

## Electronic Supplementary Information

# Absolute asymmetric photocyclization in chiral diarylethene co-crystals with octafluoronaphthalene

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## 1. Materials

Synthesis and characterization of 1,2-Bis[2-methyl-5-(1-naphthyl)-3-thienyl]perfluorocyclopentene (**1a**) and the corresponding closed-ring isomer (**1b**) are described in a previous paper.<sup>S1</sup> Octafluoronaphthalene was purchased from Tokyo Kasei Kogyo Co., Ltd.

## 2. Instrumentation

Absorption spectra in hexane were measured with a Hitachi U-3410 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W super high-pressure mercury lamp. The wavelength of the light was selected by passing the light through a Ritsu MV-10N monochromator or cut-off filters.

Absorption spectra in the single-crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Fig. S1 shows an illustration of equipments for the measurement. A 100 W halogen lamp in the microscope was used as a light source. Polarizer and analyzer were set in parallel to each other. The wavelength dependence of light intensity which transmits through the colourless crystal ( $I_0$ ) was measured by the photodetector. After irradiation with ultraviolet light to the crystal, the wavelength dependence of light intensity which transmits through the coloured crystal ( $I$ ) was measured. Based on the Lambert-Beer's law ( $A = \log(I_0/I)$ ), the absorption spectrum of photogenerated closed-ring isomer in the crystal was calculated. Polar plots of the absorbance were carried out by measuring the spectra on rotating the stage of the microscope.

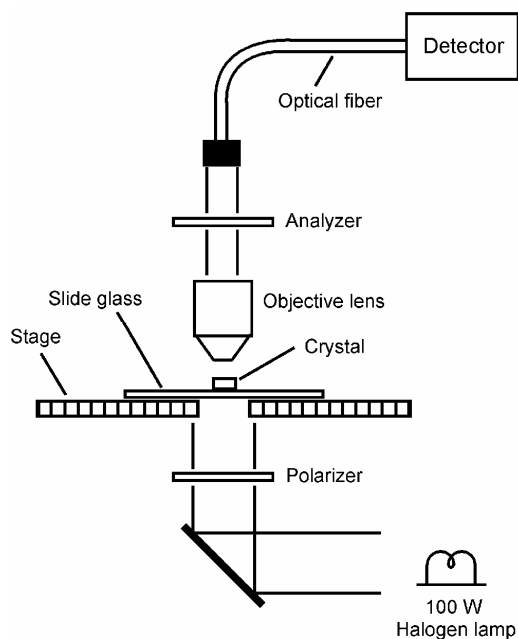


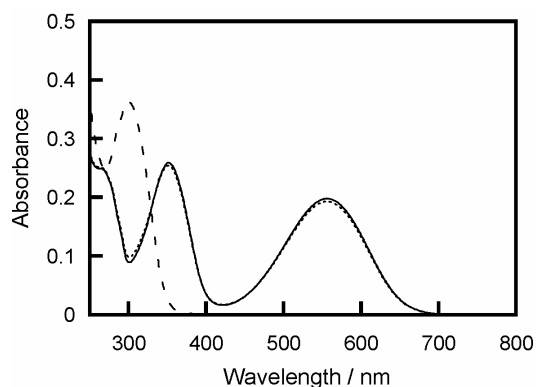
Fig. S1 Equipments for absorption spectral measurement of single crystal

CD spectra in hexane were measured with a JASCO J-820 spectropolarimeter.

HPLC analysis was performed on a Hitachi L-2130 pump coupled with a Hitachi L-2420 UV-visible detector. Products after the photocyclization reaction were separated with a chiral column (Daicel CHIRALCEL OD-H, hexane:2-propanol = 98:2, 6 mL min<sup>-1</sup>). The detection wavelength was 329 nm, which is an isosbestic point for **1a** and **1b**. The retention times for **Np<sup>F</sup>**, **1a**, (*R,R*)-**1b**, and (*S,S*)-**1b** were 16, 18, 31, and 37 min, respectively. Photoirradiation was carried out using a Keyence UV-400 LED irradiation system with a Keyence UV-50 LED light source (365 nm, 20% intensity, 1.7 mW cm<sup>-2</sup>).

X-ray crystallographic analysis was performed on a Bruker APEX CCD-based diffractometer with MoK<sub>α</sub> radiation (55 kV, 30 mA). The crystals were cooled by a low temperature controller (Japan Thermal Engineering Co., Ltd. TC-190CP-CS-K). The data were collected as a series of ω-scan frames, each with a width of 0.3°/frame. The crystal-to-detector distance was 6.051 cm. Crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by the global refinement. The structure was solved by direct methods using SHELXS-86<sup>S2</sup> and refined by full least-squares on *F*<sup>2</sup> using SHELXL-97.<sup>S3</sup> The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

### 3. Absorption spectra of diarylethene **1** in hexane



**Fig. S2** Absorption spectra of diarylethene **1** in hexane ( $1.3 \times 10^{-5}$  mol dm<sup>-3</sup>): **1a** (dashed line), **1b** (solid line) and **1** in the photostationary state under irradiation with 313 nm light (dotted line). The conversion ratio from **1a** to **1b** in the photostationary state was 98%. **1a**:  $\lambda_{\text{max}}/\text{nm}$  298 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  27 000); **1b**:  $\lambda_{\text{max}}/\text{nm}$  352 and 556 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  20 000 and 15 000).

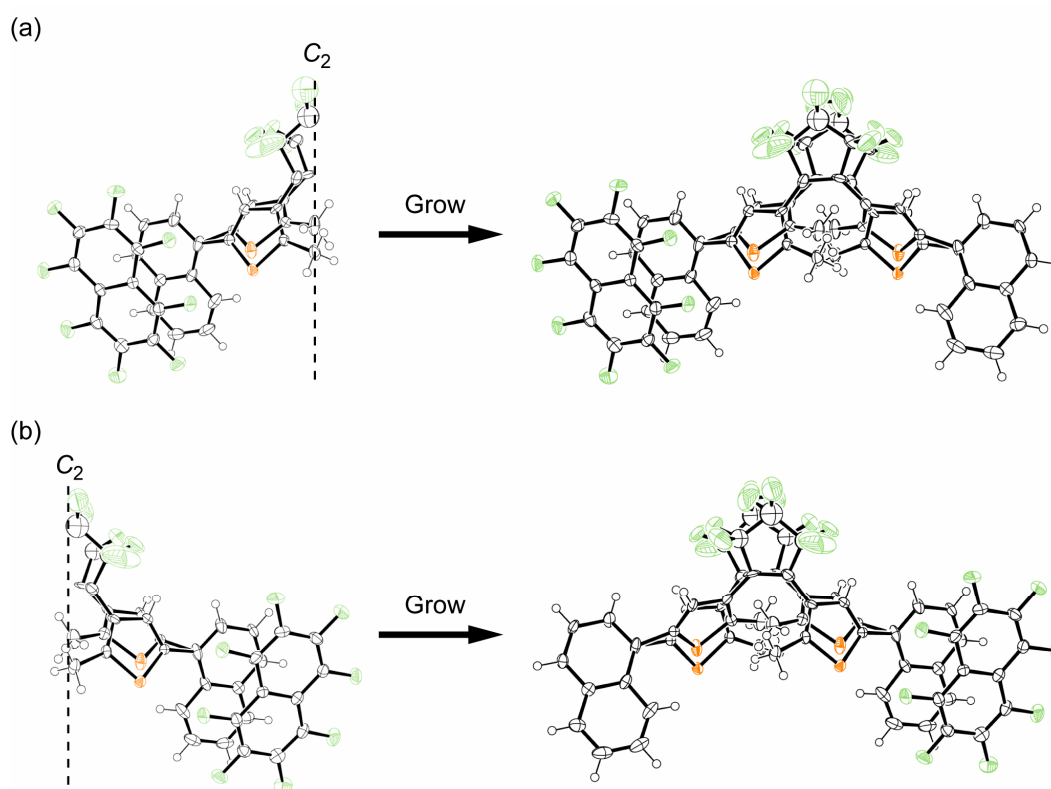
### 4. Crystallographic data for chiral co-crystal **1a**·Np<sup>F</sup>

**Table S1** Crystal data for (*P*)-**1a**·Np<sup>F</sup> and (*M*)-**1a**·Np<sup>F</sup>

	( <i>P</i> )- <b>1a</b> ·Np <sup>F</sup>	( <i>M</i> )- <b>1a</b> ·Np <sup>F</sup>
formula	C <sub>55</sub> H <sub>22</sub> F <sub>22</sub> S <sub>2</sub>	C <sub>55</sub> H <sub>22</sub> F <sub>22</sub> S <sub>2</sub>
formula weight	1164.85	1164.85
<i>T</i> /K	123(2)	123(2)
crystal system	monoclinic	monoclinic
space group	<i>C</i> 2	<i>C</i> 2
<i>a</i> /Å	37.128(5)	37.136(3)
<i>b</i> /Å	8.4977(11)	8.5070(8)
<i>c</i> /Å	7.3472(9)	7.3452(6)
$\beta$ /°	96.026(2)	96.0270(10)
<i>V</i> /Å <sup>3</sup>	2305.2(5)	2307.7(3)
<i>Z</i>	2	2
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.678	1.676
goodness-of-fit on <i>F</i> <sup>2</sup>	1.051	1.110
data/restraints/parameters	4830/1/447	4652/1/437
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0528	0.0572
<i>wR</i> <sub>2</sub> (all data)	0.1448	0.1541
Flack parameter	-0.05(12)	-0.03(14)

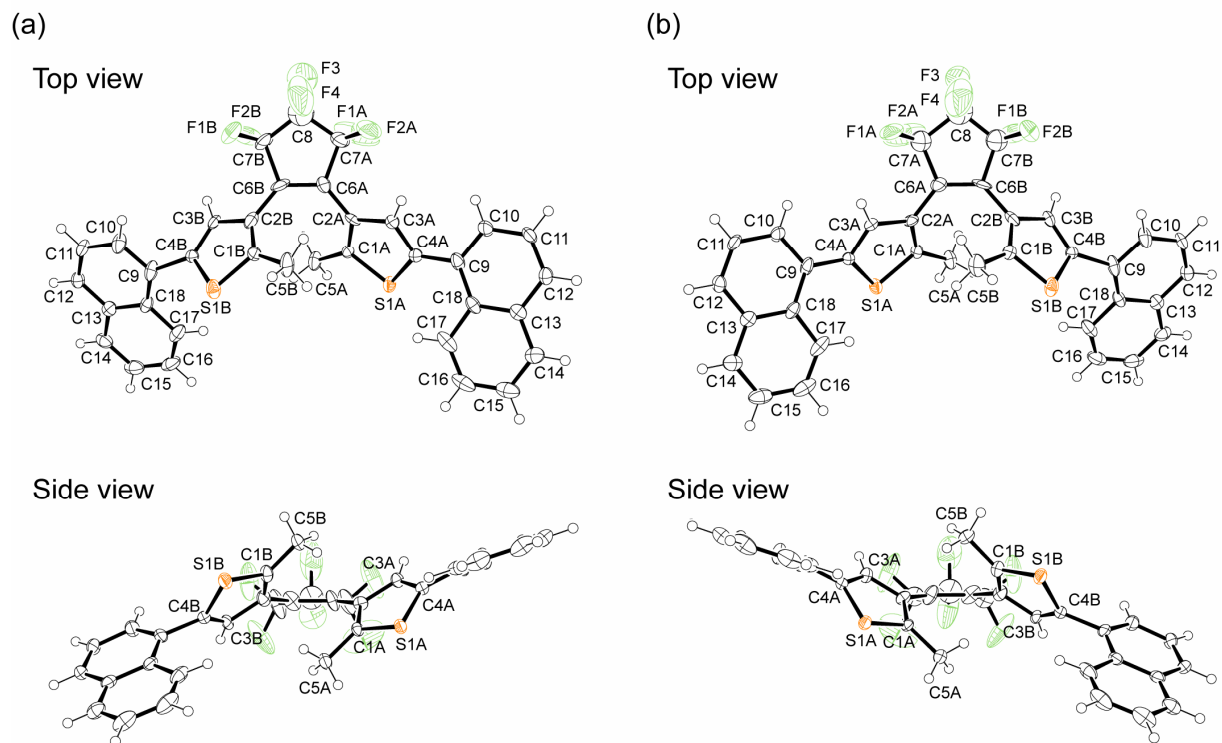
The values of the Flack parameter<sup>S4,5</sup> for (*P*)-**1a**·**Np**<sup>F</sup> and (*M*)-**1a**·**Np**<sup>F</sup> were  $-0.05(12)$  and  $-0.03(14)$ , respectively. However, a value of the Flack parameter calculated in the SHELXL-97 program is not always reliable, because the “hole-in-one” algorithm used does not involve simultaneous joint refinement of the Flack parameter with the other ones.<sup>S6</sup> Therefore, the TWIN/BASF instruction was applied in the SHELXL-97 refinement.<sup>S6,7</sup> The calculated values were  $-0.04977$  and  $-0.03480$  for (*P*)-**1a**·**Np**<sup>F</sup> and (*M*)-**1a**·**Np**<sup>F</sup>, respectively. According to these values, it is safe to say that the crystals are enantiopure and the absolute structures are correct. The high enantioselectivity in photocyclization reactions also supports the enantiopurity of the crystals.

For both (*P*)-**1a**·**Np**<sup>F</sup> and (*M*)-**1a**·**Np**<sup>F</sup>, the asymmetric unit contains a half of **1a** molecule and one of **Np**<sup>F</sup> molecule. **1a** molecule lies on a two-fold axis, and a symmetry operation of  $C_2$  builds the entire structure of the molecule. The hexafluorocyclopentene and thiophene rings are disordered to yield two equal structures in the 1:1 occupancy ratio (Fig. S3).

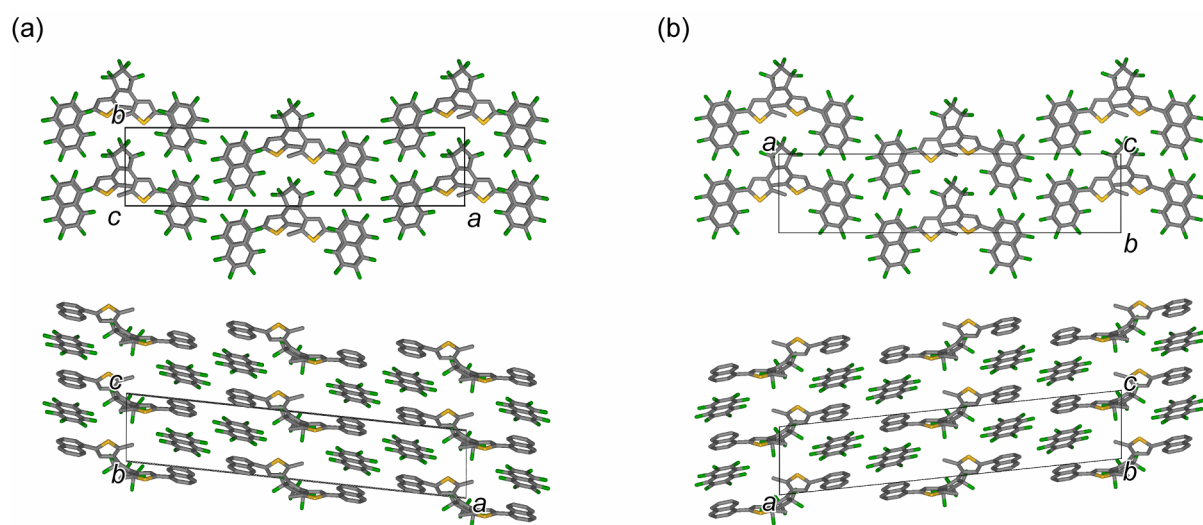


**Fig. S3** ORTEP drawings for crystals (*P*)-**1a**·**Np**<sup>F</sup> (a) and (*M*)-**1a**·**Np**<sup>F</sup> (b) with 50% thermal probability. **1a** molecule lies on a two-fold axis, and a symmetry operation of  $C_2$  build the entire structure of the molecule. The hexafluorocyclopentene and thiophene rings are disordered to yield two equal structures in the 1:1 occupancy ratio.

**1a** molecule in (*P*)-**1a**·Np<sup>F</sup> and (*M*)-**1a**·Np<sup>F</sup> adopts *P*- and *M*-helical conformations in the central hexatriene parts, respectively. The distances between the reacting carbon atoms (C1A···C1B) are 3.49 and 3.47 Å for (*P*)-**1a**·Np<sup>F</sup> and (*M*)-**1a**·Np<sup>F</sup>, respectively.

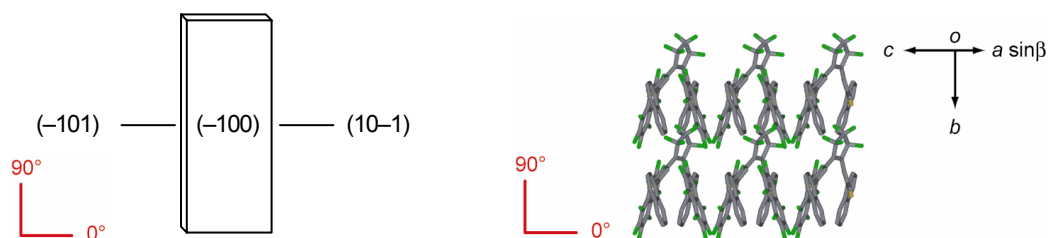


**Fig. S4** ORTEP drawings of diarylethene **1a** in crystals (*P*)-**1a**·Np<sup>F</sup> (a) and (*M*)-**1a**·Np<sup>F</sup> (b) with 50% thermal probability. Only one of the disordered structures is shown for clarity.



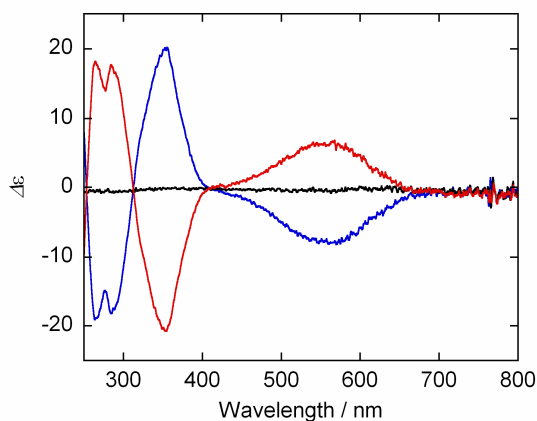
**Fig. S5** Molecular packing diagrams of crystals (*P*)-**1a**·Np<sup>F</sup> (a) and (*M*)-**1a**·Np<sup>F</sup> (b). Only one of the disordered structures is shown for clarity. Hydrogen atoms are omitted.

## 5. Shape of chiral co-crystal $1a \cdot Np^F$



**Fig. S6** Shape and face indices of crystal  $(M)\text{-}1a \cdot Np^F$  and the relationship with molecular packing.

## 6. CD spectra of diarylethene **1** in hexane



**Fig. S7** CD spectra of diarylethene **1** in hexane: **1a** (black line),  $(R,R)\text{-}1b$  (blue line) and  $(S,S)\text{-}1b$  (red line).

## References

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- S7 P. Müller ed., *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, Oxford University Press, New York, 2006.