

Examining Photoactivation of [Copper(I) bisphenanthroline]⁺ with Extended Active Space Methods Shawna Lin, Class of 2028

The discovery of metalla-photo-redox reactions in organic synthesis prompted interest regarding the involvement of metals in visible light photo-catalysis.¹ Copper(I) has emerged as a successful photosensitizer due to its fully occupied d-orbitals which restricts d-d electron transition and more metal-to-ligand charge transfer (MLCT) states.² In our research, we are studying [Copper(I) bisphenanthroline]⁺, a general representative of a copper-based redox mediator with a favorable extensive π system. When exposed to a visible light stimulant, cuprous bis-phenanthroline's filled d-orbitals on the metal and an extensive pi-network on the ligands are properties that are strongly favorable for metal-to-ligand charge transfer (MLCT).^{3,4} The efficient promotion of the electrons from the center metal to the bounded phenanthroline ligand is central to the complex's role as a photosensitizer as it results in longer excited state lifetimes and more efficient reactivities with other molecules. [Copper(I) bisphenanthroline]⁺ is a strongly correlated complex with mixing between its d, π , and π^* molecular orbitals. This means that the electronic movements cannot be adequately captured in a single configuration with a limited number of considered molecular orbitals. To provide an accurate representation of the electronic behaviors in the ground state and during MLCT, we need to refer to multiconfigurational computational methods with an extended active space.

We first adopted the geometry coordinates of the complex from a preexisting study.⁵ The geometry was initially optimized using the Density Functional Theory (DFT) for energy minimization. Localization of the orbitals was then performed using Pipek–Mezey to transform delocalized molecular orbitals into localized orbitals.⁶ These preliminary methods provide a rough estimate of the initial geometries, defining the starting orbitals in the active space for the Complete Active Space Self-Consistent Field (CASSCF) method to generate the complete set of possible configurations within the active space.

We calculated a 5-state CASSCF with an active space of 10 electrons and 9 molecular orbitals consisting of dyz, dxz, π , dz², dx²-y² occupied molecular orbitals, and four π^* unoccupied molecular orbitals. The dxy orbital isn't captured within the active space likely due to the near degeneracies of the π and d orbitals. The calculation generated the complete configuration interaction vectors for each state and the energies within the active space. In addition, we ran CAS Pair-Density Functional Theory (CAS-PDFT) to correct the static correlation-oriented reference wavefunction from CASSCF, generating the energies with greater accuracy.

Following the CAS methods, we ran DMRG-SCF and DMRG-PDFT calculations with the same active space size over 5 states and ensured minimal differences between the CAS and DMRG calculations. This indicates accuracy of the DMRG average orbital occupation values and that we are using the most optimized parameters. We then used the same parameters to extend our active space to 38 active orbitals over 5 states to capture the correlations between all d, π , and π^* molecular orbitals within the complex.

The ground state generated by the CAS methods smaller active space size showed a high degree of multiconfigurational characteristics resulting from d and π^* mixing. The overall ground state wavefunction has a 72.9% contribution from configurations displaying metal to ligand charge transfer characteristics. The extended active space DMRG calculations revealed a decrease in multiconfigurational characters in the ground state, indicating only moderate mixing. This suggests that the true characteristic of the ground state is multiconfigurational, but that DMRG reveals a more subtle multiconfigurational character. We plan to run a further 15-state DMRG calculation and compare the ground state properties and further investigate multiconfigurational characteristics.

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References

- (1) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363. <https://doi.org/10.1021/cr300503r>.
- (2) Lazorski, M. S.; Castellano, F. N. Advances in the Light Conversion Properties of Cu(I)-Based Photosensitizers. *Polyhedron* **2014**, *82*, 57–70. <https://doi.org/10.1016/j.poly.2014.04.060>.
- (3) *Employing Long-Range Inductive Effects to Modulate Metal-to-Ligand Charge Transfer Photoluminescence in Homoleptic Cu(I) Complexes | Inorganic Chemistry*. <https://pubs.acs.org/doi/full/10.1021/acs.inorgchem.2c04315> (accessed 2025-05-22).
- (4) Scaltrito, D. V.; Thompson, D. W.; O’Callaghan, J. A.; Meyer, G. J. MLCT Excited States of Cuprous Bis-Phenanthroline Coordination Compounds. *Coordination Chemistry Reviews* **2000**, *208* (1), 243–266. [https://doi.org/10.1016/S0010-8545\(00\)00309-X](https://doi.org/10.1016/S0010-8545(00)00309-X).
- (5) Gimeno, L.; Phelan, B. T.; Sprague-Klein, E. A.; Roisnel, T.; Blart, E.; Gourlaouen, C.; Chen, L. X.; Pellegrin, Y. Bulky and Stable Copper(I)-Phenanthroline Complex: Impact of Steric Strain and Symmetry on the Excited-State Properties. *Inorg. Chem.* **2022**, *61* (19), 7296–7307. <https://doi.org/10.1021/acs.inorgchem.1c03901>.
- (6) Cioslowski, J. Partitioning of the Orbital Overlap Matrix and the Localization Criteria. *J Math Chem* **1991**, *8* (1), 169–178. <https://doi.org/10.1007/BF01166933>.