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Solid-state optical properties of a chiral supramolecular fluorophore consisting of chiral (1*R*,2*R*)-1,2-diphenylethylenediamine and fluorescent carboxylic acid derivatives

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Abstract—By using (1*R*,2*R*)-1,2-diphenylethylenediamine as a chiral molecule and 2-anthracenecarboxylic acid as a fluorescent molecule, we created a chiral supramolecular organic fluorophore having circularly polarized luminescence properties in the solid-state. © 2007 Elsevier Ltd. All rights reserved.

The solid-state optical properties of organic compounds are very important physical properties to consider in the development of new functional materials. Recently, the potential application of solid-state fluorescence to organic EL (electroluminescence) and optodevice materials, etc.[1] has attracted much attention. To date, organic compounds that possess solid-state fluorescence have mostly been composed of a single molecule, and there have only been a few reports concerning supramolecular organic fluorescent complexes containing two or more organic molecules.[2] These reported complexes, however, have no circular dichroism (CD) or circularly polarized luminescence (CPL) properties because they consist of achiral molecules. Recently, we have succeeded in the development of chiral supramolecular organic complexes by combining two types of organic molecules, that is, chiral and sterically bulky molecules. These complexes have the ability to resolve racemic compounds which previously could not be resolved.[3]

In this Letter, we report the preparation and solid-state optical properties of a chiral supramolecular organic fluorophore that contains two different characteristic organic compounds. A diamine compound, (1*R*,2*R*)-1,2-diphenylethylenediamine [(1*R*,2*R*)-**1**], was used as the optically active molecule and two kinds of carboxylic acid derivatives, 2-anthracenecarboxylic acid (**2**) and 2-naphthalenecarboxylic acid (**3**), were used as the fluorescent molecules. It is predicted that the resultant supramolecular organic complex will have interesting optical properties due to the conformational synergy of the constituent molecules.
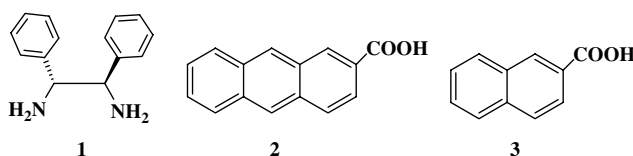
The most serious problem in applying organic fluorophores to emitter materials is fluorescence quenching in both condensed and crystalline states. Moreover, the successful measurement of a solid-state CPL spectrum of such a chiral supramolecular system has not been reported previously. Therefore, our chiral

supramolecular fluorophore is a significant advancement in solid-state chiral fluorophore development.

The complexation behavior of (1*R*,2*R*)-**1** and **2** containing an anthracene ring as the fluorescent unit was studied. Although (1*R*,2*R*)-**1** and **2** were mixed in ethanol, complex formation was not observed by UV–vis spectroscopy. Therefore, the formation of the supramolecular complex was attempted via crystallization from solution. A mixture of (1*R*,2*R*)-**1** and **2** was dissolved in ethanol and left to stand at room temperature. After 1 day, a great number of crystals **I**, constructed from (1*R*,2*R*)-**1** and **2**, were obtained.
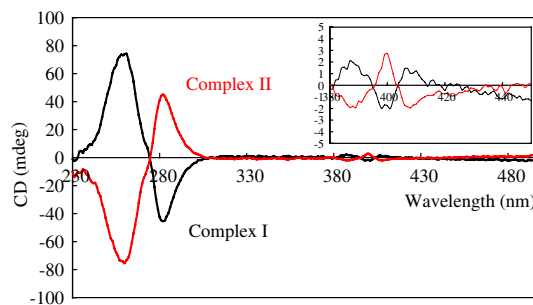
In order to study the solid-state optical properties of complex **I**, the solid-state fluorescence spectra were measured. Complex **I** showed fluorescence without quenching (Fig. 1). The solid-state fluorescence maximum of complex **I** is 432 nm and a shift (27 nm) to lower wavelength is observed relative to that of fluorescent molecule **2**. Interestingly, the solid-state fluorescence intensity of complex **I** is increased by about 4.2 times relative to **2**.

Fluorescent complex **I** is chiral, therefore it possesses both CD and CPL properties. The solid-state CD spectrum of complex **I** was measured by using a KBr pellet (Fig. 2). The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.[4]

The features in the CD spectrum originating from the anthracene ring are observed at 387, 398, and 406 nm. The circular anisotropy ($g_{CD} = \Delta OD/OD$) factor of the last Cotton effect ($\lambda^{CD} = 406$ nm) is about 0.5×10^{-3}. In order to check if the crystal caused any artifacts in the spectrum, complex **II** was prepared by using (1*S*,2*S*)-1,2-diphenylethylenediamine [(1*S*,2*S*)-**1** instead of (1*R*,2*R*)-**1**], and the CD spectrum of complex **II** was measured. A CD spectrum that was a mirror-image to that of complex **I** was observed. These results show that effective chiral transfer from chiral (1*R*,2*R*)-**1** or (1*S*,2*S*)-**1** to fluorescent molecule **2** occurred during the complexation. It was possible that the true CD spectrum of this supramolecular complex could not be observed because the complex may interact
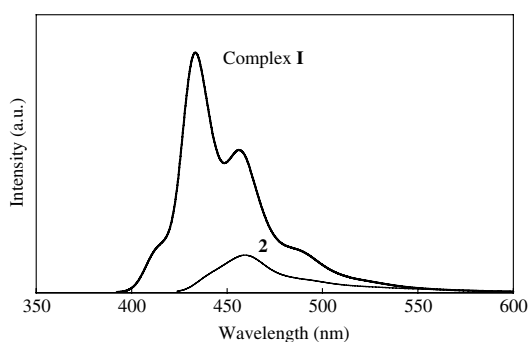
Figure 2. CD spectra of complex **I** (black line) and complex **II** (red line) in the solid-state (KBr pellets).

with the KBr matrix.[5] Therefore, the diffuse reflectance circular dichroism (DRCD) spectra of complexes **I** and **II** without the KBr matrix were measured (Fig. 3).[6] In both CD spectra with the KBr matrix and the DRCD measurements without the KBr matrix, the particle size of the crystal is about 50 μm.

The DRCD spectrum is similar to the CD spectrum, suggesting that there is no influence of the KBr matrix on the CD measurements for this type of supramolecular fluorophore. Consequently, the solid-state CPL properties of these complexes were measured by using KBr pellets.[7] In Figure 4, the CPL and fluorescence spectra of complex **I** are shown.

The fluorescence spectra using a KBr pellet are the same as that depicted in Figure 1. This result confirmed the lack of influence of the KBr matrix on these measurements. A positive CPL spectrum was obtained for complex **I**. The circular anisotropy [$g_{em} = 2(I_L - I_R)/(I_L + I_R)$] factor of complex **I** is 7.74×10^{-4}. The sign of the CPL spectrum is the same as that of the corresponding CD spectrum at the longest wavelength (406 nm). That is, the chirality of this complex in the ground state is the same as that in the excited state. To the best of our knowledge, this is the first example of a solid-state CPL property measured in such a chiral supramolecular fluorophore.

In order to elucidate the increase of the fluorescence intensity and the origin of CD and CPL properties by complexation, X-ray crystallographic analysis of complex **I** was carried out. The structure of crystal **I** is shown in Figure 5.[8]

Figure 1. Solid-state fluorescence spectra of complex **I** and fluorescent molecule **2** in the solid-state. The excitation wavelengths were 378 and 408 nm for complexes **I** and **2**, respectively. The sample thickness was 0.1 mm.
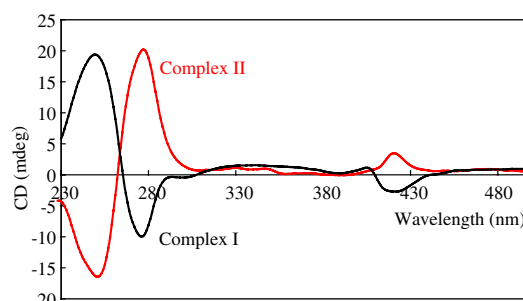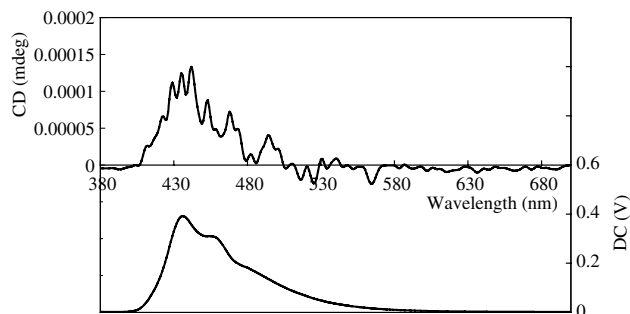

Figure 3. DRCD spectra of complex **I** (black line) and complex **II** (red line) in the solid-state.
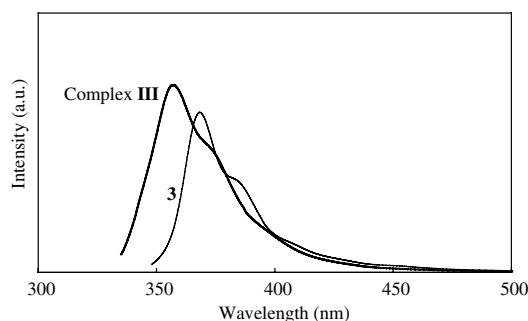
Figure 4. CPL and fluorescence spectra of complex **I** in the solid-state (KBr pellet).

As a characteristic of the structure, this crystal has a columnar supramolecular hydrogen- and ionic-bonded network around the 2_1-axis along the *b*-axis (Fig. 5a). This network is mainly formed by the ammonium hydrogen of the protonated amine (Fig. 5, indicated in green) and the carboxylate oxygen of a carboxylic acid anion (Fig. 5, indicated in blue). Complex **I** is formed by self-assembly of this 2_1-column (Fig. 5b). Fluorescence molecule **2** in complex **I** exists as a 2_1-column structure and its bonding style is a mixture of hydrogen bonds and stronger ionic bonds. Moreover, there are four kinds of CH–π interactions (2.69, 2.84, 2.87, and 2.96 Å) (Fig. 5b, indicated in red arrows) per anthracene molecule.

Unfortunately, there is no crystal structural data of molecule **2** alone. Thus, 2-naphthalenecarboxylic acid (**3**) whose crystal structure has been previously reported was used instead of molecule **2** as the fluorescent molecule.[9] In the same way, a great number of crystals **III**, constructed from (1*R*,2*R*)-**1** and **3**, were obtained by crystallization from an ethanol solution containing (1*R*,2*R*)-**1** and **3**. Complex **III** showed fluorescence with-

out quenching and the intensity is increased by about 1.4 times compared to **3** (Fig. 6). The solid-state fluorescence maximum of complex **III** is 358 nm and a shift (10 nm) to lower wavelength is observed relative to fluorescent molecule **3**.
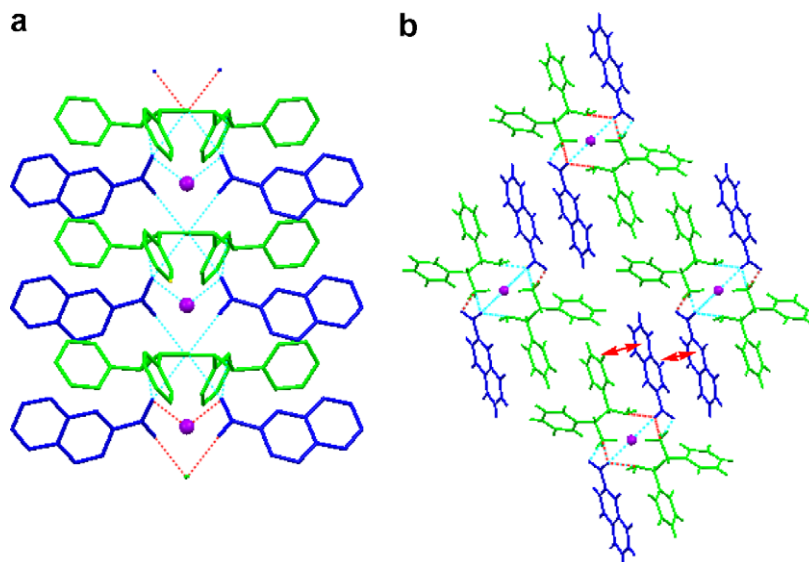
The X-ray crystal structure of complex **III** is shown in Figure 7.[10] The stoichiometry of complex **III** is (1*R*,2*R*)-**1**/**3**/H_2O = 2:2:1 and the space group is *C*2. As predicted, this crystal also has a columnar supramolecular hydrogen- and ionic-bonded network around the 2_1-axis along the *b*-axis (Fig. 7a). Complex **III** is formed by self-assembly of this 2_1-column, similar to complex **I** (Fig. 7b). In this complex, although the number of CH–π interactions is small compared to complex **I**, there are two kinds of CH–π interactions (2.68 and 2.94 Å) (Fig. 7b, indicated in red arrows) per naphthalene molecule. The configuration of the naphthalene rings between adjoining dimer columns is also side to plane as in complex **I**. On the other hand, molecule **3** alone in a crystal exists as a dimer formed by hydrogen bonding of carboxyl groups.[9] Moreover,

Figure 6. Solid-state fluorescence spectra of complex **III** and fluorescent molecule **3**. The excitation wavelengths were 323 and 335 nm for complex **III** and **3**, respectively. The sample thickness is 0.1 mm.
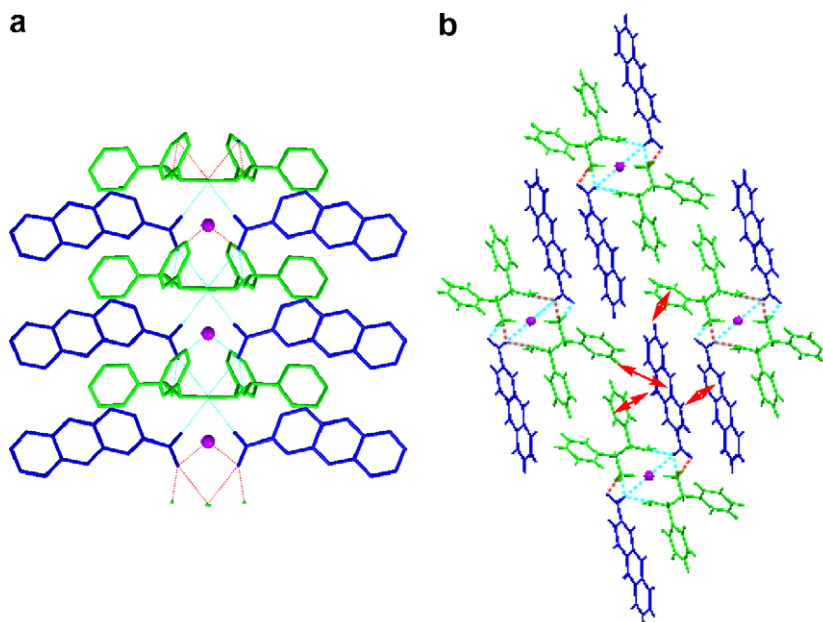
Figure 5. Crystal structure of complex **I**. (a) Columnar hydrogen- and ionic-bonded network parallel to the *b*-axis. (b) Packing structure observed along the *b*-axis. Purple balls indicate included water molecules.

Figure 7. Crystal structure of complex **III**. (a) Columnar hydrogen- and ionic-bonded network parallel to the *b*-axis. (b) Packing structure observed along the *b*-axis. Green and blue molecules indicate (1*R*,2*R*)-**1** and **3**, respectively. Purple balls indicate included water molecules.

no CH–π interaction is observed involving the naphthalene rings, and the ring configuration between the adjoining dimer columns is head to head. It can be inferred that molecule **2** also exists as a similar dimer and that the bonding and packing style changes of the fluorescence molecule, **2** or **3**, in each complex suppress the concomitant non-radiative processes and increase the fluorescence intensity of complexes **I** and **III**.

In addition, regarding the origin of CD and CPL properties, the crystal structures and theory of oscillator coupling[11] suggest that the features of the CD and CPL spectra originating from the anthracene ring are caused by interactions of the anthracene ring not into the 2_1-column but between the adjoining 2_1-columns.

In conclusion, chiral supramolecular organic fluorophores using two kinds of molecules with different characteristics (chiral and fluorescent molecules) were successfully created. The solid-state fluorescence intensity of these fluorophores was not quenched, and the solid-state CPL spectra were recorded successfully. It is expected that such supramolecular complexations will be useful in the development of chiral supramolecular fluorophores.

References and notes

1. *Organic Light-Emitting Devices*; Shinar, J., Ed.; Springer: New York, 2004.
2. (a) Mizobe, Y.; Tohnai, N.; Miyata, M.; Hasegawa, Y. *Chem. Commun.* **2005**, 1839; (b) Mizobe, Y.; Ito, H.; Hisaki, I.; Miyata, M.; Hasegawa, Y.; Tohnai, N. *Chem. Commun.* **2006**, 2126.
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.
4. Kuroda, R.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 433.
5. Braga, D.; Maini, L.; Polito, M.; Grepioni, F. *Chem. Commun.* **2002**, 2302.
6. The DRCD spectrum was measured using a Jasco J-800KCMF spectrophotometer.
7. The CPL spectrum was measured using a Jasco CPL-200 spectrophotometer. (a) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1; (b) Field, J. E.; Muller, G.; Riehl, J. P.; Venkataraman, D. *J. Am. Chem. Soc.* **2003**, *125*, 11808.
8. Crystallographic data of **I**: $(C_{14}H_{17}N_2)\cdot(C_{15}H_9O_2)\cdot 0.5H_2O$, $M = 443.53$, monoclinic, space group *C*2, $a = 27.404(3)$, $b = 5.8647(6)$, $c = 15.9321(17)$ Å, $\beta = 119.932(2)°$, $U = 2219.0(4)$ Å^3, $Z = 4$, $D_c = 1.328$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 0.085$ mm^{-1}, 7070 reflections measured, 4919 unique, final $R(F^2) = 0.0415$ using 4493 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0464$, $T = 100(2)$ K. CCDC 613387.
9. (a) Fitzgerald, L. J.; Gerkin, R. E. *Acta Crystallogr., Sect. C* **1993**, *49*, 1952; (b) Blackburn, A. C.; Fitzgerald, L. J.; Gerkin, R. E. *Acta Crystallogr., Sect. C* **1996**, *52*, 2862.
10. Crystallographic data of **III**: $(C_{14}H_{17}N_2)\cdot(C_{11}H_7O_2)\cdot 0.5H_2O$, $M = 393.47$ monoclinic, space group *C*2, $a = 25.700(3)$, $b = 5.8835(6)$, $c = 15.9181(16)$ Å, $\beta = 120.147(2)°$, $U = 2081.3(4)$ Å^3, $Z = 4$, $D_c = 1.256$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 0.081$ mm^{-1}, 9230 reflections measured, 4617 unique, final $R(F^2) = 0.0466$ using 4197 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0523$, $T = 100(2)$ K. CCDC 613388. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
11. (a) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983; (b) Berova, N.; Nakanishi, K. In *Circular Dichroism: Principles and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; pp 337–382.