

How One-photon can Induce Water Splitting into Hydrogen peroxide and Hydrogen by Aluminum Porphyrins?

Rationale of the Thermodynamics

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SI-1. Estimation of excitation energy (E_{00}) from the crossing wavelength of absorption spectra (Q-band) and fluorescence spectra of AlTMPyP(O⁻)₂ species under pH 12.5 condition.

SI-2. Estimation of saturated catalytic current from the plot between i_c vs. scan rate plot under different temperature ($T = 295-346\text{K}$) at pH 12.5 ($[\text{AlTMPyP}] = 0.2\text{mM}$, $[\text{NaOAc}] = 0.1\text{M}$)

SI-3. Extraction of k_{H_2O} and k_{OH} for AlTMPyP(OH)₂ species under pH range 7.0-9.0

SI-4. Temperature dependent cyclic voltammogram of AlTMPyP in NaOH/NaOAc condition at pH 11.0 and **50mM** Na₂CO₃ / NaOAc condition

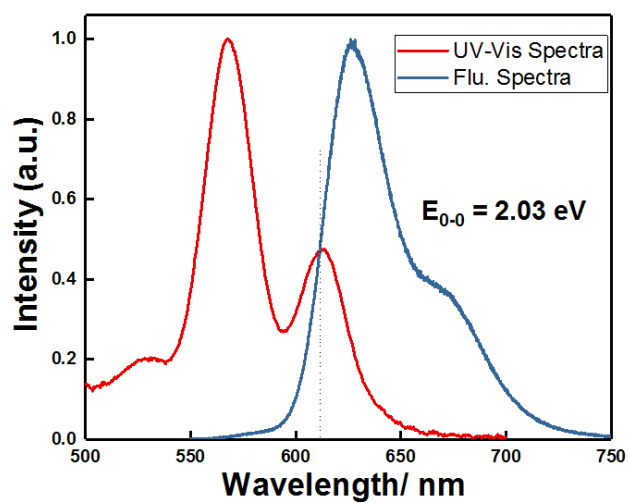


Figure S1. Estimation of excitation energy (E_{00}) from the crossing wavelength of absorption spectra (Q-band) and fluorescence spectra of AITMPyP(O⁻)₂ species under pH 12.5 condition.

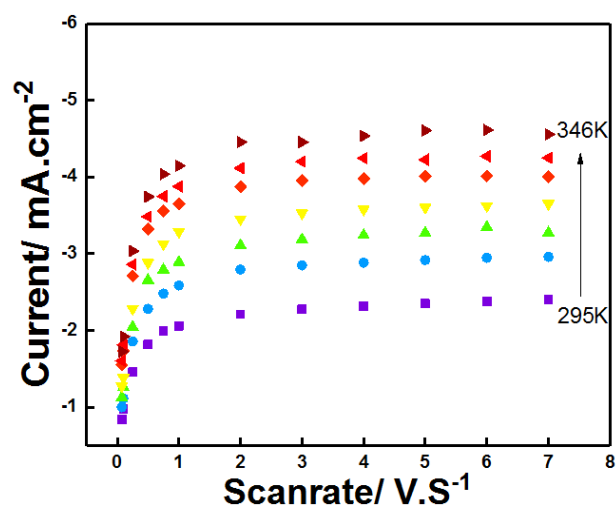


Figure S2. Estimation of saturated catalytic current from the plot between i_c vs. scanrate plot under different temperature ($T = 295\text{--}346\text{K}$) at pH 12.5 ($[\text{AITMPyP}] = 0.2\text{mM}$, $[\text{NaOAc}] = 0.1\text{M}$).

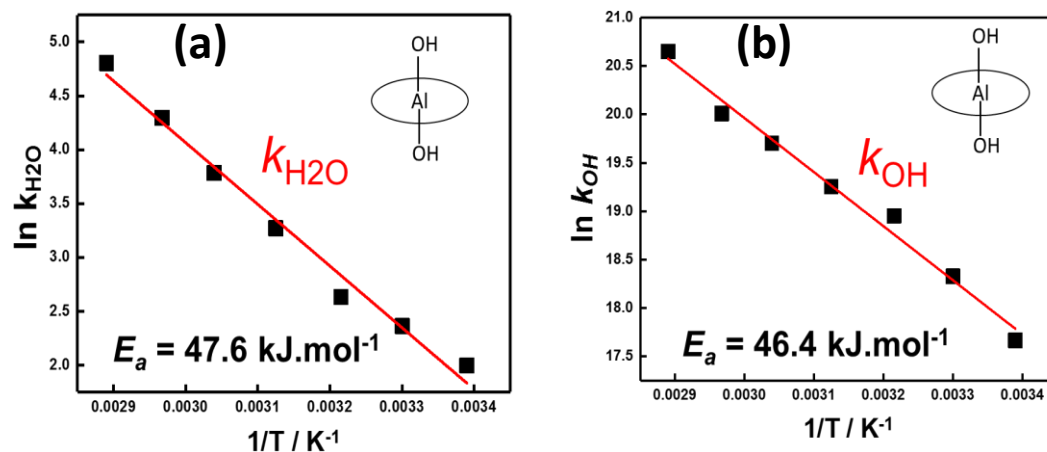


Figure S3. (a) Estimation of activation energy by Arrhenius treatment for k_{H_2O} at $T = 295\text{K} - 346\text{K}$ ($\text{pH} = 7.0 - 9.0$) and (b) k_{OH} at $T = 295\text{K} - 346\text{K}$ ($\text{pH} = 7.0 - 9.0$).

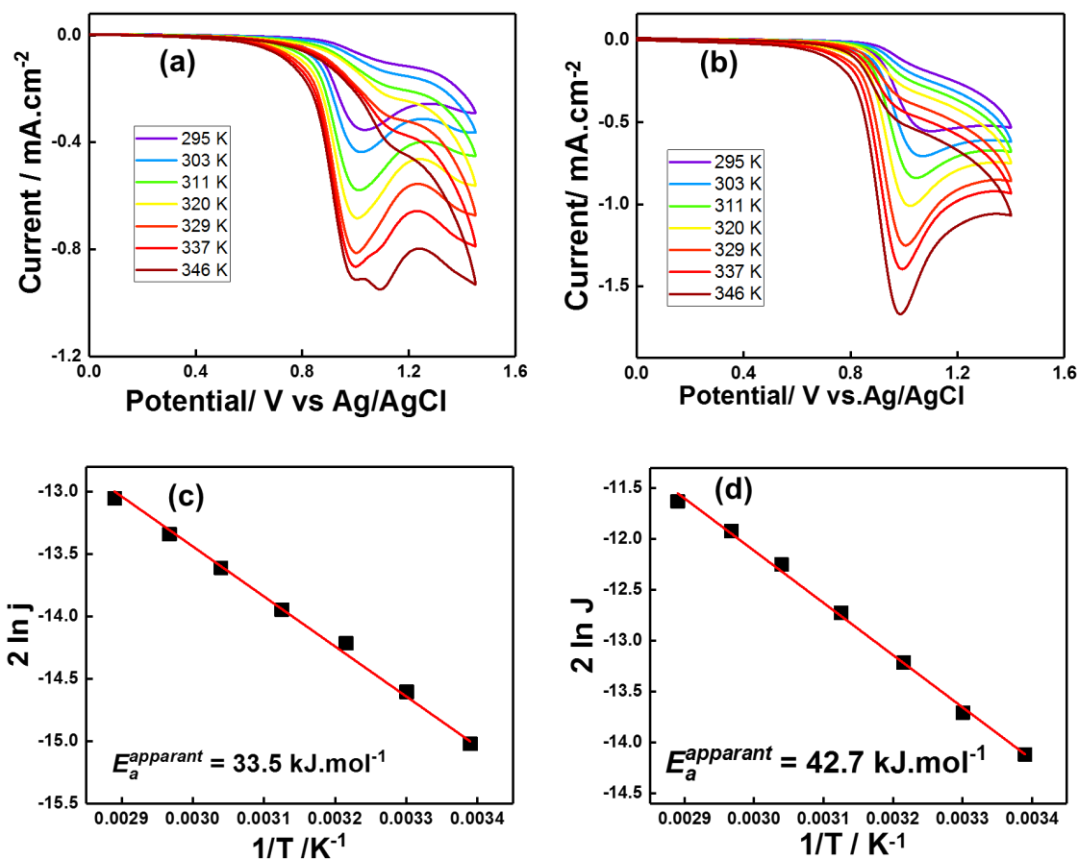


Figure S4. Temperature dependent cyclic voltammogram of AITMPyP in **(a)** NaOH/NaOAc condition at pH 11.0 **(b)** 50mM Na₂CO₃ / NaOAc condition at pH 10.9 and activation energy determined using Arrhenius plot between j^2 versus $1/T$ **(c)** NaOH/NaOAc condition at pH 11.0, **(d)** 50mM Na₂CO₃ / NaOAc condition at pH 10.9. (WE: BDD, RE: Ag/AgCl, CE:Pt, Scan rate – 100 mV/s).

Table S1. Estimation of apparent activation energies of ALTMPyP species under different pH conditions (pH 7.0-12.7)

pH	ALTMPyP Species	$E_a^{apparent}$ (kJ. mol ⁻¹)
7.0	ALTMPyP(OH) ₂	50.7
8.0	ALTMPyP(OH) ₂	48.1
9.0	ALTMPyP(OH) ₂	46.8
9.8	ALTMPyP(OH)(O ⁻)	42.4
11.0	ALTMPyP(O ⁻) ₂	33.4
11.5	ALTMPyP(O ⁻) ₂	31.7
12.0	ALTMPyP(O ⁻) ₂	27.6
12.7	ALTMPyP(O ⁻) ₂	19.8