Supporting Information for:

Anchoring a Molecular Iron Catalyst to Solar-Responsive WO_3 Improves the Rate and Selectivity of Photoelectrochemical Water Oxidation

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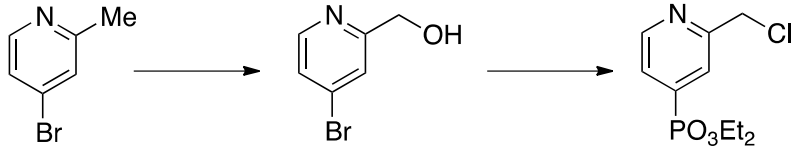
Experimental Section

General Methods

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. THF, CH_3CN, and CH_2Cl_2 were dried prior to use according to common practices. All other materials were obtained from commercial sources, and used as purchased. Column chromatography was performed using standard 200 mesh silica gel. Elemental analyses were performed by Atlantic Microlab, Inc. for C, H, N, and Cl determinations. ^{1}HNMR and ^{13}CNMR spectra were recorded in $CDCl_3$ or CD_3CN using a Varian MR400 at 400 MHz. Electrospray ionization mass spectra were collected on a Micromass LCT TOF MS through a Waters 1525 GC. UV/Visible/NIR spectroscopy was performed on an Agilent CaryWin 5000.

Synthesis



3 **4**

Preparation of **3**[1]:

4-bromo-2-methylpyridine (4.30 g, 25.0 mmol) in 100 mL $CHCl_3$ was stirred with 70 wt% *m*-CPBA (8.01 g, 32.5 mmol) open to air for 2 hours. The reaction was quenched with 15 mL saturated $NaHCO_3$, and the resulting layers were separated. The aqueous layer was extracted with 30 mL CH_2Cl_2 (2×). The combined organic layers were washed with 30 mL of 2 M HCl, dried with Na_2SO_4, filtered, and concentrated.

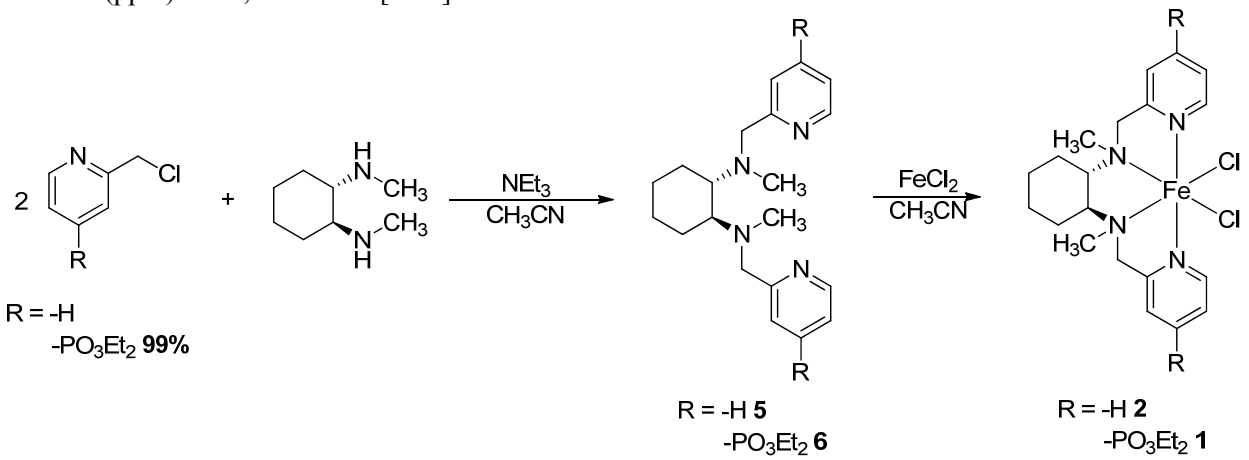
The resulting yellow oil was dissolved in 50 mL acetic anhydride and heated to 90 ºC under air overnight. The dark solution was concentrated by vacuum distillation, and the residue was cooled to room temperature and dissolved in 30 mL methanol. The resulting solution was cooled to 0 ºC. KOH (2.8 g, 50.0 mmol) was added to the chilled solution, and upon complete addition the ice bath was removed. The solution was warmed to room temperature and stirred for 3 hours. The reaction was concentrated under reduced pressure. The dark residue was taken up into 50 mL ethyl acetate and washed with saturated $NaHCO_3$. The aqueous layer was extracted with additional ethyl acetate (2× 50 mL) and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified on silica with 50% ethyl acetate/hexanes. The desired alcohol **3** (2.04 g) was isolated in 43% yield over three steps. ^{1}HNMR($CDCl_3$, ppm): 8.32 (d, 1H), 7.49 (s, 1H), 7.345 (d, 1H), 4.71 (s, 2H), 4.13 (broad, 1H); ^{13}CNMR(ppm): 161.13, 149.17, 133.79, 125.78, 124.11, 63.91; ESI-MS$^+$: $[\mathbf{3}+H]^+$ = 187.2 m/z

Preparation of **4**[1,2]:

Palladium acetate (8.5 mg, 0.038 mmol), dppf (42.0 mg, 0.076 mmol), and KOAc (16 mg, 0.17 mmol) were dissolved in 5 mL THF. Triethylamine (0.27 mL, 1.9 mmol) was added to the reaction and the solution was heated to 70 ºC under N_2 for 15 minutes. To the hot reaction, diethyl phosphite (0.16 mL, 1.27 mmol) and 4-bromo-2-(hydroxymethyl)pyridine (250 mg, 1.33 mmol) were added and the reaction was refluxed overnight. The reaction was cooled to room temperature and the reaction was concentrated under reduced pressure.

The crude residue was then taken into 5 mL of CH_2Cl_2 and cooled to 0 ºC. Thionyl chloride (0.27 mL, 3.70 mmol) in 3 mL CH_2Cl_2 was added dropwise over 5 minutes. The resulting suspension was warmed to room temperature and stirred for 4 hours in air. The reaction was concentrated, and the brown residue was taken into 25 mL CH_2Cl_2 and washed with 25 mL saturated $NaHCO_3$. The resulting aqueous layer was extracted with CH_2Cl_2 (2× 25 mL) and the combined organic layers were washed with brine. Finally,

the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. This yielded the desired product **4** (239 mg) as a brown residue that was sufficiently pure by NMR in 72% yield over two steps. ^{1}HNMR($CDCl_3$, ppm): 8.68 (t, 1H), 7.80 (d 1H), 7.57 (dd, 1H), 4.68 (s, 2H), 4.13 (m, 4H), 1.31 (t, 6H); ^{13}CNMR(ppm): 157.10, 149.69, 139.81, 124.535, 124.34, 62.835, 46.20, 16.30; ^{31}PNMR(ppm): 14.0; ESI-MS$^+$: [**4**+H]$^+$ = 263.9 m/z



General Preparation of **5** or **6**:

5: "bpmcn" R = H ^{1}HNMR($CDCl_3$, ppm): 8.46 (dd, 2H), 7.545 (m, 4H), 7.08 (q, 2H), 3.83 (q, 4H), 2.635 (d, 2H), 2.27 (s, 6H), 1.955 (d, 2H), 1.735 (d, 2H), 1.28 (d, 2H), 1.13, (d, 2H); ^{13}CNMR(ppm): 161.44, 148.57, 136.17, 122.77, 121.48, 6456, 60.46, 36.62, 25.84; ESI-MS$^+$: [**6**+H]$^+$ = 323.8 m/z

6: "tebppmcn" R = PO_3Et_2

The racemic cyclohexane diamine (54 mg, 0.38 mmol) was dissolved in 5 mL of acetonitrile. Triethylamine (0.16 mL, 1.13 mmol) and **4** (199 mg, 0.76 mmol) were added to the stirring solution. The reaction was heated to 100 ºC and attached with a long reflux condensor. After heating the reaction overnight, it was cooled to room temperature and concentrated under reduced pressure. The residue was dissolved in 10 mL CH_2Cl_2 and washed with 10 mL saturated $NaHCO_3$. The aqueous layer was extracted an additional 2 times with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated. The crude product was purified on silica with 86% ethyl acetate, 10% methanol, and 4% conc. NH_4OH (R_f ~0.5). Fractions collected from the column were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. This yielded an orange oil (173 mg, 58%). ^{1}HNMR($CDCl_3$, ppm): 8.58 (t, 2H), 7.875 (d, 2H), 7.455 (q, 2H), 4.09 (m, 8H), 3.91 (s, 4H), 2.575 (d, 2H), 2.28 (s, 6H), 1.875 (d, 2H), 1.68 (d, 2H), 1.25 (m, 14H), 1.07 (t, 2H); ^{13}CNMR(ppm): 148.98, 138.52, 136.69, 124.41, 123.22, 63.95, 62.63, 60.86, 36.78, 26.93, 25.64, 16.27; ^{31}PNMR 15.26; ESI-MS$^+$: [**5**+H]$^+$ = 597.0 m/z$^+$

General Preparation of **1** or **2**[3]:

1.0 eq. of ligand was added to 5 mL acetonitrile under N_2. To the stirring solution, 1.0 eq. of anhydrous $FeCl_2$ was added, and the reaction immediately turned from orange to purple (**1**) or yellow (**2**). The reaction was stirred overnight and concentrated under reduced pressure. If a precipitate was present, the solid was isolated as the pure product (**2**) and rinsed with diethyl ether. If no precipitate formed, the solution was concentrated and dried in a vacuum oven, yielding the pure complex. X-ray quality crystals were obtained by slow diffusion of ether into a concentrated solution of the complex in CH_3CN.

1: ^{1}HNMR(CD_3CN, ppm): 108.3, 62.07, 51.92, 51.39, 14.90, 8.0, 3.94, 2.01, 1.43, 0.16, -2.18, -2.85, -11.73; ESI-MS$^+$: [Fe(tebppmcn)Cl(CH_3CN)]$^+$ = 721.4 m/z$^+$; [Fe(tebppmcn)$(Cl)_{1.7}(HO)_{0.3}$•0.7H_2O] EA: (theory) C 46.12, H 6.59, N 7.68, Cl 8.10; (found) C 45.27, H 6.47, N 7.67, Cl 8.06

2: ^{1}HNMR(CD_3CN, ppm): 109.48, 63.25, 54.58, 51.27, 20.43, 15.46, 3.17, 2.49, 1.98, 0.10, -19.03; ESI-MS$^+$: [Fe(bpmcn)Cl(CH_3CN)]$^+$ = 423.4 m/z$^+$, [Fe(bpmcn)Cl_2•0.5H_2O] EA: (theory) C 52.20, H 6.35, N 12.17, Cl 15.41; (found) C 52.10, H 6.29, N 12.21, Cl 15.13

WO_3 was prepared by a previously reported method.[4]

Modification of WO_3 with **1**:
WO_3 electrodes were heated to 80 ^oC in a 500 μM **1**/acetonitrile solution and sealed in a vial. The anodes were soaked for 8 hours in the dark and then rinsed with excess acetonitrile and dried with N_2. This procedure resulted in a light yellow tint to the modified electrodes.

Electrochemistry

All electrochemistry was performed on either a CH Instruments CHI-600 or CHI-1000 potentiostat. All potentials are referenced to SCE (saturated calomel electrode) with saturated KCl electrolyte reference electrode (RE), and Pt was used as the counter electrode (CE) in all experiments. Non-aqueous solvents were dried prior to use and $TBAPF_6$ was recrystallized from EtOH prior to use. Glassy carbon (GC) was used as the working electrode (WE) for solution-based electrochemistry. Aqueous solutions were prepared using 18.2 Ω Milli-pore H_2O and concentrated sulfuric acid, and then pH adjusted with 7 M NaOH to obtain the desired concentration and pH. The aqueous solutions were also purged with N_2 prior to use, but were not sealed under N_2. All photoelectrochemical measurements were carried out in custom-built cells with quartz viewing windows. All illumination was carried out using a Newport Oriel 150 W Xe lamp fitted with an AM1.5G filter from Newport whose power was adjusted to 100 mW/cm^2.

Faradaic Efficiency: Oxygen Detection

Oxygen was quantified using a FOSSPOR fluorescence probe using two-point calibration at 20.90% and 0.00% O_2. O_2 evolution experiments were carried out in a custom-built two-sided cell with quartz windows, where the O_2 probe, working electrode, and reference electrode were on one side, with the temperature probe and the Pt auxiliary electrode on the other side. The solutions were purged with N_2 overnight, and then sealed under N_2 on a Schlenk line. The photoelectrode was illuminated at 100 mW/cm^2 filtered with AM 1.5G and the potential was held at 809 mV *vs.* SCE in pH 3 Na_2SO_4 (1.23 V *vs*. NHE). After collecting a stable 0% baseline for ~30 minutes, the photoanode was illuminated for ~3 hours. Following illumination, the O_2 was allowed to reach a stable O_2 level for ~30 minutes to allow for temperature fluctuations with the probe. Finally, the run was successful if the O_2 returned near 20.90% after re-exposing the O_2 probe to air. Faradaic efficiency was determined by dividing the measured moles of O_2 by the theoretical yield, determined by dividing the total charge passed during the experiment by 4F (4-electron oxidation, F = 96,485.34 C/mol e$^-$).

Faradaic Efficiency: Non-oxygen Detection

Non-oxygen by-products from photoelectrolysis were measured by quantifying the amount of Fe^{2+} that was oxidized by the non-O_2 oxidants in solution (mainly $S_2O_8^{2-}$, HSO_5^-, and H_2O_2) according to the following reactions.

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2\ SO_4^{2-} \quad (\mathbf{1})$$
$$2\ Fe^{2+} + HSO_5^- + 2H^+ \rightarrow 2\ Fe^{3+} + HSO_4^- + H_2O \quad (\mathbf{2})$$
$$2\ Fe^{2+} + H_2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O \quad (\mathbf{3})$$

The amount of Fe^{3+} generated in the second reaction was quantified by addition of excess Na(SCN). The amount of Fe^{3+} generated was determined using Beer's law and 1 mol of Fe^{3+} was generated for every 1 mol of e^- not used to oxidize water completely, and thus the Faradaic efficiency of the cells for non-O_2 production was measured. To perform the reaction, 2.0 mL of 5 mM $FeSO_4$ in 100 mM pH 3 Na_2SO_4 and 1.0 mL of the test solution were mixed and equilibrated for 15 minutes to allow for the reaction to go to completion. NaSCN was added to the solutions (~40 mM) to generate the deep red $[Fe(SCN)_6]^{3-}$ species, detectable by UV-Vis spectroscopy (ε = 172 M^{-1} cm^{-1} at λ_{max} = 465 nm). The measurement was standardized using $Ce(HSO_4)_4$. If the reactions were not carried out in aerated solutions and during the time frame of the experiments then the detected concentrations of the non-O_2 oxidants was significantly diminished.

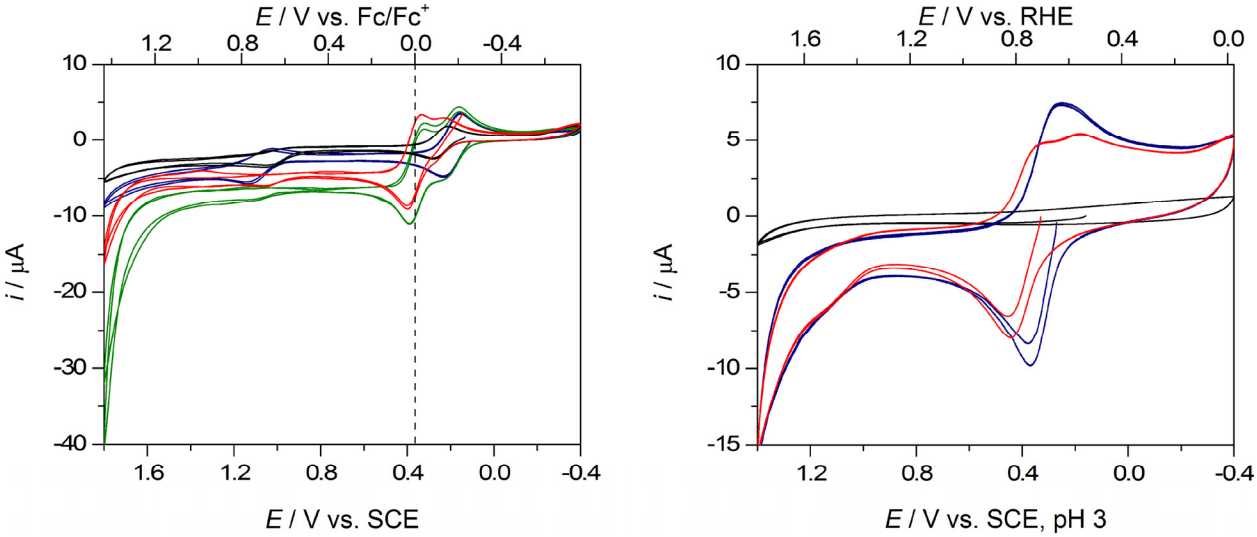


Figure S1. Left: Solution electrochemistry of 0.5 mM catalyst **1** (black) and **2** (blue) in 100 mM $TBAPF_6$ CH_3CN without Fc; 0.5 mM **1** (red) and **2** (green) with 0.5 mM Fc at 20 mV/s; Right: 1 mM **1** (red) or **2** (blue) in 100 mM Na_2SO_4 pH 3 (blank = black) at 50 mV/s using GC WE, SCE RE, Pt CE.

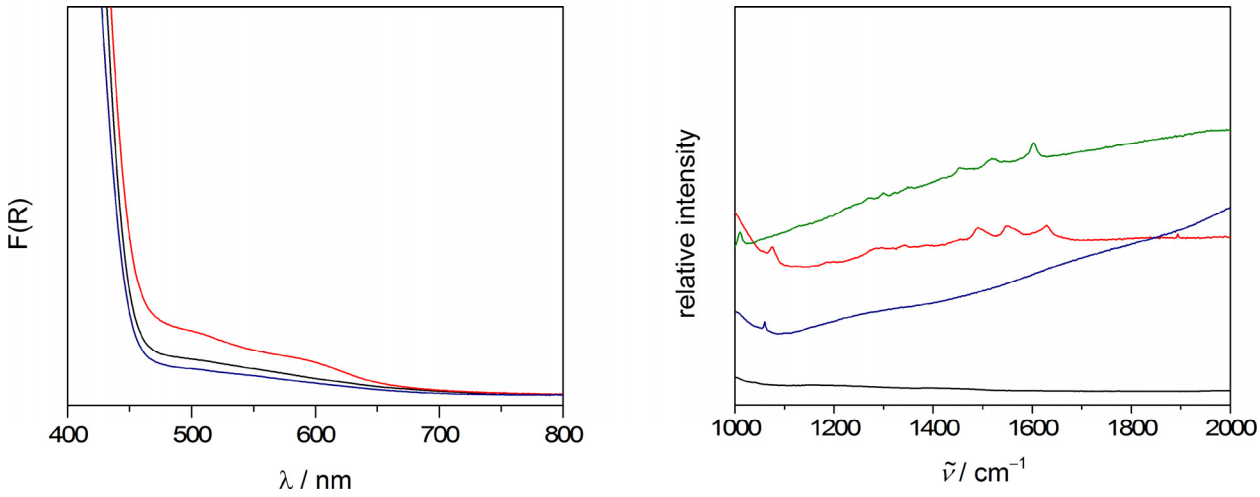


Figure S2. Left: Diffuse reflectance spectroscopy of WO_3 film (black), **1**-WO_3 before electrolysis (red) and after electrolysis (blue); Right: Raman spectroscopy of WO_3 electrode (black), **1**-WO_3 before electrolysis (red), **1**-WO_3 after electrolysis (blue), and **1** powder (green).

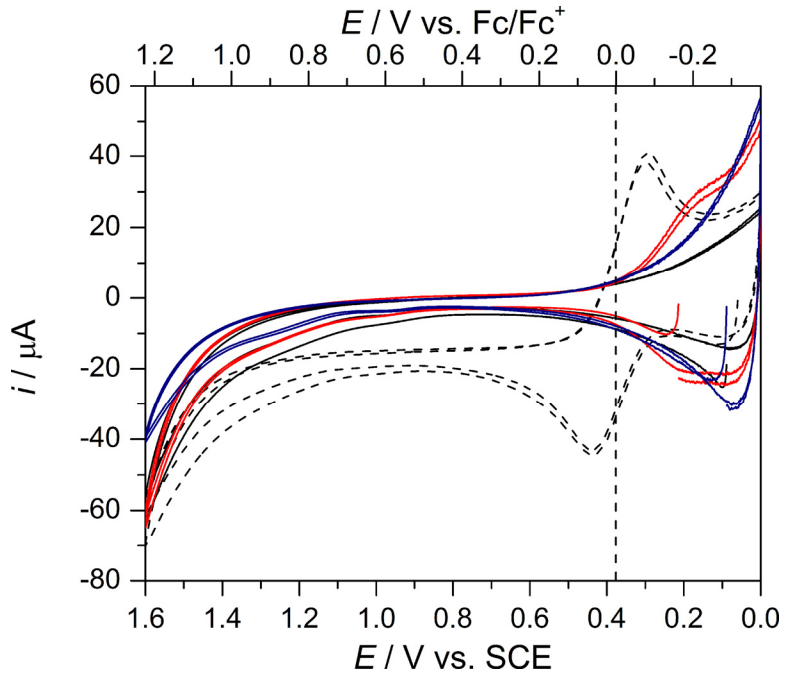


Figure S3. Cyclic voltammetry of bare WO_3 photoanode (black) with added Fc (dashed) and **1**-WO_3 photoanode before LSVs (red) and after LSVs (blue) in 100 mM $TBAPF_6$ CH_3CN; CV's recorded at 20 mV/s with SCE RE and Pt CE in the dark.

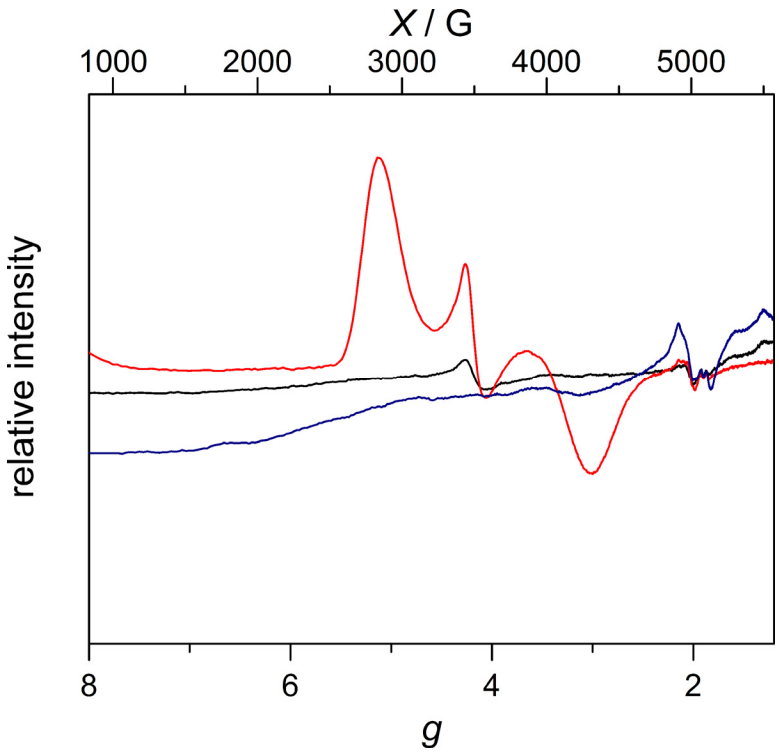


Figure S4. EPR at 4 K of 2.5 mM **1** in 100 mM $TBAPF_6$ CH_3CN at open circuit potential (black), after electrolysis at 0.6 V vs. SCE (red), and after electrolysis at 1.6 V vs. SCE (blue). Electrolysis was performed in a two compartment cell separated by a glass frit using a 1 cm^2 carbon felt electrode WE and SCE RE in one side with the 2.5 mM **1** solution and Pt mesh CE on the other side with blank electrolyte.

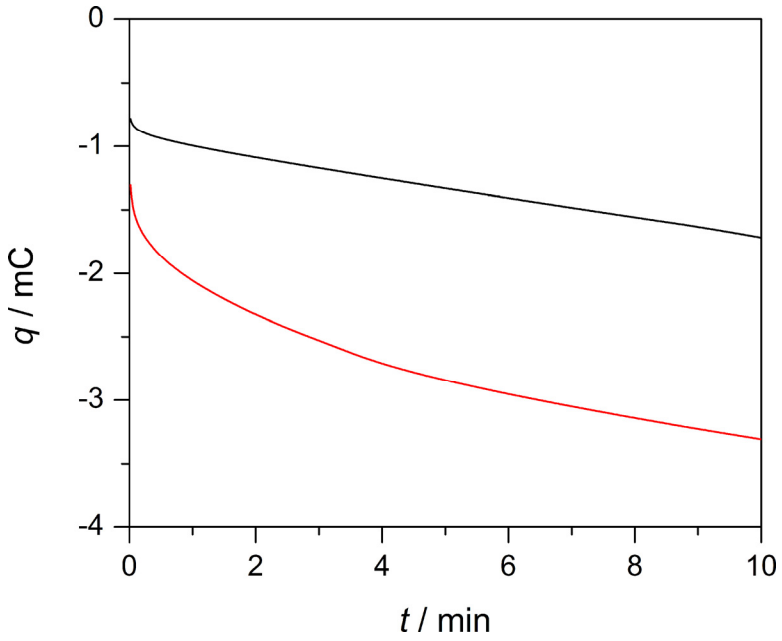


Figure S5. Bulk electrolysis (*q vs. t*) of bare WO_3 photoanode (black) and a typical **1**-WO_3 photoanode (red) before any other electrochemistry in 100 mM $TBAPF_6$ in CH_3CN; potential held at 0.43 V *vs.* Fc^+/Fc^0 (0.8 V *vs.* SCE) with SCE RE and Pt CE in the dark. The coverage of **1** on this film was 15.65 nmoles cm^{-2} based on coulometry (i.e. after 5 minutes: $n = q/F = (0.00284 - 0.00133)/96{,}485 = 15.65 \times 10^{-9}$ moles e^- passed = 15.65×10^{-9} moles Fe^{2+} oxidized to Fe^{3+})

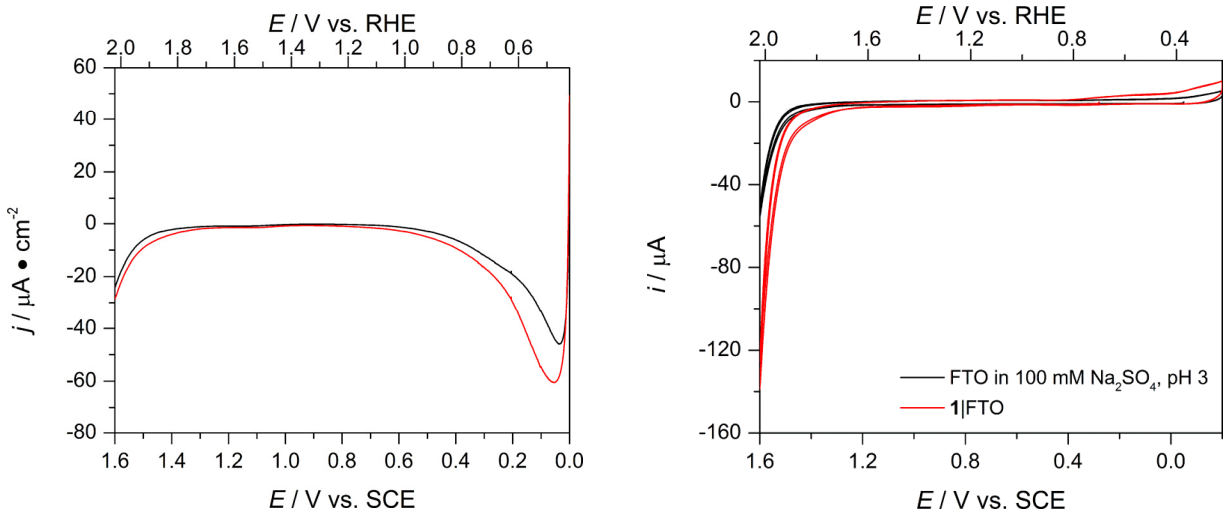


Figure S6. Left: Linear sweep voltammetry of bare WO_3 photoanode (black) and **1**-WO_3 photoanode (red) in 100 mM Na_2SO_4 pH 3; LSVs recorded at 20 mV/s with SCE RE and Pt CE in the dark. Right: CVs of **1**-FTO recorded under similar conditions.

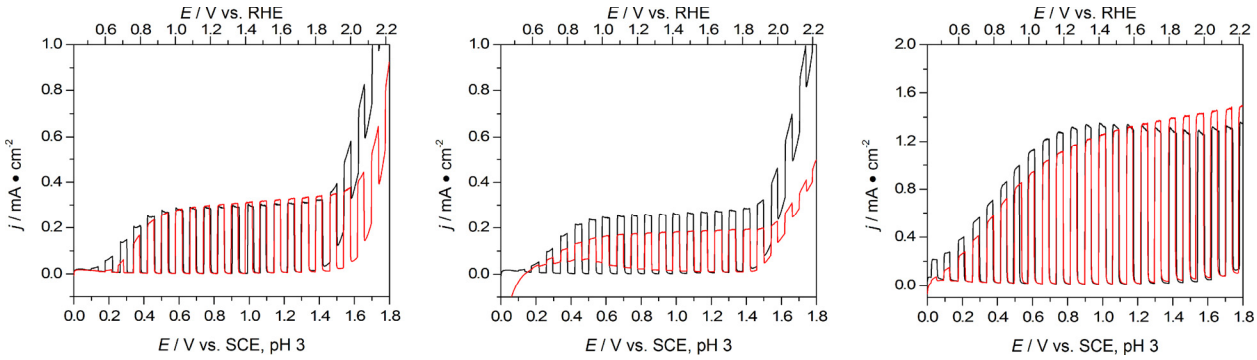


Figure S7. Left: Chopped-light LSV of a WO_3 film as prepared (black) and after soaking in CH_3CN (red); Middle: Chopped-light LSV of a WO_3 film as prepared (black) and after soaking with $FeCl_2$ (red); Right: Chopped-light LSV of a WO_3 film as prepared (black) and after soaking with tebppmcn (red) in pH 3 0.1 M Na_2SO_4, 100 mW cm^{-2} AM 1.5G illumination, 20 mV/s, Pt CE, SCE RE.

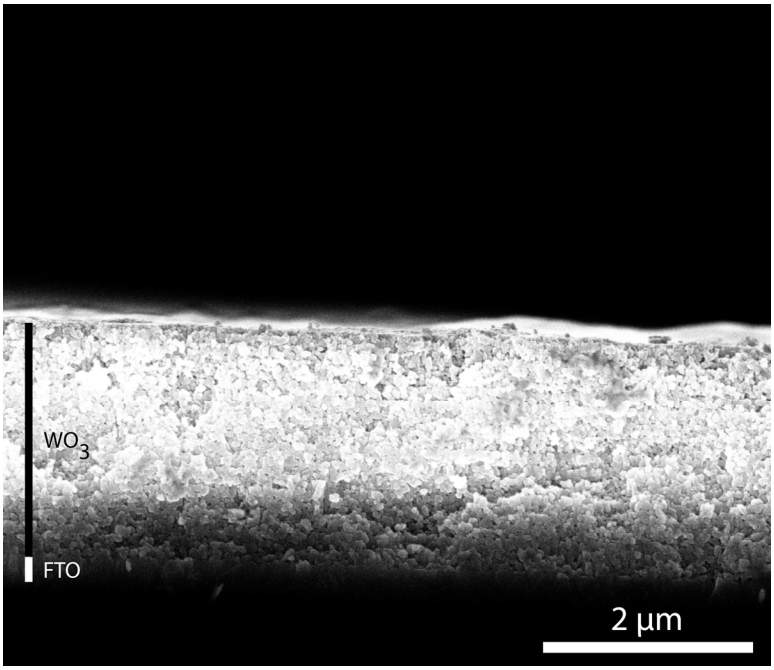


Figure S8. SEM of optimized WO_3 photoanodes with a thickness of ~1.8 µm whereas the thinner films were measured to be ~0.6 µm.

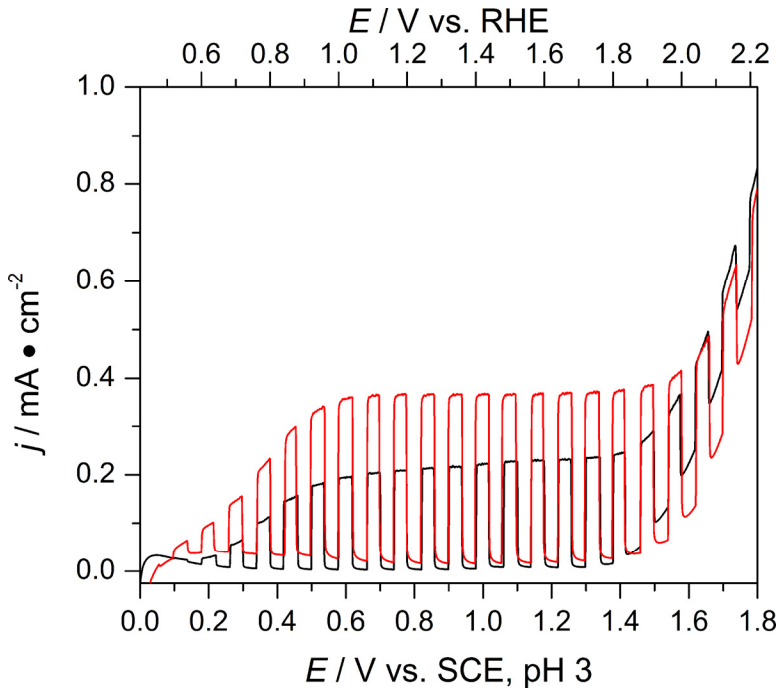


Figure S9. Chopped-light LSV of thinner photoanodes in 100 mM Na_2SO_4 at pH 3; SCE RE, Pt CE, 100 mW cm^{-2}, AM 1.5G with as prepared WO_3 (black) and **1**-WO_3 (red).

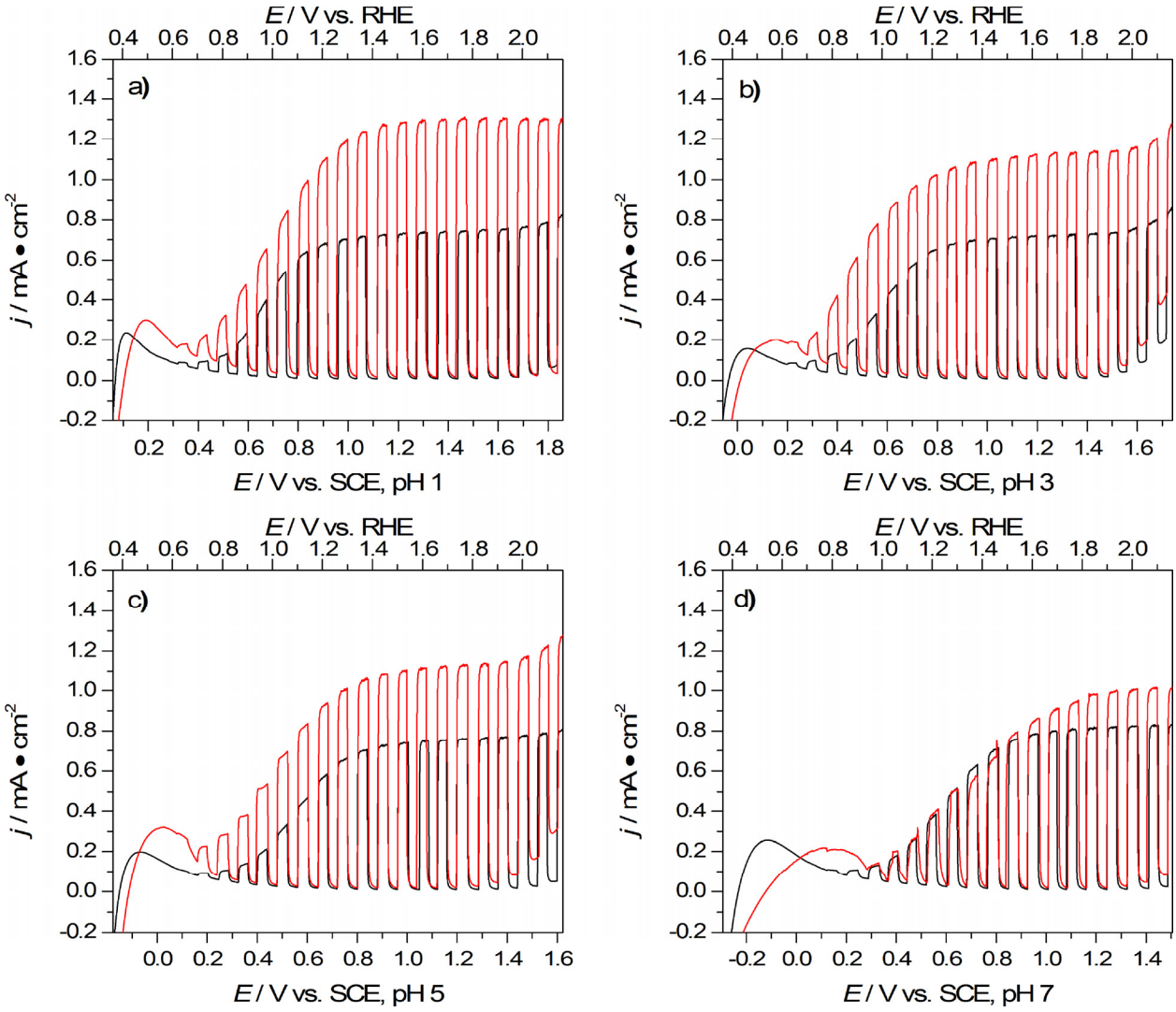


Figure S10. Chopped-light LSVs of photoanodes in 100 mM Na_2SO_4 at pH 1 (a), 3 (b), 5 (c), and 7 (d); SCE RE, Pt CE, 100 mW cm^{-2}, AM 1.5G with as prepared WO_3 (black) and **1**-WO_3 (red).

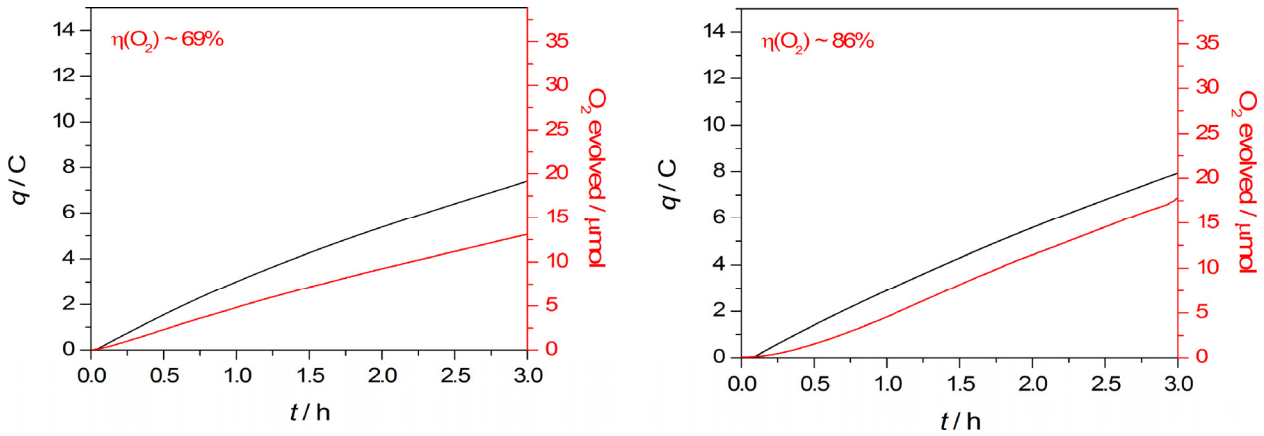


Figure S11. Additional Faradaic efficiency experiments of **1**-WO_3 photoanodes in 100 mM Na_2SO_4 pH 3; potential held at 1.23 V vs. RHE, SCE RE, Pt CE with charge passed (black) and oxygen evolution (red).

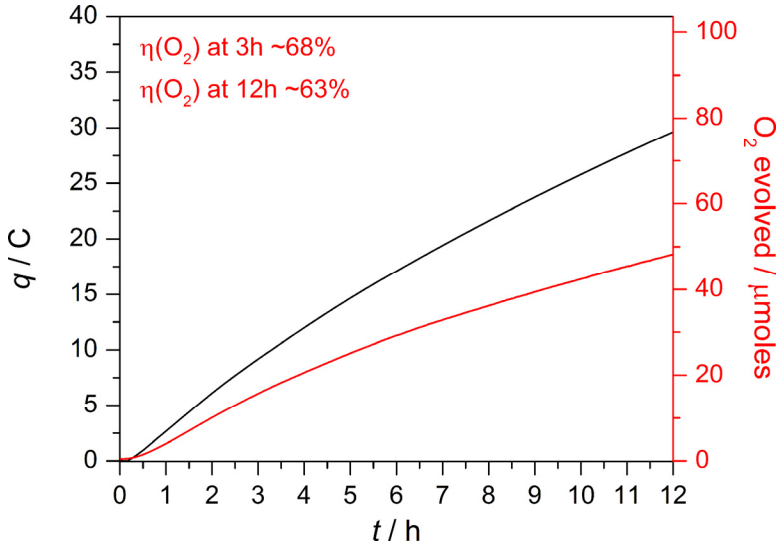


Figure S12. Faradaic efficiency of a **1**-WO_3 photoanode in 100 mM Na_2SO_4 pH 3; potential held at 1.23 V vs. RHE, SCE RE, Pt CE for 12 hours with charge passed (black) and oxygen evolution (red).

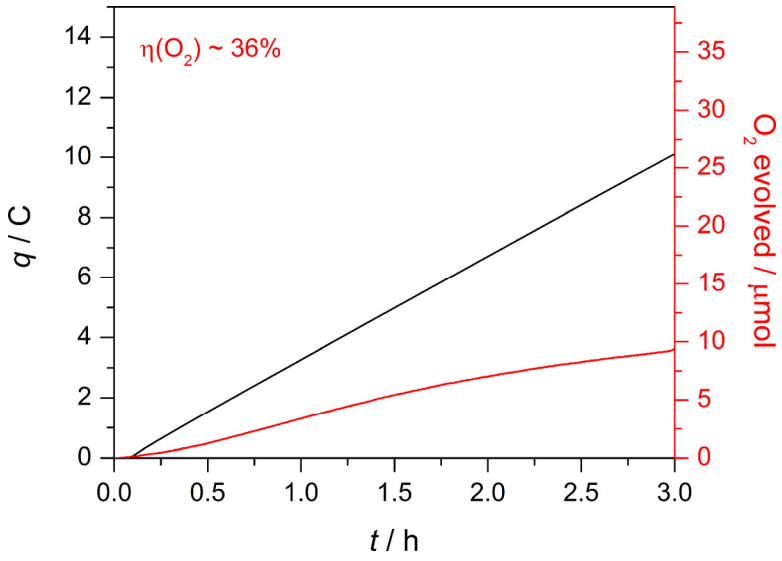


Figure S13. Faradaic efficiency of tebppmcn-WO_3 photoanode in 100 mM Na_2SO_4 pH 3; potential held at 1.23 V vs. RHE, SCE RE, Pt CE with charge passed (black) and oxygen evolution (red).

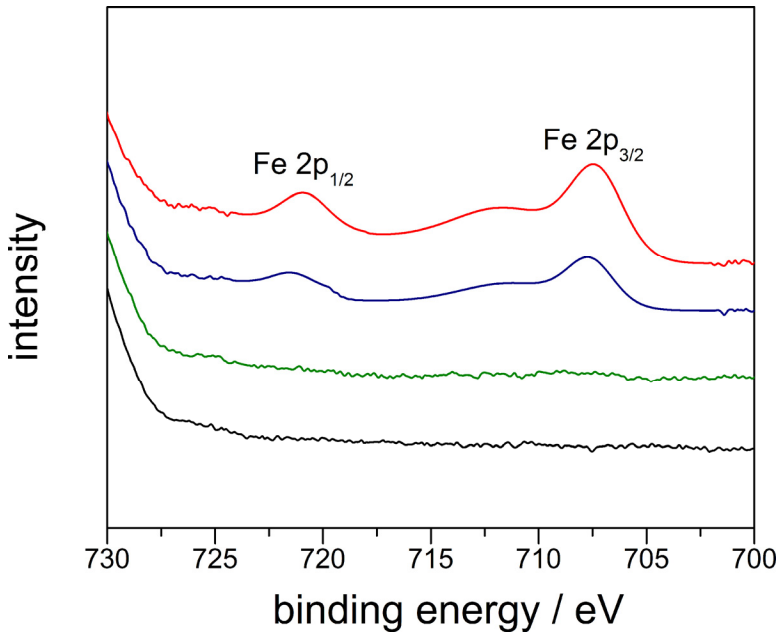


Figure S14. X-ray photoelectron spectrum of WO_3 photoanodes as prepared (black), freshly modified with **1** (red), after LSV of **1**-WO_3 in pH 3 Na_2SO_4 (blue), and after photoelectrolysis of **1**-WO_3 for 3 h (green).

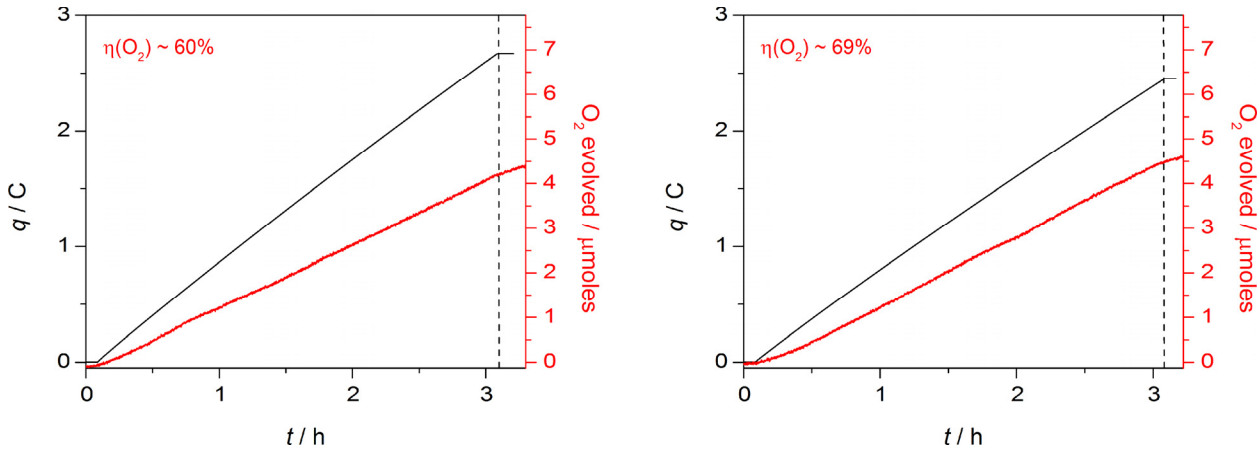


Figure S15. Left: First 3 h Faradaic efficiency experiment of a single **1**-WO_3 thinner photoanode in 100 mM Na_2SO_4 pH 3; Right: Second 3 h Faradaic efficiency experiment of a single **1**-WO_3 thinner photoanode in 100 mM Na_2SO_4 pH 3 when the potential was held at 1.23 V vs. RHE, SCE RE, Pt CE with charge passed (black) and oxygen evolution (red) the dashed line represents when the light is turned off in both plots.

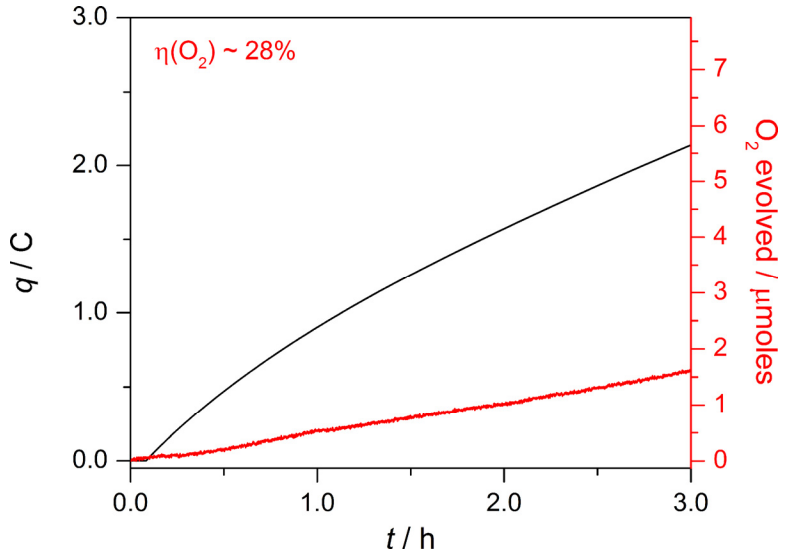
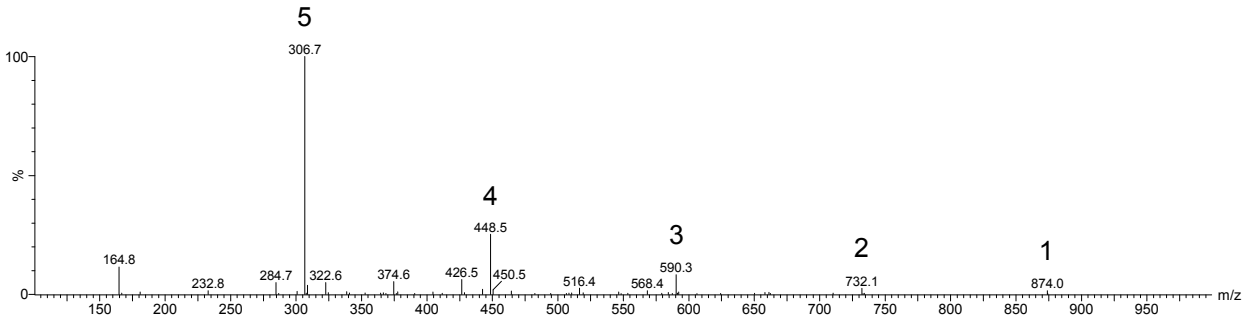


Figure S16. Faradaic efficiency of thinner WO_3 photoanode in 500 nM **1** and 100 mM Na_2SO_4 pH 3; potential held at 1.23 V vs. RHE, SCE RE, Pt CE with charge passed (black) and oxygen evolution (red).



Peak	Molecular Species	m/z$^+$	Change to Ligand
1	$[Fe^{V}(C_{28}H_{46}N_4O_6P_2)(SO_4)_2(CH_3OH)]^+$	876.2	none
2	$[Fe^{V}(C_{20}H_{30}N_4O_6P_2)(SO_4)_2]^+$	732.0	deprotected
3	$[Fe^{II}(C_{20}H_{30}N_4O_6P_2)(HO)(CH_3OH)]^+$	589.1	deprotected
4	$[Fe^{VI}(C_{28}H_{46}N_4O_6P_2)(SO_4)_2(H_2O)_3]^{2+}$	449.1	none
5	$[Fe^{VI}(C_{24}H_{38}N_4O_6P_2)(SO_4)_2(CH_3OH)]^{2+}$	306.6	partially deprotected

Figure S17. Positive electrospray ionization mass spectrometry of electrolyte after 3 hour photo-electrolysis with a **1**-WO_3 photoanode in 100 mM Na_2SO_4 pH 3 at 1.23 V vs. RHE, SCE RE, Pt CE. Table includes major peak labels and the changes to the ligand. Minor peaks were also identified, but were not included for clarity.

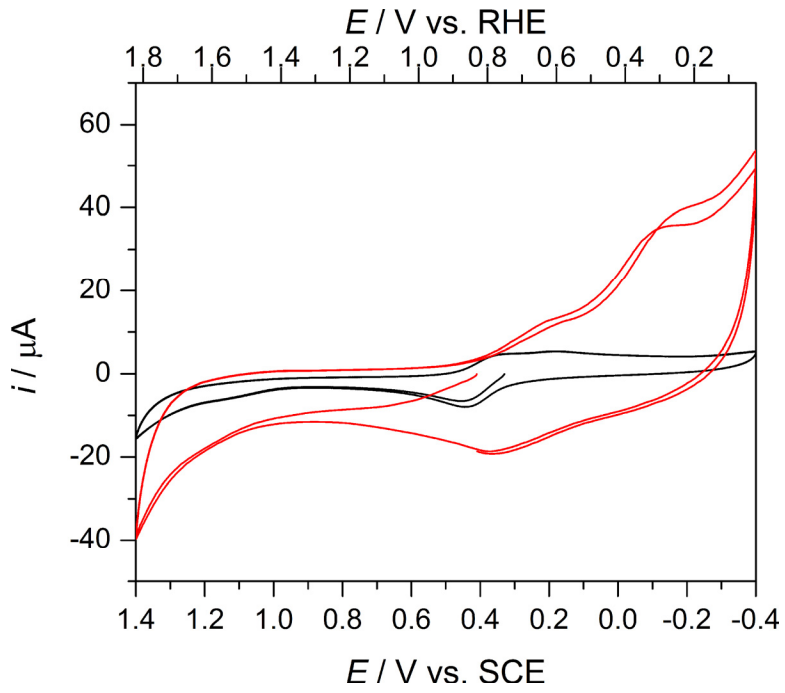


Figure S18. Cyclic voltammetry of 1 mM **1** in 100 mM Na_2SO_4 pH 3 (black) compared to a CV of a concentrated 100 mM Na_2SO_4 pH 3 solution containing **1** after a 3 hour photoelectrolysis with a **1**-WO_3 photoanode (red) recorded with GC WE, SCE RE, and Pt CE at 50 mV/s.

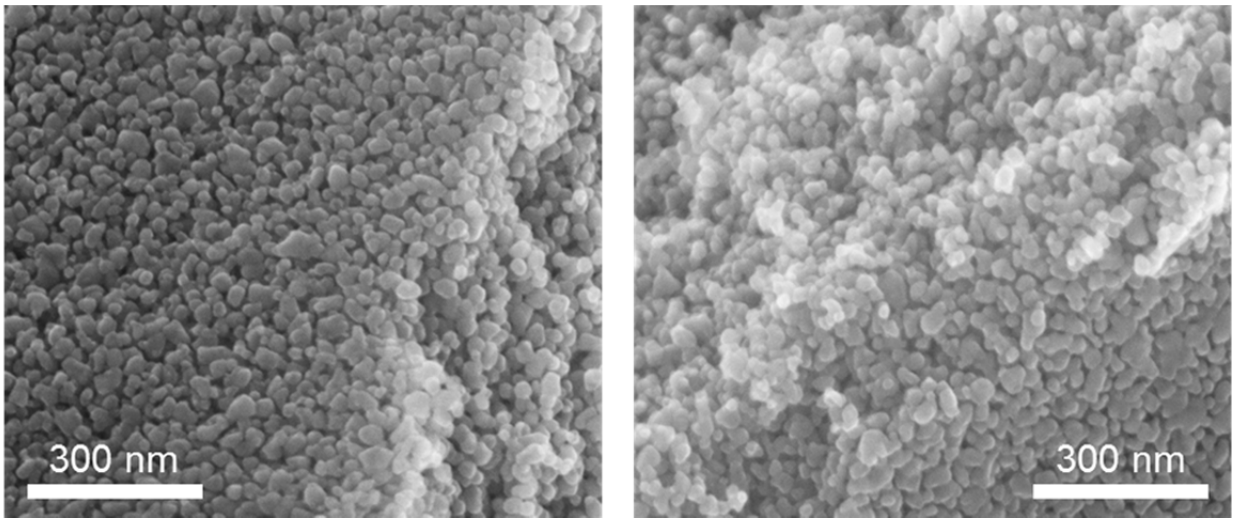


Figure S19. SEM of thinner **1**-WO_3 electrodes before (left) and after (right) 3 hour photoelectrolysis where the darker regions represent the plane or face of a larger aggregate on the electrode surface and the lighter regions are over the edge of the larger aggregates.

Table S1. Tabulated $\eta(O_2)$ % for different WO_3 and **1**-WO_3.

Entry	WO_3	**1** | WO_3	thinner WO_3	thinner **1** | WO_3
1	53	83	45	62
2	64	86	30	57
3	52	69	38	63
4	–	–	20	64
mean	56	79	33	62
std. dev.	7	9	11	3

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