A Solid-state Chiral Fluorophore Obtained from Achiral Fluorescent Biphenyl-4-carboxylic Acid and *rac*-Phenylmethylamine Derivatives

Yoshitane Imai,*[1] Katuzo Murata,[1] Hideki Matsuno,[1] Kensaku Kamon,[1] Tomohiro Sato,[2]
Reiko Kuroda,[2,3] and Yoshio Matsubara*[1]
[1]*Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,*
3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502
[2]*JST ERATO-SORST Kuroda Chiromorphology Team, 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041*
[3]*Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo,*
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902

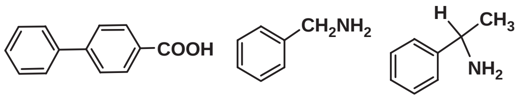
(Received April 15, 2008; CL-080390; E-mail: y-imai@apch.kindai.ac.jp, y-matsu@apch.kindai.ac.jp)

A chiral supramolecular organic fluorophore is developed by using achiral biphenyl-4-carboxylic acid and *rac*-1-phenylethylamine. This fluorophore is a spontaneously resolved chiral fluorescence system.

The potential application of solid-state fluorescence techniques to organic electroluminescence (EL) devices, optodevice materials, etc. has attracted considerable attention.[1] To date, solid-state organic fluorophores have mostly comprised a single molecule,[2] and there have been only a few reports concerning supramolecular organic fluorescent complexes containing two or more organic molecules.[3] Almost all these reported complexes, however, have no chirality. Recently, we have succeeded in developing a chiral supramolecular organic fluorophore that shows circularly polarized luminescence (CPL) in the solid state by combining two types of organic molecules—fluorescent biphenyl-4-carboxylic acid (**1**) (Chart 1) and chiral (1*R*,2*R*)-1,2-diphenylethylenediamine.[4] However, if a chiral supramolecular organic fluorophore is formed by using achiral or racemic (rac) component molecules instead of chiral component molecules, it is very useful from the viewpoint of industrialization.

In this paper, we report the formation of a chiral supramolecular organic fluorophore and its optical property; the chiral fluorophore was prepared by employing achiral or rac supramolecular building blocks. An acid molecule, achiral fluorescent biphenyl-4-carboxylic acid (**1**), was used as one of the building blocks. Achiral and rac base amine molecules, i.e., benzylamine (**2**) and *rac*-1-phenylethylamine (*rac*-**3**), respectively, were used as the other building blocks.

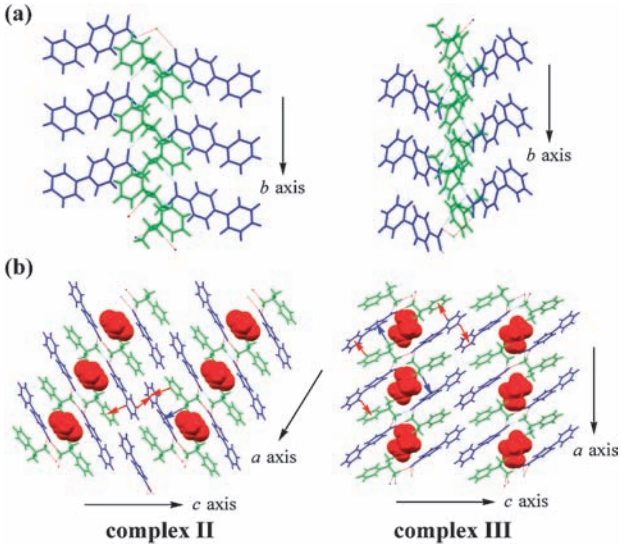
The complexation behavior of the **1**/**2** system was studied. The formation of a chiral supramolecular organic fluorophore was attempted via crystallization from MeOH and EtOH solutions. A mixture of **1** (10 mg, 0.05 mmol) and **2** (6 mg, 0.06 mmol) was dissolved in each alcohol solution (2 mL) and left to stand at room temperature. After a few days, a large number of identical crystals **I** (7 mg)[5] were obtained from both solutions. The X-ray crystal structure analysis of complex **I** is shown in Figure ESI-1.[6] Unfortunately, this complex is a rac complex. The stoichiometry of complex **I** was molecule **1**: molecule **2** = 1:1, and its space group was $P2_1/c$. This crystal had a characteristic one-dimensional (1D) columnar network structure along the *b* axis (Figure ESI-1a). The column was mainly formed by the carboxylate oxygen of a carboxylic acid anion (Figure ESI-1, indicated by the molecules in blue) and the ammonium hydrogen of a protonated amine (Figure ESI-1, indicated by the molecules in green). Complex **I** was formed by the self-assembly of the column (Figure ESI-1b). The column interacted via benzene–benzene edge-to-face interaction (3.74 Å, indicated by a red arrow in Figure ESI-1b) and CH–π interaction (3.57 Å, indicated by a blue arrow in Figure ESI-1b).[7]



1 **2** *rac*-**3**

Chart 1.

A useful feature of these supramolecular systems is that the structure of the complex can be easily controlled by changing the component molecules.[3a,8] Subsequently, *rac*-**3** is used instead of **2**. Using the same procedure, we attempt the formation of a chiral supramolecular organic fluorophore by crystallization from the MeOH and EtOH solutions. As a result, different complexes **II** and **III** are obtained, respectively.[6] The crystal



complex II **complex III**

Figure 1. Crystal structures of complexes **II** and **III**. Molecules of **1** and **3** are indicated as blue and green molecules, respectively. MeOH and EtOH molecules are indicated as red space-filling molecules. (a) View along *c* axis. 1D columnar network structure is parallel to *b* axis. (b) Packing structure observed along *b* axis. Red and blue arrows indicate benzene–benzene edge-to-face and CH–π interactions, respectively.

Table 1. Crystal forms and solid-state fluorescence spectral data of complexes **I**–**III** and fluorescent molecule **1**

Complex	Crystal form	λ_{ex}/nm	λ_{em}/nm	ϕ_{F}
I	colorless needle	324	395	0.47
II	colorless needle	321	385	0.63
III	colorless needle	327	387	0.61
Compound **1**	colorless needle	312	393	0.38

structures of complexes **II** and **III** are shown in Figure 1.[6]

Interestingly, both these complexes are chiral and are the same as those obtained from the **1**/(*R*)-**3** system.[9] The stoichiometries of complexes **II** and **III** are **1**:(*R*)-**3**:MeOH (or EtOH) = 1:1:0.5, and their space groups are *C*2. These complexes have characteristic 2_1-helical columnar hydrogen- and ion-bonded network structures along the *b* axis, similar to complex **I** (Figure 1a). Both complexes are formed by the self-assembly of these 2_1-columns, which gives rise to the channel-like cavities (Figure 1b). In complex **II**, these 2_1-columns interact by three types of benzene–benzene edge-to-face interactions (3.59, 3.64, and 3.70 Å; indicated by the red arrows in Figure 1b) and CH–π interaction (3.61 Å, indicated by a blue arrow in Figure 1b).[7] On the other hand, complex **III** has four types of benzene–benzene edge-to-face interactions (3.53, 3.62, 3.63, and 3.66 Å, indicated by the red arrows in Figure 1b) apart from CH–π interaction (3.57 and 3.80 Å, indicated by the blue arrows in Figure 1b).[7] Although the alcohol molecules (Figure 1, indicated as red space-filling molecules) are disordered, they are trapped one-dimensionally along the direction of the cavity. In one batch, chiral crystals composed of **1** and (*S*)-**3** were also obtained, respectively.[9] This shows that this system is a spontaneous resolution system.

Since this system comprises **1**, which is fluorescent, the obtained complexes may also exhibit fluorescence. In order to study the solid-state fluorescence property of this system, the solid-state fluorescence spectra of these complexes have been determined (Table 1).[6]

Although the most serious problem encountered in a solid-state organic fluorophore is fluorescence quenching in the crystalline state, this is not observed in any of the complexes obtained. A comparison of complex **I** and the fluorescent molecule **1** reveals that their solid-state fluorescence maxima (λ_{em}) are similar. However, the absolute value of the photoluminescence quantum yield (ϕ_{F}) increases from 0.38 to 0.47. On the other hand, the solid-state fluorescence maxima (λ_{em}) of complexes **II** and **III** are similar (385 and 387 nm, respectively), and small hypsochromic shifts (8 and 6 nm) are observed in these complexes relative to the hypsochromic shift of **1**. Moreover, the absolute photoluminescence quantum yields in complexes **II** and **III** ($\phi_{\mathrm{F}} = 0.63$ and 0.61) are observed to be higher than the yield in **1** ($\phi_{\mathrm{F}} = 0.38$).

A comparison of the crystal structures of complex **I** and the fluorescent molecule **1**[6] reveals that the relative arrangement of the biphenyl unit is similar in both. Although **1** exists as a dimer in the crystalline state, **1** in complex **I** comprises a strong ionic-bonded columnar network that suppresses the concomitant non-radiative processes. It can be inferred that the main reason for an increase in the photoluminescence quantum yield after complexation is the change in the bonding style of the fluorescent molecule **1**. Although the crystal structures of complexes **II** and **III** containing MeOH and EtOH are similar, a comparison of complex **II** (or **III**) and complex **I** reveals that the relative arrangement of the biphenyl unit is different. In other words, the stacking between the neighboring biphenyl units in complexes **II** and **III** is smaller than that in complex **I**. Moreover, although the bonding style of **1** is almost the same in these three complexes, the torsion angle between benzene rings of **1** in complexes **II** and **III** (39.2° for **II** and, 35.3° and 36.0° for **III**) is smaller than that in complex **I** (49.2°). It is believed that the increase in the photoluminescence quantum yields of complexes **II** and **III** is mainly caused by these structural changes, especially, the increase of planality of biphenyl unit of **1**. The fluorescent complexes **II** and **III** have chirality, and therefore, they show CPL. However, when KBr pellets were prepared for measuring the CPL spectra, all the alcohol molecules were released from the complexes. Therefore, the CPL spectra of these chiral complexes could not be measured.

In conclusion, a novel chiral supramolecular organic fluorophore was successfully prepared by using achiral **1** and *rac*-**3**. In other words, a spontaneously resolved chiral fluorescence system was found. Although many organic fluorophores lose the fluorescence property in the solid state, this chiral supramolecular fluorophore showed the fluorescence property in the solid state. This further enhanced the capability of the fluorescence system, enabling its application in the design of novel solid-state chiral supramolecular organic fluorophores.

This work was supported by the Kansai Research Foundation for technology promotion.

References and Notes

1 *Organic Light-Emitting Devices*, ed. by J. Shinar, Springer-Verlag, New York, Berlin, Heidelberg, **2004**.

2 a) K. Yoshida, Y. Ooyama, S. Tanikawa, S. Watanabe, *J. Chem. Soc., Perkin Trans. 2* **2002**, 708. b) Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels, D. Stalke, *Angew. Chem., Int. Ed.* **2003**, *42*, 783. c) J. L. Scott, T. Yamada, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1697. d) J. L. Scott, T. Yamada, K. Tanaka, *New J. Chem.* **2004**, *28*, 447. e) Y. Ooyama, K. Yoshida, *New J. Chem.* **2005**, *29*, 1204, and references cited therein.

3 a) Y. Mizobe, N. Tohnai, M. Miyata, Y. Hasegawa, *Chem. Commun.* **2005**, 1839. b) Y. Mizobe, H. Ito, I. Hisaki, M. Miyata, Y. Hasegawa, N. Tohnai, *Chem. Commun.* **2006**, 2126. c) S. Oshita, A. Matsumoto, *Langmuir* **2006**, *22*, 1943. d) Y. Mizobe, T. Hinoue, M. Miyata, I. Hisaki, Y. Hasegawa, N. Tohnai, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1162.

4 Y. Imai, K. Kawaguchi, T. Harada, T. Sato, M. Ishikawa, M. Fujiki, R. Kuroda, Y. Matsubara, *Tetrahedron Lett.* **2007**, *48*, 2927.

5 This weight is the total crop of obtained crystals in one batch.

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Distance between carbon and the center of benzene ring.

8 a) Y. Imai, T. Sato, R. Kuroda, *Chem. Commun.* **2005**, 3289. b) Y. Imai, K. Kawaguchi, T. Sato, R. Kuroda, Y. Matsubara, *Tetrahedron Lett.* **2006**, *47*, 7885.

9 The absolute configuration of **3** was determined by HPLC analysis.