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# Chiral supramolecular thiophene fluorophore consisting of thiophenecarboxylic acid derivatives

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### 1. Introduction

The solid-state optical property of organic compounds finds remarkable application in the development of new functional organic materials. The solid-state organic fluorescence property, in particular, has attracted considerable attention in the field of optoelectronics owing to its application in organic electroluminescence (EL) devices and optical sensors.<sup>1</sup> Therefore, many solid-state organic fluorophores composed of a single organic molecule have been reported, of which two-component supramolecular organic fluorophores have recently attracted greater attention.<sup>2</sup> However, most of the previously reported supramolecular organic fluorophores lack chirality and hence do not possess solid-state chiral optical properties, such as solid-state circular dichroism (CD) or circularly polarized luminescence (CPL) properties.

We recently developed a solid-state chiral supramolecular organic fluorophore composed of (R)-1-(2-naphthyl)ethylamine [(R)-1] as the chiral component molecule and 2-anthracenecarboxylic acid as the fluorescent component molecule.<sup>3</sup> The structural characteristic of this chiral supramolecular organic fluorophore is that it

### ABSTRACT

Solid-state chiral supramolecular thiophene fluorophore has been successfully prepared by using chiral (R)-1-(2-naphthyl)ethylamine and 5-bromothiophene-2-carboxylic acid. This chiral supramolecular thiophene fluorophore is formed by assembling chiral 2<sub>1</sub>-helical columnar network structures composed of (R)-1-(2-naphthyl)ethylamine and 5-bromothiophene-2-carboxylic acid. This supramolecular organic fluorophore exhibits circularly polarized luminescence (CPL) even in the solid state.

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is composed of a  $2_1$ -helical columnar hydrogen- and ionic-bonded network structure formed by the association of (*R*)-**1** and 2anthracenecarboxylic acid. The advantage of these supramolecular systems is that their physical and chemical properties can be altered by changing the component molecules.

Recently, a large number of organic functional materials consisting of a polythiophene backbone have been reported.<sup>4</sup> These polythiophene compounds show various electrochemical and photochemical properties. Therefore, it is expected that novel solidstate chiral supramolecular fluorophores may be prepared by using thiophene derivatives as one of the component molecules in supramolecular complexes.

In this study, we prepare a novel solid-state chiral supramolecular thiophene fluorophore with (R)-**1**, and study its solid-state optical properties and crystal structures. The following three basic thiophene acid derivatives are used for the preparation: 2thiophenecarboxylic acid (**2a**), 5-chlorothiophene-2-carboxylic acid (**2b**), and 5-bromothiophene-2-carboxylic acid (**2c**).





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### 2. Results and discussion

The (R)-**1**/**2a** chiral supramolecular thiophene fluorophore was first prepared via crystallization from a methanol (MeOH) solution. (R)-**1** and **2a** were dissolved in the MeOH solution and left to stand at room temperature. After a week, a large number of crystals were obtained. However, because good-quality crystals could not be obtained, the X-ray analysis was unsatisfactory. Therefore, X-ray powder diffraction (XRPD) analysis of these obtained crystals was carried out, and the results were compared to those of the XRPD analysis of component molecules (R)-**1** and **2a** (Fig. 1).



**Fig. 1.** X-ray powder diffraction (XRPD) patterns of (a) complex **I**, (b) component molecule (*R*)-**1**, and (c) component molecule **2a**.

It was found that the peaks observed in molecules (R)-1 and 2a disappeared completely and a new set of peaks had appeared. This XRPD and <sup>1</sup>H NMR<sup>5</sup> analyses revealed that novel chiral supramolecular thiophene complex I composed of (R)-1 and 2a was obtained without the crystallization solvent MeOH.

The most serious complication associated with solid-state organic fluorophores is the occurrence of fluorescence quenching in the crystalline state. In order to study the solid-state optical properties of the obtained complex **I**, it is important to record the solid-state fluorescence spectrum. However, in the present case, the solid-state fluorescence of complex **I** was hardly observed.

This prompted us to attempt the preparation of a chiral substituted supramolecular thiophene complex. The (R)-1/2b,c chiral supramolecular thiophene fluorophores were prepared via crystallization from a MeOH solution in the same manner as that used for the preparation of (R)-1/2 supramolecular complex I. (R)-1 and 2b (or 2c) were dissolved in the MeOH solution and left to stand at room temperature. After a week, a large number of crystals of complex II composed of (R)-1 and 2b, or crystals of complex III composed of (R)-1 and 2c were obtained.

To first study the solid-state optical properties of the obtained supramolecular thiophene complexes **II** and **III**, the solid-state fluorescence spectra of these complexes were recorded. The solid-state fluorescence property of complex **II** was also hardly observed (similar to complex **I**). Interestingly, complex **III** exhibited fluorescence even in the solid state. In the solid state, fluorescence maximum ( $\lambda_{em}$ ) for complex **III** is observed at 412 nm, and the absolute value of the photoluminescence quantum yield ( $\Phi_F$ ) for complex **III** is 0.38. This fluorescence of complex **III** is peculiar to the solid state. The fluorescence property of mixture of (R)-**1** and **3** in MeOH solution was hardly observed.

In order to study the trends in the solid-state chiral optical property of supramolecular thiophene fluorophore, the solid-state CD spectra of complex **II** and fluorescent complex **III** were recorded using KBr pellets. The solid-state CD and absorption spectra of complexes **II** and **III** (indicated by black lines) are shown in Fig. 2.

The shapes of the CD spectra are similar. The circular anisotropy factors ( $|g_{CD}=\Delta OD/OD|$ ) of the last Cotton effect ( $\lambda^{CD}=297$  nm for **II** 



**Fig. 2.** CD and absorption spectra of complexes (a) **II** and (b) **III** (black lines) and complexes **II'** and **III'** (gray lines) in the solid state (using KBr pellets).

and 289 nm for III) for II and III are approximately  $6.8 \times 10^{-4}$  and  $1.4 \times 10^{-3}$ , respectively. In order to check whether the complexes II and III introduced any artifacts in the spectrum, complexes II' and III' were prepared, wherein (*R*)-1 was replaced with (*S*)-(-)-1-(2-naphthyl)ethylamine [(*S*)-1]. Interestingly, when the solid-state CD spectra of complexes II' and III' were recorded (indicated by gray lines in Fig. 2), they were found to be mirror images of the CD spectra of complexes II and III. These results indicate that effective chiral transfer occurs from chiral molecule 1 to complexes II and III through complexation.

Consequently, the solid-state CPL spectra of fluorescent complexes III and III' (that show the solid-state fluorescence property) were recorded using KBr pellets. The CPL spectra were successfully observed in the solid state. The solid-state CPL and fluorescence spectra of complexes III and III' are shown in Fig. 3. Interestingly, the fluorescence spectra of these complexes recorded using KBr pellets are similar to that obtained without using KBr matrices. This result shows that the KBr matrix does not play any role in obtaining the spectrum.

A negative solid-state CPL spectrum was obtained for complex **III** whose circular anisotropy factor  $[|g_{em}=2(I_L-I_R)/(I_L+I_R)|]$  is approximately  $2.6 \times 10^{-3}$ . This shows that complex **III** 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 supramolecular thiophene organic fluorophore.

To study the crystal structures of complex **II** and fluorescent complex **III**, X-ray crystallographic analyses of complexes **II** and **III** were carried out, and the crystal structures obtained were compared. The crystal structures of complex **II** are shown in Fig. 4. The stoichiometry of **II** is (R)-**1**/**2b**=1:1, and its space group is  $P2_12_12_1$ . This complex has a characteristic  $2_1$ -helical columnar network structure along the *a*-axis (Fig. 4a). This column is mainly composed of the carboxylate oxygen of the carboxylic acid anions and the ammonium hydrogen of the protonated amine. Complex **II** is formed by the assembly of these  $2_1$ -helical columns (indicated in



**Fig. 3.** CPL and fluorescence spectra of complexes **III** (black lines) and **III**'(gray lines) in the solid state (using KBr pellets).



**Fig. 4.** Crystal structures of complex **II**: (a)  $2_1$ -helical columnar hydrogen- and ionicbonded network along *a*-axis and (b) packing structure observed along *a*-axis. The solid red arrow *A* and blue arrow *B* indicate intercolumnar naphthalene–naphthalene and naphthalene–thiophene edge-to-face interactions, respectively. The dotted red circle indicates  $2_1$ -helical column.

Fig. 4b by dotted red circle) by one intercolumnar naphthalene—naphthalene edge-to-face interaction (2.81 Å; indicated by solid red arrow *A* in Fig. 4b) between naphthalene rings in (*R*)-**1** and naphthalene—thiophene edge-to-face interaction (3.00 Å; indicated by solid blue arrow *B* in Fig. 4b) between the hydrogen atom of the naphthalene ring in (*R*)-**1** and the thiophene ring of **2b** (Fig. 4b).<sup>6</sup>

The crystal structures of fluorescent complex **III** are shown in Fig. 5. The stoichiometry of **III** is (R)-**1/2c**=1:1, and its space group is  $P2_12_12_1$ . Interestingly, in **II** and **III**, the structures of  $2_1$ -helical columns and their packing arrangements are almost identical. This complex also has a shared  $2_1$ -helical columnar network structure along *a*-axis, as observed in complex **II** (Fig. 5a). **III** is formed by assembling of these  $2_1$ -helical columns (indicated in Fig. 5b by dotted red circle) by two naphthalene–naphthalene edge-to-face interactions (2.79 and 2.98 Å; indicated by solid red arrow *A* and



**Fig. 5.** (a) Crystal structures of complex **III**: (a)  $2_1$ -helical columnar hydrogen- and ionic-bonded network along *a*-axis and (b) packing structure observed along *a*-axis. The solid red arrow *A* and blue arrow *B* indicate intercolumnar naph-thalene edge-to-face interactions. The dotted red circle indicates  $2_1$ -helical column.

blue arrow *B* in Fig. 4b, respectively) between naphthalene rings in (*R*)-1 (Fig. 5b).<sup>6</sup>

We would like to mention here that the fluorescent property of the complex is increased as the substituent in the thiophene ring changed from chlorine (Cl) to bromine (Br). First, to study the origin of the solid-state fluorescence of complex III, the solid-state fluorescence spectra of component molecules (R)-1 and 2c were recorded. Both component molecules showed fluorescence in the solid state. The solid-state  $\lambda_{em}$  of (*R*)-1 and 2c is observed at 340 and 428 nm, respectively, and the  $\Phi_{\rm F}$  of (*R*)-1 and 2c is 0.08 and 0.06 in the solid state, respectively. This result suggests that the origin of solid-state fluorescence in complex III is the thiophene unit in complex. Next, to study the origin of the difference of solid-state fluorescence between complexes II and III, the crystal structures of II and III were compared in detail. Even though the crystal structures of complexes II and III are nearly identical, the circumstances around Cl and Br in the crystal structure have a small difference. Br atom possesses a near contact toward carbon atom of the carboxylic moiety (3.55 Å), whereas the distance between Cl atom and carbon atom of the carboxylic moiety is 3.61 Å. Such interaction may reduce the spin-orbit interaction in Br atom, and decrease the nonradiative decay by enhancing the rigidity of the structure. In addition, the solid-state fluorescence spectrum of component molecule 2b was also measured. This component molecule also showed fluorescence in the solid state. The solidstate  $\lambda_{em}$  and  $\Phi_{F}$  is observed at 426 nm and 0.09, respectively. This may mean that the Cl/Br group over molecule 2 affects the excited state structures of complexes II and III rather than the ground state structures as observed in the X-ray crystal structure. The observed increase in fluorescence of complex III may be also due to the increased stabilization of its excited singlet state due to the presence of Br as compared to the Cl in complex II.

### 3. Conclusion

A chiral supramolecular thiophene fluorophore has been successfully prepared by combining chiral (R)-1-(2-naphthyl)ethylamine and 5-bromothiophene-2-carboxylic acid. This thiophene complex is found to be composed of chiral 2<sub>1</sub>-helical columnar network structure and shows CPL even in the solid state. This further enhances the potential of this fluorescence system, enabling its application in the design of novel solid-state chiral supramolecular thiophene fluorophores. A study of the complexation behavior and optical properties of the obtained complexes is expected to provide useful information for designing novel supramolecular fluorophore with thiophene units.

### 4. Experimental

### 4.1. General methods

Component molecules (R)-1 and (S)-1 were purchased from Alfa Aesar. Component molecule **2a** was purchased from Sigma–Aldrich. Component molecules **2b** and **2c** were purchased from Tokyo Chemical Industry Co., Ltd. Crystallization solvent MeOH was purchased from Wako Pure Chemical Industry. All reagents were used directly as obtained commercially.

## 4.2. Formation of complex by crystallization from MeOH solution

(*R*)-1 (8.6 mg,  $5.02 \times 10^{-5}$  mol) and each thiophenecarboxylic acid derivative ( $5.04 \times 10^{-5}$  mol) were dissolved in MeOH (3 mL) under heat and left to stand at room temperature. After one week, a large number of crystals [complex I for the (*R*)-1/2a system (6 mg), complex II for the (*R*)-1/2b system (9 mg), and complex III for the (*R*)-1/2c system (8 mg)] were obtained. The weight of crystals reported here is the total weight obtained in one batch.

### 4.3. X-ray crystallographic study of crystal

The X-ray diffraction data for single crystal of complex II were collected using RIGAKU SATURN 70R. The X-ray diffraction data for single crystal of complex III were collected using Bruker Apex. The crystal structures were solved by the direct method<sup>7</sup> and refined by full-matrix least-squares using SHELXL97.7 The diagrams were drawn using PLATON.<sup>8</sup> The absorption corrections were performed using SADABS.<sup>9</sup> The nonhydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were included in the models at their calculated positions in the riding-model approximation. Crystallographic data of II: C<sub>12</sub>H<sub>13</sub>N· C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>SCl, M=333.82, Orthorhombic, space group  $P2_12_12_1$ , a=6.414(4), b=13.712(8), c=18.334(11) Å, V=1612.5(17) Å<sup>3</sup>, Z=4,  $Dc=1.375 \text{ g cm}^{-3}$ ,  $\mu(Mo \text{ K}\alpha)=0.372 \text{ mm}^{-1}$ , 6425 reflections measured, 3161 unique, final  $R(F^2)=0.0733$  using 1341 reflections with *I*>2.0σ(*I*), *R*(all data)=0.1458, *T*=100(2) K. CCDC 809920. Crystallographic data of III: C<sub>12</sub>H<sub>13</sub>N·C<sub>5</sub>H<sub>3</sub>O<sub>2</sub>SBr, *M*=378.28, Orthorhombic, space group  $P2_12_12_1$ , a=6.4089(3), b=13.7191(7), c=18.5284(10) Å, V=1629.10(14) Å<sup>3</sup>, Z=4, Dc=1.542 g cm<sup>-3</sup>,  $\mu$ (Mo  $K\alpha$ )=2.657 mm<sup>-1</sup>, 14,384 reflections measured, 3799 unique, final  $R(F^2)=0.0304$  using 3457 reflections with  $I>2.0\sigma(I)$ , R(all data)=0.0349, T=115(2) K. CCDC 809921. Crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223 336 033; deposit@ccdc.cam.ac.uk).

### 4.4. Measurement of <sup>1</sup>H NMR spectrum

<sup>1</sup>H NMR spectrum was recorded with a JNM-AL400 spectrometer in dimethyl sulfoxide(DMSO)- $d_6$  (400 MHz).

### 4.5. Measurement of XRD spectra

X-ray powder patterns were recorded on a Rigaku RINT2500 using graphite-monochromated Cu K $\alpha$  radiation (40 kV, 80 mA). The spectra were measured at room temperature between 3° and 35° in the 2 $\theta$  scan mode with steps 0.02° in 2 $\theta$  and 3°/min.

### 4.6. Measurement of solid-state fluorescence spectra

A solid-state fluorescence spectra and absolute photoluminescence quantum yield were measured by Absolute PL Quantum Yield Measurement System (C9920-02, HAMAMATSU PHOTONICS K. K.) under air atmosphere at room temperature. The excited wavelength is 358 nm for complex **III**. The excited wavelength of (R)-**1**, **2b**, and **2c** is 258, 367, and 373 nm, respectively.

#### 4.7. Measurement of solid-state CD and absorption spectra

The CD and absorption spectra were measured using a Jasco J-800KCM spectrophotometer. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.<sup>10</sup>

### 4.8. Measurement of solid-state CPL spectrum

The CPL spectrum was measured using a Jasco CPL-200 spectrophotometer. The excited wavelength is 350 nm. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices. The power of an incident beam of the CPL spectrometer is 8.0  $\mu$ W/0.04 cm<sup>2</sup> at the installation position of sample. The CPL spectrum is approached by Simple Moving Average (SMA).

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### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.07.086.

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