ORGANIC
LETTERS

2007
Vol. 9, No. 17
3457−3460

A Solid-State Fluorescence Sensing System Consisting of Chiral (1*R*,2*S*)-2-Amino-1,2-diphenylethanol and Fluorescent 2-Anthracenecarboxylic Acid

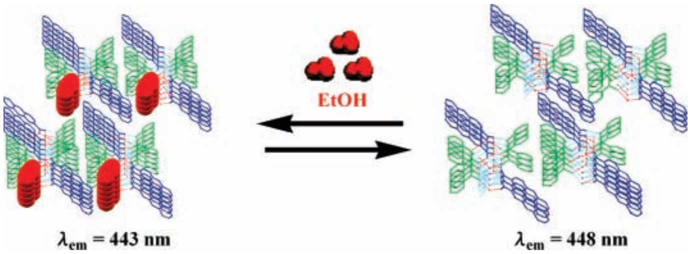
Yoshitane Imai,[*,†] Katuzo Murata,[†] Kakuhiro Kawaguchi,[†] Tomohiro Sato,[‡]
Reiko Kuroda,[‡,§] and Yoshio Matsubara*[,†]

Department of Applied Chemistry, Faculty of Science and Engineering,
Kinki University, 3-4-1 Kowakae, Higashi-Osaka, 577-8502, Japan,
JST ERATO-SORST Kuroda Chiromorphology Team, 4-7-6 Komaba, Meguro-ku,
Tokyo, 153-0041, Japan, and Department of Life Sciences, Graduate School of Arts
and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku,
Tokyo, 153-8902, Japan

y-imai@apch.kindai.ac.jp; y-matsu@apch.kindai.ac.jp

Received June 26, 2007

ABSTRACT



A solid-state fluorescence sensing system was created by using a chiral supramolecular organic fluorophore having a channel-like cavity composed of (1*R*,2*S*)-2-amino-1,2-diphenylethanol as a chiral molecule and 2-anthracenecarboxylic acid as a fluorescence molecule.

In the field of analytical chemistry, the development of a simple molecular recognition system, particularly a fluorescence sensing system, is an important issue. Recently, solid-state fluorescence sensing systems have attracted much attention as molecular sensing systems because the solid-state optical properties of organic compounds are different from the solution-state properties.[1] However, solid-state organic fluorescence indicators are mostly composed of a single molecule and require synthetic improvements for introduction of functionality. There are a few reports concerning supramolecular organic fluorescence indicators composed of two organic molecules.[2] However, they have no chirality and cannot be used as chiral indicators. Recently, we developed a chiral supramolecular organic fluorophore having circularly polarized luminescence (CPL) properties in the solid state by combining two types of organic

---

[†] Kinki University.
[‡] JST ERATO-SORST Kuroda Chiromorphology Team.
[§] The university of Tokyo.

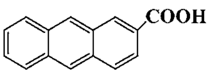
(1) (a) Yoshida, K.; Ooyama, Y.; Tanikawa, S. *J. Chem. Soc., Perkin. Trans 2* **2002**, 708. (b) Fei, Z.; Kocher, N.; Mohrschladt, C. J.; Ihmels, H.; Stalke, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 738. (c) Sott, J. L.; Yamada, T.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1697. (d) Scott, J. L.; Yamada, T.; Tanaka, K. *New J. Chem.* **2004**, *28*, 447. (e) Ooyama, Y.; Yoshida, K. *New J. Chem.* **2005**, *29*, 1204. (f) Oshita, S.; Matsumoto, A. *Langmuir* **2006**, *22*, 1943.

(2) Mizobe, Y.; Miyata, M.; Hisaki, I.; Hasegawa, Y.; Tohnai, N. *Org. Lett.* **2006**, *8*, 4295.

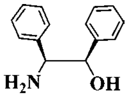
10.1021/ol701513a CCC: $37.00

molecules, i.e., fluorescent 2-anthracenecarboxylic acid (**1**) and chiral (1*R*,2*R*)-1,2-diphenylethylenediamine.[3] Unfortunately, these organic fluorophores are incapable of including a third component guest molecule and also cannot be used as fluorescence indicators.

One of the key properties of these supramolecular complexes is the ability to easily control physical and chemical properties by changing the component molecules.[4] In this paper, we report a chiral solid-state fluorescence sensing system composed of two different characteristic organic molecules (chiral and fluorescence molecules). To introduce guest inclusion ability to the supramolecular organic fluorophore, an aminoethanol molecule, (1*R*,2*S*)-2-amino-1,2-diphenylethanol [(1*R*,2*S*)-**2**], was used instead of (1*R*,2*R*)-1,2-diphenylethylenediamine as the chiral molecule. For guest molecules, three kinds of *n*-alkyl alcohols [methanol (MeOH), ethanol (EtOH), and *n*-propanol (*n*-PrOH)] having different alkyl chain lengths were used in order to study the influence of the size of the inclusion guest molecule on this system. It is predicted that the resultant supramolecular organic fluorophore will have effective fluorescence sensing ability due to the synergistic effect of conformation and optical properties.



1



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

The formation of a supramolecular organic fluorophore was attempted via crystallization from three different guest alcohol solutions. A mixture of **1** and (1*R*,2*S*)-**2** was dissolved in each guest solution and left to stand at room temperature.[5] After a few days, colorless crystals, **I** (11 mg), **II** (9 mg), and **III** (8 mg),[6] were obtained from MeOH, EtOH, and *n*-PrOH solutions, respectively. These crystals are constructed from **1** and (1*R*,2*S*)-**2**, and contain the expected alcohol molecule as guest.

Crystal forms and solid-state fluorescence spectral data of these complexes are shown in Table 1. Although many organic fluorophores lose this property in the solid state, all three complexes show fluorescence without quenching in the solid state. As the alkyl chain length of the included alcohol increases (from MeOH to EtOH), the solid-state fluorescence maximum becomes longer, e.g., 438 nm for complex **I** to 443 nm for complex **II**. On the other hand, in complex **III**, although the alkyl chain of the included alcohol (*n*-PrOH) is even longer, the solid-state fluorescence maximum becomes shorter (425 nm).

Table 1. The Crystal Forms and Solid-State Fluorescence Spectral Data of Complexes **I**−**III**

complex	crystal color	crystal shape	λ_{ex} (nm)	λ_{em} (nm)[a]
I	colorless	needle	422	438
II	colorless	needle	422	443
III	colorless	needle	422	425

[a] The thickness of sample is 0.1 mm.

To study the crystal structure of this system, X-ray crystallographic analysis of these complexes was attempted. The structure of complex **II** including EtOH is shown in Figure 1.[7] The stoichiometry of complex **II** is **1**:(1*R*,2*S*)-**2**:H_2O:EtOH = 2:2:2:1 and the space group is *P*1. As a characteristic of the structure, this crystal has a supramolecular columnar network along the *a*-axis (Figure 1a,b) that

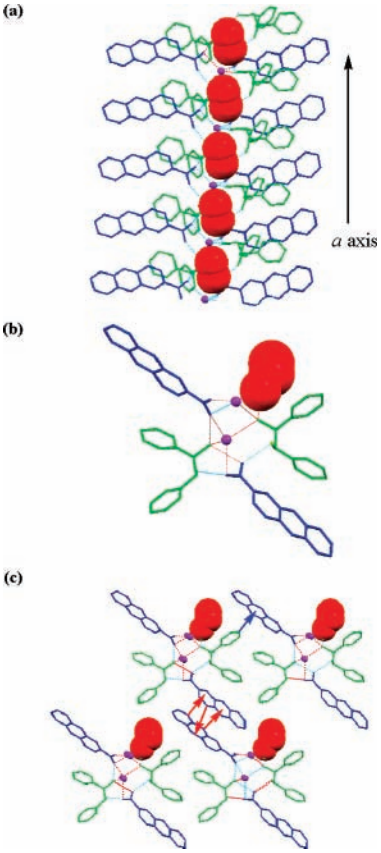


Figure 1. Crystal structure of complex **II**. (a) Columnar hydrogen- and ionic-bonded network parallel to the *a*-axis. (b) View down the *a*-axis. (c) Packing structure observed along the *a*-axis. Blue and red arrows indicate benzene−anthracene edge-to-face and anthracene−anthracene edge-to-face interactions, respectively.

---

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

(4) (a) Mizobe, Y.; Tohnai, N.; Miyata, M.; Hasegawa, Y. *Chem. Commun.* **2005**, 1839. (b) Imai, Y.; Sato, T.; Kuroda, R. *Chem. Commun.* **2005**, 3289. (c) Imai, Y.; Takeshita, M.; Sato, T.; Kuroda, R. *Chem. Commun.* **2006**, 1070. (d) Imai, Y.; Kawaguchi, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Tetrahedron Lett.* **2006**, *47*, 7885. (e) Imai, Y.; Kawaguchi, K.; Asai, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *CrystEngComm* **2007**, *9*, 467. (f) Kodama, K.; Kobayashi, Y.; Saigo, K. *Chem.-Eur. J.* **2007**, *13*, 2144. (g) Imai, Y.; Kawaguchi, K.; Murata, K.; Sato, T.; Kuroda, R.; Matsubara, Y. *Chem. Lett.* **2007**, 812. (h) Kodama, K.; Kobayashi, Y.; Saigo, K. *Cryst. Growth Des.* **2007**, *7*, 935.

(5) **1** (10 mg, 0.047 mmol) and (1*R*,2*S*)-**2** (10 mg, 0.047 mmol) were dissolved in *n*-alkyl alcohol (2 mL). After a few days, colorless crystals were deposited and collected.

(6) This weight is the total crop of obtained crystals in one batch.

is mainly formed by two types of bonds. One is an ionic bond from the ammonium hydrogen of the protonated amine (Figure 1, indicated in green) to the carboxylate oxygen of the carboxylic acid anion (Figure 1, indicated in blue). The other is a hydrogen bond formed by the hydroxyl group of (1*R*,2*S*)-**2**. The included water molecule (Figure 1, indicated as a purple ball) links the carboxyl, hydroxyl, and amino groups through hydrogen bonds and contributes to the maintenance of the column frame. Complex **II** is formed by self-assembly of this column, forming chiral channel-like cavities (Figure 1c). The guest molecule, EtOH (Figure 1, shown as red space-filling molecules), is trapped one-dimensionally along the direction of the cavity. Each EtOH molecule is connected to the column by a hydrogen bond between its own hydroxyl group and the carboxyl group of **1**. Interestingly, even when racemic (*rac*)-**2** [equimolar mixture of (1*R*,2*S*)-**2** and (1*S*,2*R*)-**2**] was used instead of the chiral (1*R*,2*S*)-**2**, the crystals obtained were identical with the chiral crystal **II** by X-ray analysis. That is, in this system, **2** can be distinguished by chirality and the complex is enantioselectively separated through the formation of the column structure and supramolecular complex.

Since complexes **I** and **III**, obtained from MeOH and *n*-PrOH solutions, respectively, were thin and needle-like, the X-ray analyses were unsatisfactory. Therefore, the X-ray powder diffraction analysis of these crystals was performed (Figure 2). Although the X-ray powder diffraction pattern of complex **I** is similar to that of complex **II**, that of complex **III** is different. However, the ^{1}H NMR analyses reveal that the host−guest ratios of all complexes are **1**:(1*R*,2*S*)-**2**:guest alcohol = 2:2:1. From these results, it is concluded that complexes **I** and **II** have similar structures, but complex **III** has a different structure. It is thought that the difference of the fluorescence maximum in complexes **I** and **II** is caused by slight changes of the distances and angles between fluorescence anthracene rings. On the other hand, the different tendency of the fluorescence maximum in crystal **III** is believed to be mainly caused by this difference in the crystal structure.

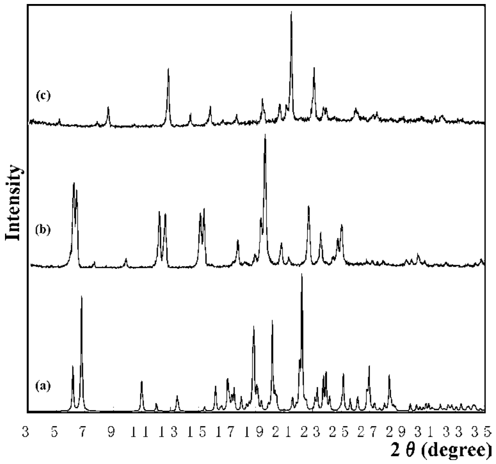


Figure 2. X-ray powder diffraction patterns of crystals (a) **II**, (b) **I**, and (c) **III**.

From X-ray analysis, it was also found that complex **II** contains benzene−anthracene edge-to-face interactions [2.63 Å (Figure 1c, indicated in blue arrows)] and anthracene−anthracene edge-to-face interactions [2.74, 2.79, and 2.99 Å (Figure 1c, indicated in red arrows)] between column structures. It is expected that these interactions prevent the channel-like cavities from collapsing and that volatile guest molecules can be discharged and adsorbed in these complexes. The discharge and adsorption behaviors of guest molecules were studied by X-ray powder diffraction analysis of complex **II** conducted under air or EtOH vapor conditions (Figure 3). EtOH was released from complex **II** by allowing it to stand in air for a few days. After ^{1}H NMR analysis confirmed that EtOH was no longer present, X-ray powder diffraction measurements of the complex were obtained. Novel complex **II-1** was observed (Figure 3b). Consequently, when complex **II-1** was placed under EtOH vapors for a few days, the X-ray powder diffraction pattern of complex **II-2**, which is similar to that of complex **II**, was observed (Figure 3c). Moreover, in complexes **I** and **III** including MeOH and *n*-PrOH, respectively, similar discharge and adsorption behaviors to that in complex **II** were observed by X-ray powder diffraction analysis (Supporting Information, Figures SI-1 and SI-2, respectively).

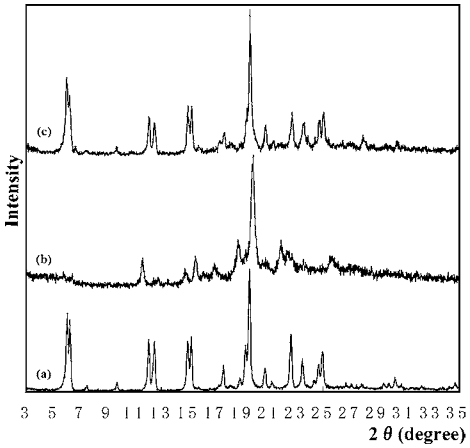


Figure 3. Changes in X-ray powder diffraction patterns of complex **II**: (a) complex **II**; (b) complex **II-1**, obtained after desorption of EtOH; and (c) complex **II-2**, obtained after readsorption of EtOH vapor.

These host systems exhibit fluorescence properties, therefore, it is expected that the solid-state fluorescence of these complexes changes reversibly according to the presence of

---

(7) Crystallographic data of **II**: $2C_{14}H_{16}NO \cdot 2C_{15}H_9O_2 \cdot C_2H_6O \cdot 2H_2O$, M = 953.10, triclinic, space group $P1$, a = 5.7753(5) Å, b = 14.7522(14) Å, c = 16.0657(15) Å, α = 116.5280(10)°, β = 91.539(2)°, γ = 94.751(2)°, U = 1217.32(19) Å^3, Z = 1, D_c = 1.300 g cm^{-3}, μ(Mo Kα) = 0.087 mm^{-1}, 10808 reflections measured, 9435 unique, final $R(F^2)$ = 0.0575 using 8491 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0641, T = 100(2) K.

guest molecules. The change of solid-state fluorescence of these complexes was examined (Figure 4). As before, the alcohol molecules were discharged from these complexes by allowing them to stand in air for a few days. After ^{1}H NMR analysis confirmed that alcohols were not included in the crystals, the solid-state fluorescence spectra were measured. In complex **I** including MeOH, the solid-state fluorescence maximum changes to 451 nm and a shift (13 nm) to longer wavelength is observed compared to that of the starting complex (Figure 4b for complex **I**). In complex **II** including EtOH, the solid-state fluorescence maximum changes to 448 nm and a shift (5 nm) to longer wavelength is observed, as in complex **I** (Figure 4b for complex **II**). On the other hand, when the *n*-PrOH molecules are discharged from complex **III**, the shift to longer wavelength in the solid-state fluorescence maximum is much larger (a shift of 24 to 449 nm) than that in complexes **I** and **II** (Figure 4b for complex **III**). After these complexes were placed under the corresponding alcohol vapor conditions for a few days, the solid-state fluorescence spectra were measured again. The solid-state fluorescence spectra returned to similar patterns as originally obtained (Figure 4c). In complex **III**, the change in the fluorescence spectrum is again different from those of complexes **I** and **II**. It is thought that this is also caused by the difference in crystal structures between complexes **I** (or **II**) and **III**.

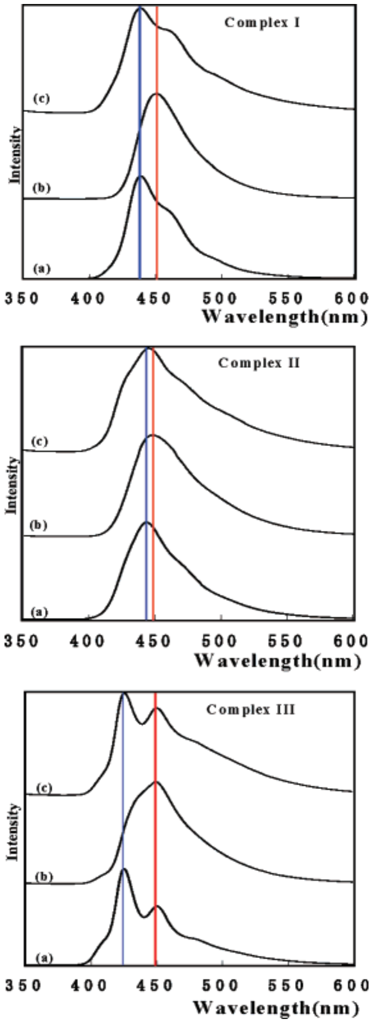


Figure 4. Change in solid-state fluorescence spectra of complexes **I**−**III**. (a) Solid-state fluorescence spectra of complexes **I**−**III**. (b) Solid-state fluorescence spectra of complexes **I-1**−**III-1**, obtained after desorption of guest. (c) Solid-state fluorescence spectra of complexes **I-2**−**III-2**, obtained after readsorption of guest vapor. Blue and red lines show the fluorescence maximum of starting complexes and complexes obtained after desorption of guest, respectively.

In conclusion, chiral supramolecular organic fluorophores having chiral channel-like cavities were successfully created by self-assembly of a hydrogen- and ionic-bonded column structure composed of 2-anthracenecarboxylic acid and (1*R*,2*S*)-2-amino-1,2-diphenylethanol. Guest molecules can be discharged and adsorbed into a channel-like cavity, and the solid-state fluorescence of the complex changes according to the presence of guest molecules. It is expected that this supramolecular organic fluorophore will be useful as a solid-state fluorescence sensing system for various guest molecules.

Supporting Information Available: X-ray crystallographic report (CIF) of complex **II** and the change of X-ray powder diffraction pattern of complexes **I** and **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL701513A