

# **Effect of Varying Ligands and Metal Centers on Metal-to-Ligand Charge Transfer in Photoemmisive d<sup>10</sup>- complexes of Group 11 Elements**

### Introduction:

The photophysical properties of luminescent transition metal complexes has been a study of sizable interest, due to the application in phosphorescent organic-light emitting diodes (PhOLEDs).<sup>[1]</sup> The fluorescent properties of these complexes are dependent on metal to ligand charge transfer (MLCT) which vary due to the metal center and ligands involved in the complex. As a cheaper and more environmentally benign option compared to other transition metals, Hsu et al. has studied the photoemmisive properties of group 11 d<sup>10</sup>complexes. The study found that rigid metal-chelating bonding, increased ligand field strength, and lower metal oxidation states play vital roles in the promotion of MLCT contributions in the emissive state of the complex.<sup>[1]</sup> In this study, bis[2-(diphenylphosphino)phenyl]ether (POP) and an aromatic dinitrogen ligand of either 2,2-bipyridine or 1,10phenanthroline were coordinated to d<sup>10</sup> transition metals Cu<sup>+</sup> and Ag<sup>+</sup>; creating four unique coordination complexes. The response of each complex can discern the extent to which each property effects MLCT and fluorescence of the compound.

### Experimental Design:

Group 11 elements Cu<sup>+</sup> and Ag<sup>+</sup> were coordinated to aromatic dinitrogen bi-dentate ligands 2,2-bipyridine or 1,10phenathroline; synthesizing four coordinate complexes. In this portion of the experiment, Ag<sup>+</sup> was complexed with 1,10phenanthroline. The reaction resulted in the formation of 1,10phenanthrolinebis[2-(diphenylphosphino)phenyl]ether silver(I) (1). The product obtained was analyzed through <sup>1</sup>H NMR, and UV-Visible spectroscopy as well as through fluorimetry and cyclic voltammetry.



**Scheme 1.** Proposed Synthetic Route to Ag(POP)(Phen); 54% yield (88 mg).

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#### Results and Discussion:

The analysis of the product's <sup>1</sup>H NMR spectra (**figure 1**) exhibited slight broadening in aromatic region; suggesting coordination between the ligands and metal center. The UV-Visible light spectra showed a maximum absorption peak at 300 nm, as opposed to the 475 nm peak as previously reported in the literature. <sup>[1]</sup> Using the maximum absorbance of 300 nm as an excitation wavelength, the fluorimetry spectra showed a weak emission at 410 nm (figure 2). The cyclic voltammogram displayed an irreversible peak reduction potential of  $\mathcal{E}^\circ$ =-0.444V (**figure 3**). The difference in reduction potential observed from the source article, 0.74 V, is likely due to the difference in the complexed ligand.





Figure 1. Fluorescence spectra of (1); peak emission at 410 nm.

Figure 3. Cyclic Voltammogram of (1). DMF; zero point referenced vs Ferrocene

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## Future Applications:

Further applications of these photoemmisive complexes are phosphorescent organic-light emitting diodes (PhOLEDs). Following the relationship between oxidation state and ligand field strength, metal-based phosphors can be designed to emit at wavelengths spanning the entirety of the visible light spectrum.<sup>[1]</sup> These diodes, using the principle of phosphorescence, can obtain higher internal efficiencies than the commonly used fluorescent OLEDs.<sup>[2]</sup> Using the effect of the ligand and metal center on the photoemission of the excited electron, complexes can be synthesized to target photoemission in the specific wavelengths needed to create the intended colors.



**Figure 4.** PhOLED inside surface of light-concentrating pyramid

#### Conclusions:

The experimental data provided insufficient evidence to claim that the synthesis of the intended product was successful. As the spectra obtained for this experiment gives no indication to the efficiency of the synthesized complex, further experimentation is needed to categorize the complex as a PhOLED. Further study of of the of the complexes can be done through electroluminescence (EL), current density-voltage-luminance (I-V-L) characteristics, and external quantum efficiency to assess the ability for PhOLED device fabrication.

#### **References:**

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