TD-DFT Studies of Highly Luminescent and Long Lived Cu(I) Complexes

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INTRODUCTION

- Luminescent copper(I) complexes are highly sought after as potential alternatives for more commonly used complexes due to the higher abundance and lower cost of copper.
- Applications include OLEDs[1] or chemical sensing, photosensitizers, and photocatalysis.[5]
- Copper(I) complexes typically exhibit photoluminescence via thermally-activated delayed fluorescence (TADF) when an energy gap between the S_1 and T_1 states (ΔE_{ST}) is small enough and/or phosphorescence induced by large spin-orbit coupling (SOC).

COMPUTATIONAL DETAILS

- Software: Gaussian 16
- CAM-B3LYP with basis set def2-TZVP and def2-SVPP was used for geometry optimizations and vibrational frequencies
- SMD solvation model (toluene and acetonitrile)
- TD-DFT (CAM-B3LYP) was used for UV-Vis spectra calculations

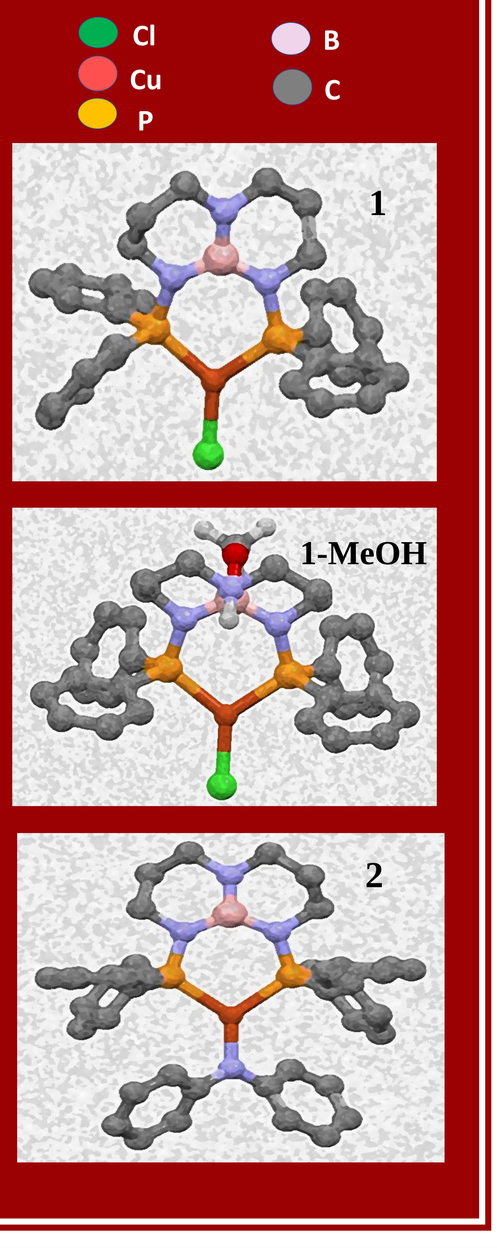
RESULTS

- Geometries of all 3-complexes were optimized with singlet and triplet spin in gas phase and in toluene and dichloromethane solvent.
- UV-vis absorption spectra's were obtained for all 3-complexes and were compared to experiment results.
- Emission energies for Phosphorescence were also calculated and compared with experimental results.

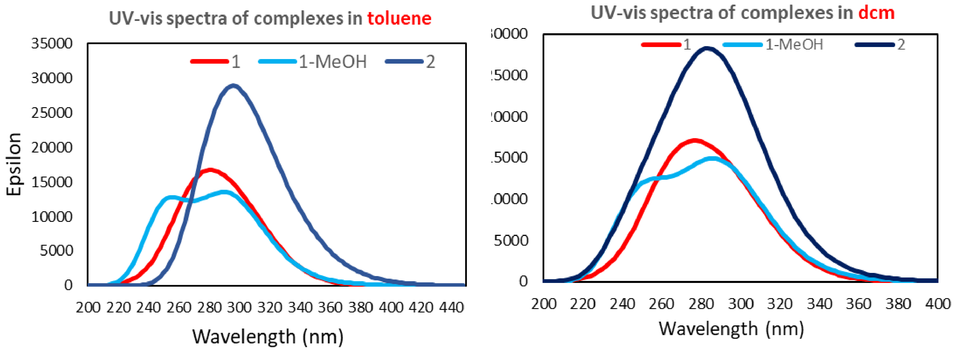
Table. Experimental and theoretical absorption data for 1, 2, and 1-MeOH.

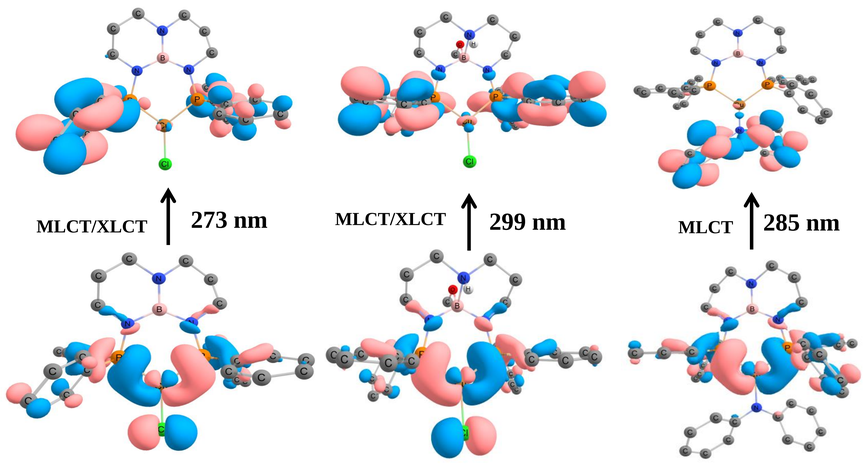
Complex	λ_{abs} nm ($\varepsilon/10^3 M^{-1}cm^{-1}$) in toluene	λ_{max} (nm) TD-DFT (toluene)
1	301 (10), 333 (sh, 9.4)	273(0.29), HOMO→LUMO+3 302(0.23), HOMO→LUMO+1
1-MeOH	(not soluble)	299(0.19)HOMO→LUMO 285(0.13) HOMO→LUMO+2
2	287 (17)	285(0.4)HOMO→LUMO+9 305(0.28)HOMO→LUMO+8

DFT OPTIMIZED COMPLEXES



UV-VIS ABSORPTION SPECTRA





EMISSION SPECTRA

	E(eV)	1	1-MeoH	2
GAS	E_{exc}	3.60	3.63	3.43
	E_p	2.18	2.07	2.20
DCM	E_{exc}	3.85	3.84	3.63
	E_p	2.17	2.30	2.02
TOLUENE	E_{exc}	3.74	3.74	3.65
	E_p	2.19	2.19	2.04

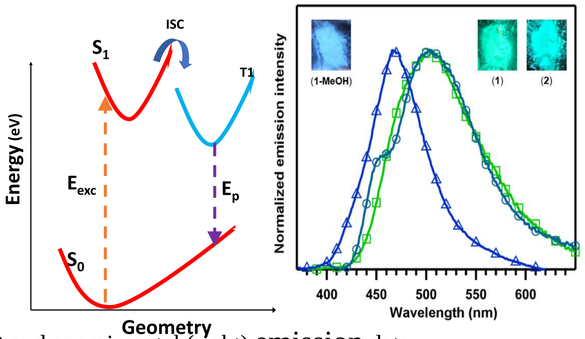


Figure. Comparison of theoretical (left) and experimental (right) emission data.

REFERENCES

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