

DFT insights into homoleptic and heteroleptic Cu(I) coordinated complexes as potential photosensitizers

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Metal coordinated complexes have important potential applications as photosensitizers and emitters, at the red to near-infrared spectral range, in photovoltaics, photocatalysis, and photodynamic therapy. Obtained insights into the relationship between the structure and optical properties of these metal coordinated complexes are important for these potential applications. Copper is a particular metal of interest, as it is both an earth abundant metal and may minimize side effects if used in a in bio- and medical applications. Our studies utilize Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) to investigate the ground and excited state properties of Cu(I) bipyridine-based complexes. Validation of the functional used in calculations was done in comparison to experimental absorbance spectra of three synthetically produced Cu(I) complexes. We investigate the effect of the conjugation length of ligands and electron donating/withdrawing ability of their substituting groups on the absorption spectra of Cu(I) homoleptic and heteroleptic complexes. Our calculations show that heteroleptic compounds result in more red-shifted absorption, up to 53 nm, compared to their homoleptic counterparts. However, binding energy calculations imply that many of the homoleptic compounds are more favorable thermodynamically, which may lead to challenges when it comes to the synthesis of their heteroleptic counterparts. Analysis of natural transition orbitals shows metal to ligand charge transfer character in the lowest optical transitions, which is a desired property for many applications of photosensitizers especially for photodynamic therapy.