

## 8.2 Dr A C Benniston, Molecular Photonics Laboratory, Newcastle University *Directed Electron Transfer*

A comprehensive understanding of electron-transfer processes is essential for further progress in many fields of chemistry, biology, physics and biochemistry. The diversity of research dependent on electron-transfer processes spans from biological enzymes to opto-driven devices, and requires an in-depth knowledge of how electrons and/or holes move through a wide variety of materials. Molecular-based assemblies, constructed to act as artificial mimics by which to probe electron-transfer events, have been widely explored. These systems generally comprise electron donor and acceptor subunits connected via an organic spacer unit. This linking group has the dual role of providing a structural scaffold for the electro-active terminals and acting as a conduit for the rapid and efficient transfer of electronic information along the molecular axis. There have been many different spacers proposed for use in concurrence with through-bond electron transfer or electron exchange. The dynamics of information transfer along these molecular spacers (i.e. wires) is very much dependent on their chemical composition; for example, the hybridisation state of any connecting carbon units. In directly fused aromatic units (e.g., phenyl, thiophene, pyrrole), electronic coupling along the poly(aryl)-based molecular wire would be expected to be modulated by the mutual orientation of adjacent aryl rings. Rapid transfer is predicted for the case where all the rings are aligned in a coplanar geometry, but transfer will be seriously impaired if several rings are held in a mutually orthogonal orientation. The ability to manipulate the relative orientation of rings offers a fascinating means by which to control or gate the electron flux, which in principal could be used to direct information along predetermined pathways.

An alternative strategy to manipulate the flow of information along a molecular axis spanning some 100 Å or so, is to utilise the rather disparate chemistry that can be attained from different types of excited states or from similar states of very different energy. The basic concept here is to set up a competition between two possible chemical processes, for example these might be intramolecular energy or electron transfer steps (Figure 1), but many other pairs of light-induced reactions are possible. The goal now is to direct the chemistry along one particular direction by careful balancing of the entire system, by perturbation of one small part of the spacer unit or by changing the experimental conditions. The most elegant way to achieve such possibilities is to use different input photon frequencies such that dissimilar excited states are populated by excitation. Provided these states have unique properties it should be possible to drive either electron transfer to an adjacent acceptor or energy transfer to a relay followed by further electron transfer. The advantage of this latter method is that no conformational switching is required, this being an essential feature of most other procedures considered for directing information flow in molecular assemblies, which would require some form of external input (i.e., electrons, protons, ions). However, the design element for molecular arrays such as that outlined in Figure 1 is far more complex since all the individual components are required to play a precise role in promoting the requisite reactions.

During the past five years, we have been actively engaged in the examination of artificial neural networks, and have carried-out substantial studies along the themes outlined above. Many of these studies have centred around photoactive ruthenium/osmium poly(pyridine) complexes and on porphyrin-based arrays such as those shown in Figure 2. The EPSRC-funded Mass Spectrometry Service at Swansea has been heavily involved in the necessary identification of the molecular systems and their precursors.

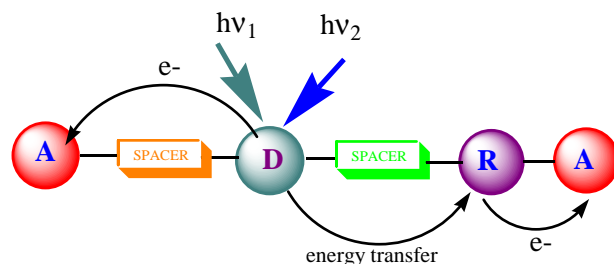


Figure 1

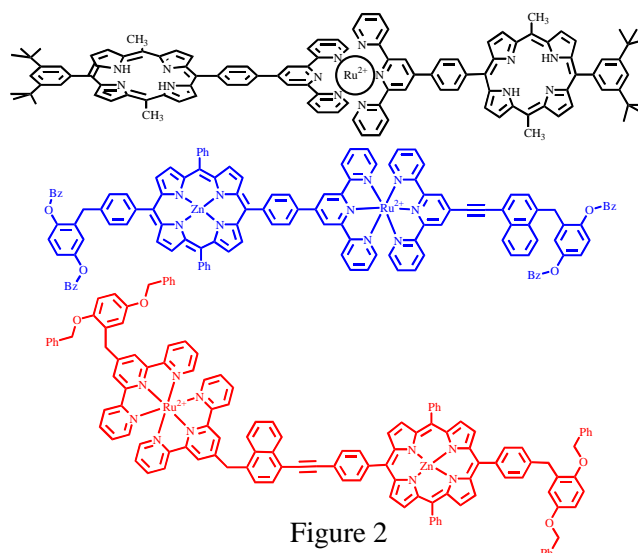


Figure 2

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