Silicon Nanocrystals Functionalized with Pyrene Units: Efficient Light-Harvesting Antennae with Bright Near-Infrared Emission

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Supporting Information

General Methods. 1H-NMR and 13C-NMR spectra were recorded on Varian INOVA 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm using tetramethylsilane as the internal reference standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). LC-electrospray ionization mass spectra were obtained with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was performed on 240-400 mesh silica gel. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware using standard inert techniques for introducing reagents and solvents. Melting points are uncorrected. TEM imaging was performed on a FEI TecnaiBiotwin TEM operated at 80 kV accelerating voltage. TEM samples were made by drop casting toluene dispersions onto carbon-coated 200 mesh copper TEM grids (Electron Microscopy Science).

1-(allyloxymethyl)pyrene synthesis. Sodium hydride (0.124 g, 5.16 mmol, 1.2 eq) was added to a mixture of 1-pyrenemethanol (1.00 g, 4.30 mmol, 1 eq), propargyl bromide (0.645 g, 5.33 mmol, 1.24 eq) in CH3CN (25 mL) at 70°C. The reaction mixture was stirred vigorously for 24 h at 70°C. After completion of the reaction, three drops of H2O were added to quench the reaction. The mixture was extracted into chloroform (3 x 5 mL). The chloroform layer was dried over MgSO4 and the solvent was removed under reduced pressure to give the crude product. The resulting residue was purified by silica column chromatography (Hexane/ EtOAc 8:2), to give the product as a yellow solid (750 mg, yield = 66%).

1H-NMR (400 MHz, CDCl3) δ: 8.38 (d, J = 9.2 Hz, 1H); 8.23-8.20 (m, 2H); 8.17-8.13 (m, 2H); 8.08-8.03 (m, 4H); 6.21-6.14 (m, 1H); 5.51 (dd, J1 = 1.6 Hz, J2 = 1.6 Hz, 1H); 5.39 (dd, J1 = 1.6 Hz, J2 = 1.6 Hz, 1H); 5.24 (s, 2H); 4.25-4.23 (m, 2H).

13C-NMR (100 MHz, CDCl3) δ: 134.9, 131.4; 131.3; 131.2; 130.8; 129.2; 127.6; 127.4; 127.3; 126.8; 125.8; 125.2; 125.1; 124.9; 124.7; 124.5; 123.3; 117.3; 71.2, 70.6. ESI-MS: 232 [M- C3H5]+

SiNC and SiNC-Py Synthesis. Si nanocrystals were synthesized following Hessel, et al.1 In a typical synthesis, 30 mL of Fox-16 (Dow Corning; 16wt% hydrogen silsesquioxane (HSQ) in isobutylmethyl ketone) is dried under vacuum on a schlenk line for 6 hours to form a white residue of HSQ, which is then transferred to a tube furnace. After purging with forming gas (93% N2, 7% H2), the tube furnace is heated to 1100°C (2.6 nm diameter) or 1200°C (5.0 nm diameter) at a heating rate of 18°C/min and then held at that temperature for an hour. The reaction product is etched with 48% HF and 37.5% HCl (10:1 v/v) in the dark for 4-6 hours and then centrifuged at
8000 rpm for 5 min. The nanocrystals are then rinsed once with deionized (DI) water, twice with ethanol, and once with chloroform. The nanocrystals are dispersed in either 5 mL of 1-dodecene, or 5 mL of 1-dodecene with 0.1 mL of 1-(allyloxymethyl)pyrene (1:36 pyrene:dodecene molar ratio) or 0.3 mL 1-(allyloxymethyl)pyrene (1:12 pyrene:dodecene molar ratio). The initially turbid dispersions are put through three freeze-pump-thaw cycles, and then heated to 170°C under N₂ flow for 12 hours. Over time, the dispersions become optically clear, indicating that passivation of Si nanocystals has occurred. The nanocrystals are then purified by transfer to a glass centrifuge tube and centrifugation at 8000 rpm for 5 min. Poorly capped nanocrystals precipitate from the mixture and are discarded. The supernatant is transferred to another glass centrifuge tube and washed with four consecutive centrifugation/precipitation cycles using toluene/ethanol solvent/antisolvent pair. The final SiNC and SiNC-Py samples were dispersed in toluene at a concentration of 5 mg/mL until further characterization.

1H and 13C NMR spectra. Figures S1-S4 show 1H and 13C NMR spectra of Py, SiNC, and SiNC-Py. 1H NMR spectra of SiNC and SiNC-Py (Figure S3) with an average diameter of 2.6 nm (Py:dodecene ratio of 1:36 used in the passivation) dispersed in CDCl₃ at room temperature provide evidence of a covalently linked surface layer. The 1H NMR spectra of SiNC show a uniform chemical environment for the alkyl chains with a single methyl resonance and several distinct methylene resonances. The 1H NMR spectrum of SiNC-Py shows additional signals compared to SiNC attributable to pyrene moieties. The molar ratio of pyrene appended groups and dodecene alkyl chains on the Si nanocrystals determined by integration of the relevant resonances in the 1H NMR spectra was 1:20, which is close to the Py:dodecene molar ratio (1:36) used in the passivation step.

Figure S1. 1HNMR (CDCl₃): 1-(allyloxymethyl)pyrene
Figure S2. $^{13}$C NMR (CDCl$_3$): 1-(allyloxymethyl)pyrene

Figure S3. $^1$H NMR spectra (400 MHz, CDCl$_3$, RT) of a) 2.6 nm SiNC and b) 2.6 nm SiNC-Py. Asterisk indicate solvent signal.
Figure S4. $^{13}$C NMR spectra (101 MHz, CDCl$_3$, RT) of 2.6 nm SiNC. Asterisk indicate solvent signal.

Transmission Electron Microscopy (TEM). Figures S5-S8 show additional TEM images of the 2.6 nm and 5.0 nm diameter SiNC and SiNC-Py samples used in the studies. Py functionalization does not affect the size of the Si nanocrystals.

Figure S5. TEM image of 2.6 nm diameter SiNC-Py.
Figure S6. TEM image of 2.6 nm diameter SiNC.

Figure S7. TEM image of 5.0 nm diameter SiNC-Py.
Figure S8. TEM image of 5.0 nm diameter SiNC.

**Photophysical measurements.** Photophysical measurements were carried out in air-equilibrated or deaerated toluene solution at 298 K. Solutions were deaerated by purging with Ar for 10 minutes. UV-visible absorbance spectra were recorded with a Perkin Elmer λ40 spectrophotometer, using quartz cells with 1.0 cm path length. Photoluminescence (PL) emission spectra were obtained with a Perkin Elmer LS-50 spectrofluorometer, equipped with a Hamamatsu R928 phototube, or an Edinburgh FLS920 spectrofluorometer equipped with a Ge-detector for emission in the NIR spectral region. Correction of the emission spectra for detector sensitivity in the 650-1200 nm spectral region was performed. PL quantum yields were measured following the method of Demas and Crosby (standard used: naphthalene in deaerated cyclohexane solution, quinine sulfate in H₂SO₄ 0.5 M, 1,1',3,3',3''-hexamethylindotricarbocyanine iodide (HITCI) in ethanol). PL lifetime measurements in the range 0.5 ns to 1 μs were performed by an Edinburgh FLS920 spectrofluorometer equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.2 ns time resolution) with a 340 nm pulsed diode and a LDH-P-C-405 pulsed diode laser. PL lifetime measurements in the range 10 μs to 1 s were performed on a Perkin Elmer LS-50 spectrofluorometer equipped with a pulsed Xe lamp. The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime, 10% on the fluorescence quantum yield.

**Additional photophysical characterization.** Figure S9 shows absorbance and PL emission spectra (b, λ_ex=378 nm) for 2.6 nm diameter SiNC and SiNC-Py made with pyrene:dodecene molar ratios of 1:12 (red line) and 1:36 (green line) dispersed in air-equilibrated toluene. The solutions are optically matched at the excitation wavelength. For most SiNC samples, the peak emission wavelength shifted to slightly longer wavelength after derivatization with pyrene. For example, Figure S9b shows the Si nanocrystal emission band shifted from 635 to 680 nm upon pyrene functionalization with a decrease of the emission quantum yield by about 30% (τ = 95 μs). The red-shift and decrease in the emission quantum yield is slightly higher with increasing Py:dodecene ratio. The reason for this peak shift and decrease in PL quantum yield is under investigation. Figure S10 shows the photoluminescence intensity decay for PL emission at 635 nm and 970 nm for SiNC with diameters of 2.6 and 5.0 nm, respectively, dispersed in air-equilibrated toluene. (λ_ex=400 nm). Figure S11 shows the photoluminescence intensity decay at 400 nm (λ_ex=345 nm) of 2.6 nm diameter SiNC-Py made with pyrene:dodecene molar ratios of 1:12 (red trace) and Py (black trace) in air-equilibrated toluene. Figure S12 shows photoluminescence excitation (PLE) spectra of the
2.6 nm and 5.0 nm diameter SiNC-Py measured by monitoring the Si nanocrystal-related emission. The appearance of the pyrene-related absorption peaks confirms that pyrene-absorption followed by energy transfer to the nanocrystals is occurring.

**Figure S9.** Absorbance (a) and photoluminescence (PL) spectra (b, \( \lambda_{ex}=378 \) nm) of 2.6 nm diameter SiNC (blue) and SiNC-Py made with pyrene:dodecene molar ratios of 1:12 (red line) and 1:36 (green line) dispersed in air-equilibrated toluene. The solutions are optically matched at the excitation wavelength.
Figure S10. Photoluminescence intensity decay at (a) 635 nm and (b) 970 nm for SiNC with diameters of 2.6 and 5.0 nm, respectively, dispersed in air-equilibrated toluene. ($\lambda_{ex}$=400 nm).
Figure S11. Photoluminescence intensity decay at 400 nm ($\lambda_{ex}=345$ nm) of 2.6 nm diameter SiNC-Py made with pyrene:dodecene molar ratios of 1:12 (red trace) and Py (black trace) in air-equilibrated toluene.

Figure S12. Photoluminescence excitation (PLE) spectra of 2.6 nm (a) and 5.0 nm (b) diameter SiNC-Py (red solid line) and SiNC (blue solid line) recorded with $\lambda_{em}= 660$ (a) and 780 nm (b). For comparison purposes, the absorption spectra of SiNC-Py are reported (red dashed line).

**Evaluation of the efficiency of energy transfer.** The efficiency of energy transfer can be estimated from the spectra reported in Figures 2b and 2d (see text) as detailed in the following:

$$\eta_{en.tr.} = \frac{(I_{obs}-I_0)}{(I_{100}-I_0)}$$

where

$I_{obs}$ is the area of the emission spectra observed for the SiNC-Py excited at 345 nm (dashed red line in Figures 2b and 2d), in which both pyrene and the Si core absorb light;

$I_0$ is the area of the emission spectrum observed for the mixture of SiNC and Py in a proper ratio to match the absorbance spectrum of the previous solution in the entire range (green line in Figures 2b and 2d);
$I_{100}$ is the area of the emission spectra observed for SiNC-Py excited at 378 nm (solid red line in Figures 2b and 2d), in which only the Si core is absorbing light, for a solution having the same absorbance at the excitation wavelength of the first case.

$I_0$ represents the emission intensity expected when energy transfer does not take place and the Si core emission is obtained only by the light at 345 nm directly absorbed by the Si core. $I_0$ has been corrected to take into account the different emission quantum yield of the Si core upon direct excitation of the silicon core for SiNC and SiNC-Py, i.e. 0.45 vs 0.40 for 5.0 nm diameter nanoparticles, respectively (Table 1).

$I_{100}$ represents the emission intensity expected when energy transfer takes place with 100% efficiency and all the absorbed light results in the Si core emission.

Figure S13 shows a schematic representation of the energy transfer process occurring in the 2.6 nm and 5.0 nm diameter SiNC-Py.

Figure S13. Energy level diagram showing the energy transfer processes and the corresponding efficiency occurring in SiNC-Py of diameter 2.6 (a) and 5.0 nm (b) upon photoexcitation of the pyrene units.

References