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Self-Assembly of Two Chiral Supramolecules with Three-Dimensional Porous Host Frameworks: $(\Delta)\{[Fe^{II}(phen)_3][Fe^{III}Na(C_2O_4)_3]\}_n$ and Its Enantiomer

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Two chiral supramolecules with enantiomeric three-dimensional porous host frameworks, $(\Delta)\{[Fe^{II}(phen)_3][Fe^{III}Na(C_2O_4)_3]\}_n$ (**1**) and $(\Lambda)\{[Fe^{II}(phen)_3][Fe^{III}Na(C_2O_4)_3]\}_n$ (**2**) (phen = 1,10-phenanthroline), have been synthesized, and their crystal structures have been determined. The structural analysis shows that compounds **1** and **2** are a pair of enantiomers, both consisting of a three-dimensional porous skeleton formed by $(\Delta)/(\Lambda)\{[Fe^{III}Na(C_2O_4)_3]^{2-}\}_n$ and guest $(\Delta)/(\Lambda)[Fe(phen)_3]^{2+}$ units. The circular dichroism spectrum measurements confirmed the optical activity and the enantiomeric nature of complexes **1** and **2**.

Supramolecular chirality is a growing topic of interest in light of its importance in biology and advanced materials.[1,2] Currently, considerable attention has been paid to the construction of chiral supramolecular aggregates through noncovalent self-assembly approaches from achiral molecular subunits,[3,4] especially to the chiral coordination polymer supramolecule. Because of the functionalization of the porous host framework that can be tuned by a choice of metal centers and organic ligands, chiral coordination polymers play a key role in molecular recognition processes.

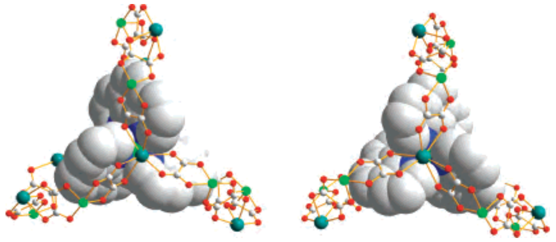

Figure 1. Perspective views (left and right) of the Δ and Λ configurations of supramolecular compounds **1** and **2**, respectively.

Selection of an appropriate multidentate ligand to link plural metal ions is a powerful way to build a chiral coordination polymer supramolecule. As a multidentate ligand, oxalate acid has been widely used in the assembly of such compounds because it can lead to abundant varieties of multidimensional coordination polymers with different kinds of topology.[5] To develop new chiral coordination polymer supramolecules, we focused our attention on metal–oxalate acid coordination polymers. Herein, we report the synthesis, crystal structure, and optical activity of a pair of oxalate coordination polymer supramolecules, $(\Delta)\{[Fe^{II}(phen)_3][Fe^{III}Na(C_2O_4)_3]\}_n$ (**1**) and $(\Lambda)\{[Fe^{II}(phen)_3][Fe^{III}Na(C_2O_4)_3]\}_n$ (**2**) (phen = 1,10-phenanthroline).

Dark-red ball-shaped single crystals of compounds **1** and **2** were obtained by a mixed solvothermal reaction of $FeCl_3$, $Na_2C_2O_4{\cdot}2H_2O$, and phen using molar ratios of 1:1:3 at about 423.15 K.[6] X-ray diffraction measurements showed that compounds **1** and **2** were enantiomers and that both crystallized in a cubic system, with chiral space group $P2_1/3$, $a = b = c = 16.1087(10)$ Å, and $Z = 2$.[7] Detailed structural

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(6) Preparation of complexes **1** and **2**: A solution of phen (3mmol) in 10 mL of methanol was added to a solution of $FeCl_3$ (1 mmol) and $Na_2C_2O_4{\cdot}2H_2O$ (1 mmol) in water (10 mL) with stirring for about 2 h. Then it was transferred into a Teflon-sealed autoclave inside a programmable electric furnace reactor. The mixed solvothermal reaction lasted for about 12 h at about 423.15 K, and then the solution was cooled to room temperature naturally. A mixture of dark-red ball-shaped single crystals of complexes **1** and **2** was obtained (yield = about 68% based on Fe). IR (KBr, cm^{-1}): 1663.93 (s), 1384.40 (s), 1246.97 (m), 874.89 (m), 788.18 (s), 727.62 (m).

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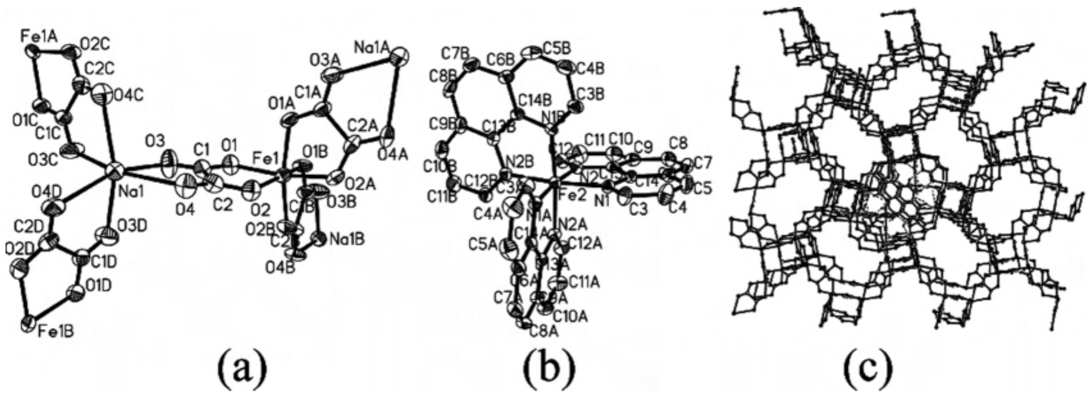

Figure 2. Perspective views of the crystallographical structure of **1**. H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (a) Basic unit of the host porous framework. (b) Guest $[Fe(phen)_3]^{2+}$ cation. (c) Supramolecule **1**. Part of the included guest molecules have been omitted. Selected bond lengths (Å) and angles (deg): Fe2−N1 1.981(4), Fe2−N2 1.977(5), Fe1−O1 2.004(5), Fe1−O2 1.999(5), Na1−O3#1 2.342(6), Na1−O4#1 2.660(6), N1−Fe2−N1#1 92.56(19), N2−Fe2−N1 83.61(18), N2#1−Fe2−N1 174.41(18), N2#2−Fe2−N1 91.68(18), N2#1−Fe2−N2 92.40-(18), O1−Fe1−O2 80.3(2), O1−Fe1−O1#3 89.4(2), O1−Fe1−O2#3 97.5(2), O3−Na1−O4 66.67(17), O3−Na1−O3#1 94.1(3), O4#1−Na1−O4#2 107.73-(17). Symmetric operation: #1, $x - {}^{1}/_{2}, -y + {}^{3}/_{2}, -z + 1$; #2, $-x + 3/2, -y + 1, z + {}^{1}/_{2}$; #3, $-x + 1, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; #4, $-z + 1, x - {}^{1}/_{2}, -y + {}^{1}/_{2}$.

analysis revealed that both compounds showed the host−guest supramolecule structure feature. The absolute configurations of **1** and **2** are as shown in Figure 1. **1** is a compound composed of the isolated Δ configuration guest ion and a three-dimensional host porous skeleton, in which all of the tris(bischelated) metallic centers also adopt the Δ configuration, while the guest ion and the host porous skeleton of compound **2** adopt a Λ configuration.[8]

Oxalate ligands and atomic Fe and Na construct the Δ configuration three-dimensional host porous skeleton of **1**; no detailed structural descriptions are presented here for **2**. Every oxalate as a tetradentate ligand connects with a Na atom using two O atoms from one side and links with a Fe atom from another side, forming two five-membered rings, Fe−O−C−C−O−Fe and Na−O−C−C−O−Na, respectively, which form the basic unit of the host framework (Figure 2a). In other words, each Fe (or Na) atom coordinates with three oxalate ligands in an octahedral geometry with D_3 symmetry to form a $(\Delta)[Fe(C_2O_4)_{3/2}]$ (or $(\Delta)[Na(C_2O_4)_{3/2}]$) node; three oxalate ligands coordinate with three Na (or Fe) atoms separately, and each of the Na (or Fe) atoms ligates with two other oxalate ligands, which results in the formation of an infinite Δ configuration three-dimensional host porous skeleton. One Fe atom coordinates with three phen ligands in an octahedral geometry, which constructs the basic Δ configuration guest unit $(\Delta)[Fe(phen)_3]^{2+}$ of compound **1**. Each $(\Delta)[Fe(phen)_3]^{2+}$ occupies one of the vacancies of the host framework (Figure 2b), in which the supramolecule **1** is formed (Figure 2c).

Because of the extremely low solubility of the obtained polymers, solid-state circular dichroism (CD) was imposed. The CD spectrum measurements in KBr pellets further confirm the optical activity and enantiomeric nature of complexes **1** and **2**.[9] The CD spectrum of **1** exhibits a negative Cotton effect at I_{max} = 256 and 420 nm and a positive dichroic signal at I = 295, 470, and 558 nm. Complex **2** shows Cotton effects of the opposite sign at the same wavelengths (Figure 3). The two normalized spectra are opposite in nature, which assesses the enantioselective character of the self-assembly, leading to the chiral supramolecules; i.e., Δ configuration porous frameworks assemble only with Δ configuration guest ions. The assembly of Δ configuration porous frameworks with a Λ configuration of guest ions is sterically forbidden.

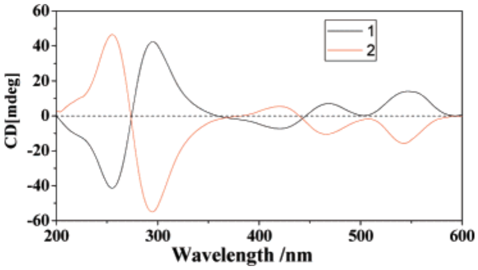

Figure 3. CD spectra of **1** (red) and **2** (black) in the solid state.

Within these supramolecules, with the exception of the effects of the ionic bonds between host anion and guest cation, there also exist different kinds of hydrogen bonds; these include C−H···O (a H···O distance of between 2.35 and 2.54 Å and a C···O distance from 3.04 to 3.14 Å) and C−H···N (mean H···N 2.60 Å and C···N 3.08 Å) bonding (see Table S1 in the Supporting Information).

In summary, two oxalate-bridged chiral coordination polymer supramolecules with three-dimensional porous host frameworks were synthesized. Analysis of the compounds synthesized shows that they are enantiomers and that the CD

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(7) Crystal data for **1**: $C_{42}H_{24}Fe_2N_6NaO_{12}$, M = 939.36, T = 293 K, cubic, space group $P2_13$, $a = b = c$ = 16.1087(10) Å, V = 4180.0(4) Å^3, Z = 4, ρ_{calcd} = 1.405 g cm^{-3}, μ = 0.805 mm^{-1}, R1 = 0.0462, wR2 = 0.1240 [$I > 2\sigma(I)$] for 3486 data and 191 parameters, S = 1.036. Crystal data for **2**: R1 = 0.0560, wR2 = 0.1360 [$I > 2\sigma(I)$] for 3105 data and 190 parameters, S = 1.011.

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(9) CD spectra were measured with a Jasco model J-810 spectropolarimeter. Measurements were made on the resulting complexes as dispersions of 0.1−1 mg in 100 mg of oven-dried KBr. Thirteen-millimeter-diameter disks were made in a standard disk press. The baseline correction was performed with the spectrum of a pure KBr disk, prepared in the same conditions. The displayed absorption spectra result from subtraction of the spectrum of a standard KBr disk.

spectrum measurements further confirm their enantiomeric nature.

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Supporting Information Available: Listings of crystallographic data for complexes **1** and **2** in CIF format and Table S1 of related hydrogen-bond parameters. Thismaterial is available free of charge via the Internet at http://pubs.acs.org.

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