

Supporting Information

**Nanoscale Assembly of Photoluminescent Quantum Dots
on the Surface of Calix[8]arene Microcrystals**

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Figure S1. TGA plots for p-tert-butylcalix[8]arene (solid line) and microcrystalline p-tert-butylcalix[8]arene (dashed line).

Figure S2. Time evolution of the PL spectra of CdSe/ZnS QDs 550 nm and C8A in toluene after 5 days of thermal treatment at 75°C. The PL intensity decreased ~15% after the thermal treatment and then increased ~35% within 7 days at room temperature ($\lambda_{\text{exc}} = 350$ nm).

Figure S3. UV-Vis spectra (left) and PL spectra (right) of 550 nm CdSe/ZnS QDs and C8A in toluene. The PL intensity increased by ~100% at room temperature within 15 days ($\lambda_{\text{exc}} = 350$ nm).

Figure S4. HRTEM images showing the QD size of a sample of C8A thermally treated batch of 550 CdSe/ZnS QDs highlighting the almost unchanged size of the QDs during the ligand exchange with C8A (~ 3.1 to 4.0 nm).

Chemicals and Synthesis. *p-tert*-butyl-calix[8]arene (C8A) was obtained from Aldrich. Toluene (ACS reagent) was from Fisher and used as purchased. 550 nm CdSe/ZnS quantum dots were prepared following the previously reported procedures:¹ TBP (tributylphosphine), TOPO (trioctylphosphine oxide), HDA (hexadecylamine) or ODP (octadecyl phosphonic acid) capped CdSe nanocrystals were synthesized using standard published methods.^{1b,1d} We deposited about five monolayers of ZnS around the CdSe cores by using the recently developed successive ion layer adsorption and reaction (SILAR) technique.^{1c} To optimize the ZnS shell growth around the CdSe core by SILAR using ZnO and S as precursors, a stock solution of 0.1 M concentration was prepared for ZnO, oleic acid and ODE (1-octadecene) that were used for Zn coating and elemental sulphur and ODE for S coating. The purified CdSe QDs were added to a reaction flask consisting of HDA and ODE where Zn and S stock solutions were added under argon flow to grow the ZnS shell. To optimize the shell growth, the reaction temperature was controlled between 200 °C to 240 °C.

Typical procedure for preparation of QD-covered C8A microcrystals: 1.3 mg, ~1 mM toluene solution of C8A was added to a $\sim 2.13 \times 10^{-4}$ mM toluene solution of CdSe/ZnS core/shell QDs. The resulting mixture was then heated at $\sim 75^\circ\text{C}$ using Tnelco (Precision Scientific Co., Chicago, USA) heating oven for a period between 4 and 7 days. The mixture was subsequently cooled to room temperature before slow evaporation of the solvent. The resulting white needles which precipitated were only visible under a microscope.

Typical procedure for the preparation of C8A microcrystals: This is similar to the above mentioned method except that no QDs were added to the solution.

UV-vis (UV) and Photoluminescence (PL) spectroscopy. UV spectra were acquired on a Perkin Elmer Lambda 45 UV-vis spectrometer, and the PL spectra were acquired on a Fluoromax-3 spectrometer (Horiba Jobin Yvon, Instruments SA) with an excitation wavelength of 350 nm, if not specified otherwise.

Fluorescence microscopy. Images were acquired with an inverted epifluorescence microscope (IX-81, Olympus) equipped with an oil immersion objective lens (UPlan S-APO100XO, Olympus) and a CCD camera (CoolSnap ES, Photometrics). Fluorescence was excited with X-Cite light source (EXFO) using FF520-Di01 dichroic mirror and FF01-500/24 excitation filter (Semrock) and collected through FF01-542/27 emission filter (Semrock). The images show $87.7 \mu\text{m} \times 66 \mu\text{m}$ areas.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-840A with a secondary electron detector and with Quartz PCI version8 imaging software for the image recording and URSA EDS as the analysis system. High-resolution images were obtained with a HITACHI S4700 using both secondary electron and backscattered electron detectors. Specific operational details (working distance, accelerating voltage, magnification, etc.) are indicated on the images.

High Resolution Transmission Electron Microscopy. HRTEM, BF- and HAADF-STEM images were obtained with a JEOL JEM-2100F field emission gun (FEG) transmission electron microscope (TEM) equipped with Gatan bright field (BF) and annular dark field (ADF) detectors. The TEM was operated at 200 kV. Samples were prepared by dispersion of one drop of toluene suspension (diluted three times using toluene from the original reaction mixture including needles and QDs) onto a carbon-coated 300 mesh Cu-grid and dried in air.

Thermogravimetric Analyses. TGA experiments were carried out on a TA Instruments 2050 (V5.4A) under flowing nitrogen (40 mL/min flow rate). Both C8A and for the C8A microrods were heated from 26 to 390 °C at a rate of 5 °C/min.

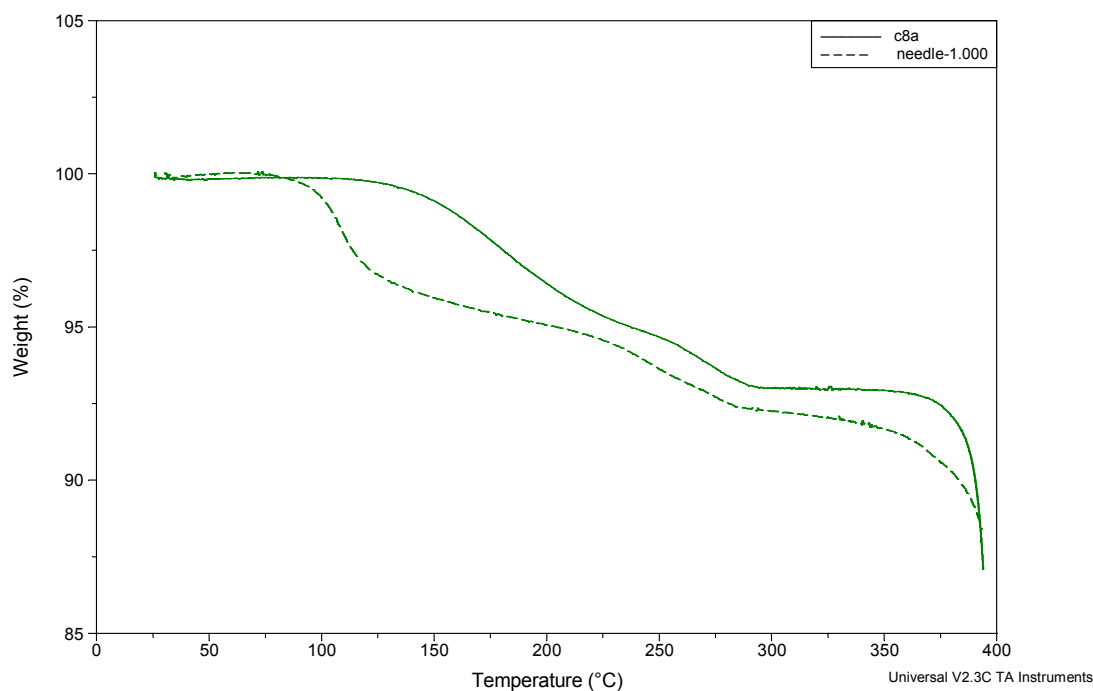


Figure S1. TGA plots for *p-tert*-butylcalix[8]arene (solid line) and microcrystalline *p-tert*-butylcalix[8]arene (dashed line).

Figure S1 shows TGA data for the as received C8A and for the C8A microrods. The first weight loss, amounting to about 5 weight per cent, is probably due to the loss of toluene. It can be easily seen that the needles (dashed line) lose about the same weight in the first event, but that the event occurs at lower temperature than for the as received C8A. The lower temperature for the first weight loss is probably due to a much smaller particle size in the case of the C8A microrods.

S4

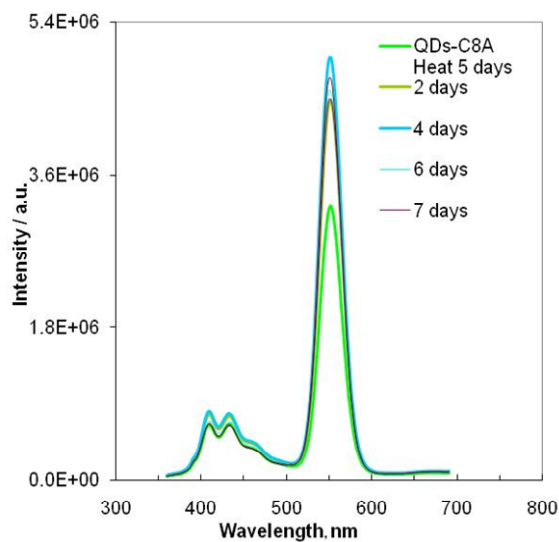


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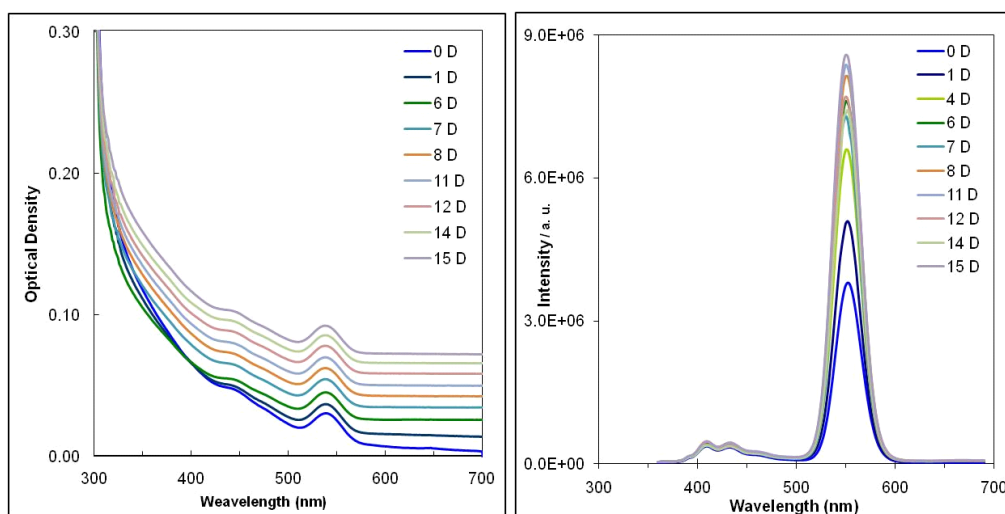


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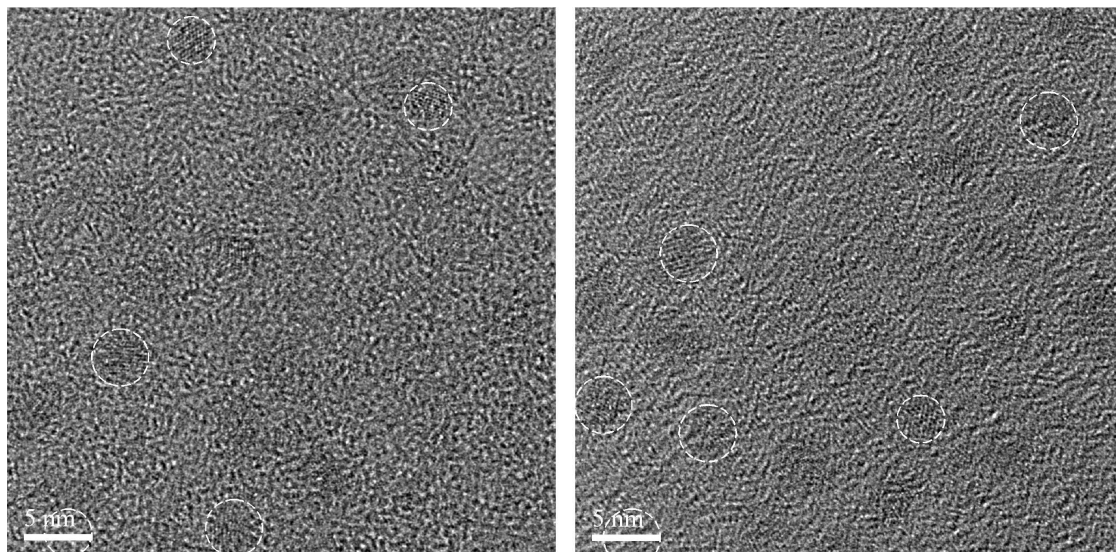


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¹ a) Ratcliffe, C. I.; Yu, K.; Ripmeester, J. A.; Zaman, M. B.; Badarau, C.; Singh, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3510–3519; b) Yu, K.; Zaman, M. B.; Singh, S.; Wang, D.; Ripmeester, J. A. *Chem. Mater.* **2005**, *17*, 2552–2561; c) Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. *J. Am. Chem. Soc.* **2003**, *125*, 12567–12575; d) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844–8850.