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Tunable Electron Density at a Rhenium Carbonyl Complex Coordinated to the Conducting Polymer Poly[5,5′-(2-thienyl)-2,2′-bithiazole]

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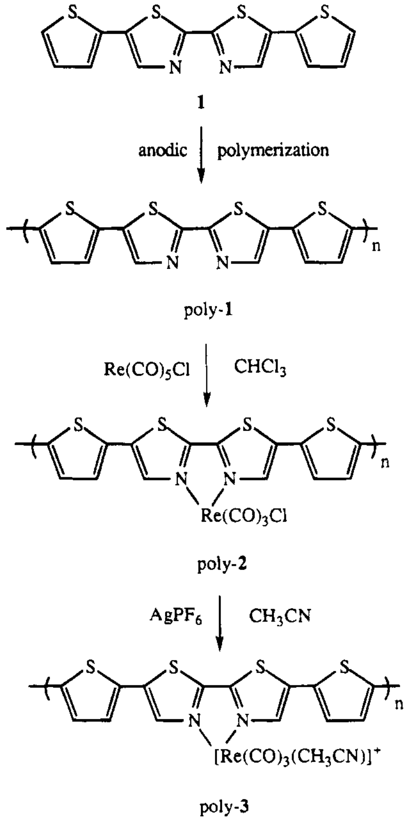
The synthesis of a conducting polymer by electropolymerization of 5,5′-(2-thienyl)-2,2′-bithiazole is reported. Films of this polymer exhibit electrochemical behavior typical of conducting polymers and have a conductivity of $\sim$0.2 Ω^{-1} cm^{-1} at 25 °C in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_2$Cl$_2$ at the potential of maximum conductivity ($\sim$+1.5 V vs Ag). The activation energy for conductivity for partially oxidized ($\sim$+1.3 V vs Ag) films is 0.25 eV. Reaction of these polymer films with refluxing solutions of Re(CO)$_5$Cl in CHCl$_3$ yields polymers in which the [Re(CO)$_3$Cl] moiety is bound to the bithiazolyl sites in the polymer. Subsequent reaction with AgPF$_6$ converts the Re centers to cationic [Re(CO)$_3$(CH$_3$CN)]$^+$ groups. These polymers were characterized by XPS and surface reflectance FTIR. The polymer containing the cationic Re groups is conducting ($\sim$2 $\times$ 10^{-3} Ω^{-1} cm^{-1} at +1.5 V vs Ag). The potential region in which the polymer is conducting does not overlap with any Re-centered oxidations, but oxidation of films of the polymer to the conducting state causes electron density to be removed from the Re center, resulting in a shift of the carbonyl stretching frequencies to higher energy. At the potential of maximum conductivity this shift is 4–6 cm^{-1}.

We report the synthesis and properties of a novel conducting polymer, poly-**1**, prepared by anodic electropolymerization of 5,5′-(2-thienyl)-2,2′-bithiazole (**1**) and subsequent reaction of the polymer to incorporate a cationic Re center (Scheme 1).

By incorporating a metal center into a conducting polymer so that the metal is coordinated to the conjugated backbone, we hoped to be able to demonstrate modulation of the electron density at the metal by varying the redox state of the polymer. We have been interested in organometallic complexes containing redox-active ligands because changing the oxidation state of such a ligand affects the properties and reactivity of the metal center.[1–3] By using a conducting polymer as the ligand, we have a continuous progression of "oxidation states" accessible to us, since changing the redox state by gradual oxidation of the polymer results in the charge being delocalized, at least partially, over the polymer backbone.[4] Chemical modification of electrode surfaces with a range of different polymers has been widely studied for its application to electrocatalysis. In the previously studied systems, the polymer acts as an inert support for an electrocatalyst, thus increasing the active area of the electrode. Our work is an example of a polymer system in which the electronic properties of the polymer could potentially be used to modify the behavior of the electrocatalytic group.[5]

Scheme 1



Tuning the properties and reactivity of metal centers by changing the electronic properties of ligands is common.[1–3] However, such changes are inevitably a combination of both steric and electronic changes, and

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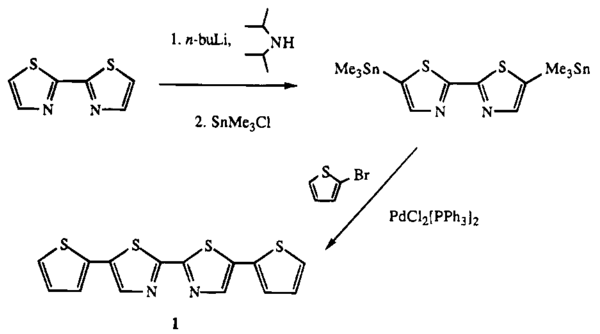
these factors are difficult to separate. Redox-active ligands may be used to tune properties with only small changes in sterics at the metal center. Moreover, these ligands permit *in situ* tuning by accessing the different redox states using electrochemical techniques. We have shown previously that changes in the oxidation state of a ferrocene pendant to a Re carbonyl complex affects the carbonyl stretching frequency in the infrared region.[6] The shifts obtained range from 2 to 33 cm^{-1} depending on the proximity and number of bonds separating the ferrocene and the metal center. Other workers have also demonstrated carbonyl shifts upon oxidation or reduction of a redox-active ligand.[7-15] Recently, we have demonstrated that changing the oxidation state of a pendant cobaltocene containing ligand on a Re carbonyl complex causes changes in the rate of a nucleophilic reaction at the carbonyl groups in the complex.[16]

In this paper we establish that oxidation of poly-**3** results in electron density changes at the Re center. We chose the cationic Re species to demonstrate this effect for several reasons. The preparation of the complexes is straightforward, and they are inert to oxygen and substitution reactions. Moreover, the metal center in these complexes is not oxidized in the potential range where the polymer is expected to be conducting, allowing investigation of the consequences of changes in the state of charge of the conducting polymer ligand. Additionally, the carbonyl ligands provide an infrared handle by which the changes in electron density at the metal center can be monitored.[6]

To introduce the metal center as close to the conjugated backbone as possible, we chose a derivative of the previously characterized Re complexes containing 2,2′-bipyridine as a ligand.[17,18] In this respect a ligand based on 2,2′-bithiazole was attractive, because this compound has the same structural basis as 2,2′-bithiophene which can be used as a precursor to polythiophene, yet it also contains an α-diimine ligating site analogous to 2,2′-bipyridine. Conducting polymers[19-25] and oligomers[26] containing bound transition metal complexes have been previously prepared; however, in most of these systems the metals are too easily oxidized and are not stable when oxidized, or the metals are too remote from the backbone of the polymer to be substantially affected by the redox changes in the polymer.

Scheme 2



Electrochemical polymerization of thiazole and 4,4′-dimethyl-2,2′-bithiazole has been attempted,[27,28] but the resulting materials are poorly conducting. The electropolymerization of monomers such as 1,4-(2′-thienyl)-benzene, 2,5-(2′-thienyl)pyridine, or 2,5-(2′-thienyl)-thiazole has been shown to yield polymers which are conducting.[29] These results provide evidence that aromatic groups that do not readily electropolymerize by themselves can be incorporated into conducting polymers by using a monomer in which the aromatic group is inserted between two thiophene groups.

Results and Discussion

Preparation and Characterization of Poly-1. The simplest polymer incorporating 2,2′-bithiazolyl units is poly-5,5′-(2,2′-bithiazole). Unfortunately, previous attempts to electropolymerize both thiazole and 4,4′-dimethyl-2,2′-bithiazole were unsuccessful.[27,28] Polythiazole was prepared chemically from 2,5-dibromothiazole using a Grignard coupling, but the measured conductivity of the material after doping was very low (10^{-7}–10^{-8} Ω^{-1} cm^{-1}).[27] We attempted to electropolymerize 2,2′-bithiazole but were unsuccessful. Although anodic current was observed, no polymer deposited on the electrode. Hence, it became necessary to synthesize modified bithiazoles from which polymers could be prepared. To this end we prepared 5,5′-(2-thienyl)-2,2′-bithiazole, **1**, prepared as shown in Scheme 2. **1** has an intense absorption band with λ_{max} = 400 nm (ϵ = 35 000 M^{-1} cm^{-1}), and a strong short-lived (<10 ns) fluorescence showing vibrational structure (Figure 1).

1 can be electropolymerized from a CH_2Cl_2 solution at +1.5 V vs Ag wire. The deposited films are black when oxidized and become red upon stepping the electrode back to 0 V. The films are insoluble in CH_2Cl_2 or CH_3CN and were characterized by cyclic voltammetry in 0.1 M [n-Bu_4N]PF_6/CH_2Cl_2 (Figure 2a). The films are durable to oxidative cycling between 0 and

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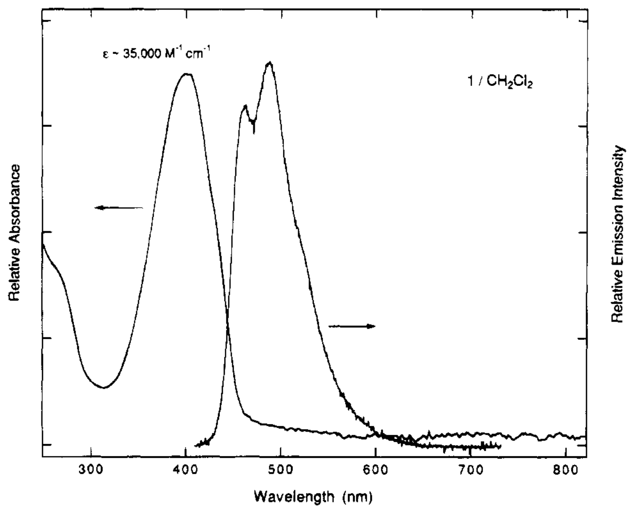

Figure 1. Absorption and emission spectra of 1.

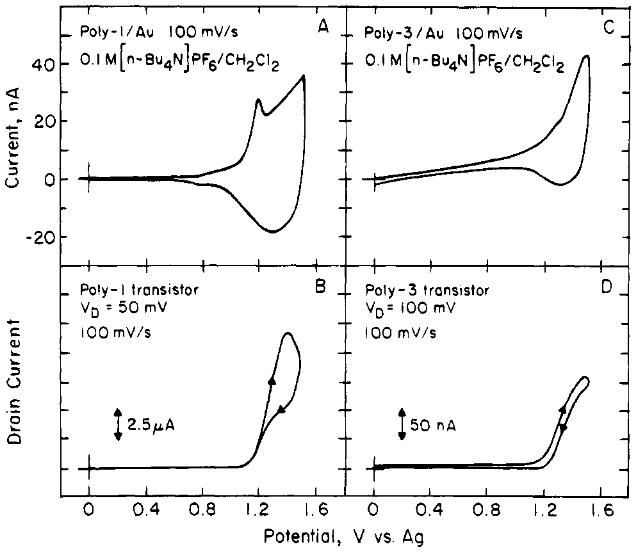

Figure 2. (a) Cyclic voltammogram of a film of poly-1 on Au microelectrodes, in 0.1 M [n-Bu_4N]PF_6/CH_2Cl_2 at 100 mV/s. (b) I_D-V_G of poly-1 on Au microelectrodes with $V_D = 50$ mV at 100 mV/s. (c) Cyclic voltammogram of a film of poly-3 on Au microelectrodes, in 0.1 M [n-Bu_4N]PF_6/CH_2Cl_2 at 100 mV/s. (d) I_D-V_G of poly-3 on Au microelectrodes with $V_D = 100$ mV at 100 mV/s. Note the different current scales in (b) and (d).

+1.4 V, and the cyclic voltammogram has the broad reversible appearance typical of the polythiophene class of conducting polymes.[30,31] Although both CH_3CN and propylene carbonate were tried as electrochemical solvents, neither solvent was suitable for characterization of the films, as degradation of the oxidized film was very rapid in these media. For example, in CH_3CN the cyclic voltammogram disappeared completely after one scan to +1.5 V.

Microelectrode devices developed in these laboratories may be used for *in situ* potential-dependent measurement of the conductivities of electropolymerized polymer films. This method has been described previously for the measurement of the conductivities of polythiophene, polypyrrole and polyacetylene films.[31-33] Using this technique we measured the drain current, I_D, as a function of gate potential, V_G, for electropolymerized films of poly-**1**. The drain current flows between the "source" and "drain" microelectrodes when the sample is conducting due to the small applied drain voltage, V_D. The drain current is proportional to the conductivity of the polymer at a given potential; hence we are able to examine the conductivity of poly-**1** as a function of potential (Figure 2b). The polymer becomes conducting at a gate potential of +1.1 V, and the conductivity reaches a maximum at ~+1.5 V vs Ag. At this maximum the conductivity is approximately 0.2 Ω^{-1} cm^{-1}. In comparison, polythiophene becomes conducting at approximately +0.75 V vs Ag.[33] The shift to more positive potentials in both the I_D-V_G and cyclic voltammogram of poly-**1** vs polythiophene is attributed to te electron-withdrawing nature of the nitrogen in the thiazole rings.

The transport of charge carriers in conducting polymers containing more than one type of heterocycle (in poly-**1**, both bithiazole and bithiophene moieties) may differ from that in conducting polymers in which the backbone contains only one type of heterocycle. In poly-**1**, the bithienyl units represent sites where a hole is more stable than on the bithiazolyl units, based on the facts that the polymerization of **1** occurs at a more positive potential than tetrathiophene and that the onset of conductivity in poly-**1** is more positive than in polythiophene. Moreover, poly-**1** is only moderately conducting, compared to polythiophene, suggesting that the bithiazole/bithiophene alternation in the backbone gives rise to the lower conductivity of poly-**1**, with the bithiazolyl units representing barriers to hole delocalization in the valence band. We studied the temperature dependence of the conductivity of poly-**1**, in order to measure the activation energy for conductivity. Because of the reactivity of highly oxidized films of poly-**1**, it was possible to study only a partially oxidized film. We find that the conductivity of a film of poly-**1** increased with increasing temperature. A plot of log σ as a function of $1/T$ plot is linear over the temperature range studied (213–298 K), and the activation energy, E_A, obtained from the slope of this plot is 0.25 eV (Figure 3). Undoped, electrochemically synthesized polythiophene is reported to have an E_A of 0.36 eV, whereas the doped material has $E_A = 0.023$ eV.[30] The sample we examined was oxidized to approximately 50% of the oxidation level at maximum conductivity, yet E_A is close to that measured for undoped polythiophene. These results suggest that the energy of the valence band of poly-**1** is indeed modulated due to the alternation of bithiazole and bithiophene units.

UV–Vis Spectroelectrochemistry of Poly-1. Spectral changes in the visible part of the spectrum upon oxidation of conducting polymers are well documented.[34] Typically, a broad band in the infrared replaces the high-energy $\pi-\pi^*$ absorption upon oxidation. The UV–vis spectrum of a film of poly-**1** which was electrochemically oxidized in 0.1 M [n-Bu_4N]PF_6/CH_2Cl_2 to +1.5 V vs Ag (Figure 4b), shows that the $\pi-\pi^*$ absorption of the neutral film (Figure 4a) is reduced in intensity, and a low-energy absorption appears. There is residual

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Table 1. Electrochemical and Infrared Spectral Data in the CO Stretching Region for 2,2′-Bithiazole and 2,2′-Bipyridine Complexes

complex	IR bands (cm^{-1})	E_{PA} ($E_{1/2}$) (V)	E_{PC} ($E_{1/2}$) (V)
(2,2′-bithiazole)$Re(CO)_3Cl$, **4**	2026; 1926; 1901[a]	+1.38[b]	(−1.11)
(2,2′-bipyridine)$Re(CO)_3Cl$	2025; 1923; 1896[c,d]	+1.35[e,f]	(−1.41)
[(2,2′-bithiazole)$Re(CO)_3(CH_3CN)]^+$, **5**	2044; 1944[a]	(+1.77)[b]	(−1.00); −1.35
[(2,2′-bipyridine)$Re(CO)_3(CH_3CN)]^+$	2032; 1942[a,g]	(+1.77)[g,h]	(−1.25)

[a] CH_2Cl_2. [b] 0.1 M [*n*-$Bu_4N]PF_6CH_3CN$ vs SCE. [c] $CHCl_3$. [d] Reference 39. [e] 0.1 M [*n*-$Bu_4N]PF_6/CH_3CN$ vs SCE. [f] Reference 17. [g] Reference 40. [h] 0.1 M [*n*-$Et_4N]ClO_4/CH_3CN$ vs SSCE.

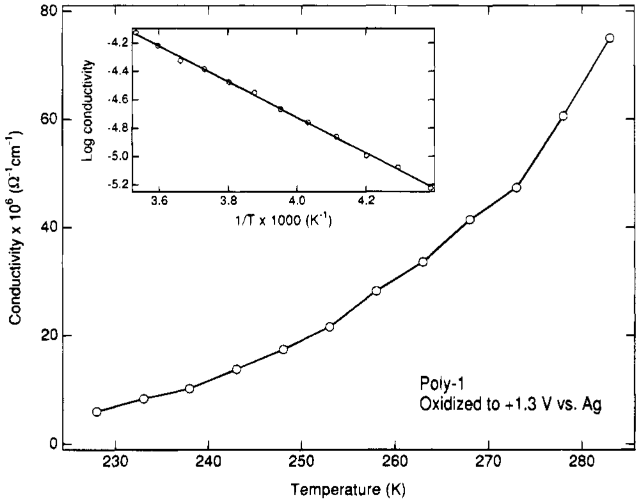


Figure 3. Temperature dependence of the conductivity of a partially oxidized film of poly-**1**. Inset: log conductivity vs 1/*T* for the same data.

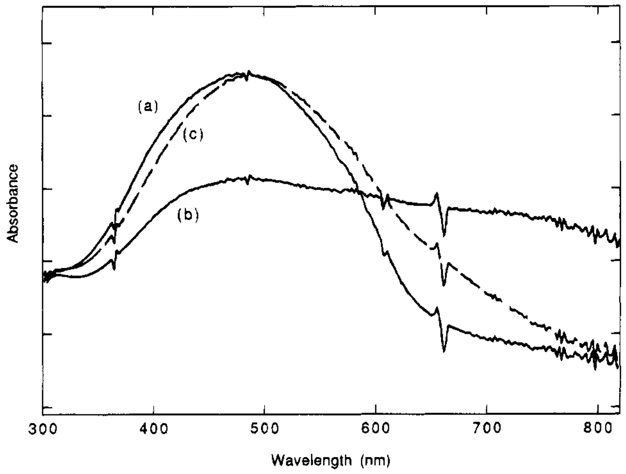
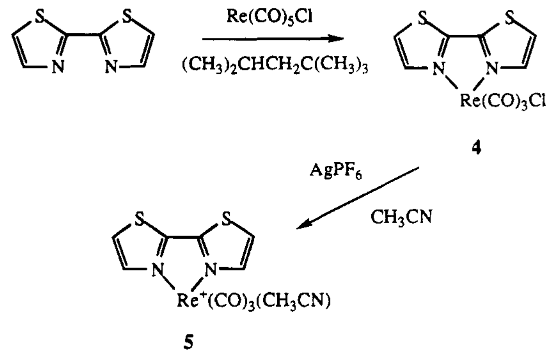


Figure 4. (a) UV−vis spectrum of poly-**1** on ITO/glass. (b) UV−vis spectrum of poly-**1** held at +1.5 V vs Ag. (c) UV−vis spectrum of poly-**1** returned to 0 V vs Ag.

Scheme 3



absorption in the 400−600-nm range suggesting incomplete oxidation. When the potential of the film is returned to 0 V vs Ag (Figure 4c), the original absorption band reappears, although there is more absorption at the low-energy end of the spectrum than previously. We attribute this to partial decomposition of the film when oxidized, consistent with the electrochemical results.

Derivatization of Poly-1. Electropolymerized films of poly-**1** react readily with $Re(CO)_5Cl$ to give poly-**2** under mild conditions. Immersion in a refluxing $CHCl_3$ solution of the Re reagent for 5 min yields derivatized films. The Re complexes (2,2′-bithiazole)$Re(CO)_3Cl$ (**4**) and (2,2′-bithiazole)$Re(CO)_3(CH_3CN)PF_6$ (**5**) were prepared in order to compare their electrochemical and spectroscopic properties (Table 1) to those of the analogous polymer confined complexes. Complexes **4** and **5** were prepared in a manner similar to that reported for the analogous (2,2′-bipyridine)$Re(CO)_3Cl$ and [(2,2′-bipyridine)$Re(CO)_3(CH_3CN)]^+$ complexes by reaction of 2,2′-bithiazole with $Re(CO)_5Cl$ followed by reaction with $AgPF_6$, Scheme 3.[17,18]

Attempted reaction of 2,2′-bithiophene with $Re(CO)_5Cl$ under the same conditions yielded only starting materials, supporting the proposal that the 2,2′-bithiazole is not ligated in an *S*,*S* fashion. The ^1H NMR spectrum of **4** shows only two resonances (8.35 and 8.25 ppm), suggesting that the 2,2′-bithiazole is bound symmetrically and ruling out the possibility of an *N*,*S*-bound complex. 2,2′-Bithiazole has been previously used as a ligand and in iridium and rhodium complexes has been demonstrated to ligate through the two nitrogen atoms.[35] Films of poly-**2** were analyzed by surface reflectance IR and X-ray photoelectron spectroscopy (XPS) to confirm that the reaction took place. The surface reflectance IR spectrum of a film of poly-**2** in the carbonyl stretching region clearly confirms that the Re is coordinated to the available bithiazole sites in the polymer in a manner analogous to that in **4** (Figure 5a,b). The peak positions of the metal carbonyl bands are close to those observed in solution for **4**. The IR spectrum shows no evidence of residual $Re(CO)_5Cl$ in the film.

The XPS spectrum of a poly-**2** film contains peaks which are assigned to Re and Cl in addition to the C, N and S observed in XPS spectra of films of poly-**1** (Figure 6). By comparison of the integrated areas of the Re 4f peaks with the areas of the S and N peaks in the XPS spectrum of poly-**2**, it is possible to calculate the extent that 2,2′-bithiazole sites in the polymer have reacted with $Re(CO)_5Cl$. This comparison shows that the amount of Re remains the same whether reaction was stopped after 5 or 30 min. However, the ratio of Re to N indicates that only 60−75% of the available reaction sites are occupied by Re. In addition, we were able to

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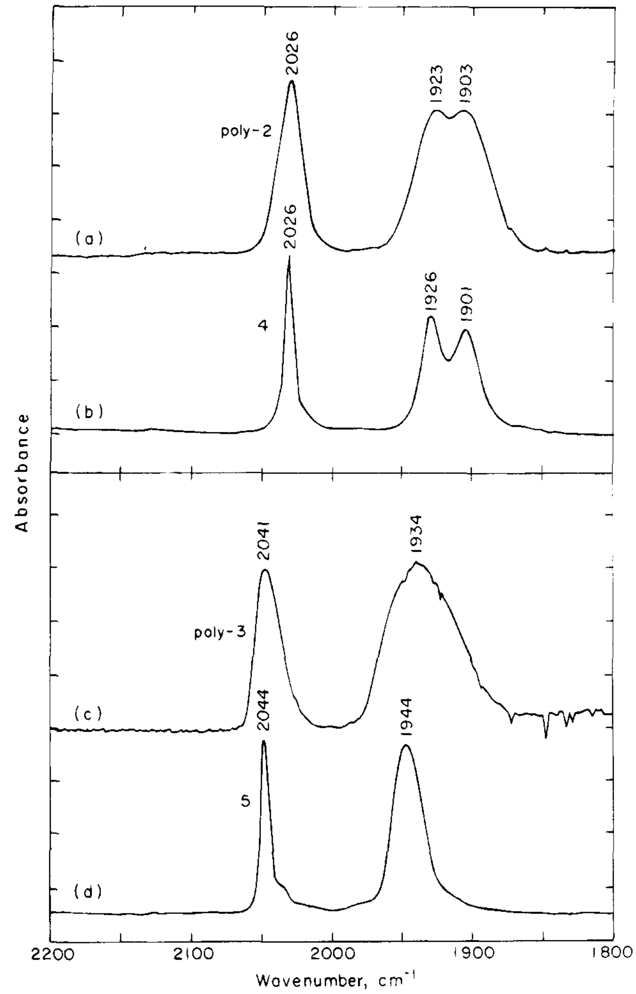


Figure 5. (a) Surface reflectance FTIR spectrum of CO stretching region of a film of poly-**2** on Pt. (b) IR of the same region of a CH_2Cl_2 solution of **4**. (c) Surface reflectance FTIR spectrum of CO stretching region of a film of poly-**3** on Pt. (d) IR of the same region of a CH_2Cl_2 solution of **5**.

use the N 1s peaks to verify the extent of reaction with $Re(CO)_5Cl$. The N 1s peak appears at 399 eV in the spectrum of poly-**1**. After the film is reacted with $Re(CO)_5Cl$ the N 1s splits into two distinct peaks, one at 399 eV, which we assign to N in unreacted 2,2′-bithiazolyl groups, and one at 400 eV assigned to N in groups which had reacted with the $[Re(CO)_3Cl]$ moiety. The N 1s peak in the XPS spectrum of a thin film of **4** on Au appears at 400 eV. The integrated areas of the two N peaks for poly-**2** indicates that approximately 60% of the N at the surface of the sample has reacted in good accord with the conclusion drawn from the Re/N ratio.

Poly-**2** can be converted quantitatively to poly-**3** by reaction of the polymer film with a solution of refluxing $AgPF_6$ in CH_3CN for 1 h (Scheme 1). Surface reflectance IR of a film of poly-**3**, shown in Figure 5c, demonstrates that complete conversion to the cationic Re occurs. The correspondence between the characteristic carbonyl bands of **5** (Figure 5d) and the IR spectrum of poly-**3** in the CO stretching region confirms the binding mode of the Re. XPS analysis of a film of poly-**3** confirms the presence of Re, S, and N as well as the unique elements F and P (Figure 6c).

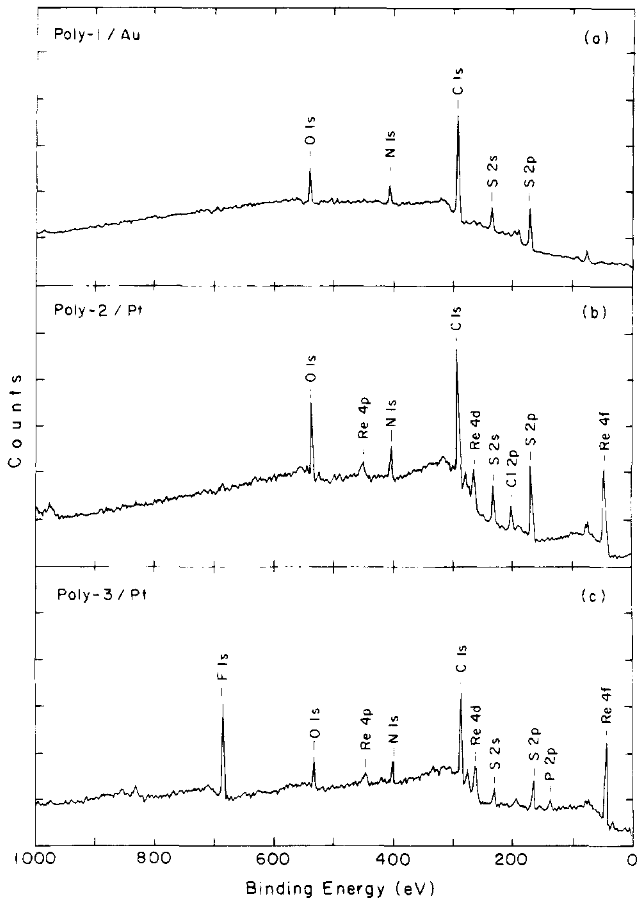


Figure 6. XPS survey scan of (a) poly-**1** on Pt; (b) poly-**2** on Pt; (c) poly-**3** on Pt.

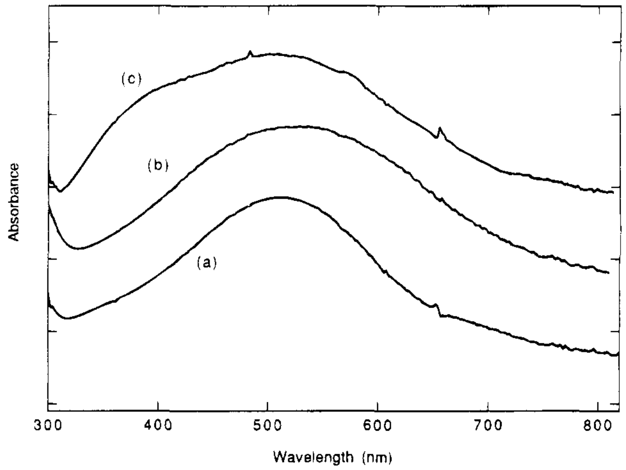


Figure 7. (a) UV–vis spectrum of a film of poly-**1** on ITO/glass. (b) UV–vis spectrum of a film of poly-**2** on ITO/glass. (c) UV–vis spectrum of a film of poly-**3** on ITO/glass.

The sequence of reactions to make poly-**3** may also be followed by UV–vis spectroscopy. The spectrum of poly-**1** contains a broad peak with $\lambda_{max} = 510$ nm (Figure 7a). Upon reaction with $Re(CO)_5Cl$ to give poly-**2**, the maximum in the absorbance spectrum shifts to 530 nm (Figure 7b). The shift in the maximum is the result of the overlap of the polymer absorption band and a low-energy Re→LCT band. In **4** the Re→LCT is found at 412 nm, and the extended conjugation in poly-**2** should shift this band to lower energy. Reaction of poly-**2** with $AgPF_6$ to give poly-**3** results in a shift in λ_{max} back to 510 nm and the development of a shoulder at approximately 400 nm (Figure 7c). We assign the band at 510 nm to the $\pi-\pi^*$ of the polymer backbone, and the band at 400 nm to the Re→LCT. The absorption

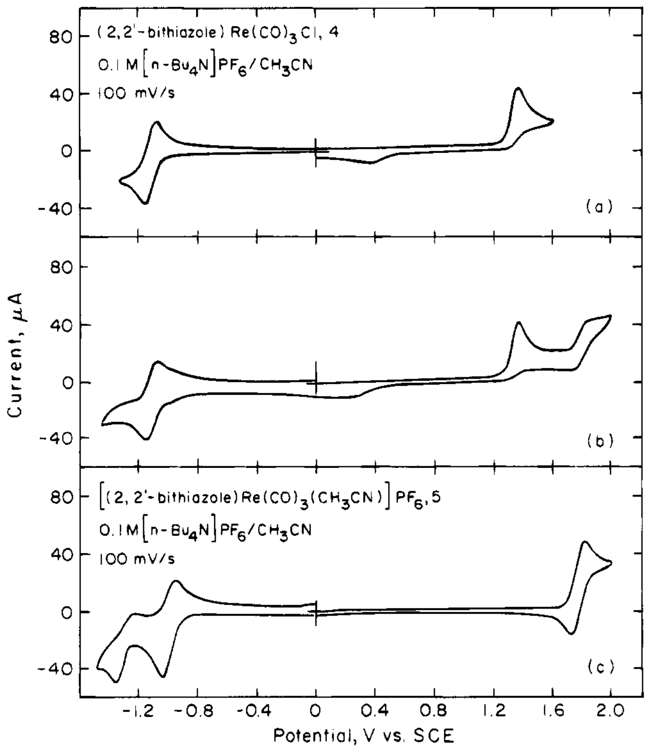


Figure 8. (a) Cyclic voltammogram of (2,2′-bithiazole)Re(CO)$_3$Cl, **4** in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN at 100 mV/s. (b) Same solution scanning to +2.0 V vs SCE. (c) Cyclic voltammogram of [(2,2′-bithiazole)Re(CO)$_3$(CH$_3$CN)]$^+$, **5** in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN at 100 mV/s.

spectrum of **5** has a peak at 336 nm with no lower energy peaks present, so in this complex the Re→LCT band must be shifted to higher energy compared to **4**. In the polymer confined complex, the extended conjugation is expected to shift this Re→LCT to lower energy than in **4**; therefore, it is reasonable that the band would appear at 400 nm.

Electrochemistry of Complexes 4 and 5. The cyclic voltammetry of **4** in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN is shown in Figure 8a. There is no evidence for electropolymerization in the potential region examined (−1.4 V to +2.0 V vs SCE). However, two waves are present, an irreversible oxidation wave and a reversible reduction wave at +1.38 V and −1.11 V vs SCE respectively (Table 1). This electrochemical behavior is very similar to that observed for other (α-diimine)Re(CO)$_3$X (X = halide) species such as (2,2′-bipyridine)Re(CO)$_3$Cl, both in the reversibility and potentials of the waves.[17]

The cyclic voltammetry of **5** in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN is shown in Figure 8c. We observe a reversible oxidation (+1.77 V vs SCE) and two reduction waves (−1.00 and −1.35 V vs SCE). The first reduction wave is reversible when the scan was reversed at −1.2 V; the second reduction was irreversible even at a high scan rate. We also found that if we scan positive of the irreversible oxidation of **4** we find a smaller reversible oxidation with $E_{1/2}$ = +1.81 V vs SCE, (Figure 8b). This wave corresponds closely to the cyclic voltammogram observed for **5**. We conclude that **4** is oxidized electrochemically to a species which loses Cl to give **5** in CH$_3$CN solution, analogous to the behavior of (2,2′-bipyridine)Re(CO)$_3$Cl upon electrochemical oxidation.[18]

The similarities between the electrochemical and spectroscopic characteristics of the 2,2′-bithiazolyl and 2,2′-bipyridyl complexes are great enough that they can be considered analogs for most purposes. Importantly, the cationic Re species **5** is difficult to oxidize and hence should not interfere with the oxidative doping of a conducting polymer to which it is pendant, provided that the potential region in which the polymer is conducting is <+1.6 V vs SCE.

Electrochemistry of Poly-2 and Poly-3. Characterization of the films of poly-**2** by cyclic voltammetry is difficult, because the potential region in which the polymer is oxidized overlaps with the region where the Re is expected to be oxidized, based on the cyclic voltammetry studies on the model complex **4**. Holding the poly-**2** film for several minutes at +1.8 V vs Ag, a potential at which we expect the Re to be oxidized, causes the growth of carbonyl bands in the IR region to be identical to those observed for the cationic complex **5**. In addition, XPS analysis of a film which was subjected to the same procedure showed the presence of F and P in the resulting film, additional evidence of conversion of the Re to a cationic center, with PF$_6^-$ from the electrolyte solution as counterion. However, the XPS results may be ambiguous since holding the films at such oxidizing potentials causes degradation of the polymer, rendering it nonconducting. For this reason, electrochemical oxidation cannot be used to quantitatively convert poly-**2** to poly-**3**, and the reaction of poly-**2** with AgPF$_6$ is therefore the preferred synthetic route to poly-**3**.

The cyclic voltammogram and I_D−V_G plot[31−33] of poly-**3** are shown in parts c and d of Figure 2, respectively. The cyclic voltammogram looks fundamentally the same as that of poly-**1**, although the small peak at +1.2 V is gone and the area under the curve is slightly reduced. The plot of the conductivity as a function of V_G indicates that the onset of conductivity is shifted slightly more positive than for poly-**1**, and the maximum drain current is about 3 orders of magnitude less than for poly-**1**, corresponding to a peak conductivity of ~2 × 10^{-3} Ω^{-1} cm^{-1}. Incorporation of the Re cation into the film reduces the conductivity significantly compared to underivatized poly-**1**. Interestingly, poly-**3** can be cycled to +1.5 V several times without any significant decrease in conductivity. The mechanism by which oxidized poly-**1** degrades during electrochemical cycling to positive potentials may therefore involve the unprotected nitrogen atom. In poly-**3** the nitrogen is "protected" by ligation with the Re and degradation by this mechanism is minimized.

IR of Reduced and Oxidized Poly-3. Electrochemical oxidation of the films of poly-**3** on an electrode surface demonstrates that the electron density at the cationic Re center can be tuned as a function of the state of charge on the polymer backbone. Surface reflectance IR measurements on films of poly-**3** which were oxidized to +1.5 V vs Ag wire in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_2$Cl$_2$ and removed from solution under potential control shows that in the oxidized film and carbonyl stretching bands shift from 2040 to 2044 cm^{-1} and from 1934 to 1940 cm^{-1}. When the same film was returned to 0 V vs Ag and the surface IR acquired the bands did not shift back completely to the original values; we attribute this to partial degradation of the oxidized film when removed from solution for an extended time. However, scanning a different sample to +1.5 V vs Ag, holding at that potential for 30 s and returning the potential to 0 V, results in a film in which the IR bands remained at the original positions.

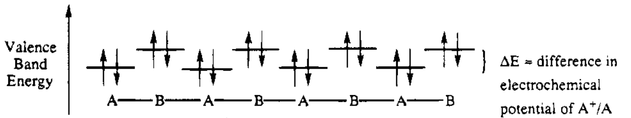
The magnitude of the shifts in the CO stretching frequencies upon oxidation of poly-**3** is related to the extent of oxidation and charge distribution in the polymer ligand. Unlike the systems we have studied previously where the redox-active pendant group has two discrete and well-defined states, the conducting polymer ligand system described in this work has an ill-defined structure in which the exact nature of the oxidized and reduced states is unclear. The shift in the carbonyl stretching frequencies upon oxidation represents the average effect on the system.

Conclusions

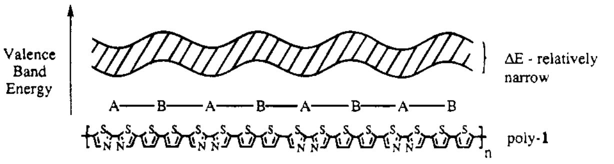
A conducting polymer system containing 2,2′-bithiazole groups derivatized with $[Re(CO)_3(CH_3CN)]^+$ groups has been described. The modified polymer is an example of a conducting polymer system in which a metal complex has been attached using the polymer as a ligand and the metal moiety remains intact when the polymer is oxidized and conducting. This stability allowed us to study the electron density at the Re as a function of the state of charge of the polymer backbone. The electron density changes which we observed were small, as measured by a shift in the carbonyl stretching frequency, but this result is not entirely unexpected, since even when the polymer is highly oxidized, the number of electrons removed per monomer unit is probably less than 1, if we assume the level of oxidation is comparable to that observed in polythiophene derivatives.[33] Additionally, the alternating structure of the backbone may localize holes away from the bithiazolyl groups, lessening the effect of oxidation even further. Even though the observed effect is relatively small, it is important to note that oxidation of both ferrocene centers in $(4\text{-ferrocenylpyridine})_2Re(CO)_3Cl$ causes a shift of only 4–7 cm^{-1} in the CO stretching frequencies.[6] This shift is probably close to what can be expected for poly-**3** in which the backbone has one hole per monomer unit, even if the hole is more localized on the bithiophene unit. However, small changes in electron density as a result of changes in the redox state of a pendant ligand have been demonstrated to alter reactivity to a remarkable extent.[16] Shifts of only 15 cm^{-1} in the carbonyl stretching frequency have been shown to result in differences of up to 200 times in the rate of nucleophilic attack at a carbonyl carbon in a Re carbonyl complex with a pendant chelating cobaltocene ligand. This illustrates that the shifts in CO stretching frequency we observe upon oxidation of poly-**3** could be significant in altering the rate of a reaction at the Re center.

We measured the activation energy for conductivity of poly-**1** to be 0.25 eV over the temperature range 213–298 K, suggesting that the energy of the valence band of poly-**1** is modulated due to the alternation of bithiazole and bithiophene units (Scheme 4). Complete localization of holes on the subunits of an $(A-B)_n$ copolymer would give rise to variation in the hole energy as represented by Scheme 4a. This describes an $(A-B)_n$ copolymer in which A and B (having differing electrochemical potentials) are linked together in a fashion which precludes delocalization of a hole. Complete delocalization of carriers in an $(A-B)_n$ copolymer would be associated with a wide valence band typical of highly conducting polymers, Scheme 4c. The intermediate case of partial delocalization is associated with a relatively narrow valence band which may vary in energy as in Scheme 4b, giving rise to activated carrier transport. We postulate that the observed decrease in the conductivity of poly-**3** upon binding the $[Re(CO)_3(CH_3CN)]^+$ group to the bithiazolyl unit in the polymer is the result of less delocalization of the charge carriers than in poly-**1**. The positive charge on the Re group is expected to make localization of holes onto the bithienyl moiety even more favorable than in poly-**1**. It should be emphasized that the simple energy diagrams in Scheme 4 are intended to describe the "valence band" for a single, linear $(A-B)_n$ chain. The conductivity of polymers is likely limited by chain-to-chain charge-transport events when there is significant delocalization along a chain. Both inter- and intrachain charge-transport events can be significant in governing the "conductivity" of so-called redox conductors such as polyvinylferrocene. Poly-**1** and poly-**3** are both likely to be best described as conducting polymers having partial delocalization, and each is less delocalized than the parent polythiophene.

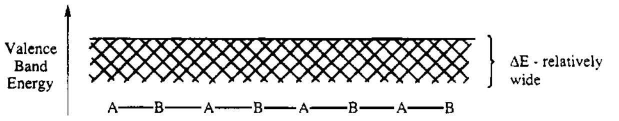
Scheme 4



(a) Completely Localized



(b) Partially Delocalized



(c) Completely Delocalized

Experimental Section

General Methods. All manipulations were carried out under air unless otherwise noted. Ether and THF were distilled from sodium benzophenone ketyl. Toluene was distilled from sodium. Chloroform and acetonitrile (Aldrich anhydrous) were used as received. Dichloromethane was distilled from P_2O_5. 2,2,4-Trimethylpentane was spectrophotometric grade. Solvents for chromatography were reagent grade and were not purified prior to use. ^1H NMR spectra were acquired on Varian XL-300 or Bruker AC-250 instruments. FTIR spectra were acquired on a Nicolet 60SX FTIR instrument. X-ray photoelectron spectra were obtained on a Surface Science Instruments Model SSX-100 spectrometer using monochromatic Al Kα radiation and operating at 10^{-8} Torr. A 1-mm spot size was used. Elemental analyses were performed by Oneida Research Services Inc. 2-Trimethylstannylthiazole[36] and 2,2′-bithiazole[37] were prepared as described in the literature.

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(2,2′-Bithiazole)Re(CO)$_3$Cl (4). 2,2′-Bithiazole (0.100 g, 5.94 mmol) and Re(CO)$_5$Cl (0.215 g, 5.94 mmol) were added to 50 mL of 2,2,4-trimethylpentane. The mixture was heated to reflux for 5 min during which time the starting materials dissolved and an orange solid precipitated. This solid was collected on a frit and was washed with hot 2,2,4-trimethylpentane to remove any residual starting materials. The solid was then dissolved in CH_2Cl_2 and reprecipitated by adding hexanes, yielding 0.236 g of **4** (84%). ^{1}H NMR (acetone-d_6) δ 8.35 (d, 3.4 Hz, 2H), 8.25 (d, 3.4 Hz, 2H). IR (CH_2Cl_2) 2028, 1926, 1902 cm^{-1}. UV–vis (THF) 412 (4700), 344 (16 000), 332 (19 000), 260 (11 000). Anal. Calcd for $C_9H_4ClO_3S_2N_2Re$: C, 22.81; H, 0.85; N, 5.91. Found: C, 22.75; H, 0.67; N, 5.88. Mp > 250 °C.

(2,2′-Bithiazole)Re(CO)$_3$(CH$_3$CN)PF$_6$ (5). A solution of (2,2′-bithiazole)Re(CO)$_3$Cl (0.435 g, 0.918 mmol) dissolved in 50 mL of acetonitrile was prepared, and $AgPF_6$ (0.400 g, 1.58 mmol) was added. The mixture was refluxed in the dark for one hour and then cooled and filtered. The solvent was removed *in vacuo*, and the residual solid dissolved in CH_2Cl_2 and filtered through a Celite plug. The solvent was removed *in vacuo* and the solids dissolved in a minimal amount of CH_3CN. Ether was added to precipitate the product as a yellow solid which was collected on a frit yielding 0.184 g of **5** (32%). ^{1}H NMR ($(CD_3)_2SO$) δ 8.40 (d, 3.0 Hz, 2H), 8.37 (d, 3.0 Hz, 2H), 2.32 (s, 3H). IR (CH_2Cl_2) 2044, 1944 cm^{-1}. UV–vis (THF) 336 (18 000). Anal. Calcd for $C_{11}H_7N_3O_3S_2PF_6Re$: C, 21.16; H, 1.13; N, 6.73. Found: C, 21.00; H, 1.04; N, 6.57. Mp 202 °C.

5,5′-(Trimethylstannyl)-2,2′-bithiazole (6). A solution of diisopropylamine (1.3 mL, 17 mmol) in 10 mL of THF was cooled to −78 °C. To this solution was added *n*-butyllithium (4.0 mL, 2.36 M in hexanes, 9.4 mmol) via syringe. The mixture was allowed to warm to room temperature for 5 min and then recooled to −78 °C. 2,2′-Bithiazole (0.75 g, 4.4 mmol) in 10 mL of THF was then added. A solid precipitated during the addition. The mixture was stirred at −78 °C for 1 hour, then trimethylstannyl chloride (9.4 mL, 1.0 M in THF, 9.4 mmol) was added, and the solution was warmed to room temperature. Stirring was continued for 2 h, after which time saturated $NaHCO_3$ (50 mL) was added followed by addition of ether (100 mL) and subsequent extraction. The organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the resulting residue was washed with hexanes, leaving a brown solid. The resulting solid was filtered yielding 1.4 g (63%) of **6**. ^{1}H NMR ($CDCl_3$) δ 7.77 (s, 2 H), 0.41 (s, 18H). Anal. Calcd for $C_{12}H_{20}N_2S_2Sn_2$: C, 29.19; H, 4.08; N, 5.67. Found: C, 29.00; H, 4.15; N, 5.80.

5,5′-(2-Thienyl)-2,2′-bithiazole (1). A solution of 2-bromothiophene (0.60 mL, 6.2 mmol), 5,5′-(trimethylstannyl)-2,2′-bithiazole (1.5 g, 3.0 mmol), and $PdCl_2[PPh_3]_2$ (90 mg, 0.13 mmol) in 20 mL of THF was prepared and refluxed for 12 h. The solvent was removed *in vacuo*, and ether was added to the residual material. The resulting yellow solid was filtered off and washed well first with ether (100 mL) and then with hexanes (100 mL). The residue was then dissolved in CH_2Cl_2 and filtered through a Celite pad, followed by sublimation *in vacuo* to yield 0.14 g (14%) **1** as a bright yellow solid. ^{1}H NMR ($CDCl_3$) δ 7.89 (s, 2H), 7.32 (d 4.5 Hz, 2H), 7.25 (d, 3.6 Hz, 2H), 7.06 (dd, 4.5 Hz and 3.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 159.3, 139.6, 134.7, 132.7, 128.2, 126.4, 126.3. UV–vis (THF) 400 (35 000), 258 (29 000). Mp 208 °C. HRMS: *m/e* 331.9569 (M$^+$ calcd for $C_{14}H_8S_4N_2$: 331.957 04).

Electrochemistry. All electrochemical measurements were conducted using a Pine RDE-4 bipotentiostat and a Kipp and Zonen *XY* recorder either in a nitrogen-filled Vacuum Atmospheres drybox or in a sealed flask under argon. Dichloromethane was distilled from P_2O_5 and stored in the drybox. [*n*-Bu$_4$N]PF$_6$ was recrystallized from ethanol and dried in a vacuum oven overnight. The reference electrode was either a silver wire or a saturated calomel electrode (SCE), and the counter electrode a 1 cm^2 piece of Pt gauze. The silver wire was referenced to the cobaltocene/cobaltocenium couple.

Anodic electropolymerizations were all conducted either on large 2 × 4 cm pieces of silicon wafers which had been coated with 1000 Å of Pt for specular reflectance spectroscopy and XPS measurements or on ITO/glass electrodes for UV–vis absorption spectroscopy. For potential dependent conductivity measurements Au microelectrode arrays were used.[38,39] The microelectrodes were cleaned by placing a drop of freshly prepared 3:1 H_2SO_4/30% H_2O_2 on the electrode for 10 s, followed by characterization in 5 mM $Ru(NH_3)_6$ aqueous solution, by recording the diffusion-limited Ru$^{2+/3+}$ reduction wave.

Polymer Preparation and Derivatization. 5,5′-(2-Thienyl)-2,2′-bithiazole was electropolymerized anodically from 5–10 mM CH_2Cl_2 solution containing 0.1 M [*n*-Bu$_4$N]PF$_6$. The working electrode was held at +1.5 V vs Ag wire for 3–4 min to derivatize the surface with polymer. The surface coverage was calculated by integration of the area under the cyclic voltammogram of the film, and assuming that oxidation to +1.5 V vs Ag corresponds to 1–2 electrons/monomer unit.[32] This procedure yields a coverage of 2×10^{-7}–5×10^{-7} mol/cm^2 of poly-**1**. The resulting films were reacted with a solution of Re(CO)$_5$Cl in $CHCl_3$ by immersing the film in the refluxing solution for 3–4 min. To remove any residual Re(CO)$_5$Cl, the film was then washed by dipping several times in a refluxing $CHCl_3$ solution. To generate the cationic Re species on the polymer, the derivatized film was refluxed in a CH_3CN solution containing $AgPF_6$ for 1 h. The film was then rinsed with hot CH_3CN to remove any residual $AgPF_6$.

The temperature-dependent conductivity measurements were performed in a nitrogen atmosphere over the temperature range 25 to −60 °C. Polymer was deposited on a microelectrode array, oxidized to +1.3 V vs Ag, and the microelectrode array placed in a narrow glass tube which was immersed into an isopropyl alcohol bath. The temperature of the bath was varied using a cold finger immersion cooler.

Spectroelectrochemistry. The FTIR spectra of the neutral polymer films were acquired using a Spectra-Tech specular reflectance accessory. The IR spectra of the polymer film as a function of potential were acquired by holding the film at a given potential until the residual current is negligible, and then removing the film while still under potential control and acquiring the IR spectrum immediately.

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