In this chapter the photochemical switching properties of the dithienylethene functional units have been employed to control the electropolymerizability of bis-terthiophene monomers onto conducting surfaces. The spectroscopic, electrochemical and photochemical properties of the monomer in solution are compared with those of the polymer formed through oxidative electropolymerization. The combination of alkene-bridged terthiophene units and the photoswitchable dithienylethene unit provides the ability to switch off and on the electropolymerizability of the monomer 4F with UV and visible light, respectively. In the open state (4Fo) electropolymerization yields alkene-bridged sexthiophene polymers through oxidative α,α-terthiophene coupling while in the closed state (4Fc) the polymerizability is switched off. The characterization and electrochromic properties of poly-4Fo are reported.

This chapter has been published in part in:
4.1 Introduction

Conjugated polymers, such as polythiophenes (PTs), offer several potential opportunities for development of organic electronic devices such as field-effect transistors, OLEDs, plastic photovoltaic cells, and electrochromic devices and sensors. These applications result from their remarkable electronic and optoelectronic properties. The flexibility of these polymer systems offered in terms of their physical characteristics and processibility sets them apart from non-molecular semiconducting and conducting materials. Although the syntheses of polymeric materials from thiophene derivatives are well known, intensive research efforts focused on the optimization of the preparation of polythiophenes is in keeping with the emergence of widespread general interest in conducting polymers (CPs) since the early 1980s. PTs are essentially prepared by means of one of two routes, i.e chemical and electrochemical polymerization. However, it is evident that polymers produced by chemical synthesis contain a significant proportion of regiochemical defects. Furthermore electrochemical polymerization of the monomer is the most convenient, simple, and robust method that can produce polymer films, the thickness of which can be controlled by variation of the electrolysis time. The in situ formation of polymers on electrode materials by electrochemical techniques is a well established approach and, has focused primarily on the fabrication of conducting polymer films, providing electroactive polymer film layers for, for example, corrosion protection and for retaining biomolecules on surfaces.

Furthermore the functionality of both monomers and polymers can be extended by introducing responsive units that can be switched between two states using external stimuli, e.g., light, heat or redox switching. For instance, the introduction of photocontrolled switching units into a monomer to control its electropolymerizability could offer considerable opportunities in device fabrication. Dithienylethene switches have proven to be good platforms on which to build functional molecular-based systems, allowing for reversible control of properties as diverse as fluorescence, self-assembly, and molecular conductivity with light. In the following paragraphs, a short overview of the electropolymerization of dithienylethene switches will be presented.

4.2 Electropolymerization of Dithienylethene onto Conducting Surfaces

Electropolymerization of dithienylethene switches onto a conducting surfaces have been investigated by Kim and co-workers. Figure 1 shows the electropolymerization of an EDOT-modified diarylethene polymer. Diarylethene (BTFTT-I) was substituted with 3,4-ethylendioxythiophene (EDOT) as the electropolymerizable group. Upon electropolymerization of the BTFTT-I monomer, red-purple polymeric films (PBTFTT-Ic) were deposited on the working electrodes; a similar film was also deposited on an electrode
Electropolymerization of Dithienylethene: ON/OFF Photoswitching of the Electropolymerizability of Terthiophenes

from the solution exposed to UV light (BTFTT-1c) through electrochemical oxidation. The driving force for the polymerization of the closed isomer is the formation of redox-stable insoluble polymer with a lower oxidation potential due to the extended π-electron conjugation of the main chain formed. The film thickness correlated linearly to the number of potential cycles indicating that film growth could be controlled by cyclic voltammetry. The film color was bleached slowly by irradiation at 532 nm, as shown in Figure 1. The slow photoresponse time allowed Kim and co-workers to achieve the oxidative polymerization of BTFTT-1 copolymerized with EDOT as shown in Figure 2. The film electrodeposited on the ITO electrode showed reversible photocurrent switching in an electrolyte solution containing a quinone/hydroquinone by alternate switching on and off with UV light. The photocurrent generation in the polymer films prepared from the mixture of EDOT and BTFTT-1 was higher than compared to the PBTFTT-1 film, and increased as the content of EDOT was increased and the maximized when the ratio between the BTFTT-1 and EDOT was 1:1. The response time for the photocurrent switching was also faster in the film, indicating the importance of film composition for photoactivity.

Figure 1. Electrochemical deposition of BTFTT-1 on an ITO electrode and spectral change of PBTFTT upon irradiation with a 532 nm laser for 0, 15, 30, 45, 60, 75, and 90 min.16a

Figure 2. Electrochemical polymerization of copolymer BTFTT-1 and EDOT and photocurrent response of the polymer films at +0.5 V in a buffer solution containing hydroquinone. Film prepared from EDOT:BTFTT (a) 2:1, (b) 1:1, (c) 0.5:1, (d) 0:1 and (e) 1:016b
Recently Feringa and co-workers reported\textsuperscript{17} a one-step method for fabricating a photoresponsive dithienylethene switch bearing electropolymerizable methoxystyryl units,\textsuperscript{18} which enabled immobilization of the photochromic unit onto conducting substrates via electropolymerization (Scheme 1). Repetitive cyclic voltammetry of 2\textsubscript{o} between 0.0 and 1.6 V vs SCE results in a steady increase in the current response at ca. 0.4 and 0.6 V which was assigned to the formation of 2\textsubscript{c}\textsuperscript{2+} (Figure 3a). The polymerization occurs upon oxidation of the methoxystyryl groups, which form radical cations and undergo radical-radical coupling\textsuperscript{18} to form dimers and oligomers. The electropolymerization of 2\textsubscript{o} leads to the formation of poly-2\textsubscript{c} as shown in Figure 3. Photochemical ring opening of poly-2\textsubscript{c} by irradiation at >420 nm yields poly-2\textsubscript{o}. The cyclic voltammetry of poly-2\textsubscript{o} shows no Faradic current from 0 to 0.6 V, in contrast to poly-2\textsubscript{c}, which shows a one-electron reversible redox process at ca. 0.34 V (Figure 3c). The poly-2\textsubscript{o} modified electrode can be converted to poly-2\textsubscript{c} through oxidative ring closure via poly-2\textsubscript{c}\textsuperscript{+}. The photochemical ring opening and subsequent electrochemical ring closure of the polymer film deposited on ITO was followed by UV/Vis spectroscopy (Figure 3d). The absorption of the closed state in the visible region decreases upon irradiation at >450 nm and increases again after electrochemical ring closure. These data show that the ability of poly-2 to switch from the open to closed forms, and vice versa, both in an electrochemical and photochemical processes, respectively, is retained in the electropolymerized state. However, the electroactive polymer is formed as layers of limited thickness, regardless of the concentration of monomer present in solution or the deposition potential or time.

\begin{center}
\textbf{Scheme 1.} A bifunctional molecule incorporating photo/electrochromic dithienylethene and electropolymerizable methoxystyryl unit 2\textsubscript{o}.
\end{center}
Electropolymerization of Dithienylethene: ON/OFF Photoswitching of the Electropolymerizability of Terthiophenes

In this chapter the focus is on the electropolymerizability of bis-terthiophene monomers which is controlled by photochromic switching of a dithienylcyclopentene molecule. The design of the present system is based on the combination of alkene bridged bithiophene or terthiophene units and the well-known photoswitchable dithienylethene photochromic units as shown in Scheme 2. The oxidative polymerization of a diarylethene substituted with mono- and bi-thiophene $3H/3F$ and $4H/4F$, respectively, is described. It is known that terthiophene can be polymerized to yield polythiophene films through oxidative polymerization. Thus an oligothiophene-modified diarylethene is a promising material to control electropolymerization of these monomers, which could allow for the direct patterned electrodeposition of dithienylethenes as thin films for organic devices.
Chapter 4

4.3 Synthesis of the Dithienylethene-Substituted Oligothiophene

Compounds 3H/3F were synthesized according to literature procedures. The syntheses of the monomers are outlined in Scheme 3. Treatment of compound 5H or 5F with n-BuLi and subsequent reaction with tri-n-butylborate results in the corresponding boronic acid intermediates, which were reacted with 5-bromo-2,2'-bithiophene in the presence of a palladium catalyst providing 4H or 4F in 60% and 26% yield, respectively. The compounds were purified by column chromatography and characterized by 1H and 13C NMR spectroscopy and mass spectroscopy.

Scheme 3. Synthetic route to dithienylethene substituted bithiophene compounds 4H and 4F.
Electropolymerization of Dithienylethene: ON/OFF Photoswitching of the
Electropolymerizability of Terthiophenes

4.4 Electronic Properties

Figure 4 shows the UV/Vis absorption spectra of the open and closed forms of diarylethene
derivatives 3H/3F and 4H/4F in acetonitrile. Comparison of the electron-rich
hexahydrocyclopentene-based compounds (3Ho/3Hc and 4Ho/4Hc) with the electron-
deficient hexafluorocyclopentene-based compounds (3Fo/3Fc and 4Fo/4Fc) shows a
bathochromic shift in the lowest energy absorption bands in both the open and closed
forms. However, the effect of incorporating the hexahydrocyclopentene group instead of a
hexafluorocyclopentene group on the absorption spectra of the dithienylethene (e.g., 3Ho:
$\lambda_{\text{max}} = 295$ nm, 3Fo: $\lambda_{\text{max}} = 312$ nm) is quite modest, especially considering the large
difference in the redox properties (vide infra) of the hexahydrocyclopentene- (3Ho and
4Ho) and hexafluorocyclopentene-(3Fo and 4Fo) compounds. Moreover, the large
bathochromic shift observed in the closed form (4Hc versus 4Fc) is not as pronounced in
the open form (4Ho versus 4Fo), and this suggests that the influence of the
hexafluorocyclopentene group on the bithiophene substituent is minor in the open form.
This difference is rationalized on the basis of the loss of conjugation of the thieryl ring with
the bridging cyclopentene in the more flexible open state. The effect of the number of
thiophene units on the dithienylethene can be seen in the spectral changes between
3H and 3F with respect to 4H and 4F. Both, the absorption maxima of the open and closed forms
of 4H and 4F are shifted to longer wavelengths by 30 to 50 nm compared to 3H and 3F. As
expected, this band shifts to longer wavelengths in the UV/Vis absorption spectrum with
increasing number of thiophenes due to the increase in the $\pi$-conjugation length in the
longer oligomers.6,8,19

<table>
<thead>
<tr>
<th></th>
<th>Abs. $\lambda_{\text{max}}$ [nm] (c [10$^3$ cm$^{-1}$ M$^{-1}$])¹</th>
<th>$E_{pa}$ [V] vs SCE ($E_{pa}$ when irr)⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Open form</td>
<td></td>
</tr>
<tr>
<td>3Ho</td>
<td>281 (14), 295 (18)</td>
<td>1.10 (irr)</td>
</tr>
<tr>
<td>4Ho</td>
<td>364 (11)</td>
<td>0.87 (irr)</td>
</tr>
<tr>
<td>3Fc</td>
<td>312</td>
<td>1.42 (irr)</td>
</tr>
<tr>
<td>4Fc</td>
<td>365 (39)</td>
<td>1.14 (irr)</td>
</tr>
<tr>
<td></td>
<td>closed</td>
<td></td>
</tr>
<tr>
<td>3Hc</td>
<td>229 (10), 311 (18), 347 (8.5), 356 (9.5), 519 (13)</td>
<td>0.54, 0.29</td>
</tr>
<tr>
<td>4Hc</td>
<td>357 (9.8), 574 (5.9)</td>
<td>0.41, 0.26</td>
</tr>
<tr>
<td>3Fc</td>
<td>605</td>
<td>0.86 (qr), 0.78 (qr)</td>
</tr>
<tr>
<td>4Fc</td>
<td>391 (28), 647 (25)</td>
<td>0.65</td>
</tr>
</tbody>
</table>

¹: Photochemistry performed in MeCN, ²: Redox measurements were carried out in 0.1 M TBAPF$_6$/DCM, ³: From reference. 22
4.5 Redox properties

The redox properties of the open and closed states $3\text{H}/3\text{F}$ and $4\text{H}/4\text{F}$ were investigated using cyclic voltammetry (CV). The closed states were prepared readily by UV irradiation at 365 nm until the photostationary state (PSS) was reached. The electrochemical properties of the hexahydro- and hexafluoro-dithienylcyclopentenes of the oxidized compounds in the +1 and +2 oxidation states are summarized in Table 4.1. In the open state, $3\text{H}$ exhibits an irreversible oxidation at $E_{p,a} = 1.10$ V (V vs SCE), leading to oxidative ring closure to $3\text{Hc}^{2+}$, which can then be reduced, first to $3\text{Hc}^+$ at 0.54 V and finally $3\text{Hc}$ at 0.29 V as shown in Figure 5a. By comparison with $3\text{F}$, the redox chemistry is characterized by an irreversible oxidation at 1.42 V, which gives rise to two quasi reversible redox waves at 0.86 and 0.78 V $\{3\text{Fc}^{2+} \rightarrow 3\text{Fc}^+ \rightarrow 3\text{Fc}\}$ as shown in Figure 5b. $3\text{F}$ in both open and closed form, displayed redox processes at more positive potentials than in $3\text{H}$. For both $4\text{H}$ and $4\text{F}$ (Figure 6), irreversible oxidation processes are observed at $E_{p,a} = 0.87$ and 1.14 V (V
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vs SCE), respectively. An irreversible oxidation process in 4Ho results in oxidative ring-closure to form 4Hc\textsuperscript{2+}, which is reduced to 4Hc\textsuperscript{+} and then to 4Hc at 0.41 and 0.26 V (Figure 6a). The redox chemistry of dithienylethene 3Ho/3Fo and 4Ho shows similar reactivity to that observed in related dithienylethene switches.\textsuperscript{20b}

The redox chemistry of the open form of 4Fo is characterized by an irreversible oxidation at 1.14 V (V vs SCE), however, on the return cycle the irreversible oxidation of 4Fo does not give rise to oxidative ring closure (e.g., to 4Fc\textsuperscript{2+}). The appearance of broad redox waves was observed and assigned to the accumulation of oxidation products on the surface of the electrode\textsuperscript{19,23} (vide infra). Cyclic voltammetry of 4Fc, obtained after irradiation of a CH\textsubscript{2}Cl\textsubscript{2} solution of 4Fo with 365 nm light for 5 min, showed reversible redox processes at 0.65 V vs SCE \{4Fc \rightarrow 4Fc\textsuperscript{2+}\} as shown in Figure 6b. However, the separation of the first and second oxidation process (\(\Delta E\)) is less than the resolution limit for both cyclic and differential pulse voltammetry (<30 mV). It is known that oligothiophenes generally tend to show less positive oxidation potentials with the addition of each thiophene unit.\textsuperscript{8,19} Hence the effect of the number of thiophene units substituted on the dithienylethene can be seen in the cyclic voltammetry of 3H and 3F with respect to 4H and 4F. Both, the oxidation potential of the open and closed forms of 4H and 4F are shifted to less positive potentials by 130 to 280 mV compared to 3H and 3F, respectively. These results were in agreement with changes in their UV/Vis spectra, respectively.

**Figure 5.** Cyclic voltammetry of a) 3Hc (top) and 3Ho (bottom), b) 3Fc (top) and 3Fo (bottom) in 0.1 M TBAPF\textsubscript{6} / CH\textsubscript{2}Cl\textsubscript{2} at 0.1 V s\textsuperscript{-1}. 
Figure 6. Cyclic voltammetry of a) 4Hc (top) and 4Ho (bottom), b) 4Fc (top) and 4Fo (bottom) in 0.1 M TBAPF$_6$ / CH$_2$Cl$_2$ at 0.1 V s$^{-1}$. The CVs of the closed forms are offset along the coordinate for clarity. The integral potential used is the open circuit potential.

In previous studies in our group,$^{20b,24}$ it has been shown that redox properties of the dithienylethenes can be tuned towards electrochemical ring-closing and ring-opening by stabilization or destabilization of the mono- and dication of the closed state, respectively. Alternatively, redox-active groups may be employed to change the direction of switching. It is important to recognize the mechanism by which these processes occur as summarized in Scheme 4. The driving force for electrochemical ring opening and closing observed in hexahydro- and hexafluoro-cyclopentene systems appears to lie in the ability of the bridging cyclopentene moiety to allow for stabilization of the dicaticonic species as depicted in Scheme 4. In ring-closure, the driving force is stabilization of the dication through (partial) delocalization of the charge over the thiophene rings. Where the communication between the rings is poor, as is the case in hexafluoro compounds, the stabilization achieved does not compensate for the loss of ring stabilization (aromaticity), and thus ring opening of the monocation/dication of the closed form is favored.

Indeed in the case of 4Fo the positive shift in the first oxidation potential compared with 4Ho is only 230 mV. This indicates that the oxidation is localized on the terthienyl moieties and not on the dithienylecyclopentene core. As a result the oxidized species is best viewed as a terthiophene radical cation and not as a [dithienylethene]$^{2+}$ species. Hence, the description of the system as a terthiophene radical cation is more apt as evidenced by the propensity for the molecule to undergo oxidative electropolymerization (vide infra) rather than ring closing as seen for 4Ho, etc. In the case of 3Ho, 3Fo, and 4Ho, which are structurally analogous to 4Fo, there is a thermal equilibrium between the dicaticonic open and closed form of dithienylethene with increased electron donating character of both the substituents on the thiienyl rings and the cyclopentene bridge moving the equilibrium toward the formation of the ring closed isomers. 3Hc, 3Fc, and 4Hc, respectively, show that they are functionally dithienylethenes. In these systems the rate of thermal ring closure upon
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Oxidation of the open form is much faster, and hence electrochemical ring closing is observed and not electropolymerization.

Scheme 4. General scheme for electrochemical processes observed in dithienylethene based system.\textsuperscript{20b}

4.6 Electropolymerization

Electropolymerization was carried out using multiple cycle cyclic voltammetry in CH$_2$Cl$_2$ solution containing ca. 2 mM of monomers and 0.1 M of TBAPF$_6$ as a supporting electrolyte. First electropolymerization of 3Ho/3Fo and 4Ho/4Fo was attempted on glassy carbon electrodes, however only 4Fo showed electropolymerization on the electrode (vide supra). The cyclic voltammogram of compound 4Fo between 0.0 and 1.20 V (vs SCE) presents an irreversible oxidation corresponding to the oxidation of the compound to the corresponding dication. Subsequent cycling leads to the emergence, at less positive potentials, of a new redox system associated with the oxidation and reduction of the polymer grafted onto the electrode surface as shown in Figure 7a. The increase in current is due to the combined electroactivity of the polymeric film building up on the electrode surface while monomer diffuses towards the electrode from the bulk of the solution. The rate of increase with respect to number of cycles is approximately linear indicating that the conductivity through the polymer is high at the scan rate employed as shown in Figure 7a (inset). During deposition the shape of the voltammogram changes from the typical shape of a diffusion controlled process into the broad shaped voltammogram of a surface-confined species since for each scan the current increases proportionally due to the oxidation and reduction of the surface-confined material. After repeated scanning, the coated electrode is removed from the monomer solution and rinsed with dichloromethane to remove mono- and oligomeric material and a smooth adherent yellow film is observed. It is evident that compound 4Fo can undergo oxidative polymerization. It has been shown already that the oxidation potential of terthiophene derivative 4Fo decreases when
increasing the chain length of this oligomer, e.g. bithiophene derivative 3Fo, $E_{pa}=1.42$; terthiophene derivative 4Fo, $E_{pa}=1.10$ V.

In a monomer-free electrolyte solution (Figure 7b), a surface-confined redox process is observed with the appearance of a reversible redox wave at 1.1 V and a quasi-reversible redox wave at ca. 0.7 V vs SCE. In order to investigate the scan rate dependence of the peak current, the polymer film coated working electrode was cycled between oxidized and reduced states over several scan rates (0.1 to 1.0 V s$^{-1}$). The scan rate dependence of the peak current shows a linear dependence on scan rate as illustrated in Figure 8. This demonstrates that the films were well-adhered and the electrochemical processes are reversible, non-diffusion-controlled, and originate from electrode-bound redox active species.\(^{25}\)

The anodic polymerization of 4Fo was successfully carried out on glassy carbon, platinum, gold, and ITO electrodes by cyclic voltammetry under various conditions, for instance in different solvents (dichloromethane and propylene carbonate), different supporting electrolytes (TBAPF$_6$ and TBAClO$_4$) and at a wide range of monomer concentrations (0.1-2.0 mM). Remarkably, the formation of the polymer film proceed smoothly at a monomer concentration $\sim 0.1$ mM and was insensitive to air and trace water (i.e. anhydrous conditions and/or Lewis acids were not required).\(^{26}\) Electrodeposition of the polymer on ITO yields an adherent yellow film which is mechanically stable (with respect to peeling), and a loss of electroactivity under repeated potential scanning is not observed. Moreover it can be stored in air for at least several days. Poly-4Fo is insoluble in CH$_2$Cl$_2$, CH$_3$CN, and toluene upon storage of the electrode for several hours in those solvents. It is not surprising as it is well known in the field of conjugated polymers that the strong $\pi$-$\pi$ interactions between the chains often lead to completely insoluble polymers.\(^{27}\)

**Figure 7.** a) Cyclic voltammetric scanning electropolymerization of 4Fo monomer in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$ cycled at 0.1 V s$^{-1}$ on gold micro electrode (10 µm diameters) *Inset:* Increase in current at 0.73 V vs SCE with number of cycles. b) Cyclic voltammogram of the polymer coated gold electrode in monomer-free 0.1 M TBAPF$_6$/CH$_2$Cl$_2$
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Figure 8. a) Cyclic voltammogram of poly-4Fo modified glassy carbon electrode in monomer free CH₂Cl₂ (0.1 M TBAPF₆) solution at 0.10, 0.20, 0.50, 0.75, and 1.00 V s⁻¹, carbon working electrode A = 0.071 cm²) b) linear dependence of current on scan rates between 0.1 and 1.0 V s⁻¹.

In the open state (4Fo) electropolymerization occurs upon oxidation of the terthiophene moieties to the cation radicals and subsequently oxidative α,α'-terthiophene coupling to yield alkene bridged sexithiophene polymers. The oxidative electropolymerization of the bis-oligothienyl-substituted dithienylethene switch is expected to result in the formation of linear polymers with the α-carbons of the outermost thienyl groups of each monomer linked to the neighboring monomers’ outermost α-carbons as illustrated in (Scheme 5).⁶,⁸

Scheme 5. General scheme represent the electropolymerization of 4Fo.
In order to confirm the electropolymerized process can only be achieved in the open state of 4Fo, we attempted to polymerize the closed form of 4F by using the isolated photocyclized compound 4Fc. After several cycles with cyclic voltammetry the increase in current due to the combined electroactivity of the polymeric film building up on the electrode surface was not observed as shown in Figure 9. Cyclic voltammetry of 4Fc showed the reversible oxidation of the dithienylcyclopentene core at 0.65 V vs SCE. When the ring closed form 4Fc is oxidized to the dicationic state the positive charge is centered in the dithienylethene core unit. Hence the cationic radical character of the terminal thiophene units are insufficient to permit $\alpha,\alpha'$-dimerization (Scheme 5). Based on earlier studies (Scheme 4), it is known that there is a thermal equilibrium between the dicationic open and closed forms of dithienylethene (i.e. between 4Fo$^{2+}$ and 4Fc$^{2+}$) with increased electron donating character of both the substituent on the thienyl rings and the cyclopentene bridge shifting the equilibrium towards the closed state. Hence it would be expected that oxidation of 4Fo would lead to formation of 4Fc$^{2+}$. However, in this system the rate of ring closure is insufficient to compete with that of the $\alpha,\alpha'$-coupling of 4Fo$^{2+}$ giving sufficient time for electropolymerization to proceed.

![Figure 9](image)

**Figure 9.** Cyclic voltammogram of 4Fc at the gold electrode in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$, scan rate 0.1 V s$^{-1}$. 

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4.7 Characterization of poly-4Fo films

4.7.1 Surface Characteristics of poly-4Fo on ITO

The contact angle of an ITO electrode before and after electropolymerization was found to change from 20° to 90-100°. No significant differences in contact angle were observed when the polymer films were prepared with different numbers of scans using cyclic voltammetry. AFM has proven to be a useful technique in studying the morphology of electodeposited polymer films on ITO surfaces. The tapping-mode AFM image of clean ITO and ITO surface on which poly-4Fo films are formed by electropolymerization are shown in Figure 10. The topographic AFM image of the clean ITO sample (Figure 10a) consists of crystalline grains. AFM topographic images after electropolymerization of 4Fo onto the ITO surface are shown in Figure 10b and Figure 10c. The surface morphology changes from crystalline grains, on bare ITO, to a globular structure on the polymer modified ITO with an approximate rms roughness of 100 nm. The phase contrast images corresponding to the topographic image is shown in Figure 10d with a surface roughness of ~100 nm. The AFM images of poly-4Fo show that under the conditions employed for electropolymerization, the ITO is covered homogeneously by the polymer film. The thickness of the polymer film can be tuned by the number of cycles used during the electropolymerization, for instance 25 cycles yields a thickness of ca. 57 nm and 50 cycles a thickness of ca. 100 nm.
4.7.2 FTIR-Raman Spectroscopy

The FT-IR spectra of monomer 4Fo and its redox polymer poly-4Fo are shown in Figure 11. The spectrum of the polymer is nearly identical to that of the monomer except for the disappearance of the band at 695 cm\(^{-1}\) (the characteristic C\(_\alpha\)-H o.o.p. deformation band at the terminal thiophene rings) and the presence of a strong band at 796 cm\(^{-1}\) (the corresponding band of the C\(_\beta\)-H o.o.p. deformation mode of the thiophene rings of the

Figure 10. a) Topographic image of bare ITO (5x5 µm\(^2\)), b) topographic image of poly-4Fo on ITO surface (5x5 µm\(^2\)), c) topographic image and d) phase contrast image of poly-4Fo on ITO surface (1.5x1.5 µm\(^2\)).
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sexithiophene band). This indicates that $\alpha$-$\beta$ and $\beta$-$\beta$ mislinkages are unlikely to occur significantly in the polymer film. Polyythiophene has been shown to proceed with a 95% preference for $\alpha,\alpha$-coupling over $\alpha,\beta$-coupling when it is synthesized electrochemically (Scheme 6). Furthermore, the strong bands at 1275, 1190, 1142, 1137, 1120, 1050, and 845 cm$^{-1}$ correspond to the main absorptions arising from the hexafluorocyclopentene ring (C-F stretching vibrations). The stretching frequencies of the C=C bonds in polysexithiophene appear in the region 1400-1500 cm$^{-1}$. The electropolymerization was confirmed by using Raman Spectroscopy to compare the spectra of the polymer with that of its monomer. In contrast to IR spectroscopy, the effect of the presence of the perfluorocyclopentene moiety has only a minor effect on the Raman spectrum (lack of strong scattering from C-F stretching vibrations). As shown in Figure 12, the polymer displayed peak broadening between 1400-1500 cm$^{-1}$, indicative of polymerized product with respect to the typical vibrational peak of C=C bonds in the thiophene unit around 1450 cm$^{-1}$, which is in agreement with that reported for polyythiophene.

Scheme 6. Competitive reactions pathways in the electropolymerization of thiophene.

Figure 11. FTIR spectra of (top) monomer 4Fo in KBr and (bottom) an electrochemically deposited film of poly-4Fo on gold surface.
4.8 Photochemical and electrochemical switching of a polymer film

The absorption spectra for monomer 4Fo and poly-4Fo are presented in Figure 13. In the neutral state the polymer exhibits an absorption maximum in the UV-Visible range, at 427 nm, and corresponds to the π-π* transition of the oligothienyl group in the backbone which is close to those observed for polythiophene (between 418-480 nm, depending on the method of preparation). The absorption maxima for poly-4Fo are expected at lower energy than for monomer 4Fo (λ_{max} = 365 nm) due to the increased conjugation of the thiényl groups in the polymer backbone. The photochemical switching of poly-4Fo was examined with UV-Vis spectroscopy. However, attempts to accomplish ring-closing of poly-4Fo using prolonged irradiation at λ = 365 nm did not result in any change to the UV-Vis spectra. It is clear that the poly-4Fo remained in the ring-open form as shown in Figure 13b. Moreover, the electrochemical switching of poly-4Fo to generate poly-4Fc was not observed. The cyclic voltammetry of poly-4Fo (quasireversible redox potential at 0.7 and 1.1 V vs SCE) was unaffected even after several scans of cyclic voltammetry Figure 14 and a new redox wave assignable to poly-4Fc was not observed at lower potential either. The cyclic voltammetry of poly-4Fo is characteristic of a sexithiophene-based polymer. Overall although successful electropolymerization of a dithienylethene 4Fo monomer was achieved at a conducting surface, the photochemical and electrochemical switching functionalities of the polymer are lost when the switching unit is immobilized (Scheme 7).
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Figure 13. a) UV-Vis spectra of 4Fo-monomer in toluene solution and poly-4Fo film electrodeposited on ITO glass; b) UV-Vis spectra of poly-4Fo on ITO before (---) and after (—) irradiation at 365 nm.

Figure 14. Repetitive cycles of poly-4Fo on a glassy carbon electrode.

Scheme 7. Attempted photo- and electrochemical switching of dithienylethene in polymer backbone.
Generally, 4Fo can be viewed as either a photochromic dithienylethene unit substituted by bis-bithiophene or as an alkene bridging terthiophene units. The bithiophene-substituted photochromic dithienylperfluorocyclopentene (4F) can be switched reversibly by UV and visible light between a colorless open state (4Fo) and a colored closed state (4Fc), respectively. In the open state (4Fo) electropolymerization yields alkene bridged sexithiophene polymers through oxidative $\alpha,\alpha$-coupling, while in the closed state (4Fc) the polymerizability is switched off (Scheme 8). The electropolymerizability of the bis-terthiophene bridged alkene has been controlled by photochemical switching of the photochromic dithienylethene unit.

Scheme 8. Photochemical switching between polymerizable (4Fo) and non-polymerizable (4Fc) states towards poly-sexithiophene bridged alkene (poly-4Fo).

### 4.9 Spectroelectrochemistry of poly-4Fo

To examine the effect of oxidation on the spectral characteristics of the electopolymerized films, in situ spectroelectrochemistry of poly-4Fo on transparent ITO was performed. The cyclic voltammograms of these films were similar to those obtained on glassy carbon, Pt or gold. Optical spectra of the films at three potentials: neutral (0.0 to 0.3 V), oxidized (0.8 V) and fully oxidized (1.3 V) were obtained. These spectra, over the range 320-1650 nm, are shown in Figure 15. The polymer exhibits a yellow color in the neutral state, with an absorption maximum at 420 nm assigned to a $\pi-\pi^*$ transition of the hexathiienyl component.
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of the polymer. Upon oxidation at 0.8 V, the polymer film becomes blue with the intensity of the 420 nm absorption band decreasing and the appearance of a new broad absorption band in the NIR region (600-1600 nm) assigned to the polaron state of mono-oxidized sexithiophene ($\lambda_{\text{max}}$ 660, 1084 nm). At 1.3 V a further change to a purple colored film is observed with broad features characteristic of a bipolaron state in the 900-1300 nm region of the electronic absorption spectrum. The coloration is easily tuned by varying the thickness of the poly-4Fo film.

![Figure 15](image1.png)

**Figure 15.** a) UV/Vis/NIR spectroelectrochemistry for polymer 4Fo on indium tin oxide (ITO) glass, Pt wire counter electrode, Ag wire pseudo reference electrode, TBAPF$_6$ supporting electrolyte (0.1 M in dichloromethane) passing from neutral to positive potentials, from 0.3 to 1.3 V, scan rate 0.1 Vs$^{-1}$ and b) color changing of a poly-4Fo film on ITO.

During redox switching, distinct color changes are observed demonstrating the potential utility of these polymers as electrochromic films. For electrochromic applications, it is most important for a polymer to switch rapidly between two colored states and to exhibit a striking color change. A square-wave potential step method coupled with optical spectroscopy known as chronoabsorptometry$^{23}$ is used to probe the transmittance changes with time during repeated potential stepping between the neutral and oxidized states. The experiments carried out by square-wave potential voltammetry showed the ability of poly-4Fo to switch between its neutral and oxidized states with a change in transmittance at fixed wavelengths (1150, 650, and 420 nm). The electrochromic switching between 0.0 to 1.3 V can be performed over multiple cycles as expected for a stable oligothiophene based polymer as shown in Figure 16. Indeed poly-4Fo is quite robust and can be switched without loss of signal. Furthermore the reversibility of the change during redox switching with full

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recovery of the initial spectrum at 0.0 V and the absence of the color change with irradiation with UV light (vide supra) confirms that ring closing does not occur in the redox polymer film either electrochemically or photochemically.

![Figure 16](image)

Figure 16 Electrochromic switching and optical absorbance monitored at 420, 650, and 1150 nm with time during repeated potential stepping between the neutral and oxidized states (0.0 V to 1.3 V) with a switching interval 10 s in a 0.1 M TBAPF$_6$ / CH$_2$Cl$_2$ medium.

### 4.10 Photo-patterning of Polymer Formation

As mentioned above, the rate of thermal ring closure upon oxidation of the open form of 4F is insufficient to compete with that of the α-α’ coupling of 4Fo$^2+$, i.e. electropolymerization is a dimerization process. The ability to control electropolymerizability by light allows for localization of polymer growth/deposition through optical patterning. Thus, using 4Fo, the controlled delivery of polymerizable monomer units to a preferred site for electropolymerization can be achieved.$^{19a}$ A solid film of 4Fc on ITO glass was irradiated with visible light (520 nm) through a mask to generate 4Fo locally. A potential of 1.3 V was applied to the ITO electrode, which resulted in polymer film formation only where the film was in the open state (4Fo) as shown in Figure 17 and Figure 18.
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**Figure 17.** 4Fc was deposited onto an ITO coated glass slide (left) and irradiated at $\lambda > 520$ nm through a patterned mask (right). The less colored pattern at the centre of the slide contains predominantly 4Fo.

**Figure 18.** Two examples of photopatterned slides that were held at 1.3 V vs SCE in propylene carbonate (0.1 M TBAPF$_6$). 4Fc when oxidized dissolves readily into solution whilst the 4Fo in the patterned areas underwent electropolymerization.

### 4.11 Conclusions

In summary, the ability to switch off and on the electropolymerizability of bis-terthiophene 4F with light is reported. In the case of 3Ho, 3Fo, and 4Ho, which are structurally analogous to 4Fo, the electrochemical driven formation of the ring closed isomers 3Hc, 3Fc, and 4Hc, respectively, was observed. This shows that they are functionally dithienylethene switches. In these systems the rate of thermal ring closure upon oxidation of the open form is much faster, and hence electrochemical ring closing is observed and not electropolymerization. Indeed 4F shows that the inherent character of a molecule (polymerizable terthiophene vs electrochromic dithienylethene) can be switched by light in a fully reversible manner. In the open state 4Fo, the terthiophene cation radical formed by oxidation reacts readily via $\alpha,\alpha'$-dimerization to form perfluorocyclopentene bridged sexithiophene polymers. In the closed state 4Fc, oxidation results in the formation of a stable dication, in which the cationic radical character at the $\alpha$-position of the two terthiophene units is insufficient for $\alpha,\alpha'$-coupling to proceed and thus the oxidized 4Fc$^{2+}$
does not engage in polymerization. The photochemical and electrochemical switching functionalities of the dithienylethene are lost when the switching unit is incorporated into the extended conjugated system of polymer which was evidenced by spectroelectrochemistry. Furthermore this system shows robustness in the electropolymerization of the monomer with respect to H2O or oxygen and the stability of the polymer after several cycles of cyclic voltammetry making this system potentially useful in controlling electropolymer deposition in a broad range of applications e.g. in conducting polymer based-devices.37

4.12 Acknowledgements

Dr. G. T. Carroll is acknowledged for the assistance with AFM measurement. The syntheses of compounds 3H/3F were performed by Dr. J. J. D. de Jong and Dr. T. Kudernac.

4.13 Experimental Section

See Chapter 2 for information on synthesis and characterization and general details.

Compound 1H, 1F, 2H, 2F, 5H, and 5F were synthesised according to the previously reported methods. UV/Vis spectra were recorded (in solution or for polymer modified ITO slides) using a JASCO 670 UV-Vis-NIR spectrometer. Electrochemical measurements were performed using a Model 630B or 760C Electrochemical Workstation (CH Instruments). 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 was employed as a working electrode (CH Instruments), a Pt wire auxiliary electrode and Ag/AgCl ion quasi reference or a SCE electrode were employed (calibrated externally using a 0.1 mM solution of ferrocene, all potentials reported are relative to the SCE). Cyclic voltammograms were obtained at sweep rate between 100 mV and 5000 mV/s. FT-IR spectra were recorded in reflectance mode using a Nicolet Nexus FTIR spectrometer. Raman Spectra were recorded at an excitation wavelength, λexc of 785 nm on gold slides on an Avalon R1-ST Raman station.

2-(5-Methyl-4-(2-(2-methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)thiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)thiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)thiophene (4H). Compound 5H (0.19 g, 0.59 mmol) was dissolved in anhydrous THF (20 ml) under nitrogen and n-BuLi (0.92 ml, 1.6 M in n-hexane, 1.47 mmol) was added slowly by syringe. This solution was stirred at room temperature for 1 h and B(OBu)3 (0.40 ml, 1.47 mmol) was added in one portion. After the mixture had been stirred for 1 h at room temperature, THF (40 ml), aqueous Na2CO3 (5 ml, 2M), 5-bromo-2,2’-bithiophene (0.57 g, 1.77 mmol) and Pd(PPh3)4 (40 mg, 0.03 mmol) were added, and the mixture heated at reflux overnight. The reaction mixture was cooled to
room temperature, H2O (10 ml) was added, the organic layer separated and the aqueous
layer extracted with ethyl acetate (2x20 ml). The combined organic layers were dried over
Na2SO4, and the solvent evaporated. The product was purified by column chromatography
on silica gel (n-heptane) to give the product as a green solid (0.2 g, 60%). m.p. = 150.6-
154.1 °C; 1H NMR (400 MHz, CDCl3) δ = 1.97 (s, 6H), 2.07 (m, 2H), 2.82 (t, 4H, J=7.7 Hz,
7.3 Hz), 6.89 (s, 2H), 6.95 (d, 2H, J=3.6 Hz), 7.00 (dd, 2H, J=5.2 Hz, 3.6 Hz), 7.04 (d, 2H,
J=3.6 Hz), 7.14 (dd, 2H, J=3.3 Hz, 1.1 Hz), 7.20 (dd, 2H, J=5.1 Hz, 1.1 Hz), 13C NMR (100
MHz, CDCl3) δ 14.7 (q), 22.3 (t), 38.4 (t), 123.4 (d), 123.5 (d), 124.2 (d), 124.6 (d), 124.5
(d), 127.8 (d), 127.7 (s), 134.3 (s), 134.6 (s), 135.5 (s), 136.4 (s), 136.5 (s), 137.2 (s); EI-
MS (M+) = 588; HRMS C31H24S6  Found 588.0180, Calcd 588.0202.

2-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)thiophen-3-
yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)-5-(thiophen-2-yl)thiophene (4F).
Compound 5F (0.21 g, 0.48 mmol) was dissolved in anhydrous diethyl ether (20 ml) under
nitrogen and n-BuLi (0.75 ml, 1.6 M in n-hexane, 1.2 mmol) was added slowly by syringe.
This solution was stirred at room temperature for 1h and B(OBu)3 ( 0.32 ml, 1.2 mmol) was
added in one portion. After the mixture had been stirred for 1h at room temperature, THF
(30 ml), aqueous Na2CO3 (5 ml, 2M), 5-bromo-2,2'-bithiophene ( 0.62 g, 1.92 mmol) and
Pd(PPh3)4 (33 mg, 0.02 mmol) were added, and the mixture 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. The product was
purified by column chromatography on silica gel (n-heptane) to give the product as a green
solid (90 mg, 26%). m.p.= 184.1-184.8 °C; 1H NMR (400 MHz, CDCl3) δ = 1.97 (s, 6H),
7.02 (m, 4H), 7.08 (d, J=4.7 Hz, 2H), 7.13(s, 2H), 7.18 (d, J=3.3 Hz, 2H), 7.23 (d, J=5.1
Hz, 2H); 13C NMR (100 MHz, CDCl3) δ = 14.5 (q), 122.5 (d), 123.9 (d), 124.2 (d), 124.6
(d), 124.7 (d), 125.5 (s), 127.9 (d), 134.7 (s), 135.3 (s), 136.8 (s), 140.8 (s); EI-MS (M+) =
696; HRMS C31H18F6S6  Found 695.9622, Calcd 695.9636;

4.14 References

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Mater. 2002, 14, 99-127


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29 Film thickness was measured by a dektak profilometer. To quickly measure the thickness profile of a film, the dektak profilometer is used. It is a surface contact measurement technique where a very low force stylus scans across a surface and measures a profile with a vertical resolution of a few nanometres over a scan length of up to millimeters.


