A conjugated polymer/redox polymer hybrid with electronic communication between metal centres

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Enhanced electrochemical charge transport rates in a conjugated metallopolymer formed by complexation of $[Ru(2,2'\text{-}bpy)_2]^{2+}$ moieties to donor N-atoms in the backbone of a benzimidazole-based polymer provide strong evidence for electronic communication between metal centres.

In the study of electrodes coated with electroactive polymers,[1,2] a clear distinction has been made between 'conducting polymers' whose redox sites are delocalised over a conjugated π system, and 'redox polymers' which have localised redox sites. Although redox polymers based on transition-metal complexes have many potential advantages in applications such as electrocatalysis and electronic devices, the development of commercial applications has been much more successful for conducting polymers.[3,4] There could therefore be significant opportunities for the exploitation of transition-metal centres in conducting polymers. Indeed, there has been much work in this area,[5] but in most cases the complex has been electronically isolated from the conjugated polymer backbone by saturated linkages. The few examples which involve direct electronic interaction between the conjugated polymer and the complex have demonstrated novel electronic, electrochemical and catalytic properties.[6–10]

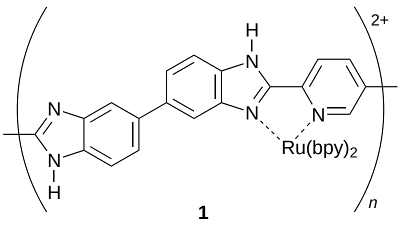
We report here a benzimidazole-based conjugated polymer with coordinated $Ru(bpy)_2^{2+}$ moieties (**1**, bpy = 2,2′-bipyridine). The Ru redox centres are coordinated to nitrogen atoms in the conjugated backbone of the polymer, providing direct electronic communication between the complex and the polymer. Work on an analogous binuclear complex (**2**) has indicated that there is a weak electronic interaction between adjacent Ru centres, which can be increased by removal of the imidazole proton.[11] These interactions are manifested most strikingly in polymer **1** by a high, pH-dependent electron transport rate.

Polymer **1** was prepared following standard literature procedures for the preparation of polybenzimidazoles[12] and $[Ru(bpy)_2L]^{2+}$ complexes[13] (glycerol was used as the solvent for complexation). Gel permeation chromatography indicated that the molar mass of the ruthenium-complexed polymer was > 50 000 g mol^{-1}. Elemental analysis indicated that *ca.* 60% of the bidentate pyridine–benzimidazole sites were occupied. Polymer films were deposited on Pt disc electrodes by evaporation of acetonitrile–water (12 : 1).

Fig. 1 shows cyclic voltammograms of a film of **1** in acetonitrile containing acid or base. The formal potentials are close to values reported for the dimer complex **2**. The shift in potential with increasing pH is due to deprotonation of the imidazole ring.

Fig. 2 shows complex impedance plots for similar films in basic (*a*) and acidic (*b*) electrolyte solutions. In each case the impedance was measured at the formal potential. These impedance data are typical for a redox polymer film on an electrode and the electron diffusion coefficient (D_e) can be obtained from the difference between the high-frequency intercept (R_{high}) and the low-frequency limiting real impedance (R_{low}): $D_e = d^2/[3(R_{low} - R_{high})C_{lf}]$, where d is the film thickness and C_{lf} is the low-frequency capacitance.[14] Values of d were obtained from the surface coverage, determined from a slow voltammogram, using a ruthenium site concentration of 1.6 m based on the dry density of similar materials.[15] Although this concentration is an estimate, it does not compromise the validity of our conclusions because (*a*) it is the same value used to obtain D_e values for the comparison material, poly-$[Ru(bpy)_2(vpy)_2]^{2+}$ (vpy = 4-vinylpyridine),[16] and (*b*) it is unlikely to be significantly overestimated, since the Ru site concentration in a $[Ru(bpy)_3][PF_6]_2$ crystal is only 1.75 m.[17] D_e values obtained from impedance measurements on **1** in acidic and basic acetonitrile were 6×10^{-9} and 1×10^{-8} cm^2 s^{-1}, respectively. For comparison, D_e for poly-$[Ru(bpy)_2(vpy)_2]^{3+/2+}$ in acetonitrile is *ca.* 7×10^{-10} cm^2 s^{-1}.[16]

In both acidic and basic media, electron transport is significantly faster in **1** than in poly-$[Ru(bpy)_2(vpy)_2]^{3+/2+}$, suggesting enhanced electronic communication between Ru centres. D_e is higher in the basic solution than in the acidic solution, consistent with the known increase in electron



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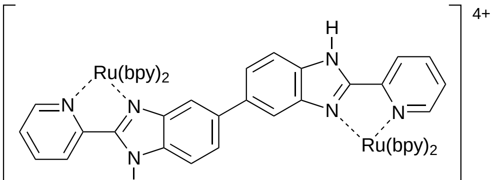

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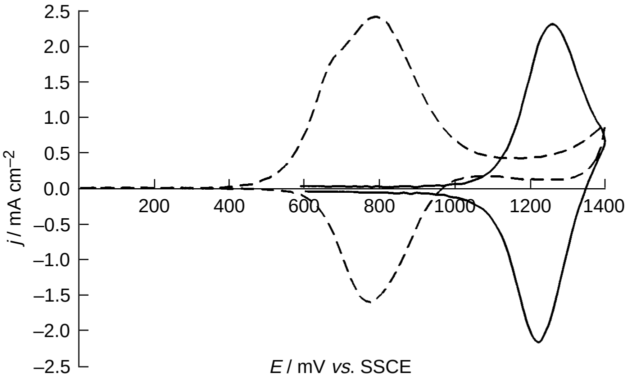

Fig. 1 Cyclic voltammograms (100 mV s^{-1}) of a Pt electrode (0.0052 cm^2) coated with a thin ($\Gamma_{Ru} = 3.6 \times 10^{-8}$ mol cm^{-2}) film of **1** in 0.1 m NEt_4ClO_4–MeCN containing *ca.* 5 mm NBu_4OH (---) or *ca.* 50 mm $HClO_4$ (—)

delocalization between Ru centres connected by a benzimidazole bridge.[11] Furthermore, D_e values for **1** were found to decrease with time spent at high potentials in the basic electrolyte (*i.e.* during impedance measurements or cyclic voltammetry), consistent with the expected deactivation (overoxidation) of the conjugated polymer backbone.[18] As far as we know, the D_e value obtained for **1** in basic acetonitrile is the highest value yet reported for a Ru–bpy based redox polymer.[19]

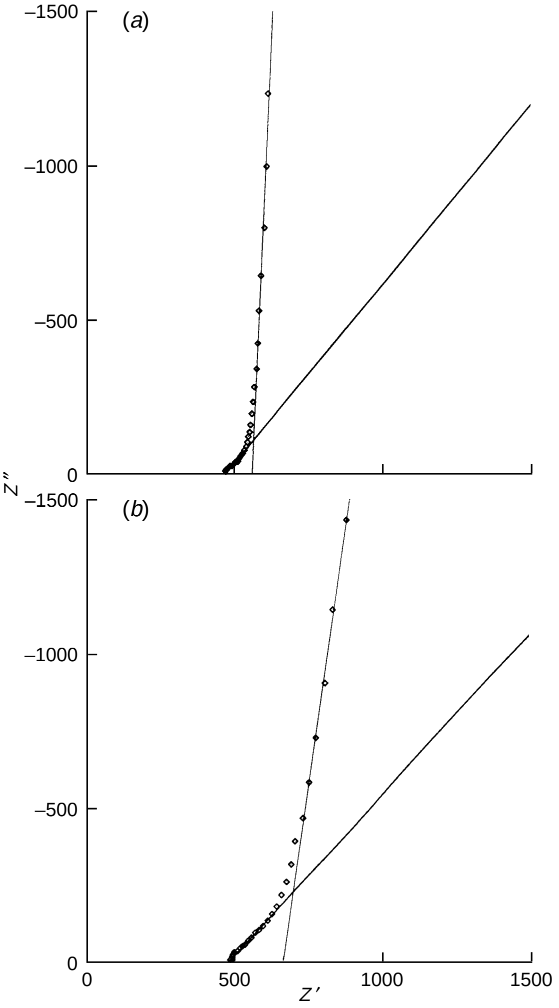

Fig. 2 Complex plane impedance plots for Pt electrodes (0.0052 cm^2) coated with thin films of **1** in 0.1 m NEt_4ClO_4–MeCN containing (*a*) *ca.* 5 mm NBu_4OH (Γ_{Ru} = 1.5 × 10^{-8} mol cm^{-2}) or (*b*) *ca.* 50 mm $HClO_4$ (Γ_{ru} = 1.4 × 10^{-8} mol cm^{-2}). Lines show extrapolations to the real axis intercepts, R_{high} and R_{low}.

These results provide conclusive evidence that the conjugated polybenzimidazole backbone of **1** is involved in electron transfer between Ru sites. Since the Ru-free polymer does not exhibit electrochemical activity in the potential region of the Ru formal potential in either medium studied, electron transport is presumably facilitated by an electronic interaction between metal centres through the polymer backbone, rather than by hopping *via* the polymer backbone. This type of long-range, multi-metal centre interaction could provide the basis for useful electrocatalytic and electronic materials.

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