Supporting information

A Simple General Chemical Etching Strategy to Generate "Ion-Imprinted" Sites on the Surface of Quantum Dots for Selective Signal Turn-On Detecting of Metal ions

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Materials and Chemicals.

All reagents used were of analytical grade. $CdCl_2 \cdot 2.5H_2O$, mercaptoproponic acid (MPA, Jingchun Chemical Reagent Co., Shanghai, China), Te powder (Guangfu Chemicals Co., Tianjing, China), and KBH_4 (Fuchen Chemicals Co., Tianjin, China) were used to prepare Hcy-capped CdTe QDs. Ultrapure water (18.2 MΩ cm) was obtained from a TKA MicroPure water purification system (Niederebert, Germany).

Apparatus.

Fluorescence measurements were performed on an F-4500 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). Absorption spectra were recorded on a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu, Japan). The X-ray diffraction (XRD) spectra were collected on a Rigaku D/max-2500 X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation. The FT-Raman spectra were recorded with a RFS 100 FI-Raman spectrometer (Bruker, Germany) equipped with a 1064 nm Nd:YAG laser system with a maximum power out of 2 W, a quartz beamsplitter, and a cryogenically cooled Ge detector.

The hyphenation of CE with ICP-MS was based on a previous work from this group.[S1] A laboratory-built CE system, composing of a 0-30 kV high-voltage power supply (Model DW 300-1, Tianjing Dongwen High-voltage power supply factory, Tianjing, China), a hydrodynamic sampling unit and a 50 μm id × 375 μm od fused-silica capillary with an effective length of 50 cm (Yongnian Optical Fiber Co., Heibei, China), was employed for separation. The power supply was operated in a voltage-controlled mode. The inlet end of the capillary was held at a positive potential and sample was hydrodynamically introduced from this end, while the outlet end was grounded. For separation, the electrophoretic voltage was set at 22 kV and the electrophoretic buffer was 10 mM NH_4Ac + 20 mM Tris (pH 8.2).

An X-series ICP-MS instrument (Thermo Elemental, Cheshire, UK) was used as the on-line detector

for CE. The MicroMist nebulizer (GE, Australia) was mounted on the standard spray chamber without any modification. A home-made interface for CE-ICP-MS was employed for connection of CE and ICP-MS. The CE outlet was grounded through a Pt electrode and the sheath flow of 0.5% v/v HNO_3 containing 1.0 μg/L ^{115}In was sucked by the nebulizer. The mixture of CE effluent and HNO_3 solution was nebulized by the MicroMist nebulizer of ICP-MS system and introduced into the ICP-MS by the nenbulizer gas.

Synthesis of MPA-Capped CdTe QDs.

CdTe QDs were prepared using the reaction between Cd^{2+} and KHTe in the presence of MPA as stabilizer according to the method of Rogach *et al.*[S2] Typically, 1 mL of 0.2 M $CdCl_2$ and 0.48 mmol of MPA were dissolved in 17 mL ultrapure water in a three-necked flask to form the cadmium precursor. The cadmium precursor was adjusted to pH 11 with 1 M NaOH and purged with Ar under continuous stirring for 30 min. Subsequently, 0.5 mL of freshly prepared 0.1 M KHTe aqueous solution from KBH_4 and Te powder was injected into the reaction system by a syringe under vigorous stirring, and the solution was heated at 100 °C for 2 h to obtain MPA-CdTe QDs. The size and concentration of the CdTe QDs were calculated to be 3.0 nm and 15 μM, respectively, according to Peng and co-workers.[S3] Batches of the obtained MPA-CdTe QDs were precipitated with ethanol, and separated by centrifugation. Finally, the purified MPA-CdTe QDs were redispersed in the Tris-HCl buffer solution (10 mM, pH 9.0).

Synthesis of ZnS QDs[S4]

1 mL of 0.2 M $Zn(NO_3)_2$ and 0.8 mmol of MPA were dissolved in 17 mL ultrapure water in a three-necked flask to form the cadmium precursor. The zinc precursor was adjusted to pH 11 with 1 M NaOH and purged with Ar under continuous stirring for 30 min. Subsequently, 1 mL of 0.2 M Na_2S was injected into the reaction system by a syringe under vigorous stirring, and the solution was heated at 50 °C for 2 h to obtain MPA-ZnS QDs. The purification procedure for ZnS was the same as that of CdTe QDs.

Synthesis of ZnSe QDs[S5]

1 mL of 0.2 M $Zn(NO_3)_2$ and 0.8 mmol of MPA were dissolved in 17 mL ultrapure water in a three-necked flask to form the cadmium precursor. The zinc precursor was adjusted to pH 11 with 1 M NaOH and purged with Ar under continuous stirring for 30 min. Subsequently, 0.5 mL of freshly prepared 0.1 M KHSe aqueous solution from KBH_4 and Se powder was injected into the reaction system by a syringe under vigorous stirring, and the solution was heated at 100 °C for 2 h to obtain MPA-ZnSe QDs. The purification procedure for ZnS was the same as that of CdTe QDs.

Procedures.

To evaluate the effect of EDTA etching on the fluorescence of CdTe QDs, 1 mL of 0.1 M Tris-HCl buffer solution (pH 9.0), 40 μL of 15 μM MPA-capped CdTe QDs, and various amounts of EDTA were sequentially added to a 10-mL calibrated test tube and further diluted to volume with ultrapure water. The solution was mixed thoroughly, and left for another 10 min to measure the fluorescence. For absorption measurements, the concentration of QDs was increased by 20-folds to ensure the absorbance of shoulder peak of CdTe QDs over 0.1. Then, the concentrations of EDTA and Cd^{2+} were also increased by 20-folds.

To investigate the fluorescence enhancement induced by Cd^{2+}, 1 mL of 0.1 M Tris-HCl buffer solution (pH 9.0), 40 μL of 15 μM MPA-capped CdTe QDs and 120 μL of 0.5 mM EDTA were sequentially added to a 10-mL calibrated test tube. The mixture was diluted to about 3 quarters of the total volume of the test tube with ultrapure water and left for 10 min. Then, Cd^{2+} standard solution was added and the mixture was further diluted to volume with ultrapure water. The solution was mixed thoroughly, and left for another 10 min to measure the fluorescence.

Analyzing the content of S in the dialyzed solution of QDs

To confirm the occurrence of MPA in the solution of EDTA-etched CdTe QDs, 5 mL of the QDs (3.6 μM)

solution, EDTA (360 μM)-etched QDs solution and Cd^{2+} (300 μM) repaired EDTA-etched QDs solution, were dialyzed against 20 mL Tris-HCl buffer (pH 9.0) for 4 h under continuous shaking. The dialysis bag has molecular weight cut-off of 12,000-14,000 (Kanmei Bioscience Technology Ltd., Beijing, China). After dialysis, the dialysates were oxidized with HNO_3 (1 mL) and concentrated by evaporation of water to final volume of 5 mL. Then, the dialysates was directly analyzed with inductively coupled plasma optical emission spectrometry to determine the concentration of S, with results of 58, 397 and 205 μM, respectively, for the above three solutions. The concentration of S (MPA) in the dialysate of EDTA-etched QDs was obviously higher than that without etching. While after adding of Cd^{2+} to the etched QDs, the concentration of S was decreased, confirming the role of Cd-MPA complex in repairing the etched QDs.

Factors Affecting the Sensitivity of the EDTA-Etched QDs for Signal Turn-on Detection of Cd^{2+}.

The concentration of EDTA had a significant effect on the fluorescence background of the probe and the sensitivity toward Cd^{2+}. Without EDTA etching, no significant change in the fluorescence of the QDs was observed upon interaction with different concentrations of Cd^{2+} from 1 to 10 μM (Fig. S3). The restored fluorescence caused by 2 μM Cd^{2+} reached maximum at EDTA concentration of 6 μM (Fig. S6). Increasing the concentration of EDTA not only increased the number of Cd^{2+} recognition sites, but also accelerated the oxidation of Te^{2-}, therefore a critical concentration which maximize the Cd^{2+} recognition sites was expected (6 μM in this case). Further increasing the concentration of EDTA would result in heavy destruction of the structure of QDs, yet decreasing the Cd^{2+} recognition ability. The concentration of EDTA investigated was in the range of 1-9 μM, significantly lower than that of Cd (40 μM) in the QDs solution. So the potential effect of extra free EDTA that would firstly catch the added Cd^{2+} to decrease the actual amount of Cd^{2+} for re-construction of EDTA-etched QDs, could be ruled out.

pH is another important factor to affect the sensitivity of Cd^{2+}-induced fluorescence restoration (Fig. S7). Maximum restoration was achieved in the pH range of 8.5-10.0. Aqueous synthesis of CdTe QDs with thiol stabilizer gave the information that the formation of Cd-MPA complex was favored in alkaline media,[S3] in accordance with the optimal pH range for fluorescence restoration by Cd^{2+}. The pH investigation also confirmed the role of Cd-MPA complex in fluorescence restoration. To guarantee the sensitivity, pH 9.0 of Tris-HCl buffer (10 mM) was employed.

Water Samples.

Two tap and two river water samples were collected locally and filtered through 0.45 μm supor filters. Before analysis, the tap water and river water samples were subjected to 5- and 10-fold dilution, respectively.

References

[S1] Y. Li, J.-M. Liu, Y.-L. Xia, Y. Jiang, X.-P. Yan, *Electrophoresis* **2008**, *29*, 4568.

[S2] W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854.

[S3] A. L. Rogach, T. Franzl, T. A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmüller, Y. P. Rakovich and J. F. Donegan, *J. Phys. Chem. C*, 2007, **111**, 14628.

[S4] J. Q. Zhuang, X. D. Zhang, G. Wang, D. M. Li, W. S. Yang, T. J. Li, *J. Mater. Chem.* **2003**, *13*, 1853.

[S5] C. Wang, X. Gao, Q. Ma, X. G. Su, *J. Mater. Chem.* **2009**, *19*, 7016.

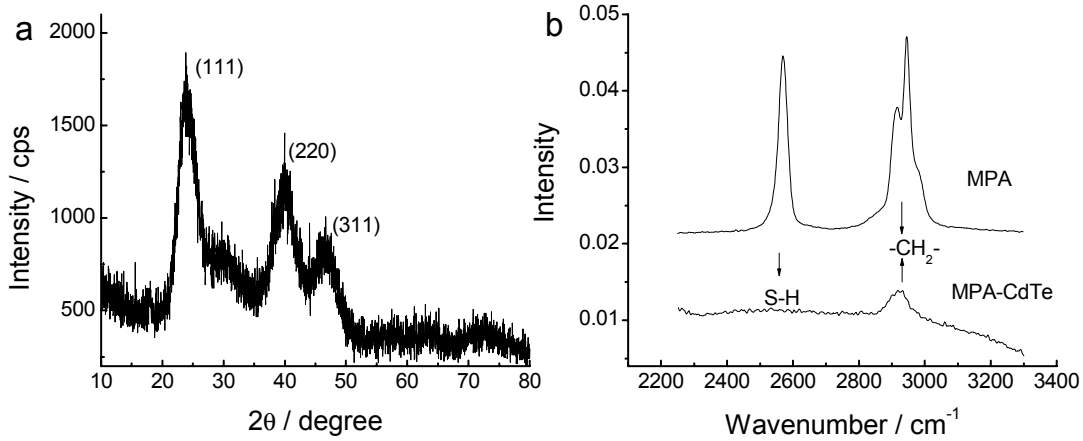

Fig. S1. a) XRD pattern of the MPA-CdTe QDs; b) FT-Raman spectra of MPA and MPA-CdTe QDs. XRD pattern of the CdTe QDs showed distinguishable (111), (220) and (311) planes of typical zinc blend structure. Owing to the covalent binding of thiol groups with Cd^{2+}, the S-H vibration (2554 cm^{-1}) in the MPA molecule disappeared whereas the characteristic peak for $–CH_2–$ (2948 cm^{-1}) still existed, confirming the interaction between MPA and CdTe core.

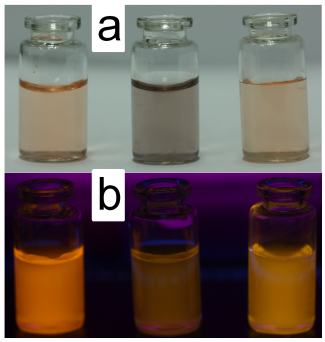

Fig. S2. Photos of MPA-CdTe QDs under irradiation with daylight (a) and UV light (b, λ_{Ex} = 365 nm). From left to right: CdTe QDs, CdTe QDs + EDTA, and CdTe QDs + EDTA + Cd^{2+}. The concentrations of MPA-CdTe QDs, EDTA and Cd^{2+} are 1.2 μM, 0.12 mM and 40 μM, respectively. All solutions were prepared in 0.01 M Tris HCl buffer of pH 9.0. The dark and opaque dispersion of QDs (middle of a) after EDTA etching indicated the oxidation of Te^{2-} to Te.

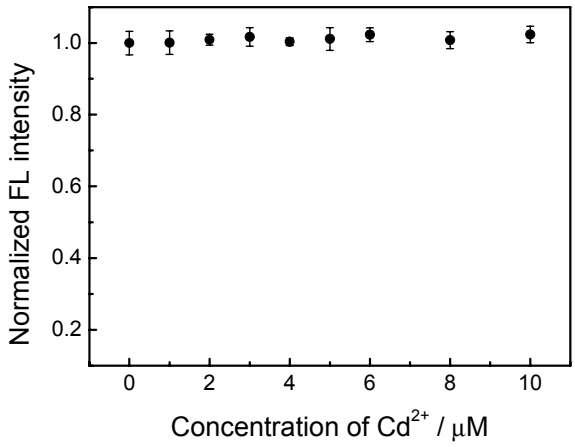

Fig. S3. The influence of Cd^{2+} on the fluorescence of MPA-CdTe QDs (60 nM).

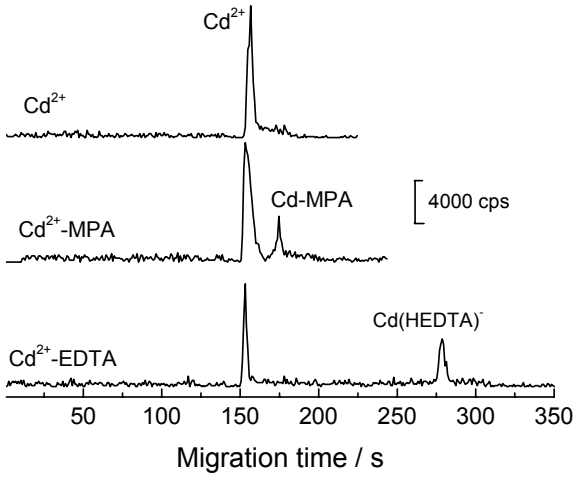

Fig. S4. Electrophoregrams of Cd^{2+}, mixture of Cd^{2+} and MPA and mixture of Cd^{2+} and EDTA. The concentration of Cd^{2+}, MPA and EDTA are 5 μM, 1 μM and 2.5 μM, respectively.

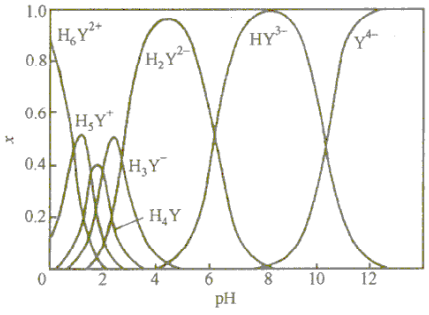

Fig. S5. Distribution of EDTA (shown as Y) as a function of pH obtained from *Handbook of Analytical Chemistry, Vol. 1*, 2nd ed., Chemical Engineering Press, Beijing, **1999**.

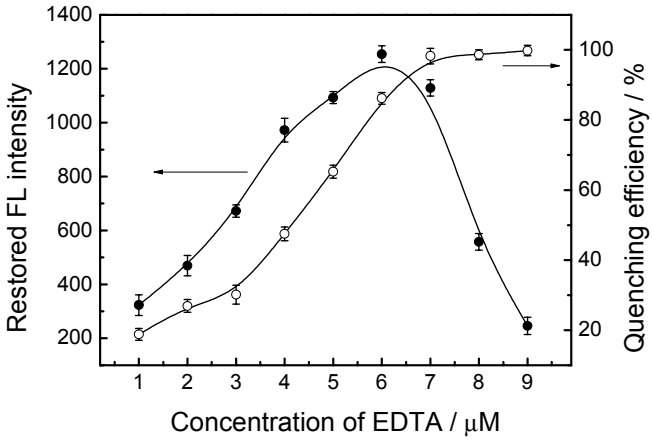

Fig. S6. EDTA concentration dependent fluorescence quenching of CdTe QDs (60 nM) and subsequent fluorescence restoration by Cd^{2+} (2 μM). All solutions were prepared in 0.01 M Tris-HCl buffer of pH 9.0.

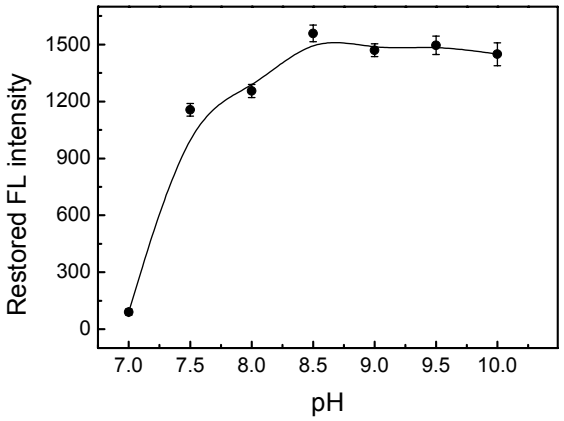

Fig. S7. Effect of sample pH (0.01 M Tris-HCl buffer) on the fluorescence restoration of Cd^{2+} (2 μM) to EDTA (6 μM)-etched CdTe QDs (60 nM).

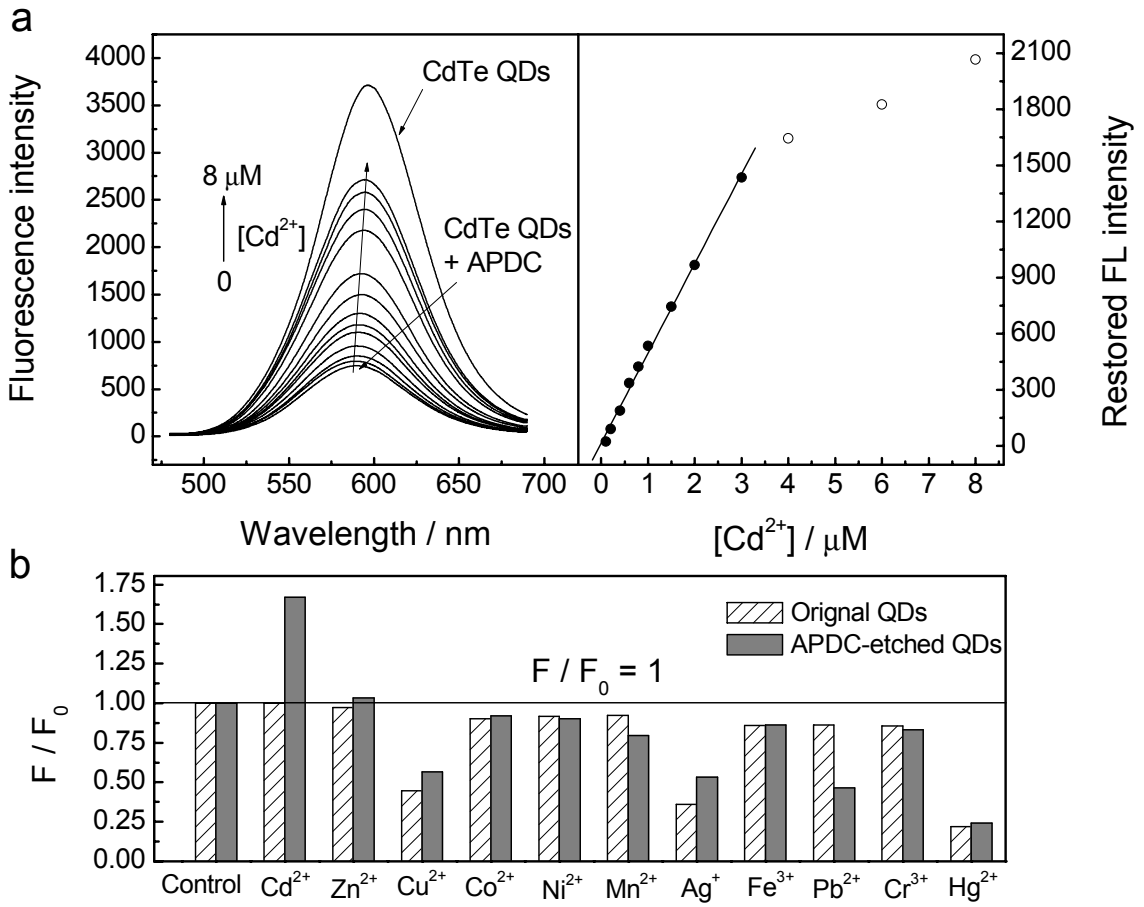

Fig. S8. a) APDC (10 μM)-etched CdTe QDs (60 nM) as a turn-on sensor for Cd^{2+}. b) selectivity comparison of original CdTe QDs and APDC-etched CdTe QDs toward transition metal ions (1 μM each). All solutions were prepared in 0.01 M Tris-HCl buffer of pH 9.0 except for the investigation of Ag^{+} (BT buffer).

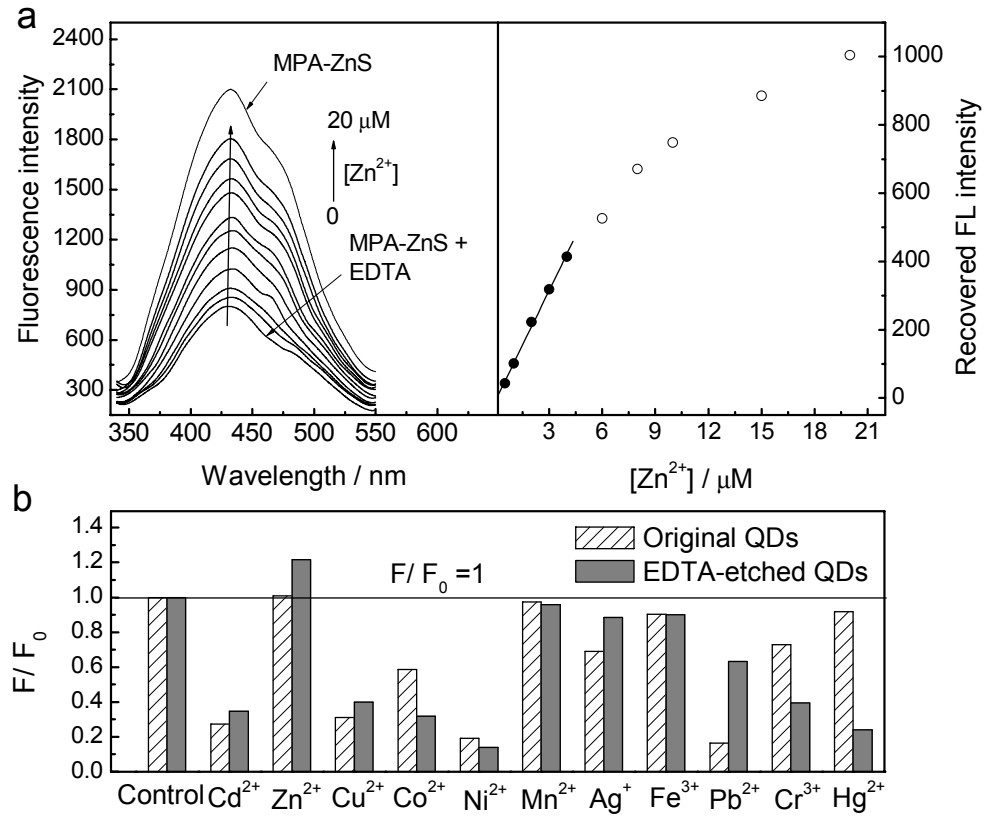

Fig. S9. a) EDTA (20 μM)-etched ZnS QDs (100 μM, as S) as a turn-on sensor for Zn^{2+}; b) selectivity comparison of original ZnS QDs and EDTA-etched ZnS QDs toward transition metal ions (2 μM each). All solutions were prepared in 0.01 M Tris-HCl buffer of pH 9.0 except for the investigation of Ag^{+} (BT buffer).

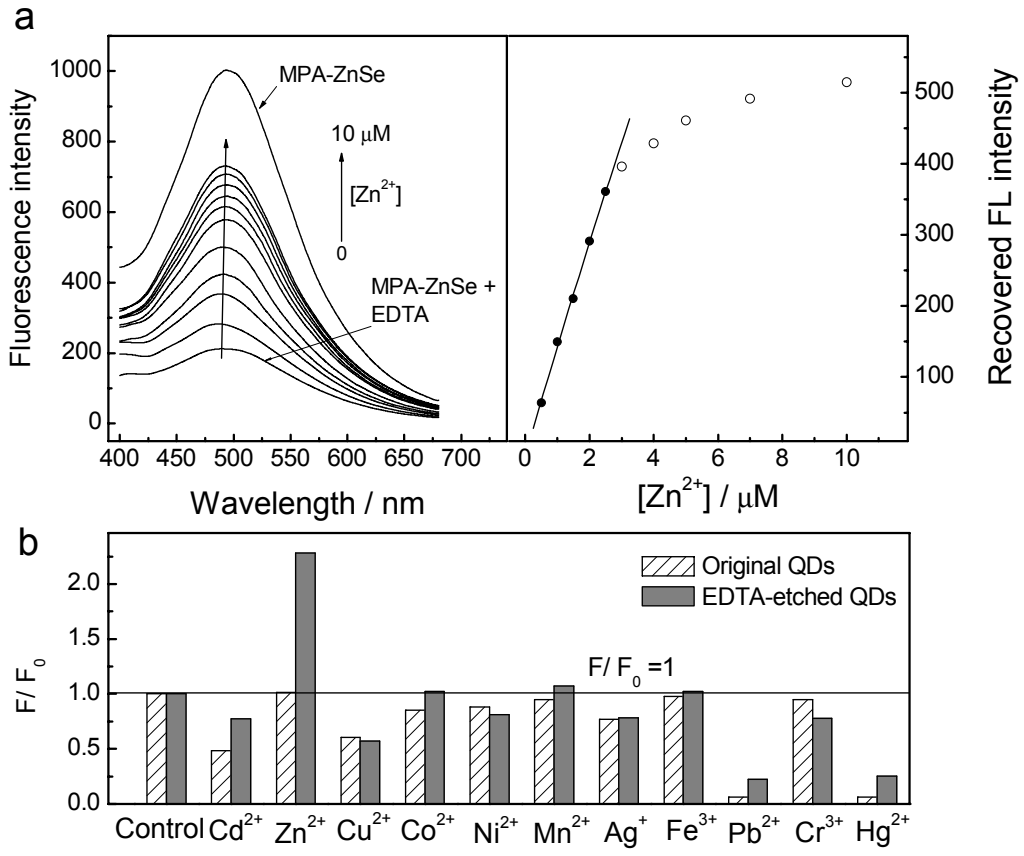

Fig. S10. a) EDTA (20 μM) -etched ZnSe QDs (100 μM, as Se) as a turn-on sensor for Zn^{2+}; b) selectivity comparison of original ZnSe QDs and EDTA-etched ZnSe QDs toward transition metal ions (2 μM each) except for the investigation of Ag^{+} (BT buffer).