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Logtenberg, Hella

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Chapter 5

Electrochemical Switching of Conductance with Diarylethene Based Redox-active Polymers

In this chapter reversible switching of conductance using redox triggered switching of a polymer modified electrode is demonstrated. A bifunctional monomer comprising a central electroswitchable core and two bithiophene units enables formation of a film through anodic electropolymerisation. The conductivity of the polymer can be switched electrochemically in a reversible manner by redox triggered opening and closing of the diarylethene unit. In the closed state the conductivity of the modified electrode is higher than in the open state.

This chapter has been published:

**Introduction**

The development of smart interfaces, which respond to external input such as heat, light and electrical stimuli, has received intense interest in recent years for applications as diverse as cell culturing\textsuperscript{12}, droplet transport\textsuperscript{3} and increasingly in the development of organic electronics.\textsuperscript{4-6} Light-switching within self-assembled monolayers,\textsuperscript{7-9} and in polymer films\textsuperscript{10-12} has been demonstrated by several groups to date,\textsuperscript{13, 14} with azobenzene,\textsuperscript{15} spiropyran\textsuperscript{16, 17} and diarylethene\textsuperscript{18} photochromic switches playing an important role as the photo-responsive elements in such systems.\textsuperscript{19-21} A major challenge associated with the use of self-assembled monolayers and thin (e.g., < 20 nm) polymer films in organic electronic devices, however, is that the magnitude of the change in conductance achievable is limited by the background tunneling current, which limits applications in organic based devices. The use of thicker films will overcome this albeit at the cost of an increase in resistance and inhibition of photoswitching due to inner filter effects.\textsuperscript{22}

Dithienylethenes have figured prominently in the development of switchable organic electronic devices, especially with regard to photoswitching of conductance, between the non-conjugated open and the conjugated closed forms.\textsuperscript{18, 23-25} Although mostly known as photochemical molecular switches, switching of dithienylethenes can also be achieved electrochemically.\textsuperscript{26-31} Due to kinetic reasons, redox switching is essentially one way in solution. However, when immobilized on electrodes, both ring opening and ring closing can be achieved electrochemically.\textsuperscript{14, 32-34} The difference in redox potentials between the open and closed states can potentially allow this class of molecular switches to function as active components in organic electronic devices, in particular in terms of switching of conductance.

Controlling the electrochemical response of electrodes through electrochemical modification using mono/multilayers of biphenyls has been demonstrated by McCreery and co-workers,\textsuperscript{35} and with phenylbithiophenes by Lacroix and co-workers.\textsuperscript{36-38} In these systems, electronic properties, including diode like behaviour, could be achieved with respect to redox active species in solution. The properties of the films once formed, however, are fixed, and although in many applications this is advantageous, exerting reversible control on the properties of the films after formation remains a key challenge.

![Figure 5-1](image.png)  
*Figure 5-1* Previous designs used as electropolymerisable diarylethene switches.
Reversible electrochemical switching in polymer films was demonstrated recently by our group using thin polystyryl-dithienylethene films (Figure 5-1, A).\(^\text{14}\) The use of styryl groups, however, limited the film thickness (< 10 nm) and adhesive stability due to the non-conductive nature of the film formed at the potentials required for polymerization. However, when a bithiophene group is attached directly to the switching unit excellent electropolymerisation behaviour is observed (Figure 5-1, B),\(^\text{39}\) and in contrast to the styryl based system film thickness was not limited by a lack of conductivity of the polymer at the potentials required for electropolymerisation. In this latter system, in the ring closed state polymerisation is not observed, and although, in general oxidation of the open form of a dithienylethene unit can lead to ring closure, polymerisation was sufficiently competitive to allow for film formation. However, photo or electrochemical switching in the polymer film formed did not occur and the resulting polymer is best viewed as an alkene spaced polysixithiophene. An important goal therefore is to combine the dithienylethene redox switchable unit with a redox active polymer backbone that facilitates charge transport through the film without loss of the dithienylethene’s switching functionality.\(^\text{40}\) However, although redox-driven switching of conductance has been shown in monolayers and doped polymer films, reversible switching of conductivity in the polymer has, so far, not been demonstrated.

In this chapter reversible switching of conductivity is shown to be possible within diarylethene based redox-active polymer films. This is achieved by combining a molecular switching unit, a dithienylethene, and an electropolymerisable bithiophene unit (Figure 5-2) without loss of redox switching properties both before and after electropolymerization. The key design aspect is the use of phenyl spacers. The phenyl groups are twisted out of plane, thereby limiting the electronic interaction between the switching unit and the polymerisable unit.\(^\text{21, 41}\) In this chapter, it is demonstrated that the polymer modified electrode formed upon electropolymerisation can undergo reversible redox driven switching between open and closed states of the dithienylethene under ambient conditions.

Figure 5-2 Bifunctional polymerisable dithienylethene switch 10.
Results and discussion

Synthesis
The bifunctional monomer 1o (Figure 5-2, where ‘o’ indicates that the dithienylethene is in the open form) used to form the switchable electropolymer comprises a central dithienylethene unit separated from the electropolymerisable units by phenyl groups. The monomer was prepared via Pd(0) catalysed cross coupling of bis(p-bromophenyl)dithienylethene with 5-tributyltin-2,2′-bithiophene (Scheme 5-1).

Scheme 5-1 Synthesis of monomer 1.

In addition two model compounds bis(p-2-dithienyl)benzene (2, Scheme 5-2) and bis(5,5′-diphenyl)dithienycyclopentene (3o, Figure 5-3) were prepared by reported procedures. The monomer 1o is photoswitchable and shows electrochemical properties similar to that of the model compound 3o. Irradiation of 1o in CH3CN at 365 nm results in a decrease in absorption at 365 nm and an increase in absorption at 550 nm, which is characteristic for ring closing of a dithienylethene switch. The absorption at 365 nm is partly due to the absorption of the bithiophene unit (vide infra, Figure 5-11).

Scheme 5-2 Synthesis of model compound 2.

Electropolymerisation
Polymerisation of 1o and model compound 2 proceeds smoothly both potentiostatically and by cyclic voltammetry on Au disk/bead, Pt disk, ITO and glassy carbon (GC) electrodes, under ambient conditions without the need to exclude water or oxygen and without addition of Lewis acids. The polymer coatings formed are mechanically stable and can be stored in air under ambient conditions for at least several weeks without significant changes in their cyclic voltammetry.

The cyclic voltammetry of 1o, 2 and 3o are shown in Figure 5-3. Upon electropolymerization of 1o two oxidation waves at 0.9 V and 1.2 V are observed in the first cycle (shown in black in the cyclic voltammetry). On the return scan, however, four reduction waves are observed
within the same potential window. In the second cycle four reversible oxidations are observed, at 0.4, 0.6, 1.0 and 1.3 V.

![Graph](image_url)

**Figure 5-3** Multi-cycle cyclic voltammetry of 1o (middle) shown together with model compounds 2 (top) and 3o (bottom) (in 0.1 M TBAPF₆ in CH₂Cl₂, GC WE, Pt-wire CE and SCE RE). In each case the first cycle is shown in black (initial potential and scan directions are 0.0 V and positive, respectively).

When comparing the electrochemistry of 1o, 2 and 3o it is apparent that the cyclic voltammetry of 1o appears to be a superposition of the voltammetry of 2 (irreversible oxidation of the bithiophene units at 0.9 V, followed by oxidative coupling) and 3o (irreversible oxidation of the dithienylcyclopentene core at 1.2 V).²⁷ Counter intuitively, however, oxidation of 1o to 1o²⁺ at 0.9 V is followed by ring closure, to form 1c²⁺ (where ‘c’ indicates that the dithienylethene is in the closed form). For 3o oxidation at 1.2 V is required to achieve oxidative ring closing of the dithienylcyclopentene. Furthermore the onset potential for electropolymerisation for 2 is 0.9 V, while for 1o electropolymerisation does not occur until 1.2 V (Figure 5-4).
Scheme 5-3 Mechanism for electropolymerisation of bis(bithiophene) functionalized dithienylcyclopentene 1o/1c.

The onset potential for polymerisation 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, Figure 5-4). 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 allowed for determination of the presence of polymer on the electrode.
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Figure 5-4  a) Cyclic voltammetry of 1o to 1.0 V; Ring closure occurs, but not polymerisation.  b) Cyclic voltammetry of 1o to 1.2 V; Ring closure occurs, and some polymerisation.  c) Cyclic voltammetry of 1o to 1.3 V; Ring closure and polymerisation occurs.

Electropolymerisation 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 (see chapter 4).
Electropolymerisation of 1o on a 10 micron diameter gold-microelectrode, 0.1 M TBAPF₆ in CH₂Cl₂, scan rate 0.1 V/s.

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.

Polymerisation can also be performed using the ring closed monomer (1c, Figure 5-7). Two additional oxidations are observed in the first cycle, indicating oxidation of the closed form first. With the exception of the first cycle the electropolymerisation of 1c is essentially identical to that of 1o.
**Figure 5-7** Polymerisation of closed form (1c) on a glassy carbon electrode, 0.1 M TBAPF₆ in CH₂Cl₂, scan rate 0.1 V/s.

Cyclic voltammetry of 1c was compared to the polymer formed directly after polymerisation, which demonstrates that the polymer is prepared in its closed form.

**Figure 5-8** Electrochemistry of 1c in solution compared to polymer (poly-1c) formed immediately after polymerisation of 1o on a glassy carbon electrode, 0.1 M TBAPF₆ in CH₂Cl₂, scan rate 0.1 V/s.
Mechanism of electropolymerisation

The unusually high overpotential for the onset of electropolymerisation is rationalised in Scheme 1. The first oxidation process (0.9 V) observed for 1o involves the peripheral bithiophene units, which is followed by intramolecular electron transfer to the dithienylethene switching unit and subsequently ring closing to form 1c$^{2+}$. This conclusion is consistent with electrochemistry of other dithienylethene switches bearing redox active side groups. For 1c the first and second oxidation processes are dithienylcyclopentene centered (Figure 5-8) and hence when oxidation of either 1o or 1c at < 1.2 V results in the formation of 1c$^{2+}$, with electrostatic interactions with the bithiophene units shifting their oxidation potential to > 1.2 V (Figure 5-3).

A redox co-polymer of repeating tetrathiophene-phenyl-dithienylcyclopentene-phenyl units is formed upon multi-cycle cyclic voltammetry of 1o. The dithienylcyclopentene component of the polymer is in the ring closed state after electropolymerisation (poly-1c, Scheme 5-3). The cyclic voltammetry of the poly-1c modified electrode in monomer free solution is shown in Figure 5-8. Two well defined reversible oxidation waves are observed at potentials similar to those of 1c in solution. Additional redox processes are observed at higher potentials that correspond to those of poly-thiophenes, as observed for poly-2.

Electrochemical switching

The switching of the polymer modified electrodes from poly-1c to poly-1o and vice versa could be achieved electrochemically (Figure 5-9). This can be monitored, without switching the material, using cyclic voltammetry, by cycling between 0.0 and 0.5 V, since ring opening is relatively slow, as shown earlier for dithienylethene based SAMs and polymers. In this range the poly-1c/poly-1c$^{+}$ redox process is observed. In the open state the Faradaic current is negligible compared to that in the closed state. Importantly the tetrathiophene units formed in the electropolymerisation are conductive upon doping at potentials intermediate of the open and closed states of the dithienylcyclopentene core, thereby enabling switching of conductivity potentiostatically through the whole film regardless of thickness.
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Figure 5-9 Electrochemical switching; ring closing of the dithienylcyclopentene unit of poly-10 to poly-1c (conditions as for Figure 5-3, in monomer free solution, initial scan shown in black).

From the closed polymer (poly-1c) spontaneous ring opening to the open polymer form (poly-10) is observed after several hours, depending on polymer film thickness, due to the presence of trapped charges within the film.\textsuperscript{46, 47} The ring opening was manifested as a disappearance of the redox waves at 0.3 and 0.6 V (i.e. the oxidation of 1c to 1c\textsuperscript{+} and 1c\textsuperscript{2+}, respectively) and an increase in the intensity of the oxidation waves above 0.8 V. Cyclic voltammetry between -0.2 and 1.4 V resulted in ring closure to restore the closed polymer poly-1c (Figure 5-9), as observed for monomer when starting the electropolymerization with the open form (vide supra).

Electrochemical ring opening was also achieved by holding the film at ca. 0.35 V or by repeated cyclic voltammetry between -0.4 and 0.4 V (Figure 5-10), i.e. only sufficiently positive to form poly-1c\textsuperscript{+}, as shown previously for monolayers of dithienylethenes.\textsuperscript{31, 33} Multiple switching cycles were performed (Figure 5-10). Holding the potential at 0.0 V for an equal period of time did not result in any change to poly-1c. Based on the fact that a decrease in signal intensity with cycle number is observed in both the switching and the control experiment, this is ascribed to gradual dissolution of the polymer into the solvent. When propylene carbonate was used as a solvent, in which the solubility of the oxidised oligomers is higher, a higher rate of dissolution was observed. A change in morphology during swelling and shrinkage of the polymer is commonly observed for organic semi-conductive polymers.\textsuperscript{48} The gradual decrease in response is likely to be solved by application in a solid state device.
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Figure 5-10 a) Cyclic voltammetry between -0.2 and 0.4 V showing the first oxidation wave of poly-1c. b) Repeated switching between poly-1c and poly-1o. Ring opening was achieved potentiostatically at 0.35 V (15 min) and closing by a single cycle between -0.2 and 1.0 V. The \( I_{p,c} \) at 0.3 V after each step is shown in black. The control shows the change in \( I_{p,c} \) at 0.3 V when the potential used was 0.0 V (over 15 min).

Spectroscopic properties
Diarylethene switches undergo substantial changes in their UV/Vis absorption spectra upon switching as observed for 1o in solution (Figure 5-11). Similarly a change in the UV/Vis absorption spectrum of poly-1o was observed upon electrochemical ring closing of the dithienylethene units in the polymer (Figure 5-11), confirming that the diarylethene unit undergoes ring closure also.

Figure 5-11 UV/Vis absorption spectrum of a) 1o (thin) and 1c (thick) in CH₃CN and b) poly-1o/c on an ITO electrode (dry slide). (Thin is ring opened, thick is after electrochemical ring closure).

The polymer films were characterised by Raman spectroscopy. At \( \lambda_{\text{exc}} \) 785 nm resonance enhancement is expected for the polaronic states (as observed before for a related sexithiophene polymer). Spectroelectrochemistry reveals the changes in the resonance Raman spectra as the potential is varied (Figure 5-12). The resonance enhancement of Raman scattering from either the central switch unit or of the tetrathiophene unit in the polymer can be expected depending on the localisation of the polarons. At all potentials greater than 0.3 V the band at 1605 cm\(^{-1}\), which is characteristic of a phenyl ring, is strongly enhanced. The broad band at 1440 cm\(^{-1}\) persists at all potentials also and is characteristic of
the C=C symmetric stretch in the oxidised thiophenes. At potentials above 0.7 V additional bands assignable to the tetrathiophene mono/bipolaron are observed at 1160 cm\(^{-1}\), 1195 cm\(^{-1}\), 1230 cm\(^{-1}\) and 1505 cm\(^{-1}\). The absence of these vibrations below 0.7 V is consistent with the assignment of the redox processes below 0.7 V as being centered on the dithienylethene unit.

![Spectroelectrochemistry of the poly-1c on a gold bead electrode, \(\lambda_{exc} = 785\) nm, at 0.3 V (black), 0.7 V (blue), 1.1 V (green) and 1.4 V (pink).](image)

**Figure S-12** Spectroelectrochemistry of the poly-1c on a gold bead electrode, \(\lambda_{exc} = 785\) nm, at 0.3 V (black), 0.7 V (blue), 1.1 V (green) and 1.4 V (pink).

**Film conductivity**

The cyclic voltammetry of decamethylferrocene, which shows a reversible redox couple at -0.1 V, was used to demonstrate the effect of switching on the conductance of a poly-1c/poly-1o modified electrode. The cyclic voltammetry of decamethylferrocene in solution using an unmodified electrode (inset) and a polymer modified electrode in both the open (red line) and closed (blue line) states are shown in Figure S-13. Despite decamethylferrocene's oxidation being 0.5 V lower than the oxidation potential of the closed state polymer film a clear difference is observed between the cyclic voltammetry of decamethylferrocene upon switching the electrode from poly-1c state to the poly-1o state. In the open state, the redox chemistry of decamethylferrocene is blocked at potentials below 0.3 V. Upon ring closing, by a single cycle between 0.0 and 1.2 V, the conductivity of the polymer film is increased and a substantial increase in decamethylferrocene signal is observed. This shift in redox potential demonstrates an electrochemically driven switching of the conductance of the electrode.
Figure 5-13 Cyclic voltammetry of decamethylferrocene (inset unmodified glassy carbon electrode with decamethylferrocene, thin/red: poly-1o, thick/blue: poly-1c)

To further characterise the change in conductivity upon switching, in situ conductivity measurements were performed using Interdigitated Microelectrode Arrays (IDA). Polymerisation was performed using cycling voltammetry at a low scan rate (Figure 5-15) until a relatively homogeneous coverage of the electrodes was observed by optical microscopy (Figure 5-14).

Initially, upon polymerisation the current at both electrodes is equal. However, once a connection between the electrodes is made, clear changes between the source and drain currents can be observed, where the anodic is higher at the second electrode and the cathodic higher at the first electrode, i.e. source-drain behaviour.49,50
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**Figure 5-15** Polymerisation on an Interdigitated Microelectrode Array (IDA) using cyclic voltammetry, electrode 1 (black), electrode 2 (red). Source drain offset = 20 mV, scan rate is 0.05 V s\(^{-1}\).

**Figure 5-16** Electrochemical ring closing on an IDA, both electrodes are cycled with the same scan rate and in the same potential window. Scan rate = 0.1 V/s, no source drain offset, electrode 1 (thick), electrode 2 (thin).

Measurements carried out at scan rates higher than 0.1 V s\(^{-1}\) show a difference between the open and closed state in the potential window of -0.2 to 0.4 V vs SCE (Figure 5-17). However, analysis of the polymer formed on an IDA with a source/drain offset of 10 mV at low scan rates (5 mV s\(^{-1}\)) resulted in spontaneous ring opening on a much shorter timescale than observed on macro electrodes (*vide supra*). This is due to the occurrence of electrochemical ring opening occurring on a shorter timescale than that of the measurement. Since the data required to determine *in situ* conductivity can only be obtained using low scan rates, this precludes accurate determination of the conductivity of the polymer in the closed state. Measurements performed at faster scan rates did show significant difference in source-drain behaviour between the open and the closed form. This is depicted in Figure 5-17. Although at these scan rate the conductance of the polymer film cannot be calculated since the measured current is mainly faradaic, still lateral current is observed for the closed polymer film and not for the open polymer film. This demonstrates an increase in conductivity upon ring closing.
Conclusions
In this chapter a new polymeric functional material is described based on a bifunctional monomer in which the electropolymerisable groups are separated from the photochromic unit by phenyl spacers. The polymerisation can be carried out under ambient conditions. It is shown that both units retain their functionality with redox driven switching achieved in the polymer modified electrodes. The phenyl spacer is a key design component as it serves to separate the functionalities of the two functional components; the central switch unit and polymerisable bithiophene units. Upon switching of the polymer to the open form, the conductivity of the polymer films at potentials below 0.8 V decreases. The redox driven switching of the conductance was demonstrated by using a modified electrode to analyse the well-known redox couple of decamethylferrocene and the behaviour of the polymer in both open and closed states was probed using IDAs.

The observed redox-driven switching in conductivity of the polymer after formation is in contrast with previously reported systems in which the properties of the polymer were controlled solely in the preparation stage\textsuperscript{35-38} or which employ photochemically induced changes.\textsuperscript{16, 17} A key challenge in organic electronics is not to simply duplicate the functions achieved already with non-molecular materials but instead to introduce new behaviour. In the present case the ability to switch conductivity reversibly between two states using electrochemical stimulus is novel. This holds considerable advantages in terms of application compared with optically switched systems as it obviates the need for optical access to an organic electronic device. Furthermore the electropolymerisation and the polymer formed is not especially sensitive to oxygen or moisture, which facilitates application and opens new opportunities in the use of dithienylethene switches as electrochemical switchable components in closed electronic devices where the delivery of optical stimuli is not possible.
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**Experimental Section**

**Materials and instrumentation**
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. Bromodithiophene\(^{51}\) and 1,2-Bis[5-(4-bromophenyl)-2-methylthien-3'-yl]cyclopentene\(^{43, 52}\) 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 λ<sub>exc</sub> 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.

**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...
Na$_2$SO$_4$ 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(PPh$_3$)$_4$ (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 SiO$_2$:K$_2$CO$_3$ = 9:1 and rinsed with toluene. The organic layer was washed with brine (2 x 100 mL), dried over Na$_2$SO$_4$ and the solvent was evaporated. The crude impurities were removed by column chromatography (SiO$_2$, toluene), to obtain > 80% yield of crude compound. Analytically pure samples of 1o as a yellow solid were obtained by batch wise preparative TLC (SiO$_2$, 85:15 pentane/CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.7, 139.1, 137.4, 136.8, 136.6, 134.8, 134.7, 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 calc for C$_{43}$H$_{33}$S$_6$, [M+H]$^+$ 741.0907, found 741.0900.

**Model compound paraphenylbisdithiophene (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 purified using column chromatography (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 ºC) $\delta$ 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-ESI$^+$ m/z calc for C$_{22}$H$_{15}$S$_6$, [M+H]$^+$ 407.00511, found 407.00491.

**References**


