## Supporting Information

# Bromosuccinimide-based Bromination and Subsequent Functionalization of Hydrogen-terminated Silicon Quantum Dots

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## **1. Experimental Details**

#### **1.1 Materials**

Hydrofluoric acid (HF, 48 wt. % in  $H_2O$ ) and anhydrous organic chemicals including chloroform (>99%), 1-octanol (C<sub>8</sub>OH, >99%), ethanol (99.5%), tert-butyldimethylsilanol (R<sub>3</sub>SiOH, 95%), trichlorosilane (99.8%), methanol (99%), N-bromosuccinimide (NBS, 99%), and 1-pyrenebutanol (99%) were purchased from Sigma-Aldrich. Methanol (ACS, Pharmco-AAPER), toluene (99.5%, BDH), and chloroform-d (CDCl<sub>3</sub>, 99.8%, Cambridge) were purchased from Fisher. All other chemicals were used as received.

#### 1.2 Synthesis of Hydrogen-terminated Si Quantum Dots (H-SiQDs)

H-SiQDs were synthesized following the sol-gel method reported in the literature. <sup>1</sup> Typically, 50 mL of water was slowly added to cooled trichlorosilane (10 mL) that was stirred and kept in a dry-ice bath (-77°C). The hydrolyzed product was washed with water to remove the HCl byproduct. The washed product was dried under vacuum at room temperature for 24 hours. Next, the hydrogen silsesquioxane (HSSQ, 1 g) was heated at a ramp rate of 18 °C/min to 1100 °C and kept for one hour under a H<sub>2</sub>/Ar (5%/95%) atmosphere, yielding SiQDs embedded in a matrix of SiO<sub>2</sub>, at a yield of 10% versus HSiQ. The SiQDs were released from the oxide with HF/ethanol (1:4 vol) etching, producing hydrogenterminated SiQDs (H-SiQDs). The H-SiQDs were extracted into toluene and the residual water was removed via three cycles of centrifugation, decanting, and suspension in ethanol. Finally, ethanol was removed under vacuum and the purified H-SiQDs were stored in a nitrogen-filled glove box for further use.

#### 1.3 Chlorination of H-SiQDs by Phosphorus Pentachloride (PCl<sub>5</sub>)

The H-SiQDs were chlorinated according to a previously reported procedure with slight modifications.<sup>2</sup> In a N<sub>2</sub>-filled glove box, the H-SiQDs prepared according to the procedure described above were dispersed into toluene (30 ml) and placed into a 50-mL flask. After phosphorous pentachloride (0.525 g, 2.52 mmol) and a few grains of benzoyl peroxide were added into the flask, the mixture was stirred for 19 hours at room temperature. 1-octanol (3.5 ml, 22.2 mmol) was added and the mixture was stirred for 5 hours. The passivated particles were then centrifuged to remove the large aggregates. The soluble particles were precipitated by methanol and the suspension was centrifuged for 20 min. The methanol was decanted and the isolated particles were dispersed in chloroform. This

precipitation and centrifugation process was repeated two more times and the functionalized SiQDs were dissolved in chloroform.

#### 1.4 Bromination and Functionalization of Triethylsilane (Et<sub>3</sub>Si-H) with 1-octanol (C<sub>8</sub>OH)

In a  $N_2$ -filled glove box, 0.50 ml of  $Et_3Si$ -H (3.1 mmol) was added to 40 mL of chloroform in a 100 mL flask. NBS (1.21 g, 6.80 mmol) was added to this mixture and the flask was stirred in the dark for 24 hours. Subsequently, 1-octanol (3.5 ml, 22.2 mmol) was added; and the system was stirred overnight. The flask was moved out of the glovebox and the solvent was removed under vacuum. The resultant product was dispersed in hexane and the succinimide white powder (that is the byproduct succinimide) was removed via centrifugation. Hexane was removed under vacuum. The final product was dispersed in chloroform.

#### 1.5 Characterization

Fourier transform infrared (FTIR) spectroscopy (Fisher, Thermo Nicolet 4700) in the attenuated total reflection mode was employed to characterize the obtained aggregates and solution residues. Each of the presented spectra is an average of 32 scans acquired at a resolution of 2 cm<sup>-1</sup> from the solution samples that were drop-cast and dried on the attenuated total reflection (ATR) crystal. Nuclear Magnetic Resonance spectroscopy (NMR, JEOL ECA-500) was employed to take the <sup>1</sup>H NMR spectra of samples suspended in CDCl<sub>3</sub> and loaded in quartz NMR tubes. UV-Vis absorption spectroscopy (UV-Vis, Shimadzu UV-1800 probe spectrophotometer) and Fluorescence spectroscopy (PL, Photon Technology International, QuantaMaster 40) were employed to take the absorption and photoluminescence (PL) spectra of samples that were diluted in chloroform in 3-mL cuvettes.

#### 2. Results and Discussion

#### 2.1 Chlorination of H-SiQDs by PCl<sub>5</sub>

**SI-Fig. 1** shows the FTIR spectra of the obtained aggregates (A) and chloroform solution (B) of the  $PCl_5$ -treated SiQDs. In **SI-Fig. 1A**, the stretching (2950 - 2895 cm<sup>-1</sup>) and bending (1450 - 1350 cm<sup>-1</sup>) modes of CH<sub>2</sub> and CH<sub>3</sub> indicate the presence of 1-octanol. The peaks at 2100 cm<sup>-1</sup> and 900 cm<sup>-1</sup>, the characteristic signals from the Si-H stretching and bending modes, respectively, indicate that  $PCl_5$  did not completely chlorinate the Si-H bonds on the SiQD surfaces, due to particle aggregation. The peak at 1050 cm<sup>-1</sup> may be assigned to either the stretching mode of Si-O-C in the attached 1-octanol or the stretching mode of Si-O-Si of surface oxides. In contrast, the FTIR spectrum of the soluble particles in **SI-Fig. 1B** does not show the unreacted Si-H signals. The sharp peak at 1030 cm<sup>-1</sup> is assigned to the Si-O-C bonds. This peak confirms the attachment of 1-octanol to the SiQDs. However, the peaks at 1300 cm<sup>-1</sup>, 900 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, ascribed to organophosphorus compounds,<sup>3</sup> are indicative of side reactions between PCl<sub>5</sub> and 1-octanol. While SiQDs can be successfully functionalized by 1-octanol through the PCl<sub>5</sub>-based pre-chlorination, extensive particle aggregation and side reactions limit the effectiveness and generality of this method.



SI-Fig. 1. FTIR spectra of the obtained aggregates (A) and solution (B) of the PCl<sub>5</sub>-treated SiQDs.

#### 2.2 Bromination and Functionalization of Triethylsilane (Et<sub>3</sub>Si-H) with 1-octanol (C<sub>8</sub>OH)

The final product is first characterized using FTIR (SI-Fig. 2). The characteristic Si-H peaks of  $Et_3Si$ -H at 2200 cm<sup>-1</sup> and 900 cm<sup>-1</sup> (visible in the black curve, SI-Fig. 2-i) disappear after bromination and passivation (red curve, SI-Fig. 2-ii). Correspondingly, the appearance of two peaks at 1080 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> support the expected formation of Si-O-C bonds.<sup>3</sup> The peak at 1700cm<sup>-1</sup> in the red spectrum can be attributed to the stretching mode of C=O from the unreacted NBS.

Further characterization is conducted using <sup>1</sup>H NMR (**SI-Fig. 3**). In the spectrum of Et<sub>3</sub>Si-H (a), the characteristic peaks at  $\delta = 0.58$  ppm (1), 0.97 ppm (2), and 3.6 ppm (3) correspond to the methyl, methylene, and Si-H, respectively. After the 1-octanol treatment (b), as expected, the signals from the Et<sub>3</sub>Si-moiety were observed at  $\delta = 0.49$  ppm (1') and 0.85 ppm (2') and the signals from the C<sub>8</sub>O-moiety are observed at  $\delta = 0.78$  ppm (10), 1.31 ppm (6-9), 1.6 ppm (4 and 5), and 2.49 ppm (3\*). The shifts of peaks 1', 2' and 3\* indicate the linkage between the Et<sub>3</sub>Si-and C<sub>8</sub>O-moieties. This linkage is further confirmed by the disappearance of the Si-H peak (3). The FTIR (**SI-Fig. 2**) and NMR (**SI-Fig. 3**) measurements confirm the expected final product of triethylsilyloxyoctane (TESO), indicating the successful bromination of Et<sub>3</sub>Si-H using NBS.



**SI-Fig. 2.** FTIR spectra of Et<sub>3</sub>Si-H (i) and the as-produced TESO (ii) to assess the bromination of Et<sub>3</sub>Si-H using NBS.



**SI-Fig. 3.** <sup>1</sup>H NMR spectra of  $Et_3Si$ -H (i) and the TESO (ii) to assess the bromination of  $Et_3Si$ -H using NBS, where symbol (•) indicates an unknown impurity in the sample.



SI-Fig. 4. XRD profile of the glass substrate used for measuring H-SiQDs.



**SI-Fig. 5.** A literature survey of the full width at half maximum (FWHM) for the PL spectra of colloidal SiQDs with their PL peak positions in the range of 650 - 690 nm,<sup>1,4-11</sup> together with the data from this work. The numbers in the symbols correspond to the reference numbers in the main text and match the reference numbers in the Supporting Information as follows:  $18 \rightarrow 4$ ,  $19 \rightarrow 5$ ,  $21 \rightarrow 1$ ,  $28 \rightarrow 6$ ,  $46 \rightarrow 7$ ,  $47 \rightarrow 8$ ,  $48 \rightarrow 10$ ,  $49 \rightarrow 10$ , and  $50 \rightarrow 11$ .



SI-Fig. 6. UV-vis absorption spectrum (blue) and PL spectrum (red) of 1-pyrenebutanol (PyOH).

### 3. References:

1 M. L. Mastronardi, F. Maier-Flaig, D. Faulkner, E. J. Henderson, C. Kubel, U. Lemmer and G. A. Ozin, Nano Letters, 2012, 12, 337-342.

- 2 M. Dasog and J. G. C. Veinot, Physica Status Solidi (a): Applications and Materials Science, 2012, 209, 1844-1846.
- 3 J. Coates, Interpretation of Infrared Spectra, A Practical Approach in Encyclopedia of Analytical Chemistry, ed. R. A. Meyers, John Wiley & Sons Ltd, Chichester, 2000.
- 4 A. Gupta, M. T. Swihart and H. Wiggers, Advanced Functional Materials, 2009, 19, 696-703.
- 5 X. Pi, T. Yu and D. Yang, Particle & Particle Systems Characterization, 2014, 31, 751-756.
- 6 J. Wang, Y. X. Liu, F. Peng, C. Y. Chen, Y. H. He, H. Ma, L. X. Cao and S. Q. Sun, Small, 2012, 8, 2430-2435.
- 7 M. L. Mastronardi, F. Hennrich, E. J. Henderson, F. Maier-Flaig, C. Blum, J. Reichenbach, U. Lemmer, C. Kuebel, D. Wang, M. M. Kappes and G. A. Ozin, *Journal of the American Chemical Society*, 2011, **133**, 11928-11931.
- 8 J. Fuzell, A. Thibert, T. M. Atkins, M. Dasog, E. Busby, J. G. C. Veinot, S. M. Kauzlarich and D. S. Larsen, *The Journal of Physical Chemistry Letters*, 2013, 4, 3806-3812.
- 9 F. J. Hua, M. T. Swihart and E. Ruckenstein, Langmuir, 2005, 21, 6054-6062.
- 10 X. G. Li, Y. Q. He and M. T. Swihart, Langmuir, 2004, 20, 4720-4727.
- 11 C. M. Hessel, E. J. Henderson, J. A. Kelly, R. G. Cavell, T.-K. Sham and J. G. C. Veinot, *Journal of Physical Chemistry C*, 2008, **112**, 14247-14254.