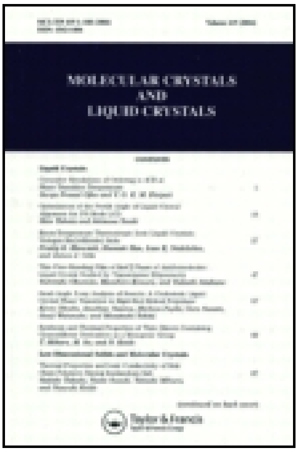

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Conductivity Studies of Metal Coordination Polymers of Cobalt, Iron, Ruthenium, and Osmium Vinylbipyridine Complexes

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Electropolymerized films of the type $[M(\text{v-bpy})_x(L)_y]$ (M = Co, Fe, Ru, Os; v-bpy = 4 vinyl,4′ methyl 2,2′ bipyridine; L = CN, v-bpy) exhibit conductivity dependent on the oxidation state of the metal as well as the backbonding ability of the coordinated ligands and the radial extension of the metal *d*-orbitals. Higher oxidation states and reduced electron density at the metal center result in higher conductivities. The reversible temperature-dependence of the conductivity supports an electron exchange model of charge transport, except for the unusual behavior observed for the $[Fe(\text{v-bpy})_2(CN)_2]$ polymer which exhibited a virtually temperature independent conductivity.

INTRODUCTION

The utility of electroactive metal-centered coordination polymers has been demonstrated in polymer modified electrodes[1] by application to electroanalysis,[2] electrocatalysis,[3] and development of electronic devices.[4] The conductivity of the polymer films is essential for these applications yet studies geared at an understanding and characterization of the energetic, molecular, and structural details of this conductivity have been limited.

The conductivity of metal-centered coordination complexes is known to vary with oxidation state. A classic example is $K_2Pt(CN)_4$, a square planar complex with minimal conductivity in the platinum (II) oxidation state. However, upon oxidation to platinum (IV), the conductivity of the complex increases by seven orders of magnitude.[5] This dramatic difference in conductivity is attributed to the occupancy of the d_z2 orbitals perpendicular to the plane of the complex. In the platinum (II) state, these d_z2 orbitals are completely filled so that conduction only occurs when an electron is excited from the d_z2 orbital to a high lying empty band, thus giving rise to semiconducting behavior. Upon oxidation to platinum (IV), these d_z2 levels are only half-filled and these empty states provide a facile conduction pathway leading to the dramatic increase in conductivity alluded to above.

An analogous model for the conductivity of redox active polymers as a function of its oxidation state has been put forth by Pickup and Murray[6] and White.[7] Conceptually identical ideas, however, were first expoused by Reilly[8] in the context of twin electrode thin layer electrochemical cells.

Metalloporphyrin and phthalocyanine polymers form an interesting class of materials for conductivity studies since both the ligand-centered π-orbitals as well as the metal-centered orbitals can participate in conduction. Hanack[9] prepared bridged phthalocyanine polymers of the type $[Fe(Pc)(\mu\text{-pyz})]_n$ (Pc = pthalocyaninato; pyz = pyrazine) which appear to involve both the transition metal and the bridging ligands in the conduction mechanism. Marks *et al.* suggest that conductivity of stacked phthalocyanine polymers is a factor of 10^2-10^3 greater along the stacking axis of a single crystal than in polycrystalline samples.[10] More recently, Collman *et al.*[11] prepared a series of ligand-bridged metalloporphyrin polymers of the type $[M(OEP)(L\text{-}L)]_n$ (M = Fe, Ru, Os; L-L = pyrazine, 4,4′-bipyridine, 1,4-diazobicyclo[2.2.2]octane; OEP = octaethylporphyrin) which exhibit highly conductive behavior when the metal centers are partially oxidized. A dependence of the conductivity on the identity of both the central transition metal and the bridging ligand was observed, however, the conductivity was metal centered and the porphyrin π-electrons were not involved. Bard, Kennedy and coworkers recently reported on charge delocalization on partially oxidized oligomeric silicon phthalocyanines.[12]

A class of materials well suited for studies of the mechanisms of charge transfer and transport through electroactive redox polymers is that comprised of transition metal complexes of the type $[M(v\text{-}bpy)_x(L)_y]$ (where M = Fe, Ru, Os, Co, Cu, Cr; v-bpy = 4 vinyl,4′ methyl 2,2′ bipyridine; L = auxiliary ligands such as cyano, chloro, phenanthroline derivatives and other chelates) which can be electropolymerized to yield stable, well-behaved, electroactive polymer films.[13] Systematic variations in the identity of the metal center and auxiliary ligands can lead to polymers with continuously varying parameters such as the extent of backbonding, the radius of the Van der Waals sphere, and the metal localized oxidation potential.[14]

In this study, we focus on the measurement of conductivity to probe the processes controlling charge transfer in redox polymers based on the above mentioned class of materials.

EXPERIMENTAL

Reagents

$[Co(v\text{-}bpy)_3]^{2+}$, $[Fe(v\text{-}bpy)_3]^{2+}$, $[Os(v\text{-}bpy)_3]^{2+}$, and $[Ru(v\text{-}bpy)_3]^{2+}$ were prepared as previously described[15] by substituting v-bpy as a ligand. $[Fe(v\text{-}bpy)_2(CN)_2]$ was synthesized as previously described[16] and purified by dissolving the complex in a minimal volume of acetonitrile and precipitating in ether. Acetonitrile (Burdick and Jackson distilled in glass) was dried over 4 Å molecular sieves. Tetra *n*-butyl ammonium perchlorate (TBAP, G. F. Smith), was recrystallized three times from ethyl acetate and dried under vacuum at 70°C for 72 hours.

Electrode fabrication

Working electrodes of two types were prepared. A macroscopic array (type 1) was prepared with three closely spaced platinum strips (25 microns thick and 1.5 mm wide) separated by 6 micron mylar sheets and sealed with Epon 828 epoxy with 14% *m*-phenylenediamine hardener (Miller-Stephenson) between glass plates, such that only the cross section of platinum would be exposed (Figure 1a). The final separation between platinum electrodes was approximately 10 microns. Electrical contact to the electrodes was via soldered wires to the platinum sheets. The electrodes were polished with 600 grit emery paper and subsequently with 1 micron diamond paste (Buehler), followed by a rinse with acetone and water.

A second microelectrode array (type 2) was fabricated at the National Nanofabrication Facility at Cornell University. A 3000 Å thick layer of SiO_2 was grown on a silicon (111) single crystal wafer substrate. The wafer was first spin-coated with HMDS (hexamethyldisilizane) primer and then with a 1 micron layer of AZ5214E image reversal resist. The resist-coated wafer was baked at 90°C for 30 minutes to cure the resist. The pattern was exposed on a Canon Pattern Aligner for optical lithography followed by a 30 minute bake at 105°C to crosslink the exposed resist. The entire wafer was then

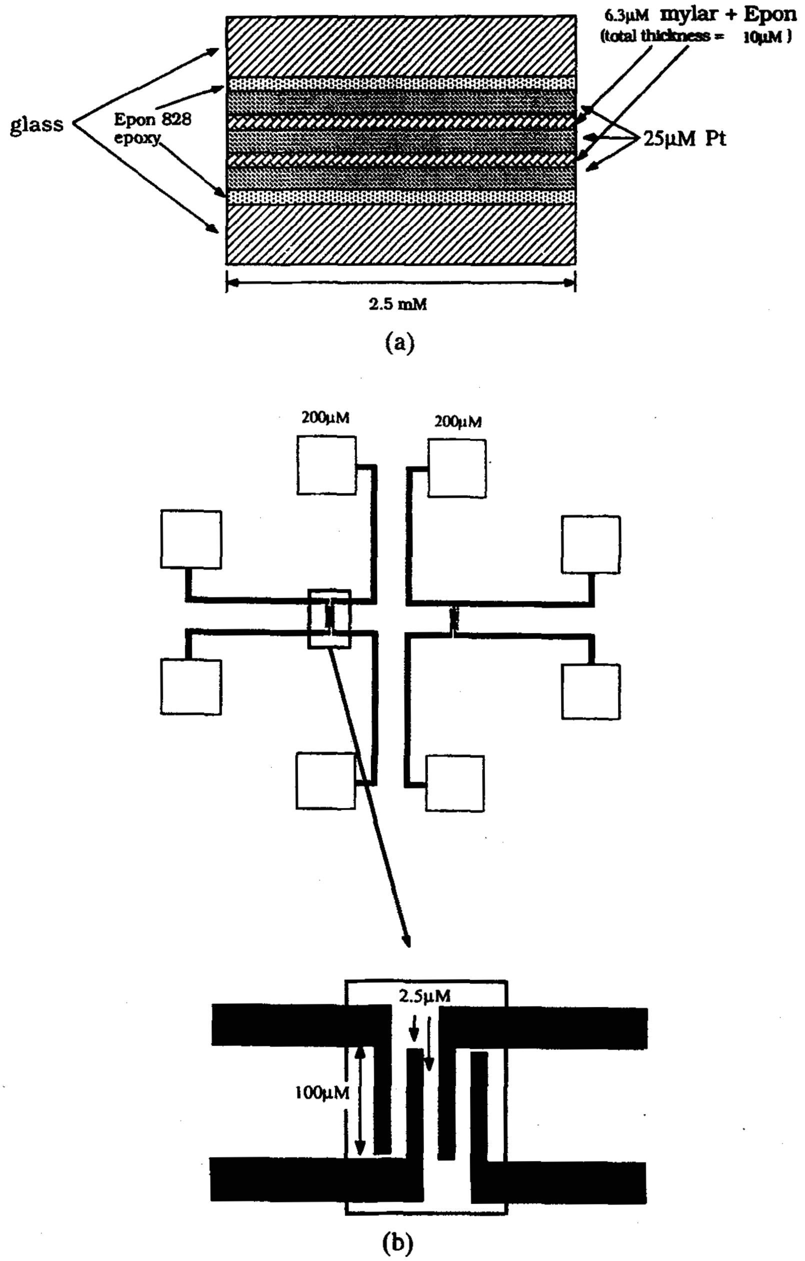

FIGURE 1 Schematic views of electrode arrays: (a) cross-sectional view of a macroscopic platinum array, type 1 (b) face view of an unmasked gold microelectrode array, type 2.

exposed to a mercury lamp (600 mJ/cm^2) to expose the remaining resist. Development of the resist was carried out in 50/50 v/v Shipley 312 developer and distilled water for 1.5 minutes. Metallization was accomplished with a CHA Industries thermal evaporator operated at 55 amps and 0.5 Å/second to deposit 50 Å of chromium (as an adhesion layer) followed by deposition of 1000 Å of gold at 35 amps and 2.5 Å/second. The lift off was achieved after a three hour soak and 10 minute sonication in *n*-butyl acetate.

Each microelectrode in the array is 2.5 microns in width and 100 microns in length. A series of electrode arrays was produced with electrode spacings varying between 1.25 and 2.5 microns. Each electrode was connected to a 200 micron square contact pad (Figure 1b). After utilizing a diamond scribe to separate the devices on the wafer, each array was mounted on a T-05 header (Platronics Seals) and connections between the contact pads and the header posts were made with 1.25 micron aluminum wire with an ultrasonic wire bonder. Headers were mounted into reusable sockets with soldered wire connections. Contact pads and other connections were masked by application of Chemgrip cement (Chemplast). Thus, only the microelectrodes were exposed during the experiment.

Instrumentation

Electrochemical experiments were performed on a Pine Instruments RD-4 bipotentiostat in the 3-electrode configuration and data were recorded on a Soltec X-Y-Y recorder. A conventional electrochemical cell was employed with a platinum counter electrode and a saturated sodium calomel reference electrode (SSCE). All potentials are referenced to this electrode without regard for the liquid junction. All experiments were carried out in a Faraday cage to minimize noise. Conductance through polymer films was measured as a voltage across a 50 Mohm high precision Victoreen resistor with a 140 mv load (Figure 2).

Temperature-controlled experiments were performed using an Omega temperature controller with two hotwatt resistive heaters inside a copper block of dimensions 9 cm × 7 cm × 2 cm insulated with a layer of teflon. A glass vial was placed in a recess in the copper block and thermal contact was made via thermally conductive paste. Temperature was monitored by a thermocouple placed inside the copper block. Temperature-controlled electrochemical experiments utilized a silver wire reference although all potentials have been converted to the SSCE reference.

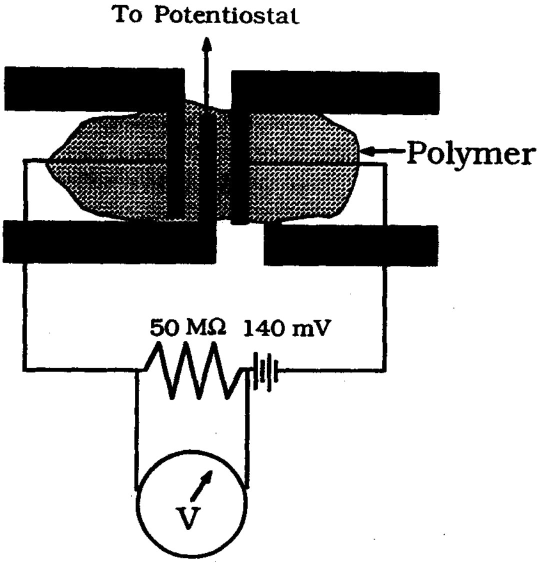

FIGURE 2 Schematic view of the electrode connections for the conductance measurements.

Procedures

Electropolymerization of the complexes was carried out in acetonitrile/0.1 M TBAP with 1 mg/ml of the complex in solution in a conventional three compartment electrochemical cell according to previously described procedures.[13] During the electropolymerization, the array of electrodes was shorted together to facilitate uniform polymer deposition. Polymer coverages of 5×10^{-9} to 8×10^{-8} mol/cm^2 were used in the conductivity experiments as these coverages were sufficient to bridge the insulating gaps between the electrodes in the array. Polymer films were viewed under a Nikon Optiphot light microscope to ensure uniform coverage.

Conductance measurements were made in a fresh acetonitrile/0.1 M TBAP solution after the modified electrodes had been rinsed in acetone and water and dried. The conductance between two noncontiguous electrodes was measured while the potential applied to the center electrode was varied, thus changing the oxidation state of the polymer film. Both current (i.e. cyclic voltammogram) and conductance were recorded simultaneously. Several repetitions of the cyclic voltammogram confirmed that the films were stable, and there was no loss of polymer material between successive scans.

RESULTS AND DISCUSSION

As would be anticipated, conductance in these electroactive polymers is dependent on the oxidation state of the metal centers within the polymer film. As shown in Figure 3a, for an electrode array modified with a film of $[Os(v\text{-}bpy)_3]^{2+}$, the conductance remained essentially constant with potential until potentials in the vicinity of the oxidation potential of the metal center were attained. At a potential corresponding to the peak current of the polymer oxidation, the polymer conductance began to increase and continued this trend for 250 mv with some lag time behind the oxidation peak of the cyclic voltammogram even for scan rates as slow as 1–5 mv/sec. Thus, upon partial oxidation of the polymer film, charge begins to be transported through electron self-exchange on the individual redox centers.

The $[Fe(v\text{-}bpy)_3]^{2+}$ polymer exhibited a peaked conductance following the peak of the current response (Figure 3b) before stabilizing at the conductance associated with the higher oxidation state. This is the anticipated response since one would expect that the conductivity would be maximal when the concentration gradients from both electrodes meet with the highest slope.[6,7,8] Conceptually this is analogous to the maximum conductance predicted by band theory for a half-filled band. We thus would anticipate maximum conductance when half of the metal centers are in the oxidized state.

This potential dependent conductance was consistently observed in all five polymers employed in this study. However, the magnitude of the conductance was strongly dependent upon the nature of both the metal center and the auxiliary ligands. For the v-bpy complexes, values normalized to the electrode coverage follow the trend Co < Fe << Ru < Os which correlates well with the atomic radius of the metal *d* orbitals[17] as illustrated in Figure 4. This trend was observed at several different polymer coverages. Values for the coverage-normalized conductivities are presented in Table I.

Further, when one of the v-bpy ligands in the $[Fe(v\text{-}bpy)_3]^{2+}$ complex is exchanged for two cyano ligands, the conductivity is increased by more than two orders of magnitude. The stronger π-acidity of the cyano groups influences the electronic structure of the metal center by an enhanced degree of π-backbonding. The ligand has low lying π orbitals capable of overlapping with the d-π orbitals of the metal, and the ligand orbitals are stable enough to accept electron density from the metal ion.[18] This backbonding has an effect analogous to partial oxidation of the metal center and enhances conduction by a process similar to introducing acceptor states into a semiconductor.

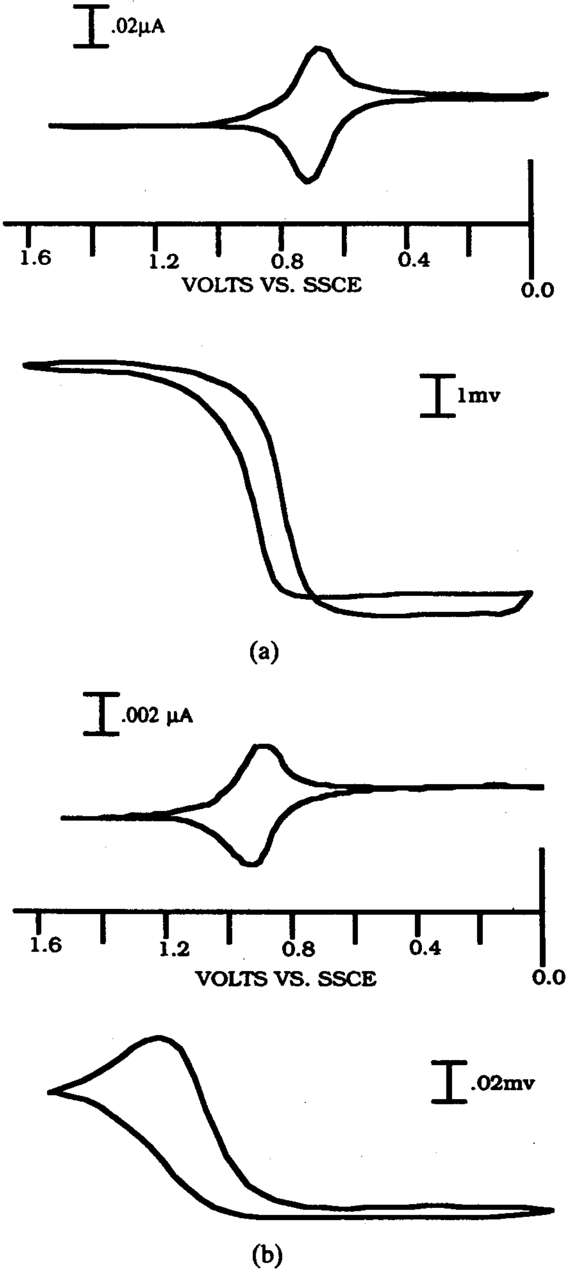

FIGURE 3 Cyclic voltammograms at 5 mv/sec and potential-dependent conductance traces in a solution of acetonitrile/0.1 M TBAP for an electrode array modified with (a) 4 × 10^{-8} mol/cm^2 of $[Os(v\text{-}bpy)_3]^{2+}$ (b) 7 × 10^{-8} mol/cm^2 of $[Fe(v\text{-}bpy)_3]^{2+}$.

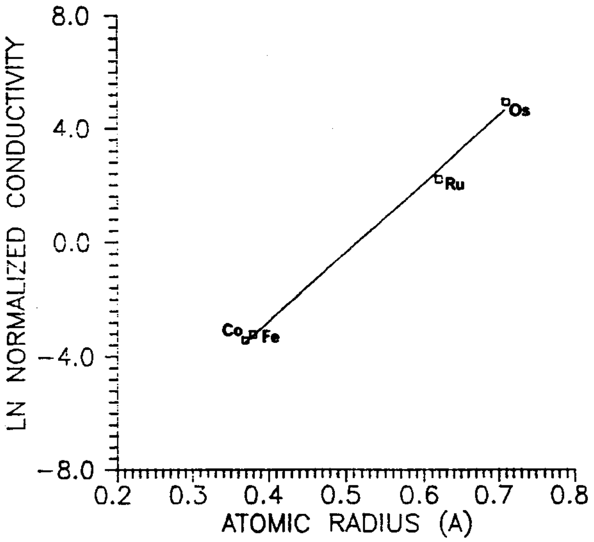

FIGURE 4 The natural logarithm of conductivities normalized for electrode coverage for each of the $[M(v\text{-bpy})_3]^{2+}$ polymer films as a function of the atomic radius of the metal *d* orbitals (where atomic radius is defined as the radius of maximum charge density), $r^2 = .99$.

Further evidence that such interactions may enhance conductivity in these polymer films comes from studies of mixed-valence dimers of both ruthenium (II) and osmium (II) which contain electrons capable of delocalizing through bridging π-acid ligands.[19]

The temperature dependence of this conductance response was also investigated. Figure 5 presents the conductance response of the $[Os(v\text{-bpy})_3]^{2+}$ polymer as a function of temperature from 0°C to 45°C illustrating a logarithmic dependence of normalized conductivity with temperature. The temperature dependence of the conductivity is often employed to determine particular conduction mechanisms. The con-

TABLE I

Normalized conductivities for single species polymers

Compound	Conductivity/Coverage
$Co(\nu\text{-bpy})_3^{2+}$	3.2×10^{-2} mol/ohm-cm^3
$Fe(\nu\text{-bpy})_3^{2+}$	4.0×10^{-2}
$Fe(\nu\text{-bpy})_2(CN)_2$	6.4
$Ru(\nu\text{-bpy})_3^{2+}$	9.0
$Os(\nu\text{-bpy})_3^{2+}$	1.4×10^2

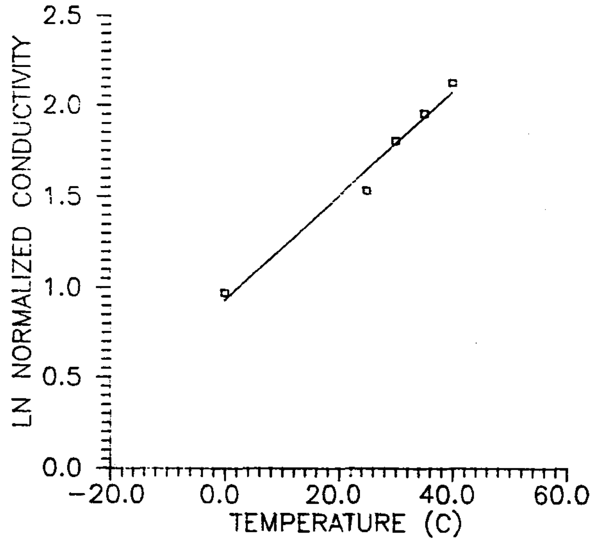

FIGURE 5 The natural logarithm of conductivity normalized for electrode coverage as a function of temperature for the $[Os(v\text{-}bpy)_3]^{2+}$ polymer, $r^2 = .98$.

ductivity of electronically conducting polymers will remain relatively constant or may decline slightly with increased temperature since the temperature induced lattice vibrations can scatter electrons and decrease their mobility. However, electron hopping and ionic conductivity mechanisms predict a logarithmic increase in conductivity with increasing temperature since the number of charge carriers will be increased and the potential barrier to electron hopping will be reduced thus increasing electron mobility.[20,21]

The conductance of the $Fe(v\text{-}bpy)_2(CN)_2$ polymer exhibited little temperature dependence though this response may not necessarily imply electronic conductivity. The $[M(v\text{-}bpy)_3]^{2+}$ polymers exhibited a reversible temperature dependent response independent of the initial direction of temperature change. Yet, the temperature dependence of the conductivity of $Fe(v\text{-}bpy)_2(CN)_2$ polymer exhibited significant hysteresis. This irreversibility is an anomaly amongst this class of polymers.

One could speculate that this difference in behavior may be due to the fact that in this particular case the individual metal complexes are initially uncharged (when the iron is in the 2+ oxidation state) and upon oxidation acquire a +1 net charge (the iron is present in the 3+ oxidation state). One would anticipate substantially different solvation and couterion transport effects in this system relative to the other ones which involve a change from 2+ to 3+ net charge. The dynamics of solvation and counterion transport may be responsible, in part, for the observed hysteresis.

This type of effect is very well documented in the modified electrode literature where the most significant deviations in voltammetric waveshapes are encountered for systems where one of the redox partners is electrically neutral (e.g. ferrocene).[22]

CONCLUSIONS

We have demonstrated that charge transport in vinyl-bipyridine based metal coordinated polymer films is dependent on the electronic state of the metal center which is influenced by its interaction with coordinated ligands and the oxidation state of the metal. We are continuing this work by examining conductivities in a wide range of electroactive polymers with finely tuned properties with respect to metal localized oxidation potential and π-acidity of the coordinating ligands. We hope to gain a better understanding of charge and energy transport in these polymers.

Acknowledgments

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