

*Supporting Information*

**Facile Electrocatalytic Proton Reduction by a [Fe-Fe]-  
Hydrogenase Active Site Model Bearing Bridging CO  
and Terminal CN<sup>-</sup> Ligand**

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**General procedure**

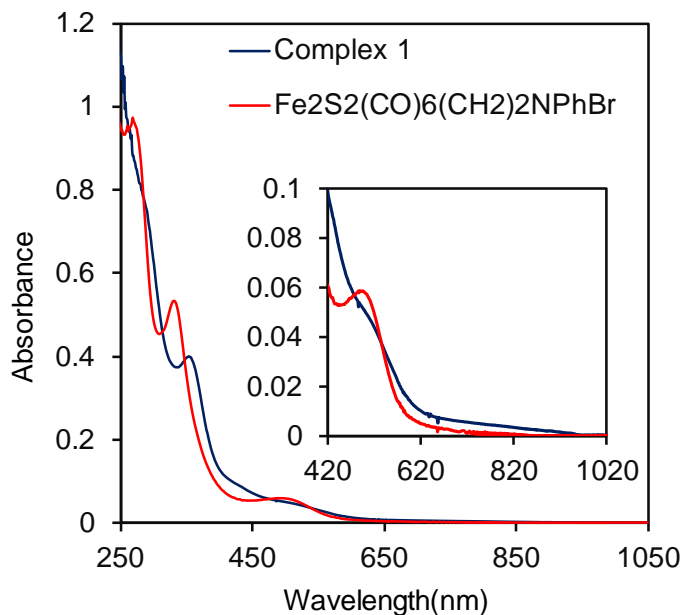
All the anaerobic experiments were performed in a MBRAUN glove box. The electrochemical studies in aqueous medium have been performed under argon environment. The solvents used were purchased from Merck Specialties, Pvt. Ltd. (India), Spectrochem Pvt. Ltd. (India), RFCL Ltd. (India), and Avra synthesis Pvt. Ltd. (India) and were used without further purifications for aerobic experiments. *p*-bromoaniline and Thionyl chloride (SOCl<sub>2</sub>) was purchased from Spectrochem Pvt. Ltd. (India). *p*-formaldehyde, tetrabutylammoniumperchlorate (TBAP), superhydride (LiBEt<sub>3</sub>H, 1 M in

THF) and tetraethylammonium cyanide ( $\text{Et}_4\text{NCN}$ ) was bought from Sigma-Aldrich chemicals Pvt. Ltd. and anhydrous  $\text{Na}_2\text{SO}_4$  and sulfuric acid (98%) was purchased from Merck (India).  $\text{SiO}_2$  (60-120 mesh) and *p*-Toluenesulfonic acid (*p*TsOH) was purchased from SISCO Pvt. Ltd. (India). These chemicals were used without further any purification. Triple distilled deionized water, has been used for all electrochemical experiments. All the column chromatographic separations were performed on  $\text{SiO}_2$  (60-100 mesh) column. Edge Plane Graphite (EPG) discs were purchased from Pine Instruments. The FT-IR data were measured on the Parkin-Elmer Frontier instrument. The  $\text{CaF}_2$  windows for FTIR spectroscopy were purchased from Sigma-Aldrich. The anaerobic setup for FTIR spectroscopy was purchased from PerkinElmer. The optically transparent thin-layer electrochemical (OTTLE) cell was purchased from the University of Reading for spectro-electrochemistry. UV-vis absorption spectra were recorded by Agilent 8453 spectrophotometer. The aerobic and anaerobic cuvettes were purchased from Starna Scientific. All the NMR spectra were recorded on the Bruker DPX-300 or DPX-500 spectrometer at room temperature. The mass spectra are recorded by QTOF Micro YA263 instrument. Elemental analyses were performed on a PerkinElmer 2400 series II CHN analyzer. The  $\text{H}_2$  gas from controlled potentiometry proton reduction was detected on a GC instrument of model no. 7890B (G3440B), serial no. CN14333203 fitted with a thermal conductivity detector (TCD). Mössbauer spectra were recorded using an alternating constant WissEl Mössbauer spectrometer, consisting of an MR 360 drive unit, an MVT 1000 velocity transducer, and an LND-45431 proportional counter mounted on an MB-600 Mössbauer bench with cryostat stand. The system was operated in a horizontal transmission geometry with source ( $^{57}\text{Co}$  in Rh-matrix), absorber and detector in a linear arrangement. The temperature was controlled and maintained using MBBC-N20106 Mössbauer cryostat for liquid nitrogen connected with Lake Shore-325 temperature controller unit. Measurements were performed at 90K. Data acquisition was performed using a 512-channel analyzer. Isomer shifts were referenced versus  $\alpha$ -iron metal foil at the same temperature. The simulation of experimental data was performed using the Normos-A Mössbauer Fit programmes Site and Dist.

**Synthesis of complex 1  $[\text{Et}_4\text{N}][\text{BrC}_6\text{H}_4\text{N}(\text{CH}_2\text{S})_2\text{Fe}_2(\text{CO})_5\text{CN}]$ :**

Complex **1** was synthesized from *p*-BrC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> (Scheme **2**). 55 mg (0.1 mmol) of *p*-BrC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> was dissolved in 20 mL of dry acetonitrile (CH<sub>3</sub>CN) in an argon glove box. Then 21 mg (0.13 mmol) of tetraethylammonium cyanide (Et<sub>4</sub>N<sup>+</sup>CN<sup>-</sup>) was added to the red solution at room temperature. Immediately, the colour of the solution changed to dark red. The reaction mixture was stirred for 24 hours and the reaction was monitored by FT-IR spectrometry time to time where appearance of a new band at 2093 cm<sup>-1</sup> was followed. After completion of the reaction (indicated by lack of increases of the IR band at 2093 cm<sup>-1</sup>) the dark red solution was evaporated to dryness under vacuum. The resulting red oil was extracted into 10 mL of THF, and this extract was filtered and concentrated to approximately 1 mL. The product was precipitated upon addition of 20 mL of hexanes and washed with hexane, toluene and ether successively to give a red brown solid product. Yield- 51 mg (79 %). <sup>1</sup>H NMR (Fig. **S10**) (300 MHz, CD<sub>3</sub>CN) δ 7.36 (d, 2H), 6.69 (d, 2H), 4.37 (s, 2H), 4.05 (s, 2H), 3.15 (q, 8H, CH<sub>2</sub>CH<sub>3</sub>N<sup>+</sup>), 1.21 (t, 12H, CH<sub>2</sub>CH<sub>3</sub>N<sup>+</sup>). <sup>13</sup>C NMR (Fig. **S11**) (300 MHz, CD<sub>3</sub>CN) δ 212.28 (CO), 145.83 (CN), 133.00 (Aromatic), 110.70 (Aromatic), 53.19 (Et<sub>4</sub>N<sup>+</sup>), 49.55 (-CH<sub>2</sub>), 7.78 (Et<sub>4</sub>N<sup>+</sup>). FT-IR (CH<sub>3</sub>CN): 2093 cm<sup>-1</sup> (s), 2033 cm<sup>-1</sup>(s), 1982 cm<sup>-1</sup>(s), 1960 cm<sup>-1</sup>(s), 1950 cm<sup>-1</sup> (s), 1922 cm<sup>-1</sup> (s); ES<sup>+</sup> Mass (TOF): ESI [m/z]<sup>-</sup> = 539.2906 (46%), [m-CO/z]<sup>-</sup> = 511.2703 (4%), [m-2CO/z]<sup>-</sup> = 483.2468 (42 %), [m-3CO/z]<sup>-</sup>=455.2113 (39%), [m-4CO/z]<sup>-</sup>=427.2468 (63%), [m-5CO/z]<sup>-</sup>=399.1537(100%); Calculated ESI-[m/z]<sup>-</sup>=539.772. [Et<sub>4</sub>N]<sup>+</sup>[BrC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>5</sub>CN]<sup>-</sup>: Elemental Analysis: C: 39.67, H: 4.01, N: 6.05; Calculated: C: 39.43, H: 4.21, N: 6.27.

**<sup>13</sup>CN analogue of Complex 1:** The <sup>13</sup>CN substituted analogue was synthesised by following the exactly similar procedure and in situ generated Et<sub>4</sub>N<sup>+</sup><sup>13</sup>CN<sup>-</sup> (1:1 Et<sub>4</sub>NBr and Na<sup>13</sup>CN) is used instead of Et<sub>4</sub>N<sup>+</sup>CN<sup>-</sup>.



**Figure S1:** UV-vis Absorption spectra of complex **1** and its precursor complex  $\text{Fe}_2\text{S}_2(\text{CO})_6(\text{CH}_2)_2\text{NPhBr}$ .

## Electrochemical Measurements

### *Cyclic Voltammetry*

The cyclic voltammograms are recorded on a CH Instrument bipotentiostat model 700E. A glassy carbon electrode and a Pt wire were used as the working and the counter electrode, respectively. The measurements were made against an Ag/AgCl aqueous reference electrode in saturated KCl solution. Anaerobic CV experiments was performed in a glove box filled with  $\text{N}_2$  or within a five-neck S3 water jacketed electrochemical cell (PINE Instruments) by thoroughly degassing the whole set up with  $\text{N}_2$  gas.at room temperature. The working glassy carbon electrode was washed and polished before use.

The cyclic voltammogram in aqueous medium was recorded in 0.1 M  $\text{KPF}_6$ -water solution with the complex **1** adsorbed on EPG disc by drop casting a solution of the complex **1** onto EPG (0.35 mm diameter) inserted in a RDE set up ((Pine Instruments) in an airtight and water jacketed electrochemical cell (Pine Instrument, RRP138). The Ag/AgCl reference (Pine instruments, RREF0021) and Pt counter (AFCTR5) electrodes were attached to this cell through air tight joints.

The cyclic voltammogram in Homogeneous medium was recorded on a bipotentiostat (CHI 700E) using glassy carbon as a working electrode. All CV data were collected in a sealed custom-made electrochemical cell. Four milliliters of 0.5 mM of compound solution in CH<sub>3</sub>CN was taken in the presence of 100 mM TBAP as the supporting electrolyte. The glassy carbon electrode was taken as the working electrode, standard double-junction silver/silver chloride as the reference electrode, and a Pt was taken as the counter electrode. The solution was deaerated by bubbling N<sub>2</sub> before recording the CV as required.

All the potentials are recorded with Ag/AgCl (sat. KCl) reference electrode at the time of experiment and transformed to NHE by adding a factor of 0.2 V to the measured values.

### ***RDE and RRDE Experiments:***

#### **a. Deposition of the catalyst on EPG Surfaces:**

The edge plane graphite (EPG) electrode was freshly polished and cleaned with polishing kit before each single experimental use. 50 µL of a dilute solution (~20mM, in CH<sub>2</sub>Cl<sub>2</sub>) of Complex **1** was uniformly distributed on the EPG disc (0.35 mm diameter). After all the CH<sub>2</sub>Cl<sub>2</sub> evaporated, the surface was washed with CHCl<sub>3</sub> thoroughly and sonicated in ethanol to remove any loosely bound catalyst on the EPG surface and washed with triple distilled water.

#### **b. RDE and RRDE Electrochemistry:**

The RDE/RRDE measurements was performed on a CHI 700E bi-potentiostat. An EPG disc was used as the working electrode which was mounted inside of a Pt ring assembly (Pine Instrument, AFE6RIP) which was mounted at the tip of a shaft (Pine Instruments, AFE6MB) which in turn was fitted to a MRS rotator. A water jacketed electrochemical cell (Pine Instrument, RRP138) was obtained where the rotor was inserted through a taper plug assembly (AC01TPA6M) which allowed free rotation of the vertical rotor while maintaining an air tight seal. An Ag/AgCl reference (Pine instruments, RREF0021) and Pt counter (AFCTR5) electrode was attached to the cell through air tight joints. The graphite surface was cleaned by polishing it uniformly on a Silicon carbide grinding paper followed

by sonication in triple distilled water. The complex was then physically adsorbed on the disc as described above.

The shaft bearing the EPG electrode and the Pt ring was vertically inserted to the water jacket cell and the cell was purged with N<sub>2</sub> for 50-60 minutes. The anaerobic HER experiments were carried out in thoroughly degassed solutions (freeze-pump-thaw) to eliminate any competing electrocatalytic Oxygen reduction reaction. Background scans were performed under same conditions with bare EPG electrodes. Linear sweep voltammetry (LSV) had been performed at various rotation rates for RDE experiments. The rotation rate for all HER study is 300 rpm if otherwise not mentioned. RRDE experiments had been done to detect hydrogen produced in the working electrode following well known protocols. The Pt-ring encircling the working electrode was held at 0.7 V potential where it oxidizes H<sub>2</sub> generated at the working electrode, where a reduction current is observed, back to H<sup>+</sup> generating an oxidation current.

### ***Controlled Potential Coulometry and Faradic Efficiency***

The controlled potential coulometry experiments were performed in the same water jacket electrochemical cell that was used for the RDE/RRDE Experiment. The Pt-counter is fitted within a separated cylindrical chamber with a frit at the bottom that maintains the junction with the electrolytic solution. This minimizes the possibility of O<sub>2</sub> incorporation in H<sub>2</sub> measurements by inverted burette set up. These experiments were performed in degassed 0.1 N H<sub>2</sub>SO<sub>4</sub> solutions at -0.4 V vs NHE for 1 hour. The shaft bearing the working electrode was rotated at 1200 rpm to disperse H<sub>2</sub> bubbles formed on the electrode into the bulk solution. The same experiment was performed with bare EPG. During electrolysis the H<sub>2</sub> generated was collected through an outlet of the cell and collected using an inverted burette setup. The ratio of the moles of H<sub>2</sub> produced in the process (estimated from the volume of H<sub>2</sub> collected) and the charge dispersed is reported as the FY.

After the catalyst solution in CH<sub>3</sub>CN (concentration 0.3 mM) was purged with N<sub>2</sub> in presence of 80 eq. of *p*TsOH, the controlled potential electrolysis was performed on a CHI 700E bipotentiostat using the glassy carbon plate electrode at -0.9 V vs. The Pt counter electrode was separated using a glass frit and aqueous Ag-AgCl reference electrode were

inserted in the cell which was connected to the inverted burette. The gaseous products evolved were collected into the burette by vertical displacement of water. The volume of water displaced during the experiment is the amount of gas evolved during the experiment. 500 $\mu$ L gas was syringed out by a gastight syringe from the head space of the cell and was injected into the inlet of the Agilent GC instrument fitted with a TCD detector. The ratio of the moles of H<sub>2</sub> produced in the process (estimated from the volume of H<sub>2</sub> collected) and the charge dispersed is reported as the FY. Additionally, these CPE experiments along with the GC analysis were conducted for several times to confirm the reproducibility of the reduced products formation.

### ***Faradic yield (FY) and TON calculation***

The CPE experiments of complex 1 in the presence of *p*TsOH at -0.9 V vs NHE, produced 0.5 ml of H<sub>2</sub> after consuming 5.12 C charge after 70 min, The volume of H<sub>2</sub> gas was measured by water replacement in an inverted burette.

The amount of H<sub>2</sub> produced = 0.5 / 22,400 mol.

FY % = 2 × amount of H<sub>2</sub> (mol) × 96,500 / charged consumed during CPE.

%FY = 82 %

Amount of catalyst in 0.3 mM in 5 mL solution = 0.3 × 5 × 10<sup>-6</sup> mol.

TON = Product / Catalyst = 14.88.

### ***Detection of H<sub>2</sub>***

H<sub>2</sub> was detected by head space gas analysis by a GC fitted with appropriate detector. The gas evolved during CPE was detected by using a GC instrument brought from Agilent Technologies with model no. 7890B (G3440B), serial no. CN14333203, fitted with TCD. Approximately 200  $\mu$ L gas was collected by a gastight syringe and was injected into the inlet of the GC.

### **FTIR-SEC data Collection:**

1 ml 4 mM of catalyst solution was prepared using CH<sub>3</sub>CN inside glove box. 1 eq. *p*TsOH was added to it. 400 μL of this mixture was injected into the OTTLE cell. Spectro-electrochemistry was performed using the OTTLE cell connected with the potentiostat (CHI 700E). The sample solution also contained 100 mM TBAP as the supporting electrolyte. A Pt-mesh working electrode, a Pt counter electrode and a Ag-wire was used as the reference electrode. The FTIR spectra were taken at different time intervals during electrolysis at different potentials. The potential of the reference electrode was calibrated using ferrocene as an internal standard in the same solvent combination.

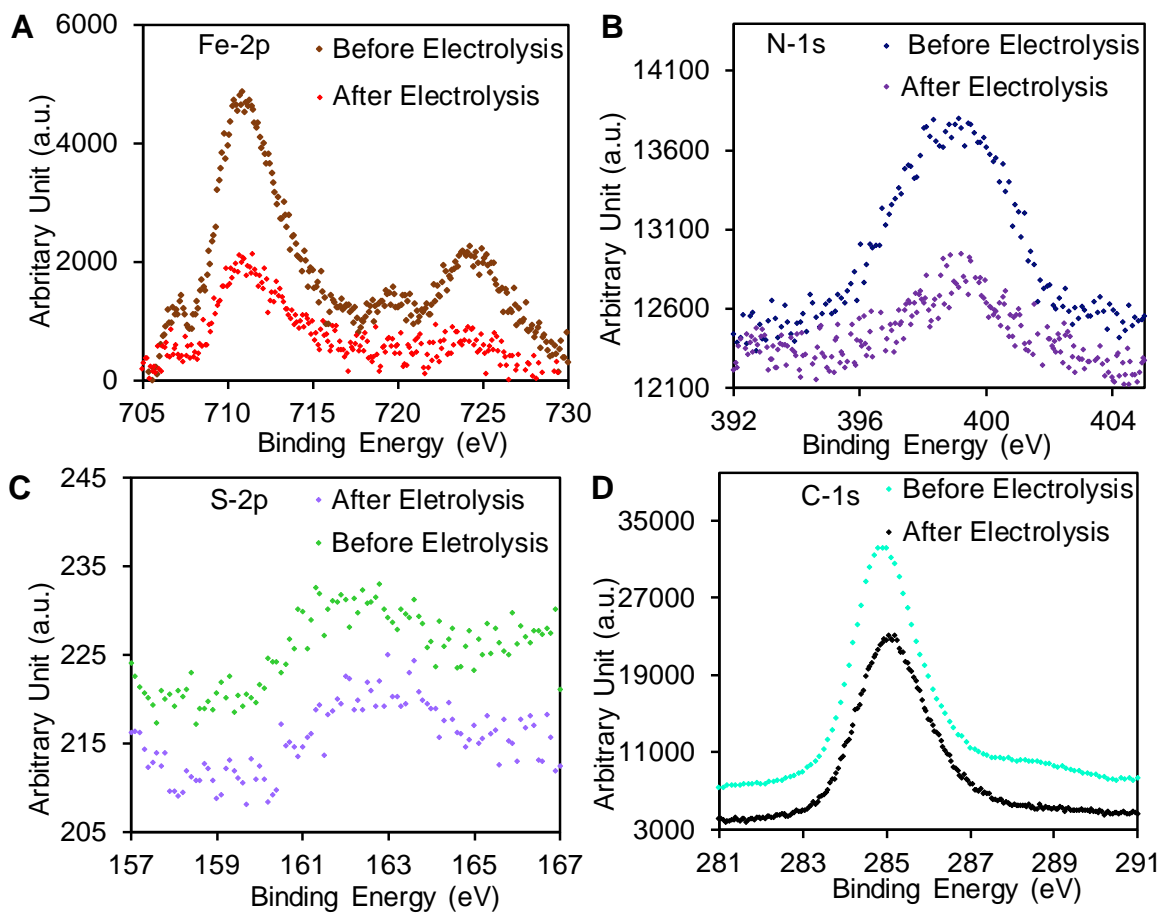
### **X-Ray Photoelectron Spectroscopy**

XPS (XPS, Omicron, model: 1712-62-11) measurement was done using a high-resolution monochromatic Mg-K $\alpha$  radiation source at 1253.6eV under 15 kV voltage and 5 mA current condition.

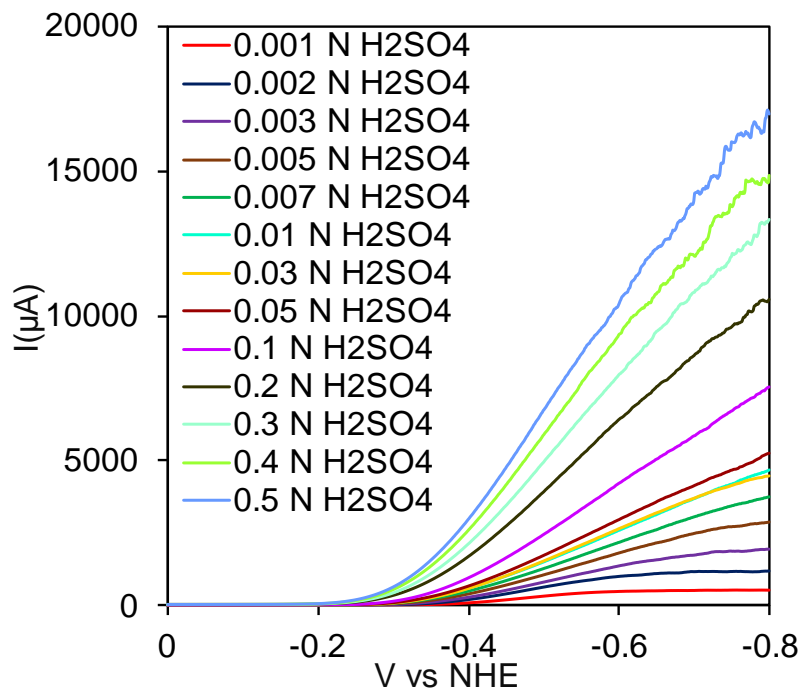
### **Density Functional Theory Calculations**

The density functional calculations are performed in gradient corrected BP86 Functional in unrestricted formalism using Gaussian 16 version C03.<sup>1-3</sup> All the Fe, C, H, N, O, S and Br atoms were optimized using 6-311g\* basis set. Frequency calculations were performed on each optimized structure using the same basis set to ensure that it was a minimum on the potential energy surface. The final energy calculations were performed using 6-311+g\* basis set on all atoms in PCM model using acetonitrile as a solvent and convergence criterion of 10<sup>-10</sup> Hartree. Basis-set superposition error has been reported to be minimal ( $\approx$ 1 kcal/mol) for anion binding at this level of theory. The shift of C-N vibration, C-O manifold and H/D isotope shifts in the SEC-FTIR data were used to judge the suitability of the DFT calculations. Comparison of the vibrational frequencies between B3LYP and BP86 reveals that the latter functional reproduced the experimental data better and was used for the electronic structure and energy calculations.

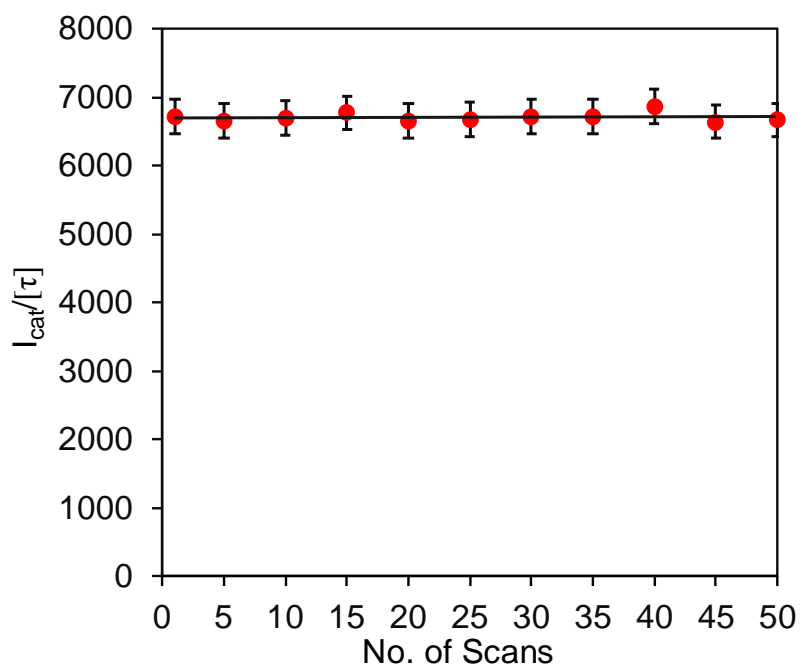




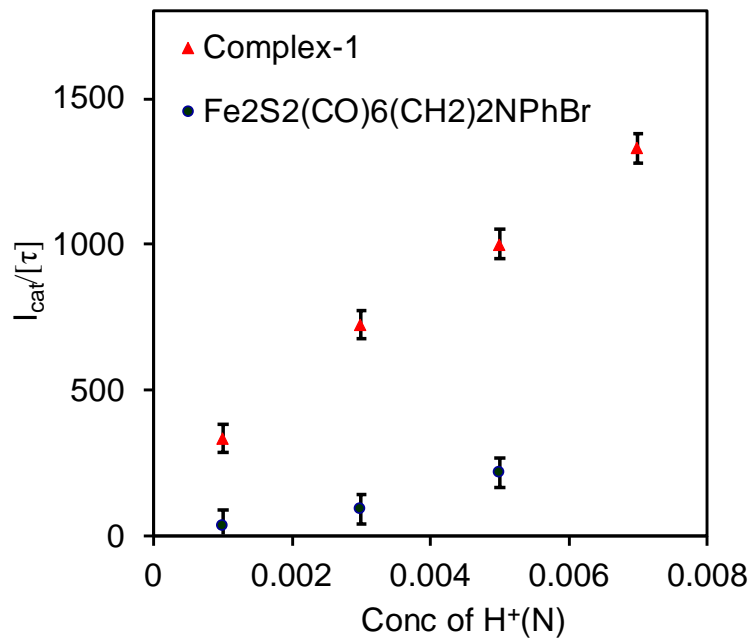
**Fig. S2.** XPS spectra of the modified EPG electrodes before and after electrolysis (A) Fe-2p, (B) N-1s, (C) S-2p and (D) C-1s.



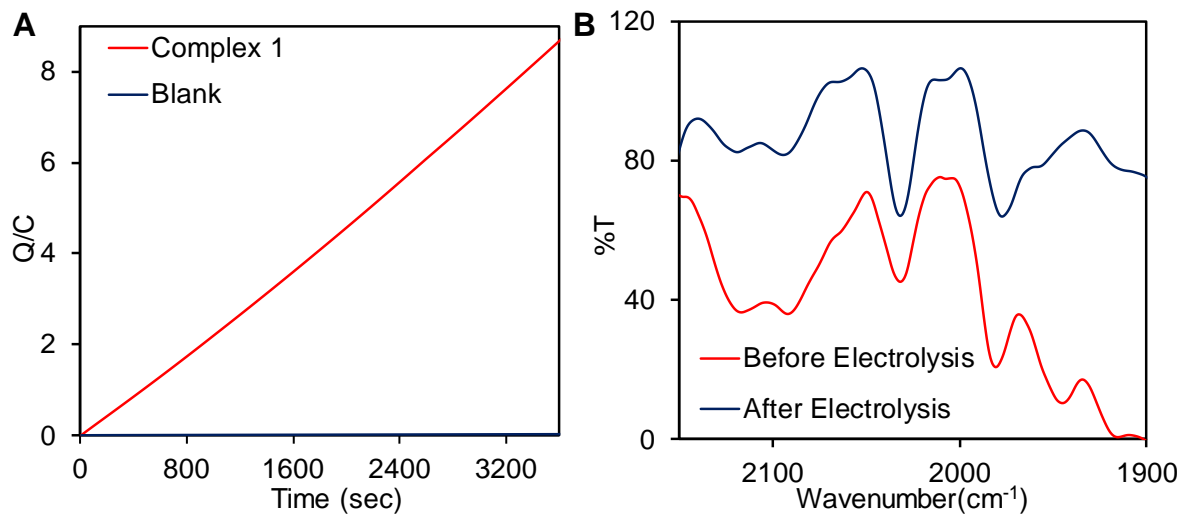
**Fig. S3.** LSV of Complex 1 physisorbed in EPG in different acid concentrations [0.001 N–0.5 N  $\text{H}_2\text{SO}_4$ ].



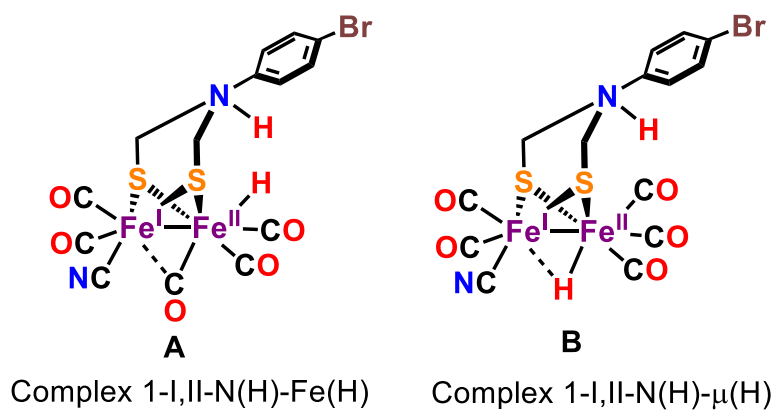
**Fig. S4:** Plot of  $I_{\text{cat}}/[\tau]$  vs number of scans.



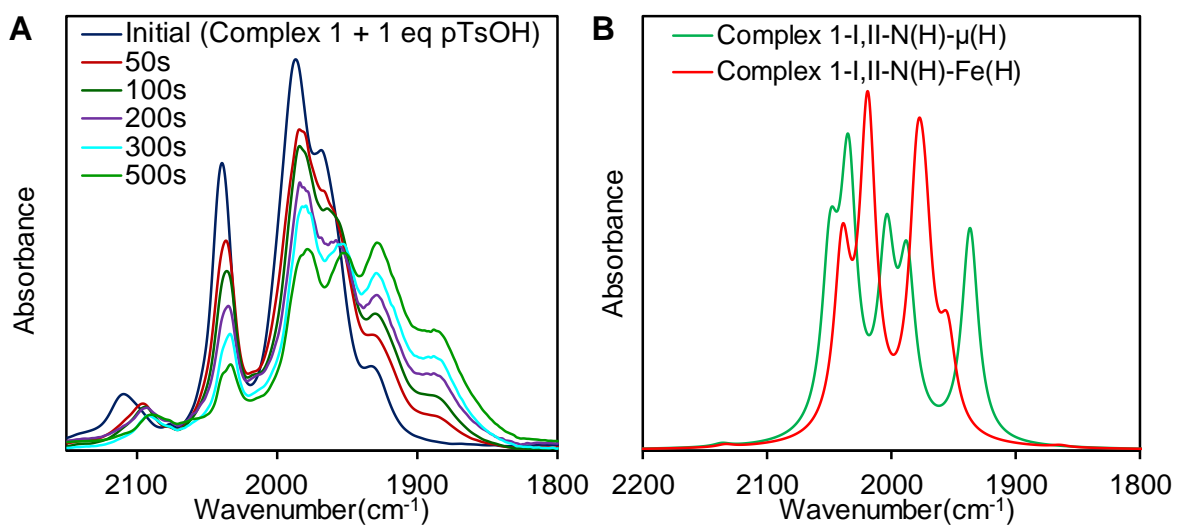
**Fig. S5:** Comparison of  $I_{cat}/[\tau]$  complex 1 and its precursor complex.



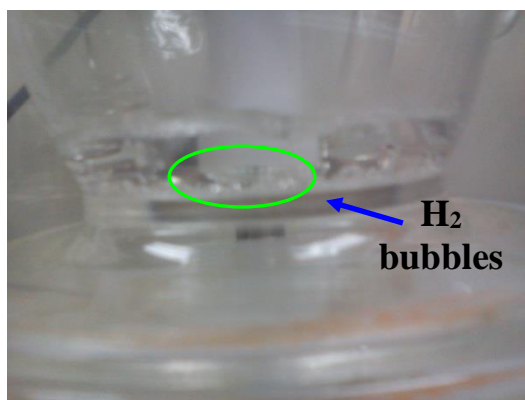
**Fig S6:** (A) Overlay of controlled potential bulk electrochemistry with the complex 1 modified EPG (red line) at -0.4 V vs NHE in 0.1 N  $H_2SO_4$  and with bare electrode (blue line) under identical conditions. (B) ATR-IR of the modified EPG electrode of complex 1 before and after 1 h bulk electrolysis at -0.4 V vs NHE.



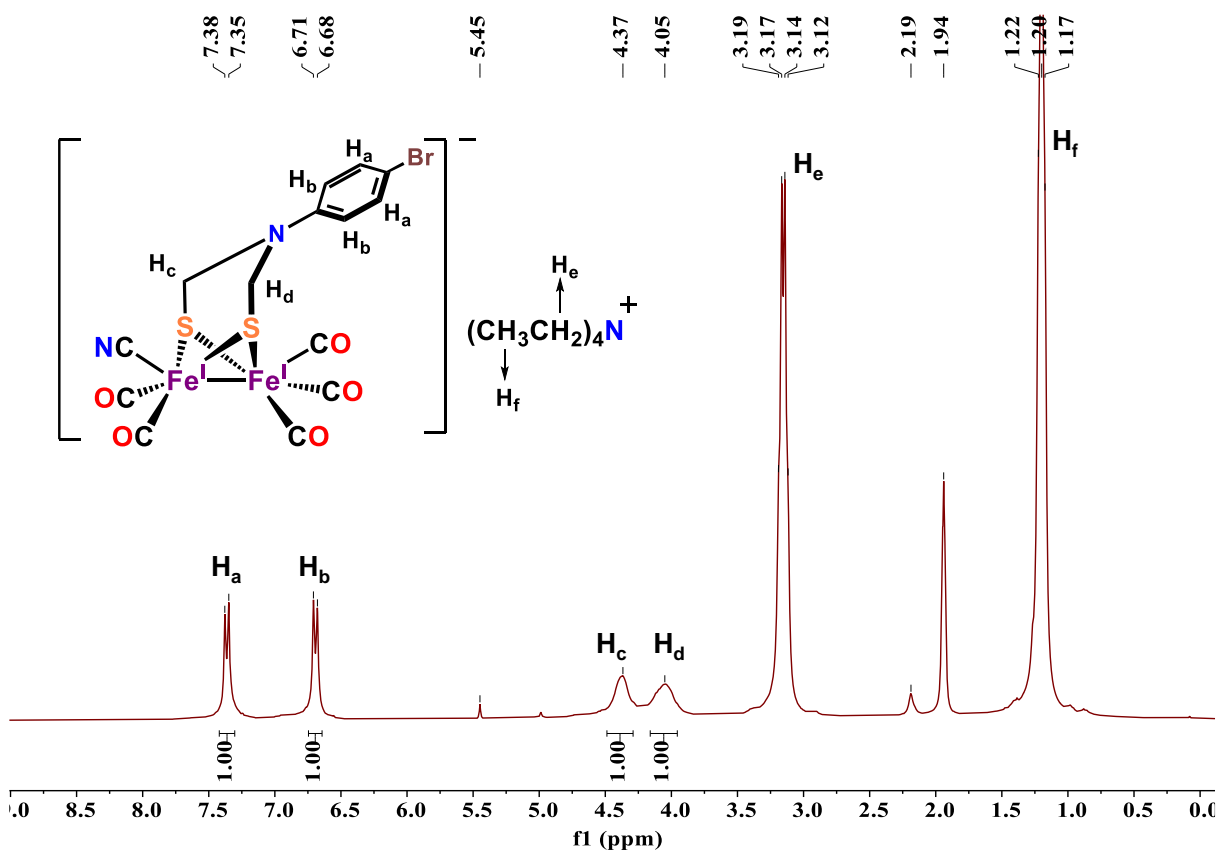
**Fig S7:** Probable Doubly protonated species.



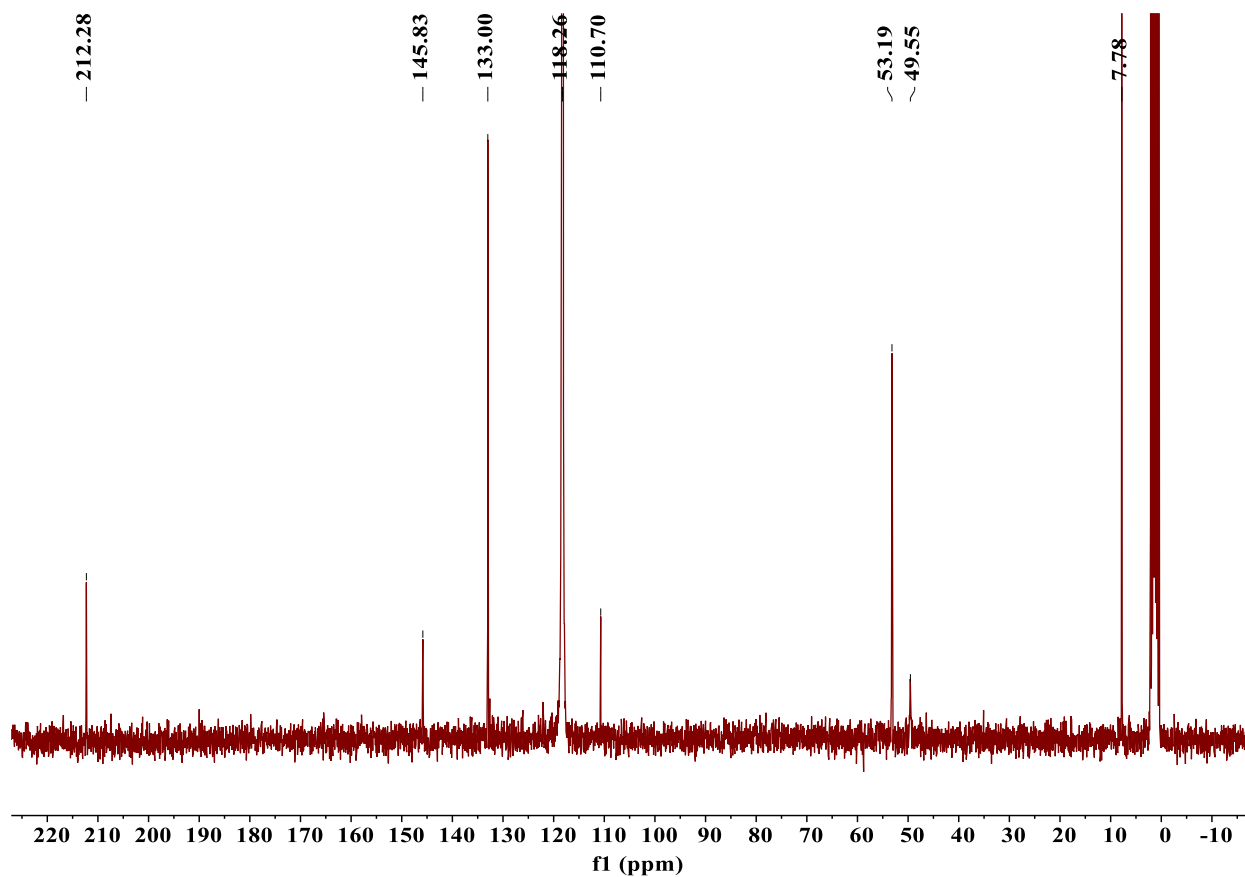
**Fig S8:** (A) FT-IR SEC data of complex **1** in presence of 1 eq. *p*-TsOH at -0.9V vs NHE, (B) Computed vibrational frequencies of two doubly protonated species **A** and **B** (Fig. **S7**).



**Fig. S9:** Photograph of the bubbles formed on the complex 1 loaded EPG surface at each scan in higher acid concentrations.



**Fig. S10.**  $^1\text{H-NMR}$  spectra of complex 1 in  $\text{CD}_3\text{CN}$ .



**Fig. S11.**  $^{13}\text{C}$ -NMR spectra of complex **1** in  $\text{CD}_3\text{CN}$ .

**Coordinates (x, y, z) of optimized structures:**

**(i)  $p\text{-BrC}_6\text{H}_4\text{N}(\text{CH}_2\text{S})_2\text{Fe}_2\text{CO}_6$  complex**

Fe	-0.94953	1.04256	-0.08184
Fe	-2.92701	-0.40776	0.05967
S	-1.30627	-0.70257	-1.57102
S	-1.19318	-0.55663	1.59565
Br	6.10447	0.43949	0.03385
C	1.79276	-1.51641	0.02512
C	0.78384	1.42288	-0.32818
O	1.84861	1.77789	-0.53337
C	-1.24837	2.24492	1.20239
O	-1.44677	2.99952	2.03619
C	-1.64058	2.10404	-1.33112
O	-2.10293	2.77162	-2.13563
C	-3.84327	0.47536	1.31342
O	-4.40813	1.05224	2.12193

C	-4.0136	0.16653	-1.24037
O	-4.6995	0.52942	-2.07834
C	-3.58469	-2.05243	0.247
N	0.52454	-2.12947	0.02854
C	2.56601	-1.44938	-1.14818
H	2.19683	-1.84098	-2.08585
C	3.83292	-0.88066	-1.14631
H	4.40086	-0.84026	-2.06763
C	4.35819	-0.36764	0.03444
C	3.62151	-0.42178	1.20991
H	4.01691	-0.011	2.1307
C	2.35046	-0.98524	1.20276
H	1.79422	-0.96756	2.12912
C	-0.26402	-2.21237	-1.16457
H	-0.96821	-3.0389	-1.07819
H	0.34465	-2.38286	-2.04433
C	-0.26097	-2.14366	1.22304
H	0.34692	-2.35174	2.09801
H	-1.01586	-2.92373	1.14659
O	-3.97407	-3.08914	0.38012

**(ii) axial-CN<sup>-</sup> complex**

Fe	-1.13075	1.15656	-0.05205
Fe	-3.02992	-0.43684	0.08292
S	-1.43318	-0.5388	-1.56214
S	-1.26382	-0.49418	1.5534
Br	6.42179	-0.08541	0.20428
C	1.89296	-1.464	-0.02074
C	0.55106	1.5846	-0.41625
O	1.61072	1.94343	-0.71348
C	-1.34264	2.31028	1.27225
O	-1.46563	3.0687	2.13838
C	-1.9445	2.22471	-1.19837
O	-2.48155	2.93234	-1.94153
C	-3.96687	0.38183	1.34461
O	-4.57996	0.92047	2.16578
C	-4.19297	0.02936	-1.17278
O	-4.96685	0.30944	-1.98687
C	-3.57571	-2.10193	0.29212
N	0.55849	-1.94311	-0.07246
C	2.77771	-1.69243	-1.0975
H	2.44635	-2.23419	-1.9871
C	4.11014	-1.27922	-1.03639
H	4.77757	-1.471	-1.87955
C	4.58838	-0.64318	0.11496
C	3.73647	-0.41484	1.19825
H	4.1028	0.09319	2.09309
C	2.39797	-0.81548	1.1267

H	1.74467	-0.57863	1.96951
C	-0.20252	-1.95718	-1.28612
H	-0.8181	-2.86952	-1.34942
H	0.45064	-1.90314	-2.16278
C	-0.2365	-2.02308	1.10986
H	0.39171	-2.21684	1.98771
H	-0.96593	-2.84105	1.00908
N	-3.9653	-3.32185	0.47492

**(iii) equatorial -CN<sup>-</sup> complex**

Fe	-1.13075	1.15656	-0.05205
Fe	-3.02992	-0.43684	0.08292
S	-1.43318	-0.5388	-1.56214
S	-1.26382	-0.49418	1.5534
Br	6.42179	-0.08541	0.20428
C	1.89296	-1.464	-0.02074
C	0.55106	1.5846	-0.41625
O	1.61072	1.94343	-0.71348
C	-1.34264	2.31028	1.27225
O	-1.46563	3.0687	2.13838
C	-1.9445	2.22471	-1.19837
O	-2.48155	2.93234	-1.94153
C	-3.96687	0.38183	1.34461
O	-4.57996	0.92047	2.16578
C	-4.19297	0.02936	-1.17278
C	-3.57571	-2.10193	0.29212
N	0.55849	-1.94311	-0.07246
C	2.77771	-1.69243	-1.0975
H	2.44635	-2.23419	-1.9871
C	4.11014	-1.27922	-1.03639
H	4.77757	-1.471	-1.87955
C	4.58838	-0.64318	0.11496
C	3.73647	-0.41484	1.19825
H	4.1028	0.09319	2.09309
C	2.39797	-0.81548	1.1267
H	1.74467	-0.57863	1.96951
C	-0.20252	-1.95718	-1.28612
H	-0.8181	-2.86952	-1.34942
H	0.45064	-1.90314	-2.16278
C	-0.2365	-2.02308	1.10986
H	0.39171	-2.21684	1.98771
H	-0.96593	-2.84105	1.00908
O	-3.92527	-3.19652	0.45614
N	-4.95948	0.30678	-1.97912

**(iv) [Fe(I)-Fe(I)NH]<sup>+</sup>-Complex**



Fe	-1.10504	1.15598	-0.08234
Fe	-3.0326	-0.43811	0.14853
S	-1.50629	-0.57679	-1.55446
S	-1.23912	-0.47509	1.57536
Br	6.49466	-0.21907	0.34242
C	1.9082	-1.43355	-0.01616
C	0.53045	1.53985	-0.62174
O	1.55382	1.89905	-1.05145
C	-1.17885	2.3104	1.23578
O	-1.20313	3.08011	2.11098
C	-2.10805	2.1833	-1.10268
O	-2.71567	2.92479	-1.75887
C	-4.04446	0.37786	1.31863
O	-4.74325	0.91349	2.08287
C	-4.29276	-0.01841	-1.21238
C	-3.61189	-2.05041	0.39292
N	0.57913	-1.87048	-0.0927
C	2.80876	-1.62819	-1.09284
H	2.47104	-2.10174	-2.01793
C	4.15284	-1.26498	-0.99192
H	4.82583	-1.43319	-1.83635
C	4.63252	-0.70508	0.19641
C	3.77035	-0.49163	1.27448
H	4.13543	-0.02572	2.19302
C	2.42239	-0.84516	1.1661
H	1.75435	-0.60615	1.99617
C	-0.17321	-1.88807	-1.32549
H	-0.70158	-2.8516	-1.43419
H	0.49617	-1.75247	-2.18178
C	-0.23073	-1.98647	1.08755
H	0.39988	-2.239	1.95051
H	-0.95886	-2.79789	0.93559
O	-3.95798	-3.14894	0.60592
N	-5.08822	0.21499	-2.04871
H	0.8268	-2.83863	-0.12924

**(v) [Fe(I)-Fe(0)NH]-Complex**

Fe	-1.69009	1.50181	0.03204
Fe	-3.13036	-0.5705	0.09429
S	-1.56047	-0.20706	-1.51898
S	-1.45152	-0.1877	1.58982
Br	7.67088	-2.43155	0.11495
C	2.16804	-1.14061	-0.07025
C	-0.12313	2.26484	0.3096
O	0.85464	2.84832	0.56914
C	-2.79581	2.27354	1.15427
O	-3.50633	2.84338	1.88719
C	-2.20362	2.53437	-1.29193

O	-2.5159	3.24446	-2.16165
C	-4.36666	-0.39068	1.31843
O	-5.21995	-0.31695	2.1142
C	-4.41516	-0.12934	-1.2385
C	-3.23039	-2.29287	-0.02697
N	0.75341	-0.82408	-0.04495
C	2.67084	-2.28105	-0.72756
H	1.98048	-2.96602	-1.23709
C	4.05516	-2.54918	-0.72366
H	4.43743	-3.43468	-1.249
C	4.92799	-1.70596	-0.04285
C	4.44044	-0.58093	0.62262
H	5.12906	0.0917	1.15104
C	3.06534	-0.28559	0.60001
H	2.67086	0.62186	1.0736
C	-0.01645	-1.21547	-1.20098
H	-0.36588	-2.27054	-1.16738
H	0.6028	-1.07513	-2.09752
C	0.10239	-1.1474	1.20723
H	0.7941	-0.92474	2.03039
H	-0.19213	-2.2192	1.27063
O	-3.26954	-3.46272	-0.09833
N	-5.22632	0.13733	-2.05058
H	0.73424	0.1753	-0.07448

**(vi) [Fe(I)-Fe(II)*t*-H]-Complex**

Fe	-0.87778	1.06828	-0.05142
Fe	-2.92679	-0.39215	0.13713
S	-1.41649	-0.58423	-1.55101
S	-1.15957	-0.59806	1.5558
Br	6.1116	0.44033	0.26666
C	1.85923	-1.51469	0.0077
C	0.69581	1.44859	-0.74554
O	1.6792	1.77412	-1.27836
C	-0.71558	2.18239	1.2977
O	-0.58178	2.90676	2.19533
C	-1.99252	2.17062	-0.87269
O	-2.62214	2.9897	-1.3942
C	-3.93784	0.42561	1.3218
O	-4.63273	0.95994	2.08065
C	-4.13852	0.11353	-1.22983
C	-3.60365	-1.97758	0.31202
N	0.54644	-2.23836	-0.08903
C	2.79427	-1.75181	-1.00701
H	2.56049	-2.3955	-1.86064
C	4.06276	-1.1685	-0.93541
H	4.79236	-1.34641	-1.72749
C	4.38371	-0.36031	0.1622

C	3.45425	-0.13852	1.18475
H	3.70845	0.49589	2.03585
C	2.18327	-0.72032	1.11098
H	1.46418	-0.51975	1.90566
C	-0.26747	-1.99238	-1.39488
H	-0.85102	-2.91646	-1.53178
H	0.47901	-1.91038	-2.19427
C	-0.33591	-2.18806	1.15665
H	0.31186	-2.47973	1.99505
H	-1.1002	-2.96257	1.00112
O	-3.98664	-3.06964	0.46211
N	-4.88254	0.39579	-2.09578
H	0.04181	0.15891	0.62608

**(vii) [Fe(I)-Fe(II)*t*-D]-Complex**

Fe	-0.75828	1.26502	-0.16465
Fe	-2.98009	-0.2805	-0.03645
S	-1.24493	-0.46212	-1.65663
S	-1.26192	-0.25794	1.57881
Br	6.52372	-0.51613	0.58824
C	1.88594	-1.49485	0.15952
C	-0.28985	2.25864	-1.51819
O	0.08872	2.90652	-2.40752
C	-0.25365	2.42144	1.03943
O	0.14785	3.17033	1.83596
C	-2.6108	1.79285	-0.18221
O	-3.32967	2.72591	-0.21529
C	-4.21304	0.12346	1.13246
O	-5.05035	0.35813	1.90702
C	-4.16778	-0.01128	-1.49889
C	-3.35647	-2.02098	-0.01772
N	0.53692	-1.87534	0.07378
C	2.80414	-1.80729	-0.8726
H	2.46838	-2.31325	-1.78071
C	4.16435	-1.51428	-0.75152
H	4.84969	-1.77316	-1.56246
C	4.64145	-0.90638	0.41346
C	3.76199	-0.57419	1.44697
H	4.12549	-0.06759	2.34429
C	2.39954	-0.85657	1.31567
H	1.72316	-0.52181	2.10443
C	-0.17267	-1.93702	-1.18224
H	-0.85716	-2.80155	-1.16824
H	0.52774	-2.05806	-2.01453
C	-0.30898	-1.84545	1.23574
H	0.28519	-2.06036	2.13357
H	-1.07345	-2.63015	1.12289
O	-3.72683	-3.12843	-0.01261

N	-4.91217	0.12792	-2.39924
H(iso=2)	0.73334	0.86946	-0.13468

**(viii) [Fe(I)-Fe(II) $\mu$ -H]-Complex**

Fe	-1.13075	1.15656	-0.05205
Fe	-3.02992	-0.43684	0.08292
S	-1.43318	-0.5388	-1.56214
S	-1.26382	-0.49418	1.5534
Br	6.42179	-0.08541	0.20428
C	1.89296	-1.464	-0.02074
C	0.55106	1.5846	-0.41625
O	1.61072	1.94343	-0.71348
C	-1.34264	2.31028	1.27225
O	-1.46563	3.0687	2.13838
C	-1.9445	2.22471	-1.19837
O	-2.48155	2.93234	-1.94153
C	-3.96687	0.38183	1.34461
O	-4.57996	0.92047	2.16578
C	-4.19297	0.02936	-1.17278
C	-3.57571	-2.10193	0.29212
N	0.55849	-1.94311	-0.07246
C	2.77771	-1.69243	-1.0975
H	2.44635	-2.23419	-1.9871
C	4.11014	-1.27922	-1.03639
H	4.77757	-1.471	-1.87955
C	4.58838	-0.64318	0.11496
C	3.73647	-0.41484	1.19825
H	4.1028	0.09319	2.09309
C	2.39797	-0.81548	1.1267
H	1.74467	-0.57863	1.96951
C	-0.20252	-1.95718	-1.28612
H	-0.8181	-2.86952	-1.34942
H	0.45064	-1.90314	-2.16278
C	-0.2365	-2.02308	1.10986
H	0.39171	-2.21684	1.98771
H	-0.96593	-2.84105	1.00908
O	-3.92527	-3.19652	0.45614
N	-4.95948	0.30678	-1.97912
H	-2.95157	1.19687	0.246

**(ix) [Fe(I)-Fe(II)-(H)-N(H)]-Complex**

Fe	-0.87778	1.06828	-0.05142
Fe	-2.92679	-0.39215	0.13713
S	-1.41649	-0.58423	-1.55101
S	-1.15957	-0.59806	1.5558
Br	6.1116	0.44033	0.26666
C	1.85923	-1.51469	0.0077

C	0.69581	1.44859	-0.74554
O	1.6792	1.77412	-1.27836
C	-0.71558	2.18239	1.2977
O	-0.58178	2.90676	2.19533
C	-1.99252	2.17062	-0.87269
O	-2.62214	2.9897	-1.3942
C	-3.93784	0.42561	1.3218
O	-4.63273	0.95994	2.08065
C	-4.13852	0.11353	-1.22983
C	-3.60365	-1.97758	0.31202
N	0.54644	-2.23836	-0.08903
C	2.79427	-1.75181	-1.00701
H	2.56049	-2.3955	-1.86064
C	4.06276	-1.1685	-0.93541
H	4.79236	-1.34641	-1.72749
C	4.38371	-0.36031	0.1622
C	3.45425	-0.13852	1.18475
H	3.70845	0.49589	2.03585
C	2.18327	-0.72032	1.11098
H	1.46418	-0.51975	1.90566
C	-0.26747	-1.99238	-1.39488
H	-0.85102	-2.91646	-1.53178
H	0.47901	-1.91038	-2.19427
C	-0.33591	-2.18806	1.15665
H	0.31186	-2.47973	1.99505
H	-1.1002	-2.96257	1.00112
O	-3.98664	-3.06964	0.46211
N	-4.88254	0.39579	-2.09578
H	0.81321	-3.2331	-0.1678
H	0.04181	0.15891	0.62608

**(x) [Fe(I)-Fe(II)-N(H)- $\mu$ (H)]-Complex**

Fe	-1.44436	1.50401	-0.15783
Fe	-3.05558	-0.54287	0.17358
S	-1.58825	-0.27237	-1.54856
S	-1.42435	-0.68438	1.84185
Br	6.76669	-1.69863	0.00069
C	2.09891	-1.12779	-0.05597
C	0.06661	2.14846	0.45313
O	0.99998	2.73754	0.8876
C	-2.64806	2.10819	0.98329
O	-3.34069	2.69087	1.72736
C	-1.71874	2.71876	-1.40215
O	-1.85711	3.56854	-2.19361
C	-4.27854	-0.28432	1.40234
O	-5.12927	-0.16646	2.18949
C	-4.32551	-0.02289	-1.13778
C	-3.26782	-2.2509	0.00105

N	0.65231	-0.94457	-0.02996
C	2.6543	-2.35614	-0.45186
H	2.01171	-3.17981	-0.77398
C	4.04288	-2.52562	-0.43744
H	4.48497	-3.47556	-0.74592
C	4.85689	-1.46468	-0.02221
C	4.30892	-0.2378	0.37772
H	4.9554	0.58478	0.69068
C	2.92024	-0.07056	0.36405
H	2.47843	0.88573	0.66397
C	-0.06063	-1.28593	-1.31585
H	-0.30705	-2.35669	-1.31412
H	0.62355	-1.05354	-2.1432
C	-0.04633	-1.63356	1.20668
H	0.73677	-1.70695	1.97334
H	-0.31843	-2.63879	0.84845
O	-3.35517	-3.4159	-0.09162
N	-5.1263	0.26961	-1.94994
H	0.41201	0.10719	0.1035
H	-2.87645	0.89877	0.3192

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