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Partial Density of States Ligand Field Theory (PDOS-LFT): Recovering A LFT-Like Picture and Application to Photo Properties of Ruthenium(II) Polypyridine Complexes

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Abstract

Gas phase density-functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are reported for a data base of 98 ruthenium(II) polypyridine complexes. Comparison with X-ray crystal geometries and with experimental absorption spectra measured in solution show an excellent linear correlation with the results of the gas phase calculations. Comparing this with the usual chemical understanding based upon ligand field theory (LFT) is complicated by the large number of molecular orbitals present and especially by the heavy mixing of the antibonding metal eg^* orbitals with ligand orbitals. Nevertheless, we show that a deeper understanding can be obtained by a partial density-of-states (PDOS) analysis which allows us to extract approximate metal t_{2g} and eg^* and ligand π^* orbital energies in a well-defined way, thus providing a PDOS analogue of LFT (PDOS-LFT). Not only do PDOS-LFT energies generate a spectrochemical series for the ligands, but orbital energy differences provide good estimates of TD-DFT absorption energies. Encouraged by this success, we use frontier-molecular-orbital-theory-like reasoning to construct a model which allows us in most, but not all, of the cases studied to use PDOS-LFT energies to provide a semiquantitative relationship between luminescence lifetimes at room temperature and liquid nitrogen temperature.

Key words: polypyridine ruthenium complexes, luminescence, density-functional theory, time-dependent density-functional theory, partial density of states

Journal of Photochemistry and Photobiology A: Chemistry Vol.348 pp 305–325(2017)

See more at: <https://arxiv.org/pdf/1707.03665.pdf>