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Supporting Information

Fluorescent Recognition of Adenosine Triphosphate and Uric Acid by two Eu-Based Metal-Organic Frameworks

Li-Juan Han,[a, b,*] Ya-Jie Kong,[a] Xing-Min Zhang,[a] Guo-Zheng Hou,[a] Hua-Chong Chen,[a] and He-Gen Zheng [b, *]

[a] *Department of Chemistry and Chemical Engineering, Jining University, Qufu, 273155, P. R. China*

[b] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China*

* Corresponding authors: hanlij78@163.com; zhenghg@nju.edu.cn

Materials and instrumentation

All reagents and solvents were commercially available and used as received without further purification. The IR absorption spectra of these complexes were recorded in the range of 400-4000 cm^{-1} by means of a Nicolet (Impact 410) spectrometer with KBr pellets. Element analyses (C, H, N) were carried out on a Perkin-Elmer model 240C analyzer. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-*Kα* radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 30 mA. TG analysis was performed on a Perkin Elmer thermogravimetric analyzer from room temperature to 1000 °C with a heating rate of 10 $K \cdot min^{-1}$ under N_2 atmosphere. Photoluminescence spectra were recorded with a PerkinElmer FS-LS55 fluorescence spectrophotometer at room temperature.

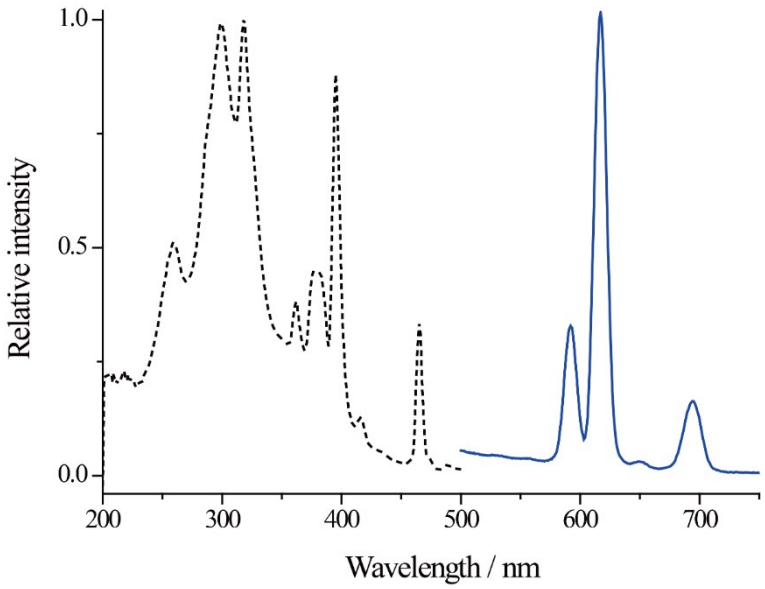


Fig. S1 Solid-state excitation (dotted black, λ_{em} = 617 nm) and emission (solid blue, λ_{ex} = 265 nm) spectra of compound **1**.

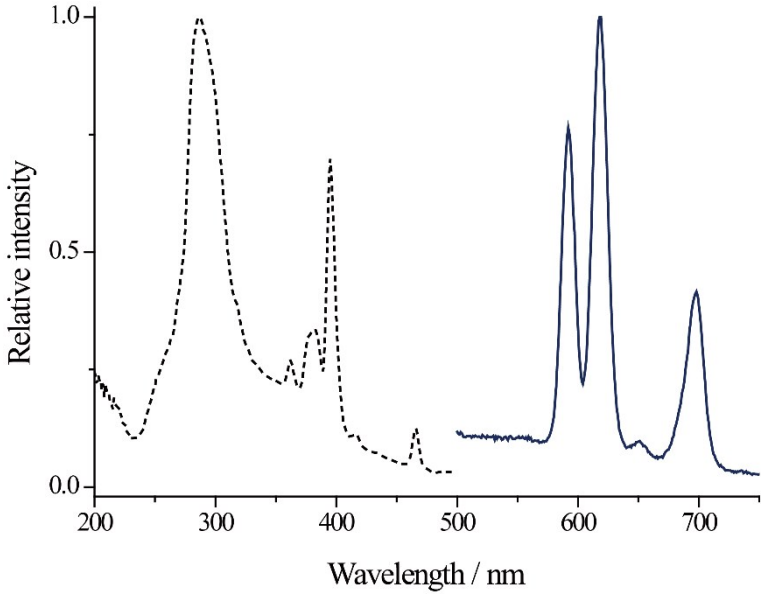


Fig. S2 Solid-state excitation (dotted black, λ_{em} = 617 nm) and emission (solid blue, λ_{ex} = 265 nm) spectra of compound **2**.

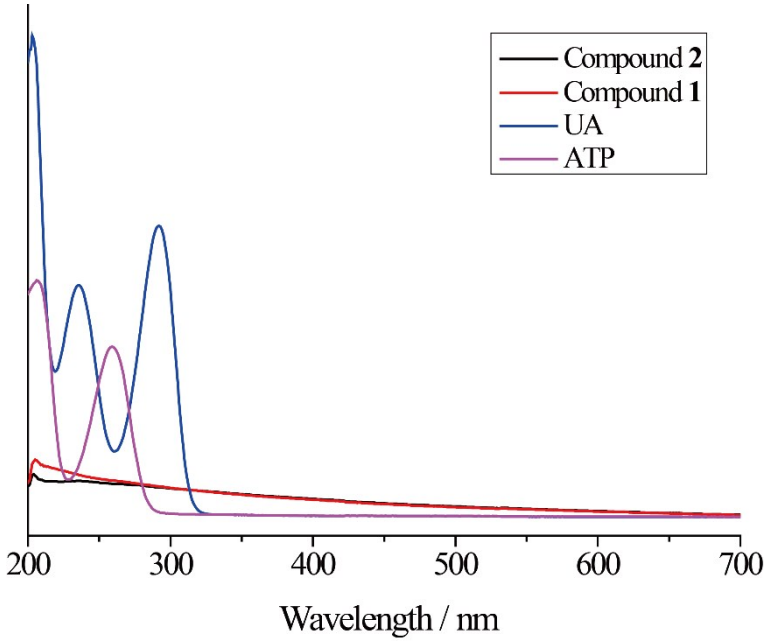


Fig. S3 Liquid UV-vis spectra of compound **1**, compound **2**, ATP and UA.

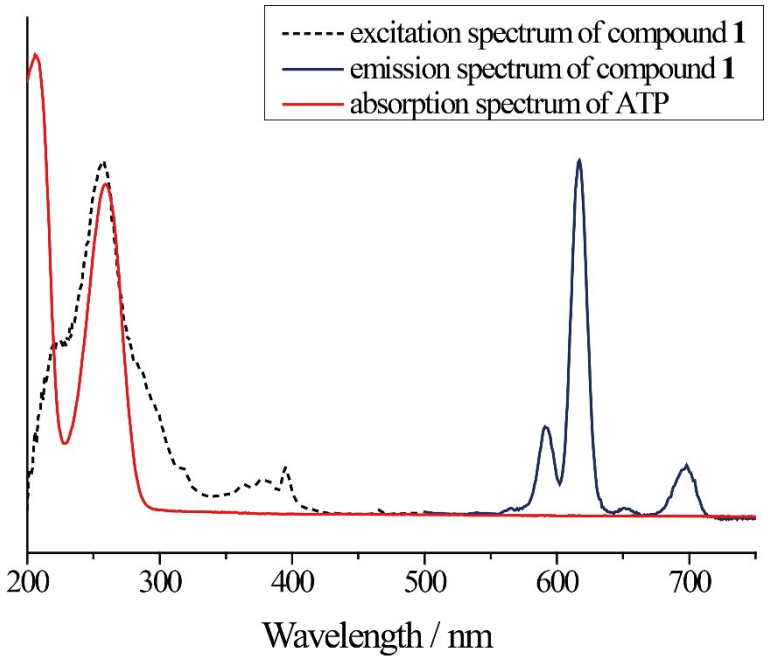


Fig. S4 Spectral overlap between the absorption spectra of ATP and the emission as well as excitation spectra of compound **1**.

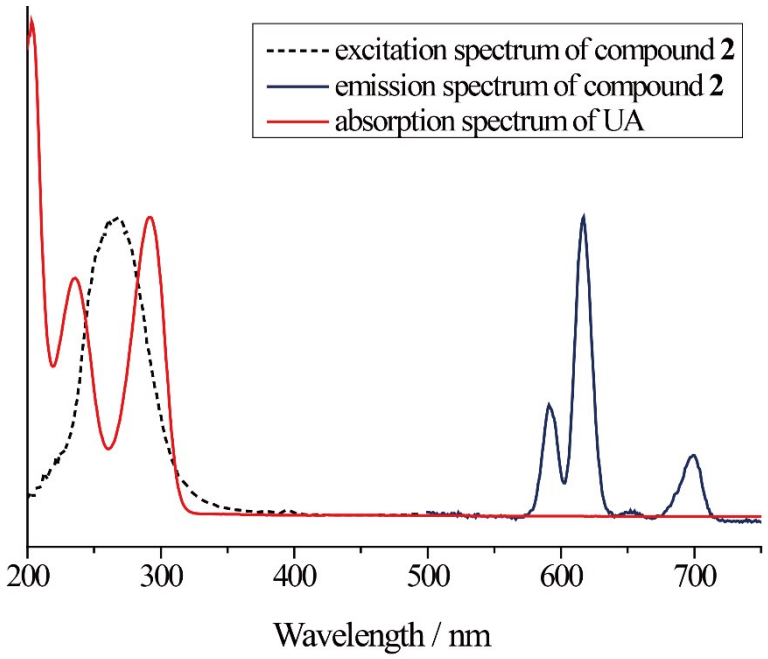


Fig. S5 Spectral overlap between the absorption spectra of UA and the emission as well as excitation spectra of compound **2**.

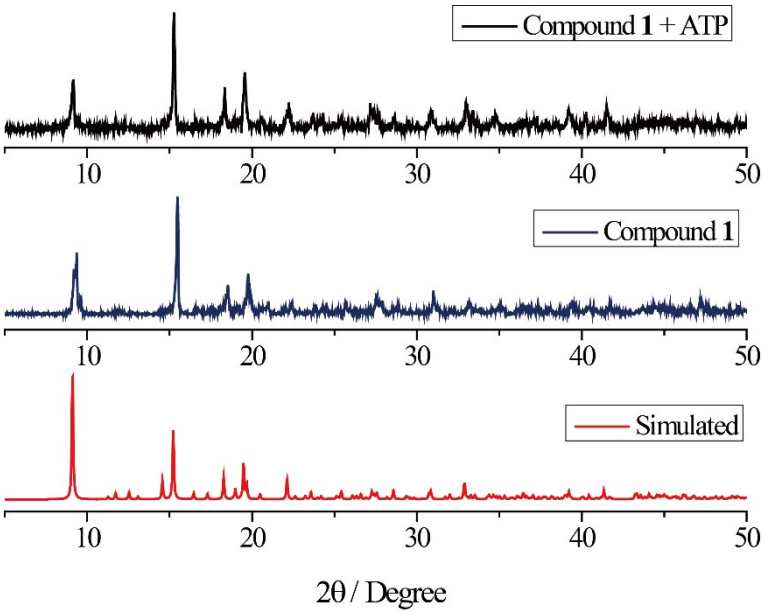


Fig. S6 PXRD of compound **1** before and after immersed in ATP 80 hours.

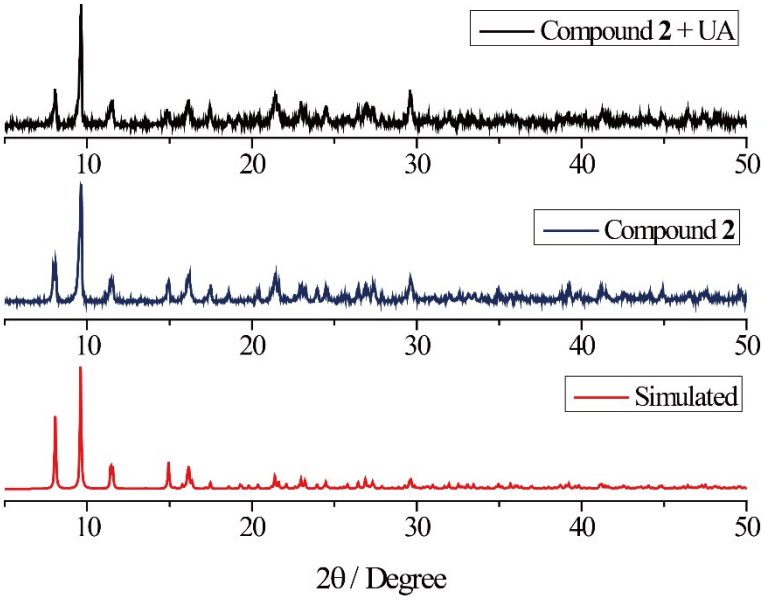
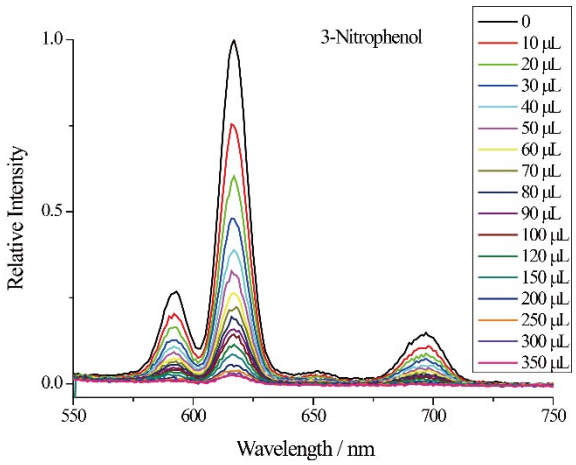
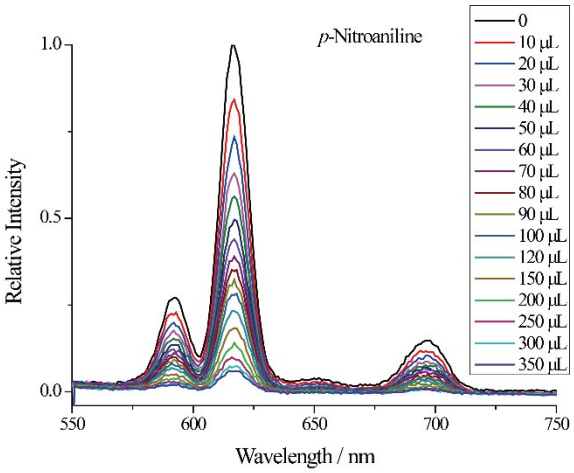
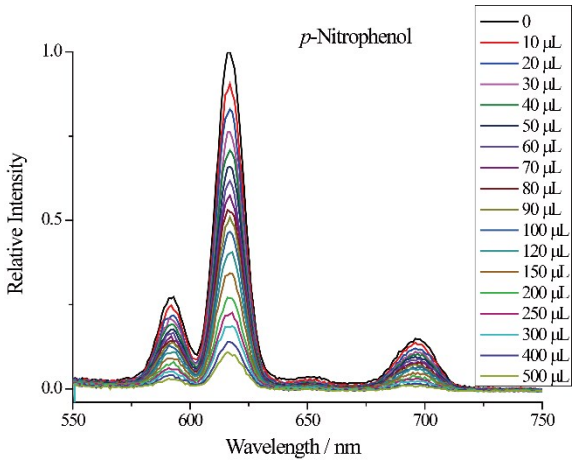
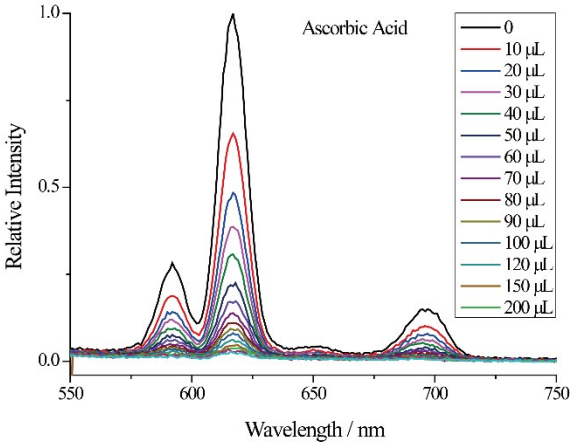


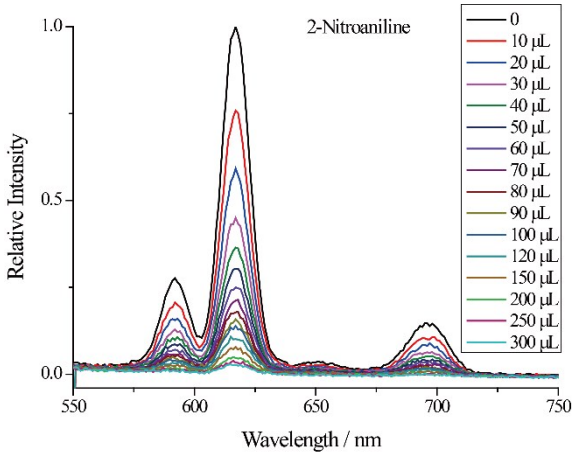
Fig. S7 PXRD of compound **2** before and after immersed in UA 80 hours.

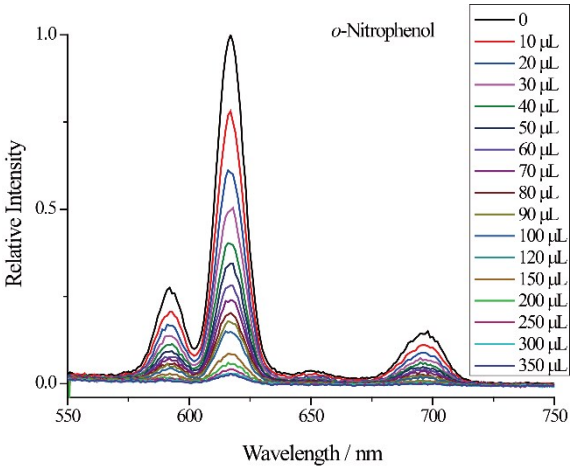

3-Nitrophenol
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
350 μL


p-Nitroaniline
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
350 μL


p-Nitrophenol
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL
500 μL


Ascorbic Acid
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL


2-Nitroaniline
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


o-Nitrophenol
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
350 μL

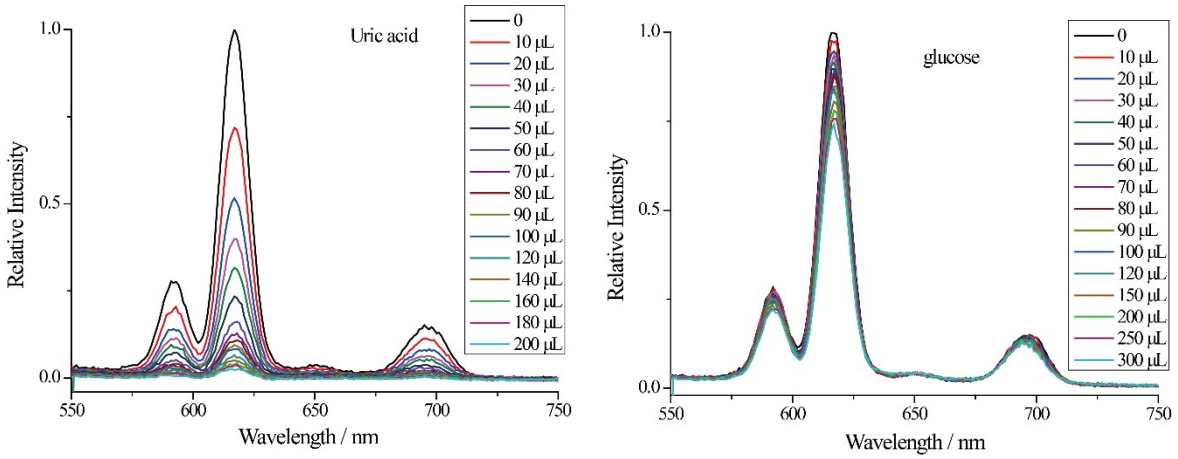
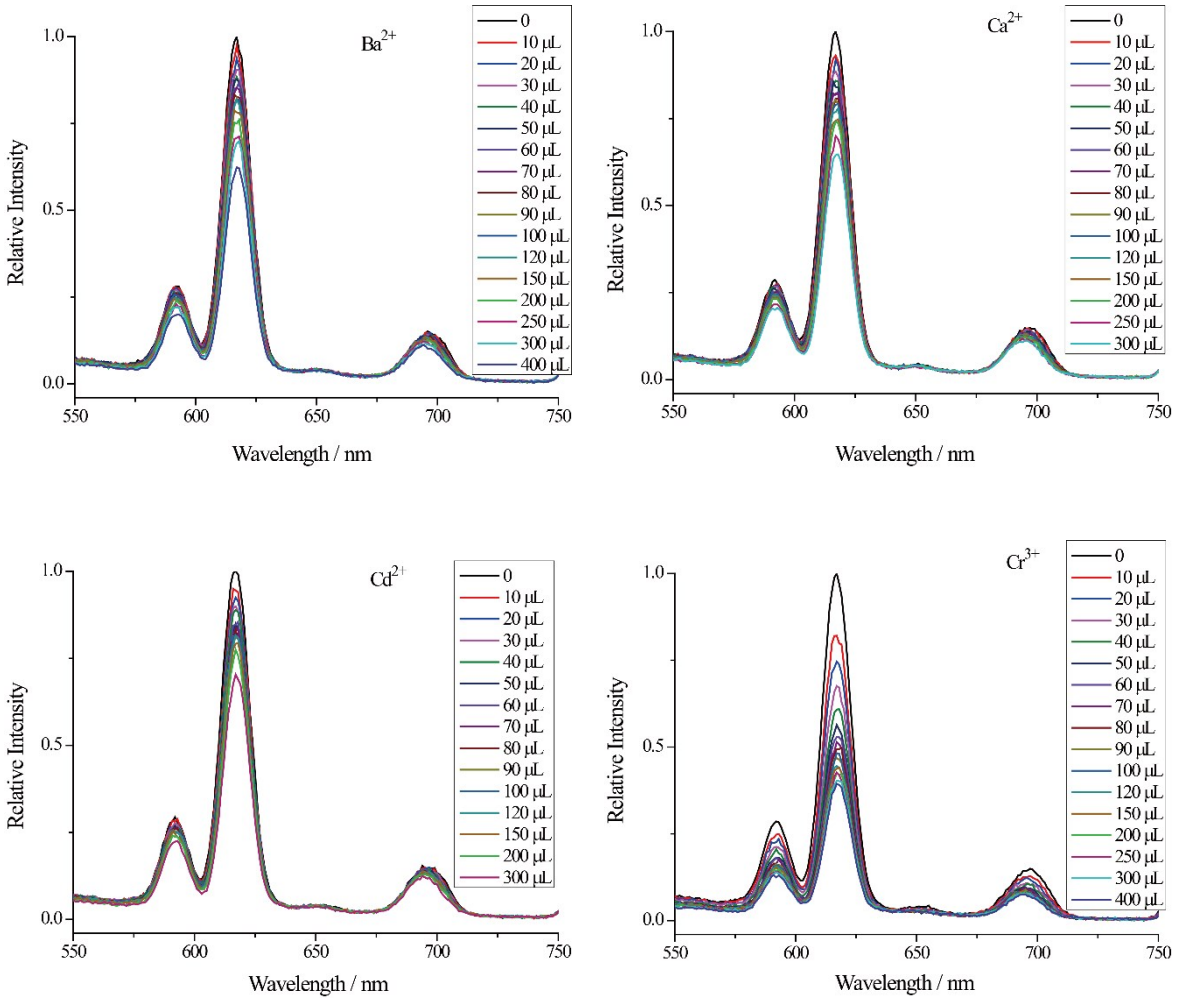
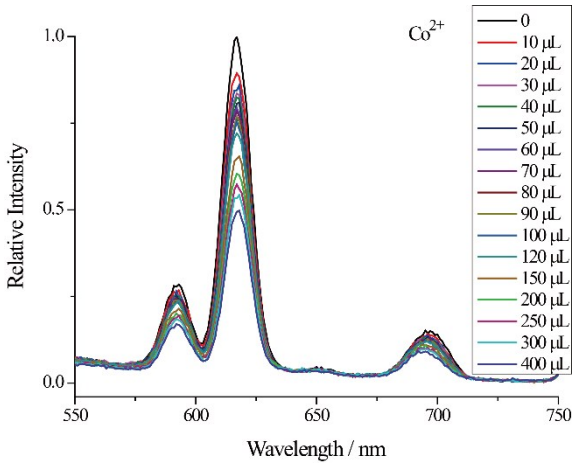
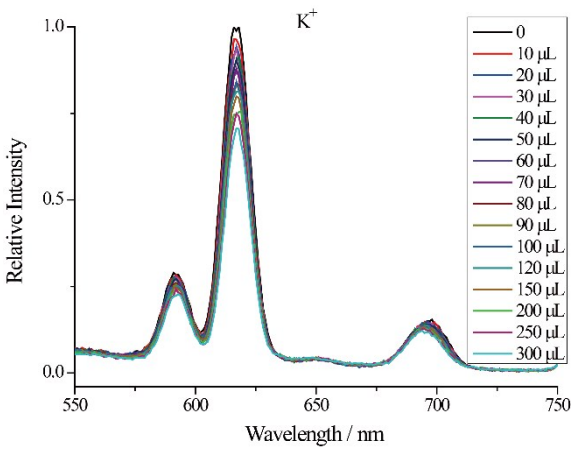
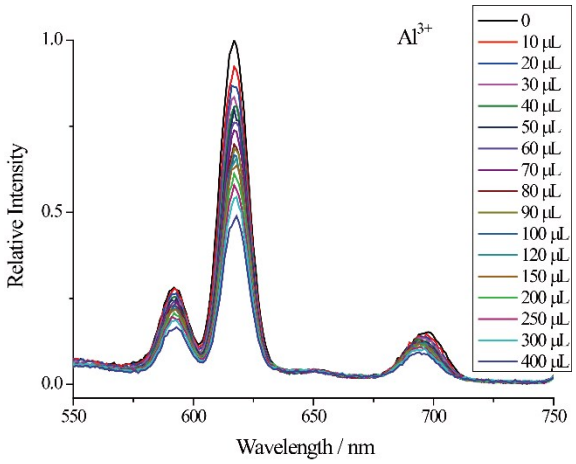


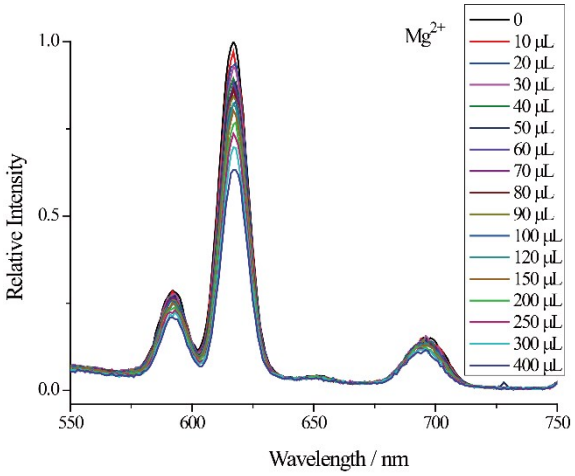
Fig. S8 Fluorescence spectra of compound **1** (ethanol suspension, 1.0 mL) before and after added various analytes (excited at 265 nm).

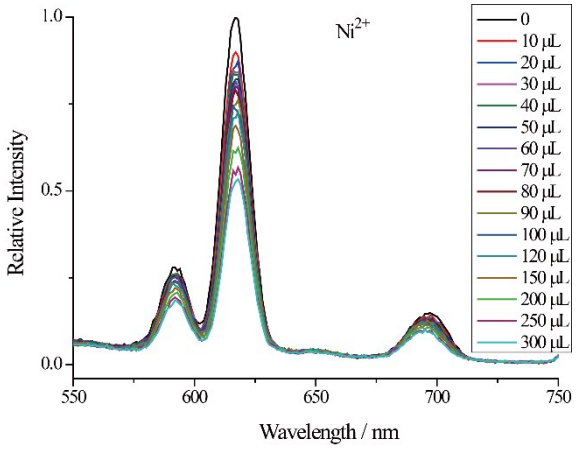


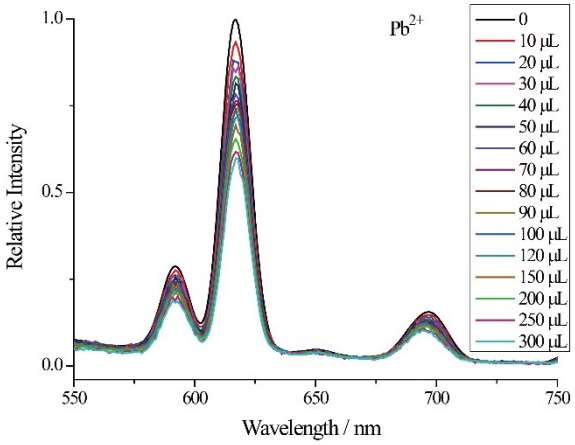

Co2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


K+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


Al3+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


Mg2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


Ni2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


Pb2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL

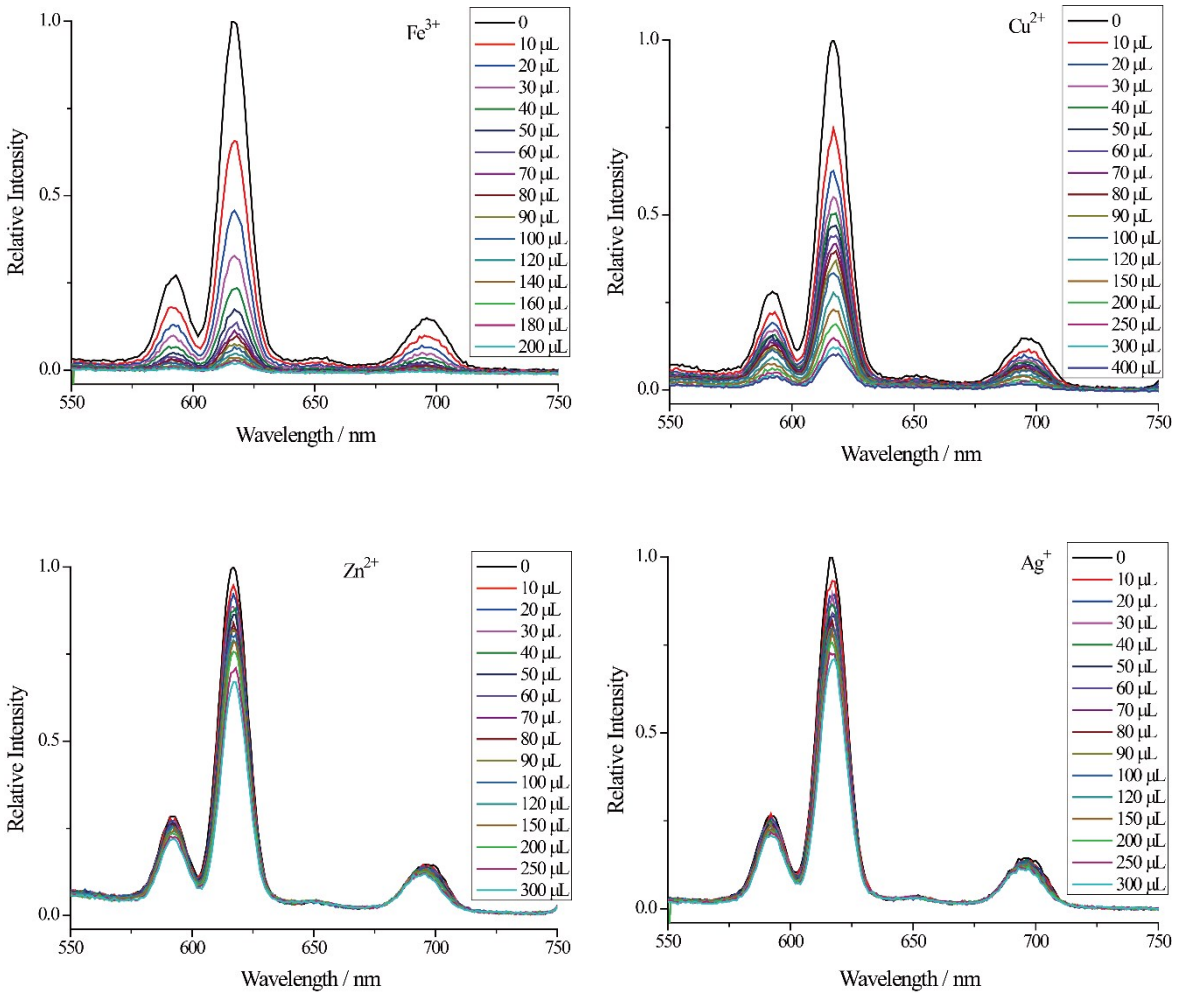
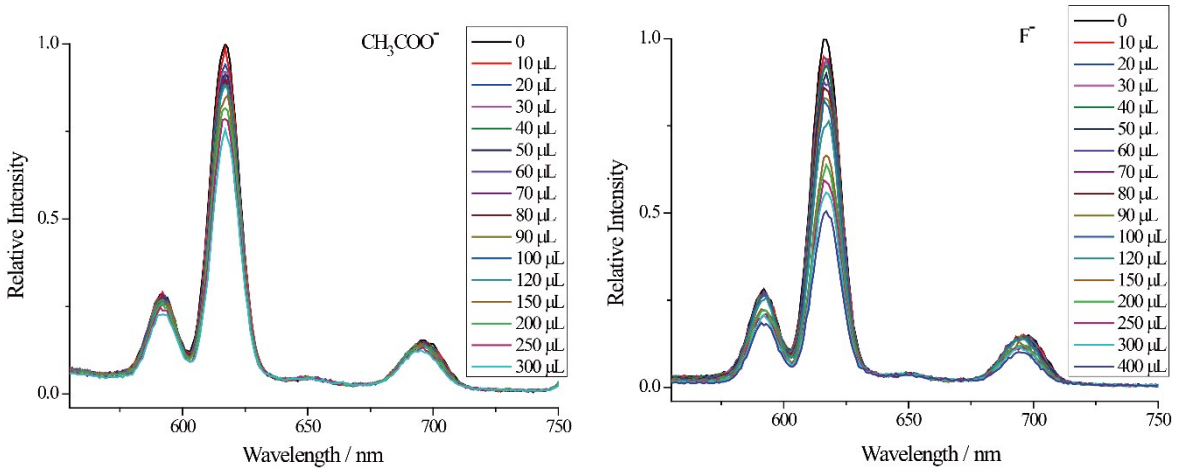
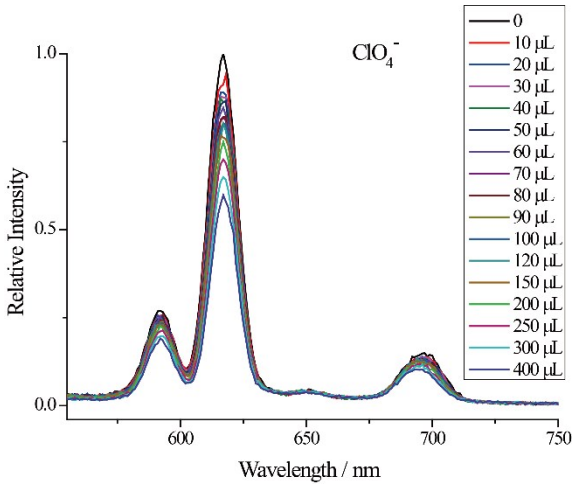
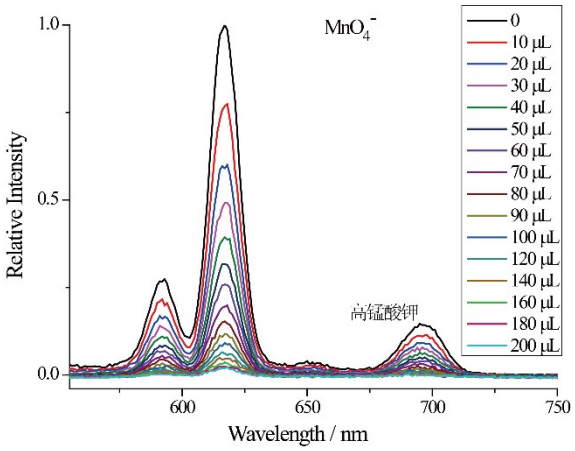
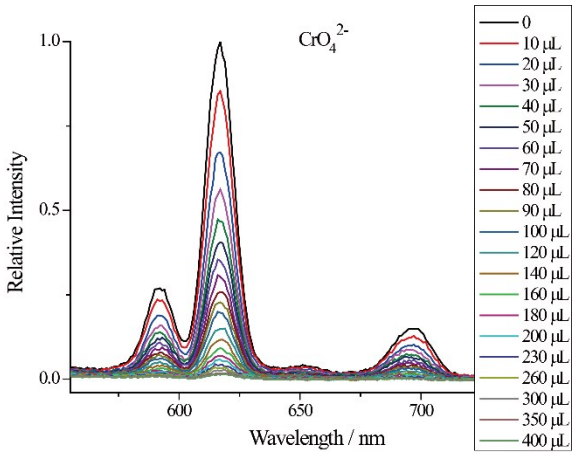


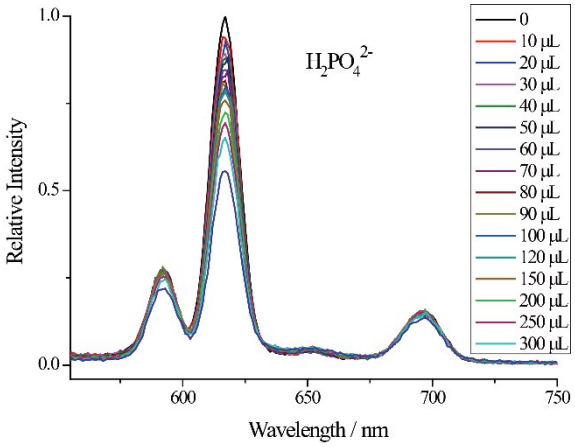
Fig. S9 Fluorescence spectra of compound **1** (ethanol suspension, 1.0 mL) before and after added different metal ions (excited at 265 nm).

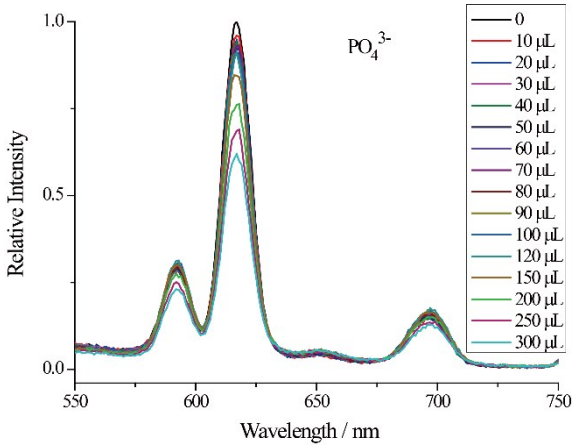


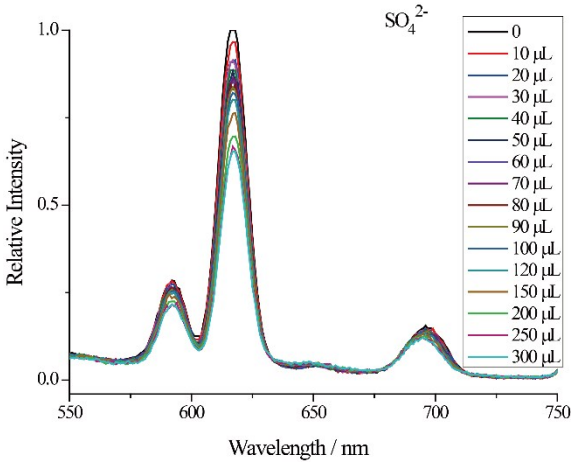

ClO_4^-
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


MnO_4^-
高锰酸钾
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL


CrO_4^{2-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
230 μL
260 μL
300 μL
350 μL
400 μL


$H_2PO_4^{2-}$
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


PO_4^{3-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


SO_4^{2-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL

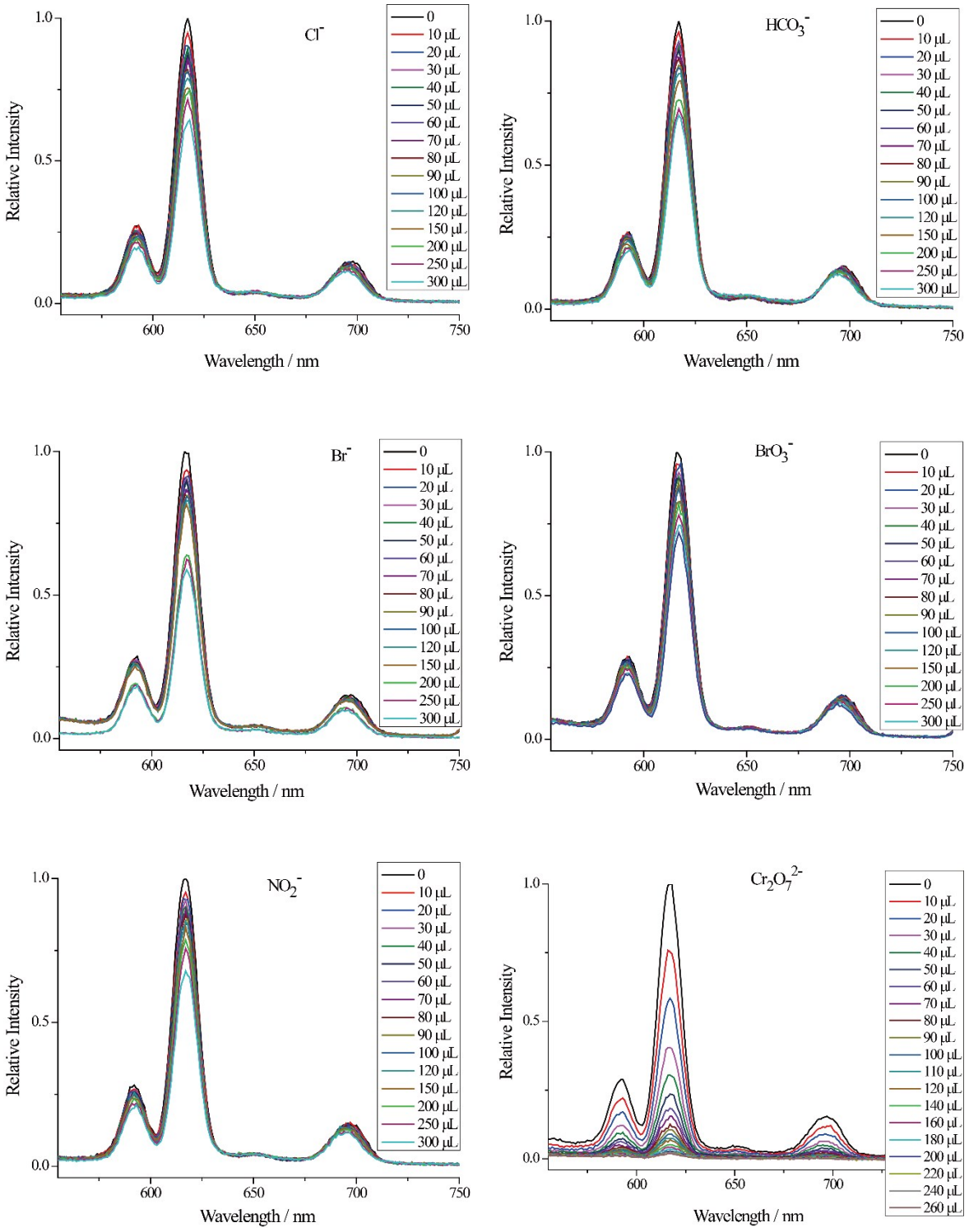
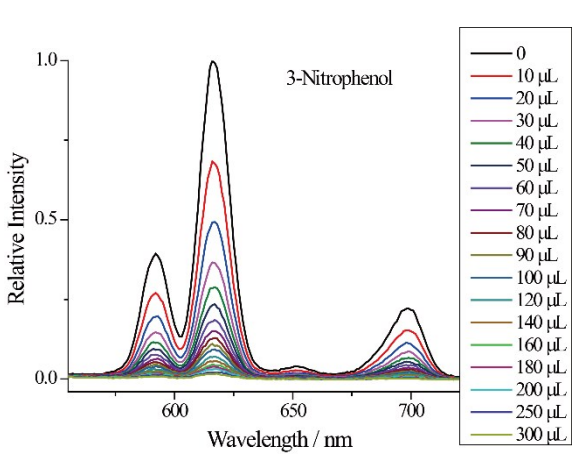
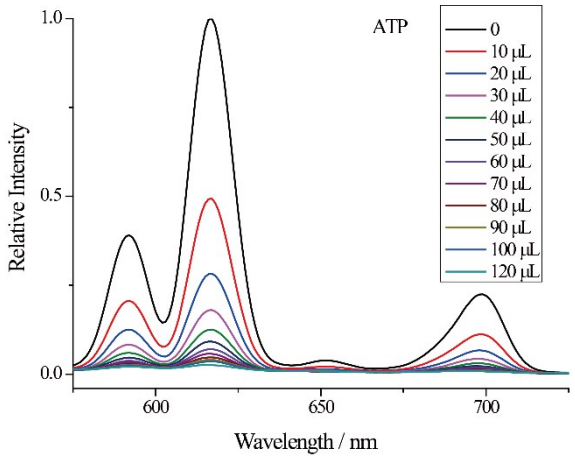
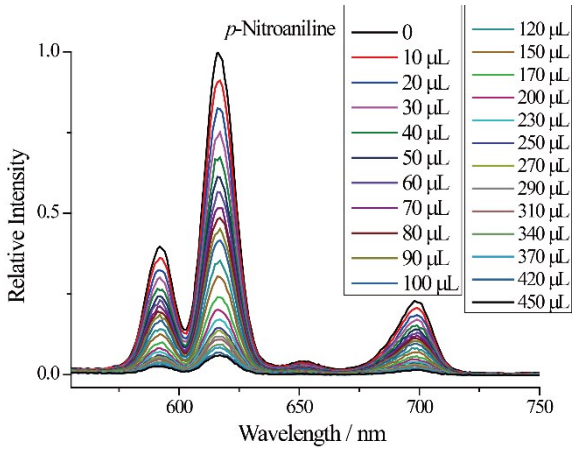
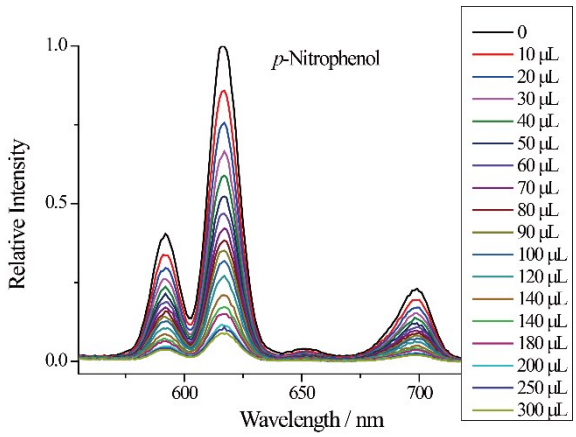


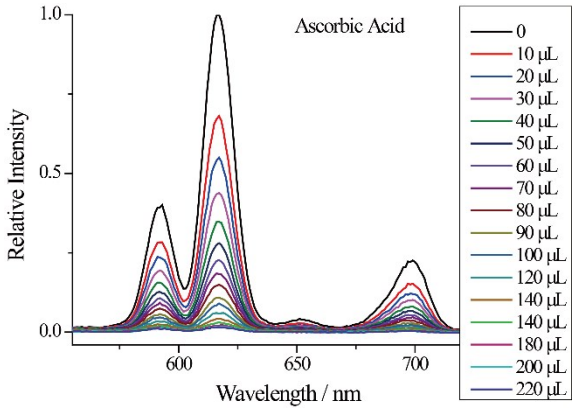
Fig. S10 Fluorescence spectra of compound **1** (ethanol suspension, 1.0 mL) before and after added different anions (excited at 265 nm).

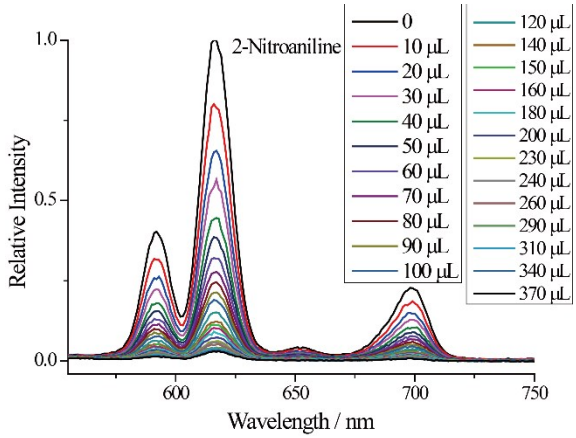

3-Nitrophenol
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
250 μL
300 μL


ATP
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL


p-Nitroaniline
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
170 μL
200 μL
230 μL
250 μL
270 μL
290 μL
310 μL
340 μL
370 μL
420 μL
450 μL


p-Nitrophenol
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
140 μL
180 μL
200 μL
250 μL
300 μL


Ascorbic Acid
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
140 μL
180 μL
200 μL
220 μL


2-Nitroaniline
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
150 μL
160 μL
180 μL
200 μL
230 μL
240 μL
260 μL
290 μL
310 μL
340 μL
370 μL

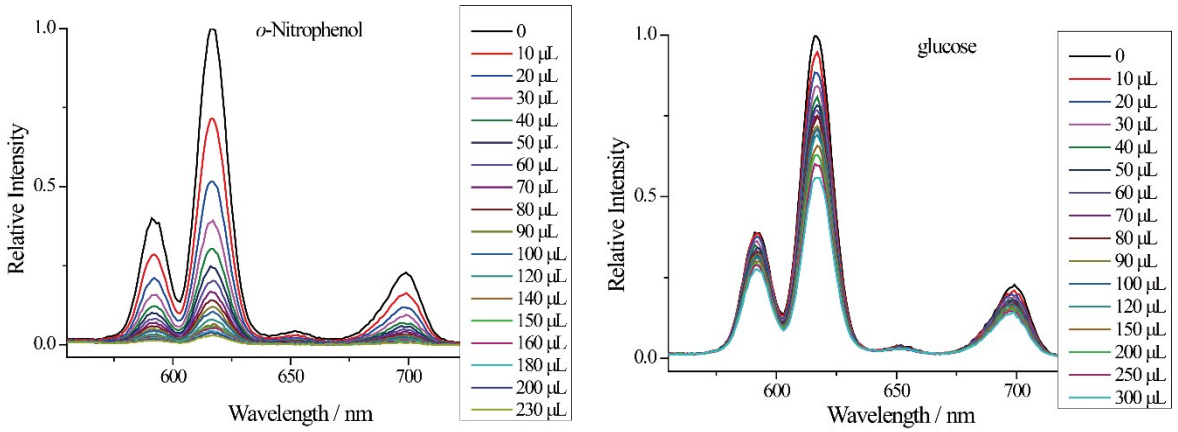
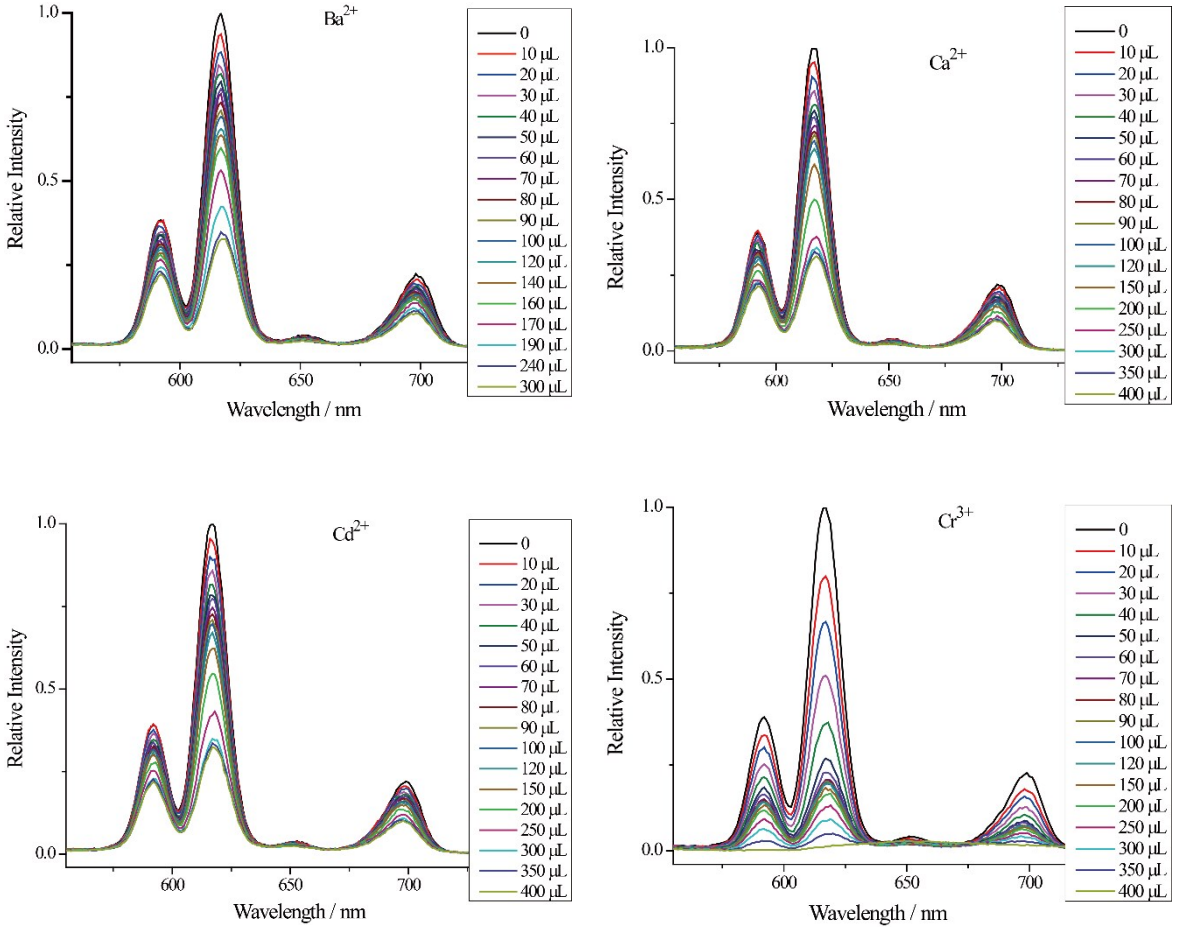
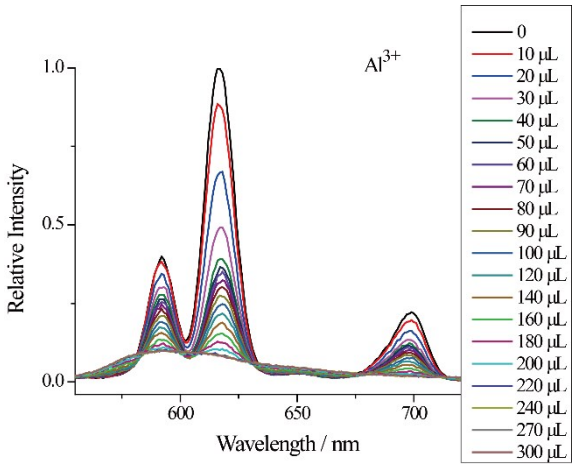
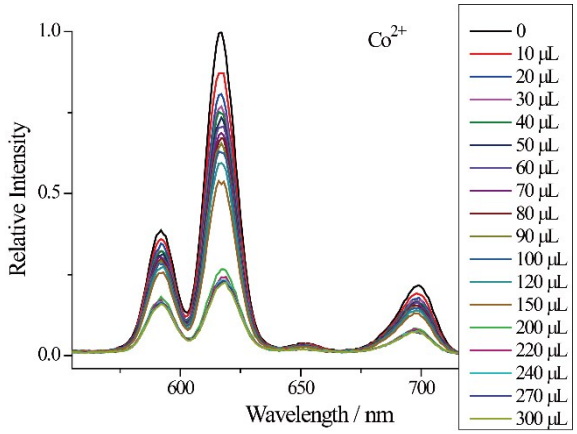
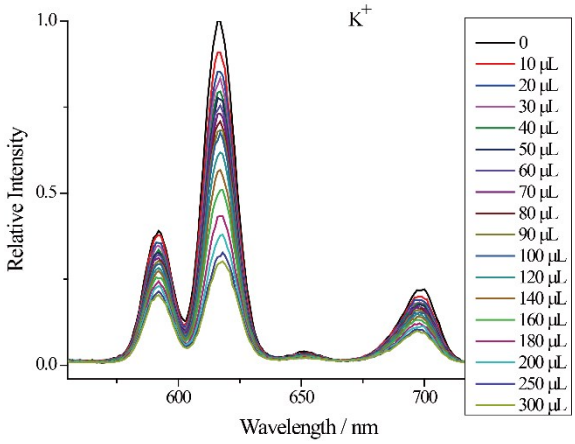


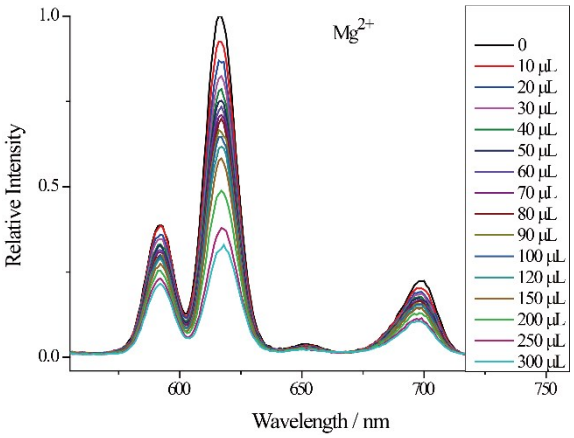
Fig. S11 Fluorescence spectra of compound **2** (ethanol suspension, 1.0 mL) before and after added various analytes (excited at 265 nm).

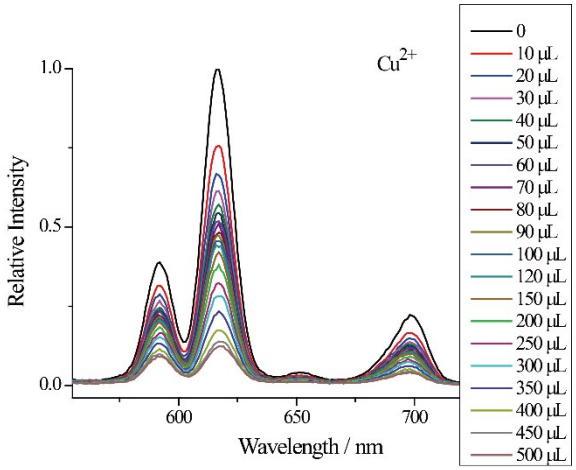


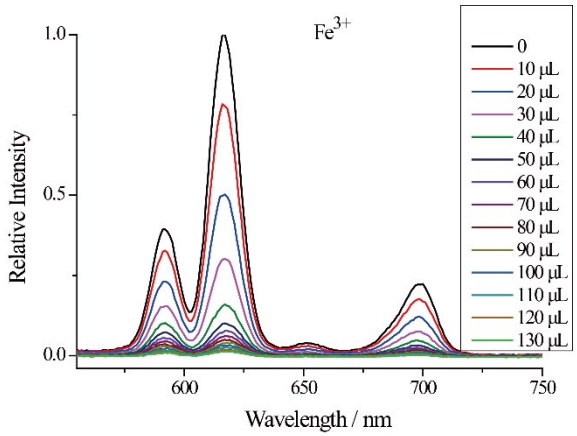

Al3+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
220 μL
240 μL
270 μL
300 μL

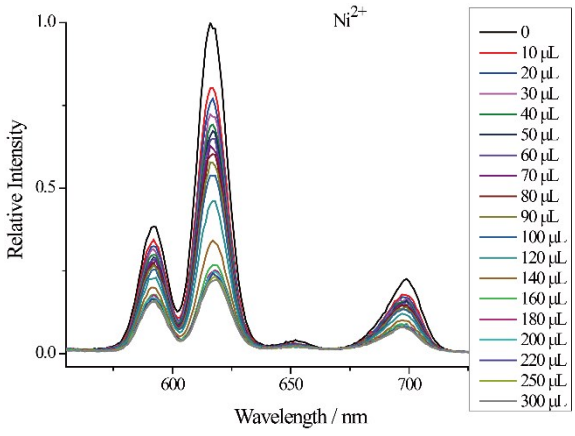

Co2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
220 μL
240 μL
270 μL
300 μL

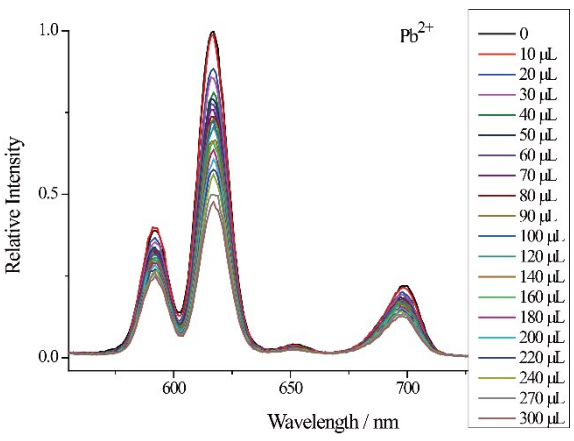

K+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
250 μL
300 μL


Mg2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


Cu2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
350 μL
400 μL
450 μL
500 μL


Fe3+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
110 μL
120 μL
130 μL


Ni2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
220 μL
250 μL
300 μL


Pb2+
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL
200 μL
220 μL
240 μL
270 μL
300 μL

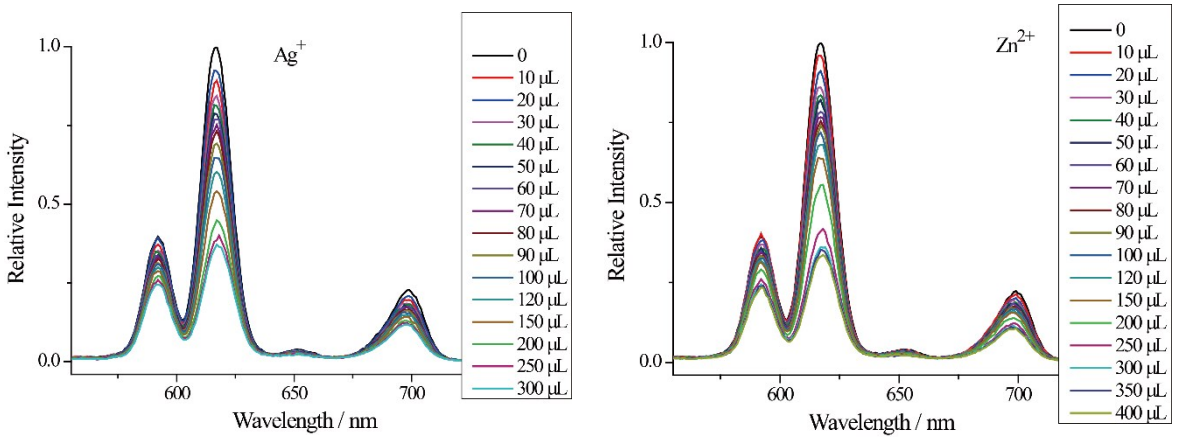
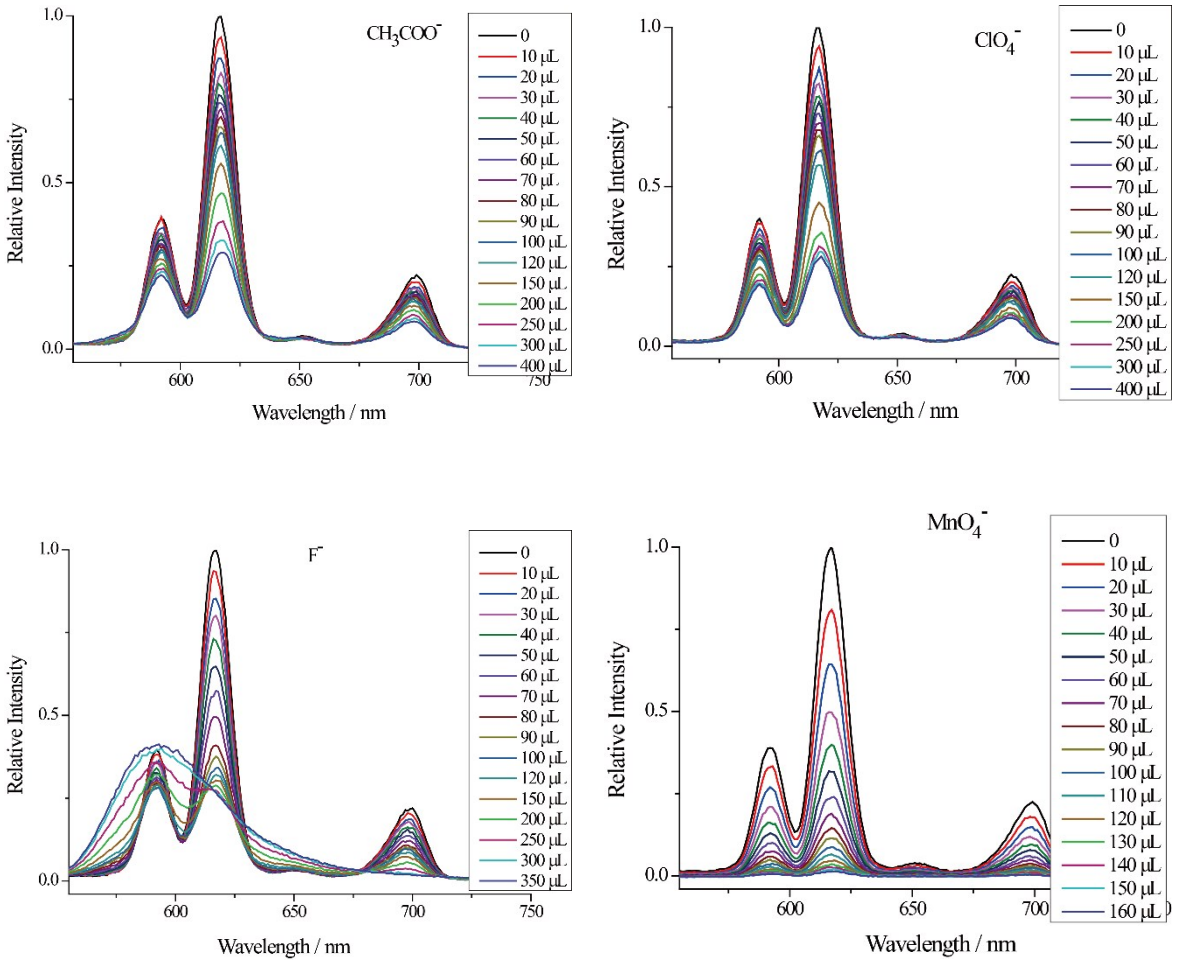
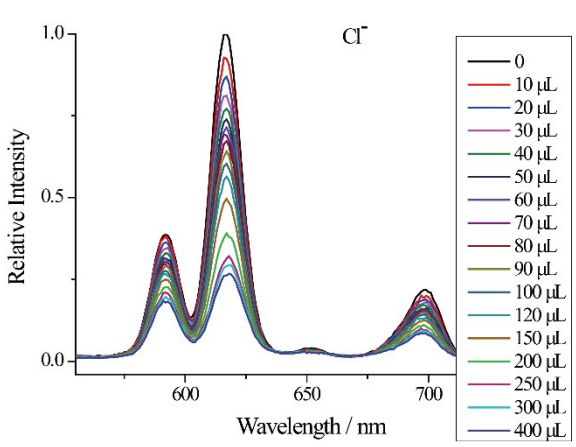
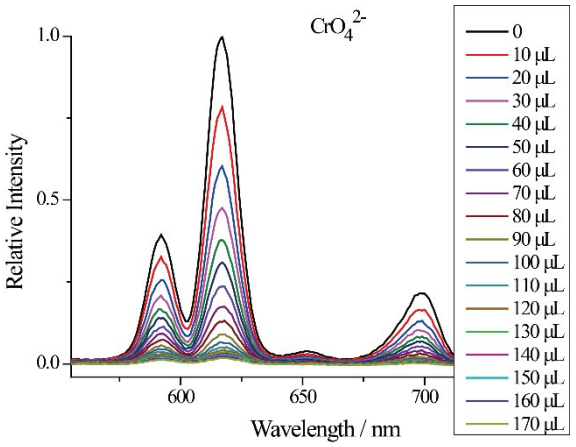
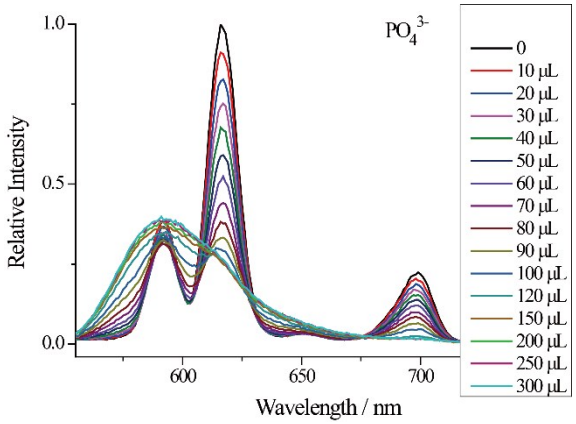


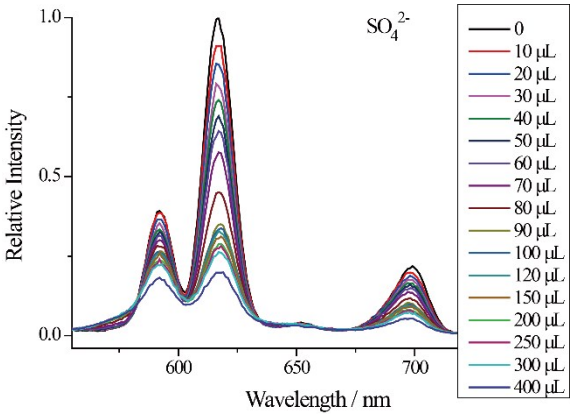
Fig. S12 Fluorescence spectra of compound **2** (ethanol suspension, 1.0 mL) before and after added different metal ions (excited at 265 nm).

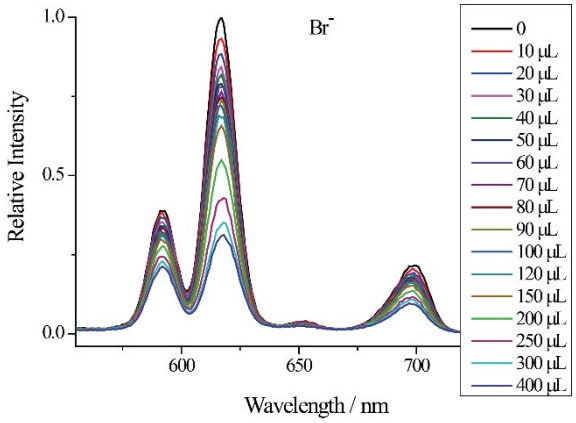


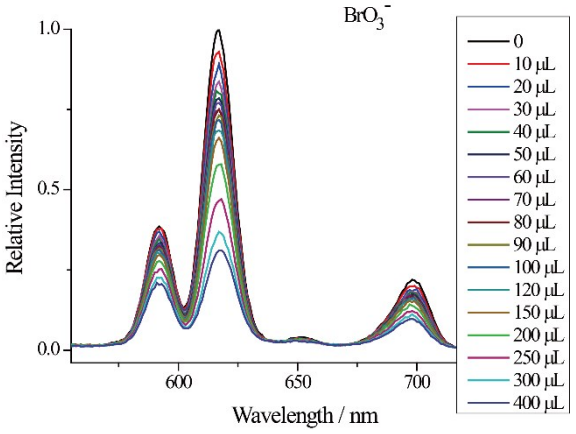

Cl^-
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL

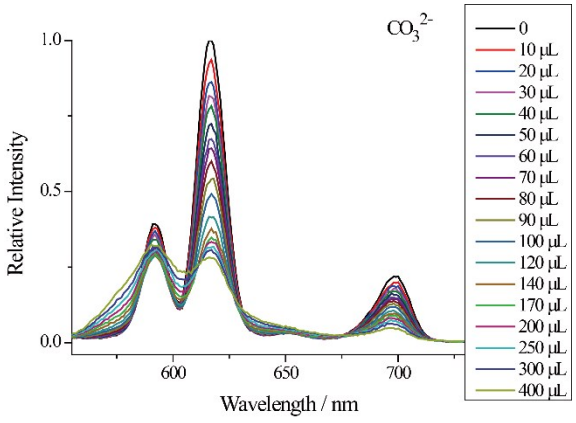

CrO_4^{2-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
110 μL
120 μL
130 μL
140 μL
150 μL
160 μL
170 μL

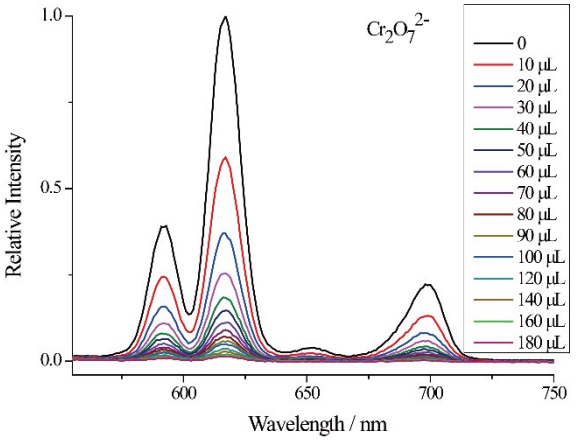

PO_4^{3-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL


SO_4^{2-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


Br^-
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


BrO_3^-
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
150 μL
200 μL
250 μL
300 μL
400 μL


CO_3^{2-}
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
170 μL
200 μL
250 μL
300 μL
400 μL


$Cr_2O_7^{2-}$
Relative Intensity
Wavelength / nm
0
10 μL
20 μL
30 μL
40 μL
50 μL
60 μL
70 μL
80 μL
90 μL
100 μL
120 μL
140 μL
160 μL
180 μL

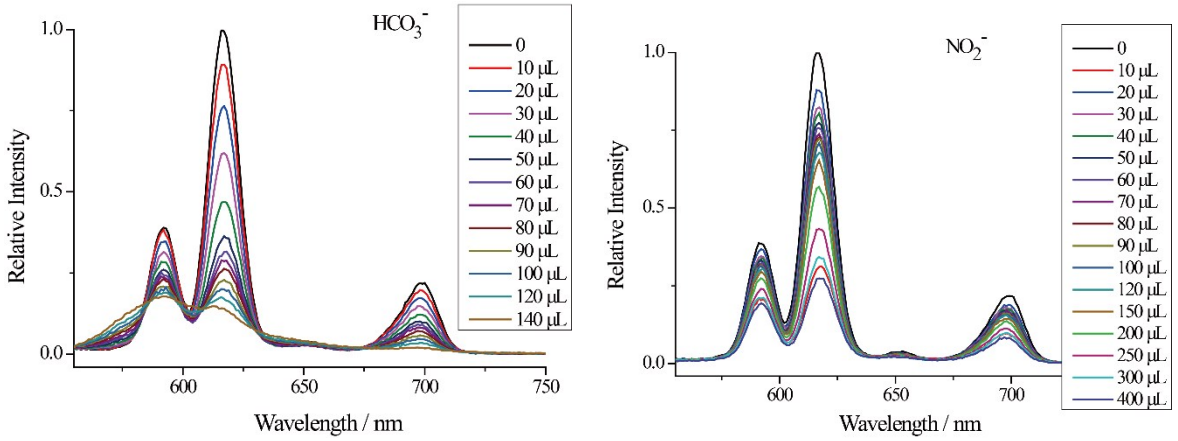


Fig. S13 Fluorescence spectra of compound **2** (ethanol suspension, 1.0 mL) before and after added different anions (excited at 265 nm).

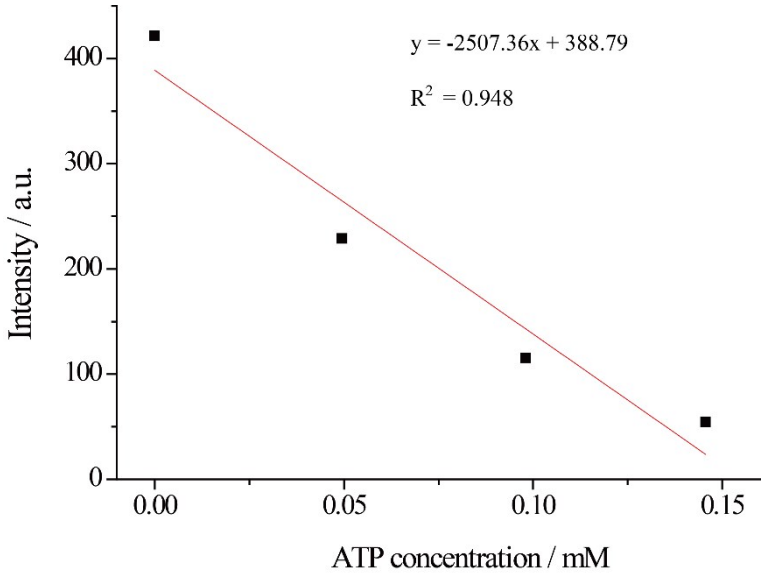


Fig. S14 The fitting curve of the emission intensity (617 nm) of compound **1** vs. ATP concentration.

Detection limit was determined according to the following definitions:

$$s_b = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

$$S = \frac{\Delta I}{\Delta c}$$

$$DL = \frac{3s_b}{S}$$

S is the slope of the calibration curve; S_b is the standard deviation for replicating detections of blank solutions.[1]

$S = 2.51 \times 10^6\ M^{-1}$

$S_b = 0.41$ (n = 11)

$DL = 3Sb / S = 0.490 \times 10^{-6}$ M = 0.490 μM (for compound **1** detecting ATP)

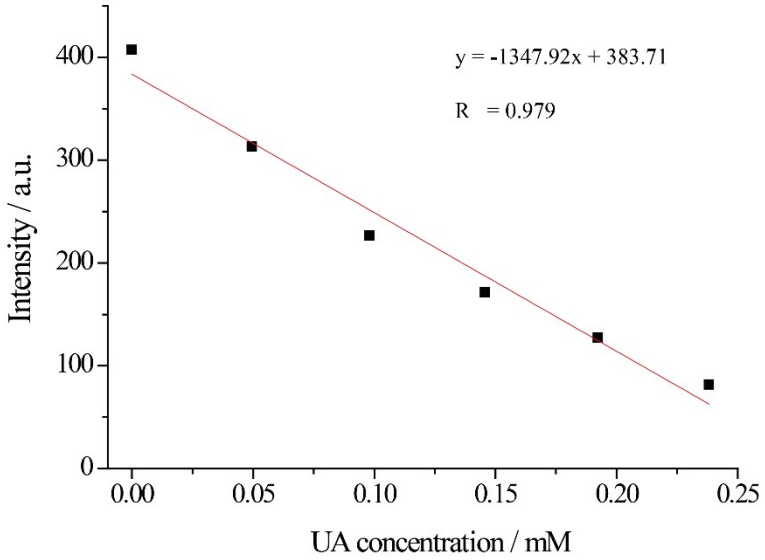


Fig. S15 The fitting curve of the emission intensity (617 nm) of compound **2** vs. UA concentration.

$S = 1.347 \times 10^6\ M^{-1}$

$S_b = 0.27$ (n = 11)

$DL = 3Sb / S = 0.601 \times 10^{-6}$ M = 0.601 μM (for compound **2** detecting UA)

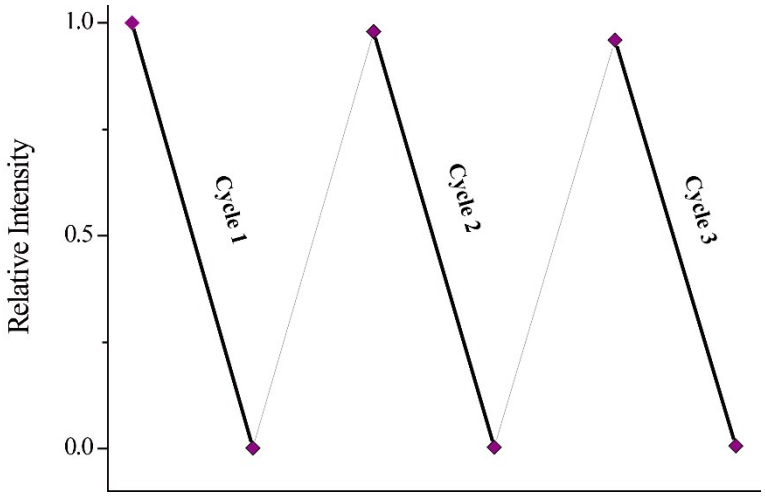


Fig. S16 Reproducibility of luminescence intensity (617 nm) of crystal powder compound **1** up to three cycles, adding ATP (100 μL).

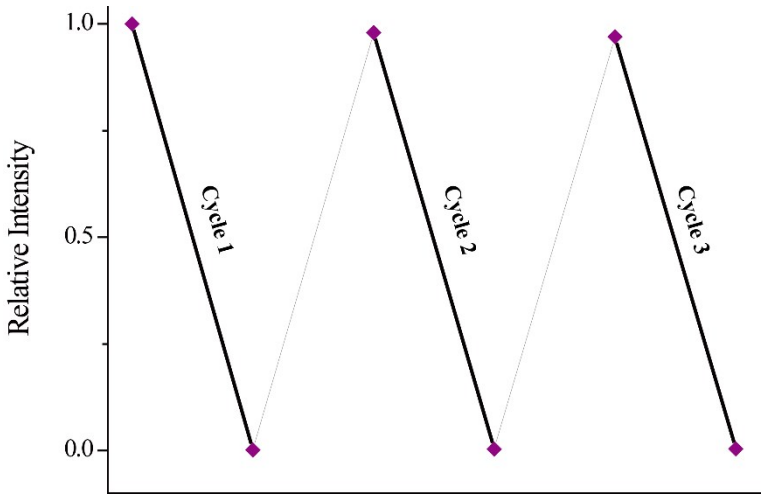


Fig. S17 Reproducibility of luminescence intensity (617 nm) of crystal powder compound **2** up to three cycles, adding UA(100 μL).

Table S1 Selected bond lengths (Å) and angles (°) for compound **1**.

Eu(1)-O(3)	2.388(2)	O(3)-Eu(1)-O(5)	77.86(9)
Eu(1)-O(5)	2.396(2)	O(3)-Eu(1)-O(8)	115.72(8)
Eu(1)-O(8)	2.426(3)	O(5)-Eu(1)-O(8)	81.60(10)
Eu(1)-O(7)	2.432(2)	O(3)-Eu(1)-O(7)	74.88(8)
Eu(1)-O(4)	2.442(3)	O(8)-Eu(1)-O(7)	84.88(10)
Eu(1)-O(2)	2.487(3)	O(5)-Eu(1)-O(4)	73.97(9)
Eu(1)-O(1)	2.501(2)	O(8)-Eu(1)-O(4)	76.59(9)
Eu(1)-O(6)	2.550(2)	O(7)-Eu(1)-O(2)	86.87(10)
		O(4)-Eu(1)-O(2)	83.82(11)
		O(3)-Eu(1)-O(1)	81.54(8)
		O(5)-Eu(1)-O(1)	74.81(9)

Table S2 Selected bond lengths (Å) and angles (°) for compound **2**.

Eu(1)-O(12)	2.3834(18)	O(12)-Eu(1)-O(8)	70.83(9)
Eu(1)-O(8)	2.402(3)	O(8)-Eu(1)-O(7)	73.44(9)
Eu(1)-O(7)	2.4249(16)	O(7)-Eu(1)-O(9)	69.53(7)
Eu(1)-O(9)	2.4305(19)	O(12)-Eu(1)-O(2)	75.47(6)
Eu(1)-O(2)	2.4500(18)	O(9)-Eu(1)-O(2)	74.87(6)
Eu(1)-O(5)	2.4896(17)	O(12)-Eu(1)-O(5)	76.98(6)
Eu(2)-O(13)	2.3154(19)	O(9)-Eu(1)-O(5)	78.16(7)
Eu(2)-O(11)#1	2.3571(16)	O(2)-Eu(1)-O(5)	68.15(6)
Eu(2)-O(5)	2.3632(16)	O(12)-Eu(1)-O(10)	75.31(7)
Eu(2)-O(3)	2.3961(18)	O(8)-Eu(1)-O(10)	79.52(12)
Eu(2)-O(1)	2.443(2)	O(7)-Eu(1)-O(10)	91.46(7)
Eu(2)-O(4)	2.450(2)	O(2)-Eu(1)-O(10)	85.66(8)
		O(8)-Eu(1)-O(6)	76.58(12)
		O(7)-Eu(1)-O(6)	76.80(6)
		O(9)-Eu(1)-O(6)	79.34(9)

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z+1/2

Table S3 Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{28}Eu_2O_{16}$	$C_{30}H_{30}Eu_2O_{15}$
Formula weight	804.33	934.48
Crystal color	Yellow	Yellow
Crystal size (mm)	0.20 x 0.18 x 0.15	0.18 x 0.15 x 0.12
Crystal system	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.909(2)	21.9083(13)
b (Å)	8.285(3)	10.1368(6)
c (Å)	10.444(3)	14.0410(8)
α (deg)	72.666(4)	0
β (deg)	74.008(4)	91.5660(10)
γ (deg)	78.581(4)	0
Volume ($Å^3$)	622.9(3)	3117.1(3)
Z	1	4
d_{calcd} (g/cm^3)	2.117	1.987
μ (mm^{-1})	5.063	4.062
F (000)	380	1816
λ (Å)	0.71073	0.71073
Temperature	293(2) K	293(2) K
θ range (deg)	2.10 to 27.00	0.93 to 27.17
h ,k, l range	-10<=h<=9	-27<=h<=27
	-10<=h<=8	-8<=h<=12
	-13<=h<=10	-17<=h<=17
Reflections collected / unique	3624 / 2625	18097 / 6816
	[R(int) = 0.0106]	[R(int) = 0.0364]
Completeness to θ	95.9 % (θ = 27.00)	98.7 % (θ = 27.17)
Data / restraints / parameters	2625 / 0 / 199	6816 / 0 / 537
Goodness-of-fit on F^2	1.044	1.126
Final R indices [I>2σ(I)] [a]	R1 = 0.0194	R1 = 0.0182
	wR2 = 0.0541	wR2 = 0.0452
R indices (all data)	R1 = 0.0195	R1 = 0.0204
	wR2 = 0.0542	wR2 = 0.0461
Largest diff. Peak	0.955	0.501
and hole($e \cdot Å^{-3}$)	and -1.124	and -0.590

References

[1] Xu, H.; Gao, J.; Qian, X.; Wang, J.; He, H.; Cui, Y.; Yang, Y.; Wang, Z.; Qian, G. Metal–organic framework nanosheets for fast response and highly sensitive luminescent sensing of Fe^{3+}. *J. Mater. Chem. A*, 2016, **4**, 10900–10905.