Electronic Supplementary Information

Photochemical control of dielectric properties based on intermolecular proton transfer in a hydrogen-bonded diarylethene crystal

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Contents

1. General

^{1}H NMR spectrum was measured with a 400 MHz NMR spectrometer (Bruker Biospin, Avance 400). Tetramethylsilane (TMS) was used as an internal standard. Mass spectrum was measured with a gaschromatography-mass spectrometer (Shimadzu, GCMS-QP2010Plus).

X-ray crystallographic analysis was performed on a CCD-based X-ray diffractometer (Bruker AXS, SMART APEX) with MoK$_\alpha$ radiation (λ = 0.71073 Å). The crystal was cooled by a low temperature controller (Japan Thermal Engineering, 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 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-90[S1] and refined by full-matrix least-squares on F^2 using SHELXL-97.[S2] The positions of the N−H hydrogen atoms were determined by difference Fourier analysis. The positions of other hydrogen atoms were calculated geometrically and refined by the riding model.

Absorption spectra in the single-crystalline phase were measured by using a polarizing microscope (Leica, DMLP) connected with a multi-channel photodetector (Hamamatsu, PMA-11). Fig. S1 shows an illustration of the equipments. The 100 W halogen lamp in the microscope was used as a light source. Polarizer and analyzer were set in parallel to each other. Wavelength dependence of the light intensity which transmits through the crystal before photoirradiation (I_0) was measured by the photodetector. After irradiation with UV light (λ = 400 nm), wavelength dependence of the light intensity which transmits through the UV-irradiated crystal (I) was measured. Based on the Lambert-Beer's law ($A = \log(I_0/I)$), absorption spectra of the photogenerated closed-ring isomer in the crystal were calculated. Polar plots of the absorbance were obtained by measuring the spectra on rotating the stage of the microscope.

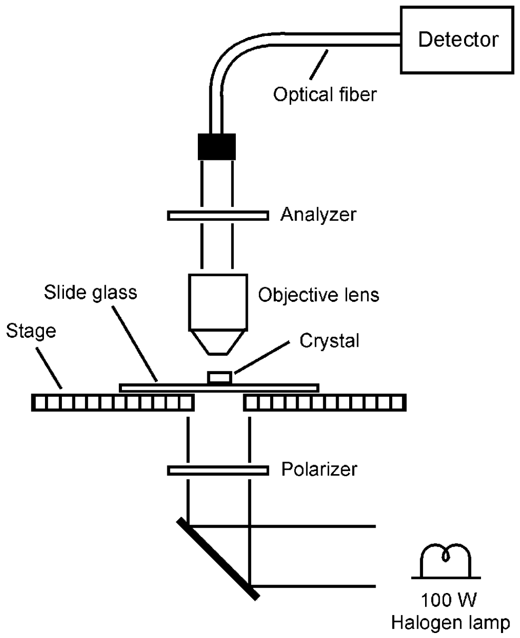
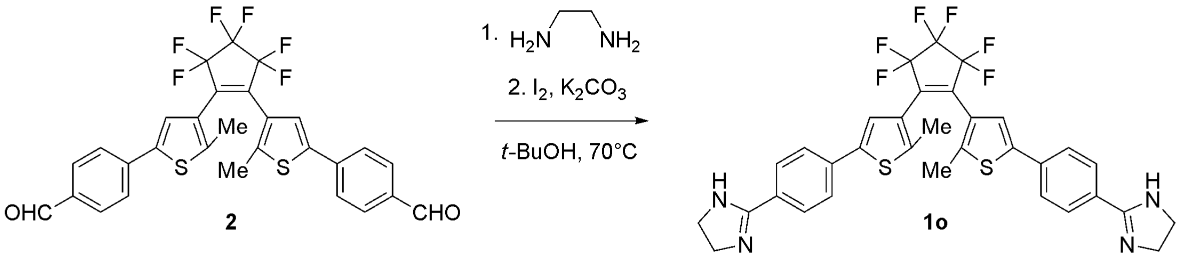


Fig. S1 Illustration of equipments for absorption spectral measurement of single crystal.

Dielectric constants of single-crystalline samples were measured by using an impedance analyzer with a dielectric interface (Solartron, 126096W). The measurements were made on single crystals with gold paste painted on to form the electrodes in a two-probe style. The crystals were set under a helium-gas atmosphere in a cryostat with optical windows (Oxford Instruments, Optistat CF). The temperature was monitored by a RhFe sensor and controlled by a temperature controller (Oxford Instruments, ITC-503S). Photoirradiation was carried out by using an UV-LED irradiation system (EXFO, OmniCure 400) and a xenon lamp irradiation system (Asahi Spectra, MAX-302).

Optimized molecular structures were calculated by using the RHF functional and the 6-31G* basis set (Gaussian 03 program).[S3]

2. Synthesis of 1o[S4]



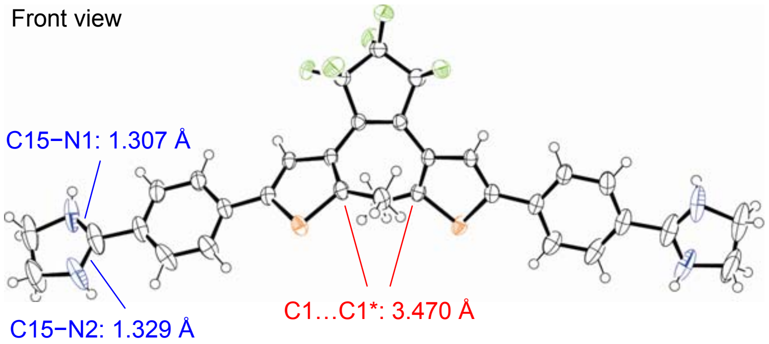
To a solution of 1,2-bis(2-methyl-5-(4-formylphenyl)-thiophen-3-yl)perfluorocyclopentene[S5] (**2**) (600 mg, 1.04 mmol) in *t*-BuOH (20 mL) and THF (30 mL) was added ethylenediamine (138 mg, 2.29 mmol) under a nitrogen atmosphere. The obtained mixture was stirred at room temperature for 30 min, and then K_2CO_3 (862 mg, 6.24 mmol) and I_2 (660 mg, 2.60 mmol) were added to the mixture and stirred at 70°C. After 4.5 h, the mixture was quenched by adding saturated aqueous Na_2SO_3 until the colour of I_2 disappeared, and then extracted with $CHCl_3$. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. After filtration, the mixture was evaporated in vacuo. Purification by recrystallization from $CHCl_3$ afforded pale yellow powders of **1o** was obtained (410 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.01 (s, 6H, CH_3), 2.40 (br, 2H, NH), 3.82 (s, 8H, CH_2CH_2), 7.34 (s, 2H, thienyl), 7.56 (d, *J* = 8.4 Hz, 4H, phenyl), 7.81 (d, *J* = 8.4 Hz, 4H, phenyl). MS (EI): *m*/*z* 655 (M^+), 612 ($M{-}CH_3$).

3. X-ray crystallographic analysis of 1o

Table S1 Crystal data for **1o**

	1o	**1o-UV**	**1o-Vis**
formula	$C_{33}H_{26}F_6N_4S_2$	$C_{33}H_{26}F_6N_4S_2$	$C_{33}H_{26}F_6N_4S_2$
formula weight	656.70	656.70	656.70
T / K	93(2)	93(2)	93(2)
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnna*	*Pnna*	*Pnna*
a / Å	11.0597(8)	11.0788(12)	11.0607(10)
b / Å	29.913(2)	29.771(3)	29.907(3)
c / Å	9.2876(7)	9.3271(10)	9.2892(8)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V / Å^3	3072.6(4)	3076.3(6)	3072.8(5)
Z	4	4	4
ρ_{calc} / g cm^{-3}	1.420	1.418	1.420
goodness-of-fit on F^2	1.102	1.118	1.163
R_1 ($I > 2\sigma(I)$)	0.0576	0.0676	0.0661
wR_2 ($I > 2\sigma(I)$)	0.1496	0.1717	0.1573
R_1 (all data)	0.0602	0.0721	0.0699
wR_2 (all data)	0.1521	0.1751	0.1600
CCDC No.	805211	805212	805213

(a) Front view



(b) Side view

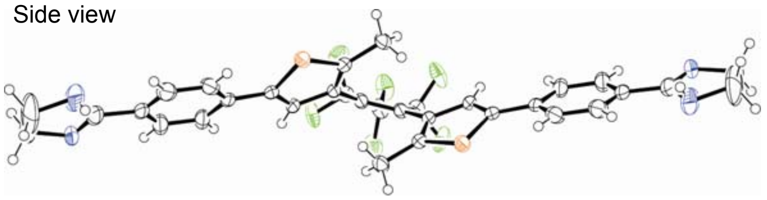


Fig. S2 ORTEP drawings of **1o**: (a) front view and (b) side view. The distance between the reacting carbon atoms C1 and C1* is 3.470 Å. The lengths of the two C–N bonds in the imidazoline ring are almost the same (C15–N1: 1.307 Å, C15–N2: 1.329 Å) as a result of the average of single (C–N) and double (C=N) bond lengths.

4. Dielectric properties of single crystal of 1o

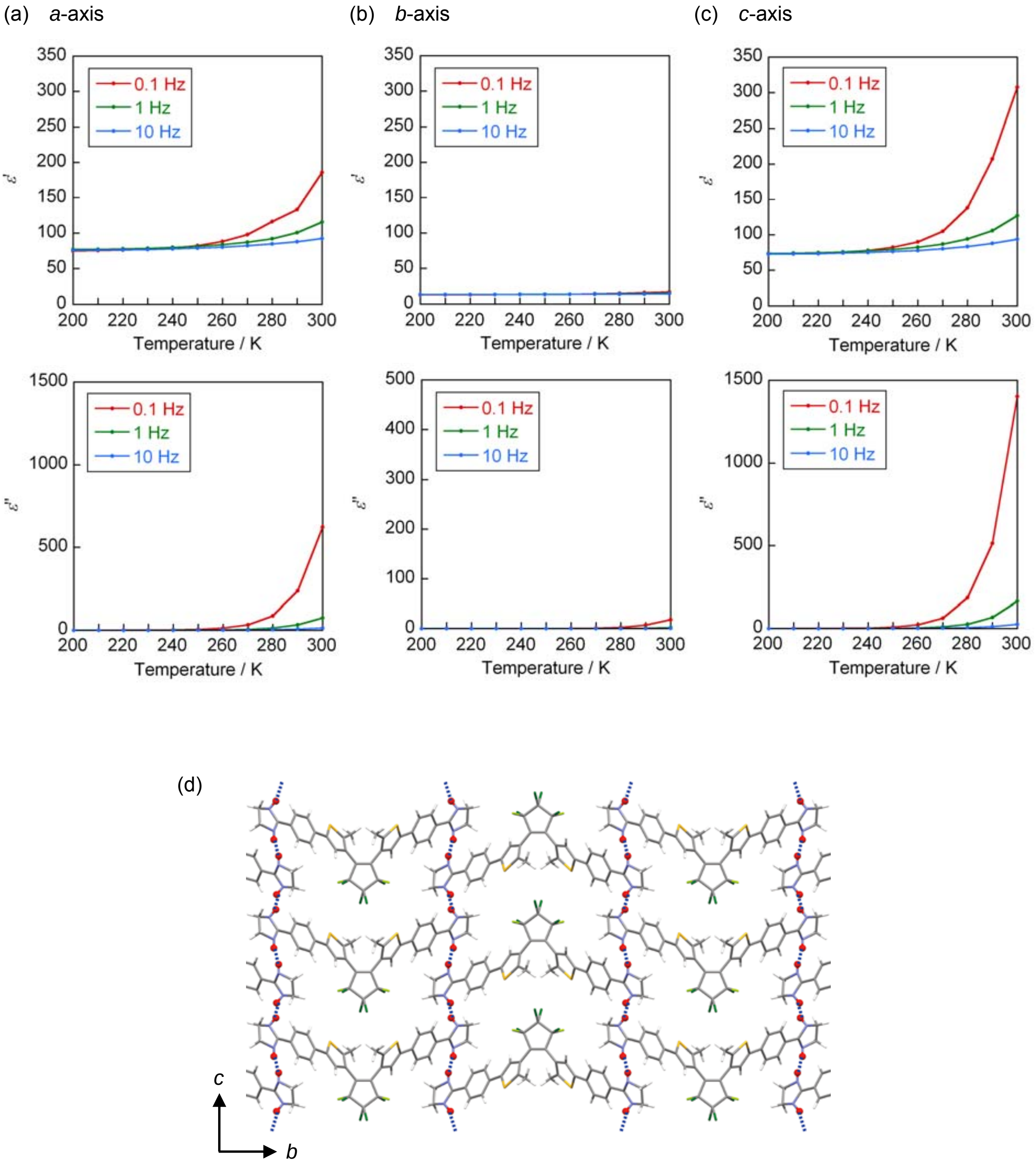


Fig. S3 Temperature-dependence of relative dielectric permittivity (ε': real part, ε'': imaginary part) of single crystal of **1o** measured along (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis at 200−300K. (d) Crystal structure of **1o** viewed along *a*-axis.

5. Photochromism of 1 in single-crystalline state

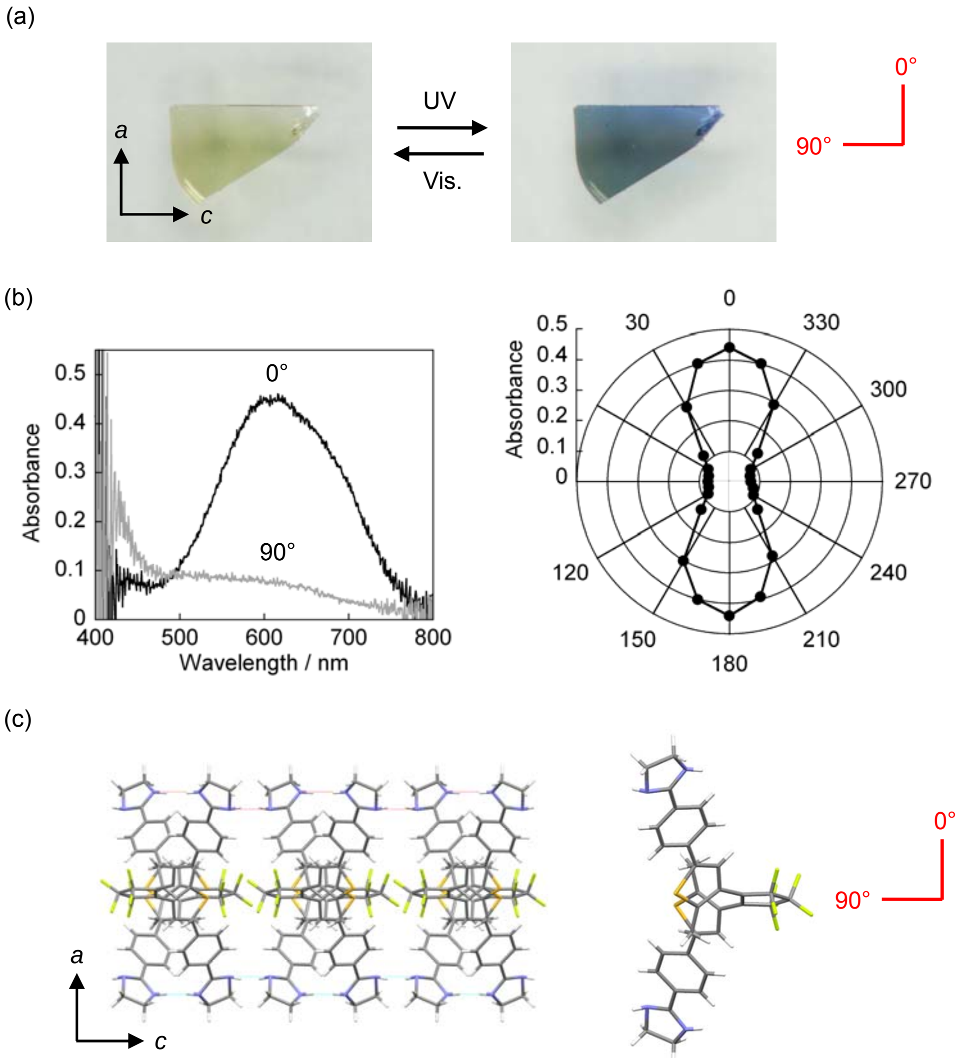


Fig. S4 (a) Photographs showing colour change of single crystal of **1o** upon photoirradiation. (b) Polarized absorption spectra of photogenerated closed-ring isomer **1c** in the single crystal measured on (0 1 0) face and polar plots of absorbance at 610 nm. (c) Crystal structure of **1o** viewed from (0 1 0) face. The absorption anisotropy shown in (b) indicates that the photochromic reaction of the diarylethene take places in the single-crystalline phase.[S6]

6. Molecular orbital calculation

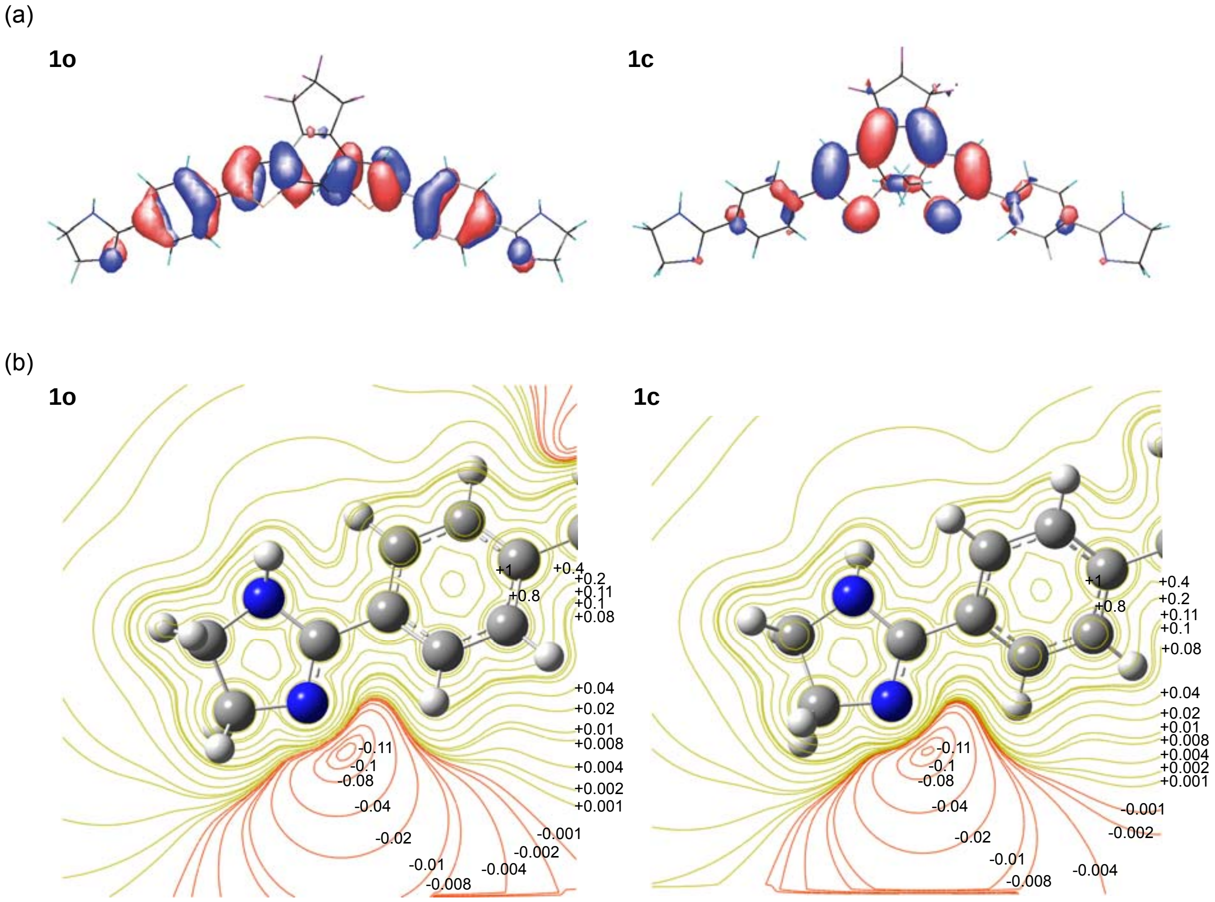
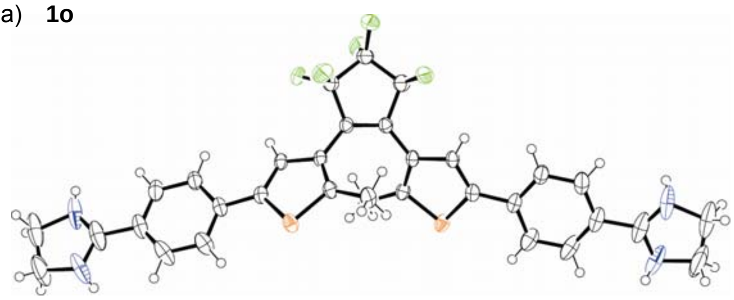


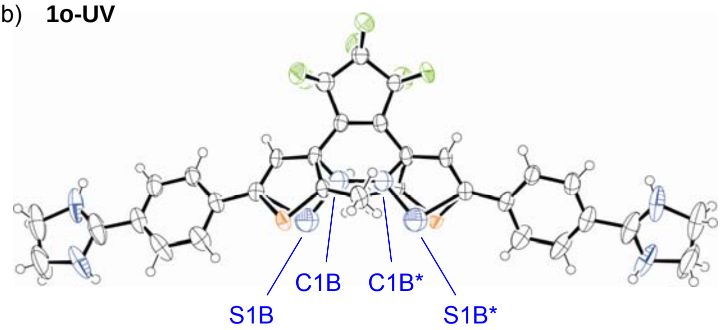
Fig. S5 (a) HOMOs and (b) contours of electrostatic potentials around imidazoline rings of open-ring isomer **1o** and closed-ring isomer **1c** calculated by RHF/6-31G*.

7. *In situ* X-ray crystallographic analysis

(a) **1o**



(b) **1o-UV**



(c) **1o-Vis**

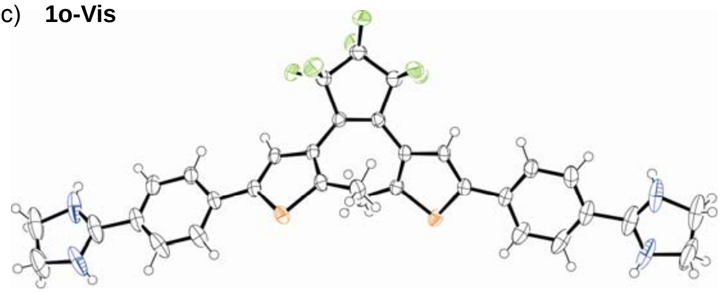


Fig. S6 ORTEP drawings for (a) **1o** (before photoirradiation), (b) **1o-UV** (after UV irradiation, $\lambda = 400$ nm), and (c) **1o-Vis** (after visible irradiation, $\lambda > 520$ nm). For **1o-UV**, carbon and sulfur atoms of the photogenerated closed-ring isomer **1c** (C1B, C1B*, S1B, S1B*) were observed. The occupancy ratio for these atoms is 9%.

8. References

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