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Complexation Behavior of a Supramolecular Organic Fluorophore Prepared by Solid-State Co-Grinding Crystallization Using 2-Anthracenecarboxylic Acid and (*R*)-1-(2-Naphthyl)ethylamine and Its Optical Properties

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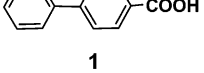
A novel crystalline supramolecular organic fluorophore having a 2_1-helical columnar structure has been prepared by solid-state co-grinding crystallization using crystals of 2-anthracenecarboxylic acid and (*R*)-1-(2-naphthyl)ethylamine. Although many organic fluorophores lose their fluorescence in the solid state, this supramolecular organic fluorophore exhibits fluorescence even in the solid state.

Introduction

The properties of crystalline organic compounds in the solid state are different to those in solution because molecules are densely packed in the solid state under the strong influence of neighboring molecules. Therefore, in the field of supramolecular organic chemistry, solid-state supramolecular systems comprising two or more organic molecules have received considerable attention,[1] particularly solid-state chiral supramolecular systems having a helical columnar structure. Various functional supramolecular organic complexes such as chiral molecular recognition complexes,[2] fluorescent molecular-sensing complexes,[3] and chiral fluorescent complexes[4] have been developed. However, these supramolecular organic complexes are formed by crystallization from solutions containing the component molecules and the crystallization process takes a long time. In recent times, the demand for a simple and economic method for the preparation of supramolecular complexes has increased. For inorganic solids and inorganic–organic hybrid materials, a solid-state synthesis under solvent-free conditions has been widely used. This method is very useful from the viewpoint of both green chemistry as well as industrial chemistry because no crystallization solvent is required and the crystallization time is short. However, it is difficult and rare to prepare crystalline supramolecular organic complexes by solid-state crystallization under solvent-free conditions by simply mixing/grinding the component crystals because the intermolecular interactions are not so strong.[5]

In this paper, we report the complexation behavior of a solid-state chiral supramolecular organic fluorophore having a helical columnar structure that was prepared by solid-state crystallization by simply mixing/grinding the component crystals. We also present its crystal structure and optical properties. Two building blocks were used in the preparation. We attempted to use three types of simple acid molecules that exhibit fluorescence, 4-biphenylcarboxylic acid (**1**), 2-naphthalenecarboxylic acid (**2**), and 2-anthracenecarboxylic acid (**3**), as one building block. For the other building block, we used a chiral amine molecule, (*R*)-1-(2-naphthyl)ethylamine [(*R*)-**4**].



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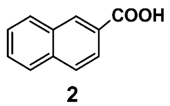

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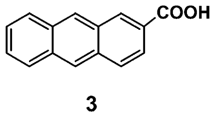

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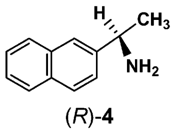

(*R*)-**4**

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Results and Discussion

The preparation of the crystalline supramolecular fluorophore by solid-state co-grinding crystallization was first attempted by mixing **1** and (*R*)-**4**. A mixture of **1** and (*R*)-**4** was ground in an agate mortar under solvent-free conditions. After grinding for 15 min, the X-ray powder diffraction pattern of the obtained product was recorded and compared with that of the component molecules (Figure 1).

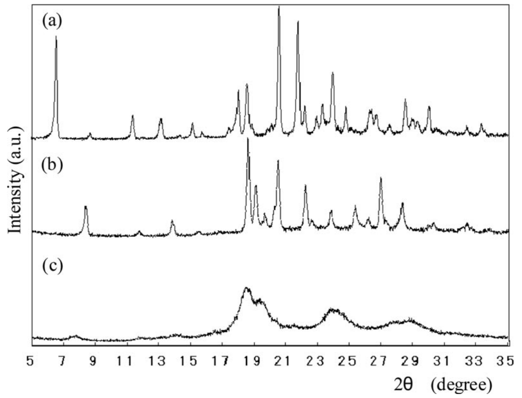

Figure 1. X-ray powder diffraction patterns of (a) crystal **1**, (b) crystal (*R*)-**4**, and (c) the product obtained from the **1**/(*R*)-**4** system.

The peaks corresponding to **1** and (*R*)-**4** disappeared in the X-ray diffraction pattern of the product. However, the X-ray diffraction pattern of the product showed the presence of an amorphous solid.

Next, we attempted to prepare the crystalline supramolecular fluorophore by using the **2**/(*R*)-**4** system. By using the same technique, a mixture of **2** and (*R*)-**4** was ground in the agate mortar for 15 min. Again, the X-ray powder diffraction pattern of the product showed the presence of an amorphous solid (Figure 2).

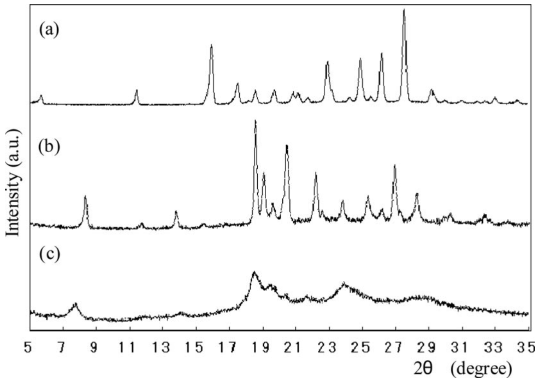

Figure 2. X-ray powder diffraction patterns of (a) crystal **2**, (b) crystal (*R*)-**4**, and (c) the product obtained from the **2**/(*R*)-**4** system.

Then **3** was used, which has a wider and more rigid aromatic unit than **2**. By using the same technique, a mixture of **3** and (*R*)-**4** was ground in the agate mortar for 15 min. As expected, and in contrast to the **1**/(*R*)-**4** and **2**/(*R*)-**4** systems, the peaks corresponding to **3** and (*R*)-**4** disappeared completely and a new set of intense peaks were observed in the X-ray powder diffraction pattern of the product (Figure 3). This shows that the novel crystals (**I**) composed of **3** and (*R*)-**4** were formed by solid-state co-grinding crystallization.

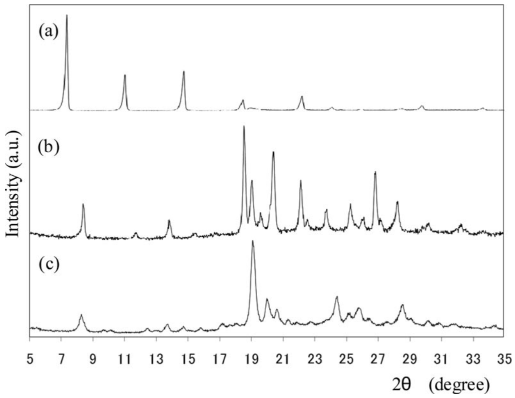

Figure 3. X-ray powder diffraction patterns for crystals of (a) **3**, (b) (*R*)-**4**, and (c) **I**.

To study the crystal structure of complex **I**, a single crystal composed of **3** and (*R*)-**4** was obtained by crystallization from a solution containing the component crystals. A mixture of **3** and (*R*)-**4** was dissolved in MeOH solution and left to stand at room temperature. After a week, good quality colorless crystals were obtained, which were subjected to X-ray crystallographic analysis. The X-ray crystal structure of the obtained complex is shown in Figure 4.

The stoichiometry of the complex **3**/(*R*)-**4** is 1:1 and its space group is $P2_12_12_1$. It has a characteristic 2_1-helical columnar network structure along the *a* axis (Figure 4a and b). The column is mainly formed through the interaction between the carboxylate oxygen of the carboxylic acid anion of **3** and the ammonium hydrogen of the protonated amine of (*R*)-**4**. The complex is formed by the self-assembly of the 2_1-columns through three types of aromatic–aromatic edge-to-face interactions (Figure 4c): One anthracene–anthracene edge-to-face interaction (2.84 Å; indicated by arrow ***A***), one anthracene–naphthalene edge-to-face interaction (3.00 Å; indicated by arrow ***B***), and two naphthalene–anthracene edge-to-face interactions (2.72 and 2.86 Å; indicated by arrows ***C***).

The X-ray powder diffraction patterns of the crystal obtained by crystallization from MeOH and the crystal obtained by solid-state co-grinding crystallization are almost identical (Figure 5). This suggests that the crystals of the supramolecular complex having a 2_1-helical columnar structure can be formed by solid-state co-grinding crystallization by simply mixing/grinding **3** and (*R*)-**4**. In other words, by the solid-state co-grinding crystallization of two appropriate component molecules, crystals of a 2_1-helical columnar complex can be obtained by the self-assembly of the columns.

In the **1**/(*R*)-**4** system, because the component molecule **1** has a biphenyl backbone with an internal rotation axis, it does not easily densely pack with another component molecule. Therefore, the supramolecular complex of this system does not form a crystal. Similarly, in the **2**/(*R*)-**4** system,

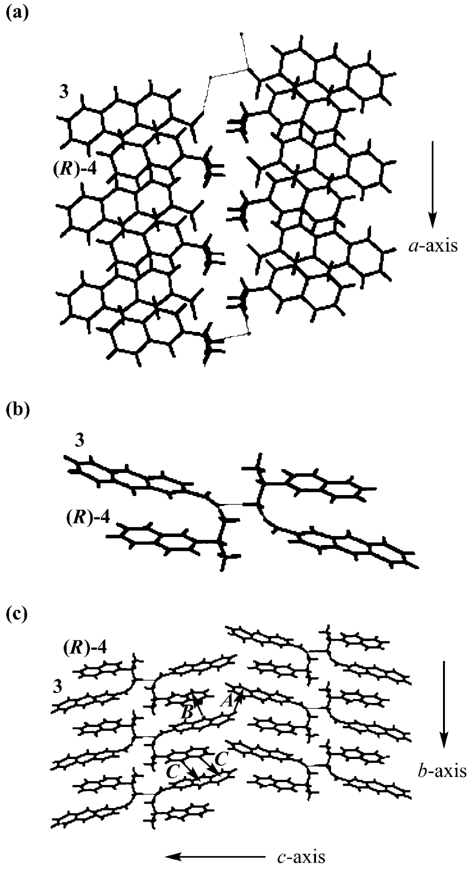

Figure 4. Crystal structure of **I**. (a) 2_1-helical columnar network structure parallel to the *a* axis. (b) View along the *a* axis. (c) Crystal-packing structure observed along the *a* axis. The arrows ***A***, ***B***, and ***C*** indicate the anthracene–anthracene edge-to-face, the anthracene–naphthalene edge-to-face, and the naphthalene–anthracene edge-to-face interactions, respectively.

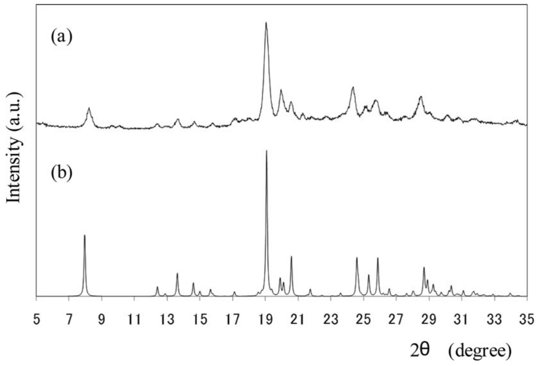

Figure 5. (a) X-ray powder diffraction patterns of crystals of **I**. (b) Pattern calculated for the crystal obtained by crystallization from solution.

despite **2** having a rigid planar aromatic moiety (naphthalene ring), the crystal of the supramolecular complex is not formed. To study the causes behind the above-mentioned phenomena in detail by X-ray crystallographic analysis, a single crystal of complex **II** composed of **2** and (*R*)-**4** was prepared by crystallization from MeOH solution. The crystal structure of **II** is shown in Figure 6. X-ray analysis revealed that the stoichiometry of **II** is the same as that of **I**, that is, **2**/(*R*)-**4** = 1:1, and that the two complexes have the same space group, that is, $P2_12_12_1$. Complex **II** also has a characteristic 2_1-helical columnar structure, similar to **I** (Figure 6a and b) and is formed by the self-assembly of the 2_1-columns through two naphthalene–naphthalene edge-to-face interactions (2.64 and 2.93 Å; Figure 6c, indicated by arrows ***A***). A comparison of the crystal structures of **I** obtained from the **3**/(*R*)-**4** system and **II** obtained from the **2**/(*R*)-**4** system shows that the number of aromatic–aromatic edge-to-face interactions in **I** is greater than that in **II**. Moreover, the melting point (224–225 °C) and the crystal density (1.32 $\mathrm{g\,cm^{-3}}$) of **I** are higher than those of **II** (202–203 °C and 1.30 $\mathrm{g\,cm^{-3}}$, respectively). These results suggest that **I** is more stable than **II**. Therefore, only **I** is formed by solid-state co-grinding crystallization by simply mixing/grinding the component crystals.

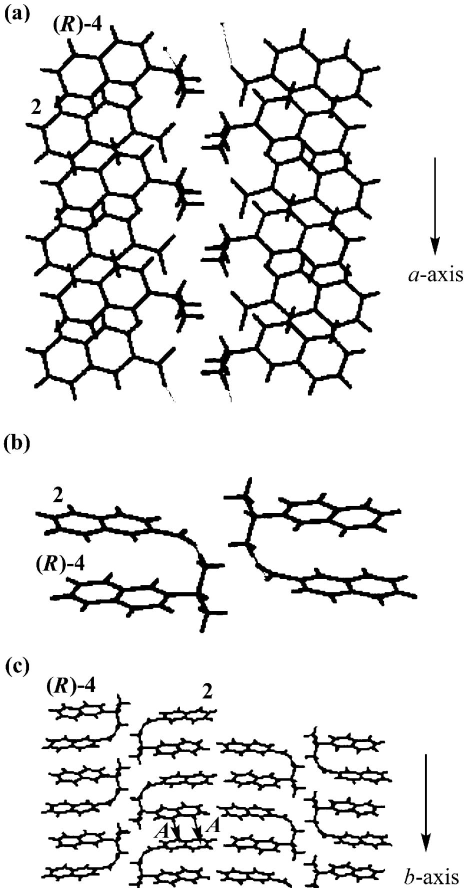

Figure 6. Crystal structure of **II**. (a) 2_1-helical columnar network structure parallel to the *a* axis. (b) View along the *a* axis. (c) Crystal-packing structure observed along the *a* axis. The arrows ***A*** indicate naphthalene–naphthalene edge-to-face interactions.

To study the asymmetric environment of **I**, its solid-state absorption and circular dichroism (CD) spectra were measured by using a KBr pellet (Figure 7). The solid-state sample was prepared according to the standard procedure employed for obtaining glassy KBr matrices. The features in the CD spectrum originating from the anthracene ring were mainly observed at 366, 389, and 400 nm (black line, Figure 7). The circular anisotropy factor ($g_{CD} = \Delta OD/OD$) of the Cotton effect at λ_{CD} = 400 nm was approximately 0.65×10^{-3}. To check if the crystal had caused any artefact in the spectrum, complex **I′** was prepared by using (*S*)-1-(2-naphthyl)ethylamine [(*S*)-**4**] instead of (*R*)-**4** and the CD spectrum of **I′** was measured (gray line, Figure 7). This spectrum was found to be a mirror image of the CD spectrum of **I**. These results show that **3** exists in an effective chiral environment in the crystalline state.

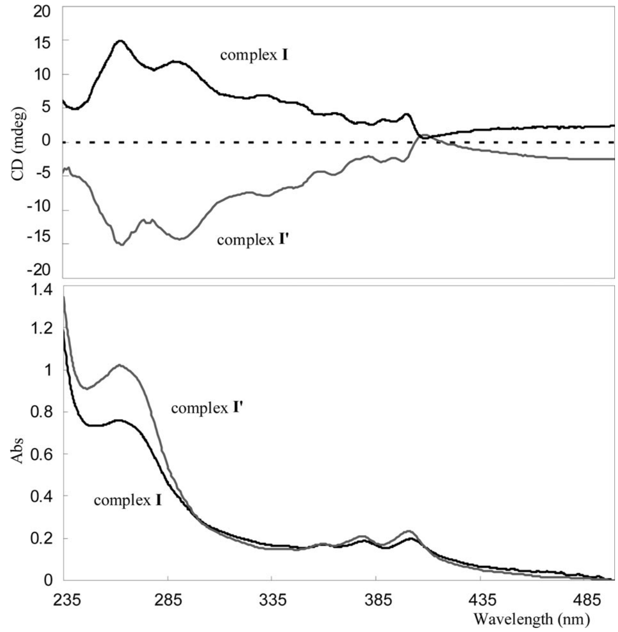

Figure 7. CD and absorption spectra of **I** (black line) and **I′** (gray line) in the solid state.

As **I** comprises **3**, which is a fluorescent molecule, **I** may also exhibit fluorescence. To study the fluorescence properties of **I**, the solid-state fluorescence spectra of **I** and **3** were recorded. Although a large number of solid-state organic fluorophores exhibit fluorescence quenching in the crystalline state, **I** did not exhibit any such phenomenon. The absolute value of the photoluminescence quantum yield (Φ_F) in **I** is 0.18. This value is higher than that of **3** (Φ_F = 0.04). On the other hand, the solid-state fluorescence maximum (λ_{em}) of **I** is 458 nm, and a small hypsochromic shift is observed relative to the λ_{em} of **3** (λ_{em} = 464 nm). Unfortunately, because there is no crystal structure data for molecule **3** alone, the structures of **I** and **3** cannot be directly compared. However, it is known that strong intermolecular π–π interactions between the fluorophores induce a decrease in the photoluminescence quantum yield in the solid state. Therefore, one of the reasons for the increase in Φ_F after complexation may be due to differences in the excited singlet state caused by changes in the relative arrangements of the fluorescent anthracene rings. Moreover, **3** may exist as a dimer due to hydrogen-bonding in the solid state. On the other hand, in **I**, **3** forms a strong hydrogen- and ionic-bonded columnar network that suppresses the concomitant nonradiative processes. It is thought that the change in the bonding mode of **3** also causes the increase in Φ_F after complexation.

Conclusions

A novel chiral supramolecular organic fluorophore with a 2_1-helical columnar structure has been successfully prepared by using 2-anthracenecarboxylic acid (**3**) and (*R*)-1-(2-naphthyl)ethylamine [(*R*)-**4**]. This crystalline supramolecular organic fluorophore was formed by solid-state crystallization by simply mixing/grinding the component crystals under solvent-free conditions. Generally, it is not easy to predict which supramolecular organic crystals will be formed by solid-state co-grinding crystallization. Therefore, it is expected that this study will provide useful information on the formation of novel supramolecular organic crystals by solid-state co-grinding crystallization. Moreover, although many organic fluorophores lose their fluorescence in the solid state, this chiral supramolecular fluorophore exhibits fluorescence even in the solid state. This further enhances the potential of this fluorescence system, enabling its application in the design of novel crystalline chiral supramolecular organic fluorophores that can be easily formed by solid-state co-grinding crystallization.

Experimental Section

General Methods: Component molecules **1**–**4** were purchased from Tokyo Kasei Kogyo Co., LTD. Methanol (MeOH) was purchased from Wako Pure Chemical Industry. All reagents were used directly as obtained commercially.

Formation of Crystalline Supramolecular Fluorophores by Solid-State Co-Grinding Crystallization: A mixture of **1** (or **2**, **3**) (0.050 mmol) and (*R*)-**4** (8.6 mg, 0.050 mmol) was ground in an agate mortar under solvent-free conditions at room temperature. After grinding for 15 min, the X-ray powder diffraction pattern of the obtained product was recorded and compared with those of the component molecules.

Formation of Single Crystals of the Supramolecular Fluorophores by Crystallization from Solution: A mixture of **3** or **2** (0.045 mmol) and (*R*)-**4** (7.7 mg, 0.045 mmol) was dissolved in MeOH solution with heating and left to stand at room temperature. After a week, good quality colorless crystals **I** (8 mg) and **II** (7 mg) were obtained, respectively. The weights given are the total crops of the crystals obtained in one batch.

X-ray Crystallographic Study of Crystal I: X-ray diffraction data for single crystals were collected by using a Bruker APEX diffractometer. The crystal structures were solved by direct methods[6] and refined by full-matrix least-squares using SHELX97.[7] The diagrams were prepared by using PLATON.[8] Absorption corrections were performed by using SADABS.[9] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. Crystallographic data for **I**: $C_{12}H_{13}N \cdot C_{15}H_{10}O_2$, M = 393.46, orthorhombic, space group $P2_12_12_1$, a = 6.1306(5), b = 7.2385(6), c = 44.562(4) Å, U =

1977.5(3) Å^3, $Z = 4$, $D_c = 1.322\ \mathrm{g\,cm^{-3}}$, $\mu(\text{Mo-}K_\alpha) = 0.083\ \mathrm{mm^{-1}}$, 12315 reflections measured, 4521 unique, final $R(F^2) = 0.0554$ using 3854 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0680$, $T = 120(2)$ K.

X-ray Crystallographic Study of Crystal II: Crystallographic data for **II**: $C_{12}H_{13}N{\cdot}C_{11}H_8O_2$, $M = 343.41$, orthorhombic, space group $P2_12_12_1$, $a = 6.2237(7)$, $b = 7.1666(8)$, $c = 39.302(4)$ Å, $U = 1753.0(3)$ Å^3, $Z = 4$, $D_c = 1.301\ \mathrm{g\,cm^{-3}}$, $\mu(\text{Mo-}K_\alpha) = 0.083\ \mathrm{mm^{-1}}$, 8744 reflections measured, 2989 unique, final $R(F^2) = 0.0734$ using 2808 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0780$, $T = 115(2)$ K.

CCDC-694979 (for **I**) and -694980 (for **II**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of XRD Spectra: X-ray powder patterns were recorded on a Rigaku RINT2500 instrument by using graphite-monochromated Cu-K_α radiation (40 kV, 80 mA). The spectra were measured at room temperature between 3 and 35° in the 2θ scan mode in steps of 0.02° and 3 °min^{-1}.

Measurement of Solid-State CD and Absorption Spectra: The CD and absorption spectra were recorded by using a Jasco J-800KCM spectrophotometer. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.[10]

Measurement of Solid-State Fluorescence Spectra: Solid-state fluorescence spectra and the absolute photoluminescence quantum yields were measured by using the Absolute PL Quantum Yield Measurement System (C9920-02, HAMAMATSU PHOTONICS K.K.) in air at room temperature. Excited wavelengths are 389 nm for complex **I** and 408 nm for component molecule **3** were used.

Acknowledgments

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