SURFACE FUNCTIONALIZATION OF SILICON QUANTUM DOTS FOR ENERGY SUSTAINABLE APPLICATIONS

By

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Abstract

Silicon quantum dots (SiQDs) are an interesting material for many opto-electronic applications due to their size-tunable optical properties, nontoxicity, abundance, and potential integration into microelectronics. Since SiQDs are highly susceptible to oxidation, a protective passivation is crucial. To this end, halogen-terminated SiQDs can be functionalized with various reagents with desired anchoring atoms. This thesis focuses on two reaction schemes for halogenated SiQDs: direct colloidal synthesis of Cl-terminated SiQDs (Cl-SiQDs) and the indirect sol-gel synthesis of Cl- and Br-terminated SiQDs (Br-SiQDs). Colloidal Cl-SiQDs were functionalized by three distinct anchoring atoms (C, N, and O) and found to be significantly oxidized. Sol-gel SiQDs were chlorinated by phosphorus pentachloride and subsequently functionalized resulting in the partial passivation and aggregation of the SiQDs. In contrast, N-Bromosuccinimide was an effective reagent to brominate SiQDs, the first demonstration to the best of our knowledge. The direct functionalization of sol-gel SiQDs by Lewis acid tris(pentafluorophenyl)boron resulted in a failure to passivated the particles due to steric hindrance.
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To my wife, for being there every step of the way.
CHAPTER 1. INTRODUCTION

1.1 Energy Sustainability
Currently, the energy mankind depends on is predominantly from non-renewable energy sources (~90% of the total energy), including petroleum, coal, natural gas, and nuclear\(^1\). These energy sources are in limited quantity and predicted to be depleted within the next 200 years\(^2\), if their consumption rates are not dramatically decreased. In addition, the energy consumption has irreversibly impaired the environment through the production of green-house gases (carbon dioxide, methane, etc.) and induced global climate change\(^3\). Thus, to ensure sufficient energy for current generations and minimizing environmental harm; it is essential to actively invest in the development of an energy-sustainable world. In energy production, the solution is to rapidly increase the portion of renewable energies (currently ~10% of the total energy use). Renewable energies include solar, wind, biomass, geothermal, and hydraulic. Among them, solar is the most abundant energy source with one hour of sunlight capable of powering the whole world for a single year.\(^4\) A fast growing and promising area is the development of cost-effective and energy-efficient photovoltaic devices to capture solar energy. In energy conversion-and-storage, transportation, and utilization, the focus is on promoting clean, reusable, and energy-efficient methods, facilities, and devices, for example, rechargeable batteries and light emitting devices (LEDs). In summary, it is an inevitable task for the entire globe to realize long-term energy sustainability.

1.2 Silicon Quantum Dots (SiQDs)

Silicon, a nontoxic and earth-abundant element, has been the primary semiconductor material since the 1950’s, due to its applications in microelectronics and photovoltaics (PVs)\(^5\). However, one key factor limiting the growth of these two applications is the fixed energy band-gap (1.1 eV) of silicon. The band-gap of a semiconductor is the energy difference between its ground (valence band) and excited states (conduction band), at which an excited electron can conduct current freely. The empty space left by the excited electron is called a hole. Before the electron and the hole separate to produce current, these two particles interact with each other and can move together as a unit called an exciton (electron-hole pair)\(^6\). The energy holding them together is called binding energy (\(E_b\)). The exciton may also relax to the ground state, through the electron and hole recombination, releasing energy in the form of light (emission) and/or heat.
The energy gap ($E_g$) during the absorption/excitation process is called the absorption band-gap (or pseudo particle band-gap, $E_{g,a}$); and the energy gap during the relaxation/emission process is called the emission band-gap (or optical band-gap, $E_{g,e}$), where $E_{g,a} = E_{g,e} + E_b$. Usually, $E_b$ is negligible compared with $E_{g,a}$ and $E_{g,e}$. Thus, $E_{g,a}$ and $E_{g,e}$ are used interchangeably as $E_g$, without differentiation, as in this thesis. For a bulk semiconductor, the size of the exciton (called Bohr diameter) is governed only by the nature (chemical composition and the crystal structure) of the material and not the material’s dimension. When the material’s dimension is smaller than the Bohr diameter, the exciton is constricted within the material’s dimensions. As a result, the $E_g$ becomes size-dependent; the smaller the size, the bigger the $E_g$. This phenomenon is called the quantum confinement effect (QCE). When all three dimensions of a crystalline semiconductor are smaller than the Bohr diameter, the particle is called a quantum dot (QD). As the QDs decrease in size, they eventually become molecules, in which the valence band maximum and conduction band minimum evolve into the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The energy-diagrams of a molecule, QD, and bulk semiconductor, shown in Fig. 1.1, demonstrates the change in $E_g$ as the dimensions of a material are reduced. The QCE enables band gap engineering with simple size control thus expanding the uses of silicon.

![Energy diagram](image_url)

Figure 1.1. Energy diagram of a molecule, semiconductor nanocrystal (QD), and bulk semiconductor. Adapted from Ref 8.
SiQDs are Si nanocrystals of \( \leq 10 \text{ nm} \) in diameter. They can find important applications in the following areas. 1) Photovoltaics: band-gaps in the range of 1.1 – 2.5 eV will allow SiQDs to absorb visible light more effectively for single-junction PV devices. Moreover, SiQDs hold the promise for fabricating multi-junction PV devices and multi-exciton PV devices\(^9\)\(^{–}\)\(^{11}\). Different layers with different band-gaps (2.5 – 1.1 eV) can be realized using SiQDs of different sizes. 2) Lithium Ion Batteries (LIBs): Si has been identified as one of the most promising anode materials for LIBs. Due to the large (400\%) volume-fluctuation associated with the lithiation/delithiation cycles, the electrode and its electrical contacts with the current collector can seriously damaged, only Si nanocrystals (< a few hundreds of nm) have demonstrated promising performance\(^{12}^{–}\)\(^{14}\). 3) LEDs: Studies have shown that SiQDs can be the active material for green to red LEDs. If their energy efficiencies can be further improved to be comparable with the prevailing materials (such as GaN and CdSe), SiQDs will open a new era of QD-LEDs\(^{15,16}\). 4) Biological labeling: Biological sensors\(^{17}\) that utilize the color-tunable photoluminescent properties of SiQDs have also been demonstrated recently. All in all, the study of SiQDs is important for moving toward an energy-sustainable society.

1.3 Synthesis and Surface Functionalization

SiQDs are isolated and/or self-standing Si nanocrystals. They are prone to undesirable oxidation and aggregation due to their large surface/volume ratios and reactive dangling-bonds\(^{18}\). Thus, one important task in SiQD applications is to stabilize SiQDs through surface functionalization using desirable molecules. The stabilization chemistry is strongly dependent on how SiQDs are synthesized and what applications are being targeted. Our research interest lies in photovoltaics applications of SiQDs. The following sections provide a review of the synthesis and surface functionalization of SiQD literature.

1.3.1 Synthesis of SiQDs

The primary synthetic methods for SiQDs are: (electro)chemical etching of bulk Si, colloidal synthesis, chemical vapor deposition (CVD), and sol-gel synthesis.

a) (Electro)chemical Etching of Bulk Si: This method produced the first Si nanostructure (nanowires) in the QCE regime, reported by Canhman in 1990\(^9\), using Si wafer as the starting material. The electrochemical etching in an acid solution generated pores; the un-etched walls turned into quantum confined nanowire arrays. By decreasing the acid concentration and current density, SiQDs are produced instead of pores on the Si wafer surface. Nychyporuk \textit{et al.}
produced 2 nm SiQDs by changing the current density, electrolyte concentration, and time. The SiQDs produced using this method are terminated with hydrogen. While this method is advantageous over others in producing highly crystalline SiQDs, the atom- and energy-efficiency is undesirably low because the majority of the material was etched away.

b) **Colloidal Synthesis:** This approach was first introduced by Heath in 1992 and systematically explored by Kauzl and Tilley. The typical procedure is to reduce a reactive silicon precursor (like SiCl₄) with a strong reducing agent (like sodium naphthalene) in organic solvents under an inert atmosphere, shown in Figure 1.2. The reaction mechanism was believed to follow the classical LaMer model. The reaction between the Si-precursor molecules and the reducing agents produces a large amount of Si-containing radicals (such as \( \text{SiCl}_3 \)) called monomers. The monomers’ supersaturation immediately triggers their polymerization and produces a burst of nuclei. The nuclei subsequently grow into larger nanocrystals (i.e., SiQDs) through monomer addition and nuclei fusion. The smaller nuclei have higher surface energy and grow faster than the larger nuclei. This phenomenon is called “self-focusing” and sufficiently enables the production of colloidal SiQDs with narrow size distribution. If the reaction duration is sufficiently long, the monomer concentration would decrease below the monomer solubility; larger SiQDs would grow at the cost of dissolution of smaller SiQDs resulting in a broader size distribution. Thus, the reaction should be terminated before entering this Ostwald ripening regime. In addition, the particle size is also dependent on several factors, such as the silicon precursor and reducing agent, their molar ratio, and auxiliary agent to form micelles. Typically, the SiQDs produced using this method are spherical and 1 to 8 nm in diameter. The freshly produced SiQDs are terminated with either a halogen (Cl or Br) or hydrogen depending on the precursor and the reducing agent used. The halogen-terminated SiQDs are highly reactive and have to be replaced by further surface functionalization with more stable ligands in the same solution.

The advantage of using this method for surface functionalization lies in the versatile surface chemistry. SiQDs synthesized by this method do not present the expected red photoluminescence matching the TEM-observed particle sizes, but always show a high energy blue emission instead. There has been a long running debate about the possible explanations for these results. Initially, the reason was attributed to either surface traps or surface oxides. Very recently, several publications have provided convincing evidence that the mysterious blue emission originates
from nitrogen impurities from the ligands and oxidation.\textsuperscript{33,34} In these studies, SiQDs were produced by two colloidal methods involving charged nitrogen compounds and by the sol-gel synthesis. The colloidal SiQDs emitted blue as previously observed. The sol-gel H-terminated SiQDs emitted red initially but began to emit blue as they were exposed to charged nitrogen compounds and oxygen. This again confirms the importance and challenge of creating oxygen free environments even when using glove boxes.

\[
\text{in } \text{SiCl}_4 + (4m-1) \left[ \begin{array}{c} \text{Na}^+ \\
\end{array} \right] \xrightarrow{\text{DME RT}} \begin{array}{c} \text{Si} \\
\end{array} + (4m-1) \text{NaCl} + (4m-1) \text{SiH}_4
\]

Figure 1.2. Diagram showing the colloidal synthesis of SiQDs using SiCl\(_4\) as the Si precursor and sodium naphthalide as the reducing agent. Adapted from Ref. 66.

c) Chemical Vapor Deposition (CVD): The CVD process is performed in a gas phase and involves decomposing Si precursors, such as silane SiH\(_4\). The decomposing stimulus can be heat, laser, or plasma. Typically, SiQDs are collected on a filter in a vacuum chamber after the pyrolysis of the precursor into radicals and then condensation into nanoparticles. Thermal pyrolysis was used extensively in the first decade of SiQD research\textsuperscript{35–37}. This technique is simple to operate, but suffers low production yield and difficult to control particle sizes. In addition, the particles are uncharged and prone to aggregation even before collection. Laser pyrolysis has similar advantages and disadvantages, in addition to the requirement of a high power laser\textsuperscript{38–40}. Plasma-enhanced CVD (PECVD)\textsuperscript{41–44} uses an argon plasma generated by applying a high electric field to decompose silane molecules. This approach several has advantages. First, particle aggregation is effectively prevented because the as-synthesized particles in the gas phase are charged. Second, production yield is greatly improved because the charged reactor walls prevent the charged SiQDs from depositing on the reactor walls. Last, the plasma-generated high temperature (up to 1000\(^\circ\text{C}\)) is only localized on the particle surfaces, effectively annealing the particles and achieving high crystallinity despite the overall low temperature of the reactor. The QD sizes are dependent on the residence time of the particles in
the plasma and the plasma power. Fig. 1.3 shows transmission electron microscopy (TEM) images of two sizes (3 nm and 5 nm) of SiQDs resulting from different residence times. Recently, another method has been reported to control the QD sizes, i.e., introducing an etchant (SF$_6$) in the plasma stream. PECVD also has the ability to attach alkenes in-situ through hydrosilylation of the particles$^{45}$. This reduces the time involved with passivation and avoids oxidation that occurs when unpassivated particles are removed from the reactor. The disadvantages of PECVD include the low production yield of the reactor (1-10mg/hr) and the use of highly reactive chemicals.

![Figure 1.3](image)

Figure 1.3. TEM images of the PECVD particles, with selected area diffraction pattern and primary particle size distribution. a-c were produced by a residence time of 1.85ms; d-f were produced with a residence time of 6.8ms. The spacing of the fringes in images b and e is 0.31 nm, which corresponds to the (111) plane in diamond cubic silicon. Adapted from Ref 33.

**d) Sol-gel Synthesis:** This multi-step method was first demonstrated by the Veinot group in 2006$^{46,47}$. First, trichlorosilane was hydrolyzed at -78°C to produce a cage structured silicon oxide—hydrogen silisesquioxane (HSQ). Second, the produced HSQ sol-gel was heated at 1100°C for one hour under a 5% H$_2$/95% Ar atmosphere, producing SiQDs embedded in a matrix of non-stoichiometric silicon oxides. Last, SiQDs were released by etching away the oxide.
matrix with HF. During the thermal treatment, the transformations begin in temperature ranges of 400°C to 900°C, through rearrangements and cross-linking among HSQ molecules. Then the Si-H bonds begin to cleave; and regions elemental silicon form through disproportionation of the (SiO)n bonds. At temperatures above 900°C, the silicon regions begin to crystallize into SiQDs. The SiQD sizes are mainly controlled by the heating temperature, as shown in Fig. 1.4. The higher the temperature, the larger the particle sizes, as confirmed by sharper x-ray diffraction (XRD) peaks (Fig. 1.4B) and red-shifted photoluminescence (PL) peaks (Fig. 1.4C). The as-synthesized SiQDs are terminated with hydrogen and hydrophobic. This method is able to control particle sizes in a wider range of 3-9 nm. The precursor, trichlorosilane, is commercially available and inexpensive, making this method easy to scale up to produce HSQ. HSQ, itself, is also an inexpensive commercial precursor that can produce SiQDs in large quantities. The drawback is the use of HF, a very hazardous chemical to remove the oxide.

![Image](image.png)

Figure 1.4. Synthesis and characterization of SiQDs by the sol-gel method. (A) The cage structure of hydrogen silsesquioxane (HSQ). (B) XRD patterns of the thermally treated HSQ 1100–1400°C under 5% H2/95% Ar. (C) HRTEM of SiQDs embedded in an oxide matrix. (D) PL spectra of SiQDs embedded in oxide matrices, obtained by heating HSQ at 900–1400°C. Adapted from Ref 38.
1.3.2 Surface Functionalization of SiQDs

As shown in the previous section, as-synthesized SiQDs are either hydrogen-terminated or halogen-terminated. Such SiQDs are too reactive to be used in real applications. Moreover, studies have shown that the surface passivation can greatly affect the electrical and optical properties of SiQDs\(^{49-52}\). Thus, further surface functionalization of SiQDs is an important task. Below, we first elaborate on the ligand effect on the band-gaps of SiQDs, and then discuss hydrosilylation of H-terminated SiQDs, and derivation of halogen terminated SiQDs.

a) The Ligand Effect on the Band-gaps of SiQDs

Theoretical studies have shown that the band gaps of SiQDs are not only determined by the QCE, but also by the electronegativity of the passivating ligands\(^{50}\) as shown in Figure 1.5.

![Figure 1.5. Band gap dependence on size and passivation. The band gap is shown as a function of the QD diameter for SiQDs with different terminations. Adapted from Ref. 50.](image)

For a 1.5nm SiQD, CH\(_3\)– and NH\(_2\)-passivation present the band gap at 3eV. When the passivation is changed to -OH or -H, the band gap increases by over 1eV. This effect is assigned to the increased charge density on the QD-ligand interface, created by the highly electronegative atoms of O and F. The charged interface can significantly influence the wave function of the exciton, and in turn the band gap. So, the extent of the influence is dependent on particle sizes, or more specifically, the ratio of the number of the charged surface atoms to the number of the core atoms. The effect of the passivation can be split into three size regimes. For SiQDs larger
than 3.7 nm, the QCE is the dominant factor, since the majority of silicon atoms are in the core. For SiQDs between 0.7 and 3.7 nm, the ligand effect is strong enough to compete with the QCE in influencing the band gap. For SiQDs < 0.7 nm, the ligand effect surmounts the QCE in governing the band gap, since nearly all Si atoms are on the surface.

b) Hydrosilylation of H-terminated SiQDs

Hydrosilylation is a process of grafting alkene or alkyne molecules onto the H-terminated SiQDs, as shown in Fig. 1.6. This process originates from the silane reduction of alkenes or alkynes, which is widely used in organic chemistry. For SiQDs, the typical alkenes are dodecene or octadecene. The grafted long carbon chains can improve SiQDs’ stability in air and solubility in organic solvents. Hydrosilylation can be conducted through thermal treatment, UV-light radiation, or metal catalysis. The thermal treatment follows a radical mechanism with a reaction time on the order of hours or minutes depending on the reaction temperature and the nature of alkene/alkyne. Unfortunately the thermal treatment cannot attach short alkenes with low boiling points due to the high temperatures used. The hydrosilylation using UV-light follows the same radical process as the thermal treatment. Since the reaction is operated at room temperature, this method is more applicable to alkenes than the thermal treatment, allowing for the attachment of small molecules of low boiling points. The disadvantage of the UV treatment is that it is not scalable. The metal catalysis typically uses a platinum catalyst. This method applies to both short and long alkenes/alkynes as well as bifunctional molecules. The disadvantage is the difficulty in removing the unreacted catalysts afterward. These hydrosilylation methods all passivate SiQDs through Si-C bonds. If the alkene/alkyne molecules have compatible functional groups (such as epoxides or carboxylic acids) on the other ends of the carbon chains, hydrosilylation can control the polarity of the functionalized SiQDs to either hydrophilic or hydrophobic. The surface coverage of alkenes through hydrosilylation has been shown to be from 30-60%, depending on the ligands used. While hydrosilylation is a robust method for attaching alkenes to the SiQD surface, it is not useful for grafting other types of molecules such as alcohols, amines, and thiols. Other functionalization methods are needed.

c) Derivation of Halogen terminated SiQDs

As described in the previous section, hydrosilylation only attach carbon chains to SiQD surfaces, and has limited flexibility in meeting the needs of a variety of applications. This inability can be overcome by replacing the H-termination on the SiQDs to halogen-termination
(i.e., F-, Cl-, and Br-), such halogenated SiQDs will allow for many kinds of nucleophilic surface functionalizations, as illustrated in Fig. 1.7.

To realize these surface functionalizations in Figure 1.7, the halogen-termination can be constructed either during or after the synthesis. In principle, the SiQDs obtained by colloidal

![Figure 1.6. The reaction mechanism of hydrosilylation of SiQDs using 1-alkene (top) and 1-alkyne (bottom). Adapted from Ref 38.](image)

![Figure 1.7. Possible surface functionalizations of halogenated SiQDs with various nucleophiles.](image)

synthesis methods are ready for versatile surface functionalization, since they are naturally halogen-terminated. Similarly, the direct synthesis of Cl-terminated SiQDs has also been
demonstrated in the PECVD method, by using SiCl₄ as the precursor. However, the particles need to be transferred to a solution for subsequent passivation, a step that increases the risk of oxidation. Thus, the best option is to conduct the post-synthesis halogenation of H-terminated SiQDs from other synthesis methods. Veinot et al. reported chlorination of sol-gel derived SiQDs, by using phosphorus pentachloride (PCl₅) as the chlorination agent. The chlorination is performed by placing phosphorus pentachloride in a toluene solvent along with H-SiQDs at room temperature. However, the reaction mechanism was unclear since PCl₅ was insoluble in the reaction solvent toluene. Bromination has only been demonstrated in the cases of large silicon nanoparticles (>100nm) and using bromine as the agent.

1.4 The Question to Be Answered

Based on the discussion above, the question identified that is attempted to be answered in this thesis: Can we develop a versatile method for surface functionalization of SiQDs?

1.5 The Proposed Research

The raised question will be answered by testing three hypotheses: 1) Cl-terminated SiQD directly obtained from colloidal synthesis would be versatile approach to various anchoring units (C, O, and N); 2) NBS would be effective agent to brominate H-terminated SiQDs; and 3) Boron-based Lewis acids would be promising agents to directly catalyze various surface functionalizations of H-terminated SiQDs. The first hypothesis was motivated by limited exploration into attaching various ligands to the SiQD surface. The second hypothesis was stimulated by the wide usage of NBS in organic chemistry to brominate alkenes and aromatics, and carbonyls. The third hypothesis was motivated by the direct reactions of alkenes, alcohols, amines, and thiols with organosilanes under the catalysis of boron-based Lewis acids. The success of these two methods, particularly the latter, will open a new door for direct functionalization of H-terminated SiQDs.

The rest of the thesis is arranged as follows: Chapter 2 covers the colloidal synthesis and surface functionalization of chlorine-terminated SiQDs; Chapter 3 describes surface functionalization of sol-gel based H-terminated SiQDs through pre-halogenation; and Chapter 4 elaborates on the direct functionalization of H-terminated SiQDs using boron-compounds as catalysts. A road map of the reaction schemes for the rest of the thesis can be seen in Fig. 1.8 below.
Figure 1.8 A road map of reaction schemes used in this thesis.
2.1 Introduction

SiQDs are being extensively researched for photovoltaic applications due to the abundance and nontoxicity of silicon. Their band gap can be tuned by controlling the particle size. As a result, SiQDs have potential applications in multi-junction solar cells and multiple-exciton generation photovoltaics (PVs). Colloidal synthesis presents a convenient and scalable route for SiQD production. As described in Chapter 1, the colloidal synthesis of SiQDs can feature a halogen (typically chlorine) passivation, which allows for a variety of reactions to further functionalize the SiQD surfaces, as shown in Fig. 1.6. This can result in SiQDs functionalized with different anchoring atoms including carbon, nitrogen, oxygen, and sulfur. Such functionalizations will enable for investigation on the impacts different ligands have on the electronic and optical properties of SiQDs. The passivation effect has been shown in theory and has yet to be observed by experiment. The ligands 1-octanol, hexylamine, and hexyllithium were chosen for the resulting attachments of O, N, and C. Typically the attachment of the ligand is examined by Fourier transform infrared spectroscopy (FTIR) to detect the vibrational modes of the carbon chains and Si-ligand mode. Another method for determining attachment is nuclear magnetic resonance (NMR). NMR is a powerful technique that can detect changes in the chemical environment of the ligand. This sensitivity enables the detection of the anchoring atom to the SiQD surface through the changes in chemical shift that occurs to the ligand after attachment. NMR can also determine the concentration of the ligand on the SiQD surface through peak integration, which is not typically investigated. The concentration can be used to determine the surface coverage of the particle, which determines solubility and protection from oxidation. NMR allows for multiple characterizations with a single technique.

If the ligand contains a fluorescent moiety, i.e., an optically active functional group, there may be energy transfer between the ligands and the SiQDs, which is important for facilitating charge separation and transportation in photovoltaic devices. There have been several studies demonstrating the energy transfer between SiQDs and optically active ligands. Currently there has been little investigation into how fluorescent moieties impacts the energy/charge transfer between SiQDs. 1-Pyrenebutanol was chosen because its emission spectrum overlaps
with the absorption spectrum of SiQDs and feasibility of attachment with the Cl-terminated SiQDs.

In this work, we functionalized chlorine-terminated-SiQDs produced via colloidal synthesis\textsuperscript{62} with 1-octanol, hexylamine, hexyllithium and 1-pyrenebutanol as shown in Fig. 2.1.

\begin{equation}
\text{m SiCl}_4 + (4m-1) \text{Na}^+ \xrightarrow{\text{DME RT}} \text{Si-Cl} + (4m-1) \text{NaCl} + (4m-1) \text{1-Octanol}
\end{equation}

Figure 2.1. Colloidal synthesis and passivation scheme of SiQDs with 1-octanol, 1-hexylamine, hexyllithium, and 1-pyrenebutanol.

2.2. Experimental Section

The chemicals used were 1,2-dimethoxyethane (anhydrous, Sigma-Aldrich), sodium metal (ACS reagent, stick dry, Sigma-Aldrich), naphthalene (99%, Sigma-Aldrich) SiCl4 (99% metal basis, Alfa Aesar), 1-octanol (anhydrous, Sigma-Aldrich), hexyllithium (2.3M in hexane, Sigma-Aldrich), hexylamine (99%, Sigma-Aldrich), 1-pyrenebutanol (99%, Sigma-Aldrich), ethanol (anhydrous, 99.9%, Sigma-Aldrich) and methanol (anhydrous, 99.8%, Sigma-Aldrich). All chemicals were used as received unless otherwise noted.

2.2.1 Synthesis of Octanol Passivated SiQDs (SiQD-OC\textsubscript{8})

A solution of sodium (0.49 g, 21.3 mmol) and naphthalene (1.362 g, 10.6 mmol) in 1,2-dimethoxyethane (25 ml) and was stirred overnight (16 hr) in a 50 ml flask to form sodium naphthlide. The sodium naphthalide solution was added rapidly via a glass syringe to a 300 ml Schlenk flask containing 1,2-dimethoxyethane (75 ml) and silicon tetrachloride (0.325 ml, 2.83 mmol) while rapidly stirring. After 1 hour, 1-octanol (1.5 ml, 9.5 mmol) was added drop wise. The mixture was stirred for 12 hours then allowed to settle for another 12 hours. The yellow solution was decanted from the solids and; the solvent was removed by vacuum resulting in
yellow liquid. The liquid was heated under vacuum to remove residual naphthalene yielding a viscous yellow oil of SiQD-OC₈, which was dissolved in chloroform.

2.2.2 Synthesis of Hexyllithium Passivated SiQDs (SiQD-C₆)

A solution of sodium (0.647g, 28.1 mmol) and naphthalene (1.365 g, 10.6 mmol) in 1,2-dimethoxyethane (25 ml) was stirred overnight (16 hr) in a 50 ml flask to form sodium naphthalide. The sodium naphthalide solution was added rapidly via a glass syringe to a 300 ml Schlenk flask containing 1,2-dimethoxyethane (75ml) and silicon tetrachloride (0.325 ml, 2.83 mmol) while rapidly stirring. After 1 hour, hexyllithium (1.0 ml, 2.3 mmol) was added drop wise. The mixture was stirred for 12 hours then allowed to settle for another 12 hours. The brown solution was decanted from the solids and; the solvent was removed by vacuum resulting in yellow liquid. The liquid was heated under vacuum to remove residual naphthalene yielding a viscous brown oil of SiQD-C₆, which was dissolved in chloroform.

2.2.3 Synthesis of Hexylamine Passivated SiQDs (SiQD-NC₆)

A solution of sodium (1.078 g, 46.89 mmol) and naphthalene (2.72 g, 21.2 mmol) in 1,2-dimethoxyethane (25 ml) was stirred overnight (16 hr) in a 50 ml flask to form sodium naphthalide. The sodium naphthalide solution was added rapidly via a glass syringe to a 300 ml Schlenk flask containing 1,2-dimethoxyethane (75 ml) and silicon tetrachloride (0.650 ml, 5.66 mmol) while rapidly stirring. After 1 hour, Hexylamine (0.735 ml, 5.56 mmol) was added drop wise. The mixture was stirred for 12 hours then allowed to settle for another 12 hours. The yellow solution was decanted from the solids and; the solvent was removed by vacuum resulting in yellow liquid. The resulting liquid was heated under vacuum to remove residual naphthalene yielding a viscous yellow oil of SiQD-NC₆, which was dissolved in chloroform.

2.2.4 Synthesis of 1-Pyrenebutanol Passivated SiQDs (SiQD-OPy)

A solution of sodium (0.117g, 5.09mmol) and naphthalene (0.660 g, 5.15 mmol) in 1,2-dimethoxyethane (25 ml) was stirred overnight (16 hr) in a 50 ml flask to form sodium naphthalide. The sodium naphthalide solution was added rapidly at room temperature via a glass syringe to a 300 ml Schlenk flask containing 1,2-dimethoxyethane (75 ml) and silicon tetrachloride (0.265 g, 2.31 mmol) while rapidly stirring. After 1 hour, 3.0 ml of a 1-pyrenebutanol solution (0.100 g, 0.364 mmol) in 1,2-dimethoxyethane was added drop wise followed by ethanol (1 ml, 17.1 mmol) after one hour. The mixture was stirred for another 10 hours then allowed to settle for another 12 hours. The yellow solution was decanted from the
solids and; the solvent was removed by vacuum resulting in yellow liquid. The liquid was heated under vacuum to remove residual naphthalene yielding a viscous yellow oil of SiQD-OPy, which was dissolved in chloroform or tetrahydrofuran (THF). AF4 was used to remove the excess 1-pyrenebutanol from the SiQD solution.

The SiQDs were characterized by using a UV-1800 Shimadzu UV Spectrophotometer (UV-Vis), a PTI Fluorescence with 914 Photomultiplier Detection system and LPS-100 Lamp Power supply (PL), a Jeol ECA-500 (NMR), a Thermo Nicolet 4700 FT-IR with Smart Orbit attachment (FTIR), and Philips/FEI CM200 Transmission Electron Microscope (TEM). For FTIR the sample was dropped onto the ATR plate and allowed to dry before 32 scans at a resolution of 2 cm\(^{-1}\) were performed. For PL the sample was placed into a quartz cuvette and which was then into the sample holder. For TEM, the SiQD samples were dropped onto a carbon film 400 square mesh copper grid purchased from Electron Microscopy Sciences.

2.3 Results and Discussion

The following subsections are a discussion on the results obtained from the previously described methodology on the attachment of the three anchoring units (C, O, and N) to the Cl-SiQDs along with the purification of SiQD-OPy by asymmetric flow field flow fractionation (AF4).

2.3.1 Characterization of 1-Octanol (HO-C\(_8\)), Hexyllithium (Li-C\(_8\)), and Hexylamine (H\(_2\)N-C\(_6\)) Passivations

The optical properties of the three SiQDs passivations were investigated by UV-Vis and photoluminescence (PL) to determine any ligand dependent effects are observed. The UV-Vis spectra (Fig. 2.2A) of these SiQDs show a peak at 275nm, similar to literature results\(^{63}\). The absorbance onsets are at 420nm, 430nm, and 400nm for SiQD-OC\(_8\), SiQD-C\(_6\), and SiQD-NC\(_6\), respectively. These results suggest that absorbance originate from the SiQD core, with little or no contribution from the ligands. The PL spectra (Fig. 2.2B) have single peaks centered at 420nm suggesting that the three particles have comparable sizes. The similarity of the peaks indicates the ligands have no impact on the optical band gap of the SiQDs. This is consistent with the theoretical results shown in Fig. 1.5, for SiQDs larger than 4 nm (see below). Recent work from the Veinot group\(^{34}\) suggests that trace amounts of oxygen and the nitrogen-containing organic compounds (e.g. tetaoctylammonium bromide) give rise to blue emissions in the range of 350 - 600 nm. This conclusion does no hold for the SiQD-OC\(_8\) and SiQD-C\(_6\) systems herein since no
nitrogen compounds were used in the synthesis. Thus, it can be speculated that the blue emissions observed in our experiments arise from oxidation of SiQDs. The results of the UV-Vis and PL measurements conclude there are no observed impacts on the optical properties due to either large SiQD sizes and/or oxidation of the particles.

The size distribution of the SiQDs after each passivation was determined with TEM (Fig. 2.3). The observed SiQDs-OC₈ (Fig. 2.3A) were found to be 4 nm to over 100 nm in diameter. It is not clear from this image if the large particles are aggregates of smaller SiQDs or individual particles. However, the PL of the SiQD-OC₈ suggests a particle size in the range of 4-5nm, which is smaller than TEM results. The image in Fig. 2.3D shows a large aggregate particle (>200nm). The energy-dispersive x-ray analysis (EDX) indicates that this particle consists of silicon and sodium chloride (NaCl), the latter being a by-product of the SiQD synthesis. Crystalline nature of the large particle suggests a NaCl crystal with small-incorporated SiQDs. Due to the low contrast of silicon, it is possible that these small particles could not be visualized by TEM. This hypothesis was tested by performing an EDX analysis to determine if there was silicon in the blank areas of the TEM grid. Fig. 2.3E shows a “blank” area of the grid with no particles. The EDX surprisingly shows silicon where no particles are observed. This suggests the presence of small particles in the SiQDs-OC₈ sample that are not discernable with TEM.
Figure 2.3. TEM and energy-dispersive x-ray analysis (EDX) of SiQDs with various terminations. TEM image of SiQD-OC$_8$ (A). TEM image of SiQD-NC$_6$ (B). TEM image of SiQD-C$_6$ (C). TEM and EDX of SiQD-OC$_8$ aggregate (D). TEM and EDX of "blank" carbon grid from of SiQD-OC$_8$ (E).

The size range of SiQD-NC$_6$ was found by TEM to be from 3-10 nm in diameter (Fig. 2.3B). The SiQD-NC$_6$ sample was composed of large aggregate particles that are approximately 15-20nm in diameter (Fig. 2.3C). Smaller particles were not observed probably due to the same reason as for SiQDs-OC$_8$. Due to these “invisible” SiQDs, it was impossible to accurately determine the sizes and size distributions of SiQDs using TEM. In addition, the particle sizes were not correlated to the PL of the SiQDs seen in Fig. 2.2.

The SiQD-C$_6$ and SiQD-NC$_6$ samples were investigated with selected area electron diffraction (SAED) (Fig. 2.4) to determine the composition of the particles. The d-spacings of 1.85Å (Figure 2.4A) and 2.44Å, 2.08Å, 1.78Å, 1.5Å, 1.2Å (Figure 2.4B) extracted from SAED are close matches to the (112), (110), (200), (003), (211) and (213) d-spacings of silicon dioxide$^{64}$. This suggests that the particles are primarily composed of silicon dioxide. Hence SiQD oxidation is the likely explanation for the observed anomalous blue emission of the passivated SiQDs. These results indicate that the colloidal synthesis method produces SiQDs with blue emissions in the presence of trace amounts of oxygen, even if there are no nitrogen compounds present in the reaction, different from the conclusion in recent literature$^{34}$. These
results along with the PL (Fig. 2.1) indicate that the abnormal optical properties of the colloidal SiQDs herein arise from a composition of silicon dioxide rather than quantum confinement. The cause of the oxidation is attributed to the extreme reactivity of Cl-SiQDs even in a glove box.

Figure 2.4. The selected area electron diffraction (SAED) of passivated SiQDs. SAED of A) SiQD-C\textsubscript{6} and B) SiQD-NC\textsubscript{6}.

The ligand attachment was investigated by FTIR (Fig. 2.5) to confirm the functionalization of the SiQDs by the desired anchoring atom. The peaks at 2900 cm\textsuperscript{-1} to 3000 cm\textsuperscript{-1}, 1500 cm\textsuperscript{-1} to 1400 cm\textsuperscript{-1}, and 700 cm\textsuperscript{-1} arise from the stretching and bending modes of CH\textsubscript{x} confirming the presence of the ligands. The peaks 1000 cm\textsuperscript{-1} to 1100 cm\textsuperscript{-1} arise from the Si-O-Si stretch, corroborating the SAED conclusion of oxidation. For the Si-OC\textsubscript{8}, The presence of the oxide peak masks the Si-O-C peak (1080-1000 cm\textsuperscript{-1}), prohibiting the confirmation of the 1-octanol attachment. The OH stretching mode from 3300 cm\textsuperscript{-1} to 3600 cm\textsuperscript{-1} suggests the presence of excess 1-octanol or hydroxyl groups on the Si surface. In the FTIR spectrum of SiQD-C\textsubscript{6}, the Si-O-Si stretching mode masks the Si-C stretch modes at 1080 cm\textsuperscript{-1} and 1020 cm\textsuperscript{-1} making the confirmation of the Si-C bond unachievable by FTIR. In the FTIR spectrum of SiQD-NC\textsubscript{6}, the primary NH bending mode at 1600 cm\textsuperscript{-1} is absent. Concurrently, the secondary NH bending mode at 1650 cm\textsuperscript{-1} appears after passivation. The peak at 3660 cm\textsuperscript{-1} in the SiQD-NC\textsubscript{6} spectrum likely corresponds to the stretching mode of N-H. The absence of a second lower wavenumber peak suggests the loss of the symmetric stretching mode of the N-H bonds. These results suggest that the ligand has attached to the SiQD surface. The Si-N stretching mode should be located at 800 cm\textsuperscript{-1} is likely masked by the C-Cl stretching mode at 774 cm\textsuperscript{-1} from chloroform in the sample. The peaks at 3060 cm\textsuperscript{-1}, and 1615-1580 cm\textsuperscript{-1} in all the SiQD spectra arise from the
aromatic compound naphthalene present due to incomplete purification. These results demonstrate that FTIR is not an effective method for the determination of the ligand attachments to SiQDs due to overlapping absorbance modes and low sensitivity to the amount of material. A more sensitive technique is needed.

Figure 2.5. FTIR spectra of SiQD-OC₈, SiQD-NC₆, and SiQD-C₆. The FTIR spectra of 1-octanol and Hexylamine are also displayed. The FTIR of Hexyllithium was not obtained due to the reactivity of the molecule.

Since FTIR was unable to conclusively confirm the functionalization of the SiQDs, NMR was employed since it can detect the environmental changes of H and C atoms that are directly attached to or adjacent to Si surface if ligand attachment occurs. The ¹H NMR (Fig. 2.6) for SiQD-OC₈ has three peaks at δ=0.89 (8), δ=1.31 (4-7), and δ=1.6 (2,3) corresponding to the methyl (8), and methylene (2-7) peaks of 1-octanol. The hydroxyl group is absent and suggests a
low concentration of excess 1-octanol. Peak 1*, the methylene proton adjacent to oxygen after functionalization, appears at $\delta=3.8$, which is shifted from unattached 1-octanol methylene (1) at $\delta=3.6$ due to the surrounding atoms (Si-O-CH$_2$-) deshielding the proton group. This indicates the attachment of 1-octanol to the SiQD surface and will allow for the concentration of 1-octanol to be determined.

![NMR spectrum of 1-Octanol and SiQD-OC8](image)

Figure 2.6. $^1$H NMR of 1-Octanol and SiQD-OC8 in chloroform with tetramethylsilane (TMS).

The $^{13}$C NMR of SiQD-OC$_8$ (Fig 2.7) agrees with the results of the $^1$H NMR. Peaks $\delta=14$ (8), $\delta=23$ (7), $\delta=26$ (6), $\delta=29.6$ (4,5), $\delta=32$ (3), $\delta=33$ (2), and $\delta=64$ (1*) correspond to the methyl (8) and methylene (2-7) groups of unattached 1-octanol. The methylene adjacent to oxygen after functionalization, 1*, shifted from the corresponding peak of the unattached ligand, 1, from $\delta=63$ to $\delta=64$. This is most likely due to the deshielding of the carbon atom caused by the 1-octanol
attachment to the SiQD surface. It is also possible that the observed shift in peak 1* is caused by the environmental change after the reaction and not the attachment to the SiQD. 2D heteronuclear correlation NMR (HETCOR) was conducted to confirm the corresponding shifts in the resonance of the methylene protons and carbon atom were coupled but not the result of a side reaction or change in chemical environment of the free ligand.

Figure 2.7. $^{13}$C NMR of 1-Octanol and SiQD-OC$_8$ in chloroform with tetramethylsilane (TMS).

In the HETCOR spectrum (Fig. 2.8), the group 1 proton and carbon couplings, where the peak $^1$H $\delta$=3.65 correlates with $^{13}$C $\delta$=63 and the peak $^1$H $\delta$=3.75 correlates with $^{13}$C $\delta$=64. These two distinct couplings confirm that the two peaks observed in the proton and carbon spectra originate from excess 1-octanol and 1-octanol attached to SiQDs. The alkyl groups from $^1$H $\delta$=0.8-2.0 (2-7) couple with the alkyl groups $^{13}$C $\delta$=14.0-35.0 (2-7) as expected. Using this information, the amount of 1-octanol attached to the SiQDs was determined to be 2.75x10$^{-2}$ mmol compared to the internal standard tetramethylsilane (TMS). The surface coverage of the 1-
octanol could not be calculated due to the wide size distribution of obtained SiQDs and significant amounts of “invisible” SiQDs in TEM as discussed previously.

The $^1$H NMR spectrum of SiQD-NC$_6$ (Fig. 2.9) shows three peaks at $\delta$=0.89 (6), $\delta$=1.31 (3-5), $\delta$=1.41 (2), and $\delta$=2.76 (1*) corresponding to the methyl (6), and methylene (2-5) peaks of hexylamine. Peak 1* appears at $\delta$=2.76, shifted from $\delta$=2.63 suggesting attachment to the SiQD. The peaks have been shifted and slightly broadened compared to unattached hexylamine. This is due to an unexpected side reaction of the amine with the solvent, chloroform, gelling the sample. The broadening of peak 1* may suggest that the attachment to the SiQD surface has restricted the degree of freedom of the proton groups.$^{65}$ $^{13}$C NMR may be able to confirm the attachment through a shift in the nitrogen adjacent methylene peak (1*). The peaks $\delta$=14 (6), $\delta$=23 (5), $\delta$=26 (4), $\delta$=32 (3), $\delta$=34 (2), and $\delta$=42 (1) observed in the $^{13}$C NMR spectrum of the SiQD-NC$_6$ (Fig. 2.10) correspond to the methyl (6) and methylene (1-5) peaks of hexylamine. As in the case of SiQD-OC$_8$, peak 1* is expected to shift downfield after the functionalization; however, the peak
shifted upfield since carbon 1* gained electron density after attachment. The peak broadening implies the attachment of hexylamine to the SiQDs as previously described. The FTIR and NMR results together confirm the attachment of hexylamine to the surface of the SiQD.

HETCOR (Fig. 2.11) was employed on the SiQD-NC$_6$ sample to confirm the peak assignment seen in Fig. 2.9 and Fig. 2.10. The $^1$H alkyl peak from $^1$H $\delta$=0.8-2.0, 2-6, couple with the alkyl groups $^{13}$C $\delta$=14.0-35.0, as expected for the methyl and methylene peaks for hexylamine. Peak 1 shows coupling between $^1$H $\delta$= 2.7 and $^{13}$C $\delta$= 42, the proton and carbon peak 1, which confirms the attachment of the hexylamine to the SiQD surface. The amount of
hexylamine attached to the SiQD surface and the surface coverage could not be determined because of a side reaction between amine and chloroform causing the sample to solidify and the wide size range of particles (see Fig. 2.2B).

The $^1$H NMR of SiQD-C$_6$ (Fig. 2.12) shows three peaks at $\delta=0.6$ (6), $\delta=0.89$ (1), and $\delta=1.3$ (2-5) which corresponded to the alkyl proton resonances of hexane attached to the SiQDs. The attached hexyl groups of the SiQD-C$_6$ shifted from the standard peak positions of hexane ($\delta=0.89$ and $\delta=1.27-1.29$ for the methyl and methylene peaks) due to being bonded to the particle surface greatly changing their chemical environment. In particular, peaks 1 and 6, the methylene and the methyl groups adjacent to the SiQD surface, shifted into two peaks at $\delta=0.89$ and $\delta=0.6$,
when they would typically be observed as a single peak at $\delta=0.89$. These results suggest the attachment of the hexyl group to the SiQD surface due to the peak shifting. The $^{13}$C NMR of the SiQD-$C_6$ sample has three groups of peaks at $\delta=13$ (6), $\delta=14$ (1), $\delta=23$ (2), $\delta=23.6$ (5), $\delta=32$ (4), and $\delta=34$ (3). These peaks show two peaks centered at the hexane positions ($\delta=14.13$, 22.17, 31.65), which would not typically be seen for hexane. This indicates a major change in the chemical environment of the hexyl group upon attachment to the SiQD. The peak shifting calls into question the peaks assignments for the attached hexane molecule. HETCOR NMR was performed to confirm the assignment of the peaks in the $^1$H and $^{13}$C spectra.

The 2D spectrum (Fig. 2.13) of the SiQD-$C_6$ couplings confirmed the peak assignments seen in the $^1$H and $^{13}$C NMR (Fig. 2.11). The peak 1 signals correspond to $^1$H $\delta=0.95$ and $^{13}$C $\delta=18$ coupling. The coupling of these peaks confirms the peak assignment and confirms the ligand attachment to the SiQD. This confirmation of the attachment allowed the amount of
Figure 2.12. $^1$H and $^{13}$C NMR of SiQD-C$_6$ in chloroform.

ligand on the SiQDs to be determined as $8.29 \times 10^{-1}$ mmol through integration of the methylene peak. Similar to the SiQD-OC$_8$ and SiQD-NC$_6$ cases, the surface coverage of the hexane could not be calculated due to the wide size range of particles.

2.3.2 Characterization and Purification of 1-Pyrenebutanol-terminated SiQDs (SiQD-OPy).

The functionalization of Cl-terminated SiQD by the fluorophore, 1-pyrenebutanol (PyOH), was conducted to study the impact of an optically active ligand on SiQD energy transfer. The UV-Vis and PL spectra of the SiQD-OPy and PyOH (Fig. 2.14) were measured to determine the effect that pyrene has on the optical properties of SiQDs (comparable SiQD-OC$_8$ sample UV-Vis and PL can be seen in Fig. 2.2). The absorption spectrum of the SiQD-OPy is nearly identical to that of pure PyOH except for an unknown single peak at 221nm. The similarity is due to the strong absorption of the pyrene masking the weaker absorption of the
Figure 2.13. HETCOR of SiQD-C₆.

SiQD. Thus, UV-Vis cannot be used to conclude if there is change in the SiQD’s absorbance or whether of PyOH has been successfully attached. The PL spectrum of the SiQD-OPy shows an additional two pyrene peaks at 397nm and 420nm with a large peak at 460nm. Upon investigation into the emission of the pyrene molecule, it was found that at pyrene concentrations greater than 0.1 mmol a peak in the range of 450-480nm will appear. This peak is due to the formation of an excimer in which two molecules interact in an excited state to form a dimer. This suggests the peak in the SiQD-OPy at 460nm forms due to pyrene excimer either in solution or on the SiQD surface. The appearance of the excimer and no observed SiQD peaks necessitates the removal of the excess PyOH from the solution to determine the impact of PyOH on the optical properties of SiQDs.

The attachment of the PyOH was examined by FTIR. The FTIR of SiQD-OPy (Fig. 2.15) shows the presence of the aromatic pyrene ring at 3020, 1620, 1245, and 1210 cm⁻¹. As in the
previous case, it was not possible to observe the Si-O-C stretching modes confirming attachment. This is due to the interference of Si-O-Si at 1000-1100 cm\(^{-1}\) formed because of oxidation. The FTIR measurement was unable to confirm the attachment of the PyOH to the SiQD surface. NMR was used to determine the attachment of the PyOH to the surface of the SiQD. The \(^1\)H NMR (Fig. 2.16) shows several peaks at \(\delta=1.7\ (3), \delta=1.9\ (4), \delta=3.46\ (2)\) and \(\delta=7.4-8.4\ (Ar)\), corresponding to the alkyl and aromatic proton resonances of PyOH respectively. The attachment of PyOH to SiQDs should shift the peak originally at \(\delta=3.68\) to higher ppm, as previously discussed. Group 1* could be assigned to \(\delta=3.83\); but the strong tetrahydrofuran (THF) peak at \(\delta=3.75\) makes it difficult to confirm the assignment. NMR confirms the presence of PyOH in the particle system but is unable to determine attachment. The results from NMR, FTIR, and PL indicate the need of further purification before characterization.

Asymmetric flow-field flow fractionation (AF4) is a size-separation technique that is able to separate particles of 1 nm to 10 \(\mu\)m in a single open channel\(^69\). AF4 uses a laminar flow profile
of the solvent through a channel in an applied field. The applied field is a cross flow of solvent that forces the particles towards an accumulation wall while diffusion causes particles motion away from the wall. These two opposing transport processes and the direct proportionality between diffusion coefficient and the hydrodynamic radius of the particles lead to different sizes occupying different velocity streams in the channel. This causes the retention to be proportional to the size. A focusing step is also used to position the particles at the same starting point in order to reduce line broadening. During the focusing step, the solvent is driven through a semi-permeable membrane on the accumulation wall. This step also allows small molecules such as excess reagent to exit the channel resulting in an on-line purification process. The focusing step results in a simple purification process allowing for a size separation without pretreatment. Thus, AF4 was employed to remove the excess PyOH out of the SiQD-OPy sample. Fig. 2.17 shows

Figure 2.15. FTIR of 1-Pyrenebutanol and the SiQD-OPy sample.
the purification results with various focusing times. During the focusing process, the carrier fluid along with the excess PyOH can exit through the permeable membrane while the SiQD-OPy is retained inside the AF4 channel. A focusing study (Fig. 2.17A) was used to determine the time needed to flush the excess PyOH out of the channel. The PyOH peak was significantly reduced when a focusing time of 6 min was used. Fig. 2.17B shows the effectiveness of focusing time on the removal of excess PyOH from the SiQD-OPy sample. The PL of the purified SiQD-OPy sample (Fig. 2.18) revealed that after purification the pyrene excimer was still present. This suggests that the PyOH excimer originated from PyOH dimers that are formed because of close
packing PyOH molecules on the SiQD surface. Unfortunately, PL could not confirm that the measured emission originated from SiQD-OPy, due to the spectral interference from the pyrene excimer. These results impeded further investigation into the energy transfer between the PyOH and the SiQDs as well as between the particles themselves.

Figure 2.17. Fractograms of A) focusing study of PyOH and B) purification of SiQD-OPy at various focusing times.

2.4 Conclusions

The synthesized chlorine-terminated SiQDs were functionalized with four different ligands with three distinct anchoring atoms (O, C, and N). The resultant SiQDs did not show ligand-dependent absorption and emission properties, because the SiQDs were outside the QCE regime and also strongly oxidized. While FTIR was unable to determine the attachment of the ligands due to interference of silicon oxide, NMR confirmed the attachment through the observation of the deshielding effect of the methylene groups adjacent to the SiQD. Two-dimensional NMR was able to differentiate between free ligand in solution from the attached ligand on the basis of the chemical shifts observed in the $^1$H and $^{13}$C NMR. In the case of the SiQD-NC$_6$, NMR confirmed the attachment of the hexlyamine but was unable to determine the amount of ligand on the SiQD. The attachment of the optically active PyOH was confirmed after the effective purification using AF4. The PyOH excimer was found to be the dominant emitting species, masking the emission from SiQDs prohibiting the energy transfer study. Moreover, the formation of silicon dioxide was observed during the synthesis of SiQDs. These results indicate
Figure 2.18. PL spectra of SiQD-OPy samples before and after the AF4 purification with a SiQD-OC₈ for reference.

that this particular solution synthesis method is prone to oxidation and explains the blue emission observed for large SiQDs. This observation is different from literature reports that the oxidation of nitrogen-containing compounds resulted in blue emissions.
CHAPTER 3. HALOGENATION OF SOL-GEL SYNTHESIZED HYDROGEN-TERMINATED SIQDs FOR SURFACE FUNCTIONALIZATION

3.1 Introduction

As discussed in Chapter 2, SiQDs synthesized using the colloidal chemistry approach can be prone to serious oxidation, because the Cl-terminated particle surfaces rapidly reacted with trace amounts of oxygen and water. It is possible that such a problem may be mitigated via halogenation of pre-made SiQDs. This ensures the SiQDs are composed of crystalline silicon and not oxide. Thus, in this chapter, the surface functionalization of sol-gel synthesized SiQDs is studied through the use of halogenation. In the literature there is only one example of the halogenation of H-terminated SiQDs demonstrated by Veinot et al., where H-SiQDs synthesized by the sol-gel method were chlorinated and functionalized with allylamine. PCl₅ is insoluble in the solvent used, toluene, severely limiting its reactivity with H-SiQDs. To mitigate this problem, a halogenation reagent that is soluble will be desirable, such as N-bromosuccinimide (NBS). NBS is a broadly used bromination reagent in organic chemistry to brominate alkenes and aromatics. It has also been shown to brominate hydrogen-terminated Si wafers. To the best of our knowledge, the use of NBS for the bromination of H-SiQDs has not been previously reported in literature.

In this Chapter, two major studies will be presented: surface functionalization of sol-gel synthesized SiQDs via chlorination (using PCl₅) and bromination using NBS. The surface functionalization includes two types of ligands: 1-octanol and tert-butyldimethylsilanol (silanol). These ligands were chosen due to the nucleophilic nature of their hydroxyl groups and our previous experience in characterization.

3.2 Experimental Section

Anhydrous chemicals chloroform, 1-octanol, chlorobenzene, and ethanol and high purity chemicals hydrofluoric acid (HF), trichlorosilane, tert-butyldimethylsilanol, benzoyl peroxide, phosphorous pentachloride, triethyldimethylsilane, methanol, and toluene were purchased from Aldrich and used as received.

3.2.2 Synthesis and etching of H-SiQDs by the sol-gel method

The H-SiQDs were synthesized following a literature procedure reported by Ozin. Hydrogen silsesquioxane (HSQ) was synthesized by placing trichlorosilane (13.4g, 99 mmol) in
a 100ml three-neck flask. The flask was placed on a Schlenck line with nitrogen gas flowing through the flask. The trichlorosilane was cooled in an acetone/dry ice bath (-78°C) for 5 min while stirring before 50 ml of water (Millipore, 18.2Ω) was injected. The mixture was allowed to warm to room temperature while stirring for 40 min producing a white precipitate and hydrochloric acid. The resulting HSQ was washed with water to remove the hydrochloric acid then placed under vacuum to dry for 24 hours. Finally 4 grams of HSQ was produced and stored under vacuum to prevent excess oxidation of Si-H bonds.

One gram of HSQ was placed into an alumina boat, which was then placed into a high temperature tube furnace. The quartz tube was purged with H₂/Ar gas (5%/95%) for 20 mins. The temperature was raised by 18°C/min to 1100°C and held at 1100°C for 1 hour with gas flowing over the boat. The Si/SiOₓ composite produced was allowed to cool to room temperature. Then 1g of the Si/SiOₓ composite was ground by mortar and pestle to produce a fine powder. This powder was placed into a Teflon bottle along with 10ml of ethanol and 40ml HF. The mixture was stirred rapidly for 4 hours etching away the SiOₓ and liberating the SiQDs from the composite. The solution was then placed into a Teflon separatory funnel along with 25ml of toluene. The mixture of H-SiQD/etch and toluene was shaken to transfer H-SiQDs into the toluene phase. The etching solution was drained from the funnel and the H-SiQD toluene phase was collected in a 20 ml vial. The H-SiQDs suspended in toluene were transferred into a glovebox. To remove residual water and etchant, the particles were removed from the toluene by a centrifuge treatment (3800 rpm for 20 min). The toluene was decanted from the particles and ethanol (10 ml) was used to redisperse the H-SiQDs. The solution was centrifuged (3800 rpm for 25 min) to remove the particles from solution and the ethanol was decanted. The ethanol dispersion and centrifuge treatment procedure was repeated once more. In the final step, the ethanol was decanted and the particles were placed under vacuum to remove any residual ethanol from the H-SiQDs before for use.

3.2.3 Chlorination of H-SiQDs by PCl₅

In a glove box, SiQDs were dispersed into 30ml of toluene or chlorobenzene and placed into a 50ml flask equipped with a stir bar. Phosphorous pentachloride (0.525 g, 2.52 mmol) was placed into the flask and capped. The mixture was stirred for 3 or 19 hours with a few grains of benzoyl peroxide. The SiQDs were filtered with a 0.2 μm filter and 1-octanol (3.5 ml, 22.2 mmol) was added and stirred for 5 hours. The particles were then centrifuged to remove
aggregates. The particles were precipitated out of solution by methanol and centrifuged for 20 min. The methanol was decanted and the isolated SiQDs were redispersed in chloroform. This precipitation and centrifuge process was repeated two more times.

A batch of H-SiQDs was dispersed in chlorobenzene along with a few grains of benzoyl peroxide. The system was then refluxed for 1.5 hr before 1-octanol (3.5 ml, 22.2 mmol) was added and stirred for 6 hours. The solution was then centrifuged to remove aggregates from solution.

To confirm PCl$_5$ could chlorinate a H-terminated Si surface, the procedure was tested on a H-terminated Si wafer. The wafer was etched with 2:1 ethanol:HF mixture for 5 minutes to remove the native oxide and terminate the surface with hydrogen. The wafer was then washed with ethanol and transferred into the glove box. Chlorobenzene (12 ml) and PCl$_5$ (0.524 g, 2.5 mmol) were added to a 20 ml vial. A stir bar was added along with the etched Si wafer. The mixture was stirred for 24 hr. The wafer was then rinsed with THF and 1-octanol (2.0 ml, 12 mmol) was added to a new vial. The mixture solution was then stirred for 24 hours before the wafer was removed and washed with hexane.

**3.2.4 Bromination of Triethylsilane by NBS**

In a glove box, 0.50 ml triethylsilane (3.1 mmol) was added into 40 ml of chloroform and placed into a 100 ml flask equipped with a stir bar. NBS (1.21 g, 6.80 mmol) was added to the flask and was capped. The flask was covered and stirred for 24 hours before 1-octanol (3.5 ml, 22.2 mmol) was added. The SiQDs were stirred overnight (16 hr). The flask was removed from the glovebox and the solvent was removed by vacuum. The product was dispersed in hexane and centrifuged to remove excess succinimide. The hexane was decanted and removed by vacuum then silane was then dispersed into chloroform.

**3.2.5 Bromination of H-SiQDs by NBS**

In a glove box, 100 mg of SiQDs were dispersed into 80 ml of chloroform and placed into a 300 ml flask equipped a stir bar. NBS (1.2 g, 6.8 mmol) was then added to the flask, capped and covered in foil. The mixture was stirred for 24 hours before 1-octanol (3.5 ml, 22.2 mmol) or tert-butyldimethylsilanol (1.2 ml, 7.6 mmol) was added and stirred overnight (16 hr). The flask was removed from the glovebox and the solvent was removed by vacuum. The resulting mixture of excess NBS, ligand and SiQDs were dispersed in hexane (30 ml) and centrifuge to remove the excess NBS. The particles dispersed in excess 1-octanol or silanol were
precipitated out of solution by methanol and centrifuged for 20 min. The methanol was decanted and the isolated SiQDs were redispersed in chloroform. This precipitation and centrifuge process was repeated two more times before the SiQDs were finally dispersed into chloroform.

The SiQDs were characterized by using a UV-1800 Shimadzu UV Spectrophotometer (UV-Vis), a PTI Fluorescence with 914 Photomultiplier Detection system and LPS-100 Lamp Power supply (PL), a Jeol ECA-500 (NMR), a Thermo Nicolet 4700 FT-IR with Smart Orbit attachment (FTIR), a Philips X’Pert X-ray diffractometer (XRD) a Philips/FEI CM200 Transmission Electron Microscope (TEM), and a Varian CP-3800 GC with a 5% diphenyl-, 5% dimethyl-polysiloxane column coupled to a Varian 1200L quadrupole MS/MS for gas chromatography mass spectrometry (GC-MS). For FTIR the sample was dropped onto the ATR plate and allowed to dry before 32 scans with a resolution of 2 cm⁻¹ were performed. For PL, the sample was transferred into a quartz cuvette, which was then placed into the sample holder. For TEM, the SiQD samples were dropped onto a carbon film 400 square mesh copper grid purchased from Electron Microscopy Sciences. GC-MS was performed by heating the injector and column to 250°C and 70°C respectfully at a gas flow rate of 1.2 ml/min with a 1:20 split. The sample was then injected and the temperature was ramped at 20°C/min to 320°C and held for 6 min.

3.3 Results and Discussion

The following subsections are a discussion on the results obtained from the previously described methodology on halogenation of H-SiQDs. The chlorination using PCl₅ based on literature was explored followed by the bromination of H-SiQD using NBS.

3.3.1 Synthesis of H-SiQDs using the sol-gel method

The H-SiQDs were produced using the sol-gel synthesis method. The particles are formed through the thermal disproportionation of a silicon oxide sol-gel in a H₂/Ar atmosphere. The dimensions and crystallinity of the SiQDs are dependent on the processing temperature of the sol-gel. This process results in composites of SiQDs and SiOₓ. The composite can be created in bulk allowing for high yields of silicon particles. The SiQDs can be freed from the oxide through the use of an HF etch. The particle size is controlled by the etching time. The resulting freestanding particles are hydrogen-terminated allowing the SiQDs to be extracted from the etching solution by organic solvents. The sol-gel synthesis method is useful for producing large amounts of H-SiQDs with controlled size.
The free standing H-SiQDs were investigated by XRD and Raman (Fig. 3.1). The broad reflections at 28°, 47°, and 56° in Fig. 3.1A were indexed to the diamond silicon planes (111), (220), and (311). The peak widths are broad due to the small particle size and thus confirming the formation of nanocrystalline silicon. The broad peak centered at 21° is from the oxide matrix. The peak observed at 517 cm\(^{-1}\) in the Raman spectrum (Fig. 3.1B) of the H-SiQDs arises from the crystalline H-SiQD differing from the bulk silicon signal of 521 cm\(^{-1}\) due to the reduction in particle size. The peak tails to lower wavenumbers (~500 cm\(^{-1}\)) due to the presence of amorphous silicon in the sample. The XRD and Raman indicated that the synthesized SiQDs are crystalline and in the nanometer size range.

Figure 3.1. XRD of SiQDs embedded in Oxide (A) and Raman spectrum of H-SiQDs (B).

### 3.3.2 Chlorination of H-SiQDs by PCl₅

The PCl₅ treatment was performed on the H-SiQD following the procedure developed by Veinot et. al.\(^{33}\) (Fig. 3.2) to determine the viability of the chlorination. The H-SiQDs produced by the sol-gel synthesis were stirred with PCl₅ in toluene for 3 hours to chlorinate the particles. The SiQDs after the chlorination formed large aggregates and precipitated out of the solution. Since PCl₅ was not very soluble in toluene, it was difficult to separate the SiQD precipitate from PCl₅. Thus, the ligand, 1-octanol, was added without removing PCl₅. The reaction system was stirred for another 5 hours producing a light yellow solution with large quantities of SiQD precipitate. The solution was centrifuged to remove precipitated SiQDs, leaving only dispersible SiQDs-OC\(_₈\) in solution. The dispersed particles were concentrated by evaporation and purified.
using three rounds precipitation and centrifugation with methanol. The purified particles were dispersed in chloroform and PL was taken on a diluted sample of SiQD-OC₈ at various excitation wavelengths (Fig. 3.3).

\[
\begin{array}{c}
\text{Si-H} + \text{PCl}_5 \rightarrow \text{Toluene} \rightarrow \text{Si-Cl} \\
\text{Si-Cl} + \text{HOR} \rightarrow \text{Toluene} \rightarrow \text{Si-OR} + \text{HCl}
\end{array}
\]

Figure 3.2. Reaction scheme for the chlorination of H-SiQDs by PCl₅.

![Figure 3.3. PL spectra of SiQD-OC₈ via pre-chlorination using PCl₅ excited by various wavelengths.](image)

The peaks were centered at 610 nm for all spectra, indicating particle size of approximately 1 nm⁵⁵. The size change is likely related to the aggregation of the SiQDs but more characterization was needed to confirm the cause. A possible explanation for the aggregation was likely due to incomplete hydrogen replacement by chlorine allowing the H-SiQDs to aggregate during the reaction. Following the literature, the PCl₅ reaction resulted in a low yield of dispersible particles suggesting further steps are needed to completely chlorinate H-SiQDs. Further investigation was conducted to prevent particle aggregation.
An increased reaction time may minimize the SiQD aggregation by allowing the chlorination to completely replace the hydrogen. To test this hypothesis, the reaction time was increased to 19 hours prolonging the SiQD exposure to PCl₅. The H-SiQDs aggregated during the reaction as previously observed in the 3 hours treatment. The ligand was then added as described previously and stirred for another 5 hours. The resulting SiQDs-OC₈ was purified as previously described resulting in soluble SiQD-OC₈ in chloroform and a solid aggregated phase. The FTIR of the aggregates and the soluble SiQD-OC₈ particles were taken (Fig. 3.4) to determine the efficiency of the chlorination. The peaks for the stretching and bending modes of CH₂ and CH₃ indicate the presence of octanol in the SiQD-OC₈ and the aggregated phase (Fig. 3.4A). The Si-H peaks at 2100 cm⁻¹ and 900 cm⁻¹ in Fig. 3.4A imply that PCl₅ did not chlorinate all the Si-H bonds on the SiQDs. This was likely due to particle aggregation, which prevents SiQD surfaces from being accessed by PCl₅. The peak at 1050 cm⁻¹ can be assigned to either the stretching mode of Si-O-C embodying the successful attachment of octanol or the stretching mode of Si-O-Si embodying oxide formation. In contrast, the FTIR spectrum of the soluble SiQD-OC₈ (Fig. 3.4B) does not indicate that presence of unreacted Si-H bonds. The sharp peak at 1030 cm⁻¹ arises from the Si-O-C bond not oxide formation which would be a broader peak. This peak confirms the attachment of octanol to the SiQDs. Unfortunately, there are also a number of peaks associated with organophosphate bonds at 1300 cm⁻¹, 900 cm⁻¹ and 600 cm⁻¹. These peaks indicate side reactions of the PCl₅ with the octanol in the system creating soluble phosphate compounds. The FTIR results confirm the octanol functionalization of SiQDs via pre-chlorination. However, the SiQD aggregation severely limits the effectiveness of chlorination.

The optical properties of the 19 hr reacted SiQD-OC₈ sample were investigated by PL (Fig. 3.5) to examine impacts by the chlorination. A heated chlorination procedure in chlorobenzene was also performed to determine if heating would promote a fast reaction avoiding SiQD aggregation. The initial SiQD-OC₈ solution, before the centrifuging, emitted red-blue suggesting the presence of two emitting species. After the precipitation and centrifuge procedure, the SiQD-OC₈ solution emitting at 630 nm and the collected methanol washing emitted at 380 nm corresponding to the dual emissions of the initial solution. The red emission results from the quantum confinement of SiQD-OC₈ in solution. The source of the blue emission is unclear, probably from heavily oxidized SiQDs produced during the PCl₅ reaction. While the possibility of oxidation in the glove box cannot be ruled out, it is more likely to occur during
sample handling during purification. The PL spectrum of the heated SiQD-OC\textsubscript{8} reaction supports a similar conclusion with a strong blue emission and the absence of the red emission indicating oxidization. These results demonstrate that the PCl\textsubscript{5} treatment is not an effective chlorination technique for H-SiQDs.

![Figure 3.4. FTIR of aggregated SiQD-OC\textsubscript{8} (A) and soluble SiQD-OC\textsubscript{8} (B).](image)

To determine if the above-described procedure actually works for chlorinating hydrogen-terminated Si surface, we performed the same reaction using Si wafer as a model system. FTIR was used to determine the attachment of octanol to the Si wafer (Fig. 3.6). The peaks corresponding to the CH\textsubscript{2} and CH\textsubscript{3} stretching and bending modes are observed at 3000 to 2800cm\textsuperscript{-1} and 1500 to 1400cm\textsuperscript{-1}, respectively. The weak signals can be ascribed to the restriction of the CH\textsubscript{2} and CH\textsubscript{3} vibrations due to the close packing of octanol. The peak at 609 cm\textsuperscript{-1} can be assigned to Si-Cl bonds that were not replaced by the 1-octanol. The strong peak at 1080 cm\textsuperscript{-1} can be assigned to the stretching mode of Si-O-C. These results together confirm the successful attachment of octanol to the Si wafer, and in turn the successful chlorination of the Si wafer using PCl\textsubscript{5}. Thus, complexity of the chlorination in the case of SiQDs was assigned to the particle aggregation.

### 3.3.3 Bromination of H-SiQDs by NBS

The bromination of H-SiQDs has not been demonstrated in literature. In silane chemistry the bromination of the Si-H bond is achieved mainly by using bromine\textsuperscript{72–74} and by NBS\textsuperscript{71,75,76}. When bromine was used as the bromination reagent, SiQDs were etched away (data not shown).
Figure 3.5. PL of SiQD-OC$_8$ after purification, methanol soluble SiQD-OC$_8$ and SiQD-OC$_8$ from the heated chlorination reaction.
Figure 3.6. FTIR of a Si wafer passivated with 1-octanol after chlorination with PCl$_5$.  

![FTIR spectrum of Si wafer]

- Vibrations at 2950 cm$^{-1}$: C-H stretch of alkyl groups
- Vibrations at 1700 cm$^{-1}$: C=O stretch of carboxylic acid
- Vibrations at 1100 cm$^{-1}$: Si-O-Si stretch
Thus, NBS was proposed as the brominating reagent following the reaction scheme in Fig. 3.7.

![Reaction Scheme](image)

Figure 3.6. Bromination and passivation of H-SiQDs through the use of NBS.

First, triethylsilane (TES) was used as the model system to study the bromination of Si-H bond. After the bromination, 1-octanol was added to functionalize the bromine-terminated TES, without the removal of NBS from the system. FTIR (Fig. 3.8), NMR (Fig. 3.9), and GC-MS (Fig. 3.10) measurements indicate the successful functionalization with octanol, which simultaneously confirmed the successful bromination. The characteristic Si-H peaks at 2200 cm\(^{-1}\) and 900 cm\(^{-1}\) of TES in the FTIR spectrum (Fig. 3.8A) are absent after the bromination and attachment of 1-octanol. The peaks at 1080 cm\(^{-1}\) and 1000 cm\(^{-1}\) are assigned to the stretching modes of Si-O-C. These results suggest the formation of the expected triethylsilyloxyoctane (TESO) molecule (Fig. 3.8B). The peak at 1700 cm\(^{-1}\), corresponding to the stretching mode of C=O, implies the presence of NBS residuals due to incomplete purification.

In the \(^1\)H NMR of TES (Fig. 3.9A), the characteristic proton groups observed at δ=0.5 (1), 0.9 (2), and 3.6(3) correspond to the methyl, methylene, and Si-H respectively. After the octanol treatment, the peaks at δ=0.89 (10), δ=1.31 (6-9), δ=1.6 (4,5), and δ=2.49 (3*), corresponding to octanol are observed along with the TES peaks as assigned in Fig. 3.9B. The peak at δ=0.89 is likely due to the incomplete removal of succinimide after the reaction was also seen in Fig. 3.8. The disappearance of the Si-H peak indicates the successful attachment of octanol through the use of NBS as a bromination reagent.

Moreover, GC-MS was also used to investigate the attachment of octanol to TES. Seven compounds are indicated in the TESO solution by GC-MS (Fig. 3.10). The main peak (4) at 6.9 min is the TESO molecule and confirms the attachment of octanol to TES with a high yield. Peak 1 was determined to be 1-bromotriethylsilane, the product of silane bromination. The presence of 1-bromotriethylsilane confirms the bromination of the H-Si bond by NBS. Peaks 2, 6, and 7 were
Figure 3.8. FTIR spectra of Triethylsilane (TES) (A) and Triethylsilyloxyoctane (TESO) (B).

Figure 3.9. $^1$H NMR spectra of Triethylsilane (TES) (A) and Triethylsilyloxyoctane (TESO) (B).
found to be 1-bromo-octane, octyloctanoic acid, and 1, 1’ oxybis-octane indicating the side reactions between octanol and excess bromine. The presence of 1-bromo-octane indicates the replacement of the octanol hydroxyl by bromine. Octyloctanoic acid and 1, 1’ oxybis-octane indicates the self-reactions of octanol through unknown mechanisms. Peaks 3 and 5 were found to be triethoxysilanol and hexaethoxysiloxane. The silanol and siloxane form through the oxidation of the silane and the subsequent condensation reaction. In short, GC-MS, along with the results of FTIR and NMR, confirms the successful bromination of TES and the subsequent octanol attachment to the brominated product. This indicates the feasibility of using NBS for the bromination of H-SiQDs.

Following the same procedure as the silane, H-SiQDs were functionalized with octanol and tert-butyldimethylsilanol (silanol) via the bromination using NBS as the bromination reagent. The size distribution of the SiQDs-silanol was 3 - 8nm, as shown by TEM in Fig. 3.11A. The size distribution of the SiQD-OC\textsubscript{8} was 4.7±1.4nm (N=43) (Fig. 3.11B). Their UV-vis and PL spectra are shown in Fig. 3.11C. The UV-Vis spectra are nearly identical to each other with absorbance onsets at 460nm. The PL spectra have peak maxima of 670nm and 690nm for SiQD-OC\textsubscript{8} and SiQD-silanol, respectively. The shift in the peak maxima is likely due to a slight size difference between these two samples, originating from the different batches of Si/SiO\textsubscript{x} used for each synthesis. The comparable widths of these two PL spectra indicate that the size distributions of these two samples are also similar.

The FTIR spectra of SiQDs-OC\textsubscript{8} and SiQDs-silanol are shown in Fig. 3.12A, together with that of H-SiQDs as comparison. The H-SiQDs sample displays the characteristic Si-H bonds at 2200 cm\textsuperscript{-1} and 900 cm\textsuperscript{-1}. The CH\textsubscript{x} peaks arise from toluene used to suspend the particles. After bromination the Si-H peaks disappeared, indicating the successful replacement of hydrogen with bromine. For the SiQD-silanol (Fig. 3.12B) and SiQD-OC\textsubscript{8} samples (Fig. 3.12C), the stretching and bending modes of CH\textsubscript{x} are observed at the expected positions: 2800-3000 cm\textsuperscript{-1}, and 1350-1480 cm\textsuperscript{-1}. The OH stretching mode at 3300 cm\textsuperscript{-1} suggests either excess ligand or surface oxidation. The broad peak centered at 1050 cm\textsuperscript{-1} in the case of the SiQD-silanol, corresponding to the Si-O-Si bond, indicates the functionalization of the SiQDs. For SiQDs-OC\textsubscript{8}, the peak centered at 1050 cm\textsuperscript{-1} suggests the attachment of octanol. Nevertheless, the presence of the peaks at 800 and 600 cm\textsuperscript{-1} implies oxidation of the SiQD surface\textsuperscript{77}. The FTIR confirms the attachment of the silanol. In contrast, the oxide peaks in the case of SiQD-OC\textsubscript{8}
Figure 3.10. GC-MS chromatograph and mass spectra of Triethylsilyloxyoctane sample.
points to the need of further investigation to confirm the successful attachment.

NMR was used to further investigate and confirm the attachment of octanol and silanol to the SiQD surface after bromination. The $^1$H NMR of the SiQD-silanol system (Fig. 3.13A) has three peaks at $\delta$= 1.2, 0.9 (2), and -0.2 (1). The first two peaks correspond to the $t$-butyl and methyl groups. The peak at 1.2 ppm arises from an unknown impurity in the solution. The absence of the Si-OH peak confirms the attachment of the silanol to the SiQDs. The peaks at $\delta$=0.89 (8), $\delta$=1.31 (4-7), $\delta$=1.6 (2,3), and $\delta$=2.49 (1) in the $^1$H NMR of SiQD-OC$_8$ (Fig. 3.12B) correspond to 1-octanol indicating the attachment to the SiQDs. The shifted methylene peak (1) at $\delta$= 3.8 suggests the attachment of octanol to the SiQDs. The broad nature of the peak indicates the restriction the methylene protons on the SiQDs$^{65}$.

The three carbon groups at $\delta$=25 (3), 18 (2), and -4 (1) in the $^{13}$C NMR of SiQD-silanol (Fig. 3.14) correspond to the $t$-butyl, quaternary, and methyl carbons of silanol. The peaks have broadened due to the restriction of the ligand on the SiQD surface. The peak broadening of the
Figure 3.12. FTIR of H-SiQDs (A), SiQD-silanol (B) SiQD-OC₈ (C).

$^{13}$C confirms the attachment of the silanol to the SiQD$^{65}$. Eight peaks are observed in the $^{13}$C NMR of the SiQD-OC₈ system at $\delta=14$ (8), $\delta=23$ (7), $\delta=26$ (6), $\delta=29.6$ (4,5), $\delta=32$ (3), $\delta=33$ (2), and $\delta=63.3$ (1) correspond to 1-octanol. The presence of these peaks as well as the methylene peak (1) at $\delta=63.3$ (shifted by 0.01 ppm) confirms the attachment of octanol to the SiQD surface.

The methylene group adjacent to the oxygen (1) in SiQD-OC₈ was further investigated by a 2D HETCOR NMR experiment (Fig. 3.15) to determine if peak 1 in the $^{13}$C spectrum (Fig. 3.14) arises from the attached ligand or the excess ligand in solution. The couplings of the proton and carbon groups 2-8 are all observed as expected. The coupling of the methylene group adjacent to the oxygen (1) at $\delta=3.6$ couples to the carbon signal at $\delta=63.3$ suggesting that the carbon peak (1) arises from the free ligand. This conflicts with the $^1$H NMR spectrum (Fig. 3.13) demonstrating a higher concentration of attached octanol than in solution. It can be speculated that the weak signal of the methylene carbon (1) is due to the methylene proton being restricted
on the SiQD surfaces, suppressing the coupling. In summary, the NMR results confirm the ligand attachments through the bromination treatment of H-SiQDs.

Figure 3.13. $^1$H NMR of SiQD-silanol (A) SiQD-OC$_8$(B).

After the functionalization and purification, both samples were well dispersed in chloroform (Fig. 3.16A). The SiQD-silanol particles were also dispersible in hexane indicating a lower surface charge than the SiQD-OC$_8$ particles. After one week of functionalization, a clear difference in solubility was observed between the two SiQD passivations (Fig. 3.16B). The SiQD-silanol sample is well dispersed in solution while the SiQD-OC$_8$ particles have aggregated and precipitated. This indicates a significant difference in the ability to prevent particle aggregation between these two ligands. The linear carbon chain of octanol perpendicular to the
Figure 3.14. $^{13}$C NMR of SiQD-silanol (A) and SiQD-OC$_8$ (B).
Figure 3.15. HECTOR Spectrum of Octanol passivated SiQDs.
SiQD surface may facilitate the interaction among different particles and then aggregation. On the contrary, the bulky structure of silanol seems effective in preventing particle aggregation. This suggests a bulky ligand may better passivate SiQDs than a linear ligand.

3.4 Conclusions

In conclusion, we have investigated surface functionalization of H-SiQDs via two methods of halogenation: chlorination using PCl\textsubscript{5} and bromination using NBS. While PCl\textsubscript{5} is able to chlorinate H-SiQD, the further octanol functionalized SiQDs were severely aggregated. Experiments in which reaction time and temperature were increased the SiQDs were oxidized as indicated by PL. These results indicate the limitation of PCl\textsubscript{5} as a reagent for H-SiQDs chlorination. In contrast, NBS has been proven an effective reagent to brominate H-SiQDs, the first demonstration to the best of our knowledge. The brominated SiQDs are further functionalized with octanol and tert-butyldimethyilsilanol at room temperature. The tert-butyldimethyilsilanol derived SiQDs show improved solubility in organic solvents and stability in air, an observation that is attributed to the bulky structure of tert-butyldimethyilsilanol. In addition, NBS has been demonstrated in bromination of triethyilsilane.
CHAPTER 4. DIRECT SURFACE FUNCTIONALIZATION UTILIZING BORON-BASED CATALYSTS

4.1 Introduction

As we showed in Chapters 2 and 3, it is challenging to functionalize H-SiQDs. While hydrosilylation is a one-step process, it can only graft alkenes or alkynes to silicon through Si-C bonds. The two-step process via pre-halogenation allows for the grafting various ligands to silicon but encounters difficulties in preventing particle oxidation. It will be highly desirable if H-SiQDs can directly be functionalized with a variety of ligands to alter the electronic properties of particles. In silane chemistry, it has been demonstrated that some boron compounds can catalyze the grafting reactions of alcohols, alkenes, thiols, and also amines\textsuperscript{78–80}. This motivated us to test the possibility of developing a one-step process to functionalize H-SiQDs with alcohols and thiols using boron-compounds as catalysts as seen in Fig. 4.1. The selected alcohol was 1-octanol; and the selected thiol was 1-hexanethiol. The selected catalysts included tris(pentafluorophenyl)boron (B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}) and boron trifluoride (BF\textsubscript{3}). Prior to functionalizing H-SiQDs, triethyilsilane (TES) was used as the model system to test the catalytic reactions.

\[
\text{SiH} + \text{HX} \xrightarrow{\text{B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} or BF\textsubscript{3}}} \text{SiX} + \text{H}_2
\]

Figure 4.1. Functionalization of H-SiQDs by boron catalysts.

4.2 Experimental section

High purity chemicals 1-octanol (99% anhydrous) and benzene (99.8% Anhydrous), triethyilsilane (99%, Aldrich), 1-hexanethiol (99%, Aldrich), tris(pentafluorophenyl)boron (95%), boron trifluoride tetrahydrofuran complex (BF\textsubscript{3}), and triphenylphosphine (PPh\textsubscript{3}) (99%) were all purchased from Aldrich and used as received.
4.2.1 Synthesis of Triethylsilyloxyoctane using B(C₆F₅)₃

In a glove box, triethylsilane (0.22 ml, 1.4 mmol) was placed into a 15ml flask along with benzene (5 ml). 1-octanol (0.22 ml, 1.4 mmol) was added to the solution followed by B(C₆F₅)₃ (54 mg, 0.099 mmol). The solution was stirred for 30 sec before the flask was capped and stirred for 21 hr. Then PPh₃ (27 mg, 0.103 mmol) was added to the solution and stirred for another 3 hr. The flask was then removed from the glovebox and the solvent was removed by vacuum. The product was a clear liquid with solid white particles. The mixture was dissolved in hexane and filtered to remove particulates.

4.2.2 Synthesis of Triethylsiylhexylthiol using B(C₆F₅)₃

In a glove box, triethylsilane (0.22 ml, 1.4 mmol) was placed into a 15ml flask along with benzene (5 ml). 1-hexanethiol (0.198 ml, 1.4 mmol) was then added to the solution followed by B(C₆F₅)₃ (51 mg, 0.099 mmol). The solution was stirred for 30 sec before the flask was capped and stirred for 21 hr. PPh₃ (41 mg, 0.15 mmol) was added to the solution and stirred for another 3 hr. The flask was then removed from the glovebox and the solvent was removed by vacuum. The product was a clear liquid with solid white particles. The mixture was dissolved in hexane and filtered to remove particulates.

4.2.3 Synthesis and etching of SiQDs (same as in 3.2.2)

The H-SiQDs were synthesized following a literature procedure reported by Ozin\textsuperscript{55}. Hydrogen silsesquioxane (HSQ) was synthesized by placing trichlorosilane (13.4 g, 99 mmol) in a 100ml three-neck flask. The flask was placed on a Schlenck line with nitrogen gas flowing through the flask. The trichlorosilane was cooled in an acetone/dry ice bath (-78°C) for 5 min while stirring before 50 ml of water (Millipore, 18.2Ω) was injected. The mixture was allowed to warm to room temperature while stirring for 40 min producing a white precipitate and hydrochloric acid. The resulting HSQ was washed with water to remove the hydrochloric acid then placed under vacuum to dry for 24 hours. Finally 4 grams of HSQ was produced and stored under vacuum to prevent excess oxidation of Si-H bonds.

One gram of HSQ was placed into an alumina boat, which was then placed into a high temperature tube furnace. The quartz tube was purged with H₂/Ar gas (5%/95%) for 20 mins. The temperature was raised by 18°C/min to 1100°C and held at 1100°C for 1 hour with gas flowing over the boat. The Si/SiOₓ composite produced was allowed to cool to room temperature. Then 1g of the Si/SiOₓ composite was ground by mortar and pestle to produce a
fine powder. This powder was placed into a Teflon bottle along with 10ml of ethanol and 40ml HF. The mixture was stirred rapidly for 4 hours etching away the SiO\textsubscript{x} and liberating the SiQDs from the composite. The solution was then placed into a Teflon separatory funnel along with 25ml of toluene. The mixture of H-SiQD/etch and toluene was shaken to transfer H-SiQDs into the toluene phase. The etching solution was drained from the funnel and the H-SiQD toluene phase was collected in a 20 ml vial. The H-SiQDs suspended in toluene were transferred into a glovebox. To remove residual water and etchant, the particles were removed from the toluene by a centrifuge treatment (3800 rpm for 20 min). The toluene was decanted from the particles and ethanol (10 ml) was used to redisperse the H-SiQDs. The solution was centrifuged (3800 rpm for 25 min) to remove the particles from solution and the ethanol was decanted. The ethanol dispersion and centrifuge treatment procedure was repeated once more. In the final step, the ethanol was decanted and the particles were placed under vacuum to remove any residual ethanol from the H-SiQDs before for use.

4.2.4 1-Octanol passivation of H-SiQD using $\text{B(C}_6\text{F}_5\text{)}_3$ and BF\textsubscript{3}

In a glove box, approximately 25 mg of H-SiQDs were dispersed in benzene (10 ml) and placed in a 25 ml flask. 1-octanol (1.0 ml, 6.3 mmol) was added to the H-SiQDs followed by $\text{B(C}_6\text{F}_5\text{)}_3$ (47 mg, 0.09 mmol). The solution was stirred for 30 sec before the flask was capped and stirred for 24hr. After 24 hr the flask was heated to 60\degree C for 2 days with stirring. The mixture was then allowed to settle resulting in a clear top layer with SiQD aggregates settled on the bottom.

4.2.5 1-Hexanethiol passivation of H-SiQD using $\text{B(C}_6\text{F}_5\text{)}_3$ and BF\textsubscript{3}

In a glove box, approx. 25mg of SiQDs were dispersed in benzene (10 ml) and placed in a 25ml flask. 1-octanol (01.0 ml, 6.3 mmol) was added to the SiQDs followed by $\text{B(C}_6\text{F}_5\text{)}_3$ (47mg, 0.09 mmol). The solution was stirred for 30 sec before the flask was capped with a septum and stirred for 24hr. After 24 hr the flask was heated to 60\degree C for 2 days with stirring. The mixture was then allowed to settle resulting in a clear top layer with SiQD aggregates settled on the bottom.

The silane derived compounds were characterized by using a UV-1800 Shimadzu UV Spectrophotometer (UV-Vis), a Jeol ECA-500 (NMR), a Thermo Nicolet 4700 FT-IR with Smart Orbit attachment (FTIR), and a Varian CP-3800 GC with a 5% diphenyl-, 5% dimethyl-polysiloxane column coupled to a Varian 1200L quadrupole MS/MS for gas chromatography.
mass spectrometry (GC-MS). For FTIR the sample was dropped onto the ATR plate and allowed to dry before 32 scans with a resolution of 2 cm⁻¹ was performed. GC-MS was performed by heating the injector and column to 300°C and 70°C respectfully at a gas flow rate of 1.2 ml/min with a 1:20 split. The sample was then injected and the temperature was ramped at 20°C/min to 320°C and held for 6 min.

4.3 Results and Discussion

The following subsections are a discussion on the results obtained from the previously described methodology on the attachment of the two ligands 1-octanol and 1-hexanethiol to triethylsilane and H-SiQDs catalyzed by B(C₆F₅)₃ and BF₃.

4.3.1 Direct attachment of 1-Octanol (Si-OR) and 1-Hexanethiol (Si-SR) to Triethylsilane

The attachment of 1-octanol and 1-hexanethiol to the triethylsilane molecule was first investigated using FTIR (Fig. 4.2). The Si-H stretching and bending modes of TES at 2100 cm⁻¹ and 900 cm⁻¹ disappeared in both cases of attachment, indicating the replacement of Si-H bonds with Si-O or Si-S bonds, i.e., the formation of Triethylsilyloxyoctane (TESO) and

![Figure 4.2. FTIR of triethylsilane, Triethylsilyloxyoctane (TESO), and triethylsilylhexylthiol (TESS).](image)
Triethylsilylhexylthiol (TESS). The peaks at 1250 cm$^{-1}$ and 735 cm$^{-1}$ are assigned to the Si-CH$_2$- vibrations originating from the TES molecules. The Si-O-C modes at 1080 cm$^{-1}$ and 1000 cm$^{-1}$ in the TESO spectrum indicates the octanol attachment. The S-C mode at 600cm$^{-1}$ in the TESS spectrum indicates presence of 1-hexanethiol. The Si-S vibration at 460 cm$^{-1}$ confirms the attachment of the thiol.

Next, NMR was employed to further study the attachments of 1-octanol and 1-hexanethiol to TES. In Fig. 4.3 the $^1$H NMR shows the spectra of TES, TESO, and TESS. The three peaks of δ=0.5 (1), 0.9 (2), and 3.8 (3) in the TES spectrum are assigned to the methyl, methylene, and Si-H groups, respectively. The additional peaks in the TESO spectrum originate from the octanol moiety: δ=0.89(10), δ=1.29(6-9), δ=1.5(4,5), and δ=3.5(3). The absence of the Si-H signal at δ= 3.6 indicates the attachment of octanol to the silicon atom. The additional peaks in the TESS spectrum originate from the hexanethiol moiety: δ=0.75(8), δ=1.2-1.3(5-7), δ=1.5(4),

![NMR Spectra](image)

Figure 4.3. $^1$H NMR of triethylsilane, Triethylsilyloxyoctane, and triethylsilylhexylthiol in chloroform.
and $\delta=2.45(3)$. The absence of the Si-H peak suggests the attachment of the thiol to the TES molecule.

![13C NMR spectra](image)

Figure 4.4. $^{13}$C NMR of triethylsilane, Triethylsilyloxyoctane, and triethylsilylhexylthiol in chloroform.

The $^{13}$C NMR spectra (Fig. 4.4) reached the same conclusion as the $^1$H NMR spectra. The methyl and methylene peaks for TES were observed at $\delta=3(1)$ and $\delta=8(2)$. After the octanol treatment, these two peaks shifted to $\delta=7$ and $\delta=4.5$, respectively, indicating the octanol attachment. The octanol-derived peaks were observed at $\delta=14\ (8), \delta=23\ (7), \delta=26\ (6), \delta=29.6\ (4.5), \delta=32\ (3), \delta=33\ (2)$, and $\delta=63\ (1)$ in the expected positions with no shifts in position observed. This result further corroborates the successful attachment of octanol. In the case of hexanethiol, we also observed the hexanethiol peaks at $\delta=14(8)\ delta=23(7), \delta=26(3), \delta=28(6), \delta=32(5)$, and $\delta=33(4)$. The TES-derived peaks were observed at $\delta=5.5$ and $\delta=7.5$ shifted in a similar fashion as the TESO molecule. Peaks 3-6 exhibit a shift from the standard hexanethiol positions, resulting from the attachment of the thiol to the TES. These results together with FTIR indicate the successful attachment of 1-hexanethiol to TES.
Furthermore, gas chromatography–mass spectrometry (GC-MS) was also implemented to confirm the attachment of hexanethiol to TES since we have less experience with the thiol attachment. The GC-MS chromatograph (Fig. 4.5) indicates the presence of five compounds in the TESS solution. The TESS molecule is the main peak (4) at 8.1 min, confirming the attachment of the hexanethiol. Peak 2 was determined to be unreacted 1-hexanethiol. Peaks 1 and 3 were found to be triethysilanol and hexaethyldisiloxane produced through oxidation and condensation of the silanol. Peak 5 is the excess PPh₃ added to the system to remove the \( \text{B}(\text{C}_6\text{F}_5)_3 \) after the reaction. The GC-MS was able to conclusively confirm the attachment of the hexanethiol using \( \text{B}(\text{C}_6\text{F}_5)_3 \) as the catalyst. These results along with FTIR and NMR strongly indicate that \( \text{B}(\text{C}_6\text{F}_5)_3 \) has potential application for the direct attachment of octanol and hexanethiol to a H-SiQD surface.

### 4.3.2 Direct attachment of 1-Octanol (Si-OR) and 1-Hexanethiol (Si-SR) to H-SiQDs

Thus, the same procedure described above for the direct attachment of octanol and hexanethiol molecules to silane molecules using \( \text{B}(\text{C}_6\text{F}_5)_3 \) as the catalyst was applied to the functionalization of H-SiQDs. After 24 hours of the H-SiQDs stirring in the presence of \( \text{B}(\text{C}_6\text{F}_5)_3 \) and the ligand, both systems (octanol and hexanethiol) showed no signs of reaction but remained a suspension of SiQDs. Then, to determine if there was an activation energy needed for the reaction to proceed, the reactions were heated to 60°C. However, at the end of the reactions, the SiQDs severely aggregated and fell out of solution. With these unsuccessful reactions, it was hypothesized that the problem may be the steric hindrance coming from the bulky \( \text{B}(\text{C}_6\text{F}_5)_3 \) molecules. To test the hypothesis, the catalyst was changed to \( \text{BF}_3 \). Unfortunately, the SiQDs treated with \( \text{BF}_3 \) aggregated in the same manner as the \( \text{B}(\text{C}_6\text{F}_5)_3 \) treated systems. The inabilities of both \( \text{B}(\text{C}_6\text{F}_5)_3 \) and \( \text{BF}_3 \) for the surface functionalization of H-SiQDs indicate that the problem may lie in the steric hindrance of SiQDs. After an extensive literature search into the reaction mechanism between \( \text{B}(\text{C}_6\text{F}_5)_3 \) and silane molecules, it was revealed that the Si-H bond coordinates with the boron center creating a partial positive charge on the silicon atom\(^8\). This activates the silicon center allowing for the ligand to undergo a nucleophilic attack on the silicon via a \( \text{S}_\text{N}_2 \) mechanism as shown in Fig. 4.6. This results in the displacement of the catalyst and the creation of the Si-X (X=O, S) bond. In the case of H-SiQDs, the coordination of the catalyst with the Si-H bond on the bulky SiQD will impede the ligand from displacing the catalyst through the \( \text{S}_\text{N}_2 \) mechanism.
Figure 4.5. GC-MS chromatograph and mass spectra of triethylsilylhexylthiol sample.
4.4 Conclusions

Lewis acids, $B(C_6F_5)_3$ and $BF_3$, were investigated for surface functionalization of H-SiQDs with octanol and hexanethiol. While the functionalization of silane (triethylsilane) molecules was successful, the attempt to functionalize the H-SiQDs failed. The reason was assigned to the steric hindrance from the SiQD surface. Nevertheless, this study does not rule out the feasibility of using other Lewis acid catalysts to functionalize H-SiQDs.
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

This thesis investigates surface functionalization of SiQDs made by colloidal synthesis and sol-gel synthesis, leaning toward their photovoltaic applications. The key findings can be summarized as follows.

In the case of colloidal-synthesized SiQDs, the directly obtained chlorine-terminated SiQDs were functionalized with four different ligands with three distinct anchoring atoms (O, C, and N). The resultant SiQDs did not show ligand-dependent absorption and emission properties since the SiQDs were outside the quantum confinement regime and strongly oxidized. While FTIR was unable to determine the attachment of the ligands due to interference of silicon oxide, NMR confirmed the attachment through the observation of the deshielding effect of the methylene groups adjacent to the SiQD. 2D NMR was able to differentiate between free ligand in solution and the attached ligand on the basis of the chemical shifts in the $^1$H and $^{13}$C NMR. In the case of the SiQD-NC$_6$, NMR confirmed the attachment of the hexylamine but was unable to determine the amount of ligand on the SiQD. The attachment of optically active PyOH was confirmed after the effective purification using AF4. The PyOH excimer was found to be the dominant emitting species, masking the emission from the SiQDs. Moreover, we observed the formation of silicon dioxide during the process of SiQDs synthesis. These results indicate that this particular solution synthesis method is highly prone to oxidation, explaining the blue emission observed for large SiQDs. This observation is different from literature reporting that the surface oxidation and presence of nitrogen-containing compounds are both necessary for the blue emission.

In the case of sol-gel synthesized SiQDs, we investigated surface functionalization of hydrogen-terminated SiQDs (H-SiQDs) via two methods of halogenation: chlorination using PCl$_5$ and bromination using NBS. While PCl$_5$ is able to chlorinate H-SiQD, the further octanol-derived SiQDs were severely aggregated. The increase in reaction time and temperature resulted in the oxidization of SiQDs. These results indicate the limitation of PCl$_5$ for chlorination of SiQDs. In contrast, NBS has been proven an effective reagent to brominate H-SiQDs, the first demonstration to the best of our knowledge. The brominated SiQDs are further functionalized with octanol and tert-butyldimethylsilanol at room temperature. The tert-butyldimethylsilanol
passivated SiQDs show better solubility in organic solvents and stability in air, originating from the bulky structure of tert-butyldimethylsilanol.

In addition, two Lewis acids, B(C$_6$F$_5$)$_3$ and BF$_3$, were also investigated for surface functionalization of sol-gel synthesized H-SiQDs with octanol and hexanethiol. While the functionalization of silane (triethylsilane) molecules was successful, the attempt of functionalizing H-SiQDs failed. The reason was assigned to the steric hindrance from the SiQD surface. Nevertheless, this study does not rule out the feasibility of using other Lewis acid catalysts to functionalize H-SiQDs.

5.2 Future work

Due to the difficulty in suppressing oxidation of the colloidal-synthesized SiQDs, future research should focus on the use of sol-gel synthesized SiQDs. With the success of bromination of H-SiQDs and the subsequent surface functionalization with octanol and silanol, one interesting study will be to use fluorophore-containing ligands, such as pyrenebutanol, to study the energy transfer between SiQDs and the ligands as well as between particles.
REFERENCES CITED


(18) Faulkner, R.; DiVerdi, J.; Yang, Y. The Surface of Nanoparticle Silicon as Studied by Solid-State NMR. *Materials (Basel).* 2012, 6, 18–46.


(60) Rosso-vasic, M.; Cola, L. De; Zuilhof, H. Efficient Energy Transfer between Silicon Nanoparticles and a Ru - Polypyridine Complex. 2009, 2, 2235–2240.


