

*Supplementary Information for*

**Invisible Photochromism of Diarylethene Derivatives**

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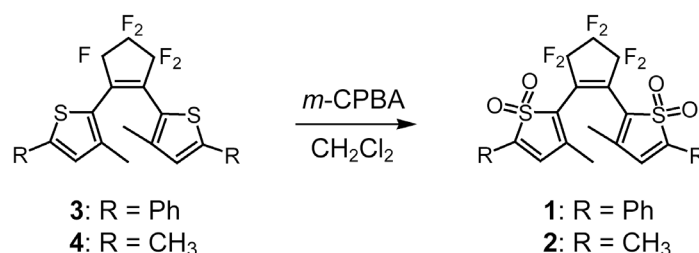
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**1. General.** Solvents used in photochemical measurements were spectroscopic grade and purified by distillation before use.  $^1\text{H}$  NMR spectra were recorded on a NMR spectrometer (Bruker-AVANCE-400, 400 MHz). Samples were dissolved in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard. Mass spectra were measured with a mass spectrometer (JEOL JMS mate II). Absorption and fluorescence spectra were measured with a Hitachi U-3500 absorption spectrophotometer and a Hitachi F-2500 fluorescence spectrophotometer, respectively. Photoirradiation was carried out using an USHIO 1 kW high-pressure mercury lamp or an USHIO 500 W xenon lamp as the light sources. Monochromic light was obtained by passing the light through a monochromator (Ritsu MV-10N) or a band-pass filter ( $\Delta\lambda_{1/2} = 15$  nm).

**2. Synthesis.** Compounds **1** and **2** were synthesized as illustrated in Scheme S1. Compound **3** and **4** were synthesized according to the literatures.<sup>S1, S2</sup> The molecules were purified by GPC and HPLC carefully. The molecular structure was confirmed by  $^1\text{H}$  NMR, elemental analysis and mass spectroscopy and purity was evaluated by HPLC.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a NMR spectrometer (Bruker AVANCE-400, 400 MHz). Samples were dissolved in  $\text{CDCl}_3$  and tetramethylsilane was used as an internal standard. Mass spectra were measured with a mass spectrometer (Shimadzu GCMS-QP5050A and JEOL JC-mate II).

Scheme S1



### 1,2-Bis(3-methyl-5-phenylthien-1,1-dioxa-2-yl)-perfluorocyclopentene (**1**)

The solution of 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**3**) (100 mg, 0.19 mmol) and 65 % *m*-chloroperoxy-benzoic acid (300 mg, 1.15 mmol) in dichloromethane (5 ml) was stirred at room temperature. After the mixture was stirred for 48 h,  $\text{NaHCO}_3$  solution was added to the reaction mixture and extracted by dichloromethane, dried over  $\text{MgSO}_4$ , filtered, and concentrated. The residue was purified by silica gel column chromatography ( $\text{AcOEt/Hexane} = 2/3$ ) and recrystallization (methanol) to give 93 mg of **1** in 84 % yield as orange crystal. mp = 200 - 202 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ); Open-ring isomer (**1a**):  $\delta$  2.26 (s, 6H), 6.78 (s, 2H), 7.42–7.44 (m, 6H), 7.68–7.70 (m, 4H); Closed-ring isomer (**1b**):  $\delta$  1.39 (s, 6H), 6.76 (s, 2H), 7.48–7.54 (m, 6H), 7.73–7.75 (m, 4H); MS ( $\text{FAB}^+$ ):  $m/z = 585$  [ $\text{M} + \text{H}$ ] $^+$ ; Anal. Calcd. for  $\text{C}_{27}\text{H}_{18}\text{F}_6\text{O}_4\text{S}_2$ : C, 55.48; H, 3.10; Found: C, 55.42; H, 3.07.

**1,2-Bis(3,5-dimethylthien-1,1-dioxa-2-yl)-perfluorocyclopentene (2)**

The solution of 1,2-bis-(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**4**) (100 mg, 0.25 mmol) and 65 % *m*-chloroperoxybenzoic acid (400 mg, 1.51 mmol) in dichloromethane (6 ml) was stirred at room temperature. After the mixture was stirred for 48 h, NaHCO<sub>3</sub> solution was added to the reaction mixture and extracted by dichloromethane, dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica gel column chromatography (AcOEt/Hexane = 3/2) and recrystallization (methanol) to give 91 mg of **2** in 79 % yield as pale yellow crystal. mp = 197 - 199 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) Open-ring isomer (**2a**): δ 2.13 (s, 6H), 2.14 (d, *J* = 1.6 Hz, 6H), 6.29 (q, *J* = 1.6 Hz, 2H); Closed-ring isomer (**2b**): δ 1.20 (s, 6H), 2.21 (d, *J* = 1.6 Hz, 6H), 6.26 (q, *J* = 1.6 Hz, 2H); MS (FAB<sup>+</sup>): *m/z* = 461 [M + H]<sup>+</sup>; Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C, 44.35; H, 3.06; Found: C, 44.35; H, 2.95.

**3. X-ray Crystallographic Analysis.** Good quality crystal of **1a**, **1b**, **2a** and **2b** were selected for the X-ray diffraction study. The data collections were performed on a Bruker Apex2 CCD-based diffractometer (55 kV, 35 mA) with Mo K $\alpha$  radiation. The crystal was cooled at 123 K using a cryostat (RIGAKU GN2). The data were collected by covering a fullsphere (**1a** and **1b**) and hemisphere (**2a** and **2b**) of the reciprocal space by combining four or three sets of runs. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by the global refinement. The structure solved by direct methods using SHELXS-97 and refined by full least-squares on  $F^2$  using SHELXL-97.

(Crystal data and structural refinement parameters)

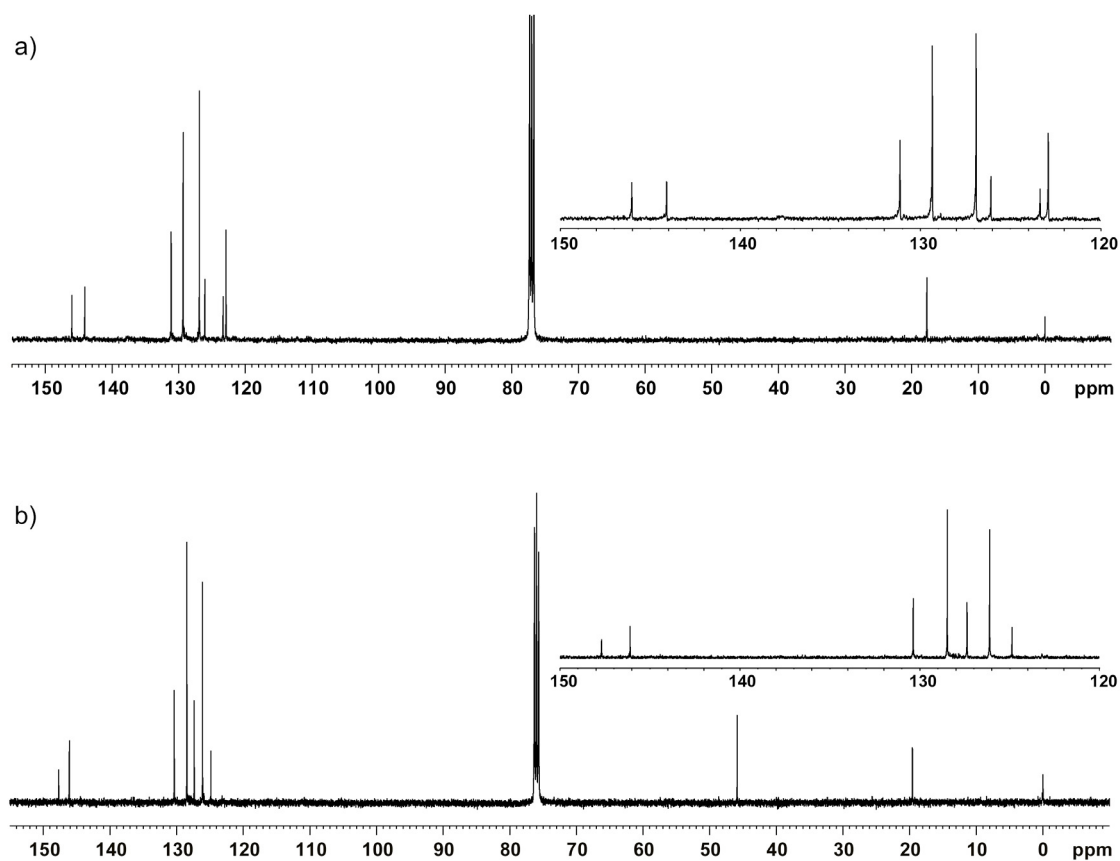
**1a:** C<sub>27</sub>H<sub>18</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>,  $M = 584.55$ , triclinic,  $a = 13.0067(11)$ ,  $b = 13.4973(11)$ ,  $c = 18.0024(15)$  Å,  $\alpha = 70.2730(10)^\circ$ ,  $\beta = 89.5390(10)^\circ$ ,  $\gamma = 61.6610(10)^\circ$ ,  $V = 2573.9(4)$  Å<sup>3</sup>,  $T = 123$  K, space group  $P-1$  (no. 2),  $Z = 4$ , 22619 reflections measured, 7520 unique ( $R_{\text{int}} = 0.0376$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.2319 (all data).

**1b:** C<sub>27</sub>H<sub>18</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>,  $M = 584.55$ , triclinic,  $a = 12.866(4)$ ,  $b = 13.907(5)$ ,  $c = 16.158(9)$  Å,  $\alpha = 95.720(6)^\circ$ ,  $\beta = 91.807(6)^\circ$ ,  $\gamma = 117.035(4)^\circ$ ,  $V = 2552.7(19)$  Å<sup>3</sup>,  $T = 123$  K, space group  $P-1$  (no. 2),  $Z = 4$ , 23480 reflections measured, 8067 unique ( $R_{\text{int}} = 0.0456$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1716 (all data).

**2a:** C<sub>17</sub>H<sub>14</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>,  $M = 460.41$ , monoclinic,  $a = 18.151(2)$ ,  $b = 8.0157(11)$ ,  $c = 12.9963(17)$  Å,  $\beta = 96.729(2)^\circ$ ,  $V = 1877.8(4)$  Å<sup>3</sup>,  $T = 123$  K, space group  $C2/c$  (no. 15),  $Z = 4$ , 5091 reflections measured, 2108 unique ( $R_{\text{int}} = 0.0282$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1305 (all data).

**2b:** C<sub>17</sub>H<sub>14</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub>,  $M = 460.41$ , monoclinic,  $a = 8.6990(14)$ ,  $b = 15.316(2)$ ,  $c = 14.199(2)$  Å,  $\beta = 97.291(2)^\circ$ ,  $V = 1876.5(5)$  Å<sup>3</sup>,  $T = 123$  K, space group  $P21/c$  (no. 14),  $Z = 4$ , 10170 reflections measured, 4011 unique ( $R_{\text{int}} = 0.0363$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.2072 (all data).

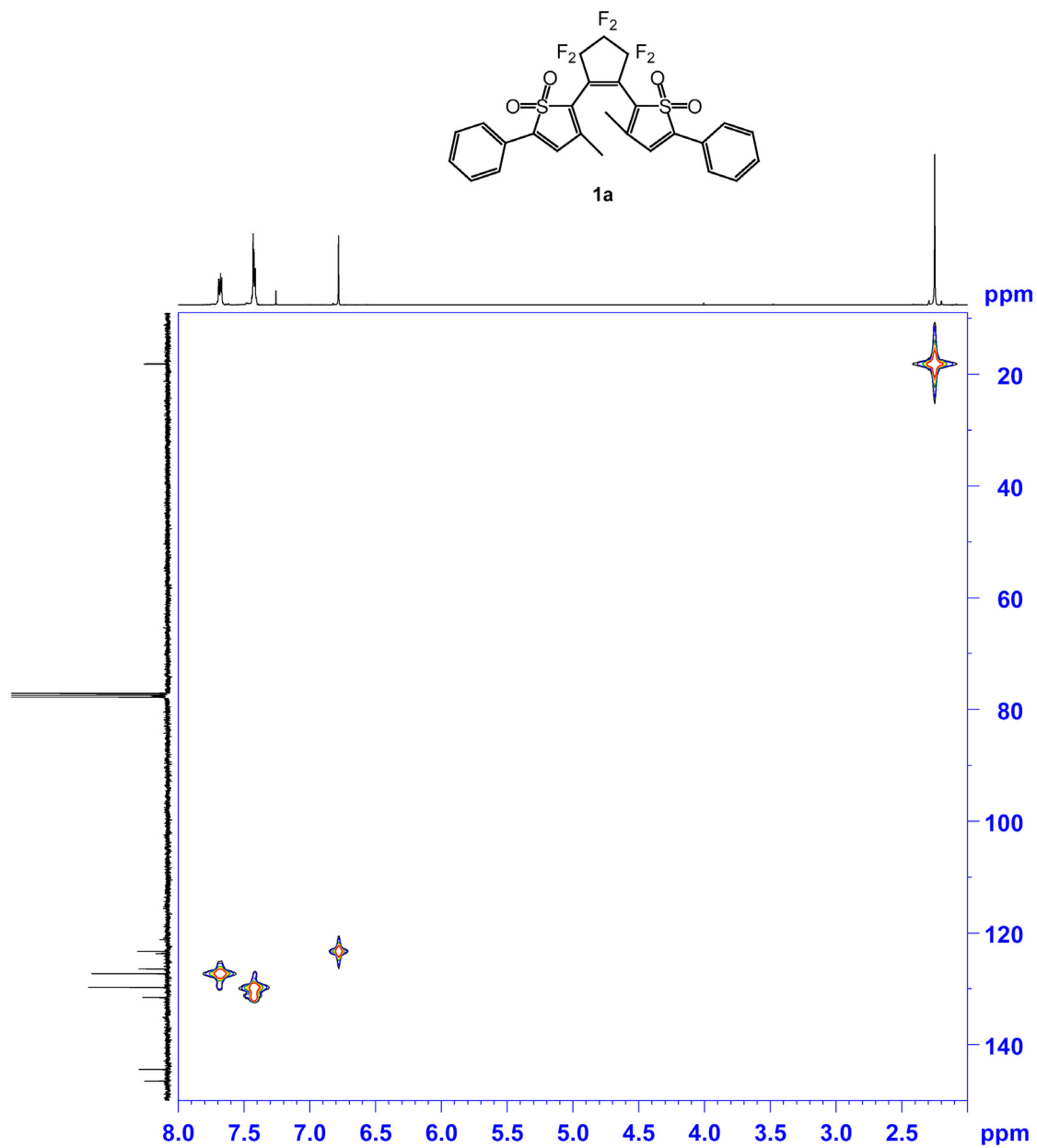
**4. NMR Measurements.** In order to confirm the photocyclization and photocycloreversion reactions, the photoinduced reaction was monitored by  $^{13}\text{C}$  NMR spectra, as shown in Figure S1. Before photoirradiation, eight carbon signals were observed in the region between 120 ppm and 150 ppm. Upon irradiation with visible light ( $\lambda > 430$  nm), the number of signals was reduced to seven and a new signal appeared at 45.89 ppm. This new signal is attributed to the reactive carbon atom by using Heteronuclear Multiple Bond Correlation (HMBC) and Heteronuclear Multiple Quantum Correlation (HMQC) measurements (see below). The signal disappeared upon irradiation with UV light (313 nm) and the original signals recovered. It is inferred from the  $^{13}\text{C}$  NMR measurement that the molecular structure before photoirradiation is the open-ring isomer and it converts to the closed-ring isomer upon visible light irradiation.



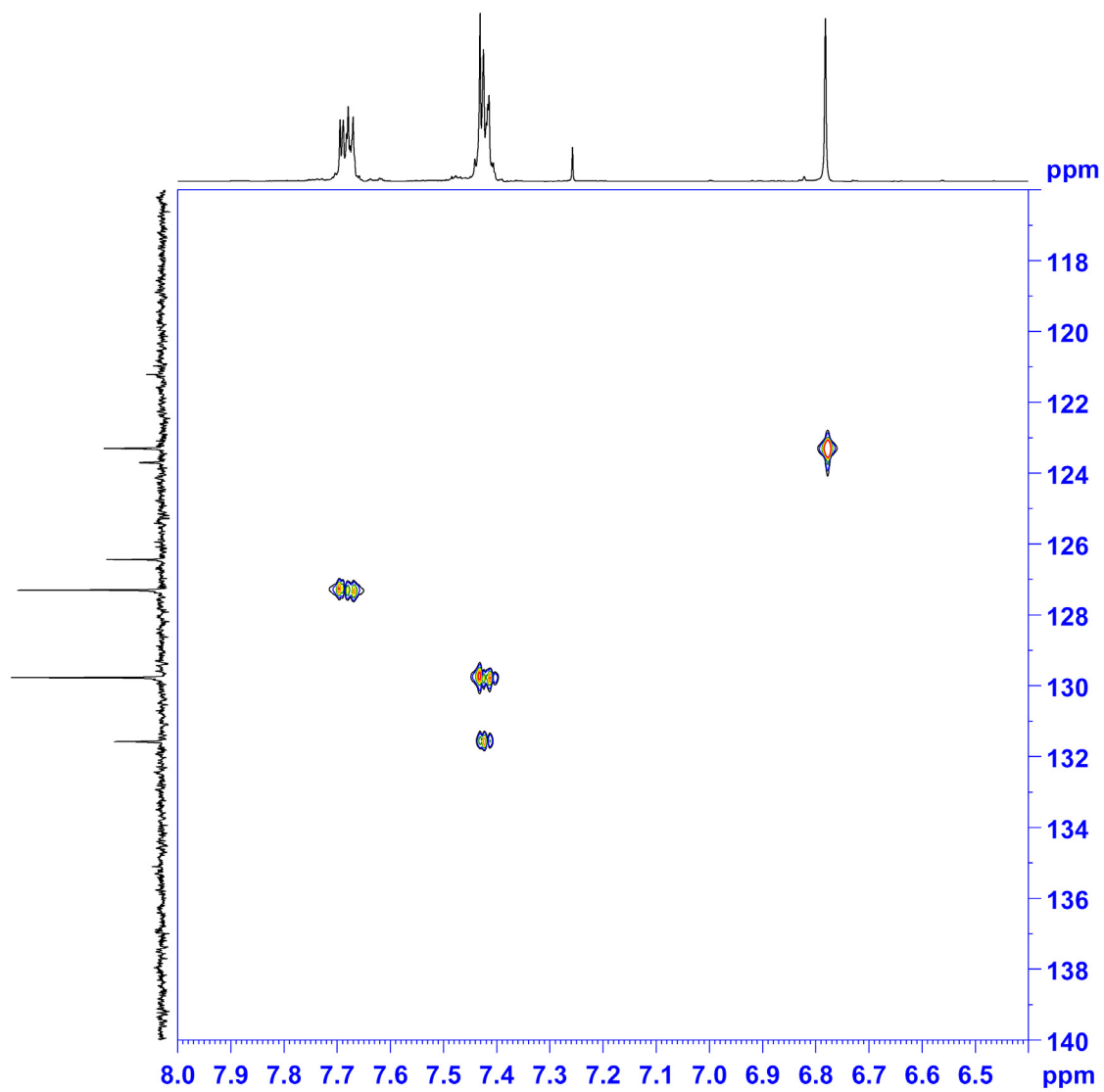
**Figure S1.**  $^{13}\text{C}$  NMR spectral changes of **1a** upon irradiation with visible light ( $\lambda > 430$  nm). (a) before and (b) after photoirradiation. Inset: Zooms of the region between 120 ppm and 150 ppm.

Compound **1a**

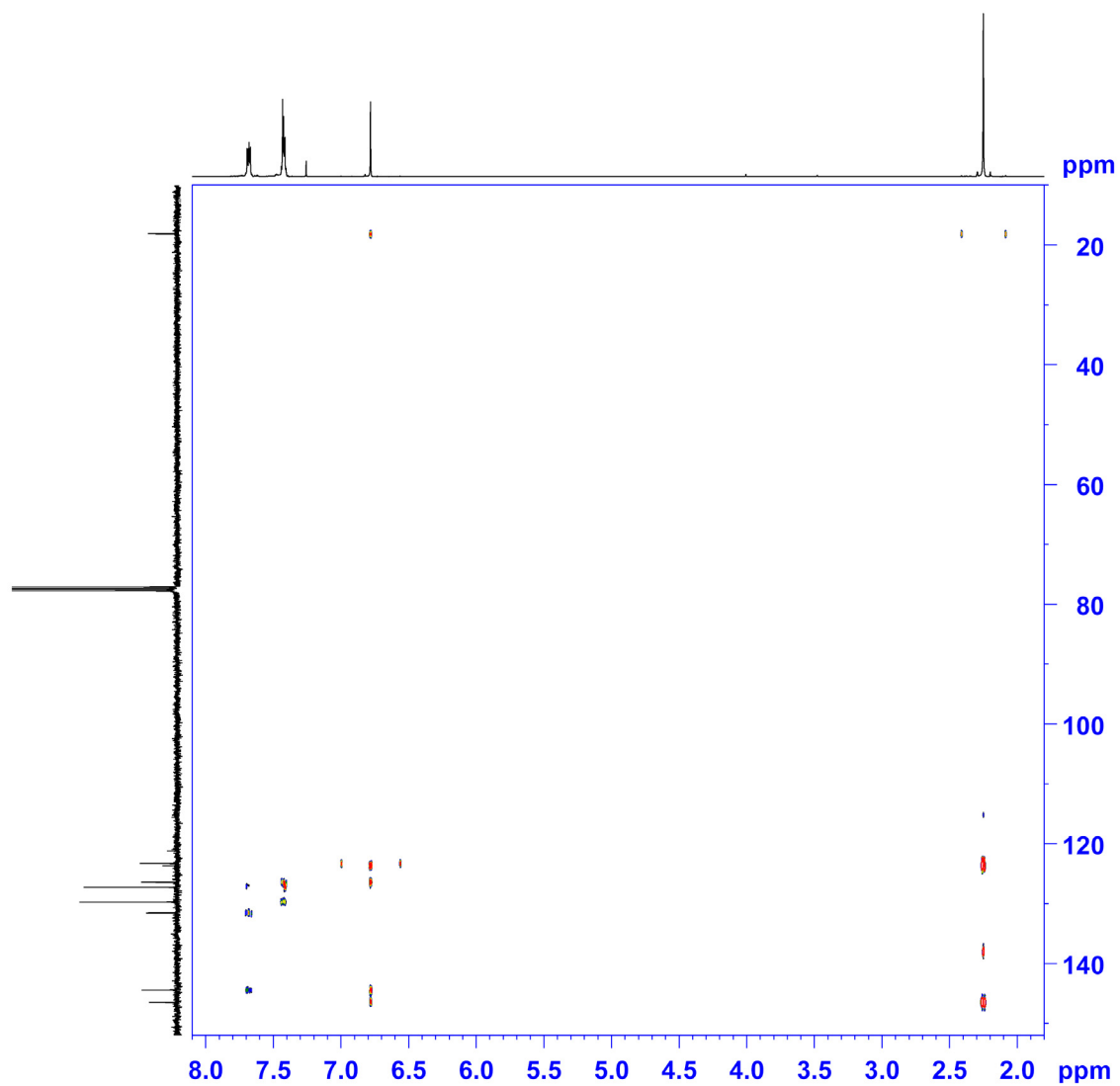
(*Heteronuclear Multiple Bond Correlation (HMBC) measurement*)



(Zoom)

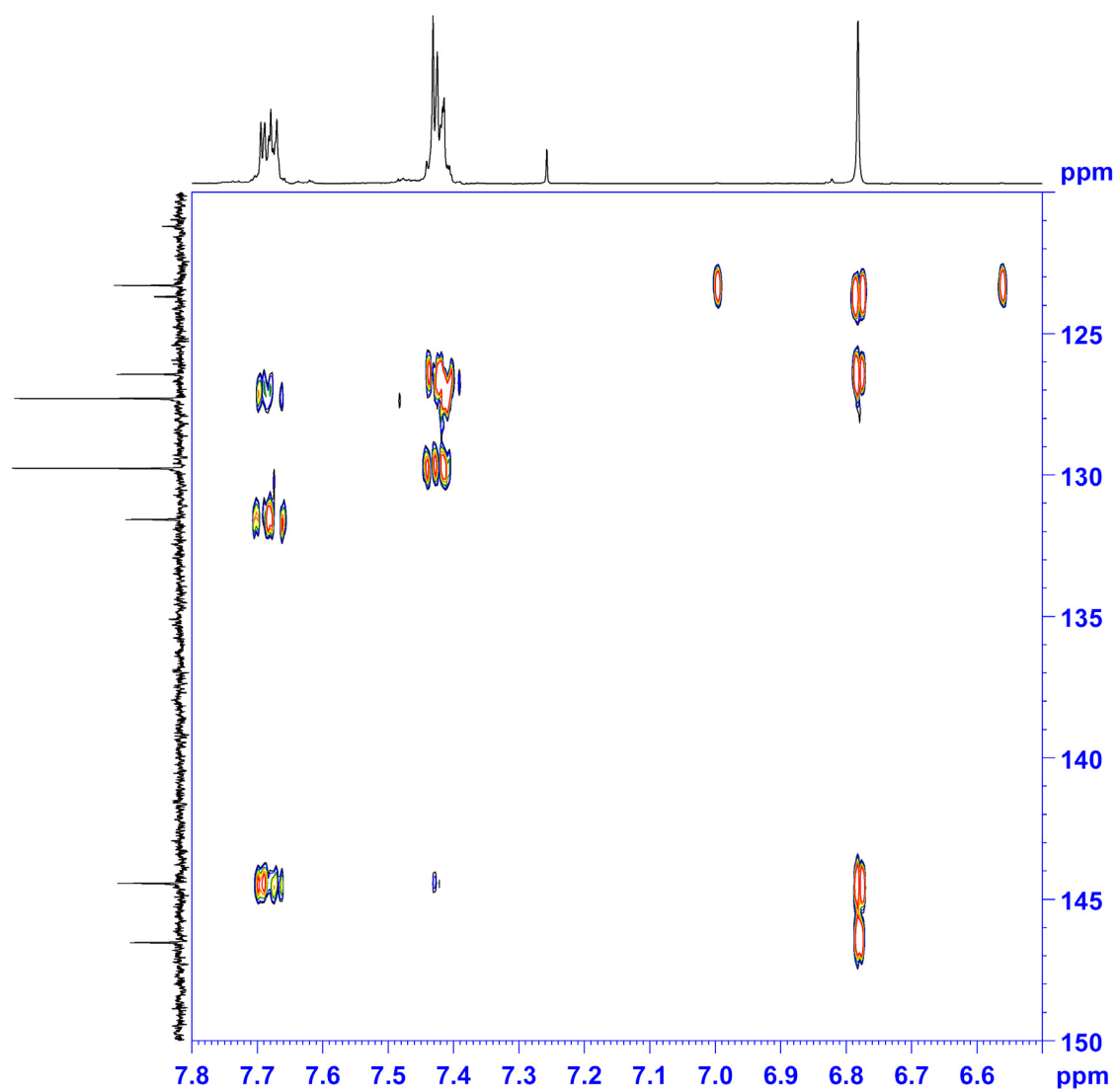


*(Heteronuclear Multiple Quantum Correlation (HMQC) measurement)*



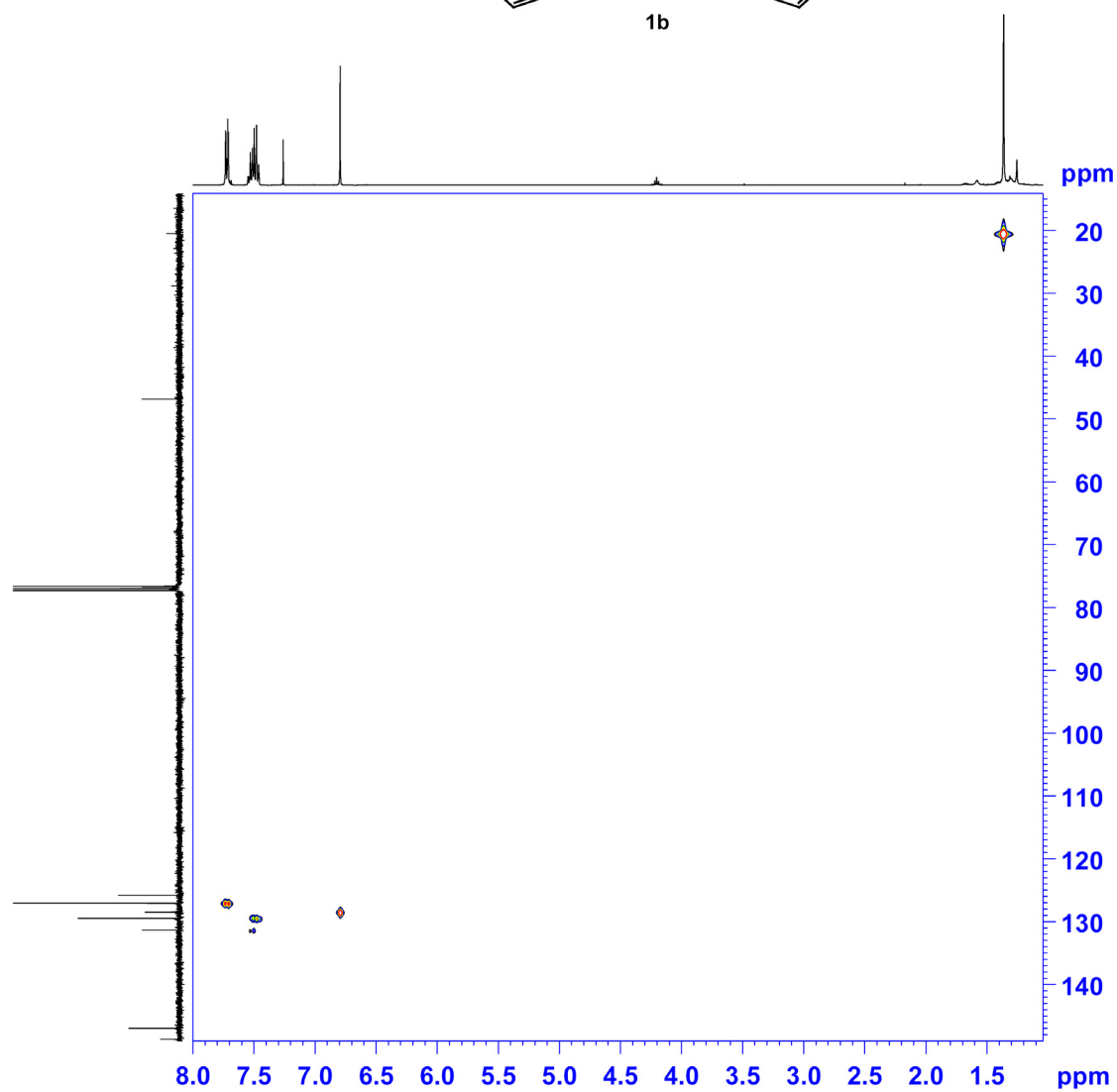
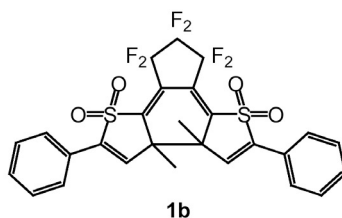


(Zoom)

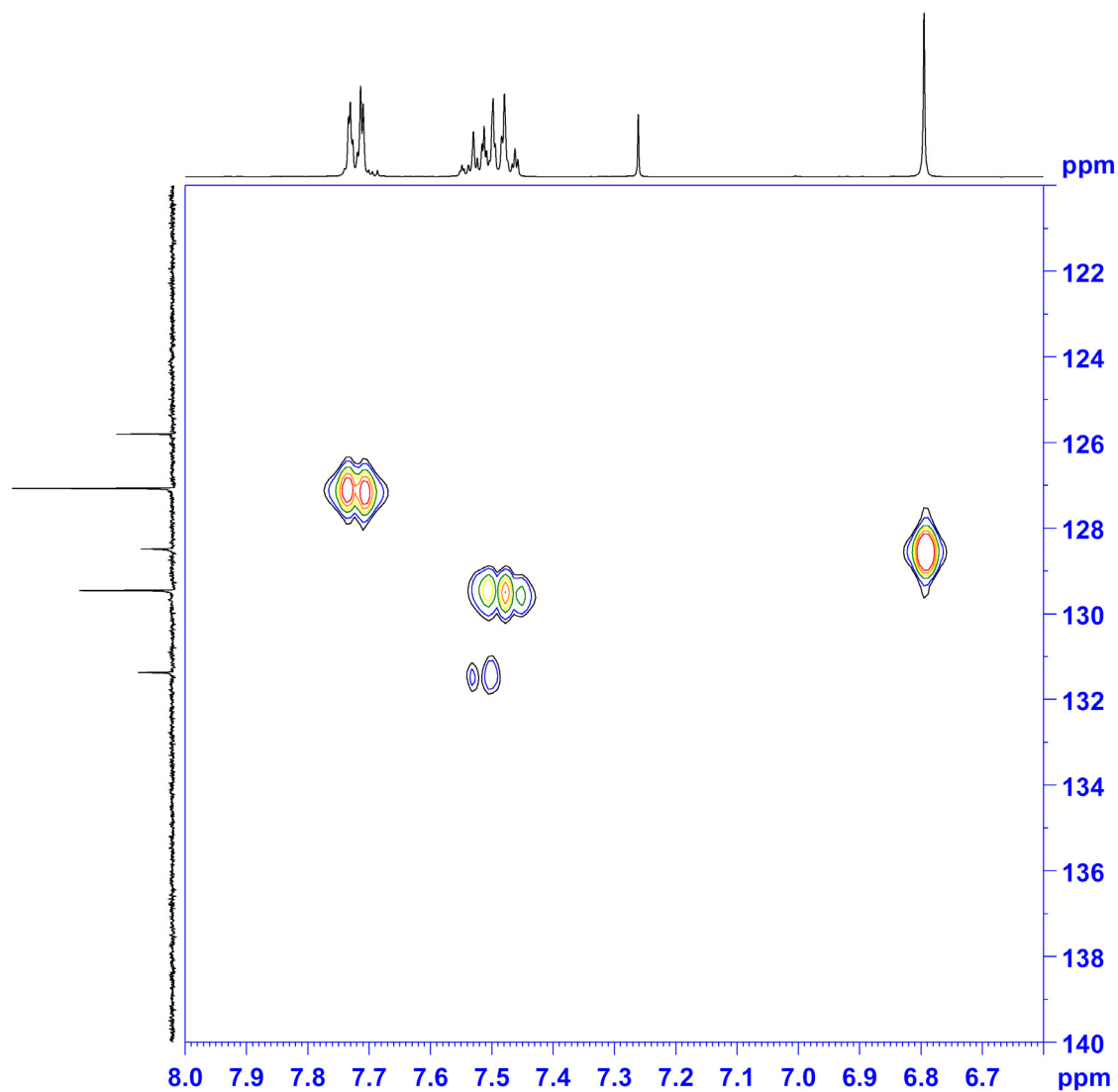


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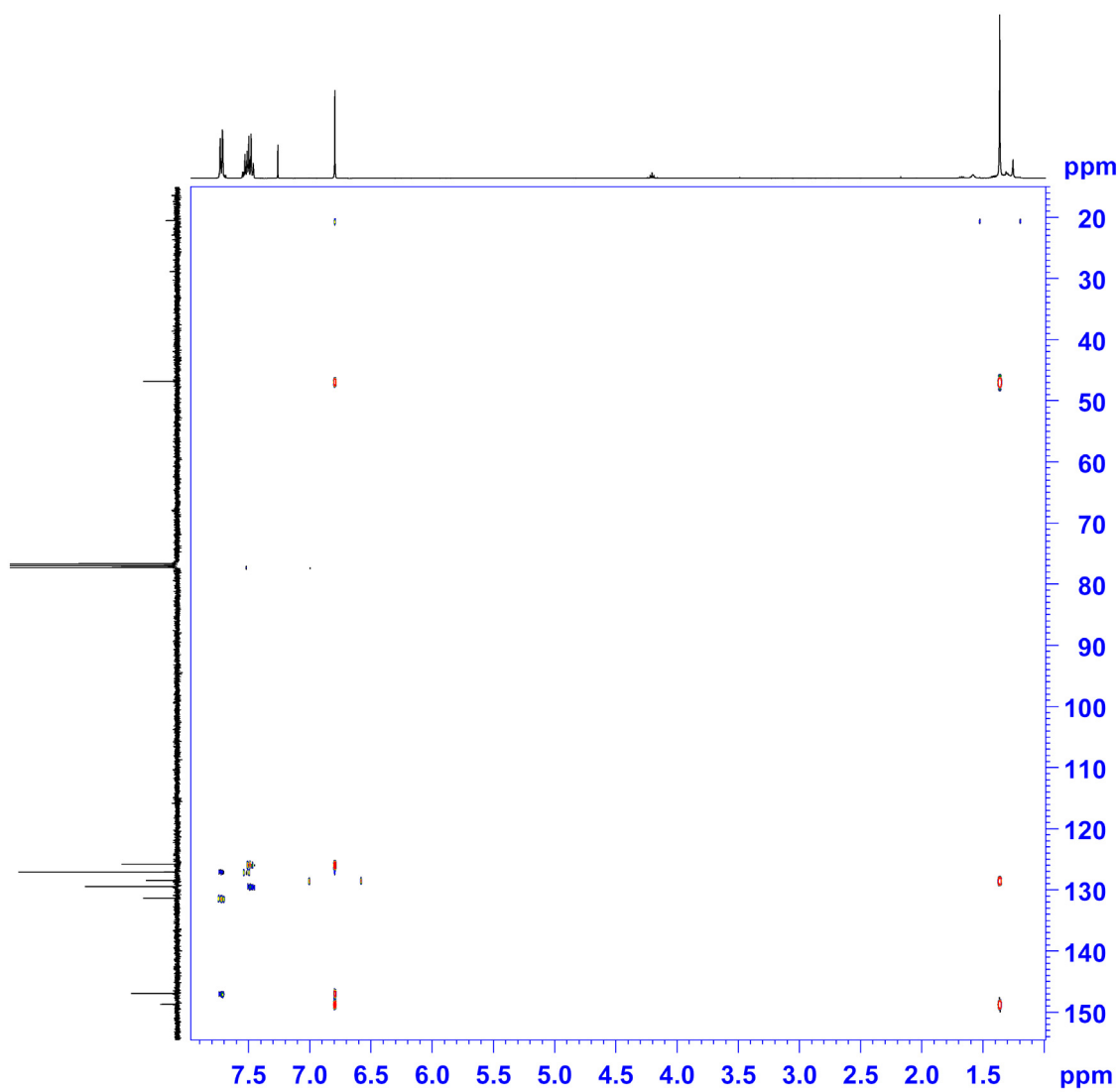
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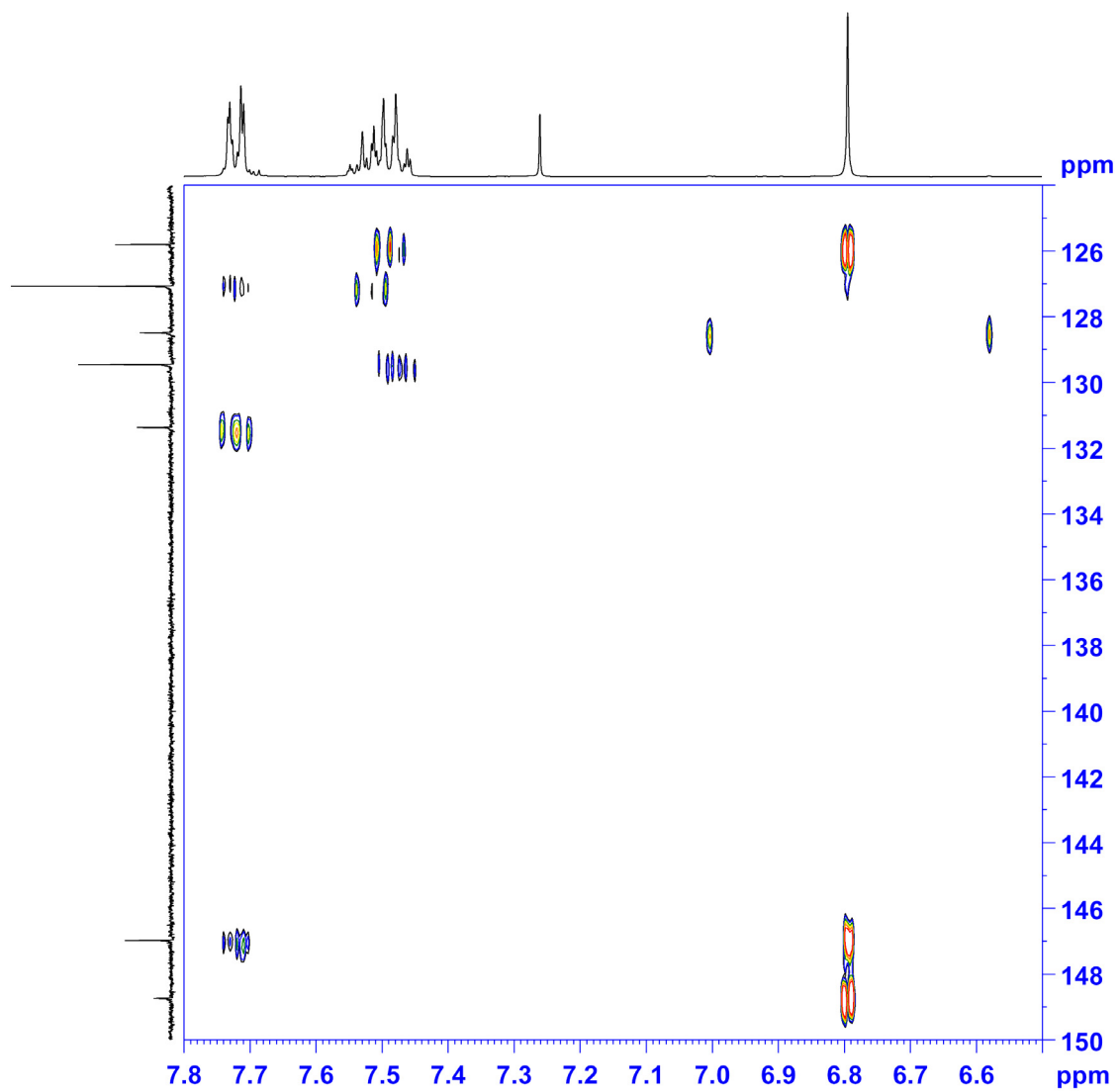
(Zoom)



*(Heteronuclear Multiple Quantum Correlation (HMQC) measurement)*

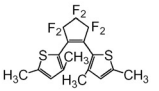
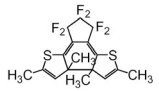
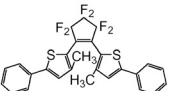
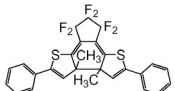
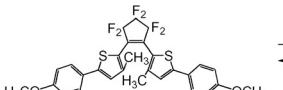
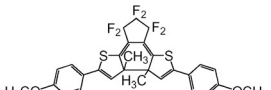
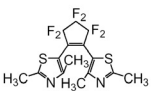
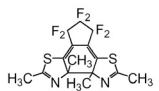
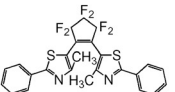
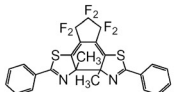
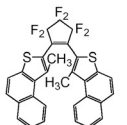
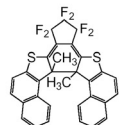

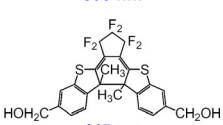
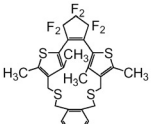
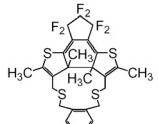
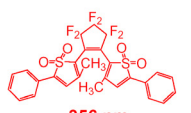
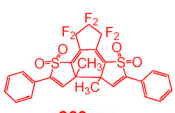
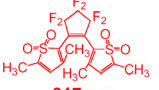
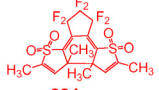


(Zoom)



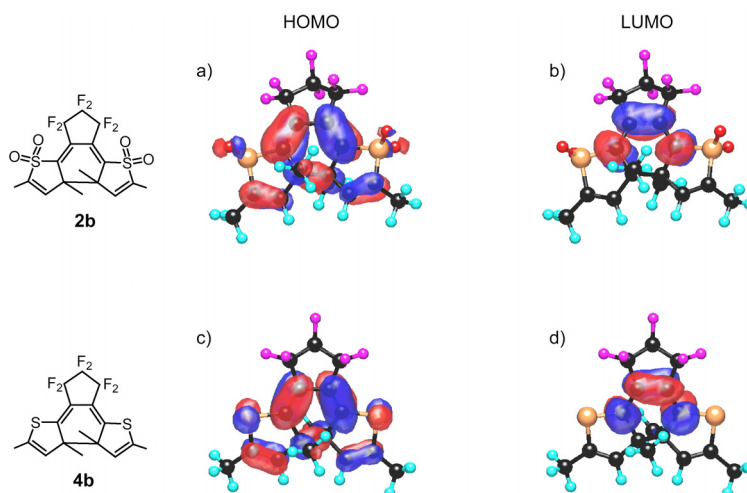
5. Table of absorption spectral changes of 2-thienylethene derivatives.

Table S1 Absorption spectral changes

Open-ring Isomer	Closed-ring Isomer	Bathochromic Shift	Ref.
 <b>336 nm</b>	 <b>425 nm</b>	<b>89 nm</b>	(S1)
 <b>370 nm</b>	 <b>438 nm</b>	<b>68 nm</b>	(S2)
 <b>385 nm</b>	 <b>440 nm</b>	<b>55 nm</b>	(S2)
 <b>320 nm</b>	 <b>391 nm</b>	<b>71 nm</b>	(S3)
 <b>363 nm</b>	 <b>406 nm</b>	<b>43 nm</b>	(S3)
 <b>380 nm</b>	 <b>500 nm</b>	<b>120 nm</b>	(S4)
 <b>337 nm</b>	 <b>445 nm</b>	<b>108 nm</b>	(S5)
 <b>340 nm</b>	 <b>460 nm</b>	<b>120 nm</b>	(S6)
 <b>356 nm</b>	 <b>260 nm</b>	<b>-96 nm</b>	(This work)
 <b>317 nm</b>	 <b>284 nm</b>	<b>-33 nm</b>	(This work)

## 6. Calculations.

The absorption spectral changes along with the photocyclization/photocycloreversion reactions of diarylethenes with oxidized thiophene rings were quite different from the changes observed for their dithienylethene analogues. In order to reveal the difference in the absorption spectral changes, molecular orbital calculation both for **2b** and for the closed-ring isomer of 1,2-bis-(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**4b**) was undertaken using standard MOPAC software with CNDO/S parameterization. Although the conformations of **2b** and **4b** are almost similar, considerable difference between the HOMO states is observed. The orbital profiles of HOMO and LUMO based on the CNDO/S parameterization are illustrated in Figure S2. In the HOMO state, the molecular orbital of **2b** is clearly separated by the oxidized sulfur atoms, while the  $\pi$ -electron of **4b** is delocalized throughout the molecule via sulfur atoms. Therefore, the spectral difference between **2b** and **4b** is attribute to the difference in the wavefunction of HOMO level. In **2b**, electrons are localized in the central cyclohexadiene structure.



**Figure S2.** CNDO/S calculation of HOMO and LUMO for **2b** (a, b) and for 1,2-bis-(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**4b**) (c, d).

## 7. References

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