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Solvation Dependent Redox-Gated Fluorescence Emission in a Diarylethene-Based Sexithiophene Polymer Film

Luuk Kortekaas and Wesley R. Browne*

Responsive surfaces have and continue to receive widespread interest[1] owing to their applications ranging from cell culturing[2] and biocompatibility,[3] to microfluidic devices,[4] droplet transport and wetting,[5] sensor technologies[6] and solar management systems,[7] and organic devices and electronics.[8] A key challenge in developing responsive surfaces is to engineer a response to external stimuli such as light, heat, redox equivalents, etc., and a common approach is to modify a surface with a self-assembled monolayer or polymer film which introduces the necessary functionality. Dual responsive systems in which two stimuli can be used orthogonally are of special interest because of the nonlinear increase in functionality (number of states) that can be achieved. In particular, the control of fluorescence intensity both through excitation intensity and a secondary control (e.g., redox potential) is highly attractive due to the ease with which the state of the surface can be read.[9] Furthermore, redox switching of polymer-modified surfaces potentially provides electrochemical control limited only by the rate of heterogeneous electron transfer between the electrode surfaces and the polymer film (i.e., rapid switching rates) and allows for potential to be used to control the extent of modulation by consideration of the Nernst equation. [10] The challenge in the field of functional redox-polymers, however, lies both within the robustness (i.e., mechanical and chemical stability and film conductivity) of the redox cycling[11] and, moreover, in the retention of the functionality of molecular components upon immobilization on surfaces.[12] Ultimately, the goal is to generate polymers in which the function of the individual units in the polymer are disrupted neither by the act of electropolymerization nor by intercomponent interactions, or cross-talk.

The diarylethene class of photochromic switches[13] have been demonstrated to be highly versatile,[14] e.g., for on/off control of molecular properties such as fluorescence,[15] redox as well as photochemically triggered switching,[16] etc., and hence their incorporation into polymer films offers considerable opportunities for photochemical and electrochemical control of surface properties.[17]

A relatively simple approach to incorporating a diarylethene switching unit into a redox polymer was demonstrated earlier by Areephan and co-workers in which it was modified by attachment of two bithiophene units directly to the diarylethene core to yield 1 (Scheme 1). In the open form, 1o underwent oxidative polymerization readily to form thick conducting films of a redox polymer (poly-1o), whereas in its closed form, 1c, polymerization was not observed upon oxidation, ascribed to the extended π-conjugation in 1c and the coupling of the “radicals” formed upon one-electron oxidation of each half of the dithienyl ethene. Hence, the system provided for photochemical on/off switching of the polymerization of 1.[18]

Although dithienylethene photochromic switches readily undergo thermal cyclization and cycloreversion upon one-electron[19] or two-electron[20] oxidation (depending on the precise structure of the diarylethene), in the case of 1 the rate of electrochemical ring closing was sufficiently low to allow for C–C coupling at the terminal thiophene carbons to be competitive and for polymer film formation to occur. The polymer films formed, however, were found to be inert to both photo- and electrochemical switching and instead the spectroscopic and electrochemical properties of poly-1 appeared to be essentially those of an alkene bridged poly-sexithiophene polymer.[21]

Spectroscopic comparison with model compound 2[22] (Scheme 2), for which the open state forms H-aggregates in solution at below 200 K, indicated that the extent of H-type interactions[23] in the polymer film was substantial and hence rapid excited state deactivation due to Davydov splitting precluded both fluorescence and photochemical switching.[24] The introduction of a phenyl spacer unit between the dithienylethene and the dithiophene units restored the switching functionality of the dithienylethene unit in a polymer film, however, the quantum yield for photochemical switching was still lower than that observed in solution.[25] The use of a methoxystyryl unit in place of the bithiophene unit also allows for electropolymerization with retention of the photo- and electrochemical switching properties of the dithienylethene unit, however, this is achieved at the cost of film thickness and poor film stability under UV irradiation.[26] Recently, we demonstrated an alternative approach toward the preparation of photochemically switchable redox-polymers in which the functional unit (a bis-spiropyran) was formed concomitant with polymerization of the monomer units. This approach provides polymer films in which the properties of the switching unit observed in solution are retained fully in the polymer.[27] With these later approaches the photochromic functionality of dithienylethene switching unit is retained, however, the opportunity to modulate the intense fluorescence of the sexithiophene unit by dual redox and photochemical control is lost. Although films of poly-1 were found to be photochemically inert and show little or no fluorescence, the excellent properties of poly-1 in regard to electropolymerization, electrochromic response, and film stability prompted us to reexamine its photochemical and photophysical properties.

In this contribution, we show that the photochemistry and photophysics of the alkene bridged sexithiophene redox
polymer formed by oxidative electropolymerization of the bis(terthiophene)-hexafluorocyclopentene photochromic switch (1) can be reactivated by immersion of the polymer film in dichloromethane. The recovery of the switching and fluorescence properties of poly-1 is ascribed to the disruption of the H-aggregation between the sexithiophene units within the polymer film, presumably due to film swelling, manifested in a loss of the structured absorption band seen in the dry state (Figure S1, Supporting Information). The reactivation is achieved without concomitant desorption of polymer film from the surface. Furthermore, we show that, in stark contrast to the polymer’s properties in the dry state, the photophysics of poly-1 are essentially as expected for both a sexithiophene in terms of fluorescence and singlet oxygen generation[28] and a dithienylethene in terms of reversible photochromic switching (i.e., cyclization and cycloreversion) and electrochemical ring closing. These data demonstrate that retention of the functional properties of the subunits within a photoswitchable polymer can be achieved through disruption of intermolecular interactions and, the corollary, that environmental conditions can be used to regain control over the photochemical and photophysical behavior of the films.

As reported earlier,[18] the terthiophene end groups of 1 can undergo oxidative coupling to form sexithiophene-linked dithienylethene polymers. The intermolecular coupling competes with electrocyclization of the dithienylethene unit. During electropolymerization reversible redox waves at 0.8 and 1.1 V emerge due to the formation of the hexafluorocyclopentene bridged sexithiophene polymer on the surface.[29] The redox polymer, poly-1, forms readily on a wide range of conducting surfaces including glassy carbon, ITO, Au, and Pt electrodes.[18]

A first indication that the photophysical properties of poly-1 films are not suppressed entirely in the film is apparent from the effect of irradiation with visible light (e.g., 420 nm) on poly-1 films on ITO immersed in acetonitrile. Rapid bleaching of the yellow film was observed in the region irradiated indicating film degradation, which was confirmed by visible absorption spectroscopy and Raman microspectroscopy (Figure 1). The degradation of the polymer film is restricted to the region.
irradiated and hence opens the possibility to photopatterning of
the slide after electropolymerization in addition to patterning
by ring closing of the monomer (1) before polymerization.

As expected, the resonance Raman spectrum of poly-1 was
observed only outside of the irradiated region. Notably, however,
the relative intensity of the Raman bands at 1455 and 1480 cm
−1 was no longer constant over the whole film, indicating that
in addition to film loss, poly-1 had undergone an additional
change in its molecular structure (e.g., cyclization of the dithie-
nyleneethene units). The presence of cyclized dithienylethene units
near the irradiated region was confirmed by comparison with
the Raman spectra of the open and closed forms of the model
compound 2 in acetonitrile and in the solid state. The band
of 2 at 1480 cm−1 increases in intensity relative to the band at
1455 cm−1 (vide infra) upon cyclization. Hence, although poly-
1 is stable to irradiation as a dry film, when immersed in solvent
it undergoes both photochemically induced cyclization of the
dithienylethene moieties and irreversible bleaching due to the
photosensitization of oxygen (for which oligothiophenes gener-
ally show good efficiency, vide infra).28 These data prompted
us to revisit the redox and photochemistry of poly-1 in solution.

Irradiation of poly-1 with red light (660 nm) had no effect
on its cyclic voltammetry. In contrast, irradiation resonant with
the absorption bands of poly-1 in air equilibrated acetonitrile
or dichloromethane results in a rapid loss in current response
at 0.8 V (Figure 2), which is consistent with the loss of visible
absorption and Raman scattering. The decrease in current was
observed both while irradiating during cyclic voltammetry and
when the irradiation was conducted only in the neutral state
(Figure S3, Supporting Information).

Recovery of the redox waves is not observed upon irradiation
at 660 nm or thermally over 3 days. Furthermore, the redox
response continues to decrease, albeit at a lower rate, even
after visible irradiation had ceased. The involvement of oxygen
was confirmed by the absence of an effect of visible irradiation
under oxygen free conditions (Figure 3, left). Irradiation of the
film under an argon atmosphere results in only a slight modi-
fication of the films redox response initially and no further
changes even under prolonged irradiation. Purging with oxygen
during irradiation results in rapid loss in the redox response
once again (Figure 3, right).

Although visible irradiation in the presence of oxygen leads
to rapid film bleaching, irradiation under argon results in
reversible changes to the voltammetry of poly-1 films. Hence
the polymer film bleaching was attributed to singlet oxygen
generation, typical of thiophenes,28 a property which is seem-
ingly restored when wetted. Comparison with zinc tetraphenyl-
porphyrin,31 confirmed the ability of the model dimer to gen-
ergate singlet oxygen with a quantum yield of greater than 10%
(Figure S4, Supporting Information). Furthermore, irradiation
of poly-1 at 365 nm under conditions where singlet oxygen
generation cannot occur, i.e., in dichloromethane under argon,

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Figure 2. Left: Continuous cyclic voltammetry during irradiation (λexc 420 nm) of a poly-1 gold disc electrode (3 mm diameter) in dichloromethane
(0.1 M TBAPF6, scan rate 0.1 V s−1, SCE reference, and platinum counter electrode) with oxygen present. Right: The evolution in current of the first and
second oxidation waves as a function of cycle number.

Figure 3. Cyclic voltammetry of a poly-1 modified platinum macro electrode (d = 3 mm) in dichloromethane (0.1 M TBAPF6, scan rate 0.1 V s−1, SCE
reference, and platinum counter electrode) while irradiating (λexc 420 nm) under argon atmosphere (left) and after oxygenation (right).
results in a minor decrease in absorbance at 410 nm and an increase in absorbance at 690 nm (Figure 4a), consistent with ring closing of the dithienylethene unit. The Raman spectrum of the slide shows an increase in the band at 1480 cm$^{-1}$ relative to 1455 cm$^{-1}$, which is also in agreement with the changes observed in solution upon going from open to closed form (Figure 5). Subsequent irradiation at 660 nm results in a recovery of the original spectrum (Figure 4b). Moreover, the cyclic voltammograms of the slide before and after switching shows that the polymer film is intact confirming that in the absence of oxygen the film indeed does not undergo photodegradation (Figure S5, Supporting Information). The photostationary state reached of the polymer is determined to be $\approx 30\%$ closed form, estimated by comparison with the absorption of the fully closed model compound 2 in solution.[21]

Although the fluorescence of poly-1 is quenched in dried films (which allows for facile recording of its resonance Raman spectra, vide supra), wetting of the film with acetonitrile results in a reappearance of weak fluorescence. In contrast, wetting with dichloromethane results in the appearance of intense fluorescence. The difference in the effect of each solvent may reflect their relative abilities to swell the polymer film and disrupt the intermolecular H-type interactions. The fluorescence rapidly decreases to close to zero again upon solvent evaporation, and ultimately to zero over the course of $\approx 40$ s (Figure S6, Supporting Information), and repeated wetting/evaporation cycles can be performed (Figure 6).

In addition to the evaporation of the solvent “switching off” the fluorescence of poly-1, electrochemical oxidation of the film has an equally pronounced effect (Figure S7, Supporting Information). The electrochemical oxidation of the film was monitored readily by in situ Raman/fluorescence spectroelectrochemistry. The relatively weak fluorescence in acetonitrile allows for simultaneous observation of both fluorescence and resonance Raman scattering from poly-1. Oxidation results in a disappearance in both the emission and Raman scattering (as neither the mono- nor dication absorb significantly at 488 nm), which both recover upon re-reduction to the neutral state.

In dichloromethane, the emission of poly-1 overwhelms the Raman scattering, but again oxidation results in a near complete loss in fluorescence, which is reversed upon re-reduction (Figure 7). A detailed analysis of the changes which occur during polarization/depolarization of the electrode with respect to emission intensity is that the initial emission (Figure 7 upper, black line) decreases to almost zero upon polarization at 1.0 V for 60 s prior to the start ($t = 0$ s) of the experiment. Afterward, the potential was stepped back to 0.0 V and held.

Figure 4. In situ switching of a poly-1 modified ITO slide to the closed form (left, $\lambda_{exc}$ 365 nm) and back (right, $\lambda_{exc}$ 660 nm) in dichloromethane under argon.

Figure 5. Raman spectrum of a) 2 c) in CH$_3$CN (PSS at 365 nm) and b) a dry poly-1 modified ITO slide after irradiation at 365 nm while immersed in dichloromethane under argon.

Figure 6. Fluorescence spectra of a poly-1 modified ITO electrode upon wetting with DCM ($\lambda_{exc}$ 405 nm).
at that potential for the remainder of the experiment, without excitation for the first 60 s. The emission spectrum obtained immediately after was weak (Figure 7 upper, red line) but recovered gradually while under irradiation toward its original state. Notably the recovery of fluorescence did not occur unless the film was under irradiation, as signified by the further recovery under on/off switching of the excitation. These data indicate that at least partial oxidatively driven cyclization of the dithienylethene units in the polymer film occurred at 1.0 V.

A key aspect of device performance is response time (switching rate). In the case of redox polymers the rate of charging and discharging of films is limited by the mobility of charge carriers in the film (i.e., intermolecular electron self-exchange rates). Hence, the response time of a film to a change in electrode potential would be expected to increase with film thickness and indeed a response time of up to tens of seconds before the fluorescence intensity reaches a steady state was observed upon film reduction at 0.0 V. Furthermore, the films described above are also sufficiently thick to observe kinetic charge trapping upon film reduction. Hence, the intrinsic response of the films to changes in electrode potential was explored using thinner films (with film thickness controlled by the number of cycles used during polymer formation), albeit with an associated decrease in absolute fluorescence intensity. Nevertheless for the thinner film, switching off the fluorescence is achieved within a few seconds, while subsequent on-switching is even faster.

Stepped polarization/depolarization of the electrode (at 0.0 and 1.0 V, respectively) for increasing periods of time under continuous irradiation at 405 nm shows the rapidity with which fluorescence can be quenched by electrochemical oxidation. Oxidation at 1.0 V resulted in a near complete switching off of the emission within several seconds. Notably, the time over which the potential is held at 1.0 V had a marked effect on the time taken for the films emission to reach maximum intensity. After several seconds at 1.0 V, switching polarization to 0.0 V resulted in a near immediate recovery in emission intensity. As the duration of oxidation increases the recovery took longer once the polarization was switched to 0.0 V. Of note is that the rate of immediate recovery of emission at 0.0 V, i.e., the re-reduction of the still open form, was relatively constant (Figure 8).

The electrochemical ring closing upon oxidation of the polymer film is therefore shown to be slowly established, as longer periods of oxidation cause a greater dependence on ring opening toward the fluorescent form (Scheme 3).

**Scheme 3.** Mechanism of the slowly established electrochemical ring closing of the polymer responsible for fluorescence quenching upon oxidation and its subsequent reactivation by irradiation with visible light.
In conclusion, the sexithiophene-diarylethene hybrid polymer, poly-1, although photochemically and photophysically inactive when dry, shows a remarkable recovery in photo-switching and fluorescence when the film is immersed in solvent, ascribed to disruption of the H-type intermolecular interactions due to solvent swelling of the film (Scheme 4).

The reactivation of the photochemical properties of the film includes oxygen sensitization, which results in oxidation and eventual film bleaching at the irradiated area, enabling facile post-polymerization patterning of films. In the absence of oxygen the cyclization of the dithienylethene moieties is driven both photochemically and electrochemically. This together with the switching of luminescence by polarization of the polymer modified electrode at 1.0 V allows for volatile information storage. Emission is reactivated by photochemical ring opening of the dithienylethene moieties upon depolarization of the electrode at 0.0 V. In summary, poly-1 modified electrodes can serve as functional memory devices, as oxidation can be used to write information, short bursts of visible light to read and long bursts to erase and re-write the state of the film. Additionally, the properties of the functional system can be tuned by varying the film thickness. Increased fluorescence intensity and photochromism is paired with longer response times due to slow diffusion of charges within the polymer film. On the other hand, a thin film allows for much faster response times with lower overall emission intensity. Ultimately, this approach of seeking to circumvent quenching effectively allows for reactivation of the functional units which were previously thought to be practically deactivated upon polymerization. Naturally although the use of volatile solvents is highly impractical for restoring switching properties in devices, these behavior can be exploited in sensing applications where solvent turns on fluorescence as a readout signal. From a photonic materials perspective, polymer film impregnation with non-volatile (high molecular weight) solvents to render the polymer in a permanently solvated state can be envisaged as a more attractive route toward incorporation in devices.

Experimental Section

**Materials:** TBAPF$_6$ (Aldrich) and spectroscopic-grade DCM (UVASOL) were used without further purification for electrochemical and spectroscopic measurements. 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 and the (2-(5-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)thiophen-2-yl)thiophene) dimer model compound were available from earlier studies. [18,22]

**Physical Methods:** UV–vis absorption spectra were obtained on an Analytik Jena Specord600 spectrometer. Electrochemical data were obtained using a 600C or 760B electrochemical workstation (CH Instruments). The working electrodes used were a Teflon-shrouded Au electrode (3 mm diameter), indium tin oxide (ITO) on glass slides (1 cm × 3 cm), and a platinum disc electrode (2 mm diameter). A platinum wire was used as an auxiliary electrode, and an Ag/AgCl or a saturated calomel electrode (SCE) was used as the reference electrode. All potential values are quoted with respect to the SCE. Cyclic voltammograms were obtained at a sweep rate of 100 mV s$^{-1}$ in anhydrous DCM containing 0.1 M TBAPF$_6$. Irradiation at 365 nm (4.1 mW), 420 nm (8 mW), 490 nm (2 mW), and 660 nm (4.5 mW) was carried out using light emitting diodes (Thorlabs). Raman spectra at 633 nm were acquired using a Olympus BX51 microscope coupled to a HeNe Laser (10 mW, Thorlabs) and a Shamrock 163 spectrograph and iDus-420-OE CCD (Andor Technology). Raman (488 nm) and fluorescence spectra were recorded using a Nikon Eclipse inverted microscope coupled to a Shamrock 3031 spectrograph and Shamrock 3031 spectrograph and iVac-OE CCD camera (Andor Technology) with excitation provided by 405 and 488 nm laser (Andor laser combiner/ATOF) using a Nikon Eclipse inverted microscope coupled to a Shamrock 3031 spectrograph and iVac-OE CCD camera (Andor Technology) with excitation provided by 405 and 488 nm laser (Andor laser combiner/ATOF) using a 60× objective. Singlet oxygen emission spectra were recorded at 405 nm excitation (50 mW, Power Technology) and an Andor idus-491-InGaAs detector coupled to a Shamrock 163 spectrograph with a 1000 nm blaze (150 l mm$^{-1}$) grating and silver coated optics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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[29] Additionally, a reversible redox wave at 0.2 V appears, of which the origin is not known.
[30] Allowing for recording of resonance Raman spectra at all wavelengths, e.g., 488 nm, without interference from fluorescence (Figure S2, Supporting Information).