Supporting Information (SI)

Reusable fluorescence coordination polymer for the detection of Zr^{4+} ions in aqueous media

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Contents

X-ray Crystallography Determination. A good quality crystal of 1 was mounted on Bruker Smart Apex CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. The structures were solved by direct methods using SHELXS-2014 [1] and refined by full-matrix least-squares on F^2 using SHELXL-2014 [2]. The program SADABS was applied to conduct the empirical absorption correction [3]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located geometrically and refined as riding atoms. The crystallographic data and selected bond lengths and bond angles have been listed in Tables S1 and S2, respectively.

Table S1. Crystal data and structure refinement for **1**.

Formula	$C_{36}H_{22}EuN_2O_7$	Z	8
FW	746.51	D_{calcd} (g cm^{-3})	1.665
Temperature	298(2) K	μ (mm^{-1})	2.161
Crystal system	Monoclinic	F(000)	2968
Space group	*C*2/*c*	Reflections collected	21587
a (Å)	24.198(5)	Independent reflections	5837
b (Å)	15.541(3)	R_{int}, R_{sigma}	0.0655, 0.0385
c (Å)	15.939(3)	GOF (F^2)	1.022
α (deg)	90°	$R_1{}^a$ (I>2σ(I))	0.0307
β (deg)	96.314(4)°	$_wR_2^b$ (I>2σ(I))	0.1091
γ (deg)	90°	$R_1{}^a$ (all data)	0.0413
V($Å^3$)	5958(2)	$_wR_2^b$ (all data)	0.1357

$R_1^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $_wR_2^b = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

Table S2. Bond lengths [Å] and angles [°] for **1**.

Eu(1)-O(2)	2.397(3)	Eu(1)-O(3)	2.388(3)
Eu(1)-O(4)$^{\#1}$	2.374(2)	Eu(1)-O(5)	2.368(2)
Eu(1)-O(6)$^{\#1}$	2.361(2)	Eu(1)-O(7)	2.520(3)
Eu(1)-N(1)	2.567(3)	Eu(1)-N(2)	2.612(4)
Eu(1)-Eu(1)$^{\#1}$	4.4061(9)		
O(4)$^{\#1}$-Eu(1)-N(1)	137.13(9)	O(4)$^{\#1}$-Eu(1)-N(2)	78.89(11)
O(3)-Eu(1)-N(1)	146.99(10)	O(3)-Eu(1)-N(2)	140.81(11)
O(2)-Eu(1)-N(1)	73.04(10)	O(2)-Eu(1)-N(2)	107.33(12)
O(7)-Eu(1)-N(1)	110.34(10)	O(7)-Eu(1)-N(2)	71.50(11)
O(6)$^{\#1}$-Eu(1)-N(2)	77.23(11)	N(1)-Eu(1)-N(2)	63.37(11)
O(6)$^{\#1}$-Eu(1)-O(5)	76.57(9)	O(6)$^{\#1}$-Eu(1)-O(4)$^{\#1}$	75.40(9)
O(6)$^{\#1}$-Eu(1)-O(3)	123.36(9)	O(5)-Eu(1)-O(4)$^{\#1}$	123.65(9)
O(5)-Eu(1)-O(3)	80.53(10)	O(4)$^{\#1}$-Eu(1)-O(3)	75.83(9)
O(6)$^{\#1}$-Eu(1)-O(2)	142.91(8)	O(5)-Eu(1)-O(2)	77.08(9)
O(4)$^{\#1}$-Eu(1)-O(2)	141.59(8)	O(3)-Eu(1)-O(2)	76.83(10)
O(6)$^{\#1}$-Eu(1)-O(7)	138.93(9)	O(5)-Eu(1)-O(7)	143.78(9)
O(4)$^{\#1}$-Eu(1)-O(7)	73.03(9)	O(3)-Eu(1)-O(7)	72.74(10)
O(2)-Eu(1)-O(7)	73.41(8)	O(6)$^{\#1}$-Eu(1)-N(1)	77.01(9)
O(5)-Eu(1)-N(1)	79.89(10)	O(5)-Eu(1)-N(2)	138.66(10)

Symmetry code: #1 -x, y, -z+1.

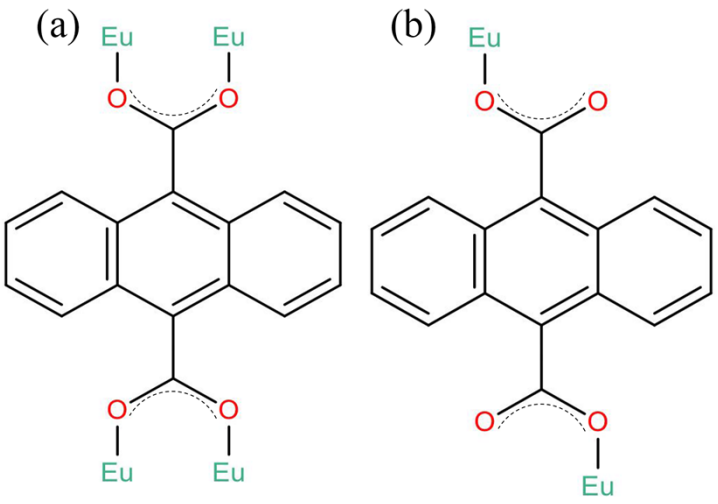


Fig. S1. Two coordination modes of ligand $\mathbf{L}^{2-}$.

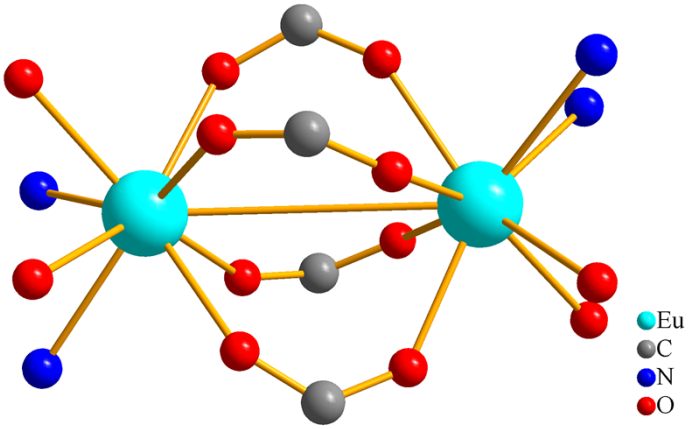


Fig. S2. The dinuclear $Eu_2(COO)_4$ unit.

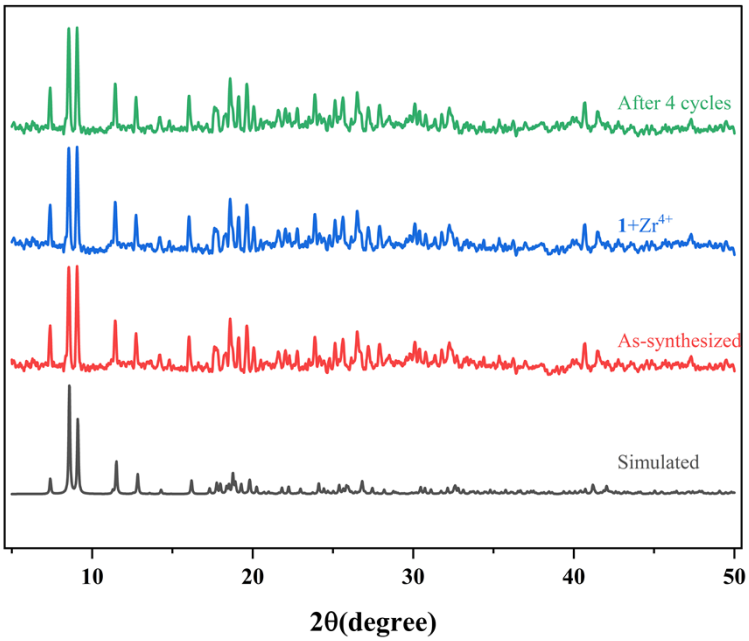


Fig. S3. The PXRD patterns of **1**.

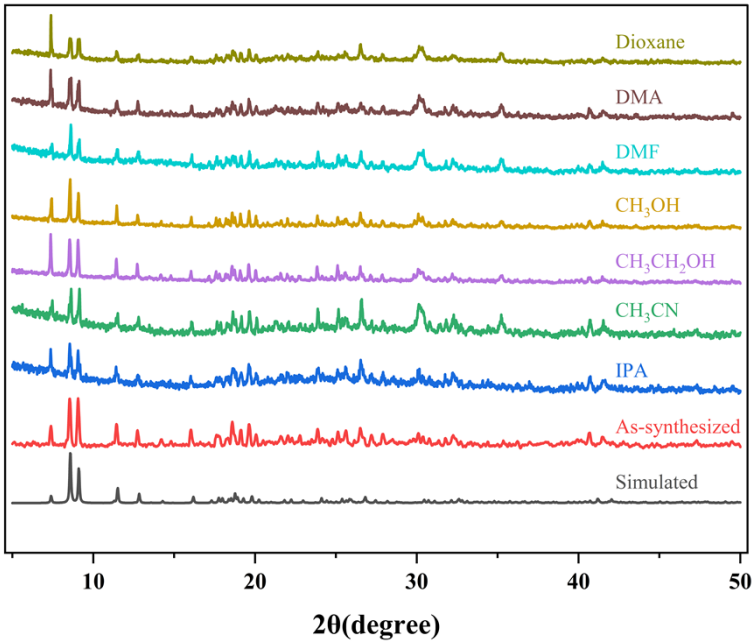


Fig. S4. PXRD patterns of compound **1** in different organic solutions.

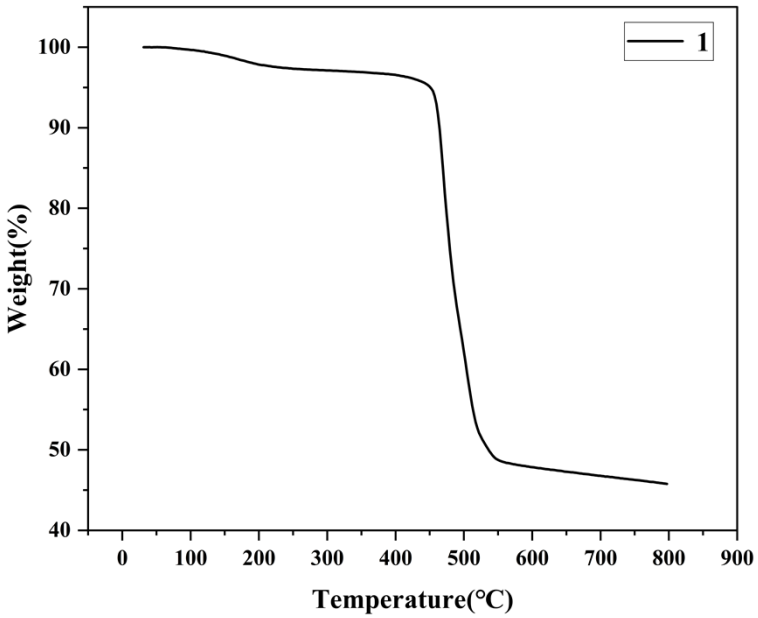


Fig. S5. The TGA curve of complex **1**.

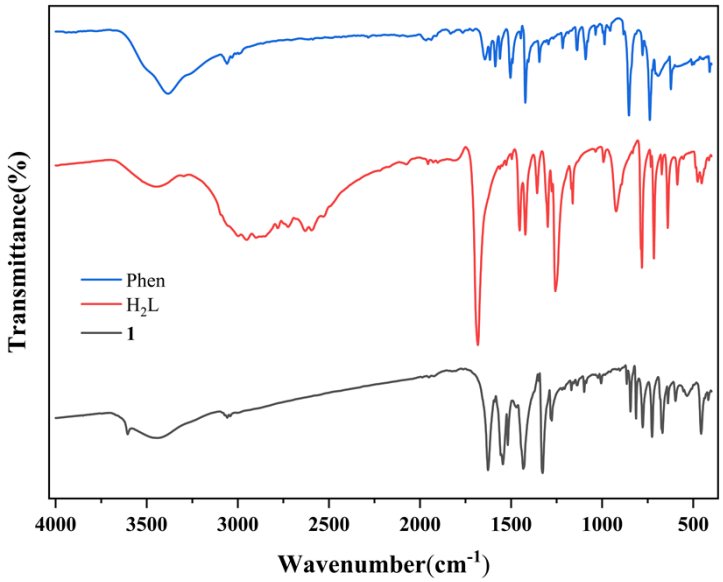


Fig. S6. IR spectra of H_2L, phen and complex **1**.

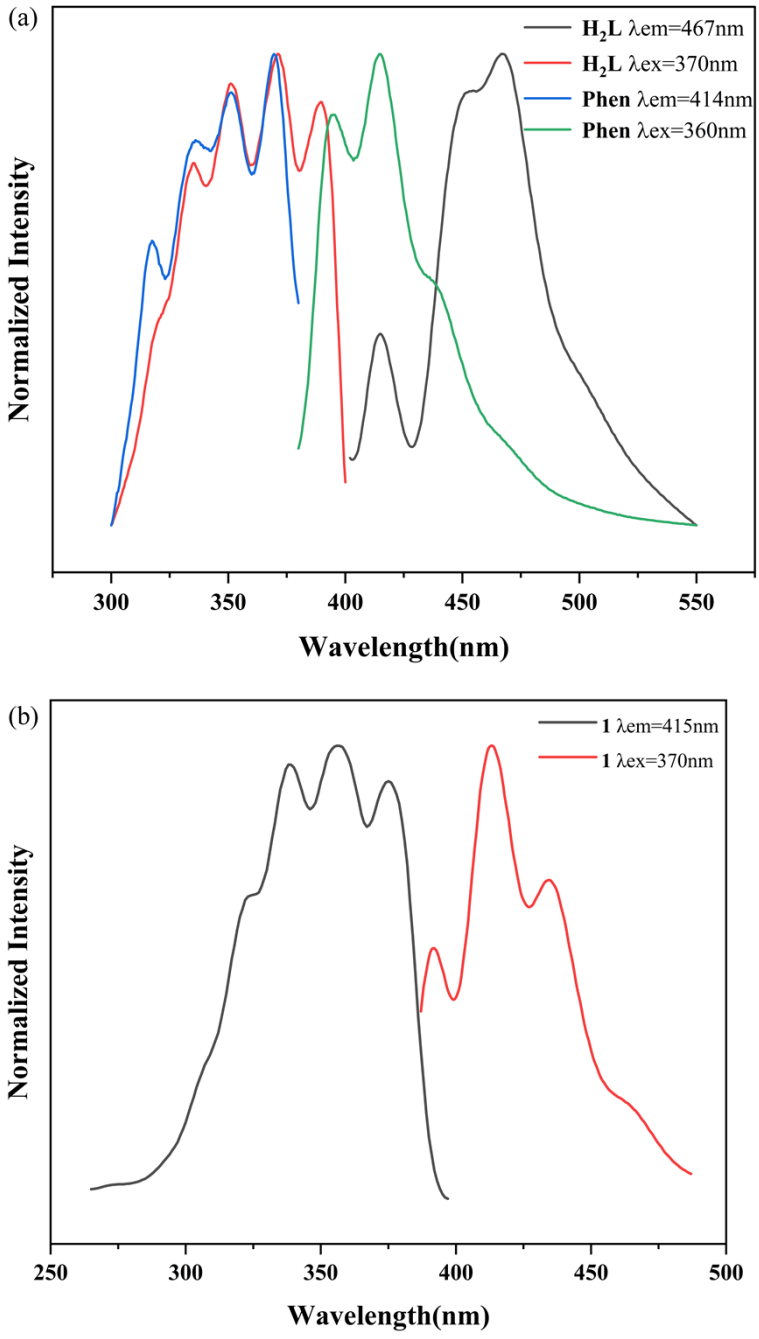


Fig. S7. (a) Excitation and emission spectra of ligands H_2L and phen in aqueous solution. (b) Excitation and emission spectra of complex **1** in aqueous solution.

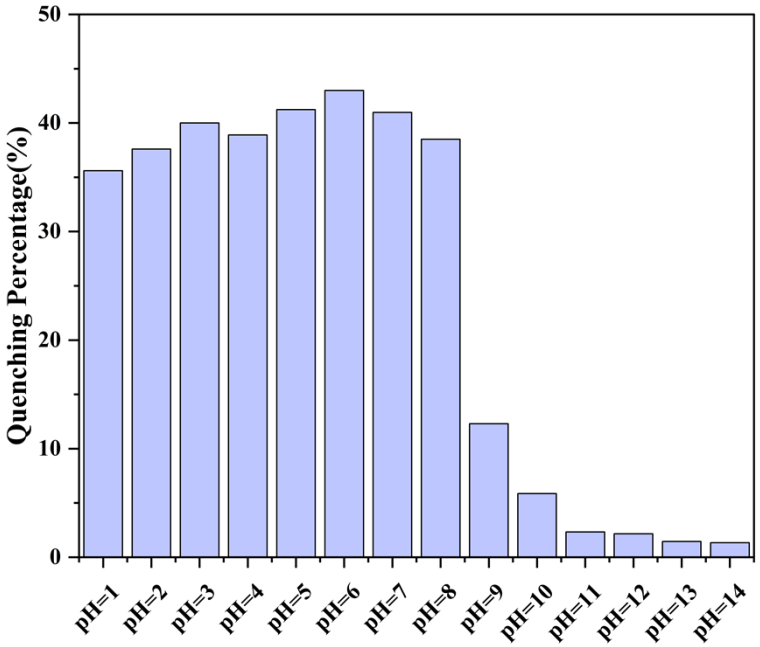
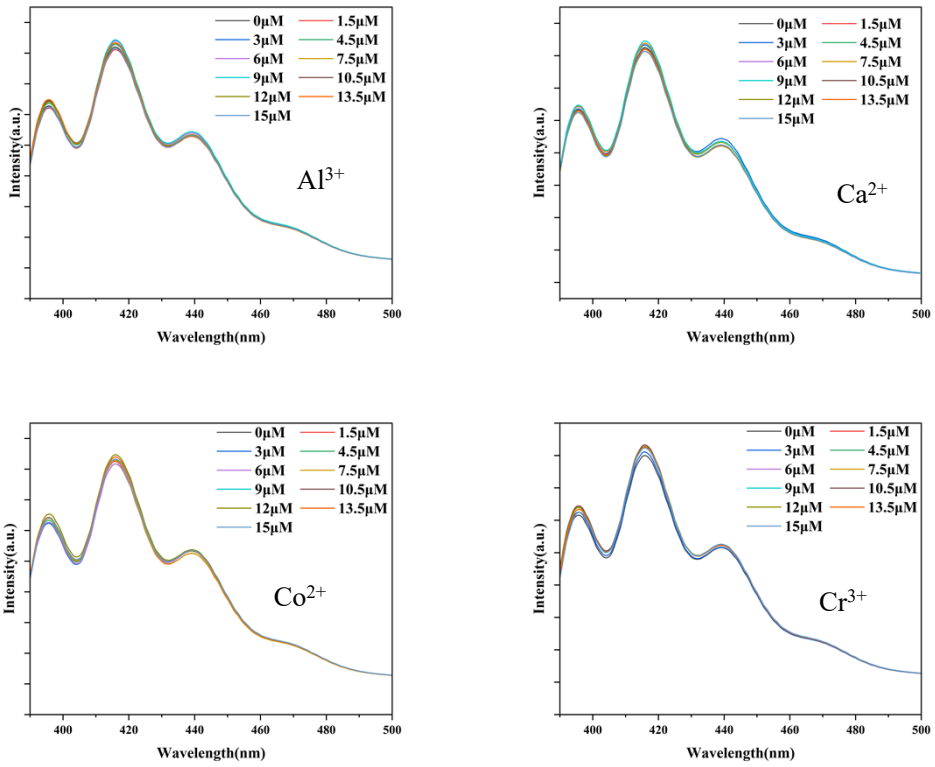
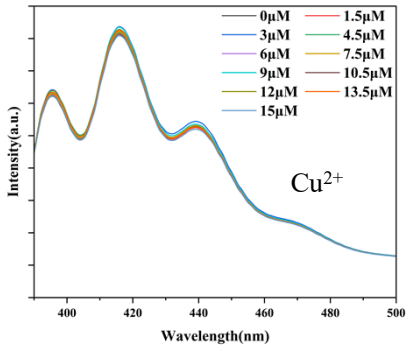
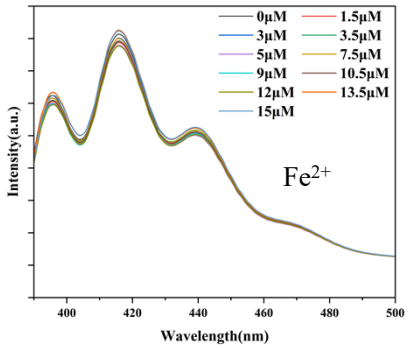
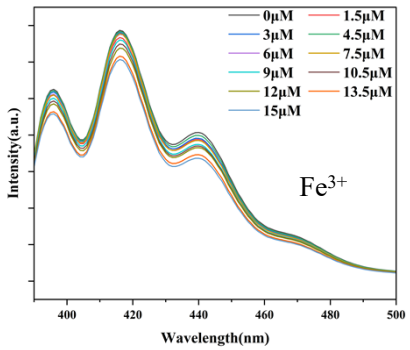


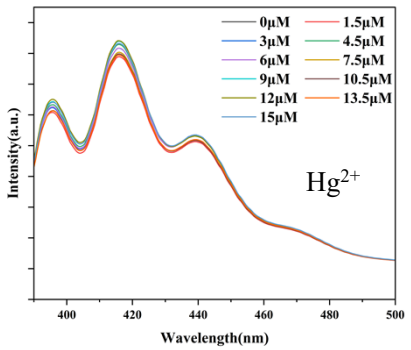
Fig. S8. Effect of pH on quenching percentage of **1**+Zr^{4+} ions.

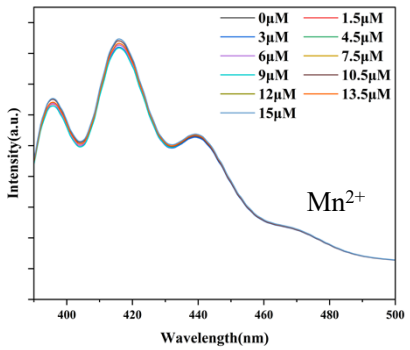


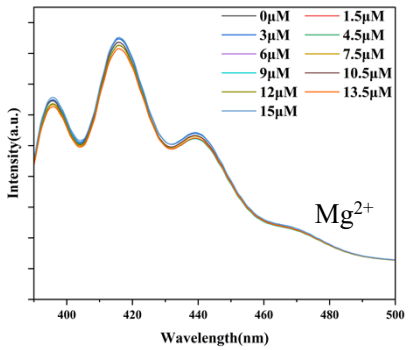

0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Cu2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)

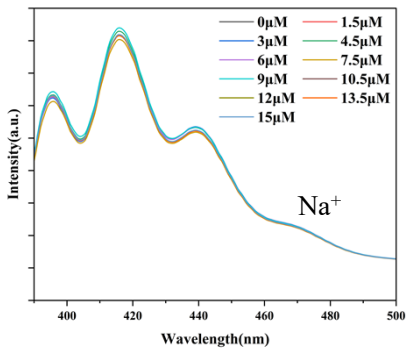

0μM
1.5μM
3μM
3.5μM
5μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Fe2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)

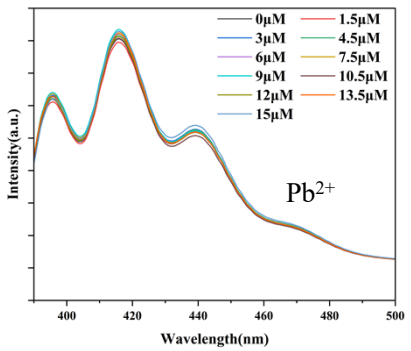

0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Fe3+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)


0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Hg2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)


0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Mn2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)


0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Mg2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)


0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Na+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)


0μM
1.5μM
3μM
4.5μM
6μM
7.5μM
9μM
10.5μM
12μM
13.5μM
15μM
Pb2+
Intensity(a.u.)
400
420
440
460
480
500
Wavelength(nm)

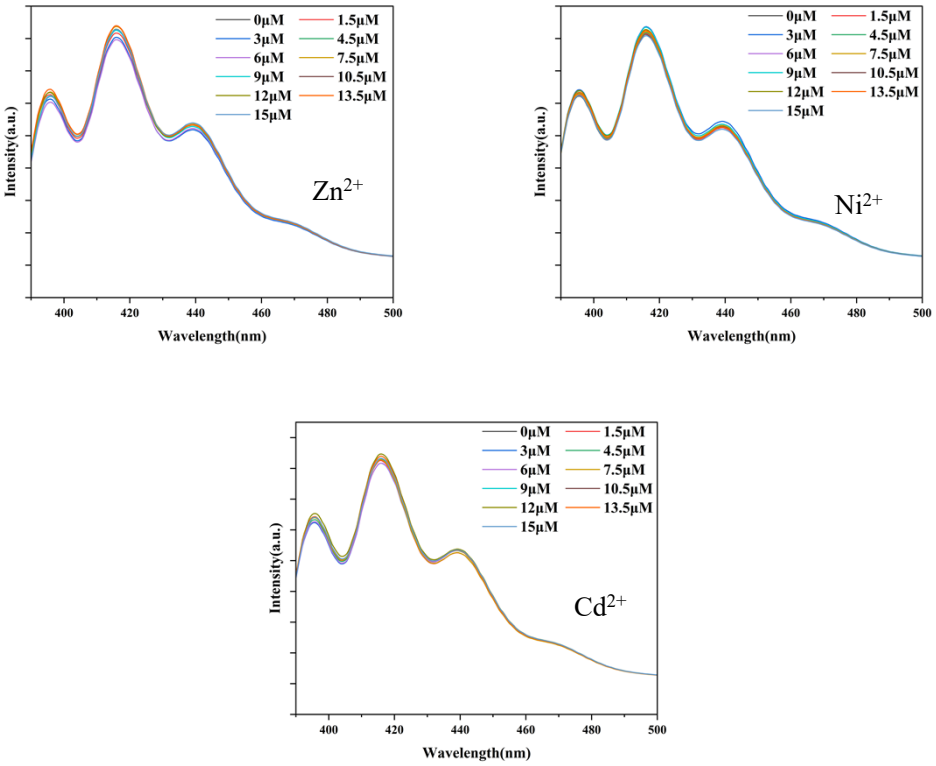


Fig. S9. PL spectra of **1** before and after adding different metal ions (excited at 370 nm).

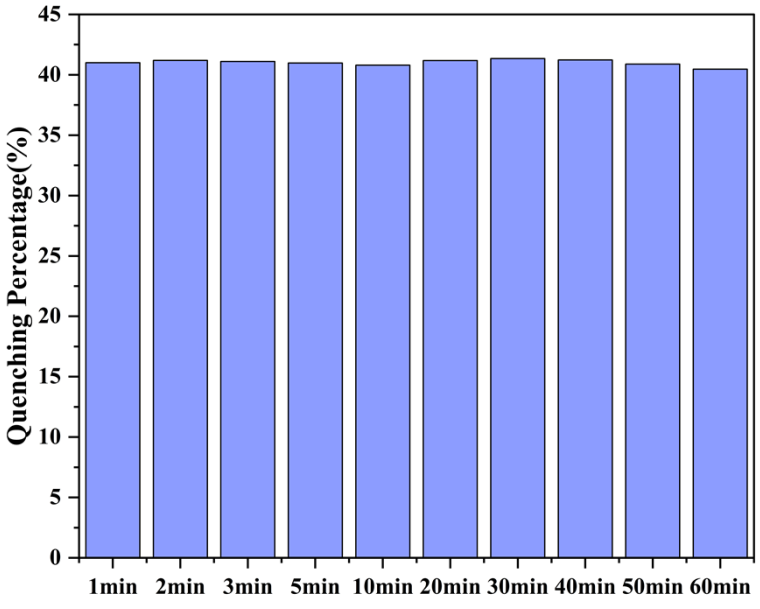


Fig. S10. Quenching percentages of **1**+Zr^{4+} ions at different times.

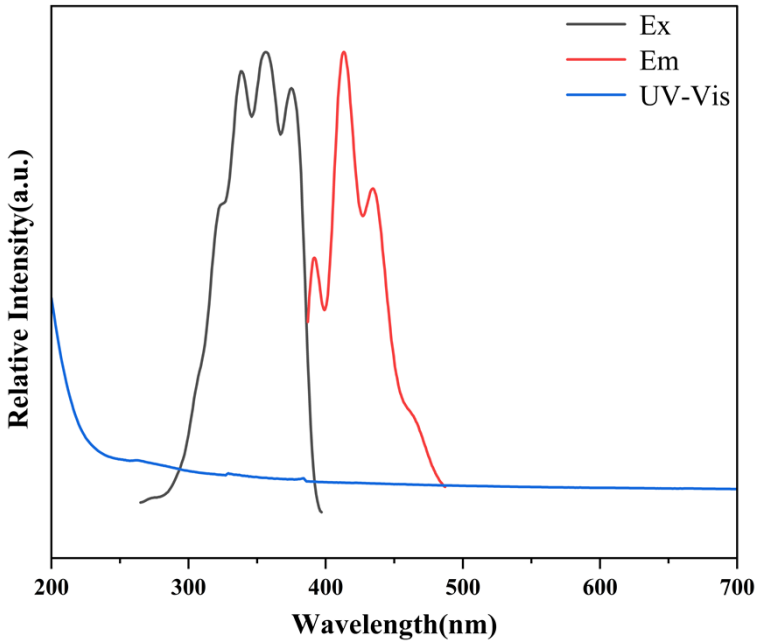


Fig. S11. The UV-Vis absorption spectra of Zr^{4+}, compared with the emission and excitation spectra of complex **1**.

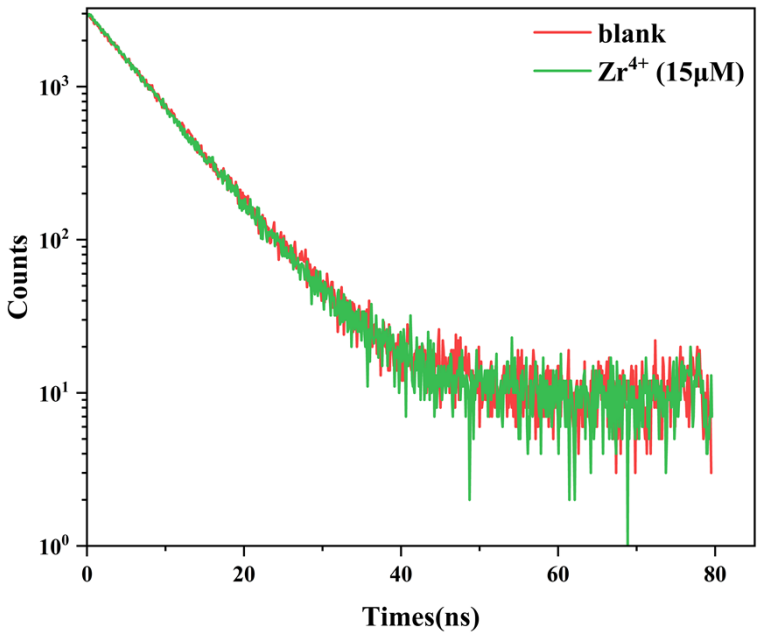


Fig. S12. Fluorescence decay curves of **1**.

References

[1] Sheldrick G. SHELXS-2014, Program for crystal structure solution. University of Göttingen, Göttingen. 2014.

[2] Sheldrick G. SHELXL-2014, Program for the refinement of crystal structures. University of Göttingen, Göttingen. 2014.

[3] Sheldrick GM. Program for empirical absorption correction of area detector data. Sadabs. 1996.