SUPPLEMENTARY MATERIAL

The decoration of each of the double layered 6-connected networks is unimportant in the determination of topology but can be seen as completing the co-ordination sphere in **2**, expanding the structure to accommodate anions in **3** or accommodating extra ligands in **4**. In **2** the triflate anions occupy the free space between the 4^4 nets of a single bilayer. In **3** the iodide ions occupy space both within a bilayer and between adjacent bilayers. The large volume within the framework of **4** accommodates not only ClO_4^- anions but also one molecule of chlorobenzene and one CH_3OH molecule per metal centre.

Crystallographic Data

Crystal data for **1**: $C_{20}H_{16}LaN_7O_{13}$, M = 701.31, monoclinic, space group $C2/c$, a=27.008(8) Å, b=13.389(4) Å, c=13.982(3) Å, β =106.29(2)º, U=4853(2) Å^3, Z=8, D_c=1.920 Mg/m^3, μ(Mo-Kα)=1.846 mm^{-1}, T = 298(2) K. 4771 unique reflections (R_{int} = 0.026). Final R_1 [4122 $I > 2\sigma(I)$] = 0.0292, $wR2$ (all data) = 0.0634.

Crystal data for **2**: $C_{33}H_{24}F_9N_6O_{17}S_3Yb$, M=1216.8, orthorhombic, space group *Pcca* (No. 54), a=16.794(3) Å, b=13.764(3) Å, c=20.044(4) Å, U=4633.4(14) Å^3, Z=4, D_c=1.744 Mg/m^3, μ(Mo-Kα)=2.264 mm^{-1}, T = 150(2) K. 5345 unique reflections (R_{int} = 0.074). Final R_1 [3592 $I > 2\sigma(I)$] = 0.0965, $wR2$ (all data) = 0.249.

Crystal data for **3**: $C_{56}H_{44}ErI_9N_{11}O_{13}$, M=2388.4, orthorhombic, space group *Pbcn*, a=43.203(8) Å, b=19.244(4) Å, c=17.167(3) Å, U=14274(8) Å^3, Z=8, D_c = 2.223 Mg/m^3, μ(Mo-Kα) = 5.13 mm^{-1}, T = 150(2) K. 15426 unique reflections (R_{int} = 0.046). Final R_1 [14261 $I > 2\sigma(I)$] = 0.079, $wR2$ (all data) = 0.169.

Crystal data for **4**: $C_{47}H_{41}Cl_4LaN_8O_{21}$, M = 1334.59, monoclinic, space group $P2_1/n$, a = 16.6846(8) Å, b = 19.8749(9) Å, c = 32.669(2) Å, β = 100.664(2)º, U = 10646(2) Å^3, Z = 8, D_c = 1.665 Mg/m^3, μ(Mo-Kα) = 1.091 mm^{-1}, T = 150(2) K. 20663 unique reflections (R_{int} = 0.118). Final R_1 [13088 $I > 2\sigma(I)$] = 0.059, $wR2$ (all data) = 0.195.

Crystal data for **5**: $C_{86.7}H_{91.8}B_2LaN_5O_{11.7}$ M = 1551.58, monoclinic, space group $C2/c$, a = 49.269(7) Å, b = 17.698(3) Å, c = 18.718(3) Å, β = 105.946(3)º U = 15693(3) Å^3, Z = 8 D_c = 1.313 Mg/m^3, μ(Mo-Kα) = 0.609 mm $^{-1}$, T = 150(2) K, 15221 unique reflections (R_{int} = 0.045). Final R_1 [9822 $I > 2\sigma(I)$] = 0.068, $wR2$ (all data) = 0.208.

Synthesis of 1 - 5

Preparation of $\{La(L)_2(NO_3)_3\}_\infty$ **1**:

A solution of L (22 mg, 0.10 mmol) in MeOH (6cm^3) was carefully mixed with a solution of $La(NO_3)_3$•$6H_2O$ (22 mg, 0.05mmol) in MeOH (6 cm^3). The reaction yielded a pale yellow crystalline product after several hours. Elemental analysis calcd (%) for $C_{20}H_{16}LaN_7O_{13}$: C 34.25, H 2.30, N 13.98; found 34.09, H 2.17, N 13.74.

Preparation of $\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$ **2**:

$Yb(CF_3SO_3)_3.xH_2O$ (31.8mg, 0.05mmol) was covered with $CHCl_3$ (5 cm^3) on top of which a solution of L (10mg, 0.05mmol) in MeOH (10 cm^3) was layered. Colourless square plate shaped crystals appeared over a period of 1 week. Elemental analysis calcd (%) for $C_{33}H_{24}F_9N_6O_{17}S_3Yb$: C 36.07, H 2.20, N 21.67; found C 35.16, H 2.52, N 20.41.

Preparation of $\{[Er(L)_5](I_3)_3(L)_{0.5}(MeOH)\}_\infty$, **3**:

$ErCl_3$ (6mg, 0.013mmol), I_2 (16.5mg, 0.065mmol) and NaI (1.8mg, 0.012mmol) was dissolved in MeOH (10 cm^3), to which a solution of L (10mg, 0.05mmol) in MeOH (10 cm^3) was added. Dark red lath shaped crystals appeared over a period of 48h. Elemental analysis calcd (%) for $C_{56}H_{43}ErI_9N_{11}O_{13}$: C 28.16, H 1.86, N 6.45; found C 27.76; H 1.96; N 6.06.

Preparation of $[La(L)_4](ClO_4)_3{\cdot}C_6H_5Cl{\cdot}CH_3OH$, **4**:

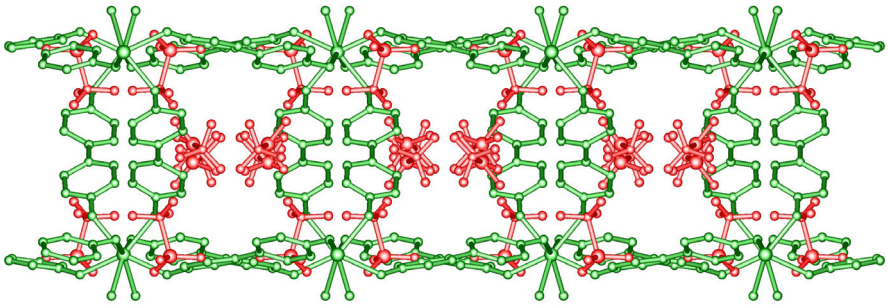
$La(ClO_4)_3{\cdot}xH_2O$ (45 mg, 0.1 mmol) was covered with chlorobenzene (10 cm^3), on which a solution of L (59 mg, 0.3 mmol) in MeOH (10 cm^3) was layered. Colourless crystals appeared at on the wall of the

vessel over a period of a week. Elemental analysis calcd (%) for $C_{47}H_{41}Cl_4LaN_8O_{21}$: C 42.30, H 3.10, N 8.40; found C 42.23, H 3.15, N 8.75.

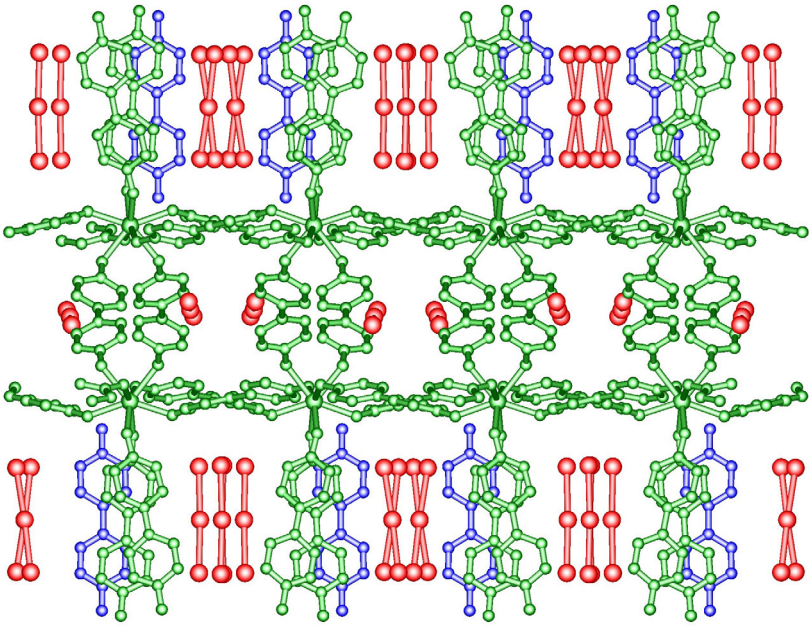
Preparation of $[La(L)_{2.5}(CH_3OH)_2(C_7H_{11}CH_2CO_2)](BPh_4)_2 \cdot 2.7CH_3OH$ **5**:

Lanthanum chloride hydrate (18 mg, 0.05 mmol) in methanol (5 cm^3) was added to a solution of 2-norbornyl acetic acid (8 mg, 0.05 mmol) and NaOMe (3 mg, 0.05 mmol) in MeOH (5 cm^3). To this solution was then added firstly a solution of sodium tetraphenylborate (51 mg, 0.15 mmol) in MeOH (5 cm^3) and secondly a solution of L (33 mg, 0.15 mmol) in MeOH (5 cm^3). The resultant white emulsion-like precipitate slowly transformed to a light yellow crystalline product in *ca*. 3 days. Yield: 47 mg (59%); anal. calcd for $C_{86.7}H_{91.8}B_2LaN_5O_{11.7}$: C 67.11, H 5.96, N 4.51; Found: C 65.80, H 5.60, N 4.52. Elemental and powder diffraction analysis indicates possible impurities of other yet unidentified products.

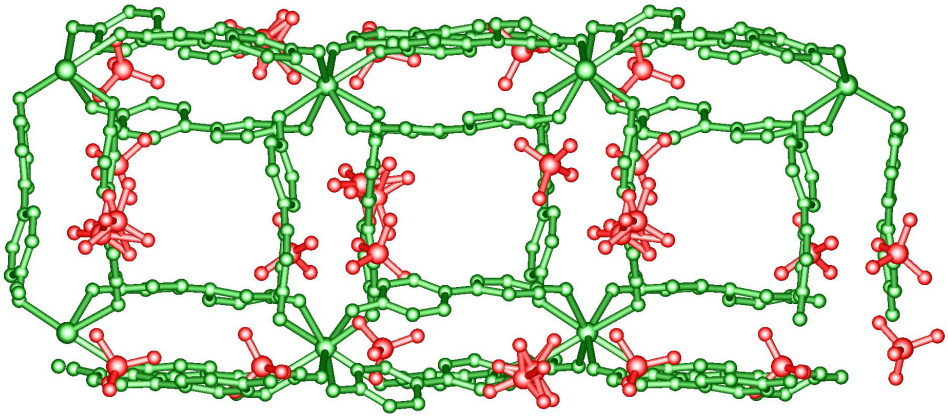
Supplementary Figures



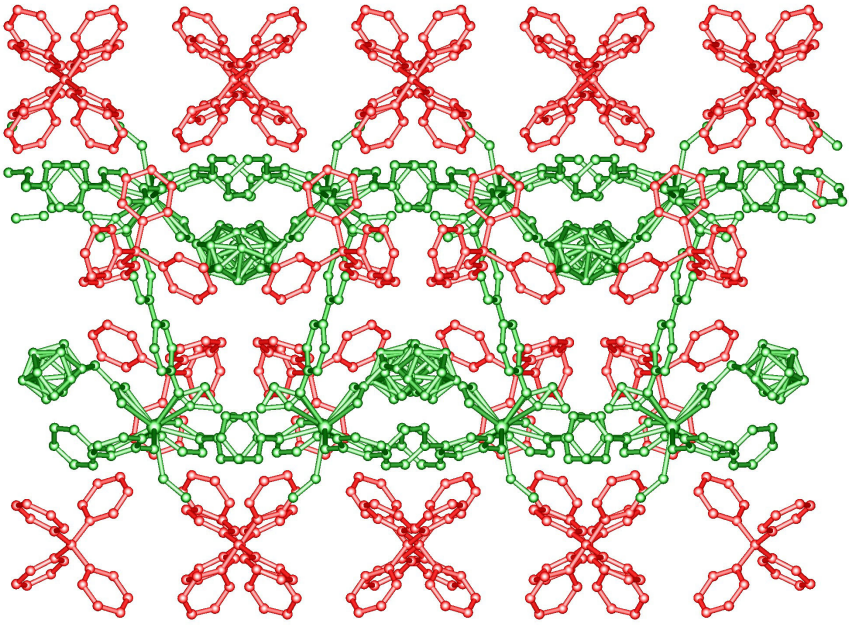
Supplementary Figure 1: Full structure of **2** showing the positions of the triflate anions (red) within the bi-layer structure (green).



Supplementary Figure 2: Full structure of **3** showing the positions of the iodide anions (red), the bi-layer structure (green) and the non-co-ordinating ligands (blue).



Supplementary Figure 3: View of the full structure of **4** positions of the perchlorate anions (red) within the bilayer structure (green).



Supplementary Figure 4: Full structure of **5** showing the position of the tetraphenylborate anions (red) and the bi-layer structure (green).

Supplementary Material (ESI) for Chemical Communications