Electronic Supplementary Material (ESI) for Analytical Methods.

Selective aqueous fluorescent probe for metal ions based on benzoyl hydrazone derivatives

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1. Experimental section

1.1. Calculation of luminescence quantum yields.

The emission quantum efficiency was determined from the slopes of a plot between the fluorescence integral and absorbance at λ_{max} of each compound compared with that of quinine sulfate in 0.1 M H_2SO_4 (for **I**, **III**) and rhodamine B in ethanol (for **II**) used as the standard with the quantum efficiency of 0.55 and 0.65 respectively. [1] The fluorescence quantum yield was measured by using

$$\Phi_f = \Phi_{f\times}^{0} \frac{F_S}{\overline{F_0}} \times \frac{A_0 n_s^2}{\overline{A_S n_0^2}} \qquad \text{(Formula S 1. 1. 1)}$$

in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples.

1.2. Measurements of fluorescence lifetimes.

Measurements of the fluorescence lifetimes were performed with standard time correlated single photon counting method. [2] Fluorescence decay curves were recorded for 10s by TCSPC. Typically, a total of 1-1×10^4 counts were collected in each decay curve. The fluorescence lifetimes were measured by using

$$\text{Fit} = A + B_1 e^{(-\frac{t}{\tau_1})} + B_2 e^{(-\frac{t}{\tau_2})} + B_3 e^{(-\frac{t}{\tau_3})} + B_4 e^{(-\frac{t}{\tau_4})} \qquad \text{(Formula S 1.2.1)}$$

to obtain the fluorescence lifetime τ_n (n=1, 2, 3, 4). [3]

1.3. Stability of benzoyl hydrazone-based fluorescent probes.

The absorption spectra of **I**, **I**-Al^{3+}, **II**, **II**-Cu^{2+}, **III**, and **III**-Zn^{2+} at time intervals of 0, 2, 6, 12, 24 and 72h in aqueous solution were obtained with an U-3900H spectrophotometer in quartz

absorption cells. The emission spectrum was recorded by F-7000 FL spectrophotometer.

1.4. DFT calculations of benzoyl hydrazone based derivatives and the complexes.

To verify the mechanism of **I**-Al^{3+}, **II**-Cu^{2+} and **III**-Zn^{2+}, geometry optimizations were performed by Gaussian 09 program. B3LYP exchange-correlation functional [4] and 6-31G* basis-set [5] were employed. SMD solvation model [6] was used to represent water solvent environment.

2. References

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6. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

Summary of Figures

Figure S 1. (left) Fluorescence spectra of probe **I** (λ_{ex}=380 nm) in the presence of various times in aqueous solution. (right) Fluorescence intensity of probe **I** at differernt times in aqueous solution in the absence and presence of Al^{3+}.

Figure S 2. (left) Fluorescence spectra of probe **II** (λ_{ex}=454 nm) in the presence of various times in aqueous solution. (right) Fluorescence intensity of probe **II** at differernt times in aqueous solution in the absence and presence of Cu^{2+}.

Figure S 3. (left) Fluorescence spectra of probe **III** (λ_{ex}=343 nm) in the presence of various times in aqueous solution. (right) Fluorescence intensity of probe **III** at differernt times in aqueous solution in the absence and presence of Zn^{2+}.

Figure S 4. The decay curve of **I** (λ_{abs}=380 nm, λ_{em}=470 nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **I** was estimated with a single exponential model. Fluorescence lifetime τ_F=297 ns.

Figure S 5. The decay curve of **I**-Al^{3+}(λ_{abs}=380nm, λ_{em}=470nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **I**-Al^{3+} was estimated with a single exponential model. Fluorescence lifetime τ_F=597 ns.

Figure S 6. The decay curve of **II** (λ_{abs}=454 nm, λ_{em}=523 nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **II** was estimated with a single exponential model. Fluorescence lifetime τ_F=269 ns.

Figure S 7. The decay curve of **II**-Cu^{2+} (λ_{abs}=454 nm, λ_{em}=523 nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **II**-Cu^{2+} was estimated with a single exponential model. Fluorescence lifetime τ_F =368 ns

Figure S 8. The decay curve of **III** (λ_{abs}=343 nm, λ_{em}=503 nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **III** was estimated with a single exponential model. Fluorescence lifetime τ_F =254 ns.

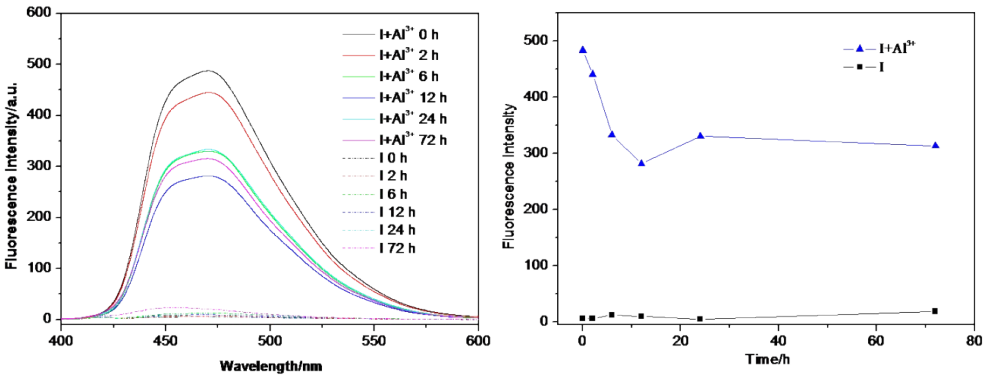
Figure S 9. The decay curve of **III**-Zn^{2+} (λ_{abs}=343 nm, λ_{em}=503 nm) in aqueous solution at ambient temperature. By using formula S 1.2.1, the lifetime of **III**-Zn^{2+} was estimated with a single exponential model. Fluorescence lifetime τ_F =359 ns

Figure S 10. Optimized structure of **I** and **I**-Al^{3+} by DFT calculation. The Al-N (1) bond length is 2.02 Å, Al-O (1) bond length is 1.99 Å and Al-O (2) bond length is 1.86 Å.

Figure S 11. Optimized structure of **II** and **II**-Cu^{2+} by DFT calculation. The Cu-N (1) bond length is 1.97 Å, Cu-N (2) bond length is 2.01 Å, Cu-O (1) bond length is 1.99 Å, Cu-O (2) bond length is 2.46 Å, Cu-O (3) bond length is 2.09 Å and Cu-O (4) bond length is 2.19 Å.

Figure S 12. Optimized structure of **III** and **III**-Zn^{2+} by DFT calculation. The Zn-N (1) bond length is 2.06 Å, Zn-N (2) bond length is 2.04 Å and Zn-O (1) bond length is 2.02 Å.

Z. Guo et al. Figure S 1.



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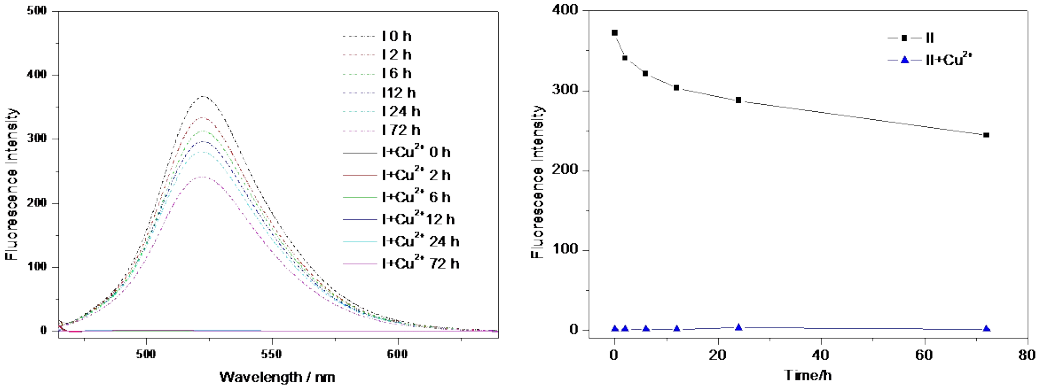

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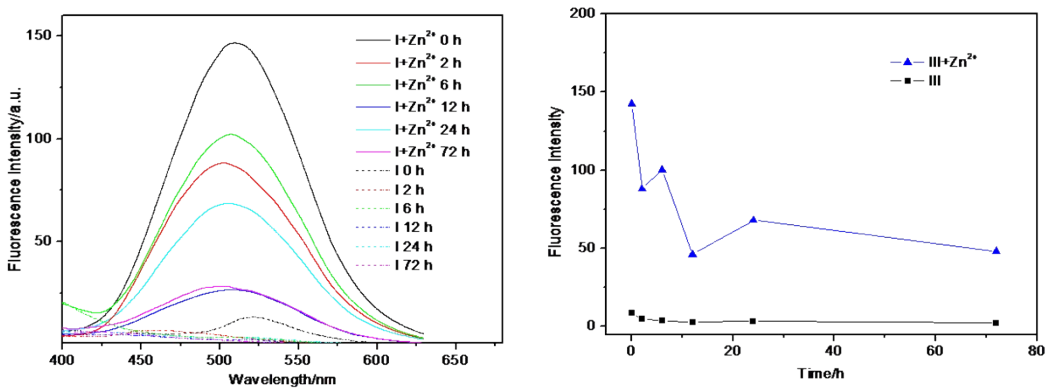

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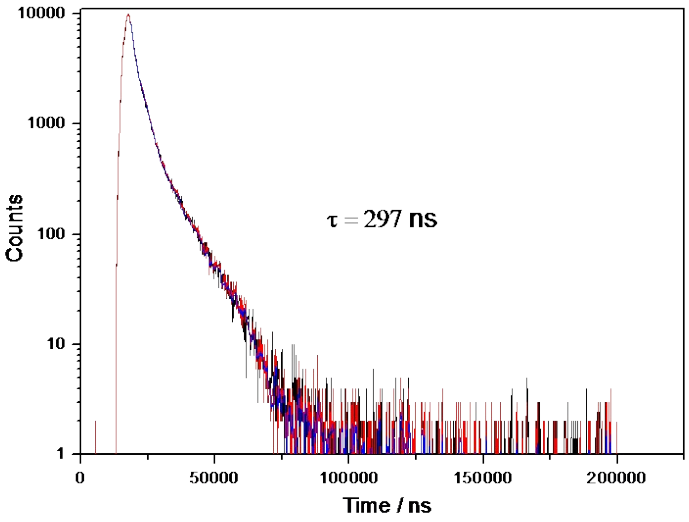

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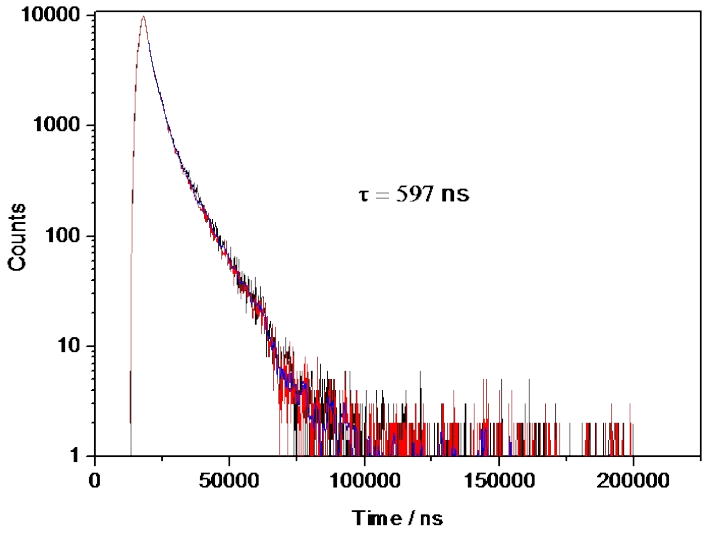

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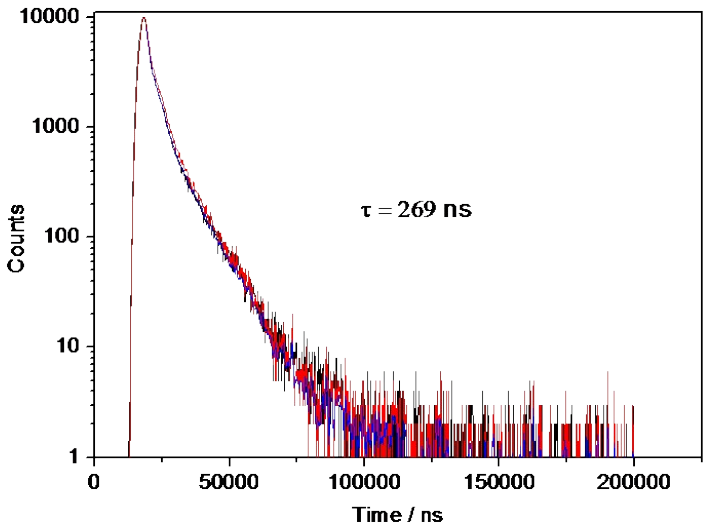

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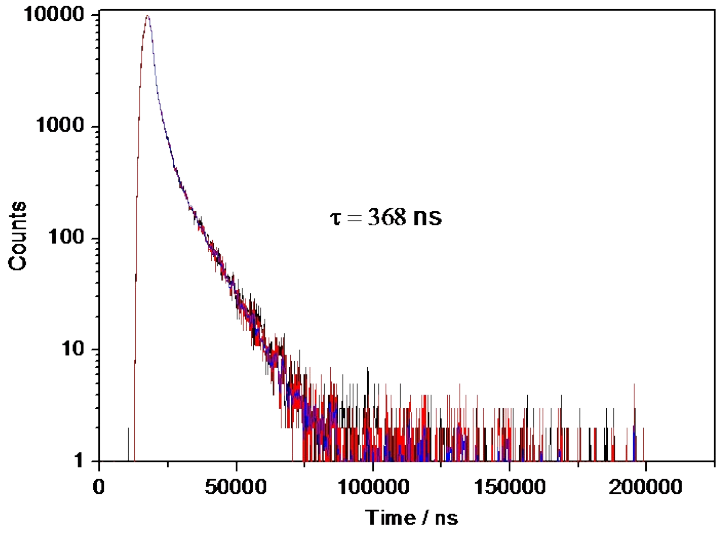

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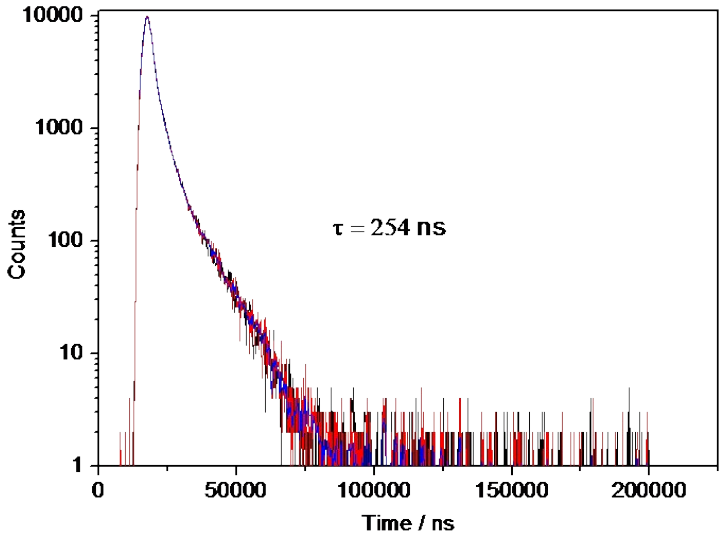

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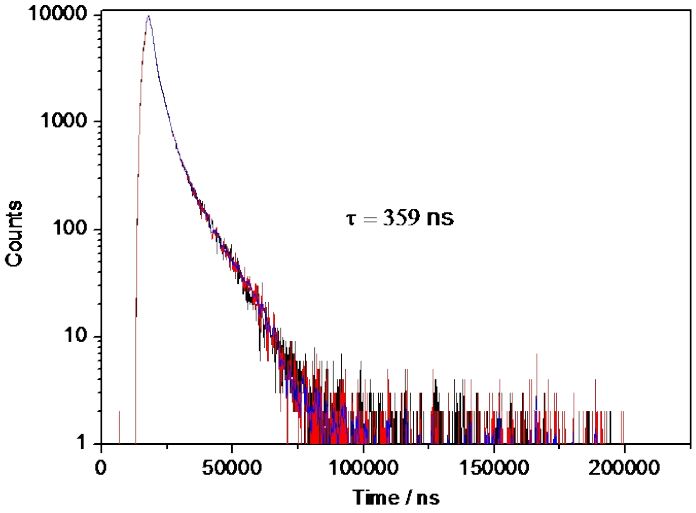

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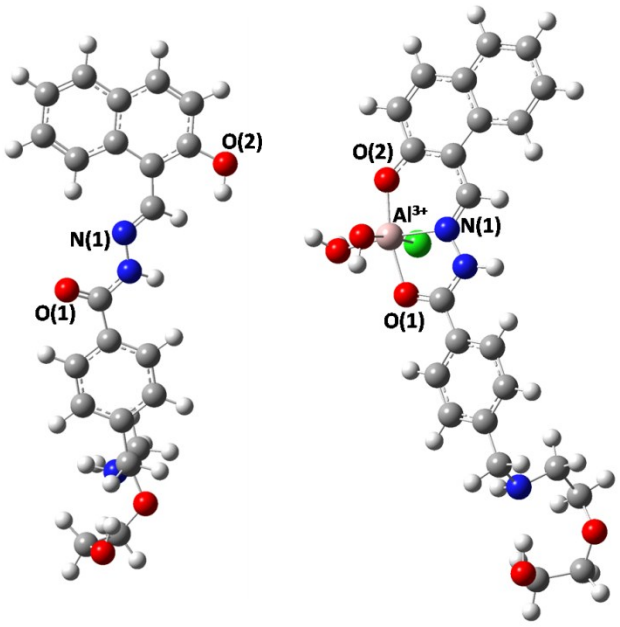
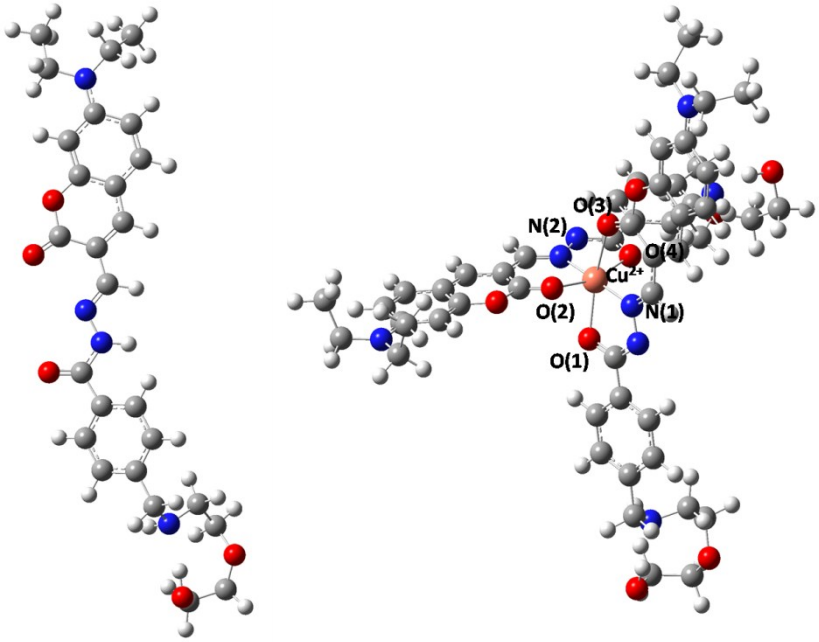


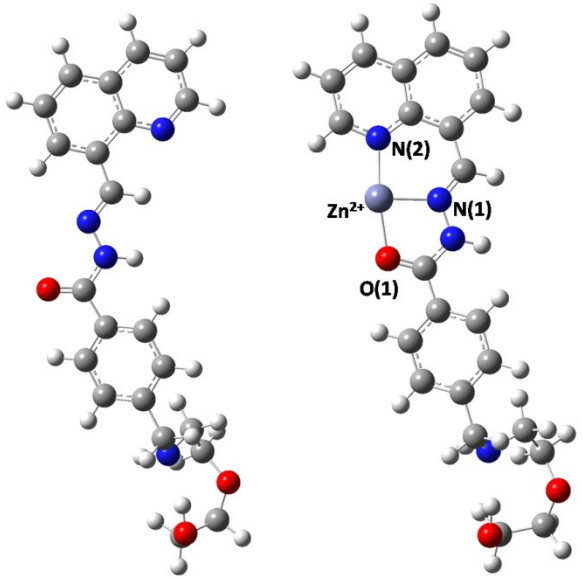
I **I-Al^{3+}**

Z. Guo et al. Figure S 11.



II **II-Cu^{2+}**

Z. Guo et al. Figure S 12.



III **III-Zn^{2+}**