Electronic Supplementary Material (ESI) for Analyst

A quantum dot-based "off-on" fluorescent probe for biological detection of zinc ions

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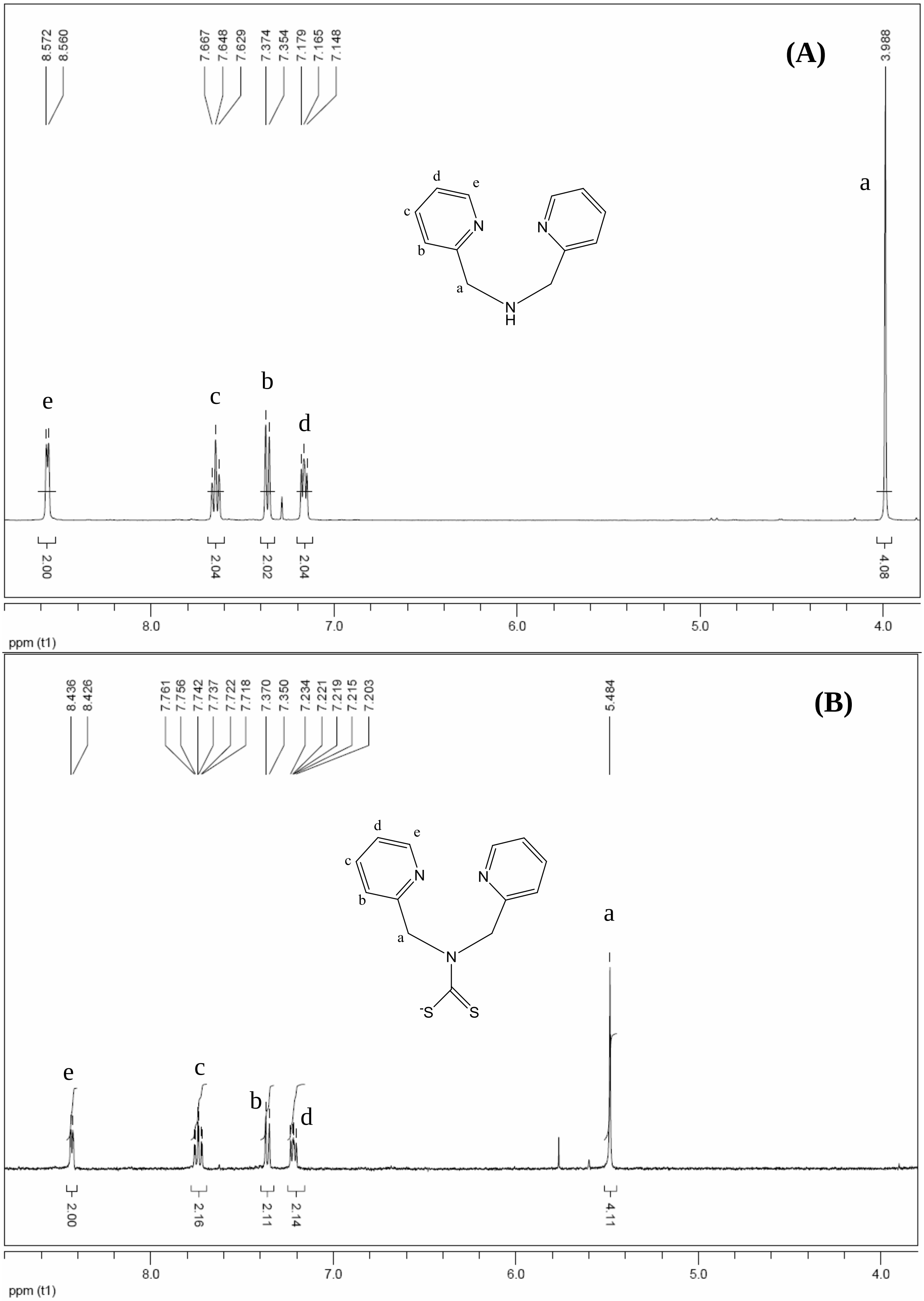

Fig. S1 ^{1}H NMR spectra of DPA and DPA-DTC in [D$_6$]DMSO.

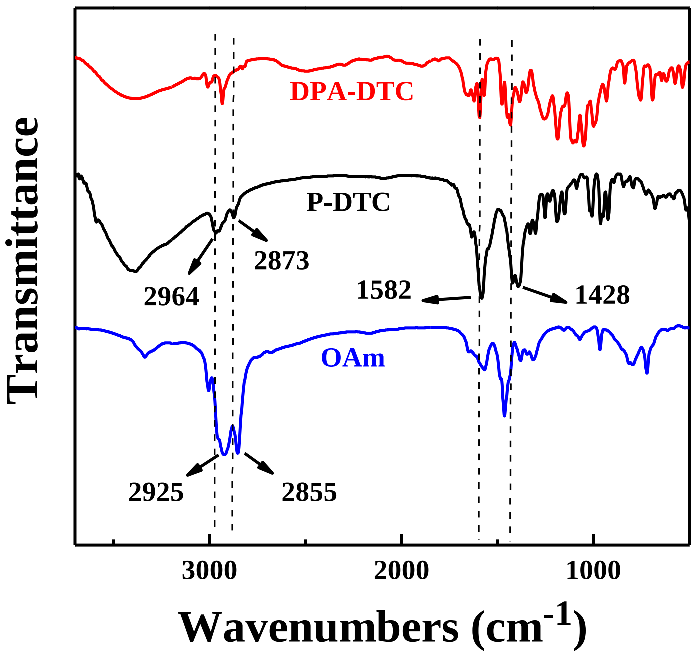

Fig. S2 The solid-state FTIR spectra of DPA-DTC, P-DTC, and OAm.

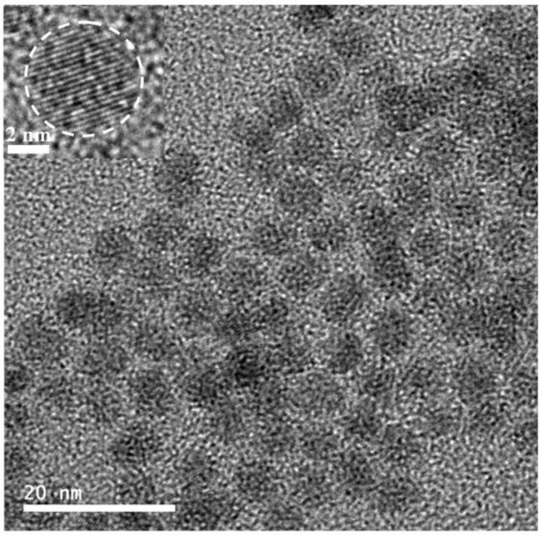

Fig. S3 Wide-field TEM image of DPA-P-DTC-QDs. The insert shows the corresponding HRTEM.

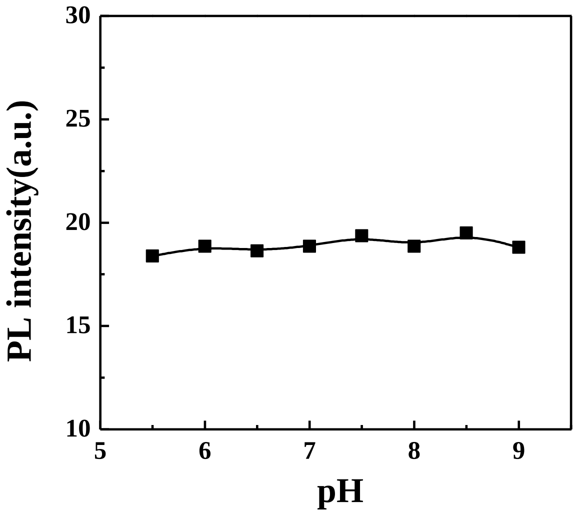

Fig. S4 The PL intensity of DPA-P-DTC-QDs at different pH values in the absence of Zn^{2+}. (λ_{ex} = 350 nm)

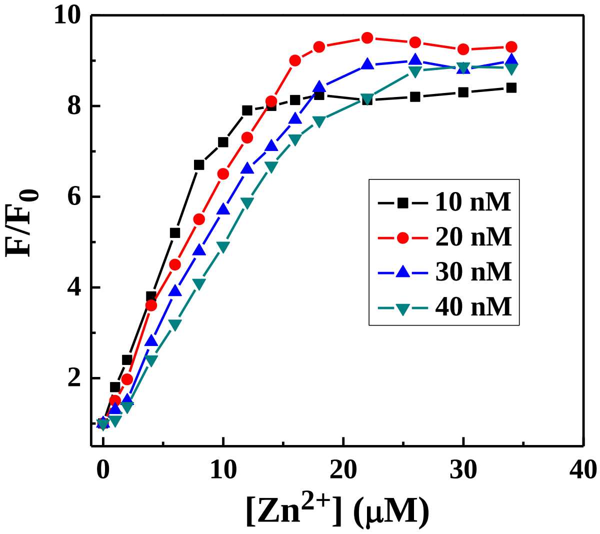

Fig. S5 The effect of the concentration of DPA-P-DTC-QDs on PL enhancement of QDs for Zn^{2+}.

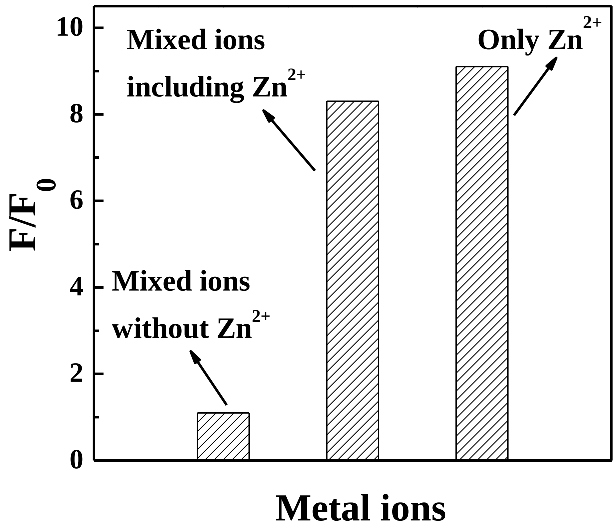

Fig. S6 Relative PL response (F/F_0) of DPA-P-DTC-QDs in the presence of (A) mixed ions including Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, and Pb^{2+} ions (each at 0.125 mM) except for Zn^{2+}, (B) mixed ions (each at 0.125 mM, no Cu^{2+}, Ag^{+}, Fe^{2+}, Fe^{3+}, and Hg^{2+} ions) containing Zn^{2+} (16 μM), and (C) only Zn^{2+} (16 μM) at pH 7.5 (PBS, 10 mM).

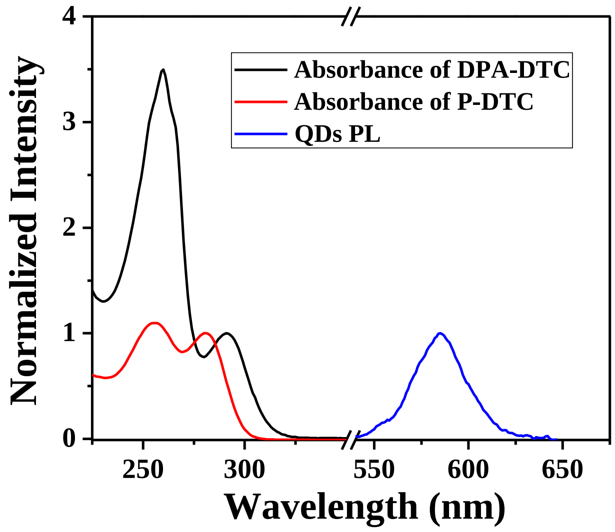

Fig. S7 Normalized absorbance of DPA-DTC and P-DTC and normalized PL intensity of CdSe/ZnS QDs.

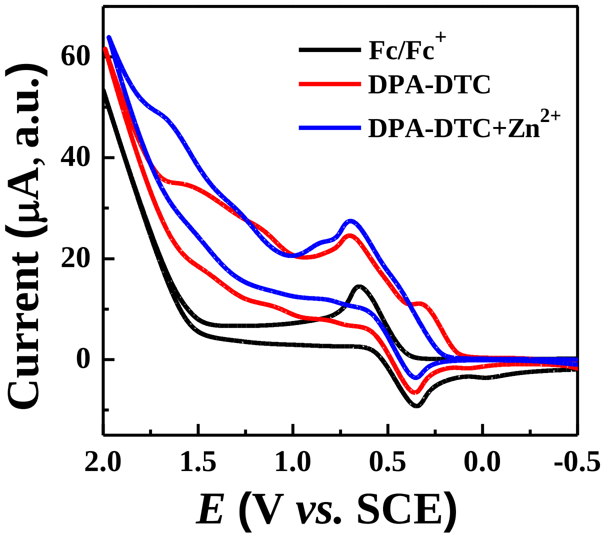

Fig. S8 Cyclic voltammograms of Fc/Fc^{+} (black curve), DPA-DTC in the absence of Zn^{2+} (red curve), and DPA-DTC in the presence of equimolar Zn^{2+} (blue curve) at scan rate 100 mV/s. For the red and blue curves, except for the reversible peaks of Fc/Fc^{+} redox couple there is a very broad and irreversible anodic peak in the range of 0.4–1.5 V, which can be assigned to the formation of dithiocarbamate radicals *via* oxidation and the subsequent dimerization of these radicals to thiuram disulfide (L. Marek, *Zeszyty Naukowe Politechniki Gdanskiej*, *Chemia*, 2003, **51**, 3–96.). This transformation should always exist in DPA-DTC containing system whether or not Zn^{2+} is present in the system. The repeated measurement gave the similar results. Thus, the equimolar Zn^{2+} addition into DPA-DTC solution only trigger the disappearance of anodic peak at 0.3 V and the occurrence of a new anodic peak at 1.7 V, which essentially reflects the energy level change of the HOMO of DPA-DTC before and after adding Zn^{2+}.

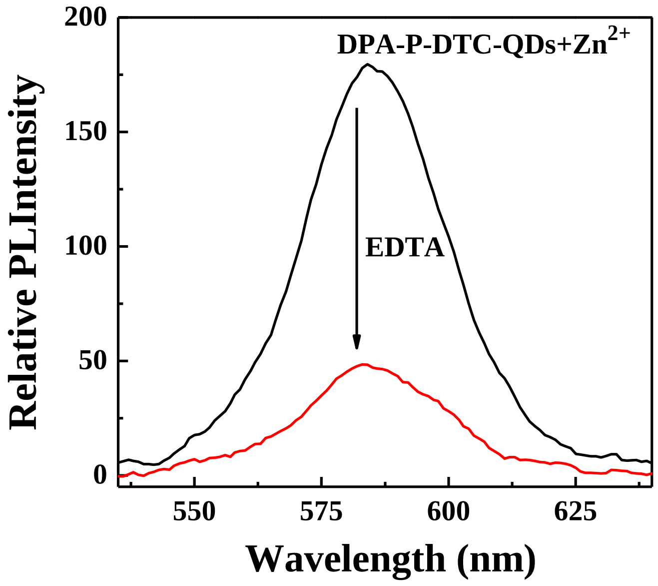

Fig. S9 The re-quenching of the recovered PL of DPA-P-DTC-QDs suspension containing Zn^{2+} (16 μM) upon the addition of EDTA (16 μM).

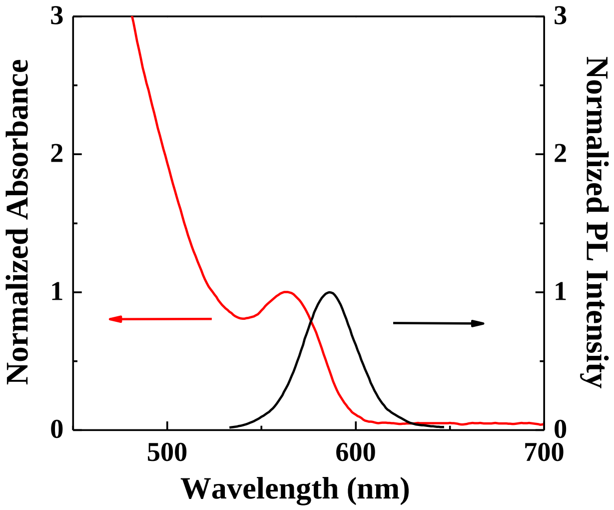

Fig. S10 The normalized UV-vis and PL spectra (λ_{ex} = 350 nm) of DPA-P-DTC-QDs in PBS (10 mM, pH 7.5).

Table S1 Fluorescence lifetime data for OAm-capped CdSe/ZnS QDs and DPA-P-DTC-QDs in the absence and presence of Zn^{2+}.

Substrate	Emission lifetimes^{a}/ns		Average lifetime^{b}
	τ_1	τ_2	$\tau_{av/ns}$
OAm-capped CdSe/ZnS QDs	6.03 (51%)	24.31 (49%)	20.56
DPA-P-DTC-QDs	2.29 (77%)	8.31 (23%)	5.41
DPA-P-DTC-QDs + Zn^{2+}	3.19 (44%)	15.65 (56%)	13.94

^{a}The PL decay was analyzed using the express $F(t) = a_1\exp(-t/\tau_1) + a_2\exp(-t/\tau_2)$, where τ_1 and τ_2 were the lifetimes. The values in parentheses indicate the fraction (%) of the corresponding lifetime component. ^{b}The average lifetime values was calculated using the expression $\tau_{av} = \sum a_i\tau_i^2 / \sum a_i\tau_i$.

Table S2. Comparison of detection performance of various QDs-based probes for Zn^{2+}.

Linear range	**Detection limit**	**Detection Probes**	**References**
0-20 μM	0.8 μM	L-cysteine-capped CdS QDs	29b
5-500 μM	2.4 μM	Azamacrocycle activated QDs	29c
10-1000 μM	0.57 μM	CdSe/ZnS core/shell QDs-zincon conjugates	29d
1.6-35 μM	1.2 μM	CdTe QDs	29e
0.3-15 μM	0.08 μM	Mn^{2+} doped ZnS QDs	29f
0.2-5.0 mM	No report	Iminodiacetate-capped CdSe/ZnS core/shell QDs	29a
0.9-16 μM	0.7 μM	DPA-P-DTC-QDs	This work