

Electronic Supplementary Information

Recent developments in the electrochemical investigations into the iron carbonyl complexes relevant to the metal centres of hydrogenases

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1. Experimental tips for electrochemistry

Inappropriate experimental conditions could severely distort the resultant cyclic voltammograms which may surrender misleading information. Losing reversibility and changes in coupled chemical reactions may be some of the distortions. Therefore, it is essential to perform electrochemistry in an appropriate solvent which is dry and oxygen-free under inert atmosphere in a gas-tight cell with a working electrode which is normally a Pt or vitreous carbon disk with diameter less than 1 mm, preferably 0.5 mm to minimize background current and the voltage resulting from cell resistance. It is also important to keep the surface fresh of the working electrode by regularly and appropriately polishing the electrode surface. It is equally important to use an appropriate reference electrode according to the medium in which the electrochemistry was performed. It needs to avoid using an aqueous reference electrode in organic media for the sake of minimizing junction potentials which will be imposed onto the potentials to be measured. In addition to these required conditions, a variety of electrochemical techniques such as varying scanning rate and temperature, switching working atmosphere, for example, from inert gas atmosphere to CO when CO is involved in the investigated system, bulk electrolysis, differential pulse voltammetry, even in combination with chemical redox reaction, sufficient information could be gathered to establish a picture for the electron transfer and coupled chemical reactions.

2. Electrochemical behaviors of complex 6 with various acids in 0.1 mol L⁻¹

[NBut₄]BF₄/ acetonitrile at room temperature

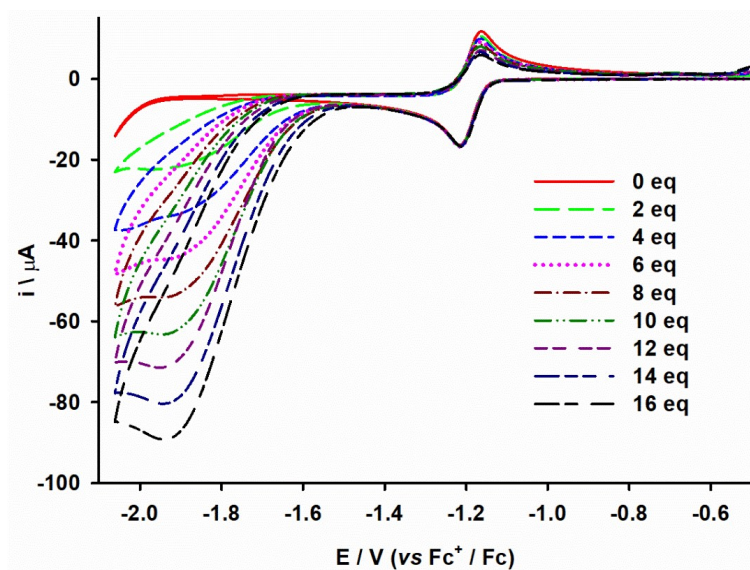


Fig. S1 Cyclic voltammograms of complex **6** upon successive addition of HAc ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

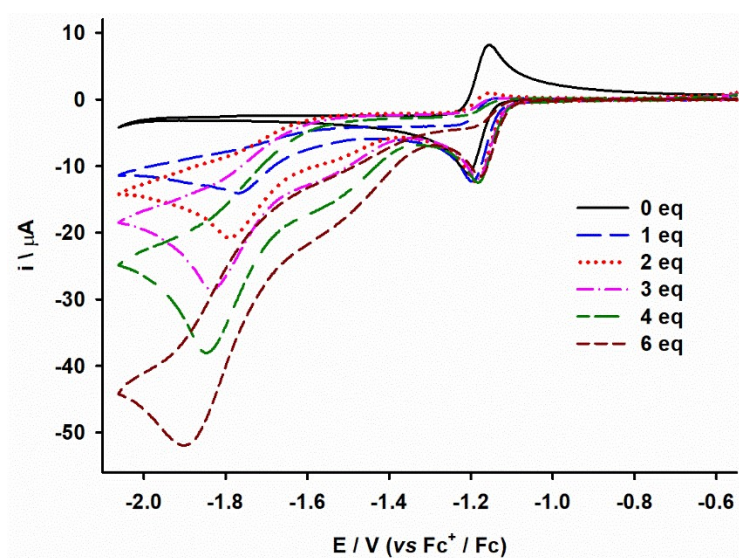


Fig. S2 Cyclic voltammograms of complex **6** upon successive addition of 2,6-dichlorobenzoic acid ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

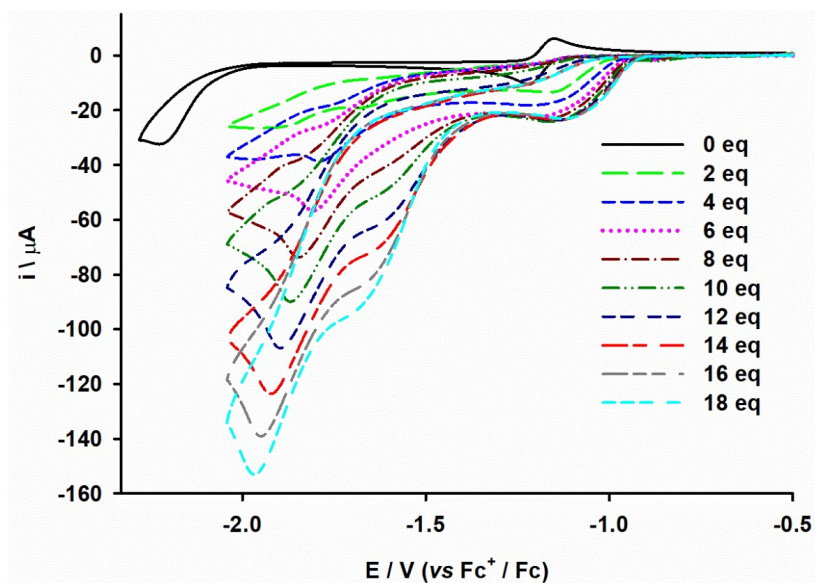


Fig. S3 Cyclic voltammograms of complex **6** upon successive addition of CF_3COOH ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

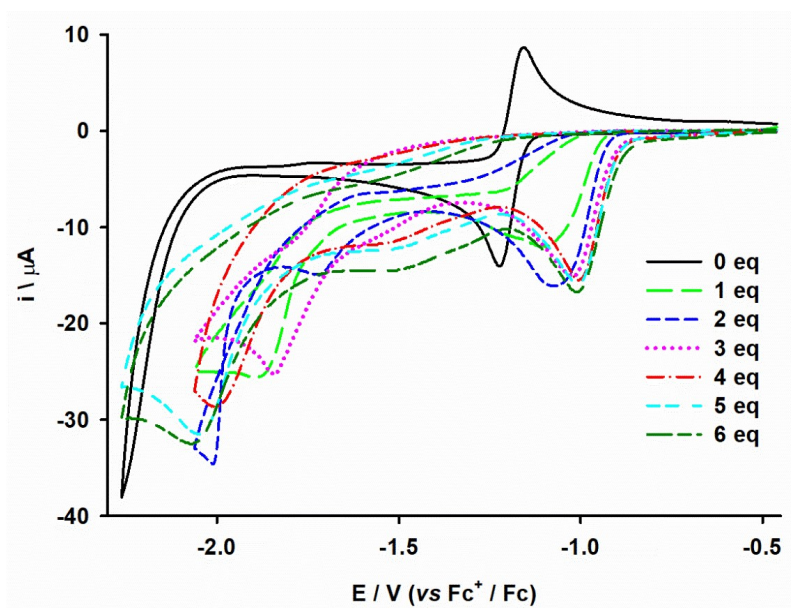


Fig. S4 Cyclic voltammograms of complex **6** upon successive addition of HOTs ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

3. Electrochemical behaviors of complex 7 with various acids in 0.1 mol L⁻¹

[NBut₄]BF₄/ acetonitrile at room temperature

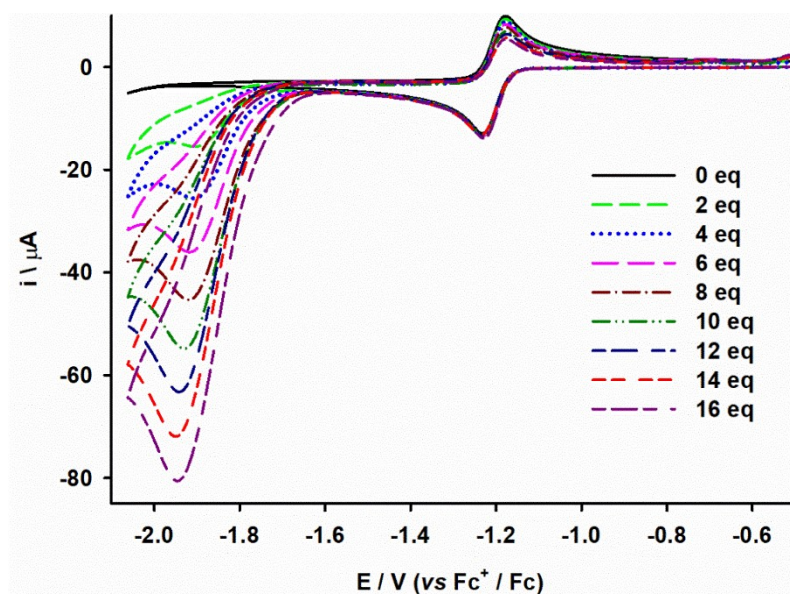


Fig. S5 Cyclic voltammograms of complex 7 upon successive addition of HAc ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

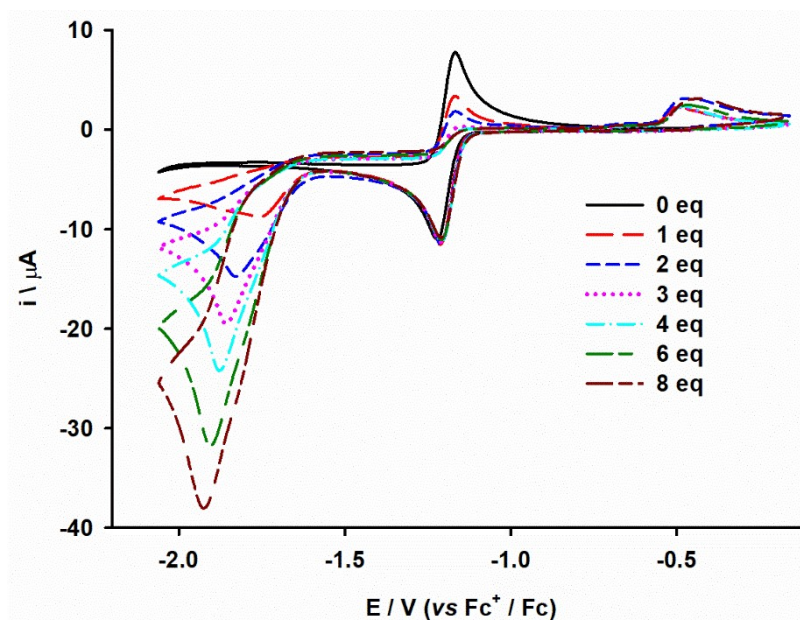


Fig. S6 Cyclic voltammograms of complex 7 upon successive addition of 2,6-dichlorobenzoic acid ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

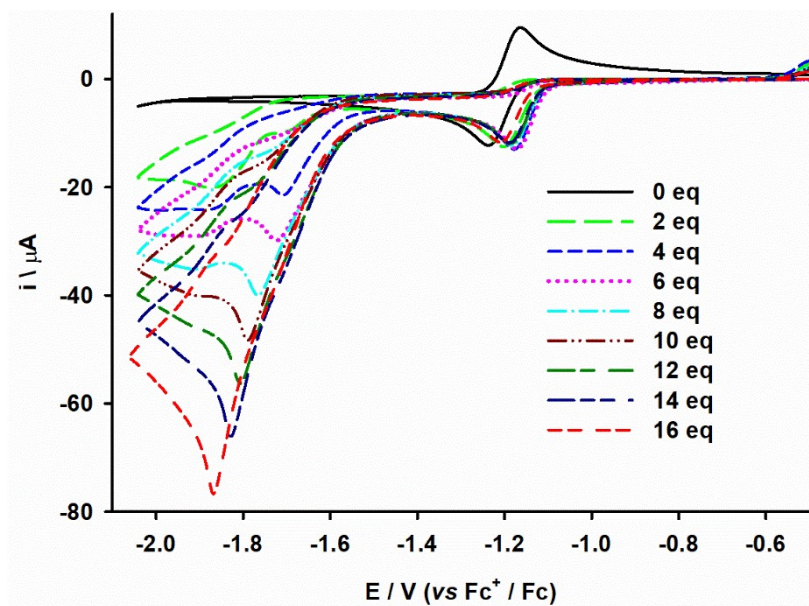


Fig. S7 Cyclic voltammograms of complex **7** upon successive addition of CF_3COOH ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

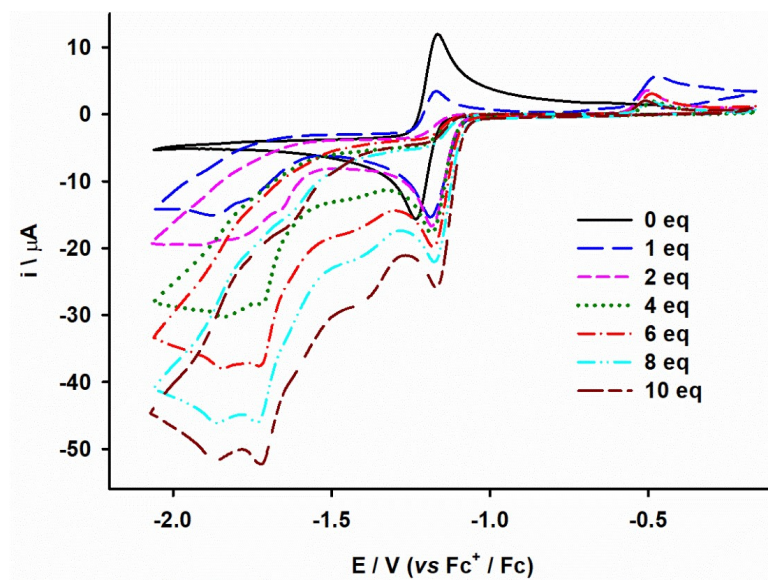


Fig. S8 Cyclic voltammograms of complex **7** upon successive addition of HOTs ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

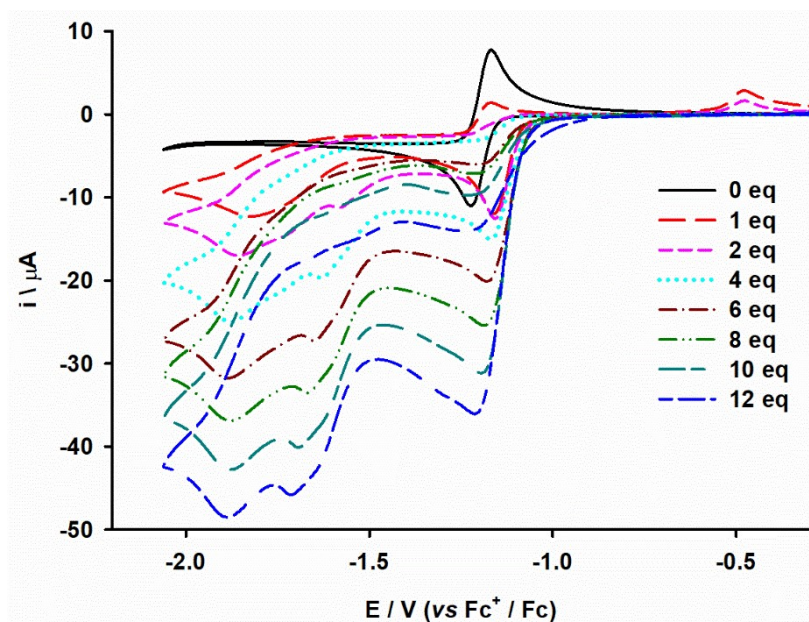


Fig. S9 Cyclic voltammograms of complex **7** upon successive addition of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

4. Electrochemical behaviors of complex **8** with various acids in 0.1 mol L^{-1}

$[\text{NBut}_4]\text{BF}_4 / \text{acetonitrile}$ at room temperature

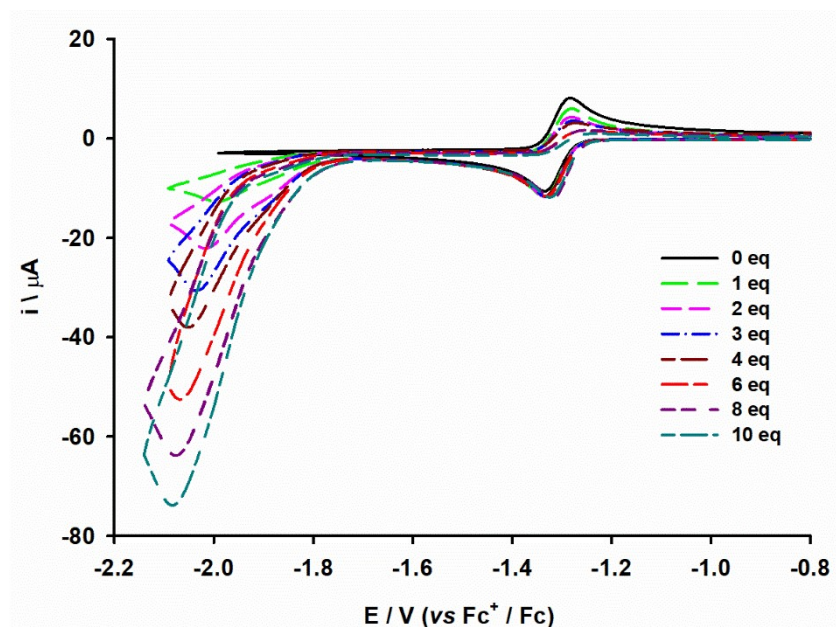


Fig. S10 Cyclic voltammograms of complex **8** upon successive addition of HAc ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

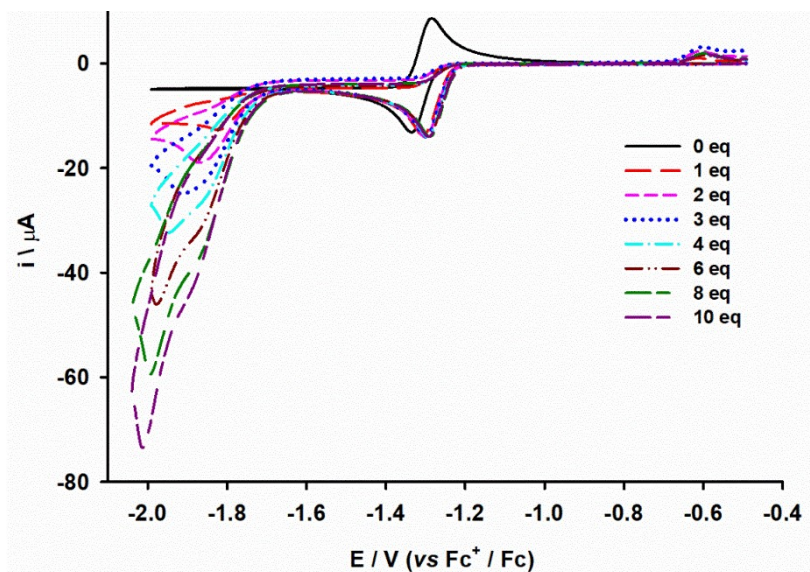


Fig. S11 Cyclic voltammograms of complex **8** upon successive addition of 2,6-dichlorobenzoic acid ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

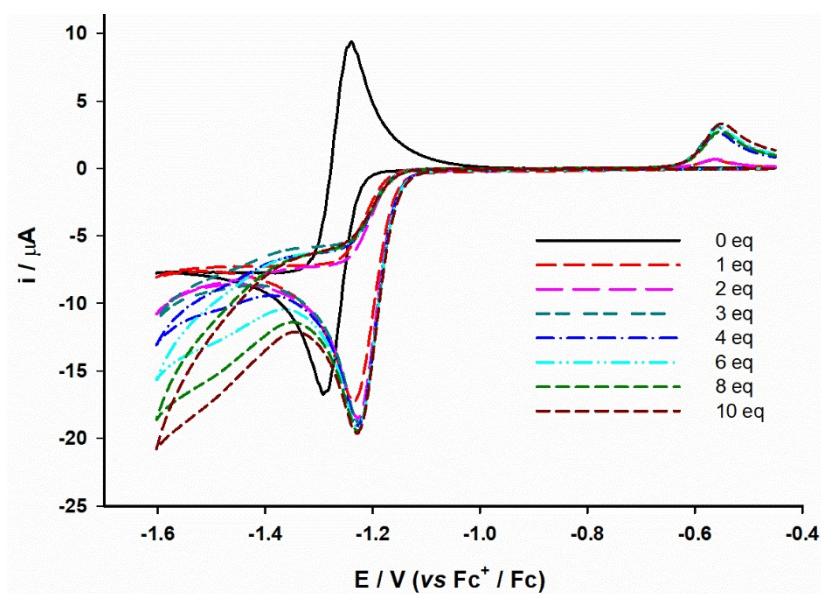


Fig. S12 Cyclic voltammograms of complex **8** upon successive addition of CF_3COOH ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

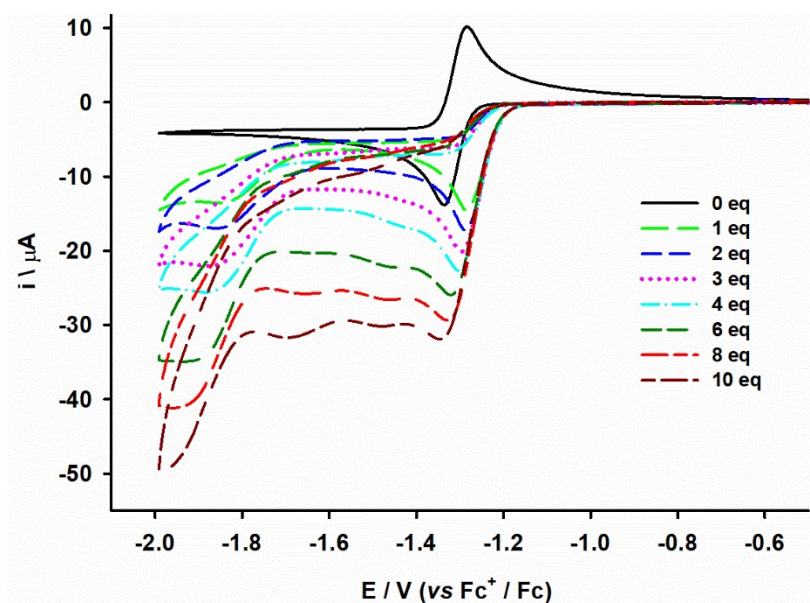


Fig. S13 Cyclic voltammograms of complex **8** upon successive addition of HOTs ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).

5. Comparison of i_{cat} for the first reduction peak against the number of equivalents of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ for complexes **6–8**

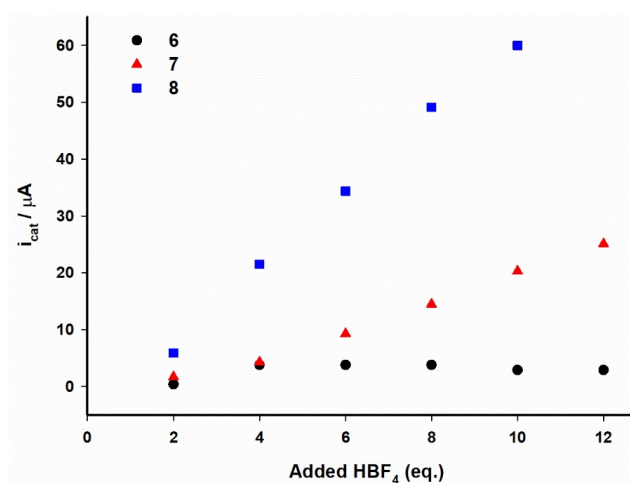


Fig. S14 Plots of i_{cat} for the first reduction peak against the number of equivalents of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ for complexes **6–8** ($c = 2.86 \text{ mmol L}^{-1}$, scanning rate = 0.1 V s^{-1}).