

# Preparation of a spontaneous resolution chiral fluorescent system using 2-anthracenecarboxylic acid†

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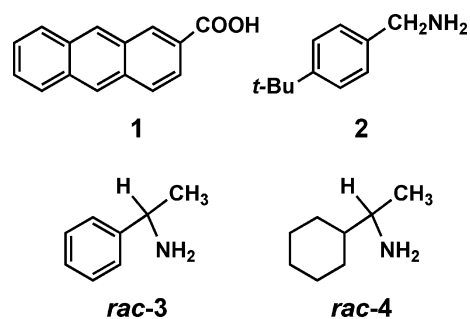
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A spontaneous resolution chiral fluorescent system is prepared by using 2-anthracenecarboxylic acid, and racemic (*rac*)-1-phenylethylamine or *rac*-1-cyclohexylethylamine. Although chiral functional organic materials are usually prepared using chiral molecules, in this system, a chiral organic fluorophore, which exhibits fluorescence in the solid state, is prepared from achiral and *rac* molecules.

## Introduction

The potential application of solid-state fluorescence techniques to organic electroluminescence (EL) devices, optoelectronic devices, *etc.* has attracted considerable attention.<sup>1</sup> In particular, the demand for a chiral fluorophore exhibiting circularly polarized luminescence (CPL) has increased. Previously reported solid-state organic fluorophores mostly comprise a single molecule,<sup>2</sup> and there are very few reports on supramolecular organic fluorophores containing two or more organic molecules.<sup>3</sup> Most of these supramolecular complexes, however, do not exhibit chirality. Recently, we have succeeded in preparing a solid-state chiral supramolecular organic fluorophore composed of two types of organic molecules—fluorescent 2-anthracenecarboxylic acid (**1**), which is one of the most famous and important fluorescent units, and chiral 2-amino-1,2-diphenylethanol.<sup>4</sup> Although chiral functional organic materials are usually prepared using chiral molecules, in this system the chiral supramolecular organic fluorophore has been obtained using achiral **1** and racemic (*rac*)-2-amino-1,2-diphenylethanol—an equimolar mixture of (1*R*,2*S*)- and (1*S*,2*R*)-2-amino-1,2-diphenylethanol. That is, this chiral fluorophore is a spontaneous resolution fluorescent system. Generally, most chiral molecules are not easily available and are more expensive than achiral or *rac* molecules. Therefore, chiral supramolecular organic fluorophores prepared using achiral or *rac* molecules can be used for the industrial production of chiral fluorophores without the use of any chiral auxiliaries, by a preferential crystallization method. As previously reported, the fluorescent **1**–2-amino-1,2-diphenylethanol system is useful for the preparation of novel chiral fluorophores. However, it is not easy to predict the formation of spontaneous resolution systems for new component molecules.

In this paper, we report the formation of a novel chiral supramolecular organic fluorophore and its optical properties; the chiral fluorophore is prepared by employing achiral or *rac* supramolecular building blocks. **1** is used as one of the acid building blocks. Achiral and *rac* amine molecules, *i.e.*, 4-*tert*-butylbenzylamine (**2**), *rac*-1-phenylethylamine (*rac*-**3**), and *rac*-1-cyclohexylethylamine (*rac*-**4**) are used as the other base building blocks.



## Results and discussion

First, the complexation behavior of the **1**–**2** system is studied. The chiral supramolecular complex is prepared *via* crystallization from an ethanol (EtOH) solution. A mixture of **1** and **2** is dissolved in the EtOH solution and allowed to stand at room temperature. After a few days, a large number of crystals of complex **I**, composed of **1** and **2**, are obtained. The X-ray crystal structure analysis of complex **I** is shown in Fig. 1†. Complex **I** is a *rac* complex. That is, the stoichiometry of complex **I** is **1** : **2** = 1 : 1, and its space group is *P*2<sub>1</sub>/*c*. This complex has a characteristic pseudo-2<sub>1</sub>-helical columnar network structure along the *b*-axis (Fig. 1a). This column is mainly formed by the carboxylate oxygens of the carboxylic acid anions (indicated by the molecules in blue in Fig. 1) and the ammonium hydrogen of the protonated amines (indicated by the molecules in green). Although complex **I** is formed by the assembly of the pseudo-2<sub>1</sub>-columns, obvious intercolumnar interactions are not present (Fig. 1b).<sup>5</sup>

A useful feature of the supramolecular system is that the structure of the supramolecular complex can be easily controlled by changing the component molecules. Thus the *rac* amine molecules (**3** and **4**) can be used instead of **2**. Next, the **1**–*rac*-**3**

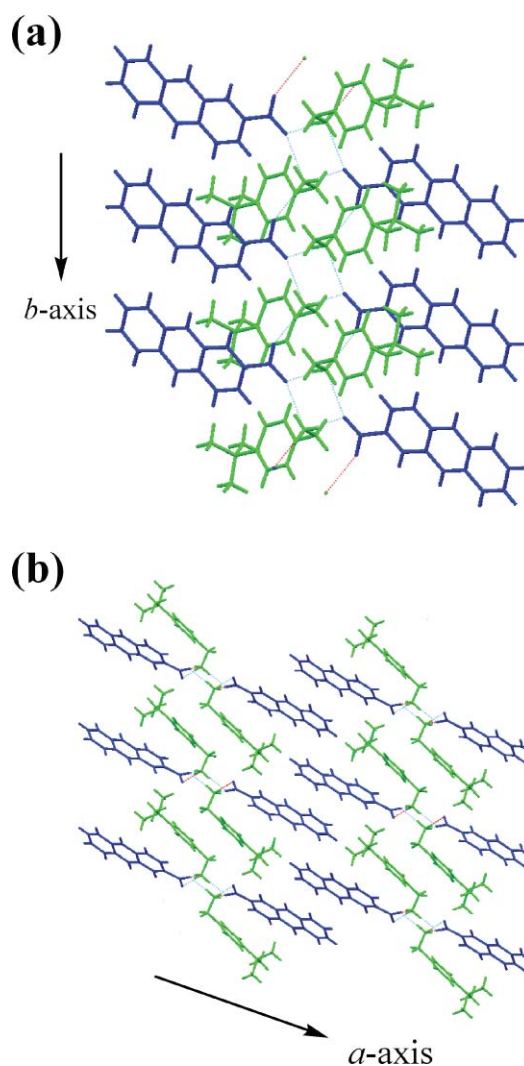
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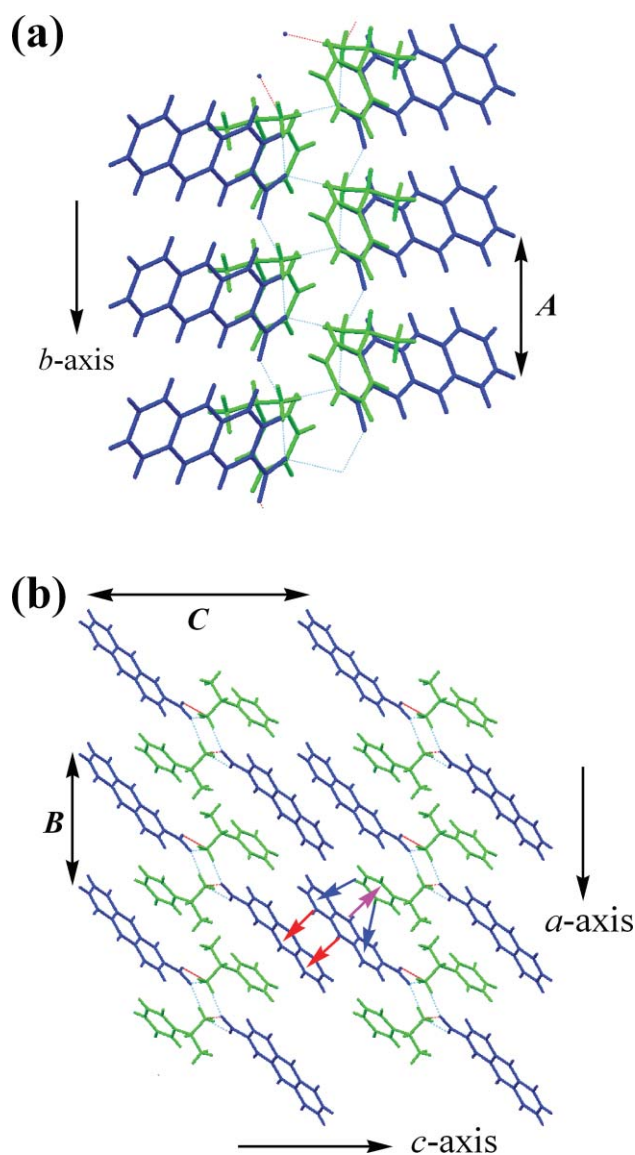
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**Fig. 1** Crystal structure of complex **I**. Molecules of **1** and **2** are indicated by the molecules in blue and green, respectively. (a) Pseudo-2<sub>1</sub>-helical columnar hydrogen- and ionic-bonded network parallel to the *b*-axis. (b) Packing structure observed along the *b*-axis.

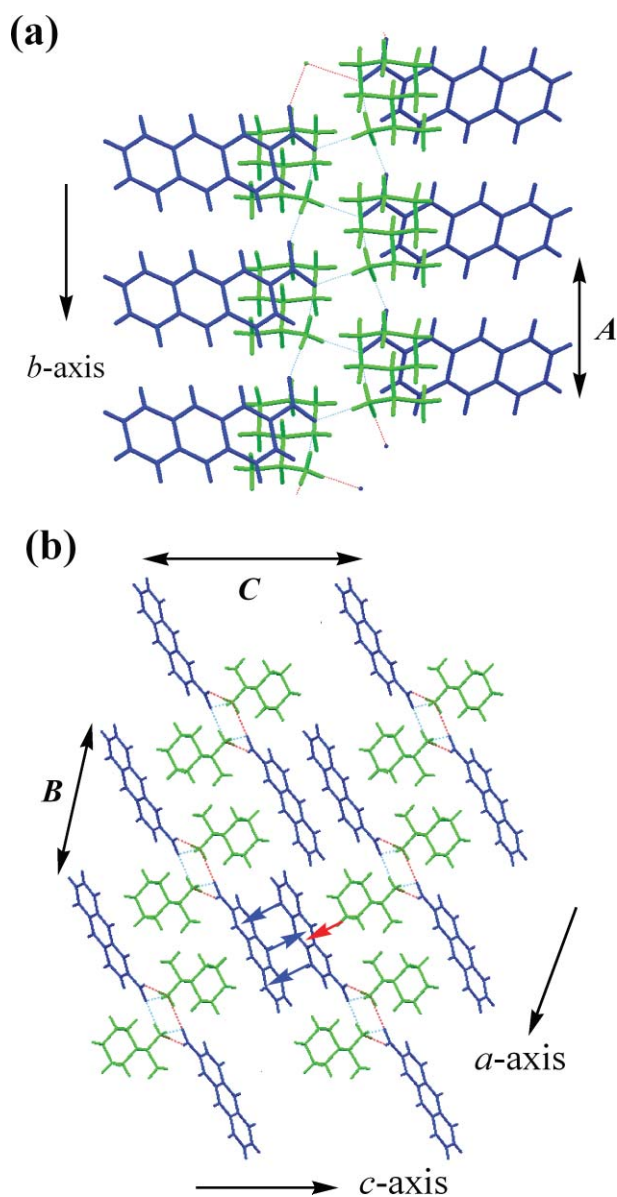
system is studied. Similarly to the preparation of the **1–2** system, the chiral fluorophore **1–3** system is prepared *via* crystallization from an EtOH solution. A mixture of **1** and *rac*-**3** is dissolved in the EtOH solution and allowed to stand at room temperature. After a few days, colorless crystals of complex **II**, consisting of **1** and **3**, are obtained. The X-ray crystal structure analysis of complex **II** is shown in Fig. 2†. Interestingly, this complex exhibits chirality and is the same as that obtained from the **1–(R)**-**3** system. The stoichiometry of complex **II** is **1** : (*R*)-**3** = 1 : 1, and its space group is *P2*<sub>1</sub>. This difference between complex **II** and the previously reported **1–2**-amino-1,2-diphenylethanol system is that the former does not contain EtOH molecules. This complex has a characteristic 2<sub>1</sub>-helical columnar network structure along the *b*-axis (Fig. 2a). This column is mainly formed by the carboxylate oxygen of the carboxylic acid anions (Fig. 2, indicated by the molecules in blue) and the ammonium hydrogen of the protonated amines (Fig. 2, indicated by the molecules in green). Complex **II** is formed by the self-assembly of the 2<sub>1</sub>-columns by two anthracene–anthracene edge-to-face interactions (2.68 and 2.85 Å, indicated



**Fig. 2** Crystal structure of complex **II**. Molecules of **1** and **3** are indicated by the molecules in blue and green, respectively. (a) 2<sub>1</sub>-Helical columnar network structure along the *b*-axis. (b) Packing structure observed along the *b*-axis. The red, blue, and purple arrows indicate the anthracene–anthracene edge-to-face, benzene–anthracene edge-to-face, and anthracene–benzene edge-to-face interactions, respectively.

by the red arrows in Fig. 2b), two benzene–anthracene edge-to-face interactions (2.74 and 2.97 Å, indicated by the blue arrows), and one anthracene–benzene edge-to-face interaction (2.92 Å, indicated by the purple arrow).

Subsequently, *rac*-**4** with a cyclohexane ring is used instead of *rac*-**3**. Using the same procedure, a chiral supramolecular organic fluorophore is prepared by crystallization from the same EtOH solution. As a result, complex **III**, containing **1** and **4** without any EtOH molecules, is obtained. The crystal structure of complex **III** is shown in Fig. 3†. Interestingly, complex **III** also exhibits chirality and is the same as that obtained from the **1–(S)**-**4** system. The stoichiometry of complex **III** is **1** : (*S*)-**4** = 1 : 1, and its space group is the same as that of crystal **II**, *i.e.*, *P2*<sub>1</sub>. This complex also has a characteristic 2<sub>1</sub>-helical columnar network structure along



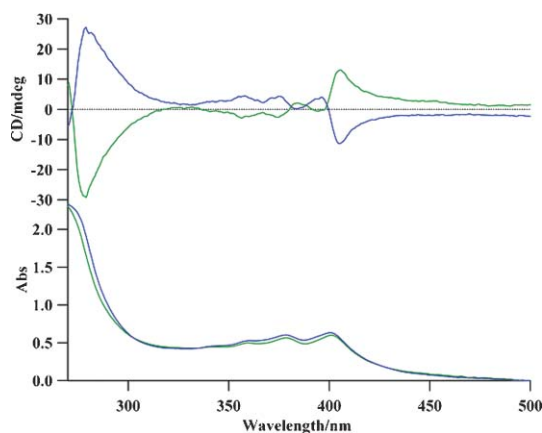
**Fig. 3** Crystal structure of complex **III**. Molecules of **1** and **4** are indicated by the molecules in blue and green, respectively. (a)  $2_1$ -Helical columnar network structure along the  $b$ -axis. (b) Packing structure observed along the  $b$ -axis. The red and blue arrows indicate the  $\text{CH}-\pi$  and anthracene-anthracene edge-to-face interactions, respectively.

the  $b$ -axis, formed by the carboxylate oxygen of the carboxylic acid anions and the ammonium hydrogen of the protonated amines (Fig. 3a). In contrast with complex **II**, complex **III** is formed by the self-assembly of the  $2_1$ -columns by one  $\text{CH}-\pi$  (3.00 Å, indicated by the red arrow in Fig. 3b) and three anthracene-anthracene edge-to-face interactions (2.74, 2.79, and 2.84 Å, indicated by the blue arrows). In both **1-rac-3** and **1-rac-4** systems, chiral crystals **II'**, composed of **1** and (*S*)-**3**, and chiral crystals **III'**, composed of **1** and (*R*)-**4**, were also obtained in each batch, respectively. This shows that these systems are spontaneous resolution systems.

From the X-ray crystallographic analysis, it is confirmed that these spontaneous resolution systems form the chiral crystals in two steps. In the first step, a chiral  $2_1$ -helical columnar structure suitable for the 1D network structure is formed by selecting the

appropriate combination from the three molecules [**1**, (*R*)-**3** (or **-4**), and (*S*)-**3** (or **-4**)]. In the second step, on the basis of the packing structure, suitable chiral crystals are formed by varying the  $2_1$ -helical column packing, *i.e.*, by the self-assembly of the  $2_1$ -helical columns with the same chirality. Moreover, by comparing the crystal structures of the chiral complexes **II** and **III** with that of the previously studied 1-2-amino-1,2-diphenylethanol system, it appears that **1**, along with the amine molecules, easily forms the  $2_1$ - or pseudo- $2_1$ -helical columnar network structure comprising two **1** and two amine molecules when observed along the column. Therefore, this system may relatively easily form chiral complexes because chiral complexes can be formed only if columns with the same chirality are assembled.<sup>6</sup>

In order to study the asymmetric environments of complexes **II** and **III**, their solid-state circular dichroism (CD) spectra have been measured using a KBr pellet. The solid-state CD and absorption spectra of complex **II** are shown in Fig. 4 (indicated by the blue line). The peaks in the CD spectrum originating from the anthracene ring are observed at 358, 375, 397, and 404 nm. The circular anisotropy ( $g_{\text{CD}} = \Delta\text{OD}/\text{OD}$ ) factor of the last Cotton effect ( $\lambda^{\text{CD}} = 404$  nm) is approximately  $-0.6 \times 10^{-3}$ . In order to check if the crystal has caused any artifact in the spectrum, complex **II'**, composed of (*S*)-1-phenylethylamine [(*S*)-**3**] instead of (*R*)-**3** is prepared, and the CD and absorption spectra of complex **II'** are measured (Fig. 4, indicated by the green line). This CD spectrum is found to be a mirror image of the CD spectrum of complex **II**.

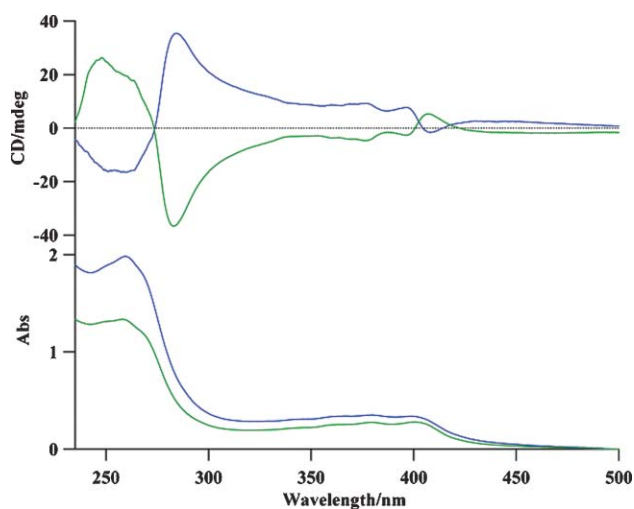


**Fig. 4** CD and absorption spectra of complexes **II** (blue line) and **II'** (green line) in the solid state (KBr pellets).

Similarly, the solid-state CD and absorption spectra of complex **III** are shown in Fig. 5 (indicated by the green line). The features in the CD spectrum originating from an anthracene ring are observed at 376, 396, and 407 nm. The  $g_{\text{CD}}$  factor of the last Cotton effect ( $\lambda^{\text{CD}} = 407$  nm) is approximately  $0.6 \times 10^{-3}$ . On the other hand, the CD spectrum of complex **III'**, composed of (*R*)-**4**, is found to be a mirror image of the CD spectrum of complex **III** (indicated by the blue line in Fig. 5). These results show that an effective chirality transfer from **3** or **4** to **1** takes place through complexation. When the CD spectra of the **1-3** system are compared to those of the **1-4** system, the two spectra are found to be similar, particularly the wavelengths and signs of the Cotton effect, and the  $g_{\text{CD}}$  factors are almost the same. This similarity is caused by the relative positions

**Table 1** Crystal shape and solid-state fluorescence spectral data of complexes **II** and **III** and fluorescent molecule **1**

	Crystal shape	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{F}}$
Complex <b>II</b>	Colorless needle	371	430	0.20
Complex <b>III</b>	Colorless needle	372	440	0.24
<b>1</b>	Yellow powder	408	464	0.04



**Fig. 5** CD and absorption spectra of complexes **III** (green line) and **III'** (blue line) in the solid state (KBr pellets).

of the anthracene rings in complexes **II** and **III** being almost the same, and does not depend on the type of amine molecule used.

Since this spontaneous resolution system comprises **1**, which is fluorescent, the obtained chiral complexes may exhibit fluorescence. In order to study the solid-state optical properties of this system, the solid-state fluorescence spectra of complexes **II** and **III** have been measured (Table 1).

Although many organic fluorophores lose their fluorescence in the solid state, complexes **II** and **III** show fluorescence even in the solid state. The solid-state fluorescence maxima ( $\lambda_{\text{em}}$ ) of complexes **II** and **III** are 430 and 440 nm, respectively, and hypsochromic shifts (34 nm for complex **II** and 24 nm for complex **III**) are observed relative to the  $\lambda_{\text{em}}$  of **1**. The absolute values of the photoluminescence quantum yield ( $\Phi_{\text{F}}$ ) of complexes **II** and **III** increase from 0.04 to 0.20 and from 0.04 to 0.24, respectively, relative to that of **1**. A comparison of the structures of complex **II** (or **III**) and **1** reveals that although **1** may exist as a dimer due to hydrogen bonding in the solid state, **1** in complexes **II** and **III** comprises a strong hydrogen- and ionic-bonded columnar network that suppresses the concomitant nonradiative processes. It is inferred that one of the reasons for the increase in  $\Phi_{\text{F}}$  after complexation is the change in the bonding style of **1**. On the other hand, when comparing complexes **II** and **III**, although  $\Phi_{\text{F}}$  and  $\lambda_{\text{em}}$  in these two complexes are different, significant differences are not observed despite using the cyclohexane ring instead of the benzene ring in complex **III**. From the detailed structural analyses, comparison of complex **II** with complex **III** shows that the distance between the anthracene rings along the column is found to slightly decrease from 6.15 Å to 6.11 Å (*A*, Fig. 2a and 3a). Although the distance between the 2<sub>1</sub>-columns (*B*, Fig. 2b and 3b) increases from 9.32 to 10.91 Å, the distance between the columns

(*C*, Fig. 2b and 3b) decreases (15.35 Å and 14.65 Å for complexes **II** and **III**, respectively). It is thought that the difference in  $\lambda_{\text{em}}$  of complexes **II** and **III** is due to the difference in the excited singlet state, mainly caused by small changes in the relative arrangements of the fluorescent anthracene rings.

## Conclusions

A novel chiral supramolecular organic fluorophore has been successfully prepared by using **1** and *rac*-**3** (or **-4**). That is, a novel spontaneous resolution chiral fluorescence system has been found. Since it is not easy to predict the structure of supramolecular organic complexes for new component molecules, it is expected that this study will provide useful information on the formation of novel spontaneous resolution systems consisting of supramolecular complexes. Moreover, although many organic fluorophores lose their fluorescence in the solid state, this chiral supramolecular fluorophore shows stronger fluorescence on complexation as compared to **1** 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 exhibiting spontaneous resolution.

## Experimental

### General methods

All reagents were used directly as obtained commercially. Component molecules **1–4** were purchased from Tokyo Kasei Kogyo Co. EtOH was purchased from Wako Pure Chemical Industry.

### Formation of the complex by crystallization from an EtOH solution

**1** (10 mg, 0.045 mmol) and an amine (0.045 mmol) were dissolved in EtOH (2 mL). After 3–5 days, a large number of crystals [crystals of complex **I** for the **1–2** system (6 mg), a mixture of crystals of complexes **II** and **II'** for the **1–3** system (5 mg), and a mixture of crystals of complexes **III** and **III'** for the **1–4** system (6 mg)] were obtained. The weight of the crystals is the total weight of crystals obtained in one batch.

### X-ray crystallographic study of the complexes

X-ray diffraction data for single crystals were collected using *BRUKER APEX*. The crystal structures were solved by the direct method<sup>7</sup> and refined by full-matrix least-squares using *SHELX97*.<sup>8</sup> The diagrams were prepared using *PLATON*.<sup>9</sup> Absorption corrections were performed using *SADABS*.<sup>10</sup> 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<sub>11</sub>H<sub>17</sub>N·C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>, *M* = 385.49, monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 18.2494(14), *b* = 6.5375(5), *c* = 17.7953(13) Å,  $\beta$  = 99.5320(10)°, *V* = 2093.8(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.223 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.077 mm<sup>-1</sup>, 12454 reflections measured, 4745 unique, final *R*(*F*<sup>2</sup>) = 0.0674 using 3578 reflections with *I* > 2.0 $\sigma$ (*I*), *R*(all data) = 0.0940, *T* = 100(2) K. CCDC 681597. Crystallographic data for **II**: C<sub>8</sub>H<sub>11</sub>N·C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>, *M* = 343.41, monoclinic, space group *P*<sub>2</sub><sub>1</sub>, *a* = 9.319(3), *b* = 6.1500(17),

$c = 15.347(4) \text{ \AA}$ ,  $\beta = 90.088(5)^\circ$ ,  $V = 879.6(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.297 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.082 \text{ mm}^{-1}$ , 7730 reflections measured, 3934 unique, final  $R(F^2) = 0.0518$  using 3257 reflections with  $I > 2.0\sigma(I)$ ,  $R(\text{all data}) = 0.0663$ ,  $T = 120(2) \text{ K}$ . CCDC 681595. Crystallographic data for **III**:  $\text{C}_8\text{H}_{17}\text{N}\cdot\text{C}_{15}\text{H}_{10}\text{O}_2$ ,  $M = 349.46$ , monoclinic, space group  $P2_1$ ,  $a = 10.9057(9)$ ,  $b = 6.1084(5)$ ,  $c = 14.6448(12) \text{ \AA}$ ,  $\beta = 102.4310(10)^\circ$ ,  $V = 952.71(14) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.218 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.077 \text{ mm}^{-1}$ , 8407 reflections measured, 4179 unique, final  $R(F^2) = 0.0453$  using 3527 reflections with  $I > 2.0\sigma(I)$ ,  $R(\text{all data}) = 0.0559$ ,  $T = 135(2) \text{ K}$ . CCDC 681596. Crystallographic data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44)1223-336-033; [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))†.

#### Measurement of solid-state CD and absorption spectra

The CD and absorption spectra were measured using a Jasco J-800KCM spectrophotometer. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.<sup>11</sup>

#### Measurement of solid-state fluorescence spectra

Solid-state fluorescence spectra and absolute photo-luminescence quantum yields were measured by an absolute PL quantum yield measurement system (C9920-02, HAMAMATSU PHOTONICS K. K.) under an air atmosphere at room temperature.

#### Acknowledgements

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