

Preparation, crystal structure, and solid-state optical property of a disulfonic acid/amine fluorescent complex composed of 4,4'-biphenyldisulfonic acid and 2-naphthylethylamine

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Abstract Solid-state disulfonic acid/amine fluorescent host complexes including methanol (MeOH) as guests were successfully prepared using 4,4'-biphenyldisulfonic acid and 2-naphthylethylamine as component molecules. Although the crystal structure of the obtained host complex is similar to that of the corresponding dicarboxylic acid/amine host complex, the solid-state photo-luminescence quantum yield of the disulfonic acid/amine fluorescent host complex is increased relative to those of the corresponding dicarboxylic acid/amine host complex.

Keywords 4,4'-Biphenyldicarboxylic acid · 4,4'-Biphenyldisulfonic acid · Crystal-engineering · Fluorescence · 2-Naphthylethylamine · Supramolecule

Introduction

The development of novel functional host system is important in the field of host–guest chemistry. In particular, solid-state organic fluorescent host systems are required because solid-state systems can directly interact with guest molecules [1–6]. Recently, solid-state supramolecular organic fluorescent hosts composed of two or more organic component molecules have attracted considerable attention [7–18]. This is because the physical and chemical

properties of these hosts for molecular recognition can be easily controlled by changing the combination of component molecules without synthetic process. Generally, in such a supramolecular system, to tune the physical and chemical properties, the component molecule is changed to another molecule with a different backbone. However, in this case, changes to the packing arrangement of component molecules may occur in the complex. As a result, problems such as changes to the inclusion styles and behaviors of guest molecules in host complex may occur. If their physical and chemical properties can be tuned without a change in the packing arrangement, it is expected that the ease of prediction and control of functionality in novel supramolecular complexes would increase.

We previously reported a solid-state supramolecular host complex (**I**) with channel-like cavities prepared by combining *rac*-2-naphthylethylamine (*rac*-**1**) and 4,4'-biphenyldicarboxylic acid (**2**) [19]. This complex has a two-dimensional (2D) layered network structure composed of *rac*-**1** and **2**. Guest methanol (MeOH) molecules were included in the channel-like cavities formed by assembling these 2D-layered network structures. Unfortunately, this host complex showed hardly any fluorescence in the solid state.

In this paper, we attempt to change the solid-state optical properties of a supramolecular host complex without a change in the packing arrangement of component molecules. Specifically, we aim to increase the solid-state fluorescence of a **1/2**-type supramolecular host complex with a biphenyl backbone without changing its packing arrangement. For this purpose, we do not alter the biphenyl backbone of the component molecule, but instead change a binding substituent of component molecule. The formation of the novel solid-state supramolecular fluorescent host complex with a biphenyl backbone that features stronger

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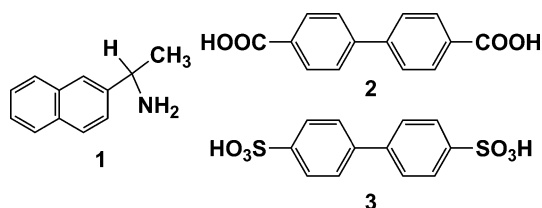


Chart 1 Component molecules of complex

solid-state fluorescence was attempted by combining 4,4'-biphenyldisulfonic acid (**3**) with a sulfonic acid group as a component molecule instead of **2** with a carboxylic acid group. As guest molecule, methanol (MeOH) was used (Chart. 1).

Experimental procedure

General methods

All reagents and solvents are commercially available. Component molecules (*R*)-**1** and (*S*)-**1** were purchased from Alfa Aesar. Component molecules **2** and **3** were purchased from Tokyo Kasei Kogyo Co. The guest MeOH solution was purchased from Wako Pure Chemical Industries. Component molecule *rac*-**1** was produced by mixing (*R*)-**1** and (*S*)-**1**.

Formation of supramolecular fluorescent host complex

Rac-**1** (8.6 mg, 5.0×10^{-5} mol) [or (*R*)-**1** (8.5 mg, 5.0×10^{-5} mol)] and **3** (7.85 mg, 2.5×10^{-5} mol) were dissolved in guest MeOH solvent (2 mL) and MeOH was slowly evaporated at room temperature for a week. MeOH was not completely evaporated. A variety of complexes [racemic complex **II** (7.2 mg) for the *rac*-**1**/**3** system and chiral complex **III** (7.5 mg) for the (*R*)-**1**/**3** system] were obtained after filtration.

Measurement of ^1H -NMR spectra

^1H -NMR spectra were recorded with a JNM-AL400 spectrometer in $\text{DMSO}-d_6$ (400 MHz).

X-ray crystallographic study of crystal

X-ray diffraction data for single crystals were collected using RIGAKU SATURN 70R. The crystal structures were solved by the direct method [20] and refined by full-matrix least-squares using SHELXL97 [20]. The diagrams were prepared using PLATON [21]. Absorption collections were performed using SADABS [22]. Nonhydrogen 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 **II**: $\text{C}_{12}\text{H}_{13}\text{N} \cdot 0.5\text{C}_{12}\text{H}_{10}\text{O}_6\text{S}_2$ with unknown solvate, $M = 328.39$, Monoclinic, space group $C2/c$, $a = 28.132(9)$, $b = 5.5892(15)$, $c = 25.421(8)$ Å, $\beta = 113.911(4)^\circ$, $V = 3654.1(19)$ Å³, $Z = 8$, $D_c = 1.194$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.190$ mm⁻¹, 8574 reflections measured, 3782 unique, final $R(F^2) = 0.0801$ using 1963 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.1317$, $T = 100(2)$ K. Disordered solvent regions were treated by SQUEEZE/PLATON [21]. CCDC 818715. Crystallographic data for **III**: $2\text{C}_{12}\text{H}_{13}\text{N} \cdot \text{C}_{12}\text{H}_{10}\text{O}_6\text{S}_2$ with unknown solvate, $M = 656.79$, Monoclinic, space group $C2$, $a = 28.100(5)$, $b = 5.5859(8)$, $c = 25.499(4)$ Å, $\beta = 114.045(2)^\circ$, $V = 3655.1(10)$ Å³, $Z = 4$, $D_c = 1.194$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 0.190$ mm⁻¹, 16222 reflections measured, 9727 unique, final $R(F^2) = 0.0584$ using 8770 reflections with $I > 2.0\sigma(I)$, $R(\text{all data}) = 0.0631$, $T = 100(2)$ K. Disordered solvent regions were treated by SQUEEZE/PLATON [21]. CCDC 818716. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; deposit@ccdc.cam.ac.uk).

Measurement of solid-state fluorescence spectra

A solid-state fluorescence spectra and absolute photoluminescence quantum yields (Φ_F) were measured by Absolute PL Quantum Yield Measurement System (C9920-02, HAMAMATSU PHOTONICS K. K.) under air atmosphere at room temperature. The excited wavelength for complexes **II** and **III** is 310 nm. The excited wavelength is 331 nm for **2** and 322 nm for **3**.

Results and discussion

The preparation of a supramolecular host complex was attempted by crystallization from the guest MeOH solution. As the component molecules, racemic amine molecule *rac*-**1** and disulfonic acid molecule **3** with a biphenyl backbone were used for the first study. A mixture of *rac*-**1** and **3** was dissolved in MeOH and left to stand at room temperature; after a week, colorless complex **II** was obtained. ^1H NMR analysis of complex **II** in dimethyl sulfoxide ($\text{DMSO}-d_6$) revealed that this complex was composed of *rac*-**1** and **3** and includes guest MeOH molecules ¹.

To investigate the crystal structure of host complex **II**, X-ray crystallographic analysis was performed.

¹ ^1H -NMR spectra are shown in S.Figs. 1 for **II** and 2 for **III**.

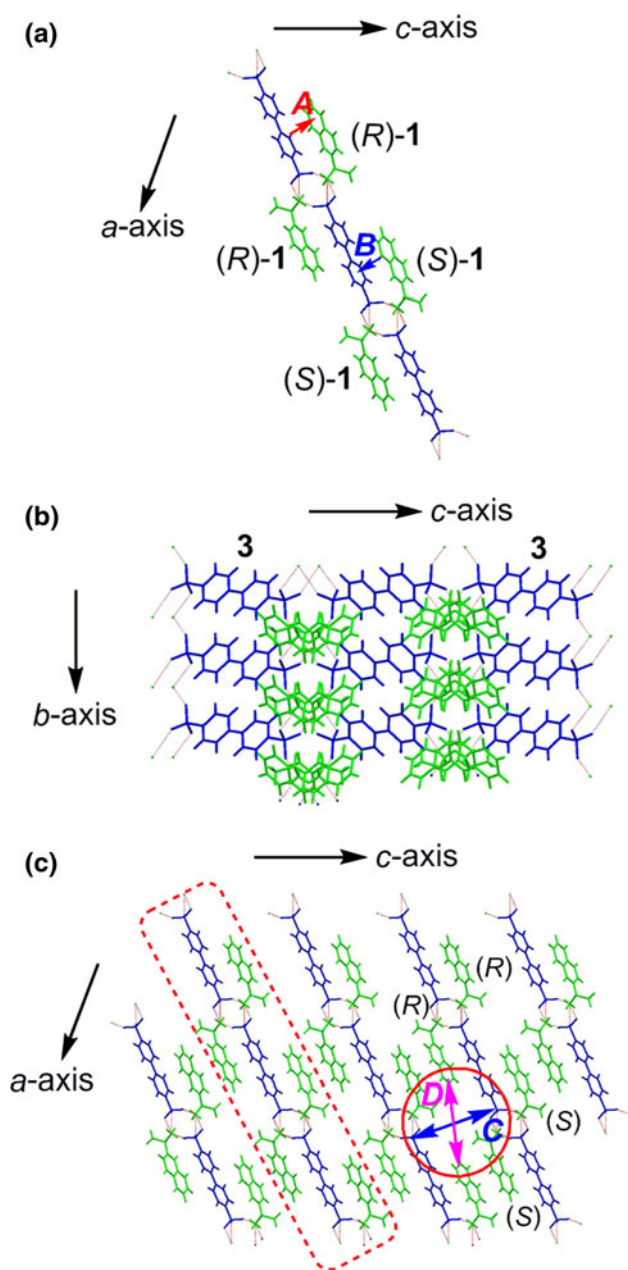


Fig. 1 Crystal structures of racemic complex **II**. Guest MeOH molecules are squeezed. (*R*) and (*S*) indicate the absolute configuration of **1**. **a** Extracted 2D-layered network structural unit observed along the *b*-axis. Red *A* and blue *B* arrows show the benzene-naphthalene and naphthalene-benzene edge-to-face interactions, respectively. **b** Extracted 2D-layered structural unit observed along the *a*-axis. **c** Channel-like cavities formed by assembly of the 2D-layered network structure observed along the *b*-axis. The dotted red rectangle shows a 2D-layered network structure. The red circle shows a channel-like cavity

Unfortunately, although this revealed the disordered nature of the guest molecules, the crystal structure of complex **II** squeezed the guest molecules, as is shown in Fig. 1.

The X-ray crystallographic analysis revealed that the stoichiometry of the host backbone in complex **II**

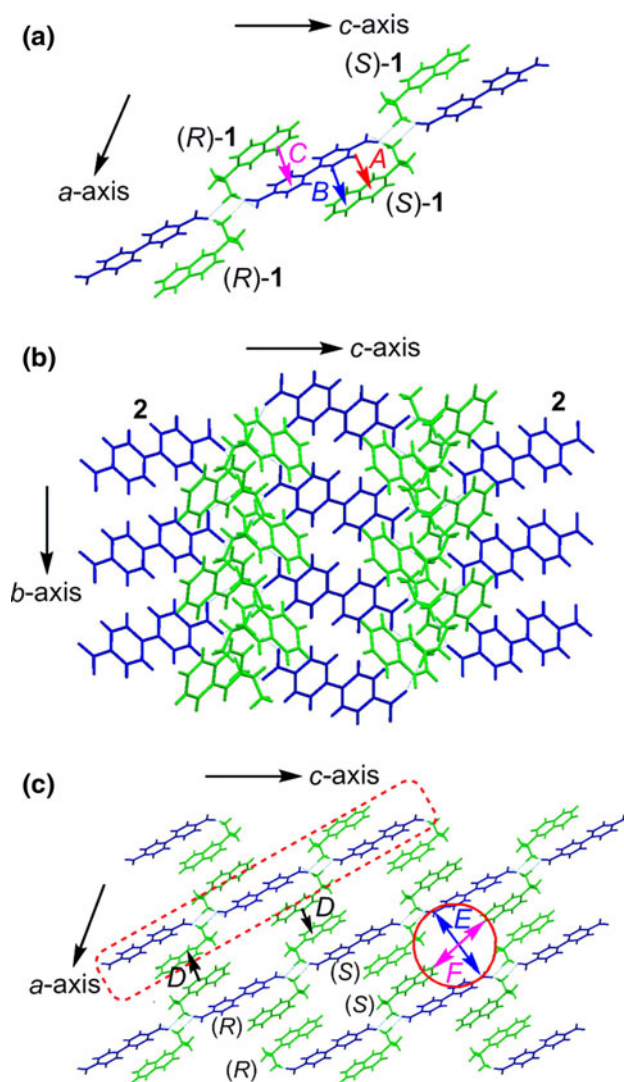


Fig. 2 Crystal structures of racemic complex **I** [19]. Guest MeOH molecules are squeezed. (*R*) and (*S*) indicate the absolute configuration of **1**. **a** Extracted 2D-layered network structural unit observed along the *b*-axis. Red *A* and blue *B* arrows show the benzene-naphthalene edge-to-face interactions. The purple *C* arrow shows naphthalene-benzene edge-to-face interaction. **b** Extracted 2D-layered structural unit observed along the *a*-axis. **c** Channel-like cavities formed by assembly of the 2D-layered network structure observed along the *b*-axis. The dotted red rectangle shows a 2D-layered network structure. The red circle shows a channel-like cavity. Black *D* arrows show naphthalene–naphthalene edge-to-face interactions

[(*R*)-**1**:(*S*)-**1**:**3**] is 1:1:1, and the complex belongs to the $C2/c$ space group. In addition, $^1\text{H-NMR}^2$ analysis shows that the ratio of guest MeOH molecules to the components of the complex ((*R*)-**1**:(*S*)-**1**:**3**:MeOH) is 1:1:1:2. Interestingly, the crystal structures of dicarboxylic acid/amine host complex **I** and disulfonic acid/amine host complex **II** are almost identical (Fig. 2 for **I**) [19].

² See footnote 1.

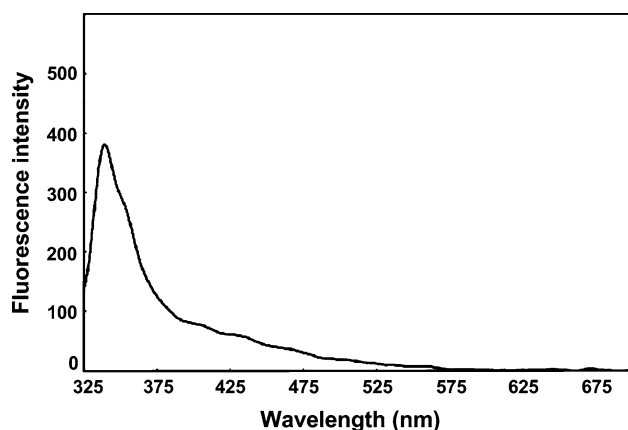


Fig. 3 Solid-state fluorescence spectrum of complex **II**

X-ray crystallographic analysis of **II** revealed that this crystal structure has a supramolecular 2D-layered hydrogen- and ionic-bonded network structure composed of **1** and **3** along the *b*- and *c*-axes, which is the same as in the crystal structure of complex **I** (Figs. 1a, b). This 2D-layered network structure is formed by the association of the ammonium hydrogen of one protonated amine in *rac*-**1** (Fig. 1; indicated in green) and the sulfoxylate oxygen of a sulfonic acid anion in **3** (Fig. 1; indicated in blue), although **1** is disordered. In addition, this layered network structure is also maintained by benzene-naphthalene edge-to-face (Fig. 1a; indicated by the red *A* arrow, 2.90 Å) and naphthalene-benzene edge-to-face (Fig. 1a; indicated by the blue *B* arrow, 2.73 Å) interactions³. The torsion angle between the benzene rings in **3** is 1.97°. The assembly of these 2D-layered network structures (Fig. 1c; indicated by the dotted red rectangle) without major interlayer interactions along the *a*-axis results in the formation of complex **II** (Fig. 1c)⁴. Similar to complex **I**, one-dimensional (1D) channel-like cavities (Fig. 1c; indicated by a solid red circle) are formed by the assembly of these 2D-layered network structures. Although the guest molecules are disordered and squeezed in these channel-like cavities, they are trapped one-dimensionally. When comparing the crystal structures of complexes **I** and **II**, although the binding substituent is different (i.e., –COOH for **I** and –SO₃H for **II**), the style of the 2D-layered network structure and their packing are almost the same. However, the sizes of the channel-like cavities in **I** and **II** are different. As the binding substituent of the biphenyl derivatives changes from a carboxylic acid group in **2** to a sulfonic acid group in **3**, the distance between the 2D-layered network structures, *E*, for **I** and, *C*, for **II** (Figs. 1c for **II** and 2c for **I**), increase from 9.88 Å in **I** to 10.50 Å in **II**. In addition, the *F* and *D* distances in **I** and **II**,

respectively, (Figs. 1c for **II** and 2c for **I**) also elongate from 8.60 Å in **I** to 9.56 Å in **II**.

To investigate the solid-state fluorescence properties of supramolecular host complex **II**, the solid-state fluorescence spectrum was measured (Fig. 3).

As expected, unlike complex **I**, which uses a carboxylic acid substituent, complex **II**, which uses a sulfonic acid substituent, showed fluorescence in the solid state despite the inclusion of guest MeOH molecules; however, the fluorescence of **II** is weak. The solid-state fluorescence maximum (λ_{em}) of complex **II** is observed at 339 nm, and the absolute value of the photoluminescence quantum yield (Φ_F) is 0.07 in the solid state, which demonstrates that this supramolecular host complex may be used as a solid-state fluorescent host. These results suggest that by the change of the binding substituent of the component molecule from a carboxylic acid group to a sulfonic acid group, the solid-state photoluminescence quantum yield can be increased without changes in the packing arrangement of component molecules.

To investigate the origin of the increase of the solid-state photoluminescence quantum yield by replacing **2** with **3**, the fluorescence properties of component molecules **2** and **3** were studied. When the solid-state fluorescence spectra of component molecules **2** and **3** were measured, both molecules **2** and **3** showed fluorescence in the solid state. The solid-state λ_{em} of molecules **2** and **3** is observed at 395 and 355 nm, respectively, and the Φ_F of **2** and **3** is both 0.19 in the solid state. They show that the increase of the solid-state photoluminescence quantum yield is caused by the slight difference of intermolecular distances between component molecules and the difference of binding strengths in complexes **I** and **II**.

Complex **II** is a racemic complex; therefore, the preparation of chiral complex **III**, comprising chiral (*R*)-**1** and **3**, was attempted by crystallization from a guest MeOH solution containing (*R*)-**1** and **3** similar to the preparation of complex **II**. This process also resulted in a colorless complex **III**, which was composed of (*R*)-**1** and **3** and included guest MeOH molecules as determined by ¹H-NMR analysis⁵.

The crystal structure of chiral complex **III** contains squeezed guest molecules, as shown in Fig. 4. X-ray crystallographic analysis revealed that (*R*)-**1** and guest molecules in this complex are also disordered. Similar to complex **II**, X-ray crystallography revealed that the stoichiometry of the host backbone in complex **III** [(*R*)-**1**:**3**] is 2:1, and this complex belongs to the *C*2 space group. ¹H-NMR⁶ analysis shows that the ratio of guest MeOH molecules to the component molecules [(*R*)-**1**:**3**:MeOH] is

³ Determined by PLATON geometry calculation

⁴ See footnote 3

⁵ See footnote 1

⁶ See footnote 1

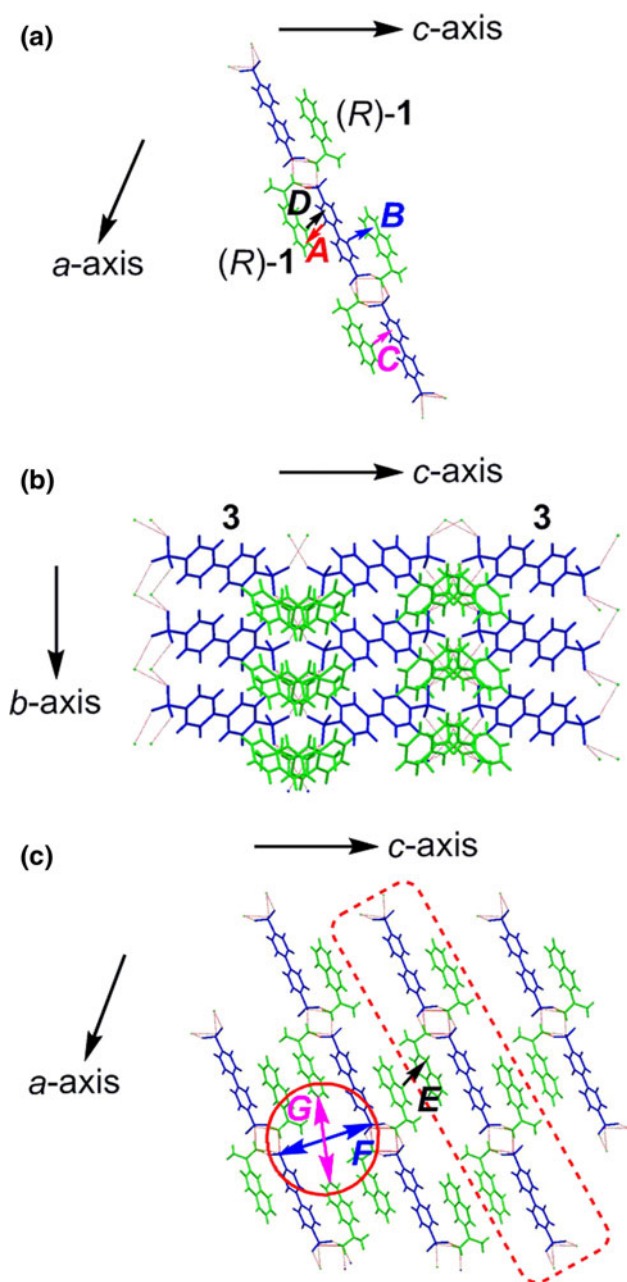


Fig. 4 Crystal structures of chiral complex **III**. Guest MeOH molecules are squeezed. **a** Extracted 2D-layered network structural unit observed along the *b*-axis. Red *A* and blue *B* arrows indicate benzene-naphthalene edge-to-face interactions. Purple *C* and black *D* arrows indicate naphthalene-benzene edge-to-face interactions. **b** Extracted 2D-layered structural unit observed along the *a*-axis. **c** Channel-like cavity formed by assembly of the 2D-layered network structure observed along the *b*-axis. The dotted red rectangle shows a 2D-layered network structure. The red circle shows a channel-like cavity. The black *E* arrow indicates the naphthalene-naphthalene edge-to-face interaction

2:1:2. The crystal structures of racemic complex **II** and chiral complex **III** are almost identical. Complex **III** also has a supramolecular 2D-layered hydrogen- and ionic-bonded network structure composed of (*R*)-**1** (Fig. 4;

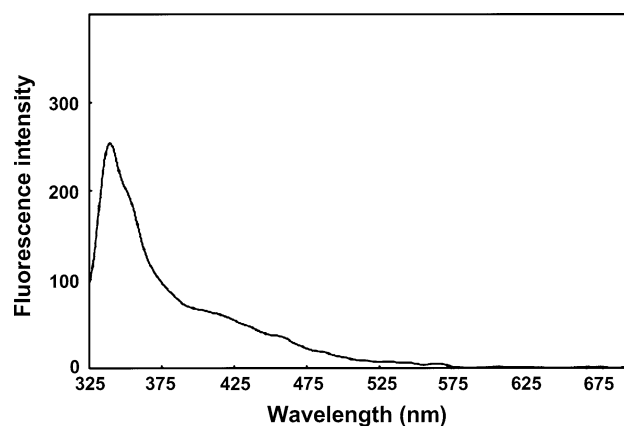


Fig. 5 Solid-state fluorescence spectrum of complex **III**

indicated in green) and **3** (Fig. 4; indicated in blue) along the *b*- and *c*-axes (Fig. 4a, b).

The layered network structure is maintained by two benzene-naphthalene edge-to-face interactions (Fig. 4a; indicated by the red *A* and blue *B* arrows, 2.89 and 2.87 Å, respectively) and two naphthalene-benzene edge-to-face interactions (Fig. 4a; indicated by the purple *C* and black *D* arrows, 2.73 and 2.75 Å, respectively)⁷. Channel-like cavities (Fig. 4c; indicated by a solid red circle) are formed by assembly of these 2D-layered network structures (Fig. 4c, indicated by the dotted red rectangle) with naphthalene-naphthalene edge-to-face interlayer interactions (Fig. 4c; indicated by the black *E* arrow, 2.86 Å)⁸. In this cavity, although the guest molecules are disordered and squeezed, the guest molecules are oriented one-dimensionally along the direction of the cavity.

The style of the 2D-layered network structures and the packing of racemic complex **II** and chiral complex **III** are almost the same (Figs. 1c and 4c). Even though the chirality of the component molecule changes from racemic to chiral (from *rac*-**1** to (*R*)-**1**), the sizes of the channel-like cavities are similar. That is, the distances between the 2D-layered network structures, *C*, (10.50 Å) in **II** and, *F*, (10.54 Å) in **III** are almost same, and the distances, *D*, (9.56 Å) in **II** and, *G*, (9.52 Å) in **III** are also similar (Figs. 1c and 4c).

Similar to racemic complex **II**, chiral complex **III** showed fluorescence in the solid state even though guest MeOH molecules are included (Fig. 5).

The solid-state λ_{em} of complex **III** is observed at 339 nm, and the Φ_F is 0.10 in the solid state. These characteristics demonstrate that this chiral supramolecular host complex may also be used as a solid-state chiral fluorescent

⁷ See footnote 3

⁸ See footnote 3

host. The same solid-state λ_{em} of the complexes is caused by the similar packing structures of the complexes.

Conclusions

A novel racemic or chiral supramolecular fluorescent host complex was prepared by combining *rac*-2-naphthylethylamine [or chiral (*R*)-2-naphthylethylamine] and 4,4'-biphenyldisulfonic acid. Although the fluorescent component molecule changes from 4,4'-biphenyldicarboxylic acid to 4,4'-biphenyldisulfonic acid, the component molecules form a similar 2D-layered network structure and the racemic (or chiral) channel-like cavities formed by the assembly of these 2D-layered network structures. Guest MeOH molecules were included in these channel-like cavities. Interestingly, the solid-state fluorescence of the supramolecular complex was successfully increased without a change in the packing arrangement by changing a binding substituent of the component molecule from a carboxylic acid to a sulfonic acid group. The prepared complexes may prove useful as a sensitive fluorescent indicator for molecular recognition. This study provides useful information for the design of novel solid-state supramolecular fluorescent host systems.

Supplementary material

¹H-NMR spectra of complexes **II** and **III**.

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