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Solid-State Chiral Supramolecular Organic Fluorophore Having a π-Conjugated Phenylene Ethynylene Unit

Takafumi Kinuta,[a] Kensaku Kamon,[a] Takunori Harada,[b] Yoko Nakano,[c]
Nobuo Tajima,[d] Tomohiro Sato,[b] Michiya Fujiki,[c] Reiko Kuroda,[b,e]
Yoshio Matsubara,*[a] and Yoshitane Imai*[a]

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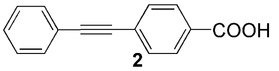
A solid-state, chiral, helical, columnar, organic fluorophore having a π-conjugated phenylene ethynylene unit was prepared by using 4-[2-(4-methylphenyl)ethynyl]benzoic acid and 1-phenylethylamine. Such a chiral π-conjugated organic fluorophore can be obtained from achiral and racemic component molecules, and it exhibits circularly polarized luminescence (CPL) in the solid state.

Introduction

Solid-state fluorophores have attracted considerable attention in the field of optoelectronic devices, including organic electroluminescence (EL) devices, light-emitting diodes (LEDs), and optical sensors.[1] Several organic fluorophores comprising a single molecule that has a phenylene ethynylene unit have been developed to tune the fluorescence wavelength by extending the π-conjugated systems.[2] Recently, solid-state supramolecular organic fluorophores comprising two organic molecules have been developed.[3] A characteristic feature of these supramolecular organic fluorophores is that their physical and chemical properties can be easily tuned by simply changing the component molecules. Moreover, they offer novel functionality due to the synergy effect between the two component molecules. Recently, we succeeded in preparing a solid-state chiral supramolecular organic fluorophore comprising two types of organic molecules – fluorescent 2-anthracenecarboxylic acid and 1-phenylethylamine (**1**).[4] Although chiral functional organic materials are usually prepared by using chiral molecules, this chiral supramolecular organic fluorophore was obtained by using achiral 2-anthracenecarboxylic acid and racemic 1-phenylethylamine (*rac*-**1**), because of the synergy effect between these two molecules in the solid state. A disadvantage of these supramolecular systems is that it is not easy to predict their formation, structure, and chemical and physical properties when new component molecules are used. Therefore, the crystal structure and chemical and physical properties of supramolecular organic complexes that are prepared by using basic supramolecular building blocks are being studied extensively as a bottom-up approach to studying solid-state supramolecular chemistry.

In this paper, we report a novel supramolecular fluorescent system having a π-conjugated fluorescence unit. A racemic amine molecule, *rac*-**1**, is used as one of the building blocks. As the other π-conjugated fluorescence building blocks, 4-phenylethynyl benzoic acid (**2**) and 4-[2-(4-methylphenyl)ethynyl]benzoic acid (**3**), which are the most basic units of the phenylene ethynylene unit, are used.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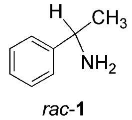
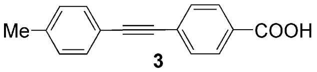

rac-**1**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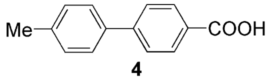
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Results and Discussion

The **1**/**2**-supramolecular organic fluorophore was studied first. The formation of the supramolecular fluorophore was attempted by crystallization from methanol (MeOH) solution. However, **2** had low solubility in MeOH. Therefore,

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[a] Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University,
3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan
Fax: +81-6-6727-2024
E-mail: y-imai@apch.kindai.ac.jp
y-matsu@apch.kindai.ac.jp
[b] JST ERATO-SORST Kuroda Chiromorphology Team,
4-7-6 Komaba, Meguro-ku, Tokyo, 153-0041, Japan
[c] Graduate School of Materials Science, Nara Institute of School and Technology,
Takayama, Ikoma, Nara, 630-0192, Japan
[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

the formation of the supramolecular organic fluorophore was attempted by using the π-conjugated component molecule **3** with a methyl group as a π-conjugated phenylene ethynylene unit. A mixture of *rac*-**1** and **3** was dissolved in MeOH and left to stand at room temperature. After a few days, colorless crystals of complex **I** comprising **1** and **3** were obtained.

In order to study the solid-state fluorescence of the supramolecular organic complex thus obtained, a solid-state fluorescence spectrum of **I** was measured. Although the most serious problem encountered in a solid-state organic fluorophore is the quenching of fluorescence in the crystalline state, **I** showed fluorescence in the solid state. Complex **I** showed a maximum solid-state fluorescence (λ_{em}) at 379 nm, and the absolute value of the photoluminescence quantum yield (Φ_F) was 0.58 in the solid state.

X-ray crystallographic analysis of **I** was attempted to study the crystal structure (Figure 1). Interestingly, this complex exhibited chirality. The stoichiometry of **I** was (*R*)-**1**/**3** = 1:1, and its space group was $P2_1$. This complex had a characteristic 2_1-helical columnar network structure along the *b* axis (Figure 1a,b). This column was mainly formed by the carboxylate oxygen atom of the carboxylic acid anions and the ammonium hydrogen atom of the protonated amine. Moreover, benzene–benzene edge-to-face interactions (2.96 Å, indicated by solid arrows *A* in Figure 1a) between the hydrogen atom of the benzene ring in **3** and the benzene ring of (*R*)-**1** were also observed.[5] Complex **I** was formed by the self-assembly of these 2_1-helical columns by three benzene–benzene edge-to-face interactions (2.93, 2.73, and 2.75 Å, indicated by solid arrows *B*–*D* in Figure 1c, respectively).[5] This shows that this chiral supramolecular organic fluorophore is a spontaneous resolution fluorescent system. In general, most chiral molecules are not easily available and are more expensive than achiral or racemic molecules. Therefore, chiral supramolecular organic fluorophores prepared by using achiral or racemic molecules can be used for the industrial production of chiral fluorophores by a preferential crystallization method without using any chiral auxiliaries.

Complex **I** is a chiral crystal; therefore, it may exhibit circularly polarized luminescence (CPL) in the solid state. To study the solid-state CPL of **I**, its solid-state circular dichroism (CD) spectrum was measured by using a KBr pellet. Solid-state samples were prepared according to the standard procedure employed for obtaining glassy KBr matrices.[6] The solid-state CD and absorption spectra of **I** are shown in Figure 2 (black line).

Peaks originating from the phenylene ethylene unit were observed in the CD spectrum at 300 and 320 nm. The circular anisotropy (g_{CD} = ΔOD/OD) factor of the last Cotton effect (λ^{CD} = 320 nm) was approximately -1.0×10^{-3}. To check whether the crystal caused any artifact in the spectrum, CD and absorption spectra of **I′**, comprising (*S*)-1-phenylethylamine [(*S*)-**1**], were measured (Figure 2, gray line). This CD spectrum was found to be a mirror image of the CD spectrum of **I**. These results show that effective chirality transfer occurred from **1** to **3** through complexation.

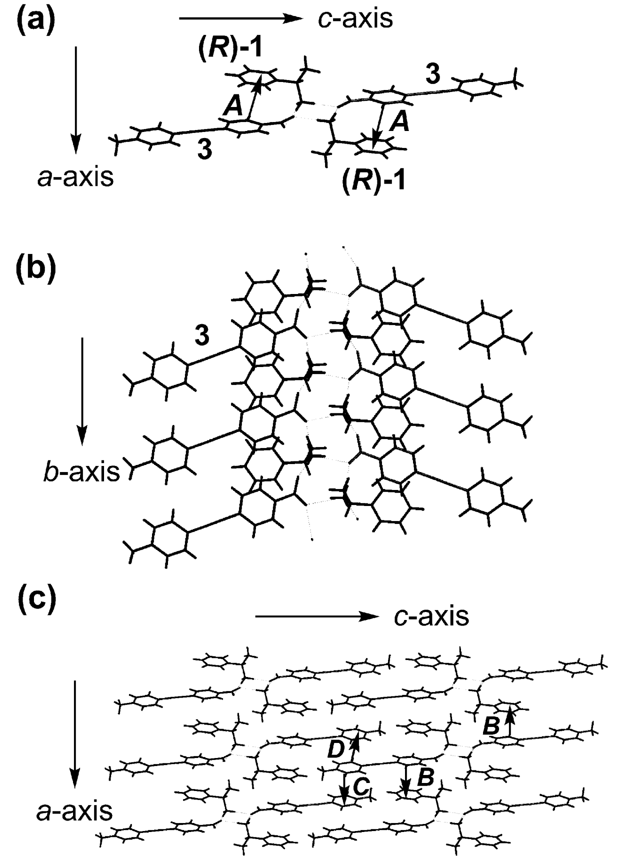

Figure 1. Crystal structure of **I**: (a) 2_1-helical columnar network structure observed along the *b* axis. The solid arrows *A* indicate the intracolumnar benzene–benzene edge-to-face interactions. (b) View along the *a* axis. (c) Packing structure observed along the *b* axis. The solid arrows *B*–*D* indicate the intercolumnar benzene–benzene edge-to-face interactions.

It is possible that the true CD spectrum of this supramolecular complex was not observed, because the complex may have interacted with the KBr matrix. Therefore, diffuse reflectance circular dichroism (DRCD) spectra of **I** and **I′** were measured without using a KBr matrix (Figure 3). The DRCD spectra were similar to the CD spectra, suggesting that the KBr matrix did not affect the CD measurements of this type of supramolecular organic fluorophore.

Next, the measurement of a solid-state CPL spectrum of **I** with a positive Cotton effect was attempted by using a KBr pellet.[6] We successfully obtained the solid-state CPL spectrum of **I** (Figure 4). A negative CPL spectrum was obtained for **I**. The circular anisotropy [$g_{em} = 2(I_L - I_R)/(I_L + I_R)$] factor of **I** was approximately -0.7×10^{-3}. This shows that the chiral supramolecular complex **I** exhibited CPL in the solid state. To the best of our knowledge, this is the first example of solid-state CPL observed in a chiral supramolecular organic fluorophore comprising a π-conjugated phenylene ethynylene unit. Thus, this shows that it may be possible to measure the solid-state CPL spectrum of a supramolecular complex comprising a π-conjugated phenylene ethynylene unit.

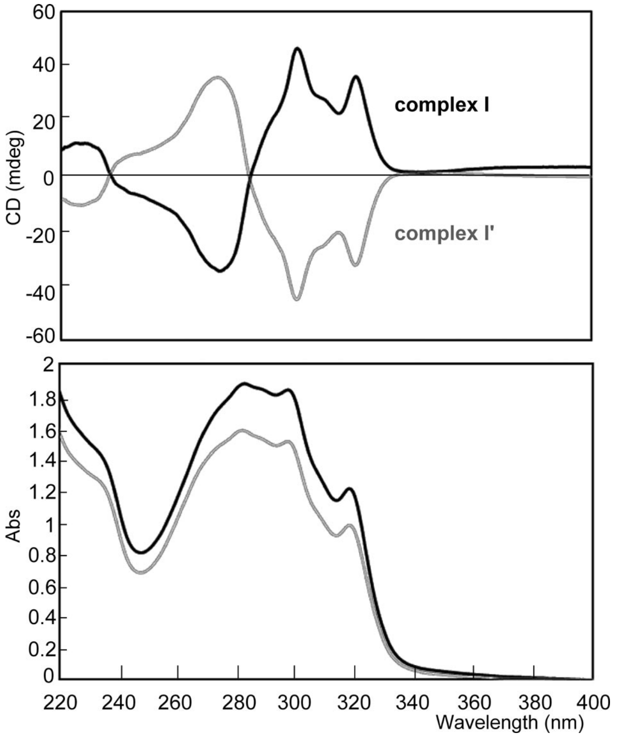

Figure 2. CD and absorption spectra of **I** (black line) and **I′** (gray line) in the solid state (KBr pellets).

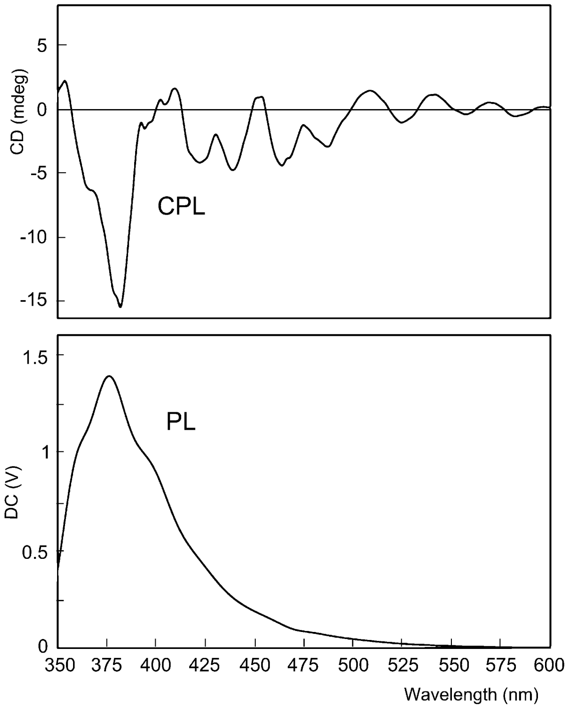

Figure 4. CPL and fluorescence spectra of **I** in the solid state (KBr pellet).

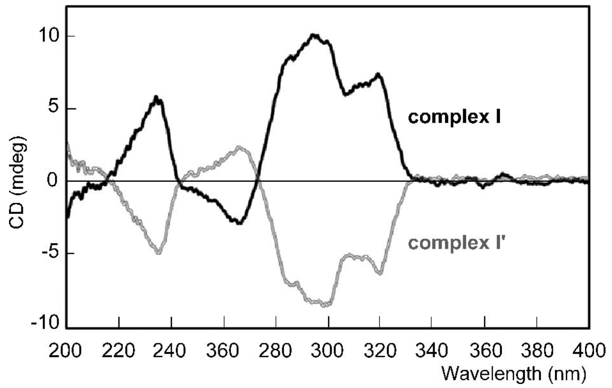

Figure 3. DRCD spectra of **I** (black line) and **I′** (gray line) in the solid state.

To study the effect of the phenylene ethynylene unit on this system, the formation of a **1**/4-methyl-4′-biphenylcarboxylic acid (**4**) supramolecular organic fluorophore was attempted by crystallization from MeOH in the same manner as described before. A mixture of *rac*-**1** and **4** was dissolved in MeOH and allowed to stand at room temperature. After a few days, a large number of crystals of complex **II** comprising **1** and **4** were obtained. X-ray crystal structure analysis of **II** was carried out (Figure 5). In contrast to **I**, this complex was a racemic complex. Thus, the stoichiometry of **II** was (*R*)-**1**/(*S*)-**1**/**4** = 0.5:0.5:1, and its space group was $P\bar{1}$. This complex also had a characteristic pseudo-2_1-helical columnar network structure comprising (*R*)-**1**, (*S*)-**1**, and **4** along the *a* axis (Figure 5a,b). This column was mainly formed by the carboxylate oxygen atom of the carboxylic acid anions and the ammonium hydrogen atom of the protonated amine. Benzene–benzene edge-to-face interactions (2.92 Å, indicated by solid arrows *A* in Figure 5a) between the hydrogen atom of the benzene ring in **4** and the benzene ring of (*R*)-**1** and (*S*)-**1** were also observed, similar to those observed in **I**.[5] Complex **II** was formed by the assembly of this pseudo-2_1-column by two benzene–benzene edge-to-face interactions (2.84 and 3.00 Å, indicated by solid arrows *B* and *C* in Figure 5c, respectively).[5] These results suggest that the ethynylene unit of component molecule **3** affected the chiral crystallization of this system.

To study the effect of the ethynylene unit on the fluorescence properties of the complex, a solid-state fluorescence spectrum of **II** was measured and compared with that of **I**. The maximum solid-state fluorescence (λ_{em}) and the absolute value of the photoluminescence quantum yield (Φ_F) of **II** were 370 nm and 0.1, respectively. Comparison of the solid-state fluorescence spectra of **I** and **II** revealed that λ_{em} changed as follows: **II** (λ_{em} = 370 nm) < **I** (λ_{em} = 379 nm). It is generally known that extension of a π-conjugated system induces a redshift in the emission wavelength,[2] that is, a small HOMO–LUMO gap induces a redshift in the emission wavelength. Therefore, the HOMO–LUMO gaps of the single molecules of **3** and **4** were studied theoretically. The theoretically calculated HOMO–LUMO gaps of the respective gas-phase molecules were 3.98 eV in the case of **3** and 4.67 eV in the case of **4**. This shows that, in this system, one of the reasons for the redshift in λ_{em} is the effect of the ethynylene unit in component molecule **3**.

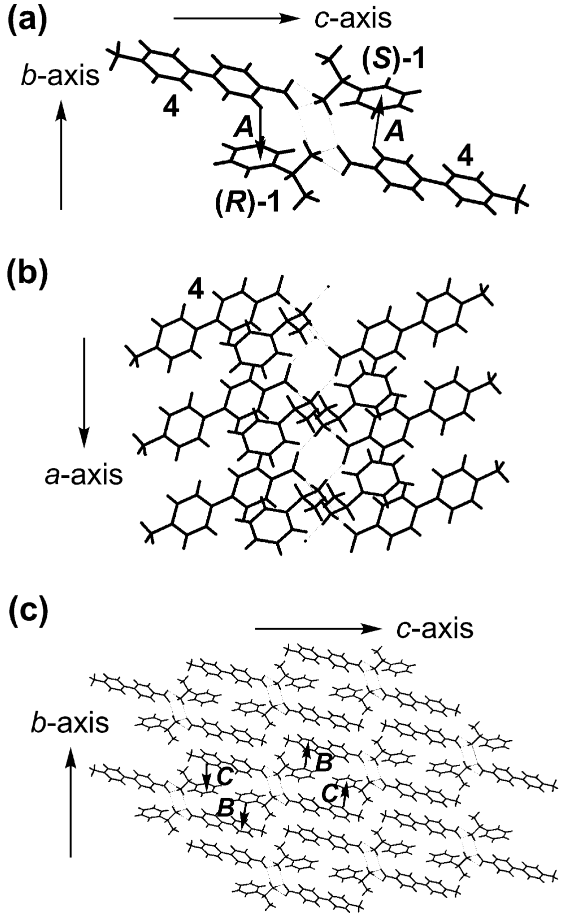

Figure 5. Crystal structure of **II**: (a) pseudo-2_1-helical columnar network structure observed along the *a* axis. The solid arrows *A* indicate the intracolumnar benzene–benzene edge-to-face interactions. (b) View along the *b* axis. (c) Packing structure observed along the *a* axis. The solid arrows *B* and *C* indicate the intercolumnar benzene–benzene edge-to-face interactions.

Conclusions

A novel, chiral, supramolecular, organic fluorophore was successfully prepared from *rac*-**1** and achiral **3**. Thus, a novel, spontaneous resolution, chiral, fluorescent system was formed. In addition, although many organic fluorophores lose their fluorescence in the solid state, this chiral supramolecular fluorophore shows stronger CPL on complexation 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 organic fluorophores having a π-conjugated phenylene ethylene unit.

Experimental Section

General Methods: Component molecule *rac*-**1** was purchased from Tokyo Kasei Kogyo Co. Component molecule **4** and MeOH were purchased from Wako Pure Chemical Industry. Reported component molecules **2** and **3** are prepared by a typical Sonogashira cross-coupling reaction.[7]

Formation of Complex by Crystallization from MeOH: Compound *rac*-**1** (10 mg, 0.083 mmol) and the carboxylic acid derivative (0.083 mmol) were dissolved in MeOH (3 mL) and left to stand at room temperature in an open air atmosphere. After 3–5 d, a large number of crystals [mixture of crystals of complexes **I** and **I′** for **1**/**3** system (15 mg) and crystals of complex **II** for **1**/**4** system (12 mg)] were obtained. The reported weight of the crystal is the total weight of the obtained crystals in one batch.

X-ray Crystallography: X-ray diffraction data for single crystals were collected by using a Bruker APEX. The crystal structures were solved by direct methods[8] and refined by full-matrix least-squares 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**: $M = 696.24$, monoclinic, space group $P2_1$, $a = 7.1842(7)$ Å, $b = 5.9850(6)$ Å, $c = 22.807(2)$ Å, $\beta = 98.001(2)°$, $V = 971.09(17)$ Å^3, $Z = 2$, $D_{\text{calcd.}} = 1.222\ \text{g cm}^{-3}$, $\mu(\text{Mo-}K_\alpha) = 0.077\ \text{mm}^{-1}$, 8445 reflections measured, 2430 unique, final $R(F^2) = 0.0549$ using 2053 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0689, $T = 115(2)$ K. Crystallographic data for **II**: $C_{22}H_{23}NO_2$, $M = 333.41$, triclinic, space group $P\bar{1}$, $a = 5.6712(6)$ Å, $b = 12.0505(13)$ Å, $c = 13.1250(15)$ Å, $\alpha = 80.777(2)°$, $\beta = 84.448(2)°$, $\gamma = 84.448(2)°$, $V = 877.86(17)$ Å^3, $Z = 2$, $D_{\text{calcd.}} = 1.261\ \text{g cm}^{-3}$, $\mu(\text{Mo-}K_\alpha) = 0.080\ \text{mm}^{-1}$, 7499 reflections measured, 3861 unique, final $R(F^2) = 0.0686$ using 3044 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0890, $T = 115(2)$ K. CCDC-733516 (for **I**) and -733517 (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: A solid-state fluorescence spectra and absolute photoluminescence quantum yield were measured with an Absolute PL Quantum Yield Measurement System (C9920–02, Hamamatsu Photonics K.K.) in an air atmosphere at room temperature. The excited wavelengths were 332 and 331 nm for complexes **I** and **II**, respectively.

Measurement of Solid-State CD and Absorption Spectra: The CD and absorption spectra were measured by using a Jasco J-800KCM spectrophotometer. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.[6]

Measurement of Solid-State CPL Spectrum: The CPL spectrum was measured by using a Jasco CPL-200 spectrophotometer. The excited wavelength was 320 nm. The solid-state sample was prepared according to the standard procedure for obtaining glassy KBr matrices.[6] The power of an incident beam of the CPL spectrometer was 8.0 μW/0.04 cm^2 at the installation position of sample. The CPL spectrum was approached by simple moving average (SMA).

Calculation Method of HOMO–LUMO Gaps of Component Molecules 3 and 4: The HOMO–LUMO gaps of component molecules **3** and **4** were calculated by the hybrid density functional theory (B3LYP functional[12]) with the cc-pVDZ[12] basis set. For calculating the HOMO–LUMO gaps of molecules in the isolated state, the molecular geometries were fully optimized by using this theory and basis set.

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[1] a) E. Weber, M. Czugler in *Topics in Current Chemistry Vol. 149: Molecular Inclusion and Molecular Recognition – Clathrates II* (Ed.: E. Weber), Springer, Berlin, **1988**, pp. 45–135; b) E. Weber in *Inclusion Phenomena and Molecular Recognition* (Ed.: J. L. Atwood), Plenum Press, New York, **1990**, vol. 4; c) J. D. Wright, *Molecular crystals*, 2nd ed., Cambridge University Press, New York, **1995**; d) J. Shinar, *Organic Light-Emitting Devices*, Springer, Berlin, **2004**; e) K. Müllen, U. Scherf, *Organic Light-Emitting Devices*, Wiley-VCH, Weinheim, **2006**; f) A. Wakamiya, Y. Inukai, S. Yamaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 15934–15935; g) C.-H. Zhao, A. Wakamiya, S. Yamaguchi, *Macromolecules* **2007**, *40*, 3898–3900; h) Y. Imai, K. Murata, K. Kawaguchi, T. Sato, N. Tajima, R. Kuroda, Y. Matsubara, *Chem. Asian J.* **2008**, *3*, 625–629, and reference cited therein.

[2] a) B. Valeur, *Molecular Fluorescence*, Wiley-VCH, Weinheim, **2005**; b) H. Langhals, T. Potrawa, H. Nöth, G. Linti, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 478–480; c) H. Langhals, R. Ismael, O. Yürük, *Tetrahedron* **2000**, *56*, 5435–5441; d) K. Yoshida, Y. Ooyama, H. Miyazaki, S. Watanabe, *J. Chem. Soc. Perkin Trans. 2* **2002**, 700–707; e) H.-C. Yeh, W.-C. Wu, Y.-S. Wen, D.-C. Dai, J.-K. Wang, C.-T. Chen, *J. Org. Chem.* **2004**, *69*, 6455–6462; f) Y. Ooyama, T. Okamoto, T. Yamaguchi, T. Suzuki, A. Hayashi, K. Yoshida, *Chem. Eur. J.* **2006**, *12*, 7827–7838; g) Y. Ooyama, K. Yoshida, *Eur. J. Org. Chem.* **2008**, *15*, 2564–2570.

[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. Imai, K. Kawaguchi, T. Harada, T. Sato, M. Ishikawa, M. Fujiki, R. Kuroda, Y. Matsubara, *Tetrahedron Lett.* **2007**, *48*, 2927–2930; f) Y. Mizobe, T. Hinoue, M. Miyata, I. Hisaki, Y. Hasegawa, N. Tohnai, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1162–1172; g) Y. Imai, K. Murata, K. Kawaguchi, T. Sato, N. Tajima, R. Kuroda, Y. Matsubara, *Chem. Asian J.* **2008**, *3*, 625–629; h) Y. Imai, K. Nagasaki, K. Murata, K. Kawaguchi, T. Harada, Y. Nakano, T. Sato, M. Fujiki, R. Kuroda, Y. Matsubara, *CrystEngComm* **2008**, *10*, 951–953; i) Y. Ooyama, K. Yoshida, *Eur. J. Org. Chem.* **2008**, 2564–2570; j) J. Luo, T. Lei, L. Wang, Y. Ma, Y. Cao, J. Wang, J. Pei, *J. Am. Chem. Soc.* **2009**, *131*, 2076–2077.

[4] Y. Imai, K. Kamon, K. Murata, T. Harada, Y. Nakano, T. Sato, M. Fujiki, R. Kuroda, Y. Matsubara, *Org. Biomol. Chem.* **2008**, *6*, 3471–3475.

[5] It was determined by PLATON geometry calculation.

[6] R. Kuroda, Y. Saito, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 433–436.

[7] C. Rafel, N. Carmen, *Chem. Rev.* **2007**, *107*, 874–922.

[8] G. M. Sheldrick, *SHELX97: Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.

[9] G. M. Sheldrick, *SHELX97: Program for the Refinement of Crystal Structures*, University of Göttingen, 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 Göttingen, Germany, **1996**.

[12] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

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