

Supporting Information

for

A surfactant-modulated fluorescent sensor with pattern recognition capability: sensing and discriminating multiple heavy metal ions in aqueous solution

Yuan Cao, Liping Ding*, Wenting Hu, Junxia Peng and Yu Fang

Key Laboratory of Applied Surface and Colloid Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, P. R. China

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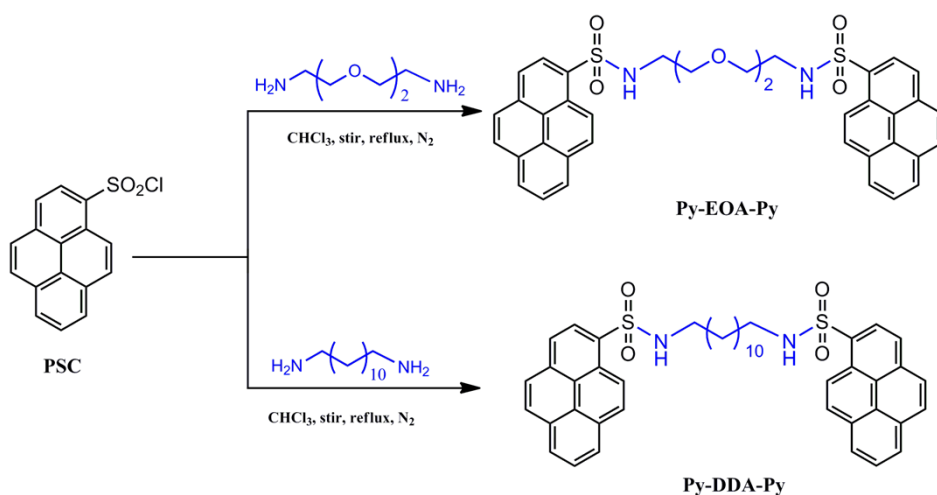
Experimental

1.1 Synthesis of N,N'-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(pyrene-1-sulfonamide) (Py-EOA-Py)

The analogous bispyrene derivative that contains two oxyethyl groups in the spacer was synthesized by reacting PSC with 2,2'-(ethane-1,2-diylbis(oxy))-diethanamine (EOA). The synthesis procedure is as follows: EOA (0.09 mL 0.68 mmol) was added into a solution of PSC (450 mg, 1.50 mmol) in CHCl_3 (200 mL) under stirring and N_2 atmosphere, then refluxed over a period of 24 h. After the mixture was cooled, it is washed with brine until the pH of the aqueous layer is neutral. Organic layers were combined and dried with anhydrous Na_2SO_4 overnight. Then it was filtered and evaporated to dryness under reduced pressure. The resulting yellow-green oil was purified by column chromatography on silica gel column with $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (v:v, 25:1) as eluent. Py-EOA-Py was obtained as a yellow solid after freeze-drying (265 mg, 86%). The synthesis route of Py-EOA-Py is shown in Scheme S1. ^1H NMR (400 MHz, CDCl_3): δ 8.91 (d, 1H), 8.66 (d, 1H), 8.17–8.02 (m, 7H), 5.71 (s, 1H), 3.29–3.24 (m, 2H), 3.14–3.04 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3): δ 134.74, 131.42, 130.83, 130.12, 130.04, 129.95, 128.01, 127.18, 126.96, 126.87, 126.80, 126.72, 125.14, 123.91, 123.75, 123.22, 70.11, 69.44, 42.98. MS (ESI, m/z): $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{38}\text{H}_{33}\text{N}_2\text{O}_6\text{S}_2$, 677.1775; found, 677.1773.

1.2 Synthesis of N,N'-(dodecane-1,12-diyl)bis(pyrene-1-sulfonamide) (Py-DDA-Py)

The control bis-pyrene derivative was synthesized using alkyl diamine as a spacer. The synthesis procedure is as follows: DDA (0.14 g 0.68 mmol) was added into a solution of PSC (450 mg, 1.5 mmol) in CHCl_3 (200 mL) under stirring and N_2 atmosphere, then refluxed over a period of 24 h. After the mixture was cooled, it was washed with brine until the pH of the aqueous layer is neutral. Organic layers were combined and dried with anhydrous Na_2SO_4 overnight. Then it was filtered and evaporated to dryness under reduced pressure. The obtained faint yellow crude product was purified by recrystallization with dichloromethane. Py-DDA-Py was obtained as a white solid after freeze-drying (387 mg, 78%). The synthesis route of Py-EOA-Py is shown in Scheme S1. ^1H NMR (400 MHz, CDCl_3): δ 8.97 (d, 1H), 8.70 (d, 1H), 8.29–8.07 (m, 7H), 4.70 (t, 1H), 2.91 (dd, 2H), 1.34–1.27 (m, 2H), 1.09–0.99 (m, 2H), 0.88 (dd, 6H). MS (ESI, m/z): $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_6\text{S}_2\text{Na}$, 751.2635; found, 751.2622.



Scheme S1. Synthesis routes of Py-EOA-Py and Py-DDA-Py

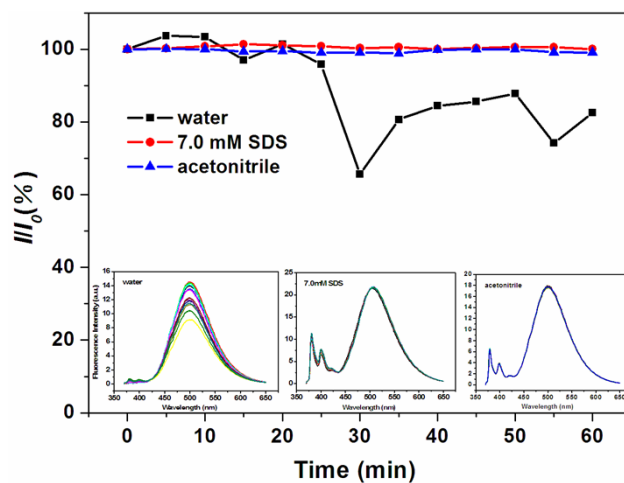


Fig. S1 Fluorescence intensity variation of Py-TOA-Py in water, 7.0 mM SDS and acetonitrile along scanning time. Inset: Fluorescence emission spectra of Py-TOA-Py in water, 7.0 mM SDS and acetonitrile along scanning time.

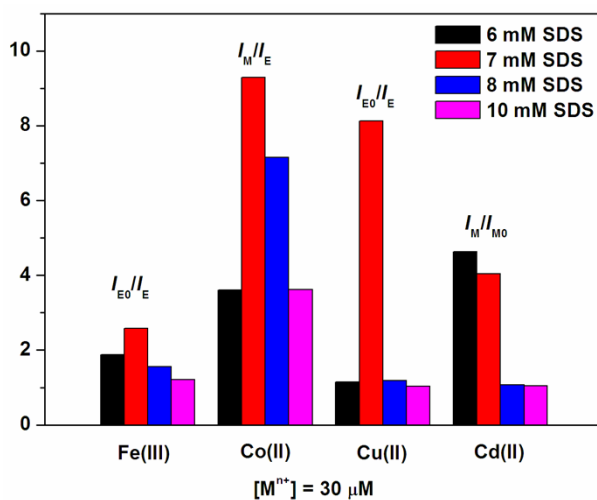


Fig. S2 Fluorescence intensity variation of Py-TOA-Py (1.0 μM) in different concentrated SDS aqueous solution upon titration of four representative metal ions at 30 μM .

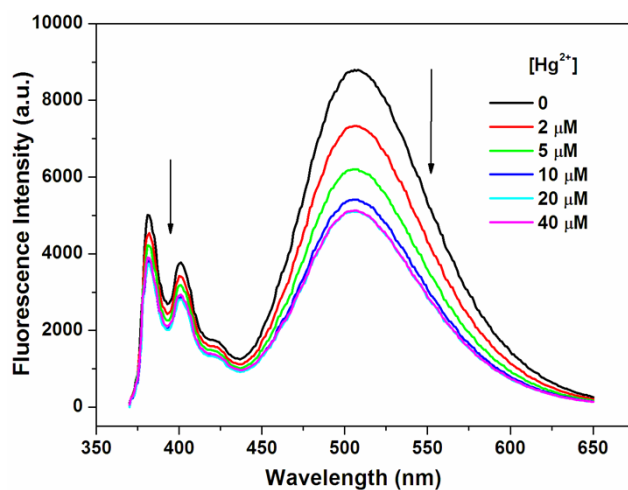
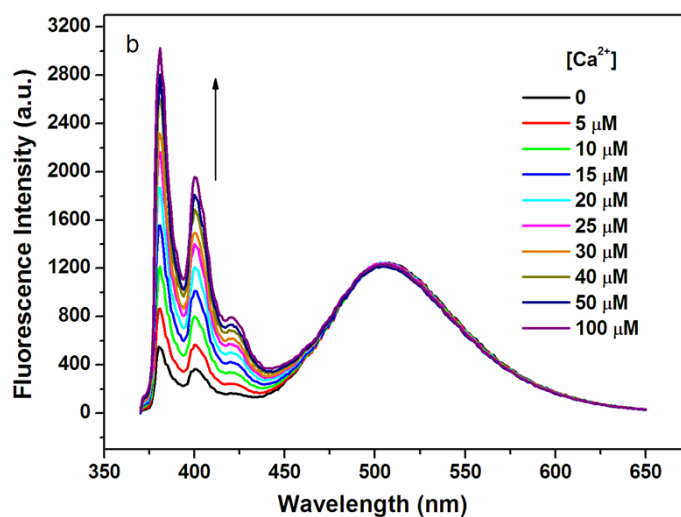
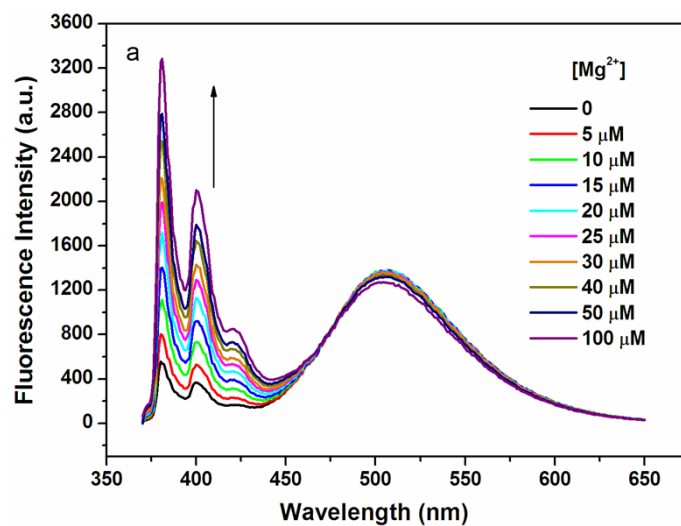


Fig. S3 Fluorescence spectra of Py-TOA-Py (1.0 μM) in 7 mM SDS aqueous solution upon addition of Hg^{2+} ions ($\lambda_{\text{ex}} = 350 \text{ nm}$).



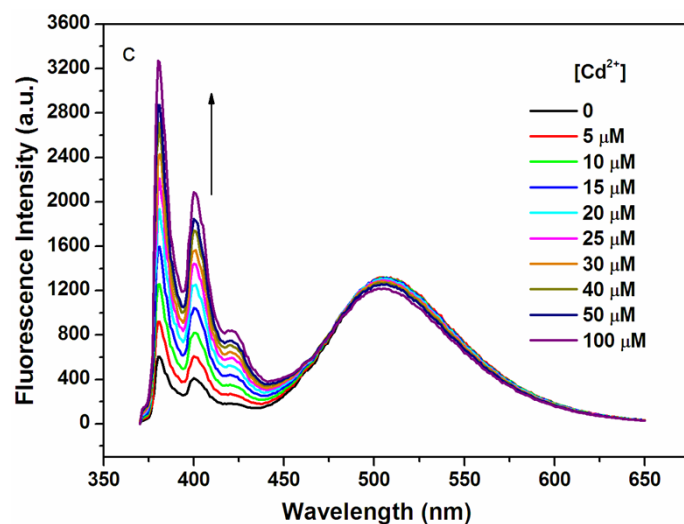


Fig. S4 Fluorescence spectra of Py-TOA-Py (1.0 μM) in 7 mM SDS aqueous solution upon addition of different metal ions: (a) Mg^{2+} ion; (b) Ca^{2+} ion; (c) Cd^{2+} ion. ($\lambda_{\text{ex}} = 350 \text{ nm}$)

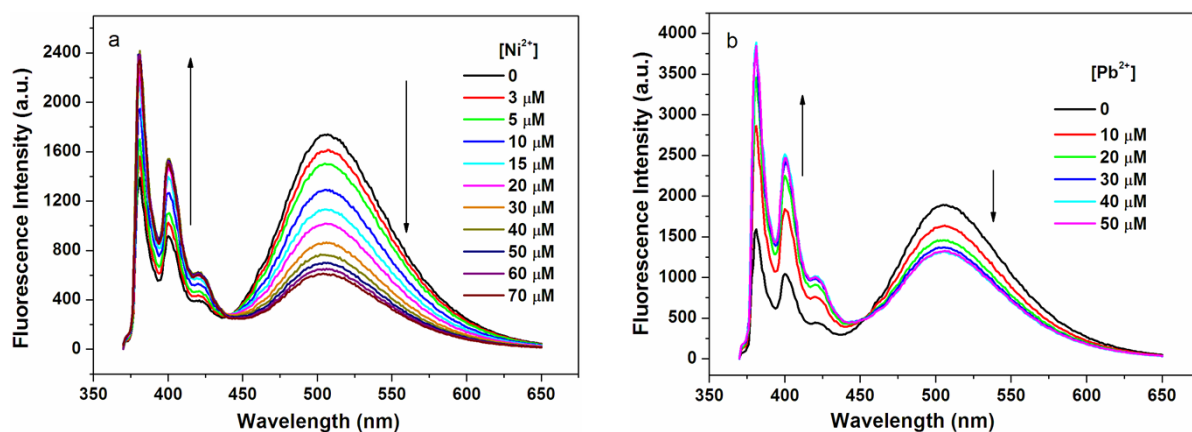
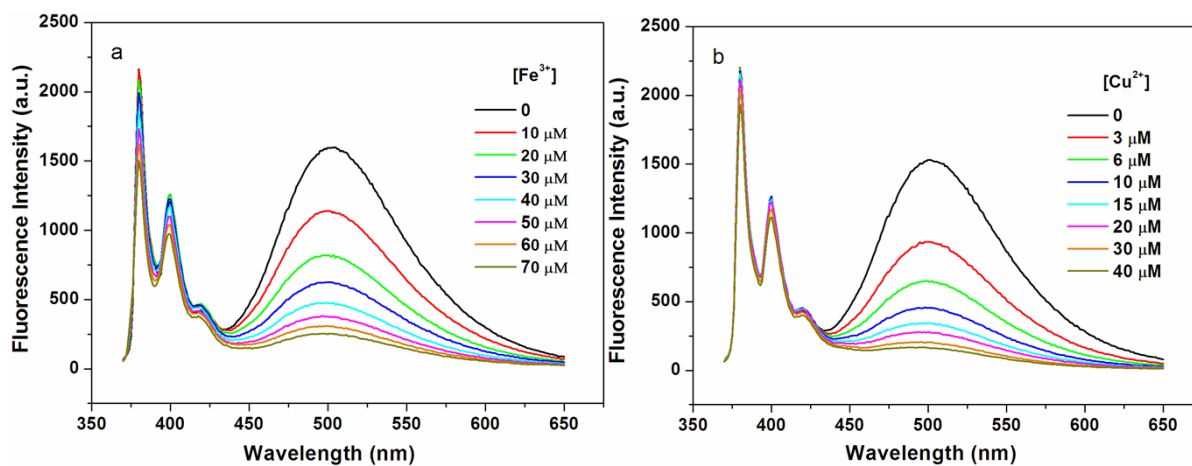


Fig. S5 Fluorescence spectra of Py-TOA-Py (1.0 μM) in 7 mM SDS aqueous solution upon addition of different metal ions: (a) Ni^{2+} ion; (b) Pb^{2+} ion. ($\lambda_{\text{ex}} = 350 \text{ nm}$)



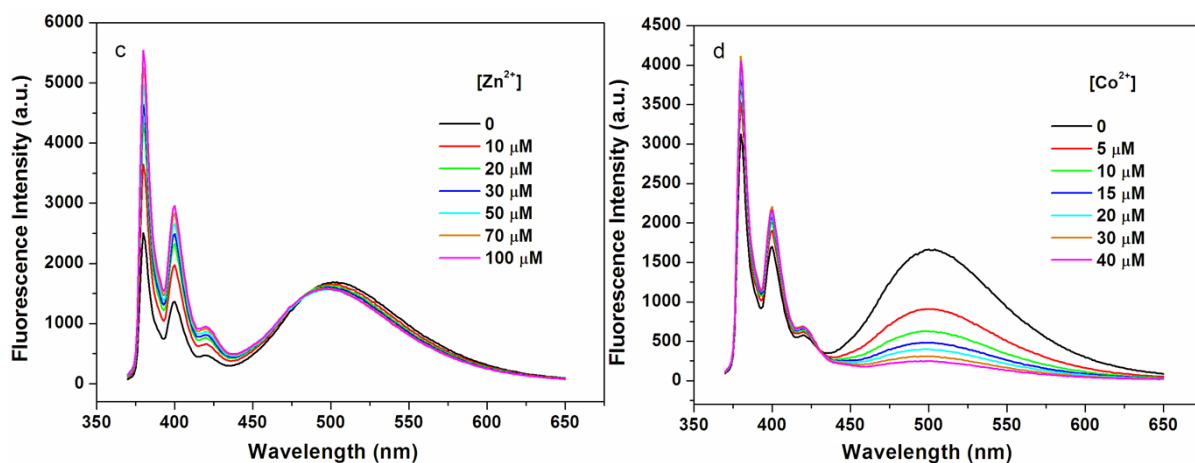


Fig. S6 Fluorescence spectra of Py-EOA-Py (1.0 μM) in 7 mM SDS aqueous solution upon addition of different metal ions: (a) Fe³⁺ ion; (b) Cu²⁺ ion; (c) Zn²⁺ ion; and (d) Co²⁺ ion. ($\lambda_{\text{exc}} = 350 \text{ nm}$)

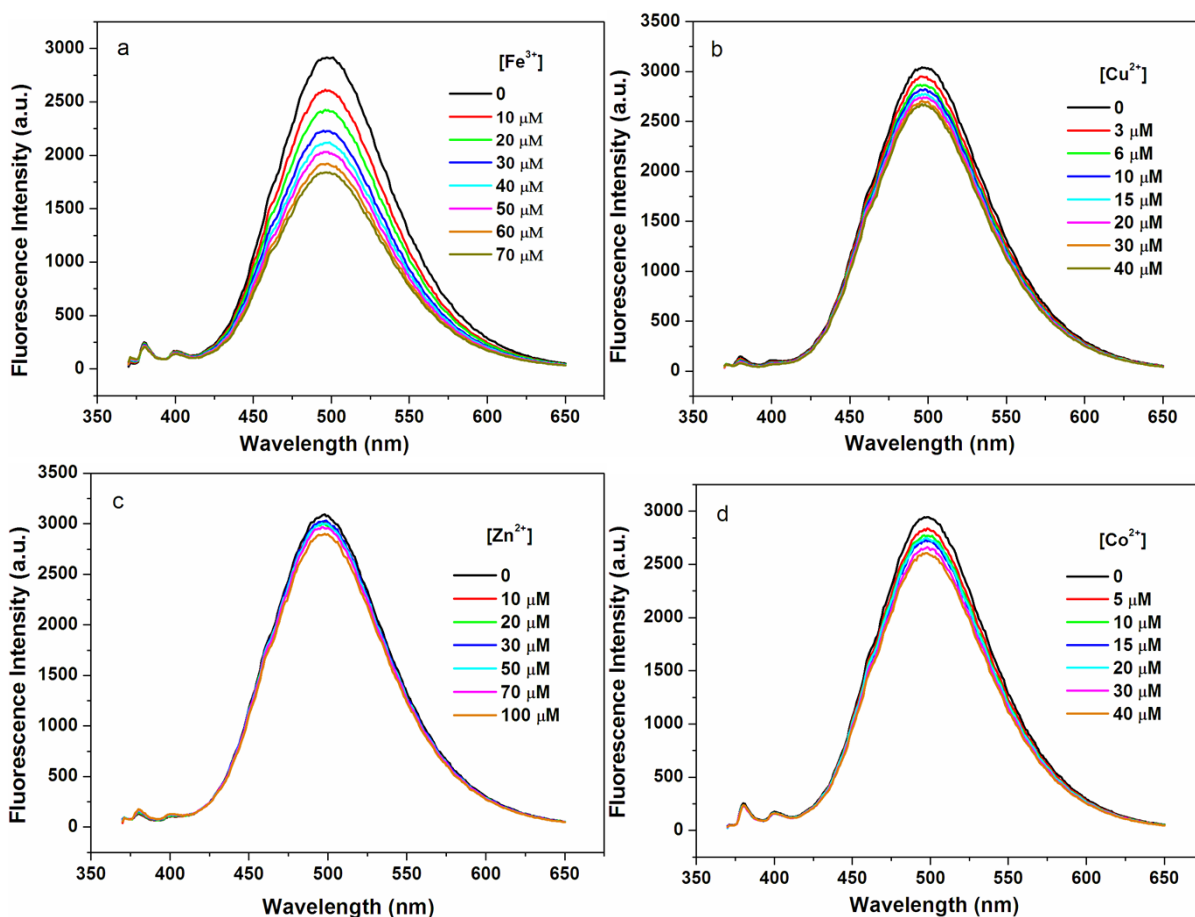


Fig. S7 Fluorescence spectra of Py-DDA-Py (1.0 μM) in 7 mM SDS aqueous solution upon addition of different metal ions: (a) Fe³⁺ ion; (b) Cu²⁺ ion; (c) Zn²⁺ ion; and (d) Co²⁺ ion. ($\lambda_{\text{exc}} = 350 \text{ nm}$)

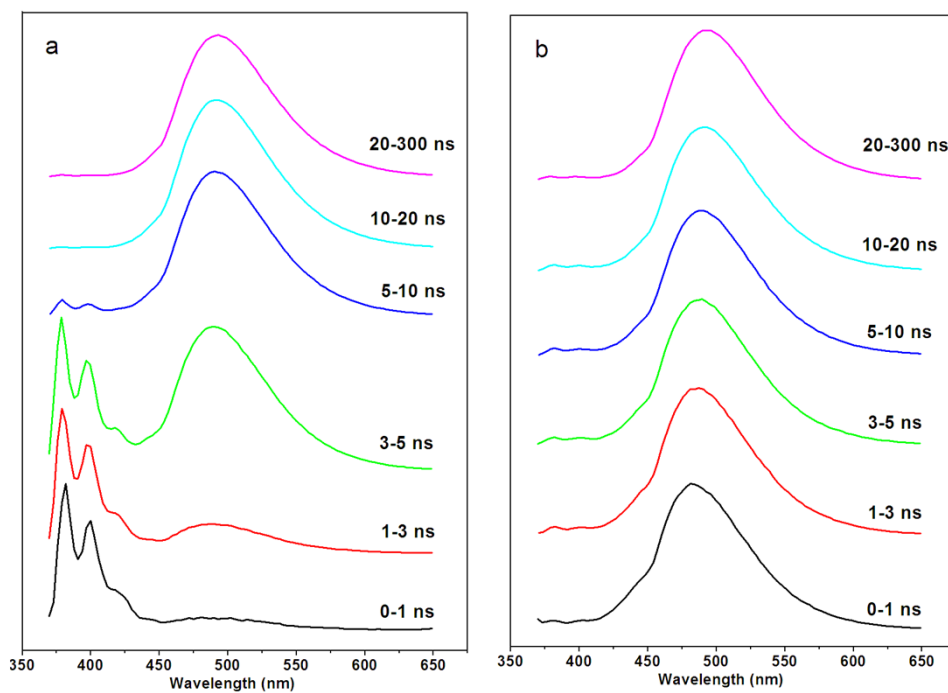
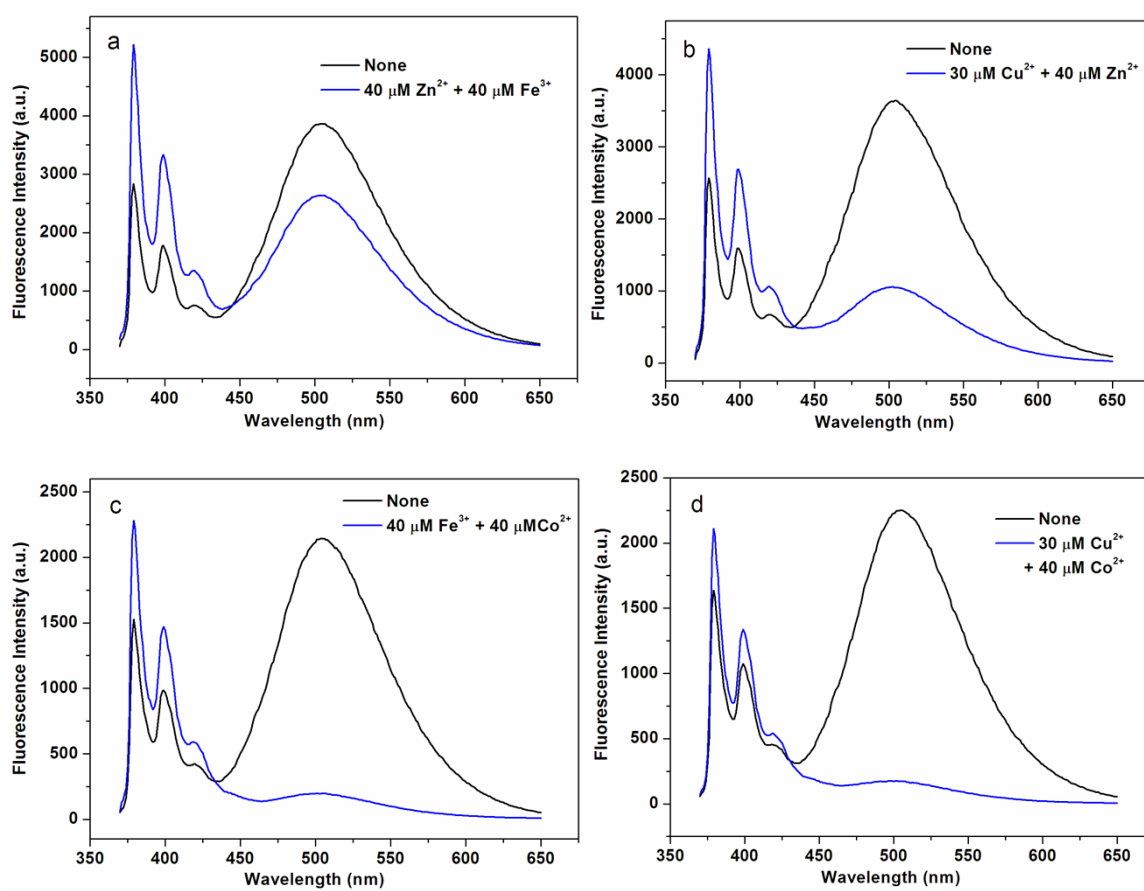


Fig. S8 Time-resolved emission spectra of Py-TOA-Py (1.0 μM) in acetonitrile (a) and water (b).



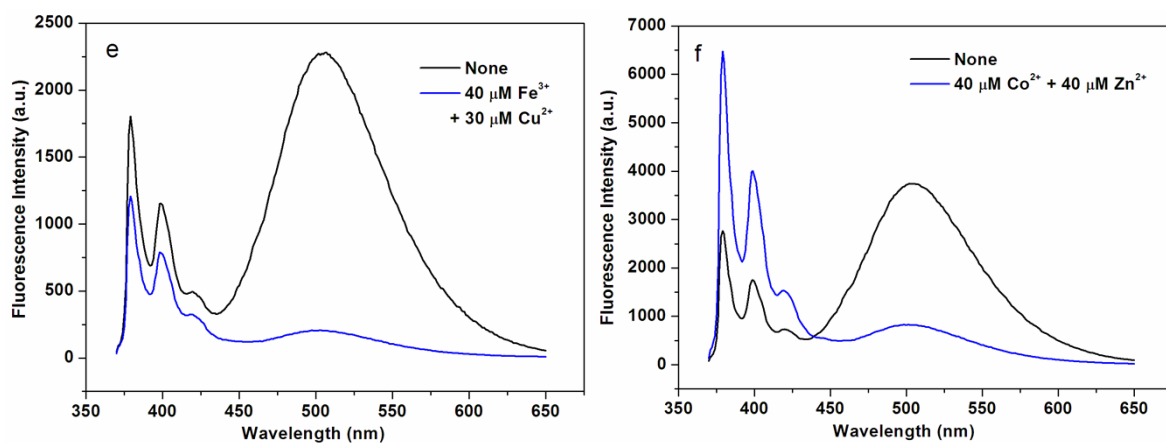


Fig. S9. Fluorescence responses of Py-TOA-Py/SDS to mixtures containing two competing metal ions: (a) Zn²⁺ and Fe³⁺; (b) Cu²⁺ and Zn²⁺; (c) Fe³⁺ and Co²⁺; (d) Cu²⁺ and Co²⁺; (e) Fe³⁺ and Cu²⁺; and (f) Co²⁺ and Zn²⁺.

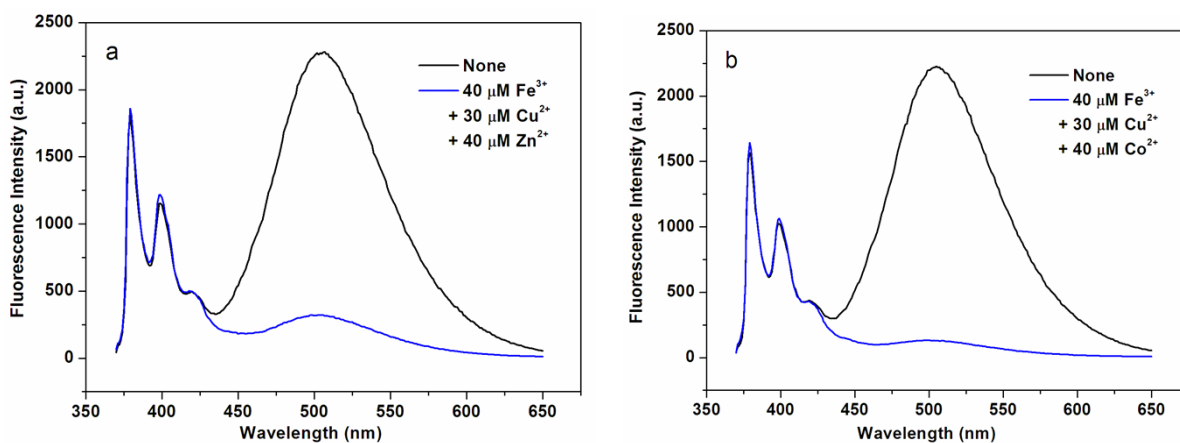


Fig. S10 Fluorescence responses of Py-TOA-Py/SDS to mixtures containing three metal ions: (a) Fe³⁺, Cu²⁺ and Zn²⁺; (b) Fe³⁺, Cu²⁺ and Co²⁺.

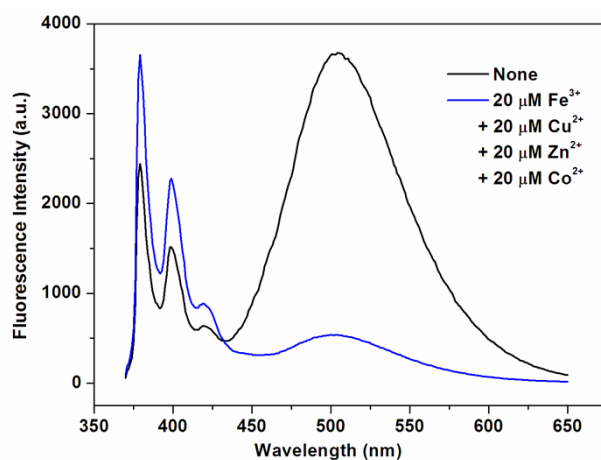


Fig. S11 Fluorescence responses of Py-TOA-Py/SDS to mixtures containing four metal ions including Fe³⁺, Cu²⁺, Zn²⁺ and Co²⁺.