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Nonclassical Tunability of Solid-State CD and CPL Properties of a Chiral 2-Naphthalenecarboxylic Acid/Amine Supramolecular Organic Fluorophore**

Noriaki Nishiguchi,[a] Takafumi Kinuta,[a] Tomohiro Sato,[a] Yoko Nakano,[b]
Hayato Tokutome,[c] Nobuo Tajima,[d] Michiya Fujiki,[b] Reiko Kuroda,[c]
Yoshio Matsubara,[a] and Yoshitane Imai*[a]

Abstract: The solid-state chiral optical properties (circular dichroism and circularly polarized luminescence) of a 2-naphthalenecarboxylic acid/amine supramolecular organic fluorophore can be controlled by changing the aryl unit of the chiral 1-arylethylamine component of the molecule rather than altering the chirality of the 1-arylethylamine itself.

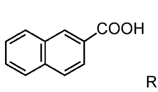
Keywords: chirality · crystal engineering · fluorescence · luminescence · supramolecular chemistry

Introduction

Solid-state organic fluorophores have attracted considerable attention in the field of optoelectronics for application in devices such as organic electroluminescence (EL) devices and optical sensors.[1] Recently, two or more component solid-state supramolecular organic fluorophores have gained considerable interest because their optical properties can be easily controlled by changing the component molecules without synthetic processes.[2] On the other hand, most of the previously reported supramolecular organic fluorophores or organic fluorophores composed of a single organic molecule were not chiral, and therefore, did not display solid-state chiral optical properties such as solid-state circular dichroism (CD) and circularly polarized luminescence (CPL).

Typically, to control the sign of the optical properties of a given chiral compound, a chiral compound with the opposite chirality is used. However, chiral compounds with opposite chirality may not be easily available. Therefore, it is desirable to develop a way of tuning the sign of the optical properties of a chiral fluorophore without using an opposite-chirality counterpart in the development of new chiral fluorescent systems.

Herein, we report the nonclassical tunability of the solid-state chiral optical properties of a new chiral two-component supramolecular organic fluorophore. The solid-state chiral optical properties of a 2-naphthalenecarboxylic acid/1-arylethylamine supramolecular organic fluorophore are tunable by changing the type of aryl unit in the chiral 1-arylethylamine component molecule, but not the chirality of the 1-arylethylamine itself. In this system, 2-naphthalenecarboxylic acid (**1**) was used as the fluorescent component molecule. Three types of chiral 1-arylethylamines, (*R*)-(+)-1-phenylethylamine ((*R*)-**2**), (*R*)-(+)-1-(*p*-tolyl)ethylamine ((*R*)-**3**), and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine ((*R*)-**4**), possessing different aryl units, but the same chirality, were used as the chiral (*R*)-(+)-1-arylethylamine component molecule.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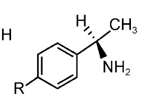
(*R*)-**2**: R = H
(*R*)-**3**: R = CH_3
(*R*)-**4**: R = OCH_3

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[a] N. Nishiguchi, T. Kinuta, T. Sato, Prof. Dr. Y. Matsubara, Dr. Y. Imai
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

[b] Dr. Y. Nakano, Prof. Dr. M. Fujiki
Graduate School of Materials Science
Nara Institute of School and Technology
Takayama, Ikoma, Nara 630-0192 (Japan)

[c] H. Tokutome, Prof. Dr. R. Kuroda
Department of Life Sciences
Graduate School of Arts and Sciences
The University of Tokyo
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902 (Japan)

[d] Dr. N. Tajima
Computational Materials Science Center
National Institute for Materials Science
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 (Japan)

[**] CD = circular dichroism, CPL = circularly polarized luminescence.

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Results and Discussion

The three versions of the chiral supramolecular organic fluorophore, **1**/(*R*)-**2**–**4**, were prepared by crystallization from a solution containing **1** and (*R*)-**2**–**4** in MeOH. Compounds **1** and (*R*)-**2** (or (*R*)-**3** or (*R*)-**4**) were dissolved in MeOH and left to stand at room temperature. After one week, a large number of crystals of complexes **I** (composed of **1** and (*R*)-**2**), **II** (composed of **1** and (*R*)-**3**), and **III** (composed of **1** and (*R*)-**4**) were obtained.

The most serious problem associated with solid-state fluorophores is the occurrence of fluorescence quenching in the crystalline state. To study the solid-state optical properties of complexes **I**–**III**, we first measured solid-state fluorescence spectra. The crystal form and solid-state fluorescence spectral data of complexes **I**–**III** are presented in Table 1.

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

Complex	Crystal color	Crystal shape	λ_{em} [nm][a]	Φ_F
I	colorless	Plate	349	0.09
II	colorless	Needle	348	0.12
III	colorless	Needle	348	0.08

[a] Excited wavelengths are 329, 330, and 327 nm for complexes **I**–**III**, respectively.

Complexes **I**–**III** all exhibit fluorescence in the solid state. The solid-state fluorescence maximum (λ_{em}) for complex **I** is observed at 349 nm and the absolute value of the photoluminescence quantum yield (Φ_F) for complex **I** is 0.09 in the solid state. The solid-state λ_{em} and Φ_F values for complexes **I**–**III** are similar, despite the use of 1-arylethylamine molecules with different aryl units.

To study the trends in the solid-state chiral optical properties (CD and CPL) of the 2-naphthalenecarboxylic acid/1-arylethylamine supramolecular organic fluorophore, the solid-state CD spectra of fluorescent complexes **I**–**III** were measured as KBr pellets. The solid-state CD and absorption spectra of complexes **I**–**III** (indicated by black lines) are shown in Figure 1. The shapes of these CD spectra are similar. Characteristic peaks of the naphthalene unit are observed between 260 and 350 nm. The circular anisotropy factors ($|g_{CD} = \Delta OD/OD|$; OD = optical density) of the last Cotton effect ($\lambda^{CD} = 330$ nm for **I**, 333 nm for **II**, and 329 nm for **III**) for **I**, **II**, and **III** are approximately 5.6×10^{-4}, 7.2×10^{-4}, and 3.7×10^{-4}, respectively.

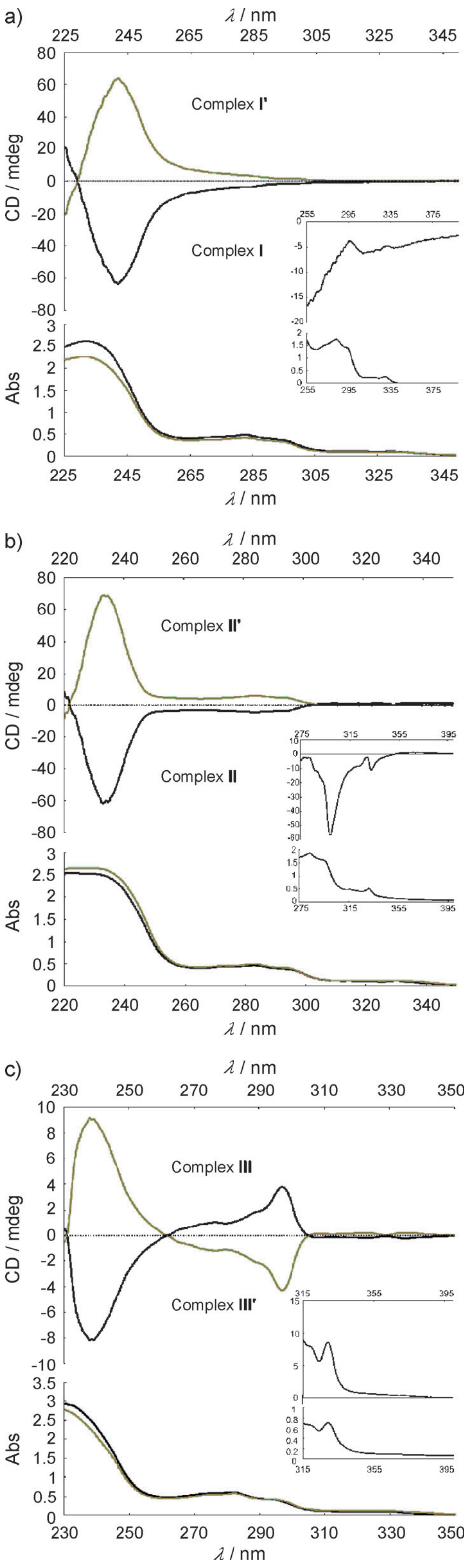

Figure 1. CD and absorption spectra of complexes a) **I**, b) **II**, and c) **III** (black lines) and complexes **I′**–**III′** (gray lines) in the solid state (as KBr pellets).

Abstract in Japanese:

本研究では、2-naphthalenecarboxylic acid/amine系光学活性超分子有機発光体の固体状態におけるキラルな光学特性[円偏光二色性(CD)及び円偏光ルミネッセンス(CPL)]をキラルなアミン構成分子1-arylethylamine のキラリティーではなく、アリール部位の種類を変えることにより、制御することに成功した。

To check whether complexes **I**–**III** introduced any artifact into the spectra, complexes **I′**–**III′** were prepared, in which compounds (*R*)-**2**–**4** were replaced with (*S*)-(−)-1-phenylethylamine ((*S*)-**2**), (*S*)-(−)-1-(*p*-tolyl)ethylamine ((*S*)-**3**), and (*S*)-(−)-1-(4-methoxyphenyl)ethylamine ((*S*)-**4**). Then, the solid-state CD spectra of complexes **I′**–**III′** were measured (indicated by gray lines in Figure 1). These CD spectra were mirror images of the CD spectra of complexes **I**–**III**. These results indicate that effective chiral transfer occurs from chiral compounds **2**–**4** to complexes **I**–**III** through complexation.

Interestingly, although chiral complexes **I**–**III** (or **I′**–**III′**) are composed of amine component molecules with the same chirality, the signs of the CD spectra of chiral complexes **I**–**III** (or **I′**–**III′**) are not all the same. That is, the signs of the CD spectra of complexes **I** and **II** at the longest wavelengths are negative (indicated by black lines in Figure 1a and b), whereas that of complex **III** is positive (indicated by black lines in Figure 1c). This shows that the solid-state CD property of the 2-naphthalenecarboxylic acid/1-arylethylamine supramolecular organic fluorophore can be controlled by changing the aryl unit in the chiral 1-arylethylamine component to another aryl unit with the same chirality.

To study the origin of the solid-state CD properties of these complexes, X-ray crystallographic analyses of complexes **I**–**III** were conducted and the resulting crystal structures of complexes **I**–**III** were compared. The crystal structures of **I** are shown in Figure 2.[3] The stoichiometry of complex **I** is 1:1 with regards to the components **1**/(*R*)-**2** and the complex is in the space group $P2_12_12_1$. This complex has a characteristic 2_1-helical columnar network structure along the *a* axis (Figure 2a and b). This column is mainly composed of the carboxylate oxygen atoms of the carboxylic acid anions and the ammonium hydrogen atoms of the protonated amine. Complex **I** is formed by the assembly of these 2_1-helical columns (indicated by the dotted circle in Figure 2c) without major intercolumnar interactions (Figure 2c).[4]

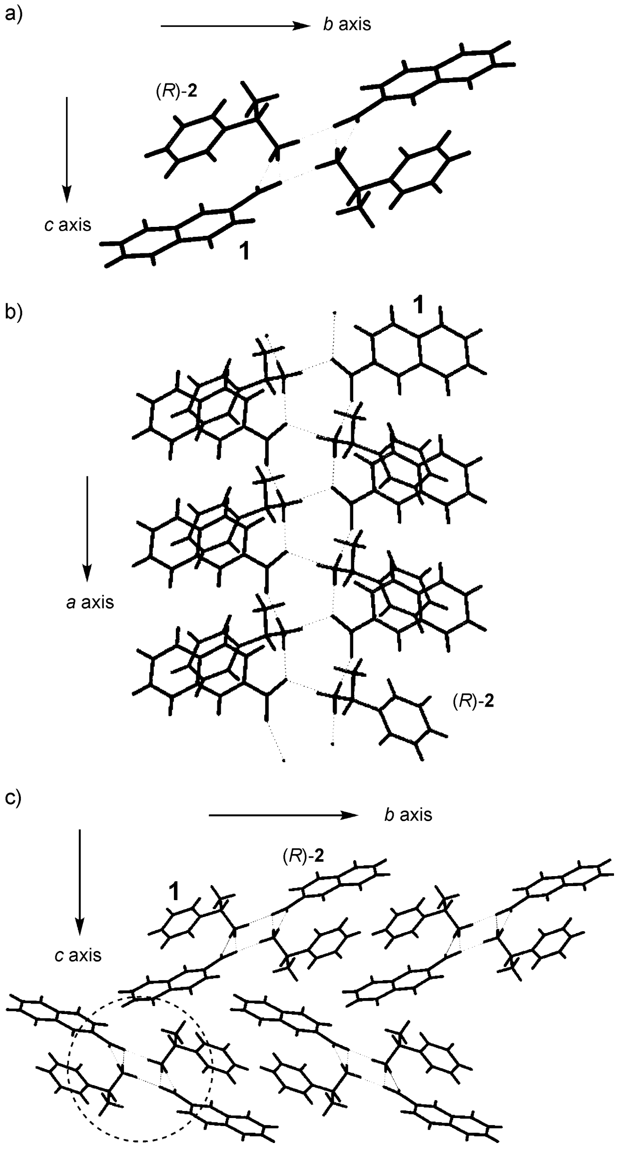

Figure 2. Crystal structures of **I**. a) 2_1-Helical columnar network structure observed along the *a* axis. b) View along the *c* axis. c) Packing structure observed along the *a* axis. The dotted circle represents a 2_1-helical columnar network structure.

The crystal structures of **II** are shown in Figure 3. The stoichiometry of **II** is 1:1 with regards to the components **1**/(*R*)-**3** and the complex is in space group $P2_12_12_1$, which is the same as that of complex **I**. This complex also has a 2_1-helical columnar network structure along the *a* axis similar to that in complex **I** (Figure 3a). Complex **II** is formed by the assembly of these 2_1-helical columns (indicated by the dotted circle in Figure 3b) through three types of intercolumnar interactions (Figure 3b):[4] 1) naphthalene–benzene edge-to-face interactions (2.80 Å, as indicated by arrow A in Figure 3b) between the hydrogen atom of the naphthalene ring in **1** and the benzene ring of (*R*)-**3**; 2) benzene–naphthalene edge-to-face interactions (2.95 Å, as indicated by arrow B in Figure 3b) between the hydrogen atom of the benzene ring of (*R*)-**3** and the naphthalene ring in **1**; and 3) naphthalene–naphthalene edge-to-face interactions between naphthalene rings in **1** (2.83 Å, as indicated by arrow C in Figure 3b). Interestingly, X-ray crystallography revealed that, although the structures of the 2_1-helical columns in complexes **I** and **II** are the same, the packing structures of the shared 2_1-helical columns are considerably different (cf. Figures 2c and 3b).

The crystal structures of **III** are shown in Figure 4. The stoichiometry of **III** is 1:1 with regards to the components **1**/(*R*)-**4** and the complex is in space group $P1$. In contrast to complexes **I** and **II**, the component molecules **1** and (*R*)-**4** form a pseudo-2_1-helical columnar network structure along the *a* axis (Figure 4a). This column is also mainly composed of the carboxylate oxygen atoms of the carboxylic acid anions and the ammonium hydrogen atoms of the protonated amine. As expected, the packing structure of this pseudo-2_1-helical column in complex **III** is also different from that of complexes **I** and **II**. In **III**, there are three types of intercolumnar interactions (Figure 4b):[4] 1) CH–π interactions

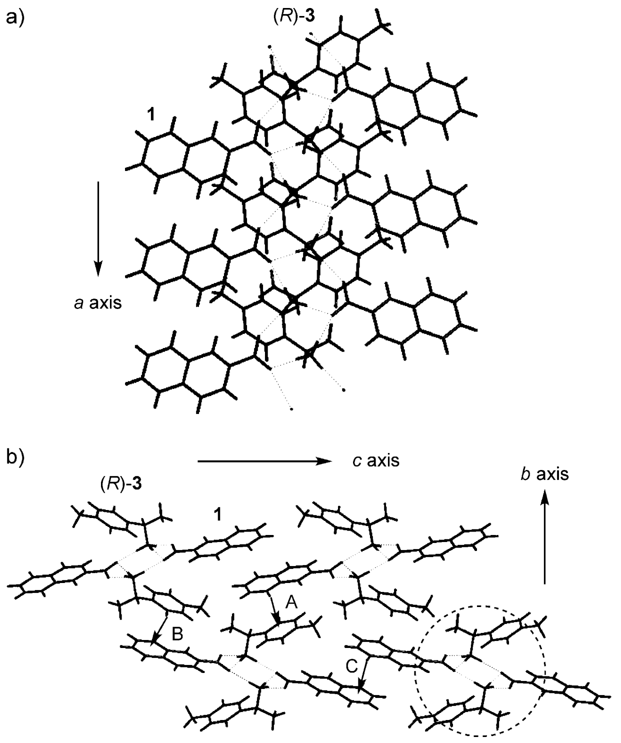

Figure 3. Crystal structures of **II**. a) 2_1-Helical columnar network structure along the *a* axis. b) Packing structure observed along the *a* axis. The dotted circle represents a 2_1-helical columnar network structure. Arrows A, B, and C indicate the intercolumnar naphthalene–benzene, benzene–naphthalene, and naphthalene–naphthalene edge-to-face interactions, respectively.

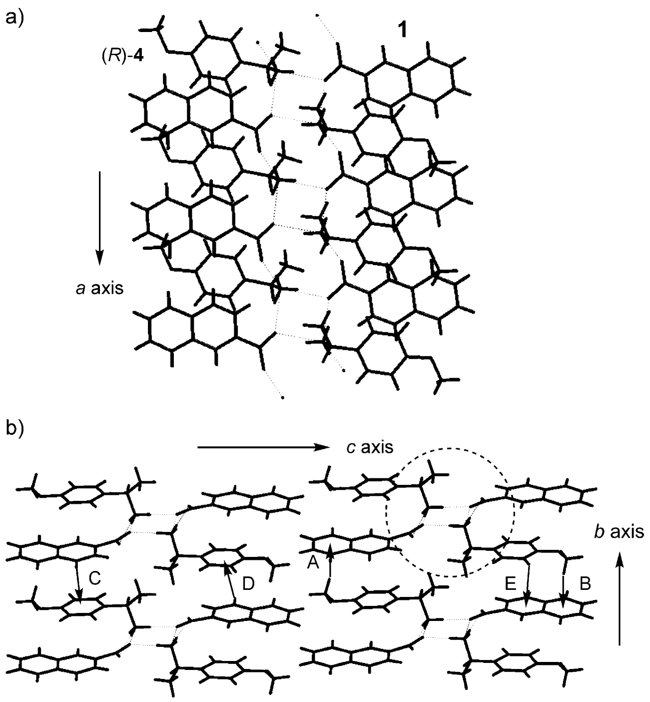

Figure 4. Crystal structures of **III**. a) Pseudo-2_1-helical columnar network structure along the *a* axis. b) Packing structure observed along the *a* axis. The dotted circle represents a helical columnar network structure. Arrows A and B indicate the intercolumnar CH–π interactions. Arrows C (or D) and E indicate the intercolumnar naphthalene–benzene and benzene–naphthalene edge-to-face interactions, respectively.

between the methyl group in (*R*)-**4** and the naphthalene ring in **1** (2.58 and 2.55 Å, as indicated by arrows A and B in Figure 4b, respectively); 2) naphthalene–benzene edge-to-face interactions (2.71 and 2.89 Å, as indicated by arrows C and D in Figure 4b, respectively) between the hydrogen atom of the naphthalene ring of **1** and the benzene ring in (*R*)-**4**; and 3) benzene–naphthalene edge-to-face interactions between the hydrogen atom of the benzene ring of (*R*)-**4** and the naphthalene ring in **1** (2.94 Å, as indicated by arrow E in Figure 4b).

Complexes **I** and **II** have negative CD intensities at 260–350 nm, which originate from the electronic absorption of molecule **1**, whereas complex **III** has a positive CD intensity in the 260–350 nm region. The origins of the chiroptical properties of complexes **I**–**III** were studied on the basis of the X-ray structures. As described earlier, we focused on the CD intensities in the longest wavelength region, 260–350 nm, because not all three complexes have the same sign despite having component amine molecules with the same chirality. The weak electronic absorption in this wavelength region, apparently originating from component molecule **1**, suggests that the corresponding CD intensities are induced by molecular structure fixation of **1** in crystals. To verify this hypothesis, the chiroptical properties of single molecules of **1** in the three complexes were examined theoretically. Figure 5 displays the calculated rotational strengths for **1** in the three crystals, in which the rotational strengths at 230–250 nm correspond to the experimentally observed strong CD intensities at 220–240 nm, whereas those at 300–350 nm correspond to the CD intensities in the longest wavelength region 260–300 nm we have focused on. Although the correlation to the experimentally observed spectra is not good, the calculated rotational strengths at 300–350 nm reproduce the main features of the CD intensities at 260–300 nm observed for the complexes. That is, we find a negative intensity of **I** (Figure 5a) and a positive intensity of **III** (Figure 5c), although the intensity of **II** is barely observed (Figure 5b). Complex **III** also has negative intensities (Figure 5d), but the positive contribution overwhelms the negative one upon summation. These rotational strengths result mainly from distortions of **1** around the C$-$CO$_2$ bond: the OC$-$CC dihedral angles are −18.6 (−15.7) in **I**, 3.9 (3.3) in **II**, and 34.9 (34.4) and −42.0° (−38.9°) in **III**. These calculated data suggest that the molecular structure fixation of **1** possibly contributes to the experimentally observed CD intensities in the 260–350 nm region.

Next, the solid-state CPL spectra of complexes **I**–**III** were measured as KBr pellets and compared. The solid-state CPL and fluorescence spectra of complexes **I**–**III** are shown in Figure 6.

The fluorescence spectra of these complexes measured as KBr pellets are similar to those of complexes obtained without using the KBr matrix. This result shows that the KBr

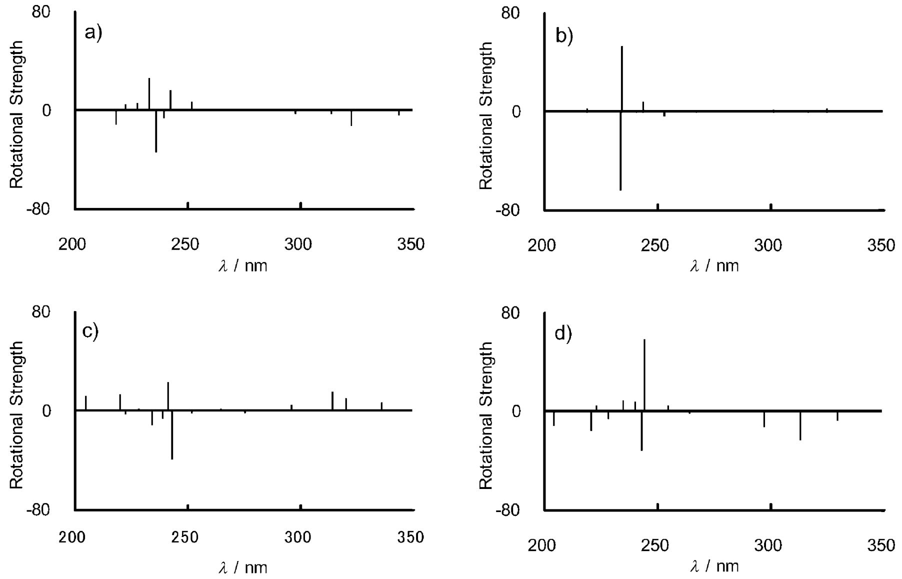

Figure 5. Calculated rotational strengths (in 10–40 erg esu cm Gauss^{-1}) and electronic excitation wavelength for molecule **1**: a) and b) molecules taking the geometries in **I** and **II**, respectively; c) and d) molecules taking the geometries in **III** (two crystallographically independent molecules).

matrix does not introduce any artifacts into measurements of the spectra. As expected, a comparison of the CPL properties of chiral complexes **I–III** indicates that the sign of the CPL spectra changes from negative for **I** and **II** to positive for **III**. The circular anisotropy factor ($g_{em} = 2(I_L - I_R)/(I_L + I_R)$) of complexes **I–III** is approximately -4.0×10^{-4}, -2.5×10^{-4}, and 7.6×10^{-4}, respectively. To the best of our knowledge, this is the first time that the sign of solid-state CD and CPL spectra in a chiral supramolecular organic fluorophore composed of 1-arylethylamine has been controlled by changing the type of aryl unit in the chiral 1-arylethylamine component molecule without changing its chirality.

Conclusions

A chiral supramolecular organic fluorophore was successfully prepared by forming a complex between achiral fluorescent 2-naphthalenecarboxylic acid and chiral (*R*)-(+)-1-arylethylamines. By changing the aryl unit in the chiral (*R*)-(+)-1-arylethylamine, the style of helical columnar network structure and its packing arrangement was changed. As a result, the signs of the solid-state CD and CPL spectra of these supramolecular fluorophores could be reversed despite using chiral amine component molecules with the same chirality. These results show that the solid-state chiral optical properties of the 2-naphthalenecarboxylic acid/amine supramolecular organic fluorophore can be controlled by replacing the aryl unit in the chiral 1-arylethylamine component molecule with another of the same chirality (that is, by changing the style of helical column and its packing structure), instead of changing the chirality of the amine component molecule in the solid state. Supramolecular organic fluorophores offering these functionalities are expected to be useful in the development of new solid-state chiral supramolecular fluorophores.

Experimental Section

General Methods

Component molecule **1** and MeOH were purchased from Wako Pure Chemical Industries. Component molecules (*R*)-**2–4** and (*S*)-**2–4** were purchased from Tokyo Kasei Kogyo. MeOH was used directly without further purification.

Formation of Complexes *I–III* by Crystallization from MeOH

Compounds **1** (11.5 mg, 6.68×10^{-5} mol) and (*R*)-**2** (or (*R*)-**3**, (*R*)-**4**; 6.68×10^{-5} mol) were dissolved in MeOH (2 mL). After one week, a large number of crystals (crystals of complexes **I** (9 mg) for the **1**/(*R*)-**2** system, **II** (10 mg) for the **1**/(*R*)-**3** system, and **III** (10 mg) for the **1**/(*R*)-**4** system) were obtained. The mass of the crystals was equal to the total mass of the crystals of complexes **I**, **II**, and **III** obtained in one batch.

Theoretical Calculations

The excitation energies and rotational strengths of **1** were calculated by the Zerner's intermediate neglect of differential overlap (ZINDO) method[5] from the molecular geometries in the complexes. In these calculations, the deprotonated form of **1** was used instead of the neutral form because the carbonate proton of **1** was transferred to the amine molecule in complexes **I–III**. These quantum chemical calculations were carried out by using the Gaussian 03 program.[6]

Measurement of Solid-State Fluorescence Spectra

The solid-state fluorescence spectra and absolute photoluminescence quantum yields were measured by using the Absolute PL Quantum Yield Measurement System (C9920-02, HAMAMATSU PHOTONICS K. K.) in air at room temperature. The excitation wavelengths were 329, 330, and 327 nm for complexes **I**, **II**, and **III**, respectively.

Measurement of Solid-State CD and Absorption Spectra

The solid-state CD and absorption spectra were measured by using a Jasco J-800 KCM spectrophotometer. The solid-state samples were prepared according to standard procedures for obtaining glassy KBr matrices.[7]

X-ray Crystallographic Study of Complexes *I–III*

X-ray diffraction data for single crystals were collected by using a BRUKER APEX diffractometer. The crystal structures were solved by a direct method[8] and refined by full-matrix least-squares using the SHELXL97 program.[8] Diagrams were prepared by using the PLATON program.[9] Absorption corrections were performed by using the SADABS program.[10] 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**: $C_8H_{11}N{\cdot}C_{11}H_8O_2$; $M = 293.35$; space group $P2_12_12_1$; $a = 6.3454(5)$, $b = 14.4425(11)$, $c = 17.3736(13)$ Å; $V = 1592.2(2)$ Å^3; $\rho_{calcd} = 1.224$ g cm^{-3}; $z = 4$; $\mu(\mathrm{Mo}_{K\alpha}) = 0.079$ mm^{-1}; 9906 reflections measured; 3648 unique: final $R(F^2) = 0.0437$ using 3194 reflec-

Figure 6. CPL and fluorescence spectra of complexes a) **I**, b) **II**, and c) **III** in the solid state (as KBr pellets).

tions with $I > 2.0\sigma(I)$; R(all data) = 0.0525; $T = 115(2)$ K. CCDC 822729 contains 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.

Crystallographic data for **II**: $C_9H_{13}N{\cdot}C_{11}H_8O_2$; $M = 307.38$; space group $P2_12_12_1$; $a = 6.0380(7)$, $b = 16.4105(18)$, $c = 16.7204(18)$ Å; $V = 1656.8(3)$ Å^3; $\rho_{\text{calcd}} = 1.232$ g cm^{-3}; $z = 4$; $\mu(\text{Mo}_{K\alpha}) = 0.079$ mm^{-1}; 10358 reflections measured; 3774 unique; final $R(F^2) = 0.0577$ using 3026 reflections with $I > 2.0\sigma(I)$; R(all data) = 0.0758; $T = 115(2)$ K. CCDC 822730 contains 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.

Crystallographic data for **III**: $C_9H_{13}NO{\cdot}C_{11}H_8O_2$; $M = 646.76$; space group $P1$; $a = 6.1134(7)$, $b = 7.2271(8)$, $c = 18.892(2)$ Å; $\alpha = 88.533(2)$, $\beta = 88.910(2)$, $\gamma = 88.428(2)°$; $V = 833.94(16)$ Å^3; $\rho_{\text{calcd}} = 1.288$ g cm^{-3}; $z = 1$; $\mu(\text{Mo}_{K\alpha}) = 0.086$ mm^{-1}; 7302 reflections measured; 5935 unique; final $R(F^2) = 0.0545$ using 4641 reflections with $I > 2.0\sigma(I)$; R(all data) = 0.0740; $T = 115(2)$ K. CCDC 822731 contains 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 CPL Spectra

The solid-state CPL spectra were measured by using a Jasco CPL-200 spectrophotometer. The excitation wavelengths were 329, 330, and 326 nm for complexes **I–III**, respectively. The solid-state samples were prepared according to standard procedures for obtaining glassy KBr matrices. The power of the incident beam of the CPL spectrometer was 0.3 mW cm^{-2} at the installation position of sample. The CPL spectrum is approached by Simple Moving Average (SMA).

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