

# Application of resonance Raman spectroscopy for a direct characterisation of the nature of the frontier orbitals in Pt(II) diimine acetylide complexes

R. D. Bennett, N. M. Shavaleev, I. V. Sazanovich and J. A. Weinstein

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

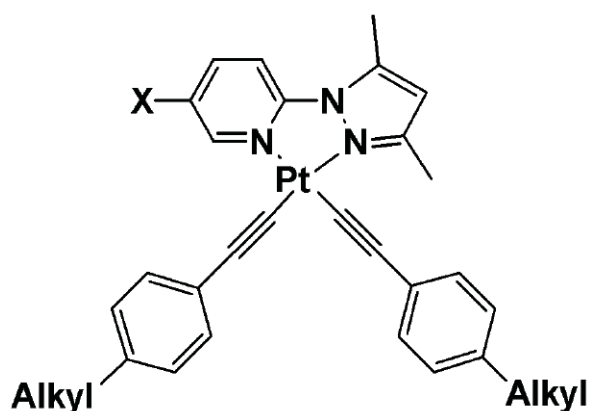
Contact | [Julia.Weinstein@Sheffield.ac.uk](mailto:Julia.Weinstein@Sheffield.ac.uk)

## Introduction

Photoinduced charge separation is at the heart of photosynthesis<sup>[1]</sup> and as such continues to attract much interest in attempts to mimic the process for artificial light energy harvesting.<sup>[2]</sup> Photoinduced charge separation occurs via the formation of a transient charge-separated excited state (CSS). In photosynthesis, the CSS triggers a cascade of dark electron transfer steps. This creates distant-separated ‘electron’ and ‘hole’ which are then engaged in catalytic redox processes. The central component of such systems is a Donor–Spacer–Acceptor module. The key to the efficient energy harvesting is the lifetime of the CS state. With greater understanding of the behaviour of the constituent parts, especially with respect to the frontier orbitals, it will be possible to design a longer lived CSS and efficient extended cascade systems.<sup>[3]</sup> One class of the Donor–Spacer–Acceptor models uses mixed ligand metal complexes, with the transition metal acting as ‘conducting spacer’. Diimine ligands are typical electron acceptors due to low-lying  $\pi^*$  orbitals. Acetylide ligands are strongly donating and hence can be used as electron donors in such assemblies (figure 1).

The nature of the HOMO in those systems is still a matter of debate. It is generally believed that the HOMO in such systems is predominantly localised on the Pt centre; although a significant contribution from the acetylide ligand is also mentioned.<sup>[4]</sup> The standard experimental technique for elucidating the nature of the frontier orbitals in transition metal complexes is UV/Vis/IR/EPR spectroelectrochemistry. However, this technique is not applicable for Pt(II) diimine acetylides because the first oxidation process of these complexes is irreversible.

Resonance Raman spectroscopy is another powerful tool to elucidate the nature of frontier orbitals, as it allows for a selective enhancement of those molecular vibrations that are coupled to the electronic transition of interest. Resonance Raman would be the method of choice to investigate electronic structure of Pt(diimine)acetylides because the  $\nu(\text{CC})$  of the acetylide ligand is strongly Raman active. However, strong emission typically emanated by Pt(II) diimine acetylide complexes precludes the use of resonance Raman spectroscopy.<sup>[5]</sup> To overcome this obstacle, we have prepared a series of Pt(II) complexes with pyridine-pyrazole acceptor ligand (figure 1). The compounds shown in figure 1 are much less emissive than the majority of Pt(II) diimine acetylides. The greatly reduced emission background enabled the first instance of



**Figure 1.** Model Pt(II) acetylide systems,  $\text{Pt}(5\text{-X-NN})(\text{-CC-Ph-CH}_3)_2$ , where NN = pyridine-pyrazole; X = H,  $\text{NO}_2$ , CN.

the use of resonance Raman spectroscopy for elucidation of the frontier orbitals in this class of compounds.

## UV/vis absorption spectra

The complexes studied have general formula  $\text{Pt}(5\text{-X-NN})(\text{-CC-Ph-CH}_3)_2$ , NN = pyridine-pyrazole, in which position 5 of the pyridine ring was modified with a different substituent X = H,  $\text{NO}_2$  and CN (figure 1). UV/Vis absorption spectra of  $\text{Pt}(5\text{-X-NN})\text{Cl}_2$  and their respective acetylide complexes (figure 2) demonstrate influence of both Cl vs. acetylide substitution, and the effect of the substitution in the pyridine ring. The absorption spectra of  $\text{Pt}(5\text{-X-NN})\text{Cl}_2$  are dominated by a strong somewhat structured band positioned at 272, 290, 305 nm for X = H, CN and  $\text{NO}_2$ , respectively. The shift to lower energies with an increase of electron acceptor ability of X indicates that this transition may have partial intra-pyridine-pyrazole charge transfer character. The lowest energy band, with much lower oscillator strength, also shifts to lower energies from 330 nm to 370 nm, and to 389 nm as electron acceptor ability of X increases. This band is tentatively assigned to the Metal-to-Ligand charge transfer transition, and, given the influence of X, it is assumed that the LUMO is at least partially localised on the pyridine ring of the pyridine-pyrazole ligand.

A substitution of Cl with acetylide ligand leads to the appearance of a new absorption band at lower energies, 370 nm (X=H), 390/420 nm (X = CN), and a broad manifold at  $>400$  nm for X= $\text{NO}_2$ . These bands are

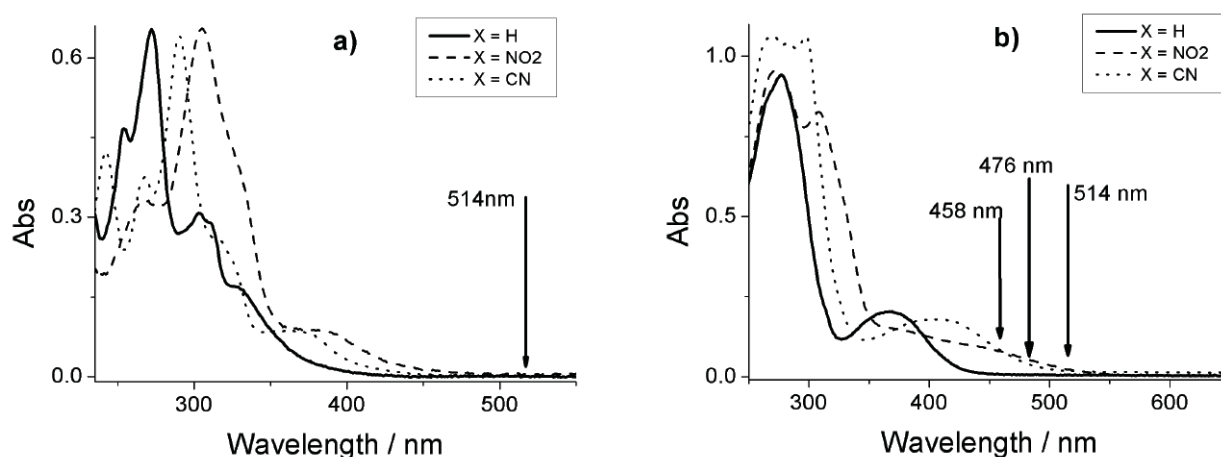


Figure 2. UV/vis absorption spectra for Pt(5-X-NN)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub> (b) and their respective chlorides (a) in CH<sub>2</sub>Cl<sub>2</sub>.

attributed to Ligand-to-Ligand Charge Transfer (LL'CT) transitions.

### Resonance Raman spectra

To investigate the nature of the HOMO and the LUMO, resonance Raman experiments were conducted with the energy of excitation in resonance with the lowest electronic transition.

**Pt(5-H-NN)Cl/Pt(5-H-NN)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub>.** Figure 3 shows the Raman spectra obtained for these complexes under 514.5 nm excitation. It should be noted that the 514.5 nm excitation is in pre-resonance with the lowest allowed electronic transition for both Cl and acetylide derivatives, and hence the resonance Raman data can be directly related to the nature of the lowest electronic transition in these complexes.

The spectrum of the Cl complex (black line, figure 3) shows several vibrations in the fingerprint region which are

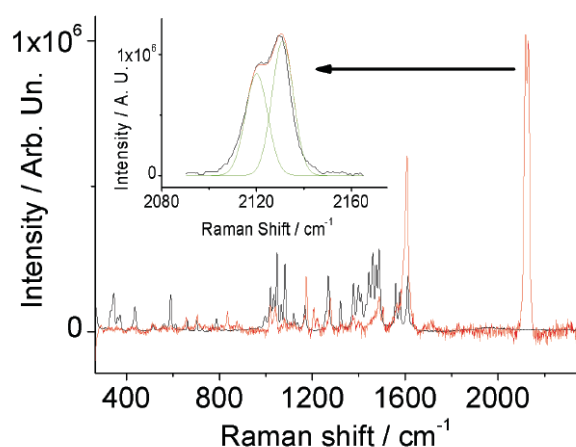


Figure 3. Resonance Raman spectrum for Pt(5-H-NN)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (red) and Raman spectrum of polycrystalline Pt(5-H-NN)Cl<sub>2</sub> (black) under 514.5 nm excitation. The inset shows Gaussian deconvolution of the acetylide band centred at ca. 2130 cm<sup>-1</sup>.

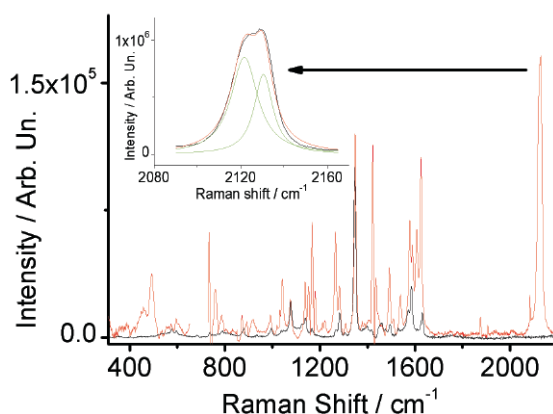
generally characteristic of coordinated diimine ligands. For example, the 1616 cm<sup>-1</sup> is typically assigned to ν(C=N) of the coordinated diimine. There is also a group of bands in the low frequency region, of which 434 cm<sup>-1</sup> vibration can be assigned to the ν(Pt-Cl) on the basis of literature data.<sup>[6]</sup> The presence of intra-diimine and Pt-Cl vibrations indicate that the 514.5 nm excitation is in resonance with an MLCT transition, supporting the initial interpretation of the UV/Vis spectra.

Substitution of the Cl ligand with acetylide leads to several changes in the resonance Raman spectrum (figure 3, red line).

- (i) The acetylide complex has a striking additional feature at 2130 cm<sup>-1</sup>. This is characteristic of an acetylide stretching vibration, and shows that the HOMO of the acetylide complex has significant acetylide character. Furthermore, the ν(C≡C) band is composed of two overlapping bands, at 2120 and 2131 cm<sup>-1</sup> (figure 3, inset). This is characteristic of symmetric and asymmetric combinations of the ν(C≡C) vibrations, and means the HOMO is delocalised over both acetylide ligands.
- (ii) Additional bands are observed at 1208/1222 cm<sup>-1</sup>. Those appear very similar to the bands present in the Raman spectrum of free Ph-C≡CH, and may indicate that the HOMO is delocalised not only over the acetylide bonds, but also over the phenyl rings of the acetylide ligands.
- (iii) The bands in the range 1000-1600 cm<sup>-1</sup> which are common to both spectra may be assigned to the pyridine pyrazole ligand. Indeed, the Raman spectrum of free pyridine shows a sympathetic pair of bands near 1000 cm<sup>-1</sup>. This shows that the LUMO has pyridine nature.

Overall, resonance Raman data for Pt(5-H-NN)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub> show enhancement of both acetylide-localised and diimine localised vibrations, supporting LL'CT assignment of the lowest electronic transition in this complex.

**Pt(5-NO<sub>2</sub>-NN-NO<sub>2</sub>)Cl/Pt(5-NO<sub>2</sub>-NN)(-CC-Ph-C<sub>7</sub>H<sub>15</sub>)<sub>2</sub>.** Figure 4 shows the Raman spectra obtained for these complexes. Similar to the X=H compound discussed



**Figure 4.** Resonance Raman spectrum for Pt(5-NO<sub>2</sub>-NN-)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub> (red) under 457.9 nm excitation and of Pt(NO<sub>2</sub>-NN)Cl<sub>2</sub> (black) under 514.5 nm excitation. The inset shows Lorenzian deconvolution of the acetylide band centred at 2130 cm<sup>-1</sup>.

above, the NO<sub>2</sub> substituted acetylide complex also has the additional feature near 2130 cm<sup>-1</sup>. This again shows that the HOMO of the acetylide substituted complex has acetylide character. The precise assignment of the transitions involved is currently underway as several electronic transitions could contribute to the data observed. DFT studies are planned in order to determine the nature of these transitions.

### Experimental

The home-built Resonance Raman set-up for solution measurements used a Coherent Innova 300 FRED Argon ion laser from the Rutherford Appleton Laboratory as an excitation source. A Bentham TM600 monochromator and an Andor iDus CCD camera comprised the detection system. A Renishaw Raman microscope (with 514.5 nm excitation) was used to measure solid samples, including chloride precursors Pt(5-X-NN)Cl<sub>2</sub>, which were not soluble enough to perform measurements in solutions.

### Conclusions

The use of the resonance Raman method has allowed us to obtain direct insight into the nature of the HOMO in Pt(II) diimine acetylide complexes. This information was inaccessible otherwise. The use of pyridine-pyrazole as diimine ligand greatly reduced emission quantum yield of these complexes if compared to the other reported Pt(II) diimine acetylides. The greatly reduced emission background enabled the use of resonance Raman spectroscopy. Pyridine pyrazole based vibrations are prominent in the resonance Raman spectra of Pt(5-X-NN)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub>, indicating that the LUMO has considerable diimine character. The strong enhancement observed for the ν(CC) vibrations at ca. 2130 cm<sup>-1</sup> in the rR spectra of Pt(NN-X)(-CC-Ph-CH<sub>3</sub>)<sub>2</sub> indicates that the HOMO resides on the acetylide ligands. The fact that 2130 cm<sup>-1</sup> band appears as an overlap of two bands, due to asymmetric and symmetric combinations of ν(C≡C) of individual acetylide ligands, indicates a delocalisation of the HOMO over both acetylide ligands. Overall, the lowest

electronic transition in the compounds studied is LL'CT in nature as the spectral features that are enhanced in the Raman spectra obtained in resonance with the lowest electronic transition are due to both the diimine and the acetylide ligands.

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