

Protonation, electrochemical properties and molecular structures of halogen-functionalized diiron azadithiolate complexes related to the active site of iron-only hydrogenases

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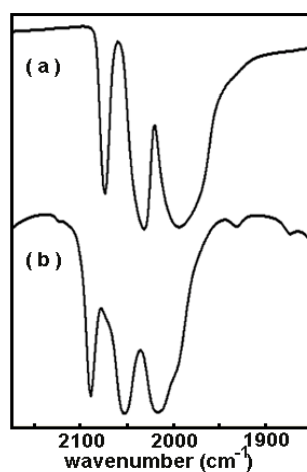


Fig. S1 The IR spectra of (a) **3** in CH₃CN, (b) + 10 equiv of HClO₄.

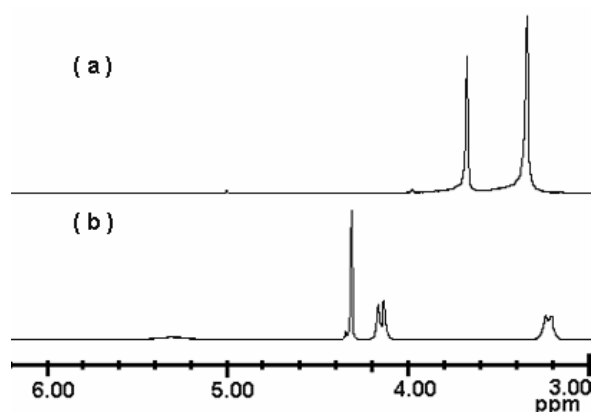


Fig. S2 The ¹H NMR spectra of (a) **3** in CD₃CN, (b) [3(NH)]⁺ in CD₃CN.

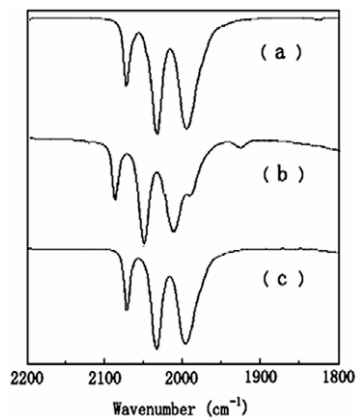


Fig. S3 IR spectra of (a) **1** in CH₃CN, (b) + 10 equiv of HClO₄, (c) [1(NH)]⁺ + 1 equiv of 4-bromoaniline in CH₃CN.

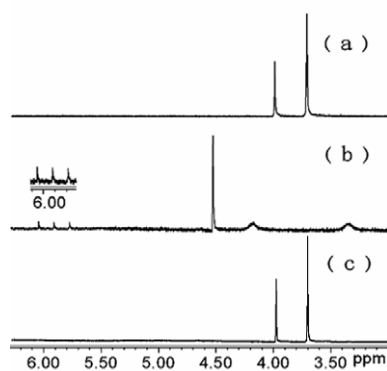


Fig. S4 ¹H NMR spectra of (a) **1** in CD₃CN, (b) [1(NH)]⁺ in CD₃CN, (c) [1(NH)]⁺ + 1 equiv of 4-bromoaniline in CD₃CN.

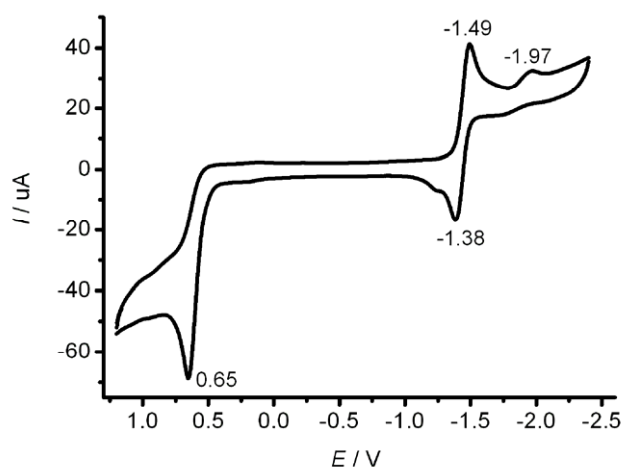


Fig. S5 The CV of complex **1**, 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN , scan rate 100 mV s^{-1} , using a non-aqueous Ag/AgNO_3 electrode as reference.

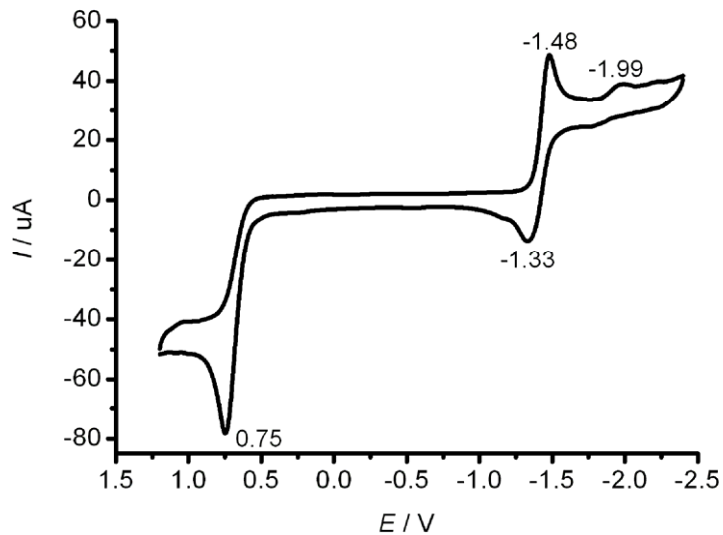


Fig. S6 The CV of complex **2**, 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN , scan rate 100 mV s^{-1} , using a non-aqueous Ag/AgNO_3 electrode as reference.

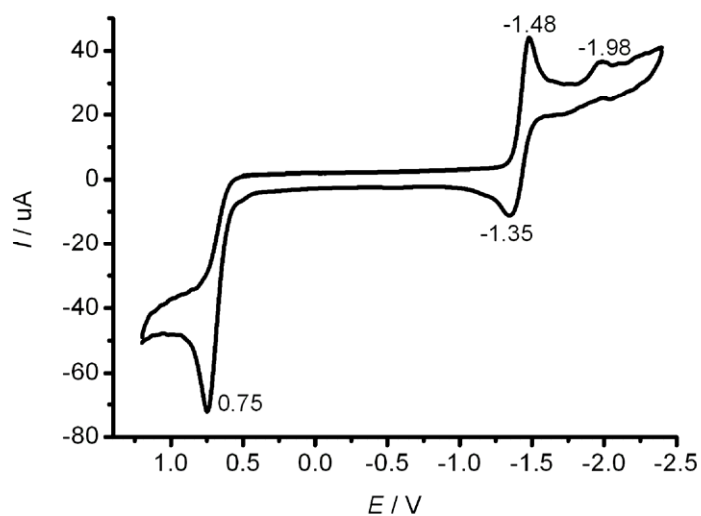


Fig. S7 The CV of complex **3**, 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN ; scan rate 100 mV s^{-1} , using a non-aqueous Ag/AgNO_3 electrode as reference.

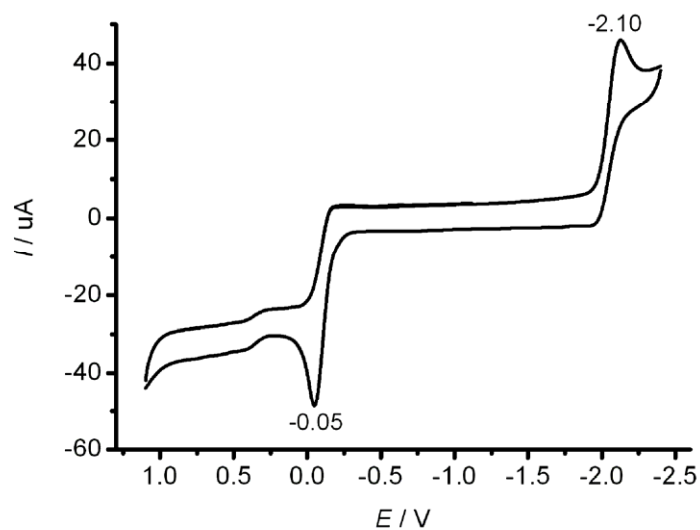


Fig. S8 The CV of complex **4**, 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN , scan rate 100 mV s^{-1} , using a non-aqueous Ag/AgNO_3 electrode as reference.

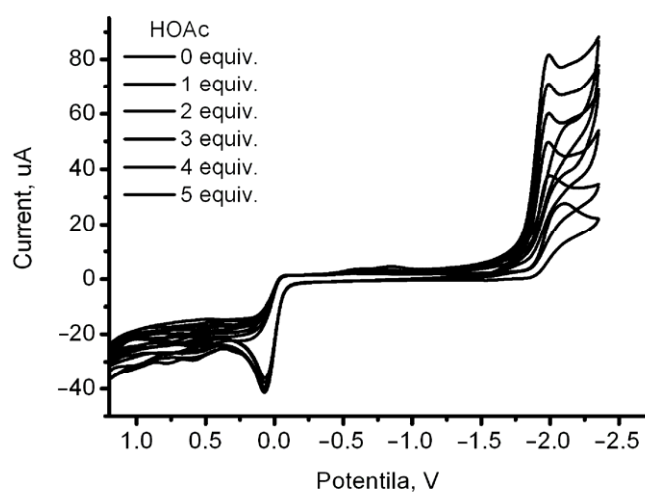
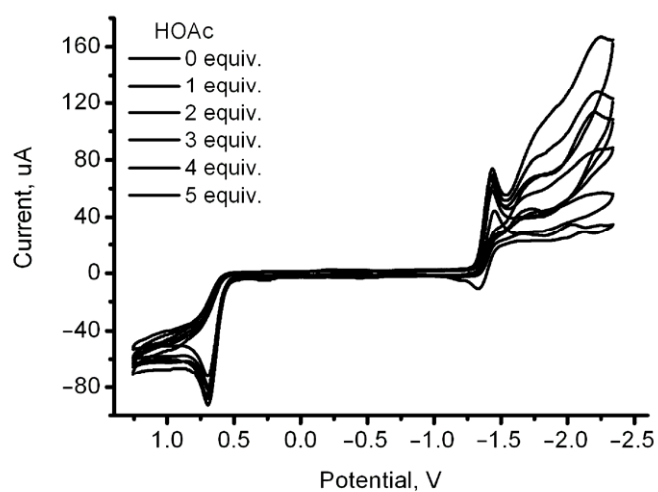


Fig. S9 Cyclic voltammograms of (top) **1** + HOAc in CH₃CN, (bottom) **4** + HOAc in CH₃CN, with 1.0 mM complex in 0.05 M *n*Bu₄NPF₆/CH₃CN at a scan rate of 100 mV s⁻¹.

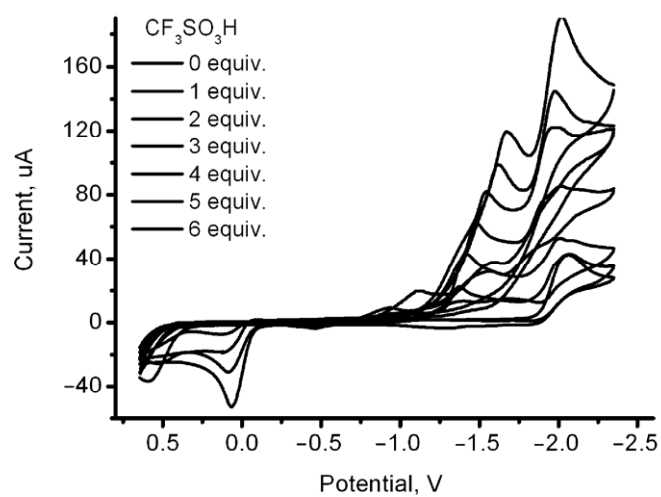
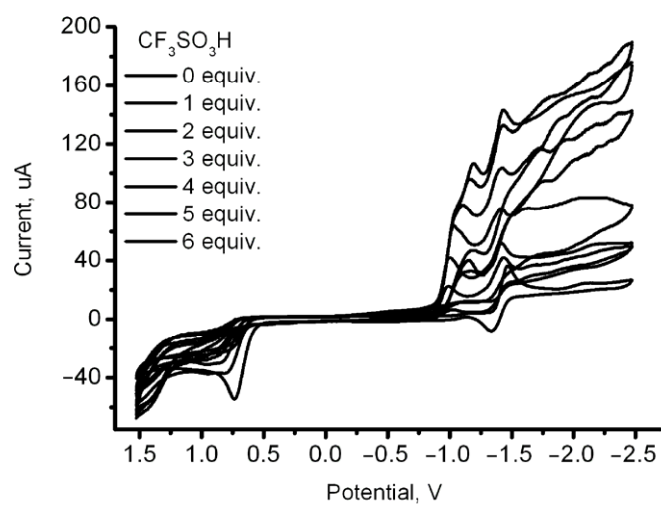


Fig. S10 Cyclic voltammograms of (top) **1** + HOTf in CH₃CN, (bottom) **4** + HOTf in CH₃CN, with 1.0 mM complex in 0.05 M *n*Bu₄NPF₆/CH₃CN at a scan rate of 100 mV s⁻¹.