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Coordination-induced assemblies of quantum dots in amphiphilic thermo-responsive block copolymer micelles: morphologies, optical properties and applications

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Experimental section

Materials

N-isopropylacrylamide (NIPAm) was purchased from Tokyo Kasei Kogyo Co. Ltd. and recrystallized by hexane. Styrene (St) was obtained from Macklin Chemical Reagent Co. Ltd, and washed three times with 1% NaOH solution, and washed with deionized water to neutral, finally distilled. Methyl methacrylate (MMA) was obtained from Macklin Chemical Reagent Co. Ltd and purified by distillation under vacuum. 8-Hydroxyquinoline (HQ) was purchased from Xiya Reagent. 5-(2-Methacryloylethyloxymethyl)-8-quinolinol (MQ) was synthesized according to a previous procedure.[1] 2,2′-Azobis(2-methylpropionitrile) (AIBN) (98%, Aldrich) was obtained from Macklin Chemical Reagent Co. Ltd and recrystallized twice from ethanol and stored in the dark at 4 °C. 4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDTPA) was purchased from

Strem Chemicals Inc. CdSe/ZnS QDs capped with octadecylamine was obtained from Suzhou Xingshuo Nanotech Co., Ltd. CdTe/ZnS QDs capped with GSH was synthesized according to previous literatures.[2,3] Thioglycolic acid (TGA, 99%), $NaBH_4$ (96%) and tellurium powder (9.8%) were obtained from Sinopharm Chemical Reagent Co., Ltd. $ZnCl_2$ (99%) and $CdCl_2 \cdot 2.5H_2O$ (99%) were obtained from Shanghai Reagent Company. Reduced Glutathione (GSH, 98%) were purchased from Beijing Jing Ke Hong Da Biotechnology Co. Ltd. 2,4,6-Trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT) in methanol (1.0 mg mL^{-1}) and 2,4-dinitrotolene (2,4-DNT) were purchased from Aladdin. The other nitro compounds such as 2-nitrotoluene (2-NT), 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT), nitrobenzene (NB), nitromethane (NM) and phenol were purchased from Macklin. $CaCl_2$, NaCl, KNO_3, $FeCl_2$, $FeCl_3$, $CoCl_2$, $Cu(NO_3)_2$, $Cd(CH_3COO)_2$ and $Hg(NO_3)_2$ were purchased from Beijing Chemical Works.

Synthesis of diblock copolymer P1

Synthesis of $P(St_{0.94}\text{-co-}MQ_{0.06})_{51}CTA$.

The typical procedure for the preparation of $P(St_{0.94}\text{-co-}MQ_{0.06})_{51}CTA$ is as follows. A mixture of St (5.63 g, 50.5 mmol), MQ (0.48 g, 1.67 mmol), CDTPA (0.01 g, 0.287 mmol), AIBN (0.04 mg, 0.22 mmol) and THF (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 °C under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in methanol and centrifugation. After repeated three times of this procedure, the product was dried under vacuum ($M_{n,NMR}$ = 5860, $M_{n,GPC}$ = 5450, M_w/M_n = 1.10).

Diblock copolymer $P(St_{0.94}\text{-co-}MQ_{0.06})_{51}\text{-}PNIPAm_{221}$ (P1) was obtained as follows. NIPAm (0.315 g, 2.78 mmol), $P(St_{0.94}\text{-co-}MQ_{0.06})_{51}CTA$ (0.2 g, 0.034 mmol), AIBN (0.0018 g, 0.011 mmol) and THF (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 °C under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in diethyl ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum. ($M_{n,NMR}$ = 31100, $M_{n,GPC}$ = 26500, M_w/M_n = 1.12).

For $P(St_{0.94}\text{-co-}MQ_{0.06})_{51}CTA$, the degree of polymerization for the MQ units (DP_{MQ}) was calculated based on the ^1H NMR data by eqn (1):

$$DP_{MQ} = \frac{A_f/2}{A_i/3} \qquad (1)$$

where A_f is the integral area of $-CH_2$ in MQ units, A_i indicates the integral area of $-CH_3$ in RAFT agent.

The DP_{NIPAm} was calculated by eqn (2):

$$DP_{St} = \frac{\dfrac{A_{7,b,d,e} - \left(\dfrac{A_f}{2} \times 3\right)}{5}}{\dfrac{A_f}{2}} \times DP_{MQ} \qquad (2)$$

$P(St_{0.94}\text{-co-}MQ_{0.06})_{51}CTA$ was used as a new RAFT agent to prepare diblock copolymer P1 with hydrophilic PNIPAm block using NIPAm as a monomer.

The DP_{NIPAm} was calculated by eqn (3):

$$DP_{NIPAm} = \frac{(A_2 - A_f)}{A_f} \times 2DP_{MQ} \tag{3}$$

The ratio of the monomer units in the P1 can be obtained by using the above calculation formula (1-3), and the results are listed in Table 1. The calculation method for DP of other polymers is similar to that of P1.

Synthesis of diblock copolymer P2

$P(NIPAm_{0.97}\text{-co-}MQ_{0.03})_{118}CTA$ was prepared as follows: A mixture of NIPAm (2.0 g, 17.7 mmol), MQ (0.157 g, 0.546 mmol), CDTPA (0.0652 g, 0.182 mmol), AIBN (0.012 g, 0.072 mmol), toluene (2.0 mL) and methanol (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 ^oC under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in diethyl ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum. ($M_{n,NMR} = 14160$, $M_{n,GPC} = 9690$, $M_w/M_n = 1.11$).

$P(NIPAm_{0.97}\text{-co-}MQ_{0.03})_{118}\text{-b-}PSt_{18}$ (P2) was obtained as follows. A mixture of St (1.0 g, 9.6 mmol), $P(NIPAm_{0.97}\text{-co-}MQ_{0.03})_{118}CTA$ (0.2 g, 0.014 mmol), AIBN (0.0016 g, 0.0096 mmol) and THF (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 ^oC under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in diethyl ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum ($M_{n,NMR}$ = 16040, $M_{n,GPC}$ = 11350, M_w/M_n = 1.27).

Synthesis of triblock copolymer P3

The typical procedure for the preparation of PNIPAm$_{67}$CTA is as follows. A mixture of NIPAm (1.0 g, 8.8 mmol), CDTPA (0.0652 g, 0.18 mmol), AIBN (0.012 g, 0.073 mmol), toluene (2.0 mL) and methanol (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 ^{o}C under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in petroleum ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum. ($M_{n,NMR}$ = 8600, $M_{n,GPC}$ = 7480, M_w/M_n = 1.10).

Synthesis of PNIPAm$_{67}$-b-P(MMA$_{0.93}$-co-MQ$_{0.07}$)$_{28}$ CTA was obtained as follows. A mixture of MMA (0.22 g, 2.19 mmol), MQ (0.033 g, 0.115 mmol), PNIPAm$_{67}$CTA (0.2 g, 0.023 mmol), AIBN (0.0015 g, 0.0092 mmol) and THF (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 ^{o}C under stirring for 4 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in petroleum ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum ($M_{n,NMR}$ = 11800, $M_{n,GPC}$ = 8420, M_w/M_n = 1.10).

$PNIPAm_{67}$-b-$P(PMMA_{0.93}$-co-$MQ_{0.07})_{28}$-b-PSt_{30} (P3) was synthesized by a similar procedure of $PNIPAm_{67}$-b-$P(PMMA_{0.93}$-co-$MQ_{0.07})_{28}CTA$. St (2.0 g, 19 mmol), $PNIPAm_{67}$-b-$P(MMA_{0.93}$-co-$MQ_{0.07})_{28}CTA$ (0.2 g, 0.017 mmol), AIBN (0.003 g, 0.018 mmol) and THF (2.0 mL) were added to a dried three-neck round bottomed flask. After the mixture was degassed with N_2 by three freeze-pump-thaw cycles, the polymerization was started by heating at 70 ^{o}C under stirring for 12 h. After the polymerization, the reaction was quenched in liquid nitrogen. The product was purified by precipitation in petroleum ether and centrifugation. After repeated three times of this procedure, the product was dried under vacuum. ($M_{n,NMR}$ = 14900, $M_{n,GPC}$ = 10000, M_w/M_n = 1.10).

Self-assembly of block copolymer in THF/water

Core-labeled micelles (CLMs), shell-labeled micelles (SLMs) and interface-labeled micelles (ILMs) were prepared via the assembly of block copolymers P1, P2 and P3, respectively. The typical procedure for the preparation of labeled micelles is as follows: 5.0 mg polymer was simultaneously dissolved in 5.0 mL THF with stirring for 30 min at room temperature to obtain a homogeneous solution. Deionized ultrapure water was added dropwise to the polymer solution at a rate 20 μL/30s until the appearance of blue opalescence, followed by stirring for 3 h. 40 mL deionized ultrapure water was added into the solution to stabilize the micelles for another 3 h. The above mixture solution was dialyzed against water for 4 days to obtain CLMs, NLMs and SLMs.

Determination of critical micelle concentration (CMC)

Pyrene was used as a fluorescence probe to determine the critical micelle concentration (CMC) of the block copolymers P1-P3. 5.0 mL polymer micelle solutions with concentration ranging from 0.1 mg/mL to 4.88×10^{-5} mg/mL were added to the vials containing pyrene, and the final concentration of pyrene was 1×10^{-6} mol/L in solution. The solutions were kept at room temperature for 7 days before measured. Fluorescence spectra of the as-prepared solutions were recorded by a fluorescence spectrophotometer from 350 to 470 nm after excitation at 335 nm.

Preparation of core-doping micelles (CDMs)

Core-doped micelles (CDMs) were prepared through co-assembly of CdSe/ZnS QDs and P1 in THF. The CdSe/ZnS QDs were stored in chloroform solvent with a concentration of 4.17 mg/mL before use. Two kinds of assemblies were prepared: 1. CdSe/ZnS QDs in $CHCl_3$ was mixed with P1 solution directly, and a radial array assembly structure will be formed at this time. 2. The $CHCl_3$ solvent in CdSe/ZnS QDs solution was dried at room temperature before mixed with P1 solution. In this case, the CdSe/ZnS QDs will be located at the core of the micelle. In the typical prepared procedure for the condition of 2, P1 (5.0 mg) was dissolved in 3.0 mL THF and stirred vigorously for 30 min to obtain a transparent solution. Different volumes of 8, 10, 15 or 20 μL CdSe/ZnS QDs (4.17 mg/mL in $CHCl_3$) were dried by solvent evaporation and 2.0 mL THF were added, and then different THF solutions of

CdSe/ZnS QDs were mixed with P1 solutions, respectively. The mixture solution was stirred for 30 min to make the coordination assembly complete. Deionized ultrapure water was dripped into the mixed solution with a rate of 20 μL/30 s until a homogeneous liquid with blue opalescence was obtained. After stirring for 2 h, 20 mL water was added to make micelles shape stable. After stirring another 2 h, THF was removed by dialysis for 4 days to obtain core-doping micelles (CDMs).

Preparation of shell-doped micelles (SDMs)

In a typical procedure, 200, 300, 400 and 500 μL CdTe/ZnS QDs were slowly injected into 4.0 mL shell-labeled micelles (SLMs) aqueous solution, respectively. The mixture was stirred 12 h under room temperature, and the QDs will be positioned on the shell of the micelles (SDMs) by coordination interaction. The absorption and fluorescent spectra were monitored.

Preparation of interface-doped micelles (IDMs)

In a typical procedure, 5 μL CdSe/ZnS QDs in THF was slowly injected into 4.0 mL interface-labeled micelles (SLMs) aqueous solution. Then, the mixture was dialyzed (MWCO = 14000 Da) for 3 days against deionized water. For comparison, 5 μL CdSe/ZnS QDs in THF was slowly injected into 4.0 mL deionized water. Then, the mixture was dialyzed (MWCO = 14000 Da) for 3 days against deionized water. After dialysis, the above solutions were fixed to 5.0 mL with deionized water. The QDs will be positioned in the interface of the micelles (IDMs) by coordination effect and hydrophobic effect. The absorption and fluorescent spectra were monitored.

Detection of TNP and Hg^{2+} by shell-doped micelles (SDMs)

For the typical TNP and Hg^{2+} detection procedure, TNP and Hg^{2+} aqueous solutions (1×10^{-4} mol L^{-1}) with different volumes were added to 4.0 mL shell-doped micelles (SDMs). Fluorescence emission spectra were recorded under 365 nm excitation. To evaluate the selectivity of our sensing system for TNP, the other nitroaromatics including TNP, TNT, 2,4-DNT, 2-NT, 1,3-DNB, 2,6-DNT, NB, NM and phenol were also detected under the same analytical conditions. And the fluorescence emission spectra of SDMs in the present of Ca^{2+}, Na^{+}, K^{+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+} and Cd^{2+} were recorded to evaluate the response for metal ions. (the concentrations of these nitroaromatics and metal ions were fixed to 1×10^{-2} mol L^{-1}).

Characterization

^{1}H NMR spectra were obtained from an AVANCE Bruker spectrometer at basic frequencies of 500 MHz for ^{1}H in $CDCl_3$ solution. The molecular weight of polymer was estimated at a flow rate of 1.0 mL min^{-1} at 25 ^{o}C by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector. THF was used as eluent, and the molecular weight was determined vs polystyrene standards. Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Magna 560 FTIR spectrometer. Transmission electron microscopy (TEM) was carried out on a JEM-2100F electron microscope. UV-vis absorption spectra were recorded on a SHIMADZU UV-2550

UV-visible spectrophotometer in the range 200-800 nm. The steady state photoluminescence spectra, excited-state decay times and photoluminescence quantum yield (QY) were measured on a fluorescence spectrofluorometer (Edinburgh FLS980) using a time-correlated single-photo counting technique. Dynamic light scattering (DLS) was carried out on a Zetasizer-nanozs.

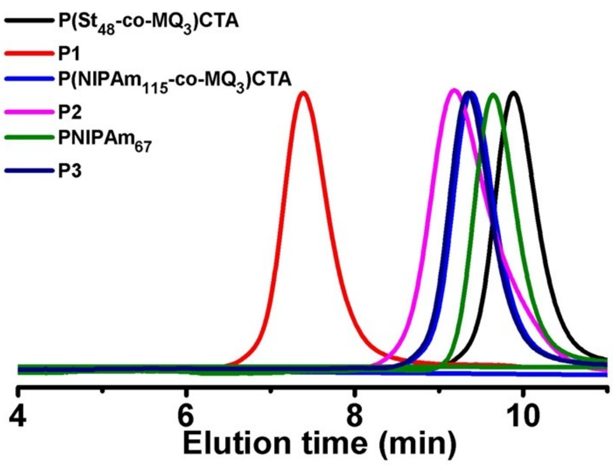

Fig. S1 GPC curves of P1-3 and their corresponding macro-RAFT agents.

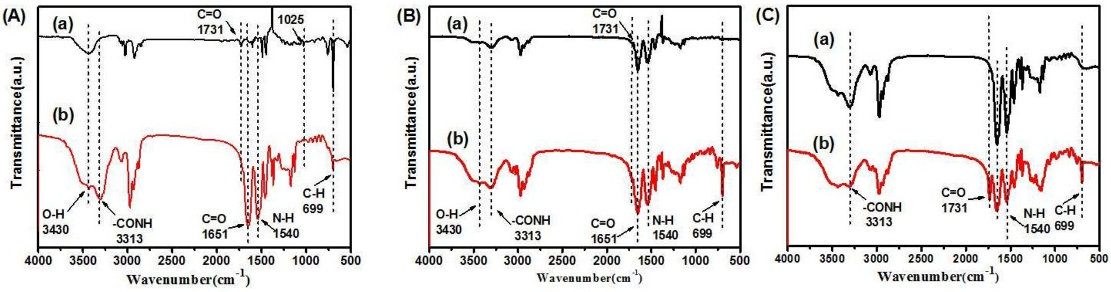

Fig.S2 FTIR spectra of (A) P($St_{0.94}$-co-$MQ_{0.06}$)$_{51}$CTA (a) and P1 (b); (B) P($NIPAm_{0.97}$-co-$MQ_{0.03}$)$_{118}$CTA (a) and P2 (b) and (C) $PNIPAm_{67}$CTA (a) and P3 (b).

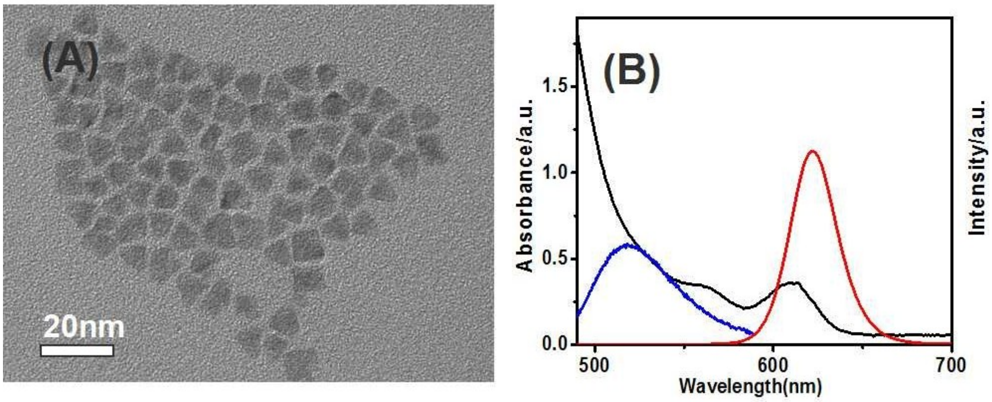

Fig. S3 (A) TEM image of CdSe/ZnS QDs; (B) fluorescence (red line) and UV-vis absorption (black line) spectra of CdSe/ZnS QDs, and PL spectrum (blue line) of CLMs-Zn complex.

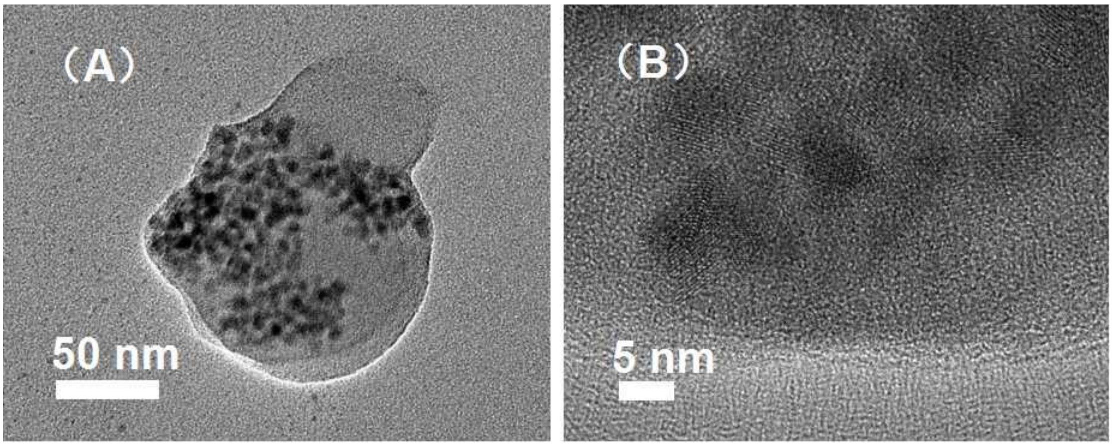

Fig. S4 (A) TEM and (B) HRTEM images of interface-doped micelles (IDMs).

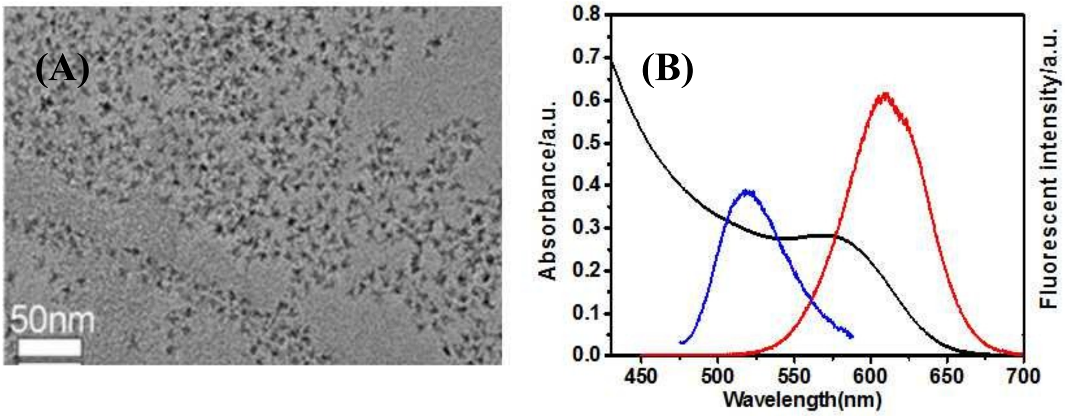

Fig. S5 (A) TEM image of CdTe/ZnS QDs; (B) fluorescence (red line) and UV-vis absorption (black line) spectra of CdTe/ZnS QDs, and emission spectrum (blue line) of Zn-SLMs complex.

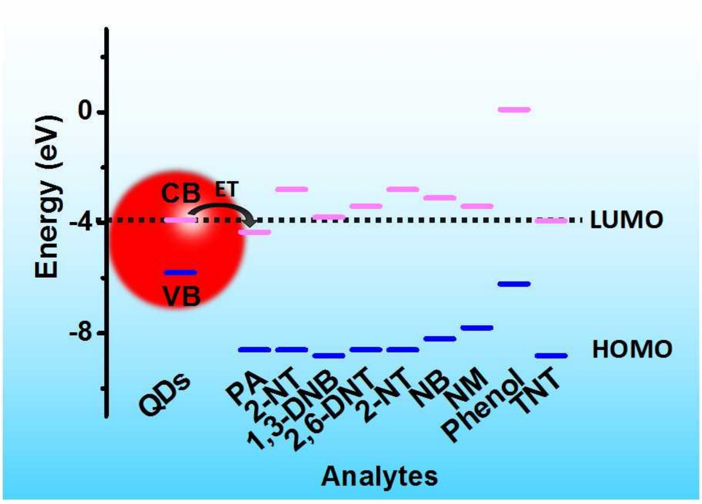

Fig. S6 HOMO and LUMO energies for CdTe/ZnS QDs and selected analytes.

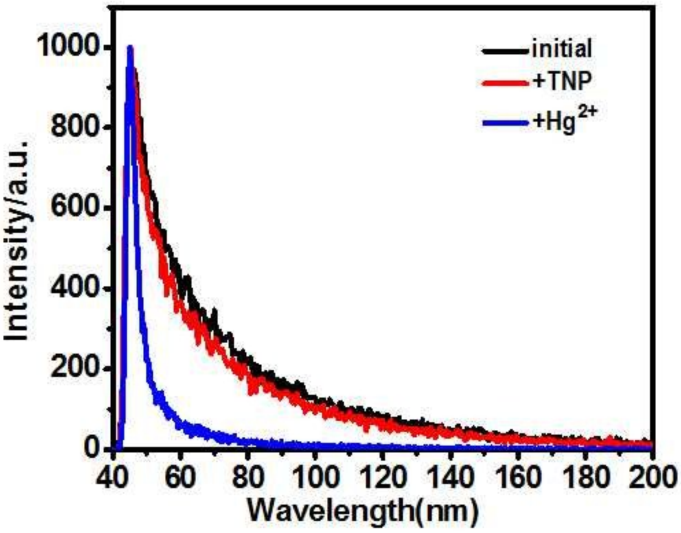

Fig. S7 Fluorescence decay curves for SDMs in aqueous solution without (black), with TNP (red) and Hg^{2+} (blue).

References:

1. N. Du, R. Tian, J. Peng and M. Lu, *J. Polym. Chem.*, 2005, **43**, 397-406.
2. H. Zhang, Z. Zhou, B. Yang and M. Gao, *J. Phys. Chem. B,* 2003, **107**, 8-17.
3. Y. F. Liu and J. S. Yu, *J. Colloid Interf. Sci.*, 2010, **351**, 1-9.