Formation of a Chiral 2D-layered Host System Composed of (1*R*,2*R*)-1,2-Diphenylethylenediamine and Benzenediacetic Acid Derivatives

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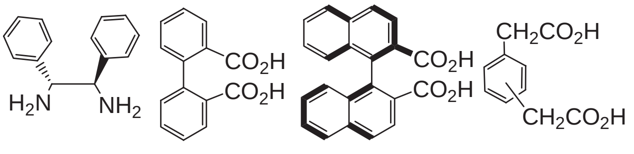
A chiral supramolecular host system was developed by combining (1*R*,2*R*)-1,2-diphenylethylenediamine and benzenediacetic acid derivatives. These supramolecular complexes are constructed by the self-assembly of a chiral 2D-layered network structure with multiple chiral points derived from chiral transfers.

Many supramolecular host compounds have been reported that include guest molecules.[1] In order to create the various shapes and properties of the cavities in these host complexes, supramolecular host complexes composed of two or three molecules have been developed.[2] However, almost all of these supramolecular host complexes have been achiral although a few chiral host complexes have been reported.[3] Recently, we reported a supramolecular host system with multiple chiral points by using a hydrogen- and ionic-bonded network composed of a diamine and a dicarboxylic acid derivative.[4] For the diamine derivative, chiral (1*R*,2*R*)-1,2-diphenylethylenediamine [(1*R*,2*R*)-**1**] was used, and either diphenic acid (**2**) or chiral (*R*)-1,1′-binaphthyl-2,2′-dicarboxylic acid [(*R*)-**3**] having an internal symmetry axis was used as the dicarboxylic acid derivative. Characteristically, these host complexes are formed by the self-assembly of a chiral 2_1-columnar hydrogen- and ionic-bonded network structure. Interestingly, in the (1*R*,2*R*)-**1**–**2** system, the axial chirality of achiral compound **2** was induced and fixed by a chiral transfer from (1*R*,2*R*)-**1** to **2**.

The advantage of these host systems is that modifying the shape and property of the cavity can easily be accomplished by changing the component molecules. In this paper, we report the formation and crystal structure of a novel chiral supramolecular host system with multiple chiral points consisting of a diamine and a dicarboxylic acid derivative. (1*R*,2*R*)-**1** was used as the diamine derivative. Three achiral diacetic acid derivatives, 1,2-, 1,3-, and 1,4-benzenediacetic acid (*o*-**4**, *m*-**4**, and *p*-**4**), were used as dicarboxylic acid derivatives (Chart 1). In order to impart flexibility for binding to the carboxylic acid derivative, an acetic acid group was used for the carboxylic acid group.



(1*R*,2*R*)-**1** **2** (*R*)-**3** **4**

Chart 1.

Formation of the (1*R*,2*R*)-**1**–**4** supramolecular host systems was attempted by adding (1*R*,2*R*)-**1** (10 mg, 0.047 mmol) and each **4** molecule (10 mg, 0.047 mmol) to a solution of MeOH (3 mL). When ortho- and meta-derivatives (*o*-**4** and *m*-**4**) were used, colorless crystals, **I** (12 mg) and **II** (10 mg), respectively, were obtained which included MeOH as a guest molecule. The para-derivative (*p*-**4**) did not form a supramolecular complex with (1*R*,2*R*)-**1**. X-ray analysis was performed to investigate the crystal structure of the supramolecular host system and the inclusion mechanism of the guest MeOH. Views of the crystal structure of **I** are shown in Figure 1.[5] The stoichiometry of crystal **I** is (1*R*,2*R*)-**1**:*o*-**4**:MeOH = 1:1:2 and the space group is $P2_12_12$. This crystal has two types of bonding networks. One is an ionic-bonded network along the *a* axis (Figure 1a), which is formed from the ammonium hydrogens of (1*R*,2*R*)-**1** (Figure 1, green molecule) and the carboxylate oxygens of *o*-**4** (Figure 1, blue molecule). The other is a hydrogen-bonded network along the *b* axis (Figure 1b). There are also CH–π interactions (Figure 1c, indicated by red arrows, 2.76 Å) between the 2-CH of the benzene ring in (1*R*,2*R*)-**1** and the benzene ring of *o*-**4** along the *a* axis. A 2D-layered network structure is maintained by these networks (Figure 1c). The included MeOH molecules (Figure 1, indicated by red spacefilling view) are linked with the carboxyl group and the amino group through hydrogen bonds along the *b* axis and are included in the 2D-layered network structure (Figure 1a). Interestingly, the two acetic acid groups on *o*-**4** exist in a *trans* conformation relative to each other. Although *o*-**4** is an achiral molecule, the conformation of the two acetic acid groups on *o*-**4** is fixed in the chiral conformation by chiral transfer from (1*R*,2*R*)-**1**. Consequently, although only one chiral molecule (1*R*,2*R*)-**1** is used, this supramolecular host has two kinds of chiral moieties in the crystal.

Views of the crystal structure of **II** are shown in Figure 2.[6] The stoichiometry of crystal **II** is (1*R*,2*R*)-**1**:*m*-**4**:MeOH = 1:1:2 and the space group is $P2_12_12$. The crystals have the same characteristic ionic- and hydrogen-bonded 2D-layered network structure composed of (1*R*,2*R*)-**1** (Figure 2, green molecule) and *m*-**4** (Figure 2, blue molecule) along the *a* and *b* axes, as in crystal **I**. The guest MeOH molecules (Figure 2, indicated by red spacefilling view) are included in this 2D-layered network structure through hydrogen bonds. However, in this crystal, CH–π interactions are not observed. The two acetic acid groups on *m*-**4** exist in a *trans* and chiral conformation by chiral transfer from the chiral (1*R*,2*R*)-**1**.

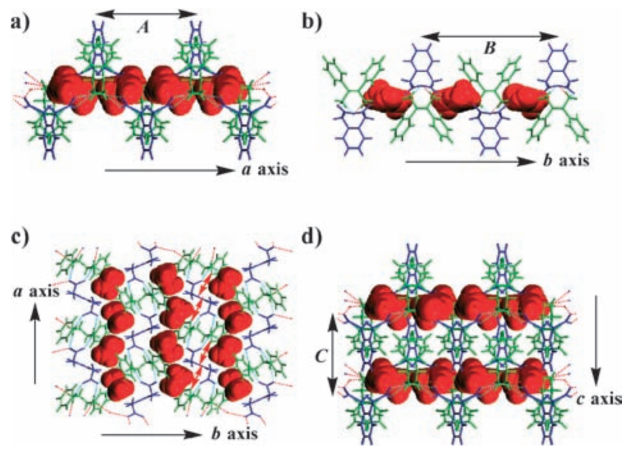


Figure 1. Crystal structure of 2D-layered network in complex **I**. (a) View down the *b* axis. (b) View down the *a* axis. (c) View down the *c* axis. (d) Packing diagram. View down the *b* axis.

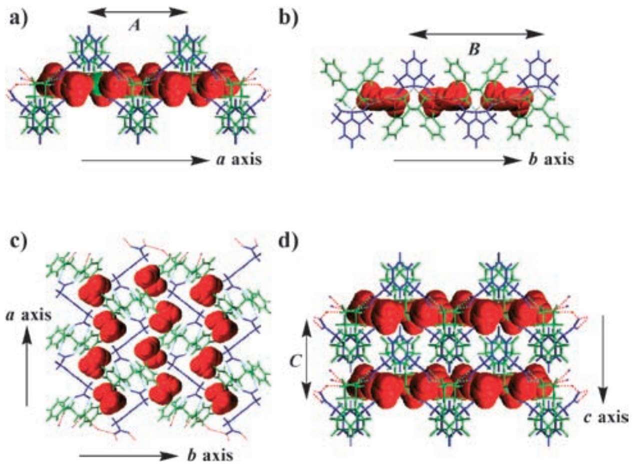


Figure 2. Crystal structure of 2D-layered network in complex **II**. (a) View down the *b* axis. (b) View down the *a* axis. (c) View down the *c* axis. (d) Packing diagram. View down the *b* axis.

In complexes **I** and **II**, the structure and packing of the chiral 2D-layered network are similar. However, as the component molecule changes from *o*-**4** to *m*-**4**, the distances between the **4** units [*A* and *B*, Figures 1a, 1b, 2a, and 2b] become longer (from 9.448 to 10.320 Å for *A*) along the *a* axis and shorter (from 16.272 to 15.886 Å for *B*) along the *b* axis. Moreover, the distance between the 2D-layered network structures [*C*, Figures 1d and 2d] becomes shorter (from 7.793 to 7.731 Å) along the *c* axis. These results suggest that the inclusion environment for guest molecules can be controlled by changing the component molecules.

In conclusion, two-component chiral host systems were created by using (1*R*,2*R*)-**1** and **4**. These supramolecular host systems are constructed by the self-assembly of a chiral 2D-layered network structure in which the guest molecules are included. Interestingly, this chiral 2D-layered network structure has multiple chiral points derived from chiral transfer from (1*R*,2*R*)-**1** to **4**. These chiral host systems may be used as chiral molecular recognition systems and asymmetric reaction fields in the future.

References and Notes

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5 Crystallographic data of **I**: $C_{14}H_{16}N_2{\cdot}C_{10}H_{10}O_4{\cdot}2CH_4O$, MW 470.56, orthorhombic, space group $P2_12_12$, $a = 9.4477(10)$, $b = 16.2721(18)$, $c = 7.7928(9)$ Å, $U = 1198.0(2)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.304\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K}\alpha) = 0.093\,\mathrm{mm^{-1}}$, 7630 reflections measured, 2807 unique, final R $(F^2) = 0.0468$ using 2212 reflections with $I > 2.0\sigma(I)$, R(all data) $= 0.0682$, $T = 100$ K. CCDC 641519.

6 Crystallographic data of **II**: $C_{14}H_{16}N_2{\cdot}C_{10}H_{10}O_4{\cdot}2CH_4O$, MW 470.56, orthorhombic, space group $P2_12_12$, $a = 10.3198(8)$, $b = 15.8863(12)$, $c = 7.7311(6)$ Å, $U = 1267.46(17)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.233\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K}\alpha) = 0.087\,\mathrm{mm^{-1}}$, 7837 reflections measured, 2877 unique, final R $(F^2) = 0.0294$ using 2785 reflections with $I > 2.0\sigma(I)$, R(all data) $= 0.0305$, $T = 100$ K. CCDC 641520. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).