Supporting Information

A Switchable Fluorescent Quantum Dot Probe Based on Aggregation /Disaggregation Mechanism

Jianbo Liu, Xiaohai Yang, Kemin Wang*, Ronghua Yang, Haining Ji, Liyan Yang and Chunlei Wu

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Key Laboratory for Bio-Nanotechnology and Molecular Engineering of Hunan Province, Hunan University, Changsha 410082, China

Experimental Section:

Materials: Cadmium perchlorate hexahydrates ($Cd(ClO_4)_2 \cdot 6H_2O$, 99%) was purchased from Acros Organics. Cysteamine (95%) and aluminum telluride (Al_2Te_3, 99.5%) were purchased from Sigma and Cerac Inc., respectively. Sodium fluoride (NaF, 98%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Zirconium Oxydichloride Octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99%) was purchased from Aldrich. Unless otherwise noted, all reagent-grade chemicals were used as received. pH of the solutions was adjusted by 0.1 M NaOH or HCl.

Synthesis of cysteamine-capped CdTe QDs. CdTe QDs stabilized by cysteamine were prepared in water, as described previously.[1] In a typical synthesis, 2.35 mmol $Cd(ClO_4)_2 \cdot 6H_2O$ is dissolved in 125 mL of degassed water, and 5.7 mmol cysteamine is added. Under stirring, H_2Te gas (generated by the reaction of 0.46 mmol Al_2Te_3 lumps with 15-20 mL of 0.5 M H_2SO_4) is passed through the solution together with a slow nitrogen flow for ~20 min. CdTe precursors are formed at this stage which is accompanied by a change of the solution color from colorless to dark red. After refluxed at 100 °C about 30 h, CdTe QDs with fluorescence peak at 594 nm ($\Phi \approx 15\%$) could be obtained. The mole concentration of CdTe QDs was determined as a procedure reported by Peng et al. [2]

Characterization: Steady-state fluorescence measurements were performed on a Hitachi FL 7000 fluorescence spectrophotometer with excitation wavelength at 400 nm. Time-resolved measurements were conducted on Fluorolog-Tau-3 spectrafluorometer (Jobin Yvon) with a NanoLED pulsed diode excitation at 461 nm. Photoluminescence quantum yield of QDs were obtained by comparing the integrated emission area to that of Rhodamine 6G in methanol assuming its photoluminescence quantum yield as 95%. Absorption spectra were recorded on a UV-Vis 1601 Shimadzu spectrophotometer. DLS experiments were carried out in a Malvern Nano-ZS system equipped with a He-Ne laser working at 633 nm to examine the hydrodynamic diameter (number-weighted mean diameter) and zeta potentials of QDs. Transmission electron microscopy (TEM) was performed on a JEOL-1230 microscope operating at an accelerating voltage of 100 kV. FTIR spectra of KBr powder-pressed pellets were recorded on a Bruker Tensor 27 spectrophotometer scanning from 4000 cm^{-1} to 500 cm^{-1}.

Figure Legend:

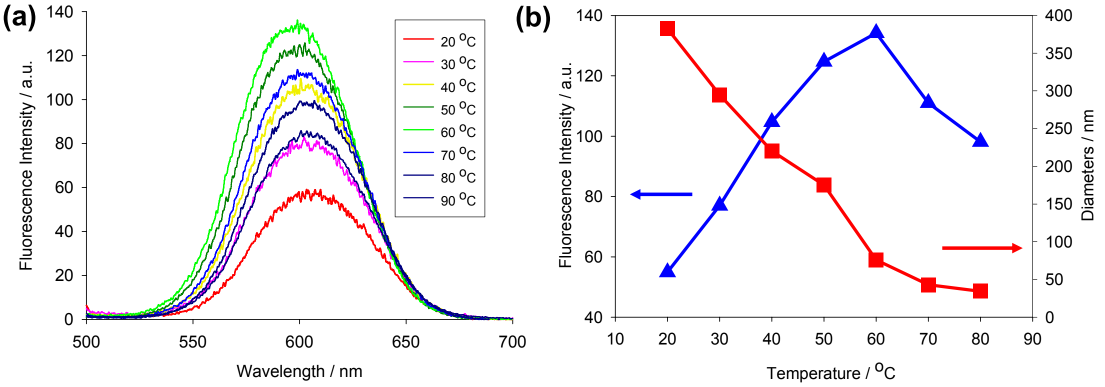


Figure S1. a) Fluorescence emission spectra of CdTe QD aggregates (1.0 µM) at different temperatures, and b) Plot of the fluorescence peak intensity and hydrodynamic diameter against the temperature. The fluorescence decreasing above 60 °C may be attributed to the self-quenching at high temperature. The experiment was performed at aqueous solution at pH 7.6. The QDs suspensions were incubated for 20 min in water bath at different temperature and then determined.

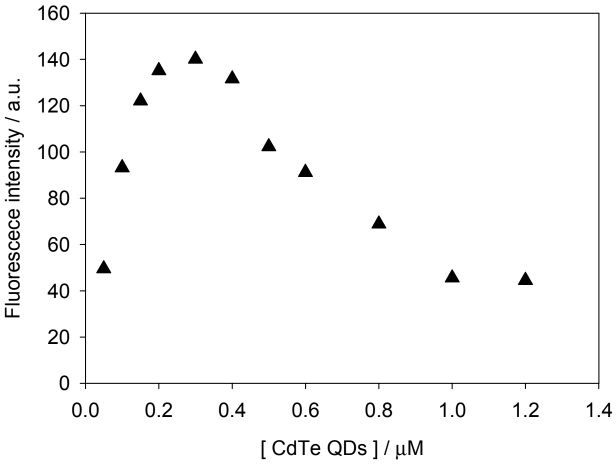


Figure S2. Fluorescence intensity of different concentration of CdTe QDs at pH 7.6. The experiment was performed at aqueous solution at room temperature.

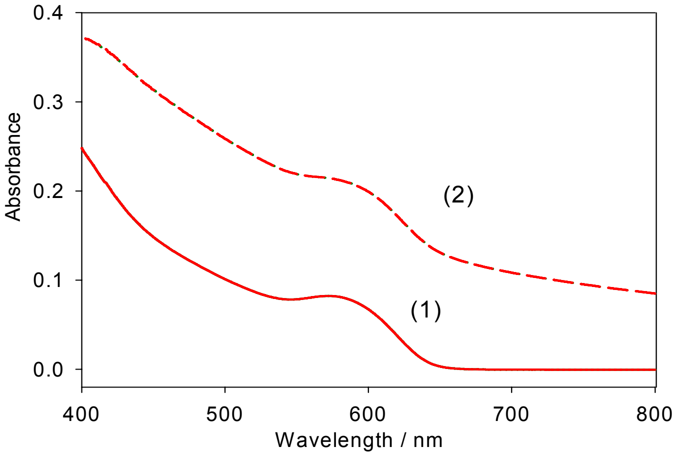
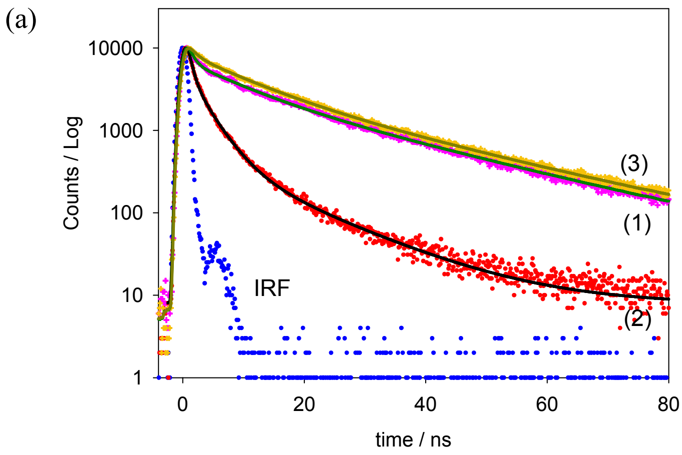


Figure S3. UV-vis absorbance spectra of cysteamine capped-CdTe QDs (1.0 µM).1) aggregate-free QDs at pH 6.0; 2) QD aggregates at pH 7.6. The experiment was performed at aqueous solution at room temperature.



(b) Fluorescence lifetime parameters for different samples studied [a]

Sample	α_1	τ_1 / ns	α_2	τ_2 / ns	α_3	τ_3 / ns	$<\tau>$/ ns [b]
(1)	29.83	8.9	61.75	25.0	8.42	0.8	18.2
(2)	46.49	3.1	18.28	13.0	35.23	0.6	2.9
(3)	38.14	9.8	57.18	26.2	4.77	1.3	18.8

[a] $\lambda_{ex} = 461$ nm, $\lambda_{em} = 600$ nm. [b] $< \tau > = \Sigma_{i} \alpha_i \tau_I$, $\chi^2 < 1.5$.

Figure S4. a) Fluorescence decay curves of CdTe QDs (1 μM). 1) aggregate-free QDs at pH 6.0, 2) aggregated QDs at pH 7.6, and 3) F^- ions triggered disaggregated QDs at pH 7.6. Solid curves showed the results of the fitting. b) Fluorescence lifetime fitting parameters for different samples studied.

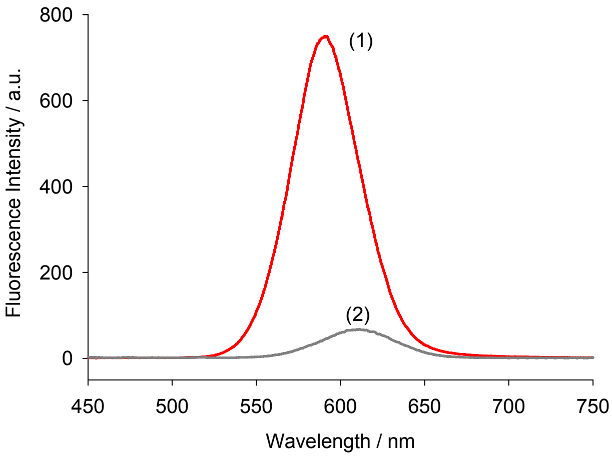


Figure S5. Fluorescence spectra of cysteamine capped-CdTe QD aggregates (1.0 μM) in the 1) presence of F^- ions (10 mM), and (2) after addition of ZrO^{2+} ions (5 mM). The experiment was performed at aqueous solution at pH 7.6 at room temperature.

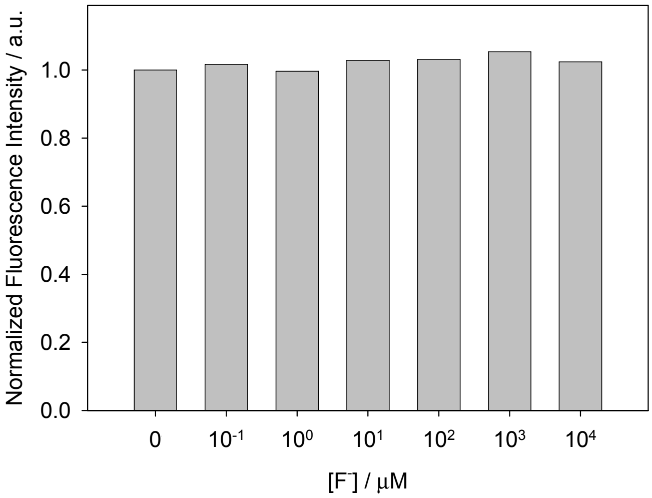


Figure S6. Influence of F⁻ ions on the fluorescence intensity of aggregate-free monomeric QDs (0.05 μM). At this concentration, CdTe QDs showed no obvious aggregation.

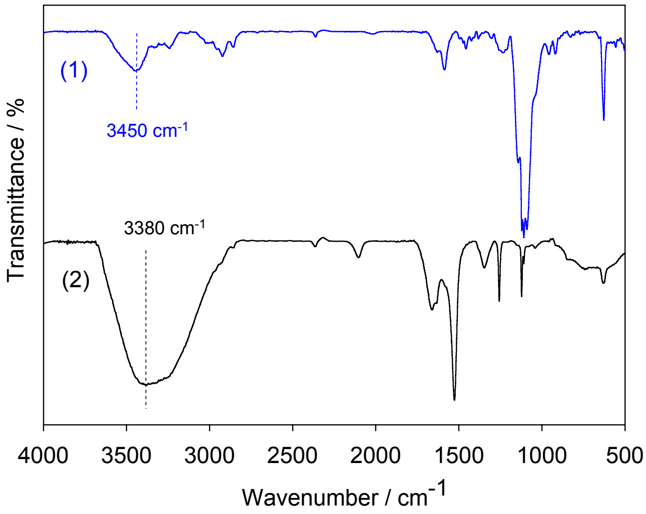


Figure S7. FTIR spectra of CdTe QD aggregates powders (1.0 μM) in the 1) absence and 2) presence of F⁻ ions (10 mM). Samples of CdTe QDs were dehydrated by vacuum freeze-drying.

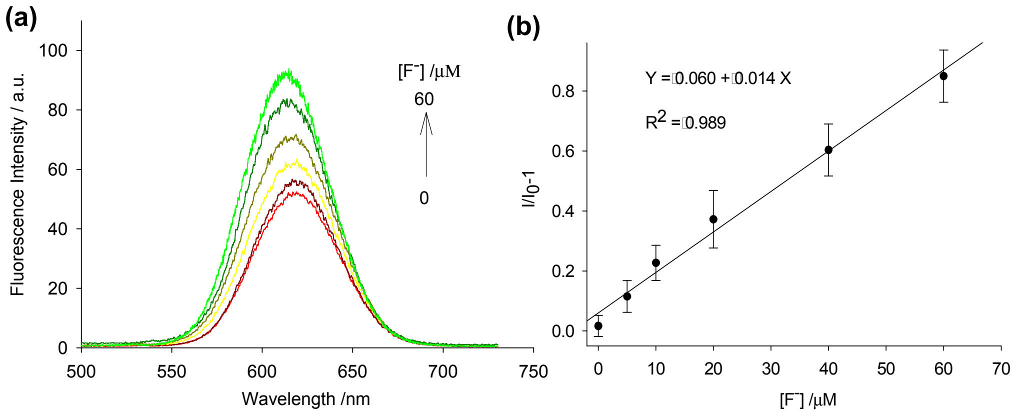


Figure S8. Estimation of the detection limit of QDs aggregates for F^- ions. a) Fluorescence spectra of QDs suspension (1.0 μM) on the addition of F^- ions (0-60 μM), and b) Corresponding relative fluorescence enhancement of QDs depended on F^- ions. Error bars represent standard deviations of three experiments. The experiment was performed at aqueous solution at pH 7.6 at room temperature.

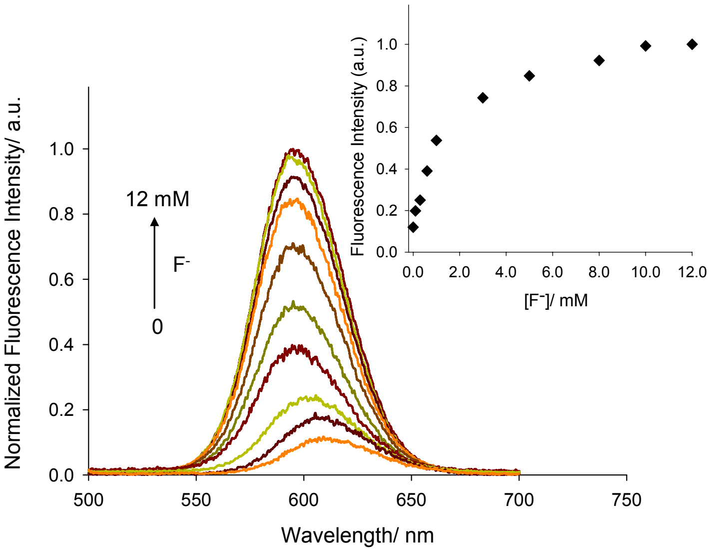


Figure S9. Fluorescence spectra change of CdTe QDs aggregate suspension (1.0 μM) up addition of F^- ions (0-12 mM). The competitive titration experiment was performed at aqueous solution at pH 7.6 at room temperature. The solution contained different ions, including 20 μM Cl^-, Br^-, I^-, SO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, HCO_3^-, NO_3^-, respectively. All the anion ions were from their sodium salts. Inset: the corresponding quantitative fluorescence intensity of QDs depended on F^- ions.

References

1 N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmuller and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 7177-7185.

2 W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.