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COMMUNICATION

Nanoscale assembly of photoluminescent quantum dots on the surface of calix[8]arene microcrystals†‡

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The layered assembly of fluorescent CdSe/ZnS quantum dots (QDs) on the surface of *p*-tert-butylcalix[8]arene microcrystals is reported.

A factor preventing a fundamental discovery from finding a practical application is often that it is difficult to scale up the desired property to technologically relevant systems (fibers, gels, and nanocomposites). Recently we have focused our efforts on interfacing light-emitting semiconductor quantum dots (QDs) with macrocyclic¹ and supramolecular² structures. In the first case, the nanocrystals were included in giant cucurbit[6]uril polymeric capsules, whereas in the second case, supramolecular gels were readily doped with QDs, which deposit on dipeptide fibers after a short exposure to ultrasound.³ The resulting xerogels showed good porosity and bright luminescence under UV light. These materials had potential as chemical sensors, since the luminescence was sensitive to the presence of free radicals near the QD surface.² Supramolecular chemistry has been applied to expand the scope of application of QDs, resulting in the preparation of new nanocomposites of calix[*n*]arenes. The usual approach used was calixarene capping of nanoparticles,^{4–8} and resulted in remarkable success in chiral surface plasmon resonance,⁹ SERS based nanosensors^{10,11} and biosensing.¹² However, there are a limited number of reports which describe new approaches for interfacing QDs with calixarenes, and exploring their potential applications.^{13–15} Here we report the one-pot preparation of *p*-tert-butylcalix[8]arene (C8A) microrods, and the capture of fluorescent QDs on their surfaces, giving materials which may find applications in wave guiding¹⁶ and Whispering-Gallery Mode (WGM) resonators¹⁷ for multiplexed sensing.

Calix[*n*]arenes are polyphenolic macrocyclic compounds recognized for their important inclusion properties (Scheme 1).^{18,19} Molecules with four (*n* = 1), six (*n* = 3), or eight (*n* = 5) phenolic units within the macrocycle are the most commonly used calixarenes.

The number of phenol groups per calixarene molecule engaged in guest recognition can vary from 3 to 8 (Scheme 1). In some cases the stereochemical orientation of the ligating arms can be controlled. For example, selective alkylation of calix[4]arene can force the molecule to adopt only one of its four possible conformations (*e.g.*, cone as in Scheme 1, partial-cone, 1,2-alternate or 1,3-alternate). On the other hand, the larger and conformationally more mobile calix[6]- and calix[8]-arenes can adapt their conformations to achieve guest recognition of complex multi-functional entities. The chemistry of these macrocycles is now well established, and efficient procedures are available to functionalize both the phenolic OH rim and the aromatic carbons with useful functional groups (–CHO, –COOH, –NH₂, –NCS,...). These kinds of functionalization can be further employed for the construction of supramolecular assemblies of higher complexity.

Crystallization of C8A in the presence or absence of photoluminescent (PL) QDs was investigated in toluene. Slow evaporation of 1 mM C8A solutions at room temperature resulted in very tiny white needles. We speculate that the growth and shape of the needles are controlled by hydrogen bonding interactions between the phenolic OH groups of self-assembling C8A molecules, since intra- and inter-molecular hydrogen bonds are expected to be significant, especially in a non-competing solvent like toluene. The ability to suspend QDs in toluene was found to be crucial to the formation of these photoluminescent composite materials, wherein the QDs are tightly bound to the surface of the calix[8]arene microrods. To prepare the composite materials, C8A (1.3 mg, ~1 mM) was added to a 100 μl (~2.13 × 10^{–4} mM) toluene solution of CdSe/ZnS core/shell

Scheme 1 Structure of quantum dots and calixarenes.

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QDs (see preparation in ESI[†], the ligands on the surface of the QDs are trioctylphosphine oxide/trioctylphosphine—TOPO/TOP—molecules). The resulting suspensions were then heated at $\sim 75^\circ\text{C}$ for periods between 4 and 7 days. The mixtures were subsequently cooled to room temperature before slow evaporation of the solvent. The resulting white needles which precipitated were only visible under a microscope, with a size too small to allow their characterization by single-crystal X-ray diffraction.²⁰

Scanning electron microscopy (SEM) of the C8A small needles showed microrods with a width of approximately 0.5–5 μm , and a length of around 20–100 μm (Fig. 1a). Flat surfaces were clearly observed, with some images occasionally showing hexagonal cross-sections (Fig. 1b). Hexagonal calixarene crystals have previously been observed for calix[4]arene derivatives.²¹

The presence of QDs during C8A crystal growth did not preclude the formation of the microrods, presumably as a consequence of the much larger concentration of C8A with respect to that of the QDs. The remarkable capture of the QDs on the surface of the C8A microrods was evidenced by high resolution transmission electron microscopy (HRTEM, Fig. 1d–f) and fluorescence microscopy (Fig. 2). HRTEM images showed multiple layers of QDs near the surface of the microrods (Fig. 1f). The mean distance between QDs was found to be ~ 5 nm. Using the intensity of QD fluorescence observed by fluorescence microscopy as an indicator of QD

Fig. 2 Fluorescence microscopy images of the QD-covered C8A microrods. The colored scale on the left is directly proportional to the concentrations of QDs (550 nm) on the surface of the C8A microrods. The yellow, red, green, and blue areas represent very strong, strong, medium, and weak fluorescence, respectively, for samples previously washed with toluene.

concentration clearly showed a non-homogeneous QD distribution on the microrod surfaces. The fact that the QDs remain bound to the surface of the rod even after several dilutions with toluene is remarkable and demonstrates some binding of the QDs on the microrod surface, presumably as a consequence of either (i) TOPO/TOP binding inside C8A cavities⁸ or (ii) ligand exchange with the aid of multivalency (multiple hydroxy–C8A interactions).²² These preliminary results are interesting because they provide an easy entry for nanocomposite materials amenable for optical physics.

We believe that a more homogeneous coverage of the microrod surfaces can be achieved by fine tuning the experimental conditions. A plausible mechanism for the formation of the C8A/QD composites relies on two successive self-assembly events: (i) growth of C8A microrods due to the large excess of calixarene in the medium and (ii) assembly of the QDs on the surface of the C8A microrods, with the aid of previously formed C8A-bound QDs. Indeed, the thermal treatment with a large excess of C8A may have resulted in significant ligand exchange on the QD surface enabling C8A to behave as a compatibility agent between the self-assembly of C8A alone and the incorporation of C8A-decorated QDs. However, on the basis of previous work using similar QDs and ligand capping or ligand exchange experiments with calixarenes⁸ or cyclodextrins,²³ a regular red shift in the QDs emission was observed. In our case, the slight decrease of PL emission at 550 nm accompanied by the increase of that in the 390–490 nm region (409 nm, 433 nm and 460 nm due to C8A) may be attributed to some ligand exchange on the surface of the QDs (*vide infra*).

Regarding the C8A assembly, efforts were devoted to get a single crystal X-ray diffraction structure, which were unsuccessful.²⁰ ¹³C solid state NMR showed almost no difference between the spectra of the C8A microrods and the as-received material (Fig. 3a). A small amount of toluene is present in both spectra (1/1 toluene/C8A ratio as calculated by TGA, see ESI[†]). Powder X-ray diffraction is consistent with the structures of the needles and the bulk C8A being quite similar. Significant differences appear in the 5–20° 2 θ region, whereas no detectable differences are observed for higher values of 2 θ (Fig. 3b).

A very small blue shift in the QDs emission combined with a significant increase of that of C8A was observed by PL spectroscopy after this synthetic procedure (Fig. 4a). After five days of thermal treatment and subsequent evaporation of toluene, the intensity of the most intense peak centered on 550 nm slightly decreased ($\sim 15\%$, redispersed sample), with a ~ 2 nm blue shift. Interestingly, we observed significant increases in the PL intensity of

Fig. 1 SEM (a and b, different magnifications) and TEM (c) images of C8A rod crystals and TEM (d–f) images of QD-covered C8A microrods. Inset in (d) shows the lattice pattern of the QDs. HAADF-STEM (e and f) images of QD-covered C8A microrods. White large areas are for the C8A microcrystals and the small white spots for the QDs.

Fig. 3 ^{13}C SSNMR spectra (a) and PXRD data (b) of commercial C8A (black trace) and C8A needles (red trace).

the 550 nm signal at room temperature within the time (no blue or red shift) after thermal treatment (Fig. S2†) or for a room temperature reaction (Fig. S3†).

Photoluminescent excitation (PLE) experiments allowed us to unambiguously assign the peaks at 409 nm, 433 nm and 460 nm to C8A and that at 550 nm to the QDs (Fig. 4b). Furthermore, high resolution TEM images showed no meaningful reduction of the bound QD sizes, which were in the range of ~ 3.1 to 4.0 nm, as compared with 3.5 ± 0.5 nm for the parent QDs. Sulfur atom replacement on the surface of the ZnS shell of QDs by oxygen atoms of cyclodextrins has been recently reported.²³ The high hydroxyl group density of C8A can cause a similar complexation behavior to that previously described for cyclodextrins. Thus one could propose a mechanism in two steps, (i) ligand exchange from TOPO to C8A (with possible multivalency effects) and (ii) crystal growth of C8A first without QDs, and second, incorporating the C8A-covered QDs during crystal growth.²⁴

In conclusion, we show that multiple layers of CdSe/ZnS nanocrystals can easily be bound to the surface of calix[8]arene microcrystals in a one-pot procedure. The C8A crystal growth as well as the respective concentrations of (i) C8A and (ii) the QDs are expected to have a significant influence over the nature and homogeneity of the resulting self-assembled nanocomposite. This approach is complementary to the recently reported preparation of fluorescent organic heterostructures²⁵ which were conceived for the development of

Fig. 4 (a) (1) PL spectrum of original 550 CdSe/ZnS QDs in toluene (2.13×10^{-4} mM), (2) PL spectrum after addition of C8A (1 mM) and (3) PL spectrum after thermal treatment for 5 days at 75°C with C8A (1 mM). The UV-vis spectrum of the original 550 CdSe/ZnS QDs in toluene is shown in green. (b) Photoluminescence excitation with emission at 409 nm, 433 nm, 460 nm, and 551 nm. Accordingly, PLE at 409 nm, 433 nm, 460 nm and the absorption ~ 360 nm are from calix[8]arene and that ~ 540 nm assigned to QD550.

novel electronic and photonic applications, such as portable display devices.

The QD fluorescence is still present on large areas of the nanocrystals after incorporation onto the microrods, and this can be of practical importance for optical applications. In addition to the well established role of QDs in bioimaging,²⁶ the fact that much of the microcrystals surface remains accessible can also be interesting for further functionalization for the preparation of multifunctional supramolecular materials.

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