

Monday 19 September 2011

11.00 am - Room 531

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Understanding the interactions of charge-transfer and ligand-centred excited states in rhenium(I) complexes: a spectroscopic and theoretical study

Complexes incorporating dipyrido[3,2-a:2',3'-c]phenazine (dppz) and its derivatives have been the subject of extensive investigation because they possess interesting photophysical properties. One striking example of this is the observation that some dppz complexes exhibit a "light switch effect", being highly emissive in aqueous solution in the presence of DNA but non-emissive in aqueous solution. Theoretical and photophysical studies suggest that the excited states of Re(I) complexes with dppz-type ligands contain closely lying ligand centered (LC) and metal-to-ligand charge-transfer (MLCT) states of differing orbital parentage. In dppz the lowest lying unoccupied MOs may have phenanthroline character, $b_1(\text{phen})$, in which the wavefunction amplitude is predominantly across the A, B and C rings (Fig. 1) or phenazine character, $b_1(\text{phz})$, in which the amplitude is on the B, D and E rings. We have investigated dppz-based ligands in which differing sulfur-bearing substituents are appended; this results in significant modifications to the electronic structure of both the ligands and their complexes. These features are analyzed using density functional theory (DFT) calculations, resonance Raman spectroscopy and excited state electronic absorption and infrared techniques. These systems possess charge-transfer states in which both ligand and metal act as donors.

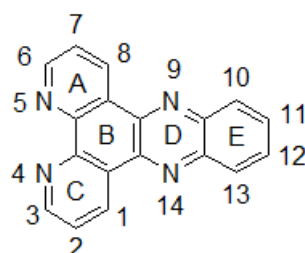


Figure 1. Dppz ligand structure with ring labels and numbering