

Modelling of spectral properties and electron transfer in Re, Ir and Pt organometallic complexes

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Femtosecond IR, absorption and emission spectroscopy experiments on a series of Re, Ir and Pt complexes identified excited states which participate to the ultra-fast intersystem crossings (~ps time scale) and mainly contribute to the photophysical properties of these molecules [1]. In order to understand the character and dynamics of optically excited states quantum chemical calculations were performed on $[\text{Re}(\text{X})(\text{CO})_3(\text{L})]^n$ (X = Cl, Br, I, im, py, protein chain; L = bpy (2,2'-bipyridine) or phen (phenantroline) systems, tetrakis(pyrophosphito)diplatin(II) complexes $[\text{Pt}_2(\text{BF}_2\text{POP})_4]^n$ and for $[\text{Ir}_2(1,8\text{-diisocyanomenthane})_4]^n$ (Ir(dimen))ⁿ.

Optimized excited-state geometries were calculated for the lowest singlet and triplet states of each complex by TD-DFT. The lowest excited states were optimized also by the unrestricted Kohn-Sham approach (UKS). DFT calculations employed the hybrid functionals either B3LYP or Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0). The solvent was described by the polarizable continuum model (PCM) (G09 program package) or conductor like screening model (COSMO) (ADF program package). Low-lying excitation energies and coupling elements between low-lying singlet and triplet states were calculated by several quantum chemical approaches which include spin orbit (SO): SO TD-DFT (ADF), SO-RASSI of MOLCAS 8.0 package based on CASSCF/MS-CASPT2.

TD-DFT results on the series of complexes well interpret main spectral characteristic of complexes in different redox states. SO-TD-DFT calculated spectra interpreted experimental UV-vis spectra including the lowest lying singlet – triplet excitations. SO calculations shown the splitting the lowest triplet states and help to understand photophysical properties. Molecular dynamic (MD) simulations on ground and the lowest triplet states followed by time DFT and TDDFT calculations at instant times were used for interpretation of time-dependent experimental data.

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References

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