# Spectroscopic Properties and Electronic Structures of Thiolate Coordinated Iron-Porphyrin NO Adducts

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Nitric oxide (NO) bound heme centers with axial cysteinate coordination are present in the active sites of fungal nitric oxide reductase ($P450_{nor}$), nitric oxide synthase (NOS) and *Cimex* nitrophorin. In this regard, we have synthesized thiolate coordinated iron-porphyrin NO complexes as models for these enzymes active sites. A series of six-coordinate Fe(II)-NO adducts $[Fe^{II}(TPP)(SR)(NO)]^-$ (TPP = tetraphenylporphyrin) with substituted thiophenolates and tetrahydrothiophene have been prepared and investigated in solution using electron paramagnetic resonance (EPR) spectroscopy[1]. From the obtained *g* values and $^{14}N$ hyperfine pattern of the NO ligand it is concluded that the coordination of thiophenolates to the Fe(II) center is weak in comparison to the corresponding 1-methylimidazole adduct and the ferrous NO adducts of $P450_{nor}$ and $P450_{cam}$[2]. The interaction of the Fe(II)-NO center with different thiolate ligands SR has also been explored computationally. The six-coordinate model complex $[Fe(P)(SR)(NO)]^-$ (P = porphine ligand) has an interesting electronic structure where NO acts as a medium strong $\sigma$ donor and $\pi$ acceptor ligand. The vibrational properties, bond distances and force constants have been determined for this model system from DFT calculations. The trend in the calculated Fe-S bond strengths follows the trend in basicity of different sulfur donors. Correspondingly, the co-ordination behavior of thiolates with Fe(III)-NO centers has been explored using UV-Vis, vibrational, and NMR spectroscopy. The initially formed $[Fe^{III}(TPP)(SR)(NO)]$ adducts show decomposition over time and the products have been analyzed using spectroscopic techniques. In addition, DFT results for these Fe(III) model systems are also presented.

1. V.K.K. Praneeth, E. Haupt, N. Lehnert, *J. Inorg. Biochem.* 2005, **99,** 940-948.
2. Y. Shiro, M. Fujii, Y. Isogai, S.-I. Adachi, T. Iizuka, E. Obayashi, R. Makino, K. Nakahara, H. Shoun, *Biochemistry.* 1995, **34**, 9052-9058.