DISSERTATION

CHLORO-, ARYL-, AND PERFLUOROALKYLFULLERENES

Submitted by

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY IGOR V. KUVYCHKO ENTITLED "CHLORO-, ARYL-, AND PERFLUOROALKYLFULLERENES" BE ACCEPTED AS FULFILLING IN PART THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

CHLORO-, ARYL-, AND PERFLUOROAKYLFULLERENES

The preparation, properties, stability, and handling of three classes of fullerene derivatives, chloro-, aryl-, and perfluoroalkylfullerenes, were studied in detail, in some cases for the first time. The same general methodology was used throughout this work: i) analytical methodology was developed and optimized using internal standards of known composition and purity; ii) the preparation of new compounds was studied by mapping the space of different reaction conditions using the newly developed analytical methods; iii) the efficient synthetic methods for the preparation of individual pure compounds were developed based on the mapping; iv) the pure compounds were characterized and their stability, or lack thereof, was studied.

The first detailed study of fullerene chlorination led to isolation and characterization of several new chlorofullerenes: *o*-$C_{60}Cl_2$; *p*-$C_{60}Cl_2$; $C_{60}Cl_4$; $C_{60}Cl_{10}$; $C_{70}Cl_6$; and $C_{70}Cl_8$. It was discovered that chlorofullerenes are generally photosensitive in solution, both in the presence and absence of air and moisture. Effective methods for handling chlorofullerenes were developed (including a specialized crystallization technique). The experimental findings and theoretical calculations revealed the fundamental patterns governing multiple additions to fullerene cages.

The efficient preparation of aryl- and perfluoroalkylfullerenes from chlorofullerene synthons was developed, leading to high yields of aryl- and mixed perfluoroethyl/hydrofullerenes (i.e., $C_{60}(C_2F_5)_5H$ and $C_{60}(C_2F_5)_3H$). The first example of

an organometallic complex of a perfluoroalkylfullerene was prepared using $C_{60}(C_2F_5)_5H$ as a synthon.

The direct addition of thermally-generated CF_3 radicals to fullerenes was also studied. A specialized reactor was designed and built in order to validate mechanistic hypotheses. Good agreement between the experimental observations and predictions based on the hypotheses was observed. It led to the development of a new approach to efficient synthesis of $C_{60}(CF_3)_n$ with low values of n, including an unprecedented selective synthesis of $C_{60}(CF_3)_2$ from unpurified fullerene extract.

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Chapter I
General Introduction

Fullerenes are unique closed three-dimensional unsaturated networks of carbon atoms. Their structures are composed of 12 pentagons and a variable number of hexagons of carbon atoms.[1] Most of the discovered fullerenes obey a so-called isolated pentagon rule (IPR) which states that the pentagons are surrounded by hexagons in stable fullerene structures.[1,2] The smallest fullerene that can satisfy the isolated pentagon rule is C_{60}.[1] On the right side of Figure I.1 is a Schlegel diagram of C_{60}, which is a common 2D representation of fullerenes (it is used extensively in the fullerene literature and in this work).[1] This simplest IPR fullerene has 30 double bonds, which are explicitly shown in the Schlegel diagram on Figure I.1 (they are usually omitted). The number of double bonds is larger for higher fullerenes.

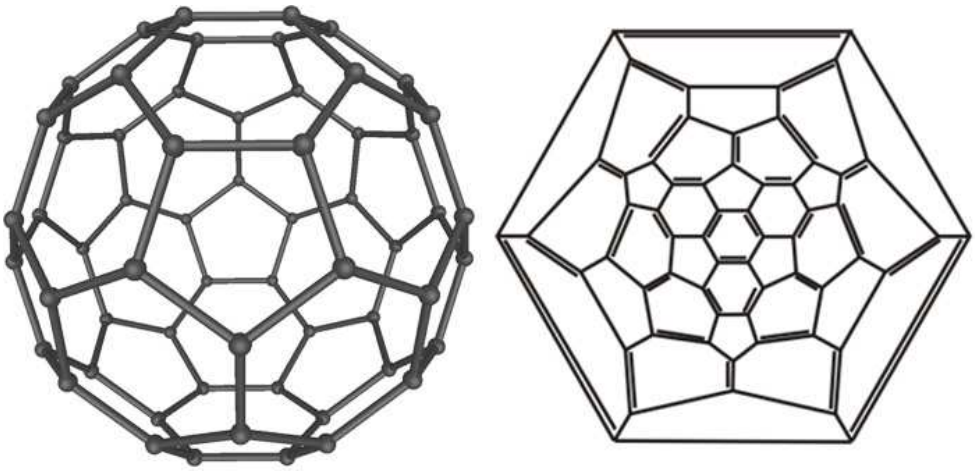

Figure I.1. The most common and simplest IPR-fullerene C_{60}. A 3D representation is shown on the left; a 2D representation of the same structure in the form of a Schlegel diagram is shown on the right (with the 30 double bonds shown explicitly).

Fullerenes can be extensively modified chemically by the addition of various groups to the double bonds of the cage, leading to a wide variety of different derivatives with particular spatial arrangements of the addends.[2] Besides their fundamental scientific interest, fullerenes and especially fullerene derivatives are promising compounds for various advanced applications, such as the development of efficient organic solar cells[3] and medical applications[4,5] (i.e., agents for photodynamic cancer therapy and magnetic resonance imaging and/or computed tomography imaging).

A deep understanding of the reactivity of fullerenes and their derivatives is clearly critical for their successful application. Despite the fact that fullerenes became available in macroscopic quantities in the beginning of 1990s,[2,6] this area is still relatively unexplored and is rapidly developing.[2] However, some areas of fullerene chemistry are fairly well-studied and understood, an example being cycloadditions to fullerene cages.[2] Nevertheless, these areas are mostly limited to fullerene derivatives that have a low number of addends (also known as substituents). There are a number of excellent reports on the reactions that only involve a single double bond of the fullerene cage (out of 30 for the simplest fullerene C_{60}) and produce well-characterized products (see ref. 2 and references therein).

The situation is much more complex for reactions involving multiple additions to fullerenes due to the large number of possible isomeric products. For example, the number of geometrically possible isomers for $C_{60}X_2$ is 23; for $C_{60}X_4$ this number is 4,190; and for $C_{60}X_6$ it is 418,470 (X = H, R, Ar, halogen, pseudohalogen, etc).[7] According to DFT (density functional theory) calculations, many of these isomers are not thermodynamically stable; however, in practice the number of observed isomers is still considerable. For example, one method of trifluoromethylation of C_{60} was reported to yield more than 60 different $C_{60}(CF_3)_n$ products.[8] The properties of these compounds are

very similar, which makes their separation in pure form highly challenging (generally fullerene derivatives are considered "pure" if their mol% purity exceeds 90%). Currently the only practical method of purification is HPLC, and multiple separation stages are often required in order to isolate a product that is both compositionally and isomerically pure.[8]

In addition to isolation in pure form, the determination of the structure (i.e., the addition pattern) of a multiply addended fullerene is another challenging problem. The best, and sometimes the only, method suitable for this is a single-crystal X-ray diffraction study. Of course this requires suitable single crystals, which are often difficult to obtain, especially if the compound in question is not very pure and/or has a low solubility. Sometimes one can use alternative methods of analysis, often in conjunction with theoretical calculations, in order to establish the addition pattern. For example, fluorofullerenes and perfluoroalkylfullerenes can be analyzed by ^{19}F NMR spectroscopy. Besides providing the molecular symmetry, the spectra contain a wealth of additional structural information such as J_{FF} coupling constants and spin-spin connectivities via COSY experiments.[9] These data can be used to narrow down the number of possible addition patterns of the compound and sometimes even to pinpoint a particular one.[9,10] It is also notable that fluorofullerenes and perfluoroalkylfullerenes have high thermal stabilities,[11] which make their analysis by mass-spectrometric methods relatively straightforward. For example, regular "harsh" ionization methods like electron impact ionization can be effectively used.[8] The availability of these reliable analytical methods has resulted in the considerable progress achieved in the areas of fluorofullerenes and perfluoroalkylfullerenes during the last 15 and 5 years, respectively.[9]

The study of chlorofullerenes (i.e., fullerene$(Cl)_n$ compounds) is an area of fullerene chemistry in which progress has been considerably slower than for fluorofullerenes and perfluoroalkylfullerenes. Chlorofullerenes are promising synthons (i.e., precursors) for

selective multiple derivatization of fullerene cages.[12,13] It was long believed that HPLC analysis and separation were not suitable for chlorofullerenes due to an early report implying that they decompose in solution or on HPLC columns.[14] For this reason, HPLC was excluded from the arsenal of methods that fullerene chemists otherwise routinely used for the analysis and separation of complex product mixtures. In addition, conventional mass spectrometry methods were found to cause an extensive and/or complete loss of chlorine atoms (with ions of the bare fullerene frequently being the only observable fullerene species in the mass spectrum). Furthermore, ^{13}C NMR spectroscopy was too limited by its low sensitivity for it to be a useful analytical method for chlorofullerenes.[15] Prior to this work, the successful crystallization of chlorofullerenes resulting in their single-crystal X-ray diffraction study was achieved exclusively under exotic high-temperature, high-pressure *in situ* conditions.[16-18] Despite these difficulties, some progress had been achieved. Many different syntheses of fullerene$(Cl)_n$ derivatives were described in the literature (see Tables II-1 and III-1 for comprehensive lists of references); however, the analysis of the resulting products was often limited to information on the average value of *n*.

This was the state of affairs when the work described in this dissertation was started. During the initial stage of this study, HPLC analysis and soft-ionization MALDI mass spectrometry was successfully introduced for the analysis of the chlorofullerene $C_{60}Cl_6$.[19] We showed that $C_{60}Cl_6$ sample does *not* undergo any detectable decomposition during HPLC analysis or separation.[19] Using this method the purification and quantitative purity determination of chlorofullerenes was achieved for the first time (through the integration of the corresponding HPLC trace; see ref. 19 for details). Moreover, it was demonstrated for the first time that the samples of $C_{60}Cl_6$ prepared via literature methods contain higher chlorinated and arylated fullerene impurities (this was shown by soft-ionization Matrix Assisted Laser Desorption Ionization, or MALDI, mass spectrometry).[19] This information

made it possible to compare several reaction conditions for $C_{60}Cl_6$ synthesis, leading to the development of an improved synthesis of this chlorofullerene.[19]

An experimental study of the performance of several analytical methods (HPLC, TGA, IR, UV-vis, ^{13}C-NMR, MALDI-MS, ESI-MS, and APCI-MS; see Appendix A.I.1 for Table of Abbreviations) was then carried out using $C_{60}Cl_6$ samples with purities ranging from 96% to 27%. This study led to the development and, importantly, validation of the analytical methodology most suitable for complex mixtures of chlorofullerenes, HPLC. Using this powerful tool, it became possible to perform the first study of $C_{60}Cl_6$ stability in solution, which led to the discovery of the photosensitivity of chlorofullerenes in solution (both in the presence and absence of moisture and air). As a result of this discovery, proper precautions were taken during the subsequent investigations of fullerene chlorination, ultimately leading to the first successful growth of X-ray quality single crystals of the chlorofullerenes $C_{60}Cl_6$ and $C_{60}Cl_{10}$ from solutions under ambient conditions (followed by single-crystal X-ray diffraction studies, see Appendix A.I.2). Using HPLC, the earlier literature reports on fullerene chlorination were reproduced and reexamined, which led to the conclusion that the majority of previously reported "pure" chlorofullerenes were really complex chlorofullerene mixtures, sometimes containing dozens of different compounds. The first detailed study of fullerene chlorination under a variety of conditions was then carried out in order to find the conditions leading to pure chlorofullerenes (or to their HPLC-separable mixtures). During this study, the space of different reaction conditions was carefully surveyed (mapped), and this approach led to the discovery of the several sets of reaction conditions that led to the formation of new chlorofullerenes. Based on these results, a number of large-scale preparative procedures for different chlrorofullerenes were developed (in the context of fullerene chemistry large scale means tens or hundreds of milligrams); this led to the isolation of new compounds in quantities sufficient for their detailed characterization and for a study of their stability.

This work is described in Chapters II and III. It was discovered that C_{60} and C_{70} chlorination under some particular conditions leads to formation of insoluble products (the vast majority of chlorofullerenes have good solubility); it was hypothesized that the insoluble products are dimeric or polymeric in nature. A dedicated study of the formation of and the properties of these products was carried out, which confirmed the viability of this hypothesis. This work is described in Chapters III and IV.

Together with the exploration of chlorofullerenes themselves, their potential as synthons for new fullerene derivatives that cannot be prepared using direct addition to the cage was investigated. Chapter V describes the work on chlorofullerene arylation. This work also relied on the same analytical methodology that was developed for chlorofullerene study. Similarly to the case of chlorofullerenes, the mapping of reaction-condition space led to the development of effective synthetic procedures for arylfullerenes.

The stability of arylfullerenes was also studied, revealing that some of them are air-sensitive and photosensitive. For this reason a class of perfluoroalkylfullerenes was studied, since these compounds possess much higher stability. This work is described in Chapter VI.[11] A unique method of preparation of perfluoroethylfullerene derivatives from chlorofullerenes was developed. Besides providing an efficient method for the synthesis of $C_{60}(C_2F_5)_n$ with low values of n (i.e., 2, 4, 6), this approach led to the discovery of the unique mixed perfluoroethyl/hydrofullerenes ($C_{60}(C_2F_5)_5H$ and $C_{60}(C_2F_5)_3H$). Using $C_{60}(C_2F_5)_5H$ as a synthon, the first organometallic complex of a perfluoroalkylfullerene anion, $Rh(C_{60}(C_2F_5)_5)$(1,5-cyclooctadiene), was prepared.

Finally, the direct addition of CF_3 groups to the fullerene cage at high temperature was studied. This work is described in Chapter VII. A phenomenological description of the mechanism of the heterogeneous fullerene trifluoromethylation was suggested. In order to validate this hypothesis, the reaction-condition space of the trifluoromethylation

process was studied (mapped) using a reactor specifically designed and fabricated for this purpose. This led to the validation of the phenomenological description of fullerene trifluoromethylation, which led the prediction and experimental realization of the first selective synthesis of $C_{60}(CF_3)_2$, as well as the development of efficient methods for the preparation of mixtures of $C_{60}(CF_3)_n$ with n = 4 and 6.

The success of this work can be largely attributed to the use of informative analytical methods that provided the capability to study the particular chemical systems in sufficient detail. This general methodology can be summarized as follows: i) the quantitative means of analysis of the molecular species under investigation was developed and validated (i.e., a suitable *analytical methodology* was created; this step relies on the availability of "reference" or "model" compounds with known structure and purity); ii) using these methods, the stability of these compounds under different conditions was studied; iii) synthetic conditions were investigated in detail by a thorough analysis of the products formed, in other words, the reaction-condition space was mapped; iv) using the results of the mapping, the optimal conditions for the efficient large-scale preparation of the particular compounds (or their separable mixtures) were chosen; v) using these conditions, particular products were prepared and isolated in large quantity in pure form in order to allow their detailed characterization by an array of analytical methods; vi) the reactivity, stability, and physical properties of these compounds were investigated. The results established during such investigations were constantly "fed back" in order to further refine the different stages of the procedure.

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Chapter II
Study of C_{60} Chlorination and C_{60} Chlorides

II.1. Introduction

The addition of substituents to one or more of the double bonds of fullerenes such as C_{60}, C_{70}, etc. is the most common way to prepare fullerene derivatives for scientific study or practical applications (e.g., solar-cell development).[1] Addition-reaction types include cycloaddition, halogenation, and electrochemical reduction followed by alkylation. However, the "direct-addition" products can potentially be converted into an even wider array of derivatives by subsequent substitution reactions, including derivatives that cannot be prepared by direct addition. In this regard, halofullerenes, $C_{60}X_n$, are arguably the most versatile class of substitution-reaction precursors, and within this class compounds the chlorofullerenes are far superior to either fluorofullerenes, for which practical amounts are only available for high values of *n* (18, 36, and 48) or bromofullerenes, which are notoriously insoluble (note that no iodofullerenes have been reported). Although there are reports of the conversion of $C_{60}F_{18}$ to $C_{60}F_{15}Ph_3$[2] and of $C_{60}Br_{24}$ to $C_{60}F_{24}$,[3] there are many more reports of the conversion $C_{60}Cl_6$ to products such as $C_{60}Me_6$ and $C_{60}Me_5Cl$,[4] $C_{60}(CH_2CH{=}CH_2)_6$ and $C_{60}(CH_2CH{=}CH_2)_5Cl$, [5] $C_{60}(OMe)_5OH$ and $C_{60}(OEt)_5OH$,[6] and $C_{60}Ar_5Cl$[7] (Ar = Ph, tolyl, anisyl, tert-butylphenyl, fluorophenyl, trimethylsilylphenyl, and thienyl). The chlorofullerenes $C_{60}Cl_6$ and $C_{70}Cl_{10}$ have also been used for the preparation of derivatives with potentially useful optical[8] and biomedical properties.[9] For all of these reasons, the synthesis of new chlorofullerenes has become an important area of research.

Compounds of the formula $C_{60}Cl_n$ were among the first derivatives of C_{60} to be reported in the literature. Mixtures of $C_{60}Cl_n$ compounds were prepared in 1991,[10,11] followed by the synthesis and structure elucidation of $C_{60}Cl_6$ in 1993.[12] Table II.1 lists all $C_{60}Cl_n$ syntheses reported prior to this work,[10-28] including the recent report of two non-isolated-pentagon-rule (non-IPR)[29] derivatives prepared by adding a small amount of chlorine gas to a carbon-arc fullerene-synthesis reactor.[28] (In this chapter, the term chlorofullerene (abbreviation CF) will be used exclusively to denote $C_{60}Cl_n$ derivatives of the only isolated-pentagon-rule[29] (IPR) isomer of C_{60} (this isomer is known as $^{\#1812}C_{60}$);[28-30] the two non-IPR $C_{60}Cl_n$ derivatives reported in 2008[28] will be denoted $^{\#1809}C_{60}Cl_8$ and $^{\#1804}C_{60}Cl_{12}$ for clarity.) Note that the majority of CFs are soluble in a variety of organic solvents.

Table II.1 reveals that several CFs other than $C_{60}Cl_6$ have been reported, and some of these have been characterized by single-crystal X-ray diffraction.[13-16] Nevertheless, it is generally acknowledged that the isolation of a crystal or a number of crystals of high compositional and isomeric purity is no guarantee that the bulk CF product is homogeneous. Except for our 2005 paper reporting an improved synthesis and method of purification of $C_{60}Cl_6$,[17] no paper reporting the synthesis of practical amounts of one or another CF has included compelling physico-chemical data regarding the composition and isomeric purity of the bulk reaction product. Since there are, in principle, thousands of theoretically, thermodynamically, and/or kinetically plausible CF isomers for each value of *n*, the burden of proof should be on the authors of synthetic papers to demonstrate the purity of their products.

In this chapter the problem of CF analysis is discussed in detail. The performance of several analytical methods for the analysis of CF mixtures was studied. Using this knowledge a reliable methodology for analysis of mixtures of CFs was developed; this approach was applied to the study of fullerene chlorination in detail. This chapter also describes several new CFs that were isolated and studied using the reliable analytical methodology.

Table II.1. Compilation of $C_{60}Cl_n$ chlorofullerene syntheses (1991-2008).[a,b]

No. [year][ref]	proposed composition[c]	proposed purity [yield]	reagents and rxn. conditions	analytical techniques used for characterization[c]	stability	solubility
1 [1991][10]	$C_{60}Cl_{\sim 24}$[d]	mxt. [n/r]	Cl_2, 250–400 °C	WI, EA, IR, (^{13}C NMR,[e] MS (FAB and FI)[f])	Cl_2 loss at 400 °C	org. solv.
2 [1991][11]	$C_{60}Cl_{12-15}$[g]	mxt. [n/r]	Cl_2, −35 °C, no light	EA, IR, XPS, (^{13}C NMR[h])	Cl_2 loss above 200 °C	$PhCH_3$, CH_2Cl_2
3 [1993][12]	$C_{60}Cl_6$[g]	n/r [100.5%][i]	ICl, C_6H_6[j]	EA, IR, UV-Vis, ^{13}C-NMR	n/r	org. solv.[k]
4 [1993][18]	$C_{60}Cl_{40}$[g]	n/r [n/r]	Cl_2, CCl_4, UV	EA, IR, UV-Vis	n/r	n/r
5 [1994][19]	$C_{60}Cl_{40}$[g]	mxt. [n/r]	Cl_2, CCl_4, UV	EA, IR, UV-Vis	Cl_2 loss at HT	CH_2Cl_2, CCl_4
6 [1996][20]	$C_{60}Cl_{12}$[g]	n/r [n/r]	ICl, C_6H_6, no light	EA, UV-Vis	n/r	C_6H_6, C_6H_{12}[l]
7 [1997][21]	$C_{60}Cl_{24}$[m]	n/r [n/r]	Cl_2, CCl_4, UV	FAB-MS	n/r	CCl_4
8 [1998][31]	$C_{60}Cl_{24}$	n/r [n/r]	Cl_2, 327 °C	IR, Raman	n/r	n/r
9 [1999][22]	$C_{60}Cl_{7-45}$[n]	mix.[o] [n/r]	Cl_2, CS_2, UV	WI, MALDI-MS, PIXE-NMP, EMP, HPLC	possible Cl_2 loss[p]	$PhCH_3$
10 [1999][23]	$C_{60}Cl_{22}$[q]	n/r [100%]	Cl_2, 200–300 °C	WI, IR	n/r	n/r
11 [2002][24]	$C_{60}Cl_{30\pm2}$[r]	n/r [n/r]	Cl_2, UV	TGA, IR, MALDI-MS	n/r	$PhCH_3$
12 [2002][32]	$C_{60}Cl_{24}$	99.9%[n/r]	Cl_2, 310 °C	HPLC, WI, UV-Vis	n/r	org. solv.
11 [2003][25]	$C_{60}Cl_6$[s]	n/r [n/r]	ICl, ODCB[t]	IR, possibly EA	n/r	C_6H_6, ODCB
12 [2003][25]	$C_{60}Cl_8$[u]	"mxt. of isomers" [80–99%]	$KICl_4$, ODCB[t]	EA, IR, (MALDI-MS, ^{13}C-NMR[h])	n/r	C_6H_6, ODCB
13 [2003][25]	$C_{60}Cl_{10}$[u]	same as above	Cl_2, ODCB[t]	same as above	n/r	C_6H_6, ODCB
14 [2003][25]	$C_{60}Cl_{12}$[u]	same as above	ICl, ODCB[t]	same as above	n/r	C_6H_6, ODCB
15 [2003][25]	$C_{60}Cl_{14}$[u]	same as above	$KICl_4$, ODCB[t]	same as above	n/r	C_6H_6, ODCB
16 [2003][25]	$C_{60}Cl_{26}$[v]	same as above	Cl_2, ODCB[t]	EA, IR, MALDI-MS, (^{13}C NMR[e])	n/r	C_6H_6, ODCB

17 [2004][26]	T_h-$C_{60}Cl_{24}$[w]	~90%[x] [n/r]	VCl_4, 160–180 °C[y]	EA, IR,[z] TGA-MS, MALDI-MS	Cl_2 loss at 280–390 °C	n/r
18 [2005][13]	T_h-$C_{60}Cl_{24}$[aa]	n/r [n/r]	VCl_4, 160-180 °C[y]	IR,[z] X-ray	Cl_2 loss at 280–390 °C	n/r
19 [2005][14]	D_{3d}-$C_{60}Cl_{30}$[aa]	"pure"[aa] [n/r]	ICl, 220-250 °C[y]	IR,[z] X-ray, TGA-MS	Cl_2 loss at 450–500 °C	ODCB[ab]
20 [2005][15]	C_2-$C_{60}Cl_{30}$[ac]	n/r [n/r]	VCl_4, 160 °C	IR,[z] X-ray	n/r	n/r
21 [2005][15]	C_1-$C_{60}Cl_{28}$[ac]	n/r [n/r]	ICl, 160 °C[v]	IR,[z] X-ray	n/r	n/r
22 [2005][17]	$C_{60}Cl_6$[ad]	90–99%[‡] [90%]	ICl, PhCl	HPLC, IR,[w] Raman,[w] ^{13}C NMR, MALDI-MS	decomp. in soln.	$PhCH_3$, $CDCl_3$
23 [2006][16]	$C_{60}Cl_6$[ae]	n/r [n/r]	$POCl_3$, 100–150 °C	IR, X-ray	n/r	n/r
24 [2007][27]	$[C_{60}Cl_5]_2$[ac]	n/r [40%]	$C_{60}Br_{24}$ + $TiCl_4$[af]	IR, X-ray	n/r	n/r
25 [2007][9]	$C_{60}Cl_6$[ag]	"as good…as..." 90%[ah] [77%]	ICl, ODCB	^{13}C NMR, IR, (ESI-MS)	n/r	CB, ODCB, $PhNO_2$
26 [2008][28]	$^{\#1809}C_{60}Cl_8$	XYZ	carbon-arc + Cl_2	^{13}C NMR, APCI-MS, X-ray	Cl_2 loss at XYZ °C	XYZXYZ
27 [2008][28]	$^{\#1804}C_{60}Cl_{12}$	XYZ	carbon-arc + Cl_2	^{13}C NMR, APCI-MS, X-ray	Cl_2 loss at XYZ °C	XYZXYZ
28 this work	*o*-$C_{60}Cl_2$	75% [5%]	ICl, CB	HPLC, UV-Vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
29 this work	*p*-$C_{60}Cl_2$	75% [5%]	ICl, CB	HPLC, UV-Vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
30 this work	$C_{60}Cl_4$	98% [25%]	ICl, CB	HPLC, UV-Vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
31 this work	$C_{60}Cl_6$	90-96% [90%]	ICl, CB	HPLC, UV-Vis, IR, Raman, APCI-MS, MALDI-MS, TGA, ^{13}C NMR, X-ray	Cl_2 loss above 250 °C light-sensitive	$PhCH_3$, CH_2Cl_2
32 this work	$C_{60}Cl_{10}$	98% [30%]	ICl, CB	HPLC, UV-Vis, IR, Raman, APCI-MS, ^{13}C NMR, X-ray	light-sensitive	$PhCH_3$, CH_2Cl_2

[a] Abbreviations: mxt. = mixture; n/r = not reported; org. solv. = organic solvents; WI = weight increase; EA = elemental analysis; TGA = thermal gravimetry analysis; UV-Vis = UV-Vis spectroscopy; UV = UV-irradiation; ODCB = *o*-dichlorobenzene; CB =

chlorobenzene; FI = field ionization; HT = high temperature; PIXE-NMP = particle induced X-ray emission/nuclear microprobe analysis; EMP = electron microprobe analysis; CF(s) = chlorofullerene(s). [b] Comments within quotation marks are verbatim statements from the indicated reference. [c] Throughout this paper CFs with reliably demonstrated bulk purity are shown with a bold font; bold font is also used to show that a particular isomerically pure CF is meant in the context; regular font is used for CFs with unknown bulk purity and for otherwise poorly defined CFs. [c] Methods in parentheses were not successful for analysis of CFs according to the statements of the authors. [d] Determined by weight increase and EA. [e] No peaks were observed in the liquid ^{13}C NMR spectrum and only broad peaks were observed in the C(sp^2) and C(sp^3) regions of the solid-state ^{13}C NMR spectrum. [f] No CF ions were observed. [g] Determined by EA. [h] Only broad unresolved peaks in the C(sp^2) and C(sp^3) regions were observed in the liquid ^{13}C NMR spectrum. [i] "quantitative yield... 100.5%" was reported in ref. 12, which implies that the authors believed the purity of $C_{60}Cl_6$ to be ca. 100%; later authors corrected the purity to ca. 75%;[22] in our earlier work we found that this procedure gives ca. 80% pure $C_{60}Cl_6$.[17] [j] A comparison of different synthetic methods for the preparation of $C_{60}Cl_6$ was reported in ref. 17 and is discussed in greater detail in this paper. [k] "The product is very soluble in benzene, carbon disulfide, and tetrachloromethane, moderately soluble in chloroform, dichloromethane, and toluene, and slightly soluble in pentane, hexane, diethyl ether and acetone." [l] "The crystals readily dissolved in benzene, cyclohexane, and other nonpolar solvents, and they have no solubility in polar solvents." [m] Determined by FAB-MS. [n] Widely different compositions were obtained by different analytical methods for the same samples of chlorofullerenes. [o] HPLC analysis shows that samples are mixtures. [p] Chlorofullerene degradation upon standing and/or analysis was reported as one of the possible explanations for widely different values of *n* determined by different analytical methods (see footnote n). [q] Determined by weight increase. [r] Based on TGA and MALDI-MS. [s] As determined by EA and IR spectroscopy (IR spectrum was in agreement with literature data).[12] [t] Ranges and/or multiple sets of reaction conditions and different chlorinating agents (ICl, ICl_3, $KICl_4$) were reported to yield these compounds. [u] Determined by EA, which was claimed to be supported by results of chemical modification followed by ESI-MS analysis; the absence of the control experiments for the selectivity of the chemical modification step makes it impossible to rely on these results. [v] Determined by EA and MALDI-MS. [w] Based on EA, TGA, IR (experimental and simulated). [x] Purity estimation was based on IR data. [y] See ref. 33 for alternative preparation procedure. [z] Theoretical simulations of the vibrational spectra

were performed along with the experimental measurements. [aa] Determined by single-crystal X-ray diffraction and experimental and simulated IR data. [ab] "$C_{60}Cl_{30}$ is insoluble in most common organic solvents such as diethyl ether, 1,4-dioxane, CH_2Cl_2, $CHCl_3$, and CCl_4; it is poorly soluble in CS_2, toluene, and chlorobenzene; and its solubility in 1,2-dichlobenzene was estimated at roughly 0.2 mg mL^{-1}." [ac] Determined by single-crystal X-ray diffraction study. [ad] Relative purity is reported, determined by integration of HPLC traces. [ae] As determined by single-crystal X-ray diffraction and IR spectroscopy. [af] See ref. 17 for alternative synthesis. [ag] As determined by ^{13}C-NMR and IR spectroscopy (experimental spectra was in agreement with the literature data, see Ref. [12]). [ah] Reported to be as good as the product of the synthesis reported in ref. 17 based on the ^{13}C NMR spectrum.

II.2. Results and Discussion

II.2.1. Chlorofullerene Purity and Analysis

A. General Comments. Analysis of all of the literature reports describing the preparation of CFs (Table II.1) revealed that, except for our earlier paper,[17] CF molecular composition and product purity was never firmly demonstrated. In the majority of those studies, CF composition and purity were not explicitly discussed, leaving the reader to assume that the reported syntheses led to pure products. In some cases, the formation of CF mixtures was suggested by ^{13}C NMR spectroscopy[10,11] or demonstrated by HPLC.[22,6] In other studies, a single CF with "90+% purity" was claimed based on ^{13}C NMR[12,9] or IR spectroscopy.[26,14]

The shortcomings of ^{13}C NMR spectroscopy as an analytical method for the quantitative determination of CF purity became obvious when the original report on the "quantitative yield" synthesis of $C_{60}Cl_6$,[12] in which the authors presumed they had prepared a pure product based on the absence of extra ^{13}C NMR peaks, was later corrected in order to explain the presence of some phenyl-containing derivatives in the products of $C_{60}Cl_6$ methylation.[22] This later report stated that the purity of $C_{60}Cl_6$ prepared by their original method was only ca. 75 mol%; the other 25 mol% consisted of phenylated derivatives and possibly $C_{60}Cl_n$ compounds with $n > 6$.[4] Our earlier study[17] confirmed this conclusion; in our hands,[17] the purity of $C_{60}Cl_6$ obtained using the original recipe[12] was 80% based on the integration of HPLC peaks.

In this section, we show that IR, UV-Vis, and ^{13}C NMR spectroscopy and the types of mass spectrometry used in the past are not well suited, alone or in combination, for a

reliable analysis of CF reaction products. In our opinion, the method best suited for establishing CF purity or for studying mixtures of CFs is HPLC (i.e., for soluble CFs), since it combines high sensitivity with the ability to separate and quantify compounds with even minor structural differences (e.g., C_{60} and He@C_{60}[34]). We previously showed that HPLC is reliable for the quantitative analysis of $C_{60}Cl_6$ samples.[17] However, this method has seen only limited use for the study of CFs by others.[22,6] We now report the successful application of HPLC for the purification and quantitative analysis of CFs other than $C_{60}Cl_6$, and present a detailed comparison of HPLC and other analytical methods mentioned earlier for the analysis of CF mixtures.

B. HPLC Analysis of Chlorofullerenes. Despite the wide application of HPLC for the purification and, in some cases, quantification of fullerene$(X)_n$ derivatives in general, there have been very few attempts to use this method for CFs. The correct choice of HPLC column is very important for the successful separation of fullerene derivatives. Specialized Cosmosil BuckyPrep columns are usually used for this task. In 1999, Heymann et al. used HPLC with Cosmosil BuckyPrep column to determine that a CF sample contained unreacted C_{60} and a mixture of various CFs.[22] In 2001, Taylor et al. used HPLC to estimate the purity of a $C_{60}Cl_6$ sample, revealing that "by-products comprise as much as 25% of the total yield" (the HPLC column used was not specified in their report, but it is likely that it was also Cosmosil BuckyPrep).[6] In 2002, Razbirin et al. used HPLC for analysis of CF sample,[32] claiming 99.9% purity of the $C_{60}Cl_{24}$ product (an ordinar C18 HPLC column was used). Later this conclusion was shown to be incorrect (an impurity of $C_{60}Cl_{30}$ was identified in the absorption spectrum of their $C_{60}Cl_{24}$);[35] this demonstrates the importance of the correct choice of HPLC column for the analysis of CFs. The reason that most chemists have not considered using HPLC for CFs may be a comment in ref. 6, in which the authors stated that $C_{60}Cl_6$ "was used without further purification *in order to avoid degradation*" (emphasis added). This statement implied that $C_{60}Cl_6$ degrades during HPLC purification. However, in 2005 we showed that no such

decomposition during HPLC processing takes place, and we demonstrated the applicability of HPLC for the analysis and purification of $C_{60}Cl_6$ (using a Cosmosil BuckyPrep column).[17]

In order to demonstrate the essential role of HPLC for the study of CFs, and also to compare it with the other analytical methods (with respect to the analysis of CFs), we prepared four samples of $C_{60}Cl_6$ of various purities using chlorobenzene as the solvent and ICl as a chlorinating agent. These are listed as samples **A**–**D** in Table II.2 and their HPLC traces are shown in Figure II.1. Sample **A** was HPLC purified as previously described[17] and was shown to be 95% pure (see below). Sample **B** is the crude product of our "seven-minute" synthesis,[17] and its HPLC trace clearly demonstrates its lower purity. Samples **C** and **D** were prepared by modifying the reaction conditions[17] to intentionally lower the purity of the product. The HPLC traces reveal a much lower purity of sample **C** and an even lower purity of sample **D**. The impurities in these $C_{60}Cl_6$ samples are unreacted C_{60} and other CFs (see below). No arylated by-products were detected in these samples by mass spectrometry, in contrast to the $C_{60}Cl_6$ sample prepared with benzene as the solvent.[17]

HPLC peak areas provide quantitative information on analyte concentrations weighted by their corresponding detector responses. If UV detection is used and analyte extinction coefficients at the detector wavelength are known, then relative molar concentrations can be deter-mined. For example, in this work the extinction coefficients of C_{60}, $C_{60}Cl_6$, and $C_{60}Cl_{10}$ were measured at multiple wavelengths (see Section A.3, Figure A.12, and Table A.9). The extinction coefficients of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ at the HPLC detector wavelength, 300 nm, are virtually the same and are twice as large as that of C_{60}. Assuming that the extinction coefficients of the other CF impurities in the HPLC traces shown in Figure II.1 are the same as that of $C_{60}Cl_6$ and $C_{60}Cl_{10}$, the molar percentages of $C_{60}Cl_6$ indicated in Figure II.1 were determined. (These molar percentages

can be recalculated in the future as extinction coefficients of other CFs become available.)

Table II.2. Chlorofullerene analysis: $C_{60}Cl_6$ samples, their purity, and analytical methods employed.

$C_{60}Cl_6$	uncorrected[a]		corrected[b]		analytical methods used					
sample	$C_{60}Cl_6$, %	C_{60}, %	$C_{60}Cl_6$, %	C_{60}, %	HPLC[c]	IR[d]	UV-Vis[d]	^{13}C NMR[e]	MS[f]	TG[g]
A	95	-	95	-	+	+	+	+	+	-
B	89	3	86	6	+	+	+	+	+	+
C	67	-	67	-	+	+	+	+	+	-
D	30	7	27	14	+	+	+	+	+	-

[a] The uncorrected values, calculated through direct integration of HPLC peaks observed at 300 nm. [b] The corrected values, calculated through direct integration of HPLC peaks observed at 300 nm, followed by normalization of C_{60} peak area (it was multiplied by 2 according to the ratio of the extinction coefficients of $C_{60}Cl_6$ and C_{60} at 300 nm). [c] Same HPLC conditions used for all experiments (50/50 toluene/heptane eluent, 5 mL/min flow rate). [d] See Figure II.1. [e] See Figure II.2. [f] APCI-MS was used, see Figure II.3. [g] See Figure II.4.

$C_{60}Cl_6$ samples **A**–**D** were also analyzed by UV-Vis, FTIR, and ^{13}C NMR spectroscopy and by APCI mass spectrometry. Sample **B** was also analyzed by TG. The UV-Vis and FTIR spectra are shown in Figure II.1; the NMR and mass spectra are shown in Figures II.2 and II.3, respectively. The UV-Vis data show the gradual smoothing of the absorption spectra as the purity of $C_{60}Cl_6$ was decreased, with the most significant difference between the spectra of samples **A** and **B** (95% and 86% pure, respectively). However, there is virtually no difference between UV-Vis spectra of samples **C** and **D**, which have very different $C_{60}Cl_6$ purities (67% and 27%, respectively). FTIR spectroscopy also has a poor sensitivity to impurities, with only minor changes observed between the spectra of samples **A**, **B**, and **C** (95, 88, 67%). ^{13}C NMR spectroscopy has an even lower sensitivity; the spectra of samples **A** and **C** are virtually identical. Only sample **D** can be identified as impure by this method. APCI mass spectra indicate the presence of $C_{60}Cl_n$ species with $n > 6$ for samples **C** and **D**, but they cannot be used to distinguish between samples **A** and **B** or between samples **C** and **D**. All of these methods are discussed in more detail in the corresponding sections below, but it is clear that they cannot provide reliable information on the molecular composition and purity of CFs, let alone a quantitative data. This demonstrates that currently HPLC is only analytical method capable of quantitative evaluation of molecular composition and purity of CFs, which makes it the method of choice for the quantitative analysis of CF samples as well as the method of choice for CF purification.

Analytes containing components with very similar retention times can be hard to analyze by HPLC due to peak overlap. The presence of hidden peaks in such cases can be revealed by changing the eluent, flow rate, or column packing material. For example, we previously reported that a sample of $C_{60}Cl_6$ was 99% pure based on its HPLC trace when toluene was used as the eluent.[17] We now report that the same sample, when eluted with 50/50 v/v toluene/*n*-heptane, showed *ca.* 4% impurity with a different retention time. Therefore, the purity of this sample was 95%, not 99%. By surveying several different

HPLC conditions, the chance of overlooking an impurity with the same retention time as the main component can be minimized.

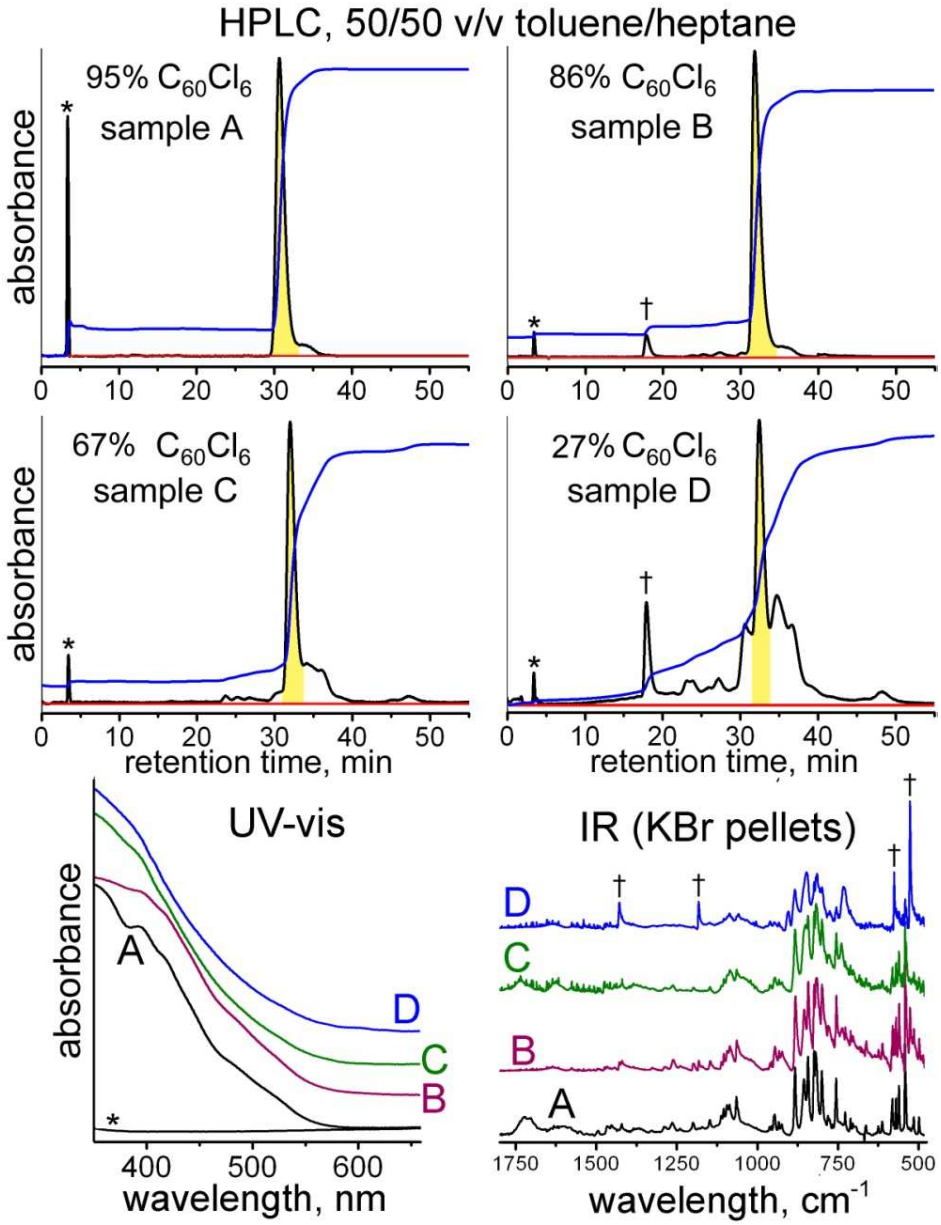


Figure II.1. HPLC traces and IR and UV-Vis spectra of $C_{60}Cl_6$ samples **A**, **B**, **C**, and **D** (95-27% purity). The shaded HPLC peaks are due to $C_{60}Cl_6$. HPLC peaks marked with daggers are due to C_{60}. HPLC peaks marked with asterisks are due to toluene (samples were injected as 100% toluene solutions; these peaks were not included in peak integration for quantitation). Same conditions were used for HPLC acquisition (50/50 v/v toluene/heptanes eluent, 5 mL/min flow rate). UV-Vis spectra are intentionally offset for clarity (samples **A–D** have virtually no absorptivity at ca. 650 nm). The UV-Vis marked with an asterisk is a toluene blank. The IR peaks marked with daggers are due to C_{60}.

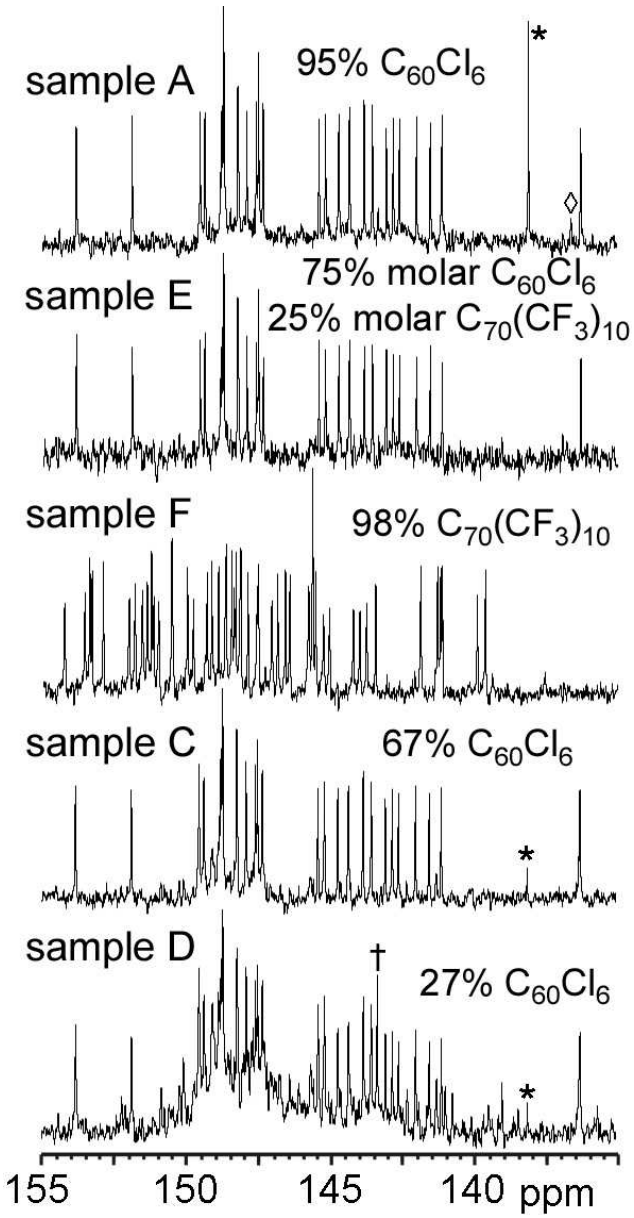


Figure II.2. ^{13}C NMR spectra of $C_{60}Cl_6$ samples **A**, **C**, **D**, **E**, and of $C_{70}(CF_3)_{10}$ sample **F**. ^{13}C NMR spectrum of sample **B** is virtually the same as the spectrum of sample **A**, although it shows a peak of C_{60} impurity. ^{13}C NMR of sample **B** is not included in the figure (it is virtually identical to ^{13}C NMR of sample **A**). The signals of the quaternary carbon of the toluene impurity are marked with asterisks. Peak marked with a dagger is due to C_{60} (sample **D**). Peak marked with a diamond is due to an unidentified impurity. Spectra expansions covering 73-52 ppm (sp^3-carbons) and 160-115 ppm ranges, signal-to-noise calculations, details of the acquisition conditions, and tables of ^{13}C chemical shifts for $C_{60}Cl_6$, $C_{60}Cl_{10}$, and $C_{70}(CF_3)_{10}$ are given in Section A.4.

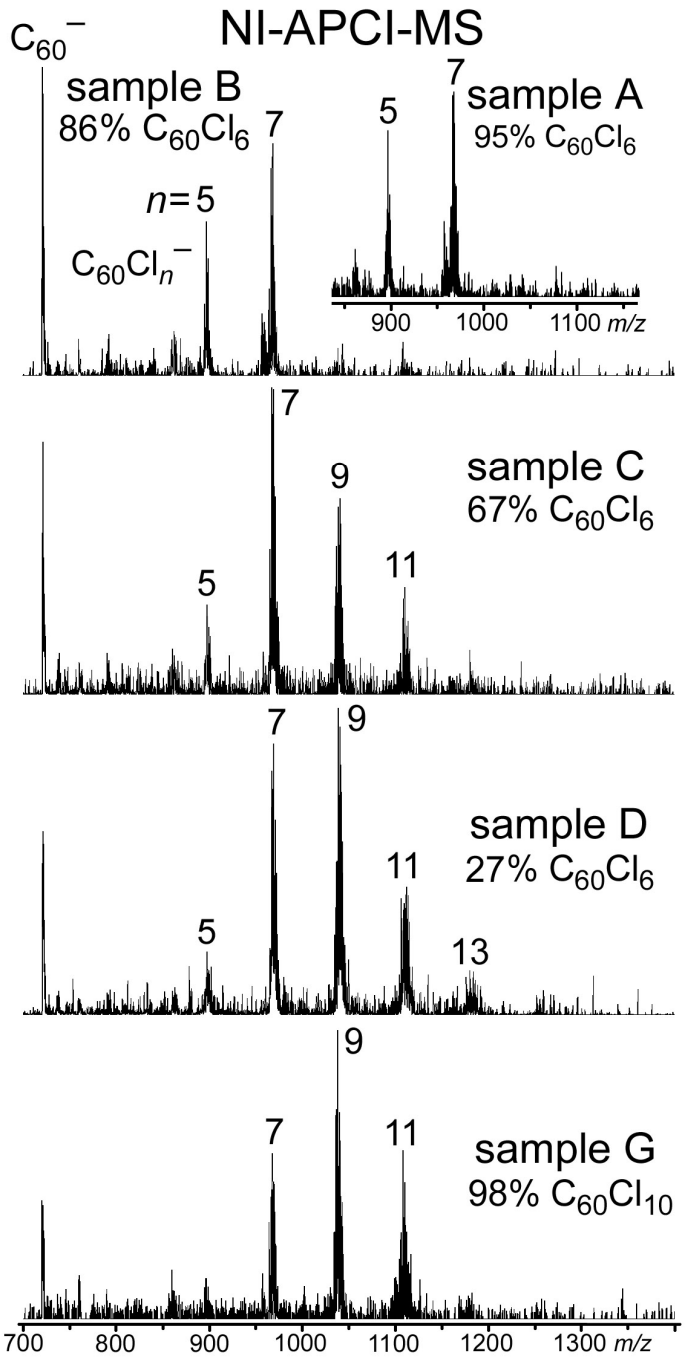


Figure II.3. NI-APCI-MS spectra of $C_{60}Cl_6$ samples **A**, **B**, **C**, **D**, and of $C_{60}Cl_{10}$ sample **G**.

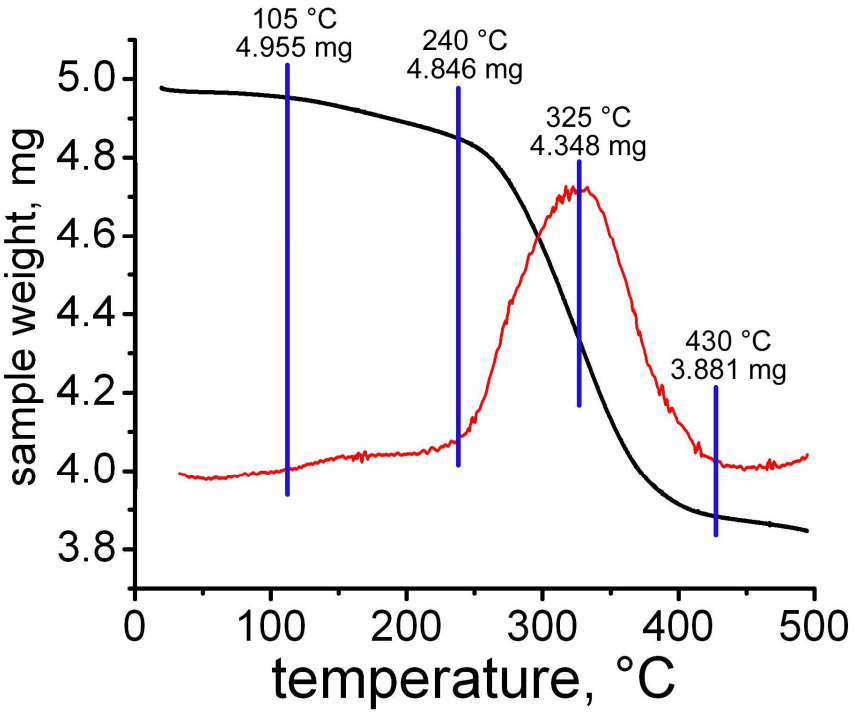


Figure II.4. TGA plot (black) and differential TGA plot (red) of 86% pure $C_{60}Cl_6$ (sample **B**). 5 °C/min heating rate was used.

C. Elemental Analysis (EA) and Thermal Gravimetry Analysis (TGA). The literature reports (see Table II.1) show that EA was the most commonly used technique for determination of the CF composition (carbon-to-chlorine ratio). However, EA is only suitable for characterization of CFs shown to be pure by other methods, since samples of CF mixtures may have the same carbon-to-chlorine ratio but drastically different composition (for example, single-isomer $C_{60}Cl_{10}$ and a mixture of $C_{60}Cl_{10}$ isomers, as well as equimolar mixtures of $C_{60}Cl_8/C_{60}Cl_{12}$ or $C_{60}Cl_4/C_{60}Cl_{16}$ or a combination of these cases). Nevertheless, in two papers the compositions of the reported CFs were determined by EA only.[20,25] In 1996, Priyadarsini et al. reported $C_{60}Cl_{12}$ preparation (see Table II.1, No. 6) and a pulse radiolysis study (of $C_{60}Cl_{12}$ and $C_{60}Cl_6$) done with an implicit assumption of the high purity of these CFs.[20] In 2003, Troshin et al. reported the preparation of $C_{60}Cl_8$, $C_{60}C_{10}$, $C_{60}Cl_{12}$, $C_{60}Cl_{14}$, and $C_{60}Cl_{26}$ (see Table II.1, No. 12–16 correspondingly), saying that "Most likely, prepared chlorofullerenes $C_{60}Cl_n$ (n = 8, 10, 12, 14, 26) consist of several isomers."[25] Our MS and HPLC analysis of all of the

aforementioned CFs (except $C_{60}Cl_{14}$) prepared according to the reported procedures[20,25] show them to be complex mixtures of multiple compositionally (and most likely isomerically) different CFs (see Sections II.2.1.B and II.2.1.G). These results demonstrate the danger of treating the average bulk elemental composition of a CF sample (given by EA) as the actual molecular composition without a sufficient proof of the sample purity.

Another method that may be used to determine the carbon-to-chlorine ratio of CF samples is thermal gravimetry analysis (TGA). The low strength of C–Cl bond allows for the decomposition to occur in the 200–500 °C temperature range, depending on the CF and the experimental conditions,[10,11,19,26,13,14] causing the loss of Cl_2 (shown by TGA-MS[26]). A parent C_{60} was detected in the products of decomposition by IR spectroscopy in two cases.[11,26] Assuming that the mass loss (Δm) of the sample in the TGA experiment is caused exclusively by chlorine evolution,[36] and that the CF decomposition is complete (which can be shown by the absence of C−Cl vibrations in the IR spectrum of the TGA residue[26]), then the Δm value accurately represents the average chlorine content (chlorine-to-carbon ratio) in the original CF sample. For example, TGA analysis of $C_{60}Cl_6$ sample **B** showed the weight loss corresponding to the composition of 5.6 chlorines per C_{60} cage (see Figure II.4, the IR spectrum of the TGA residue showed only C_{60} lines). According to the HPLC data, sample **B** contains 6% of C_{60} and 86% of $C_{60}Cl_6$. The rest of the sample is comprised of other CFs. If we approximate the average composition of the other CFs present in sample **B** as $C_{60}Cl_6$, the average composition of this sample is $C_{60}Cl_{5.6}$, in excellent agreement with the TGA results. The literature data also indicate that TGA can provide reliable compositional data for CFs: TGA analysis of $C_{60}Cl_{24}$ showed a mass loss of 56.5% (corresponding to $C_{60}Cl_{26.4}$ composition), in agreement with MALDI-MS results ($C_{60}Cl_{27}^-$ was the most intense ion observed in the mass spectrum of this sample, see section 1-2-I-G for further discussion).[26]

The EA and TGA data of CF composition can be heavily influenced by the presence of the impurities. During the course of our work we found that $C_{60}Cl_6$ retains the solvent

upon drying of the $C_{60}Cl_6$/toluene solution. In fact, ^{13}C NMR spectroscopy showed that a significant amount of toluene was present in the $C_{60}Cl_6$ sample even after 12 hours of drying under dynamic vacuum (*ca.* 0.01−0.005 torr, oil pump). A reliable EA or TGA analysis requires the absence of co-crystallized solvent (see A.3 for our CF drying procedure), which should be taken into account during CF analysis by these methods. Otherwise large errors are likely to be introduced.

In conclusion, EA and TGA methods can accurately determine the average elemental composition of solvent-free CF samples, which corresponds to the actual molecular composition for the (compositionally) pure CFs. However, both EA and TGA have a significant drawback since they require a destruction of a relatively large quantity of the sample (at least, several milligrams). However, soft-ionization mass-spectrometry can also be used to determine the molecular composition of CFs (see Section II.2.1.G). This method requires a very small amount of sample and it is insensitive to some CF contaminants like co-crystallized solvents, which makes it a method of choice for the composition determination of pure CFs and the measurement of the highest degree of chlorination for the mixtures of CFs. However, mass-spectrometry does not provide the average elemental composition of the mixture of CFs, which makes its results complementary to those of EA and TG.

D. IR and Raman Spectroscopy. IR spectroscopy is one of the most common methods of CF characterization (see Table II.1). When combined with detailed theoretical modeling, IR spectroscopy can be used for accurate structure elucidation, which was confirmed, for example, for $C_{60}Cl_{24}$ structure[26] (shown to be correct later by a single-crystal X-ray diffraction study[13]). The Raman spectroscopy of CFs is challenging due to sample decomposition (loss of chlorine) upon laser excitation and hence it is less commonly used for CF study. Raman spectra of several CFs have been reported: lower chloride $C_{60}Cl_6$,[17] and higher CFs $C_{60}Cl_{24}$, $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$.[33]

The analysis of the $C_{60}Cl_6$ samples **A**–**D** (see Figure II.1 and Table II.2) demonstrates that IR spectroscopy is not suited for the evaluation of the molecular composition and purity of CF mixtures. IR spectra of samples **A** (95% of $C_{60}Cl_6$), **B** (86%), and **C** (67%) display only minor differences, and even IR spectrum of sample **D** (containing only 27% of $C_{60}Cl_6$) is dominated by the features of $C_{60}Cl_6$ (although it is broadened and has additional peaks). Other CFs cannot be reliably identified in any of the IR spectra of samples **A-D**, either because of their insufficient concentrations or due to overlap with the intense peaks of the single major component ($C_{60}Cl_6$). However, when a component possesses a high molecular symmetry it may be detected even at low concentrations, due to the increased intensities of the degenerate vibrational modes of the molecule. It is demonstrated by the observable C_{60} peaks in the IR spectra of samples **D** (containing 14% of C_{60}) and **B** (6% of C_{60}). This effect can explain some peculiar data found in the literature.[26] In 2004 Troyanov et al. reported the synthesis of T_h-$C_{60}Cl_{24}$, arguing that "In view of the elemental analysis and IR spectroscopic data, the purity of the $C_{60}Cl_{24}$ samples should be estimated as rather high, with the major component content of at least 90%".[26] Other analytical methods described in the same study gave contradicting results, with the MALDI mass-spectrum showing $C_{60}Cl_{27}^-$ ion as the most intense peak (usually molecular ions of CFs are not observed in mass spectra due to extensive fragmentation, see Section II.2.1.G), and the TGA analysis resulting in the weight loss corresponding to $C_{60}Cl_{26.4}$ composition (observed weight loss of 56.5%, versus 54.1% corresponding to the theoretical $C_{60}Cl_{24}$ composition). When the original work did not elaborate on the discrepancy between the EA and TGA results, the presence and the intensity of the $C_{60}Cl_{27}^-$ ion in the MALDI mass-spectrum was explained[26,37] by the analyte suppression effect, causing the ions with higher number of electron-withdrawing substituents to be overrepresented relative to the concentrations of their parent CFs (due to the higher electron affinity and hence better ionization efficiency and higher stability[38,39]). The higher mass loss observed in the TGA experiment was credited to "the presence of a

small $C_{60}Cl_{28}$ impurity in the sample". In order for the latter explanation to be true, the sample has to contain 42 mol. % of $C_{60}Cl_{24}$ and 58 mol. % of $C_{60}Cl_{28}$, in other words, $C_{60}Cl_{28}$ has to be the major component! If one takes into account a possible presence of lower CFs ($C_{60}Cl_{26}$, $C_{60}Cl_{22}$), the concentration of $C_{60}Cl_{24}$ would have to be even lower in order to make up the reported average composition of $C_{60}Cl_{26.4}$. This suggests that $C_{60}Cl_{24}$ purity reported in the original study is overestimated.[26] The highly symmetric T_h-$C_{60}Cl_{24}$ is likely to dominate the IR spectrum even when present in a relatively small concentration, with the rest of the sample composed of multiple low symmetry CFs.

Under favorable conditions (when IR spectra of at least some constituents of CF mixture are known), IR spectroscopy can be used to reveal the presence of impurities in CF sample. For example, IR spectrum revealed the presence of D_{3d}-$C_{60}Cl_{30}$ in T_h-$C_{60}Cl_{24}$.[35] However, our results demonstrate that in general IR spectroscopy is not suitable for the evaluation of molecular composition and purity of CFs in mixtures, and it should be used mainly for the characterization of bonified pure CFs. These conclusions can also be expanded to other types of vibrational spectroscopy (far-IR, Raman spectroscopy).

E. UV-Vis Spectroscopy. The electronic transitions exhibited by fullerene derivatives are highly dependent on their addition pattern. The nature of the substituents has a much less pronounced effect on the UV-Vis spectra of these compounds (unless the substituents themselves absorb in the UV-Vis range of interest). These features allow one to use UV-Vis spectroscopy for elucidation of addition patterns by matching the UV-Vis spectrum of the compound in question with the reference spectra of the derivatives with known addition patterns (we use this method to evaluate the addition patterns of *o*-, *p*-$C_{60}Cl_2$ in Section I-2-4-B).[40,41] Additional structural data, such as symmetry of the compound (usually deduced from NMR spectroscopy), can be used to narrow down the list of possible addition patterns. Since this method relies on the reference UV-Vis spectra of the fullerene derivatives with known addition patterns, it is not applicable for

the compounds with unprecedented addition patterns, which have to be structurally studied by other means (see the discussion of $C_{60}Cl_{10}$ in Section II.2.4.C).

UV-Vis spectroscopy is often used for accurate measurement of concentrations. However, our study of $C_{60}Cl_6$ samples **A**–**D**, which range from 95 to 27 mol% $C_{60}Cl_6$, demonstrate that UV-Vis spectroscopy is poorly suited for even a qualitative evaluation of CF purity. As the purity of the $C_{60}Cl_6$ samples decreased, their UV-Vis spectra lost their clearly defined, if overlapped, absorption bands and became relatively featureless. Generally, the absence of well-resolved peaks in the UV-Vis spectra of CFs makes UV-Vis quantification of the molecular composition of CF mixtures close to impossible, especially if some or all of the impurities have not been characterized in 95+ mol% purity. Nevertheless, we have discovered that samples with similar amounts of the principal CF component can be distinguished from one another in *some* cases. For example, samples **A** (95 mol% $C_{60}Cl_6$) and **B** (88% $C_{60}Cl_6$) display notable differences in their UV-Vis spectra (which is probably due, in large part, to ca. 6 mol% C_{60} impurity in sample **B**).

These data demonstrate that the purity of the CF sample should be firmly established when UV-Vis spectroscopy is used for the assessment of the addition pattern, since even minor impurities can cause unpredictable changes of the UV-Vis spectrum, which in turn can deem addition pattern assignment unreliable.

F. NMR Spectroscopy. Carbon-13 NMR spectroscopy can be a powerful method for the structure elucidation of organic compounds, including fullerene derivatives. In favorable cases, the 2-D correlation technique ^{13}C INADEQUATE can reveal the connectivity of carbon atoms, making a complete peak assignment and addition-pattern determination possible.[42-47] However, it is often the case that ^{13}C NMR spectra of fullerene derivatives can only be used for the determination of molecular symmetry; a more complete analysis can be hindered by the presence of many overlapping signals. In addition, even "routine" natural-abundance ^{13}C NMR spectra of fullerene derivatives

require long acquisition times and relatively concentrated samples due to the low receptivity of the ^{13}C nucleus and the relatively low solubility of most fullerene derivatives. The only ^{13}C NMR spectra of CFs reported to date are C_s-SPP-$C_{60}Cl_6$ (ref. 12 and this work), C_s-$C_{70}Cl_{10}$,[48] and C_1-14,28,29,31,SPP-$C_{60}Cl_{10}$ (this work) No ^{13}C INADEQUATE studies of CFs have been reported.

In general NMR spectroscopy is a convenient method of purity evaluation since under favorable conditions the intensity of the peaks is directly proportional to the concentration of the corresponding compounds (taking into account their symmetry). For the following discussion we will assume that sufficiently long relaxation times (possibly combined with the use of relaxation agents) and a uniform excitation of the spectral region of interest are ensured. Then molar ratios of the sample components (CFs, without restricting the generality) can be easily calculated if they have observable and identifiable NMR signatures. If we consider that the peaks cannot be detected if their signal-to-noise (S/N) ratio is equal or below 2, then we can calculate the lower limit of molar purity (LLMP) of the major component. Assuming there are no resonances that overlap one another, the LLMP depends on the following: (i) the number of impurities (assuming the worst-case scenario of the equal concentrations of the impurities); (ii) the molecular symmetries of the impurities; (iii) the S/N ratios for the peaks of the major component; and (iv) the symmetry of the major component. For example, let us consider an asymmetric (C_1) major component, so that all of its ^{13}C peaks have the same intensity (the case of higher symmetry is similar). If the peaks of this major component are observed with S/N = 12 (i.e., a high-quality fullerene-derivative ^{13}C NMR spectrum), then the highest possible undetectable concentration of the asymmetric impurity is only 6 times smaller than the concentration of the major component. In other words, the LLMP of the major component is 87 mol% (a single C_1-impurity in a C_1-major component). The LLMP drops quickly as we increase the number of possible impurities, decrease the S/N

ratio of the spectrum, or increase the symmetry of the major component (see Section A-I-2-2 and Table A.10 for estimates of several LLMPs).

The results of a ^{13}C NMR study of several $C_{60}Cl_6$ samples with different purities confirm these conclusions. ^{13}C NMR spectra of the samples **A**, **B**, and **C** (95%, 86%, and 67% of $C_{60}Cl_6$) show $C_{60}Cl_6$ spectra with very similar quality. These spectra have the similar S/N ratios (11±2, see Section A.4), but it is still insufficient to reveal the presence of CF impurities in the samples **B** and **C**. ^{13}C NMR spectrum of the sample **E** containing 75 mol.% of C_s-$C_{60}Cl_6$ and 25 mol.% of C_1-$C_{70}(CF_3)_{10}$ showed no peaks of the latter at S/N = 6 for the peaks of the major component, in a perfect agreement with the calculated LLMP (75% for C_2-major component containing a single C_1-impurity, see Section A.4 and Figure A.13). The reference spectrum of 98% pure C_1-$C_{70}(CF_3)_{10}$ (sample **F**) is shown on Figure II-2 for comparison (see Figure A.13). Even the spectrum of sample **D** (27% of $C_{60}Cl_6$) is dominated by the lines of $C_{60}Cl_6$, although additional peaks and baseline drift become observable. The signal of a highly symmetric I_h-C_{60} (a single line marked with a dagger) can be easily identified among the peaks of $C_{60}Cl_6$ in the spectrum of sample **D**, demonstrating the importance of molecular symmetry on the detection limit (similar to the case of IR spectroscopy, see Section II.2.1.D). It is interesting that according to the HPLC data, sample **D** contains 27% of $C_{60}Cl_6$ and 14% of C_{60}, which should make ^{13}C NMR peak of C_{60} about 15 times more intense than the double-intensity peaks of C_2-$C_{60}Cl_6$. This discrepancy is likely caused by a poor solubility of C_{60} in $CDCl_3$, which was used as a solvent for NMR spectra acquisition (CFs were found to be highly soluble in $CDCl_3$, see Table A.9).

These results conclusively show that ^{13}C NMR spectroscopy cannot be used to determine the molecular compositions of CF mixtures, although NMR spectroscopy of nuclei with higher receptivities (e.g., ^{1}H and ^{19}F) *is* suited for purity evaluation (due to higher S/N ratios), these methods are not suitable for CF study. However, in 2007 Troshin et al. reported a new procedure for the preparation of $C_{60}Cl_6$, claiming that it

"gives as good results as reported recently 'seven minute' synthesis" [sic],[9] which is the $C_{60}Cl_6$ synthesis previously reported by our group.[17] In our opinion, the chemical synthesis has at least two well-defined numerical measures of its "goodness": yield and purity of the product (other parameters, like time requirements and chemicals and equipment are more difficult to quantify). With these measures of synthetic "goodness" defined, the quoted statement of the ref. 9 (quoted above) is incorrect since (i) the yield of this alternative procedure is notably lower than the yield achieved by our "seven-minute" synthesis (77%[9] versus 90%[17]) and (ii) the claim of high purity of the $C_{60}Cl_6$ product in ref. [9] was based solely on the absence of additional peaks from the ^{13}C NMR spectrum of the product (S/N = 12, see Figure A.13). Our results show that this evidence is insufficient and other analytical methods, preferably HPLC, should be employed to substantiate the claim of high $C_{60}Cl_6$ purity (the absence of product purity also makes the validity of the reported yield of 77%[9] questionable).

G. Mass Spectrometry (MS). General Comments. Due to a relatively weak bonding between chlorines and fullerene carbon cage, CFs are challenging objects for mass spectrometry. For a long time MS was thought to be unsuitable for CF analysis, since these compounds were undergoing a complete (under EI and FI conditions[10]) or partial (under FAB[21] and MALDI conditions[22,24,25]) loss of chlorine substituents (fragmentation) during the ionization process.

a. FAB-MS. The first observation of CF anions in MS experiment was reported in 1997 by Adamson et al.[21] A wide range of closed-shell CF ions ($C_{60}Cl_n^-$, n = 1–23, odd numbers only) was observed, suggesting an extensive fragmentation of the CF sample. No other example of FAB mass spectra of CFs has been reported up to date. Our experiments with FAB-MS of a variety of different CFs always resulted in a complete CF degradation yielding a parent bare-cage fullerene without any detectable CF ions, implying that this ionization technique is generally too harsh for CFs.

b. MALDI-MS. In 1999 Heymann et al. reported the first successful observation of CF ions ($C_{60}Cl_{7,9,11}^-$ and $C_{70}Cl_7^-$) using NI-MALDI with 2,5-dihydroxybenzoic acid (DHB) as a matrix.[22] However, other analytical methods used in this study (WG, PIXE-NMP, E-probe) indicated a considerably higher chlorine content of the original CF samples ($C_{60}Cl_{45-16}$ and $C_{70}Cl_{31-18}$), suggesting that an extensive fragmentation of CFs was taking place during MALDI-MS. In 2002 we showed that a sulfur matrix suppresses the fragmentation of halogenated fullerenes, allowing for the first MS observation of highly chlorinated CF ions ($C_{60}Cl_n^-$, n = 5–31, odd numbers only).[24] Later we used a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) matrix, which not only minimized fragmentation of CFs with high chlorine content, but also led to the first successful MS analysis (MALDI{DCTB}-MS) of lower CFs (a series of $C_{60}Cl_6$ samples) with a minimal fragmentation.[17] The best results were achieved using the negative-ion MS, which gave a single major peak of $C_{60}Cl_5^-$ and a minor peak of $C_{60}Cl_7^-$ (about 10% as intense as $C_{60}Cl_5^-$, resulting form chlorine addition to $C_{60}Cl_6$, see Figure II.15a) for a 95% pure sample of $C_{60}Cl_6$.[17] The positive-ion MS showed a more substantial fragmentation, with a complete range of closed- and open-shell CF ions ($C_{60}Cl_n^+$, *n* = 1, 2, 3, 4, 5, 6, 7) for the same $C_{60}Cl_6$ sample, demonstrating that negative-ion MALDI{DCTB}-MS is the method of choice for the analysis of CFs.[17] In this work we used NI-MALDI{DCTB}-MS to analyze several CF samples, including HPLC purified $C_{60}Cl_{10}$ (see Figure II.14d and Section II.2.4.C). The NI-MALDI{DCTB} mass spectrum of $C_{60}Cl_{10}$ consists of a single major peak of $C_{60}Cl_9^-$, two less intense fragment peaks of $C_{60}Cl_{5,7}^-$, and a minor peak of $C_{60}Cl_{11}^-$ (Figure II.14d), showing that fragmentation and chlorine addition are likely to be the general phenomena taking place during MALDI{DCTB}-MS of CFs (see Section II.2.1.G.b for further discussion). These processes (together with analyte suppression effects, see Section II.2.1.D and refs. [38,39]) limit the applicability of this method to the determination of the chlorine content of pure CFs and determination of the highest degree of chlorination of the CF mixture. Further

development of the MS technique targeting the suppression of the fragmentation and chlorine addition is necessary in order to make MALDI-MS suitable for studies of the molecular composition and purity of CFs. Some promising results on solvent-free sample preparation of MALDI samples (potentially suitable for insoluble CFs) were also reported.[49]

c. ESI- and APCI-MS. In this work we explored the potential of ESI- and APCI-MS for the analysis of soluble CFs for the first time. We did not observe any CF ions in either negative or positive ion ESI mass spectra using non-polar solvents like toluene and CH_2Cl_2. We found that polar solvents (CH_3OH and CH_3CN) boost the ion generation, but they also cause immediate chemical transformations of CFs (e.g., substitution of chlorines by solvent moieties). The very low selectivity of these processes and the high complexity of the mass spectra of the products precluded us from utilizing ESI-MS for CF analysis.

The APCI-MS analysis of 75% pure *o*-$C_{60}Cl_2$ (see Section II.2.4.B for synthetic details) demonstrated the formation of $C_{60}Cl^+$ ion, see Figure II.5, albeit with a low intensity. Under the same conditions 75% pure *p*-$C_{60}Cl_2$ gave raise to both $C_{60}Cl^+$ and $C_{60}Cl_2{}^+$ ions, which can be interpreted as an indication of the higher stability of the molecular ion formed from *para*-isomer of $C_{60}Cl_2$ (see Section II.2.4.B). APCI mass spectrum of 99% pure $C_{60}Cl_4$ showed a complete range of $C_{60}Cl_{1-4}{}^+$ ions, see Figure II.5 (same MS conditions were used). We were unable to observe any negative CF ions formed from *o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, and $C_{60}Cl_4$, likely due to the insufficiently high electron affinity of these CFs. APCI-MS of $C_{60}Cl_6$ gave detectable CF ions with both positive (see Figures II.3 and II.5) and negative (see Figure II.3) charge. The positive-ion APCI mass spectrum of $C_{60}Cl_6$ shows extensive fragmentation (a complete range of $C_{60}Cl_{1-6}{}^+$ ions is present). We also observed a product of chemical transformation ($C_{60}Cl_4(C_7H_7)^+$ formation, see Figures II.5 and A.17), which is likely taking place in the ion source. In the negative-ion mode the mass spectrum shows only peaks of $C_{60}Cl_5{}^-$ and $C_{60}Cl_7{}^-$ ions with similar

intensities. The NI-APCI-MS analysis of both 95% and 86% pure samples of $C_{60}Cl_6$ (samples **A** and **B**, see Figure II.3) also showed $C_{60}Cl_5^-$ and $C_{60}Cl_7^-$ peaks (with similar

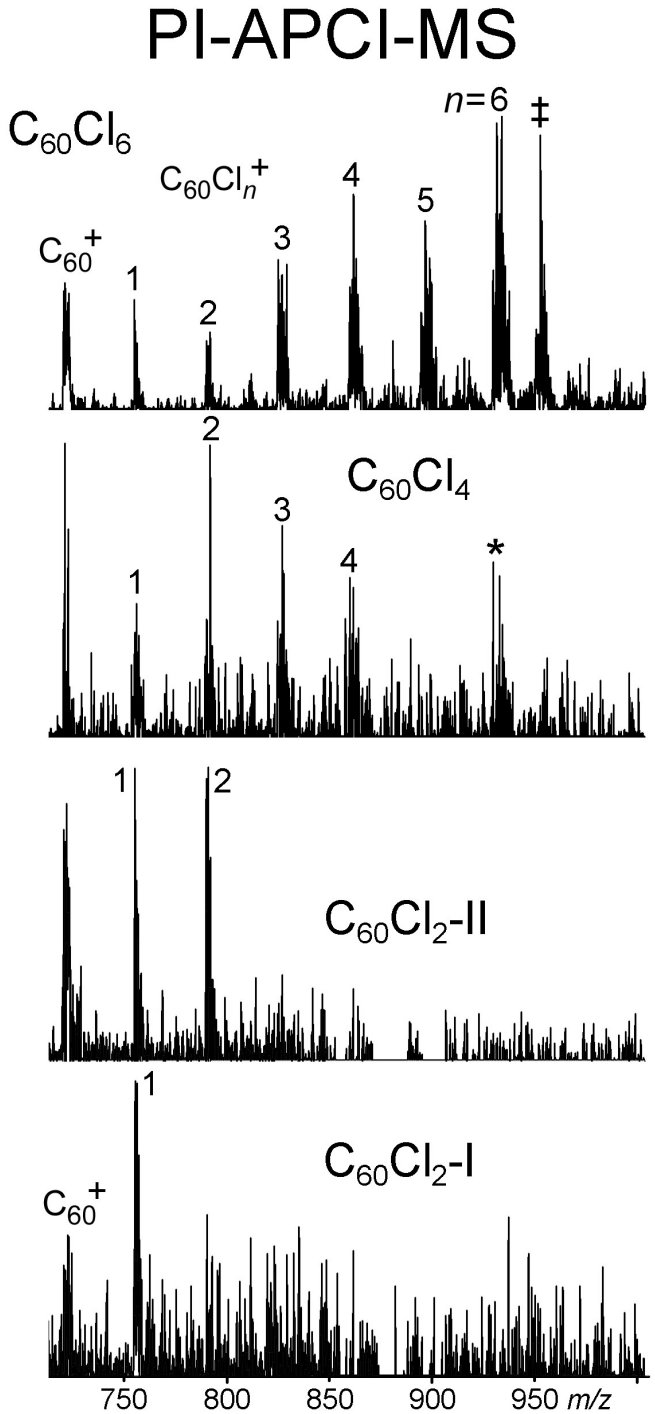


Figure I-5. PI-APCI-MS of lower CFs ($C_{60}Cl_2$-I, $C_{60}Cl_2$-II, $C_{60}Cl_4$, $C_{60}Cl_6$). A peak marked with asterisk is not due to $C_{60}Cl_6^+$ (the m/z ratio of it lower). A peak marked with double dagger is due to $C_{60}Cl_4(C_7H_7)^+$. See Figure A-I-17 for expansions and plots of theoretical isotopic distributions.

intensities) for both samples, indicating that $C_{60}Cl_7^-$ is produced from $C_{60}Cl_6$ itself (see Section II.2.1.G.b). This is also confirmed by the NI-APCI mass spectrum of a ca. 98% pure $C_{60}Cl_{10}$ sample (see Figure II.3, sample **G**), showing a prominent peak of $C_{60}Cl_{11}^-$ (accompanied with fragments $C_{60}Cl_{7,9}^-$), although there could be no more than a few percent of $C_{60}Cl_{12}$ (if any at all) present in this sample. No positive CF ions were detected during $C_{60}Cl_{10}$ study, indicating that positive-ion APCI is poorly suitable for the analysis of CFs with higher chlorine content ($C_{60}Cl_n$, $n > 6$).

These results demonstrate that chlorine addition to the CF molecules takes place for $C_{60}Cl_6$ and $C_{60}Cl_{10}$ under negative-ion APCI and MALDI mass spectrometry. This process should be strongly suppressed for higher CFs (i.e., $C_{60}Cl_{30}$) due to steric effects. Currently, we do not possess pure samples of $C_{60}Cl_n$ with $n > 10$, so we cannot experimentally study the behavior of higher CFs in MS. In order to avoid misinterpretation of the MS data, we assign the highest degree of chlorination of CF samples as a range of n(Cl) when CF ions above $C_{60}Cl_{11}^-$ are present (for pure CFs other methods should be used to corroborate n(Cl). For example, if the heaviest CF ion observed in the spectrum is $C_{60}Cl_{17}^-$, the highest CF present in the sample can be either $C_{60}Cl_{18}$ or $C_{60}Cl_{16}$ (with and without chlorine addition taking place), which we designate as $C_{60}Cl_{16/18}$.

Our work shows that APCI-MS is suitable for informative CF analysis; however, this method cannot be relied upon for the purity evaluation of CFs. So, NI-APCI mass spectra of $C_{60}Cl_6$ samples **A**, **B**, **C**, and **D** (95–27 mol% $C_{60}Cl_6$, see Figure II.3) indicate the presence of the higher chlorinated impurities only for samples **C** (67 mol% $C_{60}Cl_6$) and **D** (27 mol% $C_{60}Cl_6$). Furthermore, the NI-APCI mass spectrum of 98 mol% $C_{60}Cl_{10}$ (see Figure II.3, sample **G**) is similar to the spectrum of 67 mol% $C_{60}Cl_6$ sample **C**, demonstrating the limitations of this method.

A conclusion can be made that APCI-MS can be successfully used for the analysis of CF samples. As opposed to MALDI-MS, this method does not require a cumbersome

sample preparation, allowing one to analyze solutions of CFs. We show that APCI-MS is suitable for analysis of CFs with both low ($C_{60}Cl_n$, n = 2, 4, positive-ion MS) and high ($C_{60}Cl_n$, $n \geq 6$, negative-ion MS) chlorine content. Currently both APCI- and MALDI{DCTB}-MS cannot be used for the evaluation of molecular composition and purity of CFs, limiting their applicability to the determination of the composition of pure CFs and measurements of the highest degree of chlorination in the samples of mixtures of CFs.

H. Single-Crystal X-Ray Diffraction Study. Whenever single crystals of CFs with sufficiently high quality are obtained, this method can give the definitive information on the CF structure. [13-16] However, the formation of the quality single crystals cannot be used as an evidence for the high purity of the bulk product (although sometimes it is true). This can be illustrated by several examples. In 2005 the structure of T_h-$C_{60}Cl_{24}$ was determined, using the crystals grown from the bromine solution of the crude CF sample.[13] However, we show in this work that the originally reported 90% purity of the bulk product is likely overestimated (see Sections II.2.1.D and II.2.1.F). In 2007 the structure of $C_{60}Cl_6$ was determined by single-crystal X-ray diffraction for the first time.[16] However, the authors reported[16] that the crystals of $C_{60}Cl_6$ were mixed with the crystals of unreacted C_{60}, which comprised ca. 40% of the product (in this work we were able measure a higher-quality structure of $C_{60}Cl_6$ grown from toluene solution, see Section II.2.4.A). Another interesting example comes from this work: we obtained single crystals of $C_{60}Cl_3H$ from the solution of 99% pure $C_{60}Cl_4$, indicating that chemical transformation of $C_{60}Cl_4$ was taking place in solution under air (sample was stored in the dark at low temperature, see Section II.2.4.B). Also single-crystal X-ray diffraction study may not be able to reveal a presence of a few percent of an impurity present in the crystal itself, especially when the impurity forms a solid solution with the main component. This demonstrates that even if a single-crystal X-ray diffraction study leads to a successful

structure determination, other methods should be used for the analysis of the bulk CF samples if their molecular composition and purity are of interest.

I. Analytical Methodology for CF Investigation. Based on these results, we developed an analytical methodology for analysis and characterization of CFs that was used throughout this work. The first step of CF analysis employs HPLC (surveying several different eluents to reveal a possible peak overlap) as the only method able to determine the relative amounts of different fullerene components present in crude CF samples (see Sections II.2.3 and II.2.4). If a crude sample is found to contain a single major component with a sufficiently high purity, it can be characterized further by other methods. However, the only $C_{60}Cl_n$ that was shown to be prepared in relatively pure form (80-90%[17]) without the need of further separation is $C_{60}Cl_6$ (see ref. 17 and Sections II.2.3 and II.2.4 for the detailed discussions of CF synthesis). If a crude CF sample contains many different CFs present at similar concentrations, individual CFs have to be isolated first by HPLC separation (which can require several stages, see Sections II.2.4.B and II.2.4.C). Once individual single-isomer CFs are obtained with sufficiently high purity, they may be analyzed by MALDI- or APCI-MS in order to determine their composition. Since the extent of chloride addition is unknown for $C_{60}Cl_n$ with $n > 10$ (see Section II.2.1.G), the MS results should be corroborated for these CFs by other methods like ^{13}C-NMR or single-crystal X-ray diffraction study. Vibrational (IR and Raman) and UV-Vis spectroscopy can also be used for sufficiently pure CFs; besides being good methods of CF characterization their results can be used for structure elucidation (see Sections II.2.1.D and II.2.1.F). Methods like EA and TGA may be used too, but they require a destruction of a significant quantity of (purified) CFs, which may be prohibitive for their application.

II.2.2. Stability and Photodegradation of Chlorofullerenes

A. General Remarks. The knowledge of CF stability under various conditions is critical for their further chemical derivatization and potential applications of these compounds. The scattered data on CF stability that has been reported up to date deal almost exclusively with thermal decomposition of dry solid samples of CFs (stability of CFs in solid phase). Our previous paper briefly mentioned the question of $C_{60}Cl_6$ stability is toluene solution. In this paper we report our study of CF stability both in solid phase and in solution.

B. Stability of Chlorofullerenes in the Solid State. Published in the same journal in 1991, the first two papers dedicated to CF preparation and properties also gave the first insight into thermal stability of these compounds.[10,11] Olah et al. reported that a CF sample (average composition estimated as $C_{60}Cl_{24}$) decomposed completely into its parent fullerene upon heating at 400 °C under argon atmosphere (the exact details of the experiment were not given).[10] In the second paper, Tebbe et al. monitored the thermal decomposition of $C_{60}Cl_{12\text{-}15}$ by IR spectroscopy as the sample was heated under vacuum, observing the onset of chlorine loss at 200 °C and the completion of this process at 350 °C.[11] Much later, in 2004 and 2005, T_h-$C_{60}Cl_{24}$ and D_{3d}-$C_{60}Cl_{30}$ were studied by TG, resulting in the following ranges of decomposition temperatures: 280-390 °C (T_h-$C_{60}Cl_{24}$)[13,26] and a remarkably high 450-500 °C (D_{3d}-$C_{60}Cl_{30}$).[14] Despite the fact that the structures of these two CFs were determined by single-crystal X-ray diffraction study, the purity of the corresponding *bulk* samples was either not established reliably for T_h-$C_{60}Cl_{24}$ (see Sections II.2.1.C and II.2.1.D) or not reported for D_{3d}-$C_{60}Cl_{30}$. We also

reported a decomposition temperature of 270 °C (corresponding to the maximum rate of mass loss in a TGA experiment) for $[C_{60}Cl_5]_2$ dimer in our 2005 paper.[17,27]

Due to temperature dependency of the rate of CF decomposition, TGA is likely to give a higher decomposition temperature than methods based on prolonged annealling of CFs at the constant temperature. For example, our TGA study of $C_{60}Cl_6$ shows that the rapid mass loss starts at ca. 250 °C, reaching its maximum rate at ca. 325 °C (see A.4). A separate annealing experiment conducted at 220 °C for a period of 30 min led to the decomposition of ca. 30% of $C_{60}Cl_6$ into C_{60} (as shown by the HPLC analysis of the annealed sample), which shows that TGA somewhat overestimates the thermal stability of CFs. Furthermore, CF isomerisation and/or disproportionation may take place without chlorine loss and hence these processes may not be detectable by TGA. We did not observe any isomerization products or CFs resulting from partial chlorine loss in the annealed $C_{60}Cl_6$ sample from the aforementioned experiment (only $C_{60}Cl_6$ and C_{60} were detected by HPLC). However, when we performed similar experiment with kinetic isomer of fluorofullerene T_h-$C_{60}F_{24}$, we found that it undergoes both fluorine loss and fluorine migration during sublimation at 300 °C. This process results in the formation of C_{3v}-$C_{60}F_{18}$.[50] The contigious addition pattern of $C_{60}F_{18}$ is not a subpattern of T_h-$C_{60}F_{24}$, which features non-contigious arrangement of fluorines, implying that fluorine rearrangement is necessary for this convertion to take place. This peculiar structure makes T_h-$C_{60}F_{24}$ a more energetic kinetic isomer (both D_2 and D_{3d} isomers of $C_{60}F_{24}$ have contiguous addition patterns and are 340 and 280 kJ mol^{-1} more stable than T_h-$C_{60}F_{24}$, respectively[51]), which may provide the driving force for the thermal isomerization of this compound. Kinetically stable CFs are likely to undergo a similar thermally induced isomerisation; for example, a kinetically stable C_1-$C_{60}Cl_{30}$ (prepared at 160 °C, calculated to be 78 kJ/mol less stable than D_{3d} isomer) was reported to be converted completely into D_{3d}-$C_{60}Cl_{30}$ isomer after 2 days of heating at 300 °C (in the presence of $SbCl_5$).[15]

In conclusion, these data show that CFs have a relatively high thermal stability in the solid phase. The CFs studied up to date are less thermally stable than fluorofullerenes ($C_{60}F_{18,36,48}$ sublime unchanged at ca. 200–400 °C), but more stable than bromofullerenes, which easily lose bromine at ca. 100-220 °C,[52] following the order of the bond energy values for F-C_{60}, Cl-C_{60}, and Br-C_{60} (corresponding average values of bond enthalpy: 347, 167, 83 kJ/mol[53]). It is important that our HPLC analysis of solvent-free solid samples of $C_{60}Cl_6$ did not show any detectable changes even after ca. 6 months of storage under air at room temperature (samples were not shielded from the ambient fluorescent light in the laboratory). This demonstrates the high stability of at least some CFs upon storage, which is important for the further use of these compounds in synthetic practice.

C. Chlorofullerene Stability in Solution. The first report of the CF stability in solution was given in our earlier paper in 2005, where we found that $C_{60}Cl_6$ slowly decomposes in toluene solution (under ambient air atmosphere).[17] During our further work we found that CFs decompose in solution, making their HPLC isolation and purification impossible. In order to inhibit this degradation, we performed a detailed study of CF stability in solution.

A dedicated HPLC purified (to 95% purity) sample of $C_{60}Cl_6$ was used to prepare a stock solution in degassed, deoxydenated toluene. This solution was split into four batches that were stored for 35 days under different conditions: i) sample **I** was kept in the dark, under N_2; ii) sample **II** was kept under light, under N_2; iii) sample **III** was kept in the dark, under air; iv) sample **IV** was kept under light, under air. The solutions stored under air were also airated prior to the beginning of the experiment. All other conditions were kept the same (the containers were kept together in order to ensure the same temperature history). The four solutions were regularly analyzed by HPLC (samples of the same volueme were analyzed directly without any prior workup). The resulting HPLC

traces were arranged into 3D waterfall plots (see Figure II.6), providing a convenient way of data visualisation.

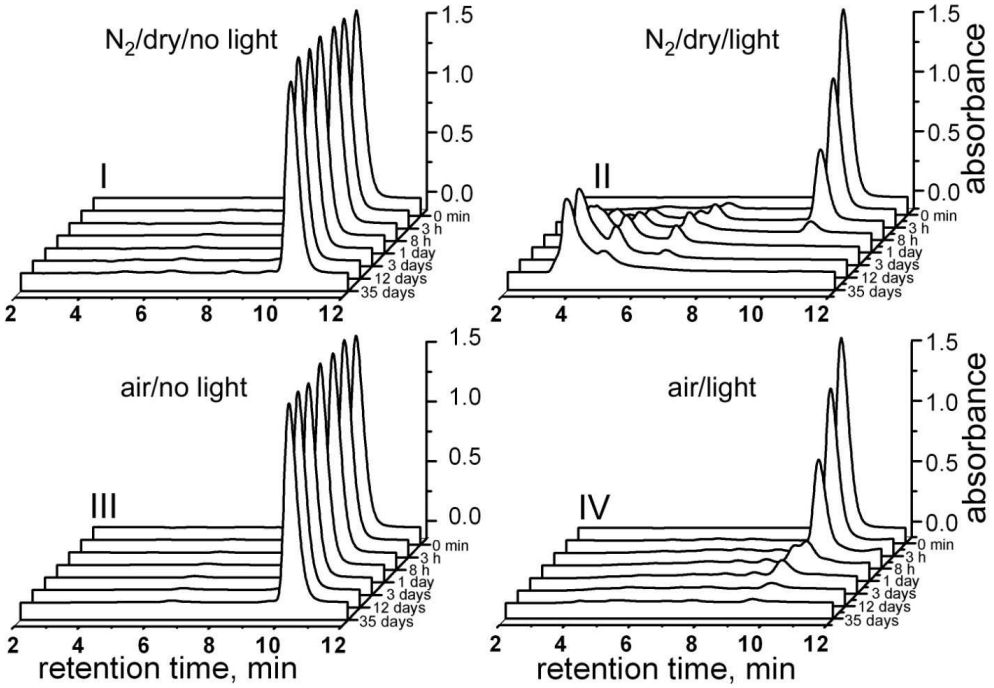


Figure II.6. HPLC monitoring of $C_{60}Cl_6$ solutions in toluene: i) sample **I** was kept in the dark, under N_2; ii) sample **II** was kept under light, under N_2; iii) sample **III** was kept in the dark, under air; iv) sample **IV** was kept under light, under air.

The results convincingly show that ambient light (regular fluorescent laboratory lightning) is the main factor that causes $C_{60}Cl_6$ degradation in solution. The half-life of $C_{60}Cl_6$ in toluene is only about 5 hours when exposed to light; in the dark the concentration of $C_{60}Cl_6$ is virtually unchanged even after 35 days of storage, both under inert atmosphere (N_2) and air. When air does not change the rate of $C_{60}Cl_6$ photodecomposition, it has a strong effect on the composition of the products, see Figures II.6 and II.7. APCI-MS analysis of sample **II** after 35 days of light exposure showed the main signal with *m/z* = 1176 Dal, corresponding to $C_{60}(C_7H_7)_5^-$ ion, see Figures II.8 and II.9. On the other hand, no fullerene-containing species could be detected by APCI-MS in sample **IV** after the same period of time (sample **IV** was kept under air). The HPLC analysis of sample **II** showed a major peak with R_f of 3.8 min with a shoulder at R_f = 4.9 min; sample **IV** gave a broad range of low-intensity peaks (both samples were

analyzed after 35 days of photodegradation, see Figure II.7), which demonstrates the non-selective degradation of the initial $C_{60}Cl_6$ photodecomposition products in the presence of air.

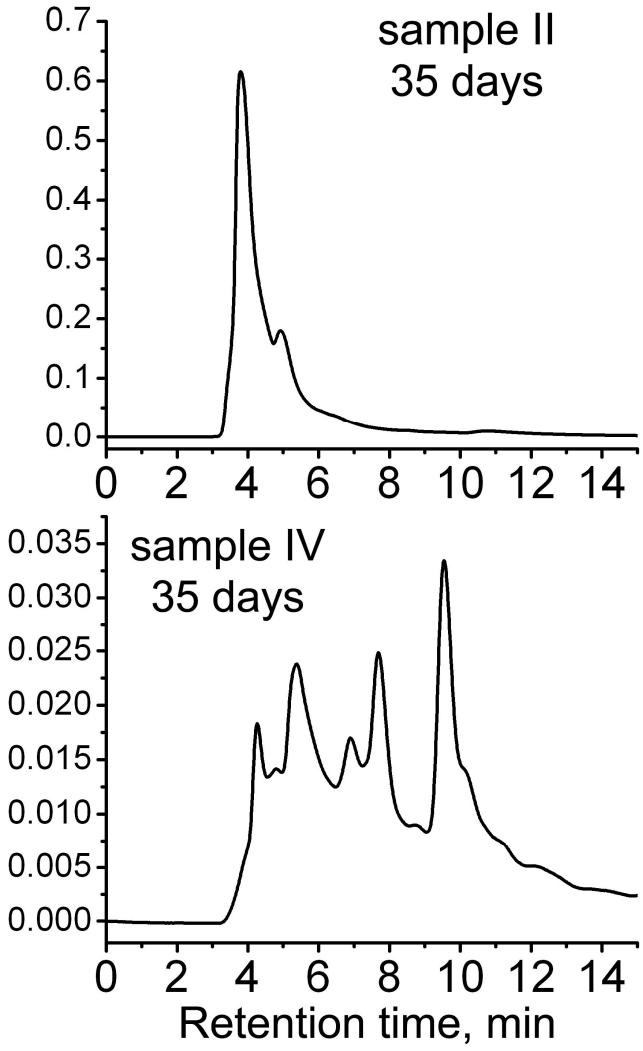


Figure II.7. Vertically-expanded HPLC traces of $C_{60}Cl_6$/toluene samples **II** and **IV** used for photosensitivity study.

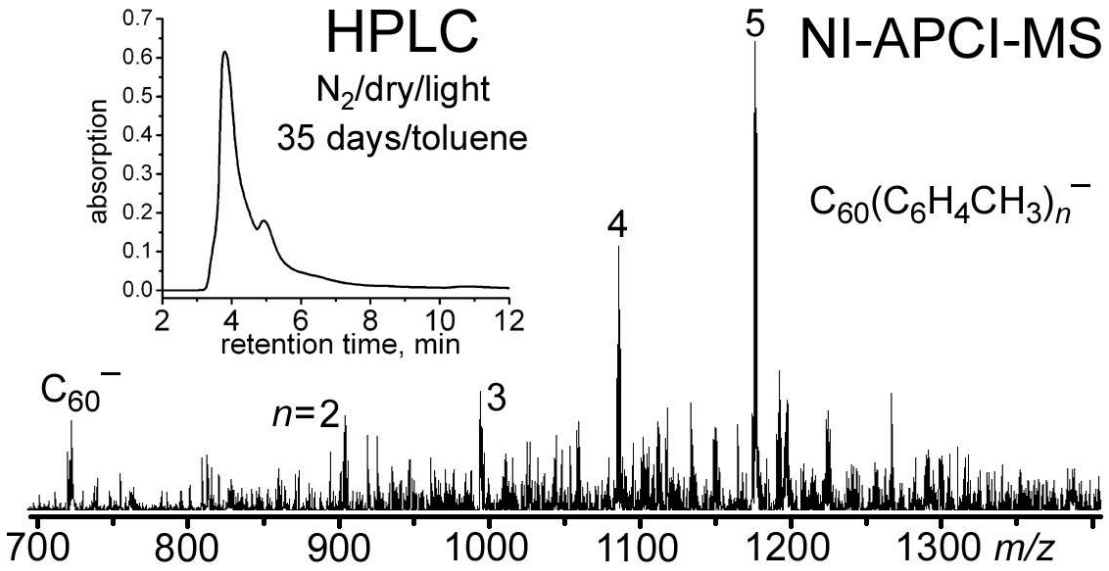


Figure II.8. NI-APCI-MS of the $C_{60}Cl_6$/toluene sample **II** after 35 under light (see Figure A.9 for experimental and calculated isotopic distributions of $C_{60}(C_6H_5CH_3)_5^-$ ion).

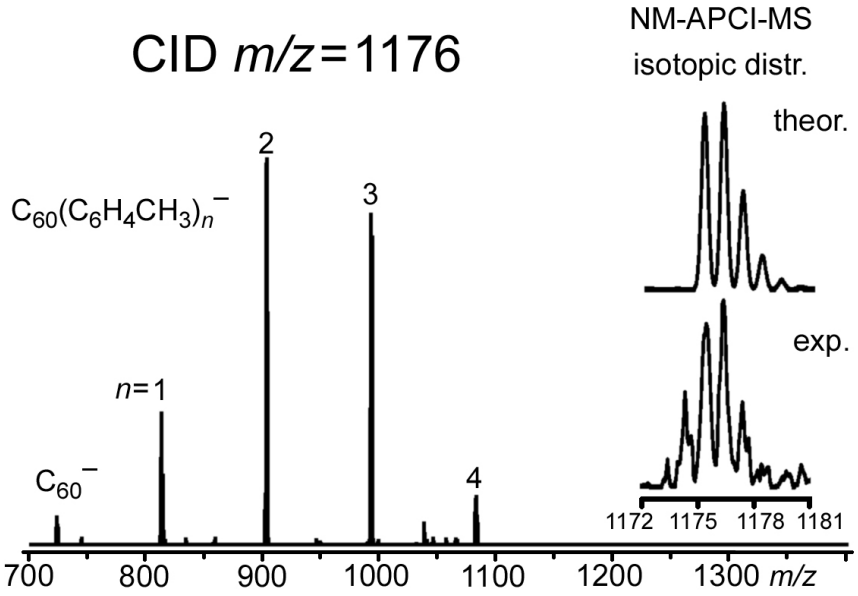


Figure II.9. Collision-induced-dissociation (CID) experiment on $C_{60}(C_6H_5CH_3)_5^-$ ion (NI-APCI-MS) from the $C_{60}Cl_6$/toluene sample **II** after 35 under light (see Figure A.9). The insert shows experimental and calculated isotopic distributions of $C_{60}(C_6H_5CH_3)_5^-$ ion (regular NI-APCI-MS).

$C_{60}Cl_6$ is also photosensitive when dissolved in dichloromethane. The analogous series of four $C_{60}Cl_6/CH_2Cl_2$ experiments showed that the rate of $C_{60}Cl_6$ photodegradion is ca. 15 times slower than in toluene, see Figure II.10.

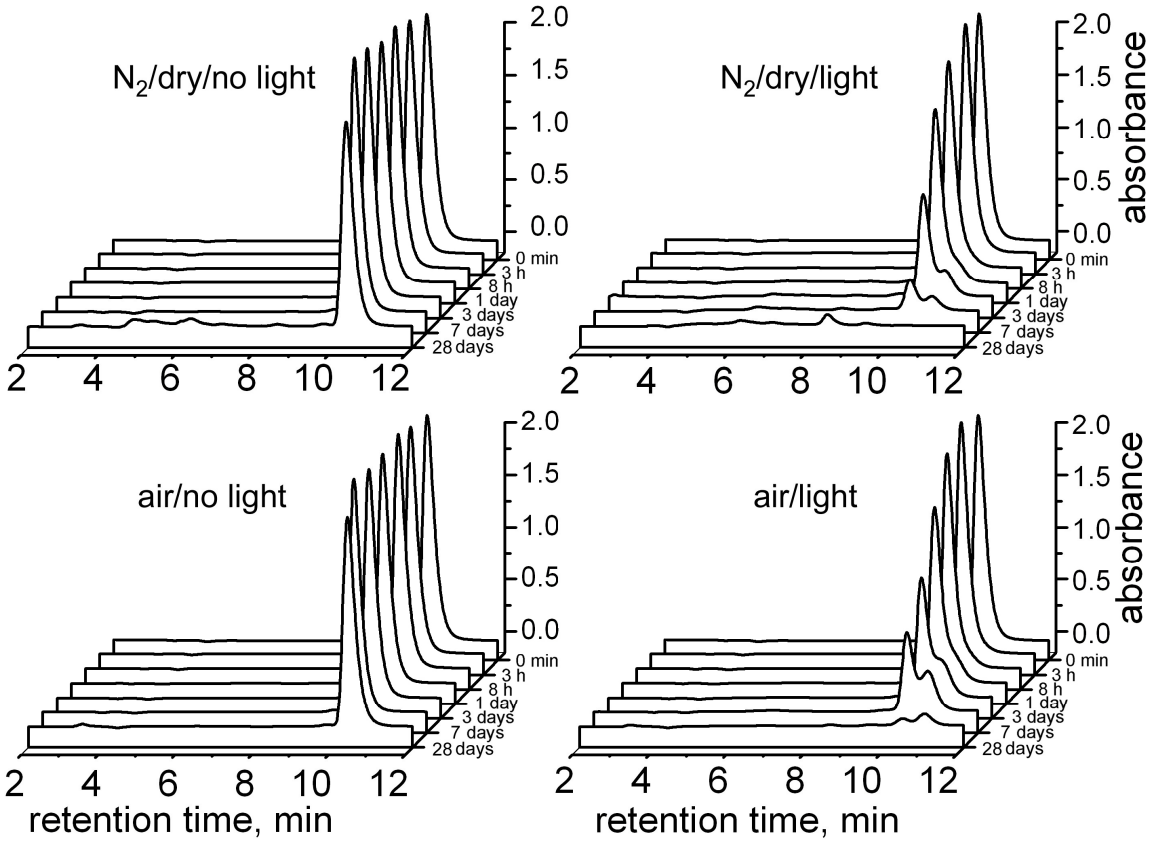


Figure II.10. Stability study of $C_{60}Cl_6$ solutions in CH_2Cl_2.

However, $C_{60}Cl_6$ appears to be slightly less stable in CH_2Cl_2 than in toluene solution during long-term storage in the absence of light (the concentration of $C_{60}Cl_6$ dropped by ca. 15% after 28 days of storage, both under N_2 and air, see Figure II.10). Again, the presence of air does not have an appreciable effect on the rate of $C_{60}Cl_6$ photodecomposition, but it changes the nature of the products. A wide range of photodecomposition products is formed under air (as shown by HPLC), when under inert atmosphere the majority of the products are insoluble, forming a fine brown precipitate. APCI-MS gave inconclusive results for both samples, but the IR spectrum of the insoluble product showed an intense broad peak centered at 1100 cm^{-1}, which coincides with the position of a ν(COC) band (a few weaker lines at lower wavenumbers were also detected, see Figure II.11). The presence of oxygen in the product is surprising since rigorously air-free conditions were employed. Although a small air leak cannot be ruled

out, more data is necessary to assess the nature of the insoluble $C_{60}Cl_6$ photodecomposition products. However, the low solubility of these products suggests that they may have polymeric nature.

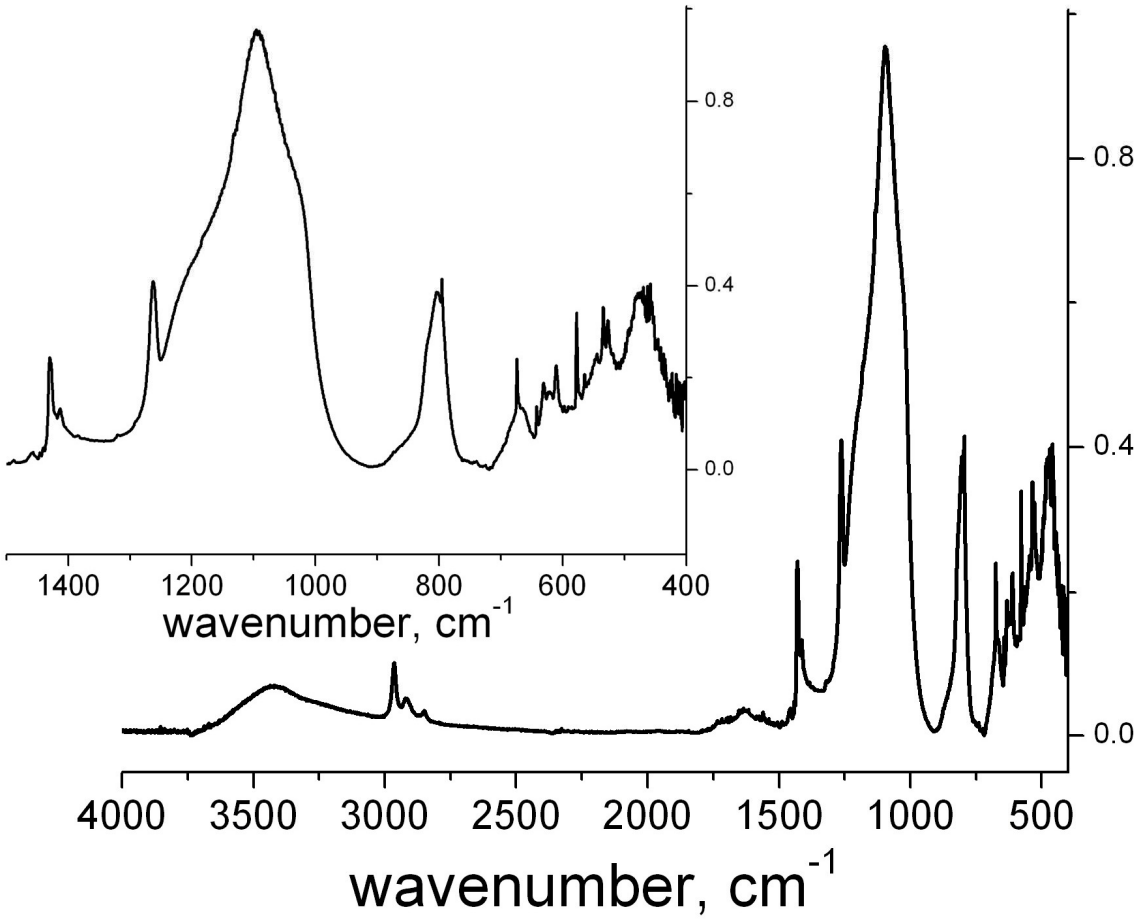


Figure II.11. IR spectrum of the insoluble residue formed after 28 days of storage of $C_{60}Cl_6/CH_2Cl_2$ solution under N_2 in the absence of light.

Similar experiments performed with toluene solutions of mixtures of CFs (containing $C_{60}Cl_{6\text{-}14}$, according to NI-APCI-MS) and 98% pure sample of $C_{60}Cl_{10}$, showed that all of these CFs are photosensitive. The half-life of $C_{60}Cl_{10}$ in toluene solution under ambient light (under air) was ca. 5-6 hours, similar to that of $C_{60}Cl_6$, see Figure II.12.

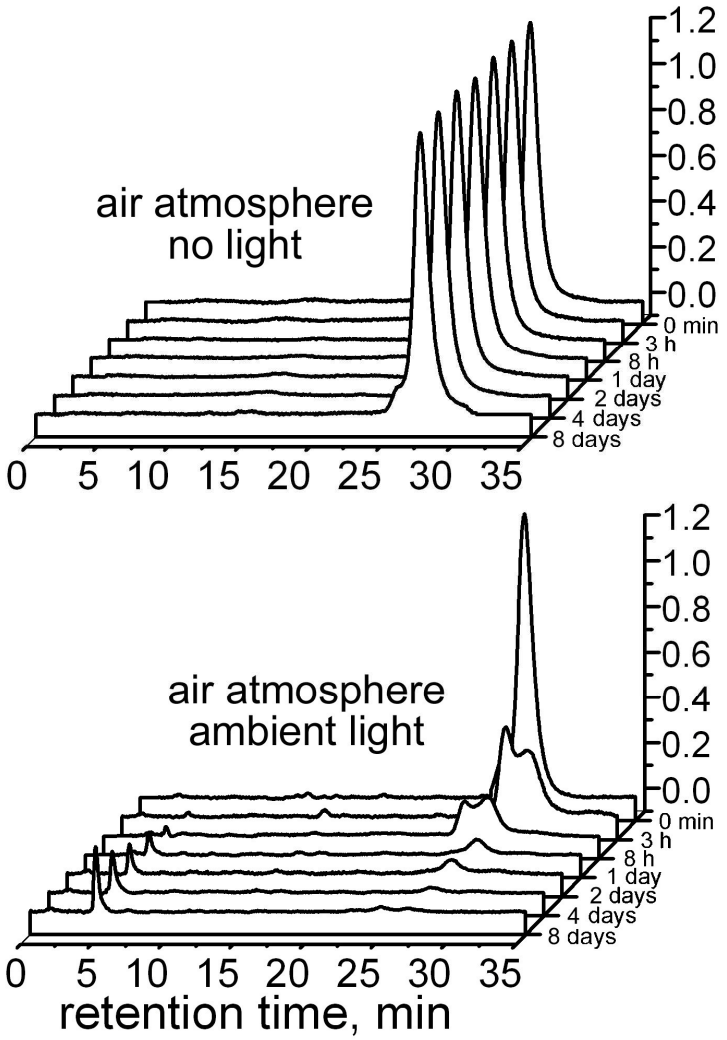


Figure II.12. HPLC monitoring of $C_{60}Cl_{10}$ solutions in toluene under air.

These results show that photosensitivity is likely to be a generic property of CFs. It can be attributed to the photoinduced homolitic cleavage of C-Cl bond, which was shown to take place during irradiation of $C_{60}Cl_6$ solution (λ = 366 nm, benzene or toluene solution), producing radical species that were observed by ESR spectroscopy.[54]

We also performed several experiments with toluene solutions of fluorofullerenes $C_{60}F_{18}$ and $C_{60}F_{36}$. The latter compound did not show any signs of decomposition in solution even after 49 days of storage (under air, both in the dark and under ambient fluorescent light) according to HPLC and APCI-MS analysis. The earlier literature report described light-induced transformation of $C_{60}F_{18}$ into $C_{60}F_{17}O(OH)$ in toluene solution

(incandescent light bulb was used as a light source).[55] Our results confirmed these findings: after 49 days of storage (under air) $C_{60}F_{18}$ was at least partially converted into oxidized fluorofullerene $C_{60}F_{17}O(OH)$ ($C_{60}F_{17}O(OH)^-$ ion was detected by APCI-MS). After 49 days there was practically no starting $C_{60}F_{18}$ left in the solution that was stored under light, when $C_{60}F_{18}$ was largely intact in the sample that was shielded from light, see Figure II.13.

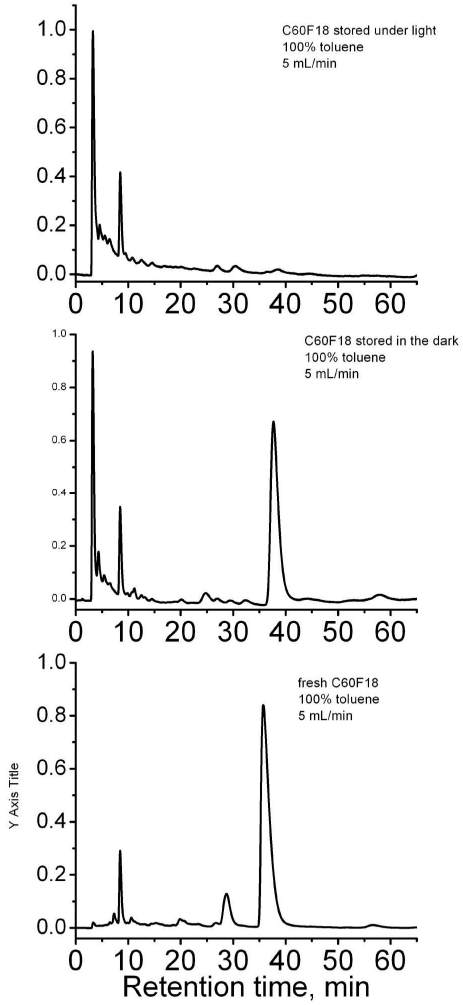


Figure II.13. HPLC analysis of $C_{60}F_{18}$ solutions in toluene under air. The top figure is HPLC trace of $C_{60}F_{18}$ solution after 49 days of storage under ambient light. The middle figure is HPLC trace of $C_{60}F_{18}$ solution after 49 days of storage in the dark. The bottom figure is HPLC trace of the fresh $C_{60}F_{18}$ solution in toluene. The peak with R_f = 38-39 min is $C_{60}F_{18}$ (a slight change of R_f between middle and bottom HPLC traces is likely due to slight impurity of heptanes present in the eluent used for the acquisition of the middle HPLC trace).

Unlike the case of $C_{60}Cl_6$/toluene no fullerene products bearing tolyl fragment(s) were detected for both $C_{60}F_{36}$ and $C_{60}F_{18}$. This suggests that when chemical transformation of some fluorofullerenes can be accelerated by light, the mechanism of this process is different from photodegradation of CFs. Based on the experimental data, it is unlikely that C-F bond dissociation takes place under ambient light irradiation in fluorofullerenes. Instead, ambient light may excite the pi-system of the fluorofullerene molecule, making its affinity for reactions with oxygen and water higher (which is already high for $C_{60}F_{18}$ that produces an oxide $C_{60}F_{18}O$ during synthesis[55]).

The observed photosensitivity of CFs in solution has not been described in the literature before,[36] so the syntheses involving CFs (either as products or as starting materials) were performed without regard to the lightning conditions. When it is difficult to accurately predict the impact of light on many of the reported synthetic procedures, some remarks can be made. Many of the synthetic procedures involving relatively short reaction times and darkly-colored reaction solutions (many CF syntheses employing ICl, ICl_3, or $KICl_4$) are unlikely to be strongly influenced by the ambient light (see Section I-2-4). Most of the reported work on CF synthesis and derivatization falls under this category, except some longer CF preparations[12,21,25] and the methoxylation of $C_{60}Cl_6$, reported to take over 5 days.[4] Many complex products of partial oxidation were obtained from the latter reaction mixture ($C_{60}Me_5O_2OH$, $C_{60}Me_5O_3H$, $C_{60}Me_5OOH$, $C_{60}Me_4PhO_2OH$[4]), which may be the result of partial photodecomposition of the starting material. This reaction would be interesting to repeat in the dark in order to check the influence of light on this process.

When the extent of photodecomposition incurred by CFs during synthesis or further derivatization can be estimated, the degradation of CFs in solutions during the workup, analysis and storage is much more difficult to account for. As we demonstrated above, a trivial step of leaving a solution of $C_{60}Cl_6$ or $C_{60}Cl_{10}$ in toluene (which is a very common solvent in fullerene chemistry) under laboratory light for 5-6 hours can lead to

decomposition of the half of the material, which can unpredictably alter the results of the analysis and further derivatization of these CFs. It is likely that many problems were encountered by the researchers during earlier studies of CFs due to photodegradation, which may justify an experimental reexamination of some of the earlier reports on CF chemistry.

We found that the solutions of all studied CFs are sufficiently stable to survive a brief (few minutes) light exposure without noticeable degradation, which makes them relatively easy to work with. However, a careful exclusion of any prolonged light irradiation is paramount for avoiding CF decomposition during storage, analysis, and possibly derivatization (see Section II.2.1.4). The discovery of CF photosensitivity allowed us to successfully isolate and study several new isomerically pure CFs (*o*-, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, $C_{60}Cl_{10}$) with a variety of analytical methods, including single-crystal X-ray diffraction study (see Appendix A.2). It is noteworthy that all of the previous X-ray quality single crystals of CFs were grown under exotic conditions, either *in situ* during a high-temperature, high-pressure ampoule synthesis or using liquid bromine as the crystallization solvent, which limited the majority of structurally studied CFs to higher chlorinated compounds ($C_{60}Cl_n$, $n \geq 24$). By using light-protected crystallization chamber we were able to successfully crystallize CFs from regular aromatic solvents (toluene), further demonstrating the importance of light-exclusion for CF study.

II.2.3. Re-Examination of Reported Chlorofullerenes: Synthesis and Product Composition

Over a dozen different CFs are listed in Table II.1. Gaseous Cl_2, ICl, ICl_3, $KICl_4$, $SbCl_5$, VCl_4, $POCl_3$, and PCl_5 were used to convert bare-cage fullerene (in one case, a bromofullerene $C_{60}Br_{24}$[26]) into CFs. The molecular composition of the bulk CF products was not discussed (or investigated), except in our earlier paper;[17] nevertheless, these products were referred to by the precise molecular formulas, leading the reader to assume their high purity. In order to determine the molecular composition and purity of these CFs, we repeated some of the published CF syntheses and analyzed the products by MALDI-MS and HPLC (see Figure II.14).

Reactions of C_{60} with elemental chlorine were the first ones used for CF preparation. Different conditions were reported to give different products: (i) high-temperature reaction with gaseous Cl_2 (tube furnace, 250–400 °C) produced mixtures of CFs with an average composition $C_{60}Cl_{\sim 24}$ (Table II.1, Nos. 1, 8, 10, 12);[10,23,31,32] (ii) low-temperature reaction with liquid Cl_2 at −35 °C gave a CF mixture with an average composition of $C_{60}Cl_{12\text{-}15}$ (Table II.1, No. 2);[11] (iii) UV-induced chlorination in liquid chlorine gave a product consisting primarily of $C_{60}Cl_{32}$ and $C_{60}Cl_{34}$ (Table II.1, No. 11);[24] (iv) UV-induced chlorination of C_{60} with Cl_2 in carbon tetrachloride or carbon disulfide solution at 25 °C generally produced CF mixtures with higher degrees of chlorination, such as $C_{60}Cl_{40}$, $C_{60}Cl_{24}$, or $C_{60}Cl_{7\text{-}40}$ (Table II.1, Nos. 4, 5, 7, 8);[18,19,21,22] (v) chlorination in *o*-dichlorobenzene solution without UV-irradiation was reported to produce a mixture of isomers of $C_{60}Cl_{10}$ or a mixture of isomers of $C_{60}Cl_{26}$, depending on reaction time (Table II.1, No. 15, 18).[25]

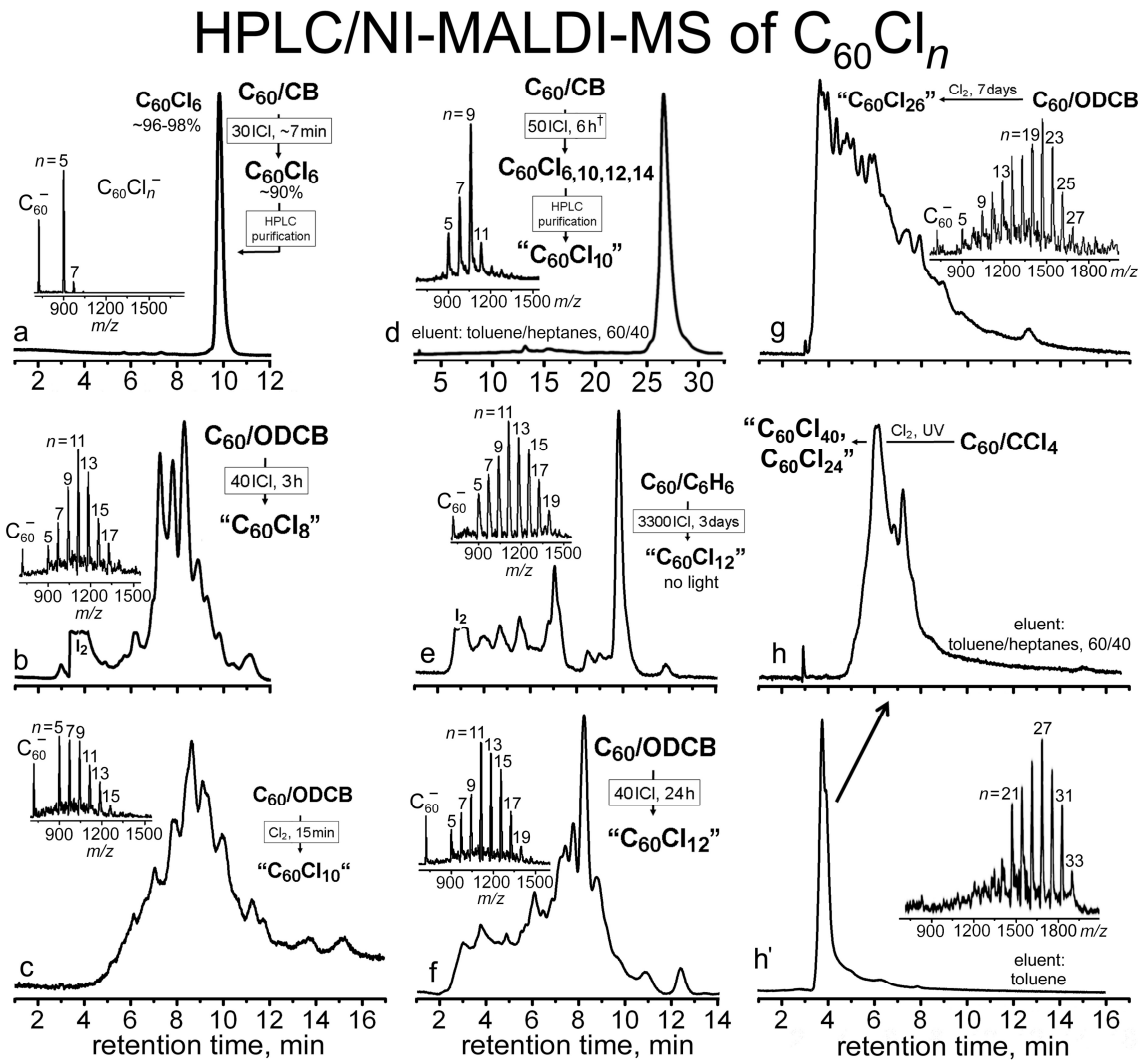


Figure II.14. HPLC and NI-MALDI-MS analysis of the reported CFs (see section IV for the detailed descriptions of the syntheses). HPLC and NI-MALDI-MS data for pure samples of $C_{60}Cl_6$ (a) and $C_{60}Cl_{10}$ (d) are included for comparison. Same HPLC conditions (5 mL/min flow rate, 300 nm detection wavelength, toluene eluent) were used during acquisition of all HPLC traces except trace h', where 60/40 toluene/heptanes eluent was used (the other HPLC conditions were the same).

In our hands, a UV-induced chlorination of C_{60} with Cl_2 in CCl_4 solution gave a light-yellow product that was soluble in CCl_4, dichloromethane, and toluene. HPLC analysis of this product showed it to be a mixture of several CFs up to $C_{60}Cl_{32/34}$ (according to NI-MALDI-MS), similar to the product of the UV-induced chlorination of C_{60} in liquid chlorine.[24] The chlorination of C_{60} solution without UV-irradation produced a mixture of CFs with a lower chlorine content of up to $C_{60}Cl_{14/16}$ in a 15-minute reaction (see

Figure II.14c) and $C_{60}Cl_{26/28}$ in a 7-day reaction (see Figure II.14g). The last two procedures were reported to yield "$C_{60}Cl_{10}$" and "$C_{60}Cl_{26}$" (quotation marks here and below are added by us), correspondingly (see Table II.1, No. 15, 18).[25] The wording used in the original report[25] may be interpreted as a claim of the compositional purity of these CFs: "Most likely, prepared chlorofullerenes $C_{60}Cl_n$ (n = 8, 10, 12, 14, 26) consist of several isomers."[25] Our analysis demonstrates that both products are mixtures of many CFs which are unlikely to be isomers with the same composition due to: i) wide range of retention times displayed by the components in HPLC traces; ii) NI-MALDI-MS showing the presence of higher CFs for "$C_{60}Cl_{10}$" product. In light of these findings (also see below) we suggest that this statement should be corrected to read: "prepared chlorofullerenes $C_{60}Cl_n$ (n = 8, 10, 12, 14, 26) consist of several isomers of several compositions", which would remove the ambiguity for the reader.

These results show that chlorination of C_{60} by chlorine can produce a variety of CFs with a different degree of chlorination depending on the conditions. However, complex mixtures of CFs are invariably produced under all of the tested conditions (see Section II.2.4 for further discussion).

The other chlorinating agent that was used for CF synthesis is iodine monochloride. The use of this reagent led to the first synthesis[12] of $C_{60}Cl_6$ in a relatively pure form (*ca.* 75-80% as we later determined).[17] A paper by Troshin et al., beside a report on the syntheses of "$C_{60}Cl_{10}$" and "$C_{60}Cl_{26}$" using chlorine, contains the descriptions of $C_{60}Cl_8$, $C_{60}Cl_{12}$, and $C_{60}Cl_{14}$ preparation by using ICl (also ICl_3 and $KICl_4$) chlorination of C_{60} in 1,2-$C_6H_4Cl_2$ solution. The exact reproduction of these preparation procedures was not possible due to insufficient description of the experiments.[25] Moreover, HPLC and NI-MALDI-MS analysis of both "$C_{60}Cl_8$" and "$C_{60}Cl_{12}$" (prepared as closely to the original recipe[25] as possible, see Table II.1, No. 14, 16) showed them to be complex mixtures (see Figure II.14b and II.14f), which contain CFs up to $C_{60}Cl_{16/18}$ and $C_{60}Cl_{18/20}$, correspondingly. The authors stated that "pure ICl_3 and ICl gave the same results as with

$KICl_4$" when the concentrations of these chlorinating agents are adjusted accordingly to molar content of chlorine. This conclusion is questionable since the analytical methods used to study the products (EA and IR spectroscopy) are not capable of giving sufficiently detailed information on the composition of CF mixtures; hence the possible differences between products formed with different chlorinating reagents may have been easily overlooked. The results of our study of C_{60} chlorination by ICl and ICl_3 also shows that different products are produced (see Section II.2.4). Another complication comes from the fact that a wet procedure was used for the synthesis of $KICl_4$, followed by 1–2 weeks of drying in a desiccator over P_4O_{10} (an analysis of the composition this reagent was not reported).[25] It is, however, known that a monohydrate $KICl_4 \cdot H_2O$ is isolated from aqueous solutions; furthermore, this compound was reported to decompose upon drying if chlorine atmosphere is not used[56] (Cl_2 atmosphere was not reported in ref. 25). ICl_4^- was also reported to form IO_3^- in aqueous solution, which makes the wet preparative procedure a poor choice, especially when a dry $KICl_4$ synthesis is known.[57] These facts made the composition of $KICl_4$ used in the original study[25] questionable, which invalidated the re-examination of the experiments that used this compound as a chlorinating agent.

Priadarsini et al. also reported a synthesis of "$C_{60}Cl_{12}$" by chlorinating a benzene solution of C_{60} with a very large excess of ICl in the absence of light (see Table II.1, No. 6; only EA was used to characterize the product, see Section II.2.1.C).[20] In our hands, however, their procedure yielded predominantly $C_{60}Cl_6$ (see Figure II.14e) heavily contaminated with CFs up to $C_{60}Cl_{18/20}$ according to MALDI-MS.

These data show that ICl (and other iodine chlorides ICl_3 and possibly $KICl_4$) produces mixtures of intermediate CFs (except $C_{60}Cl_6$, which can be prepared 90% pure[17]) when chlorination takes place in solution. When an elevated temperature is used, ICl was shown to give higher CFs ($C_{60}Cl_{24}$, $C_{60}Cl_{28}$, $C_{60}Cl_{30}$).[14,15,33] Other reagents were also used for high-temperature C_{60} chlorination. Most of them ($SbCl_5$, VCl_4, PCl_5),

similar to ICl, were reported to give higher CFs ($C_{60}Cl_{24}$,[13,26] Table II.1, No.19, 20; $C_{60}Cl_{30}$, Table II.1, No. 22;[15]), except $POCl_3$, which provides the only example of the high-temperature chlorination of C_{60} giving lower CF, $C_{60}Cl_6$ (albeit with a poor conversion of C_{60}).[16] The resulting higher CF products were usually characterized by single-crystal X-ray diffraction study, without analysis of the molecular composition and purity of the bulk CFs. The first paper that described $C_{60}Cl_{24}$ preparation reported it to be 90% pure based on its IR spectrum,[26] which is likely to be an overestimation (see Sections II.2.1.C and II.2.1.D). Highly chlorinated CFs were reported to be poorly soluble in common organic solvents, hence we did not repeat their preparations due to likely complications with HPLC and MS analysis and their lower utility for fullerene derivatization.

A conclusion can be drawn that, except $C_{60}Cl_6$, none of the reported soluble C_{60} chlorides were proven to be isolated as a single-composition single-isomer product. This shows that no lower and intermediate pure single-composition single-isomer soluble CFs ($C_{60}Cl_n$, $n < 24$) besides $C_{60}Cl_6$ (first reported[12] 15 years ago in 1993) have been prepared up to date. Our next goal was to study the chlorination of C_{60} in detail to determine conditions which would either allow for a preparation of the new pure soluble CFs, or yield a separable (by HPLC) mixture of these compounds.

II.2.4. Synthesis of New Chlorofullerenes

A. ICl, ICl_3, and Cl_2 Chlorination of C_{60}. We investigated several chlorination agents: ICl, ICl_3, and Cl_2. Despite its moisture-sensitivity and corrosiveness, ICl is easier to manipulate than ICl_3 or Cl_2 because it is a liquid (i.e., it can be added to reaction mixtures with a syringe using air-free techniques). In contrast, ICl_3 is an unstable solid that evolves Cl_2 at 25 °C (the equilibrium pressure of Cl_2 above ICl_3 is ca. 50 torr at 25 °C and increases rapidly at higher temperatures[58]). For this reason, we found it necessary to prepare ICl_3 immediately prior to use. Furthermore, in order to simplify gas manipulations, a large excess of Cl_2 was used in our synthetic reactions (i.e., degassed C_{60} solutions were saturated with Cl_2).

All three chlorinating reagents that we studied, and their reaction byproducts (ICl or I_2), were easily removed under vacuum, which simplified work-up procedures. The lack of the aqueous work-up step (necessary for chlorinating agents such as VCl_4[26]) and of the associated extractions reduced product loss and avoided any CF hydrolysis that might occur. However, it also calls for a volatile solvent to be used as a reaction medium. Hence, the chlorination experiments were performed in dry, deoxygenated chlorobenzene (CB), which we used successfully in our earlier work for the preparation of 90+% pure $C_{60}Cl_6$.[17] We found this solvent to be much less reactive towards further chlorination and fullerenyzation than benzene.[17] GC-MS analysis of the reaction mixtures showed that CB exhibits further chlorination (when Cl_2 is used) and chlorination/iodination (in case of ICl or ICl_3). The extent of CB halogenation remains small[a] for low concentrations of iodine

[a] Impurities account for only 1–2% of integrated intensity of the GC trace; no impurities were detected by the same method in CB used for this study.

chlorides (up to 0.375 mM of ICl and 0.125 mM of ICl_3), rising considerably[b] when higher concentrations of these chlorinating agents are used. According to these results, ICl_3 is a more reactive chlorinating agent than ICl (for both C_{60} and CB, see below). Both iodine chlorides are much more active towards C_6H_5Cl chlorination than Cl_2, which only gives raise to ca. 1% of higher chlorinated impurities. Both positive and negative ion APCI mass-spectrometry of the CF products showed no evidence that fullerenization of CB was taking place. This allows us to assume that CB chlorination does not influence the chlorination of C_{60} except by consumption of the chlorinating agent. Since solvent chlorination becomes significant only when large (ca. 450 equivalents) excess of ICl or ICl_3 is used, we can expect that their consumption due to solvent halogenation should have little influence on the course of C_{60} chlorination.

In this study we used fully homogenous solutions of C_{60}, with C_{60} concentration slightly below its solubility in CB (6.0 mg/mL concentration of C_{60} was used; 7.0 mg/mL was reported as C_{60} solubility in CB in ref. 59), as a system best suited for a scale-up when needed. We avoided non-homogenous conditions because our earlier work on $C_{60}Cl_6$ synthesis showed that they lead to a decrease in selectivity as well as poor C_{60} conversion.[17]

The presence of highly active chlorinating agents in the reaction mixture made it impossible to use direct sampling (analyzing equal volumes of the reaction mixture without any workup, which was used to study photodegradation of CFs) for HPLC monitoring. In order to avoid the need for accurate sampling of the reaction mixture and ensuring the quantitative transfer and injection of the products, we chose a different approach and introduced an internal standard normalization of HPLC traces. In this technique the vertical scale of HPLC traces is adjusted to keep the intensity of the peak associated with the standard compound constant, greatly simplifying the overall

[b] Impurities account for up to 25% of integrated intensity of GC traces for ca. 3.15 M of ICl and up to 36% for ca. 3.15 M of ICl_3.

procedure. The standard had to satisfy strict requirements: (i) it must not undergo any changes under the reaction conditions; (ii) it must not affect the reaction of C_{60} and the chlorinating agent in any way; (iii) it must have an R_f value different than the R_f values of the starting material and the CF products of interest; (iv) its R_f value should not be too high, otherwise it can dramatically increase duration of HPLC analyses; (v) it must give a satisfactory detector response (have a high enough extinction coefficient on the detection wavelength for the case of UV detection); and (vi) it must be soluble in the reaction media and HPLC eluent. These conditions made the choice of the standard difficult, but after testing and dismissing several candidates ($Cr(acac)_3$ due to its degradation under reaction conditions; $C_{60}F_{48}$ due to its low extinction coefficient/detector response) we chose a mixture of $C_{70}(CF_3)_{12,14}$. These compounds have convenient R_f values (3.0–3.9 min under the HPLC conditions used in this study) which did not overlap with the R_f value of C_{60} (8.2 min.) or the range of R_f values for the CF products of our reactions (4.0-10.0 min.). Furthermore, no changes were detected (by APCI-MS) in these compounds after their prolonged exposure to the most drastic chlorination conditions used it our study (highest concentrations of ICl, ICl_3, and Cl_2 in PhCl solution). Finally, control experiments showed no difference between C_{60} chlorination with and without added $C_{70}(CF_3)_{12,14}$.

The HPLC monitoring plots of C_{60} chlorination by ICl, ICl_3, and Cl_2 are given on Figures II.15 and II.16. The composition of the resulting CFs was determined by APCI-MS analysis of the HPLC separated fractions corresponding to various HPLC peaks (see Figures II.17 and II.18). Several CFs ($C_{60}Cl_2$-I, $C_{60}Cl_2$-II, $C_{60}Cl_4$, and $C_{60}Cl_{10}$) were isolated and studied in detail, which we describe in detail in Sections II.2.4.B and II.2.4.C.

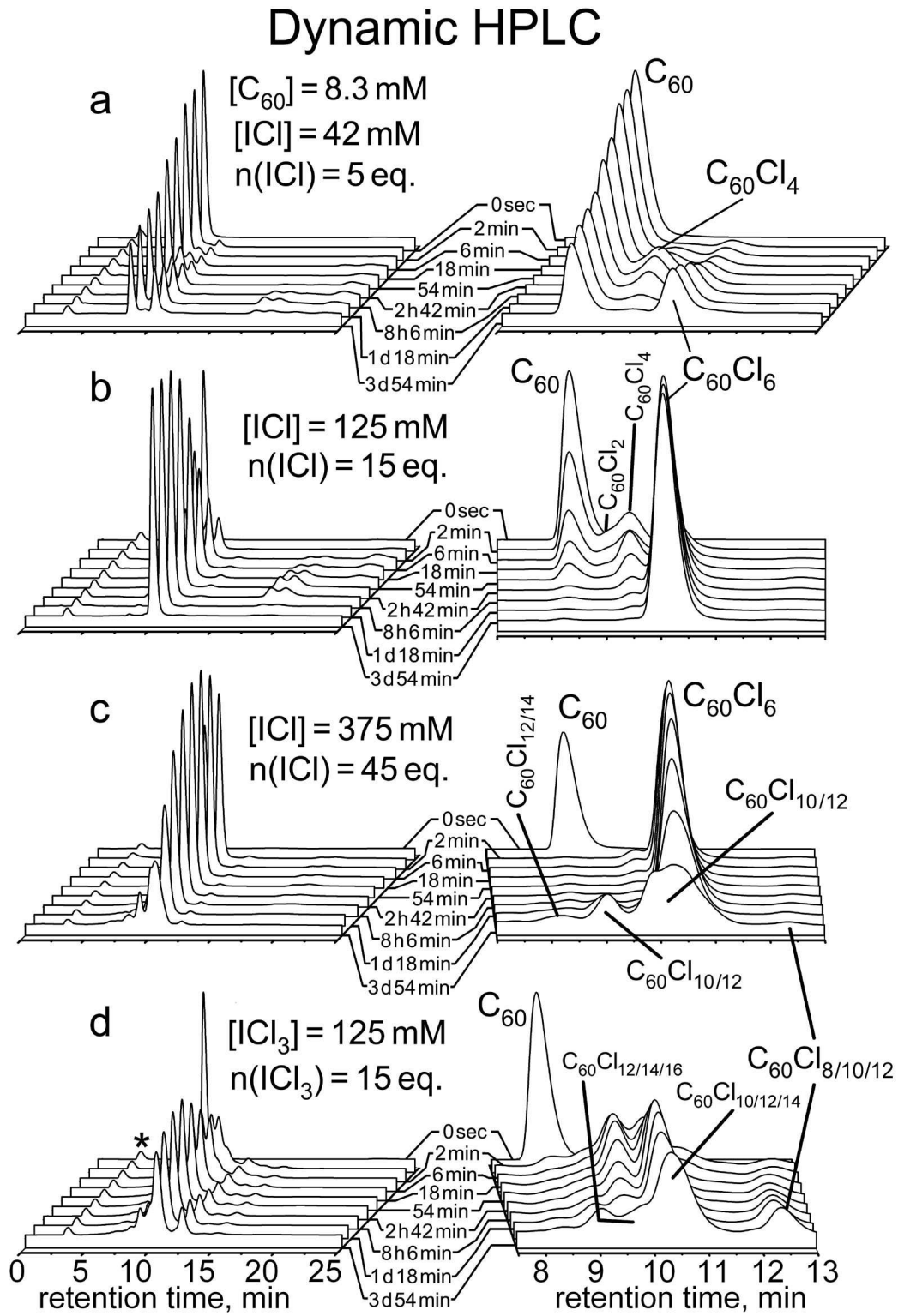


Figure II.15. HPLC monitoring of C_{60}/PhCl chlorination by ICl and ICl_3. The peak of standard, $C_{70}(CF_3)_{10,12}$, is marked with an asterisk. The composition of CFs was identified by NI-APCI-MS (MS was performed after HPLC separation).

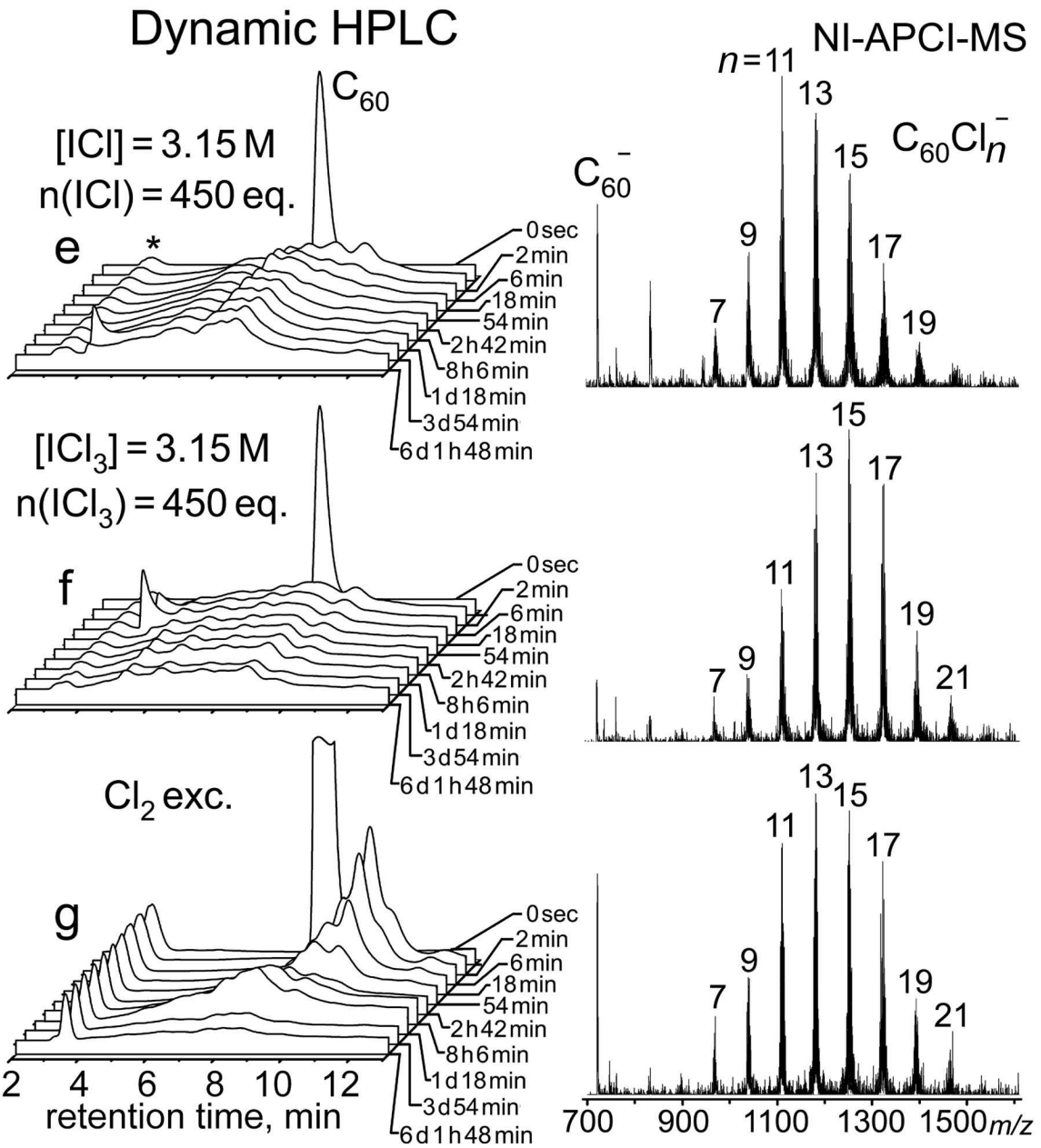


Figure II.16. Left column: HPLC monitoring of C_{60}/PhCl chlorination by large excess of ICl, ICl_3, and Cl_2. The peak of standard, $C_{70}(CF_3)_{12,14}$, is marked with an asterisk. Right column: NI-APCI-MS of the reaction mixtures after 6 d 1 h 48 min of chlorination (after HPLC separation of $C_{70}(CF_3)_{12,14}$).

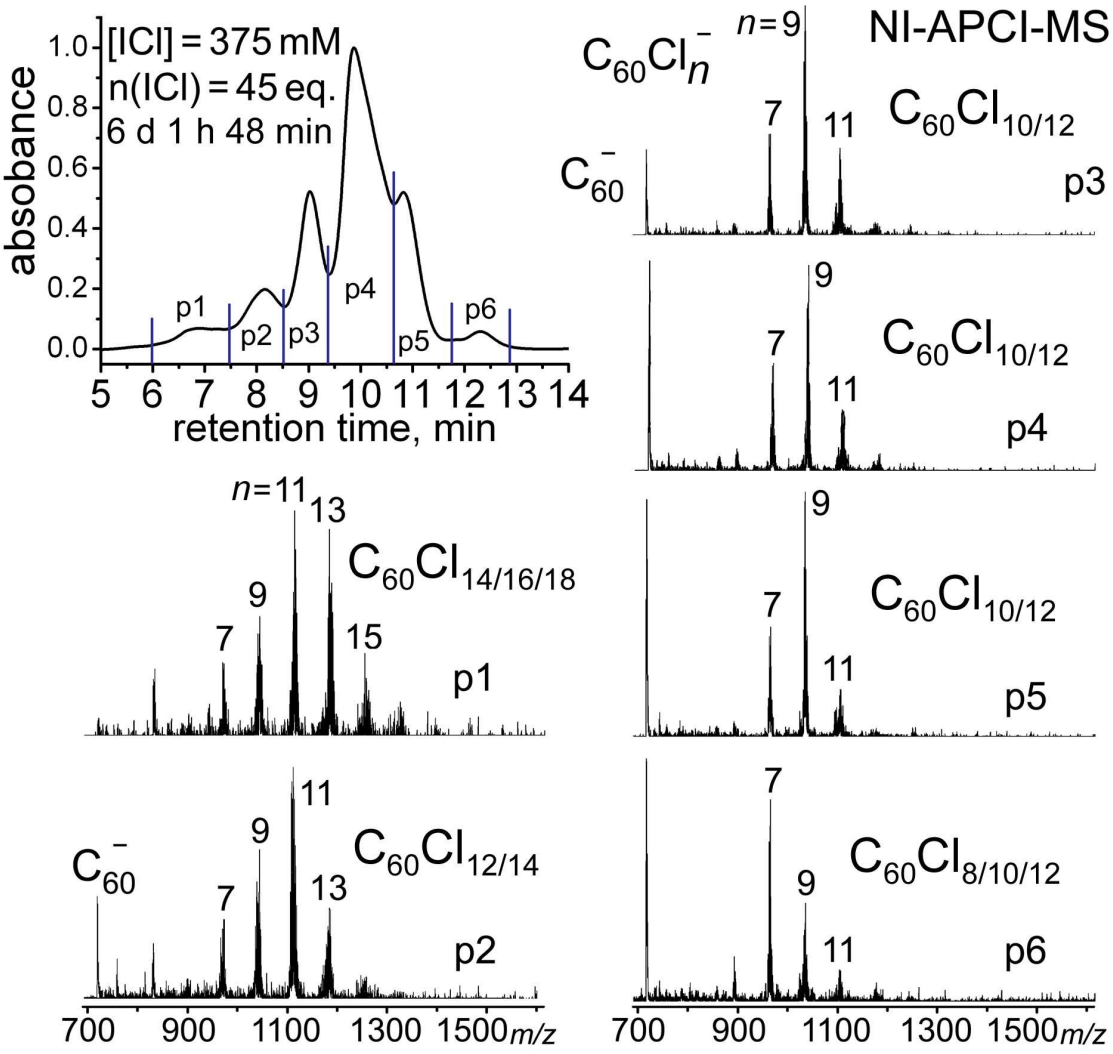


Figure II.17. The HPLC separation and NI-APCI-MS analysis of the products of C_{60} chlorination by ICl (approximate highest degrees of chlorination of the corresponding fractions are given by the mass spectra). $C_{60}Cl_8$ may be the major constituent of p6 due to $C_{60}Cl_7^-$ ion being more intense than $C_{60}Cl_9^-$; $C_{60}Cl_{11}^-$ may be due to contamination of higher $C_{60}Cl_{10/12}$. It is also possible that p7 is comprised of higher CFs $C_{60}Cl_{10/12}$.

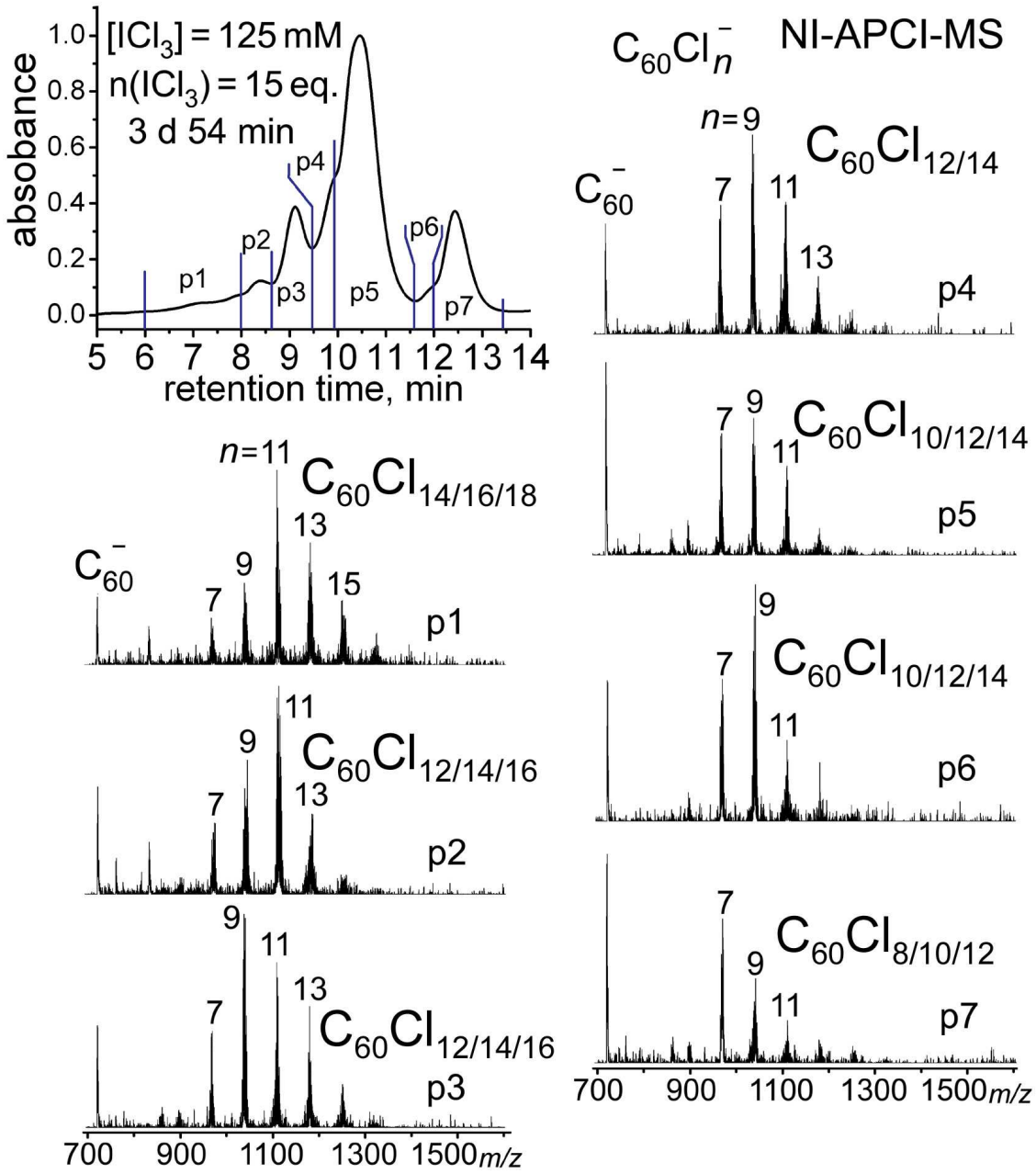


Figure II.18. The HPLC separation and NI-APCI-MS analysis of the products of C_{60} chlorination by ICl_3 (approximate highest degrees of chlorination of the corresponding fractions are given by the mass spectra). $C_{60}Cl_8$ may be the major constituent of p7 due to $C_{60}Cl_7^-$ ion being more intense than $C_{60}Cl_9^-$; $C_{60}Cl_{11}^-$ may be due to contamination of higher $C_{60}Cl_{10/12}$. It is also possible that p7 is comprised of higher CFs $C_{60}Cl_{10/12}$.

Chlorination with a low concentration of ICl (42 mM, 5 equivalents) showed that C_{60} is slowly converted into two isomers of $C_{60}Cl_2$ (*ortho*- and *para*-isomers) and a single isomer of $C_{60}Cl_4$ (see Figure II.15a). These lower CFs were observed for the first time, and later isolated and studied further (see Section II.2.4.B). $C_{60}Cl_4$ is considerably more abundant than $C_{60}Cl_2$ at any observed moment of the reaction; both isomers of $C_{60}Cl_2$ are present as a weak shoulder with a shorter R_f than $C_{60}Cl_4$ (9.0 min versus 9.4 min correspondignly). The highest concentration of $C_{60}Cl_4$ was observed after ca. 3 hours of reaction at 25 °C. The tetrachloro- compound slowly disappeared during the next 3 days with the concomitant formation of $C_{60}Cl_6$ (R_f = 10.2 min) and several weak peaks with R_f values of ca. 18–24 min (these compounds are unidentified at the present time). These changes occur at the same time as the formation of the red insoluble precipitate. In our earlier work we observed the formation of the same precipitate when low concentrations of ICl were used for C_{60} chlorination; we then hypothesized, based on IR and TGA data that this compound is $[C_{60}Cl_5]_2$ dimer.[17] This dimer was later synthesized in a sealed ampoule at high temperature and pressure, and its structure was unambiguously determined by single-crystal X-ray diffraction.[27] Based on the virtually complete agreement between the the IR spectrum of the reported $[C_{60}Cl_5]_2$ dimer and our product we can conclude that they have identical structure.[27] Therefore, the insoluble red compound we have observed is a dimeric $[C_{60}Cl_5]_2$ species (see Chapter III for further discussion of fullerene dimers). Our current hypothesis is that the lower chlorides $C_{60}Cl_{2,4}$ are converted into $C_{60}Cl_6$, $[C_{60}Cl_5]_2$, and several as-yet-unidentified compounds with long R_f values of 18–24 min, as shown in Figure II.15a.

When the concentration of ICl was increased three-fold to 0.125 mM (15 equivalents), the reaction rate increased more than three-fold but without changing the general course of the reaction, as shown in Figure II.15b. The HPLC peaks of the lower chlorides $C_{60}Cl_{2,4}$ were observed during the first 2 minutes after ICl addition. They slowly decayed during the next several hours. The faster chlorination produced a higher

concentration of $C_{60}Cl_2$, which is clearly visible on the HPLC trace after 2 min of reaction. These conditions provide a higher yield of both $C_{60}Cl_2$ isomers and $C_{60}Cl_4$, and hence they were used for a large-scale synthesis of these compounds (see Section II.2.4.B). The decay of the $C_{60}Cl_2$ and $C_{60}Cl_4$ HPLC peaks coincided with the growth of the 18–24 min weak intensity peaks and the precipitation of, presumably, $[C_{60}Cl_5]_2$, similar to the reaction at the lower concentration of ICl (42 mM, 5 eq.). The HPLC peak due to $C_{60}Cl_6$ started to grow immediately after ICl addition (the same as for the 42 mM ICl reaction). The main difference between the two reactions was the rate of chlorination; the intermediate and final products were the same.

Further increase of ICl concentration to 375 mM changes the behavior of the system (see Figure II.15c). The first observable product of C_{60} chlorination is $C_{60}Cl_6$ which dominates the HPLC trace. Low-intensity peaks of $C_{60}Cl_2$ and $C_{60}Cl_4$ are visible only during the first hour of the reaction. No peaks with longer R_f values (over 18–24 min) were observed. $[C_{60}Cl_5]_2$, which formation can be correlated with higher concentrations of $C_{60}Cl_{2,4}$, is not formed in this reaction. Further chlorination of $C_{60}Cl_6$ is observed after *ca.* 1 day of chlorination, with additional peaks of $C_{60}Cl_{10/12}$ growing at 9.3 and 9.8 min. It is interesting to note the formation of the component with R_f = 12.5 min, which persists in the reaction mixture with a practically constant concentration throughout the chlorination process. The likely composition of this compound based on NI-APCI-MS data is $C_{60}Cl_{10,12}$, although it may also be $C_{60}Cl_8$ with an impurity of higher CFs, see Figure II.17. By using ICl_3 as a chlorinating agent we were able to find conditions producing a much larger concentration of this component (see below).

The results of C_{60} chlorination suggest that selective synthesis of $C_{60}Cl_6$ can be best accomplished using higher concentrations of ICl, preferably 375 mM of ICl. These data are in agreement with our earlier work, which showed that by increasing the excess of ICl from 30 equivalents to 60 equivalents (same concentration of 6.0 mg of C_{60} per 1 mL of CB was used the earlier study) the minor peaks can be suppressed, yielding a 90% pure

material.[17] However, the higher excess of ICl requires a fast quenching of the reaction mixture, otherwise higher CFs are formed ($C_{60}Cl_n$, $n > 6$). In our earlier work[17] this fast quenching was accomplished using a flash evaporation in a specially designed apparatus; however, this study shows that the use of 375 mM of ICl (45 equivalents) yields a practically pure $C_{60}Cl_6$ (+90% pure) anywhere between 1 hour and 8 hours after the beginning of chlorination. This effectively eliminates the need for fast quenching, simplifying the synthetic procedure even more, since it can be performed in the regular Schlenk glassware.

We also tested a different chlorinating agent, ICl_3 (see Figure II.15d). It proved to be more active than ICl, causing rapid chlorination of C_{60} beyond $C_{60}Cl_6$ at 125 mM concentration (15 equivalents). The chlorination of C_{60} by ICl_3 was significantly different from ICl, causing the formation of a larger quantity of $C_{60}Cl_{8/10/12}$ with R_f of 12.5 min, which was only observed in a very low concentration when using 375 mM of ICl (see Figure II.15c). More importantly, the use of ICl_3 not only increases the rate of chlorination (when compared with ICl), it also produces higher degrees of chlorination, with $C_{60}Cl_{12/14/16}$ observed in the HPLC trace, see Figure II.18.

We suggest that CFs formed via ICl_3 chlorination are likely to be different from the products of ICl chlorination, since chlorides with the same (or very similar) R_f values apparently have higher degrees of chlorination according to APCI-MS (see Figures II.17 and II.18). This demonstrates that R_f values are likely to be insufficient for reliable CF identification, and other analytical methods, like APCI-MS, IR, UV-Vis and ^{13}C NMR spectroscopy should be used.

In order to check if a large excess of chlorinating agents is possible capable to push the reaction towards a single major component or at least a relatively simple mixture of CFs, we studied the chlorination of C_{60} under more harsh conditions (see Figure II.16). By using large concentrations (ca. 3.15 M) of ICl and ICl_3, and large excess of Cl_2, we found that mixtures of many different CFs are formed. Chlorination of C_{60} by a large

excess of Cl_2 led to a surprising result. Most of the starting C_{60} was converted into a black, practically insoluble precipitate. This compound has a relatively simple IR spectrum with some lines that can be assigned to C-Cl vibrations. According to the weight loss of this material in TGA-MS experiment, its composition can be tentatively assigned as $C_{60}Cl_{2.3}$ (chlorine evolution was observed by MS). The very low solubility of this product suggests that it may have a dimeric or a polymeric structure (see Chapter IV for further discussion). The intensity of the HPLC peaks shows a dramatic drop, which is consistent with the formation of the insoluble fullerene product. Surprisingly, even after 6 days of the reaction the HPLC analysis of the soluble CF products of this reaction shows very broad distributions, without any tendency of the conversion into a mixture with fewer components. This can be explained by the lack of chlorine migration on the fullerene cage at room temperature; at higher temperatures chlorine migration is likely to be possible, which can explain the successful isolation of higher $C_{60}Cl_n$ with n = 24, 28, 30 (see Section II.2.3 and Table II.1). [13-15,26] This suggests that some products with lower numbers of attached chlorines (and hence with longer R_fs, *ca.* 9-10 min) may have structures which are resistant towards further chlorination due to a combination of steric and electronic factors. The APCI-MS analysis of the CF products formed under these conditions (performed after HPLC separation of $C_{70}(CF_3)_{10,12}$ standard) showed the formation of $C_{60}Cl_n^-$ ions with up to 21 chlorines for ICl_3 and Cl_2 chlorination and 19 chlorines for ICl chlorination. These results allow us to estimate the maximum degree of C_{60} chlorination in PhCl solution as $C_{60}Cl_{18/20}$ for ICl and $C_{60}Cl_{20/22}$ for ICl_3 and Cl_2 chlorination.

In conclusion, the use of the dynamic HPLC method gave us a detailed insight into the course of C_{60} chlorination by several chlorinating agents under various conditions. These data gave the first evidence of the formation of lower chlorides $C_{60}Cl_{2,4}$. Furthermore, the information given by dynamic HPLC allows us to choose the optimal conditions for a large-scale preparation of +90% pure $C_{60}Cl_6$ or a particular mixture of

CFs. In the following sections we describe the successful preparation, isolation, and characterization of several new CFs (*o*-, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, and $C_{60}Cl_{10}$) which was based on this approach to the choice of the reaction conditions.

B. Synthesis, Isolation, and Characterization of *o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, and $C_{60}Cl_3H$. The large-scale synthesis of the mixture of lower CFs ($C_{60}Cl_{2,4}$) was prepared by chlorination of C_{60} solution (6.0 mg of C_{60} per 1.0 mL of CB) by ICl (125 mM). The flash-evaporation of the reaction mixture in our evaporation apparatus[17] was used to stop chlorination after only 2 minutes of the reaction, which was necessary in order to avoid further chlorination of the lower CFs into $C_{60}Cl_6$. See Figure II.19 for a technical drawing of the improved design of the evaporation apparatus.

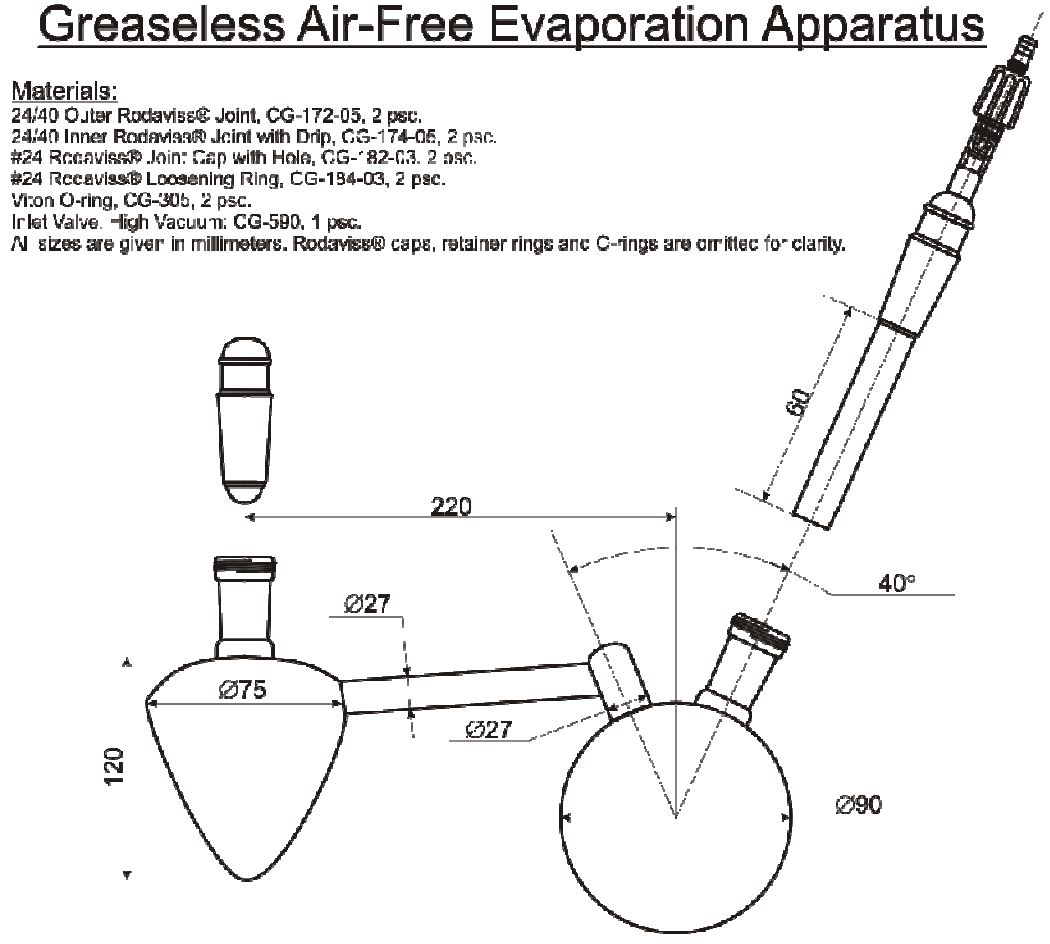


Figure II.19. Small-scale greaseless evaporation apparatus.

When a similar rate of evaporation of CB may be achieved in a rotary evaporator equipped with an oil pump,[25] we do not recommend this approach due to high corrosiveness of ICl (a polimer washer that ensures a proper seal of the rotating shaft in some models of rotary evaporators may be damaged). The resulting CF mixture was separated using a two-stage HPLC procedure, with the first stage using 100% toluene eluent, and the second stage using 50/50 toluene/*n*-heptane mixture (5 mL/min flow rate was used during both stages). The HPLC traces of the crude and partially separated CF mixtures are shown in Figure II.20. This procedure yielded a 99% pure $C_{60}Cl_4$ (according to HPLC analysis using 50/50 toluene/*n*-heptane eluent); however, both $C_{60}Cl_2$-I and *p*-$C_{60}Cl_2$ were obtained only as ca. 75% pure products due to an apparent transformation of these compounds during some of the steps of the HPLC purification. The exact nature of the transformation that these compounds are undergoing is not completely clear now and requires further study.

The compounds *o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, and $C_{60}Cl_4$ were analyzed by positive-ion APCI-MS, which provided us with their molecular composition data (see Section II.2.1.G for the discussion of the mass spectra and Figure II.5). The presence of two isomers of $C_{60}Cl_2$ suggests that both *ortho*- and *para*-isomers are formed during C_{60} chlorination by ICl at room temperature in solution (other addition patterns are likely to have much higher enthalpy of formation and hence unlikely to be formed). The UV-Vis spectrum of $C_{60}Cl_2$-I (see Figure II.21) is virtually identical with the spectrum of 1,2-substituted cycloadduct *N*-methyl[60]fullerenopyrollidine (see Figures II.22 and II.23)[60,61] which strongly suggests that it is the *ortho* isomer. The UV-Vis spectrum of $C_{60}Cl_2$-II (see Figure I-24) is very similar to the spectrum of *para*-$C_{60}(CF_3)_2$ (see Figure II.25),[62] the structure of which was first elucidated by ^{19}F NMR and DFT calculations[63] and has recently been confirmed by X-ray diffraction.[64]

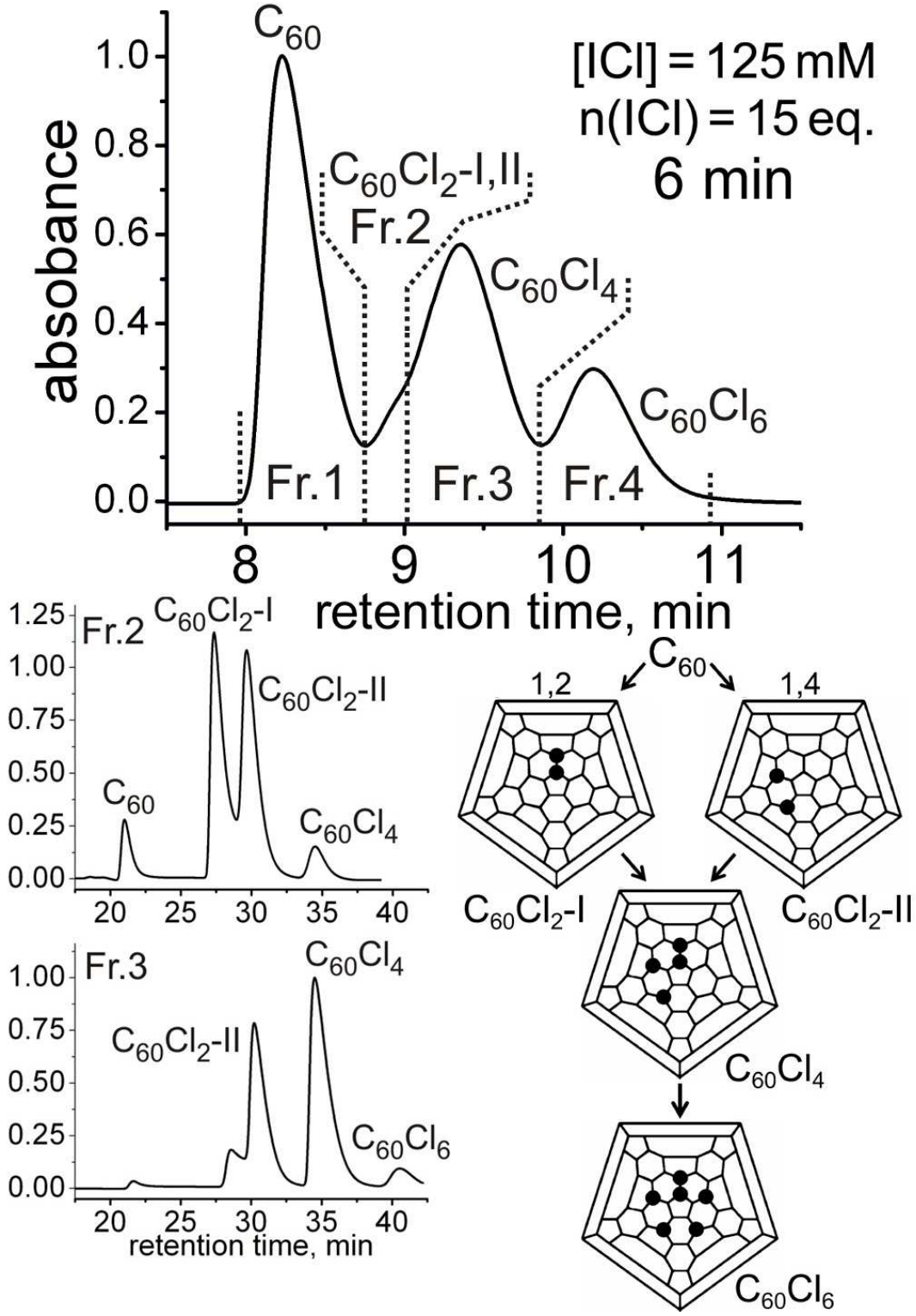


Figure II.20. Synthesis and separation of $C_{60}Cl_2$-I,II (*ortho*- and *para*-isomers) and $C_{60}Cl_4$. The pathway of C_{60} chlorination is given.

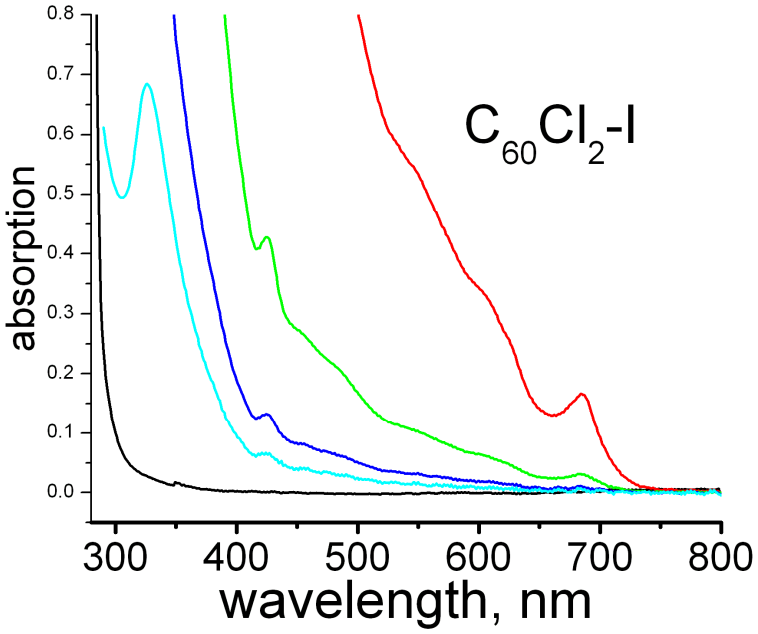


Figure II.21. UV-Vis spectra of 75% *o*-$C_{60}Cl_2$ in toluene. Bottom plot is a background spectrum of neat toluene.

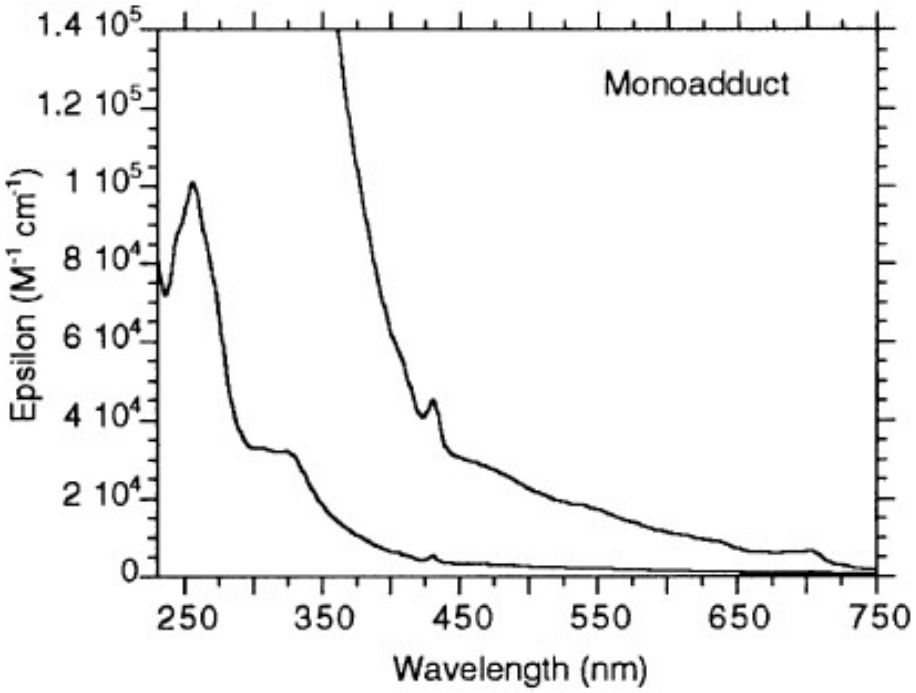


Figure II.22. UV-Vis spectra of pyrrolidine N-mTEG (mTEG = $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$) mono-adduct of C_{60} in cyclohexane. Figure is taken from ref. 60.

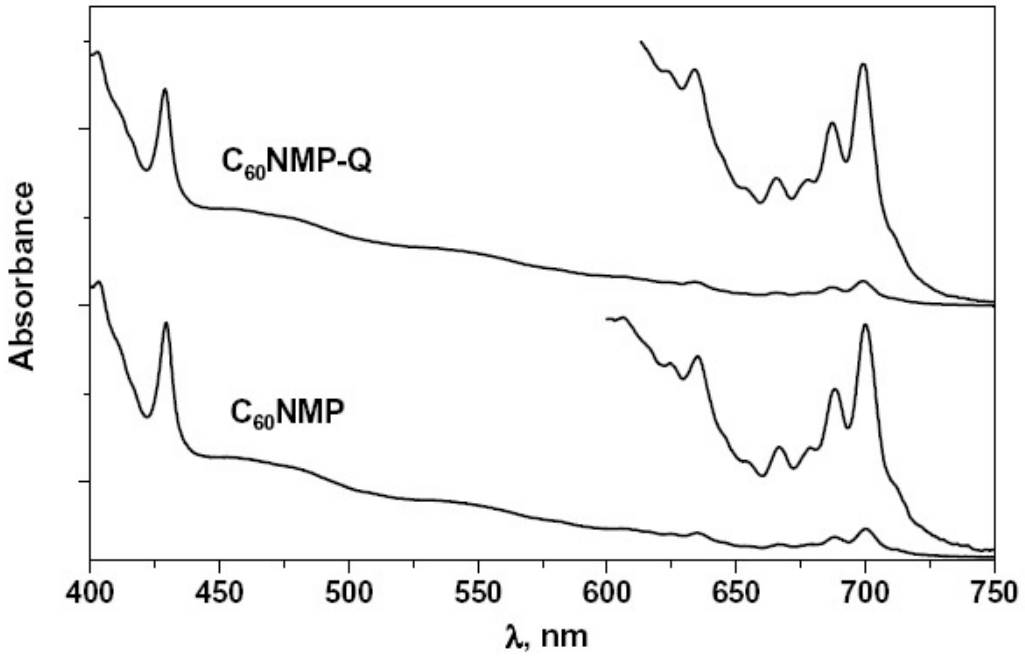


Figure II.23. UV-Vis spectra of C_{60}NMP-Q (N-methylfulleropyrrolidine-quinoline dyad) and C_{60}NMP (N-methylfulleropyrrolidine) in *n*-hexane. Figure is taken from ref. 61.

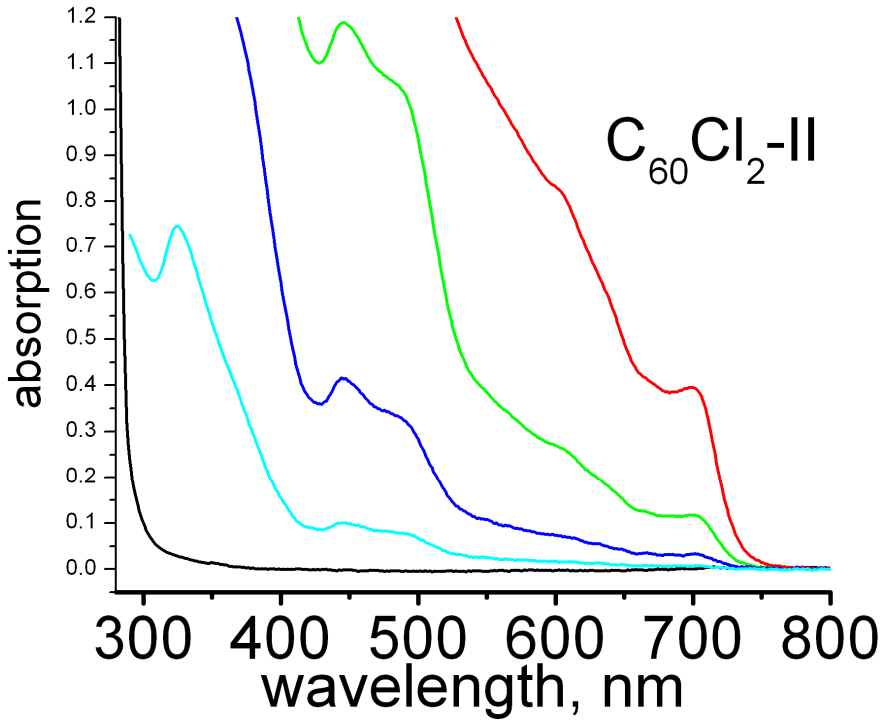


Figure II.24. UV-Vis spectra of 75% *para*-$C_{60}Cl_2$ in toluene. Bottom plot is a background spectrum of neat toluene.

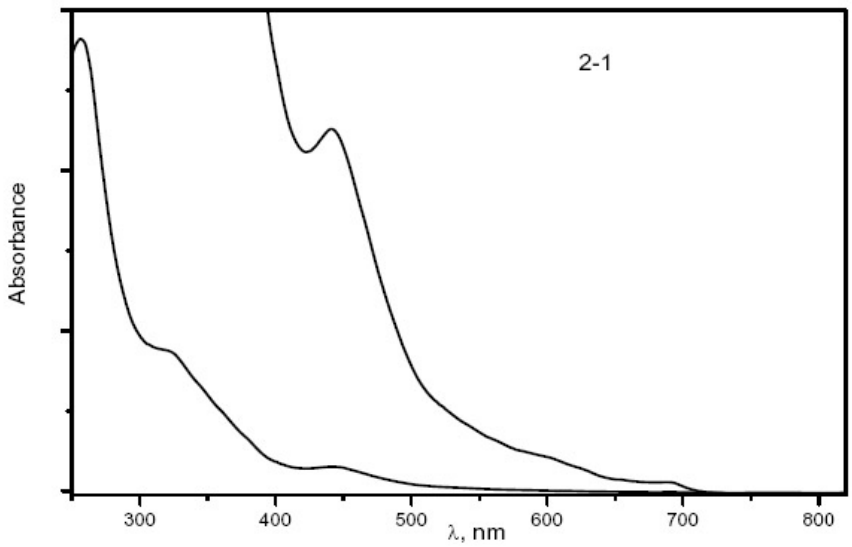


Figure II.25. UV-Vis spectra of $C_{60}(CF_3)_2$ in CH_2Cl_2. Figure is taken from Supporting Information of our earlier paper, ref. 62.

However, the spectrum of $C_{60}Cl_2$-II has an additional feature at 490 nm not found in the spectrum of *para*-$C_{60}(CF_3)_2$, which could be due to this compound or to an unidentified impurity (samples of *o*-$C_{60}Cl_2$/*p*-$C_{60}Cl_2$ were ca. 75% pure). Despite this slight irregularity in UV-Vis spectra, it is very likely that $C_{60}Cl_2$-II has a 1,4-addition pattern and is *p*-$C_{60}Cl_2$. This conclusion is also supported by the different behavior of *o*-$C_{60}Cl_2$ and *p*-$C_{60}Cl_2$ under PI-APCI-MS (see Section II.2.1.G for the discussion of the mass spectra and Figure II.5): The compound we designate as *o*-$C_{60}Cl_2$ does not form an observable molecular ion $C_{60}Cl_2^+$, but the compound we designate as *p*-$C_{60}Cl_2$, does. This is consistent with a more crowded environment of the Cl atoms in *o*-$C_{60}Cl_2$ than in *p*-$C_{60}Cl_2$.

If we assume that chlorine migration on the fullerene cage is unlikely to occur at a significant rate at 25 °C, then the structure of the tetrachloro compound we have isolated is probably 1,6,9,18-$C_{60}Cl_4$. The results shown in Figures II.15a, II.15b, and II.20 demonstrate that *o*- and *p*-$C_{60}Cl_2$ are both converted into a single isomer of $C_{60}Cl_4$, which is subsequently chlorinated to form the single isomer SPP-$C_{60}Cl_6$ (SPP = 1,6,9,12,15,18). Based on this information, $C_{60}Cl_4$ should have the 1,6,9,18 addition pattern because this

pattern (i) can form from either *o*- or *p*-$C_{60}Cl_2$ without rearrangement and (i) is a fragment of the SPP-$C_{60}Cl_6$ addition pattern. Figure II.26 shows that the UV-Vis spectrum of 99% pure $C_{60}Cl_4$ is similar to the spectrum of the structurally characterized compound 1,6,9,18-$C_{60}(CH_2Ph)_4$.[65] Nevertheless, since UV-Vis spectra of different $C_{60}R_4$ isomers are not very well resolved (see Figures II.27 and II.28), the addition-pattern assignment for $C_{60}Cl_4$ cannot be based only on its UV-Vis.[62,65]

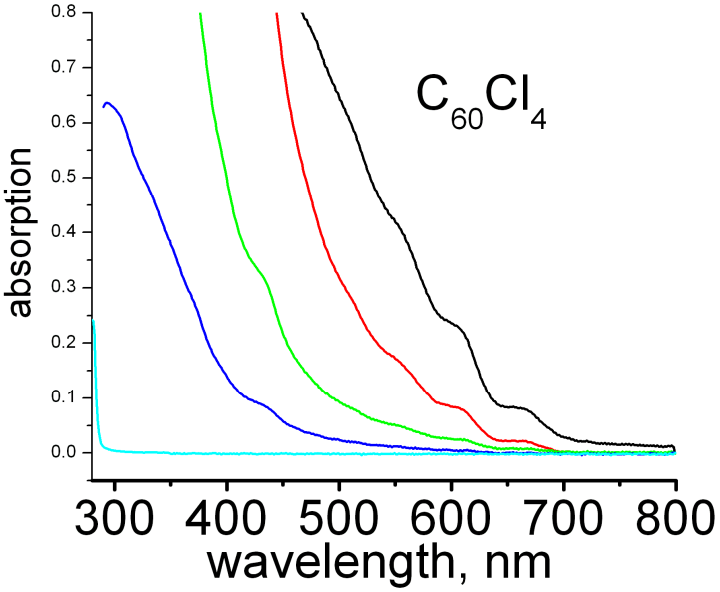


Figure II.26. UV-Vis spectra of 99% $C_{60}Cl_4$ in toluene. Bottom plot is a background spectrum of neat toluene.

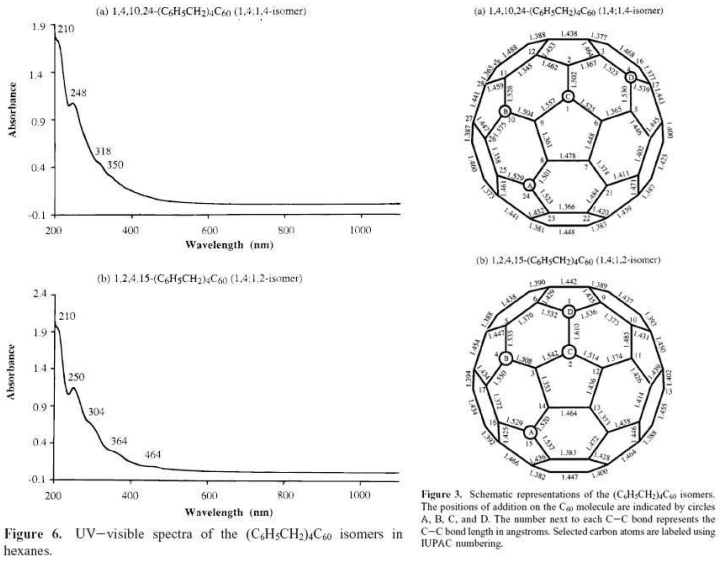


Figure 6. UV−visible spectra of the $(C_6H_5CH_2)_4C_{60}$ isomers in hexanes.

Figure 3. Schematic representations of the $(C_6H_5CH_2)_4C_{60}$ isomers. The positions of addition on the C_{60} molecule are indicated by circles A, B, C, and D. The number next to each C−C bond represents the C−C bond length in angstroms. Selected carbon atoms are labeled using IUPAC numbering.

Figure II.27. UV-Vis spectra of two different isomers of $(C_6H_5CH_2)_4C_{60}$ in hexanes. The figure is taken from ref. 65.

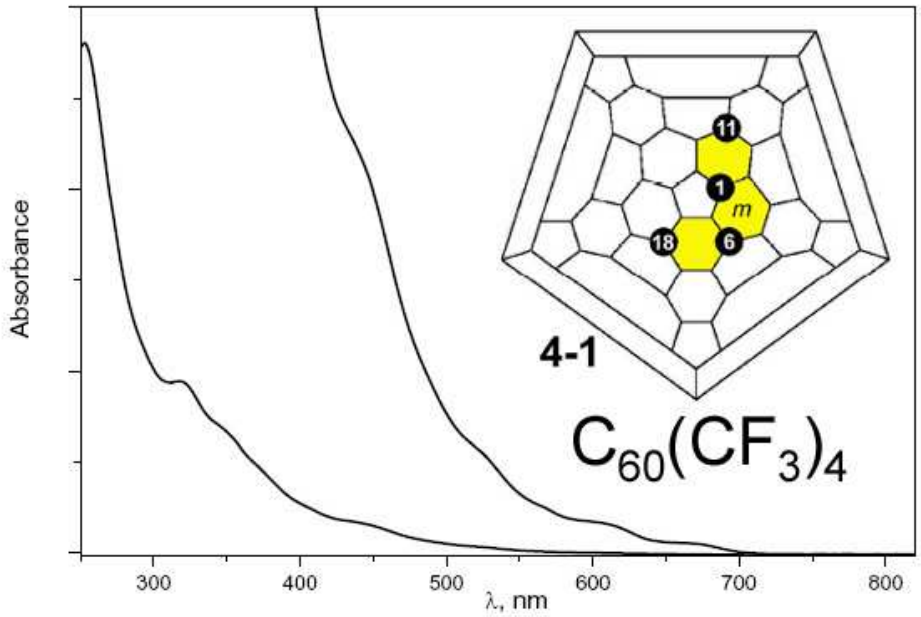


Figure II.28. UV-Vis spectra of $C_{60}(CF_3)_4$ in CH_2Cl_2. Figure is taken from Supporting Information of our earlier paper, ref. 62.

Fortunately, diffraction-quality crystals (albeit relatively poor-quality crystals) of the adventitiously substituted derivative $C_{60}HCl_3$ grew from a +3 °C toluene solution protected from light during several weeks. A preliminary single-crystal X-ray diffraction study of this compound showed that it is 1-H-6,9,18-$C_{60}Cl_3$. If we tentatively assume that the Cl/H substitution occurred without rearrangement, then the precursor of 1-H-6,9,18-$C_{60}Cl_3$ should be 1,6,9,18-$C_{60}Cl_4$. We are attempting to grow higher-quality single crystals of 1-H-6,9,18-$C_{60}Cl_3$ for a more precise structural study, but the addition pattern of this compound is no longer in question. Interestingly, the Cl atom that undergoes substitution in the putative transformation 1,6,9,18-$C_{60}Cl_4$ → 1-H-6,9,18-$C_{60}Cl_3$ is the one that is the most crowded, with one *ortho* and two *meta* Cl atom nearest neighbors.

C. Synthesis and Characterization of $C_{60}Cl_{10}$. The dynamic HPLC study of C_{60} chlorination by 375 mM ICl in chlorobenzene showed that the further chlorination of $C_{60}Cl_6$ was still rather slow under these conditions (see Figure II.15c). Therefore, we increased the concentration of ICl to *ca.* 660 mM (80 equivalents) for a large-scale preparation of $C_{60}Cl_n$ compounds with $n > 6$), and this change resulted in a reaction time

of only 6 hours. Figure II.29 shows the HPLC purification of the reaction products, which yielded a single isomer of $C_{60}Cl_{10}$ as the main product. The successful crystallization of this compound led to its unambiguous structure determination by X-ray diffraction (see Appendix A.2). The unprecedented and unexpected addition pattern of this compound, 1,6,9,12,14,15,18,28,29,31-$C_{60}Cl_{10}$, is shown in Figure II.30 (see Section II.2.5 for further discussion). Note that this asymmetric addition pattern includes the SPP-$C_{60}Cl_6$ addition pattern, suggesting that $C_{60}Cl_{10}$ might be formed by the addition of four Cl atoms to SPP-$C_{60}Cl_6$ without rearrangement.

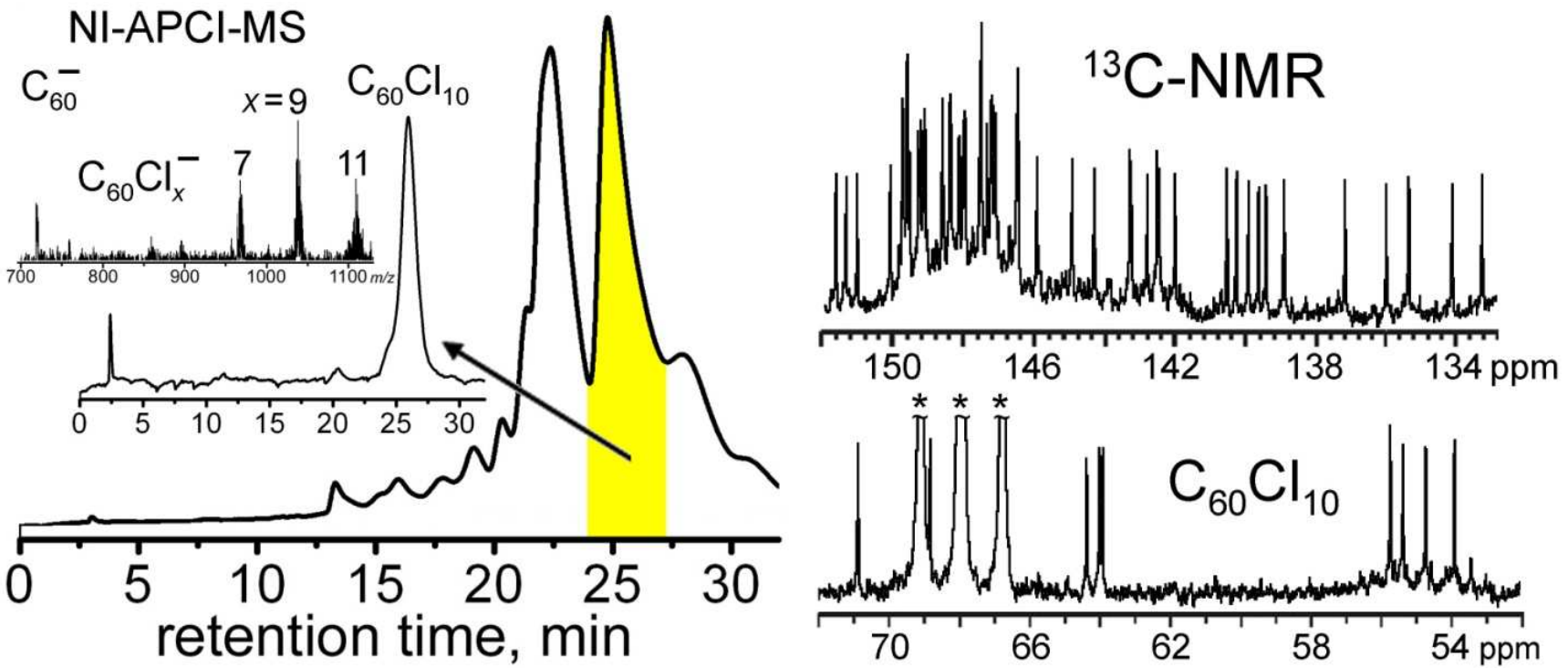


Figure II.29. $C_{60}Cl_{10}$ HPLC separation and characterization by NI-APCI-MS and ^{13}C-NMR (the starred peaks are due to unidentified organic impurity). 30/70 toluene/heptanes mixture and 7 mL/min eluent flow was used for HPLC analysis and separation.

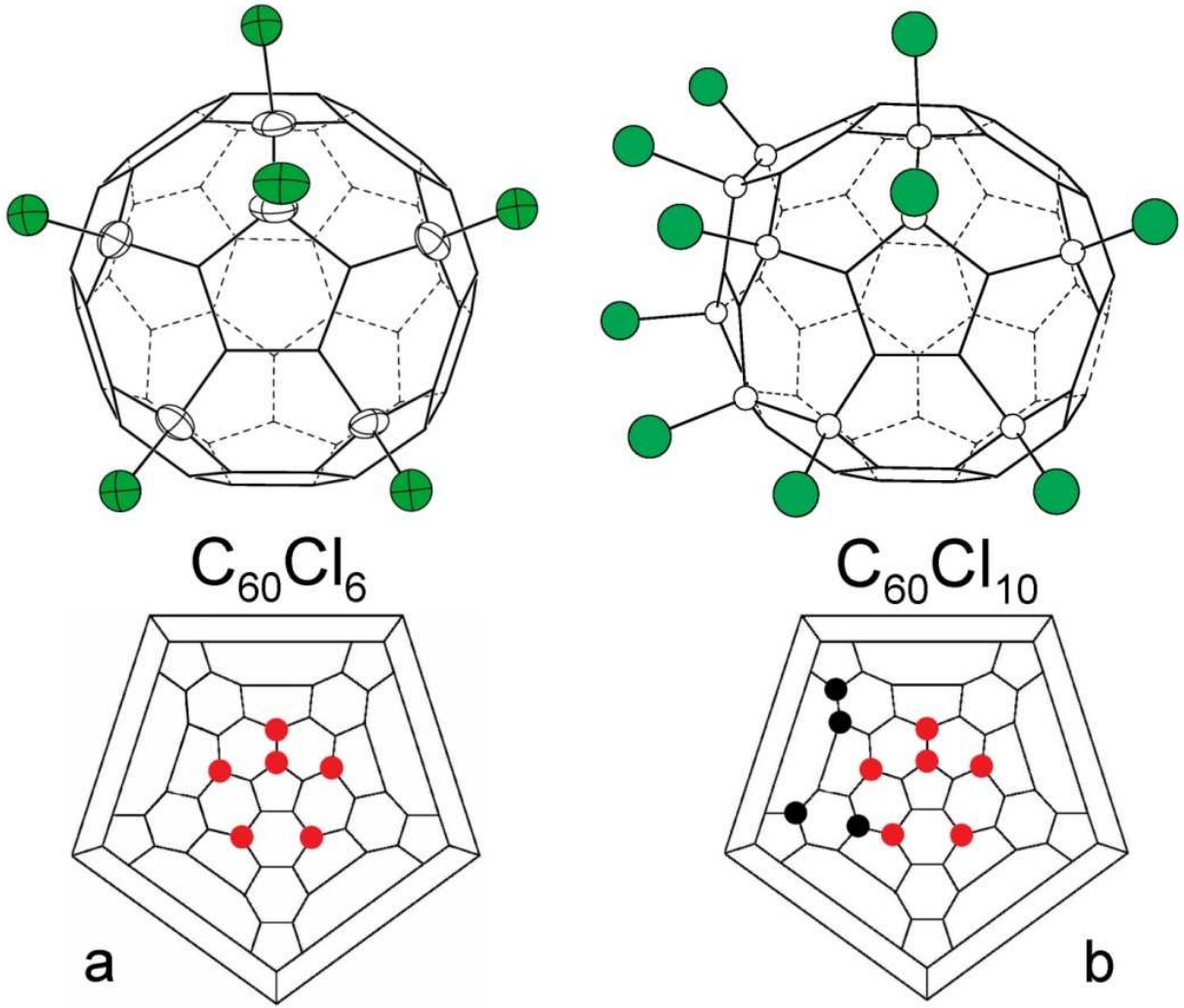


Figure II.30. Structures and Schlegel diagrams of $C_{60}Cl_6$ (a) and $C_{60}Cl_{10}$ (b) determined by single-crystal X-ray diffraction study (see Appendix A.2).

II.2.5. The Relative Stability and Stepwise Formation of $C_{60}Cl_{10}$ from C_{60}/ICl Reaction Mixtures. A DFT Frontier Orbital Analysis.

The addition to C_{60} or higher fullerenes of H, F, Cl, or Br atoms or CF_3 groups, each of which forms a 2c-2e$^-$ bond to a single cage C atom, has been extensively studied experimentally and theoretically.[1,62,64,66-68] The smaller addends H and F tend to add so that all of the newly formed C(sp^3) atoms are contiguous (one notable exception is an isomer of $C_{60}F_8$;[69] here we are only citing compounds formed by direct addition to fullerenes, not by substitution of fullerene-derivative precursors). For $n \leq 12$, the larger addends Br and CF_3 tend to form derivatives with the addends *meta* or *para* to one another, with *ortho* cage C(sp^3) atoms being rare. For example, the only bromofullerenes with neighboring C(sp^3) atoms are $C_{60}Br_6$ (one *ortho* pair),[70] and $C_{70}Br_{10}$ (one *ortho* pair).[71] Fullerene$(CF_3)_n$ compounds tend to have addition patterns that are referred to as ribbons or loops of edge-sharing *meta*- and *para*-$C_{60}(CF_3)_2$ hexagons.[62,72] Chlorine atoms are sterically in between. For $n > 2$, CFs in which *all* of the fullerene C–Cl vertexes are contiguous (e.g., D_{3d}-$C_{60}Cl_{30}$), or in which *none* of the C–Cl vertexes are contiguous (e.g. $C_{60}Cl_{24}$[13] and $C_{78}Cl_{18}$[73]), are rare. Chlorofullerenes with some C–Cl vertexes *ortho*, some *meta*, and some *para* to one another are the rule, including C_s-SPP-$C_{60}Cl_6$,[16] #1809$C_{60}Cl_8$,[28] $C_{60}Cl_{10}$ (this work), #1804$C_{60}Cl_{12}$,[28] $C_{60}Cl_{28}$,[15] C_2-$C_{60}Cl_{30}$,[15] $C_{70}Cl_{10}$,[71] $C_{70}Cl_{16}$,[74] $C_{70}Cl_{28}$,[75] and $C_{76}Cl_{18}$.[76]

Before we had determined the structure of $C_{60}Cl_{10}$ by X-ray crystallography, we tried to prepare a "short list" of plausible $C_{60}Cl_{10}$ addition patterns to begin our computational study. The only structurally characterized $C_{60}X_{10}$ compounds that are known are five isomers of $C_{60}(CF_3)_{10}$, none of which have contiguous cage C(sp^3) atoms.[62,77] The "in-

between" steric requirements of Cl atoms meant that we could not consider these five addition patterns as very likely. Furthermore, none of them are derived by adding four addends to SPP-$C_{60}(CF_3)_6$ (which, incidentally, is a known compound[78]). Nevertheless, one isomer of $C_{60}(CF_3)_{12}$ does have two SPP addition-pattern fragments on opposite poles.[79] Initially, therefore, it seemed reasonable to propose that one possible stable isomer of $C_{60}Cl_{10}$ might have the addition pattern of SPP,SPP-$C_{60}(CF_3)_{12}$ minus the Cl atoms on one of the *ortho* pairs of C(sp^3) atoms (this would leave a ribbon of three edge-sharing *para*-C_6Cl_2 hexagons on the pole opposite the SPP fragment). In a DFT study of the early stages of addition to C_{60}, Clare and Kepert calculated selected isomers of $C_{60}Cl_n$ for n = 2, 4, 6, 8, 12, 18, and 24. Plausible isomers of $C_{60}Cl_{10}$ were not mentioned, even in passing. At the HF/6-31G* level of theory, Zhao and co-workers calculated isomers of $C_{60}Cl_n$ for n = 2, 4, 6, 8. In that paper, they stated that "the HOMO [of SPP-$C_{60}Cl_6$ is]... almost evenly spread over the equator belt, implying... no preferred site for further addition."

With this limited information as a starting point, we decided that our computational study had to be as inclusive as possible. We performed an exhaustive search of all isomers of $C_{60}Cl_{10}$ formed by adding four Cl atoms to an SPP-$C_{60}Cl_6$ array. We believed that this limitation was justified because there are no reports demonstrating Cl atom rearrangement in a CF at 25 °C (there is one report that chlorination of T_h-$C_{60}Cl_{24}$ with $SbCl_5$ *at 300 °C* produces D_{3d}-$C_{60}Cl_{30}$, and the D_{3d}-$C_{60}Cl_{30}$ addition pattern cannot be derived by simply adding six Cl atoms to T_h-$C_{60}Cl_{24}$; however, T_h-$C_{60}Cl_{24}$ decomposes to C_{60} and Cl_2 at temperatures above 280 °C, so it is not clear that D_{3d}-$C_{60}Cl_{30}$ is formed in this reaction by chlorination of intact T_h-$C_{60}Cl_{24}$[13]). More than 30,000 isomers were studied at the semiempirical AM1 level. The 1,100 lowest-energy isomers from that set were recalculated at the PBE/TZ2P//AM1 level, and the 44 lowest-energy isomers from that set were recalculated at the full PBE/TZ2P level and again at the B3LYP/6-311G*//PBE/TZ2P level. The nine lowest-energy isomers from that set are shown in

Figure II.31, along with their full PBE/TZ2P and their B3LYP/6-311G*//PBE/TZ2P relative energies. Table II.3 is list of the 44 DFT-predicted lowest-energy isomers and their relative energies (0.0–23.8 kJ mol^{-1} with the PBE functional).

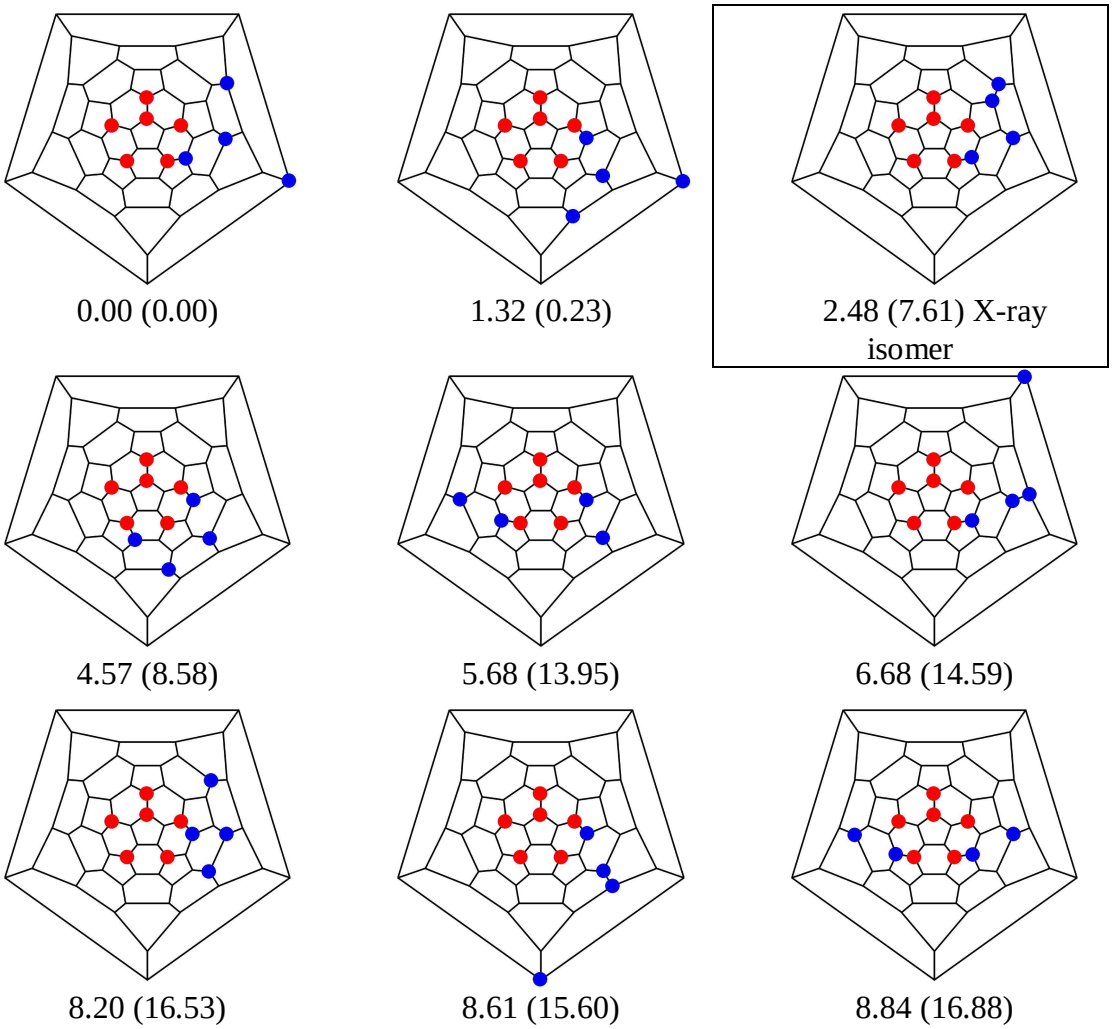


Figure II.31. Schlegel diagrams of the nine lowest-energy DFT-optimized isomers of $C_{60}Cl_{10}$ that include an SPP array of six Cl atoms (SPP = 1,6,9,12,15,18). The locants are not necessarily the lowest set of locants; they were chosen so that comparisons with 14,28,29,31,SPP-$C_{60}Cl_{10}$ can be clearly seen. The relative energies shown were determined at the B3LYP/6-311G*//PBE/TZ2P level of theory (the values in parentheses were determined at the PBE/TZ2P//PBE/TZ2P level).

Table II-3. A list of the 44 DFT-predicted lowest-energy isomers of $C_{60}Cl_{10}$ (that have the SPP-$C_{60}Cl_6$ moiety in their structure).

SPP+, non-IUPAC numbering	E, kJ/mol	E (B3LYP//PBE)	IUPAC locants numbering	added pattern (relative to SPP-$C_{60}Cl_6$)
10,12,18,21-$C_{60}Cl_{10}$	0.00	0.00	14,31,47,59	pmp
7,9,18,22- $C_{60}Cl_{10}$	1.32	0.23	13,32,51,59	pmp
2,10,13,21- $C_{60}Cl_{10}$	2.48	7.61	14,28,29,31	omp
6,9,22,31- $C_{60}Cl_{10}$	4.57	8.58	13,17,32,35	ppp
9,22,30,41- $C_{60}Cl_{10}$	5.68	13.95	14,20,31,39	p and p
10,11,17,21- $C_{60}Cl_{10}$	6.68	14.59	14,31,48,58	pop
9,10,13,22- $C_{60}Cl_{10}$	8.20	16.53	13,28,31,32	pop
8,9,22,26- $C_{60}Cl_{10}$	8.61	15.60	13,32,50,60	pop
10,21,30,41- $C_{60}Cl_{10}$	8.84	16.88	14,31,19,40	p and p
5,6,9,22- $C_{60}Cl_{10}$	9.76		13,32,34,35	omp
10,13,21,24- $C_{60}Cl_{10}$	10.21		10,14,28,31	ppp
8,26,30,41- $C_{60}Cl_{10}$	11.92		14,31,54,60	p and isolated p
6,9,10,21- $C_{60}Cl_{10}$	12.55		14,31,32,35	pop
8,26,33,39- $C_{60}Cl_{10}$	13.12		47,54,59,60	isolated pop
7,11,12,18- $C_{60}Cl_{10}$	13.27		47,48,51,59	isolated omp
6,8,26,31- $C_{60}Cl_{10}$	13.35		16,36,54,60	pmp
7,8,12,18- $C_{60}Cl_{10}$	13.63		47,50,51,59	isolated omp
7,17,18,36- $C_{60}Cl_{10}$	14.00		44,51,58,59	isoalted pop
1,2,10,21- $C_{60}Cl_{10}$	14.16		14,26,29,31	pmp
9,17,22,36- $C_{60}Cl_{10}$	15.13		13,32,44,58	p and isolated p
9,22,33,39- $C_{60}Cl_{10}$	15.15		13,32,42,56	p and isolated p
9,22,29,42- $C_{60}Cl_{10}$	15.36		13,20,32,39	p and p
5,9,22,46- $C_{60}Cl_{10}$	15.48		13,32,34,37	pmp
7,8,26,43- $C_{60}Cl_{10}$	15.50		50,51,54,60	isolated omp
11,17,34,40- $C_{60}Cl_{10}$	15.62		41,48,57,58	isolated pop
7,18,30,41- $C_{60}Cl_{10}$	15.68		14,31,53,56	p and isolated p
10,13,21,22- $C_{60}Cl_{10}$	15.70		13,14,28,31	omp
11,12,17,36- $C_{60}Cl_{10}$	15.95		44,47,48,58	isolated pmp
6,7,18,31- $C_{60}Cl_{10}$	16.05		17,35,51,59	pop
14,17,23,36- $C_{60}Cl_{10}$	16.07		11,27,44,58	pmp
10,21,34,40- $C_{60}Cl_{10}$	16.30		14,31,41,57	p and isolated p
11,15,17,36- $C_{60}Cl_{10}$	17.05		44,45,48,58	isolated omp

3,4,11,12- $C_{60}Cl_{10}$	17.92	30,33,47,48	omp
2,10,11,21- $C_{60}Cl_{10}$	18.22	14,29,31,48	"opp"
4,6,9,31- $C_{60}Cl_{10}$	18.22	17,32,33,35	omp
10,11,12,21- $C_{60}Cl_{10}$	18.31	14,31,47,48	oop
6,29,31,42- $C_{60}Cl_{10}$	20.44	17,20,35,39	p and p
7,8,9,22- $C_{60}Cl_{10}$	21.24	13,32,50,51	oop
14,15,23,34- $C_{60}Cl_{10}$	21.61	11,27,45,57	pop
6,10,21,31- $C_{60}Cl_{10}$	22.50	14,17,31,35	p and p
7,8,29,42- $C_{60}Cl_{10}$	22.98	13,32,53,54	p and isolated p
7,8,30,41- $C_{60}Cl_{10}$	23.28	14,31,53,54	p and isolated p
10,15,21,36- $C_{60}Cl_{10}$	23.31	14,31,44,45	p and isolated o
9,22,28,37- $C_{60}Cl_{10}$	23.80	7,13,24,32	p and p

The unusual and unexpected results are as follows. First, the third most stable isomer of $C_{60}Cl_{10}$ that can be made by adding four Cl atoms to SPP-$C_{60}Cl_6$ *is* the abundant isomer we have isolated and characterized by X-ray crystallography, 14,28,29,31,SPP-$C_{60}Cl_{10}$. Second, the addition pattern of 14,28,29,31,SPP-$C_{60}Cl_{10}$ is not a fragment of a known or proposed addition pattern of any $C_{60}X_n$ compound with $n > 10$. Third, all but one of the nine lowest-energy isomers are asymmetric (the least-stable of the nine isomers has C_s symmetry). Fourth, all nine involve the creation of one or two *ortho* pairs of C(sp^3) atoms *in addition to* the *ortho* pair in the original SPP array (in fact, only one of the 44 lowest-energy isomers does not have an additional *ortho* pair). Fifth, all of the Cl atoms in the first nine isomers share a hexagon with at least one other Cl atom from the SPP array (i.e., there are no isolated C_6Cl_2 hexagons and no *pmp* or p^3 ribbon of edge-sharing C_6Cl_2 hexagons that is isolated from the SPP Cl atoms for the first nine isomers). The 14th isomer (not shown), with a relative energy of 13.1 kJ mol^{-1}, is the lowest-energy isomer for which the four added Cl atoms do not share a hexagon with any of the six Cl atoms in the SPP array. Finally, the isomer referred to earlier, with an SPP array on one pole, an isolated p^3 ribbon on the other, and overall C_s symmetry, is not even among the 44 lowest-energy isomers. Its DFT-predicted relative energy is 34.2 kJ mol^{-1}. One thing

is now clear. The "flexible" steric requirements of Cl atoms will make it much more challenging to make a list of plausible addition patterns based on previously reported structures, for a given value of *n*, than for fullerene$(X)_n$ derivatives with X = H, F, Br, or CF_3.

Significantly, 28 of the 44 lowest-energy isomers of $C_{60}Cl_{10}$ have a Cl atom on either C13 or C14, including all of the first 13 isomers and 20 of the first 28 isomers. The C13–C14 bond in DFT-optimized SPP-$C_{60}Cl_6$, at 1.379 Å, is among the shortest, and presumably the most electron rich, double bonds in this molecule (only the unique bonds and atoms in C_s-symmetric SPP-$C_{60}Cl_6$ are mentioned in this paragraph; see Figure II.32 for a numbered Schlegel diagram of SPP-$C_{60}Cl_6$). The only shorter bonds in SPP-$C_{60}Cl_6$ are C2–C3, at 1.356 Å, and C10–C11, at 1.377 Å. However, none of the 44 isomers has a Cl atom on C2 or C3 and only three of the 44 isomers has a Cl atom on C10 or C11 (and one of these also has a Cl atom on C14). The next shortest double bond in SPP-$C_{60}Cl_6$ is C16–C17, at 1.383 Å, but only six of the 44 isomers has a Cl atom on C16 or C17, and two of these also have a Cl atom on C13 or C14. All of the remaining double bonds in SPP-$C_{60}Cl_6$ are 1.401 Å or longer. We shall return to this point later in this section.

To better understand the transformation of SPP-$C_{60}Cl_6$ into 14,28,29,31,SPP-$C_{60}Cl_{10}$, we considered all possible $C_{60}Cl_8$ isomers formed by adding two Cl atoms to SPP-$C_{60}Cl_6$ without any rearrangement. Calculations were performed in the same way as in the case of SPP-$C_{60}Cl_6$ (the 50 lowest-energy isomers at the B3LYP/6-311G*//PBE/TZ2P level). Nine of the first 19 lowest-energy isomers are shown in Figure II.32, along with their B3LYP/6-311G*//PBE/TZ2P relative energies. Interestingly, the most stable isomer is 14,31,SPP-$C_{60}Cl_8$ and the 28,29,SPP and 28,31,SPP isomers are no more than 21 kJ mol^{-1} higher in energy. Note that 13,32,SPP-$C_{60}Cl_8$, is the second lowest-energy isomer. It is now clear that the formation of 14,28,29,31,SPP-$C_{60}Cl_{10}$ is not only among the kinetically favored products of the further chlorination of SPP-$C_{60}Cl_6$, it is among the three most-thermodynamically-favored products as well.

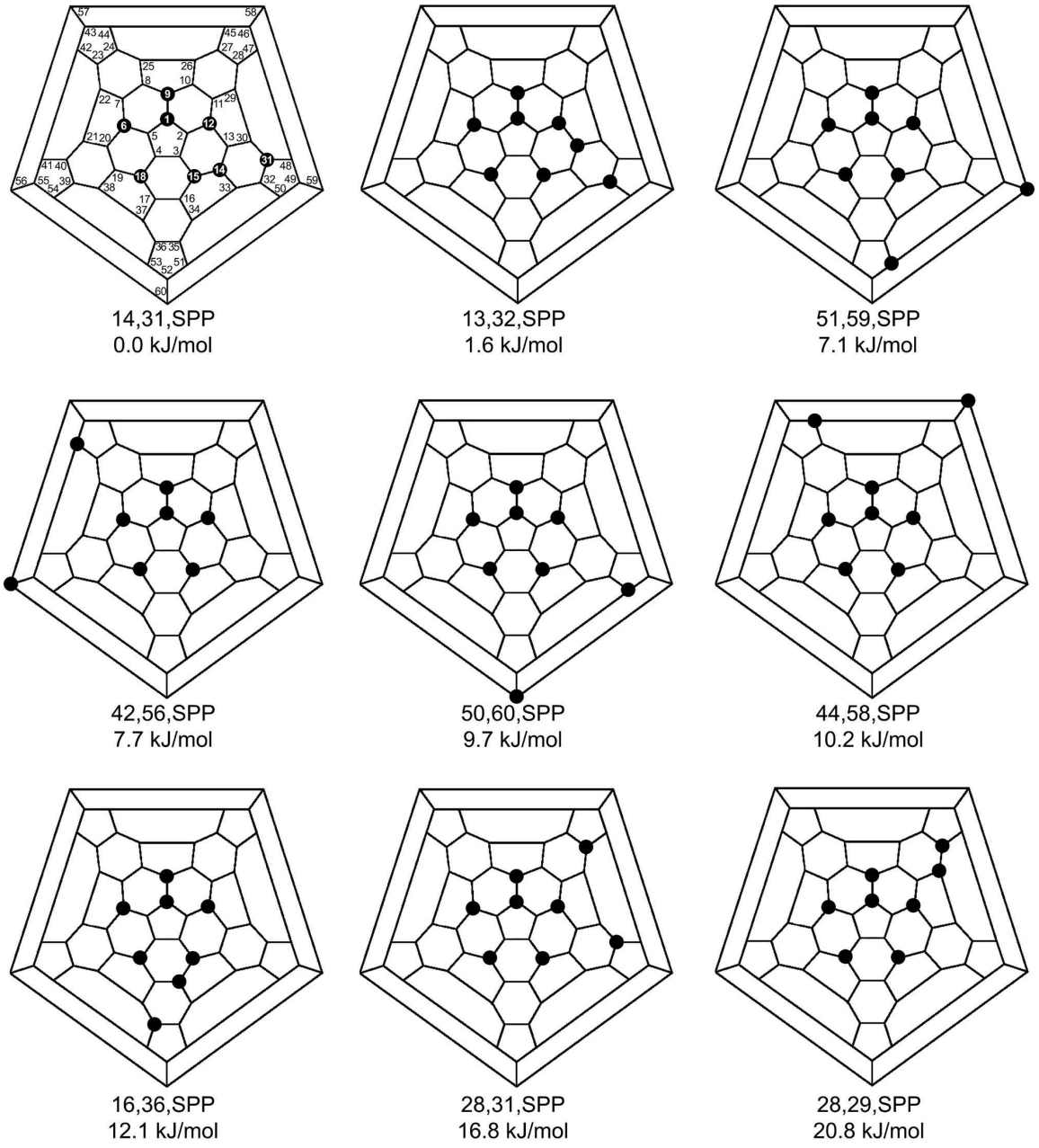


Figure II.32. Schlegel diagrams of the nine lowest-energy DFT-optimized isomers of $C_{60}Cl_8$ that include an SPP array of six Cl atoms (SPP = 1,6,9,12,15,18). The locants are not necessarily the lowest set of locants; they were chosen so that comparisons with 14,28,29,31,SPP-$C_{60}Cl_{10}$ can be clearly seen. The relative energies shown were determined at the B3LYP/6-311G*//PBE/TZ2P level of theory.

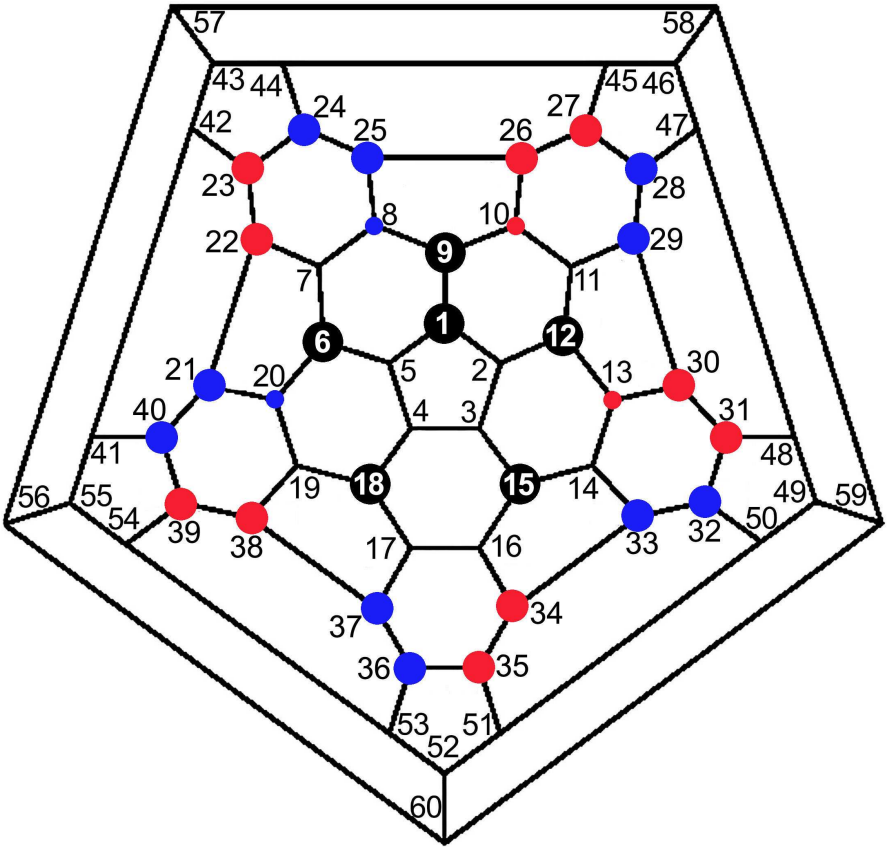


Figure II.33. Numbered Schlegel diagram of SPP-$C_{60}Cl_6$. Blue and red circles signify the HOMO of this molecule (based on DFT calculation).

Let us examine the HOMO-Schlegel diagram for SPP-$C_{60}Cl_6$, shown on Figures II.33 and II.34. There are 10 unique cage C atoms that have the most significant contributions to the HOMO, the orbital that presumably is attacked by ICl. These are C26–C35, and these are the C atoms that would form a bond to the I atom of the incoming ICl electrophile. Let us assume that any one of these ten C atoms that shares a hexagon or pentagon with a C–Cl vertex is sterically hindered, at least to some extent, from forming the linear (cage)C···I–Cl Lewis acid-base adduct. Since those atoms are C26, C29, C30, C33, and C34, that leaves C27, C28, C31, C32, and C35 as the most likely points of attack for the ICl molecule. Next, are there any differences in the bond distances for the three "double bonds" C27–C28, C31–C32, or C35–C36? The answer is no: the three B3LYP-DFT optimized distances are 1.442 ± 0.001 Å. Do they differ in their POAV

angles? The answer is no: all five are 12.0 ± 0.1 deg. Finally, the relative energies of the $C_{60}Cl_6I^+$ cationic inter-mediates are all within 3.3 kJ/mol of one another (the isomer with I^+ on C31 is the lowest).

A 3D representation of the HOMO of SPP-$C_{60}Cl_6$ is shown on Figure II.33. Perhaps it is significant that the size of the lobes on C28 and C32 are bigger (if only a little bigger) than the lobes on C27, C30, and C34. Does this mean a higher probability of the $C_{60}Cl_6I^+$ intermediate having the I atom on C28 or C32 than on C27, C31, or C35? I must ask AAP for his opinion about this.

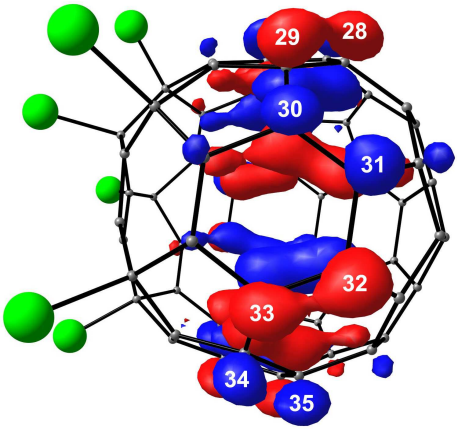


Figure II.34. A 3D representation of the HOMO of SPP-$C_{60}Cl_6$ (Note that C27 is hidden from view in this figure, but its lobe is no bigger than the lobe of C31).

Let us assume there is no rearrangement of either I or Cl atoms once they are attached to the cage (see above). In that case, we can propose that the "mechanism" of adding two Cl atoms to a pair of *ortho* positions may proceed as follows (see the Figure II.35); *para* additions would also be likely, because the positive charge in the iodo cation would be distributed on the *para* as well as the *ortho* positions. The hypothesis that an ion-pair consisting of an iodo cation and an ICl_2^- anion can exist in chlorobenzene soln. is also discussed in the MS. The mechanism is consistent with, but goes beyond, proposed mechanisms for the addition of ICl to olefins. The "beyond" part is the attack of the second ICl molecule on the cage C–I bond (the third reaction in the sequence).

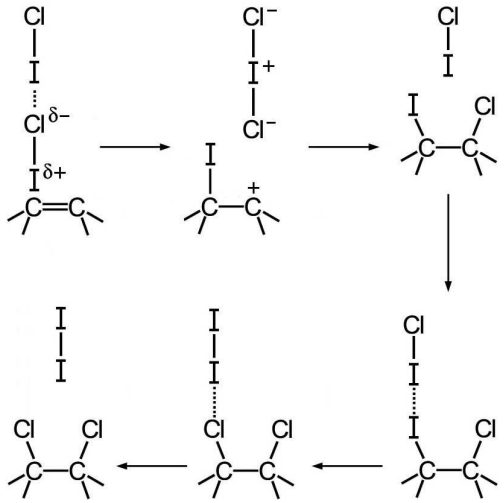
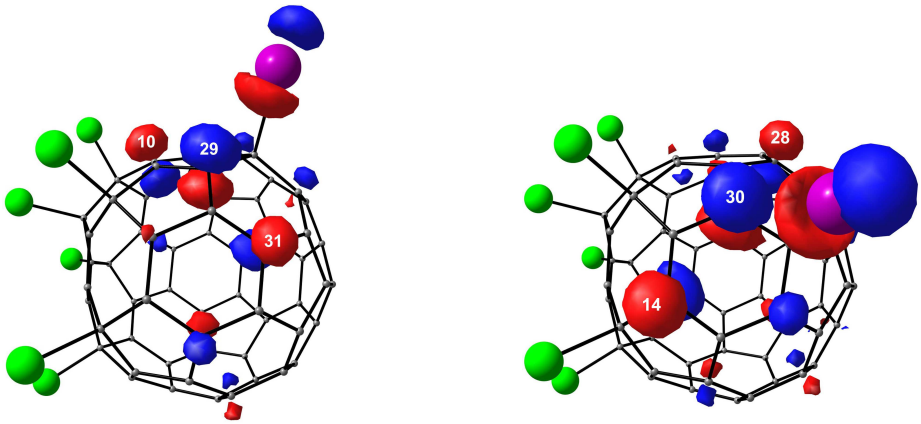


Figure II.35. The proposed mechanism of ICl addition to the double bond of the fullerene cage.

Now let us follow the frontier-orbital-based arguments that lead from SPP-$C_{60}Cl_6$ to 14,28,29,31,SPP-$C_{60}Cl_{10}$ by reactions with ICl in chlorobenzene. We will not argue that this isomer of $C_{60}Cl_{10}$ must be formed from SPP-$C_{60}Cl_6$, but rather that it is highly likely to be formed if the first intermediate, $C_{60}Cl_6I^+$, has its iodine atom on C28 or C31, which it will 40% of the time if addition of "I^+" to "the most likely points of attack" is purely statistical. Therefore, we will argue that, in retrospect, it *could* have been predicted that 14,28,29,31,SPP-$C_{60}Cl_{10}$ should be one of the major isomers of $C_{60}Cl_{10}$ formed, even if it is not the major isomer (which of course we do not know).

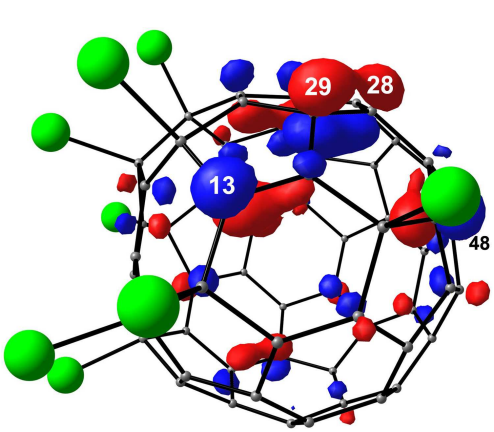
Shown on Figure II.36 are drawings of the LUMOs of *X*-I-SPP-$C_{60}Cl_6^+$ cations (*X* = 28, 31), presumably the orbitals that would be attacked by the ICl_2^- anion, transfering a Cl^- ion from ICl_2^- to the *X*-I-SPP-$C_{60}Cl_6^+$ cation.



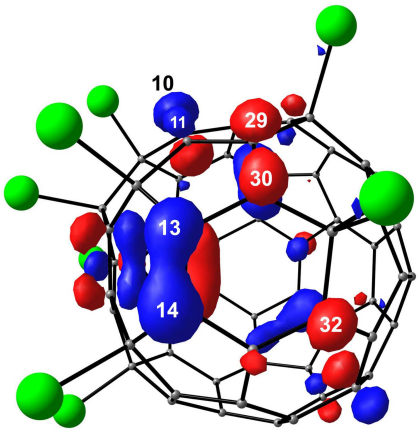
LUMO of 28-I-SPP-$C_{60}Cl_6^+$ LUMO of 31-I-SPP-$C_{60}Cl_6^+$

Figure II.36. The drawings of the LUMOs of *X*-I-SPP-$C_{60}Cl_6^+$ cations (*X* = 28, 31).

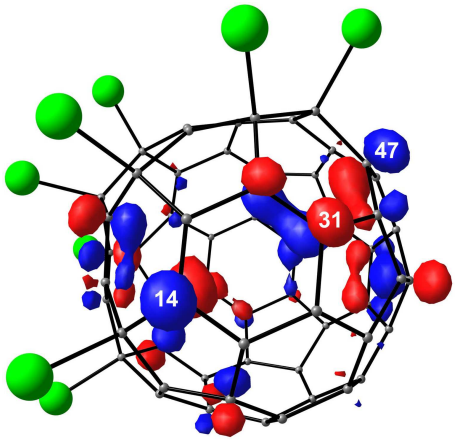
After substitution of the I atom for a Cl atom by the second ICl molecule, isomers of *X*,*Y*,SPP-$C_{60}Cl_8$ would be formed. For the 28-I-SPP-$C_{60}Cl_6^+$ cation, C10 is sterically too crowded to react with the next ICl molecule, leaving C29 and C31 as the most likely points of attack, and C31 is far less crowded than C29, which is ortho to the I atom. For the 31-I-SPP-$C_{60}Cl_6^+$ cation, C28 is far less crowded than C30 or C14. Therefore, the most likely isomers of $C_{60}Cl_8$ would be 28,29,SPP-$C_{60}Cl_8$, 28,31,SPP-$C_{60}Cl_8$, and 14,31,SPP-$C_{60}Cl_8$. The HOMOs of these three isomers are shown on Figure II.36.



HOMO of 14,31,SPP-$C_{60}Cl_8$



HOMO of 28,31,SPP-$C_{60}Cl_8$



HOMO of 28,29,SPP-$C_{60}Cl_8$

Figure II.35. The drawings of the HOMOs of *X*,Y,SPP-$C_{60}Cl_8$.

The most theromodynamically stable isomer of $C_{60}Cl_8$ is 14,31,SPP-$C_{60}Cl_8$ (see above), so we will limit our further discussion to it. From this isomer, the most likely

isomers of *Z*-I-*X*,*Y*,SPP-$C_{60}Cl_8^+$ to be formed next (taking sterics into account) would be 28-I-14,31,SPP-$C_{60}Cl_8^+$ and 29-I-14,31,SPP-$C_{60}Cl_8^+$. Both of these isomers lead to 14,28,29,31,SPP-$C_{60}Cl_{10}$. This shows that the molecular orbital analysis does allow one to predict the likely products resulting from multiple addition to fullerene cage.

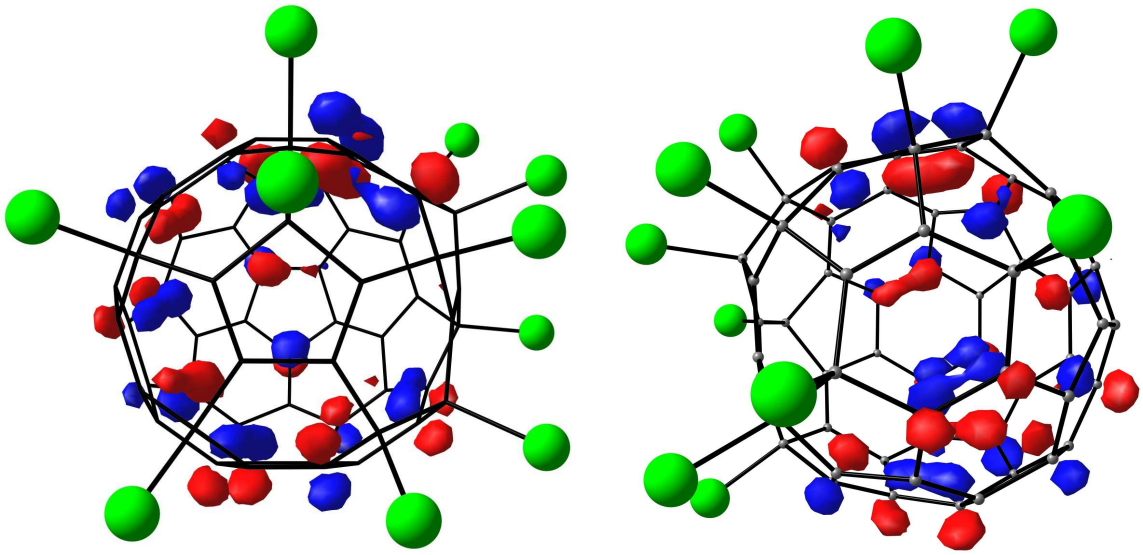


Figure II.36. The drawings of the HOMO of 14,28,29,31,SPP-$C_{60}Cl_{10}$ (two different orientations are shown).

The similar analysis of 14,28,29,31,SPP-$C_{60}Cl_{10}$ shows that HOMO of this molecule is spread across multiple cage carbons. This indicates that further chlorination of this isomer of $C_{60}Cl_{10}$ is likely to be lead to multiple isomers of $C_{60}Cl_{12}$, which lies in agreement with our observations on the higher chlorination of C_{60} (see Section II.2.4). However, in principle it is possible to predict the likely isomers resulting from such reaction using the same approach of molecular orbital analysis coupled with theoretical calculations of the thermodynamic stability of the intermediate (and final) species.

II.3. Conclusions

This study of C_{60} chlorination convincingly demonstrates the power of our methodology (that was introduced in the Preface of this dissertation) for the study of a novel class of chemical compounds. We successfully developed and validated a set of analytical methods for the first time made possible a reliably study of complex samples of chlorofullerenes, oftentimes comprised of many different individual compounds. Using this analytical methodology we were able to reexamine the majority of the literature reports dedicated to synthesis (and characterization) of chlorofullerenes. Our careful reproduction of the reported literature procedures and analysis of the resulting chlorofullerene products shows that all of them are complex mixtures of compositionally and isomerically different compounds with a sole exception of $C_{60}Cl_6$. In order to investigate C_{60} chlorination fundamentally and develop efficient methods for preparation of the single-composition, single-isomer chlorofullerenes besides $C_{60}Cl_6$ we carried out the first detailed study of this process. We studied C_{60} chlorination under several different conditions using different chlorinating agents relying on systematic mapping of the reaction space according to our general methodology. Again, this study was made possible because we were able to reliably analyze and study resulting chlorofullerene products using previously developed analytical methods. Besides a deep theoretical insight into the process of fullerene chlorination this study allowed us to discover and develop efficient syntheses and separation methods for the production of previously unknown chlorides *o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, and $C_{60}Cl_{10}$. The elucidation of the structures of these compounds (using single-crystal X-ray diffraction and UV-Vis spectroscopy) allowed us to suggest the reasons behind the observed regioselectivity of

fullerene chlorination. Using extensive theoretical calculations we were able to show that the selectivity of this process is likely to be heavily influenced by the geometry of the HOMO and SOMO orbitals of the (chloro)fullerene substrate and open-shell chlorofullerene intermediate.

Using our analytical methodology we also performed the first detailed study of chlorofullerene stability. We discovered that all chlorofullerenes that we studied are photosensitive in solution. The study of chlorofullerene stability was instrumental to the success of this work since we were able to ensure that the chlorofullerene samples under investigation do not experience degradation (by shielding them from light at all times). The knowledge of chlorofullerene stability was also crucial to our success in growing X-ray quality single crystals of these compounds from their solutions (and their further structural study). This is the first reported instance of the successful growth of chlorofullerenes single crystals under such conditions; in all earlier reports exotic and poorly reproducing methods of *in situ* crystal growth under high temperature and pressure were used. The discovery of chlorofullerene photosensitivity also raises questions of the results of earlier studies, since extensive chlorofullerene degradation in these reports cannot be ruled out (no light-shielding or photosensitivity was indicated in these earlier studies). This highlights the importance of the systematic stability study, especially when a novel class of compounds is investigated.

The highly successful application of our general methodology to the study of C_{60} chlorination and C_{60} chlorides created a need for a similar investigation of C_{70} in order to determine if the observed behavior is generic to other fullerene cages. Chapter III describes our successful application of our analytical methodology and general approach to the study of such systems to C_{70} chlorination and C_{70} chlorides.

II.4. Experimental Details

Reagents and solvents: Benzene (Sigma-Aldrich , Na), toluene (Fischer Scientific, Na), chlorobenzene (Sigma-Aldrich, CaH_2), and 1,2-dichlorobenzene (Sigma-Aldrich, CaH_2) were ACS Reagent Grade (vendor indicated in parenthesis) and were distilled from the indicated drying agent under purified N_2 atmosphere prior to use. HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), iodine monochloride (Sigma Aldrich, 99.998% trace metals basis), trans-2-[3-c-2-methyl-2-propenylidene]malononitrile (Fluka), chromium(iii) acetyl acetonate (Sigma Aldrich), and KBr (Sigma Aldrich, 99+ % FTIR grade) were used as received. All syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk techniques with vigorous stirring by a magnetic stirrer.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). Electronic spectra of dichloromethane and/or toluene solutions of chlorofullerenes were recorded using a Varian Cary 500 spectrophotometer (see Appendix I-1 for more details). ^{13}C NMR spectra were recorded at 25 °C using a Varian INOVA-unity 400 and a Varian INOVA-unity 500 spectrometers operating at 100 and 126 MHz (see Appendix I-2 for more details). MALDI mass spectra were recorded on a Kompact MALDI IV (Kratos Analytical, Manchester, UK) time-of-flight mass-spectrometer in the linear mode. A 337 nm N_2 laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. CF samples and the trans-2-[3-{4-

tert-butylphenyl}-2-methyl-2-propenyl-idene]malononitrile matrix material (DCTB) were dissolved separately in toluene and were mixed in a 1:10 mol/mol sample/DCTB ratio assuming the sample contained only $C_{60}Cl_6$. A drop of each sample/DCTB solution was deposited on a stainless steel slide by using a capillary and dried under a strong stream of cool air from an airsprayer/brush in order to achieve a uniform sample surface. APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene). Thermogravimetry was performed using a TA Instruments TGA-2950 (platinum sample pans, *ca.* 5 mg sample size, 25–500 °C temperature range).

98% $C_{70}(CF_3)_{10}$ and $C_{70}(CF_3)_{10,12}$ mixture. 98% pure $C_{70}(CF_3)_{10}$ was prepared and purified according to the procedure described in ref. [80]. $C_{70}(CF_3)_{12,14}$ mixture was isolated during HPLC purification of $C_{70}(CF_3)_{10}$ (a fraction with R_f = 2.5-3.5 min was collected using 20/80 toluene/heptanes eluent), see ref. 80.

Iodine monochloride handling and transfer. In a typical experiment, the storage container with solid ICl (a storage tube equipped with a Teflon valve and a side arm) was warmed up, the resulted liquid then measured and transferred using a warmed-up air-tight syringe (500 μL, 250 μL, and 50 μL syringes with Teflon plungers were used) equipped with a Teflon straw of sufficient volume to accommodate all of ICl (to avoid ICl contact with the stainless steel needle and a possible metallic contamination) under protective flow of purified N_2. DANGER! ICl is very volatile, extremely corrosive to metal and rubber, and moisture-sensitive.

ICl_3 preparation. ICl (12.5 μL, 0.246 mmol; or 376 μL, 7.41 mmol) was put into a small-scale, greaseless, air-free reactor (see Figure II.31) and degassed (by using two consecutive freeze-pump-thaw cycles). After degassing ICl was cooled to *ca.* −50 °C and a large excess of gaseous Cl_2 was added to it (some chlorine condensed into a liquid). The reactor was allowed to slowly warm up to room temperature (it was connected with

the atmosphere through an oil bubbler to avoid pressure build-up), which was accompanied by the change of dark-brown color of ICl into bright-yellow color of ICl_3.

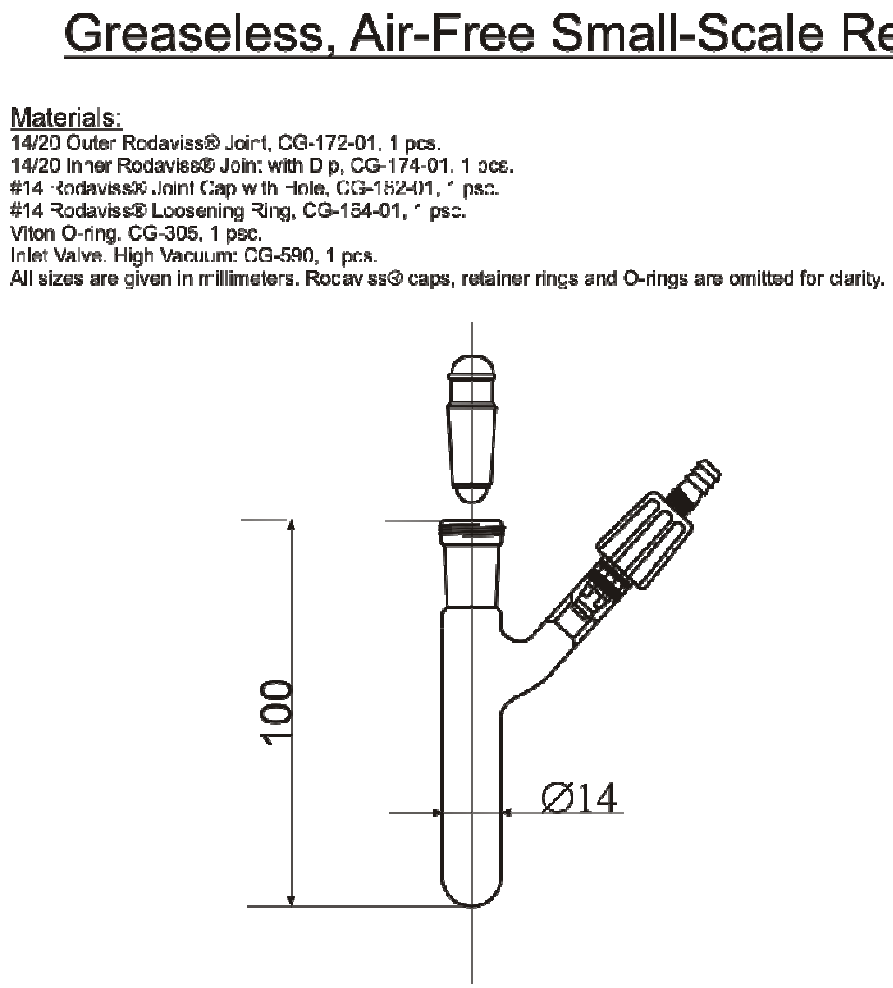


Figure II.31. Small-scale greaseless air-free reactor.

After allowing ICl_3 to stand at room temperature for 30 min the product was cooled to *ca.* −50 °C and evacuated for ~5 min in order to remove the excess of chlorine. ICl_3 was used immediately after the synthesis in the same reactor in order to avoid the need of transferring and weighting this substance. DANGER! ICl_3 is very volatile, extremely corrosive, and moisture-sensitive. ICl_3 releases chlorine upon warming, which can lead to a dangerous pressure buildup in a closed container.

CF handling. All operations involving solutions of CFs were performed either in the dark (vessels containing CF solutions were wrapped with aluminum foil) or with minimal exposure to light (the experimental operations were performed as quickly as possible under minimal illumination). The synthesis of the reported CFs were performed without any special consideration for light exclusion for an accurate reproduction of the original procedures (except $C_{60}Cl_{12}$-I synthesis, see below); however, handling and analysis of the products were in the dark or with minimal light exposure.

Synthesis of $C_{60}Cl_6$ samples A, B, C, and D. Samples **A** and **B** were prepared by adding ICl (1.600 g, 0.500 mL, 9.8 mmol, *ca.* 60 eq.) to a vigorously stirred solution of C_{60} (0.1220 g, 0.169 mmol) in CB (20 mL) at ca. 15 °C (the evaporation chamber was placed in a cool water bath) in the glass reactor of local design[17] (see Figure I-19) with pre-cooled (by liquid nitrogen) trap. Immediately after the addition of ICl, the reactor was put under dynamic vacuum (oil pump) in order to remove all volatiles (CB, excess ICl, I_2) as rapidly as possible without warming of the reaction mixture. After ca. 7 minutes the reaction mixture was evaporated to dryness. It was kept under dynamic vacuum for additional 45 min to ensure the complete removal of ICl and especially I_2. The dry product was washed off the walls of the evaporation chamber of the reactor with a minimum volume of HPLC grade CH_2Cl_2 (under air); then CH_2Cl_2 was removed under vacuum to give sample **B**, $C_{60}Cl_6$ (0.1553 g, 0.166 mmol, ca. 98% yield). Sample **A** was prepared from *ca.* 0.04 g of the sample **B** by HPLC purification (100 % toluene eluent, 5 mL/min flow, Ø10 mm × 250 mm semipreparative Cosmosil BuckyPrep column).

Sample **C** was prepared by addition of ICl (0.800 g, 0.25 mL, 4.9 mmol, ca. 60 eq.) to a vigorously stirred solution of C_{60} (0.0600 g, 0.083 mmol) in CB (10 mL) at ca. 18 °C in 50 mL Schlenk flask. Immediately after addition of ICl, the flask was put under dynamic vacuum (oil pump). After ca. 1 h the reaction mixture was evaporated to dryness; the flask was kept under dynamic vacuum for additional 6 h to the complete removal of ICl

and I_2. The product was used without further purification. The yield is not calculated due to low purity of the product.

Sample **D** was prepared by addition of ICl (0.467 g, 0.146 mL, 2.9 mmol, ca. 80 eq.) to a vigorously stirred solution of C_{60} (0.0263 g, 0.036 mmol) at ca. 20 °C in CB (4 mL) in 50 mL Schlenk flask. 15 min after ICl addition the reaction mixture was put under dynamic vacuum (oil pump). After 40 min the reaction mixture was evaporated to dryness; the flask was kept under dynamic vacuum for additional 2 h to remove ICl and I_2. The product was used without further purification. The yield is not calculated due to low purity of the product.

Photodegradation experiments: $C_{60}Cl_6$/toluene. HPLC purified and carefully dried (see Appendix I.1 for the description of the drying procedure) sample of $C_{60}Cl_6$ (6.6 mg, 7.1 μmol, prepared analogously to $C_{60}Cl_6$ sample **A**) was dissolved in dry deoxygenated toluene (50 mL) under purified N_2 atmosphere. This solution was split into four parts of approximately same volume. Parts **I** and **II** were transferred into Schlenk flasks (under N_2), when parts **III** and **IV** were transferred into 25 mL volumetric flasks with small-diameter necks and ground-glass stoppers (all reservoirs were made of colorless Pyrex glass). Solutions **III** and **IV** were aerated for 10 sec by bubbling air through them. The flasks containing solutions **I** and **III** were wrapped in aluminum foil to shield them from light, when flasks with solutions **II** and **IV** were left in the fume hood exposed to a continuous irradiation with ambient fluorescent light. All solutions were stored in the same place to ensure their equal temperature. All four flasks were tightly capped (using silicon grease) to avoid solvent loss and air contamination. Samples of the solutions **I**, **II**, **III**, and **IV** were taken (under protective flow of N_2 in case of samples **I** and **II**) regularly and analyzed immediately by HPLC (100% toluene eluent, flow 5 mL/min, 300 nm detection wavelength, Ø10 mm × 250 mm semipreparative Cosmosil BuckyPrep column, 500 μL injection volume).

Photodegradation experiments: $C_{60}Cl_6/CH_2Cl_2$. HPLC purified and carefully dried (see Appendix I-1 for the description of the drying procedure) sample of $C_{60}Cl_6$ (8.0 mg, 8.6 μmol, prepared analogously to $C_{60}Cl_6$ sample **A**) was dissolved in dry deoxygenated CH_2Cl_2 (40 mL) under purified N_2 atmosphere. This solution was split into four parts, treated, stored, and analyzed analogously to $C_{60}Cl_6$/toluene photodegradation experiments described above.

Photodegradation experiments: $C_{60}Cl_{10}$/toluene. HPLC purified and carefully dried (see Appendix I.1 for the description of the drying procedure) sample of **$C_{60}Cl_{10}$** (ca. 2 mg, 1.9 μmol, HPLC separated from the sample used for ^{13}C-NMR study of this compound, see Appendix I.2) was dissolved in HPLC grade toluene (30 mL) under air. This solution was split into two parts, which were handled and analyzed analogously to the samples **III** and **IV** of photodegradation experiments $C_{60}Cl_6$/toluene and $C_{60}Cl_6/CH_2Cl_2$ (700 μL samples were used for HPLC analysis).

Preparation of the previously reported $C_{60}Cl_n$. "$C_{60}Cl_8$". The reaction conditions were chosen in order to repeat the original preparation[25] as accurately as possible. ICl (0.0576 g, 0.018 mL, 0.35 mmol, *ca.* 40 eq.) was added to a vigorously stirred (by a magnetic stirrer) solution of C_{60} (0.0075 g, 10 μmol) at *ca.* 20 °C in ODCB (0.25 mL) in 25 mL Schlenk flask. After 3 h the reaction mixture was flash-evaporated under vacuum (oil pump), giving the orange product "$C_{60}Cl_8$".

"$C_{60}Cl_{10}$". The reaction conditions were chosen in order to repeat the original preparation[25] as closely as possible. A vigorously stirred (by a magnetic stirrer) solution of C_{60} (0.0075 g, 9 μmol) at *ca.* 20 °C in ODCB (0.25 mL) in 25 mL Schlenk flask was saturated with gaseous chlorine. Immediately after Cl_2 addition a dark precipitate was formed, which dissolved after *ca.* 10 min. After 15 min of chlorination the reaction mixture was flash-evaporated under vacuum, giving the orange product "$C_{60}Cl_{10}$".

"$C_{60}Cl_{12}$": The reaction conditions were chosen in order to repeat the original preparation[20] as closely as possible. ICl (1.600 g, 0.500 mL, 9.8 mmol, *ca.* 3300 eq.) was

added to a vigorously stirred (by a magnetic stirrer) solution of C_{60} (0.0022 g, 0.003 mmol) at *ca.* 20 °C in C_6H_6 (15 mL) in 50 mL Schlenk flask. The flask was wrapped in aluminum foil to shield the reaction mixture from light. After 3 days the volatiles were removed under vacuum, giving the orange product.

"$C_{60}Cl_{12}$". The reaction conditions were chosen in order to repeat the original preparation[25] as closely as possible. Same conditions were used as for preparation of "$C_{60}Cl_8$", but the reaction was allowed to go for 24 h. Then the reaction mixture was evaporated under vacuum (oil pump), giving the orange product "$C_{60}Cl_{12}$".

"$C_{60}Cl_{26}$". The reaction conditions were chosen in order to repeat the original preparation[25] as closely as possible. Same conditions were used as for preparation of "$C_{60}Cl_{10}$", but the chlorination was allowed to go for 7 days. After that was evaporated under vacuum, giving the orange product "$C_{60}Cl_{26}$".

"$C_{60}Cl_{40,}$ $C_{60}Cl_{24}$". The reaction conditions were chosen in order to repeat the original preparation[19,21] as closely as possible. A vigorously stirred (by magnetic stirrer) suspension of C_{60} (0.0050 g, 0.007 mmol) in CCl_4 (4 mL) in 25 mL Schlenk flask was saturated with gaseous chlorine and left to stand for 16 h. Then the yellow-green solution was irradiated by mercury arch UV-lamp for additional 24 h (Hanovia PC451050 lamp with circulated water jacket was used). The resulted yellow-greenish solution was evaporated under vacuum to give light-orange product "$C_{60}Cl_{40,}$ $C_{60}Cl_{24}$".

C_{60} chlorination study. A stock solution 1 was prepared by dissolving C_{60} (0.1205 g, 0.167 mmol) and $C_{70}(CF_3)_{12,14}$ (6.5 mg) in dry, deoxygenated CB (20.0 mL). 2.0 mL portions of this solution (containing 16.7 μmol of C_{60} each) were chlorinated by different agents in the specialized small-scale air-free greaseless reactors of local design, see Figure I-31. Experiments a, b, c, and e were performed using ICl (a. 4 μL, 0.0128 g, 79 μmol, 5 eq.; b. 12 μL, 0.0384 g, 237 μmol, 15 eq.; c. 36 μL, 0.1152 g, 0.710 mmol, 45 eq.; e. 376 μL, 1.2032 g, 7.41 mmol, 440 eq.); experiments d and f were performed using ICl_3 (d. 256 μmol, 15 eq.; f. 7.41 mmol, 440 eq); experiment g was performed by

saturating the C_{60} solution with gaseous Cl_2 (large excess was used). The reaction mixtures were left stirring at room temperature (shielded from light). Samples of the reaction mixtures were taken (under protective N_2 flow) at the regular time intervals (2 min, 6 min, 18 min, 54 min, 162 min, 8 h 6 min, 1 day 18 min, 3 days 54 min, 6 days 1 h 48 min) and flash-evaporated under vacuum. The dry samples were dissolved in toluene and analyzed by HPLC (100% toluene eluent, flow 5 mL/min, Ø10 mm × 250 mm semipreparative Cosmosil BuckyPrep column, 300 nm detection wavelength). The dry residues of the final reaction mixtures (3 days 54 min for experiments a, b, c, d and 6 days 1 h 48 min for experiments e, f, and g) were dissolved in toluene and separated from $C_{70}(CF_3)_{10,12}$ using HPLC (100% toluene eluent, flow 5 mL/min, 300 nm detection wavelength). The isolated fractions containing CFs were analyzed by APCI-MS.

***o*-, *p*-$C_{60}Cl_2$ and $C_{60}Cl_4$ preparation.** C_{60} solution (0.0705 g, 0.098 mmol) in dry, deoxygenated CB (12 mL) was mixed with ICl (75 μL, 0.2400 g, 1.48 mmol, 15 eq.) under vigorous stirring at ca. 15 °C (the evaporation chamber was placed in a cool water bath) in the glass reactor of local design[17] (see Figure II.19 for an improved greaseless design). After 1 min the reactor was evacuated (the trap was pre-cooled with liquid nitrogen) and the volatiles were quickly removed. The crude product was washed off the walls of the evaporation chamber with HPLC grade toluene, filtered and separated by HPLC. The first stage of separation was performed using neat toluene as an eluent at 5 mL/min flow rate; the second stage was done with 50/50 v/v toluene/heptanes eluent, 5 mL/min flow. The latter HPLC conditions were used for the analysis of the purified fractions.

$C_{60}Cl_{10}$ preparation. C_{60} solution (0.1200 g, 0.167 mmol) in dry, deoxygenated CB (16 mL) was mixed with ICl (0.700 mL, 2.2400 g, 13.8 mmol, 83 eq.) under vigorous stirring at *ca.* 15 °C (the evaporation chamber was placed in a cool water bath) in the glass reactor of local design[17] (see Figure I-19 for an improved greaseless design). After 45 min the reactor was evacuated (the trap was pre-cooled with liquid nitrogen) and the

volatiles were quickly removed. The crude product was washed off the walls of the evaporation chamber with HPLC grade toluene, filtered and separated by HPLC. The first stage of separation was performed using neat toluene as an eluent at 5 mL/min flow rate; the second stage was done with 50/50 v/v toluene/heptanes eluent, 7 mL/min flow. The latter HPLC conditions were used for the analysis of the purified fractions.

Growth of the single crystals of $C_{60}Cl_6$, $C_{60}Cl_{10}$, and $C_{60}Cl_3H$. Crystals of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ were grown by slow evaporation of the saturated benzene or toluene solutions (correspondingly) of the HPLC purified CFs at 23 °C in the absence of light. $C_{60}Cl_3H$ was formed from a toluene solution of 99% pure $C_{60}Cl_4$ at +3 °C during slow evaporation of the solvent in the absence of light.

II.5. List of References

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Chapter III
Study of C_{70} Chlorination and C_{70} Chlorides

III.1. Introduction

In the first chapter we discussed synthesis, analysis, and stability of soluble C_{60} chlorides, in which we describe an analytical methodology (based on HPLC followed by IR, UV-vis, and ^{13}C-NMR spectroscopy and mass-spectrometry analysis) that was developed for detailed studies of CFs (hereinafter C_{60} and C_{70} chlorofullerenes are abbreviated as CFs). We demonstrated that without using HPLC one can not get reliable data on the *molecular composition* (i.e., the amounts of compositionally and/or isomerically different CFs) and purity of bulk soluble CF samples. Many of the C_{60} chlorides reported in the earlier literature, in our study were found to be complex CF mixtures.

The summary of the available literature data on the synthesis of C_{70} chlorides is given in Table III.1. The first work was published in 1995 by Sussex group, which reported the preparation and characterization of $C_{70}Cl_{10}$ by ICl chlorination of C_{70} in benzene solution;[1] no information of the preparative procedure (such as concentrations of the reagents, reaction time and temperature, and yield and purity of the product) was given. A more detailed description of $C_{70}Cl_{10}$ synthesis was given in a later paper (the yield and purity were not reported).[2]

In 1998 Ehrhardt et al. reported that C_{70} chlorination in liquid chlorine was achieved (reaction was performed in a sealed glass ampoule during a period of 30 days).[3] The elemental analysis of the product gave an average composition of $C_{70}Cl_{12}$; the mass loss

of this CF during thermal gravimetry (see Section II.2.1.C) corresponded to much higher degree of chlorination of ca. $C_{70}Cl_{21}$.[3] The Raman spectroscopy of this product was not informative due to its strong fluorescence.[3]

In 1998 Heymann et al. reported the chlorination of C_{70} by chlorine in CCl_4 medium under UV irradiation.[4] The analysis of the $C_{70}Cl_n$ product by several analytical methods gave very different results on the degree of chlorination, which varied between n = 7 and n = 31 (see Table III.1). The chlorinated product was also analyzed by HPLC. This method demonstrated the absence of the starting material, C_{70}, however, authors did not report the number of the components observed in the HPLC trace (the corresponding HPLC trace was not shown in the paper[4]).

In 2003 Troshin et al. reported a synthesis of $C_{70}Cl_{10}$ in 1,2-dichlorobenzene (ODCB) using $KICl_4$ chlorinating agent.[5] It was stated that independently of the amount of chlorinating agent $C_{70}Cl_{10}$ was the only product formed (when less than stoichiometric amount of $KICl_4$ was used, mixtures of $C_{70}Cl_{10}$ and unreacted C_{70} were obtained).[5]

In 2005, two higher C_{70} chlorides, $C_{70}Cl_{28}$ and $C_{70}Cl_{16}$ were reported; they were prepared in sealed ampoules using transition metal chlorides[6] and $TiCl_4/Br_2$ mixture[7] correspondingly. These chlorides were structurally characterized by single-crystal X-ray diffraction study, which revealed that the crystals of both CFs contained several isomers of the corresponding composition (three isomers of $C_{70}Cl_{28}$[6] and two isomers of $C_{70}Cl_{16}$[7]).

Careful analysis of these publications revealed that none of them reported the purity of the CFs, and only in one paper[5] the yield was mentioned. Furthermore, as we have shown in Chapter II for chlorides of C_{60}, the analytical methods used in these studies (see Table III.1) simply cannot provide accurate data on the molecular composition and purity of the bulk $C_{70}Cl_n$ products.

In this chapter we study C_{70} chlorides and C_{70} chlorination using analytical methodology that we described in Chapter II.

Table III.1. Overview of reported C_{70} chlorides.[a]

No. [year][ref]	proposed composition[c]	proposed purity [yield]	reagents and rxn. conditions	analytical techniques[c]	stability	solubility
1 [1995][1]	$C_{70}Cl_{10}$[b]	n/r [qnt][c]	ICl, C_6H_6,[c] reflx.[e]	IR, UV-vis, ^{13}C NMR	slow dcmp at RT	many org. slvnts
2 [1996][8]	$C_{70}Cl_{10}$	n/r. [n/r]	ICl, C_6H_6, heat[f]	n/r	n/r	C_6H_6
3 [1998][3]	$C_{70}Cl_{12}$[e]	n/r. [n/r]	Cl_2(liq.), RT	EA, TG, (Raman[g])	Cl_2 loss at 200-300 °C	n/r
4 [1999][4]	$C_{70}Cl_{7-31}$[n]	n/r [n/r]	Cl_2, CCl_4, UV	WG, MALDI-MS, PIXE-NMP, EMP, HPLC	possible Cl_2 loss upon standing and/or analysis	CCl_4, $PhCH_3$
5 [2003][5]	$C_{70}Cl_{10}$[h]	n/r. [96%]	$KICl_4$, ODCB, RT	EA, IR	n/r	n/r
6 [2005][6]	$C_{70}Cl_{28}$[i]	n/r [n/r]	VCl_4, $SbCl_5$, PCl_5, 140–200°C[j]	IR,[k] X-ray	stable on air	poor sol. in org. slvnts
7 [2005][7]	$C_{70}Cl_{16}$[l]	n/r [n/r]	Br_2, $TiCl_4$, 60–80°C	IR,[k] X-ray	stable on air Cl_2 loss at 240-360 °C	n/r
8 [2008][9]	$C_{70}Cl_{8.4}Br_{1.6}$[m]	n/r [n/r]	Br_2, $TiCl_4$, 80–90°C	IR,[n] X-ray	n/r	n/r

[a] Abbreviations: mxt. = mixture; n/r = not reported; qnttv = quantitative; reflx. = reflux; ODCB = *o*-dichlorobenzene; EA = elemental analysis; UV = UV-irradiation; ODCB = *o*-dichlorobenzene; PIXE-NMP = particle induced X-ray emission/nuclear microprobe analysis; EMP = electron microprobe analysis. [b] As determined by ^{13}C-NMR (based on symmetry requirements). [c] Quantitative yield of this synthesis was reported in ref. [10]. [d] "Preparative details will be given in a full paper."[1]; see item 2 [1996].[8] [e] In ref. [10] it was mentioned that this reaction took 20 minutes and was conducted in boiling C_6H_6; no other preparative details (like quantities of the reagents) were reported. [f] "… the mixture was heated until reaction was complete (*ca.* 20 min)." This description is ambiguous, but based on the ref. [10] it can be presumed that reaction was performed under reflux. [g] Raman spectroscopy was not informative due to strong fluorescence. [h] As determined by EA. [i] As determined by single-crystal X-ray diffraction study (the crystals were found to contain three isomers of $C_{70}Cl_{28}$). [j] $C_{70}Br_{10}$ can also be used as a starting material, allowing to decrease the reaction time. [k] Experimental and calculated IR spectra of $C_{70}Cl_{28}$ were reported. [l] As determined by single-crystal X-

ray diffraction study (the crystals were found to contain two isomers of $C_{70}Cl_{16}$). [m] As determined by single-crystal X-ray diffraction study. [n] IR spectroscopy results were mentioned, but the spectrum itself was not reported.

III.2. Results and Discussion

III.2.1. C_{70} Chlorination

A. Dynamic HPLC Study of C_{70} Chlorination. We performed a detailed study of C_{70} chlorination using dynamic HPLC monitoring as the main analytical tool. This method allows one to quantitatively monitor the course of the reaction by HPLC analysis of the samples of the corresponding reaction mixture taken at the particular time intervals; the resulting HPLC traces are normalized (using the peak of the internal standard) and arranged into 3D waterfall plots. For a detailed discussion of this technique see Chapter II, Section II.2.4. The compositions of the crude and isolated fullerene products were determined by soft-ionization mass spectrometry (MS), and, in some cases, thermal gravimetry analysis (TGA); see Chapter II, Section II.2.1 for more details.

All of the C_{70} chlorination experiments that we performed in this work were carried out in CB solution and were shielded from light unless stated otherwise. Saturated C_{70}/CB solution ([C_{70}] = 2.3 mM according to our solubility data, see experimental section) with dissolved $C_{60}F_{48}$ internal standard were chlorinated by ICl under different conditions (experiment **a**: 42 mM of ICl; experiment **b**: 147 mM of ICl; experiment **c**: 1.13 M of ICl). Figure III.1 shows the dynamic HPLC plots for experiments **a** and **b**. The chlorination of C_{70} by 42 mM of ICl (18 eq., see Figure III.1a) leads to initial formation of the previously unknown $C_{70}Cl_6$ (after ca. 10 minutes of reaction). During the next two hours $C_{70}Cl_6$ is slowly chlorinated further into $C_{70}Cl_8$ (also a previously unknown compound). The HPLC trace of the reaction mixture after 4 hours of chlorination shows a drastic decrease of the total intensity of the peaks of C_{70} and $C_{70}Cl_n$ products; this

decrease is due to formation (and precipitation) of the previously unknown insoluble product $[C_{70}Cl_8]_2$ (see Figure III.2 for the alternative projection of the dynamic HPLC). During the next 5 days of chlorination $[C_{70}Cl_8]_2$ is slowly converted into soluble $C_{70}Cl_{10}$ as evidenced by the dynamic HPLC plot.

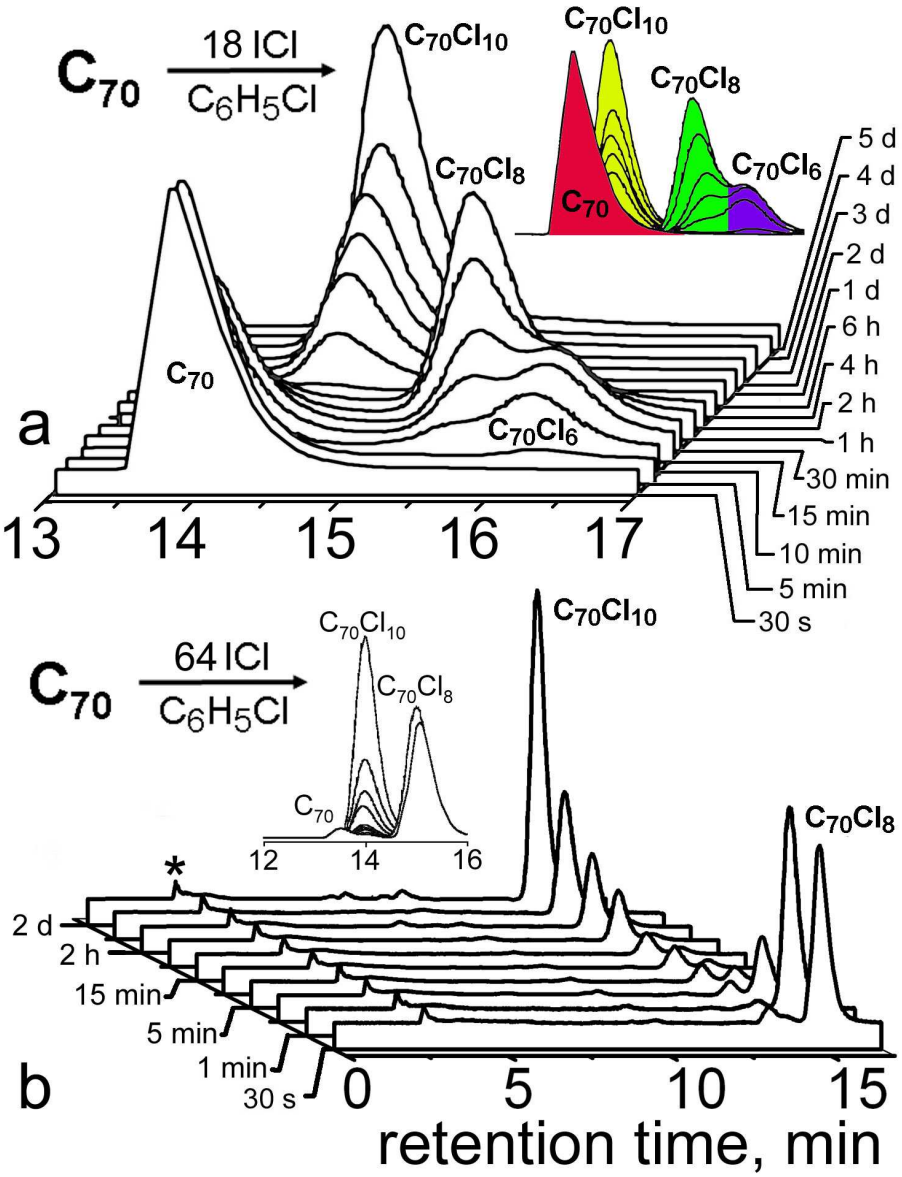

Figure III.1. Dynamic HPLC of C_{70} chlorination in chlorobenzene solution by: a) 42 mM or 14 eq. of ICl; b) 147 mM or 64 eq. of ICl. A retention time range of 0 to 13 min of plot a) is virtually identical to that of plot b). For the other perspective of plot a) see Figure III.2 (inverted direction of the reaction time axis). The peaks marked with asterisks are due to $C_{60}F_{48}$ (added as the internal standard).

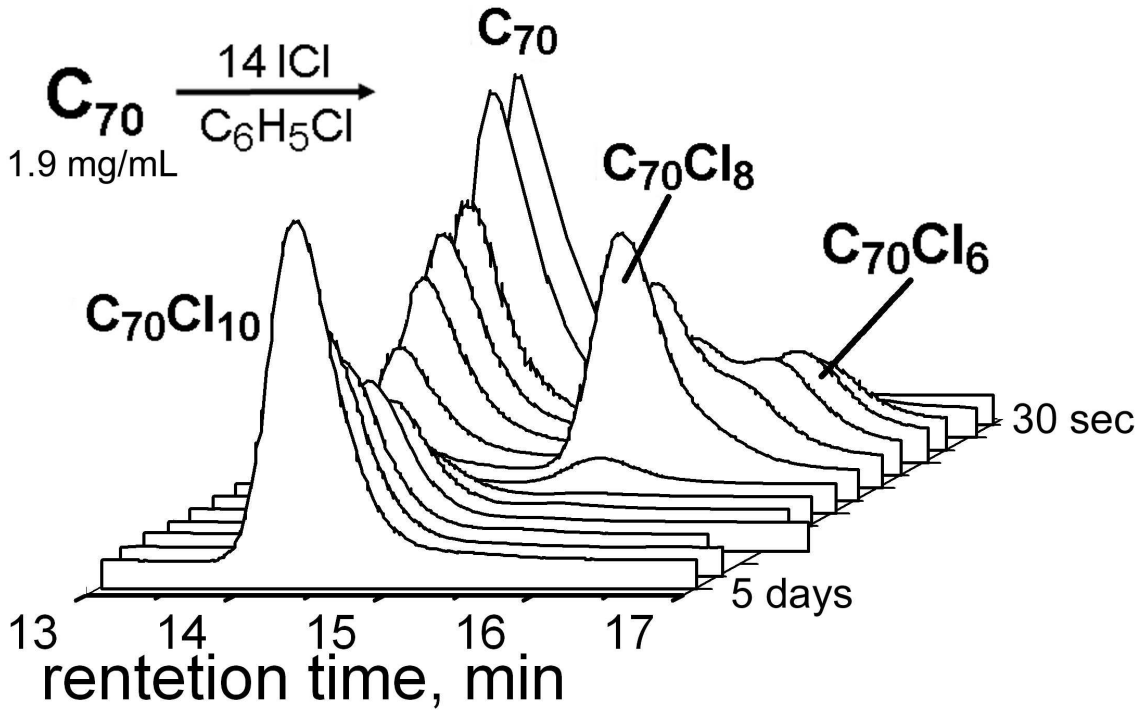

Figure III.2. Dynamic HPLC of C_{70} chlorination in chlorobenzene solution by 42 mM or 14 eq. of ICl (experiment **a**).

The higher concentration of ICl (147 mM or 64 eq., see Figure III.1b) leads to higher chlorination rate and different distribution of CF products. Under these conditions C_{70} is converted into a ca. 90% pure $C_{70}Cl_8$ within the first minute of chlorination. A peak due to $C_{70}Cl_6$ is not observed, apparently due to its rapid conversion into $C_{70}Cl_8$, which indicates that the rate of chlorination is faster for $C_{70}Cl_6$ than for $C_{70}Cl_8$. The concentration of $C_{70}Cl_8$ experiences a dramatic drop during the next 5-10 minutes of reaction. This process is not accompanied by the formation of $C_{70}Cl_{10}$, but by the precipitation of the insoluble product - a dimer $[C_{70}Cl_8]_2$. Similar to the case of C_{70} chlorination by 42 mM of ICl, $[C_{70}Cl_8]_2$ is then slowly (days) converted into $C_{70}Cl_{10}$.

C_{70} chlorination by a higher concentration of ICl (1.13 M, ca. 500 eq., exp. **c**) leads to its complete conversion into $C_{70}Cl_{10}$ within the first 5 minutes of chlorination (see Figure III.3). It is noteworthy that further chlorination of $C_{70}Cl_{10}$ is very slow even at such high concentration of ICl; it takes days for a significant conversion to occur, see

Figure III.3. Moreover, many products are formed during $C_{70}Cl_{10}$ chlorination, which indicates the poor selectivity of this process.

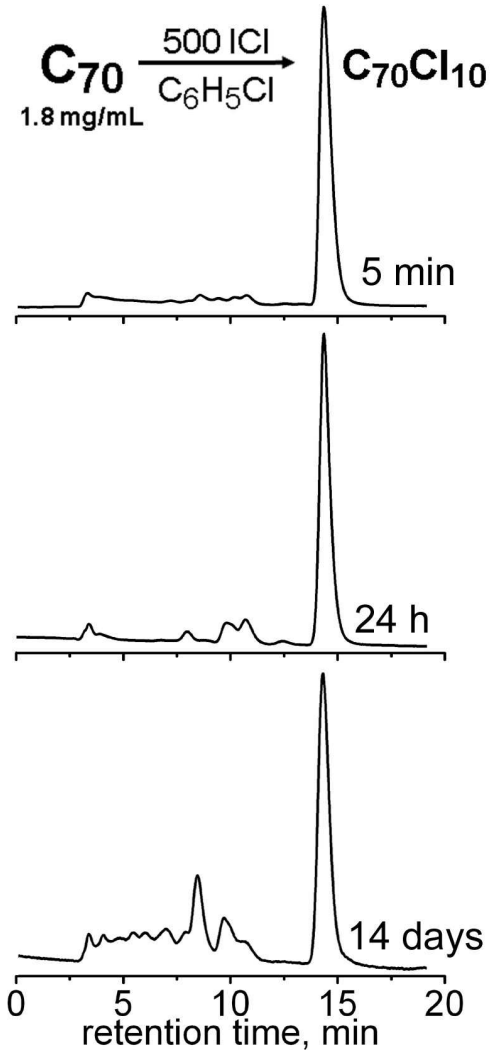

Figure III.3. C_{70} chlorination by high concentration of ICl (1.13 M, or ca. 500 eq.). The main peak is due to $C_{70}Cl_{10}$. Reaction time is given by the right side of the HPLC trace. 100% toluene eluent, 5 mL/min flow rate.

The dynamic HPLC study of C_{70} chlorination did not give any evidence for the presence of the detectable concentrations of lower chlorides $C_{70}Cl_2$ and $C_{70}Cl_4$, indicating that these chlorides may be more easily chlorinated than both C_{70} and higher chlorides ($C_{70}Cl_6$ and $C_{70}Cl_8$). Hence lower chlorination rates should be better suited for the

synthesis of these products (their further chlorination may be slow enough to allow for their accumulation in solution). When we used low concentrations of both C_{70} (to 1.52 mM) and ICl (to 20 mM)we observed the formation of a new peak with a retention time different from $C_{70}Cl_{10}$, $C_{70}Cl_8$, $C_{70}Cl_6$ and C_{70} (the conditions used for $C_{70}Cl_6$ preparation, see below). This peak is likely to be due to $C_{70}Cl_2$ or $C_{70}Cl_4$ (or their mixture); the yield of that product under these conditions is very low at best (ca. 1% according to HPLC integration). Our attempt to increase the yield by decreasing the initial concentrations of C_{70} and ICl further ([C_{70}] = 1.20 mM; [ICl] = 5 mM) was not successful due to very low rate of chlorination (practically no CFs could be detected by HPLC even after several days). A tentative conclusion can be made that lower chlorides $C_{70}Cl_2$ and $C_{70}Cl_4$ may be difficult to prepare because of their high reactivity.

B. Synthesis and Characterization of $C_{70}Cl_{10}$. Several findings from our studies of C_{70} chlorination were taken into account for the development of $C_{70}Cl_{10}$ preparation procedure: i) further ICl chlorination of $C_{70}Cl_{10}$ in PhCl is very slow; ii) further chlorination of the insoluble $[C_{70}Cl_8]_2$ product is slow (days) even with relatively high concentration of ICl (ca. 140 mM); iii) $[C_{70}Cl_8]_2$ is formed in a wide range of ICl concentrations (see above). From these observations it follows that the formation of $[C_{70}Cl_8]_2$ should be avoided if short reaction times are desired.

We found that $[C_{70}Cl_8]_2$ formation can be completely suppressed by using a sufficiently high concentration of ICl (265 mM, 250 eq.). This leads to a very fast and virtually quantitative formation of 98+% pure $C_{70}Cl_{10}$ (see Figure III.4). Since $C_{70}Cl_{10}$ is inert towards further chlorination under these conditions, rapid quenching of the reaction mixture is not critical (see experimental section). The small peaks observed between 7 and 11 minutes of retention time are due to chlorination of C_{60} impurity (ca. 1%) present in the starting C_{70} (hence the purity of $C_{70}Cl_{10}$ product can be improved by using a more pure C_{70}). The yield of $C_{70}Cl_{10}$ achieved in this synthesis is close to quantitative (ca. 99%).

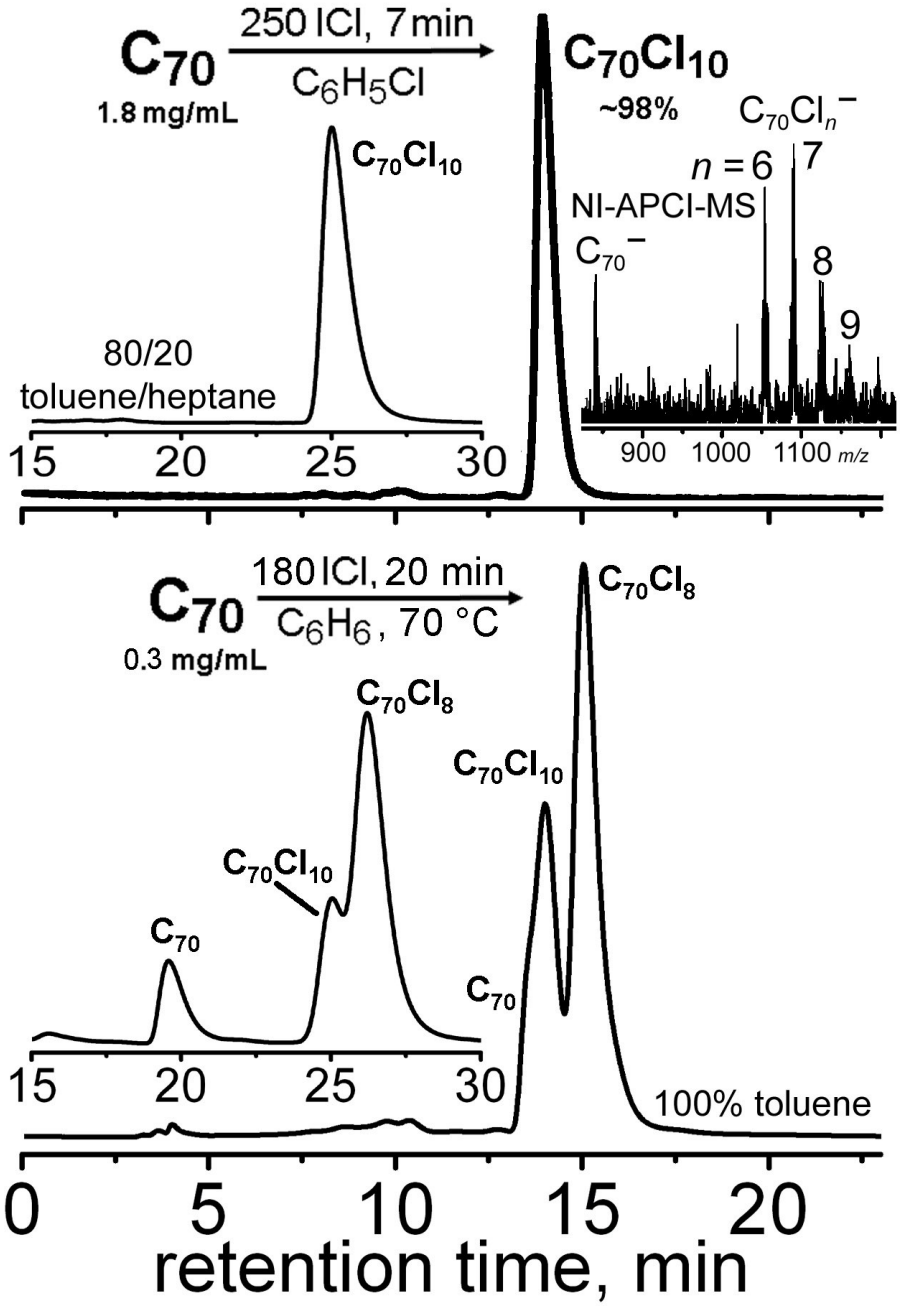

Figure III.4. Top figure: preparation and analysis of $C_{70}Cl_{10}$ by our new synthesis. Bottom figure: preparation and analysis of $C_{70}Cl_{10}$ according to the Sussex group procedure. Large-size HPLC traces were acquired using 100% toluene eluent and 5 mL/min flow rate. Small-size HPLC traces (inserts) were acquired using 80/20 v/v toluene/heptane eluent and 5 mL/min flow rate.

If lower concentration of ICl is used, a more economical $C_{70}Cl_{10}$ synthesis (in terms of ICl) may be realized. However, it will go through the stage of $[C_{70}Cl_8]_2$ precipitation,

so long reaction times (and/or higher temperatures) will be necessary to fully convert it into $C_{70}Cl_{10}$.

The very high compositional and isomeric purity of this $C_{70}Cl_{10}$ product was confirmed by HPLC analysis using several different eluents (in order to minimize the chances of overlooking potential impurities with retention times similar to $C_{70}Cl_{10}$, see Section II.2.1.B). Besides HPLC, $C_{70}Cl_{10}$ also was characterized by IR and UV-vis spectroscopy which confirmed that the product has the same spectral signatures as the $C_{70}Cl_{10}$ reported in the literature, see Figure III.5.[1]

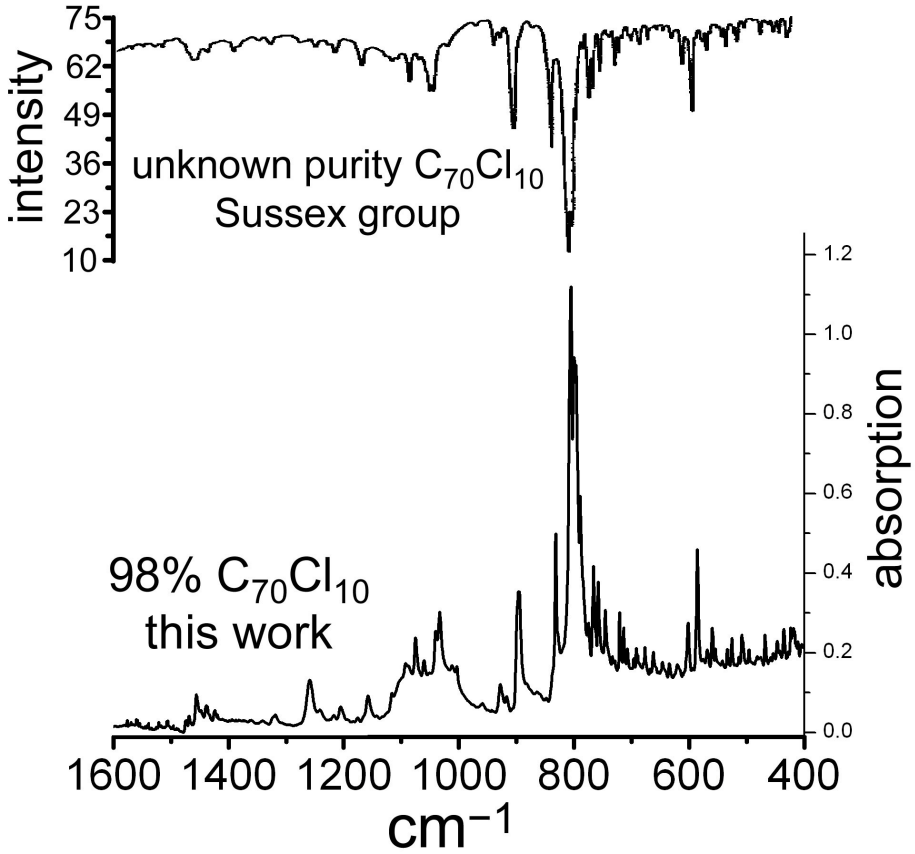

Figure III.5. Top figure: the literature IR spectrum of $C_{70}Cl_{10}$ (pressed KBr pellet, see ref.11. Bottom figure: the IR spectrum of *ca.* 98% $C_{70}Cl_{10}$ (pressed KBr pellet, this study).

In addition, for the first time $C_{70}Cl_{10}$ was characterized by mass-spectrometry (NI-APCI-MS), which showed several $C_{70}Cl_n^-$ ions with n = 6, 7, 8, 9 (see Figure III.4). The peak corresponding to $C_{70}Cl_{10}^-$ molecular ion has a very low intensity. The low stability

of the molecular ion can be rationalized by the high steric hindrance of the two chlorines occupying a 1,2-position in the structure of $C_{70}Cl_{10}$. No peak corresponding to the product of chloride addition ($C_{70}Cl_{11}^-$ ion) was observed; this shows that $C_{70}Cl_{10}$ does not add chloride ion under these conditions (or that the concentration of this ion is too low to be observed). This behavior is notably different from C_{60} chlorides: C_1-$C_{60}Cl_{10}$ forms an abundant $C_{60}Cl_{11}^-$ anion (same as $C_{60}Cl_6$ forming $C_{60}Cl_7^-$ anion) under the same MS conditions (see Section II.2.1.G).

The composition and symmetry of $C_{70}Cl_{10}$ was initially determined by ^{13}C-NMR in the original report by Sussex group.[1] The two candidates for $C_{70}Cl_{10}$ structure consistent with ^{13}C-NMR were given.[1] That paper also mentioned that these structures were consistent with ^{1}H-NOE data for $C_{70}Ph_8$ and $C_{70}Ph_{10}$ derivatives (prepared from $C_{70}Cl_{10}$ and C_{70} correspondingly), assuming to the preservation of the addition pattern of the parent CF ($C_{70}Ph_8$ addition pattern suggested[12] is a subpattern of $C_{70}Cl_{10}$). The actual description of the synthesis and characterization of these phenylated derivatives, including ^{1}H-NOE measurements, were reported in a later publication[12] in 1996. In the theoretical study (published in 1995) four candidate structures for $C_{70}Cl_{10}$ consistent with ^{13}C-NMR spectrum were given; the calculations on semiempirical level of theory suggested that an isomer with a maximum number of 1,4-chlorine additions to hexagons and no double bonds in pentagons should be preferred (see Figure III.6 for the Schlegel diagram).[10]

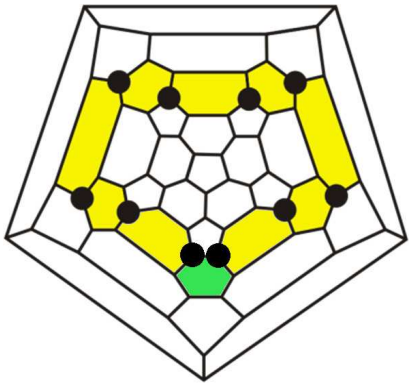

Figure III.6. Schlegel diagram of $C_{70}Cl_{10}$.

Later calculations that were done on the higher level of theory confirmed this conclusion. Up to date, the single-crystal X-ray structure of $C_{70}Cl_{10}$ has not been determined; however, single-crystal X-ray diffraction studies of $C_{70}Br_{10}$[ref] and a mixed halide $C_{70}Cl_{8.4}Br_{1.6}$[9] were shown to have the addition pattern identical to the predicted one for $C_{70}Cl_{10}$. The close similarity of the IR spectra of $C_{70}Cl_{10}$[1] and $C_{70}Br_{10}$[ref] indicate that these compounds are likely to have the same addition pattern, which further supports the proposed structure of $C_{70}Cl_{10}$.

We repeated the first synthesis of $C_{70}Cl_{10}$ reported in ref. 2 in order to compare the purity of the resulting product and its yield with those achieved in our synthetic procedure (see Figure III.4). The analysis of the product revealed that $C_{70}Cl_{10}$ constitutes only a small part of the product (ca. 20% according to HPLC trace integration), with the major product being $C_{70}Cl_8$ (ca. 70%). The unreacted C_{70} takes up ca. 10%. $[C_{70}Cl_8]_2$ formation was not observed (all product was soluble). This result puzzled us because spectroscopic data (IR and UV-vis spectra) reported in the original paper are very close to the ones obtained by us for the 98% pure $C_{70}Cl_{10}$.

The presence of $C_{70}Cl_8$ in the original product is consistent with the results of $C_{70}Cl_{10}$ phenylation reported by Sussex group (see Chapter IV);[12] however, the UV-vis and ^{13}C-NMR spectra suggest that $C_{70}Cl_{10}$ was indeed the major component of the CF sample that was synthesized in the original work.[1] Although the IR spectra of our 98% pure $C_{70}Cl_{10}$ lie in excellent agreement with the literature data published in 1995 paper (see Figure III.5), this cannot be used as an evidence for the absence or low concentration of $C_{70}Cl_8$ since the IR spectra of $C_{70}Cl_{10}$ and $C_{70}Cl_8$ are very similar. Our study of C_{70} chlorination (see above) shows that the amount of $C_{70}Cl_{10}$ in the products of C_{70} chlorination can be increased by using a longer reaction time and/or higher concentration of ICl (higher reaction temperature may also increase the yield of $C_{70}Cl_{10}$). These data suggest that different synthetic methods may have been used in different reports published by Sussex group on preparation[1,2] and chemistry of $C_{70}Cl_{10}$.[12-16] This

hypothesis can explain an excellent match between the spectroscopic data for the original $C_{70}Cl_{10}$[1] and our 98+% pure sample, which is otherwise perplexing in light of our findings. (We did not repeat the procedure reported by Troshin et al. due to the ambiguous composition of $KICl_4$ that was used in this work.[5])

C. Synthesis and Characterization of $C_{70}Cl_8$. The dynamic HPLC plot of C_{70} chlorination by 147 mM of ICl (64 eq.) suggests that these conditions can provide a highly effective method of $C_{70}Cl_8$ synthesis (see Figure III.1b). However, the dynamic HPLC plot shows that the concentration of $C_{70}Cl_8$ quickly drops due to formation of $[C_{70}Cl_8]_2$ dimer. When this insoluble side-product can be easily separated from the soluble $C_{70}Cl_8$ by filtration, its formation decreases the total yield of the latter target compound. The rate of this process is significantly lower when lower concentration of ICl is used (see Figure III.1a); however, $C_{70}Cl_6$ also becomes significantly more abundant. Separation of $C_{70}Cl_8$ and $C_{70}Cl_6$ is tedious due to their similar retention times (toluene/heptane mixed eluent and long HPLC runs have to be used for this purpose); thus from the practical standpoint it is better to avoid $C_{70}Cl_6$ formation during synthesis. Hence we chose to use conditions similar to dynamic HPLC experiment a (initial concentrations: $[C_{70}]$ = 1.9 mM; [ICl] = 96 mM, or 50 eq.) and short reaction times (1-2 minutes) for an efficient $C_{70}Cl_8$ preparation, see Figure II-. These conditions allow one to avoid the formation of $[C_{70}Cl_8]_2$ and $C_{70}Cl_6$ in appreciable quantities; however, the crude product of this procedure contains ca. 20% of unreacted C_{70}. Due to an ample difference in retention times of C_{70} and $C_{70}Cl_8$ this chloride can be easily purified to 95+% purity by a straightforward HPLC separation (see Figure III.7). The HPLC analysis of the purified $C_{70}Cl_8$ using 80/20 v/v toluene/heptane eluent also shows a single peak, which is consistent with a single-composition, single-isomer $C_{70}Cl_8$ product (see Figure III.7).

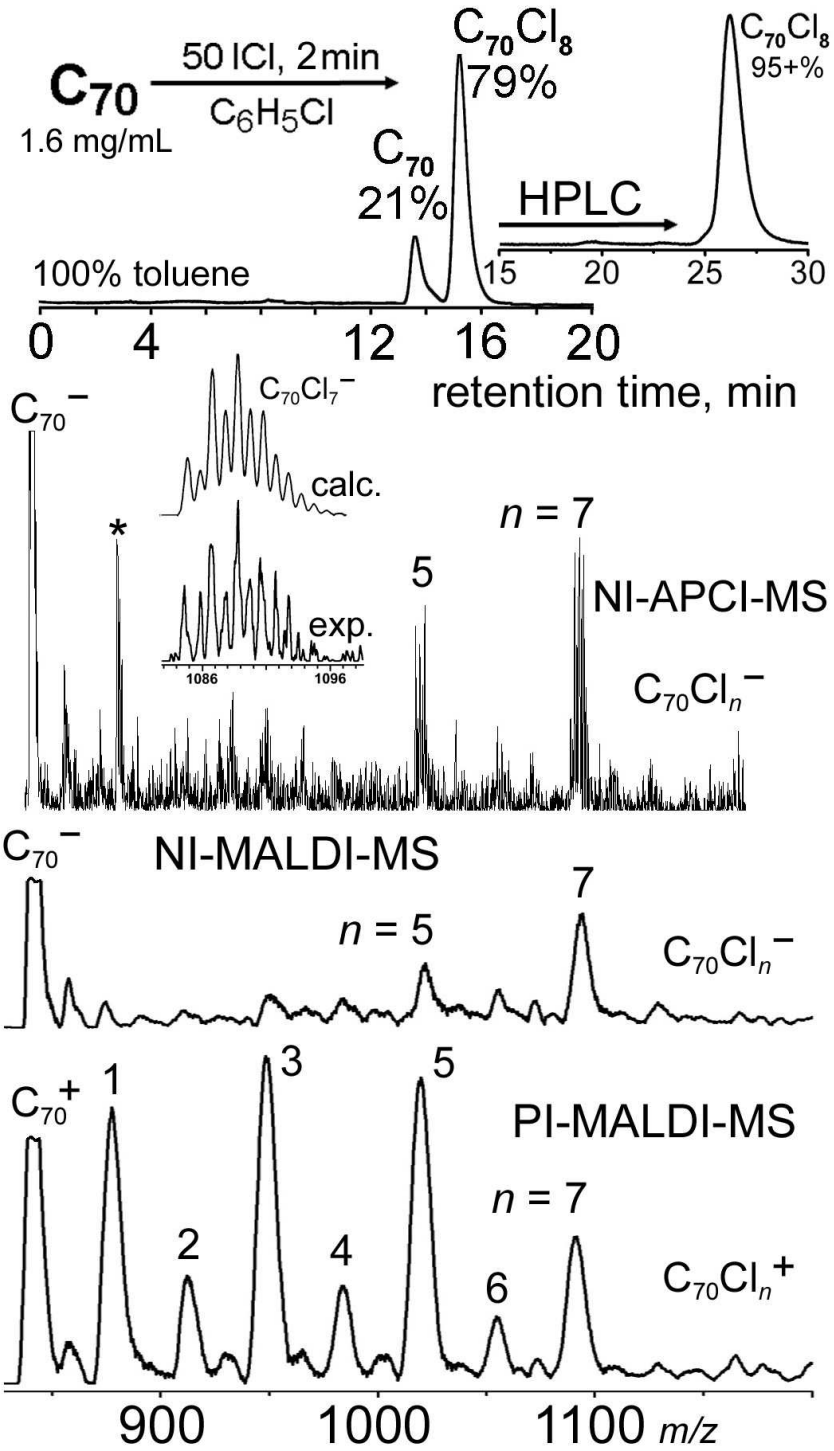

Figure III.7. Synthesis, HPLC purification and analysis of $C_{70}Cl_8$ (the small-size HPLC trace of the 95+% $C_{70}Cl_8$ was acquired using 80/20 v/v toluene/heptane eluent and 5 mL/min flow rate). NI-APCI- and NI- and PI-MALDI- mass spectra of the 95+% pure $C_{70}Cl_8$ are also shown. The insert shows experimental (NI-APCI-MS) and calculated isotopic distribution of $C_{70}Cl_7^-$ peak.

The 98% pure $C_{70}Cl_8$ was analyzed by NI-APCI- and NI- and PI-MALDI-MS (see Figure III.7). The results of NI-APCI- and NI-MALDI-MS are similar, with $C_{70}Cl_7^-$ and $C_{70}Cl_5^-$ being the two observable CF ions in both mass spectra. Similar to $C_{70}Cl_{10}$, negative-ion mass spectra of $C_{70}Cl_8$ does not show the molecular ion. There is also no indication of chloride addition (formation of $C_{70}Cl_9^-$ is not observed). The positive-ion MALDI mass spectrum of $C_{70}Cl_8$ shows a much higher extent of fragmentation (which has been observed before for MALDI-MS of $C_{60}Cl_6$[ref]), however, the heaviest observable CF ion is $C_{70}Cl_7^+$. This observation is important since in positive-ion MALDI-MS the formation of heavier CF ions (for example, formation of $C_{60}Cl_7^+$ from $C_{60}Cl_6$) has never been observed; moreover, this process is unlikely to occur. Hence, the fact that MALDI-MS analysis of the CF sample results in the heaviest (also most intense) observable CF ions having seven chlorine substituents both in positive- and in negative-ion modes strongly supports the conclusion that the composition of this CF sample is indeed $C_{70}Cl_8$.

$C_{70}Cl_8$ was also analyzed by UV-vis and IR spectroscopy. The fact that $C_{70}Cl_{10}$ is produced during further chlorination of $C_{70}Cl_8$ strongly suggests that the addition pattern of $C_{70}Cl_8$ is a sub-pattern of $C_{70}Cl_{10}$ structure (the migration of chlorine substituents on the fullerene cage at room temperature is unlikely). In the structure of $C_{70}Cl_{10}$ only two chlorines have a close 1,2-contact; the rest of the substituents occupy more energetically favorable 1,4-positions relative to each other (on the equatorial hexagons of C_{70} cage, see Figure xx for a Schlegel diagram of $C_{70}Cl_{10}$). Hence the likely addition pattern of $C_{70}Cl_8$ is a pattern of $C_{70}Cl_{10}$ with two 1,2-chlorines removed, see Figure III.8. This addition pattern was also suggested for $C_{70}Ph_8$ derivative of $C_{70}Cl_{10}$ and it is supported by ^{1}H-NOE measurements.[12] The comparison of the UV-vis spectra of $C_{70}Cl_8$ and C_s- and C_2-isomers of $C_{70}(CF_3)_8$ also supports the C_s addition pattern for $C_{70}Cl_8$, see Figure III.8.

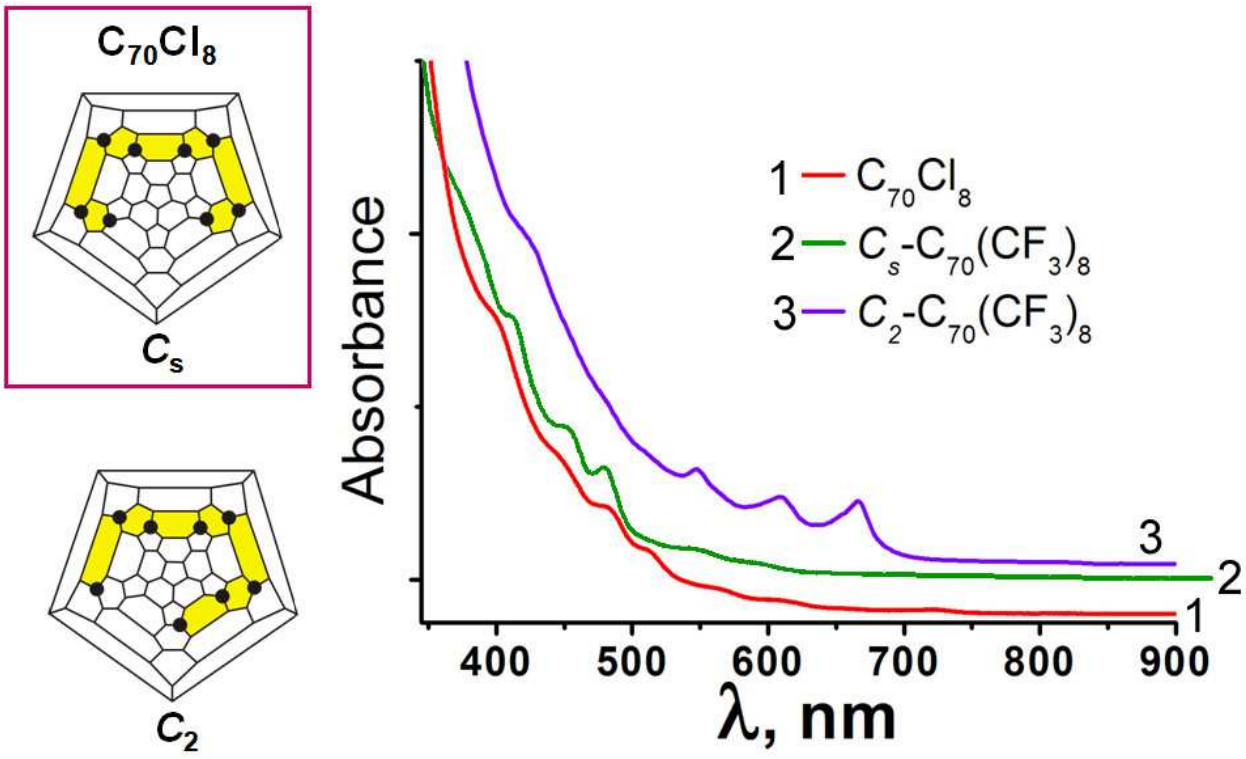

Figure III.8. UV-vis spectra of 98% pure $C_{70}Cl_8$ (1), C_s-(2) and C_2-$C_{70}(CF_3)_8$ (3).

D. Synthesis and Characterization of $C_{70}Cl_6$. Based on the dynamic HPLC data (see Figure III.1a) a preparatory procedure for $C_{70}Cl_6$ was developed. The chlorination of the diluted C_{70} solution in CB ([C_{70}] = 1.5 mM) by ICl (20 mM, 14 eq.) for a period of 90 minutes produces the highest yield of $C_{70}Cl_6$ that we were able to achieve (see Figure III.9). The crude product contains ca. 27% of $C_{70}Cl_6$, ca. 5% of $C_{70}Cl_8$, and ca. 66% of unreacted C_{70} (based on HPLC trace integration, see Figure III.9). The minor impurities include ca. 1% of C_{60} (present in the starting material) and ca. 1% of the unidentified component that may be due to lower C_{70} chlorides $C_{70}Cl_2$ and/or $C_{70}Cl_4$ (see Section II.2.1.A).

$C_{70}Cl_6$ was purified to 95+% state using HPLC (80/20 v/v toluene/heptane eluent was used). This purified product was analyzed by NI-APCI-MS, which showed $C_{70}Cl_6^-$ ion as the most abundant, with $C_{70}Cl_4^-$ and $C_{70}Cl_2^-$ peaks having smaller intensity. It is

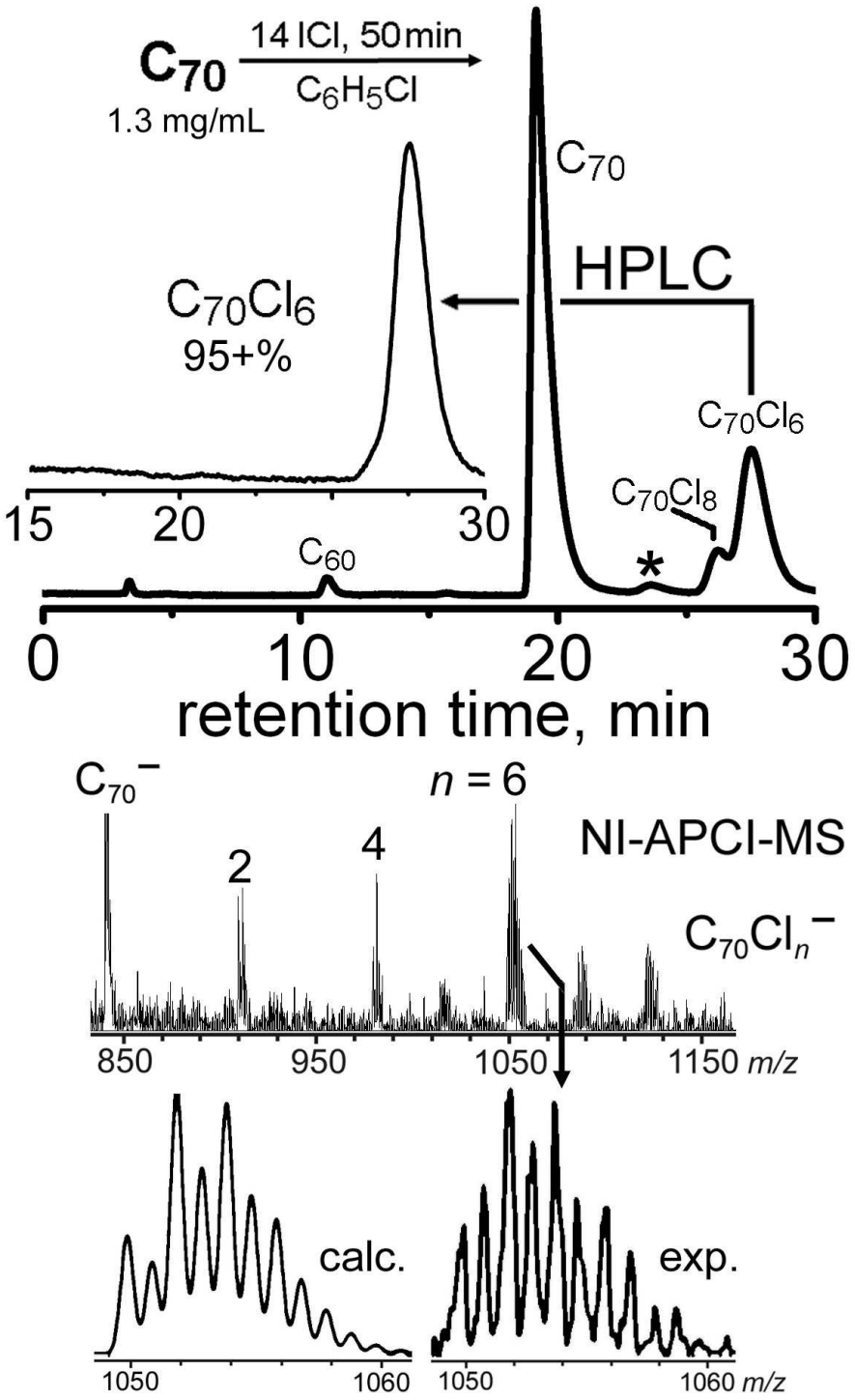

Figure III.9. Synthesis, HPLC purification and analysis of $C_{70}Cl_6$ (the small-size HPLC trace of the 95+% $C_{70}Cl_6$ was acquired using 80/20 v/v toluene/heptane eluent and 5 mL/min flow rate). The peak markes with an asterisk may be due to lower chloride(s) $C_{70}Cl_2$ and/or $C_{70}Cl_4$. NI-APCI- mass spectrum of the 95+% pure $C_{70}Cl_6$ is shown below. The bottom part of the figure shows the experimental and calculated isotopic distribution of $C_{70}Cl_6^-$ peak.

notable that mostly $C_{70}Cl_n^-$ ions with even number of chlorines are observed in this case. NI-APCI- mass spectrum of $C_{70}Cl_{10}$ shows CF ions with both even and odd number of chlorines; NI-APCI- mass spectrum of $C_{70}Cl_8$ produces mostly CF ions with odd *n*'s (see Figures III.4 and III.7, correspondingly). $C_{70}Cl_7^-$ ion is not observed in the NI-APCI- mass spectrum of $C_{70}Cl_6$, which demonstrates that addition of chloride anion to this molecule is not observed under these NI-APCI-MS conditions. A conclusion can be drawn that unlike $C_{60}Cl_6$ and $C_{60}Cl_{10}$, $C_{70}Cl_n$ (n = 6, 8, 10) do not add chloride anion in NI-APCI-MS.

The fact that $C_{70}Cl_6$ is further chlorinated into $C_{70}Cl_8$ and $C_{70}Cl_{10}$ allows us to assume that the addition pattern of this compound is a subpattern of these higher chlorides. The UV-vis spectra of C_2-$C_{70}Cl_6$ and C_2-$C_{70}(CF_3)_6$ (see Figure III.10) are similar, which allows us to suggest that these two compounds have the same addition pattern. Moreover, the theoretical calculations suggest that the C_s-symmetric alternative structure possesses a very narrow HOMO-LUMO gap, which would lead to a high polymerization tendency of this compound (this is not observed).

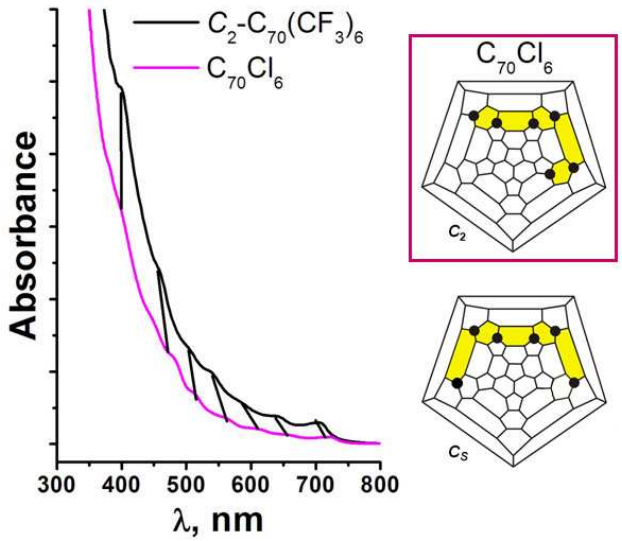

Figure III.10. UV-vis spectra of 95+% $C_{70}Cl_6$ and C_2-$C_{70}(CF_3)_6$. The likely C_2-addition pattern of $C_{70}Cl_6$ is highlighted by the red square.

E. Synthesis and Characterization of $[C_{70}Cl_8]_2$. The synthesis of $[C_{70}Cl_8]_2$ uses the same conditions as for $C_{70}Cl_8$ preparation, but longer reaction time is used (see Figure 6). 25-30 minutes of chlorination gives $[C_{70}Cl_8]_2$ with 75% yield (of the isolated compound). The thermal gravimetry showed the mass loss corresponding to $C_{70}Cl_{8.3\pm0.3}$ composition (see Figure III.11; the residue after TGA contains C_{70}, as demonstrated by IR spectroscopy). This composition is also confirmed by the results of NI- and PI-MALDI-MS: in both positive and negative modes the heaviest CF ions observable contained C_{70} with 8 chlorine substituents as the heaviest (see Figure III.11). The very poor solubility of this product can be explained by the formation of dimer $[C_{70}Cl_8]_2$, similar to the insoluble dimeric $[C_{60}Cl_5]_2$ which can be prepared using similar conditions (see Chapter IV).[17,18]

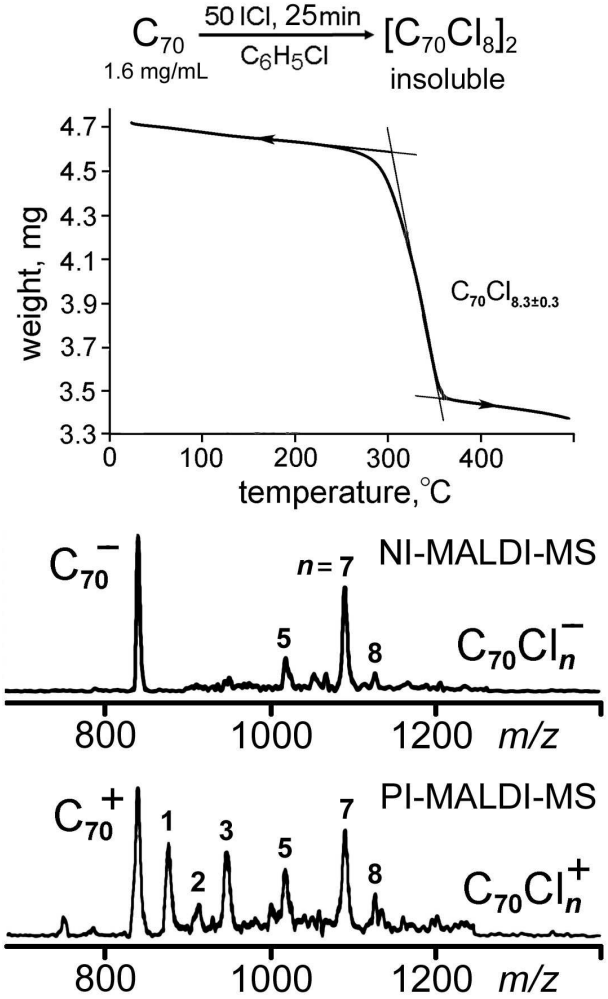

Figure III.11. Synthesis and characterization of $[C_{70}Cl_8]_2$ by TG and NI- and PI-MALDI-MS.

III.2.2. Stability and Photodegradation of $C_{70}Cl_n$

There have been scarce data reported on $C_{70}Cl_n$ stability (either in solid phase or in solution) up to date. Sussex group stated that solid $C_{70}Cl_{10}$ slowly decomposes while standing on air.[1,10,12] The authors attributed this phenomenon to the high steric hindrance and associated ease of loss of two *ortho*-chlorines present in the structure of this chloride; no experimental evidence for the formation of lower C_{70} chlorides was reported, however. In our study, no signs of decomposition of dry samples of $C_{70}Cl_{10}$ were observed even after ca. 1 year of storage (according to HPLC analysis; the samples were stored under air and under ambient laboratory light). The only other data available on the stability of $C_{70}Cl_n$ is the TG analysis of the product of C_{70} chlorination by liquid chlorine (rapid mass loss was observed between 200–300 °C).[3] No data on the stability of $C_{70}Cl_n$ in solution have been reported up to date.

Recently, we discovered that $C_{60}Cl_n$ are photosensitive to ambient laboratory light in solution, both under ambient air atmosphere and under dry nitrogen. We also found that $C_{60}Cl_6$ undergoes this photodecomposition both in aromatic and in halogenated hydrocarbon solvents (toluene and dichloromethane), although the rate of this process was significantly lower in the latter solvent. Since the nature of chemical bonding in C_{60} and C_{70} chlorides is very similar, it was worthwhile to examine stability of $C_{70}Cl_n$ in solution.

In this work, we applied the same method (dynamic HPLC monitoring) to study the stability of $C_{70}Cl_{10}$, $C_{70}Cl_8$, and $C_{70}Cl_6$ in toluene solution under different conditions. The same procedure was used for these three compounds: a sample of CF was dried and dissolved in dry, deoxygenated toluene. These solutions were split into four portions

(samples **I-IV**) each, which were stored under different conditions: i) samples **I** were kept in the dark, under N_2; ii) samples **II** were kept under light, under N_2; iii) samples **III** were kept in the dark, under air; iv) samples **IV** were kept under light, under air. The solutions stored under air were also airated prior to the beginning of the experiment. All other conditions were kept the same (the containers were kept together in order to ensure the same temperature history). The solutions were regularly analyzed by HPLC (samples of the same volume were analyzed directly without any prior workup). The resulting HPLC traces were arranged into 3D waterfall plots (see Figure III.12) which provided a detailed visual account of the CF behavior in solution.

The dynamic HPLC plots demonstrate that all three C_{70} chlorides undergo photo-induced decomposition in toluene solution, both under dry nitrogen and air atmosphere. However, the rate of photodegradation is different for different $C_{70}Cl_n$ (n = 10, 8, 6). $C_{70}Cl_{10}$ practically disappears after the first 12 hours of light exposure (with the half-life of ca. 2-3 hours, both under N_2 and air). $C_{70}Cl_8$ and $C_{70}Cl_6$ show significantly slower rates of photodecomposition (half-life values are ca. 12 hours and 24 hours correspondingly, both under N_2 and air). These half-life values are similar to the ones found for toluene solutions of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ (5-6 hours) in our earlier work (see Section II.2.2). The decomposition of $C_{70}Cl_n$ solutions in toluene is accompanied by the growth of the peaks with small retention times, which may be indicative of the formation of C_{70} derivatives carrying tolyl groups (we observed the formation of tolyl-substituted derivatives during photodecomposition of $C_{60}Cl_6$/toluene; see Section II.2.2).

The behavior of $C_{70}Cl_n$ solutions in the dark is notably different from the behavior of $C_{60}Cl_n$ solutions (the latter were found to be unchanged even after approximately one month of storage in the absence of light, see Section II.2.2). We found that the concentrations of $C_{70}Cl_{10}$ and $C_{70}Cl_6$ decrease by 15-50% after ca. 2 weeks of storage in the absence of light. The rate of this process is slightly lower for the solutions that were

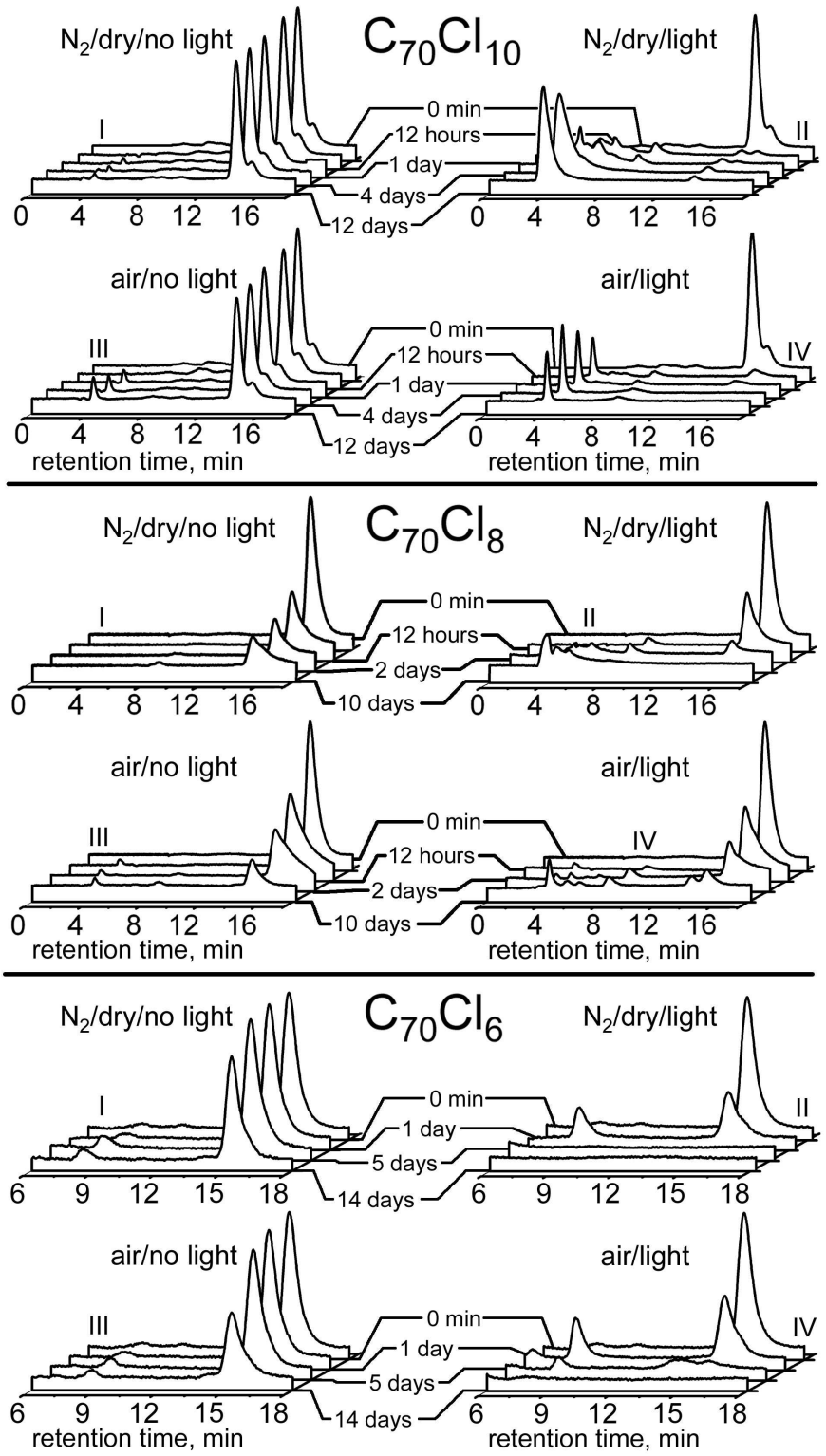

Figure III.12. Dynamic HPLC study of the stability of different $C_{70}Cl_{10}$ (top), $C_{70}Cl_8$ (middle), and $C_{70}Cl_6$ (bottom) in toluene solution under different conditions. The peak on the right side of the main peak of $C_{70}Cl_{10}$ is due to $C_{70}Cl_8$ impurity.

stored under inert and moisture-free atmosphere (as opposed to the solutions stored under air). The degradation of the $C_{70}Cl_8$ solution in the absence of light is much faster. The decrease in the $C_{70}Cl_8$ concentration is not accompanied by the growth of the peaks with small retention times (it is different from the behavior of both $C_{70}Cl_{10}$ and $C_{70}Cl_6$ under light and in the dark); rather, $C_{70}Cl_8$ is converted into an insoluble material. We did not have enough of this product to study it in detail; however, we suggest that these observations can be explained by the dimerization of $C_{70}Cl_8$ into an insoluble $[C_{70}Cl_8]_2$. The [2+2] cyclization required for such dimerization is thermally-prohibited and photo-allowed; however, the concentration of $C_{70}Cl_8$ decreases even when the corresponding solution is shielded from the light (this phenomenon requires further study). The rate of the dimerization should be proportional to the square of $C_{70}Cl_8$ concentration; this is consistent with our observations. The concentration of $C_{70}Cl_8$ drops by ca. 50% after the first 12 hours of storage; then the rate of this process decreased significantly, with some $C_{70}Cl_8$ remaining even after 10 days of storage (we can not completely rule out that a different compound with the same retention time could be formed). This suggests that the dimerization of $C_{70}Cl_8$ may lead to a complete (or at least considerable) dimerization when its solutions are concentrated during evaporation. However, we found that flash-evaporation of $C_{70}Cl_8$ solution under vacuum (solution is kept at room temperature) does not lead to any significant dimerization and does not cause an observable loss of $C_{70}Cl_8$ (this can be attributed to a relatively low solubility of $C_{70}Cl_8$ in toluene). Even after several cycles of flash-evaporation the solid $C_{70}Cl_8$ could still be redissolved (the HPLC analysis confirmed the persistence of this chloride throughout this treatment without any observable degradation). The solid dry samples of $C_{70}Cl_8$ (prepared by flash-evaporation of $C_{70}Cl_8$ solutions under vacuum) were unchanged even after several months of storage (in the absence of light in the freezer). This makes it possible to use this compound as a precursor for fullerene derivatization.

The conclusion can now be drawn that $C_{70}Cl_{10}$, $C_{70}Cl_8$, and $C_{70}Cl_6$ are light-sensitive in solution, which means that all procedures involving solutions of these materials should be done in the absence of light or with minimal light exposure (unless a particular reaction is catalyzed by light-irradiation). These data suggest that photosensitivity may be a general property of fullerene chlorides in solution. $C_{70}Cl_8$ chloride also displays a unique instability in solution even when shielded from light, which may be rationalized by its tendency to dimerize into $[C_{70}Cl_8]_2$.

III.3. Conclusions

Through the use of our analytical methodology we were able to discover several previously unknown facts about C_{70} chlorination and C_{70} chlorides. We found that C_{70} chlorination is chlorinated sequentially (same as C_{60}), so that chlorides with 6, 8, and 10 chlorine addends can be prepared and isolated in pure state. According to the experimental data, these compounds are produced as single isomers. It is notable and in earlier studies C_{70} was claimed to form a single chloride $C_{70}Cl_{10}$ during chlorination, although it is very likely that $C_{70}Cl_{10}$ reported in the earlier literature was heavily contaminated with other chlorides and unreacted C_{70}. Some experimental indications of $C_{70}Cl_2$ and/or $C_{70}Cl_4$ formation were observed; these compounds appear to be too reactive to be isolated in sufficiently large quantity to permit a more detailed study. The chlorination of $C_{70}Cl_{10}$ chloride was observed; however, this reaction appears to be very slow and poorly selective (multiple higher chlorinated products were observed). This is similar to the process of C_{60} chlorination, which selectively produces individual C_{60} chlorides (*o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$) up to the formation of $C_{60}Cl_6$; further process is also poorly selective.

The stability study of C_{70} chlorides ($C_{70}Cl_6$, $C_{70}Cl_8$, and $C_{70}Cl_{10}$) showed that all of these compounds are photosensitive (both under inert atmosphere and under air). This strongly suggests that photosensitivity may be a general property of fullerene chlorides regardless of the shape and size of the carbon cage.

These original findings provide further evidence for the power of our general methodology. Using the analytical methodology that we developed and validated for C_{60}

chlorides, we were able to carry out the first detailed study of C_{70} chlorination through the careful mapping of the reaction space. This study showed that lower C_{70} chlorides can be prepared and isolated; using this information it was straightforward to develop the procedures for the large-scale preparation of the corresponding compounds. These accomplishments, including the discovery of the photosensitivity of C_{70} chlorides, would be unlikely without the use of our approach to the study this novel class of chemical compounds.

III.4. Experimental Details

Reagents and Solvents: Benzene (Sigma-Aldrich, Na), toluene (Fischer Scientific, Na), chlorobenzene (Sigma-Aldrich, CaH_2), fluorobenzene (Sigma-Aldrich, CaH_2), and 1,2-dichlorobenzene (Sigma-Aldrich, CaH_2) were ACS Reagent Grade (vendor indicated in parenthesis) and were distilled from the indicated drying agent under purified N_2 atmosphere prior to use. $TiCl_4$ (Sigma-Aldrich) was stirred with copper powder for several days, then distilled under vacuum. HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), iodine monochloride (Sigma Aldrich, 99.998% trace metals basis), trans-2-[3-{4-tert-butylphenyl}-2-methyl-2-propenylidene]malononitrile (Fluka), chromium(iii) acetyl acetonate (Sigma Aldrich), and KBr (Sigma Aldrich, 99+ % FTIR grade) were used as received. All syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk techniques with vigorous stirring by a magnetic stirrer.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). Electronic spectra of dichloromethane and/or toluene solutions of chlorofullerenes were recorded using a Varian Cary 500 spectrophotometer. MALDI mass spectra were recorded on a Kompact MALDI IV (Kratos Analytical, Manchester, UK) time-of-flight mass-spectrometer in the linear mode. A 337 nm N_2 laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. CF samples and the trans-2-[3-{4-tert-butylphenyl}-2-methyl-2-propenyl-idene]malononitrile matrix material (DCTB) were

dissolved separately in toluene and were mixed in a 1:10 mol/mol sample/DCTB ratio assuming the sample contained only $C_{70}Cl_{10}$. A drop of each sample/DCTB solution was deposited on a stainless steel slide by using a capillary and dried under a strong stream of cool air from an airsprayer/brush in order to achieve a uniform sample surface. APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene). Thermogravimetry was performed using a TA Instruments TGA-2950 (platinum sample pans, *ca.* 5 mg sample size, 25–500 °C temperature range).

$C_{60}F_{48}$. 98+% pure $C_{60}F_{48}$ was prepared following the procedure described in ref. [19]. It was used without further purification.

Iodine Monochloride Handling and Transfer. In a typical experiment, the storage container with solid ICl (a storage tube equipped with a Teflon valve and a side arm) was warmed up, the resulted liquid then measured and transferred using an air-tight syringe (50, 250, and 500 μL syringes were used) equipped with a Teflon straw of sufficient volume to accommodate all of ICl (to avoid ICl contact with the stainless steel needle and a possible metallic contamination) under protective flow of purified N_2. DANGER! ICl is very volatile, extremely corrosive to metal and rubber, and moisture-sensitive.

CF Handling. All operations involving solutions of CFs were performed either in the dark (vessels containing CF solutions were wrapped with aluminum foil) or with minimal exposure to light (experimental operations were performed as quickly as possible under minimal illumination) unless reported otherwise. We recommend that prior to long-term storage the traces of aromatic solvents (toluene etc.) should be removed by dissolving a CF sample in HPLC grade CH_2Cl_2 and evaporating the resulting solution under vacuum (see Appendix A.I.1).

Preparation of $C_{70}Cl_{10}$. C_{70} solution (83.0 mg, 0.099 mmol) in dry, deoxygenated CB (45 mL) was mixed with ICl (1.25 mL, 4.00 g, 24.6 mmol, 250 eq.) under vigorous stirring at ca. 20 °C in the glass reactor of local design (see Figure II.19).[20] The

evaporation chamber of the apparatus was immersed in a room-temperature water bath. After 7 min the reactor was evacuated (the trap was pre-cooled with liquid nitrogen) and the volatiles were quickly removed. Longer reaction times (up to tens of minutes) are unlikely to cause a detectable decrease of the product purity. The product was washed off the walls of the evaporation chamber with a small volume of HPLC grade gave CH_2Cl_2 and transferred into a storage vessel, and then CH_2Cl_2 was removed under vacuum. This procedure 117.9 mg (0.0986 mmol, 99% yield) of 98% $C_{70}Cl_{10}$ (according to the integration of the HPLC trace collected with 100% toluene eluent at 5 mL/min flow rate).

Preparation of $C_{70}Cl_{10}$ (Sussex group[2] procedure). ICl (0.125 mL, 400 mg, 2.46 mmol, 180 eq.) was added to a vigorously stirred solution of C_{70} (11.6 mg, 0.0138 mmol) in C_6H_6 (36 mL). Then reaction mixture was heated to ca. 70 °C using preheated oil bath for 20 minutes. After heating the reaction mixture was set to cool down for 10 minutes. Then the reaction mixture was split into two parts (A and B). The part A was worked up using the original aqueous method of Sussex group. The part B of the reaction mixture was evaporated down using our evaporation apparatus. The products obtained by these two procedures were dissolved completely in toluene (no insoluble products were observed); the resulting solutions were analyzed by HPLC (100% toluene eluent at 5 mL/min flow rate). The HPLC analysis of products A and B showed only minor differences in the distribution of products. Both products contained $C_{70}Cl_8$ as the major constituent (ca. 70% according to HPLC trace integration; 80/20 toluene/heptane eluent was used) and ca. 20% of $C_{70}Cl_{10}$ (the other ca. 10% being composed of C_{70}).

Preparation of $C_{70}Cl_8$. ICl (73 μL, 233 mg, 1.44 mmol, 50 eq.) was added to a vigorously stirring solution of C_{70} (24.4 mg, 0.0290 mmol) in CB (15 mL) in evaporation apparatus. The evaporation chamber of the apparatus was immersed in a room-temperature water bath. After 90 sec the vacuum was applied and the volatiles were removed (the evaporation took ca. 2 min). The brown residue was kept under dynamic vacuum for additional 30 minutes. The crude product was dissolved in toluene (the

absence of the insoluble residue demonstrates that no significant amount of $[C_{70}Cl_8]_2$ was formed) and $C_{70}Cl_8$ was separated from C_{70} impurity by HPLC (100% toluene eluent, 5 mL/min). The yield of $C_{70}Cl_8$ is ca. 80% (based on HPLC trace integration of the crude product).

Preparation of $[C_{70}Cl_8]_2$. ICl (200 μL, 640 mg, 3.94 mmol, 50 eq.) was added to a vigorously stirring solution of C_{70} (71.1 mg, 0.0846 mmol) in CB (44 mL) in evaporation apparatus. The evaporation chamber of the apparatus was immersed in a room-temperature water bath. After 25 min the vacuum was applied and the volatiles were removed (the evaporation took ca. 8 min). The brown residue was washed off the walls of the reactor with ca. 3 mL of HPLC grade toluene. The resulting slurry was centrifuged and the brown supernatant was decanted. The insoluble residue was washed again with toluene and two more times with HPLC grade dichloromethane Centrifugation and decantation were used instead of filtration to avoid losses. The resulting light-brown solid was dried under vacuum to remove traces of solvents, giving 71.1 mg of $[C_{70}Cl_8]_2$ (0.0316 mmol, 75% yield).

Preparation of $C_{70}Cl_6$. ICl (12 μL, 36 mg, 0.22 mmol, 14 eq.) was added to a vigorously stirring solution of C_{70} (14.0 mg, 0.0167 mmol) in CB (11 mL) in evaporation apparatus. The evaporation chamber of the apparatus was immersed in a room-temperature water bath. After 1 hour and 30 minutes the vacuum was applied and the volatiles were removed (the evaporation took ca. 5 min). The brown residue was kept under dynamic vacuum for additional 30 minutes. The crude product was dissolved in 80/20 v/v toluene/heptane mixture and $C_{70}Cl_6$ was separated by HPLC (80/20 v/v toluene/heptane eluent, 5 mL/min). The yield of $C_{70}Cl_8$ is ca. 27% (based on HPLC trace integration of the crude product).

Dynamic HPLC study of C_{70} chlorination. A stock solution of C_{70} and $C_{60}F_{48}$ in PhCl (solution 1) was prepared by adding C_{70} (25.0 mg) and $C_{60}F_{48}$ (27.0 mg) to 10 mL of dry, deoxygenated PhCl. After ca. 24 hours of stirring the solution was filtered. A

stock solution of ICl in CH_2Cl_2 was prepared by dissolving ICl (312 μL, 1.00 g, or 0.62 mM) 10.0 mL of dry, deoxygenated CH_2Cl_2. The experiments were performed in the small-scale greaseless reactors of local design.

Experiment a. 2.0 mL of stock solution 1 were mixed with stock solution 2 (136 μL). Small samples of the reaction mixture were taken at regular time intervals, flash-evaporated under vacuum, dissolved in toluene and analyzed by HPLC (100% toluene eluent, 5 mL/min flow rate). Initial concentrations of the reagents: [C_{70}] = 2.3 mM; [ICl] = 42 mM (18 eq.).

Experiment b. 2.0 mL of stock solution 1 were mixed with ICl (15 μL). Small samples of the reaction mixture were taken at regular time intervals, flash-evaporated under vacuum, dissolved in toluene and analyzed by HPLC (100% toluene eluent, 5 mL/min flow rate). Initial concentrations of the reagents: [C_{70}] = 2.3 mM; [ICl] = 147 mM (64 eq.).

Experiment c. 2.0 mL of stock solution 1 were mixed with ICl (115 μL). Small samples of the reaction mixture were taken at regular time intervals, flash-evaporated under vacuum, dissolved in toluene and analyzed by HPLC (100% toluene eluent, 5 mL/min flow rate). Initial concentrations of the reagents: [C_{70}] = 2.3 mM; [ICl] = 1.13 M (490 eq.).

Photodegradation Experiments: $C_{70}Cl_{10}$/toluene. A sample of 2.7 mg of $C_{70}Cl_{10}$ (with ca. 15% $C_{70}Cl_8$ contamination) was dissolved in 30 mL of dried, deoxygenated toluene under dry N_2 atmosphere. This solution was split into four parts of approximately same volume. Parts **I** and **II** were transferred into Schlenk flasks (under N_2), when parts **III** and **IV** were transferred into 25 mL volumetric flasks with small-diameter necks and ground-glass stoppers (all reservoirs were made of colorless Pyrex glass). Solutions **III** and **IV** were aerated for 10 sec by bubbling air through them. The flasks containing solutions **I** and **III** were wrapped in aluminum foil to shield them from light, while the flasks with solutions **II** and **IV** were left in the fume hood exposed to a continuous

irradiation with ambient fluorescent light. All solutions were stored in the same place to ensure their equal temperature. All four flasks were tightly capped (using silicon grease) to avoid solvent loss and air contamination. Samples of the solutions **I**, **II**, **III**, and **IV** were taken (under protective flow of N_2 in case of samples **I** and **II**) regularly and analyzed immediately by HPLC (100% toluene eluent, flow 5 mL/min, 300 nm detection wavelength, Ø10 mm × 250 mm semipreparative Cosmosil BuckyPrep column, 500 μL injection volume).

Photodegradation Experiments: $C_{70}Cl_8$/toluene. A sample of ca. 2 mg of HPLC purified 95+% $C_{70}Cl_8$ was dissolved in 20 mL of dried, deoxygenated toluene under dry N_2 atmosphere. This solution was treated analogously to the solution of $C_{70}Cl_{10}$/toluene in the corresponding photodegradation experiment.

Photodegradation Experiments: $C_{70}Cl_6$/toluene. A sample of ca. 1 mg of HPLC purified 95+% $C_{70}Cl_6$ was dissolved in 14 mL of dried, deoxygenated toluene under dry N_2 atmosphere. This solution was treated analogously to the solution of $C_{70}Cl_{10}$/toluene in the corresponding photodegradation experiment.

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Chapter IV
Multiply-Chlorinated C_{60} and C_{70} Dimers

IV.1. Introduction

Fullerene dimers attract considerable attention both for their potential practical applications (i.e., for solar-cells),[1] as simpler models for studies of polymerized fullerene networks,[2,3] and for fundamental investigations of the chemical bonds in sterically hindered environments.[4-7] For example, a theoretical study of the conformers of $(R\text{-}C_{60}\text{-})_2$ dimers revealed an unexpected "lever" effect.[4] Several different types of fullerene dimers have been reported up to date: i) directly linked bare fullerene cages (*i.e.*, C_{60}=C_{60}[8,9] and C_{70}=C_{70}[9,10]); ii) bare fullerene cages linked through a bridge (a single atom,[11-14] two atoms,[12] or a larger chemical group[15-17]); iii) dimers of single-substituted fullerenes (directly linked with a single bond like $(R\text{-}C_{60})_2$[18,19] or through a bridge like $(H\text{-}C_{60})_2CR_2$[20]); iv) dimers of fullerene cages with multiple substituents ($(C_{60}F_{16})(C_{60})$,[21] $(C_{60}Cl_5)_2$,[22,23] $(C_{60}H_n)_2$[24]); v) dimeric complexes of charged fullerene cages.[22,25-31] Two excellent reviews on fullerene dimers are currently available;[32,33] however, the multiply substituted fullerene dimers are probably the least explored class of these compounds, with only a few examples described in the literature.[21,22,24] In this chapter we focus on this class of fullerene derivatives, specifically, on the multiply chlorinated dimers of C_{60} and C_{70} fullerenes, their synthesis and characterization.

IV.2. Results and Discussion

IV.2.1. Formation of Chlorinated Fullerene Dimers

A. Formation of $[C_{60}Cl_2]_2$. In Chapter II (Section II.2.4.A) we reported that C_{60} solution in chlorobenzene becomes black and murky due to formation of a fine black precipitate within the first 10-20 seconds after this solution is saturated with gaseous chlorine. We found that generally chlorination of C_{60} solution with Cl_2 in aromatic solvent (benzene, toluene, chlorobenzene, 1,2-dichlorobenzene) produces a complex mixture of soluble $C_{60}Cl_n$ species with maximum value of *n* of 20 or 22 (depending on the interpretation of the NI-APCI-MS data, see Sections II.2.1.G and II.2.4.A) and the black powdery product insoluble in most common organic solvents (it is very slightly soluble in carbon disulfide and 1,2-dichlorobenzene). The analysis of these black insoluble products by IR spectroscopy gave virtually identical results, leading us to the conclusion that the products have the same composition and structure (see Figure IV.1). The analysis of the black precipitate by thermal gravimetry shows the mass loss corresponding to two chlorine atoms per one fullerene cage (the rapid mass loss was observed between 200 and 280 °C at 5 °C/min heating rate, figure not shown; the IR spectrum of the TGA residue shows that it composed of C_{60}). The EI-MS study of this product shows that it decomposes giving rise to chlorine and C_{60} ions (no $C_{60}Cl_n$ ions were observed, which is consistent with a generally low stability of this species in MS conditions, see paper). The extremely low solubility of this product suggests that it is a dimer $[C_{60}Cl_2]_2$ (or possibly a polimer), since in this work we synthesized and isolated

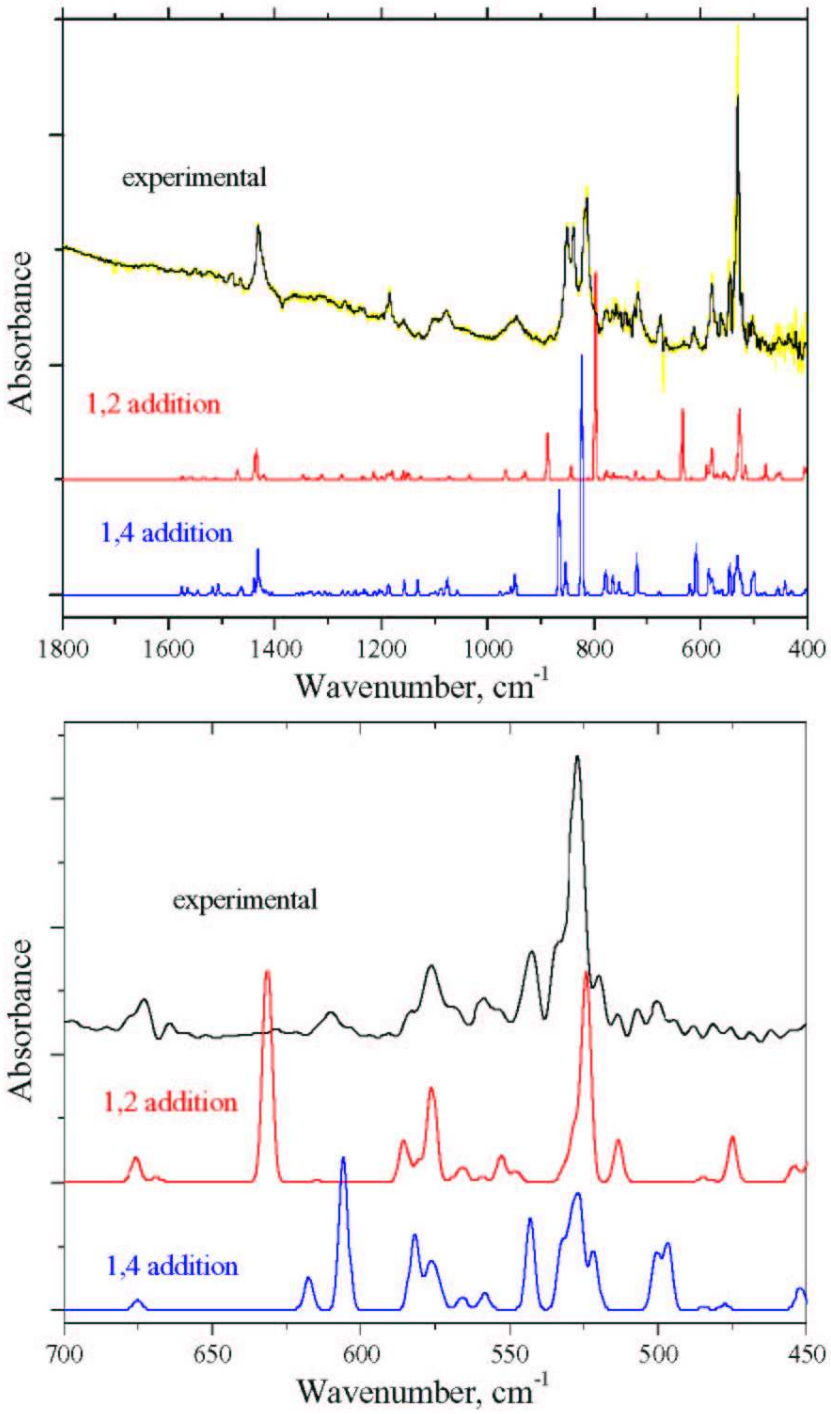

Figure IV.1. Experimental IR spectrum of $[C_{60}Cl_2]_2$ (top line) and calculated IR spectra of *o*-$C_{60}Cl_2$ and *p*-$C_{60}Cl_2$ monomeric isomers.

two isomers of monomeric $C_{60}Cl_2$ (featuring *ortho*- and *para*-addition patterns, see Chapter II) which are readily soluble in toluene and other organic solvents (like

dichloromethane). The IR spectrum of $[C_{60}Cl_2]_2$ is also consistent with this assumption due to its simplicity, see Figure IV.1. We also calculated IR spectra of two $C_{60}Cl_2$ isomers (*ortho*- and *para*-) that suggest that $[C_{60}Cl_2]_2$ is likely to feature chlorines occupying *para*-positions in the hexagon (see Figure IV.1).

We performed a series of similar experiments using different solvents (benzene and toluene) and different reaction conditions (different reaction temperature and C_{60} concentration, see Table IV.1). We found that using a higher concentration of C_{60} in the

Table IV.1. The dependence between the yield of $[C_{60}Cl_2]_2$ and the reaction conditions.

exp.	solvent	$[C_{60}]$, mg/mL	$T_{reaction}$, °C	yield of $[C_{60}Cl_2]_2$
A	benzene	1.7	+5	62
B	benzene	1.7	+20	31
C	benzene	1.7	reflux	0
D	toluene	2.8	+5	78
E	toluene	2.8	-18	88
F	toluene	2.8	-41	97
G	toluene	2.0	-41	55
H	toluene	1.0	-41	31
K	toluene	0.7	-41	9
L	toluene	0.5	-41	0
M	chlorobenzene	5.0	-41	40

starting solution and lower reaction temperature, a nearly quantitative yield of $[C_{60}Cl_2]_2$ can be achieved (97%, experiment F, see Table IV.1). The increase of the yield of the dimer with the increasing concentration of C_{60} (and corresponding concentration of the precursor species) is logical; the increase of the yield with the decreasing reaction temperature suggests that the $[C_{60}Cl_2]_2$ product is formed from an unstable precursor(s), possibly free-radical species. The lower temperature may increase the lifetime of the precursor(s), which makes dimer formation more favorable (leading to a higher yield of $[C_{60}Cl_2]_2$). It is also likely that a very low solubility of the product in toluene plays an important role in such a high yield of this product. For example, when we chlorinated a

more concentrated C_{60} solution in chlorobenzene at -41 °C, the yield of $[C_{60}Cl_2]_2$ was only 40% (Experiment M), which is considerably lower than the yield achieved at this temperature for the reaction in toluene solution (see Experiment D). We observed, however, that unlike benzene and toluene, chlorobenzene was capable to dissolve a low concentration of $[C_{60}Cl_2]_2$. This compound forms a very pale-yellow solution in chlorobenzene (and a slightly darker-colored solution in 1,2-dichlorobenzene); however, it does not show any signs of dissolving in benzene and toluene. Hence we can suggest that $[C_{60}Cl_2]_2$ may be more prone to further chlorination and dissociation when it is dissolved rather than in solid phase.

It is notable that chlorination of C_{70} under similar conditions (-15 °C, concentrated chlorobenzene solution, neat chlorine as a chlorinating agent) produces regular C_{70} chlorides ($C_{70}Cl_{10}$, $C_{70}Cl_8$, and $C_{70}Cl_6$, according to the HPLC analysis of the product); no insoluble compounds similar to $[C_{60}Cl_2]_2$ were detected.

B. Formation of $[C_{60}Cl_5]_2$. In our earlier work[23] chlorination of C_{60} solutions (in chlorobenzene and 1,2-dichlorobenzene) with low concentrations of ICl (10-20 equivalents) was shown to produce, along with soluble lower chlorides *o*-, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, and $C_{60}Cl_6$, an insoluble red product, which we identified as a dimer $[C_{60}Cl_5]_2$. This compound was also prepared by ampoule chlorination of C_{60} and structurally studied by single-crystal X-ray diffraction.[22] The use of a higher concentration of ICl (45 equivalents and more) leads to a rapid formation of $C_{60}Cl_6$, which is then slowly chlorinated further (no dimer is formed under these conditions). The yield of $[C_{60}Cl_5]_2$ is strongly dependant on the concentration of C_{60} in the initial solution. The chlorination of the diluted C_{60}/PhCl solution (0.5 mg/mL) does not yield any detectable $[C_{60}Cl_5]_2$, however, at 6 mg/mL of C_{60} in PhCl the yield of the dimer reaches ca. 30%.

C. Formation of $[C_{70}Cl_8]_2$. In Chapter III (Section III.2.1.E) we reported that chlorination of C_{70}/PhCl by lower concentrations of ICl (15-50 equivalents) leads to the formation of $C_{70}Cl_8$ (which is a readily soluble compound); this chloride rapidly

dimerizes in the reaction mixture to form a highly insoluble $[C_{70}Cl_8]_2$ (we suggested this formula in Section III.2.1.E based on the results of MALDI-MS, TG, and IR spectroscopy, see discussion and figures therein). Using this technique we prepared this dimer with a 75% yield. A flash-evaporation of the reaction mixture allows one to isolate monomeric $C_{70}Cl_8$ with a high yield (ca. 80%); the dimerization does not seem to take place in solid phase (at room temperature and at a normal pressure); in solution it appears to be strongly dependent on the concentration of $C_{70}Cl_8$ (see Section III.2.1.E for detailed discussion). The higher concentration of C_{70} leads to a rapid (within seconds) and practically quantitative conversion of the starting material into $C_{70}Cl_{10}$ which is relatively inert to the further chlorination.

The yield of $[C_{70}Cl_8]_2$ drops down sharply when lower concentration of C_{70} is used; we found that instead of dimerization $C_{70}Cl_8$ is chlorinated further into $C_{70}Cl_{10}$ under these conditions.

IV.2.2. Formation and Thermal Dissociation of $[C_{70}(CF_3)_8]_2$ Dimer

The possibility of dimerization of fullerenes with multiple substituents seems unlikely due to steric hindrance. However, the dimeric nature of $[C_{60}Cl_5]_2$ dimer was demonstrated unequivocally with single-crystal X-ray diffraction data.[22] Formation of $[C_{70}Cl_8]_2$ dimer raises more questions. A possible reason behind this behavior of $C_{70}Cl_8$ may lie in its structure, which features a "special" double bond. The addition of two chlorines to this double bond leads to the formation of $C_{70}Cl_{10}$, which may explain the unprecedented selectivity of the formation of this chloride (see Chapter III and discussion therein). According to the theoretical calculations, the majority of the HOMO electron density of $C_{70}Cl_8$ molecule resides on this double bond, which provides a likely explanation for its high reactivity. The high electron density concentrated on this double bond may facilitate the dimerization of two $C_{70}Cl_8$ molecules, however, the mode of the bonding between two $C_{70}Cl_8$ moieties in $[C_{70}Cl_8]_2$ is not currently clear. Unfortunately, our attempts at growing single-crystals of $[C_{70}Cl_8]_2$ so far were unsuccessful. Currently we are working in collaboration with Dr. Alexey Popov who employs high-level theoretical calculations in conjunction with experimental IR- and Raman-spectroscopy to answer the question of the nature of bonding between two $C_{70}Cl_8$ moieties in the dimer.

In order to overcome (at least partially) these complications and obtain some additional evidence for the possibility of $C_{70}Cl_8$ dimerization we studied a different derivative of C_{70} with the identical addition pattern – *C*$_s$-$C_{70}(CF_3)_8$ (see Figure III.8 for a Schlegel diagram showing the addition pattern). We found that this compound behaves strikingly similar to $C_{70}Cl_8$. In its regular state it is a dark-brown solid which is readily soluble in many organic solvents (i.e., toluene and dichloromethane). However, upon

standing under ambient light (under air) this compound precipitates from its highly concentrated solutions (in toluene) forming a bright-yellow solid which is practically insoluble (this experiment was performed by Dr. I. E. Kareev). Under mass-spectrometric analysis this product gave rise to the peak of $C_{70}(CF_3)_8$. Its IR spectrum was also strikingly similar to the spectrum of the initial $C_{70}(CF_3)_8$, see Figure IV.2. These observations strongly suggest that this compound has dimeric (or polymeric) nature; it is likely that it is a dimer $[C_{70}(CF_3)_8]_2$.

Due to a much higher thermal stability of trifluoromethylated derivatives (see Chapter VI) we annealed this insoluble product under high vacuum at 250 °C for a period of 30 minutes. The product changed color to dark-brown and became readily soluble in toluene; its analysis with HPLC indicated that it is identical to the original C_s-$C_{70}(CF_3)_8$. This behavior strongly supports the dimeric (or polymeric) nature $[C_{70}(CF_3)_8]_2$, especially in conjunction with the IR spectra of the starting monomeric material, dimer, and annealed dimer, see Figure IV.2. Currently Dr. Alexey Popov is working on the assignment of these changes in the IR spectra of the compounds using extensive theoretical calculations. We hope that using these data we may be able to propose a possible structure for $[C_{70}(CF_3)_8]_2$ (and $[C_{70}Cl_8]_2$).

Unfortunately, we are unable to perform a similar annealing experiment with $[C_{70}Cl_8]_2$ due to the loss of chlorine by chlorofullerenes at such temperatures. However, the dimerization of $C_{70}(CF_3)_8$ shows that this process is possible with CF_3 addends which are larger than chlorine atoms; hence, this provides an indirect support for our hypothesis of $C_{70}Cl_8$ dimerization.

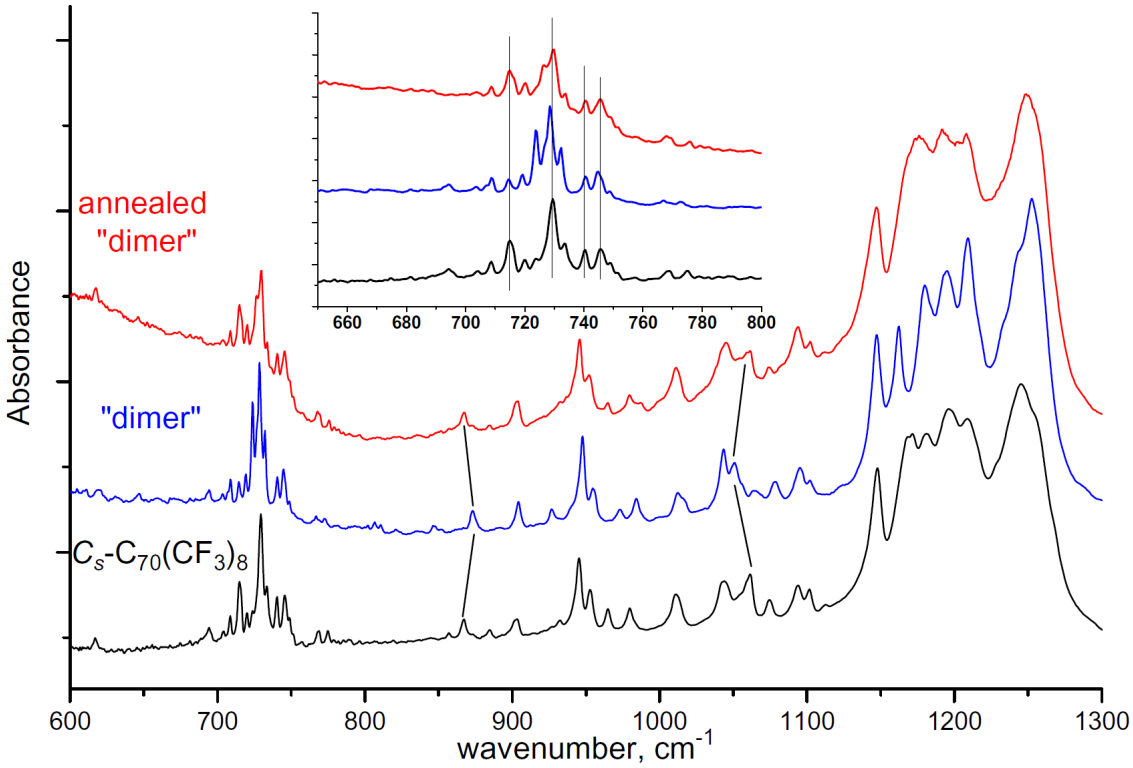

Figure IV.2. Experimental IR spectra of monomeric C_s-$C_{70}(CF_3)_8$, $[C_{70}(CF_3)_8]_2$, $[C_{70}(CF_3)_8]_2$ sample after annealing (from bottom to top) showing the changes in the IR signatures of the compounds.

IV.3. Conclusions

The results described in this chapter (and literature data, see Section III-1 and references therein) show that fullerenes are prone to the formation of dimers during radical addition reactions. These compounds display a generally poor solubility as opposed to the initial (or similar) monomeric molecules. Due to this low solubility they are challenging objects for structural studies, since the growth of the single-crystals is problematic (the single-crystals of $[C_{60}Cl_5]_2$ were produced using a high-temperature, high-pressure *in situ* method[22]); this also makes solution ^{13}C-NMR inapplicable. Currently we are attempting to use vibrational spectroscopy combined with extensive theoretical calculations in order to obtain more information on the structure of these species. An understanding of these compounds may provide a deep insight into the nature of bonding in exhohedral fullerene derivatives and steric requirements for the bond formation in such systems. Moreover, the proximity between two fullerene moieties in such dimers may find a possible application for development of solar cells or in other areas where delocalization of electron density between two (or more) fullerene cages may be of service.

The discovery of the formation of $[C_{60}Cl_2]_2$, $[C_{60}Cl_5]_2$, and $[C_{70}Cl_8]_2$ dimers also gives another striking demonstration of the power of our general methodology of investigation, rooted in the careful analysis of the products formed during various experiments. It is notable that we observed and reported a formation of $[C_{60}Cl_5]_2$ with *ca.* 30% yield in the reaction that was reported earlier and claimed to produce pure $C_{60}Cl_6$ with nearly quantitative yield.[23]

IV.4. Experimental Details

Reagents and Solvents: Benzene (Sigma-Aldrich, Na), toluene (Fischer Scientific, Na), chlorobenzene (Sigma-Aldrich, CaH_2), and 1,2-dichlorobenzene (Sigma-Aldrich, CaH_2) were ACS Reagent Grade (vendor indicated in parenthesis) and were distilled from the indicated drying agent under purified N_2 atmosphere prior to use. HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), iodine monochloride (Sigma Aldrich, 99.998% trace metals basis), trans-2-[3-{4-tert-butylphenyl}-2-methyl-2-propenylidene]malononitrile (Fluka), chromium(iii) acetyl acetonate (Sigma Aldrich), and KBr (Sigma Aldrich, 99+ % FTIR grade) were used as received. All syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk techniques with vigorous stirring by a magnetic stirrer.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). Electronic spectra of dichloromethane and/or toluene solutions of chlorofullerenes were recorded using a Varian Cary 500 spectrophotometer. MALDI mass spectra were recorded on a Kompact MALDI IV (Kratos Analytical, Manchester, UK) time-of-flight mass-spectrometer in the linear mode. A 337 nm N_2 laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. CF samples and the trans-2-[3-{4-tert-butylphenyl}-2-methyl-2-propenyl-idene]malononitrile matrix material (DCTB) were dissolved separately in toluene and were mixed in a 1:10 mol/mol sample/DCTB ratio

assuming the sample contained only $C_{70}Cl_{10}$. A drop of each sample/DCTB solution was deposited on a stainless steel slide by using a capillary and dried under a strong stream of cool air from an airsprayer/brush in order to achieve a uniform sample surface. APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene). Thermogravimetry was performed using a TA Instruments TGA-2950 (platinum sample pans, *ca.* 5 mg sample size, 25–500 °C temperature range).

Iodine Monochloride Handling and Transfer. In a typical experiment, the storage container with solid ICl (a storage tube equipped with a Teflon valve and a side arm) was warmed up, the resulted liquid then measured and transferred using an air-tight syringe (50, 250, and 500 μL syringes were used) equipped with a Teflon straw of sufficient volume to accommodate all of ICl (to avoid ICl contact with the stainless steel needle and a possible metallic contamination) under protective flow of purified N_2. DANGER! ICl is very volatile, extremely corrosive to metal and rubber, and moisture-sensitive.

CF Handling. All operations involving solutions of CFs were performed either in the dark (vessels containing CF solutions were wrapped with aluminum foil) or with minimal exposure to light (experimental operations were performed as quickly as possible under minimal illumination) unless reported otherwise. We recommend that prior to long-term storage the traces of aromatic solvents (toluene etc.) should be removed by dissolving a CF sample in HPLC grade CH_2Cl_2 and evaporating the resulting solution under vacuum.

$[C_{60}Cl_2]_2$ preparation. Experiments A, B, and C. C_{60} (200 mg) was mixed with 100 mL of dry, deoxygenated C_6H_6 and left stirring overnight. Then the solution was filtered and used for the following experiments. Experiment A. 30 mL of C_{60}/C_6H_6 solution were placed in a Schlenk flask, cooled down to +5 °C in benzene slush bath, and quickly saturated with chlorine (chlorine gas was quickly passed through the solution for *ca.* 1 minute). During the first 10-20 seconds of the reaction the color of the solution changed from dark-purple to black (due to the formation of a fine black precipitate) with yellow-

green hue. The solution was left standing at +5 °C for 2 hours to let the precipitate fall to the bottom and coagulate. The solution above the precipitate (clear yellow solution) was carefully decanted with a Paster pipette, and the precipitate was washed with toluene several times. After each wash the mixture was centrifuged, and the supernatant was decanted using a Paster pipette. During the last wash the mixture was placed in a tared vial, the supernatant was removed, the precipitate was dried under vacuum and weighted, yielding 35.0 mg of the product. If we take that C_{60} solubility in benzene is 1.7 mg/mL,[34] then the yield of the product with molecular formula $[C_{60}Cl_2]_2$ is 62%. Experiment B. 17 mL of C_{60}/C_6H_6 solution were treated as above, except the reaction was carried out at room temperature. Experiment C. Same as experiment B, but the reaction was carried out at reflux.

Experiments D, E, and F. C_{60} (120 mg) was mixed with 40 mL of dry, deoxygenated toluene and left stirring overnight. This solution was filtered and used for the following experiments. Experiment D. 10 mL of C_{60}/toluene solution was treated in a fashion of experiment A at +5 °C. Experiment E. Same as experiment D, but the reaction was carried out at -18 °C (using 1,2-dichlorobenzene slush bath). Experiment F. Same as experiment D, but the reaction was carried out at -41 °C (using chlorobenzene slush bath).

Experiments G, H, K, and L. The experiments were performed in the same fashion as experiment D. However, corresponding solutions were specially prepared using 15 mL of dry, deoxygenated toluene and a corresponding amount of C_{60} for each experiment.

Experiment M. A solution of 25 mg of C_{60} in 5 mL of dry, deoxygenated PhCl was prepared. Then it was chlorinated and the reaction mixture was worked up analogously to Experiment D.

C_{70} chlorination with Cl_2. C_{70} (21.2 mg) was dissolved in 5 mL of dry, deoxygenated PhCl. This solution was cooled to -15 °C using 1,2-dichlorobenzene slush bath and rapidly saturated with chlorine; after *ca*. 10 minutes the reaction mixture was

degassed under vacuum (the reaction vessel was kept in the same slush bath during that process). Then the reaction mixture was warmed up (no precipitate formation was visible) and the volatiles were removed under vacuum. The solid product was completely dissolved in toluene and analyzed by HPLC (using 100% toluene eluent at 5 mL/min); no insoluble product was observed.

$[C_{60}Cl_5]_2$ preparation. C_{60} (60 mg) were dissolved in 10 mL of dry, deoxygenated PhCl and left stirring overnight in the specially designed evaporation apparatus. Then 20 eq. of ICl (85 μL) were added to this solution, which was left stirring for 6 hours (at room temperature). Then the volatiles were quickly removed and the residue was washed three times with toluene (the insoluble product was centrifuged and the supernatant was carefully removed with a pipette) and then dried under vacuum. The yield of the product was *ca.* 30%.

Preparation of $[C_{70}Cl_8]_2$. ICl (200 μL, 640 mg, 3.94 mmol, 50 eq.) was added to a vigorously stirring solution of C_{70} (71.1 mg, 0.0846 mmol) in CB (44 mL) in evaporation apparatus. The evaporation chamber of the apparatus was immersed in a room-temperature water bath. After 25 min the vacuum was applied and the volatiles were removed (the evaporation took *ca.* 8 min). The brown residue was washed off the walls of the reactor with ca. 3 mL of HPLC grade toluene. The resulting slurry was centrifuged and the brown supernatant was decanted. The insoluble residue was washed again with toluene and two more times with HPLC grade dichloromethane Centrifugation and decantation were used instead of filtration to avoid losses. The resulting light-brown solid was dried under vacuum to remove traces of solvents, giving 71.1 mg of $[C_{70}Cl_8]_2$ (0.0316 mmol, 75% yield).

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Chapter V
Arylfullerenes and Their Preparation

V.1. Introduction

As we put it in the preceding chapters, a selective preparation of multiply substituted fullerenes is an extremely challenging task. Among different methods that may be used in order to accomplish this task, a selective substitution of fullerene derivatives that carry good leaving groups has a high promise. We have already explained earlier why chlorofullerenes are arguably the most suitable precursors for such reactions in the introduction to chapters II and III. However, the success of this strategy relies both on the availability of the compositionally and isomerically pure chlorofullerenes and on the efficient and selective methods for their derivatization. We have addressed and (at least partially) solved the first problem in chapters II and III; this chapter (and Chapter VI) is dedicated to the study and development of methods of chlorofullerene derivatization.

Several different methods have been reported in the literature for CF derivatization. The majority of work in this area was done by Sussex group: i) CF arylation via Friedel-Krafts aromatic substitution in the presence of Lewis acids;[1-4] ii) alkylation by methyl lithium;[5-7] iii) alkoxylation by alcohol-base mixture;[8] iv) allylation by allyltrimethylsilane in the presence of Lewis acid.[9] The Friedel-Crafts arylation was the first and most frequently studied method used for CF derivatization.[1,4,10] The arylation of $C_{60}Cl_6$ by several different aromatic substrates gave penta-arylated $C_{60}Ar_5Cl$ derivatives.[1,3] The yields of *ca.* 50-70% were reported for several $C_{60}Ar_5Cl$ products prepared from $C_{60}Cl_6$ starting material ($C_{60}Ph_5Cl$ – 68%;[1] $C_{60}(p\text{-}C_6H_4F)_5Cl$ – 63%; $C_{60}(p\text{-}C_6H_4OCH_3)_5Cl$ –

54%; $C_{60}(tolyl)_5Cl$ – 61%; $C_{60}(thienyl)_5Cl$ – 49%[3]); $C_{60}(C_6H_4\text{-}COOCH_3)_5Cl$ – 60%; $C_{60}(C_6H_4\text{-}CH(COOCH_3)_2)_5Cl$ – 50%[4]). However, in these reactions products with fewer ($C_{60}Ph_2$ and $C_{60}Ph_4$[3,11]) and larger number of substituents than six ($C_{60}Aryl_8$[3]) were also isolated. Phenylation of $C_{70}Cl_{10}$ was reported to yield $C_{70}Ph_8$ (with 66% yield).[2] $C_{70}Ph_2$, $C_{70}Ph_4$, and $C_{70}Ph_6$ were also reported to be produced under similar conditions.[2,12-14]

The fact, that arylated derivatives with fewer and larger number of substituents than the number of chlorines in the starting CF were prepared, may be interpreted in two different ways. It may indicate that the arylation of CFs is accompanied by side-processes (i.e. elimination of chlorines and/or addition of aryl groups to bare fullerene cage). Alternatively, it may be rationalized by the presence of CFs with fewer or larger number of chlorines. Earlier we found that $C_{60}Cl_6$ prepared by the same method as in ref. 3 contains CFs with more than 6 chlorines. In this work we also found that purity of $C_{70}Cl_{10}$ prepared by the method described by Sussex group is very low (ca. 20%) with the major product being $C_{70}Cl_8$ (ca. 70%, see Section III.2), which may explain the preferential formation of $C_{70}Ph_8$.[2] These problems make interpretations, and especially mechanistic considerations, unreliable.

It is also notable that a variety of the reaction conditions were used for CF arylation; $FeCl_3$ catalyst was used in the majority of the cases except for the preparation of $C_{60}(p\text{-}C_6H_4OCH_3)_5Cl$ ($TiCl_4$ was employed).[3] The aromatic substrate was always used in large excess; some substrates (benzene, fluorobenzene, toluene, and thiophene) were used as the reaction medium and solvent.[1,3] More valuable substrates were reacted with $C_{60}Cl_6$ in solution of dichloromethane (*tert*-butylbenzene, phenyltrimethylsilane, and anisole[3]) or nitrobenzene ($C_6H_5\text{-}COOCH_3$ and $C_6H_5\text{-}CH(COOCH_3)_2$[4]). In some cases, the formation of $C_{60}Ar_5Cl$ derivatives was performed at an elevated temperature (benzene, fluorobenzene, thiophene;[1,3] $C_6H_5\text{-}COOCH_3$ and $C_6H_5\text{-}CH(COOCH_3)_2$[4]). In case of $C_{60}Cl_6$ phenylation it was stated that heating is required, otherwise the reaction "take[s] many weeks".[3] For other substrates the reaction was performed at room temperature for

2-24 hours (toluene, anisole, *tert*-butylbenzene, phenyltrimethylsilane).[3] Despite the multitude of various conditions used for CF arylation by different aromatic compounds, no study that compares the effect of different reaction conditions on the yield and purity of the product has been published up to date. This makes the development of the arylation procedure for a novel CF and/or aromatic substrate more challenging and labor-consuming. Hence, we decided to study the arylation of fullerenes in detail, starting with reactivity of bare-cage C_{60} and C_{70} and proceeding to CFs. In this work we applied the techniques of dynamic HPLC monitoring and soft-ionization MS methods (ESI- and APCI-MS).

V.2. Results and Discussion

V.2.1. Selective Arylation of Chlorofullerenes

A. Arylation of Bare-Cage Fullerenes. According to the early work of Olah and co-workers,[15] C_{60} is phenylated in the presence of strong Lewis acids ($AlCl_3$ and $FeCl_3$) in benzene medium, producing mixed phenylated-protonated derivatives ($C_{60}Ph_xH_y$). No reaction was observed in the presence of weaker Lewis acids ($TiCl_4$ and $SnCl_4$).[16] The only work describing the behavior of C_{70} under similar conditions stated that no evidence of C_{70} phenylation was observed when $AlCl_3$ catalyst was used (that work was done with mixed samples of C_{60} and C_{70}).[15]

In agreement with the literature data, we found that C_{60} solution in benzene is rapidly converted into mixtures of $C_{60}Ph_xH_y$ derivatives in the presence of strong Lewis acids like $AlCl_3$ and $FeCl_3$. The maximum values of *x* and *y* observed by EI- and ESI-MS are equal to 15; the HPLC analysis of the reaction products showed them to be complex mixtures (figures not shown). A weak Lewis acid $TiCl_4$ did not catalyze this process leaving C_{60} unchanged (we performed these reactions in C_6H_6 medium). Contrary to the literature data,[15] we found that C_{70} undergoes a rapid phenylation in the presence of $FeCl_3$ in C_6H_6 medium, producing a mixture of C_{70} derivatives with 10 and 9 phenyl groups both at room temperature and under reflux, see Figure V.1. C_{70} was unchanged when $TiCl_4$ catalyst was used. This shows for the first time that both C_{60} and C_{70} possess a similar reactivity towards phenylation in benzene medium in the presence of different Lewis acids. Both of these fullerenes are easily phenylated in the presence of strong Lewis acids ($FeCl_3$), but weak Lewis acids ($TiCl_4$) are not sufficiently active to catalyze

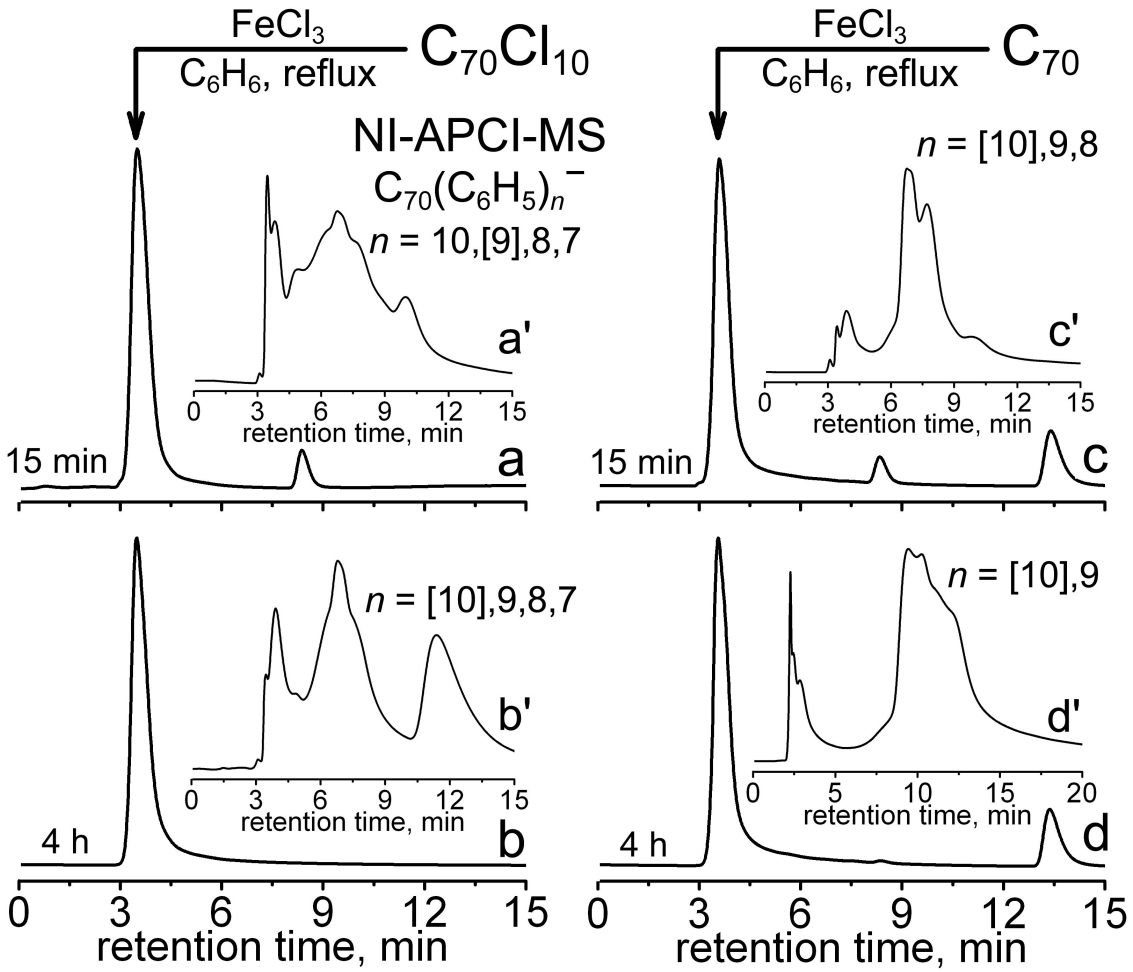

Figure V.1. Phenylation of $C_{70}Cl_{10}$ (left column) and C_{70} (right column) in refluxing dry benzene in the presence of $FeCl_3$. The upper row figures correspond to the products formed after 15 minutes of reaction; the bottom row figures correspond to the products formed after 4 hours. HPLC traces a-d were acquired using 100% toluene eluent at 5 mL/min flow rate. HPLC traces a', b', and c' were acquired using 50/50 v/v toluene/heptane mixture as an eluent at 5 mL/min flow rate. HPLC trace d' was acquired using 30/70 v/v toluene/heptane mixture as an eluent at 7 mL/min flow rate. The different values of *n* correspond to the peaks observed in the NI-APCI-MS analysis of the corresponding products; the values in [square brackets] designate the most intense peak. The NI-APCI-MS figures are not shown except for the sample a, see Figure V.2.

this process. The HPLC analysis of the products of the arylation of the bare-cage fullerenes indicate that this process is poorly selective (mixtures of products were found to be produced, see Figure V.1); hence, it is unlikely to be a viable approach to the high-yield preparation of pure arylated fullerenes. Arylation of bare-cage fullerenes by means

of metalloorganic compounds provides an effective alternative for Friedel-Crafts arylation.[17]

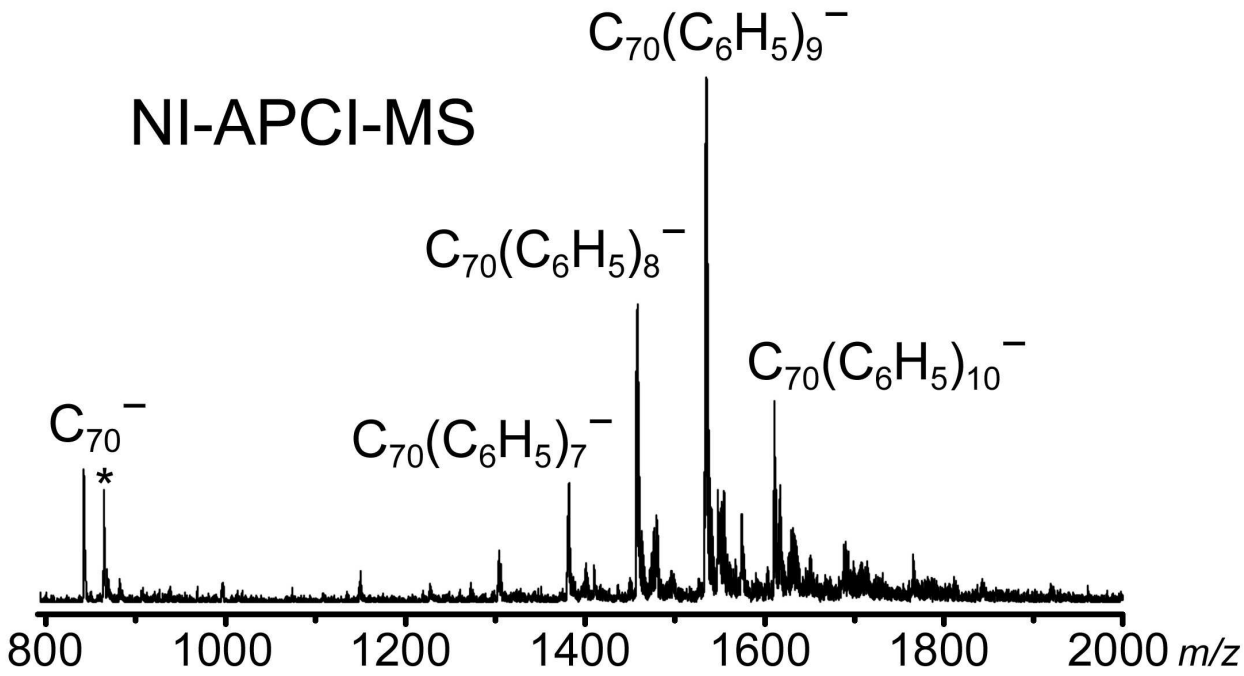

Figure V.2. NI-APCI-MS of the sample a (see Figure IV-1). The peak designated with an asterisk in due to a non-fullerene impurity.

B. Arylation of $C_{60}Cl_6$. The precise reproduction of the original conditions used for $C_{60}Ph_5Cl$ preparation[1] is complicated due to a lack of the accurate description of the procedure (the concentrations of $C_{60}Cl_6$ and $FeCl_3$ catalyst and the reaction temperature have not been reported[1]). However, we tried to follow the published description[1] as close as possible. We found that phenylation of $C_{60}Cl_6$ in benzene solution in the presence of $FeCl_3$ catalyst is a fast process both at room temperature and at 70 °C (see Figure V.3A and V.3B correspondingly). In both cases all starting material was completely consumed after 20 minutes of the reaction, and $C_{60}Ph_5Cl$ was formed as the major product (with 50% and 60% yield correspondingly, these data are obtained by integration of the HPLC traces acquired using 50/50 v/v toluene/heptane eluent, see Figures V.3A' and V.3B'; the 1H-NMR spectrum of the HPLC isolated product matched the literature data[1]). This is

contradictory to the statement of Sussex group, which indicated that at room temperature this reaction is very slow (takes "many weeks").[3]

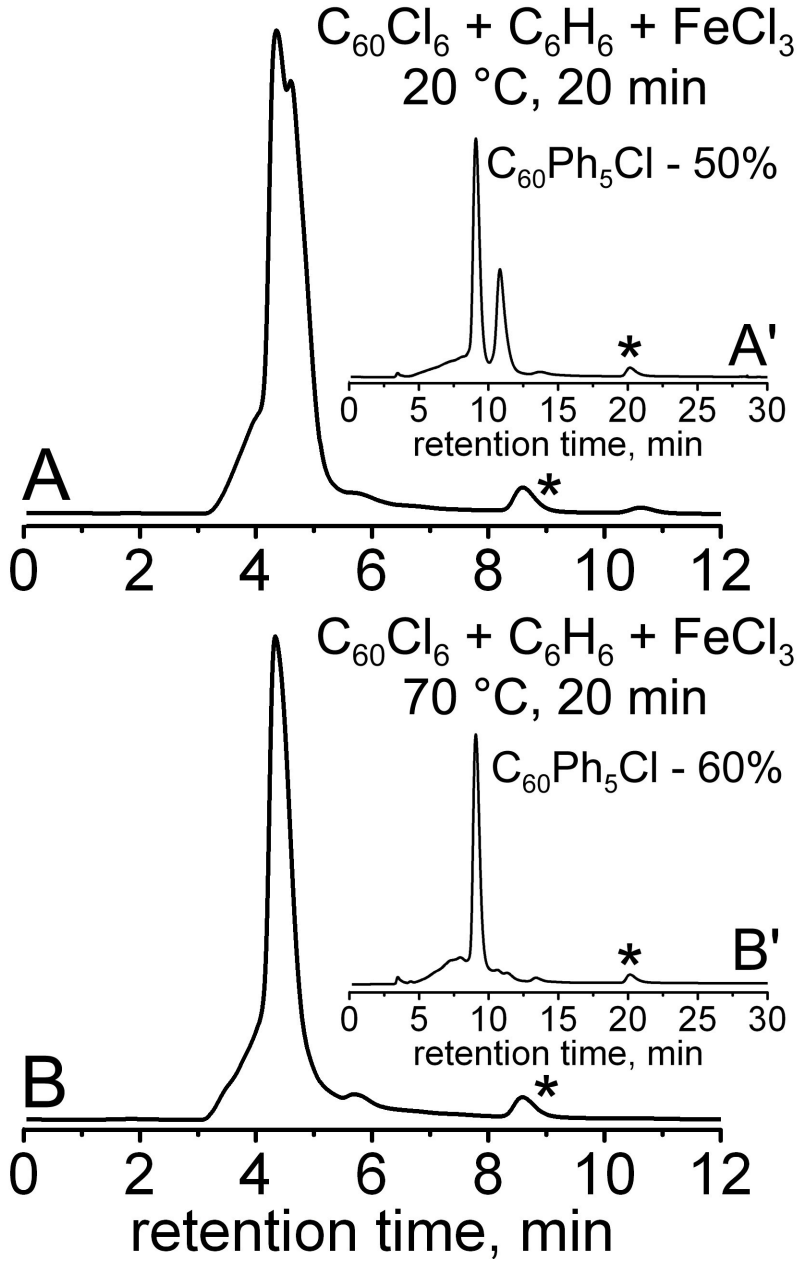

Figure V.3. Phenylation of $C_{60}Cl_6$ in benzene solution in the presence of $FeCl_3$ catalyst. HPLC traces designated by A and B were acquired using 100% toluene eluent at 5 mL/min flow rate. HPLC traces designated by A' and B' were acquired using 50/50 v/v toluene/heptane eluent at 5 mL/min flow rate. The peaks marked with asterisks are due to C_{60} (which was present as ca. 3% impurity in the starting $C_{60}Cl_6$). 90% pure starting material $C_{60}Cl_6$ was used (according to the HPLC trace integration).

In the next series of experiments we studied CF arylation using dynamic HPLC monitoring, see Figure V.4. However, the internal standard normalization (see Section II.2.4.A) was not used in these experiments due to a difficulty of finding a suitable standard. Instead, a different approach of full integral normalization was employed.

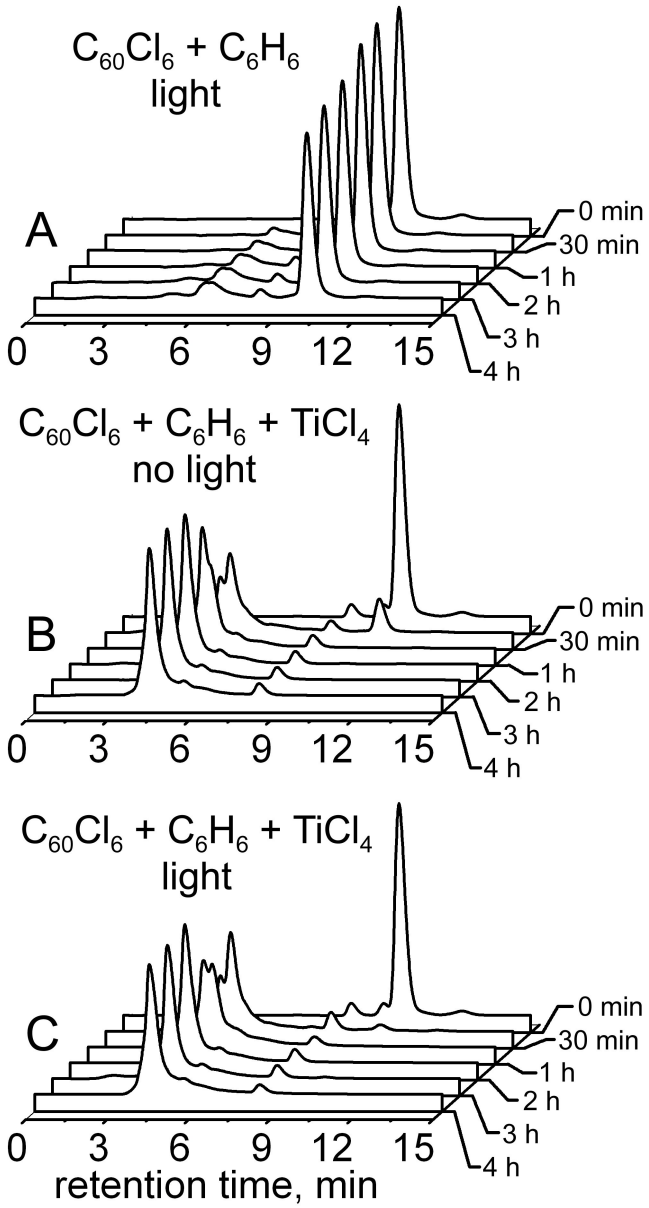

Figure V.4. Dynamic HPLC monitoring of $C_{60}Cl_6$ phenylation in benzene solution in the presence of $TiCl_4$ catalyst. The reaction mixtures A, B, and C were kept at the same distance from the light source to ensure that their temperatures are the same. The flask containing reaction mixture B was shielded from light by aluminum foil wrap.

The individual HPLC traces that comprise a dynamic waterfall plot were normalized so that their full integrals are the same. This approach is limited since it assumes that all fullerene products are representatively analyzed by HPLC (all of them are soluble) and that all of them give the same detector response (in our case, their extinction coefficients at 300 nm are the same). The deviations from these assumptions will introduce the distortions into the relative vertical intensity of the individual traces of the dynamic HPLC plots; however, for the representative purposes these deviations are unlikely to be important.

Dynamic HPLC monitoring of $C_{60}Cl_6$ phenylation in benzene solution in the presence of $TiCl_4$ catalyst showed that the use of weaker Lewis acid leads to somewhat slower reaction rate (see Figure V.4). We found that it takes ca. 2 hours for a complete conversion of the starting material into $C_{60}Ph_5Cl$ (which is a major product of this reaction). This reaction is slightly faster when it is exposed to the visible light (two 60-watt incandescent light bulbs were used to irradiate the reaction mixture C, see Figure V.4C); however, this difference is very slight. In both cases the yield of $C_{60}Ph_5Cl$ is ca. 50% (these yields are calculated by the integration of the HPLC plots of the reaction mixtures samples taken after 4 hours, acquired with 50/50 v/v toluene/heptane eluent mixture). The phenylation is very slow in the absence of Lewis acid (see Figure V.4A), with only slight decrease in the concentration of $C_{60}Cl_6$ after 4 hours (the irradiation by visible light was used; earlier we showed that $C_{60}Cl_6$ is stable in the solution of aromatics in the dark, see Section II.2.2). These results demonstrate that catalysis by Lewis acids in required for $C_{60}Cl_6$ phenylation; however, the difference between strong ($FeCl_3$) and weak ($TiCl_4$) Lewis acids is not very significant (the yields of the major product $C_{60}Ph_5Cl$ are similar in both cases).

The fluorophenylation of $C_{60}Cl_6$ was described in the literature as being very similar to the phenylation.[3] In both cases the same synthetic procedure that utilized a heating of $C_{60}Cl_6$ solution in the aromatic substrate (benzene or fluorobenzene) in the presence of

$FeCl_3$ catalyst for 20 minutes was used.[3] The penta-substituted $C_{60}Ar_5Cl$ products were reported in both cases with similar yields (68% and 61% for phenylation and fluorophenylation correspondingly; only *para*-substituted products were observed for in $C_{60}Cl_6$ fluorophenylation).[3] The dynamic HPLC plot of $TiCl_4$-catalyzed reaction shows a gradual substitution of chlorines in $C_{60}Cl_6$, which produces $C_{60}(p\text{-}C_6H_4F)_5Cl$ with ca. 70% yield after 2 days at room temperature (according to HPLC trace integration, see Figure V.5A). $FeCl_3$–catalyzed process, on the other hand, causes a very rapid (minutes)

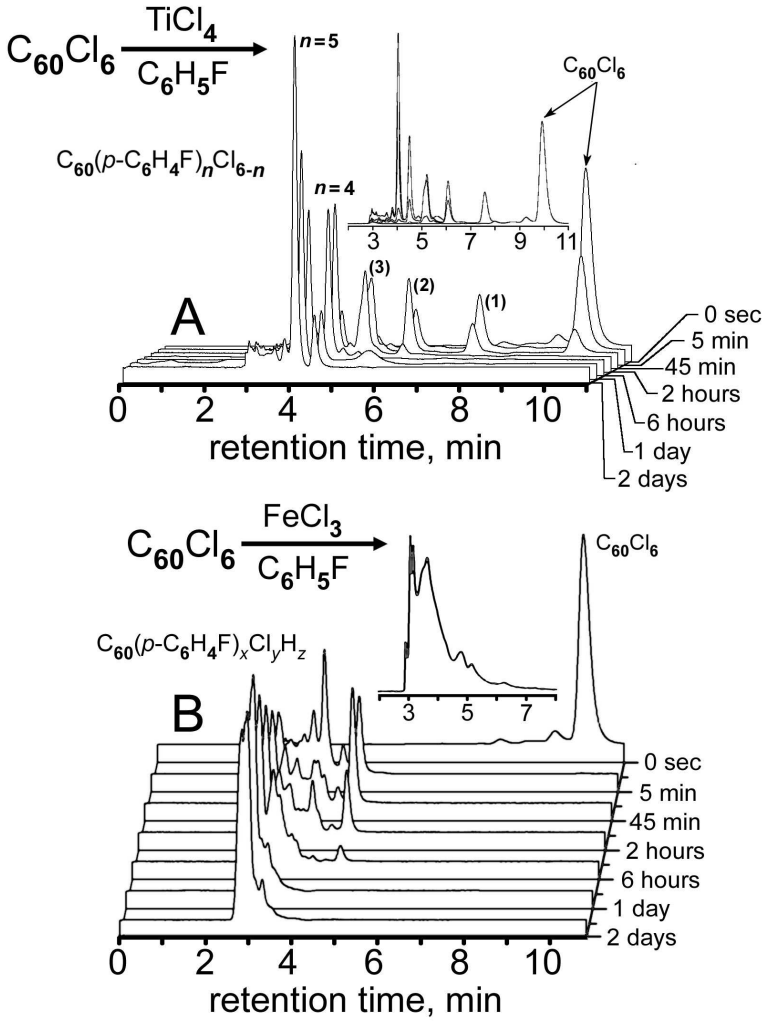

Figure V.5. Inert-atmosphere dynamic HPLC study of $C_{60}Cl_6$ arylation catalyzed by $TiCl_4$ (A) and $FeCl_3$ (B). The inserts are the expansions of the projections of the 3D plots on the retention time – vertical intensity coordinate plane. The reaction times are designated on the right side of the figure. The *n* numbers given without parenthesis were determined by FAB-MS of the isolated HPLC fractions. The *n* numbers given in parenthesis are hypothetical (plot A).

and poorly selective arylation beyond $C_{60}(p\text{-}C_6H_4F)_5Cl$ (see Figure IV-5B). The fractions designated as $C_{60}(p\text{-}C_6H_4F)_4Cl_2$ and $C_{60}(p\text{-}C_6H_4F)_5Cl$ on the plot A were isolated by HPLC and characterized by FAB-MS. $C_{60}(p\text{-}C_6H_4F)_5Cl$ was also studied by $\{^1H\}$-^{19}F-NMR, which confirmed its C_s-symmetry, consistent with the conservation of the addition pattern of $C_{60}Cl_6$ during arylation (see Figure V.6). These results are surprising since the reactivity of fluorobenzene towards electrophiles is usually lower than that of benzene. It is not clear how Sussex group was able to prepare $C_{60}(p\text{-}C_6H_4F)_5Cl$ with 61% yield using $FeCl_3$ as a catalyst.[3] We also found that fluorophenylated fullerenes are strongly air-sensitive, so a specially developed inert-atmosphere HPLC technique was used for the purification and the analysis of these products (see section on stability and experimental section).

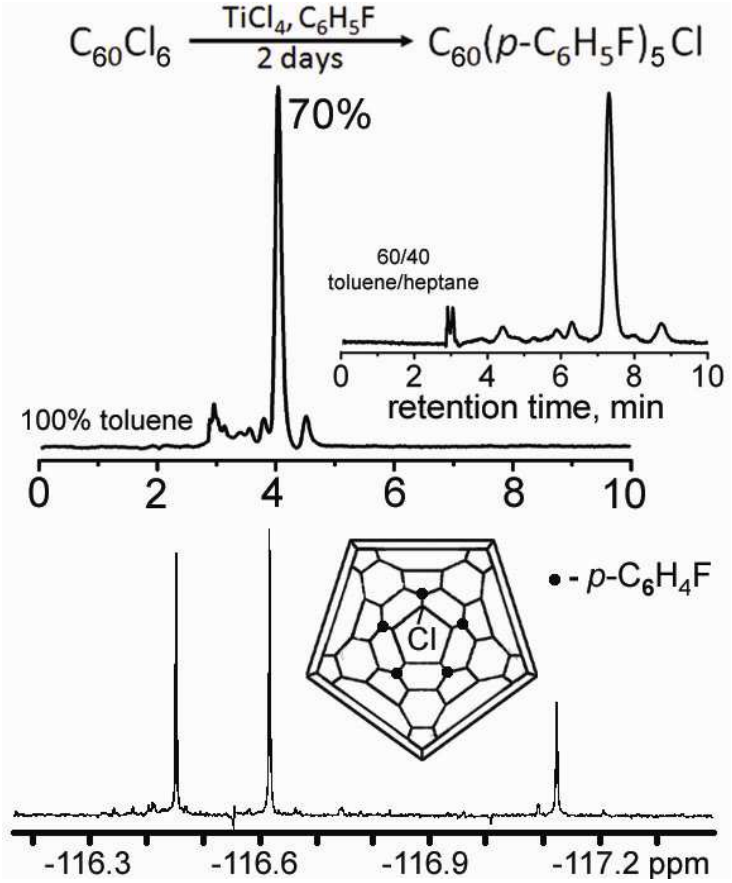

Figure V.6. The synthesis, HPLC analysis and $\{^1H\}$-^{19}F-NMR spectrum of $C_{60}(p\text{-}C_6H_4F)_5Cl$.

These results demonstrate that the optimal conditions for arylation of $C_{60}Cl_6$ are strongly dependent of the nature of the aromatic substrate. The correct choice of the reaction conditions and especially of the Lewis acid catalyst has a very strong impact on the yield and purity of the products.

C. Fluorophenylation of $C_{60}Cl_{10}$. The fluorophenylation of the 95+% $C_{60}Cl_{10}$ was carried out in solution of fluorobenzene in the presence of $TiCl_4$ catalyst (figure not shown). The dynamic HPLC study showed that although the process of fluorophenylation proceeds smoothly, the product is comprised of at least three different derivatives present in the similar concentration. It is likely that the presence of several closely spaced chlorine substituents in the structure of the starting material makes their complete substitution difficult.

D. Arylation of $C_{70}Cl_n$. We repeated the phenylation of $C_{70}Cl_{10}$, following the procedure of Sussex group.[2] According to their paper $C_{70}Ph_8$ is formed with 66% yield after 15 minutes of reflux of the benzene solution of $C_{70}Cl_{10}$ in the presence of $FeCl_3$ (the authors claimed that two chlorines were eliminated during the course of the reaction).[2] In our hands this procedure yielded a complex mixture of at least seven different C_{70} derivatives present in similar quantities (see Figure V.1a). NI-APCI-MS of this mixture showed that C_{70} species with 7, 8, 9, and 10 phenyl groups were present (the most intense ion corresponded to $C_{70}Ph_9^-$, see Figure V.2). The longer reaction time (4 hours of reflux) led to changes in the product composition (see Figure V.1b). The most intense peak observed in the NI-APCI mass spectrum of this product is $C_{70}Ph_{10}^-$, which indicates that further phenylation of C_{70} cage was achieved. However, it was also composed of at least 7 different components present in similar quantities. In view of these results we suggest that the sample of $C_{70}Cl_{10}$ used in the original work[2] of Sussex group was contaminated with $C_{70}Cl_8$ (see Section III.2.1).

The dynamic HPLC study of $C_{70}Cl_{10}$ phenylation in the presence of $TiCl_4$ (see Figure V.7) shows that the use of this weaker Lewis acid leads to slower phenylation

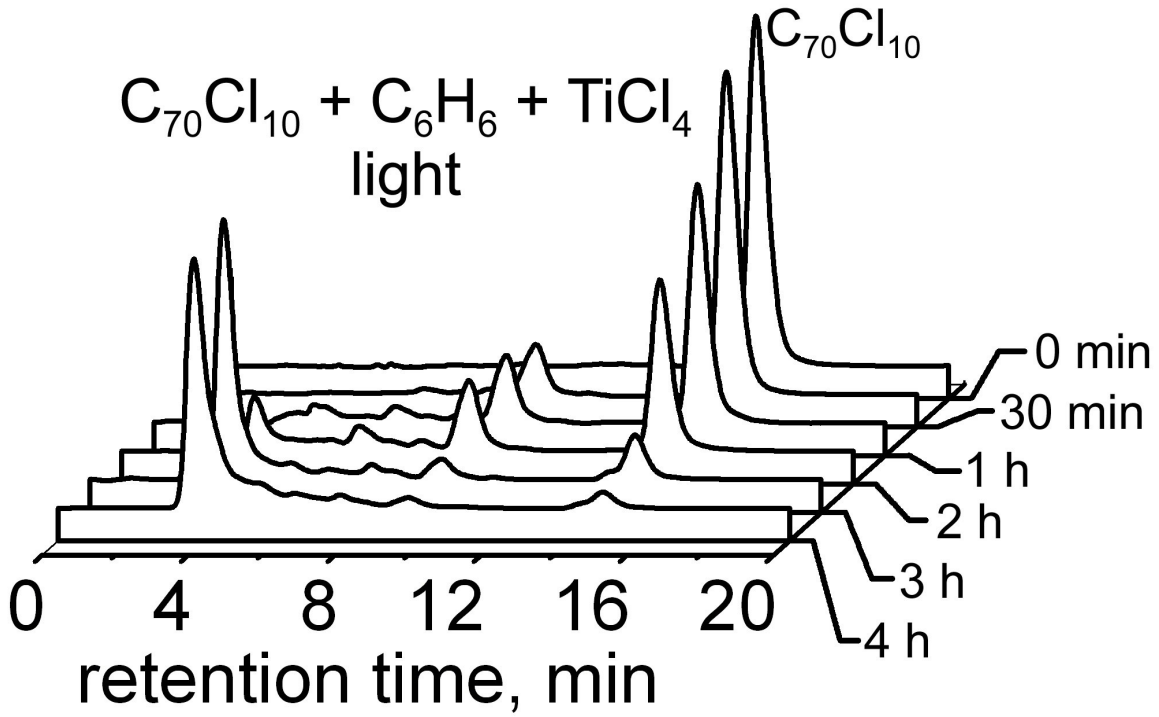

Figure V.7. Dynamic HPLC monitoring of $C_{70}Cl_{10}$ phenylation in benzene solution in the presence of $TiCl_4$ catalyst.

(as compared to the reaction catalyzed by $FeCl_3$, see Figure V.1). However, this reaction also produces mixtures of the products (with 9 and 10 phenyl substituents as determined by NI- and PI-APCI-MS, figures not shown; see Figure V.8 for the expansions of the corresponding HPLC traces). The fluorophenylation of $C_{70}Cl_{10}$ was found to proceed in a similar fashion, producing mixtures of C_{70} derivatives with 8, 9, and 10 fluorophenyl groups ($TiCl_4$ catalyst was used, see Figure V.9). The poor selectivity of $C_{70}Cl_{10}$ arylation is likely to be caused by the high steric hindrance between two chlorines that occupy *ortho*-positions (it is notable that $C_{70}Ph_{10}$ was prepared by direct phenylation of C_{70} under harsh conditions[2] rather than phenylation of $C_{70}Cl_{10}$). On the other hand, the fluorophenylation of $C_{70}Cl_8$ was found to proceed smoothly, leading to the formation of $C_{70}(p\text{-}C_6H_4F)_8$ with ca. 75% yield ($\{^1H\}$-^{19}F-NMR of this compound is consistent with the conservation of the addition pattern of $C_{70}Cl_8$ during arylation, see Figure V.10). $C_{70}Cl_8$ structure contains only chlorine substituents in *para*-positions relative to each

other; the lack of steric hindrance is likely to be the reason behind the high yield of the corresponding arylated product.

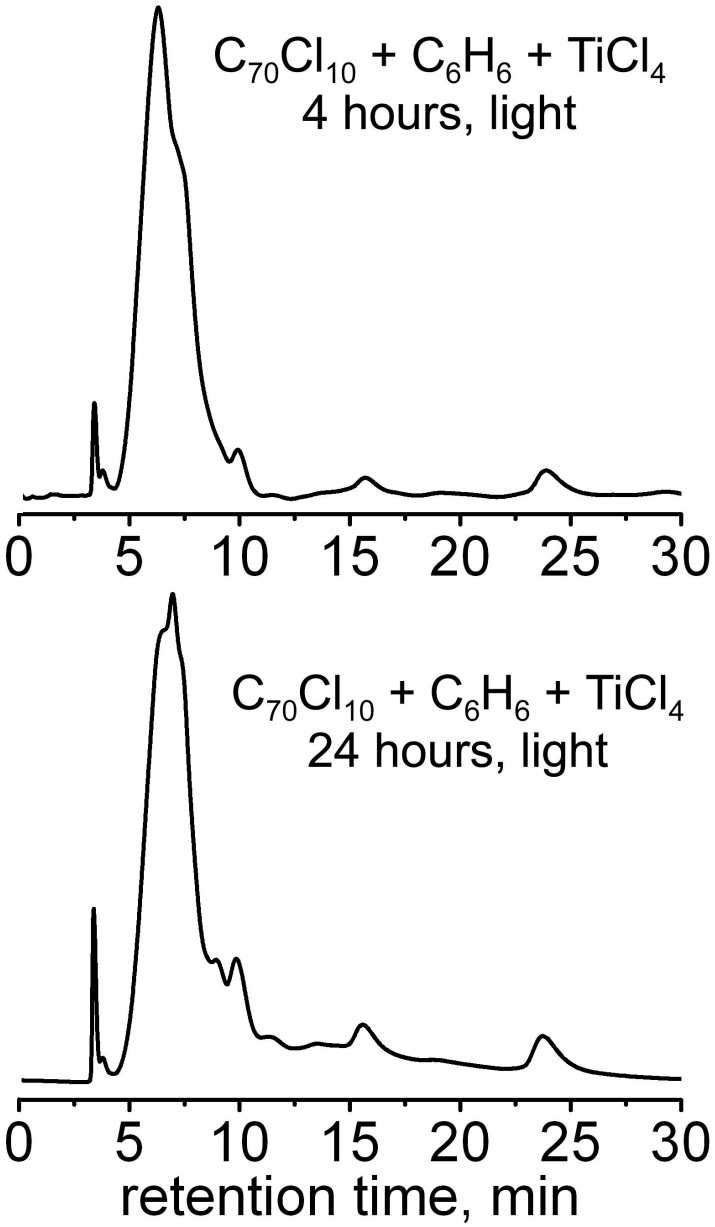

Figure V.8. The HPLC analysis of the products of $C_{70}Cl_{10}$ phenylation in the presence of $TiCl_4$ catalyst. The traces were acquired using 50/50 v/v toluene/heptane eluent with 5 mL/min flow rate.

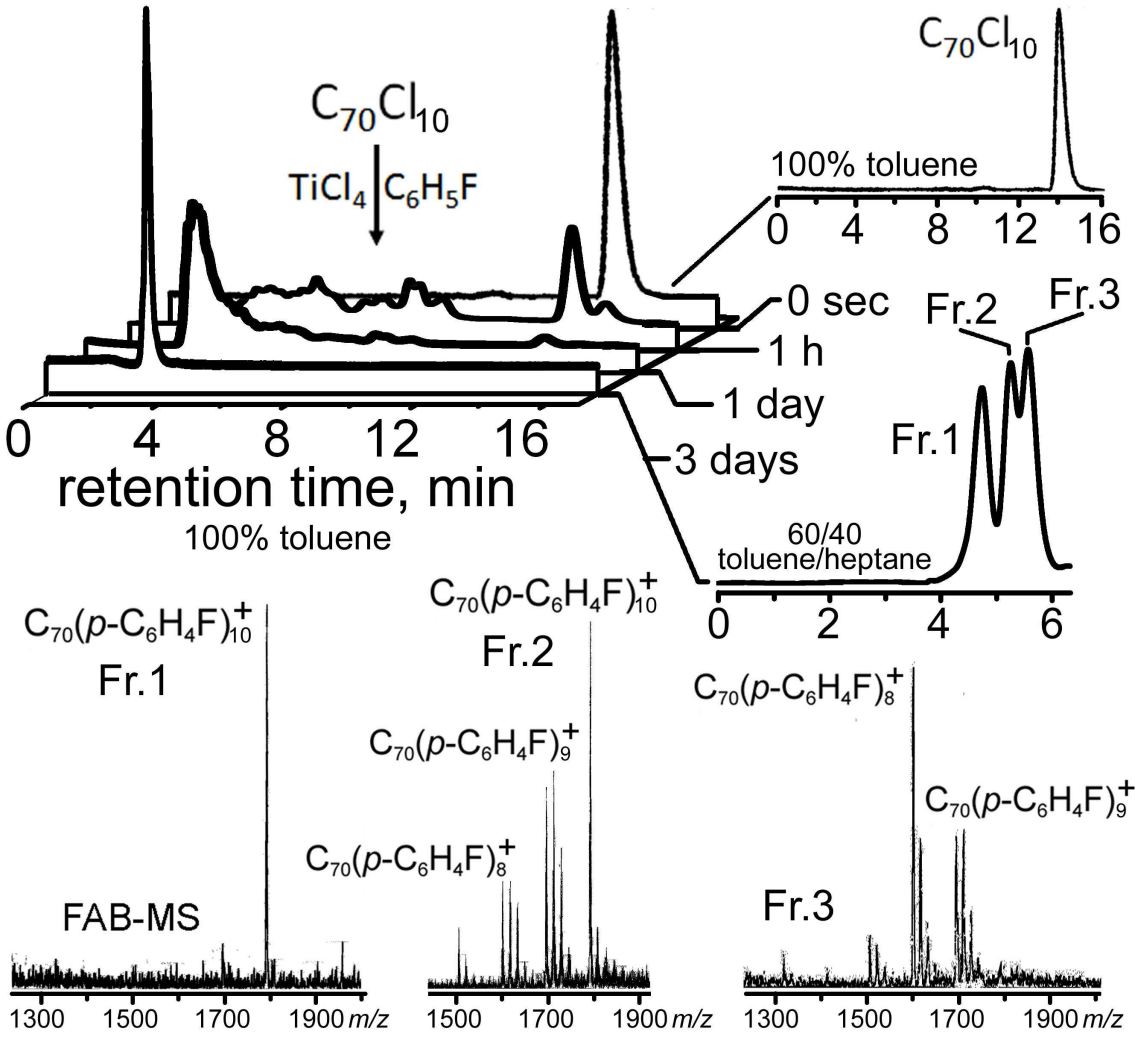

Figure V.9. Dynamic HPLC plot of $C_{70}Cl_{10}$ fluorophenylation. The HPLC trace of the starting $C_{70}Cl_{10}$ is shown in the top right corner of the figure. The crude reaction mixture after 3 days of the reaction was separated by HPLC and analyzed by FAB-MS, which are shown in the bottom part of the figure.

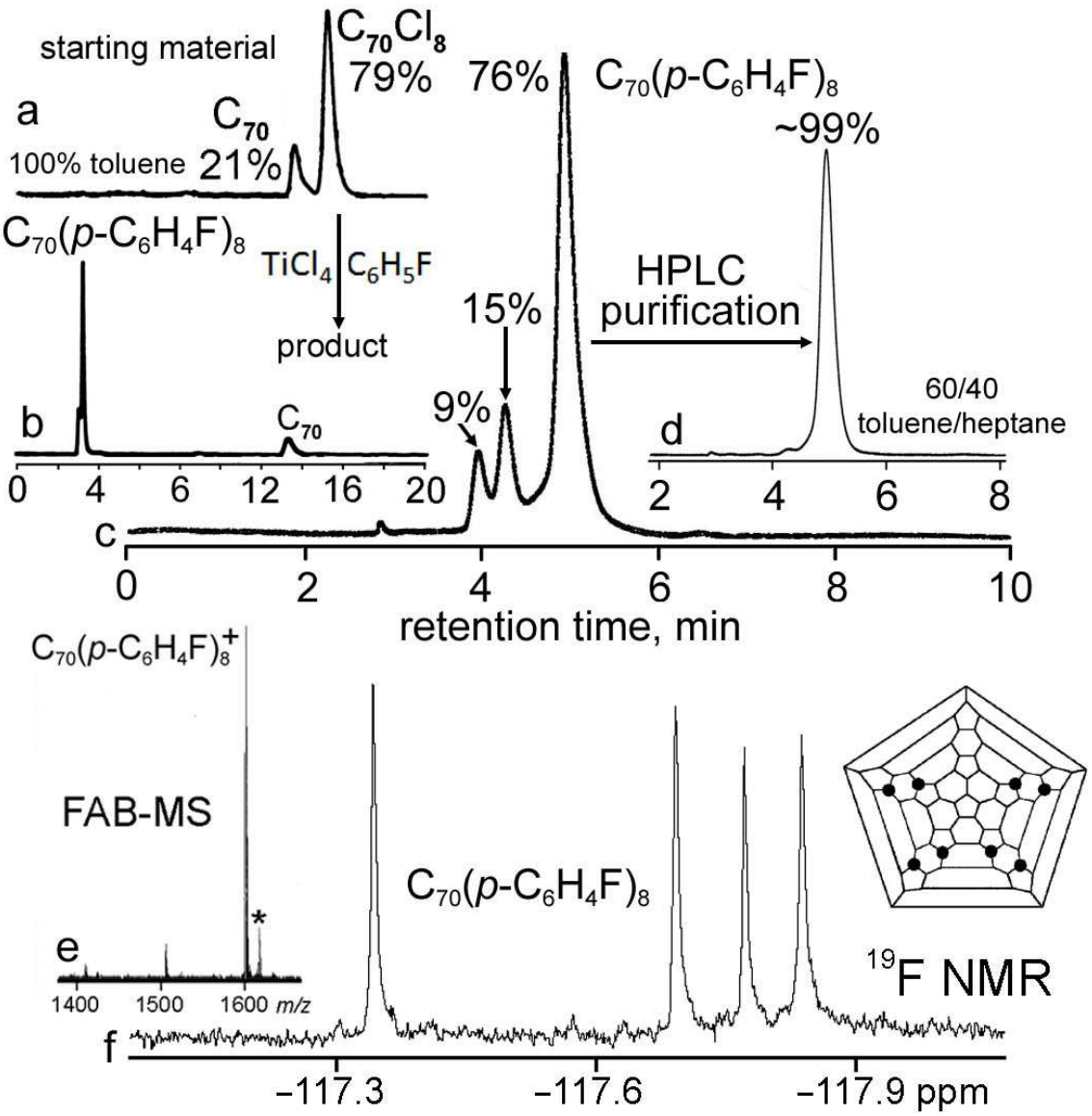

Figure V.10. $C_{70}(p\text{-}C_6H_4F)_8$ preparation, purification, and FAB-MS (plot e) and $\{^1H\}$-^{19}F-NMR (plot f) spectra. Plot a is the HPLC trace of the starting material ($C_{70}Cl_8$), plot b is the HPLC trace of the crude reaction mixture (100% toluene eluent was used in both cases). Plot c is the HPLC trace of the crude reaction mixture taken with 60/40 v/v toluene/heptane eluent. Plot d is the HPLC trace of the purified $C_{70}(p\text{-}C_6H_4F)_8$ acquired with 60/40 v/v toluene/heptane eluent.

V.2.2. Stability of Arylated Fullerenes

Numerous papers dedicated to the synthesis and study of arylated derivatives of fullerenes do not provide much information on the stability of these compounds; however, suggestions were made of their future use in the fields of solar power and biomedics. Naturally, the advanced materials for solar cell applications must possess a high degree of stability towards light-induced degradation; the biomedical applications and studies on the other hand requires a very high degree of sample purity (or an intimate knowledge of the impurities present). Besides these practical considerations, a general point should be made. The knowledge of the stability of a novel compound (or a novel class of compounds) is critical so that the steps necessary to ensure the absence of a significant, uncontrolled, and unwanted degradation during its study can be taken. Usually it is assumed that the degradation of a compound will reveal itself during the in the first stages of the study. However, it is not always true. Earlier we showed that $C_{60}Cl_n$ and $C_{70}Cl_n$ compounds decompose when irradiated with ambient light in solution (sometimes within hours). There was no mention of this phenomenon in the literature before our work, despite the fact that the first report on the preparation of a CF was published in 1991, in the very beginning of synthetic fullerene chemistry. We suggest that the report of the synthesis of a novel compound (or a class of compounds) in the field of fullerene chemistry can greatly benefit from the associated study of the stability of this compound (or a class of compounds). To keep with the spirit of this statement, we performed the first detailed study of the stability of arylated fullerenes.

Earlier the only data on the stability of arylated fullerenes was a brief mention that fluorophenylated fullerenes are more prone to oxidation than the phenylated derivatives.[3] In several papers the isolation of partially oxygenated arylated fullerenes were obtained (*i.e.*, $C_{70}Ph_9OH$, $C_{70}Ph_8O_4$, etc.); these compounds were obtained as by-products from the reaction mixtures formed during the preparation of arylated derivatives. These observations can be interpreted as indications of the air-sensitivity displayed by arylated fullerene derivatives, however, no concrete statements on that have been reported. Nowhere the need of inert-atmosphere conditions for working with arylated fullerenes was mentioned.

Despite that assuring literature data we found that all fluorophenylated fullerenes that we prepared (including 90+% pure samples of $C_{60}(p\text{-}C_6H_4F)_5Cl$ and $C_{70}(p\text{-}C_6H_4F)_8$) undergo a rapid (5-60 seconds) decomposition when their solutions are exposed to air. During this brief period of time the solutions rapidly turn cloudy forming a whitish gelatinous precipitate. When solid samples of these compounds (films prepared by evaporation of the corresponding solutions under vacuum) are exposed to air, they do not seem to change their appearance; however, they fail to redissolve, demonstrating a clear sign of degradation. If these films are kept in the vacuum or under inert atmosphere, they redissolve easily (in dry, deoxygenated toluene, which is the solvent used for all stability studies of arylated fullerenes performed in this work). The degree of air-sensitivity of these compounds does not show any obvious correlation with the presence or absence of ambient light, which suggests that fluorophenylated derivatives of fullerenes are air-sensitive independent of the lighting conditions.

The phenylated derivatives (95+% sample of $C_{60}Ph_5Cl$ and mixed sample of $C_{70}Ph_xCl_{10-x}$, x = 8, 9, 10) were found to be stable under air atmosphere. These compounds did not show any sings of degradation even after several days of storage under air (in the dark, see below). This shows that the stability of arylated fullerenes towards air depends to a great extent on the nature of the aryl group. A suggestion can be

made that more electron-withdrawing substituents of the aryl group may lead to higher air-sensitivity of the corresponding arylated fullerene; however, more experiments need to be done with various aryl groups in order to find a clear correlation.

We also studied the photosensitivity of arylated fullerenes towards ambient fluorescent light of the laboratory using 95+% pure sample of $C_{60}Ph_5Cl$ as a test compound. The technique of dynamic HPLC monitoring was used; the method was identical to one that we used to study the stability of $C_{70}Cl_n$ in the section II above and $C_{60}Cl_n$ in our earlier paper. We found that $C_{60}Ph_5Cl$ is photosensitive. No detectable decrease in the concentration of $C_{60}Ph_5Cl$ was observed even after 9 days of storage in the absence of light, both under air and under inert atmosphere. Under ambient laboratory radiation $C_{60}Ph_5Cl$ half-life was found to be *ca.* 3 days (both under inert atmosphere and under air). However, the photosensitivity of this compound may be associated with the presence of a chlorine substituent, rather than phenyl groups. More work needs to be done in order to firmly establish the stability of arylated fullerenes carrying various aryl groups under different conditions and in different solvents. However, even these limited findings show that some arylated fullerenes can be highly air-sensitive, thus putting some of the earlier results under question.

V.3. Conclusions

Our results show that although direct arylation of bare-cage fullerenes is poorly selective, similar reaction of CFs can produce arylated fullerene derivatives with multiple substituents with high yield and selectivity. However, complete substitution may be difficult to achieve when 1,2-chlorine substituents are present in the structure of the initial CF. For example, arylation of $C_{60}Cl_6$ produces $C_{60}Aryl_5Cl$ compound with a good yield for a variety of different aryl substituents; however, the synthesis of the fully-substituted $C_{60}Aryl_6$ is much more difficult to achieve (apparently, only a low-yield synthesis of $C_{60}Ph_6$ has been reported up to date). Other examples are poorly selective arylations of $C_{70}Cl_{10}$ (one 1,2-chlorine contact) and of C_1-$C_{60}Cl_{10}$ (multiple 1,2-chlorine contacts). However, $C_{70}Cl_8$ (all chlorine substituents occupying 1,4-positions relative to each other) is selectively converted into $C_{70}(p\text{-}C_6H_4F)_8$ with good yield. This shows that arylation may be a valuable generic method for derivatization of CFs that do not have (multiple) close contacts between chlorine substituents in their structure.

We found that arylated fullerenes have notably different stability depending on the nature of the aryl addends. So, fluorophenylated derivatives rapidly degrade under air atmosphere, when phenylated derivatives are stable under such conditions. We also found that $C_{60}Ph_5Cl$ compound is photosensitive both under air and under inert atmosphere. This behavior may be associated with chlorine rather than phenyl addends; however, the generic photosensitivity of arylated fullerenes (similar to the chlorofullernes) cannot be ruled out without further investigation.

The development of the efficient and selective methods of arylation of fullerene chlorides relied entirely on our general methodology of investigation. The discovery of

the limited stability of many arylated fullerenes also supports our view that stability study must be an integral part of the investigation of any novel class of chemical compounds (and/or materials).

V.4. Experimental Details

Reagents and Solvents: Benzene (Sigma-Aldrich, Na), toluene (Fischer Scientific, Na), chlorobenzene (Sigma-Aldrich, CaH_2), fluorobenzene (Sigma-Aldrich, CaH_2), and 1,2-dichlorobenzene (Sigma-Aldrich, CaH_2) were ACS Reagent Grade (vendor indicated in parenthesis) and were distilled from the indicated drying agent under purified N_2 atmosphere prior to use. $TiCl_4$ (Sigma-Aldrich) was stirred with copper powder for several days, then distilled under vacuum.[ref] HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), iodine monochloride (Sigma Aldrich, 99.998% trace metals basis), trans-2-[3-{4-tert-butylphenyl}-2-methyl-2-propenylidene]malononitrile (Fluka), chromium(iii) acetyl acetonate (Sigma Aldrich), and KBr (Sigma Aldrich, 99+ % FTIR grade) were used as received. All syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk techniques with vigorous stirring by a magnetic stirrer.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). Electronic spectra of dichloromethane and/or toluene solutions of chlorofullerenes were recorded using a Varian Cary 500 spectrophotometer. MALDI mass spectra were recorded on a Kompact MALDI IV (Kratos Analytical, Manchester, UK) time-of-flight mass-spectrometer in the linear mode. A 337 nm N_2 laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. CF samples and the trans-2-[3-{4-

tert-butylphenyl}-2-methyl-2-propenyl-idene]malononitrile matrix material (DCTB) were dissolved separately in toluene and were mixed in a 1:10 mol/mol sample/DCTB ratio assuming the sample contained only $C_{70}Cl_{10}$. A drop of each sample/DCTB solution was deposited on a stainless steel slide by using a capillary and dried under a strong stream of cool air from an airsprayer/brush in order to achieve a uniform sample surface. APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene). Thermogravimetry was performed using a TA Instruments TGA-2950 (platinum sample pans, *ca.* 5 mg sample size, 25–500 °C temperature range).

CF Handling. All operations involving solutions of CFs were performed either in the dark (vessels containing CF solutions were wrapped with aluminum foil) or with minimal exposure to light (experimental operations were performed as quickly as possible under minimal illumination) unless reported otherwise. We recommend that prior to long-term storage the traces of aromatic solvents (toluene etc.) should be removed by dissolving a CF sample in HPLC grade CH_2Cl_2 and evaporating the resulting solution under vacuum.

Inert-atmosphere HPLC. The analysis and separation of fluorophenylated fullerene derivatives were done using inert-atmosphere HPLC. The procedure uses protective positive pressure of dry nitrogen (*ca.* 5-6 psi above atmospheric pressure). This allows us to avoid placing the whole HPLC setup inside a glovebox and simply perform all the operations on the bench. The plastic effluent tube is equipped with a stainless-steel needle; when a fraction needs to be collected the operator quickly pokes it through the rubber septum of the collection flask (see Figure V.11). The collected fractions are concentrated and/or dried by vacuum-distilling the solvent into the solvent trap that is cooled with liquid nitrogen (see Figures V.11 and V.12).

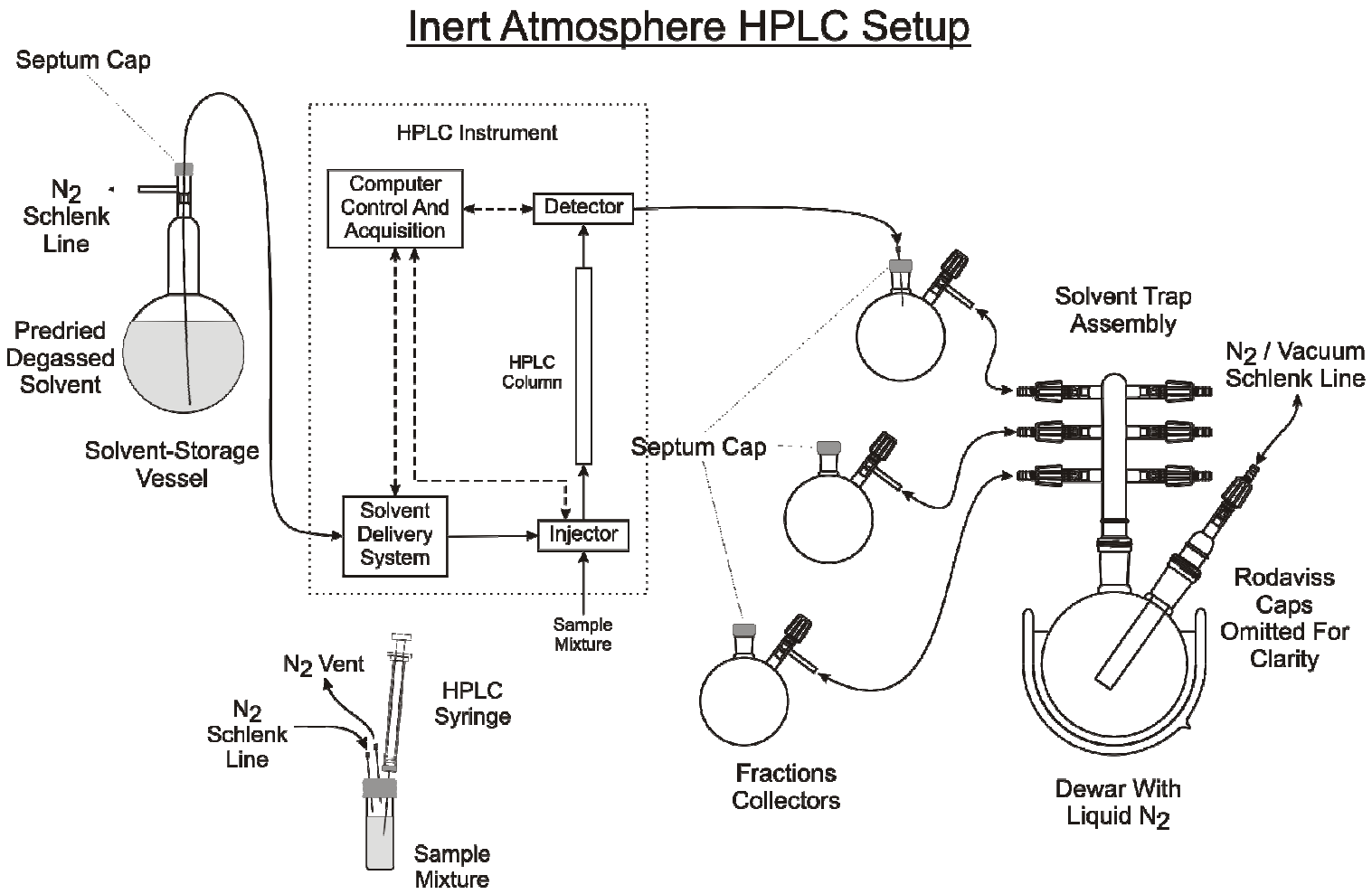

Figure V.11. The schematic representation of the inert-atmosphere HPLC setup (see also Figure IV-12). Through the use of protective atmosphere of dry nitrogen, the air-sensitive compounds can be manipulated outside of the glove-box in a convenient benchtop system.

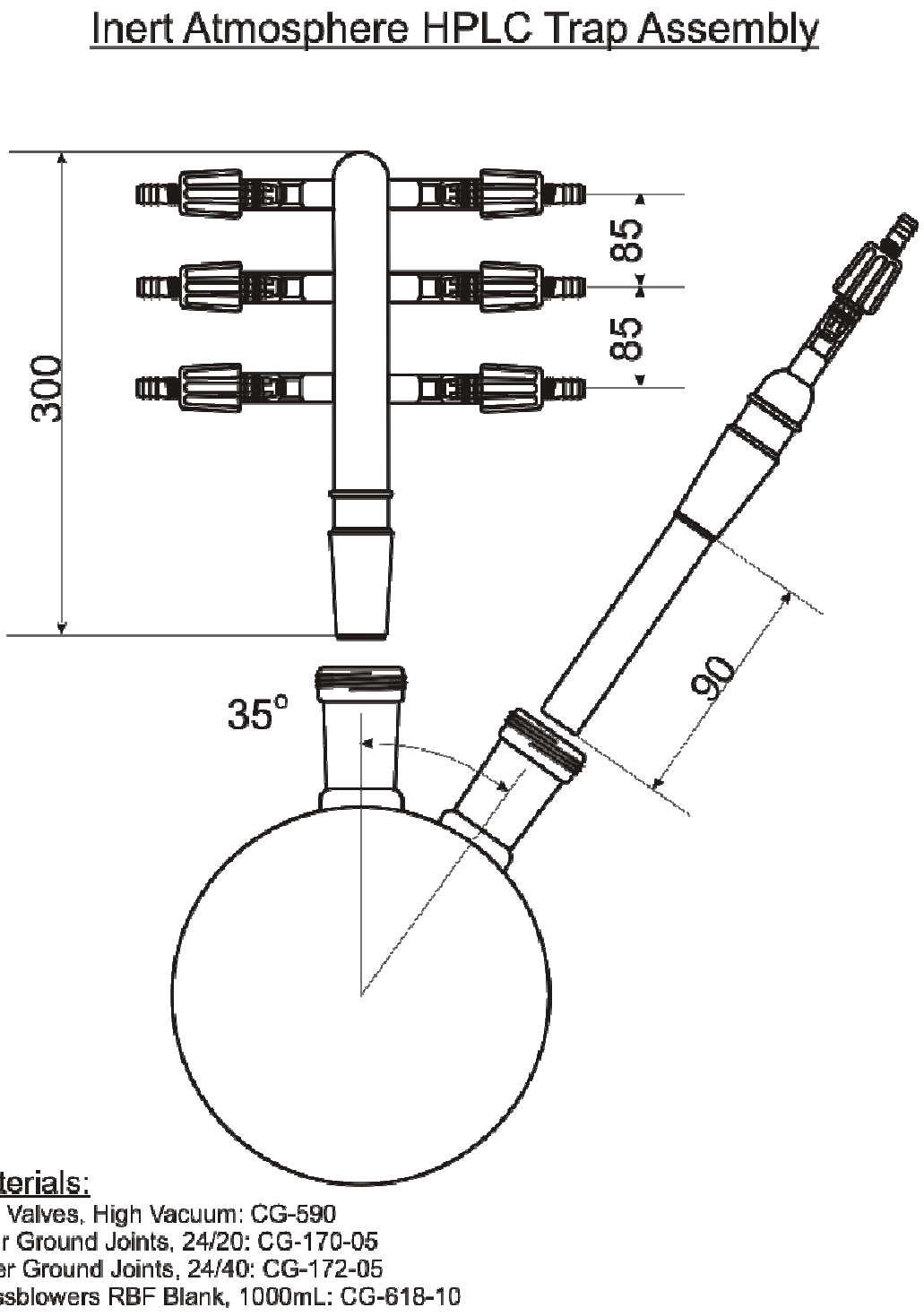

Figure V.12. The technical drawing of the inert-atmosphere HPLC trap assembly (see Figure IV-11).

C_{70} phenylation in the presence of $FeCl_3$. The arylation reactions were performed under ambient fluorescent light, under dry nitrogen atmosphere. C_{70} (3.5 mg, 0.004 mmol) was dissolved in 13 mL of dry, deoxygenated C_6H_6. About 10 mg of dry $FeCl_3$ was added to this solution, which was then mixed and split into two batches (batch A and batch B) of approximately the same size. Solution A was left stirring at room temperature; solution B was refluxed. After 15 min both reaction mixtures were quenched with aqueous HCl, washed with water, then the organic layer was separated and dried over $MgSO_4$. The resulting solutions were analyzed by HPLC and APCI-MS.

$C_{70}Cl_{10}$ phenylation in the presence of $FeCl_3$. The arylation reactions were performed under ambient fluorescent light, under dry nitrogen atmosphere. $C_{70}Cl_{10}$ (3.5 mg, 0.003 mmol) was dissolved in 9 mL of dry, deoxygenated C_6H_6. About 10 mg of dry $FeCl_3$ was added to this solution, which was then mixed and split into two batches (batch A and batch B) of approximately the same size. Solution A was left stirring at room temperature; solution B was refluxed. After 15 min both reaction mixtures were quenched with aqueous HCl, washed with water, then the organic layer was separated and dried over $MgSO_4$. The resulting solutions were analyzed by HPLC and APCI-MS.

$C_{60}Cl_6$ phenylation in the presence of $TiCl_4$. 90% pure (by HPLC trace integration) sample of $C_{60}Cl_6$ (70.5 mg, 0.0755 mmol, for preparation see Chapter I) was dissolved in 70 mL of dry, deoxygenated C_6H_6. A 5 mL sample of this solution was stored under dry nitrogen (sample A) in the clear glass flask. To the rest of the $C_{60}Cl_6/C_6H_6$ solution 5 mL of $TiCl_4$ were added. A 5 mL sample of this mixture was taken and stored under dry nitrogen in the dark (sample B). The rest of the reaction mixture were left stirring under dry nitrogen in the clear glass flask under ambient fluorescent light of the laboratory (same as sample A). All three reaction mixtures were sampled at the regular time intervals (30 min, 1 hour, 2 hours, and 3 hours); these samples were flash-evaporated under vacuum, dissolved in toluene and analyzed by HPLC (under air atmosphere). After 4 hours the reaction mixtures B and C were quenched with aqueous HCl, washed with

water, then the organic layers were separated and dried over $MgSO_4$. The resulting products were analyzed by APCI-MS and HPLC.

$C_{60}Cl_6$ phenylation in the presence of $FeCl_3$. 90% pure (by HPLC trace integration) sample of $C_{60}Cl_6$ (15.0 mg, 0.016 mmol, for preparation see ref. #) was dissolved in 15 mL of dry, deoxygenated C_6H_6. *Ca.* 10 mg of dry $FeCl_3$ was added to this solution; it was thoroughly mixed and split into two portions A and B (both were kept under dry nitrogen atmosphere under ambient fluorescent light). Portion A was kept at room temperature; portion B was heated at 70 °C. After 20 min both reaction mixtures were quenched with aqueous HCl, washed with water, then the separated organic layers were dried over $MgSO_4$.

$C_{70}Cl_{10}$ phenylation in the presence of $TiCl_4$. $C_{70}Cl_{10}$ (33.3 mg, 0.0279 mmol) was dissolved in 50 mL of dry, deoxygenated C_6H_6. Then 3 mL of $TiCl_4$ were added to it and the resulting mixture was left stirring under the atmosphere of dry nitrogen in the clear glass flask under ambient fluorescent light of the laboratory. After ca. 2 hours the reaction mixture changed color from bright-yellow to very dark-greenish. The samples of the reaction mixture were taken regularly, flash-evaporated under vacuum, dissolved in toluene, filtered, and analyzed by HPLC.

Dynamic HPLC study of $C_{60}Cl_6$ arylation. The arylation reactions were performed under ambient fluorescent light, under dry nitrogen atmosphere. 90% pure $C_{60}Cl_6$ (15.1 mg, 0.016 mmol, prepared according to ref.) was dissolved in 6 mL of dry, deoxygenated PhF. This solution was split into two batches (batch A and batch B). $TiCl_4$ (20 μL, 0.10 mmol) was added to the batch A; $FeCl_3$ (ca. 16 mg, 0.1 mmol) was added to the batch B. Both reaction mixtures were stirred vigorously. Samples of both reaction mixtures were taken at the regular time intervals and flash-evaporated; then they were dissolved in toluene, filtered, and analyzed by inert-atmosphere HPLC. Reaction mixture B changed color from orange to very dark-brown within the first 5 minutes of Lewis acid addition; the color of reaction mixture A stayed unchanged throughout the course of the reaction.

Dynamic HPLC study of $C_{60}Cl_{10}$ fluorophenylation. The reaction was performed under ambient fluorescent light, under dry nitrogen atmosphere. 95% pure $C_{60}Cl_{10}$ (*ca.* 5 mg, 0.005 mmol, prepared according to ref.) was dissolved in 3 mL of dry, deoxygenated PhF. $TiCl_4$ (200 μL, 1 mmol) was added to it and the reaction mixture was left stirring. Samples of the reaction mixture were taken at the regular time intervals and flash-evaporated; then they were dissolved in toluene, filtered, and analyzed by inert-atmosphere HPLC.

Preparation of $C_{70}(p\text{-}C_6H_4F)_8$. 80% pure $C_{70}Cl_8$ (12.6 mg, *ca.* 0.009 mmol; 20% impurity is due to C_{70}) was prepared as described above and used without HPLC purification. It was dissolved in 10 mL of dry, deoxygenated PhF; then this solution was mixed with 0.25 mL of $TiCl_4$ (1.27 mmol) and left with vigorous stirring. After three days the reaction was completely evaporated under vacuum. The residue was dissolved in dry, deoxygenated toluene under dry nitrogen atmosphere, filtered, and separated by inert-atmosphere HPLC.

Preparation of $C_{70}(p\text{-}C_6H_4F)_{10}$. 98% pure $C_{70}Cl_{10}$ (14.2 mg, *ca.* 0.012 mmol) was prepared as described above. It was dissolved in 5 mL of dry, deoxygenated PhF; then this solution was mixed with 0.25 mL of $TiCl_4$ (1.27 mmol) and left with vigorous stirring. The reaction mixture started to change color to green and fluoresce after *ca.* 12 hours. After 3 days of stirring the reaction mixture was evaporated down. The residue was dissolved in dry, deoxygenated toluene under dry nitrogen atmosphere, filtered, and separated by inert-atmosphere HPLC.

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Chapter VI
Perfluoroalkylation of Chlorofullerenes

VI.1. Introduction

In the preceding chapters we showed that chlorofullerenes and arylated fullerenes have relatively low stability and are easily decomposed. In chapters II and III we also demonstrated that chlorofullerenes are generally light-sensitive in solution (both under air and under inert atmosphere). In chapter V we determined that arylated fullerenes can be very air-sensitive; these compounds may also demonstrate light-sensitivity (similar to chlorofullerenes). Such behavior of these compounds makes their further use for the development of advanced materials questionable. In order to overcome this difficulty, we decided to use excellent properties of chlorofullerenes as precursors (see Section II.1 and V.1) and attempt to convert these compounds into fullerene derivatives with higher stability. Our choice fell on substitution of chlorines for perfluoroalkyl groups, since perfluoroalkyl fullerene derivatives (PPAFs) are one of the most (if not the most) stable among the known exohedral fullerene derivatives.[1] Moreover, PPAFs were shown to have exceptionally long lifetimes of the corresponding radical anions in solution,[2,3] and a broad range (0.8 V) of the first reduction potentials that strongly depend on the number of substituents, their nature, and especially their addition pattern .[4]

Several different methods for PPAF preparation have been described in the literature; all of them can be regarded as reactions of bare-cage fullerenes with perfluoroalkyl radicals, produced either by photolysis or thermolysis of suitable precursors.[1,3,5-10] The thermally-induced reactions are by far the most common methods of PPAF preparation

(only two papers describing photo-induced PPAF synthesis[5,11] have been published up to date); with the most common radical precursors being perfluoroalkyl iodides (silver trifluoroacetate[6,7,12] and perfluoropropionyl peroxide[5] were also used). So far there have been no reports of PPAFs preparation via *substitution* of fullerene precursor.

There are several examples of a relatively successful substitution of chlorines with methyl group in chlorofullerenes using methyl lithium;[13,14] in both cases the selectivity of the substitution process was not very high, leading to formation of compounds carrying less and more methyl groups than the number of chlorine addends in the starting material. We observed similar behavior in the preceding chapter (see Chapter V), where we showed that the selectivity of chlorofullerene arylation is oftentimes low but can be strongly increased by the careful choice of the reaction conditions (and of suitable substrate).

In this work we explored an approach based on reaction of chlorofullerenes with organometallic *perfluoroalkyl* compounds. Due to poor stability of organometallic derivatives of CF_3,[15] we focused on the study C_2F_5-Li that was successfully used in organic synthesis before.[15-17] This reagent was prepared immediately prior to use by metal-halogen exchange at low (−95 °C) temperature.[15,18]

VI.2. Results and Discussion

VI.2.1. Preparation of Fullerene$(C_2F_5)_n$ via Substitution of Chlorofullerenes

A. Reaction of $C_{60}Cl_6$ with C_2F_5Li. This reaction was carried out by mixing of freshly-prepared C_2F_5Li solution in diethyl ether with toluene solution of $C_{60}Cl_6$ (both solutions were kept at −95 °C in order to prevent C_2F_5Li degradation[18]). Then this mixture was warmed up to room temperature, evaporated down, dissolved in toluene, filtered and analyzed by HPLC. Some of the resulting crude products were separated by HPLC and individual fractions were studied in detail (see below). We found that the rate of the warm-up does not have an effect on the reaction selectivity and product distribution (see Figure VI.1). However, the stoichiometry of this reaction has a very

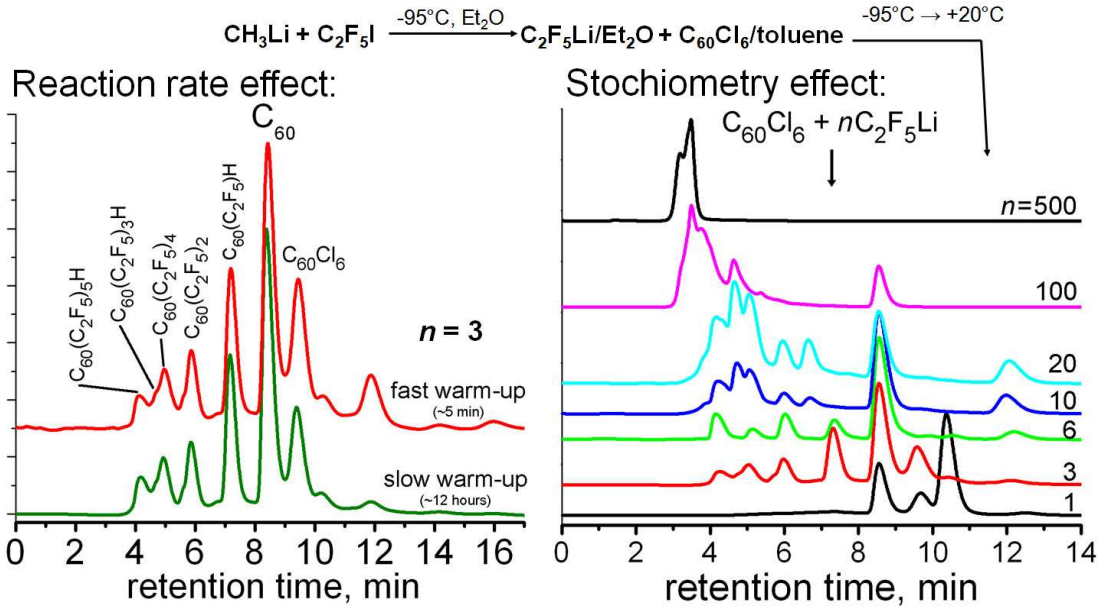

Figure VI.1. Effects of reaction rate and stoichiometry on the product distribution of $C_{60}Cl_6$ reaction with C_2F_5Li (the HPLC traces of various crude products are shown).

strong effect on the composition of the reaction products (see Figure VI.1). When low excess of C_2F_5Li is used (1-6 equivalents relative to $C_{60}Cl_6$) several products carrying between 1 and 5 C_2F_5 groups are formed (see Figure VI.1). It is notable that fullerene derivatives with both even and odd number of C_2F_5 groups are produced under these conditions; this lies in stark contrast to the results observed in radical addition reactions where only products with even number of C_2F_5 groups are formed.[19,20] The analysis of the reaction products isolated in pure form showed that derivatives with odd number of C_2F_5 groups also carry a hydrogen substituent (this was shown by ^{1}H-NMR spectroscopy). This is the first synthetic method that produces such "mixed" fullerene derivatives with relatively high selectivity. In several earlier reports the formation of perfluoroalkyl/hydrofullerenes were also detected.[5,6] However, the selectivity of these processes is very low, making it highly unlikely that they can be used for the synthesis of the particular perfluoroalkyl/hydrofullerenes.

The HPLC analysis shows (see Figure VI.1) that the reaction of C_2F_5Li with $C_{60}Cl_6$, besides the productive substitution of chlorines, also causes chlorine loss leading to formation of bare-cage C_{60}. It is also clear that this reaction is not very selective, leading to the formation of several products with C_2F_5 substituents. Both of these processes were also observed during chlorofullerene methylation[13,14] and arylation (see Chapter V). Further optimization of the reaction conditions (*i.e.*, use of different metalloperfluoroorganic reagents) may allow one to improve the selectivity and yields of this process. However, the vast majority of the reported up to date methods of fullerene perfluoroalkylation also produce (sometimes very complex) mixtures of products (see Chapter VII and references therein). These crude products are usually separated by HPLC, giving pure single-isomer, single-composition compounds. Hence, the reaction of $C_{60}Cl_6$ chlorofullerene with C_2F_5Li reagent is a useful and unique synthesis tool, since it is the only method that can relatively selectively produce derivatives with odd number of C_2F_5 groups and also derivatives with low even number of C_2F_5 groups (this is very

challenging when radical addition methods of synthesis are employed, see Chapter VII and references therein).

B. Reaction of C_{60} with C_2F_5Li. This reaction was carried out in the same fashion as reaction of $C_{60}Cl_6$ with C_2F_5Li. The products are shown in Figure VI.2. We found that this reaction produces a mixture of products when large excess of C_2F_5Li is used (the analysis of this product by APCI-MS was not successful); the use of low excess did not result in the appreciable change in C_{60}. A conclusion can be made that bare-cage C_{60} cannot be used if fullerene derivatives with 1-5 C_2F_5 groups are thought out, mandating the use of $C_{60}Cl_6$ chlorofullerene substrate.

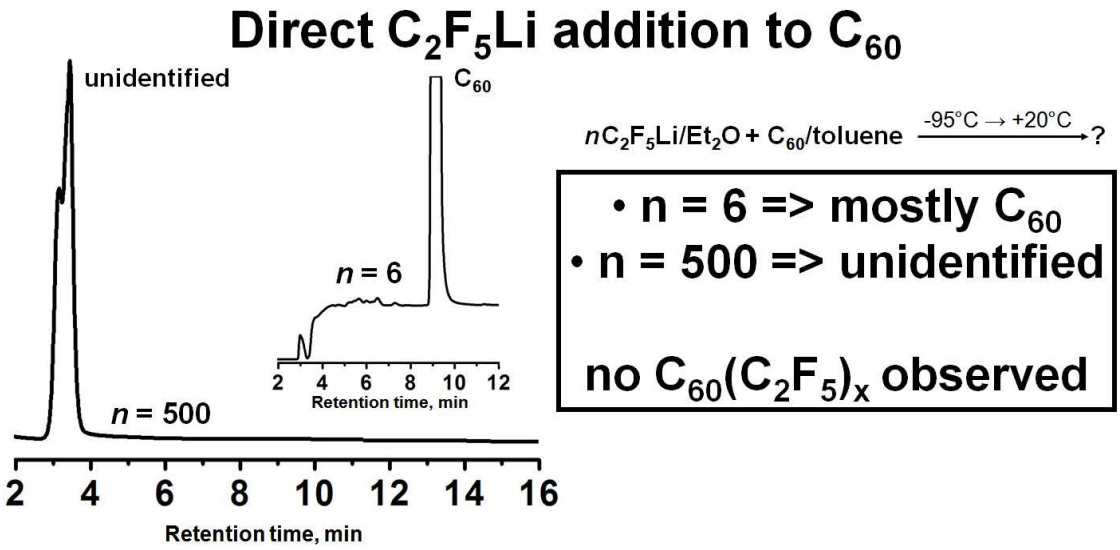

Figure VI.2. Direct addition of C_2F_5Li to C_{60}. HPLC traces of the corresponding crude products are shown.

C. Reaction of $C_{70}Cl_{10}$ with C_2F_5Li. This reaction was found to cause an extensive de-chlorination of $C_{70}Cl_{10}$ leading mostly to bare-cage C_{70}, see Figure VI.3. Using large excess of C_2F_5Li reagent complex mixtures of products carrying up to 12 C_2F_5 groups are produced (as shown by APCI-MS, figure not shown). However, the selectivity of this reaction is too low to allow for an efficient preparation of $C_{70}(C_2F_5)_n$ (or $C_{70}(C_2F_5)_mH$) derivatives.

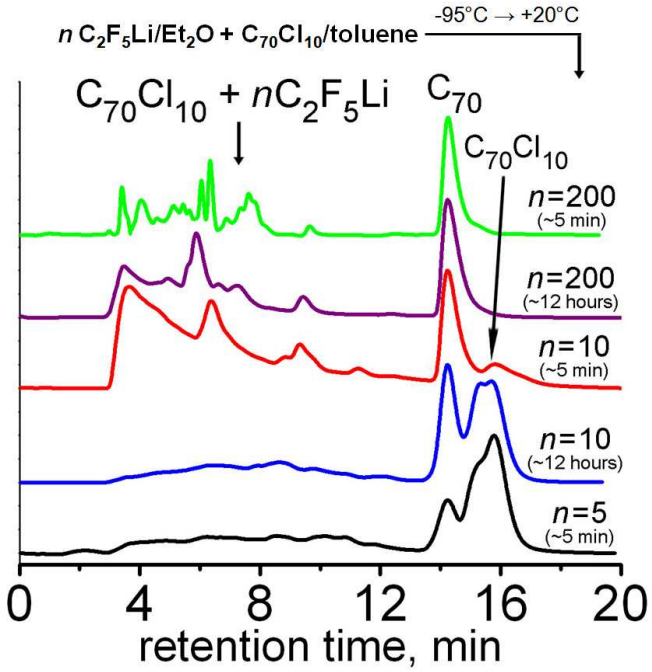

Figure VI.3. HPLC analysis of the products of $C_{70}Cl_{10}$ reaction with various amounts of C_2F_5Li reagent.

VI.2.2. Isolation and Characterization of Individual $C_{60}(C_2F_5)_n$ and $C_{60}(C_2F_5)_mH$ Compounds

Several previously unknown C_2F_5 derivatives of C_{60} were prepared by $C_{60}Cl_6$ reaction with six equivalents of C_2F_5Li (see Figure VI.1). They were isolated in pure state using HPLC and analyzed by UV-vis spectroscopy, APCI mass-spectrometry, ^{19}F- and ^{1}H-NMR spectroscopy, and single-crystal X-ray diffractometry (for $C_{60}(C_2F_5)_5H$, see Appendix A.2), see Figures VI.4 and VI.5. The presence of hydrogen substituent was established by ^{1}H-NMR spectroscopy (figure not shown).

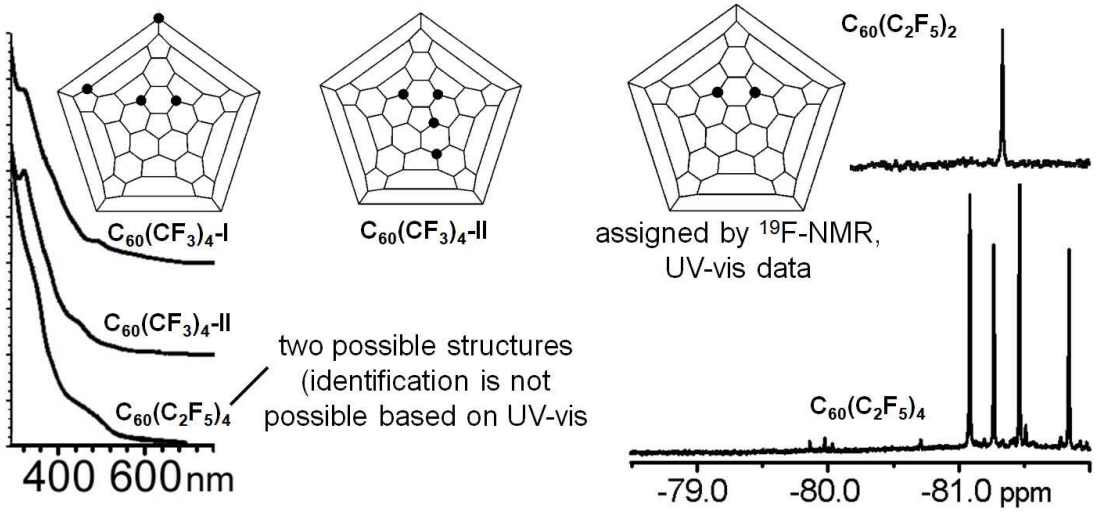

Figure VI.4. Analysis and likely addition patterns of $C_{60}(C_2F_5)_2$ and $C_{60}(C_2F_5)_2$.

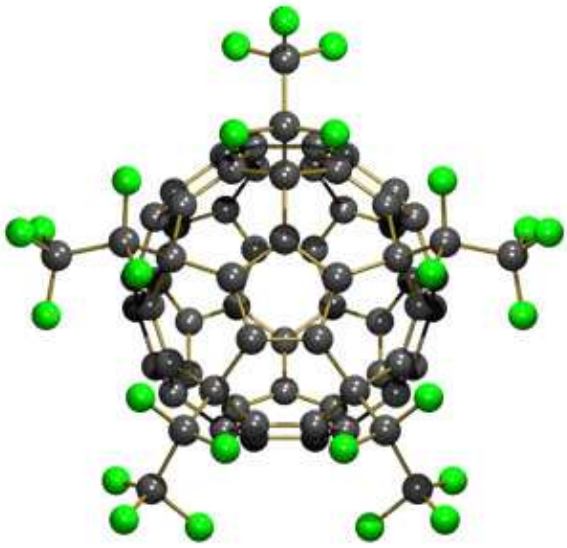

Figure VI.5. The structure of $C_{60}(C_2F_5)_5H$ determined by single-crystal X-ray diffraction study (see Appendix A.2). The addition pattern of this compound is the same as the addition pattern of the starting material $C_{60}Cl_6$.

Unfortunately, the addition pattern of $C_{60}(C_2F_5)_4$ cannot be reliably assigned based only on the results of ^{19}F-NMR and UV-vis spectroscopy (see Figure VI.4). So far our attempts at obtaining single crystals of this compound that are suitable for X-ray study were not successful.

VI.2.3. Preparation of the First Organometallic Complex of Perfluoroalkylfullerene

The structure of $C_{60}(C_2F_5)_5H$ features a cyclopentadiene ring with hydrogen substituent, surrounded with electron-withdrawing C_2F_5 groups. Such molecule should have a significant Broensted acidity, in other words, the loss of proton and formation of Cp-type negatively charged anion should be favorable. We decided to test this hypothesis by attempting to deprotonate $C_{60}(C_2F_5)_5H$ in order to produce $C_{60}(C_2F_5)_5^-$; then react this anion with an active metalloorganic precursor prone to formation of Cp-complexes. We chose to use $[RhCl(1,5\text{-}COD)]_2$ (1,5-COD = 1,5-cyclooctadiene) dimer for this role. Our attempt was successful, see Figure VI.6. The analysis of the reaction product with ^{19}F-NMR spectroscopy shows that the C_s-$C_{60}(C_2F_5)_5H$ was converted into a species with at least C_5-symmetry (the lines of C_s-$C_{60}(C_2F_5)_5H$ merged into a single peak). ^1H-NMR spectroscopy also confirmed the disappearance of the hydrogen addend that was attached to directly to the fullerene cage in C_s-$C_{60}(C_2F_5)_5H$. Finally, APCI mass-spectrometry analysis of the reaction product confirmed the formation of $C_{60}(C_2F_5)_5Rh(1,5\text{-}COD)$. This is the first reported example of the organometallic complex of fluoroalkylfullerene.

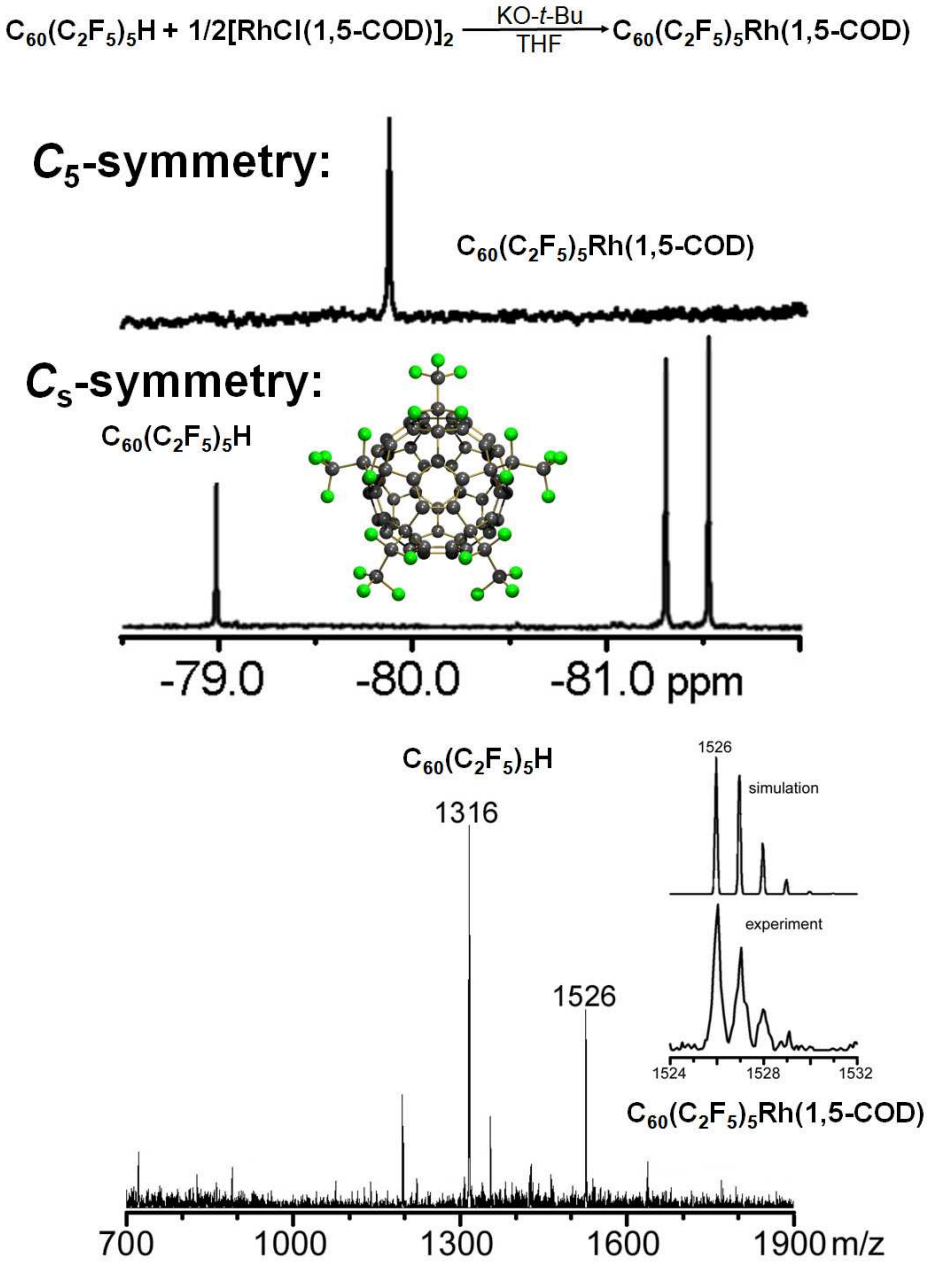

Figure VI.6. Synthesis and characterization of the first organometallic complex of fluoroalkylfullerene $C_{60}(C_2F_5)_5Rh(1,5\text{-COD})$ (1,5-COD = 1,5-cyclooctadiene).

VI.3. Conclusions

This chapter summarizes the first reported preparation of perfluoroalkyl (pentafluoroethyl) fullerene derivatives by substitution of leaving groups of *derivatized* fullerene precursor. All earlier literature methods relied exclusively on the addition of perfluoroalkyl radicals to bare-cage fullerenes, generally producing mixtures of products with even number of perfluoroalkyl substituents.[1,3,5-10] Our method of pentafluoroethylation of chlorofullerenes with C_2F_5Li reagent allows one to prepare unique fullerene derivatives with odd number of C_2F_5 substituents and a single hydrogen addend. Compounds with low even number of C_2F_5 groups can also be synthesized, which is generally difficult if direct synthetic methods are used.

The mixed pentafluoroethylated/hydrogented fullerene derivatives constitute a unique and previously unknown class of fullerene derivatives. These compounds are likely to show enhanced proton acidity. Moreover, we demonstrated that these compounds can form metallorganic complexes, which is the first reported example of such reactivity for perfluoroalkylfullerenes. However, the preparative methods that we explored so far show relatively low selectivity which complicates their wide application. More work needs to be done in order to improve the efficiency of these procedures, however, the initial success demonstrated in this work shows that this is a promising direction of further study.

VI.4. Experimental Details

Reagents and Solvents: Toluene (Fischer Scientific, Na), diethyl ether (Sigma-Aldrich, Na), and tetrahydrofuran (Sigma-Aldrich, Na) were ACS Reagent Grade (vendor indicated in parenthesis) and were distilled from the indicated drying agent under purified N_2 atmosphere prior to use. HPLC Grade toluene (Fisher Scientific was used as received. C_{60} (99.9%, Term-USA) was used as received. All syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk techniques with vigorous stirring by a magnetic stirrer. C_2F_5I was purchased from SynQuest Labs and used as received. $[RhCl(1,5\text{-}COD)]_2$ (1,5-COD = 1,5-cyclooctadiene) was purchased from Sigma-Aldrich (Reagent Grade) and used as received. $C_{60}Cl_6$ and $C_{70}Cl_{10}$ were prepared according to the procedures described in Sections II.4 and III.4.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). 100% toluene eluent at 5 mL/min flow rate was employed for trace acquisition. Electronic spectra of dichloromethane and/or toluene solutions of chlorofullerenes were recorded using a Varian Cary 500 spectrophotometer. APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene). C_2F_5I was handled and its amount was measured using vacuum system with calibrated volumes and capacitance Baratron gauge (0-1000 torr pressure range).

Experimental procedure. In a typical experiment, an excess (*ca.* 10 fold) of C_2F_5I was added to the solution of *n*-butyl lithium in ether at −95 °C (100 µL of 1.6 M solution

of n-BuLi in hexanes were dissolved in 5 mL of diethyl ether in a typical experiment; toluene slash bath is used for cooling); the amount of the initial *n*-BuLi determines the quantity of the resulting C_2F_5Li (quantitative conversion is presumed). Then this solution is added to the toluene solution of chlorofullerene maintained at −95 C° during a period of ca. 1 minute under vigorous stirring (24 mg of $C_{60}Cl_6$ were dissolved in 15 mL of toluene in a typical experiment). The resulting mixture is allowed to warm up to the room temperature; then it is evaporated down under vacuum, dissolved in toluene, and filtered. The quenching of the reaction mixture with water or aqueous acid did not result in any observable change in results of the experiment.

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Chapter VII
Direct Trifluoromethylation of Fullerenes

VII.1. Introduction

As we have shown in Chapter VI, the preparation of poly(perfluoroalkyl)fullerenes (PPAFs) via substitution of chlorofullerenes is a promising method. However, it is also limited by the selectivity and efficiency of chlorofullerene substitution, as well as availability of particular chlorofullerenes. Moreover, organometallic compounds carrying CF_3 groups are extremely unstable (see Section VI.1 and references therein), so the substitution approach is unlikely to be suitable for the preparation of perfluoromethylated fullerene derivatives. Moreover, the most populous class of PPAFs currently consists of poly(trifluoromethyl)fullerenes (PFMFs);[1-5] various fullerene cages, including endometallofullerenes[6] and TNT fullerenes,[7] carrying anywhere from two[1] to eighteen[8] CF_3 groups per cage have been isolated and studied by a wide array of structural and electrochemical[4,9] methods. The majority of these compounds are prepared as mixtures of PFMFs, which are separated into isomerically and compositionally pure products using HPLC (the yield of the individual PFMFs is generally low); however, two PFMFs can be prepared with high yield by using carefully selected synthetic conditions (S_6-$C_{60}(CF_3)_{12}$[5] and C_1-$C_{70}(CF_3)_{10}$[4]). However, reported synthetic procedures yield mostly PFMFs with higher number of substituents (six and more); the efficient large-scale preparation of PFMFs with two and four perfluoroalkyl groups has not been achieved.

Compounds carrying lower number of CF_3 groups ($n(CF_3)$ = 2, 4, 6) are especially enticing for further study since their structure preserves a large portion of the fullerene

cage intact to allow for both the efficient charge delocalization (for photo- and electrochemical applications) and the unrestricted attachment of additional substituents (for the development of advanced materials and polymers). Hence in this work we focus on the systematic study of direct trifluoromethylation of fullerenes in order to develop an efficient procedure for preparation of PFMFs with low number of addends.

VII.2. Results and Discussion

VII.2.1. Literature Methods of PFMF Preparation

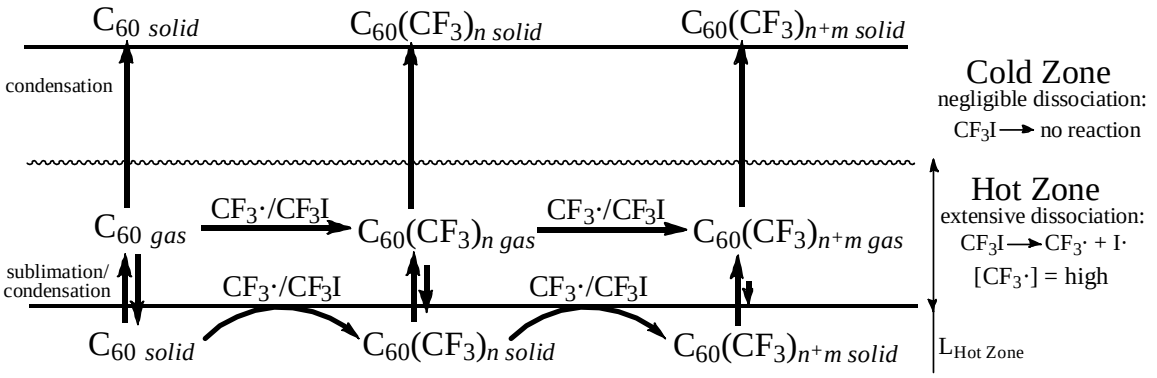
All of the reported up to date PFMF preparations are achieved by a reaction of (bare-cage) fullerene with trifluoromethyl radical precursor such as silver trifluoroacetate[1,2] or trifluoromethyl iodide in heterogeneous conditions at high temperature[3-5,10] (the only example of UV-induced reaction of C_{60} solution in benzene with CF_3I led to the formation of mixed $C_{60}(CF_3)_nH_m$ species[11]). In case of use of silver trifluoroacetate, solid $AgOOCCF_3$ is thoroughly mixed (by grinding) with fullerene, then charged in a glass insert that is sealed in a copper tube and heated. [1,2] This method produces very complex mixtures of PFMFs, including $C_{60}(CF_3)_nH_m$ compounds (*i.e.* over 60 different compounds were isolated from the products of such reaction with C_{60}[12]). These crude products can be sublimed at higher temperature (ca. 500-600 °C) in order to obtain a sublimate that does not contain $C_{60}(CF_3)_nH_m$ products (they possibly decompose); hence this sublimate is more amenable to HPLC separation (sometimes two consecutive sublimations were employed for further simplification of the product composition).[1,2] The reaction with trifluoromethyl iodide is usually performed either in the flow-tube reactor[3,10] (the tube with a sample of fullerene is heated in the furnace, and a stream of CF_3I gas is passed through it) or in the sealed glass ampoules at elevated pressure and high temperature[5,8] (*ca.* 5 bar, liquefied CF_3I is present in the cold section of the ampoule[8]). These procedures generally yield mixtures of PFMFs that are separated into isomerically and compositionally pure products by HPLC (except for the selective syntheses of S_6-$C_{60}(CF_3)_{12}$[5] and C_1-$C_{70}(CF_3)_{10}$[4]). However, CF_3I procedures have notably

better selectivity than the ones based on the use of $AgOOCCF_3$, since they do not produce partially hydrogenated products. Due to the absence of $C_{60}(CF_3)_nH_m$ products no additional sublimation(s) of the crude PFMF mixture is required for CF_3I-based procedures.

Despite a large number of publications on different synthetic methods for PFMF preparation and properties of these compounds, there are very few reports that discuss the dependence of the products (product distribution) on the reaction conditions. One of the few observations of this nature is the inverse dependence between the average number of CF_3 groups in the products of C_{60} trifluoromethylation (by CF_3I in flow-tube reactor) and the reaction temperature.[4] Also, the effect of the ratio between fullerene and $AgOOCF_3$ reagent on the product composition was studied in one paper.[13] However, no systematic study of the effects of other reaction conditions on the distribution of PFMF products have been published up to date.

VII.2.2. General Remarks on Fullerene Trifluoromethylation

Scheme VII.1 will be used for generic description of the processes that supposedly take place during heterogeneous trifluoromethylation of fullerenes at elevated temperature. Although this scheme features C_{60} fullerene and CF_3I radical source, this does not restrict its generality, since it may be used to describe similar processes with other fullerenes, radical sources, and even other phases. For example, this scheme can be adopted, with some corrections, to describe the thermally-induced trifluoromethylation of C_{60} with CF_3I in hexafluorobenzene medium (C_{60} is insoluble in C_6F_6 which makes this a heterogeneous process involving a solid and liquid phases; the corrections to the scheme include the absence of the cold zone and the high solubility of PFMF products).[11] Formation of $CF_3\cdot$ radicals is assumed to be the initial stage of the trifluoromethylation process; in case of CF_3I the extent of this process becomes considerable above 400 °C (400-600 °C temperatures are used in the literature procedures[4,10]). Hence, there are enough radicals to cause appreciable reaction within the volume of the "hot zone" (this may be regarded as a definition of the "hot zone"). In "cold zone", on the other hand, the temperature of CF_3I gas is too low to create an appreciable concentration of $CF_3\cdot$ radicals, thus we can assume that no further trifluoromethylation takes place there (this may be regarded as a definition of the "cold zone"). The trifluoromethylation of fullerenes is treated as an irreversible process; also, it is assumed that the solid products cannot sublime out of the cold zone due to insufficient temperature.



Scheme VII.1. The simplified description of the heterogeneous reaction of C_{60} with gaseous CF_3I at elevated temperature (without restricting the generality). The formation of molecular iodine and its condensation in the cold zone is not shown.

Several processes may take place in such system at the same time: i) sublimation of C_{60} from the hot zone; ii) trifluoromethylation of the surface layer of solid C_{60} (and further trifluoromethylation of so-formed solid PFMFs) in the hot zone; iii) sublimation of PFMFs from the hot zone; iv) trifluoromethylation of the subliming C_{60} and PFMFs in the gas phase; v) condensation of C_{60} and PFMFs from the gas phase into the cold zone; vi) condensation of C_{60} and PFMFs back into the hot zone. By breaking up the process of fullerene trifluoromethylation into these individual processes we can predict what reaction conditions are important and how they should effect the composition of the PFMFs prepared. We can identify two major variables that should have a strong effect on the composition of the resulting PFMFs: the concentration of $CF_3\cdot$ radicals in the hot zone and the residence time of the fullerene species. Residence time is defined here as the time a C_{60} or PFMF molecule spends either in the surface layer of solid C_{60}/PFMF particles or in the gas phase within the hot zone (i.e., in the area where it has a high probability of reacting with $CF_3\cdot$ radical(s)). It is clear that factors increasing the concentration of $CF_3\cdot$ radicals and/or residence time of fullerene species should favor the formation of PFMFs with higher number of CF_3 groups (and improve the conversion of the bare-cage fullerene). Let's discuss the effects of these factors in more detail.

The increase of the pressure of CF_3I increases the concentration of $CF_3\cdot$ radicals; hence, PFMFs with higher number of substituents, or $n(CF_3)$, should be produced. Higher gas pressure should also make the sublimation rate of C_{60} and PFMFs present in the solid state in the hot zone slower; in other words, the transport rate of these species to the cold zone should decrease. Slower transport rate of the fullerene species from the hot zone increases the residence time; hence, it causes the formation of PFMFs with higher $n(CF_3)$. According to this analysis, the increase of CF_3I pressure increases both the $[CF_3\cdot]$ and the residence time; both of them increase the degree of addition of the resulting PFMF products.

The increase of the temperature of the hot zone increases the concentration of $CF_3\cdot$ radicals; however, it also increases the rate of sublimation (especially for the higher PFMFs which have lower sublimation temperature than lower PFMFs and C_{60} itself). Hence, the increase of the hot zone temperature increases $[CF_3\cdot]$ *but* decreases the residence time, making the overall change in the PFMF composition difficult to predict.

The size of the hot zone ($L_{hot\ zone}$, see Scheme VII.1) of the reactor should not change the concentration of CF_3 radicals (assuming that the temperature of the hot zone stays constant); however, the residence time should change proportionally to it. Hence, a prediction can be made that longer hot zone should favor the formation of higher PFMFs, while shorter hot zone should lead to the preparation of lower-substituted PFMFs.

The dilution of CF_3I with an inert gas should decrease the concentration of CF_3 radicals and slow down the sublimation and increase the residence time. Hence the effect of such dilution on product distribution is difficult to predict (similar to the case of the reaction temperature).

This schematic description of trifluoromethylation process is supported by the literature data. The increase of the stoichiometric ratio between $AgOOCCF_3$ and C_{60} was reported to cause an increase of the average number of CF_3 groups in the PFMF products;[13] which is consistent with the increase of the effective concentration of CF_3

radicals. The use of large reaction zone was reported to improve the selectivity of $C_{70}(CF_3)_{10}$ synthesis in the flow-tube reactor, since less $C_{70}(CF_3)_8$ impurity was produced under these conditions (larger reaction zone increases the residence time, thus favoring the production of higher PFMFs.[4] According to our discussion, the increase of the reaction temperature may shift PFMF composition both towards lower and higher degrees of addition depending on the interplay between concentration of CF_3 radicals and the rate of the fullerene and PFMFs transport from the cold zone. The experimental data show that increase of the reaction temperature shifts the average composition of PFMFs towards lower number of addends; this can be explained by the decrease of the residence time due to faster sublimation rates (both at atmospheric pressure[10] and at *ca.* 5 bar of CF_3I[8]).

VII.2.3. Controlling the Selectivity of Fullerene Trifluoromethylation

Multiple additions to fullerenes are notoriously difficult to control. Since fullerenes are large non-aromatic networks of double bonds, it is not surprising that multiple radical additions to such compounds give rise to large number of compositionally and isomerically different products. It is logical to assume that the addition of CF_3 radical(s) to such molecular systems is either an induction-free process or the induction barrier is very small (too small to allow for a preferential formation of a PFMF with a particular number of substituents). Under such conditions the number of CF_3 groups per cage in the PFMF product depends on the number of collisions of the fullerene molecule with CF_3 radicals before it leaves the reaction zone. We assume that fullerene trifluoromethylation by CF_3I is most likely to occur through the following steps: i) formation of $CF_3\cdot$ radical by CF_3I dissociation; ii) reaction of fullerene with $CF_3\cdot$ forming an open-shell PFMF molecule; iii) reaction of this open-shell molecule with CF_3I molecule (or a less likely reaction with $CF_3\cdot$ radical), forming a closed-shell PFMF). However, as the number of CF_3 substituents attached to the fullerene cage increases, the probability of the reaction of this PFMF with CF_3 radical is likely to decrease due to shielding and effective deactivation of the substituted part of the fullerene molecule (the "sticking coefficient" for $CF_3\cdot$ reaction will be lower as compared to the reaction with bare-cage fullerene). For highly substituted PFMFs the probability of CF_3 addition should become small enough to prevent further trifluoromethylation. Such reaction regime can be called "exhaustive".

To the best of our knowledge, the "exhaustive" trifluoromethylation regime has not been practically realized up to date. For example, the highest reported PFMFs derivatives of C_{60} ($C_{60}(CF_3)_{16}$ and $C_{60}(CF_3)_{18}$[14]) have not been prepared selectively (we also reported mass-spectroscopic evidence for the formation of even higher PFMFs in various high-

temperature trifluoromethylation reactions).[15] The probable explanation for this is a transport of the higher PFMFs from the hot reaction zone to the cooler region of the reactor via sublimation (in the flow-tube system or in the sealed ampoule) before they can be "exhaustively" trifluoromethylated. It is well established that higher PFMFs have lower sublimation temperatures than lower PFMFs.[10] For example, we found that isomer 3 of $C_{60}(CF_3)_{10}$ starts subliming at *ca.* 250 °C versus *ca.* 500 °C for C_{60} (the sublimation experiments were carried out under dynamic vacuum in the hot-plate reactor, see below). We also observed a similar difference in sublimation temperature between C_1-$C_{70}(CF_3)_{10}$ and C_{70}. The sublimation temperatures of PFMFs with similar number of substituents (6-8; 10-12; etc.) is likely to be similar; thus the removal of higher PFMFs from the hot zone via sublimation is unlikely to yield a truly selective and highly tunable method for fullerene trifluoromethylation. In other words, although the reaction temperature was reported to shift the product distribution of fullerene trifluoromethylation (higher reaction temperature leads to the shift towards lower PFMF derivatives), certain narrow ranges of compositionally different PFMFs are produced. The preparation of C_1-$C_{70}(CF_3)_{10}$[4] may be considered as a very rare example of a selective trifluoromethylation procedure that uses transport of the PFMF product form the reaction zone.

Based on this discussion, a conclusion can be made that mixtures of compositionally different PFMFs should be generally produced during fullerene trifluoromethylation. However, in a situation when the probability of fullerene collision (and hence, reaction) with CF_3 radical is small, the Fullerene$(CF_3)_2$ product should be produced selectively (albeit with low fullerene conversion). In other words, in such regime a considerable portion of the bare-cage fullerene remains unchanged; however, some portion of it is converted into Fullerene$(CF_3)_2$ with high selectivity. We can call such situation a "low conversion" regime. This is the only regime of fullerene trifluoromethylation that should selectively yield Fullerene$(CF_3)_2$ product. To the best of our knowledge, this regime has not been realized in experimentally.

VII.2.4. Hot-Plate Reactor Design and Functions

The fullerene trifluoromethylation is usually carried out either in flow-tube reactors or in sealed ampoules. Good results were achieved using both of these methods (selective syntheses of C_1-$C_{70}(CF_3)_{10}$[4] in flow-tube reactor and S_6-$C_{60}(CF_3)_{12}$[5] in sealed ampoules); however, only limited number of parameters can be easily changed for the purpose of process study and/or optimization. Specifically, flow-tube reactor allows one to easily adjust the reaction temperature and the size of the hot zone (by using tube furnaces of different length); however, using this reactor with gas pressures different from atmospheric would be challenging since it would require a complex gas-handling system. Trifluoromethylation in sealed ampoules is ideally suited for smaller-scale experiments at higher pressure of CF_3I. The ampoules used for this purpose have a section that is kept at room temperature and contains the liquefied CF_3I (hence the higher pressure of CF_3I which is equal to ca. 5 bar, or saturated vapor pressure of CF_3I, under these conditions[16]). The presence of liquefied CF_3I ensures that its consumption during the course of the reaction does not lead to a large change in the reagent pressure (which would be difficult to achieve otherwise due to small internal volume of the ampoule). Although in principle the pressure of CF_3I in such ampoule can be controlled to some extent by controlling the temperature of its "cool" section,[16] it would still make lower pressures (below 100-200 torr) difficult to obtain. Moreover, the scale-up of such experiments is challenging since the small diameter of the glass tube (and hence small capacity) is required in order to ensure that the ampoule has sufficient strength to withstand the high internal pressure.

The conclusion can be drawn that the flow-tube reactor or sealed ampoules are not satisfactorily for complete control over a large number of reaction parameters. In order to study the process of fullerene trifluoromethylation in detail, we should be able to change

different parameters of the process (gas pressure and composition, reaction temperature, hot zone geometry) independently, so that the effects of these parameters on the distribution of PFMF products can be revealed. Then this information can be used to optimize the processes of fullerene trifluoromethylation; for example, the realization of the selective synthesis of Fullerene$(CF_3)_2$ (using "low conversion" regime).

In order to overcome (at least partially) the limitations of the reactors described above, we designed and built a specialized "hot-plate" reactor shown in Figure VII.1.I (gas-handling part of the reactor is omitted for clarity; see experiment section for technical details). The fullerene powder is placed on the bottom of the quartz thimble which is connected via a compression joint to a ballast volume (ca. 1 L spherical vessel) which is connected through a Teflon valve to a gas-handling system with a pressure monitoring capability (it is equipped with a capacitance 0-1000 torr pressure transducer). The ballast volume is also equipped with an additional compression joint that allows one to position additional hardware in the vicinity (or in contact) with the fullerene sample: i) thermocouple can be used to measure the temperature of the fullerene sample directly; ii) water-cooled cold finger condenser can be positioned at the various distances from the fullerene sample allowing one to change the dimensions of the hot zone (see Figure VII.1.II); iii) gas injection tube can be used to introduce a flow of CF_3I reagent (see Figure VII.1.III; in this case the excess of the reagent is vented and hence only ambient pressure reactions can be expored). The quartz thimble is inserted into a special plate furnace, so that the bottom of the quartz thimble is in contact with its "hot" plate (hence the name of the reactor). The plate furnace has a permanently installed thermocouple in order to monitor its temperature (see Figure VII.1.I). In order to achieve a better control of the size of the hot zone the heated plate of the furnace has a layer of heat insulation (spacer) with a cooled brass plate on top (the copper worm with a circulating water is soldered to it). The thickness of the spacer (made of refractory brick or fused silica wool) can be changed; it is designated as L_{spacer}. This allows one to adjust

the size of the hot zone by using spacers of different size (10 and 50 mm spacers were used in this work).

During preliminary tests we found that there is a large temperature difference between the hot plate ($T_{hot\ plate}$) of the furnace and the internal surface of the bottom of the quartz thimble ($T_{hot\ zone}$). Using the measurements with internal thermocouple and calibration experiments when we observed melting of the small samples of lead (m.p. = 327 °C) and tellurium (m.p. = 450 °C) we found that this difference changes from ca. 90 °C (at $T_{hot\ plate}$ = 400 °C) to *ca.* 150 °C (at $T_{hot\ plate}$ = 700 °C). Since it is not always convenient to use internal thermocouple in every experiment due to its contamination with reaction products and difficulty of performing quantitative tests (see below), we only monitored $T_{hot\ plate}$ during most of the experiments. $T_{hot\ zone}$ was calculated based on $T_{hot\ plate}$ and our calibration data. We also found that at least 10 °C temperature variation exists between the center and the outer sides of the bottom of the quartz thimble (at $T_{hot\ plate}$ = 600 °C and L_{spacer} = 10 mm). This variation is likely to be caused by the walls of the quartz thimble. $T_{hot\ plate}$ parameter is used throughout the work since it has a better defined value (it is measured directly in all reported experiments).

The reactor of such design is suitable for studying the effects of different reaction parameters. A wide range of CF_3I pressures can be used (1-800 torr) when the reactor is used without enforced gas flow (the large, 23 mm internal diameter of the quartz thimble ensures that natural convective mixing is unrestricted; see discussion of the flow-tube experiments below). The presence of the ca. 1 L ballast volume makes pressure variations due to gas consumption during the course of the reaction virtually negligible. This reactor is capable of using different gas mixtures (CF_3I/N_2 mixtures were prepared and used in this reactor during this work).

The gas injection tube can convert the hot-plate reactor for operation in the enforced gas-flow regime (see Figure VII.1.III). The atmospheric gas pressure (which is 640-630 torr at the elevation of our laboratory) is maintained under these conditions, in other

words, the excess gas is vented through an oil bubbler. It is notable that test experiments did not show any significant difference between the results (product distribution and fullerene conversion) produced with enforced CF_3I flow and in the isolated hot-plate reactor when the same pressure of CF_3I was maintained (other process parameters were kept constant). The results of these experiments suggest that the natural convective mixing of gas is sufficient to replenish the atmosphere of the hot zone and hence the enforced flow is not necessary in this reactor geometry. The absence of continuous gas flow also minimizes the amount of CF_3I required, hence improving the efficiency of the trifluoromethylation process.

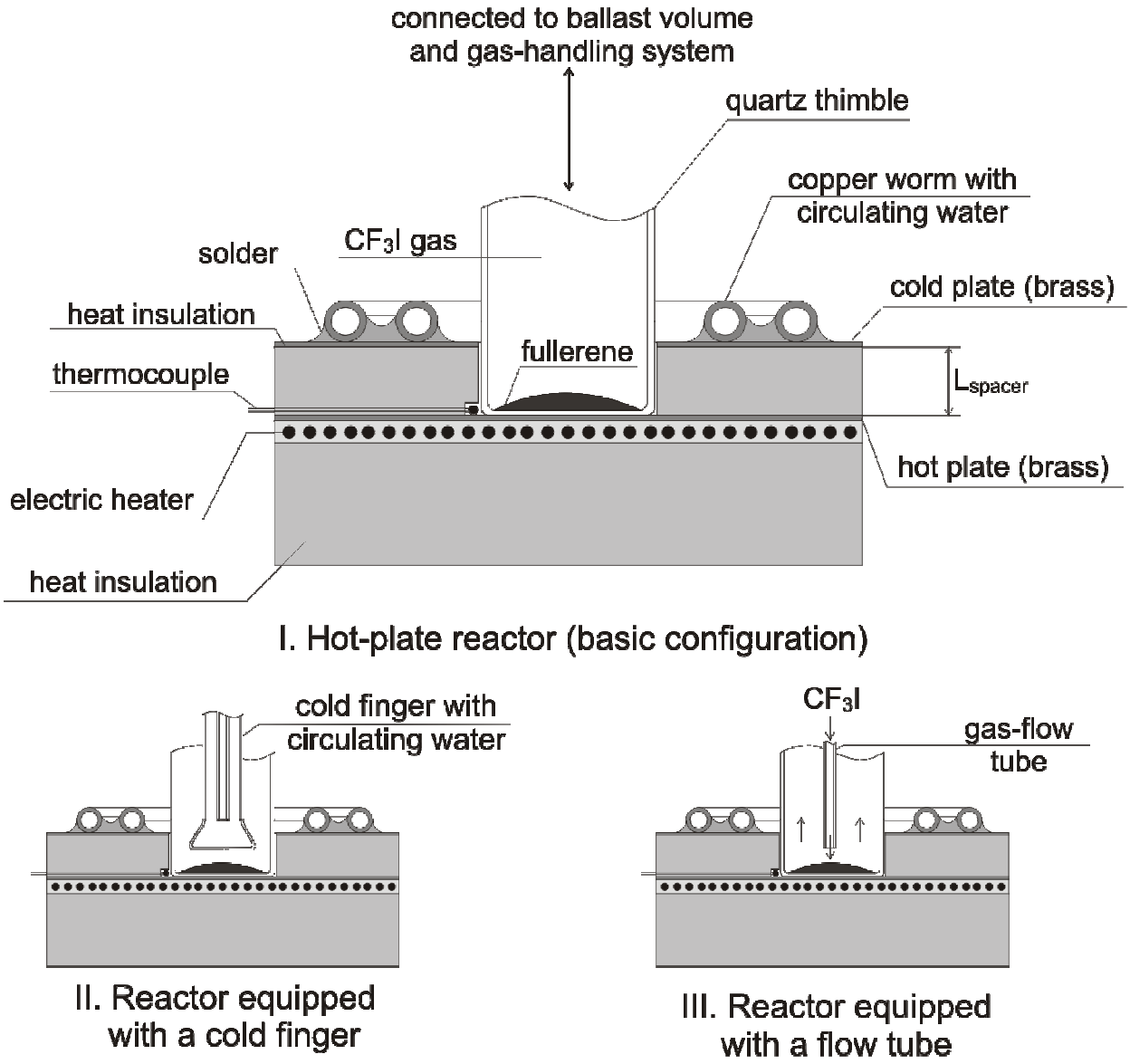


Figure VII.1. I. Basic configuration of the hot-plate reactor. II. Reactor equipped with an internal water-cooled cold finger cooler. III. Reactor equipped with an internal gas-flow tube for experiments with induced CF_3I flow.

VII.2.5. The Effect of the Reaction Parameters on the Distribution of PFMFs Formed in Hot-Plate Reactor

In order to ascertain the effects of various parameters on the trifluoromethylation process one must be able to perform a reliable comparison of the experiments (*i.e.*, compositions of the resulting PFMF products and fullerene conversion). An accurate metrological approach was developed to satisfy these requirements: i) a small and nearly constant size of fullerene samples (4.4±10% mg) was used for all exploratory experiments; ii) a charged hot-plate reactor was brought in contact with preheated furnace in order to minimize the variations of heating regime between experiments; iii) the products of the synthesis (the sublimate and the unsublimed residue) were quantitatively collected (see experimental section for the details of the procedure). HPLC analysis was used as the main analytical tool since it gives a reliable account of the composition and relative concentrations of the products (proportional to their extinction coefficients) formed in trifluoromethylation experiments. Different PFMFs and unreacted fullerene are identified by their retention times (which are generally inversely proportional to the number of CF_3 groups attached to a PFMF); this allows us to reliably compare the average composition of the crude products (*i.e.*, average number of CF_3 groups carried by a fullerene cage). APCI-MS and ^{19}F-NMR spectroscopy were also used for analysis of some samples in order to validate the results of HPLC analysis.

We performed several repetitions of the different trifluoromethylation experiments in order to establish reproducibility. We found that the composition of PFMFs produced in these experiments shows minimal variations, see Figure VII.2. However, the degree of fullerene conversion displays a more significant variation from experiment to experiment

(a possible explanation is the variation in the distribution of fullerene sample across the bottom of the quartz thimble, leading to different thickness of the fullerene layer).

During our experiments in hot-plate reactor we found that a small portion of the fullerene degrades during the high-temperature reaction (a small, *ca.* few percent, portion of the product was not soluble in toluene); this part of the product was not analyzed (it is likely to be polymerized fullerene or some carboneceous material).

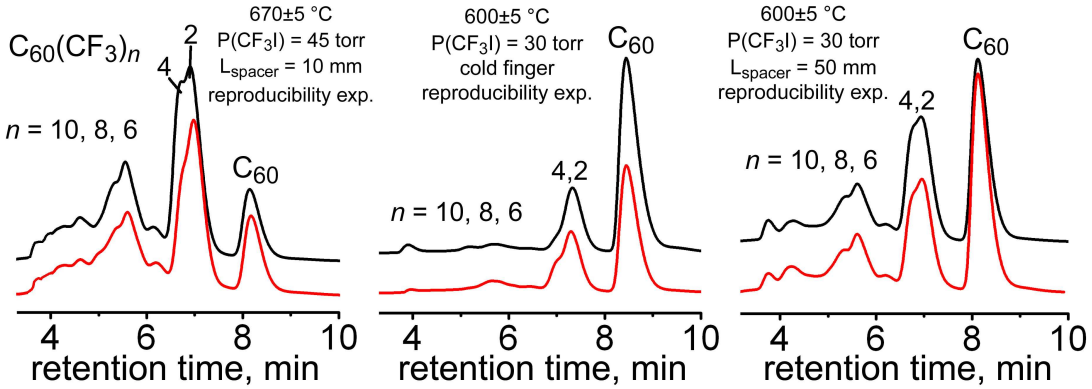


Figure VII.2. Experiments on the reproducibility of trifluoromethylation in hot-plate reactor (all experiments were performed for 30 minutes). The red and black lines are the HPLC traces corresponding to different repetitions.

A. Effect of CF_3I Pressure. The first set of experiments (set A, see Table VII.1) was performed with C_{60} at $T_{hot\ plate}$ = 600 °C ($T_{hot\ zone}$ = *ca.* 480 °C) with 10 mm spacer between the hot plate and cold plate of the furnace (L_{spacer} = 10 mm); 30 minutes reaction time was chosen. Pressure drop during the course of trifluoromethylation was negligible (1-2% of the initial reading) due to incorporation of the ballast volume (ca. 1.5 L) into the design of the hot-plate reactor. A series of different pressures of neat CF_3I was used: 5, 15, 30, 45, 135, and 410 torr. The HPLC traces of the resulting products were stacked into 3D waterfall graph in order to achieve a better visualization and easier comparison of the data (see Figure VII.3A). The waterfall plot clearly reveals a very strong effect that the pressure of CF_3I has on the composition of the reaction products. Products formed at 5 and 15 torr of CF_3I are mostly comprised of $C_{60}(CF_3)_2$ and unreacted C_{60}. As the pressure of CF_3I increases, the average composition of the reaction products increases

(the conversion of C_{60} starting material improves as well). This result is fully consistent with our description of the heterogeneous fullerene trifluoromethylation (see above). The increase in the pressure of CF_3I increases the concentration of CF_3 radicals and the residence time, thus increasing the number of CF_3 groups added to the fullerene during trifluoromethylation. The selective formation of $C_{60}(CF_3)_2$ along with a low conversion of C_{60} that takes place at lower pressure of CF_3I (5 and 15 torr) is consistent with the realization of "low conversion" regime. To the best of our knowledge, this is the first reported example of the selective preparation of Fullerene$(CF_3)_2$.

Due to the strong influence of the CF_3I pressure on the product composition we decided to explore the effects of other reaction parameters by running series of experiments at the same CF_3I pressures as in the experiments described above; a single parameter under investigation is changed between two different sets of such experiments, see Figure VII.4 and Table VII.1. The set A is chosen as the main reference point during the discussion of these experiments (see Figure VII.4A).

Table VII.1. Reaction conditions used for different trifluoromethyaltion experiments.

exp.	$T_{hot\ plate}$, °C	$T_{hot\ zone}$, °C)	L_{spacer}, mm	reaction time, min
A	600	*ca.* 480	10	30
B	600	*ca.* 480	10	90
C	550	*ca.* 450	10	30
D	670	*ca.* 530	10	30
E	600	*ca.* 480	50	30
F[a]	600	*ca.* 460	10	30
G[b]	600	*ca.* 480	10	30

[a] Cold finger is used. [b] Copper powder (*ca.* 400 mg) was mixed with fullerene samples.

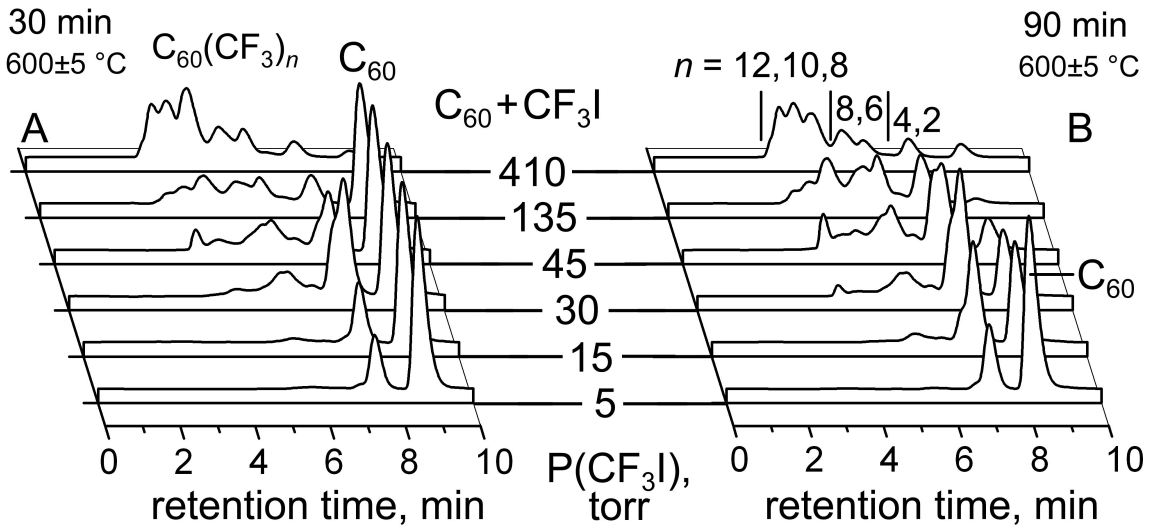


Figure VII.3. 3D waterfall plots of the normalized HPLC traces of the products of C_{60} trifluoromethylation in hot-plate reactor under different pressure of CF_3I. Sets A and B were performed under the same conditions (see Table VI-1) except for the reaction time (30 min for experiments A and 90 min for experiments B).

B. Effect of Reaction Time. The series B is an exact repeat of series A except for a longer reaction time (90 minutes; see Figure VII.4B). The 3D HPLC plot shows that longer reaction time significantly improves the conversion of C_{60}; it also slightly increases the average PFMF composition (the average number of CF_3 groups per fullerene cage in the reaction products). For example, the HPLC traces of the reaction mixtures obtained using 15 torr of CF_3I in 30- and in 90-minute reactions (see Figure VII.4B) clearly demonstrate that the second product contains a considerably higher amount of $C_{60}(CF_3)_4$. This dependence between the reaction time and the composition of the products shows that the transport of PFMFs from the hot zone is not very fast; in other words, some of the PFMFs formed after 30 minutes reaction remain within the hot zone and are trifluoromethylated further when the reaction is allowed to go for a longer time. It is most likely that these PFMFs are present in solid phase within the limits of the hot zone. This conclusion is supported by other experiments (performed under several different pressures of CF_3I) where we analyzed the sublimed products and

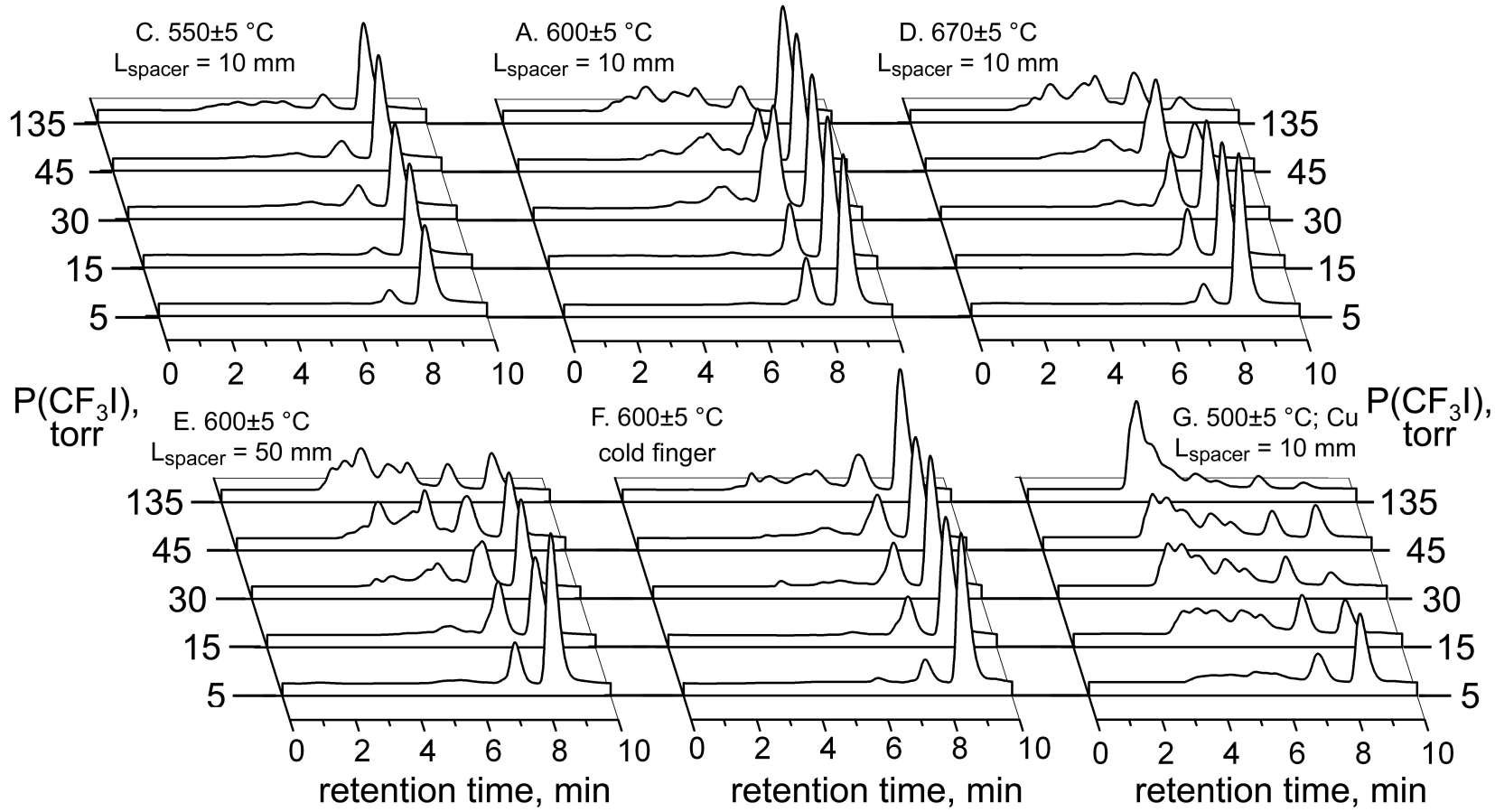


Figure VII.4. 3D waterfall plots of the normalized HPLC traces of the products of C_{60} trifluoromethylation in hot-plate reactor under different conditions (see Table VII.1).

the solid residue left on the bottom of the quartz thimble separately. We found that the solid esidues always contain some trifluoromethylated products; the sublimates, on the other hand, showed the presence of unreacted C_{60} (except for very high CF_3I pressures, *i.e.*, above 400 torr). These results lie in excellent agreement with our scheme of fullerene trifluoromethylation process (see above). They demonstrate that sublimation of both PFMFs and unreacted fullerene from the hot zone takes place; moreover, the presence of PFMFs in the solid phase in the hot zone strongly suggests that fullerene trifluoromethylation takes place on the surface of the solid fullerene/PFMF particles (and/or the condensation of PFMFs back within the volume of hot zone occurs).

C. Effect of Temperature. Sets C and D were performed using different reaction temperatures ($T_{hot\ plate}$ = 550 °C and 670 °C, see Figures VII.4C and VII.4D correspondingly, Table VII.1). The comparison of the HPLC plots corresponding to sets C, A, and D clearly demonstrates the strong effect of the reaction temperature on C_{60} conversion (at all pressures of CF_3I). This effect is possibly caused by the difference in the concentration of CF_3 radicals at these temperatures. In other words, the lower reaction temperature leads to lower concentration of CF_3 radicals and hence a lower trifluoromethylation rate (and lower conversion).

In order to compare the composition of PFMFs produced using different reaction temperatures we plotted the expansions of the individual HPLC traces without including the peak of C_{60} (see Figure VII.5). The top plot of Figure VII.5 shows such comparison between the products prepared at $T_{hot\ plate}$ = 550, 600, and 670 °C using 45 torr of CF_3I; it demonstrates that lower reaction temperature (compared with $T_{hot\ plate}$ = 600 °C as the main reference point) leads to a slight decrease in the amount of higher PFMFs. Higher reaction temperature ($T_{hot\ plate}$ = 670 °C) strongly decreases the amounts of $C_{60}(CF_3)_{10,8,6}$ while slightly increasing the concentration of $C_{60}(CF_3)_4$ (see top trace of the top Figure VII.5). We suggest that these effects could be considered as a manifestation of an interplay between the two variables that have an opposite effect on the average

composition of the trifluoromethylated products: concentration of CF_3 radicals (that increases at higher temperature and leads to higher average composition) and the transport rate (that increases at higher temperature and leads to lower residence time and lower average composition).

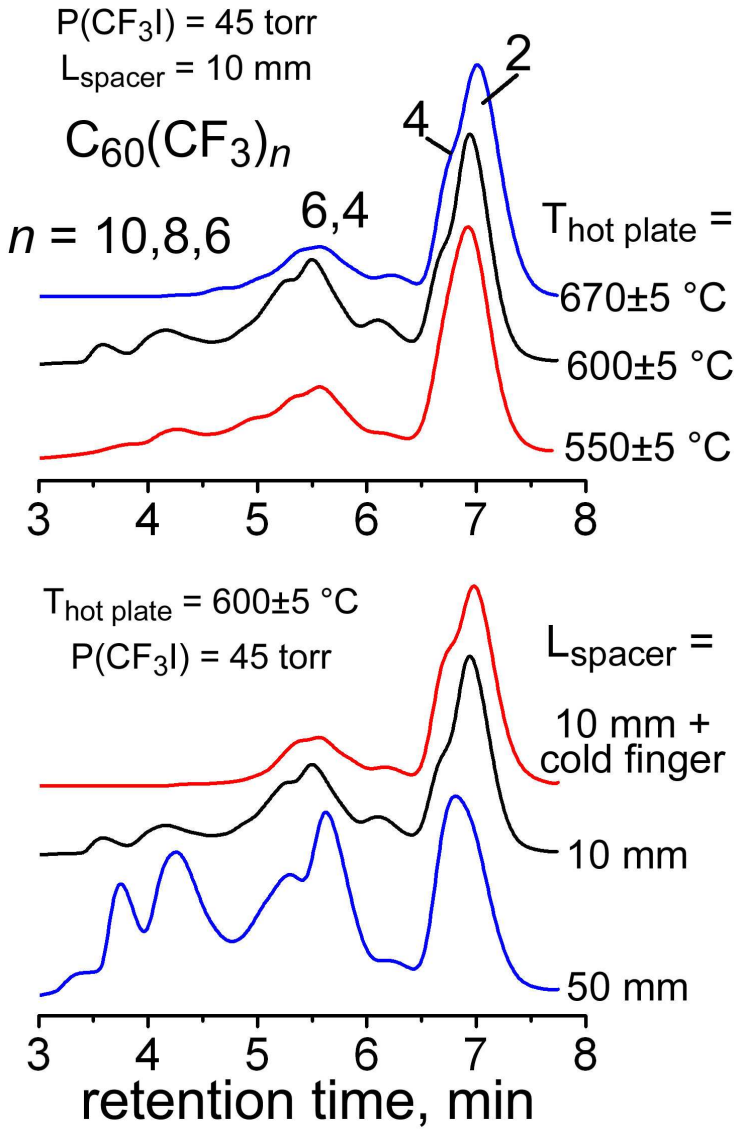


Figure VII.5. Comparison of the trifluoromethylation experiments performed at 45 torr of CF_3I at different temperatures (top figure) and different sizes of the hot zones (bottom figure).

D. Effect of the Hot Zone Size. Set E was carried out with L_{spacer} = 50 mm (versus L_{spacer} = 10 mm used for other experiments), and set F was done with a cold finger installed in the close proximity to the hot zone (*ca.* 5 mm distance between fullerene

sample in the hot zone and the tip of the cold finger was maintained). Other reaction conditions were kept identical to the set A (see Table VII.1, Figure VII.4A). The 3D HPLC plots corresponding to the sets E and F are shown on Figures VII.4E and VII.4F, correspondingly.

The experiments performed with large hot zone (set E) show better conversion of C_{60} than the reactions performed with the same pressures of CF_3I but with regular size of the reaction zone (Figure VII.4E vs. Figure VII.4A). A slight irregularity of C_{60} conversion (see Figure VII.4E, 15 torr trace) is likely due to the variation of this parameter that we observed during multiple repeats of the experiments at the same conditions (see above and Figure VII.2). This effect may be caused by the different thickness of the fullerene layer (and hence different surface area of fullerene); despite our efforts to make the loading of the hot-plate reactor as reproducible as possible, the variations of fullerene conversion were still observed (see above). The reactions done with the cold finger demonstrate lower conversion than the experiments done with the regular size of the reaction zone (Figure VII.4F vs. Figure VII.4A). This effect is consistent with the changes of the residence time due to the size of the hot zone. In other words, large hot zone leads to longer residence time and hence a more complete reaction; smaller reaction zone causes an opposite trend.

The effect of the hot zone size on the PFMF composition is very strong (see bottom part of Figure VII.5). It is clear that the large reaction zone (L_{spacer} = 50 mm) causes a strong shift of the average PFMF composition towards higher number of CF_3 groups. The decrease of the size of the hot zone causes an opposite effect – the yield of PFMFs with larger number of CF_3 groups decreases. This effect is fully consistent with the change of the residence time: longer residence time (achieved in the reactor with a large hot zone) leads to higher average composition of PFMFs; shorter residence time (small hot zone) causes an opposite effect.

The changes in the geometry of the reactor (increase of the L_{spacer} from 10 mm to 50 mm) and the introduction of the cold finger is likely to have an effect on $T_{hot\ zone}$ even though $T_{hot\ plate}$ is kept unchanged. We carried out a direct measurements of $T_{hot\ zone}$ using an internal thermocouple and found that the presence of the cold finger lowers it by ca. 20-30 °C (compared to the reactor operated with the cold finger; 10 mm spacer was used for these experiments). The increase of the size of the spacer is likely to cause a slight increase of $T_{hot\ zone}$. However, the effect of the size of the hot zone on the composition of the trifluoromethylated products is too strong to be caused by the changes in $T_{hot\ zone}$ alone (based on the results of the above study of the effect of the reaction temperature). Hence, our interpretation of the effect of the hot zone size due to changes in the residence time is probably valid.

E. Effect of the Inert (Buffer) Gas Addition. The introduction of the inert buffer gas (15 torr of N_2 to the 15 torr of CF_3I) led to a massive decrease in the conversion, with unreacted C_{60} comprising at least 95% of the product (according to the HPLC trace integration, HPLC trace not shown) as compared to the experiments performed with either with 15 or 30 torr of pure CF3I under otherwise identical conditions ($T_{hot\ plate}$ = 600 °C, L_{spacer} = 10 mm). A small amount of $C_{60}(CF_3)_2$ was also detected in the product (*ca.* 5%), which is consistent with the realization of the "low conversion" regime due to low concentration of CF_3 radicals. This direction of the study was not pursued further due to very poor fullerene conversion.

F. Effect of the Copper Metal. Copper powder is commonly used in literature studies in order to facilitate the dissociation of perfluoroalkyl iodides; for example, this technique was used for the preparation of some Fullerene$(C_2F_5)_n$ derivatives. However, it has not been used for trifluoromethylation of fullerenes. We decided to investigate the effect of copper metal present in the hot zone on this process in hot-plate reactor.

In control experiments we found that decomposition of pure CF_3I at 45 torr pressure (either with or without C_{60} present) becomes clearly visible at $T_{hot\ plate}$ = 550 °C ($T_{hot\ zone}$

= ca. 450 °C) due to formation of iodine. The introduction of powdered copper metal changed the course of CF_3I decomposition due to formation of copper iodide (scavenging of iodine). We found that formation of copper iodide, and hence the dissociation of CF_3I, begins at $T_{hot\ plate}$ = 430 °C ($T_{hot\ zone}$ = ca. 320 °C), both with and without C_{60} fullerene. These results confirmed that copper metal facilitates the decomposition of CF_3I.

We performed a series of experiments where we mixed C_{60} sample with a large excess (ca. 400 mg) of powdered copper metal and reacted this mixture with CF_3I in the hot-plate reactor (set G, see Table VII.1). The corresponding HPLC plot is shown on Figure VI-4G. Despite low reaction temperature ($T_{hot\ plate}$ = 500 °C) the presence of copper leads to very high conversion; we found that without copper C_{60} is practically unchanged under otherwise identical conditions. Even at $T_{hot\ plate}$ = 550 °C the conversion of C_{60} without copper is very low (see Figure VII.4C). The presence of copper also demonstrates a very strong effect on the average composition of PFMFs by shifting it to compounds with large number of CF_3 groups. We suggest that these effects (the formation of PFMFs with larger number of CF_3 groups and improved conversion even at low reaction temperature) are caused by the generation of a high concentration of CF_3 radicals due to reaction of CF_3I with copper. Low reaction temperature also leads to low rate of the C_{60} and PFMF sublimation from the hot zone; thus, the residence time should also increase (as compared to the experiments performed at $T_{hot\ plate}$ = 600 °C without copper, see Figure VII.4A). Both of these effects should lead to higher conversion and higher average composition of PFMF products.

The increase of the reaction temperature to $T_{hot\ plate}$ = 600 °C (in the presence of copper) lead to an increase of C_{60} conversion (the average composition of the products largely stayed unchanged, HPLC traces are not shown). However, at $T_{hot\ plate}$ = 600 °C the reaction was very vigorous and led to contamination of the ballast volume of the reactor (with a fine powder of CuI) and extensive caking of the solid residue in the hot zone. Due to these technical problems and similarity of the results to the experiments done at T_{hot}

$_{plate}$ = 500 °C, only experiments with 5 and 15 torr of CF_3I were performed at $T_{hot\ plate}$ = 600 °C.

G. Effects of the Reaction Scale. In order to study the effect of the reaction scale on PFMF composition and conversion we performed several experiments using different amounts of the initial fullerene sample (all other reaction conditions are kept the same). The results of this study are shown on Figure VII.6; the HPLC traces are normalized so that the peaks of C_{60} have the same intensity. These experiments clearly demonstrate that

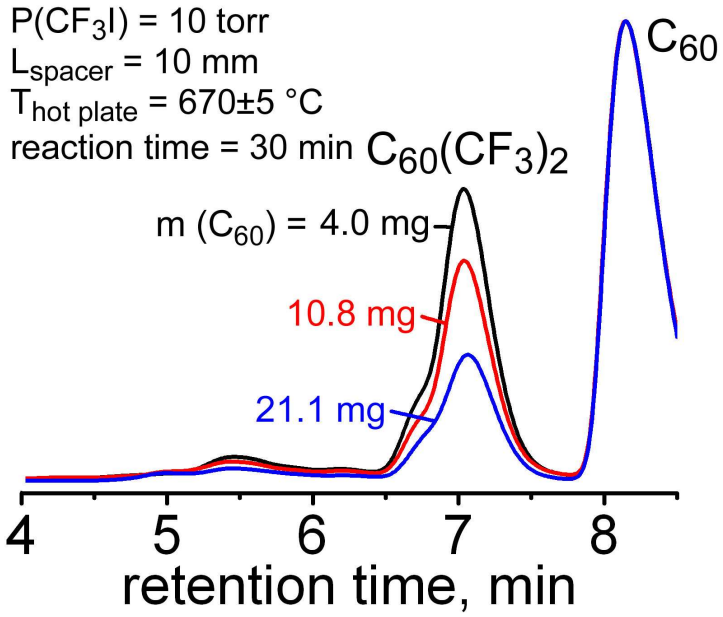


Figure VII.6. Comparison of the trifluoromethylation experiments performed with different sizes of the starting fullerene material

as we increase the size of the fullerene sample (from 4.0 mg to 10.8 mg to 21.1 mg) the yield of the PFMFs drops down. When we increased the size of C_{60} sample further to 105 mg we only obtained ca. 10 mg of $C_{60}(CF_3)_2$ product, which corresponds to 8% yield. However, the integration of the HPLC trace (taking into account different extinction coefficients of C_{60} and $C_{60}(CF_3)_2$, see experimental section) of the reaction product prepared under identical conditions from 4.0 mg of C_{60} gives a much higher yield of $C_{60}(CF_3)_2$ of ca. 40%. During the large-scale repeat of this experiment (ca. 100 mg of C_{60} was used) we observed that iodine crystals were forming on the walls of the quartz

thimble just outside of the hot zone; compared to small-scale reactions carried out under identical conditions the amount of iodine was much larger. We hypothesized that the decrease of C_{60} conversion incurred during reaction scale-up may be due to the excess of iodine vapors present in the reaction zone (which would decrease the concentration of CF_3 radicals present there). In order to check this hypothesis we repeated several large-scale experiments with a cold finger condenser positioned 20 mm above the fullerene sample as an iodine trap (putting it outside of the hot zone). We found that the presence of the cold finger increases the yield of PFMFs dramatically. Several experiments performed with this reactor geometry yielded ca. 35-40% of $C_{60}(CF_3)_2$ (65-150 mg size of the fullerene sample and 2 hour reaction time was used), see Figure VII.7. This shows that the iodine has to be removed from the hot zone of the reactor by means of the cold finger condenser in order to prevent the decrease of conversion during the scale-up of the synthetic procedure.

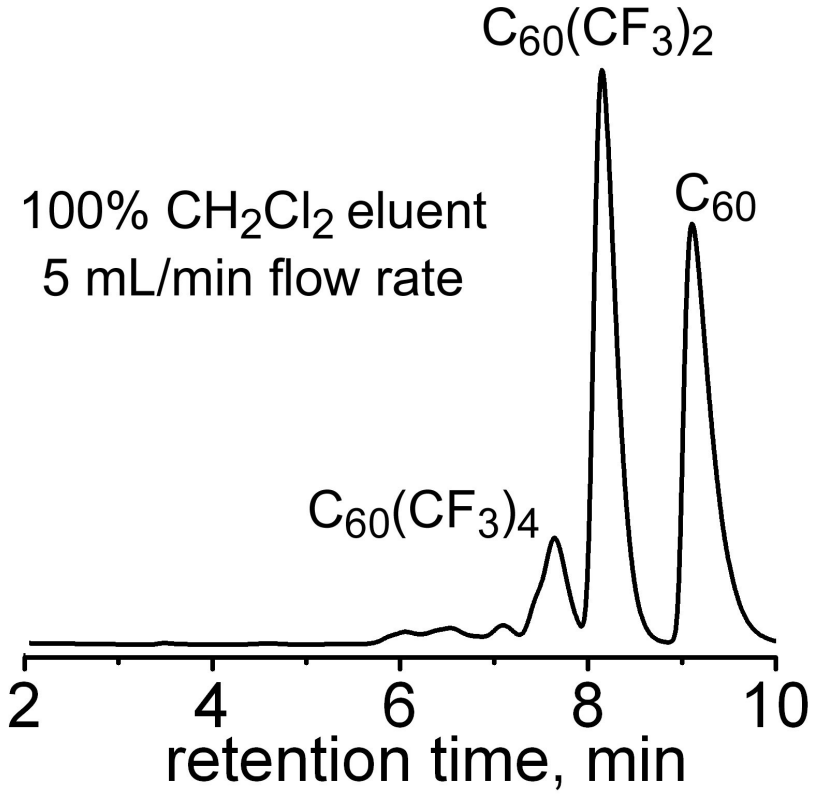


Figure VII.7. Large-scale selective synthesis of $C_{60}(CF_3)_2$ (100 mg C_{60} sample was used).

VII.2.6. Large-Scale Preparation and Purification of $C_{60}(CF_3)_2$

We performed several reactions with large samples of C_{60} using the optimized reaction conditions from Section VII.2.5.G ($P(CF_3I)$ = 10.0 torr; $T_{hot\ plate}$ = 670 °C, L_{spacer} = 10 mm). Cold finger was used in all these experiments in order to trap the iodine (distance between the tip of the cold finger and the surface of the fullerene sample was 20 mm). Different sizes of fullerene sample were used (65-150 mg, see Section VII.2.5.G); we observed that the conversion drops slightly with the increase of the amount of the starting material. This effect is likely to be due to the decrease of the surface area of the fullerene available for trifluoromethylation. We found that ca. 100 mg-sample size is optimal for our hot-plate reactor with thimble diameter of 23 mm (internal diameter), giving $C_{60}(CF_3)_2$ with ca. 40% yield. We note here, that the diameter of the quartz thimble, and hence the capacity of the reactor can be easily increased if needed. In order to increase the conversion in the large-scale reactions we increased the reaction time to 2 hours.

We found that PFMFs can be extracted from the unreacted C_{60} using C_6F_6 (fullerene is practically insoluble in it). Soxhlet extraction may be used for efficient processing of large amounts of material (which will also minimize the amount of C_6F_6). This C_6F_6 extract contains $C_{60}(CF_3)_2$ with 80+% molar purity (as determined by ^{19}F-NMR and confirmed by HPLC). This approach therefore can be used as an HPLC-free procedure for the selective preparation of $C_{60}(CF_3)_2$ with moderate purity.

In order to obtain a 99+% pure $C_{60}(CF_3)_2$ HPLC purification is necessary. We found it the most practical to extract the crude product using dichloromethane, then separate this crude mixture using 100% dichloromethane as an HPLC eluent (using Cosmosil BuckyPrep column). The use of dichloromethane elution is critical for the successful

separation since pmp-$C_{60}(CF_3)_4$ peak overlaps with $C_{60}(CF_3)_2$ when toluene (or toluene/heptane) eluent is used, see Figure VII.8.

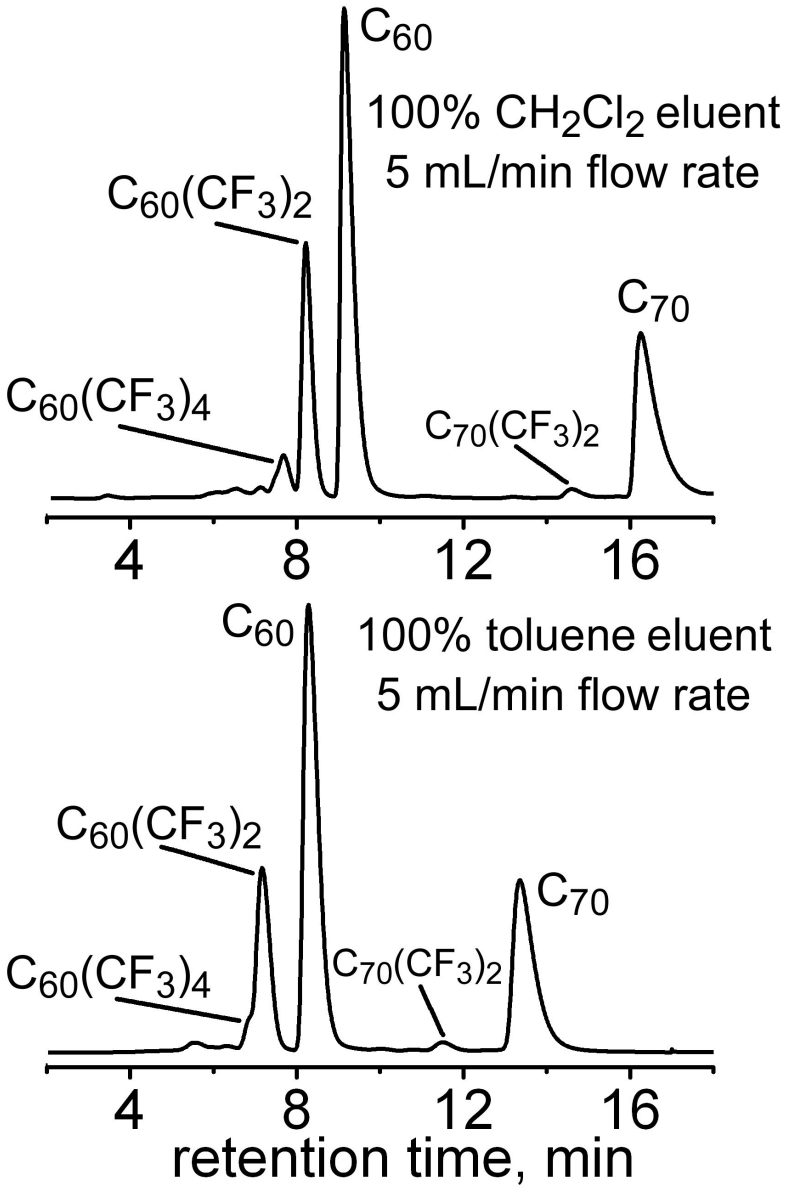


Figure VII.8. Large-scale selective synthesis of $C_{60}(CF_3)_2$ from fullerene extract. Top figure shows the HPLC trace acquired using dichloromethane eluent; bottom figure shows the HPLC trace acquired using toluene eluent (same crude product is analyzed in both cases).

$C_{60}(CF_3)_2$ can also be selectively prepared from fullerene extract (instead of pure C_{60}), see Figure VII.8. Same reaction conditions as for selective trifluoromethylation of C_{60} were used ($P(CF_3I)$ = 10.0 torr; $T_{hot\ plate}$ = 670 °C, L_{spacer} = 10 mm, ca. 100 mg sample of

fullerene extract). The product showed a slightly lower conversion of fullerene. However, $C_{60}(CF_3)_2$ was prepared with 80+% molar purity (relative to other PFMFs; the purity was measured using ^{19}F-NMR spectoscopy) and ca. 30% yield. We found that trifluoromethylation of C_{60} is preferred under these conditions as compared to C_{70} (only a very small amount of $C_{70}(CF_3)_2$ is formed, see Figure VII.8). Combined with C_6F_6 extraction this method provides a cheap and efficient way of producing 80+% pure $C_{60}(CF_3)_2$ without the use of HPLC purification.

VII.3. Conclusions

In this work we applied our general methodology to the study of the heterogeneous high-temperature trifluoromethylation of C_{60} fullerene. A dedicated metrology was developed in order to reliably compare the results of experiments performed under different conditions; thus we were able to quantitatively evaluate the distribution of different PFMFs and fullerene conversion. We also suggested the first general scheme of heterogeneous fullerene trifluoromethylation; we found that it lies in agreement with all experimental data (a specially designed hot-plate reactor was used in order to perform the carry out trifluoromethylation experiments under sufficiently well-controlled conditions). Moreover, using this scheme we were able to predict the possibility of the selective preparation of Fullerene$(CF_3)_2$ derivatives using what we called "low-conversion" regime. The hot-plate reactor allowed us to achieve the first experimental realization of selective preparation of $C_{60}(CF_3)_2$ independently of the reaction scale.

Such success of this work can be largely attributed to the use of our general methodology for the investigation of this particular system providing yet another illustration to its power.

VII.4. Experimental Details

Reagents and Solvents: HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), CF_3I, C_2F_5I, *i*-C_3F_7I (SynQuest Labs), and copper powder () were used as received.

Instruments. HPLC analysis and separation was done using Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). APCI mass-spectra were recorded on 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL/min flow, CF sample injected as solution in toluene).

Hot-plate reactor. The plate furnace of the reactor is built locally. The magnesia refractory brick is used as heat insulation (except for 10 mm spacer that is made of fused silica wool); the heating element from xxx hot plate is used as a heater (it is powered using Variac autotransformer). K-type thermocouples were used for all temperature measurements. Both the cold and the hot plate of the furnace are made of 1.25 mm brass. The thimble of the reactor is made of quartz tube (OD = 25 mm; ID = 23 mm); its total length is 150 mm (it has a bulge at 100 mm distance from the bottom in order to prevent it from being sucked into the ballast volume of the reactor). The thimble is attached to the ballast volume using Ace Glass compression joint with Viton O-ring. The ballast volume of the reactor is made of a 1 L pyrex glass flask equipped with two Ace Glass compression joint lying on the same axis, and a right-angle Teflon valve. The reactor is connected to the gas-handling system through this valve using 1/2" Cajon connector. The

gas-handling system is equipped with 0-1000 torr range Baratron (capacitance manometer) for pressure measurements.

Description of the typical experiment. A sample of starting material (3.9-4.9 mg of ground C_{60} or C_{70} straight or mixed with 400 mg of copper powder for Cu-experiments) was placed in the center of the quartz thimble of the hot-plate reactor. The reactor was evacuated, filled with a required pressure of perfluoroalkyl iodide, and isolated. The preheated plate heater/cooling plate assembly was put in place; thus the temperature ramp-up is very rapid and takes only 2-4 minutes. After 30 or 90 minutes the plate heater/cooling plate assembly was removed and the reactor was allowed to cool of for about 10 minutes. Then the thimble was removed and thoroughly washed with toluene; this solution was evaporated (in order to remove iodine) and dissolved in 10.0 mL of toluene (volumetric flask was used). Then a 500 μL sample of this solution was analyzed by HPLC (using 100% toluene as an eluent and 5 mL/min flow rate). The HPLC trace obtained in this fashion was normalized by the weight of the original fullerene sample prior to the construction of the 3D waterfall plots.

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Appendix

Table A.1. List of Abbreviations.

abbrev.	full name
CF(s)	chlorofullerene(s)
IPR	isolated pentagon rule
WI	weight increase
EA	elemental analysis
NMR	nuclear magnetic resonance
MS	mass spectrometry
FAB	fast atom bombardment
FI	field ionization
IR	infrared
XPS	x-ray photoelectron spectroscopy
UV-Vis	ultraviolet-visible spectroscopy
HT	high temperature
PIXE-NMP	particle induced X-ray emission/nuclear microprobe analysis
EMP	electron microprobe analysis
MALDI	matrix-assisted laser desorption/ionization
HPLC	high-performance liquid chromatography
TGA	thermogravimetric analysis
APCI	atmospheric pressure chemical ionization
ODCB	*ortho*-dichlorobenzene
CB	chlorobenzene

Table A.2. Crystal Data and Structure Refinements for $C_{60}Cl_6$, $C_{60}Cl_{10}$, and $C_{60}(C_2F_5)_5H$.

compound	$C_{60}Cl_6$	$C_{60}Cl_{10}$	$C_{60}(C_2F_5)_5H$
molecular formula	$C_{60}Cl_6$	$C_{60}Cl_{10}$	$C_{70}F_{25}H$
formula weight	933.30	1075.10	1316.74
crystal system	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	$C222_1$	$C2/m$
unit cell dimensions			
a (Å)	19.639(9)	9.9970(14)	14.0212(5)
b (Å)	17.258(10)	20.717(4)	14.5815(6)
c (Å)	40.11(2)	39.968(6)	20.3348(7)
α (deg)	90	90	90
β (deg)	90	90	109.163(2)
γ (deg)	90	90	90
temperature (K)	100	150	100
final R indices[a] [$I > 2\sigma(I)$]			
R_1	0.1000	0.0888	0.0635
wR_2	0.2598	0.2251	0.1580
goodness-of-fit on F_2	1.27	1.07	1.052

[a] $R_1 = (\sum \| F_o | - | F_c \|) / \sum | F_o |$; $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$.

A.3. UV-Vis Spectroscopy of C_{60} Chlorides

A. Instrumentation, Materials, and Sample Preparation. UV-vis spectra and extinction coefficients were measured using Varian Cary 500 spectrometer with digital resolution of 1 nm per data point. Tables A.3, A.4, and A.5 contain truncated UV-vis data with 5 nm spacing between datapoints. A sample of commercial C_{60} was used, with reported purity >99.5% (Term USA). It was annealed under air at +155°C for ca. 20 hours to remove traces of co−crystallized solvents. HPLC purified $C_{60}Cl_6$ (95% purity based on HPLC trace integration) and $C_{60}Cl_{10}$ (*ca.* 98% based on HPLC trace integration) were used. It was not possible to use heat treatment for removal of co-crystallized solvents from CFs due to a high probability of sample degradation. We also found that ca. 24 hours of drying under dynamic vacuum (0.01-0.005 torr) does not remove co-crystallized toluene from these compounds (its presence was detected by ^{1}H-NMR and ^{13}C-NMR). In order to solve this problem we developed a specialized drying cycle: 1) CF sample is dissolved in a minimum amount of HPLC grade CH_2Cl_2; 2) CH_2Cl_2 is removed under vacuum; 3) dry sample is kept under dynamic vacuum (0.01-0.005 torr) for ca. 3 hours. After two such cycles performed consecutively, only trace amounts of ^{1}H-impurities could be detected by ^{1}H-NMR (no CH_2Cl_2 or other solvents were detectable). 75% pure *o*-$C_{60}Cl_2$, 75% pure *p*-$C_{60}Cl_2$, and 99% pure $C_{60}Cl_4$ were used without drying (only their spectra in toluene were measured). All of these CFs were analyzed by HPLC both before and after UV−vis study to confirm the absence of decomposition.

B. UV-vis Spectra Measurements and Results. Several different concentrations were used to reliably record both short- and long-wavelength absorptions of CFs. The data are presented both in pictorial and numerical forms in the sections below. UV-vis spectra of *o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, and $C_{60}Cl_4$ were measured in toluene; UV-vis spectra of the

previously reported compounds which are likely to have the same structure are given too. UV-vis spectra of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ were measured both in toluene and in CH_2Cl_2.

Table A.3. UV-vis spectra of 75% *o*-$C_{60}Cl_2$ in toluene (C_n is concentration; $C_1 > C_2 > C_3 > C_4$).

λ, nm	***o*-$C_{60}Cl_2$, C_1, A.U.**	***o*-$C_{60}Cl_2$, C_2, A.U.**	***o*-$C_{60}Cl_2$, C_3, A.U.**	***o*-$C_{60}Cl_2$, C_4, A.U.**
800	-8.42E-04	-1.14E-03	-0.00312	-4.76E-03
795	0.00362	6.58E-04	0.0015	2.21E-03
790	0.00344	7.89E-04	1.26E-03	3.54E-05
785	0.00289	1.25E-03	-3.71E-04	-0.00192
780	0.0023	-9.57E-05	8.80E-05	-2.53E-03
775	0.00562	1.84E-03	0.00291	3.46E-03
770	0.00229	-1.14E-03	-1.23E-03	-3.21E-03
765	0.00262	8.88E-04	-1.89E-03	-7.41E-04
760	0.0056	8.63E-04	1.03E-03	6.77E-04
755	0.00464	2.43E-04	-3.70E-04	4.92E-05
750	0.00484	0.00248	5.05E-04	7.27E-04
745	0.00567	5.76E-04	-7.21E-04	-0.00173
740	0.00852	1.48E-03	0.00165	1.95E-03
735	0.00989	0.0022	9.75E-04	1.29E-03
730	0.01267	0.0019	2.91E-04	-1.10E-03
725	0.0198	4.21E-03	0.00223	3.04E-04
720	0.02661	4.62E-03	0.00122	4.64E-04
715	0.03739	0.00728	0.00145	0.00139
710	0.05143	0.00937	2.01E-03	-5.84E-04
705	0.06895	0.01253	0.00406	2.72E-03
700	0.09307	0.01849	0.00701	0.00519
695	0.11927	0.02066	0.00463	2.22E-04
690	0.15426	0.02852	0.00845	3.66E-03
685	0.16636	0.03001	0.01059	0.00577
680	0.15688	0.02865	0.00866	2.71E-03
675	0.14824	0.02688	0.00657	0.0018
670	0.13578	0.02407	0.00642	2.06E-03
665	0.13192	0.02462	0.00968	6.07E-03
660	0.12975	0.02329	0.00585	1.63E-03
655	0.13296	0.02518	0.00631	0.00228
650	0.14174	0.0263	0.00914	6.68E-03
645	0.15229	0.02781	0.00783	2.78E-03
640	0.17309	0.03354	0.00971	4.42E-03
635	0.19932	0.03625	0.01105	5.25E-03

630	0.22967	0.04191	0.0127	0.00626
625	0.2562	0.04751	0.01424	7.45E-03
620	0.27149	0.05022	0.0133	0.00413
615	0.29695	0.05554	0.01735	0.00945
610	0.31509	0.05787	0.01668	0.00586
605	0.33156	0.06208	0.01789	0.00857
600	0.34241	0.06495	0.01984	0.00874
595	0.35246	0.06616	0.01887	0.00932
590	0.36583	0.0685	0.02136	0.01169
585	0.38147	0.07125	0.02047	0.00762
580	0.40325	0.07685	0.02285	0.01134
575	0.42544	0.08019	0.0247	0.01173
570	0.44424	0.0836	0.02422	0.00937
565	0.46872	0.09022	0.02796	0.01526
560	0.48977	0.09303	0.02661	0.01067
555	0.5117	0.09908	0.02859	0.0129
550	0.53408	0.10371	0.03287	0.01788
545	0.54787	0.10509	0.03103	0.01369
540	0.56106	0.10908	0.03173	0.01374
535	0.57654	0.11215	0.03411	0.01544
530	0.5914	0.11542	0.03508	0.01613
525	0.60943	0.1191	0.03548	0.01687
520	0.63402	0.12502	0.03615	0.01447
515	0.67268	0.13441	0.04093	0.02081
510	0.7104	0.14315	0.043	0.0209
505	0.75704	0.15611	0.04669	0.02204
500	0.80779	0.16835	0.05093	0.02511
495	0.85368	0.18132	0.05465	0.02552
490	0.89894	0.19582	0.06045	0.03079
485	0.93083	0.20654	0.06228	0.02818
480	0.95759	0.21603	0.06517	0.03205
475	0.9805	0.22286	0.06867	0.03437
470	0.99806	0.23212	0.0689	0.03155
465	1.02288	0.24316	0.07367	0.03555
460	1.0478	0.25427	0.07727	0.03867
455	1.06723	0.26651	0.08143	0.04111
450	1.08034	0.27279	0.08323	0.03993
		0.2833	0.08464	0.04132
		0.29895	0.0931	0.04707
		0.33542	0.10231	0.04894
		0.39958	0.12201	0.05961
		0.42733	0.13245	0.06512
		0.41428	0.12725	0.06313

0.41186	0.12706	0.06379
0.4547	0.14006	0.06777
0.5283	0.16426	0.0839
0.5992	0.1887	0.09512
0.6975	0.22298	0.11177
0.80597	0.26423	0.13451
0.91879	0.3102	0.1578
1.02666	0.36149	0.18676
1.11274	0.41017	0.2103
1.18751	0.46617	0.24212
1.24633	0.5296	0.28013
1.28863	0.59827	0.31717
1.31362	0.6765	0.36795
1.3208	0.75647	0.42253
	0.85763	0.48745
	0.94384	0.55476
	1.01676	0.61882
	1.06475	0.668
		0.68356
		0.63728
		0.55792
		0.50699
		0.49441
		0.51011
		0.55004
		0.61185

Table A.4. UV-vis spectra of 75% *p*-$C_{60}Cl_2$ in toluene (C_n is concentration; $C_1 > C_2 > C_3 > C_4$).

λ, nm	***p*-$C_{60}Cl_2$, C_1, A.U.**	***p*-$C_{60}Cl_2$, C_2, A.U.**	***p*-$C_{60}Cl_2$, C_3, A.U.**	***p*-$C_{60}Cl_2$, C_4, A.U.**
800	1.93E-03	-9.08E-04	0	5.50E-04
795	0.00356	1.10E-03	0.00285	1.68E-04
790	0.00119	5.37E-04	1.75E-04	-2.30E-03
785	0.00295	-0.00116	-1.79E-04	-0.00111
780	0.00392	6.67E-04	2.48E-03	6.65E-04
775	0.00377	0.00225	0.0017	-3.77E-04
770	0.00362	3.16E-04	0.00114	-5.21E-04
765	0.00463	-2.60E-04	-5.12E-04	-1.88E-03
760	0.00772	2.62E-03	0.00217	1.98E-04
755	0.0091	2.45E-03	1.28E-03	-1.68E-03
750	0.01408	0.00176	-2.57E-04	-1.58E-03
745	0.02235	6.46E-03	3.45E-03	0.00137
740	0.03369	0.0092	0.00379	1.67E-04
735	0.0529	0.01372	4.74E-03	-5.80E-04
730	0.08194	0.02272	6.14E-03	6.21E-04
725	0.12822	0.03688	0.00988	2.49E-03
720	0.18852	0.05566	0.01646	3.42E-03
715	0.26534	0.0768	0.01972	0.00179
710	0.33753	0.09839	0.02589	5.41E-03
705	0.38203	0.11317	0.03136	0.00768
700	0.39525	0.11736	0.03233	0.00548
695	0.39315	0.11568	0.03167	6.05E-03
690	0.389	0.11421	0.02975	0.00585
685	0.38514	0.11446	0.0322	0.00654
680	0.38568	0.11523	0.03096	0.00556
675	0.39501	0.11536	0.02978	0.00583
670	0.40554	0.12033	0.03373	0.00892
665	0.41718	0.12543	0.03413	0.00739
660	0.42943	0.12761	0.03379	0.00713
655	0.45344	0.13511	0.03589	0.00709
650	0.49075	0.14818	0.04076	0.00798
645	0.53515	0.16306	0.04458	0.00923
640	0.57844	0.17623	0.04638	0.00906
635	0.61333	0.18781	0.05192	0.01153
630	0.64542	0.20057	0.05473	0.0127
625	0.67868	0.21063	0.05585	0.01146
620	0.7141	0.22372	0.06129	0.01382
615	0.7528	0.23947	0.06558	0.01567
610	0.78927	0.25345	0.06923	0.01581

605	0.81671	0.26329	0.0702	0.01531
600	0.83261	0.26979	0.07345	0.01689
595	0.84338	0.27524	0.07544	0.01717
590	0.86068	0.28227	0.07574	0.01615
585	0.8835	0.29221	0.08009	0.01847
580	0.90708	0.30326	0.08241	0.01916
575	0.93439	0.31706	0.08783	0.01976
570	0.95905	0.3284	0.08918	0.01931
565	0.98478	0.3428	0.09327	0.02102
560	1.00795	0.35425	0.09654	0.0212
555	1.03417	0.36819	0.09998	0.0225
550	1.06005	0.38497	0.10699	0.02505
545	1.08626	0.39931	0.11011	0.02464
540	1.1127	0.41723	0.11366	0.02505
535	1.14367	0.44352	0.12469	0.02971
530	1.18107	0.47873	0.13228	0.03126
525	1.22107	0.52781	0.14597	0.03316
520	1.25908	0.59479	0.16739	0.03945
515		0.678	0.1919	0.04534
510		0.76756	0.22241	0.05292
505		0.85521	0.25047	0.05789
500		0.93522	0.28326	0.06732
495		0.99779	0.30887	0.07452
490		1.03513	0.32345	0.07605
485		1.05322	0.3345	0.07944
480		1.06376	0.33903	0.08077
475		1.07448	0.34579	0.08295
470		1.08809	0.3515	0.08354
465		1.1064	0.3612	0.08586
460		1.13443	0.37982	0.09258
455		1.16128	0.39477	0.09462
450		1.1813	0.40893	0.09866
445		1.18765	0.41503	0.10024
440		1.17071	0.40223	0.09732
435		1.13061	0.37528	0.08972
430		1.10306	0.35905	0.0853
425		1.10566	0.36351	0.08804
420		1.13008	0.37549	0.08976
415		1.17351	0.40397	0.09664
410		1.23527	0.46041	0.11153
405		1.29149	0.53688	0.1311
400		1.31998	0.62324	0.15542
395			0.71813	0.18079

390		0.82495	0.21485
385		0.93733	0.25521
380		1.03492	0.29322
375		1.1155	0.33532
370		1.1767	0.37496
365		1.2204	0.41335
360		1.24948	0.45078
355		1.27052	0.48968
350		1.28828	0.53523
345		1.31631	0.58281
340		1.32191	0.63232
335		1.32353	0.68141
330		1.32344	0.72384
325			0.74573
320			0.72426
315			0.66819
310			0.62996
305			0.63046
300			0.65342
295			0.68993
290			0.72772

Table A.5. UV-vis spectra of 99% pure $C_{60}Cl_4$ in toluene (C_n is concentration; $C_1 > C_2 > C_3 > C_4$).

λ, nm	**$C_{60}Cl_4$, C_1, A.U.**	**$C_{60}Cl_4$, C_2, A.U.**	**$C_{60}Cl_4$, C_3, A.U.**	**$C_{60}Cl_4$, C_4, A.U.**
800	0.00E+00	0.00E+00	0	0.00E+00
795	0.01189	1.11E-03	0.0015	-1.31E-03
790	0.01231	4.89E-04	1.98E-03	-2.51E-03
785	0.01095	2.67E-04	3.80E-05	-0.00301
780	0.01373	1.96E-05	2.31E-03	-9.50E-04
775	0.01358	1.37E-04	0.00164	-2.31E-03
770	0.01296	-3.93E-04	1.20E-04	-3.07E-03
765	0.01495	-4.22E-04	1.68E-03	-1.52E-03
760	0.01411	-5.62E-04	3.37E-04	-1.79E-03
755	0.01632	-4.62E-04	1.40E-03	-1.58E-03
750	0.01477	-0.00114	2.85E-04	-2.72E-03
745	0.01519	-1.14E-03	1.23E-04	-0.00127
740	0.01764	-3.13E-04	0.0026	-1.61E-03
735	0.01629	-0.00116	9.56E-05	-3.28E-03
730	0.01766	-0.00102	1.79E-03	-1.45E-03
725	0.01945	-4.51E-04	0.00185	-2.14E-03
720	0.02174	7.08E-04	0.00196	-1.06E-03

715	0.02169	-0.00107	0.00159	-0.00255
710	0.02194	-0.00167	-3.41E-04	-3.04E-03
705	0.02747	0.00143	0.00332	-4.27E-04
700	0.02837	0.00176	0.00152	-0.00208
695	0.03198	0.00303	0.0021	-8.62E-04
690	0.04078	0.00597	0.00472	-4.76E-04
685	0.04681	0.00887	0.00304	-0.00213
680	0.05681	0.01232	0.00604	-6.73E-04
675	0.06531	0.01526	0.00516	-0.00154
670	0.07539	0.01936	0.00766	3.72E-04
665	0.08015	0.02099	0.00779	-8.78E-04
660	0.08092	0.0213	0.00611	-9.22E-04
655	0.08423	0.02189	0.00928	0.00192
650	0.08316	0.02152	0.00767	-1.73E-04
645	0.08528	0.02214	0.00767	-2.78E-04
640	0.09051	0.0235	0.00851	-5.63E-04
635	0.10159	0.02892	0.01041	5.79E-04
630	0.12127	0.03681	0.01351	0.00183
625	0.14436	0.04702	0.01403	8.95E-04
620	0.17284	0.05831	0.01836	0.00394
615	0.20203	0.07023	0.02262	0.00459
610	0.21989	0.07864	0.02301	0.00319
605	0.23118	0.08222	0.02478	0.00445
600	0.23568	0.08405	0.02458	0.00452
595	0.24233	0.08701	0.02718	0.00604
590	0.24836	0.08962	0.02744	0.00547
585	0.26079	0.09506	0.02827	0.00531
580	0.28401	0.10548	0.03326	0.0081
575	0.3061	0.11645	0.03469	0.0065
570	0.33284	0.12848	0.03806	0.00786
565	0.362	0.14207	0.04216	0.00893
560	0.38291	0.15246	0.04374	0.00861
555	0.40578	0.1644	0.04925	0.01255
550	0.41921	0.17218	0.05094	0.0116
545	0.4324	0.18025	0.05251	0.01289
540	0.44872	0.18679	0.05583	0.01314
535	0.46578	0.19714	0.05736	0.01348
530	0.49045	0.21093	0.06196	0.01476
525	0.51488	0.22477	0.06464	0.01438
520	0.54533	0.24384	0.07015	0.01733
515	0.57643	0.2645	0.07825	0.02018
510	0.60095	0.2828	0.08122	0.01932
505	0.62532	0.30121	0.08785	0.02204

500	0.6461	0.3183	0.09318	0.02384
495	0.67012	0.33991	0.0998	0.02556
490	0.69303	0.36284	0.10682	0.02602
485	0.71824	0.39146	0.11369	0.02897
480	0.74879	0.42582	0.12616	0.03326
475	0.76946	0.46126	0.13606	0.03484
470	0.78764	0.49985	0.14685	0.03743
465	0.80597	0.53972	0.16063	0.04256
460	0.81837	0.58715	0.17492	0.04667
455		0.64201	0.19376	0.05154
450		0.70652	0.2166	0.05771
445		0.7898	0.24791	0.06735
440		0.87469	0.28377	0.07764
435		0.93609	0.30984	0.08352
430		0.9672	0.32706	0.08938
425		0.99359	0.3403	0.0929
420		1.02448	0.35535	0.0975
415			0.37672	0.10382
410			0.40426	0.11208
405			0.44609	0.12548
400			0.49678	0.13926
395			0.54893	0.15691
390			0.59954	0.17281
385			0.65952	0.19223
380			0.73849	0.21948
375			0.81993	0.25048
370				0.27761
365				0.29912
360				0.32318
355				0.35348
350				0.37856
345				0.40384
340				0.43234
335				0.45873
330				0.48224
325				0.50388
320				0.52608
315				0.55441
310				0.58675
305				0.61248
300				0.62697
295				0.63519
290				0.62883

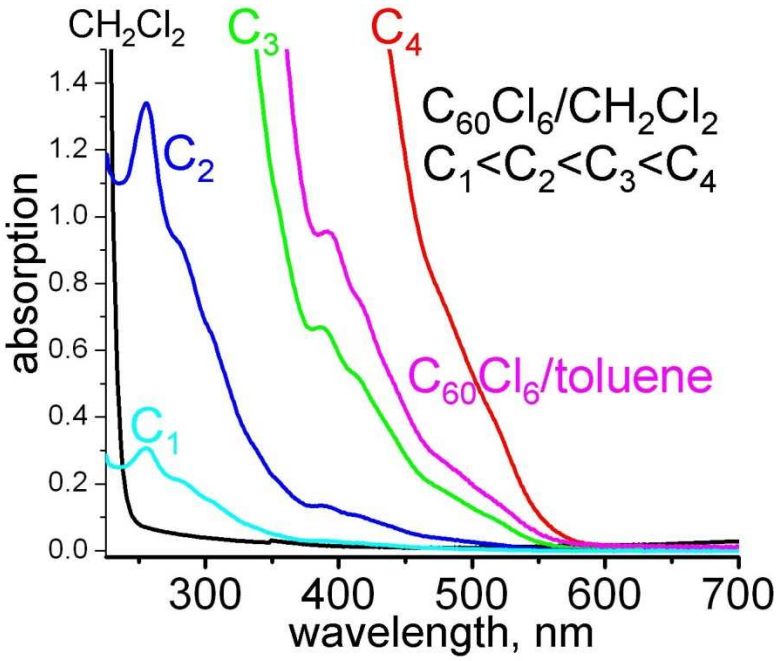

Figure A.1. UV-vis spectra of 95% $C_{60}Cl_6$ in CH_2Cl_2 and toluene solution ($C_1<C_2<C_3<C_4$ are concentrations of $C_{60}Cl_6$ in CH_2Cl_2). See Table A-1-1 for numerical data.

Table A.6. UV-vis spectra of 95% $C_{60}Cl_6$ in CH_2Cl_2 ($C_1<C_2<C_3<C_4$ are concentrations of $C_{60}Cl_6$ in CH_2Cl_2).

λ, nm	**$C_{60}Cl_6$ C_1, A.U.**	**$C_{60}Cl_6$ C_2, A.U.**	**$C_{60}Cl_6$ C_3, A.U.**	**$C_{60}Cl_6$ C_4, A.U.**
700	0.00541	0.00181	––	––
695	0.00492	0.0013	––	––
690	0.0055	0.00202	––	––
685	0.00693	0.00181	––	––
680	0.00684	0.00168	––	––
675	0.00703	0.00196	––	––
670	0.0067	0.00168	––	––
665	0.00672	0.00141	––	––
660	0.00746	0.0018	––	––
655	0.00744	0.00171	––	––
650	0.00919	0.00322	––	––
645	0.00902	0.00211	––	––
640	0.0091	0.00223	––	––
635	0.01002	0.0029	––	––
630	0.00997	0.00203	––	––
625	0.01039	0.00242	––	––
620	0.01211	0.00313	––	––
615	0.01232	0.00283	––	––
610	0.01367	0.00362	––	––
605	0.01509	0.00355	––	––
600	0.01715	0.00454	––	––

595	0.01855	0.00378	−−	−−
590	0.0189	0.00406	−−	−−
585	0.02094	0.00546	−−	−−
580	0.0264	0.00645	−−	−−
575	0.03172	0.00778	−−	−−
570	0.04184	0.01061	0.00136	−−
565	0.05312	0.01233	0.00172	−−
560	0.0673	0.01638	0.00343	−−
555	0.08579	0.02125	0.00375	−−
550	0.10911	0.02674	0.00529	−−
545	0.13728	0.03317	0.00672	−−
540	0.17118	0.04163	0.0075	0.00136
535	0.2145	0.05147	0.0101	0.00176
530	0.26219	0.06241	0.01182	0.00118
525	0.31244	0.07574	0.01489	0.00241
520	0.36229	0.08809	0.01764	0.00353
515	0.40473	0.09812	0.01938	0.00284
510	0.44449	0.10804	0.02171	0.00357
505	0.48712	0.11841	0.02396	0.00453
500	0.53117	0.12848	0.02557	0.005
495	0.58034	0.14023	0.028	0.00525
490	0.62996	0.15258	0.03043	0.00571
485	0.6809	0.16513	0.03297	0.00684
480	0.73062	0.17697	0.03582	0.00731
475	0.77503	0.18813	0.03832	0.00746
470	0.82289	0.20076	0.04039	0.00814
465	0.87875	0.21305	0.04293	0.00839
460	0.95446	0.23136	0.04598	0.00916
455	1.05538	0.25633	0.05102	0.01041
450	1.1758	0.28524	0.05781	0.01231
445	1.31061	0.31811	0.06382	0.01333
440	1.4495	0.35207	0.07175	0.01532
435	1.5794	0.38395	0.07792	0.01668
430	1.70757	0.41589	0.08437	0.01798
425	1.84502	0.44838	0.09046	0.01887
420	1.99219	0.48469	0.09751	0.02077
415	2.12477	0.51629	0.1041	0.02266
410	2.19562	0.53394	0.1076	0.02276
405	2.277	0.55426	0.11165	0.02415
400	2.42135	0.58992	0.11959	0.02603
395	2.6012	0.63314	0.12827	0.02797
390	2.71969	0.6636	0.13399	0.02919
385	2.74036	0.66842	0.13438	0.02855
380	2.7239	0.66326	0.13359	0.02934
375	2.7813	0.67844	0.13635	0.03006
370	3.00569	0.73435	0.14856	0.03241
365	3.35454	0.81655	0.16487	0.03659
360	3.71534	0.91521	0.18465	0.04099
355	−−	1.02107	0.20675	0.04689

350	--	1.11755	0.22509	0.04939
345	--	1.2612	0.25479	0.05756
340	--	1.43097	0.28925	0.06549
335	--	1.58414	0.32019	0.07268
330	--	1.75096	0.35403	0.0803
325	--	1.975	0.39943	0.09064
320	--	2.26029	0.4577	0.10439
315	--	2.56964	0.5201	0.11885
310	--	2.87695	0.58264	0.13331
305	--	3.16807	0.64305	0.14721
300	--	3.38204	0.68405	0.15648
295	--	3.6807	0.74175	0.17012
290	--	--	0.81654	0.18722
285	--	--	0.87967	0.20176
280	--	--	0.92228	0.21168
275	--	--	0.9454	0.21704
270	--	--	0.99792	0.22886
265	--	--	1.10588	0.25391
260	--	--	1.27098	0.29209
255	--	--	1.3387	0.30712
250	--	--	1.27716	0.29259
245	--	--	1.17376	0.26847
240	--	--	1.10857	0.25262
235	--	--	1.10089	0.25061
230	--	--	1.11861	0.25446

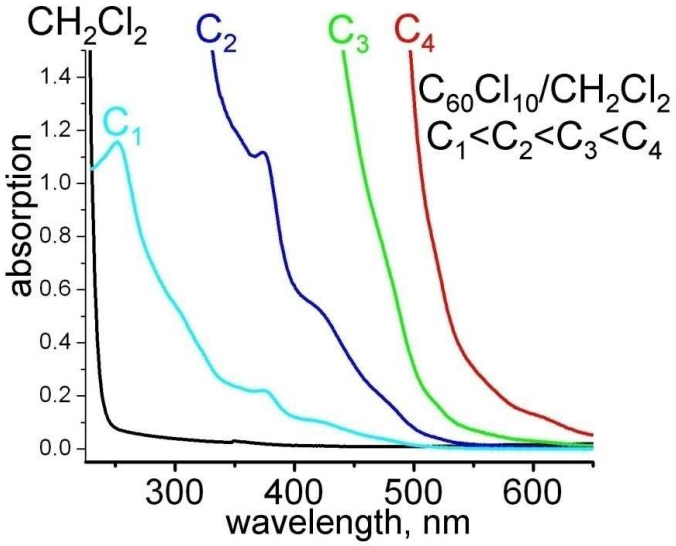

Figure A.2. UV-vis spectra of 98% $C_{60}Cl_{10}$ in CH_2Cl_2 ($C_1<C_2<C_3<C_4$ are concentrations of $C_{60}Cl_{10}$ in CH_2Cl_2). See Table A.4 for numerical data.

Table A.7. UV-vis spectra of 98% $C_{60}Cl_{10}$ in CH_2Cl_2 ($C_1<C_2<C_3<C_4$ are concentrations of $C_{60}Cl_{10}$ in CH_2Cl_2).

λ, nm	**$C_{60}Cl_{10}$ C_1, A.U.**	**$C_{60}Cl_{10}$ C_2, A.U.**	**$C_{60}Cl_{10}$ C_3, A.U.**	**$C_{60}Cl_{10}$ C_4, A.U.**
700	0.01624	0.00363	−−	−−
695	0.01961	0.00359	−−	−−
690	0.02443	0.00508	0.00128	−−
685	0.02932	0.0064	0.00109	−−
680	0.03371	0.00724	0.00153	−−
675	0.03774	0.00776	0.00171	−−
670	0.04041	0.00865	0.0011	−−
665	0.04342	0.00922	0.00172	−−
660	0.04588	0.01029	0.00277	−−
655	0.04842	0.01047	0.00235	−−
650	0.05266	0.01241	0.00314	−−
645	0.05647	0.01295	0.00319	−−
640	0.06248	0.0135	0.00301	−−
635	0.06962	0.01583	0.00406	−−
630	0.07678	0.01698	0.00337	−−
625	0.08623	0.01908	0.00358	−−
620	0.09596	0.02219	0.00564	−−
615	0.10638	0.0242	0.00529	−−
610	0.11656	0.02738	0.00702	−−
605	0.12395	0.02867	0.00669	−−
600	0.13166	0.03028	0.00725	−−
595	0.1384	0.03195	0.00798	−−
590	0.14638	0.03297	0.00743	−−
585	0.15667	0.03582	0.00825	−−
580	0.17102	0.04014	0.00969	−−
575	0.18892	0.04412	0.01031	−−
570	0.21074	0.04881	0.0119	0.00132
565	0.23184	0.05321	0.01247	0.00101
560	0.25508	0.05912	0.01433	0.00163
555	0.27934	0.06521	0.01517	0.00174
550	0.30572	0.072	0.01781	0.0028
545	0.33565	0.07853	0.01957	0.00269
540	0.37327	0.08723	0.02131	0.0035

535	0.42245	0.09958	0.02493	0.00432
530	0.49108	0.11452	0.02796	0.00391
525	0.58703	0.13752	0.03435	0.0056
520	0.69756	0.1641	0.04142	0.00691
515	0.79874	0.18738	0.04668	0.00835
510	0.91626	0.21528	0.05406	0.0092
505	1.08341	0.25545	0.0648	0.01236
500	1.32454	0.31216	0.07908	0.015
495	1.63359	0.38498	0.09778	0.0185
490	2.00999	0.47376	0.12002	0.02307
485	2.43033	0.57375	0.14571	0.02808
480	2.80482	0.66235	0.16889	0.03275
475	3.15601	0.74493	0.18935	0.03681
470	3.48397	0.82848	0.21123	0.04146
465	3.8653	0.9096	0.23228	0.0458
460	--	0.99955	0.25538	0.04962
455	--	1.11175	0.28446	0.05585
450	--	1.23987	0.31767	0.06261
445	--	1.377	0.35295	0.06914
440	--	1.5251	0.39129	0.0768
435	--	1.67842	0.43111	0.0854
430	--	1.83305	0.47157	0.09366
425	--	1.95971	0.5041	0.09916
420	--	2.05497	0.52893	0.10466
415	--	2.12321	0.54763	0.10787
410	--	2.18161	0.5624	0.11003
405	--	2.25706	0.58207	0.11414
400	--	2.37725	0.61357	0.12031
395	--	2.57491	0.66574	0.1309
390	--	2.92663	0.75668	0.1491
385	--	3.46644	0.89802	0.1771
380	--	--	1.04533	0.20663
375	--	--	1.11523	0.21932
370	--	--	1.10877	0.21861
365	--	--	1.10393	0.21768
360	--	--	1.13023	0.22195
355	--	--	1.16819	0.2304

350	−−	−−	1.2014	0.23653
345	−−	−−	1.24349	0.24586
340	−−	−−	1.3047	0.25842
335	−−	−−	1.39019	0.27765
330	−−	−−	1.54596	0.30955
325	−−	−−	1.74725	0.35052
320	−−	−−	1.93111	0.38769
315	−−	−−	2.1206	0.42647
310	−−	−−	2.33247	0.46965
305	−−	−−	2.5327	0.51012
300	−−	−−	2.69552	0.54347
295	−−	−−	2.85071	0.57538
290	−−	−−	3.04397	0.61318
285	−−	−−	3.24283	0.65649
280	−−	−−	3.48068	0.70552
275	−−	−−	3.74782	0.75992
270	−−	−−	−−	0.83452
265	−−	−−	−−	0.93751
260	−−	−−	−−	1.05272
255	−−	−−	−−	1.1388
250	−−	−−	−−	1.15229
245	−−	−−	−−	1.1228
240	−−	−−	−−	1.09356
235	−−	−−	−−	1.07011
230	−−	−−	−−	1.05421

C. Extinction Coefficient Measurements and Results. Extinction coefficients were measured for C_{60} (in CH_2Cl_2 and toluene), $C_{60}Cl_6$ (in CH_2Cl_2) and $C_{60}Cl_{10}$ (in CH_2Cl_2) using fused silica cells with 2 and 10 mm path length (see Table A.8 and Figure A.3). Each point in Table A.I.6 corresponds to the average of at least 2 experimental points. The largest error in these experiments is likely to arise from weight measurements of small (see below) samples (±0.1 mg error) and possible presence of traces of co-crystallized solvents and other trace impurities (−0.1 mg error to the weight measurement). This relates directly to the error of the extinction coefficients (assuming

that impurities do not have extremely intense UV-vis absorption bands). In order to validate our use of extinction coefficients measured in CH_2Cl_2 for conclusions on integration of HPLC data (absorption measured in toluene or various toluene/heptanes mixtures during HPLC analysis and separation) we also measured C_{60} extinction coefficients in toluene solution. Only a small shift in a position of absorption band was observed (from 330 nm in CH_2Cl_2 to 335 nm in toluene), but the extinction coefficient corresponding to this absorption maxima hardly change (55,236 $M^{-1}*cm^{-1}$ in CH_2Cl_2 and 56,949 $M^{-1}*cm^{-1}$ in toluene, falling within experimental error). This allows us to assume that extinction coefficients of chlorofullerenes are stay practically constant in toluene and CH_2Cl_2.

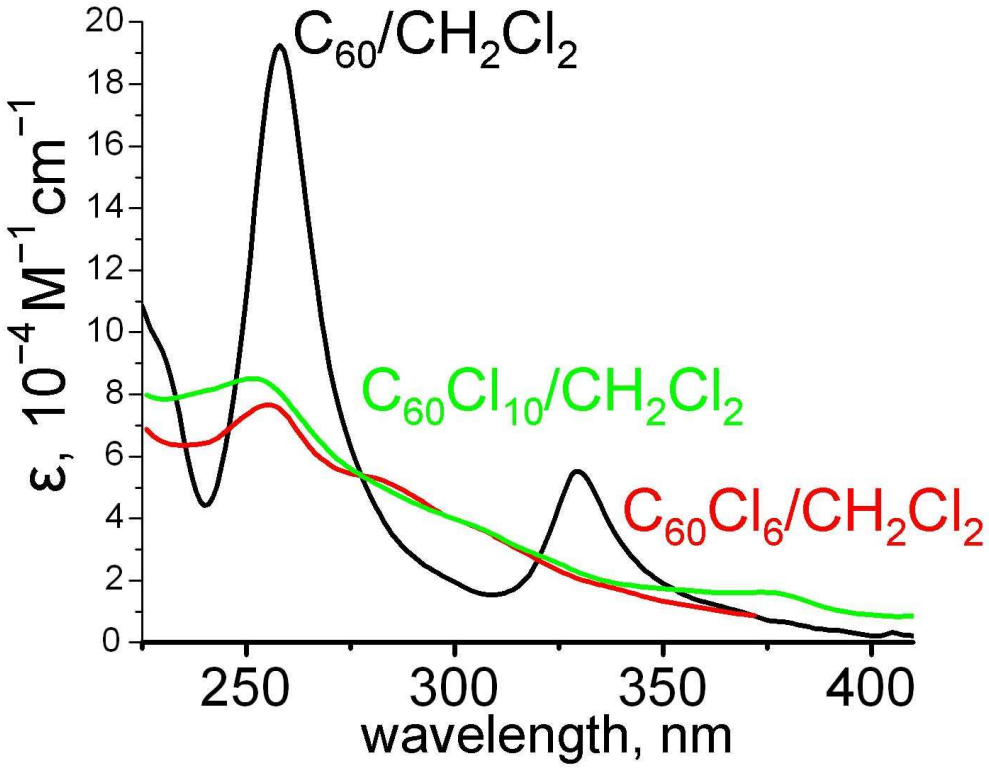

Figure A.3. Plots of $\varepsilon(C_{60})$, $\varepsilon(C_{60}Cl_6)$, and $\varepsilon(C_{60}Cl_{10})$ vs. λ measured in CH_2Cl_2.

Table A.8. $\varepsilon(C_{60})$, $\varepsilon(C_{60}Cl_6)$, and $\varepsilon(C_{60}Cl_{10})$ vs. λ measured in CH_2Cl_2 and toluene (for C_{60}).

λ, nm	**ε(C_{60} in toluene) $M^{-1}cm^{-1}$, +1/−1%**	**ε(C_{60} in CH_2Cl_2) $M^{-1}cm^{-1}$, +1/−1%**	**ε($C_{60}Cl_6$ in CH_2Cl_2) $M^{-1}cm^{-1}$, +6/−12%**	**ε($C_{60}Cl_{10}$ in CH_2Cl_2) $M^{-1}cm^{-1}$, +2/−4%**
410	2754	2185	−−	8440
405	2886	3192	−−	8430
400	3600	2151	−−	8876
395	4867	3208	−−	9659
390	5789	4064	−−	10971
385	7750	4994	−−	13050
380	9522	6396	−−	15208
375	11654	7243	−−	16167
370	14390	9403	8961	16063
365	17757	11293	9884	15967
360	21986	13051	11016	16347
355	27704	15438	12232	16883
350	34788	19081	13346	17356
345	44053	24201	14990	17965
340	53288	31976	16900	18859
335	56949	44391	18572	20236
330	49611	55236	20438	22538
325	35178	43839	23139	25477
320	24364	26594	26621	28192
315	19728	17873	30287	30993
310	19733	15411	33903	34476
305	22132	16336	37349	37452
300	25444	19421	39755	39906
295	28878	23152	43046	42394
290	33275	27820	47352	45172
285	40433	35003	50975	48432
280	−−	46738	53353	52083
275	−−	63157	54480	56078
270	−−	89016	57395	61586
265	−−	134786	63406	69120
260	−−	185549	72598	77568

255	−−	176717	76536	83848
250	−−	111918	73448	84921
245	−−	62543	67812	82941
240	−−	44075	64214	81038
235	−−	66392	63639	79420
230	−−	93591	64749	78517

D. Preparation of Solutions for Extinction Coefficient Measurements.

a. $3.42*10^{-5}$M (+6/−12%) solution of $C_{60}Cl_6$ was prepared by dissolving 1.6 mg sample in 50.0 mL of CH_2Cl_2. In order to check for any speciation equilibria, we measured extinction coefficients of the same solution diluted to 100.0 mL volume ($1.71*10^{-5}$M). The results were different by less than ±2%, pointing out to the absence of any appreciable speciation at these conditions.

b. $3.81*10^{-5}$M (+2/−4%) solution of $C_{60}Cl_{10}$ was prepared by dissolving 4.1 mg sample in 100.0 mL of CH_2Cl_2. In order to check for any speciation equilibria, we measured extinction coefficients of the same solution diluted to 250.0 mL volume ($1.52*10^{-5}$M). The results were different by less than ±2%, pointing out to the absence of any appreciable speciation at these conditions.

c. $1.37*10^{-4}$M (+1/−1% since high purity annealed sample used) solution of C_{60} was prepared by dissolving 9.9 mg sample of it in 100.0 mL of HPLC grade CH_2Cl_2. In order to check for any speciation equilibria, we measured extinction coefficients of the same solution diluted to 250.0 mL volume ($5.48*10^{-5}$M). The results were different by less than ±2%, pointing out to the absence of any appreciable speciation at these conditions. Toluene solution of C_{60} ($1.37*10^{-4}$M +1/−1%) was prepared by dissolving C_{60} quantitatively recovered from CH_2Cl_2 solutions (including all CH_2Cl_2 used to rinse the cuvettes) and dissolving it in 100.0 mL of HPLC grade toluene.

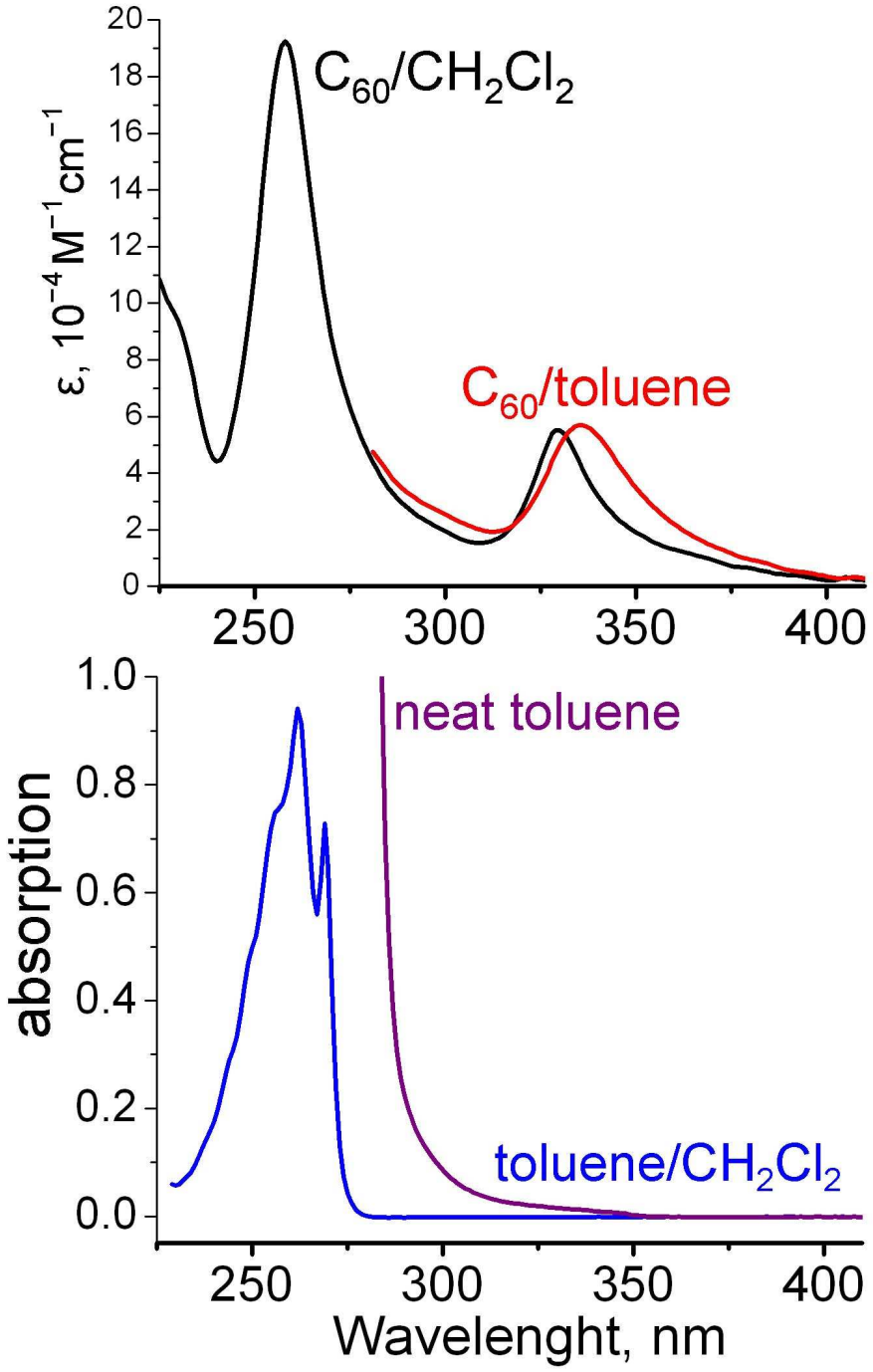

Figure A.4. Plots of $\varepsilon(C_{60})$ vs. λ measured in toluene and CH_2Cl_2 versus wavelength (upper figure); UV-vis spectra of neat toluene and toluene solution in CH_2Cl_2 (lower figure).

A.4. ^{13}C NMR study of $C_{60}Cl_6$ Samples A, B, C, D, $C_{60}Cl_{10}$, and $C_{70}(CF_3)_{10}$

Table A.9. ^{13}C-NMR sample preparation, NMR instrument/probe diameter employed.

sample	m($C_{60}Cl_6$),[a] mg	m($C_{70}(CF_3)_{10}$),[b] mg	m($Cr(acac)_3$), mg	V(solvent), mL	solvent	NMR instrument/probe diameter
95% $C_{60}Cl_6$ (sample **A**)	4.0	-	7.0	0.7	$CDCl_3$	Varian INOVA 400/5mm
75% molar $C_{60}Cl_6$ + 25% molar $C_{70}(CF_3)_{10}$ (sample **E**)	4.2	2.1	10.0	1.0	$CDCl_3$	Varian INOVA 400/5mm
98% $C_{70}(CF_3)_{10}$ (sample **F**)	-	74.6[c]	39.6	4.0	$CDCl_3$	Varian INOVA 500/10mm
67% $C_{60}Cl_6$ (sample **C**)	7.0	-	7.0	0.7	$CDCl_3$	Varian INOVA 400/5mm
27% $C_{60}Cl_6$ (sample **D**)	13.4	-	7.0	0.7	$CDCl_3$	Varian INOVA 400/5mm
$C_{60}Cl_6$[25]	no data given				CS_2/ d_{12}-cyclohexane	Bruker Avance 600MHz/no data
98%[◊] $C_{60}Cl_{10}$ (sample **G**)	-	-	40.2	4.0	$CDCl_3$	Varian INOVA 500/10mm

[a] Samples may contain up to 10% of the co-crystallized solvent (toluene) by mass. [b] 98% pure (according to HPLC trace integration) sample of $C_{70}(CF_3)_{10}$ was used. [c] $C_{70}(CF_3)_{10}$ did not fully dissolve.

A. Signal-to-Noise Measurements. In order to reliably compare the signal-to-noise (S/N) of literature ^{13}C NMR spectrum of $C_{60}Cl_6$ (O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovskiy, J. Balzarinid, R. N. Lyubovskaya, *Org. Biomol. Chem.* **2007**, *5*, 2783) with our data we decided to use peak signal-to-noise values. The maximum intensities of both signal and noise were used instead of root-mean-square intensity or integrated intensity. The maximum signal intensity was found by measuring the height of the most intense CF peak in 146-140 ppm range relative to the baseline This range conveniently hosts 12 evenly-spaced non-overlapping signals of the cage sp^2-carbons with double intensities due to C_s-symmetry of the $C_{60}Cl_6$ molecule. The peak noise level was determined by finding the maximum vertical range of the noise in the relatively signal-free area between 139.5 and 134.5 ppm and dividing it by two.

B. LLMP Calculations. Following approximations are used:

i) there is no overlap between ^{13}C NMR signals of different mixture components (reasonable because of the very small line width in ^{13}C NMR); ii) the relaxation times are the same for the same types of carbons in different fullerenes; iii) there is one main component, A, with concentration [A], and x minor components B_1, B_2… B_x, with equal concentrations $[B_1]=[B_2]=\ldots=[B_x]$; iv) all components under consideration A, B_1, B_2… B_x have the same symmetry; v) signals with S/N = 2 are indistinguishable from baseline. Then estimated **LLMP** of A on the basis of its clean (not showing any peaks of impurities) ^{13}C NMR with a given (S/N) is:

eq. 1. $$\textbf{LLMP}(C_1\text{-A}),\ \% = (S/N)/[(S/N) + 2x]*100\% = 1/[1 + 2x/(S/N)]*100\%$$

(other components have C_1 symmetry)

equation 1 is easy to adjust for the case of mixture containing components with different symmetries, e.g.:

eq. 2. **LLMP**(C_s-A), % = [(S/N)/2]/[[(S/N)/2] + 2x]*100% = 1/ [1 + 4x/(S/N)]*100%

(other components have C_1 symmetry)

Table A.10. LLMP values for different mixtures of C_1 and C_s components for S/N = 12.

Number of Bs.	**LLMP**(A), molar %	
x	A and B are C_1	A is C_s, Bs are C_1
1	86	75
2	75	60
3	67	50
4	60	43
5	55	38
10	37	23
20	23	13

C. ^{13}C NMR spectra and tabulated ^{13}C NMR data.

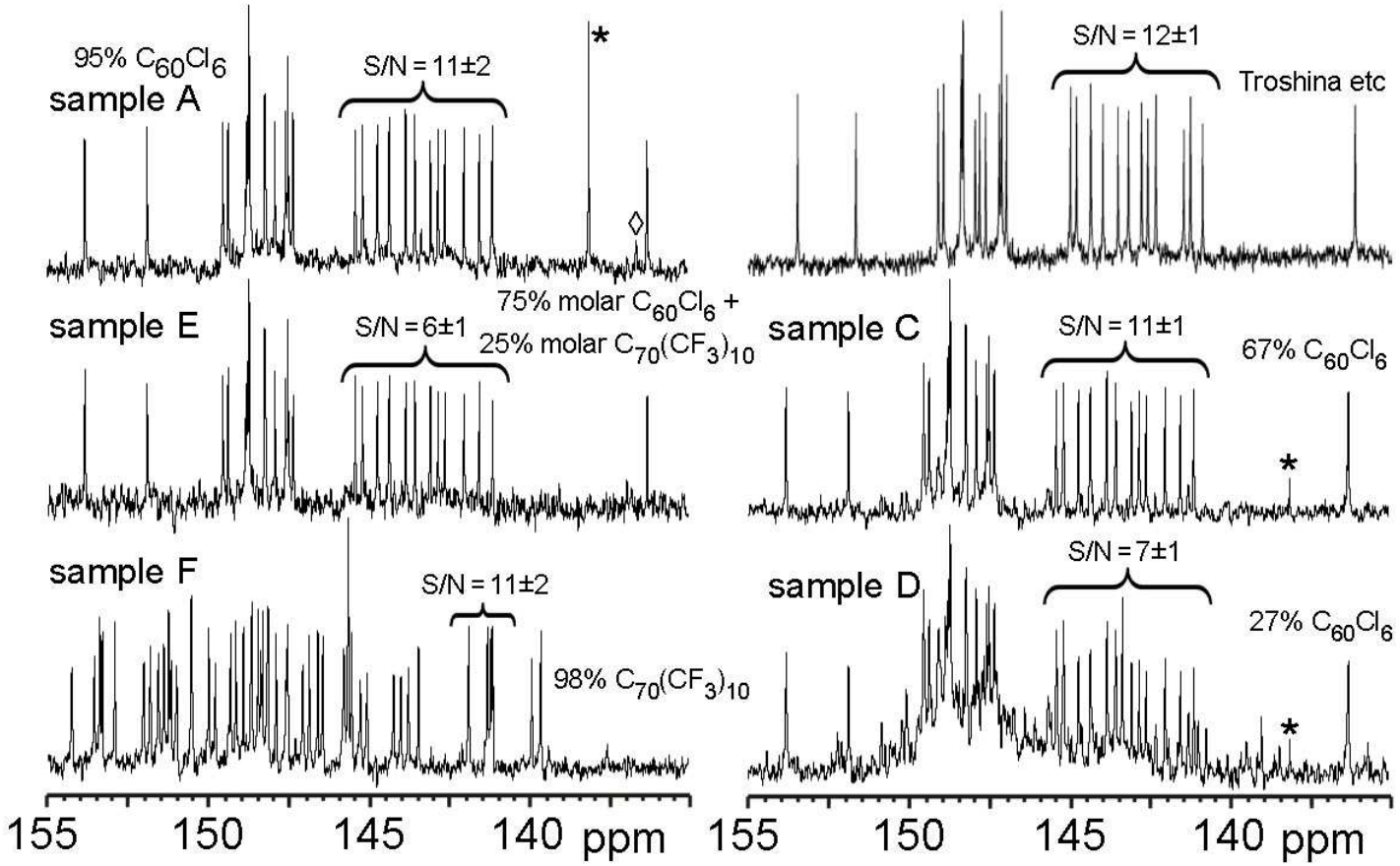

Figure A.5. ^{13}C NMR spectra of $C_{60}Cl_6$ samples **A**, **C**, **D**, **E**, $C_{70}(CF_3)_{10}$ sample **F**. The spectrum in the top right corner is reprinted with permission from O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovskiy, J. Balzarinid, R. N. Lyubovskaya, *Org. Biomol. Chem.* **2007**, *5*, 2783). The signals of the quaternary carbon of the toluene impurity are marked with asterisks. Peak marked with a dagger is due to C_{60} (sample **D**). Peak marked with a diamond is due to an unidentified impurity.

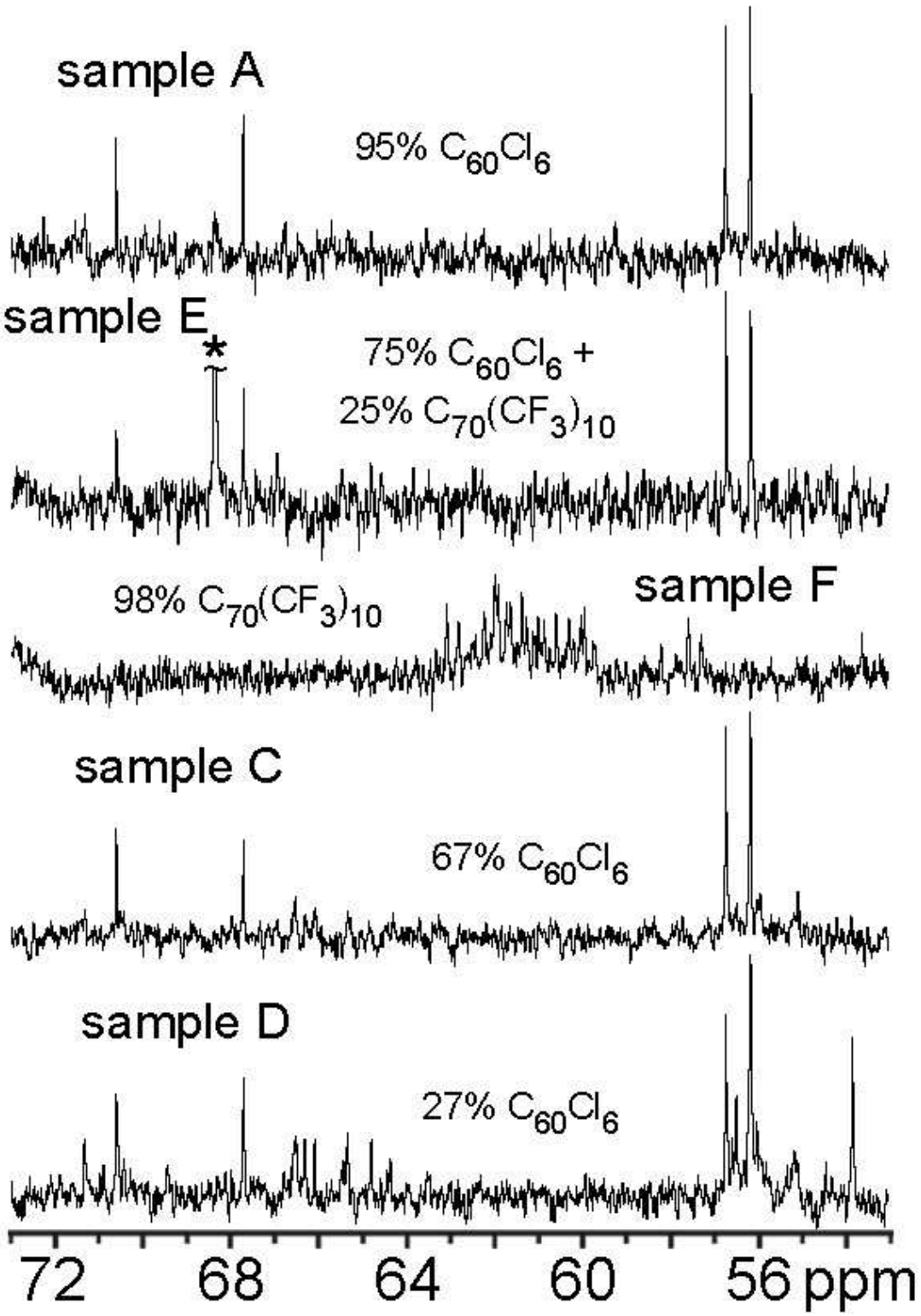

Figure A.6. ^{13}C NMR spectra of $C_{60}Cl_6$ samples **A**, **C**, **D**, **E**, and $C_{70}(CF_3)_{10}$ sample **F**. Peak marked with an asterisk is due to unidentified impurity.

Table A.11. ^{13}C-NMR peak positions and areas of $C_{60}Cl_6$ (95% pure $C_{60}Cl_6$ sample **A**).

Peak number	Chemical shift, ppm	Area under the peak, relative units
1	153.586	1.74
2	151.647	2.21
3	149.279	2.08
4	149.111	2.20
5	148.569	1.16
6	148.519	1.76
7	148.470	2.31
8	148.451	2.27
9	147.973	1.89
10	147.950	1.90
11	147.654	2.18
12	147.317	2.20
13	147.244	2.95
14	147.085	2.17
15	145.145	1.76
16	144.913	1.90
17	144.453	2.02
18	144.080	2.04
19	143.570	2.21
20	143.283	2.10
21	142.800	1.70
22	142.559	1.73
23	142.341	1.75
24	141.749	1.76
25	141.275	1.82
26	140.861	1.97
27	136.039	1.95
28	70.382	0.77
29	67.482	0.90
30	56.487	2.00
31	55.932	1.93

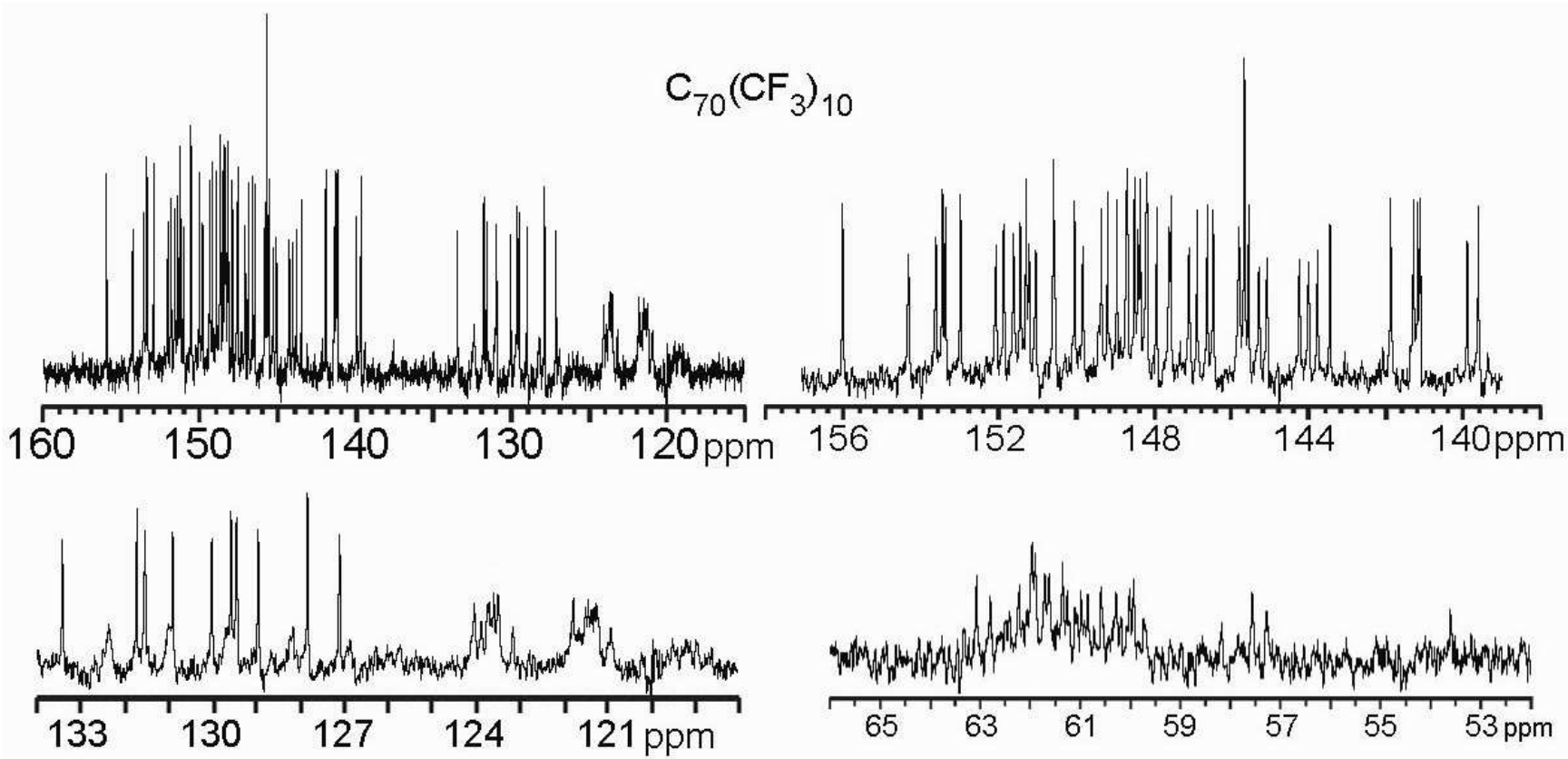

Figure A.7. Expansions of ^{13}C NMR spectrum of $C_{70}(CF_3)_{10}$ sample **F** (vertical scale is the same for all expansions).

Table A.12. ^{13}C-NMR peak positions and areas of $C_{70}(CF_3)_{10}$ (sample **F**).

Peak number	Chemical shift, ppm	Area under the peak, relative units
1	155.936	1.032
2	154.252	1.000
3	153.548	1.090
4	153.374	1.197
5	153.297	0.903
6	152.907	1.013
7	151.999	1.148
8	151.804	1.247
9	151.554	1.345
10	151.38	1.28
11	151.227	1.094
12	151.147	1.01
13	150.977	1.04
14	150.523	2.021
15	149.996	
16	149.98	1.085
17	149.772	1.046
18	149.297	1.121
19	149.136	1.093
20	148.894	0.988
21	148.6	2.247
22	148.627	
23	148.44	1.249
24	148.355	1.158
25	148.292	1.067
26	148.094	2.112
27	148.122	
28	147.872	1.009
29	147.553	1.249
30	147.507	0.83
31	147.04	1.164
32	146.841	0.959
33	146.569	1.013
34	146.421	1.03
35	145.763	1.659
36	145.619	2.415
37	145.627	
38	145.513	1.05
39	145.25	1.03
40	145.038	0.884
41	144.206	1.049
42	143.977	0.999

43	143.74	0.965
44	143.422	0.917
45	141.865	1.264
46	141.275	1.288
47	141.169	1.133
48	141.11	0.913
49	139.896	0.928
50	139.612	1.135
51	133.414	0.803
52	131.717	0.939
53	131.531	1.109
54	130.894	1.123
55	130.004	0.94
56	129.562	1.256
57	129.439	1.153
58	128.943	0.8
59	127.819	0.996
60	127.089	0.969
61	123.7	4.416 broad
62	121.44	5.296 broad
64	96.066	3.733
65	94.637	0.131
67	61.6	9.678 broad
68	50.495	-0.257

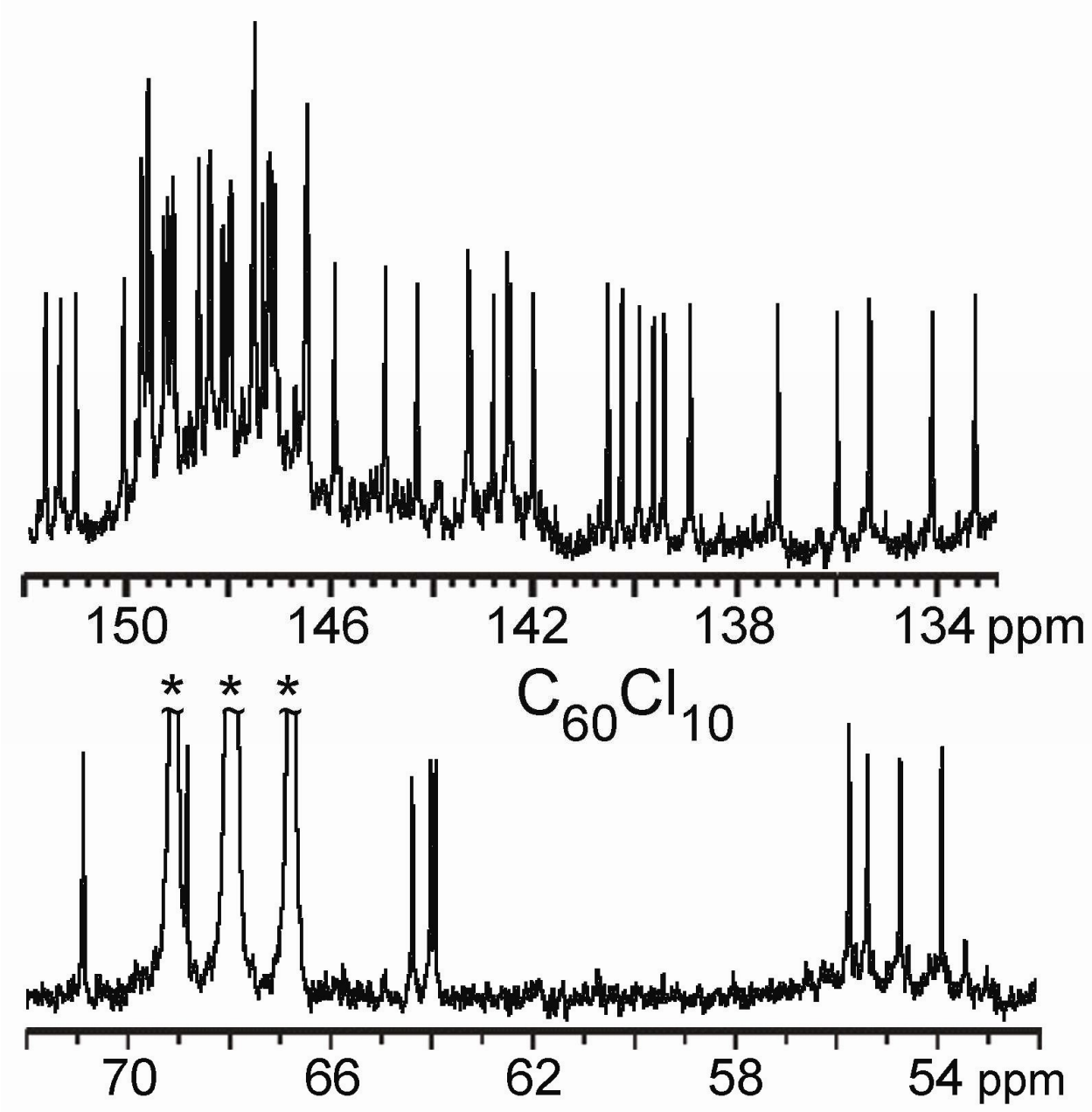

Figure A.8. Expansions of ^{13}C NMR spectrum of $C_{60}Cl_{10}$ (vertical scale is the same for all expansions). Peaks designated with asterisks are due to unidentified impurity.

Table A.13. ^{13}C-NMR peak positions and areas of $C_{60}Cl_{10}$.

Peak number	Chemical shift, ppm	Area under the peak, relative units
1	151.6	1
2	151.3	0.9
3	151	1
4	150.1	1.1
5	149.7	2.747/2
6	149.7	2.747/2
7	149.6	2.496/2
8	149.6	2.496/2
9	149.5	1.2
10	149.3	1.3
11	149.2	1.5
12	149.2	1.3
13	149.1	1.5
14	148.6	1.6
15	148.4	1.5
16	148.3	1.2
17	148.1	1.2
18	148	1.5
19	148	1.5
20	147.5	3.883/3
21	147.5	3.883/3
22	147.5	3.883/3
23	147.3	1.4
24	147.2	1.2
25	147.2	1.5
26	147.1	1.4
27	146.5	1.2
28	146.5	1.94/2
29	146.4	1.94/2
30	145.9	1
31	144.9	1.1
32	144.3	1
33	143.3	1
34	143.2	1
35	142.8	0.9
36	142.5	1.1
37	142.4	1
38	142	0.9
39	140.5	1
40	140.2	1.1
41	139.9	0.9

42	139.6	0.8
43	139.4	0.9
44	138.9	1.1
45	137.1	1.1
46	136	1.2
47	135.3	1.2
48	134.1	0.9
49	133.2	1.1
50	70.9	1.1
51	69	unknown due to overlap with the peak of impurity
52	68.8	1.1
53	64.4	1
54	64	1.1
55	63.9	1
56	55.7	1.5
57	55.3	1.1
58	54.7	1
59	53.9	1

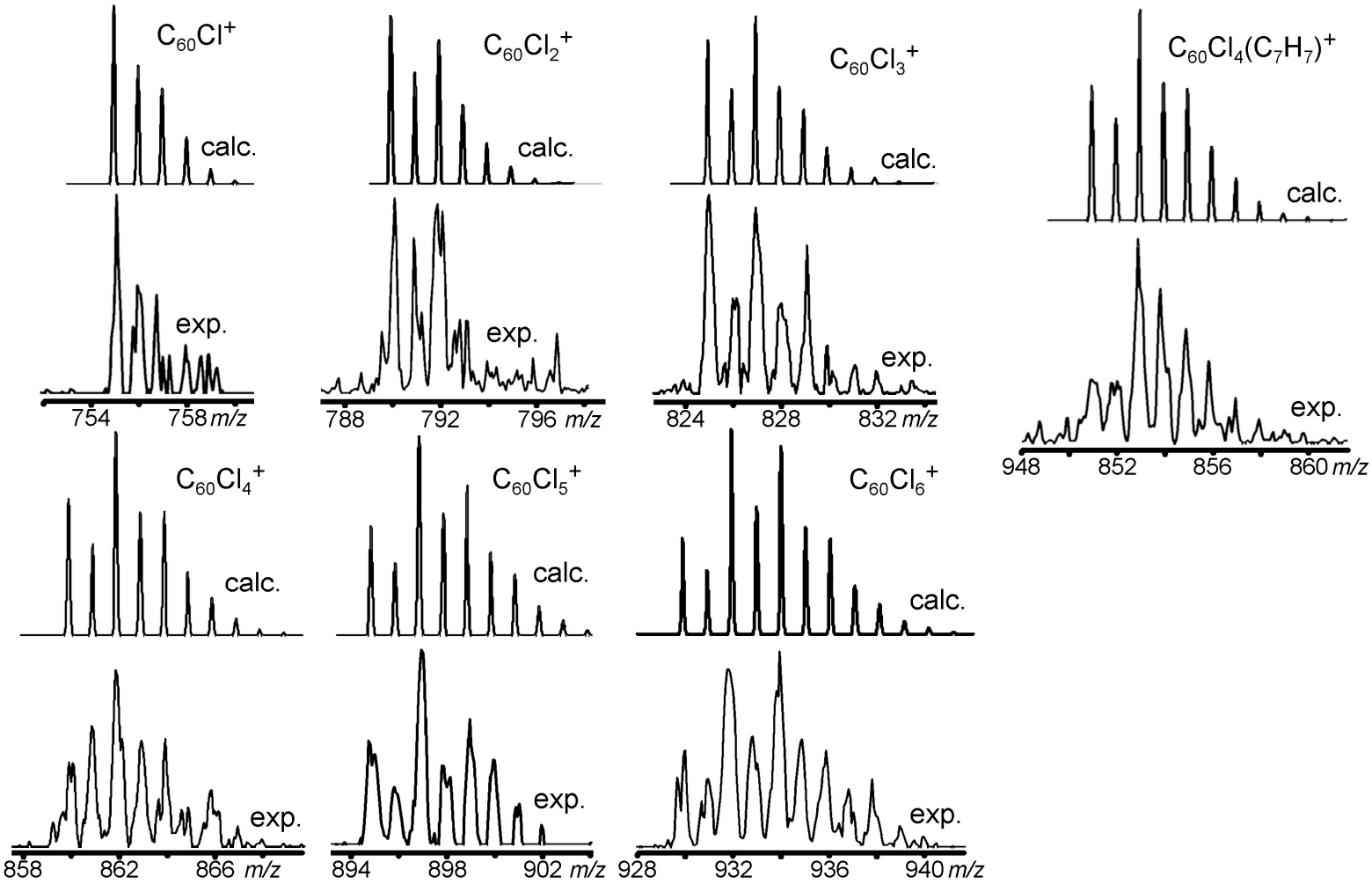

Figure A.9. Expansions of the experimental PI-APCI-MS of lower CFs (*o*-$C_{60}Cl_2$, *p*-$C_{60}Cl_2$, $C_{60}Cl_4$, $C_{60}Cl_6$) and calculated isotopic distributions of the corresponding ions.

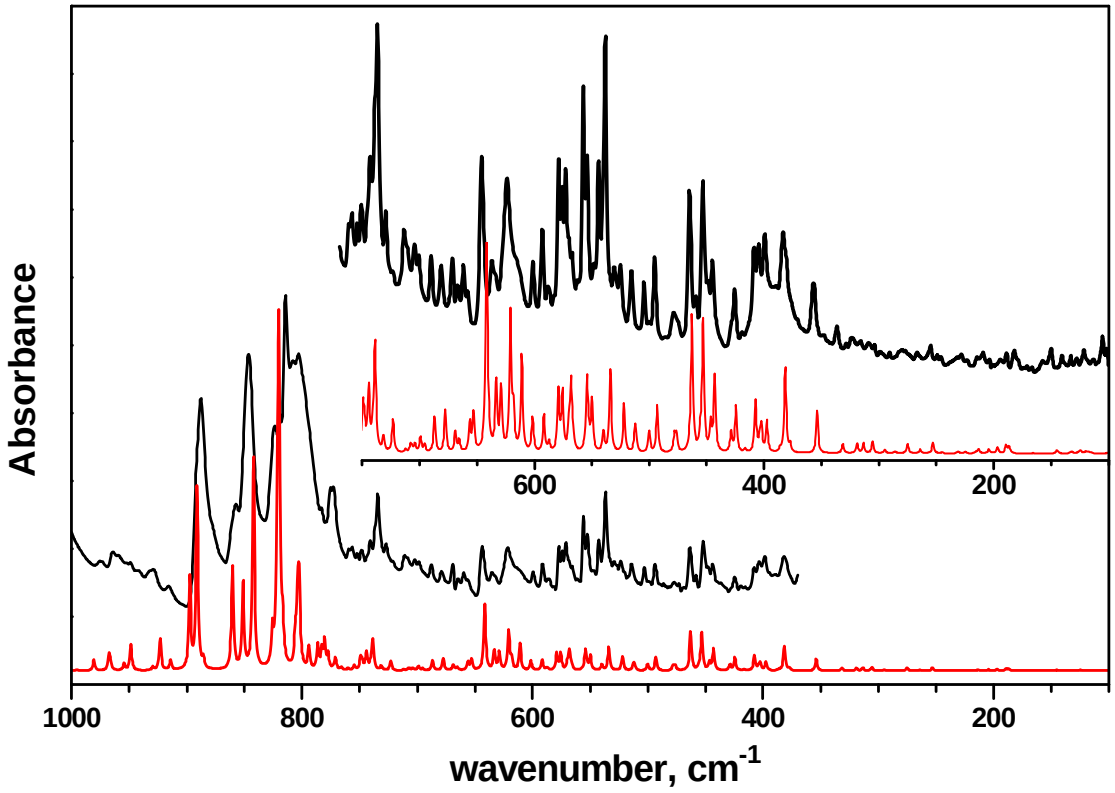

Figure A.10. Expansions of experimental (black) and simulated (red) IR spectra of $C_{60}Cl_{10}$.