DOI: 10.1002/ejoc.200900235

Solid-State Optical Properties of a Chiral Supramolecular Organic Fluorophore Consisting of Fluorescent 1-Pyrenesulfonic Acid and Amine Molecules

Yoshitane Imai,*^[a] Katuzo Murata,^[a] Yoko Nakano,^[b] Takunori Harada,^[c] Tomohiro Sato,^[c] Nobuo Tajima,^[d] Michiya Fujiki,^[b] Reiko Kuroda,^[c,e] and Yoshio Matsubara*^[a]

Keywords: Chirality / Circularly polarized luminescence / Crystal engineering / Fluorescence / Supramolecular chemistry

By using (R)-1-phenylethylamine as a chiral molecule and 1pyrenesulfonic acid as a fluorescent molecule, a chiral supramolecular organic fluorophore composed of a 2D layered structure was successfully developed. This chiral supramolecular fluorophore possesses circularly polarized luminescence (CPL) properties in the solid state. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

Introduction

Solid-state optical properties of organic compounds are very important physical properties that must be considered in the development of new functional materials. The potential application of solid-state fluorescence techniques in organic electroluminescence (EL) devices, optoelectronic devices, and so on has recently attracted much attention.^[1] To date, several organic fluorophores possessing solid-state organic fluorescence properties have been developed; however, these fluorophores are composed only of a single molecule.^[2] Recently, two-component supramolecular organic fluorophores have attracted considerable attention, as the physical and chemical properties of these fluorophores can be easily controlled by changing the component molecules.^[3] However, the study of circularly polarized luminescence (CPL) properties in these fluorophores has not been reported. We have developed a two-component, chiral supramolecular organic fluorophore exhibiting CPL in the solid state; these fluorophores were developed by combining two types of organic molecules (fluorescent carboxylic acid

[a] Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University
3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan Fax: +81-6-6727-2024
E-mail: y-imai@apch.kindai.ac.jp y-matsu@apch.kindai.ac.jp
[b] Graduate School of Materials Science, Nara Institute of School and Technology Takayama, Ikoma, Nara 630-0192, Japan
[c] JST ERATO-SORST Kuroda Chiromorphology Team

- [c] JST ERATO-SORST Kuroda Chiromorphology Team 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041, Japan
 [d] First-Principles Simulation Group, Computational Materials
- [d] First-Principles Simulation Group, Computational Materials Science Center, NIMS
- Sengen, Tsukuba, Ibaraki 305-0047, Japan

[e] Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan and achiral or chiral amine molecules).^[4] These complexes have a characteristic 1D columnar hydrogen- and ionic-bonded network structure formed by the carboxylate oxygen atom of a carboxylic acid anion and the ammonium hydrogen atom of a protonated amine.

In this paper, we report the complexation behaviors and solid-state optical properties of novel achiral and chiral supramolecular organic fluorophores composed of fluorescent sulfonic acid molecules instead of fluorescent carboxylic acid molecules. Two types of basic amine molecules were used in this study, that is, achiral benzylamine (1) and chiral (R)-1-phenylethylamine [(R)-2]. 1-Pyrenesulfonic acid (3) was used as the fluorescent sulfonic acid. To the best of our knowledge, a supramolecular organic fluorophore composed of sulfonic acid and amine molecules exhibiting CPL properties has not been reported to date. It is believed that the resultant supramolecular organic fluorophore will play an important role in the development of chiral supramolecular organic fluorophore state.



Results and Discussion

The formation of a 1/3 supramolecular organic fluorophore was first attempted by crystallization from ethanol (EtOH) solution. A mixture of 1 and 3 was dissolved in the EtOH solution and left to stand at room temperature. After





a week, a large number of supramolecular crystals (I) were obtained. Although the formation of a supramolecular organic fluorophore composed of 1 and 1-pyrenecarboxylic acid (4) was attempted in the same way, good-quality crystals were not obtained. Furthermore, the formation of a chiral supramolecular organic fluorophore composed of (R)-2 and 3 was attempted in the same way. This resulted in a large number of chiral supramolecular crystals (II) composed of (R)-2 and 3. However, powder-like solids instead of good-quality crystals composed of (R)-2 and 4 were obtained.

The most serious problem in solid-state organic fluorophores is fluorescence quenching in the crystalline state. To study the solid-state optical properties of the obtained supramolecular complexes I and II, the solid-state fluorescence spectra of these complexes were measured. Complexes I and II exhibited fluorescence in the solid state. The solid-state fluorescence maximum (λ_{em}) of complex I was observed at 466 nm, and the absolute value of the photoluminescence quantum yield (Φ_F) in complex I was 0.15 in the solid state. The values of solid-state fluorescence maximum (λ_{em}) and photoluminescence quantum yield (Φ_F) in complex II were similar to those of complex I ($\lambda_{em} = 467$ nm and $\Phi_F = 0.11$). These fluorescence emissions may originate from the excimer state of pyrene units of complexes in the solid state by comparing with that of pyrene in the crystal.^[5]

X-ray crystallographic analyses of complexes I and II were attempted to study their crystal structures. The crystal structure of complex I is shown in Figures 1 and 2.



Figure 1. Crystal structure of the extracted 2D layered network structure in complex I. Arrows A and B show pyrene–pyrene edge-to-face interactions. Arrow C shows the distance between the centers of two neighboring parallel pyrene rings. (a) View along the b axis; (b) view along the a axis.

The stoichiometry of complex I is 1/3 = 1:1 and its space group is $P2_1/c$. This crystal structure of complex I has a supramolecular 2D layered hydrogen-bonded network along the *b* and *c* axes (Figure 1, a and b). The 2D layered network structure is formed by the association of the ammonium hydrogen atom of one protonated amine in 1 and the sulfonate oxygen atom of a sulfonic acid anion in 3. Moreover, this 2D layered network structure is maintained by two types of pyrene–pyrene edge-to-face interactions (Figure 1, a and b; arrows *A* and *B*, 2.59 and 2.63 Å, respectively).^[6] The self-assembly of the 2D layered network structure (Figure 2, a and b; represented by a dotted border) without interlayer interactions along the *a* axis results in the formation of complex **I**.



Figure 2. Packing structure of complex I. The dotted borders indicate the 2D layered network structure. Arrow C shows the distance between the centers of two neighboring parallel pyrene rings. (a) Packing structure comprising 2D layered network structure observed along the b axis; (b) packing structure observed along the caxis.

The crystal structure of chiral complex II is shown in Figures 3 and 4. The stoichiometry of complex II is (R)-2/ $3/H_2O = 1:1:1$ and its space group is $P2_1$. The crystal structure of complex II has a supramolecular 2D layered hydrogen-bonded network along the a and b axes (Figure 3, a and b). This 2D layered network structure is formed by the association of the ammonium hydrogen atom of one protonated amine in 2 and the sulfonate oxygen atom of a sulfonic acid anion in 3. Moreover, the included water molecules (Figures 3 and 4, represented by black balls) link one protonated amine group of (R)-2 with two sulfonic acid anion groups of 3 through hydrogen bonds and contribute to the maintenance of the layered structure. In contrast to complex I, although aromatic-aromatic edge-to-face interactions are not observed in complex II, CH $-\pi$ interactions between the methyl group of (R)-2 and the pyrene ring of **3** are observed (Figures 3a and 4b; arrow A, 2.95 Å) in the

FULL PAPER

2D layered network structure.^[6] The self-assembly of this 2D layered structure (Figure 4, represented by dotted borders) without interlayer interactions along the *c* axis results in the formation of a chiral complex II (Figure 4).^[6]



Figure 3. Crystal structure of the extracted 2D layered network structure in chiral complex II. Water molecules are represented by black balls. Arrow *A* indicates CH– π interactions. Arrows *B* and *C* show the distance between the centers of two neighboring parallel pyrene rings. (a) View along the *a* axis; (b) view along the *c* axis.

When compared with chiral complex II, the pyrene rings in the 2D layered structure of complex I exhibit a zigzag arrangement along the c axis. However, two pyrene rings of neighboring 2D layered structure units are parallel to each other (Figure 1b). The distance between the centers of two neighboring parallel pyrene rings (Figures 1b and 2b, arrow C) is 3.59 Å. In contrast, the pyrene rings in the 2D layered structure of complex II exhibit a planar arrangement along the c axis without stacking (Figure 3, a and b). However, pyrene rings of neighboring 2D layered structure units are opposite to each other but not perfectly parallel. The distances between the centers of two neighboring pyrene rings are 4.85 and 4.15 Å, respectively (Figures 3b and 4b, arrows *B* and *C*). The solid-state fluorescence maximum (λ_{em}) and photoluminescence quantum yield ($\Phi_{\rm F}$) of complexes I and II are similar. It is believed that this similarity is due to the stacked arrangement of the pyrene rings of neighboring 2D layered structure units.

Fluorescent complex **II** is a chiral fluorophore; therefore, this fluorescence may be CPL in the solid state. To study the CPL properties of chiral complex **II**, the solid-state circular dichroism (CD) spectra of complex **II** were measured by using a KBr pellet. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.^[7] The solid-state CD and absorption spectra of complex **II** (indicated by the black line) are shown in Figure 5. Pyrene ring peaks are observed at 353 and 365 nm



Figure 4. Packing structure of chiral complex II. Water molecules are represented by black balls. The dotted borders indicate the 2D layered network structure. Arrow *A* indicates CH– π interactions. Arrows *B* and *C* show the distance between the centers of two neighboring parallel pyrene rings. (a) Packing structure comprising 2D layered network structure observed along the *a* axis; (b) packing structure observed along the *b* axis.

in the CD spectrum. The circular anisotropy ($g_{CD} = \Delta OD/OD$) factor of the last Cotton effect ($\lambda^{CD} = 365$ nm) is approximately -0.1×10^{-3} . To check if the crystal has caused any artifact in the spectrum, complex II' was prepared by using (S)-1-phenylethylamine [(S)-2], and the CD and absorption spectra of complex II' were measured (Figure 5, gray line). The CD spectrum of complex II' was found to be a mirror image of the CD spectrum of complex II. These results show that an effective chirality transfer from chiral



Figure 5. CD and absorption spectra of chiral complexes II (black line) and II' (gray line) in the solid state (KBr pellets).



unit 2 to fluorescent unit 3 takes place through complexation. Consequently, the measurement of the solid-state CPL spectrum of chiral complex II was attempted by using a KBr pellet.^[7] The CPL spectrum was successfully observed in the solid state. The solid-state CPL and fluorescence spectra of complex II are shown in Figure 6.



Figure 6. CPL and fluorescence spectra of chiral complex II in the solid state (KBr pellet).

The fluorescence spectrum obtained by using a KBr pellet is similar to the fluorescence spectrum of complex II in the solid state without KBr matrices. This result confirmed the lack of influence of the KBr matrix on this measurement. A negative CPL spectrum was obtained for complex II. The circular anisotropy $[g_{em} = 2(I_L - I_R)/(I_L + I_R)]$ factor of complex II is approximately -1.0×10^{-3} . This shows that chiral complex II exhibits CPL in the solid state. To the best of our knowledge, this is the first example of solidstate CPL observed in a chiral supramolecular organic fluorophore composed of sulfonic acid and amine molecules. In other words, it is possible to measure the solid-state CPL spectrum of a sulfonic acid/amine supramolecular complex.

Conclusions

Supramolecular organic fluorophores were successfully formed by using fluorescent 1-pyrenesulfonic acid and achiral benzylamine and chiral (R)-1-phenylethylamine. Supramolecular complexes composed of a 2D layered network structure were obtained. Most organic fluorophores lose fluorescence in the solid state; however, these supramolecular organic fluorophores exhibit fluorescence in the solid state. Especially, 1-pyrenesulfonic acid/(R)-1-phenylethylamine-supramolecular organic fluorophore exhibits solidstate CPL and its spectrum was recorded successfully. To the best of our knowledge, this is the first example of solidstate CPL observed in a chiral supramolecular organic fluorophore composed of sulfonic acid and amine molecules. It is believed that such a chiral supramolecular complex and its optical properties will be useful in the development of novel solid-state chiral fluorophores.

Experimental Section

General Methods: All reagents were used directly as obtained commercially. Compound 1 and crystallization solvent EtOH were purchased from Wako Pure Chemical Industry. Compounds (R)- and (S)-2 were purchased from Tokyo Kasei Kogyo Co., Ltd. Compounds 3 and 4 were purchased from Sigma–Aldrich Co., Ltd.

Formation of the Complex by Crystallization from EtOH Solution: Compounds 1 [or (R)-2] (0.05 mmol) and 3 (or 4) (0.05 mmol) were dissolved in EtOH solution (2 mL). After a week, a large number of crystals [crystals of complex I (10 mg) for 1/3 system, and crystals of complexes II (10 mg) and II' (9 mg) for (R)-2/3 and (S)-2/3 system, respectively] were obtained. The weight of the crystal is the total weight of the obtained crystals in one batch.

X-ray Crystallographic Study: X-ray diffraction data for single crystals were collected by using Bruker Apex. The crystal structures were solved by direct methods^[8] and refined by full-matrix leastsquares by using SHELX97.^[9] The diagrams were prepared by using PLATON.^[10] Absorption corrections were performed by using SADABS.^[11] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. Crystallographic data for I: C7H9N·C16H10O3S, M = 389.45, Monoclinic, space group $P2_1/c$, a = 16.7416(16) Å, b =10.9788(10) Å, c = 10.9788(10) Å, $\beta = 101.781(2)^{\circ}$, V =1869.8(3) Å³, Z = 4, $D_{\text{calcd.}}$ = 1.383 g cm⁻³, μ (Mo- K_{α}) = 0.198 mm⁻¹, 11315 reflections measured, 4279 unique, final $R(F^2)$ = 0.0607 using 3384 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.07767, T = 115(2) K. Crystallographic data for II: $C_8H_{11}N \cdot C_{16}H_{10}O_3S \cdot H_2O$, M = 421.49, Monoclinic, space group $P2_1, a = 8.3164(12) \text{ Å}, b = 8.6126(12) \text{ Å}, c = 14.890(2) \text{ Å}, \beta =$ 105.964(2)°, V = 1025.4(3) Å³, Z = 2, $D_{calcd.} = 1.365$ g cm⁻³, μ (Mo- K_{α} = 0.190 mm⁻¹, 3908 reflections measured, 3908 unique, final $R(F^2) = 0.0712$ using 3833 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0720, T = 115(2) K.

CCDC-720383 (for I) and -720384 (for II) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Measurement of Solid-State Fluorescence Spectra: Solid-state fluorescence spectra and absolute photoluminescence quantum yields were measured with an absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics K.K.) under air atmosphere at room temperature. The excited wavelengths were 377 and 375 nm for complexes I and II, respectively.

Measurement of Solid-State CD and Absorption Spectra: The CD and absorption spectra were measured with a Jasco J-800KCM spectrophotometer. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.^[7]

Measurement of Solid-State CPL Spectrum: The CPL spectrum was measured by using a Jasco CPL-200 spectrophotometer. The excited wavelength was 350 nm. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.^[7] The power of an incident beam of the CPL spectrometer was 8.0 μ W/0.04 cm² at the installation position of the sample. The CPL spectrum was approached by simple moving average (SMA).

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Tech-

FULL PAPER

nology, Japan (No. 20750115) and a research grant from the Research Foundation for Opto-Science and Technology.

- a) J. Shinar, Organic Light-Emitting Devices, Springer, New York, 2004; b) K. Müllen, U. Scherf, Organic Light-Emitting Devices, Wiley-VCH, Weinheim, 2006 and reference cited therein.
- [2] a) C. W. Tang, S. A. VansSlyke, Appl. Phys. Lett. 1987, 51, 913-915; b) K. Yoshida, Y. Ooyama, S. Tanikawa, J. Chem. Soc. Perkin Trans. 2 2002, 708-714; c) K.-C. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Liu, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, J. Am. Chem. Soc. 2002, 124, 11576-11577; d) Z. Fei, N. Kocher, C. J. Mohrschladt, H. Ihmels, D. Stalke, Angew. Chem. Int. Ed. 2003, 42, 783-787; e) C. J. Tonzola, M. M. Alam, W. K. Kaminsky, S. A. Jenekhe, J. Am. Chem. Soc. 2003, 125, 13548-13558; f) J. L. Sott, T. Yamada, K. Tanaka, Bull. Chem. Soc. Jpn. 2004, 77, 1697-1701; g) H.-C. Yeh, L.-H. Chan, W.-C. Wu, C.-T. Chen, J. Mater. Chem. 2004, 14, 1293-1298; h) J. L. Scott, T. Yamada, K. Tanaka, New J. Chem. 2004, 28, 447-450; i) Y. Ooyama, K. Yoshida, New J. Chem. 2005, 29, 1204-1212; j) D. Berner, C. Klein, M. D. Nazeeruddin, F. de Angelis, M. Castellani, P. Bugnon, R. Scopelliti, L. Zuppiroli, M. Graetzel, J. Mater. Chem. 2006, 16, 4468-4474; k) T. E. Kaiser, H. Wang, V. Stepanenko, F. Wuerthner, Angew. Chem. Int. Ed. 2007, 46, 5541-5544; 1) Y. Ooyama, S. Nagano, M. Okamura, K. Yoshida, Eur. J. Org. Chem. 2008, 5899-5906 and references cited therein.
- [3] a) Y. Mizobe, N. Tohnai, M. Miyata, Y. Hasegawa, Chem. Commun. 2005, 1839–1841; b) Y. Mizobe, H. Ito, I. Hisaki, M.

Miyata, Y. Hasegawa, N. Tohnai, *Chem. Commun.* **2006**, 2126–2128; c) S. Oshita, A. Matsumoto, *Langmuir* **2006**, *22*, 1943–1945; d) Y. Mizobe, M. Miyata, I. Hisaki, Y. Hasegawa, N. Tohnai, *Org. Lett.* **2006**, *8*, 4295–4298; e) Y. Mizobe, T. Hinoue, M. Miyata, I. Hisaki, Y. Hasegawa, N. Tohnai, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1162–1172; f) T. Hinoue, Y. Mizobe, I. Hisaki, M. Miyata, N. Tohnai, *Chem. Lett.* **2008**, *37*, 642–643; g) Y. Ooyama, K. Yoshida, *Eur. J. Org. Chem.* **2008**, 2564–2570; h) J. Luo, T. Lei, L. Wang, Y. Ma, Y. Cao, J. Wang, J. Pei, *J. Am. Chem. Soc.* **2009**, *131*, 2076–2077.

- [4] a) Y. Imai, K. Kawaguchi, T. Harada, T. Sato, M. Ishikawa, M. Fujiki, R. Kuroda, Y. Matsubara, *Tetrahedron Lett.* 2007, 48, 2927–2930; b) Y. Imai, K. Murata, N. Asano, Y. Nakano, K. Kawaguchi, T. Harada, T. Sato, M. Fujiki, R. Kuroda, Y. Matsubara, *Cryst. Growth Des.* 2008, 8, 3376–3379.
- [5] R. Katoh, K. Suzuki, A. Furube, M. Kotani, K. Tokumaru, J. Phys. Chem. C 2009, 113, 2961–2965.
- [6] Determined by PLATON geometry calculation.
- [7] R. Kuroda, Y. Saito, Bull. Chem. Soc. Jpn. 1976, 49, 433-436.
- [8] G. M. Sheldrick, SHELX97: Program for the Solution of Crystal Structures, University of Goettingen, Germany, 1997.
- [9] G. M. Sheldrick, SHELX97: Program for the Refinement of Crystal Structures, University of Goettingen, Germany, 1997.
- [10] A. L. Spek, PLATON: Molecular Geometry and Graphics Program, University of Utrecht, The Netherlands, 1999.
- [11] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany, 1996.

Received: March 5, 2009 Published Online: May 13, 2009