

Supplementary Information for

Supramolecular Control of Complexation Induced Fluorescence Change of Water-Soluble, β -Cyclodextrin-Modified CdS Quantum Dots

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Materials: Cadmium acetate dihydrate (98%), thiourea (99+%), *N,N*-dimethylformamide (99%, DMF), 1-adamantanecarboxylic acid (99%) were purchased from Acros. (Dimethylaminomethyl)ferrocene, ferrocenecarboxylic acid, ferrocenemethanol were purchased from Aldrich. D₂O was supplied by Cambridge Isotope Laboratories. β -cyclodextrin is donated from Cerestar. The synthesis of perthiolated β -cyclodextrin was followed by the previous report (see reference 7). The compound was fully characterized before using. All aqueous solutions were prepared by deionized water (18.1 M Ω -cm), which is passed through a four-cartridge Barnstead Nanopure II system.

Synthesis and purification of CdS quantum dots modified with perthiolated β -cyclodextrin: For a typical preparation, 25 mL of DMF containing 145 mg of cadmium acetate, 60 mg of thiourea and 120 mg of perthiolated β -cyclodextrin was refluxed under N₂ atmosphere for 10 hours. The reaction was then naturally cooled down to the room temperature. 120 mg of perthiolated β -cyclodextrin was added to the reaction mixture. The reaction was stirred under the N₂ atmosphere for one day. The DMF was removed under vacuum. The residue was re-dissolved in water and transferred to a dialysis tube. The purification of CdS quantum dots was carried out in a basic aqueous solution (pH = 12) under the N₂ atmosphere. The final solution containing CdS quantum dots inside the dialysis tube was neutralized by dialysis with neutral water. The purified CdS quantum dots were dried under the vacuum at room temperature. The final product was bright yellow powder.

TEM measurements: The TEM and HRTEM measurements were carried out on a JEOL4000FX. A few drops of CdS QD aqueous solution was transferred onto a carbon coated copper grid. The water was naturally evaporated at room temperature. The TEM and HRTEM images were obtained at 100 and 200 KeV acceleration voltages respectively. The typical images are shown in Figure 1 in the text. The size population was obtained by measuring over 100 particles from TEM images (Figure S4).

¹H NMR: ¹H NMR spectra (400 MHz) were recorded with a Varian UI400 NMR spectrometer. ¹H NMR spectra (Figure S1) of free β -CD and surface-anchored β -cyclodextrin was obtained from a D₂O solution containing either free β -CD or perthiolated β -cyclodextrin modified CdS QDs which are very similar with the results from perthiolated β -cyclodextrin modified gold nanoparticles reported previously (reference 8).

Electrochemistry Study: Square wave voltammograms (SWV) of solutions containing the ferrocene derivatives in the absence and in the presence of surface-modified CdS QDs were recorded with a CHI420 electrochemical analyzer. The experiments were done in a single-compartment glass cell fitted with a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode. The parameters used to generate the excitation function for SWV measurements were as follows: step size, 4 mV; pulse amplitude, 25 mV; frequency, 15 Hz. All experiments were carried out at room temperature in aqueous solution containing 0.1 M NaCl as the supporting electrolyte. The solutions were deoxygenated before measurements. Figure S2 shows the typical study of **FC1**.

Photon Correlation Spectroscopic (PCS) Experiments. A Coulter N4-Plus instrument was utilized to monitor the stability of surface-modified CdS QDs in aqueous solutions at room temperature. The scattered light was detected at 90° from the incident beam. The viscosity and refractive index of the CdS QD solutions were taken as identical to the values of the pure water. The particle size population of CdS QDs in the aqueous solution was not obtained from PCS measurement since the average particle diameter (4 nm from TEM) was below the detection limit of this technique. Thus, the stability of CdS QDs in aqueous solutions was monitored by checking whether these particles formed large aggregates with the time. No any signals were detected in size range between 4 nm to 1000 nm after the same solution stayed in the dark for two weeks.

UV-Vis Spectroscopic Measurements. Electronic absorption spectra of surface-modified CdS QDs in aqueous solutions were recorded with a HP8452A diode array spectrophotometer at room temperature. The stability of β -CD/CdS QD aqueous solutions was monitored by comparing their absorption spectra in a two-week period (Figure S5).

Fluorescence study. The steady-state fluorescence spectra of β -CD/CdS QD in aqueous solutions at room temperature were recorded on a Spex Fluorolog 1681 fluorophotometer controlled by DM 3000 controller. Figure 2 gives the fluorescence study of β -CD/CdS QD with ferrocene derivatives. Figure S3 provides the information about the effect of hydroquinone on the fluorescence of β -CD/CdS QDs.

Figure S1

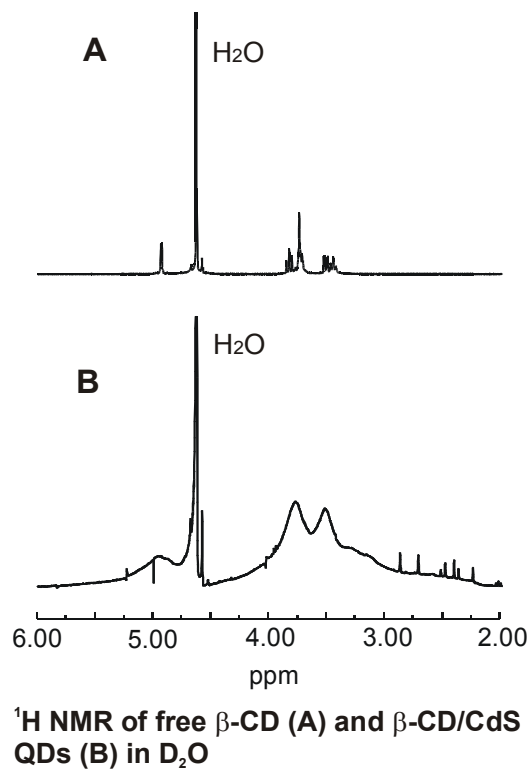
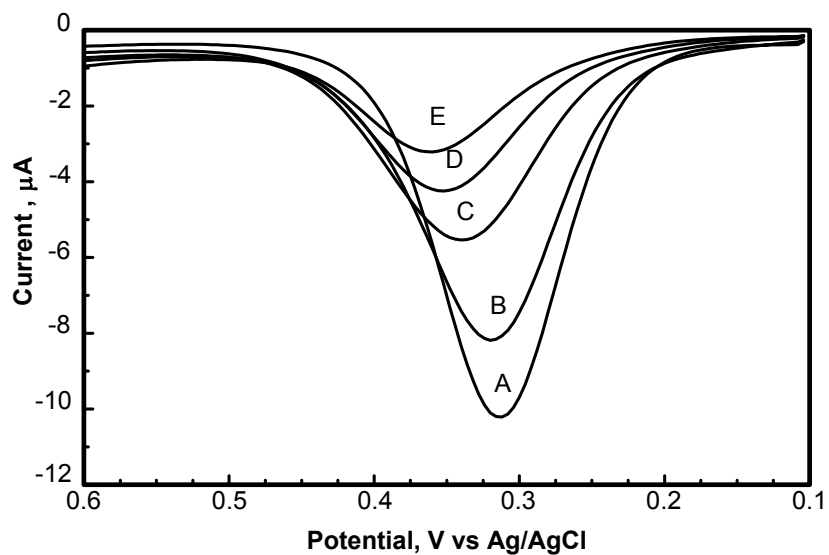
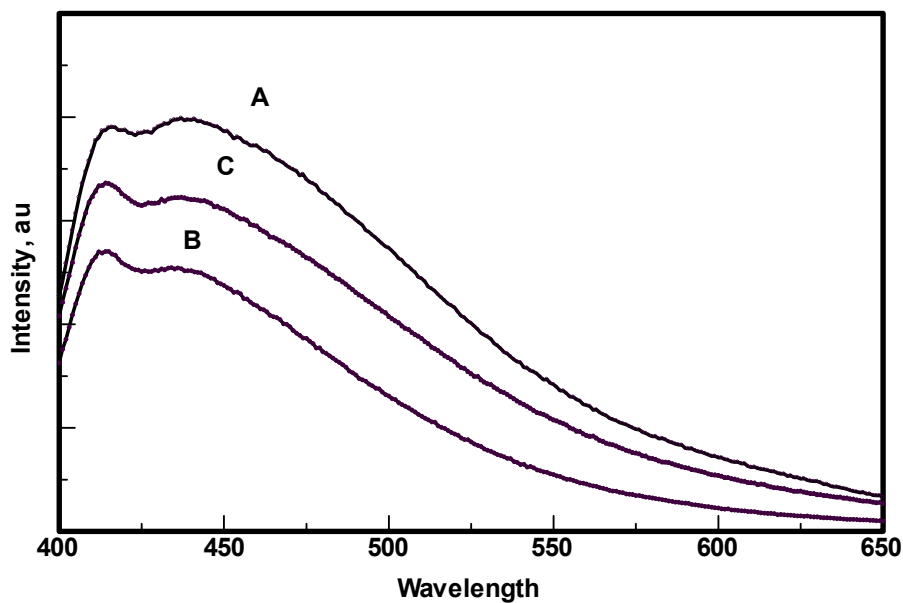


Figure S2



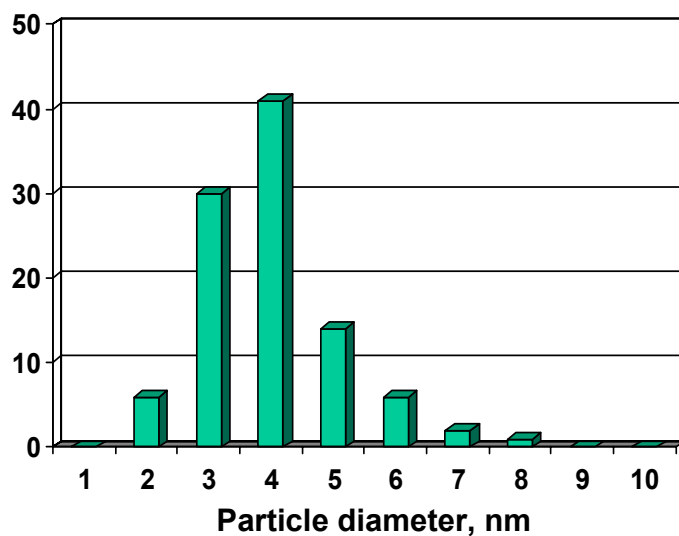
Electrochemical response (SWV) of FC1 (0.2 mM) in the presence of (A) 0 mg/mL; (B) 1.2 mg/mL; (C) 3.4 mg/mL; (D) 6.4 mg/mL and (E) 10.6 mg/mL of $\beta\text{-CD/CdS}$ QD in a 0.1 M NaCl aqueous solution at room temperature.

Figure S3



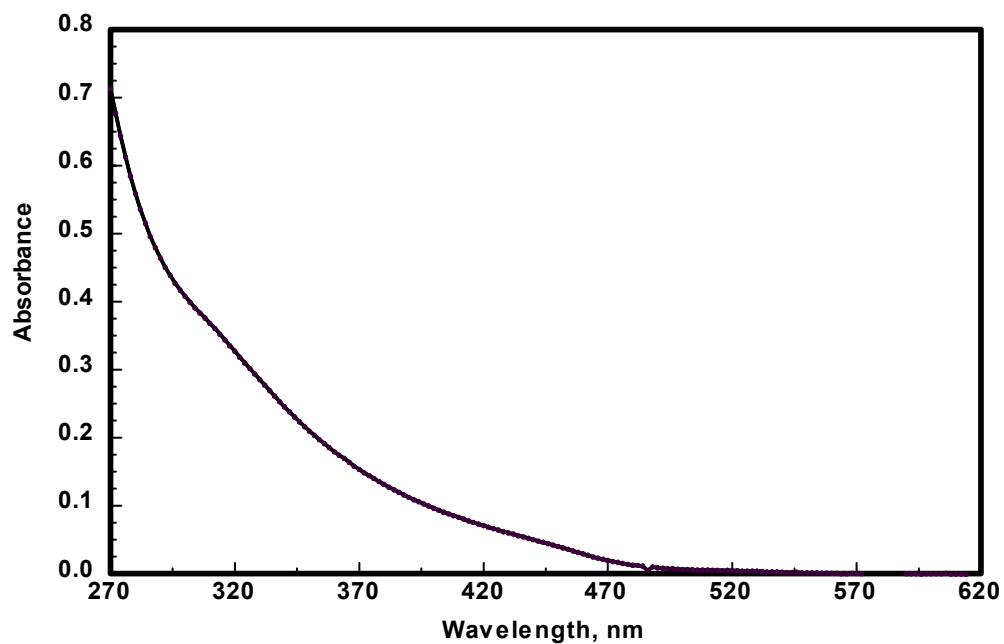
Photoluminescence of β -CD/CdS QDs. (A) Pure β -CD/CdS QDs aqueous solution; (B) in the presence of 1 mM of hydroquinone and (C) in the presence of 1 mM of hydroquinone and 2 mM of AD. The concentration of β -CD/CdS QD in all measurements was 0.1 mg/mL.

Figure S4



Relative particle size abundance (%) of β -CD/CdS QDs from TEM measurements

Figure S5



Electronic absorption spectra (overlapped) of a β -CD/CdS QD aqueous solution before and after two-week aging in the dark.