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2D Layered Supramolecular Host System Derived from a 2_1-Helical Column, Composed of 1,2-Diphenylethylenediamine and *N*-Phenyliminodiacetic Acid

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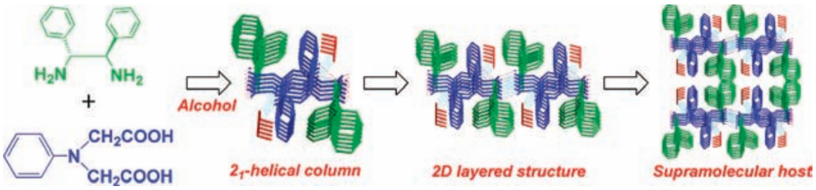
ABSTRACT



A supramolecular host system composed of a 2D layered structure was developed by combining 1,2-diphenylethylenediamine and *N*-phenyliminodiacetic acid. This 2D layered structure was formed by a hydrogen- and ionic-bonded network between 2_1-helical columns.

Many supramolecular host compounds that can accommodate guest molecules have been developed.[1] In such host systems, there has been an increased demand to facilitate the modulation of the size, shape, and functionality of the cavity that supports various guest molecules. Recently, in order to satisfy these demands, the development of supramolecular host systems composed of two or three component molecules has attracted considerable attention.[2] Among such systems, several organic supramolecular host systems composed of an amine derivative and a carboxylic acid derivative have been reported.[3] In these systems, the cavity that hosts guest molecules is formed by the self-assembly of 1D helical columnar hydrogen- and ionic-bonded network structures composed of amine and acid component molecules. Characteristically, these 1D helical columns interact with each

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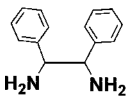
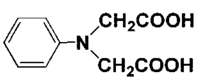
other by weak aromatic−aromatic edge-to-face or CH-π interactions. Therefore, these 1D columnar host systems accommodate guest molecules after changing to a 3D structure and rotating the helical columns in the crystal.

One characteristic of these supramolecular host systems is that the modification of the shape and properties of the cavity can easily be accomplished by changing the component molecules. Therefore, when suitable interactive substituents, for example, amine or carboxylic acid derivatives, are appropriately introduced into component molecules, 2D or 3D layered structures are expected to be formed by strong rather than weak interactions between helical columns.

In this paper, we report the formation and crystal structure of a 2D layered supramolecular host system that is derived from a 2_1-helical column composed of amine and acetic acid derivatives. Racemic and chiral (1*R*,2*R*)-1,2-diphenylethylenediamine [*rac*- and (1*R*,2*R*)-**1**, respectively] were used as amine molecules. *N*-Phenyliminodiacetic acid (**2**) having two acetic acid groups was used to obtain acetic acid molecules. In order to study the guest inclusion mechanism by X-ray crystallographic analysis, two simple *n*-alkyl alcohols [methanol (MeOH) and ethanol (EtOH)] were used as guest molecules.



***rac*-1**
(1*R*,2*R*)-1



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The complexation behavior of the *rac*-**1**/**2** host system was studied. We attempted to prepare supramolecular host complexes from guest solutions by crystallization. A mixture of *rac*-**1** (an equimolar mixture of (1*R*,2*R*)-**1** and (1*S*,2*S*)-**1**) and **2** was dissolved in MeOH and left to stand at room temperature. After 1 week, colorless crystals **I** were obtained. In order to study the mechanism of the two-component host system, the X-ray crystallographic analysis of the obtained crystals was carried out. The structure of complex **I** is shown in Figure 1.[4] Complex **I** is formed from (1*S*,2*S*)-**1** (orange-colored molecules in Figure 1), (1*R*,2*R*)-**1** (green-colored molecules in Figure 1), and **2** (blue-colored molecules in Figure 1). The stoichiometry of complex **I** is (1*S*,2*S*)-**1**:(1*R*,2*R*)-**1**:**2**:MeOH = 1:1:2:2, and the space group is $P2_1/c$. This crystal has a supramolecular helical columnar hydrogen- and ionic-bonded network around the 2_1-axis and along the *b*-axis (Figure 1a and b). This 2_1-helical column is formed by the association of the ammonium hydrogen of one protonated amine in **1** and the carboxylate oxygen of a carboxylic acid anion in **2**. Complex **I** consists of two types of chiral 2_1-helical columns with opposite chiralities: one column is composed of (1*S*,2*S*)-**1** and **2**, whereas the other is composed of (1*R*,2*R*)-**1** and **2**. Interestingly, these 2_1-helical columns with identical chiralities are connected by hydrogen bonds and ionic bonds and form a 2D layered structure along the *a*-axis (Figure 1c, represented by red-colored dotted borders). That is, one acetic acid group of the iminodiacetic acid group in **2** is used to form a 2_1-helical column with **1**, and the other is used to connect 2_1-helical columns along the *a*-axis for forming a 2D layered structure (Figure 1b, represented by purple-colored arrows). The self-assembly of these two types of 2D layered structures with different chiralities results in the formation of cavities that host guest molecules (Figure 1c). The guest MeOH molecules (Figure 1, indicated in red color or as red-colored space-filling molecules) are incorporated into the cavities by means of hydrogen bonds between the hydroxyl group of MeOH and the carboxyl group of **2**. This result suggests that, by combining a diamine molecule with a diacetic acid molecule having an iminodiacetic acid group, a supramolecular host compound composed of helical columns and having a 2D layered structure may be formed.

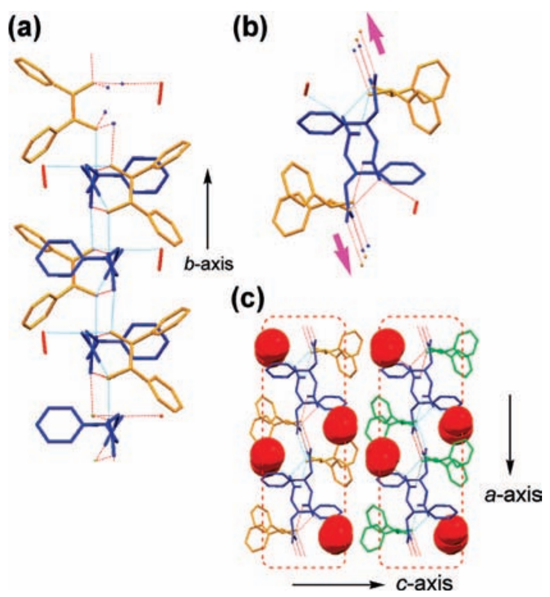

Figure 1. Crystal structure of complex **I**. (1*S*,2*S*)-**1**, (1*R*,2*R*)-**1**, **2**, and MeOH are represented as orange-, green-, blue-, and red-colored molecules, respectively. (a) 2_1-Helical column structure parallel to the *b*-axis. (b) View down the *b*-axis. The purple-colored arrows show intercolumnar interactions. (c) Packing structure comprising 2D layered structure observed along the *b*-axis. The red-colored dotted borders indicate the 2D layered structure.

Next, the inclusion of EtOH molecules was attempted by the same approach by using the *rac*-**1**/**2** system. As a result, several powder-like solids were obtained. However, due to

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(3) (a) Nakano, K.; Hishikawa, Y.; Sada, K.; Miyata, M.; Hanabusa, K. *Chem. Lett.* **2000**, 1170. (b) Imai, Y.; Kawaguchi, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron Lett.* **2006**, *47*, 7885. (c) Kodama, K.; Kobayashi, Y.; Saigo, K. *Chem. Eur. J.* **2007**, *13*, 2144. (d) Imai, Y.; Murata, K.; Kawaguchi, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Org. Lett.* **2007**, *9*, 3457. (e) Imai, Y.; Murata, K.; Matsuno, H.; Kamon, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Chem. Lett.* **2008**, *37*, 726. (f) Imai, Y.; Nagasaki, K.; Murata, K.; Kawaguchi, K.; Harada, T.; Nakano, Y.; Sato, T.; Fujiki, M.; Kuroda, R.; Matsubara, Y. *CrystEngComm.* **2008**, *10*, 951, and references therein.

(4) Crystallographic data of **I:** $C_{14}H_{16}N_2{\cdot}C_{10}H_{11}O_4N_1{\cdot}CH_4O$, $M = 453.53$, Monoclinic, space group $P2_1/c$, $a = 10.6304(8)$, $b = 10.1180(8)$, $c = 22.5404(17)$ Å, $\beta = 92.4800(10)°$, $U = 2422.1(3)$ Å^3, $Z = 4$, $D_c = 1.244$ g cm^{-3}, μ(Mo Kα) $= 0.087$ mm^{-1}, 14602 reflections measured, 5569 unique, final $R(F^2) = 0.0508$ using 4461 reflections with $I > 2.0\sigma(I)$, R(all data) $= 0.0670$, $T = 115(2)$ K. CCDC 691725.

the poor quality of the solids, their structures could not be studied by the X-ray crystallographic analysis.

When chiral 1,2-diphenylethylenediamine, i.e., (1*R*,2*R*)-**1**, is used instead of *rac*-**1**, the resulting host complex may have chiral cavities. Using the same procedure, we attempted to construct the chiral supramolecular host complex by crystallization from the same guest MeOH and EtOH solutions. A mixture of (1*R*,2*R*)-**1** and **2** was dissolved in each guest solution and left to stand at room temperature. As a result, colorless crystals [**II** in the case of the MeOH solution and **III** in the case of the EtOH solution] were obtained from each of the solutions.

In order to study the crystal structure of this two-component chiral host system, X-ray crystallographic analysis of the obtained crystals was carried out. The structure of complex **II** that includes MeOH molecules is shown in Figure 2.[5]

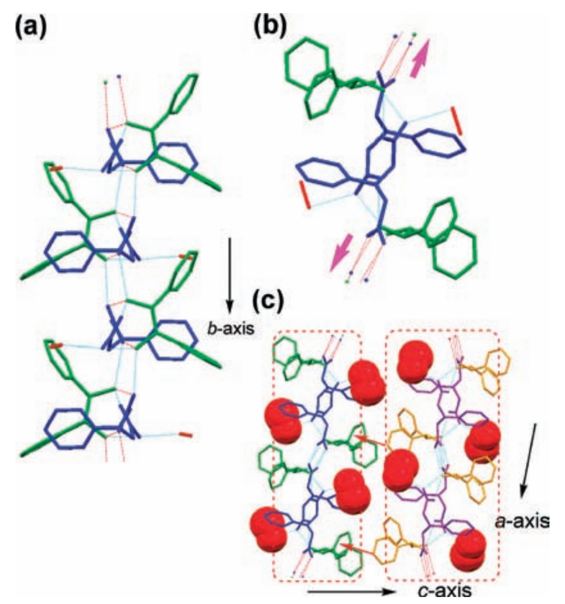

Figure 2. Crystal structure of complex **II**. The green- and orange-colored molecules represent (1*R*,2*R*)-**1** with different torsion angles. The blue- and purple-colored molecules show **2**. The MeOH molecules are shown in red. (a) 2_1-Helical column parallel to the *b*-axis. (b) View down the *b*-axis. The purple-colored arrows show intercolumnar interactions. (c) Packing structure comprising the 2D layered structure observed along the *b*-axis. The red-colored dotted borders indicate the 2D layered structure. The red-colored arrows show aromatic−aromatic edge-to-face interactions.

Although the guest MeOH molecules are partly disordered, the stoichiometry of complex **II** is (1*R*,2*R*)-**1**:**2**:MeOH = 2:2:2.5, and the space group is $P2_1$. Although this complex also has a characteristic 2_1-helical columnar network structure along the *b*-axis (Figure 2a and b), which is formed by the hydrogen- and ionic-bonded network, it has two types of 2_1-helical columns in which the torsion angles of **1** are different. One 2_1-helical column is composed of molecules of **1** (Figure 2, represented by green-colored molecules) that have a torsion angle of −49.20° (Figure 2a and b); the other column is composed of molecules of **1** (Figure 2, indicated by orange-colored molecules) that have a torsion angle of −46.28° (Figures ESI-1, Supporting Information). 2_1-Helical columns with the same torsion angle form a 2D layered structure along the *a*-axis by means of hydrogen bonds and ionic bonds (Figure 2c, indicated by red-colored dotted borders). Chiral cavities are formed by alternately arranging these 2D layered structures with different torsion angles of **1**, as shown in Figure 2c. The MeOH guest molecules (Figure 2, indicated in red or as red-colored space-filling molecules) are incorporated into the chiral cavities. In contrast to complex **I**, these 2D layered structures are maintained by aromatic−aromatic edge-to-face interactions (2.77 Å, Figure 2c, represented by red-colored arrows) between the hydrogen atom of the aromatic ring of **1** in a 2D layered structure and that of the aromatic ring of **1** in its neighboring 2D layered structure.

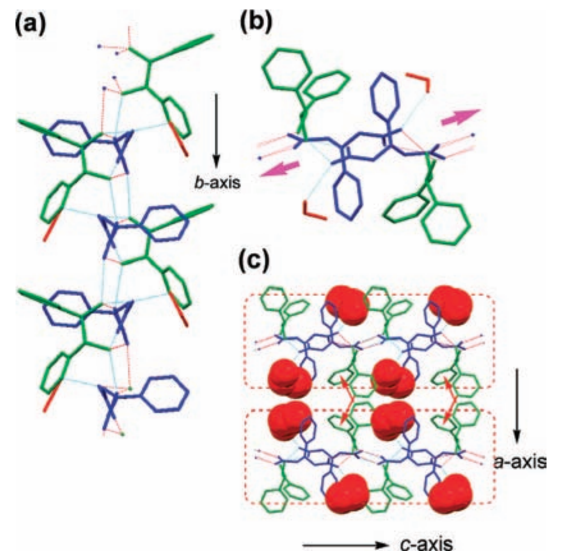

Figure 3. Crystal structure of complex **III**. (1*R*,2*R*)-**1**, **2**, and EtOH are represented by green-, blue-, and red-colored molecules, respectively. (a) 2_1-Helical column structure parallel to the *b*-axis. (b) View down the *b*-axis. The purple-colored arrows show intercolumnar interactions. (c) Packing structure comprising the 2D layered structure observed along the *b*-axis. The red-colored dotted borders indicate the 2D layered structure. The red-colored arrows show aromatic−aromatic edge-to-face interactions.

The crystal structure of complex **III** that includes EtOH molecules is shown in Figure 3.[6] The X-ray crystallographic analysis of **III** reveals that although the stoichiometry of this complex is different from that of **II** ((1*R*,2*R*)-**1**:**2**:EtOH = 1:1:1), the space group is $P2_12_12$. This complex has the same characteristic 2_1-helical column as that in complex **II** (Figure

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(5) Crystallographic data of **II:** $2C_{14}H_{16}N_2{\cdot}2C_{10}H_{11}O_4N_1{\cdot}2.5CH_4O$, $M = 923.08$, Monoclinic, space group $P2_1$, $a = 10.5997(7)$, $b = 10.0573(7)$, $c = 23.8770(17)$ Å, $\beta = 97.5940(10)°$, $U = 2523.1(3)$ Å^3, $Z = 2$, $D_c = 1.215$ g cm^{-3}, μ(Mo Kα) = 0.086 mm^{-1}, 15782 reflections measured, 9679 unique, final $R(F^2) = 0.0636$ using 8334 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0745, $T = 130(2)$ K. CCDC 691726.

3a and b). In contrast to chiral complex **II**, complex **III** has only one type of 2_1-helical column, in which the torsion angle of **1** is −41.68°. Furthermore, the 2_1-helical columns in this complex form a 2D layered structure along the *c*-axis (Figure 3c, represented by red-colored dotted borders). The interactions between the layers are aromatic−aromatic edge-to-face interactions that occur between the hydrogen atom of the aromatic ring of **1** in a 2D layered structure and that of the aromatic ring of **1** in its neighboring 2D layered structure (2.58 Å, Figure 3c, indicated by red-colored arrows), thereby forming chiral cavities (Figure 3c). The guest EtOH molecules (Figure 3, indicated in red color or as red-colored space-filling molecules) are incorporated into these chiral cavities.

Although the 2D layered structures of chiral complexes **II** and **III** are almost the same, the packing of the neighboring 2D layered structures in these complexes is slightly different. This shows that in this system as well, the size and shape of the cavities can be tuned in accordance with guest molecules because the cavities are formed by the self-assembly of 2D layered structures without strong interactions. As compared to previously reported host complexes containing a helical column without strong intercolumnar interactions,[3] the movement and rotation of the helical column in this 2D layered host complex are restricted. Therefore, in the developed system, the molecular recognition properties for guest molecules are expected to be different from those in the previously reported helical column host system.

However, a comparison of *rac*-complex **I** with chiral complexes **II** and **III** reveals that the 2_1-helical columns and 2D layered structures of each complex are the same. From this result, it is thought that 2D layered structures are also formed in the *rac*-**1**/**2** host system from the EtOH solution. However, since these 2D layered structures are unable to be densely packed by the interactions with guest EtOH molecules, poor-quality powder-like solids are obtained. This shows that the host system exhibits the property of molecular recognition for guest molecules.

In conclusion, a novel 2D layered supramolecular host system composed of two component molecules was developed. By using *N*-phenyliminodiacetic acid as a component molecule, a 2_1-helical column composed of 1,2-diphenylethylenediamine formed a 2D layered structure through hydrogen bonds and ionic bonds. This host system can accommodate guest molecules by tuning the packing of the 2D layered structure in accordance with guest molecules. Thus far, although 1,2-diphenylethylenediamine has been used as a building block in the supramolecular host complex,[3] this is the first 2D layered supramolecular host system derived from a 2_1-helical column composed of 1,2-diphenylethylenediamine. It is expected that these complexation characteristics and crystal structure data will provide useful information on the design of novel 2D- or 3D-network supramolecular host systems.

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Supporting Information Available: Crystallographic data in CIF format of complexes **I**−**III**, materials, and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystallographic data of **III:**$C_{14}H_{16}N_2{\cdot}C_{10}H_{11}O_4N_1{\cdot}C_2H_6O$, $M = 467.55$, Orthorhombic, space group $P2_12_12$, $a = 23.871(2)$, $b = 10.0306(9)$, $c = 10.6407(9)$ Å, $U = 2547.8(4)$ Å^3, $Z = 4$, $D_c = 1.219$ g cm^{-3}, μ(Mo Kα) = 0.089 mm^{-1}, 13037 reflections measured, 4348 unique, final R(F^2) = 0.0749 using 3749 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0869, T = 120(2) K. CCDC 691727. These 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 CB21EZ, U.K.; fax (+44)1223-336-033; deposit@ccdc.cam.ac.uk).