

Supporting Information for

Synthesis, Characterization, and Hydrogen Evolution Activity of Metallo-*meso*-(4-fluoro-2,6-dimethylphenyl)porphyrin Derivatives

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A. NMR Spectra

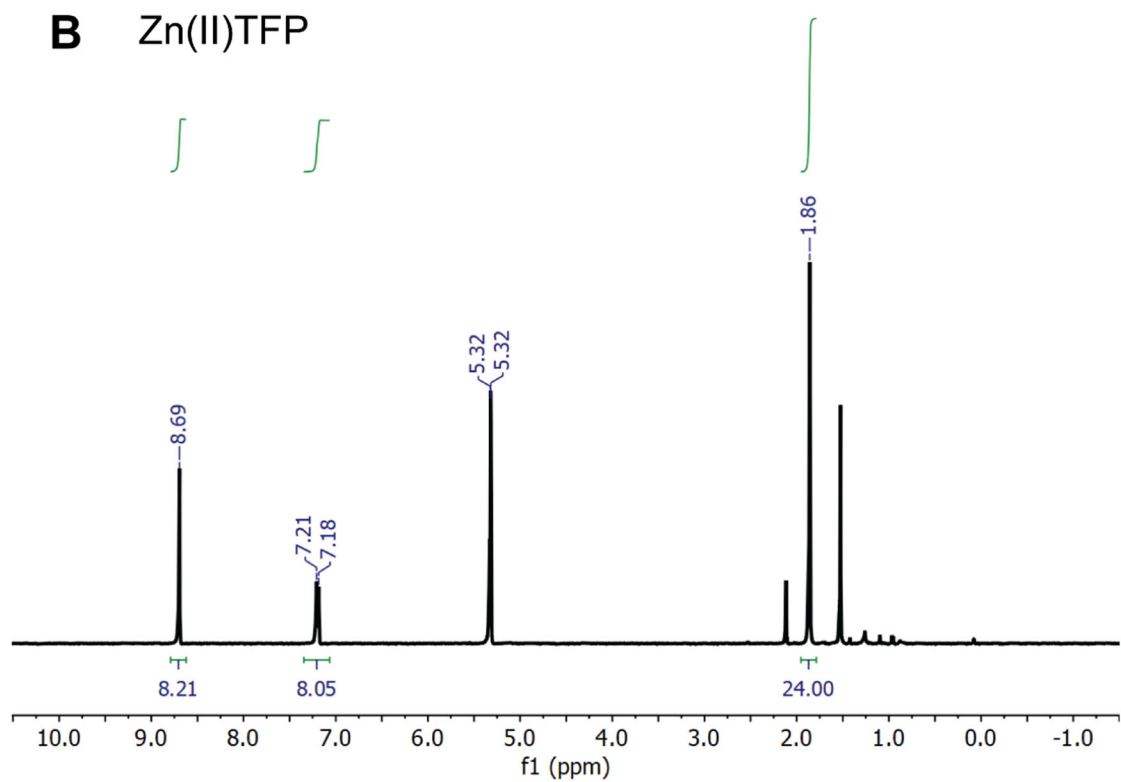
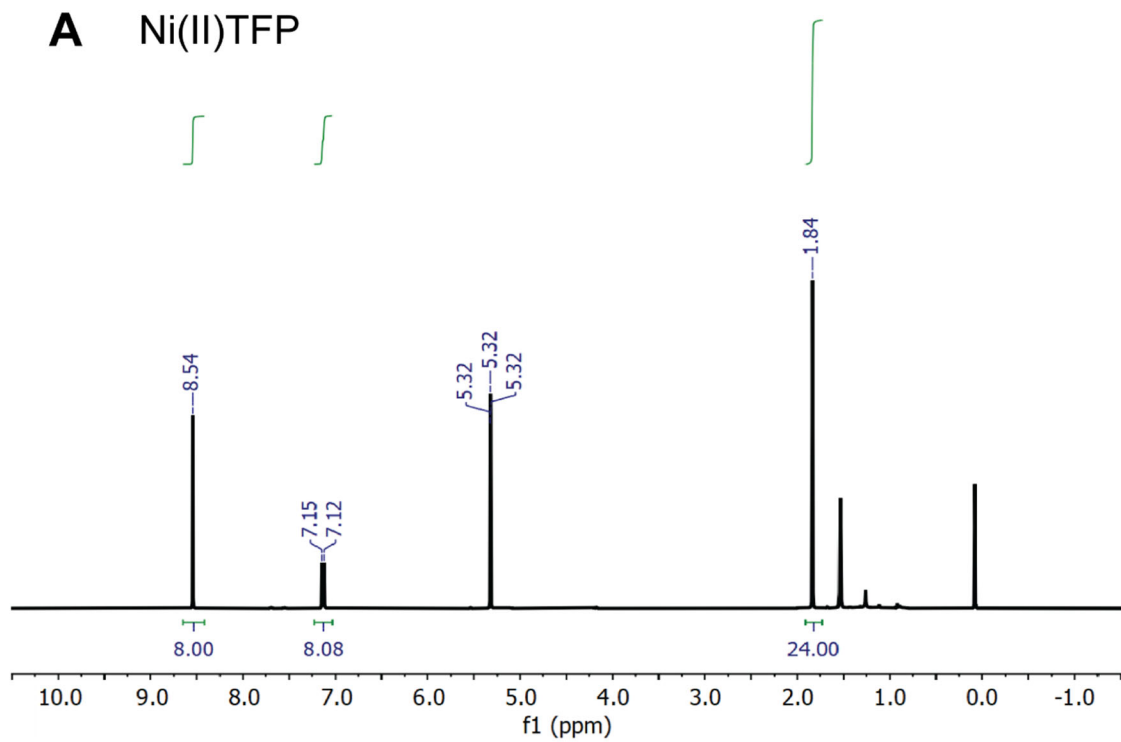


Figure S1. ^1H NMR spectra of (A) Ni(II)TFP and (B) Zn(II)TFP in DCM-d_2 solvent at 25 °C.

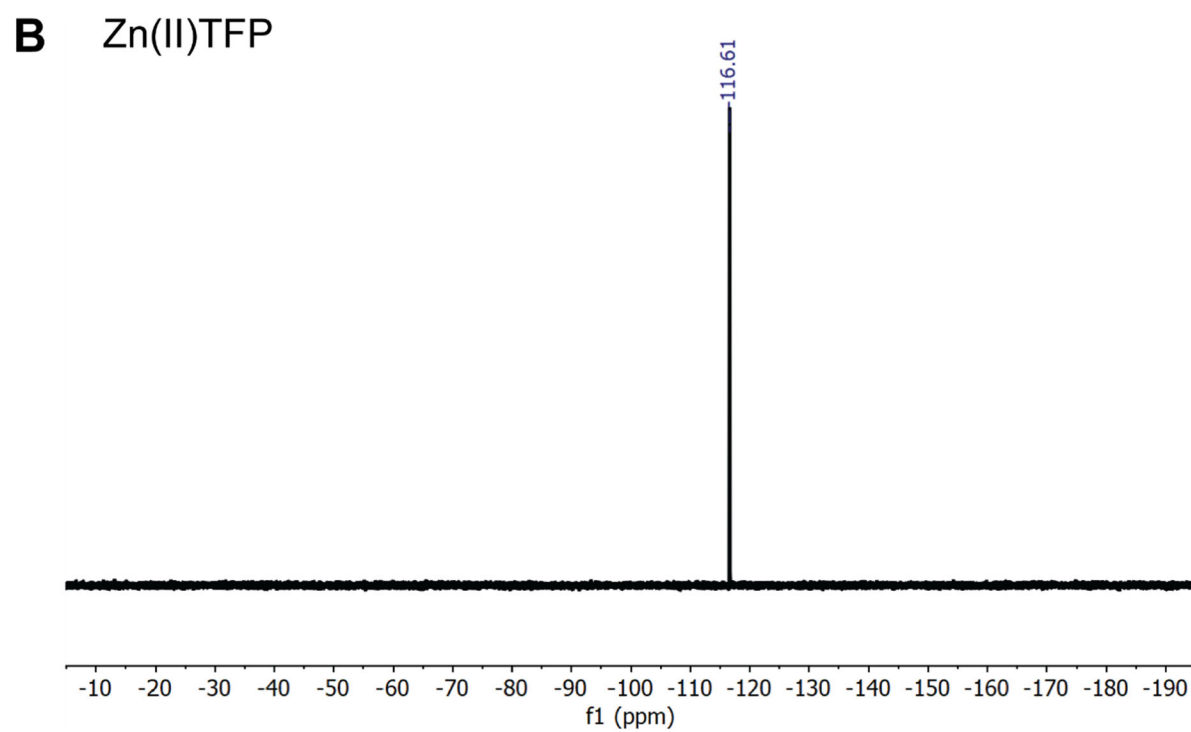
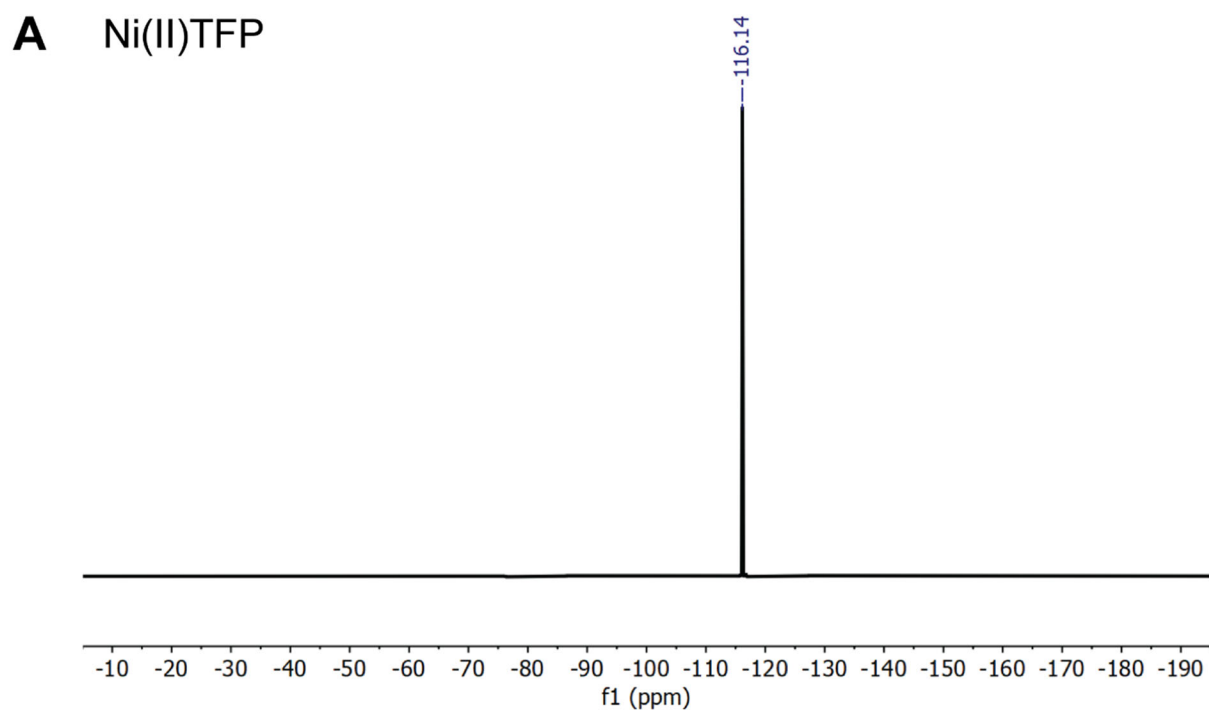


Figure S2. ^{19}F NMR spectra of (A) Ni(II)TFP and (B) Zn(II)TFP in DCM- d_2 solvent at 25 °C.

B. Crystallography

Table S1. Crystal data and structure refinement for 2H-TFP.

| | |
|---|---|
| Empirical formula | C ₅₂ H ₄₂ F ₄ N ₄ |
| Formula weight | 798.89 |
| T (K) | 100(2) |
| λ (Å) | 1.54178 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| a (Å) | 9.2143(2) |
| b (Å) | 12.7406(3) |
| c (Å) | 12.6200(3) |
| α (°) | 85.1670(10) |
| β (°) | 73.2420(10) |
| γ (°) | 71.7860(10) |
| V (Å ³) | 1347.51(5) |
| Z | 1 |
| ρ_{calcd} (mg/m ³) | 0.984 |
| μ (mm ⁻¹) | 0.548 |
| θ range for data collection (°) | 3.652 to 66.642 |
| Index ranges | $-10 \leq h \leq 10, -15 \leq k \leq 15, 0 \leq l \leq 15$ |
| Reflections collected | 4572 |
| Completeness to θ_{max} | 94.7% |
| Data/restraints/parameters | 4572 / 0 / 278 |
| GOF on F^2 | 1.086 |
| R1 | 0.0528 |
| wR2 | 0.1666 |
| Largest diff. peak, hole (e Å ⁻³) | 0.23, -0.21 |

C. Photophysics

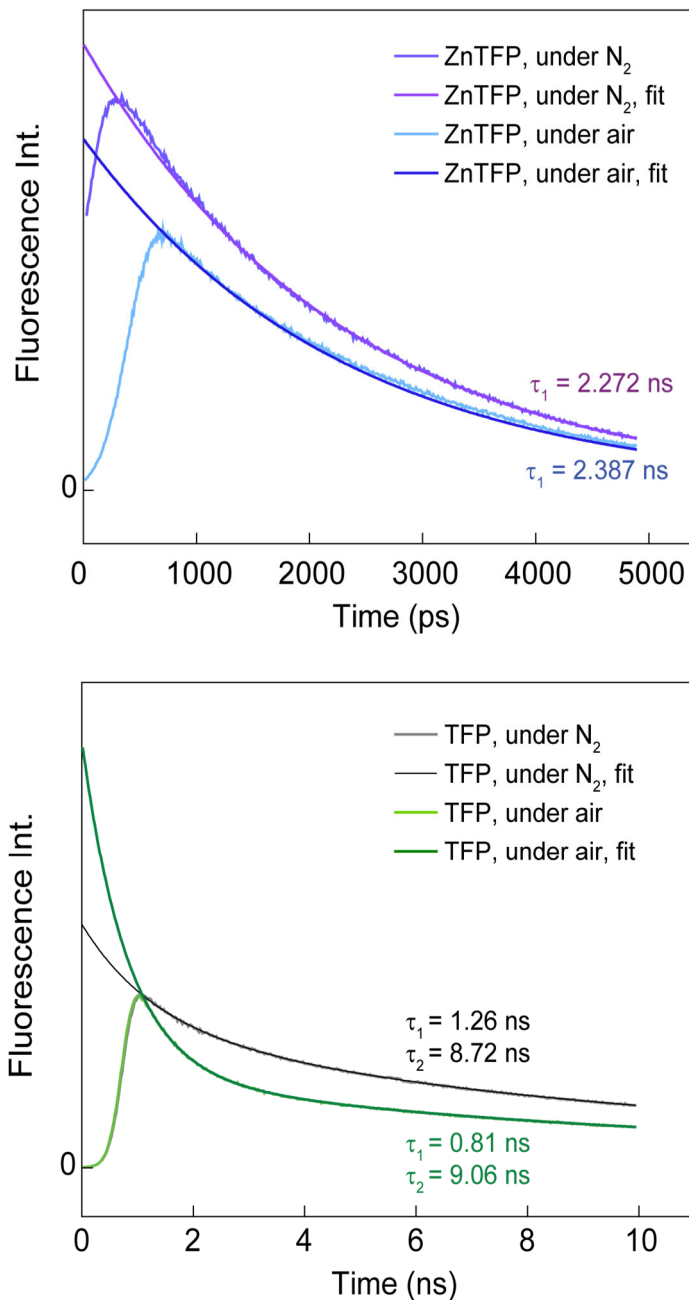


Figure S3. Lifetime decays of (top) Zn(II)TFP and (bottom) 2H-TFP emission in CH₂Cl₂ under nitrogen and in the presence of air. The observed decay “fit” traces are monophasic for Zn(II)TFP and biphasic for 2H-TFP.

D. Electrochemistry

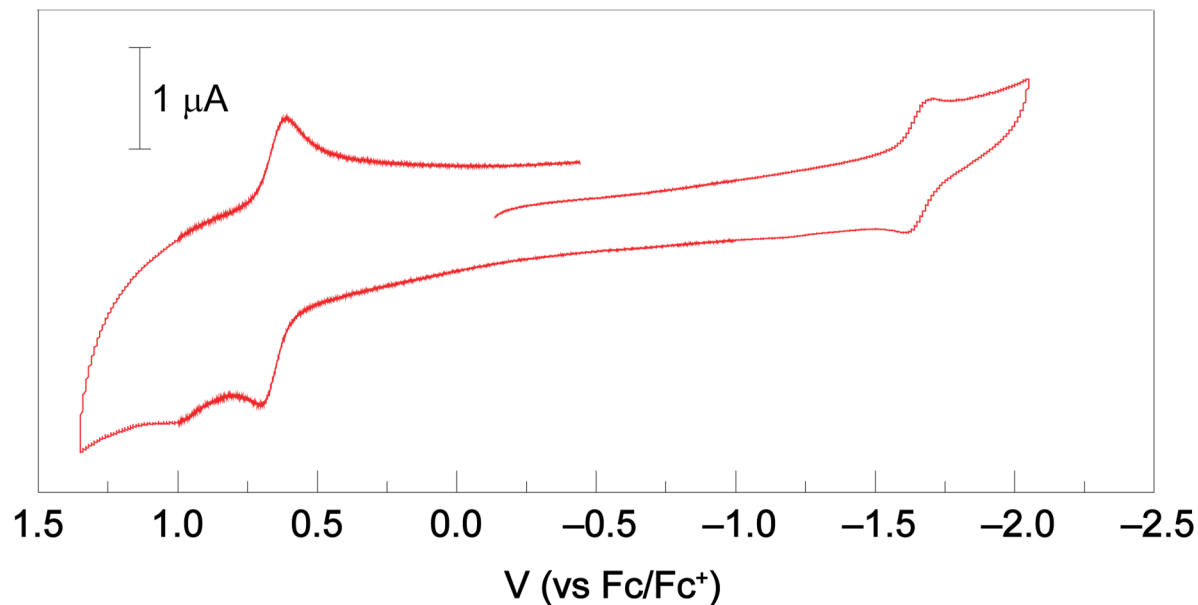


Figure S4. Cyclic voltammogram of Ni(II)TFP in CH₃CN. CV was recorded with a glassy carbon button (3 mm diameter) working electrode, Pt auxiliary electrode and Ag wire reference electrode at a scan rate of $v = 100 \text{ mV s}^{-1}$.

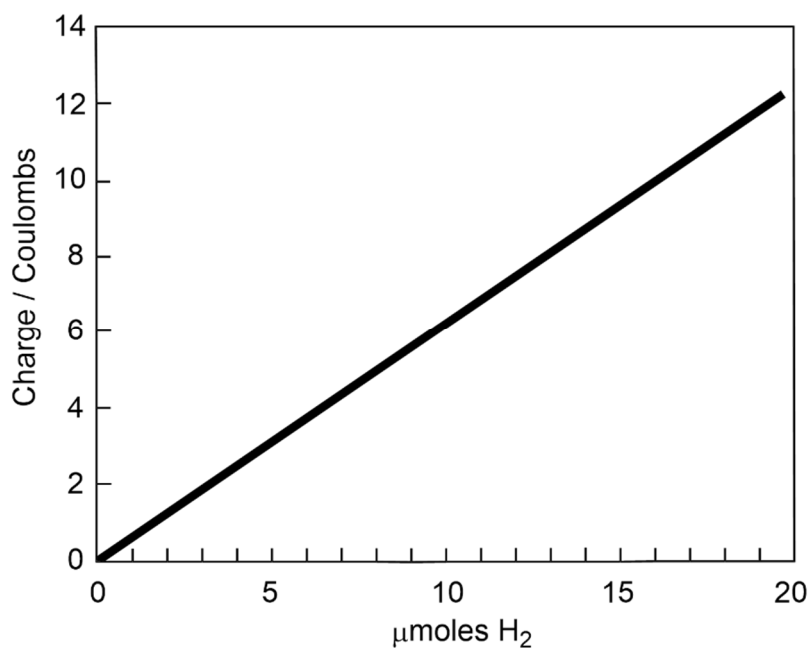


Figure S5. Plot of charge versus moles of H₂ generated by bulk electrolysis in conventional H-cell capped with rubber septums.

E. HER Catalysis

Table S2. Parameters obtained from fits of linear scan voltammogram traces.

| [BzOH] / equiv | [BzOH] / mM | i_{pl} / A^a | $TOF_{max} / s^{-1}{}^b$ | $k_{app} / M^{-1} s^{-1}{}^c$ |
|----------------|-------------|-----------------------|--------------------------|-------------------------------|
| 2 | 1.2 | 3.63×10^{-5} | 7.87 | 6.56×10^3 |
| 4 | 2.4 | 4.79×10^{-5} | 13.7 | 5.70×10^3 |
| 6 | 3.6 | 5.83×10^{-5} | 20.3 | 5.63×10^3 |
| 8 | 4.8 | 6.51×10^{-5} | 25.3 | 5.28×10^3 |

^a Current values, i , estimated from LSV traces at the inflection point prior to increase in background current of LSV traces. Current values were taken from LSV traces corrected for capacitive current at -1.0 V vs Fc⁺/Fc. ^b Calculated from eq (2) in main text for $S = 0.0707$ cm², $C_{Cu}^0 = [Cu(II)TFP] = 0.6$ mM and the diffusion constant for Cu(II)TFP to be $D_{Cu} = 5 \times 10^{-6}$ cm² s⁻¹. ^c Calculated from eq (3) in main text.

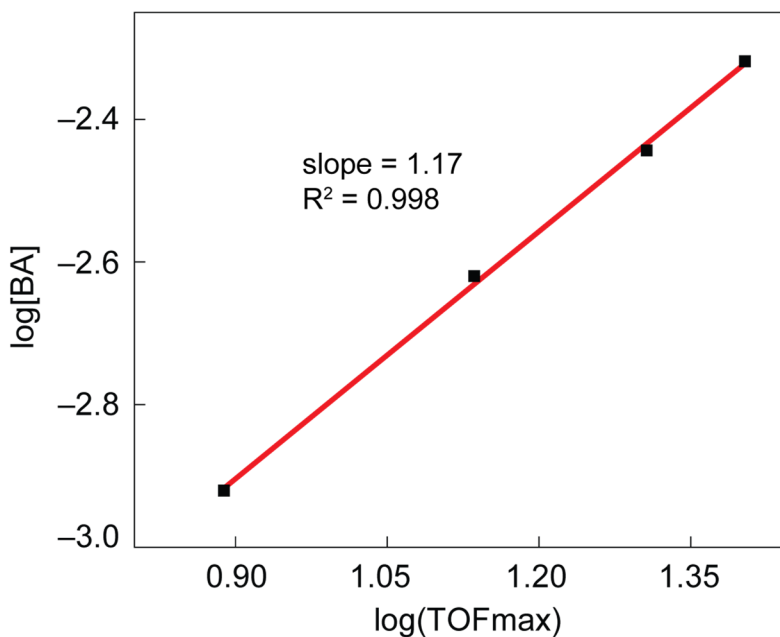


Figure S6. Plot to provide reaction order of proton concentration on HER catalysis.