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A 2D Layered Chiral Supramolecular Organic Fluorophore Composed of 1-Amino-2-indanol and Carboxylic Acid Derivatives

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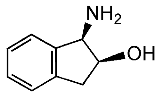
A chiral anthracenecarboxylic acid/amine supramolecular organic fluorophore composed of a 2D layered network structure was developed by combining 1-amino-2-indanol and 2-anthracenecarboxylic acid molecules. This 2D, chiral fluorophore exhibits circularly polarized luminescence (CPL) without quenching the fluorescence in the solid state.

Introduction

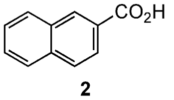
The potential application of solid-state fluorescence techniques to organic electroluminescence (EL) devices, optoelectronic devices, and so on has attracted considerable attention.[1] In particular, the demand for a chiral fluorophore exhibiting circularly polarized luminescence (CPL) as a next generation fluorophore has increased.[2] We recently developed a solid-state chiral supramolecular organic fluorophore by combining two types of organic molecules (fluorescent carboxylic acid and chiral or achiral amine molecules).[3] The optical properties of these chiral carboxylic acid/amine supramolecular organic fluorophores are such that their CPL properties are exhibited in the solid state. In addition, the structural characteristics of these chiral fluorophores are such that they are composed of a 1D columnar hydrogen- and ionic-bonded network structure formed by the carboxylate oxygen atom of a carboxylic acid anion and the ammonium hydrogen atom of a protonated amine. However, chiral carboxylic acid/amine organic fluorophores composed of 2D or 3D network structures have not been formed. Therefore, the solid-state chiral optical properties of these fluorophores, such as solid-state circular dichroism (CD) and CPL properties, which are the most fundamental and important chiral optical properties of chiral materials, have not been studied yet.

The advantage of these supramolecular organic fluorophores is that their physical and chemical properties may be easily controlled by changing the component molecules. Therefore, when suitable amine or carboxylic acid derivatives are used as component molecules, a chiral supramolecular organic fluorophore composed of a 2D or 3D network structure is expected to be formed.

In this paper, we report the formation, crystal structure, and solid-state chiral optical properties of a 2D layered chiral supramolecular organic fluorophore composed of chiral amine and fluorescent carboxylic acid derivatives. We used (1*R*,2*S*)-(+)-1-amino-2-indanol [(1*R*,2*S*)-**1**] as a chiral amine molecule. Further, we used 2-naphthalenecarboxylic acid (**2**) and 2-anthracenecarboxylic acid (**3**) as fluorescent carboxylic acid molecules.



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



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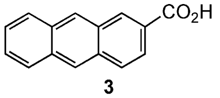

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Results and Discussion

The formation of (1*R*,2*S*)-**1**/**2** and (1*R*,2*S*)-**1**/**3** supramolecular organic fluorophores was attempted by crystallization from MeOH solution. A mixture of (1*R*,2*S*)-**1** and **2** (or **3**) was dissolved in MeOH and left to stand at room temperature. After one week, a large number of crystals **I** were obtained in the mixture of (1*R*,2*S*)-**1** and **2** in the

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MeOH solution and a large number of crystals **II** were obtained in the mixture of (1*R*,2*S*)-**1** and **3** in the MeOH solution.

An X-ray crystallographic analysis of complex **I** was first carried out to study its crystal structure. The crystal structure of complex **I** is shown in Figure 1. The stoichiometry of complex **I** is (1*R*,2*S*)-**1**/**2**/H_2O, 1:1:1 and its space group is $P2_12_12_1$. This crystal structure of complex **I** has a supramolecular 2D layered hydrogen- and ionic-bonded network structure along the *a* and *b* axes (Figure 1a,b). The 2D layered network structure is formed by the association of the ammonium hydrogen of one protonated amine in (1*R*,2*S*)-**1** and the carboxylate oxygen atom of a carboxylic acid anion in **2**. The included water molecules link two hydroxy groups of (1*R*,2*S*)-**1** with a carboxylic acid anion group of **2** through hydrogen bonds and contribute to the maintenance of the layered network structure. Moreover, this layered network structure is maintained by CH–π interactions (Figure 1a, indicated by arrow *A*, 2.61 Å).[4] The self-assembly of these 2D layered network structures (Figure 1c,d; indicated by dotted borders) without interlayer interactions along the *c* axis results in the formation of chiral complex **I**.

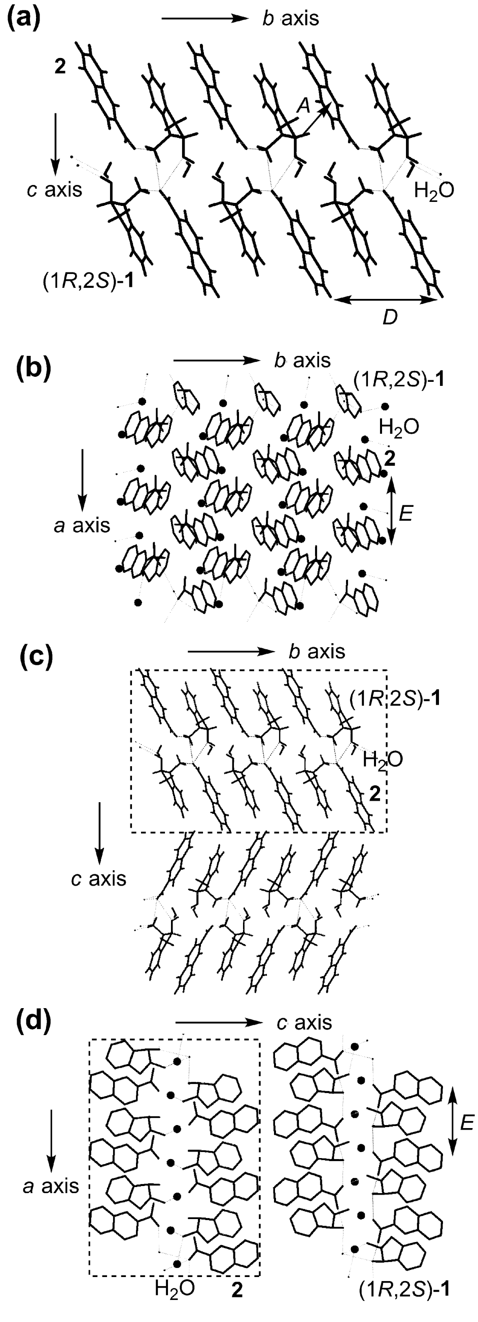

Figure 1. Crystal structure of chiral complex **I**. (a) Extracted 2D layered network structure observed along the *a* axis. The arrow *A* indicates a CH–π interaction; (b) view down the *c* axis; (c) packing structure comprising 2D layered network structure observed along the *a* axis; (d) view down the *b* axis. The dotted borders indicate the 2D layered network structure.

The biggest drawback of solid-state organic fluorophores is the phenomenon of fluorescence quenching in the crystalline state. To study the solid-state optical properties of obtained chiral complex **I**, the solid-state fluorescence spectrum of this complex was measured. Complex **I** exhibits fluorescence in the solid state. The solid-state fluorescence maximum (λ_{em}) of complex **I** is observed at 348 nm, and the absolute value of the photoluminescence quantum yield (Φ_F) in complex **I** is 0.07 in the solid state.

The crystal structure of chiral complex **II** is shown in Figure 2. This crystal structure is similar to that of complex **I**. The stoichiometry of complex **II** is (1*R*,2*S*)-**1**/**3**/H_2O, 1:1:1 and its space group is $P2_12_12_1$. The crystal structure of complex **II** also has a supramolecular 2D layered hydrogen- and ionic-bonded network formed by the association of the ammonium hydrogen of one protonated amine in (1*R*,2*S*)-**1** and carboxylate oxygen atom of a carboxylic acid anion in **3** along the *a* and *b* axes (Figure 2a,b). The included water molecules link two hydroxy groups of (1*R*,2*S*)-**1** through hydrogen bonds and contribute to the maintenance of the layered network structure. Moreover, this layered network structure is maintained by CH–π (Figure 2a; indicated by arrow *A*, 2.69 Å) and benzene–anthracene edge-to-face (Figure2a; indicated by arrow *B*, 2.91 Å) interactions.[4] In contrast to complex **I**, the self-assembly of this 2D layered network structure (Figure 2, indicated by dotted borders) with anthracene–anthracene edge-to-face interlayer interaction (Figure2c; indicated by arrow *C*, 2.77 Å) along the *c* axis results in the formation of chiral complex **II** (Figure 2).[4]

On comparing complex **II** with complex **I**, it is found that the fluorescent unit changes from the naphthalene ring to the anthracene ring when the distance between the neighboring parallel aromatic rings along the *b* axis (Figures 1a and 2a, indicated by arrows *D*) increases from 7.68 to 8.00 Å. In contrast, the distance between the neighboring parallel aromatic rings along the *a* axis (Figures 1b,d and 2b,d; indicated by arrows *E*) decreases from 6.35 to 6.27 Å.

When the solid-state optical properties of complex **II** were studied, λ_{em} and the absolute value of Φ_F of complex **II** were observed to be 440 nm and 0.16, respectively.

Fluorescent complexes **I** and **II** are chiral fluorophores; therefore, they may exhibit CPL in the solid state. However, as the fluorescence of complex **I** containing the naphthalene

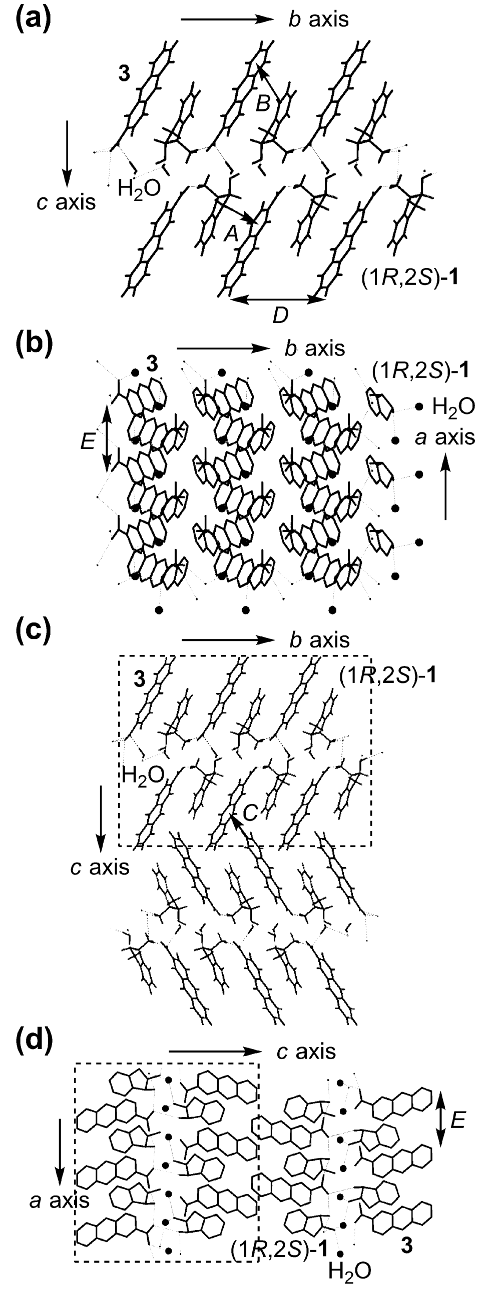

Figure 2. Crystal structure of chiral complex **II**. (a) Extracted 2D layered network structure observed along the *a* axis; the arrows *A* and *B* indicate CH–π and benzene–anthracene edge-to-face interactions, respectively; (b) view down the *c* axis; (c) packing structure comprising 2D layered network structure observed along the *a* axis; the arrow *C* indicates anthracene–anthracene edge-to-face interaction; (d) view down the *b* axis. The dotted borders indicate the 2D layered network structure.

ring is weak, we studied the solid-state chiral optical properties of complex **II** containing the anthracene ring. To study the solid-state CPL properties of chiral complex **II**, the solid-state CD spectrum of complex **II** was first measured using a KBr pellet. The solid-state CD and absorption spectra of complex **II** (indicated by the black line) are shown in Figure 3.

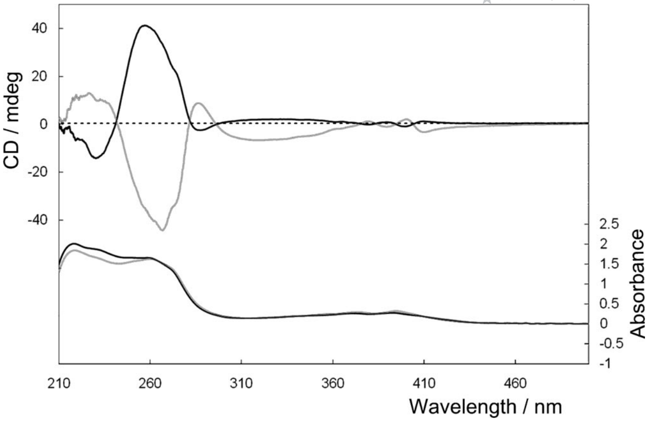

Figure 3. CD and absorption spectra of chiral complexes **II** (black line) and **II′** (gray line) in the solid state (using KBr pellets).

Anthracene ring peaks are observed at approximately 410 nm in the CD spectrum. The circular anisotropy factor (g_{CD} = ΔOD/OD) of the last Cotton effect (λ^{CD} = 410 nm) is approximately $+0.6 \times 10^{-3}$. To check whether the crystal has caused any artefact in the spectrum, the CD and absorption spectra of complex **II′**, prepared by using (1*S*,2*R*)-**1** were measured (Figure 3, indicated by the gray line). The CD spectrum of complex **II′** is found to be almost a mirror image of the CD spectrum of complex **II**. These results show that an effective chirality transfer from chiral unit **1** to fluorescent unit **3** occurs through complexation.

Consequently, the solid-state CPL spectrum of complex **II** was measured by using a KBr pellet. The CPL spectrum was successfully observed in the solid state. The solid-state CPL and fluorescence spectra of complex **II** are shown in Figure 4.

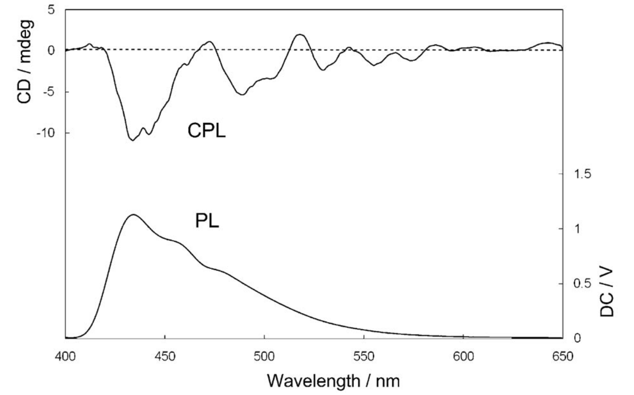

Figure 4. CPL and fluorescence spectra of chiral complex **II** in the solid state (using a KBr pellet).

The fluorescence spectrum of complex **II** obtained by using a KBr pellet is similar to that of complex **II** in the solid state without KBr matrices. This result confirmed the lack of influence of the KBr matrix on this spectrum. A negative solid-state CPL spectrum was obtained for complex **II**. The circular anisotropy factor [$g_{\mathrm{em}} = 2(I_{\mathrm{L}} - I_{\mathrm{R}})/(I_{\mathrm{L}} + I_{\mathrm{R}})$] of complex **II** is approximately -0.7×10^{-3}. This shows that complex **II** exhibits CPL in the solid state. To the best of our knowledge, this is the first instance of solid-state CPL being observed in a chiral carboxylic acid/amine supramolecular organic fluorophore composed of a 2D layered network structure.

On comparing the previously reported chiral anthracenecarboxylic acid/amine supramolecular complexes composed of a 1D columnar network structure with this 2D layered supramolecular fluorophore, although the values of λ_{em} are different, dramatic changes in the absolute values of Φ_F and g_{CD} are not observed.[3a,3b,5] However, although their g_{em} values are similar, the sign of the CD and CPL spectra are different.[3a,3b] In the 1D columnar supramolecular fluorophore, the sign of the CPL spectrum was the same as that of the corresponding CD spectrum at the longest wavelength, and the sign of the CPL spectrum in complex **II** was opposite to that of the corresponding CD spectrum (λ^{CD} = 410 nm). It is thought that the reversal of the sign of the CPL spectrum in complex **II** is caused by a local change in the packing structure of the anthracene ring induced by the incident beam when the CPL spectrum was measured in the crystalline state.

Conclusions

A chiral carboxylic acid/amine supramolecular organic fluorophore composed of a 2D layered network structure was successfully formed by using chiral (1*R*,2*S*)-(+)-1-amino-2-indanol and fluorescent 2-anthracenecarboxylic acid. This supramolecular organic fluorophore exhibited CPL in the solid state, and its CPL spectrum was recorded successfully. To the best of our knowledge, this is the first instance of solid-state CPL being observed in a chiral carboxylic acid/amine supramolecular organic fluorophore composed of a 2D layered network structure. It is believed that such a chiral supramolecular complex with such optical properties will be useful in the development of novel solid-state chiral supramolecular organic fluorophores.

Experimental Section

General Methods: All reagents were used directly as obtained commercially. Component molecules (1*R*,2*S*)-**1**, (1*S*,2*R*)-**1**, **2** and crystallization solvent MeOH were purchased from Wako Pure Chemical Industry. Component molecule **3** was purchased from Tokyo Chemical Industry Co., Ltd.

Formation of Chiral Complex by Crystallization from MeOH Solution: Compounds (1*R*,2*S*)-**1** [or (1*S*,2*R*)-**1**] (7.5 mg, 0.05 mmol) and **2** (or **3**) (0.05 mmol) were dissolved in MeOH (2 mL) and left to stand at room temperature. After a week, a large number of crystals [crystals of complex **I** (8 mg) for the (1*R*,2*S*)-**1**/**2** system, crystals of complex **II** (9 mg) for the (1*R*,2*S*)-**1**/**3** system, and complex **II′** (10 mg) for the (1*S*,2*R*)-**1**/**3** system] were obtained. The weight of the crystal is the total weight of the obtained crystals in one batch.

X-ray Crystallographic Studies: X-ray diffraction data for single crystals were collected with a Bruker Apex. The crystal structures were solved by direct methods[6] and refined by full-matrix least-squares by 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: $C_9H_{11}NO\cdot C_{11}H_8O_2\cdot H_2O$, M = 339.38, orthorhombic, space group $P2_12_12_1$, a = 6.3535(7) Å, b = 7.6779(8) Å, c = 34.701(4) Å, V = 1692.8(3) Å^3, Z = 4, $D_{calcd.}$ = 1.332 g cm^{-3}, μ(Mo-K_α) = 0.093 mm^{-1}, 14695 reflections measured, 3875 unique, final $R(F^2)$ = 0.0697 using 3084 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0911, T = 115(2) K.

Crystallographic Data for II: $C_9H_{11}NO\cdot C_{15}H_{10}O_2\cdot H_2O$, M = 389.43, orthorhombic, space group $P2_12_12_1$, a = 6.2686(3) Å, b = 8.0016(4) Å, c = 34.431(2) Å, V = 1927.66(17) Å^3, Z = 4, $D_{calcd.}$ = 1.342 g cm^{-3}, μ(Mo-K_α) = 0.091 mm^{-1}, 16982 reflections measured, 4386 unique, final $R(F^2)$ = 0.0431 using 4102 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0466, T = 115(2) K.

CCDC-745821 (for **I**) and -745822 (for **II**) contain 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 Solid-State Fluorescence Spectra: Solid-state fluorescence spectra and absolute photoluminescence quantum yield (Φ_F) were measured by Absolute PL Quantum Yield Measurement System (C9920–02, Hamamatsu Photonics K.K.) under an air atmosphere at room temperature. The excited wavelengths are 319 and 390 nm for complexes **I** and **II**, respectively.

Measurement of Solid-State CD and Absorption Spectra: The CD and absorption spectra were measured 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 CPL Spectrum: The CPL spectrum was measured by using a Jasco CPL-200 spectrophotometer. The excitation wavelength was 380 nm. The solid-state sample was prepared according to the standard procedure for obtaining glassy KBr matrices.[10] The power of an incident beam of the CPL spectrometer was 8.0 μW 0.04 cm^{-2} at the installation position of sample. The CPL spectrum was approached by Simple Moving Average (SMA).

Acknowledgments

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