Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Alkyl substituent effects in photochemical and thermal reactions of photochromic thiophene-*S*,*S*-dioxidized diarylethenes

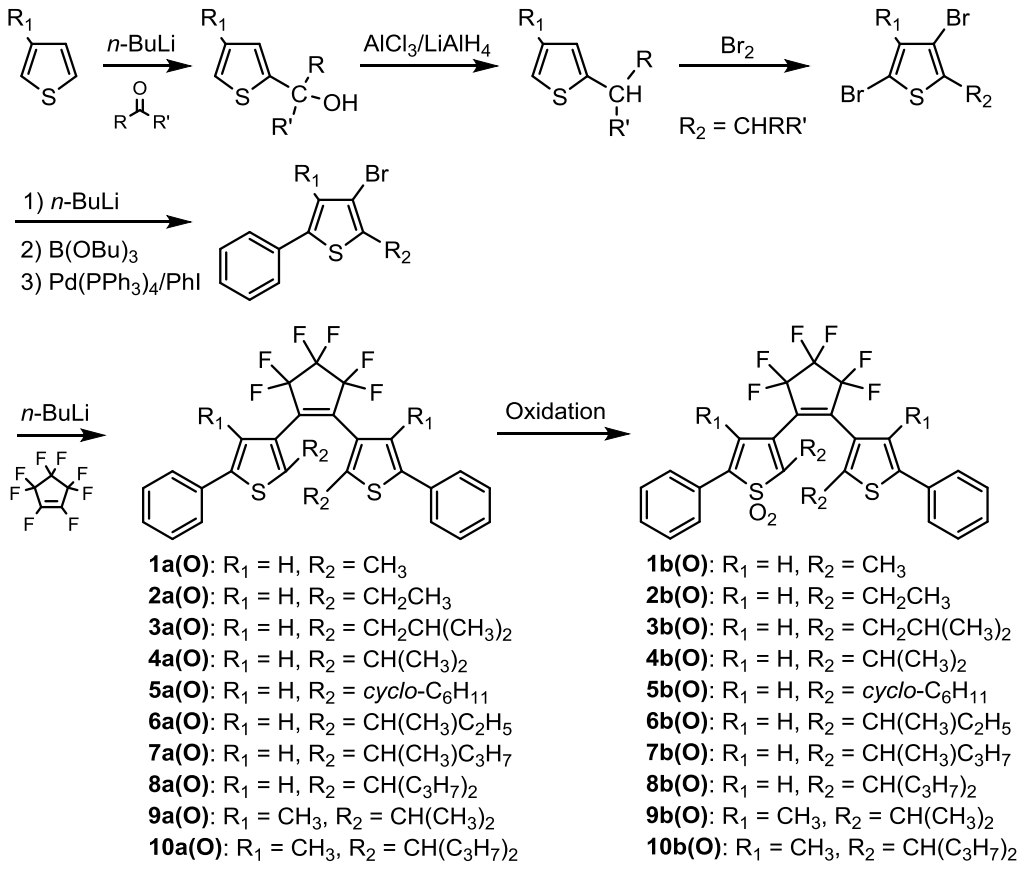
Hiroaki Shoji, Daichi Kitagawa and Seiya Kobatake*

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.

E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Tel & Fax: +81-6-6605-2797

Materials

Scheme S1 shows typical synthetic routes of diarylethens and thiophene-*S*,*S*-dioxidized diarylethenes.



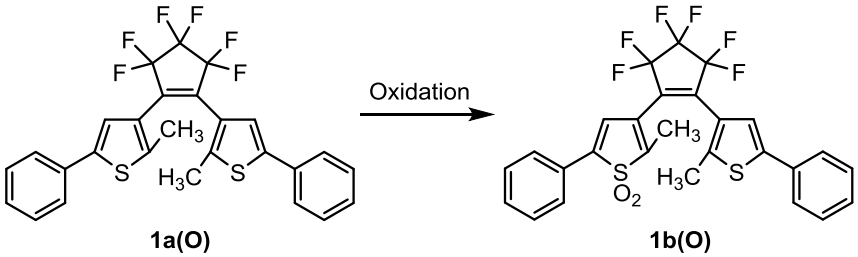
1a(O): R_1 = H, R_2 = CH_3
2a(O): R_1 = H, R_2 = CH_2CH_3
3a(O): R_1 = H, R_2 = $CH_2CH(CH_3)_2$
4a(O): R_1 = H, R_2 = $CH(CH_3)_2$
5a(O): R_1 = H, R_2 = *cyclo*-C_6H_{11}
6a(O): R_1 = H, R_2 = $CH(CH_3)C_2H_5$
7a(O): R_1 = H, R_2 = $CH(CH_3)C_3H_7$
8a(O): R_1 = H, R_2 = $CH(C_3H_7)_2$
9a(O): R_1 = CH_3, R_2 = $CH(CH_3)_2$
10a(O): R_1 = CH_3, R_2 = $CH(C_3H_7)_2$

1b(O): R_1 = H, R_2 = CH_3
2b(O): R_1 = H, R_2 = CH_2CH_3
3b(O): R_1 = H, R_2 = $CH_2CH(CH_3)_2$
4b(O): R_1 = H, R_2 = $CH(CH_3)_2$
5b(O): R_1 = H, R_2 = *cyclo*-C_6H_{11}
6b(O): R_1 = H, R_2 = $CH(CH_3)C_2H_5$
7b(O): R_1 = H, R_2 = $CH(CH_3)C_3H_7$
8b(O): R_1 = H, R_2 = $CH(C_3H_7)_2$
9b(O): R_1 = CH_3, R_2 = $CH(CH_3)_2$
10b(O): R_1 = CH_3, R_2 = $CH(C_3H_7)_2$

Scheme S1 Synthetic routes of diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes

Diarylethenes **1a(O)**,[S1] **2a(O)**,[S2] **3a(O)**,[S3] **4a(O)**,[S4] **8a(O)**,[S5] and **9a(O)**[S6] were synthesized according to methods in the literature. Thiophene-*S*,*S*-dioxidized diarylethenes **2b(O)**, **4b(O)**, and **8b(O)** were also synthesized according to methods in the literature.[S5] Other diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes were synthesized as follows.

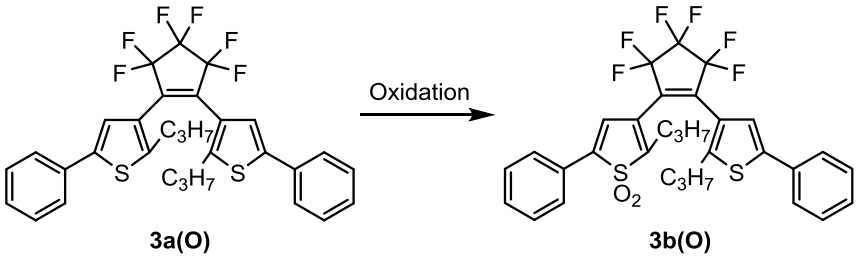
1-(1,1-Dioxide-2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclo-pentene (1b(O))



1a(O) **1b(O)**

m-Chloroperoxybenzoic acid (302 mg, 1.21 mmol) was added to the dichloromethane (5 mL) solution containing **1a(O)** (105 mg, 0.202 mmol). The mixture was stirred at room temperature for 65 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 80 : 20). Yield: 54.2 mg (49%) ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.93 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 6.77 (s, 1H, Aromatic), 7.2-7.7 (m, 11H, Aromatic). MS (FAB) *m*/*z* = 552.0652 ($[M]^+$). Calcd for $C_{27}H_{18}F_6O_2S_2$ = 552.0652.

1-(1,1-Dioxide-2-isobutyl-5-phenyl-3-thienyl)-2-(2-isobutyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (3b(O))

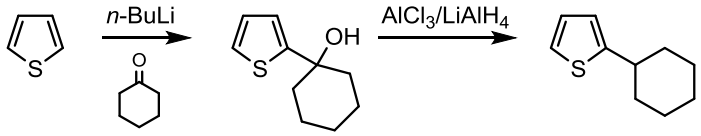


3a(O) **3b(O)**

m-Chloroperoxybenzoic acid (190 mg, 0.74 mmol) was added to the dichloromethane (5 mL) solution containing **3a(O)** (150 mg, 0.25 mmol). The mixture was stirred at room temperature for 60 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 85 : 15). Yield: 110 mg (52%) ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.96-1.31 (m, 12H, CH_3), 1.54-1.59 (m, 8H, CH_2), 2.33-2.42 (m, 2H, CH), 7.23 (s, 2H, Aromatic), 7.27-7.32 (m, 2H, Aromatic), 7.36-7.41 (m, 4H, Aromatic), 7.53-7.57 (m, 4H, Aromatic). MS (FAB)

m/*z* = 637.1678 ([M + H]$^+$). Calcd for $C_{33}H_{31}F_6O_2S_2$ = 637.1670.

2-Cyclohexylthiophene (12)

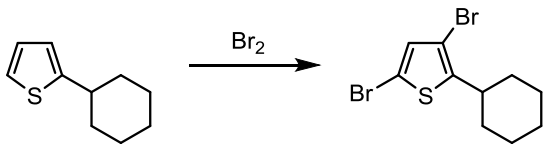


11 **12**

Thiophene (6.4 mL, 80 mmol) was stirred into dry diethyl ether (75 mL). 1.6 M *n*-BuLi/hexane solution (59 mL, 95 mmol) was slowly dropped into the solution at 0 °C and refluxed for 1.5 h. After cooling to 0 °C, cyclohexanone (10 mL, 97 mmol) was added to the reaction mixture and stirred for an hour at room temperature. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. 2-(1-Hydroxycyclohexyl)thiophene (**11**) (16 g) was obtained and was used for the following reaction without further purification.

Dry diethyl ether (75 mL) was added into a flask containing $AlCl_3$ (41 g, 310 mmol) under argon atmosphere at 0 °C, and $LiAlH_4$ (5.7 g, 150 mmol) was added to the solution. To the reaction mixture was slowly added 2-(1-hydroxycyclohexyl)thiophene (**11**) (16 g, 86 mmol) in dry diethyl ether (110 mL). After refluxed for 1.5 h, the solution was quenched with water. The residue was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Yield: 11 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.21-2.08 (m, 10H, CH_2), 2.76-2.85 (m, 1H, CH), 6.78-6.81 (m, 1H, Aromatic), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H, Aromatic), 7.11 (dd, *J* = 5.1, 1.1 Hz, 1H, Aromatic).

3,5-Dibromo-2-cyclohexylthiophene (13)

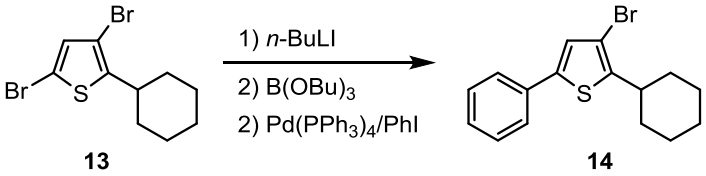


12 **13**

Bromine (7.6 mL, 150 mmol) was added dropwise into the stirring solution of 2-cyclohexylthiophene (**12**) (11 g; 69 mmol) in acetic acid (62 mL) containing water (4 mL). The reaction mixture was stirred overnight, and was extracted with diethyl ether. The organic layer was

dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane as the eluent. Yield: 14 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.16-1.46 (m, 4H, CH_2), 1.70-1.85 (m, 4H, CH_2), 1.96-2.01 (m, 2H, CH_2), 2.88-2.98 (m, 1H, CH), 6.85 (s, 1H, Aromatic).

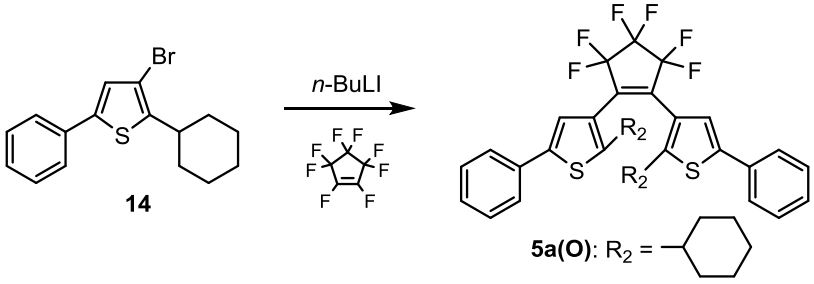
3-Bromo-2-cyclohexyl-5-phenylthiophene (14)



13 **14**

3,5-Dibromo-2-cyclohexylthiophene (**13**) (14 g, 44 mmol) was added into a flask containing dry THF (60 mL) under atmosphere. 1.6 M *n*-BuLi/hexane solution (30 mL, 36 mmol) was slowly added into the solution at −78 °C and stirred for an hour. Tri-*n*-butyl borate (13 mL, 48 mmol) was added to the mixture and stirred for an hour. After warming up room temperature, 20 wt% Na_2CO_3aq 35 mL, $Pd(PPh_3)_4$ (0.73 g, 0.16 mmol), and iodobenzene (5.6 mL, 35 mmol) was added to the reaction mixture. The reaction solution was refluxed for 13 h, and was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filterd, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 4.6 g (32%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.23-1.51 (m, 4H, CH_2), 1.74-1.87 (m, 4H, CH_2), 2.02-2.05 (m, 2H, CH_2), 2.92-3.02 (m, 1H, CH), 7.11 (s, 1H, Aromatic), 7.24-7.30 (m, 1H, Aromatic), 7.33-7.40 (m, 2H, Aromatic), 7.50-7.54 (m, 2H, Aromatic).

1,2-Bis(2-cyclohexyl-5-phenyl-3-thienyl)perfluorocyclopentene (5a(O))

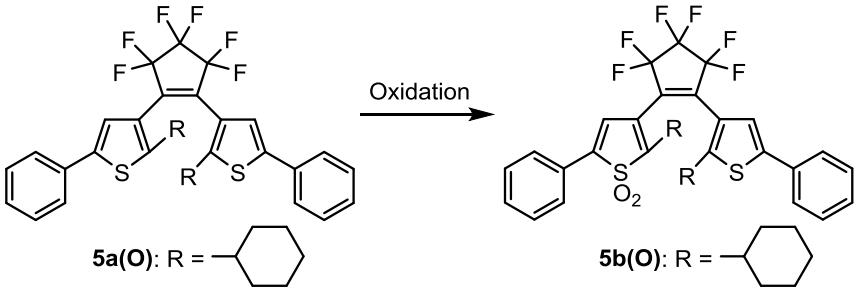


14 **5a(O)**: R_2 =

1.6 M *n*-BuLi/hexane solution (11 mL, 17 mmol) was slowly added to dry THF (65 mL) containing 3-bromo-2-cyclohexyl-5-phenylthiophene (**14**) (4.6 g, 14 mmol) at −78 °C under argon atmosphere

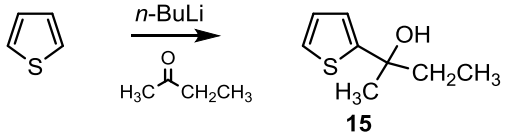
and stirred for an hour. Octafluorocyclopentene (0.95 mL, 7.3 mmol) was slowly added to the reaction mixture and stirred for 1.5 h. The mixture was quenched with water and extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 0.69 g (15%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.96-1.31 (m, 12H, CH_2), 1.54-1.59 (m, 8H, CH_2), 2.33-2.42 (m, 2H, CH), 7.23 (s, 2H, Aromatic), 7.27-7.32 (m, 2H, Aromatic), 7.36-7.41 (m, 4H, Aromatic), 7.53-7.57 (m, 4H, Aromatic). MS (FAB) *m*/*z* = 656.2006 ($[M]^+$). Calcd for $C_{37}H_{34}F_6S_2$ = 656.2006.

1-(1,1-Dioxide-2-cyclohexyl-5-phenyl-3-thienyl)-2-(2-cyclohexyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (5b(O))



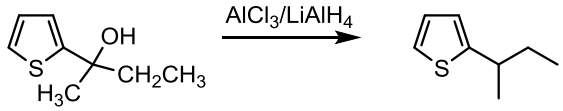
m-Chloroperoxybenzoic acid (88 mg, 0.36 mmol) was added to the dichloromethane (5 mL) solution containing **5a(O)** (100 mg, 0.15 mmol). The mixture was stirred at room temperature for 72 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 9 : 1). Yield: 14 mg (14%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.88-1.89 (m, 20H, CH_2), 2.31-2.51 (m, 2H, CH), 6.85 (s, 1H, Aromatic), 7.19 (t, *J* = 1.3 Hz, 1H, Aromatic), 7.29-7.49 (m, 4H, Aromatic), 7.53-7.57 (m, 2H, Aromatic), 7.68-7.72 (m, 2H, Aromatic). MS (FAB) *m*/*z* = 689.1984 ($[M + H]^+$). Calcd for $C_{37}H_{35}F_6O_2S_2$ = 689.1983.

2-(2-Hydroxy-2-butyl)thiophene (15)



Thiophene (17 mL, 200 mmol) was stirred into dry diethyl ether (180 mL). 1.6 M *n*-BuLi/hexane solution (150 mL, 240 mmol) was slowly added into the solution at 0 °C and refluxed for 1.5 h. After cooling to 0 °C, 2-butanone (22 mL, 240 mmol) was added to the reaction mixture and stirred for an hour at room temperature. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 7 : 3). Yield: 20 g (63%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.89 (t, *J* = 7.5 Hz, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.89 (q, *J* = 7.5 Hz, 2H, CH_2), 6.84-6.91 (m, 2H, Aromatic), 7.12-7.15 (m, 1H, Aromatic).

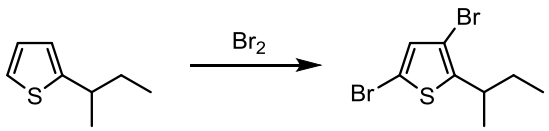
2-*sec*-Butylthiophene (16)



15 **16**

Dry diethyl ether (70 mL) was added into a flask containing $AlCl_3$ (26 g, 190 mmol) under argon atmosphere at 0 °C. $LiAlH_4$ (3.6 g, 94 mmol) was added to the solution, and 2-(2-hydroxy-2-butyl)thiophene (**15**) (7.8 g, 50 mmol) in dry diethyl ether (70 mL) was added dropwise to the reaction mixture. After refluxed for 1.5 h, the solution was quenched with water. The residue was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The solution was purified by distillation under reduced pressure (58 °C/2.7 kPa). Yield: 1.7 g (25%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.88 (t, *J* = 7.4 Hz, 3H, CH_3), 1.30 (d, *J* = 6.9 Hz, 3H, CH_3), 1.59-1.67 (m, 2H, CH_2), 2.85-2.97 (m, 1H, CH), 6.69-6.72 (m, 1H, Aromatic), 6.84 (dd, *J* = 5.1, 3.5 Hz, 1H, Aromatic), 7.04 (dd, *J* = 5.1, 1.1 Hz, 1H, Aromatic).

3,5-Dibromo-2-*sec*-butylthiophene (17)

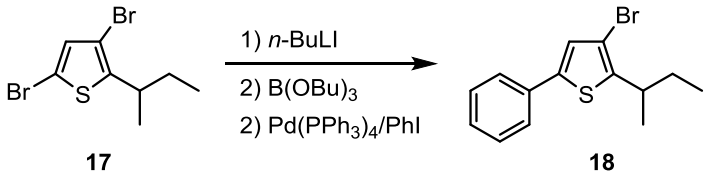


16 **17**

Bromine (1.4 g, 26 mmol) was added dropwise into 2-*sec*-butylthiophene (**16**) (1.7 g; 12 mmol) in

acetic acid (11 mL) containing water (1 mL). The reaction mixture was stirred in water bath overnight. The mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane as the eluent. Yield: 2.9 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.90 (t, *J* = 7.4 Hz, 3H, CH_3), 1.24 (d, *J* = 6.9 Hz, 3H, CH_3), 1.55-1.65 (m, 2H, CH_2), 3.01-3.13 (m, 1H, CH), 6.78 (s, 1H, Aromatic).

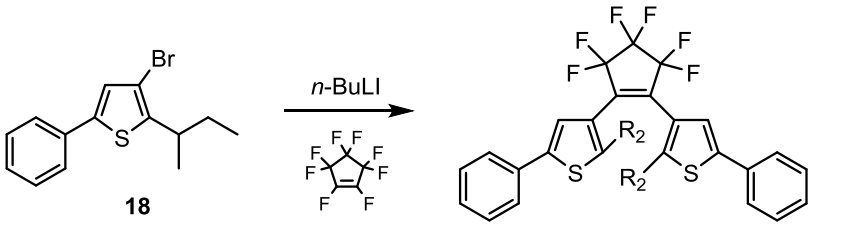
3-Bromo-2-*sec*-butyl-5-phenylthiophene (18)



17 **18**

3,5-Dibromo-2-*sec*-butylthiophene (**17**) (1.6 g, 5.4 mmol) was added into a flask containing dry THF (30 mL) under atmosphere. 1.6 M *n*-BuLi/hexane solution (3.7 mL, 5.9 mmol) was slowly dropped into the solution at −78 °C and stirred for an hour. Tri-*n*-butyl borate (2.2 mL, 8.0 mmol) was added to the mixture and stirred for an hour. After warming up room temperature, 20 wt% Na_2CO_3aq 10 mL, $Pd(PPh_3)_4$ (0.73 g, 0.10 mmol), and iodobenzene (1.1 g, 5.4 mmol) was added to reaction mixture and refluxed for 10 h. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 0.84 g (53%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.93 (t, *J* = 7.4 Hz, 3H, CH_3), 1.30 (d, *J* = 6.9 Hz, 3H, CH_3), 1.62-1.72 (m, 2H, CH_2), 3.05-3.16 (m, 1H, CH), 7.01 (s, 1H, Aromatic), 7.16-7.30 (m, 2H, Aromatic), 7.41-7.45 (m, 2H, Aromatic).

1,2-Bis(2-*sec*-butyl-5-phenyl-3-thienyl)perfluorocyclopentene (6a(O))

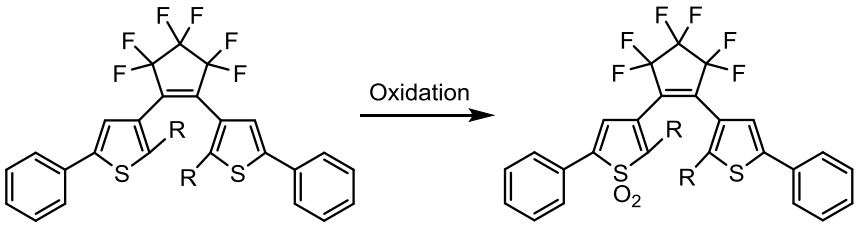


18 **6a(O)**: R_2 = $CH(CH_3)CH_2CH_3$

1.6 M *n*-BuLi/hexane solution (1.7 mL, 2.7 mmol) was slowly added to dry THF (10 mL) containing 3-bromo-2-*sec*-butyl-5-phenylthiophene (**18**) (0.70 g, 2.4 mmol) at −78 °C under argon atmosphere

and stirred for an hour. Octafluorocyclopentene (0.16 mL, 1.2 mmol) was slowly added to the reaction mixture and stirred for 2 h. The mixture was quenched with water and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 0.42 g (58%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.59 (t, *J* = 7.4 Hz, 3H, CH_3), 0.66 (t, *J* = 7.4 Hz, 3H, CH_3), 0.72 (d, *J* = 6.8 Hz, 3H, CH_3), 0.87 (d, *J* = 6.8 Hz, 3H, CH_3), 1.16-1.52 (m, 4H, CH_2), 2.44-2.55 (m, 2H, CH), 7.14 (s, 2H, Aromatic), 7.20-7.26 (m, 2H, Aromatic), 7.29-7.34 (m, 4H, Aromatic), 7.46-7.51 (m, 4H, Aromatic). MS (FAB) *m*/*z* = 604.1681 ($[M]^+$). Calcd for $C_{33}H_{30}F_6S_2$ = 604.1693.

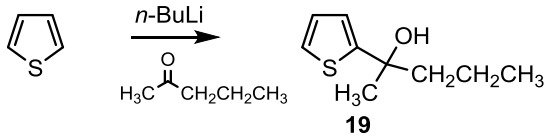
1-(1,1-Dioxide-2-*sec*-butyl-5-phenyl-3-thienyl)-2-(2-*sec*-butyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (6b(O))



6a(O): R_2 = $CH(CH_3)CH_2CH_3$ **6b(O)**: R = $CH(CH_3)CH_2CH_3$

m-Chloroperoxybenzoic acid (180 mg, 0.36 mmol) was added to the dichloromethane (5 mL) solution containing **6a(O)** (200 mg, 0.33 mmol). The mixture was stirred at room temperature for 8 days. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 9 : 1). Yield: 90 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.67-1.28 (m, 12H, CH_3), 1.45-1.88 (m, 4H, CH_2), 2.39-2.60 (m, 2H, CH), 6.86-6.89 (m, 1H, Aromatic), 7.18 (s, 1H, Aromatic), 7.30-7.49 (m, 6H, Aromatic), 7.55-7.60 (m, 2H, Aromatic), 7.69-7.73 (m, 2H, Aromatic). MS (FAB) *m*/*z* = 637.1678 ($[M + H]^+$). Calcd for $C_{33}H_{31}F_6O_2S_2$ = 637.1670.

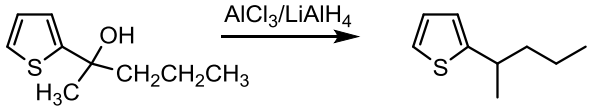
2-(2-Hydroxy-2-pentyl)thiophene (19)



19

Thiophene (7.5 mL, 72 mmol) was stirred into dry diethyl ether (85 mL). 1.6 M *n*-BuLi/hexane solution (71 mL, 110 mmol) was slowly added into the solution at 0 °C and refluxed for an hour. After cooling to 0 °C, 2-pentanone (12 mL, 110 mmol) was added to the reaction mixture and stirred for an hour at room temperature. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Yield: 15 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.90 (t, J = 7.3 Hz, 3H, CH_3), 1.26-1.39 (m, 2H, CH_2), 1.63 (s, 3H, CH_3), 1.78-1.86 (m, 2H, CH_2), 2.04 (s, 1H, OH), 6.90 (dd, J = 3.6, 1.0 Hz, 1H, Aromatic), 6.95 (dd, J = 5.0, 3.6 Hz, 1H, Aromatic), 7.19 (dd, J = 5.0, 1.0 Hz, 1H, Aromatic).

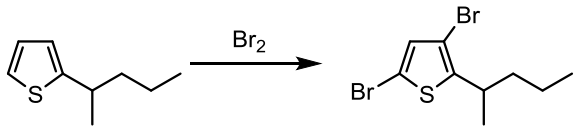
2-(2-Pentyl)thiophene (20)



19 **20**

Dry diethyl ether (90 mL) was added into a flask containing $AlCl_3$ (40 g, 300 mmol) under argon atmosphere at 0 °C. $LiAlH_4$ (5.6 g, 150 mmol) was added to the solution and 2-(2-hydroxy-2-pentyl)thiophene (**19**) (15 g, 80 mmol) in dry diethyl ether (120 mL) was slowly added into the reaction mixture. After refluxed for 1.5 h, the solution was quenched with water. The residue was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Yield: 14 g (100%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.89 (t, J = 7.3 Hz, 3H, CH_3), 1.24-1.35 (m, 5H, CH_2 and CH_3), 1.52-1.64 (m, 2H, CH_2), 2.97-3.09 (sext, J = 6.9 Hz, 1H, CH), 6.79 (d, J = 3.4 Hz, 1H, Aromatic), 6.92 (dd, J_1 = 5.1 Hz, J_2 = 3.4 Hz, 1H, Aromatic), 7.11 (dd, J_1 = 5.1 Hz, J_2 = 1.1 Hz, 1H, Aromatic)

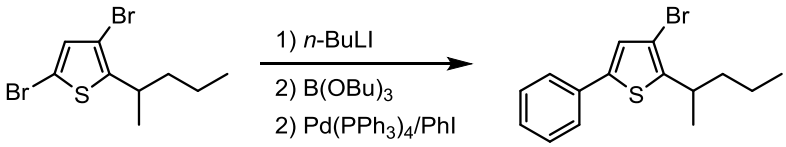
3,5-dibromo-2-(2-pentyl)thiophene (21)



20 **21**

Bromine (10 mL, 200 mmol) was added into 2-(2-pentyl)thiophene (**20**) (14 g, 90 mmol) in acetic acid (79 mL) containing water (4 mL). The reaction mixture was stirred in water bath overnight. The mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane as the eluent. Yield: 16 g (55%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.90 (t, *J* = 7.3 Hz, 3H, CH_3), 1.23 (d, *J* = 6.9 Hz, 3H, CH_3), 1.27-1.39 (m, 2H, CH_2), 1.55 (q, *J* = 7.5 Hz, 2H, CH_2), 3.19 (sext, *J* = 6.9 Hz, 1H, CH), 6.84 (s, 1H, Aromatic)

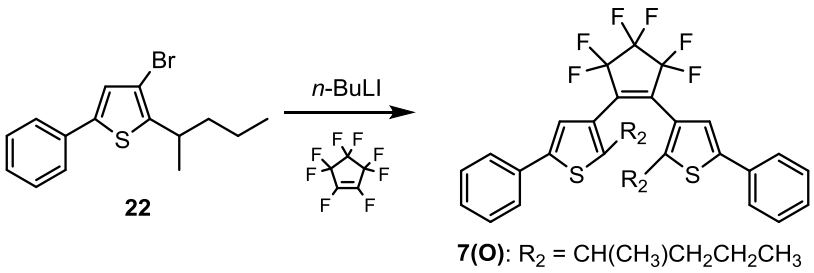
3-Bromo-2-(2-pentyl)-5-phenylthiophene (22)



21 **22**

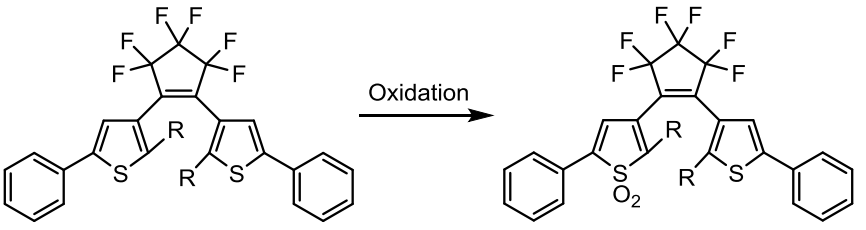
3,5-Dibromo-2-(2-pentyl)thiophene (**21**) was added into a flask containing dry THF (140 mL) under atmosphere. 1.6 M *n*-BuLi/hexane solution (20 mL, 31 mmol) was slowly added into the solution at −78 °C and stirred for an hour. Tri-*n*-butyl borate (11 mL, 42 mmol) was added to the mixture and stirred for an hour. After warming up room temperature, 20 wt% Na_2CO_3aq 60 mL, $Pd(PPh_3)_4$ (0.62 g, 0.54 mmol), and iodobenzene (4.6 g, 23 mmol) was added to the reaction mixture and refluxed for 10 h. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 5.7 g (66%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.92 (t, *J* = 7.3 Hz, 3H, CH_3), 1.30 (d, *J* = 6.9 Hz, 3H, CH_3), 1.32-1.43 (m, 2H, CH_2), 1.58-1.67 (m, 2H, CH_2), 3.22 (sext, *J* = 6.9 Hz, 1H, CH), 7.10 (s, 1H, Aromatic), 7.24-7.30 (m, 1H, Aromatic), 7.33-7.39 (m, 2H, Aromatic), 7.50-7.54 (m, 2H, Aromatic)

1,2-Bis(2-(2-pentyl)-5-phenyl-3-thienyl)perfluorocyclopentene (7a(O))



1.6 M *n*-BuLi/hexane solution (13 mL, 20 mmol) was slowly added into 3-bromo-2-(2-pentyl)-5-phenylthiophene (**22**) (5.7 g, 18 mmol) in dry THF (85 mL) at −78 °C under argon atmosphere, and the reaction mixture was stirred for an hours. Octafluorocyclopentene (1.1 mL, 8.2 mmol) was slowly added to the reaction mixture and stirred for 2 h. The mixture was quenched by water and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 1.4 g (24%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.63-0.88 (m, 12H, CH_3), 0.98-1.14 (m, 4H, CH_2), 1.25-1.48 (m, 4H, CH_2), 2.53-2.65 (m, 2H, CH), 7.22 (s, 2H, Aromatic), 7.28-7.33 (m, 2H, Aromatic), 7.37-7.42 (m, 4H, Aromatic), 7.55-7.58 (m, 4H, Aromatic). MS (FAB) *m*/*z* = 632.1998 ($[M]^+$). Calcd for $C_{35}H_{34}F_6S_2$ = 632.2006.

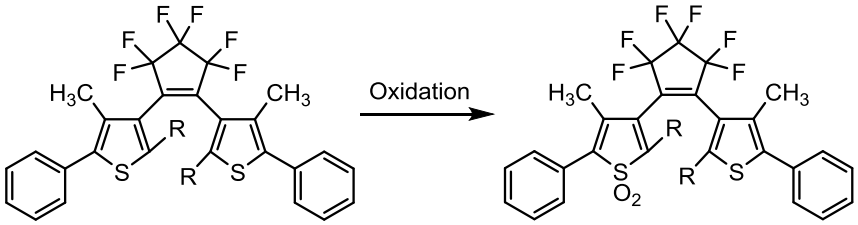
1-(1,1-Dioxide-2-(2-pentyl)-5-phenyl-3-thienyl)-2-(2-(2-pentyl)-5-phenyl-3-thienyl)-perfluorocyclopentene (7b(O))



m-Chloroperoxybenzoic acid (0.97 g, 4.0 mmol) was added to the dichloromethane (35 mL) solution containing **7a(O)** (1.0 g, 1.6 mmol). The mixture was stirred at room temperature for 48 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 9 : 1). Yield: 0.36 g (34%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.68-1.54 (m, 20H,

alkyl), 2.50-2.68 (m, 2H, CH), 7.86-7.88 (m, 1H, Aromatic), 7.16-7.18 (m, 1H, Aromatic), 7.30-7.48 (m, 6H, Aromatic), 7.55-7.58 (m, 2H, Aromatic), 7.68-7.74 (m, 2H, Aromatic). MS (FAB) *m*/*z* = 665.1990 ($[M + H]^+$). Calcd for $C_{35}H_{35}F_6O_2S_2$ = 665.1983.

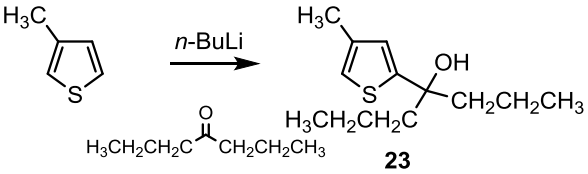
1-(1,1-Dioxide-2-isopropyl-4-methyl-5-phenyl-3-thienyl)-2-(2-isopropyl-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (9b(O))



9a(O): $R_2 = CH(CH_3)_2$ **9b(O)**: $R = CH(CH_3)_2$

m-Chloroperoxybenzoic acid (0.15 g, 0.62 mmol) was added to the dichloromethane (10 mL) solution containing **9a(O)** (0.15 g, 0.25 mmol). The mixture was stirred at room temperature for 24 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 95 : 5). Yield: 99 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.03-1.53 (m, 12H, CH_3), 1.86-2.16 (m, 6H, CH_3), 2.73-3.04 (m, 2H, CH), 7.35-7.52 (m, 10H, Aromatic). MS (FAB) *m*/*z* = 637.1672 ($[M + H]^+$). Calcd for $C_{33}H_{31}F_6O_2S_2$ = 637.1670.

2-(4-Hydroxy-4-heptyl)-4-methylthiophene (23)

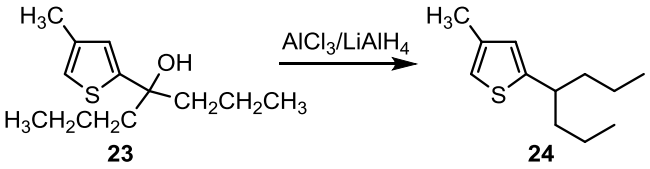


23

3-Methylthiophene (7.7 g, 78 mmol) was stirred into dry diethyl ether (70 mL). 1.6 M *n*-BuLi/hexane solution (54 mL, 86 mmol) was slowly added into the solution at 0 °C and refluxed for an hour. After cooling to 0 °C, 4-heptanone (12 mL, 86 mmol) was added to the reaction mixture and stirred for an hour at room temperature. The product was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered and concentrated. Yield: 19 g (100%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.90 (t, *J* = 7.3 Hz, 6H, CH_3), 1.19-1.43 (m, 4H, CH_2), 1.72-1.84 (m, 4H,

CH_2), 2.22 (s, 3H, CH_3), 6.66 (s, 1H, Aromatic), 6.75 (s, 1H, Aromatic)

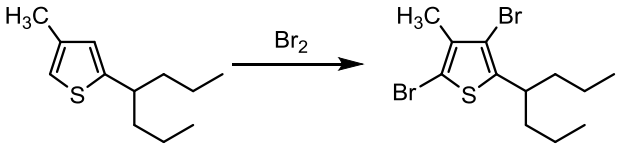
2-(4-Heptyl)-4-methylthiophene (24)



23 **24**

Dry diethyl ether (100 mL) was added into a flask containing $AlCl_3$ (44 g, 320 mmol) under argon atmosphere at 0 °C. $LiAlH_4$ (6.3 g, 160 mmol) was added to the solution and 2-(4-hydroxy-4-heptyl)-4-methylthiophene (**23**) (19 g, 88 mmol) in dry diethyl ether (130 mL) was slowly added at the reaction mixture. After refluxed for an hour, the solution was quenched with water. The residue was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Yield: 15 g (85%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.86 (t, *J* = 7.3 Hz, 6H, CH_3), 1.25 (sext, *J* = 7.3 Hz, 4H, CH_2), 1.43-1.65 (m, 4H, CH_2), 2.21 (s, 3H, CH_3), 2.73-2.82 (m, 1H, CH), 6.56 (s, 1H, Aromatic), 6.68 (s, 1H, Aromatic)

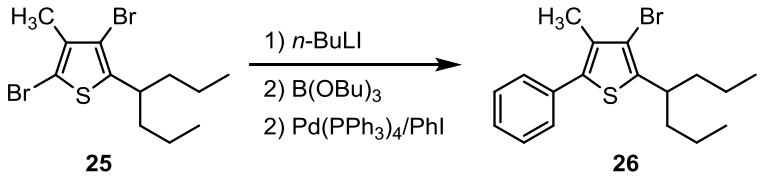
3,5-Dibromo-2-(4-heptyl)-4-methylthiophene (25)



24 **25**

Bromine (8.4 mL, 160 mmol) was added dropwise into 2-(4-heptyl)-4-methylthiophene (**24**) (15 g, 75 mmol) in acetic acid (65 mL) containing water (4 mL). The reaction mixture was stirred in water bath overnight. The mixture was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane as the eluent. Yield: 20 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.84-0.90 (m, 6H, CH_3), 1.20-1.35 (m, 4H, CH_2), 1.37-1.67 (m, 4H, CH_2), 2.18 (s, 3H, CH_3), 3.12-3.21 (m, 1H, CH).

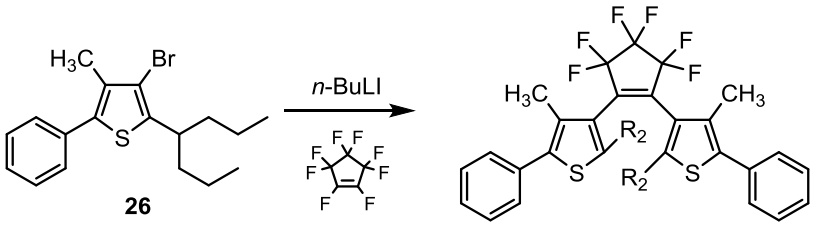
3-Bromo-2-(4-heptyl)-4-methyl-5-phenylthiophene (26)



25 **26**

3,5-Dibromo-2-(4-heptyl)-4-methylthiophene (**25**) (20 g, 57 mmol) was added into a flask containing dry THF (290 mL) under atmosphere. 1.6 M *n*-BuLi/hexane solution (40 mL, 63 mmol) was slowly dropped into the solution at −78 °C and stirred for an hour. Tri-*n*-butyl borate (23 mL, 85 mmol) was added to the mixture and stirred for an hour. After warming up room temperature, 20 wt% Na_2CO_3aq 110 mL, $Pd(PPh_3)_4$ (0.95 g, 0.83 mmol), and iodobenzene (5.4 mL, 47 mmol) were added to the reaction mixture, and the solution was refluxed overnight. The product was execrated with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 7.4 g (37%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.86-0.92 (m, 6H, CH_3), 1.26-1.38 (m, 4H, CH_2), 1.50-1.69 (m, 4H, CH_2), 2.28 (s, 3H, CH_3), 3.16-3.26 (m, 1H, CH), 7.29-7.44 (m, 5H, Aromatic).

1,2-Bis(2-(4-heptyl)-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (10a(O))

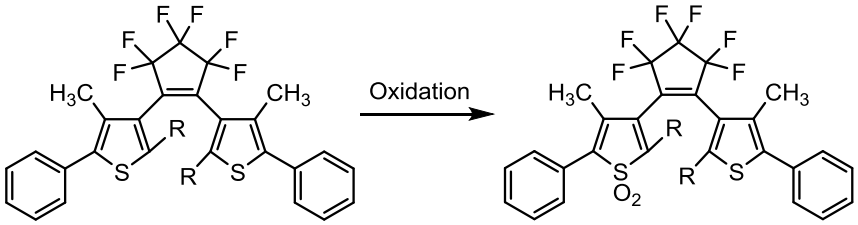


26 **10a(O)**: R_2 = $CH(CH_2CH_2CH_3)_2$

1.6 M *n*-BuLi/hexane solution (15 mL, 25 mmol) was slowly added to dry THF (90 mL) containing 3-bromo-2-(4-heptyl)-4-methyl-5-phenylthiophene (**26**) (7.4 g, 21 mmol) at −78 °C under argon atmosphere and stirred an hours. Octafluorocyclopentene (1.4 mL, 10 mmol) was slowly added to the reaction mixture and stirred an hour. The mixture was quenched with water and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel using hexane as the eluent. Yield: 0.86 g (23%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.63-1.60 (m, 28H, CH_2 and CH_3), 2.28 (d, *J* = 5.3 Hz, 6H, CH_3), 2.52-2.61 (m, 2H, CH), 7.28-7.42 (m, 10H, Aromatic). MS (FAB) *m*/*z* = 716.2944 (M^+). Calcd for

$C_{41}H_{46}F_6S_2$ = 716.2945.

1-(1,1-Dioxide-2-(4-heptyl)-4-methyl-5-phenyl-3-thienyl)-2-(2-(4-heptyl)-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (10b(O))



10a(O): R_2 = $CH(CH_2CH_2CH_3)_2$ **10b(O)**: R = $CH(CH_2CH_2CH_3)_2$

m-Chloroperoxybenzoic acid (0.17 g, 0.70 mmol) was added to the dichloromethane (10 mL) solution containing **10a(O)** (0.20 g, 0.28 mmol). The mixture was stirred at room temperature for 24 h. The solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate = 85 : 15). Yield: 54 mg (26%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.63-0.90 (m, 12H, CH_3), 1.14-1.74 (m, 16H, CH_2), 2.14 (d, *J* = 4.9 Hz, 3H, CH_3), 2.23 (d, *J* = 5.3 Hz, 3H, CH_3), 2.36-2.46 (m, 1H, CH), 2.50-2.59 (m, 1H, CH), 7.32-7.58 (m, 10H, Aromatic). MS (FAB) *m*/*z* = 748.2833 (M^+). Calcd for $C_{41}H_{46}F_6O_2S_2$ = 748.2843.

References

S1 M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.*, 2000, **122**, 4871−4876.

S2 S. Kobatake, K. Shibata, K. Uchida, M. Irie, *J. Am. Chem. Soc.*, 2000, **122**, 12135−12141 (2000).

S3 D. Kitagawa, K. Sasaki, S. Kobatake, *Bull. Chem. Soc. Jpn.*, 2000, **84**, 141−147.

S4 S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Lett.*, 2000, **29**, 1340−1341.

S5 H. Shoji, S. Kobatake, *Chem. Commun.*, 2013, **49**, 2362−2364.

S6 K. Uchida, D. Guillaumont, E. Tsuchida, G. Mochizuki, M. Irie, S. Nakamura, *J. Mol. Struct. (Theochem)*, 2002, **579**, 115−120.