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Electrochemistry of dithienylethenes and their application in electropolymer modified photo- and redox switchable surfaces

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Diarylethenes have proven to be versatile responsive components in many applications due to their photochromic properties. In recent years their potential use as redox switchable components has become increasingly apparent. Applying dithienylethenes as redox switchable components requires their immobilisation on conducting substrates and hence electropolymerisation is a promising, albeit, challenging approach to developing such systems. In this review the electrochemical properties of dithienylethenes will be discussed together with a consideration of mechanistic aspects of the switching processes observed followed by a review of recent efforts to develop dithienylethene based redox and photoswitchable redox polymers through electropolymerisation.

Introduction

Over the last decade the development of smart surfaces[1] that can respond to external stimuli, such as light, heat, redox chemistry, *etc*., has seen increasing interest in areas ranging from cell culturing,[2] droplet transport and wetting,[3,4] microfluidic devices,[5] as functional surfaces[6,7] and increasingly in the molecular and organic electronics.[8–10]

Molecular based smart surfaces are especially attractive both because of the fine control of responsive function that can be exercised through synthetic variation and by the possibility of introducing switching units with well-defined but tunable properties.[11,12] Photochromic compounds have received most attention due to their wide range of properties that can be controlled through photochemically triggered changes in molecular polarity and dipole moment. The ensemble changes in molecular properties result in macroscopic changes to surface characteristics.[13] By contrast, redox switching of molecular based modified surfaces has received less attention in part due to the challenges presented by

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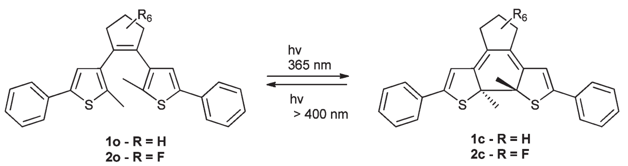

Scheme 1 Photochromic switching (ring opening and ring closing).

immobilising redox switchable molecular systems on electrodes and the relatively limited number of such systems that can provide robust switching over multiple cycles.[14]

Diarylethenes are a well-studied class of molecular photochromic switches.[15,16] Upon irradiation of the open form of a diarylethene with UV light a 6-π photocyclization reaction occurs, leading to ring closure (Scheme 1).[17] Upon irradiation with visible light the reverse 'ring opening' reaction occurs. They are of particular interest both because of their often excellent photochromic properties (closed coloured/open colourless) and thermal stability. The difference in conjugation between the two forms has been anticipated to be accompanied by a large change in molecular conductance and as a result these systems have been applied in recent years as light switchable components in molecular and organic electronics.[18–21]

Diarylethene, and especially dithienylethene, based switches have over the last decade emerged as a potentially important class of electrochromic (redox switchable) compounds in which the colour change requires only a transient application of voltage. In this review recent studies on the electrochemistry of the dithienylethenes will be discussed together with efforts towards the development of electro- and photo-responsive polymer modified electrodes in which electropolymerisation is employed to deposit the polymers. Of particular interest is the complexity that the combination of two redox active functional components (an electropolymerisable unit and an electro/photochromic unit) brings in the design of such systems.

Diarylethene electrochemistry

The possibility of redox switching the state of a dithienylethene was first noted by Kawai,[22] and later, Branda[23] and coworkers. An initial limitation to electrochemical switching of dithienylethenes was that it was perceived to be essentially one-way, *i.e.* electrochemically driven ring closing or ring opening depending on the specific structure of the switch.[22–30] Indeed early studies demonstrated that the direction of electrochemical switching was dependent on both the substituents on the thienyl rings and the nature of the central alkene, *e.g.*, perfluorocyclopentene based switches (**2o**/**2c**) undergo ring opening while perhydrocyclopentene based switches (**1o**/**1c**) undergo ring closing.[28,30] Subsequently it was demonstrated that both electrochemically induced ring opening and ring closing could be achieved under appropriate experimental conditions (*vide infra*).[24] The cyclic voltammetry of two typical dithienylethenes that exhibit opposite electrochromic behaviour is shown in Fig. 1 and 2.

In the case of the open form (**1o**) of a switch bearing phenyl substituents at the C5 position of the thienyl rings and a

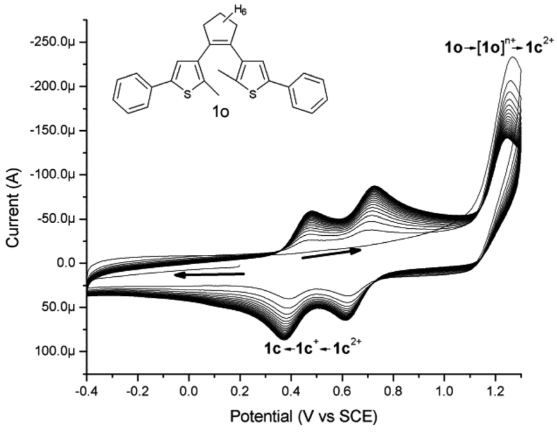

Fig. 1 Cyclic voltammetry of diarylethene **1o** in dichloromethane at 0.1 V s^{-1} at a GC electrode. Reproduced with permission from ref. 28. Copyright Wiley 2005.

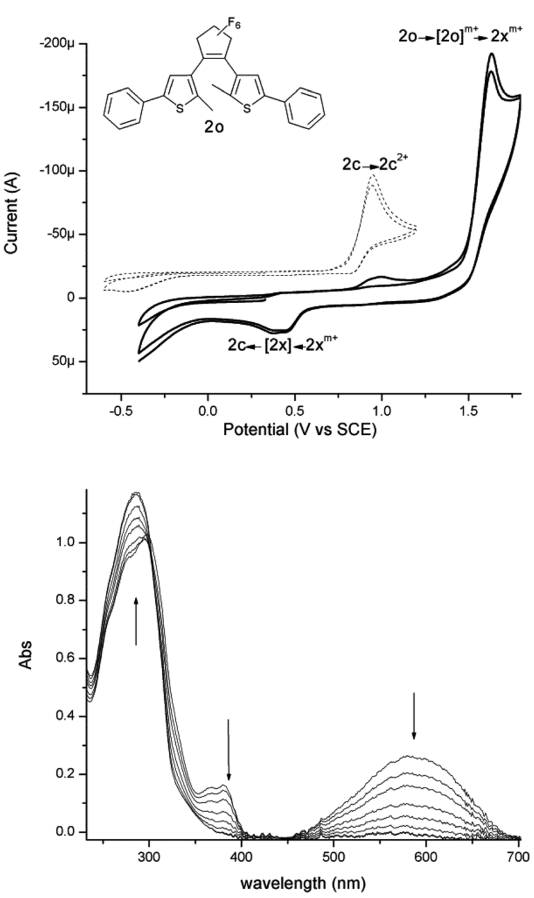

Fig. 2 Cyclic voltammetry of diarylethene **2o** in dichloromethane at 0.1 V s^{-1} at a GC electrode and UV/Vis absorption spectroelectrochemistry showing ring opening during bulk oxidation at 1.0 V to convert **2c** to **2o**. Reproduced with permission from ref. 28. Copyright Wiley 2005.

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central perhydrocyclopentene unit, when cycling towards positive potentials, an irreversible two-electron oxidation was observed at *ca.* 1.2 V *vs.* SCE (Fig. 1). On the return cycle two well resolved reductions were observed at 0.7 and 0.4 V. These reversible redox waves correspond to those of the closed form **1c**. Hence, it is apparent from cyclic voltammetry that oxidation of the open form, **1o**, leads to formation of $\mathbf{1o}^{2+}$, which undergoes immediate ring closing to $\mathbf{1c}^{2+}$. On the return cycle, $\mathbf{1c}^{2+}$ is subsequently reduced to $\mathbf{1c}^{+}$ and finally to **1c**. It should be noted that multiple successive cycles lead to a build-up of a steady state concentration of **1c** at the electrode (within the diffusion layer).

In **2o**, the perhydrocyclopentene unit of **1o** is replaced by an electron withdrawing perfluorocyclopentene unit. Again, an irreversible oxidation of the open form (**2o**) was observed, albeit at higher potential than for **1o** (Fig. 2). In stark contrast to **1o**, however, for **2o** the redox wave expected for reduction of $\mathbf{2c}^{2+}$ was not observed, and hence ring closure does not occur. Instead an, as yet, unassigned reduction was observed at 0.5 V. The cyclic voltammetry of the closed form **2c** exhibits a single irreversible oxidation at 1.0 V and it was demonstrated by UV/Vis absorption spectroelectrochemistry (Fig. 2) that oxidation of **2c** resulted in ring opening and immediate reduction to **2o**.

The effect of the central alkene unit (perhydro- *vs.* perfluoro-cyclopentene) on the direction of electrochemical switching is remarkable and allows for control of the direction of the electrochemical switching in a device by molecular design. As will be discussed below, however, an alternative approach to controlling the direction of switching is made available by immobilisation of dithienylethene switches on a surface.

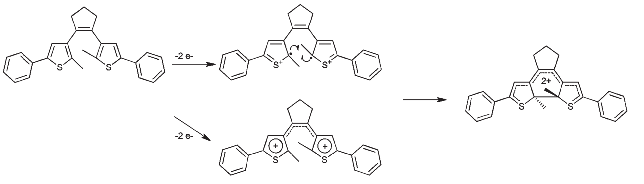
Furthermore, although the cyclopentene bridge has a dominant influence on the electrochromic behaviour of the dithienylethene switches, it should be noted that the substituents on the thienyl rings can have an equally large effect, especially where they are strongly electron withdrawing or donating (*e.g.*, chloro- or methoxy-phenyl, respectively)[28,30] and where the substituents are themselves also intrinsically redox active (*e.g.*, *N*-methyl-pyridinium).[24]

Mechanisms for electrochemical switching

Before discussing recent progress in the development of switchable electropolymerised systems it is worth considering the mechanism by which electrochemical ring opening and closing proceeds. Several recent studies on the electrochemistry of diarylethenes indicate that two general mechanisms are reasonable; where ring closing and opening proceeds *via* a monocationic species or *via* a dicationic species.

Switching *via* dicationic species

The open forms of the dithienylethenes are characterised by an irreversible two electron oxidation. For example, for the phenyl substituted dithienylethene (**1o**) a dicationic pathway can be assumed. Starting with the open form, upon oxidation at 1.2 V a dication is formed directly. This dication undergoes ring closure, driven by delocalisation of the charge over the entire conjugated system.



Scheme 2 Electrochemical ring closure *via* a dicationic state by (upper) an α-coupling mechanism and (lower) 4π-electron pericyclic ring closure.

One model that can be applied to understand the driving force behind ring closing is the radical character on the α-carbon of the thiophene (Scheme 2). α-Coupling, a mechanism invoked in thiophene polymerisation,[31] can occur to form a carbon–carbon single bond. However, whereas in thiophene polymerisation this is followed by irreversible loss of two protons, in the case of dithienylethenes this step is blocked by the methyl groups present at the α-positions. Radical coupling can potentially lead to both *trans* and *cis* products (with respect to the orientation of the two methyl groups on the central ring, Fig. 3). Steric considerations, however, should favour formation of the same product (after reduction) as formed upon photochemical ring closure, *i.e.* the *trans* product.

An alternative model that can be invoked is ring closing *via* a 4-π electron cyclisation, which proceeds in a disrotatory manner thermally (according to the Woodward–Hoffmann rules) and is analogous to the photochemical reaction in which the disrotatory cyclisation is also allowed (Scheme 2). Either pathway leads to formation of the dication of the closed form.

With regard to ring opening, for example with **2c**, the situation is somewhat more complex, due to the fact that electrochemical ring opening can proceed in principle from either the mono- or di-cationic form. The separation between the oxidation potentials required to form the mono- and the dications (ΔE) is negligible in the case of **2c** (Fig. 2) but for related switches where the phenyl ring is replaced by more electron donating moieties the separation increases.[32] In these latter cases it is apparent that the first oxidation is indeed electrochemically reversible and it is the second oxidation to form the dication that is irreversible, due to rapid ring opening.

Oxidation of the closed form of dithienylethenes to the dication ($\mathbf{c}^{2+}$) is followed by ring opening to $\mathbf{o}^{2+}$, eventually,

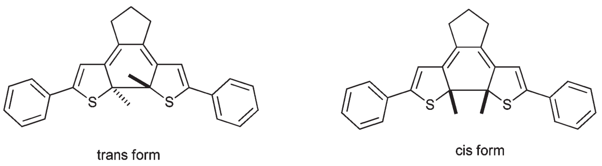


Fig. 3 *trans* and *cis* forms of a ring closed dithienylethene.

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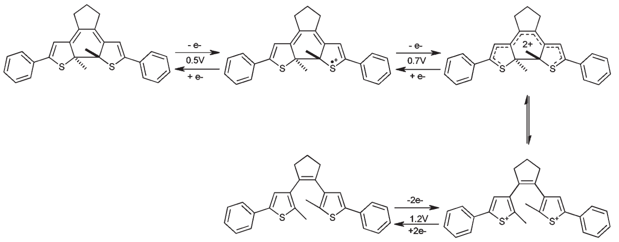
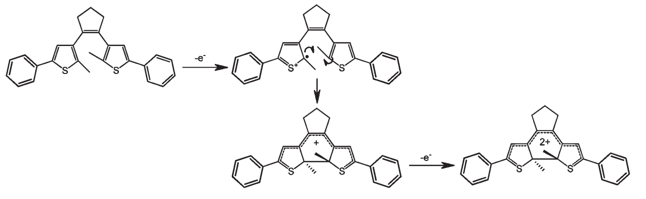


Scheme 3 Electrochemical ring opening *via* a dicationic state.



Scheme 4 Electrochemical ring closure *via* a monocationic state.

towards an equilibrium between **c**$^{2+}$ and **o**$^{2+}$. For **1o**$^{2+}$/**1c**$^{2+}$ the equilibrium lies in favour of **1c**$^{2+}$, while for **2o**$^{2+}$/**2c**$^{2+}$ it lies towards **2o**$^{2+}$. In the ring opened state, *e.g.*, **1o**$^{2+}$, rapid reduction occurs, when potentials less positive than 1.0 V are applied, to form the thermally stable **1o**. This prevents reversion to the ring closed dicationic state; in other words, the dication of the open form is trapped by the reduction to drive the equilibrium towards ring opening (Scheme 3).[29]

DFT calculations of both photochemical and electrochemical switching have been reported by Yoshizawa and co-workers.[33] They calculated the orbital energies and the barriers to ring opening/closing for the neutral, mono- and dicationic forms of **1o**/**1c**. Overall, a striking similarity in the orbital control of the electrochemically and photochemically driven ring-closing reaction was noted. As expected ring closing of **1o** to **1c** does not proceed, due to the antibonding character within the HOMO and hence spontaneous ring closing does not occur. By contrast, the HOMO − 1 of **1o** is similar to its LUMO, both of which show a favourable orientation of orbital fragments of the same phase at the ring-closing carbon atoms. Hence oxidation of **1o** to the dicationic form will lead to an electronic configuration in which the new HOMO level (*i.e.* the HOMO − 1 of **1o**) shows a bonding orbital interaction over the ring-closing carbon atoms. In the case of **1o**$^{2+}$ spontaneous ring closing is expected. By contrast, for the monocation **1o**$^{+}$, the spontaneity of the process is less certain as its SOMO (*i.e.* the HOMO of **1o**) is still populated.

Switching *via* the monocationic state

Although oxidation of the open form of the dithienylethenes is a two electron process, a second mechanism for electrochemical ring closing invokes the monocation as the species responsible. Launay and coworkers have proposed that electrochemical switching follows an ECE mechanism.[28] In this mechanism oxidation to the monocation of the open form is followed by rapid ring closure. The closed monocation is subsequently oxidised rapidly to the dication, as its oxidation potential is less positive than that of the open form (Scheme 4). The electrochemistry and kinetics of ring opening and ring closing for a series of diarylethenes was examined and the results obtained were compared with DFT calculations of the neutral and monocationic species.[34]

Recently, Fukuzumi and coworkers[35] investigated the chemical one electron oxidation of the closed forms of four perfluoro-diarylethenes, with pyridine, phenyl and methoxyphenyl substituents by stopped-flow UV/Vis absorption spectroscopy. Only the monocation of the closed and the open form were observed, which the authors proposed, supports a mechanism in which ring opening takes place *via* a monocationic species, in agreement with the conclusions of Launay and co-workers.[28]

Kinetic considerations in redox switching

Although conclusive data to support one or other mechanism are not yet available, it should be noted that any mechanism must consider disproportionation reactions. The situation is further complicated by the effect of changing the substitution on the diarylethene core and the side groups,[30] and the fact that electrochemical ring opening and closing occur at relatively high rates.

The kinetics of the electrochemically induced ring opening and closing reactions depend strongly on the experimental conditions. In a three electrode electrochemical cell, the processes observed occur within the diffusion layer at the electrode, together with its concomitant gradients of concentration of the various species involved and the presence of the electrode solution interface held at a particular potential. In contrast, the species observable when ring opening is induced by chemical (electron transfer) oxidants depends on the concentration of each component and on other factors such as the disproportionation constant ($1/K_c$) between the neutral (**c**), monocation (**c**$^{+}$) and dication (**c**$^{2+}$) of the closed form. $\{\mathbf{c} + \mathbf{c}^{2+} \Leftrightarrow 2\mathbf{c}^{+}, K_c = \exp(nF\Delta E/RT)\}$, where ΔE is the difference between the first and second oxidation potential of the closed form. With an oxidant, *e.g.*, ferrocenium or CF_3CO_2H, that is strong enough to generate the monocation of the closed form of a dithienylethene, but not strong enough to oxidise the open form, the primary species that will be observed in solution are the initially closed form, the monocation of the closed form and, increasingly, the open form. Failure to observe the dication of the closed form, however, does not prove that ring opening occurs *via* the monocation of the closed form, and *vice versa*.

The monocation of the closed form can and does disproportionate to the neutral closed form and the dication, the extent of which depends on the value of $1/K_c$, where K_c is the comproportionation constant. The dication formed will seek to establish an equilibrium with the open form dication, however once formed the dication of the open form, which is a strong oxidant, will rapidly be reduced by the neutral closed

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$$2\,\mathbf{c}^{+} \rightleftharpoons \mathbf{c} + \mathbf{c}^{2+}$$

$$\mathbf{c}^{2+} \rightleftharpoons \mathbf{o}^{2+}$$

$$\mathbf{c} + \mathbf{o}^{2+} \rightleftharpoons \mathbf{c}^{2+} + \mathbf{o}$$

Scheme 5 Equilibria and redox reactions leading to catalytic oxidative ring opening.

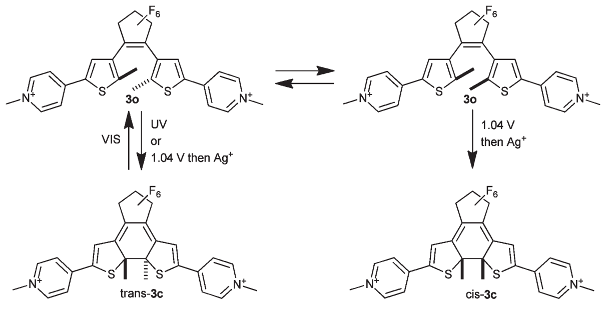
form present (Scheme 5).[22] This mechanism will be catalytic in oxidants as observed by Launay.[28]

In addition, the electrochemical switching kinetics of diarylethenes are affected strongly when incorporated into a monolayer or multi-layered material, where, due to the close packing of molecules on a surface, bimolecular reactions occur more frequently than in solution where it is under diffusion control. Therefore disproportionation reactions can proceed more rapidly on a densely packed surface. In addition the proximity to an electrode allows for rapid reduction of the open form dication.[36] These processes can be inhibited by rapid oxidation of the entire layer to the dicationic state or promoted by repetitive cyclic voltammetry and are therefore highly useful as control elements in devices.

Electrochemical switching with redox active side groups

A further complication arises where the dithienylethene is modified with redox active groups such as *N*-methylpyridinium and methoxyphenyl side groups. In the case of the phenylmethoxy modified analogue of **2o**, the first oxidation is centred on the phenylmethoxy moieties but intramolecular electron transfer occurs, for which the driving force is the formation of the more stable ring-closed dication.[28] Apart from mechanistic implications, this electron coupled ring closure needs to be taken into account when making use of electrochemical switching of diarylethenes (*vide infra*).

For example Branda and coworkers have reported the reductive electrochemical ring closing of *N*-methylpyridinium substituted dithienylperfluorocyclopentene (**3o**, Scheme 6). Reduction of **3o** at −1.0 V resulted in formation of **3c** despite the fact that it is the *N*-methylpyridine units that are formally reduced (Fig. 4).



Scheme 6 The open form of **3o** exists in two equilibrating conformers (antiparallel and parallel). Both photo- and electrochemical switching lead to formation of *trans*-**3c**, however electrochemical switching leads to an additional minor product assigned to the *cis*-**3c**.

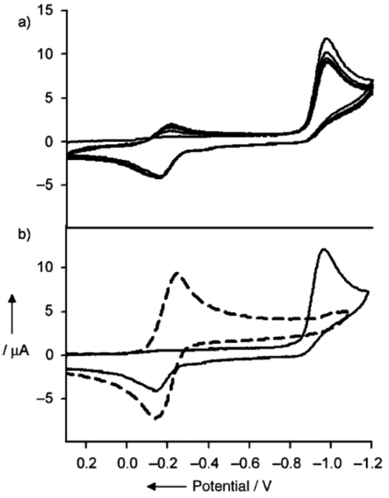


Fig. 4 (a) Cyclic voltammetry of **3o** at 0.2 V s^{-1} showing formation of **3c** after reduction at −1.0 V. (b) Before (solid line) and after (dashed line) irradiation at 365 nm. Reproduced with permission from ref. 24. Copyright Wiley 2004.

In their study of electrochemical ring closing of **3o** by Branda and coworkers,[24] a minor side-product was obtained upon electrochemical ring closure by bulk electrolysis, with chemical shifts similar to the closed form, but which was photochemically inactive (Fig. 4). This species was assigned, tentatively, to the *cis*-isomer (with respect to the two methyl groups) of the closed form, since that isomer would not be able to undergo photochemically induced, conrotatory, ring opening (Scheme 6). It should be noted however that it was obtained as a minor product, as expected based on semiempirical calculations (AM1) that indicate that the dication of the *cis*-isomer is much less thermally stable than the dication of the *trans*-isomer. The observation of a *cis*-isomer, if confirmed, would support a diradical coupling mechanism (*vide supra*).

Diarylethene modified surfaces

Several strategies have been taken to incorporate diarylethenes into devices, including coating surfaces with monolayers and SAMs (Self-Assembled Monolayers), spin coating of copolymers and modification of conducting surfaces by electropolymerisation. Although this latter approach is the topic of this review there are some aspects of the former approaches that are useful to discuss first.

Monolayer modified surfaces

A straightforward approach to modifying a surface with a dithienylethene is to form self-assembled monolayers (SAMs) on a surface using a suitable anchor group (*e.g.*, a thiol on gold). This approach has been employed by several groups and is reviewed elsewhere.[2,37,38]

A central issue in surface confinement of molecular switches is its effect on the switching function, including excited state quenching, *e.g.*, by gold,[39] or retardation of thermal relaxation processes.[14] In the case of dithienylethenes,

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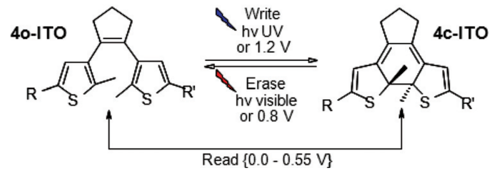

Scheme 7 Photo- and electrochromic diarylethenes when formed as monolayers on ITO electrodes can be switched in both directions electrochemically and photochemically.

the relatively minor change in shape upon switching between open and closed forms and the thermal stability of both forms mean that steric inhibition of switching in the solid state is not generally a significant problem.[40,41]

Monolayers of diarylethenes on transparent electrode surfaces (ITO) have been shown to be switchable using both UV and visible irradiation and by applying certain potentials (Scheme 7).[36] Although monolayers of diarylethenes on gold electrodes have shown limits to their photochemical switching performance, redox switching was essentially unaffected.[42] Hence the ability to switch dithienylethenes electrochemically is especially useful in surface confined systems.

A limitation that is particularly of concern in SAMs when used in devices, *i.e.* sandwiched between two electrodes, is that of pinhole defects, which short circuit the device. Besides that, monolayers are also sufficiently thin to allow for tunnelling over an insulating layer to occur. This limits the magnitude of the effects that can be achieved upon switching (*e.g.*, conductivity switching). Nevertheless, there are strategies to circumvent such issues and indeed photoswitching of conductance in devices has been reported already.[18–21]

Polymer modified surfaces

An alternative approach to surface immobilisation is through polymerisation and strategies including Pd-catalyzed coupling reactions, ring-opening-metathesis polymerisation and electropolymerisation have been employed.[43] Diarylethenes have been incorporated into polymers using all of these strategies and an overview of the progress in this area was recently given by Tian and coworkers.[44] In the present review we focus on the use of electropolymerisation to immobilise dithienylethene switches on surfaces. Electropolymerisation has several advantages, in particular with regard to immediate surface deposition upon polymerisation provided that adhesion of the growing polymer film to the surface is sufficiently strong. In addition, the polymer is fully addressable electrochemically once deposited. Due to a wide choice of electrode surfaces available, electropolymerised materials can be characterised by several spectroscopy and microscopy techniques; including AFM, SEM, UV/VIS, IR and Raman spectroscopy, electrochemical quartz crystal microbalance, *etc*.

Nevertheless several challenges are presented by this approach, in particular the necessity for wet electrochemistry. This can present limitations in certain device applications where the presence of an electrolyte can cause interference and in the case of large area electrodes where iR drop can affect uniformity of coverage. Furthermore, in order to immobilise a dithienylethene switch by electropolymerisation the polymer formed needs to be conductive at the onset potential for monomer oxidation in order for film thickness to be varied by deposition time.

Perhaps the most critical aspect in the use of electropolymerisation to adhere active units, such as dithienylethenes, is the inherent stability of the polymer backbone with respect to adhesion. Poor adhesion can result in the polymer film flaking off either upon drying or as the polymer film is oxidised or reduced (due to swelling by influx of ions). In the case of dithienylethenes, as will be discussed below, generally oxidation of the dithienylethene unit occurs prior to oxidation of the electropolymerisable unit and hence the solubility changes dramatically. If a relatively apolar solvent is chosen, such as dichloromethane, solubility will decrease upon oxidation facilitating deposition.

Several polymerisable units are immediate candidates including thiophenes, pyrroles and methoxystyryls. In general, oligothiophenes have shown good adhesion to many electrode surfaces, especially to gold electrodes. By contrast pyrrole based polymers show limited film adherence in organic solvents in the absence of water but have the advantage that polymerisation can be performed in water.[45] In the case of methoxystyryl units the key challenge is the limit to polymer film thickness presented by the relatively high oxidation potentials required to form the polymer film (*vide infra*).

Polythiophene based switchable polymers

A relatively straightforward approach to modifying surfaces through electropolymerisation is to combine a diarylethene unit with bithiophenes as in **5**, which was prepared by a Pd-catalysed Suzuki coupling between bromobithiophene and the boronic ester derivative of the diarylethene switch (Scheme 8).[46] The dithienylethene switches obtained underwent photochemically induced ring opening and closing in solution. The perhydrocyclopentene bridged analogue of **5** showed electrochemical ring closing by cyclic voltammetry. For the perfluorocyclopentene bridged **5c**, a reversible two-electron oxidation was observed at 0.7 V (Fig. 5). However, for the open form, **5o**, although an irreversible oxidation was observed at 1.1 V, the return cycle did not show the characteristic reduction of the closed form dication. Instead, over multiple cycles a redox polymer deposited on the surface of the electrode. Hence in this system the polymerisation was switched on or off depending on the state of the central dithienylethene unit.

The reason for the difference in polymerisability between the dicationic open and closed forms can be understood by considering that the mechanism for thiophene polymerisation depends on the radical character of the terminal thiophenes. In the dication of the closed form the positive charge is delocalised on the central switch unit and hence the rate of α-coupling is not competitive with the rate of diffusion from the

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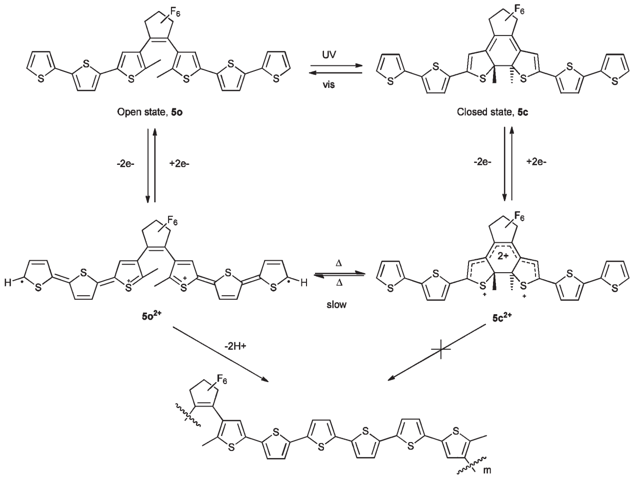


Scheme 8 Electropolymerisation of **5** proceeds *via* the open state (**5o**) only and competes with ring closing to form $\mathbf{5c}^{2+}$.

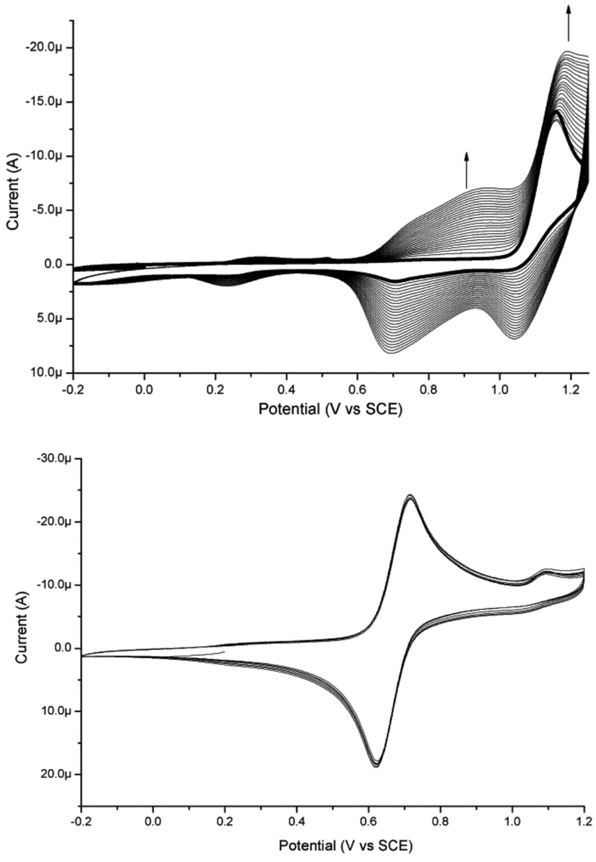


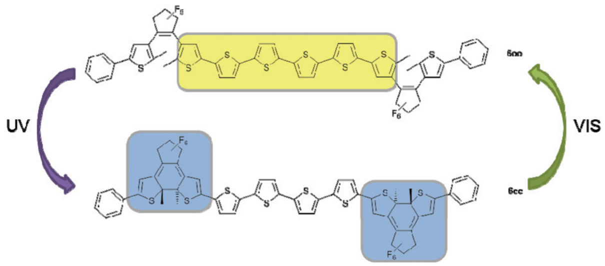
Fig. 5 Electrochemistry of **5** on a platinum electrode. (upper) The open form (**5o**) shows deposition due to electropolymerisation, while (lower) the closed form (**5c**) shows reversible redox chemistry and no polymer formation. Reproduced with permission from ref. 46. Copyright ACS 2008.

electrode precluding polymer formation. By contrast, for the open form the dication has sufficient radical character at the terminal thiophenes for α-coupling to proceed at a rate that is competitive with diffusion and, more importantly, with ring closing of the dithienylethene core (Scheme 8). For the perhydrocyclopentene bridged analogue ring closure upon oxidation proceeds at a much faster rate precluding the formation of a polymer film.

Oxidative polymerisation of **5o** provided mechanically robust polymer modified electrodes. The polymer film thickness could be controlled by deposition time or number of cycles, since the polymer film formed is conductive in the potential range necessary for monomer oxidation. However, the polymer formed did not show switching properties typical of the monomers and instead were best described as alkene bridged sexithiophene polymers. Despite the lack of switching in the polymer films, a key advantage of this system is the relative ease by which the films can be formed and especially the fact that Lewis acids, such as $BF_3{\cdot}OEt_2$, are not necessary. This was critical as the switching unit is decomposed in the presence of Lewis acids.

The absence of photochemical switching could be ascribed to intramolecular quenching by the sexithiophene units. This aspect was explored through the use of a model system, specifically a sexithiophene end-capped with two phenylthiophene perfluorocyclopentene units, prepared by electro-dimerisation of a mono-bithiophene diarylethene.[47] In this model compound switching was demonstrated in solution and hence the presence of a sexithiophene unit could not in itself result in loss of photochemical activity (Scheme 9). However, temperature dependent (*J*-)aggregation in solution was observed, which resulted in quenching of both fluorescence and photochemistry indicating that intermolecular interactions were responsible for the loss of photochemical activity in the polymer film.[48] With regard to electrochemical ring closing, its absence in the polymer can be rationalised by considering that extending a π-system beyond six thiophene rings does not increase stability and hence the driving force for ring closure (increased stability) is absent.[49,50]

Recently, Kim and co-workers reported a polymerisable EDOT-based diarylethene switch (Scheme 10).[51–53] The more readily oxidised EDOT unit reduced the synthetic complexity of the system as it enables polymerisation even with only one thiophene unit. The monomer was prepared using Pd-catalyzed Stille coupling and the compound was polymerised on ITO slides and Pt disc electrodes by repetitive cyclic



Scheme 9 Photoswitching of both dithienylethene units in a sexithiophene based double switch can be achieved despite potential quenching by the sexithiophene unit.[48]

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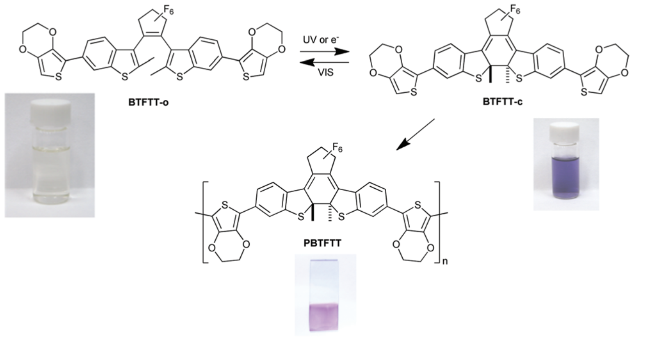


Scheme 10 EDOT based diarylethene polymerisation occurs *via* the closed form to produce coloured polymer films. Reproduced with permission from ref. 51. Copyright Elsevier 2007.

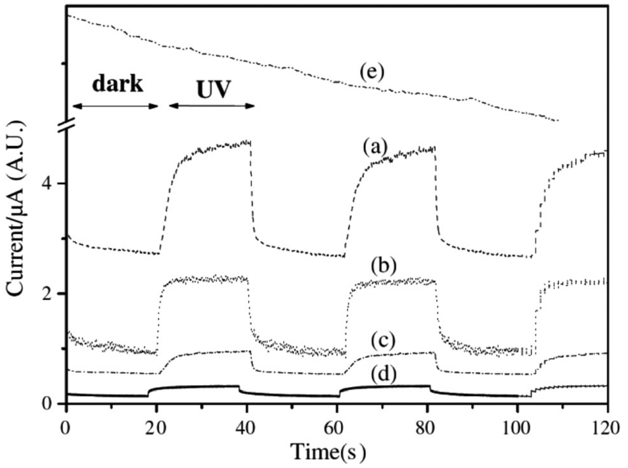
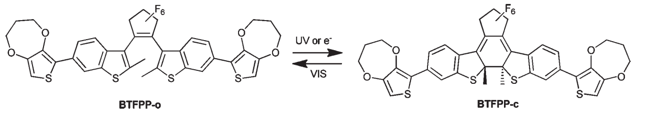


Fig. 6 Photocurrent response at +0.5 V of an EDOT based diarylethene polymer upon irradiation with UV-light in a buffer solution containing hydroquinone. Film prepared from (a) EDOT (2×10^{-3} M) and BTFTT (1×10^{-3} M), (b) EDOT (1×10^{-3} M) and BTFTT (1×10^{-3} M), (c) EDOT (0.5×10^{-3} M) and BTFTT (1×10^{-3} M), (d) BTFTT (1×10^{-3} M) and (e) EDOT (1×10^{-3} M). Reproduced with permission from ref. 52. Copyright Elsevier 2008.

voltammetry. The polymer film was formed, as determined by cyclic voltammetry, UV/Vis absorption and FTIR spectroscopy, with the diarylethene unit in the closed form. The polymer formed showed electrochromic behaviour and was applied as a switchable photocurrent generator.[52]

Upon irradiation with UV light an increase in photocurrent was obtained, which showed fast switching to a low current state when irradiation ceased (Fig. 6).[52] Although not discussed by the authors, it is possible that UV irradiation resulted in a steady state between photochemical ring closing and electrochemical ring opening.

A ProDOT derivative of the same diarylethene was also prepared (Scheme 11).[53] Direct electropolymerisation onto an ITO slide was not successful due to the higher solubility of the oligomers that form initially, which precludes nucleation of the polymer on the electrode surface. However, copolymerisation with EDOT on PEDOT-coated ITO slides successfully yielded a diarylethene switch containing material.



Scheme 11 A ProDOT based electropolymerisable diarylethene switch.[53]

The electrochromic properties of the formed polymer were demonstrated over a potential range from −1.8 V to 1.7 V. Although the photo- or redox switching properties of the polymers were not investigated in these studies, the latter case demonstrates the potential for multi-layered and multifunctional systems formed by co-electropolymerisation and the much improved stability and reduced onset potential for electropolymerisation provided for by EDOT and ProDOT units.

Poly-vinylphenylene based switchable polymers

Separating the moieties responsible for polymerisation from those that provide the switching function, while being desirable, presents synthetic challenges. Not least due to the fact that the desired properties, in terms of polymerisation, restrict the conditions that can be applied in the monomer's synthesis. Nevertheless the use of a spacer to separate the two components (switchable and polymerisable) has been shown to help to retain the functionality of each component.

Wesenhagen *et al*. have used the approach of separation of the polymerisable and switchable units using phenyl spacers.[54] In this system a diarylethene was coupled to two polymerisable methoxy styryl groups (**6o**) prepared *via* Horner–Wadsworth–Emmons coupling of an aldehyde with a methoxyphenyl phosphonate to yield the styryl functionality in a single step.

Polymer films were formed by cyclic voltammetry as depicted in Fig. 7. However, in contrast to thiophene based systems discussed above, although initially a linear increase in current density was observed, as the film thickness increased the rate of polymer growth decreased sharply and then

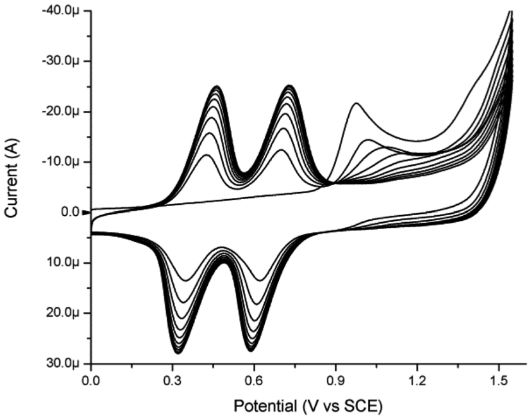


Fig. 7 Cyclic voltammetry of **6o** showing electropolymerisation. Reproduced with permission from ref. 54. Copyright ACS 2008.

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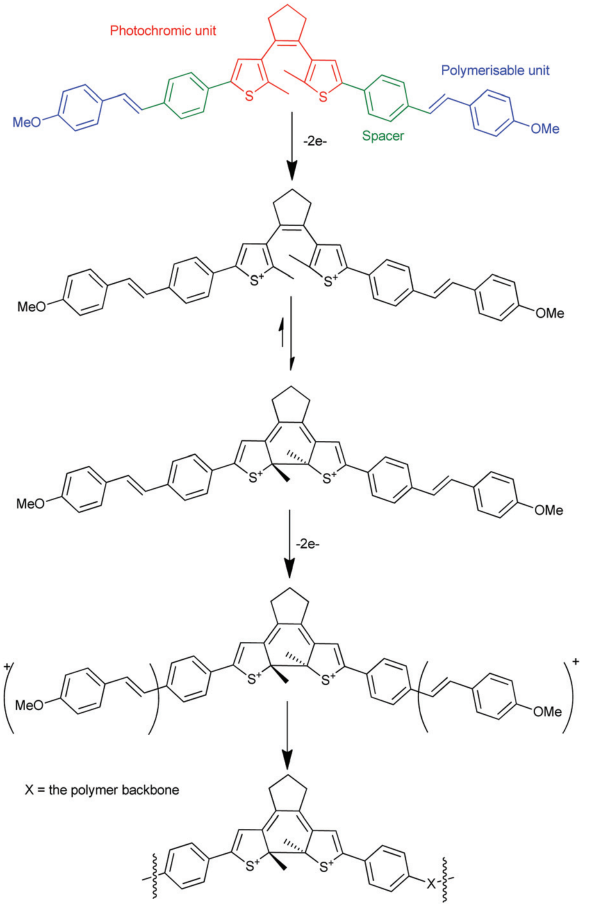


Scheme 12 Oxidation of **6o** to **6o**$^{2+}$ is followed by immediate ring closing to **6c**$^{2+}$. Subsequent polymerisation of poly-**6c** proceeds until the film thickness is sufficient to block electron transfer and prevent further polymerisation.

stopped completely. Indeed film thicknesses were relatively uniform regardless of the conditions employed and of the order of 5–10 equiv. monolayers. The origin of this effect is that, in contrast to thiophene based polymers, the film formed is insulating at the potentials required to oxidise the methoxyphenylstyryl unit. Hence the polymerisation is limited to the thickness over which direct charge transfer from the electrode to the monomer can take place.

The mechanism of polymerisation is depicted in Scheme 12. The least positive oxidation is that of the dithienylethene core and hence as the potential is increased oxidation followed by ring closing to form the dication of the closed form occurs. Subsequently, above 1.2 V oxidation of the methoxyphenylstyryl unit occurs, which results in polymerisation and film formation.

The polymer film formed was found to undergo both electrochemical ring opening, by cycling between 0.0 V and 0.9 V (*i.e.* to potentials less positive than the oxidation potential of the open form) and ring closing by cycling between 0.0 V and 1.3 V (see Fig. 8). Photochemical ring opening could be achieved as well, however, although evidence for ring closing upon irradiation at 365 nm was obtained, rapid polymer film degradation was also observed.

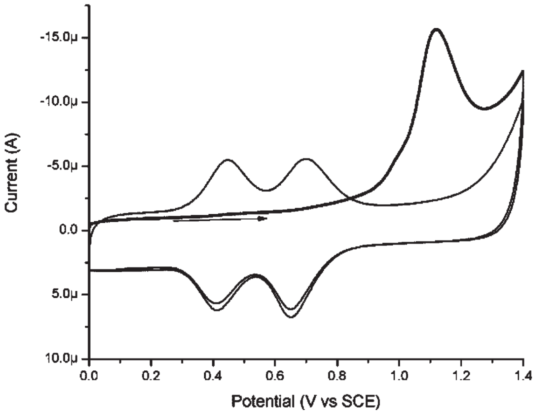
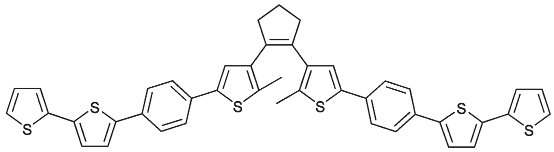


Fig. 8 Cyclic voltammetry of poly-**6o** obtained by electrochemical ring opening poly-**6c**. Reproduced with permission from ref. 54. Copyright ACS 2008.



Scheme 13 Dithienylethene containing bithiophene polymerisable groups separated using a phenyl spacer to allow for switching in the formed polymeric material.[55]

In this last example, several challenges facing the development of photo- and redox switchable polymer films formed by electropolymerisation are apparent. In particular the compatibility of the switching unit with the polymerisable unit and the polymer backbone, both during polymerisation and also subsequently during switching events, is critical. Recently, a modified design was reported wherein the methoxyphenylstyryl polymerisable unit was replaced by a bithiophene unit (Scheme 13).[55] In this case the switching properties were retained in the polymer films formed also. However, in contrast to the former system, the thickness of the polymer films was not limited by lack of conductivity.

Challenges in redox switching of surface properties

In applying the approach of deposition of redox switchable polymers using electropolymerisation, two primary challenges are faced. The first is the analysis of the materials formed, which is typically carried out using voltammetric techniques, *e.g.*, a scan rate dependence of the cyclic voltammetry reveals the thickness of the film, but is limited by diffusion of charges through the film. In addition, while determining film conductivity, *e.g.*, in dual electrode source/drain experiments,[56] the slow scan rates which are employed can cause the material to undergo redox switching of the dithienylethenes (*i.e.* from closed to open states), complicating otherwise routine experiments. When flat electrodes are used surface analytical

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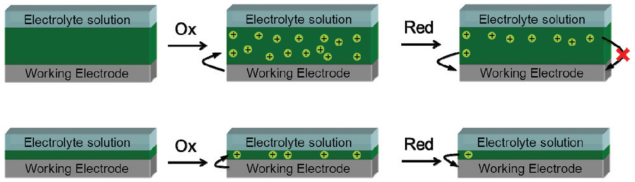

Scheme 14 When a film is oxidised electrochemically (*e.g.*, p-doped), neutralisation of the charges by, in this case, reduction is prevented in thicker films by the rapid formation of a non-conductive layer at the electrode. The trapped charges in the polymer film are concentrated at the polymer solution interface. Reproduced with permission from ref. 58. Copyright RSC 2012.

techniques are often applied to further analyse the formed polymers. FTIR, UV/Vis-NIR absorption spectroscopy and XPS can provide information about the molecular composition of the polymer and the presence of counterions and SEM and AFM provide insight into the morphology of the material. However, when such films are incorporated into devices, the limited access can present considerable challenges in characterisation, especially when the devices are operating.

An example of the challenges faced in applying redox switchable polymer modified electrodes is in controlling changes in electrode–solution interfaces and the responsiveness of the film, especially in microfluidic devices where such interactions dominate fluid flow behaviour.[57] With thicker polymer films, current outputs are increased allowing for easier characterisation of switching events. However, the responsiveness of the system in terms of switching times decreases also with an increase of film thickness. Critically, as a film is neutralised, and hence conductivity of the film decreases, the region furthest from the electrode and in contact with solution may not in fact undergo reduction (*i.e.* charges are trapped). This results in a loss of switching functionality of the polymer modified surface with respect to surface–solution interactions (Scheme 14).

In confined environments such as microfluidic channels, controlling polymer film growth and thickness is not trivial and hence *in situ* analysis methods are essential. Logtenberg *et al*. have recently demonstrated one approach in the analysis of films formed in microfluidic channels by electropolymerisation of **5**.[58] In this study resonance Raman spectroscopy (at λ_{785} nm) was employed to identify the presence of mono- and bi-polarons in the film (both species absorb strongly at 785 nm), when the film was oxidised and when in a fully reduced state (Fig. 9). Two advantages of using Raman microscopy for this analysis were that, in contrast to cyclic voltammetry, Raman microscopy addressed the entire volume of the film and measurements could be performed *in situ*.

Conclusions

The versatility of dithienylethenes as redox switchable molecular components, although less explored than photochemical switching, shows considerable promise in the development of novel modified electrode surfaces in which both light and electrochemical potential can be used as triggers. Although the mechanisms by which electrochemical switching proceeds still present questions, the general design rules in terms of molecular structure are sufficiently well developed to allow for prediction of the behaviour of dithienylethenes once incorporated in redox polymer films. In addition, several designs have been described and it is clear that the primary consideration is that the properties of the polymerisable unit are orthogonal to those of the switching unit. These considerations extend to the polymer backbone also, the redox properties of which should enable control of polymer thickness and not interfere with redox induced switching.

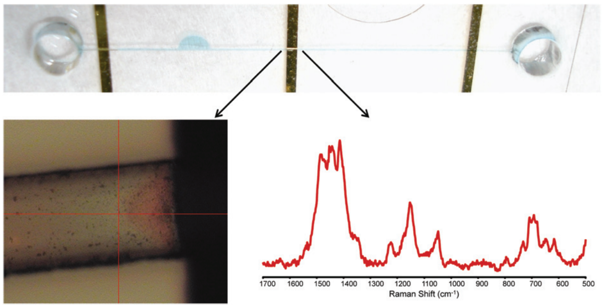

Fig. 9 An electrode in a microfluidic channel was modified by electropolymerisation of **5o**. Analysis by Raman spectroscopy *in situ* demonstrated that electrochemical reduction of the film was incomplete with poly-**5o**$^+$ remaining in the film. Reproduced with permission from ref. 58. Copyright RSC 2012.

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