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Polymerization of thiophene containing cyclobutadiene Co cyclopentadiene complexes

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Abstract

To understand the charge transport ability of the metal coordinated cyclobutadiene, a series of cyclobutadiene cobalt cyclopentadiene (CbCoCp) complexes containing electrochemically polymerizable thiophene units were synthesized. The complexes were electrochemically polymerized and the resulting polymers were characterized by cyclic voltammetry, in situ conductivity and UV–vis spectroelectrochemistry. Several different derivatives of the CbCoCp complexes and a model study suggested that if the oxidation of the organic fragment was above $\mathrm{Co^{I/II}}$ redox couple of the CbCoCp complex, detrimental side reactions occured. Side reactions did not occurred if the oxidation of the organic fragment was below the metal oxidation.

Keywords: Organometallic polythiophene derivatives; Conducting organometallic polymers; Cyclobutadiene cobalt complexes

1. Introduction

Conducting polymers with metals incorporated into the polymer structure, known as conducting metallopolymers, are potentially useful materials in such applications as molecular actuators, electrocatalysts, sensors and NLO active materials [1,2]. The synthesis of new conducting metallopolymers is valuable in that these new polymers can further increase the knowledge of how these materials function and interact. In this regard, a new conducting metallopolymer was designed with the incorporation of cyclobutadiene cobalt cyclopentadiene (CbCoCp) complexes. CbCoCp complexes have been shown to be highly versatile, as demonstrated by the fact that these complexes have been utilized in liquid crystals, as the rigid structural feature for a molecular motor, macrocycle linkages, and as groups to facilitate through space charge delocalization [3].

The most important reason why CbCoCp was selected for this study is that the conjugation and charge migration of these polymers involves an interesting unit, namely the metal coordinated Cb. The free Cb molecule is a highly unstable antiaromatic system [4]. The metal coordinated Cb, however, is extremely stable and displays some of the properties typical of aromatic systems [5]. We viewed that this pseudo aromaticity of the metal coordinated Cb system may instill interesting and useful properties into a conducting polymer. Charge migration through the Cb segment is of particular interest since it involves not only the pure carbon orbitals of the Cb ligand but also the π-bound metal orbitals acting as a single delocalized molecular structure. Conducting polymers with π-bound metals incorporated into their structure, e.g. ferrocene polymers, have been previously synthesized [6]. These polymers are in contrast to the majority of conducting metallopolymers with segmented structures that have clearly delineated metal and conjugated polymer portions [2(d),7]. The latter polymers have well defined molecular orbital structures that can lead to independent polymer and metal charge migration.

Complexes of CbCoCp have previously been incorporated by Bunz and co-workers into conjugated polymers as polyphenyleneethylene derivatives or 1,3-diethynynl Cb homopolymers [8]. These materials were mostly studied for their liquid crystalline properties although the polybutadiyne Cb derivatives have been

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investigated for the delocalization through the Cb unit [9]. An oligomeric model study demonstrated a bathochromic shift in the UV–vis absorption as the number of monomer units increased [10]. This result supported the idea that some delocalization through the CbCoCp system was possible. Charge migration through the Cb system, however, was not investigated. Charge migration through a conjugated system is related to delocalization but also requires other properties such as the ability to stabilize cations and anions. Thus, the electrochemical characterization of the conjugated polymers containing CbCoCp poses a necessary step into understanding these polymers.

Another appeal of the CbCoCp system is that the $Co^{I/II}$ redox couple is present in the same region as the redox window of typical conducting polymers [11]. This allows for the examination of a central theme in metal containing conducting polymers, namely how the metal redox properties affect the overall characteristics of the conducting polymer [7]. The consideration of the metal–polymer orbital interactions and the effect of these interactions on charge migration is critical for the design and application of future conducting metallopolymers.

In the design of the polymers, it was assumed that the ethyne units would not allow facile charge migration since polyphenyleneethynylenes and its derivatives behave poorly under standard electrochemical conditions [12]. However, if instead thiophene units are selected as the conducting linkage then electrochemical characterization is possible [13]. Furthermore, a thiophene based monomer allows for versatile monomer syntheses and gives access to an oxidative polymerization route in the polymer synthesis. This manuscript describes the synthesis, cyclic voltammetry, conductivity, and UV–vis measurements of polythiophene analogues derived from the polymerization of thiophene containing CbCoCp complexes. It was discovered that the relative position of the thiophene fragment oxidation to the $Co^{I/II}$ redox couple determined the stability of the CbCoCp complex to the polymerization conditions.

2. Experimental

2.1. General comments

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer and are referenced to residual $CHCl_3$ (7.27 ppm for ^1H and 77.23 ppm for ^{13}C) or $CHDCl_2$ (5.32 ppm for ^1H and 54.00 ppm for ^{13}C). Melting points are uncorrected. High-resolution mass spectra (HRMS) were determined on a Bruker Daltonics APEX II 3 Tesla FT-ICR-MS. The Pd catalysts and $CpCo(CO)_2$ were received from Strem. All other chemicals were received from Aldrich. The solvents were dried by passing through activated alumina and de-oxygenated by Ar purge or purified by a SPS-400-5 solvent purification system (Innovative Technologies). All air sensitive manipulations were performed using standard Schlenk techniques. Electrochemical measurements were performed in a nitrogen glovebox with an Autolab II with PGSTAT 30 potentiostat (Eco Chemie). The electrolyte solution for all electrochemical measurements, 0.1 M $(n\mathrm{Bu})_4NPF_6$ in dry CH_2Cl_2, was stored over 4 Å molecular sieves in a glovebox. The quasi-internal reference electrode was an Ag wire submersed in 0.01 M $AgNO_3$/0.1 M $(n\mathrm{Bu})_4NPF_6$ in anhydrous acetonitrile and a Pt wire or gauze was used as a counter electrode. All potentials were referenced to the Fc/Fc^+ couple. A 2 mm^2 Pt button (Bioanalytical), 5 μm Pt interdigitated microelectrodes (Abtech Scientific, Inc.) or indium tin oxide coated unpolished float glass slide (Delta Technologies) were used as the working electrodes. Absorption spectra were collected on an Agilent 8453 diode array spectrophotometer. The GPC analysis was performed using a PLgel 5 μm Mixed-C column (300 mm × 7.5 mm) and a diode detector at 254 nm with a flow rate of 1 ml/min in THF. The molecular weights were reported relative to polystyrene standards purchased from Polysciences Inc. A Dektak 6M stylus profiler (Veeco) was used to measure the film thickness of the polymers grown onto interdigitated microelectrodes. XPS measurements were collected on a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer.

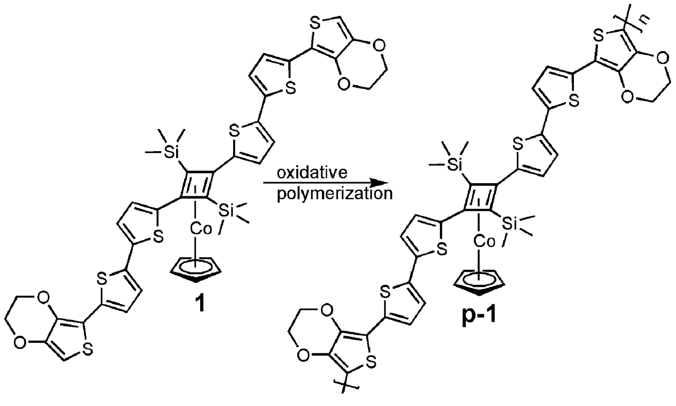
3. Results and discussion

3.1. Synthesis

The synthesis of the CbCoCp complexes was accomplished by the dimerization of the appropriate alkynes with cyclopentadiene cobalt dicarbonyl ($CpCo(CO)_2$) or a derivative of the complex [14]. The desired ethynes were synthesized by Songashira type cross-coupling reaction with an aryl halide [15]. The full synthetic details are reported in the supplementary information. The complexes were characterized by NMR, mass spectrometry and single crystal X-ray diffraction. The electrochemical synthesis of the polymers was achieved by anodic electrochemical polymerization utilizing repeated cyclic voltammetry (CV) scans that deposited an insoluble polymer of unknown molecular weight onto the working electrode.

3.2. EDOT containing complex

Complex **1** was the only complex synthesized that could be electrochemically polymerized while appearing to keep the CbCoCp complexes of the polymer intact, as shown in Scheme 1. The oxidation potential of the thiophene fragment in complex **1** is lower than the $Co^{I/II}$ redox couple by virtue of a 3,4-



Scheme 1.

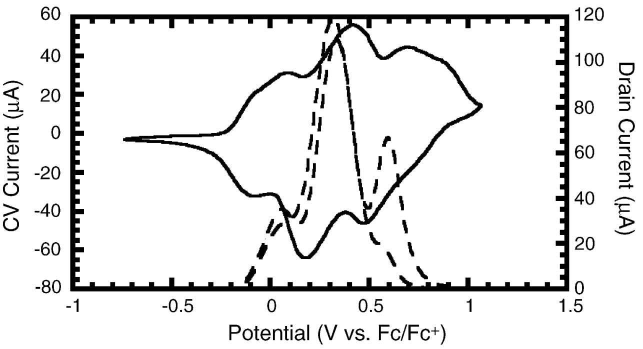


Fig. 1. Cyclic voltammogram (solid line) at 100 mV/s and in situ conductivity (dashed line) of **p-1** grown onto interdigitated 5 µm Pt microelectrodes at 5 mV/s with 40 mV offset potential between the working electrodes.

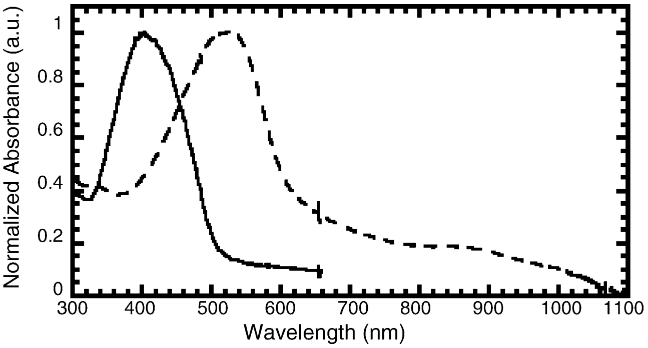


Fig. 2. UV–vis absorption spectra of complex **1** (bold line) and **p-1** (dashed line) coating an ITO slide.

ethylenedioxythiophene (EDOT) unit connected to the end of a bithiophene fragment. Without the EDOT group, the oxidation potential of the pure bithiophene fragment is above the $Co^{I/II}$ redox. A series of these CbCoCp complexes with bithiophene as the polymerizable unit was synthesized and the characterization of the resulting polymers from these complexes will be discussed vide infra.

The CV's and in situ conductivity of **p-1** is shown in Fig. 1. The CV of **p-1** had three waves with half wave potentials ($E_{1/2}$'s) of −0.03, 0.34 and 0.58 V. The peak at 0.34 V was assigned as the metal based redox wave wave. This assignment was based on two factors. First, the approximate potential value of the peak is near the expected value for this type of CbCoCp complex. The basis for this expectation is the fact that CbCoCp complex with four aryl groups attached to the Cb ring has an $E_{1/2}$ of approximately 0.5 V for the $Co^{I/II}$ redox couple and a CbCoCp complex with four alkyl groups attached to the Cb has an $E_{1/2}$ of approximately 0.1 V for the $Co^{I/II}$ redox couple [11,16]. Assuming that a trimethyl silyl (TMS) group has the same inductive donating ability as an alkyl group, the $E_{1/2}$ for $Co^{I/II}$ redox couple for complex **1** should be near 0.3 V. Secondly, the prominent shape of the wave at 0.34 V resembled the metal wave seen previously in ferrocene oligomer work [17]. The peaks at −0.03 and 0.58 V were assigned as the oxidations of the organic fragment.

The use of Pt interdigitated microelectrodes as the working electrode in the electrochemical cell allowed the conductivity of the polymer to be measured in situ [18]. The in situ conductivity of **p-1** displayed an onset of the conductivity at −0.1 V. From the in situ conductivity profile it can be interpreted that the oxidation of the Co centers enhanced the conductivity of the polymer since in these measurements the drain current is directly proportional to the conductivity of the polymer. The measurement of the polymer film thickness permitted the maximum absolute conductivity of **p-1** to be measured (uncorrected for the resistance of the leads) at 0.31 S cm^{-1} [19]. These results suggested that the incorporation of the CbCoCp structure, at the very least, does not inhibit charge migration.

To further characterize the resulting polymer, a polymer film was grown on indium tin oxide (ITO) coated glass slide and spectroelectrochemistry was performed on the resulting film. The spectroelectrochemistry of **p-1** suggested that the metal coordinated Cb has a moderate charge migration ability. The monomer **1** in the solid state had a λ_{max} of 403 nm and the neutral polymer **p-1** had a λ_{max} of 518 nm, which corresponded to a bathochromic shift of 115 nm as seen in Fig. 2.

Fig. 3 shows that the oxidation of the polymer up to 0.4 V produced a broad absorption from approximately 660 to 850 nm. This result was consistent with the results of the in situ conductivity of the polymer which suggested that the metal center oxidation enhances the conductivity of the polymer. It can be seen that the oxidation of **p-1** at potentials of 0.4 V and higher gave rise to a band that tailed into the maximum observable wavelengths for our UV–vis instrument (1100 nm). The intensity of this long wavelength absorption band grew larger as the potential of the electrochemical cell was increased.

As mentioned earlier, the polymers that result from the bithiophene based monomers have significantly different behavior than **p-1**. The series of synthesized bithiophene complexes is shown in Scheme 2. The resulting polymer from complex **2** that provides the most direct comparison to **p-1**. The CV of **p-2** had two waves, a smaller wave at approximately −0.4 V and a larger broad wave at 0.5 V, as shown in Fig. 4. The in situ conductivity of **p-2** had an onset of conductivity at approximately 0.65 V and the drain current did not plateau even to the edge of the solvent window [20]. Conducting polymers display finite windows of conduction and the fact that **p-2** did not display a plateau or reduction suggested that the bands responsible for conduction were not depleted at these potentials [21]. The wave at −0.4 V

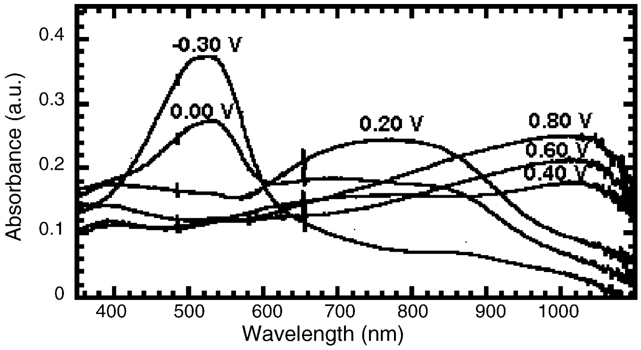
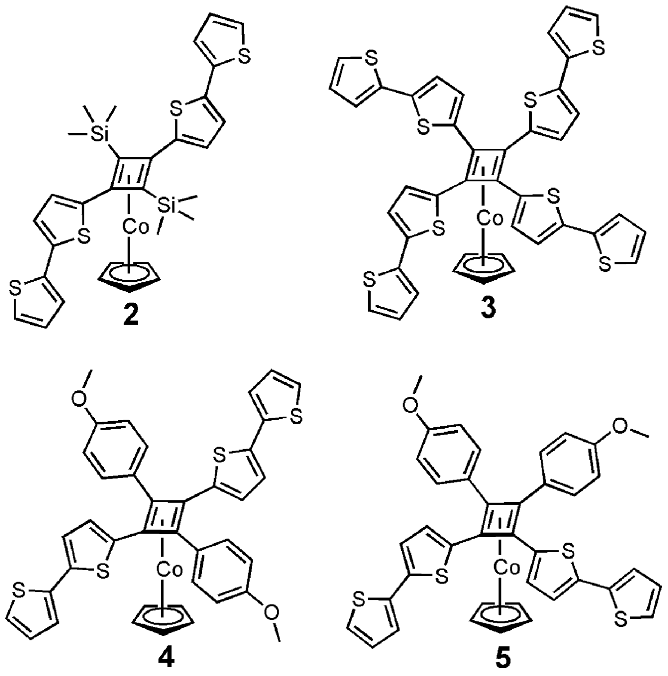


Fig. 3. Changes in the UV–vis absorption at different potentials for a film of **p-1** grown onto ITO.



Scheme 2.

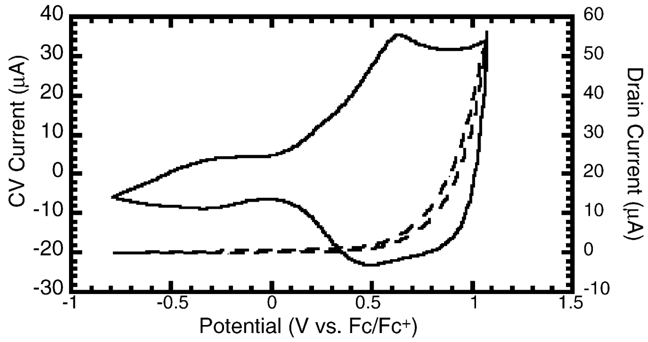


Fig. 4. Cyclic voltammogram (solid line) at 100 mV/s and in situ conductivity (dashed line) of **p-2** grown onto interdigitated 5 μm Pt microelectrodes. The same in situ conductivity conditions for **p-1** were used for **p-2**.

did not seem to alter the conductivity of the polymer. The absolute conductivity of **p-2** was $1.4 \times 10^{-3}\ \mathrm{S\,cm^{-1}}$.

The polymer from the tetrakis bithiophene complex, **p-3**, had similar electrochemical properties as **p-2**, as shown in Fig. 5.

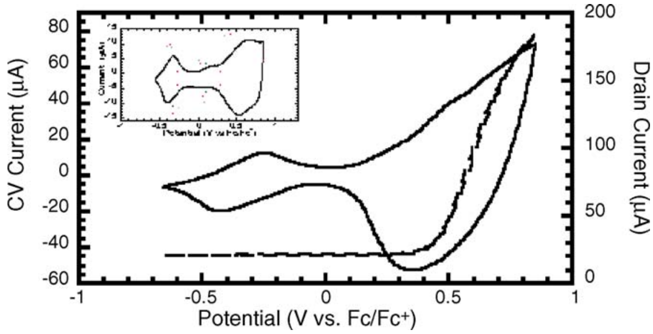


Fig. 5. Cyclic voltammogram (solid line) at 100 mV/s and in situ conductivity (dashed line) of **p-3** grown onto interdigitated 5 μm Pt microelectrodes. Inset is the CV of **p-3** on a 2 $\mathrm{mm^2}$ Pt button.

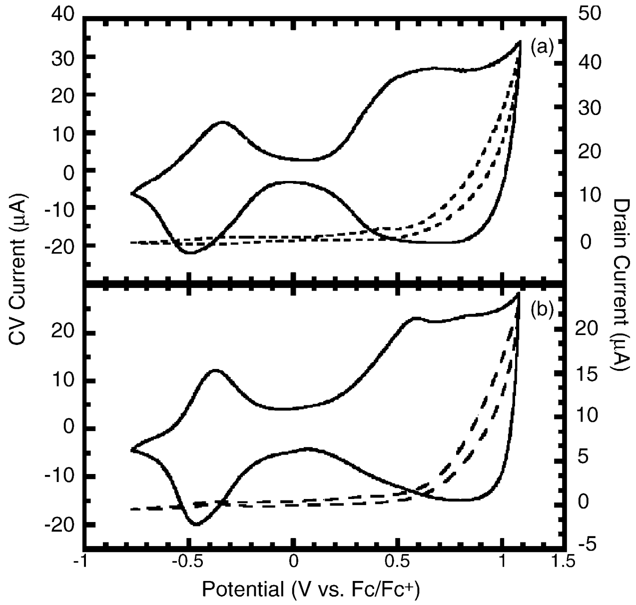


Fig. 6. (a) Cyclic voltammogram (solid line) at 100 mV/s and in situ conductivity (dashed line) of **p-5**; (b) cyclic voltammogram (solid line) at 100 mV/s and in situ conductivity (dashed line) of **p-4**.

This result was unusual since **p-3** should be a highly cross-linked polymer and this cross-linking may affect the three-dimensional conduction network of the polymer [22]. Unlike **p-2**, the CV profile of **p-3** seemed to depend on the type of electrode used for the polymerization, as shown in the inset of Fig. 5. The absolute conductivity of **p-3** was $7.3 \times 10^{-4}\ \mathrm{S\,cm^{-1}}$.

In order to probe how the relative position of the bithiophene segments affected the electrochemistry of the resulting polymers, two anisole derivatives, **4** and **5** were synthesized. Anisole was chosen since the TMS substitution produced only the *trans* isomer in significant yields and the *cis* isomer could not be isolated. The methoxy groups also increased the polarity difference between the two isomers and thus facilitated the chromatographic separation of the two isomers. The cyclic voltammograms of both isomers were very similar to those of **p-2** and **p-3**, as shown in Fig. 6. The CV's of both **p-4** and **p-5** exhibited waves in similar regions to the two waves that were present in **p-2** and **p-3**. One slight difference was that the current ratio of the wave near −0.4 to the wave near 0.5 V was larger for **p-4** and **p-5** than for **p-2** and **p-3**. The onsets of conductivity for **p-4** and **p-5** appeared at approximately 0.1 V higher than those of **p-2** and **p-3**. The in situ conductivities of **p-4** and **p-5** also displayed a larger hysteresis than either **p-2** or **p-3** and this result suggested greater structural reorganization in the oxidatively doped state. A minor difference between **p-4** and **p-5** was that **p-4** displayed a very slight drain current (conductivity) in a potential range near −0.4 V while the in situ conductivity of **p-5** displayed only the background Faradic current at those potentials. It is not certain whether the different conjugation pathways of these polymers or their different morphologies were the source of these differences. This is a central problem of conducting polymers and requires macroscopic orientation to elucidate the causes of bulk properties [23]. The absolute conductivities of **p-4** and **p-5** were in the same range as **p-3**.

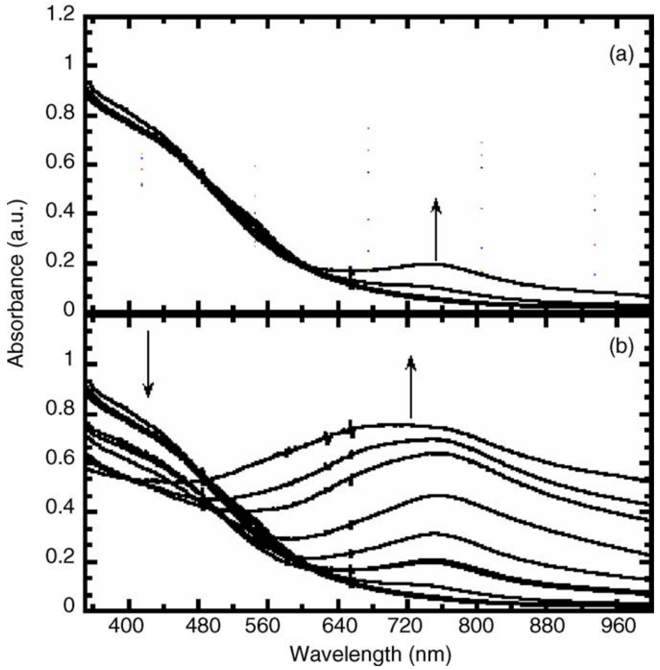


Fig. 7. (a) Changes in the UV–vis absorption of a film of **p-3** grown onto ITO when the potential of the electrochemical cell was changed from −1.00 to −0.20 in 0.20 V intervals; (b) changes in the UV–vis absorption of a film of **p-3** grown onto ITO when the potential of the electrochemical cell was changed from −1.00 to 1.00 in 0.20 V intervals.

The spectroelectrochemistry of **p-3** is shown in Fig. 7. The inherent absorption of the ITO coated glass substrate obscured most of the UV–vis spectra of the neutral polymer below 350 nm, allowing observation of only a large shoulder extending from 350 to 800 nm. As the polymer film was oxidized, the shoulder in the 350–500 nm region decreased in intensity and a new peak grew in at 735 nm. This response occurred in potential regions of the first wave (−0.85 to −0.25 V) as well as the second wave (0.00 to 1.05 V) in the CV of the polymer film. However, at the higher potentials of the second wave, the changes in the UV–vis spectrum were more dramatic. The tailing of the peak at 735 nm to longer wavelengths is typical of conducting polymers and bands in the NIR region are often attributed to delocalized charges [24]. This result agreed with in situ conductivity results that the changes in the conductivity of the polymer film occurred in this region. The rest of the polymers, **p-2**, **p-4** and **p-5**, had similar spectroelectrochemistry to **p-3**. The polymers displayed new longer wavelength absorptions at potentials near −0.5 V and they displayed much larger changes in absorption at potentials above 0.20 V. For the anisole polymers, there was a difference between isomers. The absorption maximum for oxidized *cis* isomer polymer, **p-5**, was at 656 nm while the absorption of the oxidized **p-4** was at 729 nm, as shown in Fig. 8. As with the in situ conductivity, the origin of this difference cannot be fully elucidated at present, but it does suggest greater delocalization in **p-4** (*trans* isomer).

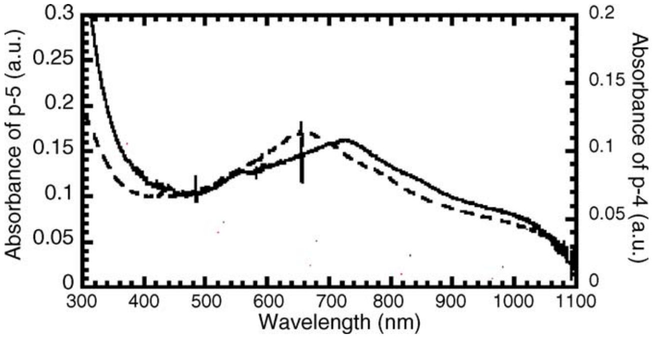


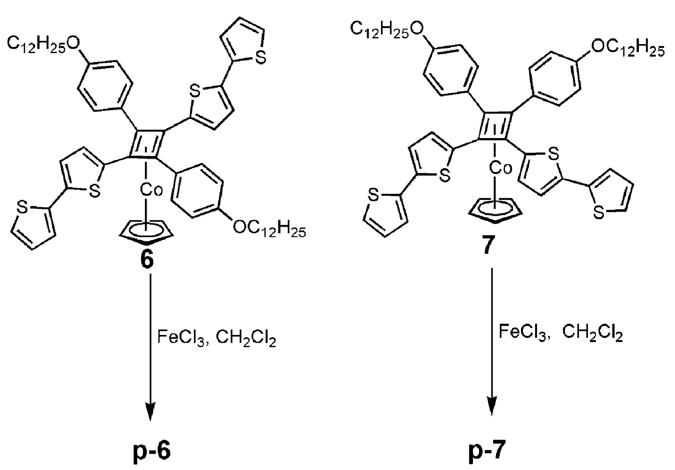
Fig. 8. UV–vis absorption of the oxidized **p-4** (solid line) and **p-5** (dashed line) grown onto ITO.

Overall, only minor differences were observed for the electrochemistry of the polymers **p-2**, **p-3**, **p-4** and **p-5**. These results suggest that effects such as cross-linking or regiochemical issues do not significantly affect the electrochemistry of the resulting polymers. The results of the electrochemistry also lead to the conclusion that the composition of **p-2**, **p-3**, **p-4** and **p-5** is significantly different than **p-1**. This conclusion raised two important questions; what is the composition of **p-2** and similar polymers and why is the composition of **p-1** different than **p-2** and similar polymers.

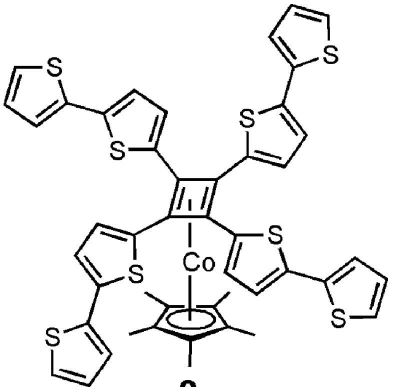
3.3. Composition

As an initial attempt to understand the composition of the polymer, X-ray photoelectron spectroscopy (XPS) was performed on polymer films grown on ITO or polished steel. The XPS confirmed the presence of cobalt in all the polymers. As another method to understand the composition of these polymers, monomers **6** and **7** were synthesized in an attempt to produce soluble versions of the polymers, as shown in Scheme 3. The polymerization was performed by $FeCl_3$ oxidation in dry CH_2Cl_2 to produce soluble oligomers with $M_n = 6570$ g/mol; PDI = 1.56 for **p-6** and $M_n = 3830$ g/mol; PDI = 2.04 for **p-7** according to gel permeation chromatography (GPC) analysis. While ^{1}H demonstrated that the CoCp fragments were in place, a suitable ^{13}C was not observed for the polymers to confirm the presence of the Cb ring.

One method to determine the composition of **p-2** and similar polymers is to change the Cp ligand to 1,2,3,4,5-pentamethylcyclopentadiene (Cp*) ligand, as exemplified by



Scheme 3.



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Scheme 4.

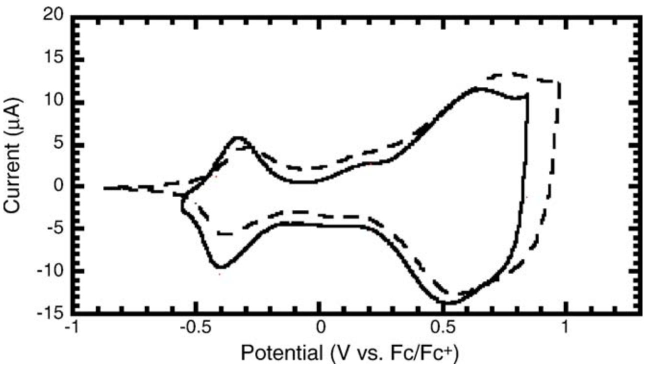
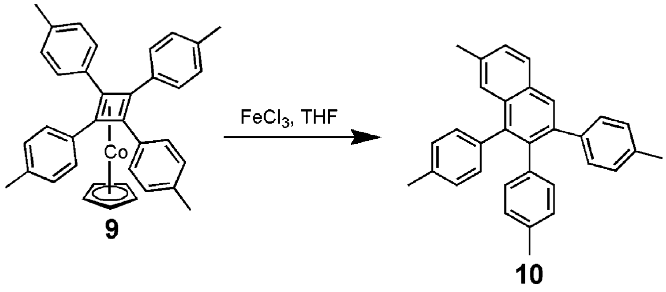


Fig. 9. Cyclic voltammogram (solid line) of **p-3** and **p-8** (dashed line) at 100 mV/s on a 2 mm^2 Pt button.

complex **8** in Scheme 4. The Cp* ligand has a well known inductive effect that lowers the metal oxidation of a sandwich complex [25]. The CV results of **p-8**, as shown in Fig. 9, were not significantly different from those of **p-3**.

This fact suggested that in **p-2** and similar polymers, side reactions had occurred. One possible side reaction that could have occurred in these polymers is a ligand (e.g., thiophene) promoted insertion of the Co metal center into the Cb ring, as shown in Scheme 5. A Co insertion into Cb ring has been observed but it is usually thermally promoted [26]. The potential Co$^{III/IV}$ redox couple of the cobaltacyclopentadiene species is approximately −0.4 V and all the polymers derived from the bithiophene monomers had a wave at this potential [27]. Polymers of a similar molecular structure have been synthesized and these polymers have CV's similar to the polymers derived from the bithiophene monomers [28]. If the metal insertion does occur, the effect of the change in the Cp ligand on the shift in the oxidation potential of metal center would be significantly decreased. This effect is caused by the different orbital overlaps in a metallocyclopentadiene or similar complex versus a metal sandwich complex [29].

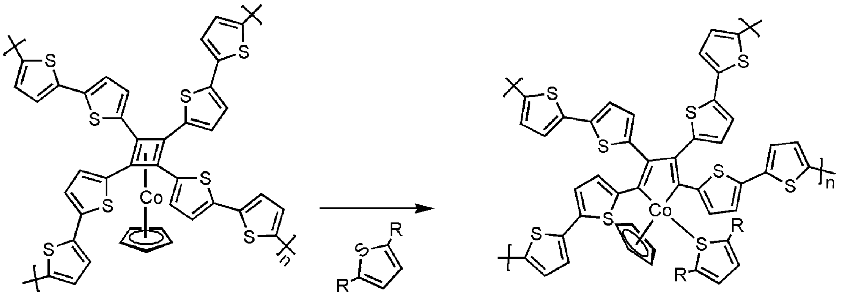


Scheme 6.

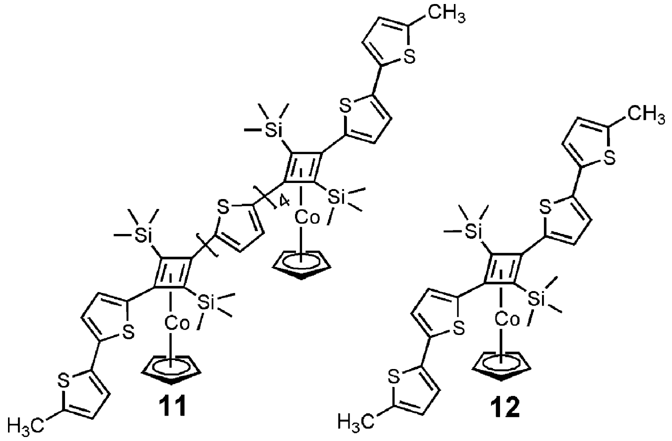
However, another factor to consider is if the CoCp fragment was completely removed from polymer. This factor was considered by the oxidation of the complex **9** in the presence of a ligand like THF to see what possible products would occur, as shown in Scheme 6. The result was a rearrangement of the Cb ring that created a naphthalene structure. If this reaction did occur then it should place an aryl group in the main chain of a polythiophene. Typically, polythiophene derivatives with aryl groups substituted in the main polymer chain tend to act as at least partially π-delocalized polymers [30]. The polymers like **p-2** did not seem to act as fully π-delocalized polymers and these types of aryl substituted polythiophene derivatives tend not to have any electroactivity in region near −0.4 V. However, the electroactivity in region near −0.4 V could be due to an impurity, like completely disproportionated Co^{2+} centers, so this possibility cannot be completely ruled out.

3.4. Model study

To understand why the CbCoCp complexes in polymers like **p-2** appear to decompose, it is important to understand the metal to metal interaction within the polymer. There are three types of metal to metal interaction; charge hopping, mediated and superexchange. The charge hopping is similar to outer sphere electron transfer [31]. The mediated interaction is a two-step process involving metal to polymer electron exchange then polymer to metal electron exchange [32]. To maximize this



Scheme 5.



Scheme 7.

interaction, the oxidation waves of the metal and the polymer should be closely matched as possible. The superexchange interaction involves interactions similar to those observed in mixed-valance metal complexes and the methods to describe the mixed valence interactions can be applied to the conducting polymer systems [33]. To assess the metal to metal communication in the **p-2** and similar polymers, model compounds **11** and **12** were synthesized, as shown in Scheme 7. The CV's of both models were quasireversible. The results of this model study were clearly displayed in differential pulse voltammetry (DPV) of the models as seen in Fig. 10. The DPV displayed two peaks for complex **12** and three peaks for complex **11**. Both models display peaks near 0.30 and 0.50 V. Complex **11** also displayed an additional peak at 0.9 V. The peaks near 0.3 V were assigned to $Co^{I/II}$ redox couple using the same arguments as the wave assignment in **p-1**. Since only a single redox event for Co metal centers of complex **11** was observed, it was concluded that there was not significant electronic communication between the metal centers through the thiophene bridge [34]. This result suggested that a superexchange type interaction was not likely. The DPV of complex **11** also demonstrated that the thiophene fragment oxidation was clearly separate from the $Co^{I/II}$ redox couple which decreased the probability of mediated type interaction. Without a superexchange or mediated mechanism for the communication between the metal centers, the only possible interaction is the charge hopping mechanism. Since charge hopping is an inefficient mechanism for metal to metal communication, the oxidized metal centers would remain in isolated sites within the polymer. This isolation could be the cause of the side reactions. In comparison, the metal to metal interactions of **p-1** are significantly enhanced by having the thiophene fragment oxidation below the $Co^{I/II}$ redox couple. When the Co sites are oxidized in **p-1**, the polymer is already in a conductive state which should greatly facilitate the metal to metal interactions.

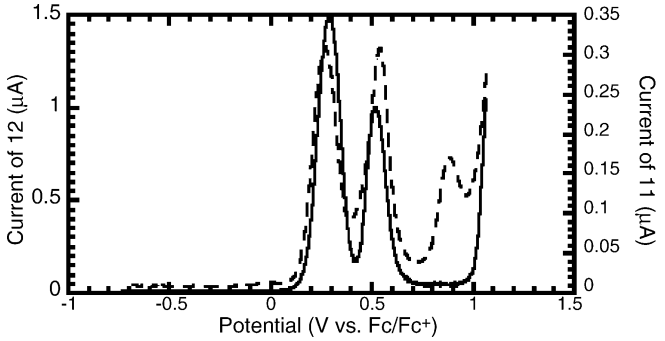


Fig. 10. Differential pulse voltammetry of complex **11** (dashed line) and complex **12** (solid line) with a pulse height of 10 mV and scan rate of 2 mV/s on a 2 mm^2 Pt button.

The significant improvement in the electroactive properties (e.g., conductivity) from **p-1** to **p-2** and similar polymers could be, in part, attributed to a better conjugation of the polymer with the Cb unit in the polymer main chain than the metal inserted into the polymer main chain. However, the fact that monomer **1** has a terthiophene fragment whereas monomer **2** has a bithiophene fragment may also account for the increase in conjugation length from **p-1** to **p-2**. Since these polymers should have significantly different molecular structures, a comparison between the polymers has a limited value but it appears that the metal coordinated Cb has a moderate ability to allow charge migration.

4. Conclusion

A series of CbCoCp complexes containing thiophene units were synthesized and polymerized electrochemically. The viability of an oxidative polymerization with these CbCoCp complexes was determined by the relative position of the oxidation potential for the thiophene fragment. According to the electrochemical characterization, if the oxidation potential of the thiophene fragment was below the $Co^{I/II}$ redox couple then the CbCoCp complex remained intact. If the oxidation potential of the thiophene fragment was above the $Co^{I/II}$ redox couple then it appeared that there was some decomposition of the CbCoCp complexes during the polymerization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2006.03.014.

References

[1] (a) P.G. Pickup, J. Mater. Chem. 9 (1999) 1641;
(b) M.O. Wolf, Adv. Mater. 13 (2001) 545;
(c) R.P. Kingsborough, T.M. Swager, Prog. Inorg. Chem. 48 (1999) 123.
[2] (a) S.S. Zhu, T.M. Swager, J. Am. Chem. Soc. 119 (1997) 12568;
(b) R.P. Kingsborough, T.M. Swager, J. Am. Chem. Soc. 121 (1999) 8825;
(c) J. Buey, T.M. Swager, Angew. Chem. Int. Ed. 39 (2000) 608;
(d) R.P. Kingsborough, T.M. Swager, Chem. Mater. 12 (2000) 872;

(e) A. Vigalok, Z. Zhu, T.M. Swager, J. Am. Chem. Soc. 123 (2001) 7917;
(f) T. Shioya, T.M. Swager, Chem. Commun. (2002) 1364.

[3] (a) M. Altmann, U.H.F. Bunz, Angew. Chem. Int. Ed. Engl. 34 (1995) 569;
(b) X. Zheng, M.E. Mulcahy, D. Horinek, F. Galeotti, T.F. Magnera, J. Michl, J. Am. Chem. Soc. 126 (2004) 4540;
(c) G.A. Virtue, N.E. Coynr, D.G. Hamilton, J. Org. Chem. 67 (2002) 6856;
(d) M.E. Stoll, S.R. Lovelace, W.E. Geiger, H. Schimanke, I. Hyla-Kryspin, R. Gleiter, J. Am. Chem. Soc. 121 (1999) 9343.

[4] G. Mair, Angew. Chem. Int. Ed. Engl. 27 (1988) 309.

[5] J.D. Fiztpatrick, L. Watts, G.F. Emerson, R. Petit, J. Am. Chem. Soc. 87 (1965) 3254.

[6] (a) M.O. Wolf, Y. Zhu, Adv. Mater. 12 (2000) 599;
(b) Y. Zhu, M.O. Wolf, Chem. Mater. 11 (1999) 2995;
(c) S.J. Higgins, C.L. Jones, S.M. Francis, Synth. Met. 98 (1999) 211;
(d) D.A. Foucher, B. Tang, I. Manners, J. Am. Chem. Soc. 114 (1992) 6246;
(e) M.A. Bureteau, T.D. Tilly, Organometallics 13 (1997) 4367.

[7] B.J. Holliday, T.M. Swager, Chem. Commun. (2005) 23.

[8] (a) I.L. Rozhanskii, I. Tomita, T. Endo, Macromolecules 30 (1997) 1222;
(b) M. Altmann, V. Enkelmann, G. Lieser, U.H.F. Bunz, Adv. Mater. 7 (1995) 726.

[9] (a) M. Altmann, U.H.F. Bunz, Marcomol. Rapid Commun. 15 (1994) 785;
(b) W. Steffen, K. Bernhard, M. Altmann, U. Scherf, K. Stitzer, H. zur Loye, U.H.F. Bunz, Chem. Eur. J. 7 (2001) 117.

[10] M. Altmann, V. Enkelmann, F. Beer, U.H.F. Bunz, Organometallics 15 (1996) 394.

[11] U. Koelle, Inorg. Chim. Acta 47 (1981) 13.

[12] D. Ofer, T.M. Swager, M.S. Wrighton, Chem. Mater. 7 (1995) 418.

[13] T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, Handbook of Conducting Polymers, Marcel Dekker, New York, 1998.

[14] (a) M.D. Rausch, R.A. Genetti, J. Am. Chem. Soc. 89 (1967) 5502;
(b) A. Clearfield, R. Gopal, M.D. Rausch, E.F. Tokas, F.A. Higbie, I. Bernal, J. Organomet. Chem. 135 (1977) 229.

[15] K. Songashira, Y. Tohda, N. Hagihara, Tetraherdon Lett. 50 (1975) 4467.

[16] R. Roers, F. Rominger, R. Gleiter, Tetrahedron Lett. 39 (1998) 6695.

[17] Y. Zhu, M.O. Wolf, J. Am. Chem. Soc. 122 (2000) 10121.

[18] H.S. White, G.P. Kittlesen, M.S. Wrighton, J. Am. Chem. Soc. 106 (1984) 5375.

[19] (a) G. Zotti, G. Schiavon, Synth. Met. 39 (1990) 183;
(b) G. Schiavon, S. Sitran, G. Zotti, Synth. Met. 32 (1989) 209.

[20] A.J. Bard, L.R. Faulker, Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wily and Sons, USA, 2001.

[21] D. Ofer, R.M. Crooks, M.S. Wrighton, J. Am. Chem. Soc. 112 (1990) 7869.

[22] (a) S. Jang, G.A. Sotzing, M. Marquez, Macromolecules 37 (2004) 4351;
(b) B. Stepp, S.T. Nguyen, Macromolecules 37 (2004) 8222.

[23] L.T. Tolbert, Acc. Chem. Res. 25 (1992) 561.

[24] (a) A.O. Patil, A.J. Heeger, F. Wudl, Chem. Rev. 88 (1988) 183;
(b) X. Chen, O. Inganäs, J. Phys. Chem. 100 (1996) 15202.

[25] R.J. Schaller, G. Haberhauer, R. Gleiter, F. Rominger, Eur. J. Inorg. Chem. (2002) 2296.

[26] R. Gleiter, D.B. Werz, Organometallics 24 (2005) 4316.

[27] R.S. Kelly, W.E. Geiger, Organometallics 6 (1987) 1432.

[28] (a) I. Matsuoka, K. Aramki, H. Nishihara, J. Chem. Soc. Dalton Trans. (1998) 147;
(b) I. Matsuoka, H. Yoshikawa, M. Kurihara, H. Nishihara, Synth. Met. 102 (1999) 1519.

[29] E.J. Miller, S.J. Landon, T.B. Brill, Organometallics 4 (1985) 533.

[30] J.R. Reynolds, J.P. Ruiz, A.D. Child, K. Nayak, D.S. Marynick, Macromolecules 24 (1991) 678.

[31] J.D. Atwood, Inorganic and Organometallic Reaction Mechanisms, Wiley, New York, 1997.

[32] C.G. Cameron, T.J. Pittman, P.G. Pickup, J. Phys. Chem. B 105 (2001) 8838.

[33] (a) M.B. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 10 (1967) 247;
(b) G.C. Allen, N.S. Hush, Prog. Inorg. Chem. 8 (1967) 357;
(c) K.D. Demadis, C.M. Hartshorn, T.J. Meyer, Chem. Rev. 101 (2001) 2655.

[34] F. Paul, C. Lapinte, Coord. Chem. Rev. 178–180 (1998) 431.