Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Construction of a 1-D Sm(III) coordination polymer with long-chain Schiff base ligand: Dual-emissive response to metal ions

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1. General Procedures

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. The Schiff-base ligands H_2L was prepared according to well established procedures.[1] 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 100^{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. 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 experiments were carried out at room temperature. DMF was used in the measurements of NMR, UV-vis absorption, excitation and emission spectra. For the emission spectra of the Sm(III) complex, the excitation wavelength (λ_{ex}) is 365 nm.

Ref. (1) Lam, F.; Xu, J.-X.; Chan, K.-S. *J. Org. Chem*., **1996**, *61*, 8414-8418.

2. ^{1}H NMR spectrum of H_2L

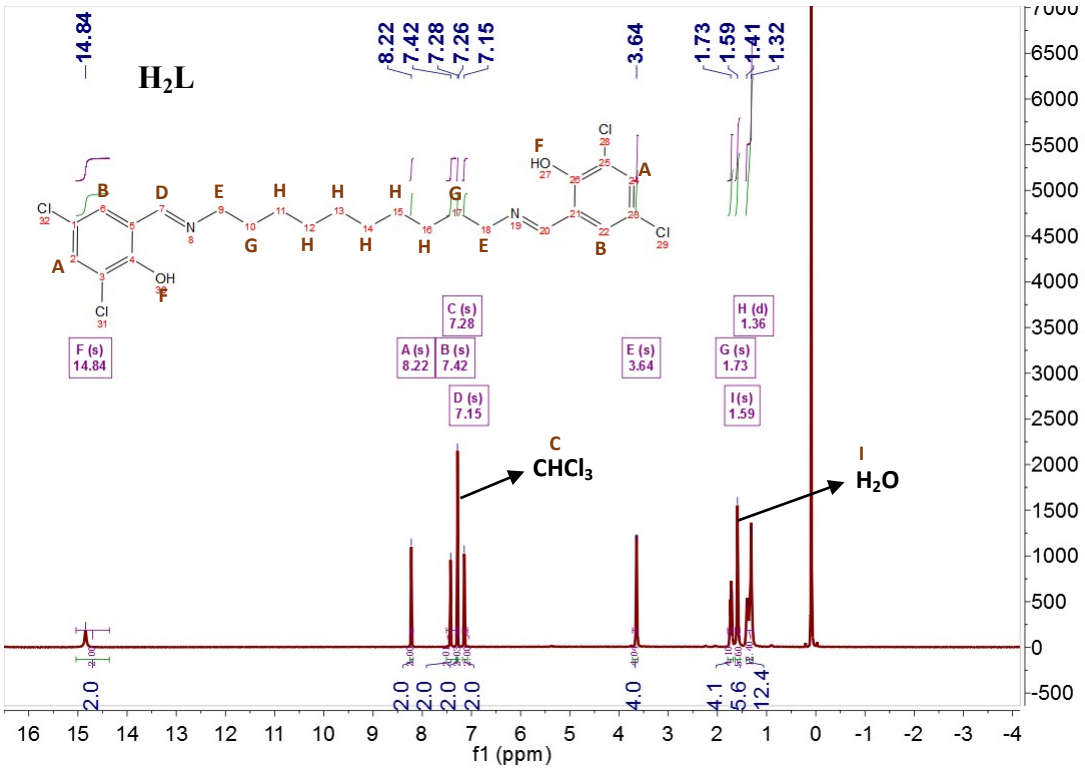


Figure S1. ^{1}H NMR spectrum of H_2L in $CDCl_3$ at room temperature (with assignment of protons from "A" to "I").

3. IR spectra of H_2L and complex 1

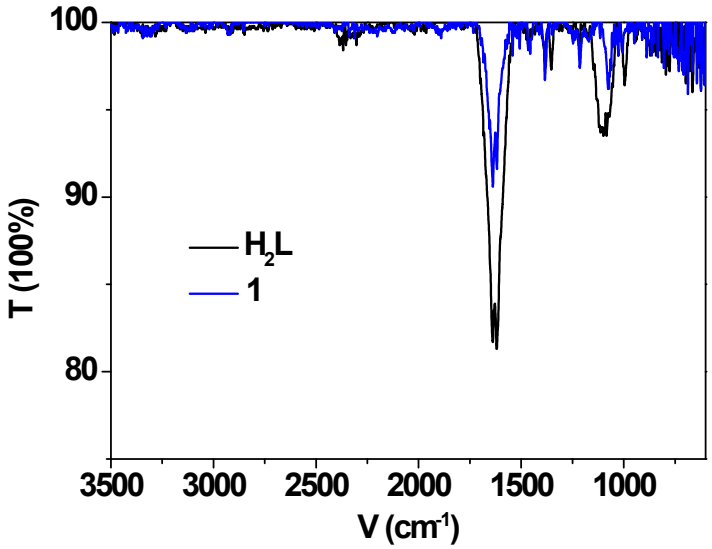


Figure S2. IR spectra of H_2L and complex **1**.

4. Powder XRD patterns of 1

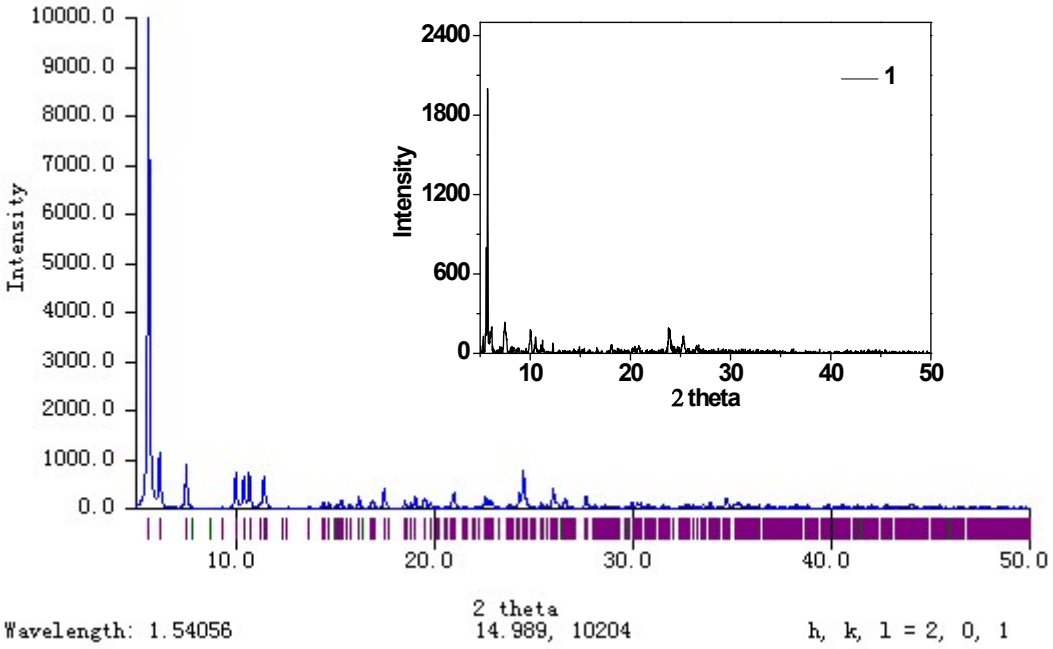


Figure S3. Powder XRD patterns of **1**.

5. The thermogravimetric analysis of 1

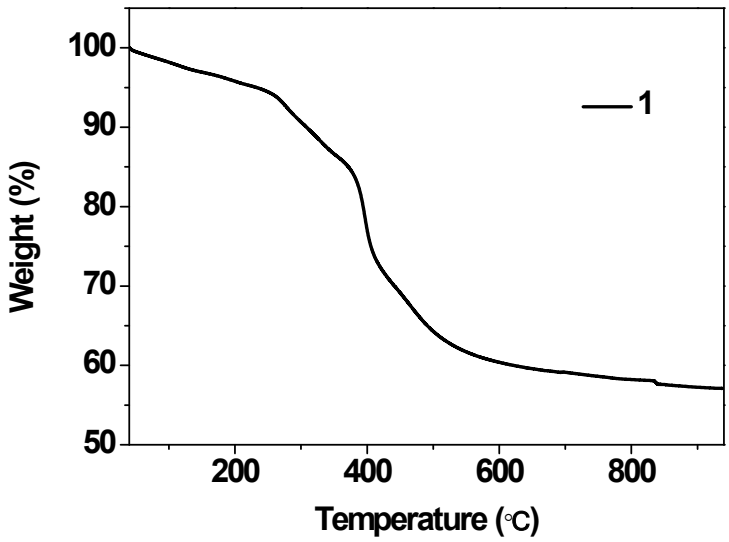


Figure S4. The thermogravimetric analysis of **1**.

6. ^{1}H NMR spectrum of 1

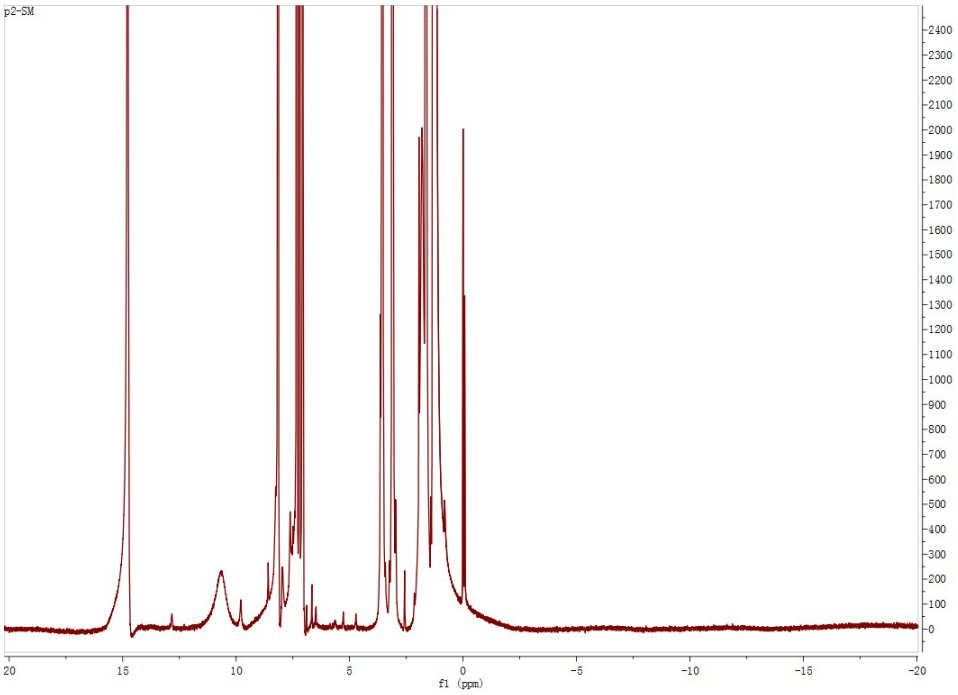


Figure S5. ^{1}H NMR spectra of **1** in *d*-DMF at room temperature.

7. The excitation and emission spectra of the free H_2L

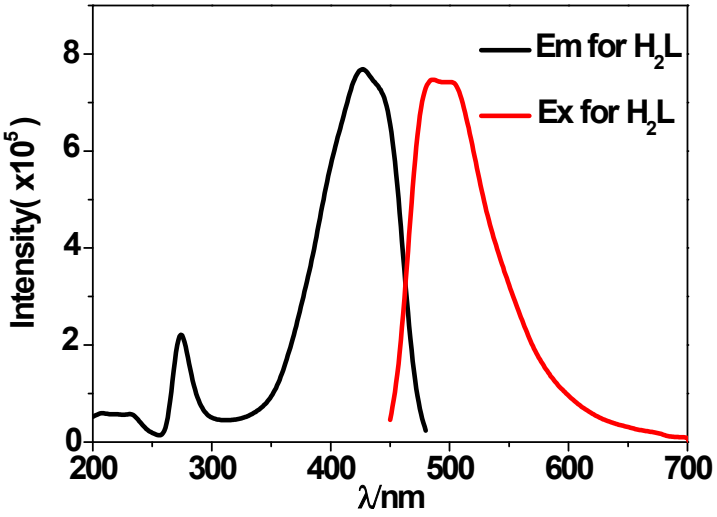


Figure S6. The excitation and emission spectra of the free H_2L in DMF at room temperature. (λ_{ex} = 420 nm, λ_{em} = 500 nm)

8. The lanthanide visible and NIR emission lifetimes of 1

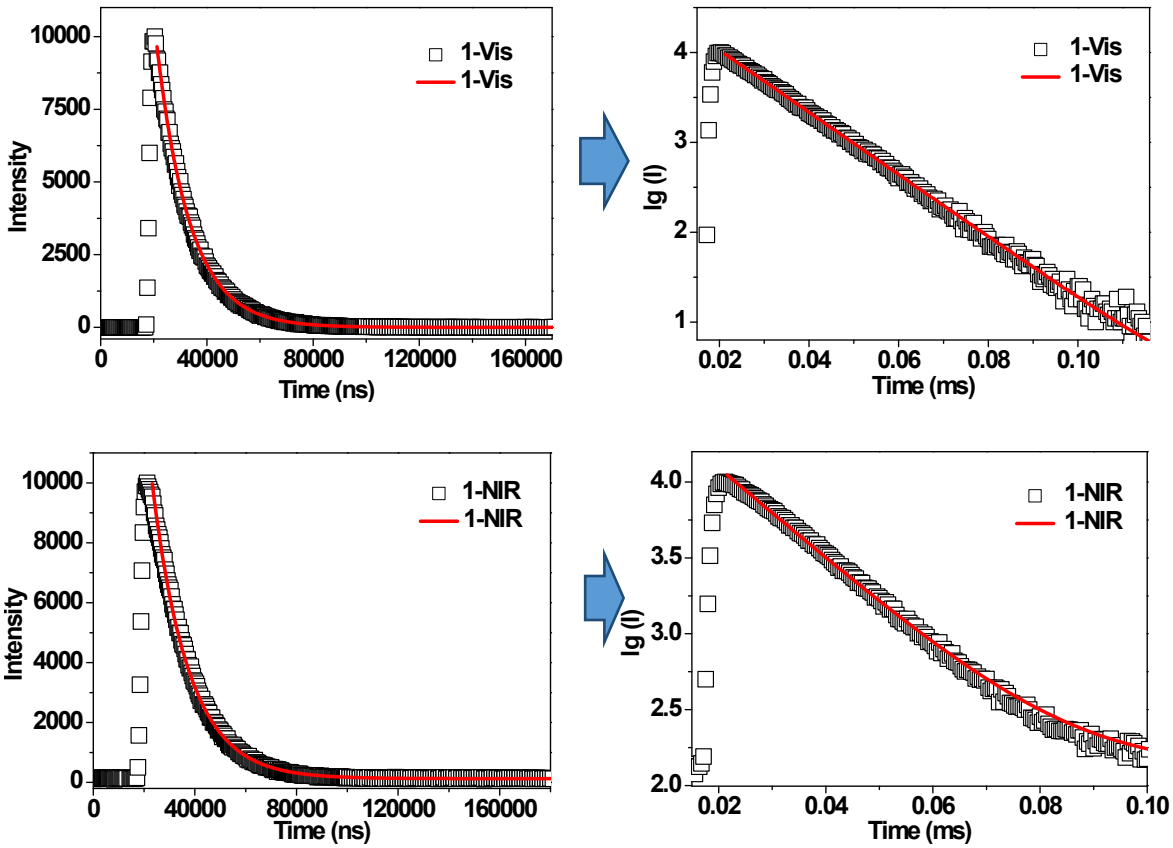
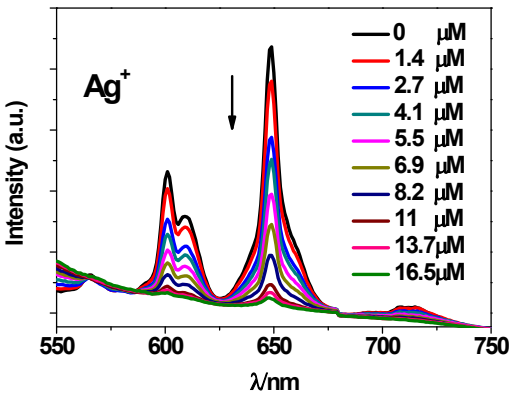
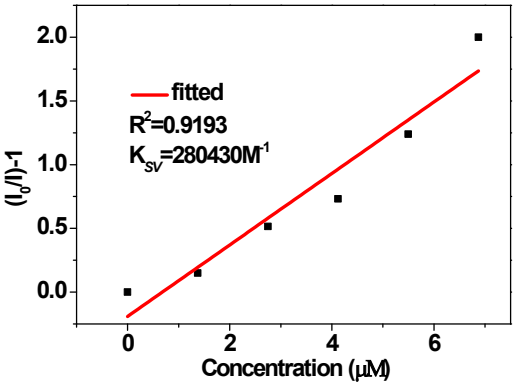
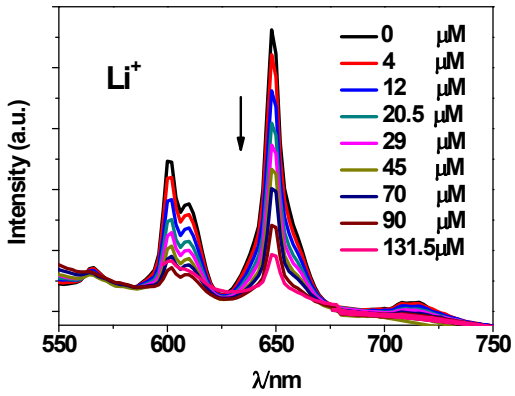


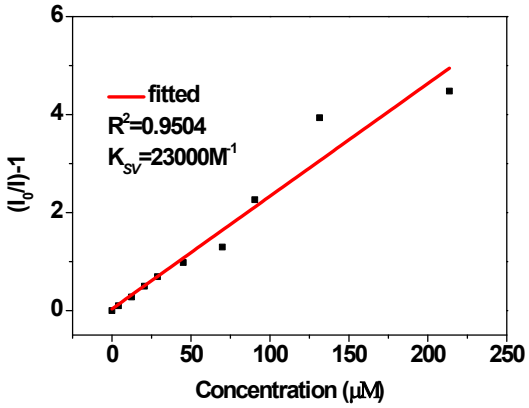
Figure S7. The lanthanide visible and NIR emission lifetimes of **1** in DMF at room temperature.

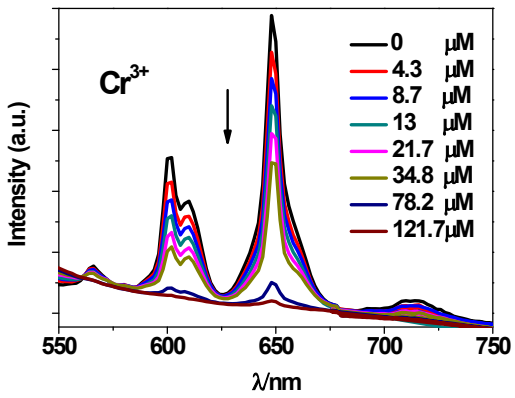
9. Visible lanthanide luminescence response of 1 to the addition of metal ions

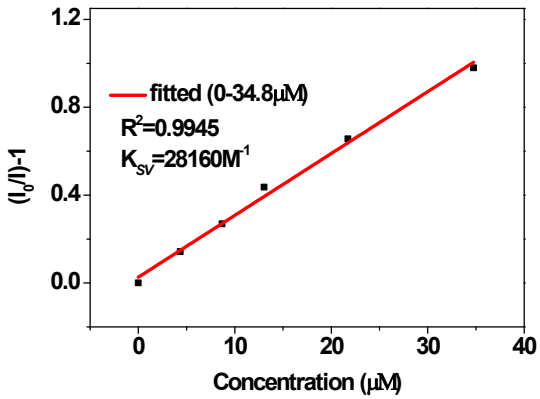


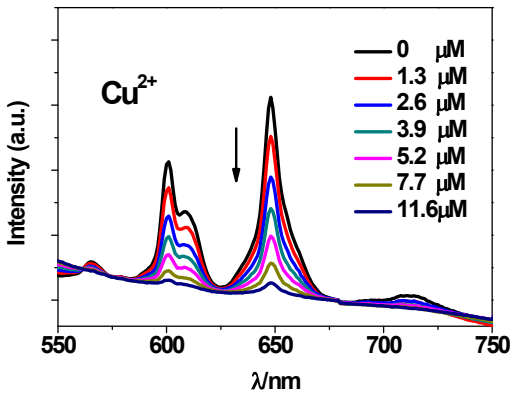


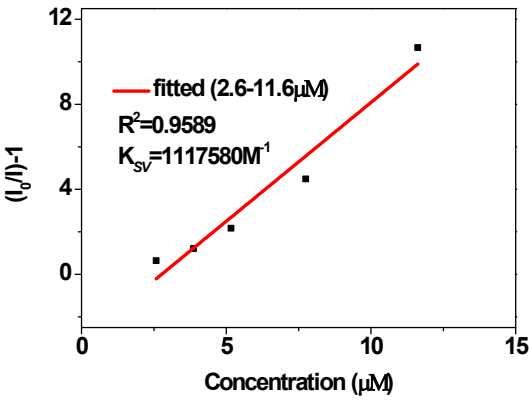


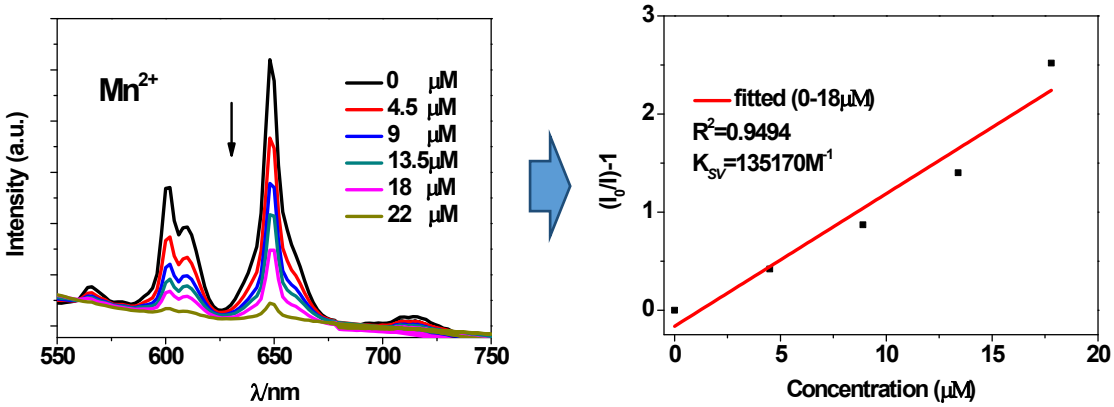


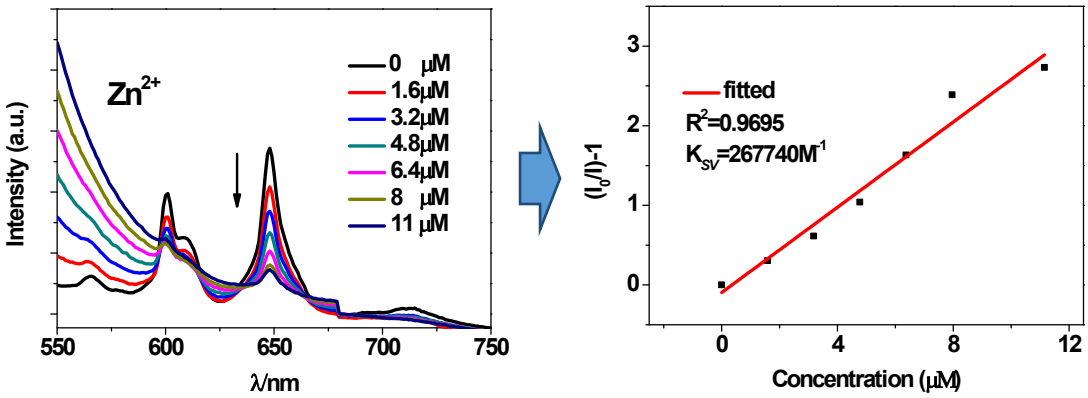









Mn2+
0 μM
4.5 μM
9 μM
13.5μM
18 μM
22 μM
Intensity (a.u.)
λ/nm
fitted (0-18μM)
R2=0.9494
KSV=135170M-1
(I0/I)-1
Concentration (μM)


Zn2+
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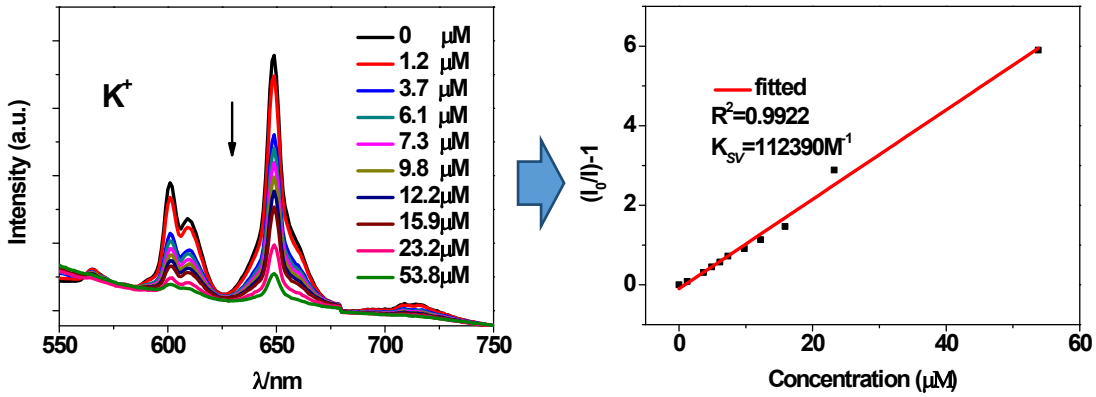
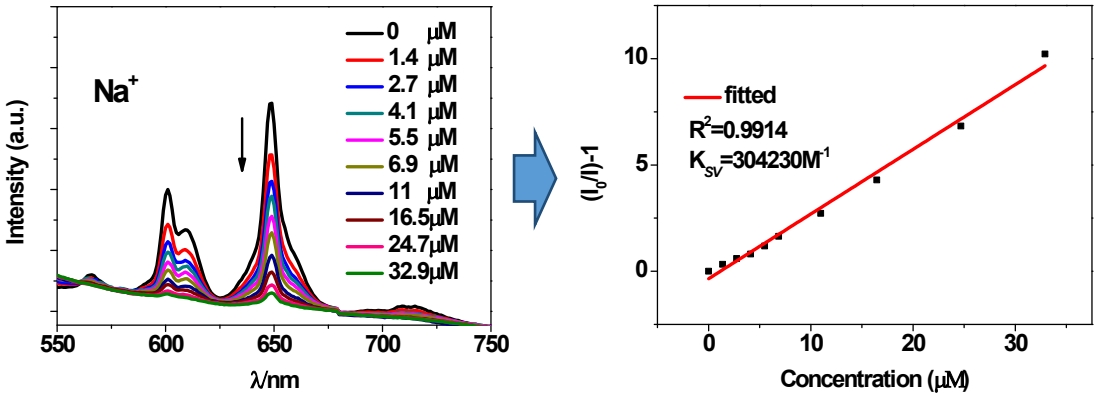
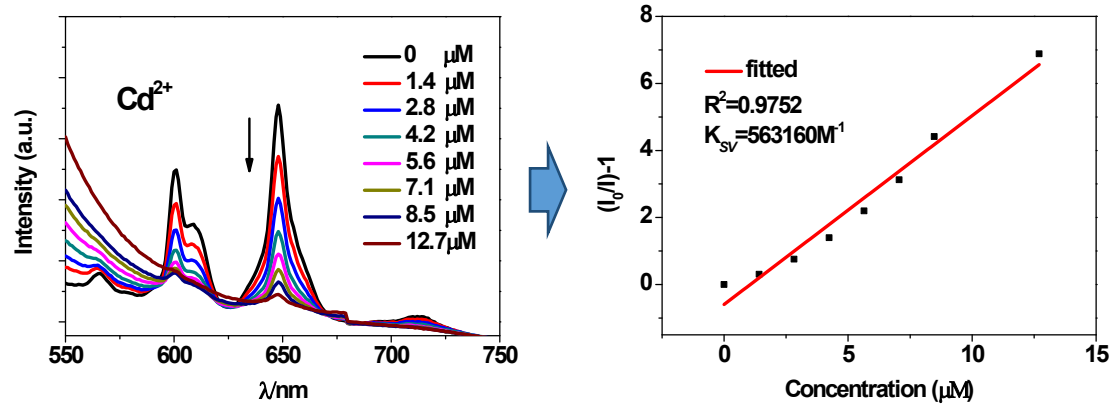
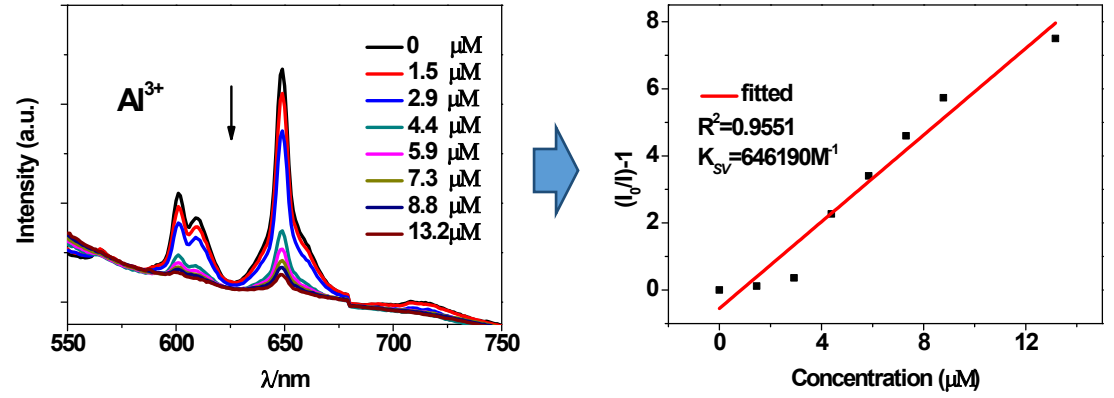
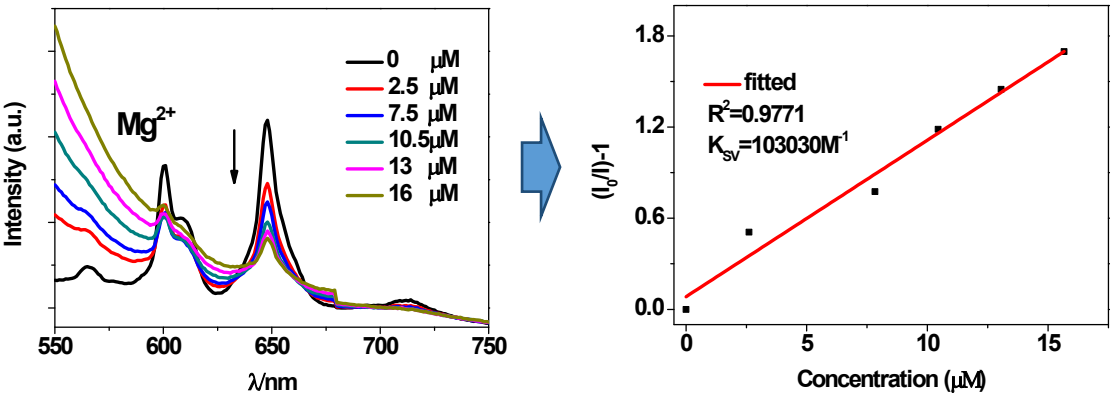
1.6μM
3.2μM
4.8μM
6.4μM
8 μM
11 μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9695
KSV=267740M-1
(I0/I)-1
Concentration (μM)

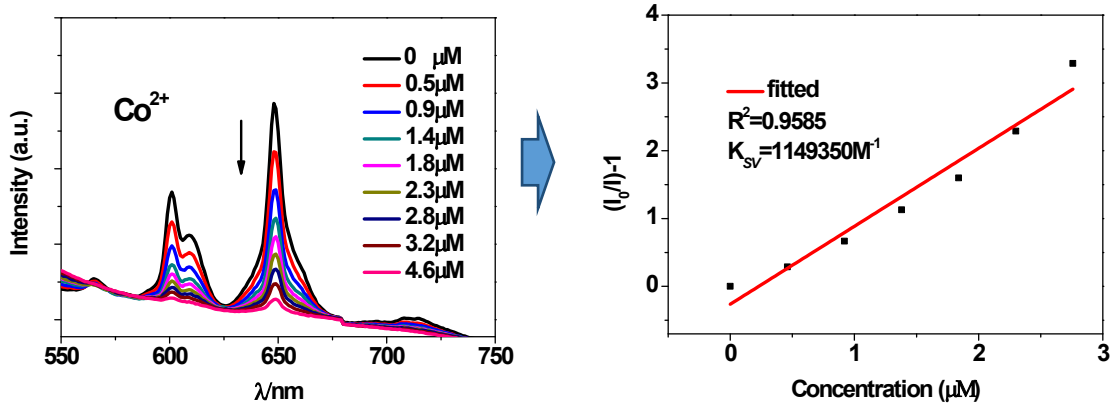

K+
0 μM
1.2 μM
3.7 μM
6.1 μM
7.3 μM
9.8 μM
12.2μM
15.9μM
23.2μM
53.8μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9922
KSV=112390M-1
(I0/I)-1
Concentration (μM)


Na+
0 μM
1.4 μM
2.7 μM
4.1 μM
5.5 μM
6.9 μM
11 μM
16.5μM
24.7μM
32.9μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9914
KSV=304230M-1
(I0/I)-1
Concentration (μM)


Cd2+
0 μM
1.4 μM
2.8 μM
4.2 μM
5.6 μM
7.1 μM
8.5 μM
12.7μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9752
KSV=563160M-1
(I0/I)-1
Concentration (μM)


Al3+
0 μM
1.5 μM
2.9 μM
4.4 μM
5.9 μM
7.3 μM
8.8 μM
13.2μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9551
KSV=646190M-1
(I0/I)-1
Concentration (μM)


Mg2+
0 μM
2.5 μM
7.5 μM
10.5μM
13 μM
16 μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9771
KSV=103030M-1
(I0/I)-1
Concentration (μM)


Co2+
0 μM
0.5μM
0.9μM
1.4μM
1.8μM
2.3μM
2.8μM
3.2μM
4.6μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9585
KSV=1149350M-1
(I0/I)-1
Concentration (μM)

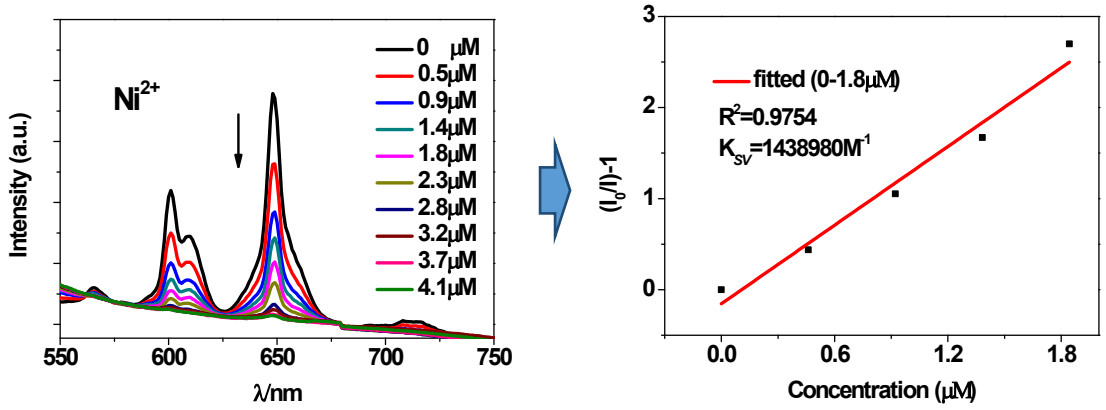
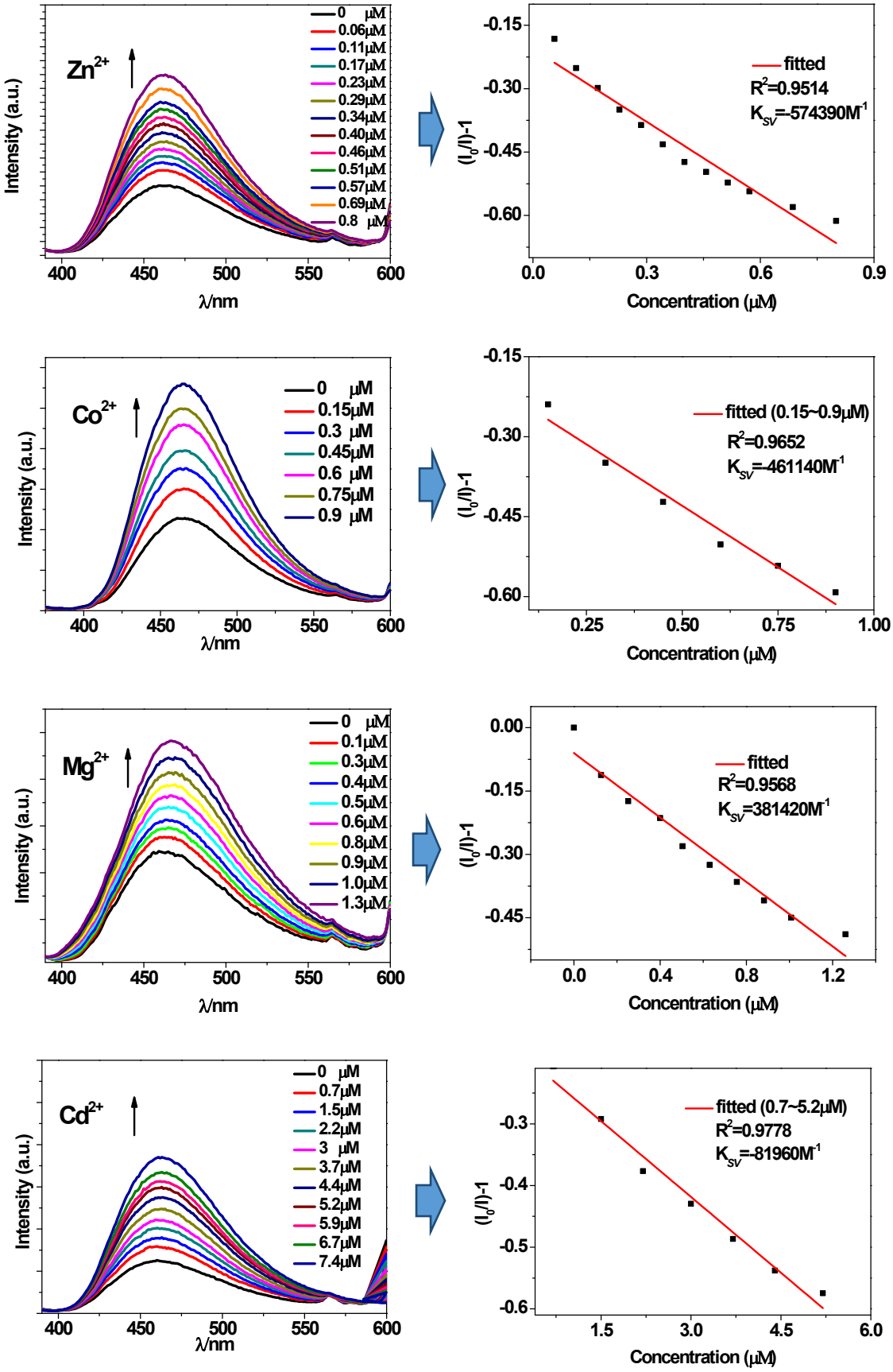
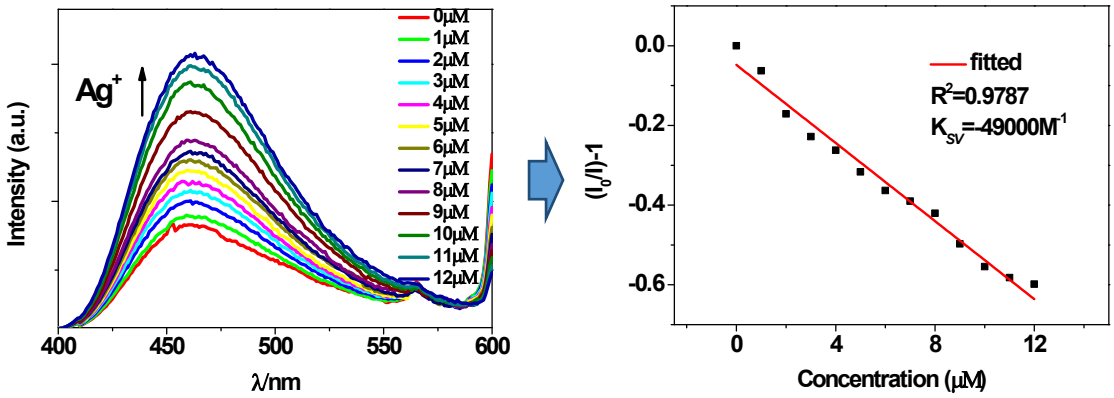
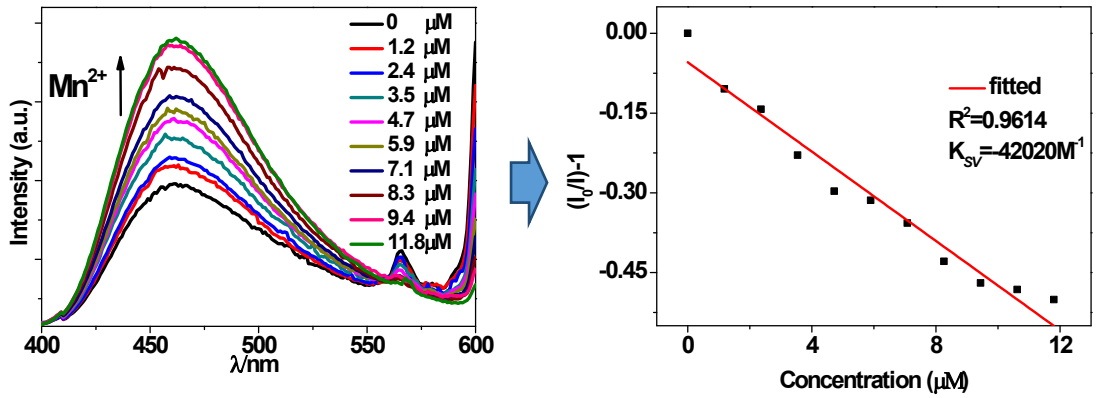


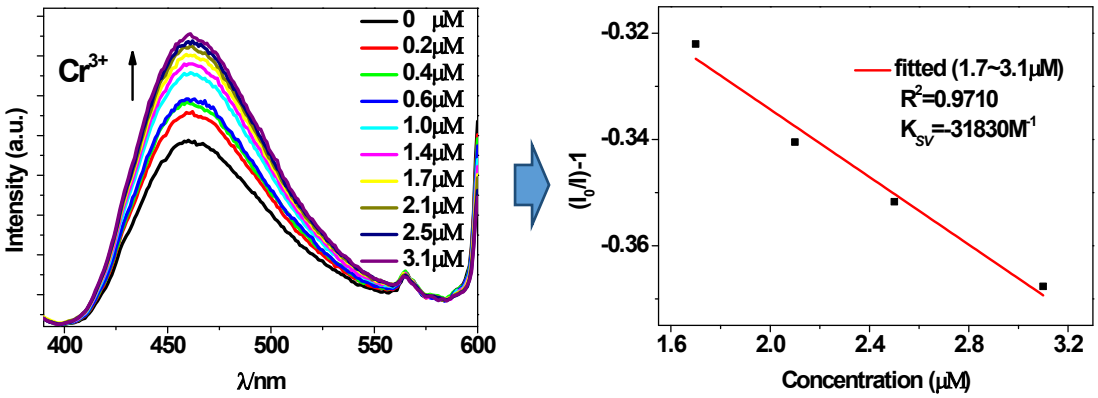
Figure S8. Visible lanthanide luminescence response of **1** (50 μM) to the addition of metal ions.

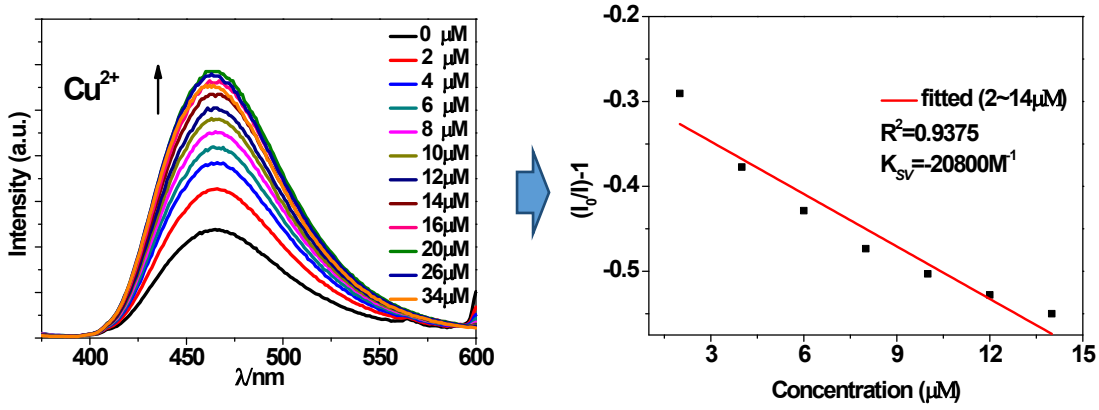
10. Ligand-centered emission response of 1 to the addition of metal ions




Ag+
0μM
1μM
2μM
3μM
4μM
5μM
6μM
7μM
8μM
9μM
10μM
11μM
12μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9787
KSV=-49000M-1
(I0/I)-1
Concentration (μM)


Mn2+
0 μM
1.2 μM
2.4 μM
3.5 μM
4.7 μM
5.9 μM
7.1 μM
8.3 μM
9.4 μM
11.8μM
Intensity (a.u.)
λ/nm
fitted
R2=0.9614
KSV=-42020M-1
(I0/I)-1
Concentration (μM)


Cr3+
0 μM
0.2μM
0.4μM
0.6μM
1.0μM
1.4μM
1.7μM
2.1μM
2.5μM
3.1μM
Intensity (a.u.)
λ/nm
fitted (1.7~3.1μM)
R2=0.9710
KSV=-31830M-1
(I0/I)-1
Concentration (μM)


Cu2+
0 μM
2 μM
4 μM
6 μM
8 μM
10μM
12μM
14μM
16μM
20μM
26μM
34μM
Intensity (a.u.)
λ/nm
fitted (2~14μM)
R2=0.9375
KSV=-20800M-1
(I0/I)-1
Concentration (μM)

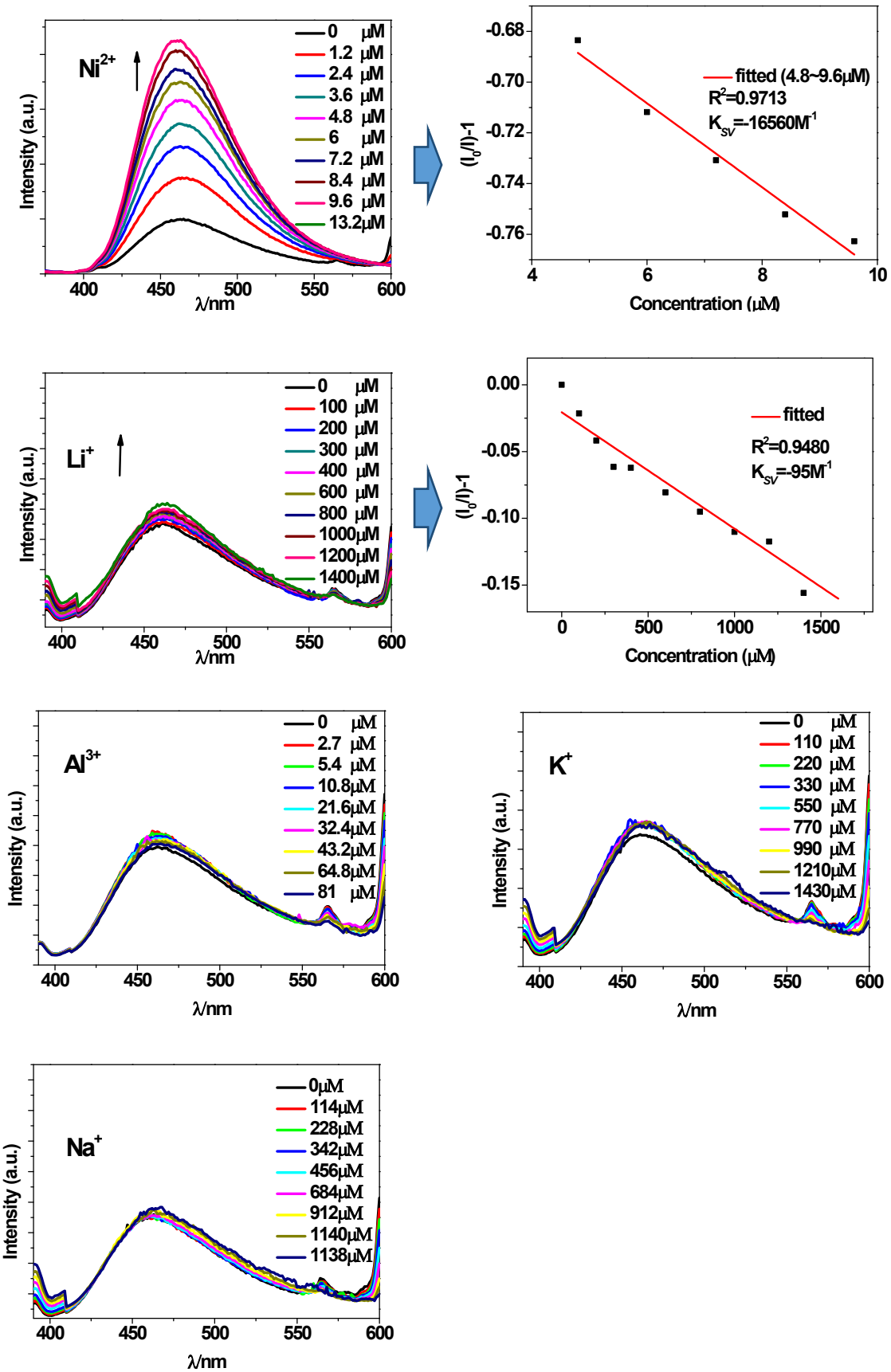


Figure S9. Ligand-centered emission response of **1** (50 μM) to the addition of metal ions.

11. X-Ray Crystallography

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

Sm(1)-O(1)	2.329(15)	O(1)-Sm(1)-O(5)	126.4(6)
Sm(1)-O(4)	2.351(14)	O(4)-Sm(1)-O(5)	82.9(5)
Sm(1)-O(2)	2.452(16)	O(2)-Sm(1)-O(5)	73.9(5)
Sm(1)-O(3)	2.471(12)	O(3)-Sm(1)-O(5)	66.7(4)
Sm(1)-N(4)	2.613(16)	N(4)-Sm(1)-O(5)	130.1(5)
Sm(1)-O(5)	2.674(16)	O(1)-Sm(1)-O(6)	80.6(6)
Sm(1)-O(6)	2.717(17)	O(4)-Sm(1)-O(6)	128.9(6)
Sm(1)-N(1)	2.778(18)	O(2)-Sm(1)-O(6)	69.7(6)
O(1)-Sm(1)-O(4)	150.5(3)	O(3)-Sm(1)-O(6)	70.0(5)
O(1)-Sm(1)-O(2)	80.6(6)	N(4)-Sm(1)-O(6)	134.9(5)
O(4)-Sm(1)-O(2)	108.2(5)	O(5)-Sm(1)-O(6)	46.5(3)
O(1)-Sm(1)-O(3)	108.1(5)	O(1)-Sm(1)-N(1)	69.0(5)
O(4)-Sm(1)-O(3)	85.2(5)	O(4)-Sm(1)-N(1)	87.2(5)
O(2)-Sm(1)-O(3)	136.5(3)	O(2)-Sm(1)-N(1)	70.2(5)
O(1)-Sm(1)-N(4)	90.9(5)	O(3)-Sm(1)-N(1)	153.2(4)
O(4)-Sm(1)-N(4)	68.1(5)	N(4)-Sm(1)-N(1)	82.4(2)
O(2)-Sm(1)-N(4)	152.6(5)	O(5)-Sm(1)-N(1)	137.5(5)
O(3)-Sm(1)-N(4)	71.0(4)	O(6)-Sm(1)-N(1)	132.7(6)