Construction and Structural Investigation of Helical Coordination Network Formed by the Self-assembly of Triple Helicate with Macrocyclic Framework and Lanthanum Cations

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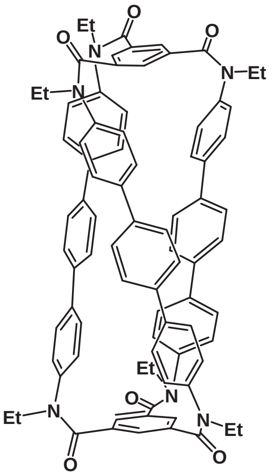
A triple helicate, a macrocyclic aromatic amide with a helical structure, is complexed with La(III) ion leading to the self-assembly of a helical coordination polymer. Each La(III) atom is coordinated by a pair of oxygen of the tertiary benzenetrianilide moieties from two adjacent ligands, resulting in the formation of chiral infinite coordination networks of alternating La(III) atoms and ligands. Here, we demonstrate that the chirality of a one-dimensional polymeric structure in the crystal was derived from T-shaped aromatic–aromatic (CH–π) interactions of each molecule twisted in the same direction.

Helical structures have attracted considerable recent interest for the development of new functional materials. This has been due to their many exploitable properties such as chemical transport, catalysis, separation, and molecular sensing.[1] Various promising synthetic methods for producing well-defined network architectures have been reported; noncovalent syntheses using metal coordination and hydrogen bonding have been the most common approach.[2] Over recent decades, a number of helical structures have been successfully designed and synthesized by the selection of the metal's coordination preferences and ligand geometry. However, except for cucurbituril[3] and calixarene,[4] large molecules with macrocyclic frameworks built of covalent bondings for use as a ligand for construction of huge helical structures have been less explored. Herein, we present the design, synthesis, and structural analysis of a one-dimensional helical chain in a crystal obtained by the self-assembly of an exo-ditopic macrocyclic ligand and a La(III) ion.

The creation of the helical coordination polymer discussed here stems from a La(III) ion and a triple helicate **1** (Scheme 1), which is a macrocyclic aromatic amide structure synthesized from aromatic diamine and 1,3,5-benzenetricarboxylic acid in high yield.[5] It is composed of three arranged *p*-terphenyl moieties covalently linked by two of the tertiary benzenetrianilide group in a propeller-like *syn* conformation at both ends to form a rigid, helical structure. The helicity was derived from intramolecular tilted T-shaped aromatic–aromatic (CH–π) interactions between each of the *N*-phenyl rings.[6] La(III) ions were chosen as the metal because they form kinetically labile complexes with the carbonyl group.

Single crystals of $[\mathbf{1}\cdot\mathrm{La(OTf)_3}]_n$ (**2**) were grown by layering a solution of $\mathrm{La(OTf)_3}$ in acetonitrile over a solution of ligand **1** in chloroform and isolated in 90% yield.[7] X-ray crystallographic analysis revealed that the product was an infinite helical network structure formed by lanthanum atoms alternating with ligand **1** that are mutually bridging (Figure 1). The crystals are in a triclinic cell, and the helical structure was solved with space group $P\bar{1}$, which contains a racemic mixture of both right- and left-handed helical coordination polymers per unit cell (Figure 2). Both enantiomers of the helical polymeric strand extend on the plane of the *a* and *b* axes, and the racemic row of the helicates piles up with chloroform and water molecules in the direction of the *c*-axis, resulting in the optical inactivity of the crystal. The fragment that determines the pitch of the helix is composed of a lanthanum atom and a ligand molecule.

Lanthanum atoms are each coordinated to a pair of oxygen of the tertiary benzenetrianilide moieties to give a $\mathrm{LaO_2}$ coordi-



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Scheme 1.

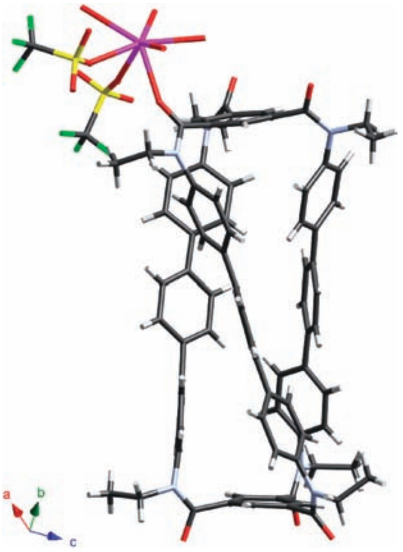

Figure 1. Asymmetric unit of the crystal structure of **2**. Chloroform, non-coordinate triflate ion, and non-coordinate water molecule are omitted for clarity.

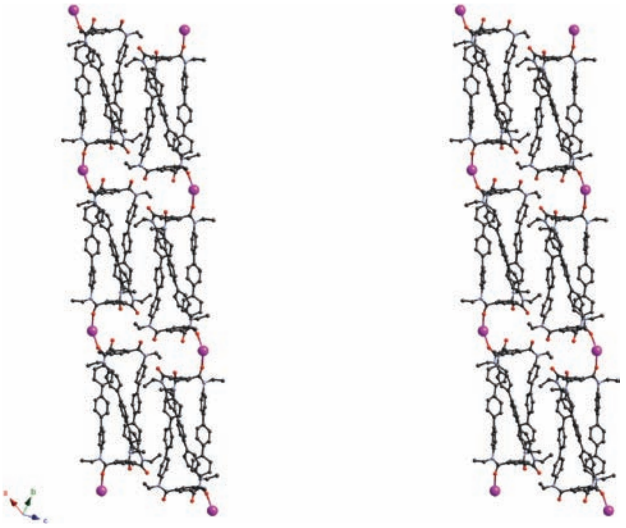

Figure 2. A portion of the structure showing the packing of **2** (stereoview). Chloroform, water molecules, triflate ions, and hydrogen atoms are omitted for clarity.

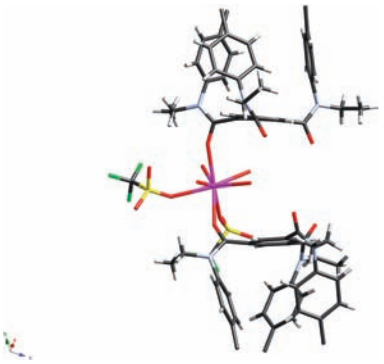

Figure 3. View around the La(III) ion of **2**.

nation environment; the O–La–O angle is 144.4°, the La–O distances are 2.44 and 2.45 Å, and the interplanar (OLa/LaO) dihedral angles are 84.5 and 99.6° (Figure 3). The remaining coordination sites are occupied by four monodentate waters and two monodentate triflate ions, showing that a lanthanum atom possesses eight-coordinate environment. Another non-coordinate triflate ion is located near the helical framework (it is omitted for clarity in the figures).

The tricarbonyl trianilide moieties of polymer **2** exist in conformations similar to those observed in ligand **1**, where the torsion angle of the six amide bonds (C_{Ph}–C–N–C_{Ph}) are 8.8, 13.7, 28.8, 3.7, 16.0, and 18.8°, those of Ar–CO are 89.2, 56.7, 86.6, 64.6, 60.0, and 60.3°, and those of Ar–NC_{Et} are 72.1, 62.1, 68.2, 69.0, 69.3, and 65.5° (averaged torsion angles in **2** are 15.0, 69.6, and 67.7°, respectively) (Figure 3). The angle of the twist between two benzenetricarbonyl moieties at both ends of the ligand is 90°. The ring center–ring center distances of each of the two phenylene groups are 5.29, 5.21, and 5.23 Å (upper), 4.57, 4.89, and 5.00 Å (middle), and 4.84, 5.57, and 5.49 Å (bottom) (Figure 1).

The observed helical structure is derived form a propeller-like chiral conformation due to intramolecular tilted T-shaped aromatic–aromatic (CH–π) interactions between each of the *N*-phenyl rings of the ligand. The conformational motion of the ligand in the coordination polymer can be restricted by fixing the chiral element of the tricarbonyl trianilide moieties through metal–ligand complexation, leading to the chiral single-stranded helical polymer in the crystal.

In conclusion, we have designed and synthesized a helical coordination polymer as a racemic mixture of left- and right-handed helices by the complexation of helical macrocyclic aromatic amides and La(III) ions. The self-assembly of macrocyclic components through metal-coordination can be regarded as an approach suitable for not only the development of novel coordination networks but also ordered arrangements into one-dimensional arrays. With the same combination of ligand and metal, the generation of optically pure left- or right-handed helices using chiral anions is currently under investigation.

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7 Elemental Analysis Calcd for $\mathbf{1}\cdot La(OTf)_3\cdot 5H_2O\cdot CHCl_3$: C, 51.38; H, 4.07; N, 4.09%. Found: C, 51.11; H, 4.02; N, 4.12%. X-ray data were collected on a Bruker Apex2 CCD detector. The crystal structure was solved by direct methods SHELXS-97 (Sheldrick, 1997) and refined by full-matrix least-squares SHELXL-97 (Sheldrick, 1997). Most non-hydrogen atoms were refined anisotropically, but some atoms were refined isotropically because of the large disorder. All hydrogen atoms were included as their calculated positions. Crystal data for **2**: $C_{84}H_{72}N_6O_6\cdot La\cdot(CF_3SO_3)_2\cdot 4H_2O$, CF_3SO_3, $CHCl_3$, H_2O; $M_r = 2057.04$ g mol^{-1}, Triclinic, $P\bar{1}$, colorless plate measuring $0.10 \times 0.05 \times 0.02$ mm^3, $T = 90$ K, $a = 13.7251(14)$ Å, $b = 18.1828(16)$ Å, $c = 20.7849(16)$ Å, $\alpha = 109.059(4)°$, $\beta = 98.172(5)°$, $\gamma = 94.173(4)°$, $V = 4813.4(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.419$ Mg m^{-3}, $\mu = 0.678$ mm^{-1}, $T_{max} = 0.9866$, $T_{min} = 0.9353$, GOF on $F^2 = 1.023$, $R_1 = 0.0875$, $wR_2 = 0.2154$ ($[I > 2\sigma(I)]$), $R_1 = 0.1503$ and $wR_2 = 0.2449$ (all data). CCDC-293729.

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