

ABSTRACTS

24: Ottó Horváth, Zsolt Valicsek, Gergely Harrach, György Lendvai, Melinda A. Fodor, Spectroscopic and photochemical properties of water-soluble metalloporphyrins of distorted structure, *Coord. Chem. Rev.* 256 (2012) 1531– 1545

The location of the metal center in the porphyrin complexes strongly depends on its size, charge and spin multiplicity. Metal ions can form normal (in-plane) metalloporphyrins, or several of them, being too large to fit into the coordination cavity of the porphyrin ring, are located above the ligand plane, resulting in out-of-plane (OOP) complexes. The distorted structure of the latter type induces special photophysical and photochemical features that are characteristic of all OOP complexes. Efficient LMCT processes can take place upon excitation of these compounds. In this paper we review the results of recent studies on water-soluble (1:1) porphyrin complexes of several metal ions to reveal how the size (and partly the oxidation state) of the metal center influences their structure and photoinduced behavior. Besides, the effects of the pre-distortion (via bromination) and the charge of the porphyrin ligand on the structure and photoreactivity of these complexes are also discussed. While the porphyrin complex of Ag^{2+} ($r_{\text{ion}} = 94 \text{ pm}$) formed in the reaction of the Ag^+ ion and the TSPP^{6-} ligand ($\text{H}_2\text{TSPP}^{4-} = 5,10,15,20\text{-tetrakis(4-sulfonatophenyl)porphyrin anion}$) displays OOP features, the corresponding complex of also open-shell Au^{3+} ($r_{\text{ion}} = 85 \text{ pm}$) is unambiguously of planar structure, which does not show any fluorescence and photoredox degradation. In the case of the anionic complex of Cd^{2+} ($r_{\text{ion}} = 95 \text{ pm}$), octabromination of the TSPP^{6-} ligand results in significant red-shifts in the absorption and emission spectra, dramatically diminishes the fluorescence quantum yield and lifetime, and turns the photodegradation into a very oxygen-sensitive reaction. The axial coordination of HO^- ligand further increases the distortion and photoreactivity. The efficiency for the photoinduced LMCT reaction of the cationic complex of Bi^{3+} ($r_{\text{ion}} = 103 \text{ pm}$) formed with the TMPyP^{2+} ligand ($\text{H}_2\text{TMPyP}^{4+} = 5,10,15,20\text{-tetrakis(1-methyl-4-pyridinium)porphyrin cation}$) is significantly lower than that for anionic BiTSPP^{3-} , due to the weaker Lewis-basicity of the positively charged porphyrin. DFT calculations of the geometrical structures show good correlations with the observed photophysical and photochemical properties. Deviating from the inner-sphere LMCT reaction of OOP complexes, the cationic ligand (such as TMPyP^{2+} and TAPP^{2+} ($\text{H}_2\text{TAPP}^{4+} = 5,10,15,20\text{-tetrakis(4-trimethylammonium phenyl)porphyrin cation}$)) is favorable for the outer-sphere photoinduced reduction of the metal center in the in-plane manganese(III) porphyrins because the anionic porphyrin ligands of higher Lewis-basicity stabilize the +3 oxidation state. The cationic porphyrin ligands enhance the formation of manganese(II) complexes with OOP characteristics, and can be utilized in photocatalytic systems applicable for water splitting.