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Supporting Information

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Conformational Control of Photochromic Reactivity in a Diarylethene Single Crystal

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Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer and a Jeol A-400 spectrometer, respectively. Tetramethylsilane was used as an internal standard. High performance liquid chromatography (HPLC) was carried out using a Hitachi L-7100/L-7400/D-2500 connected with a silicagel column (Wako Wakosil 5SIL). Mass spectra were taken with a Jeol JMS-AX500 mass spectrometer. Absorption spectra in hexane were measured with a Hitachi U-3410 absorption spectrophotometer. Solvents used were spectroscopic grade and purified by distillation before use. Absorption spectra in a single-crystalline phase were measured using a Nikon E600POL polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel each other. Photoirradiation was carried out using a 100 W mercury short arc lamp. The wavelength of the light used (366 nm) was selected by passing the light through a band pass filter. X-ray crystallographic analysis of single crystals was carried out using a Bruker SMART CCD X-ray diffractometer or a Rigaku RAXIS X-ray diffractometer with MoK$_\alpha$ radiation (λ = 0.71073 Å) and a graphite monochromator. The cell constants were calculated by the global refinement. The structure was solved by direct methods using SHELXS-86 and refined by full least-squares on F^2 using SHELXL-97.

1,2-Bis(2-methoxy-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) was synthesized as follows. To dry THF (150 mL) containing 2,4-dibromo-5-methoxy-3-methylthiophene (7.3 g, 0.026 mol) was added a 15% *n*BuLi hexane solution (17 mL, 0.028 mol) at –78 °C. Tributyl borate (10 mL, 0.037 mol) was slowly added to the reaction mixture at –78 °C, and the mixture was stirred for 3 h. Iodobenzene (5.3 g, 0.026 mol), 20 wt% Na_2CO_3 (aq) (60 mL), and $Pd(PPh_3)_4$ (1.0 g, 0.87 mmol) were added to the mixture, and the mixture was refluxed for 5 h at 70 °C to form 5.4 g of 3-bromo-2-methoxy-4-methyl-5-phenylthiophene (**3**) (Yield: 73%). To the solution of **3** (5.0 g, 0.018 mmol) in dry THF (15 mL), a 15% *n*BuLi hexane solution (11 mL; 0.018 mol) was added at –78 °C. Then, to the solution was added 1.2 mL (0.0089 mol) of octafluorocyclopentene to yield 2.0 g of **1a** (Yield: 38%). **1a**: m.p. 117.5-118.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 2.10$ (s, 6H, Me), 3.78 (s, 6H, MeO), 7.2-7.5 ppm (m, 10H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$ (Me), 61.3 (MeO), 110.2 (3-thienyl), 111.5 (CF_2), 116.0 (CF_2), 124.4 (5-thienyl), 127.1 (Ph), 128.6 (Ph), 129.1 (Ph), 130.5 (4-thienyl), 134.1 (Ph), 139.5 (C=C), 163.4 ppm (2-thienyl); FAB HRMS (*m/z*) $[M]^+$ calcd for $C_{29}H_{22}F_6O_2S_2$: 580.0965; found: 580.0966; UV/Vis (*n*-hexane): λ_{max} (ε) = 288 nm (28600 $M^{-1}cm^{-1}$).

The closed-ring isomer **1b** was isolated by passing a photostationary solution containing **1a** and **1b** through a HPLC (silica-gel column, hexane/ethyl acetate (98:2) as the eluent). **1b**: ^{1}H NMR (200 MHz, $CDCl_3$, TMS): $\delta = 1.98$ (s, 6H, Me), 3.86 (s, 6H, MeO), 7.2-7.5 ppm (m, 10H, Ph); MS: *m/z*: 580 $[M^+]$; UV/Vis (*n*-hexane): λ_{max} (ε) = 617 nm (12000 $M^{-1}cm^{-1}$).