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Synthesis of Dendritic Ligands Containing Ferrocene for Quantum Dots (QDs) and Characterization of QD-ligands Hybrid System

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Synthesis of Dendritic Ligands Containing Ferrocene for Quantum Dots (QDs) and Characterization of QD-ligands Hybrid System

Abstract
Ligands for nanocrystals (NCs) have been widely studied beyond its role as a capping agent to applications such as tuning self-assembled properties of nanocrystals. Recent studies show that functionalized ligands can introduce precise control over charge and energy transfer of semiconductor NCs, or quantum dots (QDs). This can be used in various applications in optoelectronic devices, such as solar cells and light emitting diodes, or even further photocatalysis, and biological imaging. Herein, this project describes the design and synthesis of a series of novel dendritic ligands containing active moiety with efficient synthetic route for developing dendron series to graft onto the surface of CdSe/CdS core shell QDs. For active site in the ligand, ferrocene (Fc) was used because of its chemical stability and the ease of the Fc/Fc⁺ redox couple. To characterize the series of ligands, Nuclear magnetic resonance (NMR) spectroscopy and mass spectroscopy studies were performed to analyze and confirm molecular structure of compounds. In addition, the synthesized ligands were grafted onto QDs and self-assembly of NCD. For characterization of this hybrid system, the changes of energy dynamics were studied by Ultraviolet-visible spectroscopy (UV-Vis) and Fluorescence spectrometer. As a result, the quenching effect was observed as placed Fc near QDs and degree of quenching also varies. This study reveals that active moiety Fc introduced optical dynamic changes in absorbance and fluorescence when anchored on QDs surfaces compared to QD-as synthesized. This project will be a capstone for enhancing mechanistic understanding of how charge transfers between active moiety and QDs. The series of samples of ligands and QD-Fc ligand hybrids were successfully made as a part of collaboration work with Prof. Baxter group at Drexel University, for ultrafast spectroscopic analysis which will enable ultimate understanding of direct charge and energy flow.

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AN ABSTRACT OF THE CAPSTONE REPORT OF

Jung Mi Park for the degree of Master of Chemical Sciences

Title: Synthesis of Dendritic Ligands Containing Ferrocene for Quantum Dots (QDs) and Characterization of QD-ligands Hybrid System

Project conducted at: University of Pennsylvania
Department of Chemistry
231 S. 34th Street, Philadelphia, PA 19104-6323
Supervisor: Prof. Christopher B. Murray
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Abstract approved: Prof. Christopher B. Murray, Principle Investigator

Ligands for nanocrystals (NCs) have been widely studied beyond its role as a capping agent to applications such as tuning self-assembled properties of nanocrystals. Recent studies show that functionalized ligands can introduce precise control over charge and energy transfer of semiconductor NCs, or quantum dots (QDs). This can be used in various applications in optoelectronic devices, such as solar cells and light emitting diodes, or even further photocatalysis, and biological imaging. Herein, this project describes the design and synthesis of a series of novel dendritic ligands containing active moiety with efficient synthetic route for developing dendron series to graft onto the surface of CdSe/CdS core shell QDs. For active site in the ligand, ferrocene (Fc) was used because of its chemical stability and the ease of the Fc/Fc^+ redox couple. To characterize the series of ligands, Nuclear magnetic resonance (NMR) spectroscopy and mass spectroscopy studies were performed to analyze and confirm molecular structure of compounds. In addition, the synthesized ligands were grafted onto QDs and self-assembly of NCD. For characterization of this hybrid system, the changes of energy dynamics were studied by Ultraviolet-visible spectroscopy (UV-Vis) and Fluorescence spectrometer. As a result, the quenching effect was observed as placed Fc near QDs and degree of quenching also varies. This study reveals that active moiety Fc introduced optical dynamic changes in absorbance and fluorescence when anchored on QDs surfaces compared to QD-as synthesized. This project will be a capstone for enhancing mechanistic understanding of how charge transfers between active moiety and QDs. The series of samples of ligands and QD-Fc ligand hybrids were successfully made as a part of collaboration work with Prof. Baxter group at Drexel University, for ultrafast spectroscopic analysis which will enable ultimate understanding of direct charge and energy flow.
Synthesis of Dendritic Ligands Containing Ferrocene for Quantum Dots (QDs) and Characterization of QD-ligands Hybrid System by Jungmi Park

A CAPSTONE REPORT submitted to the University of Pennsylvania in partial fulfillment of the requirements for the degree of Master of Chemical Sciences

Presented on May 8, 2019
Commencement on May 19, 2019

APPROVED:

[Signature]

Prof. Christopher B. Murray, representing Materials Chemistry

I understand that my Capstone Report will become part of the permanent collection of the University of Pennsylvania Master of Chemical Sciences Program. My signature below authorizes release of my final report to any reader upon request.

[Signature]

Jung Mi Park, Author
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Introduction

Ligands for nanocrystals (NCs) have been widely studied for the past decades, extending beyond its role as a capping agent to applications such as tuning self-assembled properties of nanocrystals. Many groups have shown great quality of self-assembly of NCs, using various ligands either synthesis or post-synthesis ligand exchange. The significance of good self-assembly behavior of NCs has been addressed for better understanding of NCs’ properties. Recently, the group showed tuning physical arrangement of NCs system using ‘Janus’ ligands, which are both hydrophilic and hydrophobic. Developing novel ligands as a way to change surface chemistry of NCs system will suggest wide range of understanding relationship between ligands with different functionalities, as well as help NCs build array of more complicated structure of small materials such as the anisotropic shape of particles.

Recent studies show that functionalized can introduce precise control over charge and energy transfer of semiconductor NCs, or quantum dots (QDs). This can be used in various applications in optoelectronic devices such as solar cells and light emitting diodes, photocatalysis, and biological imaging. Previous reports have shown that placing redox active species on the surface of QDs may introduce many advantages. First, a redox active species near the surface can modulate photoluminescence by participating in the transfer of charges with QDs. Applying external potential or introducing oxidizing/reducing (ox/redox) reagents could control the redox state of redox-active ligands. Lastly, the photogenerated charges in QD can participate in ox/redox reactions in the NC organic shells. All these properties can be used in sensing, catalysis, or optoelectronic devices.

Herein, the goal of this project is to design and synthesize a series of novel dendritic ligands containing active moiety, then to graft ligands onto the surface of CdSe/CdS core shell QDs. QDs will be provided by Natalie Gogotsi, 4th year PhD student in Murray’s group, who is part of this research study.

For active site in the ligand, ferrocene (Fc) will be used because of its chemical stability and the ease of the Fc/Fc⁺ redox couple. Recent studies have shown that Fc and ferrocenyl derivatives near QDs can affect hole transfer rates and photoluminescence quenching efficiency of photoexcited QDs. Developing from this idea, employing scaffolds that can introduce various moieties will be capstone for changing dynamics of NCs array. Therefore, Fc will be harnessed to the targeted novel series of ligands (Fc 1-4). Functionalization of QDs with tailored dendrimer incorporating acceptors will be studied with varying distance between moieties and QDs and density of packing around the spherical structure. Dendrimers are stable and robust stabilizers for many indirect syntheses of NCs, being used at the post-synthesis ligand exchange step.

Two dendritic backbones with hydrophobic alkyl chains will be synthesized, one with lower generation, denoted R₁ in Figure 1, and higher generations with steric bulkiness, denoted as R₂, for physically separating active moieties in the QD arrays. This QD-Fc ligands hybrid study will advance understanding of photophysical properties of inorganic/organic interfaces at molecular energy level.

As shown in Figure 1, the active moiety, Fc, will be incorporated in the dendrimer precursors, using click chemistry followed by reduction step to obtain the target Fc ligands.
Fc ligands will serve as post-synthesis ligands for QDs which will be grafted with the binding thiol (-SH) in the ligands. The use of proper binding group in the ligands is important to successfully cap the Fc ligands and also prevent Fc from binding onto surface of QDs. Triazole ring in the structure has some affinity to QDs. Thiol (-SH) is the most common binding group for CdSe/Cds QDs and will be mainly used for this project.\textsuperscript{30}

**Figure 1.** Experimental Approach for Target Molecules

In addition to the short chain of ligands \textbf{Fc 1} and \textbf{2}, two different dendritic ligands \textbf{Fc 3} and \textbf{4} will also be made for locating Fc on the periphery of the dendron in different numbers, meaning that physical space will be changed between each Fc by varying linear (\(R_1\)) to bulky side chains (\(R_2\)). To characterize the series of ligands, Nuclear magnetic resonance (NMR) spectroscopy and mass spectroscopy studies will be performed to analyze and confirm molecular structure of compounds. In addition, the synthesized ligands \textbf{Fc 1-4} will be grafted onto QDs by post-synthesis ligand exchange method, and self-assembly of NCD hybrids will be studied by transmission electron microscopy (TEM) for visualization of QD arrays, estimating different interparticle spacing. The change of energy dynamics will be studied by Ultraviolet-visible (UV-Vis) and Fluorescence spectroscopy for understanding of photophysical properties of inorganic/organic interfaces at molecular energy level.
Materials and Methods

Materials

Potassium Iodide (99 %), Sodium Azide (≥99.5%), 12-azidododecylphosphonic acid (≥ 95 %), (+)-sodium L-ascorbate (≥ 98 %) and p-toluenesulfonyl chloride (≥ 98 %) were purchased from Sigma-Aldrich and used without further purification. Methyl 3,4,5-trihydroxybenzoate (98 %), 1-bromodecane (97 %), 4-methyl diterbutyl pyridine (≥ 99 %), and lithium aluminum hydride (95 %) were purchased from Aldrich and used without further purification. Copper (II) sulfate (98 %), 2,6-ditertbutyl 4-methyl pyridine (98 %), (1R)-(−)-10-camphorsulfonic acid (98 %) and oxalyl chloride (98 %) were purchased from Acros Organics. Ferrocenecarboxylic acid (99%) was purchased from Chem Impex Int’s Inc.. Thionyl chloride (≥ 98 %) was purchased from TCI and used without further purification. All chemicals were used as received. Potassium carbonate (reagent grade), sodium sulfate (anhydrous, reagent grade), silica gel (230-400 mesh, grade 60), triethyl amine (reagent grade), dimethylfomamide, tetrahydrofuran, methanol, hexanes, and ethyl acetate were purchased from Fisher Scientific and used without further purification. 11,11'-disulfanediylbis(undecan-1-ol) was used store in the lab cabinet prepared by previous reported literature.13 All solvents were ACS grade or higher. Dichloromethane was purchased from Fisher Scientific and was dried with activated molecular sieves (3A, 4 to 8 mesh, purchased from Acros Organics) before use.

Techniques

NMR. 1H NMR (500 MHz) and 13C NMR (126 MHz) spectra were recorded on Bruker UNI500 or BIODRX500 NMR spectrometer. 1H and 13C chemical shifts (δ) are reported in ppm while coupling constants (J) are reported in Hertz (Hz). The multiplicity of signals in 1H NMR spectra is described as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet), “p” (pentet), “dd” (double of doublets) and “m” (multiplet). All spectra were referenced using solvent residual signals (CDCl3: 1H, δ 7.27 ppm; 13C, δ 77.2 ppm). Reaction progress was monitored by thin-layer chromatography using silica gel coated plates or 1H NMR. Compounds were purified by filtration, precipitation, crystallization or flash column chromatography using silica gel (Acros Organics, 90 Å, 35-70 μm) as indicated in corresponding procedures.

Mass Spectroscopy. Electro spray ionization (ESI) was performed on Waters SQD equipped with an Acuity UPLC. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed on Ultraflex III (Maldi-Tof-Tof) mass spectrometer using dithranol as the matrix.

Optical Extinction Spectra. Optical extinction spectra were collected using a Cary 5000 UV-VIS-NIR, for solid films. Spectral band-pass was set to 2 nm and integration time to 0.25 s. Solution-phase measurements were collected on an Analytical Spectral Devices QSP 350-2000 UV-VIS-NIR spectrometer.

Electron Microscopy. TEM micrographs were collected using a JEOL 1400 microscope operated at 120 kV. The TEM was calibrated using a MAG*I*CAL® TEM calibration standard.
Prop-2-ynyl Ferrocenyl-1-carboxylate 3. To an oven dried round bottom flask was added ferrocenecarboxylic acid 1 (0.5 g, 1.48 mmol) and anhydrous CH₂Cl₂ (20 mL). The solution was stirred for 10 minutes under nitrogen atmosphere before oxalyl chloride (0.53 g, 4.45 mmol) was added, then the reaction mixture was stirred at room temperature for 3 hours under nitrogen. The reaction mixture was then concentrated under reduced pressure, and the crude product was dissolved in anhydrous CH₂Cl₂ (20 mL) and cooled to -10 °C. To the stirred solution was added propargyl alcohol (0.26 g, 0.65 mmol), Et₃N (0.30 g, 2.97 mmol, 0.41 mL), and DMAP (0.05 g, catalytic amount). The reaction mixture was allowed to warm up to room temperature and stirred overnight, then was washed with 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (100:0 → 80:20 hexane:ethyl acetate) to afford pure 3 as orange crystal (1.09g, 1.2 mmol, 96% yield). 1H NMR (CDCl₃) δ 7.25 (s, 2H), 4.01 (q, J = 6.2 Hz, 6H), 3.87 (s, 3H), 3.24 (t, J = 7.0 Hz, 2H), 1.80 (p, J = 6.8 Hz, 4H), 1.73 (p, J = 7.0 Hz, 2H), 1.58 (p, J = 6.8 Hz, 2H), 1.47 (t, J = 7.7 Hz, 6H), 1.37 – 1.23 (m, 44H), 0.87 (t, J = 6.8 Hz, 6H); 13C NMR (126 MHz, CDCl₃) δ 170.88, 78.42, 77.23, 77.18, 76.98, 76.72, 74.46, 71.49, 71.05, 70.13, 69.94, 69.70, 69.61, 69.57, 60.23, 51.35, 31.43, 22.51, 20.93, 14.07, 14.02; AMM-ESI (m/z): calcd. for C₁₄H₁₂Fe₂O₂, 268.1087; found 268.0169

Disulfanediyli bis(11-mercaptoundecyl ferrocenyl acetate) 4. To an oven dried round bottom flask was added ferrocenecarboxylic acid (0.25 g, 1.087 mmol) and anhydrous CH₂Cl₂ (20 mL). The solution was stirred for 10 minutes under nitrogen atmosphere before oxalyl chloride (0.53 g, 4.45 mmol) was added, then the reaction mixture was stirred at room temperature for 3 hours under nitrogen. The reaction mixture was then concentrated under reduced pressure, and the crude product was dissolved in anhydrous CH₂Cl₂ (20 mL) and cooled to -10 °C. To the stirred solution was added 11,11’-disulfanediylbis(undecan-1-ol) (0.20 g, 0.49 mmol), Et₃N (0.44 g, 4.348 mmol, 0.41 mL), and DMAP (0.05 g, catalytic amount). The reaction mixture was allowed to warm up to room temperature and stirred overnight, then was washed with 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (100:0 → 90:10 hexane:ethyl acetate) to afford pure 4 as dark browns crystal (0.317 g, 0.234 mmol, 46% yield). 1H NMR (500 MHz, Chloroform-d) δ 4.80 (dd, J = 2.6, 1.3 Hz, 2H), 4.38 (td, J = 2.3, 1.2 Hz, 2H), 4.27 – 4.06 (m, 7H), 2.67 (t, J = 7.3 Hz, 2H), 1.82 – 1.49 (m, 4H), 1.49 – 1.13 (m, 15H); 13C NMR (126 MHz, CDCl₃) 171.90, 100.14, 77.45, 77.20, 76.95, 71.69, 71.34, 70.25, 69.87,
To an oven dried round bottom flask was added disulfide 4, sodium borohydride (50 mg, 0.876 mmol) and ZrCl₄ (0.002 g catalytic amount) in THF (20 mL), Methanol (2 mL) and Water (2 mL). The solution was stirred for 3h. The reaction mixture was protonated with 6N HCl, before the aqueous layer was extracted with chloroform (2 x 50 mL) and the organic layer was washed with 1N HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure to yield Fc 1. The crude product was used for ligand exchange without further purification as dark brown crystals (45 mg, 0.74 mmol, 90% yield). ¹H NMR (500 MHz, Chloroform-d) δ 4.80 (dd, J = 2.6, 1.3 Hz, 2H), 4.38 (td, J = 2.3, 1.2 Hz, 2H), 4.27 – 4.06 (m, 7H), 2.67 (t, J = 7.3 Hz, 2H), 1.82 – 1.49 (m, 4H), 1.49 – 1.13 (m, 15H). ¹³C NMR (126 MHz, CDCl₃) 171.90, 100.14, 77.45, 77.20, 76.95, 71.69, 71.34, 70.25, 69.87, 64.46, 39.33, 29.74, 29.69, 29.66, 29.47, 29.41, 29.39, 29.09, 28.70, 26.24.; AMM-ESI (m/z): calcd. for C₄₄H₆Fe₂O₄S₂ 831.2867; found 831.2874

Fc 2. To an oven dried round bottom flask was added 3 (50 mg, 1.865 mmol) and 12-azidododecylphosphonic (49.39 mg, 3.7 mmol) in THF (20 mL). To a stirred solution were added copper (II) sulfate (0.05 g, catalytic amount), L-Sodium ascorbate (5 mg, catalytic amount) and water (4 mL). The solution was stirred for 5 minutes at room temperature until blue Copper (II) sulfate turned dark brown then the reaction mixture was refluxed at 70 °C for 36 hours. The reaction was cooled to room temperature and a mixture was then concentrated under reduced pressure, and the crude product was dissolved in CHCl₃ (20 mL). Then solution was washed with 6 M HCl (2 x 50 mL) and 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure. The crude product was precipitated out with 6M HCl and 1 M NaOH and the filtrate was washed with hexane (92.4 mg, 1.14 mmol, 74% yield). AMM-ESI (m/z): calcd. for C₂₅H₃₆Fe₃O₃S₅P 535.1786; found 545.1812

Methyl 7-hydroxy-2,2-dimethylbenzo[d][1,3]dioxole-5-carboxylate, 6. To an oven dried round bottom flask were added methyl 3,4,5-trihydroxybenzoate (2.5 g, 13.5 mmol) and dried toluene (50 mL). To a stirred solution were added (1R)-(-)-10-camphorsulfonic
acid (0.1 g, catalytic amount) and 2,2-dimethoxypropane (10 mL). The solution was stirred for was refluxed at 120 °C for 9 hours under nitrogen using a Dean Stark Trap to remove water. The reaction was cooled to room temperature and a mixture was then concentrated under reduced pressure. The crude was purified by column chromatography 100:25 hexanes:ethyl acetate) to afford pure 5 as brown crystals (2.04 g, 9.35 mmol, 70% yield).

Methyl 7-((11-azidoundecyl)oxy)-2,2-dimethylbenzo[d][1,3]dioxole-5-carboxylate, 8. To a stirred solution of 6 (2.02 g, 9.01 mmol) and 7 (4.97 g, 13.5 mmol) in DMF (45 mL) were added potassium iodide (0.1 g, catalytic amount) and K2CO3 (2.5 g, 18.02 mmol). The resulting mixture was stirred at 80 °C for 12 hours. The reaction was cooled to room temperature, diluted with CHCl3 (200 mL) and then washed with H2O (3 x 100 mL) and 1 M HCl (3 x 100 mL). The organic layer was dried over anhydrous Na2SO4, filtered, and the filtrate was concentrated under reduced pressure to yield pure orange solid (3.3 g, 8.7 mmol, 96% yield).

Methyl 3-((11-azidoundecyl)oxy)-4,5-dihydroxybenzoate, 9. To a stirred solution of 8 (3.3 g, 8.95 mmol) in DCM (30 mL) was added TFA (1.06 g, 8.95 mmol) until the solution turned to dark brown. The resulting mixture was stirred for 4h at room temperature. The reaction was concentrated under reduced pressure and dissolved in methanol, then concentrated again under reduced pressure. This process was repeated (100 mL x 3) to form crystalline, then filtered with hexane and filtrate was collected as dark orange solids (2.1 g, 5.4 mmol, 60% yield).

Methyl 3-((11-azidoundecyl)oxy)-4,5-bis(dodecyloxy)benzoate, 12. To a stirred solution of 9 (1 g, 2.98 mmol) and 1-bromododecane (1.78 g, 6.7 mmol) in DMF (25 mL) was added, K2CO3 (18.7 g, 135.5 mmol) and the resulting mixture was stirred at 80 °C for 12 hours. The reaction was cooled to room temperature, diluted with CHCl3 (200 mL) and then washed with H2O (3 x 100 mL) and 1 M HCl (3 x 100 mL). The organic layer was dried over anhydrous Na2SO4, filtered, and the filtrate was concentrated under reduced pressure. The product was purified by dissolving in small amount of CHCl3 and precipitated out by adding excess MeOH affording pure 12 as a white solid (2.5 g, 5.24 mmol, 85% yield).
Methyl 3,4,5-tris(dodecyloxy)benzoate, 20. To. As for 12. Methyl 3,4,5-trihydroxybenzoate 5 (5g, 27.17 mmol) and 1-bromododecane 2 (27g, 108.4 mmol) in DMF (45 mL) was added K$_2$CO$_3$ (18.7g, 135.5 mmol) and the resulting mixture was stirred at 80 °C for 12 hours. The precipitate was collected by filtration and dried obtain pure 8 as a white solid (15.61g, 20.8 mmol, 85% yield).

3,4,5-Tris(octadecyloxy)phenylmethanol, 21. To a stirred solution of LiAlH$_4$ (2.64 g, 69.4 mmol) in THF (100 mL) at 0 °C was added 4 (15.6g, 23.13 mmol) portion wise over a period of 10 minutes, and the resulting mixture was stirred at 0 °C for 30 minutes under nitrogen atmosphere. The reaction mixture was then allowed to warm up to room temperature for 30 minutes after which it was stirred at 60 °C for an additional 3 hours. Then, it was cooled to 0 °C and quenched slowly by adding small portions of cold water while monitoring the evolution of hydrogen bubbles. The mixture was then concentrated under reduced pressure, dissolved in CHCl$_3$ (200 mL) and washed with 1 M HCl (2 x 100 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in the smallest possible amount of warm CHCl$_3$ and mixed with MeOH to induce precipitation. The precipitate was collected by filtration and dried to obtain pure 21 as a white solid (13.41g, 20.2, 96 % yield).

5-(Chloromethyl)-1,2,3-tris(octadecyloxy)benzene, 11. To a stirred solution of 21 (13.41 g, 20.28 mmol) in CH$_2$Cl$_2$ (100 mL) was added DMF (0.05 mL), and thionyl chloride (7.23 g, 60.85 mmol, 4.37 mL), and the resulting mixture was stirred for 3 hours at room temperature under nitrogen atmosphere. The reaction mixture was then concentrated under reduced pressure and the residue was dissolved in the smallest possible amount of warm CHCl$_3$ and mixed with MeOH to induce precipitation. The precipitate was collected by filtration and dried to obtain pure 11 as a white solid (12.83g, 13.04 mmol, 98% yield).
Methyl 3-((11-azidoundecyl)oxy)-5-((3,4,5-tris(dodecyloxy)benzyl)oxy)-4-(3,4,5-tris(dodecyloxy)phenoxy)benzoate, 13. To a stirred solution of benzoyl methyl ester 9 (0.71 g, 1.87 mmol) and 11 (3.18 g, 4.68 mmol) in DMF (45 mL) was added K$_2$CO$_3$ (0.73 g, 5.30 mmol) and KI (0.1 g, catalytic amount) and the resulting mixture was stirred at 80 °C for 12 hours. The reaction was cooled to room temperature, diluted with CHCl$_3$ (200 mL) and then washed with 1 M HCl (3 x 50 mL) and H$_2$O (3 x 50 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and the filtrate was concentrated under reduced pressure. The product was purified using column chromatography (100:2 hexanes:ethyl acetate) to afford pure 13 as a pale yellow oil (0.67 g, 0.48 mmol, 40% yield).

3-((11-Azidoundecyl)oxy)-4,5-bis(dodecyloxy)benzoic acid, 13. To a stirred solution of 12 (1.8 g, 2.87 mmol) in THF (10 mL) was added KOH (0.4 g, 9.39 mmol), H$_2$O (2 mL), and MeOH (2 mL). The reaction mixture was stirred at 80 °C for 4 hours. The solvents were evaporated under reduced pressure, and the resulting product was acidified with 1 M HCl before being extracted with chloroform (3 x 75 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and the filtrate was concentrated under reduced pressure to yield 14 as a pure white solid (1.7 g, 2.8 mmol, 99 % yield).
3-((11-Azidoundecyl)oxy)-5-((3,4,5-tris(dodecyloxy)benzyl)oxy)-4-(3,4,5 tris(dodecyloxy)phenoxy)benzoic acid, 15. To a stirred solution of 12 (0.66g, 0.51 mmol) in THF (10 mL), H₂O (2 mL), and MeOH (2 mL) was added KOH (0.1164g, 0.277 mmol). The reaction mixture was stirred at 80 °C for 16 hours. The solvents were evaporated under reduced pressure, and the resulting product was acidified with 1 M HCl before being extracted with chloroform (3 x 75 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure to yield 15 as a pale-yellow oil (0.67 g, 0.51 mmol, 99 % yield).

Disulfanediylbis(undecane-11,1-diyl) bis(3,4,5-tris(dodecyloxy)benzoate)), 16. To an oven dried round bottom flask was added 14 (1.0 g, 1.48 mmol) and CH₂Cl₂ (20 mL). The solution was stirred for 10 minutes under nitrogen atmosphere before thionyl chloride (0.53 g, 4.45 mmol) was added, then the reaction mixture was stirred at room temperature for 3 hours under nitrogen. The reaction mixture was then concentrated under reduced pressure, and the crude product was dissolved in CH₂Cl₂ (20 mL) and cooled to -10 °C. To the stirred solution was added 21 (0.26 g, 0.65 mmol), Et₃N (0.30 g, 2.97 mmol, 0.41 mL), and DMAP (0.05 g, catalytic amount). The reaction mixture was allowed to warm up to room temperature and stirred overnight, then was washed with 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (100:1 hexanes:ethyl acetate) to afford pure 22 as a white solid (1.09 g, 1.3 mmol, 96% yield).
Disulfanediylbis(undecane-11,1-diyl)bis(3-((11-azoundecyl)oxy)-5-((3,4,5-tris(dodecyloxy)benzyl)oxy)-4-(3,4,5-tris(dodecyloxy)phenoxy)benzoate), 17. To an oven dried round bottom flask was added 15 (1.0 g, 1.48 mmol) and CH₂Cl₂ (20 mL). The solution was stirred for 10 minutes under nitrogen atmosphere before thionyl chloride (0.53 g, 4.45 mmol) was added. The solution was cooled at 0 °C for 10 minutes under nitrogen atmosphere before 2,6-ditert butyl 4-methyl pyridine (0.228 g, 1.11 mmol) and thionyl chloride (0.14 g, 1.11 mmol) were added, then the reaction mixture was stirred at room temperature for 3 hours under nitrogen. The reaction mixture was then concentrated under reduced pressure, and the crude product was dissolved in CH₂Cl₂ (20 mL) and cooled to -10 °C. To the stirred solution was added 11,11'-disulfanediylbis(undecan-1-ol) (0.26 g, 0.65 mmol), NEt₃ (0.30 g, 2.97 mmol, 0.41 mL), and DMAP (0.05 g, catalytic amount). The reaction mixture was allowed to warm up to room temperature and stirred overnight, then was washed with 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (100:10 hexanes:ethyl acetate) to afford pure 17 as a pale yellow solid (1.09 g, 1.3 mmol, 96% yield).

Disulfanediylbis(undecane-11,1-diyl) bis(3-((11-(4-(acetoxyferrocenyl)-1H-1,2,3-triazol-1-yl)undecyl)oxy)-4,5-bis(dodecyloxy)benzoate), 18. To an oven dried round bottom flask was added 16 (95 mg, 0.357 mmol) and THF (20 mL). To a stirred solution were added the alkynyl intermediate 3 and Copper (II) sulfate (5 mg, catalytic amount), L-Sodium ascorbate (5 mg, catalytic amount) and water (4 mL). The solution was stirred for 5 minutes at room temperature until blue Copper (II) sulfate turned dark brown then the reaction mixture was refluxed at 70 °C for 36 hours. The reaction was cooled to room temperature and a mixture was then concentrated under reduced pressure, and the crude product was dissolved in CHCl₃ (20 mL). The crude product was purified with column
chromatography (100:15 hexanes:ethyl acetate) to afford pure 18 as brown solid (125 mg, 0.08 mmol, 28% yield). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.26 (s, 2H), 5.37 (s, 2H), 4.82 (s, 2H), 4.56 – 4.20 (m, 6H), 4.22 – 3.80 (m, 12H), 2.68 (t, $J$ = 7.4 Hz, 2H), 2.05 – 1.87 (m, 2H), 1.74 (dddd, $J$ = 43.3, 29.7, 14.6, 7.2 Hz, 11H), 1.47 (q, $J$ = 7.7 Hz, 8H), 1.42 – 1.04 (m, 62H), 0.89 (t, $J$ = 6.7 Hz, 7H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.70, 166.44, 152.74, 143.22, 142.29, 125.03, 123.89, 108.01, 107.97, 77.36, 77.11, 76.85, 73.44, 71.55, 71.53, 70.51, 70.26, 69.74, 69.14, 65.11, 57.32, 50.43, 39.10, 31.90, 30.34, 30.29, 29.71, 29.70, 29.68, 29.66, 29.64, 29.61, 29.53, 29.51, 29.48, 29.44, 29.38, 29.36, 29.34, 29.32, 29.30, 29.27, 29.23, 29.19, 28.98, 28.73, 28.51, 26.50, 26.07, 26.03, 25.99, 22.67, 14.11.

Disulfanediylbis(undecane-11,1-diyl) bis (3-((11-(4-(acetoxyferrocenyl)-1H-1,2,3-triazol-1-yl)undecyl)oxy)-4,5-bis(3,4,5-tris(dodecyloxy)benzyl)oxy)benzoate), 19. To an oven dried round bottom flask was added 17 (50 mg, 0.187 mmol) and THF (20 mL). To a stirred solution were added the propargyl ester intermediate 3 and Copper (II) sulfate (0.05 g, catalytic amount), L-Sodium ascorbate (5 mg, catalytic amount) and water (4 mL). The solution was stirred for 5 minutes at room temperature until blue Copper (II) sulfate turned dark brown then the reaction mixture was refluxed at 70 °C for 48 hours. The reaction was cooled to room temperature and a mixture was then concentrated under reduced pressure, and the crude product was dissolved in CHCl$_3$ (20 mL). The crude product was purified with column chromatography (100:10 hexanes:ethyl acetate) to afford pure 19 as dark brown solid (86 mg, 0.06 mmol, 34% yield). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.67 (s, 1H), 7.34 (s, 1H), 6.63 (s, 5H), 5.32 (s, 2H), 5.00 (d, $J$ = 17.3 Hz, 5H), 4.89 (s, 2H), 4.47 (s, 2H), 4.27 (t, $J$ = 6.8 Hz, 3H), 4.20 (s, 6H), 4.01 (t, $J$ = 6.5 Hz, 3H), 3.89 (tt, $J = 15.7, 6.5$ Hz, 15H), 2.67 (t, $J = 7.3$ Hz, 2H), 1.89 (s, 2H), 1.81 (d, $J = 7.1$ Hz, 3H), 1.74 (p, $J = 7.5$ Hz, 17H), 1.69 – 1.59 (m, 4H), 1.44 (dq, $J = 22.8, 7.5$ Hz, 2OH), 1.27 (d, $J = 11.7$ Hz, 149H), 0.88 (t, $J = 6.8$ Hz, 23H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.91, 166.38, 153.39, 153.12, 152.56, 142.22, 138.04, 138.00, 132.70, 131.94, 125.72, 109.44, 106.74, 105.91, 77.42, 77.17, 76.91, 75.26, 73.52, 73.49, 71.90, 69.33, 69.23, 69.14,
Fc 3. As for Fc 1. \(50 \text{ mg, } 0.123 \text{ mmol}\) in dried THF (20 mL). The solution was stirred for 6 h at room temperature under flow of nitrogen. The reaction affords crude Fc 3 as brown solid. The reaction was not purified and used for the next step (38 mg, 0.08 mmol, 76\% yield). \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta 6.54 \text{ (s, 2H), 4.87 – 4.70 (m, 5H), 4.57 (s, 2H), 4.39 – 4.30 (m, 7H), 4.24 (d, } J = 18.0 \text{ Hz, 9H), 4.02 – 3.88 (m, 23H), 3.73 (h, } J = 3.9, 3.5 \text{ Hz, 61H), 3.67 – 3.53 (m, 5H), 2.74 – 2.59 (m, 4H), 2.15 (s, 21H), 1.92 – 1.68 (m, 97H), 1.49 – 1.40 (m, 24H), 1.36 – 1.22 (m, 207H), 0.86 (t, } J = 6.7 \text{ Hz, 24H).}

**General procedure for QD-Fc Ligand Hybrids**

A solution of 10 mg of ligands (Fc 1 - 4) dissolved in 10 mL solution of 1.8 mg/mL TOPO-capped CdS/CdSe core-shell QDs in chloroform and the resulting mixture was stirred at room temperature for 16 h while mildly heated at 55 °C. The reaction was cooled to room temperature and transferred to 50 mL centrifuge tubes and dissolved in 30 mL of chloroform. Ethanol (10 mL) was added until precipitation observed. The resulting precipitate was collected by centrifugation (8000 rpm, 3 minutes) and the supernatant liquid was discarded. The solid was redispersed in hexane (acetonitrile for ligand Fc 2) and precipitated by addition of ethanol. This step was repeated at least twice to remove any excess ligands. QD-Fc **ligand hybrids** were characterized by UV VIS nd Fluorescence spectroscopy. Each specie was diluted in chloroform (2 mg/mL). The solution was transferred to 4 clear side glass cuvette for measurements.
Results and Discussion

Ligand Synthesis and Design

A series of Fc ligands (Fc 1-4) with dendritic backbones were designed, to allow for varying the distance between the surface of QDs and active moieties at present on the periphery of the dendrons.

Scheme 1. Synthesis of Ferrocene ester intermediates.

\[ \text{Reagents and conditions: (i) Oxalyl chloride, 2,6-di-tert-butyl-4-methylpyridine, anhydrous dichloromethane (DCM), r.t, 3 h, under nitrogen, (ii) anhydrous DCM, propargyl alcohol, DMAP, and triethyl amine, r.t, 16 h under nitrogen.} \]

To obtain the targeted Fc ligands (Fc 1-4), a Fc propargyl ester intermediate, 3, was first synthesized for a triple bond to allow for click chemistry to be employed, for efficient generation of the series. The starting material, Ferrocenecarboxylic acid 1, was first chlorinated and then propargyl alcohol was added to ferrocene acid chloride 2 in a one-pot-two-step synthesis process (Scheme 1). Fc 1 was synthesized by the same one pot synthesis, but disulfide bearing molecule 11,11’-disulfanediylbis(undecan-1-ol) was added to afford the disulfide 4. Reduction with sodium borohydride catalyzed by zirconium chloride (Scheme 2a) produces the target molecule Fc 1.

The targeted Fc 2 was synthesized using click chemistry in good yield (ca. 70%). The reaction utilized in this project was a 1,3-cycloaddition between an azide and terminal alkyne catalyzed by copper and sodium-L ascorbate under heating and microwave radiation in the settings (Scheme 2b). This reaction was used as a key step to link our active moiety Fc with a choice of series of dendritic backbone in later steps as well.

The series of dendritic backbones were synthesized following convergent growth of dendrons starting from reacting readily available methyl gallate (methyl 3,4,5-trihydroxybenzoate) 5 with 2,2-dimethoxy propane to selectively protect two hydroxy sites. The remaining hydroxyl group in compound 6 was reacted with azide bearing 7, to yield compound 8. The intermediate 8 was deprotected by trifluoroacetic acid to give 9. Then, the choice of adding benzyl chloride 10 or dodecylbromide 11 will determine whether dendrons to build lower (R_1) or higher (R_2) generations. Two equivalents of chlorinated intermediate 10 to grow lower generation and 11 for higher generation backbone were grown by same Williamson etherification reaction under mild basic condition to give access to give corresponding 12 or 13 with 90% yield. Hydrolysis of the methyl ester functional groups with potassium hydroxide gave access to the carboxylic acids compound 14 or 15 in high yield (ca. 90%). Then, the one-pot-two-step process employed previously was utilized to add thiol-containing binding groups, to give backbones 16 or 17. The disulfide 16 and 17 will be used for click reaction before reducing...
to thiol, because azide is another possible 11,11’-disulfanediylbis(undecan-1-ol) active site for reduction as well. (Scheme 3).

**Scheme 2. Synthesis of Fe 1 and Fe 2**

*a*

For the targeted ligands Fe 3-4, Fe propargyl ester intermediate 3 was attached to disulfide backbones 16 or 17 using click chemistry, resulting disulfide dendrons with 18 or 19 in relatively lower yield (ca. 35%) compared to shorter ligand Fe 2 (ca. 70%).

While conventional disulfide reductions were reported with small molecule synthesis, bulky dendritic backbones cause steric hinderance, possibly restricting access to the sulfur atoms, creating difficulties for fully reducing the molecule. Reduction of 18 by NaBH₄ with ZrCl₄ as a catalyst was performed. Fe 3 was observed in H-NMR, and the crude used for post-synthesis ligand exchange without further purification, because any unbound remaining compounds can be separated out during reaction with QDs. More precise control of reagents and condition will be carried out for bulkier backbone clicked moiety as remaining future work (Scheme 4). Then, the series of ligands Fe 1-3, were grafted onto the CdSe/CdS QDs with capping ligands, trioctylphosphine oxide (TOPO), prepared by the group member. The reaction was carried out under mild heating at 55 °C and stirred for 16 h. The hybrids were precipitated out with the choice of antisolvent, acetonitrile, and the QD particles were collected by centrifugation. This step was repeated several times to remove any remaining unbound ligands (Figure 2).
Scheme 3. Synthesis of Dendritic Backbones

*Reagents and conditions: (i) Anhydrous toluene, r.t, 3h, under nitrogen then consequently; (ii) K₂CO₃, KI, DMF, 80 °C, 12 h; (iii) TFA, 60 °C, 4 h, reflux (iv) KOH, THF/water (5:1), 80 °C, 4 h for 12, 16 h for 13; (v) SOCl₂, anhydrous DCM, r.t., 3 h for 14 and add 2,6-ditert butyl 4-methylpyridine for 15; then, Et₃N, DMAP, anhydrous DCM, −10 °C → r.t., 12 h;
Scheme 4. Preparation of Reagent 11

(ii) K$_2$CO$_3$, KI, DMF, 80 °C, 12 h; (vi) LiAlH$_4$, THF, 60 °C, 3 h; (vii) SOCl$_2$, anhydrous DCM, r.t., 3 h

Figure 2. Synthesis of QD-Fc ligand hybrids
Scheme 5. Synthesis of Fe 3 and Fe 4

*Reagents and conditions: (i) (iv) CuSO₄ (cat.), L-ascorbate, THF/water (5:1), 75 °C, 36 h, 48 h for 17; (ii) NaBH₄, ZrCl₄ (cat.), 60 °C, 4 h, reflux
Optical Characterization

A series of ligands Fc 1-4 was completed to determine where the acetylferrocene are present in the UV region. Peaks between 200 nm to 300 nm, and small peak at 450 nm (Figure 3a and b) were observed. These peaks correspond to the data of acetylferrocene compounds.\textsuperscript{29}. This data will be used for comparison between bare ligands and QD-ligand hybrids in absorbance spectra.

![Absorbance Spectra](image)

**Figure 3.** Absorbance Spectra of Fc containing species a) Fc 1-4, b) Fc-disulfide intermediates

After performing the ligand exchange, both absorbance and fluorescence were measured with a control sample of QDs containing TOPO. Fluorescence measurement demonstrate a photoluminescence change of QDs by the presence of Fc.
Absorbance spectra indicates QD-ligands hybrids only show minor changes in spectra comparing from contrast sample QDs-as synthesized. However, only different absorption peak occurred at 590 nm for QD-Fc 3, which was found to be indicated from using different batch of QDs and confirmed by emission spectra as well. This is evidence to support that there was neither transfer to surface defect nor structural transformation of QDs during the progress of ligand exchange (Figure 4).

Quenching of photoluminescence was observed by placing Fc in proximity to the QDs as evidenced by fluorescence studies. This study preliminarily implies that quenching efficiency of each QD ligands depends on length of ligands (Figure 5). To further analyze
the degree of quenching relative to the length of ligands or number of Fc near the QD surface, \textbf{Fc 3} should be grafted onto the same size QDs as used for other samples.
Conclusions and Future Work

This project studied a novel system with Fc as an acceptor embedded on dendritic backbones and indicates their impact on QDs’ photophysical energy system. An efficient synthetic route for novel functionalized ligands with dendritic backbones has been achieved. Dendrimers also enhanced stability of both ligands and QD hybrids as it showed chemical stability without decomposition when stored at room temperature for long time. This study demonstrates QDs-Fc ligands exchange reaction is solution-processable even with highly hydrophobic backbones. Characterization of each intermediate was carried out, understanding chemical structures from molecular to supramolecular extent. There was a synthetic challenge of reducing disulfide bond to thiol. To address the limited reaction with the bulky dendritic molecules, the organometallic catalyst was used to partially improve the reaction with bulky dendritic molecule. The active moiety Fc revealed optical dynamic changes in absorbance and fluorescence when anchored on QDs surface. Mechanistic details of how charge transfers between Fc and core-shell structure of CdSe/CdS QDs will be further studied by analyzing signal decay in ultrafast spectrometry. The QD-Fc ligand hybrid samples will be visualized through TEM. To generate coherent emission range of peak in both fluorescence and absorbance, Fc 3 ligand will be grafted onto the same size QDs as used for Fc 1 and Fc 2. This project implies valuable crude data, that will be used to direct the assembly of NCD hybrids into superstructures with featured optoelectronic properties and translated into next-generation nanomaterials. The computational study of measuring charge transfer will be completed by a collaborator, Prof. Baxte in Drexel University, using ultrafast spectroscopy instrument.
References


Appendix 1. NMR Spectra for 3 a) $^1$H NMR, b) $^{13}$C NMR
Appendix 2. NMR Spectra for 4 a) $^1$H NMR, b) $^{13}$C NMR
Appendix 3. NMR Spectra for Fe 1 a) $^1$H NMR, b) $^{13}$C NMR
Appendix 4. NMR Spectra for 18 a) $^1$H NMR, b) $^{13}$C NMR
Appendix 5. NMR Spectra for 19 a) $^1$H-NMR, b) $^{13}$C-NMR
Appendix 6. $^1$H-NMR Spectra for Fe 3