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Homochiral 3D lanthanide coordination networks with an unprecedented $4^9 6^6$ topology

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Homochiral 3D metal–organic open frameworks based on enantiopure atropisomeric dicarboxylic acid bridging ligands and dilanthanide secondary building units exhibit an unprecedented $4^9 6^6$ topology, and possess ethoxy-protected BINOL functionalities that are pointing toward the open channels.

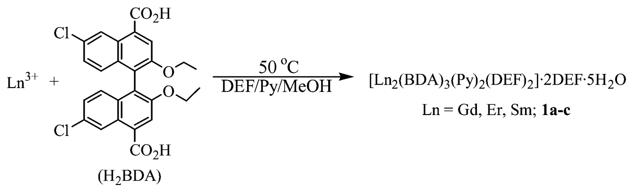
The field of metal–organic coordination networks (MOCNs) has witnessed tremendous success in the synthesis and structural characterization of numerous interesting metal–organic frameworks with novel topologies over the past decade.[1–5] The nature of metal–ligand coordination bonds not only allows the systematic variation of the structures and therefore potential fine-tuning of the functions of MOCNs, but also detailed structural interrogations using single-crystal X-ray crystallography owing to the general ease of crystal growth of MOCNs. The synthesis of homochiral, porous materials *via* the combination of metal–organic secondary building units (SBUs) and enantiopure bridging ligands represents a particularly interesting objective to us because such chiral porous MOCNs can be exploited for potential applications in heterogeneous asymmetric catalysis and enantioselective separations.[3c,6] Herein we wish to report the synthesis and characterization of 3D homochiral open frameworks based on dilanthanide carboxylates with an unprecedented six-connected $4^9 6^6$ topology.

Enantiopure 6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene-4,4′-dicarboxylic acid (H_2BDA), was prepared from readily available chiral 1,1′-bi-2-naphthol (BINOL).[7] Homochiral lanthanide carboxylates with the general formula of $[Ln_2(BDA)_3(DEF)_2(py)_2]\cdot 2DEF\cdot 5H_2O$ (Ln = Gd, Er, Sm, **1a-c**; DEF = *N*,*N*′-diethylformamide; py = pyridine) were prepared in 30–45% yields by treating hydrated lanthanide salts and H_2BDA in a mixture of DEF, MeOH and Py at 50 °C (Scheme 1).† **1a–c** are stable in air and insoluble in water and common organic solvents. The IR spectra of **1a–c** exhibit bands characteristic of carboxylate groups at 1650–1320 cm^{-1}. Thermogravimetric analyses (TGA) show that **1a–c** loses 11.7–11.9% of total weight between 20–180 °C, corresponding to the loss of two DEF and five water guest molecules (expected 11.7–12.0%). **1a–c** further loses 14.5–14.6% of total weight between 180–380 °C, corresponding to the loss of coordinated pyridine and DEF molecules (expected 14.5–14.7%). The formulations of **1a–c** are supported by microanalysis results.

A single-crystal X-ray diffraction study‡ performed on **1a** reveals a 3D network that crystallizes in the chiral space group $C222_1$. The asymmetric unit of **1a** consists of one gadolinium center, one and a half *trans*-BDA groups, and one pyridine and two DEF molecules. Two types of BDA ligands exist in **1a**: BDA^A contains one bridging carboxylate group and one chelating carboxylate group, whereas BDA^B contains two bridging carboxylate groups. The basic building unit for **1a** contains two crystallographically equivalent Gd centers that are quadruply bridged by four carboxylate groups of two BDA^A and two BDA^B dianions in a *syn–syn* fashion with a Gd···Gd separation of 3.710(1) Å (Fig. 1(a)). The binaphthyl subunits of BDA^A and BDA^B have dihedral angles of 71.7 and 93.6°, respectively. Each Gd center also coordinates to a chelating carboxylate group of a BDA^A anion, a DEF molecule, and a pyridine molecule to afford a distorted square antiprism geometry.

Each digadolinum core in **1a** is linked by four BDA^A and two BDA^B ligands to six adjacent digadolinum cores to form two independent hexagonal 6^3 grids in the *ab* and *ac* planes, respectively, and result in a unique 3D neutral framework with a 1D channel running parallel the *a*-axis, as shown in Fig. 1(b). The structure can be classified as a $4^9 6^6$ topological type built upon six-connected nodes as defined by Wells,[8] as shown in Fig. 2(a). To our knowledge, the structure of **1a** represents the first coordination framework exhibiting a $4^9 6^6$ topology. Both the ethoxy-protected BINOL functionalities and the chlorine atoms are pointing towards the channel, leading to an asymmetric 1D channel with a cross-section of ~3.1 × 6.2 Å that is occupied by two DEF and five water guest molecules (Fig. 2(b)).

3D inorganic solids with six connectivity are rather common with the familiar example of the NaCl lattice exhibiting a $4^{12}6^3$



Scheme 1 Synthesis of **1a–c**.

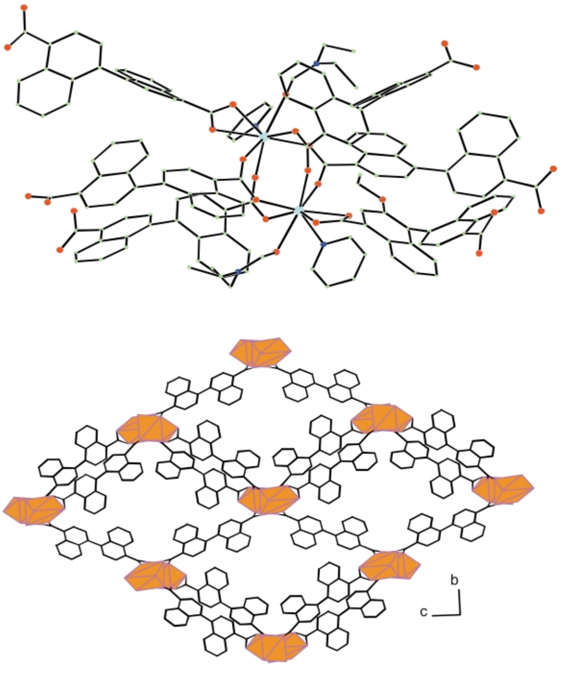


Fig. 1 (Top) The digadolinium building unit of **1a**. The DEF and water guest molecules are omitted. (Bottom) Polyhedral presentation of the 3D network of **1a** along the *a* axis.

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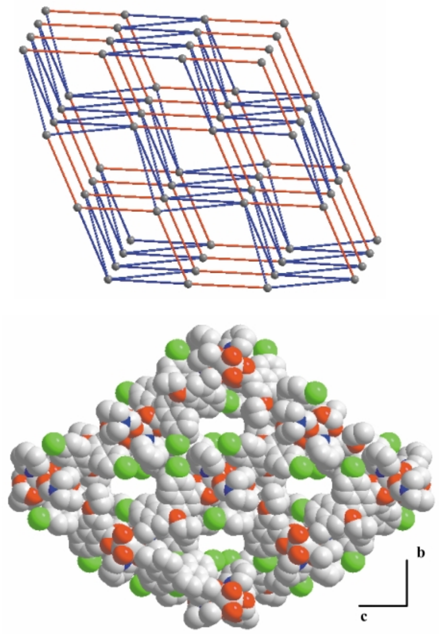

Fig. 2 (a) Schematic illustrating the $4^9 6^6$ topology of 3D network of **1a**. The digadolinium SBUs are shown as grey balls, and the blue and red lines represent BDA^A and BDA^B bridging ligands, respectively. (b) A space-filling model of **1a** as viewed down the *a* axis. The DEF and water guest molecules are omitted for clarity.

topology,[8] but examples of six-connected coordination networks are still rare due to steric bulk of most commonly used organic ligands. The use of metal clusters as the building block can more readily accommodate the steric demands of organic linkers, and thus provides an interesting pathway for the generation of MOCNs with six or higher connectivity. Indeed, several six-connected $4^{12}6^3$ MOCNs have been reported recently, but there are no precedents of six-connected MOCNs of $4^9 6^6$ topology.[9]

Single-crystal and powder X-ray diffraction studies have established (*S*)-**1b** is isostructural to (*S*)-**1a**, while cell parameter determinations and XRPD indicate that (*S*)-**1c** is also isostructural to (*S*)-**1a**.§ We have also prepared (*R*)-**1a** using (*R*)-H_2DBA. Solid-state circular dichroism spectra of compound **1a** made from (*R*)- and (*S*)-H_2DBA are exact mirror images (Fig. 3), and conclusively demonstrate that compounds **1a** made from (*R*)- and (*S*)-H_2BDA are supramolecular enantiomers. Solid-state CD spectra of compound (*S*)-**1b** and (*S*)-**1c** are essentially the same as that of (*S*)-**1b**.

In conclusion, we have developed a rational synthetic approach toward homochiral materials based on 3D coordination networks using enantiopure dicarboxylate ligands and dilanthanide SBUs as the building blocks. To the best of our knowledge, compounds **1a–c** represent the first examples of homochiral 3D lanthanide–organic coordination polymers. Furthermore, the $4^9 6^6$ topology exhibiting by **1a–c** is unprecedented, and should provide an interesting framework for the construction of other interesting coordination networks. Ongoing work is aimed at increasing the porosity of these frameworks through structural modifications of atropisomeric dicarboxylic acid bridging ligands, and the exploitation of these novel homochiral porous coordination networks in enantioselective processes.

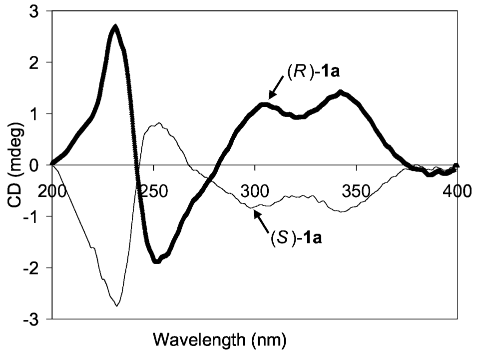

Fig. 3 Solid-state CD spectra of (*R*)- and (*S*)-**1a**.

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Notes and references

† A mixture of $Gd(NO_3)_2 \cdot 6H_2O$ and H_2BDA (0.015 mmol) was placed in a small vial containing DEF (2.5 mL), MeOH (0.5 mL) and pyridine (0.25 mL). The vial was sealed, heated at 50 °C for 72 h, and allowed to cool to room temperature. Crystals of **1a** suitable for X-ray diffraction was filtered off, washed with diethyl ether and dried in air. The Er and Sm complexes **1b** and **1c** were prepared similarly. Yield: **1a**, 42%; **1b**, 37%; **1c**, 31%. Anal. calc. for $C_{108}H_{108}Cl_6Gd_2N_6O_{22}$, **1a**: C, 52.74; H, 4.84; N, 3.42. Found: C, 52.68; H, 4.73; N 3.37%. Anal. calc. for **1b**: C, 52.32; H, 4.80; N, 3.39. Found: C, 52.45; H, 4.73; N 3.36%. Anal. calc. for **1c**: C, 53.04; H, 4.86; N, 3.44. Found: C, 52.98; H, 4.60; N 3.45%.

‡ X-Ray single-crystal diffraction data for **1a** and **1b** were collected on a Siemens SMART CCD diffractometer. *Crystal data* for **1a**: orthorhombic, space group $C222_1$, a = 12.816(3), b = 34.481(7), c = 24.816(5) Å, U = 10967(4) Å^3, Z = 4, D_c = 1.435 g cm^{-3}, μ(Mo-Kα) = 1.416 mm^{-1}. Least-squares refinement based on 12076 reflections with $I > 2\sigma(I)$ and 600 parameters led to convergence, with a final $R1$ = 0.045, $wR2$ = 0.114 and GOF = 1.12. Flack parameter = 0.003(12). *Crystal data* for **1b**: orthorhombic, space group $C222_1$, a = 12.776(3), b = 34.298(7), c = 24.724(5) Å, U = 10833(4) Å^3, Z = 4, D_c = 1.65 g cm^{-3}, μ(Mo-Kα) = 1.758 mm^{-1}. Least-squares refinement based on 12898 reflections with $I >$ 2σ(*I*) and 600 parameters led to convergence, with a final $R1$ = 0.047, $wR2$ = 0.110 and GOF = 1.06. CCDC reference numbers 181475 and 181476. See http://www.rsc.org/suppdata/cc/b2/b204249e for crystallographic data in CIF or other electronic format.

§ Unit cell parameters for **1c**: orthorhombic, a = 12.816(2), b = 34.232(4), c = 24.982(3) Å, U = 10960(2) Å^3.

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