Control of circularly polarized luminescence (CPL) properties by supramolecular complexation†

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The sign of circularly polarized luminescence (CPL) of a chiral 2_1-helical columnar organic fluorophore was successfully controlled in the solid-state by changing an achiral fluorescence component molecule, and not by using a chiral component molecule with opposite chirality.

The solid-state optical properties of organic compounds are very important physical properties to be considered in the development of new functional materials. The potential application of solid-state fluorescence techniques to organic electroluminescence (EL) devices, optoelectronic devices, *etc*., has recently attracted much attention.[1] Thus far, most organic compounds that possess solid-state fluorescence properties are composed of a single molecule,[2] and only a few reports about supramolecular organic fluorophores composed of two or more organic molecules are available.[3] These reported fluorophores, however, do not have circularly polarized luminescence (CPL) properties, because they consist of achiral molecules. Recently, we developed a chiral supramolecular organic fluorophore with CPL properties in the solid state, by combining two types of organic molecule: chiral (1*R*,2*R*)-1,2-diphenylethylenediamine [(1*R*,2*R*)-**1**] and fluorescent 2-anthracenecarboxylic acid (**2**) (Fig. 1).[4] Typically, this complex has a 2_1-helical columnar hydrogen- and ionic-bonded network, formed by the carboxylate oxygen of a carboxylic acid anion and the ammonium hydrogen of a protonated amine. Usually, in order to control the CPL sign, a chiral compound with opposite chirality is used. However, such compounds are not easily available. Therefore, the control of the CPL sign of chiral fluorophores without the use of these chiral compounds may be useful in their development.

One of the key properties of supramolecular complexes composed of two or more component molecules is the ability to easily control their physical and chemical properties by changing their component molecules.[5] Moreover, the resultant supramolecular complex may have an effective functionality due to the synergistic effect of packing and the properties of its component molecules in the solid state. In this Letter, we report the control of the CPL properties of a two-component chiral supramolecular organic fluorophore by changing an achiral fluorescent component molecule in the solid-state, not using a chiral component molecule with opposite chirality. The same chiral amine molecule, (1*R*,2*R*)-**1**, was used as one of the two component molecules. 2-Anthraceneacetic acid (**3**) was used instead of the carboxylic acid derivative, **2**, as the achiral fluorescent component molecule.

3 was prepared by following a procedure discussed in a previous report.[6] The formation of a supramolecular organic fluorophore was attempted *via* crystallization from an ethanol (EtOH) solution. A mixture of (1*R*,2*R*)-**1** and **3** was dissolved in EtOH and left to stand at room temperature. After a week, a large number of crystals (**I**), composed of (1*R*,2*R*)-**1** and **3**, were obtained.

The most serious problem in solid-state organic fluorophores is fluorescence quenching in the crystalline state. In order to study the solid-state optical properties of complex **I**, its solid-state fluorescence spectrum was measured. Complex **I** showed fluorescence without quenching, and the solid-state fluorescence maximum of complex **I** was observed at 435 nm, with a shift in the maximum by 66 nm to a lower wavelength being observed relative to the maximum of **3**. The absolute value of the photoluminescence quantum yield in complex **I** ($\Phi_F = 0.06$) increased by approximately double that of **3** in the solid-state.

Fluorescent complex **I** is a chiral crystal; therefore, its fluorescence may be CPL. In order to study the CPL of complex **I**, its solid-state CD spectrum was measured by using a KBr pellet (Fig. 2, blue line). Solid-state samples were prepared according to a standard procedure for obtaining glassy KBr matrices.[7] Features in the CD spectrum originating from an anthracene ring were observed at 346, 365, 385 and

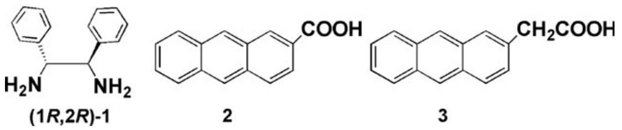

Fig. 1 Structures of compounds **1**, **2** and **3**

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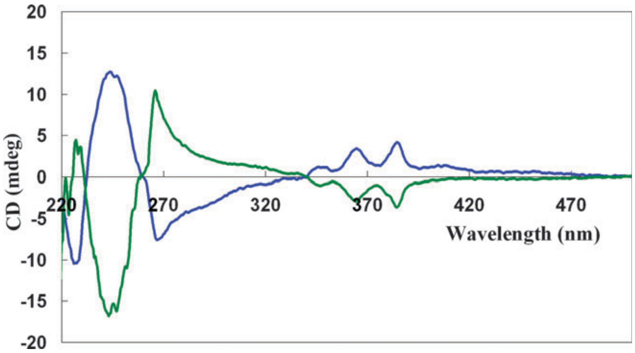

Fig. 2 The CD spectra of complexes **I** (blue line) and **I′** (green line) in the solid-state (using a KBr pellet).

405 nm. The circular anisotropy (g_{CD} = ΔOD/OD) factor of the last Cotton effect (λ^{CD} = 405 nm) was approximately 0.3×10^{-3}. In order to check whether the crystal caused any artifacts in the spectrum, complex **I′** was prepared by using (1*S*,2*S*)-1,2-diphenylethylenediamine [(1*S*,2*S*)-**1**] instead of (1*R*,2*R*)-**1**, and its CD spectrum was measured (Fig. 2, green line). This spectrum was found to be a mirror image of that of complex **I**. When the CD spectrum of complex **I** was compared to that of complex **II**, composed of (1*R*,2*R*)-**1** and **2**, the two spectra were found to be similar; in particular, the sign of the last Cotton effect (λ^{CD} = 406 nm for complex **II**) showed the same positive sign[4] and the g_{CD} factor of complex **II** was close to that of complex **I** (approximately 0.5×10^{-3}).

Consequently, the measurement of the solid-state CPL spectrum of complex **I** was attempted by using a KBr pellet, and was successfully observed (Fig. 3, blue line).

The circular anisotropy [$g_{em} = 2(I_L - I_R)/(I_L + I_R)$] factor of complex **I** was approximately -0.9×10^{-3}, and was close to that of complex **II** ($g_{em} = 0.8 \times 10^{-3}$).[8] Interestingly, although the CPL sign of the spectrum of complex **II** was positive (Fig. 3, orange line), that of complex **I** was negative, despite using the same chiral component molecule (1*R*,2*R*)-**1**.[4] Moreover, in complex **I**, the CPL sign of the spectrum was different to that of the corresponding CD spectrum at the longest wavelength (λ^{CD} = 405 nm). In fact, when the CD spectrum was measured after the measurement of CPL, its sign was positive. To the best our knowledge, this is the first example of the CPL sign of a supramolecular fluorophore being controlled by changing an achiral component molecule in the solid-state.

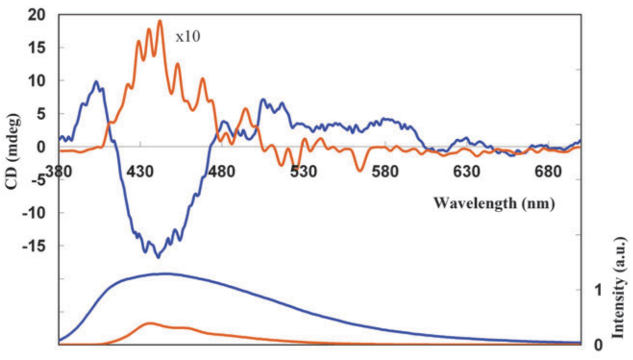

Fig. 3 CPL and fluorescence spectra of complexes **I** (blue line) and **II** (orange line) in the solid-state (using a KBr pellet).

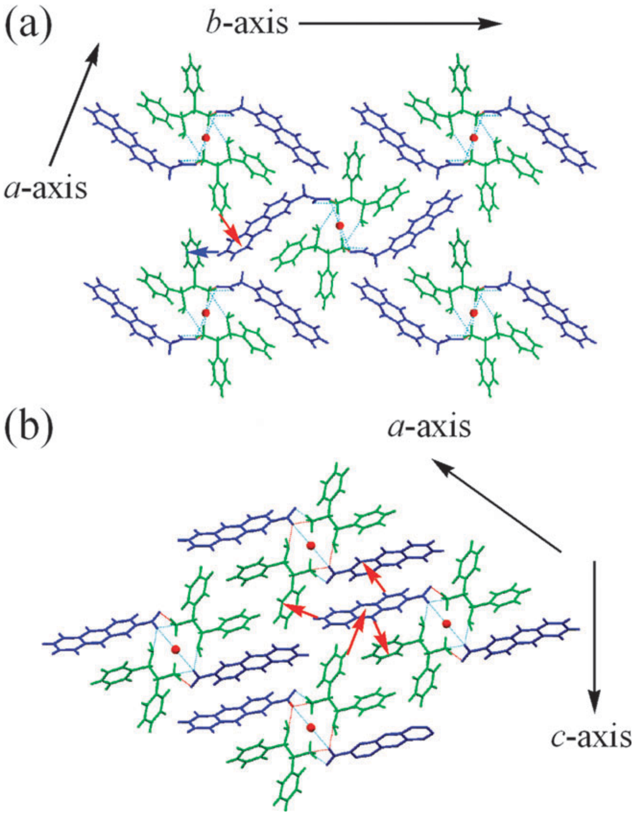

Fig. 4 The crystal structures of complexes **I** and **II**. (a) Packing structure observed along the c-axis for complex **I**; (b) packing structure observed along the b-axis for complex **II**.[4] Red and blue arrows indicate aromatic–aromatic edge-to-face interactions.

To study the optical properties of complex **I**, an X-ray crystallographic analysis was attempted, and its crystal structure is shown in Fig. 4. The stoichiometry of complex **I** is (1*R*,2*R*)-**1** : **3** : H_2O = 2 : 2 : 1 and the space group is $P2_12_12$. As expected, this crystal has a 2_1-helical columnar hydrogen- and ionic-bonded network along the *c*-axis, similar to that of complex **II**.[4] The columns are mainly formed by the carboxylate oxygens of carboxylic acid anions (Fig. 4, the molecules shown in blue) and the ammonium hydrogens of protonated amines (Fig. 4, the molecules shown in green). The included water molecules (Fig. 4, shown by red spheres) link the carboxyl and amino groups through hydrogen bonds, and contribute to the maintenance of the columnar frame. Complex **I** is formed by the self-assembly of these 2_1-columns (Fig. 4(a)). Interestingly, although complexes **I** and **II** have a similar chiral 2_1-helical columnar structure, the packing structure of the 2_1-columns of complex **I** is different from that of the 2_1-columns of complex **II** (Fig. 4(b)). That is, although the anthracene rings between adjoining 2_1-columns are zigzag in complex **II**, the rings in complex **I** lie vertically between the 2_1-columns. Moreover, although there are four aromatic–aromatic edge-to-face interactions (2.69, 2.84, 2.87 and 2.96 Å, shown by red arrows in Fig. 4(b)) per anthracene ring in complex **II**, there are only two aromatic–aromatic edge-to-face interactions in complex **I** (2.95 and 2.98 Å, shown by red and blue arrows in Fig. 4(a)) per anthracene ring.

From the crystal structures and CD spectra, it is evident that, although the packing structure of the anthracene ring in complexes **I** and **II** is different, the chirality of both the complexes in the ground state is the same. Regarding the origin of the CD and CPL properties, the crystal structures and oscillator coupling theory[9] suggest that the features of the CD and CPL spectra originating from the anthracene ring are mainly caused by interactions of the anthracene ring with the adjoining 2_1-helical columns. Therefore, it is thought that the reversed CPL sign of the spectrum between complexes **I** and **II** is caused by a local change in packing structure of the anthracene ring in crystalline-state complex **I**. That is, in complex **I**, a local structural change in the crystalline state is induced by the incident beam, only when the CPL spectrum is measured. A comparison of the crystal structures of complexes **I** and **II** shows that in complex **I**, the number and distances of aromatic–aromatic edge-to-face interactions are lesser and greater, respectively, than those in complex **II**. Moreover, the melting point (210–218 °C) and crystal density (1.303 g cm^{-3}) of complex **I** are lower than those of complex **II** (238–245 °C and 1.328 g cm^{-3}, respectively). These results also support the proposed mechanism.

In conclusion, chiral 2_1-helical columnar organic fluorophores were successfully formed by using fluorescent 2-anthraceneacetic acid and chiral 1,2-diphenylethylenediamine. In this system, the CPL sign of the chiral fluorophore could be successfully controlled by changing an achiral fluorescence component molecule, despite the use of a chiral component molecule with opposite chirality in the solid-state. It is expected that such chiral supramolecular complexes, and their optical properties will be useful in the development of novel solid-state chiral fluorophores.

Experimental

Formation of complex I

A mixture of (1*R*,2*R*)-**1** (10 mg, 0.047 mmol) and **3** (11 mg, 0.047 mmol) was dissolved in EtOH (4 mL) and left to stand at room temperature. After a week, a large number of crystals (**I**), composed of (1*R*,2*R*)-**1** and **3**, were obtained. The weight of the total crop of crystals from one batch was 9.0 mg.

Measurement of solid-state fluorescence spectra

Solid-state fluorescence spectra and absolute photoluminescence quantum yields were measured using an Absolute PL Quantum Yield Measurement System (C9920-02, Hamamatsu Photonics K. K.). The excited wavelength was 372 nm.

Measurement of CD spectra

CD spectra were measured using a Jasco J-800KCM spectrophotometer.

Measurement of CPL spectra

CPL spectra were measured using a Jasco CPL-200 spectrophotometer.[10] The excited wavelength was 350 nm. CPL spectra was approached by a simple moving average (SMA). The power of an incident beam of the CPL spectrometer was 8.0 μW 0.04 cm^{-2} at the installation position of sample.[9]

X-Ray crystallographic study

X-Ray diffraction data for single crystals were collected using a Bruker Apex diffractometer. The crystal structures were solved by the direct method and refined by full-matrix least-squares using SHELX97. The structure diagrams were prepared using PLATON. **Crystallographic data for I:** $C_{14}H_{17}N_2 \cdot C_{16}H_{11}O_2 \cdot 0.5H_2O$, M = 457.55, orthorhombic, space group $P2_12_12$, a = 16.2996(18), b = 24.900(3), c = 5.7470(7) Å, U = 2332.5(5) Å^3, Z = 4, D_C = 1.303 g cm^{-3}, μ(Mo K$_\alpha$) = 0.083 mm^{-1}, 14 524 reflections measured, 3150 unique, R_{int} = 0.1124, final $R(F^2)$ = 0.0639, w$R2$ = 0.0927, using 2230 reflections with $I > 2.0\sigma(I)$, R (all data) = 0.1043, T = 100(2) K.†

References

1. *Organic Light-Emitting Devices*, ed. J Shinar, Springer-Verlag, New York, 2004.
2. (*a*) K. Yoshida, Y. Ooyama and S. Tanikawa, *J. Chem. Soc., Perkin Trans. 2*, 2002, 708; (*b*) Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels and D. Stalke, *Angew. Chem., Int. Ed.*, 2003, **42**, 783; (*c*) J. L. Scott, T. Yamada and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1697; (*d*) J. L. Scott, T. Yamada and K. Tanaka, *New J. Chem.*, 2004, **28**, 447; (*e*) Y. Ooyama and K. Yoshida, *New J. Chem.*, 2005, **29**, 1204; (*f*) S. Oshita and A. Matsumoto, *Langmuir*, 2006, **22**, 1943.
3. (*a*) Y. Mizobe, N. Tohnai, M. Miyata and Y. Hasegawa, *Chem. Commun.*, 2005, 1839; (*b*) Y. Mizobe, H. Ito, I. Hisaki, M. Miyata, Y. Hasegawa and N. Tohnai, *Chem. Commun.*, 2006, 2126.
4. Y. Imai, K. Kawaguchi, T. Harada, T. Sato, M. Ishikawa, M. Fujiki, R. Kuroda and Y. Matsubara, *Tetrahedron Lett.*, 2007, **48**, 2927. The CSD Refcode for complex **II** is GIKYUV.
5. (*a*) Y. Imai, T. Sato and R. Kuroda, *Chem. Commun.*, 2005, 3289; (*b*) Y. Imai, K. Kawaguchi, K. Asai, T. Sato, R. Kuroda and Y. Matsubara, *CrystEngComm*, 2007, **9**, 467; (*c*) K. Kodama, Y. Kobayashi and K. Saigo, *Chem.–Eur. J.*, 2007, **13**, 2144; (*d*) Y. Imai, K. Kawaguchi, K. Murata, T. Sato, R. Kuroda and Y. Matsubara, *Chem. Lett.*, 2007, 812; (*e*) K. Kodama, Y. Kobayashi and K. Saigo, *Cryst. Growth Des.*, 2007, **7**, 935; (*f*) Y. Imai, K. Kawaguchi, K. Murata, T. Sato, R. Kuroda and Y. Matsubara, *Cryst. Growth Des.*, 2007, **7**, 1676.
6. N. Acto and E. Erliner, *J. Am. Chem. Soc.*, 1964, **86**, 3312.
7. R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 433.
8. I_L and I_R are the intensity of left and right circular polarized emissions.
9. (*a*) N. Harada and K. Nakanishi, *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, 1983; (*b*) N. Berova and K. Nakanishi, in *Circular Dichroism: Principles and Applications*, ed. N Berova, K Nakanishi and R. W. Woody, Wiley-VCH, New York, 2nd edn, 2000, pp. 337–382.
10. (*a*) J. P. Riehl and F. S. Richardson, *Chem. Rev.*, 1986, **86**, 1; (*b*) J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, *J. Am. Chem. Soc.*, 2003, **125**, 11808.