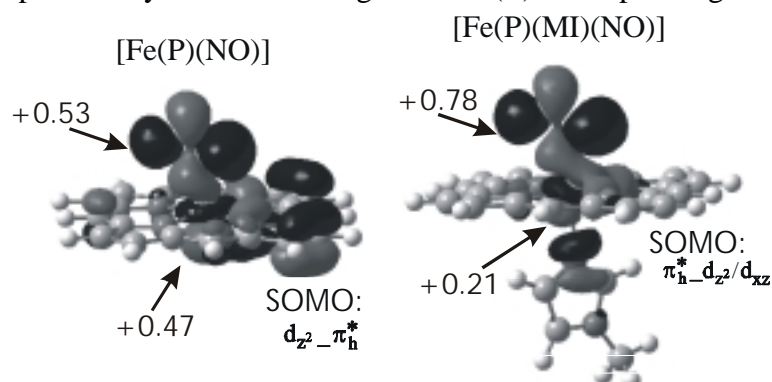


# Electronic Structure of Five- vs. Six-coordinate Fe(II)-Porphyrin NO Adducts: Effects of Binding the axial N-Donor Ligand

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Iron(II)-porphyrin NO adducts play a key role in the mechanisms of many metalloproteins including nitrite and nitric oxide reductases, nitric oxide synthase and guanylate cyclase. In this study, the spectroscopic properties and the electronic structures of five- and six-coordinate Fe(II)-porphyrin NO complexes are presented. Coordination of N-donor ligands L to five-coordinate [Fe(TPP\*)(NO)] (TPP\* = tetraphenylporphyrin type ligand) is studied in solution using UV-Vis absorption and NMR spectroscopies to monitor the formation of [Fe(TPP\*)(L)(NO)] and [Fe(TPP\*)(L)<sub>2</sub>]. The differences in the electronic structures of the five- and six-coordinate Fe(II)-NO complexes are investigated using vibrational and magnetic circular dichroism (MCD) spectroscopies coupled to density functional (DFT) calculations [1]. In the five-coordinate complex, a strong Fe-NO  $\sigma$  bond between  $\pi_h^*$  and  $d_{z^2}$  is present which leads to a large transfer of spin density from the NO ligand to Fe(II) corresponding to an electronic structure with noticeable



**Figure 1:** Contour plots of the SOMOs of five- and six-coordinate Fe(II)-porphyrin NO adducts. The numbers given in the Figure represent the calculated spin densities (P = porphine, MI = 1-methylimidazole).

Fe(I)-NO<sup>+</sup> character. On coordination of the sixth ligand, the spin density is pushed back from the iron toward the NO ligand resulting in an Fe(II)-NO(radical) type electronic structure.

[1] (a) V. K. K. Praneeth, F. Neese, N. Lehnert *Inorg. Chem.* **2005**, asap. (b) V. K. K. Praneeth, C. Näther, G. Peters, N. Lehnert, *Manuscript in preparation*