Three-State Photochromic Switching in a Silyl Bridged Diarylethene Dimer

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Materials. All solvents employed were of UVASOL grade or better and used as received unless stated otherwise. Aldrich silica gel Merck grade 935 (2300-400 mesh) used for column chromatography and Sigma-Aldrich preparative TLC plates (20x20 cm², 2000 µm) with fluorescent indicator were used. All reagents employed in synthetic procedures were of reagent grade or better and were also used as received unless stated otherwise. 5-Chloro-3-(2-(5-chloro-2-methylthiophene-3-yl)cyclopent-1-enyl)-2-methylthiophene (5Ho), 5-chloro-3-(2-(5-chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2-methylthiophene (5Fo), 3-(2-(5-chloro-2-methylthiophene-3-yl)-cyclopent-1-enyl)-5-(phenyl)-2-methylthiophene (4Ho) and 3-(2-(5-chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-5-(phenyl)-2-methylthiophene (4Fo) were prepared following our reported procedures.¹

UV-Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Electro-spray ionization mass spectra were recorded on a Triple Quadrupole LC/MS/MS Mass spectrometer (API 3000, Perkin-Elmer Sciex Instruments). A sample (2 µl) was taken from the reaction mixture at the indicated times (vide infra) and was diluted in CH₃CN (1 ml) before injection in the mass spectrometer (via syringe pump). Mass spectra were measured in positive mode and in the range of m/z 100-1500. Ion-spray voltage: 5200 V, orifice: 15 V, ring: 150 V, Q0: -10 V. ¹H-(400.0 MHz) and ¹³C-NMR (100.6 MHz) spectra were recorded on a Varian Mercury Plus. Chemical shifts are denoted relative to the solvent residual peak (¹H: CDCl₃ 7.26 ppm; ¹³C: CDCl₃ 77 ppm). HPLC was performed on Shimadzu LC-20 equipped with a Whelk-01 column.
Synthesis spectroscopic and analytical data

5-Chloro-3-(2-(5-(4-methoxyphenyl)-2-methylthiophene-3-yl)cyclopent-1-enyl)-2-methylthiophene (6Ho). To a solution of 5-chloro-3-(2-(5-chloro-2-methylthiophene-3-yl)cyclopent-1-enyl)-2-methylthiophene (5Ho) (3.01 g, 9.18 mmol) in THF (100 ml) was added n-BuLi (5.74 ml, 1.6 M in hexane, 9.18 mmol) under nitrogen atmosphere. After 1 h, B(OBu)₃ (3.71 ml, 13.7 mmol) was added and the mixture was stirred for 1 h at room temperature. A separate flask was charged with p-iodoanisole (2.14 g, 9.18 mmol), [Pd(PPh₃)₄] (0.31 g, 0.27 mmol), THF (25 ml), aqueous Na₂CO₃ (2 M, 20 ml) and ethylene glycol (20 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly. The reaction mixture was heated a reflux overnight, cooled to room temperature, diluted with diethyl ether (200 ml) and washed with H₂O (200 ml). The aqueous layer was extracted with diethyl ether (200 ml) and washed with H₂O (200 ml). The combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford (6Ho) as a viscous oil (2.28 g, 62%).

¹H NMR (400 MHz, CDCl₃) δ 1.92 (s, 3H), 2.01 (s, 3H), 2.03-2.11 (m, 2H), 2.74-2.85 (m, 4H), 3.83 (s, 3H), 6.66 (s, 1H), 6.90 (s, 1H), 6.91 (d, J=8.8 Hz, 2H), 7.45 (d, J=8.79 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.12 (q), 14.26 (q), 22.84 (t), 38.27 (t), 38.39 (t), 55.22 (q), 114.11 (d), 122.62 (d), 124.82 (d), 126.47 (d), 126.76 (d), 127.22 (s), 133.15 (s), 133.31 (s), 133.45 (s), 135.10 (s), 135.31 (s), 136.11 (s), 139.64 (s), 158.78 (s). EI-MS (m/z): 400 (M⁺, 100); HRMS (m/z), 400.0721, calcd 400.0722.
(4-(2-(5-(4-Methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)trimethylsilane (1Ho). To a solution of 6Ho (0.40 g, 1 mmol) in THF (5 ml) was added t-BuLi (0.94 ml, 1.6 M in hexane, 1.5 mmol) at 0°C under nitrogen atmosphere. The mixture was stirred for 1 h at room temperature. Trimethylsilylchloride (0.25 ml, 2 mmol) was added slowly and the reaction mixture was stirred for 2-3 h. Subsequently the mixture was quenched with saturated aq. NH₄Cl (10 ml). The organic layer was separated and the aqueous layer extracted with diethyl ether (2x10 ml). The organic layers were combined and dried over Na₂SO₄. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford (1Ho) as a viscous oil (0.33 g, 74%).

1H-NMR (CDCl₃, 400 MHz) δ: 0.27 (s, 9H), 1.93 (s, 3H), 2.06 (s, 3H), 2.10 (m, 2H), 2.84 (t, J=7.33 Hz, 4H), 3.83 (s, 3H), 6.85 (s, 1H), 6.87 (s, 1H), 6.91 (d, J= 9.10Hz, 2H), 7.41 (d, J=8.80 Hz, 2H); 13C NMR (100 MHz, CDCl₃) δ: -0.12 (q), 14.09 (q), 14.25(q), 23.08 (t), 38.24 (t), 38.27 (t), 55.29 (q), 114.11 (d), 123.11 (d), 126.54 (d), 127.52 (s), 133.32 (s), 134.38 (s), 134.76 (s), 135.40 (d), 135.71 (s), 136.50 (s), 137.26 (s), 139.26 (s), 140.05 (s), 158.74 (s); EI-MS (m/z): 438 (M⁺, 100); HRMS (m/z), 438.1524, calcd 438.1507.

(3-(2-(4-(4-Methoxyphenyl)-2-methylcyclopenta-1,4-dienyl)cyclopent-1-enyl)-4-methylcyclopenta-1,3-dienyl)(4-(2-(5-(4-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5methylthiophen-2-yl)dimethylsilane (2H(O-O)). Compound
6Ho (0.83 g, 2.07 mmol) was dissolved in anhydrous THF (15 ml) under nitrogen atmosphere and t-BuLi (2.07 ml, 1.5M in pentane, 3.1 mmol) was slowly added by syringe at 0 °C. The mixture was stirred for 1h at room temperature and dichlorodimethylsilane (0.13 ml, 1 mmol) was added dropwise. This solution was stirred for 2 h at room temperature. The reaction mixture was hydrolyzed with saturated aq. NH₄Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2), dried over Na₂SO₄, and the solvent evaporated. The product was purified by column chromatography on silica gel (heptane/ethyl acetate 9/1) to give (2H(O-O)) as a pink oil (0.34 g, 42%). ¹H NMR (400 MHz, CDCl₃) δ 0.47 (s, 6H), 1.88 (s, 6H), 2.00 (s, 6H), 2.03-2.06 (m, 4H), 2.77-2.82 (m, 8H), 3.77 (s, 6H), 6.82 (s, 2H), 6.85 (d, J=8.80 Hz, 4H), 6.95 (s, 2H), 7.37 (d, J=8.80 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ -0.25 (q), 14.16 (q), 14.30 (q), 23.04 (t), 38.30 (q), 53.30 (q), 114.12 (d), 123.04 (d), 126.55 (d), 127.51 (s), 133.26 (s), 133.35 (s), 134.52 (s), 134.60 (s), 136.45 (s), 136.71 (d), 137.43 (s), 139.33 (s), 141.05 (s), 158.76 (s); Maldi-TOF 788.4 (M⁺); Anal. calcd. for C₄₆H₄₈O₂S₄Si : C, 70.01, H, 6.13, S, 16.25. Found: C, 70.40, H, 6.52, S, 15.75

Photoisomer of 2(O-O) [2(C-O) and 2(C-C)]
A heptane solution of 2(O-O) was irradiated with 312 nm light until it reached the PSS. The compounds were separated by preparative thin layer chromatography (heptane:ethylacetate=95:5).

2(C-O)
Purple Solid: ¹H-NMR (CDCl₃, 400 MHz) δ: 0.44 (s, 3H), 0.45 (s, 3H), 1.81-1.85 (m, 2H), 1.86 (s, 3H), 1.89 (s, 3H), 1.94 (s, 3H), 2.02 (s, 3H), 2.04-2.08 (m, 2H), 2.36 (t, J=6.97, 7.33 Hz, 2H), 2.42 (t, J=7.33, 7.33 Hz, 2H), 2.82 (t, J=7.33, 7.33 Hz, 4H), 3.80 (s, 3H), 3.82 (s, 3H), 6.05 (s, 1H), 6.25 (s, 1H), 6.84 (s, 1H), 6.86 (d, J=8.69 Hz, 4H), 7.39 (d, J=9.16 Hz, 2H), 7.44 (d, J=8.80 Hz, 2H). ¹³C-NMR (CDCl₃, 100 MHz)
\( \delta \) -0.24, 14.17, 14.20, 14.30, 14.35, 23.05, 25.30, 38.29, 38.36, 55.32, 55.34, 113.85, 114.14, 114.16, 123.00, 123.04, 126.55, 126.57, 127.40, 127.50, 128.15, 130.87, 132.51, 133.26, 133.35, 134.53, 136.45, 136.71, 136.86, 137.43, 139.33, 141.04, 146.35, 158.76. Maldi-TOF 788.4 (M+)

![Chemical Structure](image)

**2(C-C)**

\(^1\)H-NMR (CDCl₃, 400 MHz) \( \delta \) 0.41 (s, 6H), 1.81-1.85 (m, 4H), 1.89 (s, 6H), 1.95 (s, 6H), 2.39-2.45 (m, 8H), 3.82 (s, 6H), 6.17 (s, 2H), 6.26 (s, 2H), 6.86 (d, \( J=8.79 \) Hz, 4H), 7.44 (d, \( J=8.80 \) Hz, 4H). \(^{13}\)C-NMR (CDCl₃, 100 MHz) \( \delta \) -2.79, 14.03, 23.09, 38.36, 55.35, 113.88, 114.17, 119.92, 126.54, 127.38, 128.68, 128.79, 130.87, 131.22, 134.47, 141.19, 141.64, 144.79, 146.44, 159.88. Maldi-TOF 788.5 (M+)

![Chemical Structure](image)

**3-(2-(5-Chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-
5-(4-methoxyphenyl)-2-methylthiophene (6Fo).** To a solution of 5-chloro-3-(2-(5-chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2-methylthiophene (5Fo) (1.2 g, 2.76 mmol) in Et₂O (50 ml) was added \( n \)-BuLi (2.0 ml, 1.6 M in hexane, 3.31 mmol) under nitrogen atmosphere. After 1h, B(OBu)₃ (1.12 ml, 4.14 mmol) was added and the mixture was stirred for 1 h at room temperature. A separate flask was charged with \( p \)-iodoanisole (1.94 g, 8.28 mmol), [Pd(PPh₃)₄] (95 mg, 0.082 mmol), THF (50 ml), aqueous Na₂CO₃ (2 M, 10 ml) and ethylene glycol
(10 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly. The reaction mixture was heated at reflux overnight, cooled to room temperature, diluted with diethyl ether (100 ml) and washed with H₂O (100 ml). The aqueous layer was extracted with diethyl ether (100 ml). The combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford 6Fo as a brown solid (0.91 g, 65%). M.p.= 112-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 1.89 (s, 3H), 1.96 (s, 3H), 3.84(s, 3H), 6.92 (d, J=8.8 Hz, 3H), 7.12(s, 1H), 7.49 (d, J=8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.33 (q), 14.43 (q), 55.35 (q), 114.38 (d), 121.01 (d), 124.39 (s), 125.38 (s), 125.65 (d), 126.02 (s), 126.89 (d), 127.66 (s), 140.26 (s), 140.45 (s), 142.39 (s), 159.55 (s). EI-MS (m/z): 508 (M⁺, 100); HRMS (m/z), 508.014, calcd 508.015.

Bis(4-(3,3,4,4,5,5-hexafluoro-2-(5-(4methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)dimethylsilane (2Fo). To a solution of 6Fo (0.22 g, 0.4 mmol) in Et₂O (10 ml) was added t-BuLi by syringe (0.44 ml, 1.5 M in hexane, 0.6 mmol) under nitrogen atmosphere at room temperature. The mixture was stirred for 1h at room temperature and dichlorodimethylsilane (40 µl, 0.33 mmol) was added dropwise. This solution was stirred for 2 h at room temperature. The reaction mixture was hydrolyzed with saturated aq. NH₄Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2). The organic layers were dried over Na₂SO₄, and the solvent evaporated. The product (2Fo) was purified by column chromatography on silica gel (heptane) to give compound as viscous oil (0.13 g, 59%). ¹H NMR (400 MHz, CDCl₃) δ 0.59 (s, 6H), 1.8 (s, 6H), 2.00 (s, 6H), 3.82 (s, 6H), 6.90 (d, J=8.80 Hz, 4H), 7.13 (s, 2H), 7.20 (s, 2H), 7.45 (d, J=8.43 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ -0.62 (q), 14.15 (q), 14.40 (q), 55.34 (q), 114.36 (d),
Dimethylbis(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopentenyl)thiophen-2-yl)silane (3H(O-O)). To a solution of 3-(2-(5-chloro-2-methylthiophene-3-yl)-cyclopent-1-enyl)-5-(phenyl)-2-methylthiophene (4H0). (0.40 g, 1.0 mmol) in Et2O (20 ml) was added t-BuLi by syringe (1.0 ml, 1.5 M in hexane, 1.5 mmol) under nitrogen atmosphere at room temperature. The mixture was stirred for 1h at room temperature and dichlorodimethylsilane (0.13 ml, 1.0 mmol) was added dropwise. This solution was stirred for 2 h at room temperature. The reaction mixture was hydrolyzed with saturated aq. NH4Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2), dried over Na2SO4, and the solvent evaporated. The product was purified by column chromatography on silica gel (heptane) to give 3H(O-O) as viscous oil (0.14 g, 37%). 1H NMR (400 MHz, CDCl3) δ 0.43 (s, 6H), 1.86 (s, 6H), 1.96 (s, 6H), 2.02 (m, 4H), 2.75 (m, 8H), 6.90 (s, 2H), 6.91 (s, 6H), 7.17 (m, 2H), 7.26 (t, J=7.32 Hz, 7.69 Hz, 4H), 7.41 (d, J=7.32 Hz, 4H); 13C NMR (100 MHz, CDCl3) δ -0.25 (q), 14.24 (q), 14.28 (q), 23.05 (t), 38.27 (t), 38.29 (t), 124.09 (d), 125.26 (d), 126.82 (d), 128.69 (d), 133.32 (s), 134.41 (s), 134.53 (s), 134.76 (s), 136.58 (s), 136.64 (d), 137.37 (s), 139.42 (s), 141.06 (s). EI-MS (M+): 728 (M+); Elemental analysis Found C 72.40, H 6.36, S 16.95 Calcd C 72.48, H 6.08, S 17.59
Bis(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)dimethylsilane (3Fo). To a solution of 3-(2-(5-chloro-2-methylthiophene-3-yl)-3,4,4,5,5-hexafluorocyclopent-1-enyl)-5-(phenyl)-2-methylthiophene (4Fo) (0.51 g, 1.0 mmol) in Et₂O (20 ml) was added t-BuLi by syringe (1.0 ml, 1.5 M in hexane, 1.5 mmol) under nitrogen atmosphere at room temperature. The mixture was stirred for 1h at room temperature and dichlorodimethylsilane (96 µl, 0.75 mmol) was added dropwise. Stirring for 2 h at room temperature where up the reaction mixture was hydrolyzed with saturated aq. NH₄Cl (15 ml), and the aqueous layer was extracted with diethyl ether (2x 20 ml), dried over Na₂SO₄, and the solvent evaporated. The product was purified by column chromatography on silica gel (heptane) to give 3F(O-O) as a viscous oil (0.18 g, 37%). ¹H NMR (400 MHz, CDCl₃) δ 0.59 (s, 6H), 1.86 (s, 6H), 1.99 (s, 6H), 7.20 (s, 2H), 7.24 (s, 2H), 7.30 (m, 2H), 7.37 (t, J=7.7, 7.7 Hz, 4H), 7.52 (d, J=7.7 Hz, 4H) ; ¹³C NMR (100 MHz, CDCl₃) δ -0.61 (q), 14.23 (q), 14.38 (q), 122.41 (d), 125.55 (d), 125.73 (s), 126.78 (s), 127.88 (d), 128.96 (d), 133.28 (s), 135.28 (d), 135.72 (s), 141.11 (s), 142.20 (s), 148.16 (s); Maldi-TOF (M⁺): 944.3
Spectroscopic and HPLC data

Figure S1. $^1$H NMR (400 MHz) spectra of a) 2H(O-O), b) 2H(C-O) and c) 2H(C-C) in CDCl$_3$. 
Figure S2 HPLC chromatograph of 2H(O-O) 4.5 min, 2H(C-O) 5.7 min, and 2H(C-C) 6.7 min, respectively. Whelk-01 column and isopropanol:heptane = 99.9:0.1 eluent.

Photochromism

Figure S3. UV.Vis spectral changes of 2H(C-C) upon irradiation with >455 nm light at 298 K in isomethylpentane to the fully open state 2H(C-C).
**Figure S4.** UV-Vis spectral changes a) $2\text{H(C-O)}$ to $2\text{H(O-O)}$ and b) $2\text{H(C-C)}$ to $2\text{H(O-O)}$ when irradiated with visible light $> 455$ nm; $2\times10^{-5}$ M in acetonitrile.

**Figure S5.** UV/VIS spectral changes of 1Ho upon irradiation with 312-nm light; $10^{-5}$ M in heptane.
**Figure S6.** UV/VIS spectral changes of $2\text{F(O-O)}$ upon irradiation with 312-nm light; $10^{-5}$ M in heptane.

**Figure S7.** UV/VIS spectral changes of $3\text{F(O-O)}$ upon irradiation with 312-nm light; $1.2 \times 10^{-5}$ M in heptane.
Figure S8. UV/VIS spectral changes of 3H(O-O) upon irradiation with 312-nm light; 2 x 10^{-5} M in heptane.