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Photoswitchable Sexithiophene-Based Molecular Wires

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Photoswitchable sexithiophene molecular wires.

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Supporting Information

Experimental

Materials and synthesis. Uvasol-grade solvents (Merck) were employed for all spectroscopic and electrochemical measurements. All reagents employed in synthetic procedures were of reagent grade or better, and used as received unless stated otherwise. **A** 2-(5-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-chlorothiophen-3-yl)cyclopent-1-enyl)-5-chloro)thiophene and **B** 2-(5-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-chloro)thiophene (see scheme 1) were prepared according to procedures reported previously.¹

2-(5-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)thiophen-2-yl)thiophene. (3) **A** (0.28 g, 0.58 mmol) was dissolved in anhydrous diethyl ether (20 mL) under nitrogen and t-BuLi (0.58 mL, 1.5 M in hexane, 0.87 mmol) was added slowly by syringe. This solution was stirred at room temperature for 1 h and B(OBu)₃ (0.25 mL, 0.87 mmol) was added in one portion. After the mixture had been stirred at room temperature for 1 h, THF (30 mL), aqueous Na₂CO₃ (5 mL, 2M), 2-bromo-5-(thiophen-2-yl)thiophene (0.37 g, 1.16 mmol) and Pd(PPh₃)₄ (20 mg, 0.017 mmol) were added, and the mixture was heated at reflux overnight. The reaction mixture was cooled to room temperature, H₂O (10 mL) was added, the organic layer separated and the water layer extracted with ethyl acetate (2x20 mL). The combined organic layers were dried over Na₂SO₄ and the solvent evaporated in vacuo. The product was purified by column chromatography

(heptane) to yield a powder (0.15 g, 44%). m.p.= 126-130 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.95 (s, 3H), 1.99 (s, 3H), 7.03 (m, 2H), 7.08 (d, $J=3.7$ Hz, 1H), 7.14(s, 1H), 7.18 (d, $J=3.3$ Hz, 1H), 7.23 (m, 1H), 7.28 (m, 2H), 7.39 (m, 2H), 7.55 (d, $J=7.7$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 14.40, 14.54, 122.26, 122.0, 123.87, 124.22, 124.57, 124.69, 125.56, 125.63, 125.68, 127.90, 128.97, 133.23, 134.79, 135.19, 136.75, 136.78, 140.83, 141.29, 142.33. EI-MS (M^+) = 608; HRMS: calc. for $\text{C}_{29}\text{H}_{18}\text{F}_6\text{S}_4$ 608.0195, found 608.0215.

2-(5-(4-(2-(5-chloro-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-5-methylthiophen-2-yl)thiophen-2-yl)thiophene. (4) B (1.08g, 2.4 mmol) was dissolved in anhydrous diethyl ether (60 mL) under dinitrogen and *n*-BuLi (1.70 mL, 1.6 M in hexane, 2.64 mmol) was added slowly by syringe. This solution was stirred at room temperature for 1 h and $\text{B}(\text{O}i\text{Bu})_3$ (0.80 mL, 2.64 mmol) was added in one portion. After the mixture had been stirred at room temperature for 1 h, THF (100 mL), aqueous Na_2CO_3 (10 mL, 2M), 2-bromo-5-(thiophen-2-yl)thiophene (1.60 g, 4.8 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (86 mg, 0.07 mmol) were added and the mixture heated at reflux overnight. The reaction mixture was cooled to room temperature, H_2O (50 mL) was added, the organic layer separated and the water layer extracted with ethyl acetate (2 x 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent evaporated in vacuo. The product was purified by column chromatography (heptane) to yield a purple solid (0.67 g, 47%). m.p.= 121-124 °C. ^1H NMR (400 MHz, CDCl_3) δ 1.91 (s, 3H), 1.97 (s, 3H), 6.93 (s, 1H), 7.04-7.10 (m, 4H), 7.2 (m, 1H), 7.25(m,1H). ^{13}C NMR(100MHz, CDCl_3) δ 14.41, 14.44, 122.39, 123.93,124.25, 124.67, 124.77 , 125.56, 127.93, 134.65, 135.41, 136.75, 136.87, 140.50, 140.79. EI-MS (M^+) = 566; HRMS. calc for $\text{C}_{23}\text{H}_{13}\text{F}_6\text{S}_4\text{Cl}_1$ 565.9492, found 565.9519.

Electrochemical α -dimerization of 3 and 4 to 1 and 2, respectively

Compound **3** or **4** (40 mg of each) were dissolved in 80 mL of CH_3CN (0.1 M KPF_6) and placed in an undivided cell containing a vitreous carbon reticulated working electrode, an SCE reference electrode and a carbon rod counter electrode. The α -dimerization was carried out at 1.2 V vs SCE yielding an intense green solution. After electrolysis was completed, a potential of 0.2 V was applied for 10 min. The solvent was removed in vacuo and the residue

dissolved in dichloromethane and filtered to remove the KPF₆ electrolyte. The products were isolated as yellow solids after evaporation of the solvent.

1 (15 mg, 38%). ¹H NMR (400 MHz, CDCl₃) δ 1.95 (s, 6H), 1.98 (s, 6H), 7.04 (d, J=4.0 Hz, 2H), 7.09 (m, 4H), 7.14 (s, 2H), 7.27 (d, J=5.5 Hz, 4H), 7.31 (d, J=7.3 Hz, 2H), 7.39 (dd, J=7.7, 7.3 Hz, 4H), 7.54 (d, J=7.3 Hz, 4H) ¹³C NMR (100 MHz, CDCl₃) δ 14.48, 14.61, 122.35, 122.83, 124.50, 124.55, 124.58, 124.61, 124.68, 124.70, 124.74, 125.62, 125.71, 125.74, 127.96, 129.02, 133.27, 135.06, 135.11, 135.38, 136.04, 136.26, 141.00, 141.31, 142.35. Maldi-Tof MS C₅₈H₃₄F₁₂S₈ = 1214.1 (M+ calc.1214.0)

2 (28 mg, 69 %). ¹H NMR (400 MHz, CDCl₃) δ 1.89 (s, 6H), 1.95 (s, 6H), 6.90 (d, J=4.7 Hz, 2H), 7.00-7.09 (m, 8H), 7.17 (d, J=5.5 Hz, 1H), 7.31 (d, J=5.13 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 14.41, 14.45, 122.48, 122.74, 124.12, 124.23, 124.27, 124.30, 124.73, 125.30, 125.40, 125.60, 127.46, 127.87, 128.81, 129.79, 130.97, 131.83, 134.21, 134.78, 135.27, 135.36, 136.59, 136.66, 136.77, 137.25, 140.51, 140.88, 141.05 Maldi-Tof MS C₄₆H₂₄F₁₂S₈Cl₂ = 1131.9 (M⁺ calc. 1131.9)

X-Ray Structural analysis of **100**

Suitable orange colored crystals were obtained for **100** by recrystallisation from chloroform. A crystal with the dimensions of 0.41 x 0.37 x 0.13 mm was mounted on top of a glass fiber and aligned on a Bruker² SAMRT APEX CCD diffractometer (Platform with full three-circle

gonimeter). The diffractometer was equipped with a 4K CCD detector set 60.0 mm from the crystal. The crystal was cooled to 100(1) K using the *Bruker KRYOFLEX* low-temperature device. Intensity measurements were performed using graphite monochromated Mo-K α radiation from a sealed ceramic diffraction tube (*SIEMENS*). Generator settings were 50 KV/ 40 mA. *SMART* was used for preliminary determination of the unit cell constants and data collection control. The intensities of reflections of a hemisphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω . A total of 1800 frames were collected with an exposure time of 10.0 seconds per frame. The overall data collection time was 7.9 h. Data integration and global cell refinement was performed with the program *SAINT*.² The final unit cell was obtained from the *xyz* centroids of 4182 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*)², and reduced to F_o .² The program suite *SAINTPLUS* was used for space group determination (*XPREP*).² The CIF is available to download from the Cambridge Crystallographic Data Centre (<http://www.ccdc.cam.ac.uk/deposit>) deposit number CCDC 711773.

Table 1. Crystallographic parameters

Compound	1
Formula	C ₅₈ H ₃₄ F ₁₂ S ₈ ·2(CHCl ₃)
fw (g mol ⁻¹)	1454.15
Crystal dimension (mm)	0.41 x 0.37 x 0.13
color	Orange

habit	Platelet
Crystal system	Triclinic
Space group, no. ³	<i>P</i> -1, 2
a (Å)	8.9801(14)
b (Å)	12.322 (2)
c (Å)	14.597 (2)
V (Å ³)	1518.4 (4)
Z'	0.5
P (g cm ⁻³)	1.590
T (K)	100 (1)
μ (cm ⁻¹)	6.36
Number of reflections	6029
Number of refinement parameters	390
Final agreement factors:	
$wR(F^2)$	0.1408
$R(F)$	0.0511
GooF	1.036
Crystal dimension (mm)	0.41 x 0.37 x 0.13

¹H NMR spectra were recorded at 400 MHz; ¹³C NMR spectra at 100.6 MHz. All spectra were recorded at ambient temperature, with the residual proton signals of the solvent as an internal reference. Chemical shifts are reported relative to TMS. CI and EI mass

spectra were recorded on a Jeol JMS-600 mass spectrometer in the scan range of m/z 50–1000 with an acquisition time between 300 and 900 ms and a potential between 30 and 70 V. MALDI-TOF spectra were recorded on an Applied Biosystems Voyager-DE Pro.

Electrochemical measurements were carried out on a Model 630B Electrochemical Workstation (CHInstruments). Analyte concentrations were typically 0.5–1 mM in anhydrous dichloromethane containing 0.1 M TBAPF₆ (except where stated otherwise in the text). Unless otherwise stated, a Teflon-shrouded glassy carbon working electrode (CHInstruments), a Pt wire auxiliary electrode and SCE or non-aqueous Ag/Ag⁺ ion reference electrode were employed. Reference electrodes were calibrated with 0.1 mM solutions of ferrocene (0.38 V versus SCE in 0.1M TBAPF₆/ CH₃CN). Solutions for reduction measurements were deoxygenated by purging with dry N₂ gas (presaturated with solvent) prior to the measurement. Cyclic voltammograms were obtained at sweep rates of between 10 mVs⁻¹±1 and 50 Vs⁻¹±1. For reversible processes the half-wave potential values are reported. Redox potentials are ±10 mV. Spectroelectrochemistry UV/Vis absorption spectra (accuracy ±2 nm) were recorded on a Hewlett-Packard UV/Vis 8453 diode array spectrometer or on a JASCO 560 UV/Vis near-IR spectrometer. Emission spectra were recorded using a JASCO 6200 fluorimeter.

Computational Methods: Density functional theory (DFT) calculations were carried out with the GAUSSIAN 03W (rev. B.04) program package.⁴ All the calculations were performed on systems in the gas phase using the Becke's three-parameter hybrid functional⁵ with the LYP correlation functional⁶ (B3LYP) and 6-31G(d) basis set.

*Redox properties of terthiophenes **3o** and **4o***

The redox chemistry of **3o** and **4o** is characterized by an irreversible oxidation at $E_{p,a} = 1.13$ V (V vs SCE) and $E_{p,a} = 1.34$ V (V vs SCE), respectively, leading to **3o**²⁺ and **4o**²⁺ species. The return cycle does not indicate that the formation of **3c**²⁺ and **4c**²⁺ occurs (i.e. oxidatively driven ring closure is not observed by the appearance of redox waves at potentials corresponding to those of the closed forms, Figure S1). The closed states (**3c/4c**), formed by

irradiation with UV light, show less positive redox potentials than in the open state, and indicating destabilization of the HOMO in the closed state. For the closed form **4c**, a quasi-reversible oxidation is observed at 0.92 V (V vs SCE). The separation of the first and second oxidation processes (ΔE) is less than the resolution limit for both cyclic and differential pulse voltammetry (< 30 mV). However, for **3c**, the two fully reversible oxidation processes are observed at 0.78 and 0.95 V (V vs SCE), assigned to two one-electron oxidation steps (Figure S1). In contrast to other perfluoro-cyclopentene bridge dithienylethenes,⁷ the current intensity of **3o** and **4o** upon scanning through multiple scans does not decrease and a quasi-reversible redox wave appears at lower potential following the initial cycle, indicating accumulation of oxidation products on the surface of the electrode. This suggests that the oxidation of monomers **3o** and **4o** may result in α -dimerization.⁸

Figure S1 Cyclic voltammogram of a) **3o/3c** and b) **4o/4c** (1 mM in 0.1 M TBAPF₆/CH₂Cl₂, scan rate 0.1 Vs⁻¹, glassy carbon electrode vs SCE). The coordinate axes of the voltammograms of **3c** and **4c** have been offset by -10 μA for clarity.

Infrared Spectroscopy

Figure S 2 FTIR spectra of (a) **1oo** (solid line) and **3o** (dotted line) and (b) **2oo** (solid line) and **4o** (dotted line), deposited from dichloromethane solution onto KBr powder. The main absorptions arising from the perfluorocyclopentene ring are denoted by arrows and the o.o.p absorptions by solid arrow.

Electronic absorption and emission spectroscopy

Figure S 3 UV-Vis absorption of **100**, **200**, **30** and **40** and the fluorescence spectra of a) **100** and b) **200** ca. 1×10^{-5} M in heptane solution.

Photochemistry

Figure S 4 a) UV/VIS spectral changes of **1a** upon irradiation at λ_{exc} 312 nm. b) Photochromic bleaching of **1c** upon irradiation at $\lambda_{exc} > 520$ nm.

Figure S 5 a) UV/VIS spectral changes of **2a** upon irradiation at λ_{exc} 312 nm. b) Photochromic bleaching of **2c** upon irradiation at $\lambda_{exc} > 520$ nm.

Figure S 6 a) Decrease in fluorescence intensity of (a) **1a** (λ_{ex} = 350 nm) and (b) **2a** (λ_{ex} = 430 nm), 1×10^{-5} M in hexane solution at 298 K, upon irradiation at λ_{ex} 365 nm.

Spectroelectrochemistry

Figure S 9 Spectral changes following oxidation of a) **100** and b) **200** with $\text{CF}_3\text{CO}_2\text{H}$ in CH_2Cl_2 . Absorption maxima for **100/200**, respectively, are at 6751/6733 and 12722/12614 and 14432/14400 cm^{-1} .

*Ring opening of **1cc** to **100** by electrochemical oxidation.*

Figure S 10 Spectroelectrochemistry of **1cc** upon oxidation at 0.9 V, followed by reduction at -0.3 V in 0.1 M $\text{TBAClO}_4/\text{DCM}$

*Temperature dependence of the thermal reversion of **1cc** to **1oo***

Figure S 11. Left: UV-vis absorption spectrum of **1oo** and at the photostationary state (**1cc**, PSS_{365 nm}) and after heating at 80 °C for 24 h. **Right:** Kinetics of reversion of **1cc** (PSS_{365 nm}) at 90 °C, 80 °C, and 60 °C

HPLC analysis of a mixture of **1oo** (labeled o-o), **1co** (labeled c-o) and **1cc** (labeled c-c) and their respective UV-Vis absorption spectra.

Frontier molecular orbital diagrams

HOMO

LUMO

a) **1oo**

b) **1co**

c) **1cc**

Figure S 13. Frontier molecular orbitals of a) **1oo**, b) **1co**, c) **1cc** calculated using the B3LYP/6-31G(d) method.

NMR Spectral Data

^1H NMR spectrum of compound **1oo**

^{13}C NMR spectrum of compound **1oo**

¹H NMR spectrum of compound **200**

¹³C NMR spectrum of compound **200**

¹H NMR spectrum of compound **30**

¹³C NMR spectrum of compound **30**

¹H NMR spectrum of compound **40**

¹³C NMR spectrum of compound **40**

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