

ABSTRACTS

10: Zsolt Valicsek, Gábor Eller, Ottó Horváth: Equilibrium, photophysical and photochemical examination of anionic lanthanum(III) mono- and bisporphyrins: the effects of the out-of-plane structure, *Dalton Trans.*, 41 (2012) 13120-13131

Lanthanum(III) ion forms kinetically labile complexes with the 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin anion ($\text{H}_2\text{TSP}^{4-}$), the compositions and formation constants of which significantly depend on the presence of potential axial ligands (at 0.01 M). Deviating from the chloride ion, acetate coordinating to the metal center hinders the formation of bisporphyrin complex. In these lanthanum(III) complexes, the metal center, due to its large ionic radius (103.2 pm), is located out of the ligand plane, distorting it. Accordingly, the absorption and fluorescence spectra of these coordination compounds display special properties characteristic of the so-called sitting-atop (SAT) or out-of-plane (OOP) porphyrin complexes. Metalation significantly decreases the quantum yield of the fluorescence from the S_1 excited state. Quantum chemical calculations (DFT) confirm the considerable OOP displacement of the La(III) center (about 120 pm in the monoporphyrin complexes). The monoporphyrins display efficient fluorescence ($\Phi \approx 0.03$), while the bisporphyrin does not emit. Differing from the normal (in-plane) metalloporphyrins, excitation of these lanthanum(III) porphyrins leads to an irreversible ligand-to-metal charge transfer (LMCT) followed by the opening of the porphyrin ring, which is also typical of OOP complexes. Dissociation releasing free-base porphyrin can also be observed upon irradiation of the monoporphyrin in acetate solution, while in the presence of chloride ions interconversions of the mono- and bisporphyrins may also take place beside the irreversible photoredox reaction.