Supplementary Material

Photoswitchable Fluorescent Diarylethene Derivatives with Thiophene 1,1-Dioxide Groups: Effect of Alkyl Substituents at the Reactive Carbons

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| Solvent         | 1b  | 2b  | 3b  | 4b  | 5b  |
|-----------------|-----|-----|-----|-----|-----|
| n-Hexane (εr = 1.89) | 0.31| 0.54| 0.53| 0.38| 0.55|
| 1,4-Dioxane (εr = 2.22) | 0.07| 0.42| 0.42| 0.42| 0.50|
| 2MeTHF (εr = 6.97)   | 0.04| 0.30| 0.30| 0.35| 0.35|
| 2-Propanol (εr = 20.1) | 0.03| 0.25| 0.23| 0.34| 0.28|
| Ethanol (εr = 25.3)  | 0.02| 0.18| 0.19| 0.32| 0.27|
Scheme S1. Syntheses of compounds 2a–5a.
2f
To a dry THF solution (110 mL) containing 2e [S1] (3.0 g, 11 mmol) was slowly added 1.6 M n-BuLi hexane solution (7.6 mL, 12 mmol) at −78°C under a nitrogen atmosphere and the mixture was stirred for 15 min at that temperature. A dry THF solution (10 mL) containing octafluorocyclopentene (0.83 mL, 6.2 mmol) was slowly added at −78°C and the mixture was stirred overnight at that temperature. The reaction was stopped by adding water. The resulting mixture was extracted with ethyl acetate and the organic layer was washed with brine, dried over MgSO4, filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 2f (1.1 g, 35%).

1H NMR (400 MHz, CDCl3, TMS) δ 0.92 (t, 3H, J = 7.6 Hz), 1.02 (t, 3H, J = 7.6 Hz), 2.08 (d, 3H, J = 1.6 Hz), 2.16 (d, 3H, J = 2.4 Hz), 2.41-2.73 (m, 4H), 7.27-7.43 (m, 10H); MS (EI) m/z 576 [M]+.

2a
To a CH2Cl2 solution (30 mL) containing 2f (43 mg, 0.075 mmol) was added 77% m-chloroperbenzoic acid (0.51 g, 2.3 mmol) and the mixture was stirred for 4 days at room temperature. The resulting mixture was treated with aqueous Na2S2O3 and extracted with CHCl3. The organic layer was washed with brine, dried over MgSO4, filtrated, and concentrated. The residue was purified by preparative thin-layer silica gel column chromatography (hexane : ethyl acetate = 3 : 1) to give 2a (27 mg, 56%).

1H NMR (400 MHz, CDCl3, TMS) δ 1.38-1.43 (m, 6H), 1.89 (s, 4H), 1.97 (s, 2H), 2.47-2.74 (m, 4H), 7.44-7.55 (m, 10H); MS (EI) m/z 640 [M]+.
**4-Methyl-2-propylthiophene (3c)**

To a dry THF solution (180 mL) containing di-sec-butylamine (9.8 mL, 57 mmol) and \(N,N,N',N'-\)tetramethylethylenediamine (8.5 mL, 57 mmol) was slowly added 1.6 M \(n\)-BuLi hexane solution (36 mL, 58 mmol) at \(-78^\circ\)C under a nitrogen atmosphere and the mixture was stirred for 30 min at that temperature. After warmed up to 0°C, the mixture was stirred for 30 min. After cooled down to \(-78^\circ\)C again, 3-methylthiophene (5.0 mL, 52 mmol) was slowly added and the mixture was stirred for 1 hour. 1-Iodopropane (5.6 mL, 57 mmol) was slowly added and the mixture was stirred for 30 min. After warmed up to room temperature, the mixture was stirred for 16 hours and then dilute HCl was added. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 3c (4.3 g, 59%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) 0.97 (t, 3H, \(J = 7.6\) Hz), 1.67 (sext, 2H, \(J = 7.6\) Hz), 2.73 (t, 2H, \(J = 7.6\) Hz), 6.58 (s, 1H), 6.66 (m, 1H); MS (EI) \(m/z\) 140 \([\text{M}]^+\).

**2,4-Dibromo-3-methyl-5-propylthiophene (3d)**

To a THF solution (200 mL) containing 3c (4.2 g, 30 mmol) was added \(N\)-bromosuccinimide (12 g, 67 mmol) at 0°C and the mixture was stirred overnight. The resulting mixture was treated with aqueous Na\(_2\)S\(_2\)O\(_3\) and extracted with ethyl acetate. The organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 3d (6.3 g, 70%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) 0.98 (t, 3H, \(J = 7.6\) Hz), 1.65 (sext, 2H, \(J = 7.6\) Hz), 2.73 (t, 2H, \(J = 7.6\) Hz), 6.58 (s, 1H), 6.66 (m, 1H); MS (EI) \(m/z\) 296 [M]+, 298 [M+2]+, 300 [M+4]+.

**3-Bromo-4-methyl-5-phenyl-2-propylthiophene (3e)**

To a dry THF solution (250 mL) containing 3d (9.0 g, 30 mmol) and tributyl borate (8.9 mL, 33 mmol) was slowly added 1.6 M \(n\)-BuLi hexane solution (21 mL, 34 mmol) at \(-78^\circ\)C under a nitrogen atmosphere and the mixture was stirred for 1 hour at that temperature. After warmed up to \(-20^\circ\)C, dilute HCl was added. After warmed up to room temperature, Pd(PPh\(_3\))\(_4\) (1.7 g, 1.5 mmol), iodobenzene (3.7 mL, 33 mmol), and saturated aqueous K\(_2\)CO\(_3\) (30 mL) was added and the mixture was refluxed for 7 hours. The resulting mixture was extracted with ethyl acetate and the organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 3e (6.4 g, 73%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) 1.02 (t, 3H, \(J = 7.6\) Hz), 1.71 (sext, 2H, \(J = 7.6\) Hz), 2.27 (s, 3H), 2.79 (t, 2H, \(J = 7.6\) Hz), 7.31-7.41 (m, 5H); MS (EI) \(m/z\) 294 [M]+, 296 [M+2]+.
3f
To a dry THF solution (70 mL) containing 3e (2.0 g, 6.8 mmol) was slowly added 1.6 M n-BuLi hexane solution (4.7 mL, 7.5 mmol) at –78°C under a nitrogen atmosphere and the mixture was stirred for 10 min at that temperature. A dry THF solution (10 mL) containing octafluorocyclopentene (0.54 mL, 4.0 mmol) was slowly added at –78°C and the mixture was stirred overnight at that temperature. The reaction was stopped by adding water. The resulting mixture was extracted with ethyl acetate and the organic layer was washed with brine, dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 3f (1.0 g, 49%).

1H NMR (400 MHz, CDCl₃, TMS) δ 0.92 (t, 3H, J = 7.6 Hz), 1.02 (t, 3H, J = 7.6 Hz), 1.46-1.77 (m, 4H), 2.08 (d, 3H, J = 1.6 Hz), 2.16 (d, 3H, J = 2.8 Hz), 2.41-2.72 (m, 4H), 7.27-7.42 (m, 10H); MS (EI) m/z 604 [M]+.

3a
To a CH₂Cl₂ solution (250 mL) containing 3f (1.4 g, 2.3 mmol) was added 77% m-chloroperbenzoic acid (12 g, 53 mmol) and the mixture was stirred for 3 days at room temperature. The resulting mixture was treated with aqueous Na₂S₂O₃ and extracted with CHCl₃. The organic layer was washed with aqueous NaOH and brine, dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography (CHCl₃) to give 3a (1.0 g, 65%).

1H NMR (400 MHz, CDCl₃, TMS) δ 1.01-1.06 (m, 6H), 1.72-2.04 (m, 4H), 1.89 (s, 3.8H), 1.95 (s, 2.2H), 2.27-2.66 (m, 4H), 7.43-7.55 (m, 10H); MS (EI) m/z 668 [M]+.

4a
To a CH₂Cl₂ solution containing 4f [S2] (0.53 g, 0.88 mmol) was added 77% m-chloroperbenzoic acid (4.0 g, 18 mmol) and the mixture was stirred for 3 days at room temperature. The resulting mixture was treated with aqueous K₂CO₃ and aqueous Na₂S₂O₃ and extracted with CHCl₃. The organic layer was washed with brine, dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography (CHCl₃) to give 2a (32 mg, 5%).

1H NMR (400 MHz, CDCl₃, TMS) δ 1.39 (d, 5H, J = 6.8 Hz), 1.47 (d, 5H, J = 6.8 Hz), 1.51 (d, 2H, J = 6.8 Hz), 1.93 (d, 1.5H, J = 2.4 Hz), 2.02 (d, 4.5H, J = 3.2 Hz), 2.74-2.81 (m, 2H), 7.46-7.55 (m, 10H); MS (EI) m/z 668 [M]+.
2-Isobutyl-4-methylthiophene (5c)
To a dry THF solution (180 mL) containing di-sec-butylamine (9.8 mL, 57 mmol) and \(N,N,N',N'-\)tetramethylethylenediamine (8.5 mL, 57 mmol) was slowly added 1.6 M \(n\)-BuLi hexane solution (36 mL, 58 mmol) at \(-78^\circ\)C under a nitrogen atmosphere and the mixture was stirred for 1 hour at that temperature. 3-Methylthiophene (5.0 mL, 52 mmol) was slowly added and the mixture was stirred for 1 hour. 1-Iodo-2-methylpropane (7.4 mL, 64 mmol) was slowly added and the mixture was stirred for 1 hour. After warmed up to room temperature, the mixture was stirred overnight and then dilute HCl was added. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 5c (2.3 g, 29%).

\[\text{1H NMR (400 MHz, CDCl}_3, \text{TMS}) \delta 0.94 (d, 6H, } J = 7.6 \text{ Hz), 1.86 (m, 1H), 2.21 (s, 3H), 2.62 (dd, 2H, } J = 7.2 \text{ Hz, 0.8 Hz), 6.56 (s, 1H), 6.67 (m, 1H); MS (EI) } m/z 154 [M]^+.\]

2,4-Dibromo-5-isobutyl-3-methylthiophene (5d)
To a THF solution (140 mL) containing 5c (2.1 g, 14 mmol) was added \(N\)-bromosuccinimide (5.3 g, 30 mmol) at 0°C and the mixture was stirred overnight. The resulting mixture was treated with aqueous Na\(_2\)S\(_2\)O\(_3\) and extracted with ethyl acetate. The organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 5d (1.6 g, 36%).

\[\text{1H NMR (400 MHz, CDCl}_3, \text{TMS}) \delta 0.95 (d, 6H, } J = 6.8 \text{ Hz), 1.92 (m, 1H), 2.18 (s, 3H), 2.62 (d, 2H, } J = 7.2 \text{ Hz); MS (EI) } m/z 310 [M]^+, 312 [M+2]^+, 314 [M+4]^+.\]

3-Bromo-2-isobutyl-4-methyl-5-phenylthiophene (5e)
To a dry THF solution (45 mL) containing 5d (1.4 g, 4.5 mmol) and tributyl borate (1.2 mL, 4.5 mmol) was slowly added 1.6 M \(n\)-BuLi hexane solution (3.1 mL, 5.0 mmol) at \(-78^\circ\)C under a nitrogen atmosphere and the mixture was stirred for 1 hour at that temperature. After warmed up to room temperature, dilute HCl was added. Pd(PPh\(_3\))\(_4\) (0.26 g, 0.22 mmol), iodobenzene (0.50 mL, 4.5 mmol), and saturated aqueous K\(_2\)CO\(_3\) (20 mL) was added and the mixture was refluxed for 7 hours. The resulting mixture was extracted with ethyl acetate and the organic layer was washed with brine, dried over MgSO\(_4\), filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 5e (0.73 g, 53%).

\[\text{1H NMR (400 MHz, CDCl}_3, \text{TMS}) \delta 1.00 (d, 6H, } J = 6.8 \text{ Hz), 2.00 (m, 1H), 2.27 (s, 3H), 2.71 (d, 2H, } J = 7.2 \text{ Hz), 7.29-7.42 (m, 5H); MS (EI) } m/z 308 [M]^+, 310 [M+2]^+.\]
**5f**

To a dry THF solution (20 mL) containing 5e (0.60 g, 1.9 mmol) was slowly added 1.6 M n-BuLi hexane solution (1.3 mL, 2.1 mmol) at –78°C under a nitrogen atmosphere and the mixture was stirred for 15 min at that temperature. A dry THF solution (5 mL) containing octafluorocyclopentene (0.14 mL, 1.0 mmol) was slowly added at –78°C and the mixture was stirred for 1 hour at that temperature. After warmed up to room temperature, the mixture was stirred for 5 hours. The reaction was stopped by adding water. The resulting mixture was extracted with diethyl ether and the organic layer was washed with brine, dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give 5f (0.20 g, 34%).

1H NMR (400 MHz, CDCl₃, TMS) δ 0.86 (m, 7H), 0.95 (d, 3H, J = 6.8 Hz), 1.04 (d, 2H, J = 6.8 Hz), 1.82-2.01 (m, 2H), 2.05-2.07 (m, 2.6H), 2.20-2.30 (m, 4.5H), 2.38-2.60 (m, 2.9H), 7.28-7.45 (m, 10H); MS (EI) m/z 632 [M]+.

**5a**

To a CH₂Cl₂ solution (25 mL) containing 5f (0.16 g, 0.25 mmol) was added 77% m-chloroperbenzoic acid (1.7 g, 7.6 mmol) and the mixture was stirred for 2 days at room temperature. The resulting mixture was treated with aqueous K₂CO₃ and aqueous Na₂S₂O₃ and extracted with CHCl₃. The organic layer was washed with brine, dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography (CHCl₃) and HPLC (Wakosil 5SIL φ20 mm × 250 mm, hexane : ethyl acetate = 9 : 1, 10 mL/min, 313 nm) to give 5a (0.10 g, 56%).

1H NMR (400 MHz, CDCl₃, TMS) δ 0.97-1.08 (m, 12H), 1.92 (d, 3H, J = 2.0 Hz), 1.97 (d, 3H, J = 1.6 Hz), 2.03-2.21 (m, 2H), 2.44-2.75 (m, 4H), 7.45-7.55 (m, 10H); MS (EI) m/z 696 [M]+.