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)°, 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 > 2σ(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 > 2σ(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 > 2σ(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)°, 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 > 2σ(I)] = 0.059, wR2 (all data) = 0.195.
Crystal data for 5: C_{86.7}H_{91.8}B_{2}La_{N}O_{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)° U = 15693(3) Å^3, Z = 8 D_x = 1.313 Mg/m^3, μ(Mo-Kα) = 0.609 mm^{-1}, T = 150(2) K, 15221 unique reflections (R(int) = 0.045). Final R₁ [9822 I > 2σ(I)] = 0.068, wR2 (all data) = 0.208.

Synthesis of 1 - 5

Preparation of {La(L)_{2}(NO_{3})_{3}}_{∞}, 1:
A solution of L (22 mg, 0.10 mmol) in MeOH (6 cm^3) was carefully mixed with a solution of La(NO_{3})_{3}•6H_{2}O (22 mg, 0.05 mmol) 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_{7}O_{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_{3}SO_{3})_{3}}_{∞}, 2:
Yb(CF_{3}SO_{3})_{3}•xH_{2}O (31.8 mg, 0.05 mmol) was covered with CHCl_{3} (5 cm^3) on top of which a solution of L (10 mg, 0.05 mmol) 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_{9}N_{6}O_{17}S_{3}Yb: 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)}_{∞}, 3:
ErCl_{3} (6 mg, 0.013 mmol), I_{2} (16.5 mg, 0.065 mmol) and NaI (1.8 mg, 0.012 mmol) was dissolved in MeOH (10 cm^3), to which a solution of L (10 mg, 0.05 mmol) in MeOH (10 cm^3) was added. Dark red lath shaped crystals appeared over a period of 48 h. Elemental analysis calcd (%) for C_{56}H_{43}Er_{3}I_{9}N_{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}•C_{6}H_{5}Cl•CH_{3}OH, 4:
La(ClO_{4})_{3}•xH_{2}O (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 the wall of the
vessel over a period of a week. Elemental analysis calcd (%) for C_{47}H_{41}Cl_{4}LaN_{8}O_{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_{3}OH)_{2}(C_{7}H_{11}CH_{2}CO_{2})](BPh_{4})_{2}·2.7CH_{3}OH 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_{2}LaN_{5}O_{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).