Supplemental Information for

# Thermal bleaching reactions of photochromic diarylethenes with thiophene-*S*,*S*-dioxide for a light-starting irreversible thermosensor

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### **Experimental**

#### General

Spectroscopic grade solvents were used and purified by distillation before use. <sup>1</sup>H NMR spectra were recorded at 300 MHz using a BRUKER AV-300N spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Mass spectra were obtained using a JEOL JMS-700/700S mass spectrometer. Absorption spectra were obtained using a JASCO V-560 absorption spectrophotometer. High-performance liquid chromatography (HPLC) was carried out using a Hitachi L-7150/L-2400 HPLC system equipped with a KANTO CHEMICAL Mightysil Si 60 column.

#### Materials

1,2-Bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4a**) and 1,2-bis-(2-isopropyl-5-phenyl-3-thienyl)perfluorocyclopentene (**5a**) were synthesized according to methods described in the literature.<sup>S1,S2</sup> 1,2-Bis(2-(4-heptyl)-5-phenyl-3-thienyl)perfluorocyclopentene (**6a**) was synthesized from thiophene as follows.

# 2-(4-Hydroxy-4-heptyl)thiophene

Thiophene (6.0 mL, 75 mmol) was added to dry ether (65 mL). To the solution was added dropwise 1.6 M *n*-BuLi hexane solution (55 mL, 88 mmol) at 0 °C, and the mixture was refluxed for 1 h. After cooling to 0 °C, 4-heptanone (12 mL, 86 mmol) was added to the reaction mixture, and the mixture was stirred for 1 h at room temperature. The organic layer extracted with ether was dried over MgSO<sub>4</sub>, filtered and concentrated. Yield: 15 g (100%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta = 0.89$  (t, J = 7.3 Hz, 6H, CH<sub>3</sub>), 1.2–1.4 (m, 4H, CH<sub>2</sub>), 1.7–1.9 (m, 4H, CH<sub>2</sub>), 1.95 (s, 1H, OH), 6.85 (dd, J = 1.1 and 3.5 Hz, 1H, Aromatic), 6.95 (dd, J = 3.5 and 5.0 Hz, 1H, Aromatic), 7.15 (dd, J = 1.1 and 5.0 Hz, 1H, Aromatic).

# 2-(4-Heptyl)thiophene

Dry ether (90 mL) was added into a flask containing  $AlCl_3$  (40 g, 0.30 mol) under argon atmosphere at 0 °C. To the solution was added LiAlH<sub>4</sub> (5.6 g, 0.15 mol), and then 2-(4-hydroxy-4-heptyl)thiophene (15 g, 76 mmol) in dry ether (120 mL) was added dropwise to the reaction mixture. After refluxed for 1.5 h, the solution was quenched by adding water. The mixture was extracted with ether, dried over MgSO<sub>4</sub>, filtered and concentrated. Yield: 13 g (94%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta = 0.86$  (t, J = 7.3 Hz, 6H, CH<sub>3</sub>), 1.1–1.3 (m, 4H, CH<sub>2</sub>), 1.4–1.7 (m, 4H, CH<sub>2</sub>), 2.8–3.0 (m, 1H, CH), 6.75 (d, J = 3.5 Hz, 1H, Aromatic), 6.91 (dd, J = 3.5 and 5.1 Hz, 1H, Aromatic), 7.12 (d, J = 5.1 Hz, 1H, Aromatic).

# 3,5-Dibromo-2-(4-heptyl)thiophene

Bromine (8.0 mL, 155 mmol) was added dropwise into a flask containing 2-(4-heptyl)thiophene 13 g (71 mmol), acetic acid (64 mL) and water (4 mL). The reaction mixture was stirred overnight. The reaction mixture was neutralized and extracted with ether. The organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was purified by column chromatography using hexane as the eluent. Yield: 12 g (50%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta = 0.88$  (t, J = 6.9 Hz, 6H, CH<sub>3</sub>), 1.1–1.3 (m, 4H, CH<sub>2</sub>), 1.4–1.7 (m, 4H, CH<sub>2</sub>), 3.0–3.2 (m, 1H, CH), 6.83 (s, 1H, Aromatic)

## 3-Bromo-2-(4-heptyl)-5-phenylthiophene

3,5-Dibromo-2-(4-heptyl)thiophene (11 g, 31 mmol) was added into a flask containing dry THF (165 mL) under argon atmosphere. To the solution was added dropwise 1.6 M *n*-BuLi hexane solution (23 mL, 37 mmol) at -78 °C, and then the reaction mixture was stirred for 1 h at that temperature. Tri-*n*-butyl borate (13 mL, 48 mmol) was added to the mixture, and then the mixture was stirred for 1 h. After warmed up room temperature, 20 wt% Na<sub>2</sub>CO<sub>3</sub>aq (60 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.73 g, 0.63 mmol) and iodobenzene (2.9 mL, 26 mmol) was added to reaction mixture, and then the reaction mixture was refluxed for 6 h. The product was extracted with ether. The organic layer was dried over MgSO<sub>4</sub>, filterd and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent.

Yield: 8.5 g (81%)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta = 0.86-0.94$  (m, 6H, CH<sub>3</sub>), 1.2–1.4 (m, 4H, CH<sub>2</sub>), 1.4–1.7 (m, 4H, CH<sub>2</sub>), 3.0–3.3 (m, 1H, CH), 7.09 (s, 1H, Aromatic), 7.3–7.6 (m, 5H, Aromatic).

1,2-Bis(2-(4-heptyl)-5-phenyl-3-thienyl)perfluorocyclopentene (6a)

1.6 M *n*-BuLi hexane solution (13 mL, 20 mmol) was added dropwise to dry THF (85 mL) containing 3-bromo-2-(4-heptyl)-5-phenylthiophene (4.8 g, 14 mmol) at -78 °C under argon atmosphere, and then the mixture was stirred for 1 h.

Octafluorocyclopentene (0.95 mL, 7.1 mmol) was added dropwise to the reaction mixture, and then the mixture was stirred for 2 h. The mixture was quenched by water and extracted with ether. The organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent.

Yield: 1.3 g (27%)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta = 0.63$  (t, J = 6.8 Hz, 12H, CH<sub>3</sub>), 0.8–1.1 (m, 8H, CH<sub>2</sub>), 1.2–1.5 (m, 8H, CH<sub>2</sub>), 2.4–2.6 (m, 2H, CH), 7.2–7.6 (m, 12H, Aromatic). HR-MS (FAB) m/z = 688.2633 (M<sup>+</sup>). Calcd for C<sub>39</sub>H<sub>42</sub>F<sub>6</sub>S<sub>2</sub> = 688.2632.

Synthesis of thiophene-S,S-dioxidized diarylethenes

The oxidation of diarylethenes was carried out under the conditions shown in Table S1. A typical example is as follows:

*m*-Choroperoxybenzoic acid (93 mg, 0.36 mmol) was added into a flask containing dichloromethane (5 mL) and a diarylethene (0.15 mmol). The mixture was stirred for 48 h at room temperature. The solution was extracted with dichloromethane. The organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 9 : 1).

1-(1,1-Dioxide-2-ethyl-5-phenyl-3-thienyl)-2-(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**): Yield = 65%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ = 1.06 (t, *J* = 7.6 Hz, 3H, CH<sub>3</sub>), 1.27 (t, *J* = 7.5 Hz, CH<sub>3</sub>), 2.42 (q, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 2.55 (q, *J* = 7.5 Hz, 2H, CH<sub>2</sub>), 6.72 (s, 1H, Aromatic), 7.34–7.46 (m, 7H, Aromatic), 7.56–7.59 (m, 2H, Aromatic), 7.63–7.66 (m, 2H, Aromatic). HR-MS (FAB) m/z = 581.1043 ([M+H]<sup>+</sup>). Calcd for C<sub>29</sub>H<sub>23</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> = 581.1044 (M+H).

1-(1,1-Dioxide-2-isopropyl-5-phenyl-3-thienyl)-2-(2-isopropyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2a**):Yield = 73%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  = 1.13 (d, *J* = 7.1 Hz, 6H, CH<sub>3</sub>), 1.25 (d, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 2.72–2.95 (m, 2H, CH), 6.79 (s, 1H, Aromatic), 7.15 (s, 1H, Aromatic), 7.30–7.47 (m, 6H, Aromatic), 7.53–7.57 (m, 2H, Aromatic), 7.65–7.71 (m, 2H, Aromatic). HR-MS (FAB) *m*/*z* = 609.1332 ([M+H]<sup>+</sup>). Calcd for C<sub>31</sub>H<sub>27</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> = 609.1357 (M+H).

1-(1,1-Dioxide-2-(4-heptyl)-5-phenyl-3-thienyl)-2-(2-(4-heptyl)-5-phenyl-3-thienyl)perfluorocyclopentene (**3a**): Yield = 39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  = 0.63–1.61 (m, 28H), 2.34–2.56 (m, 2H, CH), 6.91 (s, 1H, Aromatic), 7.2–7.5 (m, 7H, Aromatic), 7.5–7.6 (m, 2H, Aromatic), 7.7–7.8 (m, 2H, Aromatic). HR-MS (FAB) *m*/*z* = 720.2524 (M<sup>+</sup>). Calcd for C<sub>39</sub>H<sub>42</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub> = 720.2530.

### Photochromism

Photocyclization and cycloreversion quantum yields were determined in hexane as relative quantum yields using diarylethene derivatives whose quantum yields have already been determined.<sup>S3</sup> The photocyclization and photocycloreversion reactions were followed by absorption spectra. The samples were not degassed.

# Thermal bleaching reaction

The thermal reaction of the diarylethene closed-ring isomer was carried out in toluene as follows. The diarylethene open-ring isomer was put in an optical quartz cell degassed and sealed under vacuum. The solution in the cell was irradiated with 313 nm light to give the closed-ring isomer. The photoirradiation was carried out using a 200-W mercury-xenon lamp (MORITEX MUV-202) as the light source. Monochromic light was obtained by passing the light through a monochromator (Jobin–Yvon H10 UV). The cell was placed in a constant temperature chamber (ESPEC ST-110) or a temperature control unit (JASCO FTC-505S) during the thermal bleaching reaction. The reaction yields were periodically determined by absorption spectroscopic measurement.

Reactant	Substituent R	[Reactant] /M	[ <i>m</i> -CPBA] /M	[Reactant] [ <i>m</i> -CPBA]	Time/h	Product	Yield (%)
4a	CH <sub>2</sub> CH <sub>3</sub>	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	2.8	2.5	1a	65
5a	CH(CH <sub>3</sub> ) <sub>2</sub>	$3.9 \times 10^{-2}$	$9.9 \times 10^{-2}$	2.5	3.0	2a	73
6a	CH(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	$3.0 \times 10^{-2}$	$7.2 \times 10^{-1}$	2.4	2.0	<b>3</b> a	39



	2c	2d	2e	
Empirical formula	$C_{31}H_{26}F_6S$	$C_{28}H_{20}F_6S$	$C_{31}H_{26}F_6S$	
Formula weight	544.59	502.51	544.59	
Temperature/K	123	123	123	
Crystal system	Triclinic	monoclinic	Monoclinic	
Space group	P 1	$P2_{1}/c$	C2/c	
Unit cell dimensions	a = 9.636(1) Å	a = 6.720(3) Å	a = 38.047(4) Å	
	b = 11.181(1) Å	b = 21.116(12) Å	b = 6.0219(6) Å	
	c = 13.591(2) Å	c = 16.274(9) Å	c = 23.213(3) Å	
	$\alpha = 96.222(4)^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	
	$\beta = 107.826(3)^{\circ}$	$\beta = 95.32(4)^{\circ}$	$\beta = 101.266(3)^{\circ}$	
	$\gamma = 108.034(3)^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	
Volume/Å <sup>3</sup>	1291.6(3)	2299(2)	5216.0(10)	
Ζ	2	4	8	
Density/g cm <sup><math>-3</math></sup>	1.400	1.452	1.387	
Goodness-of-fit on $F^2$	1.069	1.008	1.074	
Final $R [I > 2\sigma(I)]$	R1 = 0.0882	R1 = 0.0613	R1 = 0.0786	
	wR2 = 0.2434	wR2 = 0.1509	wR2 = 0.2012	
<i>R</i> (all data)	R1 = 0.1325	R1 = 0.1080	R1 = 0.1300	
	wR2 = 0.2766	wR2 = 0.1668	wR2 = 0.2251	
CCDC No.	917414	917415	917416	

# Table S2 X-ray crystallographic data for **2c**, **2d** and **2e**.



**Fig. S1** HPLC charts of (a) **2a**, (b) **2b** and (c) after thermal reaction of **2b** for 15 min at 100 °C in toluene. HPLC measurement was carried out using hexane/ethyl acetate (95:5) as the eluent after evaporation of toluene. The intensity was detected by absorbance at 254 nm in hexane/ethyl acetate (95:5).



Fig. S2  ${}^{1}$ H NMR spectra of (a) 2c, (b) 2d and (c) 2e in CDCl<sub>3</sub>.



**Fig. S3** FAB mass spectra (low resolution) of (a) **2c**, (b) **2d** and (c) **2e**. Each mass number in high resolution and the exact mass are also shown in Figure.



Fig. S4 The reaction mechanism proposed for formation of 2c, 2d and 2e.

#### References

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