Supporting Information for:

Ligand tuning in $Cu(pyalk)_2$ water oxidation electrocatalysis

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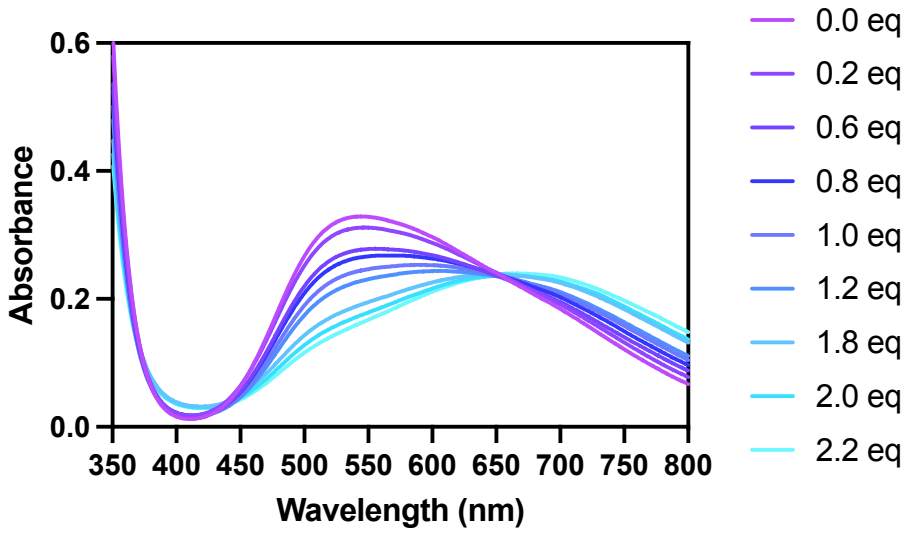

Figure S1. Titration of $Cu(pyalk)_2$ with HCl.

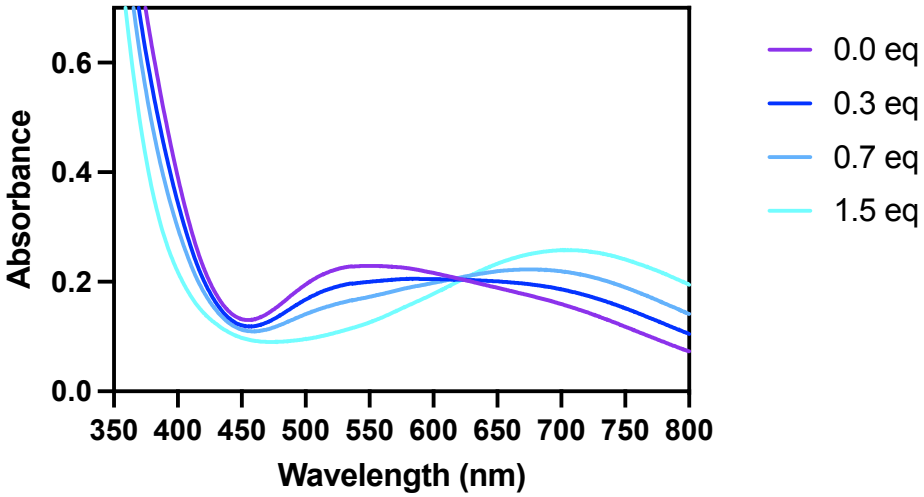

Figure S2. Titration of $Cu(4\text{-}MeOOCpyalk)_2$ with HCl.

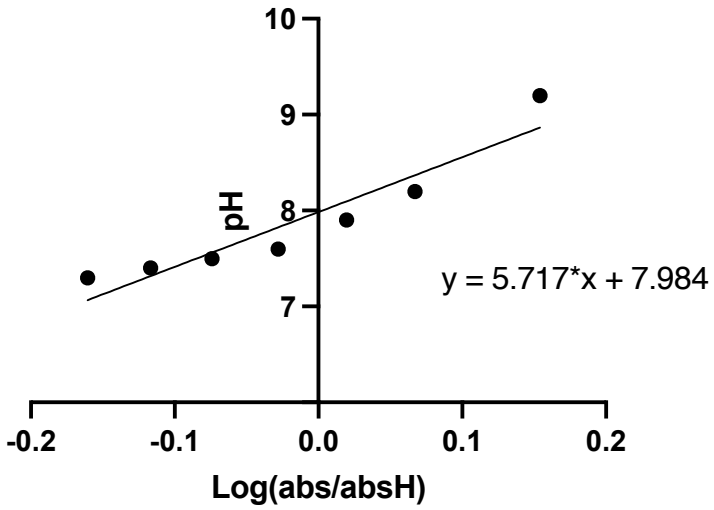

Figure S3. An example of a plot for pK_a determination. The y-intercept corresponds to the measured pK_a, as determined from the Henderson-Hasselbach equation.

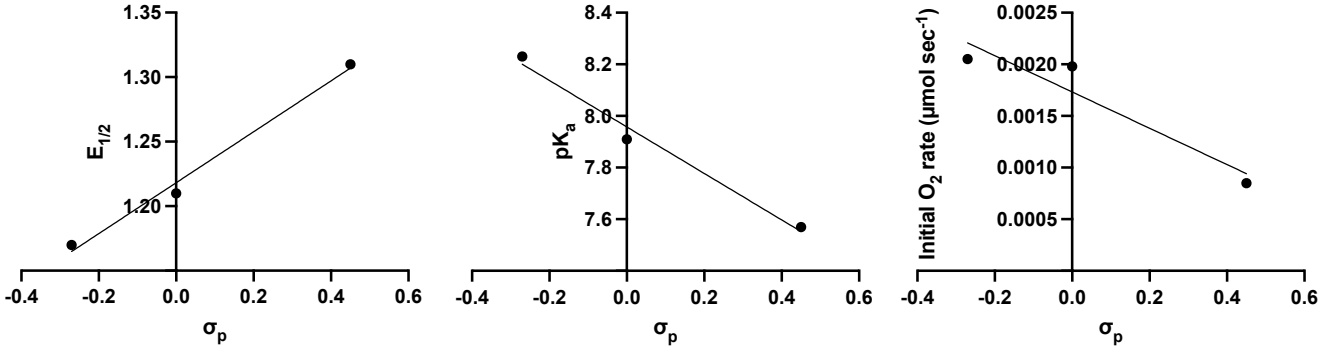

Figure S4. Plots of $E_{1/2}$, pK_a, and initial rate vs. σ_p Hammett parameters for **1**-**3**.

σ_p = –0.27 (-OMe), 0 (-H), 0.45 (-COOMe).

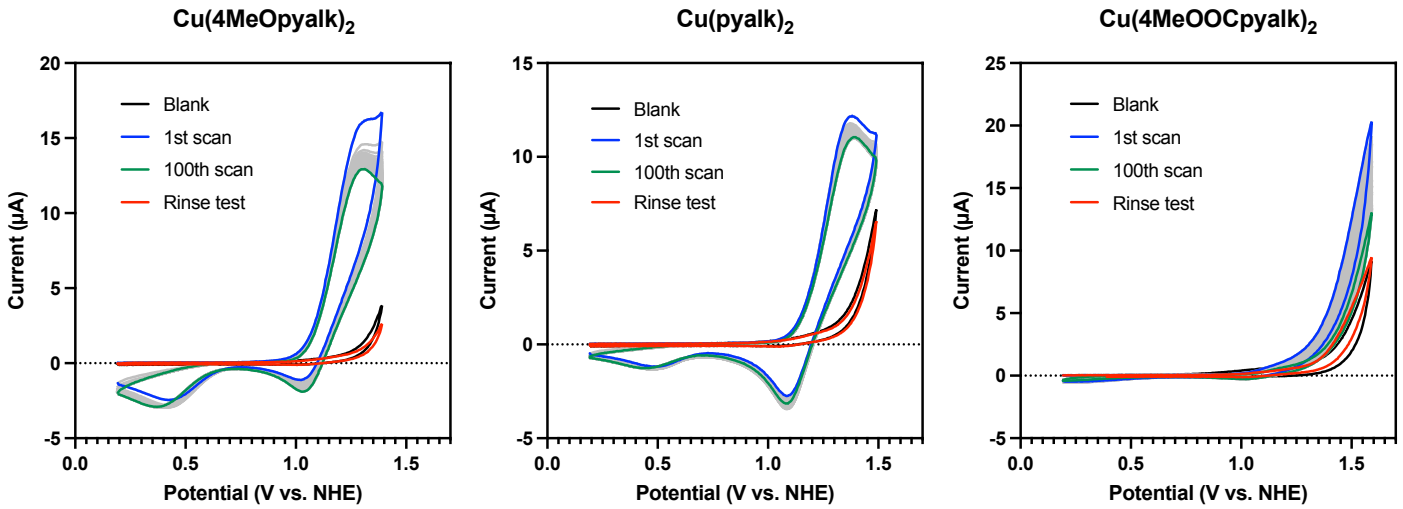

Figure S5. Repeated CVs of **3** (left), **2** (right), and **1** (center), in 0.1 M KNO_3 adjusted to pH 11. BDD working electrode; Pt wire auxiliary electrode; Ag/AgCl (sat'd KCl) reference electrode (0.199 V vs. NHE); scan rate: 100 mV/s. After 100 repeated scans, the electrode was rinsed, not polished, and placed in a fresh electrolyte solution at pH 11 (red trace).

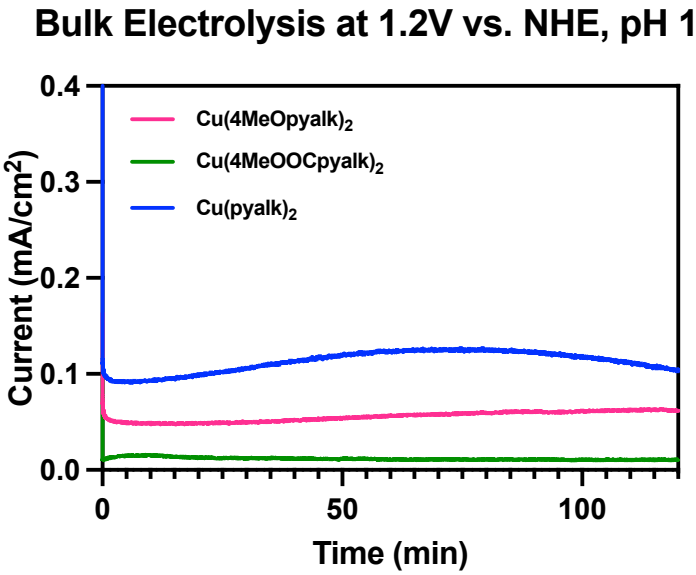

Figure S6. Controlled potential electrolysis at 1.2 V vs. NHE for 2 mM complex in 0.1 M KNO_3 electrolyte, at pH 11.5. Working electrode: 1 cm^2 fluorine-doped tin oxide coated glass, counter electrode: Pt mesh, reference electrode: Ag/AgCl, sat'd KCl.

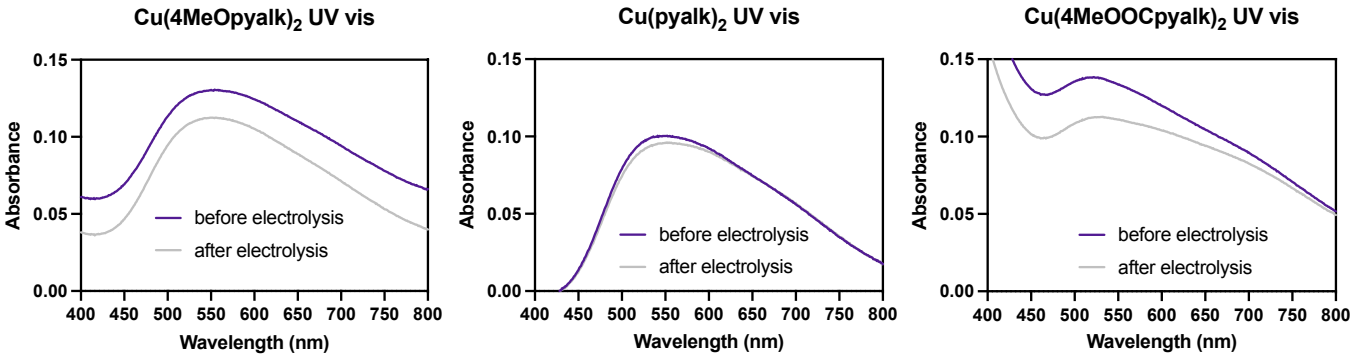

Figure S7. UV-visible spectra before and after controlled potential electrolysis for complexes **1**-**3**, showing degradation.

Complex	% degradation (at λ_{max}) after 2 h electrolysis
Cu(4-MeOpyalk)$_2$ (**3**)	14
Cu(pyalk)$_2$ (**1**)	5
Cu(4-MeOOCpyalk)$_2$ (**2**)	17

Table S1. Percent degradation for complexes **1**-**3** after 2 hours of bulk electrolysis at 1.2 V vs. NHE, assessed by comparing the absorption at λ_{max} before and after electrolysis.

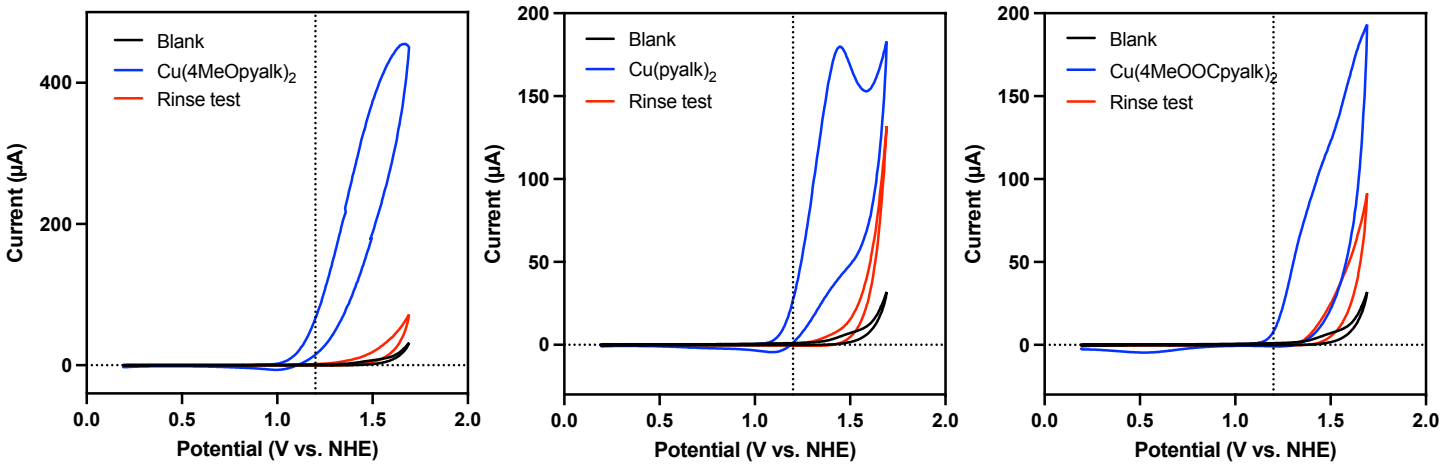

Figure S8. CVs of FTO electrodes after two hours of electrolysis after being rinsed, but not polished, and placed in a fresh solution of 0.1 M KNO_3 adjusted to pH 11. The black trace is a new FTO electrode, the blue trace is a solution of complexes **3** (left), **1** (center), and **2** (right), respectively, and the red trace is the electrode after electrolysis in fresh electrolyte solution. The dotted line indicates the potential of bulk electrolysis. Pt wire auxiliary electrode; Ag/AgCl (sat'd KCl) reference electrode (0.199 V vs. NHE); scan rate: 100 mV/s.

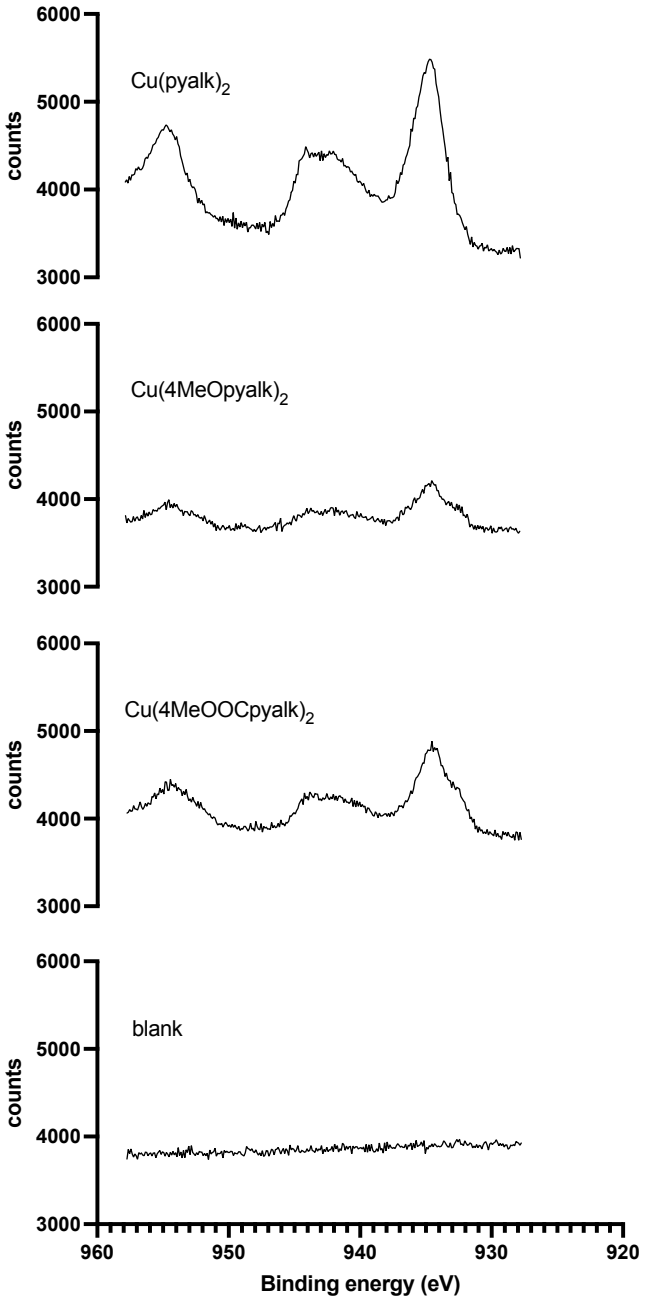

Figure S9. X-ray photoelectron spectroscopy of the FTO electrodes after two hours of electrolysis, showing Cu 2p peaks indicating copper on the surface. The spectra were energy corrected by the adventitous C 1s peak.

X-ray diffraction refinement details:

Table S2. Crystal data and structure refinement for **2** and **3**.

Identification code	007a-23002 (**2**)	007c-20025 (**3**)
Empirical formula	C20 H24 Cu N2 O6	C18 H24 Cu N2 O4
Formula weight	451.95	395.93
Temperature	93(2) K	93(2) K
Wavelength	1.54184 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/m
Unit cell dimensions	a = 6.8532(6) Å	a = 15.8992(3) Å
	b = 7.9673(7) Å	b = 6.9499(2) Å
	c = 9.5580(8) Å	c = 7.9839(2) Å
	α = 95.023(7)°.	α = 90°.
	β = 109.051(8)°.	β = 92.630(2)°.
	γ = 91.326(7)°.	γ = 90°.
Volume	490.66(8) $Å^3$	881.27(4) $Å^3$
Z	1	2
Density (calculated)	1.530 Mg/m^3	1.492 Mg/m^3
Absorption coefficient	1.927 mm^{-1}	1.264 mm^{-1}
F(000)	235	414
Crystal size	0.200 x 0.050 x 0.050 mm^3	0.200 x 0.180 x 0.080 mm^3
Crystal color and habit	Brown Plate	Purple Plate
Diffractometer	Rigaku Saturn 944+ CCD	Dectris Pilatus 3R
Theta range for data collection	4.920 to 66.880°.	3.200 to 28.281°.
Index ranges	-8<=h<=8, -9<=k<=9, -11<=l<=11	-21<=h<=21, -9<=k<=9, -10<=l<=10
Reflections collected	3484	11437
Independent reflections	3484 [R(int) = 0.0464]	1187 [R(int) = 0.0201]
Observed reflections (I > 2sigma(I))	3377	1181
Completeness to theta = 66.880°	99.0 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75266	1.00000 and 0.80519
Solution method	SHELXT-2014/5	SHELXT-2014/5
Refinement method	SHELXL-2014/7	SHELXL-2014/7
Data / restraints / parameters	3484 / 0 / 137	1187 / 0 / 76
Goodness-of-fit on F^2	1.095	1.144
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.1000	R1 = 0.0192, wR2 = 0.0524
R indices (all data)	R1 = 0.0374, wR2 = 0.1009	R1 = 0.0193, wR2 = 0.0525
Largest diff. peak and hole	0.584 and -0.396 e.$Å^{-3}$	0.412 and -0.297 e.$Å^{-3}$