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Self-Assembly and Chiral Recognition of a Two-Dimensional Coordination Polymer from a Chiral Nickel(II) Macrocyclic Complex and Trimesic Acid

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A two-dimensional chiral open framework, $[Ni(L^{R,R})]_3[C_6H_3(COO)_3]_2\cdot 12H_2O\cdot CH_3CN$ (**3**), is prepared from a nickel(II) macrocyclic complex with chiral pendants and benzenetricarboxylate in $MeCN/H_2O$ and characterized [$L^{R,R}$ = 1,8-bis[(*R*)-α-methylbenzyl]-1,3,6,8,10,13-hexaazacyclotetradecane]. The open framework shows selective chiral recognition by interactions between the solid **3** and *rac*-1,1′-bi-2-naphthol.

Currently, chiral metal−organic coordination compounds are highly desirable because of their potential and/or practical applications such as chiral recognition, chiral catalysis, enantioselective sorption, and chiral magnetism.[1] However, the preparation of such functional supramolecules is still one of the main challenges in chemistry and materials science. To date, several chiral coordination polymers including chiral moieties have been reported.[2] For instance, a homochiral metal−organic framework composed of a zinc(II) ion and chiral organic building block has large chiral one-dimensional (1D) channels and showed interesting enantioselective separation and catalysis.[1b] Recently, we have reported the structures and circular dichroism (CD) spectra of two macrocyclic nickel(II) complexes bearing chiral pendant arms, i.e., $[Ni(L^{R,R})](ClO_4)_2$ (**1**) and $[Ni(L^{S,S})](ClO_4)_2$ (**2**), where $L^{R,R/S,S}$ = 1,8-bis[(*R*/*S*)-α-methylbenzyl]-1,3,6,8,10,13-hexaazacyclotetradecane,[3] in which they can be chiral building blocks. Thus, these can be utilized for the preparation of chiral open frameworks displaying chiral recognition because they have chiral pendants to interact with chiral molecules and vacancies in the axial positions.[3,4] Therefore, our strategy for recognizing enantiopure components selectively is based on interactions of the chiral pendant groups and guest molecules. Herein, we report the self-assembly, structure, characterization, and chiral recognition of a two-dimensional (2D) chiral open framework.

From the self-assembly of **1** with deprotonated 1,3,5-benzenetricarboxylic acid, BTC^{3-} in $MeCN/H_2O$,[5] a 2D supramolecular chiral network of $[Ni(L^{R,R})]_3[C_6H_3(COO)_3]_2\cdot 12H_2O\cdot CH_3CN$ (**3**) has been obtained as a pink solid.[6] Compound **3** is insoluble in water and common organic solvents such as MeCN, MeOH, EtOH, tetrahydrofuran, and *N*,*N*-dimethylformamide. **3** is the first 2D chiral open framework assembled from a nickel(II) macrocyclic complex with chiral pendants. Furthermore, the chiral open framework **3** showed that it can selectively recognize *R* species from racemic 1,1′-bi-2-naphthol.

Coordination polymer **3** crystallizes in the monoclinic $P2_1$ space group (chiral), and the unit cell includes two fundamental building units, $[Ni(L^{R,R})]_3[C_6H_3(COO)_3]_2$.[7]

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(6) Characterization of **3**: The nickel(II) complex **1** (1.61 g, 2.41 mmol) was dissolved in MeCN (40 mL), and a solution containing 1,3,5-benzenetricarboxylic acid (H_3BTC; 338 mg, 1.61 mmol) and triethylamine (0.67 mL) in a mixture of MeCN and H_2O (3:1, v/v, 16 mL) was added dropwise. The color changed pale pink and formed pale-pink powders, which were collected by filtration, washed with MeCN, H_2O, and diethyl ether, and dried in air (yield: 1.45 g, 99%). Pale-pink crystals of **3** suitable for X-ray crystal analysis were obtained by layering of the MeCN solution of **1** on the mixture of a MeCN and H_2O solution of H_3BTC with triethylamine for several days. Anal. Calcd for $C_{92}H_{147}N_{19}Ni_3O_{24}$: C, 53.18; H, 7.14; N, 12.82. Found: C, 53.20; H, 7.04; N, 13.00. IR (KBr, cm^{-1}): ν_{NH} 3290, 3172; ν_{CH} 3031, 2926; ν_{COO} 1608, 1564, 1427; ν_{bz} 1453.

(7) Crystal and structure refinement parameters for **3**: at 294(2) K, $C_{90}H_{120}N_{18}Ni_3O_{12}$, fw = 1822.17 g/mol, monoclinic, space group $P2_1$, a = 16.512(1) Å, b = 21.437(1) Å, c = 19.547(1) Å, β = 103.945(2)°, V = 6715.1(6) Å^3, Z = 2, d_{calcd} = 0.901 g/cm^3 without guests, μ(Mo Kα) = 0.464 mm^{-1}, R1 = 0.1098 [$I > 2\sigma(I)$], wR2 = 0.3038. Data were collected on an ADSC Quantum 210 detector at Beamline 4A MXW of The Pohang Light Source using graphite-monochromated Mo Kα (λ = 0.900 00 Å) radiation. Structure was solved by direct methods and refined by full-matrix least-squares refinement using the *SHELXL97* programs.

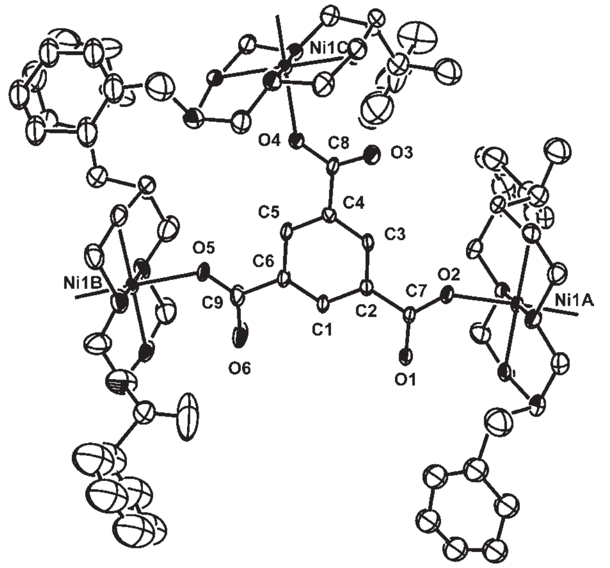

Figure 1. ORTEP drawing of the trinuclear unit of **3** with an atomic numbering scheme (thermal ellipsoid at 15% probability).

An ORTEP view of the trinuclear unit of **3** is shown in Figure 1. The coordination geometry around the nickel(II) ion is a tetragonally distorted octahedral structure. The nickel(II) ion is coordinated with four secondary amine donors of the macrocycle as well as two oxygen atoms from two BTC^{3-} ions. The average Ni−N and Ni−O bond distances are 2.037(4) and 2.145(3) Å, respectively. As shown in Figure 1, the pendant arms are clearly shown in the *R* conformations in the crystal structure. Because each nickel(II) ion is coordinated with two BTC^{3-} ions and each BTC^{3-} connects three nickel(II) macrocyclic units, the stoichiometry of the network is $Ni^{2+}:BTC^{3-}$ = 3:2, which gives rise to 2D layers extending along the *ac* plane. In the structure of a 2D sheet, six nickel(II) macrocyclic complexes and six BTC^{3-} ions form a parallelogram, which is a basic motif of **3** (Figure 2a).[8] The metal−metal distances around BTC^{3-} ions are Ni1A−Ni1B = 11.173(2) Å, Ni1A−Ni1C = 9.746(2) Å, and Ni1B−Ni1C = 8.262(2) Å, respectively. Because the benzene ring of the BTC^{3-} ion is a plane, the 2D layer is nearly flat. Thus, all of the six macrocyclic complexes and the six BTC^{3-} ions are located in the same plane. The free C−O bond distances of the BTC^{3-} ions (1.225−1.281 Å) are therefore comparable to those of the coordinated C−O bond distances (1.206−1.254 Å). The 2D layers are stacked as separated by 10.719 Å, and the closest metal−metal distance between the layers is 10.995 Å. The packing structure for the multilayers shows that the void space is generated in the solid (Figure 2b).

Calculations using *PLATON* indicate that **3** has 42.7% of the void volume occupied by solvent molecules.[9] The guest solvent molecules are included in the cavities and between the layers; however, these could not be located in the X-ray structure because of severe thermal disorder. Therefore, the identity and number of the guest molecules were determined from IR spectra, elemental analysis, and thermogravimetric analysis (TGA) data.

The TGA trace of **3** shows a weight loss of 7.1% at 93 °C, which corresponds to the loss of guest molecules, i.e., water and acetonitrile. No chemical decomposition was observed up to 160 °C. At temperatures higher than 160 °C, the compound decomposed (Figure S1 in the Supporting Information, SI). The CD spectrum of **3** shows a positive peak at 725 nm indicative of the chirality of **3** (Figure S2 in the SI). In addition to the effective magnetic moments (μ_{eff}) of **3**, there is a weak antiferromagnetic interaction between 2 and 300 K (Figure S3 in the SI).[10]

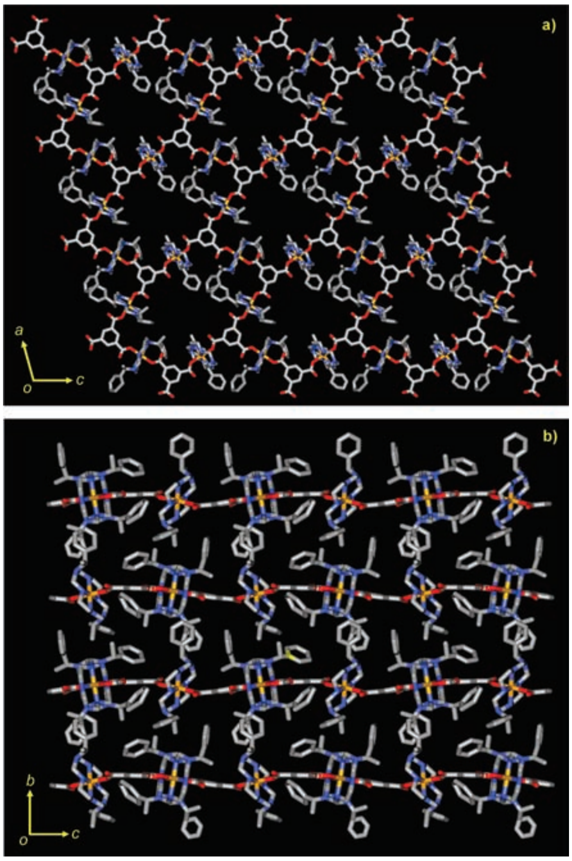

Figure 2. (a) Top view of a 2D framework of **3**. (b) Side view of 2D layers of **3** (orange, nickel(II); red, oxygen; blue, nitrogen; gray, carbon).

To identify the chiral recognition of **3**, chiral high-performance liquid chromatography (HPLC) was used for *rac*-1,1′-bi-2-naphthol and *rac*-2,2,2-trifluoro-1-(9-anthryl)ethanol in a CH_2Cl_2 solution (see the SI). The recognition experiments were performed in CH_2Cl_2 at room temperature with the solid dried at 80 °C for 3 h. When the desolvated solid **3** was immersed in CH_2Cl_2 containing a measured amount of 2,2,2-trifluoro-1-(9-anthryl)ethanol, the ratio of (*R*)- and (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol was not changed in chiral chromatograms. This means that the solid **3** cannot discriminate the (*R*)- and (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol molecules. However, that of (*R*)- and (*S*)-1,1′-bi-2-naphthol was changed significantly after immersion of **3** in a CH_2Cl_2 solution including *rac*-1,1′-bi-2-naphthol. That is, the quantity of (*R*)-1,1′-bi-2-naphthol decreased because of interactions (i.e., adsorption) with **3**. Thus, the result indicates that **3** recognizes *R* species from racemate 1,1′-bi-2-naphthol selectively. In order to check systematically, we have examined the ratio and time dependences for interaction and/or binding between **3** and *rac*-1,1′-bi-2-naphthol. The optimized ratio

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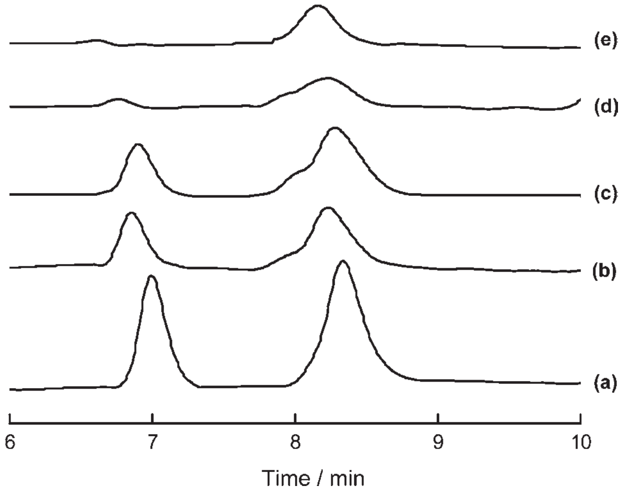

Figure 3. Chromatograms for 1,1′-bi-2-naphthol obtained by consecutive immersion and filtration of the solid **3** and *rac*-1,1′-bi-2-naphthol solution (left, *R*; right, *S*): (a) after two times; (b) after three times; (c) after four times; (d) after six times; (e) after eight times. The eluent was 10% isopropyl alcohol in hexane, and the injection volume was 5 μL. The flow rate was 1.5 mL/min, and the detection wavelength was 254 nm.

and immersion time of the solid **3** and *rac*-1,1′-bi-2-naphthol were 5:1 (% ee = 11.4) and 2 h (% ee = 10.6) (Tables S1 and S2 in the SI). On the basis of these results, we performed the chiral discrimination of *rac*-1,1′-bi-2-naphthol through immersion and filtration repeatedly. As shown in Figure 3 (Table S3 in the SI), remarkably, the optical purity of *rac*-1,1′-bi-2-naphthol became about 92% ee as the experirment was repeated eight times. The optical purity (92% ee) is comparable to that (100% ee) obtained by resolution of *rac*-1,1′-bi-2-naphthol using (*S*)-proline via a cyclic borate ester.[11] Therefore, this confirms that the solid **3** can recognize (*R*)-1,1′-bi-2-naphthol. As well, the solid **3** potentially can be used as chiral materials for chiral separation and column chromatography. The volume of the 1,1′-bi-2-naphthol molecule is much greater than the cavities of the framework of **3**. Thus, the chiral recognition can be attributed to intercalation and/or adsorption between the layers.

In summary, we have prepared and characterized a chiral 2D coordination polymer for the first time by using a nickel(II) macrocyclic complex with chiral pendant groups and benzenetricarboxylate. Significantly, the chiral coordination polymer **3** showed chiral recognition for (*R*)-1,1′-bi-2-naphthol selectively. Further studies on the mechanism of the chiral recognition and fabrication of new chiral complexes and open frameworks showing chiral resolution are ongoing.

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Supporting Information Available: Detailed experiments for chiral HPLC, X-ray crystallographic data for **3** in CIF format, and TGA data, a CD spectrum, and magnetic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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