Supporting Information

Construction of a Crystalline 14-metal Zn-Nd Rectangular Nanocluster with Dual-emissive Response towards Metal Ions

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Contents

1. General Procedures

Metal salts and solvents were purchased from Meryer and used directly without further purification. All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Physical measurements: NMR: AVANCE III AV500. 500 spectrometer (^{1}H, 500 MHz) at 298 K; IR: Nicolet IS10 spectrometer; Powder XRD: D8ADVANCE. Elemental analyses (C, H, N) of compounds were carried out on a EURO EA3000 elemental analysis after dried in an oven at 120^{o}C for 2 h. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. The thermogravimetric analyses (TA) were carried out on a TA Instruments Q600. Field emission scanning electron microscopy (FESEM) images and EDX spectra were recorded on a Nova NanoSEM 200 scanning electron microscope. Conductivity measurement was carried out with a DDS-11 conductivity bridge for 10^{-4} M solution in CH_3CN. Absorption spectra were obtained on a UV-3600 spectrophotometer.

Photophysical Studies Visible and NIR luminescence spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. Liquid nitrogen cooled Ge PIN diode detector was used to detect the NIR emissions from 800 nm to 1700 nm. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. The quantum yields (Φ_{em}) were obtained by using an integrating sphere, according to eqn $\Phi_{em} = N_{em} / N_{abs}$, where N_{em} and N_{abs} are the numbers of emitted and absorbed photons, respectively. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

2. The IR spectra of the free ligand H_2L and 1

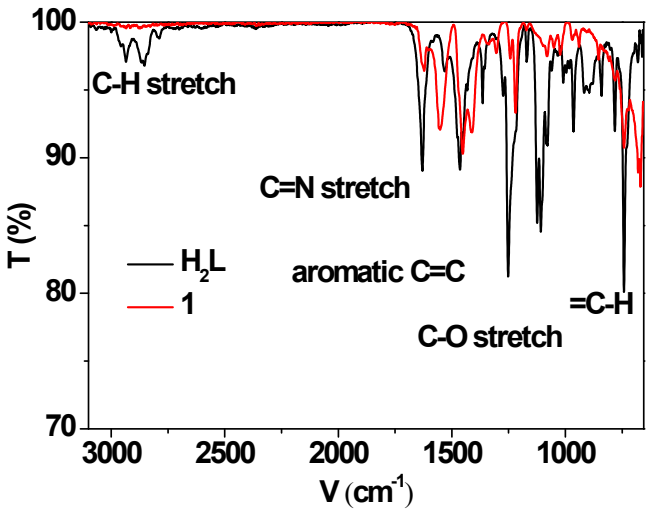


Figure S1. The IR spectra of the free ligand H_2L and **1**.

3. Powder XRD patterns of 1

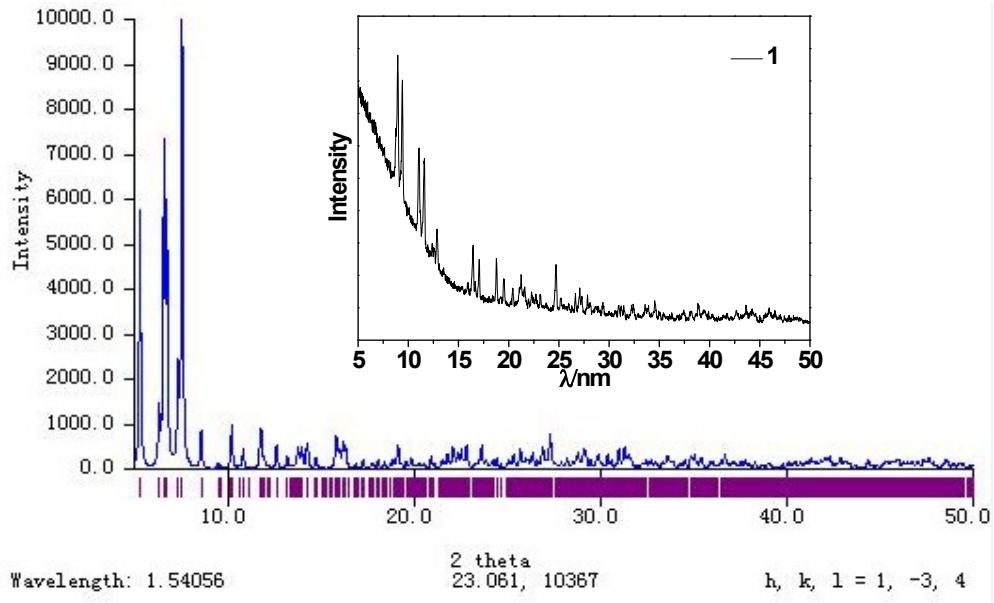


Figure S2. Powder XRD patterns of **1**.

4. The thermogravimetric analysis of 1

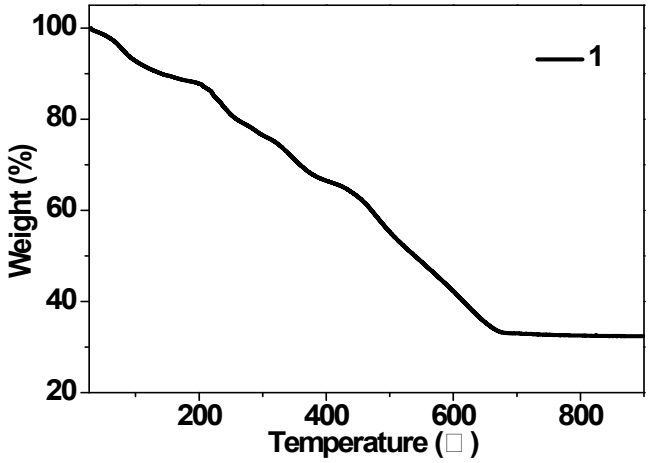


Figure S3. The thermogravimetric analysis of **1**.

5. The NIR lanthanide luminescence lifetime of 1

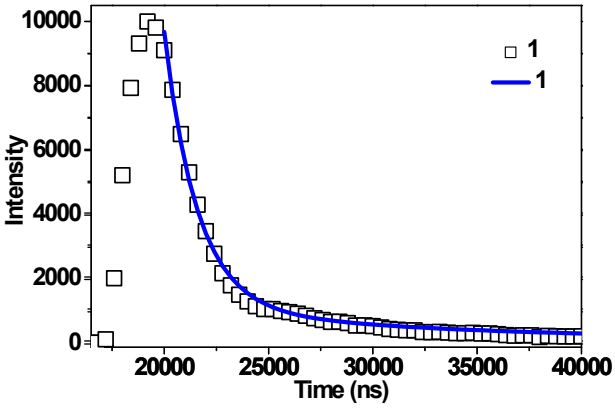
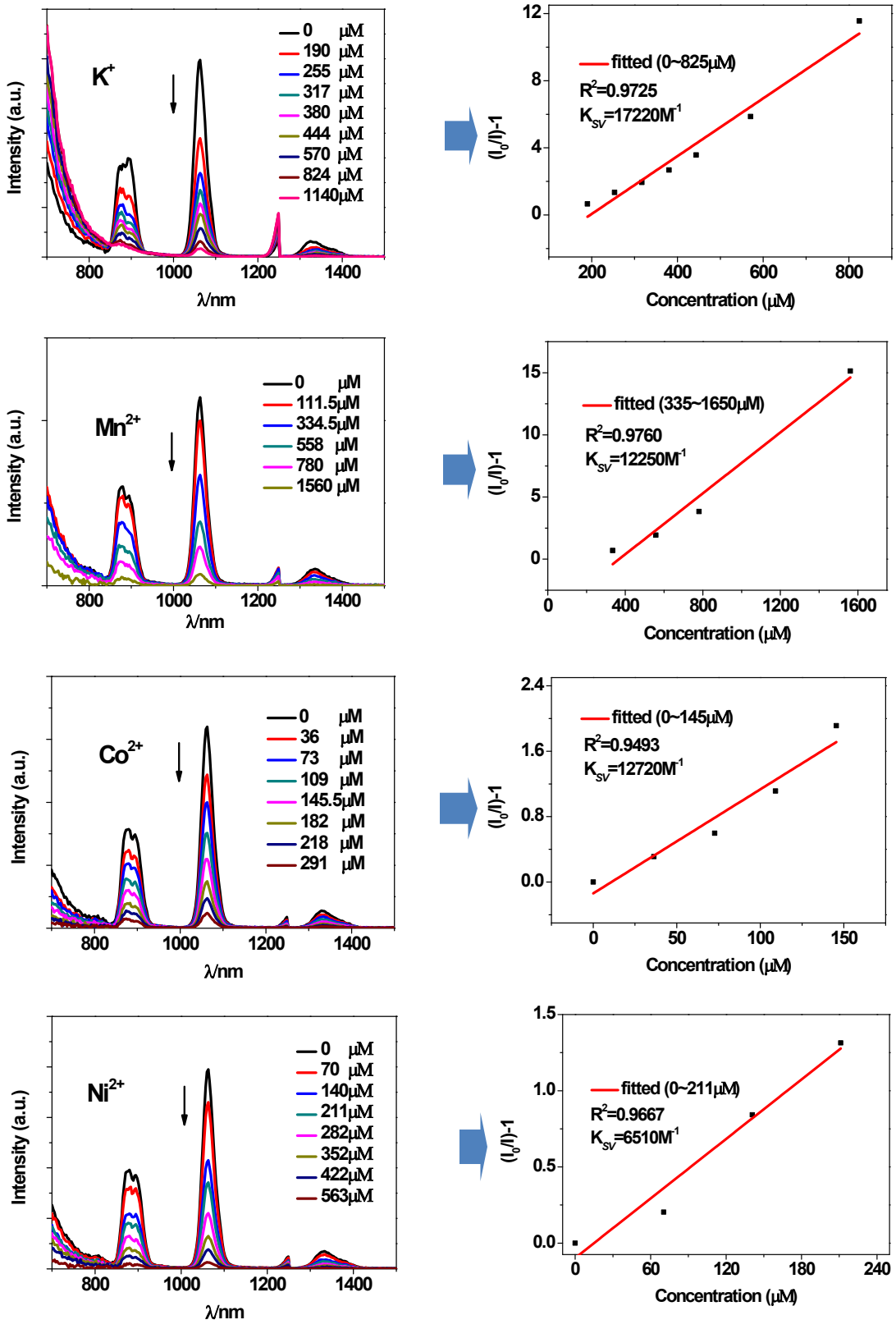
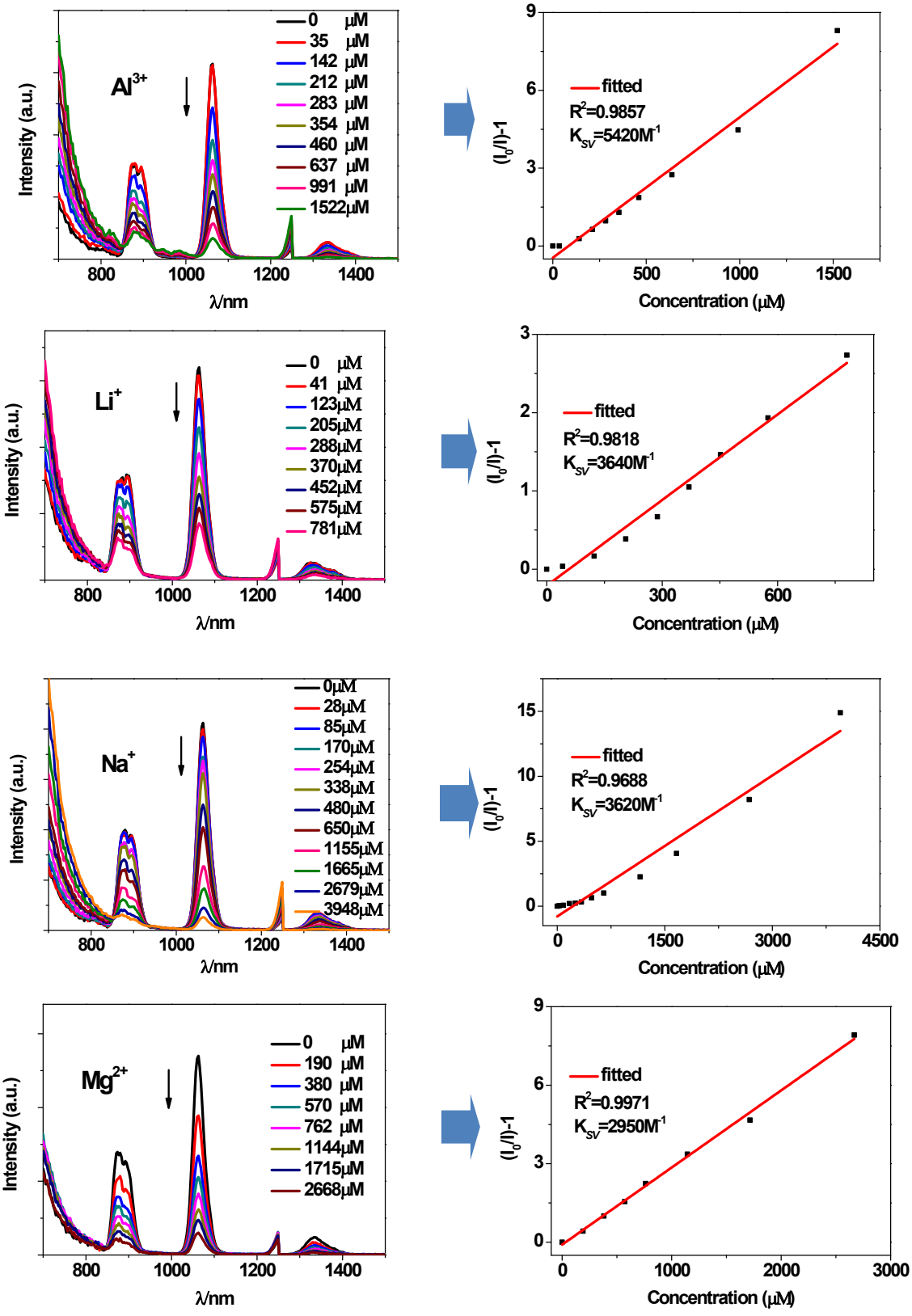
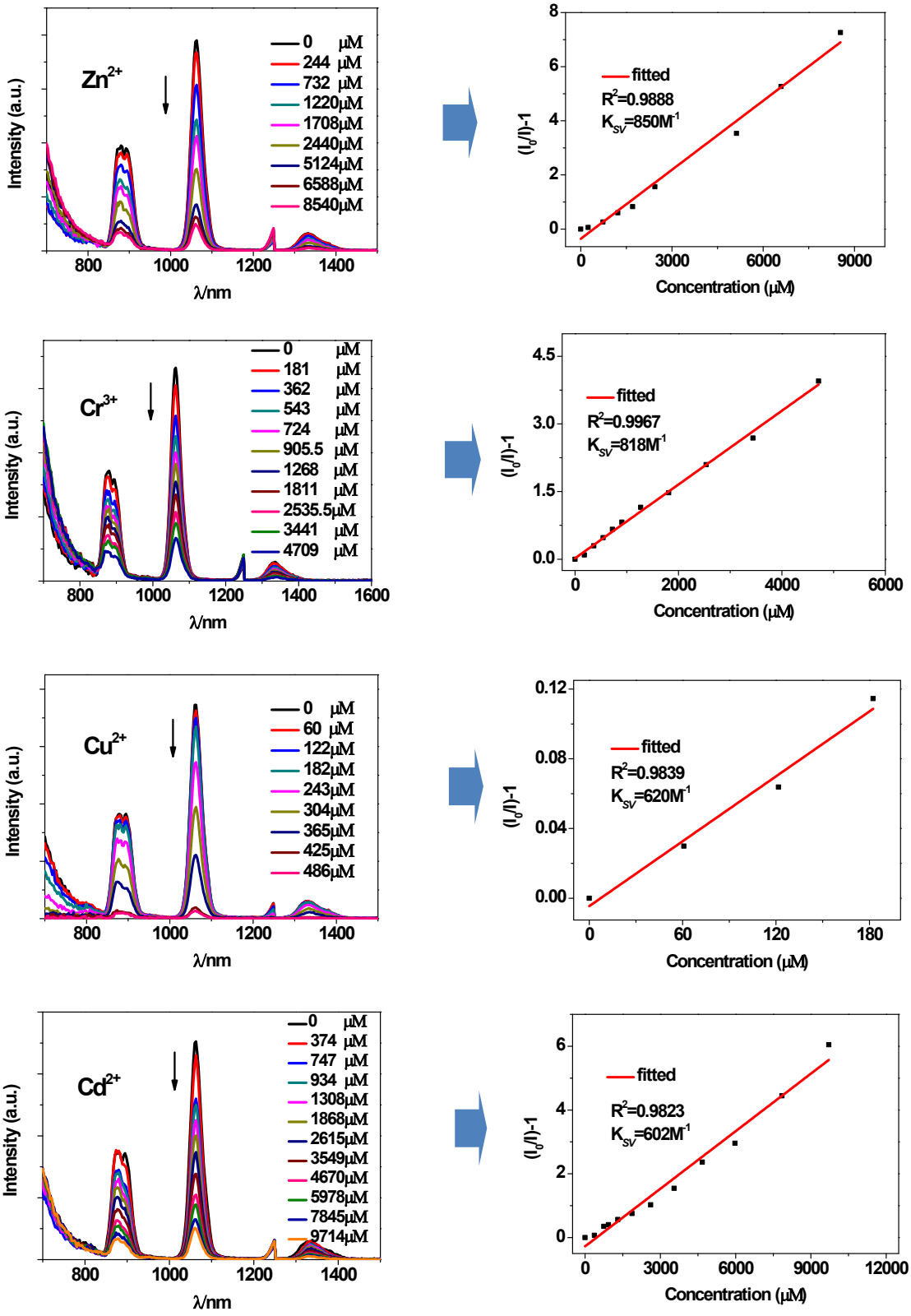


Figure S4. The NIR lanthanide luminescence lifetime of **1** in CH_3CN.

6. NIR lanthanide luminescent sensing of 1 towards metal ions




Al3+
0 μM
35 μM
142 μM
212 μM
283 μM
354 μM
460 μM
637 μM
991 μM
1522μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9857
KSV=5420M-1
(I0/I)-1
Concentration (μM)
Li+
0 μM
41 μM
123μM
205μM
288μM
370μM
452μM
575μM
781μM
fitted
R2=0.9818
KSV=3640M-1
Na+
0μM
28μM
85μM
170μM
254μM
338μM
480μM
650μM
1155μM
1665μM
2679μM
3948μM
fitted
R2=0.9688
KSV=3620M-1
Mg2+
0 μM
190 μM
380 μM
570 μM
762 μM
1144μM
1715μM
2668μM
fitted
R2=0.9971
KSV=2950M-1


Zn2+
Intensity (a.u.)
λ/nm
0 μM
244 μM
732 μM
1220μM
1708μM
2440μM
5124μM
6588μM
8540μM
fitted
R2=0.9888
KSV=850M-1
(I0/I)-1
Concentration (μM)
Cr3+
0 μM
181 μM
362 μM
543 μM
724 μM
905.5 μM
1268 μM
1811 μM
2535.5μM
3441 μM
4709 μM
fitted
R2=0.9967
KSV=818M-1
Cu2+
0 μM
60 μM
122μM
182μM
243μM
304μM
365μM
425μM
486μM
fitted
R2=0.9839
KSV=620M-1
Cd2+
0 μM
374 μM
747 μM
934 μM
1308μM
1868μM
2615μM
3549μM
4670μM
5978μM
7845μM
9714μM
fitted
R2=0.9823
KSV=602M-1

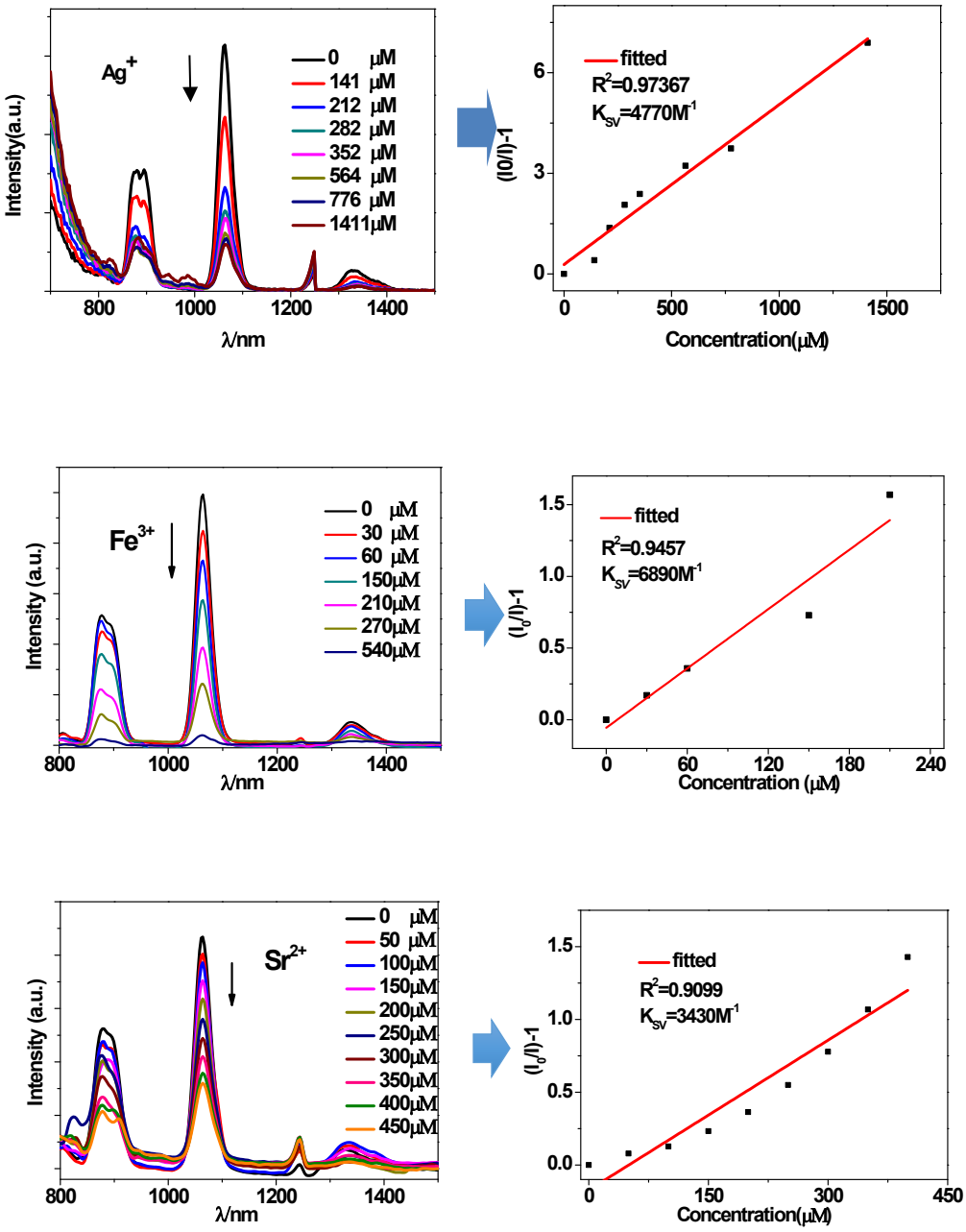
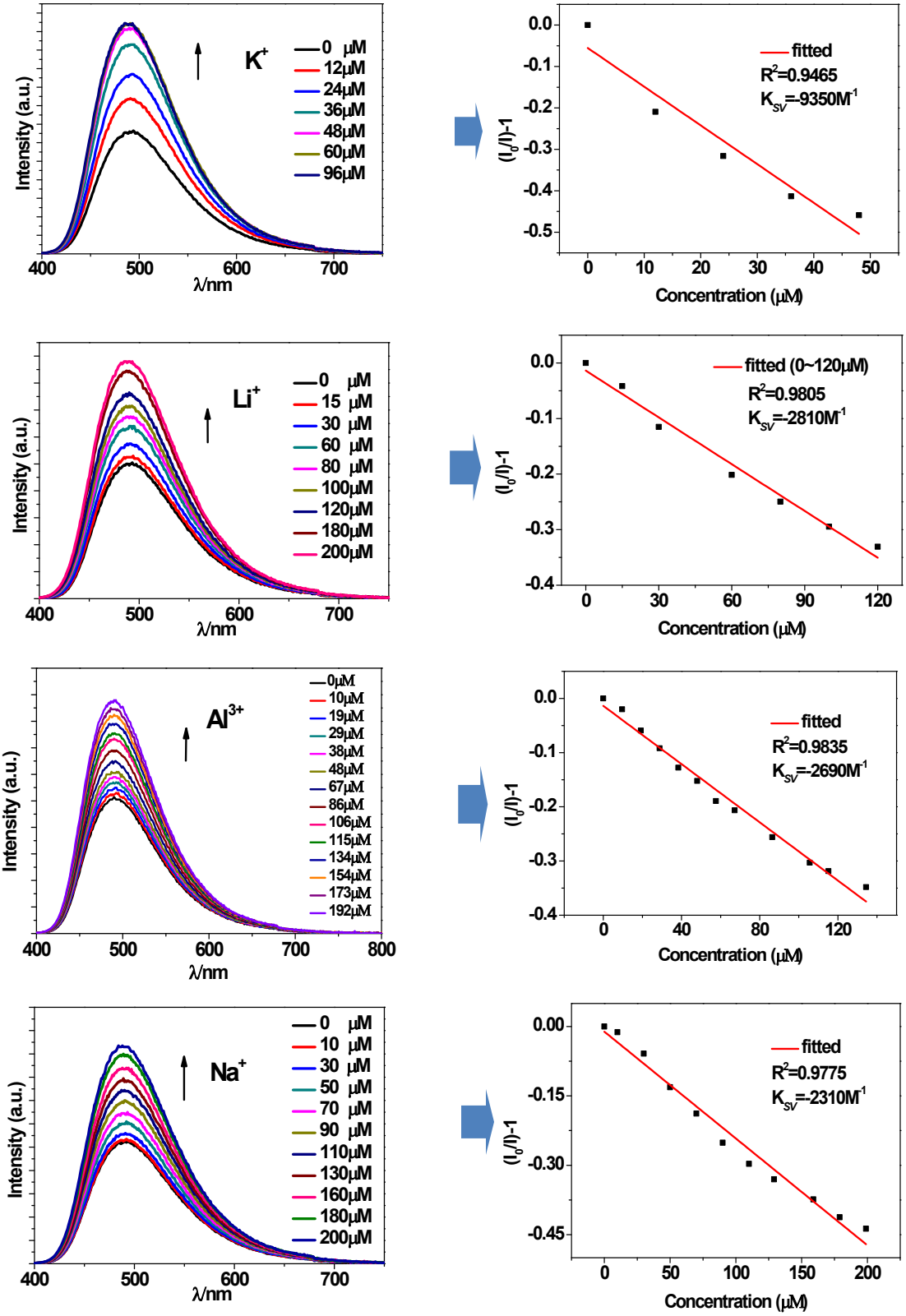
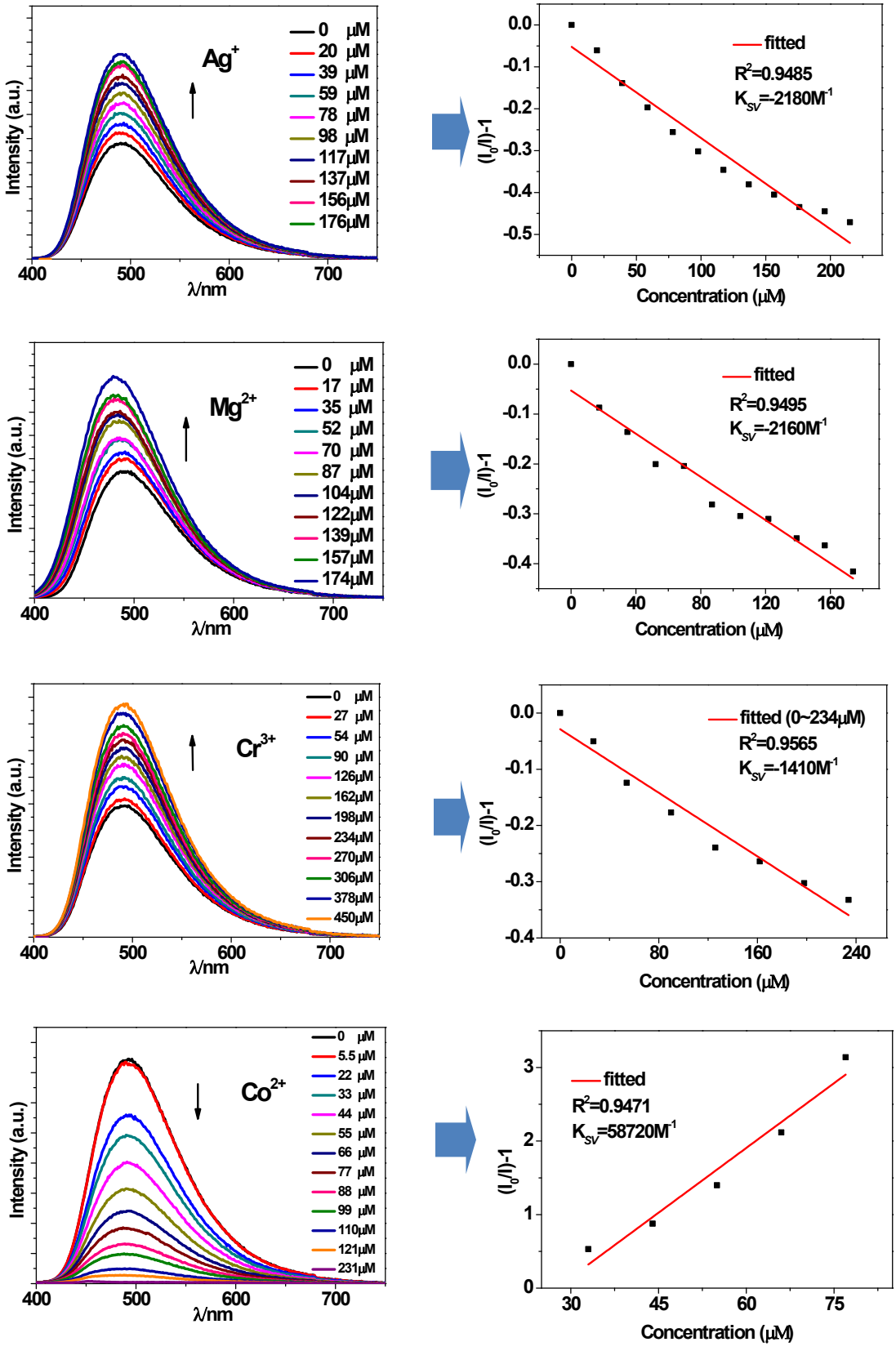
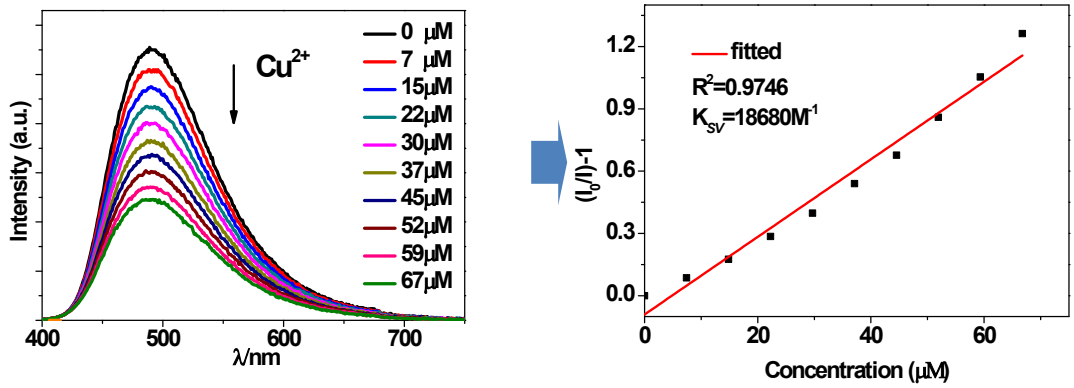


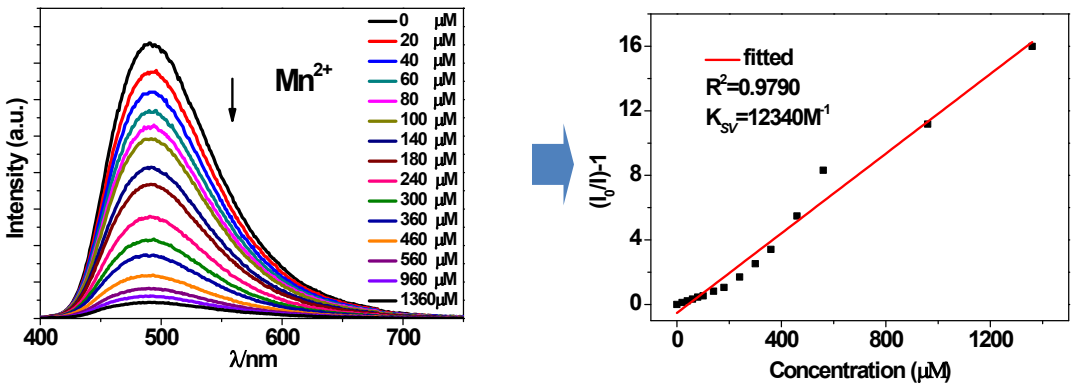
Figure S5. NIR lanthanide Luminescent sensing of **1** (60 μM) towards metal ions.

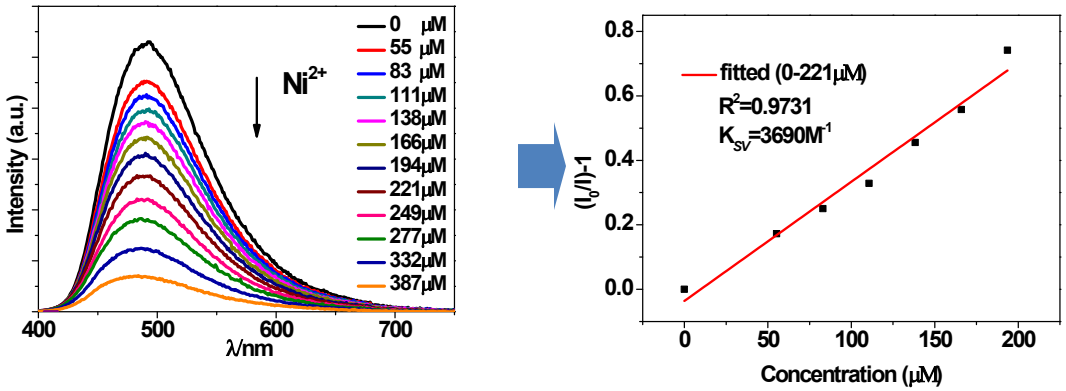
7. Visible emission response of 1 to metal ions

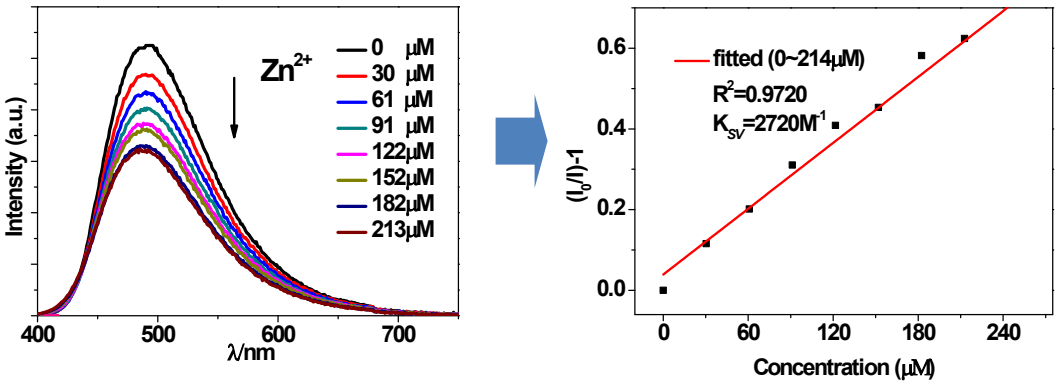



Ag+
0 μM
20 μM
39 μM
59 μM
78 μM
98 μM
117μM
137μM
156μM
176μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9485
KSV=-2180M-1
(I0/I)-1
Concentration (μM)
Mg2+
0 μM
17 μM
35 μM
52 μM
70 μM
87 μM
104μM
122μM
139μM
157μM
174μM
fitted
R2=0.9495
KSV=-2160M-1
Cr3+
0 μM
27 μM
54 μM
90 μM
126μM
162μM
198μM
234μM
270μM
306μM
378μM
450μM
fitted (0~234μM)
R2=0.9565
KSV=-1410M-1
Co2+
0 μM
5.5 μM
22 μM
33 μM
44 μM
55 μM
66 μM
77 μM
88 μM
99 μM
110μM
121μM
231μM
fitted
R2=0.9471
KSV=58720M-1


Cu2+
0 μM
7 μM
15μM
22μM
30μM
37μM
45μM
52μM
59μM
67μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9746
KSV=18680M-1
(I0/I)-1
Concentration (μM)


Mn2+
0 μM
20 μM
40 μM
60 μM
80 μM
100 μM
140 μM
180 μM
240 μM
300 μM
360 μM
460 μM
560 μM
960 μM
1360μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9790
KSV=12340M-1
(I0/I)-1
Concentration (μM)


Ni2+
0 μM
55 μM
83 μM
111μM
138μM
166μM
194μM
221μM
249μM
277μM
332μM
387μM
Intensity (a.u.)
λ/nm
fitted (0-221μM)
R2=0.9731
KSV=3690M-1
(I0/I)-1
Concentration (μM)


Zn2+
0 μM
30 μM
61 μM
91 μM
122μM
152μM
182μM
213μM
Intensity (a.u.)
λ/nm
fitted (0~214μM)
R2=0.9720
KSV=2720M-1
(I0/I)-1
Concentration (μM)

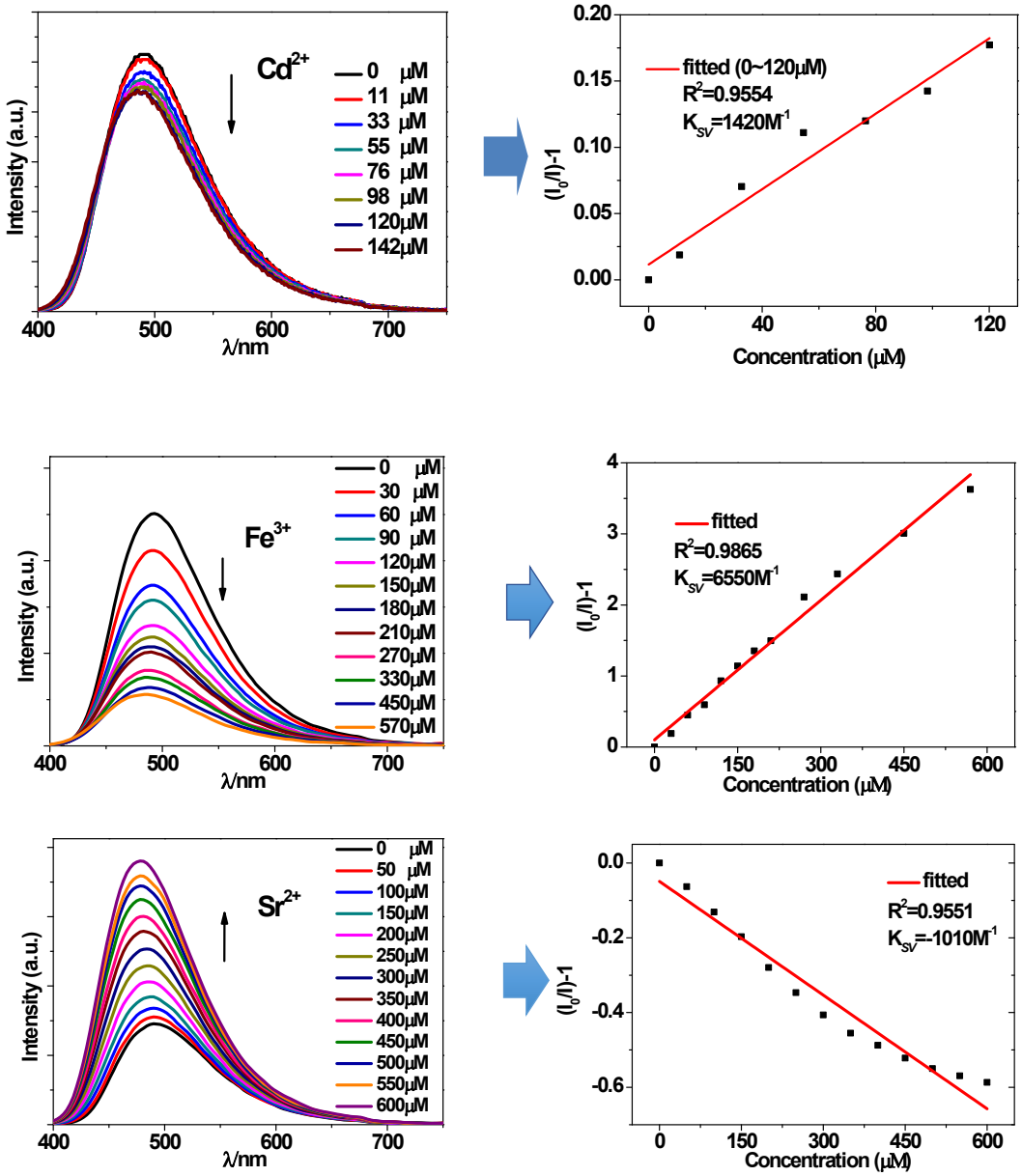


Figure S6. Visible emission response of **1** (60 μM) to metal ions.

8. The radii of added metal ions

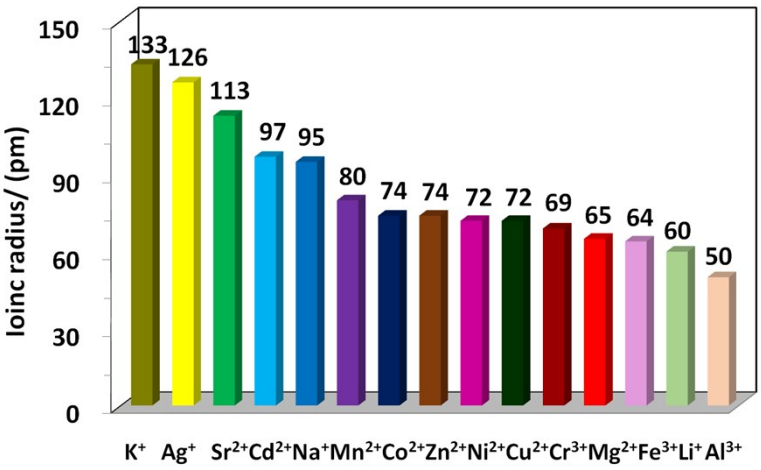


Figure S7. The radii of added metal ions.

9. UV-Vis spectra of 1 with the addition of Co^{2+} ion

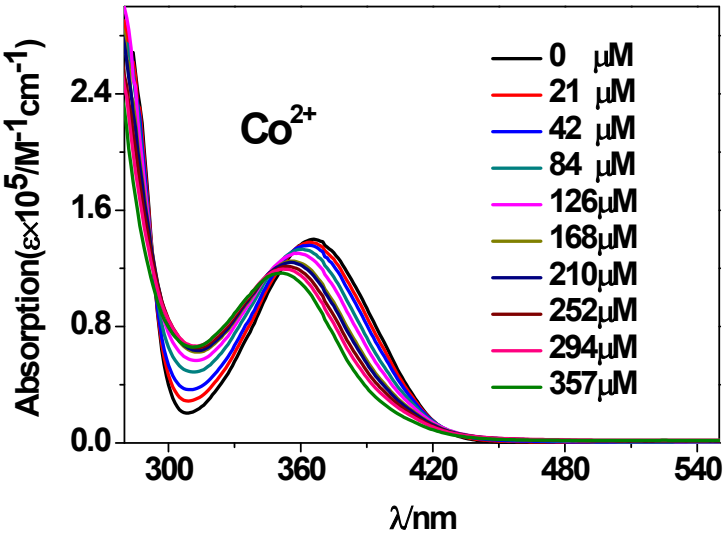


Figure S7. UV-Vis spectra of **1** (60 μM) with the addition of Co^{2+} ion.

10. X-Ray crystallography

Table S1. Selected Bond Lengths (Å) and Angles (°) for **1**.

Nd(1)-O(2)	2.485(4)	Zn(2)-O(22)	1.982(6)
Nd(1)-O(27)	2.493(4)	Zn(2)-O(29)	2.098(4)
Nd(1)-O(12)	2.498(5)	Zn(2)-O(33)	2.444(9)
Nd(1)-O(10)	2.500(4)	Zn(3)-O(34)	1.934(5)
Nd(1)-O(8)	2.540(4)	Zn(3)-O(13)	1.951(5)
Nd(1)-O(31)	2.547(5)	Zn(3)-O(15)	1.964(5)
Nd(1)-O(26)	2.608(4)	Zn(3)-O(30)	2.005(4)
Nd(1)-O(9)	2.624(4)	O(2)-Nd(1)-O(27)	63.52(13)
Nd(1)-O(7)	2.627(4)	O(2)-Nd(1)-O(12)	138.09(14)
Nd(1)-O(1)	2.653(4)	O(27)-Nd(1)-O(12)	140.83(14)
Nd(1)-N(3)	2.916(6)	O(2)-Nd(1)-O(10)	76.71(15)
Nd(2)-O(21)#1	2.395(4)	O(27)-Nd(1)-O(10)	77.43(14)
Nd(2)-O(14)	2.408(5)	O(12)-Nd(1)-O(10)	78.62(15)
Nd(2)-O(9)	2.414(4)	O(2)-Nd(1)-O(8)	92.09(14)
Nd(2)-O(16)	2.442(5)	O(27)-Nd(1)-O(8)	142.16(15)
Nd(2)-O(20)	2.493(4)	O(12)-Nd(1)-O(8)	76.69(16)
Nd(2)-O(11)	2.507(4)	O(10)-Nd(1)-O(8)	127.14(15)
Nd(2)-O(19)#1	2.608(4)	O(2)-Nd(1)-O(31)	72.08(14)
Nd(2)-O(30)	2.664(4)	O(27)-Nd(1)-O(31)	72.40(13)
Nd(2)-O(26)	2.666(4)	O(12)-Nd(1)-O(31)	137.61(14)
Nd(3)-O(18)	2.408(4)	O(10)-Nd(1)-O(31)	143.70(15)
Nd(3)-O(7)	2.440(4)	O(8)-Nd(1)-O(31)	72.66(15)
Nd(3)-O(21)#1	2.451(4)	O(2)-Nd(1)-O(26)	111.29(13)
Nd(3)-O(19)	2.486(4)	O(27)-Nd(1)-O(26)	51.33(12)
Nd(3)-O(21)	2.496(4)	O(12)-Nd(1)-O(26)	107.68(13)
Nd(3)-O(28)	2.502(4)	O(10)-Nd(1)-O(26)	105.58(13)
Nd(3)-O(11)	2.543(4)	O(8)-Nd(1)-O(26)	126.24(13)
Nd(3)-O(26)#1	2.545(4)	O(31)-Nd(1)-O(26)	70.19(14)
Nd(3)-O(23)	2.585(4)	O(2)-Nd(1)-O(9)	115.47(13)
Nd(3)-N(3)#1	2.970(6)	O(27)-Nd(1)-O(9)	70.80(13)
Nd(4)-O(17)	2.413(5)	O(12)-Nd(1)-O(9)	70.04(14)
Nd(4)-O(32)	2.429(4)	O(10)-Nd(1)-O(9)	50.05(13)
Nd(4)-O(25)	2.432(5)	O(8)-Nd(1)-O(9)	146.46(15)
Nd(4)-O(5)	2.472(4)	O(31)-Nd(1)-O(9)	132.04(14)
Nd(4)-O(35)	2.489(5)	O(26)-Nd(1)-O(9)	63.01(13)
Nd(4)-O(28)	2.502(4)	O(2)-Nd(1)-O(7)	130.70(13)
Nd(4)-O(23)	2.529(4)	O(27)-Nd(1)-O(7)	124.73(12)
Nd(4)-O(29)	2.561(4)	O(12)-Nd(1)-O(7)	70.73(14)
Nd(4)-O(6)	2.615(4)	O(10)-Nd(1)-O(7)	148.95(15)
Nd(4)-N(4)	2.959(6)	O(8)-Nd(1)-O(7)	50.21(13)
Zn(1)-O(5)	2.064(4)	O(31)-Nd(1)-O(7)	67.24(13)
Zn(1)-O(2)#1	2.075(4)	O(26)-Nd(1)-O(7)	79.83(11)
Zn(1)-N(2)	2.082(5)	O(9)-Nd(1)-O(7)	112.21(12)
Zn(1)-N(1)#1	2.099(5)	O(2)-Nd(1)-O(1)	59.97(14)
Zn(1)-O(27)#1	2.130(4)	O(27)-Nd(1)-O(1)	118.02(13)
Zn(1)-O(32)	2.286(4)	O(12)-Nd(1)-O(1)	79.36(14)
Zn(2)-O(34)	1.906(5)	O(10)-Nd(1)-O(1)	67.09(14)
Zn(2)-O(24)	1.937(5)	O(8)-Nd(1)-O(1)	62.86(13)

O(31)-Nd(1)-O(1)	110.52(15)	O(7)-Nd(3)-O(21)#1	110.65(13)
O(26)-Nd(1)-O(1)	169.12(12)	O(18)-Nd(3)-O(19)	82.23(15)
O(9)-Nd(1)-O(1)	113.44(13)	O(7)-Nd(3)-O(19)	80.80(13)
O(7)-Nd(1)-O(1)	110.67(13)	O(21)#1-Nd(3)-O(19)	133.89(13)
O(2)-Nd(1)-N(3)	84.98(14)	O(18)-Nd(3)-O(21)	139.97(14)
O(27)-Nd(1)-N(3)	25.85(14)	O(7)-Nd(3)-O(21)	70.41(13)
O(12)-Nd(1)-N(3)	131.13(15)	O(21)#1-Nd(3)-O(21)	72.20(14)
O(10)-Nd(1)-N(3)	96.10(15)	O(19)-Nd(3)-O(21)	70.38(13)
O(8)-Nd(1)-N(3)	134.76(15)	O(18)-Nd(3)-O(28)	75.43(15)
O(31)-Nd(1)-N(3)	63.49(15)	O(7)-Nd(3)-O(28)	132.29(14)
O(26)-Nd(1)-N(3)	26.65(14)	O(21)#1-Nd(3)-O(28)	73.66(13)
O(9)-Nd(1)-N(3)	69.96(14)	O(19)-Nd(3)-O(28)	131.88(13)
O(7)-Nd(1)-N(3)	100.23(14)	O(21)-Nd(3)-O(28)	144.50(13)
O(1)-Nd(1)-N(3)	143.26(15)	O(18)-Nd(3)-O(11)	82.05(14)
O(21)#1-Nd(2)-O(14)	148.86(15)	O(7)-Nd(3)-O(11)	66.74(13)
O(21)#1-Nd(2)-O(9)	122.73(13)	O(21)#1-Nd(3)-O(11)	69.64(12)
O(14)-Nd(2)-O(9)	75.45(16)	O(19)-Nd(3)-O(11)	146.35(13)
O(21)#1-Nd(2)-O(16)	92.88(16)	O(21)-Nd(3)-O(11)	104.89(13)
O(14)-Nd(2)-O(16)	76.61(18)	O(28)-Nd(3)-O(11)	71.47(13)
O(9)-Nd(2)-O(16)	143.66(16)	O(18)-Nd(3)-O(26)#1	129.38(14)
O(21)#1-Nd(2)-O(20)	119.97(13)	O(7)-Nd(3)-O(26)#1	132.93(13)
O(14)-Nd(2)-O(20)	86.93(16)	O(21)#1-Nd(3)-O(26)#1	72.74(12)
O(9)-Nd(2)-O(20)	77.55(14)	O(19)-Nd(3)-O(26)#1	68.17(13)
O(16)-Nd(2)-O(20)	78.22(16)	O(21)-Nd(3)-O(26)#1	66.32(12)
O(21)#1-Nd(2)-O(11)	71.12(12)	O(28)-Nd(3)-O(26)#1	94.45(13)
O(14)-Nd(2)-O(11)	99.00(16)	O(11)-Nd(3)-O(26)#1	142.18(12)
O(9)-Nd(2)-O(11)	66.18(13)	O(18)-Nd(3)-O(23)	80.85(14)
O(16)-Nd(2)-O(11)	141.61(15)	O(7)-Nd(3)-O(23)	145.75(13)
O(20)-Nd(2)-O(11)	140.11(14)	O(21)#1-Nd(3)-O(23)	102.77(12)
O(21)#1-Nd(2)-O(19)#1	69.88(12)	O(19)-Nd(3)-O(23)	70.54(13)
O(14)-Nd(2)-O(19)#1	130.90(15)	O(21)-Nd(3)-O(23)	114.73(12)
O(9)-Nd(2)-O(19)#1	111.32(14)	O(28)-Nd(3)-O(23)	64.23(13)
O(16)-Nd(2)-O(19)#1	71.72(16)	O(11)-Nd(3)-O(23)	135.20(13)
O(20)-Nd(2)-O(19)#1	50.79(13)	O(26)#1-Nd(3)-O(23)	51.36(12)
O(11)-Nd(2)-O(19)#1	128.92(13)	O(18)-Nd(3)-N(3)#1	105.36(16)
O(21)#1-Nd(2)-O(30)	76.51(12)	O(7)-Nd(3)-N(3)#1	147.90(14)
O(14)-Nd(2)-O(30)	72.36(15)	O(21)#1-Nd(3)-N(3)#1	86.89(13)
O(9)-Nd(2)-O(30)	122.23(14)	O(19)-Nd(3)-N(3)#1	68.09(14)
O(16)-Nd(2)-O(30)	69.21(15)	O(21)-Nd(3)-N(3)#1	91.17(14)
O(20)-Nd(2)-O(30)	144.47(14)	O(28)-Nd(3)-N(3)#1	77.52(14)
O(11)-Nd(2)-O(30)	73.12(13)	O(11)-Nd(3)-N(3)#1	145.16(14)
O(19)#1-Nd(2)-O(30)	126.10(13)	O(26)#1-Nd(3)-N(3)#1	25.99(14)
O(21)#1-Nd(2)-O(26)	65.77(12)	O(23)-Nd(3)-N(3)#1	25.41(14)
O(14)-Nd(2)-O(26)	140.04(14)	O(17)-Nd(4)-O(32)	145.46(17)
O(9)-Nd(2)-O(26)	64.89(13)	O(17)-Nd(4)-O(25)	132.37(17)
O(16)-Nd(2)-O(26)	135.68(15)	O(32)-Nd(4)-O(25)	81.19(16)
O(20)-Nd(2)-O(26)	80.22(13)	O(17)-Nd(4)-O(5)	103.74(16)
O(11)-Nd(2)-O(26)	70.00(13)	O(32)-Nd(4)-O(5)	67.31(13)
O(19)#1-Nd(2)-O(26)	64.62(12)	O(25)-Nd(4)-O(5)	83.56(15)
O(30)-Nd(2)-O(26)	133.67(11)	O(17)-Nd(4)-O(35)	71.54(19)
O(18)-Nd(3)-O(7)	76.97(15)	O(32)-Nd(4)-O(35)	138.26(16)
O(18)-Nd(3)-O(21)#1	143.24(14)	O(25)-Nd(4)-O(35)	72.04(18)

O(5)-Nd(4)-O(35)	137.29(16)	O(23)-Nd(4)-O(29)	109.56(13)
O(17)-Nd(4)-O(28)	80.81(15)	O(17)-Nd(4)-O(6)	67.46(16)
O(32)-Nd(4)-O(28)	83.74(14)	O(32)-Nd(4)-O(6)	125.44(14)
O(25)-Nd(4)-O(28)	126.43(15)	O(25)-Nd(4)-O(6)	76.23(17)
O(5)-Nd(4)-O(28)	135.10(14)	O(5)-Nd(4)-O(6)	61.33(14)
O(35)-Nd(4)-O(28)	87.04(16)	O(35)-Nd(4)-O(6)	78.80(16)
O(17)-Nd(4)-O(23)	70.17(15)	O(28)-Nd(4)-O(6)	147.92(15)
O(32)-Nd(4)-O(23)	75.31(14)	O(23)-Nd(4)-O(6)	106.27(14)
O(25)-Nd(4)-O(23)	152.59(15)	O(29)-Nd(4)-O(6)	143.31(14)
O(5)-Nd(4)-O(23)	74.55(13)	O(17)-Nd(4)-N(4)	99.70(17)
O(35)-Nd(4)-O(23)	135.36(17)	O(32)-Nd(4)-N(4)	76.68(14)
O(28)-Nd(4)-O(23)	65.05(13)	O(25)-Nd(4)-N(4)	101.74(17)
O(17)-Nd(4)-O(29)	118.30(16)	O(5)-Nd(4)-N(4)	142.40(15)
O(32)-Nd(4)-O(29)	72.31(14)	O(35)-Nd(4)-N(4)	78.13(16)
O(25)-Nd(4)-O(29)	75.67(15)	O(28)-Nd(4)-N(4)	24.71(15)
O(5)-Nd(4)-O(29)	136.81(14)	O(23)-Nd(4)-N(4)	86.51(14)
O(35)-Nd(4)-O(29)	70.42(15)	O(29)-Nd(4)-N(4)	26.07(15)
O(28)-Nd(4)-O(29)	50.78(13)	O(6)-Nd(4)-N(4)	156.25(15)