Electronic Supplementary Information

Asymmetric photoreaction of a diarylethene in hydrogen-bonded cocrystals with chiral molecules

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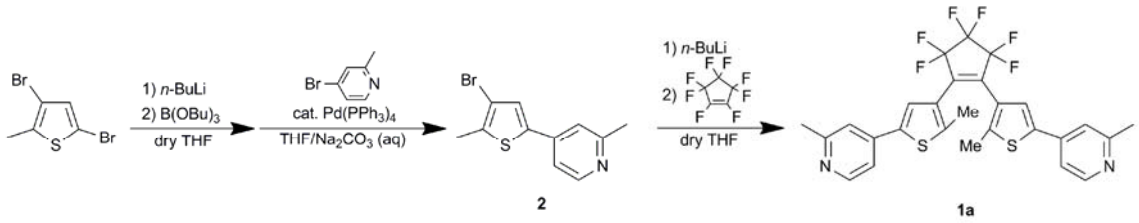
General

Recrystallization solvents used of guaranteed reagent grade and were purchased from Kanto Kagaku. 1,1'-Bi-2-naphtol was purchased from Tokyo Kasei Kogyo. ^{1}H NMR spectra were recorded by using a Bruker Biospin Avance 400 spectrometer (400 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were recorded by using a Shimadzu GCMS-QP2010Plus mass spectrometer. Absorption spectra in solution were measured by using a Hitachi U-4100 absorption spectrophotometer. Photoirradiation was carried out by using an Ushio 500 W xenon short-arc lump. Monochromic light was obtained by passing the light through a monochrometer (Jobin Yvon, H-10 UV). Absorption spectra in the single-crystalline phase were measured by using a Leica DM 2500P polarizing microscope connected to a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out by using a Keyence UV-400 ultraviolet LED. HPLC analysis was performed on a Hitachi L-2130 pump coupled with a Hitachi L-2420 UV-visible detector. Products after photocyclization reactions were separated with a chiral column (column: DAICEL CHIRALCEL OJ-RH, eluent: 20 mM NH_4HCO_3 aqueous solution adjusted to pH 9.0 by adding diethylamine : acetonitrile = 60 : 40, flow rate: 1 mL/min, detection wavelength: 580 nm).

Synthesis



2-(2-Methyl-4-pyridyl)-4-bromo-5-methylthiophene (**2**)

To a dry THF solution (30 mL) containing 2,4-dibromo-5-methylthiophene (5.5 g, 60.6 mmol) was added 1.6 M *n*-butyl lithium hexane solution (40 mL, 64 mmol) at −78°C under nitrogen atmosphere, and the reaction mixture was stirred for 15 min at that temperature. Tri-*n*-butyl borate (24 mL, 91 mmol) was added to reaction mixture at −78°C, and stirred for 2 h at that temperature. After the addition of a small amount of water, the reaction mixture was warm up to the room temperature. To the reaction mixture were added 20 wt% sodium carbonate water solution (120 mL), 4-bromo-2-methylpyridine (10.4 g, 60.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (7.0 g, 6.1 mmol) at room temperature. The reaction mixture was refluxed for 12 h. The reaction mixture was neutralized with hydrochloric acid, and then was extracted with diethyl ether. The organic layer was dried with magnesium sulfate, filtered, and concentrated. The residue was purified by alumina column chromatography using hexane as the eluent to give **2** (9.63 g, 59 %) as pale yellow powders. δ_H (400 Hz; $CDCl_3$; Me_4Si) 2.44 (s, 3H), 2.57 (s, 3H), 7.18 (d, J = 5.2 Hz, 1H), 7.24 (s, 1H), 7.24 (s, 1H), 7.29 (s, 1H), 8.46 (d, J = 5.2 Hz, 1H); m/z (EI) 267 $(M)^+$, 269 $(M+2)^+$.

1,2-Bis(2-methyl-5-(2-methyl-4-pyridyl)-3-thienyl)perfluorocyclopentene (**1a**)

To a dry THF solution (250 mL) containing **2** (9.50 g, 35.4 mmol) was added 1.6 M *n*-butyl lithium hexane solution (23 mL, 37 mmol) at −78°C under nitrogen atmosphere, and the reaction mixture was stirred for 15 min at that temperature. Octafluorocyclopentene (2.4 mL, 18 mmol) was added to the reaction mixture at −78°C, and the reaction mixture was stirred for 2 h at that temperature. The reaction mixture was extracted with diethyl ether. The organic layer was dried with magnesium sulfate, filtered, and concentrated. The residue was purified by alumina column chromatography using hexane as the eluent to give **1a** (3.12 g, 32 %) as white powders. δ_H (400 Hz; $CDCl_3$; Me_4Si) 1.99 (s, 6H), 2.59 (s, 6H), 7.22 (d, J = 5.2 Hz, 2H), 7.27 (s, 2H), 7.45 (s, 2H), 8.49 (d, J = 5.2 Hz, 2H); m/z (EI) 550 $(M)^+$.

X-ray crystal structure analysis

X-ray crystal structure analysis of single-component crystal of **1a** was performed using a Bruker APEX CCD-based diffractometer (55 kV, 30 mA) with Mo Kα radiation (0.71073 Å). The crystals were cooled with a cryostat. The data was collected as a series of ω-scan frames, each with a width of 0.3°/frame. The crystal-to-detector distance was 6.049 cm. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by a global refinement. The structures were solved by direct methods using SHELXS-97, and refined by full least-squares on F^2 using SHELXL-97. The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

X-ray crystal structure analysis of cocrystals was performed using a Bruker APEX2 Ultra CCD-based diffractometer (50 kV, 50 mA) with Cu Kα radiation (1.54178 Å). The crystals were cooled with a cryostat. The data were collected as a series of ϕ- and ω-scan frames, each with a width of 0.5°/frame. The crystal-to-detector distance was 4.053 cm. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by a global refinement. The structures were solved by direct methods using SHELXS-97, and refined by full least-squares on F^2 using SHELXL-97. The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

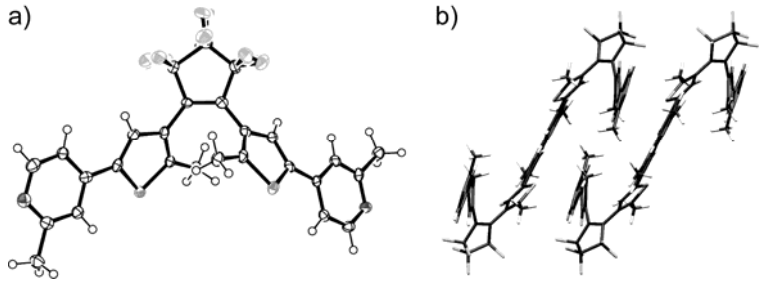


Fig. S1 (a) ORTEP drawing of **1a**, (b) molecular packing of **1a**

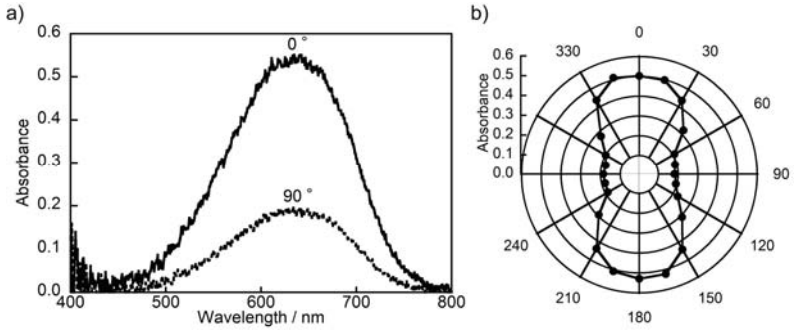


Fig. S2 (a) Absorption spectra of blue-coloured single crystal of **1a** measured on (001) face (θ = 0° and 90°), (b) Polar plots of absorbance of 641 nm.

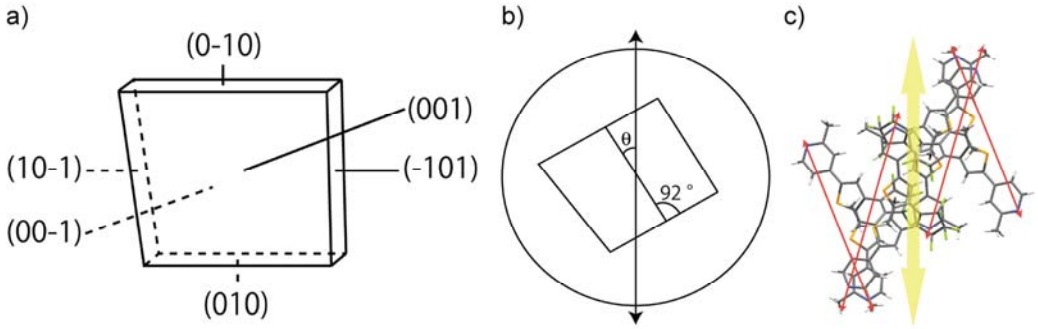


Fig. S3 (a) Miller indices of single crystal **1a**, (b) Polarized angle (arrow: direction of incident light), (c) Molecular packing of **1a** viewed from (001) surface (θ = 0°, red arrow: long axis of **1a**, yellow arrow: direction of incident light).

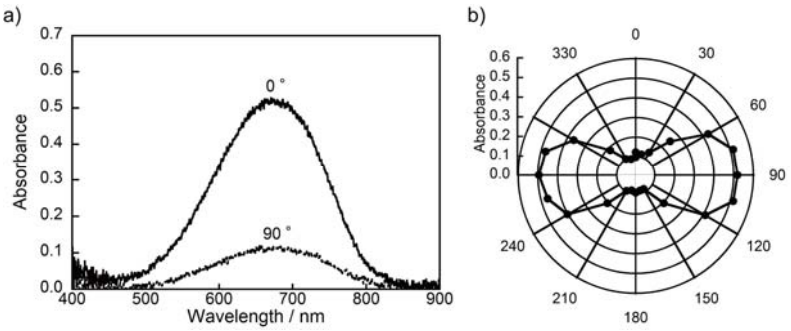


Fig. S4 (a) Absorption spectrum chiral crystal **1a**·(*R*)-**BINOL** ($\theta = 0°$ and 90°), (b) Polar plots of absorbance at 673 nm.

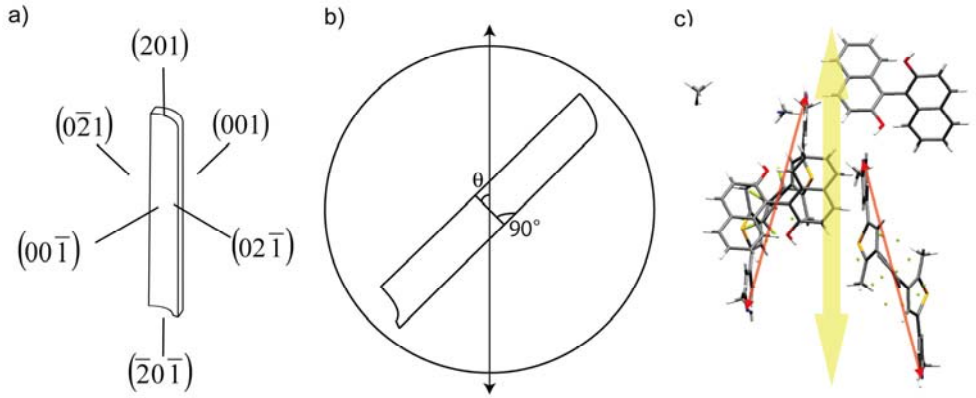


Fig. S5 (a) Miller indices of single crystal **1a**·(*R*)-**BINOL**, (b) Polarized angle (arrow: direction of incident light), (c) Molecular packing of **1a**·(*R*)-**BINOL** at (00−1) surface ($\theta =$ 90°, red arrow: long axis of **1a**, yellow arrow: direction of incident light).

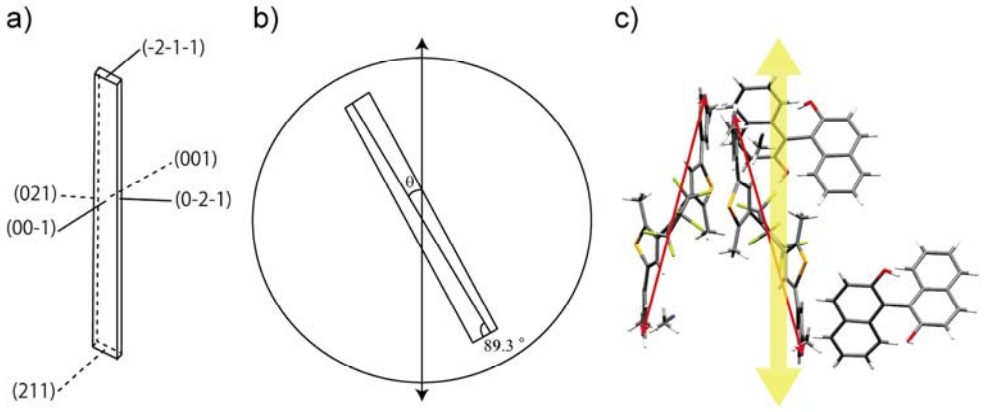


Fig. S6 (a) Miller indices of single crystal **1a**·(*S*)-**BINOL**, (b) Polarized angle (arrow: direction of incident light), (c) Molecular packing of **1a**·(*S*)-**BINOL** at (00−1) surface ($\theta = 0°$, red arrow: long axis of **1a**, yellow arrow: direction of incident light).

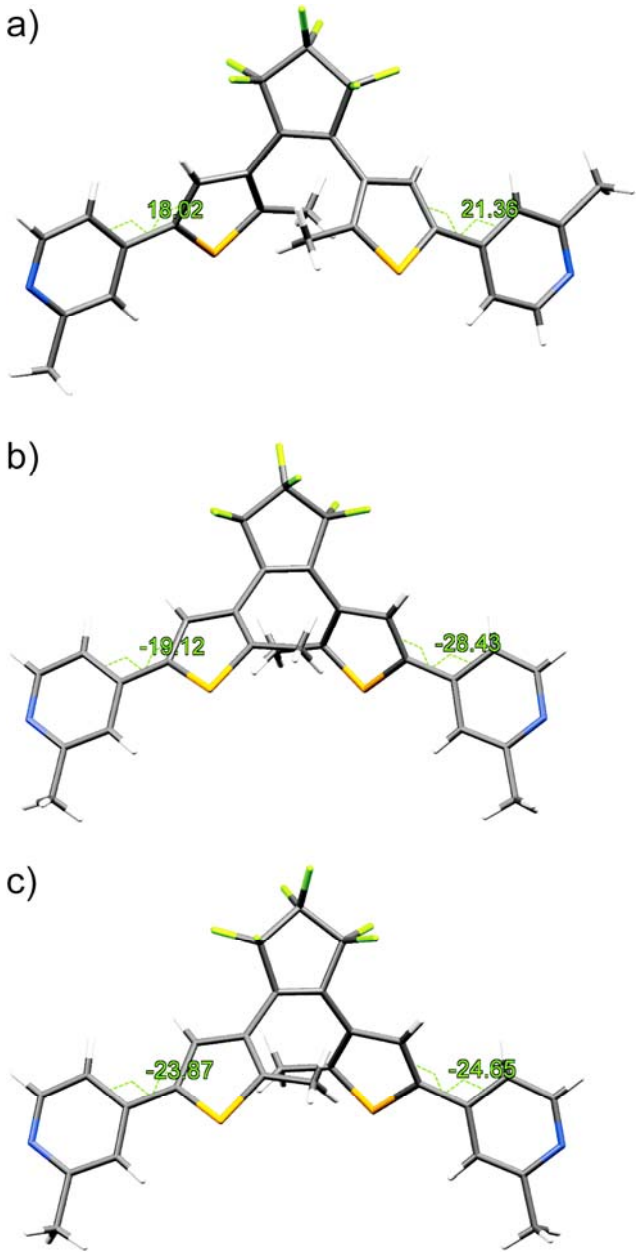


Fig. S7 Dihedral angels of thienyl and pyridyl rings of **1a** in single crystal of **1a** (a) and in chiral cocrystal of **1a**·(*R*)-**BINOL** (b, c).