

Research Interests: Electrochemistry, modified electrodes, electrocatalysis, solar energy conversion, coordination compounds, conducting polymers, redox polymers



The aim of our research is to understand molecular and materials redox reactions of both fundamental and technological relevance. We are seeking to prepare novel sensors and devices by chemical modification of the electrode surface with monolayers or multilayers (polymers and redox-active inorganic materials). The synthetic aspect of the work is crucial as it allows the redox properties to be carefully tuned to the application in mind.

### Luminescent Polymers

In recent years there has been a revolution in organic display devices with the discovery that polyphenylene vinylene (PPV) conjugated polymers are efficient emitters of light in LED-type thin-film devices. Two aspects are being addressed in this project: (i) the effect of bulky substituent groups and/or physical separation of the polymer chains on the luminescence efficiency; (ii) the enhancement of luminescence efficiency through energy transfer to metal complexes tethered to the polymer chain. The latter work involves innovative synthesis of ligand-bearing monomers which are coupled by efficient routes such as Suzuki coupling. We are also using modern living polymerisation methods to synthesise soluble block copolymers. This work is in collaboration with the Organic Semiconductor Centre here in St Andrews which is fully equipped for polymer and device characterization.[Ref. 1]

### Conducting polymer and redox-polymer electrodes

The luminescent polymers described above are also electroactive, and their redox properties are highly relevant to device function. Redox properties are also fundamental to the understanding of ferromagnetic and electrochromic polymer properties. In addition, some of these polymers may be grown electrochemically. All these polymers lend themselves well to characterisation using electrochemistry, spectroelectrochemistry, EPR and magnetic susceptibility methods[Ref 2]. An amperometric adenosine sensor based on a novel operating principle involving the use of a cascade of three enzymes has been miniaturised using conducting polymer immobilisation techniques. This should vastly extend its capabilities, particularly for the monitoring of adenosine uptake in the muscles of small animals and in patients with spinal injuries.[Ref 3]

### Metal Complexes in Redox Catalysis and Materials

Metal complexes which are robust in several oxidation states have been examined as electrocatalysts, dye sensitizers for solar cells and electrochromic materials. These include Ru and Os complexes of chelating ligands and Ni and Co macrocyclic complexes. The properties are studied using the latest electrochemical and spectroelectrochemical methods.[Refs 4 and 5] In collaboration with Dr Mark Muldoon and Dr NP Botting we are developing a research programme in the electrosynthesis of organic compounds in ionic liquids using metal complexes as redox catalysts. Ionic liquids are attractive electrolytes since they are sufficiently conducting that no added salts are necessary, and they are also non-volatile, simplifying separation of the electrogenerated products

### Representative Publications

1. *Effect of meta-linkages on the photoluminescence and electroluminescence properties of light-emitting polyfluorene alternating copolymers*, J. Ritchie, J. A. Crayston, J.P.J. Markham and I. D. W. Samuel, *J. Mater. Chem.*, **2006**, 16, 1651.
2. *Electrochemical Deposition of Poly(trans-[RuCl<sub>2</sub>(4-vinylpyridine)<sub>4</sub>]) and its Reductive Desorption: Cyclic Voltammetry and Electrochemical Quartz Microbalance Studies* Merlin C.E. Bandeira, Joe A. Crayston, Andrew Glidle and César V. Franco, *Phys. Chem. Chem. Phys.*, **2007**, 9, 1003-1012.
3. *A three-enzyme microelectrode sensor for detecting purine release*, E. Llaudet, N.P. Botting, J.A. Crayston, N. Dale, *Biosensors & Bioelectronics* **2003**, 18, 43.
4. *Ruthenium Complexes of 2-(2-Pyridyl)benzimidazole as Photosensitisers for Dye-Sensitized Solar Cells*, H. Yi, J. A. Crayston, J.T.S. Irvine, *J. Chem. Soc., Dalton Trans.* **2003**, 685.
5. *A SERRS spectroscopic investigation of nickel(II) porphyrin complexes adsorbed at electrochemical interfaces* B. D. Alexander, J. A. Crayston and T. J. Dines, *Phys. Chem. Chem. Phys.*, **2004**, 6, 3576.