

Modulation of Heterogeneous Electron Transfer Dynamics: Osmium Bis-Bipyridyl Triazole Monolayers

Darren A. Walsh, Tia E. Keyes, Robert J. Forster
National Centre for Sensor Research
Dublin City University
Ireland

Direct modulation of bridge-mediated electron transfer dynamics has wide-ranging implications, from sensor development to understanding biological electron transfer reactions. The structure of the bridging ligand between electron donor and acceptor moieties can drastically affect the rate of electron transfer. An important goal is to develop systems in which the bridge structure can be reversibly altered by a change in the local microenvironment, so as to modulate the rate of electron transfer. These systems can provide an insight into the role of bridge electronic levels in mediated electron transfer reactions.

In this contribution, we report on the formation of spontaneously adsorbed monomolecular films of $[\text{Os}(\text{bpy})_2 \text{4-bpt Cl}]\text{PF}_6$, where bpy is 2,2'-bipyridyl and 4-bpt is 3,5-bis(pyridin-4-yl)-1,2,4-triazole, at platinum microelectrodes (Figure 1). Monolayers of this complex are highly stable over a wide range of pH values ($1.0 < \text{pH} < 12.0$) and exhibit remarkably ideal voltammetric responses (Figure 2). The 4-bpt bridge is electroactive and is capable of undergoing a protonation/deprotonation reaction depending on the pH of the contacting electrolyte solution. Probing the pH dependence of the interfacial capacitance reveals that the surface pK_a of the 4-bpt ligand is 7.0 ± 0.6 . This value differs from that found in solution and may be due to partial solvation of the adsorbates within the monolayer.

High speed chronoamperometry has been used to probe the rate of electron transfer across the electrode/monolayer interface. Significantly, upon protonation of the 4-bpt bridge, the standard heterogeneous electron transfer rate constant, k^0 , decreases from 1.60×10^6 to $1.9 \times 10^5 \text{ s}^{-1}$ for the reduction process and from 2.67×10^6 to $4.5 \times 10^4 \text{ s}^{-1}$ for the oxidative process.

Electron rich bridging ligands of this type have previously been shown to support superexchange mechanisms.¹ Electron superexchange may be the dominant mechanism if the LUMO of the bridge is close in energy to the metal $d\pi$ orbitals of the remote redox centre. In contrast, if the HOMO of the bridge is closer in energy to the metal $d\pi$ orbitals, hole superexchange may be the dominant mechanism. Protonation of the 4-bpt bridging ligand in this monolayer system decreases the electron density on the ligand, making it harder to oxidise and easier to reduce the bridge. This will cause the formal potential of the HOMO and LUMO of the bridge to shift in a positive potential direction, increasing the metal $d\pi$ -HOMO separation. This is illustrated in Figure 3. The *increased* energy gap between the metal $d\pi$ orbitals and the bridge HOMO causes an overall *decrease* in the rate of electron transfer. Therefore, it appears that the bridge mediated redox reaction occurs via a hole superexchange mechanism.

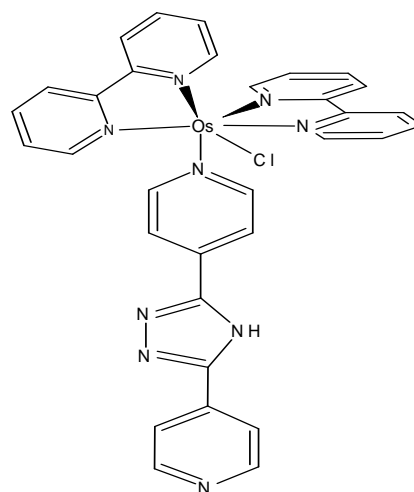


Figure 1 Structure of $[\text{Os}(\text{bpy})_2 \text{4-bpt Cl}]\text{PF}_6$

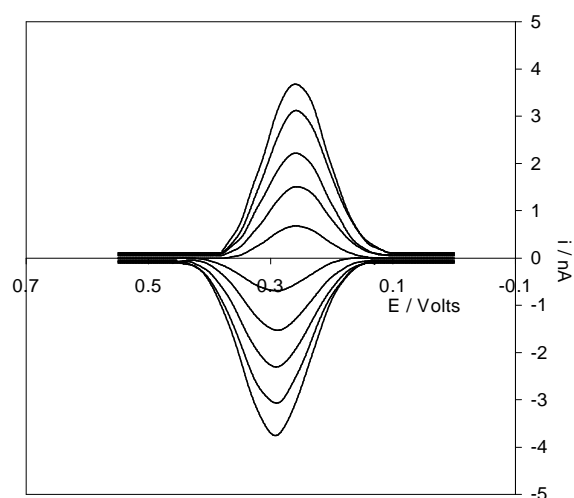


Figure 2 Voltammetric response of monolayers of $[\text{Os}(\text{bpy})_2 \text{4-bpt Cl}]\text{PF}_6$ at varying scan rates. Scan rates are (from top to bottom) 2.0, 1.6, 1.2, 0.8 and 0.4 V s^{-1} . The radius of the platinum microelectrode is 25 μm . The supporting electrolyte is 0.1 M LiClO_4 .

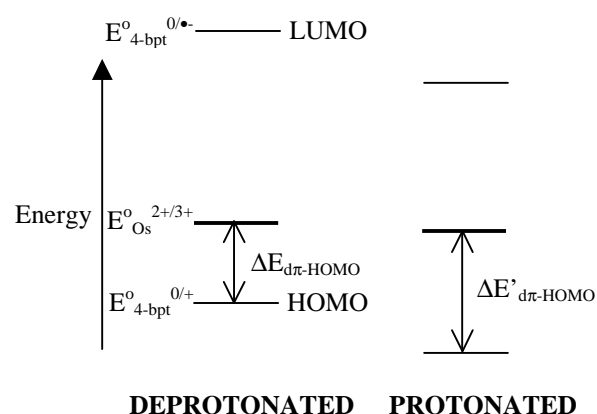


Figure 3 Proposed effect of protonation of the 4-bpt bridging ligand on hole superexchange.

REFERENCES

- 1 Barigelletti, F., De Cola, L., Balzani, V., Hage, R., Haasnoot, J. G., Reedijk, J., Vos, J. G., *Inorg. Chem.*, **1991**, *30*, 641.