

# Emissive State Characterization of Homoleptic Ir(III)-Complexes for Solid-State Lighting

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## I. INTRODUCTION

Organic materials have had a large impact on current concepts and strategies to devise solid-state lighting and modern display technologies. Due to their highly efficient (near unity quantum efficiency) luminescence, OLEDs with doped-in phosphorescent emitters have been an area of much attention. Phenyl-pyridine (ppy), a commonly used ligand within Ir-complexes for OLEDs, has been experimentally observed to be “tunable” across the visible spectrum by simply altering the structure of the ligand [1]. However, the relation between emissive characteristics and the molecular structure has not been well understood hitherto, providing a barrier into designing new phosphorescent-emitters.

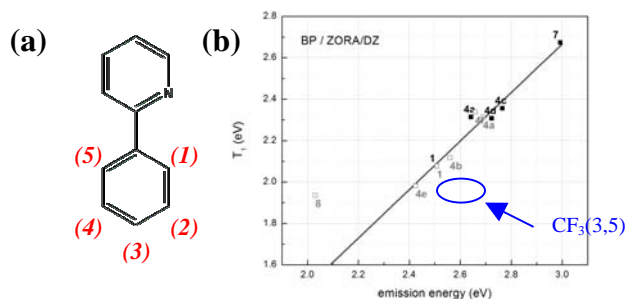
The goal of the project is to identify the primary mechanisms that characterize the phosphorescence properties of organic emitters by employing computational methods to calculate the electronic structure in ppy-based ligands. Examining how structure affects wavelength emission and stability may be useful for providing systematic approach to designing new organic emitters.

## II. PROCEDURE

Various computational software packages were utilized for geometry optimization, quantitative estimates of the emissive states for both the free-ligand and metal-complex, and visualization of frontier orbitals. The structure of the ppy molecule, along with its derivatives, *e.g.*, arising from F and CF<sub>3</sub> substitutions (Figure 1a), were generated in ArgusLab, and subsequently exported for geometry optimization and HOMO/LUMO visualization into AMPAC(AM1). The molecules (ligand and complex) in their ground state were simulated using ADF(DFT, BP/ZORA), which provided the lowest singlet/triplet to ground-state energies. An initial DFT geometry optimization with determination of the HOMO/LUMO energies preceded the excited state calculations. Additionally, we were able to calculate the extent of participation due to the Ir- metal in the complexes. Finally, the orbitals of the complexes were visualized with JAGUAR(DFT, BP86/LACPV\*\*).

## III. RESULTS AND DISCUSSION

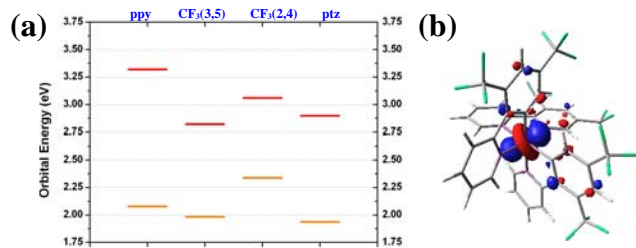
The trends in the first-triplet ( $T_1$ ) to ground-state transitions (that account for the phosphorescence emissions) agree well with the emission energies observed in experiments [1,2]. As one representative example, Figure 1b highlights this correlation for the ppy and CF<sub>3</sub>-substituted ppy-ligands, showing a consistent ~0.3eV underestimate of  $T_1$  energies from published values. One can also observe that the coordination to Iridium has an overwhelming effect on the transition energies when comparing the complex to the free-ligand case. However, the positioning of the substituent groups on the ligand appears to have an effect on the energies, as well (Figure 2a). In the case of CF<sub>3</sub> substitution, for example, the Ir-Complex with substituents in (3,5) position demonstrates a red-shift while in (2,4) a



**Figure 1** – (a) Phenyl-Pyridine and Substitution Locations  
(b) Published Emission Values vs Calculated Ir-  $T_1$  Energies

blue-shift in the emission energy for with respect to the unsubstituted ppy ligand.

Figure 2b shows a representative plot of the HOMO in the Ir-complex. The significant contribution of the metal  $dz^2$  orbital readily indicates a strong influence of the Iridium, as a result of which the HOMO energy is significantly increased with respect to the free ligand. In accordance to expectation, attaching electron-withdrawing CF<sub>3</sub> groups was found to affect the LUMO energies more pronounced than the HOMO ones.



**Figure 2** – (a)  $T_1$  Energies of Four Ligands (Ligand top, Ir- bottom)  
(b) HOMO plot (Isovalue=-0.005) for CF<sub>3</sub>(2,4)-substituted ppy

## IV. CONCLUSION

The effect of ligand alteration is only feasibly apparent in the full Ir-complex models. The predicted  $T_1$  energies as well as the HOMO/LUMO gaps are well in agreement with published trends. Owing to the metal-free nature of the LUMO, its modification has a more direct impact on the emission characteristics of the complex.

## V. REFERENCES

- [1] Sajoto, T., et al. “Blue and Near-UV Phosphorescence from Iridium Complexes with Cyclometalated Pyrazolyl or N-Heterocyclic Carbene Ligands”. *Inorganic Chemistry* (2005).
- [2] Coppo, P., et al. “Tuning Iridium(III) Phenylpyridine Complexes in the ‘almost blue’ region”. *Chemical Communications* (2004).

## IV. ACKNOWLEDGEMENTS

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