Photoswitchable sexithiophene molecular wires.

Jetsuda Areephong, Johannes H. Hurenkamp, Maaike T. W. Milder, Auke Meetsma, Jennifer L. Herek, Wesley R. Browne, Ben L. Feringa*

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-chlorothiophene and B 2-(5-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-chlorothiophene (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. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (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=3.3Hz, 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$_3$) $\delta$ (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 C$_{29}$H$_{18}$F$_6$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 (1.08 g, 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 B(OBu)$_3$ (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$_2$CO$_3$ (10 mL, 2M), 2-bromo-5-(thiophen-2-yl)thiophene ( 1.60 g, 4.8 mmol) and Pd(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$_2$O (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$_2$SO$_4$ 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. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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).$^{13}$CNMR(100MHz,CDCl$_3$)$\delta$ 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 C$_{23}$H$_{13}$F$_6$S$_4$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$_3$CN (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 KPF$_6$ electrolyte. The products were isolated as yellow solids after evaporation of the solvent.

1 (15 mg, 38%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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) $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.48, 14.61, 122.35, 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 C$_{58}$H$_{34}$F$_{12}$S$_8$ = 1214.1 (M$^+$ calc. 1214.0)

2 (28 mg, 69 %). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 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 C$_{46}$H$_{24}$F$_{12}$S$_8$Cl$_2$ = 1131.9 (M$^+$ calc. 1131.9)

X-Ray Structural analysis of 1oo

Suitable orange colored crystals were obtained for 1oo 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 Bruker$^2$ 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-Kα 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. 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), and reduced to $F_o^2$. The program suite SAINTPLUS was used for space group determination (XPREP). 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

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>fw (g mol⁻¹)</td>
</tr>
<tr>
<td>Crystal dimension (mm)</td>
</tr>
<tr>
<td>color</td>
</tr>
<tr>
<td>Habit</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group, no.</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
<tr>
<td>V (Å³)</td>
</tr>
<tr>
<td>Z'</td>
</tr>
<tr>
<td>P (g cm⁻³)</td>
</tr>
<tr>
<td>T (K)</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
</tr>
</tbody>
</table>

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

\(^1\)H NMR spectra were recorded at 400 MHz; \(^{13}\)C 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 and 50 Vs⁻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. All the calculations were performed on systems in the gas phase using the Becke’s three-parameter hybrid functional with the LYP correlation functional (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 Eₚ,a = 1.13 V (V vs SCE) and Eₚ,a = 1.34 V (V vs SCE), respectively, leading to 3o²⁺ and 4o²⁺ species. The return cycle does not indicate that the formation of 3c²⁺ and 4c²⁺ 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, 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.

Figure S1 Cyclic voltammogram of a) 3o/3c and b) 4o/4c (1 mM in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$, scan rate 0.1Vs$^{-1}$, glassy carbon electrode vs SCE). The coordinate axes of the voltammograms of 3c and 4c have been offset by -10 µA for clarity.
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. 1x10^-5 M in heptane solution.
Photochemistry

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

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

**Figure S 6** a) Decrease in fluorescence intensity of (a) 1o ($\lambda_{\text{ex}} = 350$ nm) and (b) 2o ($\lambda_{\text{ex}} = 430$ nm), 1x10$^{-5}$ M in hexane solution at 298 K, upon irradiation at $\lambda_{\text{ex}}$ 365 nm.
Spectroelectrochemistry

**Figure S 9** Spectral changes following oxidation of a) 1oo and b) 2oo with CF₃CO₂H in CH₂Cl₂. Absorption maxima for 1oo/2oo, respectively, are at 6751/6733 and 12722/12614 and 14432/14400 cm⁻¹.

*Ring opening of 1cc to 1oo 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 TBAClO₄/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

a) $\text{HOMO}$

b) $\text{LUMO}$

c) $\text{B3LYP/6-31G(d)}$ method.

Figure S 13. Frontier molecular orbitals of a) $\text{1oo}$, b) $\text{1co}$, c) $\text{1cc}$ calculated using the

B3LYP/6-31G(d) method.
**NMR Spectral Data**

**1H NMR spectrum of compound 100**

Chemical shifts (ppm): 7.14, 7.08, 7.07, 7.04, 7.03, 7.55, 7.53, 7.41, 7.37, 7.30, 7.27, 7.25, 7.14, 7.08, 7.07, 7.04, 7.03

**13C NMR spectrum of compound 100**

Chemical shifts (ppm): 142.35, 141.31, 141.00, 136.26, 136.04, 135.83, 135.11, 135.06, 133.27, 129.02, 127.96, 125.74, 125.71, 125.62, 124.74, 124.70, 124.68, 124.61, 124.58, 124.55, 124.50, 122.83, 122.35, 121.32, 77.32, 77.00, 76.68, 14.61, 14.48
H NMR spectrum of compound 200 ppm (t1)

C NMR spectrum of compound 200 ppm (t1)
H NMR spectrum of compound 3o

C NMR spectrum of compound 3o
$^1\text{H}$ NMR spectrum of compound 40

$^1\text{C}$ NMR spectrum of compound 40

Chemical shifts:

- $^1\text{H}$ NMR: 7.236, 7.226, 7.224, 7.178, 7.171, 7.169, 7.088, 7.073, 7.063, 7.036, 7.027, 7.024, 7.017, 7.015, 6.916
- $^1\text{C}$ NMR: 140.79, 140.50, 136.87, 136.75, 135.41, 134.65, 127.93, 125.56, 124.77, 124.67, 124.25, 123.93, 122.39, 77.31, 77.60, 76.68, 14.44, 14.41


