

Supporting Information

Quantum dots based turn-on fluorescent probes for anion sensing

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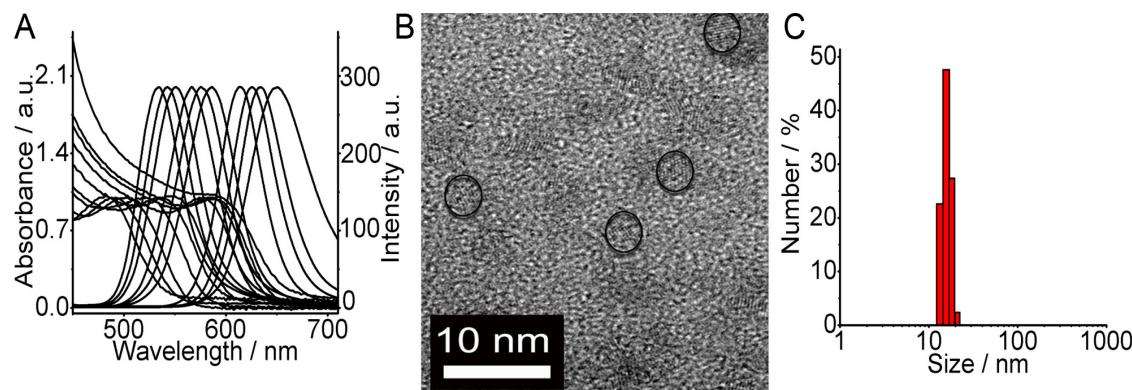


Fig. S1 (A) UV-Vis absorption and fluorescence spectra of TGA-capped CdTe QDs obtained at different reflux time (from 1 to 25 h). (B) TEM image of TGA-capped CdTe QDs with emission peak at 575 nm. (C) The hydrodynamic diameter of TGA-capped CdTe QDs shown in Fig. S1B determined by DLS. CdTe QDs are chosen here because of their high emission quantum yields and precisely manipulating synthesis. As shown in Fig. S1A, the emission wavelengths can be continually tuned from 534 to 650 nm by simply increasing reflux time from 1 h to 25 h. Accordingly, their sizes increase from 3.0 to 4.3 nm. The fluorescence quantum yields of the QDs are 10-45% depending on their particle sizes. The absorption spectra exhibit no any obvious scattering at whole wavelength region, indicates well dispersion of the as-prepared CdTe QDs because of strong electrostatic repulsion effect. Fig. S1B shows the typical TEM image of the CdTe QDs (emission wavelength is centered at 575 nm), their TEM size is about 3.3 ± 0.5 nm, which is in good agreement with the result estimated by UV-Vis absorbance. As shown in Fig. S1C, the DLS size of the QDs with 575 nm emission wavelength is about 14 nm. The larger DLS size may be ascribed to the formation of some oligomers of QDs (dimer, trimmer, and so on) during prerequisite by ethanol. (*J. Am. Chem. Soc.*, 2011, **133**, 18062.)

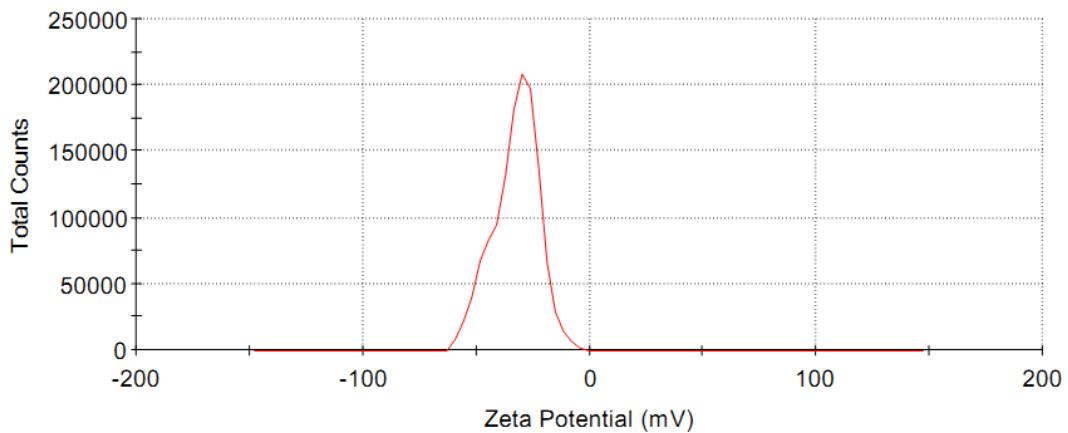


Fig. S2 ξ -potential of TGA-capped CdTe QDs.

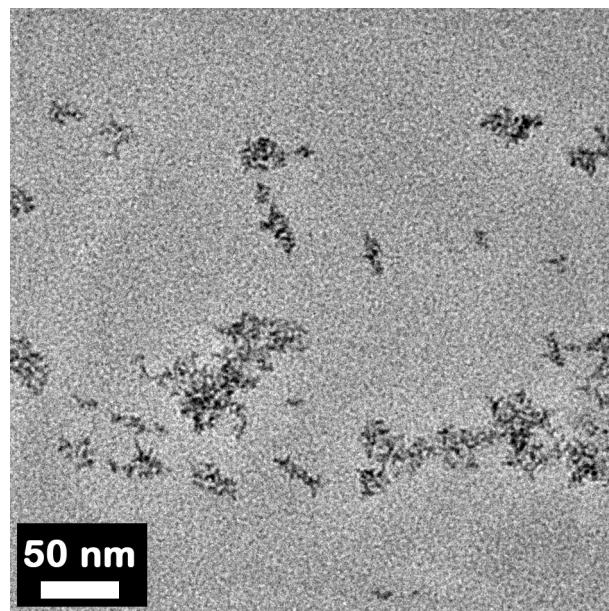


Fig. S3 TEM image of TGA-capped CdTe QDs in the presence of 20 μM Ca^{2+} ions.

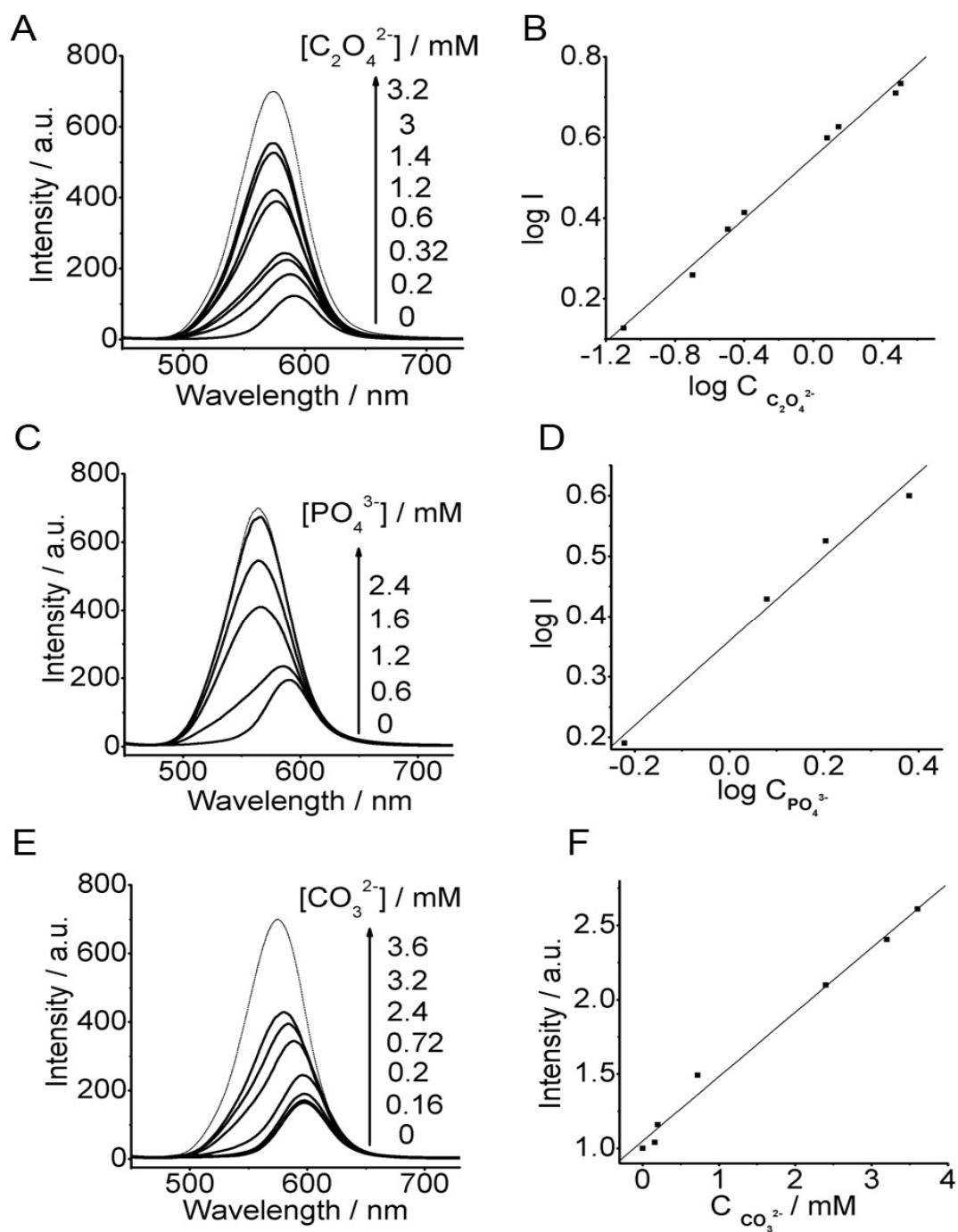


Fig. S4 A, C and E: Evolutions of fluorescence spectra of QDs-Ca²⁺ system with increasing different concentrations of C₂O₄²⁻, PO₄³⁻, CO₃²⁻ ions, respectively. B, D and F: Linear plots of the fluorescence intensity against the concentration of C₂O₄²⁻, PO₄³⁻ and CO₃²⁻ ions, respectively. The detection limits of the three anions are 9, 48, 200 μM, respectively.

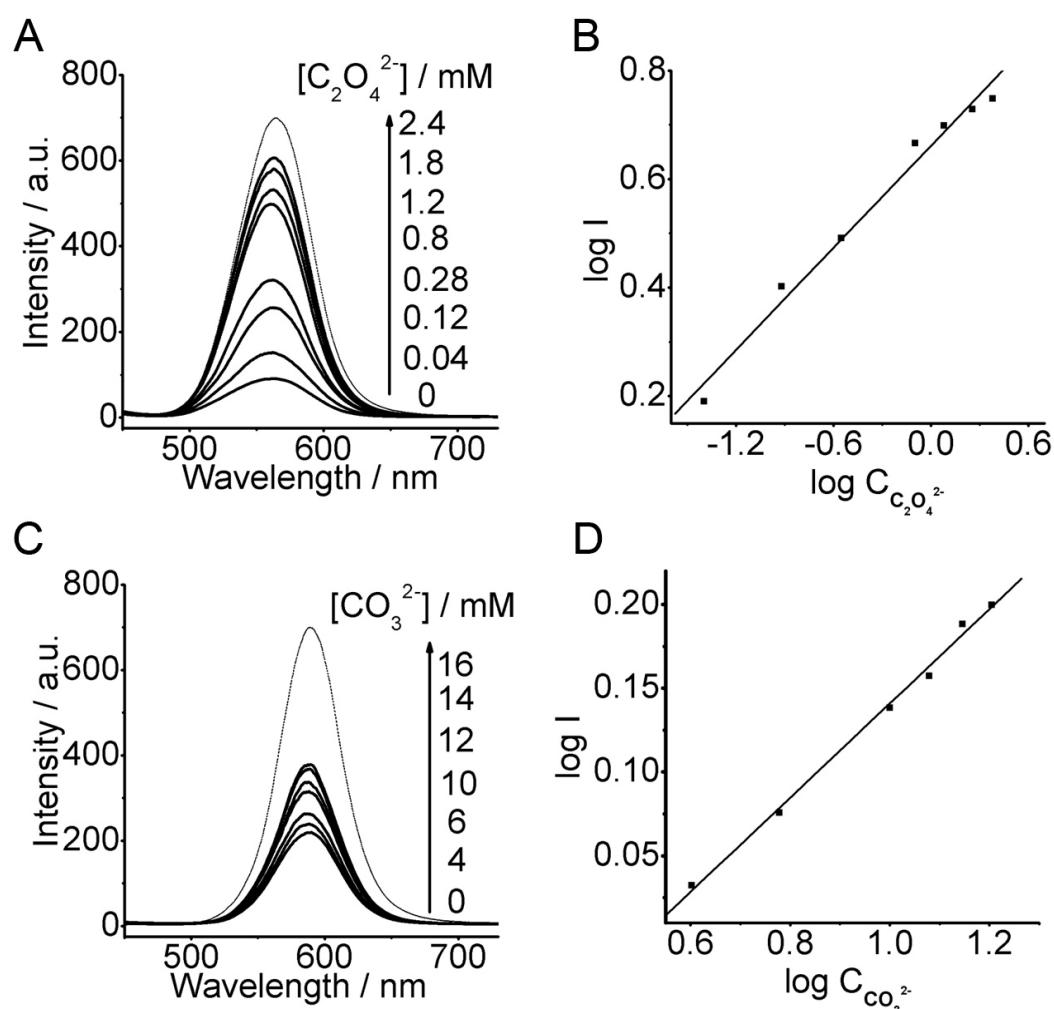


Fig. S5 A and C: Evolutions of fluorescence spectra of QDs-Ni²⁺ system with increasing different concentrations of $\text{C}_2\text{O}_4^{2-}$ and CO_3^{2-} ions. B and D: Linear plots of the fluorescence intensity against the concentration of $\text{C}_2\text{O}_4^{2-}$ and CO_3^{2-} ions. The detection limits of the two anions are 3.6 and 2500 μM .

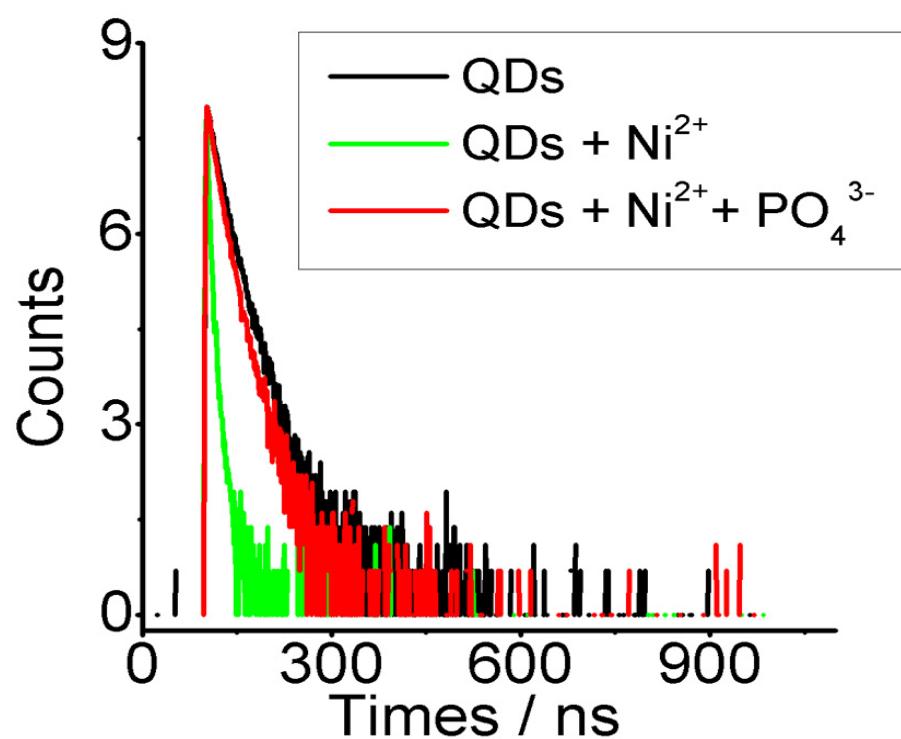


Fig. S6 Fluorescence decay curves of CdTe QDs, QDs-Ni²⁺ system and QDs-Ni²⁺-PO₄³⁻.

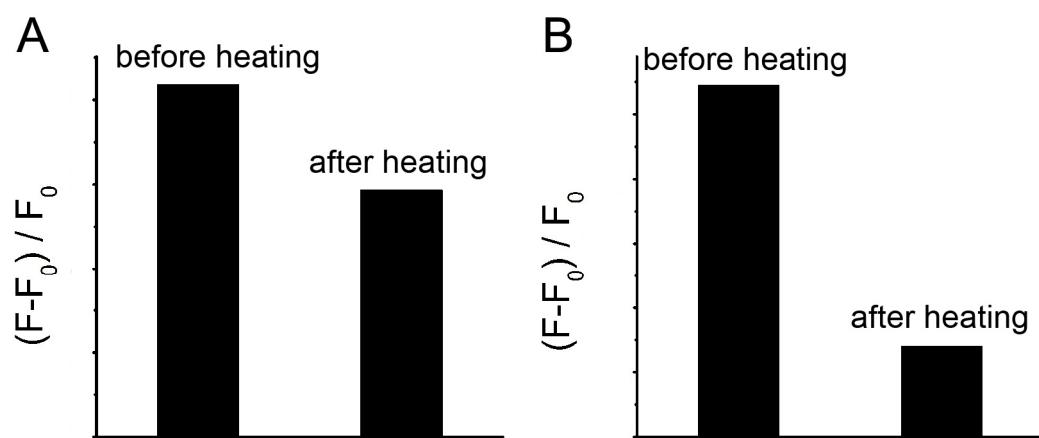


Fig. S7 Selective detection for PO_4^{3-} in the mixtures of $\text{PO}_4^{3-}\text{-C}_2\text{O}_4^{2-}$ (A) and $\text{PO}_4^{3-}\text{-CO}_3^{2-}$ (B) after removing CO_3^{2-} and $\text{C}_2\text{O}_4^{2-}$ by heating, respectively. The mixtures were firstly tuned to acidic (pH 1-3) and heated to boiling for several hours. After the solutions cooled in the air, they were tuned back to neutral by NaOH. The concentrations of PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$ and CO_3^{2-} are 6 mM, 3 mM and 40 mM, respectively.

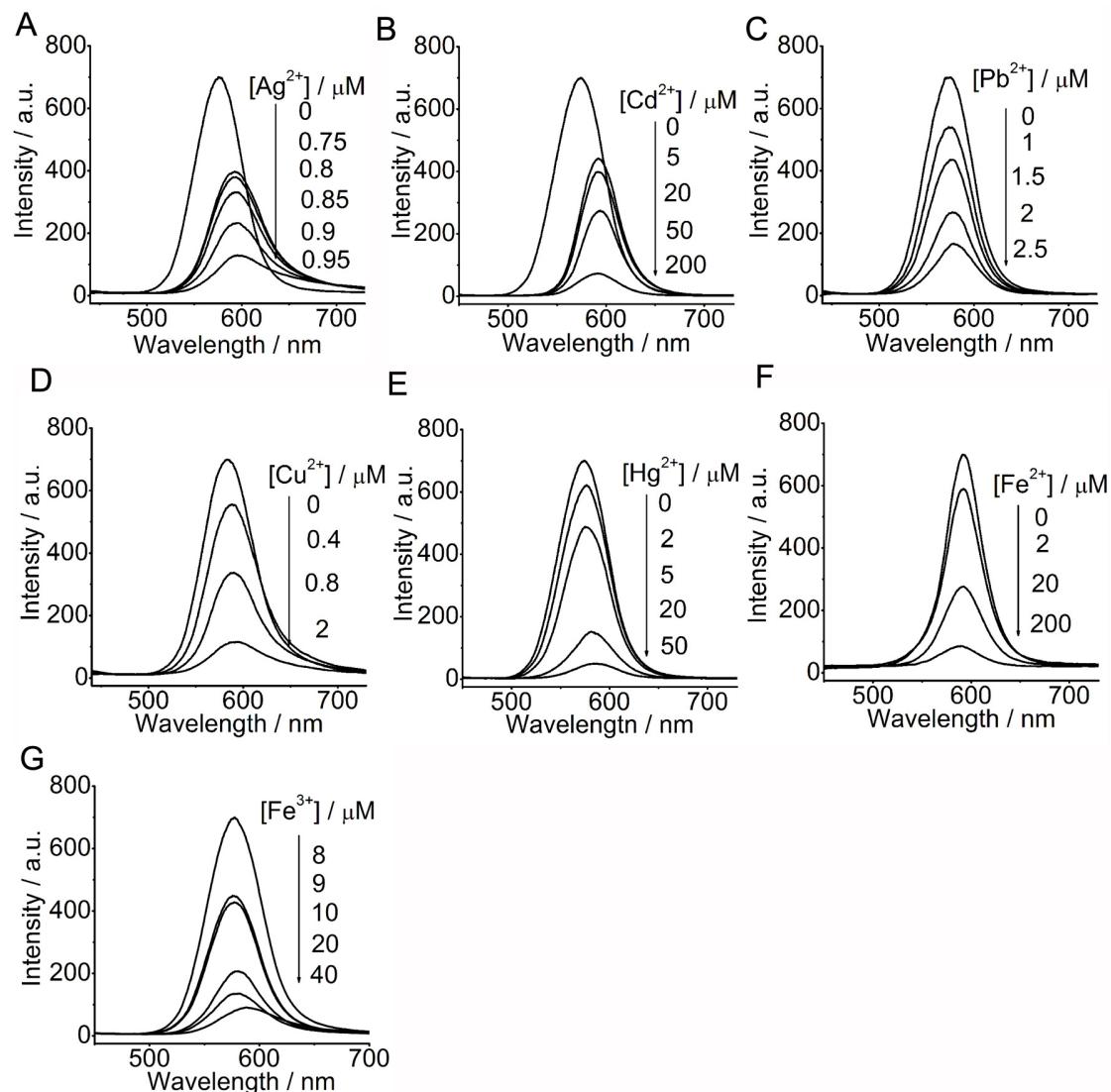


Fig. S8 Evolutions of fluorescence spectra of TGA-capped QDs with increasing different concentrations of various heavy metal ions.

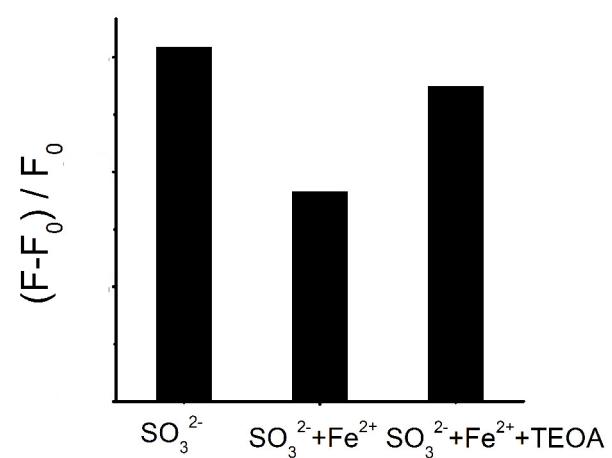


Fig. S9 Triethanolamine (TEOA) acts as masking agent for Fe^{2+} . The concentrations of SO_3^{2-} , Fe^{2+} and TEOA are 7.6 mM, 4 μM and 20 μM , separately.

Table S1 Fluorescence decay time (τ), quantum yield (Qy), radiative (kr) and nonradiative (knr) rate constants of CdTe QDs at different systems.

Sample	τ/ns	Qy	Kr/S^{-1}	KnR/S^{-1}
CdTe QDs	23.46	0.331	1.41×10^4	2.84×10^4
QDs-Ni ²⁺ system	6.79	0.071	1.04×10^4	1.37×10^5
QDs-Ni ²⁺ + PO ₄ ³⁻	20.17	0.244	1.21×10^4	3.73×10^4

Nonradiative (k_{nr}) and radiative (k_{r}) rate constants can therefore be calculated using the following equation:¹

$$k_r = \frac{Q_y}{\tau}$$

$$\tau = \frac{1}{k_r + k_{\text{nr}}}$$

References

1. Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: New York, 2001.