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Electron Transport in Conjugated Metallopolymers

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Summary: Superexchange interactions between metal centers coordinated to various conjugated polymer backbones have been shown to enhance the rate of electron transport through the polymer. Results for Ru and Os bipyridine moieties complexed to polybenzimidzoles and poly(bithiophene-co-bithiazole)s are reviewed. The evidence for superexchange mediated electron transport, and the factors that influence the rate of electron hopping between metal centers, are discussed.

Keywords: charge transport; conjugated polymers; electrochemistry; metal-polymer complexes; superexchange

Introduction

Electron transport through molecular materials is of immense fundamental importance to diverse fields of science ranging from the study of redox proteins,[1,2] to the development of molecular electronic devices.[3,4] The broad field of conducting polymers is built upon this phenomenon, and photosynthesis and respiration could not occur without it. It will be crucial to the development of nano-electronics technology.

The work reviewed in this paper was designed to demonstrate and develop a new mechanism for electron transport in molecular materials, based on the well known phenomenon of electronic coupling (superexchange) between metal complexes bound to the same ligand.[5] Thus, metal complexes have been bound to conjugated polymers such that there are superexchange interactions between them through the polymer chains (Structures **1** and **2**). Electron transport rates in these materials have been measured by electrochemical impedance spectroscopy. Their dependence on variables such as the metal centre (Ru or Os), the structure of the polymer backbone, and pH, clearly demonstrate the enhancement of electron transport rates in these materials by a superexchange mechanism.

This work draws on the extensive literature on redox polymers[6-9] and conducting polymers,[10,11] and the concept of hybridization of these materials that has been developed over the past

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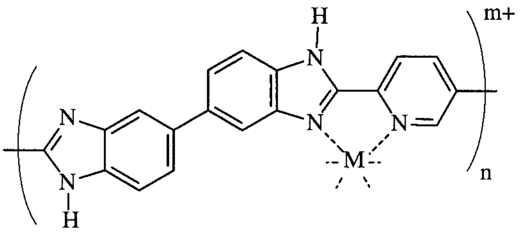
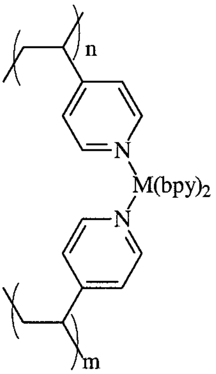
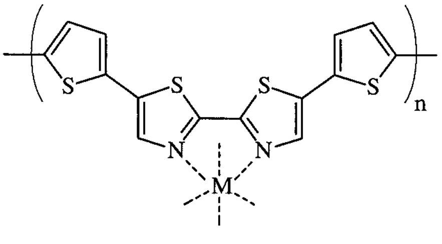
decade.[12-14] Similar materials have been reported by Swager and coworkers,[15] and Wolf and Wrighton.[16]



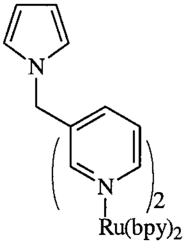
1Ru: M = Ru(bpy)2; $D_eC_M^2 = 1.5 \times 10^{-14}$
1Os: M = Os(bpy)2; $D_eC_M^2 = 0.71 \times 10^{-14}$



3Ru: M = Ru(bpy)2; $D_eC_M^2 = 0.18 \times 10^{-14}$
3Os: M = Os(bpy)2; $D_eC_M^2 = 1.2 \times 10^{-14}$



2Ru: M = Ru(bpy)2; $D_eC_M^2 = 32 \times 10^{-14}$
2Os: M = Os(bpy)2; $D_eC_M^2 = 5.8 \times 10^{-14}$



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The synthesis and characterization of the metallopolymers discussed here as well as details of the electron transport measurements have been described elsewhere.[17-20] A variety of techniques have been used for the electron transport measurements, and these are compared in detail in ref.[17]. Results are expressed as $D_eC_M^2$ values, where D_e is the effective diffusion coefficient for electron transport and C_M is the concentration of metal centres, since it is difficult to accurately determine C_M. It is assumed in the discussion that variations in C_M between materials are small relative to the variations in D_e.[19]

Results and Discussion

Effect of the Polymer Backbone. The structures of the polymers discussed here are shown as Structures **1-3** (bpy = 2,2'-bipyridine) together with $D_eC_M^2$ values (in mol^2 cm^{-4} s^{-1}). In polymers **1** and **2** the metal is complexed to a conjugated backbone, and so these polymers exhibit enhanced electron transport rates relative to the non-conjugated reference materials, **3**. The role of the HOMO of the conjugated backbone in enhancing electron transport is illustrated in Figure 1, where electron transport rates are plotted as a function of the estimated energy gap between the metal d orbitals and the HOMO of the polymer. These energy gaps were estimated from the difference between the M(III/II) formal potential and the formal potential for oxidation of the polymer backbone.[18,20] The latter was estimated to be ≥ 2.2 eV for **1Ru** and **1Os**.[21]

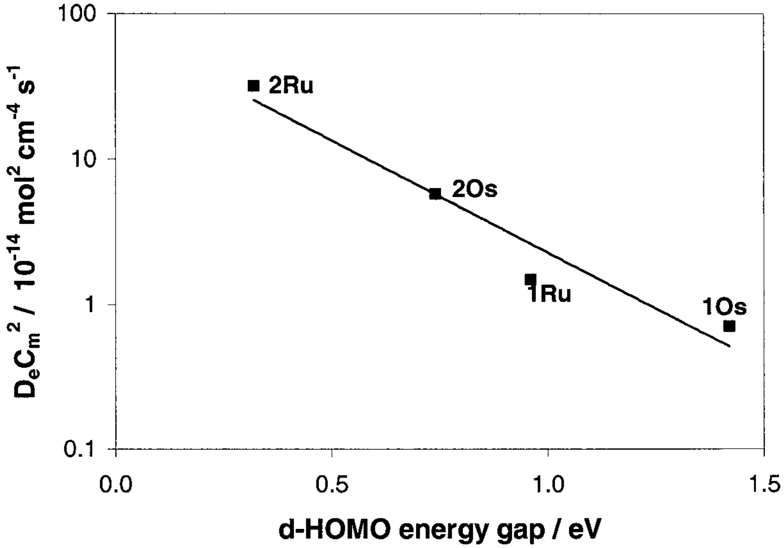

Figure 1. Electron transport rate as a function of the estimated energy gap between the metal d orbitals and the HOMO of the polymer.

The data in Figure 1 show that the electron transport rate increases greatly as the d-HOMO energy gap is decreased. Data for the two different types of polymer (polybenimidazole or poly(bithiophene-co-bithiazole)) fit an exponential relationship quite well. As illustrated in Figure

2, hole-type superexchange involves the bridging ligand's HOMO and is therefore enhanced by decreasing the d-HOMO gap. The data in Figure 1 therefore strongly implicate the involvement of a hole-type superexchange process in electron transport in these materials. There is evidence that electron-type superexchange becomes dominant for Os-benzimidazole polymers.[22]

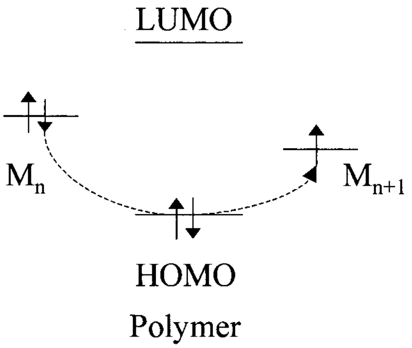

Figure 2. Schematic diagram of hole-type superexchange.

The enhanced electron transport rates observed for the conjugated polymers **1** and **2** could be explained by mediation of electron transfer between metal centres by the conjugated backbone. The distinction between this and a superexchange mechanism is subtle,[12] depending on whether there is an intermediate state in which the hole (for hole-type mediation) is located on the polymer backbone.

Arguments against the dominance of a mediated mechanism for polymers **1** and **2** have been made elsewhere.[17,19] However, there are cases in which mediation is the dominant charge transport process, and it is relevant to discuss them here.

Zotti et al[23] have shown that electron transfer rates between metal sites in polythiophenes with pendant ferrocene moieties are enhanced when a conjugated linkage is used. Ochmanska and Pickup[24] have explored the effect of copolymerization of $[Ru(2,2'\text{-bipyridine})_2(3\text{-}\{\text{pyrrol-1-ylmethyl}\}\text{pyridine})_2]^{2+}$ (**4**) with 3-methylthiophene on its electron transport properties. The homopolymer of the complex shows no electrochemistry or conductivity due to the pyrrole moieties, while copolymerization with 3-methylthiophene generates redox waves and conductivity due to oligo-thiophene linkages. Moreover, these conjugated linkages enhance the rate of electron transfer between Ru centres by mediation. Superexchange is not possible because of the saturated linkage between the complex and the conjugated linkages. A particularly important finding from this work, in the present context, was that mediation of electron transport between Ru sites was accompanied by a distortion from the normal wave-shape for redox conduction. This therefore appears to be a useful diagnostic for mediated electron transport. The fact that it is not observed for polymers **1** and **2** (i.e. that $D_eC_M^2$ is not potential dependent) provides strong evidence that they do not exhibit significant mediated electron transport.

Effect of the Metal. It is very significant that for the conjugated polymers **1** and **2** $D_eC_M^2$ values are higher for the Ru complex than for the Os complex, while this is reversed for the non-conjugated polymer **3**. This is consistent with domination of the charge transport rate by hole-type superexchange for the conjugated polymers, and outer sphere electron transfer for **3**. The higher redox potential of Ru relative to Os causes a decrease in the d-HOMO energy gap, and therefore enhances hole-type superexchange. On the other hand, the larger Os centre enhances the rate of outer sphere electron exchange.[25]

Effect of pH. A dinuclear complex based on the structure of polymer **1Ru** has been shown to exhibit enhanced superexchange when deprotonated.[26] The imidazole of polymer **1Ru** has a pK_a of 5.5, and its deprotonation produces changes in electrochemistry and electronic absorption similar to those seen for the dinuclear complex.[17] It also leads to a significant increase in the electron transport rate of the polymer,[17] consistent with dominance of electron transport by superexchange. Deprotonation of the Os polymer, **1Os**, causes a decrease in $D_eC_M^2$, suggesting that electron-type superexchange is dominant in this case.[20]

Degradation of the Polymer Backbone. The role of a conjugated polymer backbone can be exposed by disruption of the conjugation. This can conveniently be achieved by brief exposure of the polymer to potentials that are sufficiently high to cause overoxidation, which involves nucleophilic attack of the conjugation pathway by water or other species.[27]

The electron transport rate of **1Ru** was found to decrease with time at high potentials, indicating that it was enhanced by the conjugated backbone.[17] This phenomenon was investigated in much more detail for **2Ru** and **2Os**.[19] For the Os polymer, the potential at which disruption of conjugation begins is much higher than the redox potential of the Os, and so $D_eC_M^2$ values could be compared before and following complete disruption of the conjugation. A decrease of a factor of 7 was observed, indicating that the conjugated backbone plays a major role in electron transport. For **2Ru**, the Ru oxidation and polymer overoxidation processes overlap, and so $D_eC_M^2$ decreases while it is being measured (as for **1Ru**[17]). Full disruption of conjugation resulted in a ca. 7 fold decrease, again indicating that the conjugated backbone is responsible for the extremely high electron transport rates observed for **2Ru**.

Conclusions

The combined evidence for a superexchange electron transport mechanism for polymers **1-2** is very strong. Electron transport is fastest in the Ru complexes and involves a hole-type mechanism. The highest rates are obtained by minimizing the energy gap between the Ru d orbitals and the HOMO of the polymer. An electron-type mechanism may dominate for some Os complexes (e.g. **1Os**).

Acknowledgements

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