Supporting Information

First NIR luminescent polymeric high-nuclearity Cd-Ln nanoclusters from a long-chain Schiff base ligand

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1. General Procedures

All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Physical measurements: NMR: VARIAN UNITY-plus. 600 spectrometer (^{1}H, 600 MHz) at 298 K; Powder XRD: SMART APE II DUO; IR: FTIR-650 spectrometer. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses (C, H, N) were carried out on a EA1112 elemental analysis. 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, and excitation and emission spectra on a QuantaMaster PTI fluorimeter.

2. Synthesis of 1-3

$\{[La_6Cd_{22}Cl_{14}(OH)_2L_{10}(OAc)_{26}](EtOH)_5(EtOEt)_2(MeOH)_{10}(H_2O)_{15}\}_n$ (**1**). $Cd(OAc)_2{\cdot}2H_2O$ (0.50 mmol, 0.1322 g), $LaCl_3{\cdot}6H_2O$ (0.10 mmol, 0.0353 g) and H_2L (0.20 mmol, 0.0770 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 two weeks. The crystals were filtered off, washed with EtOH (5 ml) and dried in the air for one week. Yield (based on $Cd(OAc)_2{\cdot}2H_2O$): 0.1131 g (53 %). m. p. > 212 ^oC (dec.). Elemental analysis: Found: C, 34.62; H, 4.42; N, 2.73 %. Calc. for $C_{280}H_{356}Cd_{22}Cl_{14}N_{20}La_6O_{99}(EtOH)_5(EtOEt)_2(MeOH)_{10}(H_2O)_{15}$: C, 34.76; H, 4.44; N, 2.70 %. IR (cm^{-1}): 2930 (m), 1633 (s), 1572 (s), 1465 (s), 1210 (m), 1077 (m), 1012 (w), 959 (w), 851 (w), 742 (m), 670 (w), 615 (w).

$\{[Nd_6Cd_{22}Cl_{14}(OH)_2L_{10}(OAc)_{26}](EtOH)_7(EtOEt)_3(MeOH)_9(H_2O)_{10}\}_n$ (**2**). The procedure was the same as that for **1** using $NdCl_3{\cdot}6H_2O$ (0.10 mmol, 0.0359 g). Pale yellow single crystals of **2** were formed after two weeks. Yield (based on $Cd(OAc)_2{\cdot}2H_2O$): 0.1242 g (58 %). m. p. > 215 ^oC (dec.). Elemental analysis: Found: C, 35.57; H, 4.45; N, 2.70 %. Calc. for $C_{280}H_{356}Cd_{22}Cl_{14}N_{20}Nd_6O_{99}(EtOH)_7(EtOEt)_3(MeOH)_9(H_2O)_{10}$: C, 35.31; H, 4.49; N, 2.68 %. IR (CH_3OH, cm^{-1}): 2921 (m), 1635 (s), 1573 (s), 1467 (s), 1212 (m), 1078 (m), 1013 (w), 960 (w), 852 (w), 740 (m), 672 (w), 616 (w). ^1H NMR (600 MHz, CD_3OD): δ (ppm) -14.634, -9.853, -8.525, -8.248, -6.436, -5.066, -4.402, -3.851, -2.143, -1.546, -0.609, 0.059, 0.286, 0.696, 0.862, 1.820, 2.102, 3.310, 3.701, 4.350, 5.389, 6.000, 6.166, 6.572, 6.740, 6.771, 6.851, 6.980, 7.095, 7.177, 7.984, 8.116, 8.207, 8.287, 8.616, 9.003, 9.100, 9.804, 9.905, 10.592, 10.766, 11.090, 11.252, 12.029, 14.042, 16.869.

$[Yb_6Cd_{18}Cl_6(OH)_2L_9(OAc)_{28}](EtOH)_5(EtOEt)(MeOH)_{16}(H_2O)_{20}$ (3). The procedure was the same as that for **1** using $YbCl_3{\cdot}6H_2O$ (0.10 mmol, 0.0388 g). Pale yellow single crystals of **3** were formed after two weeks. Yield (based on $Cd(OAc)_2{\cdot}2H_2O$): 0.1517 g (65 %). m. p. > 195 ^oC (dec.). Elemental analysis: Found: C, 35.32; H, 4.78; N, 2.67 %. Calc. for $C_{254}H_{320}Cd_{18}Cl_6N_{18}Yb_6O_{94}(EtOH)_5(EtOEt)(MeOH)_{16}(H_2O)_{20}$: C, 35.58; H, 4.84; N, 2.63 %. IR (CH_3OH, cm^{-1}): 2926 (m), 1634 (s), 1576 (s), 1467 (s), 1410 (m), 1340 (m), 1210 (m), 1235 (m), 1076 (m), 1015 (m), 958 (w), 854 (w), 741 (m), 660 (m).

3. Views of crystal structures of 1 and 3

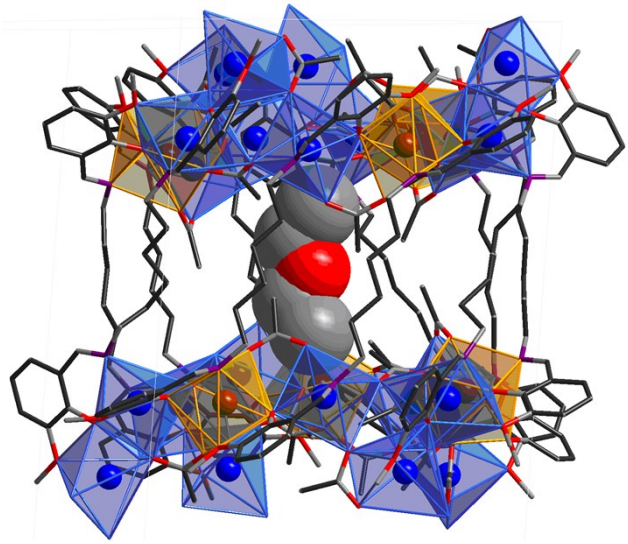


Fig. S1. A view along the *b*-axis of the crystal structure of **1** with enclosed diethyl ether.

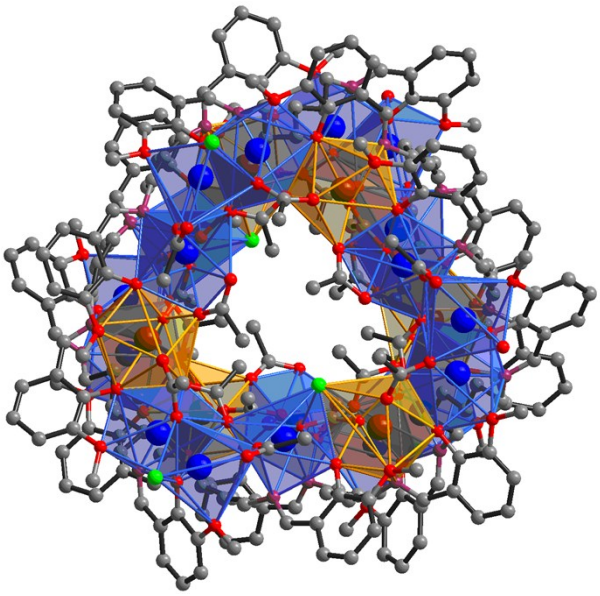
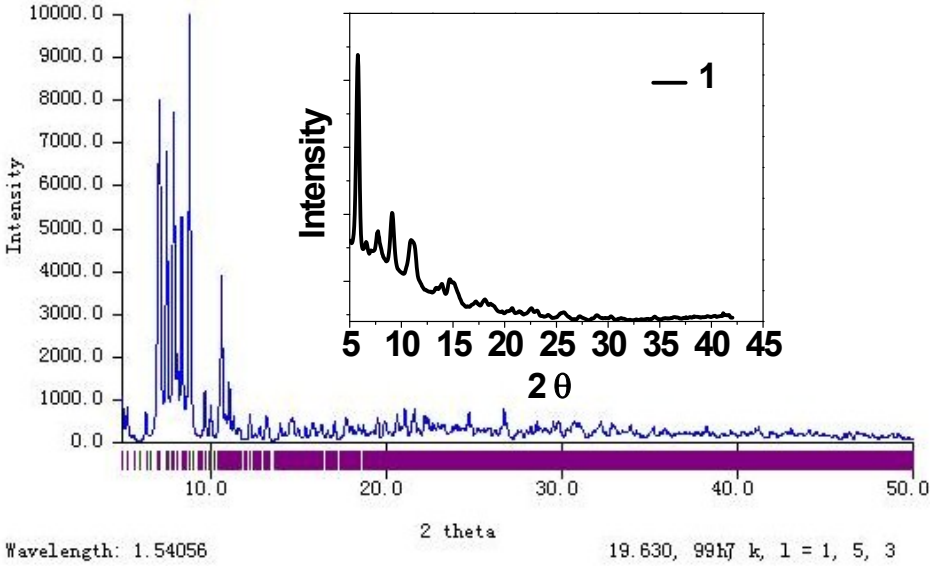
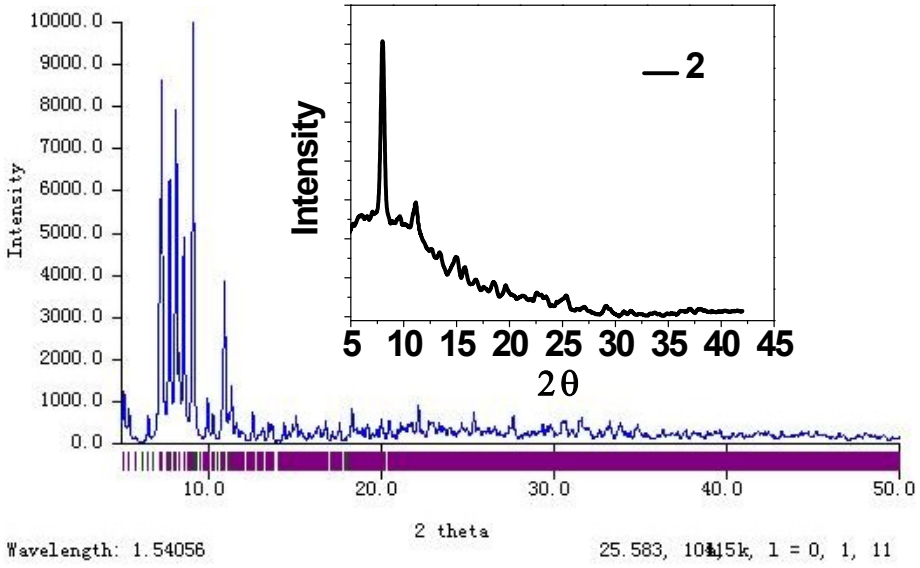


Fig. S2. A view along the *ac*-axis of the crystal structure of **3**.

4. Powder XRD patterns of 1-3





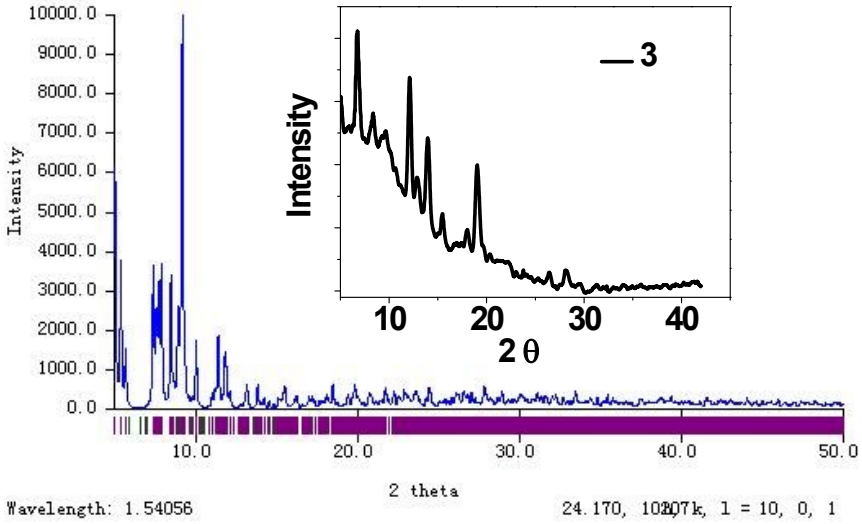


Figure S3. Powder XRD patterns of **1-3**

5. ^{1}H NMR spectra of 1-3

^{1}H NMR experiments were performed on a Bruker Avance III NMR spectrometer at 500.13MHz, equipped with a 5 mm room temperature probe (Bruker Instruments Inc., Germany), and reported as parts per million (ppm) from the internal standard TMS (solvent, $CDCl_3$). The experimental conditions are as follows: spectrometer frequency 500.13 MHz, spectral width (SW) 10 ppm, pulse 90°, acquisition time (AQ) 5.40 s, relaxation delay (RD) 2.00 s, and Fourier Transform (FT) size 32K data point. An exponential window function with a line-broadening factor of 1 Hz was applied to the FID before Fourier transformation.

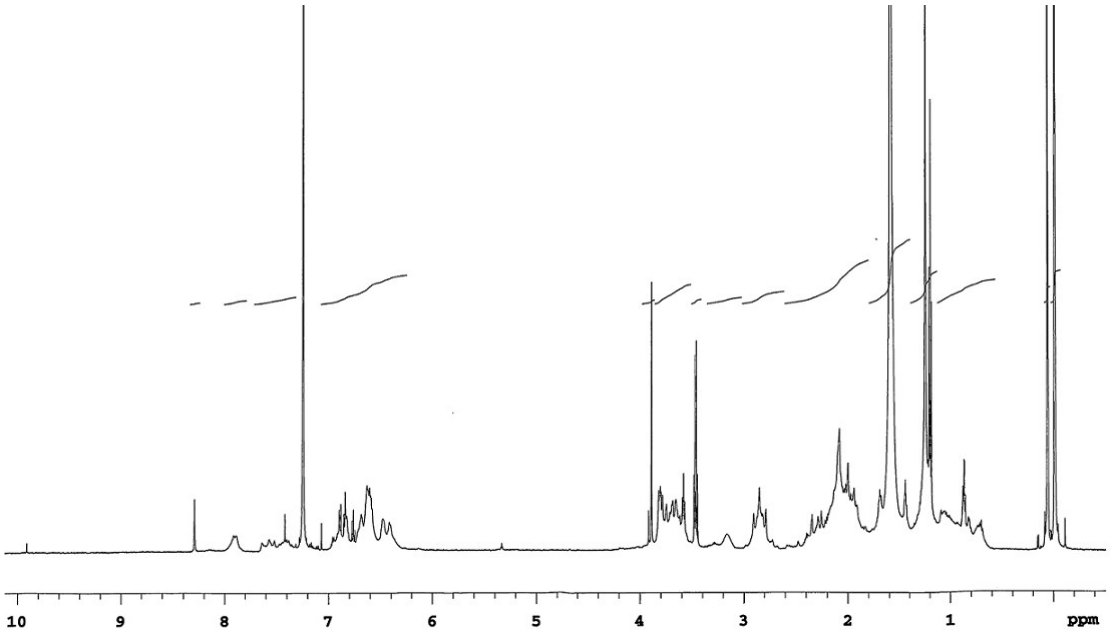
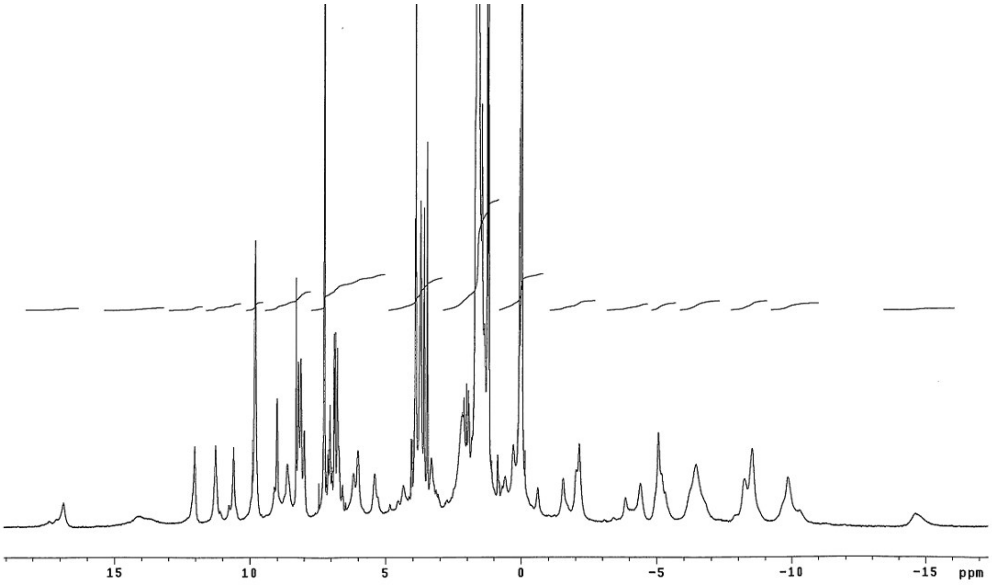
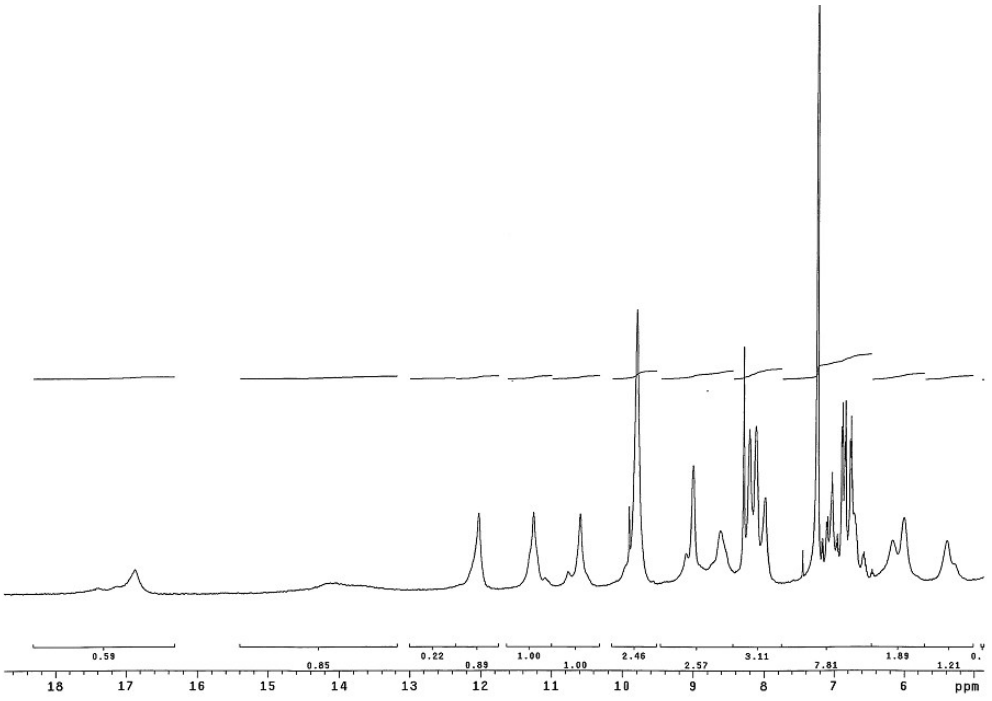


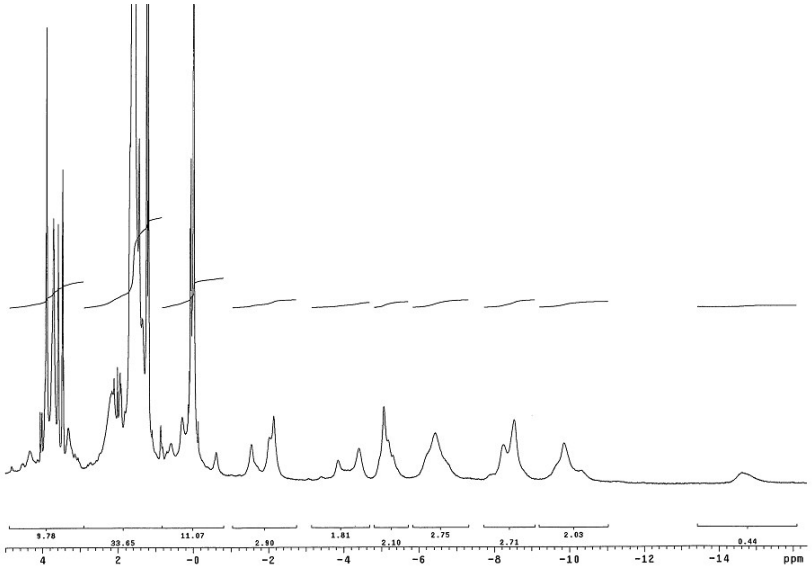
Fig. S4. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 298K.


15
10
5
0
-5
-10
-15
ppm

(a)


0.59
0.85
0.22
0.89
1.00
1.09
2.46
2.57
3.11
7.81
1.89
1.21
18
17
16
15
14
13
12
11
10
9
8
7
6
ppm

(b)



(c)

Fig. S5. ^{1}H NMR spectrum of **2** in $CDCl_3$ at 298K.

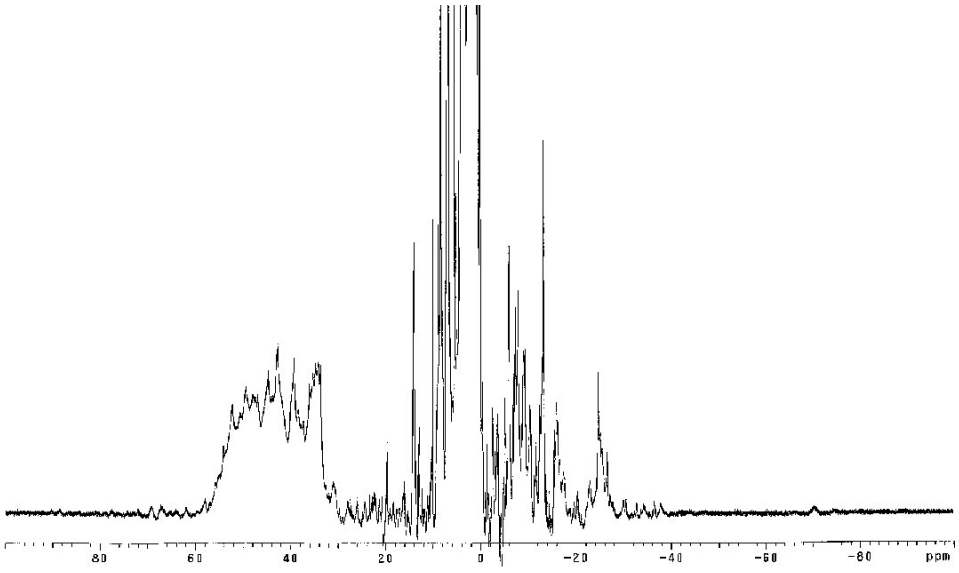


Fig. S6. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 298K.

6. The NIR luminescence spectrum of 2 and 3 in the solid state

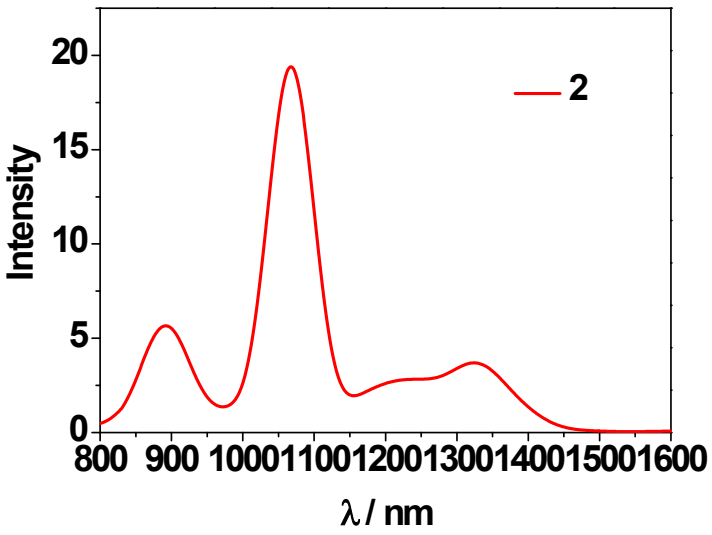


Fig. S7. The NIR luminescence spectrum of **2** in the solid state.

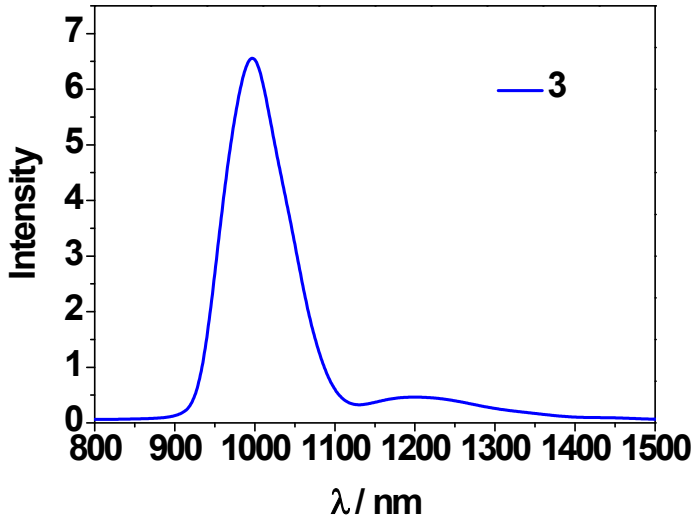


Fig. S8. The NIR luminescence spectrum of **3** in the solid state.

7. X-Ray Crystallography

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

For the crystal structures of **1**-**3**, some uncoordinated solvent molecules such as CH_3OH, C_2H_5OH, $C_2H_5OC_2H_5$ 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**-**3** (CCDC reference numbers 1417785-1417787) are presented in Table S1 and selected bond lengths are given in Tables S2-S4. 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	$C_{280}H_{356}Cd_{22}Cl_{14}N_{20}La_6O_{99}$	$C_{280}H_{356}Cd_{22}Cl_{14}N_{20}Nd_6O_{99}$	$C_{254}H_{320}Cd_{18}Cl_6N_{18}Yb_6O_{94}$
Fw	9388.41	9420.39	8403.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	C222
a [Å]	25.333(11)	24.724(5)	41.918(8)
b [Å]	24.730(10)	24.125(5)	23.335(5)
c [Å]	40.341(19)	39.007(8)	41.805(8)
α [deg]	90	90	90
β [deg]	97.579(16)	97.61(3)	113.62(3)
γ [deg]	90	90	90
V / [Å^3]	25053(20)	23062(8)	37467(13)
d / [g/cm^3]	1.245	1.357	1.490
Z	2	2	4
T [K]	190(1)	190(1)	190(1)
F(000)	9208	9244	16432
μ, mm^{-1}	1.540	1.793	2.588
θ rang, deg	1.31-25.00	2.97-24.98	3.00-25.00
reflns meads	42864	39887	32716
reflns used	42864	39887	32716
params	1990	1990	1793
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0932, 0.2440	0.0561, 0.1375	0.0428, 0.0986
R1, wR2 (all data)	0.1488, 0.2715	0.0873, 0.1480	0.0598, 0.1036
Quality of fit	1.043	1.066	1.050

[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**.

La(1)-O(4)	2.330(9)	Cd(4)-O(35)	2.321(9)
La(1)-O(24)	2.367(9)	Cd(4)-O(12)	2.323(9)
La(1)-O(2)	2.375(8)	Cd(4)-O(11)	2.557(10)
La(1)-O(28)	2.465(8)	Cd(5)-O(14)	2.285(10)
La(1)-O(21)	2.475(10)	Cd(5)-O(39)	2.309(12)
La(1)-O(26)	2.490(10)	Cd(5)-O(38)	2.314(10)
La(1)-N(2)	2.616(11)	Cd(5)-O(13)	2.463(10)
La(1)-O(1)	2.682(9)	Cd(5)-O(40)	2.472(10)
La(2)-O(12)	2.356(8)	Cd(5)-Cl(5)	2.523(4)
La(2)-O(32)	2.373(10)	Cd(6)-O(41)	2.269(9)
La(2)-O(10)	2.386(9)	Cd(6)-N(8)	2.296(11)
La(2)-O(33)	2.391(9)	Cd(6)-O(43)	2.338(11)
La(2)-O(35)	2.462(10)	Cd(6)-O(16)	2.339(9)
La(2)-O(37)	2.488(12)	Cd(6)-O(36)	2.408(9)
La(2)-N(6)	2.638(11)	Cd(6)-O(40)	2.555(10)
La(2)-O(9)	2.661(11)	Cd(7)-O(7)#1	2.273(8)
La(3)-O(42)	2.346(10)	Cd(7)-O(47)	2.330(9)
La(3)-O(44)	2.391(9)	Cd(7)-N(4)#1	2.334(13)
La(3)-O(16)	2.399(8)	Cd(7)-O(46)	2.343(9)
La(3)-O(18)	2.404(8)	Cd(7)-O(18)	2.358(8)
La(3)-O(47)	2.465(9)	Cd(7)-O(17)	2.512(9)
La(3)-O(45)	2.470(9)	Cd(8)-O(7)#1	2.326(9)
La(3)-O(15)	2.625(9)	Cd(8)-O(46)	2.332(8)
La(3)-N(9)	2.648(12)	Cd(8)-O(8)#1	2.457(8)
Cd(1)-N(3)	2.284(11)	Cd(8)-Cl(4)	2.574(4)
Cd(1)-O(6)	2.291(8)	Cd(8)-Cl(7)#2	2.581(4)
Cd(1)-O(28)	2.310(9)	Cd(8)-Cl(7)	2.655(4)
Cd(1)-O(25)	2.311(10)	Cd(9)-N(10)	2.315(11)
Cd(1)-O(4)	2.369(8)	Cd(9)-O(20)	2.320(8)
Cd(1)-O(3)	2.563(9)	Cd(9)-O(48)	2.336(8)
Cd(2)-O(6)	2.301(9)	Cd(9)-Cl(3)	2.641(4)
Cd(2)-O(30)	2.331(11)	Cd(9)-Cl(2)	2.674(4)
Cd(2)-O(25)	2.349(10)	Cd(9)-Cl(4)	2.855(4)
Cd(2)-O(5)	2.413(12)	Cd(10)-O(20)	2.335(9)
Cd(2)-Cl(6)	2.490(4)	Cd(10)-O(22)	2.374(9)
Cd(2)-O(29)	2.507(10)	Cd(10)-O(19)	2.463(8)
Cd(3)-O(31)	2.286(11)	Cd(10)-O(49)	2.469(10)
Cd(3)-N(5)	2.309(11)	Cd(10)-Cl(1)	2.495(4)
Cd(3)-O(10)	2.359(8)	Cd(10)-Cl(3)	2.592(4)
Cd(3)-O(27)	2.375(8)	Cd(11)-N(1)	2.262(9)
Cd(3)-O(34)	2.387(10)	Cd(11)-O(23)	2.266(10)
Cd(3)-O(29)	2.499(11)	Cd(11)-O(2)	2.336(8)
Cd(4)-O(14)	2.293(9)	Cd(11)-O(22)	2.345(9)
Cd(4)-N(7)	2.320(12)	Cd(11)-Cl(2)	2.584(4)
Cd(4)-O(38)	2.321(10)	Cd(11)-O(21)	2.642(9)

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

Nd(1)-O(4)	2.301(5)	Cd(4)-O(35)	2.296(5)
Nd(1)-O(24)	2.303(5)	Cd(4)-O(12)	2.306(5)
Nd(1)-O(2)	2.336(5)	Cd(4)-O(11)	2.501(5)
Nd(1)-O(26)	2.408(5)	Cd(5)-O(14)	2.235(5)
Nd(1)-O(28)	2.409(5)	Cd(5)-O(38)	2.269(5)
Nd(1)-O(21)	2.427(5)	Cd(5)-O(39)	2.274(6)
Nd(1)-N(2)	2.548(6)	Cd(5)-O(13)	2.408(6)
Nd(1)-O(1)	2.607(5)	Cd(5)-O(40)	2.409(5)
Nd(2)-O(33)	2.307(5)	Cd(5)-Cl(5)	2.459(2)
Nd(2)-O(12)	2.311(5)	Cd(6)-O(41)	2.205(5)
Nd(2)-O(32)	2.321(5)	Cd(6)-N(8)	2.280(6)
Nd(2)-O(10)	2.337(5)	Cd(6)-O(43)	2.282(5)
Nd(2)-O(37)	2.404(5)	Cd(6)-O(16)	2.325(5)
Nd(2)-O(35)	2.432(5)	Cd(6)-O(36)	2.387(5)
Nd(2)-N(6)	2.547(6)	Cd(6)-O(40)	2.486(5)
Nd(2)-O(9)	2.597(6)	Cd(7)-O(7)#1	2.243(5)
Nd(3)-O(44)	2.310(5)	Cd(7)-N(4)#1	2.256(7)
Nd(3)-O(42)	2.311(5)	Cd(7)-O(46)	2.264(5)
Nd(3)-O(16)	2.346(5)	Cd(7)-O(47)	2.287(5)
Nd(3)-O(18)	2.354(5)	Cd(7)-O(18)	2.325(5)
Nd(3)-O(45)	2.405(5)	Cd(7)-O(17)	2.454(5)
Nd(3)-O(47)	2.414(5)	Cd(8)-O(7)#1	2.245(5)
Nd(3)-N(9)	2.543(7)	Cd(8)-O(46)	2.314(5)
Nd(3)-O(15)	2.560(5)	Cd(8)-O(8)#1	2.413(5)
Cd(1)-N(3)	2.242(6)	Cd(8)-Cl(7)#2	2.495(2)
Cd(1)-O(25)	2.257(5)	Cd(8)-Cl(4)	2.526(2)
Cd(1)-O(6)	2.266(5)	Cd(8)-Cl(7)	2.607(2)
Cd(1)-O(28)	2.277(5)	Cd(9)-O(20)	2.249(5)
Cd(1)-O(4)	2.344(5)	Cd(9)-N(10)	2.259(6)
Cd(1)-O(3)	2.505(5)	Cd(9)-O(48)	2.274(5)
Cd(2)-O(6)	2.231(5)	Cd(9)-Cl(3)	2.587(2)
Cd(2)-O(30)	2.256(6)	Cd(9)-Cl(2)	2.596(2)
Cd(2)-O(25)	2.284(5)	Cd(9)-Cl(4)	2.785(2)
Cd(2)-O(5)	2.380(6)	Cd(10)-O(22)	2.270(5)
Cd(2)-Cl(6)	2.417(2)	Cd(10)-O(20)	2.287(5)
Cd(2)-O(29)	2.436(5)	Cd(10)-O(49)	2.409(5)
Cd(3)-O(31)	2.268(5)	Cd(10)-O(19)	2.409(5)
Cd(3)-N(5)	2.276(6)	Cd(10)-Cl(1)	2.440(2)
Cd(3)-O(34)	2.287(5)	Cd(10)-Cl(3)	2.545(2)
Cd(3)-O(10)	2.321(5)	Cd(11)-O(23)	2.230(5)
Cd(3)-O(27)	2.353(5)	Cd(11)-N(1)	2.245(6)
Cd(3)-O(29)	2.414(5)	Cd(11)-O(22)	2.293(5)
Cd(4)-O(14)	2.236(5)	Cd(11)-O(2)	2.315(5)
Cd(4)-O(38)	2.264(5)	Cd(11)-Cl(2)	2.545(2)
Cd(4)-N(7)	2.272(7)	Cd(11)-O(21)	2.626(5)

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

Yb(1)-O(19)	2.205(4)		
Yb(1)-O(2)	2.252(4)	Cd(3)-O(6)	2.344(4)
Yb(1)-O(18)	2.264(4)	Cd(3)-O(5)	2.498(4)
Yb(1)-O(23)	2.274(4)	Cd(4)-N(4)	2.306(5)
Yb(1)-O(46)	2.318(4)	Cd(4)-O(8)	2.311(4)
Yb(1)-O(44)	2.348(4)	Cd(4)-O(30)	2.331(4)
Yb(1)-N(9)	2.521(5)	Cd(4)-O(33)	2.337(4)
Yb(1)-O(1)	2.526(4)	Cd(4)-O(31)	2.358(4)
Yb(2)-O(29)	2.218(4)	Cd(4)-Cl(3)	2.5434(18)
Yb(2)-O(8)	2.236(4)	Cd(5)-O(32)	2.211(5)
Yb(2)-O(6)	2.240(4)	Cd(5)-O(10)	2.243(4)
Yb(2)-O(28)	2.278(4)	Cd(5)-O(35)	2.270(5)
Yb(2)-O(26)	2.333(4)	Cd(5)-O(9)	2.397(5)
Yb(2)-N(3)	2.491(5)	Cd(5)-Cl(2)	2.467(2)
Yb(2)-O(7)	2.533(4)	Cd(5)-O(31)	2.568(4)
Yb(2)-Cl(3)	2.8575(19)	Cd(6)-O(10)	2.220(4)
Yb(3)-O(37)	2.218(4)	Cd(6)-N(5)	2.269(5)
Yb(3)-O(14)	2.234(4)	Cd(6)-O(35)	2.270(4)
Yb(3)-O(12)	2.238(4)	Cd(6)-O(34)	2.271(4)
Yb(3)-O(39)	2.286(5)	Cd(6)-O(12)	2.325(4)
Yb(3)-O(36)	2.297(4)	Cd(6)-O(11)	2.498(4)
Yb(3)-O(34)	2.373(4)	Cd(7)-N(7)	2.304(5)
Yb(3)-N(6)	2.476(5)	Cd(7)-O(38)	2.323(4)
Yb(3)-O(13)	2.584(4)	Cd(7)-O(14)	2.324(4)
Cd(1)-O(24)	2.232(5)	Cd(7)-O(43)	2.339(4)
Cd(1)-N(1)	2.276(5)	Cd(7)-O(41)	2.438(4)
Cd(1)-O(2)	2.283(4)	Cd(7)-O(40)	2.443(5)
Cd(1)-O(20)	2.292(4)	Cd(7)-O(39)	2.460(5)
Cd(1)-O(25)	2.358(4)	Cd(8)-O(16)	2.228(4)
Cd(1)-O(21)	2.613(5)	Cd(8)-O(42)	2.280(4)
Cd(1)-O(23)	2.648(4)	Cd(8)-O(45)	2.293(4)
Cd(2)-O(4)	2.219(4)	Cd(8)-O(15)	2.426(4)
Cd(2)-O(22)	2.261(5)	Cd(8)-O(41)	2.430(4)
Cd(2)-O(27)	2.287(4)	Cd(8)-Cl(1)	2.4541(15)
Cd(2)-O(47)	2.306(6)	Cd(9)-O(16)	2.236(4)
Cd(2)-O(21)	2.382(5)	Cd(9)-N(8)	2.244(5)
Cd(2)-O(3)	2.438(5)	Cd(9)-O(45)	2.260(4)
Cd(3)-N(2)	2.264(5)	Cd(9)-O(44)	2.276(4)
Cd(3)-O(27)	2.265(4)	Cd(9)-O(18)	2.322(4)
Cd(3)-O(4)	2.272(4)	Cd(9)-O(17)	2.509(4)
Cd(3)-O(26)	2.310(4)		