MCD spectroscopy and TD-DFT calculations of Metal Porphyrinoids

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Optical spectroscopy has long been used to study the electronic structure of metal porphyrinoids. The energies and the relative intensities of the major $\pi \rightarrow \pi^*$ bands are based primarily on the magnetic properties of the four frontier π-MOs and can be described qualitatively by Gouterman's 4-orbital model [1]. Electronic excitation of metal porphyrinoids induces strong magnetic dipole moments within $\pi\pi^*$ excited states due to the circular movement of charge on the inner perimeter of the heteroaromatic ligand, which is analogous to current loop experiments within elementary physics. Absorption of left and right circularly polarized photons results in differing directions of circular charge circulation and induced magnetic moments that are aligned either with or against the *z*-axis of light propagation. When a magnetic field is applied parallel to the beam of a CD spectrometer, Zeeman splitting of states information can be derived from the resulting magnetic circular dichroism (MCD) spectrum. Historically, MCD spectroscopy provided the ground and excited state orbital degeneracy information, which was required to fully assign the optical spectra of many biologically significant metal porphyrinoids.

A systematic study of the UV-visible absorption and MCD spectra and B3LYP based TD-DFT calculations of a wide range of planar and saddled synthetic Zn(II) porphyrinoids is reported. The study demonstrates that trends in the induced magnetic dipole based properties of the optical spectra are reproduced successfully by the TD-DFT technique and these trends are sensitive to even small changes in the planar geometry of the porphyrinoid ligand. Recent advances by Seth *et al.* in the application of TD-DFT to the three Faraday terms [2] point the way towards a future renaissance for MCD spectroscopy within porphyrinoid research in applications such as the modeling of ligand non-planarity within heme-binding proteins. Until recently, research on TD-DFT had focused primarily on the absorption spectrum and the electric dipoles generated by the linear translation of charge along the *x*-, *y*- and *z*-axes.

References: [1] Mack, J.; Stillman, M. J. in *Handbook of Porphyrins and Related Macrocycles*, Kadish, K.; Smith, K.; Guilard, R., Eds., Academic Press, New York, 2003; Vol. 16, Ch. 103, pp 43-116. [2] M. Seth, T. Ziegler, A. Banerjee, J. Autschbach, S. J. A. van Gisbergen, E. J. Baerends *J. Chem. Phys.* **2004**, *120*, 10942.