

Supporting Information

Cyclodextrin modified quantum dots with tunable liquid-like behaviour

Juan Zhou, Jin Huang, Demei Tian, and Haibing Li*

Experimental sections

Materials

All chemicals used were of analytical grade or of the highest purity available. Cadmium oxide (CdO, 99.99%), zinc acetate (ZnAc₂, 99%), trioctylphosphine (TOP, 90%), oleic acid (OA, 99.99%), selenium (powder, 99.99%), sulphur (powder, 99.99%), octadecenoic acid (ODE, 90%), α -cyclodextrin (α -CD), poloxamer 188 (P188, 99%) purchased from Aldrich (Milwaukee, WI, USA).

1. Preparation of OA-capped oil-soluble Cd_{1-x}Zn_xSe_{1-y}S_y QDs (OA-QDs)

Oleic acid (OA)-capped Cd_{1-x}Zn_xSe_{1-y}S_y QDs was synthesized according to a literature procedure^[1] with little modification. Selenium and sulfur powder reserve liquids were prepared as follows. Selenium powder (31.2 mg, 0.4 mmol) were mixed with sulfur powder (32 mg, 1 mmol) in a two-necked flask. TOP (1.5 mL) was injected into the flask after repeated three times evacuation and ventilation with nitrogen. Then reacting with ultrasound technique until the solution turned transparent and colorless. At the mean time, CdO (25.8 mg, 0.2 mmol), ZnAc₂ (365 mg, 1 mmol) and OA (8.8 mL) were mixed in a three-neck flask. After three times evacuation and ventilation with nitrogen, ODE (10 mL) was added and followed with stirring under 294 °C. At this time, the as-prepared reserved liquids were injected into the three-neck

flask rapidly with long pinhead, and then reduce the temperature to 280 °C. Finally, OA-capped $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$ QDs have been collected after 4 minutes reaction and washing with acetone twice. The as-synthesized OA-QDs were dispersed in chloroform and stored in a refrigerator for further investigation.

2. Preparation of water-soluble 1830-QDs

Water-soluble 1830-QDs were synthesized *via* a typical emulsion volatile method. Simply in manipulation, the oil-soluble OA-QDs (1 mL) were added dropwise into 1830 aqueous solutions (10^{-3} M, 20 mL) with uniform stirring under 50 °C. Once the chloroform volatilized completely, the solution changed from emulsible to transparent aqueous. After purification by centrifugating at 10000 rpm for 5 min and removing the precipitates, water-soluble 1830-QDs were obtained, and 1830-QDs nanofluids were acquired after removing the solvent by means of rotary evaporation and vacuum drying for about two days.

3. Preparation of superamolecular QDs nanofluids based on inclusion interactions between α -CD and PEG chains

Based on the well-known inclusion interaction between α -CD and PEG chains, α -CD (16 mg) was added into the aqueous solutions of freshly prepared 1830-QDs (40 mL) using the aforementioned technique and proportion. By stirring overnight under room temperature, the mixture was purified *via* centrifugation at 10000 rpm for 5 min. After that, solvents were removed and vacuum dried under room temperature. The resultant waxy-like material was collected after two days or longer.

Characterization

Transmission electron microscopy (TEM) was carried out on a JEOL-JEM 2010 electron microscope operating at 200 kV. Infrared spectra (IR) were collected on a Thermo Nicolet NEXUS IR spectrometer in the wavenumber range 400-4000 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on Varian Mercury VX600 instrument (DMSO-*d*₆, 600 MHz, 298 K) with TMS as the internal standard. The fluorescence spectra were acquired on a right-angle fluorescence spectroscopy (Cary Eclipse Fluorescent Spectrometer, FL1008M018), with excitation wavelength of 450 nm and slits width of 5. Thermogravimetric analysis (TGA) were measured with the temperature rising from 30 to 700 °C under nitrogen flowing, with a heating rate of 20 $\text{K}\cdot\text{min}^{-1}$. Differential scanning calorimetric (DSC) analysis was carried out with the following procedure: a cycles of heating from 30 °C to 100 °C, holding for 1.0 min at 100 °C, and then cooling to -50 °C at a heating rate of 20 $\text{K}\cdot\text{min}^{-1}$ under nitrogen protection. All of the mentioned photographic images were shot by a digital camera.

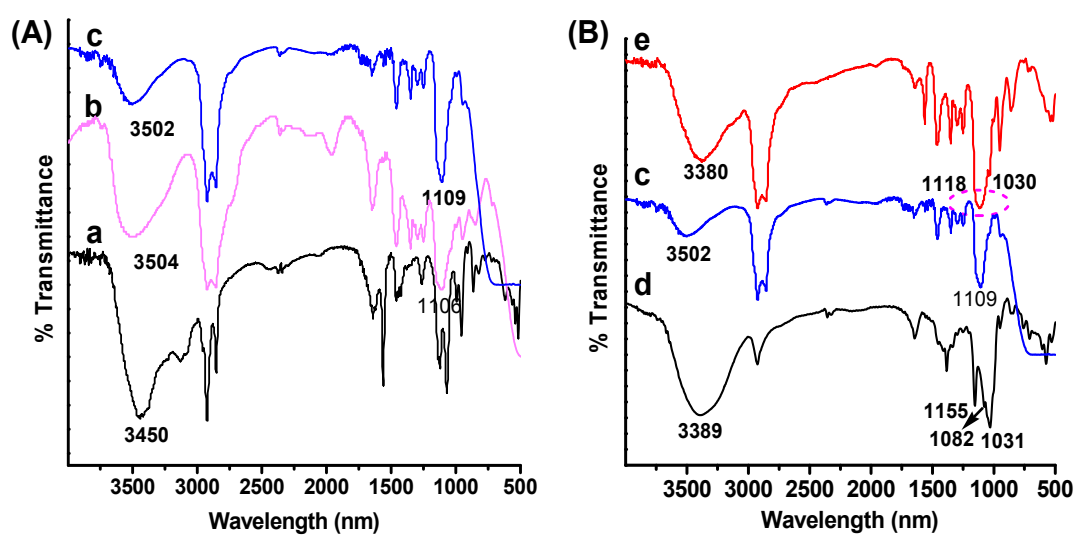


Fig. S1 FT-IR spectra of (A) OA-CdSe/ZnS QDs (a); pure 1830 (b); 1830-QDs (c), and (B) pure α -CD (d); 1830-QDs-CD (e).

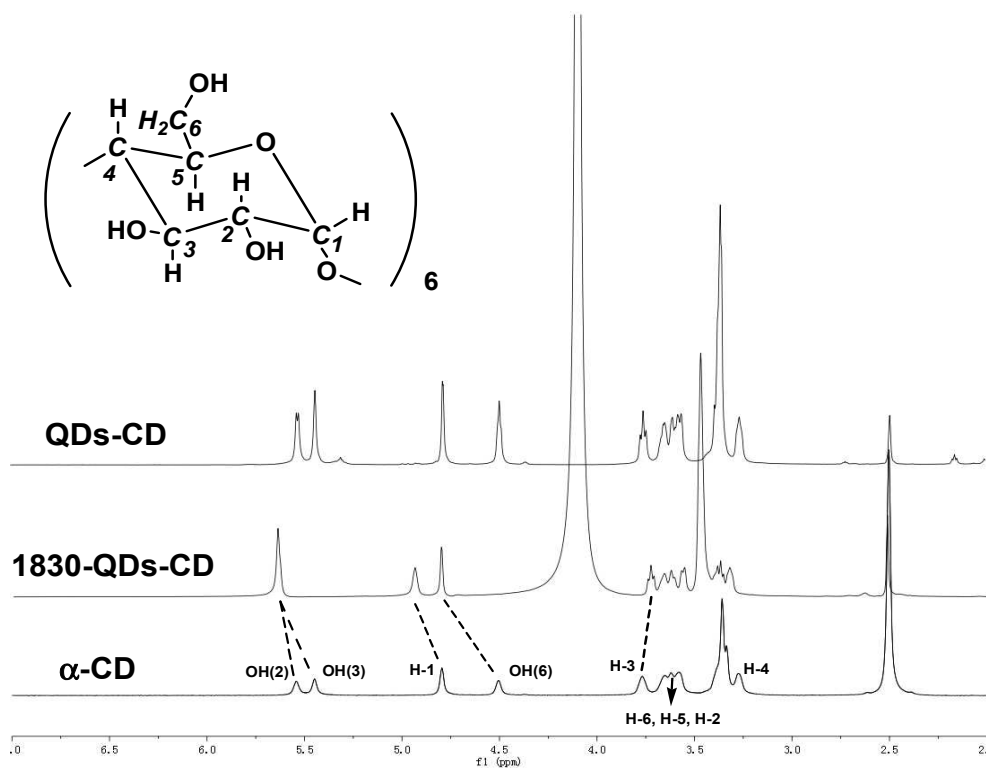


Fig. S2 ^1H NMR spectra (DMSO-*d*₆, 600 MHz, 298 K) of mixed QDs-CD, the resultant 1830-QDs-CD and pure α -CD. The material of QDs-CD is formed by mixing OA-CdSe/ZnS QDs with α -CD in the solvent of DMSO-*d*₆. By comparison, the obvious shift of H-3 and H-5 of α -CD proved the inclusion interactions between PEG chains and α -CD, comparing with QDs-CD which excluded the affection of QDs. On the other hand, the changes of outside proton of H-2, H-4, H-6 and OH(2), OH(3), OH(6) is caused by the hydrogen bonding between α -CD molecules.

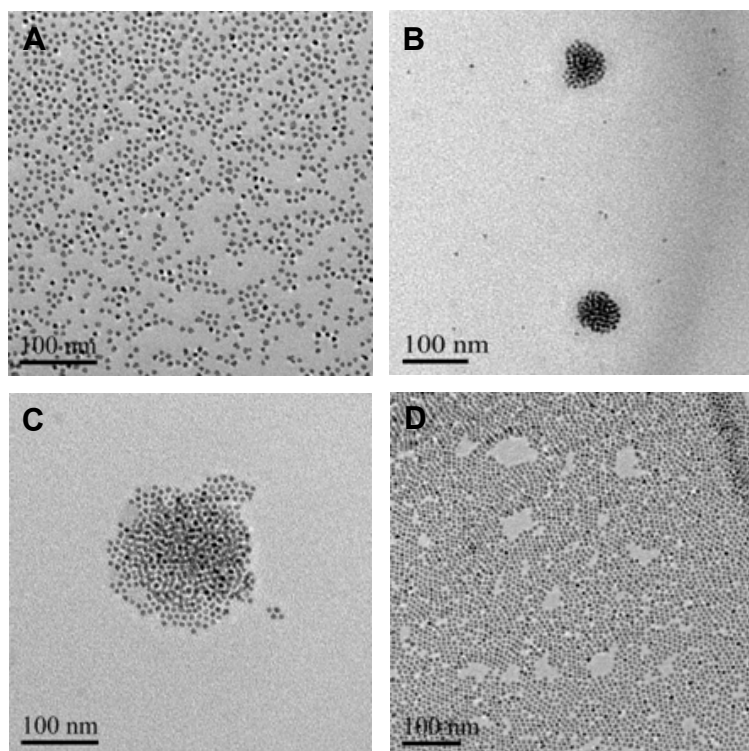


Fig. S3 TEM images of OA-QDs (A), 1830-QDs (B), 1830-QDs added with α -CD and stirring for 2 hours (C) and 12 hours (D).

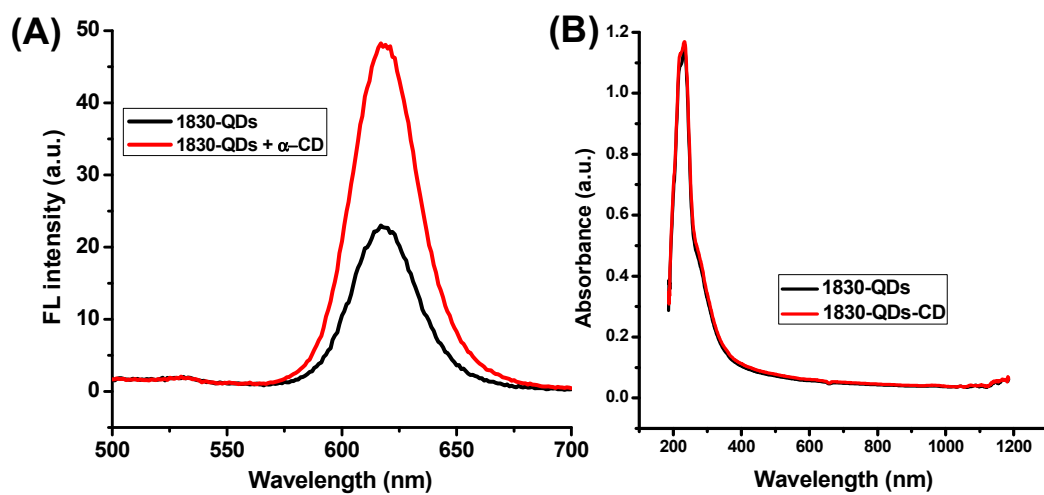


Fig. S4 (A) Fluorescent spectra of water-soluble 1830-QDs (black line) and 1830-QDs reacting with α -CD for 12 hours (red line), and (B) corresponding UV-vis spectra of 1830-QDs and 1830-QDs-CD. As can be seen, the fluorescent intensity obviously enhanced twice compared with 1830-QDs.

Reference

- [1] W. K. Bae, K. Char, H. Hur, S. Lee, *Chem. Mater.* 2008, **20**, 531.