DFT Study of Ligand Effects on Tungsten Coordinated Complexes

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Understanding the optical properties of metal coordinated complexes is crucial for their applications as red to near-infrared emitters and photosensitizers. This prompts applications in photocatalysis, isomerization, photovoltaics, and photodynamic therapy. The focus on tungsten is particularly crucial since earth abundant metals have the potential to yield more economic research and development processes. Varying the ligands on these types of complexes has the ability to red shift the absorption spectra to better fit the above applications. Our investigations of the ground and excited state properties of tungsten pyridyl-imidazole coordinated complexes were calculated using density functional theory (DFT) and time-dependent DFT (TD-DFT). The computations were validated by comparing calculated optical spectra with experimental data. It was found that the B3LYP functional best aligned with experimental data. A comparison of the effects of increasing conjugation of the pyridyl-imidazole ligand and substituting groups was performed. It was found that ligands with increasing conjugation are more redshifted. Increasing the length of the carbon chain on the substitution group has no effect on the spectra, while adding electron donating (EDG) and electron withdrawing (EWG) to the substitution group causes a slight blue-shift and red-shift, respectively. Comparisons were also made between having the carbonyl ligands and replacing them with pyridine or bipyridine. Our calculations predict that replacing the carbonyl ligands with pyridine or bipyridine redshifts the spectra from around 500 nm up to 700 nm-1000 nm, while also increasing the optical activity of the lowest-energy transition in some cases.