Supporting information

The Ferrocene Effect: Enhanced Electrocatalytic Hydrogen Production using meso-Tetraferrocenyl porphyrin Palladium (II) and Copper (II) Complexes

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Equation 1.

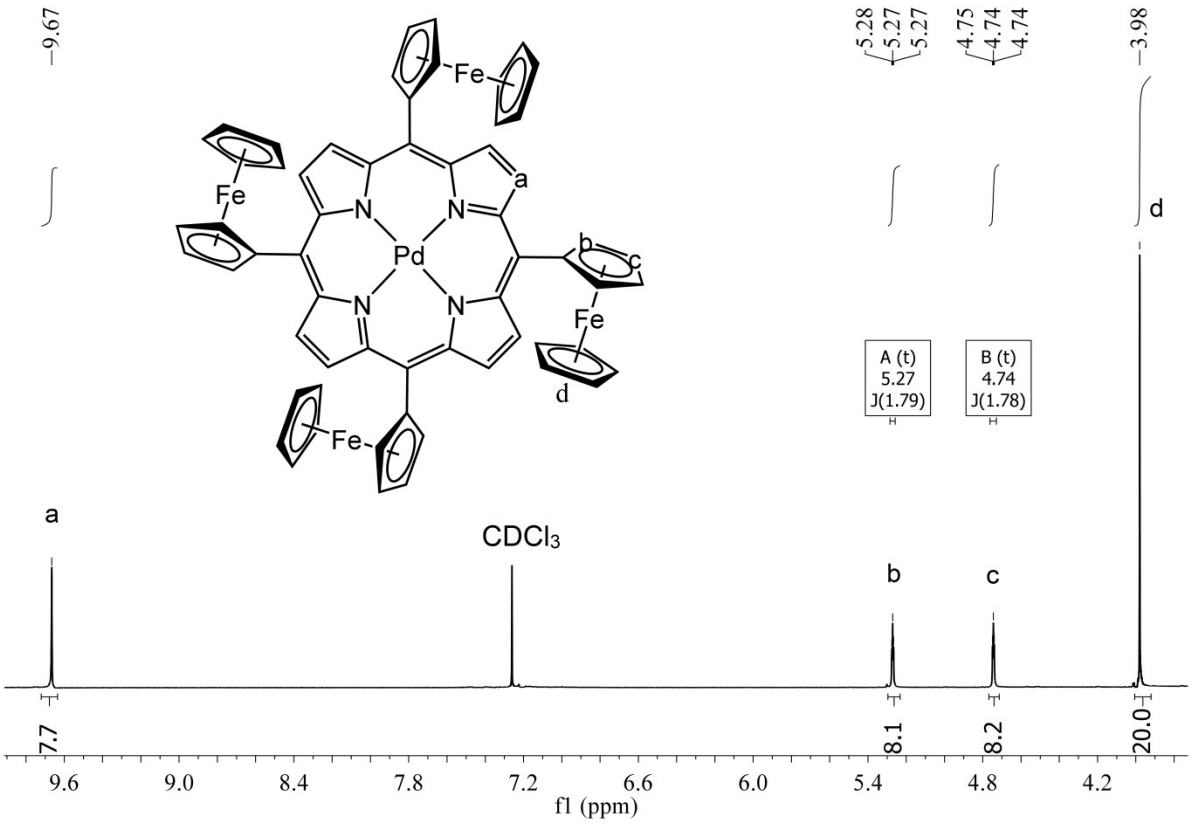
$$E_{1/2} = E_{H^+/H_2}^{o} - \frac{2.303 \times RT}{F} pK_a + \varepsilon_D - \frac{RT}{2F} ln \frac{C_0}{C_{H_2}^{o}}$$

Were $E_{H^+/H_2}^{o} = -0.62\ V$ is the standard potential for the reduction of protons in DMF, R = 8.617 x 10^{-5} is the Boltzmann constant, T – absolute temperature, F = 96485 C mol^{-1} is the Faraday constant, $pK_a = 6 \pm 0.3$ is the dissociation constant of TFA in DMF, $\varepsilon_D = 40\ mV$ is the correction factor which reflects the difference in diffusion coefficients of the acid and H_2, C_0 - the total concentration of acid, $C_{H_2}^{o} = 1.9\ mmol\ L^{-1}$ the saturating concentration of dissolved H_2 under 1 bar H_2.

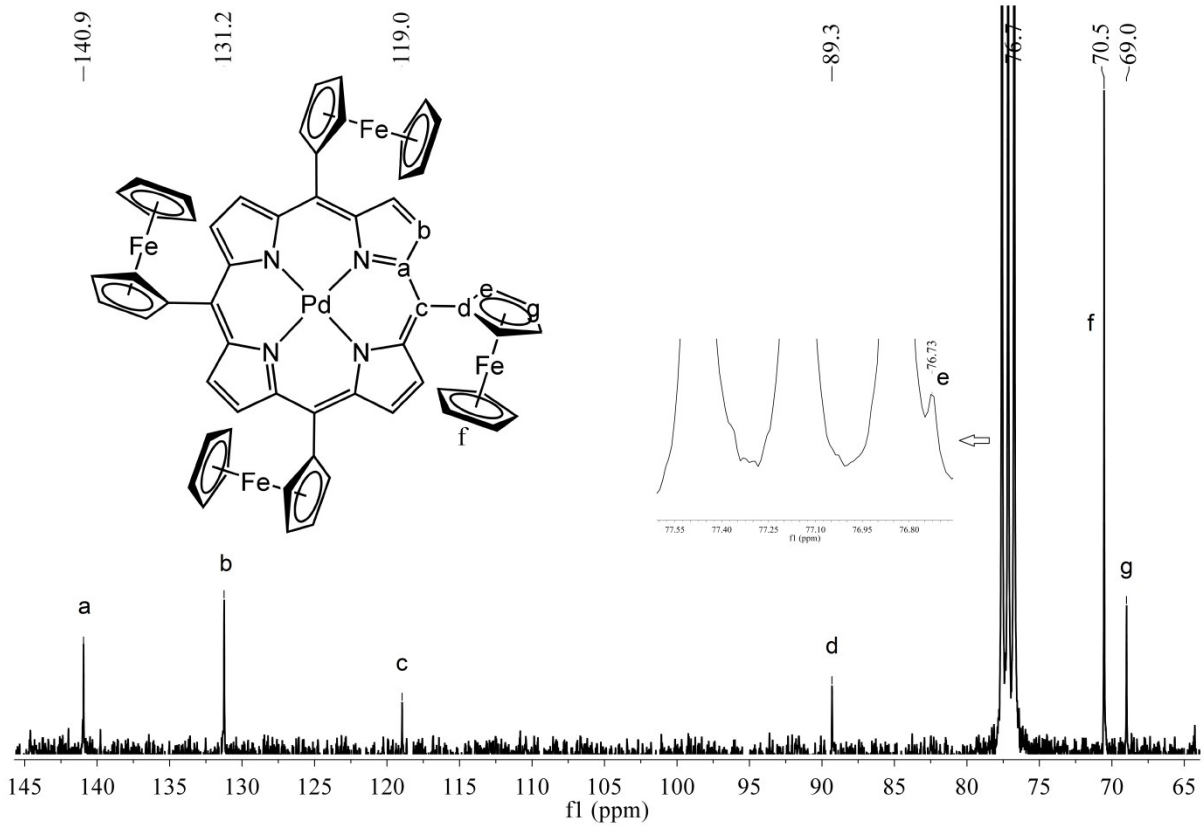
Table. Comparison of selected calculated and observed bond lengths.

Method	Fe-C bond lenghs / Å	Pd-N / Å
B3PW91/3-21G*[a]	2.05 (meso) 2.03 (free)[b]	2.03
X-ray crystallography	2.05[c]	2.009(9)[d]

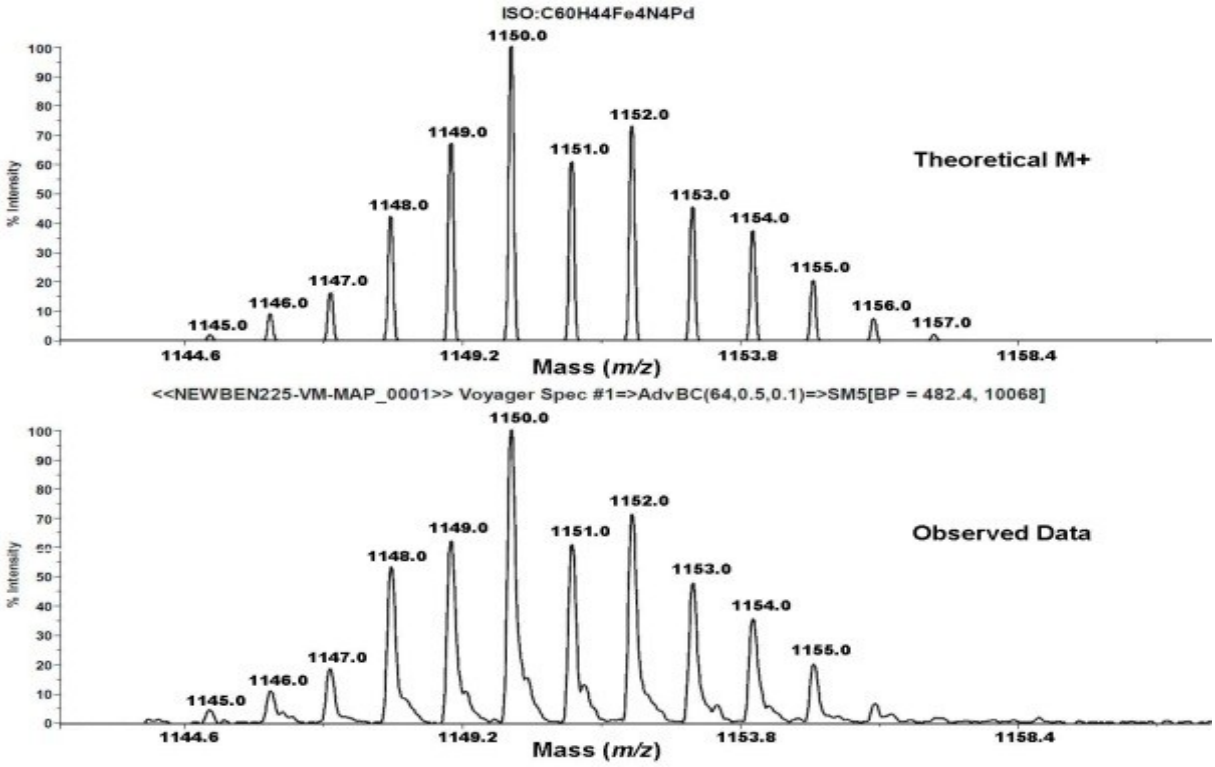
[a]Calculated using Gaussian 09, [b]Average value for the two Cp rings, [c]Taken from Dunitz *et al.* (*Acta. Cryst.* **1956,** 9, 373), [d]Standard deviation in bracket and taken from Fleischer *et al.* (*J. Am. Chem. Soc.,* **1964**, 86, 2342) for palladium(II) tetraphenylporphine.


9.67
5.28
5.27
5.27
4.75
4.74
4.74
3.98
Fe
Fe
Fe
Fe
N
N
N
N
Pd
a
b
c
d
A (t)
5.27
J(1.79)
B (t)
4.74
J(1.78)
a
CDCl3
b
c
d
7.7
8.1
8.2
20.0
9.6
9.0
8.4
7.8
7.2
6.6
6.0
5.4
4.8
4.2
f1 (ppm)

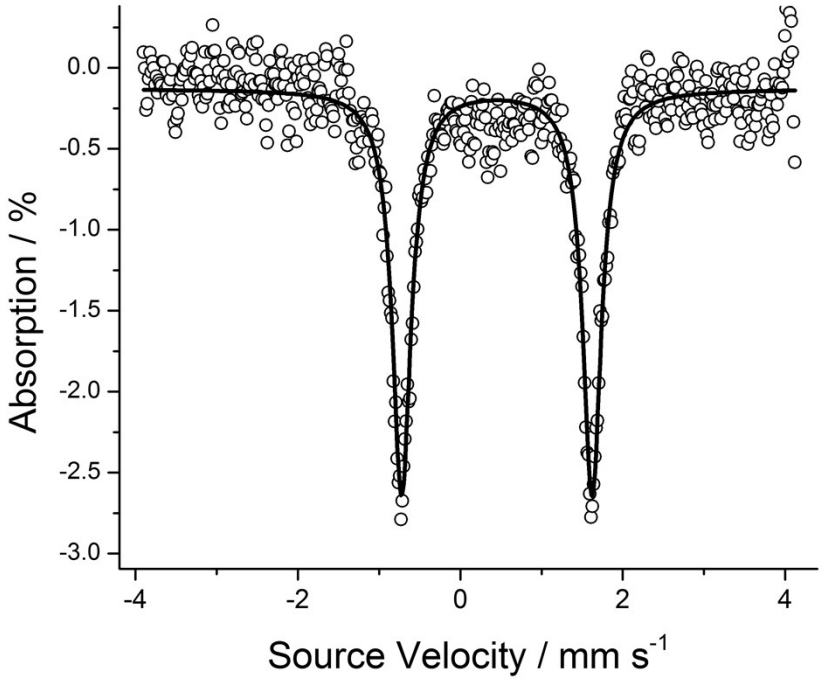
S1. ^{1}H-NMR spectrum of **PdTFcP** in $CDCl_3$.



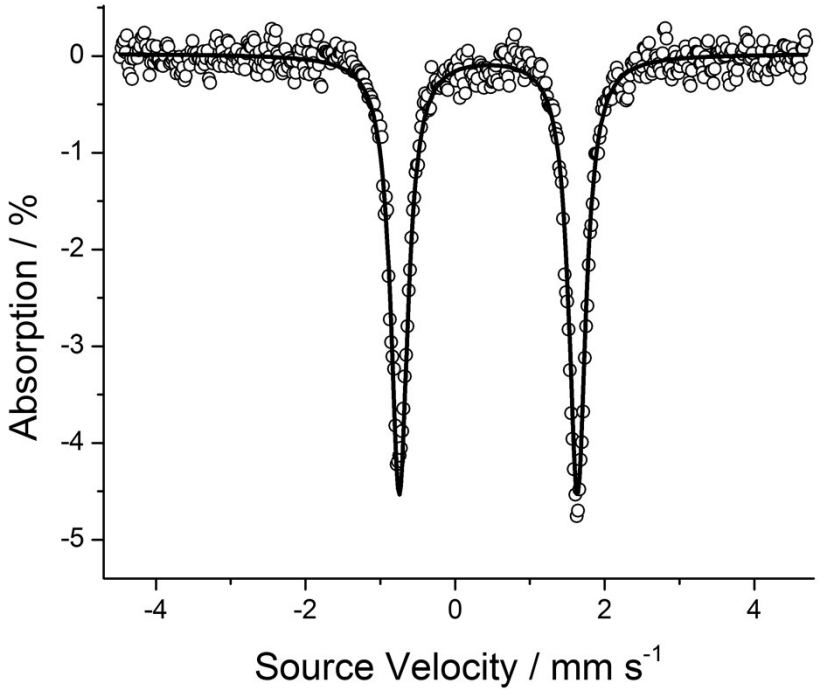
S2. ^{13}C-NMR spectrum of **PdTFcP** in $CDCl_3$.



S3. Maldi-TOF mass spectrum of **PdTFcP**.



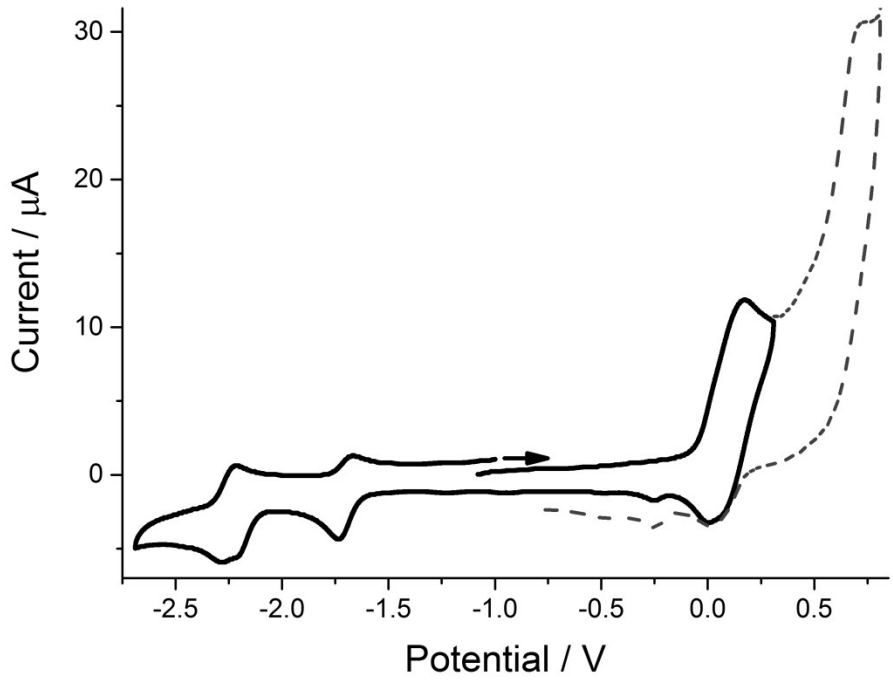
S4. The room temperature ^{57}Fe Mössbauer spectrum for **CuTFcP**.



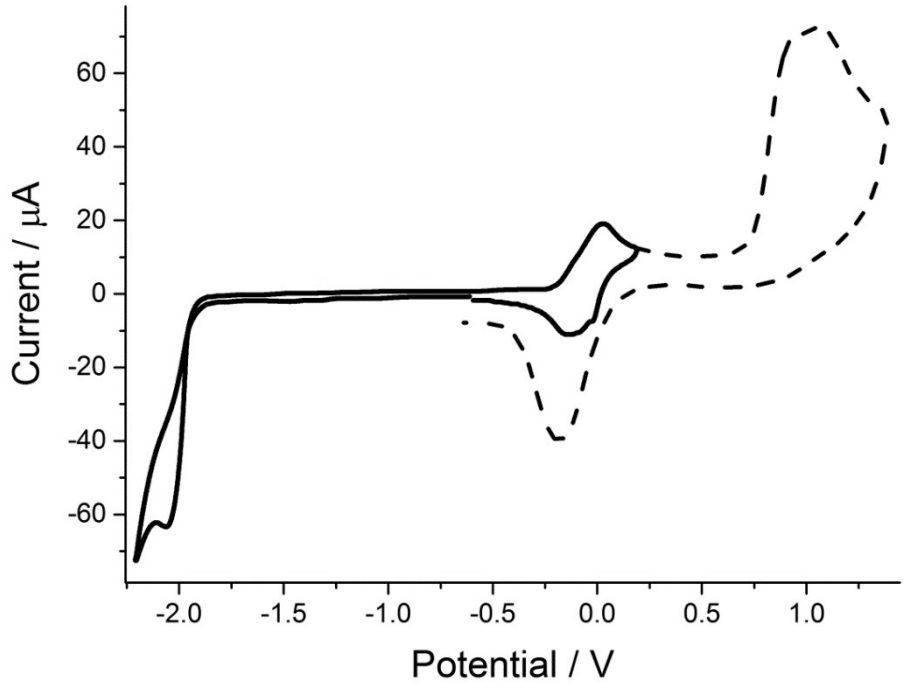
S5. Room temperature ^{57}Fe Mössbauer spectrum for **PdTFcP**.

Compound	Temp, K	Isomer Shift δ, mm/s	Quadrupole Splitting ΔEQ, mm/s
PdTFcP	7 K	0.55	2.39
	293 K	0.44	2.34
CuTFcP	293 K	0.45	2.35
H_2TFcP	293 K	0.45	2.35
Fc	293 K	0.45	2.39

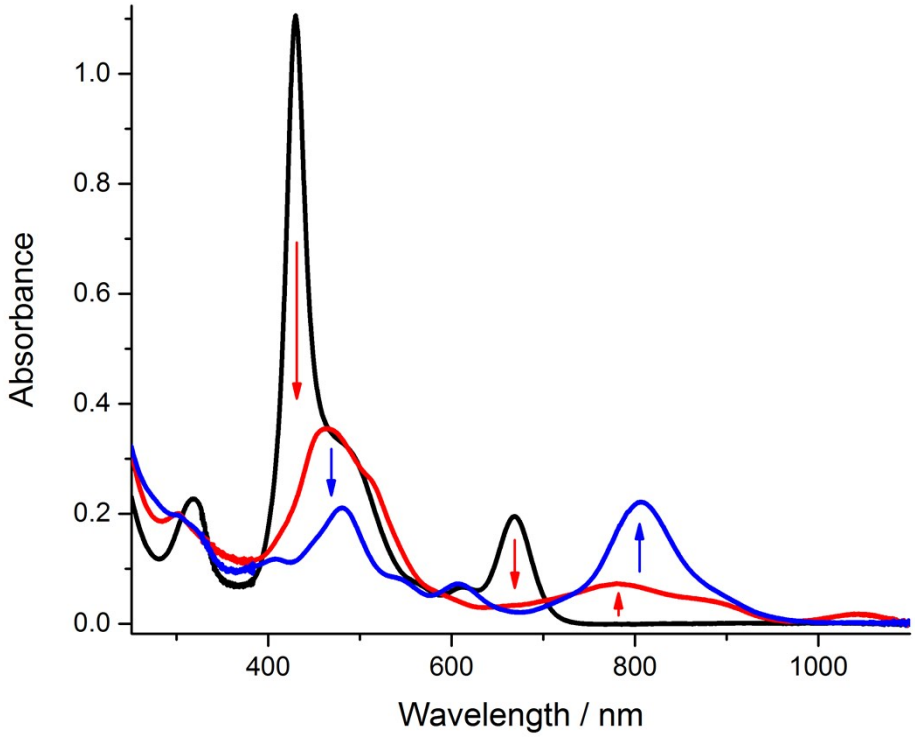
S6. Experimental Mössbauer parameters for **PdTFcP**, **CuTFcP** and reference **H_2TFcP**, **Fc**.



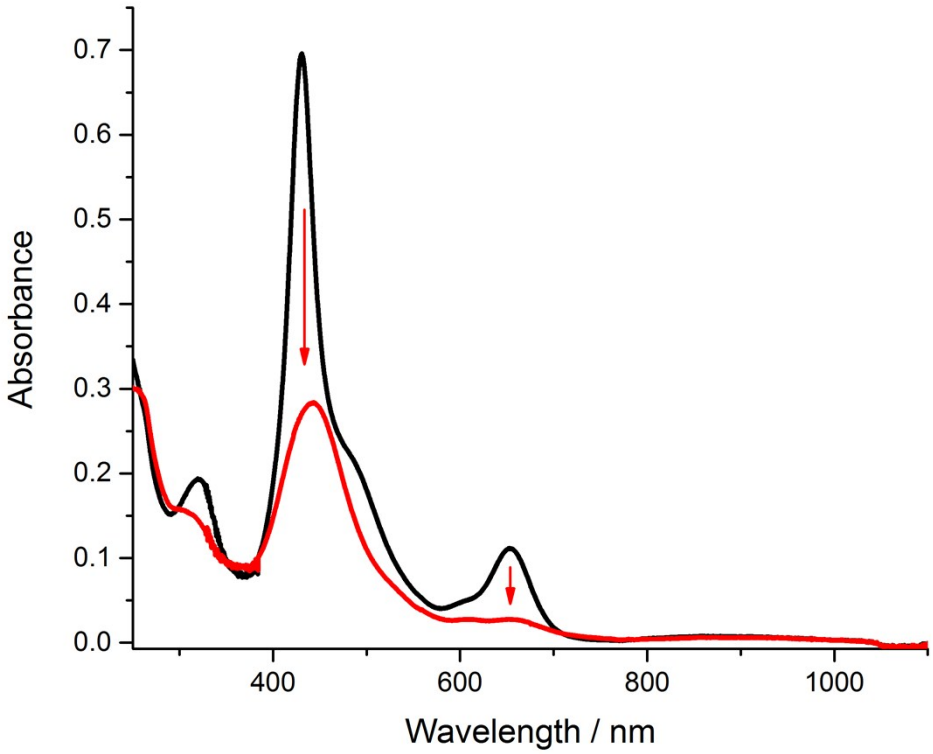
S6. Cyclic voltammogram recorded for **CuTFcP** in DMF containing 0.2 M TBATFB vs Fc^{+}/Fc. The dashed line shows the additional irreversible oxidation peak when the potential window was increased.



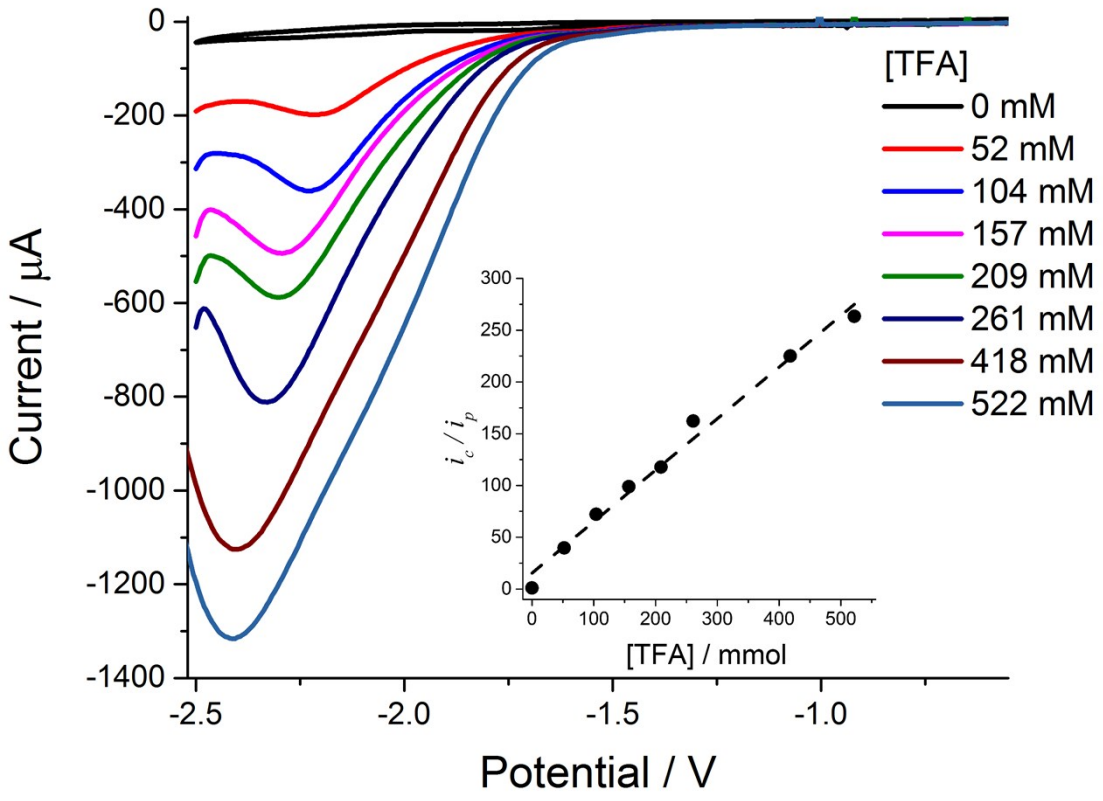
S7. Cyclic voltammogram recorded for **PdTFcP** in DCM containing 0.2 M TBATFB vs Fc^{+}/Fc. The dashed line shows the additional irreversible oxidation peak when the potential window was increased.



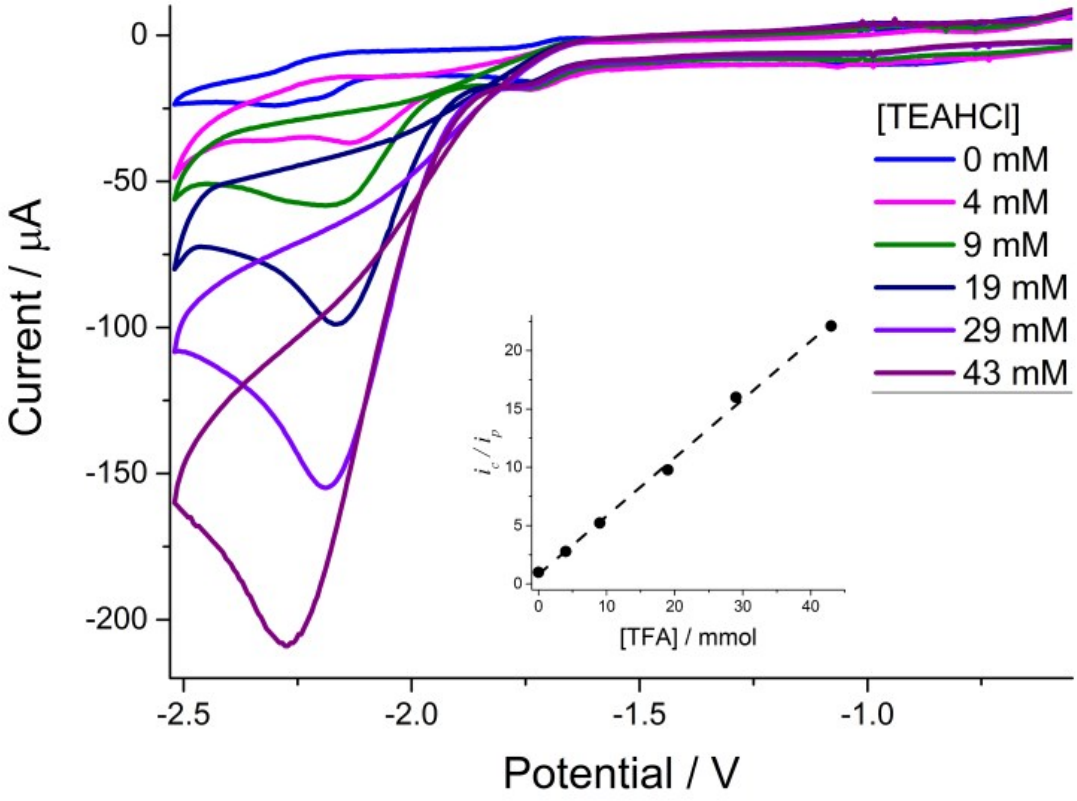
S8. Electronic absorption spectra for **CuTFcP** in THF at the start (black) and after reduction at -1.3 V (red) and -1.7 V (blue) vs Ag wire.



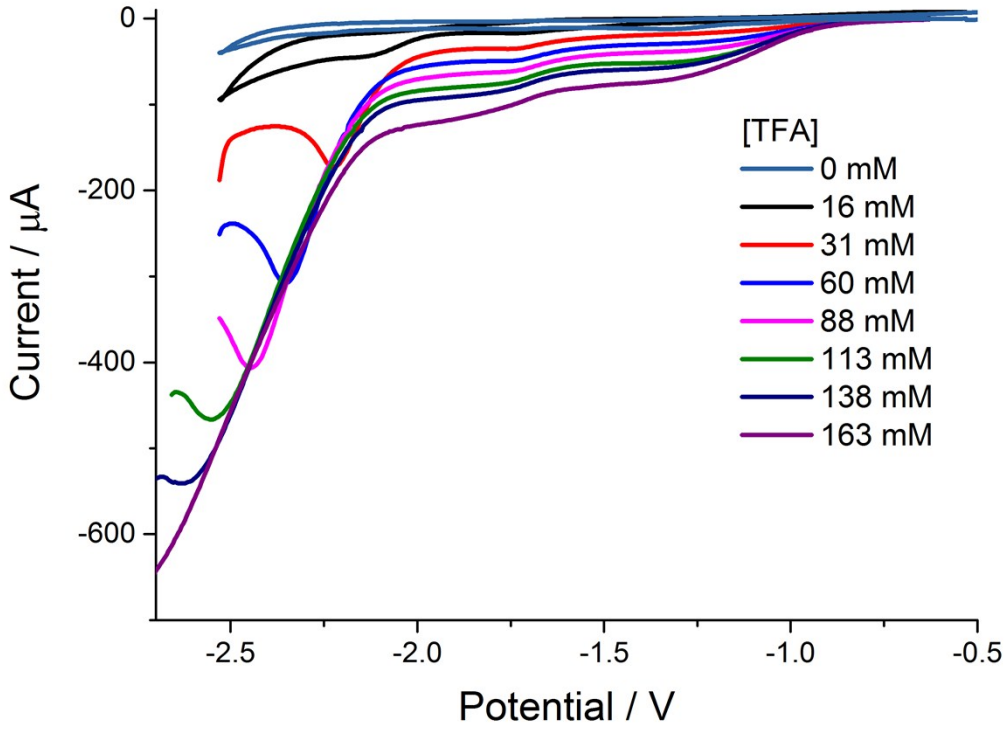
S9. Electronic absorption spectra for **PdTFcP** in THF/DMF at the start (black) and after oxidation at +0.9 V (red) vs Ag wire.



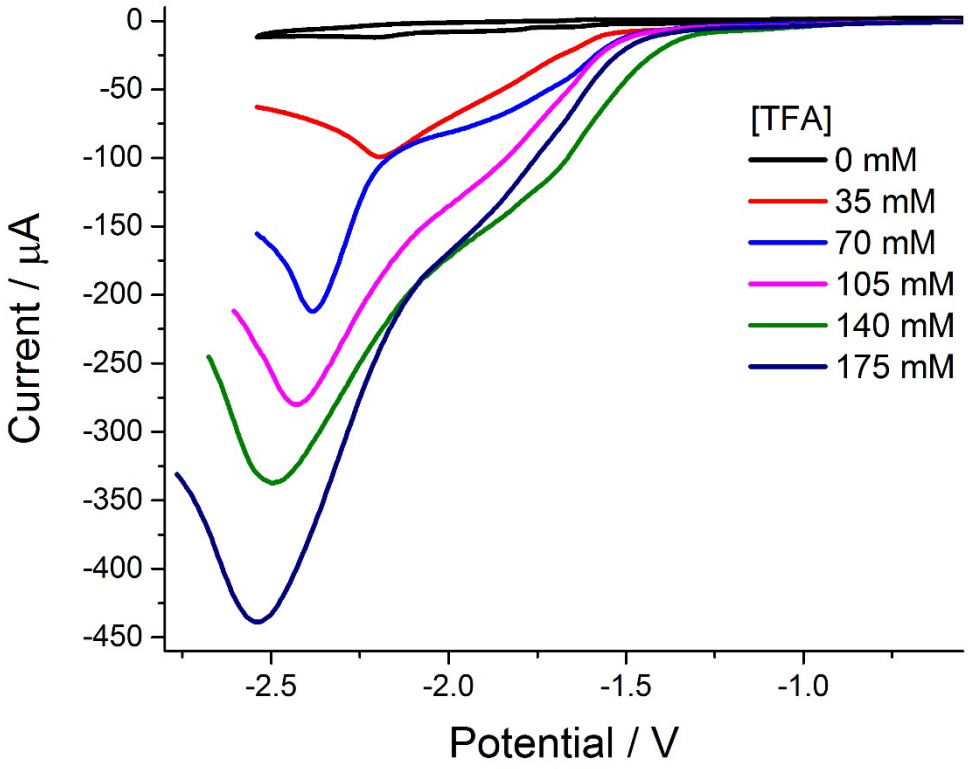
S10. Selected linear sweep voltammograms for **CuTFcP** (1 mM) at a glassy carbon electrode in DMF in the presence of increasing quantities of TFA. Voltammograms show that the addition of hydrochloride leads to the appearance of an irreversible wave of increasing amplitude corresponding to the reduction of protons catalyzed by the complex. Conditions: T = 298 K, scan rate 100 mVs^{-1}. Supporting electrolyte: 0.2 M TBATFB. Insert shows relationship between i_c/i_p and concentration of acid.



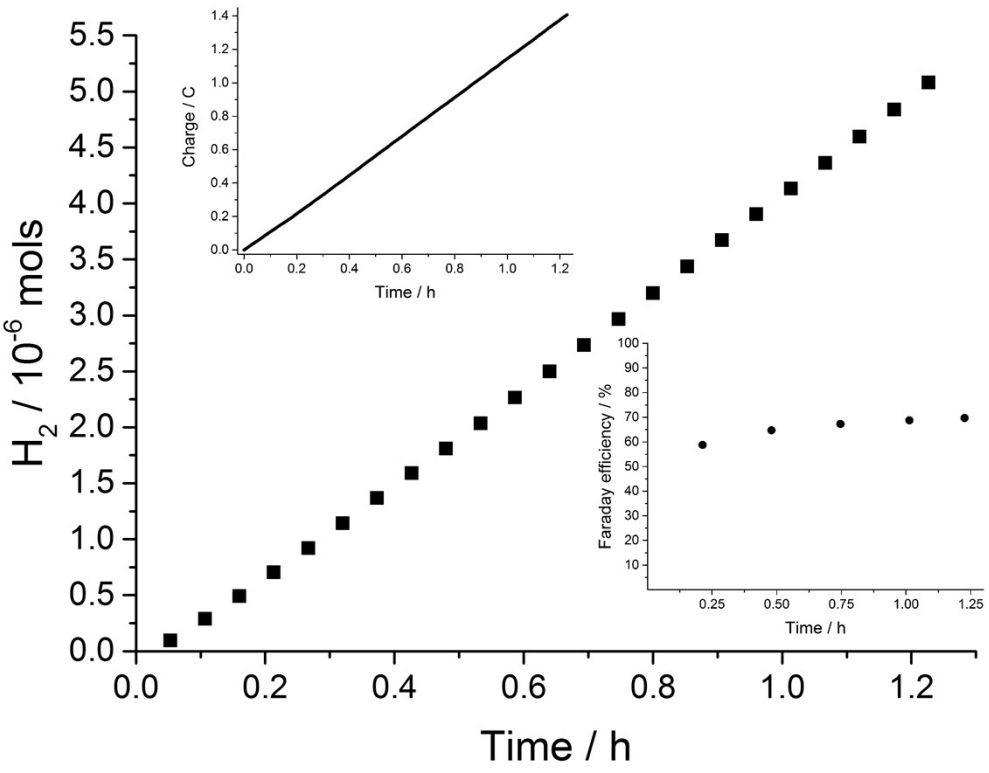
S11. Selected cyclic voltammograms for **CuTFcP** (1 mM) at a glassy carbon electrode in DMF in the presence of increasing quantities of TEAHCl. Voltammograms show that the addition of hydrochloride leads to the appearance of an irreversible wave of increasing amplitude corresponding to the reduction of protons catalyzed by the complex. Conditions: T = 298 K, scan rate 100 mVs^{-1}. Supporting electrolyte: 0.2 M TBATFB. Insert shows relationship between i_c/i_p and concentration of acid.



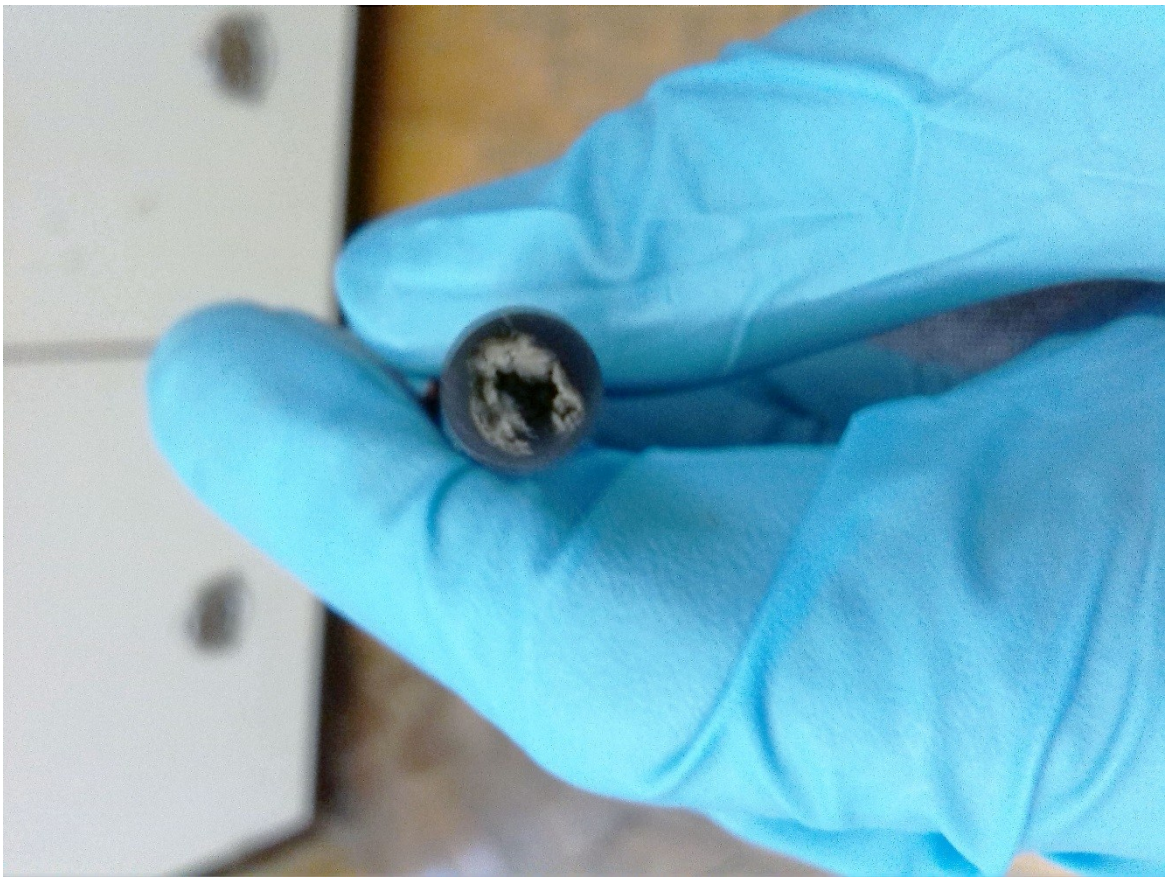
S12. Selected linear sweep voltammograms for **NiTFcP** (1 mM) at a glassy carbon electrode in dry DMF in the presence of increasing quantities of TFA. Voltammograms show that the addition of acid leads to the appearance of an irreversible wave of increasing amplitude corresponding to the reduction of TFA catalyzed by the complex. Conditions:T = 298 K, scan rate = 100 mV s^{-1}. Supporting electrolyte: 0.2 M TBATFB.



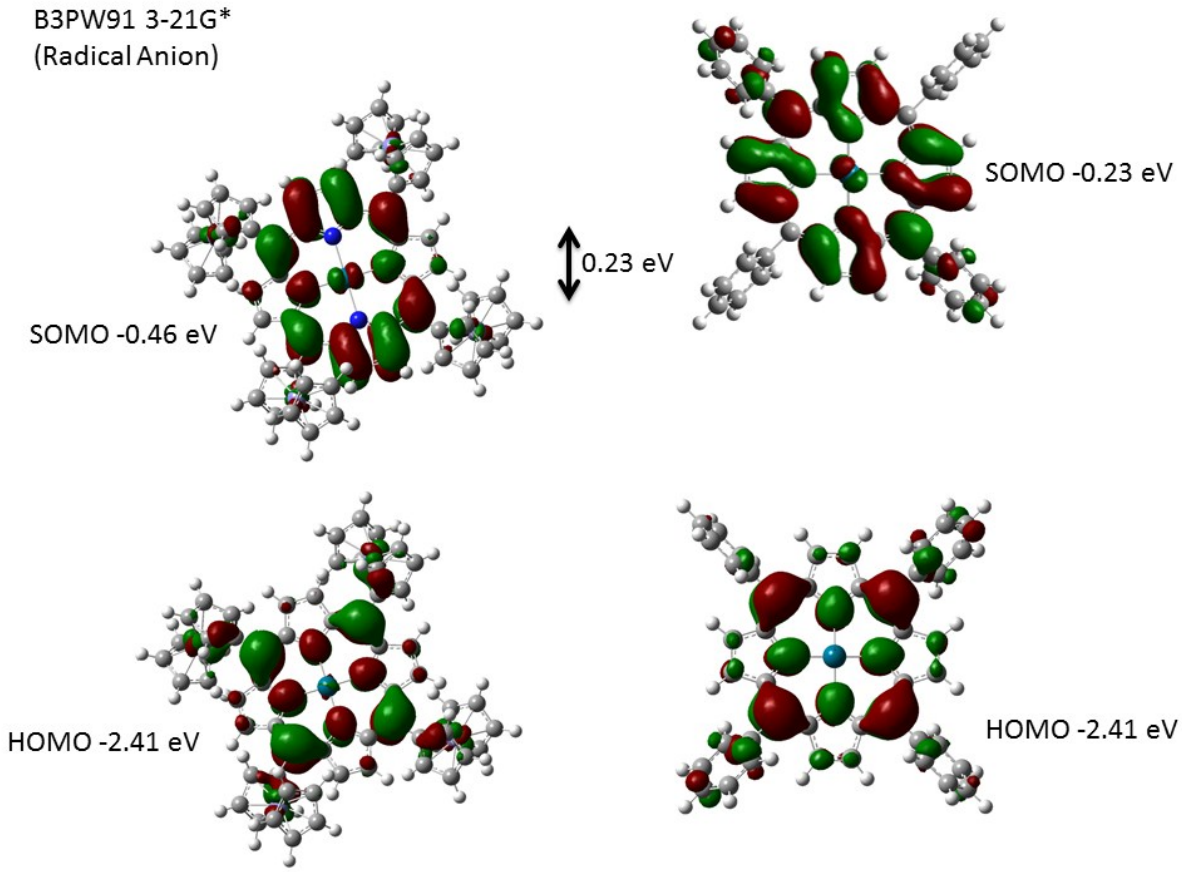
S13. Selected linear sweep voltammograms for **PdTPP** (1 mM) at a glassy carbon electrode in dry DMF in the presence of increasing quantities of TFA. Voltammograms show that the addition of acid leads to the appearance of an irreversible wave of increasing amplitude corresponding to the reduction of TFA catalyzed by the complex. Conditions:T = 298 K, scan rate = 100 mV s^{-1}. Supporting electrolyte: 0.2 M TBATFB.



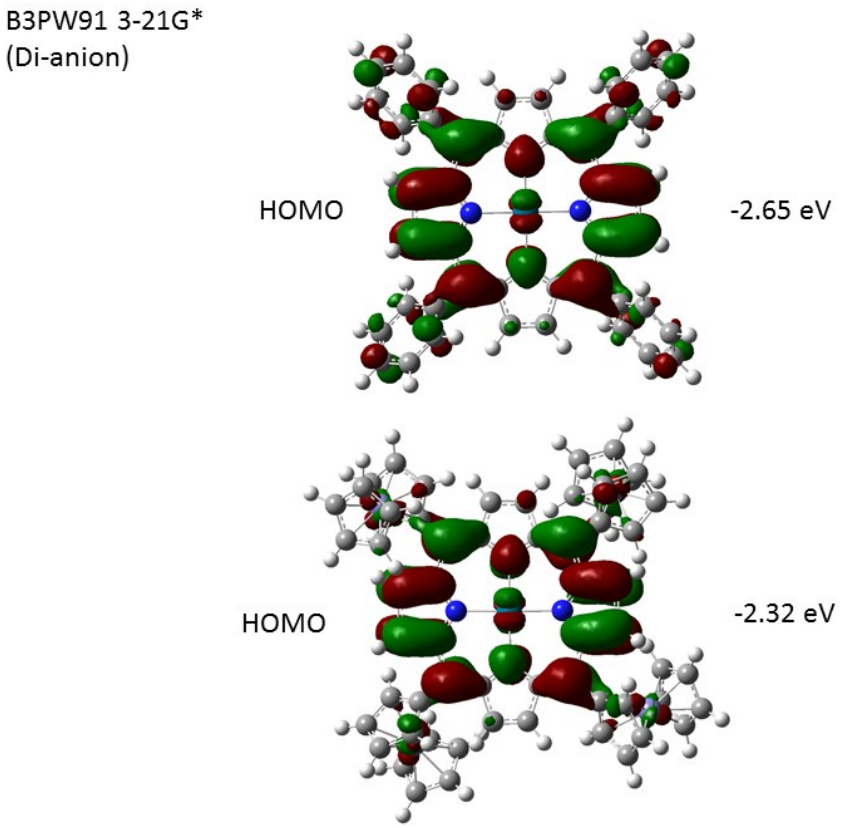
S14. Electrocatalytic hydrogen production vs time, charge vs time (left top insert) and Faradaic efficiency vs time (right bottom insert) by applying -1.5 V vs SCE to a glassy carbon electrode in 0.2 M $TBABF_4$ solution of DMF containing 50 mM TFA and 0.1 mM **PdTFcP**.



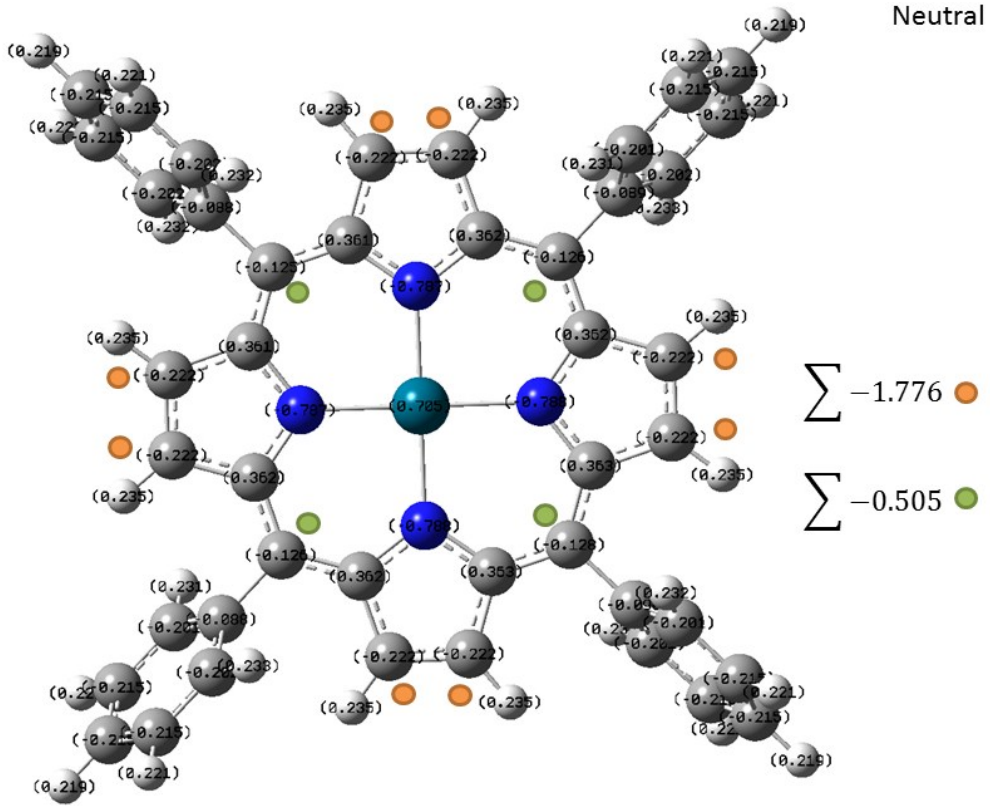
S15. Picture of the glassy carbon electrode after H_2 production using **PdTFcP** and TFA as the acid source.



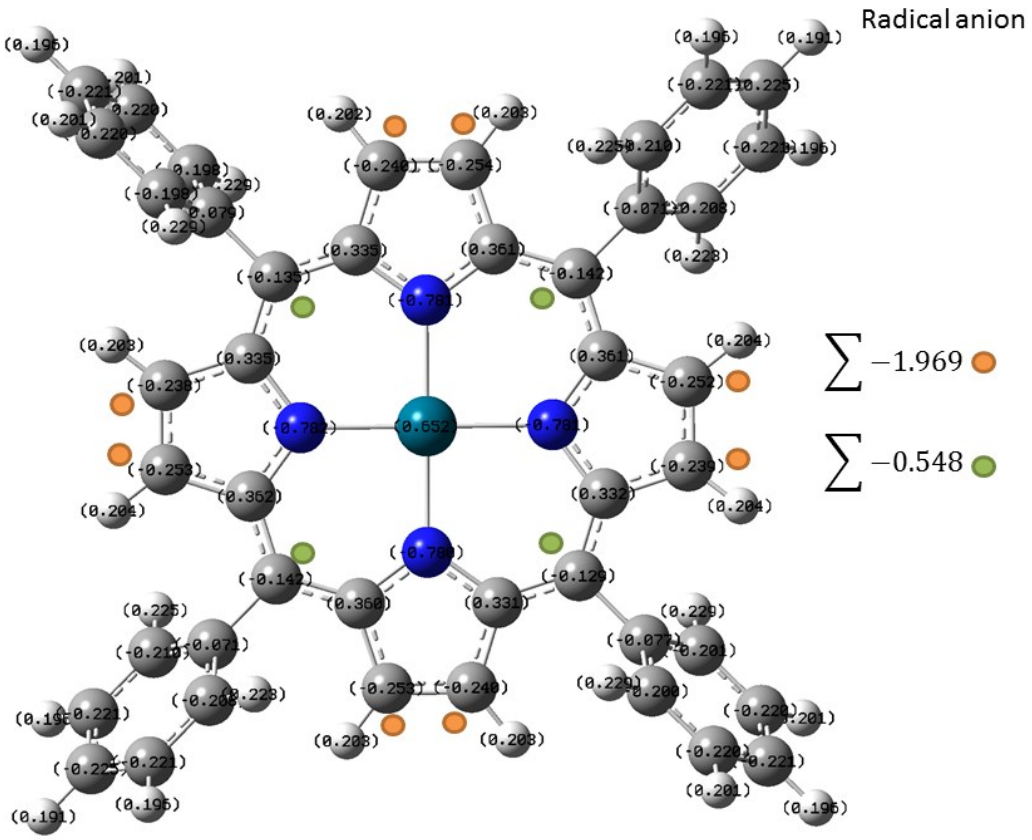
S16. Computer calculated molecular orbitals for **PdTFcP**$^{\bullet-}$ (left) and **PdTPP**$^{\bullet-}$ (right) using the B3PW91 function and a 3-21G* basis set.



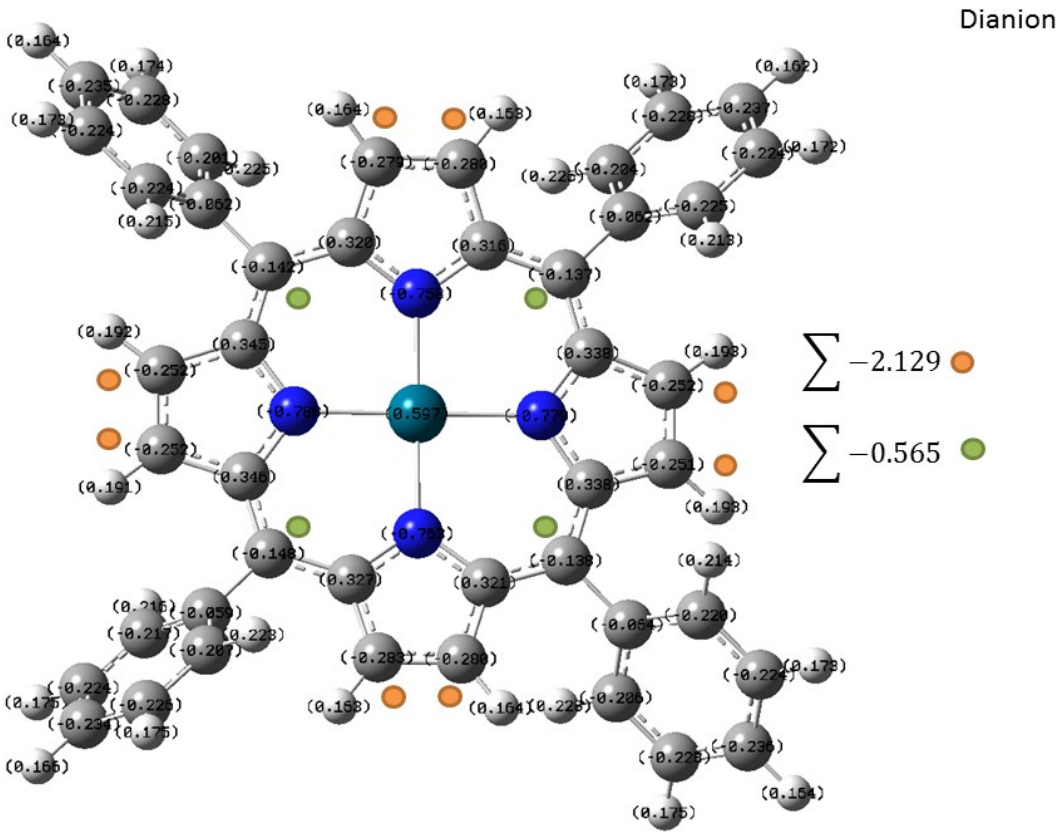
S17. Computer calculated HOMOs for **PdTPP**$^{2-}$ (top) **PdTFcP**$^{2-}$ (bottom) using the B3PW91 function and a 3-21G* basis set.



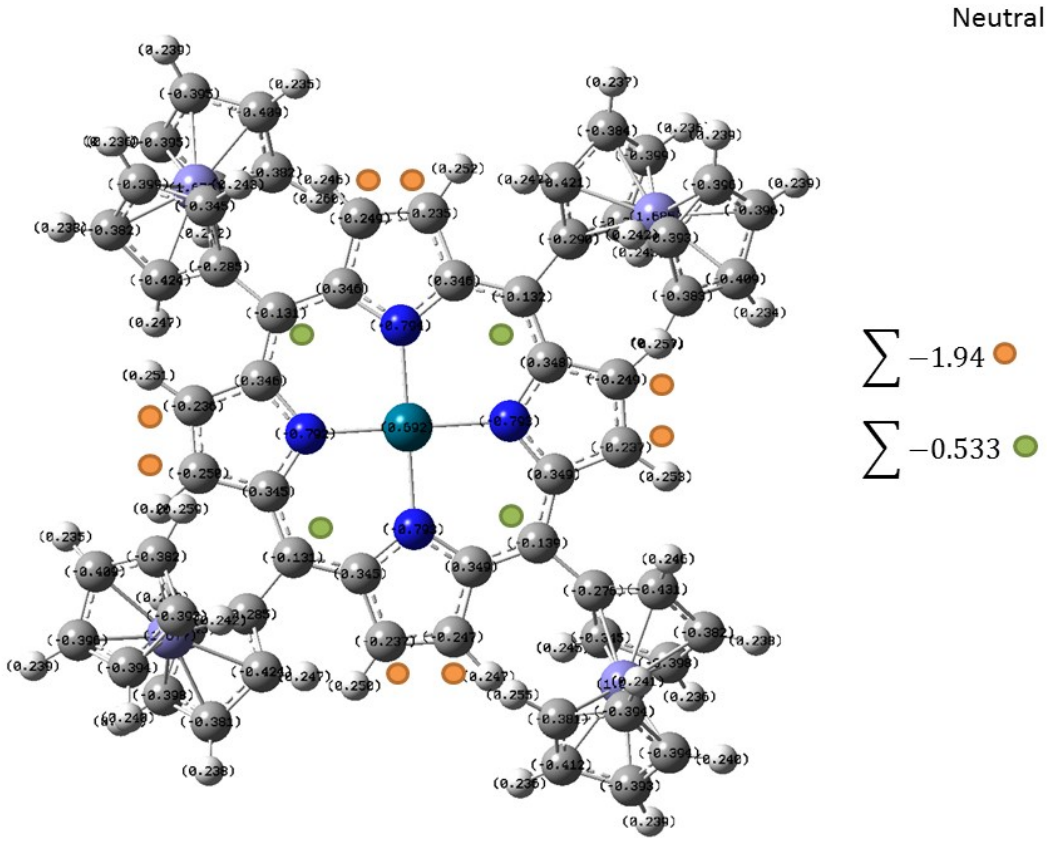
S18. Computer calculated Mulliken Charges (MC) for **PdTPP** using the B3PW91 function and a 3-21G* basis set.



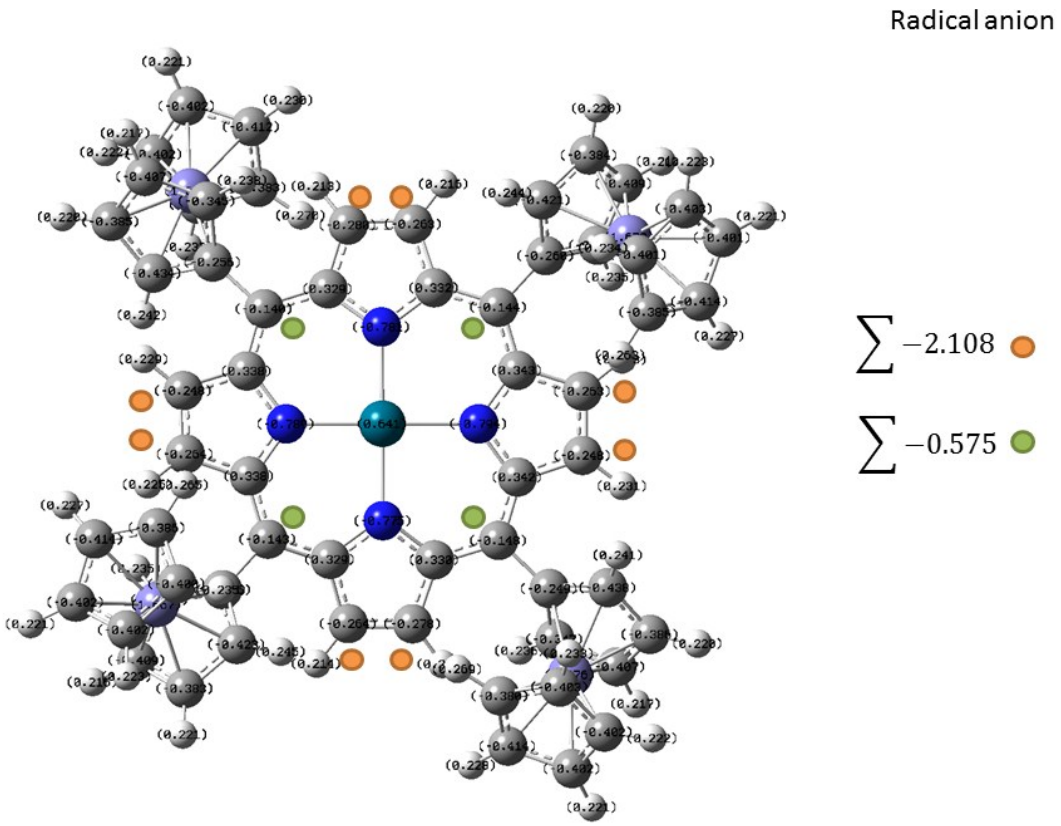
S19. Computer calculated Mulliken Charges (MC) for **PdTPP**$^{\bullet-}$ using the B3PW91 function and a 3-21G* basis set.



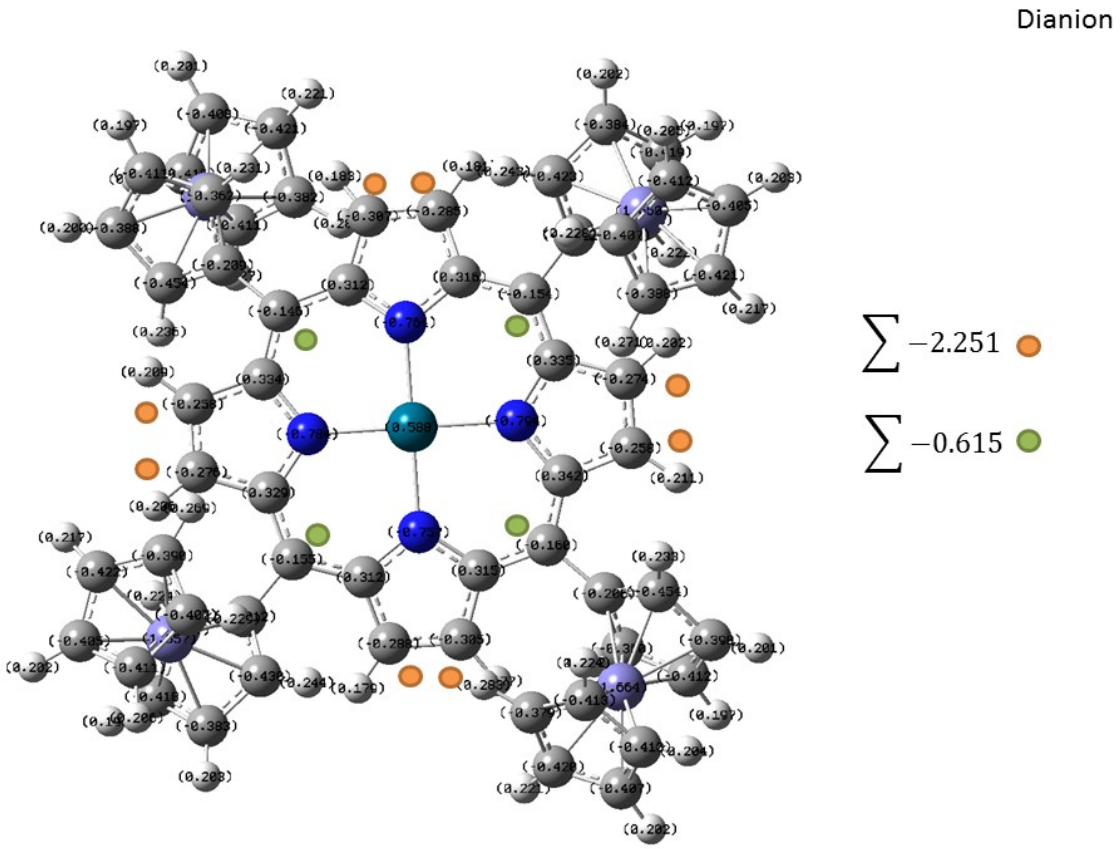
S20. Computer calculated Mulliken Charges (MC) for **PdTPP^{2-}** using the B3PW91 function and a 3-21G* basis set.



S21. Computer calculated Mulliken Charges (MC) for **PdTFcP** using the B3PW91 function and a 3-21G* basis set.



S22. Computer calculated Mulliken Charges (MC) for **PdTFcP**$^{\bullet-}$ using the B3PW91 function and a 3-21G* basis set.



S23. Computer calculated Mulliken Charges (MC) for **PdTFcP^{2-}** using the B3PW91 function and a 3-21G* basis set.