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Metal-Containing Conjugated Oligo- and Polythiophenes

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Summary: Conjugated polymers containing metal groups are an important class of new materials that may find application as sensors, non-linear optical materials and in molecular electronics. Polythiophenes are an extensively studied class of conjugated polymers, that can be easily modified synthetically, and may be prepared using a variety of methods. Metal groups pendant to polythiophene backbones modulate the electronic, optical and redox properties of the conjugated backbone and can introduce novel structural motifs to these materials. Functionalization of oligo- and polythiophenes by Fe, Pd and Ru containing groups is discussed, along with the properties of some of these materials.

Keywords: conductivity; conjugated polymers; electropolymerization; metal-containing polymers; optical properties; redox properties

Introduction

Polymers containing transition-metal complexes attached to or directly in a π-conjugated backbone are a promising class of modern materials. These hybrids of π-conjugated organic and transition-metal containing polymers allow the electronic properties of the conjugated backbone to be combined with the electronic, optical and catalytic properties of metal complexes. π-Conjugated organic polymers, including polyacetylene, polypyrrole, and polythiophene, as well as oligomers of these materials, have been studied extensively.[1] These materials are endowed with many important properties, such as non-linear optical properties, electronic conductivity and luminescence, and have been proposed for use in many applications including chemical sensors, electroluminescent devices, electrocatalysis, batteries, smart windows and memory devices.[1, 2]

Synthetic approaches to metal-containing conjugated polymers include condensation routes,[3,4] ring-opening metathesis polymerization,[5,6,7] and electropolymerization.[8]

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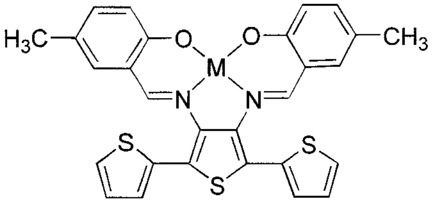
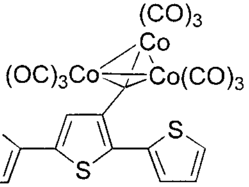
Electropolymerization was first used to prepare organic polymers such as polythiophene and polyaniline,[9] and results in deposition of insoluble electrogenerated material directly onto the electrode surface as a thin film. This allows oxidative or reductive doping to the conductive form to be achieved *in situ* electrochemically, allowing these polymers to be easily switched from the conductive to insulating state. Our group has focussed on preparing materials based on oligo- and polythiophenes due to their relative ease of synthesis relative to other conjugated materials.

Many different structural motifs have been incorporated into electropolymerized polythiophenes containing metals, including pendant Schiff base complexes[10] (**1**) or metal clusters[11] (**2**), and the properties of films of these materials explored.



1 M = Co, Zn, Cu



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We have shown that electropolymerization of the ferrocene-containing monomer **4** and **5** (prepared as shown in Figure 1) results in films that show electroactivity both due to the $Fe^{II/III}$ couple and oxidation of the thiophene groups.[12]

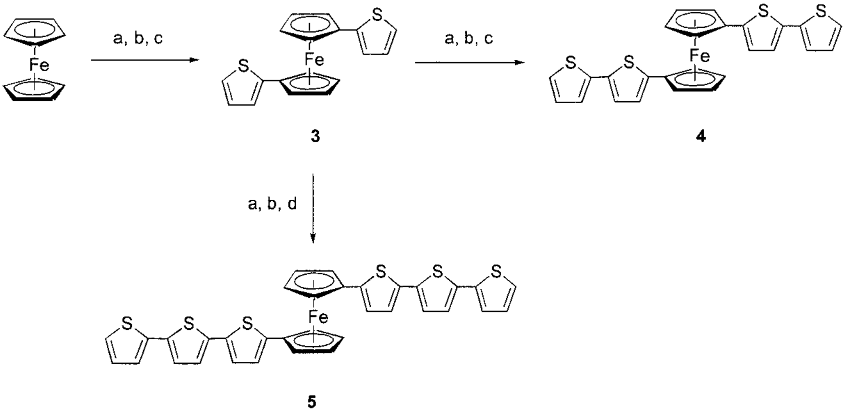


Figure 1. Synthesis of monomers **4** and **5**. Reagants: (a) BuLi, TMEDA, THF/hexanes. (b) $ZnCl_2$, THF. (c) 2-bromothiophene, $Pd(PPh_3)_4$, THF. (d) 5-bromo-2,2'-bithiophene, $Pd(PPh_3)_4$, THF.

Upon oxidation of a film of poly-**4** to a potential at which the ferrocenyl groups are oxidized, changes are observed in the UV-vis spectra of the films. Two bands are observed, at 495 and 1 395 nm. The broad, higher energy band is predominantly due to the π-π^* transition with contributions from Cp→Fe^{III} LMCT also possible; and the band with λ_{max} at 1 395 nm is assigned as a charge transfer band from the oligothiophene group to the Fe^{III}. Further oxidation of a poly-**4** film to 1.5 – 1.7 V vs. SCE results in the appearance of a very broad absorption between 400 and 1 600 nm. The appearance and positions of these bands suggest that they arise due to transitions to intergap states in the oxidized polymers, similar to transitions which appear upon oxidation of polythiophene.[13]

Pd-containing polymers may be prepared by electropolymerization of monomers **7**-**9**.[14, 15] These monomers are prepared by reaction of $PdCl_2$ with the phosphine substituted terthiophene **6** as shown in Figure 2.

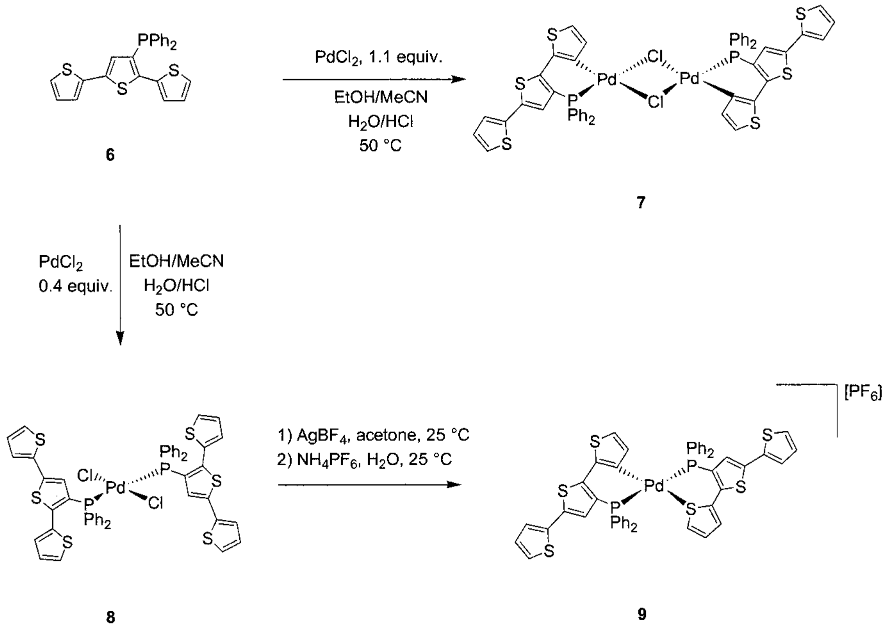


Figure 2. Synthesis of Pd containing monomers **7**-**9**.

Pd complexes **7**-**9** all electropolymerize when solutions of these monomers are scanned repeatedly over their whole oxidation range. Poly-**7** forms as a purple film that is conductive (10^{-3} S cm^{-1}) when oxidized. Poly-**8** forms as a red film and the voltammogram of the film shows a broad redox feature between +0.7 and +1.6 V, similar to that observed for poly-**7**. The maximum conductivity of oxidized poly-**8** is 3×10^{-4} S cm^{-1}, determined *in situ* by deposition of the film on interdigitated Pt microelectrodes. Similarly, electropolymerization of **9** (Figure 3) gave red films (reduced) with a conductivity of 10^{-4} S cm^{-1} when oxidized.

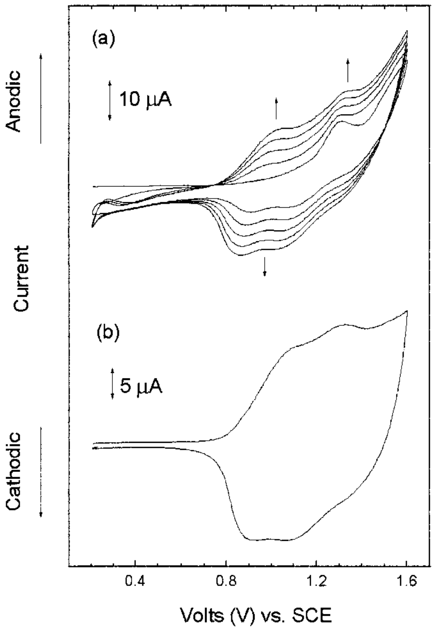
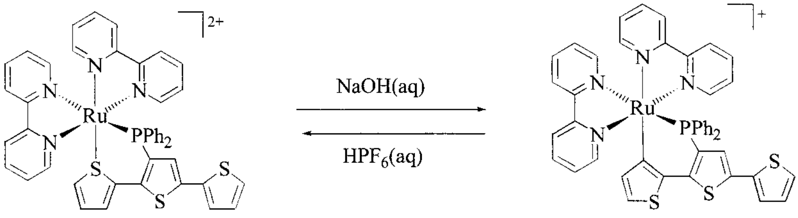


Figure 3. Cyclic voltammetry of **9** in CH_2Cl_2 containing 0.1 M $[(n\text{-Bu})_4NPF_6]$, scan rate = 200 mV/s. (a) Multiple scans from +0.20 to +1.60V. (b) Scan of a film of poly-**9** on a gold electrode.

The spectrum of neutral poly-**8** shows a broad absorbance at λ_{max} = 442 nm which shifts to 766 nm upon oxidation. The spectra of neutral poly-**9** contain broadened bands with λ_{max} at 454. The band maxima for poly-**8** and poly-**9** are red-shifted from those of their corresponding monomers, however they are also blue-shifted with respect to that of poly-**7** (522 nm). This is due to these materials being composed of oligomers with longer conjugation lengths than their corresponding monomers, but with shorter conjugation than in poly-**7**. The observed conductivity in poly-**7** results primarily from charge delocalization along the extended polythiophene chains and π-stacking rather than through the metal bridges in this material.

Our group is interested in conjugated polymers in which coordination of a metal group to an oligothiophene segment may be controllably altered via switching between two different modes, and to examine resulting differences in the structural, chemical, and physical properties of the material. We have prepared Ru(II) bipyridyl phosphinoterthiophene complexes **10** and **11** in which the terminal thiophene is *S*- or *C*-coordinated.[16] Reaction of **10** with NaOH in an acetonitrile-water emulsion resulted in cyclometallation to **11**. Addition of a drop of HPF_6 at room temperature to a solution of **11** results in rapid conversion to **10** (Figure 4).



10 **11**

Figure 4. Acid/base switching of thiophene coordination mode in complexes **10** and **11**.

The switch in coordination mode results in significant changes to the π→π* and MLCT transitions. In the UV-vis absorption spectrum (Figure 2), a shift of the terthiophene π→π* transition from a shoulder at ~316 nm in **10** to 350 nm in **11** occurs, the Ru d→bpy π* MLCT is also red-shifted from 394 nm to 456 nm, and a slight shift was observed for the bpy π→π* transition.

The $Ru^{2+/3+}$ and terthiophene oxidation potentials of **10** and **11** were measured by cyclic voltammetry. The lowest oxidation waves are assigned to the $Ru^{2+/3+}$ process (quasireversible for **10** when the scan is reversed immediately after the wave). The large shift of the $Ru^{2+/3+}$ oxidation wave of **10** to a substantially lower redox potential in **11** is consistent with the decreased energy of the MLCT transition. The terthiophene oxidation for **10** is most likely the second wave shown, and also shifts to a substantially lower position in **11** (second wave); consistent with the decreased energy of the terthiophene π→π* transitions.

Although complexes **10** and **11** do not electropolymerize, the synthesis of longer oligomers should allow access to polymeric materials exhibiting the switching observed for these model systems.

Conclusions

A variety of structural motifs have been observed for metal-oligothiophene complexes which can be electropolymerized to give polymeric films. Introduction of ferrocene groups into a conjugated polythiophene backbone results in conductive materials in which charge transfer states arise upon oxidation of the ferrocene groups. Pd-containing polymers in which the Pd is directly bonded to the conjugated backbone were described. Complexes with pendant $Ru(bpy)_2$ groups attached to an oligothiophene backbone via two different coordination modes may be reversible switched using acid and base. Substantial electronic differences between the two coordination modes manifest themselves in changes in the redox and spectroscopic behavior of these complexes. Polymers containing these pendant groups may be useful in sensing applications.

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