Supporting Information

Construction of Luminescent high-nuclearity Zn-Ln Rectangular Nanoclusters with Flexible Long-chain Schiff Base Ligands

Shiqing Wang, Xiaoping Yang, Ting Zhu, Le Bo, Ruifu Wang, Shaoming Huang, Chengri Wang, Dongmei Jiang, Hongfen Chen and Richard A. Jones

Contents

1. General Procedures

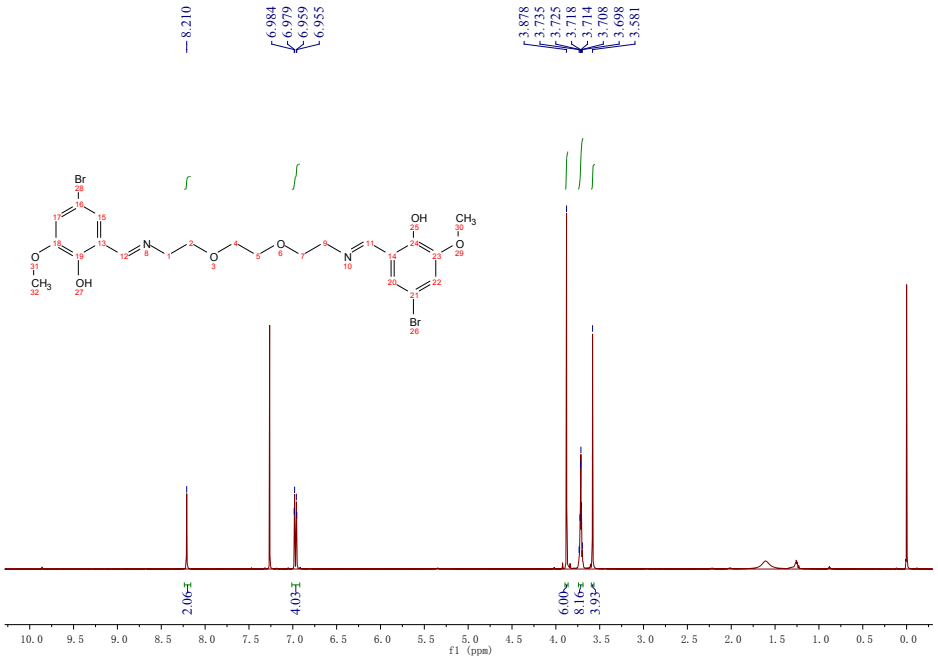
All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Metal salts and other solvents were purchased from Aldrich and used directly without further purification. The Schiff-base ligands $H_2L^{1,2}$ were prepared according to well-established procedures.[1] Physical measurements: NMR: AVANCE III AV500. 500 spectrometer (^{1}H, 500 MHz) at 298 K; Powder XRD: Rigaku R-AXIS RAPID II; IR: Nicolet IR 200 FTIR spectrometer. Elemental analyses (C, H, N) were carried out on a EURO EA3000 elemental analysis. Melting points were obtained in sealed glass capillaries under dinitrogen and

are uncorrected. Conductivity measurements were carried out with a DDS-11 conductivity bridge for 10^{-3} M solutions in CH_3CN. Absorption spectra were obtained on a UV-3600 spectrophotometer, and excitation and emission spectra on a FLS 980 fluorimeter.

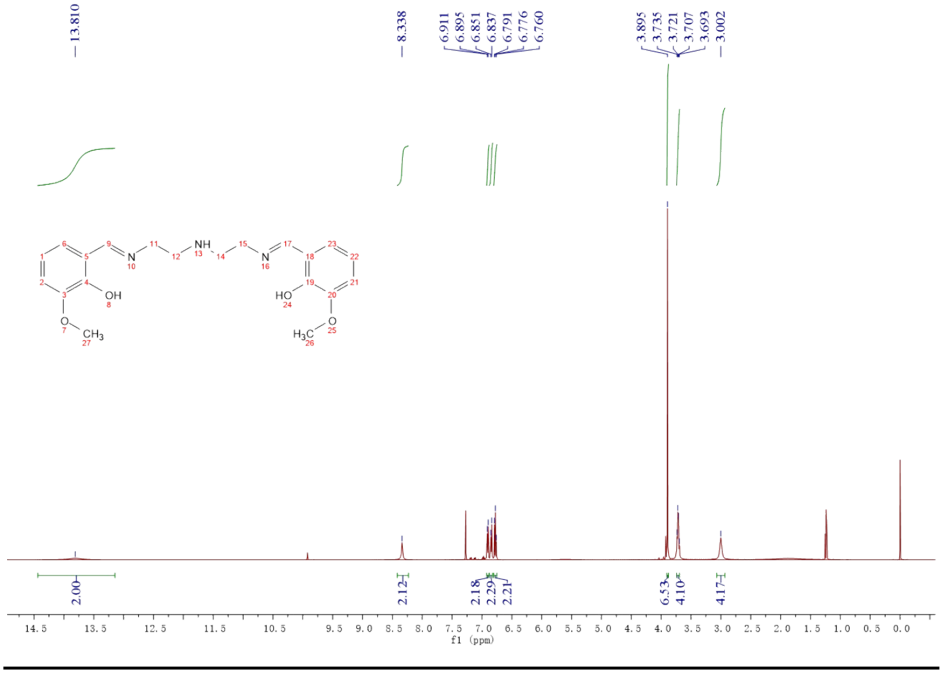
2. Synthesis of $H_2L^{1,2}$ and 1-3

Synthesis of ligand H_2L^1. 5-bromo-2-hydroxy-3-methoxybenzaldehyde (6.8 mmol, 1.5831 g) was dissolved in 10 mL EtOH, and a solution of 1,8-diamino-3,6-dioxaoctane (3.4 mmol, 0.5075 g) in 20 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 2.5 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 a yellow product. Yield (based on 1,8-diamino-3,6-dioxaoctane): 6.21g (82.08%). m. p. = 39.6 ^oC. ^1H NMR (500 MHz, $CDCl_3$): 8.210 (2H), 6.955-6.984 (4H), 3.878 (6H), 3.698-3.735 (8H), 3.581 (4H). Elemental analysis: Found: C, 45.54; H, 4.46; N, 4.78%; Calc. for $C_{22}H_{28}N_2O_6Br_2$: C,45.84; H, 4.91; N, 4.86%. IR (CH_3CN, cm^{-1}): 1640 (m), 1450 (m), 1250 (s), 1180 (w), 1110 (s), 1080(m), 964 (m), 903(w), 845 (w), 775 (m), 740 (s).

Synthesis of ligand H_2L^2. 2-Hydroxy-3-methoxybenzaldehyde (9.6 mmol, 1.4512 g) was dissolved in 10 mL EtOH, and a solution of diethylenetriamine (4.6 mmol, 0.4775 g) in 20 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 2.5 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 a yellow product. Yield (based on 1,8-diamino-3,6-dioxaoctane): 5.96g (97.5%). m. p. = 42.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$): 8.338 (2H), 6.760-6.911 (6H), 3.985 (4H), 3.693-3.735 (6H), 3.002 (4H). Elemental analysis: Found: C, 45,69; H, 5.08; N, 5.07%; Calc. for $C_{20}H_{24}N_3O_4$: C, 45.84; H, 4.91; N, 4,86%. IR (CH_3CN, cm^{-1}): 1630 (m), 1470 (m), 1250 (s), 1180 (w), 1120 (s), 1080(m), 964 (m), 903(w), 845 (w), 775 (m), 735 (s).



(a)



(b)

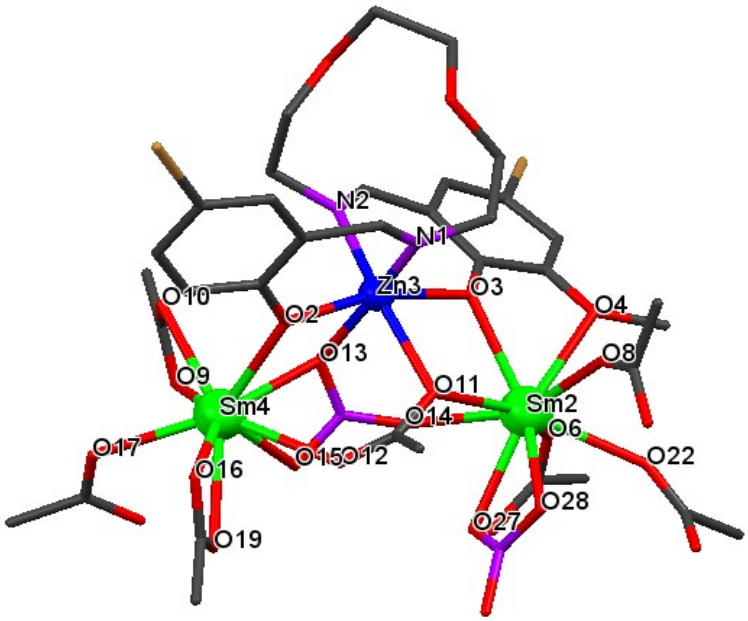
Figure S1. ^{1}H NMR spectra of H_2L^1 and H_2L^2.

$[Sm_8Zn_6(L^1)_2(OAc)_{20}(O)_2(NO_3)_4(OH)_4]$ (**1**). In the presence of $N(CH_2CH_3)_3$ (1.08 mmol/L, 1 mL), a mixture of the Schiff-base ligand H_2L^1 (0.4 mmol, 0.148 g) with $Zn(OAc)_2{\cdot}2H_2O$ (0.4 mmol, 0.0878 g) and $Sm(NO_3)_3{\cdot}6H_2O$ (0.4 mmol, 0.1778 g) in MeOH/EtOH (1:2, 15 ml) was stirred and heated under reflux for 10 minutes. The mixture was allowed to cool and then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale yellow crystals of **1** were obtained after one week. Yield (based on $Sm(NO_3)_3{\cdot}6H_2O$): 0.036 g (20 %). m.p. > 229 ℃ (dec.). Elemental analysis: Found: C, 22.59; H, 2.63; N, 2.13 %. Calc. for $C_{62}H_{74}Zn_6N_6Sm_8O_{66}(EtOH)_5(H_2O)$: C, 22.53; H, 2.87; N, 2.19 %. IR (CH_3OH, cm^{-1}): 1535 (s), 1400 (s), 1340 (w), 1286 (w), 843 (m), 763 (m), 748 (m), 690 (m).

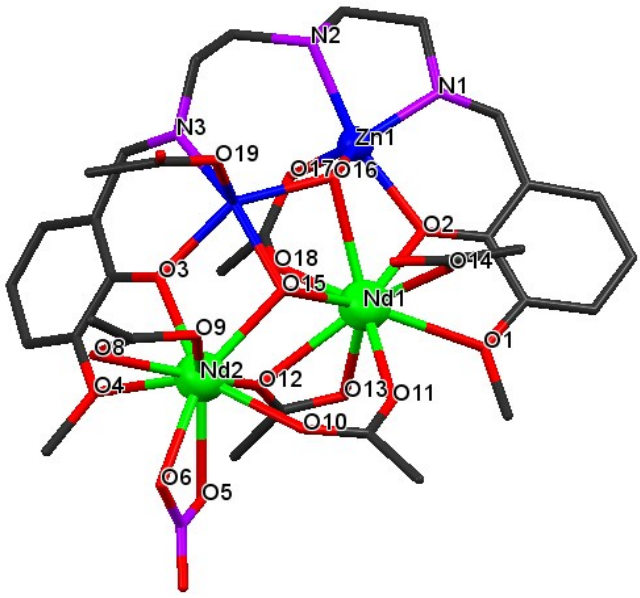
$[Nd_8Zn_6(L^1)_2(OAc)_{20}(O)_2(NO_3)_4(OH)_4]$ (**2**). The procedure was the same as that for **1** using $Nd(NO_3)_3.6H_2O$ (0.4 mmol, 0.1753 g). Purple crystals of **2** were formed after two weeks. Yield (based on $Nd(NO_3)_3{\cdot}6H_2O$): 0.021 g (24 %). m.p. > 231 ℃ (dec.). Elemental analysis: Found: C, 19.24; H, 2.87; N, 1.44 %. Calc. for $C_{62}H_{74}Zn_6N_6Nd_8O_{66}(EtOH)_7(MeOH)(H_2O)_5$: C, 18.82; H, 2.40; N, 1.88 %. IR (CH_3OH, cm^{-1}): 1535 (s), 1406 (s), 1346 (w), 1286 (w), 1021 (w), 839 (m), 763 (m), 746 (m), 690 (m).

$[Nd_4Zn_4(L^2)_2(OAc)_{10}(NO_3)_2(OH)_4]$ (**3**). The procedure was the same as that for **1** using $Nd(NO_3)_3{\cdot}6H_2O$ (0.4 mmol, 0.1753 g) and H_2L^2 (0.4 mmol , 0.1481 g). Yellow crystals of **3** were formed after one week. Yield (based on $Nd(NO_3)_3{\cdot}6H_2O$): 0.1084 g (46 %). m.p. > 266 ℃ (dec.). Elemental analysis: Found: C, 30.62; H, 3.81; N, 4.23 %. Calc. for $C_{60}H_{82}Zn_4N_8Nd_4O_{38}(EtOH)_7$: C, 30.96; H, 3.87; N, 4.66 %. IR (CH_3OH, cm^{-1}): 1630 (m), 1570 (s), 1460 (s), 1420 (s), 1310 (m), 1220 (s), 1080 (m), 972 (w), 859 (w), 742 (s).

3. Coordination modes of Schiff base ligands and metal ions in 1 and 3



(a)



(b)

Figure S2. Coordination modes of Schiff base ligands and metal ions in **1** (a) and **3** (b).

4. Space filling view of 3

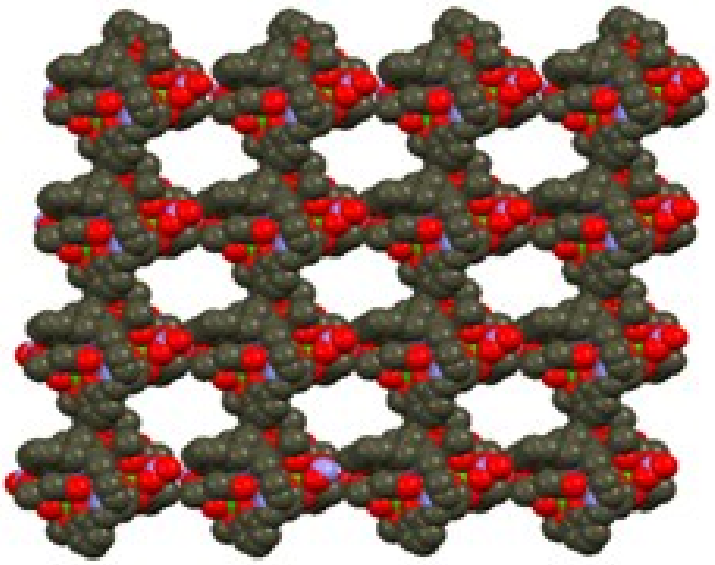


Figure S3. Space filling view of **3** along the *a*-axis showing the open porous structure.

5. Powder XRD patterns of 1 and 3

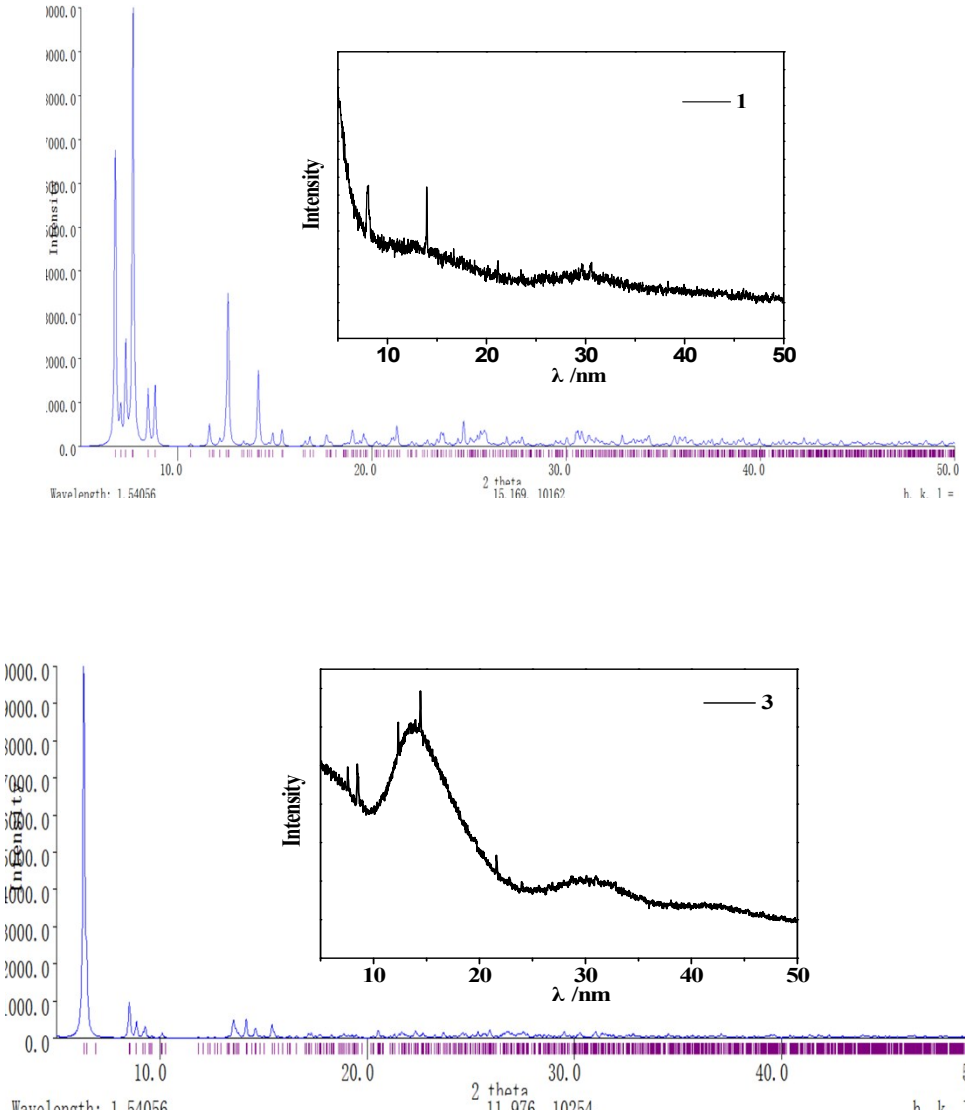


Figure S4. Powder XRD patterns of **1** and **3**.

6. The thermogravimetric analyses of 1 and 3

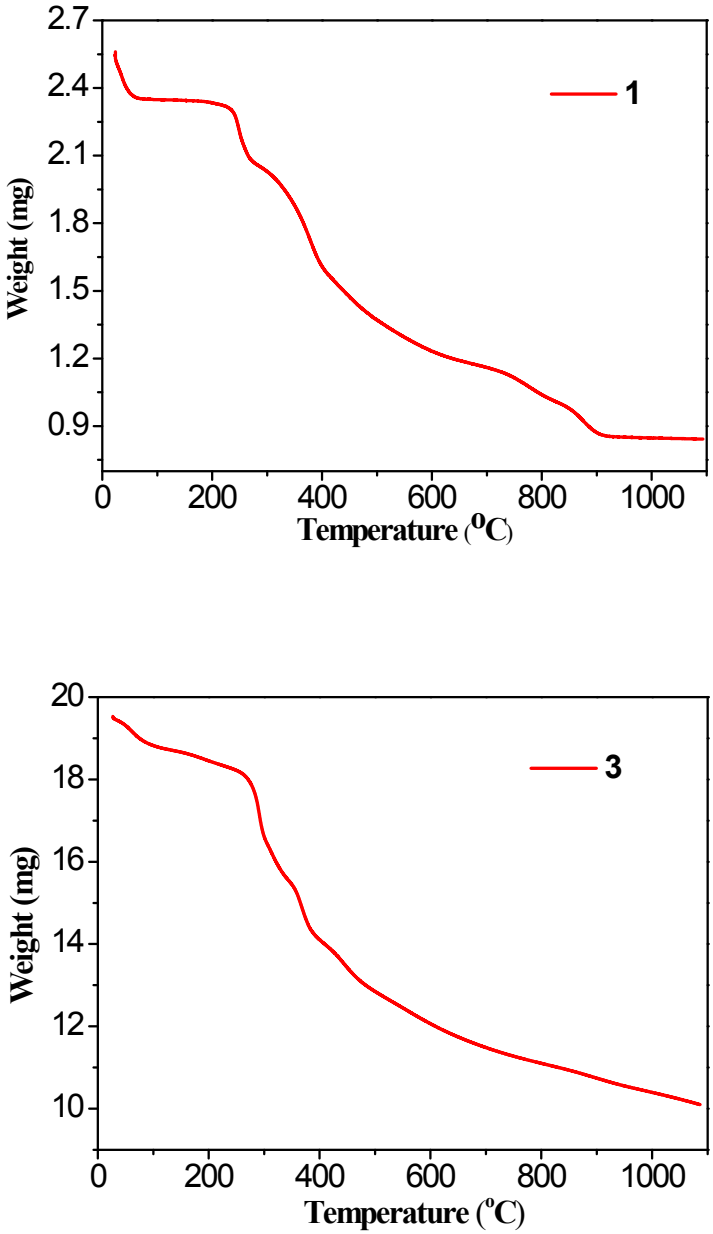


Figure S5. The thermogravimetric analyses of **1** and **3**.

7. Photophysical properties of the free ligands $H_2L^{1,2}$

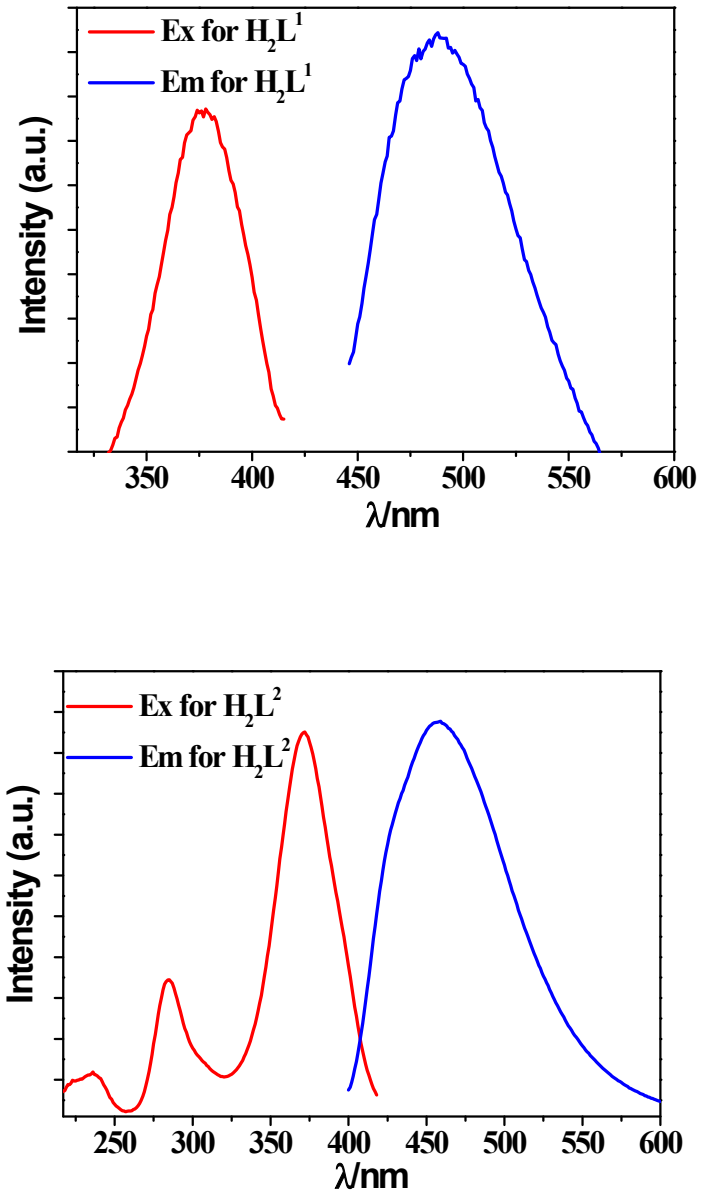
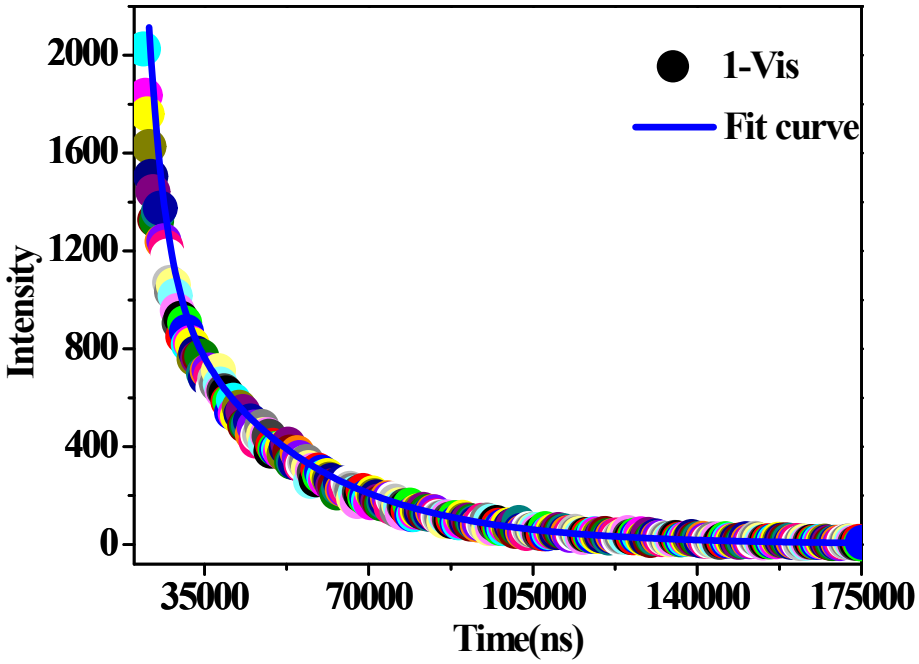
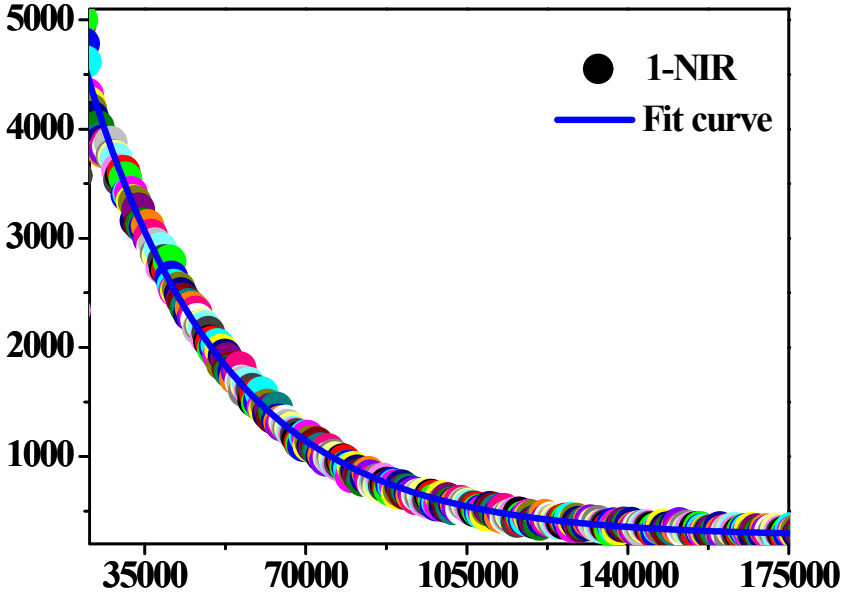


Figure S6. Excitation and emission spectra of free ligands $H_2L^{1,2}$ in CH_3CN.

8. Fluorescence lifetimes of 1-3 in solution





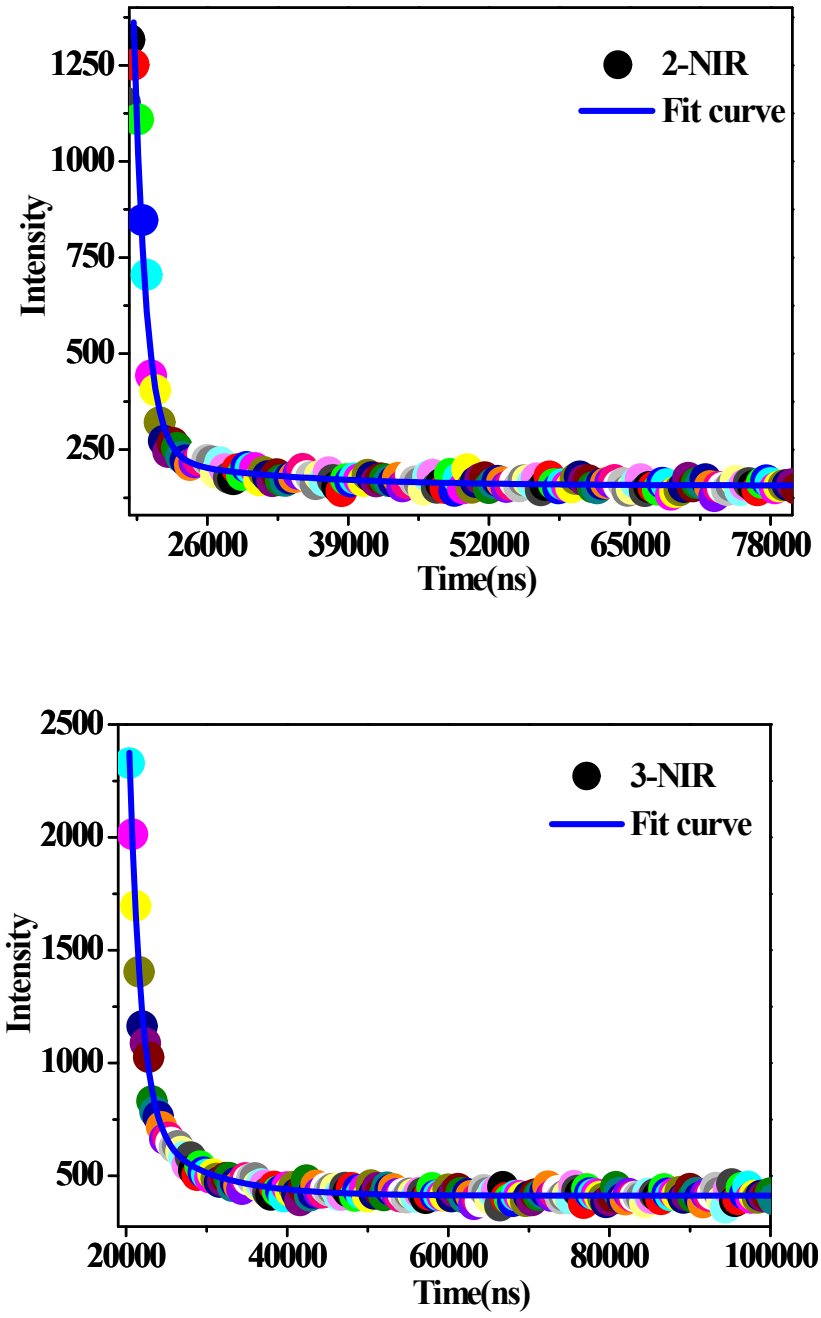


Figure S7. Fluorescence lifetimes of **1-3** in solution

9. Single Crystal 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] Crystal dimensions: **1**: 0.11, 0.13, 0.18 mm; for **2**: 0.15, 0.18, 0.21 mm; for **3**: 0.13, 0.18 0.19 mm.

Crystallographic data for **1-3** are presented in Table S1 and selected bond lengths are given in Tables S2-S4. (CCDC reference numbers 1551284-1551286). See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format).

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. Crystal data and structure refinement for **1-3**.

	1	**2**	**3**
Formula	$C_{87}H_{124}Br_4Sm_8N_8O_{76}Zn_6$	$C_{88}H_{128}Br_4Nd_8N_8O_{77}Zn_6$	$C_{66}H_{102}Nd_4N_8O_{46}Zn_4$
Fw	4404.60	4395.76	2582.00
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a [Å]	14.4478(11)	14.4850(15)	14.087(5)
b [Å]	14.9363(12)	14.9498(16)	14.640(5)
c [Å]	20.1881(15)	20.261(2)	14.997(5)
α [deg]	69.7890(10)	69.988(2)	62.231(3)
β [deg]	76.1150(10)	75.909(2)	87.122(4)
γ [deg]	89.1930(10)	89.461(2)	64.738(4)
V / [Å^3]	3957.5(5)	3985.4(7)	2431.8(13)
d / [g/cm^3]	1.848	1.831	1.763
Z	1	1	1
T [K]	223(1)	223(1)	223(1)
F(000)	2122	2128	1282
μ, mm^{-1}	4.903	4.529	3.155
θ rang, deg	1.11-25.00	1.59-25.00	1.77-25.00
reflns meads	28092	23649	11748
reflns used	13722	13627	8253
params	883	883	577
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0507, 0.1538	0.0457, 0.1297	0.0500, 0.1466
R1, wR2 (all data)	0.0779, 0.2141	0.0743, 0.1668	0.0635, 0.1656
Quality of fit	1.097	1.051	1.060

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. $w=1/[\sigma^2(F_o^2)+(0.075P)^2]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$.

Table S2. Selected Bond Lengths (Å) and Angles (°) for **1**.

Sm(1)-O(5)	2.384(7)	Zn(3)-O(13)	2.081(7)
Sm(1)-O(20)	2.387(7)	Zn(3)-N(2)	2.084(9)
Sm(1)-O(19)	2.468(7)	Zn(3)-N(1)	2.084(9)
Sm(1)-O(30)	2.468(6)	Zn(3)-O(2)	2.133(7)
Sm(1)-O(27)	2.490(7)	Zn(3)-O(11)	2.296(7)
Sm(1)-O(20)#1	2.490(6)	O(5)-Sm(1)-O(20)	145.1(3)
Sm(1)-O(21)	2.526(6)	O(5)-Sm(1)-O(19)	77.2(3)
Sm(1)-O(15)	2.532(7)	O(20)-Sm(1)-O(19)	109.2(2)
Sm(1)-O(14)	2.575(6)	O(5)-Sm(1)-O(30)	81.9(3)
Sm(1)-N(4)	2.972(9)	O(20)-Sm(1)-O(30)	132.5(2)
Sm(2)-O(8)	2.429(8)	O(19)-Sm(1)-O(30)	81.5(2)
Sm(2)-O(6)	2.440(8)	O(5)-Sm(1)-O(27)	78.5(3)
Sm(2)-O(22)	2.454(9)	O(20)-Sm(1)-O(27)	73.1(2)
Sm(2)-O(11)	2.459(7)	O(19)-Sm(1)-O(27)	134.4(2)
Sm(2)-O(27)	2.488(7)	O(30)-Sm(1)-O(27)	131.8(2)
Sm(2)-O(3)	2.491(7)	O(5)-Sm(1)-O(20)#1	140.3(3)
Sm(2)-O(28)	2.518(8)	O(20)-Sm(1)-O(20)#1	69.7(3)
Sm(2)-O(14)	2.562(6)	O(19)-Sm(1)-O(20)#1	70.4(2)
Sm(2)-O(4)	2.634(7)	O(30)-Sm(1)-O(20)#1	71.4(2)
Sm(2)-N(3)	2.895(11)	O(27)-Sm(1)-O(20)#1	141.2(3)
Sm(3)-O(25)	2.382(9)	O(5)-Sm(1)-O(21)	81.4(3)
Sm(3)-O(9)	2.391(8)	O(20)-Sm(1)-O(21)	70.9(2)
Sm(3)-O(20)#1	2.425(7)	O(19)-Sm(1)-O(21)	66.7(2)
Sm(3)-O(32)	2.433(10)	O(30)-Sm(1)-O(21)	146.6(2)
Sm(3)-O(29)	2.490(8)	O(27)-Sm(1)-O(21)	72.0(2)
Sm(3)-O(21)#1	2.511(7)	O(20)#1-Sm(1)-O(21)	105.2(2)
Sm(3)-O(30)	2.601(7)	O(5)-Sm(1)-O(15)	129.6(2)
Sm(3)-O(18)	2.655(7)	O(20)-Sm(1)-O(15)	71.8(2)
Sm(3)-O(15)	2.672(7)	O(19)-Sm(1)-O(15)	133.1(2)
Sm(4)-O(2)	2.442(7)	O(30)-Sm(1)-O(15)	68.4(2)
Sm(4)-O(13)	2.467(7)	O(27)-Sm(1)-O(15)	91.8(2)
Sm(4)-O(17)	2.492(8)	O(20)#1-Sm(1)-O(15)	66.5(2)
Sm(4)-O(16)	2.534(8)	O(21)-Sm(1)-O(15)	142.3(2)
Sm(4)-O(12)	2.546(8)	O(5)-Sm(1)-O(14)	81.2(2)
Sm(4)-O(10)	2.548(8)	O(20)-Sm(1)-O(14)	103.2(2)
Sm(4)-O(9)	2.596(8)	O(19)-Sm(1)-O(14)	146.6(2)
Sm(4)-O(15)	2.619(7)	O(30)-Sm(1)-O(14)	70.4(2)
Sm(4)-O(19)#1	2.629(7)	O(27)-Sm(1)-O(14)	63.4(2)
Sm(4)-O(1)	2.655(8)	O(20)#1-Sm(1)-O(14)	115.0(2)
Sm(4)-N(4)	2.914(11)	O(21)-Sm(1)-O(14)	134.4(2)
Zn(1)-O(31)#1	1.923(11)	O(15)-Sm(1)-O(14)	51.3(2)
Zn(1)-O(33)	1.931(13)	O(5)-Sm(1)-N(4)	105.6(3)
Zn(1)-O(26)	1.946(11)	O(20)-Sm(1)-N(4)	86.6(3)
Zn(1)-O(18)	1.998(7)	O(19)-Sm(1)-N(4)	148.8(3)
Zn(2)-O(7)	1.900(13)	O(30)-Sm(1)-N(4)	68.3(3)
Zn(2)-O(31)	1.911(13)	O(27)-Sm(1)-N(4)	75.3(2)
Zn(2)-O(28)	2.120(8)	O(20)#1-Sm(1)-N(4)	91.6(2)
Zn(2)-O(23)	2.23(2)	O(21)-Sm(1)-N(4)	144.4(2)
Zn(2)-O(24)	2.304(15)	O(15)-Sm(1)-N(4)	26.1(2)
Zn(3)-O(3)	2.066(7)	O(14)-Sm(1)-N(4)	25.2(2)

O(8)-Sm(2)-O(6)	133.0(3)
O(8)-Sm(2)-O(22)	74.5(3)
O(6)-Sm(2)-O(22)	70.4(3)
O(8)-Sm(2)-O(11)	80.2(3)
O(6)-Sm(2)-O(11)	145.4(3)
O(22)-Sm(2)-O(11)	140.0(3)
O(8)-Sm(2)-O(27)	127.8(3)
O(6)-Sm(2)-O(27)	81.5(3)
O(22)-Sm(2)-O(27)	88.2(3)
O(11)-Sm(2)-O(27)	83.3(2)
O(8)-Sm(2)-O(3)	84.3(3)
O(6)-Sm(2)-O(3)	102.0(3)
O(22)-Sm(2)-O(3)	138.3(3)
O(11)-Sm(2)-O(3)	67.0(2)
O(27)-Sm(2)-O(3)	132.3(2)
O(8)-Sm(2)-O(28)	76.7(3)
O(6)-Sm(2)-O(28)	117.6(3)
O(22)-Sm(2)-O(28)	70.2(3)
O(11)-Sm(2)-O(28)	74.1(3)
O(27)-Sm(2)-O(28)	51.1(2)
O(3)-Sm(2)-O(28)	139.1(3)
O(8)-Sm(2)-O(14)	151.7(3)
O(6)-Sm(2)-O(14)	69.8(2)
O(22)-Sm(2)-O(14)	133.8(3)
O(11)-Sm(2)-O(14)	75.5(2)
O(27)-Sm(2)-O(14)	63.6(2)
O(3)-Sm(2)-O(14)	73.0(2)
O(28)-Sm(2)-O(14)	109.7(2)
O(8)-Sm(2)-O(4)	77.8(3)
O(6)-Sm(2)-O(4)	66.2(2)
O(22)-Sm(2)-O(4)	79.8(3)
O(11)-Sm(2)-O(4)	124.5(2)
O(27)-Sm(2)-O(4)	147.6(3)
O(3)-Sm(2)-O(4)	60.6(2)
O(28)-Sm(2)-O(4)	144.8(2)
O(14)-Sm(2)-O(4)	104.3(2)
O(8)-Sm(2)-N(3)	102.7(3)
O(6)-Sm(2)-N(3)	100.1(3)
O(22)-Sm(2)-N(3)	78.8(3)
O(11)-Sm(2)-N(3)	77.0(3)
O(27)-Sm(2)-N(3)	25.2(3)
O(3)-Sm(2)-N(3)	141.8(3)
O(28)-Sm(2)-N(3)	26.0(3)
O(14)-Sm(2)-N(3)	86.0(3)
O(4)-Sm(2)-N(3)	157.6(3)
O(25)-Sm(3)-O(9)	73.4(3)
O(25)-Sm(3)-O(20)#1	142.4(3)
O(9)-Sm(3)-O(20)#1	122.7(3)
O(25)-Sm(3)-O(32)	81.7(4)
O(9)-Sm(3)-O(32)	138.6(3)
O(20)#1-Sm(3)-O(32)	97.2(3)
O(25)-Sm(3)-O(29)	96.3(3)
O(9)-Sm(3)-O(29)	75.3(3)
O(20)#1-Sm(3)-O(29)	120.0(3)
O(32)-Sm(3)-O(29)	75.2(3)
O(25)-Sm(3)-O(21)#1	88.1(3)
O(9)-Sm(3)-O(21)#1	68.8(2)
O(32)-Sm(3)-O(21)#1	143.6(3)
O(29)-Sm(3)-O(21)#1	140.9(3)
O(25)-Sm(3)-O(30)	141.1(3)
O(9)-Sm(3)-O(30)	109.9(2)
O(20)#1-Sm(3)-O(30)	70.2(2)
O(32)-Sm(3)-O(30)	71.0(3)
O(29)-Sm(3)-O(30)	50.7(2)
O(21)#1-Sm(3)-O(30)	130.1(2)
O(25)-Sm(3)-O(18)	68.9(3)
O(9)-Sm(3)-O(18)	127.0(3)
O(20)#1-Sm(3)-O(18)	75.5(2)
O(32)-Sm(3)-O(18)	69.7(3)
O(29)-Sm(3)-O(18)	143.3(3)
O(21)#1-Sm(3)-O(18)	74.1(2)
O(30)-Sm(3)-O(18)	122.9(3)
O(25)-Sm(3)-O(15)	137.8(3)
O(9)-Sm(3)-O(15)	64.8(2)
O(20)#1-Sm(3)-O(15)	65.2(2)
O(32)-Sm(3)-O(15)	135.3(3)
O(29)-Sm(3)-O(15)	79.4(3)
O(21)#1-Sm(3)-O(15)	71.8(2)
O(30)-Sm(3)-O(15)	64.4(2)
O(18)-Sm(3)-O(15)	134.4(2)
O(2)-Sm(4)-O(13)	64.2(2)
O(2)-Sm(4)-O(17)	138.5(2)
O(13)-Sm(4)-O(17)	140.5(3)
O(2)-Sm(4)-O(16)	92.5(3)
O(13)-Sm(4)-O(16)	142.1(3)
O(17)-Sm(4)-O(16)	76.8(3)
O(2)-Sm(4)-O(12)	71.6(2)
O(13)-Sm(4)-O(12)	72.6(2)
O(17)-Sm(4)-O(12)	137.4(3)
O(16)-Sm(4)-O(12)	71.7(3)
O(2)-Sm(4)-O(10)	75.6(3)
O(13)-Sm(4)-O(10)	77.1(3)
O(17)-Sm(4)-O(10)	80.1(3)
O(16)-Sm(4)-O(10)	128.1(3)
O(12)-Sm(4)-O(10)	142.5(3)
O(2)-Sm(4)-O(9)	114.6(2)
O(13)-Sm(4)-O(9)	69.7(2)
O(17)-Sm(4)-O(9)	70.9(3)
O(16)-Sm(4)-O(9)	147.4(3)
O(12)-Sm(4)-O(9)	132.3(3)
O(10)-Sm(4)-O(9)	50.3(3)
O(2)-Sm(4)-O(15)	111.9(2)
O(13)-Sm(4)-O(15)	51.3(2)
O(17)-Sm(4)-O(15)	106.8(2)
O(16)-Sm(4)-O(15)	124.9(2)
O(12)-Sm(4)-O(15)	70.9(2)
O(10)-Sm(4)-O(15)	106.0(3)
O(9)-Sm(4)-O(15)	63.0(2)

O(2)-Sm(4)-O(19)#1	131.4(2)	O(33)-Zn(1)-O(26)	114.6(5)
O(13)-Sm(4)-O(19)#1	123.2(2)	O(31)#1-Zn(1)-O(18)	115.9(4)
O(17)-Sm(4)-O(19)#1	70.5(2)	O(33)-Zn(1)-O(18)	115.6(4)
O(16)-Sm(4)-O(19)#1	50.6(2)	O(26)-Zn(1)-O(18)	102.4(4)
O(12)-Sm(4)-O(19)#1	67.4(2)	O(7)-Zn(2)-O(31)	118.5(6)
O(10)-Sm(4)-O(19)#1	150.1(3)	O(7)-Zn(2)-O(28)	101.0(5)
O(9)-Sm(4)-O(19)#1	112.0(2)	O(31)-Zn(2)-O(28)	93.8(4)
O(15)-Sm(4)-O(19)#1	78.0(2)	O(7)-Zn(2)-O(23)	118.9(8)
O(2)-Sm(4)-O(1)	61.8(2)	O(31)-Zn(2)-O(23)	120.9(6)
O(13)-Sm(4)-O(1)	119.9(2)	O(28)-Zn(2)-O(23)	88.3(6)
O(17)-Sm(4)-O(1)	77.7(2)	O(7)-Zn(2)-O(24)	89.3(6)
O(16)-Sm(4)-O(1)	64.1(3)	O(31)-Zn(2)-O(24)	92.9(6)
O(12)-Sm(4)-O(1)	111.8(3)	O(28)-Zn(2)-O(24)	163.1(5)
O(10)-Sm(4)-O(1)	65.9(3)	O(23)-Zn(2)-O(24)	75.0(7)
O(9)-Sm(4)-O(1)	111.9(3)	O(3)-Zn(3)-O(13)	95.2(3)
O(15)-Sm(4)-O(1)	170.3(2)	O(3)-Zn(3)-N(2)	91.3(3)
O(19)#1-Sm(4)-O(1)	111.6(3)	O(13)-Zn(3)-N(2)	90.7(3)
O(2)-Sm(4)-N(4)	85.4(3)	O(3)-Zn(3)-N(1)	99.5(3)
O(13)-Sm(4)-N(4)	25.7(2)	O(13)-Zn(3)-N(1)	161.8(3)
O(17)-Sm(4)-N(4)	130.6(3)	N(2)-Zn(3)-N(1)	99.6(3)
O(16)-Sm(4)-N(4)	133.7(3)	O(3)-Zn(3)-O(2)	164.3(3)
O(12)-Sm(4)-N(4)	63.8(3)	O(13)-Zn(3)-O(2)	76.5(3)
O(10)-Sm(4)-N(4)	96.1(3)	N(2)-Zn(3)-O(2)	102.0(3)
O(9)-Sm(4)-N(4)	69.5(3)	N(1)-Zn(3)-O(2)	86.7(3)
O(15)-Sm(4)-N(4)	26.8(2)	O(3)-Zn(3)-O(11)	77.4(3)
O(19)#1-Sm(4)-N(4)	98.7(2)	O(13)-Zn(3)-O(11)	83.5(3)
O(1)-Sm(4)-N(4)	145.1(3)	N(2)-Zn(3)-O(11)	166.7(3)
O(31)#1-Zn(1)-O(33)	102.8(6)	N(1)-Zn(3)-O(11)	89.3(3)
O(31)#1-Zn(1)-O(26)	105.5(5)	O(2)-Zn(3)-O(11)	88.3(3)

Table S3. Selected Bond Lengths (Å) and Angles (°) for **2**.

Nd(1)-O(5)	2.410(7)	Zn(3)-N(1)	2.074(8)
Nd(1)-O(20)	2.451(6)	Zn(3)-N(2)	2.079(8)
Nd(1)-O(30)	2.487(6)	Zn(3)-O(13)	2.089(6)
Nd(1)-O(19)	2.491(6)	Zn(3)-O(2)	2.152(6)
Nd(1)-O(27)	2.498(6)	Zn(3)-O(11)	2.283(6)
Nd(1)-O(20)#1	2.504(6)	O(5)-Nd(1)-O(20)	145.1(2)
Nd(1)-O(21)	2.558(6)	O(5)-Nd(1)-O(30)	82.0(2)
Nd(1)-O(15)	2.568(6)	O(20)-Nd(1)-O(30)	132.5(2)
Nd(1)-O(14)	2.588(6)	O(5)-Nd(1)-O(19)	77.9(2)
Nd(1)-N(4)	2.998(8)	O(20)-Nd(1)-O(19)	108.70(19)
Nd(2)-O(6)	2.422(7)	O(30)-Nd(1)-O(19)	81.1(2)
Nd(2)-O(22)	2.469(8)	O(5)-Nd(1)-O(27)	78.6(2)
Nd(2)-O(8)	2.474(7)	O(20)-Nd(1)-O(27)	72.9(2)
Nd(2)-O(11)	2.473(6)	O(30)-Nd(1)-O(27)	132.5(2)
Nd(2)-O(27)	2.508(6)	O(19)-Nd(1)-O(27)	134.8(2)
Nd(2)-O(3)	2.517(6)	O(5)-Nd(1)-O(20)#1	139.8(2)
Nd(2)-O(28)	2.551(7)	O(20)-Nd(1)-O(20)#1	70.5(2)
Nd(2)-O(14)	2.571(6)	O(30)-Nd(1)-O(20)#1	70.0(2)
Nd(2)-O(4)	2.649(7)	O(19)-Nd(1)-O(20)#1	69.99(19)
Nd(2)-N(3)	2.974(11)	O(27)-Nd(1)-O(20)#1	141.5(2)
Nd(3)-O(25)	2.400(7)	O(5)-Nd(1)-O(21)	82.3(2)
Nd(3)-O(20)#1	2.413(6)	O(20)-Nd(1)-O(21)	70.20(19)
Nd(3)-O(9)	2.417(6)	O(30)-Nd(1)-O(21)	146.43(19)
Nd(3)-O(32)	2.435(8)	O(19)-Nd(1)-O(21)	66.7(2)
Nd(3)-O(21)#1	2.522(6)	O(27)-Nd(1)-O(21)	72.2(2)
Nd(3)-O(29)	2.527(8)	O(20)#1-Nd(1)-O(21)	105.48(19)
Nd(3)-O(30)	2.609(7)	O(5)-Nd(1)-O(15)	129.1(2)
Nd(3)-O(18)	2.674(6)	O(20)-Nd(1)-O(15)	72.17(19)
Nd(3)-O(15)	2.690(6)	O(30)-Nd(1)-O(15)	68.5(2)
Nd(4)-O(2)	2.459(6)	O(19)-Nd(1)-O(15)	132.86(19)
Nd(4)-O(13)	2.502(6)	O(27)-Nd(1)-O(15)	91.60(19)
Nd(4)-O(17)	2.519(7)	O(20)#1-Nd(1)-O(15)	66.23(17)
Nd(4)-O(12)	2.539(7)	O(21)-Nd(1)-O(15)	141.9(2)
Nd(4)-O(16)	2.555(7)	O(5)-Nd(1)-O(14)	80.9(2)
Nd(4)-O(10)	2.557(7)	O(20)-Nd(1)-O(14)	103.22(18)
Nd(4)-O(9)	2.588(7)	O(30)-Nd(1)-O(14)	71.02(19)
Nd(4)-O(15)	2.622(6)	O(19)-Nd(1)-O(14)	147.0(2)
Nd(4)-O(19)#1	2.642(6)	O(27)-Nd(1)-O(14)	63.37(19)
Nd(4)-O(1)	2.668(6)	O(20)#1-Nd(1)-O(14)	114.39(18)
Nd(4)-N(4)	2.943(9)	O(21)-Nd(1)-O(14)	134.72(19)
Zn(1)-O(31)#1	1.924(9)	O(15)-Nd(1)-O(14)	51.08(18)
Zn(1)-O(33)	1.935(10)	O(5)-Nd(1)-N(4)	105.0(2)
Zn(1)-O(26)	1.977(9)	O(20)-Nd(1)-N(4)	87.0(2)
Zn(1)-O(18)	2.000(7)	O(30)-Nd(1)-N(4)	68.6(2)
Zn(2)-O(31)	1.899(10)	O(19)-Nd(1)-N(4)	148.6(2)
Zn(2)-O(7)	1.917(10)	O(27)-Nd(1)-N(4)	75.3(2)
Zn(2)-O(28)	2.109(6)	O(20)#1-Nd(1)-N(4)	91.2(2)
Zn(2)-O(23)	2.125(17)	O(21)-Nd(1)-N(4)	144.5(2)
Zn(2)-O(24)	2.318(17)	O(15)-Nd(1)-N(4)	26.1(2)
Zn(3)-O(3)	2.069(6)	O(14)-Nd(1)-N(4)	25.0(2)

O(6)-Nd(2)-O(22)	69.8(3)
O(6)-Nd(2)-O(8)	133.6(3)
O(22)-Nd(2)-O(8)	74.9(3)
O(6)-Nd(2)-O(11)	145.6(2)
O(22)-Nd(2)-O(11)	140.4(2)
O(8)-Nd(2)-O(11)	79.4(2)
O(6)-Nd(2)-O(27)	80.7(2)
O(22)-Nd(2)-O(27)	88.3(3)
O(8)-Nd(2)-O(27)	127.7(2)
O(11)-Nd(2)-O(27)	84.0(2)
O(6)-Nd(2)-O(3)	102.5(2)
O(22)-Nd(2)-O(3)	138.1(3)
O(8)-Nd(2)-O(3)	84.4(2)
O(11)-Nd(2)-O(3)	66.58(19)
O(27)-Nd(2)-O(3)	132.2(2)
O(6)-Nd(2)-O(28)	117.1(2)
O(22)-Nd(2)-O(28)	70.8(3)
O(8)-Nd(2)-O(28)	76.5(2)
O(11)-Nd(2)-O(28)	74.3(2)
O(27)-Nd(2)-O(28)	51.24(19)
O(3)-Nd(2)-O(28)	138.9(2)
O(6)-Nd(2)-O(14)	69.9(2)
O(22)-Nd(2)-O(14)	133.7(3)
O(8)-Nd(2)-O(14)	151.4(2)
O(11)-Nd(2)-O(14)	75.68(19)
O(27)-Nd(2)-O(14)	63.48(19)
O(3)-Nd(2)-O(14)	72.92(18)
O(28)-Nd(2)-O(14)	109.51(19)
O(6)-Nd(2)-O(4)	66.6(2)
O(22)-Nd(2)-O(4)	79.7(3)
O(8)-Nd(2)-O(4)	78.5(2)
O(11)-Nd(2)-O(4)	123.89(19)
O(27)-Nd(2)-O(4)	147.3(2)
O(3)-Nd(2)-O(4)	60.44(19)
O(28)-Nd(2)-O(4)	145.2(2)
O(14)-Nd(2)-O(4)	104.0(2)
O(6)-Nd(2)-N(3)	99.6(3)
O(22)-Nd(2)-N(3)	78.8(3)
O(8)-Nd(2)-N(3)	102.1(3)
O(11)-Nd(2)-N(3)	77.7(2)
O(27)-Nd(2)-N(3)	25.6(2)
O(3)-Nd(2)-N(3)	142.0(2)
O(28)-Nd(2)-N(3)	25.6(2)
O(14)-Nd(2)-N(3)	86.3(2)
O(4)-Nd(2)-N(3)	157.5(2)
O(25)-Nd(3)-O(20)#1	142.2(2)
O(25)-Nd(3)-O(9)	74.1(2)
O(20)#1-Nd(3)-O(9)	122.8(2)
O(25)-Nd(3)-O(32)	81.0(3)
O(20)#1-Nd(3)-O(32)	96.7(3)
O(9)-Nd(3)-O(32)	139.1(3)
O(25)-Nd(3)-O(21)#1	88.2(3)
O(9)-Nd(3)-O(21)#1	67.9(2)
O(32)-Nd(3)-O(21)#1	143.7(3)
O(25)-Nd(3)-O(29)	96.5(3)
O(20)#1-Nd(3)-O(29)	119.5(2)
O(9)-Nd(3)-O(29)	76.3(2)
O(32)-Nd(3)-O(29)	75.0(3)
O(21)#1-Nd(3)-O(29)	141.0(2)
O(25)-Nd(3)-O(30)	141.1(3)
O(20)#1-Nd(3)-O(30)	69.39(19)
O(9)-Nd(3)-O(30)	110.9(2)
O(32)-Nd(3)-O(30)	70.9(3)
O(21)#1-Nd(3)-O(30)	130.14(19)
O(29)-Nd(3)-O(30)	51.0(2)
O(25)-Nd(3)-O(18)	68.4(2)
O(20)#1-Nd(3)-O(18)	75.43(19)
O(9)-Nd(3)-O(18)	126.8(2)
O(32)-Nd(3)-O(18)	69.3(3)
O(21)#1-Nd(3)-O(18)	74.5(2)
O(29)-Nd(3)-O(18)	142.9(2)
O(30)-Nd(3)-O(18)	122.1(2)
O(25)-Nd(3)-O(15)	138.2(2)
O(20)#1-Nd(3)-O(15)	65.51(18)
O(9)-Nd(3)-O(15)	64.52(19)
O(32)-Nd(3)-O(15)	135.8(3)
O(21)#1-Nd(3)-O(15)	71.49(19)
O(29)-Nd(3)-O(15)	79.7(2)
O(30)-Nd(3)-O(15)	64.93(18)
O(18)-Nd(3)-O(15)	134.36(18)
O(2)-Nd(4)-O(13)	64.45(19)
O(2)-Nd(4)-O(17)	138.0(2)
O(13)-Nd(4)-O(17)	140.6(2)
O(2)-Nd(4)-O(12)	71.4(2)
O(13)-Nd(4)-O(12)	72.1(2)
O(17)-Nd(4)-O(12)	138.0(2)
O(2)-Nd(4)-O(16)	92.3(2)
O(13)-Nd(4)-O(16)	141.9(2)
O(17)-Nd(4)-O(16)	76.9(2)
O(12)-Nd(4)-O(16)	71.9(2)
O(2)-Nd(4)-O(10)	75.9(2)
O(13)-Nd(4)-O(10)	77.4(2)
O(17)-Nd(4)-O(10)	79.5(2)
O(12)-Nd(4)-O(10)	142.4(2)
O(16)-Nd(4)-O(10)	128.2(2)
O(2)-Nd(4)-O(9)	115.0(2)
O(13)-Nd(4)-O(9)	70.1(2)
O(17)-Nd(4)-O(9)	70.6(2)
O(12)-Nd(4)-O(9)	132.3(2)
O(16)-Nd(4)-O(9)	147.1(2)
O(10)-Nd(4)-O(9)	50.2(2)
O(2)-Nd(4)-O(15)	111.65(19)
O(13)-Nd(4)-O(15)	50.82(17)
O(17)-Nd(4)-O(15)	107.56(19)
O(12)-Nd(4)-O(15)	70.5(2)
O(16)-Nd(4)-O(15)	124.9(2)
O(10)-Nd(4)-O(15)	106.0(2)
O(9)-Nd(4)-O(15)	63.3(2)

O(2)-Nd(4)-O(19)#1	130.5(2)	O(33)-Zn(1)-O(26)	114.4(4)
O(13)-Nd(4)-O(19)#1	122.88(18)	O(31)#1-Zn(1)-O(18)	115.7(3)
O(17)-Nd(4)-O(19)#1	71.6(2)	O(33)-Zn(1)-O(18)	115.0(4)
O(12)-Nd(4)-O(19)#1	67.0(2)	O(26)-Zn(1)-O(18)	102.9(3)
O(16)-Nd(4)-O(19)#1	50.1(2)	O(31)-Zn(2)-O(7)	118.7(5)
O(10)-Nd(4)-O(19)#1	150.5(2)	O(31)-Zn(2)-O(28)	93.7(4)
O(9)-Nd(4)-O(19)#1	112.64(19)	O(7)-Zn(2)-O(28)	100.3(4)
O(15)-Nd(4)-O(19)#1	78.40(18)	O(31)-Zn(2)-O(23)	121.7(6)
O(2)-Nd(4)-O(1)	61.1(2)	O(7)-Zn(2)-O(23)	117.2(7)
O(13)-Nd(4)-O(1)	119.3(2)	O(28)-Zn(2)-O(23)	91.7(5)
O(17)-Nd(4)-O(1)	77.9(2)	O(31)-Zn(2)-O(24)	92.2(6)
O(12)-Nd(4)-O(1)	111.9(2)	O(7)-Zn(2)-O(24)	91.4(5)
O(16)-Nd(4)-O(1)	64.8(2)	O(28)-Zn(2)-O(24)	162.4(5)
O(10)-Nd(4)-O(1)	65.4(2)	O(23)-Zn(2)-O(24)	71.1(6)
O(9)-Nd(4)-O(1)	111.4(2)	O(3)-Zn(3)-N(1)	99.5(3)
O(15)-Nd(4)-O(1)	169.4(2)	O(3)-Zn(3)-N(2)	90.8(3)
O(19)#1-Nd(4)-O(1)	112.2(2)	N(1)-Zn(3)-N(2)	98.5(3)
O(2)-Nd(4)-N(4)	85.2(2)	O(3)-Zn(3)-O(13)	94.8(2)
O(13)-Nd(4)-N(4)	25.29(19)	N(1)-Zn(3)-O(13)	162.6(3)
O(17)-Nd(4)-N(4)	131.2(2)	N(2)-Zn(3)-O(13)	91.1(3)
O(12)-Nd(4)-N(4)	63.3(2)	O(3)-Zn(3)-O(2)	164.7(2)
O(16)-Nd(4)-N(4)	133.5(2)	N(1)-Zn(3)-O(2)	86.6(3)
O(10)-Nd(4)-N(4)	96.2(2)	N(2)-Zn(3)-O(2)	102.3(3)
O(9)-Nd(4)-N(4)	70.0(2)	O(13)-Zn(3)-O(2)	77.2(2)
O(15)-Nd(4)-N(4)	26.80(19)	O(3)-Zn(3)-O(11)	77.9(2)
O(19)#1-Nd(4)-N(4)	98.8(2)	N(1)-Zn(3)-O(11)	89.4(3)
O(1)-Nd(4)-N(4)	144.1(2)	N(2)-Zn(3)-O(11)	167.1(3)
O(31)#1-Zn(1)-O(33)	103.9(5)	O(13)-Zn(3)-O(11)	84.0(2)
O(31)#1-Zn(1)-O(26)	105.0(4)	O(2)-Zn(3)-O(11)	88.2(2)

Table S4. Selected Bond Lengths (Å) and Angles (°) for **3**.

Nd(1)-O(2)	2.306(6)	O(13)-Nd(1)-O(12)	51.3(2)
Nd(1)-O(11)	2.311(7)	O(2)-Nd(1)-O(1)	63.9(2)
Nd(1)-O(15)	2.329(6)	O(11)-Nd(1)-O(1)	75.5(2)
Nd(1)-O(14)	2.341(7)	O(15)-Nd(1)-O(1)	152.7(2)
Nd(1)-O(18)	2.378(7)	O(14)-Nd(1)-O(1)	76.0(2)
Nd(1)-O(13)	2.464(7)	O(18)-Nd(1)-O(1)	119.1(2)
Nd(1)-O(12)	2.547(7)	O(13)-Nd(1)-O(1)	69.8(2)
Nd(1)-O(1)	2.564(7)	O(12)-Nd(1)-O(1)	116.7(2)
Nd(1)-O(16)	2.614(6)	O(2)-Nd(1)-O(16)	66.4(2)
Nd(2)-O(15)	2.291(6)	O(11)-Nd(1)-O(16)	137.0(2)
Nd(2)-O(12)	2.299(6)	O(15)-Nd(1)-O(16)	66.96(19)
Nd(2)-O(10)	2.327(7)	O(14)-Nd(1)-O(16)	74.9(2)
Nd(2)-O(3)	2.374(6)	O(18)-Nd(1)-O(16)	68.2(2)
Nd(2)-O(9)	2.417(7)	O(13)-Nd(1)-O(16)	139.9(2)
Nd(2)-O(8)	2.423(8)	O(12)-Nd(1)-O(16)	115.6(2)
Nd(2)-O(5)	2.528(8)	O(1)-Nd(1)-O(16)	124.3(2)
Nd(2)-O(4)	2.541(7)	O(15)-Nd(2)-O(12)	73.6(2)
Nd(2)-O(6)	2.548(8)	O(15)-Nd(2)-O(10)	77.6(2)
Nd(2)-N(4)	2.950(10)	O(12)-Nd(2)-O(10)	85.0(3)
Zn(1)-O(16)	1.968(6)	O(15)-Nd(2)-O(3)	66.4(2)
Zn(1)-O(17)	2.006(7)	O(12)-Nd(2)-O(3)	78.7(2)
Zn(1)-N(1)	2.065(8)	O(10)-Nd(2)-O(3)	143.3(2)
Zn(1)-O(2)	2.110(6)	O(15)-Nd(2)-O(9)	78.4(2)
Zn(1)-N(2)	2.158(8)	O(12)-Nd(2)-O(9)	150.6(3)
Zn(2)-O(19)	2.021(6)	O(10)-Nd(2)-O(9)	80.2(3)
Zn(2)-O(16)	2.028(6)	O(3)-Nd(2)-O(9)	98.4(2)
Zn(2)-O(3)	2.057(6)	O(15)-Nd(2)-O(8)	116.0(3)
Zn(2)-O(15)	2.064(6)	O(12)-Nd(2)-O(8)	150.6(3)
Zn(2)-N(3)	2.067(8)	O(10)-Nd(2)-O(8)	123.5(3)
O(2)-Nd(1)-O(11)	137.5(2)	O(3)-Nd(2)-O(8)	80.5(3)
O(2)-Nd(1)-O(15)	133.3(2)	O(9)-Nd(2)-O(8)	53.5(3)
O(11)-Nd(1)-O(15)	80.8(2)	O(15)-Nd(2)-O(5)	133.7(2)
O(2)-Nd(1)-O(14)	83.4(2)	O(12)-Nd(2)-O(5)	69.6(2)
O(11)-Nd(1)-O(14)	74.4(3)	O(10)-Nd(2)-O(5)	72.3(3)
O(15)-Nd(1)-O(14)	84.7(2)	O(3)-Nd(2)-O(5)	129.6(2)
O(2)-Nd(1)-O(18)	75.2(2)	O(9)-Nd(2)-O(5)	128.1(3)
O(11)-Nd(1)-O(18)	140.4(3)	O(8)-Nd(2)-O(5)	109.8(3)
O(15)-Nd(1)-O(18)	87.9(2)	O(15)-Nd(2)-O(4)	126.5(2)
O(14)-Nd(1)-O(18)	142.4(2)	O(12)-Nd(2)-O(4)	79.3(2)
O(2)-Nd(1)-O(13)	96.5(2)	O(10)-Nd(2)-O(4)	144.6(2)
O(11)-Nd(1)-O(13)	80.5(3)	O(3)-Nd(2)-O(4)	63.6(2)
O(15)-Nd(1)-O(13)	119.7(2)	O(9)-Nd(2)-O(4)	126.0(2)
O(14)-Nd(1)-O(13)	141.6(2)	O(8)-Nd(2)-O(4)	73.0(3)
O(18)-Nd(1)-O(13)	72.5(3)	O(5)-Nd(2)-O(4)	72.5(3)
O(2)-Nd(1)-O(12)	135.0(2)	O(15)-Nd(2)-O(6)	145.5(3)
O(11)-Nd(1)-O(12)	74.4(3)	O(12)-Nd(2)-O(6)	119.8(3)
O(15)-Nd(1)-O(12)	68.5(2)	O(10)-Nd(2)-O(6)	72.7(3)
O(14)-Nd(1)-O(12)	141.5(2)	O(3)-Nd(2)-O(6)	143.6(3)
O(18)-Nd(1)-O(12)	66.1(2)	O(9)-Nd(2)-O(6)	79.7(3)

O(8)-Nd(2)-O(6)	69.2(3)	O(17)-Zn(1)-O(2)	96.1(3)
O(5)-Nd(2)-O(6)	50.6(3)	N(1)-Zn(1)-O(2)	86.5(3)
O(4)-Nd(2)-O(6)	88.0(3)	O(16)-Zn(1)-N(2)	100.9(3)
O(15)-Nd(2)-N(4)	145.0(3)	O(17)-Zn(1)-N(2)	94.2(3)
O(12)-Nd(2)-N(4)	94.6(3)	N(1)-Zn(1)-N(2)	81.4(3)
O(10)-Nd(2)-N(4)	68.5(3)	O(2)-Zn(1)-N(2)	166.0(3)
O(3)-Nd(2)-N(4)	144.9(3)	O(19)-Zn(2)-O(16)	109.5(3)
O(9)-Nd(2)-N(4)	103.3(3)	O(19)-Zn(2)-O(3)	109.4(3)
O(8)-Nd(2)-N(4)	90.6(3)	O(16)-Zn(2)-O(3)	138.1(3)
O(5)-Nd(2)-N(4)	25.5(3)	O(19)-Zn(2)-O(15)	96.5(2)
O(4)-Nd(2)-N(4)	81.3(3)	O(16)-Zn(2)-O(15)	84.0(2)
O(6)-Nd(2)-N(4)	25.3(3)	O(3)-Zn(2)-O(15)	76.6(2)
C(26)-Nd(2)-N(4)	96.5(3)	O(19)-Zn(2)-N(3)	99.9(3)
O(16)-Zn(1)-O(17)	115.9(3)	O(16)-Zn(2)-N(3)	97.5(3)
O(16)-Zn(1)-N(1)	136.6(3)	O(3)-Zn(2)-N(3)	90.8(3)
O(17)-Zn(1)-N(1)	107.0(3)	O(15)-Zn(2)-N(3)	161.9(3)
O(16)-Zn(1)-O(2)	83.1(2)		