Electronic Supplementary Information for

Cu^I SNS Triazole and Imidazole Pincers as Electrocatalyst Precursors for the Production of Solar Fuels

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1. General Methods

General methods. Except where noted, reactants were used as received from commercial sources without further purification. Synthesees of the ligands and the metallated complexes were performed as previously reported. Tetrabutyl ammonium hexafluorophosphate (TBA PF_6) was recrystallized from ethanol then dried under high vacuum for 24 hours before use. Metal complexes were stored in low-light in the glovebox conditions to prevent light exposure and degradation. All NMR spectra were gathered on a Bruker Avance-III 300 MHz NMR Spectrometer at room temperature with chemical shifts reported with respect to internal proton or carbon solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively.

Isopropylimidazole and isopropyltriazole were prepared according to literature procedures.[1, 2] 2,6-Bis(N-isopropyl-N'-methyleneimidazole)pyridine bromide, 2,6-bis(N-isopropyl-N'-methylenetriazole)pyridine bromide, 2,6-bis(N-isopropyl-N'-methyleneimidazole-2-thione)pyridine ($C_{19}H_{25}N_5S_2$), and 2,6-bis(N-isopropyl-N'-methylenetriazole-2-thione)pyridine ($C_{17}H_{23}N_7S_2$) were prepared following literature procedures.[3]

*Synthesis of Bis-[(κ³-S,S,N)(2,6-bis){[N-isopropyl-N'-methylene]triazole-2-thione} pyridine copper(I) tetrafluoroborate (**1**) (https://doi.org/10.1016/j.ica.2019.118996)*

In a 100 mL round bottom flask, 0.134 g (3.44 x10^{-4} mol) of ($C_{17}H_{23}N_7S_2$) was combined with 0.0824 g (3.47 x 10^{-4} mol) of copper(II) tetrafluoroborate ($Cu(BF_4)_2$) and dissolved in

15 mL of acetonitrile. The solution was refluxed for 20 hours. During the reaction time, the reaction solution became darker in orange color. The following day, the solvent was removed under reduced pressure. Yield: 0.194 g (74.8 %). Pale yellow crystals for X-ray diffraction were grown by a slow vapor diffusion of diethyl ether in to an acetonitrile solution containing the copper complex.

The mass of the titled product after recrystallization was 0.097 g (52.2 %)

Anal. Calc. for $C_{17}H_{23}CuN_7S_2BF_4$ (539.89): C, 37.82; H, 4.29; N, 18.16. Found: C, 37.87; H, 4.08; N, 18.09.

High-resolution electrospray mass spectrometry (positive ion mode) m/z = 452.09699 (molecular ion).

High-resolution electrospray mass spectrometry (negative ion mode) m/z = 87.01856 (molecular ion).

^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.02 (s, 2H, triazole CH); 8.28 (m, 1H, pyridine CH); 8.01 (m, 2H, pyridine CH); 5.55 (s, 4H, CH_2); 4.93 (septet, 2H, 3J = 6.6 Hz, isopropyl H); 1.37 (d, (^{3}J=6.6 Hz), 12 H, iPr CH_3).

^{13}C {^{1}H} NMR (DMSO-d_6, 75 MHz), δ 159.25; 153.98; 142.28 (triazole CH); 141.59 (pyridine para-CH); 126.43 (pyridine meta-CH); 51.18 ($H_3C\mathit{C}HCH_3$); 50.10 (CH_2); 20.61 (iPr CH_3).

*Synthesis of Bis-[(κ³-S,S,N)(2,6-bis){[N-isopropyl-N'-methylene]imidazole-1-ylidene-2-thione} pyridine copper(I) tetrafluoroborate (**2**)*

https://doi.org/10.1016/j.ica.2019.118996

In a 100 mL round bottom flask, 0.217 g (5.60 x10^{-4} mol) of ($C_{19}H_{25}N_5S_2$) was combined with 0.136 g (5.60 x 10^{-4} mol) of copper(II) tetrafluoroborate: $Cu(BF_4)_2$ and dissolved in 10 mL of acetonitrile. The solution was refluxed for 20 hours. During the reaction time, the solution changed color from orange to dark brown. The following day, the solvent was removed under reduced pressure. Yield: 0.282 g (93.6 %). Olive green crystals for X-ray diffraction were grown by a slow vapor diffusion of diethyl ether into an acetonitrile solution containing the copper complex. The mass of the titled product after recrystallization was 0.200 g (66.6 %)

Anal. Calc. for $C_{19}H_{25}CuN_5S_2BF_4$ (537.91): C, 42.42; H, 4.68; N, 13.02. Found: C, 42.25; H, 4.43; N, 12.95.

High-resolution electrospray mass spectrometry (positive ion mode) m/z = 450.09455 (molecular ion).

High-resolution electrospray mass spectrometry (negative ion mode) m/z = 87.01923 (molecular ion).

^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.24 (m, 1H, pyridine CH); 8.00 (m, 2H, pyridine CH); 7.66 (m, 2H (J = 2 Hz), imidazole CH); 7.55 (m, 2H (J = 2 Hz), imidazole CH); 5.50 (broad s, 4H, CH_2); 4.83 (septet, 2H, (^{3}J = 6.9 Hz), *i*Pr-H); 1.41 (d, (^{3}J = 6.6 Hz), 12 H, *i*Pr CH_3).

^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz), δ 154.75; 153.37; 141.55 (pyridine CH); 126.06 (pyridine CH); 119.98 (imidazole CH); 116.51 (imidazole CH); 51.96 (CH_2); 50.06 ($H_3C\mathit{C}HCH_3$); 21.30 (*i*Pr CH_3).

Gas Chromatography Three headspace injections were performed after each of the electrolyses were completed. Gas chromatographic analysis was performed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) in series with a Carboxen -1010 PLOT capillary column. Argon was used as the carrier gas. Flow rate was 3 mL/min. Flow and make up was 6 mL/min. Reference gas flow is 19 mL/min. The FID has no auxiliary gas, air flow was at 350 mL/min and H_2 was at 35 mL/min. The inlet was heated to 200°C and the oven started at a temperature of 35°C which was held for 8 minutes before a ramp of 20°C/min up to 195°C which was held for 1 minute. A gas-tight analytical syringe (Hamilton 1750, 500 μL) was used to collect 200 μL aliquots for analysis.

2. Cyclic Voltammograms

A standard three electrode setup with a glassy carbon working electrode (3mm, Bioanalytical Systems), a platinum wire counter electrode, and a silver wire single junction pseudo-reference were used for Cyclic Voltammograms (CVs). For electrolysis experiments a carbon cloth counter and working electrode was used in place of the platinum wire. Ferrocene was used an external standard. All experiments were done with a rigorous exclusion of air using an argon purge unless otherwise noted. All data workup was done via OriginPro vb9.4.0.220 software. CV data were collected on a Bio-Logic Systems SP150 potentiostat.

Cyclic Voltammetry: A solution of 0.1 M tetra-N-butylammonium hexafluorophosphate (TBA PF_6) and 5.0 mM of compound was prepared in 4 mL of dry acetonitrile. The solution was bubbled with argon and CV data were obtained from -0.4 V to -3.2 V vs Fc/Fc^+. The solution was then saturated with CO_2 and CVs were collected from -0.4 V to -3.2 V vs Fc/Fc^+. Finally, a proton concentration dependence was performed by adding varying amounts of 2,2,2-trifluoroethanol (TFE) the CVs were run at the same potentials.

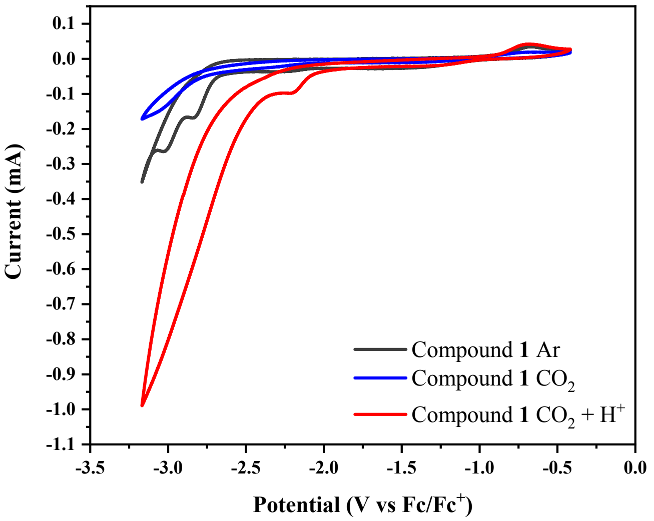


Figure S1. Cyclic Voltammogram of 5 mM Compound **1** in MeCN with 0.1 M TBA PF$_6$ as a supporting electrolyte. Scans were run under argon atmosphere (black), CO$_2$ atmosphere (blue), and CO$_2$ atmosphere with 100 µL TFE as a proton source (red).

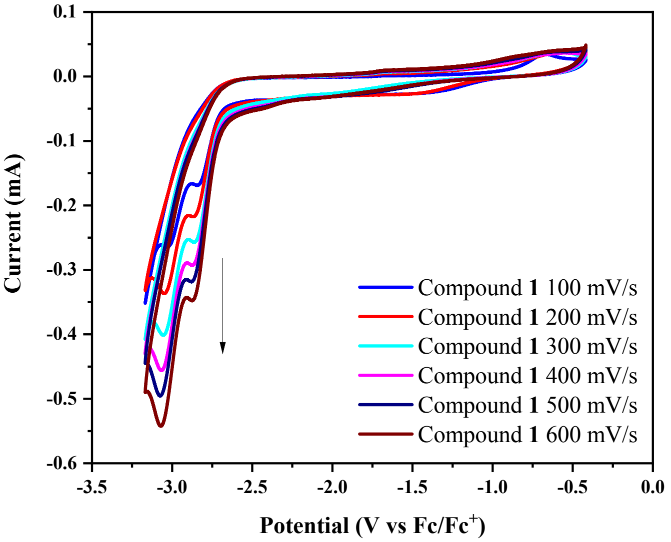


Figure S2. Scan Rate Dependence of Compound **1** by Cyclic Voltammetry: 5 mM Compound **1** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte under inert argon atmosphere. Arrow indicates increasing scan rates.

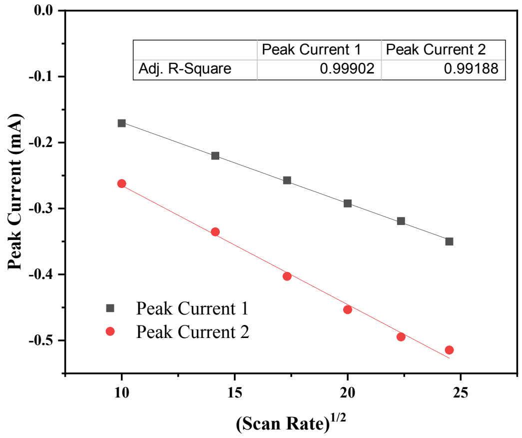


Figure S3. Sevçik plot showing linear behavior of peak current vs. scan rate$^{1/2}$ for Compound **1**: the peak at -2.8 V (peak current 1, black) and -3 V (peak current 2, red).

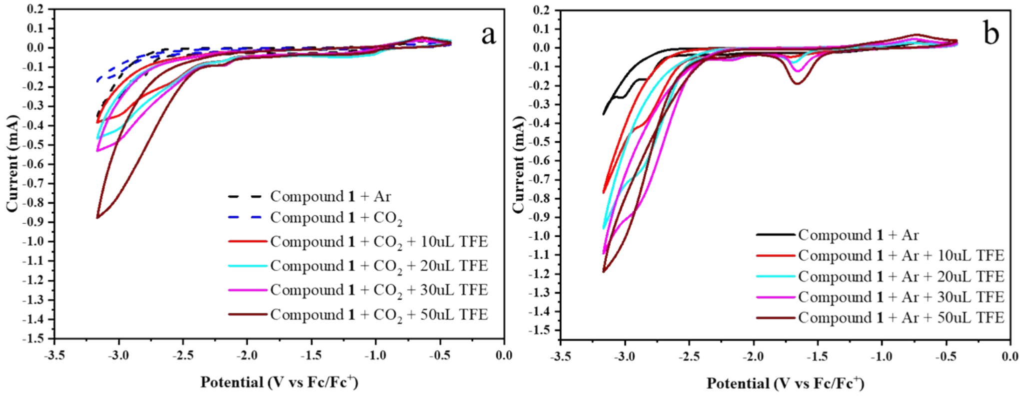


Figure S4. Proton dependence of Compound **1** by Cyclic Voltammetry: 5 mM Compound **1** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte. *Left a* Scans were taken at 100 mV/s under inert Ar atmosphere, CO_2, CO_2 with 10, 20, 30, and 50 µL TFE. *Right b* All scans were collected at 100 mV/s under inert Ar atmosphere but with varying TFE concentrations of 10, 20, 30, and 50 µL for comparison.

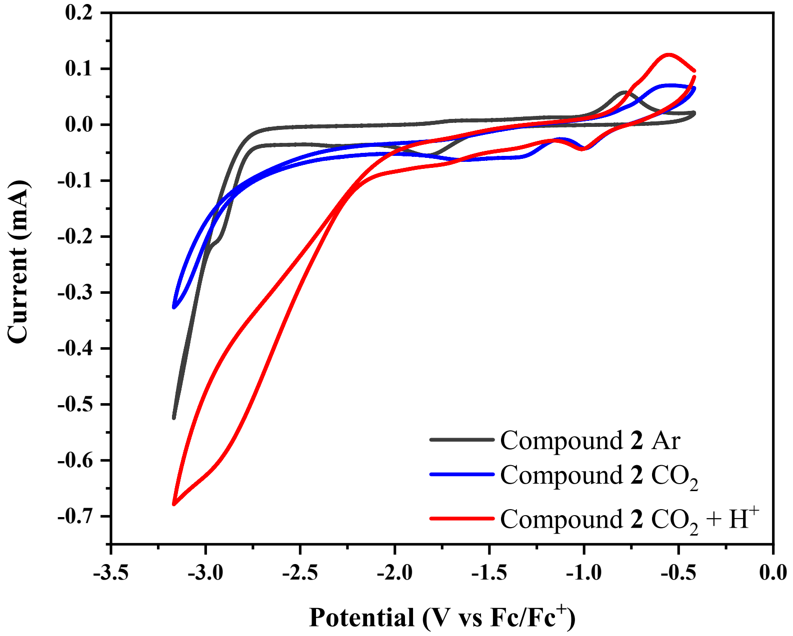


Figure S5. Cyclic Voltammogram of 5 mM Compound **2** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte. Scans were run under argon atmosphere (black), CO_2 atmosphere (blue), and CO_2 atmosphere with 100 µL TFE as a proton source (red).

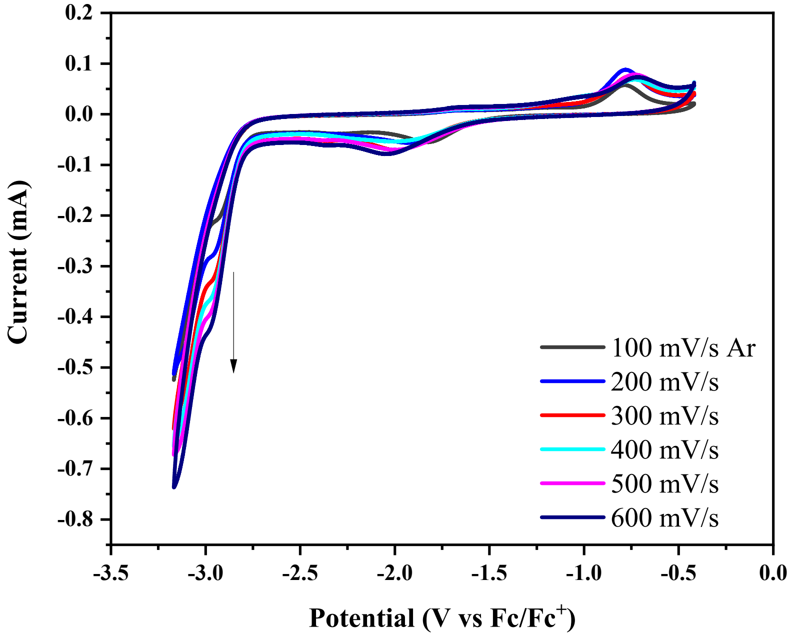


Figure S6. Scan Rate Dependence of Compound **2** by Cyclic Voltammetry: 5 mM Compound **2** in MeCN with 0.1 M TBA PF_6 as a supporting electrolyte under inert argon atmosphere. Arrow indicates increasing scan rate.

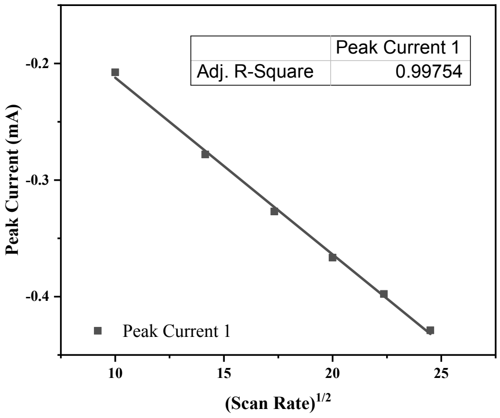


Figure S7. Sevçik plot showing linear behavior of peak current vs scan rate$^{1/2}$ for Compound **2.**

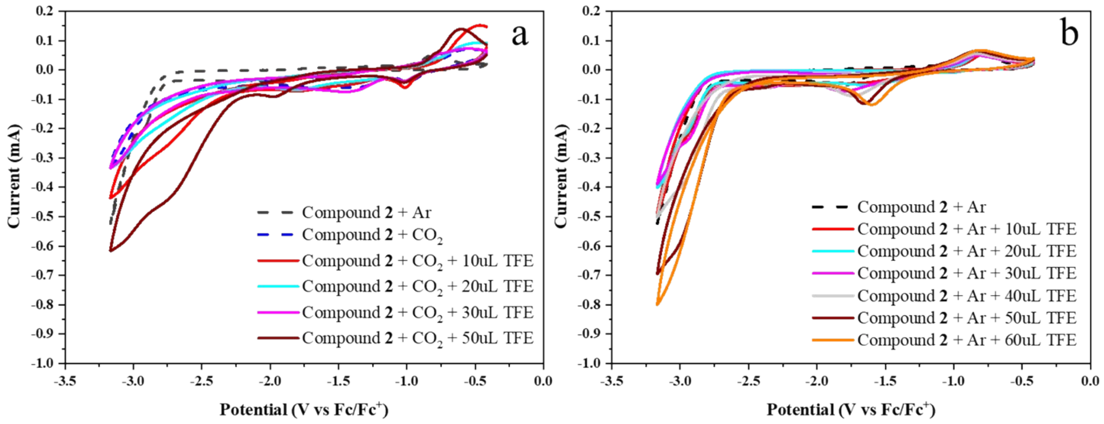


Figure S8. Proton dependence of Compound **2** by Cyclic Voltammetry: 5 mM Compound **2** in MeCN with 0.1 M TBA PF$_6$ as a supporting electrolyte. *Left a* Scans were taken at 100 mV/s under inert Ar atmosphere, CO$_2$, CO$_2$ with 10, 20, 30, 40, 50, and 60 µL TFE. *Right b* All scans were collected at 100 mV/s under inert Ar atmosphere but with varying TFE concentrations of 10, 20, 30, 40, 50, and 60 µL for comparison.

3. Bulk Electrolyses

Controlled-potential electrolyses were run for 1 h at -2.7 V vs Fc/Fc$^+$ in a custom built Schlenk electrolysis H-cell divided by a glass frit under an atmosphere of Ar. The working and counter electrodes were high-surface area 3x4 cm carbon cloth pieces (FuelCellEarth) and the reference electrode was a single-junction BASI Ag reference electrode.

Compound 1

Charge Passed: 183 C

Table S1. Hydrogen Quantitation for Compound 1

H_2 product	# Moles[a]	Turnover$_{obs}$[b,c]	% Faradaic Efficiency[d]
Run 1	6.32E-04	24.29	66.38
Run 2	6.16E-04	23.68	64.70
Run 3	6.39E-04	24.58	67.17
Average:	**6.29E-04**	**24.18**	**66.09**

[a]Number of moles is calculated from the integration values from the GC-TCD injection against a calibration curve of known analyte concentration [b] Turnover number is calculated based on the number of moles from the GC quantitation divided by the # of moles of catalyst added to the system [c] given that not all catalyst molecules are in direct contact with the electrode during the experiment, the turunover number is labeled as Turnover$_{obs}$ and is an underestimation of the true number [d] The Faradaic efficiency is calculated based on the overall amount of charge passed through the cell against the amount of observed product with 2e$^-$/mol analyte and 96485 C/mol.

Table S2. CO Quantitation for Compound 1

CO product	# Moles[a]	Turnover$_{obs}$[b,c]	% Faradaic Efficiency[d]
Run 1	9.97E-05	3.73	10.48
Run 2	1.06E-04	4.07	11.17
Run 3	1.09E-04	4.19	11.41
Average:	**1.04E-04**	**4.00**	**11.02**

[a]Number of moles is calculated from the integration values from the GC-TCD injection against a calibration curve of known analyte concentration [b] Turnover number is calculated based on the number of moles from the GC quantitation divided by the # of moles of catalyst added to the system [c] given that not all catalyst molecules are in direct contact with the electrode during the experiment, the turunover number is labeled as Turnover$_{obs}$ and is an underestimation of the true number [d] The Faradaic efficiency is calculated based on the overall amount of charge passed through the cell against the amount of observed product with 2e$^-$/mol analyte and 96485 C/mol.

Compound 2

3.9 mM

Charge Passed 178.3 C

Table S3. H_2 Quantitation for Compound 2

H_2 product	# Moles[a]	Turnover$_{obs}$[b,c]	% Faradaic Efficiency[d]
Run 1	0.000573	7.35	62.03
Run 2	0.000528	6.76	57.09
Run 3	0.000725	9.29	78.42
Average:	**0.000608**	**7.80**	**65.84**

[a]Number of moles is calculated from the integration values from the GC-TCD injection against a calibration curve of known analyte concentration [b] Turnover number is calculated based on the number of moles from the GC quantitation divided by the # of moles of catalyst added to the system [c] given that not all catalyst molecules are in direct contact with the electrode during the experiment, the turunover number is labeled as Turnover$_{obs}$ and is an underestimation of the true number [d] The Faradaic efficiency is calculated based on the overall amount of charge passed through the cell against the amount of observed product with 2e$^-$/mol analyte and 96485 C/mol.

Table S4. CO Quantitation for Compound 2

CO product	# Moles[a]	Turnover$_{obs}$[b,c]	% Faradaic Efficiency[d]
Run 1	5.42E-05	0.695	5.87
Run 2	5.07E-05	0.649	5.48
Run 3	4.00E-05	0.513	4.33
Average:	**4.83E-05**	**0.619**	**5.23**

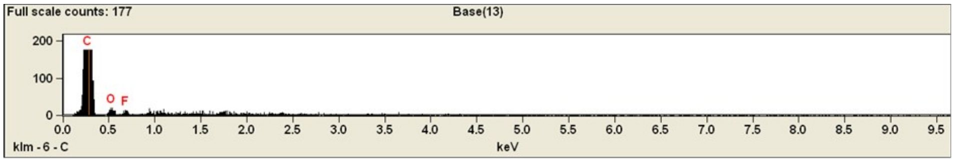
[a]Number of moles is calculated from the integration values from the GC-TCD injection against a calibration curve of known analyte concentration [b] Turnover number is calculated based on the number of moles from the GC quantitation divided by the # of moles of catalyst added to the system [c] given that not all catalyst molecules are in direct contact with the electrode during the experiment, the turunover number is labeled as Turnover$_{obs}$ and is an underestimation of the true number [d] The Faradaic efficiency is calculated based on the overall amount of charge passed through the cell against the amount of observed product with 2e$^-$/mol analyte and 96485 C/mol.

Table S5. CO and H_2 Quantitation statistics

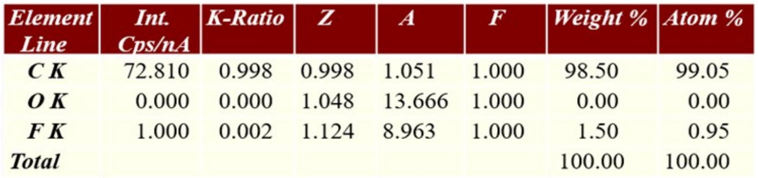
Compound	Avg CO Faradaic Efficiency	CO FE Standard Deviation	Avg H_2 Faradaic Efficiency	H_2 FE Standard Deviation	Avg Total FE%
Compound 1	11.02 %	±0.40 %	66.09 %	±1.03 %	77.10 %
Compound 2	5.23 %	±0.65 %	65.84 %	±9.11 %	71.07 %

4. SEM with EDS Analysis

Surface elemental analyses were performed at the CU Boulder COSINC-CHR Facility on a Field Emission Scanning Electron Microscope (FESEM) JEOL JSM-7401F with a beam cross section of one nanometer, a cold cathode field emission gun equipped with two detectors (in lens and lens backscatter). Elemental analyses of the electrolysis electrode surfaces were performed on this FESEM using an energy dispersive X-ray spectrometer (EDS).



Acc.Voltage: 15.0 kV Take Off Angle: 27.1 deg.



Element Line	*Int. Cps/nA*	*K-Ratio*	*Z*	*A*	*F*	*Weight %*	*Atom %*
C K	72.810	0.998	0.998	1.051	1.000	98.50	99.05
O K	0.000	0.000	1.048	13.666	1.000	0.00	0.00
F K	1.000	0.002	1.124	8.963	1.000	1.50	0.95
Total						100.00	100.00

Figure S9. EDS analysis of the carbon plate electrolysis working electrode after catalytic experiments.

References

1. A.A. Grindev, I.M Mihaltseva, *Synth. Commun.* **1994**, *24*, 1547-1555.

2. P.G. Bulger, I.F. Cottrell, C.J. Cowden, A.J. Davies, U-H. Dolling, *Tetrahedron Lett.* **2000**, *41*, 1297-1301.

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