

Introduction

Over the last few years the field of coordination chemistry of ruthenium has grown. Ruthenium (II) and ruthenium (III) carry oxidation states that accommodate six-coordinated octahedral configurations in which attached ligands can determine its chemical and optical properties.

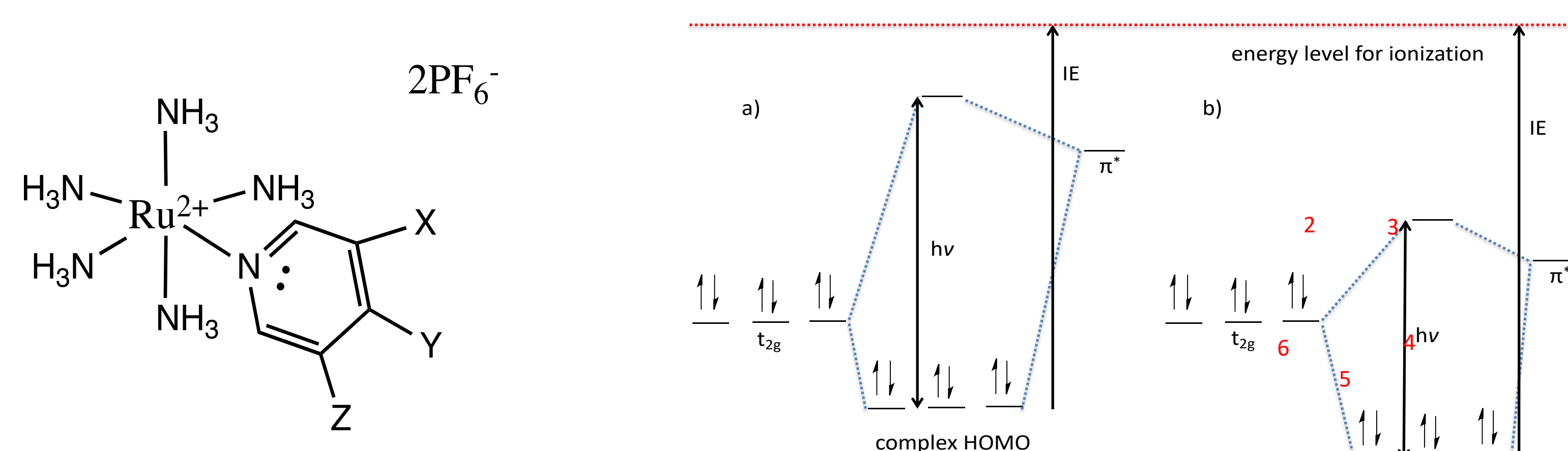


Figure 1: General ruthenium (II) pentammine complex (left) showing general substituents changes on the X, Y, and Z positions of sixth ligand, which were pyridine analogues. Molecular orbital (MO) diagram of the ruthenium complex with (a) electron donating groups (H, methyl) and with (b) electron withdrawing groups (Cl, Br)

Connelly et al. showed that when an electron is excited and a visible color change is seen, an electron gets delocalized from the ruthenium t_{2g} orbital to some anti-bonding region (π^*) on the substituted pyridine.¹ The MO diagram (a) above shows the mixing between a d₆ metal's t_{2g} and a ligand π^* orbital. Our goal was to show that changing the substituents on the pyridine would change the energy of the π^* orbital (coming from a ligand). More specifically, a more electron-withdrawing substituent on X, Y or Z of our ruthenium complex would lower in energy of the π^* . (Shown by MO diagram (b)) This would also decrease the energy level of the HOMO of the complex, leading to a greater ionization energy, thus greater voltage for oxidation. A more basic polar solvent, such as DMSO, would also lower the energy of the complex HOMO.

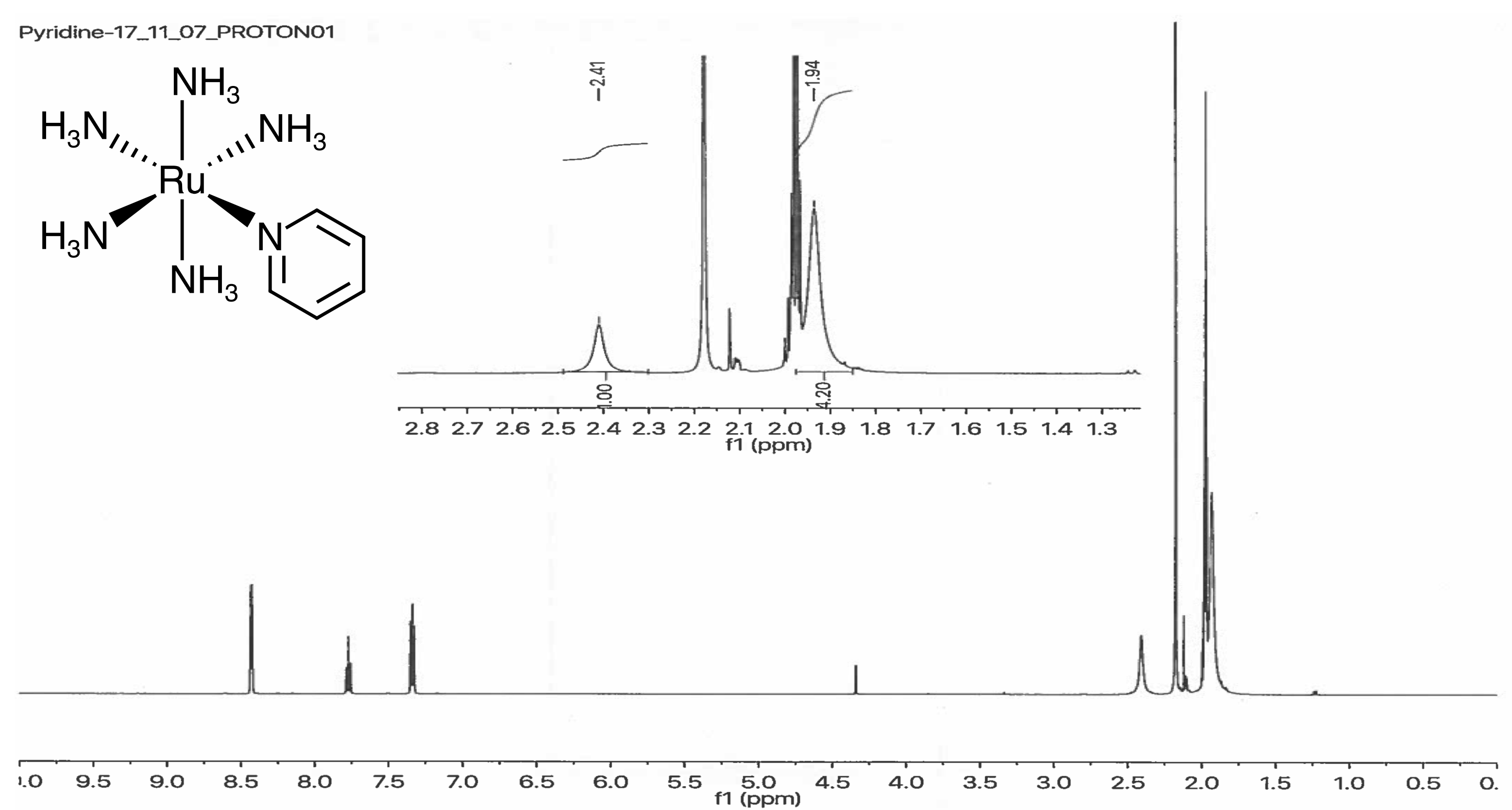
Questions to be answered: 1) How easily can each complex be oxidized? 2) How will each substituent and their position on the pyridine ligand affect energy levels? 3) Will data support previously conducted computational methods showing that this type of transition is chemically allowed?

Methods

Using three complimentary techniques (¹H₁ NMR, UV/Vis spectrometry, and electrochemical voltammetry) data was gathered on ruthenium (II) coordination compounds.

1) ¹H₁NMR

Shows us the chemical composition differences between each complex. Shifting of peaks up field or downfield was substituent dependent.



Methods cont.

2) UV/Visible Spectroscopy

In the field of inorganic chemistry, color is commonly associated with d-d transitions. In transition metal complexes a change in electron distribution between the metal and a ligand gives rise to charge transfer (CT) bands when performing Ultraviolet/visible spectroscopy.² When the ruthenium pyridine complex absorbs light, the electron is promoted from the HOMO to the LUMO. The homo has more ruthenium character from the t_{2g} orbitals so the electron is considered to be from the ruthenium. The LUMO has more pyridine character (from the π^* orbitals) so when the promotion of the e⁻ occurs, the transition is called metal to ligand charge transfer (MLCT). Upon changing the substituents to more electron withdrawing groups, the π^* orbitals lower in energy which then lower the octahedral splitting of the MO. This allows for an electron to be promoted from the HOMO to LUMO with less energy. According to $E=hc/\lambda$, the energy required to promote the e⁻ (i.e. the absorbed light) lowers in energy from uv-vis region towards more visible (see figure 2). This shift of absorbed light causes the complex to absorb lower energy light turning the complex from yellow to red.

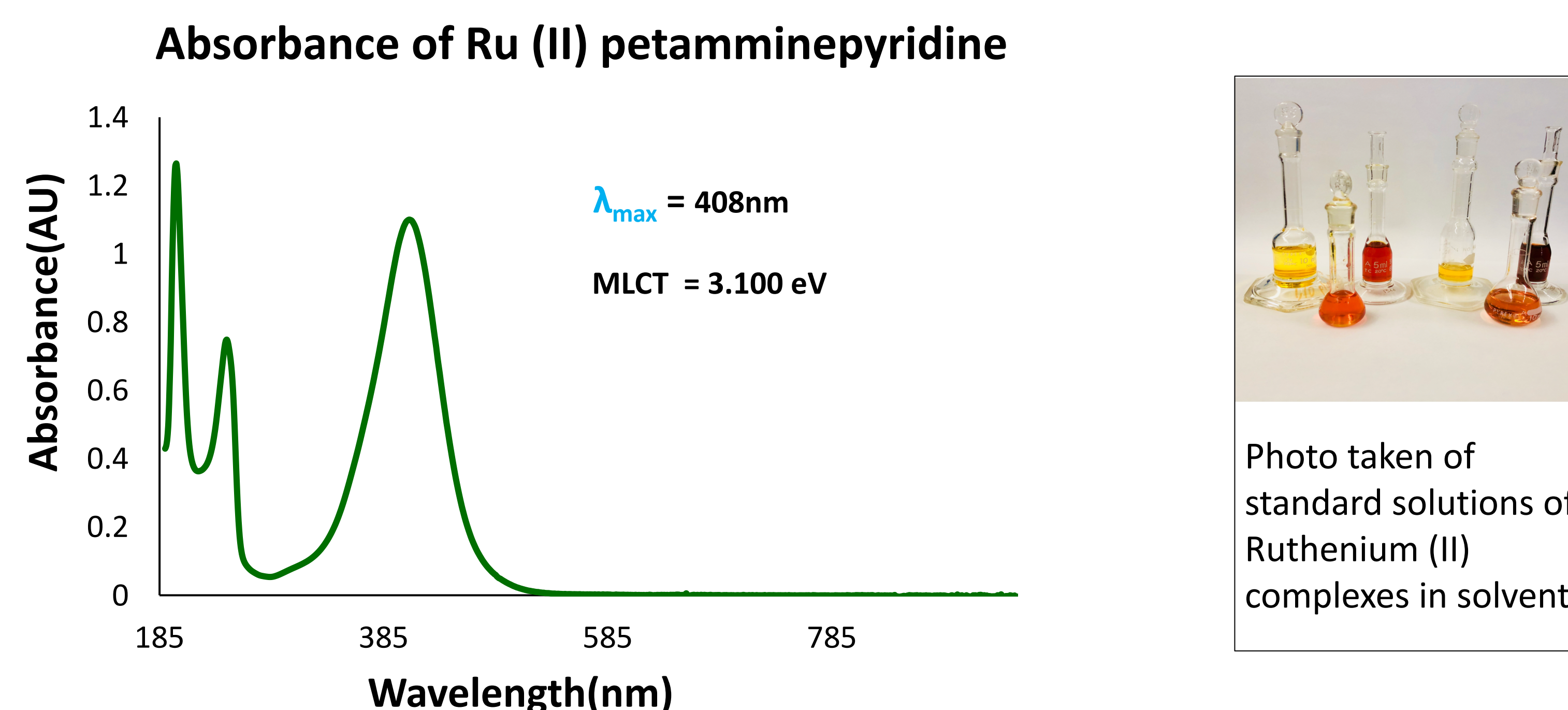
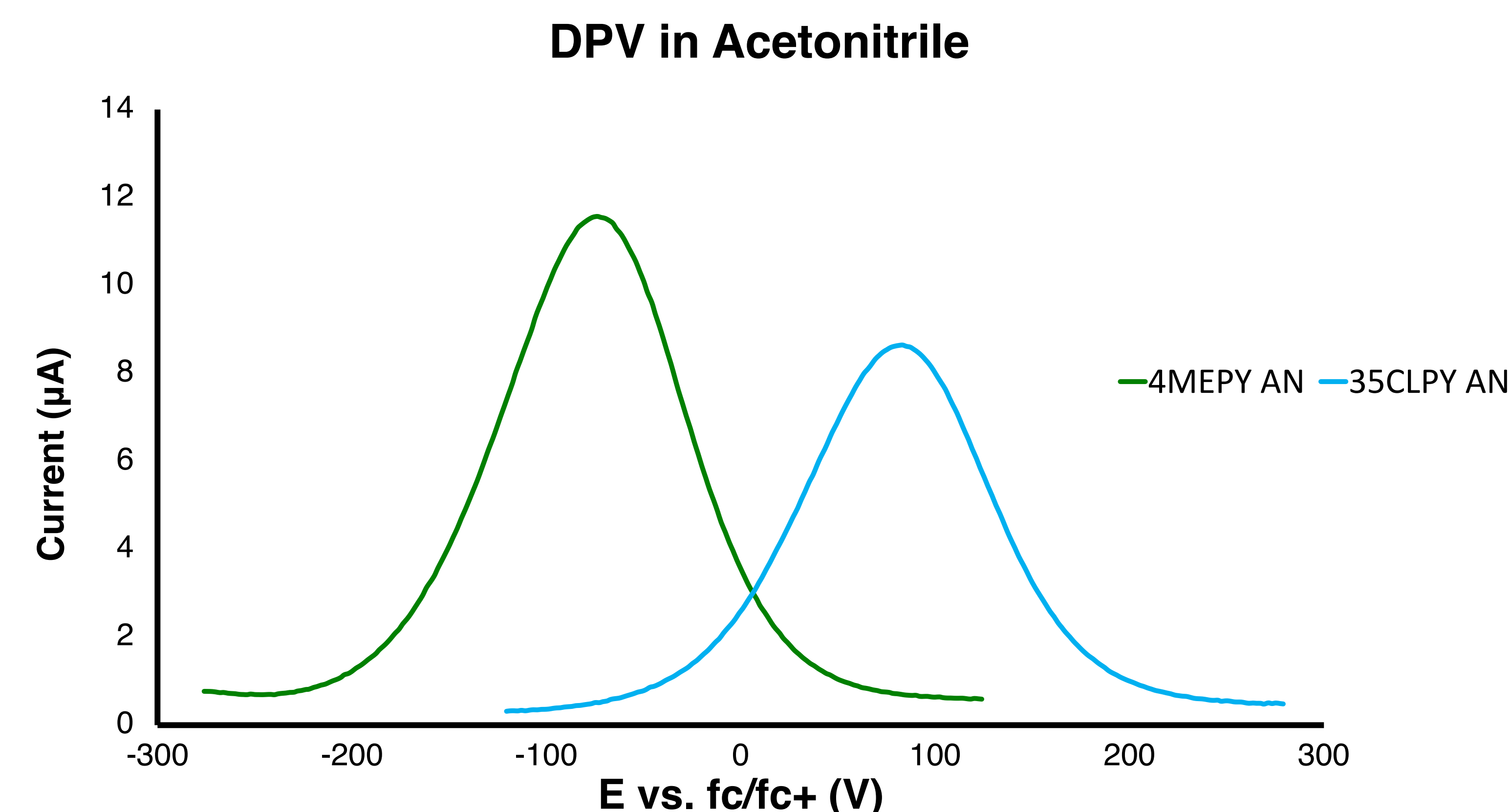


Figure 2: UV-vis of ruthenium pentamminepyridine (left) and representative stock solutions of ruthenium complexes (right) showing color changes.

3) Voltammetry – 3 Electrode System

Voltammetry such as differential pulse voltammetry (DPV) reveals the energy required to oxidize (remove an electron from) ruthenium(II). When a ligand attached to ruthenium (II) has an electron-withdrawing substituent, such as 3,5-dichloropyridine (blue), more voltage is required when compared with ruthenium with a ligand containing an electron-donating substituent, such as 4-methylpyridine (green). These samples were solvated in acetonitrile.



Results

Data was collected using the three complimentary methods and the calculated E_{1/2} values, MLCT energies and H₁ NMR chemical shifts support computational methods showing the presence of d-d orbital back bonding of the substituted ruthenium complexes. The comparison of E_{1/2} and MLCT values show that symmetry would allow for the excitation of an electron from the t_{2g} to π^* orbital would be symmetrically allowed. Computational analysis were carried out with a Gaussian program on Ru (II) complexes by Dr. Jeff Curtis in order to optimize geometry of the HOMO and LUMO states of the free ligands and predict this allowed symmetry.

The 3 position on the ligand has closer proximity to ruthenium and more molecular orbital overlap. Results show that ligand substitution on that position result in lower energy in comparison to substitution on the 4 position (para to the ruthenium metal). The lower the energy the more allowed it is for the excitation of an electron into the π^* orbital of the ligand. Results also show that the exchange of a bromine for a chlorine substituent does not effect the oxidation and no significantly greater red shift occurs in the UV/Vis spectra.

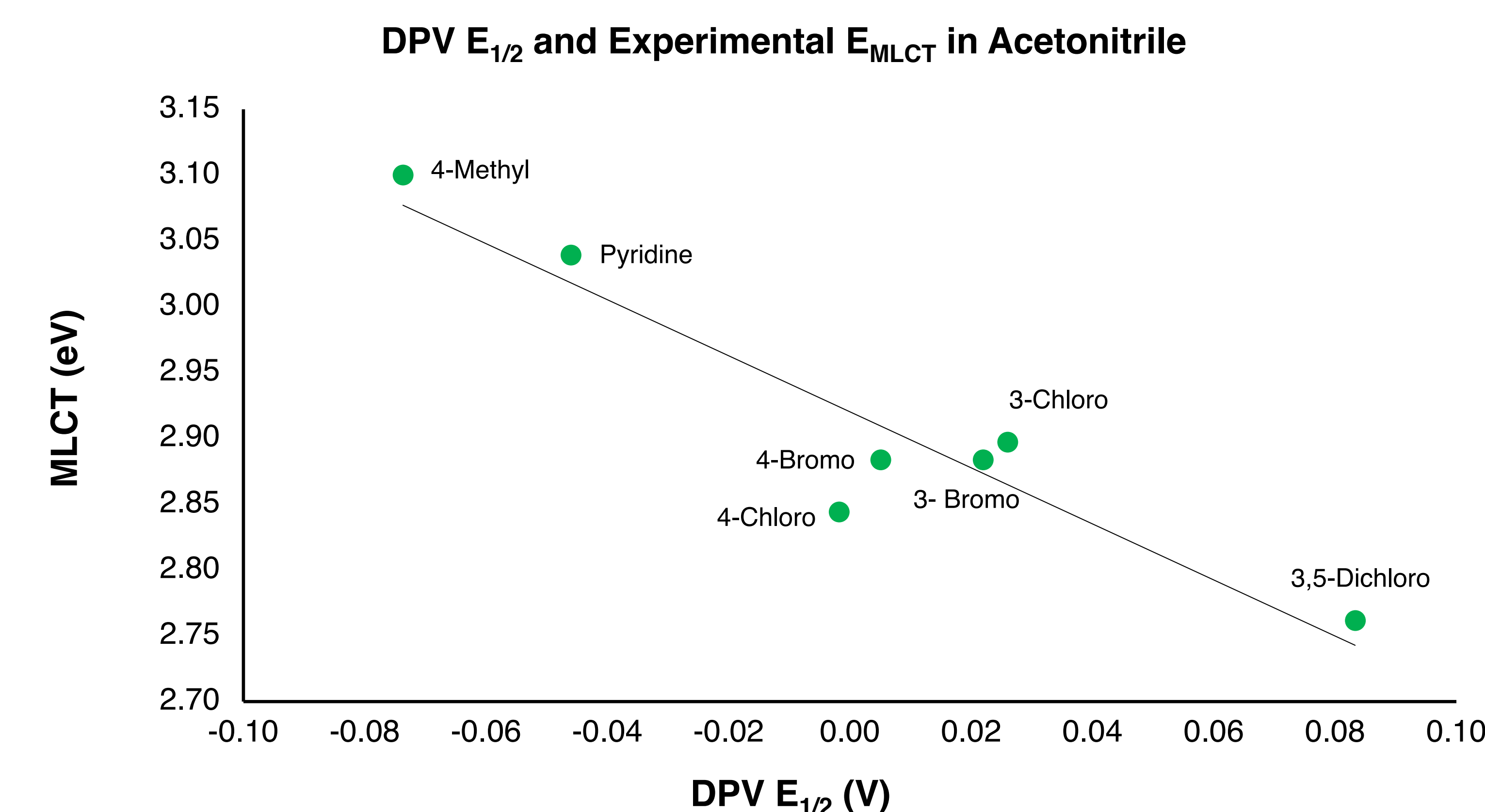


Figure 3: Comparison of E_{1/2} and MLCT energy values of all tested ruthenium (II) complexes.

References

¹ Chemical Redox Agents for Organometallic Chemistry, Neil G. Connelly*,† and and William E. Geiger*,‡ Chemical Reviews 1996 96 (2), 877-910 DOI: 10.1021/cr940053x

²Chem Libre Texts. "Metal to Ligand and Ligand to Metal Charge Transfer Bands." Chem Libre Texts, National Science Foundation , 15 Mar. 2017

³Paris, J. P., and Warren W. Brandt. "Charge Transfer Luminescence of a Ruthenium(II) Chelate." Communications to the Editor 81 (1959): 5001-002.

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