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Electronic Supplementary Information

Fluorescence Resonance Energy Transfer-Based Ratiometric Fluorescent Assay for Highly Sensitive and Selective Determination of Sulfide Anion

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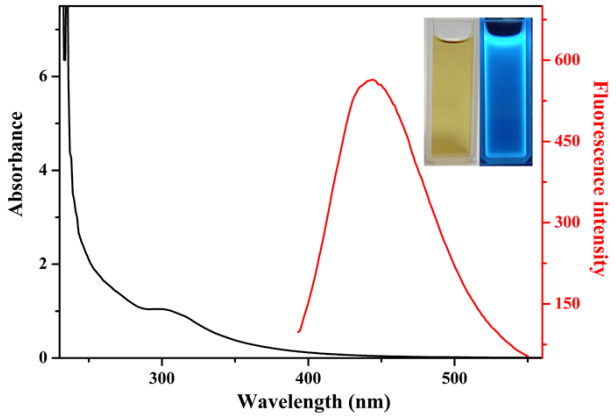

Fig. S1. The UV-vis absorption and fluorescence spectrum of the as-prepared CNPs, inset: CNPs solution under visible (left) and ultraviolet (right) light.

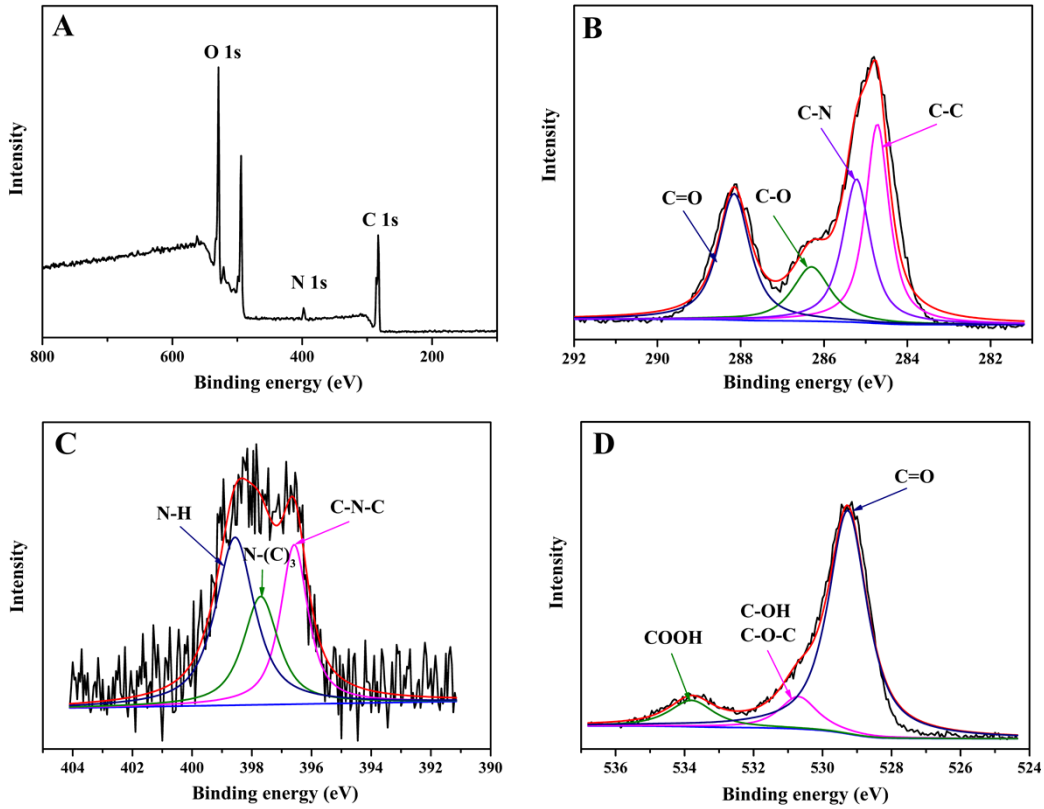

Fig. S2. (A) The XPS survey spectrum of as-prepared CNPs, (B) C 1s, (C) N 1s and (D) O 1s high-resolution spectra of the as-prepared CNPs.

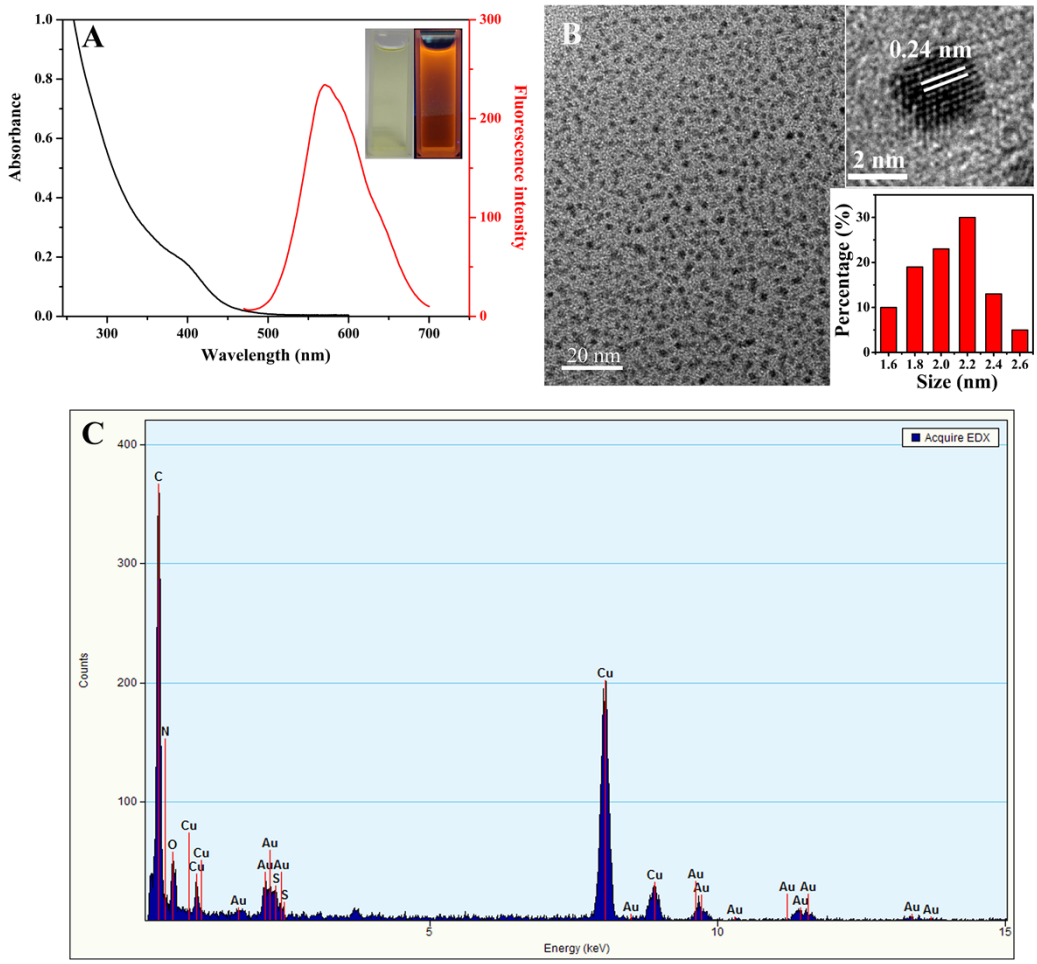

Fig. S3. (A) The UV-vis absorption and fluorescence spectrum of the as-synthesized Au NCs, inset: Au NCs solution under visible (left) and ultraviolet (right) light, (B) TEM image of Au NCs, inset: the corresponding HRTEM (top) and the size distribution histograms of Au NCs (bottom), (C) Energy-dispersive X-ray (EDX) of Au NCs.

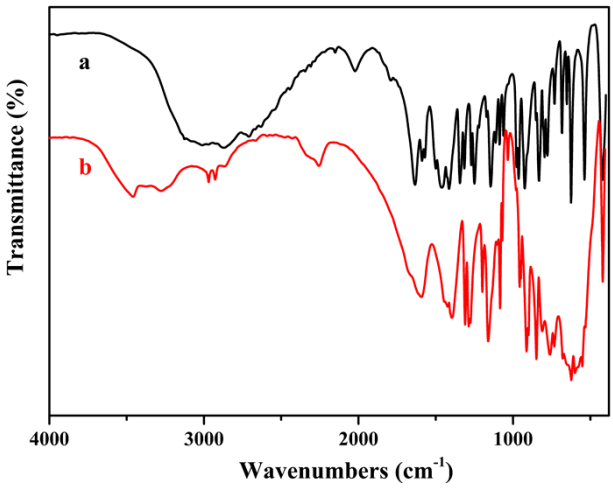

Fig. S4. FT-IR spectra of histidine (curve a) and trisodium citrate dihydrate (curve b).

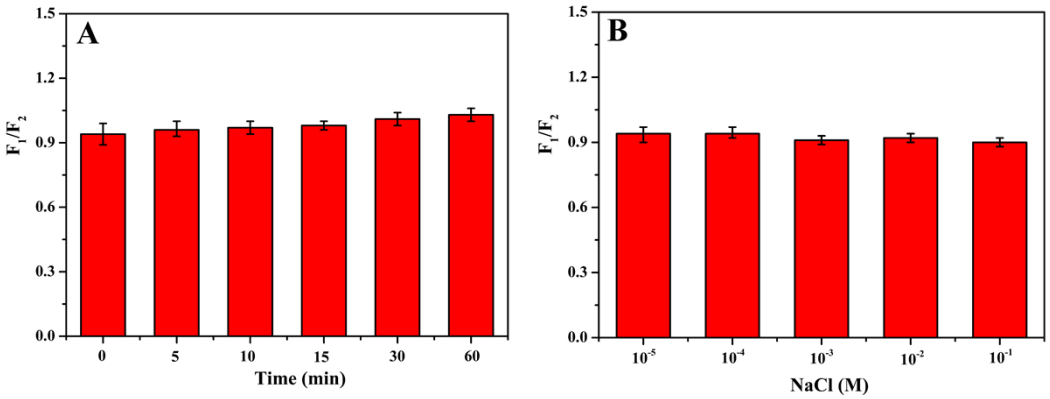

Fig. S5. (A) Photostability of the nanohybrid CNPs-Au NCs estimated by the 375 nm xenon lamp equipped in the fluorescence spectrometer, (B) Stability of the nanohybrid CNPs-Au NCs in the presence of various concentrations of NaCl. The error bars represent standard deviations based on three independent measurements.

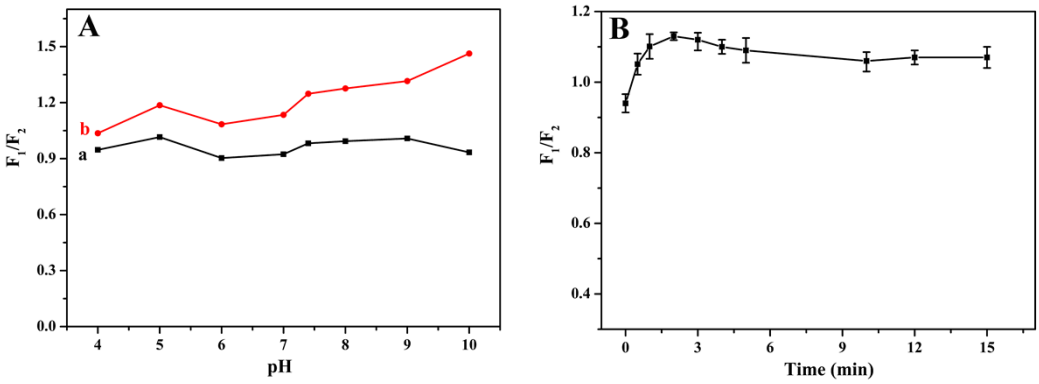

Fig. S6. (A) Effect of pH on the sensing system in the absence (curve a) and presence of S^{2-}(curve b), (B) Time-dependent fluorescence intensity ratio (F_1/F_2) of the nanohybrid CNPs-Au NCs as a function of time ([S^{2-}] = 10 μM). The error bars represent standard deviations based on three independent measurements.

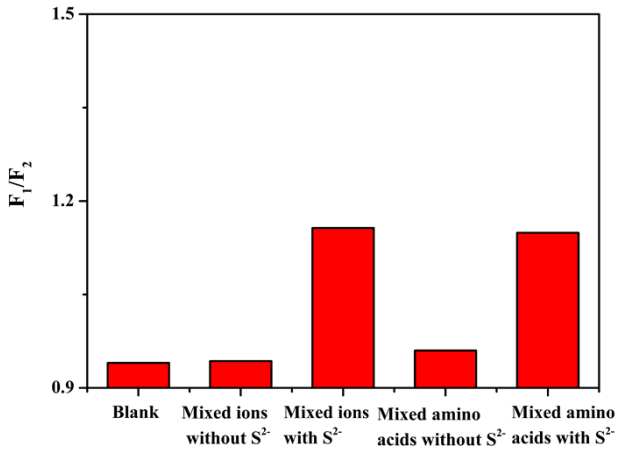

Fig. S7. The difference in the fluorescence intensity ratio (F_1/F_2) of the nanohybrid CNPs-Au NCs under various conditions (mixed ions including F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, SCN^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{2-}, Na^+ and K^+; mixed amino acids involving glutathione, cysteine, histidine, lysine, arginine, serine, glutamic acid, urea and uric acid; the concentration of all interference was 100 μM, respectively; $[S^{2-}]$ = 10 μM).

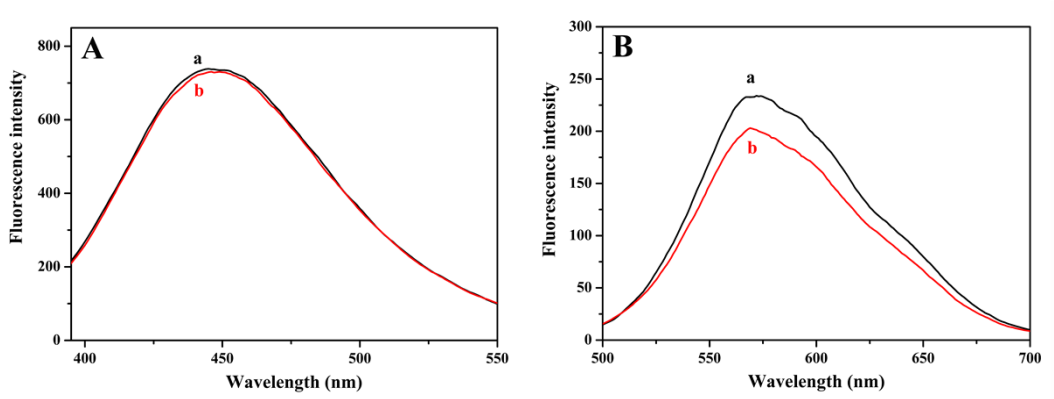

Fig. S8. (A) Fluorescence spectra of free CNPs (curve a) and CNPs in the presence of S^{2-} (curve b; [S^{2-}] = 500 μM). (B) Fluorescence spectra of free Au NCs (curve a) and Au NCs in the presence of S^{2-} (curve b; [S^{2-}] = 50 nM).

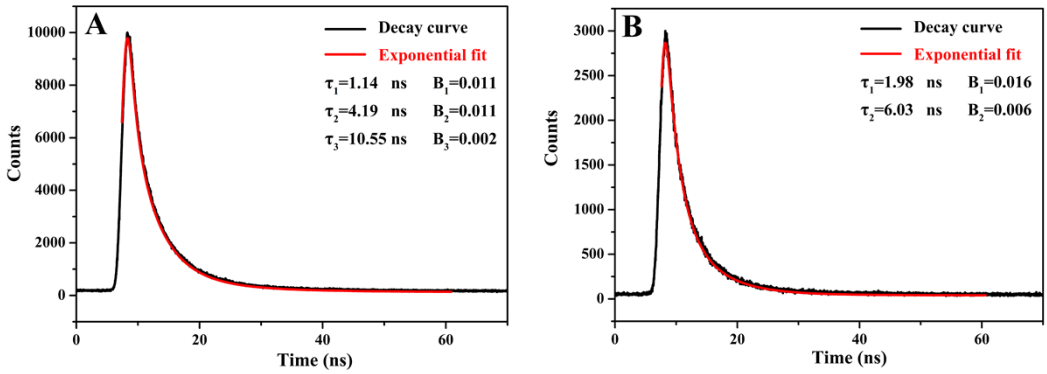

Fig. S9. (A) The fluorescence decay and exponential fitting curve of CNPs without Au NCs in aqueous solution at room temperature. (B) The fluorescence decay and exponential fitting curve of CNPs with Au NCs in aqueous solution at room temperature.

Lifetime measurements

The fluorescence decay traces of CNPs were fitted to a three -exponential function: [1]

$$I(t) = B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3} \quad (1)$$

where t is time and B_i is a weighing parameter combined with each decay time, τ_i. An average amplitude-weighted lifetime was defined as [1]:

$$\tau_{avg} = \frac{\sum B_i \tau_i^2}{\sum B_i \tau_i} \quad (2)$$

where τ_{DA} and τ_D, designate the lifetimes measured for a donor (CNPs) with and without an acceptor (Au NCs), respectively.

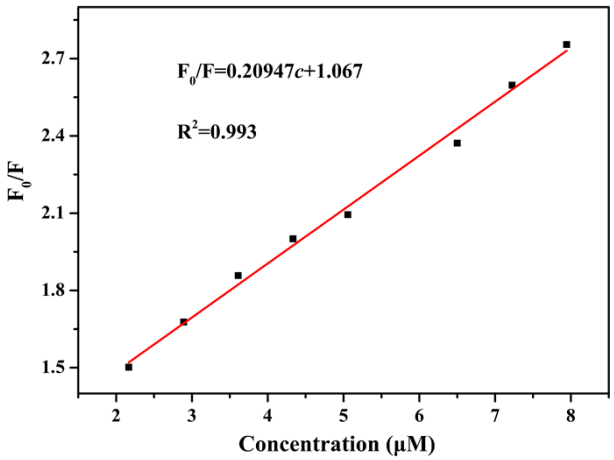

Fig. S10. Stern-Volmer plot for the fluorescence of CNPs quenched by different concentrations of Au NCs.

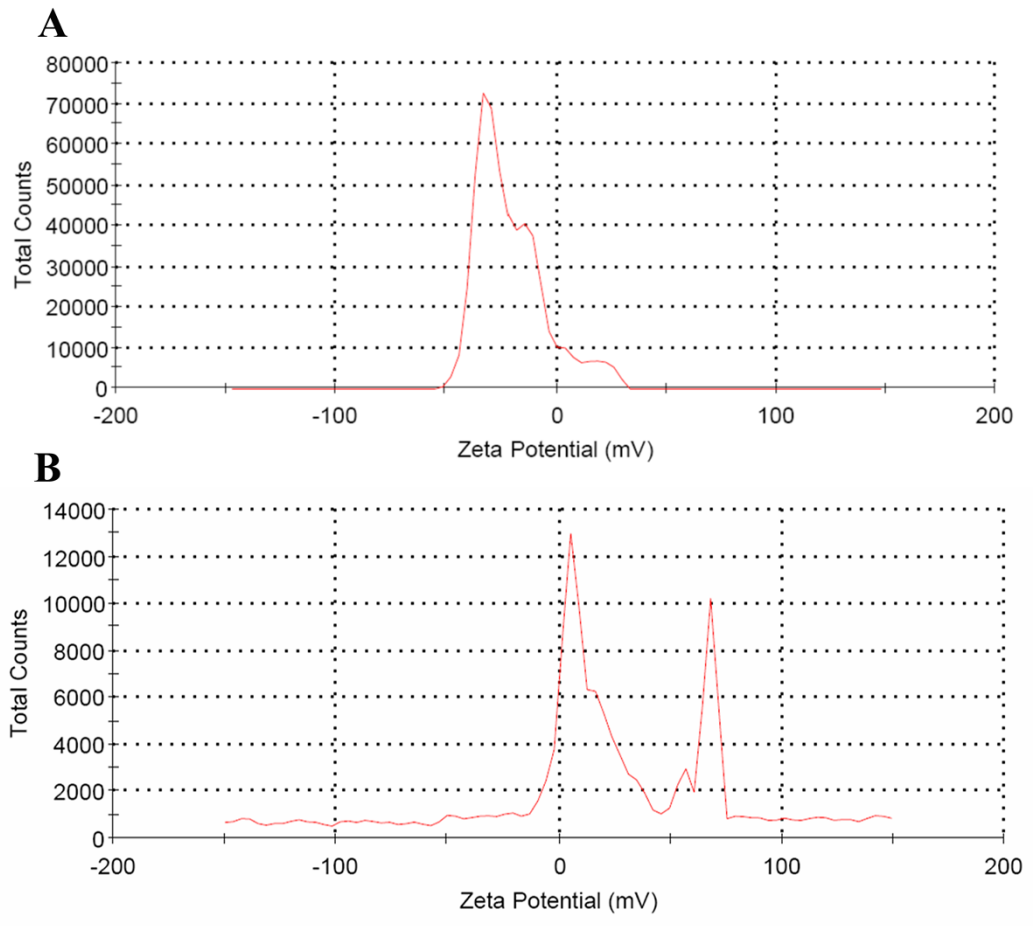

Fig. S11. (A) Zeta potential spectrum of CNPs in aqueous solution at room temperature. (B) Zeta potential spectrum of Au NCs in aqueous solution at room temperature.

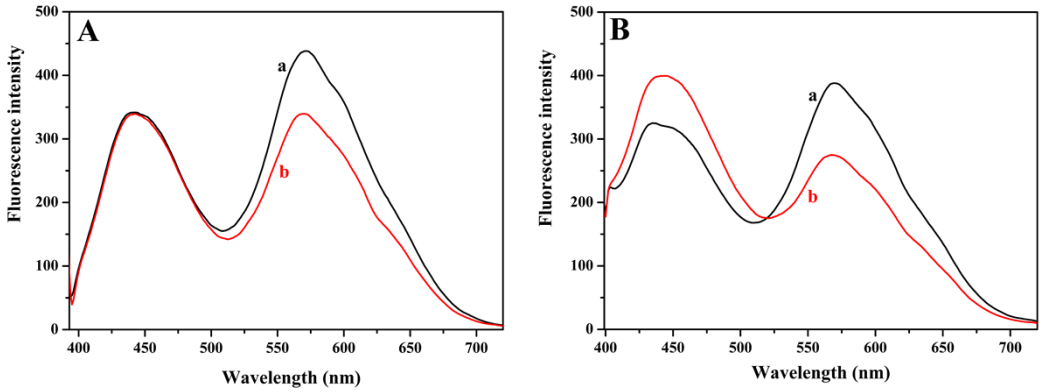

Fig. S12. (A) The fluorescence spectra of the mixture solution of CNPs and Au NCs in the absence (curve a) and presence of S^{2-} (curve b; [S^{2-}] = 33 μM). (B) The fluorescence spectra of nanohybrid CNPs-Au NCs in the absence (curve a) and presence of S^{2-} (curve b; [S^{2-}] = 33 μM).

Calculation of FRET efficiency

The quenching efficiency, *E*, can be extracted from the steady-state and/or time-resolved fluorescence profiles, adopting the following expressions:[1]

$$E = 1 - \frac{F_{DA}}{F_D} \tag{3}$$

where F_{DA} and F_D are the fluorescence intensity of the donor in the presence or absence of the acceptor, respectively.

Calculation of the Förster Radius [2, 3]

$$E = \frac{R_0^6}{R_0^6 + r^6} \tag{4}$$

$$R_0^6 = \frac{9000(In10)k^2\Phi}{128\pi^5 Nn^4} J \tag{5}$$

$$J = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \tag{6}$$

R_0 is the Förster Radius where the FRET efficiency is observed at 50%, and *r* is distance between energy donor and energy acceptor; k^2 denotes a dipole-dipole interaction between donor and acceptor, typically k^2 =2/3; *n* is the refractive index of the medium (*n* = 1.33 in water); *N* is Avogadro's number; *Φ* is the quantum yield of the donor; *J* is the associated spectral overlap integral, expressing the degree of spectral overlap between the absorption of acceptor and the emission of donor; $F_D(\lambda)$ is the fluorescence intensity of the donor at the wavelength of λ, and ε_A (λ) is the molar absorption coefficient of the acceptor at the wavelength of λ. Table S1 displays the parameters used to calculate FRET between CNPs and Au NCs.

Table S1 Parameters used to Calculate FRET between CNPs and Au NCs.

E	Φ	J (cm^3 M^{-1})	R_0 (nm)	r (nm)
0.24	0.112	3.16×10^{-13}	4.3	5.2

References

1. F. Aldeek, X. Ji and H. Mattoussi, *J. Phys. Chem. C,* 2013, **117**, 15429-15437.
2. W. Zhai, C. Wang, P. Yu, Y. Wang and L. Mao, *Anal. Chem.*, 2014, **86**, 12206-12213.
3. W. Wang, Y. C. Lu, H. Huang, A. J. Wang, J. R. Chen and J. J. Feng, *Biosens. Bioelectron.*, 2015, **64**, 517-522.