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Spectroelectrochemical Study of 2,2′:5′,2″-Terthiophene Polymerization at a Liquid/Liquid Interface Controlled by Potential-Determining Ions

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ABSTRACT: Heterogeneous electron transfer (HET) from an aqueous redox couple, Ce(III):Ce(IV) to 2,2′:5′,2″-terthiophene (3T) in 1,2-dichloroethane was investigated using potential-determining ions to establish an interfacial Galvani potential difference. The reaction was found to be potential dependent, and different thiophene oligomers species were identified spectroelectrochemically depending on the interfacial potential and the concentration of 3T present in the organic phase. At low concentrations, sexithiophene and its bipolaron were found to be the main products. At higher concentrations an insoluble black polymer was precipitated at the interface and sexithiophene radical cations and radical cation dimers were found to be present in solution.

Introduction

Conducting polymers have been the subject of a huge amount of research in the past 20 years, due to their many potential applications as light-emitting diodes, lightweight battery electrodes, selective membranes, and electrochromic devices.[1] We have recently reported the electropolymerization of 2,2′,5′,2″-terthiophene at the interface between two immiscible electrolyte solutions (ITIES), initiated by a heterogeneous electron transfer (HET) between an aqueous redox couple (Ce(III):Ce(IV)) and the terthiophene monomer in 1,2-dichloroethane (1,2-DCE).[2] The polymerization of surface-active pyrroles at the water/1,2-DCE interface has also been observed by surface tension measurements[3] and electrosynthesis of polyphenylpyrrole coated silver particles at a liquid−liquid interface has been accomplished by an EC-type mechanism where the polyphenylpyrrole facilitates the transfer of the silver ions from the aqueous to the organic phase where a slow homogeneous electron transfer from the monomer to the metal ion leads to polymerization and metal cluster growth.[4] Here we report on the electropolymerization of 2,2′:5′,2″-terthiophene (3T) at the ITIES where the interfacial potential is controlled by partitioning ions.

Electron transfer that occurs across the interface between two immiscible liquids has been studied over the past 20 years. Shafer et al., in their study of electron-transfer reactions between hydrophobic metallocenes and aqueous redox couples, discuss the history and theory of these reactions.[5] At a liquid/liquid interface, ions which partition between the phases set up an interfacial Galvani potential difference, $\Delta_o{}^w\phi$, which is governed by:[6]

$$\Delta_o^w\phi = \Delta_o^w\phi_i^0 + \frac{RT}{z_iF}\ln\frac{a_i^o}{a_i^w}$$

where $\Delta_o^w\phi_i^0$ is the standard transfer potential, z_i is the ionic charge, a_i^o is the activity of the ion i in the organic phase and a_i^w is its activity in the aqueous phase. Partitioning ion experiments coupled with visible spectroscopy were used to study the oxidation of tin biphthalocyanine by HET at the liquid/liquid interface,[7] where the various oxidation states absorb at well-defined and separate wavelengths. Partitioning ions at the liquid/liquid interface obviously has implications for phase transfer catalysis, and the partitioning of ions at the liquid−liquid interface has been applied to two-phase azo-coupling reactions,[8] electron-transfer reactions of hydrophobic metallocenes with aqueous redox couples,[5] the Williamson ether synthesis,[9] two-phase permanganate oxidation,[10] and the S_N2 formation of 2-hydroxy-3-methylbutyric acid from 2-bromo-3-methylbutyric acid.[11]

The liquid−liquid interface is defect free, making it an ideal substrate for interfacial nucleation studies, and a rate law has been derived for the deposition of metallic particles at the liquid−liquid interface where no preferential nucleation sites are present.[12] Electrochemical formation of heterocyclic polymers occurs by an E(CE)n mechanism, where the initial electrochemical step is the loss of an electron from the monomer to form a radial cation which then dimerizes, and the dimer is subsequently oxidized. However, 3-dimensional polymer growth also requires the precipitation of oligomers from solution.[13] The study of polymerization at a liquid/liquid interface using potential-determining ions is a potentiostatic method, and potentiostatic methods have been found to be more effective for polymer formation than potentiodynamic ones.[14]

In this paper, we demonstrate that with low concentrations of 3T in the organic phase the hexamer of thiophene, sexithiophene (6T), can be synthesized at the liquid/liquid interface. Oligothiophenes can be considered as short-chain models for regiochemically well-defined polythiophenes.[15] Long chain oligothiophenes have also been investigated as molecular wires.[16] High concentrations of 3T led to precipitation of polymer at the interface, with identification of soluble intermediates, which was compared to similar studies at solid electrodes.[17]

Experimental Section

The electrochemical nature of the reaction was confirmed by cyclic voltammetric experiments using a typical four

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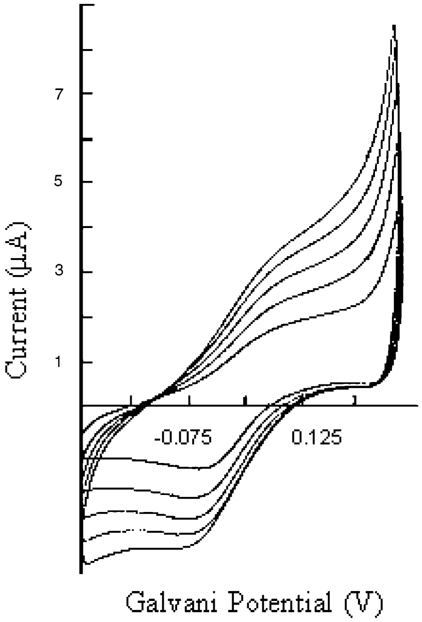

Figure 1. Representative cyclic voltammogram for cell 1 in the presence of 0.1 mM 2,2:5′,2″-terthiophene. Sweep rate equals 25, 50, 75, 100, and 125 mV s^{-1}.

electrode-cell configuration at the ITIES.[18] 1,2-Dichloroethane (1,2-DCE) (Fluka 99.5%) was the organic phase. Here, 18.2 mΩ water prepared using the Maxima ultrapure water system (Elga Ltd.) was the aqueous phase. 2,2′:5′,2″-Terthiophene (Fluka >99%), cerous(III) sulfate anhydrous (Fluka ~ 97%), cerium(IV) sulfate (Aldrich 99%), lithium sulfate, Li_2SO_4, (Fluka >99.0%), tetraphenylarsonium chloride, TPAsCl, (Fluka, 95%), and tetraethylammonium chloride, TEACl, (Fluka ≥ 99.5%) were used as received. Tetrapropylammonium chloride, TPrACl, was prepared by neutralizing tetrapropylammonium hydroxide (Fluka ≥ 99.5%) with hydrochloric acid, by filtration and by drying. Tetraphenylarsonium tetraphenylborate chloride, $TPAsTPBCl_4$ and tetraphenylarsonium tetrakis(pentafluorophenyl)borate, $TPAsTPBF_{20}$, were prepared as in the literature.[19] In experiments where partitioning ions were used to set the interfacial Galvani potential, the setup simply consisted of Pyrex test tubes, 20 mL volume, with a diameter of 2.5 cm diameter. The aqueous phase (10 mL) was added to the organic phase (5 mL), and the tubes were shaken to ensure maximum contact between the phases. Visible absorption spectra were measured and recorded using a Cary 1E U. V.-visible spectrophotometer (Varian Optical Spectroscopy Instruments).

Results and Discussion

1. Heterogeneous Electron Transfer from 2,2′:5′,2″-Terthiophene to an Aqueous Redox Couple at the Liquid/Liquid Interface in the Four-Electrode Cell Controlled Potentiodynamically. Cell 1. Ag/AgCl/1 mM TPAsCl (aq)/1 mM $TPAsTPBF_{20}$, *a* mM 3T (o)//0.1 M Li_2SO_4, 0.2 M H_2SO_4, 0.1 M $Ce(SO_4)_2$, 0.01 M $Ce_2(SO_4)_3$ (aq)/Pt.

Figure 1 shows a typical cyclic voltammogram of the charge transfer that occurs for Cell 1 in a four-electrode cell when it lies between Ce(III)/Ce(IV) in the aqueous phase and 3T in the organic phase, where the 3T concentration is 0.1 mM. This transfer was not found to occur in the absence of either the aqueous redox couple or 3T, and therefore was assigned to the HET reaction:

$$3T(o) + Ce^{4+}(aq) \leftrightarrow 3T^{\bullet +}(o) + Ce^{3+}(aq)$$

Table 1. Interfacial Galvani Potential Difference at the Interface Determined by Partitioning Ion Concentration

concentrations	$\Delta^w{}_o\phi$ (mV)
$TPrATPBF_{20}$ (5 mM), TPrACl (2 mM)	−85 (potential A)
$TEATPBF_{20}$ (5 mM), TEACl (0.5 mM)	84 (potential B)
$TEATPBF_{20}$ (5 mM), TEACl (0.01 mM)	185 (potential C)

The peak-to-peak separation was ~120 mV, indicative of a reversible electron-transfer reaction at a liquid−liquid interface.[20] The peak height current was found to be proportional to the square root of the sweep rate, indicating a diffusion-controlled reaction.[21]

A peak to peak separation of 60 mV was found for ion transfer of TEA^+ or $TPrA^+$ in Cell 1 in the absence of terthiophene. The literature values for $\Delta_o^w\phi_{TEA}^{+o}$ and $\Delta_o^w\phi_{TPrA}^{o+}$ are +44 and −91 mV, respectively,[22] and this value was used to calculate the $\Delta_o^w\phi_{1/2}$ for the electron-transfer reaction between 3T and the Ce(IV):Ce(III) aqueous redox couple as 24 mV.

Increasing the concentration of 3T in Cell 1 to 1 mM or above led to the formation of a thin green layer at the interface, even in the absence of an applied potential. A similar spontaneous reaction has also been observed for the dimethylferrocene/hexacyanoferrate system, which had been previously investigated as an "ideal" system for investigating HET at the liquid/liquid interface.[23−25] However, when there is a high concentration of dimethylferrocene present, a potential independent blue precipitate was found to form in the aqueous phase.[26]

2. Polymerization at the Liquid/Liquid Interface Using the Potential-Determining Ion To Establish the Interfacial Galvani Potential Difference. To determine if the reaction between Ce(IV):Ce(III) and 3T is potential-dependent, potential-determining ions were used to establish the interfacial potential difference on contact of the two phases. TEA^+ and $TPrA^+$ were selected as the potential dependent ions. The Galvani half-wave potentials, $\Delta_o^w\phi'_i$, of the potential-determining ions were determined by finding the half wave potential of ion transfer, $\Delta_o^w\phi^\circ_{1/2}$. The Galvani potential, $\Delta_o^w\phi$, in the system for phase transfer catalysis can then be calculated using the equation:

$$\Delta_o^w = \Delta_o^w\phi_i{}^\circ + \frac{RT}{F}\ln\frac{\alpha_i{}^{(o)}\gamma_i{}^{(o)}c_i{}^{(o)}}{c_i{}^{(w)}}$$

where a_i is the activity of species i, α_i is the degree of disassociation, γ_i is the activity coefficient, and c_i is its concentration. The interfacial potential was set to points corresponding to different points on the cyclic voltammogram. In this way the effect of potential and monomer concentration on the mechanism could be observed. Cell 2 describes the partitioning ion experiments. The polymerization reaction was studied at the three potentials given in Table 1 for a range of monomer concentrations.

Cell 2. 5 mM $TPAsTPBF_{20}$ and *a* M 2,2′:5′,2″-terthiophene and 5 mM $TEATPBF_{20}$ or 5 mM $TPrATPBF_{20}$ (o)//0.1 M Li_2SO_4 and 0.2 M H_2SO_4 and 0.1 M $Ce(SO_4)_2$ and 0.01 M $Ce_2(SO_4)_3$ and *b* mM TEACl or *c* mM TPrACl.

Figure 2 shows the spectra obtained for the reaction of 0.5 mM 3T at various potentials. Immediately upon contact of the aqueous phase there was a distinctly different color change in the organic phase at each

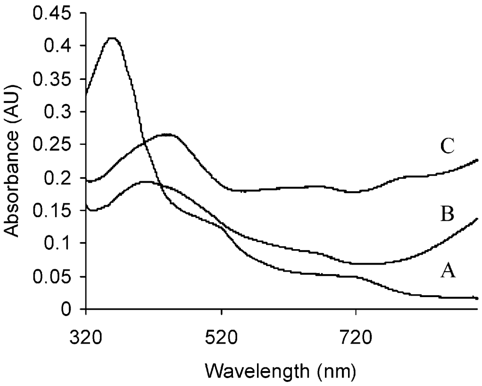

Figure 2. Visible spectra showing the effect of potential on the reactions of 0.5 mM 2,2:5′,2″-terthiophene in cell 2. Solutions were diluted by a factor of 10.

potential, indicating that the reaction is potential dependent. However no solid polymer was precipitated at the interface at any of the three potentials. The organic phase at potential A was red, that at potential B was brown, and that at potential C was green in color. At potential A the peak at 353 nm due to terthiophene[27] is the strongest peak, but there are also shoulders in the 520 and 720 nm regions which are not present for neutral 3T in the absence of the aqueous redox couple, indicating that some reaction is taking place. From Figure 1 it can be seen that the $\Delta_o^w\phi_{1/2}$ of electron transfer for cell 1 is 24 mV, and therefore, no electron transfer would be expected at −85 mV. However at this potential, some electron transfer coupled to ion transfer may be taking place. At this potential, chloride ions are transferred to the organic phase, possibly causing an electron to be transferred from the organic to the aqueous phase to maintain electroneutrality,[28] resulting in the formation of terthiophene radical cations.

To assign the absorbance at 520 and 720 nm, the possible reactions of oxidation were considered. The radical cation $3T^{\bullet+}$ is a possibility, as it has an absorbance at approximately 520−530 nm, depending on solvent.[29] The dimerization of $3T^{\bullet+}$ was reported by Hill et al. in 1992, where the dimer showed absorbance bands at 466 and 708 nm.[31] The shoulder at 720 nm therefore strongly suggests the presence of the $3T^{\bullet+}$ dimer. The bipolaron $3T^{2+}$ absorbance has been reported at 833 nm and does not appear to be present. Two radical cations could also react to form 6T, which has an absorbance in the 430−440 nm range,[27,29] and therefore could also be present in small amounts. The organic phase at this potential was red in color and the color did not diminish over the 2 h when the phases were in contact, or after removal of a portion for dilution. Therefore, the radical cation and radical cation dimer are very stable in 1,2-DCE in the presence of 5 mM $TPAsTPBF_{20}$. In contrast, 2,5″-dimethylterthiophene radical cation in acetonitrile/tetrabutylammonium fluoroborate has been reported to be unstable.[30]

Further increasing the potential (potential B) leads to the emergence of a peak at 446 nm, which is that of the neutral 6T—the product of dimerization of the starting terthiophene. At potential B the 3T and 6T peaks seem to overlap, while at potential C the concentration of 6T has increased, and the 3T peak is no longer visible. At potential C there are slight shoulders at 680 and 780 nm, which are assigned to the sexithiophene radical cation $6T^{\bullet+}$ and its π dimer. The absorbance at the positive potentials begin to increase at ~820 nm and is still rising at 900 nm. Caspar et al.[29] attributed the bands in this region to terthiophene bipolarons, suggesting that the quinoid resonance structure of the bipolaron would be stable and would be analogous to the site of charged storage in bulk polythiophene. They found that the terthiophene bipolaron absorbed at 833 nm and the sexithiophene bipolaron absorbed at 1019 nm, which is out of range of this experiment but could be present as the absorbance is rising in that direction. Sato et al. also found $6T^{2+}$ to have absorbance in this region.[31]

The reactions occurring when 5 mM 3T is present in the organic phase may then be summarized as follows: the electron transfer that occurs at the liquid/liquid interface is

$$3T(o) + Ce^{4+}(aq) - 3T^{\bullet+}(o) + Ce^{3+}(aq)$$

At lower potentials, this reaction may be the result of electron-transfer coupled to the ion transfer of chloride ions. At higher potentials, radical cation formation is followed by a chemical dimerization to form sexithiophene:

$$2\ 3T^{\bullet+}(o) - 6T(o) + 2H^{+}$$

In the dimerization step a proton is formed for each electron, which is removed from the 3T in the electrochemical step. The protons should partition into the aqueous phase, and this would maintain the overall electroneutrality of the system as protons and electrons are both being transferred from the organic to the aqueous phase. However, as there was a high concentration of acid in the aqueous phase due to the presence of the sulfuric acid, no attempt was made to detect pH changes.

As increasing the oligomers chain length lowers the oxidation potential the 6T must then also be oxidized. The peaks due to the 6T radical cation and radical cation dimer present at high interfacial potentials confirm this.

$$6T + Ce^{4+}(aq) - 6T^{\bullet+}(o) + Ce^{3+}(aq)$$

At this concentration, it seems that there is an insufficient concentration of sexithiophene radical cations to react further, as there is no evidence of longer oligomers in solution. The presence of sexithiophene bipolarons may be due to disproportionation of the radical cation.

$$2\ 6T^{\bullet+}(o) - 6T + 6T^{2+}$$

The green color of the solution at potential C is due to the absorbance of the $6T^{2+}$ species. This is also the color of the precipitate formed in the four-electrode cell at higher initial monomer concentrations. Therefore, this film may not be a higher polymer but simply lower bipolaron species.

Decreasing the concentration of 3T to 0.25 mM led to the formation of organic phases that were very similar to those obtained at 0.5 mM. The main difference is that at potential C the peak due to the neutral 3T is still visible. As the potential is sufficient to oxidize all the 3T, some disproportionation must be occurring for radical cations that remain unreacted due to concentration limitations.

$$2\ 3T^{\bullet+}(o) - 3T + 3T^{2+}$$

When 5 mM 3T is present in the organic phase there is some insoluble black polymer formed at the liquid/

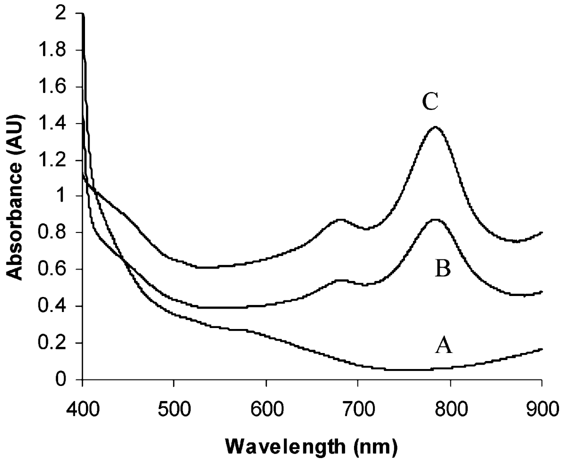

Figure 3. Visible spectra showing the effect of potential on the reactions of 5 mM 2,2:5′,2″-terthiophene in cell 2. Solutions were diluted by a factor of 10.

liquid interface at all three potentials. The amount of 3T remaining was calculated using the Beer–Lambert law[32] for each potential and found to be 4.98, 1.52 and 1.13 mM at potentials A, B, and C, respectively. The spectra of the organic phase after 2 h reaction time for 5 mM terthiophene is shown in Figure 3. At potential A there is a shoulder in the 500–600 nm region which could be assigned to $3T^{•+}$, but most of the 3T remains unreacted. At potentials B and C, two very distinct peaks emerge at 775 and 670 nm, and the 6T peak at 446 nm is not very distinct, indicating that the 6T formed has reacted further. The peak at 778 nm is due to the radical cation $6T^{•+}$, and the peak at 675 nm is due to the formation of a π-dimer of $6T^{•+}$. This behavior, where a sexithiophene radical cation dimer has an absorbance with higher energy than that of the radical cation, has been observed before.[33,34] The peak at 675 nm has a lower absorbance than that of the radical cation peak at 775 nm but increases at the same rate with the increase in potential from A to C. This behavior was previously observed by Casado et al.[33] for a dimethyl end-capped sexithiophene film. It has been argued that more polar solvents can disperse the charge and minimize the Coulombic repulsions resulting in a higher degree of dimerization than in less polar solvents such as dichloromethane,[34] but Apperloo et al. found that unsubstituted conjugated oligomers were more likely to dimerize in apolar solvents.[35]

The main reaction occurring at this concentration is the dimerizarion of sexithiophene radical cations that appear to precipitate at the interface.

$$2\ 6T^{•+}(o) - 12T(\text{precipitate}) + 2H^{+}$$

When the terthiophene concentration was increased to 50 mM, a thick black polymer layer was formed at the interface. This black layer settled to the bottom of the container with time indicating that it consisted of long oligomers which were no longer soluble in 1,2-DCE. The organic layer was removed before settling and the spectra were similar to those for 5 mM 3T, with the $6T^{•+}$ radical cation present in the same amount, despite the 10-fold increase in starting 3T concentration. 6T has a lower oxidation potential than 3T due to the increased conjugation stabilizing the radical cation, so at lower concentrations the reaction terminated at this stage due to concentration effects. At higher concentrations, all the sexithiophene formed can react further to form longer insoluble oligomers. Further increasing the monomer concentration does not significantly affect the height of the sexithiophene radical cation, indicating that it remains at a steady state during polymerization. Hoier and Park[18] also found that a radical cation of the trimer or quatramer remained present at a steady state during the polymerization of 3-methylthiophene in propylene carbonate.

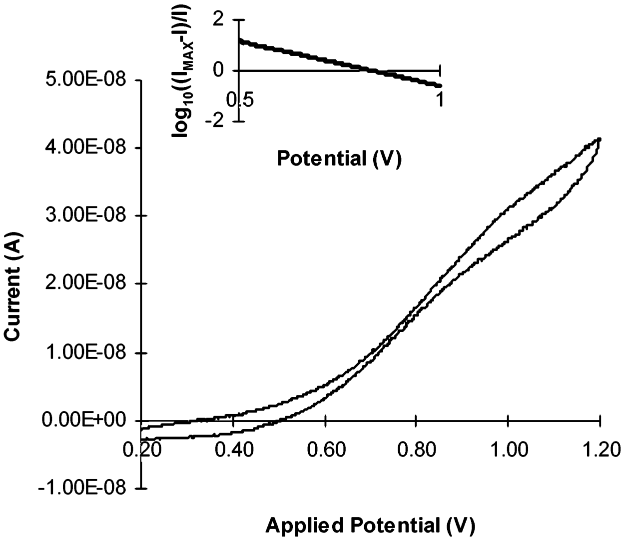

Figure 4. Redox reaction of 0.1 mM 2,2′:5′,2″-terthiophene in Cell 3.

The existence of the $6^{•+}$ radical cation in solution suggest that 1,2-DCE would be a good solvent for the polymerization of terthiophene at solid electrodes as it can solvate long radical cations and therefore the oligomers which precipitate onto the electrode would have long chain lengths.

3. Polymerization of 2,2′:5′,2″-Terthiophene at Planar Electrodes. The polymerization of 3T at a solid electrode in $TPAsTPBF_{20}$/DCE was carried out for comparison to liquid/liquid result. Cell 3 was used to study the oxidation at a 25 μm gold microelectrode.

Cell 3. Ag/AgCl/1 mM TPAsCl (o)/5 mM $TPAsTPBF_{20}$ + x mM 3T (1,2-DCE)/Au.

To confirm that the 3T radical cation formation at low concentrations is reversible, oxidation of 0.01 mM 3T was carried out with 5 mM $TPAsTPBF_{20}$ as the supporting electrolyte; see Figure 4. At this low concentration, 3T is reversibly oxidized with $E_{1/2}$ of 0.82V. Continuous cycling does not change the CV shape, and the current does not decrease. Semilogarithmic analysis of the data shows that the reaction is reversible.[38] It appears that at such low concentrations the radical cations formed by oxidation are not present in sufficient number to react and cause a polymerization reaction. When the 3T concentration was increased to 50 mM, a CV typical of conducting polymer formation was obtained; see Figure 5. Oxidation begins at 0.7 V, followed by a large increase in current after 1.1 V due to polymer deposition. On the cathodic sweep, there is a large negative peak due to stripping of the supporting anion from the polymer, i.e., conversion of the polyterthiophene from the conducting to the insulating form. The concentration and nature of the supporting electrolyte anion was found to have a large effect on the polymerization. When the $TPAsTPBF_{20}$ concentration was increased from 5 to 20 mM, no reaction was found

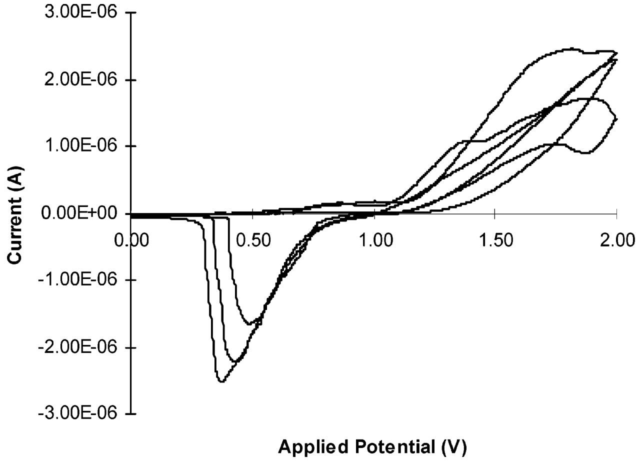

Figure 5. Redox reaction of 50 mM 2,2′:5′,2″-terthiophene in Cell 3.

to occur. In addition, polymerization of 50 mM 3T with 5 mM was carried out at a gold macroelectrode with a surface area of 0.127 cm^2, leading to the formation of a well-adhered polymer film that could be reversibly cycled between the neutral polymer, which was red in color, and the oxidized form, which was black. Therefore, the large TPBF$_{20}^-$ anion is suitable as the counterion for the electrochromic redox reaction.

Conclusions

In this paper, we have demonstrated that potential-determining ions can be used to set the interfacial Galvani potential difference at a liquid−liquid interface, an allow different oligothiophene species to be identified depending on interfacial potential and starting 2,2′:5′,2″-terthiophene concentration. Choosing a low concentration of 3T in the organic phase led to a simple synthetic route to unsubstituted sexithiophene, and is important due to the many potential applications of thiophene in devices such as thin film transistors, light-emitting diodes, and light-modulators.[36,37] Future work in this area will include isolating, purifying, and further characterizing the sexithiophene, as well as varying the organic solvent and starting oligomers in an attempt to isolate other soluble long chain thiophene oligomers. At higher 3T concentration a black powdery deposit of polymer was formed at the liquid−liquid interface. The sexithiophene radical cation was found to exist in solution at a constant concentration independent of starting terthiophene concentration.

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