

## **Nitric Oxide Reactivity with Iron Porphyrins**

Abhishek Dey

School of Chemical Science, Indian Association for the Cultivation of Science, 2A Raja SC Mullick Road,  
WB, India 700032  
*abbeyde@gmail.com*

Ferrous nitrosyl  $\{\text{FeNO}\}^7$  species are intermediates common to the catalytic cycles of  $\text{Cd}_1\text{NiR}$  and  $\text{CcNiR}$ , two heme-based nitrite reductases (NiR), and its reactivity vary dramatically in these enzymes. The former reduces  $\text{NO}_2^-$  to  $\text{NO}$  in the denitrification pathway while the latter reduces  $\text{NO}_2^-$  to  $\text{NH}_4^+$  in dissimilatory nitrite reduction. With very similar electron transfer partners and heme based active sites, the origin of this difference in reactivity has remained unexplained. Differences in the structure of the heme  $d_1$  ( $\text{Cd}_1\text{NiR}$ ), which bears electron-withdrawing groups and has saturated pyrroles, relative to heme  $c$  ( $\text{CcNiR}$ ) is often invoked to explain these reactivities. A series of iron porphyrinoids, designed to model the electron-withdrawing peripheral substitution as well as the saturation present in heme  $d_1$  in  $\text{Cd}_1\text{NiR}$ , and their  $\text{NO}$  adducts are synthesized and their properties are investigated. The data clearly show that the presence of electron-withdrawing groups (EWG) and saturated pyrroles together in a synthetic porphyrinoid (FeDEsC) weakens the Fe-NO bond in  $\{\text{FeNO}\}^7$  adducts along with decreasing the bond dissociation free energies ( $\text{BDFE}_{\text{NH}}$ ) of the  $\{\text{FeHNO}\}^8$  species. The EWG raises the  $E^0$  of  $\{\text{FeNO}\}^{7/8}$  process, making the electron transfer (ET) facile, but decreases the  $\text{pK}_a$  of  $\{\text{FeNO}\}^8$  species, making protonation (PT) difficult, while saturation has the opposite effect. The weakening of the Fe-NO bonding biases the  $\{\text{FeNO}\}^7$  species of FeDEsC for  $\text{NO}$  dissociation, as in  $\text{Cd}_1\text{NiR}$ , which is otherwise set-up for a proton coupled electron transfer (PCET) to form a  $\{\text{FeHNO}\}^8$  species eventually leading to its further reduction to  $\text{NH}_4^+$ .