Tuning Mechanism in a Two-Component Columnar Host System Composed of 1,2-Diphenylethylenediamine and 1,1′-Binaphthyl-2,2′-dicarboxylic Acid

Yoshitane Imai,[*,†] **Kakuhiro Kawaguchi,**[†] **Katuzo Murata,**[†] **Tomohiro Sato,**[‡] **Reiko Kuroda,**[‡,§] **and Yoshio Matsubara**[*,†]

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan, JST ERATO-SORST Kuroda Chiromorphology Team, 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041, Japan, and Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo, 153-8902, Japan

y-imai@apch.kindai.ac.jp; y-matsu@apch.kindai.ac.jp

ABSTRACT
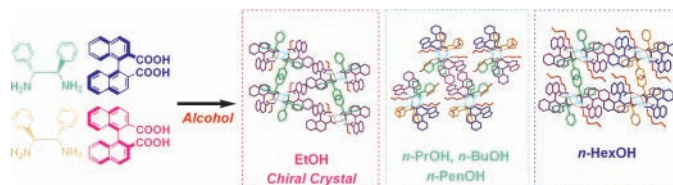
In a two-component columnar host system composed of racemic (*rac*)-1,2-diphenylethylenediamine and *rac*-1,1′-binaphthyl-2,2′-dicarboxylic acid, a cavity tuning mechanism resulted from changes in the structure of the columns using a specific combination of the following four molecules: (1*R*,2*R*)-1, (1*S*,2*S*)-1, (*R*)-2, and (*S*)-2.

Many organic supramolecular host−guest systems have been reported, and increasing attention has been devoted to the possibility of modulating the size and shape of cavities in order to include various guest molecules and increase the molecular recognition ability of the complexes.[1] In order to achieve this, supramolecular organic host systems composed of two molecules have been developed.[2] These systems allow the precise control of the cavity by varying the arrangement of the two-component molecules in the crystalline state. We have recently developed a two-component host system that capitalizes on a hydrogen- and ionic-bonded network. Chiral 1,2-diphenylethylenediamine is used as one of the two components; the other one is biphenylacetic acid, diphenic acid, or 1,1′-binaphthyl-2,2′-dicarboxylic acid.[3] Characteristically, these host systems are formed by the self-assembly of

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† Kinki University.
‡ JST ERATO-SORST Kuroda Chiromorphology Team.
§ The university of Tokyo.

(1) (a) Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds. *Inclusion Compounds*; Academic Press: New York, 1984; Vols. 1−3. (b) Walba, D. M.; Clark, N. A.; Razavi, H. A.; Parmar, D. S. In *Inclusion Phenomenon and Molecular Recognition*; Atwood, J. L., Ed.; Plenum Press: New York, 1990. (c) Lehn, J.-M., Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Eds. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vols. 1−11. (d) Atwood, J. L., Steed, J. W., Eds. *Encyclopedia of Supramolecular Chemistry*; Mercel Dekker: New York, 2004. (e) Toda, F., Bishop, R., Eds. *Perspectives in Supramolecular Chemistry*; John Wiley & Sons: Chichester, UK, 2004; Vol. 8.

(2) (a) Sada, K.; Shiomi, N.; Miyata, M. *J. Am. Chem. Soc.* **1998**, *120*, 10543. (b) Nakano, K.; Hishikawa, Y.; Sada, K.; Miyata, M.; Hanabusa, K. *Chem. Lett.* **2000**, 1170. (c) Kobayashi, Y.; Kodama, K.; Saigo, K. *Org. Lett.* **2004**, *6*, 2941. (d) Kodama, K.; Kobayashi, Y.; Saigo, K. *Chem.−Eur. J.* **2007**, *13*, 2144. (e) Imai, Y.; Kawaguchi, K.; Murata, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Chem. Lett.* **2007**, 812. (f) Kodama, K.; Kobayashi, Y.; Saigo, K. *Cryst. Growth Des.* **2007**, *7*, 935. (g) Imai, Y.; Kawaguchi, K.; Murata, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Cryst. Growth Des.* **2007**, *7*, 1676 and references cited therein.

(3) (a) Imai, Y.; Sato, T.; Kuroda, R. *Chem. Commun.* **2005**, 3289. (b) Imai, Y.; Takeshita, M.; Sato, T.; Kuroda, R. *Chem. Commun.* **2006**, 1070. (c) Imai, Y.; Kawaguchi, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron Lett.* **2006**, *47*, 7885. (d) Imai, Y.; Kawaguchi, K.; Asai, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *CrystEngComm* **2007**, *9*, 467.

a 1D columnar hydrogen- and ionic-bonded network structure that lacks strong interactions between individual columns. Therefore, these systems can include guest molecules by changing the packing arrangement of the 1D columns.

In this paper, we report a new type of tuning mechanism in a two-component columnar host system. A diamine molecule, racemic (*rac*)-1,2-diphenylethylenediamine (*rac*-**1**) (an equimolar mixture of (1*R*,2*R*)-**1** and (1*S*,2*S*)-**1**), and dicarboxylic acid, *rac*-1,1′-binaphthyl-2,2′-dicarboxylic acid (*rac*-**2**), were used as the component molecules.
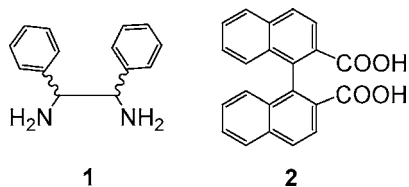
Recently, it has been reported that a *rac*-**1**−*rac*-**2** host system can contain *n*-propanol (*n*-PrOH), *n*-butanol (*n*-BuOH), and *n*-pentanol (*n*-PenOH) as guest molecules.[4] The obtained complexes consist of a similar 1D columnar supramolecular hydrogen- and ionic-bonded network (Figure 1). This 1D column (blue circle in Figure 1), which is
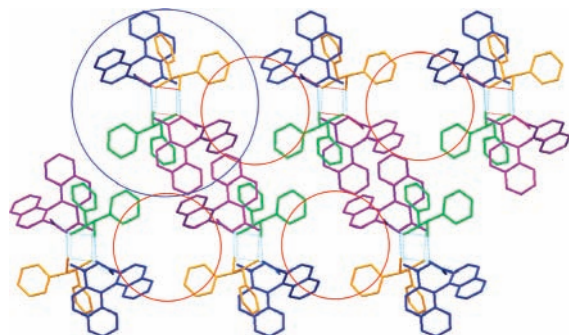

Figure 1. Cavities formed by self-assembly of 1D column composed of (1*R*,2*R*)-**1** (indicated in green), (1*S*,2*S*)-**1** (orange), (*R*)-**2** (blue), and (*S*)-**2** (purple) molecules. The blue and red circles indicate 1D column and cavities containing the guest molecules, respectively. Guest molecules are omitted.

pseudo-centrosymmetric, is composed of (1*R*,2*R*)-**1** (Figure 1, indicated in green), (1*S*,2*S*)-**1** (orange), (*R*)-**2** (blue), and (*S*)-**2** (purple) molecules, and their linkages consist mainly of ammonium hydrogen atoms obtained by the protonation of an amine in **1** and carboxylate oxygens from the carboxylic acid anion of **2**. Cavities (red circles in Figure 1) that contain the guest molecules are formed by the self-assembly of this 1D column. These cavities can include *n*-alkyl alcohol molecules by changing the packing arrangement of the 1D columns.

In this study, in order to investigate the tuning mechanism of the cavity in detail, two *n*-alkyl alcohols with longer or

shorter alkyl chains [*n*-hexanol (*n*-HexOH) and ethanol (EtOH)] were used as the guests. The inclusion of guest molecules was carried out by crystallizing the complex from the "guest solutions" in which **1** and **2** were dissolved in a solution of the guest molecule.[5] As a result, an inclusion complex [**I** for the *n*-HexOH system (12 mg)[6] and **II** for the EtOH system (14 mg)[7]] was obtained from each solution. In order to investigate the inclusion mechanism of this system, the resulting crystals were subjected to X-ray analysis. The structure of crystal **I** is shown in Figure 2.[8]

The stoichiometry of crystal **I** is (1*R*,2*R*)-**1**:(1*S*,2*S*)-**1**:(*R*)-**2**:(*S*)-**2**:*n*-HexOH = 0.5:0.5:0.5:0.5:1, and its space group is $P2_1/c$. This complex also possesses a columnar supramolecular hydrogen- and ionic-bonded network along the *b*-axis (Figure 2a,b). The column structure, a chiral 2_1-helical column structure along the *b*-axis, is different from that of past complexes. The complex consists of two types of chiral 2_1-helical columns with opposite chiralities—one is composed of (1*R*,2*R*)-**1** (Figure 2, indicated in green) and (*S*)-**2** (purple), and the other is composed of (1*S*,2*S*)-**1** (orange) and (*R*)-**2** (blue). In both of the columns, the linkages consist mainly of ammonium hydrogen atoms from protonated amines in **1** and carboxylate oxygens from the carboxylic acid anion of **2**. Each column interacts via the naphthalene−naphthalene edge-to-face interactions along the *c*-axis (2.93 Å, indicated by red arrows in Figure 2c). The self-assembly of these 2_1-helical columns with different chiralities leads to the formation of channel-like cavities along the *b*-axis (Figure 2c). *n*-HexOH is trapped one-dimensionally along the direction of the cavity by the hydrogen bonding between the hydroxyl group of *n*-HexOH and either the amino group of **1** or the carboxyl group of **2**.

The structure of crystal **II** containing EtOH is shown in Figure 3.[9]

This crystal also comprises a 2_1-helical columnar supramolecular hydrogen- and ionic-bonded network composed of (1*R*,2*R*)-**1** (Figure 3, indicated in green) and (*S*)-**2** (purple), similar to crystal **I** (Figure 3a,b). However, the packing style of this 2_1-column is different from that of complex **I** (Figure 3c). Interestingly, crystal **II** is formed by the self-assembly of a 2_1-column structure with the same chirality. That is, this crystal is a chiral crystal, and the formed channel-like

(4) Imai, Y.; Kawaguchi, K.; Tajima, N.; Sato, T.; Kuroda, R.; Matsubara, Y. *Chem. Commun.* **2008**, 362.

(5) A mixture of (1*R*,2*R*)-**1** (5 mg, 0.024 mmol), (1*S*,2*S*)-**1** (5 mg, 0.024 mmol), (*R*)-**2** (8 mg, 0.024 mmol), and (*S*)-**2** (8 mg, 0.024 mmol) was dissolved in *n*-HexOH or EtOH (2 mL) and left to stand at room temperature. After a few days, several colorless crystals were produced.

(6) This weight is the total crop of obtained crystals in one batch.

(7) This weight is the total crop of obtained chiral crystals in one batch.

(8) Crystallographic data of **I**: $C_{14}H_{18}N_2′C_{22}H_{12}O_4′C_6H_{14}O$, $M = 656.79$, monoclinic, space group $P2_1/c$, $a = 10.468(1)$, $b = 10.849(1)$, $c = 29.562-(3)$ Å, $\beta = 95.784(2)°$, $U = 3340.1(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.306$ g·cm^{-3}, μ(Mo Kα) = 0.085 mm^{-1}, 27758 reflections measured, 7702 unique, final $R(F^2) = 0.0831$ using 5289 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.1319, $T = 120(2)$ K; CCDC 652860.

(9) Crystallographic data of **II**: $C_{14}H_{18}N_2′C_{22}H_{14}O_4′C_2H_6O$, $M = 600.69$, orthorhombic, space group $P2_12_12_1$, $a = 10.204(1)$, $b = 10.835(1)$, $c = 27.774(3)$ Å, $U = 3070.5(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.299$ g·cm^{-3}, μ(Mo Kα) = 0.086 mm^{-1}, 27237 reflections measured, 7099 unique, final $R(F^2) = 0.0671$ using 4689 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.1169, $T = 120(2)$ K; CCDC 668015. 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, UK; fax: (+44)1223−336-033; deposit@ccdc.cam.ac.uk).
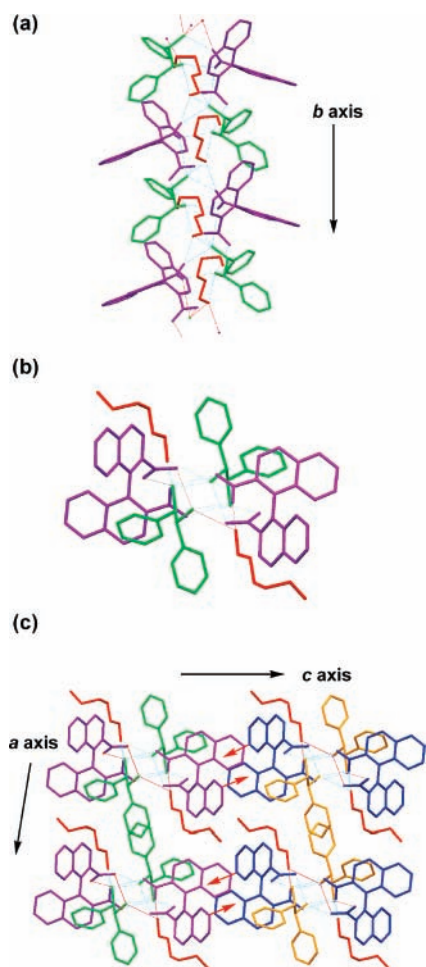
Figure 2. Crystal structure of complex **I**. (a) Column structure is parallel to the *b*-axis. (b) View down the *b*-axis. (c) Packing structure observed along the *b*-axis. The red arrows indicate naphthalene−naphthalene edge-to-face interactions.

Figure 3. Crystal structure of complex **II**. (a) Column structure is parallel to the *b*-axis. (b) View down the *b*-axis. (c) Packing structure observed along the *b*-axis. The red molecules indicate EtOH. The red and purple arrows indicate naphthalene−naphthalene edge-to-face and benzene−naphthalene edge-to-face interactions, respectively.

cavities have the same chirality in one crystal. The space group is $P2_12_12_1$, and the stoichiometry of (1*R*,2*R*)-**1**:(*S*)-**2**: EtOH = 1:1:1. Each column interacts via naphthalene−naphthalene edge-to-face and benzene−naphthalene edge-to-face interactions along the *c*-axis (2.49 and 2.75 Å, indicated by red and purple arrows in Figure 3c, respectively). EtOH is trapped one-dimensionally along the direction of the chiral channel-like cavity by the hydrogen bonding between the hydroxyl group of EtOH and either the amino group of **1** or the carboxyl group of **2**. In one batch, chiral crystals with an opposite chirality to crystal **II** were obtained. These results suggest that this system may be induced and controlled to form chiral crystals according to the guest achiral *n*-alkyl alcohol.

In conclusion, from X-ray crystallographic analyses, it can be observed that, in this two-component host system composed of *rac*-1,2-diphenylethylenediamine and *rac*-1,1′-binaphthyl-2,2′-dicarboxylic acid, suitable cavities are formed via recognition of the guest molecule in two steps. In the first step, a 1D columnar structure suitable for the guest molecule is 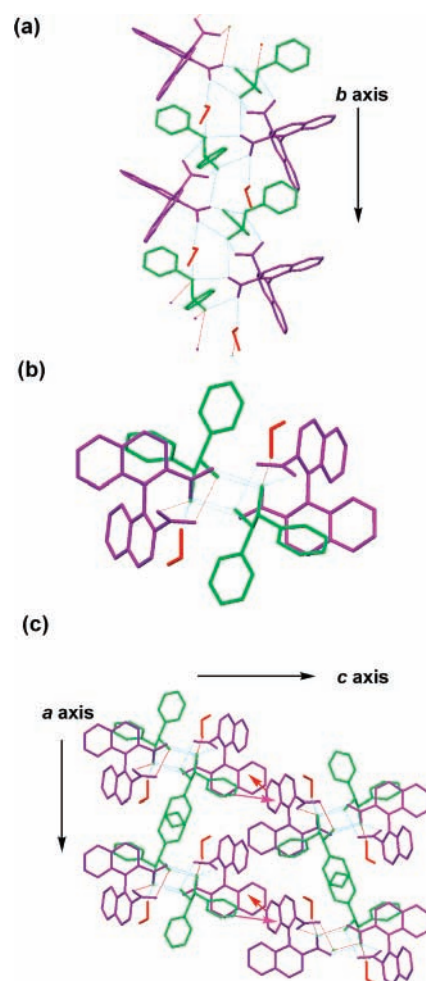formed by selecting a combination from among the four molecules [(1*R*,2*R*)-**1**, (1*S*,2*S*)-**1**, (*R*)-**2**, and (*S*)-**2**], and in the second step, achiral (or chiral) cavities suitable for the guest molecule are formed by a variation in the 1D column packing arrangement. Until now, the solvent effect in the hydrogen-bonded network structure has not been widely studied.[10] This study is expected to be useful for analyzing the inclusion mechanisms of multicomponent host systems and designing new types of molecular host systems.

Supporting Information Available: Crystallographic reports (CIF) of complexes **I** and **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Kojima, M. *J. Am. Chem. Soc.* **2002**, *124*, 629. (b) Khatua, S.; Harada, T.; Kuroda, R.; Bhattacharjee, M. *Chem. Commun.* **2007**, 3927.