

DETERMINATION OF THE EXCITED STATE STRUCTURE OF POLYPYRIDYL COMPLEXES USING TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY AND DENSITY FUNCTIONAL THEORY.

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Keywords: polypyridyl complexes, MLCT excited state, DFT, transient resonance Raman, spectroelectrochemistry

Abstract: Structural changes in polypyridyl complexes, on going to metal-to-ligand charge-transfer (MLCT) excited states, are probed using computational chemistry in conjunction with Raman spectroscopy. For the complexes containing the ligand dipyrido[2,3-a:3',2'-c]phenazine (ppb) there are very small structural changes on population of MLCT states.

Polynuclear metal complexes with bridging polypyridyl ligands have considerable utility as photocatalysts and as multi-electron transfer agents. The active species in many of these cases are MLCT excited states and redox states respectively. We have studied dipyrido[2,3-a:3',2'-c]phenazine (ppb) and some of its analogues (Fig. 1). Complexes with ppb show very interesting excited state properties that are attributed to the rigid structure of the ligand and the small coordinate displacements on going from ppb to ppb⁻. [1]

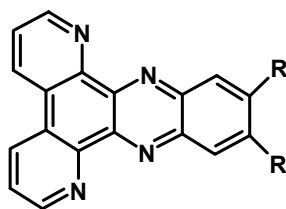


Fig. 1. Structure of ppb (R=H). The substituted analogues: ppbCl₂ (R=Cl) and ppbMe₂ (R=CH₃) have also been studied.

Density functional theory (DFT) calculations have been shown to be effective in modelling the vibrational spectra and structure of polypyridyl ligands and their radical anions.[2,3] We have used computational methods to interpret the spectral features of the ground state complexes and their MLCT excited states.

The structure of ppb and ppb⁻ were calculated using DFT (B3LYP/6-31G(d)). Reduction of ppb can be used as a model to determine structural changes that occur upon forming an MLCT excited state of ppb complexes. The structural differences between the neutral ligand and radical anion are relatively small; notably the phenazine ring shows rather small perturbations of the CC linkages across the ring. The excited state structure of Ru(II) complexes of ppb have also been modelled (B3LYP functional with the LANL2DZ and 6-31G(d) basis sets). Transient Raman spectra of Ru(II) complexes with ppb have been measured and analysed in comparison to the calculated spectra. Raman spectroelectrochemistry of Cu(I) ppb complexes is also used to experimentally obtain ppb⁻ features.

The ground state resonance Raman spectrum of [Ru(bpy)₂(ppb)]²⁺ (bpy=2,2'-bipyridine), Fig. 2(a), shows enhancement of bpy and ppb modes through their respective MLCT transitions. Pulsed laser excitation, Fig. 2 (b) and (c), results in spectral changes in which the bpy bands are reduced in

intensity, the 1522, 1259 and 1210 cm^{-1} ppb bands are bleached and new features appear at 1420, 1291 and 1232 cm^{-1} . These are attributed to ppb^- .

The ground state resonance Raman spectrum of the complex, $[\text{Cu}(\text{PPh}_3)_2(\text{ppb})\text{Cu}(\text{PPh}_3)_2]^{2+}$, Fig. 2(e), shows enhancement of ppb modes. Electrochemical reduction of the copper complex results in a resonance Raman spectrum, Fig. 2 (d), that differs from the parent complex – we attribute this to the ppb^- features. These may be compared to the calculated radical anion bands; those predicted at 1588, 1577, 1452, 1347, 1311 1277 and 1192 cm^{-1} are observed at 1594, 1576, 1466, 1341, 1310, 1266 and 1197 cm^{-1} in the reduced copper(I) complex. These bands appear in the transient resonance Raman spectrum of $[\text{Ru}(\text{CN})_4\text{ppb}]^{2-}$.

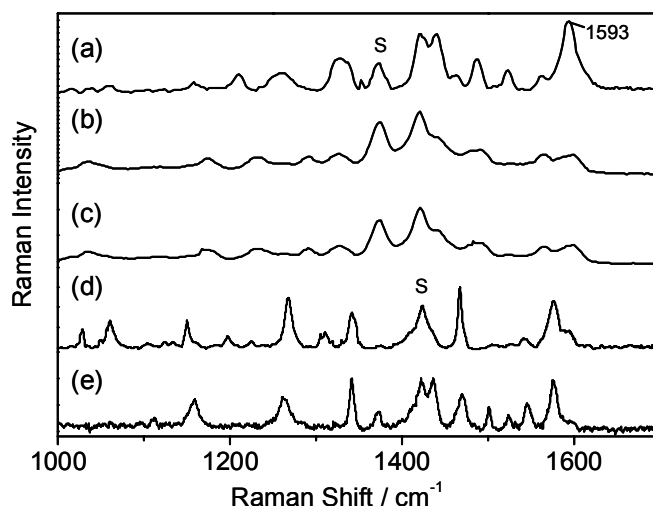


Figure 2. Resonance Raman spectra of: $[\text{Ru}(\text{bpy})_2(\text{ppb})]^{2+}$ MeCN (a) 356.4 nm CW excitation, (b) 354.7 nm pulsed excitation, 4 mJ per pulse, (c) 354.7 nm pulsed excitation, 1 mJ per pulse, and (d) $[\text{Cu}(\text{PPh}_3)_2(\text{ppb})\text{Cu}(\text{PPh}_3)_2]^+$ CH_2Cl_2 514 nm CW excitation, (e) $[\text{Cu}(\text{PPh}_3)_2(\text{ppb})\text{Cu}(\text{PPh}_3)_2]^{2+}$ 514 nm CW excitation.

The structure of the radical anion species may be calculated and compared to experimental data.[4] These show that a number of bands are very similar in frequency across the series as they represent modes in which the dominant bond length distortions for the normal modes are unaffected by reduction. The spectral variation across the series suggests that the singly occupied molecular orbital for the radical anions is delocalised over much of the ligand. The calculated structure for the radical anion is very similar to that of the neutral ligand - this suggests why MLCT excited states from ppb are very long-lived. It may be possible to rationally design long-lived MLCT excited states utilising DFT calculations.

Acknowledgements:

Support from the The MacDiarmid Institute for Advanced Materials and Nanotechnology is gratefully acknowledged. SLH thanks the Foundation for Research Science and Technology for the award of a PhD scholarship.

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