Influence of Metals, Ligand π-Conjugation and Electron Donating/Withdrawing Groups on Photophysical Properties of Organometallic Complexes

Haley Woods, Wenfang Sun, and Svetlana Kilina

Chemistry and Biochemistry Department
North Dakota State University

Photodynamic therapy (PDT) is a promising tool for cancer treatment and diagnosis of various cancers. PDT works through a mechanism of photoexcitation of an organic or metal-organic compound, i.e. a photosensitizer (PS), followed by the intersystem crossing from singlet to triplet excited state and finalized by energy or electron transfer to molecular oxygen to produce a reactive oxygen species that can promote malignant cell death. Development of new PSs with absorption at the near-IR range that can deeply penetrate through tissues and long triplet lifetime providing enough time for energy/electron transfer is crucial for improvement of the therapeutic outcomes. To establish the relationship between photophysical properties and molecular structures that enables a systematic design procedure for novel PS with improved PDT performances, time-dependent density functional theory (TD-DFT) calculations are performed on several PS candidates. Our calculations show red-shifted absorption for PS complexes with Ir(III) centers, relative to Ru(II) and Os(II) centers. Increase in the π-conjugation length of thiophene ligands also facilitates absorption redshift. Changing the electron donating/withdrawing abilities of substituting groups (NO_2, H, and NH_2) on the terpyridine ligands shows no dramatic effect on major absorption peaks. However, NO_2 substituent results in an optically dark S_1 exciton compared to H and NH_2 substituents. Mixing of the lowest triplet state, T_1, with optically dark S_1 is expected to increase the lifetime of T_1 state. Thus, our calculations predict that complexes with NO_2 substituents are likely to provide better PS candidates for the generation of reactive oxygen species needed for treatment of a broader scope of cancer types.