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Tunable Redox and Optical Properties Using Transition Metal-Complexed Polythiophenes

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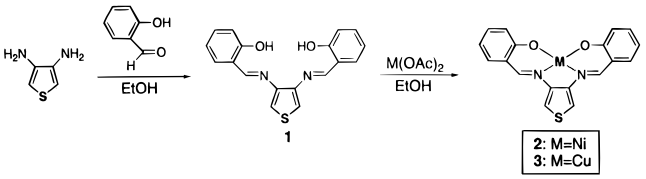
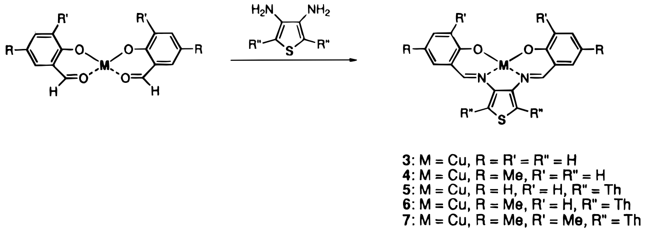
We report the synthesis and electropolymerization of the first salicyclidene-based transition metal-complexed thiophene, in which the metal is in direct electronic communication with the conjugated π-backbone, yielding a highly electroactive and electrochromic material. In addition, this system possesses multiple polymerization sites that can be selectively activated to give polymers composed of different backbones. While there are several examples of pyrrole and thiophene-based heterocycles containing transition metal complexes attached *via* pendant side chains, these systems display little electronic interaction between the metal and conjugated chain.[1] Metal-containing polymers, in which the metal is coordinated to the polymer chain, are interesting from the standpoint that the conjugated backbone can help stabilize redox activity, affording a continuum of accessible states. Directly complexed pyridyl and bis(thiazolyl) polymers have been studied; however, metal complexation was possible only after polymerization of the metal-free monomer.[2] With this methodology difficulty can arise in assessing the degree to which coordination occurs, and it would be of great convenience if such polymers could be obtained from prepurified, complexed monomers. Peng and Yu have reported a poly(*p*-phenylenevinylene)-based polymer containing ionic ruthenium centers bound to bipyridyl (BPY) units incorporated into the polymer backbone.[3] Chemical polymerization was effected by utilizing a metal-complexed monomer, thus affording a material for which the metal content was known. In this instance polymerization was not possible with uncomplexed monomer. Furthermore, while this is a very attractive system, the choice of metal for this system is limited to those which will form stable complexes with the BPY monomer and does not bind the palladium catalyst. During the preparation of this manuscript, Zhu and Swager reported on Ru−BPY_3 complexes having terminal thiophenes attached as electropolymerizable sites.[4] These considerations propelled us toward synthesizing directly-complexed, metal-containing, electropolymerizable molecules where the metal type will have a dramatic influence on the polymer's resultant properties. We have specifically designed these polymers for their metal-dependent electrochromic properties.

Our group has long been interested in the use of low-oxidation potential thiophene-based monomers which, when polymerized, form electroactive materials possessing novel electronic properties.[5] Such polymers have proved useful as components in dual-polymer electrochromic devices constructed in our laboratories,[6] and introduction of metal centers into these systems could afford a highly compatible material possessing the ability to be tuned over a wide color range. (Lifetimes of polymer-based electrochromic devices are controlled by this chemical compatibility.) Using this background for the incorporation of transition metals into such polymers, we elected to append the tetradentate coordinating bis(salicylidene)-type ligand onto a thiophene core. The selection of Schiff base ligand systems was founded upon their ease of synthesis, their ability to complex many transition metals indiscriminantly, and their robust nature, which inhibits decomplexation under a broad set of conditions.[7] Utilizing thiophene as the keystone of this macrocyclic ligand, the 3- and 4-positions of the ring were used as assembly points for imine functionalities, leaving the more reactive 2- and 5-sites open for electrochemical polymerization or further functionalization. These materials present synthetic flexibility not possible with other systems.

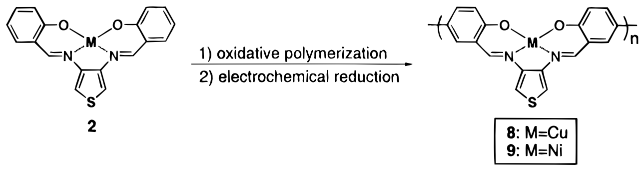
Scheme 1



Scheme 2



The ligand SALOTH (**1**) was synthesized, as outlined in Scheme 1, *via* the condensation of salicylaldehyde with 3,4-thiophenediamine,[8] which was obtained by reduction of 2,5-dibromo-3,4-dinitrothiophene.[9] Metal complexation was achieved by addition of the ligand dissolved in a hot ethanolic solution to nickel or copper acetate in hot ethanol, and subsequent cooling afforded microcrystals of the target molecules **2** and **3** in good yield.[10] As the uncomplexed ligand is somewhat unstable in solution, we opted to prepare subsequent complexes by the more direct route[7c] of first combining the salicylaldehyde species and metal acetate and then condensing this complex with the corresponding diamine, as illustrated in Scheme 2. The electrochemical properties of Cu−SALOTH (**3**) were investigated to determine its propensity toward electropolymerization. Repeated potential cycling between −0.5 V and +0.9 V *versus* Ag/Ag^+ (all further potentials will be referenced *versus* this reference electrode) of monomer **3** in 0.1 M $TBAClO_4/CH_2Cl_2$ showed both monomer oxidation and electropolymerization to form an electroactive film, as shown in eq 1.



As illustrated by the current response from the repeated scans in Figure 1, a clean monomer oxidation is observed with a sharp onset at 0.72 V and a peak potential for monomer oxidation ($E_{p,m}$) at 0.89 V. The first return scan showed a substantial reduction with a peak at 0.55 V. Repeated scanning to +0.9 V showed the rapid growth of the polymer redox at 0.6−0.7 V and 0.4−0.55 V for the oxidation and reduction, respectively.

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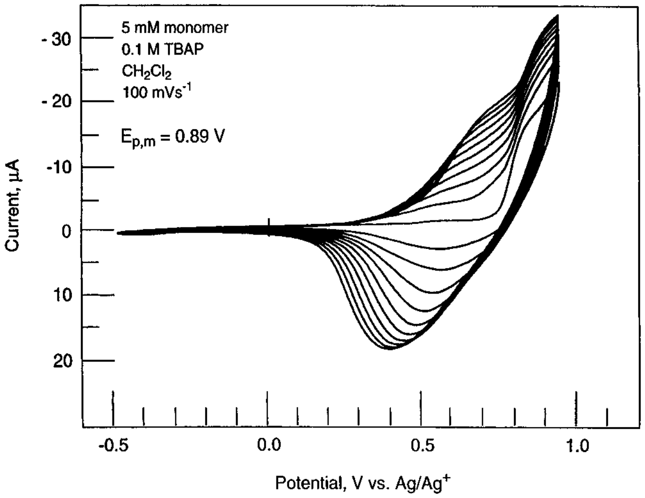


Figure 1. First five repeated potential scans of Cu−SALOTH (**3**) during electropolymerization. Electroactivity increases with each subsequent scan, indicative of a conducting polymer film forming on the working electrode.

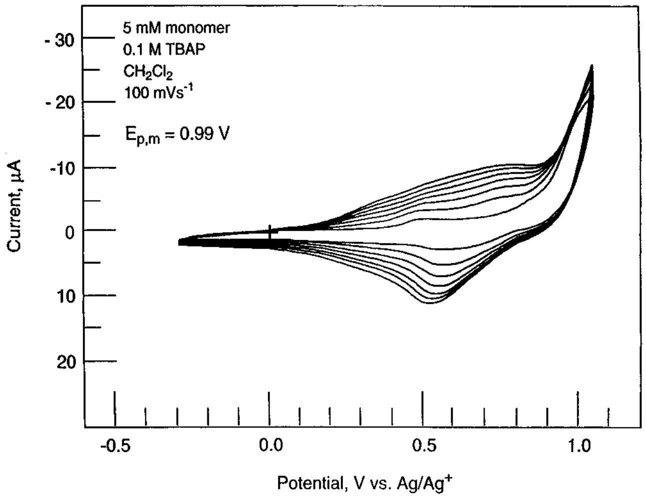


Figure 2. First five repeated potential scans of Cu−BTh−Me_2SALOTH (**6**) during electropolymerization. Again the increased peak current is expected for a film possessing a greater surface area than the bare metal electrode.

The increased peak current at $E_{p,m}$ observed with repeated scanning is expected for a conducting polymer film that is forming with a greater surface area than the bare metal electrode.

All polymer films of the complexed ligands grown on a platinum button were discovered to be quite durable and removal required the use of an abrasive pad. Upon washing and equilibrating, the redox switching properties of polymer **8** in monomer-free electrolyte were probed, and the film's redox activity was found to be rather stable, exhibiting less than a 7% loss of electroactivity after 50 repeated scans between −0.5 and +1.0 V. Upon both redox cycling and potential stepping of films grown on ITO glass, the polymer is highly electroactive and electrochromic, switching between transparent light green (reduced) and transparent dark green (oxidized). Similar behavior was also discovered for the analogously prepared nickel-containing polymer **9**, alternating between transparent orange (reduced) and transparent green (oxidized). In all cases the copper complex was more soluble than the nickel derivative; therefore, to help eliminate any complications due to poor solubility, only the copper series was fully studied.

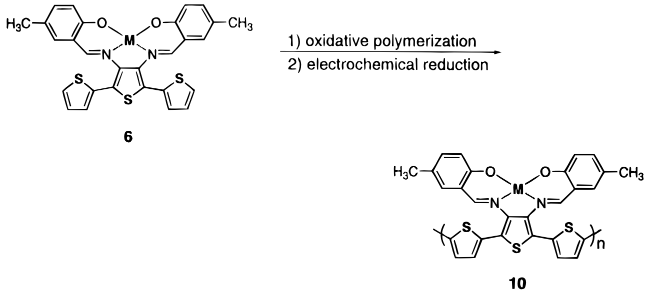
These electrochemical results are in accordance with previous investigations of the oxidations of several nickel−, copper−, and zinc−salicylaldimine chelates, which polymerize upon oxidation in poor donor solvents (e.g., CH_2Cl_2, CH_3CN.)[11−14] It has been well established with these systems that, in the case of the nickel derivatives, oxidation of nickel(II) to nickel(III) results in rapid internal electron transfer, allowing for oxidative polymerization through radical coupling.[12]

We have found that blocking of the position *para* to the phenolic oxygen in Cu−MeSALOTH (**4**) prevents polymerization. Repeated potential scans of this molecule shows a quasi-reversible copper-centered redox process with no indication of increased electroactivity (i.e. no film growth). Thus, it seems apparent that polymerization of the SALOTH complexes proceeds through the *para* carbon, as was shown in eq 1. Such behavior was also discovered in the previously studied transition metal bis(salicylaldimine) compounds.[11−14]

The next step in our investigation was to extend the conjugation length of the heterocyclic core. Previous studies in our laboratories,[5d,f] and others,[15] have shown dramatic decreases in oxidation potential by going from monocyclic to tricyclic monomers. BTh−SALOTH complexes **5**−**7** were synthesized using methodology analogous to that utilized for synthesizing the SALOTH family but, instead, replacing 3,4-diaminothiophene with 3′,4′-diamino-2,2′:5′,2″-terthiophene.

The simplest of the BTh−SALOTH complexes, **5**, exhibited electrochemical behavior similar to that of **3**, with the exception that higher potentials (ca. 0.9 V) were required to effect electropolymerization. It is very likely that the resulting polymer is a mixture of phenylene and thienylene linkages. We again employed the blocking technique to help elucidate the mode by which polymerization of the BTh−SALOTH moieties proceeded. Cu−BTh−Me_2SALOTH (**6**) was found to polymerize under conditions that its less conjugated cousin **4** did not. Most noteworthy is the fact that the repeated potential scans of **6** are significantly altered relative to the previously investigated complexes. As illustrated in Figure 2, anodic and cathodic peaks, likely due to the thienylene backbone, initiate and grow in at potentials well below those associated with metal oxidation. Even the initial scan contains these "low-potential" features.

Blocking of both *ortho* and *para* sites in Cu−BTh−Me_4SALOTH (**7**) still did not prevent electropolymerization. Furthermore, the electrochemistry of **7** very closely resembled that of **6** with the presence of the low-potential peaks. Thus, it appears that blocking the carbon *para* to the phenolic oxygen results in a polymer chain different in constitution than the unblocked analogues. We attribute this new behavior exhibited by the methylated BTh−SALOTH complexes to be the result of forming a redox active polymer possessing the polythiophene backbone such as for **10** shown in eq 2.



In conclusion, we have developed a new family of electrogenerated, electroactive polymers having a transition metal directly complexed to the conjugated backbone. Switching the polymerization site is quite novel and can afford polymer chains with uniquely different architectures. Future work will focus on exploiting the electropolymerization of other novel metal-containing monomers, as well as, further probing of the effects that metal type imparts on tuning the electronic properties of the polymer backbones to which they are affixed.

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