

# Ligand Substitution and Conformational Control of a Metal-Site Redox Function

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Our research focuses on understanding mechanisms of redox-linked ligand-substitution reactions at the heme centers. We are probing redox reactivity, ligand-substitution dynamics and other conformational processes in ligand-switching *Geobacter* cytochromes as well as a number of other heme proteins. These studies not only explore important problems in coordination chemistry and ET mechanisms but could also provide valuable insights for the design of molecular systems with switchable ET properties for solar-energy harvesting.

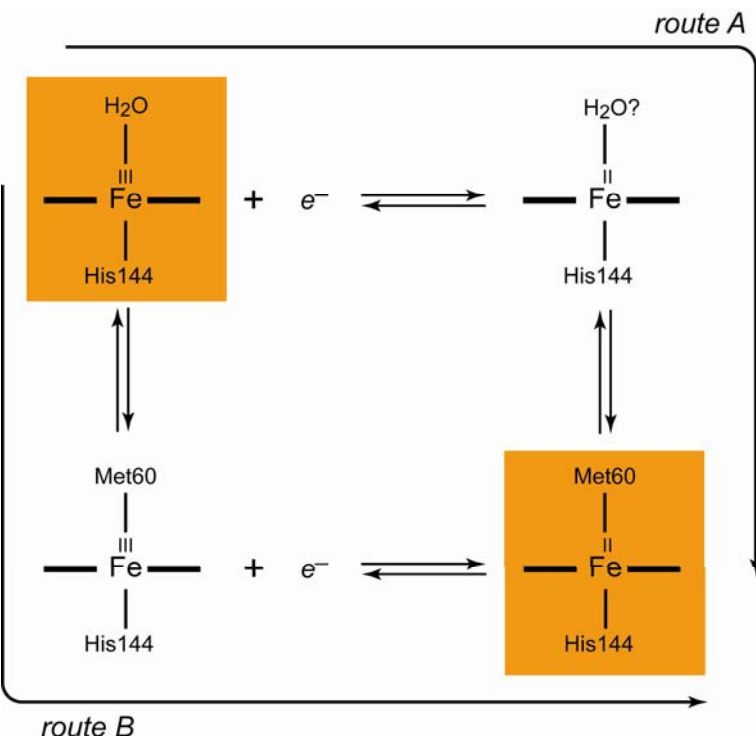


Figure 1

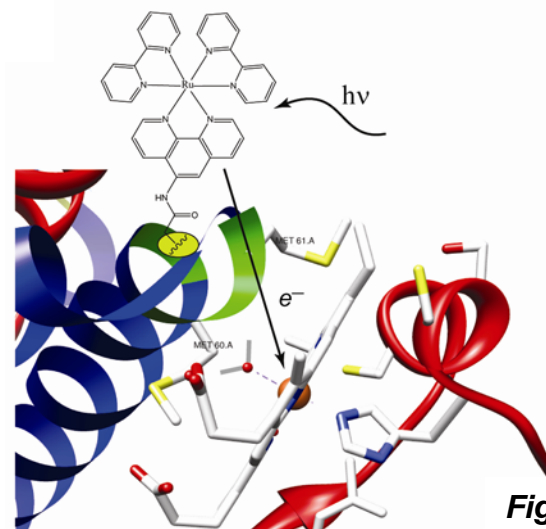


Figure 2

We have designed a system to examine reduction and accompanying conformational changes in two *Geobacter* cytochromes GSU0582 and GSU0935 through kinetics of photoinduced (route A) and thermal (route B) reactions (Figure 1). In Ru-labeled proteins with short Ru-Fe distances (Figure 2) the redox transformation is rate-limited by the ligand substitution. We correlate these kinetics with steps in the folding pathway of *Geobacter* cytochromes and find that surrounding protein matrix plays an important role in driving these redox rearrangements.