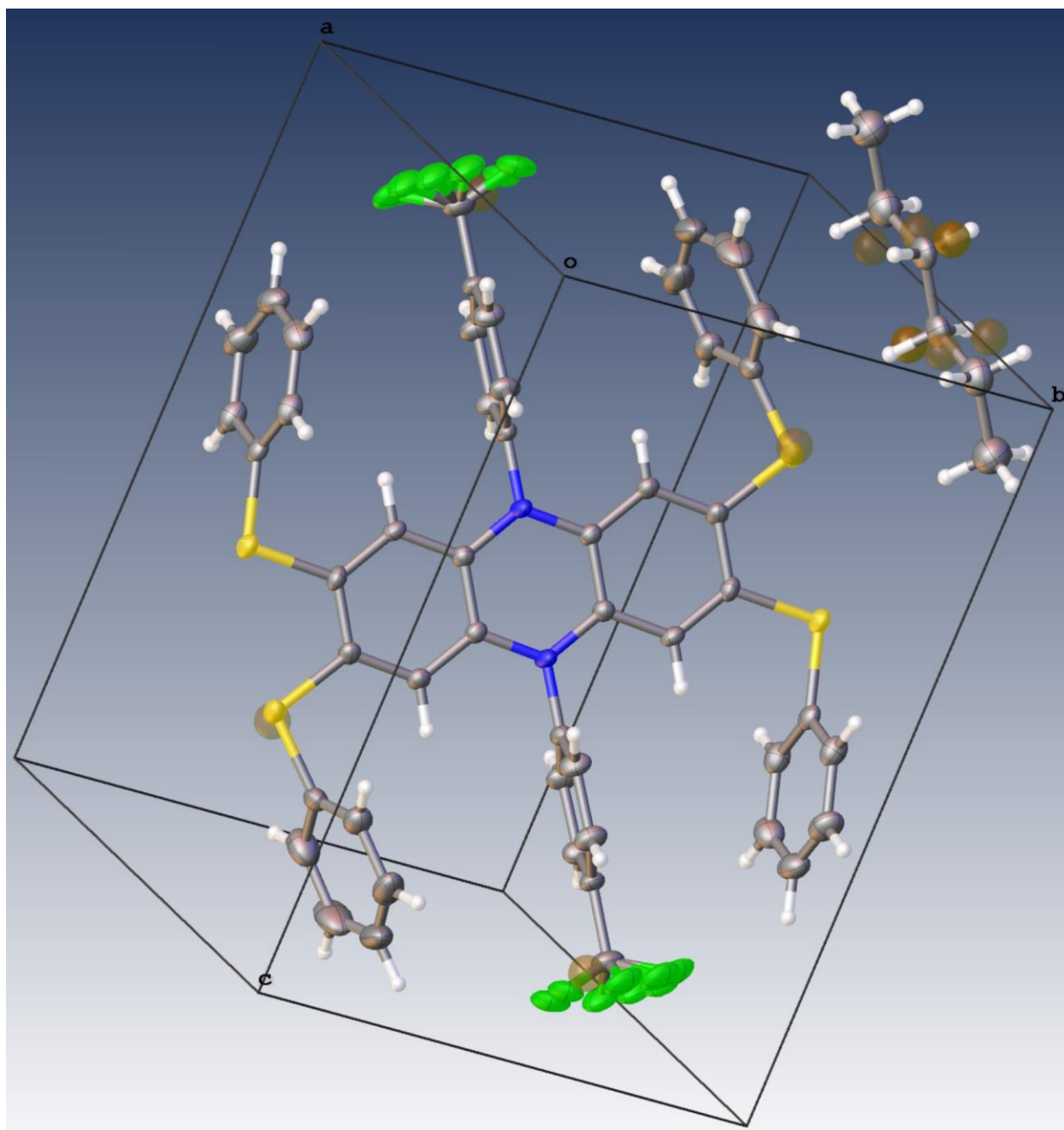


Figure A4.19. Crystal structure of PC 3 with one solvent (hexane) molecule.

PHOTOCATALYST CHARACTERIZATION

UV-visible Spectroscopy

DMAc or EtOAc was used as the solvent for UV-vis spectroscopy. All samples were analyzed in 1 cm pathlength quartz cuvettes. The molar absorptivity ($\epsilon_{\text{max,abs}}$) of each PC was determined using the following procedure: a stock solution of the PC was prepared in DMAc or

EtOAc. The stock solution was then diluted to produce six solutions of different concentrations with a maximum absorbance roughly between 0 and 2. The $\epsilon_{\text{max,abs}}$ for PCs 1 and 2 in DMAc were reported from prior work.¹

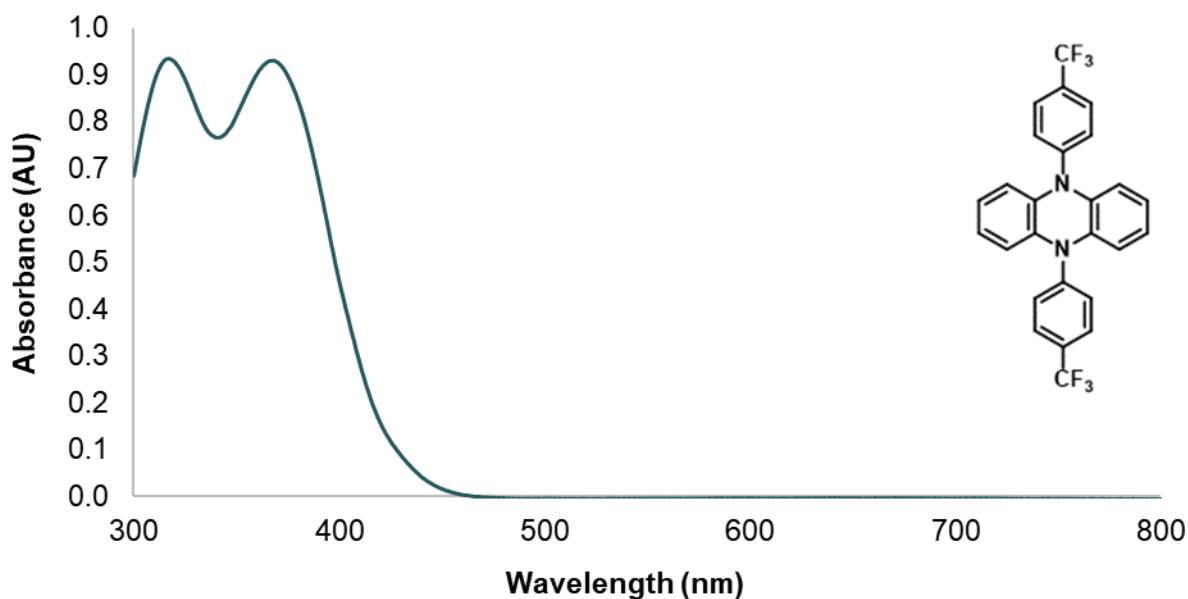


Figure A4.20. UV-visible absorption spectrum for PC 1 in DMAc.

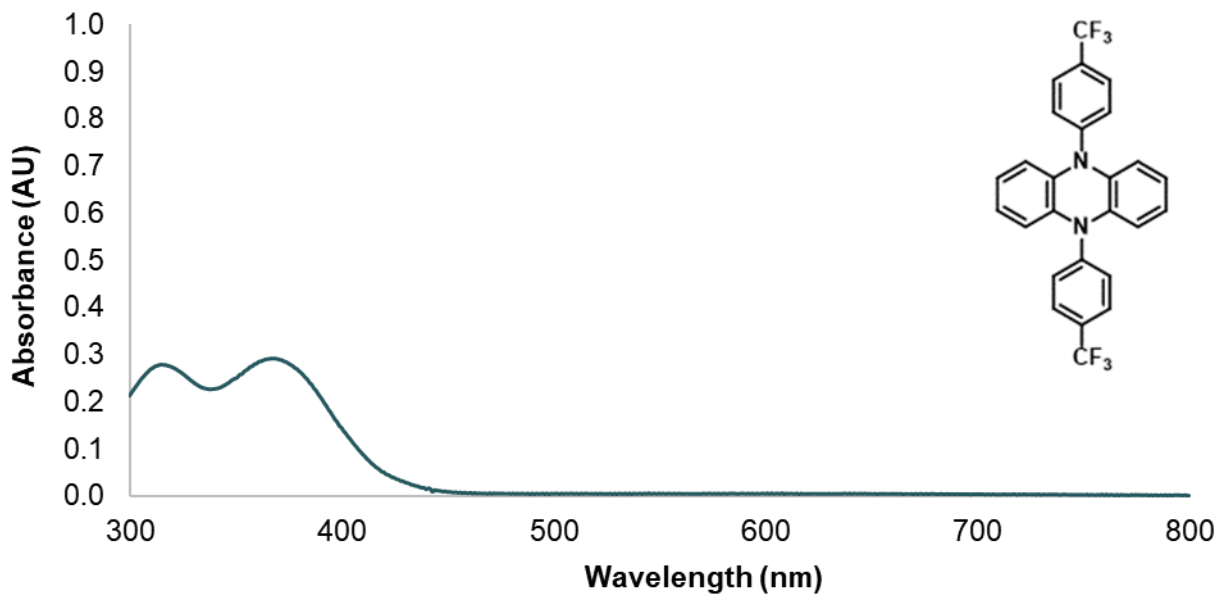


Figure A4.21. UV-visible absorption spectrum for PC 1 in EtOAc.

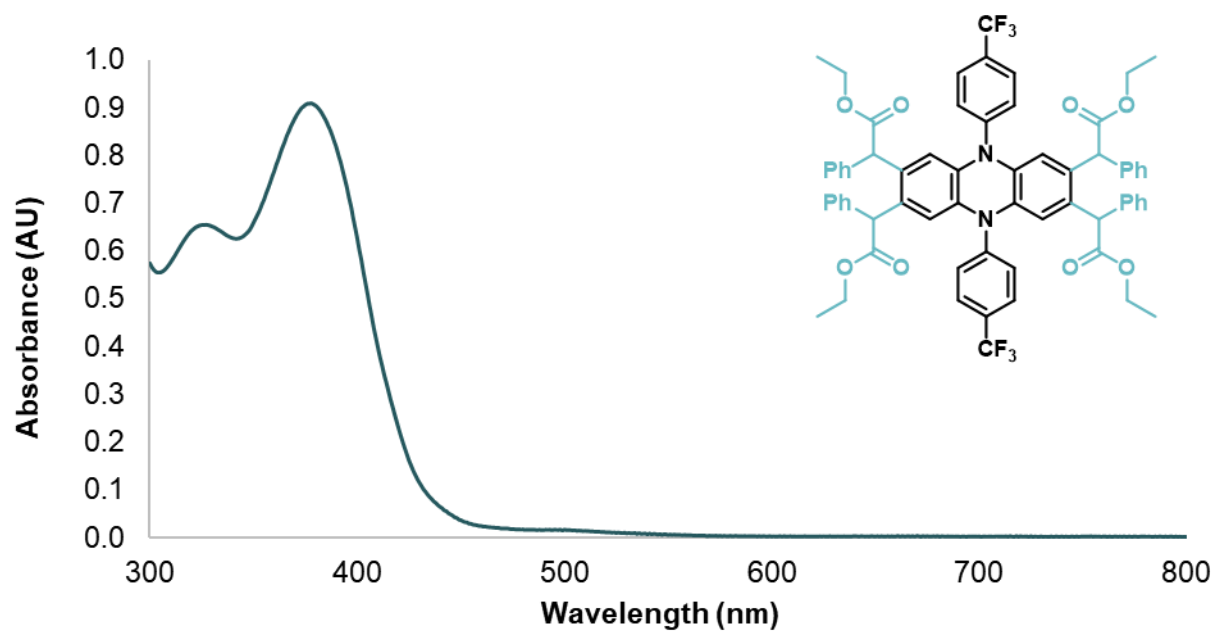


Figure A4.22. UV-visible absorption spectrum for PC 2 in DMAc.

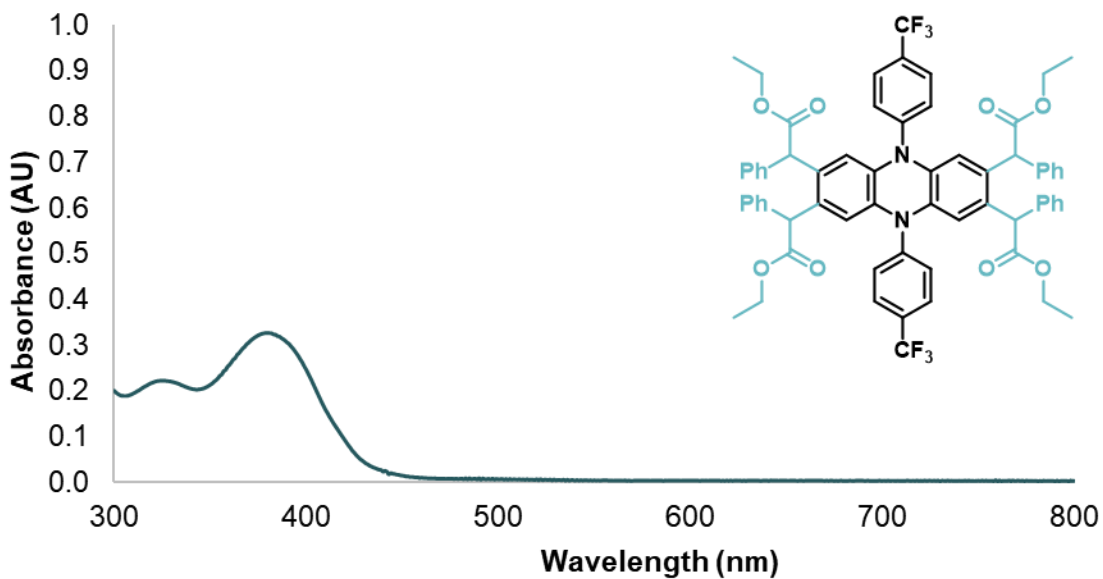


Figure A4.23. UV-visible absorption spectrum for PC 2 in EtOAc.

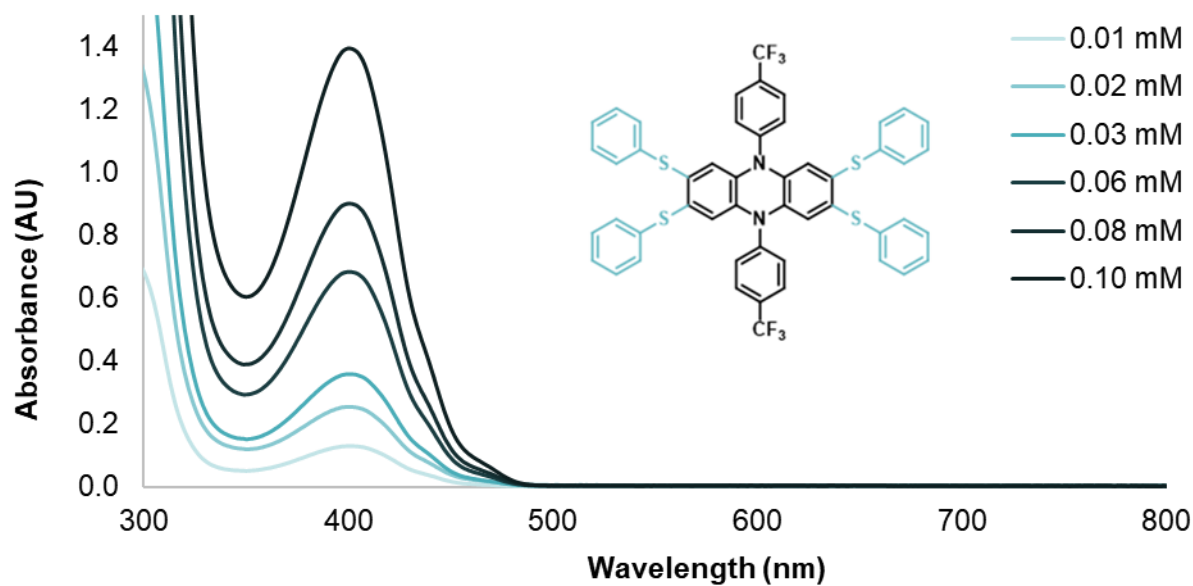


Figure A4.24. UV-visible absorption spectra for PC **3** in DMAc.

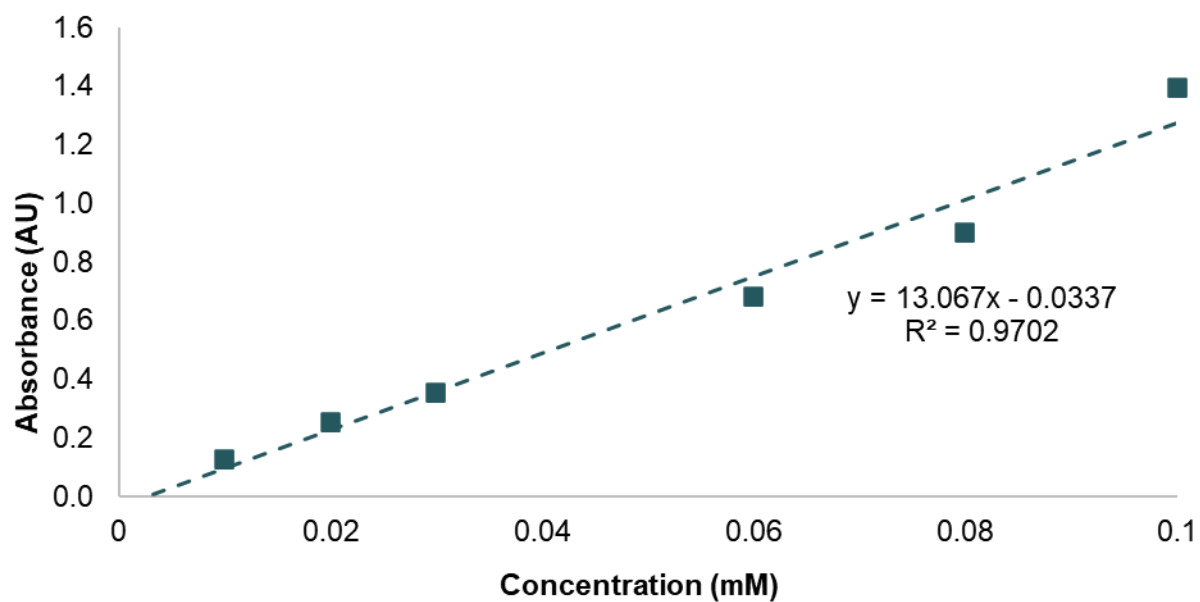


Figure A4.25. Beer's law curve used to determine the $\epsilon_{\text{max,abs}}$ of PC **3** in DMAc.

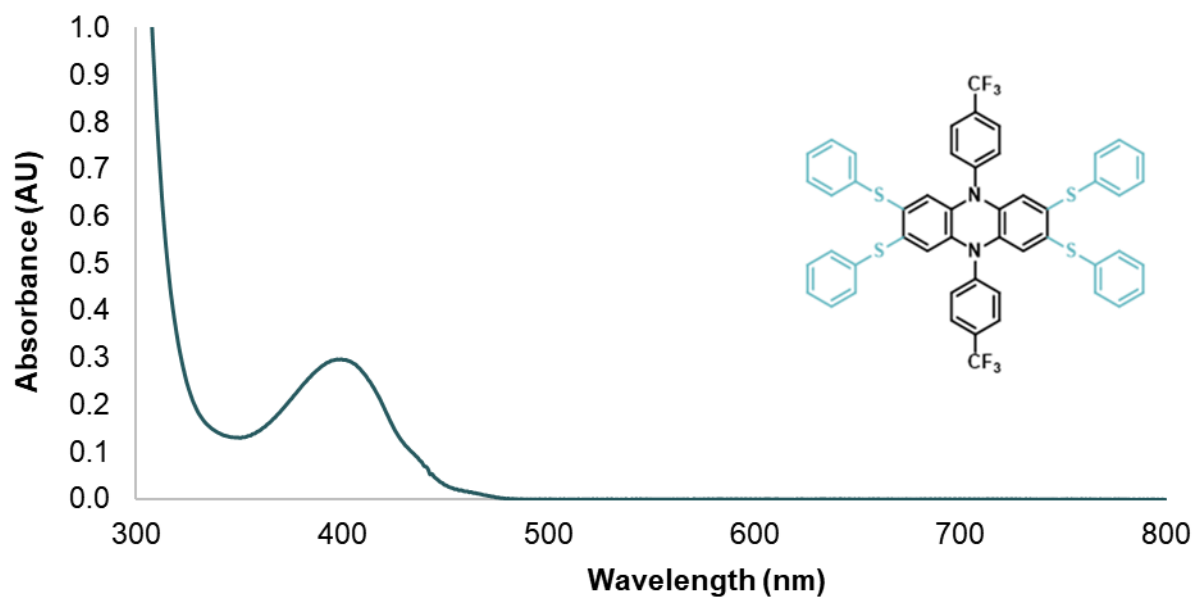


Figure A4.26. UV-visible absorption spectrum for PC 3 in EtOAc.

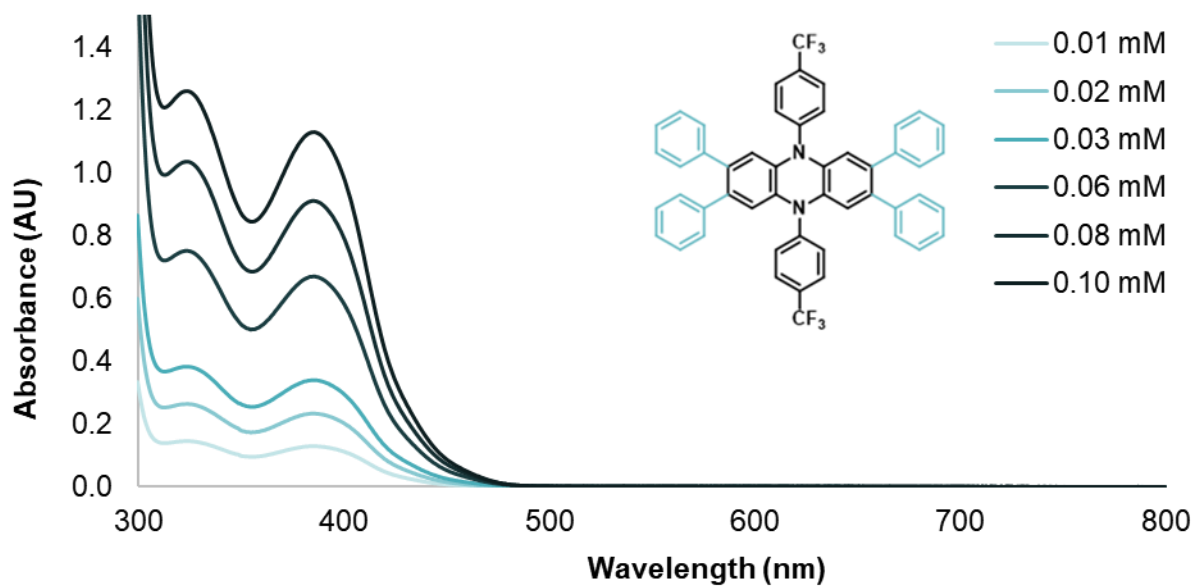


Figure A4.27. UV-visible absorption spectra for PC 4 in DMAc.

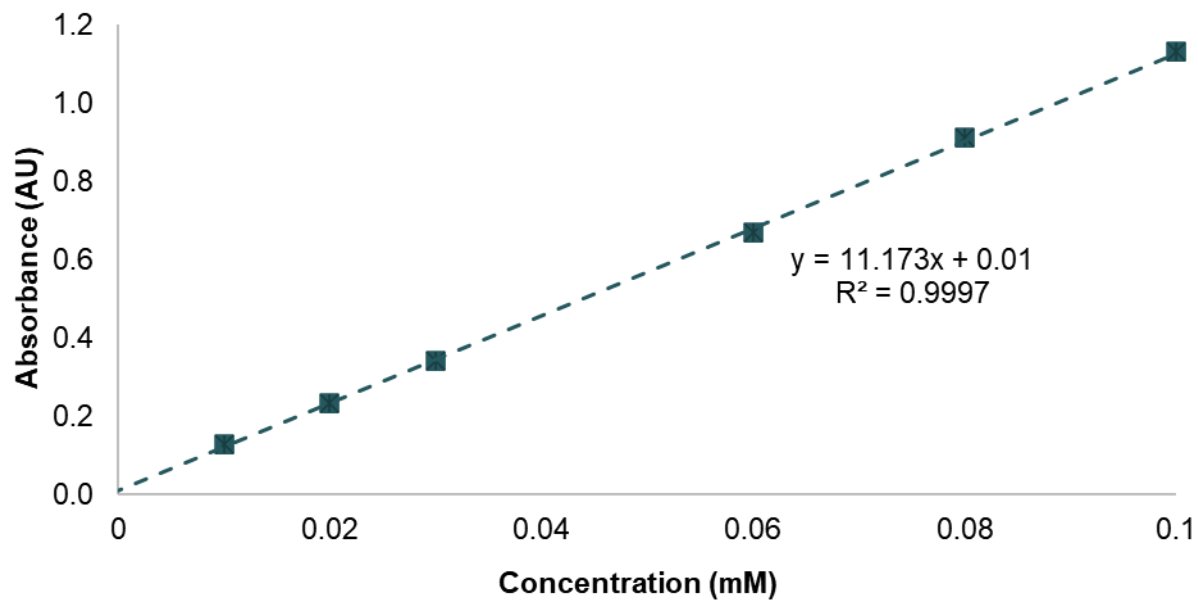


Figure A4.28. Beer's law curve used to determine the $\epsilon_{\text{max,abs}}$ of PC 4 in DMAc.

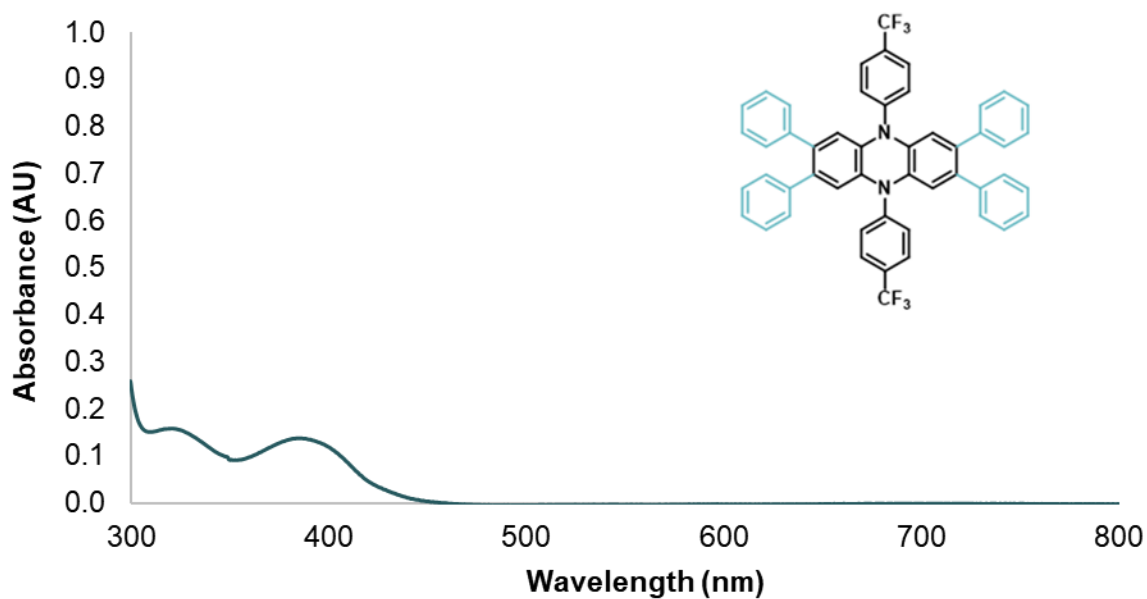


Figure A4.29. UV-visible absorption spectrum for PC 4 in EtOAc.

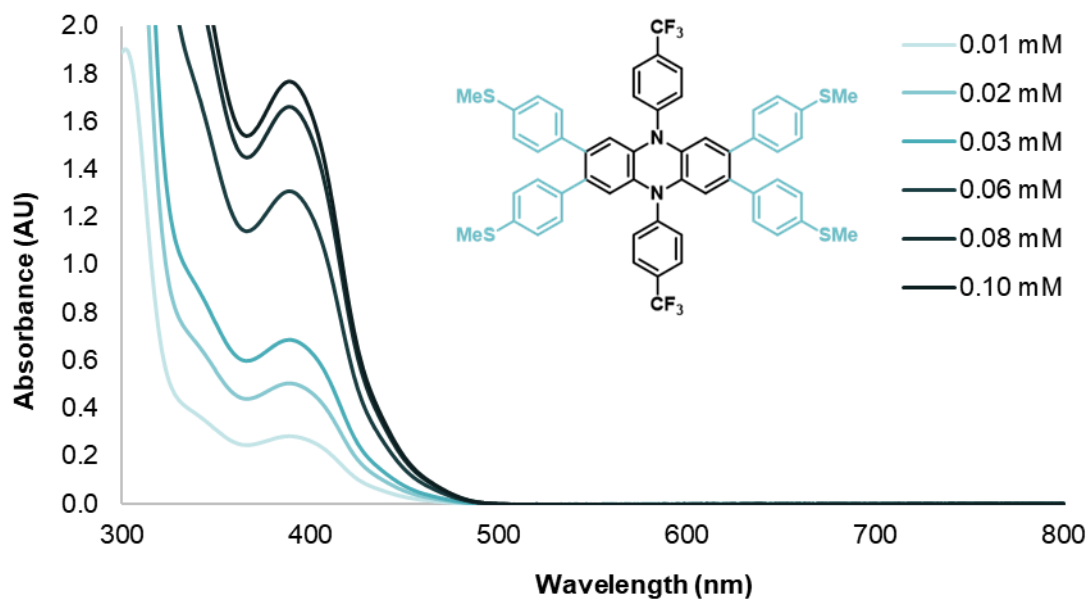


Figure A4.30. UV-visible absorption spectra for PC 5 in DMAc.

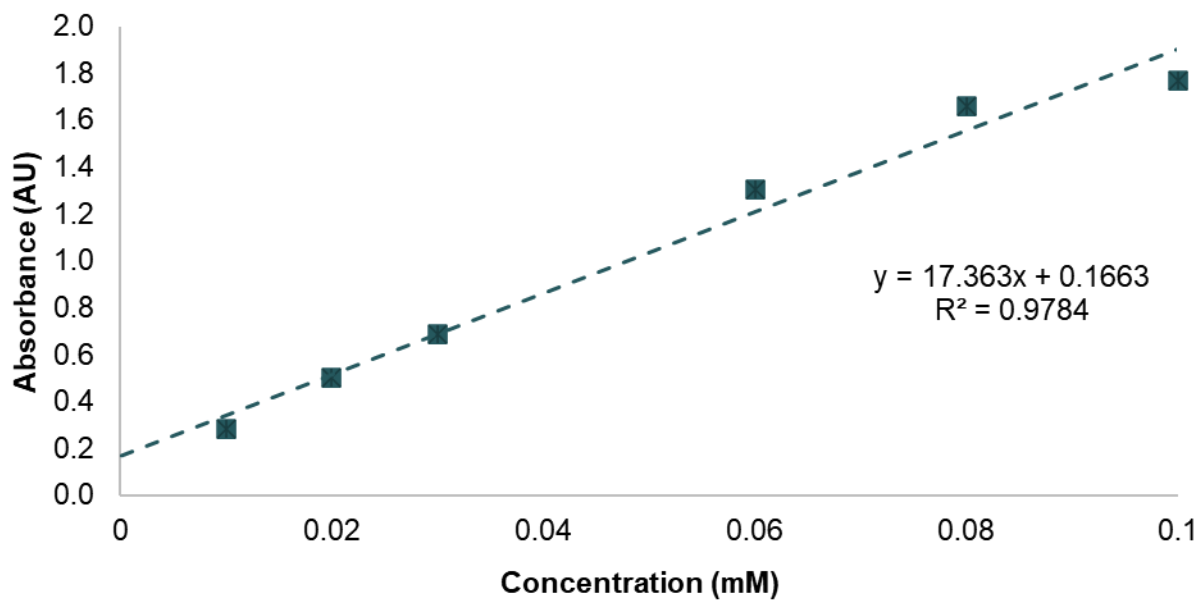


Figure A4.31. Beer's law curve used to determine the $\epsilon_{\text{max,abs}}$ of PC 5 in DMAc.

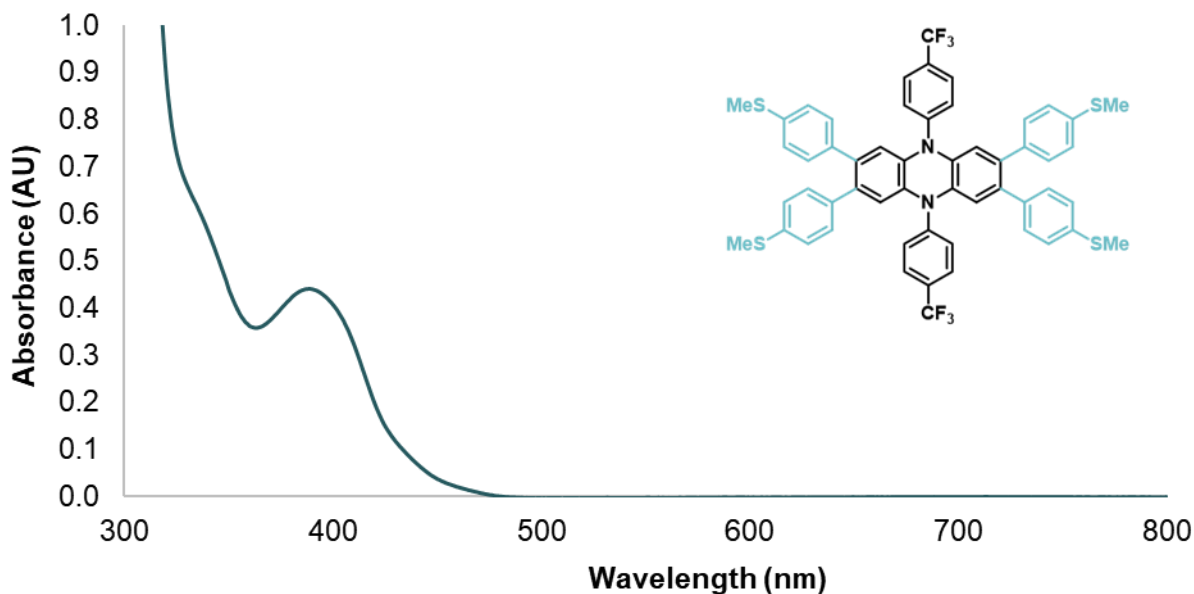


Figure A4.32. UV-visible absorption spectrum for PC **5** in EtOAc.

Fluorescence Spectroscopy

Solutions of each PC were prepared open to air in DMAc or EtOAc at a concentration that resulted in an absorbance < 0.5 AU. All samples were analyzed in 1 cm pathlength quartz cuvettes. The emission spectra of each solution were measured using the wavelength of maximum absorption ($\lambda_{\text{max,abs}}$) as the excitation wavelength.

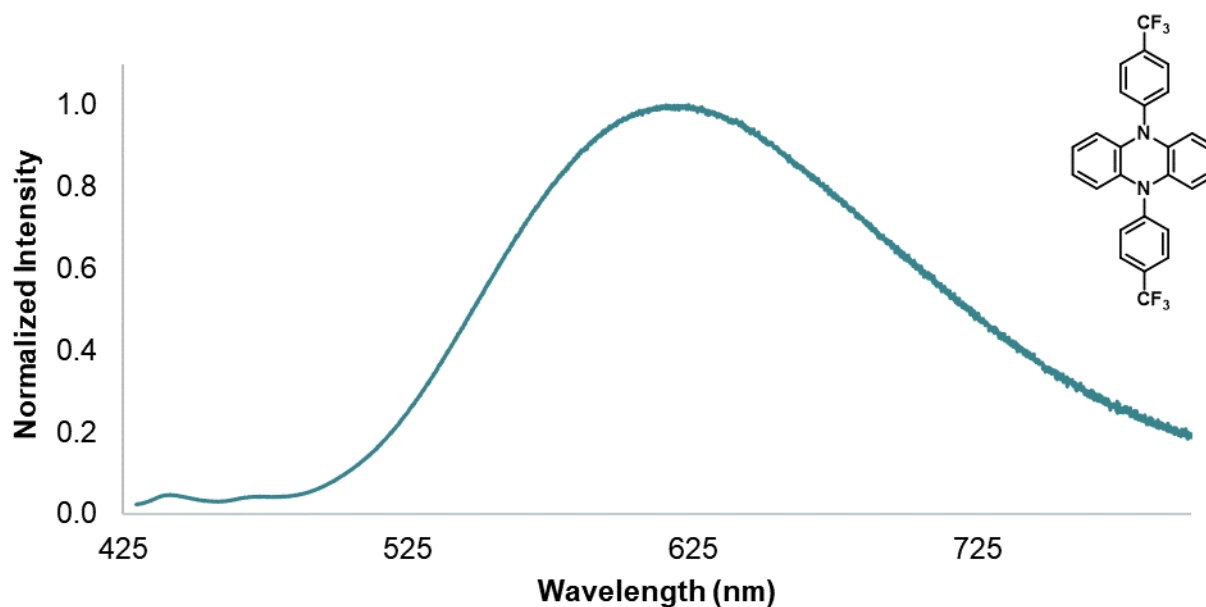


Figure A4.33. Fluorescence spectrum for PC **1** in DMAc.

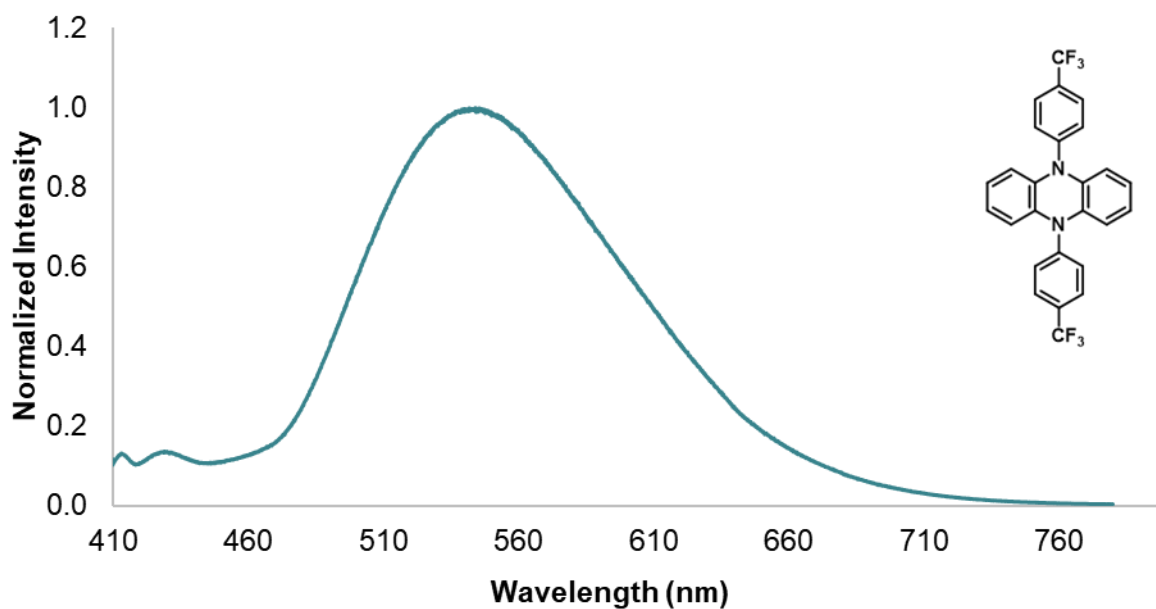


Figure A4.34. Fluorescence spectrum for PC **1** in EtOAc.

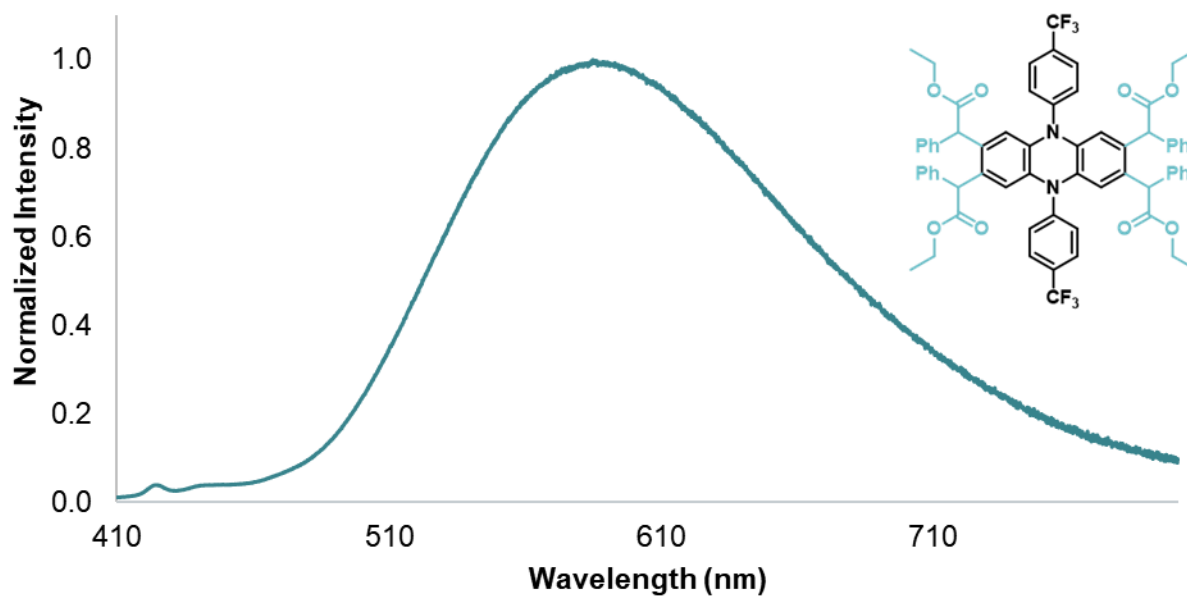


Figure A4.35. Fluorescence spectrum for PC **2** in DMAc.

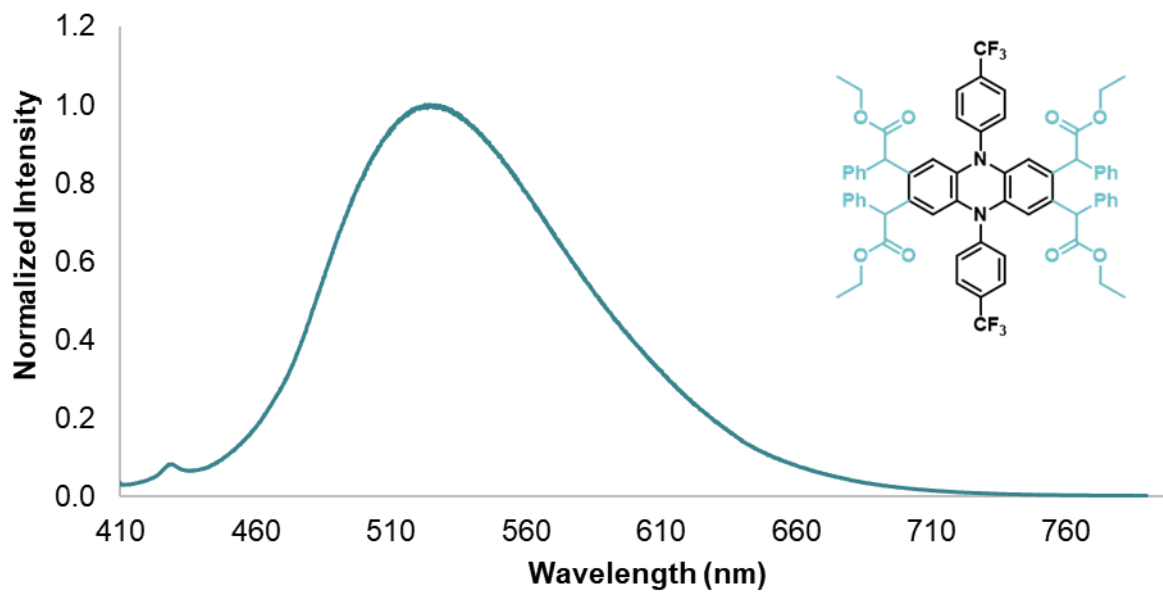


Figure A4.36. Fluorescence spectrum for PC **2** in EtOAc.

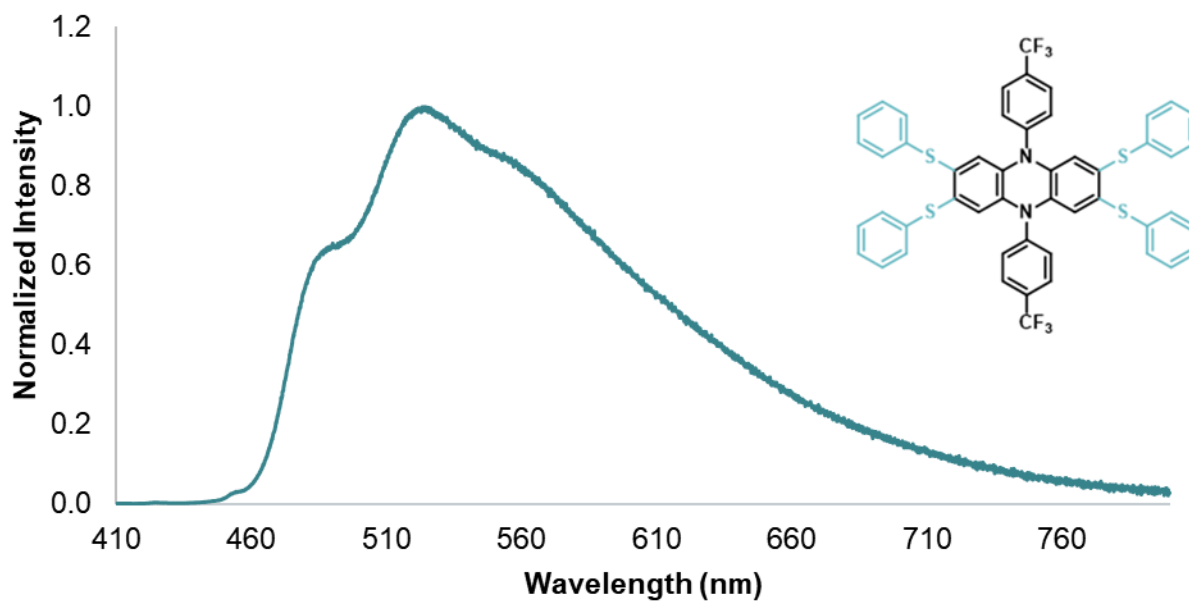


Figure A4.37. Fluorescence spectrum for PC **3** in DMAc.

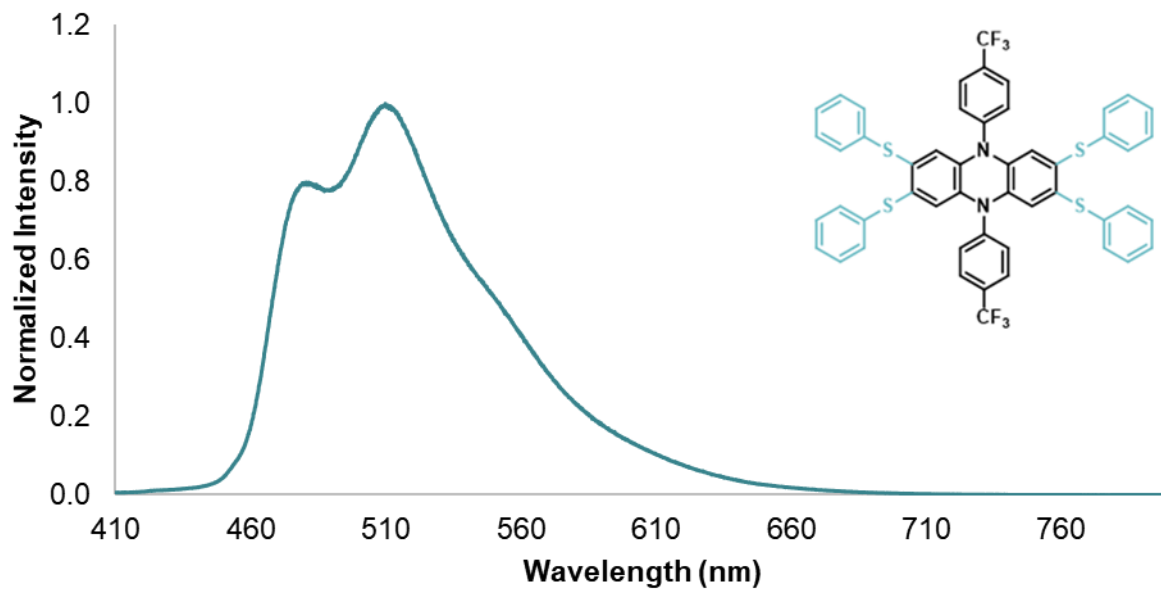


Figure A4.38. Fluorescence spectrum for PC 3 in EtOAc.

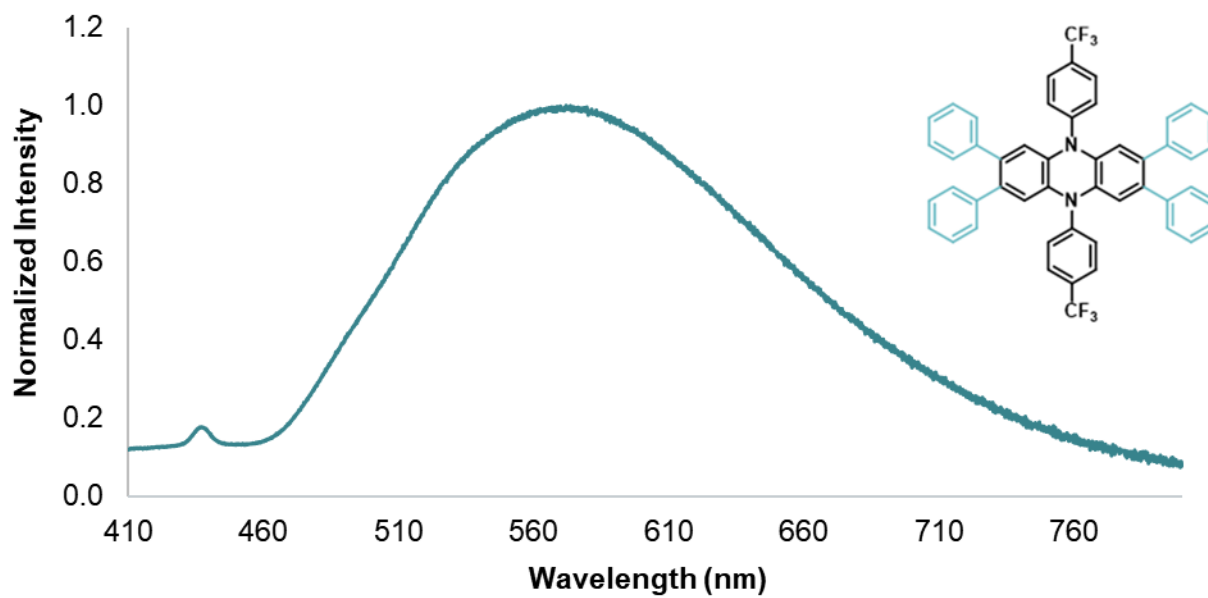


Figure A4.39. Fluorescence spectrum for PC 4 in DMAc.

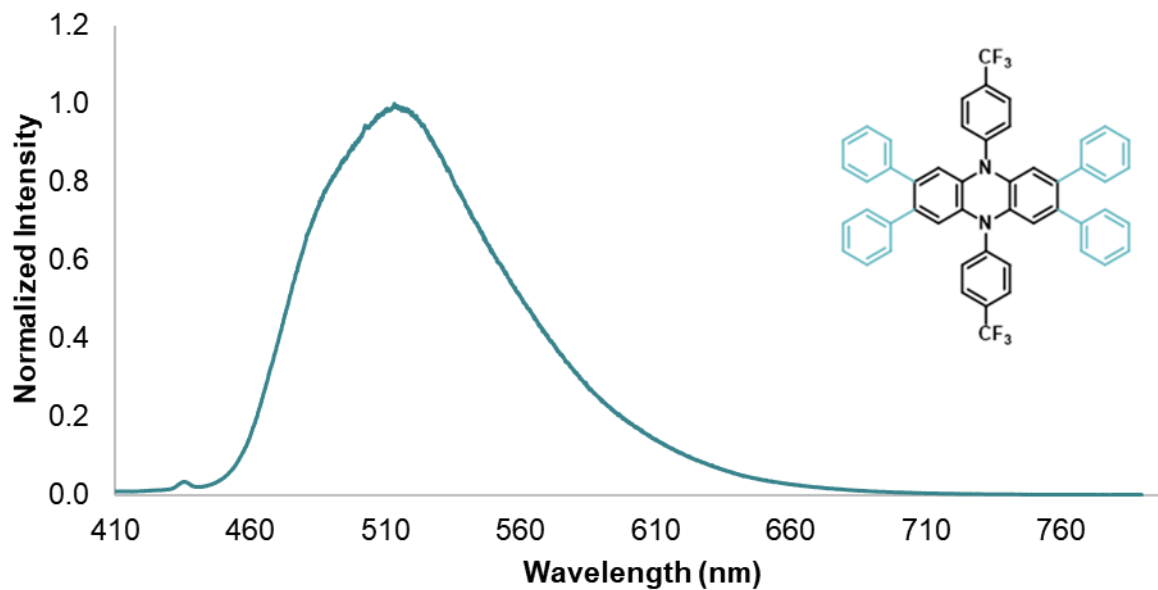


Figure A4.40. Fluorescence spectrum for PC 4 in EtOAc.

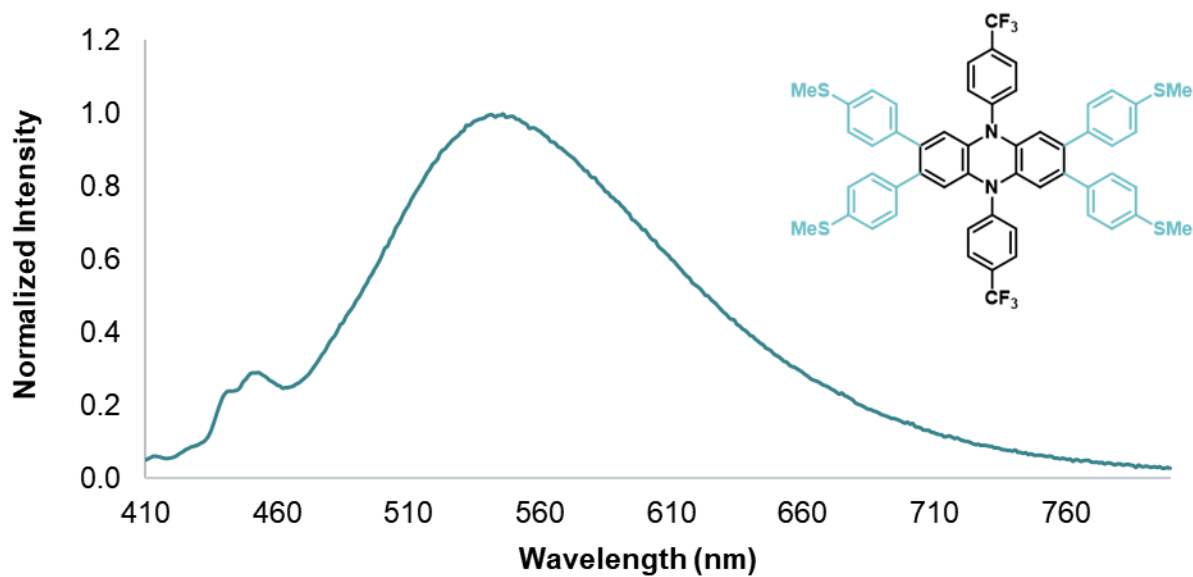


Figure A4.41. Fluorescence spectrum for PC 5 in DMAc.

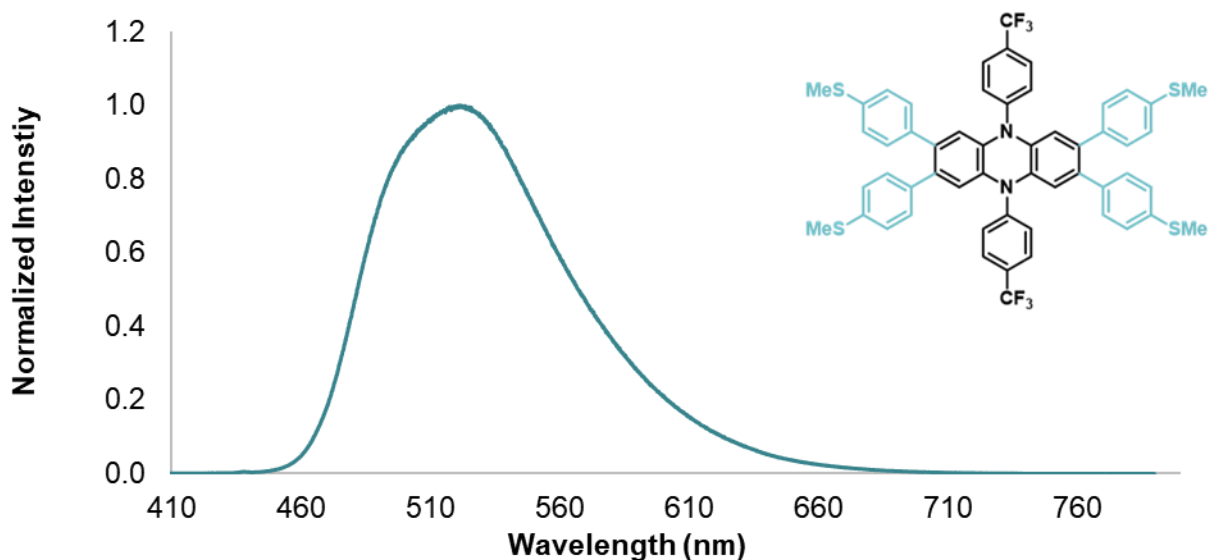


Figure A4.42. Fluorescence spectrum for PC 5 in EtOAc.

Comparison of Emission Spectra under Nitrogen and Oxygen

Solutions of each PC were prepared in DMAc in a nitrogen filled glovebox at a concentration that resulted in an absorbance < 0.5 AU. All samples were analyzed in 1 cm pathlength quartz cuvettes. The emission spectra of each solution were measured using the wavelength of maximum absorption ($\lambda_{\text{max,abs}}$) as the excitation wavelength. After the emission spectrum was measured under nitrogen, the same cuvette was exposed to oxygen (open to air) for 72 hours and the emission spectrum was measured again with the same instrument settings.

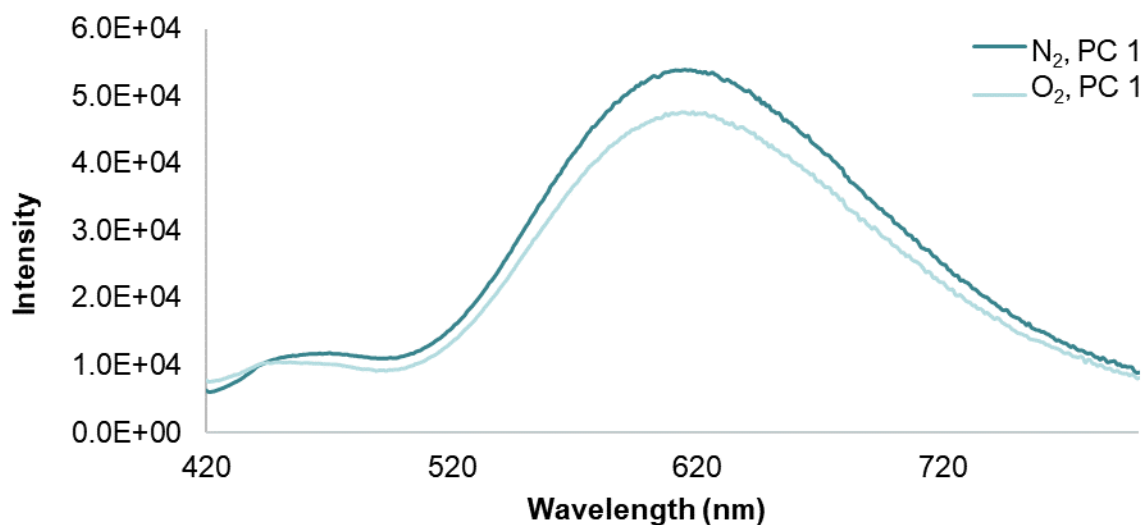


Figure A4.43. Emission spectra for PC 1 in DMAc under nitrogen (dark turquoise) and oxygen (light turquoise). No shift in the $\lambda_{\text{max,em}}$ or other change was observed between nitrogen and oxygen.

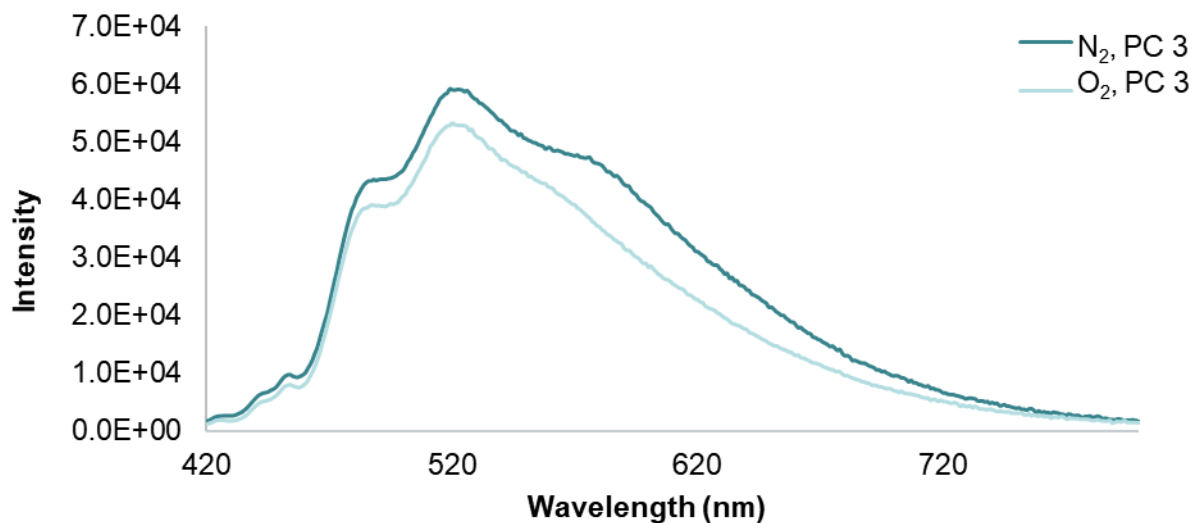


Figure A4.44. Emission spectra for PC 3 in DMAc under nitrogen (dark turquoise) and oxygen (light turquoise). The emission feature associated with the $\lambda_{\text{max,em}}$ and the most blue-shifted emission feature do not change in wavelength or flatten between nitrogen and oxygen, however the most red-shifted peak notably decreases (flattens out) after exposure to oxygen. The change in the red-shifted emission feature under oxygen suggests phosphorescence that is quenched by oxygen, supporting occupancy of an emissive triplet excited state.

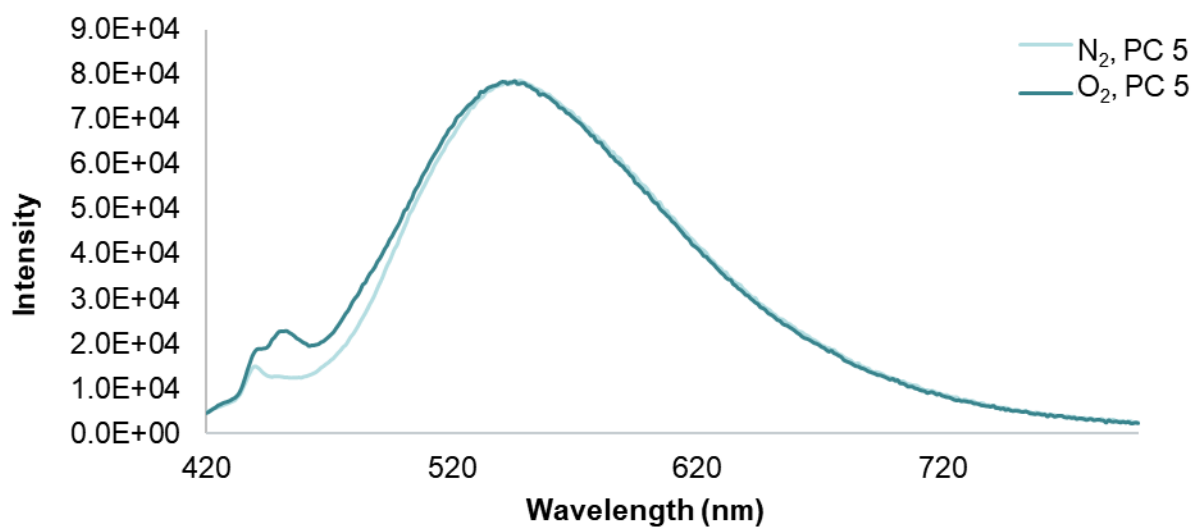


Figure A4.45. Emission spectra for PC 5 in DMAc under nitrogen (dark turquoise) and oxygen (light turquoise). No shift in the $\lambda_{\text{max,em}}$ or other change was observed between nitrogen and oxygen.

Solvatochromism

Solutions of each PC were prepared in solvents of varying polarity (ϵ = dielectric constant): 1-hexene (2.07), benzene (2.27), dioxane (2.21), THF (7.43), pyridine (13.0), and DMF (37.2) at concentrations of 0.1 – 1.0 mM. All samples were analyzed in 1 cm pathlength quartz cuvettes via fluorescence spectroscopy to obtain the emission spectra.

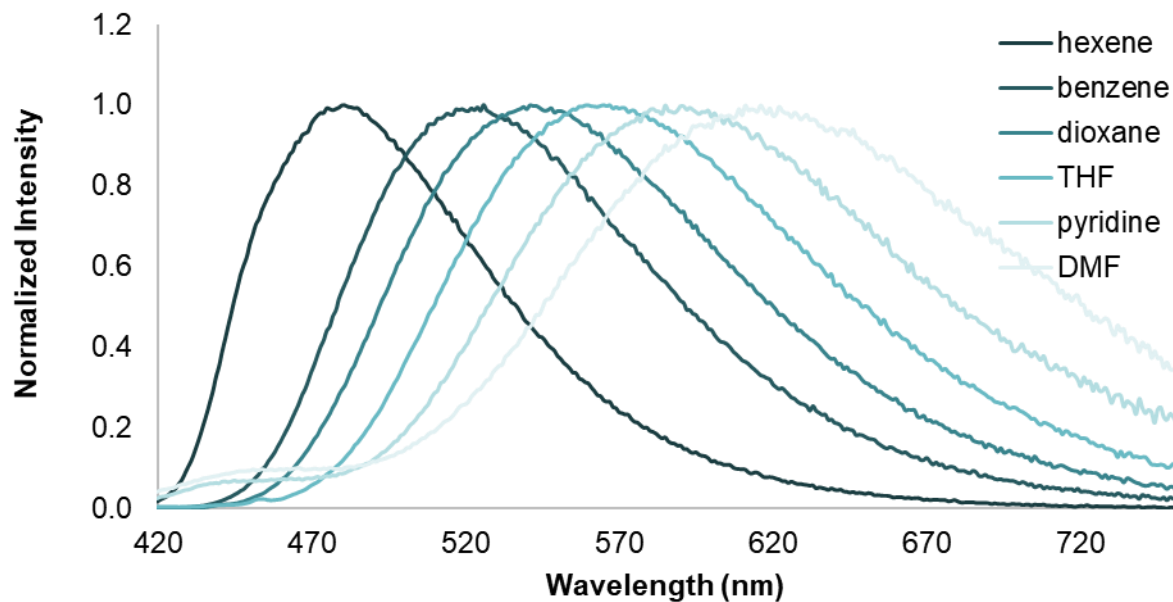


Figure A4.46. Overlaid emission profiles of PC 1 in different polarity solvents.

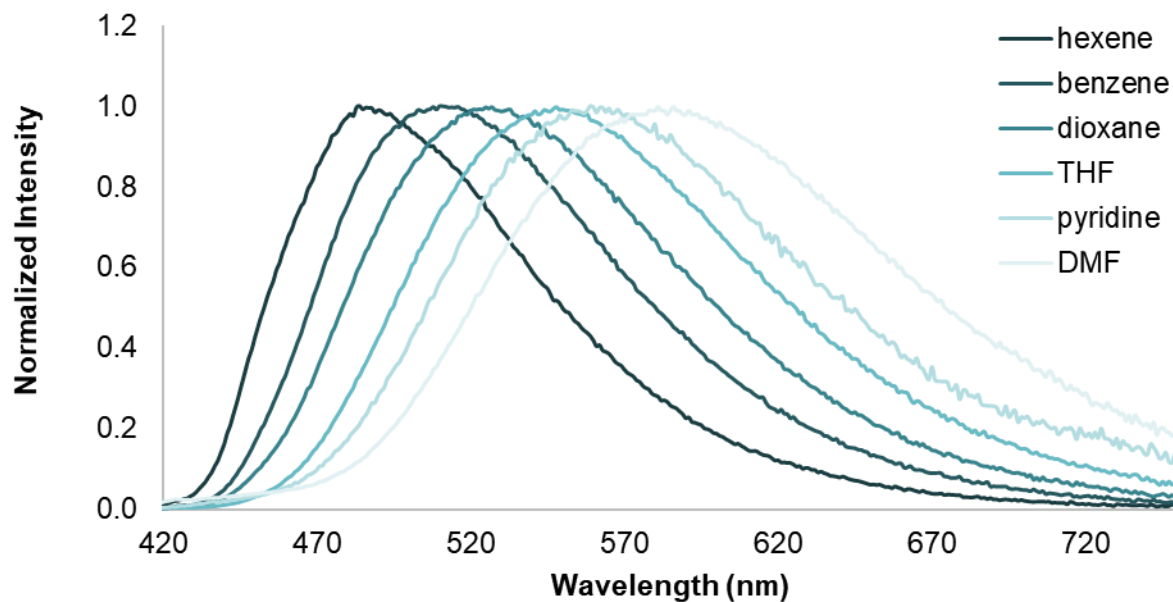


Figure A4.47. Overlaid emission profiles of PC 2 in different polarity solvents.

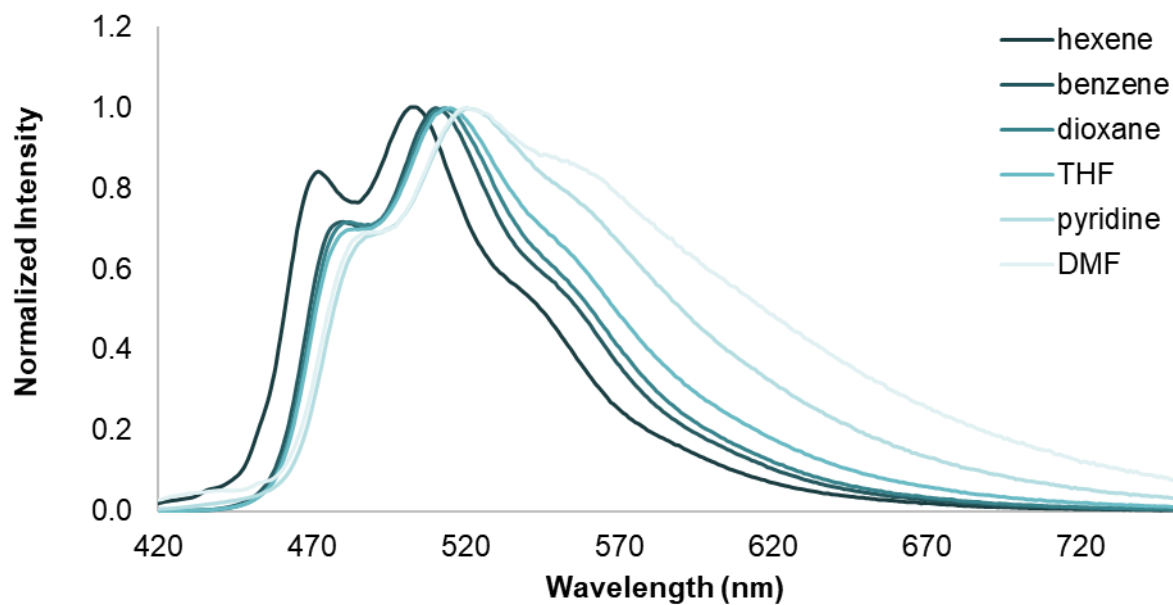


Figure A4.48. Overlaid emission profiles of PC 3 in different polarity solvents.

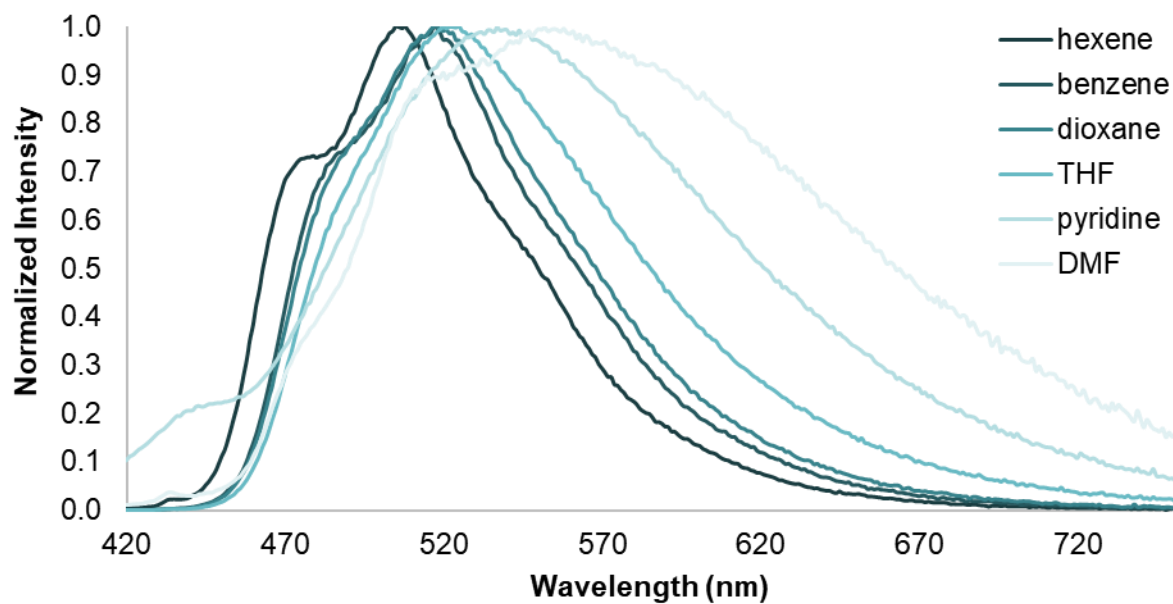


Figure A4.49. Overlaid emission profiles of PC 4 in different polarity solvents.

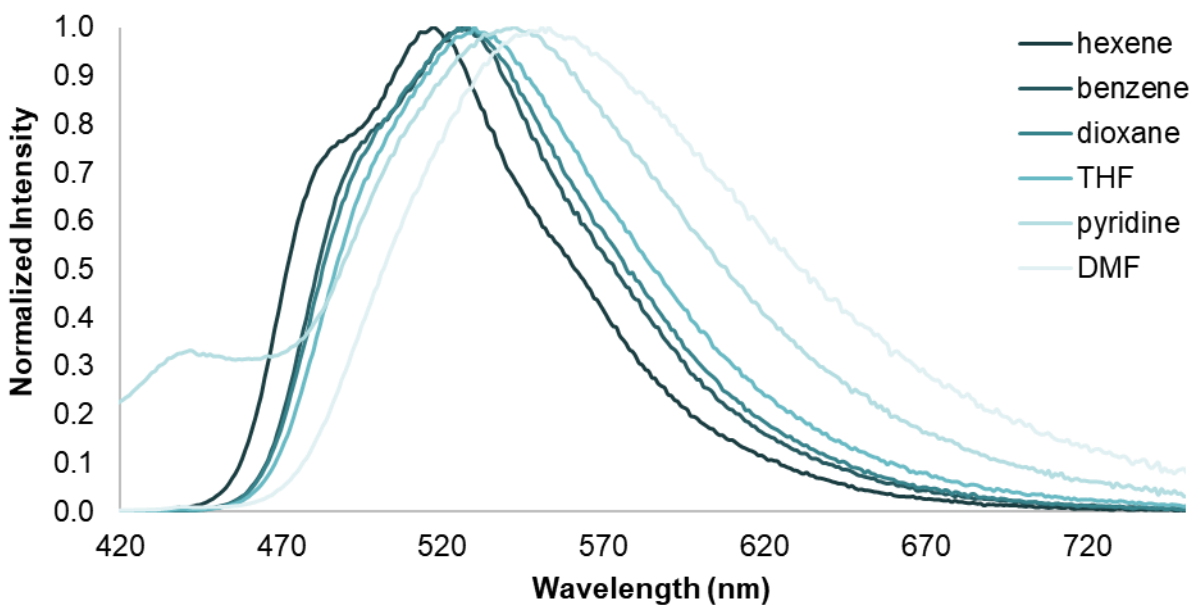


Figure A4.50. Overlaid emission profiles of PC 5 in different polarity solvents

Time Correlated Single Photon Counting

The singlet excited state lifetime for PCs 1-5 were measured by TCSPC. The PC solutions were prepared in DMAc in a nitrogen filled glovebox in air-free cuvettes. Measurements were performed until a maximum count value of 10,000 counts was achieved, and the data were fit with biexponential tail fits. The data indicate that single excited state lifetimes (τ_{S1}) follow the same trend that most of the photophysical properties follow (parent, alkyl, aryl, heteroatom).

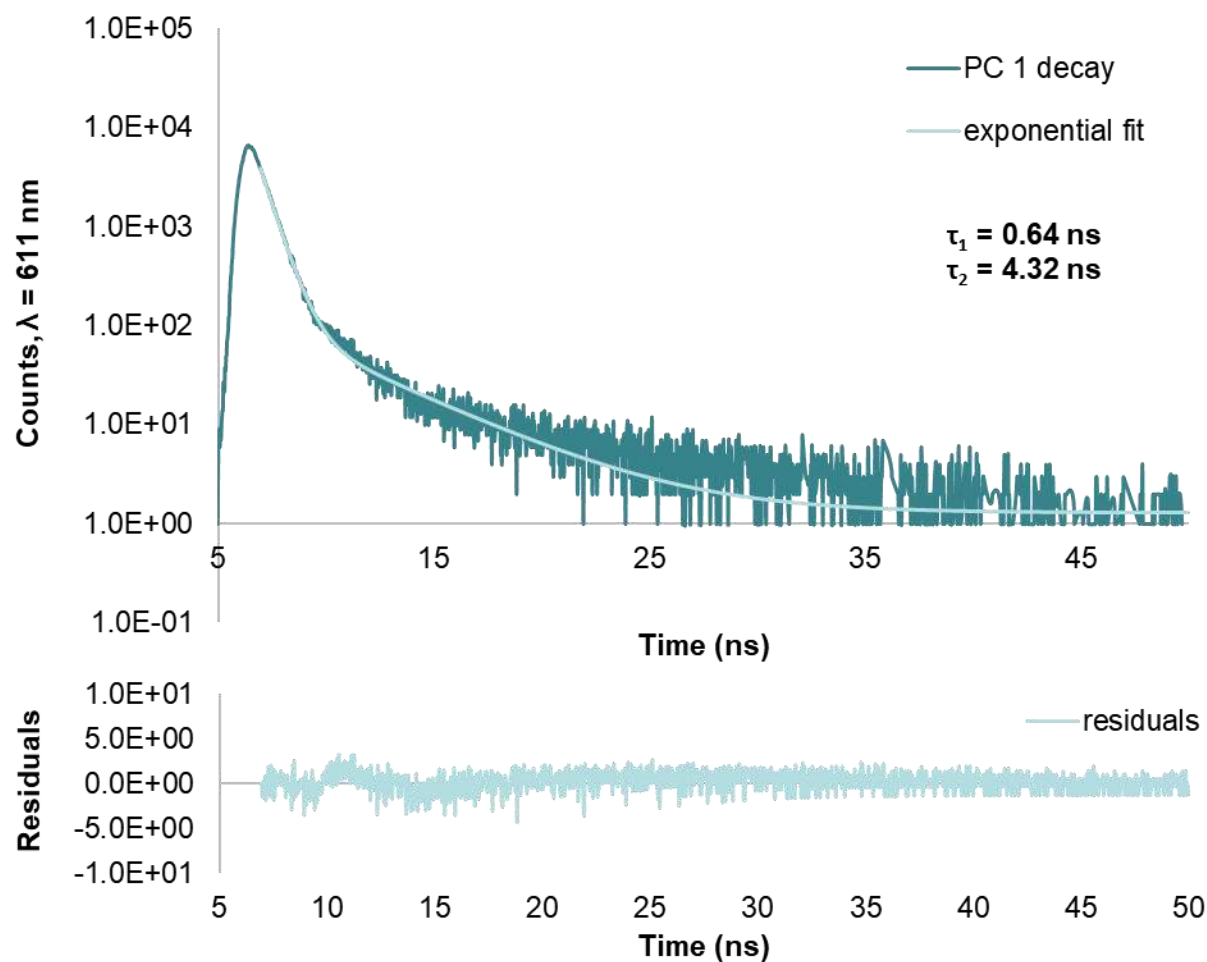


Figure A4.51. Fluorescence decay curve of PC **1** (dark turquoise) with biexponential fit of the decay data (light turquoise), $\lambda_{\text{ex}} = 368$ nm, $\lambda_{\text{em}} = 611$ nm. The data on the bottom shows the residuals from the biexponential fit of the data.

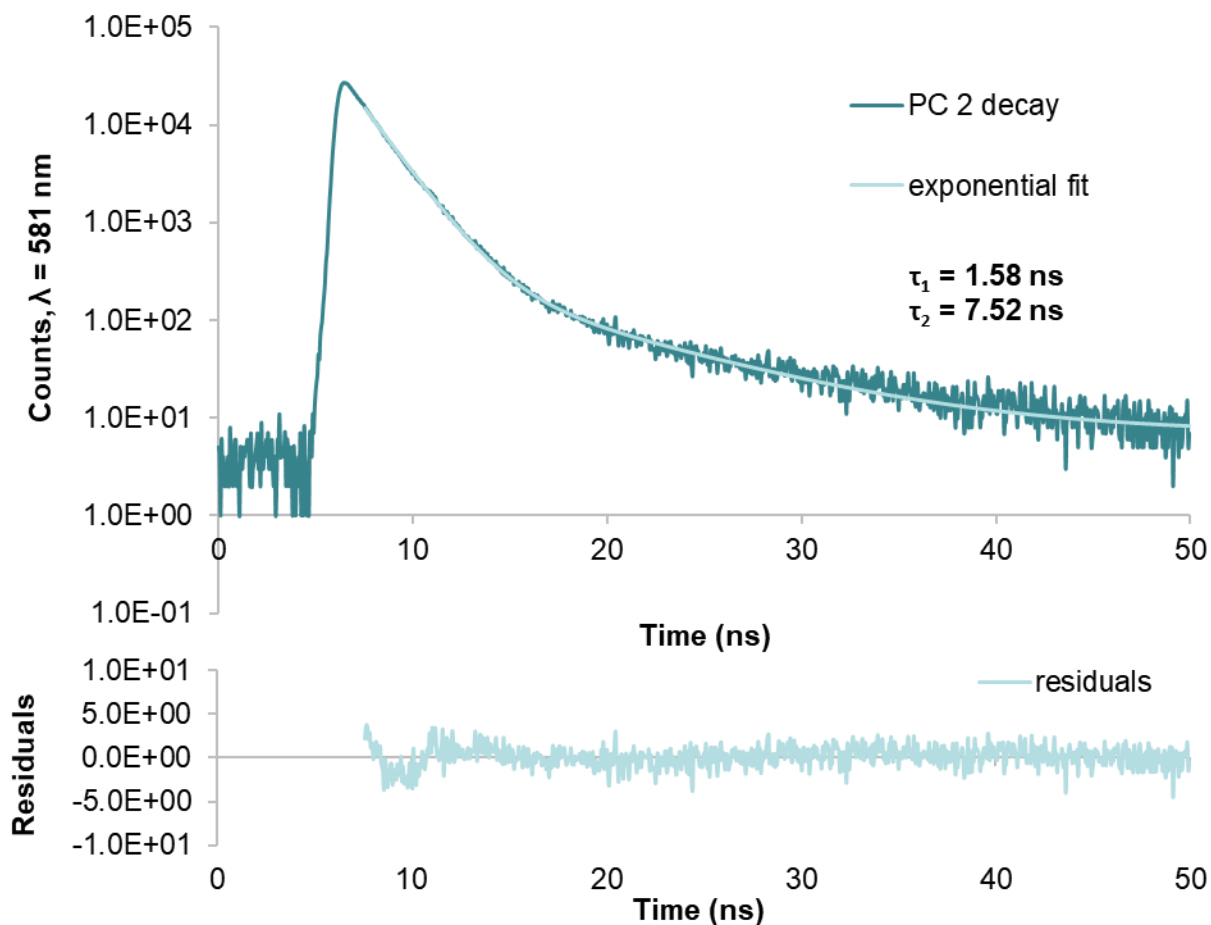


Figure A4.52. Fluorescence decay curve of PC 2 (dark turquoise) with biexponential fit of the decay data (light turquoise), $\lambda_{\text{ex}} = 378$ nm, $\lambda_{\text{em}} = 581$ nm. The data on the bottom shows the residuals from the biexponential fit of the data.

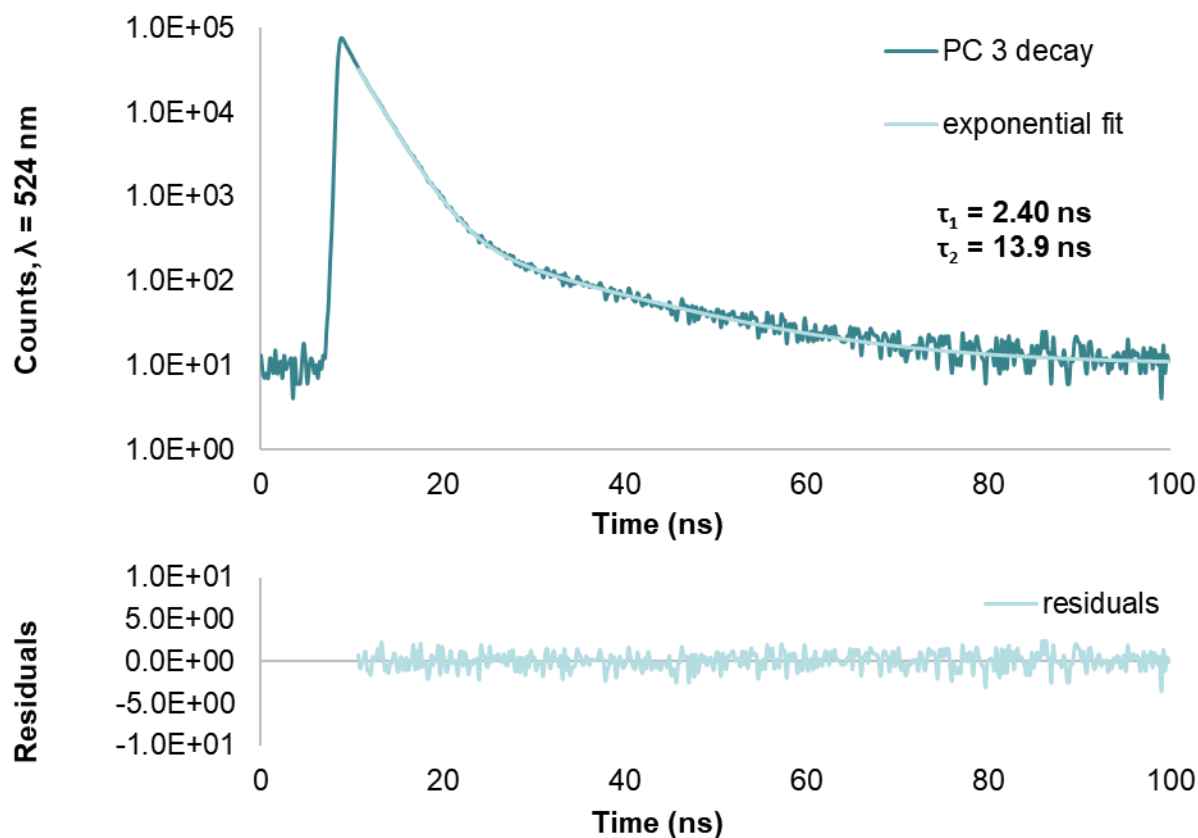


Figure A4.53. Fluorescence decay curve of PC **3** (dark turquoise) with biexponential fit of the decay data (light turquoise), $\lambda_{\text{ex}} = 400$ nm, $\lambda_{\text{em}} = 524$ nm. The data on the bottom shows the residuals from the biexponential fit of the data.

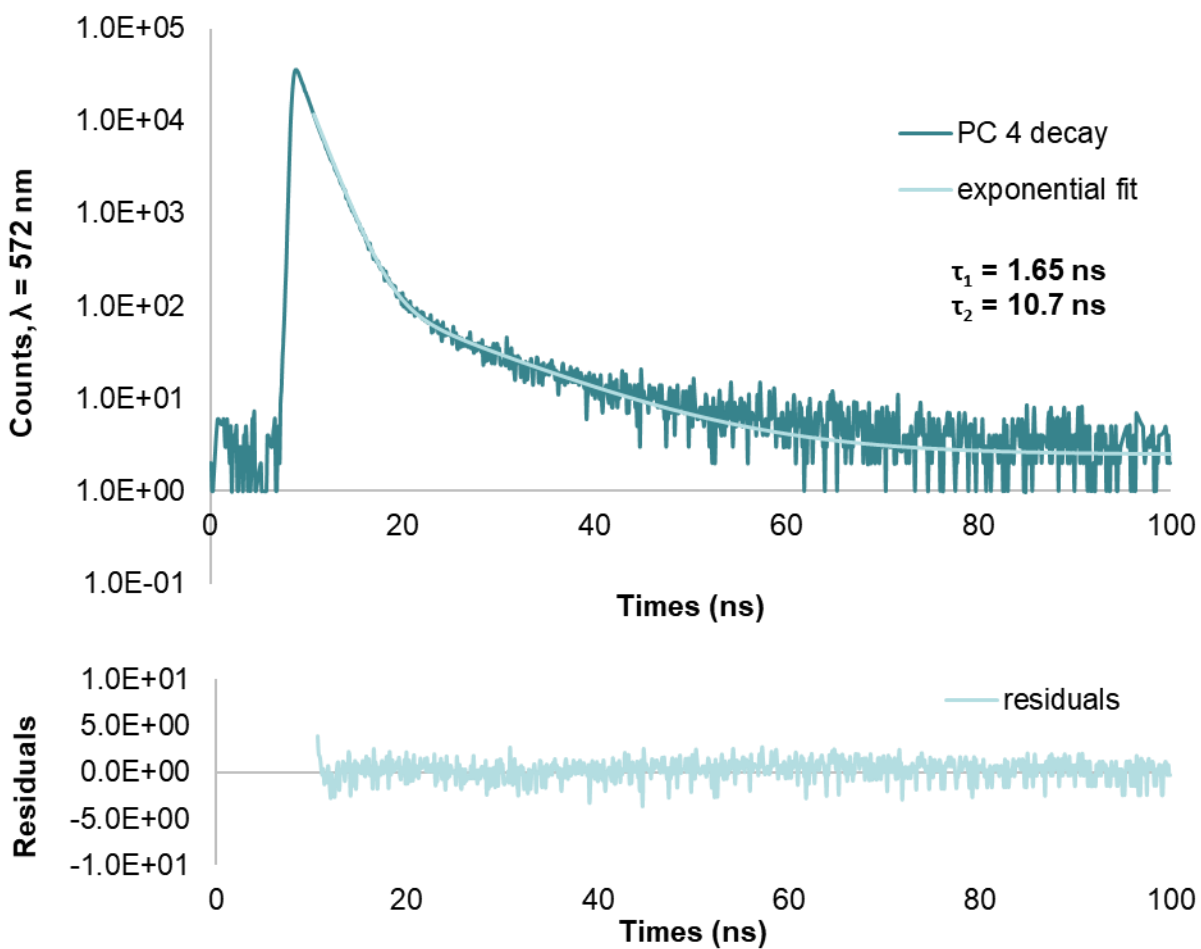


Figure A4.54. Fluorescence decay curve of PC 4 (dark turquoise) with biexponential fit of the decay data (light turquoise), $\lambda_{\text{ex}} = 385$ nm, $\lambda_{\text{em}} = 572$ nm. The data on the bottom shows the residuals from the biexponential fit of the data.

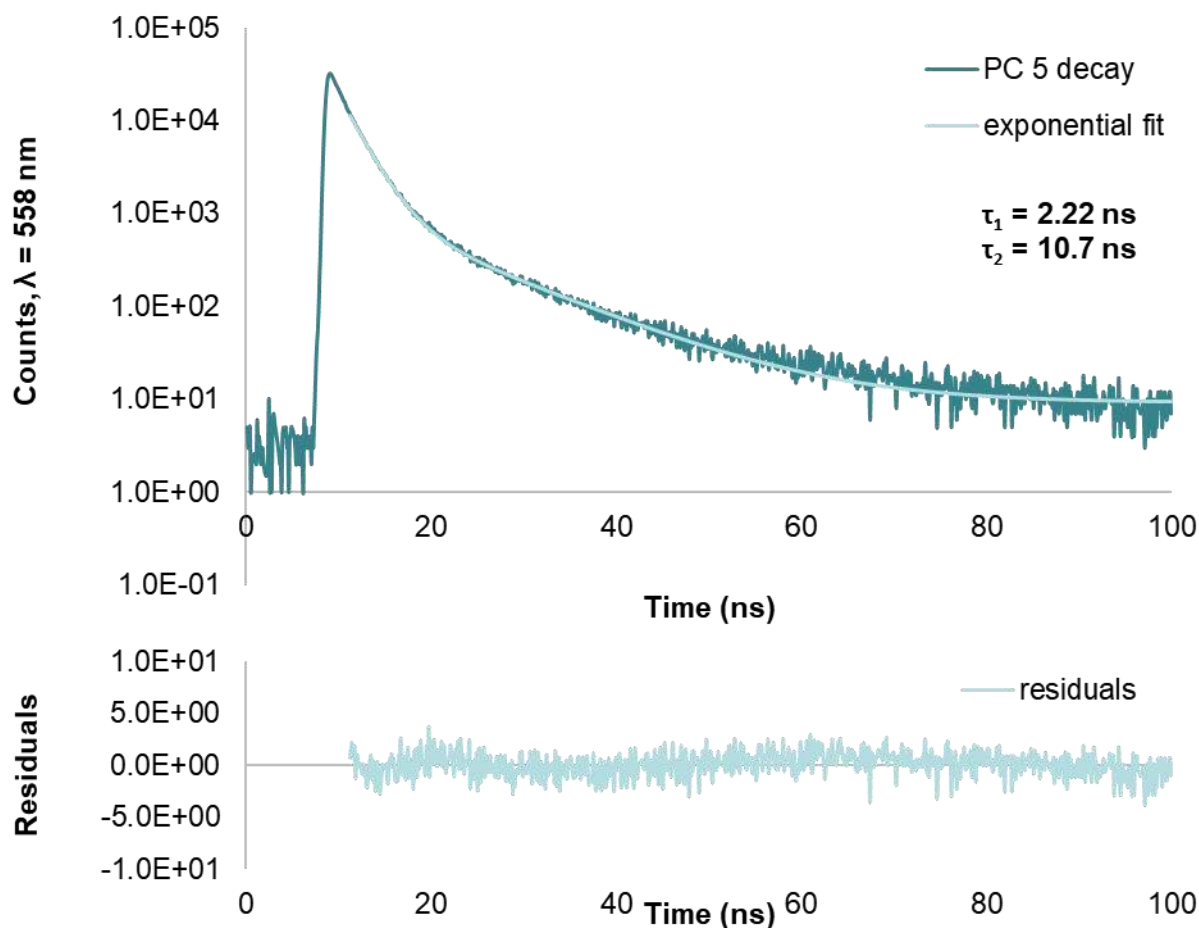


Figure A4.55. Fluorescence decay curve of PC **5** (dark turquoise) with biexponential fit of the decay data (light turquoise), $\lambda_{\text{ex}} = 389 \text{ nm}$, $\lambda_{\text{em}} = 588 \text{ nm}$. The data on the bottom shows the residuals from the biexponential fit of the data.

Cyclic Voltammetry

Samples were characterized by cyclic voltammetry in DMAc or EtOAc. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate (NBu₄PF₆) in DMAc and 0.03 M NBu₄PF₆ in EtOAc due to solubility, the working electrode was a glassy carbon disk, the counter electrode was a Pt disk, and the reference electrode was Ag/AgNO₃ (0.01 M in acetonitrile with 0.1 M NBu₄PF₆ supporting electrolyte).

Potentials were converted versus the saturated calomel electrode (SCE) by adding 0.298 V to the potentials versus Ag/AgNO₃. Prior to measurement, the solutions were sparged with N₂ for 10-15 minutes.

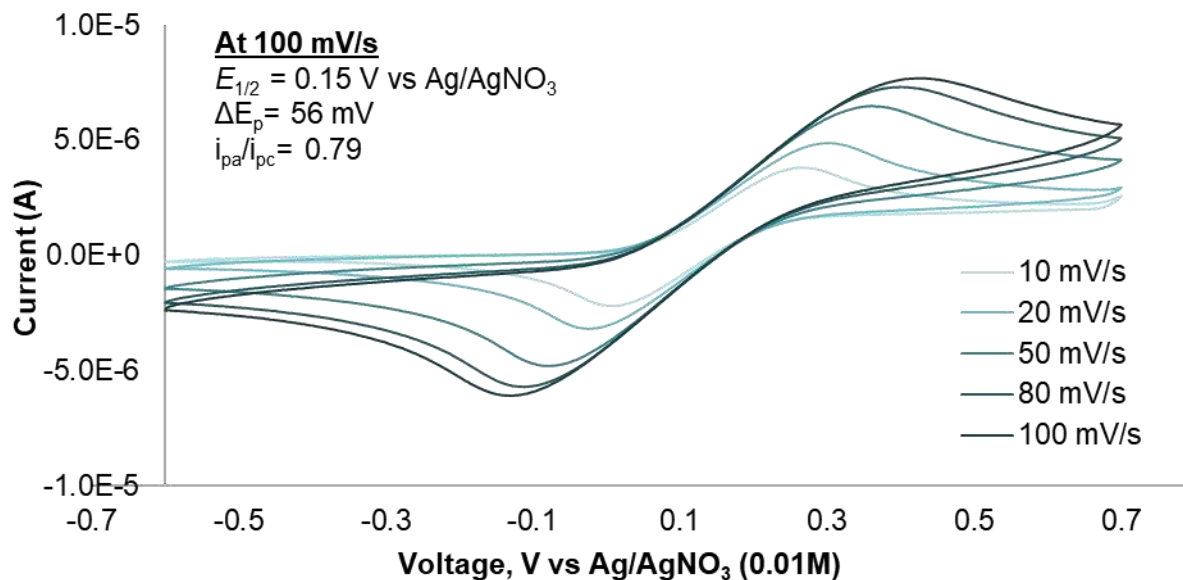


Figure A4.56. Cyclic voltammograms of PC **1** in EtOAc at various scan rates.

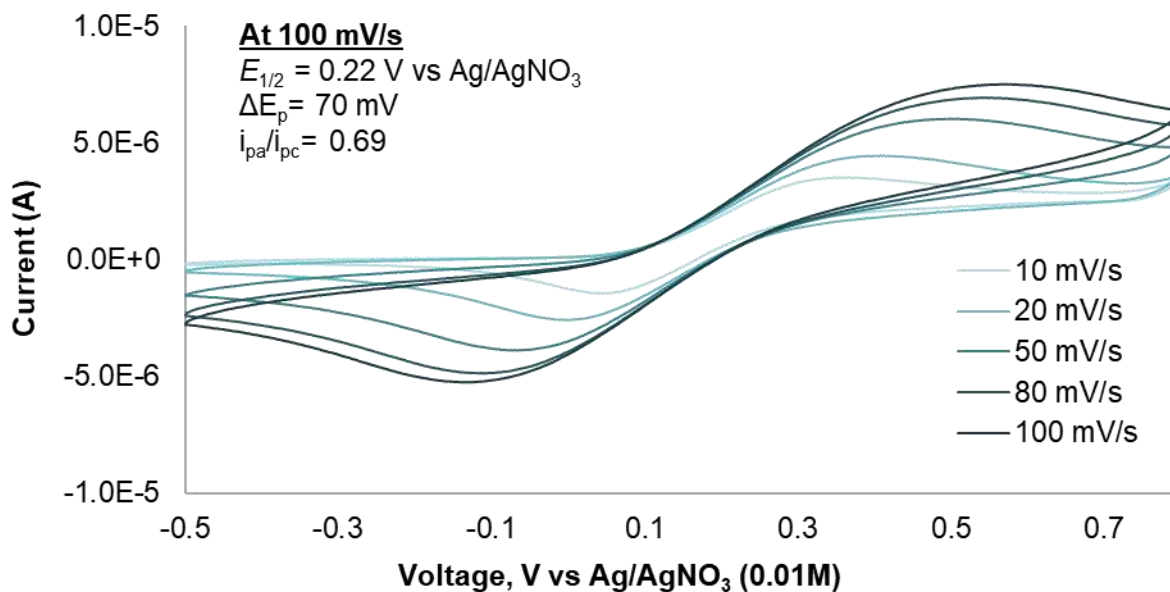


Figure A4.57. Cyclic voltammograms of PC **2** in EtOAc at various scan rates.

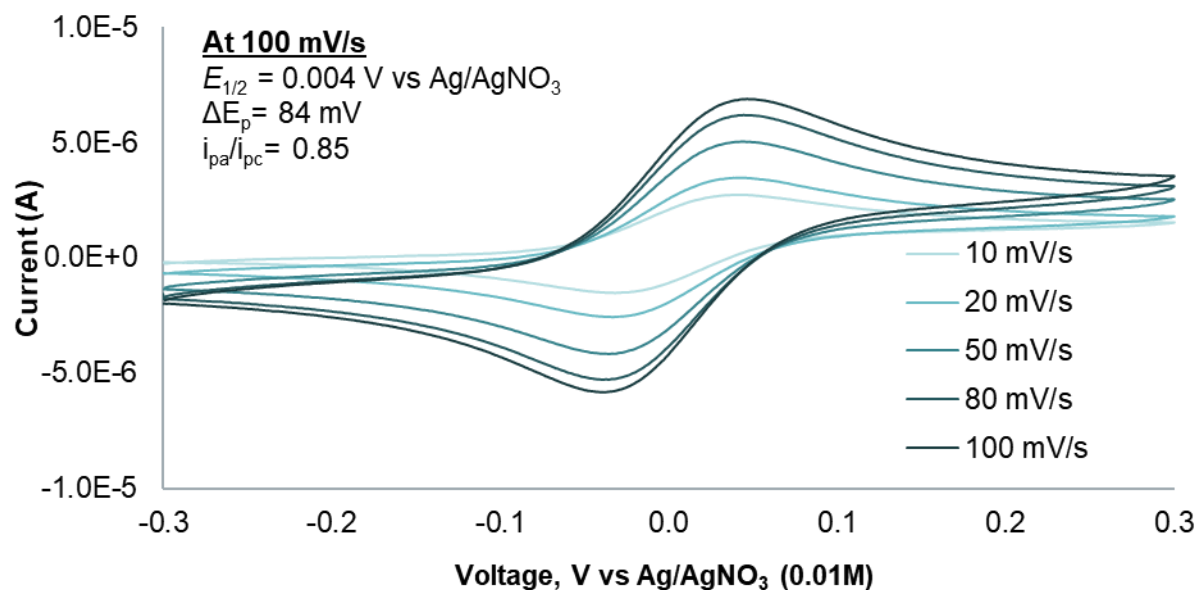


Figure A4.58. Cyclic voltammograms of PC **3** in DMAc at various scan rates.

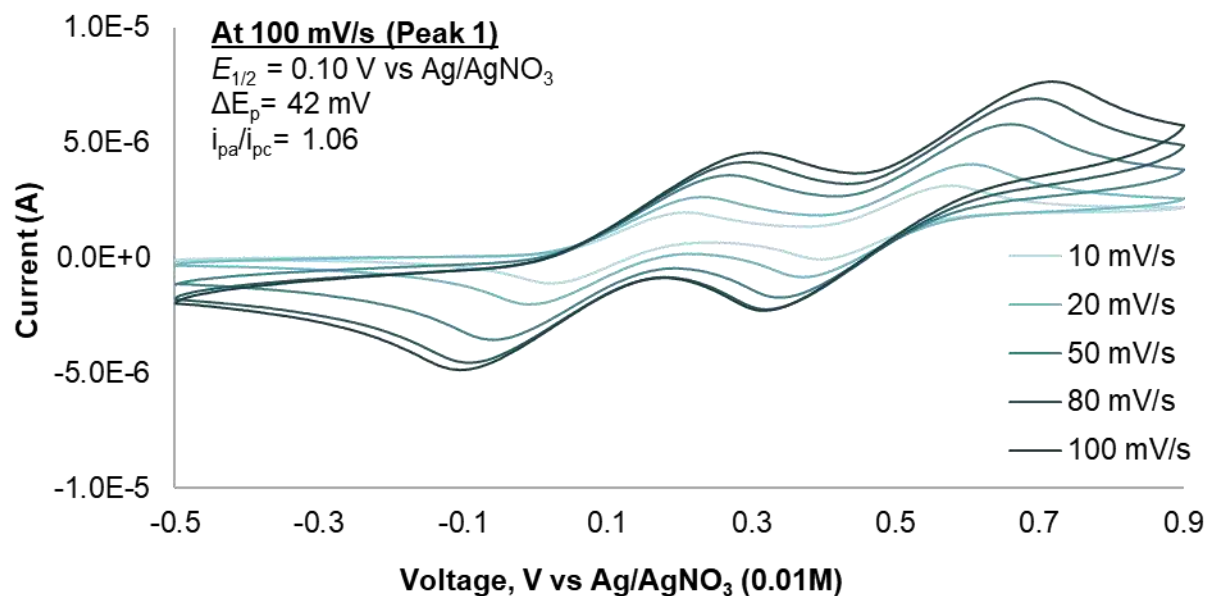


Figure A4.59. Cyclic voltammograms of PC **3** in EtOAc at various scan rates.

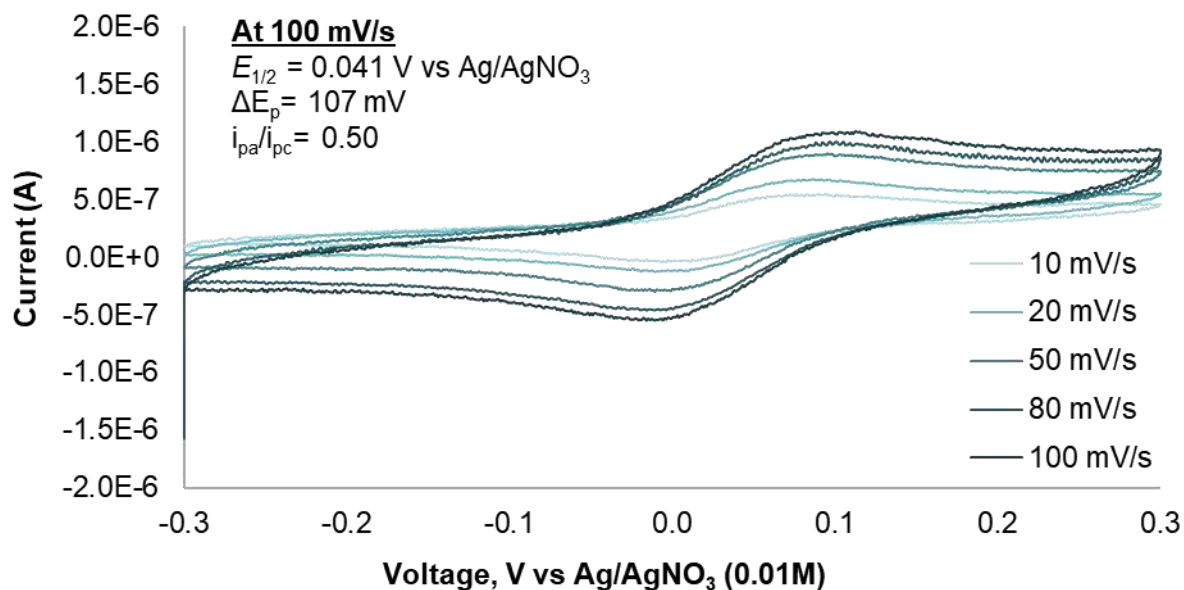


Figure A4.60. Cyclic voltammograms of PC 4 in DMAc at various scan rates.

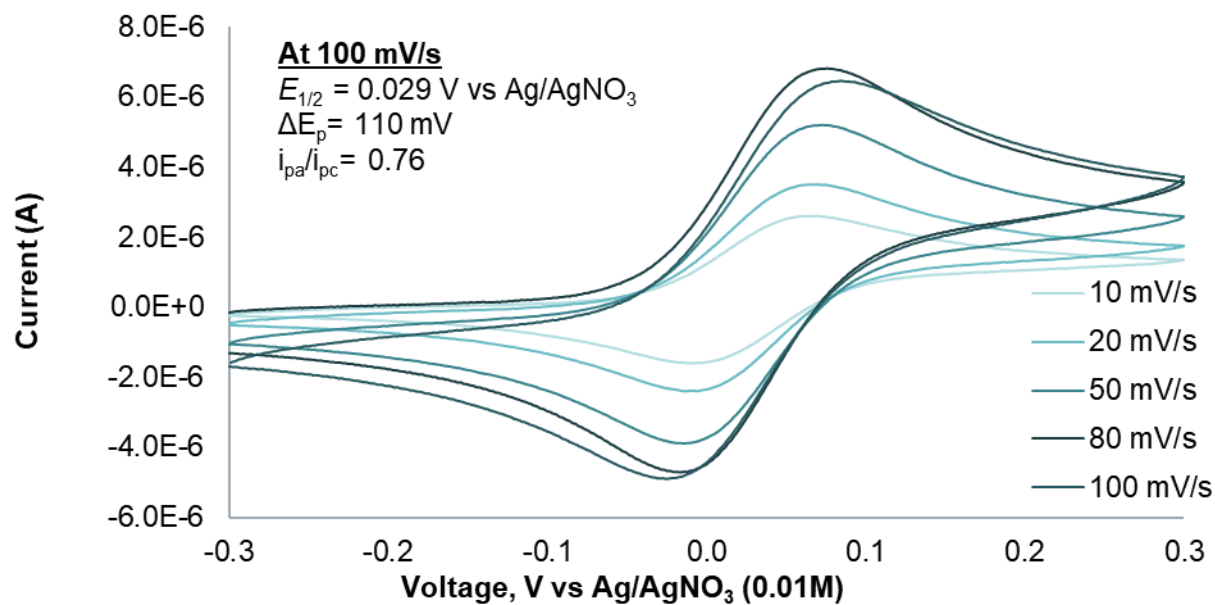


Figure A4.61. Cyclic voltammograms of PC 5 in DMAc at various scan rates.

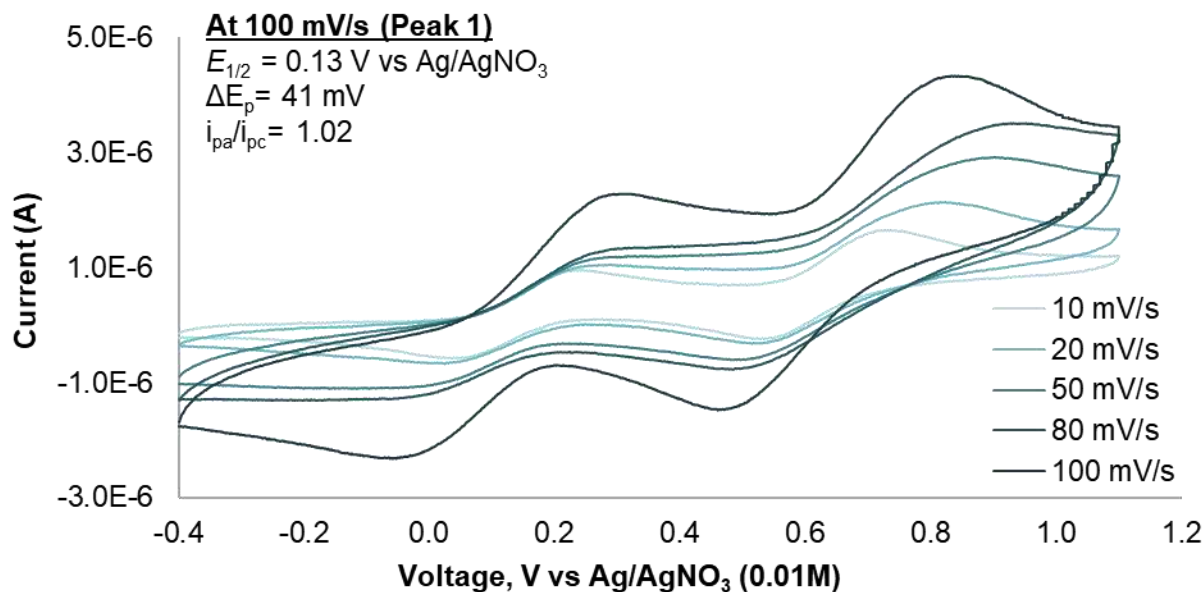


Figure A4.62. Cyclic voltammograms of PC **5** in EtOAc at various scan rates.

Evaluation of Trends in $E_{S1}^{\circ*}$ vs Stokes Shift with Data from Prior Work

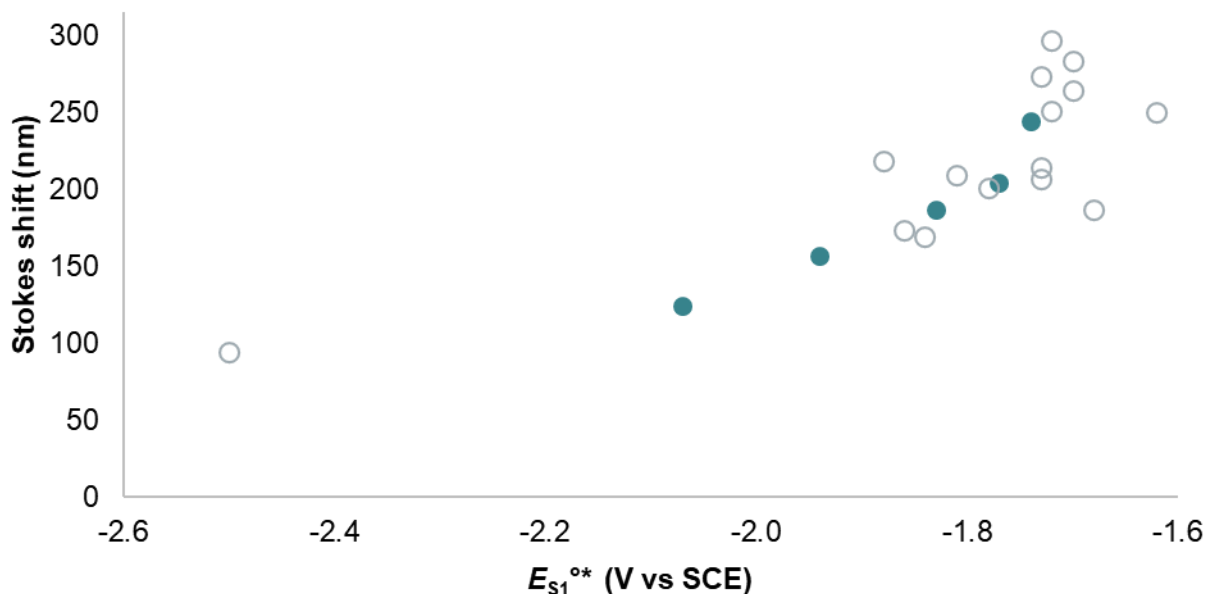


Figure A4.63. Trends in $\Delta\lambda$ vs $E_{S1}^{\circ*}$ and $\Delta\epsilon_{em}$ vs $E_{S1}^{\circ*}$ in DMAc including data points in grey from PCs characterized in prior work (see Table A4.2X for citations). Inclusion of PCs from prior work indicates that other phenazine PCs generally fit the trend observed herein – a more reducing $E_{S1}^{\circ*}$ corresponds to a smaller Stokes shift (indicative of more LE character).

Table A4.2. Previously reported E_{S1}^{0*} and Stokes Shifts for dihydrophenazine PCs.

PC ^a	$E_{S1}^{0*}(^2PC^{*+}/^1PC^*)$ (V vs SCE) ^b	$\Delta\lambda$ (nm) ^c	Reference
1	-1.70	283	3
2	-1.72	297	3
1b	-1.70	264	3
2b	-1.73	273	3
3a	-1.68	187	2
3b	-1.86	173	2
3c	-1.84	169	2
3d	-1.81	209	2
3e	-1.88	218	2
3a	-1.78	201	4
3b	-1.72	251	4
4	-2.50	94	4
4a	-1.73	207	4
5a	-1.73	214	4
5b	-1.62	250	4

^aPC nomenclature from reference ^bSinglet excited state reduction potentials were determined from the $E_{1/2}$ and singlet (E_{S1}) energies measured in DMAc. ^cStokes shift = $\Delta\lambda = \lambda_{\max,em} - \lambda_{\max,abs}$.

Change in Dipole Moment Calculation

The change in the dipole $\Delta\mu$ moment between the ground state and the first excited state can be estimated using the Lippert-Mataga equation^{7,8}:

$$\Delta\nu = \frac{2}{hc} \frac{\Delta\mu^2}{a^3} \Delta f + c$$

Where $\Delta\nu$ is the observed Stokes shift (cm^{-1}) in a given solvent, Δf is the orientation polarizability, which is dependent on the solvent's refractive index and dielectric constant, c is the speed of light, h is Planck's constant, $\Delta\mu$ is the change in dipole upon excitation, a is the radius of the solvent sphere surrounding the molecule, which was estimated using a spherical approximation using half the length of the DFT optimized molecule. The Stokes shifts ($\Delta\nu$) were plotted as a function of solvent orientation polarizability (Δf) in various solvents; $\Delta\mu$ can be extracted from the slope.

Table A4.3. Summary of photophysical, electrical and optical properties for PCs 1 in various solvents.

Solvent	Dielectric Constant (ϵ)	Refractive Index (n, 20°C)	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
Hexene	2.07	1.38	368	480
Benzene	2.27	1.50	370	526
1,4-Dioxane	2.21	1.42	368	541
Ethyl Acetate	6.08	1.37	367	544
Tetrahydrofuran	7.43	1.41	367	565
Pyridine	13.0	1.51	367	585
DMF	37.2	1.43	367	616
DMAc	37.8	1.42	368	615

Table A4.4. Summary of photophysical, electrical and optical properties for PCs 2 in various solvents.

Solvent	Dielectric Constant (ϵ)	Refractive Index (n, 20°C)	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
Hexene	2.07	1.38	375	484
Benzene	2.27	1.50	376	510
1,4-Dioxane	2.21	1.42	375	527
Ethyl Acetate	6.08	1.37	380	525
Tetrahydrofuran	7.43	1.41	375	548
Pyridine	13.0	1.51	378	559
DMF	37.2	1.43	376	586
DMAc	37.8	1.42	378	584

Table A4.5. Summary of photophysical, electrical and optical properties for PC 3 in various solvents.

Solvent	Dielectric Constant (ϵ)	Refractive Index (n, 20°C)	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
Hexene	2.07	1.38	396	502
Benzene	2.27	1.50	401	510
1,4-Dioxane	2.21	1.42	399	513
Ethyl Acetate	6.08	1.37	400	510
Tetrahydrofuran	7.43	1.41	398	515
Pyridine	13.0	1.51	400	520
DMF	37.2	1.43	402	520
DMAc	37.8	1.42	400	524

Table A4.6. Summary of photophysical, electrical and optical properties for PC 4 in various solvents.

Solvent	Dielectric Constant (ϵ)	Refractive Index (n, 20°C)	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
Hexene	2.07	1.38	391	505
Benzene	2.27	1.50	387	517
1,4-Dioxane	2.21	1.42	386	518
Ethyl Acetate	6.08	1.37	386	514
Tetrahydrofuran	7.43	1.41	384	525
Pyridine	13.0	1.51	386	537
DMF	37.2	1.43	385	552
DMAc	37.8	1.42	385	572

Table A4.7. Summary of photophysical, electrical and optical properties for PC 5 in various solvents.

Solvent	Dielectric Constant (ϵ)	Refractive Index (n, 20°C)	$\lambda_{\text{max,abs}}$ (nm)	$\lambda_{\text{max,em}}$ (nm)
Hexene	2.07	1.38	385	517
Benzene	2.27	1.50	390	527
1,4-Dioxane	2.21	1.42	387	528
Ethyl Acetate	6.08	1.37	389	521
Tetrahydrofuran	7.43	1.41	388	530
Pyridine	13.0	1.51	391	542
DMF	37.2	1.43	385	551
DMAc	37.8	1.42	389	546

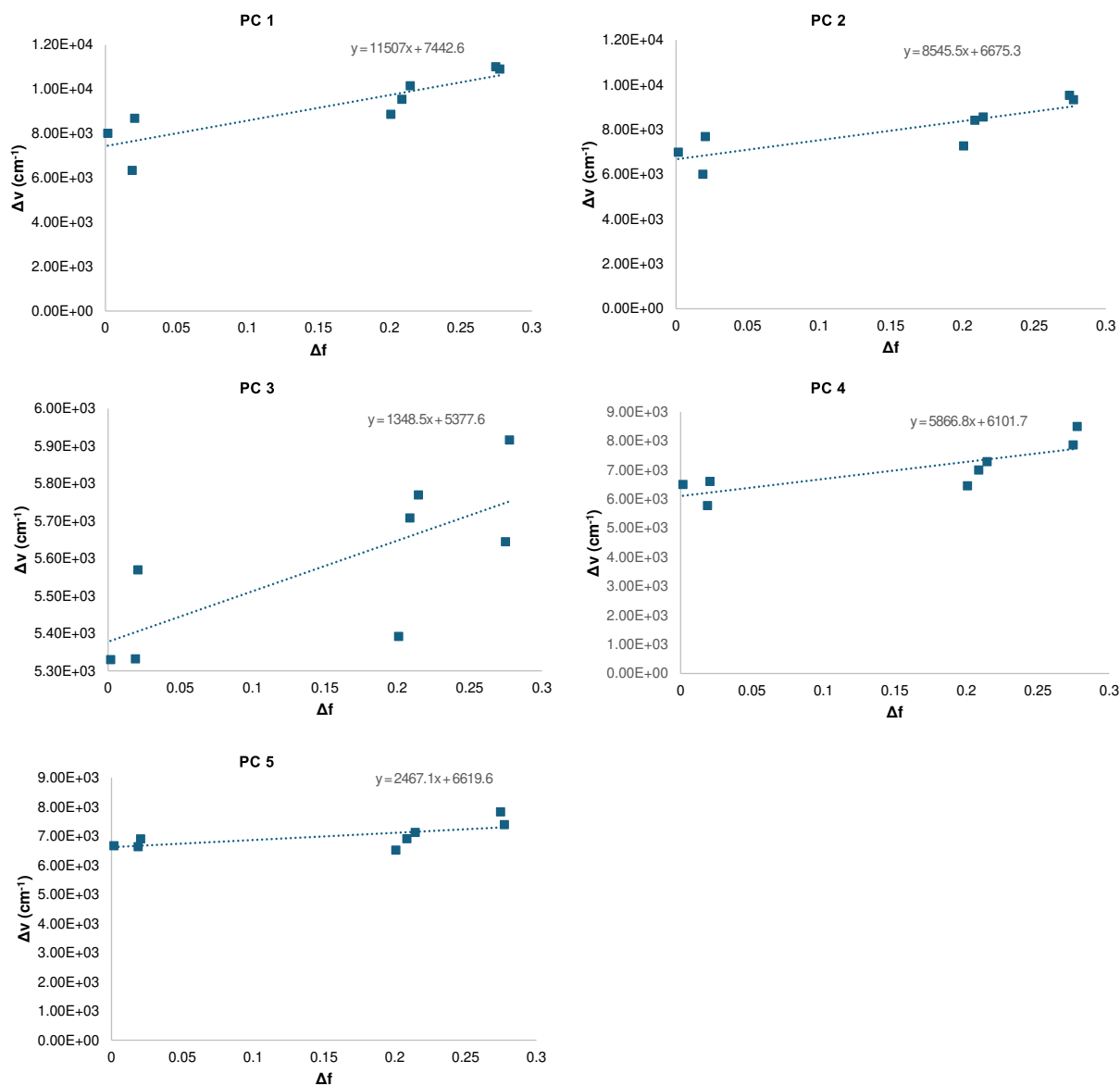


Figure A4.64. Lippert-Mataga plots for PC 1, PC 2, PC 3, PC 4 and PC 5 in various solvents. Stokes shift ($\Delta\nu$) is plotted as a function of solvent orientation polarizability (Δf).

SUPPLEMENTAL POLYMERIZATION DATA

Reaction conditions unless stated otherwise were $[\text{MMA}]:[\text{DBMM}]:[\text{PC}] = [1000]:[10]:[1]$, 1.00 mL of solvent (EtOAc or DMAc), 1.00 mL of monomer (MMA or *n*-BA) in scintillation vials in a N_2 filled glovebox with stir bars. O-ATRP was run with a white LED beaker as the light source.

To monitor polymerizations, 0.1 mL aliquots were removed periodically using a nitrogen purged syringe and needle. Aliquots were quenched in a deuterated chloroform containing 250 ppm butylated hydroxytoluene (BHT). These solutions were then transferred to an NMR tube for ^1H NMR analysis to determine the extent of monomer conversion. Afterwards, solutions were dried and dissolved in unstabilized THF for GPC analysis to obtain number average molecular weight (M_n) and dispersity (D).

Analysis of polymer molecular weights were performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μm MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using THF as the eluent at a flow rate of 1.0 mL/min. A dn/dc value of 0.084 was used for PMMA molecular weight analysis and 0.065 for P(*n*-BA).

Kinetics for O-ATRP of MMA in DMAc

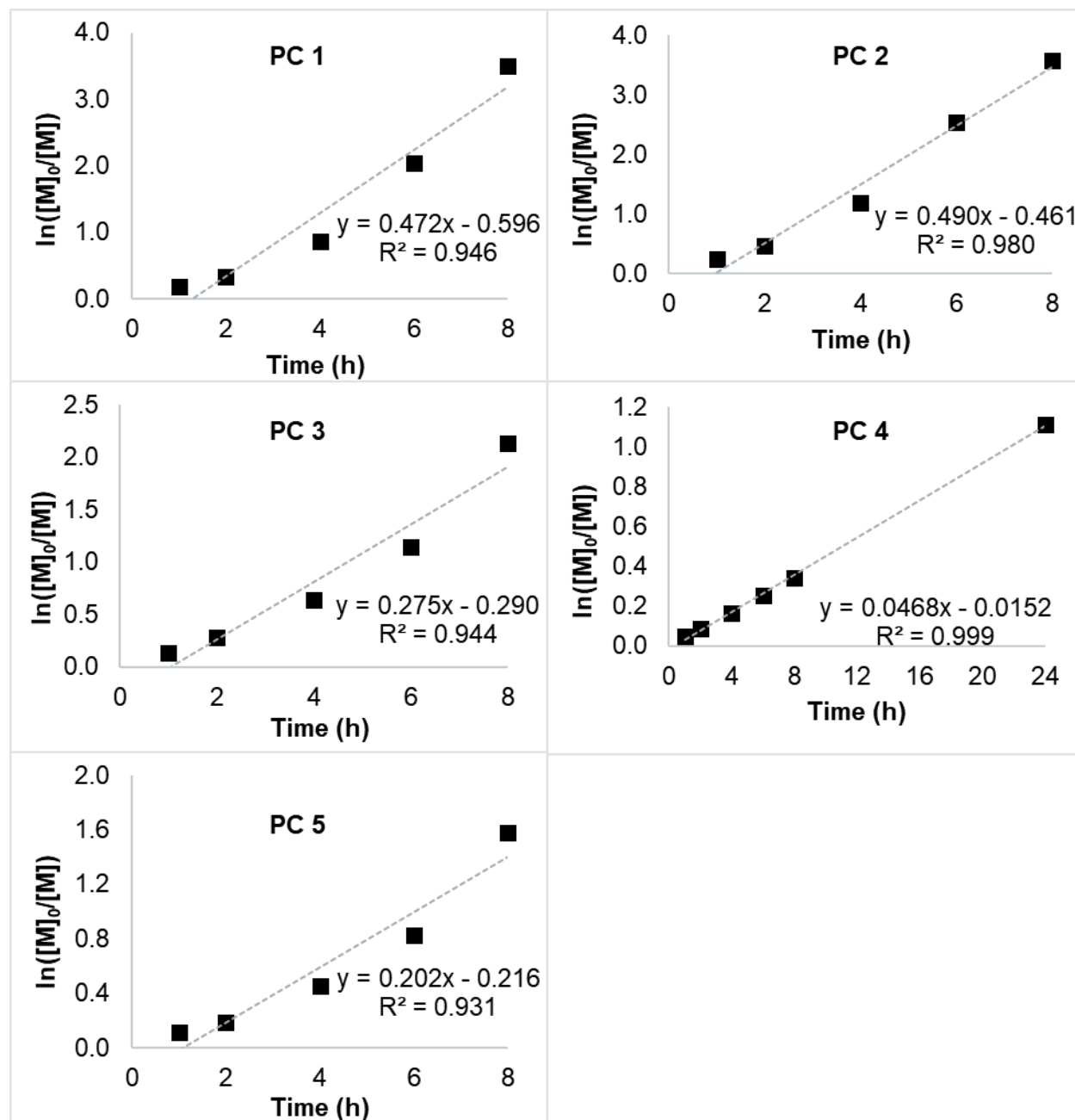


Figure A4.65. Pseudo-first-order kinetics plots for O-ATRP of MMA run in DMAc with PCs 1-5. Timepoints taken at 1, 2, 4, 6, and 8 hours, additional timepoint taken at 24 hours for PC 4.

Kinetics for O-ATRP of MMA in EtOAc

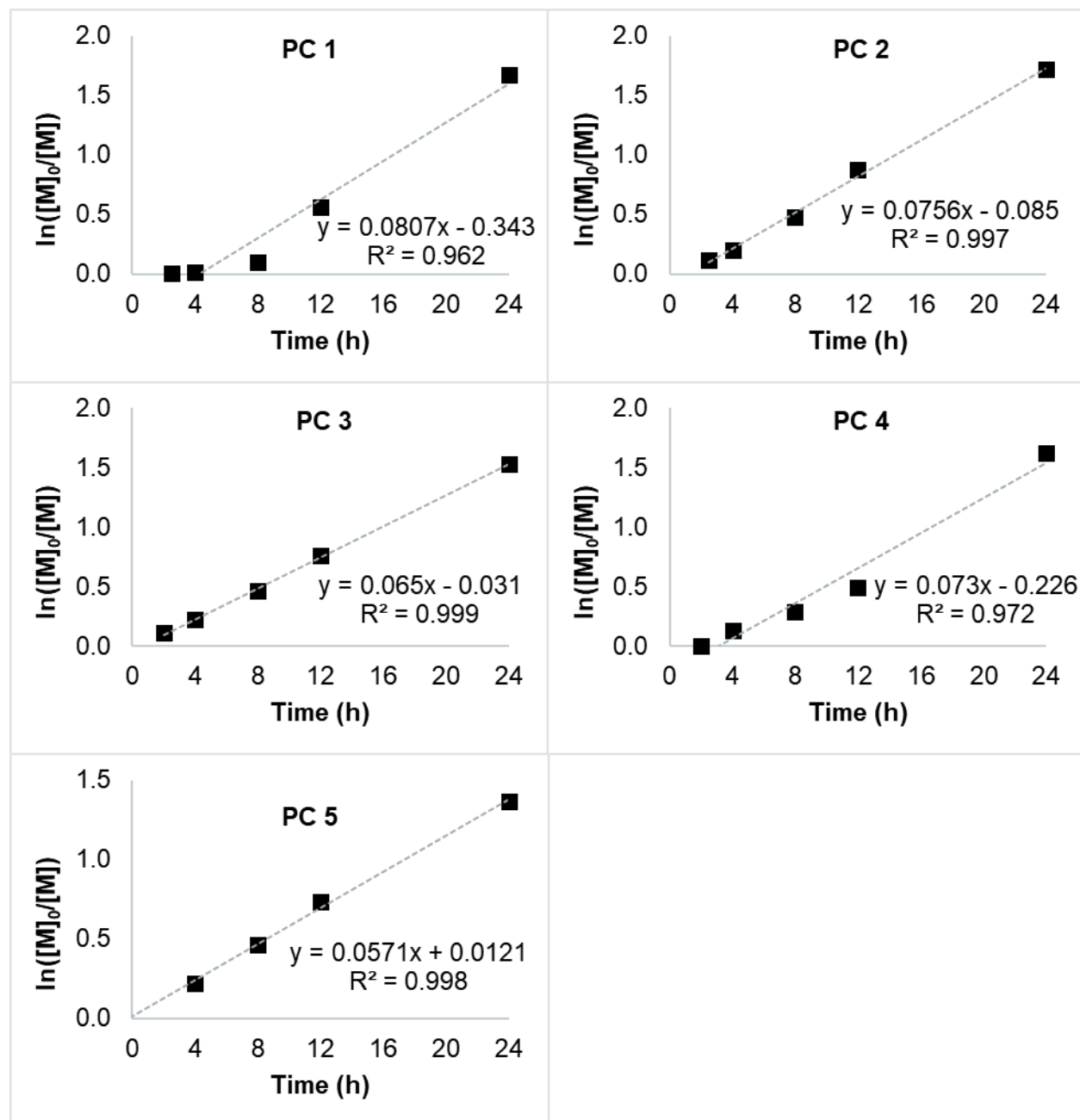


Figure A4.66. Pseudo-first-order kinetics plots for O-ATRP of MMA run in EtOAc with PCs 1-5. Timepoints taken at 2, 4, 8, 12, and 24 hours.

O-ATRP of MMA at Varied PC loadings

O-ATRP of MMA at varied PC loadings were run and analyzed as described at the beginning of the Supplemental Polymerization Data section.

Table A4.8. Results from O-ATRP of MMA in EtOAc for varied PC loadings.

PC	PC loading (ppm)	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
1	100	95.4	9.81	10.4	1.16	94
1	10	83.3	8.59	7.85	1.91	109
2	100	93.6	9.62	9.79	1.15	98
2	10	91.5	9.41	12.1	1.26	78
2	1	34.6	3.72	11.2	1.54	33
3	100	96.8	9.94	10.4	1.13	95
3	10	97.8	10.1	10.3	1.32	97
3	1	55.6	5.82	7.65	1.47	76
4	100	95.6	9.83	10.1	1.29	98
4	10	96.7	9.94	10.0	1.26	99
4	1	64.2	6.68	9.70	1.55	69
5	100	85.4	8.80	8.55	1.13	103
5	10	95.8	9.84	10.3	1.24	96
5	1	87.8	9.04	13.1	1.33	69

Conditions: [MMA]:[DBMM] = [1000]:[10], PC loading is relative to mols of monomer, 1.00 mL of EtOAc, 1.00 mL of MMA. ^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering. ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

O-ATRP at DP = 500 for PCs 2, 3, and 5

Table A4.9. Results from O-ATRP of MMA in EtOAc using PCs 2, 3, and 5 targeting DP= 500

PC	DP	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
2	500	80.4	40.5	35.3	1.27	115
3	500	74.6	37.6	29.3	1.37	128
5	500	90.8	45.7	39.9	1.40	115

Conditions: [MMA]:[DBMM]:[PC] = [1000]:[X]:[1], X = 4(S1); 2(S2); 1(S3), 2.00 mL EtOAc was used instead of 1.00 mL to avoid high viscosities, 1.00 mL of MMA. ^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering. ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

Control Reactions for MMA

O-ATRP control reactions were set up as described at the beginning of the Supplemental Polymerization Data section with the differences noted in Table A4.10 below. These control reactions indicate that PC 3 is acting as a photoredox catalyst that mediates O-ATRP of MMA.

Table A4.10. O-ATRP controls using PC 3 for polymerization of MMA in EtOAc.

ID	Control	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
A	No PC	7.4	0.99	36.1	1.76	2.8
B	No DBMM	83.2	8.58	14.2	1.83	61
C	No PC, no DBMM	2.9	0.54	175	1.95	0.3
D	No light	0	-	-	-	-

Conditions: [MMA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of EtOAc, 1.00 mL of MMA unless otherwise noted. ^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering. ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

O-ATRP of *n*-BA in DMAc and EtOAc

O-ATRP of *n*-BA at varied PC loadings were run and analyzed as described at the beginning of the Supplemental Polymerization Data section.

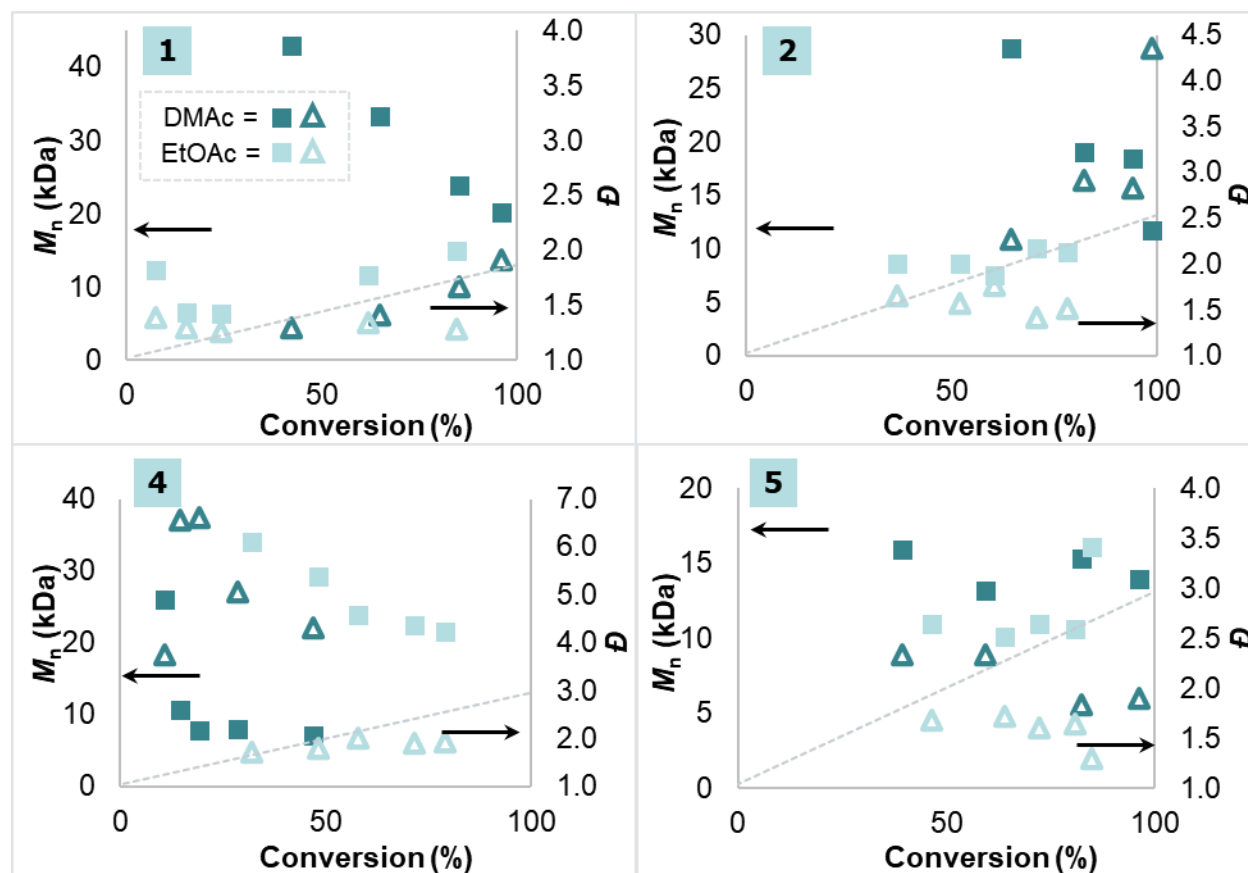


Figure A4.67. Conditions: $[n\text{-BA}]:[\text{DBMM}]:[\text{PC}] = [1000]:[10]:[1]$, 1.00 mL of solvent (DMAc or EtOAc), 1.00 mL of *n*-BA. Plots of M_n vs monomer (*n*-BA) conversion to polymer (squares) and D (triangles, secondary y-axis) for each time point in DMAc (dark turquoise) and EtOAc (light turquoise), PCs 1-5. $M_{n,theo}$ values are represented by the dashed grey line.

Table A4.11. O-ATRP results using PCs 1-5 for the polymerization of *n*-BA in DMAc and EtOAc.

PC	Solvent	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
1	DMAc	96.2	12.6	20.2	1.91	62
2	DMAc	99.0	13.0	11.7	4.36	110
3	DMAc*	97.7	12.5	13.4	1.38	95
4	DMAc*	47.1	6.29	7.11	4.32	88
5	DMAc	96.3	13.0	13.9	1.90	91
1	EtOAc	84.7	11.1	15.0	1.29	74
2	EtOAc	78.3	10.3	9.68	1.51	106
3	EtOAc	71.6	9.43	9.75	1.24	97
4	EtOAc	79.2	10.4	21.5	1.93	48
5	EtOAc	85.0	11.2	16.1	1.30	69

Conditions: [*n*-BA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of solvent (DMAc or EtOAc), 1.00 mL of MMA. ^aConversion determined by ¹H NMR at 8 hours, *4 hours (DMAc) or 24 hours (EtOAc). ^bDetermined by GPC with multi-angle light scattering. ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

Kinetics for O-ATRP of *n*-BA in DMAc

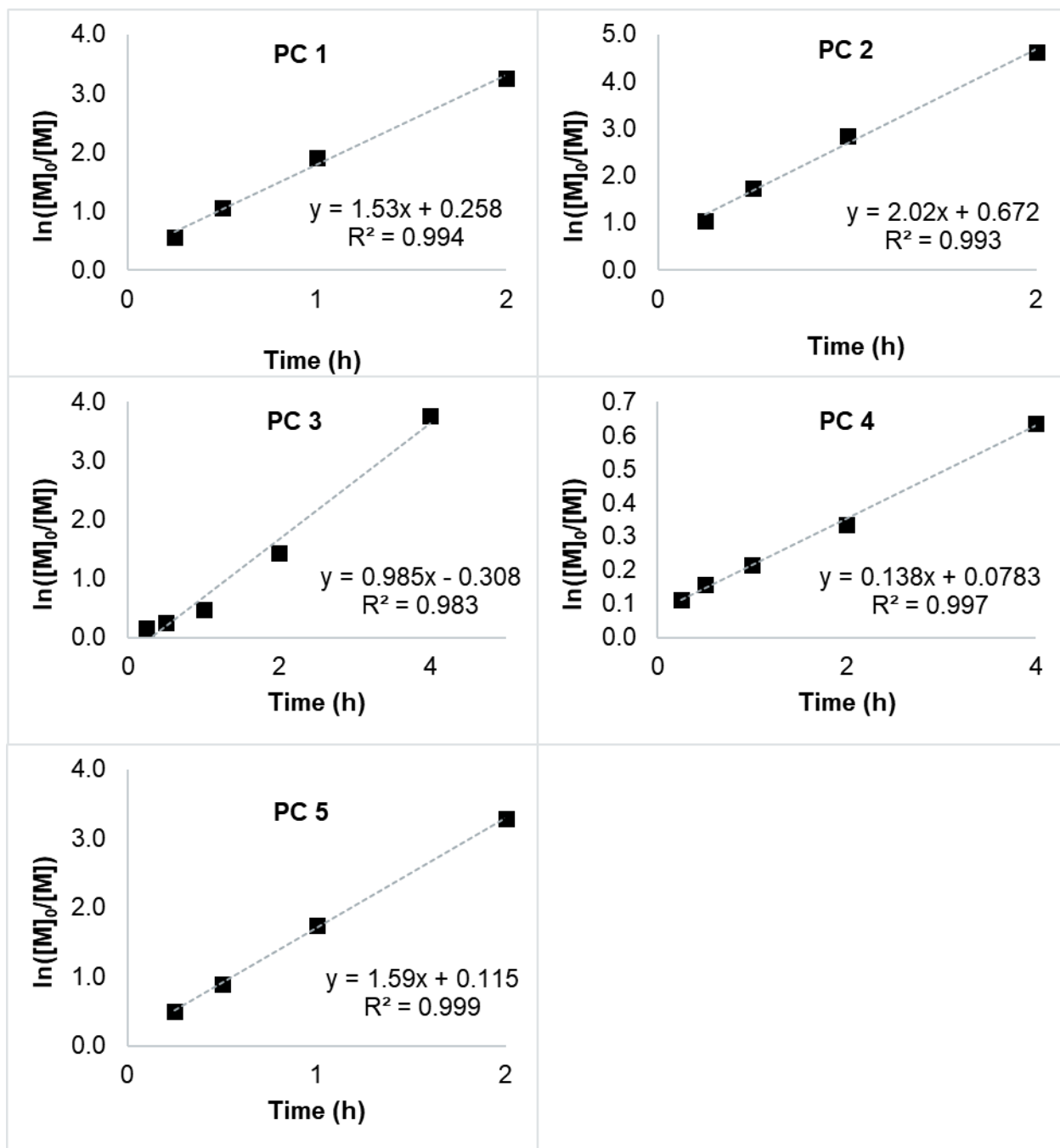


Figure A4.68. Pseudo-first-order kinetics plots for O-ATRP of *n*-BA run in DMAc with PCs 1-5. Timepoints taken at 15 min, 30 min, 1 hour, and 2 hours (and 4 hours for PC 3 and 4).

Kinetics for O-ATRP of *n*-BA in EtOAc

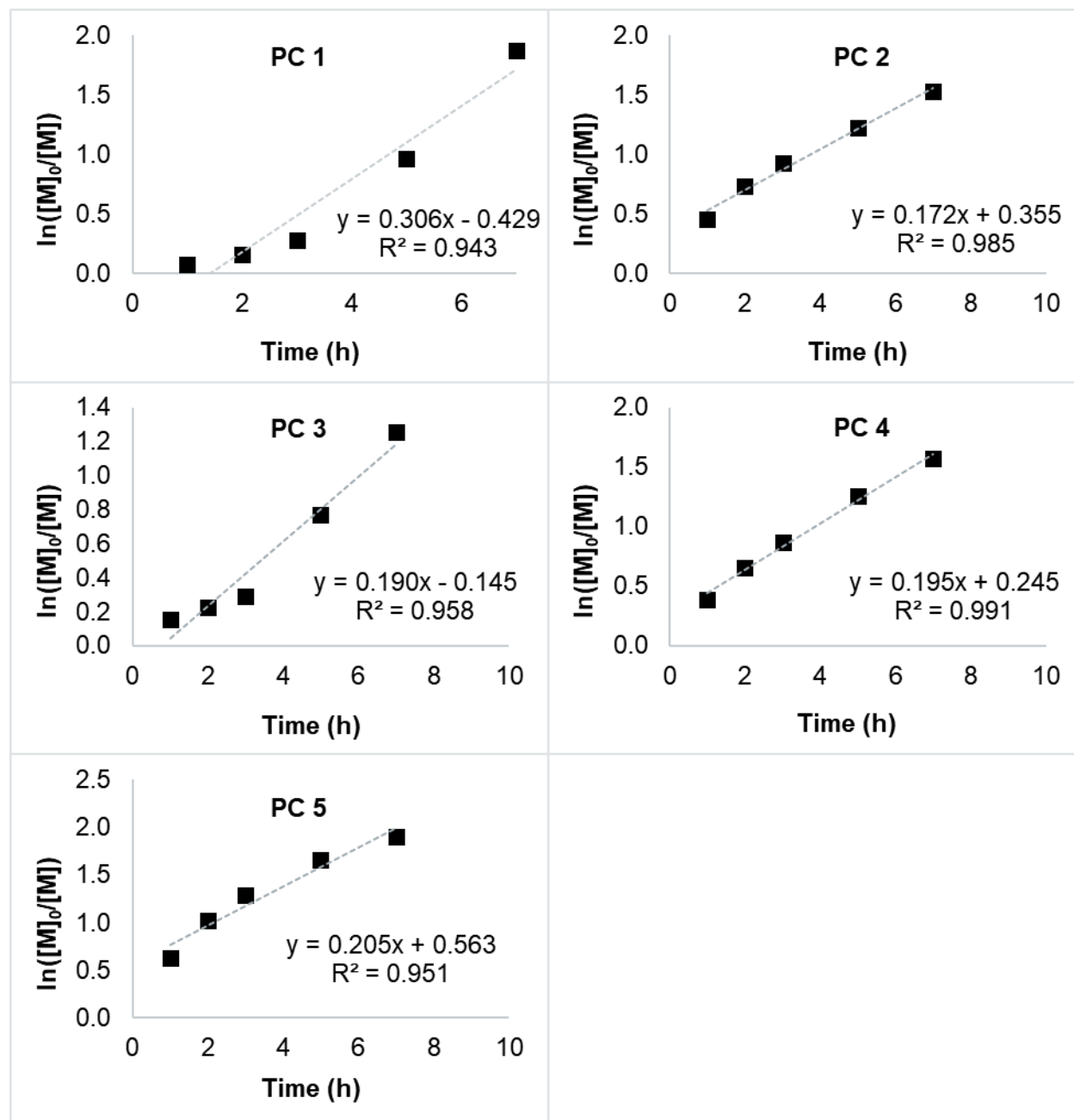


Figure A4.69. Pseudo-first-order kinetics plots for O-ATRP of *n*-BA run in EtOAc with PCs 1-5. Timepoints taken at 1, 2, 3, 5, and 7 hours.

Control Reactions for *n*-BA

O-ATRP control reactions were set up as described at the beginning of the Supplemental Polymerization Data section with the differences noted in Table A4.12 below. These control reactions indicate that PC 3 is acting as a photoredox catalyst that mediates O-ATRP of *n*-BA.

Table A4.12. O-ATRP controls using PC 3 for polymerization of *n*-BA in EtOAc.

ID	Control	Conv. (%) ^a	$M_{n, \text{theo}}$ (kDa)	$M_{n, \text{exp}}$ (kDa) ^b	$\bar{D}^b$	I^* (%) ^c
A	No PC	9.9	1.52	65.4	1.93	2.0
B	No DBMM	69.5	9.16	86.6	2.22	11
C	No PC, no DBMM	0	-	-	-	-
D	No light	0	-	-	-	-

Conditions: [*n*-BA]:[DBMM]:[PC] = [1000]:[10]:[1], 1.00 mL of EtOAc, 1.00 mL of *n*-BA. ^aConversion determined by ¹H NMR at 24 hours. ^bDetermined by GPC with multi-angle light scattering. ^c $I^* = (M_{n, \text{theo}} / M_{n, \text{exp}}) \times 100$.

COMPUTATIONAL METHODOLOGY

All density functional theory (DFT) calculations were carried out in *Gaussian 16* version C01.⁹ The long range separated dispersion-corrected ω B97X-D^{10,11} functional and Pople's double- ζ valence 6-31+G(d,p)¹²⁻¹⁶ basis set were used to optimize all stationary points. Single-point energy calculations were performed using the hybrid meta-GGA M06-2X¹⁷ functional applied with Grimme's D3 dispersion¹⁸ in conjunction with the def2-SVPD^{19,20} (for C and H) and def2-TZVPD^{20,21} (for O, S and N) basis sets. Solvation effects were accounted in geometry optimizations and single-point energy calculations by using the SMD²² variation of the integral equation formalism variant of the polarizable continuum model²³⁻²⁶ (IEF-PCM) under the presence of solvent, dimethylacetamide (smd, solvent= *N,N*-dimethylacetamide).

Vibrational frequencies were calculated to verify that stationary points were minima on the potential energy surface (PES). Computed thermochemistry data were corrected using the *Goodvibes*²⁷ program at 273.15 K. *Goodvibes* performs quasi-harmonic corrections to the

computed vibrational entropies following Grimme's quasi-harmonic approximation (QHA) model²⁸ with a frequency cut-off value of 100 cm⁻¹. Also, a standard state correction to 1 M solution from gas phase at 1 atm (option “-c 1”) was used. Conformation sampling was performed manually.

From the optimized geometry, single point time-dependent density functional theory (TD-DFT) calculations were performed at the (SMD= *N,N*-dimethylacetamide) ω B97X-D/6-31+G(d,p) level of theory to calculate the predicted percentage contribution of corresponding orbitals involved in the photoexcitation. Only orbital contributions $\geq 10\%$ were considered.

*Pymol*²⁹ and *Gaussview* were employed to generate all of the molecular graphics. The isovalue used for molecular orbitals is 0.02.

Table A4.13. Compiled thermochemical data computed at the (SMD= *N,N*-dimethylacetamide) M06-2x(D3)/def2-TZVPD(def2-SVPD for C & H)// (SMD= *N,N*-dimethylacetamide) ω B97X-D/6-31+G**

Structure	E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
1	-1708.02	-1708.58	0.36617	-1707.63	0.087972	0.079499	-1707.72	-1707.71
2	-3699.57	-3701.07	0.981397	-3698.52	0.1836	0.160839	-3698.7	-3698.68
3	-4224.01	-4225.23	0.697509	-4223.26	0.146142	0.128757	-4223.41	-4223.39
4	-2631.26	-2632.56	0.691959	-2630.52	0.133433	0.117409	-2630.65	-2630.64
5	-4381.09	-4382.48	0.808467	-4380.22	0.1657	0.144197	-4380.39	-4380.37

Cartesian Coordinates:

1	Eopt -1708.575553			C	-0.702156	-1.217541	-0.091086
C	-0.708091	3.634871	-0.362198	C	-1.381186	-2.425044	-0.234832
C	-1.397169	2.425876	-0.221862	H	-2.465003	-2.437514	-0.218299
C	-0.710175	1.222061	-0.085045	C	-0.683977	-3.628541	-0.382301
C	0.701115	1.226830	-0.099284	C	0.701355	-3.623662	-0.397856
C	1.377154	2.435245	-0.249593	C	1.393227	-2.415375	-0.265253
C	0.677254	3.639524	-0.376088	H	-2.481032	2.431058	-0.205491
C	0.709047	-1.212702	-0.105966	H	2.461051	2.447488	-0.255311

H	2.477210	-2.419994	-0.273073	F	7.582876	1.014835	0.880144
C	2.812228	0.011645	0.081188	H	1.259849	-4.547538	-0.510136
C	3.513178	0.032625	-1.122828	H	1.229605	4.567796	-0.482291
C	3.493424	-0.010411	1.296476	H	-1.268753	4.559362	-0.457198
C	4.904163	0.031752	-1.116010	H	-1.238376	-4.556317	-0.481929
C	4.882936	-0.012758	1.309021	126			
H	2.931139	-0.026694	2.224428	2		Eopt	-3701.072729
C	5.582239	0.009073	0.101220	C	-3.640755	-0.548597	-0.313351
H	5.416561	-0.031912	2.254041	C	-2.419566	-1.221675	-0.178223
N	1.383645	0.008796	0.085342	C	-1.210284	-0.559056	-0.030758
N	-1.381290	-0.000519	0.114076	C	-1.210698	0.844866	0.013260
C	-2.810089	-0.005725	0.118057	C	-2.422713	1.512879	-0.088732
C	-3.517282	0.004085	-1.085929	C	-3.641993	0.847719	-0.267996
C	-3.484866	-0.021341	1.333612	C	1.214057	0.844599	0.013951
C	-4.904759	-0.000532	-1.070331	C	1.213392	-0.559332	-0.030335
C	-4.877722	-0.026734	1.355080	C	2.422679	-1.222234	-0.176528
H	-2.918855	-0.029266	2.259396	H	2.417353	-2.305113	-0.184938
C	-5.579723	-0.016821	0.153208	C	3.643861	-0.549204	-0.312165
H	2.968473	0.049175	-2.061487	C	3.645327	0.847168	-0.266317
H	-2.976283	0.015662	-2.026811	C	2.426296	1.512469	-0.085990
H	-5.457928	0.008749	-2.004187	H	-2.414604	-2.304509	-0.187308
H	-5.402700	-0.038660	2.303403	H	-2.411705	2.595561	-0.035593
H	5.448639	0.047789	-2.053212	H	2.415258	2.595115	-0.031142
C	-7.081873	-0.006633	0.141140	C	0.000813	2.946873	-0.121541
C	7.084014	-0.005734	0.144246	C	0.011320	3.373378	-1.451587
F	-7.620481	-0.118664	1.369419	C	-0.014011	3.867193	0.918571
F	-7.576872	1.134965	-0.394525	C	0.005282	4.729547	-1.738563
F	-7.592434	-1.017193	-0.600115	C	-0.020836	5.231848	0.634710
F	7.647928	0.086026	-1.074417	H	-0.022113	3.516385	1.945276
F	7.564128	-1.140116	0.707439	C	-0.012743	5.654646	-0.690884

H	-0.033770	5.950311	1.446432	C	-6.831652	-2.415938	0.757400
N	0.001766	1.544237	0.170801	C	-4.955872	-1.672969	2.066242
N	0.001498	-1.266050	0.090641	C	-7.486612	-2.825882	1.914058
C	0.000311	-2.652253	-0.270260	H	-7.316157	-2.538264	-0.209340
C	0.006920	-3.013166	-1.619626	C	-5.613076	-2.077243	3.229660
C	-0.010468	-3.622698	0.723154	H	-3.975030	-1.213670	2.140177
C	0.002075	-4.353362	-1.973025	C	-6.878037	-2.654846	3.158933
C	-0.015934	-4.971923	0.372322	H	-8.475421	-3.270116	1.845839
H	-0.015841	-3.322878	1.765894	H	-5.133187	-1.931608	4.193200
C	-0.010153	-5.328733	-0.972166	H	-7.390068	-2.964459	4.065214
H	0.023437	2.640272	-2.252172	C	-5.703318	1.627035	0.957962
H	0.015315	-2.241272	-2.382985	C	-7.034292	1.210657	0.966815
H	0.007074	-4.638786	-3.020240	C	-5.087272	1.953992	2.169657
H	-0.025394	-5.730120	1.147173	C	-7.740697	1.110974	2.165777
H	0.013893	5.065810	-2.770477	H	-7.517884	0.940337	0.031272
C	-0.012412	-6.771448	-1.388458	C	-5.790670	1.863574	3.366961
C	-0.009989	7.116906	-1.034011	H	-4.047901	2.270194	2.180090
F	-0.065603	-7.623322	-0.348429	C	-7.119605	1.435642	3.369499
F	-1.065620	-7.066813	-2.186364	H	-8.771539	0.769128	2.157276
F	1.094711	-7.095693	-2.098324	H	-5.298403	2.116573	4.301568
F	-1.015619	7.440876	-1.879783	H	-7.663807	1.350627	4.305503
F	1.134499	7.489502	-1.656085	C	5.565043	-1.836712	0.818484
F	-0.139113	7.913647	0.042397	C	6.837379	-2.415989	0.752402
C	-4.913146	-1.371967	-0.480644	C	4.964445	-1.672956	2.065316
C	-4.929808	1.663726	-0.348504	C	7.494935	-2.825761	1.907632
H	-5.563351	1.235759	-1.132770	H	7.319654	-2.538452	-0.215438
C	4.916144	-1.372341	-0.481480	C	5.624260	-2.077081	3.227316
C	4.933195	1.662877	-0.348704	H	3.983725	-1.213715	2.141316
H	5.565210	1.234731	-1.134136	C	6.889099	-2.654610	3.153834
C	-5.559193	-1.836635	0.820683	H	8.483599	-3.269984	1.837263

H	5.146505	-1.931405	4.191908	C	3.816383	-4.725215	-1.664685
H	7.403157	-2.964096	4.059010	H	3.502395	-5.509809	-0.978142
C	5.709199	1.626109	0.956234	H	2.982724	-4.416810	-2.299660
C	7.040287	1.210048	0.962466	H	4.646119	-5.074182	-2.283241
C	5.095420	1.952878	2.169109	H	5.656014	-0.764883	-1.008638
C	7.749029	1.110436	2.160043	H	-5.654225	-0.764652	-1.006262
H	7.522116	0.939891	0.025966	C	-4.631639	-2.521304	-1.447482
C	5.801159	1.862550	3.365047	O	-4.721009	-2.417327	-2.653850
H	4.055999	2.268867	2.181502	O	-4.231688	-3.633914	-0.831084
C	7.130194	1.434913	3.364980	C	-3.812214	-4.723275	-1.667388
H	8.779928	0.768814	2.149516	H	-3.496549	-5.508259	-0.982001
H	5.310664	2.115396	4.300624	H	-4.642204	-5.072614	-2.285383
H	7.676234	1.349981	4.299919	H	-2.979654	-4.413129	-2.302947
C	4.651668	3.089557	-0.812877	94			
C	-4.648244	3.090352	-0.812835	3		Eopt	-4225.233335
O	-4.189323	3.098335	-2.066403	C	-0.658052	-3.646506	-0.210159
O	-4.808796	4.095912	-0.154643	C	-1.348879	-2.430450	-0.276028
O	4.188640	3.097385	-2.064946	C	-0.693456	-1.223233	-0.469328
O	4.815986	4.095303	-0.155905	C	0.706427	-1.219505	-0.614126
C	-3.777831	4.370767	-2.587641	C	1.387569	-2.425210	-0.566759
H	-3.359037	4.161857	-3.571188	C	0.729151	-3.641130	-0.349333
H	-4.633864	5.043573	-2.676269	C	0.698697	1.206039	-0.631529
H	-3.019584	4.819822	-1.941696	C	-0.700961	1.202680	-0.485715
C	3.777478	4.370064	-2.585804	C	-1.364034	2.408078	-0.306390
H	3.350807	4.160518	-3.565828	H	-2.439288	2.394281	-0.191671
H	3.025766	4.823210	-1.935193	C	-0.680915	3.628964	-0.252681
H	4.635173	5.039720	-2.682174	C	0.706044	3.630934	-0.396563
C	4.633392	-2.522027	-1.447495	C	1.371754	2.416871	-0.601887
O	4.720585	-2.418501	-2.654066	H	-2.424378	-2.421772	-0.161633
O	4.235503	-3.634641	-0.829868	H	2.462795	-2.422789	-0.694496

H	2.446721	2.420350	-0.731847	F	7.623829	-1.074944	-0.690244
C	2.809405	-0.000340	-0.650157	S	-1.517785	-5.193049	0.075771
C	3.342332	0.013528	0.637602	S	-1.548173	5.173690	0.019075
C	3.644462	-0.008507	-1.763882	S	1.626789	5.165945	-0.348597
C	4.720273	0.020178	0.816710	S	1.660108	-5.169480	-0.279240
C	5.023786	-0.002066	-1.589371	C	-3.219900	-4.680615	-0.112585
H	3.211509	-0.019578	-2.758702	C	-3.974568	-4.348392	1.014862
C	5.554436	0.012909	-0.299335	C	-3.782224	-4.581845	-1.388507
H	5.679440	-0.008413	-2.454465	C	-5.286221	-3.901024	0.862808
N	1.388109	-0.006117	-0.830485	H	-3.532922	-4.419358	2.004149
N	-1.403591	-0.013032	-0.541427	C	-5.091616	-4.129660	-1.534084
C	-2.801125	-0.012537	-0.233558	H	-3.191705	-4.838827	-2.262724
C	-3.220493	-0.011624	1.098440	C	-5.842250	-3.784368	-0.410122
C	-3.729839	-0.004934	-1.267707	H	-5.867471	-3.634928	1.740002
C	-4.576053	0.002464	1.393404	H	-5.523281	-4.042917	-2.526535
C	-5.092035	0.010049	-0.975615	H	-6.860083	-3.425295	-0.527249
H	-3.386302	-0.006231	-2.296917	C	-3.251491	4.637865	-0.065575
C	-5.507406	0.017030	0.352454	C	-3.889405	4.533683	-1.304801
H	2.677565	0.019468	1.495723	C	-3.932583	4.297021	1.105666
H	-2.482767	-0.018416	1.894675	C	-5.201178	4.069203	-1.370603
H	-4.905874	0.005533	2.427413	H	-3.355974	4.796660	-2.213201
H	-5.815284	0.020272	-1.783076	C	-5.245854	3.835383	1.033287
H	5.134377	0.031605	1.818381	H	-3.432045	4.373001	2.066134
C	-6.969016	0.031028	0.700660	C	-5.877906	3.715453	-0.203505
C	7.047652	0.019568	-0.139250	H	-5.691956	3.978585	-2.334818
F	-7.765172	0.180782	-0.374420	H	-5.769872	3.561471	1.943572
F	-7.358712	-1.112435	1.313113	H	-6.897253	3.346073	-0.258737
F	-7.279391	1.031444	1.556558	C	3.237226	-4.564163	0.311964
F	7.440411	0.054135	1.147611	C	4.330529	-4.528587	-0.554961
F	7.619690	1.085371	-0.747378	C	3.368555	-4.106552	1.627110

C	5.553572	-4.026468	-0.108123	H	2.370023	2.516914	0.054770
H	4.223698	-4.873589	-1.578830	C	3.635454	0.785893	0.080918
C	4.587710	-3.595158	2.062361	C	3.671895	-0.611087	0.010165
H	2.516155	-4.134673	2.299374	C	2.461997	-1.313228	-0.113493
C	5.681108	-3.552875	1.195516	H	-2.490090	2.402066	0.034250
H	6.400078	-3.993314	-0.787049	H	-2.380905	-2.511513	-0.163757
H	4.683915	-3.228212	3.079767	H	2.499296	-2.394506	-0.183092
H	6.629058	-3.148355	1.536930	C	0.066290	-2.809367	-0.297858
C	3.210608	4.580352	0.244403	C	0.088823	-3.461397	0.933107
C	3.349721	4.136382	1.563438	C	0.076978	-3.535812	-1.486309
C	4.302106	4.547866	-0.624870	C	0.122354	-4.851015	0.980119
C	4.575158	3.641844	2.000430	C	0.110493	-4.924385	-1.444714
H	2.498643	4.161990	2.237485	H	0.059178	-3.009991	-2.435327
C	5.531470	4.063051	-0.176246	C	0.131572	-5.575385	-0.210283
H	4.189296	4.882024	-1.651689	H	0.120082	-5.494327	-2.368340
C	5.667075	3.603324	1.131499	N	0.032427	-1.381831	-0.351064
H	4.677523	3.285328	3.020939	N	-0.033319	1.396940	-0.283570
H	6.376777	4.032768	-0.856797	C	-0.066488	2.824267	-0.265622
H	6.620171	3.212422	1.474394	C	-0.111321	3.508908	0.949839
90				C	-0.053810	3.519422	-1.470024
4		Eopt	-2632.562291	C	-0.146271	4.896244	0.957345
C	-3.670069	0.612474	0.073770	C	-0.086968	4.911680	-1.467769
C	-2.460143	1.319568	-0.018529	H	-0.018381	2.969777	-2.405026
C	-1.234939	0.680700	-0.155022	C	-0.132882	5.592098	-0.254127
C	-1.201376	-0.727574	-0.188389	H	0.080034	-2.880191	1.849755
C	-2.396423	-1.429024	-0.103021	H	-0.119884	2.951075	1.880821
C	-3.638706	-0.785127	0.016756	H	-0.183578	5.432641	1.900213
C	1.234255	-0.669844	-0.191655	H	-0.077534	5.453103	-2.406788
C	1.200506	0.738275	-0.153168	H	0.139786	-5.358800	1.937705
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C	0.183315	-7.076768	-0.193755
F	-0.078790	7.655190	-1.435366
F	-1.344909	7.546405	0.316950
F	0.804346	7.619324	0.540940
F	0.077715	-7.594688	1.044034
F	1.342088	-7.549755	-0.712208
F	-0.807493	-7.628807	-0.931349
C	4.849821	1.625268	0.282664
C	5.119785	2.698633	-0.574745
C	5.728911	1.377904	1.345193
C	6.246796	3.497001	-0.384187
H	4.449648	2.901458	-1.406000
C	6.854381	2.175014	1.537382
H	5.528192	0.556141	2.026705
C	7.119931	3.236008	0.670899
H	6.444085	4.320329	-1.064618
H	7.523661	1.968846	2.367624
H	7.999142	3.855946	0.819396
C	4.936022	-1.399418	0.026936
C	5.088879	-2.469729	0.916627
C	5.981308	-1.110259	-0.859971
C	6.260630	-3.225020	0.929029
H	4.288954	-2.704583	1.613924
C	7.152075	-1.864204	-0.849177
H	5.875134	-0.290547	-1.564858
C	7.297858	-2.922984	0.047883
H	6.363593	-4.046800	1.631815
H	7.951012	-1.626319	-1.545519
H	8.211832	-3.509453	0.057283
C	-4.923784	1.394869	0.263240

C	-5.238398	2.448191	-0.603854
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C	-6.957714	1.861889	1.504173
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C	-7.266748	2.903550	0.628675
H	-6.632401	4.004534	-1.111988
H	-7.620937	1.631655	2.332959
H	-8.173855	3.484030	0.768658
C	-4.862688	-1.634244	0.044087
C	-5.916336	-1.415039	-0.852747
C	-4.966218	-2.693269	0.954103
C	-7.047505	-2.227106	-0.832644
H	-5.847562	-0.605170	-1.573456
C	-6.098454	-3.506384	0.976121
H	-4.159277	-2.873652	1.659529
C	-7.144415	-3.274612	0.084013
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106			
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C	-2.428578	1.369735	-0.172048
C	-1.216272	0.701058	-0.279744
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C	1.224093	-0.702845	-0.272064

C	1.220877	0.706288	-0.278142	H	-0.007026	-5.185579	2.190245
C	2.429863	1.380449	-0.167487	C	-0.053587	7.087041	-0.475002
H	2.430420	2.464357	-0.137096	C	0.018345	-7.064825	0.196615
C	3.659252	0.708380	-0.070238	F	0.391022	7.618538	-1.630666
C	3.664862	-0.690895	-0.097411	F	-1.315512	7.552111	-0.301916
C	2.438709	-1.369707	-0.185375	F	0.685942	7.633423	0.513726
H	-2.434341	2.453609	-0.143369	F	-0.090954	-7.484400	1.470670
H	-2.432943	-2.463984	-0.222508	F	1.158169	-7.609184	-0.292728
H	2.451409	-2.453389	-0.219659	F	-0.994758	-7.641845	-0.490245
C	0.009634	-2.816886	-0.237056	C	4.893495	1.524491	0.092239
C	0.001196	-3.371820	1.040817	C	5.174807	2.579265	-0.785280
C	0.019421	-3.633137	-1.365543	C	5.794122	1.281771	1.133186
C	0.000653	-4.753829	1.195905	C	6.320041	3.352297	-0.636742
C	0.019709	-5.014787	-1.215906	H	4.496532	2.791256	-1.607390
H	0.026183	-3.182799	-2.352759	C	6.944501	2.050766	1.293704
C	0.008573	-5.568306	0.065257	H	5.598825	0.478123	1.837355
H	0.027751	-5.655051	-2.092342	C	7.221045	3.093733	0.404787
N	0.006982	-1.396473	-0.396834	H	6.514088	4.157474	-1.340560
N	0.000964	1.388958	-0.412119	H	7.611044	1.825017	2.118536
C	-0.001951	2.816630	-0.423492	C	4.912111	-1.503126	-0.070892
C	-0.018451	3.525725	0.777518	C	5.064909	-2.547066	0.850308
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C	-0.021475	4.914424	0.758710	C	6.220193	-3.318919	0.877808
C	0.009729	4.879219	-1.666643	H	4.275061	-2.751340	1.568202
H	0.025244	2.919238	-2.566581	C	7.114981	-2.037912	-0.957763
C	-0.003720	5.585385	-0.465548	H	5.860096	-0.475632	-1.709036
H	-0.006195	-2.721141	1.909602	C	7.261594	-3.069933	-0.026181
H	-0.028663	2.986626	1.719463	H	6.311270	-4.115304	1.612076
H	-0.036448	5.467635	1.691874	H	7.893215	-1.820023	-1.680546
H	0.019045	5.402198	-2.616426	C	-4.892578	1.503291	0.087757

C	-5.178629	2.556485	-0.790116	H	-10.678281	-4.122903	-1.128621
C	-5.791247	1.257906	1.129774	C	-9.559063	3.446935	1.934493
C	-6.326365	3.325628	-0.640666	H	-9.853780	2.406304	1.780425
H	-4.501942	2.770542	-1.612995	H	-8.976627	3.545322	2.853420
C	-6.944147	2.022946	1.291146	H	-10.460592	4.057760	2.023179
H	-5.592302	0.455379	1.834204	C	9.558304	3.479255	1.930960
C	-7.225240	3.064567	0.402084	H	8.979243	3.573899	2.852399
H	-6.523858	4.129907	-1.344547	H	9.854625	2.439672	1.772893
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C	-4.897693	-1.525011	-0.072042				
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C	-5.044113	-2.568924	0.850255				
C	-7.099582	-2.070703	-0.954693				
H	-5.853179	-0.503284	-1.709424				
C	-6.195795	-3.346013	0.880424				
H	-4.252159	-2.768930	1.567040				
C	-7.239918	-3.102549	-0.021938				
H	-7.879964	-1.856969	-1.676392				
H	-6.281954	-4.142078	1.615628				
S	8.698101	-4.109351	0.090607				
S	-8.671454	-4.148426	0.098504				
S	-8.663990	4.102030	0.505663				
S	8.656323	4.136093	0.507280				
C	9.797075	-3.463803	-1.192904				
H	9.357604	-3.567737	-2.187596				
H	10.066471	-2.422216	-1.002987				
H	10.700879	-4.075745	-1.142971				
C	-9.777116	-3.507327	-1.181484				
H	-10.050044	-2.466830	-0.990645				
H	-9.340502	-3.609482	-2.177614				

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