Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Improved Photon Absorption in Dye-Functionalized Silicon Nanocrystals Synthesized via Microwave-Assisted Hydrosilylation

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1. PLQY of (C6) - SiNc synthesized under various experimental conditions

(C6)-SiNc were synthesized in the microwave reactor using different temperatures and reaction time. The conditions giving the highest PLQY are temperature - 230 °C and reaction time – 120 min.

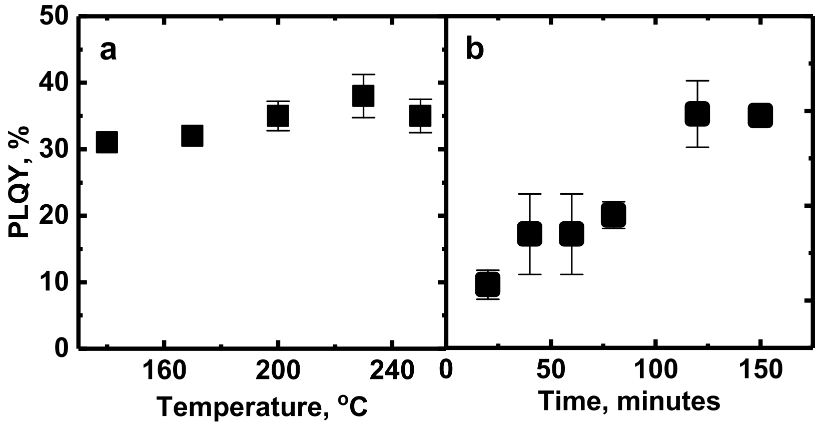

Figure S1. (a): PLQY of (C6) - SiNc as function of temperature of hydrosilylation reaction performed in the MW reactor; (b): PLQY of (C6) - SiNc as function of reaction time of hydrosilylation reaction performed in the microwave reactor. The error bars represent results repeated five times (for several chosen conditions)

2. Absorption spectra of dye (1) before and after 120 minutes thermal treatment at 230 °C.

The solutions of dyes (1), (2) and (3) in toluene were treated in the microwave reactor for 240 minutes at 230°C in order to evaluate chemical stability of the dyes. The absorption spectra measured before and after the treatment indicate that dyes are relatively stable. Only 6 % degradation was observed for the dye (1), whereas dye (2) remains unchanged during the process. The dye (3) demonstrates the fastest degradation rate. Degradation of 36 % of the dye (1) was observed after the 240 min treatment at 230°C.

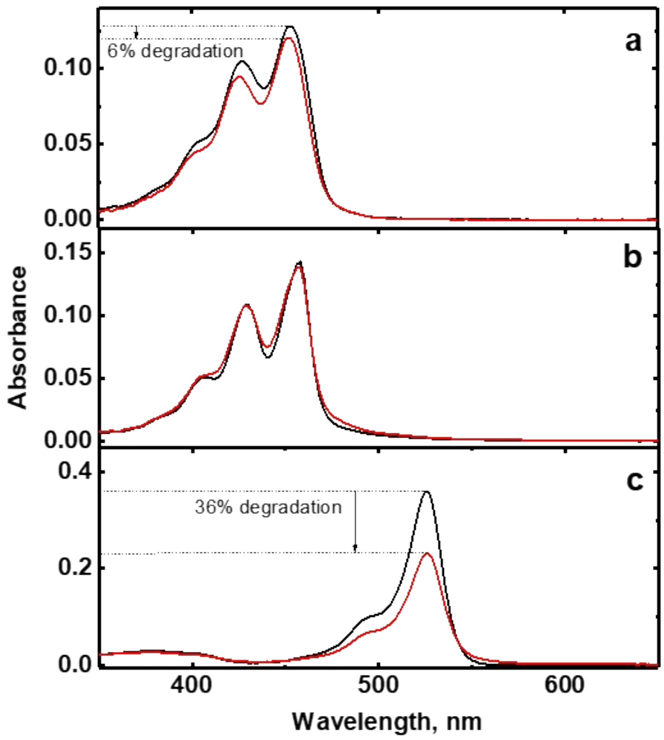

Figure S2. (a): absorption spectra of dye (1) in toluene before (black) and after (red) the treatment in the microwave reactor; (b): absorption spectra of dye (2) in toluene before (black) and after (red) the treatment in the microwave reactor. (c): absorption spectra of dye (3) in toluene before (black) and after (red) the treatment in the microwave reactor. The treatment conditions: 240 minutes at 230 °C.

3. Size distribution of SiNc measured via dynamic light scattering

The average size (hydrodynamic diameter) and size distribution of (C6) - SiNc, (C6) - (1) - SiNc, (C6) - (2) - SiNc, and (C6) - (3) - SiNc were characterized using dynamic light scattering method.

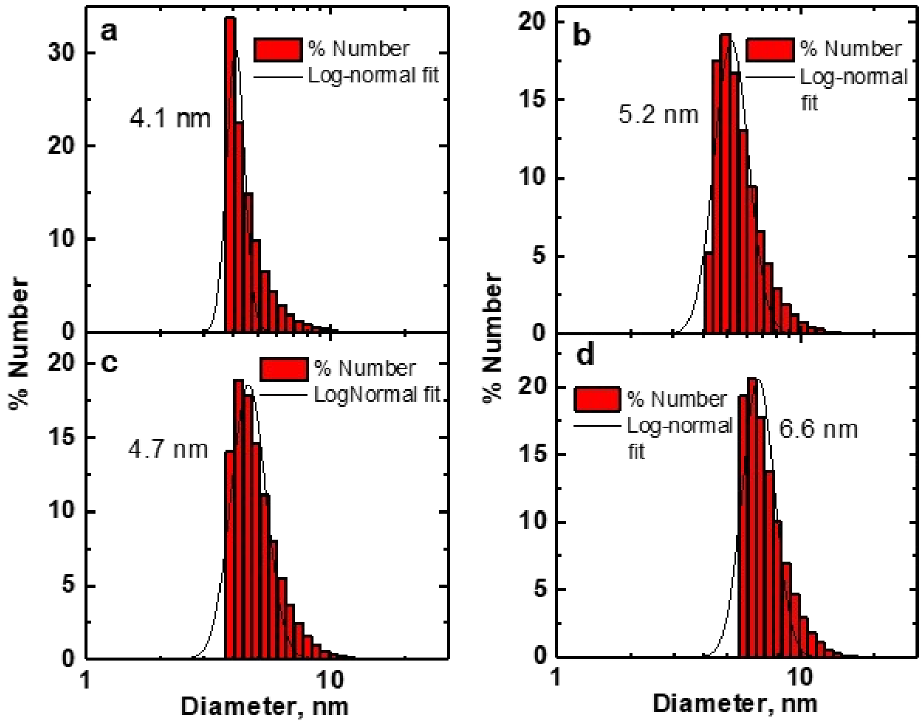

Figure S3. Particle size distribution measured with dynamic light scattering after functionalization in the MW reactor (a): (C6) - SiNc; (b): (C6) - (1) - SiNc; (c): (C6) - (2) - SiNc; and (d): (C6) - (3) - SiNc.

4. Absorption and emission spectra of the dye (1), dye (2) and dye (3).

The dyes (1) and (2) demonstrate strong light absorption between 400 and 460 nm. The dye (3) absorbs between 490 and 540 nm. The dyes (1) and (2) show similar PL spectra with PL maximum of 462 nm and 456 nm respectively. The dye (3) demonstrates green emission with maximum of 537 nm.

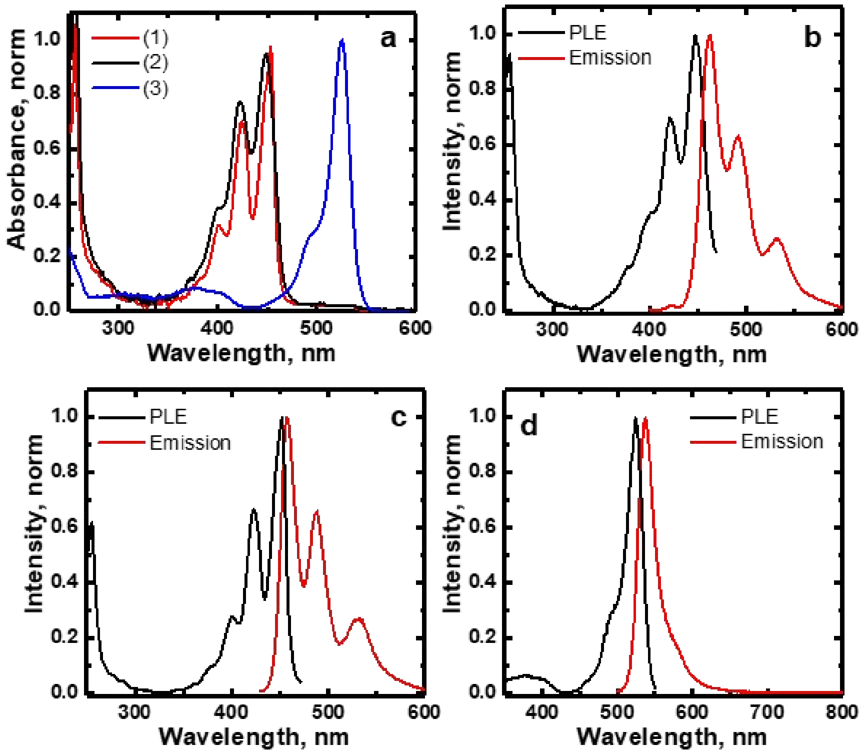

Figure S4. (a): absorption spectra of solutions of 3-ethenylperylene (1), 3-ethynylperylene (2) and ethenyl-m-phenyl-BODIPY (3) in hexane. (b), (c) and (d): PLE and PL spectra of solutions of 3-ethenylperylene, 3-ethynylperylene and ethenyl-m-phenyl-BODIPY in hexane, respectively.

5. Absorbance of (C6) - SiNc, (C6) - (1) - SiNc, (C6) - (2) - SiNc and (C6) - (3) - SiNc at different concentrations.

The extinction coefficients in hexane for five different wavelengths were calculated using the dependence of the absorbance on the concentration of (C6) - SiNc, (C6) - (1) - SiNc, (C6) - (2) - SiNc and (C6) - (3) - SiNc solutions.

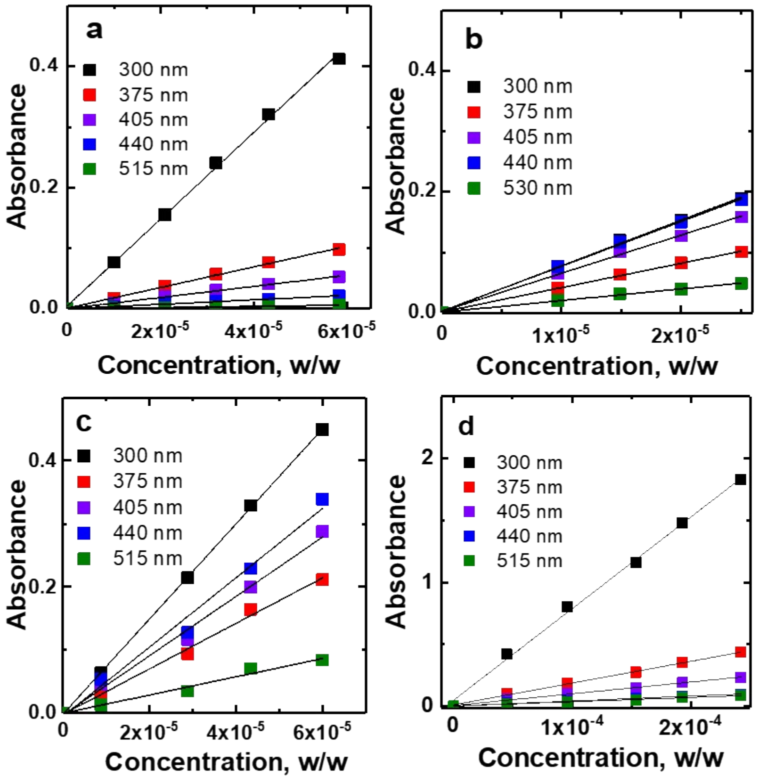

Figure S5. Estimation of the absorption coefficients at different wavelengths for the solutions of (a): (C6) - SiNc; (b): (C6) - (1) - SiNc; (c): (C6) - (2) - SiNc and (d): (C6) - (3) - SiNc in hexane.

6. Absorption and PLE spectra of physical mixtures of (C6) - SiNc and the dyes in hexane.

The PLE spectra demonstrate that the NIR emission of SiNc cannot be achieved via the dye absorption if the dyes are not attached to SiNc.

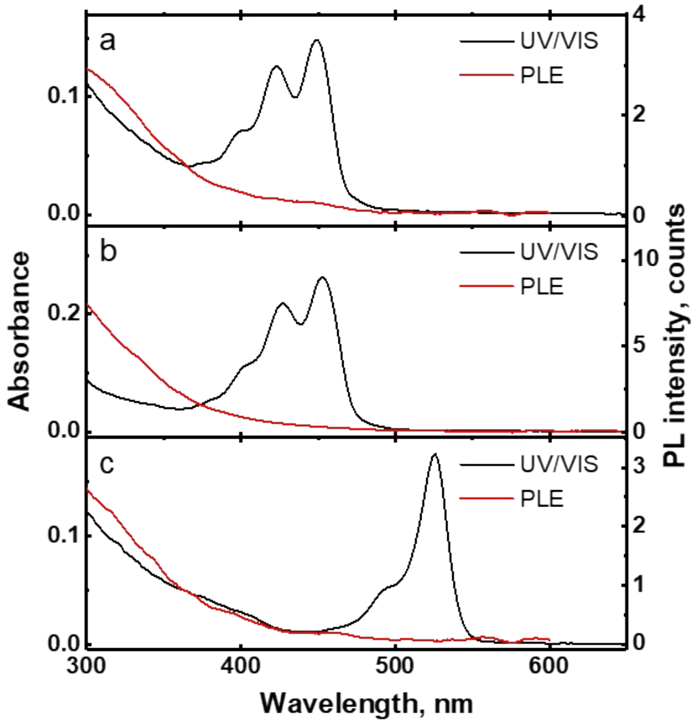

Figure S6. Absorption (black lines) and PLE (red lines) spectra of the physical mixture of (C6) - SiNc and dye (1) - (a), dye (2) - (b), dye (3) – (c). The PLE spectra were measured at fixed luminescence wavelength of 830 nm.

7. Comparison of FTIR spectra of (C6)-SiNc and (C6)-(1)-SiNc.

The FTIR spectra indicate that surface of both (C6)-SiNc and (C6)-(1)-SiNc is slightly oxidized.

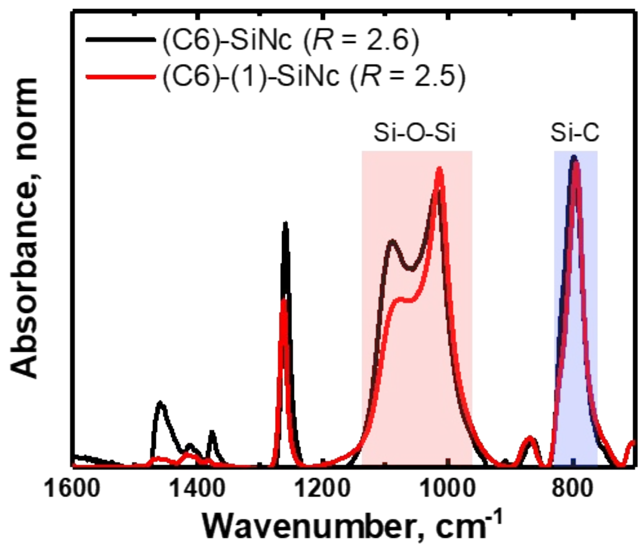

Figure S7. FTIR spectra of (C6) - SiNc and (C6) - (1) - SiNc. The spectra were normalized using the Si - C peak at 800 cm^{-1}.

8. Photoluminescence decays for solutions of dyes (1), (2) and (3) in hexane.

The PL decay of dye (2) demonstrates lifetime of 4.1 ns, whereas the decay of the dye (3) – 7.1 ns.

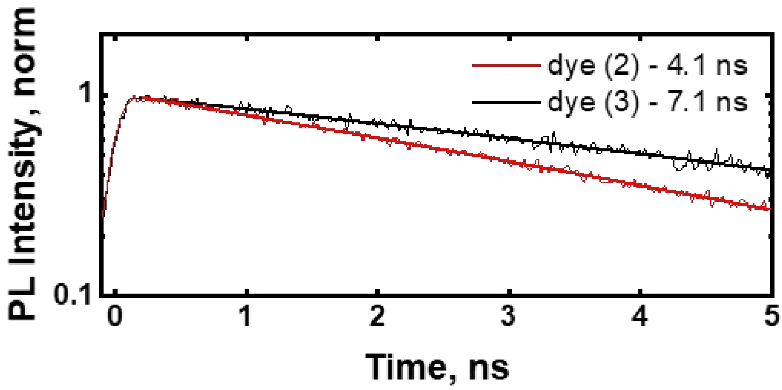

Figure S8. Short-time (ns) decays of the visible PL for dye (2) (red) and dye (3) (blue) dissolved in hexane. The lifetimes are obtained with the monoexponential fit.

9. Photoluminescence decays for solution of (C6) - (2) - SiNc in hexane.

PL decays for NIR and visible emission for (C6) - (2) - SiNc dispersed in hexane demonstrate lifetime of 72 μs and 3.8 ns, respectively.

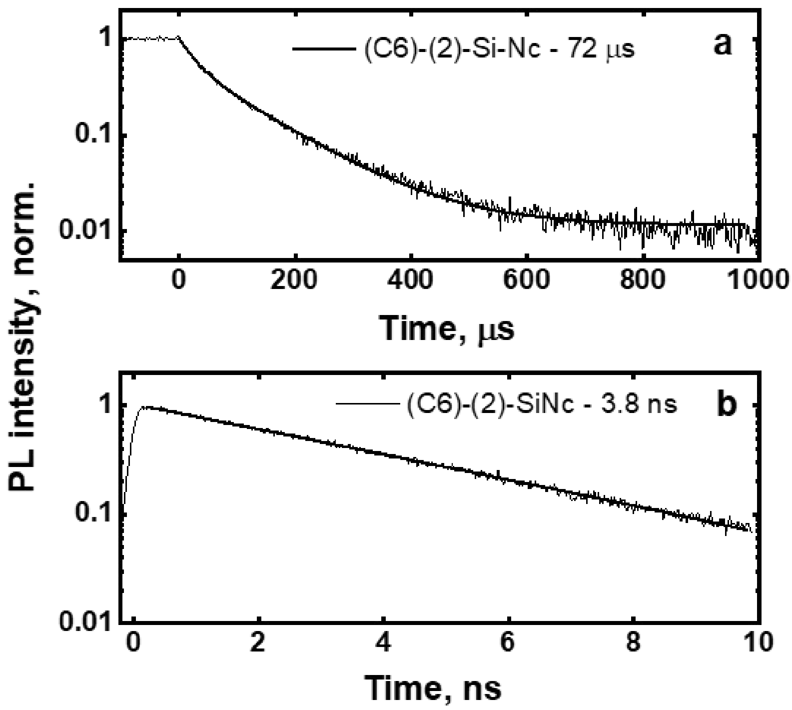

Figure S9. (a): long-time (μs) decay of the NIR PL of (C6) - (2) – SiNc. The lifetimes is average lifetimes estimated with equation 3 using the biexponential fit; (b): short-time (ns) decay of the visible PL of (C6) - (2) - SiNc. The lifetime is obtained with the monoexponential fit.

10. Photoluminescence decays for solution of (C6)-(3)-SiNc in hexane.

The PL decay for visible emission of (C6)-(3)-SiNc dispersed in hexane demonstrates lifetime of 0.3 ns.

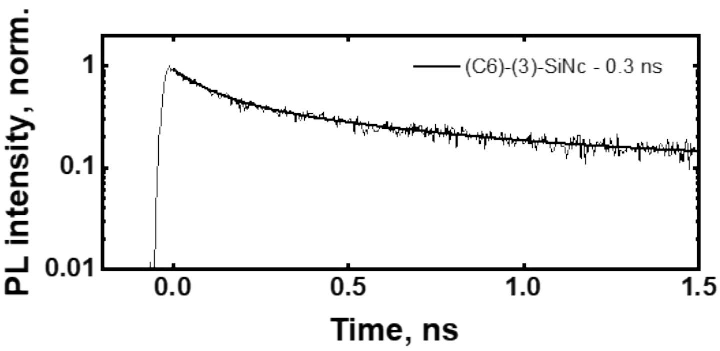

Figure S10. short-time (ns) decay of the visible PL for (C6) - (3) - SiNc. The lifetime was estimated with equation 3 using the biexponential fit.

11. Spectral profiles for LEDs used in photophysical experiments.

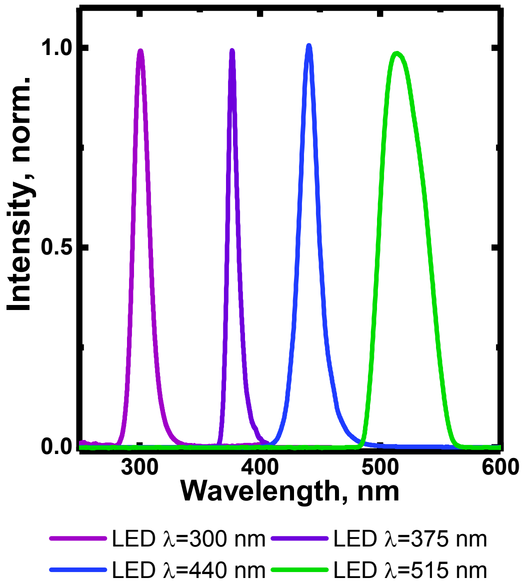

Figure S11. Spectral profiles of LED sources used in photophysical experiments.

12. Scheme of the setup for measurement of absolute PLQY.

The LED beam was focused by the lens and directed into the integrating sphere (Labsphere) with a diameter of 15 cm. The optical fiber with a diameter of 1 mm (FP1000URT, Thorlabs) was used to collect the emission from the integrating sphere and transfer it to the spectrometer (AS 5216 DLL, Avantes).

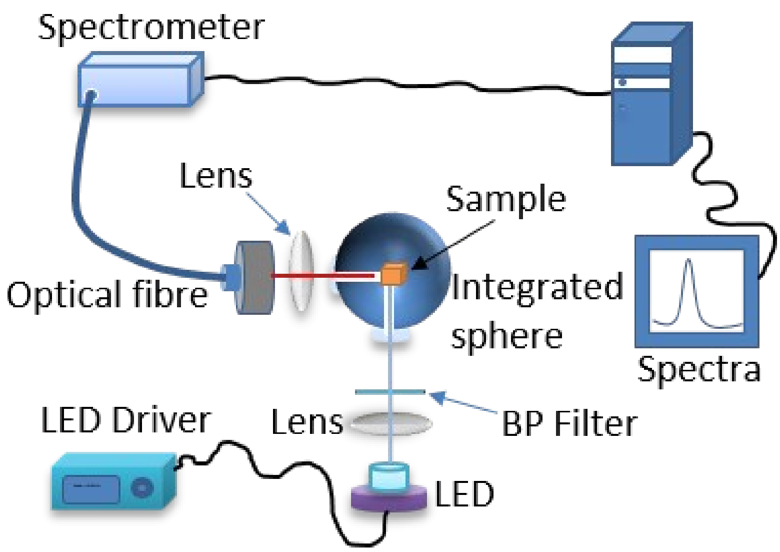

Figure S12. Scheme of the setup for measurement of absolute PLQY.