"Lanthanide coordination polymers with pyridyl-*N*-oxide or carboxylate functionalised host ligands"

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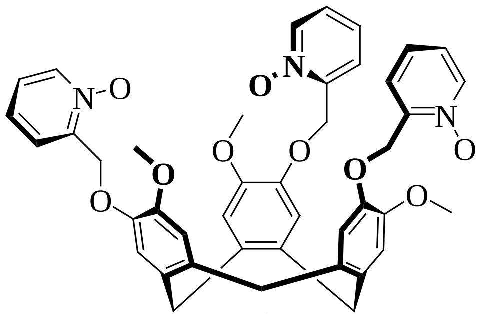
Supplementary Information

Synthesis:

Chemicals were obtained from commercial sources and used without further purification. Ligands *tris*(2-pyridylmethyl-*N*-oxide)cyclotriguaiacylene **L1**, *tris*(4-pyridylcarboxy-*N*-oxide)cyclotriguaiacylene **L2** and *tris*(4-carboxybenzyl)cyclotriguaiacylene **L3**, were synthesised according to literature methods from cyclotriguaiacylene (CTG).[1-3] Infra-red spectra were recorded as solid phase samples on a Perkin-Elmer FT-IR Spectrometer and microanalyses were performed by the University of Leeds microanalytical service using a Carlo Erba Elemental Analyser MOD 1106 spectrometer after drying samples at 80 ˚C under vacuum. Thermogravimetric analyses were performed on a TA instruments SDT Q600 machine.



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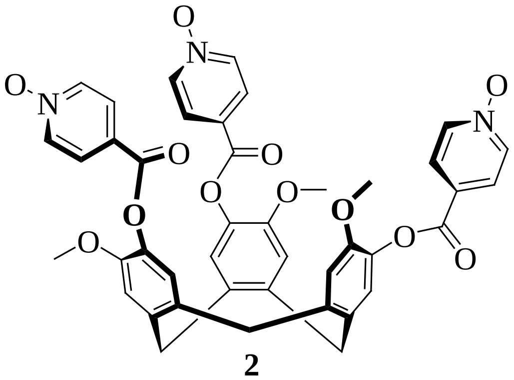

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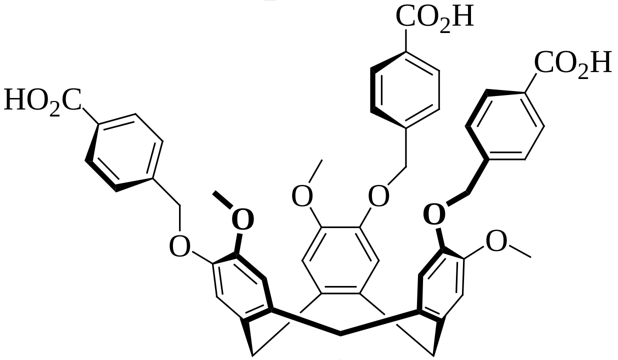

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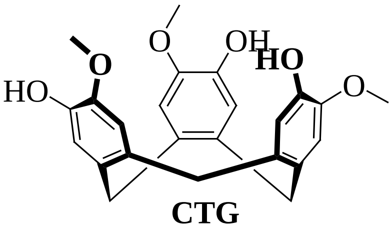


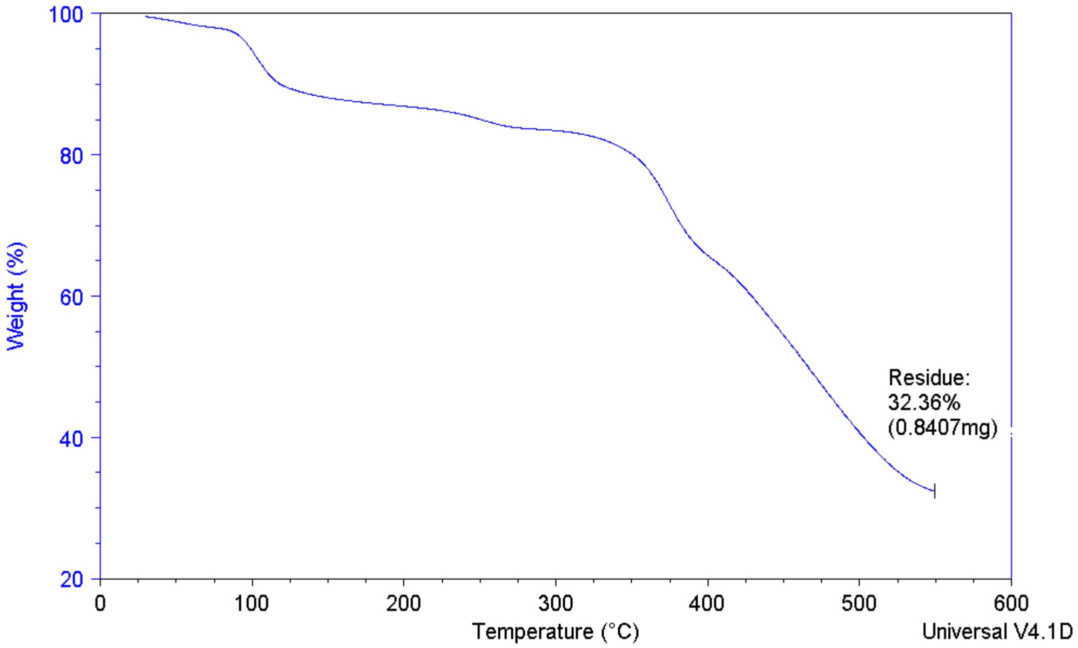
CTG

Preparation of {[Gd(L1)(NO_3)$_3$].DMF}$_\infty$: Complex 1. Gd(NO_3)$_3$·6(H_2O) (10.15 mg, 0.0225 mmol) and **L1** (5.11 mg, 0.0075 mmol) were dissolved in DMF (~ 1 mL) and diethyl-ether vapours were diffused into the solution. Small off-white needles formed after 14 days, and were analyzed via single crystal X-ray analysis. Yield 9.8 mg. Analysis for {[Gd(**L1**)(NO_3)$_3$].DMF.H_2O}$_\infty$ $C_{45}H_{48}GdN_7O_{20}$ (%

calculated, found) C (46.13, 46.15), H (4.16, 3.90), N (8.42, 8.15). Infrared analysis (FT-IR, cm^{-1}) 3458 (broad), 3140, 2985, 2328, 1672, 1609, 1518, 1454, 1384, 1295, 1266, 1212, 1142, 1090, 1058, 1029, 1011, 950, 858, 816, 766, 741, 698, 600, 569, 550.

Preparation of $\{[Sm(L2)Cl(DMF)_3]\cdot[SmCl_5(DMF)]\cdot 1.5(DMF)\}_\infty$: Complex 2. $SmCl_3\cdot 6(H_2O)$ (11.41 mg, 0.0225 mmol) and **2** (5.09 mg, 0.0075 mmol) were dissolved in DMF (~ 1 mL) and diethyl-ether vapours were diffused into the solution. Yellow needles formed after 21 days, and were analyzed via single crystal X-ray analysis. Yield 5.9 mg. Analysis for $\{[Sm(\mathbf{L2})Cl(DMF)_3]\cdot[SmCl_5(DMF)]\cdot 3(H_2O)\}_\infty$ $C_{57}H_{74}Cl_6N_{8.5}O_{20}Sm_2$: (% calculated, found) C (39.53, 39.75), H (4.01, 4.35), N (5.71, 5.35). Infrared analysis (FT-IR, cm^{-1}) 3119, 2938, 1745, 1628, 1505, 1484, 1443, 1404, 1252, 1163, 1139, 1052, 927, 861, 830, 746, 679, 630, 581, 497, 484, 470.

Preparation of $\{[Eu(L3)(DMF)(H_2O)]\cdot(DMF)_{1.5}(H_2O)\}_\infty$: Complex 3. $Eu_2(oxalate)_3\cdot xH_2O$ (30 mg, 0.053 mmol) and **L3** (15 mg, 0.019 mmol) were suspended in a mixture of H_2O (2 mL, acidified with 1 drop of HCl) and DMF (2 mL) in a sealed Parr vessel and heated to 150 °C at a rate of 1 °C *per* minute, held at 150 °C for 48 hours and then slowly cooled to room temperature at a rate of 0.1 °C *per* minute. The colourless crystals of $\{[Eu(\mathbf{L3})(DMF)(H_2O)]\cdot 1.5(DMF)(H_2O)\}_\infty$ were collected by filtration and washed with diethyl ether. Yield 12 mg. Microanalysis indicates that the bulk sample contains additional lanthanide salts. Infrared analysis (FT-IR, cm^{-1}) 1631 (m), 1608 (m), 1573 (s), 1503 (w), 1436 (w), 1406 (s), 1360 (s), 1275 (w), 1258 (w), 1214 (w), 1177 (w), 1142 (w), 1112 (w), 1083 (w), 1033 (w), 1016 (w), 990 (m), 853 (m), 780 (s), 717 (w), 679 (w), 650 (w), 615 (w).



S1. TGA of $\{[Eu(\mathbf{L3})(DMF)(H_2O)]\cdot 1.5(DMF)(H_2O)\}_\infty$.

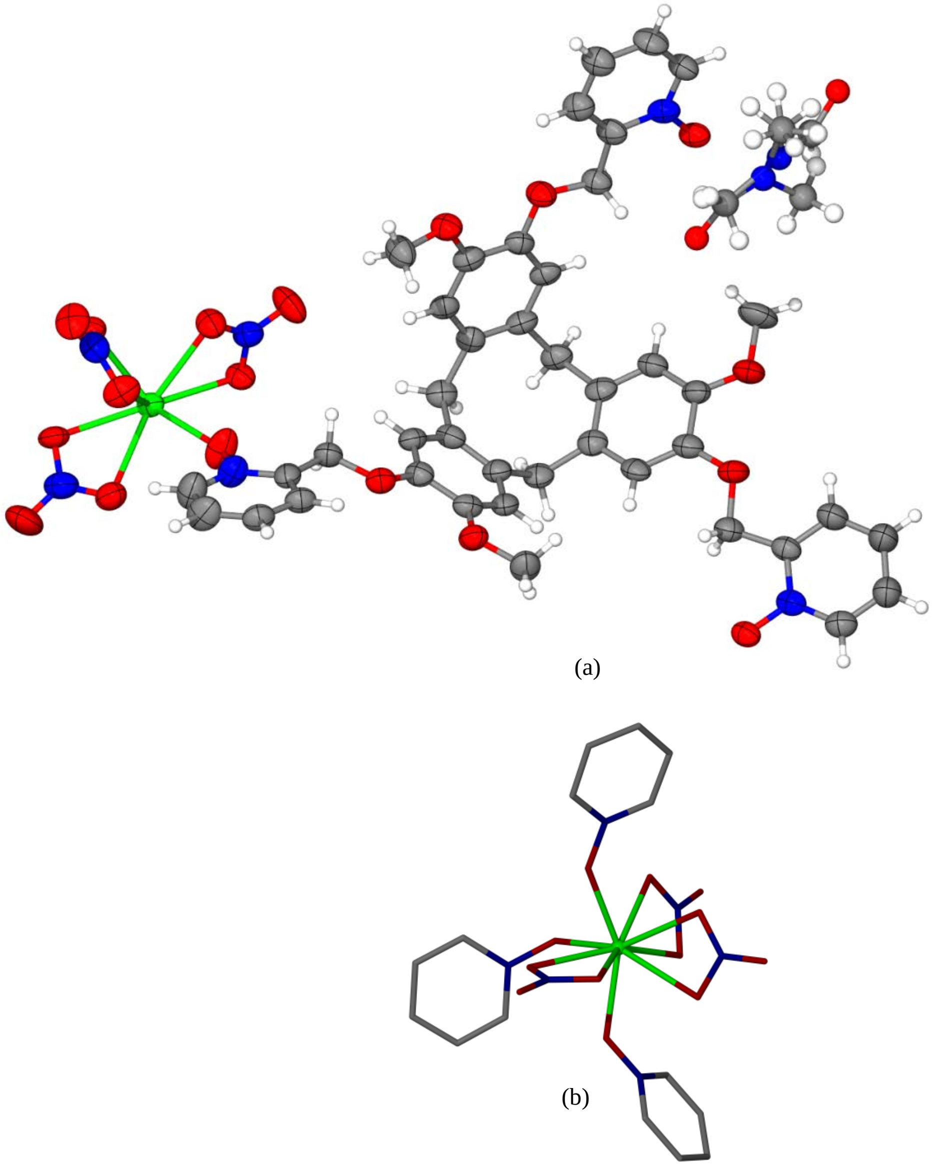
Crystal structure analysis:

Crystals were mounted on a glass or MiTeGen fibre tip under oil and flash frozen to 150(1) K using a stream of cold N_2. Data were collected on a Bruker-Nonius X8 diffractometer with an Mo-rotating anode (λ = 0.71073 Å). Data were corrected for Lorenztian and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix on F^2 using SHELXL-97, interfaced through the X-seed interface.[4,5] Unless otherwise specified, all non-hydrogen atoms were refined as anisotropic, and hydrogen positions were included at geometrically estimated positions. Molecular graphics were obtained using POV-RAY through the X-Seed interface. Additional details are given below and data collections and refinements summarised in Table S1.

Complex 1: The solvent DMF molecule was refined isotropically and modelled as disordered across two positions, each at 50% occupancy. C-O bond lengths of the disordered DMF were restrained to be chemically reasonable.

Complex 2: Two methyl groups of ligand **L2** were refined as being disordered across two positions, one with OMe in two positions each at 50% occupancy, and the other with the CH_3 group across two positions at 75:25 occupancy. The coordinated DMF of the [$SmCl_5$(DMF)] was refined as disordered across two positions each at 50% occupancy. Two uncoordinated solvent DMF molecules were refined isotropically and one shows a symmetry-related disorder and was refined at 50% occupancy. Some bond lengths of this DMF were restrained to be chemically reasonable.

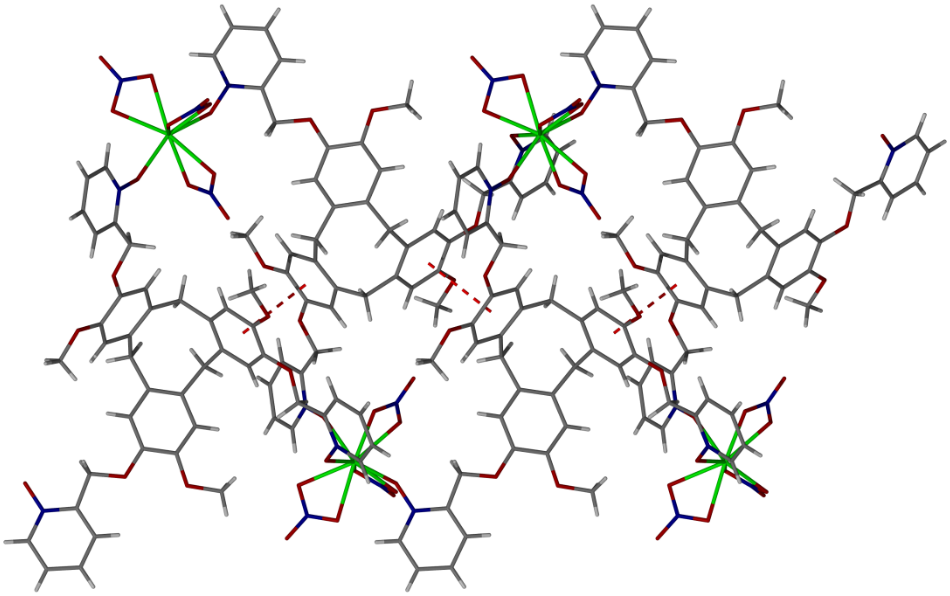
Complex 3: DMF ligand and DMF and water solvent were refined isotropically and the DMF ligand was refined with group displacement parameters for C/N atoms and a C-N bond was restrained to be chemically reasonable. A disordered water molecule was refined across two positions each at 50% occupancy.



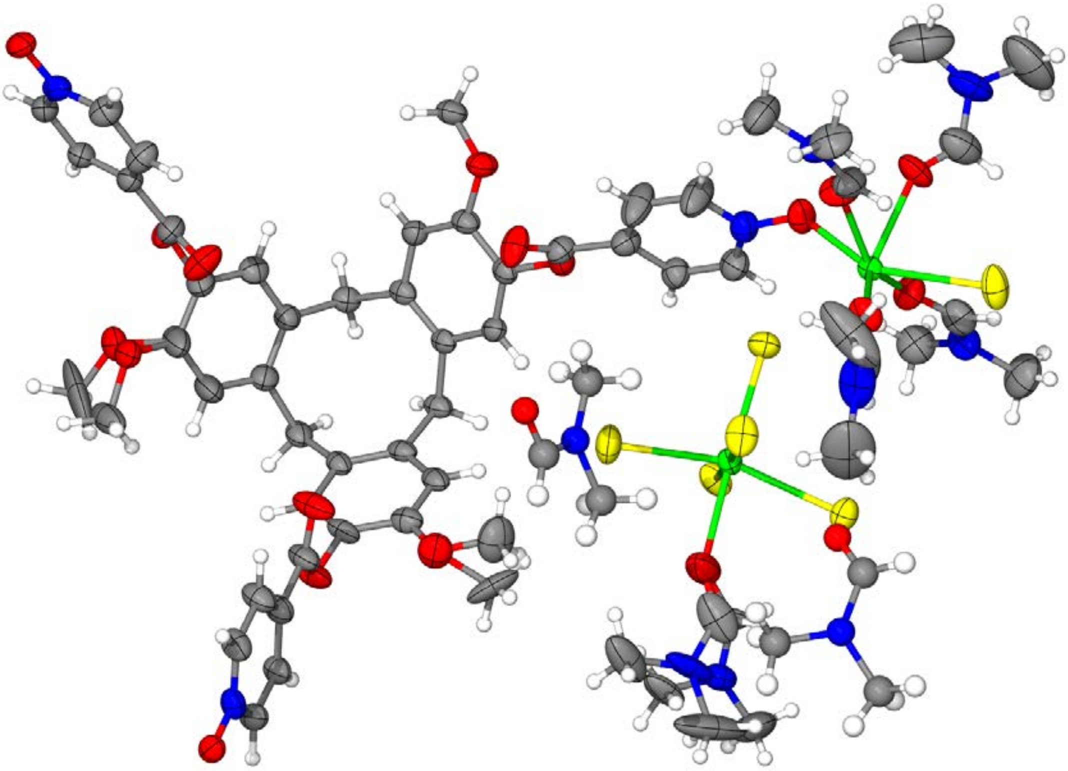
(a)

(b)

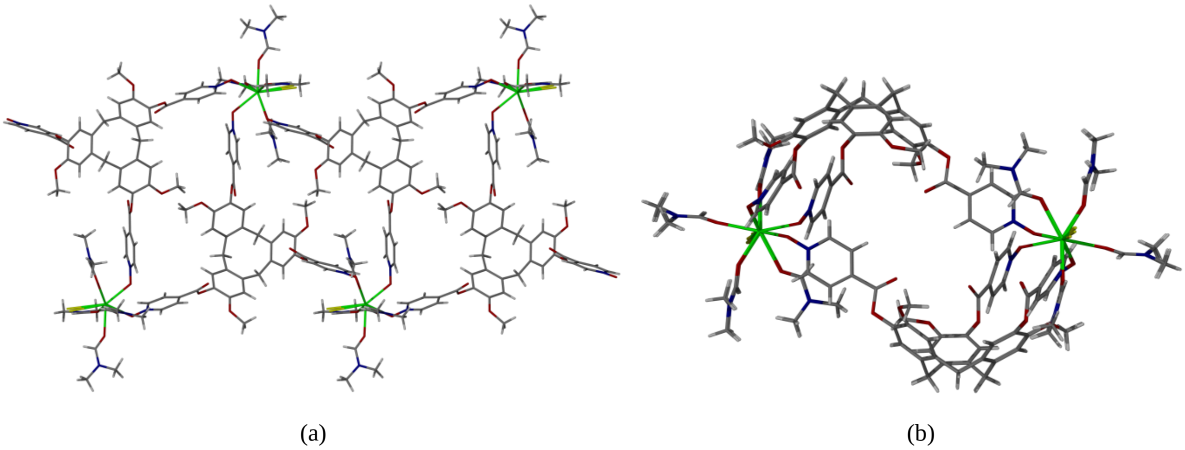
S1. (a) Asymmetric unit for complex **1**. Thermal ellipsoid parameters set at 50 % probability. Solvent DMF refined isotropically. (b) Highlighting the approximately octahedral geometry around each Gd(III) centre and *meridional* arrangement of ligands and anions. Atoms are colour-coded as follows: Green (gadolinium), grey (carbon), blue (nitrogen), red (oxygen) and white (hydrogen).



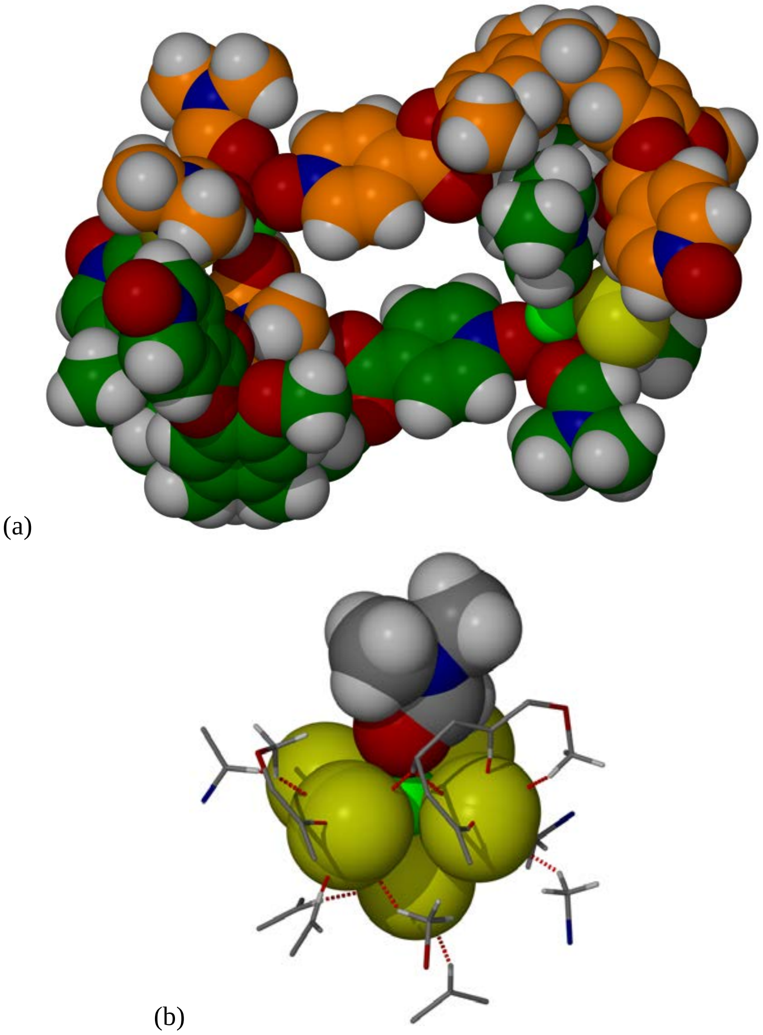
S2. Part of the packing diagram in complex **1**, displaying the π-π interactions (red, hashed lines) between ligands within each homochiral 1-D chain. Solvent DMF omitted for clarity.



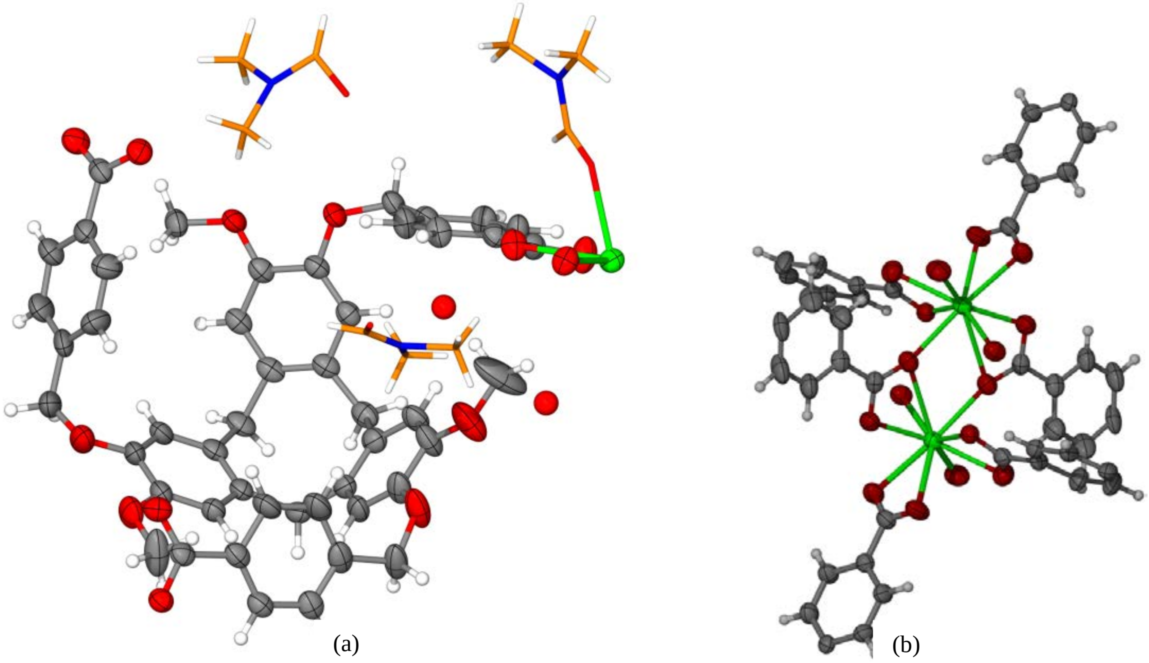
S3. Asymmetric unit for complex **2**, depicting the approximate C_3-symmetry of the ligand, and disorder models. Thermal ellipsoid parameters set at 50 % probability with isotropically refined DMFs set as arbitrary spheres. Light green = Sm; yellow = chloride.



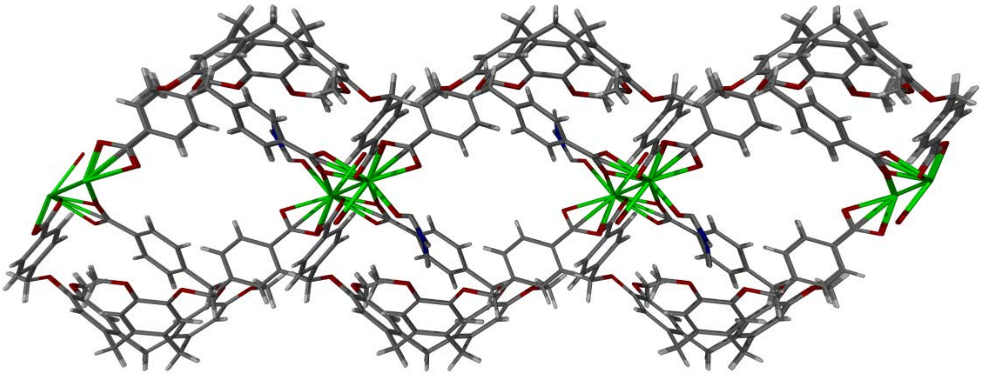
S4. 1-D ladder formation in complex **2**, with solvent DMF and anionic $[SmCl_5(DMF)]^{2-}$ lattice guest omitted. (a) Head-to-head arrangement of ligands in the 1-D ladder, as viewed down the crystallographic *a*-*c* plane. (b) The resultant quasi-cylindrical shape when viewed down the crystallographic *c*-axis.



S5. (a) Space-filling view highlighting the intermolecular host-guest interactions within complex **2**. Ligands are colour-coded based on the individual 1-D chain to which they belong. Solvent DMF and anionic $[SmCl_5(DMF)]^{2-}$ lattice guest are omitted for clarity; (b) anionic $[SmCl_5(DMF)]^{2-}$ lattice guest within the relatively well-defined, electropositive pocket. The anionic $[SmCl_5(DMF)]^{2-}$ guest is displayed using a space-filling model. Close contacts (Cl-H, within 3 Å) are shown *via* the hashed, red lines.



S6. (a) Asymmetric unit for Complex **3**, depicting the approximate C_3-symmetry of the ligand and intracavity DMF guest, shown in orange. Thermal ellipsoid parameters set at 50 % probability with isotropically refined atoms set to arbitrary spheres or sticks. (b) Displaying the two carboxylate binding modes within the Eu_2 dimer that affords the two-tiered 2-D sheets. Each Eu(III) centre is 9-coordinate and the crystallographic centre of inversion lies between the two Eu(III) cations.



S7. The free space observed when looking though the 2-D sheet and viewed down the crystallographic *a* axis. Solvent DMF excluded for clarity.

Table S1: Details of data collection and structure refinements

	$[Gd(L1)(NO_3)_3]$. DMF	**$[Sm(L2)Cl(DMF)_3]$ ·$[SmCl_5(DMF)]$· 1.5(DMF)**	**[Eu(L3)(DMF) $(H_2O)]$·1.5(DMF) (H_2O)**
Formula	$C_{45}H_{45}GdN_7O_{19}$	$C_{61.5}H_{78.5}Cl_6N_{9.5}O_{18.5}Sm_2$	$C_{55.5}H_{60.5}EuN_{2.5}O_{16.5}$
Mr	1146.14	1760.24	1178.52
Crystal colour and shape	yellow, needle	Yellow, block	yellow, block
Crystal size (mm)	0.10 x 0.08 x 0.01	0.24 x 0.18 x 0.14	0.60 x 0.44 x 0.14
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*P*-1	*P*-1
a (Å)	44.860(4)	12.7326(12)	14.2284(10)
b (Å)	15.1635(14)	16.1047(13)	14.7501(11)
c (Å)	15.6748(14)	19.7002(17)	16.4083(12)
α (^{0})	90	103.648(2)	76.082(4)
β (^{0})	97.550(4)	94.159(3)	70.013(3)
γ (^{0})	90	94.159(3)	61.718(3)
V (Å^3)	10570.2(17)	3911.0(6)	2837.0(4)
Z	8	2	2
ρ_{calc} (g.cm^{-3})	1.440	1.495	1.380
θ range (^{0})	1.42 – 26.73	1.06– 27.28	1.33 – 25.00
No. data collected	34505	61774	73244
No. unique data	10958	17431	9928
R_{int}	0.0958	0.0517	0.0489
No. obs. Data ($I > 2\sigma(I)$)	6048	12627	9299
No. parameters	633	933	632
No. restraints	2	4	1
R_1 (obs data)	0.0698	0.0504	0.0701
wR_2 (all data)	0.2194	0.1494	0.1947
S	1.006	1.038	1.168
Residual $e_{min,max}$	-1.536, 2.280	-1.559, 2.920	-1.936, 1.976

(1) Canceill, J.; Gabard, J.; Collet, A. *J. Am. Chem. Soc* **1983**, 122.
(2) Zhan, H.-Q.; Jiang, X.-K.; Li, Z.-T. *Chinese Journal of Chemistry* **2001**, *19*, 147.
(3) Henkelis, J. J.; Barnett, S. A.; Harding, L. P.; Hardie, M. J. *Inorg Chem* **2012**.
(4) Sheldrick, G. *Acta Crystallographica Section A* **2008**, *64*, 112.
(5) Barbour, L. J. *Supramol. Chem.* **2001**, *1*, 189.