A PHOTOPHYSICAL INVESTIGATION OF NICKEL TETRAPYRROLE MACROCYCLES

ANDREY V. ZAMYATIN, *Del Mar Photonics,Inc., 4119 Twilight Ridge, San Diego, CA 92130*; MICHAEL A.J. RODGERS, *Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green, Ohio, 43403*.

The porphyrins are an important class of chromophores with high stability and efficient light absorption ability in the visible and near-infrared regions of the optical spectrum. Porphyrins have a set of highly delocalized π-orbitals situated on the carbon-nitrogen framework. When such a ligand is coordinated to a centrally-located metal atom of the transition series, having incompletely filled d-orbitals (Ni, Co, Fe, Cu, etc.), the π- and d-manifolds can interact. As a result the excited state deactivation dynamics becomes very dependent on the electronic nature of the central metal. This work has two major parts. The first part focuses on the investigation of dual excited states of some Ni(II) porphyrins. Dual excited states are molecular entities that have absorbed two successive photons to generate molecular states with electronic excitation in two distinct regions of the metalloporphyrin. The dual excited states were studied by means of femtosecond two-pump-one-probe transient absorption spectroscopy. Two successive pulses of 400 nm and 550 nm were used for excitation. Based on the kinetic and spectral information of the observed transients we propose a mechanism for the Ni(II) porphyrin dual excited state deactivation involving formation of an intramolecular charge transfer state. The second part concerns the photophysical studies of Ni(II) meso-tetraphenyl tetrabenzoporphyrin (NiTPTBP). The excited states metal-ligand dynamics of Ni(II)TPTBP have been investigated using time-resolved absorption spectroscopy in different solvents. The DFT computations revealed the presence of two ligand-to-metal charge transfer states located close in energy to the ^{3}(d,d) state. These LMCT states are responsible for the lifetime dependence on solvent polarity. Upon photoexcitation two competing processes depopulate the porphyrin lowest singlet excited state S_1. One involves the charge transfer states manifold and another involves the metal excited state manifold