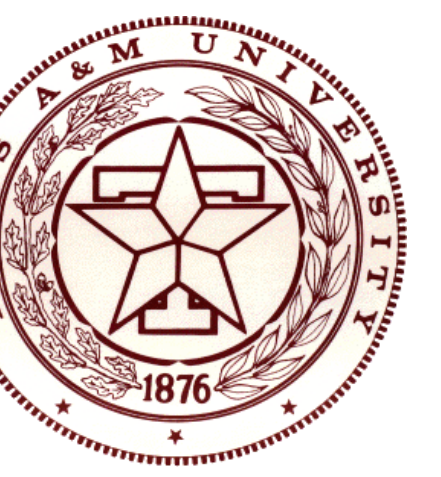




# Unleashing a Pendant Base by Reduction-Induced Hemilability in $MN_2S_2 \cdot Fe(NO)_2$ Complexes

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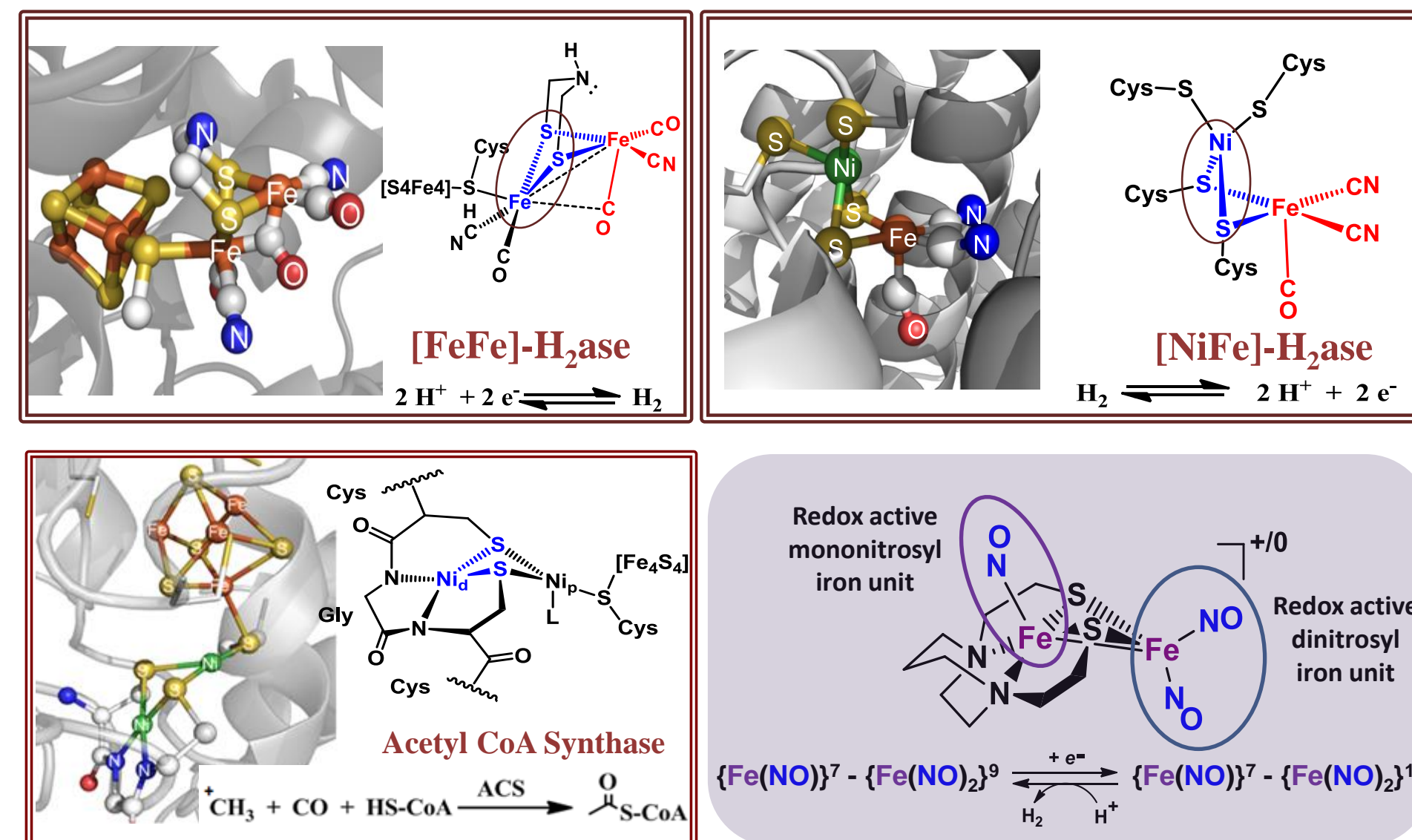
## Introduction

The plethora of bimetallic active sites in biology has motivated the search for heterobimetallic small molecule models as found in the active sites of [NiFe]-, [FeFe]-hydrogenases, CO-dehydrogenases and acetyl coA synthase.<sup>1-4</sup>

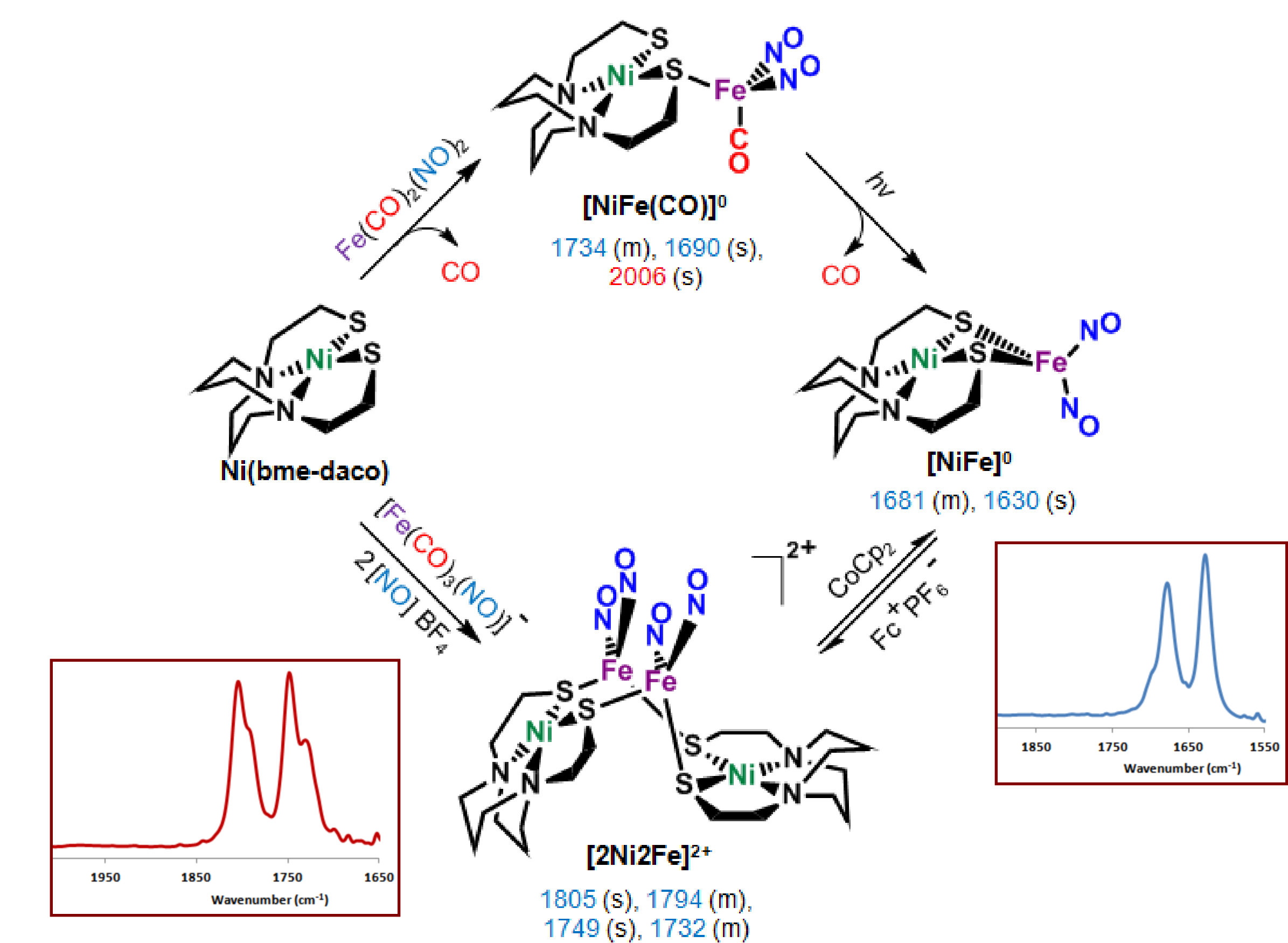
Metallothiolates ( $MN_2S_2$ ) as redox-active bridging ligands, have been developed in heterobimetallics that show electronic cooperativity between two metal centers.<sup>5</sup>

Recent studies of  $[MN_2S_2 \cdot Fe(CO)(\eta^5-C_5H_5)]^+$  ( $M = Ni^{2+}, Fe(NO)^{2+}$ ), showed hemilability of the bridging *cis*-dithiolates upon sequential reductions and protonations, allowing  $H_2$  production under electrochemical conditions. Computation-assisted structure-function analysis delineated a reductive ( $\mu$ -S)Fe(CO)( $\eta^5-C_5H_5$ ) bond cleavage that creates a site for proton uptake at iron (becoming a hydride) and at S (remaining a proton) yielding an acid-base pair.<sup>6</sup>

Earlier studies using redox-active,  $(N_2S_2)Fe(NO)$ , bound to non-innocent iron dinitrosyl unit, isolated in two redox states,  $\{Fe(NO)_2\}^{9/10}$ , illustrated modest electrocatalysis for proton reduction. Electrochemical studies showed two single-electron reduction events assigned to  $\{Fe(NO)_2\}^{9/10}$  and  $\{Fe(NO)_2\}^{7/8}$  couples. The  $\{Fe(NO)_2\}^{9/10}$  couple was the catalytically active center for electrochemical proton reduction in the presence of strong acid  $HBF_4 \cdot Et_2O$ .<sup>7</sup>

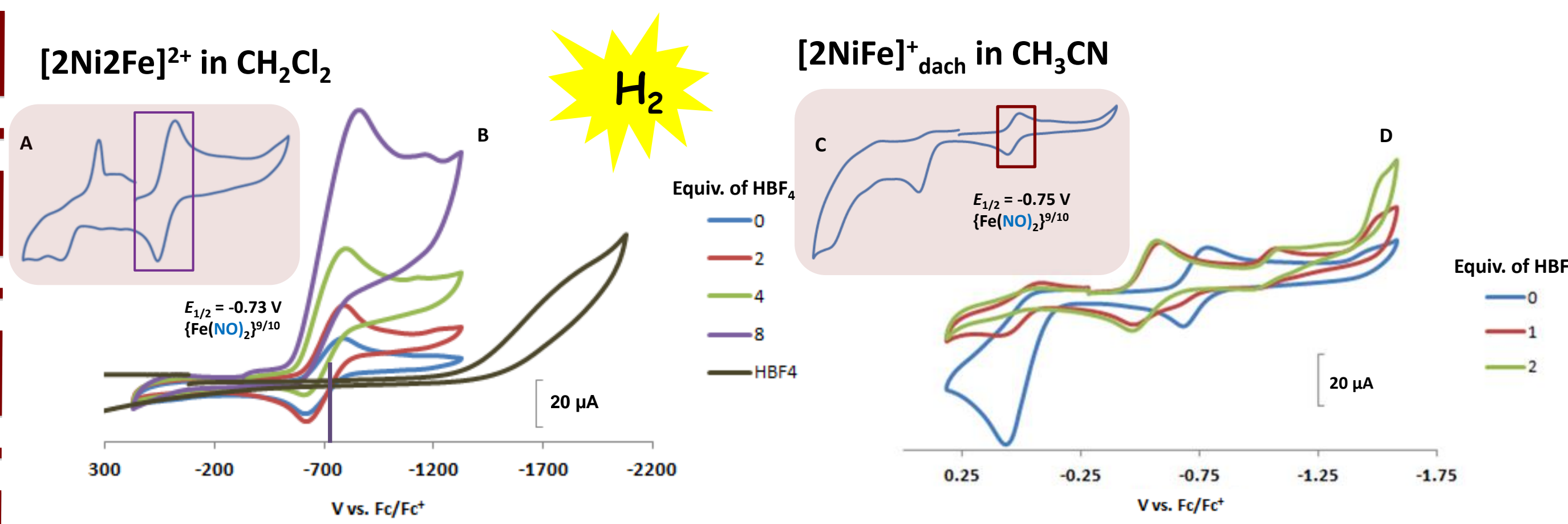


## Synthesis of [NiFe]<sup>0</sup> and [NiFe(CO)]<sup>0</sup> Neutral Complexes and [2Ni2Fe]<sup>2+</sup> Complex as BF<sub>4</sub><sup>-</sup> Salt.

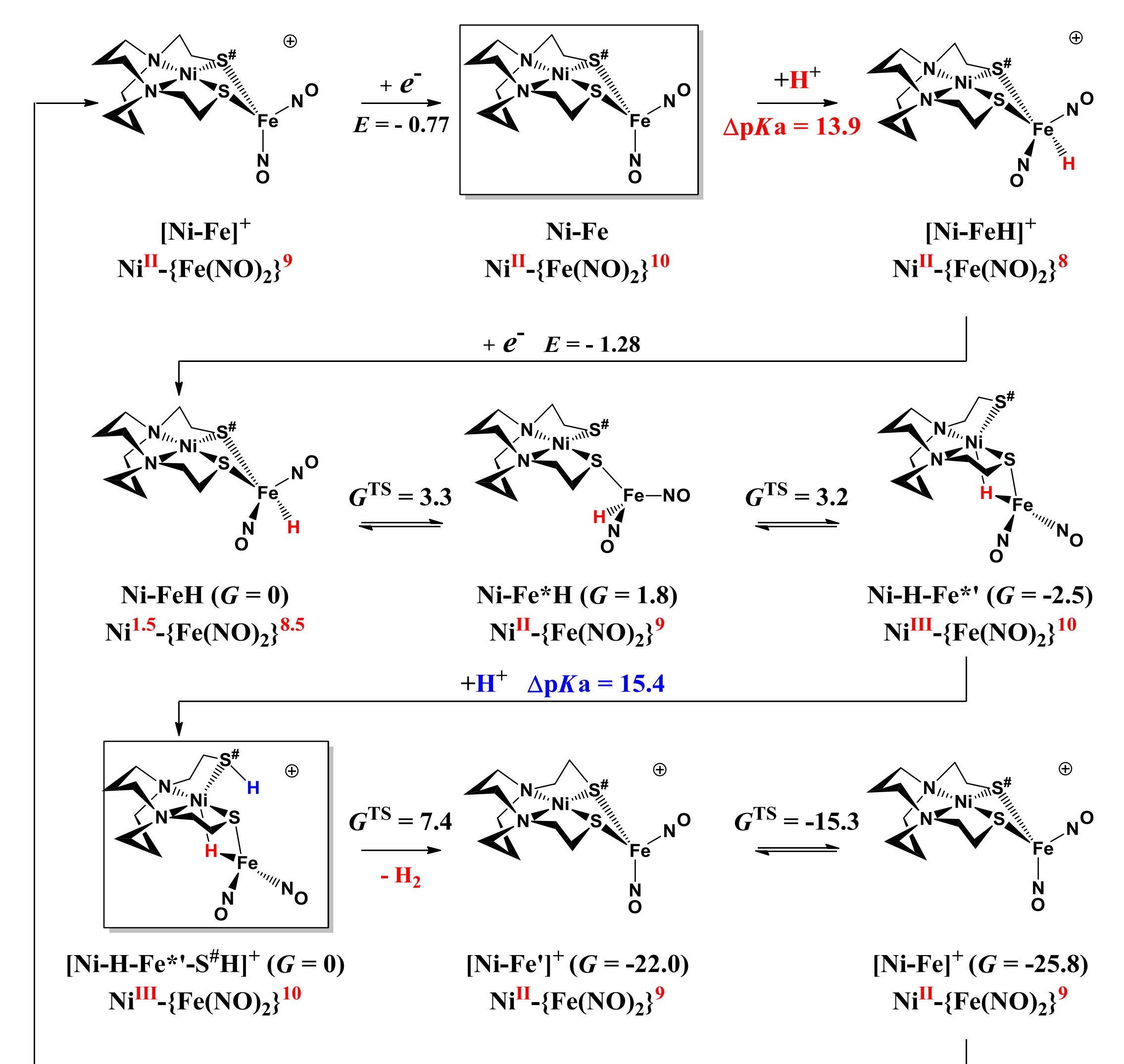


## Electrochemical Studies

### Cyclic Voltammograms of [2Ni2Fe]<sup>2+</sup> and [2NiFe]<sup>dach</sup> in Presence of HBF<sub>4</sub>·Et<sub>2</sub>O

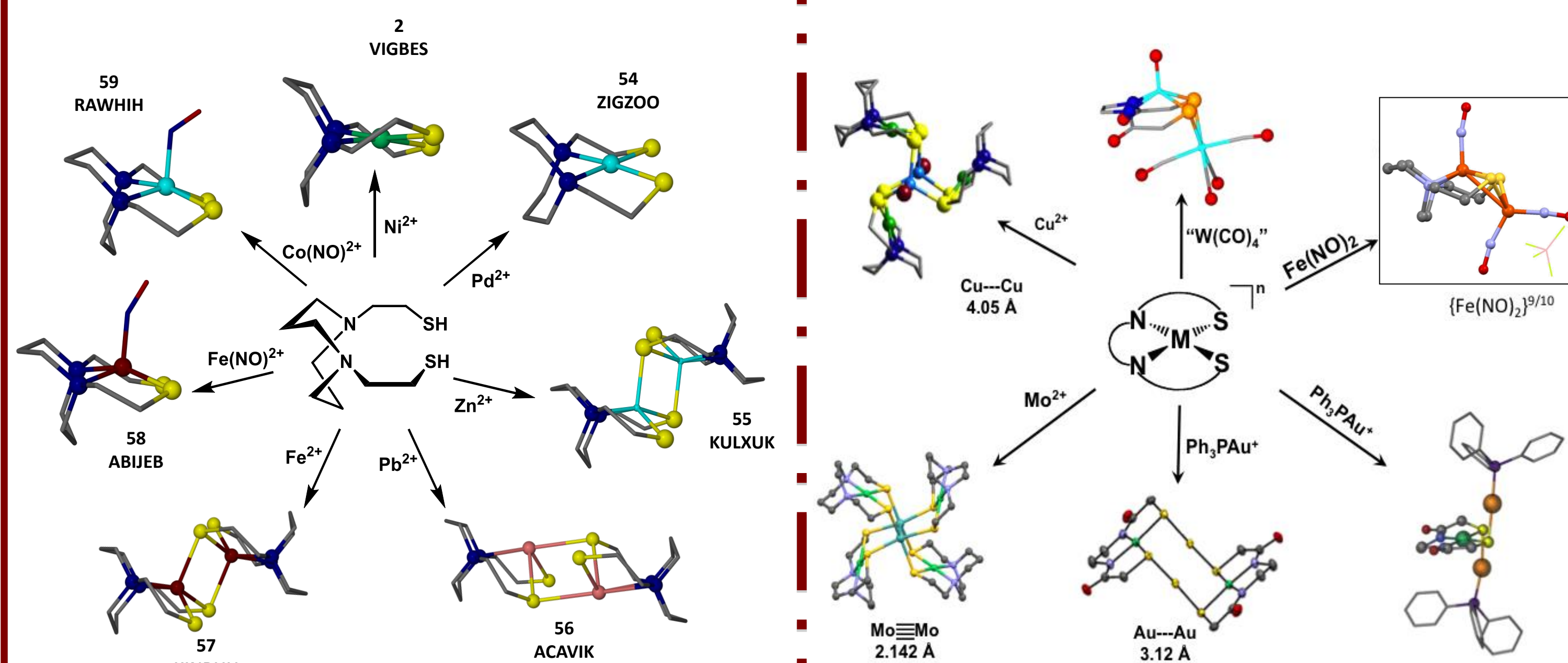


## Computational Mechanistic Study

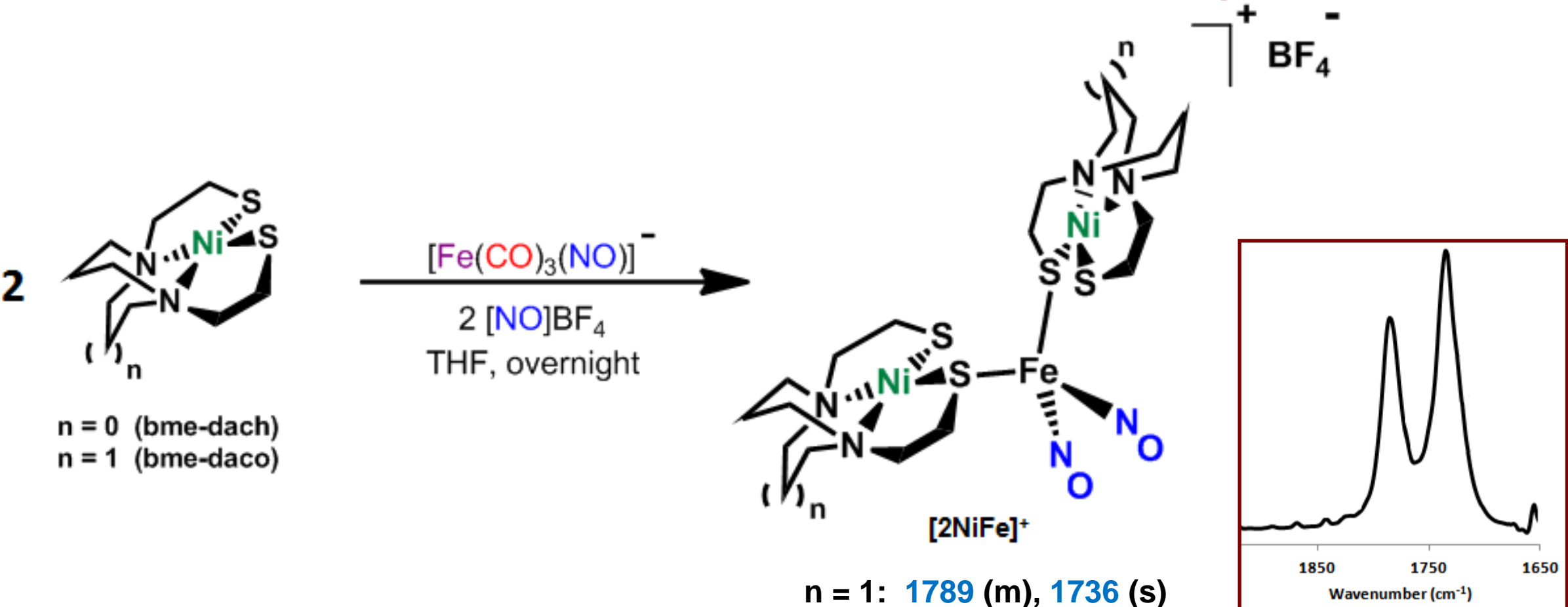


## N<sub>2</sub>S<sub>2</sub> Ligands with Thiolates "Tamed" by Metals<sup>5</sup>

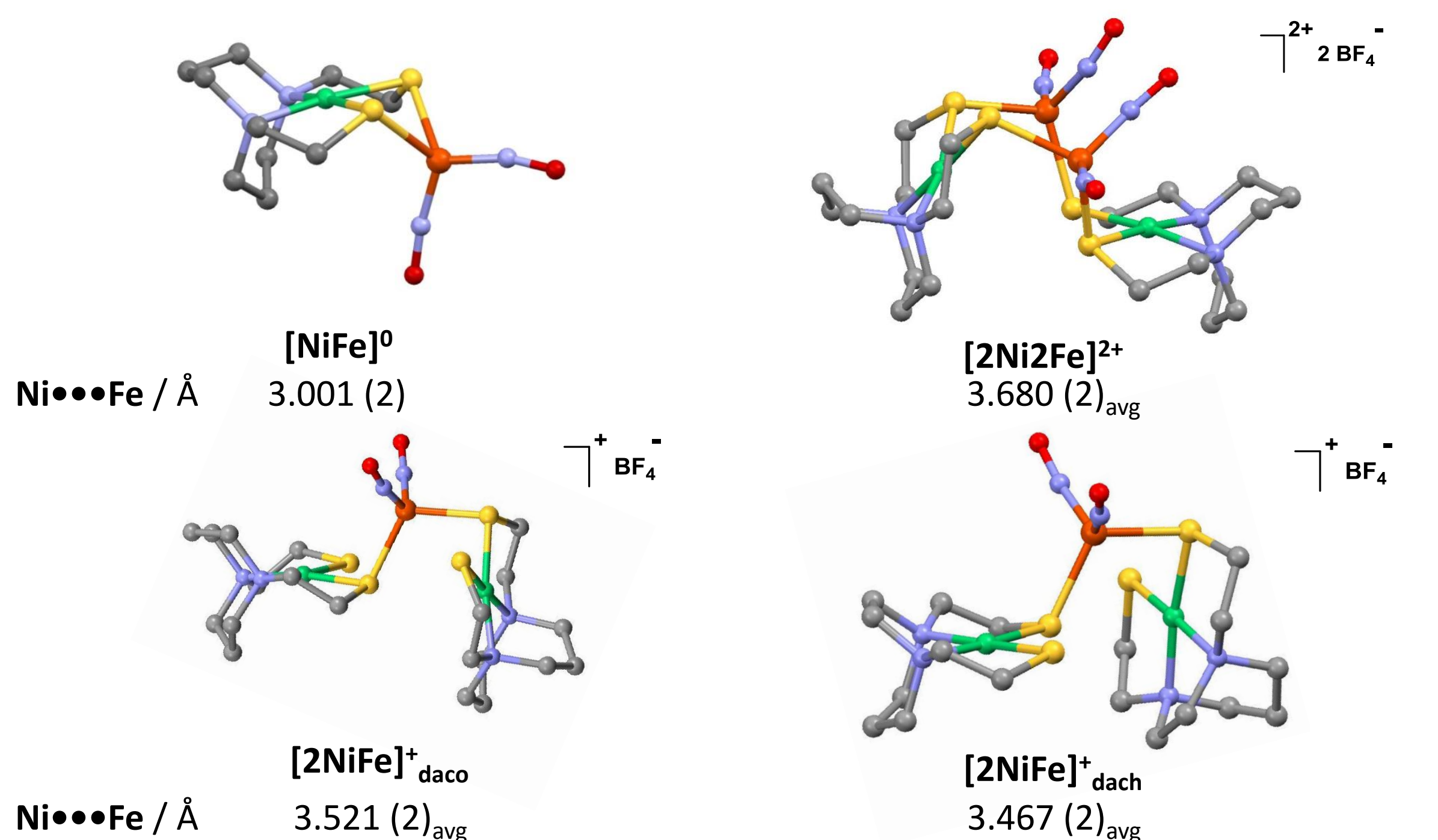
## MN<sub>2</sub>S<sub>2</sub> Metalloligands at Work: Bidentate Bridging to Single Metals<sup>5</sup>



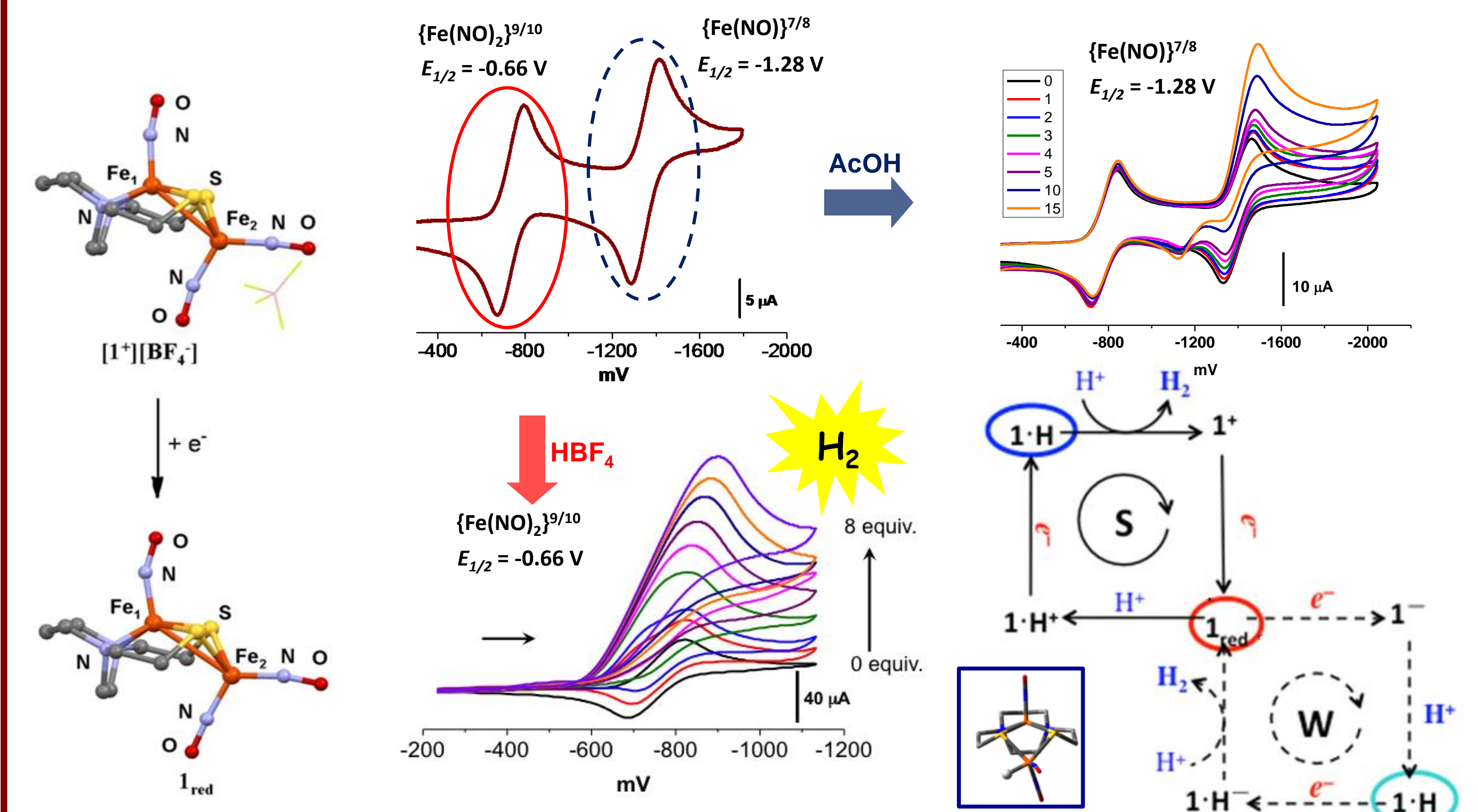
## Synthesis of [2NiFe]<sup>+</sup> Complex as BF<sub>4</sub><sup>-</sup> Salt



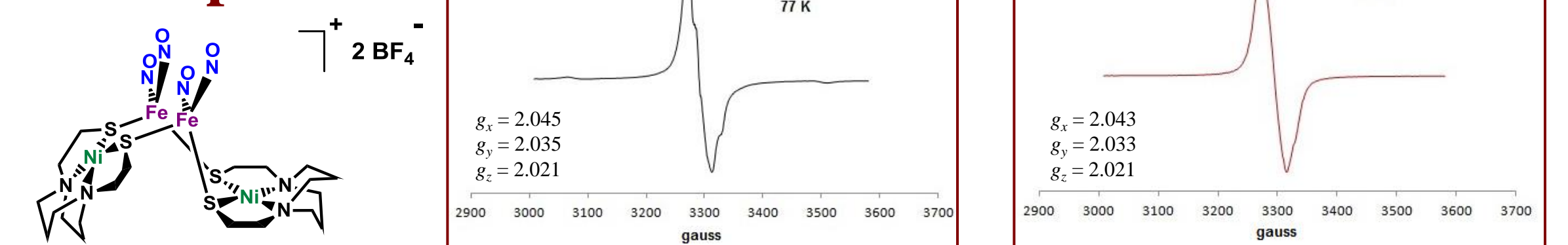
## Molecular Structures with Redox Non-Innocent {Fe(NO)<sub>2</sub>}<sup>9/10</sup> Acceptor



## Heterobimetallic DNIC as an Electrocatalyst for Proton Reduction<sup>7</sup>



## EPR Spectra



## Conclusions

- 1) Redox innocent  $Ni(N_2S_2)$ , instead of  $(NO)Fe(N_2S_2)$ , yields  $[Ni^I(N_2S_2) \cdot Fe(NO)_2]^{0+}$  complexes that elucidates or clarifies the dinitrosyl unit as catalytically active center for proton reduction.
- 2) Libraries of receivers and donors provide a rich field for catalyst development.
- 3) Preliminary DFT computations suggest that sulfur – iron bond cleavage provides the needed pendant base effect for proton uptake.
- 4) Complex  $[2Ni2Fe]^{2+}$  produces  $H_2$  under electrocatalytic conditions in presence of 50 equivalents of  $HBF_4 \cdot Et_2O$ . The headspace gas from bulk electrolysis contains  $H_2$ , detected by gas chromatography.
- 5) The internally generated pendant base is a design feature that can be optimized in catalyst development.

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