Electron Transport in a Conjugated Metallopolymer Containing Binuclear Osmium Centers with Strong Electronic Communication

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Conjugated metallopolymers in which metal sites are in direct electronic communication with a conjugated organic backbone have recently been attracting increasing attention.[1,2] Studies of electron transport in these materials provide insight into long-range electron-transfer mechanisms and will likely be important in the development of viable molecular electronic devices and electrocatalytic polymers.

The ability of conjugated linkages to provide an effective pathway for electron transfer between metal sites has been demonstrated in a number of polymeric systems. Zotti et al.[3] have shown that electron-transfer rates between metal sites in polythiophenes with pendant ferrocene moieties are enhanced when a conjugated linkage is used. We have shown that coordination of $Ru(bpy)_2^{2+}$ (bpy = 2,2'-bipyridine) moieties to a conjugated polybenzimidazole provides a rapid electron-transfer pathway by superexchange interactions between metal sites.[4,5] Zhu and Swager[6] have reported enhanced conductivities in a Cu(II/I) metallopolymer with a bpy-*co*-(3,4-ethylenedioxythiophene) backbone.

We now report a new benzimidazole based conjugated metallopolymer in which pairs of coordinated Os(III/II) sites interact strongly across a pyrazine bridge (structure **1**). There is also a much weaker interaction between adjacent binuclear centers through the much longer bibenzimidazole bridge. Interestingly, the 50:50 Os(III):Os(II) mixed valence state of the polymer is poorly conducting, while peak conductivities are observed for the 75:25 and 25:75 states. A higher peak conductivity for the former suggests that long-range electron transfer in the polymer occurs via electron superexchange through the π^* orbitals of the conjugated backbone.

Polymer **1** was prepared following standard literature procedures for the preparation of polybenzimidazoles[7] and [Os-(bpy)$_2$L]$^{2+}$ complexes[8] (glycerol was used as the solvent for complexation). Gel permeation chromatography indicated that the molar mass of the Os-complexed polymer was >50000 g mol^{-1}. Elemental (C, H, and N) analysis was consistent with the proposed structure (with residual glycerol) and indicated that ca. 95% of the bidentate pyrazine–benzimidazole sites were occupied. Polymer films were deposited on Pt disk electrodes by evaporation of a water-saturated nitromethane solution of the polymer.

Figure 1 shows cyclic voltammograms of a film of **1**. The appearance of two Os(III/II) waves separated by 320 mV confirms that there are strong interactions between Os sites across the pyrazine linkage. Based on results for an analogous Ru complex
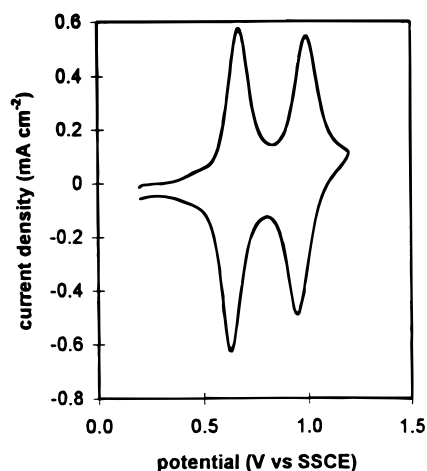
Figure 1. Cyclic voltammogram (20 mV/s) of a Pt electrode coated with a thin film of **1** ($\Gamma_{Os} = 5.9 \times 10^{-8}$ mol cm^{-2}) in a 2:1 CH$_2$Cl$_2$ + CH$_3$CN mixture containing 0.1 M Et$_4$NClO$_4$ and ca. 50 mM HClO$_4$.
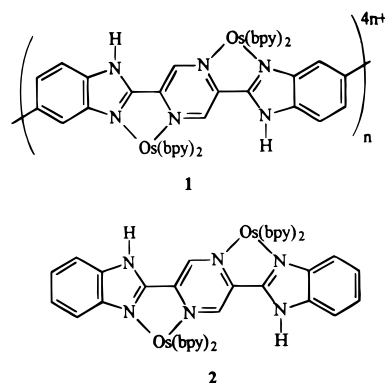
with a lower metal loading, the redox wave for mononuclear sites is expected to occur at approximately the same formal potential as the first wave for the binuclear sites. The similar sizes of the two waves in Figure 1 therefore indicate that most of the Os sites are binuclear, as indicated by the C, H, N analysis. The fact that the first wave is slightly larger than the second is consistent with the estimated 95% occupancy of sites. The formal potentials in Figure 1 are close to values obtained by us for the analogous dimer complex, **2**.

Electron transport in a thin film of **1** was investigated in situ by dual electrode voltammetry,[9] in which the polymer layer is sandwiched between a Pt electrode and a porous gold film. Figure 2 shows the results of an experiment in which a fixed potential difference (10 mV) was maintained between the Pt and Au electrodes while the potentials of both were slowly scanned relative to a reference electrode. The resulting currents have been converted to electronic conductivities by applying Ohm's law and scaling for the dimensions of the polymer film. The thickness of the film was estimated from the surface coverage, determined from a slow voltammogram, using an Os site concentration of 1.5 M based on the dry density of poly-[Os(bpy)$_2$(4-vinylpyridine)$_2$]$^{2+}$,[9] with which comparisons are made below.

The appearance of two peaks in the conductivity profile, corresponding to the two formal potentials observed in cyclic voltammetry, is perhaps surprising since mixed-valence materials are normally most conductive in the 50:50 state.[10–12] However,

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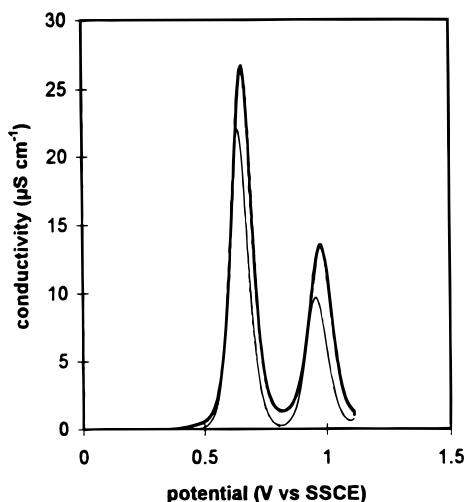(5) Cameron, C. G.; Pickup, P. G. *J. Am. Chem. Soc.* Submitted for publication.

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Figure 2. Electronic conductivity vs potential plots for a thin film of **1** ($\Gamma_{Os} = 1.6 \times 10^{-7}$ mol cm^{-2}) in a 2:1 CH$_2$Cl$_2$ + CH$_3$CN mixture containing 0.1 M Et$_4$NClO$_4$ and ca. 50 mM HClO$_4$. The thinner line is for the reverse scan.

in this case electrons are trapped on the pyrazine-bridged binuclear sites in the 50:50 mixed-valence state because of the relatively large amount of energy required for an electron to hop from one Os(III)−Os(II) site to another (the consequent production of an Os(III)−Os(III) site and an Os(II)−Os(II) site requires an energy of 0.32 eV). The low conductivity at ca. 0.8 V corresponding to the 50:50 mixed-valence state also shows that electron hopping via redox sites on the polymer backbone (mediated pathway defined in ref 2) is not a significant electron-transfer pathway.

Perhaps the most interesting feature of the conductivity profiles shown in Figure 2 is the difference in the heights of the two peaks. This is reproducible over multiple scans, and so is not due to degradation of the polymer. Clearly, electron hopping between binuclear centers is faster when the polymer is predominantly in the Os(II) state. There are a number of factors that could be responsible for this difference. Structural changes accompanying partial oxidation, including solvent and counterion uptake, may influence the overlap of the metal and polymer orbitals and may also influence the rate of electron exchange between Os sites on adjacent chains. In addition, the small fraction of mononuclear sites present may have disproportionately large electron exchange kinetics. However, since electron transport in this polymer appears to be dominated by superexchange through the polymer chains, a more likely explanation is that the higher D_e for the first wave is due to a better match of orbital energies. In this case, the fact that electron hopping is faster for higher energy electrons would indicate that superexchange between Os sites in adjacent binuclear segments occurs via the LUMO of the polymer π-system (electron-type superexchange).

Electron diffusion coefficients (D_e) in **1** were determined[9] from a dual electrode voltammetry experiment in which the gold film was maintained at 0.3 V while the potential of the Pt electrode was scanned through the Os(III/II) waves. Values of $(1.3 \pm 0.6) \times 10^{-8}$ and $(7.0 \pm 2.5) \times 10^{-9}$ cm^2 s^{-1} (averages and standard deviations for two films) were obtained for the first and second waves, respectively. For comparison, D_e for poly[Os(bpy)$_2$(4-vinylpyridine)$_2$]$^{3+/2+}$ in acetonitrile is $(8 \pm 3) \times 10^{-9}$ cm^2 s^{-1},[9] while for poly[Os(bpy)$_2$(4-py-NHCOCH=CHPh)$_2$]$^{3+/2+}$ it is only $(1.5 \pm 0.9) \times 10^{-9}$ cm^2 s^{-1}.[13] Thus electron transport appears to be faster in **1** than in nonconjugated Os(III/II) polymers, indicating enhanced long-range electronic communication between Os centers. This difference is particularly important in light of the higher rigidity of **1** which would be expected to lead to slower electron transport if the only mechanism involved was outer-sphere electron transfer.

These results clearly indicate that electron transfer between the Os$_2$−pyrazine moieties in **1** involves superexchange through the conjugated polymer backbone. Such long-range interactions between metal centers will certainly be a crucial feature of future electrocatalytic and electronic materials.

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