

Photophysical Properties of Phosphorescent Chelate Complexes with Iridium^{III}: A Quantum Chemical Study

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We have employed combined density functional theory and multi-reference configuration interaction (DFT/MRCI) methods including spin-orbit coupling (SOC) effects to investigate the photophysics of homoleptic and heteroleptic chelate complexes of the iridium^{III} ion. A critical evaluation of our quantum chemical approaches shows that a perturbational treatment of SOC is the method of choice for computing the UV/Vis spectrum of these heavy transition metal complexes while multi-reference spin-orbit configuration interaction is preferable for calculating the phosphorescence rates. The particular choice of the spin-orbit interaction operator is found to be of minor importance. Intersystem crossing (ISC) rates have been determined by Fourier transformation of the time correlation function of the transition including Dushinsky rotations. In addition to reproducing the correct orders of magnitude for the ISC rates and the individual phosphorescence emission probabilities, our theoretical study gives insight into the underlying mechanisms.