Supporting Information

Electrochemical Switching of Conductance with Diarylethene Based Redox-active Polymers

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**Experimental Section**

**General Remarks**

All chemicals were used as received from commercial resources without further purification. THF was distilled from sodium and benzophenone under N₂ atmosphere. NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz). Chemical shifts are denoted in δ (ppm) referenced to the residual solvent peak. Coupling constants J are denoted in Hz. Mass spectra were recorded on a Thermo Scientific LTQ-Orbitrap-XL. Bromodithiophene¹ and 1,2-Bis[5-(4-bromophenyl)-2-methylthien-3'-yl]cyclopentene² were prepared according to literature procedures.

Electrochemical measurements were performed using a CH Instruments, model 630B or 760C, electrochemical workstation. Analyte concentrations were typically 0.5 to 2 mM in anhydrous CH₂Cl₂ containing 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF₆). A Teflon shrouded glassy carbon, gold or platinum microelectrode and indium tin oxide (ITO) coated glass slides were employed as a working electrodes (CH Instruments). A Pt wire auxiliary electrode and Ag/AgCl quasi reference or a SCE electrode were employed (calibrated externally using 0.1 mM solution of ferrocene, all potentials reported are relatively to SCE).

UV/Vis spectra were recorded on an Analytik Jena Specord S600 diode array spectrometer. Raman spectra were measured using a Perkin Elmer Raman station at λₑxc 785 nm (80 mW at sample). For Raman spectroelectrochemistry a gold bead working electrode was employed (formed by melting gold wire using a hydrogen flame). The bead was cleaned electrochemically by oxidation in 0.5 M H₂SO₄ (aq) and subsequent stripping in 0.1 M HCl (aq) followed by cycling between -0.4 to 1.2 V vs Hg/HgSO₄ in 0.5 M H₂SO₄ (aq) for 20 cycles. Raman spectra are solvent subtracted and baseline corrected unless noted otherwise.

**Scheme S 1 Synthesis of monomer**

![Scheme S 1 Synthesis of monomer](image)

2-methyl-3-[2-(2-methyl-5-{4-[5-(thiophen-2-yl)thiophen-2-yl]phenyl}thiophen-3-yl)cyclopent-1-en-1-yl]-5-[4-{5-thiophen-2-yl}thiophen-2-yl]phenyl]thiophene (1o)

Bromodithiophene (215 mg, 0.88 mmol) was dissolved in anhydrous THF (30 ml) under a nitrogen atmosphere and n-BuLi (0.55 mL of a 1.6 M solution in hexane, 0.88 mmol) was added at -78 °C. After 1 hour of stirring at this temperature, Bu₃SnCl (325 mg, 0.99 mmol) was added and the reaction mixture was allowed to warm to r.t. while stirring for an additional hour. The solution was diluted with Et₂O (50 mL) and washed with sat. NaHCO₃ (50 mL), water (50 mL) and brine (50 mL). The combined organic extracts were dried over Na₂SO₄ and the solvent was evaporated to give the crude stannane that was used in the next step without further purification. 1,2-Bis[5-(4-bromophenyl)-2-methylthien-3'-yl]cyclopentene (0.250 g, 0.44 mmol), 5-tributyltin-2,2'-bithiophene (0.88 mmol) and DMF (10 mL) were purged with argon for 10 minutes. Pd(PPh₃)₄ (50.8 mg, 0.044 mmol) was added and the reaction mixture was heated under reflux for 24 h. After cooling down to r.t., toluene (100 mL) was added and the crude was filtered over SiO₂:K₂CO₃ = 9:1 and rinsed with toluene. The organic layer was washed with brine (2 x 100 mL), dried over Na₂SO₄ and the solvent was evaporated. The crude impurities were removed by column chromatography (SiO₂, toluene), to obtain > 80% yield of crude compound. Analytically pure samples of 1o as a yellow solid were obtained by batch wise preparative TLC (SiO₂, 85:15 pentane/CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.6 Hz, 4H), 7.50 (d, J = 8.6 Hz, 4H),...
7.25 – 7.21 (m, 4H), 7.20 (dd, J = 3.6, 1.1 Hz, 2H), 7.15 (d, J = 3.8 Hz, 2H), 7.07 (s, 2H), 7.03 (dd, J = 5.1, 3.6 Hz, 2H), 2.86 (t, J = 7.4 Hz, 4H), 2.15 – 2.05 (m, 2H), 2.03 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 142.7, 139.1, 137.4, 136.8, 136.6, 134.8, 133.7, 132.6, 127.9, 125.9, 125.6, 124.6, 124.4, 124.1, 123.6, 123.5, 38.5, 23.0, 14.5. HRMS-APCI+ m/z calcd for C43H33S6, [M+H]+ 741.0907, found 741.0900.

Fig. S 1 ¹H NMR of 1o in CDCl3

Fig. S 2 13C NMR of 1o in CDCl3

Model compound paraphenylbisdithiophene (2)

Scheme S 2 Synthesis of model compound 2
[2,2'-bithiophen]-5-yltributylstannane (496 mg, 1.09 mmol), 1,4-diiodobenzene (168 mg, 0.51 mmol) and DMF (10 mL) were purged with argon for 10 minutes. Pd(PPh$_3$)$_4$ (59 mg, 0.05 mmol) was added and the reaction mixture was heated under reflux for 16 h. After cooling down to r.t., toluene (100 mL) was added and the organic layer was washed with brine (2 x 100 mL), dried over Na$_2$SO$_4$ and the solvent was evaporated. The crude mixture was chromatographed (SiO$_2$/K$_2$CO$_3$ (10/1), 2 to 10% EtOAc/pentane) to obtain 2 (78 mg, 18%) as a yellow solid. Analytical pure sample was obtained (13 mg, 3%) after recrystallization in hexane/benzene 1:1.

$^1$H NMR (400 MHz, C$_6$D$_6$, 40 °C) δ 7.40 (s, 4H), 7.06 (d, $J = 3.4$ Hz, 2H), 6.99 (d, $J = 3.7$ Hz, 2H), 6.94 (d, $J = 3.8$ Hz, 2H), 6.77 (d, $J = 5.0$ Hz, 2H), 6.70 (dd, $J = 4.9, 3.7$ Hz, 2H). HRMS-ESII$^+$ m/z calcd for C$_{22}$H$_{15}$S$_4$, [M+H]$^+$ 407.00511, found 407.00491.

Fig. S3 $^1$H NMR of 2 in C$_6$D$_6$
The onset potential for polymerization and the onset potential for ring closure were determined by increasing the maximum potential by 0.1 V increments (three cyclic voltammograms are shown below). In each case a cyclic voltammogram was recorded followed by a second cyclic voltammogram after stirring the solution for several seconds. Examination of the initial sweep from 0.0 to 0.8 V for the second cycle allows for determination of the presence of polymer on the electrode.

Fig. S4 Cyclic voltammetry of 1o to 1.0 V; Ring closure occurs, but not polymerization.

Fig. S5 Cyclic voltammetry of 1o to 1.2 V; Ring closure occurs, and some polymerization

Fig. S6 Cyclic voltammetry of 1o to 1.3 V; Ring closure and polymerization occurs.
Electropolymerization using a microelectrode allows for better resolution of the redox processes. The increased current at 0.4 V as the polymer layer becomes thicker is due to discharge of trapped charges from a preceding cycle.

![Graph](image)

**Fig. S 7** Electropolymerization of 1o on a 10 micron diameter gold-microelectrode

The scan rate dependence of the cyclic voltammetry of poly-1c in monomer free solution shows a linear relation between current and scan rate, consistent with the surface confined nature of the process. The large peak to peak separation at higher currents observed is due to IR drop.

![Graph](image)

**Fig. S 8** Scan rate dependence of poly-1c on a gold-disk macro electrode, 0.1 M TBAPF₆ in DCM. (left) Relation between maximum current at ca. 0.4 V and scan rate. (right)

Polymerization can also be performed using the ring closed monomer (1c).

![Graph](image)

**Fig. S 9** Polymerization of closed form (1c) on a glassy carbon electrode, 0.1 M TBAPF₆ in DCM, scan rate 0.1 V/s.
Cyclic voltammetry of 1c was compared to the polymer formed directly after polymerization, which demonstrates that the polymer is prepared in its closed form.

![Graph showing cyclic voltammetry comparison](image)

**Fig. S 10** Electrochemistry of 1c in solution compared to polymer (poly-1c) formed immediately after polymerization of 1o on a glassy carbon electrode, 0.1 M TBAPF$_6$ in DCM, scan rate 0.1 V/s.

Polymerization on Interdigitated Microelectrode Arrays (IDA) was performed for In situ conductivity studies. The coverage was assessed using optical microscopy. Film thickness can be controlled by varying either or both the scan rate, switching potential or number of cycles or, when deposition is potentiostatic, by controlling both the deposition potential and the time.

![Images of IDA with different film thicknesses](image)

**Fig. S 11** (Upper) thick polymer film modified IDA, (middle) thin polymer film modified IDA, (lower) clean IDA showing the interdigitated platinum electrodes (electrodes are 5 µm wide and 5 µm apart)
Differences in conductivity and switching behavior between different IDAs were quite pronounced and due to differences in film thickness, i.e. full coverage of the IDA was obtained with both a relatively thin and a relatively thick polymer film. Conclusions reached regarding polymer film thickness were based on optical microscopy and the faradaic current after polymerization. Fast electrochemically induced ring opening was observed for the thick polymer films. The thin polymer films behaved more similarly to macro-electrodes and showed relatively slow ring opening.

A further difference in conductivity over the polymer film was also observed when analyzed in monomer free solution between the freshly formed (wet) polymer modified electrode and after having been stored for 24 h in air. On macro-electrodes the storing overnight in air shows little if any effect on the cyclic voltammetry. By contrast for polymer modified IDAs substantial changes were observed that impact on the measured conductivity. Possibly the connection between the two electrodes was damaged upon drying of the polymer film.

![Graph showing differences in conductivity](image)

**Fig. S 12** In situ conductivity on a freshly formed IDA (lower) and on the same IDA the next day (upper) using the exact same settings, $\Delta V = 20$ mV, scan rate = 0.01 V/s.

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