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Formation of chiral 2_1-helical columnar host system with phenylacetylene unit by using (1*R*,2*S*)-2-amino-1,2-diphenylethanol

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Abstract

A tunable supramolecular phenylacetylene host system with a chiral channel-like cavity is developed by using (1*R*,2*S*)-2-amino-1,2-diphenylethanol. This host system possesses a chiral 2_1-helical columnar structure; chiral cavities are constructed by the self-assembly of the 2_1-helical column, and guest molecules are included by varying the packing of this column.

Keywords: (1*R*,2*S*)-2-Amino-1,2-diphenylethanol; 2_1-Helical column; Phenylacetylene; Solid-state host system; Supramolecule

1. Introduction

In the field of host–guest chemistry, solid-state fluorescence host systems have received considerable interest as molecular host systems because the solid-state optical properties of organic compounds are different from their solution-state properties.[1] In particular, supramolecular organic fluorescence host systems comprising two or more organic molecules have been developed, because the physical and chemical properties of these supramolecular host systems can be controlled easily by simply changing the component molecules.[2] However, it is not easy to forecast the structure of supramolecular organic complexes for new component molecules. Moreover, a supramolecular fluorescence host system with a chiral cavity has not been reported. Therefore, the method of obtaining structural information on chiral supramolecular organic complexes by using basic fluorescence supramolecular building blocks has attracted considerable attention as a bottom-up approach for studying supramolecular fluorescence chemistry. Recently, we developed a solid-state fluorescence host system by using a chiral supramolecular organic fluorophore possessing a chiral channel-like cavity.[3] This supramolecular fluorophore comprises (1*R*,2*S*)-2-amino-1,2-diphenylethanol [(1*R*,2*S*)-**1**] as the chiral unit and 2-anthracenecarboxylic acid as the fluorescence unit. In this host system, guest molecules can be discharged from and adsorbed into a channel-like cavity, and the solid-state fluorescence of the complex changes depending on the presence of guest molecules.

In this paper, we report the formation and structural information on a chiral supramolecular organic host system by employing a novel combination of supramolecular building blocks—(1*R*,2*S*)-**1** and phenylacetylenecarboxylic acid (**2**). Recently, several organic fluorophores comprising a single molecule possessing a phenylacetylene unit have been developed by expanding π-conjugated systems in order to increase the photoluminescence quantum yield and tune the fluorescence wavelength.[4] Therefore, **2**, which is the most basic unit of the phenylacetylene unit, is used as a supramolecular building block although itself hardly has the fluorescence property.[5] For guest molecules, three kinds of *n*-alkyl alcohols—*n*-propanol (*n*-PrOH), *n*-butanol (*n*-BuOH), and

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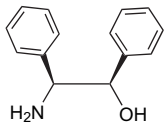
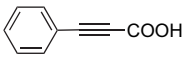
n-pentanol (*n*-PenOH)—possessing different alkyl chain lengths are used in order to study the influence of the size of the constituent guest molecule on the host system. It is expected that this study will provide useful information on the construction of novel supramolecular fluorescence host systems with a phenylacetylene unit.



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



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2. Results and discussion

We attempted to prepare the supramolecular host complex by crystallization from guest solutions. A mixture of (1*R*,2*S*)-**1** and **2** was dissolved in *n*-PrOH and left to stand at room temperature. After a few days, colorless crystals **I** were obtained. From X-ray crystal structure analysis, these crystals were found to comprise (1*R*,2*S*)-**1** and **2**, as shown in Figure 1.

The stoichiometry of complex **I** is (1*R*,2*S*)-**1**/**2**/*n*-PrOH=1:1:1, and the space group is $P2_12_12_1$. This crystal has a characteristic 2_1-helical columnar network structure along the *a*-axis (Fig. 1a and b), which is mainly formed by two types of bonds. One is an ionic bond between the ammonium hydrogen of the protonated amine (Fig. 1, indicated by green molecules) and the carboxylate oxygen of the carboxylic acid anion (Fig. 1, indicated by blue molecules). The other is a hydrogen bond formed by the hydroxyl group of (1*R*,2*S*)-**1**. Expectedly, complex **I** is formed by the self-assembly of the 2_1-column, which gives rise to chiral channel-like cavities (Fig. 1c). Characteristically, these channel-like cavities are maintained by benzene–benzene edge-to-face interactions (2.97 Å, Fig. 1c, indicated by red arrows) between the hydrogen atom of the benzene ring in **2** and the benzene ring of (1*R*,2*S*)-**1**. The guest molecules, *n*-PrOH molecules (Fig. 1, shown as red space-filling molecules), are trapped one-dimensionally along the direction of the cavity. Each *n*-PrOH molecule is connected to the column by a hydrogen bond between its own hydroxyl group and the carboxyl group of **2** and between its own hydroxyl group and the amino group of (1*R*,2*S*)-**1**.

In complex **I**, because the cavities are formed by the self-assembly of the 2_1-helical columns without strong interactions, the size and shape of the cavities can be varied. Therefore, a variety of guest molecules may be included by varying these parameters. Further, the complexation behavior of two other types of *n*-alkyl alcohol with longer alkyl chains (*n*-BuOH and *n*-PenOH) was investigated by using them as guest molecules. Good quality colorless crystals, **II** and **III**, were obtained from *n*-BuOH and *n*-PenOH solutions, respectively, and their crystal structures were analyzed. The crystal structure of complex **II** containing *n*-BuOH is shown in Figure 2.

X-ray analysis revealed that the stoichiometry of these complexes is the same as that of **I**, i.e., (1*R*,2*S*)-**1**/**2**/*n*-BuOH=1:1:1, with the same $P2_12_12_1$ space group. Expectedly, these crystals share the characteristic 2_1-helical columnar structure observed in crystal **I** (Fig. 2a). Moreover, the chiral channel-like cavities of these complexes are formed by the self-assembly of a 2_1-helical column, and the packing style of this column is similar to that of complex **I**. In these complexes also, the *n*-BuOH guest molecules (Fig. 2, shown as

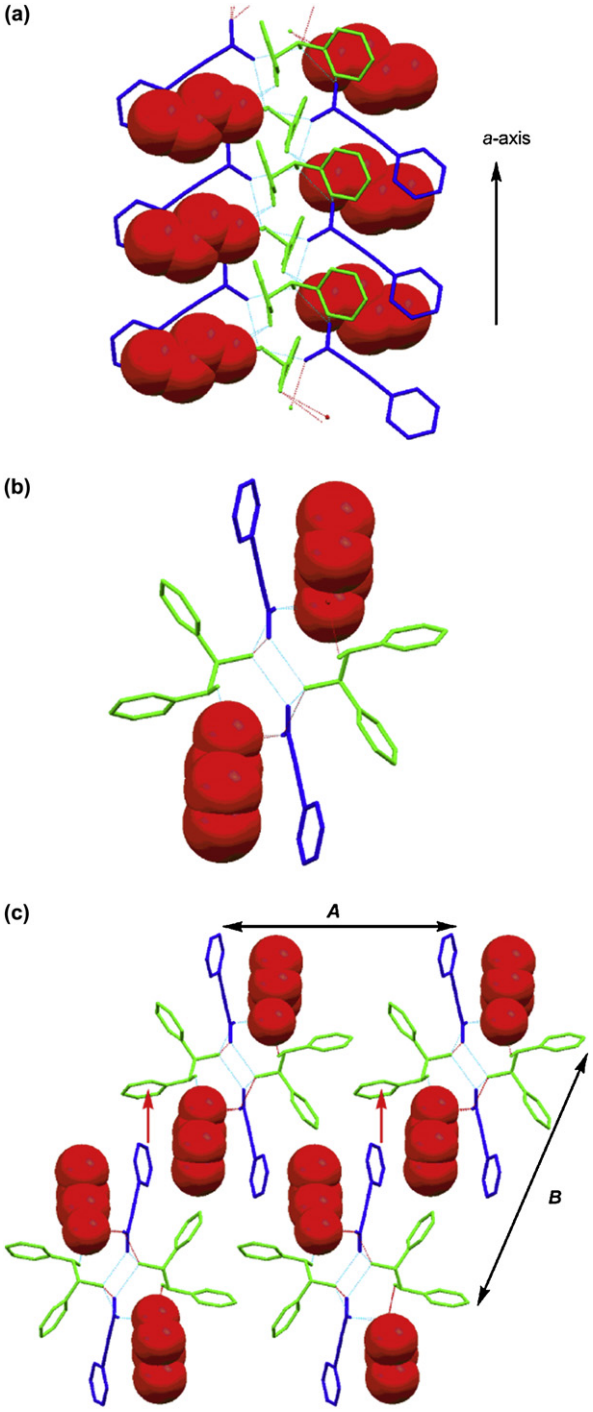

Figure 1. Crystal structure of complex **I**. *n*-PrOH molecules are shown as red space-filling molecules. (a) The 2_1-helical columnar hydrogen- and ionic-bonded network is parallel to the *a*-axis. (b) View down the *a*-axis. (c) Packing structure observed along the *a*-axis. Red arrows indicate benzene–benzene edge-to-face interactions.

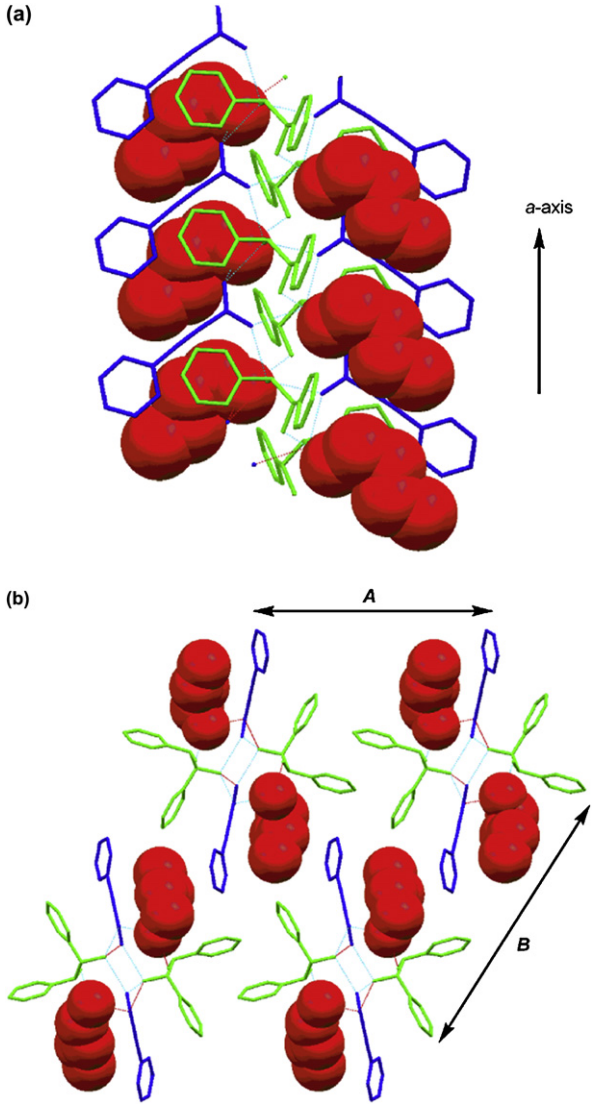

Figure 2. Crystal structure of complex **II**. (1*R*,2*S*)-**1** and **2** are shown as green and blue molecules, respectively. *n*-BuOH molecules are shown as red space-filling molecules. (a) The 2_1-helical columnar hydrogen- and ionic-bonded network is parallel to the *a*-axis. (b) Packing structure observed along the *a*-axis.

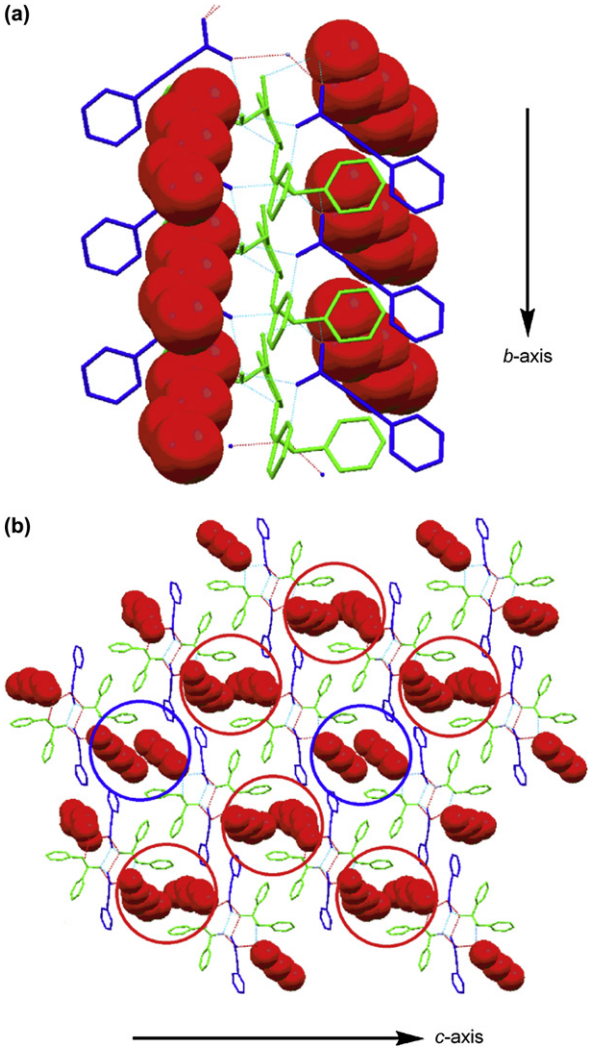

Figure 3. Crystal structure of complex **III**. (1*R*,2*S*)-**1** and **2** are shown as green and blue molecules, respectively. *n*-PenOH molecules are shown as red space-filling molecules. (a) The 2_1-helical columnar hydrogen- and ionic-bonded network is parallel to the *b*-axis. (b) Packing structure observed along the *b*-axis.

red space-filling molecules) are trapped in the cavities by two hydrogen bonds that occur between the hydroxyl group of the guest molecules and the carboxyl group of **2** and between the hydroxyl group of the guest molecules and the amino group of (1*R*,2*S*)-**1**. Although the packing style of the column is similar to that of complex **I**, the size of the chiral channel-like cavity varies. As the alkyl chain of *n*-alkyl alcohol becomes longer (from *n*-PrOH to *n*-BuOH), the distance between the 2_1-helical columns along the *b*-axis (***A***, Figs. 1c and 2b) decreases (14.53 and 14.40 Å for **I** and **II**, respectively), while the distance between the 2_1-helical columns along the *c*-axis (***B***, Figs. 1c and 2b) increases (18.15 and 18.21 Å for **I** and **II**, respectively). This shows that this host system can include guest molecules by varying the shared 2_1-helical columns.

Furthermore, the crystal structure of complex **III**, which contains *n*-PenOH, is studied and shown in Figure 3.

X-ray analysis revealed that this inclusion crystal has the same stoichiometry as that of the previously described crystals **I** and **II**, i.e., (1*R*,2*S*)-**1**/**2**/*n*-PenOH=1:1:1, and the $P2_1$ space group. This crystal also shows the same 2_1-helical columnar hydrogen- and ionic-bonded network that is observed in crystals **I** and **II** (Fig. 3a). The chiral channel-like cavities of these complexes are formed by the self-assembly of the 2_1-helical column (Fig. 3b). *n*-PenOH molecules (Fig. 3, indicated as red space-filling molecules) are trapped as guests in the cavities by the same hydrogen bonds as in the case of crystals **I** and **II**. Interestingly, in this complex, the packing style of the 2_1-helical column is quite different from that for complexes **I** and **II** (Fig. 3b). In other words, two *n*-PenOH guest molecules are included in one cavity when observed along the column. Moreover, *n*-PenOH molecules are arranged in two types of inclusion styles in the cavities (red and blue circles, respectively). From these results, it is inferred that this host

system can dramatically change the packing style of the shared 2_1-helical columns for large guest molecules.

Recently, we have reported that the photoluminescence quantum yield of complex is increased compared to that of the component fluorescent molecule by supramolecular complexation.[6] Then, the fluorescence properties of these complexes were studied. However, the absolute values of the photoluminescence quantum yields (Φ_F) in complexes **I**–**III** were 0.01 or less in the solid state.

3. Conclusion

A chiral host system with a crystal structure is formed by combining (1*R*,2*S*)-2-amino-1,2-diphenylethanol and phenylacetylenecarboxylic acid. All the complexes produced share the chiral 2_1-helical columnar structure; chiral channel-like cavities are constructed by the self-assembly of this column, and guest molecules can be included by varying the packing of this column. Until now, although 2-amino-1,2-diphenylethanol is used as a unit of host complex, this is the first information on the complexation with acetylenecarboxylic acid group.[7] It is expected that these complexation characteristics and the crystal structure data will provide useful information on the design of novel chiral supramolecular fluorescence host systems possessing a *long* π-conjugated phenylacetylene unit.

4. Experimental

4.1. General methods

All reagents were used directly as obtained commercially. Component molecule (1*R*,2*S*)-**1** was purchased from Tokyo Kasei Kogyo Co. Component molecule **2** and guest solutions were purchased from Wako Pure Chemical Industry.

4.2. Formation of host complex

(1*R*,2*S*)-**1** (10 mg, 0.047 mmol) and **2** (7 mg, 0.048 mmol) were dissolved in an *n*-alkyl alcohol (2 mL). After 1–4 days, colored crystals [crystal **I** for *n*-PrOH (7 mg), crystal **II** for *n*-BuOH (8 mg), and crystal **III** for *n*-PenOH (7 mg)] were deposited and collected, respectively. This weight is the total crop of obtained crystals in one batch.

4.3. X-ray crystallographic study of crystal

X-ray diffraction data for single crystals were collected using *BRUKER APEX*. The crystal structures were solved by the direct method[8] and refined by full-matrix least-squares using *SHELX97*.[9] The diagrams were prepared using *PLATON*.[10] Crystallographic data for **I**: $C_{14}H_{15}NO\cdot C_9H_6O_2\cdot C_3H_8O$, M=419.50, orthorhombic, space group $P2_12_12_1$, a=6.0736(5), b=14.5337(12), c=26.171(2) Å, U=2310.1(3) Å^3, Z=4, Dc=1.206 g cm^{-3}, μ(Mo Kα)=0.081 mm^{-1}, 20,462 reflections measured, 3119 unique, final $R(F^2)$=0.0674 using 2546 reflections with $I>2.0\sigma(I)$, R(all data)=0.0893, T=120(2) K. CCDC 676466. Crystallographic data for **II**: $C_{14}H_{15}NO\cdot C_9H_6O_2\cdot C_4H_{10}O$, M=433.53, orthorhombic, space group $P2_12_12_1$, a=6.2169(6), b=14.3972(14), c=26.154(3) Å, U=2341.0(4) Å^3, Z=4, Dc=1.230 g cm^{-3}, μ(Mo Kα)=0.082 mm^{-1}, 14,473 reflections measured, 3138 unique, final $R(F^2)$=0.0523 using 2428 reflections with $I>2.0\sigma(I)$, R(all data)=0.0794, T=120(2) K. CCDC 676467. Crystallographic data for **III**: $3C_{14}H_{15}NO\cdot 3C_9H_6O_2\cdot 3C_5H_{12}O$, M=1342.66, monoclinic, space group $P2_1$, a=25.713(2), b=5.9107(5), c=25.857(2) Å, β=106.595(2)°, U=3766.1(6) Å^3, Z=2, Dc=1.184 g cm^{-3}, μ(Mo Kα)=0.078 mm^{-1}, 21,624 reflections measured, 8486 unique, final $R(F^2)$=0.0691 using 6326 reflections with $I>2.0\sigma(I)$, R(all data)=0.1004, T=120(2) K. CCDC 676468. In crystal **III**, the anomalies found with the temperature factors are due to disorderings. The correctness of the assignment of atomic species to those atoms was confirmed by inspecting hydrogen bond schemes. Crystallographic 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).

4.4. Measurement of solid-state fluorescence spectra

A solid-state fluorescence spectra and absolute photoluminescence quantum yields were measured by Absolute PL Quantum Yield Measurement System (C9920-02, HAMAMATSU PHOTONICS K. K.). The excitation wavelength for **2** and complexes **I**–**III** is 308, 311, 318, and 320 nm, respectively.

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