Sonochemical Synthesis of Cyclodextrin-Coated Quantum Dots for Optical Detection of Pollutant Phenols in Water

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A simple, rapid sonochemical procedure for the preparation of highly fluorescent and water-soluble CdSe/ZnS quantum dots (QDs) using α-, β-, and γ-cyclodextrin (CD) as surface-coating agents is reported. The water-soluble QDs were characterized by luminescence spectroscopy, UV−vis spectroscopy, FT-IR spectroscopy, NMR spectroscopy, and transmission electron microscopy (TEM). The quantum yields (QYs) of α-CD-QDs, β-CD-QDs, and γ-CD-QDs in water were about 45, 39, and 27%, respectively. The *n*-CD-QDs allow highly sensitive determination of phenols by changing CD coating via fluorescence intensity quenching. The α-CD-QDs and β-CD-QDs are sensitive toward *p*-nitrophenol and 1-naphthol, respectively. Under optimal conditions, the relative fluorescence intensities of α-CD/CdSe/ZnS QDs and β-CD/CdSe/ZnS QDs both decreased linearly with increasing *p*-nitrophenol and 1-naphthol in the concentration range of 0.01−100 μM, with the corresponding detection limits (3σ) of 7.92×10^{-9} and 4.83×10^{-9} M, respectively. However, the sensitivity of *n*-CD-QDs toward other phenols, including *o*-nitrophenol, *m*-nitrophenol, 2-naphthol, *o*-cresol, *m*-cresol and *p*-cresol, are negligible. It is found that *p*-nitrophenol and 1-naphthol can quench the luminescence of α-CD-QDs and β-CD-QDs in a concentration-dependent manner that is best described by a Stern−Volmer-type equation. The possible underlying mechanism is discussed.

Introduction

Semiconductor quantum dots (QDs) with superior optical and electronic properties have gained increasing attention in materials chemistry in recent years.[1,2] The QDs have been used widely as fluorescence probes in biology and medicine, and more recently in analytical chemistry. It is known that molecular recognition structures are powerful tools for organizing nanoparticles in solution.[3,4] Introduction of an organic ligand onto the surface of nanoparticles affords the stability of these nanoentities in different solvents and the desired surface functionality.[5] Therefore, it is expected that a chemical sensing system based on QDs can be developed using fluorescence changes induced by molecular recognition at the surface of QDs.[6] Within this scheme, artificial receptor-modified nanoparticles are an interesting research topic.[7,8] For instance, Chen and co-workers have synthesized 15-crown-5 functionalized CdSe/ZnS QDs as a sensing unit toward K^+ in aqueous solution.[9] Calixarene-modified CdTe with a highly sensitive determination of PAHs[10] and pesticides[11] was synthesized by our group. Cyclodextrins (CDs) are cyclic oligosaccharides that consist of six, seven, or eight glucopyranose units in α, β, and γ forms, respectively. They are well-known for forming an inclusion complex with various guest molecules because of their special molecular structure—hydrophobic internal cavity and hydrophilic external surface.[12,13] Thus, CDs have attracted great interest in supramolecular chemistry. CDs and CD derivatives have been used in the modification of TiO_2 and CdS colloids,[14,15] gold, platinum, and palladium nanoparticles,[16−20] and in the phase transfer of oleic acid-stabilized iron oxides and silver from organic solutions to aqueous media through the formation of inclusion complexes with α-CD.[21] Liu and co-workers found that CdS and CdSe/CdS QDs could be modified by monothiolated β-CD to achieve good water

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solubility.[22,23] However, the synthesis of thiolated CD is difficult and the fluorescence property of CD-coated QDs for molecule recognition has not been fully explored. We have synthesized water-soluble QDs by a simple sonochemical method using parent CDs as surface-coating agents. A fluorescence chemosensor resulting from molecule recognition on the surface of QDs has been developed.

Phenols are found in disinfectants and antiseptics, and are widely used as intermediates of dyes in organic synthesis processes; consequently, they have a high potential for environmental pollution. The environmental concern results from the high level of toxicity of phenols to mammals, fish and other aquatic organisms. Hence, the detection of trace amounts of phenols is very important for evaluating the total toxicity of an environmental water sample. Several methods, such as liquid chromatography,[24,25] gas chromatography,[26,27] and capillary electrophoresis,[28] have been used for detection of phenols in water samples are described in the literature. However, these techniques usually require complicated sample pretreatment and are not suitable for continuous on-site monitoring. Fluorescence detection has been used extensively as an analytical technique with high levels of sensitivity and selectivity. To the best of our knowledge, the use of CD-functionalized QDs as selective probes for fluorescence determination of phenols is almost unexplored.

Here, we report the synthesis of the water-soluble semiconductor CdSe/ZnS QDs by a simple sonochemical method using α-, β-, and γ-CDs as surface-coating agents. Their potential application as selective fluorescent probes for the determination of phenols by changing the surface-coating layer with different CDs was investigated.

Experimental Section

Materials and Reagents. All chemicals used were of analytical grade or of the highest purity available. Cadmium oxide (99.99%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 90%), selenium powder (99.99%), hexamethyldisilathiane ($(TMS)_2S$), and α- and γ-cyclodextrin were purchased from Aldrich (Milwaukee, WI,). Hexylphosphonic acid (HPA) was obtained from Alfa Aesar (Karlsruhe, Germany). β-Cyclodextrin was purchased from Tianjin Chemical Factory, China. *o*-Nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 1-naphthol, 2-naphthol, *o*-cresol, *m*-cresol and *p*-cresol were obtained from Shanghai Chemical Factory, China. All phenol samples were prepared with water and stored at room temperature. The water used in this experiment was purified by distillation of deionized water.

Characterization. UV−vis absorption spectra were acquired with a TU-1901 UV−vis spectrometer (Beijing Purkinje General Instrument Co. Ltd.). Fluorescence spectra were obtained with a Fluoromax-P luminescence spectrometer (HORIBA Jobin Yvon Inc.). IR spectra were measured with a NEXUS FT/IR spectrometer (Thermo Nicolet Co.). Transmission electron micrographs (TEM) were recorded with a JEOL-JEM 2010 electron microscope operating at 200 kV. The ^{31}P NMR spectra were recorded at 162 MHz on a Varian Mercury 400 spectrometer with H_3PO_4 as external standard.

Preparation of CdSe/ZnS QDs. The synthesis of TOPO-capped CdSe QDs was essentially as described by Peng and co-workers,[29] but with some slight modifications. Briefly, 0.03 g of CdO (0.233 mmol), 0.11 g of HPA, and 3.5 g of TOPO were mixed together and heated at 300−320 °C under a flow of argon for 15−20 min, and CdO was dissolved in HPA and TOPO. The solution of selenium was injected swiftly and a change of solution color to red was observed. After injection, CdSe nanocrystals were left to grow for about 20 min at 250 °C. Then, the precursors prepared from $(TMS)_2S$ and $Zn(AcO)_2$ were added dropwise into a freshly prepared solution of CdSe at 200 °C.[30] Thus, the CdSe/ZnS core/shell quantum dots were prepared in TOPO as the solvent. The TOPO-QDs were purified by precipitation in anhydrous methanol and centrifugation. The precipitate was washed with anhydrous methanol to remove residual TOPO.

Preparation of *n*-CD QDs. The *n*-CD QDs were prepared by the following sonochemical method. Briefly, 0.5 mg of TOPO-capped CdSe/ZnS QDs was dispersed in 1 mL of anhydrous ethanol and 5.29 μmol of CD powder was added. The mixture was placed in a high-intensity ultrasonic bath (Xinzhi Co., Xinzhi, China; SB−120D, 120 W) for about 30 min at room temperature. When the reaction was finished, a rosy precipitate was obtained. The precipitate was separated by centrifuging at 10 000 rpm for 5 min. The final product was purified further by cycles of centrifuging in water to remove unreacted cyclodextrins and dispersed in 20 mL of water for further investigation.

Results and Discussion

Characterizations of *n*-CD/CdSe/ZnS QDs. The UV−vis spectra of the CD-QDs are shown in Figure 1. There is no difference in the position or width of the absorbance bands at 575 nm from hydrophobic QDs, which suggests that the modified CD-QDs in water retain the optical properties of the original QDs. The inset shows the fluorescence (FL) spectra of *n*-CD-QDs in water and TOPO-QDs in chloroform. The FL spectra of CD-QDs exhibit no obvious shift in emission wavelength. The quantum yields (QYs) of *n*-CD-QDs ($n = \alpha, \beta$, or γ) in water were measured in comparison with the value of rhodamine B (QY = 89%, EtOH) as a criterion at room temperature, which were about 45, 39, and 27%, respectively. The TEM images (Figure 2) demonstrate that the sizes of the hydrophobic QD particles and α-CD QDs are virtually identical, indicating that the modified particles are monodisperse and uniform in water. Similar phenomena were observed for β-CD QDs and γ-CD QDs (see the Supporting Information, Figure S1).

Spectra A and B in Figure 3 depict typical transmission IR spectra of parent β-CD and β-CD-capped CdSe/ZnS QDs, respectively. The gross resemblance in both spectral features and peak positions for several vibrational modes guarantees a successful attachment of CD onto CdSe/ZnS QDs. For example, the strong band at 1157 cm^{-1} corresponds to the

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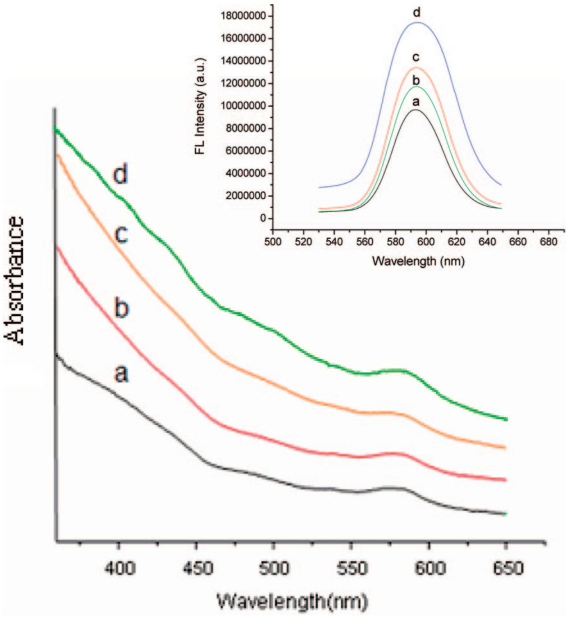

Figure 1. UV−vis spectra of (a) TOPO-coated CdSe/ZnS QDs in chloroform, (b) α-CD-CdSe/ZnS QDs in water, (c) β-CD-CdSe/ZnS QDs in water, and (d) γ-CD-CdSe/ZnS QDs in water. The inset shows fluorescence spectra of (a) γ-CD/CdSe/ZnS QDs in water, (b) α-CD/CdSe/ZnS QDs in water, (c) β-CD/CdSe/ZnS QDs in water, and (d) CdSe/ZnS QDs in chloroform (Ex: 450 nm).

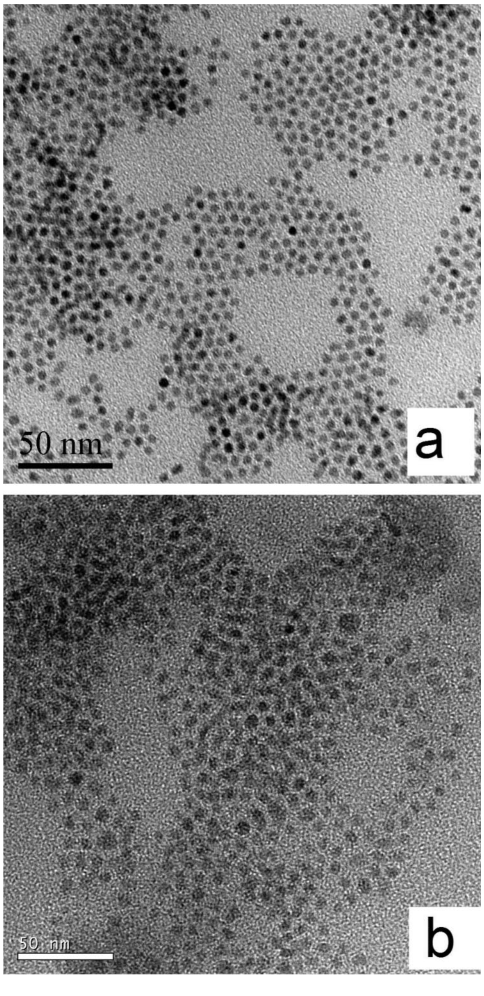

Figure 2. TEM images of (a) original CdSe/ZnS QDs in CHCl$_3$, (b) α-CD/CdSe/ZnS QDs in water. All scale bars are 50 nm.

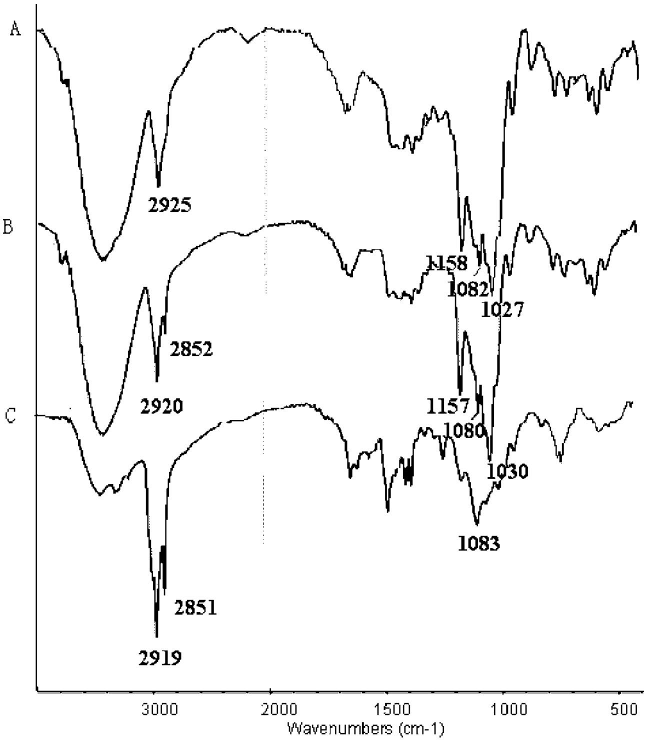

Figure 3. IR spectra of (A) pure β-CD, (B) β-CD/CdSe/ZnS QDs sample, and (C) TOPO-capped CdSe/ZnS QDs.

asymmetric glycosidic vibration v_{a} (C—O—C); the bands at 1080 and 1030 cm^{-1} correspond to the coupled stretch vibration, v(C—C/C—O); and the broadband at 3400 cm^{-1} arises from the O—H vibrations. The appearance of this IR band and those in the fingerprint regions indicate clearly that CDs cannot be removed from the solid materials by extensive washing with deionized water; thus, β-CD molecules have covered the surface of the particles after the phase transfer process. However, the IR spectrum of β-CD-capped CdSe/ZnS QDs seems to have subtle differences from the CD, which can be assigned qualitatively to TOPO (see Figure 3C). It is worth pointing out that the shift at 1030 cm^{-1} of the C—C/C—O stretch vibration in the spectrum of the β-CD/CdSe/ZnS QD complex[31,32] and the typical symmetric stretch peak of the alkyl chain of TOPO (2852 cm^{-1}), missing in the case of pure β-CD, are indicative of an inclusion-type interaction for the β-CD/ TOPO-CdSe/ZnS QDs complex. This result indicates that TOPO exists in the CD-capped CdSe/ZnS QDs, although the peak of P═O at 1083 cm^{-1} for TOPO is overlapped by v(C—C/C—O) coupled stretch vibration (1080 cm^{-1}).

A ^{31}P NMR experiment was conducted to afford more insight into the surface of CD-QDs (see the Supporting Information, Figure S2). A ^{31}P signal observed at 36 ppm, which is different from the ^{31}P signals of free TOPO ligand (47 ppm) and TOPO-capped QDs (25 ppm),[33] corresponds to TOPO after modification with CD. The ^{31}P signal of QDs shifts to 36 ppm, may be because phosphorus chemical

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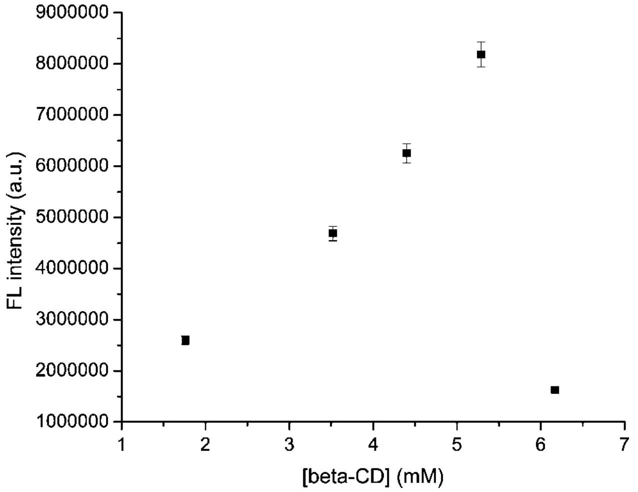

Figure 4. Effect of dosage of β-CD on the fluorescence intensity of β-CD/CdSe/ZnS QDs (Ex: 450 nm).

environments of TOPO changed to TOPO-CD complexes formed on the surface of QDs.

Preparation of *n*-CD QDs. The phase transfer of the QDs was conducted by ultrasonic irradiation of a mixture of TOPO-coated CdSe/ZnS QDs and CD in anhydrous ethanol. This method is based on the formation of a host−guest complex between the passivated ligand (TOPO) and CD by hydrophobic interaction. Ethanol was used as the solvent for this reaction, since the CD inclusion complex is very unstable in low polarity such as chloroform. Other polar solvents including acetonitrile, methanol, and tetrahydrofuran also worked. The control experiments that use conventional heating were carried out. However, these methods failed to transfer QDs to the aqueous solution.

The dosage of CD has an important effect on the quality of *n*-CD-QDs. The fluorescence intensity increases dramatically with increasing dosage of CD. Beta-CD was added to a solution of 0.5 mg/mL of CdSe/ZnS QDs in anhydrous ethanol to final concentrations of 1.76, 3.52, 4.40, 5.29, and 6.17 mM in the resulting CD QD aqueous solution. Figure 4 shows that the dosage of β-CD has an important effect on the fluorescence of the QDs after phase transfer. At a low dosage of β-CD (1.76, 3.52, and 4.40 mM), translucent suspension was obtained only after phase transition. In these cases, although some CdSe/ZnS QDs were transferred into the aqueous phase, many of the transferred particles were not stable. As the dosage of β-CD increased in the range 4.93−5.64 mM, stable and transparent QDs were obtained in aqueous solution. When the dosage of CD was very high (6.17 mM), although phase transfer was achieved efficiently, the resulting complex was found to be unstable in water, because high CD concentration would induce the resulting QDs aggregated caused by plenty of CD concentrated at the QDs surface. A similar phenomenon was observed when α-CD and γ-CD were used as surface-coating agents.

There have been a number of studies of the effects of surface ligand adsorption on the luminescence of quantum dots.[34−37] Ginger and co-workers reported that addition of alkylamines to CdSe quantum dots resulted in both quenching and enhancement, depending on the concentration of the amine.[38] These results are compatible with our CD concentration-dependent experiments. At concentrations of CD between 0.88 and 5.29 mM, the FL intensity of the resulting CD-QD increases with increasing concentration of CD. We adopted the basic Langmuir model to describe the data (see the Supporting Information, part C), and calculated the surface coverage at various concentrations of CD. The surface coverage increases with increasing concentration of CD. Under optimal conditions, the surface coverage is 65% at 5.29 mM β-CD, and 5.29 mM CD was chosen to modify the QDs in all experiments.

The results obtained in experiments using 0.5 mg/mL CdSe/ZnS QDs showed that an effective phase transfer was achieved in the case of a relatively high concentration of CD (4.93−5.64 mM). Under these conditions, a number of CD molecules are available for each QD and this can explain the more efficient complexation of alkyl chains.

It is known that CD is composed of hydrophobic cavities that can form inclusion complexes with various organic molecules with hydrophobic groups.[15] TOPO can be included by CD because of the interaction between the hydrocarbon tail of the former, and the hydrophobic cavity of the latter thus pulls QDs into water because of the hydrophilic outer cavity of CD. This concentration-dependent effect further suggests that formation of the complex between TOPO and CD is essential for the transfer of QDs to the aqueous phase. When the concentration of CD is too low, only small portions of surface-bound TOPO molecules on the surfaces of QDs form complexes with the CD, which is not sufficiently hydrophilic for the stabilization of nanoparticles in the aqueous phase. At relatively high concentrations of CD, substantial amounts of TOPO molecules could form host−guest complexes with CD, which lead to the increase of the stability of QDs in the hydrophilic medium.

Time-dependent experiments were performed by exposing a solution of CdSe/ZnS QDs and β-CD to ultrasonic irradiation for 20, 30, 40, and 60 min. The FL intensity and emission wavelength of CD QDs exhibit no significant difference.

Photostability of CD QDs. The stability of CD QDs in water is estimated by measurement of the emission intensity and the quantum yield as a function of time at 5 °C (see the Supporting Information, part E). The results showed that the CD QDs were stable for several days in water. The effect of pH in a range between 1 and 13 on the emission of CD QDs was examined (see the Supporting Information, part F), and it was found that the FL intensity of CD QDs in the pH interval 6.0−9.0 was very stable.

Detection of Phenols. Figure 5 shows the FL response of *n*-CD-QDs to 10^{-4} M phenols, including *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 1-naphthol, 2-naphthol, *o*-

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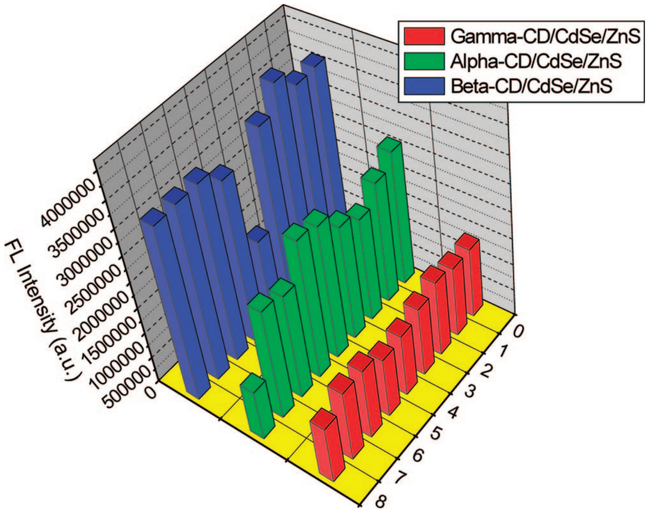

Figure 5. Effect of 1 × 10^{-4} M relevant phenols on the fluorescence of α-CD/CdSe/ZnS QDs, *β*-CD/CdSe/ZnS QDs, and *γ*-CD/CdSe/ZnS QDs (from 0 to 8: control, *o*-cresol, *m*-cresol, *p*-cresol, 1-naphthol, 2-naphthol, *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol). The fluorescence measurement was made at 10 min after phenol addition.

cresol, *m*-cresol and *p*-cresol. It was shown that *p*-nitrophenol and 1-naphthol can quench the luminescence of α-CD QDs and *β*-CD QDs, respectively; but all of the phenols had very little effect on *γ*-CD QDs.

Panels A and B in Figure 6 show the effect of increasing concentrations of *p*-nitrophenol on the fluorescence spectrum of the α-CD QDs, and 1-naphthol on the fluorescence spectrum of *β*-CD QDs, respectively. It was found that *p*-nitrophenol quenches the fluorescence of α-CD QDs, and 1-naphthol quenches the fluorescence of *β*-CD QDs in a concentration-dependent manner that is best described by a Stern−Volmer-type equation

$$I_{\max}/I = 1 + K_{\mathrm{sv}}[\mathrm{S}]$$

where I and $I_{\max}$ are the fluorescence intensities of the CD-QDs at a given related concentration of phenols and in a phenol-free solution, respectively. K_{SV} is the Stern−Volmer quenching constant, and [S] is the concentration of phenols. The dependence of $I_{\max}/I$ as a function of [S] is shown in Figures 7 and 8. The K_{sv} terms are 11 490 and 25 020 M^{-1}. The detection limits (DLs), calculated following the 3σ IUPAC criteria, are 7.92 × 10^{-9} M (0.69 ng/mL) and 4.83 × 10^{-9} M (1.10 ng/mL), which is the level of detection by current chromatographic techniques. For example, Ye and co-workers used HPLC-MS for the determination of nine phenols with DLs of 0.1−2 ng/mL.[24] GC-MS has been used for the detection of phenol compounds with the DLs in a range of 10−100 ng/L.[26]

In contrast to the typical Stern−Volmer quenching behavior driven by a collision between quencher and luminescent molecules, the quenching luminescence of the CD QDs is attributed to the fact that the phenol molecules can enter the cavity of the CD and compete with TOPO to form an inclusion complex. When the phenols are added into aqueous solution, they can be embedded into the cavities of CDs and destabilize the TOPO−CD complex, which leads to CDs being peeled off the surface of QDs and then TOPO-capped CdSe/ZnS QDs are exposed to water, and the fluorescence is quenched by water. The possible underlying mechanism is illustrated in Figure 9. When phenols were added to a CD QD solution, rosy precipitates could be observed by the naked eye on the bottom of the vial about 10 min later. It should be noted that the precipitates cannot be redispersed in water. The precipitates were washed several times with water, and confirmed by the FT/IR spectrometer (see the Supporting Information, Figure S7). The characteristic band associated with CD nearly disappears, suggesting that the precipitates have very few of the adsorbed CD remaining. This result provided further support for the proposed mechanism. Some published studies also indicate that the quenching mechanism deviates from Stern−Volmer behavior but is in accord with the Stern−Volmer equation. For example, Rosenzweig and co-workers reported that Cu^{2+} quenched the fluorescence of thioglycerol-capped CdS QDs by a redox reaction on the surface of QDs, and the quenched fluorescence intensity of thioglycerol-capped CdS QDs is dependent on the concentration of copper ions and can be best described by a Stern−Volmer type equation.[5]

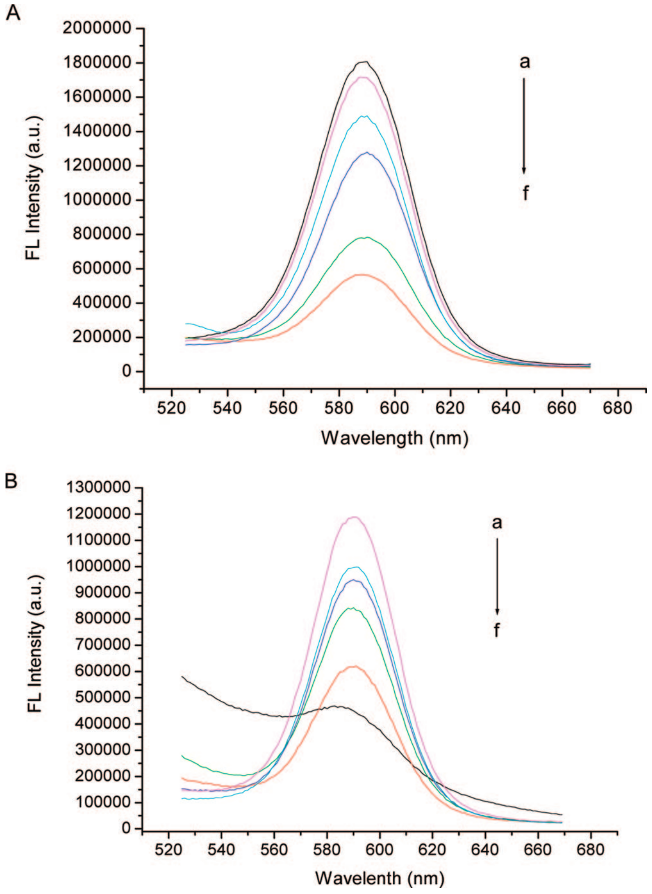

Figure 6. Effect of (A) *p*-nitrophenol concentration on the FL intensity of α-CD/CdSe/ZnS QDs and (B) 1-naphthol concentration on the FL intensity of *β*-CD/CdSe/ZnS QDs (from a to f: 0, 1 × 10^{-8}, 1 × 10^{-7}, 1 × 10^{-6}, 1 × 10^{-5}, 1 × 10^{-4} M).

The surface-tagged CD should have an important role in recognition of the phenols. Because of the fixed size of the cyclodextrin cavity, only guest molecules of the appropriate size and structure can be included in the cavity. Larger or smaller guests, or guests with an inappropriate structure, can achieve only partial inclusion, which results in weak supramolecular interaction. Among the CDs, α-CD has the smallest cavity and, in general, is selective toward single-

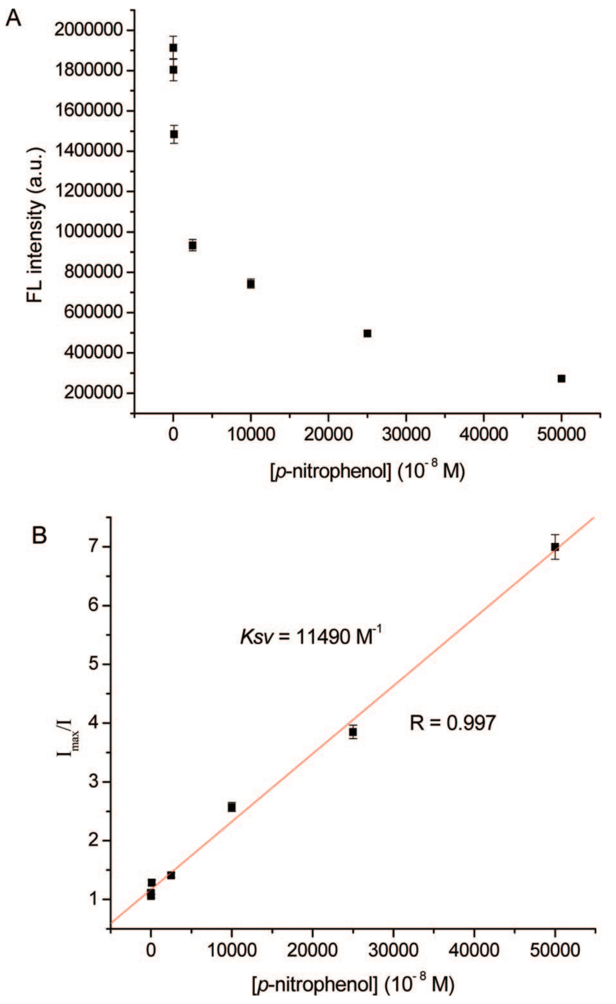

Figure 7. (A) Effect of *p*-nitrophenol concentration on the fluorescence of α-CD/CdSe/ZnS showing decreasing emission with increasing *p*-nitrophenol concentration. (B) Stern-Volmer plot of *p*-nitrophenol concentration dependence of the FL intensity with a 0.997 correlation coefficient.

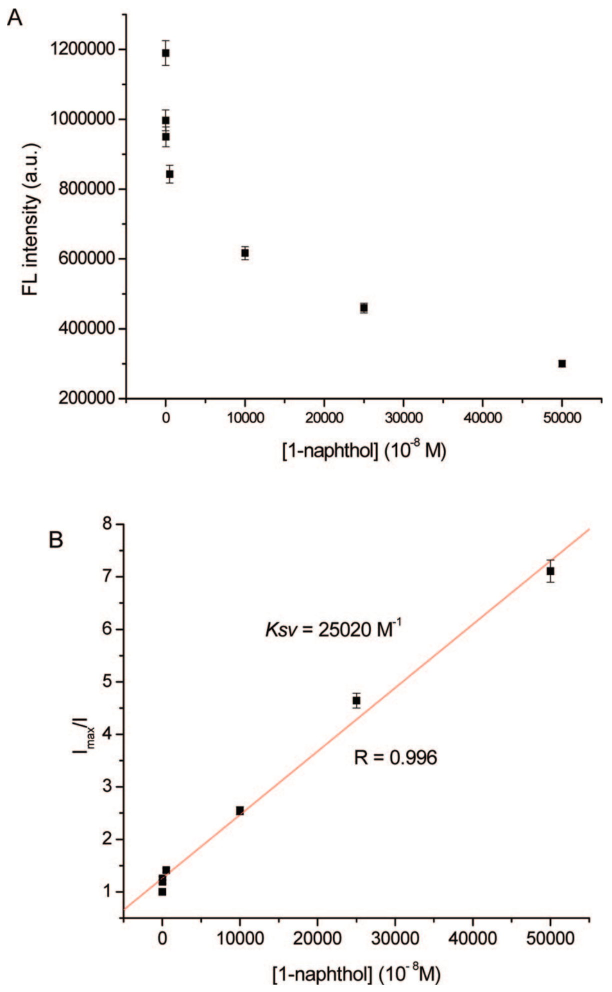

Figure 8. (A) Effect of 1-naphthol concentration on the fluorescence of β-CD/CdSe/ZnS QDs showing decreasing emission with increasing 1-naphthol concentration. (B) Stern-Volmer plot of 1-naphthol concentration dependence of the FL intensity with a 0.996 correlation coefficient.

ring aromatic compounds (i.e., nitrophenols), whereas β-CD with a larger cavity is more selective toward molecules containing two aromatic rings (i.e., naphthols), and γ-CD is more selective toward compounds containing three or more aromatic rings.[39,40]

The selectivity of structural isomers (*o*-, *m*-, and *p*-nitrophenols, 1- and 2-naphthols) can be explained by the binding constants (K_B) of CD/isomer complexes. According to the literature,[41] the K_B of nitrophenol/α-CD complexes with *o*-, *m*- and *p*-nitrophenols is 152.4, 135.1, and 628.5 M^{-1}, respectively. The K_B of *p*-nitrophenol with α-CD is higher than that of *o*- and *m*-nitrophenols. That is to say, *p*-nitrophenol is preferentially bound with α-CD than *o*- and *m*-nitrophenol. For *p*-nitrophenol, it can form a stable inclusion complex with α-CD because of the most compatible size and steric arrangement with the α-CD cavity, and the nitro group locates into the cavity with the hydroxyl groups interacting with the secondary hydroxyl of the cyclodextrin.[42] The stability constants (log *K*) for the supramolecular system formed by 1-naphthol/β-CD and 2-naphthol/β-CD are 3.07 and 2.7, respectively.[43] Therefore, it is reasonable to believe that the 1-naphthol/β-CD complex is more stable than the 2-naphthol/β-CD complex, which finally results in 1-naphthol selectively quenching the luminescence of β-CD modified QDs.

Detection of Prepared and Real Samples. The potential interference in phenol detection from coexisting species was studied in samples of *p*-nitrophenol and 1-naphthol, which were constructed by adding coexisting components to standard solutions. As shown in Table 1, the values for these two samples are identical with the expected values, and the recovery and relative standard deviation are very satisfactory. In addition, the synthesized nanoparticles were used to determine real samples. As can be seen in Table 2, the results are very close to those detected by HPLC and LC-MS. Compared with HPLC and LC-MS methods, the results obtained by these three methods are in good agreement, and the sensitivity of the present study was better. Therefore,

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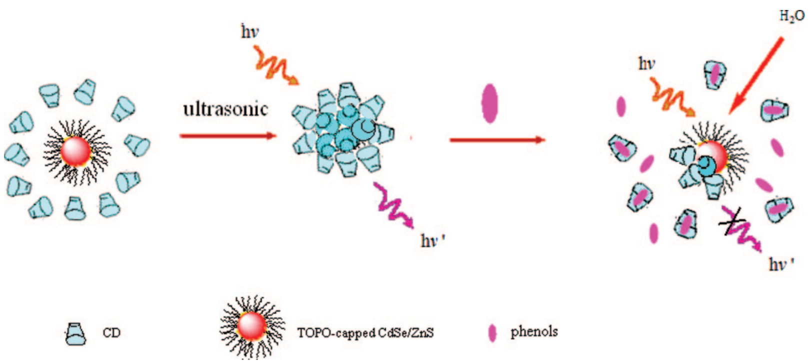

Figure 9. Possible mechanism of (A) *p*-nitrophenol quenching the fluorescence of α-CD/CdSe/ZnS QDs and (B) 1-naphthol quenching the fluorescence of *β*-CD/CdSe/ZnS QDs.

Table 1. Results of the Analysis of Prepared Samples[a]

			this method			
phenols	amount in sample (μg mL^{-1})	main interferents	amount found (μg mL^{-1})	average recovery (n = 5) (%)	R.S.D.(%)	amount found by HPLC (μg mL^{-1})
p-nitrophenol	2.5	phenols[b];	2.48	99.2	1.7	2.45
(α-CD QDs)	4.0	nitrobenzene; naphthalene; biphenyl	3.98	99.5	1.3	4.03
1-naphthol	2.5		2.55	102.0	2.5	2.52
(*β*-CD QDs)	4.0		3.92	98.0	1.9	3.97

[a] Concentration of each interferent, 3.0 μg mL^{-1}, pH 7. [b] Phenols: all phenols used in this work.

Table 2. Analytical Results for the Detection of Phenols in Real Samples[a]

	content of phenols (μg mL^{-1})		
sample	this method	HPLC	LC-MS
1	nd[b]	nd	nd
2	33.2	32.5	31.8
3	46.3	46.8	47.2

[a] Sample 1: lake water; wastewater sample 2 contains *p*-nitrophenol, wastewater sample 3 contains 1-naphthol. Wastewater samples were obtained from Chuyuan Fine Chem. Co. [b] nd means <DL.

the CD-QDs had a good specificity to phenols, and this method is applicable to the ultrasensitive and rapid detection of phenols.

Conclusion

We have presented a simple and convenient sonochemical method for the preparation of water-soluble and stable CdSe/ZnS QDs using cyclodextrins as surface-coating agents. The *n*-CD QDs have a high level of emission efficiency in aqueous solution. In this work, CDs were used as surface-coating agents of QDs, and as acceptors toward *p*-nitrophenol and 1-naphthol, thus affording a very sensitive detection system for analysis of phenol isomers. We believe that the surface architectures of QDs on introducing the CDs-based host−guest recognition would afford a variety of molecular sensing systems for chemical and bioanalytical sensing in aqueous media.[21]

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Supporting Information Available: TEM images of *β*-CD-QDs and *γ*-CD-QDs, approximate number of CD molecules on each quantum dot, synthesis of water-soluble CdSe QDs with different sizes using *β*-CD as surface-coating agents by sonochemical route, photostability of CD QDs, effect of pH on the luminescence response of CD QDs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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