

A Solid-State Fluorescent Host System with a 2₁-Helical Column Consisting of Chiral (1*R*,2*S*)-2-Amino-1,2-diphenylethanol and Fluorescent 1-Pyrenecarboxylic Acid

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Abstract: A solid-state fluorescent host system was created by self-assembly of a 2₁-helical columnar organic fluorophore composed of (1*R*,2*S*)-2-amino-1,2-diphenylethanol and fluorescent 1-pyrenecarboxylic acid. This host system has a characteristic 2₁-helical columnar hydrogen- and ionic-bonded network. Channel-like cavities are formed by self-assembly of this column, and vari-

ous guest molecules can be included by tuning the packing of this column. Moreover, the solid-state fluorescence of this host system can change accord-

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ing to the included guest molecules. This occurs because of the change in the relative arrangement of the pyrene rings as they adjust to the tuning of the packing of the shared 2₁-helical column, according to the size of the included guest molecules. Therefore, this host system can recognize slight differences in molecular size and shape.

Introduction

In the field of host-guest chemistry, the development of a functional host system is an important issue. Recently, solid-state organic fluorescence host systems have attracted much attention because the solid-state optical properties of organic compounds are different from their solution-state properties.^[1]

In particular, from the viewpoint of synthesis and functionality, supramolecular organic fluorescence host systems composed of two or more organic molecules are increasingly desirable.^[2] That is, the resultant supramolecular organic fluorophore exhibits effective fluorescence properties owing to the synergistic effects of the packing style and the optical properties of the component molecules in the supramolecular complex. Recently, we developed chiral supramolecular organic fluorophores that exhibit circularly polarized luminescence (CPL) properties in the crystalline state by combining two types of organic molecules, that is, fluorescent 2-anthracenecarboxylic acid and chiral (1*R*,2*R*)-1,2-diphenylethylenediamine molecules.^[3] Moreover, a solid-state fluorescence host system composed of 2-anthracenecarboxylic acid and (1*R*,2*S*)-2-amino-1,2-diphenylethanol ((1*R*,2*S*)-**1**) was also developed. In this host system, the solid-state fluorescence of the complex changes according to the presence of included guest molecules.^[4] Thus, the structural, physical, and chemical properties of these supramolecular host systems can be controlled easily by simply changing the component molecules without the need for further synthesis. However, it is not so easy to predict these properties of supramolecular complexes when new component molecules are used.

Herein we report a solid-state host system that consists of two organic molecules. This host system can include a varie-

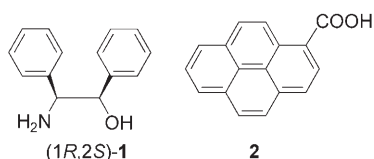
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ty of guest molecules and exhibits fluorescence properties. The first molecule is the fluorescent 1-pyrenecarboxylic acid (**2**), which is sterically larger than 2-anthracenecarboxylic



acid. The second molecule, (1*R*,2*S*)-**1**, was used because of the high possibility of forming columnar structures when using chiral acid/amine salts.^[4,5] That is, if the cavities are formed by the self-assembly of columns, the size and shape of the cavities may be tuned by changing the packing of these columns, and a variety of guest molecules may be included. For the guest molecules, four *n*-alkyl alcohols of differing chain lengths (MeOH, EtOH, *n*PrOH, and *n*BuOH) were used to study the influence of the size of the included guest molecule on this system.

Results and Discussion

The formation of supramolecular fluorescent organic host systems was attempted by crystallization from the four guest alcohol solutions. A mixture of (1*R*,2*S*)-**1** and **2** was dissolved in each of the guest alcohols and left to stand at room temperature. After a few days, colorless crystals of **I–IV** were obtained from the solutions in MeOH, EtOH, *n*PrOH, and *n*BuOH, respectively. These crystals were constructed from (1*R*,2*S*)-**1** and **2**, and included the alcohol as guest molecules.

The crystal forms and the solid-state fluorescence data of these complexes and of the component fluorescent molecule **2** are listed in Table 1 and their spectra are shown in Figure 1. Although many organic fluorophores lose this

Table 1. The crystal form and solid-state fluorescence spectral data of **I–IV** and fluorescent molecule **2**.

Complex	Color	Shape	λ_{em} [nm] ^[a]	ϕ_F
I	colorless	plate	483	0.08
II	colorless	plate	451	0.17
III	colorless	plate	477	0.07
IV	colorless	plate	461	0.18
2	yellow	powder	526	0.01

[a] The excitation wavelength is 379 nm in all cases.

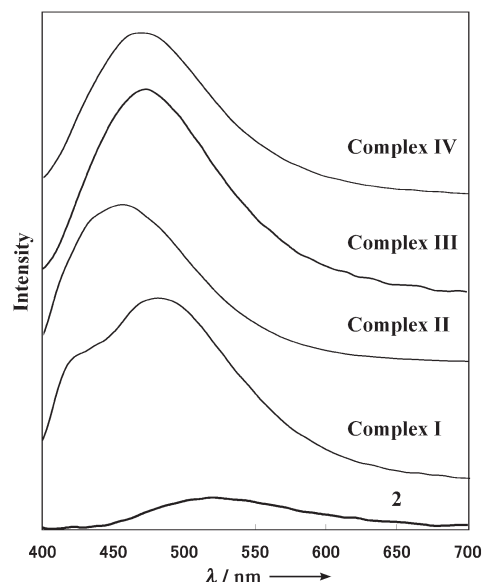


Figure 1. Solid-state fluorescence spectra of complexes **I–IV** and fluorescent molecule **2**. The excitation wavelength is 379 nm in all cases.

property in the solid state, complexes **I–IV** show fluorescence in the solid state. It is well known that oxygen molecules affect the transition fluorescence emission of the pyrene. Interestingly, although the absolute value of the photoluminescence quantum yield in component fluorescent molecule **2** is very small ($\phi_F=0.01$), that of complexes **I–IV** increased by 7–18 times relative to that of **2**, even in the presence of air. On comparison of these spectra with the published data of pyrene, it is thought that these complexes exhibit excimer emissions.^[6] Moreover, the solid-state fluorescence spectra depend on the included guest alcohols. As the alkyl-chain-length increases, the solid-state fluorescence maximum changes to a shorter wavelength, with the exception of complex **II**. These results suggest that this system can be used as a fluorescent host system for included guest molecules.

To study the guest-inclusion mechanism and fluorescence properties of this system, X-ray crystallographic analyses of these complexes were attempted. The structure of complex **I** including MeOH is shown in Figure 2. The stoichiometry of complex **I** is (1*R*,2*S*)-**1**/2/MeOH=1:1:1 and the space group is *C*2. As expected, this crystal has a 2₁-helical columnar supramolecular hydrogen- and ionic-bonded network along

Abstract in Japanese:

本研究では、光学活性分子アミノエタノール誘導体(1*R*,2*S*)-2-amino-1,2-diphenylethanol ((1*R*,2*S*)-**1**)と蛍光分子1-pyrenecarboxylic acid (**2**)とを組み合わせることにより、固体状態においてゲスト包接特性と蛍光特性を有する発光性ホストシステムの開発を行った。(1*R*,2*S*)-**1**と**2**をゲストMeOH、EtOH、*n*-PrOH、*n*-BuOH溶液からそれぞれ結晶化させたところ、対応するゲスト分子含有錯体(**I–IV**)を得た。これら錯体の固体状態蛍光スペクトルを測定したところ、蛍光スペクトルは、取り込むゲスト分子に応じて、違いが見られた。X線結晶構造解析の結果、すべての錯体は、構成分子である**1**と**2**のカルボキシル基とアミノ基による、類似した2₁-ヘリカルカラムを構築していたが、ゲスト分子に応じて、パッキング構造に大きな違いが見られた。蛍光スペクトルの違いは、このようなパッキング構造の違いに起因するものと考えられる。

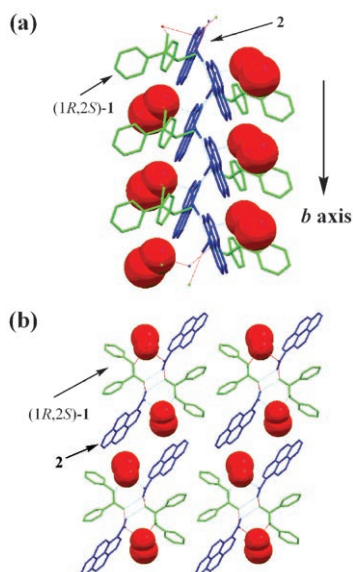


Figure 2. Crystal structures of complex **I**. a) 2_1 -Helical columnar hydrogen- and ionic-bonded network parallel to the b axis. b) Packing structure observed along the b axis.

the b axis (Figure 2a). This network is mainly formed by the ammonium hydrogen atom of one protonated amine and the carboxylate oxygen atom of a carboxylic acid anion. Chiral channel-like cavities are formed by self-assembly of this 2_1 -column (Figure 2b). In this cavity, MeOH (Figure 2, space-filling molecules) is included one-dimensionally along the direction of the cavity. Each MeOH molecule is connected to the 2_1 -column by two hydrogen bonds. One hydrogen bond is between the hydroxy group of MeOH and the carboxylate ion derived from **2**. The other is between the hydroxy group of MeOH and the hydroxy group of (1R,2S)-**1**.

In a similar way, we examined good-quality colorless crystals of **III** and **IV**, which were obtained from solutions in n PrOH and n BuOH, respectively. X-ray crystallographic analyses revealed that these inclusion crystals have the same stoichiometry and space group, that is, (1R,2S)-**1**/2/ n PrOH or n BuOH=1:1:1 and the space group is $P2_1$. The crystal structures of complex **III** are shown in Figure 3. Complex **III** also shows a similar 2_1 -helical columnar hydrogen- and ionic-bonded network, as in crystal **I** (Figure 3a). However, the packing style of this 2_1 -column is different from that of complex **I** (Figure 3b). In complex **I**, the channel-like cavity is surrounded by two pyrene groups when observed along the b axis, but in complex **III**, the channel-like cavity is surrounded by four pyrene groups and the volume of the cavity becomes larger than that of complex **I**. n PrOH (Figure 3, space-filling molecules) is included as a guest in the cavities by two hydrogen bonds between the hydroxy group of n PrOH and the carboxylate ion derived from **2**, and between the hydroxy group of n PrOH and the hydroxy group of (1R,2S)-**1**. In this complex, the channel-like cavity is maintained by benzene–pyrene edge-to-face interactions (Figure 3b, arrows, 2.97 Å).

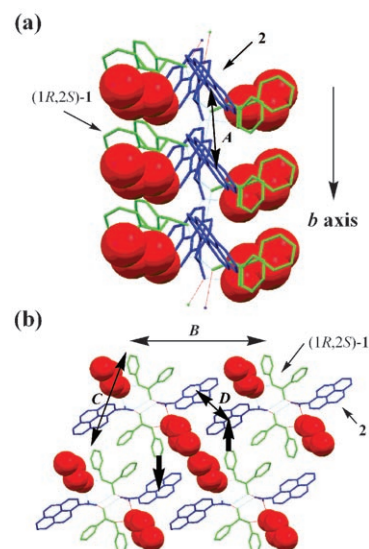


Figure 3. Crystal structures of complex **III**. a) 2_1 -Helical columnar hydrogen- and ionic-bonded network parallel to the b axis. b) Packing structure observed along the b axis. Arrows show benzene–pyrene edge-to-face interactions.

The crystals of complex **IV** also share a characteristic 2_1 -helical column structure, as in crystals **I** and **III** (Figure 4a). In addition, similar channel-like cavities are formed by the self-assembly of a 2_1 -column along the b axis, as in crystal **III** (Figure 4b).

In complexes **III** and **IV**, although the packing style of the 2_1 -column is almost the same, the size of the cavity changes according to the guest molecule. That is, as the alkyl chain of the n -alkyl alcohol becomes longer (from n PrOH to n BuOH), the distance between the 2_1 -columns (**B** and **C**,

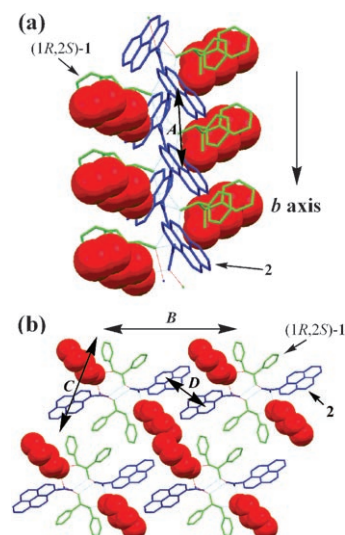


Figure 4. Crystal structures of complex **IV**. a) 2_1 -Helical columnar hydrogen- and ionic-bonded network parallel to the b axis. b) Packing structure observed along the b axis.

Figures 3b and 4b) becomes greater (17.77 Å to 17.96 Å and 13.55 Å to 13.70 Å, respectively).

As complex **II** obtained from EtOH formed only very thin crystals, X-ray crystallographic analysis was unsatisfactory. Therefore, X-ray powder diffraction analyses of all these crystals were attempted (Figure 5).

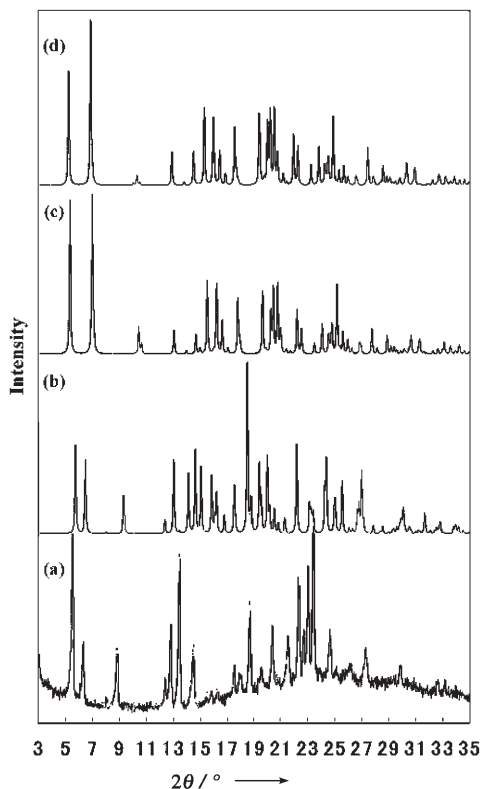


Figure 5. X-ray powder diffraction patterns of a) **II**, b) **I**, c) **III**, and d) **IV**.

The X-ray powder diffraction patterns of complexes **I–IV** are similar, especially at low angles. The X-ray powder diffraction patterns of complexes **III** and **IV** were almost identical, indicating that packing of the 2_1 -column is the same, even if the included alcohol is different (Figures 5c and d). Moreover, the ^1H NMR spectroscopic analysis of complex **II** reveals that it has the same stoichiometry, that is, (1*R*,2*S*)-**1**/**2**/EtOH = 1:1:1, as crystals **I**, **III**, and **IV**. From these results, it is assumed that complex **II** also shares a similar 2_1 -helical columnar hydrogen- and ionic-bonded network as the other complexes, but the packing of the 2_1 -column is different. In other words, this host system includes guest molecules by tuning the packing of the shared 2_1 -helical column.

In this host system, the photoluminescence quantum yield increases upon supramolecular complexation. Unfortunately, there is no crystal data for fluorescent component molecule **2** alone. However, it is reported that 1-naphthalenecarboxylic acid in its crystalline state exists as a dimer formed by hydrogen bonding of the carboxyl groups.^[7] Therefore, it can be inferred that **2** also exists as a similar dimer in the solid

state. On the other hand, in these complexes, **2** is built into a stronger helical columnar hydrogen- and ionic-bonded network that suppresses the concomitant nonradiative processes. Although the packing structures of **2** and these complexes cannot be compared directly, such a change in the bonding style of **2** in each complex probably also increases the photoluminescence quantum yield of complexes **I–IV**. Furthermore, the solid-state fluorescence spectra of this host system depend on the included guest molecules. From structural analyses, the relative arrangement of the pyrene rings in complexes **I**, **II**, and **III** (or **IV**) changes as they adjust to the tuning of the packing of the shared 2_1 -helical column, according to the size of the included alcohol. This tuning of the pyrene rings causes a guest dependency of the solid-state fluorescence spectra in complexes **I**, **II**, and **III** (or **IV**). On the other hand, although the packing of the shared 2_1 -helical column is similar in complexes **III** and **IV**, the solid-state fluorescence spectra are clearly different. From structural analyses, when comparing complex **III** with complex **IV**, the distance between the pyrene rings along the column increases from 6.06 Å to 6.15 Å (**A**, Figures 3a and 4a). Moreover, the intermolecular distance between the pyrene rings of adjoining 2_1 -columns (**D**, Figures 3b and 4b) increases from 6.17 Å to 6.33 Å. These changes in intermolecular distance between the adjoining pyrene rings cause the changes in the fluorescence spectra of complexes **III** and **IV**.

Conclusions

A novel supramolecular fluorescence host system with chiral channel-like cavities was successfully created by self-assembly of a 2_1 -helical columnar hydrogen- and ionic-bonded network composed of (1*R*,2*S*)-**1** and **2**. This host system shares a similar 2_1 -helical column structure; channel-like cavities are constructed by self-assembly of this 2_1 -column and guest molecules are included one-dimensionally along the cavity by tuning the packing of this column. Supramolecular complexation allows an increase in the photoluminescence quantum yield of the complexes relative to that of the component fluorescent molecule. The solid-state fluorescence spectra change according to the included guest molecules owing to the slight variation in molecular size and shape. This property further enriches the ability of the chiral fluorescence host system and could be of potential use in the design of novel solid-state fluorescence host systems for molecular recognition.

Experimental Section

Formation of Supramolecular Fluorescence Complexes with Guest Alcohol Molecules

(1*R*,2*S*)-**1** (10 mg, 0.047 mmol) and **2** (12 mg, 0.047 mmol) were dissolved in the respective *n*-alkyl alcohol (2 mL). After a few days, colorless crystals formed (**I** (10 mg) from MeOH, **II** (9 mg) from EtOH, **III** (8 mg) from *n*PrOH, and **IV** (8 mg) from *n*BuOH) and were collected. (The given weight is that of the total crop of crystals obtained in one batch.)

Measurement of Solid-State Fluorescence Spectra

Solid-state fluorescence spectra and absolute photoluminescence quantum yields were measured on an Absolute PL Quantum Yield Measurement System (C9920-02, Hamamatsu Photonics K.K.) under air at room temperature.

X-ray Crystallographic Study of **I**

X-ray diffraction data for single crystals were collected on a Bruker Apex. The crystal structures were solved by direct method and refined by full-matrix least-squares by using SHELX97. The diagrams were prepared with PLATON. Crystallographic data of **I**: C₁₄H₁₆NO·C₁₇H₉O₂·CH₄O, *M* = 491.56, monoclinic, space group *C*2, *a* = 30.857(4), *b* = 6.1523(7), *c* = 13.6925(15) Å, β = 98.788(2)°, *V* = 2568.9(5) Å³, *Z* = 4, ρ_{calcd} = 1.271 g cm⁻³, μ_{MoKα} = 0.083 mm⁻¹, 8030 reflections measured, 5266 unique, final *R*(*F*²) = 0.0600 by using 4528 reflections with *I* > 2σ(*I*), *R* (all data) = 0.0706, *T* = 120(2) K, CCDC-654189. Crystallographic data can be obtained free of charge at 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; e-mail: deposit@ccdc.cam.ac.uk).

X-ray Powder Diffraction Pattern of **II**

X-ray powder patterns were recorded on a Rigaku RINT2500 by using graphite-monochromated CuKα radiation (40 kV, 80 mA). The spectra were measured at room temperature between 3° and 35° in the 2θ scan mode with steps of 0.02° in 2θ and 3°/min. Powder X-ray diffraction data (Å (*I*/*I*₀)): 16.0 (1.00), 14.0 (0.35), 10.0 (0.34), 6.90 (0.49), 6.57 (0.92), 6.10 (0.37), 4.75 (0.52), 4.36 (0.37), 4.13 (0.28), 3.98 (0.62), 3.92 (0.29), 3.86 (0.67), 3.80 (0.89), 3.61 (0.30), 3.27 (0.21).

X-ray Crystallographic Study of **III**

Crystallographic data of **III**: C₁₄H₁₆NO·C₁₇H₉O₂·C₂H₆O, *M* = 519.61, monoclinic, space group *P*2₁, *a* = 13.5541(13), *b* = 6.0649(6), *c* = 17.7744(16) Å, β = 110.931(2)°, *V* = 1364.7(2) Å³, *Z* = 2, ρ_{calcd} = 1.265 g cm⁻³, μ_{MoKα} = 0.082 mm⁻¹, 8502 reflections measured, 5414 unique, final *R*(*F*²) = 0.0579 by using 4224 reflections with *I* > 2σ(*I*), *R* (all data) = 0.0800, *T* = 100(2) K, CCDC-654190.

X-ray Crystallographic Study of **IV**

Crystallographic data of **IV**: C₁₄H₁₆NO·C₁₇H₉O₂·C₃H₈O, *M* = 533.64, monoclinic, space group *P*2₁, *a* = 13.699(3), *b* = 6.1484(14), *c* = 17.961(4) Å, β = 110.921(4)°, *V* = 1413.0(5) Å³, *Z* = 2, ρ_{calcd} = 1.254 g cm⁻³, μ_{MoKα} = 0.081 mm⁻¹, 8704 reflections measured, 5920 unique, final *R*(*F*²) = 0.0794 by using 2517 reflections with *I* > 2σ(*I*), *R* (all data) = 0.1742, *T* = 120(2) K, CCDC-654191.

Measurement of ¹H NMR Spectra

¹H NMR spectra were recorded on a Varian Mercury M300 Spectrometer.

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