

## Professor Malcolm Halcrow

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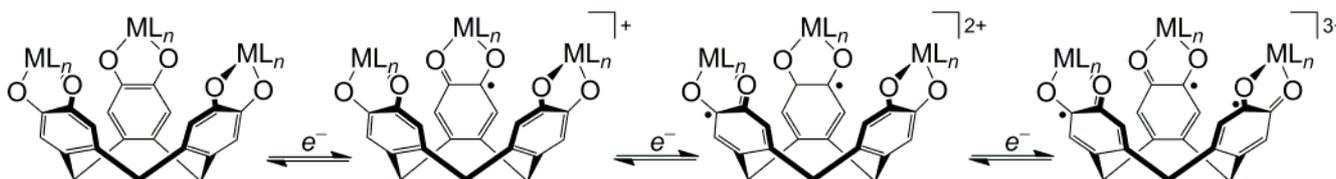
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### Metal Complexes of Radical Ligands – Electron Hopping Leading to Novel Optical Properties

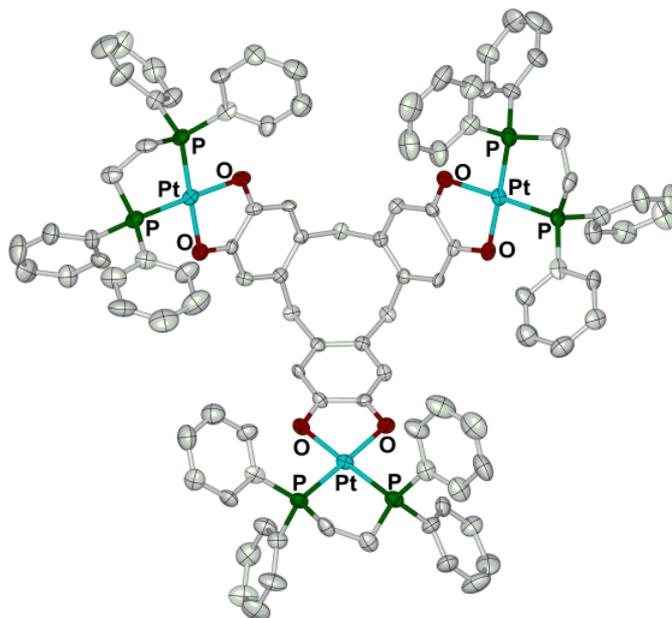
This project involves the synthesis, electrochemistry and host:guest chemistry of metal complexes of redox-active (“non-innocent”) ligands.<sup>[1]</sup>

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 catechol groups that can each bind a metal ion.<sup>[2]</sup> The platinum complex in the Figure exhibits three reversible low-potential oxidations in its cyclic voltammogram, corresponding to step-wise oxidation of its three catechol 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.<sup>[2,3]</sup> 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;<sup>[3,4]</sup> 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).



Crystal structure of a platinum/phosphine complex containing three linked catechol centres.<sup>[2]</sup>

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

### References

1. W. Kaim, ‘Manifestations of noninnocent ligand behavior’, *Inorg. Chem.*, **2011**, *50*, 9752–9765.
2. J. J. Loughrey, N. J. Patmore, S. Sproules, M. A. Halcrow *et al*, ‘Platinum(II) complexes of mixed-valent radicals derived from cyclotricatechylene, a macrocyclic tris-dioxolene’, *Chem. Sci.*, **2015**, *6*, 6935–6948.
3. J. J. Loughrey, S. Sproules, E. J. L. McInnes, M. J. Hardie and M. A. Halcrow, ‘Stable mixed-valent radicals from platinum(II) complexes of a bis-dioxolene ligand’, *Chem. Eur. J.*, **2014**, *20*, 6272–6276.
4. S. Greatorex and M. A. Halcrow, ‘Highly porous hydrogen-bond networks from a triptycene-based catechol’, *CrystEngComm*, **2016**, *18*, 4695–4698.