Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Intramolecular Stabilization of a Catalytic [FeFe]-Hydrogenase Mimic Investigated by Experiment and Theory

Indresh Kumar Pandey,[a] Mookan Natarajan,[a] Hemlata Faujdar,[a] Firasat Hussain,[a] Matthias Stein*[b] and Sandeep Kaur-Ghumaan*[a,b]

[a] Department of Chemistry, University of Delhi, Delhi-110007, India

[b] Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, 39106, Magdeburg, Germany

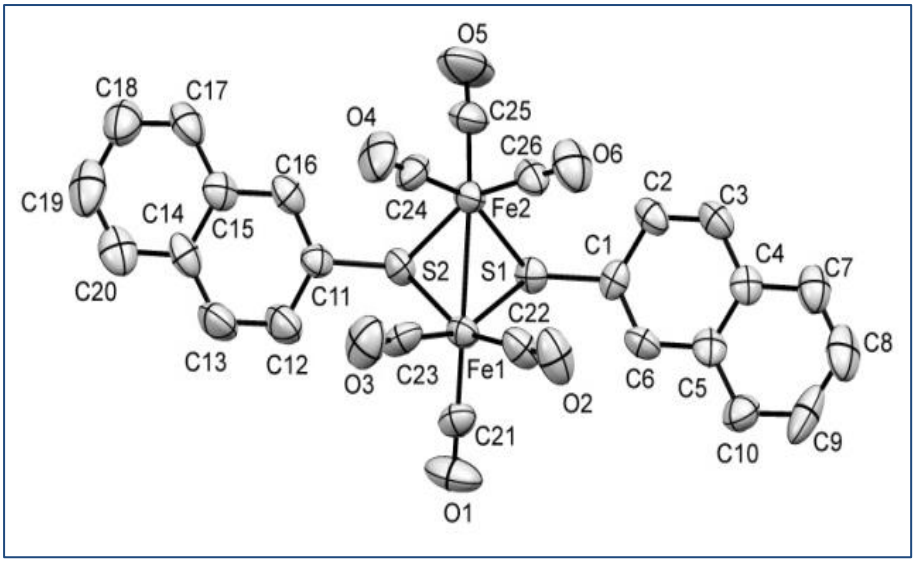


Fig. S1 Molecular structure of $[Fe_2(CO)_6(\mu\text{-naphthalene-2-thiolate})_2]$ **1**. Hydrogen atoms have been omitted for clarity.

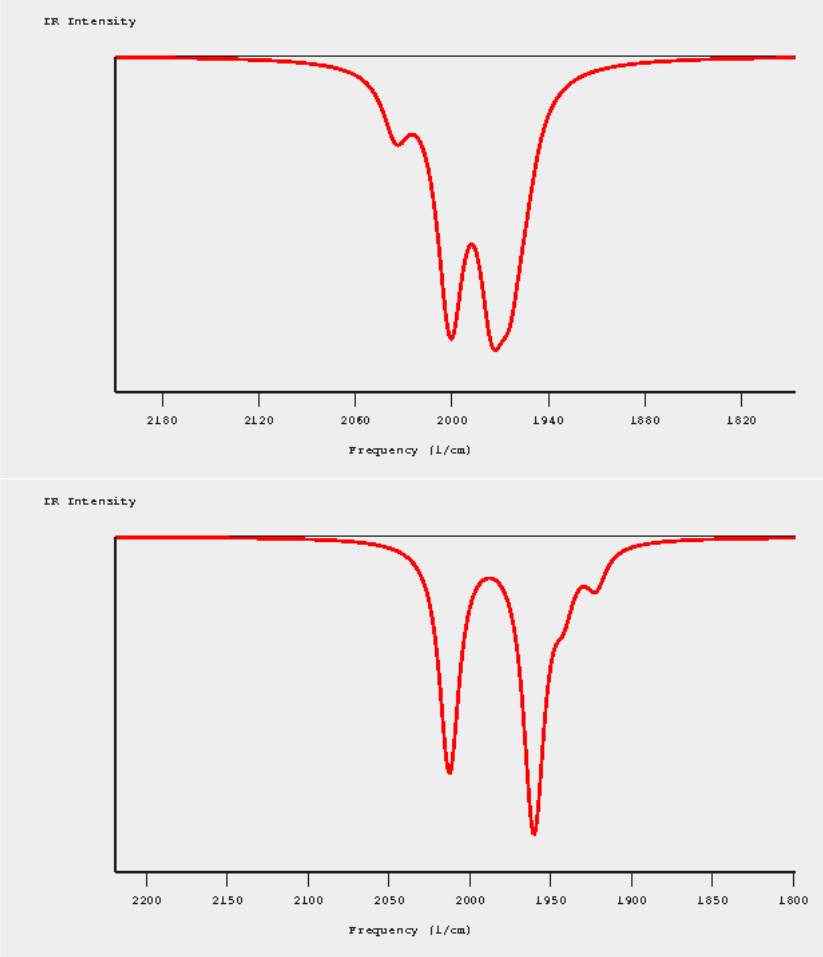


Fig. S2. Calculated IR spectra of complexes **1** and **2**. In **1** peaks at 2035 cm^{-1} correspond to CO_{sym}, 2001 $cm^{-1}CO_{asym}$ and 1975, 1964, 1955 and 1954 cm^{-1} to CO_{basal} and CO_{axial} symmetric and asymmetric molecular vibrations. In **2**, vibrations at 2013 cm^{-1} correspond to CO_{sym}, at 1962 cm^{-1} to CO_{asym} basal, 1959 $cm^{-1}CO_{sym}$ basal, 1942 $cm^{-1}CO_{axial}$, 1922 $cm^{-1}CO_{basal}$asym.

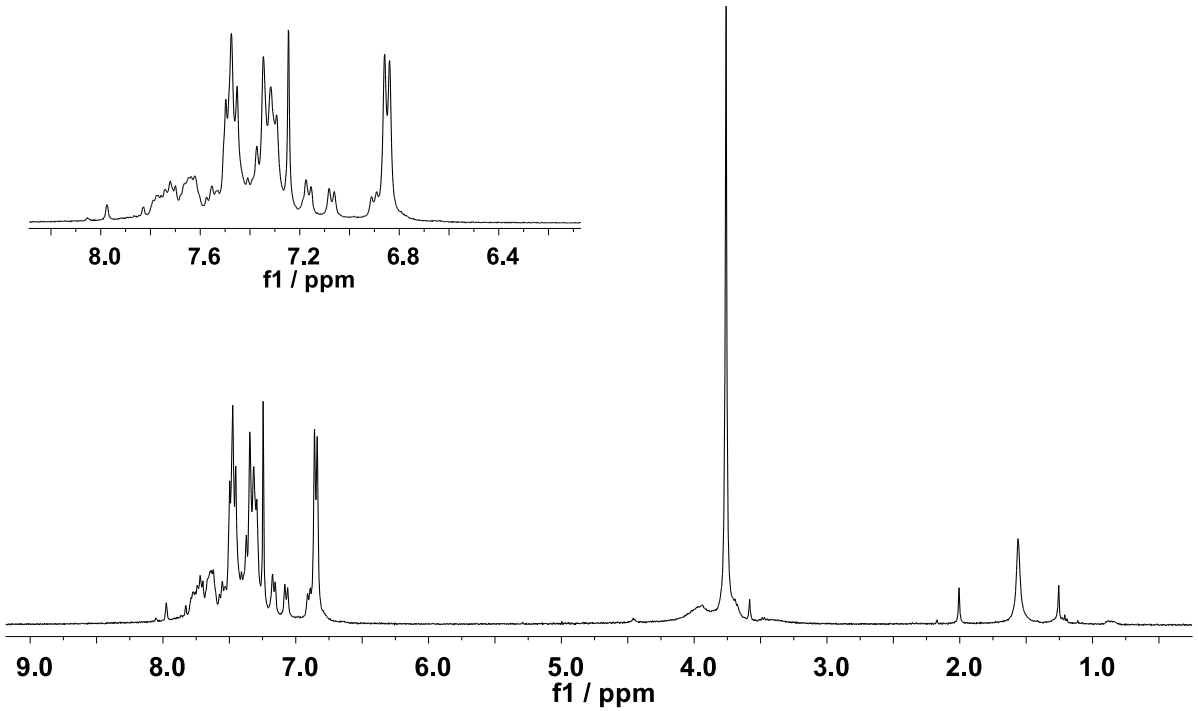


Fig. S3. ^{1}H NMR spectrum of complex **2** in $CDCl_3$.

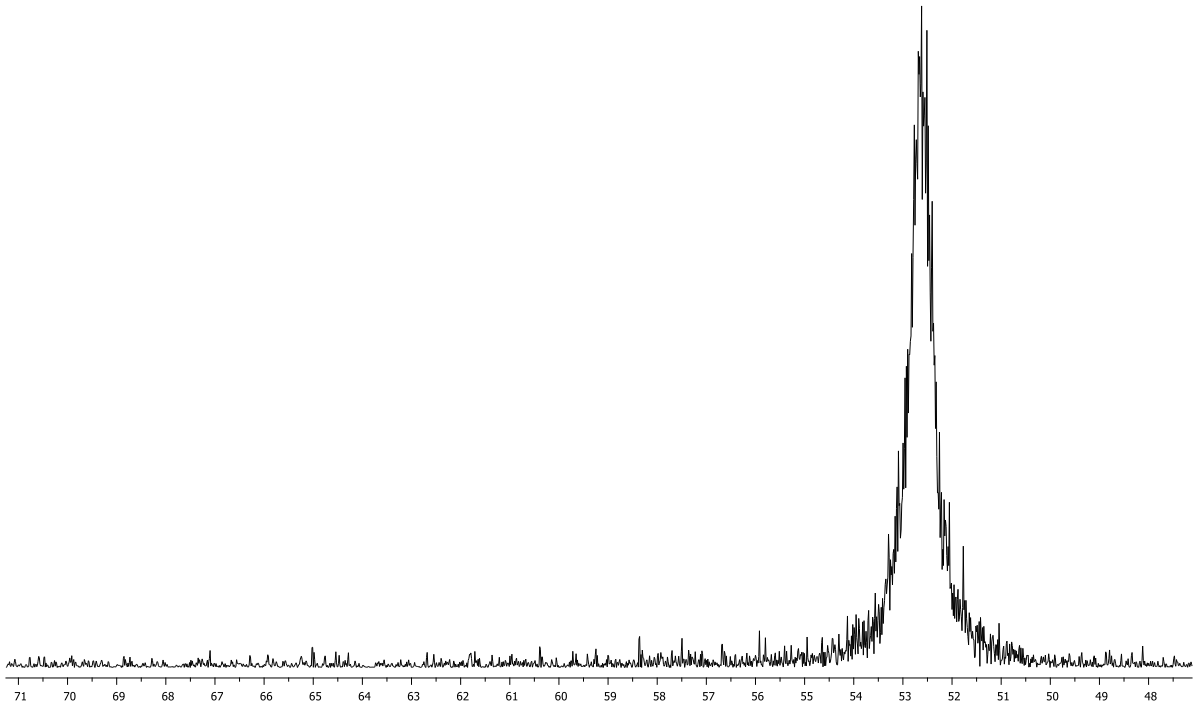


Fig. S4. ^{31}P $\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$.

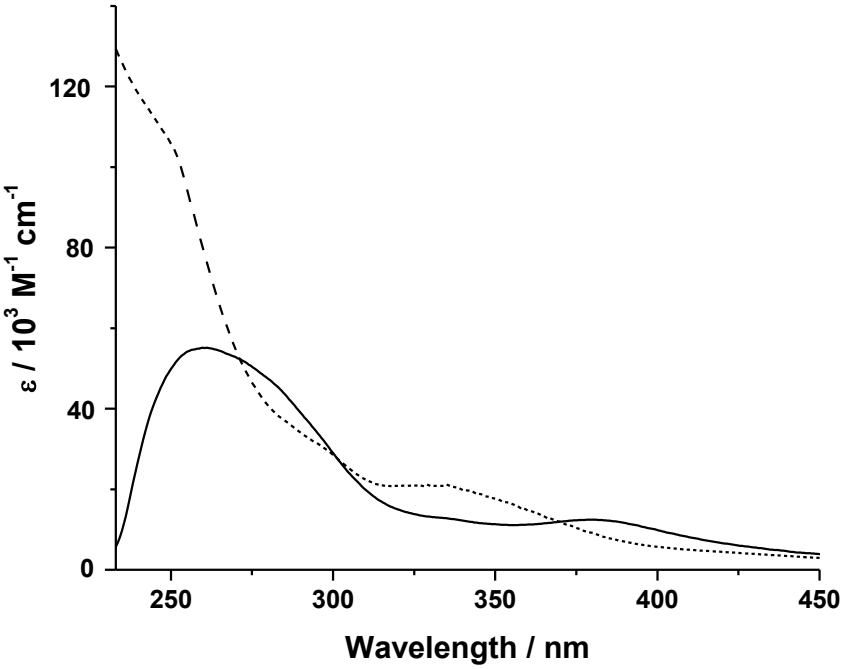


Fig. S5. UV-Vis spectra of complexes **1** (-----) and **2** (——) in dichloromethane.

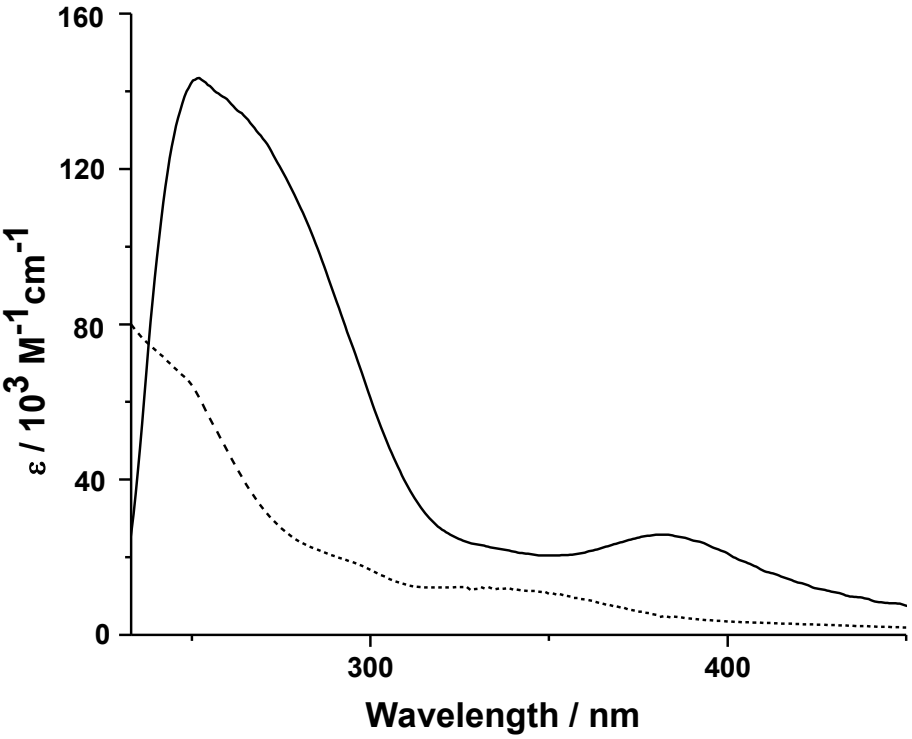


Fig. S6. UV-Vis spectra of complexes **1** (-----) and **2** (──) in acetonitrile.

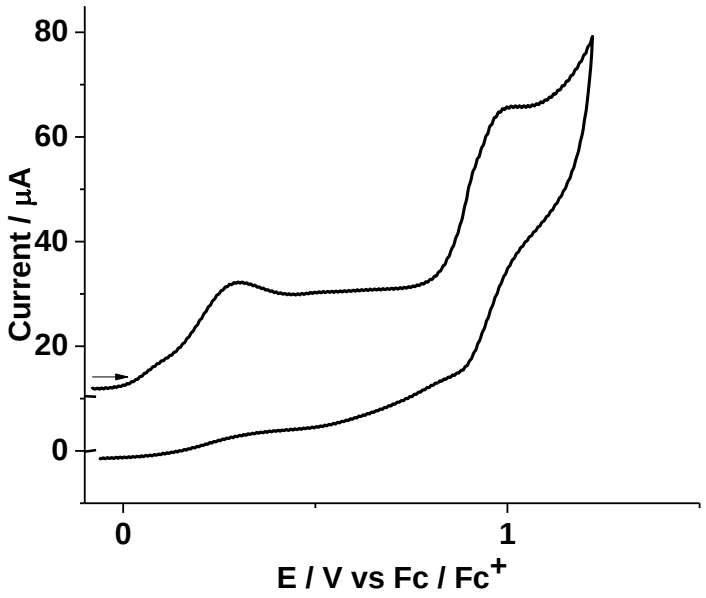


Fig. S7. Cyclic voltammogram (oxidation) for complex **2** (1.2 mM) in acetonitrile at a scan rate of 0.1 Vs^{-1}.

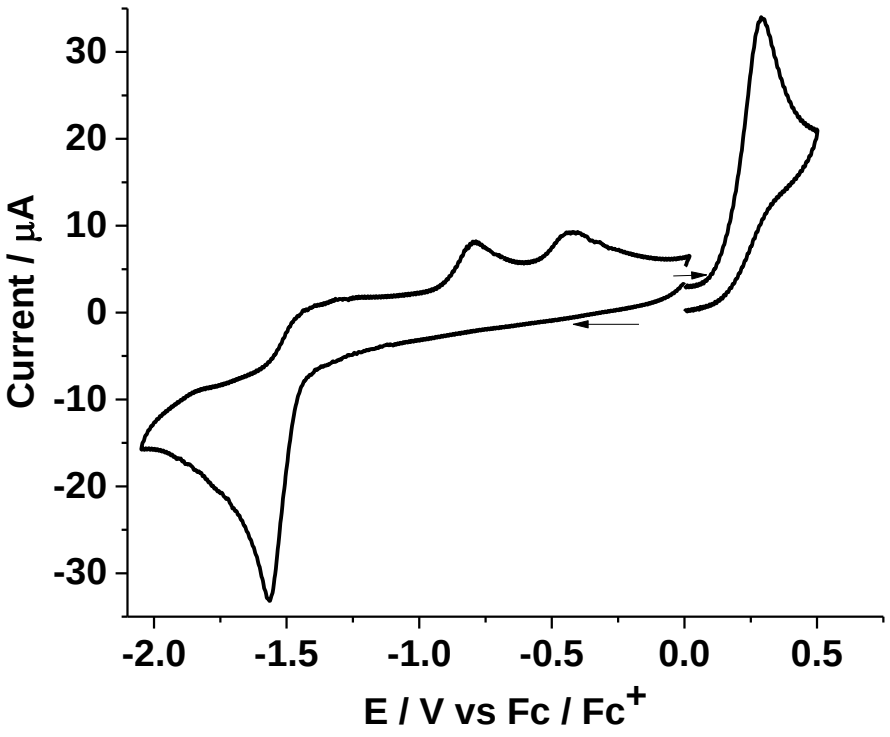


Fig. S8. Cyclic voltammograms for complex **2** (1.47 mM) in acetonitrile at a scan rate of 0.1 Vs^{-1}.

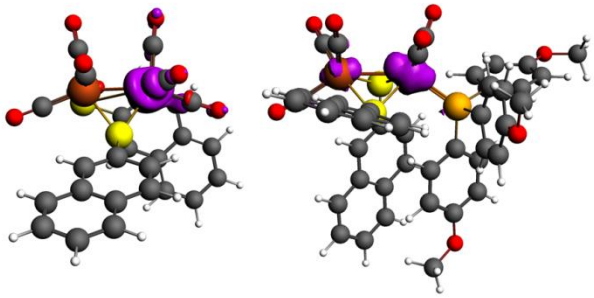


Fig. S9. Calculated unpaired spin density distribution of $\mathbf{1}^-$ (left) and $\mathbf{2}^-$ (right) at an isocontour value of 0.004 e^-/a_0^3.

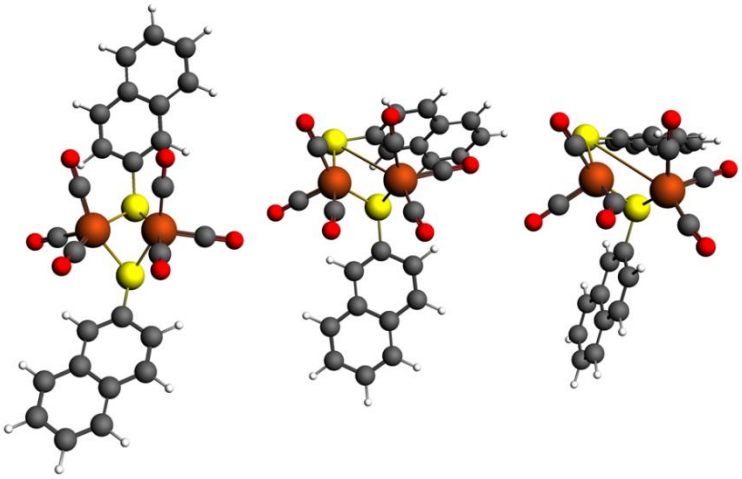


Fig. S10. Optimized structures of complexes **1**, $\mathbf{1}^-$ and $\mathbf{1}^{2-}$. Reduction leads to breakage and dissociation of one bridging μ-naphthalene-2-thiolate which obstructs the complex' catalytic activity.

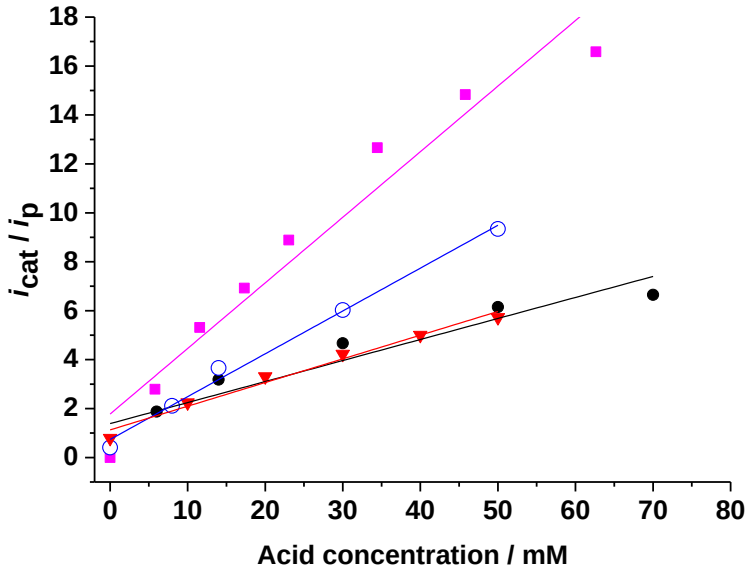


Fig. S11 Plot of i_{cat}/i_p vs. acid concentration for **2** (1.62 mM) (■), **1** (1 mM) (●), **B** (1 mM) (○) and **C** (2 mM) (▼) in presence of acetic acid at a scan rate of 0.1 Vs^{-1}.The negative sign for the current has been ignored. For complexes **1**, **B** and **C** the data were generated from literature values.[25, 26] (see manuscript for references). Lines are best fit lines to the data.

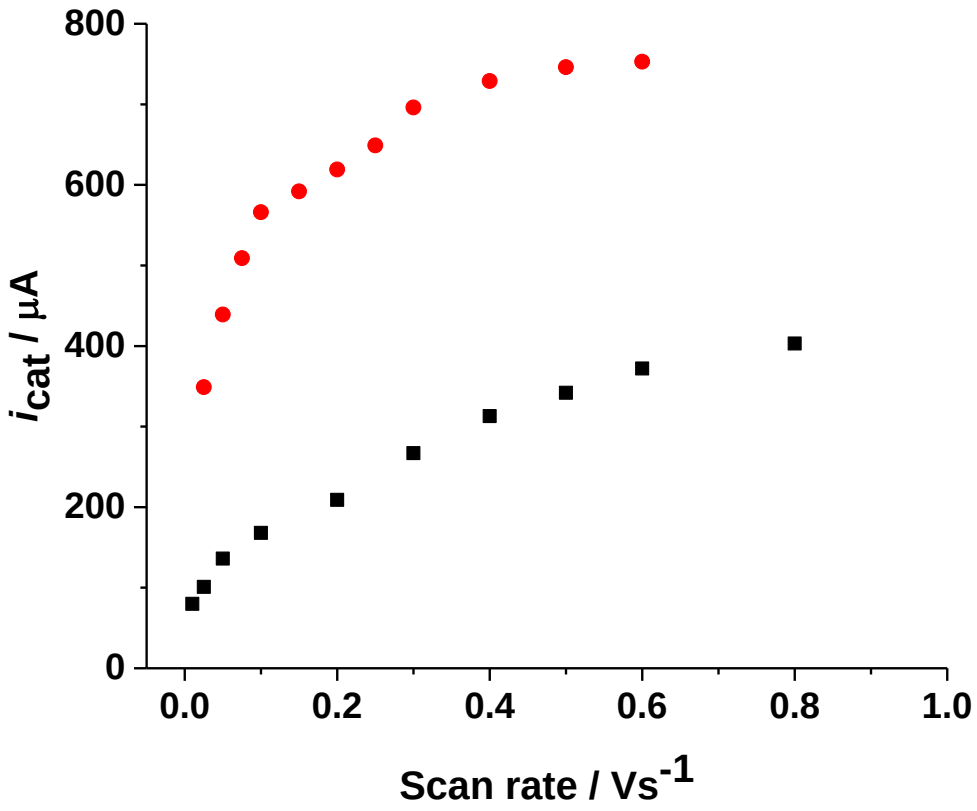


Fig. S12. Plot of i_{cat} (mA) vs. scan rate (V/s) for complex **2** (0.65 mM) with 20.8 mM (■) and 62 mM (●) acetic acid in 0.1 M $[NBu_4][PF_6]$ / MeCN.

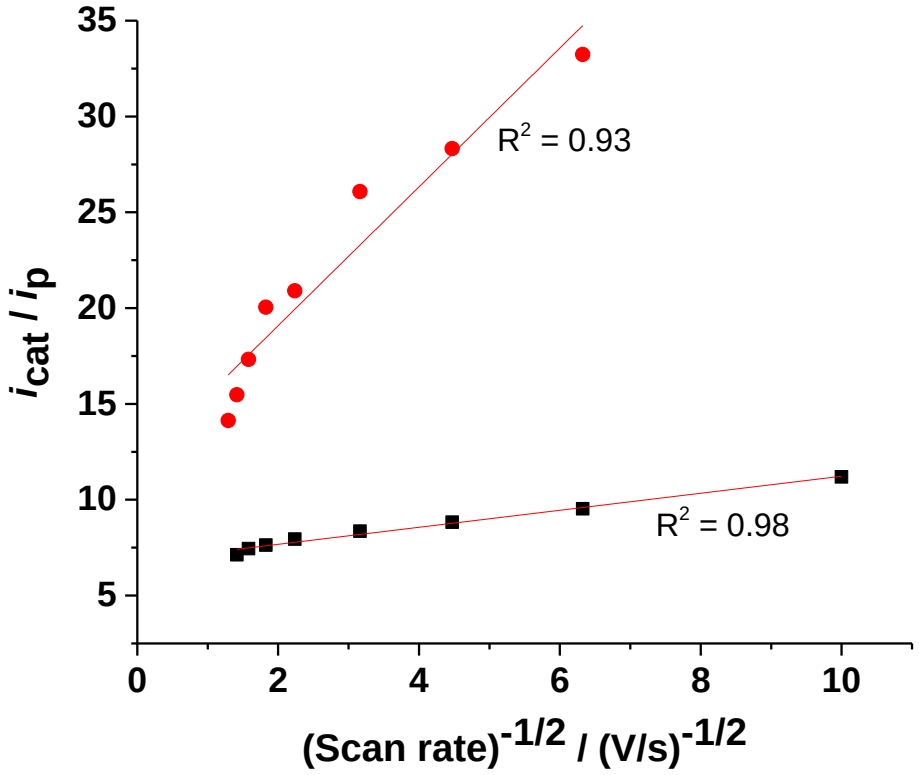


Fig. S13. Plot of i_{cat} / i_p vs. 1/scan rate$^{1/2}$ for complex **2** (0.65 mM) with 20.8 mM (■) and 62 mM (●) acetic acid in 0.1 M [NBu_4][PF_6] / MeCN.

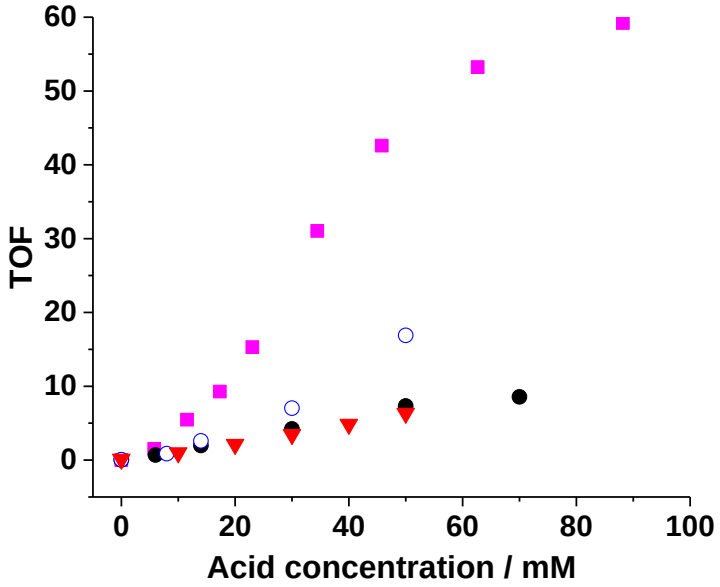


Fig. S14 Dependence of TOF for **2** (1.62 mM) (■), **1** (1 mM) (●), **B** (1 mM) (○) and **C** (2 mM) (▼) upon acetic acid concentration in 0.1 M n-Bu_4NPF_6 / MeCN at a scan rate of 0.1 V s^{-1}. For complexes **1**, **B** and **C** the data were generated from literature values.[25, 26] (see manuscript for references)

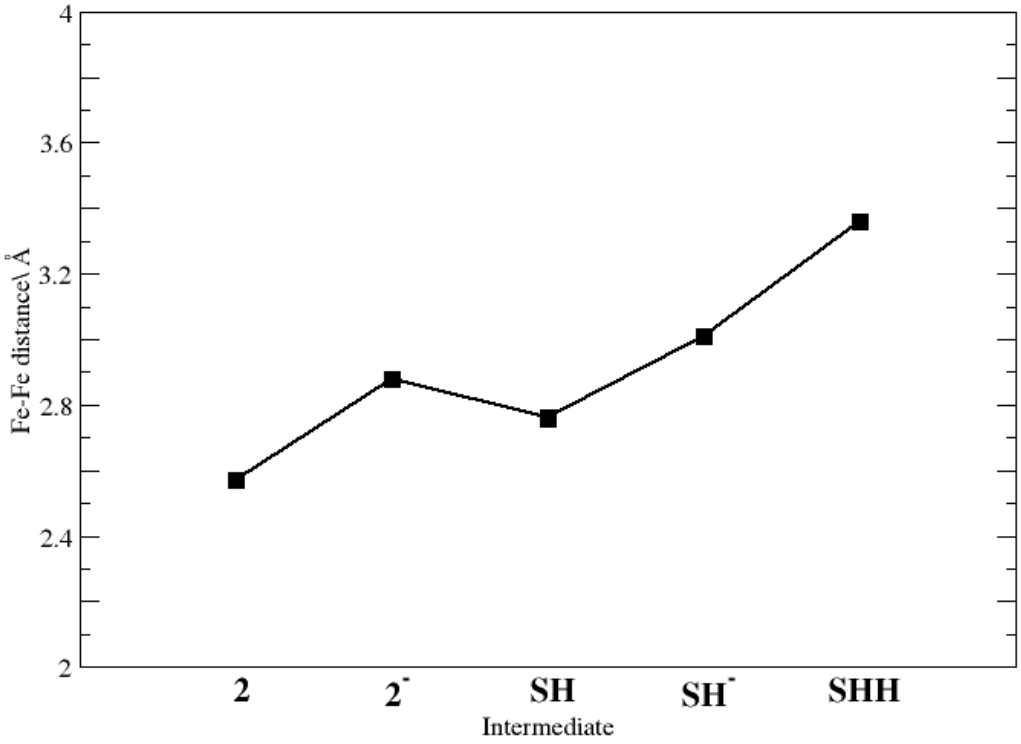


Figure S15. Calculated Fe…Fe distances in Å for reaction intermediates during proton reduction by catalyst **2**.

Table S1. Electronic structure of the mono- and two-fold oxidized forms $\mathbf{2}^{+}$ and $\mathbf{2}^{2+}$. Structural parameters, spin density distribution in $\mathbf{2}^{+}$ and atomic charges indicate a metal-based oxidation.-

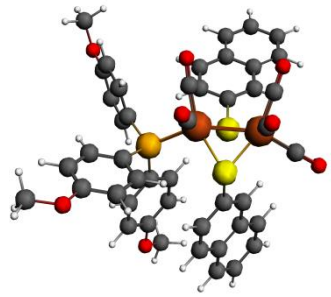
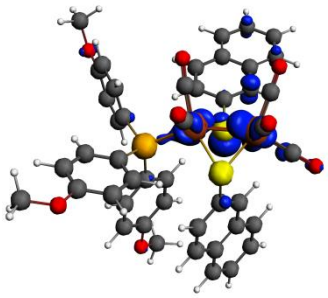
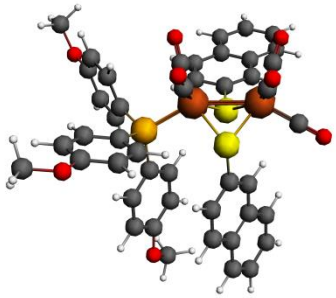
Complex		Fe Atomic Charges	Fe-Fe Distance in Å
2		- 0.127 / -0.094	2.57
$\mathbf{2}^{+}$	 	- 0.101 / -0.065 (unpaired spin density + 0.247 / + 0.358)	2.66
$\mathbf{2}^{2+}$		- 0.091 / - 0.044	2.69

Table S2 UV-Vis data for complexes **1** and **2**.

Complex	**λ_{max}/nm ($\varepsilon/10^3 M^{-1}cm^{-1}$)**	
	CH_3CN	**CH_2Cl_2**
1	249 (sh, 65), 346 (12)	250 (sh, 104), 339 (20)
2	252 (14), 381 (26)	259 (55), 385 (13)

Table S3 Crystallographic parameters and refinement details for complex **1**.

	1
Formula sum	$C_{26}H_{14}Fe_2O_6S_2$
Formula weight	598.19
Crystal system	orthorhombic
Space group	P bc a
a (Å)	25.5454)
b (Å)	26.670(4)
c (Å)	7.3447(10)
α (^{o})	90
β (^{o})	90
γ (^{o})	90
V (Å^3)	5003.9(13)
T (K)	293(2)
Z	8
F_{000}	2416.0
ρ_{calcd} (g cm^{-3})	1.588
R_1 [$I > 2\sigma(I)$]	0.0923
wR_2 [$I > 2\sigma(I)$]	0.2031

Table S4 Selected bond lengths (Å) and angles (^{o}) for complex **1**.

Bond lengths		Bond angles	
Fe(1)-S(2)	2.261(3)	S(2)-Fe(2)-S(1)	74.21(10)
Fe(1)-S(1)	2.274(3)	S(2)-Fe(2)-Fe(1)	56.41(8)
Fe(2)-S(2)	2.276(3)	S(1)-Fe(2)-Fe(1)	56.74(8)
Fe(2)-S(1)	2.278(3)	S(2)-Fe(1)-S(1)	74.57(10)
Fe(1)-Fe(2)	2.491(2)	S(1)-Fe(1)-Fe(2)	56.90(8)
Fe(1)-C(21)	1.795(12)	S(2)-Fe(1)-Fe(2)	56.98(8)
Fe(1)-C(22)	1.763(12)	Fe(1)-S(1)-Fe(2)	66.35(8)
Fe(1)-C(23)	1.768(13)	Fe(1)-S(2)-Fe(2)	66.61(9)
Fe(2)-C(24)	1.777(12)	C(22)-Fe(1)-C(21)	101.3(5)
Fe(2)-C(25)	1.793(13)	C(24)-Fe(2)-C(25)	101.2(5)
Fe(2)-C(26)	1.771(12)		
C(1)-S(1)	1.797(10)		
C(11)-S(2)	1.801(10)		
C(21)-O(1)	1.133(11)		
C(24)-O(4)	1.135(12)		

Table S5 Crystallographic parameters and refinement details for complex **2**.

	2
Formula sum	$C_{46}H_{35}Fe_2O_8P_1S_2$
Formula weight	922.53
Crystal system	triclinic
Space group	P-1
a (Å)	12.1078(5)
b (Å)	13.5576(6)
c (Å)	14.6711(6)
α (^{o})	72.688(4)
β (^{o})	67.446(4)
γ (^{o})	82.128(4)
V (Å^3)	2122.64(16)
T (K)	150(2)
Z	2
F_{000}	948.0
ρ_{calcd} (g cm^{-3})	1.443
R_1 [$I > 2\sigma(I)$]	0.0428
wR_2 [$I > 2\sigma(I)$]	0.0911

Table S6. Selected bond lengths (Å) and angles (^{o}) for **2**.

Bond lengths		Bond angles	
Fe(1)-S(1)	2.2584(7)	S(1)-Fe(2)-S(2)	80.40(3)
Fe(1)-S(2)	2.3063(8)	S(1)-Fe(2)-Fe(1)	56.05(2)
Fe(2)-S(1)	2.2661(7)	S(2)-Fe(2)-Fe(1)	57.31(2)
Fe(2)-S(2)	2.2715(8)	S(1)-Fe(1)-S(2)	79.82(3)
Fe(1)-Fe(2)	2.5169(5)	S(1)-Fe(1)-Fe(2)	56.35(2)
Fe(1)-P(1)	2.2538(7)	S(2)-Fe(1)-Fe(2)	55.99(2)
Fe(1)-C(4)	1.781(3)	Fe(1)-S(1)-Fe(2)	67.60(2)
Fe(1)-C(5)	1.778(3)	Fe(2)-S(2)-Fe(1)	66.70(2)
Fe(2)-C(1)	1.802(3)	C(5)-Fe(1)-P(1)	97.13(9)
Fe(2)-C(2)	1.766(3)	C(4)-Fe(1)-P(1)	98.39(9)
Fe(2)-C(3)	1.794(4)	C(5)-Fe(1)-C(4)	90.72(13)
C(6)-S(2)	1.789(3)	C(2)-Fe(2)-C(1)	98.54(14)
C(37)-S(1)	1.781(3)	P(1)-Fe(1)-S(1)	106.54(3)
C(1)-O(1)	1.147(3)	P(1)-Fe(1)-S(2)	103.01(3)
C(4)-O(4)	1.145(3)	P(1)-Fe(1)-Fe(2)	152.74(3)
		C(1)-Fe(2)-Fe(1)	152.23(9)

Table S7. Energies (E), enthalpies (H) and Gibbs free energies (G) of calculated complexes and intermediates in kcal/mol.

	Complex				
BP86/TZP	**1**	**1^-**	**2**	**2^-**	**2^{2-}**
E	-8058.63	-8106.52	-14337.17	-14381.01	-14361.28
Acetonitrile	-8063.08	-8141.42	-14347.48	-14421.06	-14481.62
H	-7834.20	-7884.08	-13876.99	-13923.01	-13905.81
Acetonitrile	-7838.65	-7918.98	-13887.30	-13963.06	-14026.16
G	-7900.02	-7949.44	-13970.64	-14015.98	-13997.71
Acetonitrile	-7904.47	-7984.34	-13980.95	-14056.03	-14118.06
B3LYP/TZP	**1**	**1^-**	**2**	**2^-**	**2^{2-}**
E	-9401.73	-9450.34	-16603.00	-16648.25	-16616.24
Acetonitrile	-9406.95	-9485.26	-16613.24	-1189.07	-16737.83
H	-9177.30	-9227.90	-16142.82	-16190.25	-16160.78
Acetonitrile	-9182.52	-9262.82	-16153.06	-16231.07	-16282.13
G	-9243.12	-9293.26	-16236.47	-16283.22	-16252.68
Acetonitrile	-9248.34	-9328.18	-16246.71	-16324.04	-16374.03

Table S8. Calculated energies (E), enthalpies (H) and Gibbs free energies (G) of reaction intermediates of complex **2** in kcal/mol.

ECEC	**Complex**		
BP86/TZP	**$2SH_{SH}$**	**$2H_{terminal}$**	**$2H_{bridging}$**
E	-14385.46	-14395.58	-14402.14
Acetonitrile	-14396.63	-14404.58	-14410.86
H	-13921.34	-13931.43	-13937.89
Acetonitrile	-13932.51	-13939.84	-13946.61
G	-14012.85	-14024.26	-14032.67
Acetonitrile	-14024.02	-14032.67	-14041.39
B3LYP/TZP			
E	-16667.27	-16681.91	-16682.53
Acetonitrile	-16678.72	-16690.22	-16691.02
H	-16205.15	-16217.66	-16218.28
Acetonitrile	-16214.60	-16225.97	-16227.36
G	-16294.66	-16310.48	-16313.06
Acetonitrile	-16306.11	-16318.79	-16322.14

Table S9. Calculated energies (E), enthalpies (H) and Gibbs free energies (G) of reaction intermediates of complex **2** in kcal/mol.

ECEC	**Complex**	
BP86/TZP	**$2H^-_{terminal}$**	**$2H^-_{bridging}$**
E	-14443.99	-14474.44
Acetonitrile	-14479.87	-14483.61
H	-13980.57	-13984.84
Acetonitrile	-14016.46	-14021.04
G	-14071.77	-14079.04
Acetonitrile	-14107.86	-14115.24
B3LYP/TZP		
E	-16716.54	-16724.83
Acetonitrile	-16752.52	-16762.82
H	-16253.13	-16262.26
Acetonitrile	-16289.11	-16300.25
G	-16344.53	-16356.46
Acetonitrile	-16380.51	-16394.45

Table S10. Calculated energies (E), enthalpies (H) and Gibbs free energies (G) of reaction intermediates of complex **2** in kcal/mol.

ECEC	**Complex**	
BP86/TZP	**$2H^-_{terminal}$**	**$2H^-_{bridging}$**
E	-14443.99	-14474.44
Acetonitrile	-14479.87	-14483.61
H	-13980.57	-13984.84
Acetonitrile	-14016.46	-14021.04
G	-14071.77	-14079.04
Acetonitrile	-14107.86	-14115.24
B3LYP/TZP		
E	-16716.54	-16724.83
Acetonitrile	-16752.52	-16762.82
H	-16253.13	-16262.26
Acetonitrile	-16289.11	-16300.25
G	-16344.53	-16356.46
Acetonitrile	-16380.51	-16394.45