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Novel sulfoxide-introducing reaction and photochromic reactions of ethenylsulfinyl derivatives of dithienylethenes

Mahmut Kose*

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan

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Abstract

New diarylethenes possessing one or two arenesulfinylethenyl moieties were casually synthesised. The photochromic and chiroptical properties of 1,2-bis-2-{2-methyl-5-[2-(4-toluenesulfinyl)ethenyl]-3-thienyl}-3,3,4,4,5,5-hexafluorocyclopentene were examined. While its colouring quantum yield by 313-nm irradiation ($\Phi_{O\rightarrow C}$) was as large as 0.46, its bleaching quantum yield by 621-nm irradiation ($\Phi_{O\rightarrow C}$) was negligibly small. Diels–Alder reaction of 2-(4-toluenesulfinyl)-1,4-benzoquinone with diarylethenes with the structure of 1-aryl-2-(5-ethenyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene gave, instead of the expected Diels–Alder cycloadduct or its derivatives, 1-aryl-2-{2-methyl-5-[2-(4-toluenesulfinyl)ethenyl]-3-thienyl}-3,3,4,4,5,5-hexafluorocyclopentene.

Keywords: Photochromism; Diarylethenes; Diels–Alder reaction; Arenesulfinylethenyl group; Quantum yield

1. Introduction

Thermally irreversible photochromic compounds such as fulgides [1], diarylethenes [2], and the arylbutadiene systems [3,4] are potential candidates for rewritable high-density optical memory media. The major requirements for the memory application are thermal stability, fatigue resistance, and non-destructive readout capability. Diarylethenes are the best candidate because they equip most of the necessary properties. Particularly, the thermal stability and fatigue resistance are the most notable features of the diarylethenes [5]. Since the first report of diarylethenes by Irie and Mohri [6], many research groups are engaged in the research of photochromic diarylethenes. Extensive researches on diarylethenes are mostly devoted to derivatisation of main structure, as well as the characterisation of photochromic behaviour both in solution and crystalline states. In this paper, we report two new diarylethenes **1*O*** and **2*O*** that have the novel arenesulfinylethenyl group. They were unexpectedly obtained from the thermal reaction of 2-(4-toluenesulfinyl)-1,4-benzoquinone [7] with 2-methyl-5-ethenyl-3-thienyl moiety of diarylethene derivatives. The mechanism of formation of the new compounds was discussed, and their photochromic properties were examined.

2. Results and discussions

The ethenyl-substituted diarylethenes **9** and **10**, the diene moieties of the Diels–Alder reactions, were synthesised in good yields as shown in Scheme 1. The dienophile of the Diels–Alder reaction, 2-(4-toluenesulfinyl)-1,4-benzoquinone (PTSQ), was prepared from 1,4-dimethoxybenzene and methyl 4-toluenesulfinate with the procedures reported by Carreño et al. [7].

When the diarylethene possessing one 5-ethenyl-substituted thiophene **9** was refluxed in toluene in the presence of excess amount of PTSQ, an unexpected compound **1*O*** was obtained in 30% yield in place of the expected Diels–Alder adduct or its oxidation product. Because the new compound **1*O*** showed photochromism, it still had the bisarylcyclopentene skeleton. In addition, it had a trans disubstituted double bond (^{1}H NMR δ 6.47, 1H, d, J = 15.2 Hz, δ 7.56, 1H, d, J = 15.2 Hz), 4-tolyl group (^{1}H NMR δ 2.43, 3H, s, δ 7.33, 2H, d, J = 8.0 Hz, δ 7.78, 2H, d, J = 8.4 Hz), and a sulfoxide group (IR 1085 and 1047 cm^{-1}). As it showed the molecular ion peak at 582 by mass spectroscopy, it was suggested that it has the structure depicted as **1*O*** in Scheme 1.

* Present address: Department of Chemistry, Faculty of Art and Science, Zonguldak Karaelmas University, Zonguldak 67100, Turkey. Tel.: +90-532-220-1241; fax: +90-372-257-4181.
E-mail address: mkose@karaelmas.edu.tr (M. Kose).

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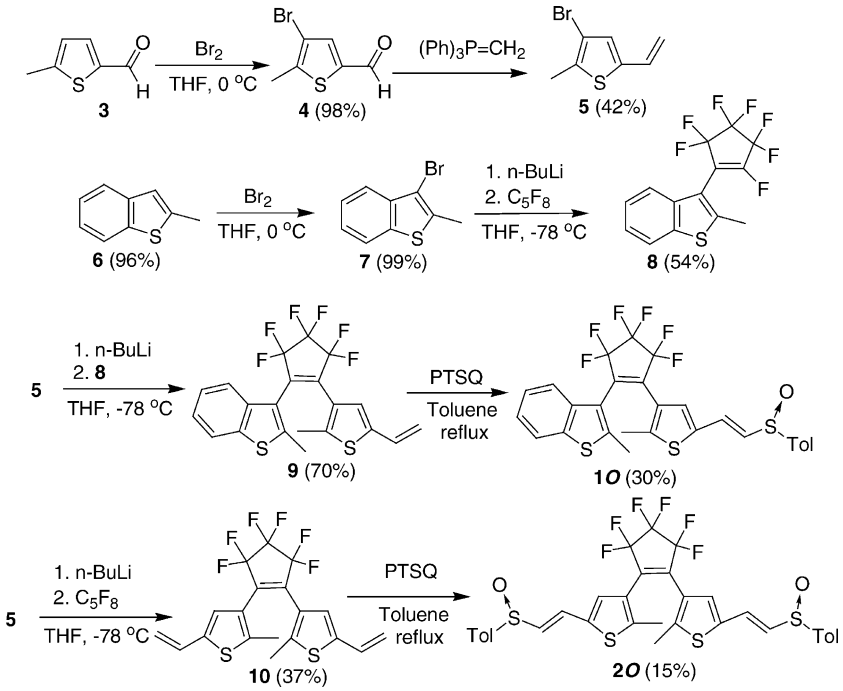
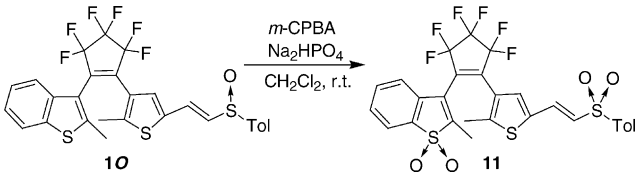


Scheme 1. Synthesis of **1*O*** and **2*O***.



Scheme 2. *m*-CPBA oxidation of **1*O***.

Although all attempts to obtain crystals of **1*O*** were unsuccessful, **11**, an oxidation product of **1*O*** by 3-chloroperoxybenzoic acid, gave suitable crystals for X-ray crystallographic analysis (Scheme 2). The ORTEP drawing of **11** is shown in Fig. 1. It confirmed the structure of **1*O*** unequivocally.

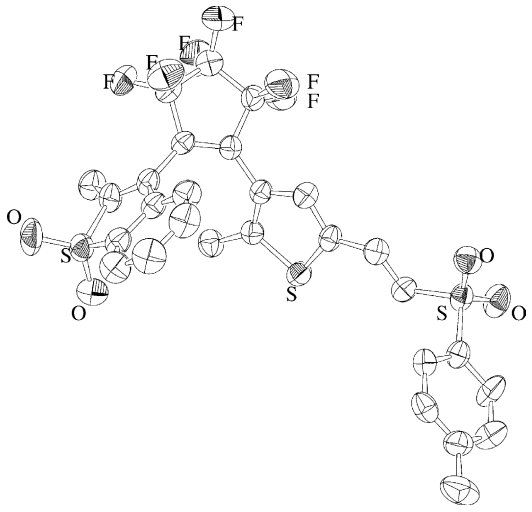


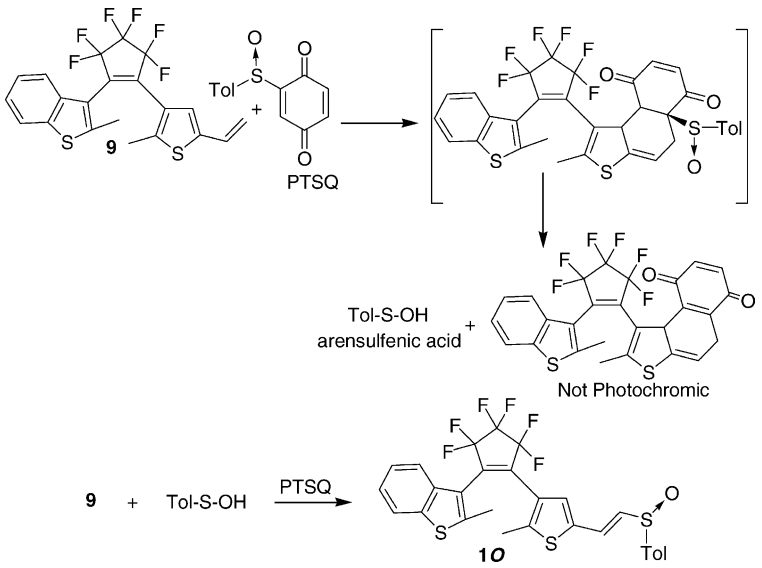
Fig. 1. ORTEP drawing of **11**.

The following multi-step mechanism has been proposed to explain the formation of **1*O*** (Scheme 3). Initially, a Diels–Alder cycloadduct was formed. Then the regeneration of quinone moiety by elimination of arenesulfenic acid took place. The arenesulfenic acid reacted with the double bond of the starting diarylethene to give a saturated sulfoxide. The regiochemistry of the addition was governed by steric congestion. Finally dehydrogenation was occurred by PTSQ to give **1*O***.[1] The arenesulfenic acid eliminations from bicyclic sulfoxides [8,9] and their addition to alkenes and alkynes [10] under reflux condition are well known.

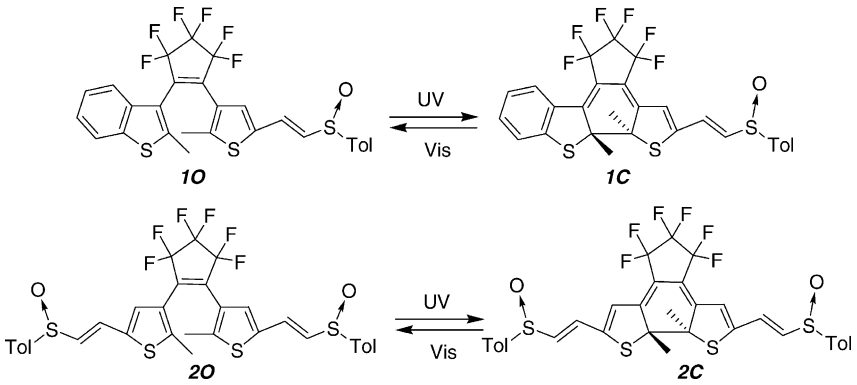
Similarly, **2*O*** was obtained from **10** which had two ethenylthiophene moieties.

Irradiation of **1*O*** and **2*O*** in toluene with UV light caused a colourless to blue (**1*O***) and deep blue-green (**2*O***) colour change, respectively, due to the formation of **1*C*** and **2*C***. The coloured forms returned very slowly to the initial colourless forms upon exposure to white light in toluene (Scheme 4).

[1] Composition of the reaction mixture after work up: when the starting diarylethene (Rf = 0.66 with AcOEt (20%)/hexane) was completely disappeared from the reaction mixture, mainly three new spots appeared on TLC (in AcOEt (20%)/hexane). Upper spot (Rf = 0.65), isolated only a few milligrams, was photochromic. After further purification it was proved that it was a mixture of two photochromic compounds (red and blue coloured) and their ^{1}H NMR and mass spectra were too complicated to elucidate. Middle large yellow spot (Rf = 0.38) was not photochromic and it was a mixture of starting PTSQ, and an unidentified starting diarylethene-related product. Lower spot (Rf = 0.28) was the main photochromic **1*O***.



Scheme 3. Proposed mechanism of the formation of **1*O***.



Scheme 4. Photoreactions of **1*O*** and **2*O***.

The absorption spectra of **1*O*** and its photostationary states of 313-nm light irradiation are shown in Fig. 2.

The quantum yields of the ring closure ($\Phi_{O\rightarrow C}$) for **1*O*** and **2*O*** and ring opening ($\Phi_{O\rightarrow C}$) by 313-nm light for the coloured forms **1*C*** and **2*C*** were measured. Although the bleaching quantum yields of **1*C*** and **2*C*** were tried to measure, they were negligibly small. For example, the bleaching quantum yield of **2*C*** with 621-nm light irradiation was calculated to be 0.0032, which is too small to discuss quantitatively. The low quantum yields for the bleaching reactions are similar to those reported for diarylethenes with the extended conjugation on the side chains [11]. The colouring quantum yields are listed in Table 1, together with the absorption spectral data.

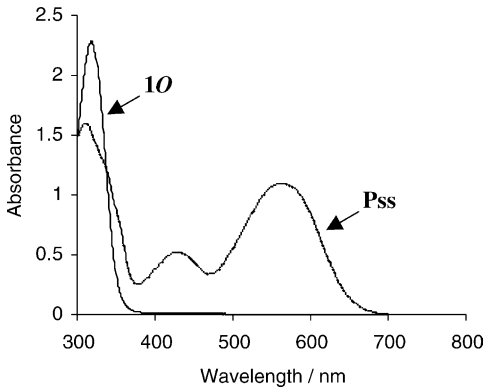


Fig. 2. Absorption spectral change of **1*O*** in toluene (1.10×10^{-4} mol dm^{-3}) irradiated with 313-m light.

When **2*O*** was irradiated with 313 nm light, a racemic mixture of **2*C*** was formed [12]. Optical resolution of **2*C*** was carried out using an HPLC apparatus equipped with Daicel OD-H chiral column. Then, optical rotation of the faster moving enantiomer was measured. The specific rotation $[\alpha]_{820}$ was -156° ($l = 10$ cm, 0.000073 g ml^{-1} in toluene at 26.5 °C, $\lambda = 820$ nm). CD spectra of the faster and slower moving enantiomers of **2*C*** were shown in Fig. 3. As was expected, they were almost the mirror images to each other.

In conclusion, the author has synthesised two new diarylethenes with one or two arylsulfinylethenyl functional

Table 1
Absorption spectral data and quantum yields of **1*O***, **1*C*** and **2*O***, **2*C*** in toluene

	1*O*	**1*C***	**2*O***	**2*C***
λ_{max} (nm)	319	564	318	621
ε_{max} ($mol^{-1}\,dm^3\,cm^{-1}$)	20,800	10,000	20,500	6,800
Φ_{313}	$\Phi_{O\rightarrow C} = 0.32$	$\Phi_{O\rightarrow C} = 0.05$	$\Phi_{O\rightarrow C} = 0.46$	$\Phi_{O\rightarrow C} = 0.012$

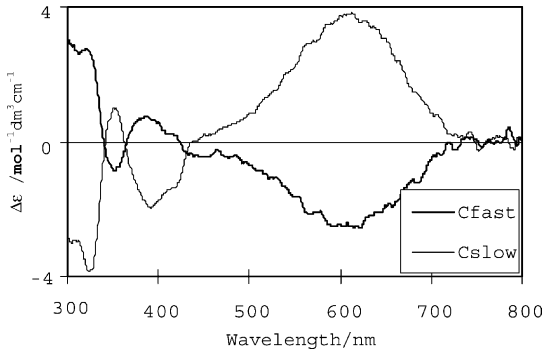


Fig. 3. CD spectra of optically resolved **2*C***.

groups by a novel synthetic method. The mechanism of their formation was proposed. Interestingly, although the colouring quantum yields are large, the bleaching quantum yields are negligibly small. The coloured form **2*C*** was optically resolved and their chiroptical properties were clarified.

3. Experimental

3.1. General

^{1}H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHZ), or a JEOL JNM-AL400 FT NMR (400 MHz) spectrometers in $CDCl_3$. The signals are expressed as parts per million down field from tetramethylsilane, used as an internal standard (δ-value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were measured using a Perkin-Elmer 1650 FT-IR spectrometer. Low- and high-resolution mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. Melting points were not corrected. UV-Vis spectra were recorded on a JASCO UBest-50 UV-Vis spectrophotometer or a JASCO V-550 UV-Vis spectrophotometer.

Photochemical reactions at 313 nm in toluene were carried out in a 10 mm path length quartz cell using a 500 W high-pressure mercury lamp (Ushio Electronic), from which the 313-nm emission line was separated by filters (5 cm water filter, a UV-D35 glass filter; 5 cm aqueous $NiSO_4{\cdot}H_2O$ solution; 1 cm aqueous K_2CrO_4–NaOH solution; and 1 cm aqueous potassium hydrogen phthalate solution). During the photoreaction, solutions in the quartz-cell were stirred continuously.

Chemical reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and dichloromethane was distilled from CaH_2 immediately before use. Solutions were dried over anhydrous sodium sulphate. Flash column chromatographic separation was carried out on Merck Kieselgel 60 (230–400 mesh) using ethyl acetate and hexane as the eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25-mm thick TLC plates.

3.2. Synthesis

3.2.1. 4-Bromo-5-methylthiophene-2-carbaldehyde (*4*)

Bromine (1.23 ml, 23.8 mmol) was added to a stirring solution of 5-methylthiophene-2-carbaldehyde **3** (2 g, 15.9 mmol) in dry THF (60 ml) under a nitrogen atmosphere at 0 °C. After 1 h stirring the reaction mixture was allowed to warm up to room temperature and was left overnight. The reaction was quenched by the successive addition of the aqueous solutions of 10% $Na_2S_2O_3$ and 10% $NaHCO_3$, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane (2.5–5%) as the eluent, to afford **4** (3.21 g, 98%.). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.49 ppm (3H, s), 7.59 (1H, s), 9.78 (1H, s). IR (KRS-5, Nujol) ν (cm^{-1}) 2982, 2831, 1748, 1687, 1440, 1373, 1221, 1135, 838, 798. Mp 45–50 °C.

3.2.2. 4-Bromo-2-ethenyl-5-methylthiophene (*5*)

A hexane solution of butyl lithium (13.8 ml, 1.57 mol dm^{-3}, 21.6 mmol) was added to a stirring solution of methyltriphenylphosphonium bromide (8.57 g, 24 mmol) in dry THF (100 ml) at 0 °C under a nitrogen atmosphere, and the temperature was raised to room temperature. After a 20-min stirring, a solution of 4-bromo-5-methylthiophene-2-carbaldehyde **4** (2.5 g, 12 mmol) in dry THF (20 ml) was added via cannula. The reaction mixture was kept stirred at room temperature for 1 h. After the reaction was quenched by adding water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using hexane as the eluent, to give **5** (1.82 g, 75%) as a viscous oil. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.37 ppm (3H, s), 5.12 (1H, d, $J = 10.88$ Hz), 5.47 (1H,

d, $J = 17.16$ Hz), 6.65 (1H, dd, $J = 17.16$ Hz, 10.89), 6.77 (1H, s). IR (KBr) ν (cm^{-1}) 3088, 2980, 2920, 2854, 1740, 1621, 1533, 1372, 1241, 1218, 1046, 976, 898, 827, 793.

3.2.3. 3-Bromo-2-methylbenzo[b]thiophene (7)

Bromine (1.12 ml, 22 mmol) was added to a stirring solution of 2-methyl-benzo[*b*]thiophene **6** (2.68 g, 18 mmol) in dry THF (150 ml) under a nitrogen atmosphere at 0 °C. After 3 h stirring, the reaction was quenched by the successive addition of the aqueous solutions of 10% $Na_2S_2O_3$ and 10% $NaHCO_3$, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using hexane as the eluent, to give **7** (4.046 g, 99%.). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.56 ppm (3H, s), 7.35–7.44 (2H, m), 7.70–7.74 (2H, m), IR (KRS-5, neat) ν (cm^{-1}) 3059, 2917, 2849, 1432, 1253, 920, 749, 726.

3.2.4. 1-(2-Methyl-3-benzo[b]thienyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (8)

A hexane solution of butyl lithium (12.34 ml, 1.57 mol dm^{-3}, 19.37 mmol) was added to a stirring solution of 3-bromo-2-methylbenzo[*b*]thiophene **7** (4 g, 17.6 mmol) in dry THF (150 ml) at −78 °C under a nitrogen atmosphere. After 30 min stirring at −78 °C, octafluoro-cyclopentene (7.1 ml, 52.8 mmol) was added to the reaction mixture via cannula. The reaction mixture was kept stirring at −78 °C for 2 h, and left overnight to let the temperature rise to room temperature. After the reaction was quenched by adding water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using 100% hexane, then ethyl acetate/hexane (2.5–5%) as the eluent, to give **8** as the white solid (3.26 g, 54%.).^{1}H NMR (270 MHz, $CDCl_3$): δ 2.52 (3H, s), 7.33–7.43 (2H, m), 7.49 (1H, d, $J = 7.59$ Hz) 7.80 (1H, d, $J = 7.26$ Hz). IR (KBr) ν (cm^{-1}) 3069, 2930, 2858, 1703, 1272, 1127, 975, 758. LRMS (EI, 70 eV) *m/z* (rel intensity), 340 (M^+, 100), 339 (31), 147 ($(M\text{-}C_5F_7)^+$, 13). Found: *m/z* 340.0157. Calcd for $C_{14}H_7F_7S$: M, 340.0139. Mp 45–47 °C.

3.2.5. 1-(2-Methyl-3-benzo[b]thienyl)-2-(5-ethenyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (9)

A hexane solution of butyl lithium (1 ml, 1.57 mol dm^{-3}, 1.59 mmol) was added to a stirring solution of 4-bromo-2-ethenyl-5-methylthiophene **5** (322 mg, 1.59 mmol) in dry THF (8 ml) at −78 °C under a nitrogen atmosphere. After 30 min stirring at −78 °C, a solution of 1-(2-methyl-3-benzo[*b*]thienyl)-2,3,3,4,4,5,5-heptafluorocyclopentene **8** (360 mg, 1.06 mmol) in dry THF (10 ml) was added to the reaction mixture via cannula. The reaction mixture was kept stirring at −78 °C for 2 h and left overnight to let the temperature rise to room temperature. After the reaction was quenched by adding water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using 100% hexane, then ethyl acetate/hexane (2.5–5%) as the eluent, to give **9** as a white solid (332 mg, 70%.).^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (3H, s), 2.20 (3H, s), 5.03 (1H, d, $J = 10.8$ Hz), 5.32 (1H, d, $J = 17.6$ Hz), 6.55 (1H, dd, $J = 17.4$, 10.6 Hz), 6.77 (1H, s), 7.25 (2H, dt, $J = 8.0$, 1.2 Hz), 7.47 (1H, d, $J = 7.6$ Hz), 7.67 (1H, dd, $J = 8.0$, 1.2 Hz). LRMS (EI, 70 eV) *m/z* (rel intensity), 444 (M^+, 100), 429 (50), 413 (24), 395 (19). Found: *m/z* 444.0427. Calcd for $C_{21}H_{14}F_6S_2$: M, 444.0441. IR (KBr) ν (cm^{-1}) 3059, 1820, 1622, 1435, 1330, 1276, 1253, 1190, 1249, 969, 908, 893, 759, 734, 654, 633, 574, 534. Mp 96–98 °C.

3.2.6. 1-(2-Methyl-3-benzo[b]thienyl)-2-{2-methyl-5-[2-(4-toluenesulfinyl)ethenyl]-3-thienyl}-3,3,4,4,5,5-hexafluorocyclopentene (1O)

A solution of ethenyl-substituted diarylethene **9** (200 mg, 0.45 mmol) and 2-(4-toluenesulfinyl)-1,4-benzoquinone (660 mg, 2.7 mmol) in 10 ml toluene was refluxed for 10 h under a nitrogen atmosphere. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel using 100% hexane, then ethyl acetate/hexane (5–30%) as the eluent, to give **1*O*** (78 mg, 30%) as a colourless amorphous-like solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (3H, s), 2.27 (3H, s), 2.43 (3H, s), 6.47 (1H, d, $J = 15.2$ Hz), 7.16 (1H, s), 7.33 (2H, d, $J = 8.0$ Hz), 7.3–7.36 (2H, m), 7.49 (1H, d, $J = 7.2$ Hz), 7.56 (1H, d, $J = 15.2$ Hz), 7.73 (1H, dd, $J = 7.2$, 2.0 Hz), 7.78 (2H, d, $J = 8.4$ Hz). LRMS (EI, 70 eV) *m/z* (rel intensity), 582 (M^+, 6), 442 ((M-4-toluenesulfinic acid)$^+$, 100), 427 (29), 411 (15). IR (KRS-5, Nujol) ν (cm^{-1}) 2932, 2853, 1605, 1274, 1146, 1085, 1047, 961, 895, 837, 660. Mp 55–60 °C.

3.2.7. 1,2-Bis(5-ethenyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (10)

A hexane solution of butyl lithium (4.18 ml, 1.58 mol dm^{-3} in hexane, 6.68 mmol) was added to a stirring solution of 4-bromo-2-ethenyl-5-methylthiophene **5** (1.21 g, 5.96 mmol) in dry THF (30 ml) at −78 °C under a nitrogen atmosphere. After 30 min stirring at −78 °C, octafluorocyclopentene (0.36 ml, 2.68 mmol) was added to the solution via cannula. The reaction mixture was kept stirring at −78 °C for 1 h, and then at room temperature for 1.5 h. After the reaction was quenched by adding water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column

chromatography on silica gel using 100% hexane as the eluent, to give **10** as a white solid (920 mg, 37%.). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.89 (6H, s (ap)), 2.37 (6H, s (p)), 5.15 (2H, d, $J = 10.89$ Hz), 5.47 (2H, d, $J = 17.16$ Hz), 6.70 (2H, dd, $J = 17.16, 10.89$ Hz), 6.91 (2H, s). LRMS (EI, 70 eV) *m/z* (rel intensity), 420 (M^+, 77), 404 (100), 372 (23), 335 (10), 321 (7), 287 (9), 210 (6). Found: *m/z* 420.0418. Calcd for $C_{19}H_{14}F_6S_2$: M, 420.0441. IR (Nujol) ν (cm^{-1}) 2977, 2882, 2837, 1622, 1339, 1275, 982, 898, 738. Mp 123–125 °C.

*3.2.8. 1,2-Bis{2-methyl-5-[2-(4-toluenesulfinyl)ethenyl]-3-thienyl}-3,3,4,4,5,5-hexafluorocyclopentene (**2O**)*

A solution of ethenyl-substituted diarylethene **10** (201 mg, 0.48 mmol) and 2-(4-toluenesulfinyl)-1,4-benzoquinone (950 mg, 3.82 mmol) in 8 ml toluene was refluxed for 9 h under a nitrogen atmosphere. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane(5–30%) as the eluent, to give **2*O*** (51 mg, 15%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (6H, s), 2.44 (6H, s), 6.56 (2H, d, $J = 15.14$ Hz), 7.22 (2H, s), 7.35 (4H, d, $J = 8.54$ Hz), 7.63 (2H, d, $J = 15.14$ Hz), 7.80 (4H, d, $J = 8.06$ Hz). ^{13}C NMR of **2*C*** (100 MHz, $CDCl_3$): δ 21.7, 29.73, 66.8, 124.9, 128.0, 129.85, 129.95, 130.15, 133.04, 134.75, 136.35, 145.17, 149.2, 152.1. LRMS (EI, 70 eV) *m/z* (rel intensity), 681 ((M-CH_3)$^+$, 4), 679 (9), 667 (12), 605 ((M-tolyl)$^+$, 12), 593 (12), 543 (13), 531 ((M-toluenesulfinylvinyl)$^+$, 14), 493 (20), 455 (20), 443 (21), 431 (30), 381 (31), 343 (32), 331 (31), 281 (55), 269 (31), 243 (39), 231 (52), 219 (70), 181 (100). IR (KRS-5, Nujol) ν (cm^{-1}) 2979, 1732, 1596, 1443, 1322, 1274, 1147, 1125, 1084, 1044, 970, 832, 811, 714, 658, 601, 537.

*3.2.9. 1-{2-Methyl-5-[2-(4-toluenesulfonyl)ethenyl]-3-thienyl}-2-(2-methyl-1,1-dioxo-3-benzo[b]thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**11**)*

To a CH_2Cl_2 (1 ml) solution of **1*O*** (30 mg, 0.052 mmol) was added Na_2HPO_4 (38 mg, 0.268 mmol) and 3-chloroperoxybenzoic acid (*m*-CPBA) (17 mg, 0.098 mmol) and the mixture was stirred at room temperature under a nitrogen atmosphere for overnight. After the reaction was quenched by adding 10% aq. $NaHCO_3$, the mixture was extracted with ethyl acetate. The organic layer was washed with sat. aq. NaCl, dried with anhydrous Na_2SO_4, and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane (20–60%) as the eluent to give **11** (21 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (3H, s), 2.20 (3H, s), 2.44 (3H, s), 6.53 (1H, d, $J = 15.2$ Hz), 7.10 (1H, d, $J = 7.2$ Hz), 7.17 (1H, s), 7.35 (2H, d, $J = 8.0$ Hz), 7.5 (2H, m), 7.58 (1H, d, $J = 15.2$ Hz), 7.75 (1H, d, $J = 2.0$ Hz), 7.79 (2H, d, $J = 8.4$ Hz). The crystals of **11** suitable for X-ray crystallographic analysis were obtained by recrystallisation from a mixture of ether–ethyl acetate. The crystallographic data for **11** are shown in Table 2.

Table 2
Crystallographic data of **11**

Empirical formula	$C_{28}H_{20}F_6O_4S_3$
Formula weight	630.63
Crystal colour, habit	Pale pink, prismatic
Crystal size (mm)	0.30 × 0.15 × 0.10
Crystal system	Triclinic
Lattice type	Primitive
a (Å)	10.743(3)
b (Å)	11.681(4)
c (Å)	12.53(1)
α (°)	76.21(2)
β (°)	110.63(4)
γ (°)	90.29(2)
Volume (Å^3)	1423(1)
Space group	$P\bar{1}$ (no. 2)
Z	2
Density (calculated) (g cm^{-3})	1.471
Residuals: *R*; R_w (all data)	0.103; 0.154
Residuals: *R*1 (for $I > 2.0 > \sigma(I)$)	0.062
Goodness-of-fit indicator	1.97

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