Supporting Information

Self-Assembly of NIR-luminescent 30-metal Drum-like and 12-metal rectangular-like d-f Nanoclusters with Long-chain Schiff Base Ligands

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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 ligand $H_2L^{1,2}$ was prepared according to well-established procedures.[1] Physical measurements: NMR: VARIAN UNITY-plus. 600 spectrometer (^{1}H, 600 MHz) at 298 K; Powder XRD: Rigaku R-AXIS RAPID II; IR: FTIR-650 spectrometer. 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. Elemental analyses (C, H, N) were carried out on a EA1112 elemental analyses. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1200EX transmission electron microscope. 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, excitation and emission spectra on a QuantaMaster PTI fluorimeter.

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

2. Synthesis of 1-4

$[Nd_6Cd_{24}(L^1)_{11}(OAc)_{43}(OH)]$ (**1**). $Cd(OAc)_2{\cdot}2H_2O$ (0.52 mmol, 0.1382 g), $Nd(OAc)_3{\cdot}4H_2O$ (0.12 mmol, 0.0472 g) and H_2L^1 (0.26 mmol, 0.1001 g) were dissolved in 50 mL MeOH at room temperature, and a solution of NaOH in EtOH (0.03 mol/L, 10 ml) was then added. The resulting solution was stirred and heated under reflux for 30 mins. It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale yellow crystals were obtained after one week. The crystals were filtered off, washed with EtOH (5 ml) and dried in the air for one week. Yield (based on $Nd(OAc)_3{\cdot}4H_2O$): 0.0661 g (32 %). m. p. > 195 ^oC (dec.). Elemental analysis: Found: C, 37.95; H, 4.72; N, 2.76 %. Calc. for $C_{328}H_{413}Cd_{24}N_{22}Nd_6O_{131}(EtOH)_7(EtOEt)_2(MeOH)_9(H_2O)_{12}$: C, 38.13; H, 4.73; N, 2.73 %. IR (cm^{-1}): 2358 (m), 1630 (s), 1558 (s), 1420 (s), 1298 (m), 1213 (s), 1078 (m), 955 (m), 851 (w), 741 (s), 668 (m). ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) -14.628 (5H), -9.818 (13H), -8.500 (14H), -8.206 (5H), -6.458 (18H), -5.083 (16H), -4.406 (8H), -3.854 (6H), -2.133 (9H), -1.536 (5H), 0.066 (20H), 0.281 (6H), 0.880 (15H), 1.278 (30H), 1.369 (8H), 1.435 (10H), 2.178 (6H), 3.300 (4H), 3.451 (10H), 3.578 (5H), 3.701 (15H), 3.880 (8H), 4.350 (8H), 5.385 (8H), 5.993 (4H), 6.141 (6H), 6.768 (15H), 6.965 (10H), 7.105 (15H), 7.173 (4H), 7.993 (10H), 8.110 (15H), 8.199 (10H), 8.287 (5H), 8.606 (8H), 9.089 (8H), 9.793 (14H), 10.587 (6H), 11.248 (6H), 12.023 (5H), 16.868 (4H).

$[Yb_6Cd_{24}(L^1)_{11}(OAc)_{43}(OH)]$ (**2**). The procedure was the same as that for **1** using $Yb(OAc)_3{\cdot}4H_2O$ (0.12 mmol, 0.0508 g). Pale yellow single crystals of **2** were formed after one week. Yield (based on $Yb(OAc)_3{\cdot}4H_2O$): 0.0945 g (45 %). m. p. > 198 ^oC (dec.). Elemental analysis: Found: C, 37.52; H, 4.95; N, 2.60 %. Calc. for $C_{328}H_{413}Cd_{24}N_{22}Yb_6O_{131}(EtOH)_{12}(EtOEt)_2(MeOH)_{13}(H_2O)_{15}$: C, 37.67; H, 4.93; N, 2.59 %. IR (cm^{-1}): 2396 (w), 1638 (m), 1577 (s), 1406 (s), 1298 (m), 1240 (m), 1212 (s), 1167 (w), 1074 (m), 954 (m), 858 (w), 740 (s), 668 (m).

$[Nd_4Zn_8(L^2)_2(OAc)_{20}(OH)_4]$ (**3**). $Zn(OAc)_2 \cdot 2H_2O$ (0.52 mmol, 0.1149 g), $Nd(OAc)_3 \cdot 4H_2O$ (0.12 mmol, 0.0472 g) and H_2L^2 (0.26 mmol, 0.1409 g) were dissolved in MeOH (50 mL) at room temperature, and a solution of NaOH in EtOH (0.03 mol/L, 10 ml) was then added. The resulting solution was stirred and heated under reflux for 30 mins. It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale yellow crystals were obtained after one week. The crystals were filtered off, washed with EtOH (5 ml) and dried in the air for one week. Yield (based on $Nd(OAc)_3 \cdot 4H_2O$): 0.0712 g (60 %). m. p. > 182 ^oC (dec.). Elemental analysis: Found: C, 31.28; H, 4.05; N, 1.48 %. Calc. for $C_{97}H_{150}Br_4Nd_4N_4O_{59}Zn_8$: C, 31.23; H, 4.02; N, 1.50 %. IR (cm^{-1}): 2915 (w), 1636 (m), 1570 (s), 1303 (m), 1210 (m), 1159 (w), 1066 (m), 961 (s), 868 (s), 740 (s), 637 (m).

$[Yb_4Zn_8(L^2)_2(OAc)_{20}(OH)_4]$ (**4**). The procedure was the same as that for **3** using $Yb(OAc)_3 \cdot 4H_2O$ (0.12 mmol, 0.0508 g). Pale yellow single crystals of **4** were formed after one week. Yield (based on $Yb(OAc)_3 \cdot 4H_2O$): 0.0876 g (75 %). m. p. > 185 ^oC (dec.). Elemental analysis: Found: C, 30.36; H, 3.87; N, 1.42 %. Calc. for $C_{97}H_{150}Br_4Yb_4N_4O_{59}Zn_8$: C, 30.30; H, 3.90; N, 1.46 %. IR (cm^{-1}): 2853 (m), 1635 (m), 1579 (s), 1549 (s), 1453 (s), 1307 (s), 1239 (s), 1214 (s), 1080 (m), 964 (m), 855 (w), 742 (m), 643 (m).

3. Energy dispersive X-ray (EDX) spectrum of 1.

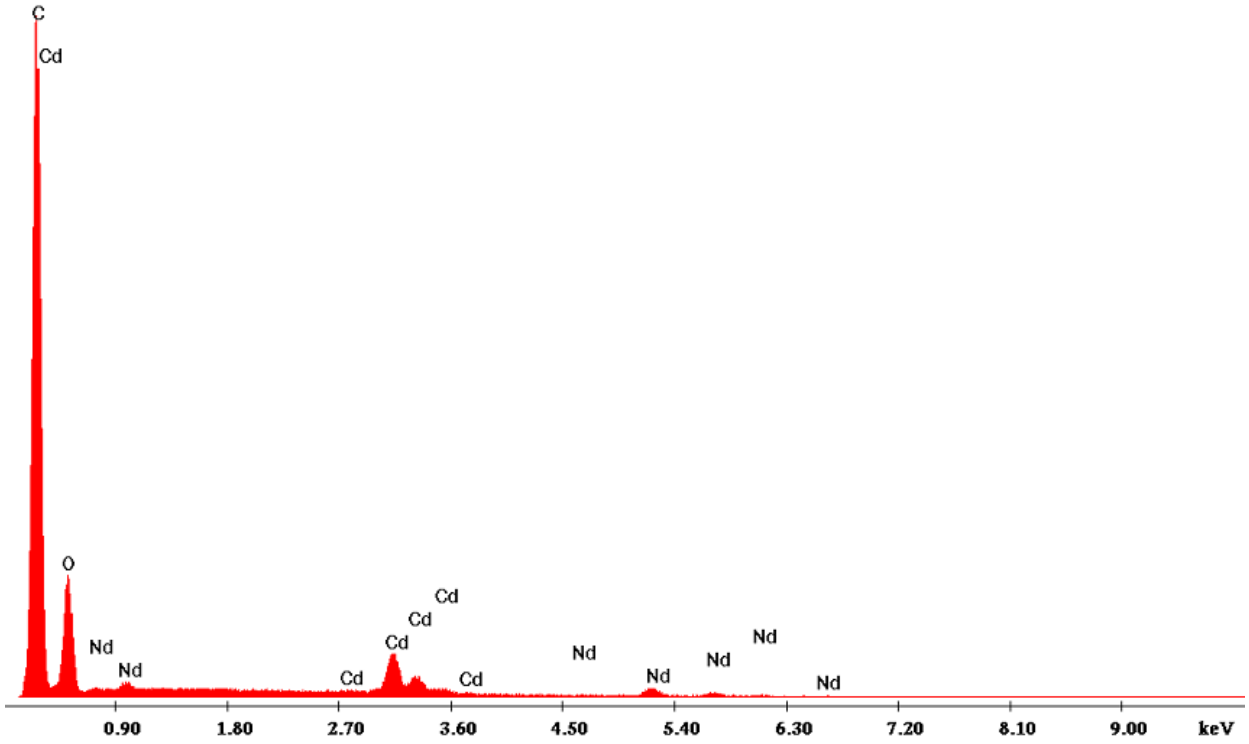
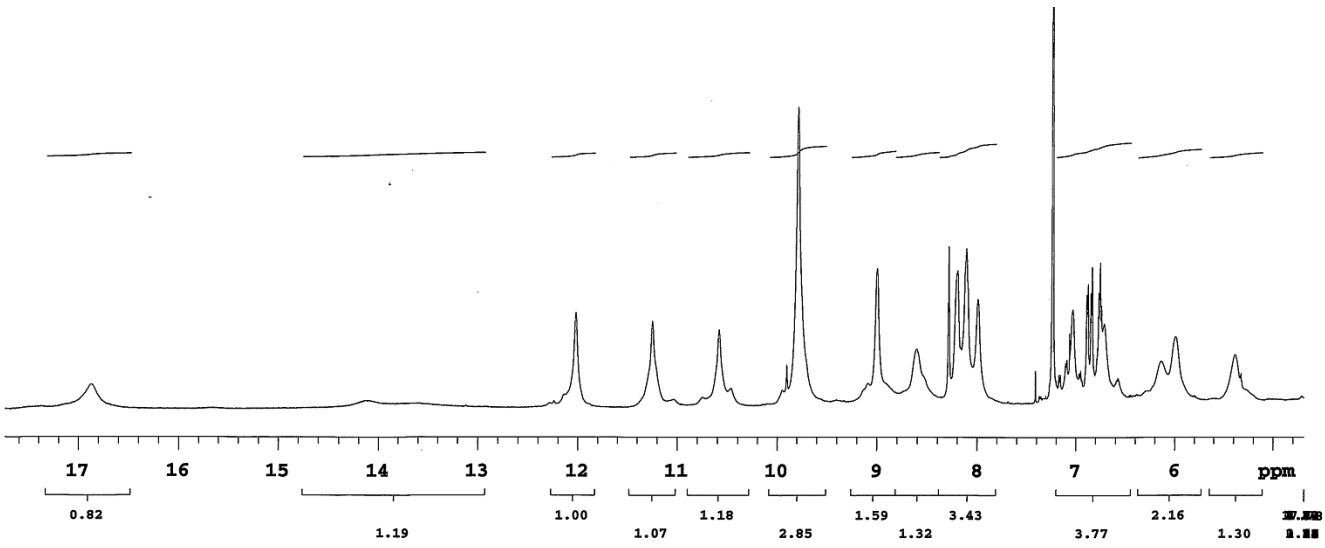
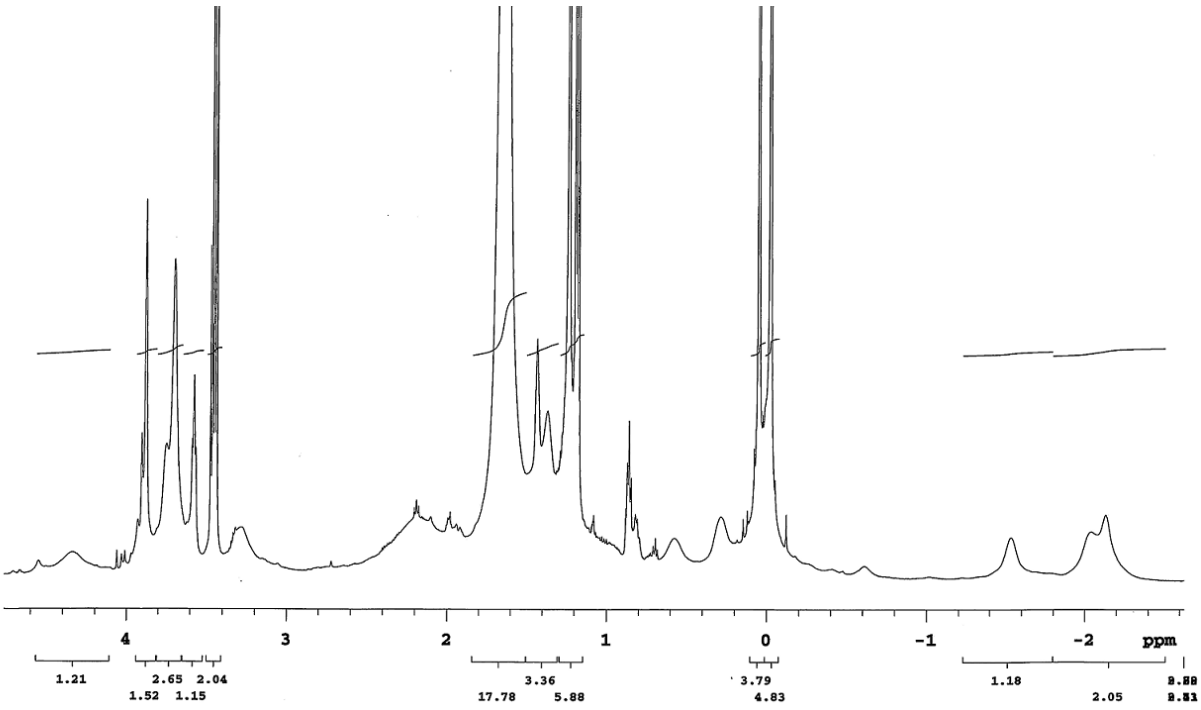


Figure S1. Energy dispersive X-ray (EDX) spectrum of **1**.

4. ^{1}H NMR spectra of 1 and 2



(a)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3
2
1
0
-1
-2
ppm
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2.04
1.52
1.15
3.36
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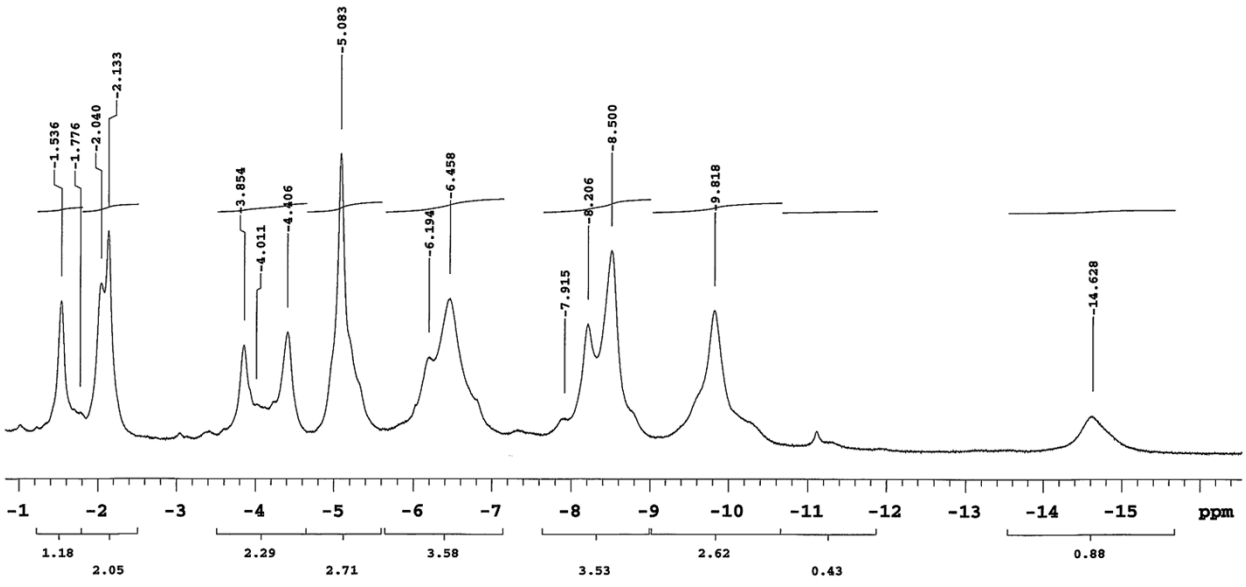
5.88
3.79
4.83
1.18
2.05

(b)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-1.776
-2.040
-2.133
-3.854
-4.011
-4.406
-5.083
-6.194
-6.458
-7.915
-8.206
-8.500
-9.818
-14.628
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
ppm
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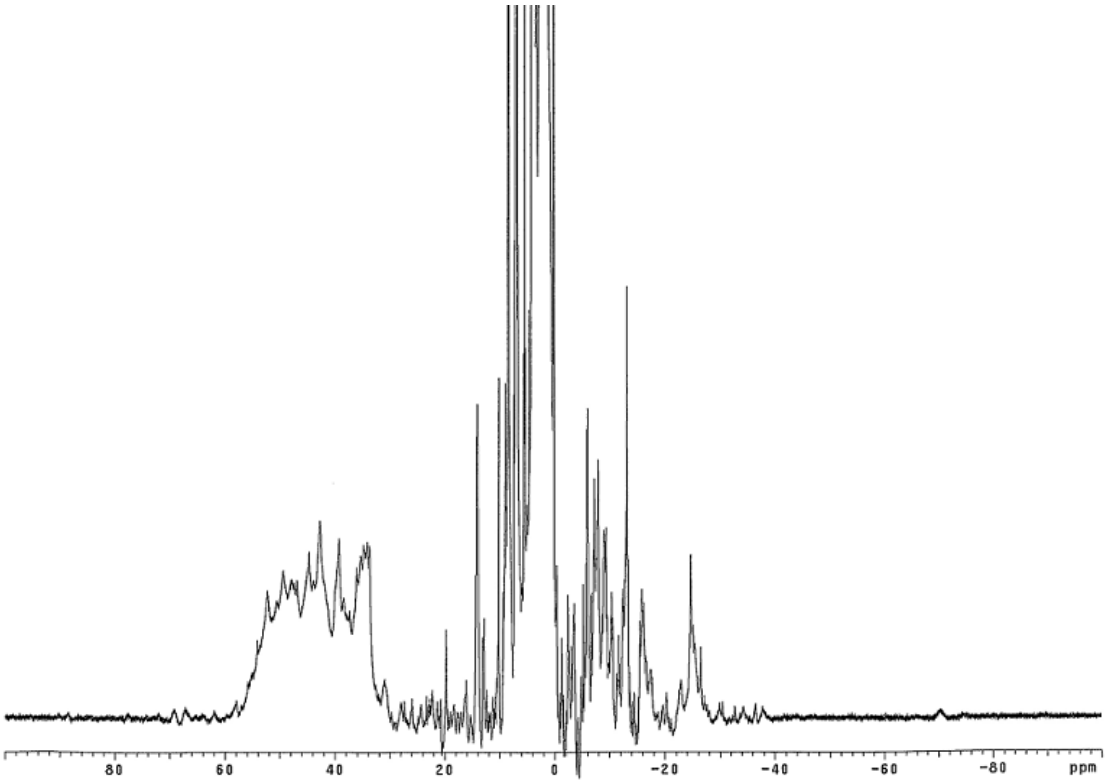
2.71
3.58
3.53
2.62
0.43
0.88

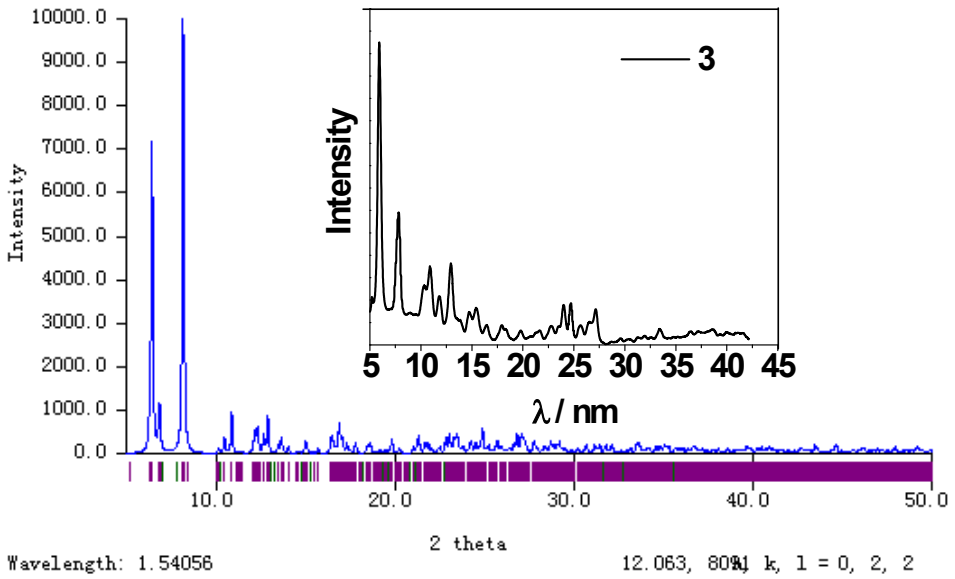
(c)



(d)

Figure S2. ^{1}H NMR spectrum of **1** (a-c) and **2** (d) in $CDCl_3$.

5. Powder XRD patterns of 3 and 4, and the thermogravimetric analysis of 1



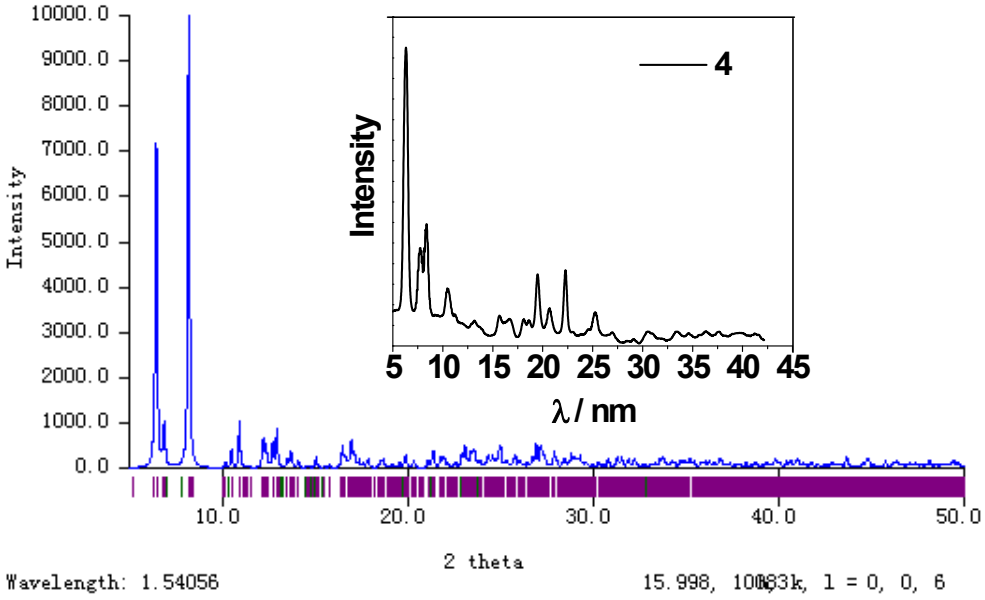


Figure S3. Powder XRD patterns of **3** and **4**.

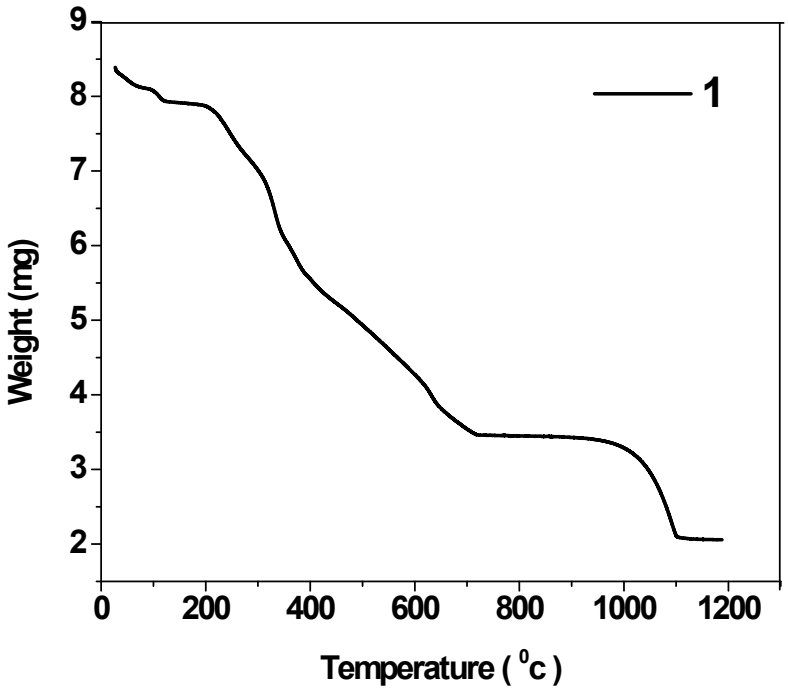
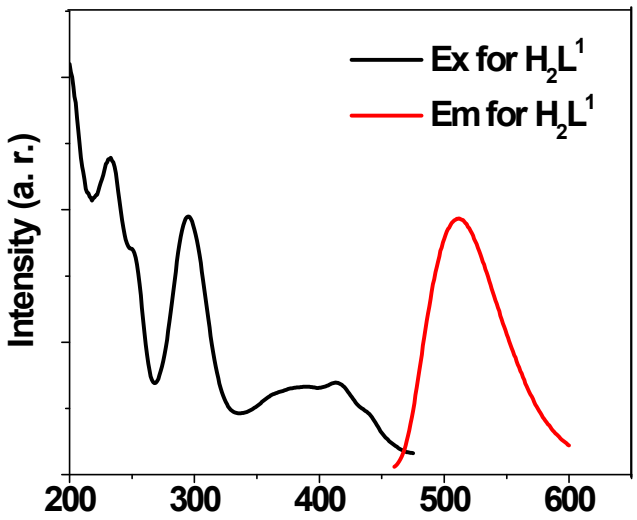
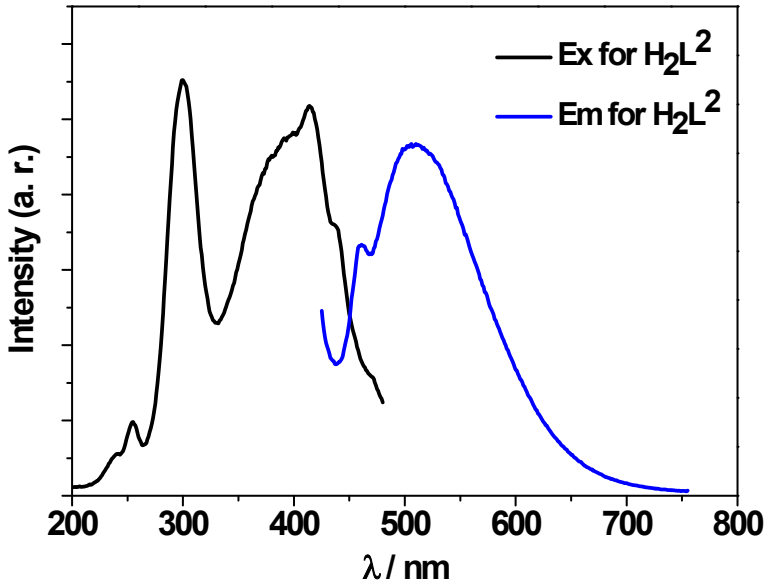


Figure S4. The thermogravimetric analysis of **1**.

6. Photophysical properties of the free $H_2L^{1,2}$ and 3d-4f clusters

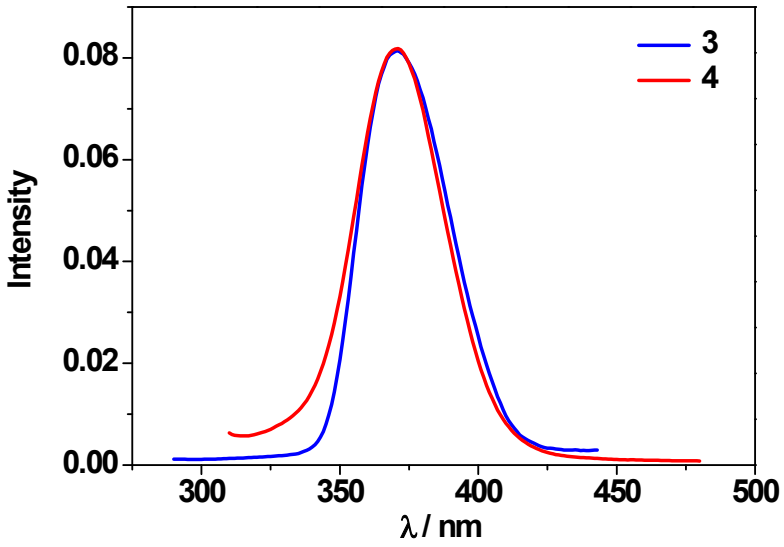


(a)

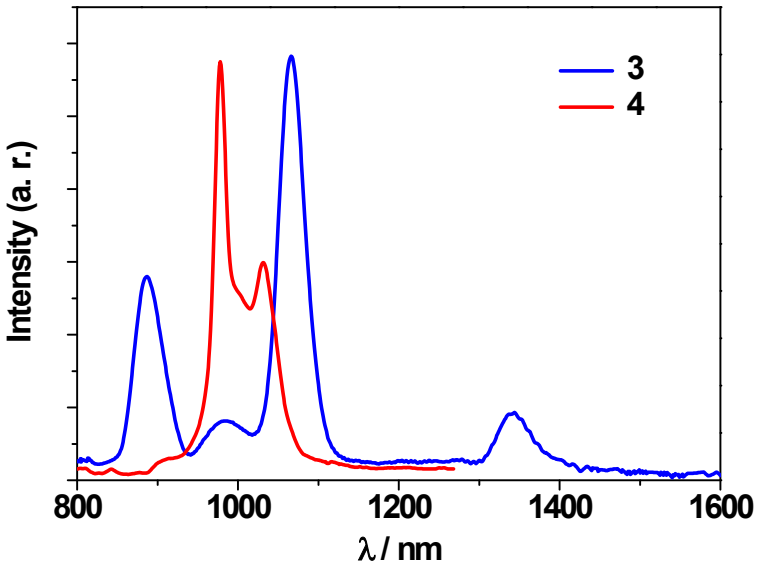


(b)

Figure S5. Excitation and emission spectra of free ligands H_2L^1 (a) and H_2L^2 (b) in CH_3CN.

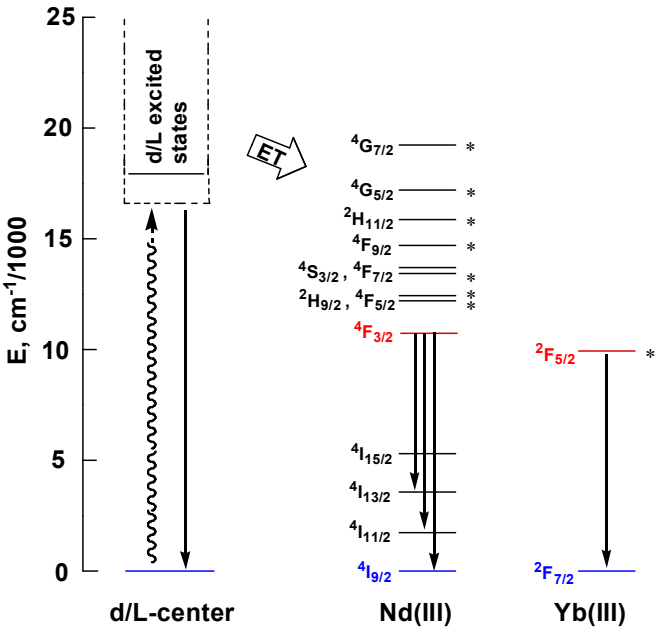


(a)



(b)

Figure S6. Excitation (a) and emission (b) spectra of **3** and **4** in CH_3CN.



Scheme S1. Relevant energy levels in **1-4** (Those marked with ***** can act as energy acceptors by either Förster or Dexter mechanism).

7. X-Ray Crystallography

Data were collected on a Rigaku Saturn Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 223 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]

Crystallographic data for **1-4** are presented in Table S1 and selected bond lengths are given in Tables S2-S5. (CCDC reference numbers 1023236, 1023237, 983620 and 1011985). 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 **1-4**.

	1	**2**	**3**	**4**
Formula	$C_{328}H_{413}Cd_{24}Nd_6N_{22}O_{131}$	$C_{328}H_{413}Cd_{24}Yb_6N_{22}O_{131}$	$C_{97}H_{150}Br_4Nd_4N_4O_{59}Zn_8$	$C_{97}H_{150}Br_4Yb_4N_4O_{59}Zn_8$
Fw	10322.84	10495.64	3727.26	3842.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	C2/c	C2/c
a [Å]	35.277(7)	35.136(7)	27.503(6)	27.466(6)
b [Å]	29.064(6)	29.045(6)	16.362(3)	16.258(3)
c [Å]	49.662(10)	49.536(10)	33.940(7)	33.847(7)
α [deg]	90	90	90	90
β [deg]	93.81(3)	94.13(3)	91.17(3)	91.29(3)
γ [deg]	90	90	90	90
V / [Å^3]	50806(18)	50420(18)	15270(5)	15111(5)
d / [g/cm^3]	1.350	2.155	1.621	1.689
Z	4	4	2	2
T [K]	223(1)	223(1)	223(1)	223(1)
F(000)	20380	20620	7390	7550
μ, mm^{-1}	1.647	1.647	3.690	4.830
θ rang, deg	3.00-25.00	0.91-25.00	1.56-25.00	1.46-25.00
reflns meads	343760	333694	42384	21562
reflns used	86623	85857	13167	12847
params	4576	4592	816	816
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0874, 0.2337	0.1114, 0.2964	0.0762, 0.2172	0.0815, 0.2377
R1, wR2 (all data)	0.1587, 0.2441	0.1560, 0.3307	0.1019, 0.2653	0.1025, 0.2616
Quality of fit	1.014	1.097	1.057	1.058

[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**.

Nd(1)-O(30)	2.281(8)	Cd(1)-O(30)	2.334(9)
Nd(1)-O(69)	2.299(9)	Cd(1)-O(29)	2.534(8)
Nd(1)-O(67)	2.320(9)	Cd(2)-O(129)	2.108(15)
Nd(1)-O(26)	2.339(9)	Cd(2)-O(34)	2.249(10)
Nd(1)-O(72)	2.414(10)	Cd(2)-O(71)	2.276(10)
Nd(1)-O(73)	2.416(9)	Cd(2)-O(75)	2.301(10)
Nd(1)-O(25)	2.589(8)	Cd(2)-O(33)	2.397(11)
Nd(1)-N(15)	2.590(11)	Cd(2)-O(76)	2.421(10)
Nd(2)-O(80)	2.290(10)	Cd(3)-O(77)	2.257(9)
Nd(2)-O(42)	2.302(10)	Cd(3)-O(38)	2.268(10)
Nd(2)-O(78)	2.333(11)	Cd(3)-O(79)	2.274(9)
Nd(2)-O(82)	2.360(11)	Cd(3)-N(19)	2.312(12)
Nd(2)-O(38)	2.371(10)	Cd(3)-O(76)	2.357(10)
Nd(2)-O(83)	2.410(9)	Cd(3)-O(74)	2.374(9)
Nd(2)-O(37)	2.590(10)	Cd(4)-O(2)	2.169(15)
Nd(2)-N(21)	2.605(12)	Cd(4)-N(1)	2.238(16)
Nd(3)-O(14)	2.290(9)	Cd(4)-O(81)	2.277(14)
Nd(3)-O(18)	2.296(10)	Cd(4)-O(42)	2.283(11)
Nd(3)-O(57)	2.321(9)	Cd(4)-O(83)	2.333(10)
Nd(3)-O(59)	2.375(9)	Cd(4)-O(41)	2.375(16)
Nd(3)-O(55)	2.385(10)	Cd(5)-O(45)	2.129(19)
Nd(3)-O(62)	2.432(9)	Cd(5)-O(2)	2.321(16)
Nd(3)-N(9)	2.544(12)	Cd(5)-O(131)	2.401(13)
Nd(3)-O(13)	2.575(9)	Cd(5)-O(46)	2.422(11)
Nd(4)-O(102)	2.298(10)	Cd(5)-O(81)	2.460(15)
Nd(4)-O(19)	2.329(11)	Cd(5)-O(1)	2.614(13)
Nd(4)-O(99)	2.344(11)	Cd(6)-O(6)	2.192(9)
Nd(4)-O(15)	2.399(10)	Cd(6)-O(47)	2.213(10)
Nd(4)-O(95)	2.416(11)	Cd(6)-N(3)	2.265(13)
Nd(4)-O(97)	2.418(10)	Cd(6)-O(84)	2.282(11)
Nd(4)-O(20)	2.577(11)	Cd(6)-O(46)	2.320(11)
Nd(4)-N(8)	2.591(13)	Cd(6)-O(52)	2.578(10)
Nd(5)-O(43)	2.299(9)	Cd(7)-O(10)	2.178(11)
Nd(5)-O(123)	2.344(10)	Cd(7)-O(6)	2.238(9)
Nd(5)-O(39)	2.352(9)	Cd(7)-N(5)	2.279(13)
Nd(5)-O(125)	2.358(9)	Cd(7)-O(48)	2.366(9)
Nd(5)-O(122)	2.425(10)	Cd(7)-O(51)	2.412(9)
Nd(5)-O(118)	2.439(11)	Cd(7)-O(52)	2.446(9)
Nd(5)-N(20)	2.544(11)	Cd(8)-O(54)	2.230(9)
Nd(5)-O(44)	2.600(9)	Cd(8)-O(10)	2.264(11)
Nd(6)-O(116)	2.299(10)	Cd(8)-O(50)	2.291(12)
Nd(6)-O(27)	2.303(10)	Cd(8)-O(48)	2.318(9)
Nd(6)-O(31)	2.318(10)	Cd(8)-O(49)	2.393(13)
Nd(6)-O(111)	2.343(11)	Cd(8)-O(9)	2.459(11)
Nd(6)-O(110)	2.410(12)	Cd(8)-O(53)	2.539(10)
Nd(6)-O(107)	2.420(11)	Cd(9)-O(56)	2.216(9)
Nd(6)-N(14)	2.559(12)	Cd(9)-O(14)	2.298(9)
Nd(6)-O(32)	2.590(10)	Cd(9)-O(58)	2.305(9)
Cd(1)-O(34)	2.200(10)	Cd(9)-N(7)	2.322(11)
Cd(1)-N(17)	2.246(13)	Cd(9)-O(53)	2.388(10)
Cd(1)-O(73)	2.259(9)	Cd(9)-O(51)	2.416(10)
Cd(1)-O(71)	2.273(9)	Cd(10)-N(11)	2.218(12)

Cd(10)-O(60)	2.229(9)	O(78)-Nd(2)-O(82)	75.4(4)
Cd(10)-O(22)	2.244(9)	O(80)-Nd(2)-O(38)	85.9(2)
Cd(10)-O(18)	2.325(9)	O(42)-Nd(2)-O(38)	131.1(3)
Cd(10)-O(62)	2.328(9)	O(78)-Nd(2)-O(38)	75.7(2)
Cd(10)-O(17)	2.568(10)	O(82)-Nd(2)-O(38)	108.5(3)
Cd(11)-O(22)	2.261(8)	O(80)-Nd(2)-O(83)	78.1(3)
Cd(11)-O(60)	2.267(8)	O(42)-Nd(2)-O(83)	70.2(3)
Cd(11)-O(66)	2.273(10)	O(78)-Nd(2)-O(83)	85.8(3)
Cd(11)-O(63)	2.322(13)	O(82)-Nd(2)-O(83)	77.8(3)
Cd(11)-O(65)	2.411(10)	O(38)-Nd(2)-O(83)	157.8(2)
Cd(11)-O(21)	2.438(10)	O(80)-Nd(2)-O(37)	142.4(2)
Cd(11)-O(64)	2.523(14)	O(42)-Nd(2)-O(37)	78.5(4)
Cd(12)-O(68)	2.264(9)	O(78)-Nd(2)-O(37)	110.7(3)
Cd(12)-N(13)	2.291(11)	O(82)-Nd(2)-O(37)	69.6(3)
Cd(12)-O(70)	2.293(9)	O(38)-Nd(2)-O(37)	62.5(3)
Cd(12)-O(26)	2.346(8)	O(83)-Nd(2)-O(37)	137.5(2)
Cd(12)-O(61)	2.381(9)	O(80)-Nd(2)-N(21)	74.4(2)
Cd(12)-O(65)	2.436(10)	O(42)-Nd(2)-N(21)	68.4(4)
O(30)-Nd(1)-O(69)	115.1(2)	O(78)-Nd(2)-N(21)	140.7(3)
O(30)-Nd(1)-O(67)	148.0(2)	O(82)-Nd(2)-N(21)	139.6(3)
O(69)-Nd(1)-O(67)	76.5(3)	O(38)-Nd(2)-N(21)	75.3(4)
O(30)-Nd(1)-O(26)	132.6(3)	O(83)-Nd(2)-N(21)	114.3(3)
O(69)-Nd(1)-O(26)	85.9(2)	O(37)-Nd(2)-N(21)	78.0(4)
O(67)-Nd(1)-O(26)	75.5(2)	O(14)-Nd(3)-O(18)	128.4(3)
O(30)-Nd(1)-O(72)	82.0(2)	O(14)-Nd(3)-O(57)	87.0(2)
O(69)-Nd(1)-O(72)	146.1(3)	O(18)-Nd(3)-O(57)	118.7(2)
O(67)-Nd(1)-O(72)	75.0(3)	O(14)-Nd(3)-O(59)	107.3(2)
O(26)-Nd(1)-O(72)	104.1(2)	O(18)-Nd(3)-O(59)	81.5(2)
O(30)-Nd(1)-O(73)	70.9(2)	O(57)-Nd(3)-O(59)	140.3(3)
O(69)-Nd(1)-O(73)	80.1(3)	O(14)-Nd(3)-O(55)	77.2(2)
O(67)-Nd(1)-O(73)	82.8(3)	O(18)-Nd(3)-O(55)	149.4(2)
O(26)-Nd(1)-O(73)	156.4(2)	O(57)-Nd(3)-O(55)	73.8(3)
O(72)-Nd(1)-O(73)	78.5(3)	O(59)-Nd(3)-O(55)	73.8(3)
O(30)-Nd(1)-O(25)	77.3(3)	O(14)-Nd(3)-O(62)	161.1(2)
O(69)-Nd(1)-O(25)	141.0(2)	O(18)-Nd(3)-O(62)	70.5(2)
O(67)-Nd(1)-O(25)	113.4(2)	O(57)-Nd(3)-O(62)	80.5(3)
O(26)-Nd(1)-O(25)	62.5(3)	O(59)-Nd(3)-O(62)	74.8(3)
O(72)-Nd(1)-O(25)	68.9(2)	O(55)-Nd(3)-O(62)	85.6(3)
O(73)-Nd(1)-O(25)	137.0(2)	O(14)-Nd(3)-N(9)	73.7(3)
O(30)-Nd(1)-N(15)	71.2(3)	O(18)-Nd(3)-N(9)	70.6(4)
O(69)-Nd(1)-N(15)	74.9(2)	O(57)-Nd(3)-N(9)	76.9(3)
O(67)-Nd(1)-N(15)	139.8(2)	O(59)-Nd(3)-N(9)	142.3(3)
O(26)-Nd(1)-N(15)	74.8(3)	O(55)-Nd(3)-N(9)	139.3(3)
O(72)-Nd(1)-N(15)	138.9(2)	O(62)-Nd(3)-N(9)	116.6(3)
O(73)-Nd(1)-N(15)	118.8(2)	O(14)-Nd(3)-O(13)	63.5(3)
O(25)-Nd(1)-N(15)	75.1(3)	O(18)-Nd(3)-O(13)	73.3(3)
O(80)-Nd(2)-O(42)	113.3(3)	O(57)-Nd(3)-O(13)	145.5(2)
O(80)-Nd(2)-O(78)	77.6(4)	O(59)-Nd(3)-O(13)	70.0(2)
O(42)-Nd(2)-O(78)	149.8(3)	O(55)-Nd(3)-O(13)	113.3(2)
O(80)-Nd(2)-O(82)	144.9(4)	O(62)-Nd(3)-O(13)	132.3(2)
O(42)-Nd(2)-O(82)	81.7(3)	N(9)-Nd(3)-O(13)	77.8(3)

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

Yb(1)-O(69)	2.306(9)	Cd(1)-N(17)	2.337(14)
Yb(1)-O(26)	2.308(9)	Cd(1)-O(29)	2.579(9)
Yb(1)-O(30)	2.315(9)	Cd(2)-O(129)	2.165(18)
Yb(1)-O(67)	2.323(10)	Cd(2)-O(34)	2.248(9)
Yb(1)-O(72)	2.392(9)	Cd(2)-O(71)	2.286(10)
Yb(1)-O(73)	2.434(10)	Cd(2)-O(75)	2.341(11)
Yb(1)-O(25)	2.555(9)	Cd(2)-O(33)	2.407(12)
Yb(1)-N(15)	2.601(12)	Cd(2)-O(76)	2.410(11)
Yb(2)-O(80)	2.258(12)	Cd(3)-O(77)	2.236(10)
Yb(2)-O(42)	2.326(12)	Cd(3)-O(38)	2.272(11)
Yb(2)-O(82)	2.337(13)	Cd(3)-O(79)	2.278(9)
Yb(2)-O(78)	2.373(13)	Cd(3)-N(19)	2.350(13)
Yb(2)-O(38)	2.376(11)	Cd(3)-O(74)	2.392(11)
Yb(2)-O(83)	2.376(10)	Cd(3)-O(76)	2.400(11)
Yb(2)-N(21)	2.568(12)	Cd(4)-O(2)	2.201(14)
Yb(2)-O(37)	2.586(15)	Cd(4)-N(1)	2.293(19)
Yb(3)-O(14)	2.292(8)	Cd(4)-O(42)	2.346(13)
Yb(3)-O(57)	2.331(9)	Cd(4)-O(83)	2.346(11)
Yb(3)-O(18)	2.342(9)	Cd(4)-O(81)	2.357(17)
Yb(3)-O(55)	2.369(9)	Cd(4)-O(41)	2.44(3)
Yb(3)-O(59)	2.390(10)	Cd(5)-O(45)	2.18(2)
Yb(3)-O(62)	2.456(9)	Cd(5)-O(2)	2.248(15)
Yb(3)-N(9)	2.560(13)	Cd(5)-O(46)	2.438(12)
Yb(3)-O(13)	2.591(9)	Cd(5)-O(131)	2.453(16)
Yb(4)-O(102)	2.282(11)	Cd(5)-O(1)	2.517(17)
Yb(4)-O(19)	2.310(12)	Cd(5)-O(81)	2.617(16)
Yb(4)-O(99)	2.316(10)	Cd(6)-O(47)	2.186(8)
Yb(4)-O(95)	2.390(10)	Cd(6)-O(6)	2.193(9)
Yb(4)-O(97)	2.397(11)	Cd(6)-N(3)	2.282(12)
Yb(4)-O(15)	2.402(9)	Cd(6)-O(84)	2.290(11)
Yb(4)-O(20)	2.522(12)	Cd(6)-O(46)	2.308(12)
Yb(4)-N(8)	2.597(12)	Cd(6)-O(52)	2.580(13)
Yb(5)-O(125)	2.320(10)	Cd(7)-O(10)	2.167(11)
Yb(5)-O(43)	2.320(9)	Cd(7)-O(6)	2.196(9)
Yb(5)-O(39)	2.321(9)	Cd(7)-O(48)	2.327(9)
Yb(5)-O(123)	2.323(11)	Cd(7)-N(5)	2.330(15)
Yb(5)-O(122)	2.416(13)	Cd(7)-O(51)	2.414(9)
Yb(5)-O(118)	2.430(9)	Cd(7)-O(52)	2.417(11)
Yb(5)-O(44)	2.552(9)	Cd(8)-O(54)	2.223(9)
Yb(5)-N(20)	2.570(14)	Cd(8)-O(10)	2.258(12)
Yb(6)-O(116)	2.298(11)	Cd(8)-O(48)	2.311(9)
Yb(6)-O(27)	2.316(9)	Cd(8)-O(50)	2.325(13)
Yb(6)-O(31)	2.326(11)	Cd(8)-O(9)	2.480(12)
Yb(6)-O(111)	2.344(10)	Cd(8)-O(49)	2.503(17)
Yb(6)-O(110)	2.410(12)	Cd(8)-O(53)	2.534(9)
Yb(6)-O(107)	2.444(9)	Cd(9)-O(56)	2.257(12)
Yb(6)-N(14)	2.539(13)	Cd(9)-O(14)	2.304(8)
Yb(6)-O(32)	2.628(11)	Cd(9)-O(58)	2.317(9)
Cd(1)-O(34)	2.239(10)	Cd(9)-N(7)	2.337(12)
Cd(1)-O(30)	2.286(10)	Cd(9)-O(53)	2.387(10)
Cd(1)-O(73)	2.292(10)	Cd(9)-O(51)	2.406(8)
Cd(1)-O(71)	2.293(9)	Cd(10)-N(11)	2.214(14)

Cd(10)-O(22)	2.248(10)	O(82)-Yb(2)-O(78)	74.8(5)
Cd(10)-O(60)	2.257(10)	O(80)-Yb(2)-O(38)	84.9(3)
Cd(10)-O(18)	2.296(9)	O(42)-Yb(2)-O(38)	129.2(4)
Cd(10)-O(62)	2.298(9)	O(82)-Yb(2)-O(38)	109.7(4)
Cd(10)-O(17)	2.571(9)	O(78)-Yb(2)-O(38)	76.4(3)
Cd(11)-O(22)	2.236(10)	O(80)-Yb(2)-O(83)	78.8(4)
Cd(11)-O(66)	2.248(12)	O(42)-Yb(2)-O(83)	72.5(3)
Cd(11)-O(60)	2.261(9)	O(82)-Yb(2)-O(83)	76.7(5)
Cd(11)-O(63)	2.326(14)	O(78)-Yb(2)-O(83)	84.8(4)
Cd(11)-O(65)	2.386(9)	O(38)-Yb(2)-O(83)	157.3(3)
Cd(11)-O(21)	2.457(11)	O(80)-Yb(2)-N(21)	74.9(3)
Cd(11)-O(64)	2.527(14)	O(42)-Yb(2)-N(21)	67.4(4)
Cd(12)-O(68)	2.285(8)	O(82)-Yb(2)-N(21)	139.4(4)
Cd(12)-O(70)	2.286(8)	O(78)-Yb(2)-N(21)	141.1(3)
Cd(12)-N(13)	2.305(12)	O(38)-Yb(2)-N(21)	73.9(4)
Cd(12)-O(26)	2.350(9)	O(83)-Yb(2)-N(21)	116.1(3)
Cd(12)-O(61)	2.360(10)	O(80)-Yb(2)-O(37)	143.0(3)
Cd(12)-O(65)	2.450(9)	O(42)-Yb(2)-O(37)	77.7(5)
O(69)-Yb(1)-O(26)	85.4(2)	O(82)-Yb(2)-O(37)	68.8(4)
O(69)-Yb(1)-O(30)	116.8(2)	O(78)-Yb(2)-O(37)	109.5(3)
O(26)-Yb(1)-O(30)	132.9(3)	O(38)-Yb(2)-O(37)	63.2(4)
O(69)-Yb(1)-O(67)	76.1(3)	O(83)-Yb(2)-O(37)	136.8(3)
O(26)-Yb(1)-O(67)	76.7(2)	N(21)-Yb(2)-O(37)	78.5(4)
O(30)-Yb(1)-O(67)	145.9(2)	O(14)-Yb(3)-O(57)	86.5(2)
O(69)-Yb(1)-O(72)	145.9(3)	O(14)-Yb(3)-O(18)	128.6(3)
O(26)-Yb(1)-O(72)	104.3(2)	O(57)-Yb(3)-O(18)	119.7(3)
O(30)-Yb(1)-O(72)	80.6(2)	O(14)-Yb(3)-O(55)	76.6(2)
O(67)-Yb(1)-O(72)	74.6(3)	O(57)-Yb(3)-O(55)	74.1(3)
O(69)-Yb(1)-O(73)	80.0(3)	O(18)-Yb(3)-O(55)	149.0(2)
O(26)-Yb(1)-O(73)	155.6(2)	O(14)-Yb(3)-O(59)	106.7(3)
O(30)-Yb(1)-O(73)	71.5(2)	O(57)-Yb(3)-O(59)	140.5(3)
O(67)-Yb(1)-O(73)	80.9(3)	O(18)-Yb(3)-O(59)	81.2(3)
O(72)-Yb(1)-O(73)	78.5(3)	O(55)-Yb(3)-O(59)	73.3(3)
O(69)-Yb(1)-O(25)	141.7(2)	O(14)-Yb(3)-O(62)	161.8(2)
O(26)-Yb(1)-O(25)	63.7(3)	O(57)-Yb(3)-O(62)	81.5(3)
O(30)-Yb(1)-O(25)	75.9(3)	O(18)-Yb(3)-O(62)	69.6(2)
O(67)-Yb(1)-O(25)	114.7(2)	O(55)-Yb(3)-O(62)	86.9(3)
O(72)-Yb(1)-O(25)	68.4(2)	O(59)-Yb(3)-O(62)	75.1(3)
O(73)-Yb(1)-O(25)	136.5(2)	O(14)-Yb(3)-N(9)	73.8(4)
O(69)-Yb(1)-N(15)	75.0(3)	O(57)-Yb(3)-N(9)	76.2(2)
O(26)-Yb(1)-N(15)	75.0(3)	O(18)-Yb(3)-N(9)	71.6(3)
O(30)-Yb(1)-N(15)	72.3(4)	O(55)-Yb(3)-N(9)	138.9(2)
O(67)-Yb(1)-N(15)	140.6(3)	O(59)-Yb(3)-N(9)	142.9(2)
O(72)-Yb(1)-N(15)	139.0(3)	O(62)-Yb(3)-N(9)	116.1(3)
O(73)-Yb(1)-N(15)	119.1(3)	O(14)-Yb(3)-O(13)	63.4(3)
O(25)-Yb(1)-N(15)	75.4(3)	O(57)-Yb(3)-O(13)	144.9(2)
O(80)-Yb(2)-O(42)	113.9(3)	O(18)-Yb(3)-O(13)	73.0(3)
O(80)-Yb(2)-O(82)	144.6(5)	O(55)-Yb(3)-O(13)	112.8(2)
O(42)-Yb(2)-O(82)	82.3(3)	O(59)-Yb(3)-O(13)	70.1(2)
O(80)-Yb(2)-O(78)	78.0(4)	O(62)-Yb(3)-O(13)	131.8(2)
O(42)-Yb(2)-O(78)	150.9(3)	N(9)-Yb(3)-O(13)	78.1(3)

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

Yb(1)-O(16)	2.420(8)	O(5)-Yb(1)-O(25)	69.9(3)
Yb(1)-O(12)	2.431(8)	O(6)-Yb(1)-O(25)	116.6(3)
Yb(1)-O(18)	2.450(8)	O(10)-Yb(1)-O(25)	73.0(3)
Yb(1)-O(5)	2.486(7)	O(16)-Yb(1)-O(2)	95.4(3)
Yb(1)-O(6)	2.487(7)	O(12)-Yb(1)-O(2)	129.1(3)
Yb(1)-O(10)	2.492(9)	O(18)-Yb(1)-O(2)	73.7(3)
Yb(1)-O(25)	2.498(9)	O(5)-Yb(1)-O(2)	141.0(3)
Yb(1)-O(2)	2.526(9)	O(6)-Yb(1)-O(2)	133.5(3)
Yb(1)-O(1)	2.661(8)	O(10)-Yb(1)-O(2)	74.6(3)
Yb(2)-O(14)	2.420(8)	O(25)-Yb(1)-O(2)	71.2(3)
Yb(2)-O(6)	2.437(7)	O(16)-Yb(1)-O(1)	68.6(3)
Yb(2)-O(22)	2.440(8)	O(12)-Yb(1)-O(1)	71.0(2)
Yb(2)-O(19)	2.458(9)	O(18)-Yb(1)-O(1)	69.0(3)
Yb(2)-O(7)	2.480(9)	O(5)-Yb(1)-O(1)	140.4(3)
Yb(2)-O(4)	2.515(8)	O(6)-Yb(1)-O(1)	131.5(2)
Yb(2)-O(23)	2.516(8)	O(10)-Yb(1)-O(1)	127.3(3)
Yb(2)-O(5)	2.522(8)	O(25)-Yb(1)-O(1)	111.6(3)
Yb(2)-O(3)	2.734(8)	O(2)-Yb(1)-O(1)	59.8(3)
Zn(1)-O(26)	1.939(12)	O(14)-Yb(2)-O(6)	89.8(3)
Zn(1)-O(2)	1.956(9)	O(14)-Yb(2)-O(22)	76.3(3)
Zn(1)-O(9)	1.970(12)	O(6)-Yb(2)-O(22)	139.5(3)
Zn(1)-N(1)	1.973(15)	O(14)-Yb(2)-O(19)	74.9(3)
Zn(2)-O(5)	1.941(8)	O(6)-Yb(2)-O(19)	76.7(3)
Zn(2)-O(15)	1.954(10)	O(22)-Yb(2)-O(19)	132.8(3)
Zn(2)-O(21)	1.965(9)	O(14)-Yb(2)-O(7)	137.0(3)
Zn(2)-O(13)	2.024(10)	O(6)-Yb(2)-O(7)	87.1(3)
Zn(3)-O(6)	1.932(8)	O(22)-Yb(2)-O(7)	78.6(3)
Zn(3)-O(20)	1.941(9)	O(19)-Yb(2)-O(7)	144.7(3)
Zn(3)-O(11)	1.945(9)	O(14)-Yb(2)-O(4)	130.8(3)
Zn(3)-O(17)	1.999(9)	O(6)-Yb(2)-O(4)	135.1(2)
Zn(4)-O(8)	1.936(9)	O(22)-Yb(2)-O(4)	77.5(3)
Zn(4)-O(24)	1.968(9)	O(19)-Yb(2)-O(4)	94.3(3)
Zn(4)-O(4)	1.970(8)	O(7)-Yb(2)-O(4)	75.3(3)
Zn(4)-N(2)	2.014(10)	O(14)-Yb(2)-O(23)	142.7(3)
O(16)-Yb(1)-O(12)	77.2(3)	O(6)-Yb(2)-O(23)	67.1(3)
O(16)-Yb(1)-O(18)	135.7(3)	O(22)-Yb(2)-O(23)	139.9(3)
O(12)-Yb(1)-O(18)	77.7(3)	O(19)-Yb(2)-O(23)	71.7(3)
O(16)-Yb(1)-O(5)	75.1(3)	O(7)-Yb(2)-O(23)	73.2(3)
O(12)-Yb(1)-O(5)	86.3(3)	O(4)-Yb(2)-O(23)	68.3(3)
O(18)-Yb(1)-O(5)	138.3(3)	O(14)-Yb(2)-O(5)	73.2(3)
O(16)-Yb(1)-O(6)	131.1(3)	O(6)-Yb(2)-O(5)	65.8(3)
O(12)-Yb(1)-O(6)	72.6(2)	O(22)-Yb(2)-O(5)	73.8(3)
O(18)-Yb(1)-O(6)	72.9(3)	O(19)-Yb(2)-O(5)	130.0(3)
O(5)-Yb(1)-O(6)	65.6(3)	O(7)-Yb(2)-O(5)	66.5(3)
O(16)-Yb(1)-O(10)	145.1(3)	O(4)-Yb(2)-O(5)	135.7(3)
O(12)-Yb(1)-O(10)	135.0(3)	O(23)-Yb(2)-O(5)	117.9(3)
O(18)-Yb(1)-O(10)	74.3(3)	O(14)-Yb(2)-O(3)	73.2(3)
O(5)-Yb(1)-O(10)	91.7(3)	O(6)-Yb(2)-O(3)	143.5(3)
O(6)-Yb(1)-O(10)	65.9(3)	O(22)-Yb(2)-O(3)	68.4(3)
O(16)-Yb(1)-O(25)	72.2(3)	O(19)-Yb(2)-O(3)	67.9(3)
O(12)-Yb(1)-O(25)	145.0(3)	O(7)-Yb(2)-O(3)	127.3(3)
O(18)-Yb(1)-O(25)	136.9(3)	O(4)-Yb(2)-O(3)	58.6(2)

O(23)-Yb(2)-O(3)	107.9(3)	O(21)-Zn(2)-O(13)	101.3(4)
O(5)-Yb(2)-O(3)	134.0(3)	O(6)-Zn(3)-O(20)	116.4(3)
O(26)-Zn(1)-O(2)	106.6(4)	O(6)-Zn(3)-O(11)	113.0(4)
O(26)-Zn(1)-O(9)	113.3(5)	O(20)-Zn(3)-O(11)	104.2(4)
O(2)-Zn(1)-O(9)	118.9(5)	O(6)-Zn(3)-O(17)	105.2(3)
O(26)-Zn(1)-N(1)	113.5(6)	O(20)-Zn(3)-O(17)	106.3(4)
O(2)-Zn(1)-N(1)	94.1(5)	O(11)-Zn(3)-O(17)	111.8(4)
O(9)-Zn(1)-N(1)	109.2(6)	O(8)-Zn(4)-O(24)	108.0(4)
O(5)-Zn(2)-O(15)	109.0(4)	O(8)-Zn(4)-O(4)	121.1(4)
O(5)-Zn(2)-O(21)	115.0(4)	O(24)-Zn(4)-O(4)	110.9(4)
O(15)-Zn(2)-O(21)	111.3(4)	O(8)-Zn(4)-N(2)	108.7(4)
O(5)-Zn(2)-O(13)	110.6(4)	O(24)-Zn(4)-N(2)	112.6(4)
O(15)-Zn(2)-O(13)	109.4(5)	O(4)-Zn(4)-N(2)	95.0(4)

Table S5. Selected Bond Lengths (Å) and Angles (°) for **4**.

Yb(1)-O(16)	2.420(8)	O(16)-Yb(1)-O(12)	77.2(3)
Yb(1)-O(12)	2.431(8)	O(16)-Yb(1)-O(18)	135.7(3)
Yb(1)-O(18)	2.450(8)	O(12)-Yb(1)-O(18)	77.7(3)
Yb(1)-O(5)	2.486(7)	O(16)-Yb(1)-O(5)	75.1(3)
Yb(1)-O(6)	2.487(7)	O(12)-Yb(1)-O(5)	86.3(3)
Yb(1)-O(10)	2.492(9)	O(18)-Yb(1)-O(5)	138.3(3)
Yb(1)-O(25)	2.498(9)	O(16)-Yb(1)-O(6)	131.1(3)
Yb(1)-O(2)	2.526(9)	O(12)-Yb(1)-O(6)	72.6(2)
Yb(1)-O(1)	2.661(8)	O(18)-Yb(1)-O(6)	72.9(3)
Yb(2)-O(14)	2.420(8)	O(5)-Yb(1)-O(6)	65.6(3)
Yb(2)-O(6)	2.437(7)	O(16)-Yb(1)-O(10)	145.1(3)
Yb(2)-O(22)	2.440(8)	O(12)-Yb(1)-O(10)	135.0(3)
Yb(2)-O(19)	2.458(9)	O(18)-Yb(1)-O(10)	74.3(3)
Yb(2)-O(7)	2.480(9)	O(5)-Yb(1)-O(10)	91.7(3)
Yb(2)-O(4)	2.515(8)	O(6)-Yb(1)-O(10)	65.9(3)
Yb(2)-O(23)	2.516(8)	O(16)-Yb(1)-O(25)	72.2(3)
Yb(2)-O(5)	2.522(8)	O(12)-Yb(1)-O(25)	145.0(3)
Yb(2)-O(3)	2.734(8)	O(18)-Yb(1)-O(25)	136.9(3)
Zn(1)-O(26)	1.939(12)	O(5)-Yb(1)-O(25)	69.9(3)
Zn(1)-O(2)	1.956(9)	O(6)-Yb(1)-O(25)	116.6(3)
Zn(1)-O(9)	1.970(12)	O(10)-Yb(1)-O(25)	73.0(3)
Zn(1)-N(1)	1.973(15)	O(16)-Yb(1)-O(2)	95.4(3)
Zn(2)-O(5)	1.941(8)	O(12)-Yb(1)-O(2)	129.1(3)
Zn(2)-O(15)	1.954(10)	O(18)-Yb(1)-O(2)	73.7(3)
Zn(2)-O(21)	1.965(9)	O(5)-Yb(1)-O(2)	141.0(3)
Zn(2)-O(13)	2.024(10)	O(6)-Yb(1)-O(2)	133.5(3)
Zn(3)-O(6)	1.932(8)	O(10)-Yb(1)-O(2)	74.6(3)
Zn(3)-O(20)	1.941(9)	O(25)-Yb(1)-O(2)	71.2(3)
Zn(3)-O(11)	1.945(9)	O(16)-Yb(1)-O(1)	68.6(3)
Zn(3)-O(17)	1.999(9)	O(12)-Yb(1)-O(1)	71.0(2)
Zn(4)-O(8)	1.936(9)	O(18)-Yb(1)-O(1)	69.0(3)
Zn(4)-O(24)	1.968(9)	O(5)-Yb(1)-O(1)	140.4(3)
Zn(4)-O(4)	1.970(8)	O(6)-Yb(1)-O(1)	131.5(2)
Zn(4)-N(2)	2.014(10)	O(10)-Yb(1)-O(1)	127.3(3)

O(25)-Yb(1)-O(1)	111.6(3)	O(6)-Yb(2)-O(3)	143.5(3)
O(2)-Yb(1)-O(1)	59.8(3)	O(22)-Yb(2)-O(3)	68.4(3)
O(14)-Yb(2)-O(6)	89.8(3)	O(19)-Yb(2)-O(3)	67.9(3)
O(14)-Yb(2)-O(22)	76.3(3)	O(7)-Yb(2)-O(3)	127.3(3)
O(6)-Yb(2)-O(22)	139.5(3)	O(4)-Yb(2)-O(3)	58.6(2)
O(14)-Yb(2)-O(19)	74.9(3)	O(23)-Yb(2)-O(3)	107.9(3)
O(6)-Yb(2)-O(19)	76.7(3)	O(5)-Yb(2)-O(3)	134.0(3)
O(22)-Yb(2)-O(19)	132.8(3)	O(26)-Zn(1)-O(2)	106.6(4)
O(14)-Yb(2)-O(7)	137.0(3)	O(26)-Zn(1)-O(9)	113.3(5)
O(6)-Yb(2)-O(7)	87.1(3)	O(2)-Zn(1)-O(9)	118.9(5)
O(22)-Yb(2)-O(7)	78.6(3)	O(26)-Zn(1)-N(1)	113.5(6)
O(19)-Yb(2)-O(7)	144.7(3)	O(2)-Zn(1)-N(1)	94.1(5)
O(14)-Yb(2)-O(4)	130.8(3)	O(9)-Zn(1)-N(1)	109.2(6)
O(6)-Yb(2)-O(4)	135.1(2)	O(5)-Zn(2)-O(15)	109.0(4)
O(22)-Yb(2)-O(4)	77.5(3)	O(5)-Zn(2)-O(21)	115.0(4)
O(19)-Yb(2)-O(4)	94.3(3)	O(15)-Zn(2)-O(21)	111.3(4)
O(7)-Yb(2)-O(4)	75.3(3)	O(5)-Zn(2)-O(13)	110.6(4)
O(14)-Yb(2)-O(23)	142.7(3)	O(15)-Zn(2)-O(13)	109.4(5)
O(6)-Yb(2)-O(23)	67.1(3)	O(21)-Zn(2)-O(13)	101.3(4)
O(22)-Yb(2)-O(23)	139.9(3)	O(6)-Zn(3)-O(20)	116.4(3)
O(19)-Yb(2)-O(23)	71.7(3)	O(6)-Zn(3)-O(11)	113.0(4)
O(7)-Yb(2)-O(23)	73.2(3)	O(20)-Zn(3)-O(11)	104.2(4)
O(4)-Yb(2)-O(23)	68.3(3)	O(6)-Zn(3)-O(17)	105.2(3)
O(14)-Yb(2)-O(5)	73.2(3)	O(20)-Zn(3)-O(17)	106.3(4)
O(6)-Yb(2)-O(5)	65.8(3)	O(11)-Zn(3)-O(17)	111.8(4)
O(22)-Yb(2)-O(5)	73.8(3)	O(8)-Zn(4)-O(24)	108.0(4)
O(19)-Yb(2)-O(5)	130.0(3)	O(8)-Zn(4)-O(4)	121.1(4)
O(7)-Yb(2)-O(5)	66.5(3)	O(24)-Zn(4)-O(4)	110.9(4)
O(4)-Yb(2)-O(5)	135.7(3)	O(8)-Zn(4)-N(2)	108.7(4)
O(23)-Yb(2)-O(5)	117.9(3)	O(24)-Zn(4)-N(2)	112.6(4)
O(14)-Yb(2)-O(3)	73.2(3)	O(4)-Zn(4)-N(2)	95.0(4)