

Surface Functionalization of Colloidal Silicon-based Quantum Dots



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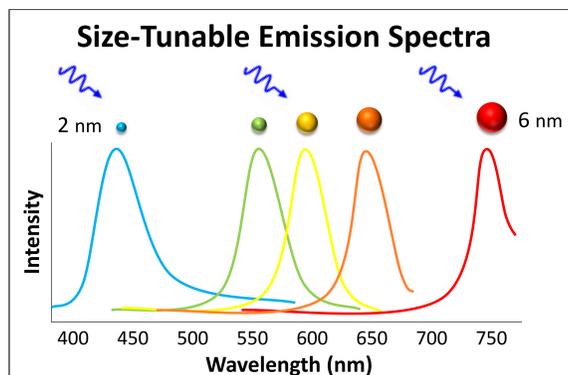
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Alternative Passivation Method to Improve Electronic Coupling

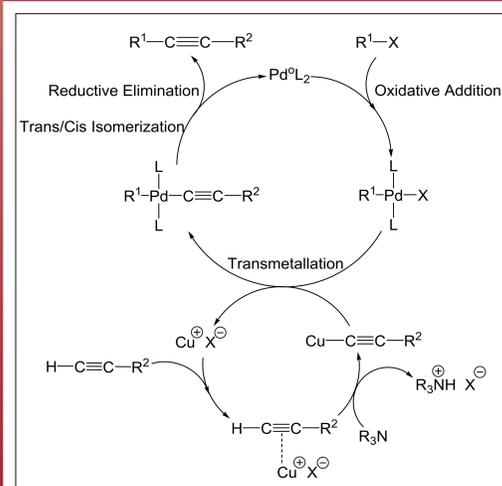
Silicon-based quantum dots (SiQDs) have been of recent interest due to their distinctive electronic properties that lead to applications in photovoltaics, fluorescent bio-labeling, organic light emitting diodes, and more.¹ A quantum dot is a semiconductor nanocrystal in which the band gap is inversely related to the size of the dot, leading to size-tunable emission spectra. Most quantum dots are presently based on heavy metal semiconductors that contain toxic and expensive elements such as cadmium, selenium, and lead.



The purpose of this project is to connect conjugated organic ligands to SiQDs with vinyl linkages in attempt to improve energy absorption and energy transfer within and between the dots. The surface passivation of these environmentally benign SiQDs leads to significant orbital redistributions that can increase resistance to oxidation, improve solubility, and alter the band gap.

The method presented here involves a palladium catalyzed cross-coupling reaction to synthesize the ligands followed by a hydrosilylation reaction to form a vinylic connection between the ligands and the SiQDs.

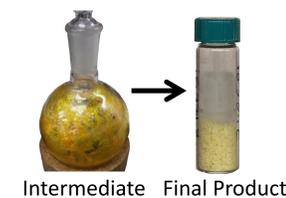
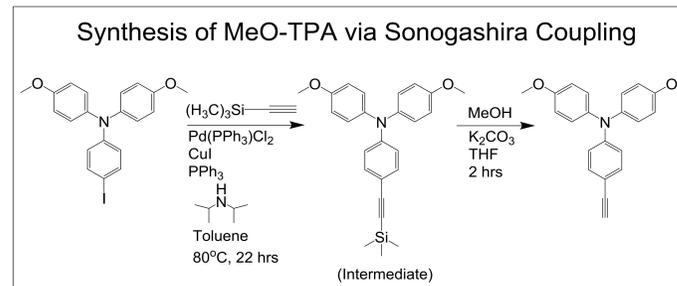
Mechanism of Ligand Synthesis



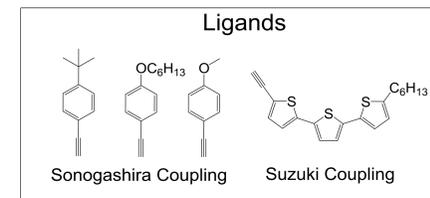
The Sonogashira cross-coupling mechanism consists of a palladium catalyst cycle and a copper cocatalyst cycle coupled by transmetalation. The reaction requires an amine base and takes place in anhydrous and anaerobic conditions.²

Ligand Synthesis and SiQD Attachment Process

1. Synthesis of electron-donating capping groups

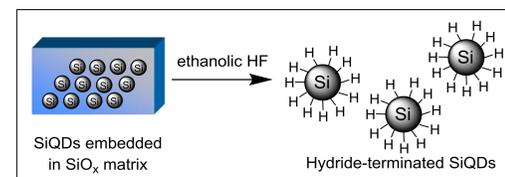


The MeO-TPA synthesis is shown above from a total of five ligands. Some reactions were repeated with varying conditions to increase yield and simplify purification. Products were characterized with FT-IR, NMR, and GC-MS.

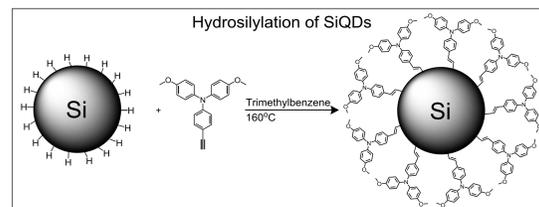


2. Preparation of hydride-terminated SiQDs

After the silicon oxide matrix was etched in the dark, dots were purified by centrifugation of three rinses with methanol and one rinse with chloroform.



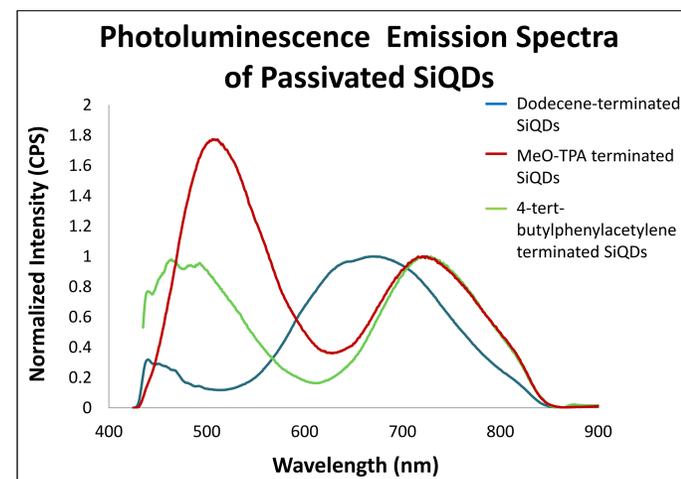
3. Ligand attachment to SiQDs



Dots were available to perform hydrosilylation reactions with synthesized MeO-TPA (shown) and purchased 4-tert-butylphenylacetylene.

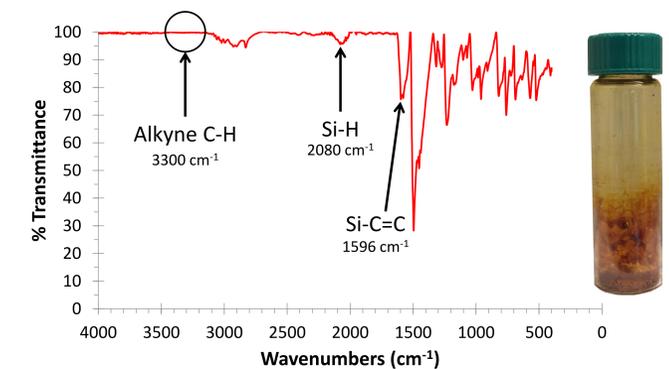
4. Characterization of functionalized SiQDs

The dot-ligand systems were characterized with FT-IR, UV-Vis, and PL/PLE. The PL graph shown to the right includes two peaks for the MeO-TPA system: the left peak is emitted by the ligand itself and right peak is emitted by the dot-ligand system.



System Characterization by FT-IR

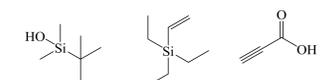
The FT-IR confirms ligand attachment based on the absorption peaks of the MeO-TPA starting material and the replacement of the terminal alkyne C-H peak at 3300 cm⁻¹ with the Si-C=C peak at 1596 cm⁻¹. The minor Si-H peak at 2080 cm⁻¹ indicates that the bulky ligand may have prevented some hydrides from reacting.



Conclusions and Future Work

This work demonstrates the feasibility of creating Si-C=C linkages to peripheral aromatic groups using mild chemistry. The passivation of SiQDs with MeO-TPA was performed by synthesis of the ligand, etching the dots, and a hydrosilylation reaction for attachment. The product was confirmed in the FT-IR spectrum by the replacement of the terminal alkyne with a vinylic attachment. The PL spectrum is red-shifted by 50 nm, indicating energy transfer from the surface species to the SiQD core as incident photons excite electrons from the HOMO (localized on the ligands) to the LUMO (localized on the dot). Therefore, the MeO-TPA capping group effectively tuned the electronic band gap of the SiQDs. Further, the dot-ligand systems are soluble and resistant to oxidation.

Ligands for Future Synthesis/Attachment



Continued research will be focused on exploring various ligand attachments to SiQDs in attempt to engineer the electronic, optical, and processing properties of the system.

Acknowledgments

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