Supplementary Information for:

Effects of Different Metal Ions on the Fluorescence of CdSe/ZnS Quantum Dots Capped with Various Thiolate Ligands

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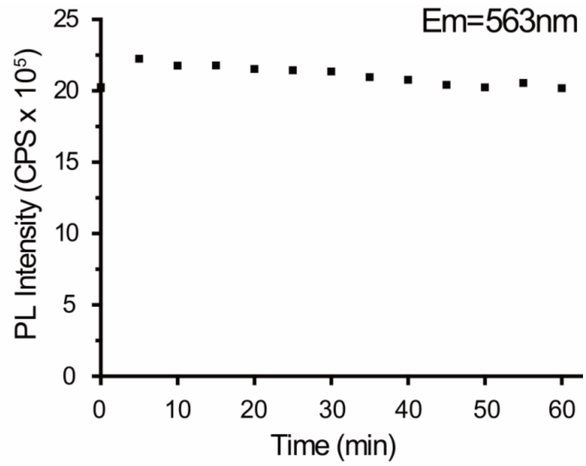

Fig. S1 Fluorescence stability test of Cys-QDs (λ_{em} = 563 nm). The PL spectra were recorded at an interval of 5 minutes in phosphate buffer (20 mM, pH 7.2), λ_{ex} = 350 nm.

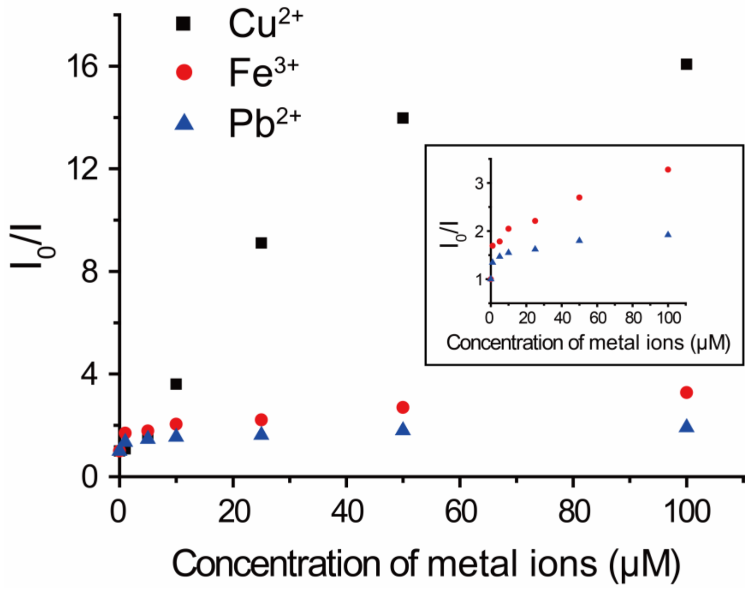

Fig. S2 Stern-Volmer plots for the PL quenching of MPA-QDs in the presence of various concentrations of Cu^{2+}, Fe^{3+}, and Pb^{2+}, respectively. Inset: expanded view of the Stern-Volmer plots for Fe^{3+} and Pb^{2+} group. The PL data were obtained in phosphate buffer (20 mM, pH 7.2), λ_{ex} = 350 nm. $C_{[metal\ ions]}$ = 0, 1, 5, 10, 25, 50, 100 μM.

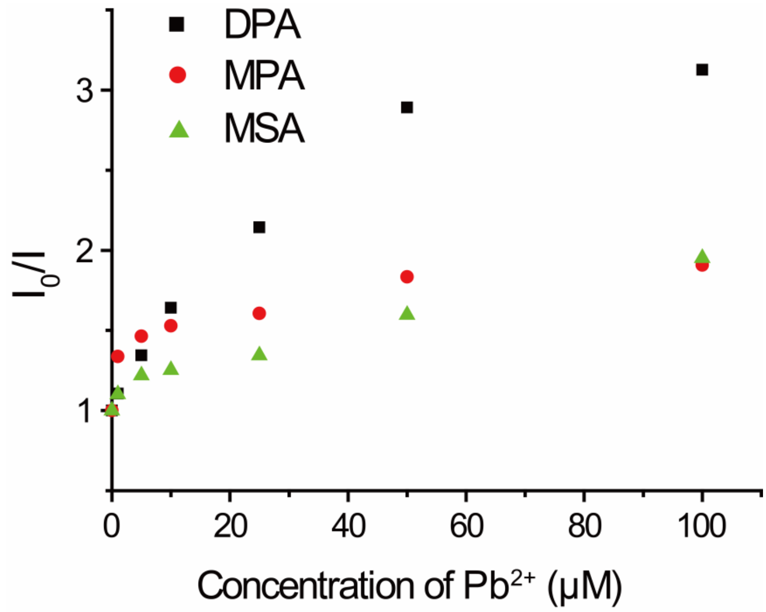

Fig. S3 Stern-Volmer plots for the PL quenching of DPA-QDs, MPA-QDs, and MSA-QDs in the presence of various concentrations of Pb^{2+}. The PL data were obtained in phosphate buffer (20 mM, pH 7.2), λ_{ex} = 350 nm. $C_{[Pb]}$ = 0, 1, 5, 10, 25, 50, 100 μM.

In addition to the fluorescence recovery experiments, we also performed fluorescence decay experiments to investigate the mechanisms of fluorescence quenching induced by metal ions (Fig. S4 and Table S1). All the obtained PL decay curves could be well fitted by a biexponential function:

$$I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$$

The derived QD lifetimes are comprised of two parts: short-lived component (τ_1) and long-lived component (τ_2), where the former is associated with core-state recombination and the latter attributed to surface-related emission.[1-2] Fig. S4 shows three typical PL decay curves for Cys-QDs before and after the addition of Cu^{2+} and Ni^{2+}. The corresponding time-resolved fluorescence parameters were summarised in Table S1. As can be clearly seen, the addition of 5 μM Cu^{2+} could induce a significant decrease of QD lifetime. Furthermore, the intensity average lifetime $<\tau_{i0}>$ and amplitude average lifetime $<\tau_{a0}>$ were reduced from 14.39 ns and 8.46 ns to 6.19 ns and 1.28 ns, respectively.

$$<\tau_{i0}>=(a_1\tau_1^2+a_1\tau_1^2)/(a_1\tau_1+a_1\tau_2)$$

$$<\tau_{a0}>=(a_1\tau_1+a_1\tau_2)/(a_1+a_1)$$

More importantly, the contribution of long-lived emission to the total PL intensity dramatically decreased in the presence of 5 μM Cu^{2+}, which was indicative of destruction of the surface state of QDs,[2] in accordance with the fluorescence recovery experiments. On the other hand, the average lifetime $<\tau_{i0}>$ and $<\tau_{a0}>$ were much less affected by the introduction of Ni^{2+}. And only a slight decrease was observed in the contribution of long-lifetime component τ_2, implying that the Cys-QD surface was almost intact when exposed to Ni^{2+}.

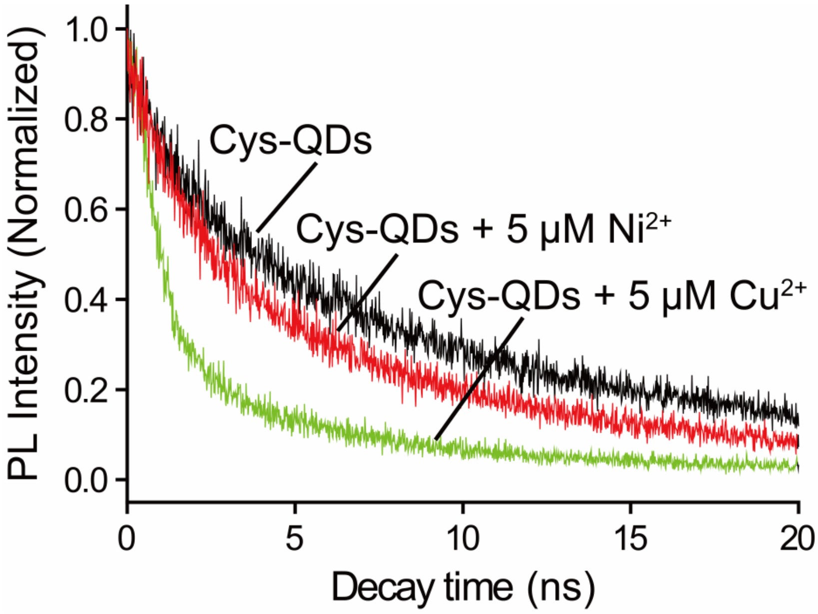

Fig. S4 Fluorescence decay profiles of Cys-QDs in the absence or presence of Cu^{2+} (5 μM) and Ni^{2+} (5 μM), respectively. The luminescence of Cys-QDs was monitored at λ_{max} = 563 nm with a 340 nm excitation laser in phosphate buffer (20 mM, pH 7.2).

Table S1 Time-resolved fluorescence parameters of Cys-QDs for various concentrations of Cu^{2+} and Ni^{2+}. The luminescence of Cys-QDs was monitored at λ_{max} = 563 nm with a 340 nm excitation laser in phosphate buffer (20 mM, pH 7.2).

Metal ions [μM]	τ_1 [ns] (b_1)[a]	τ_2 [ns] (b_2)[a]	$<\tau_{i0}>$[b] [ns]	$<\tau_{a0}>$[c] [ns]	χ^2
0	2.66 (0.19)	17.12 (0.81)	14.39	8.46	1.03
1 (Cu^{2+})	1.52 (0.24)	14.60 (0.76)	11.49	4.79	1.28
5 (Cu^{2+})	0.61 (0.44)	10.67 (0.56)	6.19	1.28	1.67
1 (Ni^{2+})	2.39 (0.22)	15.91 (0.78)	12.96	7.12	1.06
5 (Ni^{2+})	2.23 (0.28)	13.97 (0.72)	10.72	5.69	1.13

[a]: Contribution of τ_i is given as b_i, $b_i = a_i\tau_i/(a_1\tau_1 + a_1\tau_2)$.
[b]: Intensity average lifetime $<\tau_{i0}>$ is calculated as $<\tau_{i0}> = (a_1\tau_1^2 + a_1\tau_1^2)/(a_1\tau_1 + a_1\tau_2)$.
[c]: Amplitude average lifetime $<\tau_{a0}>$ is calculated as $<\tau_{a0}> = (a_1\tau_1 + a_1\tau_2)/(a_1 + a_1)$.

References

1 X. Y. Wang, L. H. Qu, J. Y. Zhang, X. G. Peng and M. Xiao, *Nano. Lett.*, 2003, **3**, 1103-1106.

2 K. Santhosh, S. Patra, S. Soumya, D. C. Khara and A. Samanta, *ChemPhysChem*, 2011, **12**, 2735-2741.