Supporting Information for:

# Bandgap Tuning of Silicon Quantum Dots by Surface Functionalization with Conjugated Organic Groups

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## I. Material Synthesis and Preparation

All chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise noted. The NMR experiments were carried out on a JEOL 400 MHz nuclear magnetic resonance spectrometer at room temperature. The UV/Vis was measured on Beckman DU-800 UV/Vis spectrometer. The PL and PLE measurement were performed on Horiba Fluorolog system using long pass filter plates (up to 590 nm) to remove any disturbances from 1$^{st}$ and 2$^{nd}$ order excitations. An excitation wavelength of 365 nm was used for all samples in this study unless otherwise noted. FT-IR spectra were obtained from a Nicolet™ iS™ 50 FT-IR Spectrometer with an ATR crystal. All spectra were taken immediately after purification to minimize the exposure of samples to ambient oxygen. Transmission electron microscopy (TEM) and electron diffraction were used to examine the size, morphology, and crystallinity of the resulting SiQDs. Suspensions of the SiQDs were prepared by mixing the solids with dichloromethane (DCM). Drops of the suspension were allowed to dry on SiNx coated TEM grids (SimPore, Inc.) and subsequently examined in a Philips CM200 equipped with a UHR polepiece and operated at 200 keV. Bright field TEM images and selected area diffraction patterns of the SiQDs are given in Figure 5 in the main manuscript. Quantifying the size using 329 SiQDs from the TEM images, a log-normal distribution was observed, with a mean value of 5 ± 2 nm and mode of 2.8 nm. Electron diffraction patterns indexed well to Si, albeit with broad diffraction lines that can be attributed to the small particle sizes.

**Synthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-trimethylsilyl)ethynyl)phenyl)aniline.**

4-iodo-N,N-bis(4-methoxyphenyl)aniline (1.0g, 2.32 mmol), $Pd(PPh_3)Cl_2$ (8.0 mg, 0.5% M), CuI (2.2 mg, 0.5% M), 10 ml triethylamine and trimethylsilylacetylene (0.4 ml, 2.78 mmol) were dispersed in 10 ml toluene (anhydrous). Three cycles of vacuum/$N_2$ refill were applied to the system to remove water and $O_2$. The mixture was heated to 80°C for 12 hours under $N_2$ protection. After reaction completion, the solvent was removed by reduced pressure distillation and the residue was purified by silica gel chromatography using $CH_2$:$Cl_2$ and hexane (1:2) as eluent to receive a light yellow oil (0.86 g, 92%). $^1$H NMR ($CDCl_3$, $\delta$): 7.23 (d, 2H, J = 8 Hz), 7.03 (d, 4H, J = 8Hz), 6.82 (d, 4H, J = 8Hz), 6.78 (d, 2H, J = 8Hz), 3.79 (s, 6H), 0.22 (s, 9H).

**Synthesis of 4-ethynyl-N,N-bis(4-methoxyphenyl)aniline (MeOTPA).** 4-methoxy-N-(4-methoxyphenyl)-N-(4-(trimethylsilyl)ethynyl)phenyl)aniline (0.7 g) was dissolved in a mixed solvent of 20 ml THF and 20 ml methanol. $K_2CO_3$ (3.9 g) was added and the mixture was stirred for 12 hours in ambient condition. After reaction completion, the solvents were removed by rotary evaporator and the residue was purified by silica gel chromatography three times using $CH_2$:$Cl_2$ and hexane (1:2) as eluent to receive a colorless oil (0.52 g, 91%). $^1$H NMR ($CDCl_3$, $\delta$): 7.25 (d, 2H, J = 8 Hz), 7.05 (d, 4H, J = 8Hz), 6.83 (d, 4H, J = 8Hz), 6.79 (d, 2H, J = 8Hz), 3.79 (s, 6H), 2.98 (s, 1H). $^{13}$C NMR ($CDCl_3$,$\delta$): 156.48, 149.30, 140.18, 133.06, 127.29, 119.01, 114.95, 112.68, 84.45, 75.85, 55.58.

**Synthesis of MeOTPA Model Compound.** Triethylvinylsilane (214 mg, 1.50 mmol), 4-iodo-4,4-dimethoxytriphenylamine (500 mg, 1.15 mmol), $Pd[P(t\text{-butyl})_3]_2$ (30 mg, 0.06 mmol), $Cy_2NCH_3$ (0.3 mL, 1.28 mmol), and anhydrous toluene (15 mL) were charged to a 50 mL Schlenk flask in a nitrogen-filled glovebox. The flask was removed from the glovebox, purged and refilled three times with argon, and heated (under argon) at 80 °C for 18 hours. Purified by 4:1 silica gel:activated carbon column in a gradient of hexanes to ethyl acetate. Solvents were removed by rotary evaporator to yield the MeOTPA model compound as a gray, highly viscous oil (441 mg, 85%). $^1$H NMR ($C_6D_6$, δ): δ 0.68 (m, 6 H, SiC*H*$_2$CH$_3$), 1.05 (t, 9 H, SiCH$_2$C*H*$_3$), 3.30 (s, 6 H, OC*H*$_3$), 6.34 (d, 1 H, ArCHC*H*), 6.72 (d, 4 H, Ar*H*), 7.00 (d, 1 H, ArC*H*CH), 7.09 (d, 6 H, Ar*H*), 7.30 (d, 2 H, Ar*H*). $^{13}$C NMR ($C_6D_6$, δ): 4.36, 8.11, 55.35, 115.48, 121.51, 122.51, 127.25, 132.07, 141.73, 145.79, 149.60, 156.89.

**Preparation of hydrogenated SiQDs.** The hydrogenated SiQDs were synthesized following literature procedure reported by Veinot.[1,2] The hydrogen silsesquioxane based precursor (HSQ) was synthesized by placing trichlorosilane (13.4g, 99 mmol) in a 100ml three-neck flask equipped with a stir bar, Schlenk line adapter, and capped with two septa. The flask was placed on a Schlenk line with nitrogen gas flowing through the flask. The trichlorosilane was cooled in an acetone/dry ice bath (−78 $^o$C) for 5 min while stirring before 50 ml of water (Millipore, 18.2W) was slowly injected while stirring. The mixture was allowed to warm to room temperature with stirring for 40 min. This produced a white precipitate and hydrochloric acid. The resulting insoluble hydrogen silsesquioxane based precursor material (HSQ), was washed with water to remove the hydrochloric acid then placed under vacuum to dry for 24 hours. One

gram of HSQ was placed into an alumina boat that was then inserted in a high temperature tube furnace. The quartz tube was purged with $H_2$/Ar gas (5%/95%) for 20 min. The temperature was raised by 18°C /min to 1100°C and held there for 1 hour with gas flowing over the boat. The Si/SiOx resultant composite was allowed to cool to room temperature.

**Etching of SiQDs**. To the Si/SiOx composite (250 mg) were added with 9 ml ethanol and 20 ml HF (40%) in a HDPE container. After 4 hours etching, the hydrogenated SiQDs were extracted by 20 ml trimethylbenzene. The SiQDs dispersed in trimethylbenzene were separated by centrifuge (13000 rpm, 5 min) to produce the SiQDs as a plug in the bottom of the tube that were washed by ethanol three times.

**Preparation of 1-decyl-SiQDs.** Trimethylbenzene (20ml) was added to freshly etched/washed SiQDs and the turbid mixture was transferred to a schlenk flask under Ar protection. 1-decene (0.5 ml) was injected into the flask and the mixture was evacuated and refilled with Ar three times. Under the protection of Ar flow, the mixture was heated to 160°C for 12 hours, during which the reaction became a solution. Upon reaction completion, the flask was cooled to room temperature followed by the addition of 50 ml methanol. The 1-decene passivated SiQDs were separated by centrifuge (13000 rpm, 5 mins) and washed by methanol three times to recover a yellow powder.

**Preparation of MeOTPA-SiQDs.** The preparation of MeOTPA functionalized SiQDs followed the same procedure used to prepare 1-decene passivated SiQDs. To make both 1-decene passivated and MeOTPA functionalized SiQDs comparable with each other, the hydrogenated SiQDs passivated by 1-decene and functionalized by MeOTPA were from the same batch of HF etching. A large excess of 300 mg MeOTPA was used for the reactions. After reaction/purification, a yellow powder was obtained.

## II. XPS analysis and results

XPS analysis of SiQDs was performed on a Kratos Nova X-ray photoelectron spectrometer with a monochromatic Al Kά source operated at 300 W. Samples were pressed onto non-conductive tape adhesive, and during spectra acquisition, were subject to charge compensation using low energy electrons. A minimum of three areas per sample were analyzed. Survey and high-

resolution spectra of C1s, O1s, N1s and Si 2p were acquired at pass energy of 160 eV and 20 eV, respectively. Data analysis included linear background subtraction, smoothing, charge referencing and curve-fitting, performed using CasaXPS software. Each Si peak contains $2p_{3/2}$ and $2p_{1/2}$ components constrained to have ratio of 0.67 and separation by 0.6 eV.

**Table S1.** XPS quantification results reporting elemental composition in atomic percent.

| **Sample** | **C 1s** | **O 1s** | **Si 2p** | **N 1s** | **C/Si** |
|---|---|---|---|---|---|
| MeOTPA-SiQDs | 72.1±0.5 | 11.4±0.3 | 13.6±0.3 | 2.9±0.1 | 5.3 |
| Decyl-SiQDs | 74.9±0.3 | 6.2±0.1 | 18.9±0.2 | 0.0 | 4.0 |

**Table S2.** XPS quantification results for SiQDs after TGA analysis in nitrogen to 1000°C. Elemental composition is reported in atomic percent.

| **Sample** | **C 1s** | **O 1s** | **Si 2p** | **N 1s** | **C/Si** |
|---|---|---|---|---|---|
| MeOTPA-SiQDs | 32.9 | 41.9 | 24.3 | 0.9 | 1.4 |
| Decyl-SiQDs | 16.5 | 47.6 | 35.9 | 0.0 | 0.5 |

## III. FT-IR and Photoexcitation (PLE) Spectra

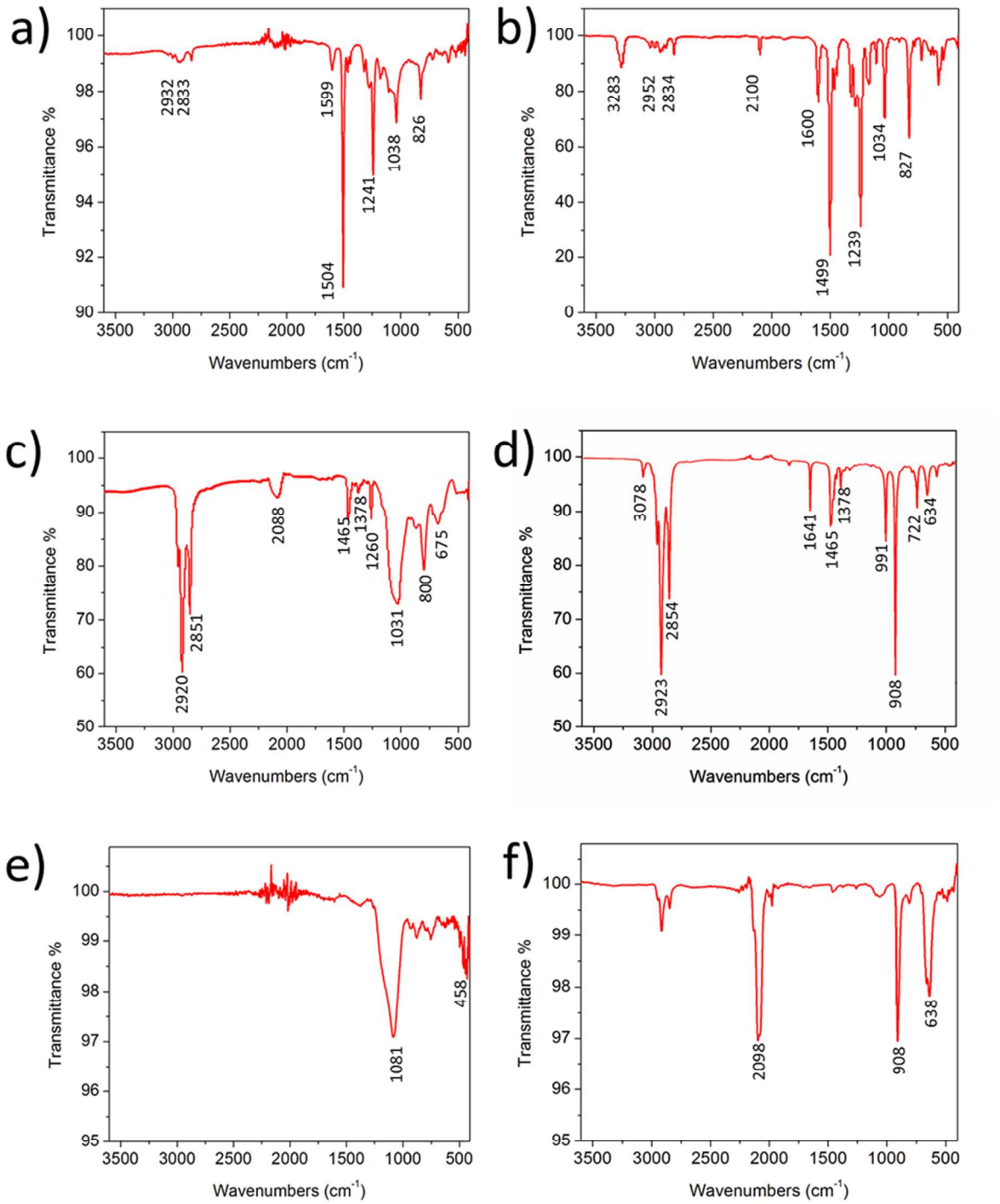



**Figure S1** FT-IR of a) MeOTPA-SiQDs; b) MeOTPA starting material; c) decyl-SiQDs; d) 1-decene starting material; (e) oxidized SiQDs; f) hydride terminated SiQD (starting material).

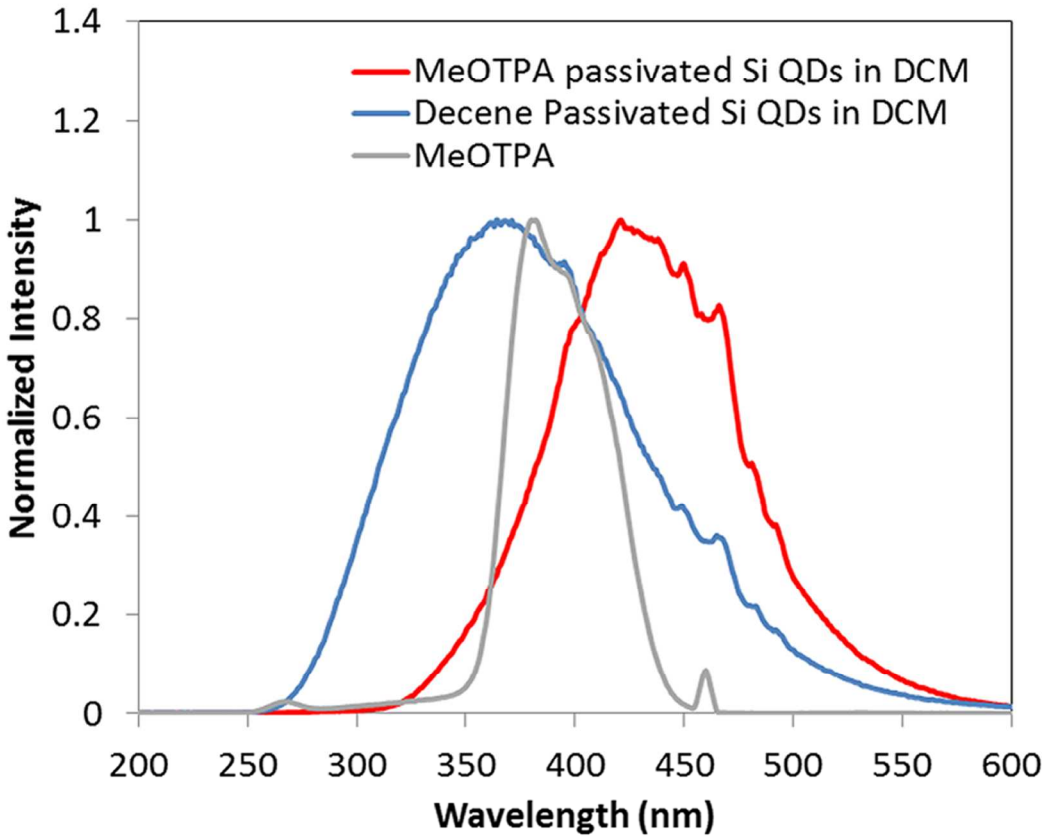



**Figure S2.** Photoexcitation (PLE) spectra of MeOTPA ligand (measured at 460 nm), decyl SiQDs (measured at 679 nm) and MeOTPA-SiQDs (measured at 749 nm). The PLE peak of MeOTPA-SiQDs (422 nm) shows a 55 nm red-shift compared with the PLE peak of decyl SiQDs (367 nm).

## IV. Comparison of Absorption Spectra for Hydrogen and Decyl Termination

The absorption spectrum of H-terminated $Si_{465}$ was computationally evaluated and compared with the absorption spectrum of the same dot but with 12 symmetrically positioned H atoms replaced by a decyl ligand. The result, shown in Figure S3, indicates that the decyl termination does not alter the absorption spectrum of the dot.

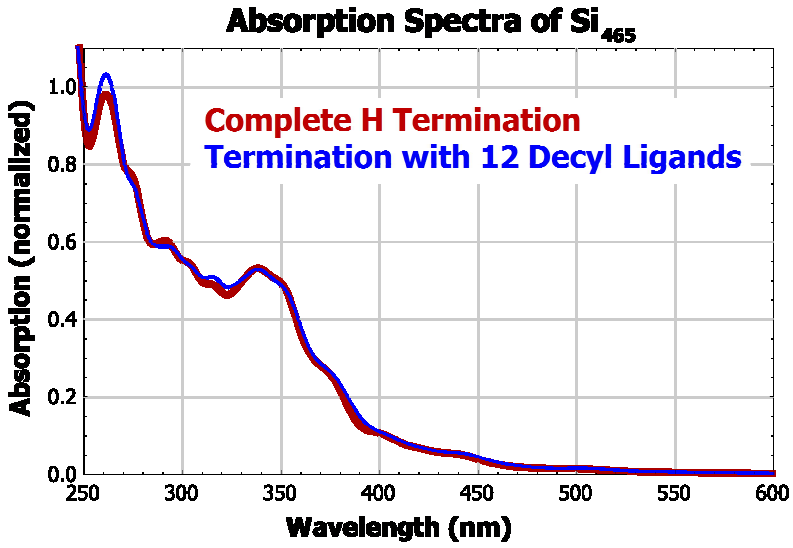
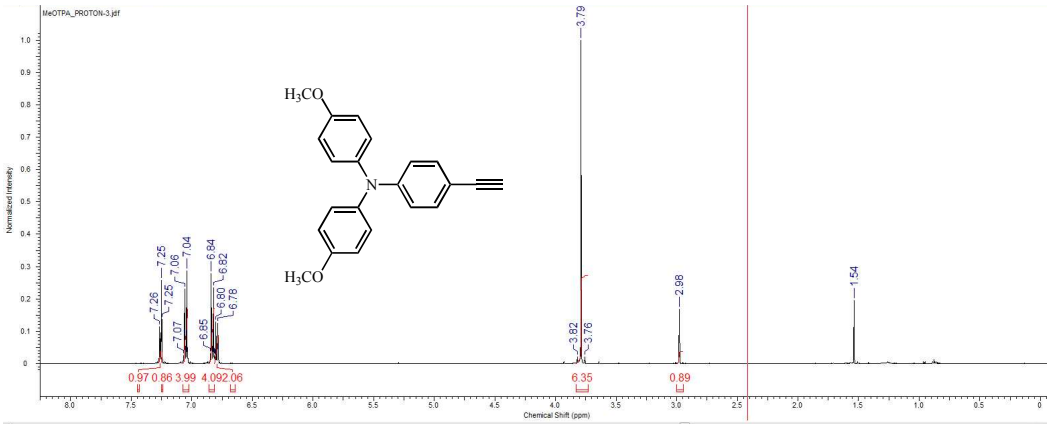


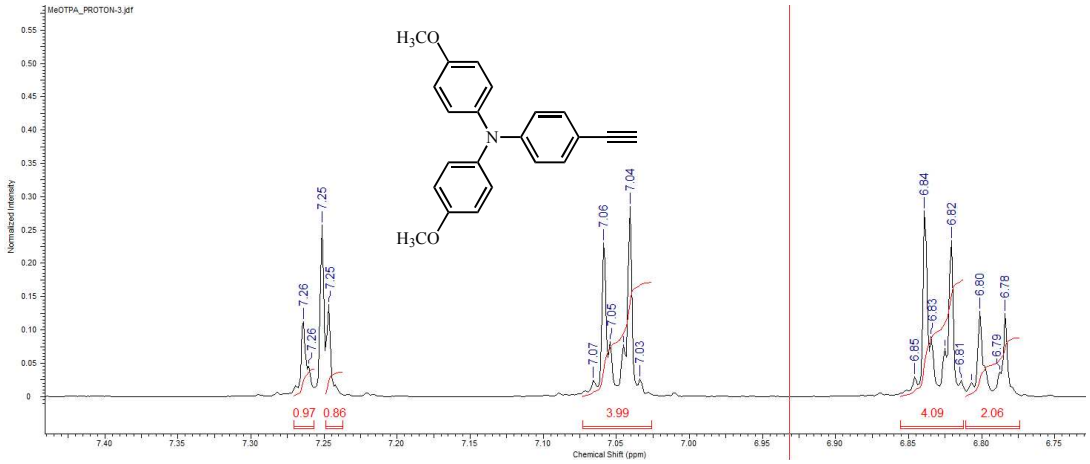

**Figure S3.** TD-DFT absorption spectrum of $Si_{465}$ dot with complete H-termination (red) and T-termination but with 12 H atoms replaced by decyl ligands (blue).

## V. $^{1}$H and $^{13}$C NMR analysis.

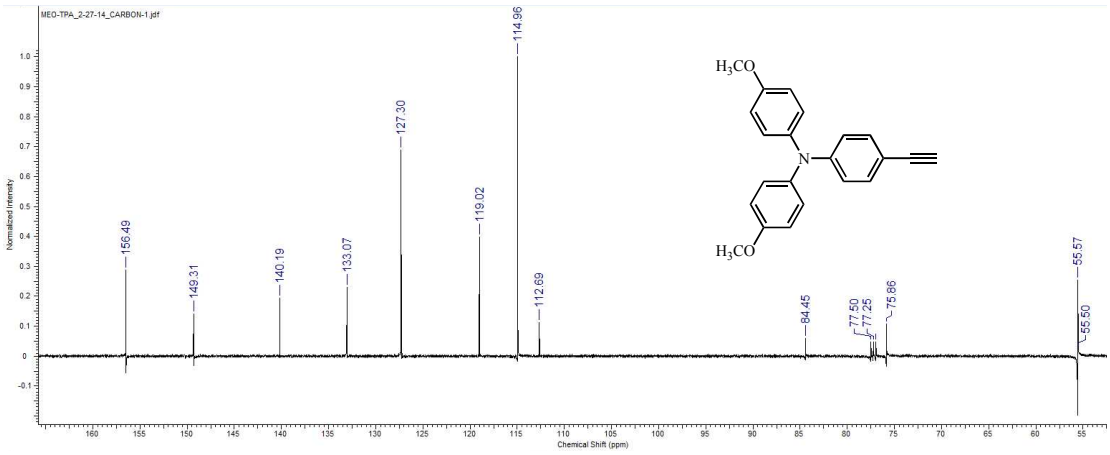
a.



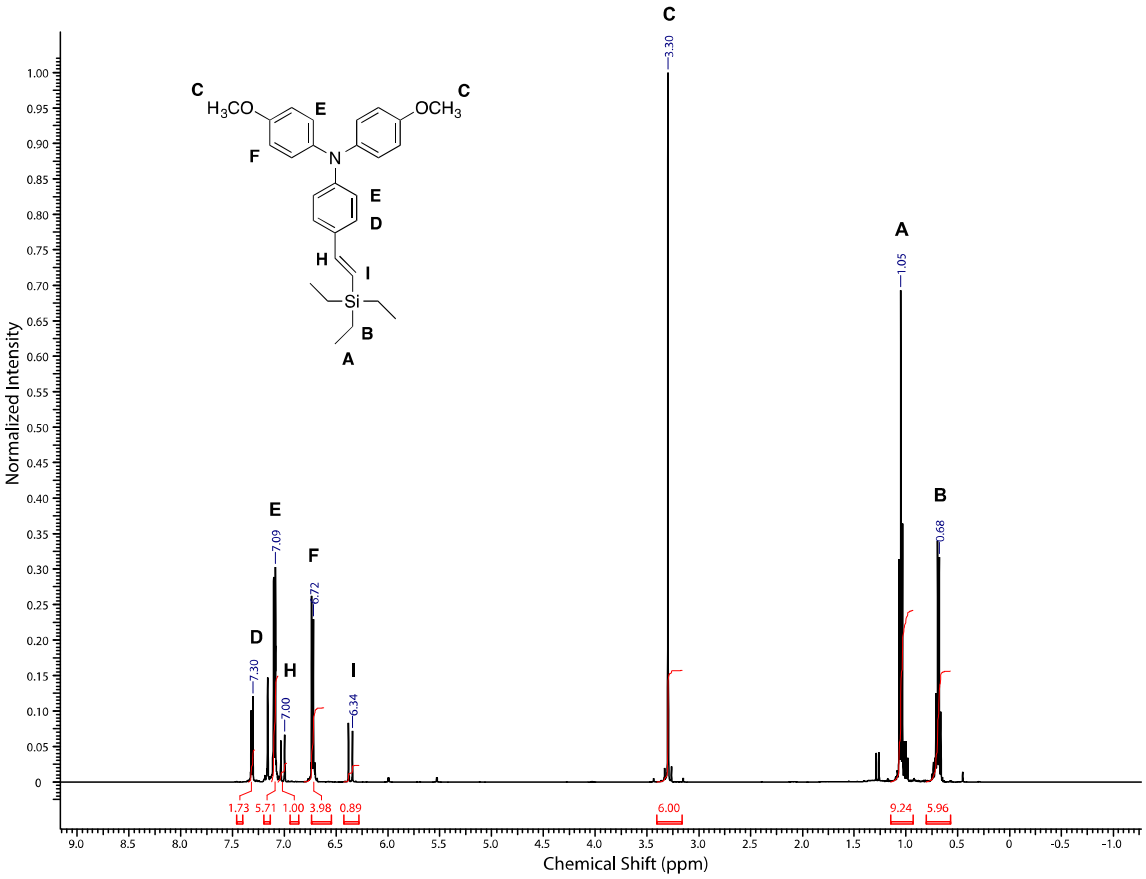

b.




c.



d.


C
H3CO
E
OCH3
C
F
N
E
D
H
I
Si
B
A
Normalized Intensity
Chemical Shift (ppm)
7.30
7.09
7.00
6.72
6.34
3.30
1.05
0.68
1.73
5.71
1.00
3.98
0.89
6.00
9.24
5.96

e.

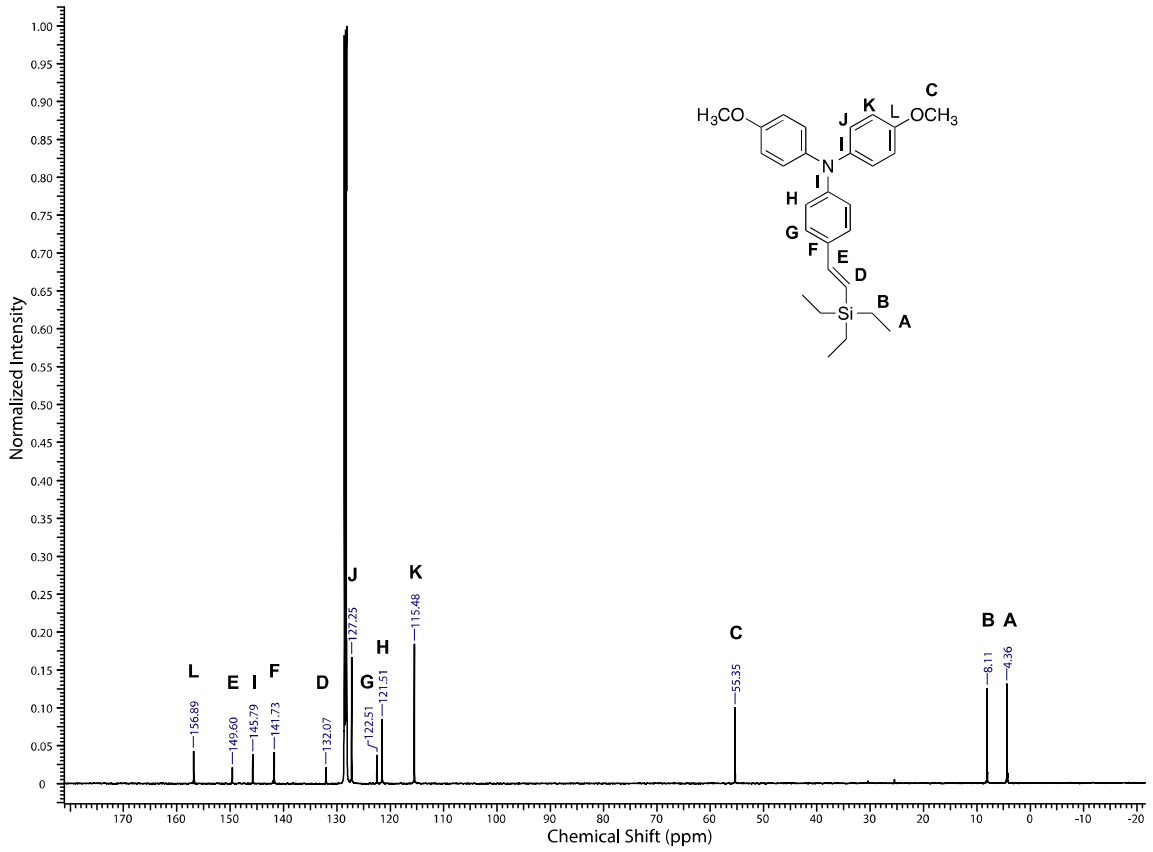



**Figure S4.** a) $^{1}$H-NMR of MeOTPA ligand, b) $^{1}$H-NMR of MeOTPA ligand (aromatic region), c) $^{13}$C-NMR of MeOTPA ligand, d) $^{1}$H-NMR of MeOTPA model compound, e) $^{13}$C-NMR of MeOTPA model compound.

## VI. Cyclic voltammetry (CV) analysis

Cyclic voltammetry (CV) analysis of SiQDs was performed with a VersaSTAT 3 CV instrument, at a scan rate of 0.05 V/s. Samples were prepared in an electrolyte of 0.1M tetrabutylammonium hexafluorophosphate (TBAPF6) in dichloromethane (DCM), at a concentration of approximately 1 mg/ml. The redox potentials of all samples were referenced to a ferrocene/ferrocenium

standard. For each sample the oxidation onset was found and added to the known vacuum energy of ferrocene (4.8 V), to obtain their respective HOMO levels. A summary of this information is presented in Figure S5.

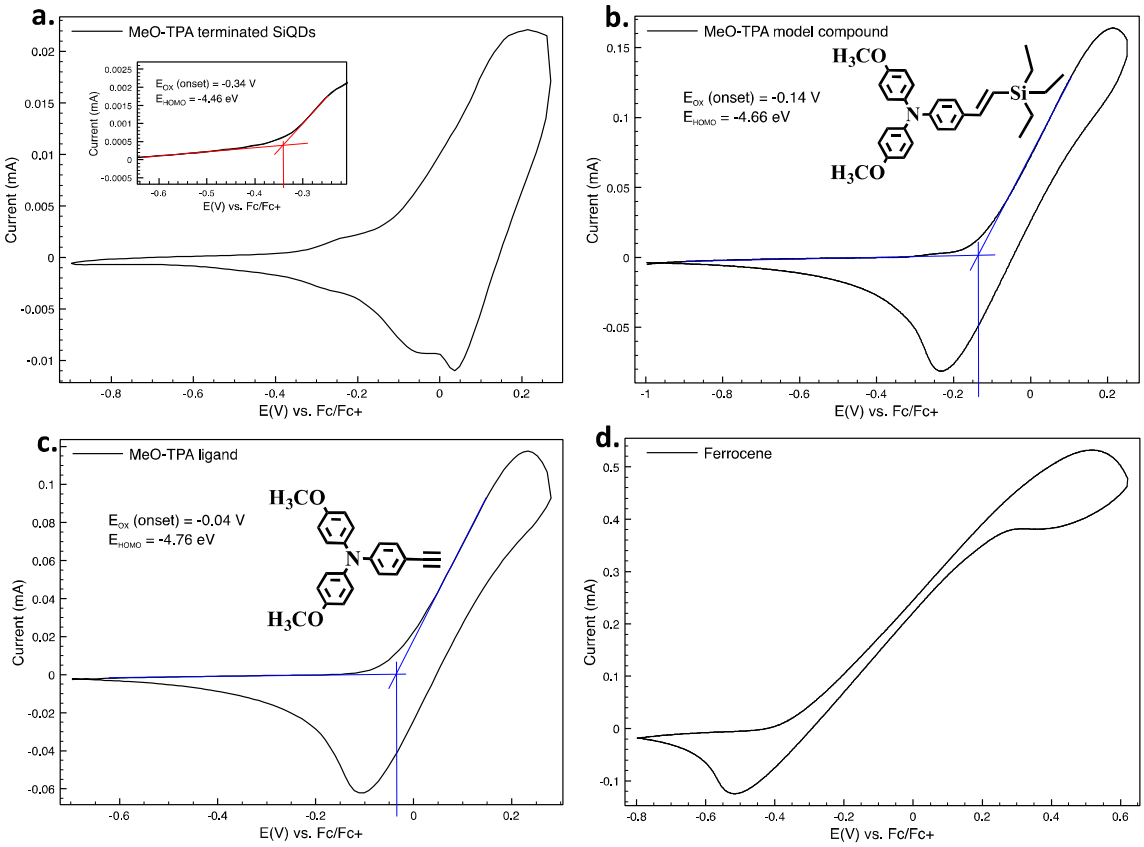



**Figure S5.** Cyclic voltammetry (CV) measurements on a. MeOTPA-SiQDs; b. MeOTPA model compound; c. MeOTPA ligand; and d. ferrocene (control). No CV response observed for decyl-SiQDs.

## VII. TGA Data

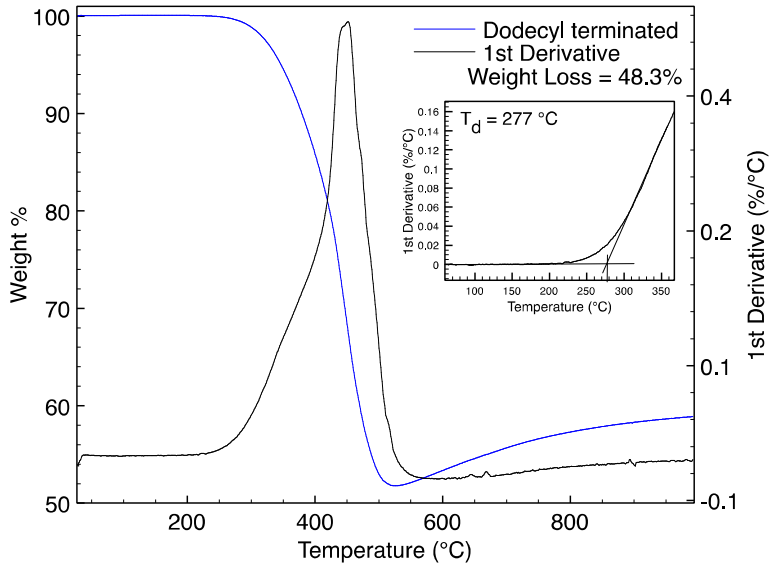



**Figure S6.** TGA data for dodecyl-SiQDs

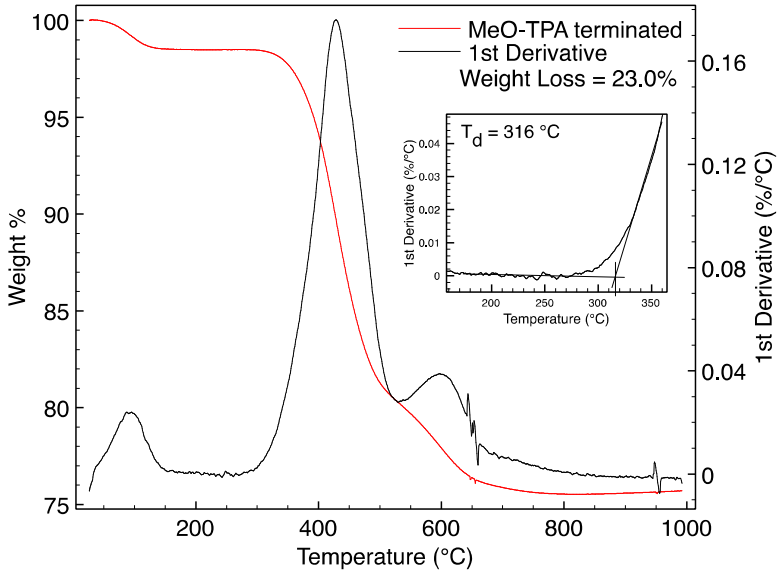



**Figure S7.** TGA data for MeOTPA-SiQDs

## VIII. TEM Images

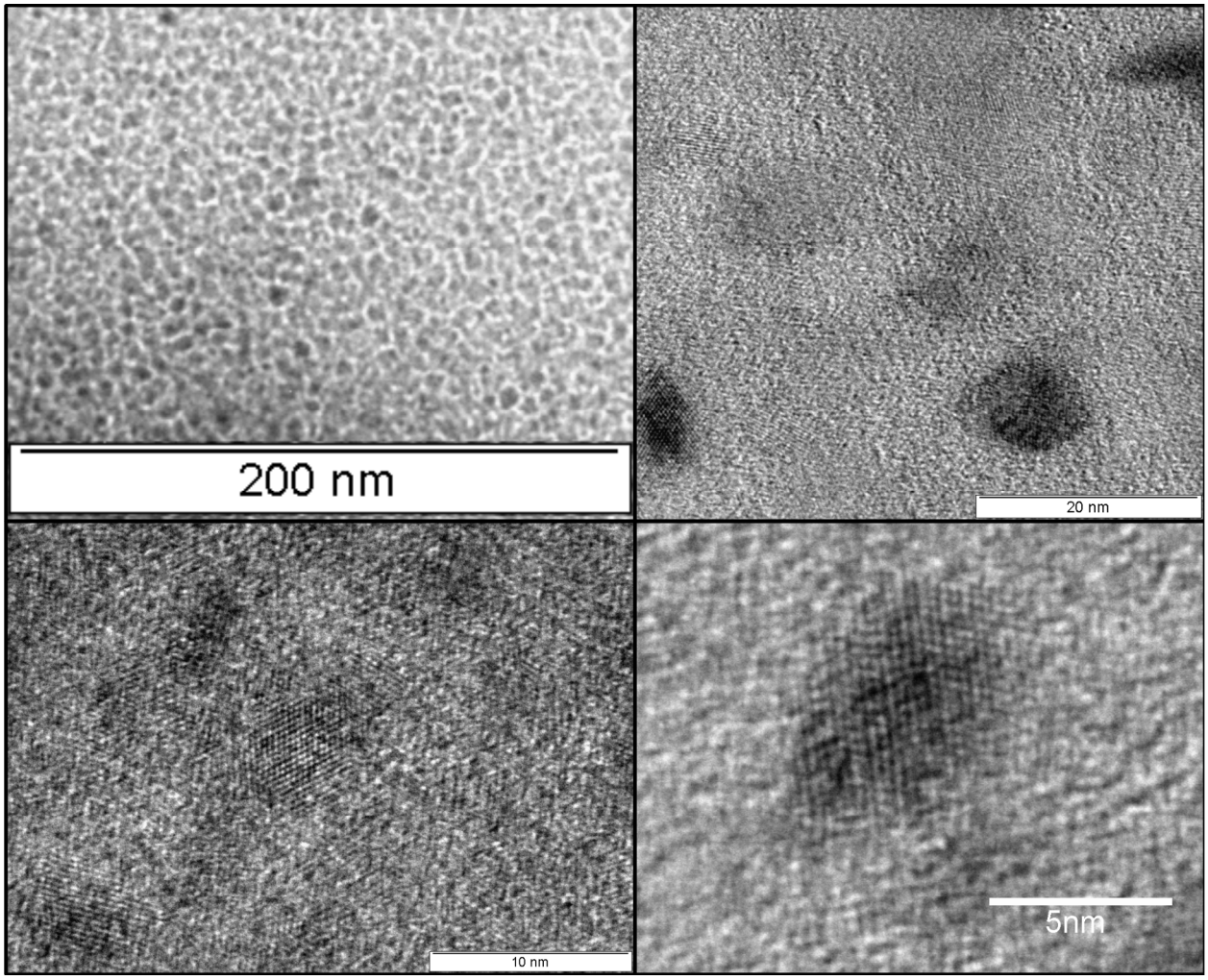



**Figure S8.** Representative TEM images of SiQDs at different length scales.

## References:

(1) Henderson, E. J.; Kelly, J. A.; Veinot, J. G. C. *Chem*. *Mater*. **2009**, 21, (22), 5426-5434.

(2) Mastronardi, M. L.; Maier-Flaig, F.; Faulkner, D.; Henderson, E. J.; Kübel, C.; Lemmer, U.; Ozin, G. A. *Nano Lett.* **2012,** 12, (1), 337-342.

(3) Hessel, C. M.; Henderson, E. J.; Veinot, J. G. C. *Chem*. *Mater*. **2006**, 18, (26), 6139-6146.