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Direct Insights into Metal-Induced Conductivity Enhancement in Conducting Metallopolymers

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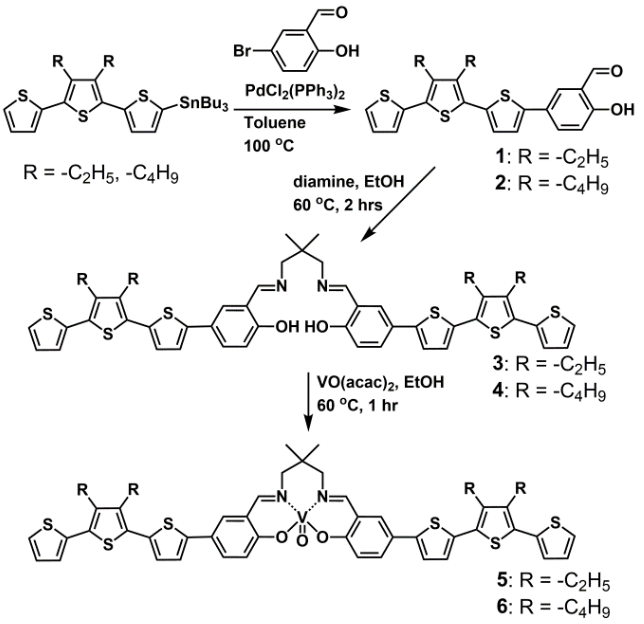
Conducting polymers of a Schiff-base ligand and the corresponding oxo-vanadium (IV) complex have been synthesized, characterized, and studied. The metal-free ligand polymer allows for direct comparison between the properties of the ligand polymer and corresponding conducting metallopolymer. The role of the metal centers in the conducting metallopolymer is elucidated unambiguously.

Conducting metallopolymers have been extensively studied recently due to the potential for these hybrid materials to impact various applications including sensing,[1-3] catalysis,[4-6] light-emitting diodes,[7,8] and energy generation and storage.[9,10] The incorporation of metal centers into polymeric organic backbones not only makes these materials multi-functional, but also changes the properties such as electroactivity and conductivity of the resulting materials when compared to the individual inorganic and organic segments alone.[11-14] Therefore, a detailed understanding of the interactive role of the transition metals in conducting metallopolymers will provide insight for the rational design of materials for specific applications. Swager *et al.* reported that matching of the metal center redox properties with that of the organic backbone of the conducting polymer greatly enhances the electroactivity of the conducting metallopolymer.[15] They also suggested that the situation where the redox potential of the organic backbone is lower than or the same as that of the metal redox potential should create materials with enhanced electron mobility. However, electrochemistry of Schiff-base metallopolymer films, in most cases, is dominated by the organic backbone making it difficult to elucidate the role and interaction of the metal centers in this class of polymers.[15,16] Additionally, it is important to note that attempts to prepare polymers from metal-free Schiff-base ligand monomers by electropolymerization have been reported to be unsuccessful, resulting in a lack of ligand-based polymer characterization.[15,16] For this reason no direct comparison between ligand polymers and metallopolymers has been reported previously (i.e., electropolymerized conducting metallopolymers).

In this contribution, we report the synthesis, characterization, and study of a novel metal-free (ligand-based) conducting polymer and the corresponding oxo-vanadium (IV/V) conducting metallopolymer that allows for a further understanding of the role of the metal centers in metal-containing conducting polymers. To our knowledge, this is the first time that a Schiff-base ligand polymer has been successfully prepared and characterized. The information obtained from the ligand polymer properties allows for a direct comparison to those of the conducting metallopolymer and helps to elucidate the role of the metal centers. Furthermore, in this study the behavior of conducting metallopolymer materials where the redox potential of the metal centers is higher than that of the organic



Scheme 1. Synthesis of ligand and metal complex monomers.

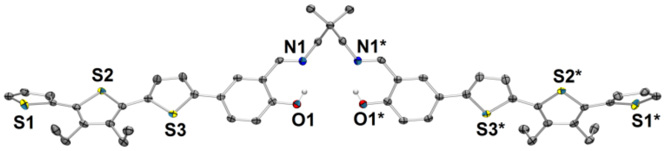


Figure 1. ORTEP diagram of **3**, drawn with the thermal ellipsoids at the 30% probability level. Hydrogen atoms (with the exception of the phenol hydrogens) have been omitted for clarity.

backbone was investigated. This will serve to complement previously reported studies in which the metal redox potential is lower than or overlapped with that of the organic backbone.[15]

The synthesis of polymerizable Schiff-base ligands which are symmetrically substituted with terthiophene moieties and the corresponding oxo-vanadium (IV) metal complex monomers is shown in Scheme 1 (see ESI). The dialkylterthiophene segments were chosen as the electropolymerizable segment due to the readily accessible oxidation potential of terthiophene and the low oxidation potential of the resulting sexithiophene units in the target conducting polymers. The alkyl chains on the middle thiophene rings were used to increase the solubility of the metal complex and to create a polymeric system with high summetry therefore eliminating complications associated with regioregularity of sidechain substituents. The metal complex was prepared by reacting the ligand with vanadyl acetylacetonate and the presence of the vanadium (IV) metal center in the resulting complex was confirmed by electron paramagnetic resonance (Figure S1, ESI). The solid-state structure of the diethyl substituted ligand (**3**) was also determined by single-crystal X-ray diffraction analysis (Figure 1). The structure of **3** in the solid-state displays an *E* conformation about both imine bonds resulting in a ligand which is preorganized into the appropriate conformation to bind to the metal center. There is a twist angle of 45.7^o between the two iminophenol rings. The inner and the middle thiophene rings are almost co-planar to the iminophenol ring with twist angles of 14.9^o and 21.4^o, respectively. The terminal thiophene ring, however, twists significantly from the iminophenol ring (53.9^o) and were modeled with static disorder of the sulfur atoms over two sites.

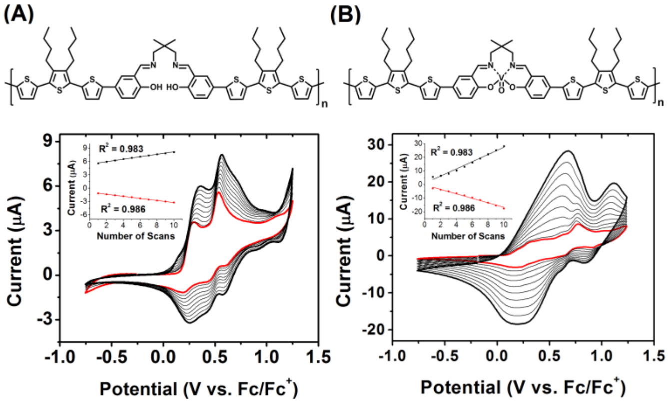


Figure 2. Polymer structures and electropolymerization of ligand **4** (A) and vanadyl complex **6** (B). Insets show the linear relationship between current at peak oxidation/reduction potentials and number of scans.

It was reported previously that a Schiff-base ligand monomer with monothiophene substitutents, *N*,*N*'-ethylene*bis*(2-thienyl)salcylidenimine, (**L^{I}**, ESI) was not electropolymerizable and it was explained as being due to the high redox potential of the organic backbone.[15-17] However, our studies in this work revealed that the growth of poly-**L^{I}** is a concentration dependent process. When varying the concentration of the ligand monomer **L^{I}**, it is possible to obtain the corresponding polymer by electropolymerization grown onto various electrodes (Figure S2, ESI) at low concentrations (ca. 10^{-4} M). This effect of concentration on electropolymerization was explained by nucleation and growth mechanisms. The increase in monomer concentration favors the nucleation under diffusion control and decreases the polymer growth rate.[18]

Due to the facile solubility of the dibutyl compounds in organic solvents, we have prepared and characterized the conducting polymers based on this system. Polymer films were formed by electropolymerization of ligand **4** and metal complex **6** using cyclic voltammetry (CV) onto various working electrodes (Figure 2). The electrode-confined polymer films were characterized using electrochemical methods, X-ray photoelectron spectroscopy (XPS), *in situ* conductivity measurements, and UV-Vis-NIR spectroelectrochemistry. Study of the scan-rate dependence of the observed peak current of the polymer films (Figure S3, ESI) in pure electrolyte solution revealed a linear relationship of observed current with the scan rate in the range of 10-500 mV/s, which is an indication of highly electroactive polymer films which are porous to electrolyte ions. Composition of the oxo-vanadium (IV/V) conducting metallopolymer, poly-**6**, was determined by quantitative XPS analysis, which yielded an atomic ratio of vanadium:sulfur = 1:5.75. This is consistent with the predicted stochiometric ratio of 1:6 in the proposed polymer structure (Figure S4, ESI).

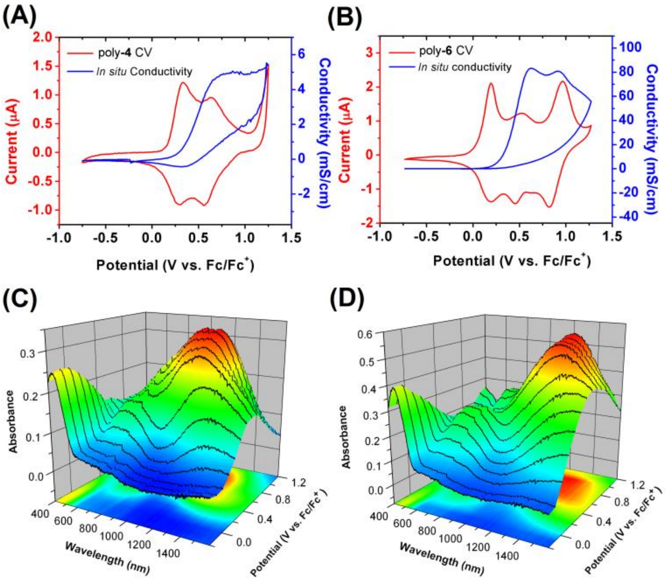


Figure 3. Cyclic voltammograms and *in situ* conductivity profiles of ligand polymer, poly-**4** (A) oxo-vanadium (IV/V) conducting metallopolymer, poly-**6** (B). UV-Vis-NIR spectroelectrochemistry of poly-**4** (C) and poly-**6** (D).

The cyclic voltammogram of poly-**4** (Figure 3A, red line) shows two oxidation peaks at 0.30 V and 0.72 V, corresponding to the formation of phenoxy radicals localized on the salpen groups and polarons on the oligothiophene backbone, respectively. CV of the oxo-vanadium (IV/V) conducting metallopolymer poly-**6**, however, reveals three oxidation peaks at 0.22, 0.50, and 0.95 V (Figure 3B, red line). The first two peaks are attributed to organic backbone oxidation as observed in poly-**4** but at lower potentials due to increased conjugation, while the new peak at 0.95 V is assigned to the redox potential of the vanadium metal center, corresponding to the $V^{4+/5+}$ redox process.

In situ conductivity measurements of poly-**4** and poly-**6** were conducted using 10 μm Pt interdigitated microelectrodes.[19] The conductivity profile of poly-**4** reveals a maximum at ~ 0.73 V (Figure 3A, blue line), corresponding to the potential of the second oxidation process in the CV (Figure 3A, red line). This suggests that the first redox process of the polymer does not contribute to the overall conductivity. As discussed above, this redox potential is attributed to the oxidation of the phenoxy groups of salpen ligands. The radical cations are highly localized on the iminophenol ring and are therefore not involved in the conduction process. The conductivity corresponding to the second redox process is assigned to the formation of polarons on the oligothiophene backbone, which are highly mobile. This is completely consistent with the observed trends in the spectroelectrochemistry spectra (*vida infra*). The conductivity profile of poly-**6** is distinguished from poly-**4** by two features: the appearance of a new peak and the magnitude of the measured conductivity. There are two peaks in the poly-**6** conductivity profile (Figure 3B, blue line). The initial peak corresponds to the potential for the second redox process, the formation of polarons as observed in poly-**4** while the second peak occurs at the potential that is assigned to the $V^{4+/5+}$ redox couple. The appearance of the new peak in the poly-**6** conductivity profile is clear evidence for direct contribution of the metal centers to the polymer conductivity. Furthermore, it should be noted that the second maximum in the conductivity profile of poly-**6** (0.91 V, Figure 3B, blue line) occurs at a potential slightly less positive than the peak current of the vanadyl redox event (0.95 V, Figure 3B, red line). This indicates that the mechanism of charge transport in the highly conductive form of poly-**6** involves redox conductivity enhanced by inner sphere electron transfer in a mixed valence redox state ($V^{4+/5+}$) of the conducting metallopolymer. The electronic delocalization under this applied potential is further aided by the mobile charge carriers that are present on the oligothiophene segments which bridge the redox-active metal centers. The importance of the metal ions is further shown by the relative magnitudes of the conductivity profiles, where the peak conductivity of poly-**6** (83.4 mS/cm) is more than an order of magnitude higher than that of poly-**4** (5.0 mS/cm).

The conjugated systems of poly-**4** and poly-**6** were investigated by UV-Vis-NIR spectroelectrochemistry. Polymer films were grown onto ITO-coated glass and subsequently oxidized incremently to potentials between 0 and 1.2 V vs Fc/Fc^+ while UV-Vis-NIR absorption spectra were taken at each potential. The spectroelectrochemical spectra of poly-**4** and poly-**6** are presented in Figure 3C and 3D, respectively. At low potentials, both polymers show two new bands at around 700 and 1300 nm. This is attributed to the formation of the polarons when the two polymers are partially oxidized. At higher potentials, these two bands merge into a single band at 1150 nm for the poly-**4** and 1250 nm for poly-**6**. These bands are assigned as the formation of bipolarons generated when additional electrons are removed from the polymer chains thus converting polarons to bipolarons. The appearance of the bipolaron band of poly-**6** relative to that of poly-**4** at longer wavelength is an indication of a more conjugated system which allows increased delocalization of the mobile charge species. This suggests that the metal centers in the oxo-vanadium (IV/V) conducting metallopolymer contribute to the overall conjugation pathway. The spectoelectrochemical data also support the observations in the CVs of poly-**4** and poly-**6**, which showed the redox potentials of the organic backbone in the conducting metallopolymer slightly lower than those in the ligand polymer.

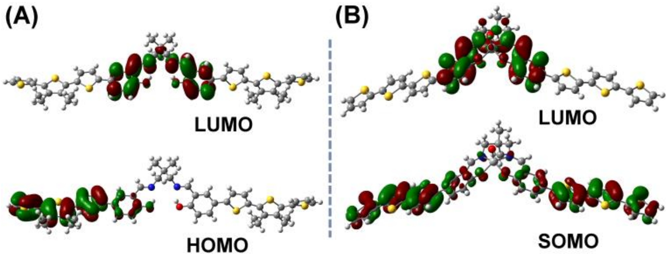


Figure 4. Calculated frontier molecular orbitals of **3** (A) and a vanadyl complex, **7** (B).

To further understand the effect of the metal centers on the electronic structure of the metal-free (ligand-based) conducting polymer and the corresponding oxo-vanadium (IV/V) conducting metallopolymer, DFT calculations were performed to explore the frontier orbital spatial distributions of electron density on the ligand and vanadyl complex. The atomic coordinates from the crystal structure of **3** were used to calculate the frontier molecular obitals of the ligand in a single point calculation while an optimized structure was computed and used for the vanadyl monomer, **7**. Figure 4 shows the HOMO/SOMO and LUMO of ligand **3** and vanadyl complex **7**. The results show the involvement of the vandyl center in the overall conjugation of the metal complex monomer, especially in the LUMO, while there is an interruption in conjugation of the ligand monomer at the aliphatic bridge (2,2-dimethylpropyl). The incorporation of the vanadyl center also makes the complex become more planar, which should enhance any interchain interaction between polymer chains, a factor that contributes to conductivity enhancement.[20]

Conclusions

In summary, we have reported the synthesis, characterization, and study of novel conducting polymers of a Schiff-base ligand and the corresponding vanadyl conducting metallopolymer. The successful synthesis of the ligand polymer has created a direct comparison and enabled studies to elucidate the role of the metal centers in Schiff-base conducting metallopolymers. Spectroelectrochemistry revealed a more delocalized conjugation system in the metallopolymer, which is attributed to the incorporation of the metal centers. Conductivity measurements show an increase in redox conductivity of the metallopolymer compared to that of the ligand polymer by more than an order of magnitude. These studies suggest that the metal-induced conductivity enhancement results from facile inner sphere electron transfer in a mixed valence redox state of the conducting metallopolymer. Further investigation is focused on the effect of the organic backbone conjugation length on electrochemical properties and conductivity of this type of metallopolymer.

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Notes and references

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† *Crystal data* for **3**: $C_{51}H_{50}N_2O_2S_6$, M = 915.29, orange, needle, monoclinic, *C12/c1*, a = 37.215(8), b = 14.101(3), c = 9.619(2) Å, $\alpha = \beta$ = 90, γ = 96.595(5)°, V = 5014.3(18) $Å^3$, T = 153 K, Z = 4, D_c = 1.212 mg/cm^3, 21117 reflections measured, 4349 independent reflections (R_{int} = 0.0998), $R[I>2\sigma(I)]$ = 0.0726, $wR2$ = 0.1735.

Electronic Supplementary Information (ESI) available: Experimental details, electrochemical data, XPS, and EPR data. CCDC 1051308. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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