

Supporting Information for

**Diiron azadithiolate cluster supported on carbon nanotubes  
for efficient electrocatalytic proton reduction**

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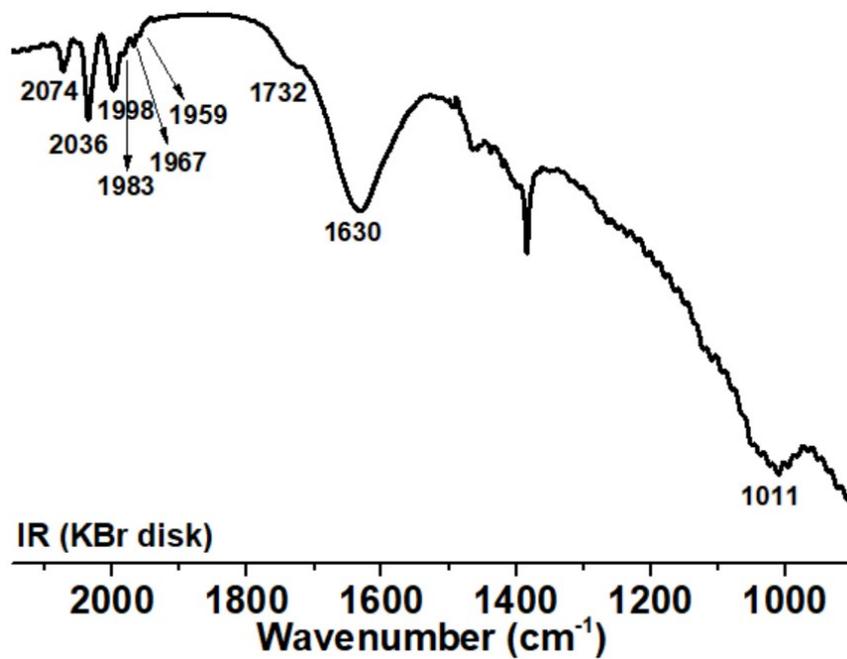
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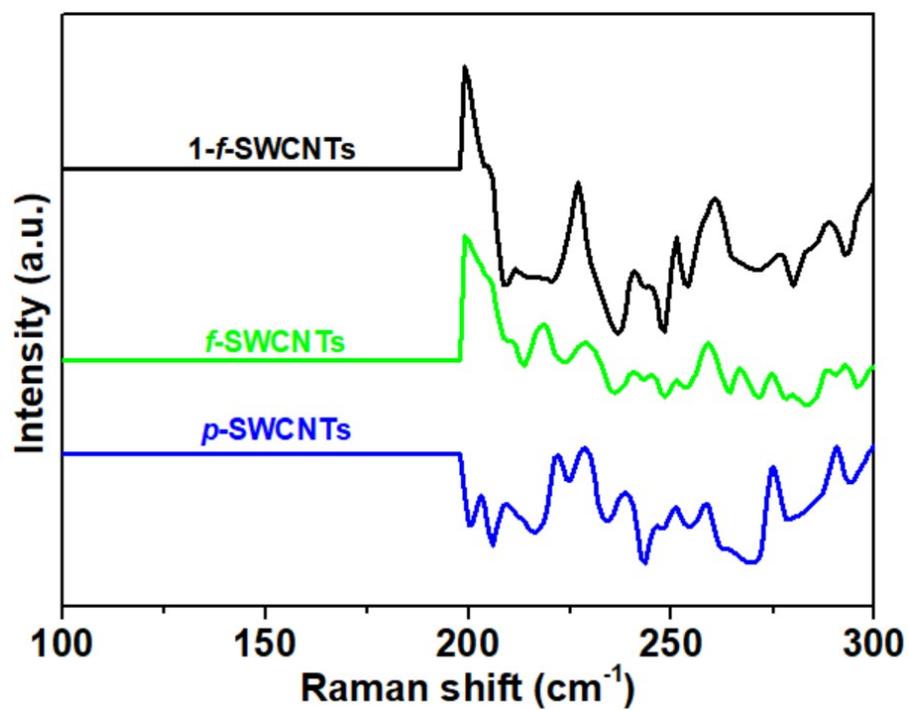
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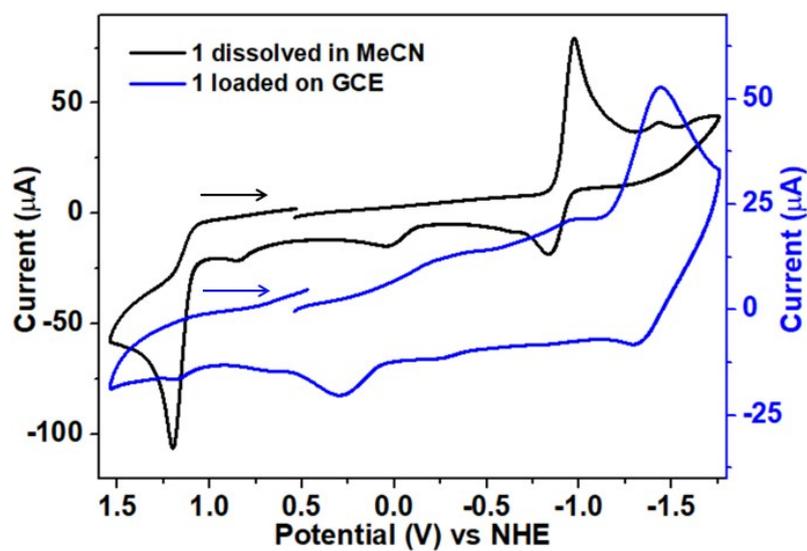
## I. Relevant spectroscopic and electrochemical data of 1-*f*-SWCNTs and 1



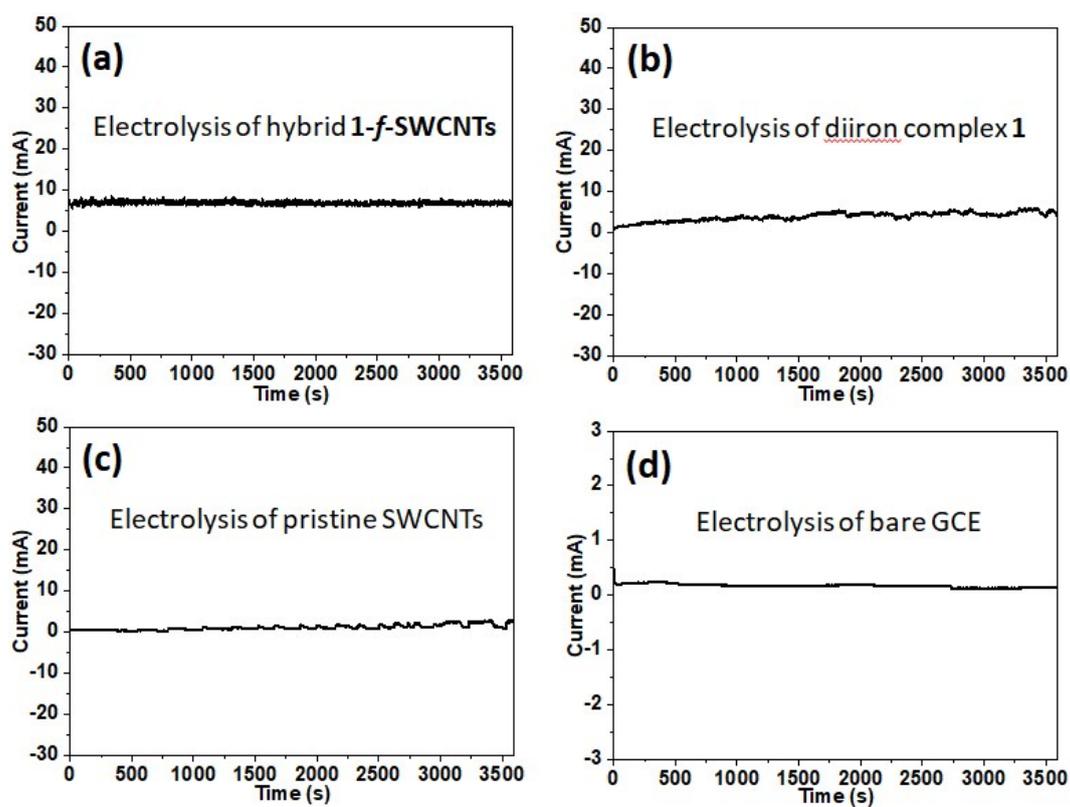
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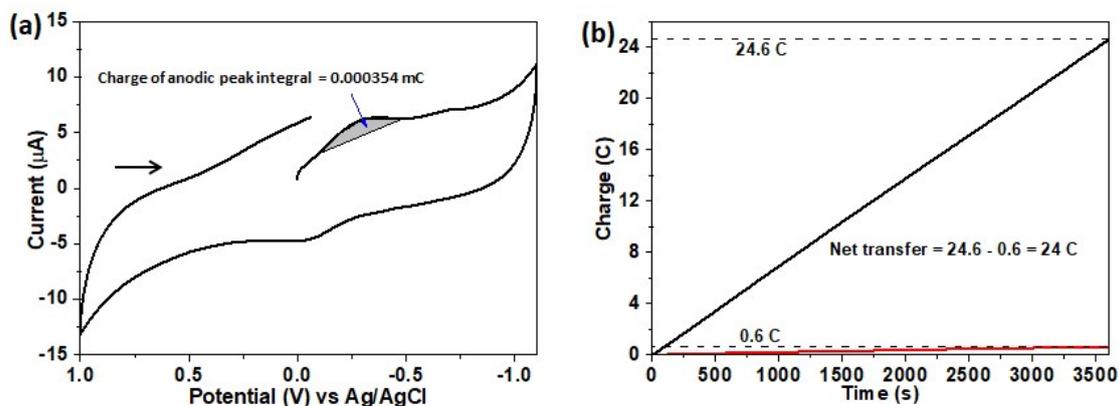


**Fig. S3.** Cyclic voltammeteries of diiron compound **1** dissolved in MeCN (1.0 mM, black line) and loaded on GCE electrode (0.71 mg cm<sup>-2</sup> loading, blue line) in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/MeCN solution at a scan rate of 0.05 V s<sup>-1</sup>. Data in MeCN were recorded using a nonaqueous Ag/AgNO<sub>3</sub> (0.01 M in MeCN) reference electrode and are further referred to the normal hydrogen electrode (NHE) for comparison.



**Fig. S4.** Controlled-potential electrolysis experiments of (a) hybrid 1-f-SWCNTs, (b) compound 1, (c) pristine SWCNTs absorbed respectively on GCE electrodes with loading of  $0.71 \text{ mg cm}^{-2}$  and (d) bare GCE electrode at  $-0.90 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  (sat.  $\text{KCl}$ ) in  $0.2 \text{ N H}_2\text{SO}_4$  solution.

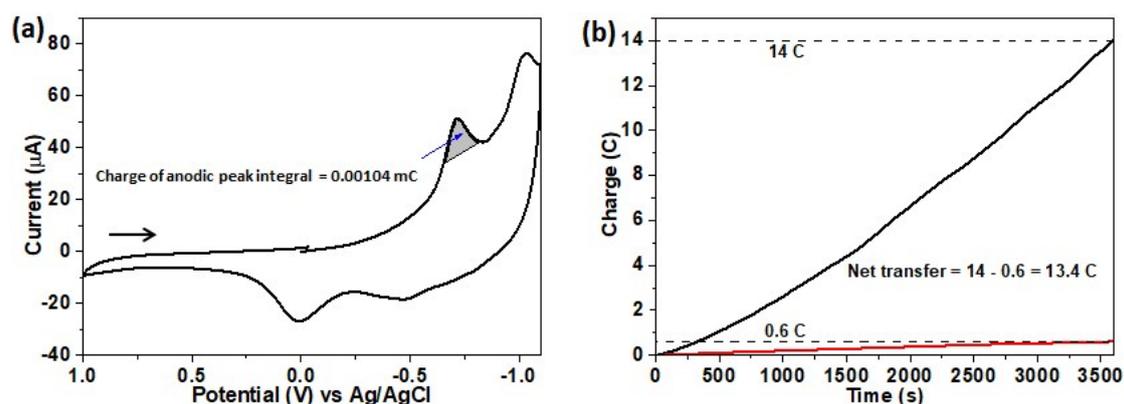
## II. TON and TOF calculations of materials 1-f-SWCNTs and 1



**Fig. S5.** (a) Cyclic voltammetry of hybrid **1-f-SWCNTs** (loading of  $0.71 \text{ mg cm}^{-2}$ ) absorbed on GCE electrode in  $0.1 \text{ M Na}_2\text{SO}_4/\text{H}_2\text{O}$  at a scan rate of  $0.05 \text{ V s}^{-1}$ . (b) Controlled potential electrolysis of hybrid **1-f-SWCNTs** (loading of  $0.71 \text{ mg cm}^{-2}$ ) absorbed on GCE electrode and bare GCE electrode at  $-0.9 \text{ V vs Ag/AgCl}$  (sat. KCl) in  $0.2 \text{ N H}_2\text{SO}_4$  solution.

TON and TOF calculation for the **1-f-SWCNTs** hybrid [1-4]:

- (1) From the CV curve shown in Fig. S4a, the charge of anodic peak integral is estimated to  $3.54 \times 10^{-7} \text{ C}$ . Thus, we converted this charge to the moles of catalyst **1-f-SWCNTs** on the GCE electrode (division by faraday constant), *i.e.*,  $n(\text{catalyst}) = Q/(F \times 1) = 3.54 \times 10^{-7} \text{ C}/96500 \text{ C} \cdot \text{mol}^{-1} = 0.37 \times 10^{-11} \text{ mol}$ .
- (2) From the CPE experiment shown in Fig. S4b, the neat charge passed on the **1-f-SWCNTs/GCE** electrode is equal to  $24 \text{ C}$  with 1 hour. Thus, we converted this charge to the moles of transfer electron on the GCE electrode (division by faraday constant), *i.e.*,  $n(e^-) = Q/F = 24 \text{ C}/96500 \text{ C} \cdot \text{mol}^{-1} = 2.48 \times 10^{-4} \text{ mol}$ . According to the reaction  $2\text{H}^+ + 2e^- = \text{H}_2$ , the moles of  $\text{H}_2$  produced is estimated from the moles of transfer electron on the GCE electrode (division by 2), *i.e.*,  $n(\text{H}_2) = n(e^-)/2 = 2.48 \times 10^{-4} \text{ mol}/2 = 1.24 \times 10^{-4} \text{ mol}$ .
- (3) According to the equations:  $\text{TON} = n(\text{H}_2)/n(\text{catalyst})$  and  $\text{TOF} = \text{TON}/t$ , the TON for hybrid **1-f-SWCNTs** is estimated to be  $\sim 3.4 \times 10^7$  after 1h and thus the TOF value is  $9444 \text{ s}^{-1}$ .



**Fig. S6.** (a) Cyclic voltammetry of compound **1** (loading of  $0.71 \text{ mg cm}^{-2}$ ) absorbed on GCE electrode in  $0.1 \text{ M Na}_2\text{SO}_4/\text{H}_2\text{O}$  at a scan rate of  $0.05 \text{ V s}^{-1}$ . (b) Controlled potential electrolysis of compound **1** (loading of  $0.71 \text{ mg cm}^{-2}$ ) absorbed on GCE electrode and bare GCE electrode at  $-0.9 \text{ V vs Ag/AgCl}$  (sat. KCl) in  $0.2 \text{ N H}_2\text{SO}_4$  solution.

TON and TOF calculation for compound **1** [1-4]:

- (1) From the CV curve shown in Fig. S5a, the charge of anodic peak integral is estimated to  $1.04 \times 10^{-6} \text{ C}$ . Thus, we converted this charge to the moles of catalyst **1** on the GCE electrode (division by faraday constant), *i.e.*,  $n(\text{catalyst}) = Q/(F \times 1) = 1.04 \times 10^{-6} \text{ C} / 96500 \text{ C} \cdot \text{mol}^{-1} = 1.08 \times 10^{-11} \text{ mol}$ .
- (2) From the CPE experiment shown in Fig. S5b, the neat charge passed on the **1** /GCE electrode is equal to  $13.4 \text{ C}$  with 1 hour. Thus, we converted this charge to the moles of transfer electron on the GCE electrode (division by faraday constant), *i.e.*,  $n(e^-) = Q/F = 13.4 \text{ C} / 96500 \text{ C} \cdot \text{mol}^{-1} = 1.39 \times 10^{-4} \text{ mol}$ . According to the reaction  $2\text{H}^+ + 2e^- = \text{H}_2$ , the moles of  $\text{H}_2$  produced is estimated from the moles of transfer electron on the GCE electrode (division by 2), *i.e.*,  $n(\text{H}_2) = n(e^-)/2 = 1.39 \times 10^{-4} \text{ mol} / 2 = 0.70 \times 10^{-4} \text{ mol}$ .
- (3) According to the equations:  $\text{TON} = n(\text{H}_2)/n(\text{catalyst})$  and  $\text{TOF} = \text{TON}/t$ , the TON for complex **1** is estimated to be  $\sim 0.6 \times 10^7$  after 1h and thus the TOF value is  $1667 \text{ s}^{-1}$ .

## References:

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- [3] S. Dey, A. Rana, S. G. Dey and A. Dey, Electrochemical hydrogen Production in acidic water by an azadithiolate bridged synthetic hydrogenase mimic: Role of aqueous solvation in lowering overpotential, *ACS Catal.*, 2013, **3**, 429–436.
- [4] M. E. Ahmed, S. Dey, B. Mondal and A. Dey, H<sub>2</sub> Evolution catalyzed by FeFe-hydrogenase synthetic model covalently attached to graphite surface, *Chem. Commun.*, 2017, **53**, 8188–8191.

### III. Crystallographic and spectroscopic data of compound 1

**Table S1.** Details of crystallographic data and structure refinement for compound 1

Identification code	Compound 1
CCDC number	2044503
Empirical formula	C <sub>16</sub> H <sub>13</sub> Fe <sub>2</sub> NO <sub>7</sub> S <sub>2</sub> ·0.5H <sub>2</sub> O
Formula weight	516.12
Temperature /K	150(2)
Crystal system	orthorhombic
Space group	Pbcn
a /Å	28.3033(7)
b /Å	10.6482(3)
c /Å	13.0200(4)
α /°	90
β /°	90
γ /°	90
Volume /Å <sup>3</sup>	3923.95(19)
Z	8
ρ <sub>calc</sub> /g cm <sup>-3</sup>	1.747
μ /mm <sup>-3</sup>	14.239
F(000)	2088.0
Crystal size/mm <sup>3</sup>	0.18 × 0.17 × 0.16
Radiation	CuKα (λ = 1.54178)
2θ range for data collection /°	8.872 to 132
Index ranges	-17 ≤ h ≤ 33, -12 ≤ k ≤ 12, -15 ≤ l ≤ 11
Reflections collected	8004
Independent reflections	3401 [R <sub>int</sub> = 0.0919, R <sub>sigma</sub> = 0.1167]
Data/restraints/parameters	3401/15/258
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0853, wR <sub>2</sub> = 0.2154
Final R indexes [all data]	R <sub>1</sub> = 0.1120, wR <sub>2</sub> = 0.2442
Largest diff. peak/hole / e Å <sup>-3</sup>	1.57/-1.12

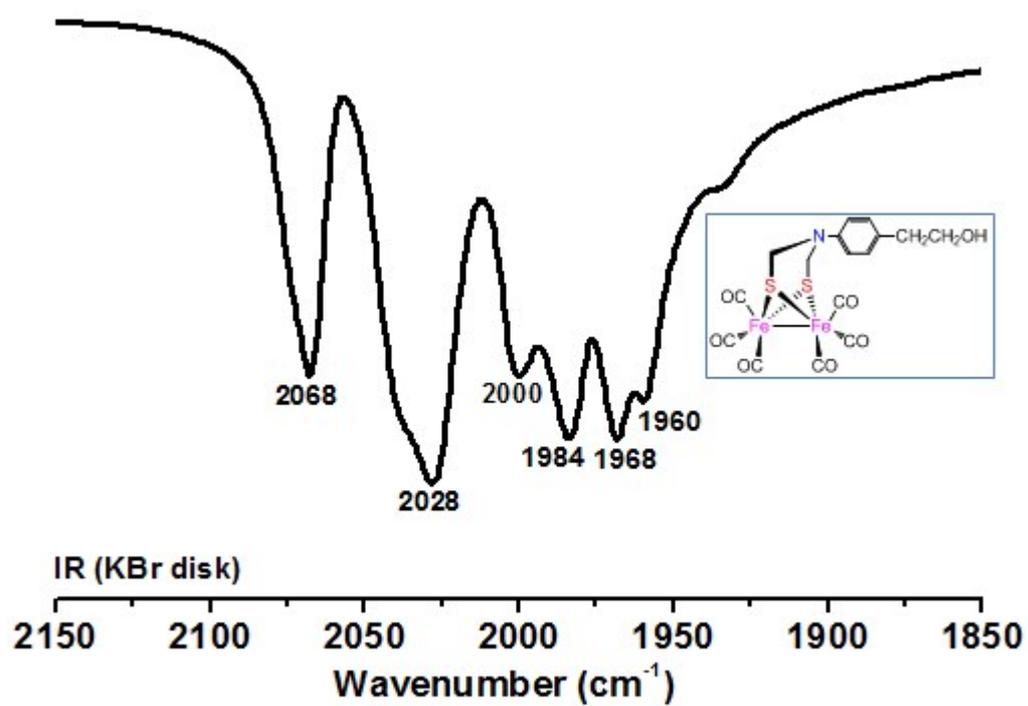
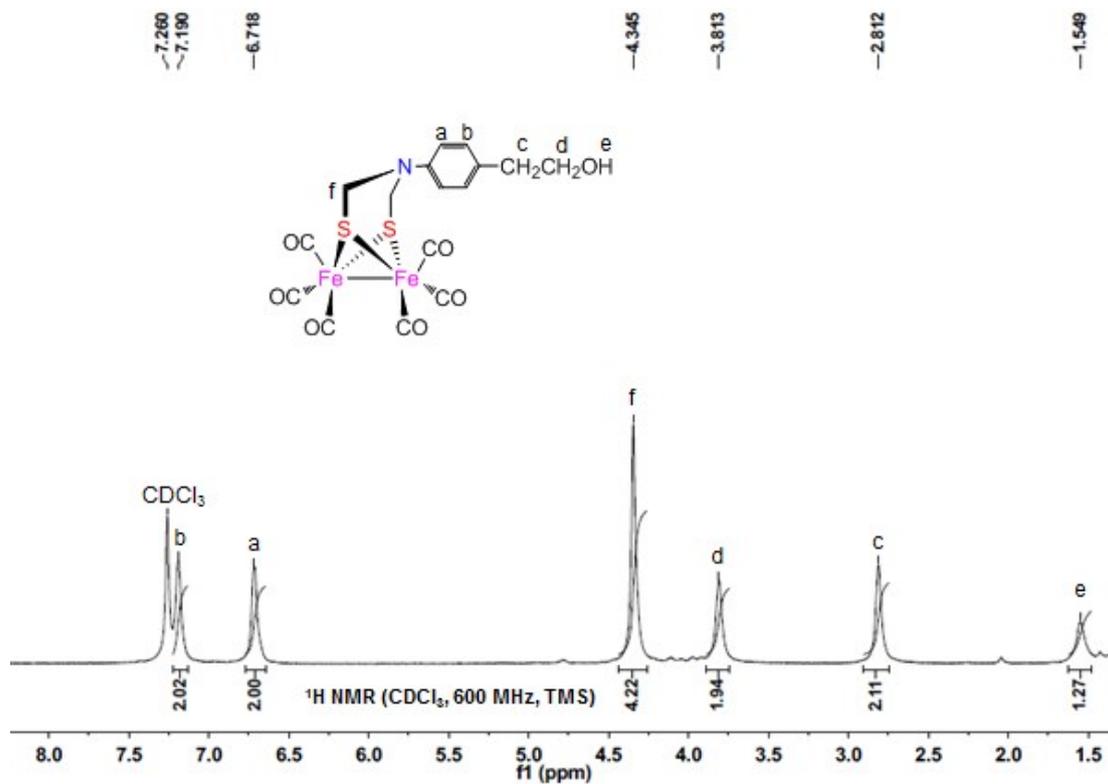
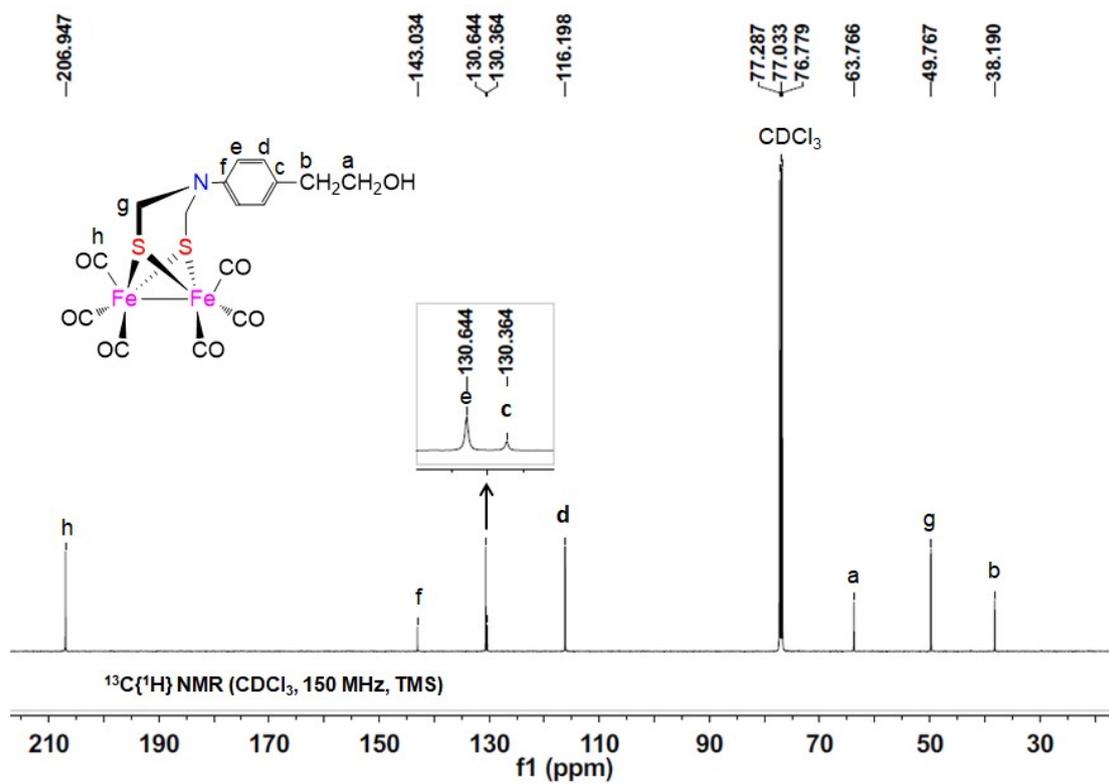


Fig. S7. FT-IR spectrum (KBr disk) of compound 1.



**Fig. S8.**  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum of compound 1.



**Fig. S9.** <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>, 25°C) spectrum of compound 1.