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Supramolecular control of complexation-induced fluorescence change of water-soluble, β-cyclodextrin-modified CdS quantum dots†

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The fluorescence of β-cyclodextrin-modified CdS quantum dots can be reversibly tuned by introducing different substrates in aqueous media.

There is growing interest in using size-dependent optoelectronic properties of semiconductor quantum dots (QDs) for chemical and biological applications.[1,2] For example, surface-modified QDs were used as fluorescent probes for DNA hybridization and conformation change.[3] Another area of focus is to utilize analyte-induced fluorescence change as a general approach for the development of QD-based fluorescence sensors.[4] But, controlling the fluorescence change of QDs by reversibly binding the analytes on particle surfaces is still a big challenge.[5] This Communication addresses this issue by using β-cyclodextrin (β-CD)-modified CdS quantum dots (β-CD/CdS-QDs) as a proof-of-concept fluorescence sensor system. In this study, the fluorescence of water-soluble β-CD/CdS-QDs is tuned through non-covalent interactions between the surface-anchored artificial host and the molecular guest on the CdS surfaces providing a novel example of QD-based heterosupramolecular systems as fluorescence sensors.

A one-pot approach has been developed for the preparation of β-CD/CdS-QDs. Briefly, a dimethylformamide (DMF) solution containing cadmium acetate, thiourea and perthiolated β-CD[6] (PSH-β-CD, Chart 1) was refluxed for several hours under a N_2 atmosphere (ESI†). Particle formation was evidenced by the appearance of a bright yellow color in the reaction mixture. After the introduction of more PSH-β-CD at room temperature, the reaction mixture was stirred for one day and the DMF then removed under vacuum. The solid residue was re-dissolved in water and purified by dialysis. The final β-CD/CdS-QDs were obtained as a bright yellow powder. As expected, these particles were very soluble in water yielding a stable, clear solution for several weeks as monitored by Photon Correlation Spectroscopic (PCS) and UV-vis measurements (ESI†). The quantum yield of these particles in aqueous solution was estimated as 0.02 by using fluorescein as the standard.[7] The broad ^{1}H NMR signals afforded by β-CD/CdS-QDs in D_2O (ESI†) unequivocally indicate the surface attachment of β-CD on CdS QDs.[6,8] The average particle size obtained from TEM measurements (Fig. 1, and ESI†) is 4 nm in diameter. The surface coverage of β-CD on the particles was estimated as 80% by elemental analysis.

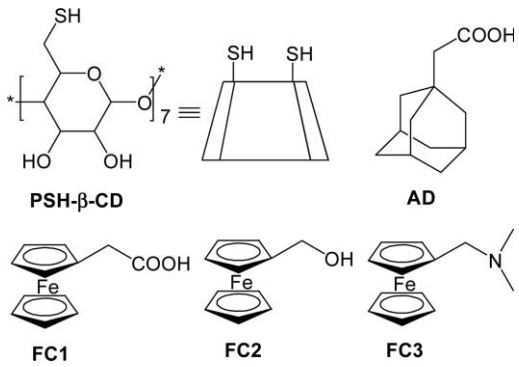

Chart 1

We then wished to use these β-CD/CdS-QDs as a prototype to test if we can reversibly tune the fluorescence of QDs by introducing host–guest recognition at the particle surfaces. Several organic molecules were used to test this concept since they are excellent guests for complexation with β-CD (Chart 1).[9] As expected, surface-anchored β-CDs on CdS QDs still retain their host capability to include molecular guests in their hydrophobic cavities. In a set of square wave voltammogram (SWV) studies, the half-wave potential of **FC1** (ESI†) shifted to more positive value as β-CD/CdS-QDs were introduced. Simultaneously, the peak current was dramatically reduced. This finding is consistent with the previous reported by Kaifer and co-workers on β-CD-modified gold nanoparticles.[6] The ^{1}H NMR study of **FC1** in the presence or absence of β-CD/CdS-QDs in D_2O also showed a similar result to that observed from β-CD-modified gold nanoparticles.[8]

Irradiation (360 nm) of these particles in water led to a typical two-band fluorescence emission (Fig. 2, line A), which was also seen in other QD systems.[3b] The sharp band centered at 410 nm is attributed to the band-edge emission. A broad band ranging from 430 to 630 nm is believed to be from trap-state emissions. Addition of 1 mM of **FC3** caused a significant decrease in the band-edge emission (Fig. 2, line B). However, introduction of the same amount of 1-adamantanecarboxylic acid, **AD**, being an excellent guest for β-CD, did not change the fluorescence under identical conditions. It is noted that these surface-modified CdS QDs can '*selectively*' respond to different analytes by the change in fluorescence emission although both **AD** and **FC3** are effectively complexed with β-CD on particle surfaces. This unique selectivity was employed to *reversibly* tune the fluorescence of the CdS QDs. Addition of 2 mM of **AD** in a β-CD/CdS-QD solution containing 1 mM of **FC3** led to the recovery of 90% of the original fluorescence of the CdS QDs in the absence of **FC3**. (Fig. 2, line C). Since **AD** is an excellent guest for the complexation with β-CD, the **FC3** molecules were replaced by **AD** inside the surface-anchored β-CD cavities (Scheme 1) resulting in a decrease in the total concentration of **FC3** on the particle surface. Thus, the fluorescence of

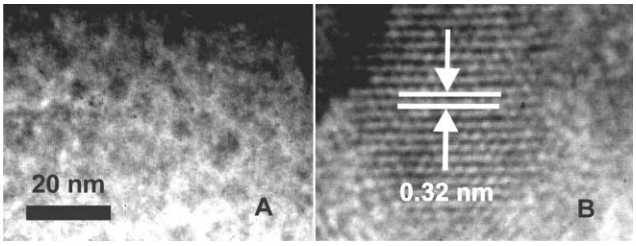

Fig. 1 TEM (A) and HRTEM (B) of β-CD/CdS-QDs.

† Electronic supplementary information (ESI) available: detailed preparation and characterization of β-CD-modified CdS nanoparticles. See http://www.rsc.org/suppdata/cc/b4/b409075f/

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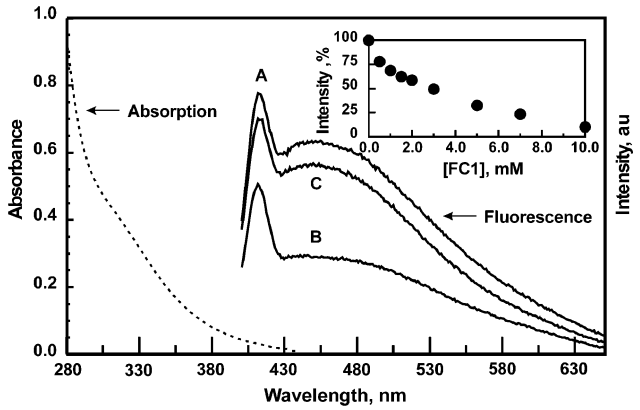
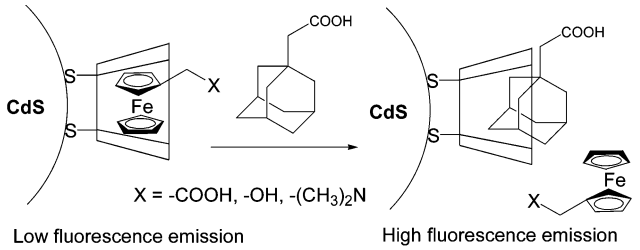


Fig. 2 UV-vis absorption (dotted line) and photoluminescence (solid lines) of β-CD/CdS-QDs. (A) Pure β-CD/CdS-QD aqueous solution; (B) in the presence of 1 mM of **FC3**; and (C) in the presence of 1 mM of **FC3** and 2 mM of **AD**. Inset: fluorescence (normalized) of β-CD/CdS-QD with respect to the concentration of **FC1**. The concentration of β-CD/CdS-QD in all measurements was 0.1 mg mL^{-1}.



Scheme 1

β-CD/CdS-QDs can be *reversibly* tailored by the introduction of host–guest chemistry on the surfaces of these particles.

It is noted that major approaches used to alter the fluorescence of QDs in previous reports were the direct physical adsorption or chelation of metal ions on their surfaces.[4,10] Thus, the current study provides the first case of using neutral molecules for reversible control of the fluorescence of QDs in aqueous solutions. The non-covalent interactions of different guest molecules with β-CDs on CdS QDs are the mechanism for the control of the fluorescence intensity of β-CD/CdS-QDs in aqueous solutions. Interestingly, the complexation of **FC1** inside the surface-anchored β-CD on CdS surfaces also dramatically changed the fluorescence emission. The fluorescence response of CdS QDs with respect to the concentration of **FC1** showed a typical binding isotherm. Up to 95% of its original intensity was diminished when 10 mM of **FC1** existed in a β-CD/CdS-QD aqueous solution (Fig. 2, inset).

In some early studies,[11] triethylamine was used as an electron donor for the enhancement of fluorescence emission by modifying surface defects on CdS. But this effect was not observed from a β-CD/CdS-QD aqueous solution. As discussed before, both **AD** and **FC1** contained a carboxyl group but only **FC1** acted as an effective quencher. Therefore, we believe that the carboxyl group is not a key factor to the fluorescence quench. Addition of **FC2** into a β-CD/CdS-QD aqueous solution also caused a similar decrease in fluorescence emission under identical experimental conditions even though it has a different functional group from **FC1** and **FC3**. Since these three ferrocene derivatives have different functional groups, we conclude that the fluorescence quench in this study was not due to the direct physical adsorption of these analytes with a specific functional group. Instead, the nature of the ferrocene, being a redox-active moiety in three ferrocene derivatives, may play a key role in the interaction with CdS QDs leading to the fluorescence quench. It should be noted that such reversible control of the fluorescence of β-CD/CdS-QDs can be achieved not only by the ferrocene/adamantane pair, but also by other guest molecules.‡ Addition of hydroquinone in a β-CD/CdS-QD aqueous solution caused a decrease in the fluorescence intensity of QDs, very similar to the cases that occurred in the presence of the ferrocene derivatives (ESI†). The fluorescene of this solution was recovered after the introduction of **AD**. A detailed study on the quench mechanism is currently in progress and will be reported in due course.

In summary, we have prepared water-soluble, β-CD-modified CdS QDs. The surface-immobilized β-CDs still retain the capability of engaging molecular recognition at QD surfaces in aqueous solutions. In addition, these receptor-modified QDs have been successfully employed as a proof-of-concept system to selectively and reversibly control the analyte-induced fluorescence change of QDs by introducing host–guest chemistry on these particles. The extension of the molecular recognition concept to other QD systems with different receptors may lead to the development of practical heterosupramolecular systems for chemical and biological sensing in aqueous media.

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Notes and references

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