Supporting Information

NIR luminescence for the detection of metal ions and nitro explosives based on a grape-like nine-nuclear Nd(III) nanocluster

Hongfen Chen, Xiaoping Yang, Dongmei Jiang, Desmond Schipper and Richard A. Jones

Contents

1. Materials and methods

The reagents and solvents were purchased from standard commercial suppliers. ^{1}H (500 MHz) NMR spectra were recorded on a AVANCE III AV500 spectrometer at 298 K. Elemental analyses for C, H, and N were performed on a EURO EA3000 elemental analysis. Melting points were determined on a Büchi melting point apparatus and are uncorrected. Powder XRD spectra were obtained on a D8ADVANCE diffractometer. Infrared and electronic absorption spectra were carried out on a Nicolet IS10 spectrometer and UV-3600 spectrophotometer, respectively. Conductivity measurements were carried out with a DDS-11 conductivity bridge. Field emission scanning electron microscopy (FESEM) images and energy dispersive X-ray spectroscopy (EDX) spectra were acquired on a Nova NanoSEM 200 scanning electron microscope.

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. Synthesis of the Schiff base ligand H_2L^1

2-Hydroxy-2-methoxybenzaldehyde (5.0 mmol, 0.7608 g) was dissolved in 10 mL EtOH, and a solution of 4-{3-[4-(2-amino-ethyl)-phenoxy]-phenoxy}-phenylamine (2.5 mmol, 0.8010 g) in 20 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 3.5 hours. It was allowed to cool and was then filtered. The solid was washed with EtOH (3×5 ml) and then dried in the air at room temperature to give orange product. Yield (based on 4-{3-[4-(2-amino-ethyl)-phenoxy]-phenoxy}-phenylamine): 1.4128 g (96%). m.p. = 139.2°C. Elemental analysis: Found: C, 73.50; H, 5.58; N, 4.80%. Calc. for $C_{36}H_{32}N_2O_6$: C, 73.45; H, 5.48; N, 4.76%. IR (CH_3CN, cm^{-1}): 1610 (m), 1447 (s), 1241 (s), 1170 (m), 1130 (w), 1092 (w), 950 (m), 836 (m), 772 (m), 730 (m), 686 (m). ^1H NMR (500 MHz, DMSO) δ = 13.20 (s, 2H), 8.96 (s, 2H), 7.49 (d, 2H), 7.42 (t, 3H), 7.22 (d, 2H), 7.15 (dd, 4H), 6.91 (t, 3H), 6.81 (dd, 2H), 6.71 (d, 2H), 3.82 (s, 6H), 1.34 (d, 4H).

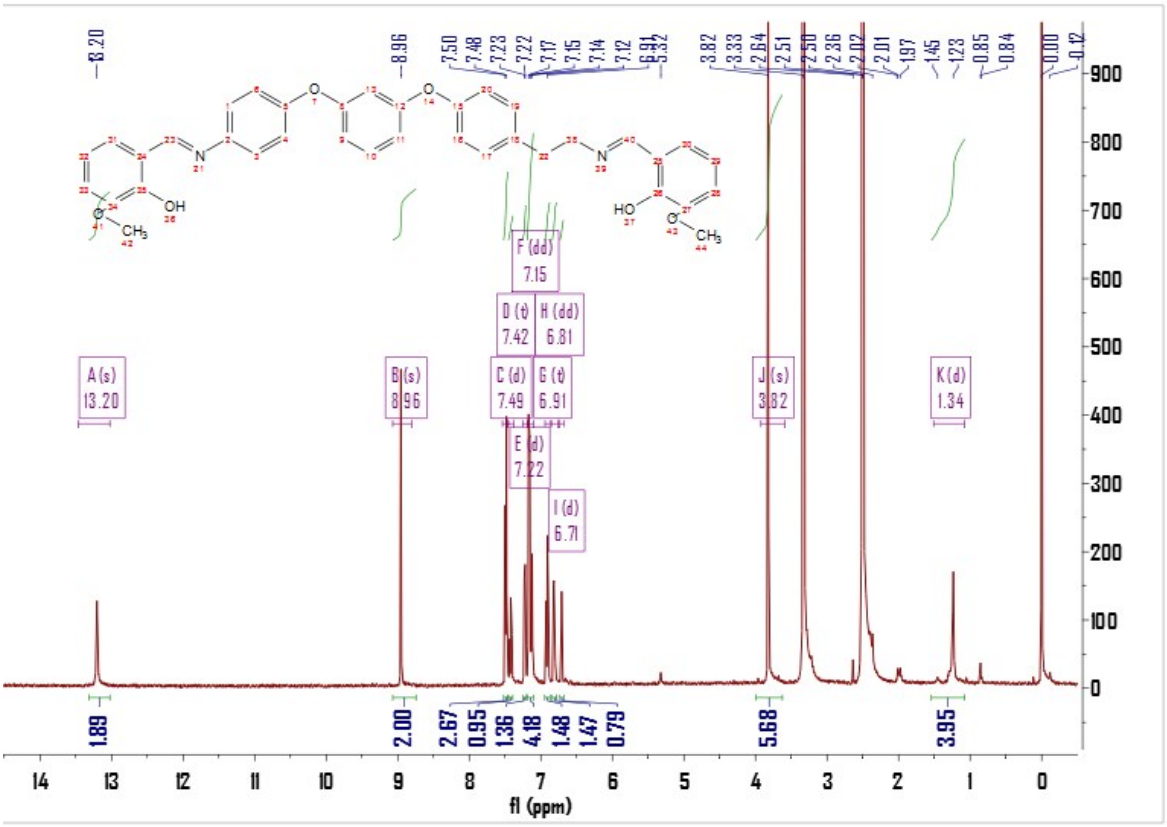
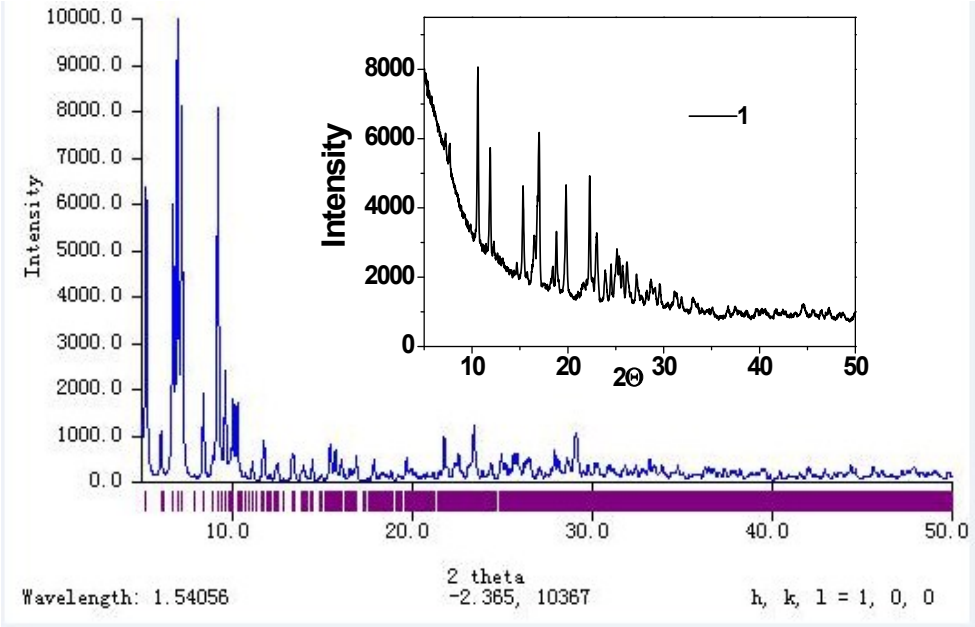


Figure S1. ^1H NMR spectrum of H_2L^1 in DMSO.

3. Powder XRD patterns of 1 and 2



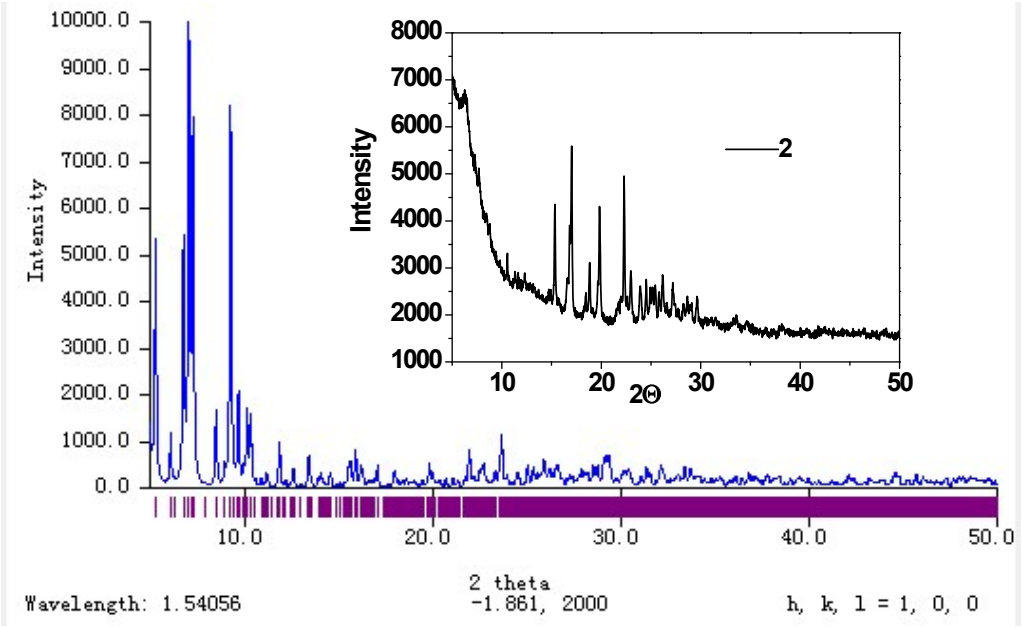


Figure S2. Powder XRD patterns of **1** and **2** (the insert pictures were obtained from experiments).

4. The IR spectra of H_2L^1 and 1-2

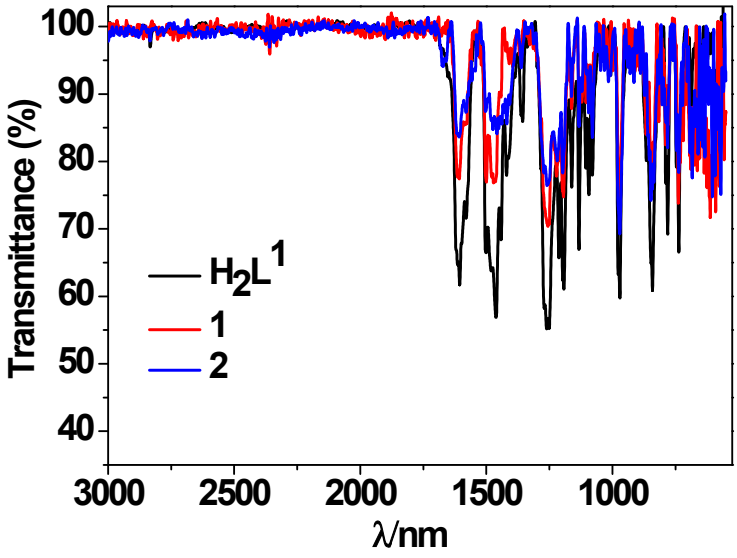


Figure S3. Infrared spectra of H_2L^1 and **1**-**2** .

5. The thermogravimetric analysis of 1-2

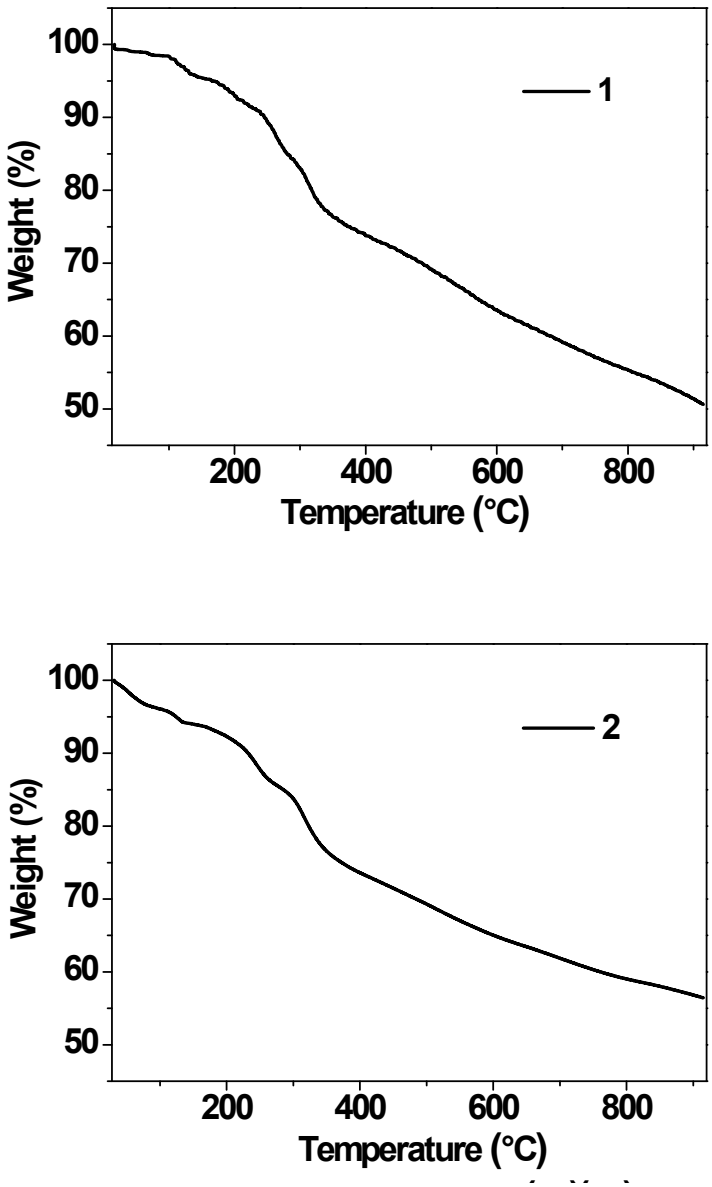


Figure S4. The thermogravimetric analysis of **1**-**2**.

6. UV-Vis spectra of the mixture of H_2L^1 and H_2L^2, and the clusters 1 and 2

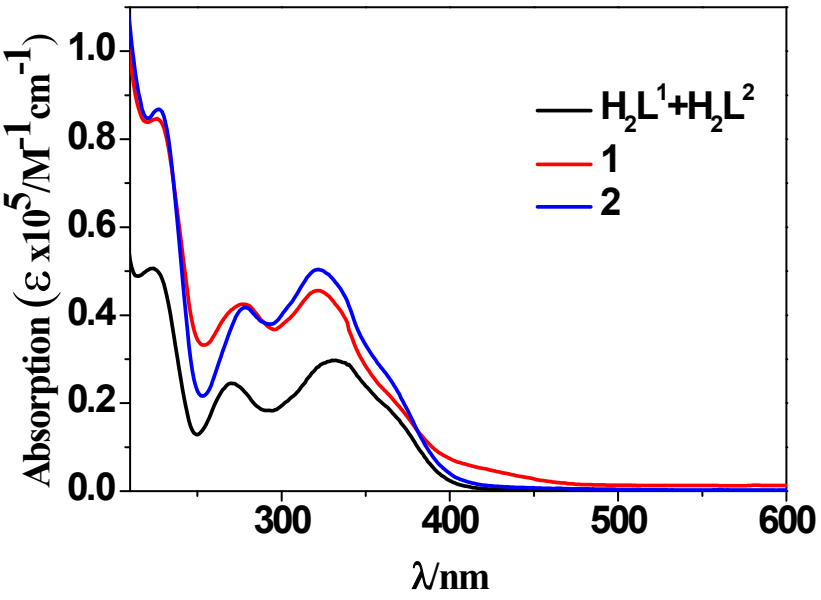


Figure S5. UV-Vis spectra of the mixture of H_2L^1 and H_2L^2, and the clusters **1** and **2** in CH_3CN.

7. The excitation and visible emission spectra of H_2L^1 and 2

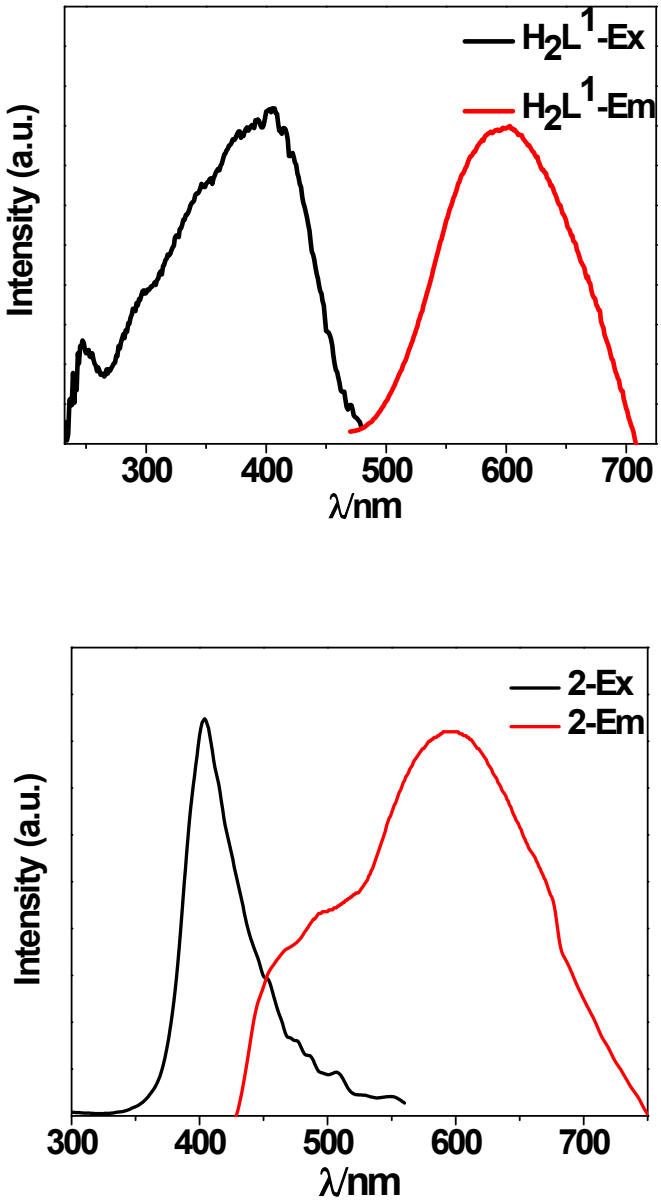


Figure S6. The excitation and visible emission spectra of H_2L^1 and **2** in CH_3CN.

8. The emission lifetimes of 1 and 2

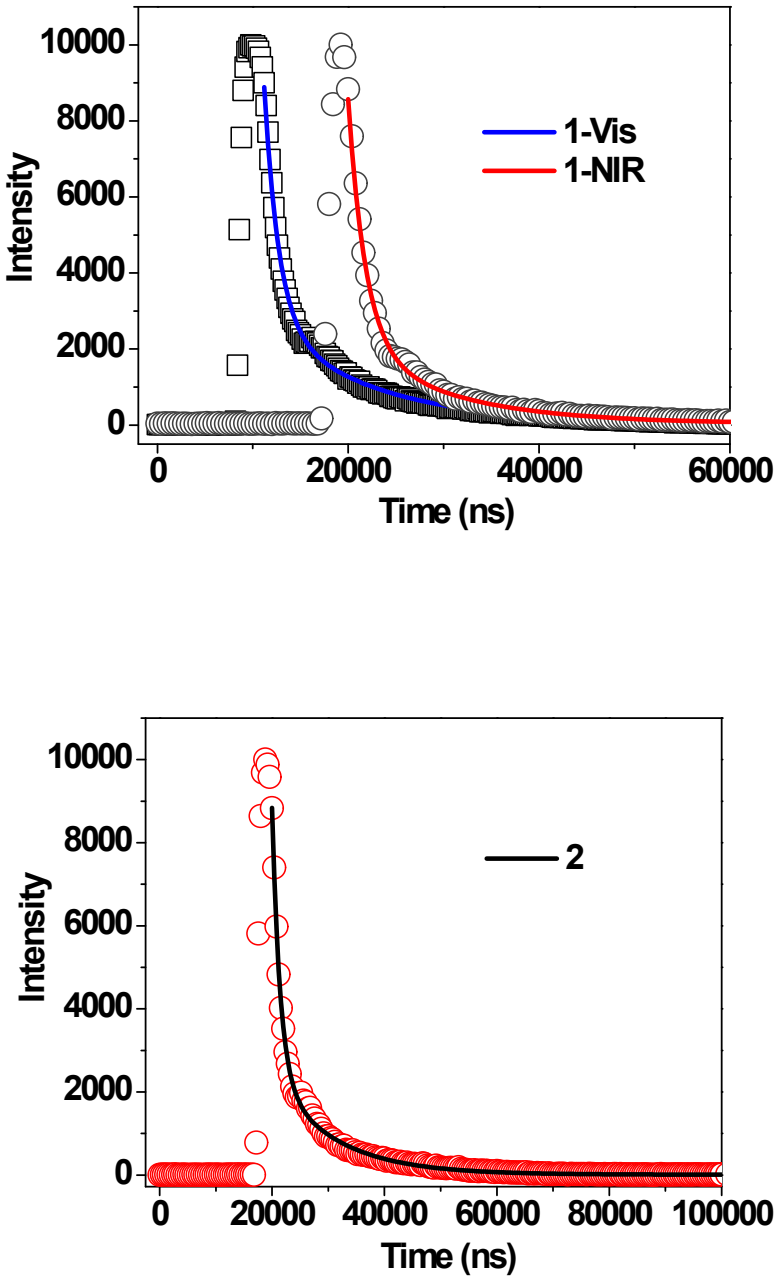
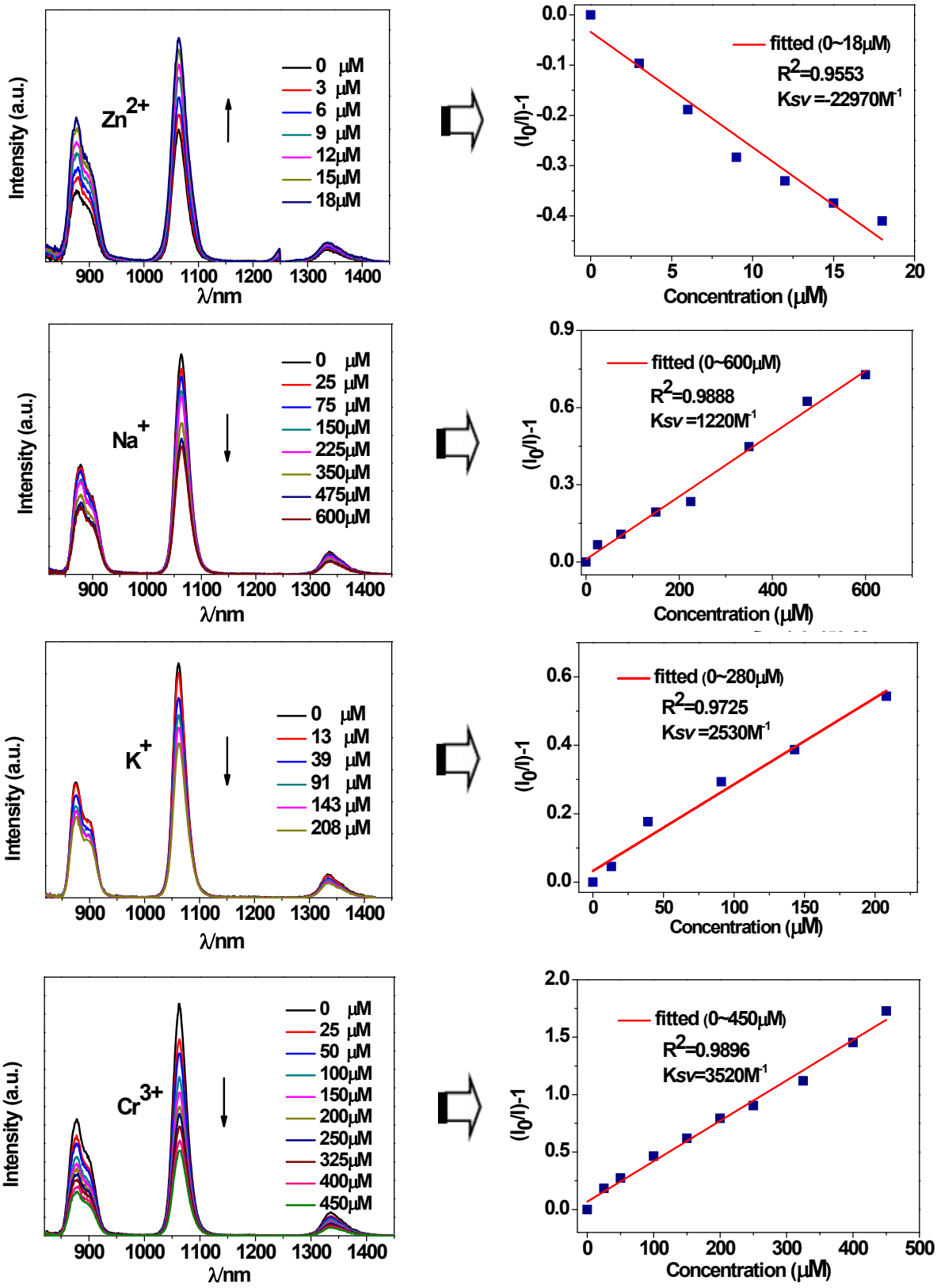
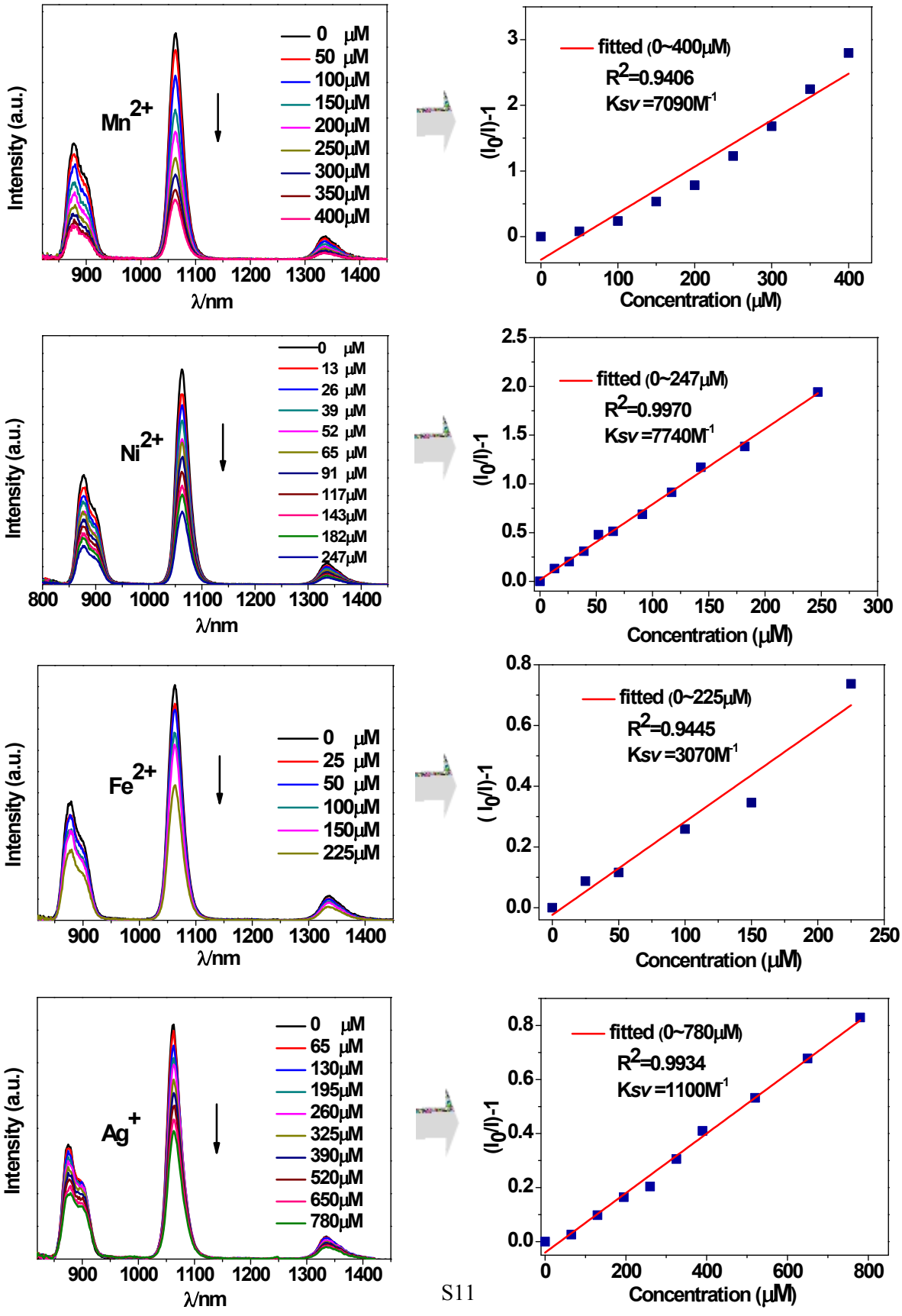


Figure S7. The visible and NIR emission lifetimes of **1** and **2** in CH_3CN.

9. NIR luminescent sensing of 1 towards metal ions




Intensity (a.u.)
λ/nm
Mn2+
0 μM
50 μM
100μM
150μM
200μM
250μM
300μM
350μM
400μM
fitted (0~400μM)
R2=0.9406
Ksv =7090M-1
(I0/I)-1
Concentration (μM)
Ni2+
0 μM
13 μM
26 μM
39 μM
52 μM
65 μM
91 μM
117μM
143μM
182μM
247μM
fitted (0~247μM)
R2=0.9970
Ksv =7740M-1
Fe2+
0 μM
25 μM
50 μM
100μM
150μM
225μM
fitted (0~225μM)
R2=0.9445
Ksv =3070M-1
Ag+
0 μM
65 μM
130μM
195μM
260μM
325μM
390μM
520μM
650μM
780μM
fitted (0~780μM)
R2=0.9934
Ksv =1100M-1

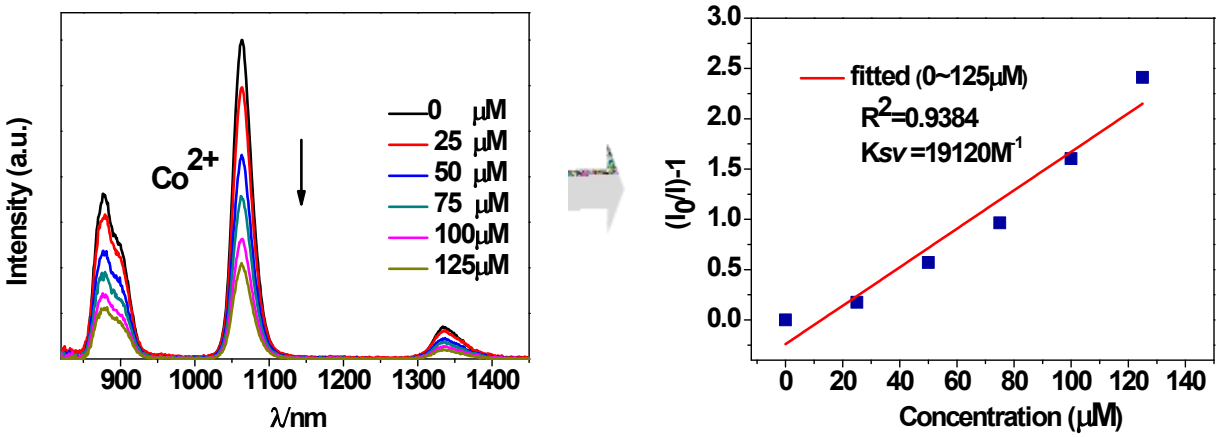


Figure S8. NIR luminescent sensing of **1** (60 μM) towards metal ions in DMF.

10. Visible emission response of 1 to metal ions and HMX

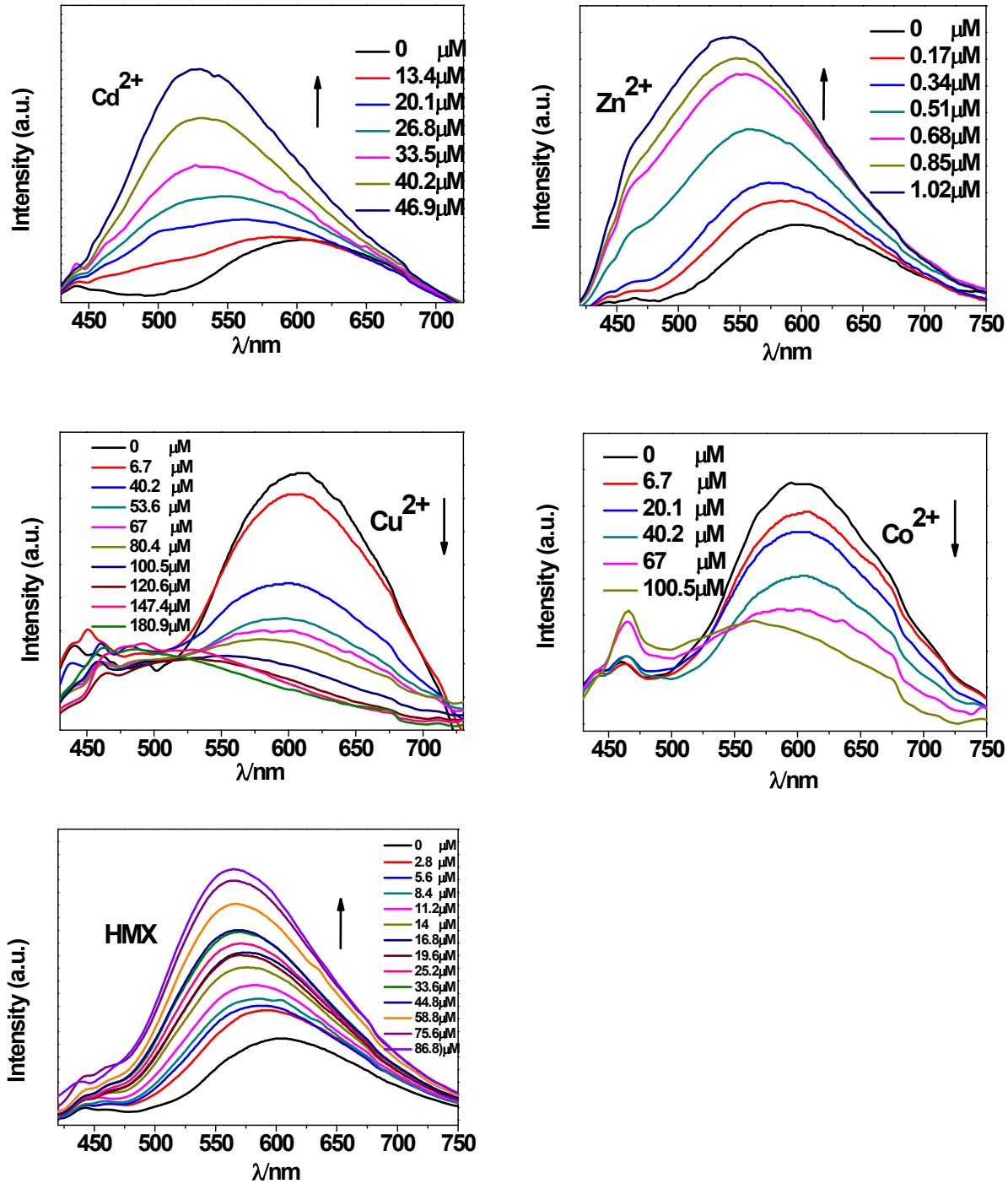


Figure S9. Visible emission response of **1** (60 μM) to metal ions and HMX

11. UV-Vis spectra of 1 with the additional of Zn^{2+} ion and HMX

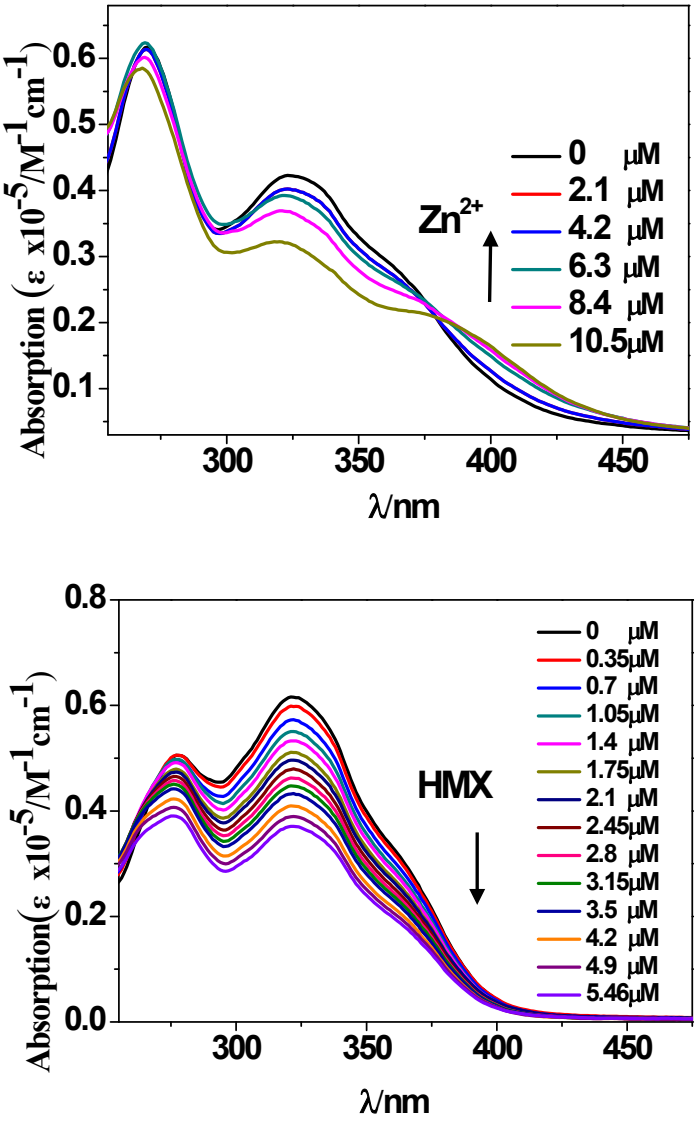
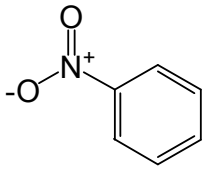
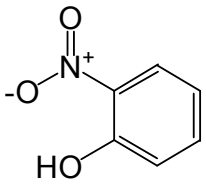


Figure S10. UV-Vis spectra of **1 (**3 μM**)** with the additional of different concentrations of Zn^{2+} ion and HMX in DMF.

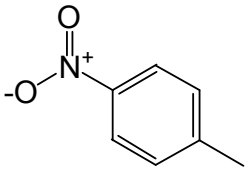
12. The structures of explosives



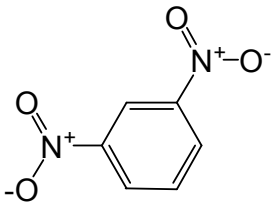
nitrobenzene (**NB**)



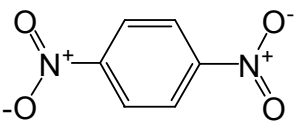
2-nitrophennol (**2-NP**)



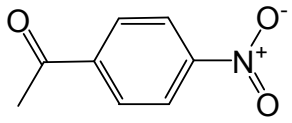
4-nitrotoluene (**4-NT**)



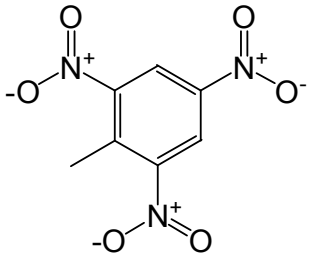
1,3-dinitrobenzene (**1,3-DNB**)



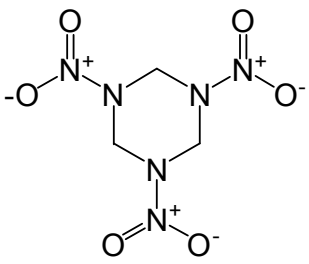
1,4-dinitrobenzene (**1,4-DNB**)



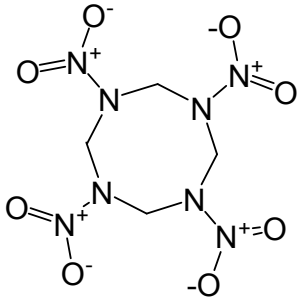
4-nitrobenzene acetophenone(**4-NBAP**)



2,4,6-trinitrotoluene (**TNT**)



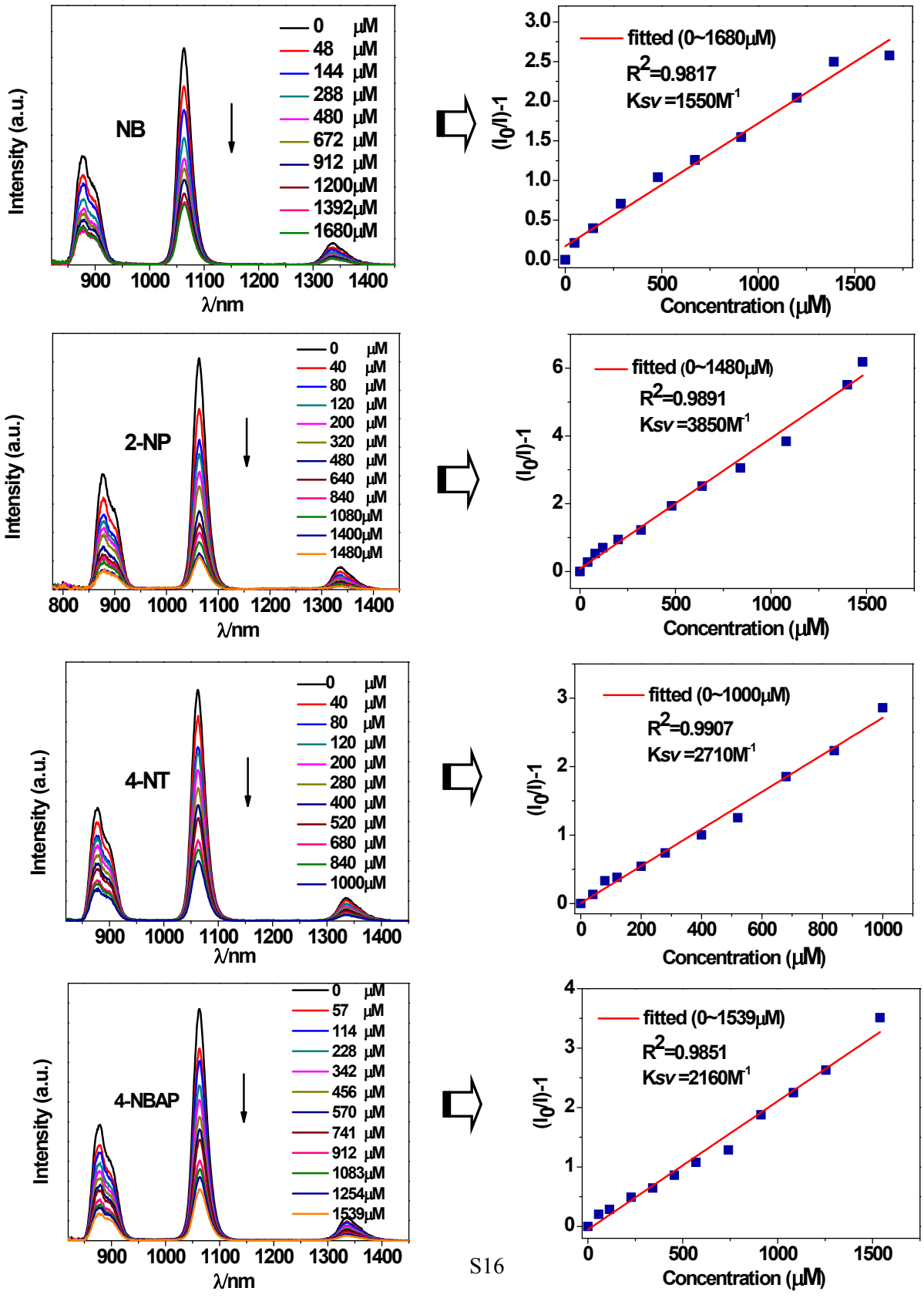
cyclotrimethylene trinitramine (**RDX**)



cyclotetramethylene tetranitramine (**HMX**)

Scheme S1. The structures of explosives.

13. NIR luminescence sensing of 1 towards nitro explosives



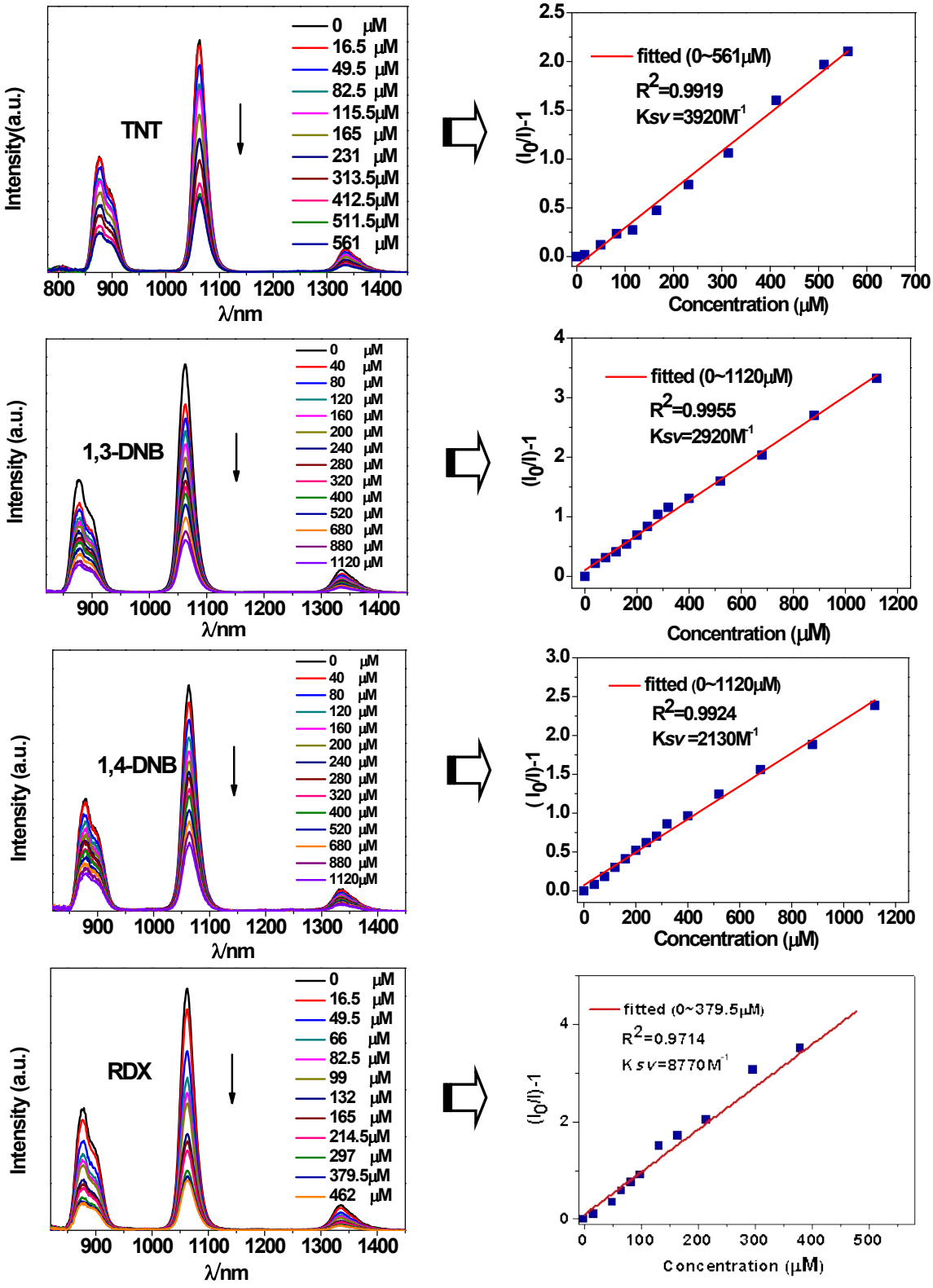


Figure S11. NIR luminescent sensing of **1** (60μM) towards nitro explosives in CH_3CN.

14. MS(ESI) spectrum of 1 before and after the addition of Cd^{2+} ion

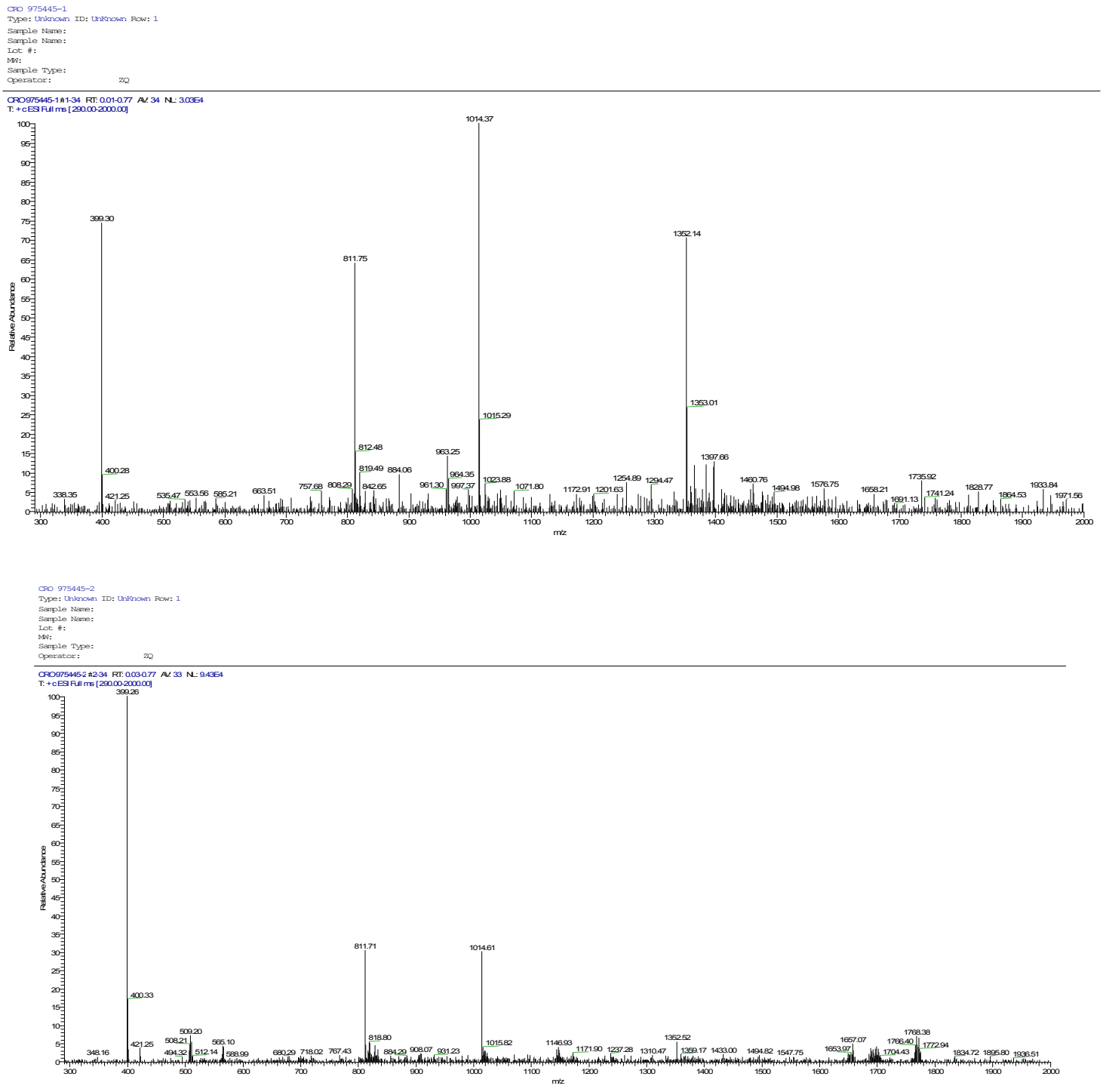


Figure S12. MS(ESI) spectra of **1** before (**a**) and after (**b**) the addition of Cd^{2+} ion.

15. X-Ray Crystallography

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

Nd(1)-O(27)	2.341(11)	Nd(6)-O(24)	2.540(11)
Nd(1)-O(34)	2.389(9)	Nd(6)-O(44)	2.599(12)
Nd(1)-O(50)	2.398(9)	Nd(7)-O(36)	2.363(12)
Nd(1)-O(33)	2.402(9)	Nd(7)-O(30)	2.367(10)
Nd(1)-O(35)	2.411(11)	Nd(7)-O(50)	2.379(10)
Nd(1)-O(31)	2.421(9)	Nd(7)-O(35)	2.409(11)
Nd(1)-O(22)	2.421(10)	Nd(7)-O(51)	2.411(10)
Nd(1)-O(20)	2.462(9)	Nd(7)-O(46)	2.418(11)
Nd(2)-O(2)	2.343(10)	Nd(7)-O(49)	2.437(10)
Nd(2)-O(43)	2.349(10)	Nd(7)-O(11)	2.445(11)
Nd(2)-O(33)	2.370(10)	Nd(8)-O(51)	2.351(10)
Nd(2)-O(41)	2.402(10)	Nd(8)-O(47)	2.367(12)
Nd(2)-O(6)	2.405(10)	Nd(8)-O(13)	2.390(14)
Nd(2)-O(42)	2.442(11)	Nd(8)-O(8)	2.392(13)
Nd(2)-O(34)	2.493(9)	Nd(8)-O(9)	2.455(14)
Nd(2)-N(1)	2.592(14)	Nd(8)-O(45)	2.461(13)
Nd(2)-O(7)	2.727(11)	Nd(8)-O(10)	2.492(12)
Nd(3)-O(51)	2.334(10)	Nd(8)-O(11)	2.588(11)
Nd(3)-O(18)	2.340(12)	Nd(8)-O(14)	2.629(11)
Nd(3)-O(16)	2.371(11)	Nd(9)-O(3)	2.308(12)
Nd(3)-O(12)	2.394(13)	Nd(9)-O(48)	2.331(13)
Nd(3)-O(20)	2.437(9)	Nd(9)-O(31)	2.335(10)
Nd(3)-O(14)	2.446(11)	Nd(9)-O(30)	2.400(11)
Nd(3)-O(22)	2.458(10)	Nd(9)-O(29)	2.408(17)
Nd(3)-O(21)	2.587(12)	Nd(9)-O(38)	2.409(13)
Nd(3)-O(13)	2.794(16)	Nd(9)-O(35)	2.426(11)
Nd(4)-O(15)	2.340(12)	Nd(9)-O(4)	2.575(11)
Nd(4)-O(20)	2.354(9)	O(27)-Nd(1)-O(34)	79.5(4)
Nd(4)-O(33)	2.373(9)	O(27)-Nd(1)-O(50)	141.5(4)
Nd(4)-O(2)	2.432(10)	O(34)-Nd(1)-O(50)	79.5(3)
Nd(4)-O(40)	2.439(12)	O(27)-Nd(1)-O(33)	81.1(3)
Nd(4)-O(19)	2.449(14)	O(34)-Nd(1)-O(33)	72.1(3)
Nd(4)-O(18)	2.481(12)	O(50)-Nd(1)-O(33)	121.7(3)
Nd(4)-O(41)	2.542(11)	O(27)-Nd(1)-O(35)	111.5(4)
Nd(4)-O(1)	2.598(11)	O(34)-Nd(1)-O(35)	143.1(4)
Nd(5)-O(37)	2.337(12)	O(50)-Nd(1)-O(35)	70.5(4)
Nd(5)-O(25)	2.361(11)	O(33)-Nd(1)-O(35)	142.6(4)
Nd(5)-O(31)	2.374(9)	O(27)-Nd(1)-O(31)	75.9(4)
Nd(5)-O(39)	2.382(13)	O(34)-Nd(1)-O(31)	81.7(3)
Nd(5)-O(50)	2.420(10)	O(50)-Nd(1)-O(31)	69.4(3)
Nd(5)-O(30)	2.424(10)	O(33)-Nd(1)-O(31)	147.8(3)
Nd(5)-O(24)	2.438(11)	O(35)-Nd(1)-O(31)	68.2(4)
Nd(5)-O(32)	2.446(11)	O(27)-Nd(1)-O(22)	81.8(4)
Nd(6)-O(34)	2.321(9)	O(34)-Nd(1)-O(22)	144.3(3)
Nd(6)-O(28)	2.369(11)	O(50)-Nd(1)-O(22)	131.2(3)
Nd(6)-O(5)	2.414(11)	O(33)-Nd(1)-O(22)	75.2(3)
Nd(6)-O(23)	2.418(11)	O(35)-Nd(1)-O(22)	72.3(4)
Nd(6)-O(6)	2.426(9)	O(31)-Nd(1)-O(22)	122.5(3)
Nd(6)-O(26)	2.444(11)	O(27)-Nd(1)-O(20)	141.1(3)
Nd(6)-O(43)	2.476(10)	O(34)-Nd(1)-O(20)	110.8(3)

O(50)-Nd(1)-O(20)	76.9(3)	O(20)-Nd(3)-O(14)	75.7(3)
O(33)-Nd(1)-O(20)	67.9(3)	O(51)-Nd(3)-O(22)	106.3(3)
O(35)-Nd(1)-O(20)	83.1(3)	O(18)-Nd(3)-O(22)	78.1(4)
O(31)-Nd(1)-O(20)	141.3(3)	O(16)-Nd(3)-O(22)	76.2(4)
O(22)-Nd(1)-O(20)	68.3(3)	O(12)-Nd(3)-O(22)	131.3(4)
O(2)-Nd(2)-O(43)	142.9(4)	O(20)-Nd(3)-O(22)	68.1(3)
O(2)-Nd(2)-O(33)	71.2(3)	O(14)-Nd(3)-O(22)	142.8(3)
O(43)-Nd(2)-O(33)	140.9(3)	O(51)-Nd(3)-O(21)	139.8(4)
O(2)-Nd(2)-O(41)	73.1(4)	O(18)-Nd(3)-O(21)	72.0(4)
O(43)-Nd(2)-O(41)	99.2(4)	O(16)-Nd(3)-O(21)	72.8(4)
O(33)-Nd(2)-O(41)	68.5(3)	O(12)-Nd(3)-O(21)	80.1(4)
O(2)-Nd(2)-O(6)	140.2(4)	O(20)-Nd(3)-O(21)	113.8(3)
O(43)-Nd(2)-O(6)	68.4(3)	O(14)-Nd(3)-O(21)	147.5(4)
O(33)-Nd(2)-O(6)	95.4(3)	O(22)-Nd(3)-O(21)	51.3(3)
O(41)-Nd(2)-O(6)	137.9(4)	O(51)-Nd(3)-O(13)	64.1(4)
O(2)-Nd(2)-O(42)	73.7(4)	O(18)-Nd(3)-O(13)	126.1(5)
O(43)-Nd(2)-O(42)	69.6(4)	O(16)-Nd(3)-O(13)	76.0(4)
O(33)-Nd(2)-O(42)	132.4(4)	O(12)-Nd(3)-O(13)	49.0(4)
O(41)-Nd(2)-O(42)	71.3(4)	O(20)-Nd(3)-O(13)	128.2(4)
O(6)-Nd(2)-O(42)	131.9(4)	O(14)-Nd(3)-O(13)	62.0(4)
O(2)-Nd(2)-O(34)	133.4(3)	O(22)-Nd(3)-O(13)	152.1(4)
O(43)-Nd(2)-O(34)	70.1(3)	O(21)-Nd(3)-O(13)	118.0(4)
O(33)-Nd(2)-O(34)	70.8(3)	O(15)-Nd(4)-O(20)	81.3(4)
O(41)-Nd(2)-O(34)	68.6(3)	O(15)-Nd(4)-O(33)	148.7(3)
O(6)-Nd(2)-O(34)	69.4(3)	O(20)-Nd(4)-O(33)	70.2(3)
O(42)-Nd(2)-O(34)	115.9(3)	O(15)-Nd(4)-O(2)	141.3(4)
O(2)-Nd(2)-N(1)	74.2(4)	O(20)-Nd(4)-O(2)	136.1(3)
O(43)-Nd(2)-N(1)	90.7(4)	O(33)-Nd(4)-O(2)	69.6(3)
O(33)-Nd(2)-N(1)	124.1(4)	O(15)-Nd(4)-O(40)	73.8(4)
O(41)-Nd(2)-N(1)	137.4(4)	O(20)-Nd(4)-O(40)	89.8(4)
O(6)-Nd(2)-N(1)	84.3(4)	O(33)-Nd(4)-O(40)	117.5(4)
O(42)-Nd(2)-N(1)	73.8(4)	O(2)-Nd(4)-O(40)	93.4(4)
O(34)-Nd(2)-N(1)	151.6(4)	O(15)-Nd(4)-O(19)	89.9(5)
O(2)-Nd(2)-O(7)	80.0(4)	O(20)-Nd(4)-O(19)	121.6(4)
O(43)-Nd(2)-O(7)	125.0(3)	O(33)-Nd(4)-O(19)	94.1(4)
O(33)-Nd(2)-O(7)	65.7(3)	O(2)-Nd(4)-O(19)	78.3(4)
O(41)-Nd(2)-O(7)	132.3(4)	O(40)-Nd(4)-O(19)	142.4(5)
O(6)-Nd(2)-O(7)	60.5(3)	O(15)-Nd(4)-O(18)	70.8(4)
O(42)-Nd(2)-O(7)	136.6(4)	O(20)-Nd(4)-O(18)	71.0(4)
O(34)-Nd(2)-O(7)	107.3(3)	O(33)-Nd(4)-O(18)	87.4(4)
N(1)-Nd(2)-O(7)	66.0(4)	O(2)-Nd(4)-O(18)	123.5(4)
O(51)-Nd(3)-O(18)	142.8(4)	O(40)-Nd(4)-O(18)	141.8(4)
O(51)-Nd(3)-O(16)	69.1(4)	O(19)-Nd(4)-O(18)	51.9(4)
O(18)-Nd(3)-O(16)	144.4(4)	O(15)-Nd(4)-O(41)	121.6(4)
O(51)-Nd(3)-O(12)	113.1(4)	O(20)-Nd(4)-O(41)	79.0(3)
O(18)-Nd(3)-O(12)	86.9(5)	O(33)-Nd(4)-O(41)	66.2(3)
O(16)-Nd(3)-O(12)	91.9(5)	O(2)-Nd(4)-O(41)	69.2(4)
O(51)-Nd(3)-O(20)	75.6(3)	O(40)-Nd(4)-O(41)	51.9(4)
O(18)-Nd(3)-O(20)	72.0(4)	O(19)-Nd(4)-O(41)	146.1(4)
O(16)-Nd(3)-O(20)	119.0(4)	O(18)-Nd(4)-O(41)	145.5(4)
O(12)-Nd(3)-O(20)	148.3(4)	O(15)-Nd(4)-O(1)	78.6(4)
O(51)-Nd(3)-O(14)	71.8(4)	O(20)-Nd(4)-O(1)	157.4(4)
O(18)-Nd(3)-O(14)	82.8(4)	O(33)-Nd(4)-O(1)	131.6(3)
O(16)-Nd(3)-O(14)	131.8(4)	O(2)-Nd(4)-O(1)	62.8(4)
O(12)-Nd(3)-O(14)	78.4(4)	O(40)-Nd(4)-O(1)	74.9(4)

O(19)-Nd(4)-O(1)	68.7(4)	O(23)-Nd(6)-O(24)	51.9(4)
O(18)-Nd(4)-O(1)	111.2(4)	O(6)-Nd(6)-O(24)	140.9(3)
O(41)-Nd(4)-O(1)	103.1(4)	O(26)-Nd(6)-O(24)	67.8(4)
O(37)-Nd(5)-O(25)	85.4(4)	O(43)-Nd(6)-O(24)	133.8(3)
O(37)-Nd(5)-O(31)	144.7(4)	O(34)-Nd(6)-O(44)	129.2(4)
O(25)-Nd(5)-O(31)	109.4(3)	O(28)-Nd(6)-O(44)	145.8(4)
O(37)-Nd(5)-O(39)	95.3(5)	O(5)-Nd(6)-O(44)	70.3(4)
O(25)-Nd(5)-O(39)	146.2(4)	O(23)-Nd(6)-O(44)	81.6(4)
O(31)-Nd(5)-O(39)	89.3(4)	O(6)-Nd(6)-O(44)	100.6(4)
O(37)-Nd(5)-O(50)	86.1(4)	O(26)-Nd(6)-O(44)	66.9(4)
O(25)-Nd(5)-O(50)	71.3(3)	O(43)-Nd(6)-O(44)	60.9(3)
O(31)-Nd(5)-O(50)	69.9(3)	O(24)-Nd(6)-O(44)	118.4(4)
O(39)-Nd(5)-O(50)	142.5(4)	O(36)-Nd(7)-O(30)	77.1(4)
O(37)-Nd(5)-O(30)	77.1(4)	O(36)-Nd(7)-O(50)	87.1(4)
O(25)-Nd(5)-O(30)	138.0(4)	O(30)-Nd(7)-O(50)	71.3(4)
O(31)-Nd(5)-O(30)	70.5(4)	O(36)-Nd(7)-O(35)	144.5(4)
O(39)-Nd(5)-O(30)	74.1(4)	O(30)-Nd(7)-O(35)	69.7(4)
O(50)-Nd(5)-O(30)	69.7(3)	O(50)-Nd(7)-O(35)	70.9(3)
O(37)-Nd(5)-O(24)	146.0(4)	O(36)-Nd(7)-O(51)	143.3(4)
O(25)-Nd(5)-O(24)	77.6(4)	O(30)-Nd(7)-O(51)	138.3(3)
O(31)-Nd(5)-O(24)	69.3(3)	O(50)-Nd(7)-O(51)	110.8(3)
O(39)-Nd(5)-O(24)	83.7(4)	O(35)-Nd(7)-O(51)	72.0(4)
O(50)-Nd(5)-O(24)	115.1(3)	O(36)-Nd(7)-O(46)	80.9(4)
O(30)-Nd(5)-O(24)	133.8(4)	O(30)-Nd(7)-O(46)	136.0(4)
O(37)-Nd(5)-O(32)	73.6(5)	O(50)-Nd(7)-O(46)	70.0(4)
O(25)-Nd(5)-O(32)	75.9(4)	O(35)-Nd(7)-O(46)	114.9(4)
O(31)-Nd(5)-O(32)	140.2(4)	O(51)-Nd(7)-O(46)	76.1(4)
O(39)-Nd(5)-O(32)	71.9(5)	O(36)-Nd(7)-O(49)	109.8(4)
O(50)-Nd(5)-O(32)	142.6(4)	O(30)-Nd(7)-O(49)	82.4(4)
O(30)-Nd(5)-O(32)	132.1(4)	O(50)-Nd(7)-O(49)	144.8(4)
O(24)-Nd(5)-O(32)	73.9(4)	O(35)-Nd(7)-O(49)	78.4(4)
O(34)-Nd(6)-O(28)	82.1(4)	O(51)-Nd(7)-O(49)	74.2(4)
O(34)-Nd(6)-O(5)	140.1(4)	O(46)-Nd(7)-O(49)	141.3(4)
O(28)-Nd(6)-O(5)	76.3(4)	O(36)-Nd(7)-O(11)	75.2(4)
O(34)-Nd(6)-O(23)	135.6(4)	O(30)-Nd(7)-O(11)	133.1(4)
O(28)-Nd(6)-O(23)	82.6(4)	O(50)-Nd(7)-O(11)	142.6(4)
O(5)-Nd(6)-O(23)	74.4(4)	O(35)-Nd(7)-O(11)	138.1(4)
O(34)-Nd(6)-O(6)	71.9(3)	O(51)-Nd(7)-O(11)	71.4(3)
O(28)-Nd(6)-O(6)	74.0(4)	O(46)-Nd(7)-O(11)	74.8(4)
O(5)-Nd(6)-O(6)	70.1(4)	O(49)-Nd(7)-O(11)	72.6(4)
O(23)-Nd(6)-O(6)	141.1(4)	O(51)-Nd(8)-O(47)	91.5(4)
O(34)-Nd(6)-O(26)	84.1(4)	O(51)-Nd(8)-O(13)	70.9(5)
O(28)-Nd(6)-O(26)	139.3(4)	O(47)-Nd(8)-O(13)	135.1(5)
O(5)-Nd(6)-O(26)	133.0(4)	O(51)-Nd(8)-O(8)	152.3(4)
O(23)-Nd(6)-O(26)	80.9(4)	O(47)-Nd(8)-O(8)	82.1(5)
O(6)-Nd(6)-O(26)	136.1(4)	O(13)-Nd(8)-O(8)	94.8(5)
O(34)-Nd(6)-O(43)	70.9(3)	O(51)-Nd(8)-O(9)	139.7(4)
O(28)-Nd(6)-O(43)	136.9(3)	O(47)-Nd(8)-O(9)	128.8(4)
O(5)-Nd(6)-O(43)	103.6(4)	O(13)-Nd(8)-O(9)	78.1(5)
O(23)-Nd(6)-O(43)	139.7(4)	O(8)-Nd(8)-O(9)	52.9(5)
O(6)-Nd(6)-O(43)	66.1(3)	O(51)-Nd(8)-O(45)	76.0(4)
O(26)-Nd(6)-O(43)	71.6(4)	O(47)-Nd(8)-O(45)	139.2(5)
O(34)-Nd(6)-O(24)	83.7(3)	O(13)-Nd(8)-O(45)	77.6(5)
O(28)-Nd(6)-O(24)	72.7(4)	O(8)-Nd(8)-O(45)	125.3(5)
O(5)-Nd(6)-O(24)	120.0(4)	O(9)-Nd(8)-O(45)	72.6(4)

O(51)-Nd(8)-O(10)	119.9(4)	O(3)-Nd(9)-O(30)	130.1(4)
O(47)-Nd(8)-O(10)	74.7(5)	O(48)-Nd(9)-O(30)	80.2(4)
O(13)-Nd(8)-O(10)	150.0(5)	O(31)-Nd(9)-O(30)	71.6(3)
O(8)-Nd(8)-O(10)	84.5(5)	O(3)-Nd(9)-O(29)	80.9(6)
O(9)-Nd(8)-O(10)	77.7(5)	O(48)-Nd(9)-O(29)	86.2(6)
O(45)-Nd(8)-O(10)	78.5(5)	O(31)-Nd(9)-O(29)	103.5(5)
O(51)-Nd(8)-O(11)	69.9(3)	O(30)-Nd(9)-O(29)	141.8(5)
O(47)-Nd(8)-O(11)	72.5(4)	O(3)-Nd(9)-O(38)	79.0(5)
O(13)-Nd(8)-O(11)	131.8(4)	O(48)-Nd(9)-O(38)	89.4(5)
O(8)-Nd(8)-O(11)	132.0(4)	O(31)-Nd(9)-O(38)	101.5(4)
O(9)-Nd(8)-O(11)	117.9(4)	O(30)-Nd(9)-O(38)	73.8(4)
O(45)-Nd(8)-O(11)	66.7(4)	O(29)-Nd(9)-O(38)	142.0(5)
O(10)-Nd(8)-O(11)	50.1(4)	O(3)-Nd(9)-O(35)	128.4(4)
O(51)-Nd(8)-O(14)	68.3(3)	O(48)-Nd(9)-O(35)	81.8(4)
O(47)-Nd(8)-O(14)	69.8(4)	O(31)-Nd(9)-O(35)	69.4(3)
O(13)-Nd(8)-O(14)	65.3(4)	O(30)-Nd(9)-O(35)	68.9(4)
O(8)-Nd(8)-O(14)	84.3(4)	O(29)-Nd(9)-O(35)	73.9(5)
O(9)-Nd(8)-O(14)	120.5(4)	O(38)-Nd(9)-O(35)	142.6(4)
O(45)-Nd(8)-O(14)	134.8(4)	O(3)-Nd(9)-O(4)	64.5(4)
O(10)-Nd(8)-O(14)	143.8(4)	O(48)-Nd(9)-O(4)	76.3(4)
O(11)-Nd(8)-O(14)	121.5(3)	O(31)-Nd(9)-O(4)	138.5(4)
O(3)-Nd(9)-O(48)	140.8(4)	O(30)-Nd(9)-O(4)	136.7(4)
O(3)-Nd(9)-O(31)	74.0(4)	O(29)-Nd(9)-O(4)	72.2(5)
O(48)-Nd(9)-O(31)	145.2(4)	O(38)-Nd(9)-O(4)	70.1(4)

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

Gd(1)-O(27)	2.275(11)	Gd(7)-O(35)	2.294(9)
Gd(1)-O(50)	2.309(10)	Gd(7)-O(36)	2.323(12)
Gd(1)-O(35)	2.341(10)	Gd(7)-O(50)	2.323(10)
Gd(1)-O(22)	2.364(12)	Gd(7)-O(30)	2.331(11)
Gd(1)-O(34)	2.373(11)	Gd(7)-O(46)	2.354(12)
Gd(1)-O(33)	2.390(11)	Gd(7)-O(51)	2.358(11)
Gd(1)-O(20)	2.405(10)	Gd(7)-O(49)	2.396(12)
Gd(1)-O(31)	2.415(10)	Gd(7)-O(11)	2.421(11)
Gd(2)-O(2)	2.288(12)	Gd(8)-O(51)	2.301(10)
Gd(2)-O(43)	2.306(11)	Gd(8)-O(13)	2.305(14)
Gd(2)-O(41)	2.329(10)	Gd(8)-O(8)	2.347(14)
Gd(2)-O(33)	2.340(11)	Gd(8)-O(47)	2.355(13)
Gd(2)-O(6)	2.372(12)	Gd(8)-O(10)	2.398(12)
Gd(2)-O(42)	2.412(12)	Gd(8)-O(45)	2.429(13)
Gd(2)-O(34)	2.431(10)	Gd(8)-O(9)	2.474(14)
Gd(2)-N(1)	2.592(14)	Gd(8)-O(11)	2.505(13)
Gd(2)-O(7)	2.694(14)	Gd(8)-O(14)	2.624(11)
Gd(3)-O(18)	2.268(12)	Gd(9)-O(3)	2.246(14)
Gd(3)-O(16)	2.304(14)	Gd(9)-O(48)	2.282(12)
Gd(3)-O(12)	2.329(13)	Gd(9)-O(31)	2.294(10)
Gd(3)-O(51)	2.348(10)	Gd(9)-O(30)	2.340(10)
Gd(3)-O(20)	2.393(11)	Gd(9)-O(38)	2.343(13)
Gd(3)-O(14)	2.419(12)	Gd(9)-O(29)	2.394(14)
Gd(3)-O(22)	2.442(13)	Gd(9)-O(35)	2.398(10)
Gd(3)-O(21)	2.472(14)	Gd(9)-O(4)	2.568(13)
Gd(3)-O(13)	2.924(15)	O(27)-Gd(1)-O(50)	141.5(4)
Gd(4)-O(15)	2.294(13)	O(27)-Gd(1)-O(35)	112.1(4)
Gd(4)-O(20)	2.319(11)	O(50)-Gd(1)-O(35)	67.2(4)
Gd(4)-O(33)	2.341(11)	O(27)-Gd(1)-O(22)	80.4(4)
Gd(4)-O(40)	2.372(12)	O(50)-Gd(1)-O(22)	131.2(4)
Gd(4)-O(2)	2.390(12)	O(35)-Gd(1)-O(22)	74.4(4)
Gd(4)-O(18)	2.444(12)	O(27)-Gd(1)-O(34)	80.3(4)
Gd(4)-O(19)	2.483(13)	O(50)-Gd(1)-O(34)	80.8(4)
Gd(4)-O(41)	2.505(12)	O(35)-Gd(1)-O(34)	142.0(4)
Gd(4)-O(1)	2.579(12)	O(22)-Gd(1)-O(34)	143.5(4)
Gd(5)-O(31)	2.255(10)	O(27)-Gd(1)-O(33)	81.2(4)
Gd(5)-O(37)	2.278(11)	O(50)-Gd(1)-O(33)	123.6(4)
Gd(5)-O(39)	2.312(13)	O(35)-Gd(1)-O(33)	143.4(4)
Gd(5)-O(25)	2.361(12)	O(22)-Gd(1)-O(33)	74.6(4)
Gd(5)-O(30)	2.374(12)	O(34)-Gd(1)-O(33)	71.9(4)
Gd(5)-O(50)	2.378(10)	O(27)-Gd(1)-O(20)	141.1(4)
Gd(5)-O(24)	2.400(11)	O(50)-Gd(1)-O(20)	77.3(3)
Gd(5)-O(32)	2.409(13)	O(35)-Gd(1)-O(20)	82.2(4)
Gd(6)-O(34)	2.280(10)	O(22)-Gd(1)-O(20)	68.7(4)
Gd(6)-O(26)	2.338(13)	O(34)-Gd(1)-O(20)	111.1(4)
Gd(6)-O(28)	2.343(11)	O(33)-Gd(1)-O(20)	68.6(4)
Gd(6)-O(23)	2.388(12)	O(27)-Gd(1)-O(31)	77.0(4)
Gd(6)-O(5)	2.396(11)	O(50)-Gd(1)-O(31)	67.2(4)
Gd(6)-O(43)	2.397(11)	O(35)-Gd(1)-O(31)	67.7(4)
Gd(6)-O(6)	2.429(13)	O(22)-Gd(1)-O(31)	123.4(4)
Gd(6)-O(24)	2.514(12)	O(34)-Gd(1)-O(31)	81.6(3)
Gd(6)-O(44)	2.615(13)	O(33)-Gd(1)-O(31)	148.0(4)

O(20)-Gd(1)-O(31)	140.0(3)	O(51)-Gd(3)-O(22)	107.4(4)
O(2)-Gd(2)-O(43)	144.9(4)	O(20)-Gd(3)-O(22)	67.6(4)
O(2)-Gd(2)-O(41)	74.5(4)	O(14)-Gd(3)-O(22)	143.2(4)
O(43)-Gd(2)-O(41)	100.1(4)	O(18)-Gd(3)-O(21)	72.7(4)
O(2)-Gd(2)-O(33)	69.9(4)	O(16)-Gd(3)-O(21)	72.8(5)
O(43)-Gd(2)-O(33)	141.4(4)	O(12)-Gd(3)-O(21)	79.9(5)
O(41)-Gd(2)-O(33)	68.8(4)	O(51)-Gd(3)-O(21)	140.0(4)
O(2)-Gd(2)-O(6)	137.2(5)	O(20)-Gd(3)-O(21)	114.2(4)
O(43)-Gd(2)-O(6)	68.8(4)	O(14)-Gd(3)-O(21)	146.8(4)
O(41)-Gd(2)-O(6)	137.9(4)	O(22)-Gd(3)-O(21)	52.1(4)
O(33)-Gd(2)-O(6)	94.3(4)	O(18)-Gd(3)-O(13)	125.6(4)
O(2)-Gd(2)-O(42)	74.2(5)	O(16)-Gd(3)-O(13)	75.7(4)
O(43)-Gd(2)-O(42)	71.1(4)	O(12)-Gd(3)-O(13)	48.0(4)
O(41)-Gd(2)-O(42)	73.0(4)	O(51)-Gd(3)-O(13)	62.5(4)
O(33)-Gd(2)-O(42)	132.9(4)	O(20)-Gd(3)-O(13)	127.7(4)
O(6)-Gd(2)-O(42)	132.7(4)	O(14)-Gd(3)-O(13)	60.7(4)
O(2)-Gd(2)-O(34)	133.5(4)	O(22)-Gd(3)-O(13)	153.0(4)
O(43)-Gd(2)-O(34)	69.9(4)	O(21)-Gd(3)-O(13)	118.1(4)
O(41)-Gd(2)-O(34)	67.7(4)	C(87)-Gd(3)-O(13)	140.0(5)
O(33)-Gd(2)-O(34)	71.8(4)	O(15)-Gd(4)-O(20)	82.8(4)
O(6)-Gd(2)-O(34)	70.4(4)	O(15)-Gd(4)-O(33)	150.0(4)
O(42)-Gd(2)-O(34)	117.2(4)	O(20)-Gd(4)-O(33)	70.9(4)
O(2)-Gd(2)-N(1)	75.2(4)	O(15)-Gd(4)-O(40)	74.4(5)
O(43)-Gd(2)-N(1)	89.3(4)	O(20)-Gd(4)-O(40)	90.5(4)
O(41)-Gd(2)-N(1)	139.1(4)	O(33)-Gd(4)-O(40)	118.7(4)
O(33)-Gd(2)-N(1)	123.8(4)	O(15)-Gd(4)-O(2)	140.8(4)
O(6)-Gd(2)-N(1)	82.6(4)	O(20)-Gd(4)-O(2)	135.6(4)
O(42)-Gd(2)-N(1)	72.7(5)	O(33)-Gd(4)-O(2)	68.2(4)
O(34)-Gd(2)-N(1)	150.4(4)	O(40)-Gd(4)-O(2)	94.4(5)
O(2)-Gd(2)-O(7)	76.7(4)	O(15)-Gd(4)-O(18)	70.0(4)
O(43)-Gd(2)-O(7)	126.1(4)	O(20)-Gd(4)-O(18)	69.9(4)
O(41)-Gd(2)-O(7)	129.9(4)	O(33)-Gd(4)-O(18)	87.3(4)
O(33)-Gd(2)-O(7)	63.2(4)	O(40)-Gd(4)-O(18)	140.9(4)
O(6)-Gd(2)-O(7)	60.9(4)	O(2)-Gd(4)-O(18)	123.5(4)
O(42)-Gd(2)-O(7)	134.9(4)	O(15)-Gd(4)-O(19)	89.6(5)
O(34)-Gd(2)-O(7)	107.9(4)	O(20)-Gd(4)-O(19)	121.2(4)
N(1)-Gd(2)-O(7)	66.9(4)	O(33)-Gd(4)-O(19)	92.1(4)
O(18)-Gd(3)-O(16)	145.3(5)	O(40)-Gd(4)-O(19)	142.7(5)
O(18)-Gd(3)-O(12)	88.7(5)	O(2)-Gd(4)-O(19)	77.0(4)
O(16)-Gd(3)-O(12)	89.5(5)	O(18)-Gd(4)-O(19)	53.0(4)
O(18)-Gd(3)-O(51)	143.1(4)	O(15)-Gd(4)-O(41)	123.5(4)
O(16)-Gd(3)-O(51)	68.8(4)	O(20)-Gd(4)-O(41)	78.7(4)
O(12)-Gd(3)-O(51)	110.4(4)	O(33)-Gd(4)-O(41)	65.9(4)
O(18)-Gd(3)-O(20)	71.7(4)	O(40)-Gd(4)-O(41)	53.1(4)
O(16)-Gd(3)-O(20)	119.8(4)	O(2)-Gd(4)-O(41)	69.6(4)
O(12)-Gd(3)-O(20)	149.7(4)	O(18)-Gd(4)-O(41)	144.1(4)
O(51)-Gd(3)-O(20)	76.9(4)	O(19)-Gd(4)-O(41)	144.8(4)
O(18)-Gd(3)-O(14)	82.3(4)	O(15)-Gd(4)-O(1)	76.1(4)
O(16)-Gd(3)-O(14)	131.0(4)	O(20)-Gd(4)-O(1)	156.8(4)
O(12)-Gd(3)-O(14)	78.0(5)	O(33)-Gd(4)-O(1)	131.9(4)
O(51)-Gd(3)-O(14)	71.8(4)	O(40)-Gd(4)-O(1)	75.0(4)
O(20)-Gd(3)-O(14)	76.8(4)	O(2)-Gd(4)-O(1)	64.8(4)
O(18)-Gd(3)-O(22)	78.3(4)	O(18)-Gd(4)-O(1)	110.4(4)
O(16)-Gd(3)-O(22)	77.4(4)	O(19)-Gd(4)-O(1)	68.5(4)
O(12)-Gd(3)-O(22)	131.9(5)	O(41)-Gd(4)-O(1)	105.3(4)

O(31)-Gd(5)-O(37)	145.9(4)	O(6)-Gd(6)-O(24)	139.9(4)
O(31)-Gd(5)-O(39)	87.7(4)	O(34)-Gd(6)-O(44)	129.8(4)
O(37)-Gd(5)-O(39)	96.9(5)	O(26)-Gd(6)-O(44)	65.5(4)
O(31)-Gd(5)-O(25)	110.4(4)	O(28)-Gd(6)-O(44)	145.7(4)
O(37)-Gd(5)-O(25)	84.0(5)	O(23)-Gd(6)-O(44)	79.0(4)
O(39)-Gd(5)-O(25)	146.2(5)	O(5)-Gd(6)-O(44)	70.6(4)
O(31)-Gd(5)-O(30)	69.5(3)	O(43)-Gd(6)-O(44)	61.9(4)
O(37)-Gd(5)-O(30)	79.2(4)	O(6)-Gd(6)-O(44)	102.3(4)
O(39)-Gd(5)-O(30)	74.4(4)	O(24)-Gd(6)-O(44)	117.7(4)
O(25)-Gd(5)-O(30)	138.1(4)	O(35)-Gd(7)-O(36)	143.8(4)
O(31)-Gd(5)-O(50)	68.7(4)	O(35)-Gd(7)-O(50)	67.7(4)
O(37)-Gd(5)-O(50)	87.7(4)	O(36)-Gd(7)-O(50)	88.4(4)
O(39)-Gd(5)-O(50)	140.8(4)	O(35)-Gd(7)-O(30)	68.5(4)
O(25)-Gd(5)-O(50)	73.0(4)	O(36)-Gd(7)-O(30)	78.1(4)
O(30)-Gd(5)-O(50)	68.2(4)	O(50)-Gd(7)-O(30)	69.9(4)
O(31)-Gd(5)-O(24)	69.3(4)	O(35)-Gd(7)-O(46)	113.4(4)
O(37)-Gd(5)-O(24)	144.7(4)	O(36)-Gd(7)-O(46)	80.7(5)
O(39)-Gd(5)-O(24)	83.0(5)	O(50)-Gd(7)-O(46)	69.9(4)
O(25)-Gd(5)-O(24)	77.5(4)	O(30)-Gd(7)-O(46)	134.6(4)
O(30)-Gd(5)-O(24)	133.3(4)	O(35)-Gd(7)-O(51)	74.0(4)
O(50)-Gd(5)-O(24)	114.5(4)	O(36)-Gd(7)-O(51)	142.0(4)
O(31)-Gd(5)-O(32)	140.9(4)	O(50)-Gd(7)-O(51)	112.2(3)
O(37)-Gd(5)-O(32)	71.6(5)	O(30)-Gd(7)-O(51)	138.1(4)
O(39)-Gd(5)-O(32)	72.8(5)	O(46)-Gd(7)-O(51)	77.5(4)
O(25)-Gd(5)-O(32)	75.5(4)	O(35)-Gd(7)-O(49)	81.0(4)
O(30)-Gd(5)-O(32)	132.4(4)	O(36)-Gd(7)-O(49)	109.1(5)
O(50)-Gd(5)-O(32)	143.8(4)	O(50)-Gd(7)-O(49)	144.5(4)
O(24)-Gd(5)-O(32)	74.8(4)	O(30)-Gd(7)-O(49)	83.4(4)
O(34)-Gd(6)-O(26)	84.6(4)	O(46)-Gd(7)-O(49)	141.7(4)
O(34)-Gd(6)-O(28)	82.3(4)	O(51)-Gd(7)-O(49)	72.7(4)
O(26)-Gd(6)-O(28)	139.7(4)	O(35)-Gd(7)-O(11)	139.3(4)
O(34)-Gd(6)-O(23)	135.9(4)	O(36)-Gd(7)-O(11)	75.2(4)
O(26)-Gd(6)-O(23)	79.3(4)	O(50)-Gd(7)-O(11)	143.9(4)
O(28)-Gd(6)-O(23)	84.1(4)	O(30)-Gd(7)-O(11)	134.5(4)
O(34)-Gd(6)-O(5)	140.3(4)	O(46)-Gd(7)-O(11)	75.7(4)
O(26)-Gd(6)-O(5)	132.3(4)	O(51)-Gd(7)-O(11)	69.4(4)
O(28)-Gd(6)-O(5)	76.2(4)	O(49)-Gd(7)-O(11)	71.6(4)
O(23)-Gd(6)-O(5)	74.7(4)	O(51)-Gd(8)-O(10)	121.1(4)
O(34)-Gd(6)-O(43)	71.0(4)	O(13)-Gd(8)-O(10)	148.7(5)
O(26)-Gd(6)-O(43)	71.5(4)	O(8)-Gd(8)-O(10)	83.1(5)
O(28)-Gd(6)-O(43)	137.0(4)	O(47)-Gd(8)-O(10)	73.3(5)
O(23)-Gd(6)-O(43)	138.1(4)	O(51)-Gd(8)-O(45)	75.3(4)
O(5)-Gd(6)-O(43)	103.6(4)	O(13)-Gd(8)-O(45)	77.7(5)
O(34)-Gd(6)-O(6)	72.0(4)	O(8)-Gd(8)-O(45)	125.8(5)
O(26)-Gd(6)-O(6)	136.6(4)	O(47)-Gd(8)-O(45)	138.6(5)
O(28)-Gd(6)-O(6)	73.7(4)	O(10)-Gd(8)-O(45)	80.4(5)
O(23)-Gd(6)-O(6)	141.9(4)	O(51)-Gd(8)-O(9)	140.8(4)
O(5)-Gd(6)-O(6)	70.1(4)	O(13)-Gd(8)-O(9)	76.5(5)
O(43)-Gd(6)-O(6)	66.5(4)	O(8)-Gd(8)-O(9)	52.5(5)
O(34)-Gd(6)-O(24)	83.0(4)	O(47)-Gd(8)-O(9)	127.6(5)
O(26)-Gd(6)-O(24)	68.5(4)	O(10)-Gd(8)-O(9)	76.0(5)
O(28)-Gd(6)-O(24)	72.2(4)	O(45)-Gd(8)-O(9)	73.5(5)
O(23)-Gd(6)-O(24)	52.9(4)	O(51)-Gd(8)-O(11)	68.9(4)
O(5)-Gd(6)-O(24)	120.2(4)	O(13)-Gd(8)-O(11)	134.0(5)
O(43)-Gd(6)-O(24)	133.8(4)	O(8)-Gd(8)-O(11)	132.8(5)

O(47)-Gd(8)-O(11)	71.4(4)	O(31)-Gd(9)-O(38)	100.9(4)
O(10)-Gd(8)-O(11)	52.3(4)	O(30)-Gd(9)-O(38)	74.6(4)
O(45)-Gd(8)-O(11)	67.3(4)	O(3)-Gd(9)-O(29)	80.2(5)
O(9)-Gd(8)-O(11)	118.2(4)	O(48)-Gd(9)-O(29)	88.2(5)
O(51)-Gd(8)-O(14)	68.8(4)	O(31)-Gd(9)-O(29)	103.7(5)
O(13)-Gd(8)-O(14)	67.0(4)	O(30)-Gd(9)-O(29)	142.5(4)
O(8)-Gd(8)-O(14)	83.8(4)	O(38)-Gd(9)-O(29)	141.3(5)
O(47)-Gd(8)-O(14)	69.8(4)	O(3)-Gd(9)-O(35)	130.0(4)
O(10)-Gd(8)-O(14)	142.1(4)	O(48)-Gd(9)-O(35)	82.6(4)
O(45)-Gd(8)-O(14)	134.8(4)	O(31)-Gd(9)-O(35)	68.7(4)
O(9)-Gd(8)-O(14)	121.3(4)	O(30)-Gd(9)-O(35)	66.6(3)
O(11)-Gd(8)-O(14)	120.3(4)	O(38)-Gd(9)-O(35)	141.0(4)
O(3)-Gd(9)-O(48)	140.1(5)	O(29)-Gd(9)-O(35)	76.5(4)
O(3)-Gd(9)-O(31)	75.0(4)	O(3)-Gd(9)-O(4)	65.4(5)
O(48)-Gd(9)-O(31)	144.9(4)	O(48)-Gd(9)-O(4)	74.7(5)
O(3)-Gd(9)-O(30)	129.1(5)	O(31)-Gd(9)-O(4)	140.2(4)
O(48)-Gd(9)-O(30)	81.0(4)	O(30)-Gd(9)-O(4)	136.1(4)
O(31)-Gd(9)-O(30)	69.4(4)	O(38)-Gd(9)-O(4)	68.9(5)
O(3)-Gd(9)-O(38)	77.9(5)	O(29)-Gd(9)-O(4)	73.1(5)
O(48)-Gd(9)-O(38)	88.6(5)	O(35)-Gd(9)-O(4)	142.3(4)