Supporting Information

Self-assembly of High-nuclearity Lanthanide-based Nanoclusters for Potential Bioimaging Applications

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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 ligands H_2L[1-3] were prepared according to well-established procedures.[1] 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 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) F. Lam, J.-X. Xu, K.-S. Chan, *J. Org. Chem.* **1996**, *61*, 8414-8418.

Cytotoxicity assays: The proliferation of exponential phase cultures were carried out using either an A549 or an AGS cancer cell line. A549 cells were seeded in 96-well microliter plates at 1000 cells/well and allowed to adhere overnight in 100 μL RPMI 1640 medium supplemented with 2 mM L-glutamine, 10% heat inactivated fetal bovine serum, and antibiotics (200 U/cm3 penicillin and 200 μg/cm3 streptomycin). AGS cells were seeded in 96-well microliter plates at 8000 cells/well, grown in F-12 medium supplemented with 10% heat inactivated fetal bovine serum, 100 U/ml penicillin, and 100 µg/ml streptomycin, and allowed to adhere for 1 day. Cell viability was assessed by tetrazolium salt reduction. Stock solutions of $[Nd_8Cd_{24}L_{12}(OAc)_{44}Cl_4]$ (**1**), neodymium chloride, or H_2L ligand (all 5 mM) in 50/50 methanol/water were formulated and then diluted in medium for secondary stocks of 20–200 μM depending on the complex being tested. Secondary stock solutions were serially diluted in medium and immediately added to wells, whereupon plates were incubated at 37 $^\circ$C under a 5% CO_2/95% air atmosphere. After a total of: 1 day for the A549 cells and 3 days with the AGS cells, a 50 μL aliquot of 3 mg/mL tetrazolium dye, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT, Sigma

Chemical), was added to each well, followed by a 4-hour incubation at 37 °C. The medium was then removed and the resulting formazan was dissolved in 50 μL DMSO and absorbances measured at 560–650 nm using a microplate reader (Molecular Devices, Sunnyvale, CA). Absorbances were corrected for background and the values normalized to wells containing untreated cells to allow plate-to-plate comparison. The data are shown as mean inhibition of proliferation or growth as a percentage of control cells proliferation or growth from 2–3 replicate values.

Microscopy: Luminex MicroPlex Microspheres (6μm cross-linked polystyrene beads with surface carboxyl groups) were loaded with **3** by drying 12.5×10^6 beads under high vacuum for 24 hours. The dried beads were resuspended in chloroform/methanol solution (1 mL, 50:50) containing **3** (5 mg) and the suspension placed on a slow rotation (2 days). The suspension was then centrifuged, the supernatant discarded and the beads washed with MeOH (3×1 mL) followed by drying under high vacuum (24 h.). The loaded beads were then resuspended in PBS and imaged using epifluorescence microscopy using a Life Technologies EVOS FL Auto Cell Imaging System equipped with EVOS Light Cube Qdot 605 and EVOS Light Cube Qdot 655 filters. The Qdot 605 has an excitation maximum of 455 ± 45nm and an emission maximum of 605 ± 15nm. The Qdot 655 has an excitation maximum of 455 ± 45nm and an emission maximum of 655 ± 15nm.

2. Synthesis of 1-5

$[Nd_8Cd_{24}L_{12}(OAc)_{44}Cl_4](EtOH)_7(EtOEt)_2(MeOH)_{11}(H_2O)_{13}$ (**1**). $Cd(OAc)_2 \cdot 2H_2O$ (0.1382 g, 0.52 mmol) and $NdCl_3 \cdot 6H_2O$ (0.0431 g, 0.12 mmol) of were dissolved in MeOH (60 mL) at room temperature, and H_2L (0.1073 g, 0.26 mmol) and Et_3N (0.30 mmol in EtOH 10 mL) were then added. The resulting solution was stirred and heated under reflux (30 min.). 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 were obtained after two weeks. The crystals were filtered off, washed with EtOH (5 ml) and dried in the air. Yield (based on $NdCl_3 \cdot 6H_2O$): 0.0656 g (35 %). m. p. > 206 ^oC (dec.). Elemental analysis: Found: C, 38.35; H, 4.40; N, 3.11 %. Calc. for $C_{376}H_{490}Cd_{24}Cl_4N_{24}Nd_8O_{136}(EtOH)_7(EtOEt)_2(MeOH)_{11}(H_2O)_{13}$: C, 39.04; H, 4.95; N, 2.67 %. IR (CH_3OH, cm^{-1}): 3374 (w), 2930 (w), 1631 (m), 1572 (s), 1470 (m), 1410 (s), 1347 (w), 1307 (m), 1238 (m), 1212 (s), 1080 (m), 1048 (m), 963 (w), 849 (m), 738 (s), 673 (s), 640 (m). ^1H NMR (600 MHz, CD_3OD): δ (ppm) -9.950 (7H), -7.970 (15H), -5.764 (8H), -5.032 (12H), -4.471 (2H), -4.064 (6H), -3.778 (6H), -3.343 (3H), -2.053 (12H), -1.643 (6H), -1.376 (6H), -1.086 (6H), -0.974 (6H), 0.020/0.059 (32H), 0.614 (6H), 1.207/1.318 (100H), 1.600/1.724 (130H), 3.016 (6H), 3.457/3.575/3.687/3.895 (100H), 6.359/6.645/6.755/6.858 (40H), 7.244 (16H), 7.427 (6H), 7.896 (6H), 8.286 (20H), 9.293 (7H), 9.570 (6H), 9.913 (10H), 11.090 (5H), 11.851 (5H), 11.974 (5H), 14.194 (5H), 16.936 (3H).

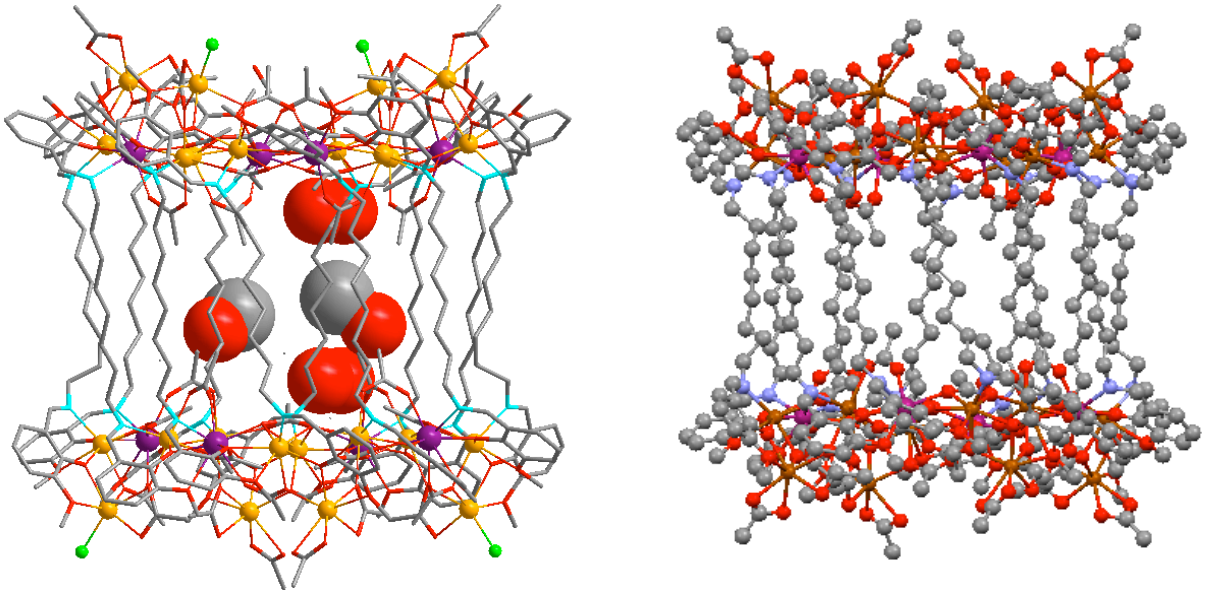
$[Yb_8Cd_{24}L_{12}(OAc)_{44}Cl_4](EtOH)_5(EtOEt)_3(MeOH)_{10}(H_2O)_{17}$ (**2**). The procedure was the same as that for **1** using $YbCl_3 \cdot 6H_2O$ (0.0466 g, 0.12 mmol). Pale yellow single crystals of **2** were formed after two weeks. Yield (based on $YbCl_3 \cdot 6H_2O$): 0.0581 g (30 %). m. p. > 209 ^oC (dec.). Elemental analysis: Found: C, 37.67; H, 4.50; N, 3.03 %. Calc. for $C_{376}H_{490}Cd_{24}Cl_4N_{24}Nd_8O_{136}(EtOH)_5(EtOEt)_3(MeOH)_{10}(H_2O)_{17}$: C, 38.18; H, 4.87; N, 2.62 %. IR (CH_3OH, cm^{-1}): 2930 (w), 1635 (m), 1576 (s), 1468 (m), 1407 (s), 1340 (w), 1309 (m), 1238 (m), 1212 (s), 1078 (m), 1020 (m), 962 (m), 854 (m), 735 (s), 676 (m), 638 (m). ^1H NMR (600 MHz, CD_3OD): δ (ppm) -18.204, -17.628, -16.449, -14.371, -12.824, -11.828, -10.708, -8.966, -8.697, -7.773, -6.829, -5.223, -4.976, -4.786, -4.606, -4.221, -3.975, -3.658, -3.320, -2.875, -2.466, -2.055, -1.861, -1.031, 0.053, 1.665, 3.705, 4.958, 6.752, 7.242, 7.446, 8.270, 9.407, 9.900, 10.943, 13.227, 14.149, 14.778, 17.533.

$[Sm_8Cd_{24}L_{12}(OAc)_{48}](EtOH)_{11}(EtOEt)_3(MeOH)_8(H_2O)_{10}$ (**3**). The procedure was the same as that for **1** using $Sm(OAc)_3 \cdot 4H_2O$ (0.0482 g, 0.12 mmol). Pale yellow single crystals of **3** were formed after one week. Yield (based on $Sm(OAc)_3 \cdot 4H_2O$): 0.0525 g (27 %). m. p. > 205 ^oC (dec.). Elemental analysis: Found: C, 39.23; H, 4.37; N, 2.33 %. Calc. for $C_{376}H_{490}Cd_{24}Cl_4N_{24}Nd_8O_{136}(EtOH)_{11}(EtOEt)_3(MeOH)_8(H_2O)_{10}$: C, 39.86; H, 5.08; N, 2.62 %. IR (CH_3OH, cm^{-1}): 2926 (w), 1631 (m), 1575 (s), 1558 (s), 1471 (m), 1410 (s), 1306 (m), 1212 (s), 1074 (m), 1016 (w), 966 (w), 854 (w), 734 (s), 665 (w).

$[Nd_8Ni_6L_6(OAc)_{24}(EtOH)_6(H_2O)_2]$ (**4**). $Ni(OAc)_2 \cdot 2H_2O$ (0.1108 g, 0.52 mmol) and $Nd(OAc)_3 \cdot 4H_2O$ (0.0472 g, 0.12 mmol) of were dissolved in MeOH (60 mL) at room temperature, and H_2L (0.1073 g, 0.26 mmol) and Et_3N (0.30 mmol in EtOH 10 mL) were then added. The resulting solution was stirred and heated under reflux (30 min.). The mixture was allowed to cool and then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale green crystals were obtained after two weeks. The crystals were filtered off, washed with EtOH (5 ml) and dried in the air. Yield (based on $Nd(OAc)_3 \cdot 4H_2O$): 0.0322 g (35 %). m. p. > 255 ^oC (dec.). IR (CH_3OH, cm^{-1}): 2929 (w), 1630 (m), 1572 (s), 1433 (s), 1402 (s), 1340 (w), 1302 (m), 1205 (s), 1167 (w), 1074 (m), 1020 (m), 970 (w), 846 (m), 777 (w), 731 (s), 665 (m), 611 (m).

$[Yb_8Ni_6L_6(OAc)_{24}(EtOH)_6(H_2O)_2]$ (**5**). The procedure was the same as that for **4** using $Yb(OAc)_3 \cdot 4H_2O$ (0.0506 g, 0.12 mmol). Pale green single crystals of **5** were formed after two weeks. Yield (based on $Yb(OAc)_3 \cdot 4H_2O$): 0.0303 g (31 %). m. p. > 258 ^oC (dec.). IR (CH_3OH, cm^{-1}): 2950 (w), 1627 (s), 1570 (s), 1435 (s), 1400 (s), 1341 (w), 1305 (m), 1206 (s), 1075 (m), 1021 (m), 846 (m), 778 (w), 730 (s), 665 (m).

3. Views of crystal structures of 1 and 3



(a) (b)

Fig. S1. A view along the *a*-axis of the crystal structures of **1** (a) and **3** (b).

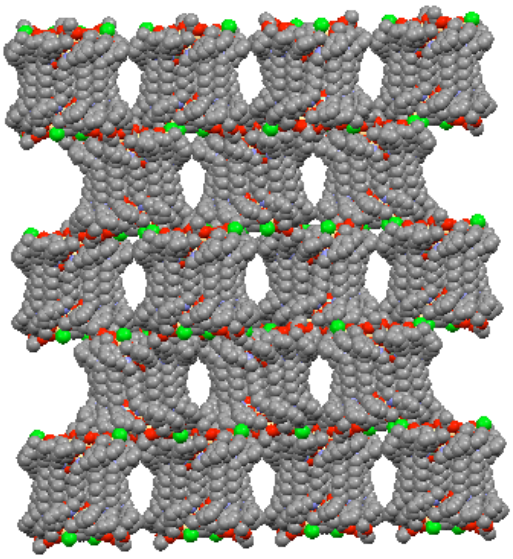
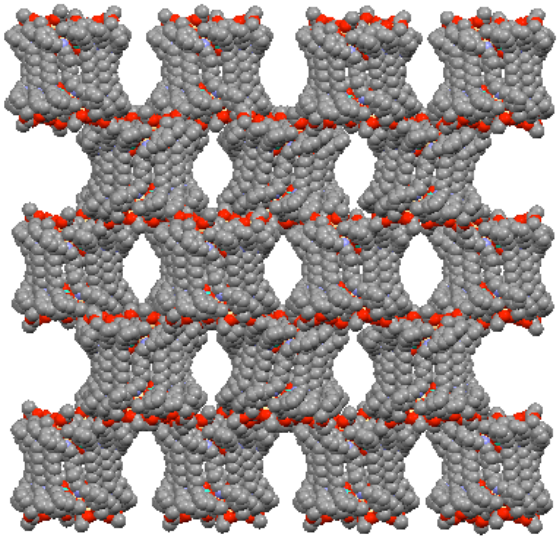
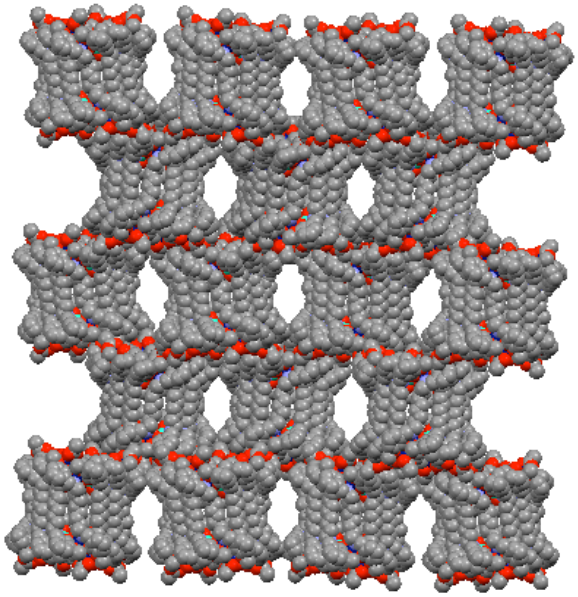


Fig. S2. Space filling view of **1** along the *b*-axis showing the open mesoporous structure.



(a)



(b)

Fig. S3. Space filling views of **3** along *a*- (top) and *b*- (bottom) axis showing the open mesoporous structure.

4. Dynamic light scattering (DLS) data for H_2L and 1

Size Distribution Report by Volume

v2.2

Malvern

Sample Details

Sample Name:	H2L-C8 DCM 2		
SOP Name:	DCM.sop		
General Notes:			
File Name:	Nd32-C8 REDO.dts	**Dispersant Name:**	DCM
Record Number:	9	**Dispersant RI:**	1.424
Material RI:	1.59	**Viscosity (cP):**	0.4300
Material Absorbtion:	0.010	**Measurement Date and Time:**	Tuesday, April 07, 2015 11:4...

System

Temperature (°C):	25.0	**Duration Used (s):**	70
Count Rate (kcps):	265.2	**Measurement Position (mm):**	1.25
Cell Description:	Disposable sizing cuvette	**Attenuator:**	11

Results

			Size (d.nm):	**% Volume:**	**St Dev (d.nm):**
Z-Average (d.nm):	229.5	**Peak 1:**	1.609	100.0	0.5288
PdI:	0.476	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.154	**Peak 3:**	0.000	0.0	0.000

Result quality : Refer to quality report

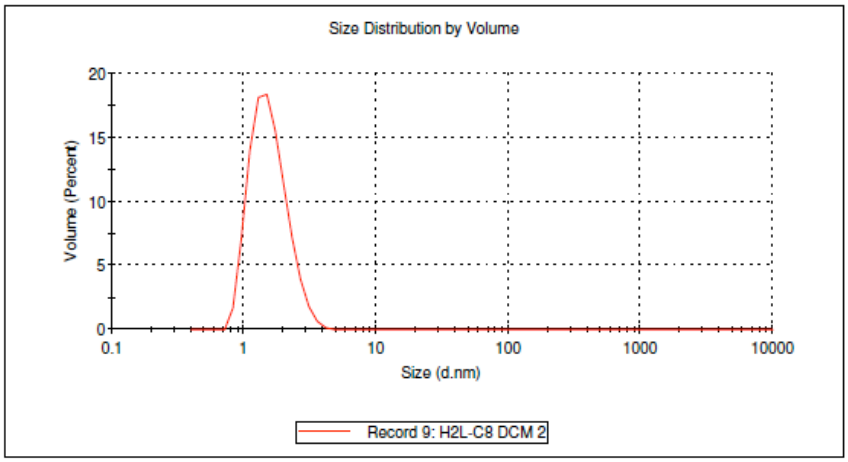


Fig. S4. Dynamic light scattering data for ligand H_2L

Size Distribution Report by Volume

v2.2

Malvern

Sample Details

Sample Name:	Nd32-C8 DCM 3		
SOP Name:	DCM.sop		
General Notes:			
File Name:	Nd32-C8 REDO.dts	**Dispersant Name:**	DCM
Record Number:	4	**Dispersant RI:**	1.424
Material RI:	1.59	**Viscosity (cP):**	0.4300
Material Absorbtion:	0.010	**Measurement Date and Time:**	Wednesday, March 25, 201...

System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	365.6	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	11

Results

			Size (d.nm):	**% Volume:**	**St Dev (d.nm):**
Z-Average (d.nm):	323.1	**Peak 1:**	267.6	0.0	67.24
PdI:	0.398	**Peak 2:**	2.335	100.0	0.5610
Intercept:	0.645	**Peak 3:**	0.000	0.0	0.000

Result quality : Refer to quality report

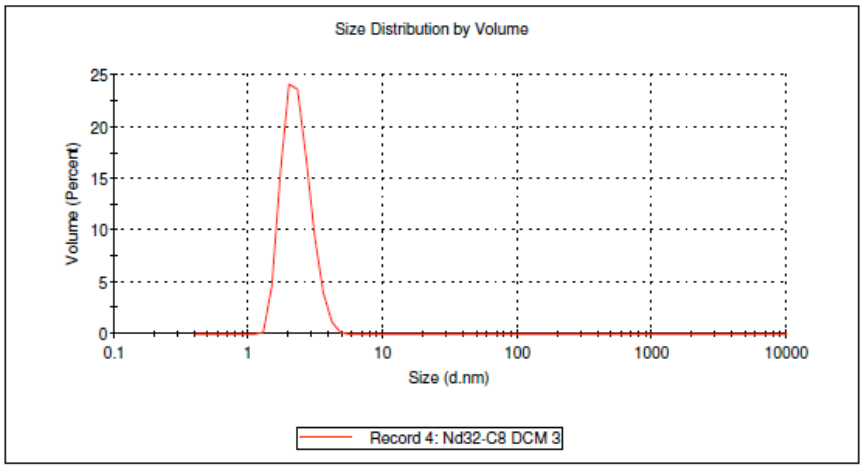
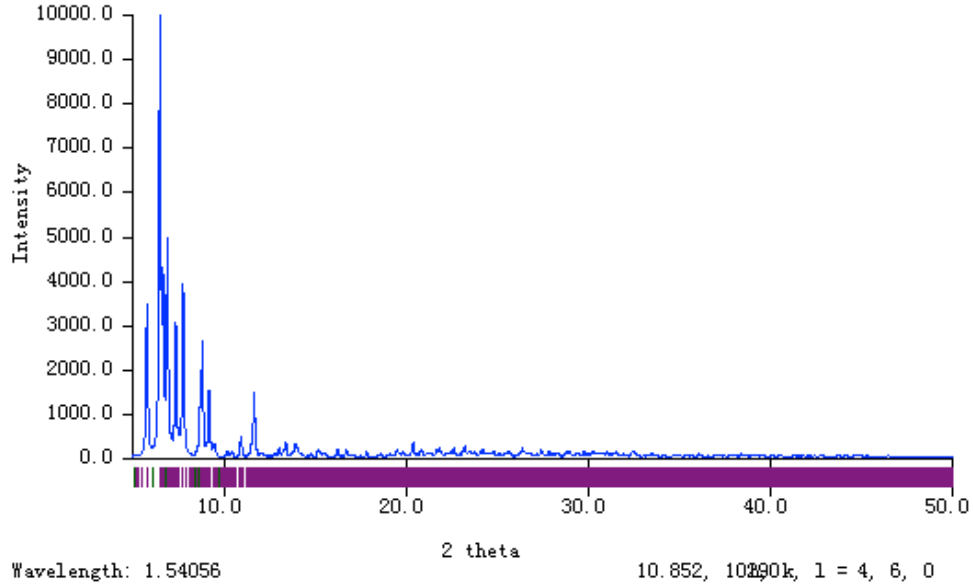
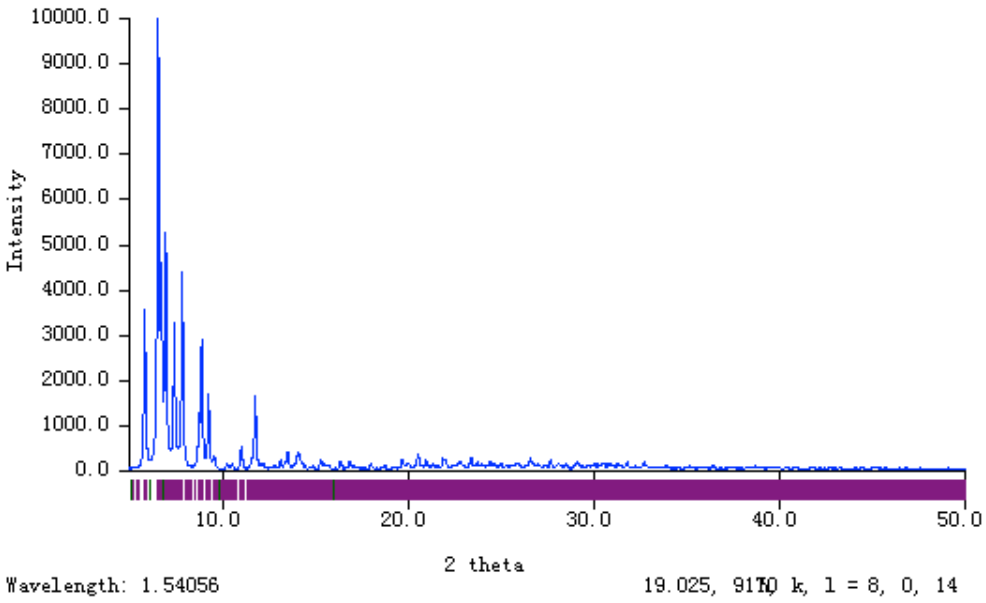
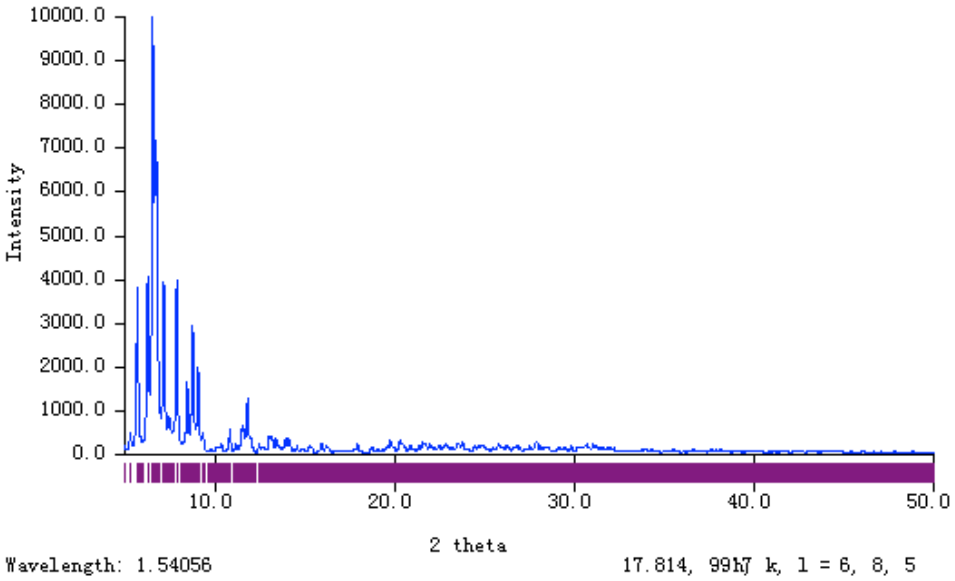


Fig. S5. Dynamic light scattering data for **1**.

5. Powder XRD patterns of 1-5



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3000.0
2000.0
1000.0
0.0
Intensity
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30.0
40.0
50.0
2 theta
Wavelength: 1.54056
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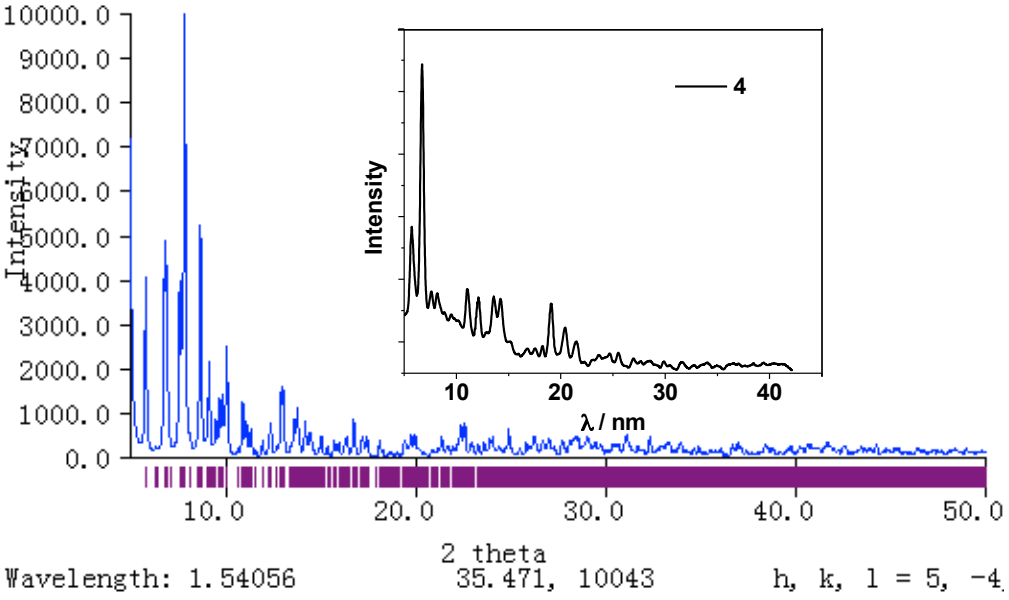
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8000.0
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1000.0
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Intensity
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20.0
30.0
40.0
50.0
2 theta
Wavelength: 1.54056
35.471, 10043
h, k, l = 5, -4
Intensity
4
10
20
30
40
λ / nm

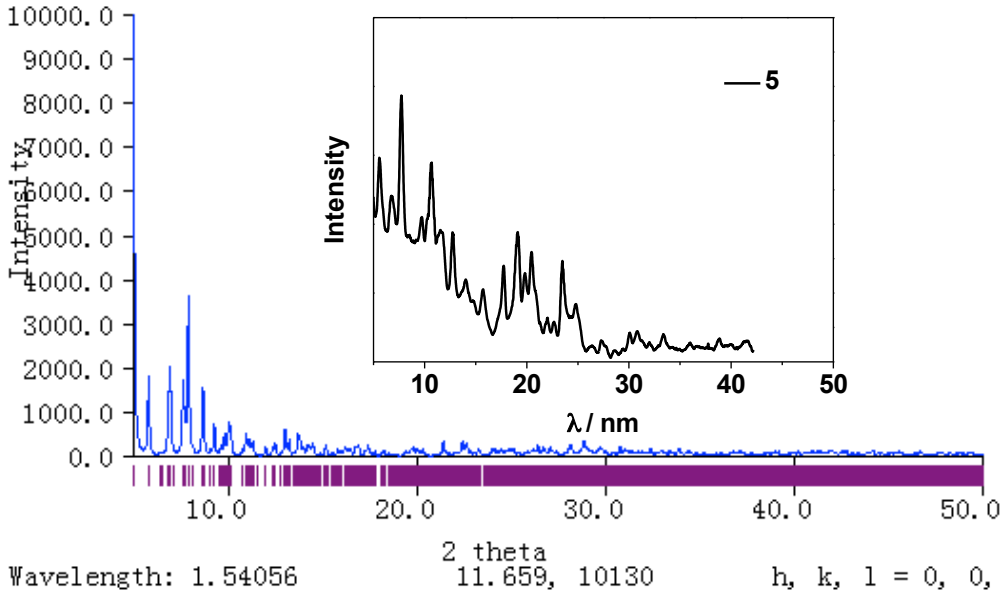


Figure S6. Powder XRD patterns of **1-5**

6. ^{1}H NMR spectra of 1 and 2

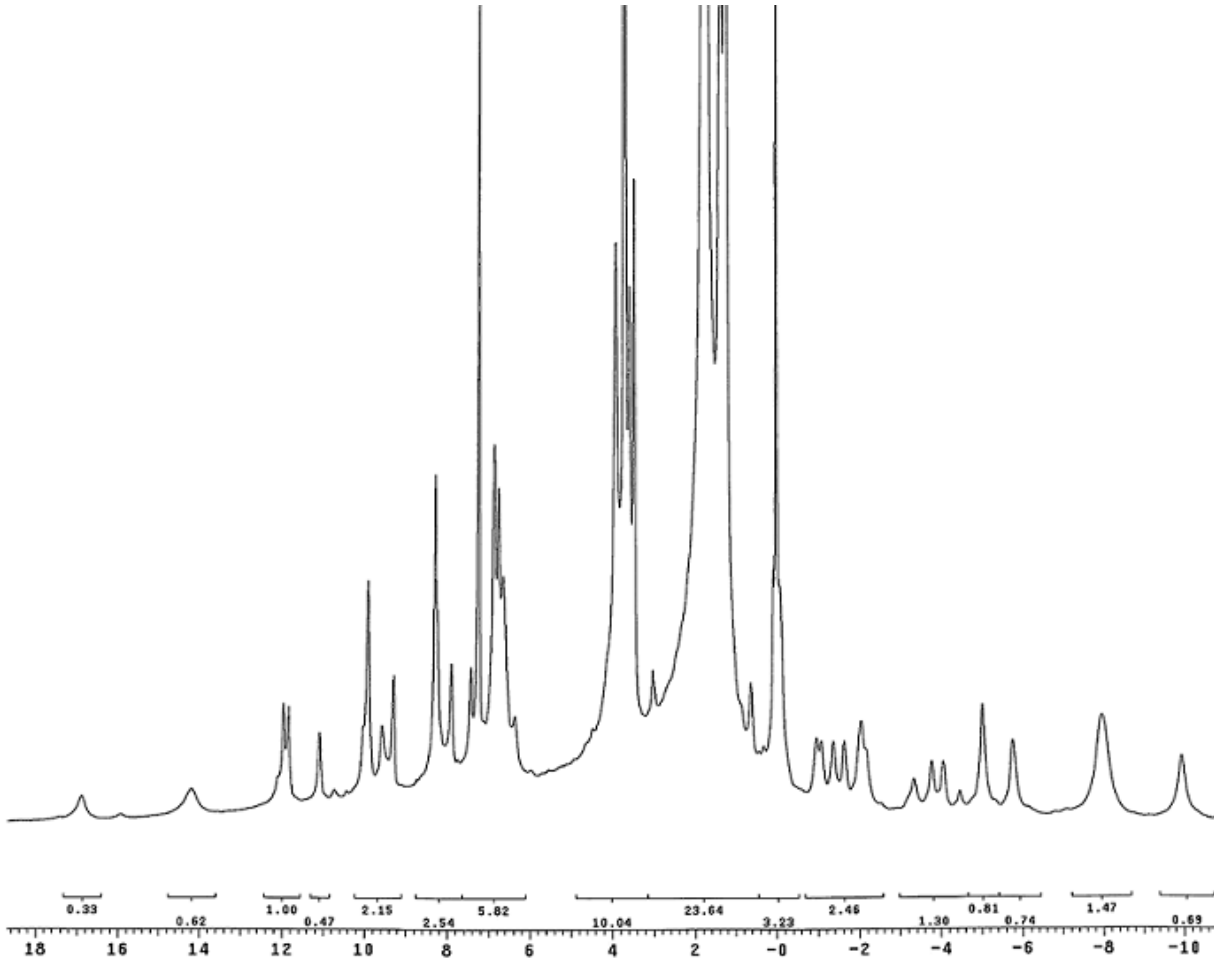
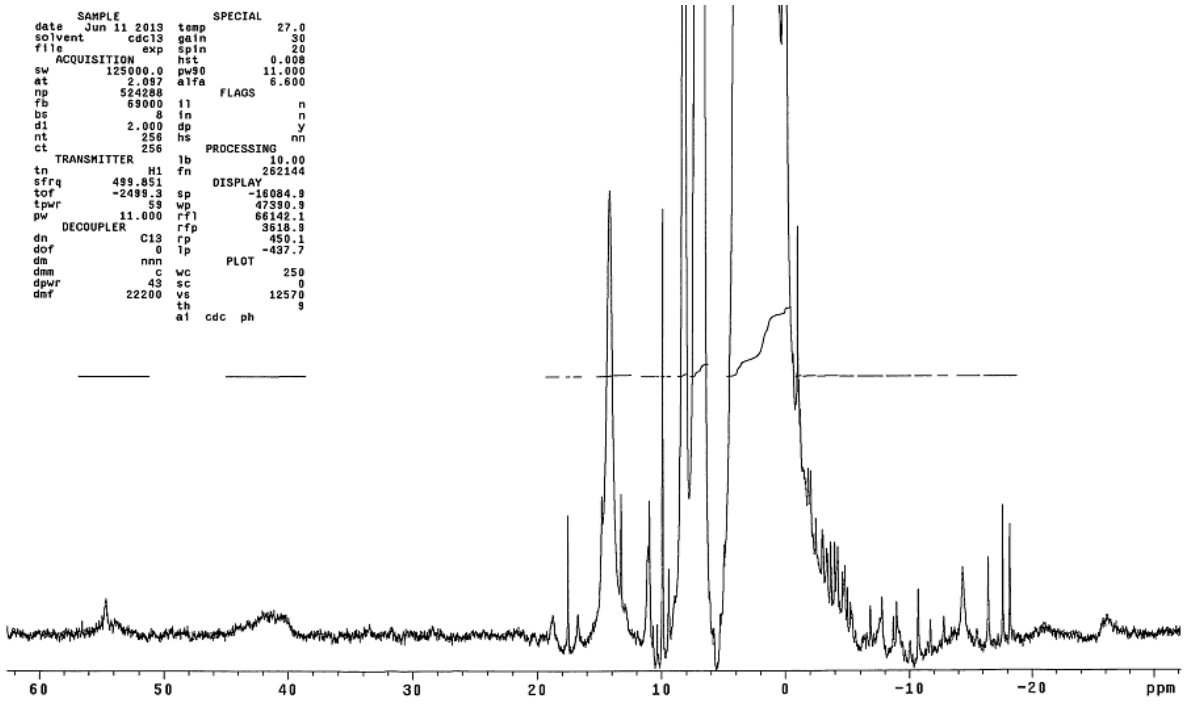


Fig. S7. ^{1}H NMR spectrum of **1** in $CDCl_3$.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fb 69000
bs 8
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nt 256
ct 256
TRANSMITTER
tn H1
sfrq 499.851
tof -2499.3
tpwr 59
pw 11.000
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 43
dmf 22200
SPECIAL
temp 27.0
gain 30
spin 20
hst 0.008
pw90 11.000
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 10.00
fn 262144
DISPLAY
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wp 47390.9
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rp 450.1
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th 9
al cdc ph
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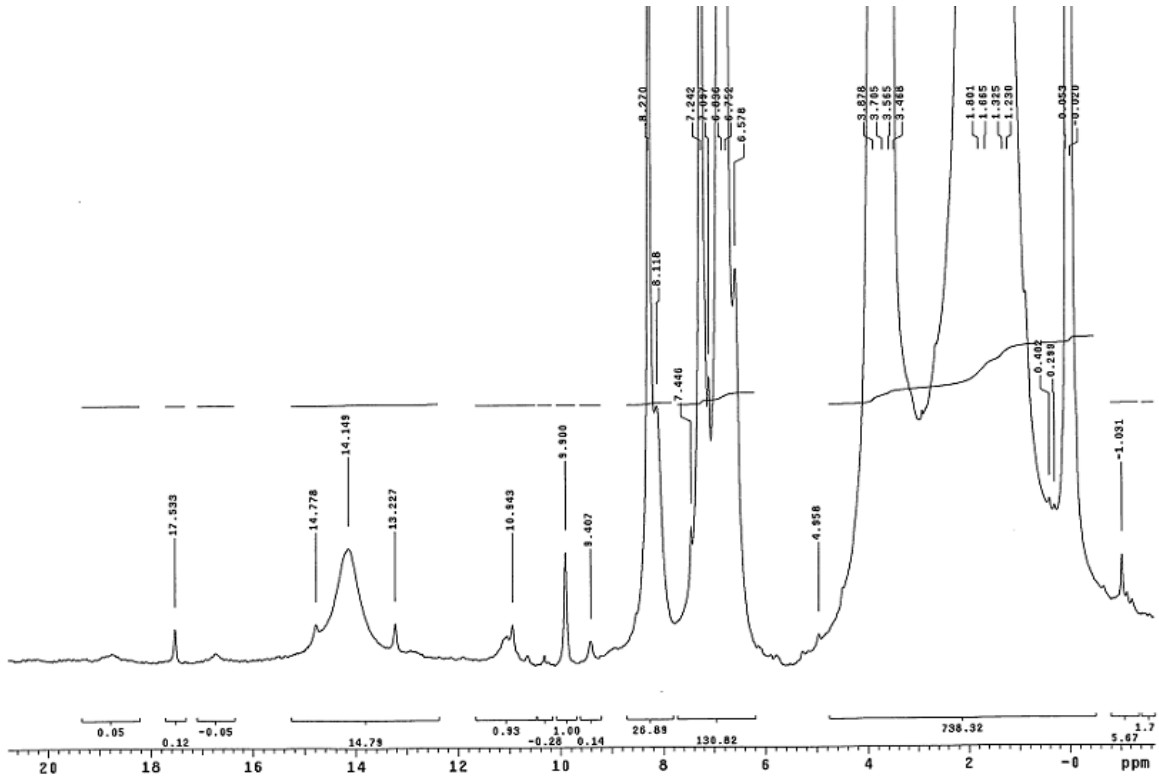
40
30
20
10
0
-10
-20
ppm

(a)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6.756
6.578
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3.765
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3.468
1.801
1.685
1.325
1.230
0.053
-0.020
0.402
0.298
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17.533
14.778
14.149
13.227
10.643
9.900
9.467
4.958
0.05
0.12
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0.93
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1.7
20
18
16
14
12
10
8
6
4
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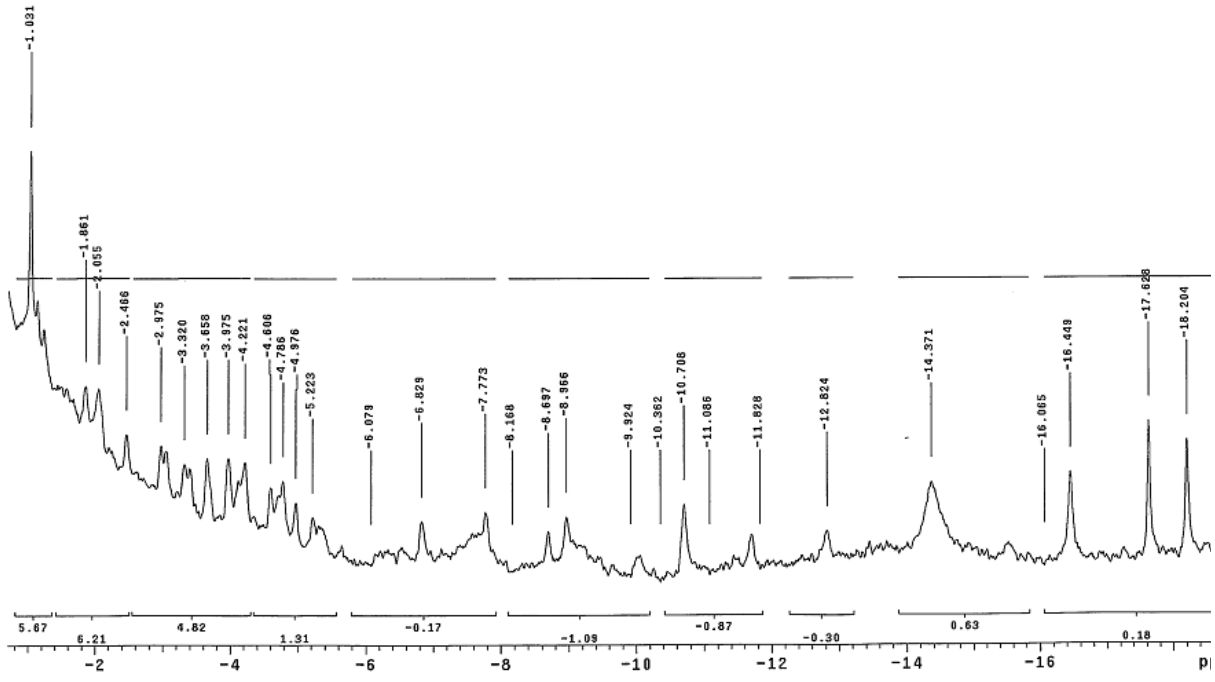
ppm

(b)



(c)

Fig. S8. ^{1}H NMR spectrum of **2** in $CDCl_3$.

7. Excitation spectrum of 3

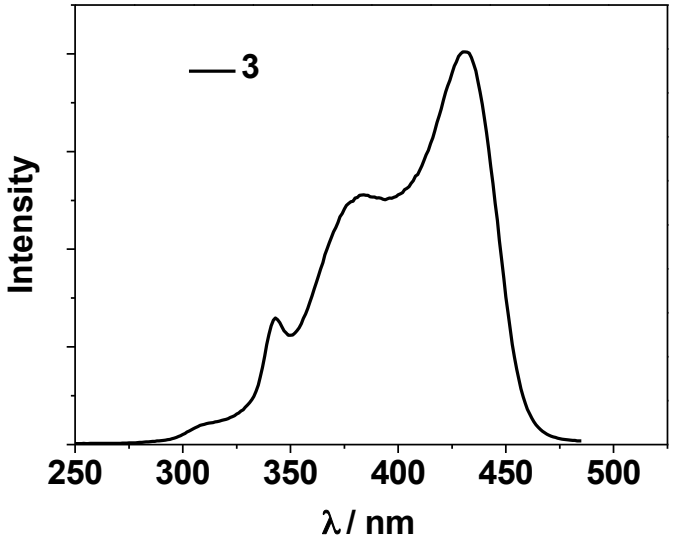


Fig. S9. Excitation spectrum of **3** in CH_3CN.

8. Cytotoxicity data for A549 cells

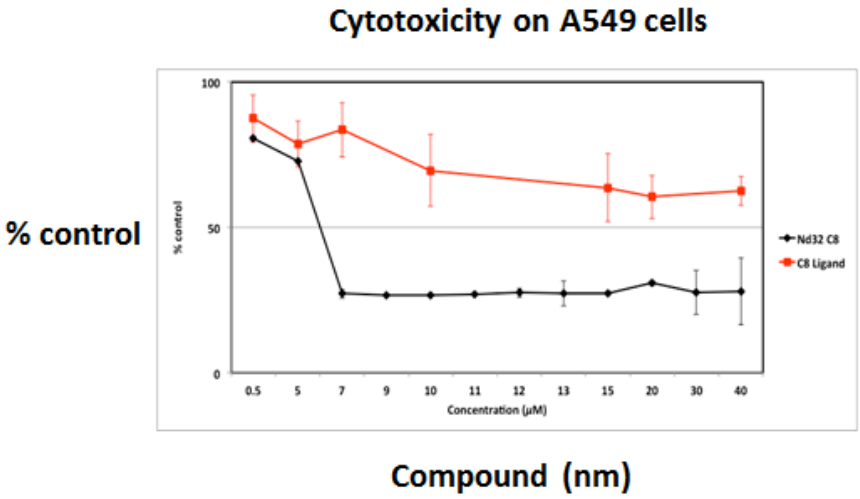


Fig. S10. Cytotoxicity data for **1** on A549 cancer cells.

9. 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 Cd-Ln clusters **1-3**, 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 **1-5** are presented in Table S1 and selected bond lengths are given in Tables S2-S6. (CCDC reference numbers 1007468, 1007469, 1007472-1007474). 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**-**5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{376}H_{490}Cd_{24}Cl_4N_{24}Nd_8O_{136}$	$C_{376}H_{490}Cd_{24}Cl_4N_{24}Yb_8O_{136}$	$C_{384}H_{504}Cd_{24}Sm_8N_{24}O_{144}$	$C_{218}H_{328}N_{12}Nd_8Ni_6O_{94}$	$C_{224}H_{342}N_{12}Yb_8Ni_6O_{94}$
Fw	11515.24	11745.64	11660.52	6127.10	6507.68
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Triclinic
Space group	Fddd	Fddd	C222	P-1	P-1
a [Å]	54.405(11)	54.070(11)	56.782(11)	13.7021(5)	13.643(3)
b [Å]	61.195(12)	60.708(12)	62.983(13)	19.5675(9)	19.294(4)
c [Å]	91.022(18)	90.132(18)	44.704(9)	31.9547(13)	31.918(6)
α [deg]	90	90	90	103.934(3)	103.53(3)
β [deg]	90	90	90	95.761(2)	95.86(3)
γ [deg]	90	90	90	105.409(2)	106.04(2)
V / [Å^3]	303043(99)	295857(102)	159876(55)	7891.9(6)	7725(3)
d / [g/cm^3]	1.010	1.055	0.969	1.289	1.399
Z	16	16	4	1	1
T [K]	223(1)	223(1)	223(1)	223(1)	223(1)
F(000)	91232	92512	46208	3120	3282
μ, mm^{-1}	1.257	1.738	1.248	1.711	2.828
θ rang, deg	2.95-24.84	3.01-25.00	2.99-25.00	1.49-25.00	3.00-25.00
reflns meads	63253	63271	139515	173694	46990
reflns used	63253	63271	139515	27125	26679
params	2575	2575	5140	1576	1612
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.1034, 0.2692	0.0955, 0.2258	0.1089, 0.2519	0.0762, 0.1682	0.0876, 0.2092
R1, wR2 (all data)	0.1798, 0.3134	0.2013, 0.2420	0.2276, 0.3063	0.1188, 0.1914	0.1439, 0.2499
Quality of fit	0.935	1.065	0.863	1.113	1.036

[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(2)	2.225(9)	Cd(4)-O(9)	2.461(12)
Nd(1)-O(30)	2.239(10)	Cd(4)-O(38)	2.461(9)
Nd(1)-O(6)	2.279(9)	Cd(4)-O(35)	2.494(15)
Nd(1)-O(33)	2.319(9)	Cd(5)-O(14)	2.264(10)
Nd(1)-O(28)	2.332(10)	Cd(5)-O(39)	2.284(11)
Nd(1)-O(31)	2.332(10)	Cd(5)-O(41)	2.295(10)
Nd(1)-N(3)	2.510(12)	Cd(5)-N(7)	2.338(13)
Nd(1)-O(1)	2.528(10)	Cd(5)-O(34)	2.364(9)
Nd(2)-O(42)	2.256(11)	Cd(5)-O(38)	2.400(10)
Nd(2)-O(45)	2.261(11)	Cd(6)-O(22)	2.219(10)
Nd(2)-O(18)	2.264(10)	Cd(6)-O(46)	2.269(10)
Nd(2)-O(14)	2.270(10)	Cd(6)-N(11)	2.275(13)
Nd(2)-O(40)	2.316(12)	Cd(6)-O(44)	2.303(9)
Nd(2)-O(44)	2.344(10)	Cd(6)-O(18)	2.323(10)
Nd(2)-N(9)	2.526(14)	Cd(6)-O(17)	2.519(12)
Nd(2)-O(13)	2.559(10)	Cd(7)-O(51)	2.234(11)
Nd(3)-O(59)	2.207(10)	Cd(7)-O(7)	2.303(10)
Nd(3)-O(19)	2.244(10)	Cd(7)-O(48)	2.314(10)
Nd(3)-O(15)	2.263(10)	Cd(7)-N(4)	2.333(12)
Nd(3)-O(57)	2.286(10)	Cd(7)-O(53)	2.352(10)
Nd(3)-O(56)	2.334(10)	Cd(7)-O(50)	2.415(11)
Nd(3)-O(54)	2.363(11)	Cd(8)-O(55)	2.272(10)
Nd(3)-N(8)	2.480(13)	Cd(8)-O(11)	2.276(10)
Nd(3)-O(20)	2.508(10)	Cd(8)-O(49)	2.293(12)
Nd(4)-O(47)#1	2.239(9)	Cd(8)-O(12)	2.405(11)
Nd(4)-O(7)#1	2.265(10)	Cd(8)-O(50)	2.424(10)
Nd(4)-O(52)#1	2.290(11)	Cd(8)-Cl(2)	2.458(7)
Nd(4)-O(3)#1	2.292(10)	Cd(9)-O(11)	2.227(10)
Nd(4)-O(68)	2.324(10)	Cd(9)-O(55)	2.265(10)
Nd(4)-O(64)	2.340(9)	Cd(9)-O(15)	2.289(10)
Nd(4)-N(2)#1	2.520(12)	Cd(9)-N(6)	2.295(11)
Nd(4)-O(8)#1	2.590(10)	Cd(9)-O(54)	2.315(9)
Cd(1)-O(22)#1	2.246(10)	Cd(9)-O(16)	2.530(10)
Cd(1)-O(25)	2.296(13)	Cd(9)-O(53)	2.642(9)
Cd(1)-O(46)#1	2.313(11)	Cd(10)-O(58)	2.282(10)
Cd(1)-O(26)	2.408(10)	Cd(10)-N(10)	2.286(13)
Cd(1)-O(21)#1	2.409(11)	Cd(10)-O(19)	2.312(10)
Cd(1)-Cl(1)	2.450(5)	Cd(10)-O(60)	2.337(10)
Cd(2)-O(27)	2.216(9)	Cd(10)-O(63)	2.369(9)
Cd(2)-O(2)	2.292(8)	Cd(10)-O(61)	2.457(10)
Cd(2)-N(1)	2.293(11)	Cd(11)-O(23)	2.275(10)
Cd(2)-O(29)	2.316(10)	Cd(11)-O(62)	2.292(9)
Cd(2)-O(43)	2.382(9)	Cd(11)-O(66)	2.300(10)
Cd(2)-O(26)	2.434(10)	Cd(11)-O(67)	2.334(9)
Cd(3)-O(6)	2.231(9)	Cd(11)-O(61)	2.424(10)
Cd(3)-O(10)	2.238(10)	Cd(11)-O(65)	2.494(10)
Cd(3)-O(32)	2.262(9)	Cd(11)-O(24)	2.508(9)
Cd(3)-N(5)	2.295(13)	Cd(12)-O(23)	2.248(9)
Cd(3)-O(33)	2.322(9)	Cd(12)-N(12)	2.273(13)
Cd(3)-O(5)	2.548(10)	Cd(12)-O(67)	2.277(10)
Cd(3)-O(34)	2.599(9)	Cd(12)-O(64)	2.303(9)
Cd(4)-O(32)	2.277(10)	Cd(12)-O(3)#1	2.324(10)
Cd(4)-O(10)	2.291(9)	Cd(12)-O(4)#1	2.547(10)
Cd(4)-O(37)	2.360(10)	Cd(12)-O(63)	2.591(9)
Cd(4)-O(36)	2.381(12)		

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

Yb(1)-O(30)	2.217(10)	Cd(4)-O(38)	2.429(9)
Yb(1)-O(2)	2.246(11)	Cd(4)-O(9)	2.452(11)
Yb(1)-O(6)	2.262(10)	Cd(4)-O(35)	2.465(17)
Yb(1)-O(28)	2.304(9)	Cd(5)-O(14)	2.262(10)
Yb(1)-O(31)	2.335(11)	Cd(5)-O(41)	2.302(10)
Yb(1)-O(33)	2.349(10)	Cd(5)-O(39)	2.308(11)
Yb(1)-N(3)	2.485(13)	Cd(5)-O(34)	2.339(10)
Yb(1)-O(1)	2.512(11)	Cd(5)-N(7)	2.359(15)
Yb(2)-O(18)	2.217(9)	Cd(5)-O(38)	2.377(10)
Yb(2)-O(42)	2.242(11)	Cd(6)-O(22)	2.226(10)
Yb(2)-O(14)	2.275(10)	Cd(6)-N(11)	2.247(13)
Yb(2)-O(45)	2.300(12)	Cd(6)-O(46)	2.276(11)
Yb(2)-O(40)	2.303(12)	Cd(6)-O(18)	2.283(11)
Yb(2)-O(44)	2.334(11)	Cd(6)-O(44)	2.303(9)
Yb(2)-N(9)	2.516(14)	Cd(6)-O(17)	2.491(13)
Yb(2)-O(13)	2.523(12)	Cd(6)-O(43)#1	2.589(10)
Yb(3)-O(15)	2.189(12)	Cd(7)-O(51)	2.266(12)
Yb(3)-O(59)	2.213(13)	Cd(7)-O(48)	2.272(11)
Yb(3)-O(19)	2.223(12)	Cd(7)-O(7)	2.274(11)
Yb(3)-O(57)	2.259(12)	Cd(7)-N(4)	2.316(13)
Yb(3)-O(56)	2.320(13)	Cd(7)-O(53)	2.322(11)
Yb(3)-O(54)	2.352(11)	Cd(7)-O(50)	2.365(11)
Yb(3)-N(8)	2.465(16)	Cd(8)-O(55)	2.226(12)
Yb(3)-O(20)	2.543(13)	Cd(8)-O(49)	2.263(12)
Yb(4)-O(47)#1	2.190(11)	Cd(8)-O(11)	2.285(12)
Yb(4)-O(7)#1	2.241(10)	Cd(8)-O(12)	2.355(12)
Yb(4)-O(3)#1	2.250(10)	Cd(8)-O(50)	2.420(11)
Yb(4)-O(68)	2.298(12)	Cd(8)-Cl(2)	2.428(7)
Yb(4)-O(52)#1	2.312(14)	Cd(9)-O(11)	2.216(12)
Yb(4)-O(64)	2.336(9)	Cd(9)-N(6)	2.271(13)
Yb(4)-N(2)#1	2.473(13)	Cd(9)-O(15)	2.278(12)
Yb(4)-O(8)#1	2.563(10)	Cd(9)-O(55)	2.294(11)
Cd(1)-O(22)#1	2.239(11)	Cd(9)-O(54)	2.295(10)
Cd(1)-O(25)	2.279(14)	Cd(9)-O(16)	2.511(11)
Cd(1)-O(46)#1	2.283(11)	Cd(10)-O(58)	2.280(11)
Cd(1)-O(26)	2.401(11)	Cd(10)-O(19)	2.287(12)
Cd(1)-O(21)#1	2.414(11)	Cd(10)-N(10)	2.306(15)
Cd(1)-Cl(1)	2.418(6)	Cd(10)-O(60)	2.310(12)
Cd(2)-O(27)	2.204(9)	Cd(10)-O(63)	2.343(11)
Cd(2)-O(2)	2.244(10)	Cd(10)-O(61)	2.417(11)
Cd(2)-O(29)	2.295(11)	Cd(11)-O(23)	2.230(12)
Cd(2)-N(1)	2.298(13)	Cd(11)-O(62)	2.256(11)
Cd(2)-O(43)	2.353(10)	Cd(11)-O(66)	2.289(11)
Cd(2)-O(26)	2.398(11)	Cd(11)-O(67)	2.307(9)
Cd(3)-O(10)	2.184(10)	Cd(11)-O(61)	2.424(10)
Cd(3)-O(6)	2.222(10)	Cd(11)-O(65)	2.464(11)
Cd(3)-O(32)	2.244(9)	Cd(11)-O(24)	2.467(11)
Cd(3)-N(5)	2.271(14)	Cd(12)-N(12)	2.237(14)
Cd(3)-O(33)	2.317(9)	Cd(12)-O(23)	2.242(11)
Cd(3)-O(5)	2.529(10)	Cd(12)-O(67)	2.257(11)
Cd(3)-O(34)	2.610(9)	Cd(12)-O(64)	2.261(9)
Cd(4)-O(32)	2.257(10)	Cd(12)-O(3)#1	2.262(11)
Cd(4)-O(10)	2.272(10)	Cd(12)-O(4)#1	2.527(12)
Cd(4)-O(37)	2.304(10)	Cd(12)-O(63)	2.588(11)
Cd(4)-O(36)	2.341(12)		

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

Sm(1)-O(53)	2.124(16)	Cd(4)-O(69)	2.371(13)
Sm(1)-O(4)	2.183(14)	Cd(4)-O(67)	2.501(15)
Sm (1)-O(51)	2.260(12)	Cd(5)-O(12)	2.219(15)
Sm (1)-O(2)	2.300(14)	Cd(5)-O(71)	2.229(16)
Sm (1)-O(94)	2.3067(13)	Cd(5)-O(73)	2.268(12)
Sm (1)-O(50)	2.318(14)	Cd(5)-O(70)	2.275(15)
Sm (1)-N(1)	2.505(18)	Cd(5)-O(69)	2.468(14)
Sm (1)-O(3)	2.587(15)	Cd(5)-O(11)	2.488(15)
Sm (2)-O(10)	2.138(11)	Cd(5)-O(72)	2.629(19)
Sm (2)-O(63)	2.258(19)	Cd(6)-O(73)	2.210(12)
Sm (2)-O(62)	2.271(14)	Cd(6)-N(6)	2.24(2)
Sm (2)-O(65)	2.274(16)	Cd(6)-O(12)	2.317(14)
Sm (2)-O(58)	2.329(14)	Cd(6)-O(68)	2.328(12)
Sm (2)-O(8)	2.346(13)	Cd(6)-O(14)	2.329(17)
Sm (2)-O(9)	2.522(14)	Cd(6)-O(13)	2.522(14)
Sm (2)-N(4)	2.529(16)	Cd(6)-O(67)	2.567(15)
Sm (3)-O(78)	2.186(11)	Cd(7)-N(8)	2.305(18)
Sm (3)-O(75)	2.233(14)	Cd(7)-O(76)	2.308(14)
Sm (3)-O(14)	2.254(14)	Cd(7)-O(77)	2.316(14)
Sm (3)-O(16)	2.254(15)	Cd(7)-O(16)	2.334(13)
Sm (3)-O(68)	2.317(14)	Cd(7)-O(81)	2.382(12)
Sm (3)-O(74)	2.370(12)	Cd(7)-O(79)	2.453(14)
Sm (3)-N(7)	2.416(17)	Cd(8)-O(18)	2.290(15)
Sm (3)-O(15)	2.545(13)	Cd(8)-O(85)	2.314(16)
Sm (4)-O(22)	2.231(11)	Cd(8)-O(80)	2.314(16)
Sm (4)-O(20)	2.238(16)	Cd(8)-O(84)	2.322(15)
Sm (4)-O(87)	2.266(14)	Cd(8)-O(17)	2.366(17)
Sm (4)-O(89)	2.288(13)	Cd(8)-O(79)	2.370(15)
Sm (4)-O(86)	2.300(13)	Cd(8)-O(83)	2.617(17)
Sm (4)-O(82)	2.395(12)	Cd(9)-O(18)	2.255(15)
Sm (4)-N(10)	2.472(19)	Cd(9)-N(9)	2.262(19)
Sm (4)-O(21)	2.480(15)	Cd(9)-O(85)	2.265(15)
Cd(1)-O(54)	2.272(14)	Cd(9)-O(20)	2.289(15)
Cd(1)-O(4)	2.283(13)	Cd(9)-O(82)	2.304(12)
Cd(1)-O(52)	2.291(14)	Cd(9)-O(19)	2.522(15)
Cd(1)-O(57)	2.332(14)	Cd(9)-O(81)	2.589(14)
Cd(1)-O(56)	2.347(18)	Cd(10)-O(90)	2.238(14)
Cd(1)-N(2)	2.36(2)	Cd(10)-O(88)	2.303(14)
Cd(2)-O(55)	2.269(19)	Cd(10)-O(93)	2.316(15)
Cd(2)-O(6)	2.311(12)	Cd(10)-O(22)	2.346(12)
Cd(2)-O(61)	2.362(15)	Cd(10)-N(11)	2.390(19)
Cd(2)-O(60)	2.39(2)	Cd(10)-O(91)	2.406(15)
Cd(2)-O(59)	2.43(2)	Cd(11)-O(96)	2.236(14)
Cd(2)-O(56)	2.481(19)	Cd(11)-O(24)	2.252(13)
Cd(2)-O(5)	2.587(19)	Cd(11)-O(49)	2.305(12)
Cd(3)-O(6)	2.177(14)	Cd(11)-O(92)	2.320(16)
Cd(3)-O(8)	2.242(13)	Cd(11)-O(23)	2.466(16)
Cd(3)-O(61)	2.256(15)	Cd(11)-O(91)	2.514(15)
Cd(3)-O(58)	2.301(12)	Cd(11)-O(95)	2.629(18)
Cd(3)-N(3)	2.316(17)	Cd(12)-N(12)	1.92(2)
Cd(3)-O(7)	2.552(17)	Cd(12)-O(2)	2.126(17)
Cd(3)-O(57)	2.635(15)	Cd(12)-O(24)	2.259(14)
Cd(4)-O(64)	2.216(13)	Cd(12)-O(49)	2.282(12)
Cd(4)-O(66)	2.259(13)	Cd(12)-O(94)	2.359(2)
Cd(4)-N(5)	2.323(18)	Cd(12)-O(1)	2.510(16)
Cd(4)-O(10)	2.340(13)		

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

Nd(1)-O(17)	2.307(9)	Nd(4)-O(31)	2.355(7)
Nd(1)-O(2)	2.342(8)	Nd(4)-O(25)	2.373(8)
Nd(1)-O(19)	2.397(8)	Nd(4)-O(40)	2.489(8)
Nd(1)-O(16)	2.406(8)	Nd(4)-O(24)	2.511(8)
Nd(1)-O(13)	2.437(8)	Nd(4)-O(19)	2.531(8)
Nd(1)-O(21)	2.441(8)	Nd(4)-O(22)	2.537(8)
Nd(1)-O(37)	2.459(9)	Nd(4)-O(21)	2.613(8)
Nd(1)-O(14)	2.553(9)	Nd(4)-O(23)	2.641(8)
Nd(1)-O(1)	2.600(9)	Nd(4)-O(20)	2.713(8)
Nd(2)-O(26)	2.315(9)	Ni(1)-O(11)#1	2.009(9)
Nd(2)-O(6)	2.337(8)	Ni(1)-O(15)	2.037(9)
Nd(2)-O(20)	2.358(8)	Ni(1)-N(6)#1	2.077(10)
Nd(2)-O(24)	2.397(7)	Ni(1)-N(1)	2.077(10)
Nd(2)-O(28)	2.403(7)	Ni(1)-O(2)	2.088(8)
Nd(2)-O(29)	2.464(8)	Ni(1)-O(13)	2.134(8)
Nd(2)-O(38)	2.475(8)	Ni(2)-O(3)	2.007(8)
Nd(2)-O(5)	2.558(8)	Ni(2)-O(30)	2.026(8)
Nd(2)-O(27)	2.592(8)	Ni(2)-N(2)	2.044(10)
Nd(3)-O(32)	2.308(8)	Ni(2)-N(3)	2.079(11)
Nd(3)-O(33)	2.353(8)	Ni(2)-O(6)	2.081(7)
Nd(3)-O(36)	2.380(9)	Ni(2)-O(28)	2.191(9)
Nd(3)-O(10)	2.380(8)	Ni(3)-O(10)	2.012(10)
Nd(3)-O(23)	2.405(8)	Ni(3)-O(7)	2.019(9)
Nd(3)-O(22)	2.506(8)	Ni(3)-N(4)	2.027(12)
Nd(3)-O(9)	2.520(9)	Ni(3)-N(5)	2.069(11)
Nd(3)-O(39)	2.531(7)	Ni(3)-O(34)	2.073(7)
Nd(3)-O(35)	2.613(9)	Ni(3)-O(36)	2.194(8)
Nd(4)-O(18)	2.345(9)		

Table S6. Selected Bond Lengths (Å) for **5**.

Yb(1)-O(17)	2.319(9)	Yb(4)-O(31)	2.353(9)
Yb(1)-O(2)	2.354(8)	Yb(4)-O(25)	2.384(9)
Yb(1)-O(16)	2.400(10)	Yb(4)-O(40)	2.478(8)
Yb(1)-O(19)	2.408(8)	Yb(4)-O(24)	2.513(8)
Yb(1)-O(21)	2.425(8)	Yb(4)-O(19)	2.525(8)
Yb(1)-O(13)	2.435(8)	Yb(4)-O(22)	2.534(8)
Yb(1)-O(37)	2.450(9)	Yb(4)-O(21)	2.589(9)
Yb(1)-O(14)	2.550(10)	Yb(4)-O(23)	2.640(9)
Yb(1)-O(1)	2.623(9)	Yb(4)-O(20)	2.709(8)
Yb(2)-O(26)	2.311(9)	Ni(1)-O(11)#1	2.019(10)
Yb(2)-O(6)	2.333(9)	Ni(1)-O(15)	2.049(9)
Yb(2)-O(20)	2.359(8)	Ni(1)-N(6)#1	2.068(12)
Yb(2)-O(28)	2.404(9)	Ni(1)-O(2)	2.088(8)
Yb(2)-O(24)	2.408(8)	Ni(1)-N(1)	2.092(11)
Yb(2)-O(29)	2.450(9)	Ni(1)-O(13)	2.155(9)
Yb(2)-O(38)	2.478(8)	Ni(2)-O(3)	2.036(8)
Yb(2)-O(5)	2.551(9)	Ni(2)-O(30)	2.041(9)
Yb(2)-O(27)	2.582(9)	Ni(2)-N(2)	2.055(11)
Yb(3)-O(32)	2.299(9)	Ni(2)-N(3)	2.071(12)
Yb(3)-O(10)	2.349(8)	Ni(2)-O(6)	2.092(8)
Yb(3)-O(33)	2.378(9)	Ni(2)-O(28)	2.197(10)
Yb(3)-O(23)	2.389(8)	Ni(3)-O(7)	2.008(9)
Yb(3)-O(36)	2.394(10)	Ni(3)-N(4)	2.022(12)
Yb(3)-O(22)	2.502(9)	Ni(3)-O(10)	2.049(10)
Yb(3)-O(39)	2.530(8)	Ni(3)-O(34)	2.068(9)
Yb(3)-O(9)	2.538(9)	Ni(3)-N(5)	2.084(11)
Yb(3)-O(35)	2.630(9)	Ni(3)-O(36)	2.211(9)
Yb(4)-O(18)	2.347(9)		

END