This proposal is representative of the projects currently on offer in our group. For more details of active research projects, please visit our webpage at: http://www.chem.leeds.ac.uk/People/Halcrow.html

**Metal Complexes of Radical Ligands – Electron Hopping Leading to Novel Optical Properties**

This project involves the synthesis, electrochemistry and host-guest chemistry of metal complexes of redox-active ("non-innocent") ligands.[1]

We are investigating metal complexes containing multiple redox-active organic ligand centres, with a view to producing a new class of mixed-valent molecules and materials. An example is cyclotricatechylene, a cyclic molecule containing three covalently linked catecholate groups that can each bind a metal ion.[2] The platinum complex in the Figure exhibits three reversible low-potential oxidations in its cyclic voltammogram, corresponding to step-wise oxidation of its three catecholate groups to semiquinone radical centres:

The radical oxidation products have intense colours, with strong absorptions in the visible and near-IR regions. This reflects the hopping of unpaired electrons around the macrocycle, between aromatic rings.[2,3] Near-IR absorbers like these, whose absorptions can be switched on and off electronically, can be very useful in fibre-optic communications devices.

Current work aims to add more steric protection to these ligand radicals, to improve their stability at room temperature,[3,4] to incorporate these radicals into extended framework ("MOF") structures with similar electron-hopping properties; and, to design new ligands with different numbers and topologies of redox centres. This project involves organic and inorganic synthesis, crystallography, electrochemistry and other techniques for studying radical products (EPR, UV/vis/NIR and IR spectroscopies, magnetic measurements and DF calculations).

Please contact Prof Malcolm Halcrow (m.a.halcrow@leeds.ac.uk) for further details about this opportunity.

**References**