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Photophysics and Excited State Reactions of $[Ru(bpy)_2dppn]^{2+}$: A Computational Study

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Photodynamic Therapy (PDT) applied to cancer is a treatment that has as its principle the use of a compound, the photosensitizer (PS), that is photoactivated through the incidence of radiation of a specific wavelength, which will culminate in cytotoxicity to cancer cells through the generation of reactive oxygen species (ROS)[1]. The $[Ru(bpy)_2dppn]^{2+}$ (dppn = benzo[i]-dipyrido[3,2-a:2',3'-c]phenazine) complex (Figure 1) has been demonstrated to be an efficient PS. It can work through a so-called "dual-channel" reaction[2,3], where its T_1 state (local excitation) can generate singlet oxygen through Energy Transfer (ENT), and its T_2 state (charge transfer) can oxidize guanine (GUA) nucleobases when intercalating with DNA. In this work, we used DFT and TD-DFT in the investigation of the photophysics of the complex in water, and its suitability as a photosensitizer (PS) PDT. For that, the thermodynamics of electron transfer (ET) and energy transfer (ENT) reactions in the excited state with molecular oxygen and guanosine-5'-monophosphate (GMP) were investigated. The overall intersystem crossing (ISC) rate constant was approximately 10^{12} s^{-1}, indicating that this process is highly favorable, and the triplet excited states are populated. The triplet excited states are known to lead to photoreactions between the PS and species of the medium or directly with nucleobases. Here, we show that the Ru-dppn complex can react favorably to oxidize the GMP and generate singlet oxygen. Furthermore, this complex can also act as an intercalator between DNA base pairs and undergo dual-channel reactions. It has been proposed that the T_2 excited state is responsible for oxidizing the GMP, but we show that T_1 is thermodynamically capable of undergoing the same reaction.

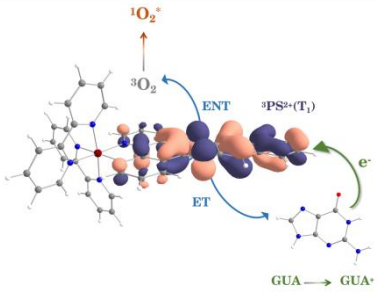

Figure 1. Dual-channel reaction of the $[Ru(bpy)_2dppn]^{2+}$ complex as a PS.

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