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Electronic Supplementary Information

Cyclodextrin Capped CdTe Quantum Dots as Versatile Fluorescence Sensors for Nitrophenol Isomers

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Experimental

1. Materials

Tellurium (Te), cadmium chloride hydrate ($CdCl_2$•$2.5H_2O$), 3-mercaptopropionic acid (3-MPA) and three nitrophenols (ONP, MNP and PNP) were purchased from aladdin (Shanghai, China). Sodium borohydride ($NaBH_4$), thiourea and β-CD were purchased from Energy Chemical Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used directly without further purification. All aqueous solutions were prepared with deionized water.

2. Preparation of mono-6-thio-β-cyclodextrin-capped CdTe quantum dots

2.1 Synthesis of 6-thio-β-CD

Mono-6-deoxy-6-(p-tolylsulfonyl)-β-cyclodextrin (TsCD) was synthesized according to our previous protocol.[1] Upon twice recrystallization of TsCD with DI-water, thiourea (4.4 g, 57.8 mmol) and TsCD (4.0 g, 3.1 mmol) was added to a mixed solution of 80% (v/v, methanol-water).[2] The mixture was kept stirred and refluxed for 48 h. Then, the solvent was removed under vacuum and the white crude product was added into methanol (60 mL) and stirred for 1.5 h. After filtration, the white precipitate was obtained and further dissolved in 10% NaOH aqueous solution with stirring for 5 h at 50 °C. The mixture was then adjusted to pH 2.0 with 10% HCl after cooling to room temperature. Trichloroethylene (10 mL) was added to the solution with stirring for 3 h and the white solid was obtained after filtration. The crude product was recrystallized using water and acetone and dried under vacuum.

2.2 Synthesis of 3-MPA surface coated CdTe QDs

Under the protection of nitrogen, Te (31.3 mg, 0.3 mmol) and excess $NaBH_4$ (113.5 mg, 0.3 mmol) was added to oxygen-free DI-water (5 mL) in an ice-bath. An achromatic NaHTe solution was obtained after 4 h. Upon the NaHTe solution was completed, $CdCl_2 \cdot 2.5H_2O$ (68.5 mg, 0.3 mmol) was added in DI-water (100 mL) under stirring, followed by the addition of 26 μL of 3-mercaptopropionic acid (3-MPA) as stabilizer. The pH of the solution was adjusted to 8.0 using 1.0 mol/L NaOH solution. Then, the as-prepared NaHTe solution (1 mL) was injected to the mixture with stirring for 20 min to form 3-MPA stabilized CdTe precursors (the pH of colloid solution may reach ~10.0 after the addition of NaHTe).[3] The mixture was heated to 90 °C and refluxed under the nitrogen atmosphere for 1-6 h to obtain different particle size of 3-MPA capped CdTe QDs. The molar ratio of Cd^{2+}/3-MPA/Te^{2-} was 1:1:0.2.

2.3 Synthesis of mono-6^A^-thio-β-CD-capped CdTe QDs

$CdCl_2 \cdot 2.5H_2O$ (68.5 mg, 0.3 mmol) and 3-MPA stabilizer (26 μL 0.3 mmol) was added to 50 ml of deionized water and stirred for 10 min, followed by the addition of mono-6-thio-β-CD aqueous solution (172.7 mg in 50 mL of DI-water). The pH of the solution was adjusted to 8.0 by 1.0 mol/L NaOH solution. The whole system was deaerated with N_2 bubbling for 20 min before the injection of NaHTe solution (1 mL). After stirring for 20 min, the resulting mixture was refluxed at 90 ^oC under nitrogen atmosphere for 1-6 h to afford mono-6-thio-β-CD-capped CdTe QDs. The molar ratio of Cd^{2+}/3-MPA/mono-6-thio-β-CD/Te^{2-} was 1:1:0.5:0.2. The β-CD-capped CdTe QDs obtained at different reflux time exhibited different particle sizes.

2.4 Purification and photoluminescence measurement procedure

Both CdTe QDs and mono-6-thio-β-CD-capped CdTe QDs were centrifuged and washed with anhydrous ethanol and DI-water three times. The obtained powder was dried in a vacuum for 1 h and dissolved in phosphate buffer solution (0.2 M, pH 7.2) to the original volume. Nitrophenol isomers were dissolved in anhydrous ethanol and diluted to different normal concentration. In a sample vial (5 mL), 0.3 mL of the as-prepared QDs solution was added and diluted to 3 mL with phosphate buffer solution. Afterwards, 20 μL of anhydrous ethanol or nitrophenol isomer solution was added to the QDs solution. The mixture was shaken thoroughly and sonicated for 2 min. The sample solution was then transferred into 1.0 cm standard quartz cuvettes to record the photoluminescence spectrum. All samples were excited at 340 nm and the fluorescence emission signal was monitored at 546 nm or 572 nm. The excitation and emission slit widths were set at 3 nm and 1.5 nm, respectively.

3. Characterization.

The nuclear magnetic resonance (NMR) analysis was carried out on a Bruker AVANCE 500 (500 MHz, Bruker Daltonics, Bremen, Germany). The absorption spectra were obtained from an Evolution 220 UV-vis instrument (Thermo Fisher Scientific, USA). Fourier-transform infrared spectra (FTIR) were recorded on Thermo Scientific Nicolet iS-10 FT-IR (Thermo Fisher Scientific, USA). The morphology of samples was observed on a JEM–2100 transmission electron microscope (JEOL, Japan). Photoluminescence spectra were collected on a RF-5301 luminescence spectrometer (Shimadzu, Japan)

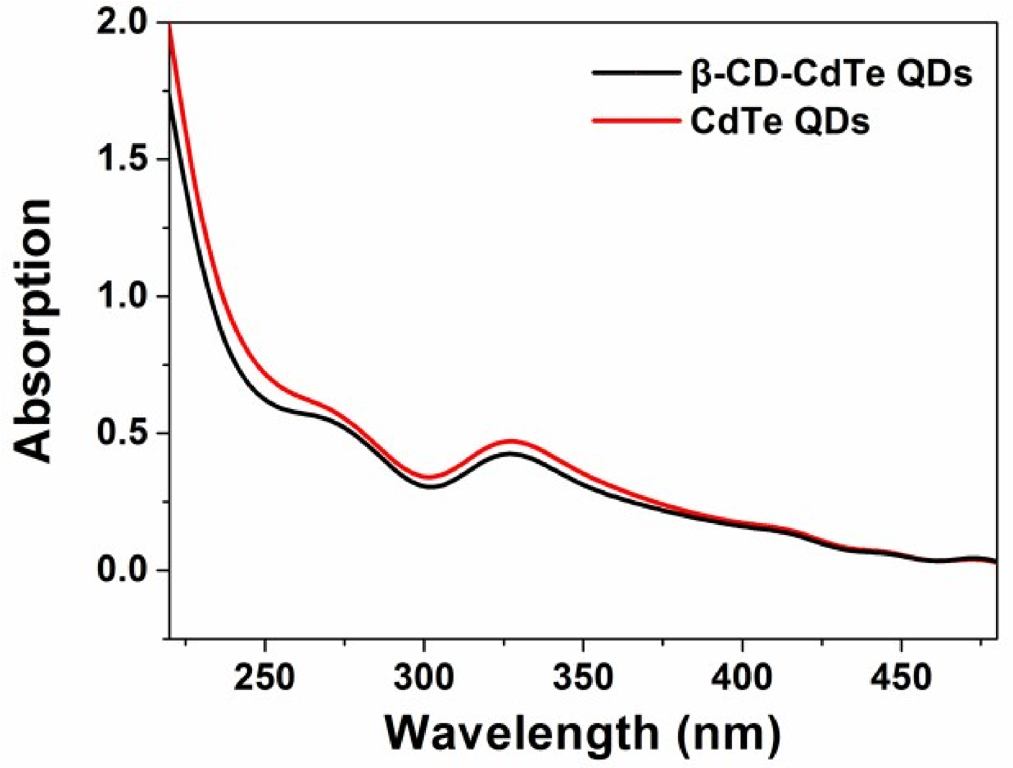

Fig. S1 UV-vis spectra of CdTe ODs and β-CD-CdTe QDs.

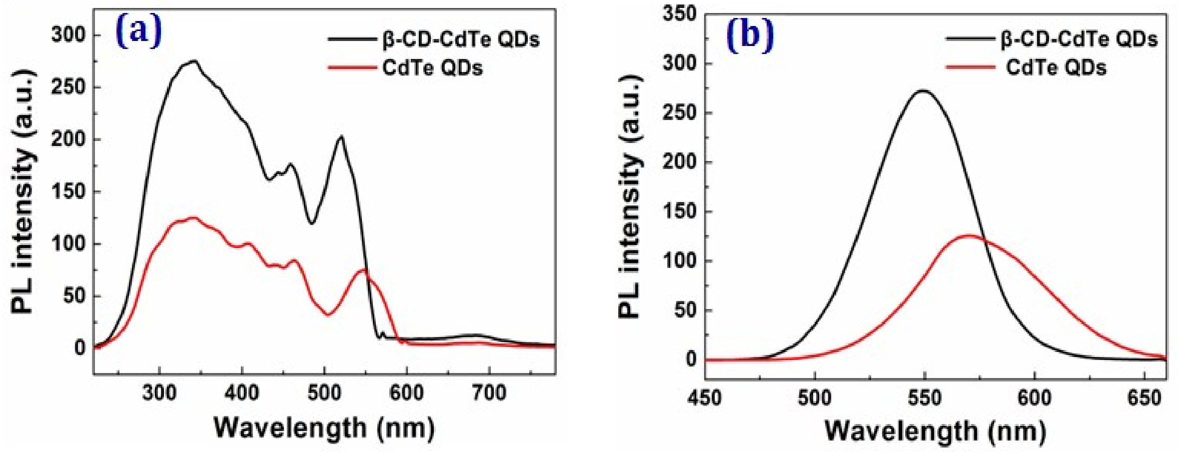

Fig. S2 The excitation (left) and emission (right) spectra of CdTe QDs and β-CD-CdTe QDs in aqueous solution.

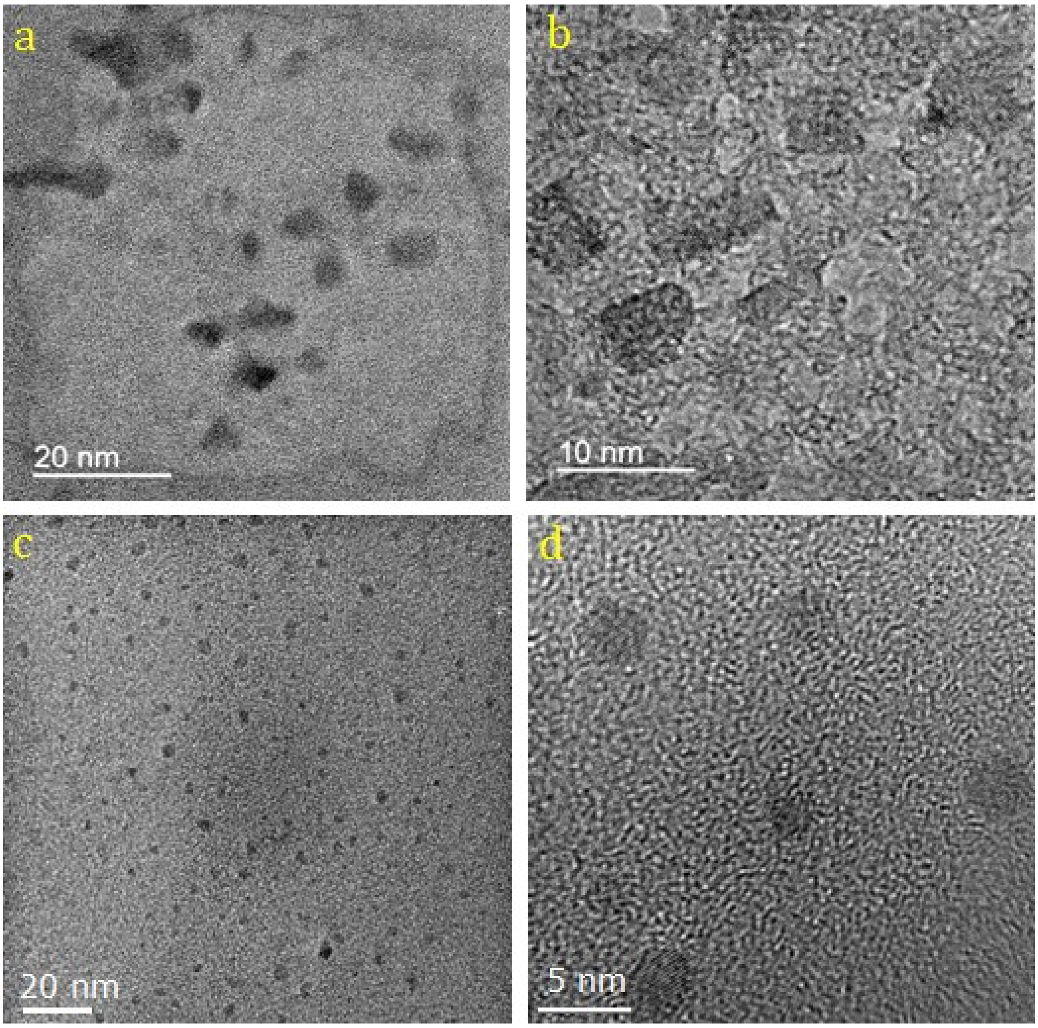

Fig. S3 TEM image of (a,b) CdTe QDs and (c,d) β-CD-CdTe QDs with different magnifications.

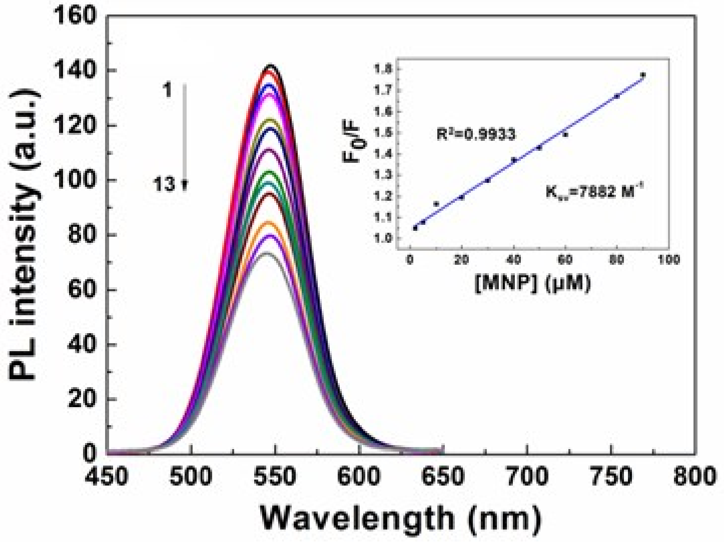

Fig. S4 PL spectra of β-CD-CdTe QDs-MNP solution containing 0, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μM MNP for Curves 1-13, respectively. Inset: Stern-Volmer plot of MNP.

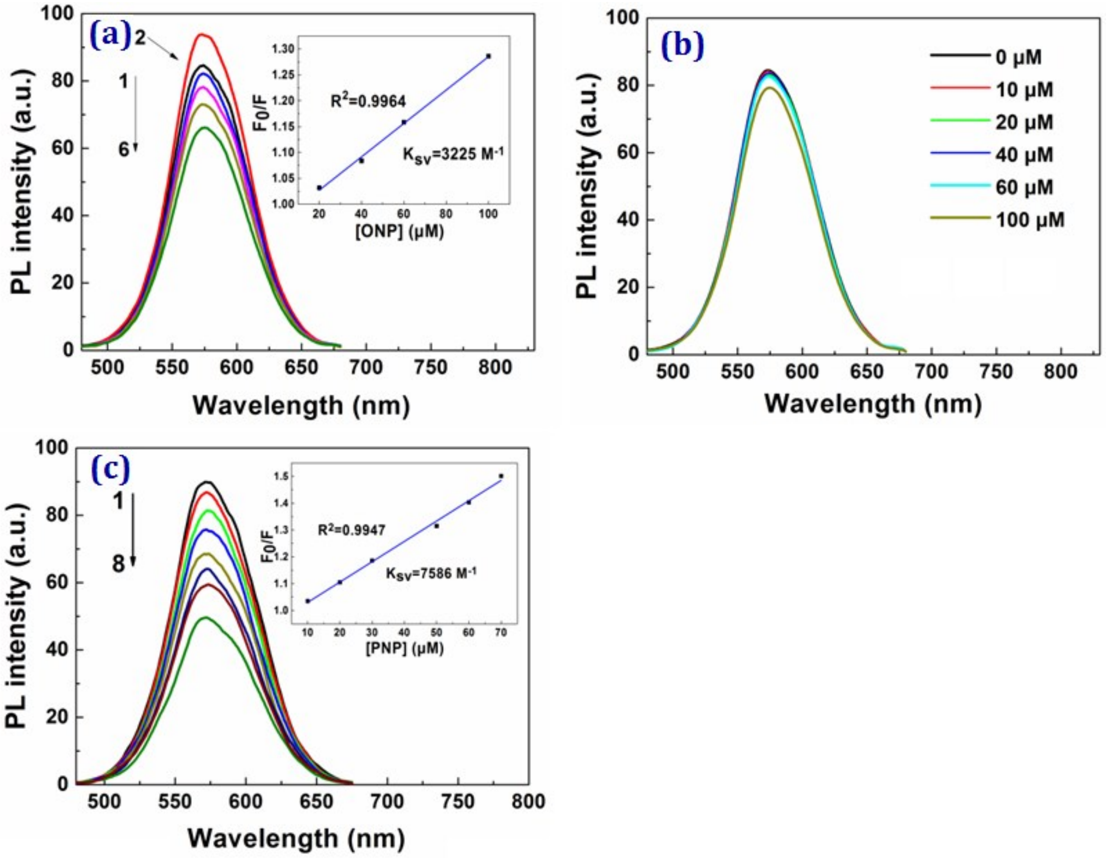

Fig. S5 PL spectra of CdTe QDs mixture solutions with (a) 0, 10, 20, 40, 60 and 100 μM ONP; (b) 0, 10, 20, 40, 60, 100 μM MNP; (c) 0, 10, 20, 30, 50, 60, 70 and 100 μM PNP, respectively. Inset: Stern-Volmer plots of ONP (a) and PNP (c).

References

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