Emissive or non-emissive? TDDFT-CASSCF calculations to rationalize phosphorescence rates of Ru(II) polypyridyl complexes

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Light-activation processes in organometallic complexes are a promising field with strong applications in e.g. artificial photosynthesis or dye sensitized solar cells. Concerning these photocatalytic systems, light-harvesting antenna complexes are usually activated through high-absorbing low-lying metal-to-ligand charge transfer (MLCT) states that undergo efficiently intersystem crossing (ISC) to ^{3}MLCT states, which feature lifetimes up to microseconds and hence allow for electron transfer processes. Additionally, effective phosphoresce emission can also be achieved in some cases, as e.g. in Ir cyclometalated complexes, and thus making them good candidates as photoactive systems in light emitting diodes technology.

To get an insight into the photophysical properties of systems with more than one hundred atoms, state of the art calculations involve the use of DFT theory and its time-dependent (TD-DFT) version. When considering solvent effects and using a hybrid functional, DFT and TD-DFT methods provide a fairly good agreement with the experimental absorption and emission spectra.[1] After irradiation, ISC between the singlet and triplet manifolds takes place, due to large spin-orbit couplings (SOC). To determine the SOC matrix elements a multiconfigurational method (as e.g. the Complete Active Space Self Consistent Field, CASSCF) is demanded. Here we present a mixed DFT/CASSCF methodology to rationalize the phosphorescence radiative rates; which determine, together with the non-radiative decays, the quantum yields. Using such methodology, we have successfully rationalized the very different emissive behaviour of two similar Ru complexes.

[1] B. Beyer, C. Ulbricht, D. Escudero, C. Friebe, A. Winter, L. González, U. Schubert. *Organometallics,* **2009,** *28*, 5478–5488.