Supporting Information

Construction of 14-metal lanthanide nanorings with NIR luminescent response to 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 dinitrogen atmospheres using standard Schlenk techniques. Physical measurements: NMR: AVANCE III AV500. 500 spectrometer (^{1}H, 500 MHz) at 298 K; Powder XRD: D8ADVANCE; IR: Nicolet IS10 spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses (C, H, N) were carried out on a EURO EA3000 elemental analysis. Conductivity measurement was carried out with a DDS-11 conductivity bridge for 10^{-4} M solution in CH_3CN. Dynamic light scattering (DLS) measurement was carried out on a Malvern Zetasizer Nano ZS for 10^{-5} M solution in CH_3CN. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova NanoSEM 200 scanning electron microscope. Absorption spectra were obtained on a UV-3600 spectrophotometer, and excitation and emission spectra on a FLS 980 fluorimeter.

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 equation $\Phi_{em} = N_{em} / N_{abs}$, 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. Synthesis of 1 and 2

Synthesis of $[Nd_{14}(HL)_2L_{20}(DMF)_8(H_2O)_8]$ (1). $Nd(OAc)_3 \cdot 4H_2O$ (0.40 mmol, 0.1573 g) and H_2L (2,3-dihydroxybenzaldehyde) (0.60 mmol, 0.0829 g) were dissolved in 30 mL EtOH and 5 mL DMF at room temperature, and then 10 ml EtOH solution of triethylamine (1.0 mol/L) was added. The mixture was stirred under reflux for 30 minutes, and then filtered. Red crystals were obtained after one week by the slow diffusion of diethyl ether into the filtrate. The solid product of **1** was dried in the oven at 120 °C for five hours. Yield (based on H_2L): 0.0636 g (40 %). m. p. > 190 °C (dec.). Elemental analysis: Found: C, 37.28; H, 2.77; N, 1.89 %. Calc. for $C_{178}H_{162}N_8Nd_{14}O_{82}$: C, 37.22; H, 2.84; N, 1.95 %. IR (KBr, cm^{-1}): 1632 (s), 1581 (m), 1534 (m), 1459 (m), 1406 (m), 1336 (w), 1306 (w), 1265 (s), 1202 (vs), 1157 (w), 1083 (m), 1059 (m), 861 (s), 781 (m), 728 (s), 659 (m), 614 (s).

Synthesis of $[Gd_{14}(HL)_2L_{20}(DMF)_8(H_2O)_8]$ (2). The procedure was the same as that for **1** using $Gd(OAc)_3 \cdot 4H_2O$ (0.40 mmol, 0.1625 g) and H_2L (0.60 mmol, 0.0829 g). Yield (based on H_2L) 0.0593 g (36 %). m. p. > 188 °C (dec.). Elemental analysis: Found: C, 36.28; H, 2.79; N, 1.93 %. Calc. for $C_{178}H_{162}N_8Gd_{14}O_{82}$: C, 36.07; H, 2.76; N, 1.89 %. IR (KBr, cm^{-1}): 1635 (s), 1555 (m), 1535 (w), 1463 (m), 1439 (m), 1412 (w), 1273 (s), 1195 (s), 1081 (s), 1015 (w), 860 (s), 739 (vs), 674 (s), 629 (s), 617 (s).

3. IR spectra of free ligand H_2L and clusters 1 and 2.

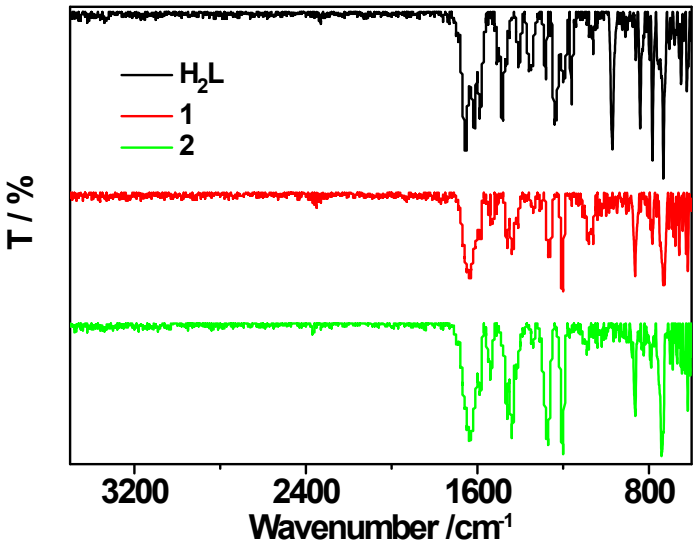
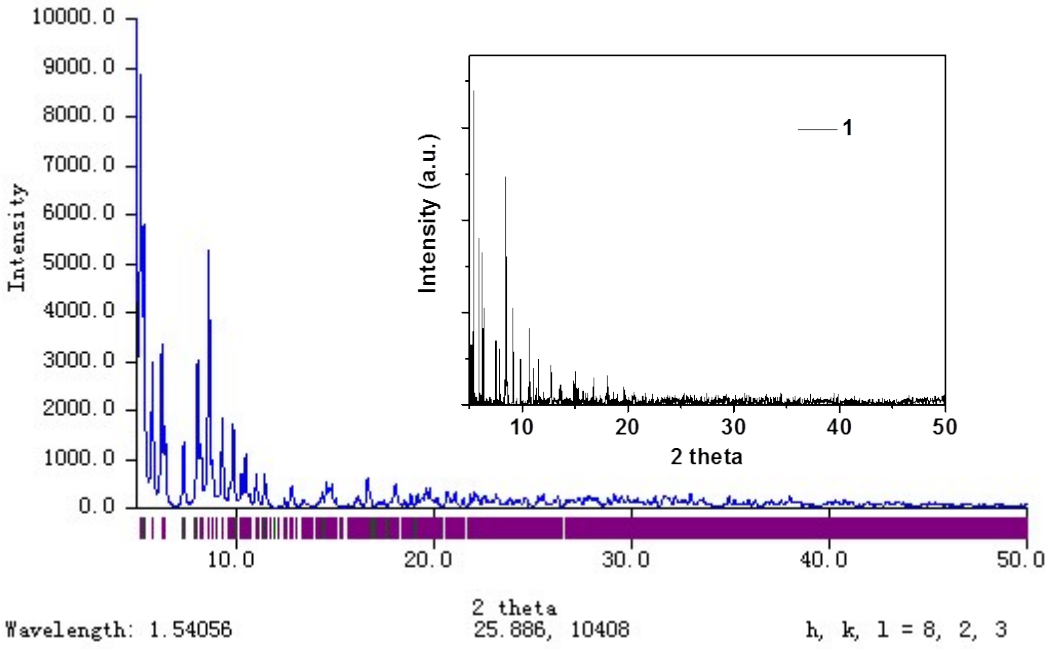


Figure S1. IR spectra of free ligand H_2L and clusters **1** and **2**.

4. Powder XRD patterns of 1 and 2



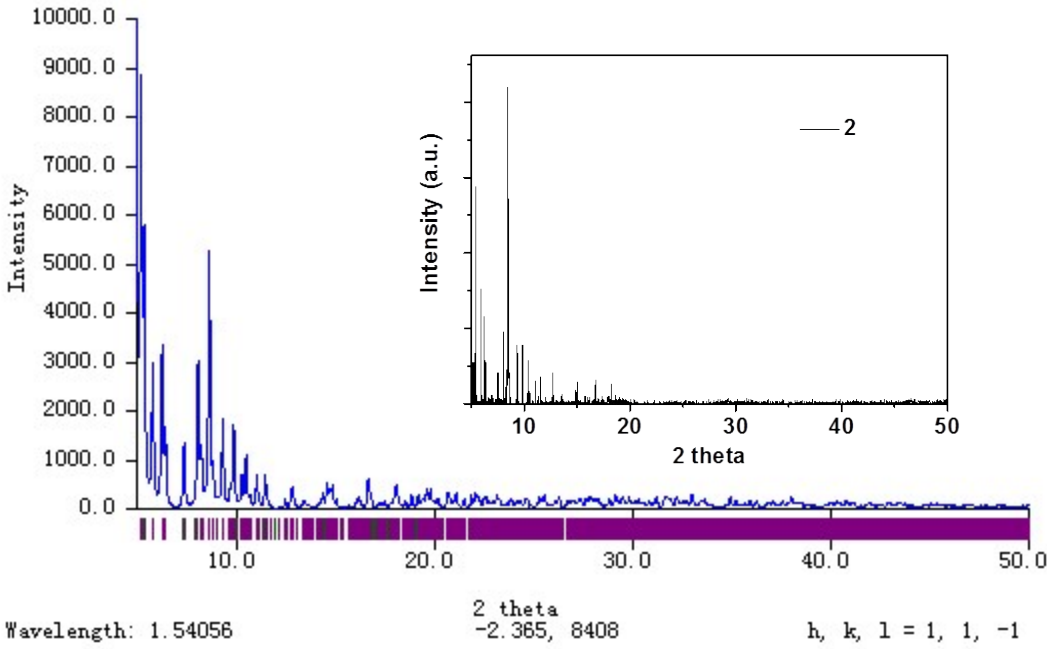


Figure S2. Powder XRD patterns of **1** and **2**.

5. UV-vis spectra of the free ligand H_2L and clusters 1 and 2

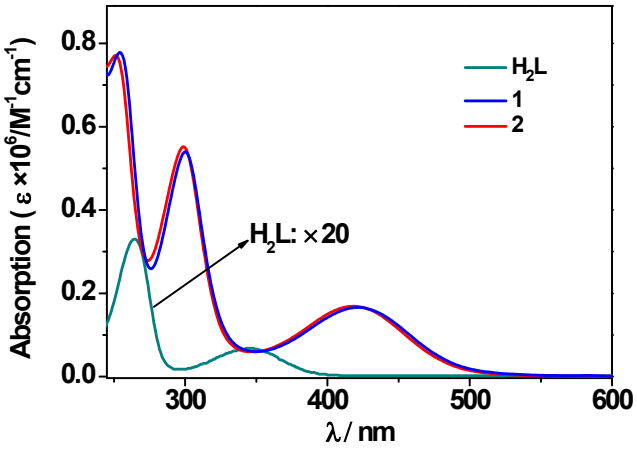


Figure S3. UV-vis absorption spectra of the free ligand H_2L and clusters **1** and **2** in CH_3CN. (C = 5×10^{-6} M)

6. Excitation and visible emission spectra of 1 and 2

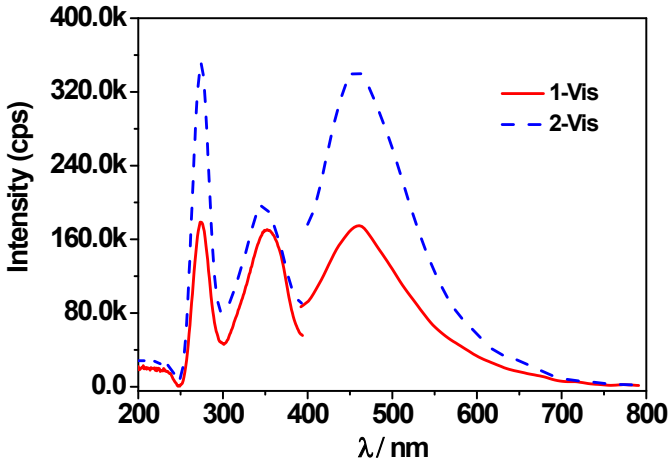


Figure S4. Excitation and visible emission spectra of **1** and **2** in CH_3CN ($C = 1 \times 10^{-5}$ M). (Emission spectra: λ_{ex} = 273 nm for **1** and 274 nm for **2**; Excitation spectra: λ_{em} = 461 nm for **1** and 457 nm for **2**)

7. The emission lifetime of 1

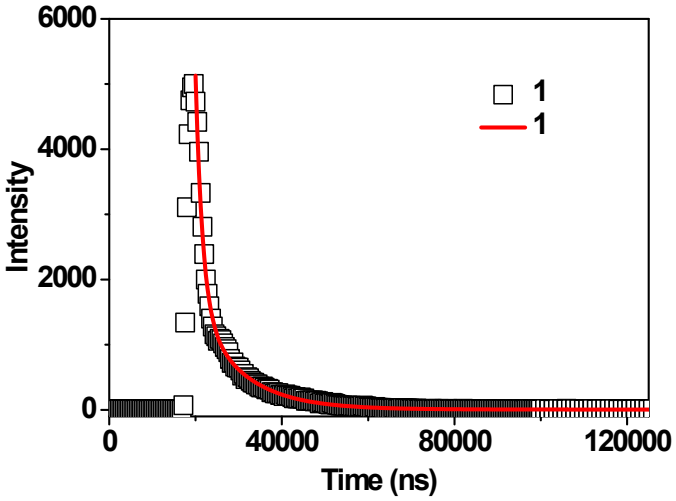


Figure S5. The NIR emission lifetime of **1** in CH_3CN.

8. The emission spectrum of 2 at 77 K

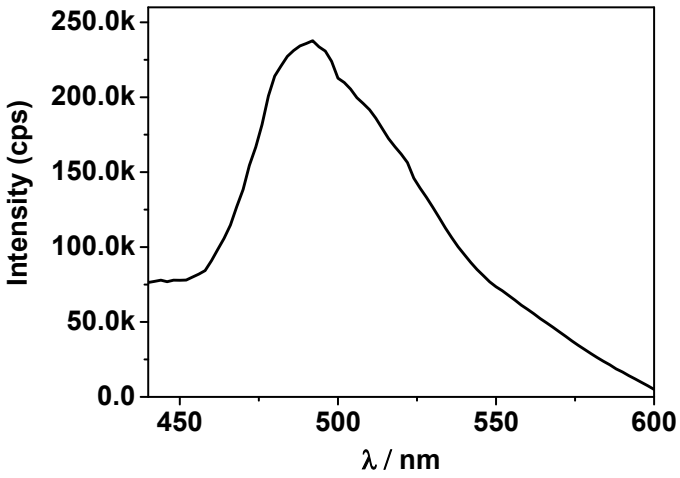
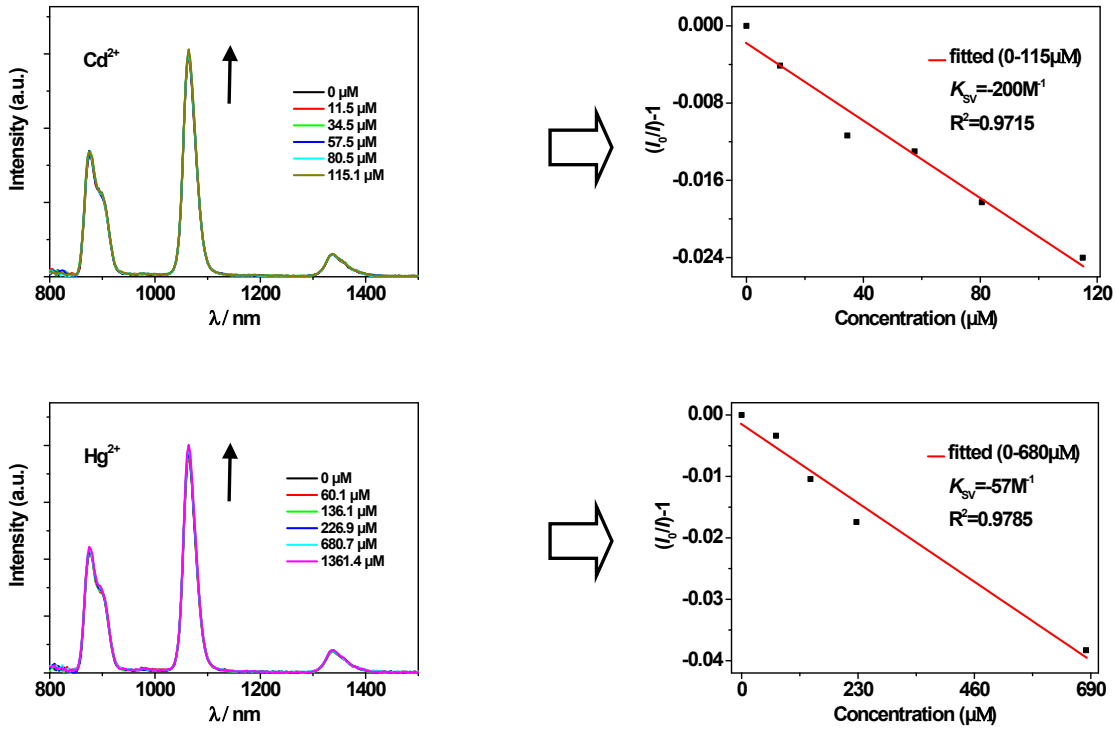
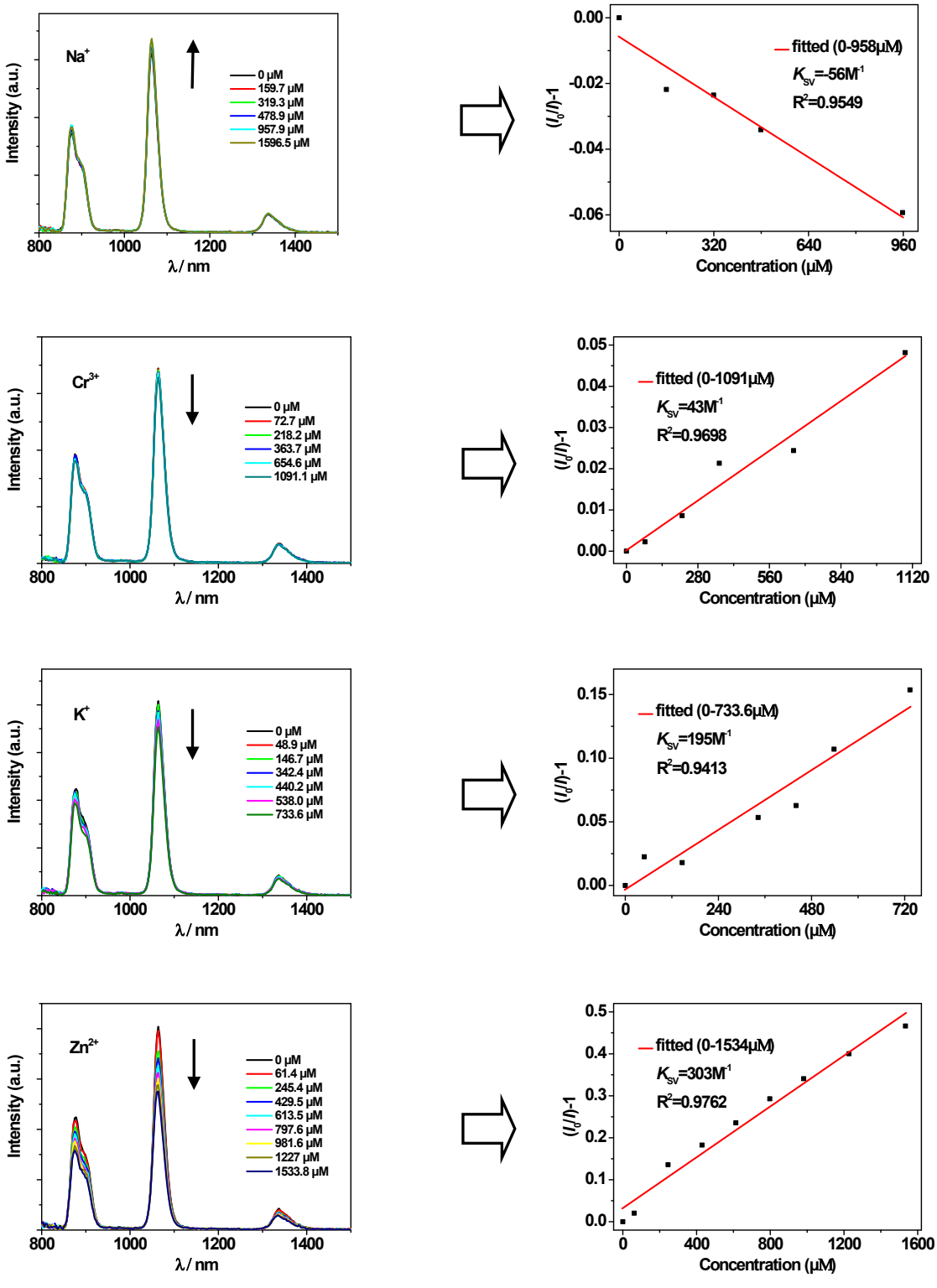
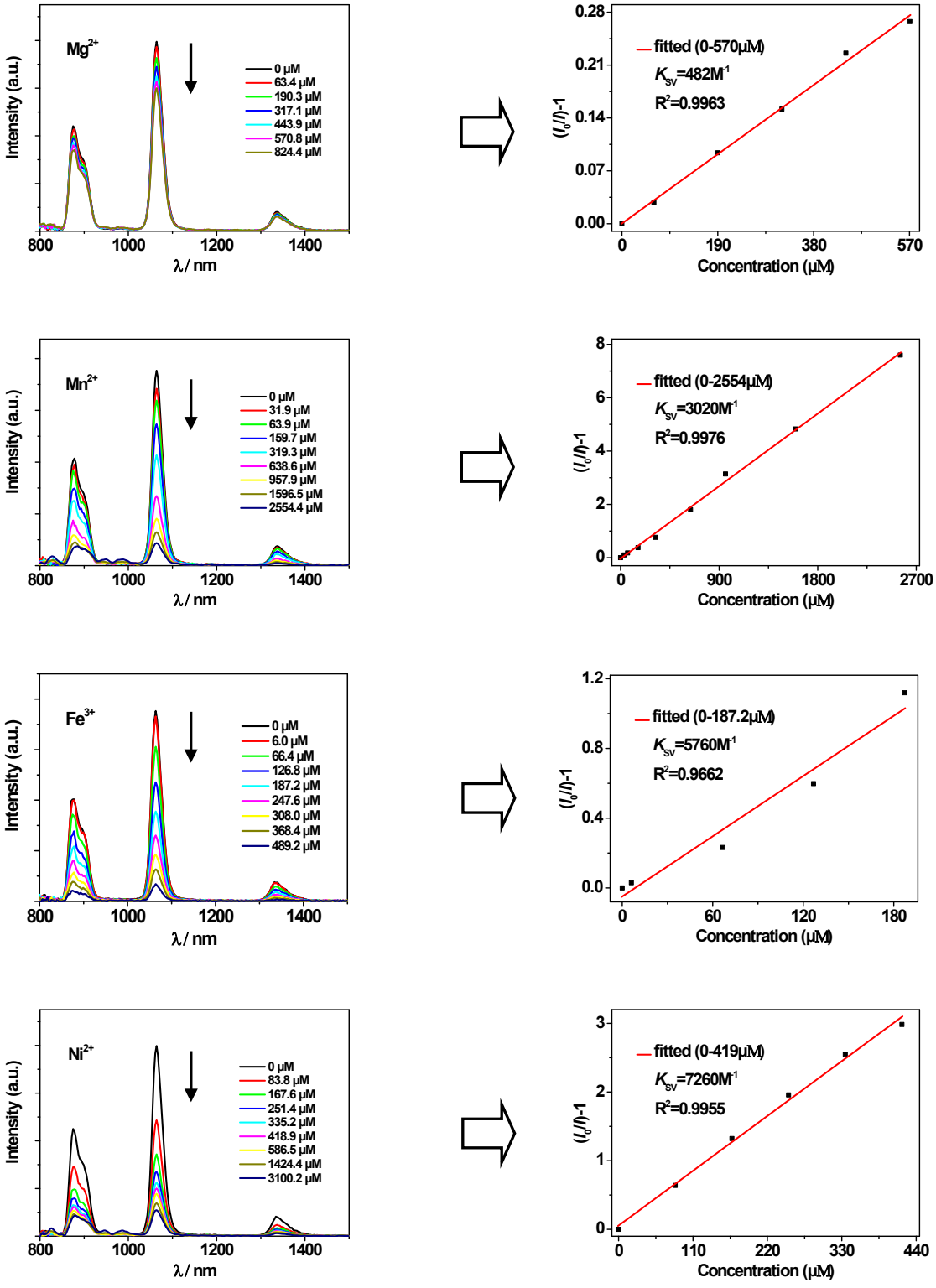


Figure S6. The emission spectrum of **2** (10 μM) in CH_3CN at 77 K. (λ_{ex} = 392 nm)

9. NIR luminescent sensing of 1 to metal cations




Na+
0 μM
159.7 μM
319.3 μM
478.9 μM
957.9 μM
1596.5 μM
Intensity (a.u.)
λ/ nm
fitted (0-958μM)
K_{SV}=-56M^{-1}
R^2=0.9549
(I_0/I)-1
Concentration (μM)
Cr3+
0 μM
72.7 μM
218.2 μM
363.7 μM
654.6 μM
1091.1 μM
fitted (0-1091μM)
K_{SV}=43M^{-1}
R^2=0.9698
K+
0 μM
48.9 μM
146.7 μM
342.4 μM
440.2 μM
538.0 μM
733.6 μM
fitted (0-733.6μM)
K_{SV}=195M^{-1}
R^2=0.9413
Zn2+
0 μM
61.4 μM
245.4 μM
429.5 μM
613.5 μM
797.6 μM
981.6 μM
1227 μM
1533.8 μM
fitted (0-1534μM)
K_{SV}=303M^{-1}
R^2=0.9762


Mg2+
0 μM
63.4 μM
190.3 μM
317.1 μM
443.9 μM
570.8 μM
824.4 μM
Intensity (a.u.)
λ/ nm
fitted (0-570μM)
KSV=482M-1
R2=0.9963
(I0/I)-1
Concentration (μM)
Mn2+
0 μM
31.9 μM
63.9 μM
159.7 μM
319.3 μM
638.6 μM
957.9 μM
1596.5 μM
2554.4 μM
fitted (0-2554μM)
KSV=3020M-1
R2=0.9976
Fe3+
0 μM
6.0 μM
66.4 μM
126.8 μM
187.2 μM
247.6 μM
308.0 μM
368.4 μM
489.2 μM
fitted (0-187.2μM)
KSV=5760M-1
R2=0.9662
Ni2+
0 μM
83.8 μM
167.6 μM
251.4 μM
335.2 μM
418.9 μM
586.5 μM
1424.4 μM
3100.2 μM
fitted (0-419μM)
KSV=7260M-1
R2=0.9955

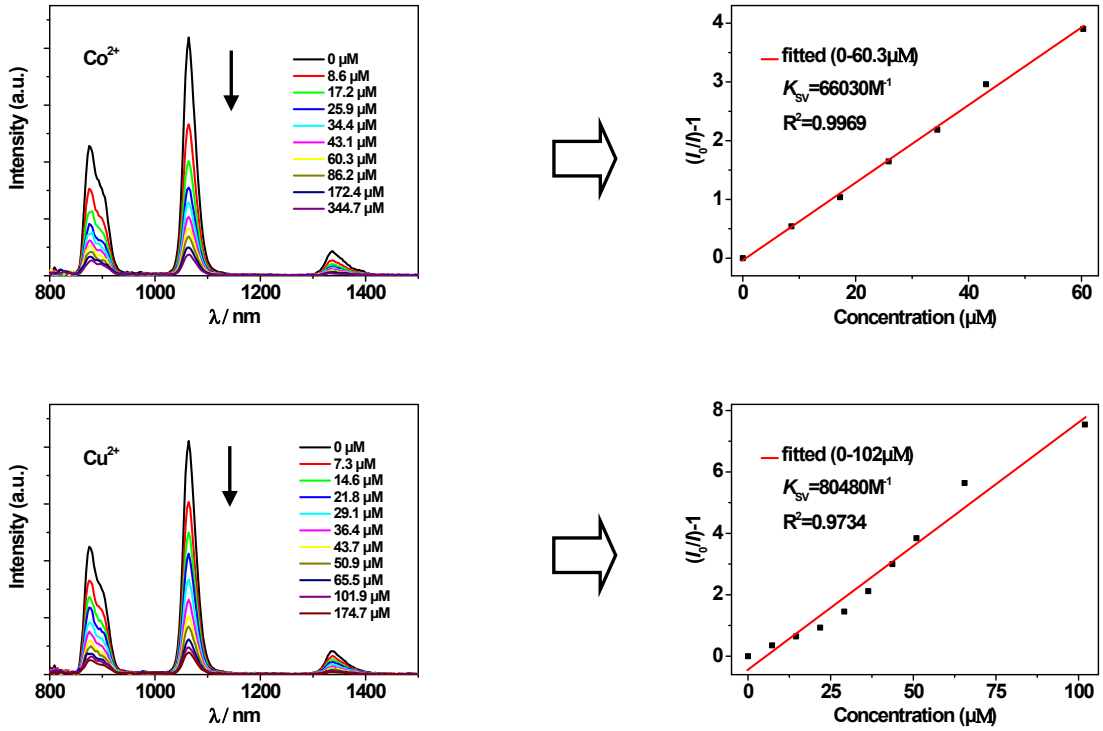
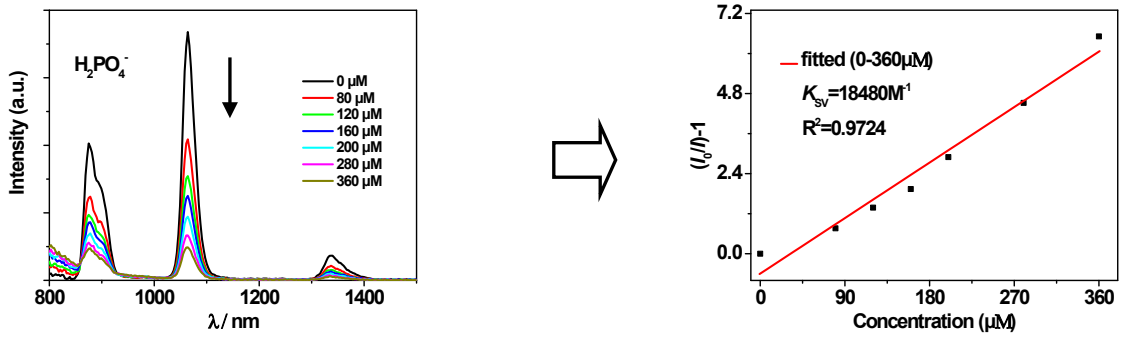
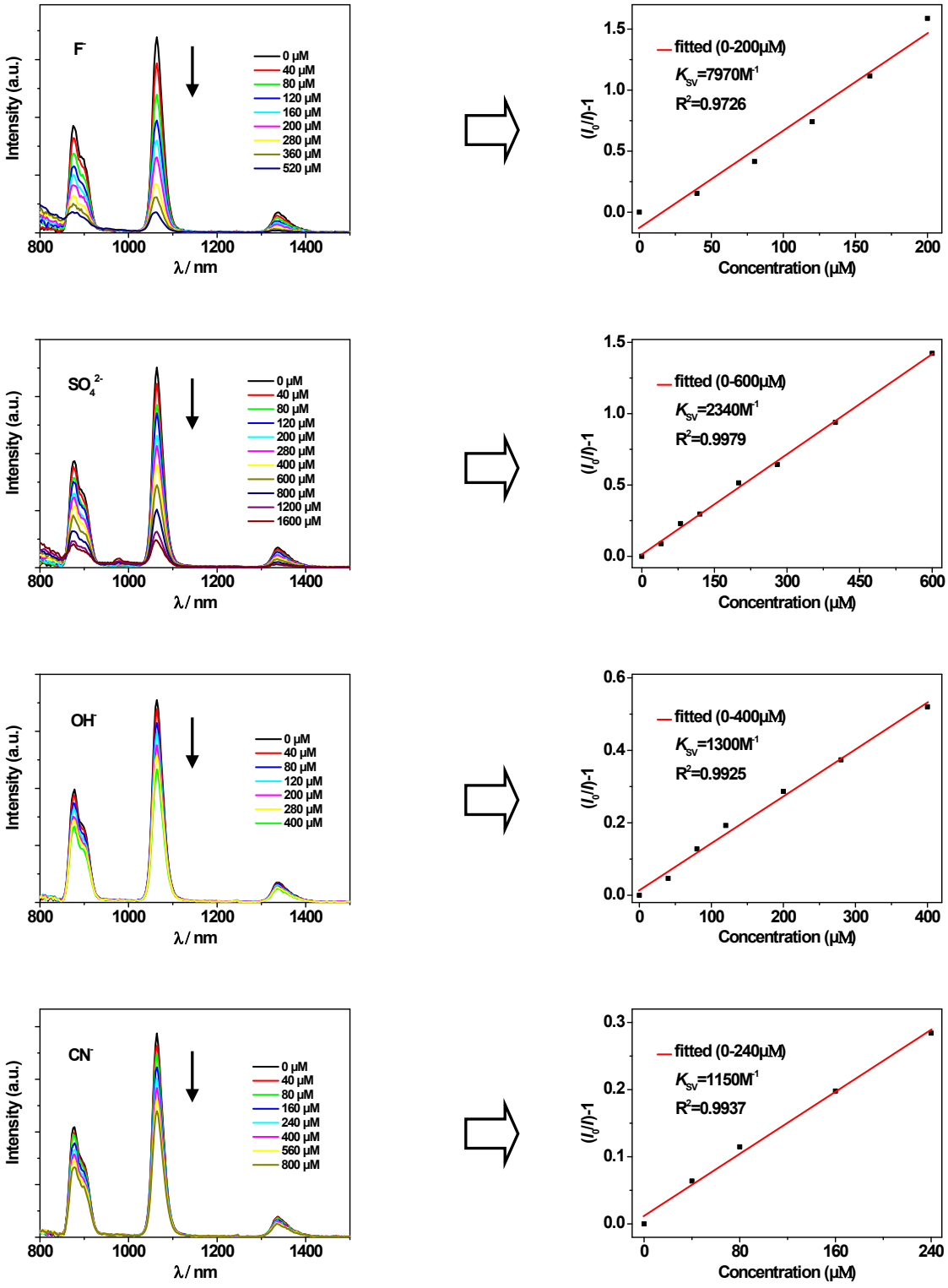
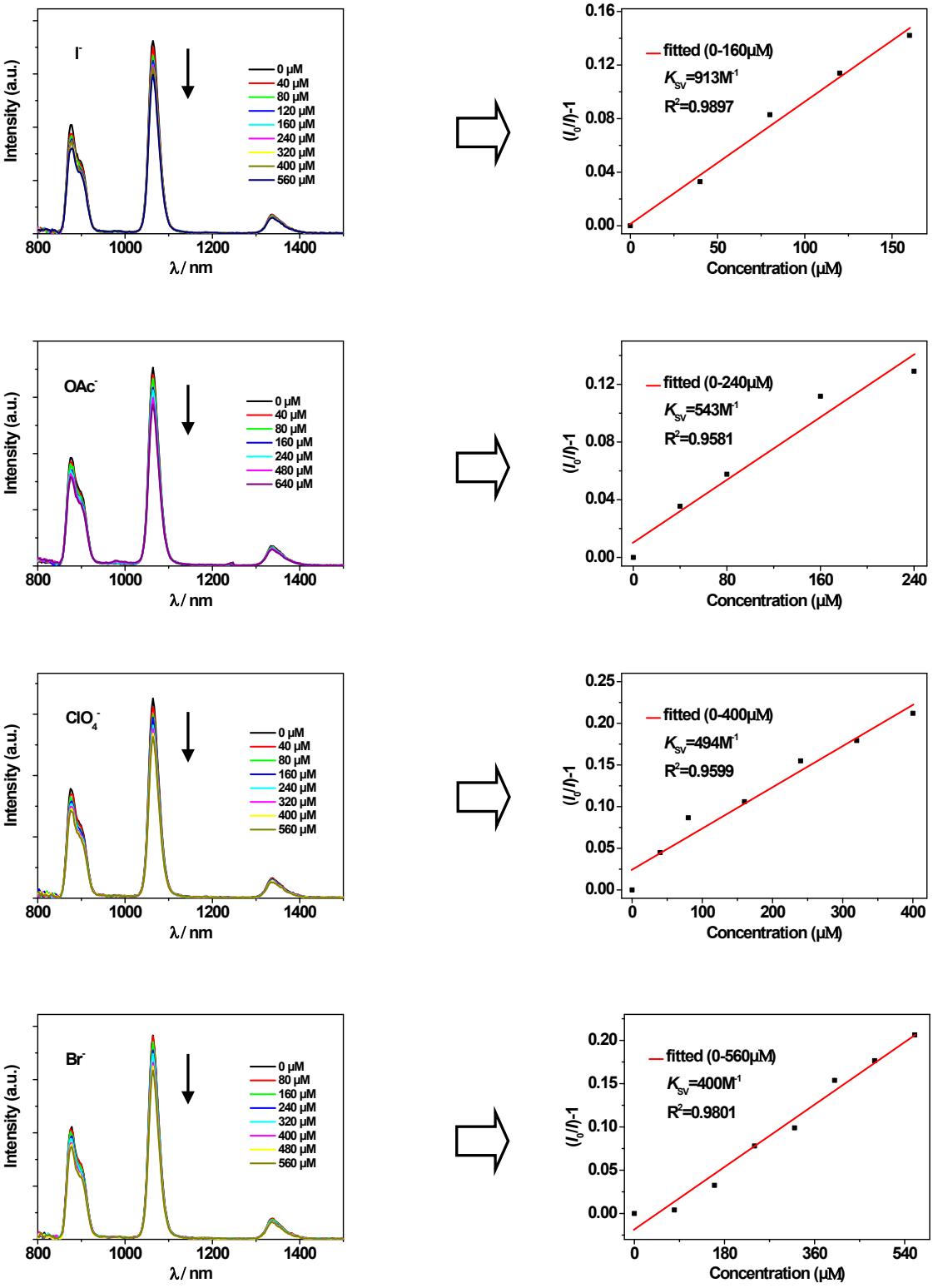


Figure S7. NIR luminescent sensing of **1** (10 μM) to metal cations in CH_3CN (λ_{ex} = 414 nm).

10. NIR luminescent sensing of 1 to anions




F-
0 μM
40 μM
80 μM
120 μM
160 μM
200 μM
280 μM
360 μM
520 μM
Intensity (a.u.)
λ/ nm
fitted (0-200μM)
K_{SV}=7970M^{-1}
R^2=0.9726
(I_0/I)-1
Concentration (μM)
SO_4^{2-}
0 μM
40 μM
80 μM
120 μM
200 μM
280 μM
400 μM
600 μM
800 μM
1200 μM
1600 μM
Intensity (a.u.)
λ/ nm
fitted (0-600μM)
K_{SV}=2340M^{-1}
R^2=0.9979
(I_0/I)-1
Concentration (μM)
OH-
0 μM
40 μM
80 μM
120 μM
200 μM
280 μM
400 μM
Intensity (a.u.)
λ/ nm
fitted (0-400μM)
K_{SV}=1300M^{-1}
R^2=0.9925
(I_0/I)-1
Concentration (μM)
CN-
0 μM
40 μM
80 μM
160 μM
240 μM
400 μM
560 μM
800 μM
Intensity (a.u.)
λ/ nm
fitted (0-240μM)
K_{SV}=1150M^{-1}
R^2=0.9937
(I_0/I)-1
Concentration (μM)


I-
Intensity (a.u.)
λ/ nm
0 μM
40 μM
80 μM
120 μM
160 μM
240 μM
320 μM
400 μM
560 μM
fitted (0-160μM)
K_{SV}=913M-1
R2=0.9897
(I0/I)-1
Concentration (μM)
OAc-
0 μM
40 μM
80 μM
160 μM
240 μM
480 μM
640 μM
fitted (0-240μM)
K_{SV}=543M-1
R2=0.9581
ClO4-
0 μM
40 μM
80 μM
160 μM
240 μM
320 μM
400 μM
560 μM
fitted (0-400μM)
K_{SV}=494M-1
R2=0.9599
Br-
0 μM
80 μM
160 μM
240 μM
320 μM
400 μM
480 μM
560 μM
fitted (0-560μM)
K_{SV}=400M-1
R2=0.9801

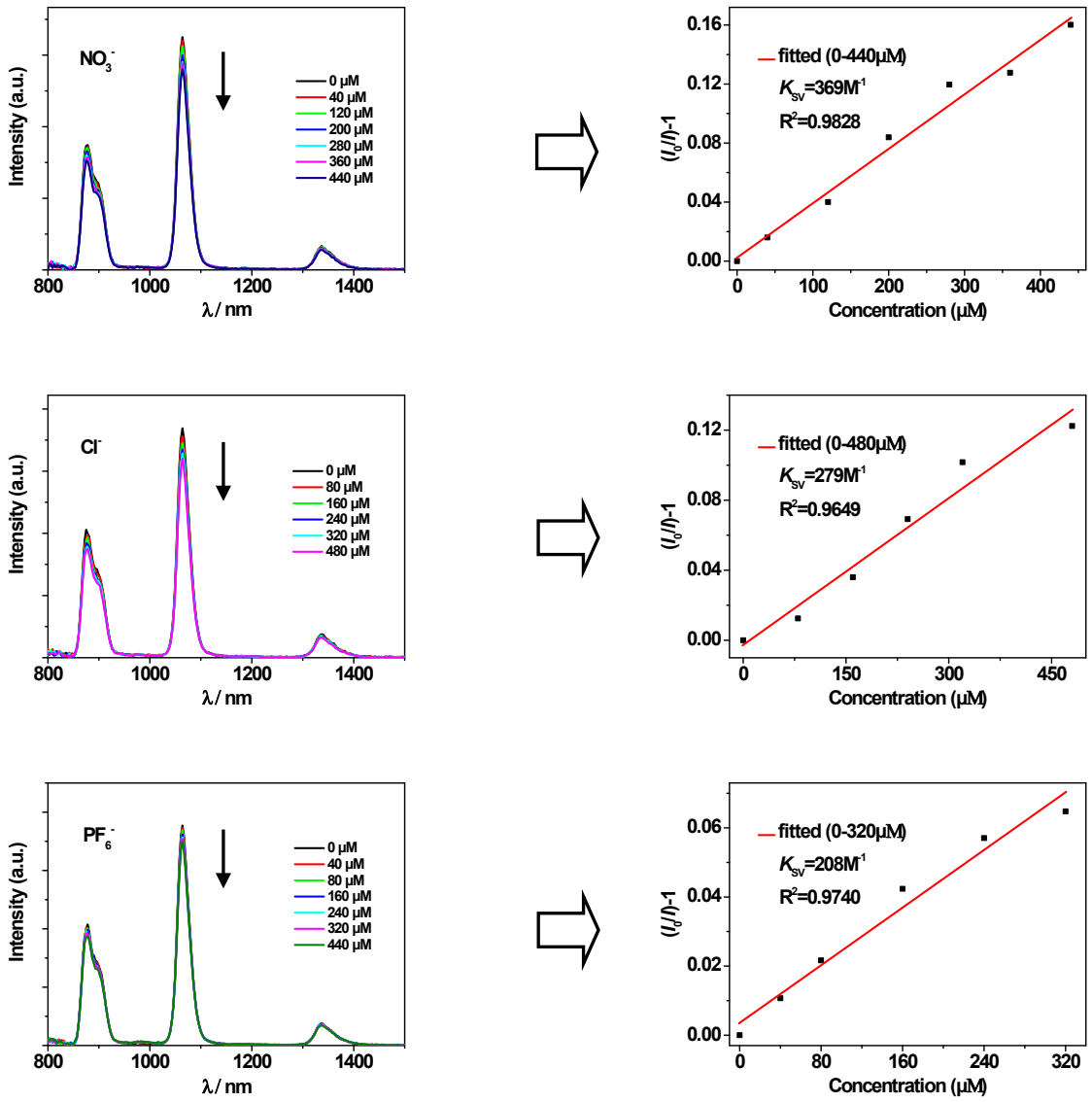
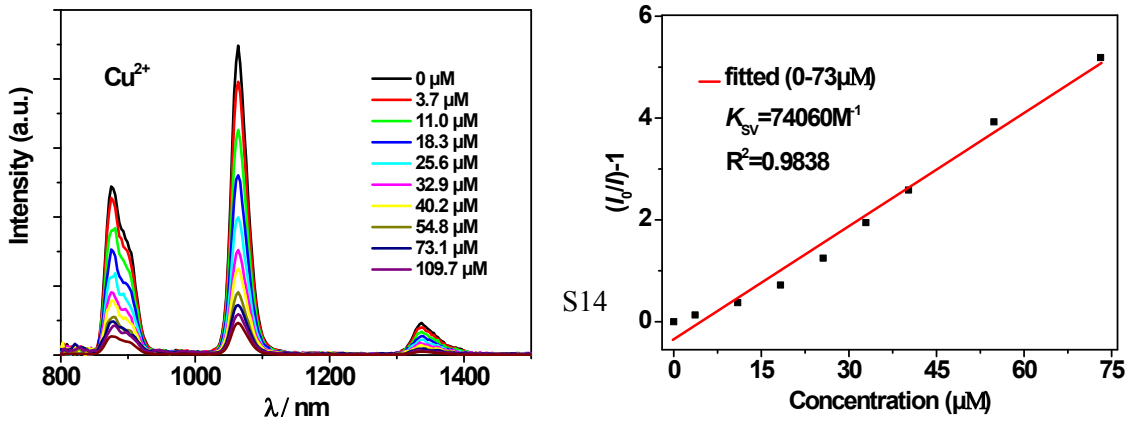
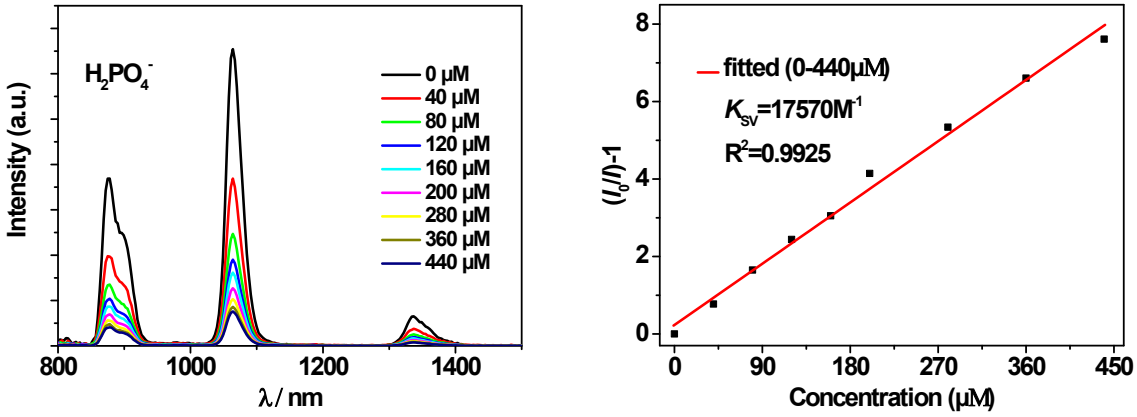


Figure S8. NIR luminescent sensing of **1** (10 μM) to anions in CH_3CN (λ_{ex} = 414 nm).

11. The luminescent response of the recycled sample of 1 to Cu(II) and $H_2PO_4^-$ ions



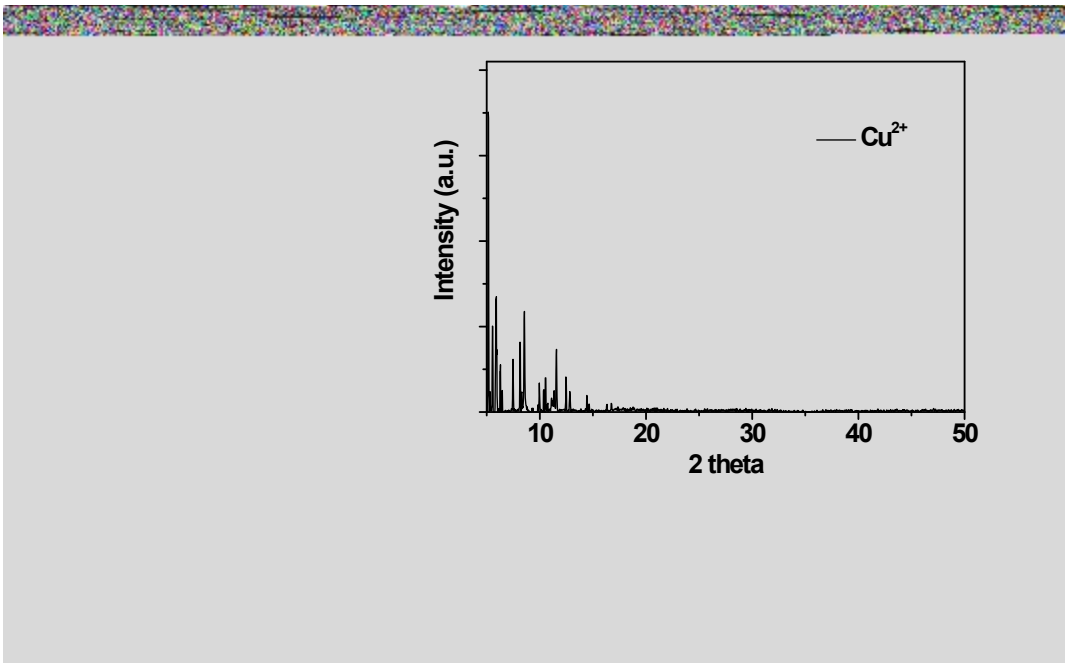
(a)



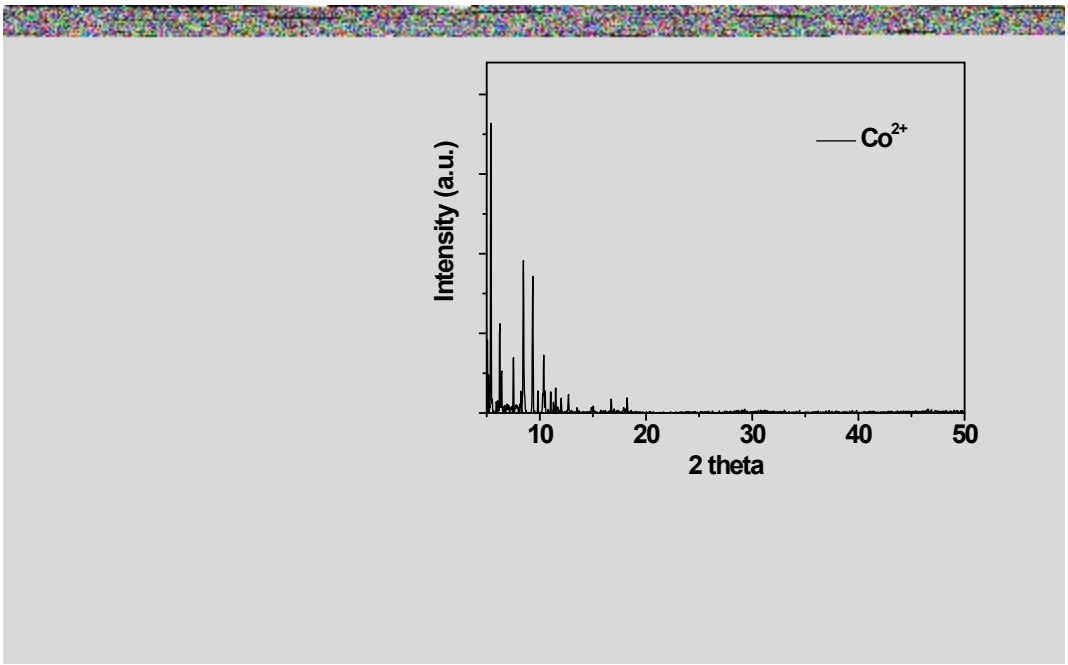
(b)

Figure S9. The luminescent response of the recycled sample of **1** (10 μM) to Cu(II) (**a**) and $H_2PO_4^-$ (**b**) ions in CH_3CN. (λ_{ex} = 414 nm)

12. Powder XRD patterns of 1 after soaked in the Cu(II) and Co(II) solutions



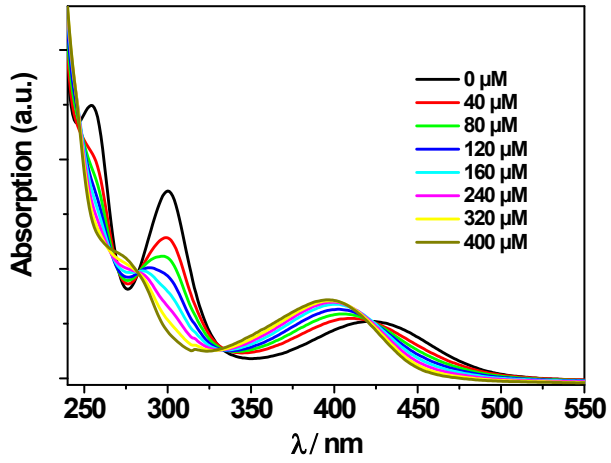
(a)



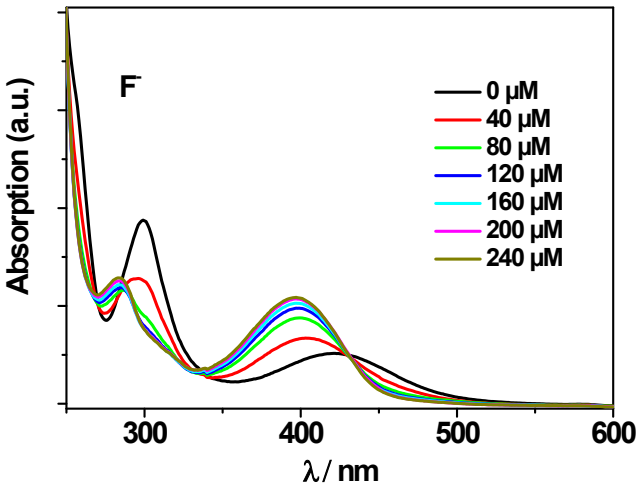
(b)

Figure S10. Powder XRD patterns of **1** after soaked in the Cu(II) (**a**) and Co(II) (**b**) solutions.

13. UV-vis spectral titration of 1 with the additional of $H_2PO_4^-$ and F^-



(a)



(b)

Figure S11. UV-vis spectral titration of **1** (5 μM) with the additional of $H_2PO_4^-$ (**a**) and F^- (**b**) ions in CH_3CN.

14. UV-vis spectral titration of 1 with the additional of some other ions

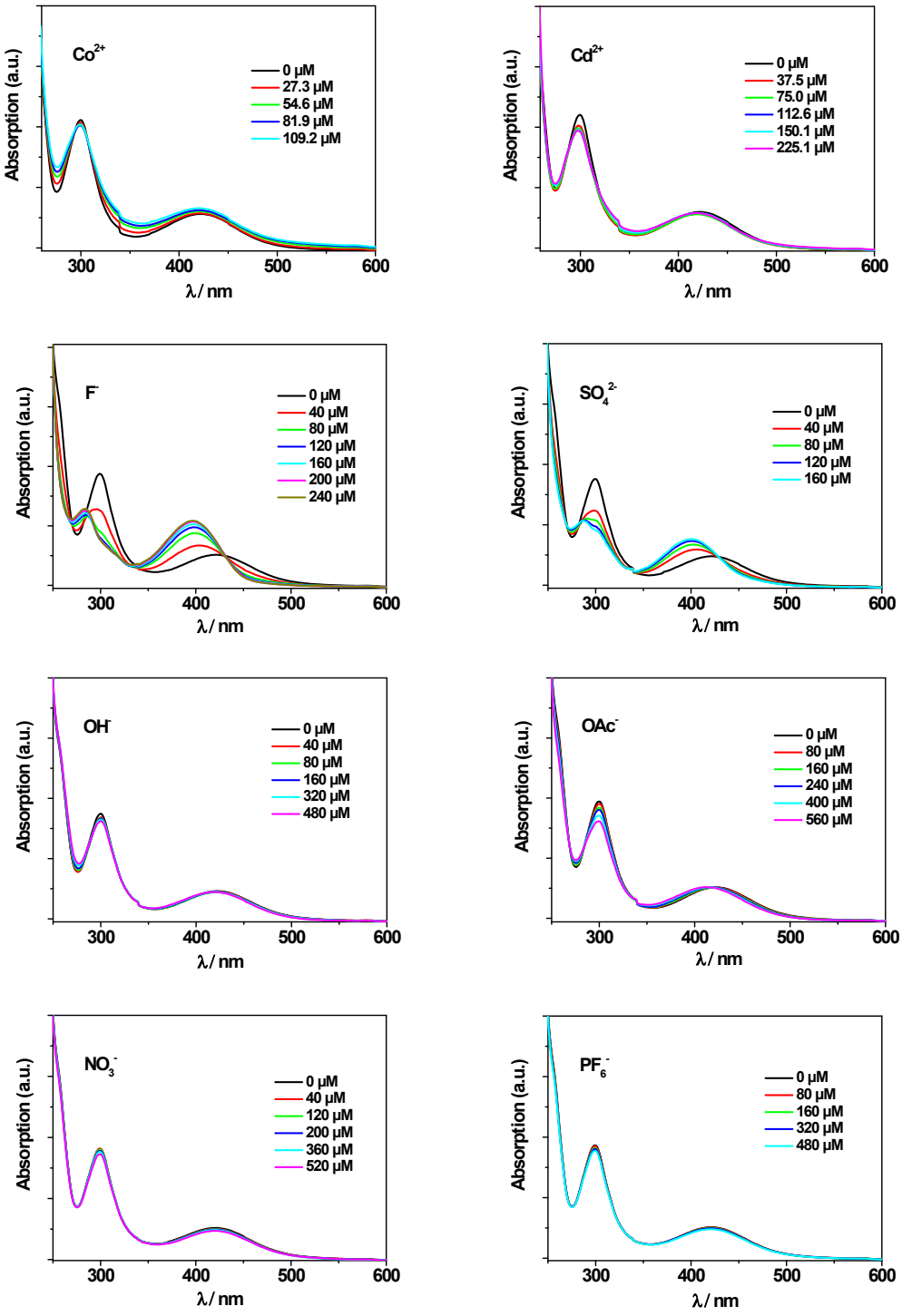


Figure S12. UV-vis spectral titration of **1** (5 μM) with the additional of some other ions in CH_3CN.

15. X-Ray Crystallography

Data were collected on a Smart APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 190 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. Data reduction was performed using DENZO-SMN.[1] The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[2] Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[3]

For the crystal structures of **1** and **2**, some uncoordinated solvent molecules such as EtOH and H_2O molecules were found to be badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE (Sluis and Spek, 1990) in PLATON98 (Spek, 1998). PLATON98 was used as incorporated in WinGX (Farrugia, 1999). Selected bond lengths and angles are given in Tables S1 and S2. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format (CCDC numbers: 1994064-1994065).

For **1**: $C_{178}H_{162}N_8Nd_{14}O_{82}$, monoclinic, space group C2/c, a = 34.000(4), b = 21.258(3), c = 37.580(4) Å, α = 90°, β = 104.305(3)°, γ = 90(2)°, V = 26320(5) Å^3, Z = 4, Dc = 1.450 g cm^{-3}, μ(Mo-Kα) = 2.778 mm^{-1}, F(000) = 11128, T = 190 K. R_1 = 0.0620, wR_2 = 0.1716, GOF = 1.057.

For **2**: $C_{178}H_{162}Gd_{14}N_8O_{82}$, monoclinic, space group C2/c, a = 33.900(6), b = 21.086(3), c = 37.720(6) Å, α = 90°, β = 104.641(3)°, γ = 90(2)°, V = 26087(7) Å^3, Z = 4, Dc = 1.509 g cm^{-3}, μ(Mo-Kα) = 3.575 mm^{-1}, F(000) = 11352, T = 190 K. R_1 = 0.0902, wR_2 = 0.1866, GOF = 1.086.

Ref. (1) DENZO-SMN. (**1997**). Z. Otwinowski, W. Minor, *Methods in Enzymology*, 276: *Macromolecular Crystallography, Part A*, 307 – 326, C. W. J. Carter, M. I. Simon, R. M. Sweet, Editors, Academic Press.

(2) G. H. Sheldrick, SHELX 97, *A software package for the solution and refinement of X-ray data*; University of Göttingen: Göttingen, Germany, **1997**.

(3) D. T. Cromer, J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, **1974**, Table 2.2A.

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

Nd(1)-O(2)	2.351(14)	Nd(6)-O(19)	2.420(17)
Nd(1)-O(3)	2.399(14)	Nd(6)-O(25)	2.535(16)
Nd(1)-O(8)	2.408(14)	Nd(6)-O(22)	2.541(16)
Nd(1)-O(11)	2.442(14)	Nd(6)-O(23)	2.566(15)
Nd(1)-O(27)#1	2.474(15)	Nd(7)-O(10)#1	2.335(14)
Nd(1)-O(37)	2.488(17)	Nd(7)-O(2)#1	2.335(15)
Nd(1)-O(10)	2.525(14)	Nd(7)-O(27)	2.373(14)
Nd(1)-O(7)	2.539(17)	Nd(7)-O(29)	2.384(14)
Nd(1)-O(38)	2.646(19)	Nd(7)-O(23)	2.410(15)
Nd(2)-O(3)	2.353(15)	Nd(7)-O(26)	2.415(13)
Nd(2)-O(8)	2.367(14)	Nd(7)-O(1)#1	2.428(15)
Nd(2)-O(34)	2.377(16)	Nd(7)-O(28)	2.491(16)
Nd(2)-O(11)	2.402(15)	O(2)-Nd(1)-O(3)	68.7(5)
Nd(2)-O(9)	2.415(15)	O(2)-Nd(1)-O(8)	134.1(5)
Nd(2)-O(5)	2.427(14)	O(3)-Nd(1)-O(8)	65.6(5)
Nd(2)-O(4)	2.506(18)	O(2)-Nd(1)-O(11)	92.9(4)
Nd(2)-O(12)	2.581(14)	O(3)-Nd(1)-O(11)	67.6(5)
Nd(2)-O(39)	2.66(2)	O(8)-Nd(1)-O(11)	66.2(4)
Nd(3)-O(6)	2.315(16)	O(2)-Nd(1)-O(27)#1	67.8(5)
Nd(3)-O(15)	2.354(15)	O(3)-Nd(1)-O(27)#1	132.9(5)
Nd(3)-O(33)	2.362(13)	O(8)-Nd(1)-O(27)#1	155.5(5)
Nd(3)-O(14)	2.390(16)	O(11)-Nd(1)-O(27)#1	131.5(5)
Nd(3)-O(9)	2.389(14)	O(2)-Nd(1)-O(37)	137.6(5)
Nd(3)-O(5)	2.397(14)	O(3)-Nd(1)-O(37)	139.0(5)
Nd(3)-O(16)	2.634(15)	O(8)-Nd(1)-O(37)	80.2(5)
Nd(3)-O(12)	2.638(13)	O(11)-Nd(1)-O(37)	78.6(5)
Nd(4)-O(21)	2.344(15)	O(27)#1-Nd(1)-O(37)	87.0(5)
Nd(4)-O(17)	2.370(15)	O(2)-Nd(1)-O(10)	66.8(5)
Nd(4)-O(33)	2.375(13)	O(3)-Nd(1)-O(10)	111.7(5)
Nd(4)-O(32)	2.419(13)	O(8)-Nd(1)-O(10)	128.1(5)
Nd(4)-O(14)	2.441(16)	O(11)-Nd(1)-O(10)	65.9(5)
Nd(4)-O(36)	2.455(18)	O(27)#1-Nd(1)-O(10)	65.6(5)
Nd(4)-O(13)	2.559(17)	O(37)-Nd(1)-O(10)	71.9(5)
Nd(4)-O(16)	2.633(16)	O(2)-Nd(1)-O(7)	135.8(5)
Nd(4)-O(40)	2.677(17)	O(3)-Nd(1)-O(7)	114.0(5)
Nd(5)-O(32)	2.347(13)	O(8)-Nd(1)-O(7)	70.1(5)
Nd(5)-O(30)	2.403(13)	O(11)-Nd(1)-O(7)	130.0(5)
Nd(5)-O(20)	2.408(13)	O(27)#1-Nd(1)-O(7)	86.1(5)
Nd(5)-O(17)	2.427(14)	O(37)-Nd(1)-O(7)	71.2(5)
Nd(5)-O(35)	2.459(14)	O(10)-Nd(1)-O(7)	134.1(5)
Nd(5)-O(18)	2.470(13)	O(2)-Nd(1)-O(38)	73.3(6)
Nd(5)-O(21)	2.497(14)	O(3)-Nd(1)-O(38)	72.0(5)
Nd(5)-O(41)	2.538(13)	O(8)-Nd(1)-O(38)	96.1(5)
Nd(5)-O(31)	2.544(15)	O(11)-Nd(1)-O(38)	139.6(5)
Nd(6)-O(20)	2.356(14)	O(27)#1-Nd(1)-O(38)	78.9(5)
Nd(6)-O(18)	2.392(14)	O(37)-Nd(1)-O(38)	136.5(6)
Nd(6)-O(26)	2.398(13)	O(10)-Nd(1)-O(38)	134.0(6)
Nd(6)-O(30)	2.406(12)	O(7)-Nd(1)-O(38)	66.9(6)
Nd(6)-O(29)	2.422(13)	O(3)-Nd(2)-O(8)	66.9(5)

O(3)-Nd(2)-O(34)	83.8(5)	O(5)-Nd(3)-O(16)	138.1(5)
O(8)-Nd(2)-O(34)	140.1(5)	O(6)-Nd(3)-O(12)	113.1(5)
O(3)-Nd(2)-O(11)	69.0(5)	O(15)-Nd(3)-O(12)	146.8(5)
O(8)-Nd(2)-O(11)	67.5(5)	O(33)-Nd(3)-O(12)	78.9(4)
O(34)-Nd(2)-O(11)	77.2(5)	O(14)-Nd(3)-O(12)	136.6(5)
O(3)-Nd(2)-O(9)	133.3(5)	O(9)-Nd(3)-O(12)	65.0(4)
O(8)-Nd(2)-O(9)	66.4(5)	O(5)-Nd(3)-O(12)	67.2(4)
O(34)-Nd(2)-O(9)	136.3(5)	O(16)-Nd(3)-O(12)	73.0(4)
O(11)-Nd(2)-O(9)	94.1(5)	O(21)-Nd(4)-O(17)	68.9(5)
O(3)-Nd(2)-O(5)	150.9(5)	O(21)-Nd(4)-O(33)	135.0(5)
O(8)-Nd(2)-O(5)	131.5(5)	O(17)-Nd(4)-O(33)	95.9(4)
O(34)-Nd(2)-O(5)	86.9(5)	O(21)-Nd(4)-O(32)	68.9(5)
O(11)-Nd(2)-O(5)	135.2(5)	O(17)-Nd(4)-O(32)	65.7(4)
O(9)-Nd(2)-O(5)	69.4(5)	O(33)-Nd(4)-O(32)	66.3(5)
O(3)-Nd(2)-O(4)	82.2(6)	O(21)-Nd(4)-O(14)	150.8(5)
O(8)-Nd(2)-O(4)	123.5(5)	O(17)-Nd(4)-O(14)	133.3(5)
O(34)-Nd(2)-O(4)	75.6(6)	O(33)-Nd(4)-O(14)	68.9(5)
O(11)-Nd(2)-O(4)	142.1(5)	O(32)-Nd(4)-O(14)	133.0(5)
O(9)-Nd(2)-O(4)	123.8(5)	O(21)-Nd(4)-O(36)	81.9(5)
O(5)-Nd(2)-O(4)	68.7(5)	O(17)-Nd(4)-O(36)	76.1(5)
O(3)-Nd(2)-O(12)	133.6(5)	O(33)-Nd(4)-O(36)	137.1(5)
O(8)-Nd(2)-O(12)	109.1(4)	O(32)-Nd(4)-O(36)	138.0(5)
O(34)-Nd(2)-O(12)	71.7(5)	O(14)-Nd(4)-O(36)	86.1(6)
O(11)-Nd(2)-O(12)	67.5(5)	O(21)-Nd(4)-O(13)	81.7(5)
O(9)-Nd(2)-O(12)	65.5(4)	O(17)-Nd(4)-O(13)	138.0(5)
O(5)-Nd(2)-O(12)	67.7(4)	O(33)-Nd(4)-O(13)	125.9(5)
O(4)-Nd(2)-O(12)	126.0(5)	O(32)-Nd(4)-O(13)	130.5(5)
O(3)-Nd(2)-O(39)	89.9(6)	O(14)-Nd(4)-O(13)	69.2(6)
O(8)-Nd(2)-O(39)	71.6(6)	O(36)-Nd(4)-O(13)	70.4(5)
O(34)-Nd(2)-O(39)	137.5(6)	O(21)-Nd(4)-O(16)	132.8(5)
O(11)-Nd(2)-O(39)	138.6(6)	O(17)-Nd(4)-O(16)	67.0(5)
O(9)-Nd(2)-O(39)	74.6(6)	O(33)-Nd(4)-O(16)	66.1(4)
O(5)-Nd(2)-O(39)	78.6(6)	O(32)-Nd(4)-O(16)	106.1(4)
O(4)-Nd(2)-O(39)	61.9(6)	O(14)-Nd(4)-O(16)	66.5(5)
O(12)-Nd(2)-O(39)	134.5(5)	O(36)-Nd(4)-O(16)	72.2(5)
O(6)-Nd(3)-O(15)	84.2(5)	O(13)-Nd(4)-O(16)	122.8(5)
O(6)-Nd(3)-O(33)	81.0(5)	O(21)-Nd(4)-O(40)	85.7(5)
O(15)-Nd(3)-O(33)	133.4(5)	O(17)-Nd(4)-O(40)	137.4(5)
O(6)-Nd(3)-O(14)	91.4(6)	O(33)-Nd(4)-O(40)	78.1(5)
O(15)-Nd(3)-O(14)	66.5(5)	O(32)-Nd(4)-O(40)	73.6(4)
O(33)-Nd(3)-O(14)	69.9(5)	O(14)-Nd(4)-O(40)	84.2(5)
O(6)-Nd(3)-O(9)	132.8(6)	O(36)-Nd(4)-O(40)	135.1(5)
O(15)-Nd(3)-O(9)	82.3(5)	O(13)-Nd(4)-O(40)	65.1(5)
O(33)-Nd(3)-O(9)	137.4(4)	O(16)-Nd(4)-O(40)	139.7(5)
O(14)-Nd(3)-O(9)	123.1(5)	O(32)-Nd(5)-O(30)	153.1(4)
O(6)-Nd(3)-O(5)	66.8(5)	O(32)-Nd(5)-O(20)	135.4(5)
O(15)-Nd(3)-O(5)	97.2(5)	O(30)-Nd(5)-O(20)	67.4(5)
O(33)-Nd(3)-O(5)	116.5(5)	O(32)-Nd(5)-O(17)	65.9(4)
O(14)-Nd(3)-O(5)	154.7(5)	O(30)-Nd(5)-O(17)	132.9(5)
O(9)-Nd(3)-O(5)	70.3(5)	O(20)-Nd(5)-O(17)	99.1(4)
O(6)-Nd(3)-O(16)	145.2(5)	O(32)-Nd(5)-O(35)	81.8(5)
O(15)-Nd(3)-O(16)	109.5(5)	O(30)-Nd(5)-O(35)	83.5(5)
O(33)-Nd(3)-O(16)	66.2(4)	O(20)-Nd(5)-O(35)	139.3(5)
O(14)-Nd(3)-O(16)	67.2(5)	O(17)-Nd(5)-O(35)	79.9(4)
O(9)-Nd(3)-O(16)	81.6(5)	O(32)-Nd(5)-O(18)	129.3(4)

O(30)-Nd(5)-O(18)	65.9(4)	O(19)-Nd(6)-O(25)	71.9(5)
O(20)-Nd(5)-O(18)	70.2(5)	O(20)-Nd(6)-O(22)	80.9(5)
O(17)-Nd(5)-O(18)	67.1(5)	O(18)-Nd(6)-O(22)	132.7(5)
O(35)-Nd(5)-O(18)	72.2(5)	O(26)-Nd(6)-O(22)	129.3(5)
O(32)-Nd(5)-O(21)	67.6(5)	O(30)-Nd(6)-O(22)	67.0(5)
O(30)-Nd(5)-O(21)	134.0(5)	O(29)-Nd(6)-O(22)	86.4(5)
O(20)-Nd(5)-O(21)	68.0(5)	O(19)-Nd(6)-O(22)	68.7(5)
O(17)-Nd(5)-O(21)	65.6(5)	O(25)-Nd(6)-O(22)	138.7(5)
O(35)-Nd(5)-O(21)	140.6(5)	O(20)-Nd(6)-O(23)	138.9(5)
O(18)-Nd(5)-O(21)	108.4(4)	O(18)-Nd(6)-O(23)	148.5(5)
O(32)-Nd(5)-O(41)	87.5(4)	O(26)-Nd(6)-O(23)	63.8(5)
O(30)-Nd(5)-O(41)	86.7(4)	O(30)-Nd(6)-O(23)	115.7(4)
O(20)-Nd(5)-O(41)	74.1(4)	O(29)-Nd(6)-O(23)	68.1(5)
O(17)-Nd(5)-O(41)	134.7(5)	O(19)-Nd(6)-O(23)	73.6(5)
O(35)-Nd(5)-O(41)	134.1(4)	O(25)-Nd(6)-O(23)	113.7(5)
O(18)-Nd(5)-O(41)	141.1(5)	O(22)-Nd(6)-O(23)	66.0(5)
O(21)-Nd(5)-O(41)	70.6(4)	O(10)#1-Nd(7)-O(2)#1	70.3(5)
O(32)-Nd(5)-O(31)	70.6(5)	O(10)#1-Nd(7)-O(27)	70.2(5)
O(30)-Nd(5)-O(31)	83.0(5)	O(2)#1-Nd(7)-O(27)	69.8(5)
O(20)-Nd(5)-O(31)	131.2(5)	O(10)#1-Nd(7)-O(29)	106.3(5)
O(17)-Nd(5)-O(31)	128.8(5)	O(2)#1-Nd(7)-O(29)	150.2(5)
O(35)-Nd(5)-O(31)	68.3(5)	O(27)-Nd(7)-O(29)	138.4(5)
O(18)-Nd(5)-O(31)	131.7(4)	O(10)#1-Nd(7)-O(23)	153.2(5)
O(21)-Nd(5)-O(31)	119.7(5)	O(2)#1-Nd(7)-O(23)	125.1(5)
O(41)-Nd(5)-O(31)	66.0(5)	O(27)-Nd(7)-O(23)	93.6(5)
O(20)-Nd(6)-O(18)	72.4(5)	O(29)-Nd(7)-O(23)	71.4(5)
O(20)-Nd(6)-O(26)	146.2(4)	O(10)#1-Nd(7)-O(26)	88.0(5)
O(18)-Nd(6)-O(26)	90.8(5)	O(2)#1-Nd(7)-O(26)	137.5(5)
O(20)-Nd(6)-O(30)	68.2(4)	O(27)-Nd(7)-O(26)	68.5(5)
O(18)-Nd(6)-O(30)	67.1(4)	O(29)-Nd(7)-O(26)	69.9(5)
O(26)-Nd(6)-O(30)	132.5(4)	O(23)-Nd(7)-O(26)	65.9(5)
O(20)-Nd(6)-O(29)	135.5(5)	O(10)#1-Nd(7)-O(1)#1	131.5(5)
O(18)-Nd(6)-O(29)	86.3(4)	O(2)#1-Nd(7)-O(1)#1	72.8(5)
O(26)-Nd(6)-O(29)	69.6(5)	O(27)-Nd(7)-O(1)#1	123.4(5)
O(30)-Nd(6)-O(29)	67.6(4)	O(29)-Nd(7)-O(1)#1	90.9(5)
O(20)-Nd(6)-O(19)	72.0(5)	O(23)-Nd(7)-O(1)#1	75.2(5)
O(18)-Nd(6)-O(19)	133.2(5)	O(26)-Nd(7)-O(1)#1	140.3(5)
O(26)-Nd(6)-O(19)	102.4(5)	O(10)#1-Nd(7)-O(28)	74.1(5)
O(30)-Nd(6)-O(19)	123.6(5)	O(2)#1-Nd(7)-O(28)	80.2(5)
O(29)-Nd(6)-O(19)	140.4(5)	O(27)-Nd(7)-O(28)	139.2(5)
O(20)-Nd(6)-O(25)	75.7(5)	O(29)-Nd(7)-O(28)	70.6(5)
O(18)-Nd(6)-O(25)	70.7(5)	O(23)-Nd(7)-O(28)	126.7(5)
O(26)-Nd(6)-O(25)	71.0(5)	O(26)-Nd(7)-O(28)	129.4(5)
O(30)-Nd(6)-O(25)	130.6(5)	O(1)#1-Nd(7)-O(28)	69.5(5)
O(29)-Nd(6)-O(25)	133.5(5)		

Table S2. Selected Bond Lengths (Å) and angles (°) for **2**.

Gd(1)-O(3)	2.35(3)	Gd(6)-O(19)	2.50(3)
Gd(1)-O(2)	2.36(3)	Gd(6)-O(23)	2.522(19)
Gd(1)-O(8)	2.41(2)	Gd(6)-O(22)	2.60(3)
Gd(1)-O(27)#1	2.45(2)	Gd(7)-O(2)#1	2.29(3)
Gd(1)-O(7)	2.51(4)	Gd(7)-O(27)	2.32(3)
Gd(1)-O(11)	2.51(2)	Gd(7)-O(10)#1	2.32(3)
Gd(1)-O(37)	2.51(2)	Gd(7)-O(23)	2.36(2)
Gd(1)-O(10)	2.55(2)	Gd(7)-O(29)	2.37(2)
Gd(1)-O(38)	2.61(4)	Gd(7)-O(1)#1	2.38(3)
Gd(2)-O(3)	2.30(3)	Gd(7)-O(28)	2.46(3)
Gd(2)-O(8)	2.33(3)	Gd(7)-O(26)	2.49(3)
Gd(2)-O(34)	2.45(4)	O(3)-Gd(1)-O(2)	70.6(9)
Gd(2)-O(5)	2.40(2)	O(3)-Gd(1)-O(8)	63.2(9)
Gd(2)-O(11)	2.43(2)	O(2)-Gd(1)-O(8)	133.7(10)
Gd(2)-O(9)	2.45(3)	O(3)-Gd(1)-O(27)#1	133.6(10)
Gd(2)-O(4)	2.52(3)	O(2)-Gd(1)-O(27)#1	65.6(10)
Gd(2)-O(12)	2.56(2)	O(8)-Gd(1)-O(27)#1	158.0(10)
Gd(2)-O(39)	2.75(5)	O(3)-Gd(1)-O(7)	115.0(9)
Gd(3)-O(15)	2.28(3)	O(2)-Gd(1)-O(7)	136.6(10)
Gd(3)-O(5)	2.31(2)	O(8)-Gd(1)-O(7)	70.1(10)
Gd(3)-O(33)	2.35(3)	O(27)#1-Gd(1)-O(7)	88.3(10)
Gd(3)-O(6)	2.36(3)	O(3)-Gd(1)-O(11)	67.1(9)
Gd(3)-O(9)	2.39(3)	O(2)-Gd(1)-O(11)	94.0(9)
Gd(3)-O(14)	2.45(3)	O(8)-Gd(1)-O(11)	66.8(8)
Gd(3)-O(12)	2.58(3)	O(27)#1-Gd(1)-O(11)	129.2(8)
Gd(3)-O(16)	2.62(2)	O(7)-Gd(1)-O(11)	128.7(9)
Gd(4)-O(14)	2.36(3)	O(3)-Gd(1)-O(37)	137.9(9)
Gd(4)-O(21)	2.38(2)	O(2)-Gd(1)-O(37)	137.8(9)
Gd(4)-O(33)	2.38(3)	O(8)-Gd(1)-O(37)	81.5(9)
Gd(4)-O(17)	2.40(3)	O(27)#1-Gd(1)-O(37)	87.1(9)
Gd(4)-O(32)	2.40(3)	O(7)-Gd(1)-O(37)	68.6(9)
Gd(4)-O(36)	2.42(4)	O(11)-Gd(1)-O(37)	78.6(8)
Gd(4)-O(40)	2.49(3)	O(3)-Gd(1)-O(10)	110.2(10)
Gd(4)-O(13)	2.54(3)	O(2)-Gd(1)-O(10)	65.8(9)
Gd(4)-O(16)	2.71(3)	O(8)-Gd(1)-O(10)	128.7(8)
Gd(5)-O(32)	2.31(2)	O(27)#1-Gd(1)-O(10)	64.4(8)
Gd(5)-O(20)	2.37(3)	O(7)-Gd(1)-O(10)	134.3(9)
Gd(5)-O(17)	2.39(3)	O(11)-Gd(1)-O(10)	64.8(8)
Gd(5)-O(30)	2.40(2)	O(37)-Gd(1)-O(10)	73.7(9)
Gd(5)-O(21)	2.44(3)	O(3)-Gd(1)-O(38)	75.5(11)
Gd(5)-O(35)	2.47(3)	O(2)-Gd(1)-O(38)	73.7(12)
Gd(5)-O(18)	2.48(2)	O(8)-Gd(1)-O(38)	96.1(10)
Gd(5)-O(41)	2.56(2)	O(27)#1-Gd(1)-O(38)	78.4(10)
Gd(5)-O(31)	2.61(3)	O(7)-Gd(1)-O(38)	67.2(12)
Gd(6)-O(26)	2.32(3)	O(11)-Gd(1)-O(38)	142.6(11)
Gd(6)-O(20)	2.40(3)	O(37)-Gd(1)-O(38)	133.7(12)
Gd(6)-O(29)	2.41(2)	O(10)-Gd(1)-O(38)	133.2(11)
Gd(6)-O(30)	2.42(3)	O(3)-Gd(2)-O(8)	65.2(9)
Gd(6)-O(25)	2.43(3)	O(3)-Gd(2)-O(34)	84.3(10)
Gd(6)-O(18)	2.45(2)	O(8)-Gd(2)-O(34)	139.6(9)

O(3)-Gd(2)-O(5)	153.8(8)	O(5)-Gd(3)-O(16)	137.4(8)
O(8)-Gd(2)-O(5)	129.0(9)	O(33)-Gd(3)-O(16)	68.5(9)
O(34)-Gd(2)-O(5)	89.9(9)	O(6)-Gd(3)-O(16)	145.3(8)
O(3)-Gd(2)-O(11)	69.1(8)	O(9)-Gd(3)-O(16)	79.8(9)
O(8)-Gd(2)-O(11)	69.2(8)	O(14)-Gd(3)-O(16)	67.1(9)
O(34)-Gd(2)-O(11)	75.6(9)	O(12)-Gd(3)-O(16)	72.3(8)
O(5)-Gd(2)-O(11)	133.9(7)	O(14)-Gd(4)-O(21)	150.8(10)
O(3)-Gd(2)-O(9)	131.7(11)	O(14)-Gd(4)-O(33)	69.8(11)
O(8)-Gd(2)-O(9)	66.6(10)	O(21)-Gd(4)-O(33)	134.1(10)
O(34)-Gd(2)-O(9)	136.7(10)	O(14)-Gd(4)-O(17)	134.1(10)
O(5)-Gd(2)-O(9)	67.0(9)	O(21)-Gd(4)-O(17)	69.0(8)
O(11)-Gd(2)-O(9)	94.2(8)	O(33)-Gd(4)-O(17)	93.8(8)
O(3)-Gd(2)-O(4)	83.6(10)	O(14)-Gd(4)-O(32)	134.5(10)
O(8)-Gd(2)-O(4)	120.1(10)	O(21)-Gd(4)-O(32)	66.8(9)
O(34)-Gd(2)-O(4)	79.2(11)	O(33)-Gd(4)-O(32)	67.4(9)
O(5)-Gd(2)-O(4)	70.3(9)	O(17)-Gd(4)-O(32)	64.1(9)
O(11)-Gd(2)-O(4)	144.2(10)	O(14)-Gd(4)-O(36)	87.4(11)
O(9)-Gd(2)-O(4)	121.5(10)	O(21)-Gd(4)-O(36)	81.2(10)
O(3)-Gd(2)-O(12)	134.1(8)	O(33)-Gd(4)-O(36)	137.8(10)
O(8)-Gd(2)-O(12)	109.0(9)	O(17)-Gd(4)-O(36)	76.8(11)
O(34)-Gd(2)-O(12)	73.2(9)	O(32)-Gd(4)-O(36)	136.0(10)
O(5)-Gd(2)-O(12)	67.1(7)	O(14)-Gd(4)-O(40)	84.2(10)
O(11)-Gd(2)-O(12)	66.9(8)	O(21)-Gd(4)-O(40)	86.7(8)
O(9)-Gd(2)-O(12)	64.3(10)	O(33)-Gd(4)-O(40)	75.9(8)
O(4)-Gd(2)-O(12)	128.4(10)	O(17)-Gd(4)-O(40)	134.5(10)
O(3)-Gd(2)-O(39)	90.0(12)	O(32)-Gd(4)-O(40)	71.2(8)
O(8)-Gd(2)-O(39)	68.6(12)	O(36)-Gd(4)-O(40)	138.3(10)
O(34)-Gd(2)-O(39)	140.6(12)	O(14)-Gd(4)-O(13)	66.2(10)
O(5)-Gd(2)-O(39)	78.4(12)	O(21)-Gd(4)-O(13)	84.7(10)
O(11)-Gd(2)-O(39)	137.7(12)	O(33)-Gd(4)-O(13)	126.0(9)
O(9)-Gd(2)-O(39)	72.3(12)	O(17)-Gd(4)-O(13)	139.7(10)
O(4)-Gd(2)-O(39)	61.4(14)	O(32)-Gd(4)-O(13)	132.7(10)
O(12)-Gd(2)-O(39)	132.1(12)	O(36)-Gd(4)-O(13)	69.1(11)
O(15)-Gd(3)-O(5)	95.6(9)	O(40)-Gd(4)-O(13)	70.2(11)
O(15)-Gd(3)-O(33)	132.6(10)	O(14)-Gd(4)-O(16)	66.8(9)
O(5)-Gd(3)-O(33)	117.5(9)	O(21)-Gd(4)-O(16)	132.6(8)
O(15)-Gd(3)-O(6)	80.0(10)	O(33)-Gd(4)-O(16)	66.6(9)
O(5)-Gd(3)-O(6)	70.8(8)	O(17)-Gd(4)-O(16)	67.4(8)
O(33)-Gd(3)-O(6)	80.4(8)	O(32)-Gd(4)-O(16)	108.1(8)
O(15)-Gd(3)-O(9)	83.4(10)	O(36)-Gd(4)-O(16)	71.9(10)
O(5)-Gd(3)-O(9)	69.5(9)	O(40)-Gd(4)-O(16)	138.4(8)
O(33)-Gd(3)-O(9)	137.9(8)	O(13)-Gd(4)-O(16)	118.8(10)
O(6)-Gd(3)-O(9)	134.8(8)	O(32)-Gd(5)-O(20)	133.8(9)
O(15)-Gd(3)-O(14)	68.0(10)	O(32)-Gd(5)-O(17)	65.5(9)
O(5)-Gd(3)-O(14)	155.5(9)	O(20)-Gd(5)-O(17)	101.3(10)
O(33)-Gd(3)-O(14)	68.7(11)	O(32)-Gd(5)-O(30)	152.9(10)
O(6)-Gd(3)-O(14)	88.0(9)	O(20)-Gd(5)-O(30)	69.1(9)
O(9)-Gd(3)-O(14)	123.5(11)	O(17)-Gd(5)-O(30)	131.8(9)
O(15)-Gd(3)-O(12)	147.6(10)	O(32)-Gd(5)-O(21)	67.1(9)
O(5)-Gd(3)-O(12)	68.2(7)	O(20)-Gd(5)-O(21)	67.0(9)
O(33)-Gd(3)-O(12)	79.2(8)	O(17)-Gd(5)-O(21)	68.0(9)
O(6)-Gd(3)-O(12)	117.4(9)	O(30)-Gd(5)-O(21)	134.9(8)
O(9)-Gd(3)-O(12)	64.8(10)	O(32)-Gd(5)-O(35)	83.7(9)
O(14)-Gd(3)-O(12)	135.0(9)	O(20)-Gd(5)-O(35)	139.0(9)
O(15)-Gd(3)-O(16)	109.8(10)	O(17)-Gd(5)-O(35)	77.7(9)

O(30)-Gd(5)-O(35)	81.2(8)	O(26)-Gd(6)-O(23)	63.8(7)
O(21)-Gd(5)-O(35)	141.7(8)	O(20)-Gd(6)-O(23)	140.6(7)
O(32)-Gd(5)-O(18)	128.4(8)	O(29)-Gd(6)-O(23)	65.8(7)
O(20)-Gd(5)-O(18)	72.2(8)	O(30)-Gd(6)-O(23)	114.1(8)
O(17)-Gd(5)-O(18)	65.9(8)	O(25)-Gd(6)-O(23)	116.9(8)
O(30)-Gd(5)-O(18)	66.2(8)	O(18)-Gd(6)-O(23)	146.6(7)
O(21)-Gd(5)-O(18)	108.5(9)	O(19)-Gd(6)-O(23)	75.5(8)
O(35)-Gd(5)-O(18)	70.2(9)	O(26)-Gd(6)-O(22)	130.0(8)
O(32)-Gd(5)-O(41)	87.5(8)	O(20)-Gd(6)-O(22)	79.7(8)
O(20)-Gd(5)-O(41)	71.8(8)	O(29)-Gd(6)-O(22)	88.8(8)
O(17)-Gd(5)-O(41)	135.4(9)	O(30)-Gd(6)-O(22)	69.3(8)
O(30)-Gd(5)-O(41)	88.0(7)	O(25)-Gd(6)-O(22)	138.4(8)
O(21)-Gd(5)-O(41)	69.1(8)	O(18)-Gd(6)-O(22)	133.8(9)
O(35)-Gd(5)-O(41)	136.3(10)	O(19)-Gd(6)-O(22)	68.0(10)
O(18)-Gd(5)-O(41)	141.4(7)	O(23)-Gd(6)-O(22)	66.3(7)
O(32)-Gd(5)-O(31)	70.0(9)	O(2)#1-Gd(7)-O(27)	68.9(10)
O(20)-Gd(5)-O(31)	130.8(9)	O(2)#1-Gd(7)-O(10)#1	70.9(9)
O(17)-Gd(5)-O(31)	126.8(9)	O(27)-Gd(7)-O(10)#1	69.9(9)
O(30)-Gd(5)-O(31)	83.7(9)	O(2)#1-Gd(7)-O(23)	126.4(8)
O(21)-Gd(5)-O(31)	118.5(9)	O(27)-Gd(7)-O(23)	97.4(8)
O(35)-Gd(5)-O(31)	69.7(9)	O(10)#1-Gd(7)-O(23)	154.6(9)
O(18)-Gd(5)-O(31)	132.7(8)	O(2)#1-Gd(7)-O(29)	151.1(10)
O(41)-Gd(5)-O(31)	67.0(8)	O(27)-Gd(7)-O(29)	138.0(9)
O(26)-Gd(6)-O(20)	145.4(10)	O(10)#1-Gd(7)-O(29)	105.0(8)
O(26)-Gd(6)-O(29)	70.9(11)	O(23)-Gd(7)-O(29)	69.1(7)
O(20)-Gd(6)-O(29)	135.1(9)	O(2)#1-Gd(7)-O(1)#1	73.5(9)
O(26)-Gd(6)-O(30)	133.2(9)	O(27)-Gd(7)-O(1)#1	123.9(9)
O(20)-Gd(6)-O(30)	68.2(9)	O(10)#1-Gd(7)-O(1)#1	131.9(10)
O(29)-Gd(6)-O(30)	67.2(9)	O(23)-Gd(7)-O(1)#1	73.5(8)
O(26)-Gd(6)-O(25)	69.5(9)	O(29)-Gd(7)-O(1)#1	91.3(9)
O(20)-Gd(6)-O(25)	76.1(9)	O(2)#1-Gd(7)-O(28)	81.1(10)
O(29)-Gd(6)-O(25)	131.8(8)	O(27)-Gd(7)-O(28)	137.6(9)
O(30)-Gd(6)-O(25)	128.7(9)	O(10)#1-Gd(7)-O(28)	72.4(10)
O(26)-Gd(6)-O(18)	91.1(8)	O(23)-Gd(7)-O(28)	124.7(9)
O(20)-Gd(6)-O(18)	72.3(8)	O(29)-Gd(7)-O(28)	70.7(9)
O(29)-Gd(6)-O(18)	86.1(7)	O(1)#1-Gd(7)-O(28)	71.1(9)
O(30)-Gd(6)-O(18)	66.4(8)	O(2)#1-Gd(7)-O(26)	138.2(11)
O(25)-Gd(6)-O(18)	68.4(8)	O(27)-Gd(7)-O(26)	69.6(10)
O(26)-Gd(6)-O(19)	99.3(10)	O(10)#1-Gd(7)-O(26)	90.9(9)
O(20)-Gd(6)-O(19)	73.6(9)	O(23)-Gd(7)-O(26)	63.8(7)
O(29)-Gd(6)-O(19)	140.5(8)	O(29)-Gd(7)-O(26)	68.9(11)
O(30)-Gd(6)-O(19)	126.4(9)	O(1)#1-Gd(7)-O(26)	136.9(9)
O(25)-Gd(6)-O(19)	72.9(9)	O(28)-Gd(7)-O(26)	130.0(9)
O(18)-Gd(6)-O(19)	133.2(9)		