

Synthesis and characterisation of three di-iron tetracarbonyl complexes related to the di-iron centre of [FeFe]-hydrogenase and their protonating, electrochemical investigations

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1. Synthesis

2-Hydroxymethyl-2-methyl-1,3-bis(toluene-4-sulfonyloxy)-propane

A solution of 1,1,1-tris(hydroxymethyl)ethane (26.4g, 0.22mol) in pyridine (150ml) was cooled to ice temperature on stirring. To the pre-cooled solution was dropwise added a solution of tosyl chloride (83.9g, 0.44mole) in pyridine (200ml). The mixture was stirred at room temperature overnight and then poured into ice water. The pH was adjusted to acidic and oily liquid formed at the bottom of the beaker. The aqueous phase was decanted off and the residue was washed with H₂SO₄ (0.5M) and water. The oily liquid was then purified by chromatography on silica gel with ethyl acetate/petroleum ether (1/1, V/V) as the eluent. A white solid (64.0g, 68.1%) was obtained. ¹H NMR (CDCl₃): δ 0.81 (s, 3H, CCH₃), 2.39 (s, 6H, 2×PhCH₃), 3.37 (s, 2H, CCH₂OH), 3.8 (q, 4H, 2×CH₂OTs), 7.29 (d, *J* = 8.4, 4H, PhH), 7.67 (d, *J* = 8.0, 4H, PhH).

2-Hydroxymethyl-2-methyl-1,3-bis(thiocyano)-propane

A mixture of 2-Hydroxymethyl-2-methyl-1,3-bis(toluene-4-sulfonyloxy)-propane (10.5g, 25mmol) and potassium thiocyanate (41g, 425mmol) in DMF (100ml) was heated at 110 °C for 18 hours. The solvent was removed under reduced pressure on hot to give a light brown solid. The solid was dissolved in water (80ml) and extracted with ethyl acetate (50ml × 4). The organic phase was dried (MgSO₄) and the solvent

was removed under vacuum after filtration, which afforded a brown liquid. The brown liquid was purified by chromatography on silica gel with ethyl acetate/petroleum ether (1/2, V/V) as the eluent and an off-white liquid was obtained (3.4g, 68%).

$^1\text{H NMR}(\text{CDCl}_3)$: 1.167(s, 3H, CCH_3), 1.809 (t, ill-resolved, 2H, CCH_2OH), 3.113 (d, $J = 13.9\text{Hz}$, 2H, CCH_2SCN), 3.206 (d, $J = 13.7\text{Hz}$, 2H, CCH_2SCN), 3.656 (d, $J = 4.4\text{Hz}$, 2H, CCH_2OH); IR ν_{SCN} (neat): 2159cm^{-1} .

2-Hydroxymethyl-2-methyl-propane-1,3-dithial

To a suspension of LiAlH_4 (2.0g, 51mmol) in dry THF (20ml) was drop wise added a solution of 2-Hydroxymethyl-2-methyl-1,3-bis(thiocyano)-propane (3.4g, 17mmol) in dry THF (60ml) at ice temperature on stirring. After the addition, the mixture temperature was heated to 55°C overnight. Then the reaction was cooled with an ice bath and *extremely carefully* quenched with degassed H_2SO_4 (0.5M, 60mL). The ice bath was removed and the mixture was stirred for 15min. The mixture was extracted with degassed ethyl acetate ($30\text{ml} \times 4$). The combined extracts were dried (MgSO_4) and the solvents were removed to give a pungent yellow liquid (2.5g, 80%).

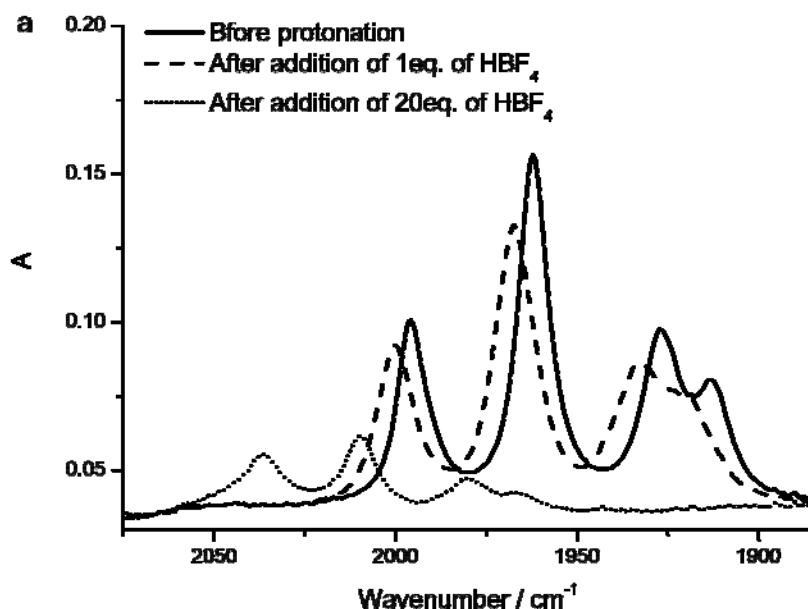
$^1\text{H NMR}(\text{CDCl}_3)$: 0.945 (s, 3H, CCH_3), 1.249 (t, $J = 8.7\text{Hz}$, 2H, CCH_2SH), 1.645 (t, ill-resolved, 1H, CCH_2OH), 2.584 (d, $J = 8.8\text{Hz}$, 4H, $2 \times \text{CH}_2\text{SH}$), 3.538 (d, $J = 4.6\text{Hz}$, 2H, CCH_2OH); IR ν_{SH} (neat): 2559cm^{-1} .



A solution of 2-Hydroxymethyl-2-methyl-propane-1,3-dithial (0.2 g, 1.3 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (0.66 g, 1.3mmol) in toluene (20 mL) was allowed to stir for 2.5h at 110°C.

Then the solvent was removed under reduced pressure, and the crude product was purified by chromatography on silica gel with ethyl acetate / petroleum ether (1/4, V/V) as the eluent. Complex **1** was obtained as a red solid (0.38 g, 68%). IR $\nu(\text{CO})$ (MeCN): 2074s, 2034s, 1998s cm^{-1}

2. Infrared spectra of the complexes 2, 4 and their protonated species



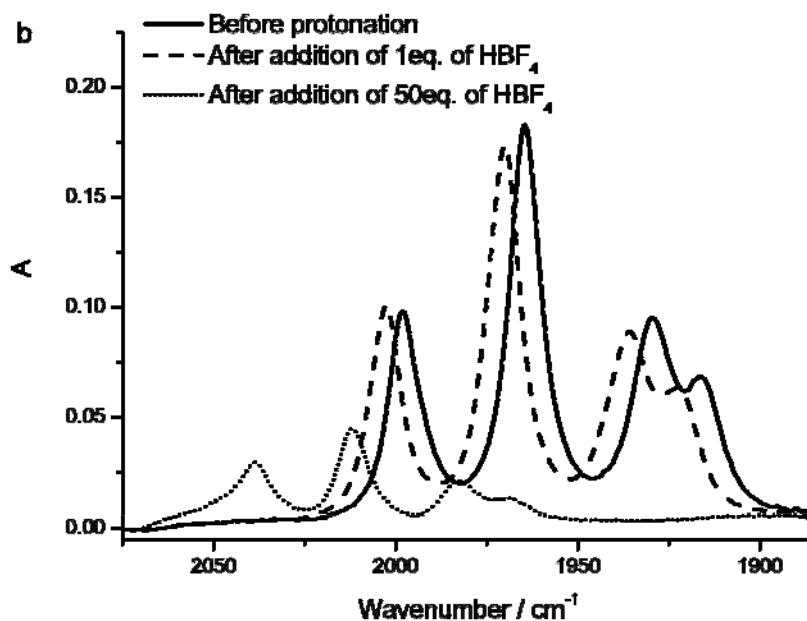


Fig. S2. Protonation reactions of 2(a) and 4(b) in acetonitrile solution.

3. Correlation of the infrared absorption bands of the protonated species against those of their parent complexes

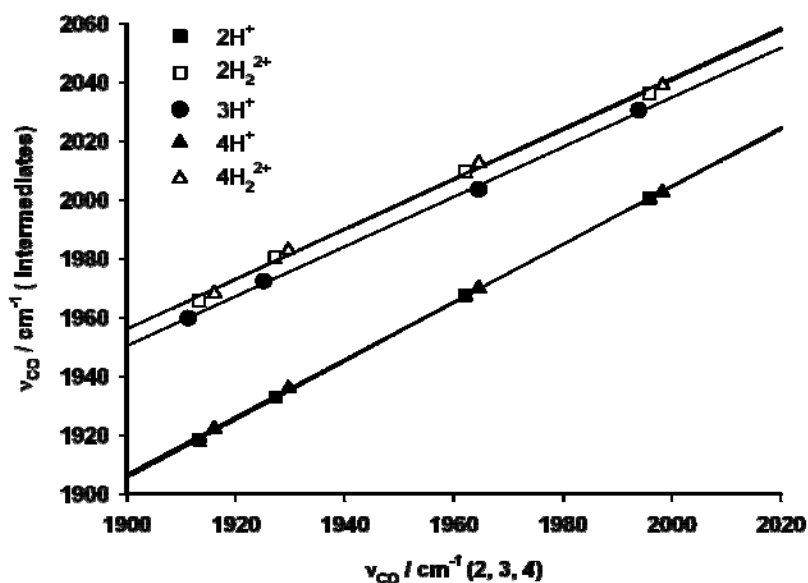
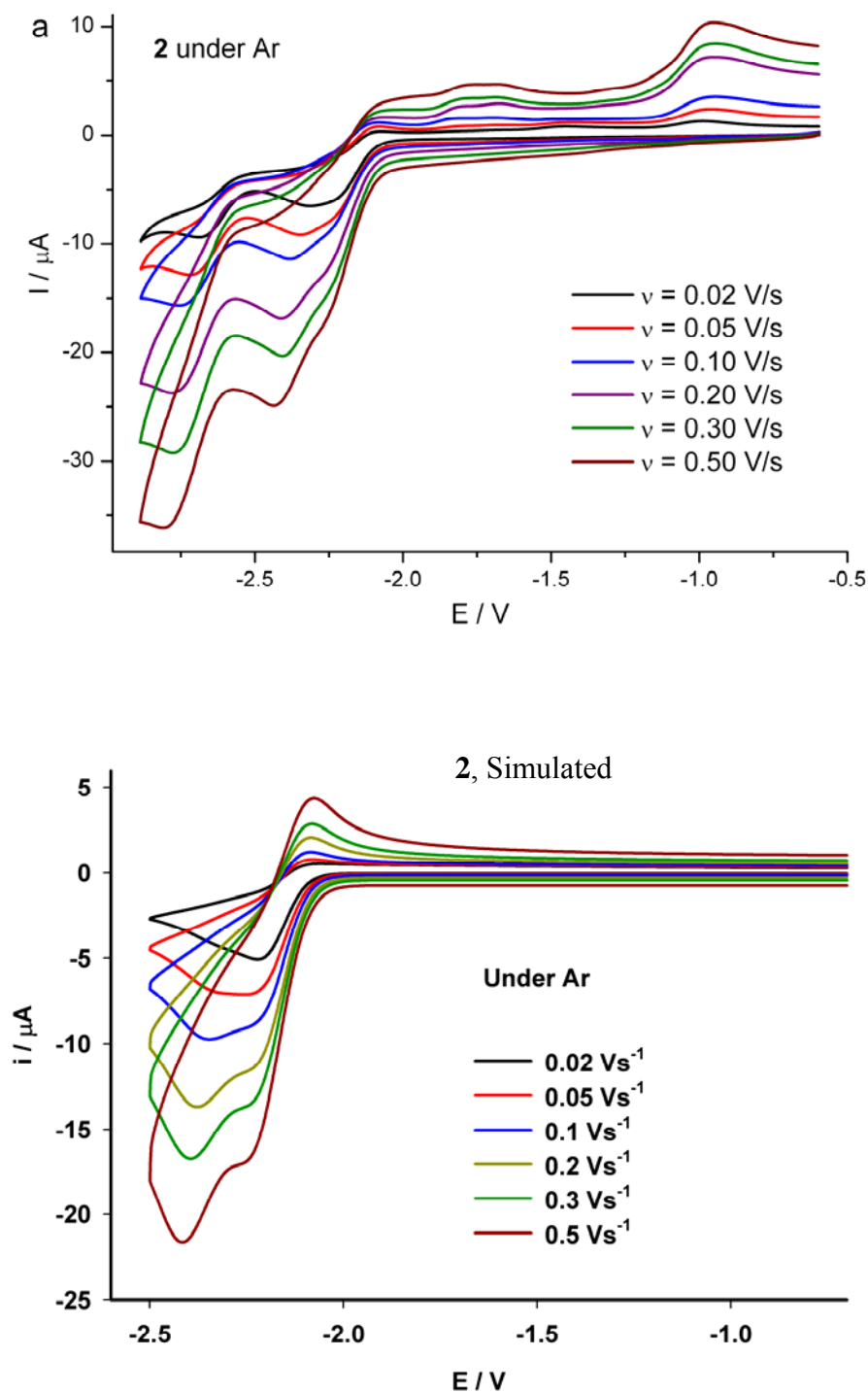
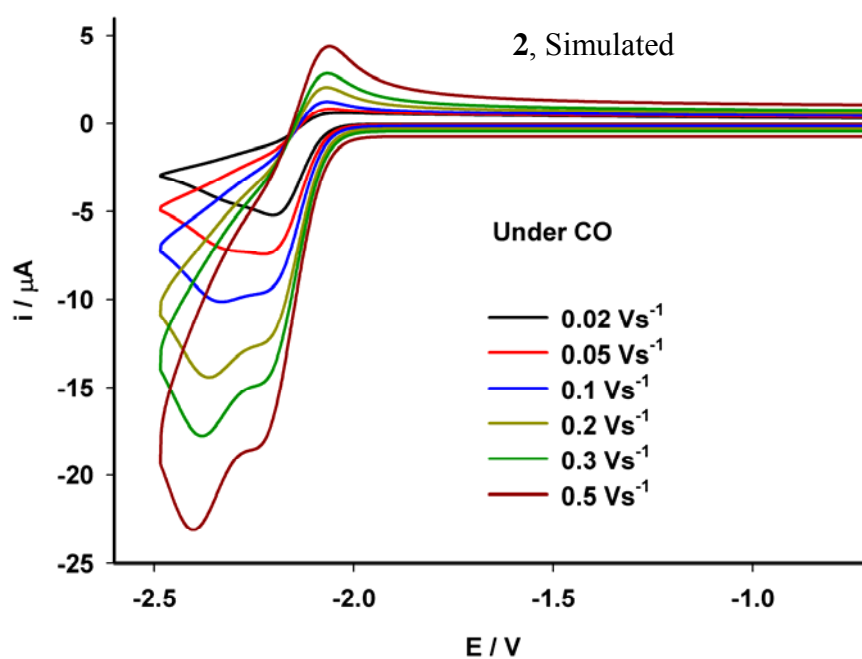
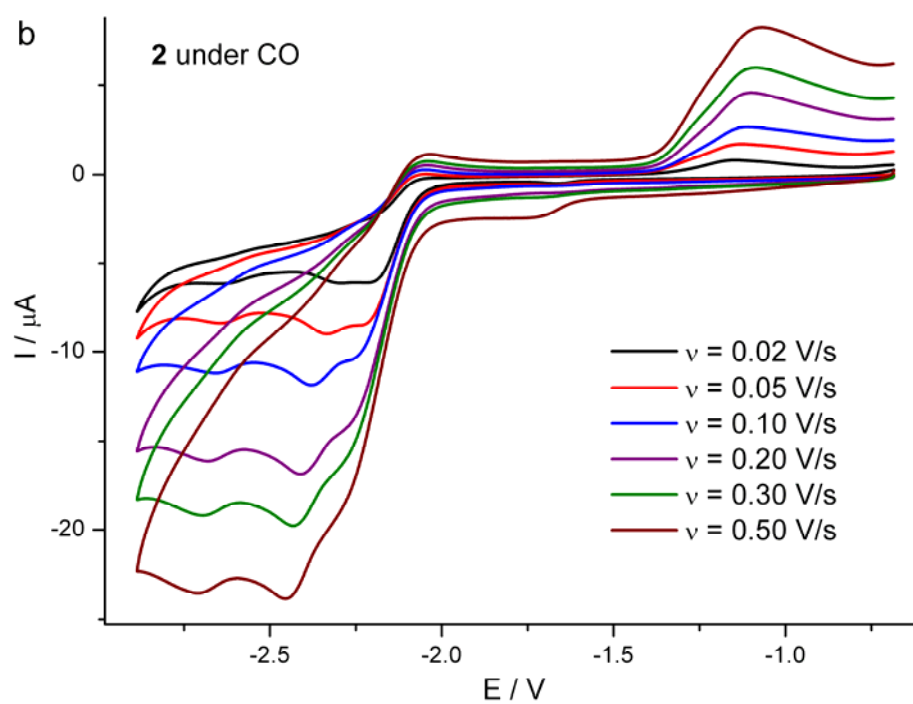
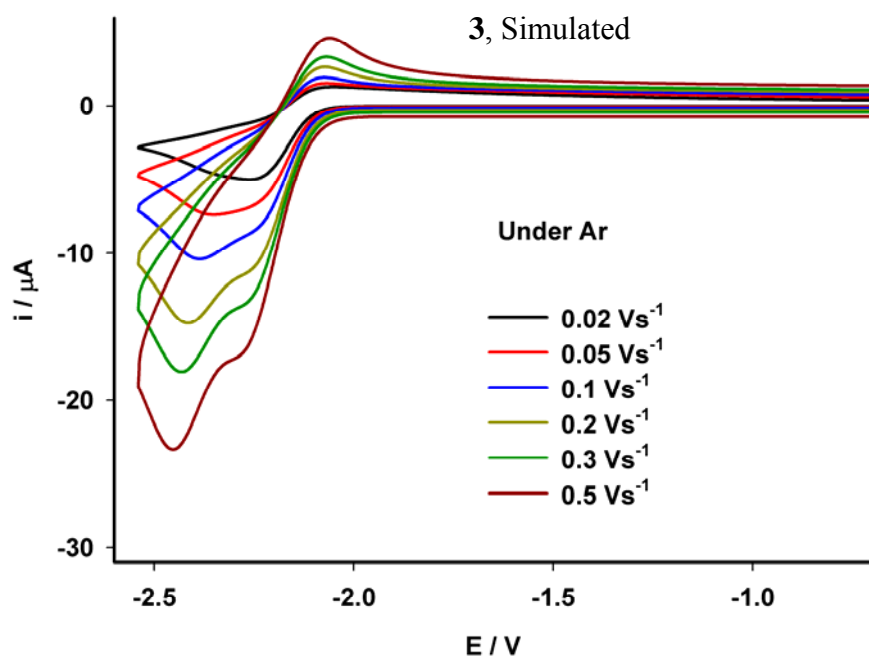
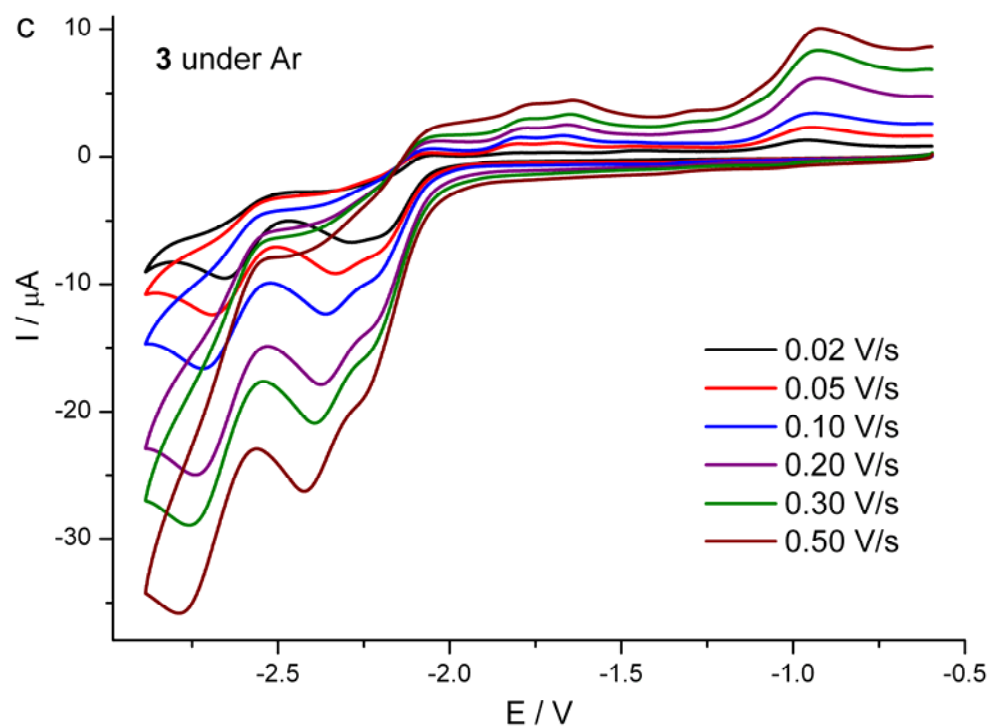


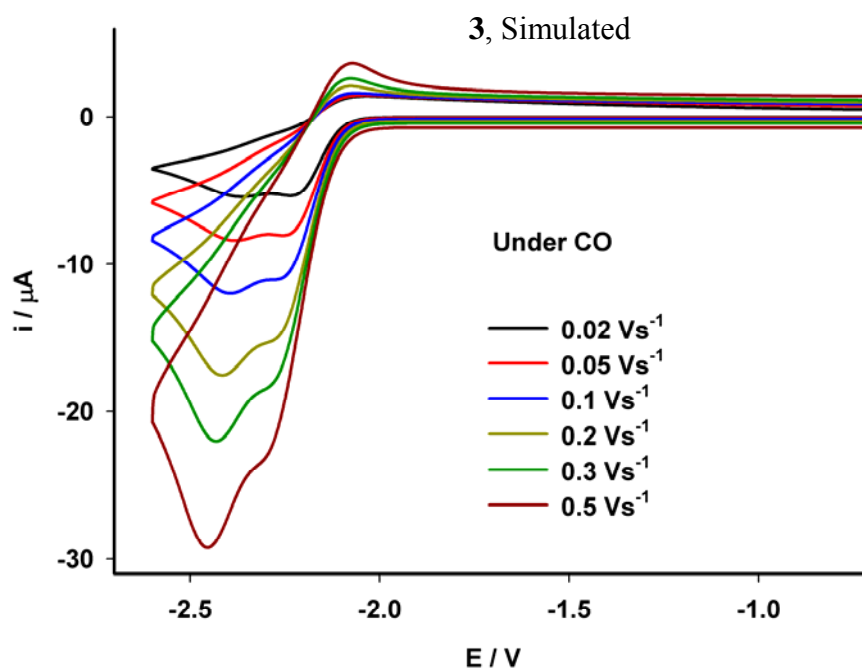
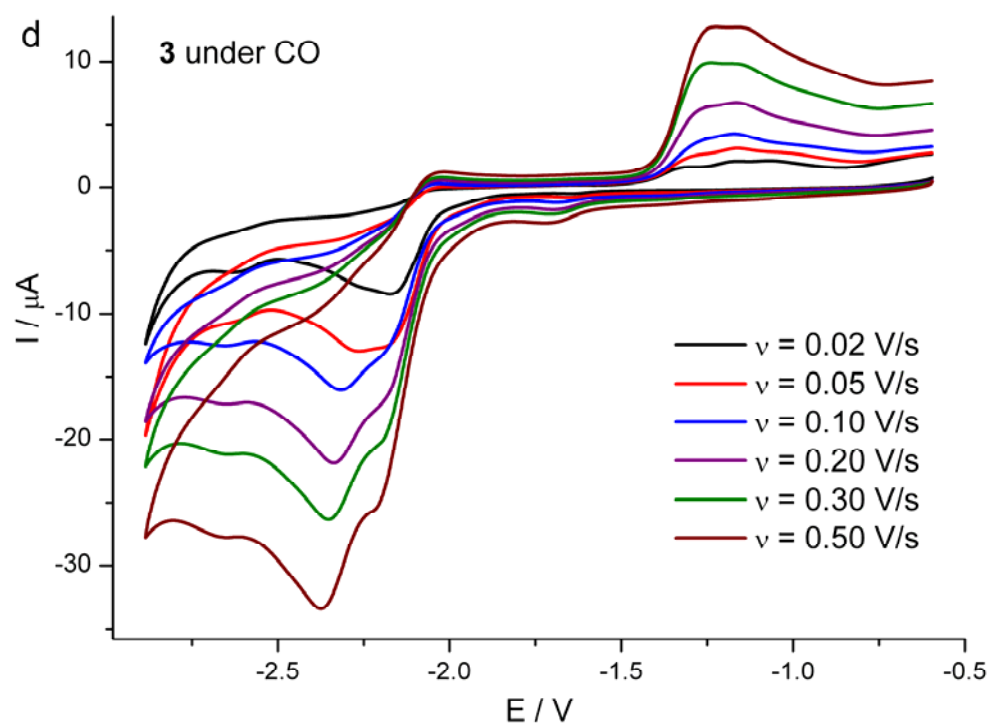
Fig. S3 Linear correlation of the infrared absorption bands of the protonated species against those of their parent complexes.

4. Electrochemistry of the complexes 2, 3 and 4 under Ar/CO atmosphere at varying scanning rates









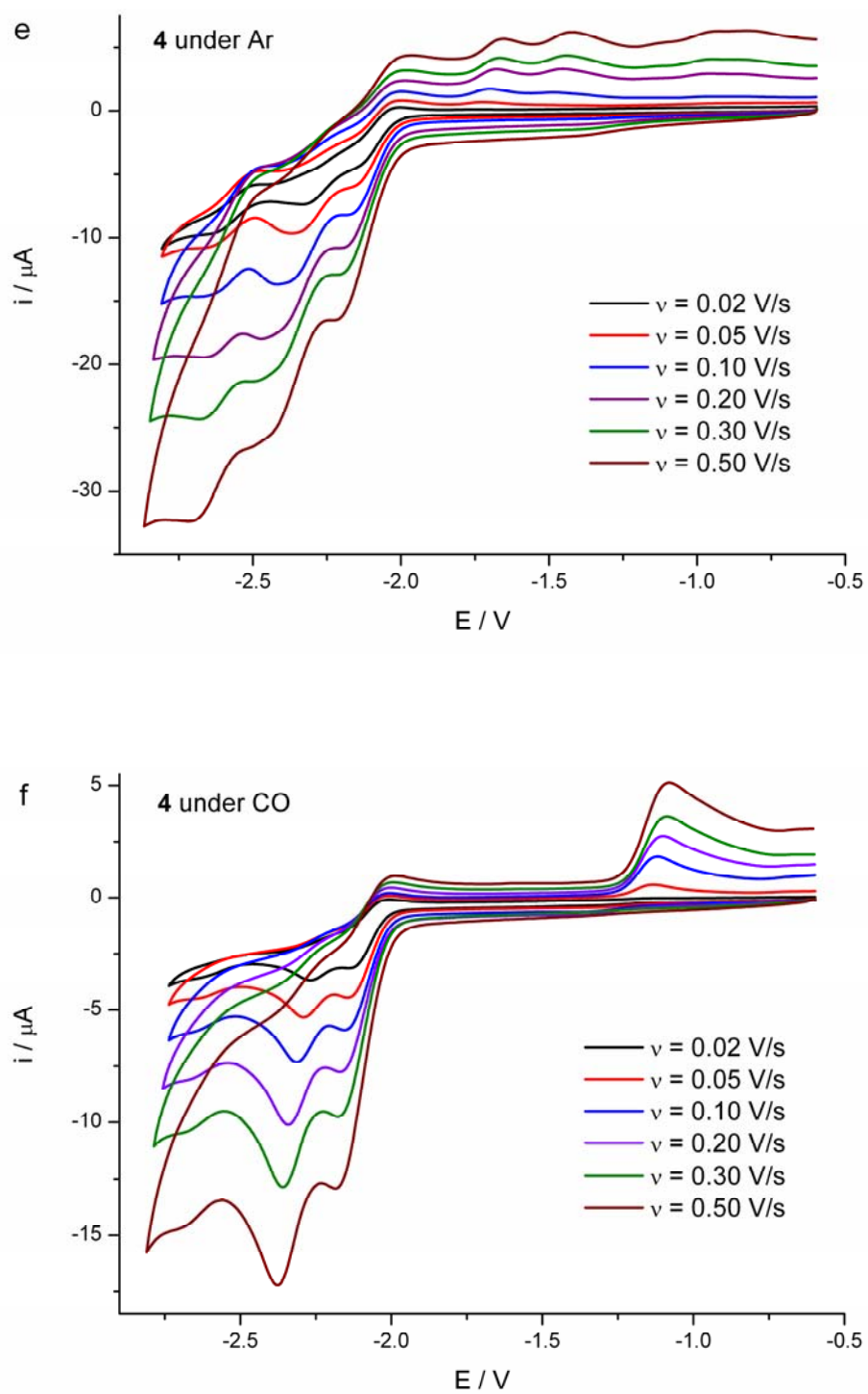
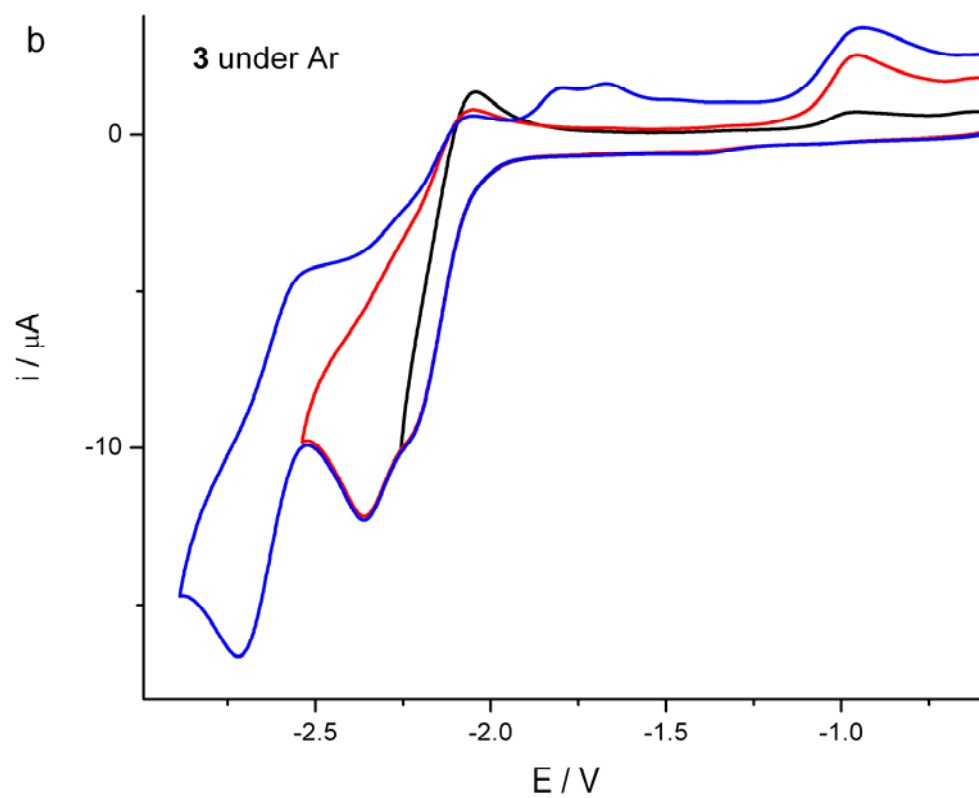
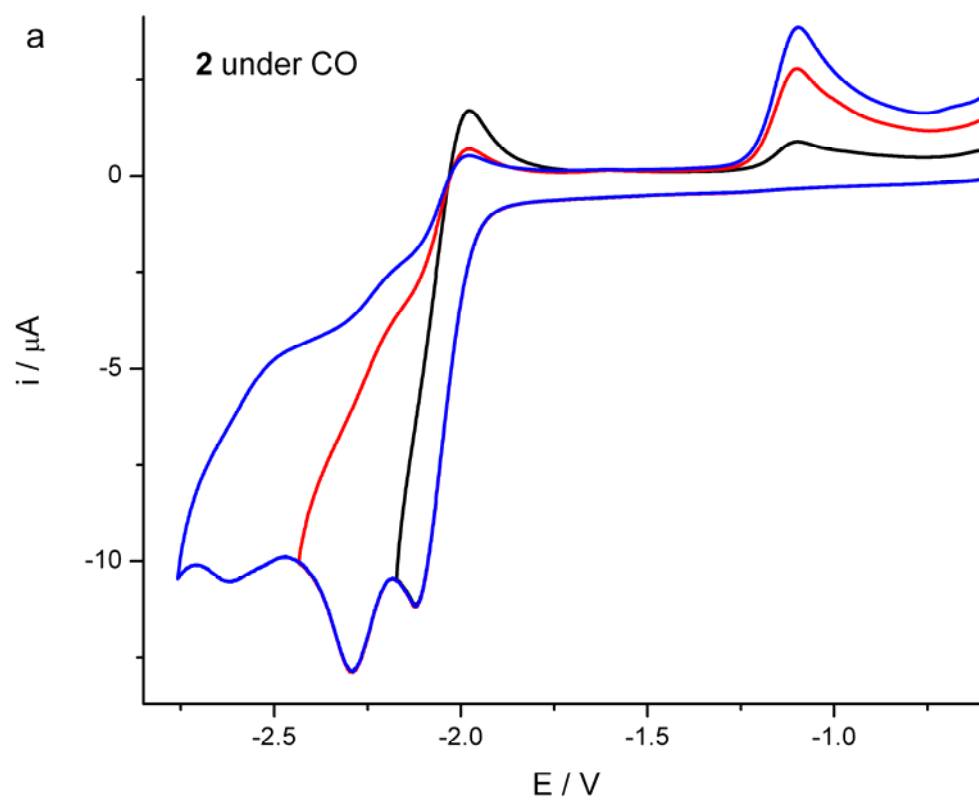


Fig. S4 Cyclic voltammograms of the complex **2**, **3** and **4** at different scanning rate under Ar / CO atmosphere.

5. Electrochemistry of the complexes 2, 3 and 4 under Ar / Co atmosphere at different scanning potential ranges



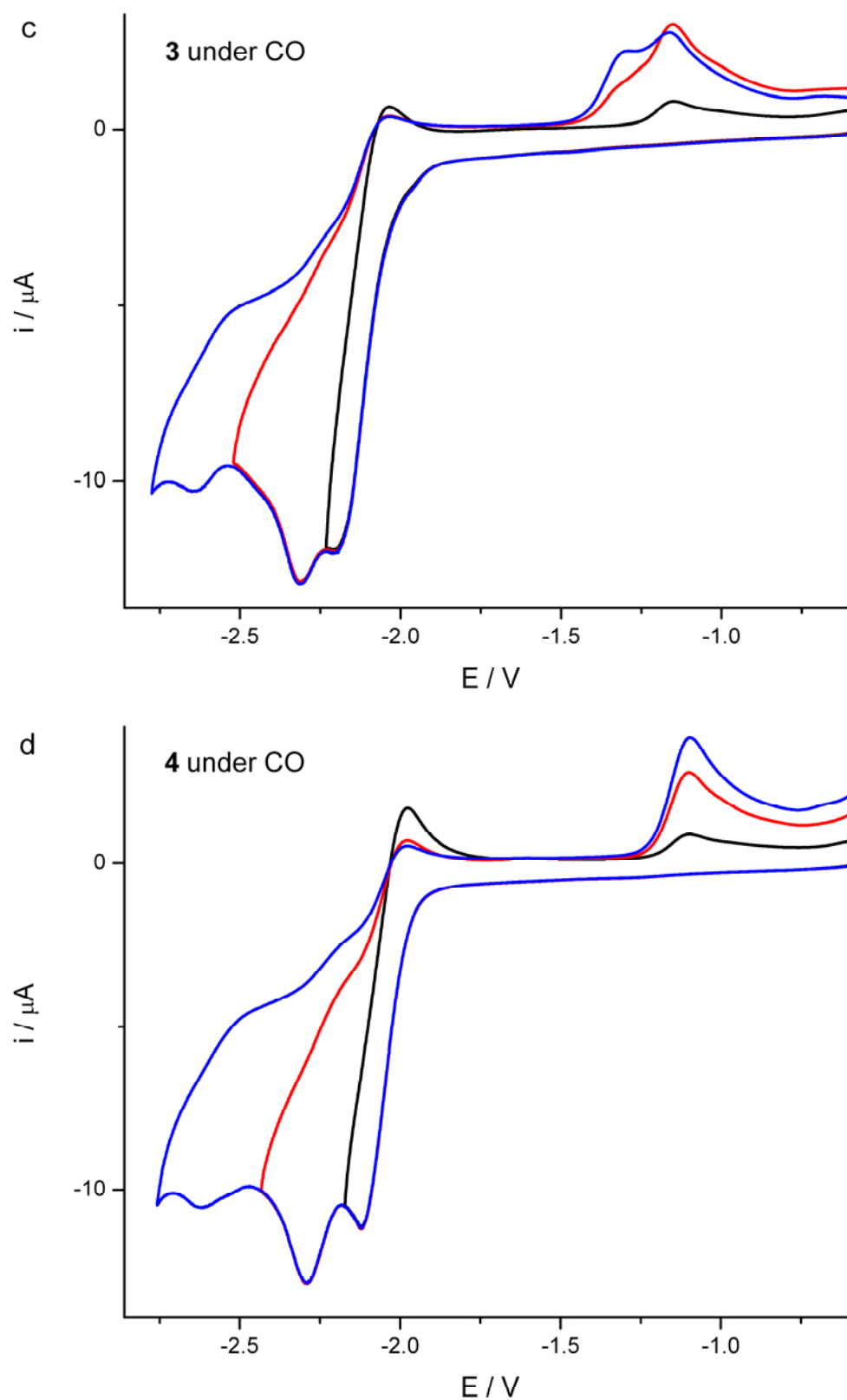


Fig. S5 Cyclic voltammograms of the complex **2**, **3** and **4** at different scanning potential ranges under Ar/CO atmosphere, scanning rate = $0.1\text{V}\cdot\text{s}^{-1}$.

6. Simulated cyclic voltammograms for the complex **2** at various scanning potential ranges

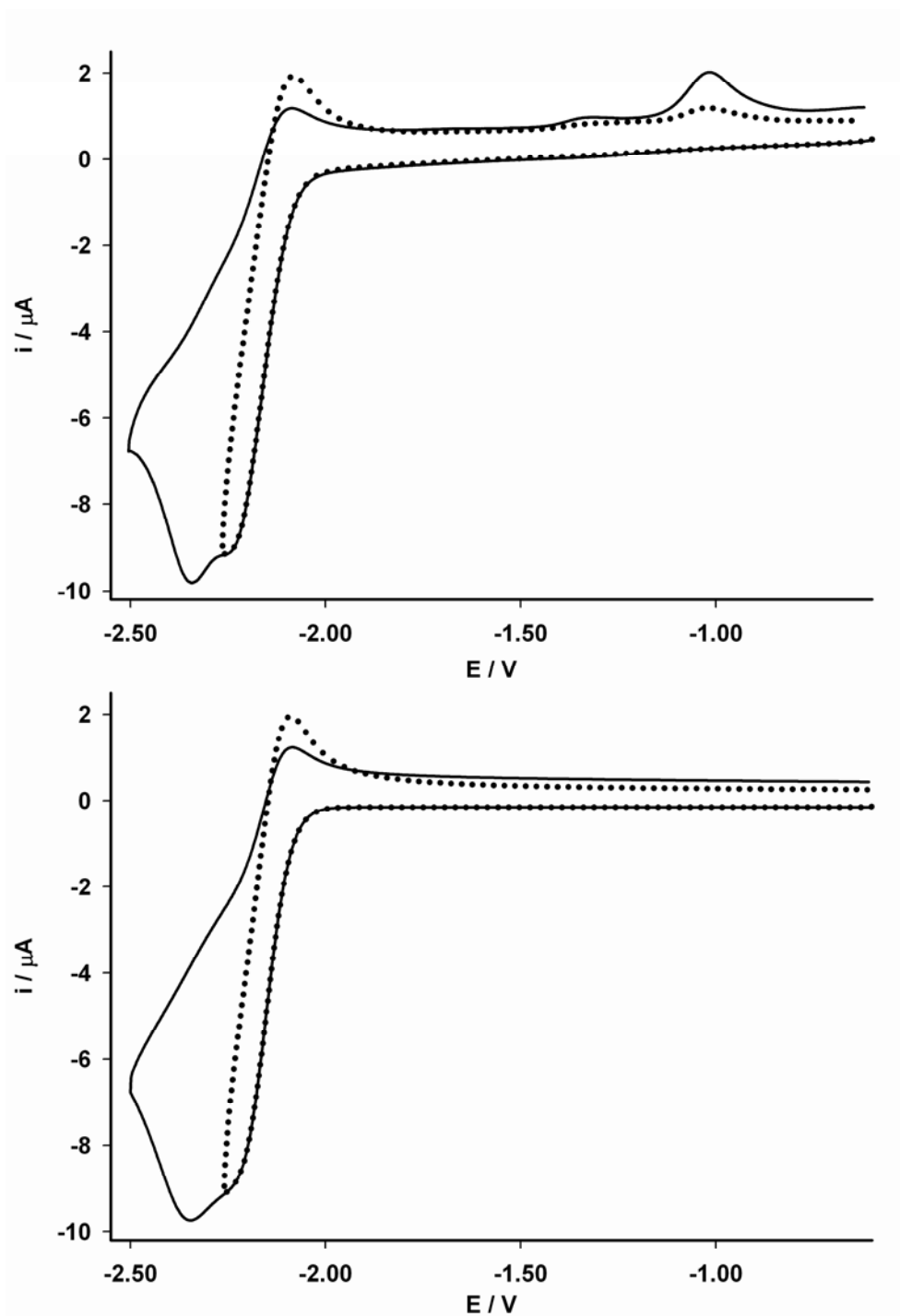


Fig. S6 Cyclic voltammograms of the complex **2** at various scanning potential ranges under Ar atmosphere (Bottom: simulated ones).

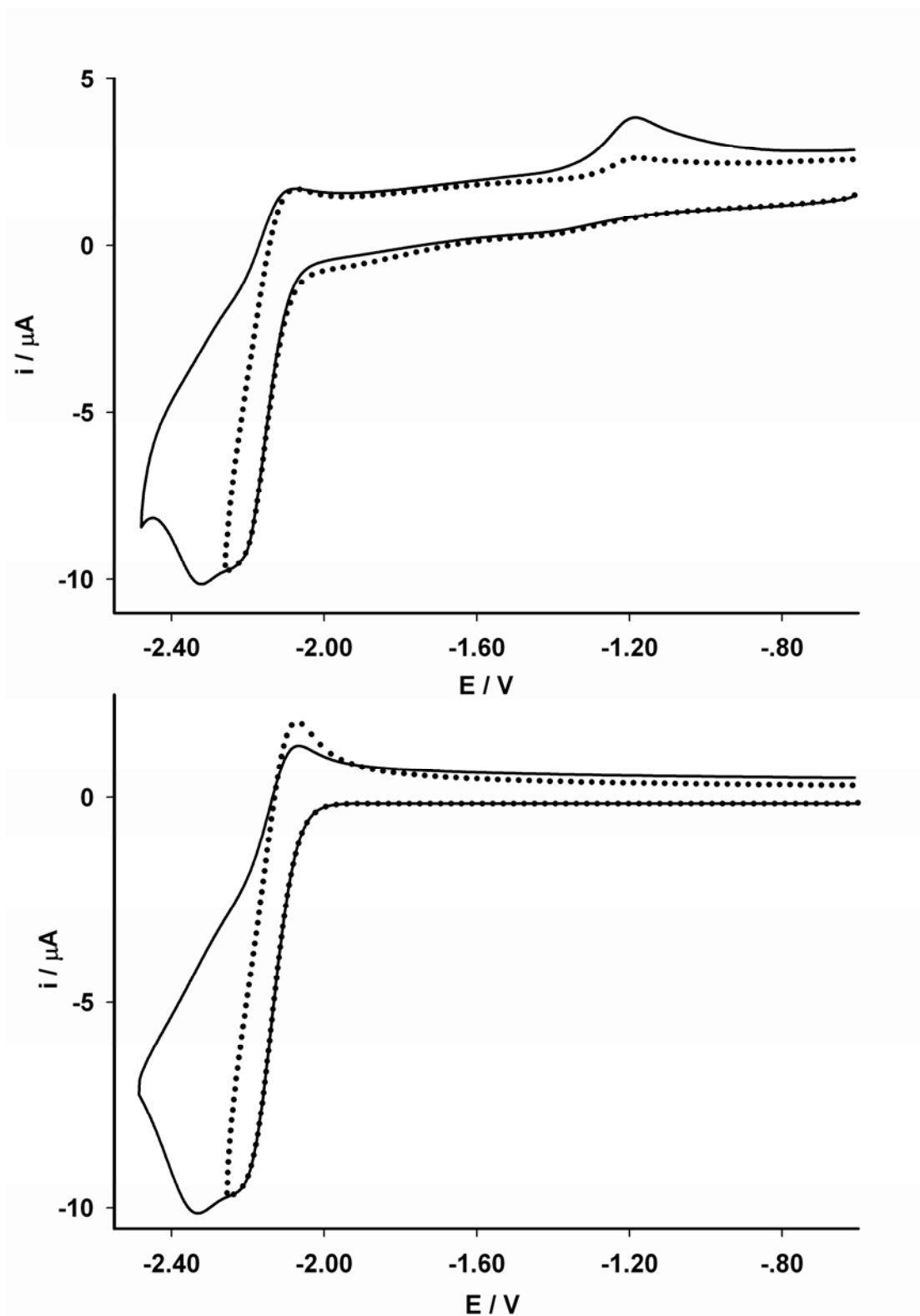


Fig. S7 Cyclic voltammograms of the complex 2 at various scanning potential ranges under CO atmosphere (Bottom: simulated ones).

7. Simulated and experimental cyclic voltammograms for the complex 4

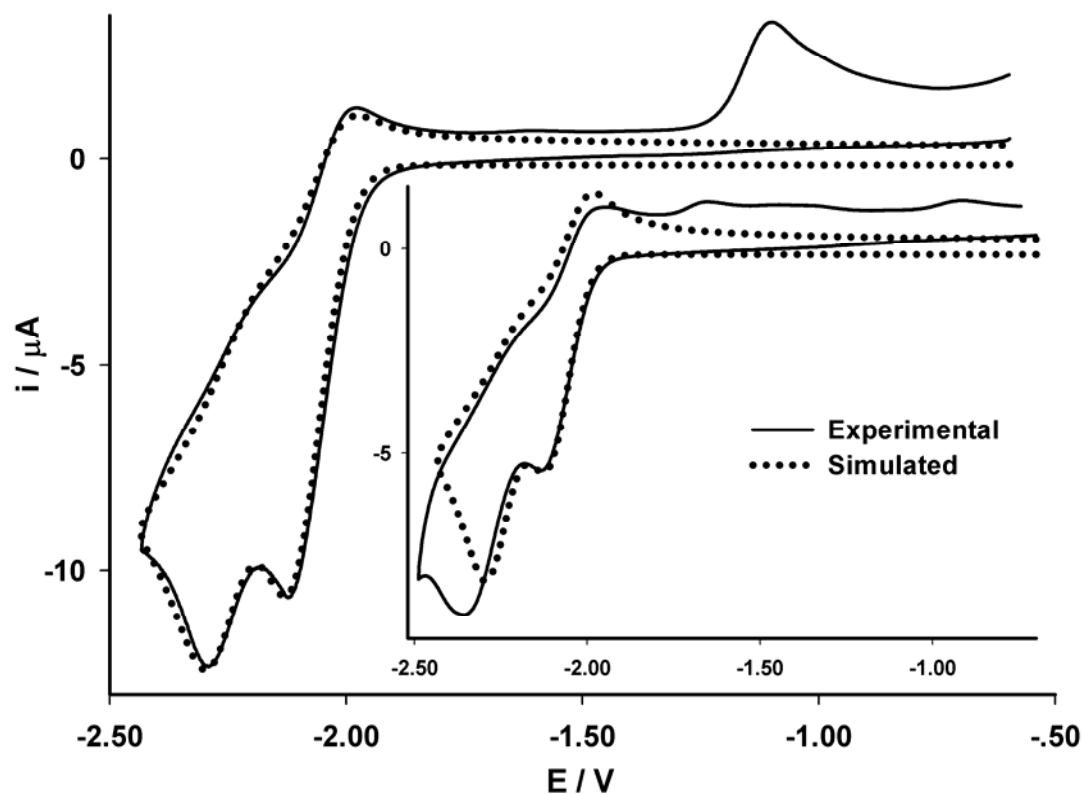
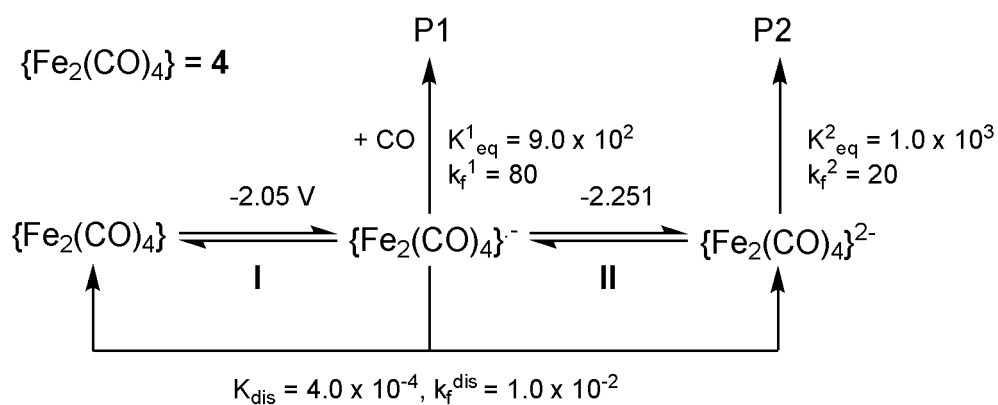


Fig. S8 Simulated and experimental cyclic voltammograms of the complex 4 under Ar atmosphere at 0.1 Vs^{-1} at 298 K. Inset: under CO atmosphere.

8. Electrochemical mechanism for the complex 4



Scheme S1 Proposed mechanism for the complex 4.