Supporting material

for

The Reactivity of Molecular Oxygen and Reactive Oxygen Species with [FeFe] Hydrogenase Biomimetics: Reversibility and the Role of the Second Coordination Sphere

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Table S1. Reduction potential of 1^{adt}, 2^{pdt}, relevant oxidants and reductants used in this study

Compound	E / vs Fc ⁺ /Fc	Ref
$Cr(C_6H_6)_2^+/Cr(C_6H_6)_2$	-1.15 V	1
$Co(C_5H_5)_2^+/Co(C_5H_5)_2$	-1.33 V	1
Co(Me ₅ H ₅) ₂ ⁺ / Co(Me ₅ H ₅) ₂	-1.94 V	1
O_2/O_2	-1.27 V	2
$1^{\mathrm{adt}}/1^{\mathrm{adt}}$	-1.6 V	3
$2^{\text{pdt}}/2^{\text{pdt}}$	-1.6 V/-1.7 V	4
O-2 ^{pdt} / O-2 ^{pdt-}	-1.58 V	4b

Table S2. Infrared absorption bands of carbonyl groups from relevant 1^{adt} and 2^{pdt} species in this study.

Complex	Wavenumber (CO)/cm ⁻¹	Ref
1 ^{adt} /2 ^{pdt}	2074, 2033, 2000, 1989 (CH ₂ Cl ₂)	This study
^a 1 ^{adt-}	2006, 1942, 1910 (CH ₃ CN)	5
^a 2 ^{pdt-}	2006, 1942, 1915, 1899 (THF)	4a
^b H-1 ^{adt}	2025, 1965, 1935 (CH ₃ CN)	6
^c H-1 ^{pdt}	2072, 2043, 1993 (CH ₂ Cl ₂)	7
O-2 ^{pdt}	2081, 2042, 2017, 1995 (Toluene)	4b
	2083, 2045, 2017, 2000 (CH ₂ Cl ₂)	
^a O-1 ^{adt-}	2038, 1997, 1957, 1946 (CH ₂ Cl ₂)	This study
^a O-2 ^{pdt-}	2020, 1960, 1891 and a broad shoulder peak between	This study
	1950 and 1910 (CH ₂ Cl ₂)	

^{a,} one-electron reduced species. ^bone-electron reduced species with a protonated bridgehead N atom in 1^{adt} . ^cone-electron reduced species with a bridged hydride (µ-H) between the diiron centre.



Figure S1. Voltammograms of 1^{adt} , 2^{pdt} and molecular O₂ in acetonitrile. The redox peaks for superoxide (blue trace, in the absence of acid) and perhydroxyl (magenta trace, in the presence of acid) occur in the more positive potential than proton reduction mediated by 1^{adt} and 2^{pdt} (red trace). A) The black trace: 1.2 mM 1^{adt} . The red trace: 1.2 mM 1^{adt} and c.a. 1.2 mM trichloroacetic acid. The blue trace: 0.27 mM O₂ (dry air). The magenta trace: 0.27 mM O₂ and 1 mM trichloroacetic acid. B) The black trace: 1 mM 2^{pdt} . The red trace: 1 mM 2^{pdt} and 1 mM chloroacetic acid. The glassy carbon electrode was used as a working electrode. A Pt counter electrode and a non-aqueous reference electrode containing Ag/Ag(NO3) 0.01 M dissolved in acetonitrile were employed. Tetrabutylammonium hexafluorophosphate, 0.1 M was used as the supporting electrolyte. The air used for electrochemical experiments was

passed through a packed column with silica gels. (i.e. dry air) The 21% O₂-saturated acetonitrile was prepared by purging with dry air for an hour before electrochemical experiments. The scan rate: 0.1 V/sec.



Figure S2. The reaction of 1^{adt} and 2^{pdt} with decamethylcobaltocene (CoCp₂*) The complex 1^{adt} (0.5 mM) or 2^{pdt} (0.5 mM) were mixed with more than 2 equivalents of CoCp₂*. Resulting products were exposed to air for 30 seconds.



Figure S3. The role of water and O_2 . Ten equivalents of cobaltocene and oxygen-free DI water (20 uL) were added. For the pink lines, molecular oxygen was purged into a mixture containing 1^{adt} (or 2^{pdt}) (0.67 mM), CoCp₂ and oxygen-free DI water.



Figure S4. Mass spectrum after mixing 1^{adt} and $CoCp_2$ with O_2 . $CoCp_2$ was used as a reductant and the mass assigned for the oxygenated 1^{adt} is 401.76 amu. The theoretical value for the oxygenated 1^{adt} (O- 1^{adt}) is 402.82 amu. Other major mass peaks correlated to the loss of the numbers of CO ligands were observed. In control experiments, the peak at 166.27 amu (the inset figure) was observed when injecting a mixture of $CoCp_2 + O_2$. No peak was observed when injecting 1^{adt} alone.



Figure S5. Mass spectrum after mixing 1^{adt} and $Cr(bz)_2$ with O_2 . $Cr(bz)_2$ was used as a reductant and the mass assigned for the oxygenated 1^{adt} is 401.75 amu. Other major mass peaks correlated to the loss of the numbers of CO ligands were observed. The theoretical value for the oxygenated 1^{adt} (O- 1^{adt}) is 402.82 amu.



Figure S6. Mass spectrum after mixing 1^{adt} and $CoCp_2$ with ${}^{16}O_2$ and ${}^{18}O_2$. In the upper figure, $CoCp_2$ was used as a reductant and the mass assigned for the oxygenated 1^{adt} is 401.60 amu. The theoretical value for the oxygenated 1^{adt} (O- 1^{adt-}) is 402.82 amu. When mixing a solution containing 1^{adt} and $CoCp_2$ with ${}^{18}O_2$, the extra peak for 403.60 amu was observed.



Figure S7. Mass spectrum after mixing 2^{pdt} and cobaltocene with O₂. The mass assigned for the oxygenated 2^{pdt} was observed at 402.59 amu. The theoretical value for the oxygenated 2^{adt} (O- 2^{adt-}) is 401.83 amu.



Figure S8. 10 K EPR signal of O-1^{adt-} and O-2^{pdt-}. A mixture solution of 1^{adt} (1.3mM, black line) or 2^{pdt} (1.3mM, red line) and 10 equivalents of cobaltocene was mixed with O₂ respectively. The arrow indicates the *g* value. EPR spectra were recorded at 10 K, microwave power 1 mW, frequency 9.28 GHz, modulation amplitude 10 G, modulation frequency 100 kHz.



Figure S9. The time course of O-1^{adt-} recorded in UV-visible and IR absorption spectroscopy. The UV-visible spectra (Figure S9a) and corresponding IR spectra (Figure S9b) were recorded at every 2 minutes respectively after adding the excess of O₂ into a mixture containing 4 eq of CoCp₂ and 1eq of **1^{adt}** (0.47 mM). The half-life time for **O-1^{adt-}** is 3.6 minutes fitting the peak at 605 nm (as shown in the inset figure in Figure S8a). The half-life time for **O-1^{adt-}** estimated by IR absorption (Figure S9c) is 5.0 minutes at 1946 cm⁻¹, 5.8 minutes at 1959 cm⁻¹ and 4.9 minutes at 2074 cm⁻¹ fitting the first 20 minutes of IR absorption results. After 20 minutes, the rate of the peak intensity decreased at 1946 and 1959, and the peak intensity increased at 2074 cm⁻¹ became much slower and no distinct absorption peak observed in the UV-visible spectrum, suggesting that another new species is formed.



Figure S10. The generation of water during the deoxygenation process of O-1^{adt-}. In the upper part of the figure, IR spectra show that the absorption of water gradualy increased during the deoygenation process of O-1^{adt-}. The spike peaks of the spectrum recorded at 0 minute ascribe to air inside the sample chamber of the IR spectrometer. In the middle part of the figure, the IR spectra for reduced cobatocene alone (dark navy-color line) and a solution of reduced cobaltocene reacting with dioxygen (red and blue line) were recorded. In the lower part of the figure, The magenta trace, "H₂O in DCM", referes to 10µL DI dissolved in 1mL DCM and the green trace, "H₂O₂ in DCM" indicates 10µL 30% H₂O₂ dissolved in 1mL DCM.



Figure S11. The effect of temperature on the stability of O-1^{adt-}. For the preparation of O-1^{adt-}, a mixture solution of 4 eq of $CoCp_2$ and 1 eq of 1^{adt} (0.5 mM) was mixed with 4 eq of O_2 . Samples were stored at room temperature (R.T.) or -30°C freezer inside the glovebox.



Figure S12. The reactivity of 1^{adt} and 2^{pdt} with an O-atom donor reagent, *meta*chloroperoxybenzoic acid (mCPBA). IR spectra were recorded 30 minutes after mixing mCPBA and 1^{adt} (or 2^{pdt}) inside the glovebox. The concentration of 1^{adt} and 2^{pdt} were 0.52 mM.



Figure S13. The effect of superoxide on 1^{adt} and 2^{pdt} . The superoxide was added to react with 1^{adt} and 2^{pdt} (0.5 mM) respectively. For the blue line, cobaltocene was added after mixing 1^{adt} or 2^{pdt} with superoxide. For the magenta line, molecular oxygen was purged into a mixture containing 1^{adt} or 2^{pdt} with CoCp₂. Ten equivalents of CoCp₂ against 1^{adt} or 2^{pdt} were used. The superoxide solution was prepared by mixing KO₂ (0.1 M) and 18-crown-6 ether (0.4 M). Mix 71 µL superoxide solution with 357 µL stock solution containing 1^{adt} and 2^{pdt} .



Figure S14. The effect of peroxide on 1^{adt} and 2^{pdt} . The H₂O₂ solution (30% (W/W) H₂O₂ in H₂O) was added to react with 1^{adt} and 2^{pdt} (0.5 mM) respectively. For the green line, oxygenfree H₂O₂ was added to a mixture containing 1^{adt} and CoCp₂. For the blue line, an aliquot of H₂O₂ was added into O-1^{adt-} or O-2^{pdt-}(prepared by mixing a solution containing 1^{adt} (or 2^{pdt}) and CoCp₂ with O₂ (i.e. magenta line)). Ten equivalents of CoCp₂ against 1^{adt} or 2^{pdt} were used. A 6 µL aliquot of H₂O₂ was added to a 494 µL mixture solution containing 1^{adt} or 2^{pdt} .



Figure S15. The reactivity of acids with O- 2^{pdt} . Two equivalents of acids against the starting concentration of 2^{pdt} (0.36 mM) were added after mixing the solution of 8 eq of CoCp₂ and 1 eq of 2^{pdt} with the excess of O₂. In the control experiments (upper parts of the figure), only DCM solvent, instead of the solution of acids, was added. The black line refers to the sample 2^{pdt} only.



Figure S16. The effect of reductants on O-1^{adt-}. The various mixtures of 1 eq of 1^{adt} (0.36 mM) and different amount of $CoCp_2$ (4eq , 10 eq and 20 eq) reacted with 4 eq of O₂ respectively. The spectrum was collected at different time points. (Black : 3 mins, Red :23 mins , blue :65 mins and Grey : 20 hrs.) The samples were stored in the glovebox at room temperature. The UV-visible absorption peaks for reduced CoCp₂ was still observed for the mixtures prepared with 10 eq and 20 eq of CoCp₂ after 20 hrs.



Figure S17. The IR spectra recorded after reacting a mixture of 1^{adt} and $CoCp_2$ with ${}^{18}O_2$ vs ${}^{16}O_2$ respectively. A mixture of 1^{adt} (4.44 mM) and 5 eq of CoCp₂ reacted with ${}^{18}O_2$ and ${}^{16}O_2$ respectively. The IR spectra were collected at 1 min (magenta and red traces) and 25 mins (grey and black traces) after addition of O₂, respectively. The corresponding region for v_{S=0} absorption is shown in Figure 4 of the main manuscript.



Figure S18. The stability of oxygenated 2^{pdt} . A mixture solution of 1 equivalent of 2^{pdt} (0.5 mM) and 10 equivalents of CoCp₂ was purged with molecular oxygen and then the sample solution was recorded with an IR spectrometer. Every spectrum was recorded at every 2 minutes. The spike peaks from the spectrum recorded at 0 minute attributes to air inside the sample chamber of an IR spectrometer.

DFT calculation results



Figure S19. The DFT-calculated IR absorption bands for ¹⁶O-1^{adt-} and ¹⁸O-1^{adt-} respectively.

For the structure of **O-1^{adt-}**, it is highly unlikely that the μ -oxo diiron(II, II), end-on peroxide diiron (II,II) or bis(μ -oxo) diiron(III,III) species are the oxygenated species since the low-valent diiron,(I,0) state are supported by IR and EPR. Another possible oxygenated species was (μ -oxo) diiron (I, 0) but the calculated IR spectrum suggests five v_{CO} bands instead of four v_{CO} observed from experiments. (Figure S19 b) An average shift of c.a. 40 cm⁻¹ to lower frequencies was observed for carbonyl ligands compared to experimental data. (Table S1)



Figure S20. The DFT-calculated IR absorption bands of v_{CO} from 1^{adt} and $O-1^{adt-}$ with different postulated structure and oxidation states.

Optimized Geometry 1^{adt} Fe₂(adt)(CO)₆ (Fe₂C₈NH₅S₂O₆)

С	1.008125000	9.676460000	0.464106000
С	0.405054000	9.688218000	2.811290000
С	-2.422070000	8.437173000	0.914903000
С	-2.203962000	6.067876000	2.203775000
С	-1.628568000	6.153075000	-0.275589000
С	2.837577000	6.868083000	2.126557000
С	0.906218000	5.259593000	3.037018000
С	1.414049000	5.205427000	0.548439000
Fe	-1.235052000	7.137123000	1.157394000
Fe	1.140499000	6.475502000	1.761749000
Ν	1.375973000	9.974460000	1.808144000
Η	2.303610000	9.619019000	2.047936000
0	-2.846253000	5.371324000	2.868570000
0	-1.900308000	5.523866000	-1.208242000
0	0.767655000	4.459229000	3.861493000
0	1.595761000	4.369679000	-0.231474000
S	0.608586000	7.878702000	0.030135000
S	-0.148078000	7.890930000	3.021805000
0	3.957596000	7.052415000	2.362246000
0	-3.213891000	9.269656000	0.764650000
Η	0.799481000	9.952056000	3.801211000
Η	-0.524642000	10.245730000	2.624024000
Н	0.106261000	10.235349000	0.173586000
Η	1.833123000	9.927808000	-0.215129000

$1^{adt-} \ [Fe_2(adt)(CO)_6]^- \ Fe_2C_8NH_5S_2O_6$

С	0.994674000	9.600056000	0.460504000
С	0.361018000	9.615314000	2.816106000
С	-2.443223000	8.596060000	0.909131000
С	-2.283215000	6.102779000	2.122392000
С	-1.753072000	6.260660000	-0.317196000
С	2.949256000	6.989456000	2.118277000
С	1.085806000	5.284670000	3.093708000
С	1.492399000	5.170010000	0.634187000
Fe	-1.342861000	7.200697000	1.114767000
Fe	1.266100000	6.464836000	1.803220000
Ν	1.354366000	9.898671000	1.818252000
Η	2.244438000	9.454878000	2.061955000
0	-2.932342000	5.389324000	2.782079000
0	-2.042076000	5.653310000	-1.272053000
Ο	0.983215000	4.499632000	3.951835000
0	1.671424000	4.309273000	-0.135217000

S	0.619918000	7.810134000	0.011738000
S	-0.187284000	7.828479000	3.037287000
0	4.101408000	7.093029000	2.304845000
0	-3.305803000	9.373497000	0.761629000
Η	0.747411000	9.911066000	3.801719000
Η	-0.557281000	10.183270000	2.600050000
Η	0.089819000	10.162360000	0.182304000
Η	1.822647000	9.887292000	-0.202922000

$\textbf{O-1}^{adt} \ Fe_2(\textbf{OSCH}_2\textbf{NHCH}_2\textbf{S})(\textbf{CO})_6 \ (Fe_2C_8\textbf{NH}_5\textbf{S}_2\textbf{O}_7)$

0.991961000	9.718103000	0.361091000
0.411842000	9.700072000	2.711912000
-2.439568000	8.483738000	0.835710000
-2.262534000	6.103644000	2.067592000
-1.648430000	6.163181000	-0.401568000
2.848686000	6.915978000	1.999634000
0.982513000	5.243908000	2.884233000
1.414378000	5.226332000	0.372635000
-1.265235000	7.164808000	1.047138000
1.161806000	6.487393000	1.628277000
1.368513000	10.002083000	1.709539000
2.306336000	9.667753000	1.938486000
-2.923027000	5.411312000	2.716346000
-1.911729000	5.540143000	-1.338499000
0.872440000	4.426882000	3.694517000
1.585725000	4.409406000	-0.426578000
0.588558000	7.918262000	-0.074622000
-0.114157000	7.874618000	2.789608000
3.964149000	7.122074000	2.236752000
-3.229506000	9.318047000	0.689363000
0.808514000	9.876873000	3.720374000
-0.531088000	10.246461000	2.560474000
0.087462000	10.277354000	0.080986000
1.813400000	9.974561000	-0.319727000
-0.568995000	7.634625000	4.201680000
	0.991961000 0.411842000 -2.439568000 -2.262534000 -1.648430000 2.848686000 0.982513000 1.414378000 -1.265235000 1.161806000 1.368513000 2.306336000 -2.923027000 -1.911729000 0.872440000 1.585725000 0.588558000 -0.114157000 3.964149000 -3.229506000 0.808514000 -0.531088000 0.087462000 1.813400000 -0.568995000	0.9919610009.7181030000.4118420009.700072000-2.4395680008.483738000-2.2625340006.103644000-1.6484300006.1631810002.8486860006.9159780000.9825130005.2439080001.4143780005.226332000-1.2652350007.1648080001.36851300010.0020830002.3063360009.667753000-2.9230270005.411312000-1.9117290005.5401430000.8724400004.4268820001.5857250004.4094060000.5885580007.918262000-0.1141570007.8746180003.9641490007.122074000-3.2295060009.3180470000.8085140009.876873000-0.53108800010.2464610000.8746200010.2773540001.8134000009.974561000-0.5689950007.634625000

$\textbf{O-1}^{adt-} [Fe_2(\textbf{OSCH}_2\textbf{NHCH}_2\textbf{S})(\textbf{CO})_6]^- (Fe_2C_8\textbf{NH}_5\textbf{S}_2\textbf{O}_7)$

С	0.922953000	9.606556000	0.244970000
С	0.461900000	9.618866000	2.630254000
С	-2.503971000	8.649957000	0.914237000
С	-2.343133000	6.135100000	2.098905000
С	-1.923591000	6.317813000	-0.376154000

С	2.899863000	7.032052000	2.247758000
С	0.927780000	5.142169000	2.786448000
С	1.869434000	5.315880000	0.446354000
Fe	-1.425679000	7.235431000	1.062487000
Fe	1.308805000	6.465638000	1.677601000
Ν	1.376336000	9.920625000	1.574660000
Η	2.292068000	9.499199000	1.752966000
0	-2.995934000	5.435901000	2.766411000
0	-2.244120000	5.722370000	-1.325198000
0	0.746111000	4.264953000	3.534015000
0	2.240306000	4.566595000	-0.364808000
S	0.532464000	7.801432000	-0.122069000
S	-0.102901000	7.816524000	2.751897000
0	3.971289000	7.206703000	2.686172000
0	-3.338971000	9.461610000	0.809635000
Η	0.922129000	9.799084000	3.612058000
Η	-0.471118000	10.195371000	2.531481000
Η	0.000281000	10.163492000	0.021921000
Η	1.703834000	9.882536000	-0.476762000
0	-0.514120000	7.651756000	4.200119000

$\mu\text{-}O\text{-}1^{adt} \quad [FeOFe(SCH_2NHCH_2S)(CO)_6] \quad (Fe_2C_8NH_5S_2O_7)$

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С	0.934495000	9.492026000	0.429914000
С	0.350110000	9.471857000	2.824170000
С	-2.284676000	8.631574000	0.892191000
С	-2.679245000	6.345133000	2.134469000
С	-2.035798000	6.360192000	-0.412539000
С	2.838633000	7.077862000	2.110735000
С	1.369037000	5.145324000	3.117601000
С	1.972103000	5.154811000	0.554324000
Fe	-1.419975000	7.072383000	1.101853000
Fe	1.274756000	6.278924000	1.746888000
Ν	1.267602000	9.794301000	1.781870000
Н	2.232312000	9.566388000	2.017487000
0	-3.462071000	5.836278000	2.809107000
0	-2.400943000	5.866945000	-1.387368000
0	1.383028000	4.403762000	3.998597000
0	2.374553000	4.414989000	-0.231206000
S	0.566858000	7.677310000	-0.018386000
S	-0.171888000	7.653711000	3.018147000
0	3.889954000	7.503514000	2.345583000
0	-2.898889000	9.599530000	0.734502000
Η	0.789311000	9.740902000	3.792635000
Η	-0.598873000	10.012647000	2.696894000

Η	0.029392000	10.032615000	0.116818000
Н	1.768369000	9.775019000	-0.224143000
0	-0.423533000	5.425232000	1.340930000

μ -O-1^{adt-} [FeOFe(SCH₂NHCH₂S)(CO)₆]⁻ (Fe₂C₈NH₅S₂O₇)

С	1.060503000	9.463923000	0.647569000
С	0.010633000	9.746793000	2.860607000
С	-2.314777000	8.657953000	0.872120000
С	-2.761479000	6.473100000	2.209412000
С	-1.916926000	6.269750000	-0.282440000
С	2.961770000	6.858037000	1.662742000
С	1.610083000	5.074222000	2.940544000
С	2.071241000	4.833883000	0.258465000
Fe	-1.453697000	7.134267000	1.198275000
Fe	1.419384000	6.011982000	1.446651000
Ν	1.202265000	9.775210000	2.034953000
Η	1.953263000	9.231681000	2.467851000
0	-3.598673000	6.032203000	2.873680000
0	-2.199657000	5.668730000	-1.229666000
0	1.696475000	4.408856000	3.891840000
0	2.566161000	4.027836000	-0.423378000
S	0.540409000	7.724256000	0.097115000
S	-0.695462000	8.085700000	3.275008000
0	3.987325000	7.406187000	1.796121000
0	-2.895332000	9.637075000	0.641099000
Η	0.256071000	10.193729000	3.835852000
Η	-0.756932000	10.378217000	2.387887000
Η	0.308574000	10.126389000	0.192137000
Η	2.021263000	9.617010000	0.136457000
0	-0.407863000	5.496237000	1.500177000

References

(1) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877-910.

(2) Peover, M. E.; White, B. S. Electrolytic Reduction of Oxygen in Aprotic Solvents: The Superoxide Ion. *Electrochim Acta* **1966**, *11*, 1061-1067.

(3) Bourrez, M.; Steinmetz, R.; Gloaguen, F. Mechanistic Insights into the Catalysis of Electrochemical Proton Reduction by a Diiron Azadithiolate Complex. *Inorg. Chem.* **2014**, *53*, 10667-10673.

(4) (a) Borg, S. J.; Behrsing, T.; Best, S. P.; Razavet, M.; Liu, X. M.; Pickett, C. J. Electron Transfer at a Dithiolate-Bridged Diiron Assembly: Electrocatalytic Hydrogen Evolution. *J. Am. Chem. Soc.* **2004**, *126*, 16988-16999; (b) Liu, T. B.; Li, B.; Singleton, M. L.; Hall, M. B.; Darensbourg, M. Y. Sulfur Oxygenates of Biomimetics of the Diiron Subsite of the [FeFe]-

Hydrogenase Active Site: Properties and Oxygen Damage Repair Possibilities. J. Am. Chem. Soc. 2009, 131, 8296-8307.

(5) Wang, S.; Aster, A.; Mirmohades, M.; Lomoth, R.; Hammarström, L. Structural and Kinetic Studies of Intermediates of a Biomimetic Diiron Proton-Reduction Catalyst. *Inorg. Chem.* **2018**, *57*, 768-776.

(6) Aster, A.; Wang, S.; Mirmohades, M.; Esmieu, C.; Berggren, G.; Hammarström, L.; Lomoth, R. Metal Vs. Ligand Protonation and the Alleged Proton-Shuttling Role of the Azadithiolate Ligand in Catalytic H_2 Formation with FeFe Hydrogenase Model Complexes. *Chem. Sci.* **2019**, 10, 5582-5588.

(7) Liu, Y.-C.; Chu, K.-T.; Huang, Y.-L.; Hsu, C.-H.; Lee, G.-H.; Tseng, M.-C.; Chiang, M.-H. Protonation/Reduction of Carbonyl-Rich Diiron Complexes and the Direct Observation of Triprotonated Species: Insights into the Electrocatalytic Mechanism of Hydrogen Formation. *ACS Catal.* **2016**, *6*, 2559-2576.