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Electronic Supplementary Information

Enhancement in catalytic proton reduction by an internal base in a diiron pentacarbonyl complex: its synthesis, characterisation, inter-conversion and electrochemical investigation

Zhimei Li,[1] Zhiyin Xiao,[2] Fenfen Xu,[1] Xianghua Zeng,[2] and Xiaoming Liu*[2]

[1]School of Chemistry, Nanchang University, Nanchang 330031, China

[2]College of Biological, Chemical Sciences and Engineering, Jiaxing University,
Jiaxing 314001, China

Email: xiaoming.liu@mail.zjxu.edu.cn; xiaoming.liu@ncu.edu.cn

Tel./Fax: +86 (0)573 83643937

1 Synthesis of the ligand (H_2L)

1.1 2-methyl-2-(pyridin-2-yl) propane-1, 3-diol

A mixture of 2-ethylpyridine (15 mL, 14.06 g, 0.131 mol) and an aqueous solution of formaldehyde (40%, 45 mL, 0.653 mol) was heated at 135 °C for 40 h in an autoclave. After being cooled down to room temperature, the solution was extracted with ethyl acetate (20 mL × 3). The organic phase was washed with saturated aqueous NaCl solution (3 × 20 mL) and dried with anhydrous Na_2SO_4. A brown oily liquid was accrued after the removal of the solvent under vacuum, in which there were three components, the starting material, monohydroxymethylated and the desired dihydroxymethylated as indicated by TLC. The crude product was purified with flash chromatography using gradient eluents. The starting material was first washed out using a mixture of ethyl acetate, n-hexane and ethanol at a ratio of 10:5:1. Then the eluting ratio was switched to 10:3.3:1 to successively elute the monohydroxymethylated, and then the dihydroxymethylated components. The former was collected as a yellow oily liquid and the latter as an orange viscous oily liquid (6.5 g, yield: 30%). ^1H NMR($CDCl_3$, ppm): 1.33 (s, 3H), 4.05 (s, 4H), 4.81 (t, 2H, J = 6.0 Hz), 7.22 (t, 2H, J = 2.76 Hz), 7.72 (s, H), 8.48 (s, H). ^{13}C NMR ($CDCl_3$, ppm): 18.5, 43.8, 75.6, 121.8, 137.0, 148.2, 165.1. MS (EI): (M+1)/z = 168.2. Micro analysis (%) for $C_9H_{13}NO_2$ (167.21), calculated (found): C, 64.65 (64.99); H, 7.84 (7.98); N, 8.38 (7.32).

1.2 2-methyl-2-(pyridin-2-yl) propane-1, 3-diyl-bis (4-methylbenzenesulfonate)

To an ice-bath pre-cooled solution of 2-methyl-2-(pyridin-2-yl)propane-1,3-diol (3.81 g, 0.023 mol) in pyridine (20 mL) was dropwise added a solution of toluenesulfonyl chloride (10.88 g, 0.057 mol) in pyridine (15 mL) through a pressure-equalized dropping funnel. The reaction was stirred at ambient temperature overnight and quenched with ice (45 g). When the ice melted, a white solid (7.2 g, yield: 66%) was isolated, washed with water (3 × 8 mL), diethyl ether (2 × 8 mL) and dried in vacuum. FTIR (nujol) $\upsilon_{S=O}$: 1374.1, 1260.9 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.30 (s, 3H), 2.45 (s, 6H), 4.27 (s, 4H), 7.15 (m, 2H), 7.27 (d, 4H, J = 8 Hz), 7.60 (d, 1H, J = 8 Hz) , 7.63 (d, 4H, J = 5.6 Hz), 8.34 (d, 1H, J = 4.4Hz). ^{13}C NMR (CDCl$_3$, ppm): 19.5, 21.7, 44.9, 72.8, 121.5, 129.8, 134.5, 144.8, 148.9, 159.3. MS (ES): (M+1) / z = 476.3. Microanalysis (%) for $C_{23}H_{25}NO_6S_2$ (475.58), calculated (found): C, 58.09 (58.03); H, 5.30 (5.38); N, 2.92 (3.07); S, 13.48 (13.63).

1.3 2-(2-methyl-1, 3-dithiocyanatopropan-2-yl) pyridine

A mixture of 2-methyl-2-(pyridin-2-yl) propane-1, 3-diyl-bis (4-methylbenzenesulfonate) (0.90 g, 1.89 mmol) and KSCN (2.2 g, 22.8 mmol) was suspended in DMF (8 mL). The reaction was heated at 110 °C for 4 h under stirring. Part of the solvent was removed on hot to give a paste which was dissolved in water

(7 mL). The mixture was repeatedly extracted using ethyl acetate (10 mL × 5). The organic phase was combined and dried with anhydrous Na_2SO_4. After the removal of the solvent, the crude product was purified by flash chromatography using a mixture of ethyl acetate (40%) and n-hexane (60%) as eluent. A pale yellow solid (0.2 g, 50%) was collected and dried with anhydrous Na_2SO_4 after the solvents were removed from the combined collected fractions containing the desired complex using rotary evaporator. FTIR (nujol) υ_{SCN}: 2158.5 cm^{-1}; ^1H NMR ($CDCl_3$, ppm): 1.25 (s, 3H), 3.41 (s, 2H), 3.70 (s, 2H), 7.30 (t, 1H, J = 9.96 Hz), 7.40 (t, 1H, J = 6.16 Hz), 7.78 (d, 1H, J = 6.16 Hz), 8.6 3(d,1H, J = 3.28 Hz). ^{13}C NMR ($CDCl_3$, ppm): 22.3, 44.3, 46.7, 112.8, 121.2, 123.2, 137.4, 149.1, 159.6. MS (EI): (M+1)/z = 250.03, (M-CN)/z = 222.97. Microanalysis (%) for $C_{11}H_{11}N_3S_2$ (249.36), calculated (found): C, 52.98 (52.81); H, 4.45 (4.72); N, 16.85 (16.44).

1.4 2-methyl-2-(pyridin-2-yl) propane-1,3-dithiol

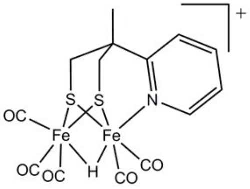
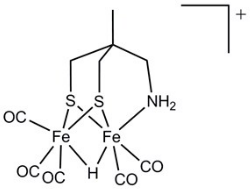
To a pre-cooled (ice bath) suspension of $LiAlH_4$ (0.777 g, 0.02 mmol) in anhydrous diethyl ether (20 mL) was added 2-(2-methyl-1, 3-dithiocyanatopropan-2-yl)pyridine (1.276 g , 5.1 mmol) in small portions to avoid vigorous reaction. The reaction was refluxed at 45 °C under N_2 overnight. After being cooled down to ice temperature, an aqueous solution of NH_4Cl (sat.) was added into the reaction with great care at the first a few drops of the saturated ammonium chloride solution to quench the reaction. The mixture was extracted with degassed ethyl acetate (20 mL × 4) and the organic phase was combined and dried with dried with anhydrous Na_2SO_4. Removing the solvent under reduced pressure yielded a yellow oily liquid of pungent smell (0.95 g, 93%). FTIR (neat): $\upsilon_{SH} = 2556.4\ cm^{-1}$. MS (ES): (M+1)/z = 199.87. ^1H NMR ($CDCl_3$, ppm): 1.18 (br, 2H, -SH), 1.43 (s, 3H, $-CH_3$), 2.83 (q, 2H, $-CH_2$), 3.08 (q, 2H, $-CH_2$), 7.09 (t, J = 3.42 Hz, 1H, Py-H), 7.23 (d, J = 7.86 Hz, 1H, Py-H), 7.59 (d, J = 7.44 Hz, 1H, Py-H), 8.53 (d, J = 4.24 Hz, 1H, Py-H). In practice, the ligand was used for next step reaction without further purification.

2. Tables and figures.

Table S1 X-ray crystallographic details of complexes **1** and **2H**$^+$.

	1	**2H**$^+$
Empirical formula	$C_{14}H_{11}Fe_2NO_5S_2$	$C_{15}H_{12}Fe_2NO_6S_2BF_4$
M_w	449.06	564.89
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/c
a / Å	9.5512(6)	14.5080(4)
b / Å	11.9757(8)	11.7408(3)
c / Å	14.9165(10)	13.0329(4)
α / °	90	90
β / °	93.128(1)	108.12
γ / °	90	90
V / Å^3	1703.64(19)	2109.86(10)
Z	4	4
T / K	298	298
Density$_{cal}$ / g·cm^{-3}	1.751	1.778
Crystal description	Block	Block
Crystal colour	Dark green	Dark red
Crystal size / mm	0.39 × 0.34 × 0.12	0.28 × 0.22 × 0.22
μ / mm^{-1}	1.971	1.640
F [000]	904.0	1128.0

Table S2 Frequencies of carbonyl groups in two hydride complexes in dichloromethane.

Formula	**structure**	**Frequencies (cm^{-1})**
$[Fe_2(\mu\text{-}H)\{(SCH_2)_2C(CH_3)(2\text{-}Py)\}(CO)_5]^+$ **(1H$^+$)**		2114, 2064, 2023
$[Fe_2(\mu\text{-}H)\{(SCH_2)_2C(CH_3)(2\text{-}CH_2NH_2)\}(CO)_5]^+$		2111, 2056, 2009

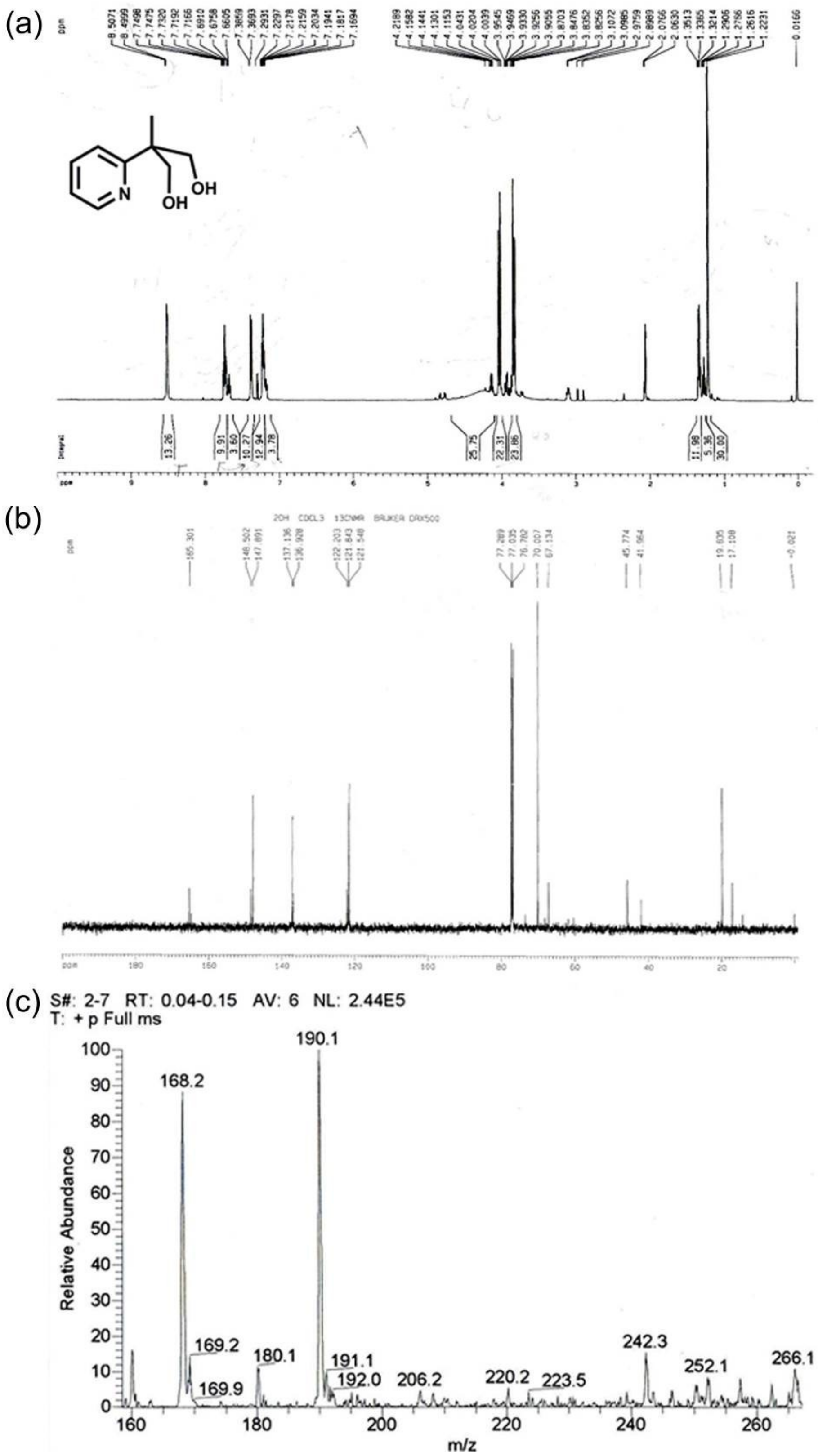


Fig. S1 Characterizations of 2-methyl-2-(pyridin-2-yl) propane-1, 3-diol: (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) MS spectra.

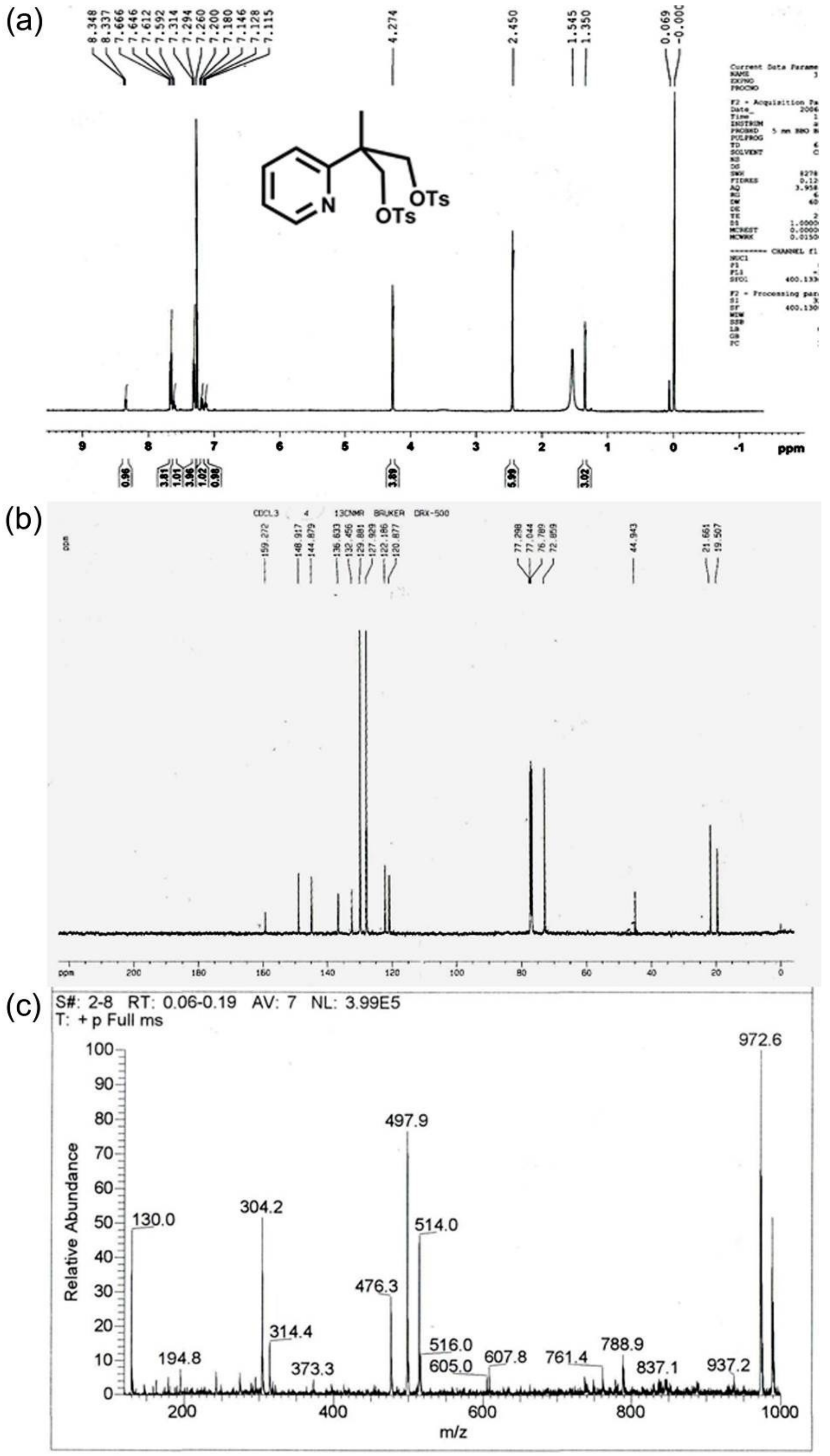


Fig. S2 Characterizations of 2-methyl-2-(pyridin-2-yl) propane-1, 3-diyl-bis (4-methylbenzenesulfonate): (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) MS spectra.

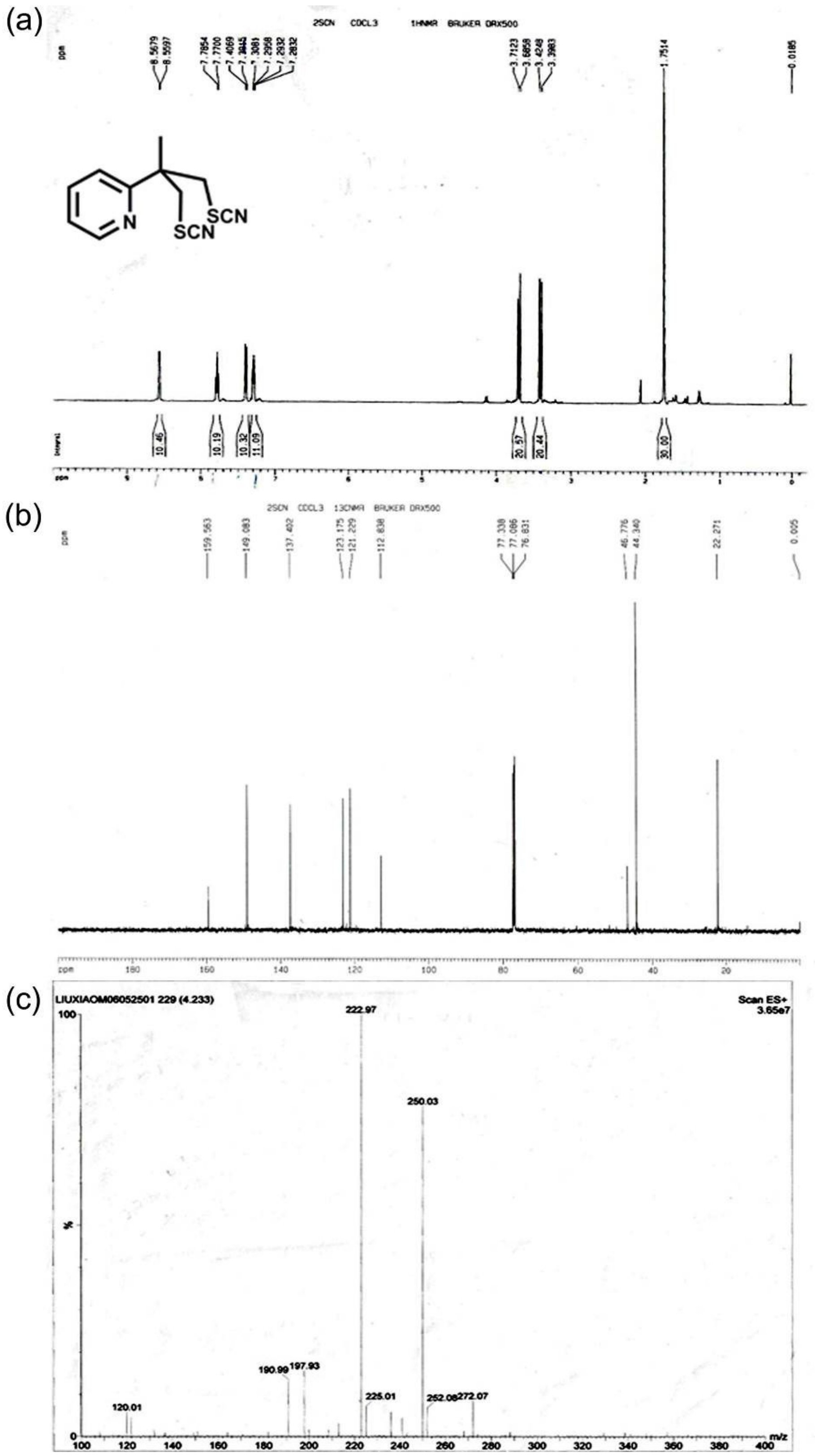


Fig. S3 Characterizations of 2-(2-methyl-1, 3-dithiocyanatopropan-2-yl) pyridine: (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) MS spectra.

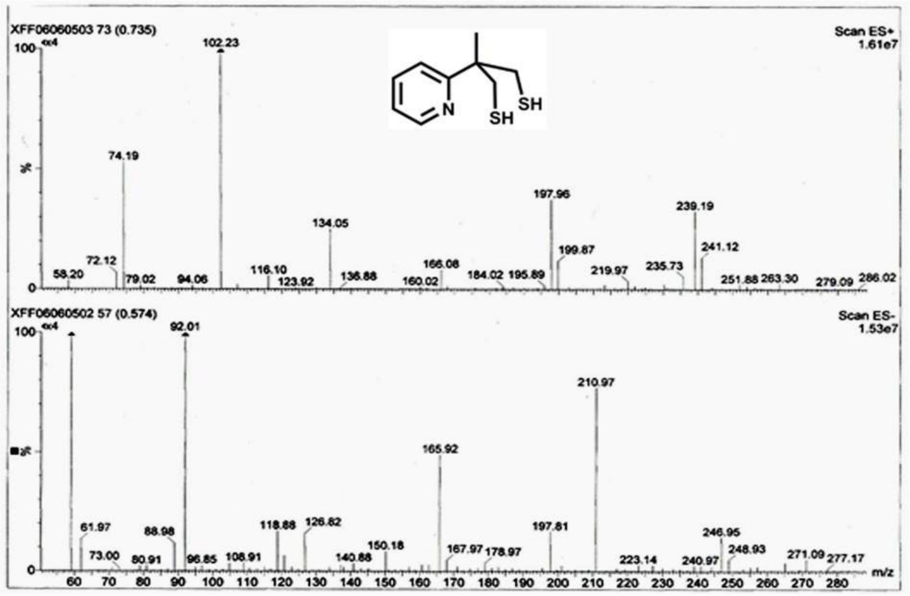


Fig. S4 Characterizations of 2-methyl-2-(pyridin-2-yl) propane-1,3-dithiol: MS spectra.

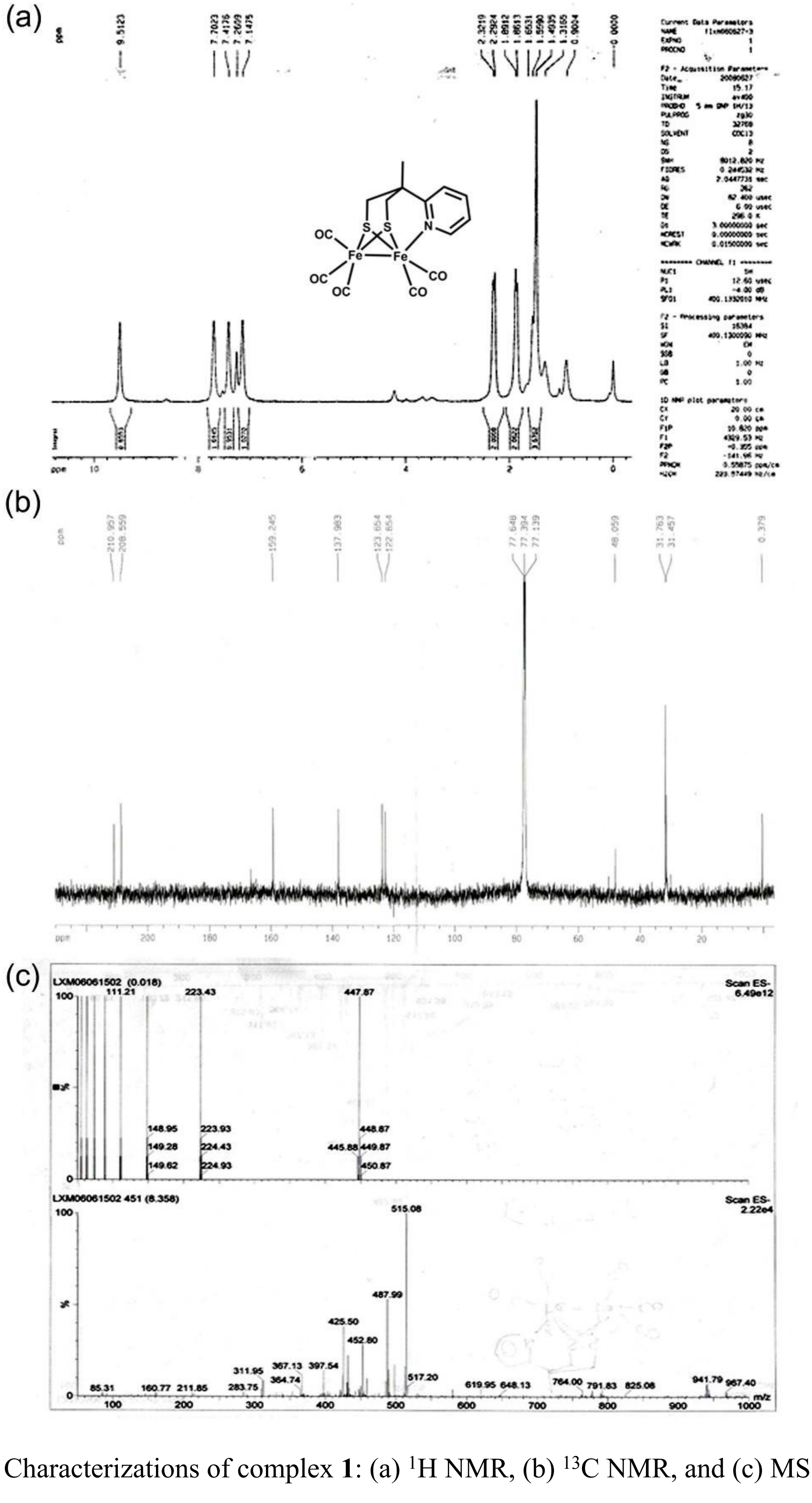


Fig. S5 Characterizations of complex **1**: (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) MS spectra.

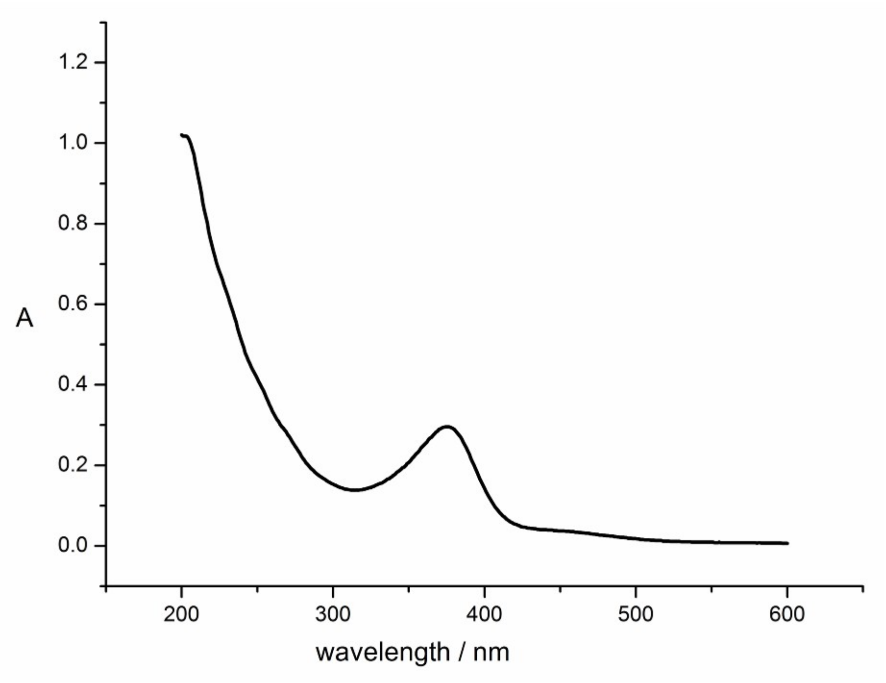


Fig. S6 UV-Vis spectrum of complex **1** in MeCN.

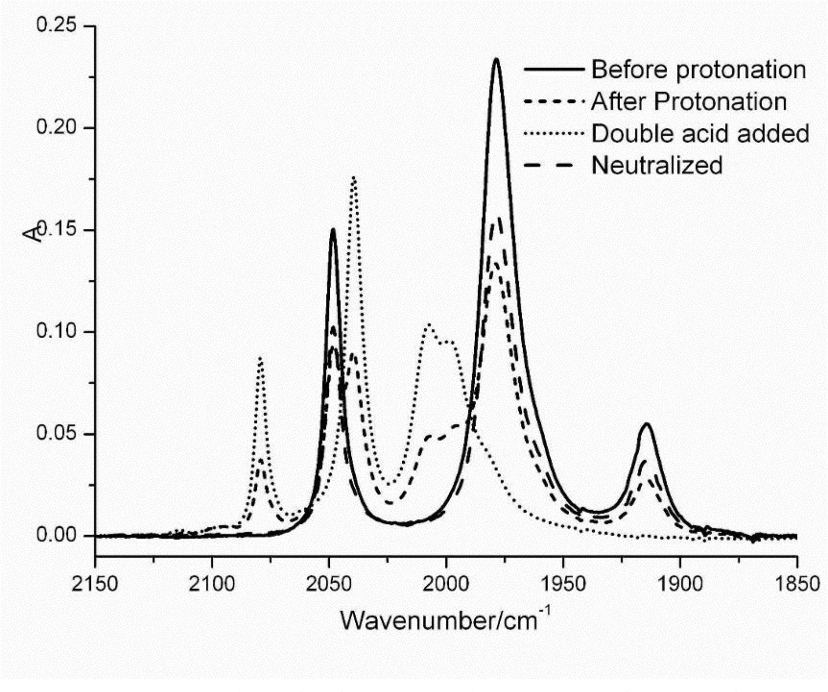


Fig. S7 FTIR spectra of reactions both protonation of complex **1** and *in-situ* deprotonation of complex **2H**$^+$ in acetonitrile solution under N_2 atmosphere at room temperature.

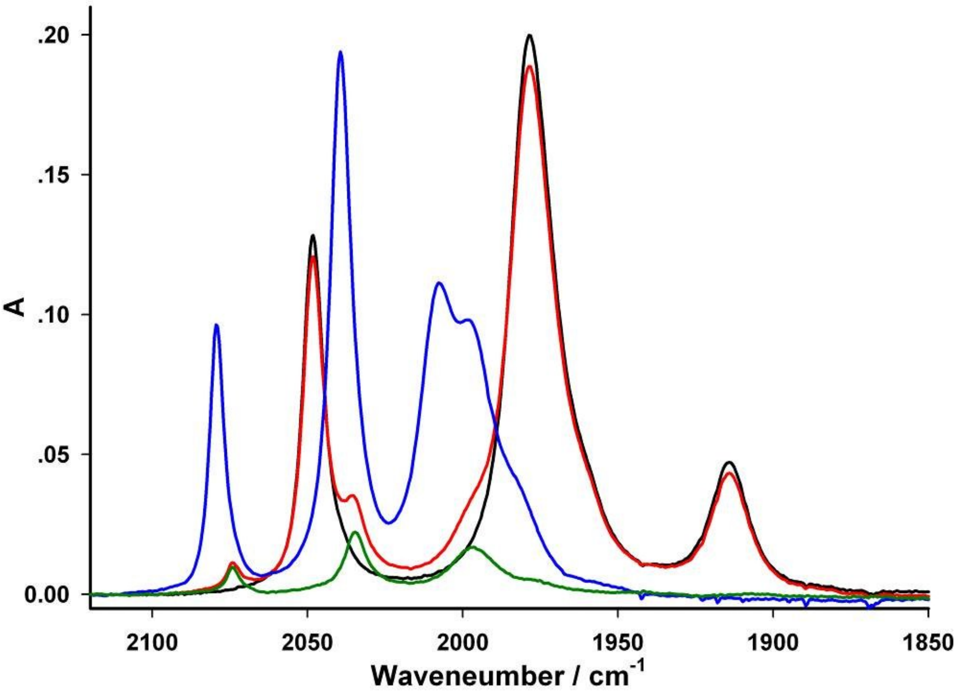


Fig. S8 FTIR spectra of the complexes in MeCN: **1** under N_2 (balck) / CO (1 atm., red), **2H$^+$** (blue) and **2** (green) abstracted from the spectrum (red) of complex **1** under CO.

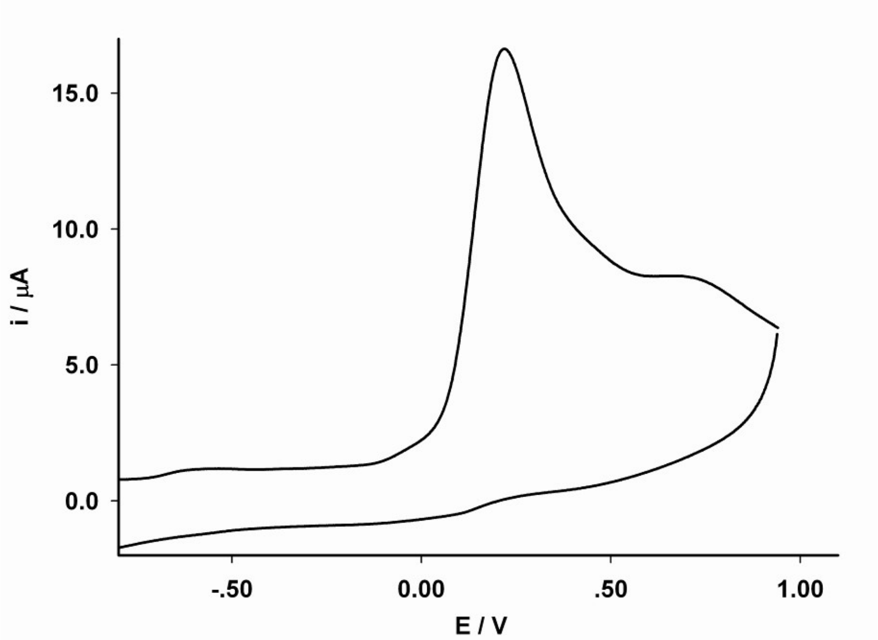


Fig. S9 Oxidation process of complex **1** (3.2 mmol L^{-1}) in DCM (ν = 0.1 mV s^{-1}, T = 298 K).

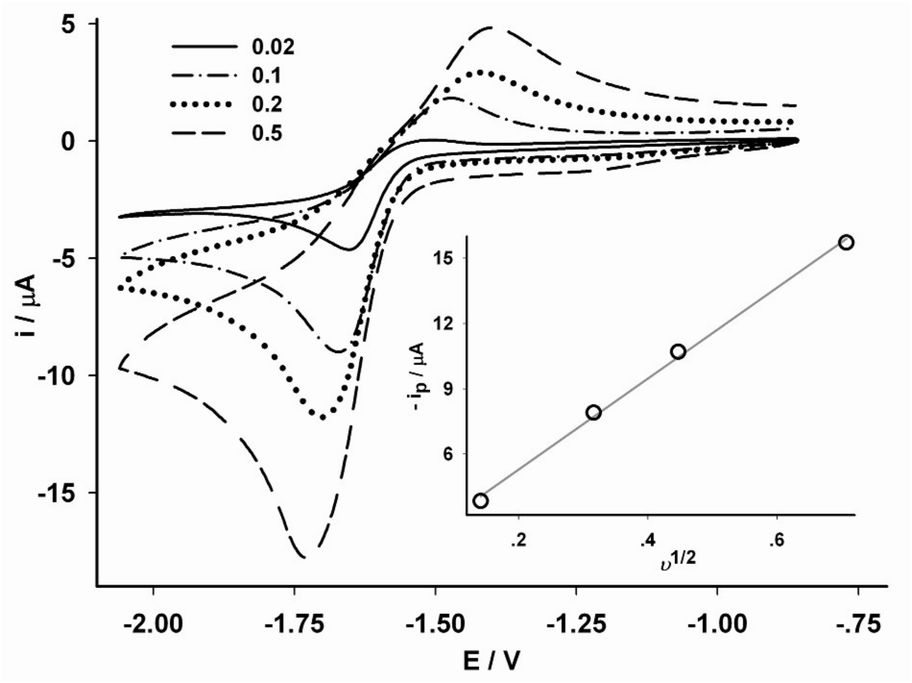


Fig. S10 Cyclic voltammograms of complex **1** (2.5 mmol L^{-1}) at various scanning rates (V s^{-1}) under CO atmosphere (Inset: the plot of the reduction peak current *versus* the square-root of the scanning rate).

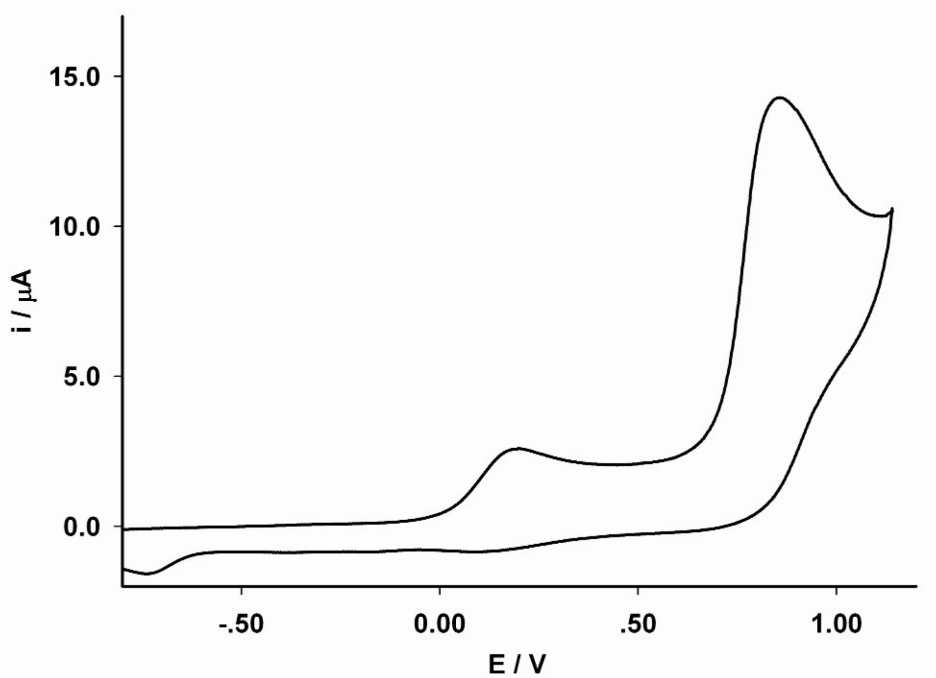


Fig. S11 Oxidation processes of complex **2H$^+$** (3.2 mmol L^{-1}) in DCM (ν = 0.1 mV s^{-1}, T = 298 K).

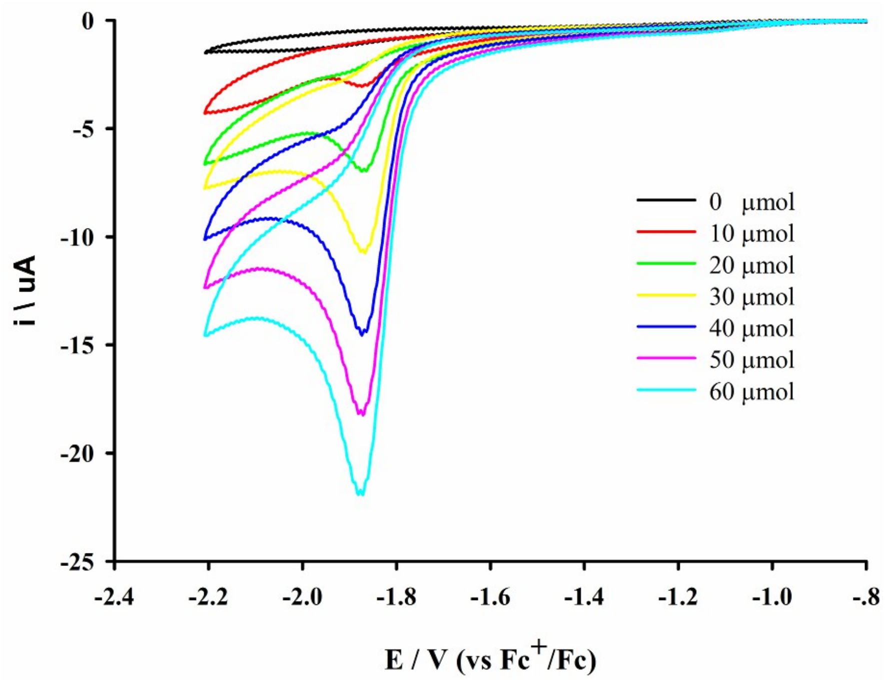


Fig. S12 Electrochemical responses of vitreous carbon disk (ϕ = 1 mm) with the addition of lutidinium (1 equivalent ~ 10 μmol) under Ar atmosphere in DCM at the scanning rate of 0.1 Vs^{-1} at 298 K.

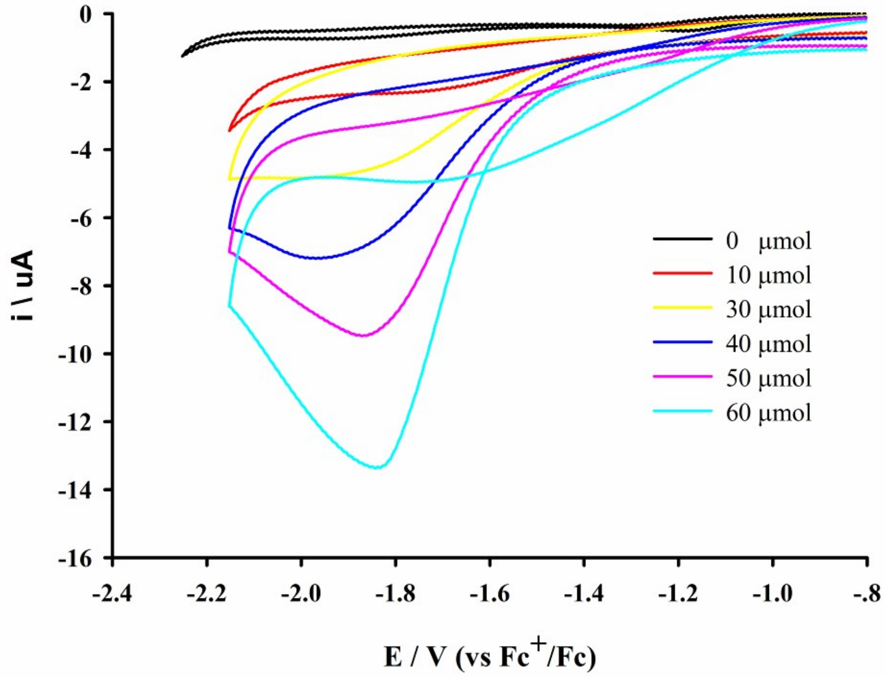


Fig. S13 Electrochemical responses of vitreous carbon disk (ϕ = 1 mm) with the addition of $HBF_4 \cdot Et_2O$ (1 equivalent ~ 10 μmol) under Ar atmosphere in DCM at the scanning rate of 0.1 Vs^{-1} at 298 K.

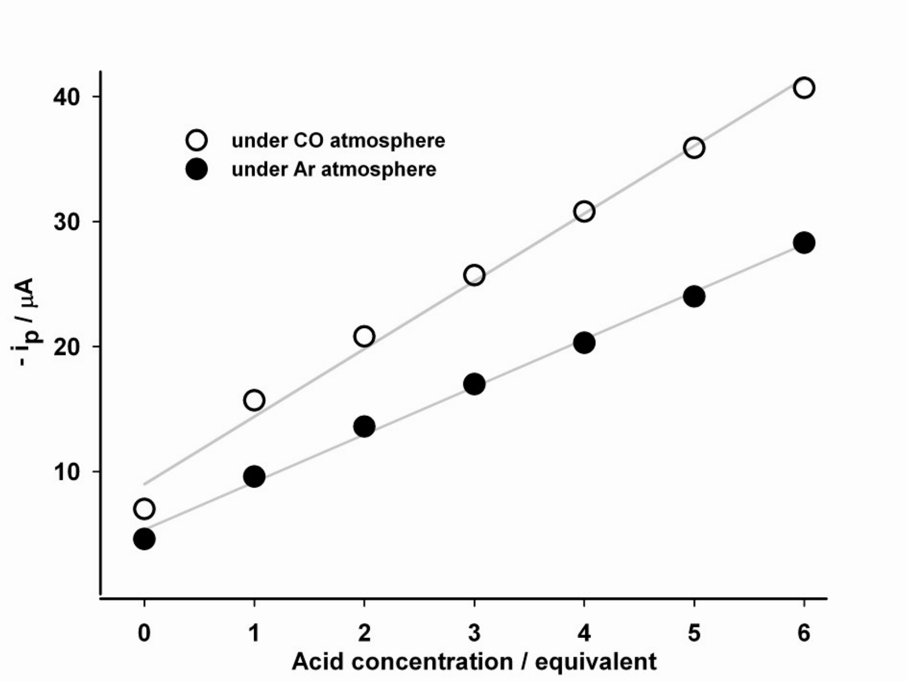


Fig. S14 Peak current *vs*. the acid ($HBF_4 \cdot Et_2O$) concentration for the first reduction process of complex **2H**$^+$ under either CO or Ar atmosphere.