Supporting Information

Anion dependent self-assembly of 56-metal Cd-Ln nanoclusters with enhanced near-infrared luminescence properties

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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 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: Nicolet IR 200 FTIR spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses (C, H, N) were carried out on a Varian EL elemental analyzer. Conductivity measurements were carried out with a DDS-11 conductivity bridge for 10^{-3} M solutions in CH_3CN. 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 BECKMAN DU 640 spectrophotometer,

excitation and emission spectra on a QuantaMaster PTI fluorimeter. The intrinsic quantum yields (Φ_{Ln}) of Nd^{3+} and Yb^{3+} emissions in **1-4** are calculated by using $\Phi_{Ln} = \tau/\tau_0$ (τ, observed emission lifetime; τ_0, the natural lifetime of Ln^{3+}: 250 μs for Nd^{3+}, 2000 μs for Yb^{3+}).[2,3]

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

(2) Meshkova, S. B.; Topilova, Z. M.; Bolshoy, D. V.; Beltyukova, S. V.; Tsvirko, M. P.; Venchikov, V. Y.; Ya, V. *Acta Phys*. *Pol*. *A*, **1999**, *95*, 983-990.

(3) Klink, S. I.; Grave, L.; Reinhoudt, D. N.; Veggel, F. C. J. M. v. *J. Phys*. *Chem*. *A*, **2000**, *104*, 5457-5468.

2. Synthesis of 1-4

$[Nd_8Cd_{24}L_{12}(OAc)_{48}]$ (**1**). 0.52 mmol (0.1382 g) of $Cd(OAc)_2{\cdot}2H_2O$ and 0.12 mmol (0.0472 g) of $Nd(OAc)_3{\cdot}4H_2O$ were dissolved in 60 mL MeOH at room temperature, and 0.26 mmol (0.1409 g) H_2L and 0.30 mmol Et_3N in 10 ml EtOH were then added. The resulting solution was stirred and heated under reflux for 30mins. 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 $Nd(OAc)_3{\cdot}4H_2O$): 0.111 g (52 %). m. p. > 195 ^oC (dec.). Elemental analysis: Found: C, 32.77; H, 3.89; N, 2.40 %. Calc. for $C_{360}H_{426}Br_{24}Cd_{24}N_{24}Nd_8O_{144}(EtOH)_8(MeOH)_{12}(H_2O)_{15}$: C, 32.85; H, 3.92; N, 2.37 %. IR (CH_3OH, cm^{-1}): 3946 (m), 1633 (m), 1557 (s), 1405 (s), 1306 (m), 1213 (s), 1080 (m), 1026 (w), 963 (m), 875 (m), 740 (s), 662 (w).

$[Yb_8Cd_{24}L_{12}(OAc)_{48}]$ (**2**). The procedure was the same as that for **1** using $Cd(OAc)_2{\cdot}2H_2O$ (0.1382 g, 0.52 mmol) and $Yb(OAc)_3{\cdot}4H_2O$ (0.0506 g, 0.12 mmol). Pale yellow single crystals of **2** were formed after one week. Yield (based on $Yb(OAc)_3{\cdot}4H_2O$): 0.1193 g (55 %). m. p. > 203 ^oC (dec.). Elemental analysis: Found: C, 32.15; H, 3.63; N, 2.45 %. Calc. For $C_{360}H_{426}Br_{24}Cd_{24}N_{24}Yb_8O_{144}(EtOH)_6(MeOH)_{10}(H_2O)_{11}$: C, 32.34; H, 3.72; N, 2.37 %. IR (CH_3OH, cm^{-1}): 2932 (m), 1633 (m), 1574 (s), 1435 (s), 1307 (m), 1212 (s), 1168 (w), 1079 (m), 1043 (m), 962 (s), 872 (s), 741 (m), 669 (w).

$[Nd_{12}Cd_{44}L_{20}Cl_{30}(OAc)_{54}]$ (**3**). The procedure was the same as that for **1** using $Cd(OAc)_2{\cdot}2H_2O$ (0.1382 g, 0.52 mmol) and $NdCl_3{\cdot}6H_2O$ (0.0431 g, 0.12 mmol). Pale yellow single crystals of **3** were formed after one week. Yield (based on $NdCl_3{\cdot}6H_2O$): 0.0870 g (40 %).

m. p. > 210 °C (dec.). Elemental analysis: Found: C, 30.49; H, 3.26; N, 2.53 %. Calc. for $C_{550}H_{639}Br_{40}Cd_{44}Cl_{31}N_{40}Nd_{12}O_{190}(EtOH)_9(MeOH)_8(H_2O)_{16}$: C, 30.57; H, 3.35; N, 2.46 %. IR (CH_3OH, cm^{-1}): 2962 (m), 1634 (s), 1556 (s), 1435 (s), 1305 (m), 1211 (s), 1080 (s), 877 (s), 800 (w), 742 (s), 665 (w). ^1H NMR (600 MHz, CD_3OD): δ(ppm) -16.121 (4H), -11.505 (4H), -9.895 (12H), -7.897 (24H), -5.736 (8H), -5.027 (12H), -4.471 (6H), -4.053 (6H), -3.757 (6H), -3.313 (4H), -3.178 (2H), -2.436 (2H), -2.041 (12H), -1.643 (8H), -1.368 (8H), -1.087 (6H), -0.971 (6H), -0.117/0.029/0.55 (40H), 0.611 (8H), 0.826 (8H), 1.095/1.205/1.320/1.375 (100H), 1.671/1.800 (90H), 3.019 (12H), 3.457/3.578/3.679/3.896 (78H), 5.945 (4H), 6.325 (4H), 6.420 (6H), 6.7630 (12H), 6.756 (18H), 6.881 (18H), 7.118 (6H), 7.419 (6H), 7.749 (6H), 7.896 (12H), 8.226 (12H), 8.291 (18H), 8.617 (2H), 9.095 (2H), 9.285 (12H), 9.549 (6H), 9.891 (18H), 10.003 (6H), 10.395 (2H), 10.707 (4H), 11.075 (6H), 11.841 (6H), 11.961 (6H), 12.088 (2H), 14.202 (6H), 15.932 (2H), 16.886 (4H).

$[Yb_{12}Cd_{44}L_{20}Cl_{30}(OAc)_{54}]$ (**4**). The procedure was the same as that for **1** using $Cd(OAc)_2{\cdot}2H_2O$ (0.1382 g, 0.52 mmol) and $YbCl_3{\cdot}6H_2O$ (0.0466 g, 0.12 mmol). Pale yellow single crystals of **4** were formed after one week. Yield (based on $YbCl_3{\cdot}6H_2O$): 0.0715 g (32 %). m. p. > 212 °C (dec.). Elemental analysis: Found: C, 30.05; H, 3.19; N, 2.50 %. Calc. for $C_{550}H_{639}Br_{40}Cd_{44}Cl_{31}N_{40}Yb_{12}O_{190}(EtOH)_{12}(MeOH)_6(H_2O)_{11}$: C, 30.14; H, 3.30; N, 2.42 %. IR (CH_3OH, cm^{-1}): 3000 (m), 1633 (s), 1434 (s), 1309 (m), 1259 (m), 1205 (s), 1105 (s), 1035 (s), 870 (s), 746 (m), 673 (w).

3. Intermolecular interactions in 3

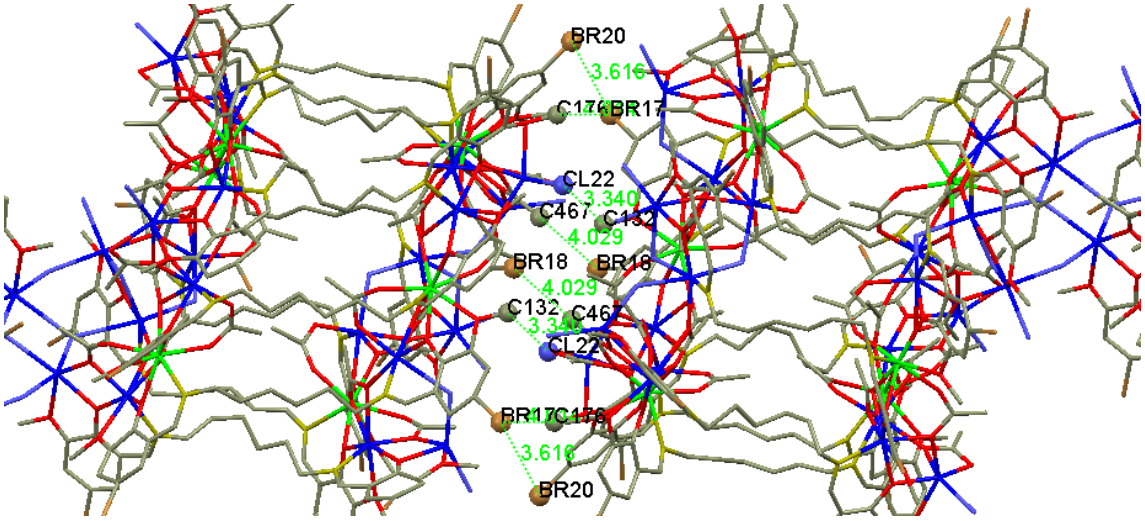
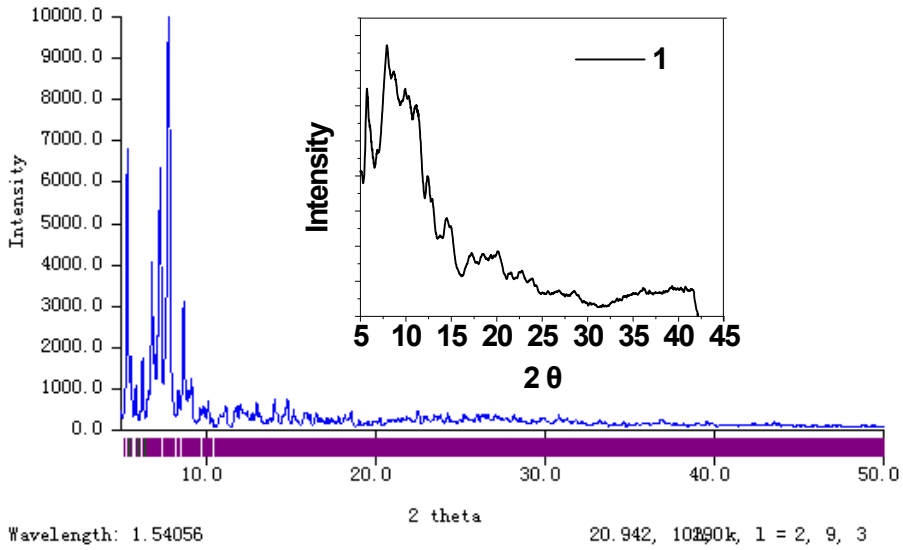
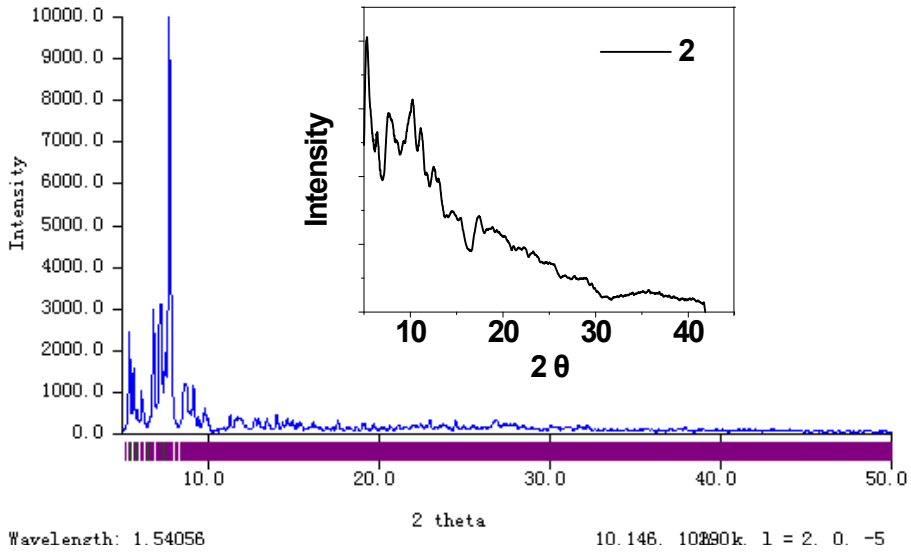


Fig. S1 Intermolecular interactions between the 16-metal rings of two face-to-face closed molecules in **3**: (1) Br···H-C interactions: Br(17)···C(176) 4.014 Å, Br···H-C(176) 3.219 Å, Br-H-C 141.33°; Br(18)···C(467) 4.029 Å, Br···H-C(467) 3.478 Å, Br-H-C 118.73°. (2) Br···Br interactions: Br(17)···Br(20) 3.616 Å. (3) Cl···H-C hydrogen bonds: Cl(22)···C(132) 3.340 Å, Cl(22)···H-C(132) 2.723 Å, Cl-H-C 122.57°.

4. Powder XRD patterns of 1-4

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40
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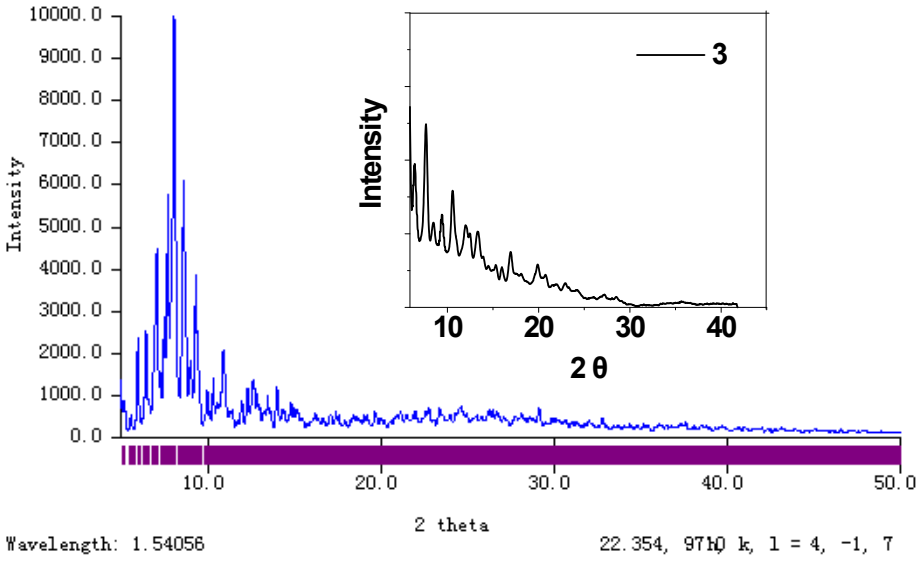
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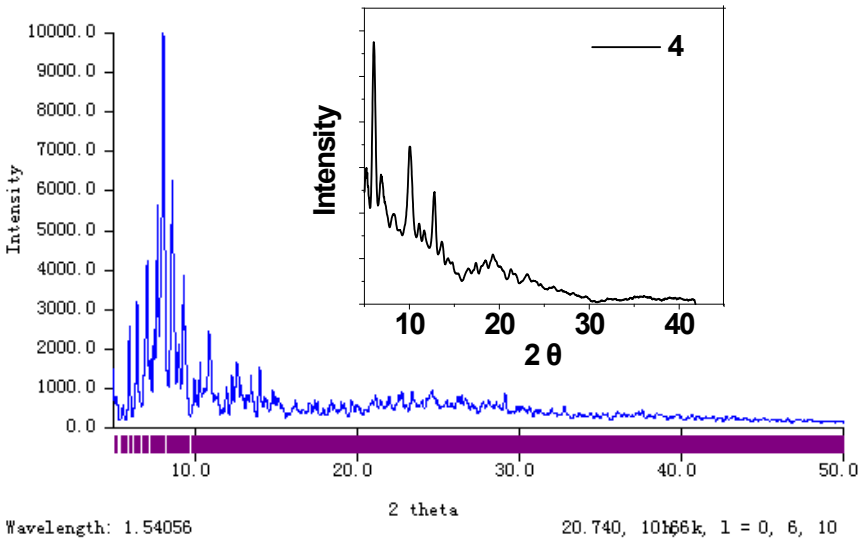
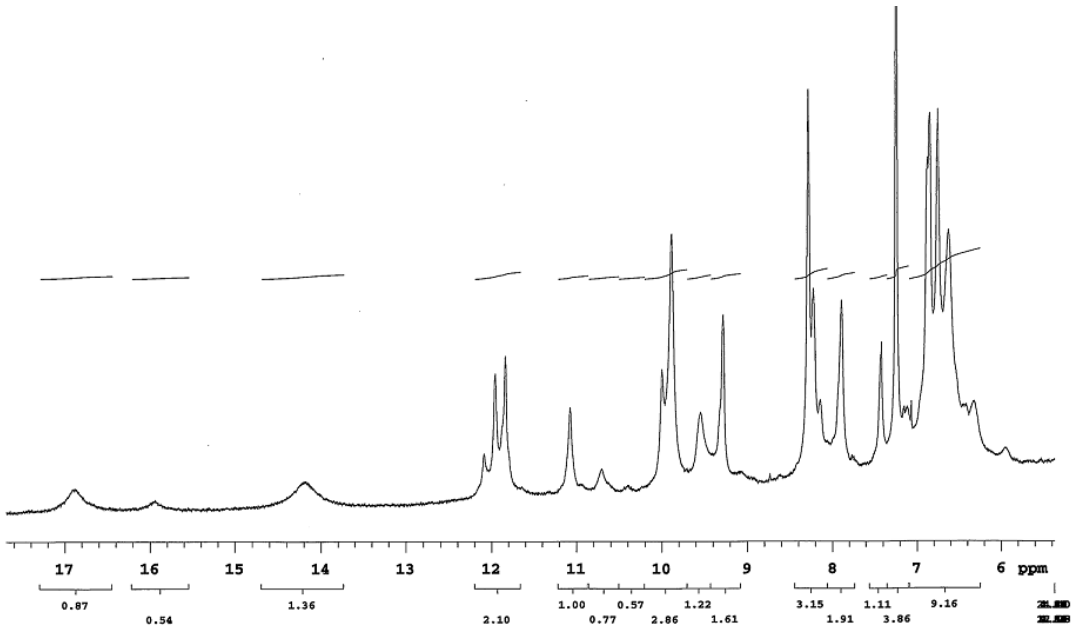
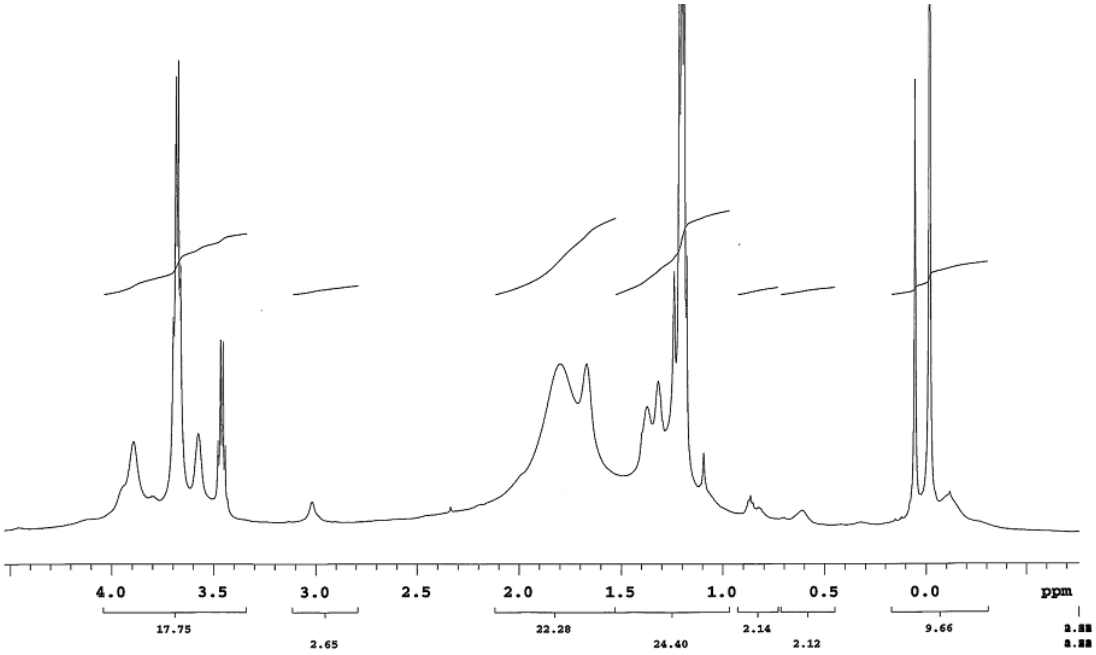


Fig. S2 Powder XRD patterns of **1**-**4**

5. ^{1}H NMR spectra of 3 and 4



(a)



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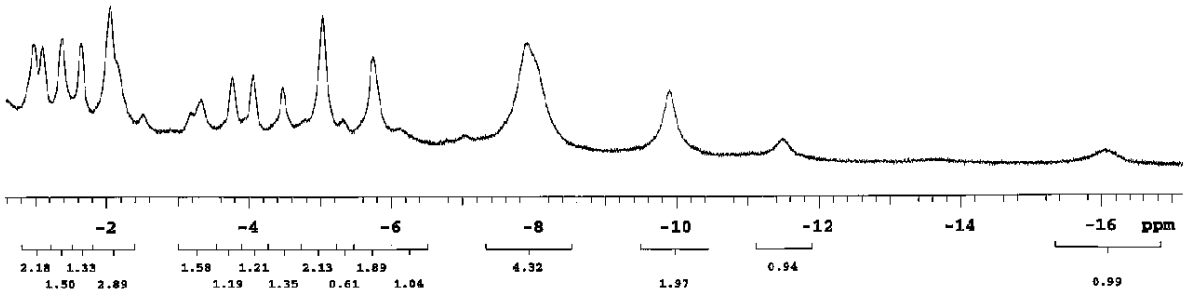

(c)

Fig. S3 ^{1}H NMR spectrum of **3** in $CDCl_3$.

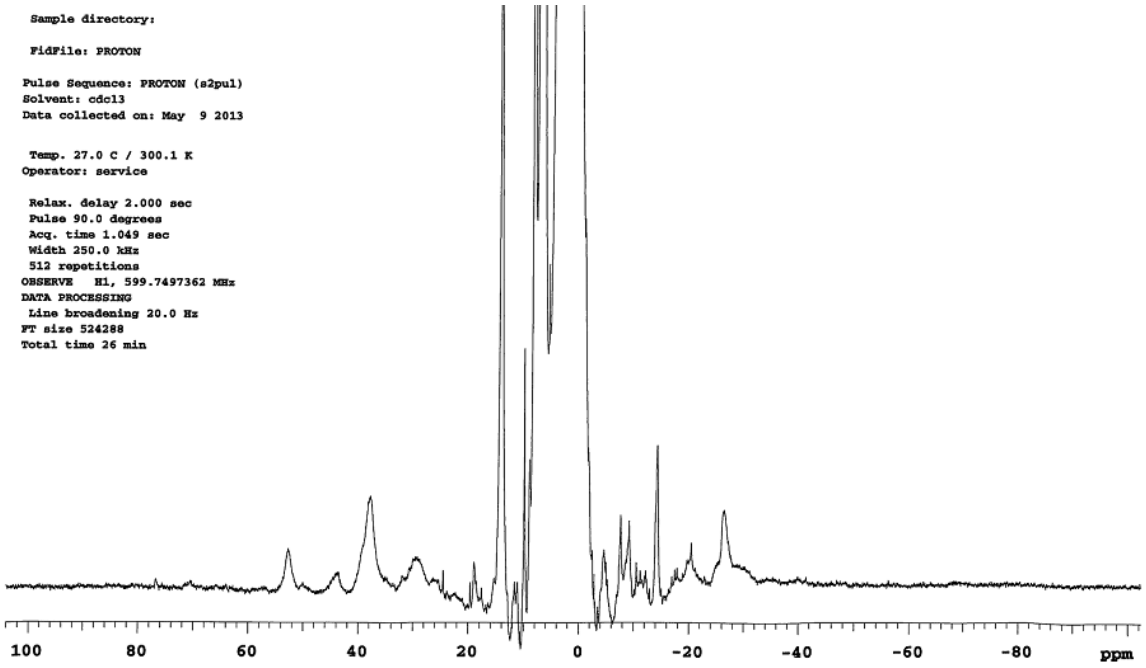

Fig. S4 ^{1}H NMR spectrum of **4** in $CDCl_3$.

6. Photophysical properties of the free H_2L and 1-4

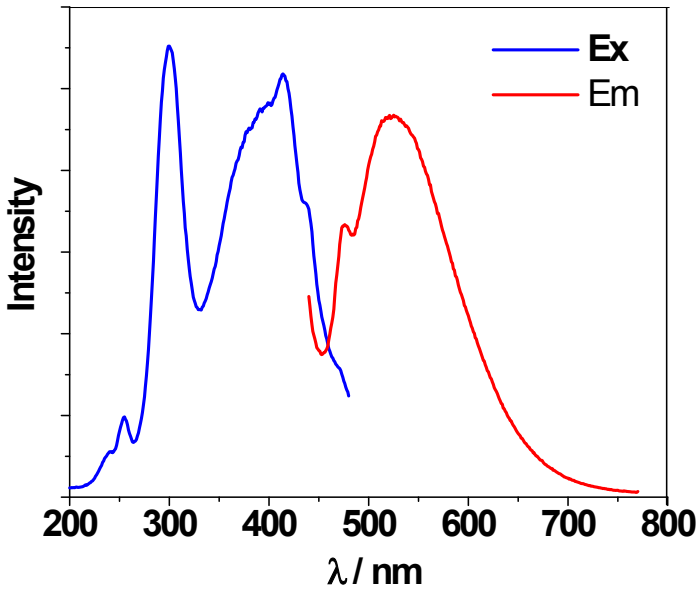

Fig. S5 Excitation and emission spectra of free H_2L in CH_3CN.

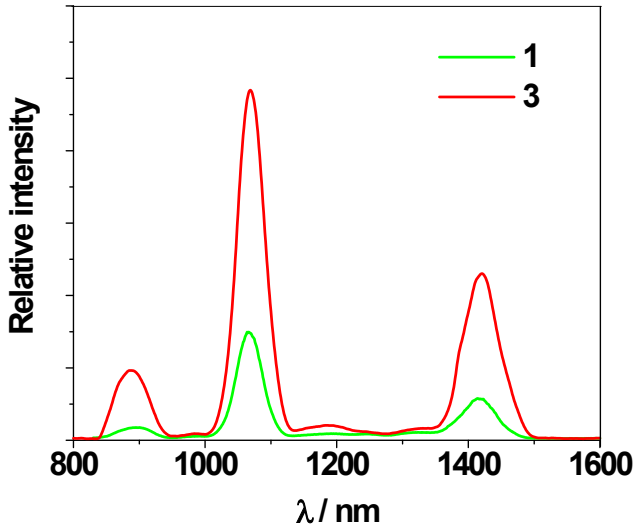

Fig. S6 The NIR emission spectra for Cd-Nd nanoclusters **1** and **3** with the same absorbance value at λ_{ex} = 380 nm in CH_3CN.

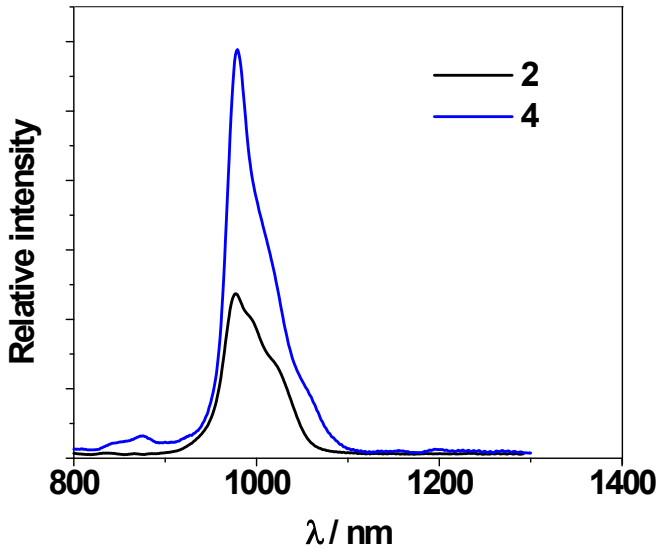

Fig. S7 The NIR emission spectra for Cd-Yb nanoclusters **2** and **4** with the same absorbance value at λ_{ex} = 380 nm in CH_3CN.

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]

For the crystal structures of **1**-**4**, some uncoordinated solvent molecules such as CH_3OH, $C_2H_5OC_2H_5$ 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). Crystallographic data for **1**-**4** are presented in Table S1 and selected bond lengths are given in Tables S2-S5. (CCDC reference numbers 972369-972372). 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	$C_{360}H_{426}Br_{24}Cd_{24}N_{24}Nd_8O_{144}$	$C_{360}H_{426}Br_{24}Cd_{24}N_{24}Yb_8O_{144}$	$C_{550}H_{639}Br_{40}Cd_{44}Cl_{31}N_{40}Nd_{12}O_{190}$	$C_{550}H_{639}Br_{40}Cd_{44}Cl_{31}N_{40}Yb_{12}O_{190}$
Fw	13162.61	13393.01	21821.84	22167.44
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	P2(1)/c	P-1	P-1
a [Å]	31.070(6)	30.073(6)	25.510(5)	25.508(5)
b [Å]	41.338(8)	41.754(8)	42.220(8)	42.215(8)
c [Å]	48.828(10)	48.731(10)	44.450(9)	43.977(9)
α [deg]	90.00	90.00	66.84(3)	66.85(3)
β [deg]	97.22(3)	96.21(3)	87.11(3)	86.45(3)
γ [deg]	90.00	90.00	77.59(3)	77.32(3)
V / [Å^3]	62216(21)	60831(21)	42956(15)	42464(15)
d / [g/cm^3]	1.405	1.462	1.687	1.734
Z	4	4	1	1
T [K]	223(1)	223(1)	223(1)	223(1)
F(000)	25512	25832	20996	21236
μ, mm^{-1}	3.057	3.674	3.795	4.426
θ rang, deg	2.96-25.00	2.99-25.00	3.00-25.00	2.99-25.00
reflns meads	104188	103341	149063	145233
reflns used	104188	103341	149063	145233
params	5258	5246	8034	8065
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0953, 0.2139	0.0923, 0.2092	0.0971, 0.2265	0.0920, 0.1949
R1, wR2 (all data)	0.2110, 0.2475	0.1869, 0.2294	0.2329, 0.2468	0.2140, 0.2554
Quality of fit	0.959	1.119	1.073	1.104

[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) for **1**.

Nd(1)-O(92)	2.27(5)	Nd(7)-O(47)	2.39(5)
Nd(1)-O(46)	2.28(5)	Nd(7)-O(142)	2.39(6)
Nd(1)-O(2)	2.34(5)	Nd(7)-O(140)	2.42(6)
Nd(1)-O(90)	2.36(5)	Nd(7)-N(24)	2.62(7)
Nd(1)-O(93)	2.39(5)	Nd(7)-O(4)	2.63(6)
Nd(1)-O(49)	2.42(5)	Nd(8)-O(15)	2.29(5)
Nd(1)-O(45)	2.56(5)	Nd(8)-O(111)	2.30(5)
Nd(1)-N(1)	2.62(7)	Nd(8)-O(107)	2.31(5)
Nd(2)-O(10)	2.31(5)	Nd(8)-O(11)	2.35(5)
Nd(2)-O(56)	2.31(6)	Nd(8)-O(106)	2.37(5)
Nd(2)-O(58)	2.32(5)	Nd(8)-O(103)	2.45(5)
Nd(2)-O(14)	2.36(5)	Nd(8)-N(6)	2.60(6)
Nd(2)-O(61)	2.39(5)	Nd(8)-O(16)	2.64(4)
Nd(2)-O(59)	2.43(5)	Cd(1)-O(6)	2.20(6)
Nd(2)-O(9)	2.66(6)	Cd(1)-O(94)	2.30(5)
Nd(2)-N(7)	2.67(6)	Cd(1)-N(3)	2.32(7)
Nd(3)-O(22)	2.31(5)	Cd(1)-O(2)	2.34(5)
Nd(3)-O(70)	2.34(6)	Cd(1)-O(49)	2.35(6)
Nd(3)-O(71)	2.35(6)	Cd(1)-O(1)	2.54(6)
Nd(3)-O(68)	2.36(5)	Cd(1)-O(50)	2.63(5)
Nd(3)-O(73)	2.37(6)	Cd(2)-O(52)	2.25(8)
Nd(3)-O(26)	2.38(5)	Cd(2)-O(6)	2.26(6)
Nd(3)-N(13)	2.61(7)	Cd(2)-O(53)	2.27(6)
Nd(3)-O(21)	2.65(5)	Cd(2)-O(94)	2.27(5)
Nd(4)-O(96)	2.28(6)	Cd(2)-O(51)	2.43(6)
Nd(4)-O(34)	2.34(5)	Cd(2)-O(54)	2.45(5)
Nd(4)-O(80)	2.34(6)	Cd(2)-O(5)	2.52(7)
Nd(4)-O(38)	2.36(5)	Cd(3)-O(10)	2.26(5)
Nd(4)-O(83)	2.38(6)	Cd(3)-O(55)	2.30(5)
Nd(4)-O(82)	2.45(5)	Cd(3)-O(57)	2.30(5)
Nd(4)-N(19)	2.56(6)	Cd(3)-O(50)	2.34(5)
Nd(4)-O(33)	2.64(5)	Cd(3)-O(54)	2.35(5)
Nd(5)-O(27)	2.31(5)	Cd(3)-N(5)	2.36(7)
Nd(5)-O(121)	2.31(6)	Cd(4)-O(18)	2.25(5)
Nd(5)-O(23)	2.33(5)	Cd(4)-O(60)	2.28(5)
Nd(5)-O(123)	2.33(5)	Cd(4)-N(9)	2.31(7)
Nd(5)-O(114)	2.38(5)	Cd(4)-O(14)	2.32(5)
Nd(5)-O(120)	2.40(5)	Cd(4)-O(61)	2.32(5)
Nd(5)-N(12)	2.56(6)	Cd(4)-O(13)	2.55(6)
Nd(5)-O(28)	2.60(5)	Cd(4)-O(62)	2.63(6)
Nd(6)-O(35)	2.27(6)	Cd(5)-O(64)	2.25(8)
Nd(6)-O(133)	2.27(6)	Cd(5)-O(63)	2.27(8)
Nd(6)-O(39)	2.29(6)	Cd(5)-O(18)	2.30(5)
Nd(6)-O(135)	2.36(6)	Cd(5)-O(66)	2.31(7)
Nd(6)-O(128)	2.43(6)	Cd(5)-O(60)	2.31(5)
Nd(6)-O(130)	2.44(6)	Cd(5)-O(65)	2.40(6)
Nd(6)-O(40)	2.62(7)	Cd(5)-O(17)	2.48(6)
Nd(6)-N(18)	2.65(7)	Cd(6)-O(69)	2.27(5)
Nd(7)-O(97)	2.26(6)	Cd(6)-O(67)	2.29(6)
Nd(7)-O(100)	2.29(6)	Cd(6)-O(22)	2.32(5)
Nd(7)-O(3)	2.36(6)	Cd(6)-N(11)	2.32(6)

Cd(6)-O(62)	2.39(5)	Cd(10)-O(42)	2.22(5)
Cd(6)-O(65)	2.39(6)	Cd(10)-N(21)	2.23(7)
Cd(7)-N(15)	2.23(7)	Cd(10)-O(84)	2.27(5)
Cd(7)-O(72)	2.24(6)	Cd(10)-O(38)	2.28(5)
Cd(7)-O(26)	2.26(5)	Cd(10)-O(82)	2.33(5)
Cd(7)-O(30)	2.28(5)	Cd(10)-O(81)	2.60(5)
Cd(7)-O(73)	2.38(5)	Cd(10)-O(37)	2.64(5)
Cd(7)-O(25)	2.62(6)	Cd(11)-O(84)	2.22(5)
Cd(8)-O(75)	2.22(8)	Cd(11)-O(88)	2.24(6)
Cd(8)-O(77)	2.23(7)	Cd(11)-O(86)	2.26(6)
Cd(8)-O(72)	2.27(6)	Cd(11)-O(42)	2.28(5)
Cd(8)-O(30)	2.30(6)	Cd(11)-O(87)	2.43(5)
Cd(8)-O(78)	2.48(6)	Cd(11)-O(41)	2.43(6)
Cd(8)-O(29)	2.55(6)	Cd(11)-C(306)	2.72(9)
Cd(8)-O(76)	2.62(11)	Cd(12)-O(89)	2.28(5)
Cd(9)-O(79)	2.24(6)	Cd(12)-O(46)	2.30(5)
Cd(9)-N(17)	2.29(8)	Cd(12)-O(91)	2.30(5)
Cd(9)-O(95)	2.33(5)	Cd(12)-N(23)	2.31(7)
Cd(9)-O(34)	2.33(5)	Cd(12)-O(81)	2.40(5)
Cd(9)-O(74)	2.37(5)	Cd(12)-O(87)	2.43(5)
Cd(9)-O(78)	2.42(6)		

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

Yb(1)-O(50)	2.281(10)	Yb(7)-O(35)	2.323(10)
Yb(1)-O(46)	2.302(9)	Yb(7)-O(111)	2.358(10)
Yb(1)-O(2)	2.355(11)	Yb(7)-O(116)	2.412(10)
Yb(1)-O(52)	2.359(11)	Yb(7)-N(18)	2.578(15)
Yb(1)-O(55)	2.371(11)	Yb(7)-O(40)	2.611(10)
Yb(1)-O(57)	2.425(10)	Yb(8)-O(98)	2.279(10)
Yb(1)-O(45)	2.567(9)	Yb(8)-O(3)	2.298(11)
Yb(1)-N(1)	2.595(13)	Yb(8)-O(47)	2.334(9)
Yb(2)-O(66)	2.241(11)	Yb(8)-O(101)	2.336(10)
Yb(2)-O(14)	2.312(10)	Yb(8)-O(100)	2.360(10)
Yb(2)-O(10)	2.315(9)	Yb(8)-O(108)	2.417(10)
Yb(2)-O(64)	2.334(10)	Yb(8)-N(24)	2.561(12)
Yb(2)-O(74)	2.361(10)	Yb(8)-O(4)	2.616(12)
Yb(2)-O(68)	2.382(11)	Cd(1)-O(6)	2.199(10)
Yb(2)-N(7)	2.550(13)	Cd(1)-N(3)	2.224(13)
Yb(2)-O(9)	2.608(10)	Cd(1)-O(56)	2.282(11)
Yb(3)-O(78)	2.255(10)	Cd(1)-O(2)	2.298(10)
Yb(3)-O(22)	2.296(9)	Cd(1)-O(57)	2.321(10)
Yb(3)-O(76)	2.323(10)	Cd(1)-O(1)	2.564(10)
Yb(3)-O(79)	2.338(10)	Cd(2)-O(61)	2.251(11)
Yb(3)-O(26)	2.345(11)	Cd(2)-O(56)	2.255(11)
Yb(3)-O(81)	2.408(10)	Cd(2)-O(6)	2.271(11)
Yb(3)-N(13)	2.598(12)	Cd(2)-O(60)	2.340(16)
Yb(3)-O(21)	2.617(11)	Cd(2)-O(62)	2.341(9)
Yb(4)-O(88)	2.284(11)	Cd(2)-O(5)	2.523(13)
Yb(4)-O(38)	2.293(10)	Cd(3)-O(63)	2.229(12)
Yb(4)-O(34)	2.302(12)	Cd(3)-N(5)	2.317(13)
Yb(4)-O(90)	2.316(10)	Cd(3)-O(10)	2.325(9)
Yb(4)-O(93)	2.368(11)	Cd(3)-O(65)	2.328(10)
Yb(4)-O(92)	2.408(13)	Cd(3)-O(58)	2.370(10)
Yb(4)-N(19)	2.584(12)	Cd(3)-O(62)	2.403(10)
Yb(4)-O(33)	2.606(11)	Cd(4)-O(18)	2.215(10)
Yb(5)-O(136)	2.281(11)	Cd(4)-N(9)	2.285(12)
Yb(5)-O(11)	2.283(10)	Cd(4)-O(67)	2.301(10)
Yb(5)-O(15)	2.297(11)	Cd(4)-O(14)	2.313(10)
Yb(5)-O(134)	2.324(13)	Cd(4)-O(74)	2.319(10)
Yb(5)-O(137)	2.332(12)	Cd(4)-O(13)	2.544(10)
Yb(5)-O(139)	2.396(12)	Cd(4)-O(73)	2.640(10)
Yb(5)-O(16)	2.563(14)	Cd(5)-O(71)	2.269(10)
Yb(5)-N(6)	2.571(13)	Cd(5)-O(67)	2.268(11)
Yb(6)-O(123)	2.277(11)	Cd(5)-O(70)	2.293(11)
Yb(6)-O(27)	2.329(11)	Cd(5)-O(18)	2.296(10)
Yb(6)-O(122)	2.336(12)	Cd(5)-O(17)	2.410(11)
Yb(6)-O(23)	2.339(9)	Cd(5)-O(72)	2.453(10)
Yb(6)-O(125)	2.339(12)	Cd(5)-O(69)	2.579(13)
Yb(6)-O(127)	2.422(11)	Cd(6)-O(75)	2.192(10)
Yb(6)-N(12)	2.616(14)	Cd(6)-O(77)	2.301(11)
Yb(6)-O(28)	2.635(10)	Cd(6)-N(11)	2.312(11)
Yb(7)-O(114)	2.288(9)	Cd(6)-O(22)	2.316(10)
Yb(7)-O(39)	2.310(9)	Cd(6)-O(72)	2.370(10)
Yb(7)-O(110)	2.322(11)	Cd(6)-O(73)	2.370(10)

Cd(7)-O(30)	2.244(10)	Cd(10)-O(94)	2.258(10)
Cd(7)-N(15)	2.248(12)	Cd(10)-N(21)	2.259(13)
Cd(7)-O(80)	2.275(9)	Cd(10)-O(38)	2.301(11)
Cd(7)-O(26)	2.286(10)	Cd(10)-O(92)	2.343(10)
Cd(7)-O(81)	2.327(10)	Cd(10)-O(37)	2.591(11)
Cd(7)-O(25)	2.547(11)	Cd(11)-O(54)	2.250(13)
Cd(8)-O(30)	2.261(10)	Cd(11)-O(96)	2.270(14)
Cd(8)-O(80)	2.261(10)	Cd(11)-O(42)	2.283(10)
Cd(8)-O(86)	2.287(14)	Cd(11)-O(94)	2.325(10)
Cd(8)-O(84)	2.348(17)	Cd(11)-O(53)	2.387(11)
Cd(8)-O(85)	2.467(12)	Cd(11)-O(41)	2.468(11)
Cd(8)-O(83)	2.494(13)	Cd(11)-O(95)	2.597(16)
Cd(8)-O(29)	2.510(12)	Cd(11)-C(310)	2.74(2)
Cd(9)-O(87)	2.292(11)	Cd(12)-O(51)	2.267(11)
Cd(9)-O(89)	2.295(10)	Cd(12)-O(46)	2.292(10)
Cd(9)-O(34)	2.316(10)	Cd(12)-N(23)	2.301(12)
Cd(9)-O(82)	2.353(9)	Cd(12)-O(49)	2.312(10)
Cd(9)-N(17)	2.377(13)	Cd(12)-O(91)	2.354(11)
Cd(9)-O(85)	2.415(12)	Cd(12)-O(53)	2.431(10)
Cd(10)-O(42)	2.229(10)		

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

Nd(1)-O(168)	2.284(14)	Cd(1)-O(160)	2.290(16)
Nd(1)-O(161)	2.294(19)	Cd(1)-O(192)	2.322(15)
Nd(1)-O(71)	2.361(18)	Cd(1)-O(76)	2.44(2)
Nd(1)-O(75)	2.367(16)	Cd(1)-O(159)	2.57(2)
Nd(1)-O(160)	2.447(19)	Cd(2)-O(192)	2.163(17)
Nd(1)-O(188)	2.505(18)	Cd(2)-O(184)	2.26(2)
Nd(1)-N(36)	2.57(2)	Cd(2)-O(79)	2.308(18)
Nd(1)-O(72)	2.578(17)	Cd(2)-Cl(10)	2.414(10)
Nd(2)-O(43)	2.182(19)	Cd(2)-O(80)	2.44(2)
Nd(2)-O(182)	2.27(2)	Cd(2)-O(183)	2.50(2)
Nd(2)-O(180)	2.343(18)	Cd(3)-O(181)	2.248(18)
Nd(2)-O(47)	2.41(2)	Cd(3)-O(187)	2.298(17)
Nd(2)-O(178)	2.424(16)	Cd(3)-O(43)	2.346(19)
Nd(2)-O(176)	2.557(19)	Cd(3)-O(183)	2.365(18)
Nd(2)-O(44)	2.567(15)	Cd(3)-N(22)	2.41(2)
Nd(2)-N(24)	2.61(3)	Cd(3)-O(159)	2.52(2)
Nd(3)-O(63)	2.232(18)	Cd(4)-O(176)	2.18(2)
Nd(3)-O(59)	2.253(19)	Cd(4)-N(26)	2.23(3)
Nd(3)-O(173)	2.339(19)	Cd(4)-O(47)	2.278(17)
Nd(3)-O(171)	2.360(15)	Cd(4)-O(51)	2.290(18)
Nd(3)-O(166)	2.382(18)	Cd(4)-O(177)	2.31(2)
Nd(3)-O(170)	2.413(16)	Cd(4)-O(48)	2.49(2)
Nd(3)-N(40)	2.59(2)	Cd(5)-O(51)	2.18(2)
Nd(3)-O(60)	2.601(17)	Cd(5)-O(177)	2.24(2)
Nd(4)-O(46)	2.26(2)	Cd(5)-Cl(9)	2.311(12)
Nd(4)-O(152)	2.285(14)	Cd(5)-Cl(13)	2.443(11)
Nd(4)-O(42)	2.289(18)	Cd(5)-O(52)	2.45(3)
Nd(4)-O(150)	2.338(18)	Cd(6)-N(28)	2.22(2)
Nd(4)-O(157)	2.370(16)	Cd(6)-O(175)	2.29(2)
Nd(4)-O(155)	2.499(18)	Cd(6)-O(55)	2.296(18)
Nd(4)-N(21)	2.652(19)	Cd(6)-Cl(11)	2.572(9)
Nd(4)-O(45)	2.699(17)	Cd(6)-Cl(15)	2.572(8)
Nd(5)-O(54)	2.241(16)	Cd(6)-Cl(13)	2.941(10)
Nd(5)-O(142)	2.338(16)	Cd(7)-O(55)	2.298(18)
Nd(5)-O(144)	2.352(15)	Cd(7)-O(174)	2.378(17)
Nd(5)-O(148)	2.358(18)	Cd(7)-Cl(12)	2.409(9)
Nd(5)-O(58)	2.369(16)	Cd(7)-O(56)	2.489(19)
Nd(5)-O(140)	2.432(18)	Cd(7)-Cl(11)	2.514(9)
Nd(5)-O(57)	2.588(17)	Cd(7)-Cl(8)	2.71(2)
Nd(5)-N(27)	2.59(2)	Cd(8)-N(30)	2.15(2)
Nd(6)-O(134)	2.256(16)	Cd(8)-O(172)	2.204(14)
Nd(6)-O(70)	2.272(16)	Cd(8)-O(174)	2.273(17)
Nd(6)-O(135)	2.317(16)	Cd(8)-O(59)	2.336(17)
Nd(6)-O(154)	2.318(16)	Cd(8)-Cl(15)	2.550(9)
Nd(6)-O(74)	2.385(15)	Cd(9)-O(166)	2.205(19)
Nd(6)-O(137)	2.496(17)	Cd(9)-O(169)	2.236(17)
Nd(6)-N(33)	2.61(2)	Cd(9)-O(67)	2.242(19)
Nd(6)-O(73)	2.710(16)	Cd(9)-N(32)	2.28(2)
Cd(1)-O(79)	2.17(2)	Cd(9)-O(63)	2.325(17)
Cd(1)-O(75)	2.239(18)	Cd(9)-O(64)	2.563(19)
Cd(1)-N(38)	2.26(2)	Cd(10)-O(163)	2.177(17)

Cd(10)-O(67)	2.263(17)	Cd(16)-O(61)	2.50(2)
Cd(10)-O(169)	2.31(2)	Cd(16)-Cl(7)	2.530(8)
Cd(10)-Cl(14)	2.438(8)	Cd(16)-Cl(1)	2.537(7)
Cd(10)-O(164)	2.458(17)	Cd(17)-N(39)	2.253(19)
Cd(10)-O(68)	2.51(2)	Cd(17)-O(62)	2.341(17)
Cd(11)-O(162)	2.238(18)	Cd(17)-O(138)	2.372(19)
Cd(11)-N(34)	2.30(3)	Cd(17)-Cl(7)	2.546(7)
Cd(11)-O(71)	2.336(16)	Cd(17)-Cl(5)	2.619(7)
Cd(11)-O(167)	2.337(15)	Cd(18)-O(66)	2.180(15)
Cd(11)-O(165)	2.463(16)	Cd(18)-O(136)	2.249(14)
Cd(11)-O(164)	2.474(16)	Cd(18)-O(137)	2.302(15)
Cd(11)-C(546)	2.75(3)	Cd(18)-O(70)	2.353(19)
Cd(12)-O(149)	2.244(16)	Cd(18)-N(31)	2.422(18)
Cd(12)-O(46)	2.32(2)	Cd(18)-O(69)	2.517(17)
Cd(12)-O(151)	2.334(18)	Cd(19)-O(66)	2.240(14)
Cd(12)-O(147)	2.374(19)	Cd(19)-O(136)	2.266(15)
Cd(12)-N(23)	2.40(2)	Cd(19)-O(65)	2.411(18)
Cd(12)-O(146)	2.508(19)	Cd(19)-Cl(2)	2.514(7)
Cd(13)-O(145)	2.19(2)	Cd(19)-Cl(1)	2.533(8)
Cd(13)-O(50)	2.213(17)	Cd(19)-Cl(2)	2.661(8)
Cd(13)-O(143)	2.228(16)	Cd(20)-N(35)	2.17(2)
Cd(13)-O(49)	2.35(2)	Cd(20)-O(153)	2.280(13)
Cd(13)-O(146)	2.38(2)	Cd(20)-O(133)	2.297(17)
Cd(13)-Cl(6)	2.443(9)	Cd(20)-O(74)	2.327(14)
Cd(14)-O(50)	2.202(18)	Cd(20)-O(158)	2.382(17)
Cd(14)-O(148)	2.264(18)	Cd(20)-O(132)	2.495(14)
Cd(14)-O(143)	2.278(15)	Cd(20)-O(134)	2.581(15)
Cd(14)-N(25)	2.35(2)	Cd(21)-O(131)	2.204(17)
Cd(14)-O(54)	2.358(16)	Cd(21)-O(78)	2.233(18)
Cd(14)-O(53)	2.592(19)	Cd(21)-O(77)	2.26(2)
Cd(15)-O(141)	2.215(15)	Cd(21)-O(156)	2.270(16)
Cd(15)-N(29)	2.266(19)	Cd(21)-Cl(3)	2.497(9)
Cd(15)-O(139)	2.293(14)	Cd(21)-O(132)	2.620(16)
Cd(15)-O(58)	2.390(19)	Cd(22)-O(156)	2.253(16)
Cd(15)-Cl(5)	2.575(9)	Cd(22)-O(157)	2.272(15)
Cd(15)-O(140)	2.617(15)	Cd(22)-O(42)	2.273(16)
Cd(15)-C(542)	2.75(3)	Cd(22)-N(37)	2.31(2)
Cd(16)-O(62)	2.329(15)	Cd(22)-O(78)	2.361(19)
Cd(16)-O(139)	2.330(14)	Cd(22)-O(41)	2.571(18)
Cd(16)-Cl(4)	2.486(7)		

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

Yb(1)-O(161)	2.276(16)	Cd(1)-O(79)	2.24(2)
Yb(1)-O(168)	2.301(14)	Cd(1)-O(75)	2.276(17)
Yb(1)-O(71)	2.305(15)	Cd(1)-N(38)	2.31(2)
Yb(1)-O(75)	2.339(17)	Cd(1)-O(192)	2.325(17)
Yb(1)-O(188)	2.454(19)	Cd(1)-O(76)	2.406(19)
Yb(1)-N(36)	2.465(11)	Cd(2)-O(192)	2.191(18)
Yb(1)-O(160)	2.472(18)	Cd(2)-O(79)	2.291(19)
Yb(1)-O(72)	2.496(18)	Cd(2)-O(184)	2.30(2)
Yb(2)-O(43)	2.211(19)	Cd(2)-O(80)	2.36(3)
Yb(2)-O(182)	2.29(2)	Cd(2)-Cl(10)	2.423(10)
Yb(2)-O(180)	2.319(18)	Cd(2)-O(183)	2.52(2)
Yb(2)-O(178)	2.362(17)	Cd(3)-O(181)	2.241(17)
Yb(2)-O(47)	2.401(18)	Cd(3)-N(22)	2.29(2)
Yb(2)-O(176)	2.44(2)	Cd(3)-O(187)	2.296(18)
Yb(2)-O(44)	2.515(15)	Cd(3)-O(43)	2.342(19)
Yb(2)-N(24)	2.61(2)	Cd(3)-O(183)	2.34(2)
Yb(2)-C(241)	3.21(3)	Cd(3)-O(159)	2.475(19)
Yb(3)-O(63)	2.240(17)	Cd(4)-O(47)	2.186(18)
Yb(3)-O(173)	2.273(15)	Cd(4)-O(176)	2.26(2)
Yb(3)-O(59)	2.287(16)	Cd(4)-O(177)	2.289(18)
Yb(3)-O(171)	2.321(14)	Cd(4)-N(26)	2.29(3)
Yb(3)-O(166)	2.375(16)	Cd(4)-O(51)	2.29(2)
Yb(3)-O(170)	2.398(16)	Cd(4)-O(48)	2.49(2)
Yb(3)-N(40)	2.57(2)	Cd(5)-O(51)	2.23(2)
Yb(3)-O(60)	2.612(15)	Cd(5)-O(177)	2.327(18)
Yb(4)-O(42)	2.251(16)	Cd(5)-Cl(9)	2.355(14)
Yb(4)-O(46)	2.259(18)	Cd(5)-Cl(13)	2.373(10)
Yb(4)-O(150)	2.292(17)	Cd(5)-O(52)	2.46(2)
Yb(4)-O(157)	2.313(16)	Cd(6)-N(28)	2.19(3)
Yb(4)-O(152)	2.324(15)	Cd(6)-O(175)	2.20(2)
Yb(4)-O(155)	2.374(16)	Cd(6)-O(55)	2.303(18)
Yb(4)-N(21)	2.57(2)	Cd(6)-Cl(11)	2.566(9)
Yb(4)-O(45)	2.655(18)	Cd(6)-Cl(15)	2.582(8)
Yb(4)-C(249)	3.20(4)	Cd(6)-Cl(13)	2.962(9)
Yb(5)-O(54)	2.256(15)	Cd(7)-O(55)	2.279(18)
Yb(5)-O(148)	2.316(18)	Cd(7)-Cl(12)	2.407(8)
Yb(5)-O(58)	2.327(16)	Cd(7)-O(174)	2.408(16)
Yb(5)-O(144)	2.355(16)	Cd(7)-Cl(11)	2.482(9)
Yb(5)-O(142)	2.371(15)	Cd(7)-O(56)	2.54(2)
Yb(5)-O(140)	2.483(16)	Cd(7)-Cl(8)	2.68(2)
Yb(5)-O(57)	2.529(16)	Cd(8)-N(30)	2.12(2)
Yb(5)-N(27)	2.62(2)	Cd(8)-O(172)	2.226(15)
Yb(6)-O(134)	2.248(15)	Cd(8)-O(174)	2.295(16)
Yb(6)-O(154)	2.314(16)	Cd(8)-O(59)	2.326(16)
Yb(6)-O(74)	2.319(15)	Cd(8)-Cl(15)	2.515(8)
Yb(6)-O(135)	2.343(14)	Cd(9)-O(166)	2.164(16)
Yb(6)-O(70)	2.352(15)	Cd(9)-O(67)	2.231(15)
Yb(6)-O(137)	2.478(15)	Cd(9)-O(169)	2.261(17)
Yb(6)-N(33)	2.601(17)	Cd(9)-N(32)	2.28(2)
Yb(6)-O(73)	2.650(15)	Cd(9)-O(63)	2.285(19)
Cd(1)-O(160)	2.217(17)	Cd(9)-O(64)	2.561(17)

Cd(10)-O(163)	2.202(18)	Cd(16)-Cl(1)#1	2.518(7)
Cd(10)-O(67)	2.238(15)	Cd(16)-Cl(7)	2.564(8)
Cd(10)-O(169)	2.319(18)	Cd(16)-O(61)	2.57(2)
Cd(10)-Cl(14)	2.447(8)	Cd(17)-N(39)	2.203(18)
Cd(10)-O(164)	2.460(15)	Cd(17)-O(62)	2.334(15)
Cd(10)-O(68)	2.496(19)	Cd(17)-O(138)	2.338(16)
Cd(10)-C(552)	2.74(2)	Cd(17)-Cl(7)	2.506(7)
Cd(11)-O(162)	2.273(16)	Cd(17)-Cl(5)	2.599(7)
Cd(11)-N(34)	2.28(2)	Cd(18)-O(66)	2.199(16)
Cd(11)-O(71)	2.323(15)	Cd(18)-O(136)	2.247(14)
Cd(11)-O(167)	2.378(14)	Cd(18)-O(137)	2.262(14)
Cd(11)-O(165)	2.386(16)	Cd(18)-N(31)	2.342(18)
Cd(11)-O(164)	2.445(15)	Cd(18)-O(70)	2.372(17)
Cd(12)-O(149)	2.176(17)	Cd(18)-O(69)	2.453(16)
Cd(12)-O(46)	2.22(2)	Cd(19)-O(66)	2.188(15)
Cd(12)-O(151)	2.283(16)	Cd(19)-O(136)	2.287(15)
Cd(12)-N(23)	2.38(2)	Cd(19)-O(65)	2.399(17)
Cd(12)-O(147)	2.384(16)	Cd(19)-Cl(2)	2.524(7)
Cd(12)-O(146)	2.554(17)	Cd(19)-Cl(1)	2.529(7)
Cd(13)-O(145)	2.15(2)	Cd(19)-Cl(2)#1	2.646(7)
Cd(13)-O(50)	2.211(19)	Cd(20)-N(35)	2.24(2)
Cd(13)-O(143)	2.254(19)	Cd(20)-O(74)	2.290(14)
Cd(13)-O(146)	2.336(18)	Cd(20)-O(133)	2.297(15)
Cd(13)-O(49)	2.41(2)	Cd(20)-O(153)	2.346(15)
Cd(13)-Cl(6)	2.440(8)	Cd(20)-O(158)	2.396(15)
Cd(14)-O(50)	2.170(19)	Cd(20)-O(132)	2.498(16)
Cd(14)-O(148)	2.242(17)	Cd(20)-O(134)	2.572(15)
Cd(14)-O(143)	2.308(17)	Cd(21)-O(131)	2.145(19)
Cd(14)-O(54)	2.338(15)	Cd(21)-O(156)	2.222(17)
Cd(14)-N(25)	2.38(2)	Cd(21)-O(78)	2.236(17)
Cd(14)-O(53)	2.534(17)	Cd(21)-O(77)	2.25(2)
Cd(14)-C(532)	2.71(2)	Cd(21)-Cl(3)	2.486(8)
Cd(15)-O(141)	2.191(16)	Cd(21)-O(132)	2.569(16)
Cd(15)-N(29)	2.21(2)	Cd(21)-C(520)	2.61(2)
Cd(15)-O(139)	2.300(14)	Cd(22)-N(37)	2.205(11)
Cd(15)-O(58)	2.385(17)	Cd(22)-O(42)	2.229(14)
Cd(15)-O(140)	2.556(16)	Cd(22)-O(156)	2.231(16)
Cd(15)-Cl(5)	2.563(8)	Cd(22)-O(157)	2.260(16)
Cd(16)-O(139)	2.300(14)	Cd(22)-O(78)	2.281(18)
Cd(16)-O(62)	2.337(14)	Cd(22)-O(41)	2.545(19)
Cd(16)-Cl(4)	2.467(7)		