



Vabilo na predavanje / Invitation to the Lecture

Prof. Dr. Oliver Kühn

Institute of Physics, University of Rostock, Albert-Einstein-Straße 23-24, 18059 Rostock, Germany

Ponedeljek / Monday 29. 5. 2023, ob / at 13:00

Velika predavalnica na Kemijskem inštitutu / Great Lecture Hall, National Institute of Chemistry; Hajdrihova 19, Ljubljana

Photophysics of Iron Complexes. A Challenge to Theory

Transition metal complexes are widely used as catalysts, photosensitizers and dyes. In particular, the six-coordinated ruthenium(II) and iridium(III) polypyridine complexes have found numerous applications in photocatalysis, light-harvesting technologies including dye-sensitized solar cells. However, due to the costs of rare metals, it is desirable to switch to the more abundant and economically feasible complexes of copper or iron. The application of such complexes is rather limited due to fast deactivation of metal-to-ligand charge-transfer (MLCT) states via metal-centered (MC) ones to the ground state. This relaxation limits the initial charge separation in MLCT states desirable for further redox reactions. Thus, the search for novel complexes with long-lived MLCT states and strategies concerning their rational design are highly warrant.

Density Functional Theory appears attractive for the characterization of the photophysical properties of transition metal complexes. In particular the use of nonempirical optimal tuning of long-range corrected functionals seems to be ideally suited for a reliable description of MLCT states. The tuning guarantees that, for a given system, the optimized functional fulfills certain properties of the otherwise unknown exact functional. In this contribution optimal tuning of functionals will be discussed for the case of iron complexes. Strong mixing between states of different character as well as the overall high density of states make these systems a particularly challenging case. While some properties as the optical spectrum often are well reproduced, the underlying potential energy surfaces, and thus the dynamics after photoexcitation, might be rather sensitive to the tuning parameters. Comparison with experimental data or with multireference CASPT2 calculations can be incorporated into the tuning strategy as an additional empirical handle. Overall, however, it must be stated that we are far away from having a black box method for the theoretical design of iron complexes.

S.I. Bokarev, O.S. Bokareva, O. Kühn, A Theoretical Perspective on Charge Transfer in Photocatalysis. The Example of Ir-Based Systems. *Coord. Chem. Rev.* **2015**, 304–305, 133.

O.S. Bokareva, O. Baig, M.J. Al-Marri, O. Kühn, L. González, The Effect of N-Heterocyclic Carbene Units on the Absorption Spectra of Fe(II) Complexes: A Challenge for Theory. *PCCP* **2020**, 22, 27605.

J. P. Zobel, A. Kruse, O. Baig, S. Lochbrunner, S. I. Bokarev, O. Kühn, L. Gonzalez, O. S. Bokareva, Can range-separated functionals be optimally tuned to predict spectra and excited state dynamics in photoactive iron complexes? *Chemical Science* **2023**, 14, 1491.

M. Bauer, J. Steube, A. Pöpcke, O. Bokareva, T. Reuter, S. Demeshko, R. Schoch, S. Hohloch, F. Meyer, K. Heinze, O. Kühn, S. Lochbrunner, Janus-type emission from a cyclometalated Iron (III) complex, *Nature Chemistry* **2023**, 15, 468.



info: janez.mavri@ki.si

Vljudno vabljeni / Kindly invited