SUPPORTING INFORMATION

Three-State Photochromic Switching in a Silyl Bridged Diarylethene Dimer

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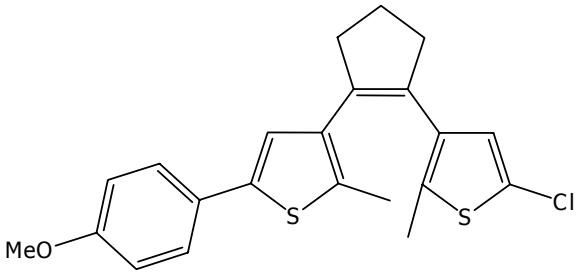
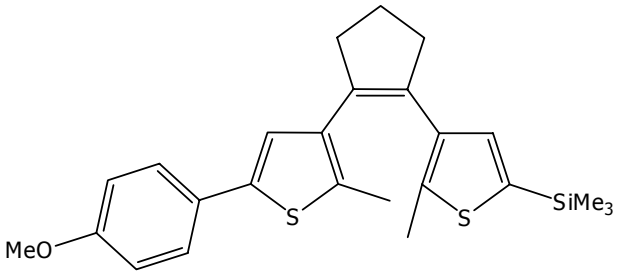
Materials. All solvents employed were of UVASOL grade or better and used as received unless stated otherwise. Aldrich silica gel Merck grade 935 (2300-400 mesh) used for column chromatography and Sigma-Aldrich preparative TLC plates (20x20 cm^2, 2000 μm) with fluorescent indicator were used. All reagents 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 CH_3CN (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. ^{1}H-(400.0 MHz) and ^{13}C-NMR (100.6 MHz) spectra were recorded on a Varian Mercury Plus. Chemical shifts are denoted relative to the solvent residual peak (^{1}H: $CDCl_3$ 7.26 ppm; ^{13}C: $CDCl_3$ 77 ppm). HPLC was performed on Shimadzu LC-20 equipped with a Whelk-01 column.

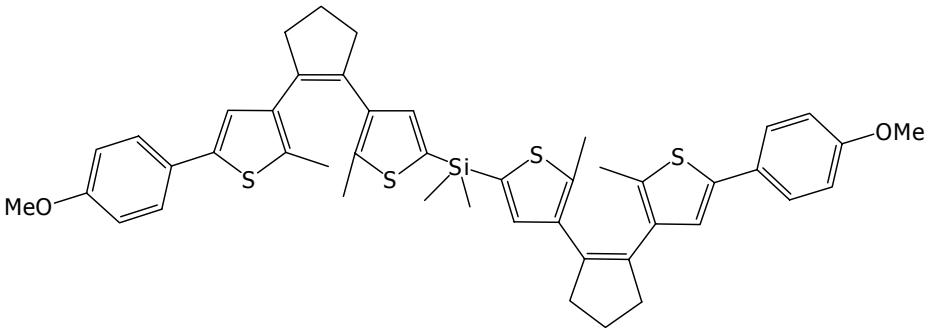
Synthesis spectroscopic and analytical data



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 1h, $B(OBu)_3$ (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), $[Pd(PPh_3)_4]$ (0.31 g, 0.27 mmol), THF (25 ml), aqueous Na_2CO_3 (2 M, 20 ml) and ethylene glycol (20 drops). The mixture was heated to 80 ^oC 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 H_2O (200 ml). The aqueous layer was extracted with diethyl ether (200 ml). The combined organic layer was dried over Na_2SO_4. 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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (s), 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^{o}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. NH_4Cl (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 Na_2SO_4. 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%). ^{1}H-NMR ($CDCl_3$, 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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.

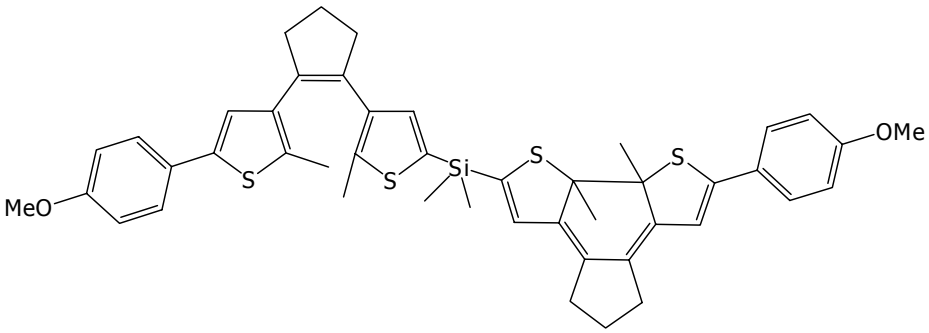


(3-(2-(4-(4-Methoxyphenyl)-2-methylcyclopenta-1,4-dienyl)cyclopent-1-enyl)-4-methylcyclopenta-1,3-dienyl)(4-(2-(5-(4-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5methylthiophen-2-yl)dimethylsilane (2H(O-O)). Compound

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 ^{o}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. NH_4Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2), dried over Na_2SO_4, 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{46}H_{48}O_2S_4Si$: 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)]

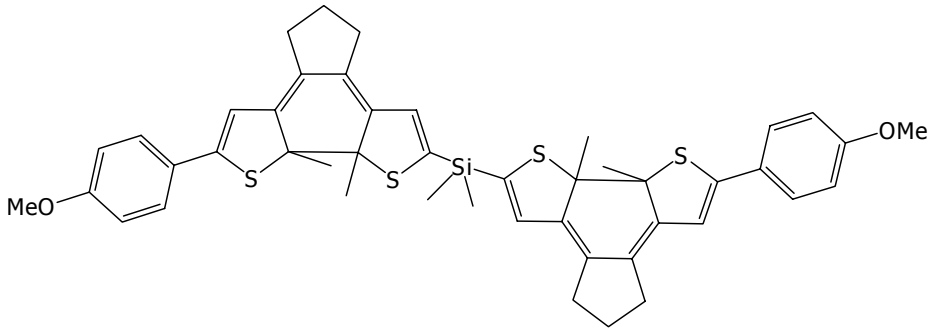
A heptane solution of 2(O-O) was irradiated with 312 nm light until it reached the PSS. The compounds were separated by preparative thin layer chromatography (heptane:ethylacetate=95:5).



2(C-O)

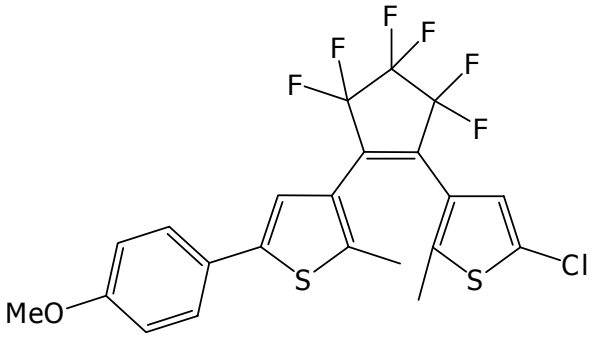
Purple Solid: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.44 (s, 3H), 0.45 (s, 3H), 1.81.1.85 (m, 2H), 1.86 (s, 3H), 1.89 (s, 3H), 1.94 (s, 3H), 2.02 (s, 3H), 2.04-2.08 (m, 2H), 2.36 (t, J=6.97, 7.33 Hz, 2H), 2.42 (t, J=7.33, 7.33 Hz, 2H), 2.82 (t, J=7.33, 7.33 Hz, 4H), 3.80 (s, 3H), 3.82 (s, 3H), 6.05 (s, 1H), 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).^{13}C-NMR ($CDCl_3$, 100 MHz)

δ: -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^+)



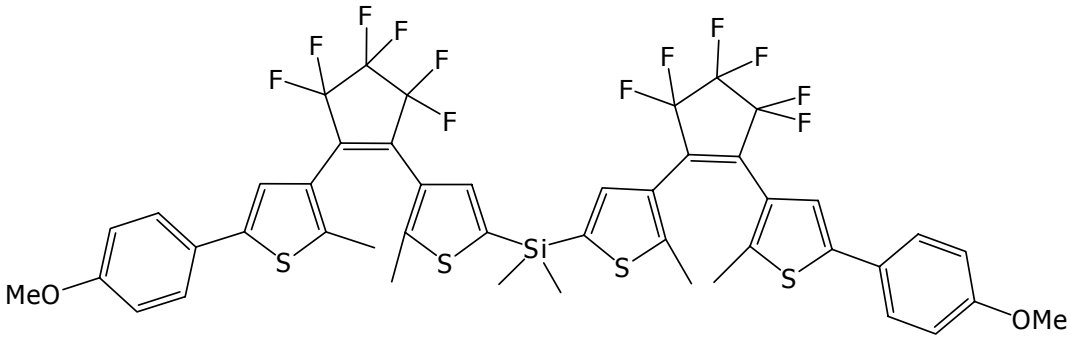
2(C-C)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 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 ($CDCl_3$, 100 MHz) δ: -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^+)



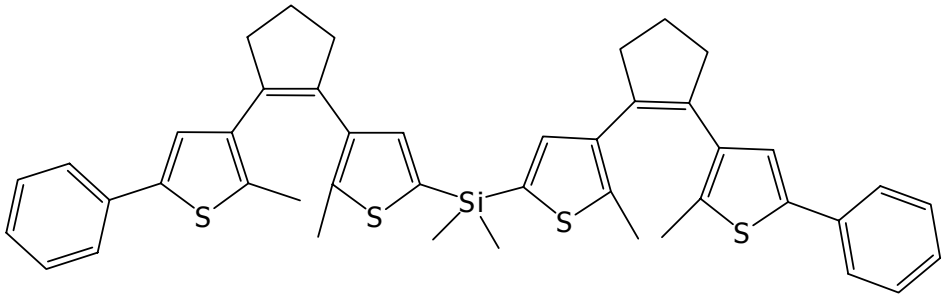
3-(2-(5-Chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-5-(4-methoxyphenyl)-2-methylthiophene (6Fo). To a solution of 5-chloro-3-(2-(5-chloro-2-methylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2-methylthiophene (**5Fo**) (1.2 g, 2.76 mmol) in Et_2O (50 ml) was added *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), [$Pd(PPh_3)_4$] (95 mg, 0.082 mmol), THF (50 ml), aqueous Na_2CO_3 (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 H_2O (100 ml). The aqueous layer was extracted with diethyl ether (100 ml). The combined organic layer was dried over Na_2SO_4. 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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.

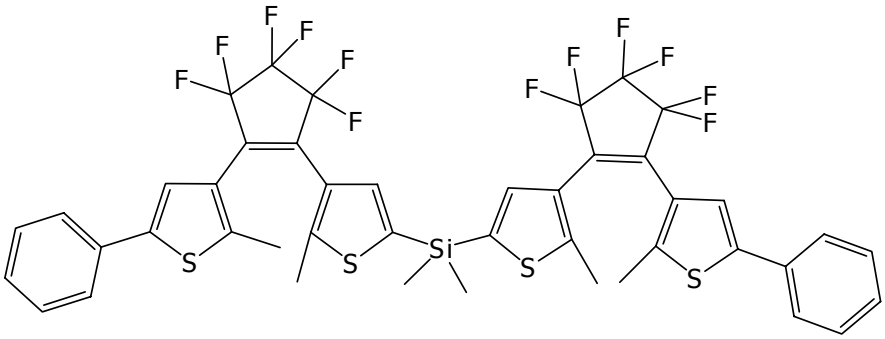


Bis(4-(3,3,4,4,5,5-hexafluoro-2-(5-(4methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)dimethylsilane (2Fo). To a solution of **6Fo** (0.22 g, 0.4 mmol) in Et_2O (10 ml) was added *t*-BuLi by syringe (0.44 ml, 1.5 M in hexane, 0.6 mmol) under nitrogen atmosphere at room temperature. 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. NH_4Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2). The organic layers were dried over Na_2SO_4, 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.62 (q), 14.15 (q), 14.40 (q), 55.34 (q), 114.36 (d),

121.24 (d), 125.61 (s), 126.15 (s), 126.87 (d), 135.32 (d), 135.66 (s), 140.13 (s), 142.13 (s), 148.15 (s), 159.49 (s); Maldi-TOF (M^+): 1004.2300



Dimethylbis(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-enyl)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 (**4Ho**). (0.40 g, 1.0 mmol) in Et_2O (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. NH_4Cl (15 ml), and the aqueous layer was extracted with diethyl ether (20 ml x 2), dried over Na_2SO_4, 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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, 7.69Hz, 4H), 7.41 (d, J=7.32 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 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)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-5-(phenyl)-2-methylthiophene (**4Fo**) (0.51 g, 1.0 mmol) in Et_2O (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. NH_4Cl (15 ml), and the aqueous layer was extracted with diethyl ether (2x 20 ml), dried over Na_2SO_4, 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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) ; ^{13}C NMR (100 MHz, $CDCl_3$) 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

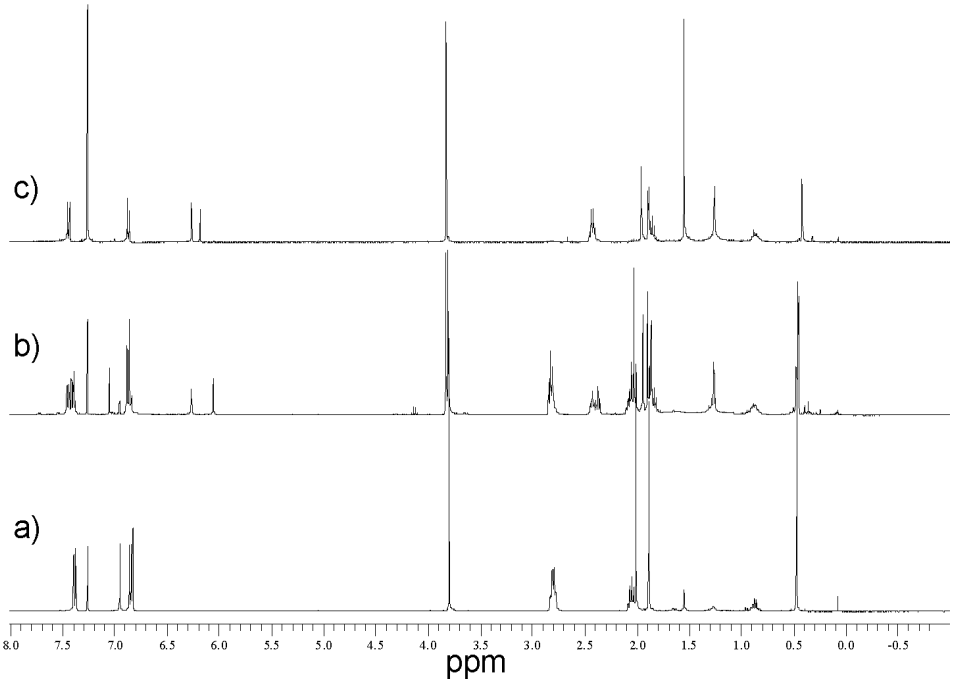


Figure S1. ^{1}H NMR (400 MHz) spectra of a) **2H**(O-O), b) **2H**(C-O) and c) **2H**(C-C) in $CDCl_3$.

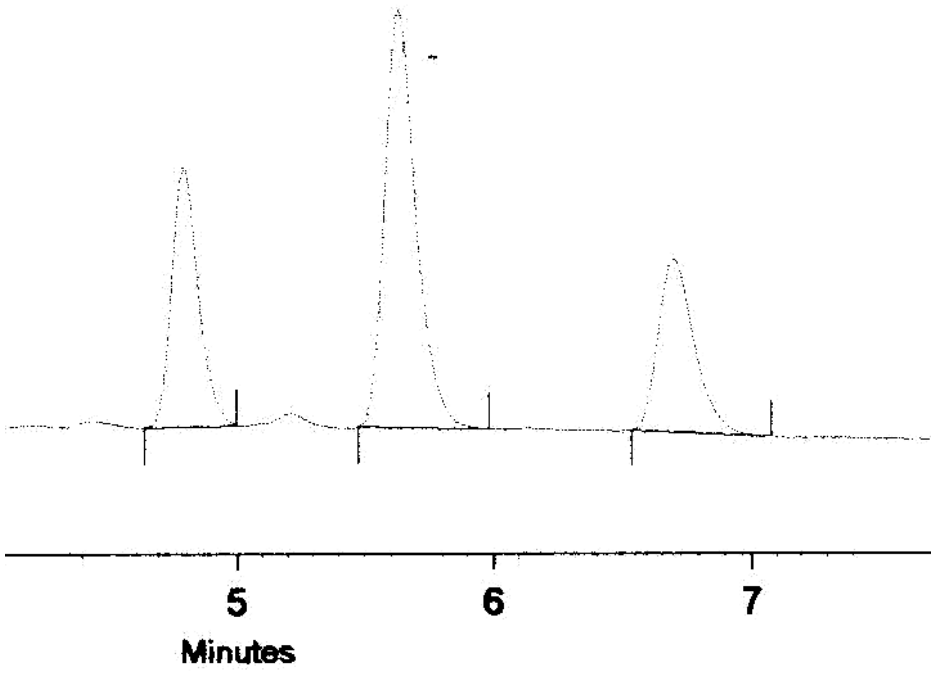


Figure S2 HPLC chromatograph of **2H(O-O)** 4.5 min, **2H(C-O)** 5.7 min, and **2H(C-C)** 6.7 min, respectively. Whelk-01 column and isopropanol:heptane = 99.9:0.1 eluent.

Photochromism

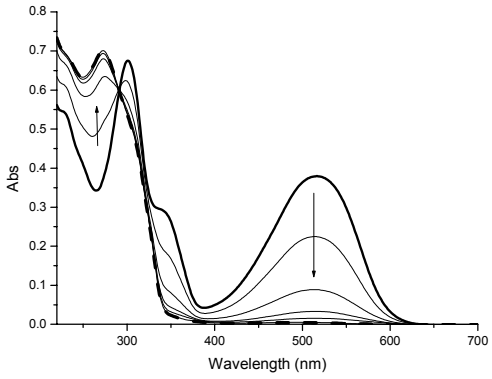


Figure S3. UV.Vis spectral changes of **2H**(C-C) upon irradiation with >455 nm light at 298 K in isomethylpentane to the fully open state **2H**(C-C).

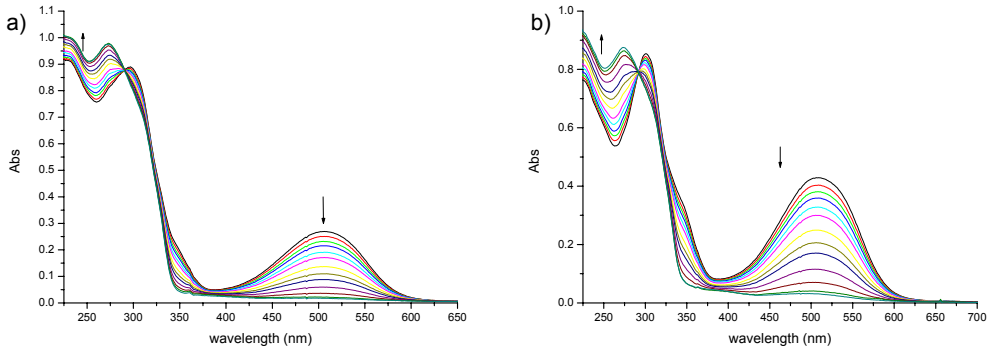


Figure S4. UV-Vis spectral changes a) **2H(C-O)** to **2H(O-O)** and b) **2H(C-C)** to **2H(O-O)** when irradiated with visible light > 455 nm; $2x10^{-5}$ M in acetonitrile

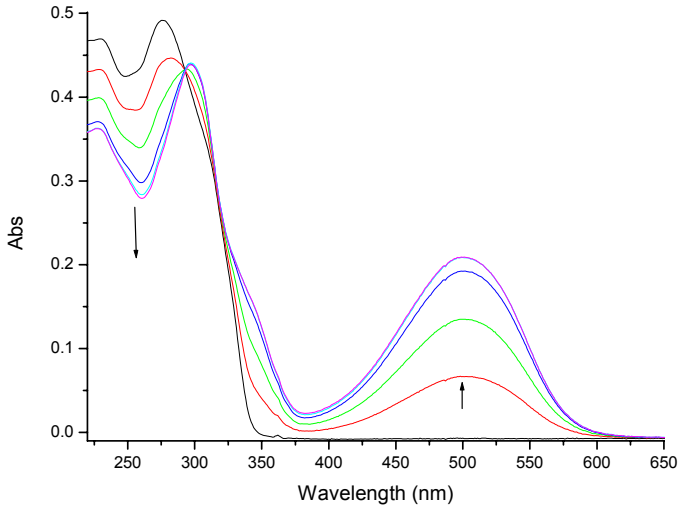


Figure S5 UV/VIS spectral changes of **1Ho** upon irradiation with 312-nm light; 10^{-5} M in heptane**.**

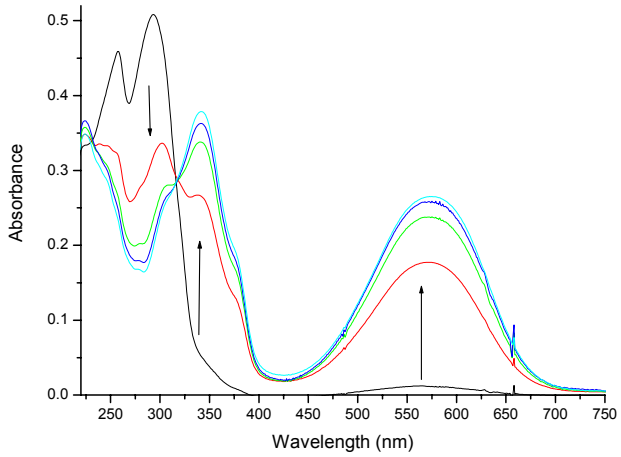


Figure S6. UV/VIS spectral changes of **2F(O-O)** upon irradiation with 312-nm light; 10^{-5} M in heptane**.**

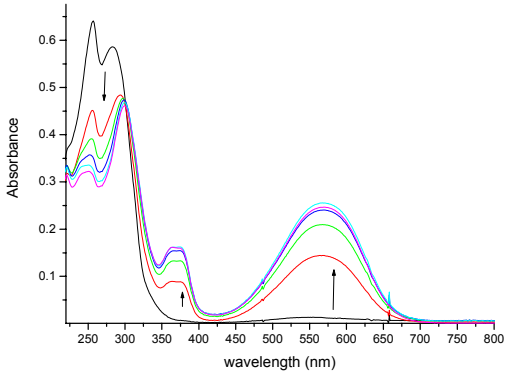


Figure S7. UV/VIS spectral changes of **3F(O-O)** upon irradiation with 312-nm light; 1.2 x 10^{-5} M in heptane**.**

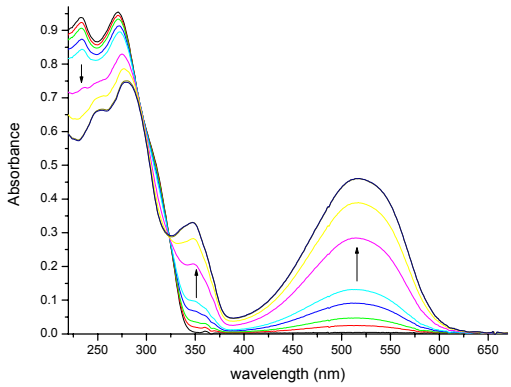


Figure S8. UV/VIS spectral changes of **3H(O-O)** upon irradiation with 312-nm light; 2 x 10^{-5} M in heptane**.**

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