

Introduction

In complexes with multiple closed-shell metal ions, it may be possible to observe an attractive interaction between two discrete metal centers known as metallophilicity.^{1,3,4} This type of interaction is particularly notable in structures bearing larger Group 11 ions including Ag^I and Au^I; although Cu^I is now also becoming prevalent within this class of bimetallic moieties.¹⁻⁴ Through careful assessment of hard-soft acid-base theory, it is possible to develop ligand systems that can selectively coordinate to two non-identical and distinct metal centers in solution.¹⁻⁴ Other major factors in ligand assessment is the incorporation of ligands with different molecular rigidity (to test the strength of metallophilicity if present) as well as variances in steric hindrance and extension of π -conjugation (to assess changes in luminescence based on external coordination or ion- π stacking interactions).¹⁻⁴ With these considerations in mind it is possible to create a library of ligands to coordinate in a bimetallic system that will result in a plethora of different emissions based on the changes in luminescence combination(s) of these factors present. The following serves to highlight the design, synthesis, characterization and photophysical analysis of a small library of Au^I...Cu^I bimetallic complexes for the assessment of their optical properties in hopes to help advance knowledge in contemporary and developing emissive technologies.

Complex Design and Synthesis

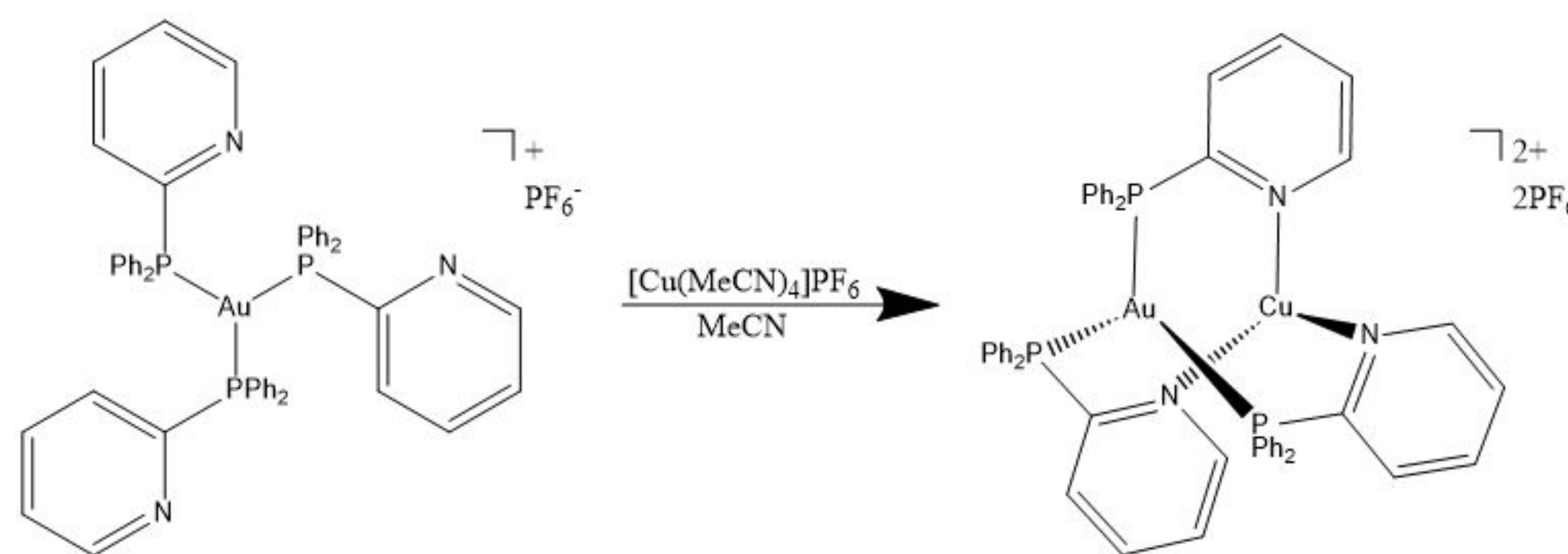
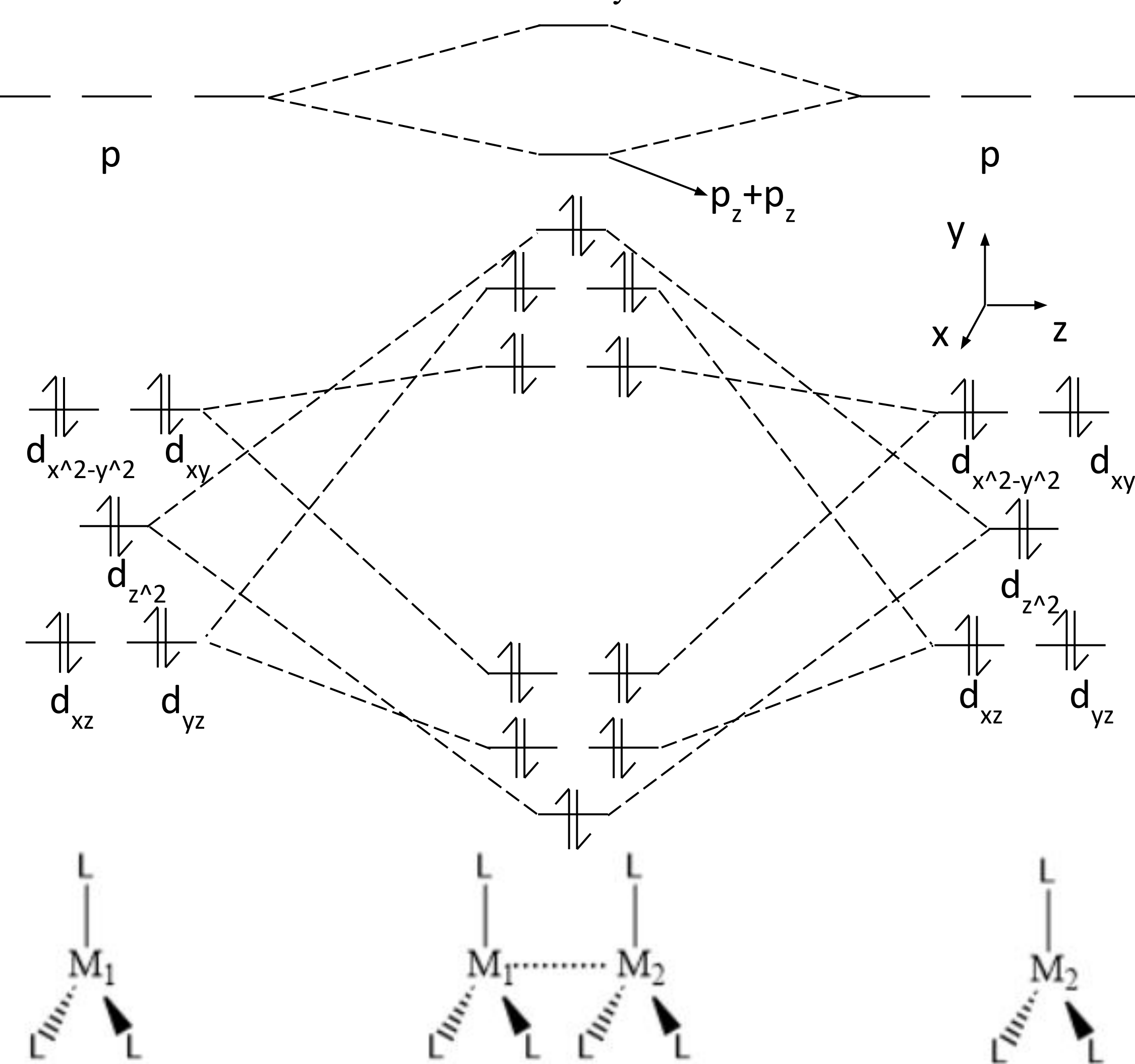


Figure 1: Synthetic route leading to a bimetallic Au^I...Cu^I complex containing multiple equivalents of a phosphinopyridine ligand of choice, with each metal center being electronically countered by a hexafluorophosphate anion. This is a relatively efficient and popular approach to the generation of multimetallic compounds due to the coordinative selectivity provided by careful control of hard-soft acid-base theory.

Figure 2: Simplified depiction of an orbital splitting diagram corresponding to the addition of two trigonal planar metal centers resulting in a metallophilic interaction.



The synthetic pathway starts with a reductive transmetalation reaction to reduce the Au(III) ion present in chloroauric acid tetrahydrate to a Au(I) ion. This could be completed through the introduction of tetrahydrothiophene in dilute ethanol followed by separation. The previously synthesized chloro(tetrahydrothiophene)gold(I) complex is taken up in dichloromethane along with three equivalents of 2-(diphenylphosphino)pyridine. A subsequent addition of methanolic potassium hexafluorophosphate is sufficient to perform a metathesis reaction in situ, pairing the gold complex with the hexafluorophosphate anion and forming potassium chloride as a side product. The reaction mixture is then filtered through celite before crashing the product out of solution upon the addition of copious diethyl ether. Upon drying, the monometallic Au(I) species appeared as a colorless powder, which did not show any emission when illuminated under a UV lamp (365 nm). Finally, as shown in Figure 1, the gold complex is taken in the presence of tetrakis(acetonitrile)copper(I) hexafluorophosphate in minimal acetonitrile in order to form the bimetallic moiety shown. The final product of the synthesis is a pale yellow, powdery solid. When illuminated under a UV lamp, the complex does not have very strong emission but more so than that of the starting material. In order to achieve a variety of different emissive properties, a plethora of vapor diffusion setups were used to acquire different sets of crystal structures. While diethyl ether was consistently utilized as the counter solvent, different systems were developed using acetone, acetonitrile, dichloromethane, methanol and nitromethane. These particular solvents were chosen as they are all polar enough to dissolve the complex and vary in overall molecular structure. This allows for different polymorphs or pseudopolymorphs of the same bimetallic complex, which vary completely in emissive properties as a result of the different locations of solvent molecules and hexafluorophosphate anions relative to the inner coordination sphere. These different external ligations also have the potential to affect the Au^I...Cu^I distance via the induction of van der Waal's forces about the Cu-center which results in an attractive interaction between the metal centers.

Experimental, Results and Discussion

In some instances, same solvent solvent system would yield a combination of polymorphs with different luminescent properties in the same vessel. This would lead to meticulous manual separation under UV light. Despite these slight difficulties, it was possible to obtain various sets of crystalline material with unique colored emissions. Additionally, each solvent of choice is a suitable spectroscopic handle in each method used to confirm the structure of each product. This is particularly notable in methods such as IR and NMR spectroscopy, although changes in luminescent properties can also be detected in both UV-vis and fluorescence spectroscopy. Different changes in emission can be assessed quantitatively between each system using fluorescence spectroscopy, which also gives insight into the interactions between the inner and outer coordination spheres which cause these changes. However the true determination of metallophilicity in any of these systems is through comparison of metal-metal distances observed within these complexes using single crystal X-ray diffractometry, with what has been previously determined in hetero-bimetallic complexes.

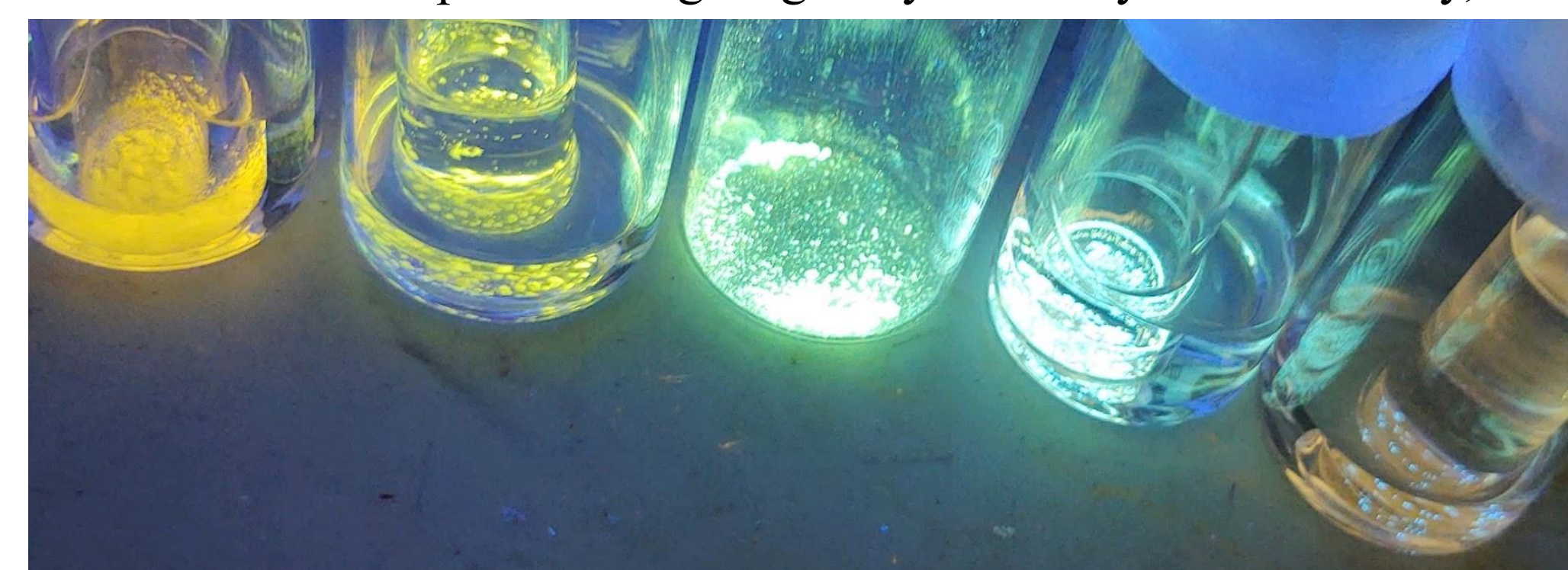


Figure 3: Crystals of [Au(PPh₂Py)₃Cu][(PF₆)₂] made using diethyl ether and (from left to right) acetonitrile, nitromethane, acetone, dichloromethane and methanol.

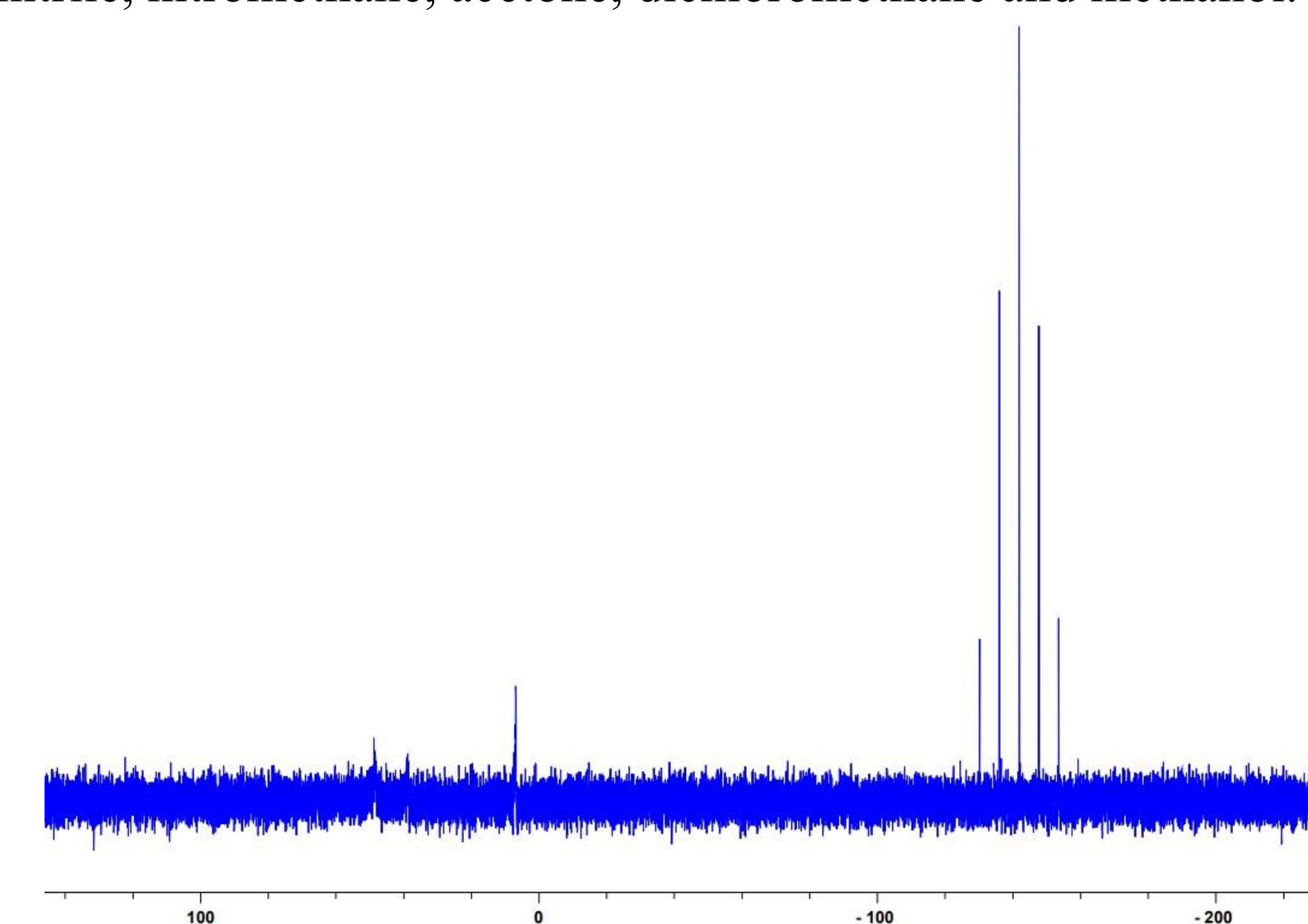


Figure 4: ³¹P NMR Spectra of [Au(PPh₂Py)₃Cu][(PF₆)₂] at room temperature (300 MHz).

Conclusions and Future Work

An efficient route to the generation of bimetallic Au^I...Cu^I moieties has been expanded upon with a change in counter-anion presence about a previously studied bimetallic scaffold. This further widens the plethora of options to choose from when considering different luminescent metal organic frameworks. Future work includes the expansion to different coordinating solvents for crystallization, along with full spectroscopic analysis (UV-vis, IR, NMR, Fluorescence). Single crystal X-ray diffractometry is essential for determining the potential metallophilic interactions present in these compounds. Additionally, the same experiments will be invoked on bimetallic structures containing the remaining phosphinopyridine ligands shown in Figure 8. These structural changes will affect not only the synthetic route to the final bimetallic complex prior to crystallization, but may also prove to have their own intrinsic effects on the luminescent properties of a given Au^I...Cu^I complex.

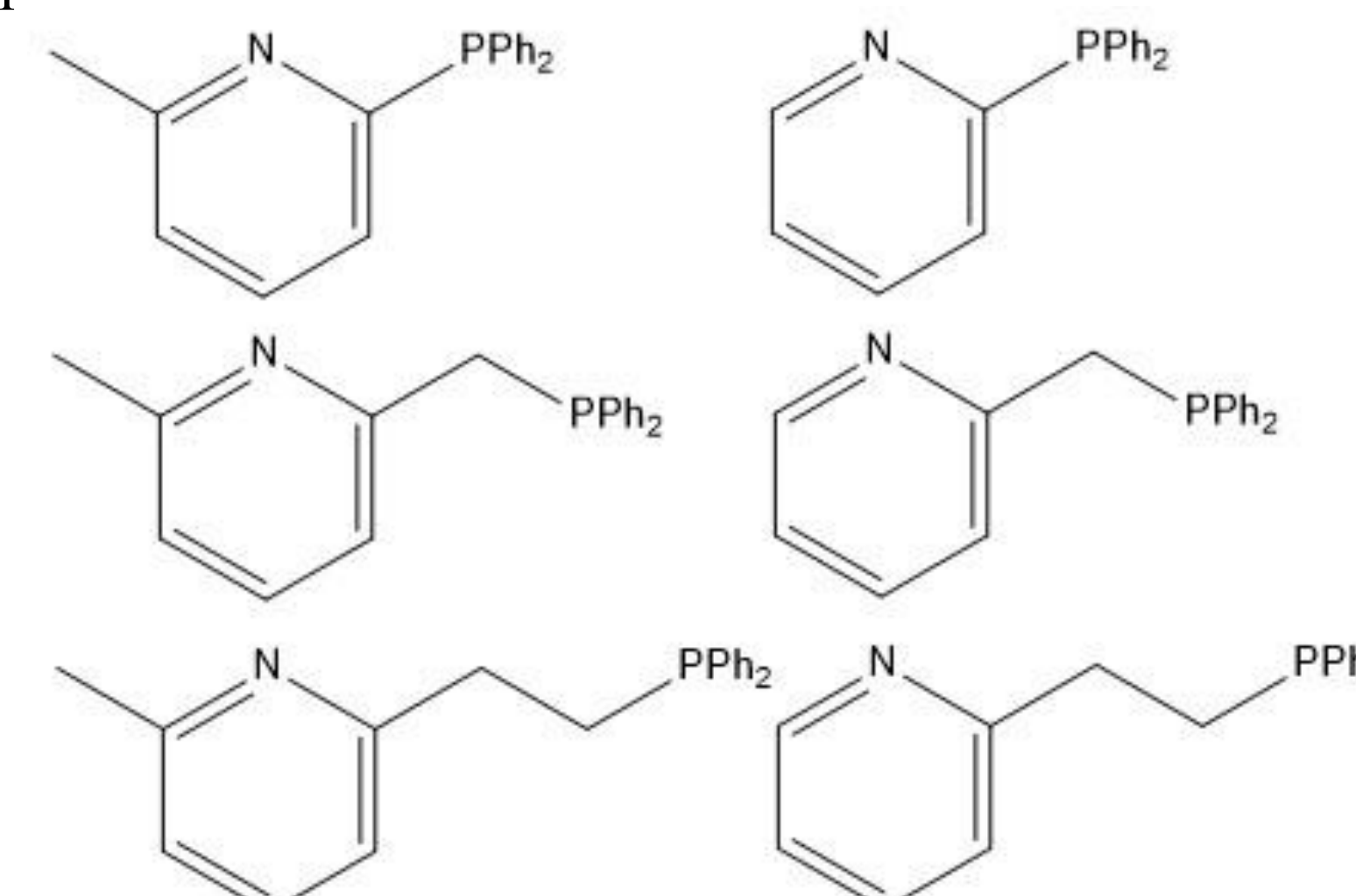


Figure 8: Complete library of ligands which are to be investigated in the Au^I...Cu^I bimetallic systems, based on variance in steric hindrance and their resulting synthetic/electronic properties.

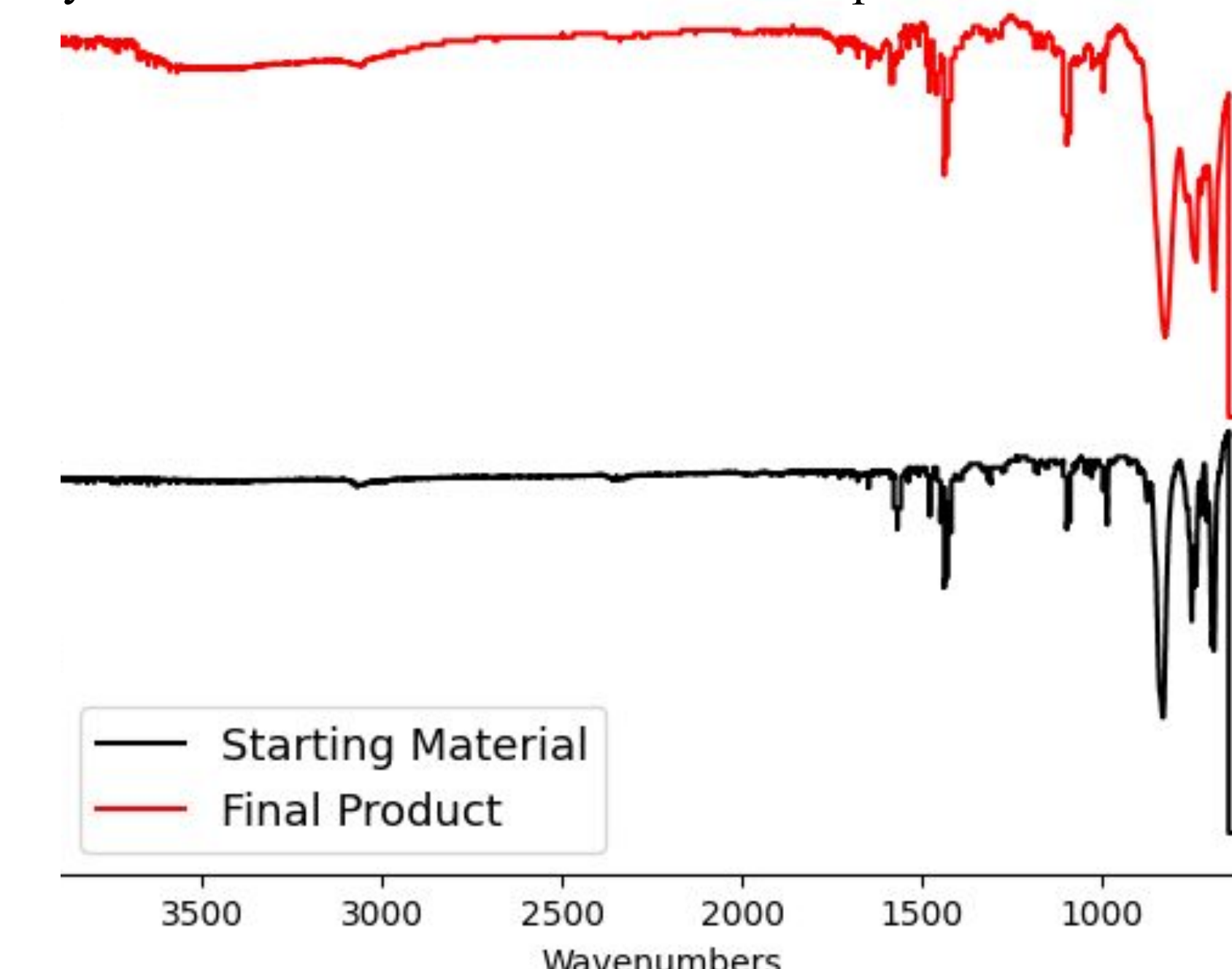


Figure 5: IR Spectra obtained for [Au(PPh₂Py)₃](PF₆) (black), [Au(PPh₂Py)₃Cu][(PF₆)₂] (red).

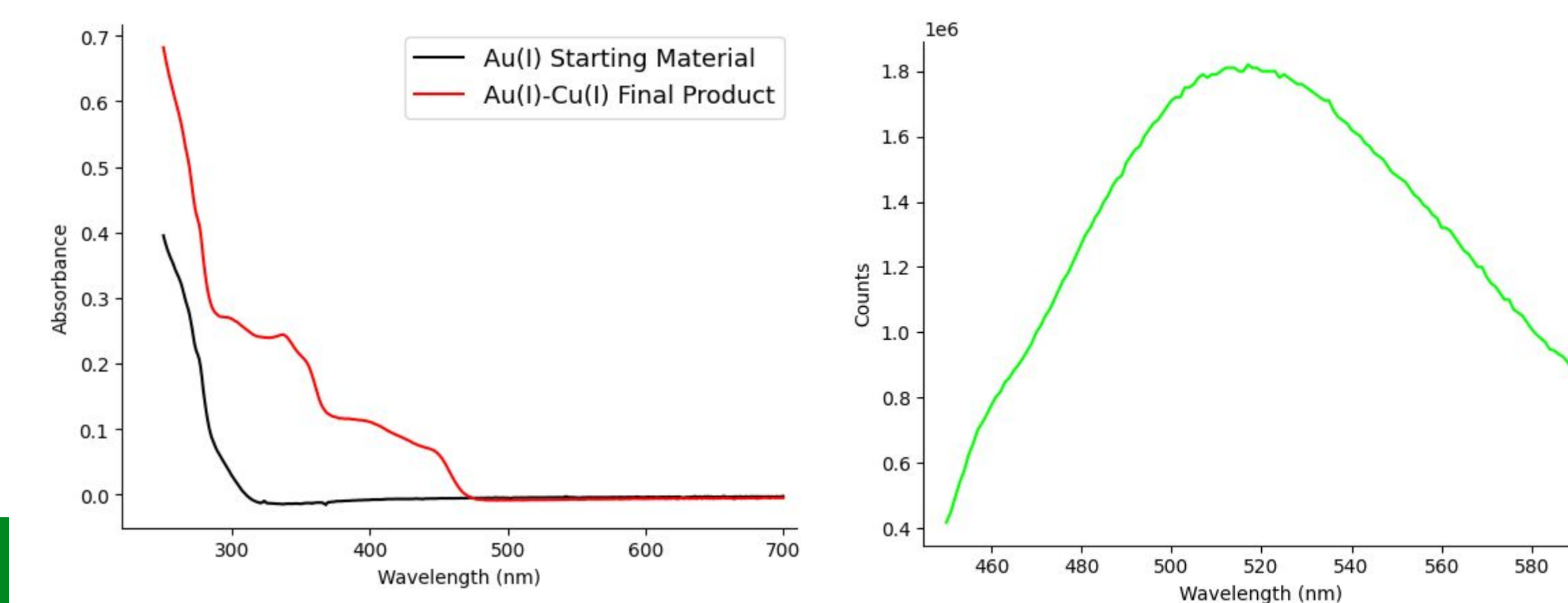


Figure 6: UV-vis Spectra obtained for [Au(PPh₂Py)₃](PF₆) and [Au(PPh₂Py)₃Cu][(PF₆)₂].

Figure 7: Fluorescence Spectra obtained for [Au(PPh₂Py)₃Cu][(PF₆)₂] crystallized using acetone and diethyl ether.

References

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