Supplementary Material (ESI) for Chemical Communications

Supporting Information

Photoluminescent Quantum Dot - Cucurbituril Nanocomposites

Minjie Li, Md. Badruz Zaman, David Bardelang, Xiaohua Wu, Dashan Wang, James C. Margeson, Donald M. Leek, John A. Ripmeester, Christopher I. Ratcliffe, Quan Lin, Bai Yang, Kui Yu.

Figure S1. TEM and HR (High Resolution) TEM images of samples of the reaction mixture illustrating the presence of empty CB[6] based polymer [a) and b)] and QD loaded polymer [c) to k)]. High resolution images enabled to directly prove the presence of QDs inside the growing sheets of the bubble-like polymer [d), h), j), k)]. An additional area of the sample [m), n), o)] shows a bunch-like zone of the polymer with growing spheres having entrapped QDs before the sphere release from the polymer. QD loaded cucurbituril capsules are also shown in pictures l) and p). All the pictures are from samples taken at 10 hours of reaction time except for l) and p) for which the samples were taken at 20 hours of reaction time. Method B.

Figure S2. (a) TEM and (b) HR (High Resolution) TEM images of cucurbituril capsules with encapsulated ME-capped QDs. Experimental conditions are identical to those mentioned in Figure S1. Pictures are from samples submitted to UV for 20 hours. Method B.

Figure S3. TEM [a), b), c), d)] and HRTEM [e)] images of hollow CB capsules having QDs inside their core [e)]. HAADF-TEM picture of the corresponding capsules [f)]. Images of the rice-shaped capsules ([g), h)] with ME-capped QDs inside [i), j)] together with longer fiber-like aggregates [k)] and ME-capped QDs inside the rice-type capsule [l)]. Images a) to f) are from samples taken at 22 hours of reaction time (10 hours with 8 lamps at 350 nm followed by 12 hours with 8 lamps at 300 nm). Images g) to l) are from samples taken at 32 hours of reaction time (10 hours more exposure to UV light with 8 lamps at 250 nm). Method A.

NMR. All the solution NMR spectra were recorded using a Bruker DRX-400 spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C in DMSO-d_6 or CH_3OH-d_4. Standard Bruker pulse sequences were used for all experiments.

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 (Jobin Yvon Horiba, Instruments SA) with a 450 W Xe lamp as the excitation source and an excitation wavelength of 350 nm and 500 nm if not specified.

Scanning Electron Microscopy. Images were acquired on a Hitachi S-4800 Cold Field Emission Scanning Electron Microscope (SEM). This instrument was fitted with two secondary detectors and images were acquired using a mixed image of the two signals at a working distance of 8 mm. An Oxford Inca Energy Dispersive Spectrometer (EDS) was also attached to the instrument to provide elemental analysis of the image area. Images were acquired at a beam energy of 2 keV and a current of 5 μA. A series of magnifications of regions of interest was imaged to show the morphology of the studied dry materials deposited onto aluminium stubs on adhesive carbon tape.

Transmission Electron Microscopy. The transmission electron microscope (TEM) samples were prepared by drop casting the solutions contaning the QD entrapped capsules onto a carbon-coated 300-mesh TEM copper grid. The dried grid was loaded into a double-tilt sample holder. The TEM samples were examined on a Philips CM20 STEM equipped with a Gatan UltraScan 1000 CCD camera; the TEM was operated at 80 kV.

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 annual dark field (ADF) detectors. The TEM was operated at 200 kV. Sample preparation was similar to that of TEM section above.

Quantum Dots were prepared following the previously reported procedures: [1] TBP (tributylphosphine), TOPO (trioctylphosphine oxide), HDA (hexadecylamine) or SA (stearic 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 adhesion 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.

Preparation of methanol soluble QDs: It is well established that different synthetic approaches considering different surface ligands are responsible for different dispersion abilities in polar and non polar solvents. Mercaptoundecanoic acid (MUA) and mercaptoethanol (ME) were selected for a ligand exchange reaction with the previously prepared QDs.

1) For the MUA ligand exchange reaction, the purified CdSe/ZnS QDs were dispersed in 1 mL of a toluene/hexanes mixture. An approximate 1000 times molar excess of MUA was added under stirring. The mixture was then heated up to ca. 100°C under vacuum to remove the toluene/hexanes mixture of solvents. The temperature was subsequently decreased to ~ 80°C under nitrogen. After 3 hours, around 2.5 mL of DMSO were added (temperature between 40 and 50°C) and the reaction flask kept overnight with stirring at room temperature. Chloroform was finally added to precipitate the resulting MUA-coated CdSe/ZnS QDs, hereafter refered to as MUA-capped QDs. Alternatively, centrifugation was used (3700 rpm for ca. 15 min) to obtain the MUA-capped QDs that were easily dispersed in methanol.

2) For the ME ligand exchange reaction, about 2500 times molar excess of ME was added to the purified CdSe/ZnS QDs in hexanes. The mixture was heated up to ca. 100°C under vacuum to remove hexanes and the reaction mixture cooled down to approximately 90°C under nitrogen for 3 hours. After cooling to room temperature, chloroform was added to precipitate the resulting ME-decorated CdSe/ZnS QDs, hereafter refered to as ME-capped QDs. Centrifugation could again be used (3900 rpm for ca. 30 min) finally affording the targeted ME-capped QDs that were easily dispersed in methanol.

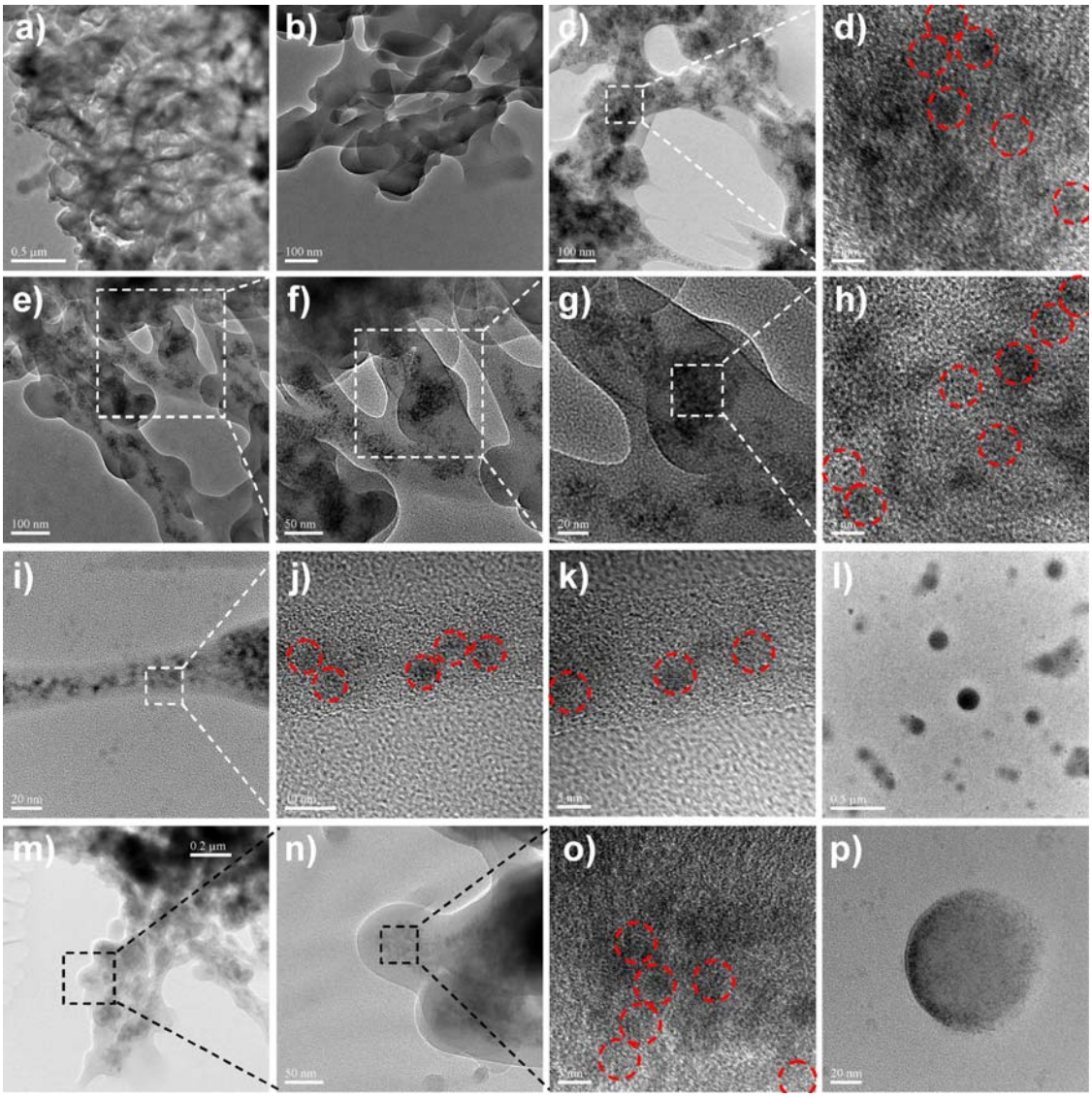
Synthesis of CB[6] derivatives: CB[6] was prepared according to literature procedures.[2] ^{1}H NMR in [D_2O / CF_3COOD / D_2SO_4 (300 μL / 300 μL / 50 μL)]: δ = 5.81 (d, 2H), 5.59 (s, 1H), 4.32 (d, 2H).[3]

CB[6]-$(OH)_{12}$ synthesis was adapted from a previously reported procedure:[4] 2g of CB[6] and 7.8g of potassium persulfate were added to 100 mL of distilled water in a 250 mL 3-neck flask equipped with a thermometer and a condenser. The mixture was bubbled with nitrogen (high purity) for at least half an hour before heating to 85°C. The bubbling tube (glass or polymer) tip may get stuck by CB particles. A slow stirring speed and gentle nitrogen bubbling were found to be better for the reaction. After the reaction is finished (6 hours), the reaction mixture was allowed to cool down to room temperature before standing in the reaction vessel overnight. The

solid was then filtered out. The filtrate was condensed to around half of its volume, transfered to a 250 mL beaker and put fully open into a bigger beaker partially filled with acetone before sealing. More acetone can be added after some of it has diffused into the small beaker. Three weeks of diffusion were usually enough to get most of the product. Special care had to be taken owing to the white precipitate that was often only made of salts and the occurrence of the product by acetone precipitation was monitored by ^{1}H NMR in DMSO-d_6. Finally, the product was filtered out, washed with acetone and dried in an oven affording 0.95 g of an off white product (40% yield). ^{1}H NMR in DMSO-d_6: δ = 7.87 (s, 12H), 5.34 (d, 12H), 4.43 (d, 12H).

CB[6]-(Oallyl)$_{12}$ synthesis was adapted from a previously reported procedure:[4] 10 mL of anhydrous DMSO were first introduced in a 250 mL Erlenmeyer with a magnetic stirrer before introduction in an ice-water bath until DMSO started to solidify on the walls under stirring. A DMSO solution (10 mL) of NaH (1.576 g, 37.4 mmol, 60% dispersion in mineral oil) was then introduced in the Erlenmeyer under stirring. Another 50 mL of a DMSO solution of dried CB[6]-(OH)$_{12}$ (2.8 g, 1.64 mmol) was then slowly added before standing at room temperature for 1 hour. Allyl bromide (3.2 mL, 37.4 mmol) was then added to the reaction mixture at 0°C before stirring at room temperature for 12-14 hours. After the reaction was finished, the reaction mixture was poured into 600 mL of ice water. The precipitate was filtered and washed thoroughly with water and diethyl ether before drying under vacuum. Alternatively, CB[6]-(Oallyl)$_{12}$ can be purified pouring about 200 mL of diethyl ether to the reaction mixture in DMSO and water under stirring, then stop stirring and leave the two phases to separate. The product is just at the interface and can thus be collected before centrifugation. The resulting solid was washed with water and diethyl ether thoroughly to get the product that was dried under vacuum and kept in a dark vial in the fridge (0.9 g, 23% yield). ^{1}H NMR in CH_3OH-d_4: δ = 5.95 (m, 12H), 5.78 (d, J = 15.5 Hz, 12H), 5.42-5.25 (dd, 24H), 4.44 (d, 12H), 4.15 (s, 24H).

QD@CB-capsule preparation: CB[6]-(Oallyl)$_{12}$ (3.12 mg, 1.9 μmol) and 3,6-dioxa-octane-1,8-dithiol (13.84 mg, 76 μmol) were added to a preliminary prepared 3 mL mercaptoundecanoïc acid (MUA) or 2-mercaptoethanol (ME) functionalized QDs methanolic solution in a 15 mL quartz tube before bubbling nitrogen for three minutes and sealing with parafilm. The tube was then introduced into a Rayonet photochemical reactor (model RMR-600, four watt lamps) and the reaction maintained at room temperature [2 setups have been used. Method A: successive use of low power (8 lamps at 350 nm for 10 hours), then medium power (8 lamps at 300 nm for 12 hours) and finally high power (8 lamps at 250 nm for 10 hours); Method B: 4 lamps at 250 nm and 4 lamps at 300 nm for a total reaction time of 20 hours]. The volume can also be reduced by a factor of one third for the reaction to take place in a 1 mL UV or PL cuvette. Dialysis can be used to purify the material taking two days (refreshing the solvent each 5-10 hours). The molecular weight cut off for the dialysis tube (regenerated cellulose) was from 8 K to10 K. The volume ratio of CB capsule solution to free solvent is about 1:100. The use of either chloroform solutions of QDs or peptide (FmocLeuLeuOH) functionalized QDs in methanol (enhanced solubility) were also not possible due to the QDs decomposition in the conditions of the reaction. We used various concentrations of QDs in different reaction entries and characterized those reaction samples using UV, PL and TEM. Our results demonstrate that the CB capsule will contain QDs at the end of the reaction, provided the QDs are soluble enough. Simply, the higher the concentration of QDs used in the reaction, the higher the amount of QDs trapped inside the polymeric capsules.



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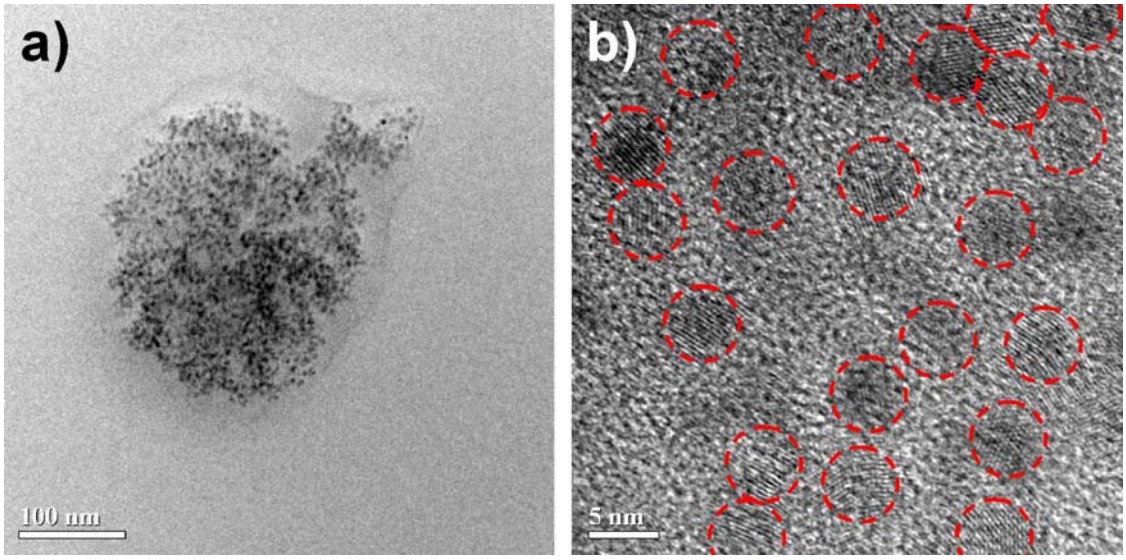

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The proportion of the cucurbituril capsules having ME-capped QDs entrapped in their core greatly increased (up to approximately 90%) by using a concentrated solution of the QDs with 100 μL of ME added to enhance the QDs solubility. However, we also observed slight capsule deformation in regard of the ideal spherical shape, this likely coming from the additional amount of ME with its thiol group probably competing during the polymerization reaction.