Supplementary Material

Disclosure of the hydrogen evolution mechanism on [FeFe]- hydrogenases-inspired molecular catalysts – a DFT study

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Reduction potential calculation

Table S1. Experimental redox potential and calculated redox potential by PBE and BP86 for the 1st and 2nd electron reduction of molecular catalysts

		Experimental	Cal (PBE)	Cal (BP86)
1	1st reduction	−1.51	−1.60	−1.54
	2nd reduction	−2.28	−2.27	−2.23
2	1st	−1.68	−1.8	−1.76
3	1st	−1.98	−1.93	−1.84
4	1st	−1.94	−1.95	
5	1st	−2.08	−2.13	
6	1st	−1.19	−1.28	−1.02
	2nd	−1.66	−1.70	−1.65
7	1st	−1.33	−1.47	−1.43
	2nd	−1.31	−1.29	−1.61
8	1st	−1.784	−1.86	

Experimental values are from Felton *et al.*[1] and Cal (PBE) and Cal (BP86) values are from A. Y. Siyao Qiu and Chenghua Sun, unpubl. data.
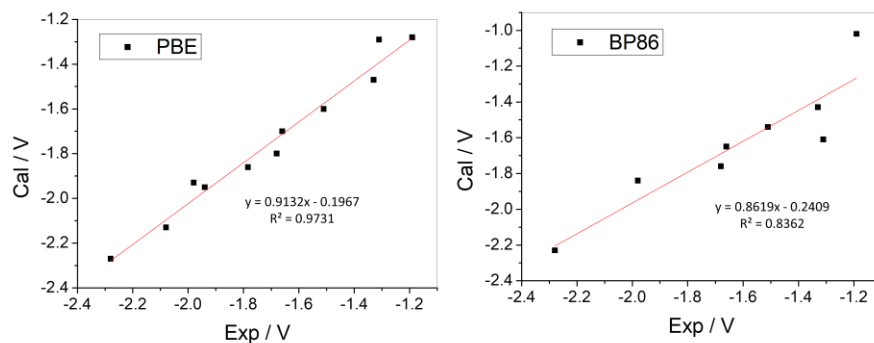

Figure S1. Experimental redox potential *v.* calculated redox potential for the one- and two-electron reduction of molecular catalysts.

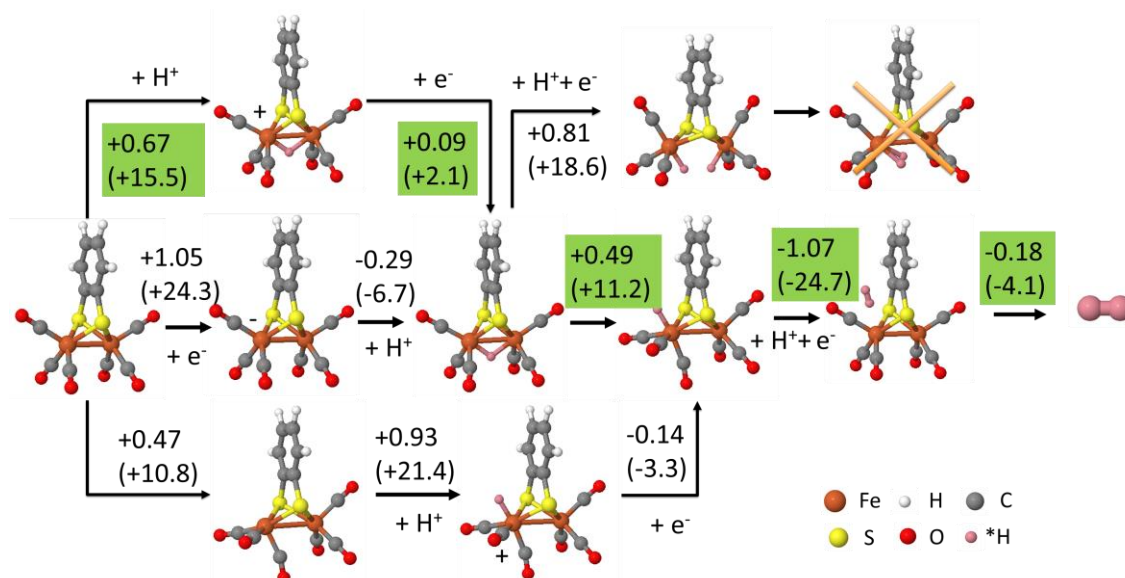# HER pathway of FeFe molecular catalysts

Figure S2. HER pathway followed by the (μ-bdt)Fe$_2$(CO)$_6$ molecular catalysts. Gibbs free energy differences, in electronvolts (kcal/mol).

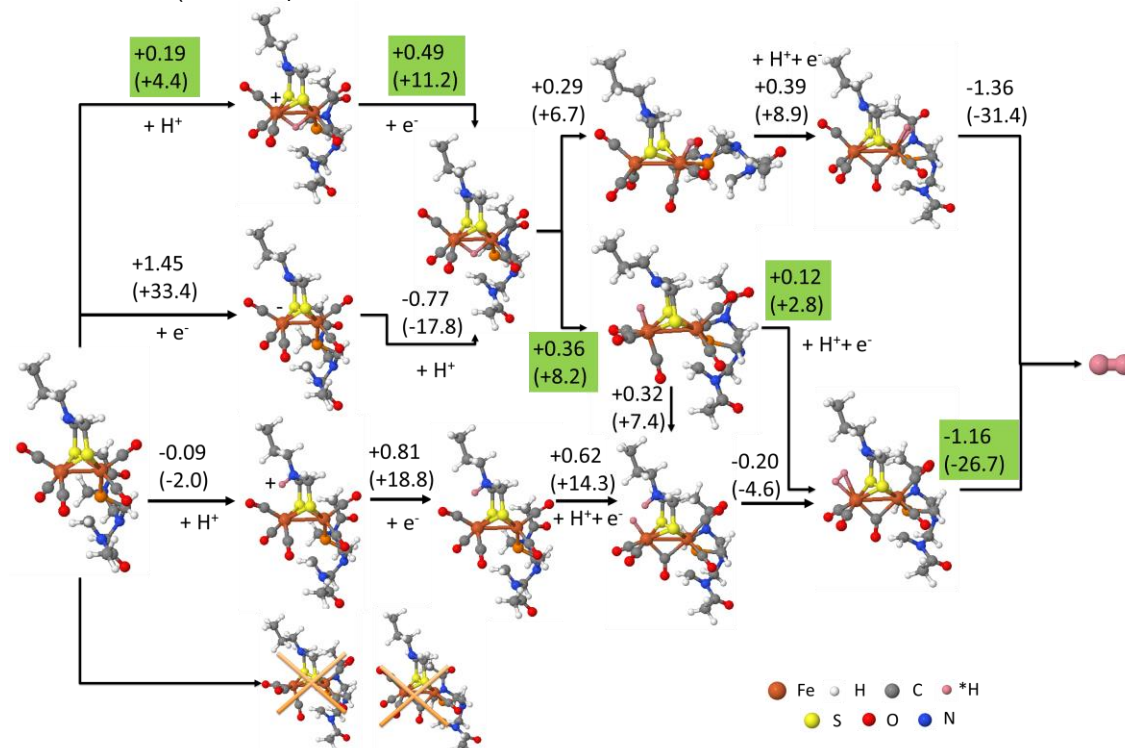**Figure S3.** HER pathway followed by the CH$_3$CH$_2$CH$_2$N(μ-SCH$_2$)$_2$[Fe$_2$(CO)$_5$DAPTA] (2-DAPTA) molecular catalysts. Gibbs free energy differences, in electronvolts (kcal/mol).

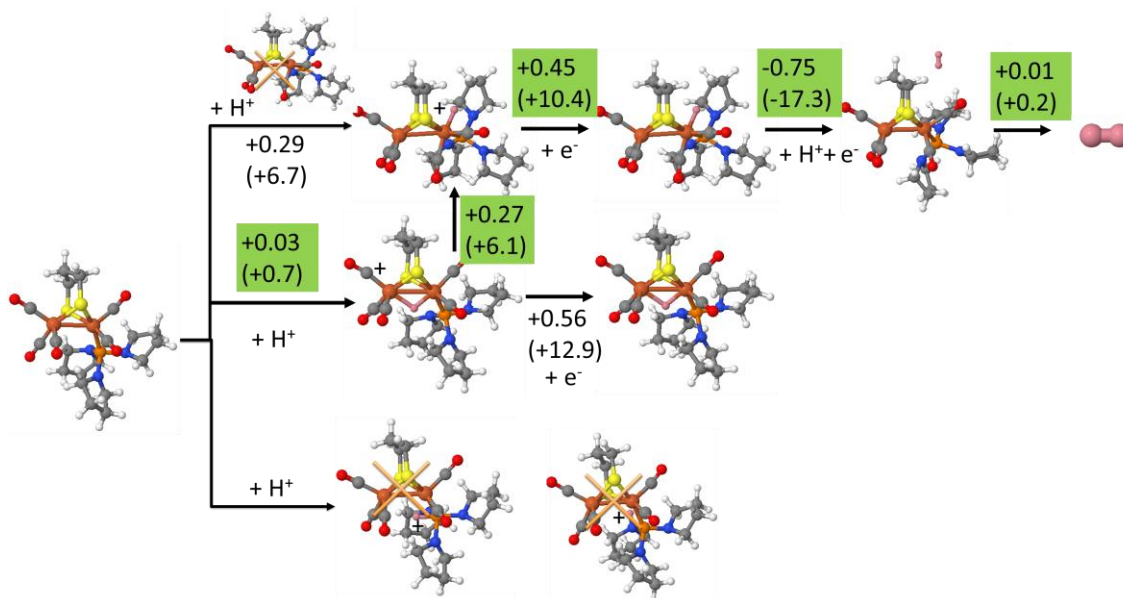**Figure S4.** HER pathway followed by the (μ-pdt)Fe$_2$(CO)$_5$P(NC$_4$H$_8$)$_3$ molecular catalysts. Gibbs free energy differences, in electronvolts (kcal/mol).
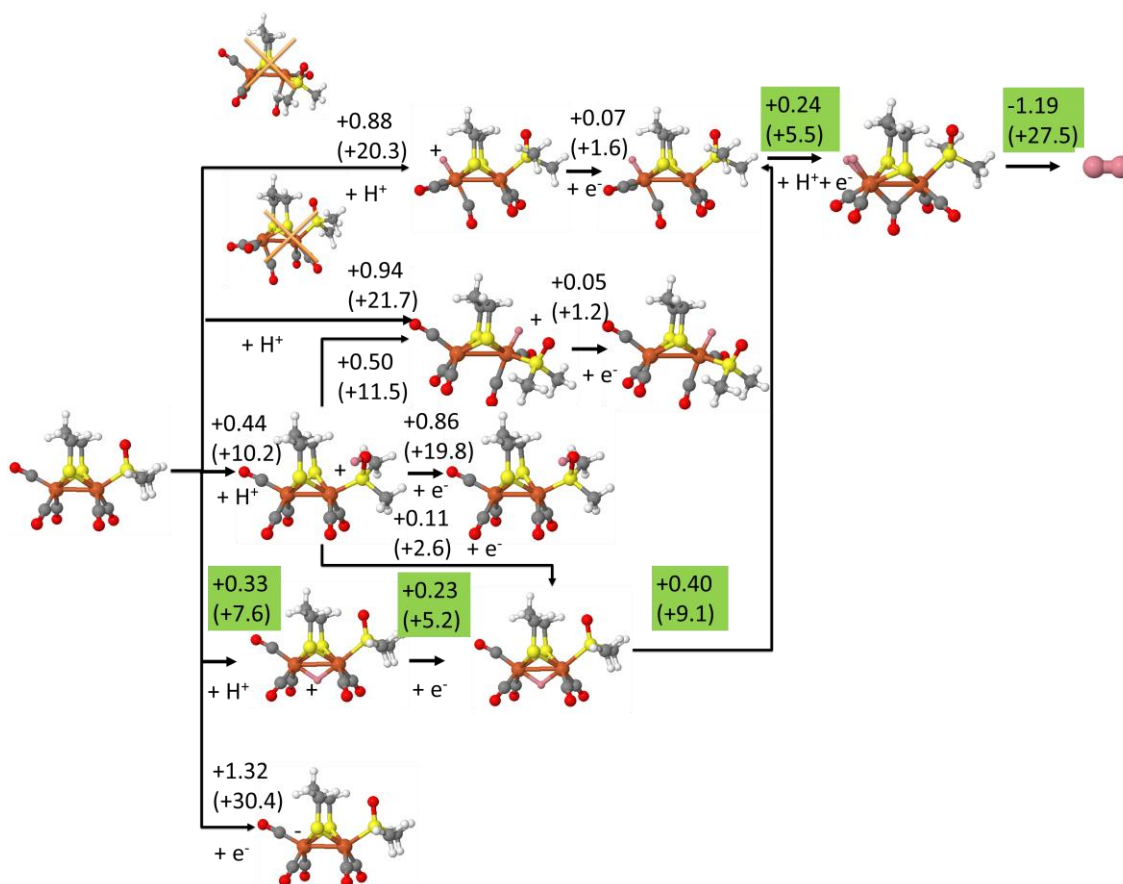
Figure S5. HER pathway followed by the (μ-SCH$_2$CH$_2$CH$_2$S)-Fe$_2$(CO)$_5$SO(CH$_3$)$_2$ molecular catalysts. Gibbs free energy differences, in electronvolts (kcal/mol).
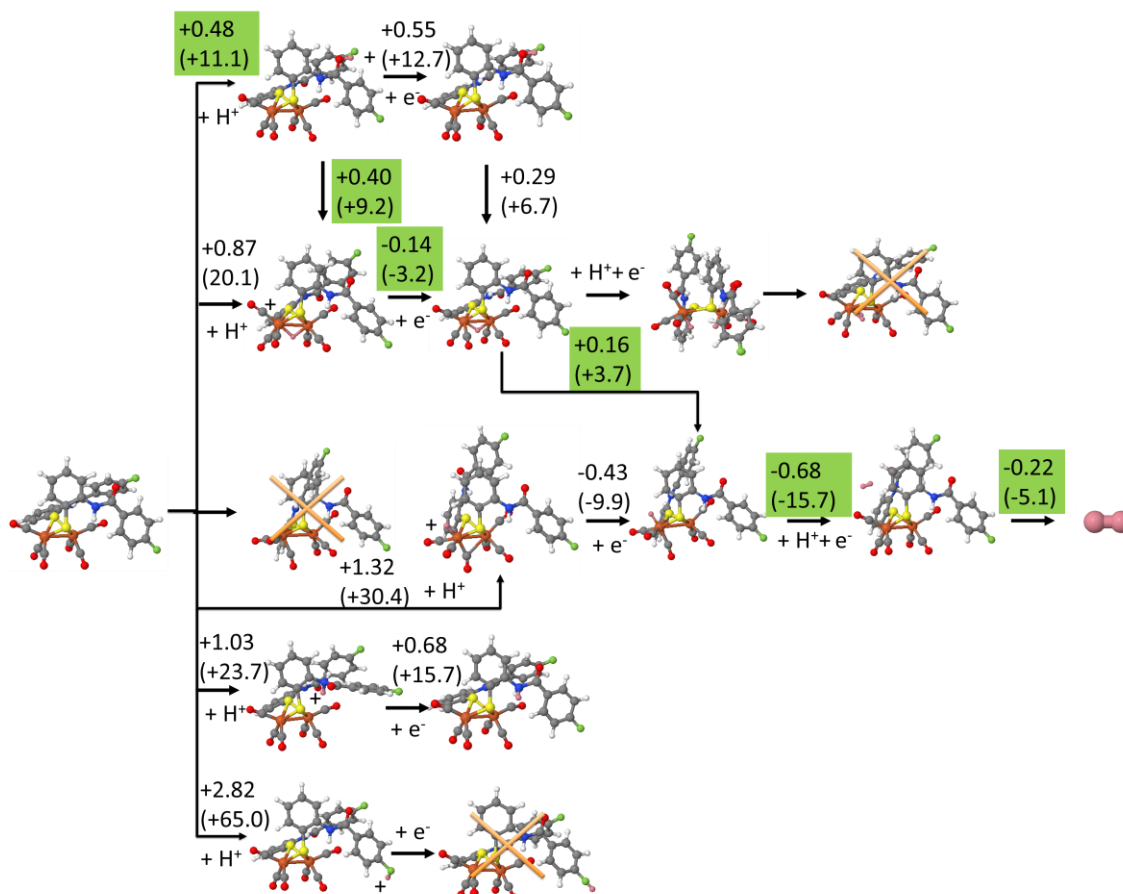
Figure S6. HER pathway followed by the [μ-S-2-(4-FC$_6$H$_4$)CONHC$_6$H$_4$]$_2$Fe$_2$(CO)$_6$ molecular catalysts. Gibbs free energy differences, in electronvolts (kcal/mol).

References

[1]   Felton GAN, Mebi CA, Petro BJ, Vannucci AK, Evans DH, Glass RS, Lichtenberger DL, Review of electrochemical studies of complexes containing the Fe$_2$S$_2$ core characteristic of [FeFe]-hydrogenases including catalysis by these complexes of the reduction of acids to form dihydrogen. *J. Organometallic Chem.* 2009, 694 (17), 2681–2699.