

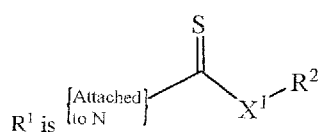
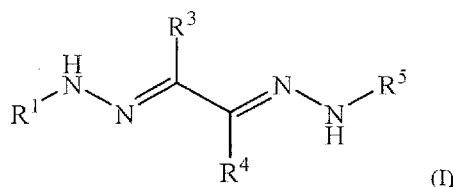
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PREPARATION AND THEIR USES(57) Abstract: In some embodiments, this application relates to inventive compounds (e.g., Formula (I), Formula (II), thiosemicarbazones and/or thiosemicarbazones and then metal (e.g., zinc, cobalt, nickel, or copper) complexes, and extended structures thereof), methods for preparation of the inventive compounds, compositions comprising the inventive compounds (e.g., anode, cathodes, catalysts (e.g., electrocatalysts), glassy carbon electrodes, carbon paste electrodes, covalently modified carbon (e.g., modified graphene)), electrochemical cells comprising compositions that comprise one or more inventive compounds, fuel cells comprising compositions that comprise one or more inventive compounds, uses of one or more inventive compounds to produce H₂ (e.g., via an electrochemical cell), and uses of one or more inventive compounds to create energy from H₂ (e.g., via a fuel cell). Additional embodiments of the invention are also discussed herein.

**COMPOUNDS, RELATED COMPOSITIONS, CATALYSTS,
ELECTROCHEMICAL CELLS, FUEL CELLS, THEIR PREPARATION AND
THEIR USES**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/348,420, filed June 10, 2016, which is herein incorporated by reference in its entirety. This application also claims the benefit of U.S. Provisional Application No. 62/436,490, filed December 20, 2016, which is herein incorporated by reference in its entirety.

GOVERNMENT RIGHTS

[0002] This invention was made with government support under CHE1361728 awarded by the National Science Foundation. The U.S. Government has certain rights in the invention.

BACKGROUND

[0003] Rising energy demands, coupled with growing concerns of repercussion from global climate change, have ignited considerable interest in the development of carbon neutral energy systems. Hydrogen is a promising component of these systems representing a light weight, energy dense energy carrier. Hydrogen evolution reactions (HERs), which involve a two-electron reduction of protons, can be used to store energy in H₂, with subsequent energy release through hydrogen oxidation reactions (HORs).

Platinum is a catalyst for HER and HOR, yet its scarcity and high costs limit practical large scale application.

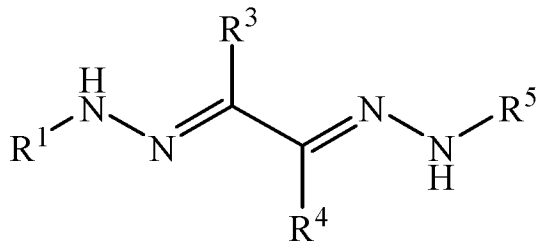
[0004] In addition, there remains a broader need for catalysts, related compounds, related compositions, and related electrochemical cells that have more desirable properties compared than currently exist, such as but not limited to: better efficiency (e.g., lower overpotential and higher turnover frequency), less expensive to produce, more easily synthesized, and more robust.

[0005] Certain embodiments of the invention can address one or more of the deficiencies discussed above.

[0006] In some embodiments, this application relates to inventive compounds (e.g., Formula (I), Formula (II), thiosemicarbazones and/or thiosemicarbazones and their metal (e.g., zinc, cobalt, or copper) complexes, and extended structures thereof), methods for preparation of the inventive compounds, compositions comprising the inventive compounds (e.g., anode, cathodes, catalysts (e.g., electrocatalysts), glassy carbon electrodes, carbon paste electrodes, covalently modified carbon (e.g., modified graphene)), electrochemical cells comprising compositions that comprise one or more inventive compounds, fuel cells comprising compositions that comprise one or more inventive compounds, uses of one or more inventive compounds to produce H₂ (e.g., via an electrochemical cell), and uses of one or more inventive compounds to create energy from H₂ (e.g., via a fuel cell). Additional embodiments of the invention are also discussed herein.

SUMMARY

[0007] Some embodiments of the present invention include a compound selected



from Formula (I),

(I), and

[0008] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof.

[0009] Some embodiments of the present invention include a compound selected from Formula (II), M·L (II) and

[0010] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof.

[0011] Yet other embodiments include a catalyst (e.g., an electrocatalyst) comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both. Some embodiments encompass an anode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both. Other embodiments include a cathode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both.

[0012] Still other embodiments of the invention include an electrochemical cell comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both. Additional embodiments include a fuel cell comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both.

[0013] Some embodiments of the invention include a method for producing H₂ comprising contacting, in an electrochemical cell, a first composition comprising a compound of Formula (I), a compound of Formula (II), or both with a second composition comprising water. Additional embodiments include a method for producing electricity comprising contacting, in a fuel cell, a first composition comprising a compound of Formula (I), a compound of Formula (II), or both with a second composition comprising H₂.

[0014] Further embodiments encompass a method for preparing a compound of Formula (I) comprising any suitable method, such as those disclosed herein, or a method for preparing a compound of Formula (II) comprising any suitable method, such as those disclosed herein. Additional embodiments encompass a method for preparing a catalyst (e.g., an electrocatalyst) comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both, comprising any suitable method, such as those disclosed herein. Still other embodiments include a method for preparing an anode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both, comprising any suitable method, including those disclosed herein. Still further embodiments include a method for preparing a cathode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both, comprising any suitable method, such as those disclosed herein.

[0015] Other embodiments of the invention are also disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the description of specific embodiments presented herein.

[0017] **FIG. 1. Electrocatalytic H₂ evolution and H₂ oxidation.** (A) Cyclic voltammograms of 3 mM ZnL in methanol with (from bottom to top) no added acid, 6 mM CH₃COOH, 9 mM CH₃COOH, and 12 mM CH₃COOH. Data collected at a scan rate of 0.5 V/s in the presence of 0.1 M Bu₄NPF₆ as supporting electrolyte. (B) Plot of i_{cat} versus [CH₃COOH] for 3 mM ZnL (upper lines at 3 mM CH₃COOH) at scan rates of 0.2 (Δ), 0.3 ($\circ$), 0.4 ($\square$), and 0.5 ($\diamond$) V/s and 3 mM H₂L (lower lines at 3 mM CH₃COOH) at scan rates of 0.2(Δ), 0.5 ($\diamond$), and 1.0 ($\times$) V/s. (C) Cyclic voltammograms of 0.3 mM ZnL in methanol under 1 atm. H₂ (from top to bottom at 1.00 V) with no added base, 3 mM (CH₃CH₂)₃N, 6 mM (CH₃CH₂)₃N, 12 mM (CH₃CH₂)₃N, 21 mM (CH₃CH₂)₃N, and 30 mM (CH₃CH₂)₃N. Data collected at a scan rate of 0.5 V/s in the presence of 0.1 M Bu₄NPF₆ as supporting electrolyte. (D) Plot of i_{cat}/i_p versus [(CH₃CH₂N)₃] for 0.3 mM ZnL under 1 atm. H₂ (clustered lines second from the top) and 3 mM H₂L under 1 atm. H₂ (top line and bottom two lines) at scan rates of 0.2(Δ), 0.5 ($\diamond$), and 1.0 ($\times$) V/s.

[0018] **FIG. 2. Mechanistic Studies of H₂ evolution.** (A) Plot of charge versus time recorded during bulk electrolysis of 0.1 mM ZnL and 12 mM CH₃COOH in methanol with 0.1 M Bu₄NPF₆ as supporting electrolyte. (B) Comparisons of experimental (solid) and simulated (dotted) cyclic voltammograms for 3 mM ZnL and 12 mM CH₃COOH in methanol with 0.1 M Bu₄NPF₆ as supporting electrolyte at scan rates

of (from bottom to top) 0.3, 0.4, and 0.5 V/s. (C) Concurrent catalytic pathways for hydrogen evolution through homo-coupling of neutral $\text{Zn}(\text{HL}\cdot)$ radicals and hetero-coupling of a neutral $\text{Zn}(\text{HL}\cdot)$ and cationic $[\text{Zn}(\text{H}_2\text{L}\cdot)]^+$ radicals.

[0019] **FIG. 3. Energy profile along with spin densities of species involved in**

5 **catalyzed H_2 evolution.** Spin-density profiles for $\text{Zn}(\text{HL}\cdot)$ (A), and $[\text{Zn}(\text{H}_2\text{L}\cdot)]^+$ (B). (C)

Relative energies (ZPE corrected) for H_2 evolution through the hetero-coupling of

$\text{Zn}(\text{HL}\cdot)$ and $[\text{Zn}(\text{H}_2\text{L}\cdot)]^+$ using the B97-D/6-311G(d) level of theory. (D) Structure of

the singlet $[\text{Zn}_2(\text{H}_3\text{L}\cdot_2)]^+$ transition state through the hetero-coupling pathway. See Fig. 20

for further information regarding the HER mechanism, analysis of the eigenvector

10 associated with the imaginary frequency $i1572\text{ cm}^{-1}$, and the charge densities of atoms for

H_2 evolution with respect to intrinsic reaction coordinate (IRC).

[0020] **FIG. 4. ZnL in acetonitrile CV, $v = 0.2\text{ V/s}$ - 0.1 M Bu_4NPF_6**

acetonitrile solution with 3 mM ZnL vs Fc^+/Fc^0 .

[0021] **FIG. 5. ZnL HER acid concentration dependent CVs, $v = 0.2\text{ V/s}$ - 0.1**

15 M Bu_4NPF_6 acetonitrile solution with increasing concentrations of acid; vs Fc^+/Fc^0 .

[0022] **FIG. 6. H_2L HER acid dependent CVs, $v = 0.5\text{ V/s}$ - 0.1 M Bu_4NPF_6**

methanol solution with increasing concentrations of acid; vs Fc^+/Fc (lowest concentration at bottom).

[0023] **FIG. 7. H_2L HOR base concentration dependent CVs, $v = 0.5\text{ V/s}$ -**

20 H_2L HOR, H_2 atmosphere with increasing $[\text{Et}_3\text{N}]$, vs Fc^+/Fc^0 (highest concentration of base at bottom).

[0024] **FIG. 8. GC-TCD Readout** - GC readouts of gas sampled every 30 minutes during 2.5 hour electrolysis of ZnL.

[0025] **FIG. 9. ZnL Diffusion Limited CV Overlay** - 0.1 M Bu₄NPF₆ methanol solution with 3 mM ZnL run from $v = 0.1 - 1.0$ V/s vs Ag/AgCl (highest mV/s at bottom).

[0026] **FIG. 10. Peak currents vs square root of scan rate** - 0.1 M Bu₄NPF₆ methanol solutions with 3 mM ZnL, plot showing peak current plotted against the square root of the scan rate from diffusion limited CVs.

[0027] **FIG. 11. ZnL concentration dependent CVs, $v = 0.5$ V/s** - 0.1 M Bu₄NPF₆ methanol solution with 12 mM acetic acid added with increasing ZnL concentrations; vs Ag/AgCl (highest ZnL concentration at bottom).

[0028] **FIG. 12. Plot of $[ZnL]^2$ vs catalytic current, $v = 0.5$ V/s.**

[0029] **FIG. 13. Simulation of experimental data using DigiElch** - ZnL HER CV Simulations of experimental data; 12 mM [acid]; $v = 0.2 - 0.5$ V/s vs Fc⁺/Fc⁰ (lowest V/s at bottom).

[0030] **FIG. 14. Simulation of experimental data using DigiElch** - ZnL HER CV Simulations of experimental data; 12 mM [acid]; $v = 0.6 - 5.0$ V/s vs Fc⁺/Fc⁰ (lowest V/s at bottom).

[0031] **FIG. 15. Simulation of experimental data using DigiElch** - ZnL HER CV Simulations of experimental data; 6 mM [acid]; $v = 0.2 - 0.5$ V/s vs Fc⁺/Fc⁰ (lowest V/s at bottom).

[0032] **FIG. 16.** Optimized structure of $[\text{ZnHL}]^+$ with protonation on hydrazino nitrogen.

[0033] **FIG. 17.** Optimized structure of $[\text{ZnHL}]^+$ with protonation on sulfur.

[0034] **FIG. 18.** Optimized structure of $[\text{ZnHL}]^+$ with protonation on amine
5 nitrogen.

[0035] **FIG. 19.** Optimized structure of $[\text{ZnHL}]^+$ with protonation on zinc.

[0036] **FIG. 20.** Transition state analysis of $[\text{Zn}_2\text{H}_3\text{L}_2]^+$ - (Upper) Transition state geometry of $[\text{Zn}_2\text{H}_3\text{L}_2]^+$ along the HER pathway, shown with active N-H bond lengths associated with the imaginary frequency $i1572\text{ cm}^{-1}$, and equilibrium bond
10 lengths in parentheses. (Lower) Charge densities of atoms near H_2 evolution with respect to IRC; N-H of $[\text{Zn}(\text{HL})]^+$ (bottom and top curves), and N-H of $\text{Zn}(\text{H}_2\text{L})$ (curves 2nd from top and 2nd from bottom).

[0037] **FIG. 21.** UV-Vis spectra from Spectroelectrochemical Electrolysis - (Upper) UV spectra recorded every 15 minutes during the electrolysis of 1 mM ZnL
15 under applied potential of -1.7 V in 0.1 M Bu_4NPF_6 methanol solution. (Lower) Blow up of 350-500 nm region showing isosbestic point at 400 nm.

[0038] **FIG. 22.** CV after ZnL electrolysis - CV of ZnL after electrolysis in 0.1 M Bu_4NPF_6 methanol solution with 12 mM acetic acid added. $v = 0.2\text{ V/s}$ vs Fc^+/Fc^0 .

[0039] **FIG. 23.** Overview of reactivity using non-innocent ligands.

[0040] **FIG. 24.** Electrochemical Characterization - CVs of CuL^1 in 0.1 M
20 Bu_4NPF_6 ACN solution at scan rates of (from inside to outside, at peak) 0.1, 0.2, 0.3, 0.4,

0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 V/s. CuL^1 . (Inset: Cottrell plot of peak current vs square root of scan rate.)

[0041] **FIG. 25. Homogeneous Catalytic Hydrogen Evolution: Cyclic**

Voltammetry - (A) CVs (from bottom to top) of 0.6 mM CuL^1 in 0.1M Bu_4NPF_6 ACN

5 with 0.0244 M CH_3COOH , 0.0448 M CH_3COOH , 0.0896 M CH_3COOH , 0.134 M

CH_3COOH , 0.179 M CH_3COOH , 0.244 M CH_3COOH , and 0.269 M CH_3COOH , (Inset:

Blow up of CV showing shift of Cu^{III} reduction event.); **(B)** Plot of i_{cat}/i_p vs $[\text{CH}_3\text{COOH}]$

for 0.60 mM CuL^1 at scan rates of 0.20 (X), 0.50 (●) and 1.00 (*) V/s; **(C)** Catalytic Tafel

Plot of CuL^1 with comparison of performance for hydrogen evolution with those of

10 others reported in literature. ♦: $\text{Co}^{\text{II}}(\text{dmgH})_2\text{py}$; ●: $[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}^{\text{Ph}})_2]^{2+}$; ■: NiL^2 ; ▲: ZnL^1 ; X: H_2L^1 .

[0042] **FIG. 26. Cyclic Voltammetry - (A)** CVs (from bottom to top) of 0.6 mM

CuL^1 in 0.1M Bu_4NPF_6 DMF with 0.0244 M CH_3COOH , 0.0672 M CH_3COOH , 0.112 M

CH_3COOH , 0.157 M CH_3COOH , 0.202 M CH_3COOH , 0.246 M CH_3COOH , 0.269 M

15 CH_3COOH , and 0.292 M CH_3COOH . **(B)** Plot of i_{cat}/i_p vs $[\text{CH}_3\text{COOH}]$ for 0.6 mM

CuL^1 at scan rates of 0.20 (♦), 0.50 (■) and 1.00 (▲) V/s. **(C)** CVs of 0.6 mM CuL^1 in

0.1M Bu_4NPF_6 DMF with 0.292 M CH_3COOH at scan rates from 0.1 to 1.0 V/s. **(D)** Plot

of i_{cat} vs scan rate for 0.6 mM CuL^1 in 0.1M Bu_4NPF_6 DMF with 0.292 M CH_3COOH .

[0043] **FIG. 27. Kinetic Isotope Effects (KIE) - (A)** CVs of 0.6 mM CuL^1 in

20 0.1 M Bu_4NPF_6 ACN solution with 0.269 M acetic acid at (from top to bottom) 0 mole %

of CD_3COOD , 20 mole % of CD_3COOD , 40 mole % of CD_3COOD , 60 mole % of

CD_3COOD , 80 mole % of CD_3COOD , and 100 mole % of CD_3COOD mole % of

CD_3COOD . **(B)** Plot of KIE vs % CD_3COOD .

[0044] **FIG. 28. Controlled Potential Electrolysis (CPE)** - CPE of 0.6 mM CuL^1 in 0.1 M Bu_4NPF_6 ACN (left-most and second from left) or 0.1 M Bu_4NPF_6 DMF (second from right and right-most) solutions with 0.292 M CH_3COOH added; 0.1 M Bu_4NPF_6 DMF with 0.292 M CH_3COOH , no CuL^1 (overlaps with x-axis, zero apparent charge)).

[0045] **FIG. 29. Control Experiments** - (A) CVs run in 0.1 M Bu_4NPF_6 ACN solutions, showing blank ACN (bottom), with 0.0672 M acetic acid added (dashed - middle), and with 0.0672 M acetic acid and 0.6 mM CuL^1 (top). (B) CVs run in 0.1 M Bu_4NPF_6 DMF solutions, showing blank DMF (solid), with 0.0224 M acetic acid added (dashed), and with 0.0224 M acetic acid and 0.6 mM CuL^1 (top).

[0046] **FIG. 30. Post-electrolysis “dip-test” of film** - Performed on working electrode post CPE. Electrode washed with D.I water and immersed into a fresh solution of 0.1 M Bu_4NPF_6 ACN (bottom), and upon addition of 0.292 M CH_3COOH (top).

[0047] **FIG. 31. Film analysis** - Calculated (left bar) and XPS experimental (right bar) relative atomic mass percent for post-electrolysis CuL^1 derived films. Error bars show $\pm 3\sigma$ for 4 experimental measurements.

[0048] **FIG. 32. UV-Visible spectrum of CuL^1** - titrated with CH_3COOH (from top to bottom); 0.022 M, 0.044 M, 0.056 M, 0.067 M, 0.089 M, 0.112 M, 0.134 M, 0.157 M, 0.202 M, 0.244 M, 0.269 M, 0.292 M, 0.337 M, and 0.382 M.

[0049] **FIG. 33. ORTEP representation of $[\text{Cu}(\text{L}^1\text{H}_2)(\text{ClO}_4)]\text{ClO}_4$** - Selected distances (Å): Cu-N1 1.9579(18), Cu-N4 1.9557(18), Cu-S1 2.2462(6), Cu-S2 2.2593(6), Cu-O1 2.5166(16), Cu...O7 2.9233(19), N2-H2n 0.78(3), N3-H3n 0.76(3), N4-N5 1.364(2), N5-H5n 0.78(2), N6-H6n 0.78(3). Selected angles (°): N1-Cu-N4 78.80(7), N1-

Cu-S1 86.88(6), N4-Cu-S(2) 86.08(5), S1-Cu-S2 108.02(2), N2-N1-Cu 118.19(14), N1-N2-H2n 121(2), N5-N4-Cu 119.13(14), N4-N5-H5n 119.9(19).

[0050] **FIG. 34. Proposed mechanism of hydrogen evolution by CuL¹.**

[0051] **FIG. 35. Energetic Stability from DFT - (A)** Energetic stability of
5 protonated species, [CuL¹H]⁺ (S = ½). **(B)** Energetic Stability of protonated / reduced species, CuL¹H (S = 0), B3LYP/6-311g(d,p).

[0052] **FIG. 36. Energetic Stability from DFT -** Energetic stability of the protonated / reduced / protonated species, [CuL¹H₂]⁺, in the singlet (S = 0) and triplet (S = 1) electronic states, B3LYP/6-311g(d,p).

10 [0053] **FIG. 37. Energetic Stability from DFT - (A)** Energetic stability of CuL¹H₂ (S = ½). **(B)** Spin-density map of CuL¹H₂ with second protonation on N4, B3LYP/6-311g(d,p).

[0054] **FIG. 38. Qualitative frontier molecular orbital diagram highlighting site of reduction.**

15 [0055] **FIG. 39. Full ORTEP view of [Cu(L¹H₂)(ClO₄)]ClO₄.**

[0056] **FIG. 40. Open circuit potential measurement in 0.1 M Bu₄NPF₆ acetonitrile solution (top) and in 0.1 M Bu₄NPF₆ DMF solution (bottom) with 0.269 M acetic acid added.**

[0057] **FIG. 41. GC-TCD readout for gaseous product identification from**
20 **electrolysis**

[0058] **FIG. 42. 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ acetonitrile HER CVs scanned at 0.2 V/s.**

[0059] **FIG. 43.** 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ acetonitrile HER CVs scanned at 0.5 V/s.

[0060] **FIG. 44.** 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ acetonitrile HER CVs scanned at 1.0 V/s.

5 [0061] **FIG. 45.** [CuL¹] dependence in 0.1 M Bu₄NPF₆ acetonitrile with 0.269 M CH₃COOH HER CVs.

[0062] **FIG. 46.** Plot of i_p vs [CuL¹] in 0.1 M Bu₄NPF₆ acetonitrile with 0.269 M CH₃COOH.

10 [0063] **FIG. 47.** 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ DMF; HER CVs scanned at 0.2 V/s.

[0064] **FIG. 48.** Plot of i_{cat}/i_p vs [CH₃COOH]; $\nu = 0.2$ V/s.

[0065] **FIG. 49.** 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ DMF; HER CVs scanned at 0.5 V/s.

[0066] **FIG. 50.** Plot of i_{cat}/i_p vs [CH₃COOH]; $\nu = 0.5$ V/s.

15 [0067] **FIG. 51.** 0.6 mM CuL¹ in 0.1 M Bu₄NPF₆ DMF; HER CVs scanned at 1.0 V/s.

[0068] **FIG. 52.** Plot of i_{cat}/i_p vs [CH₃COOH]; $\nu = 1.0$ V/s.

[0069] **FIG. 53.** Plot of scan rate vs TOF for CuL¹ in DMF.

[0070] **FIG. 54.** Dip test post electrolysis in DMF.

20 [0071] **FIG. 55.** ¹H NMR spectrum of [CuL¹].

[0072] **FIG. 56.** ¹H NMR spectrum of [CuL¹H]⁺.

[0073] **FIG. 57.** Spin-density map of CuL¹ (S=1/2).

[0074] **FIG. 58.** Spin-density map of $[\text{CuL}^1\text{H}]^+$.

[0075] **FIG. 59.** Energetic stability of the protonated / reduced species, CuL^1H , in the singlet ($S = 0$) and triplet ($S = 1$) electronic states.

[0076] **FIG. 60.** Full CV of CuL^1 .

5 [0077] **FIG. 61.** High resolution (top) XPS of copper atoms and low resolution of entire adsorbed film (bottom).

[0078] **FIG. 62.** Post CV dip-test after 50 CV Cycles.

[0079] **FIG. 63.** Post CV dip-test after 50 CV Cycles.

[0080] **FIG. 64.** CV of Asymmetric Cu ligand - CVs of CuL^{10a} in CH_3CN with
10 increasing $[\text{H}^+]$.

[0081] **FIG. 65.** GCE (Glass Carbon Electrode) polarization curves -

Polarization curves in $0.5 \text{ H}_2\text{SO}_4 (\text{aq})$ with modified GCE (working), Pt (counter), and Ag/AgCl (3.5 M KCl) (reference) electrodes.

[0082] **FIG. 66.** Carbon Paste Electrode (CPE) analysis – (a) SEM image of
15 CPE- CuL^1 ; (b) Nyquist plot of CPE- CuL^1 ; Polarization curves for modified CPEs.

DETAILED DESCRIPTION

[0083] While embodiments encompassing the general inventive concepts may take diverse forms, various embodiments will be described herein, with the understanding
20 that the present disclosure is to be considered merely exemplary, and the general inventive concepts are not intended to be limited to the disclosed embodiments.

[0084] In some embodiments, this application relates to inventive compounds (e.g., Formula (I), Formula (II), thiosemicarbazones and/or thiosemicarbazones and their metal (e.g., zinc, cobalt, or copper) complexes, and extended structures thereof), methods for preparation of the inventive compounds, compositions comprising the inventive compounds (e.g., anode, cathodes, catalysts (e.g., electrocatalysts), glassy carbon electrodes, carbon paste electrodes, covalently modified carbon (e.g., modified graphene)), electrochemical cells comprising compositions that comprise one or more inventive compounds, fuel cells comprising compositions that comprise one or more inventive compounds, uses of one or more inventive compounds to produce H₂ (e.g., via an electrochemical cell), and uses of one or more inventive compounds to create energy from H₂ (e.g., via a fuel cell). Additional embodiments of the invention are also discussed herein.

[0085] As used herein (unless otherwise specified), the term “alkyl” means a monovalent, straight or branched hydrocarbon chain. For example, the terms “C₁-C₇ alkyl” or “C₁-C₄ alkyl” refer to straight- or branched-chain saturated hydrocarbon groups having from 1 to 7 (e.g., 1, 2, 3, 4, 5, 6, or 7), or 1 to 4 (e.g., 1, 2, 3, or 4), carbon atoms, respectively. Examples of C₁-C₇ alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, n-hexyl, and n-septyl. Examples of C₁-C₄ alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, and t-butyl.

[0086] As used herein (unless otherwise specified), the term “alkenyl” means a monovalent, straight or branched hydrocarbon chain that includes one or more (e.g., 1, 2, 3, or 4) double bonds. Examples of alkenyl groups include, but are not limited to, vinyl,

allyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, and 5-hexenyl.

[0087] As used herein (unless otherwise specified), the term “alkoxy” means any of the above alkyl groups which is attached to the remainder of the molecule by an oxygen atom (alkyl-O-). Examples of alkoxy groups include, but are not limited to, methoxy (sometimes shown as MeO-), ethoxy, isopropoxy, propoxy, and butyloxy.

[0088] As used herein (unless otherwise specified), the term “alkynyl” means a monovalent, straight or branched hydrocarbon chain that includes one or more (e.g., 1, 2, 3, or 4) triple bonds and that also may optionally include one or more (e.g. 1, 2, 3, or 4) double bonds in the chain. Examples of alkynyl groups include, but are not limited to, ethynyl, 1-propynyl, 2-propynyl, 1-butylnyl, 2-butylnyl, 3-butylnyl, 1-pentylnyl, 2-pentylnyl, 3-pentylnyl, 4-pentylnyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, and 5-hexynyl.

[0089] As used herein (unless otherwise specified), the term “aryl” means a monovalent, monocyclic or bicyclic, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 member aromatic hydrocarbon group which, when unsubstituted. Examples of aryl groups include, but are not limited to, phenyl, naphthyl, pyrene, tolyl, and xylyl. For an aryl that is bicyclic, one or both rings can be substituted.

[0090] As used herein (unless otherwise specified), the term “cycloalkyl” means a monovalent, monocyclic or bicyclic, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 membered hydrocarbon group. The rings can be saturated or partially unsaturated. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and bicycloalkyls (e.g., bicyclooctanes such as [2.2.2]bicyclooctane or [3.3.0]bicyclooctane, bicyclononanes such as

[4.3.0]bicyclononane, and bicyclodecanes such as [4.4.0]bicyclodecane (decalin), or spiro compounds). For a monocyclic cycloalkyl, the ring is not aromatic. For a bicyclic cycloalkyl, if one ring is aromatic, then the other is not aromatic. For a bicyclic cycloalkyl, one or both rings can be substituted.

5 [0091] As used herein (unless otherwise specified), the term “halogen” means monovalent Cl, F, Br, or I.

[0092] As used herein (unless otherwise specified), the term “heteroaryl” means a monovalent, monocyclic or bicyclic, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 membered, hydrocarbon group, where 1, 2, 3, 4, 5, 6, 7, 8, or 9 carbon atoms are
10 replaced by a hetero atom independently selected from nitrogen, oxygen, or sulfur atom, and the monocyclic or bicyclic ring system is aromatic. Examples of heteroaryl groups include, but are not limited to, thienyl (or thiophenyl), furyl, indolyl, pyrrolyl, pyridinyl, pyrazinyl, oxazolyl, thiazolyl, quinoliny, pyrimidinyl, imidazolyl, 1-methyl-imidazolyl, triazolyl, tetrazolyl, 1H-pyrazol-4-yl, 1-Me-pyrazol-4-yl, pyridin-3-yl, pyridin-4-yl, 3,5-
15 dimethylisoxazolyl, 1H-pyrrol-3-yl, 3,5-di-Me-pyrazolyl, and 1H-pyrazol-4-yl. For a bicyclic heteroaryl, if one ring is aryl, then the other is heteroaryl. For a bicyclic heteroaryl, one or both rings can have one or more hetero atoms. For a bicyclic heteroaryl, one or both rings can be substituted. An N-heteroaryl means a heteroaryl that comprises one or more N (e.g., 1, 2, 3, 4, 5, 6, 7, or 8); an N-heteroaryl may also
20 comprise other hetero atoms.

[0093] As used herein (unless otherwise specified), the term “heterocyclyl” means a monovalent, monocyclic or bicyclic, 5, 6, 7, 8, 9, 10, 11, or 12 membered, hydrocarbon, where 1, 2, 3, 4, 5, or 6 carbon atoms are replaced by a hetero atom

independently selected from nitrogen atom, oxygen atom, or sulfur atom, and the monocyclic or bicyclic ring system is not aromatic. Examples of heterocyclyl groups include, but are not limited to, tetrahydropyran, pyrrolidinyl (e.g., pyrrolidin-1-yl, pyrrolidin-2-yl, pyrrolidin-3-yl, or pyrrolidin-4-yl), piperazinyl (e.g., piperazin-1-yl, piperazin-2-yl, piperazin-3-yl, or piperazin-4-yl), piperidinyl (e.g., piperidin-1-yl, piperidin-2-yl, piperidin-3-yl, or piperidin-4-yl), and morpholinyl (e.g., morpholin-1-yl, morpholin-2-yl, morpholin-3-yl, or morpholin-4-yl). For a bicyclic heterocyclyl, if one ring is aromatic (e.g., monocyclic aryl or heteroaryl), then the other ring is not aromatic. For a bicyclic heterocyclyl, one or both rings can have one or more hetero atoms. For a bicyclic heterocyclyl, one or both rings can be substituted. An N-heterocyclyl means a heterocyclyl that comprises one or more N (e.g., 1, 2, 3, 4, 5, or 6); an N-heterocyclyl may also comprise other hetero atoms.

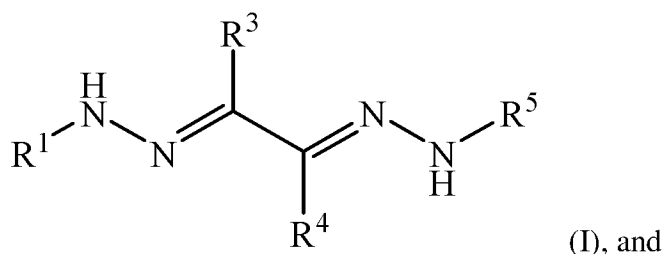
[0094] As used herein (unless otherwise specified), the term “hetero atom” means an atom selected from nitrogen atom, oxygen atom, or sulfur atom.

[0095] As used herein (unless otherwise specified), the terms “hydroxy” or “hydroxyl” indicates the presence of a monovalent -OH group.

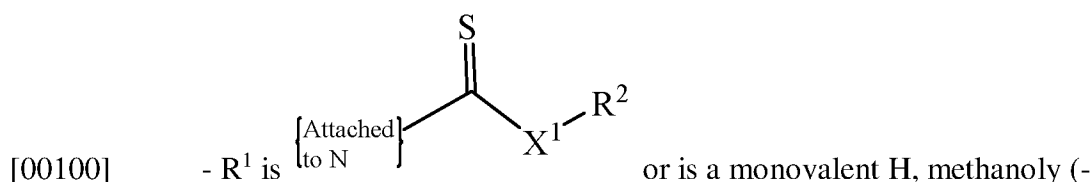
[0096] As used herein (unless otherwise specified), the term “substituted” (e.g., as in substituted alkyl) means that one or more hydrogen atoms of a chemical group (with one or more hydrogen atoms) can be replaced by one or more non-hydrogen substituents selected from the specified options. The replacement can occur at one or more positions. The term “optionally substituted” means that one or more hydrogen atoms of a chemical group (with one or more hydrogen atoms) can be, but is not required to be substituted.

[0097] Some compounds of the invention can have one or more chiral centers and can exist in and be isolated in optically active and racemic forms, for any of the one or more chiral centers. Some compounds can exhibit polymorphism. The compounds of the present invention encompass any optically active, racemate, stereoisomer form, polymorphism, or mixtures thereof. If a chiral center does not provide an indication of its configuration (i.e., R or S) in a chemical structure, it should be considered to represent R, S or a racemate.

[0098] Some embodiments of the invention include compounds of Formula (I),



[0099] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein



COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl),

C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

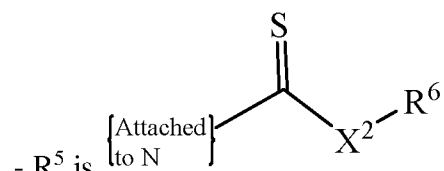
[00101] - X¹ is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more (e.g., 0, 1, or 2) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00102] - R² is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00103] - R³ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene),

cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00104] - R⁴ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00105]  or is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00106] - X² is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more (e.g., 0, 1, or 2) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

[00107] - R⁶ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇

alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl.

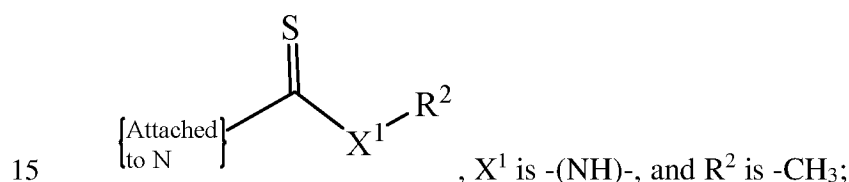
[00108] In some embodiments, the compound of Formula (I) comprises one or more of the following:

10 [00109] (a) R³ is the same as R⁴;

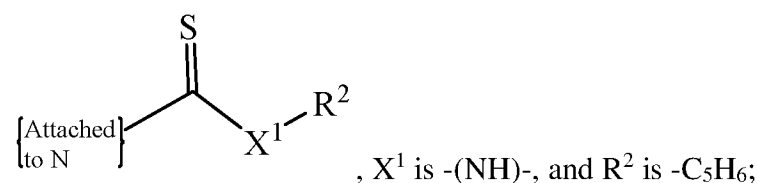
[00110] (b) R³ is the same as R⁴ and R¹ is the same as R⁵;

[00111] (c) R³ is the same as R⁴, X¹ is -(NH)-, X² is -(NH)-, and R² is the same as R⁶;

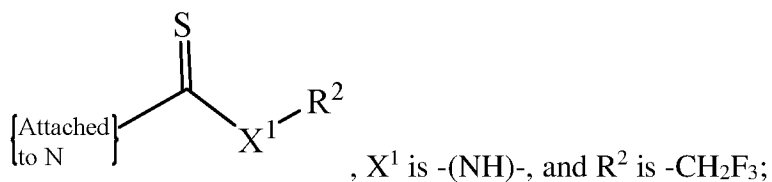
[00112] (d) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is



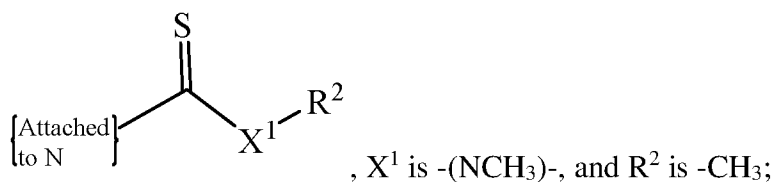
[00113] (e) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is



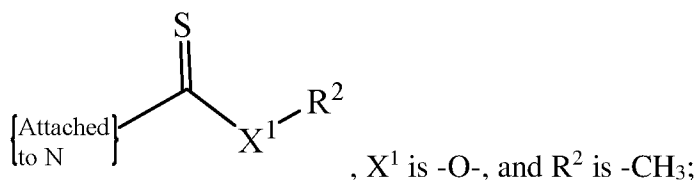
[00114] (f) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



[00115] (g) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



5 [00116] (h) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is

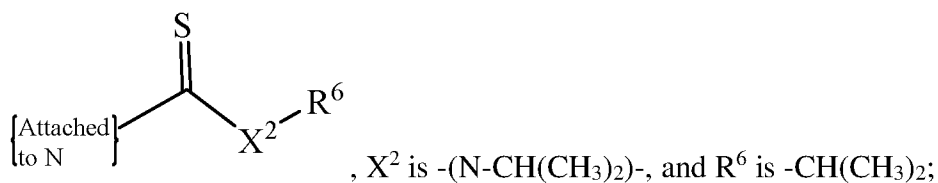


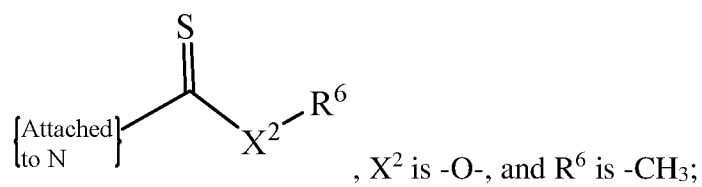
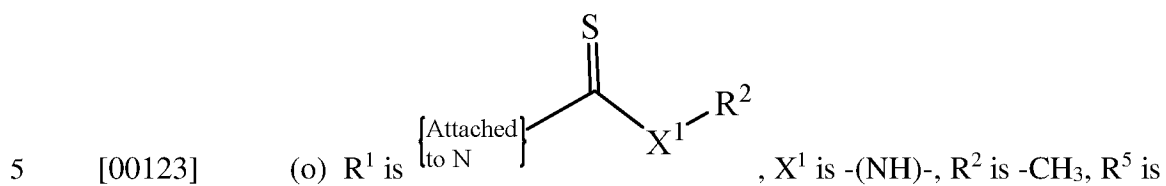
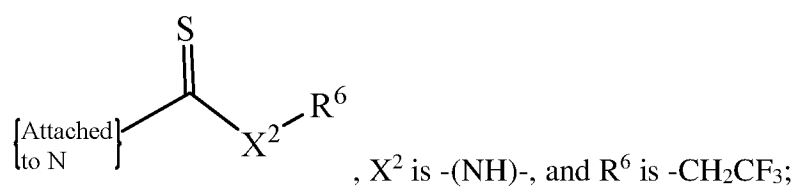
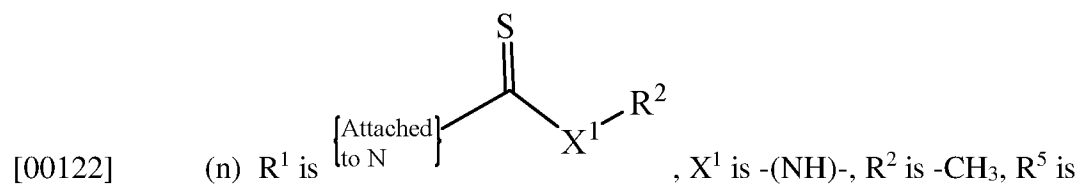
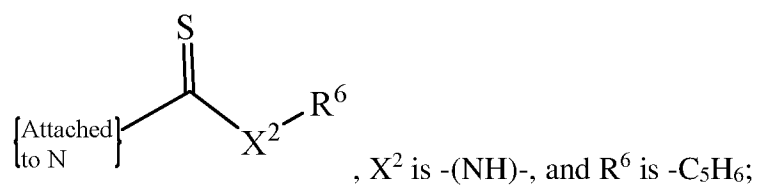
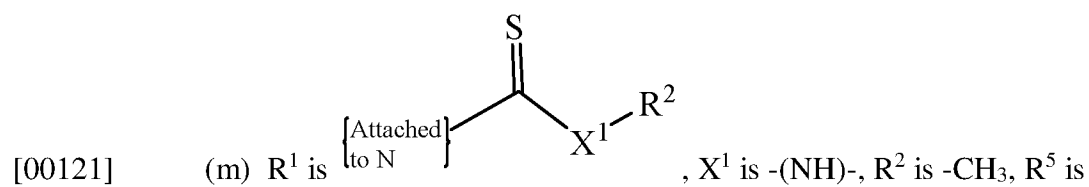
[00117] (i) R^3 is the same as R^4 and R^3 is methyl;

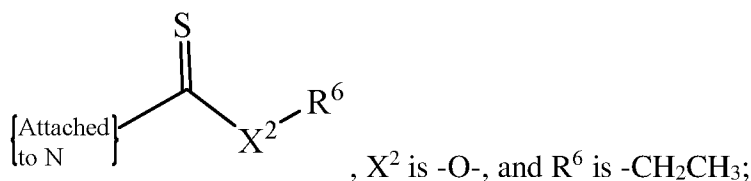
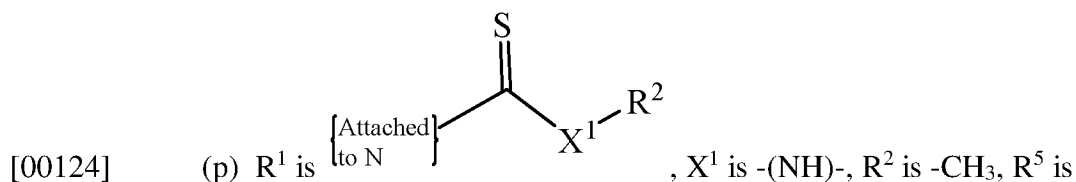
[00118] (j) R^3 is the same as R^4 and R^3 is ethyl;

[00119] (k) R^3 is methyl and R^4 is phenyl;

10 [00120] (l) R^1 is $\left\{ \begin{array}{l} \text{Attached} \\ \text{to N} \end{array} \right\} \text{---} \text{C}(=\text{S})\text{---} \text{X}^1\text{---} \text{R}^2$, X^1 is $-(\text{NH})-$, R^2 is $-\text{CH}_3$, R^5 is







[00125] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

[00126] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

5 [00127] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

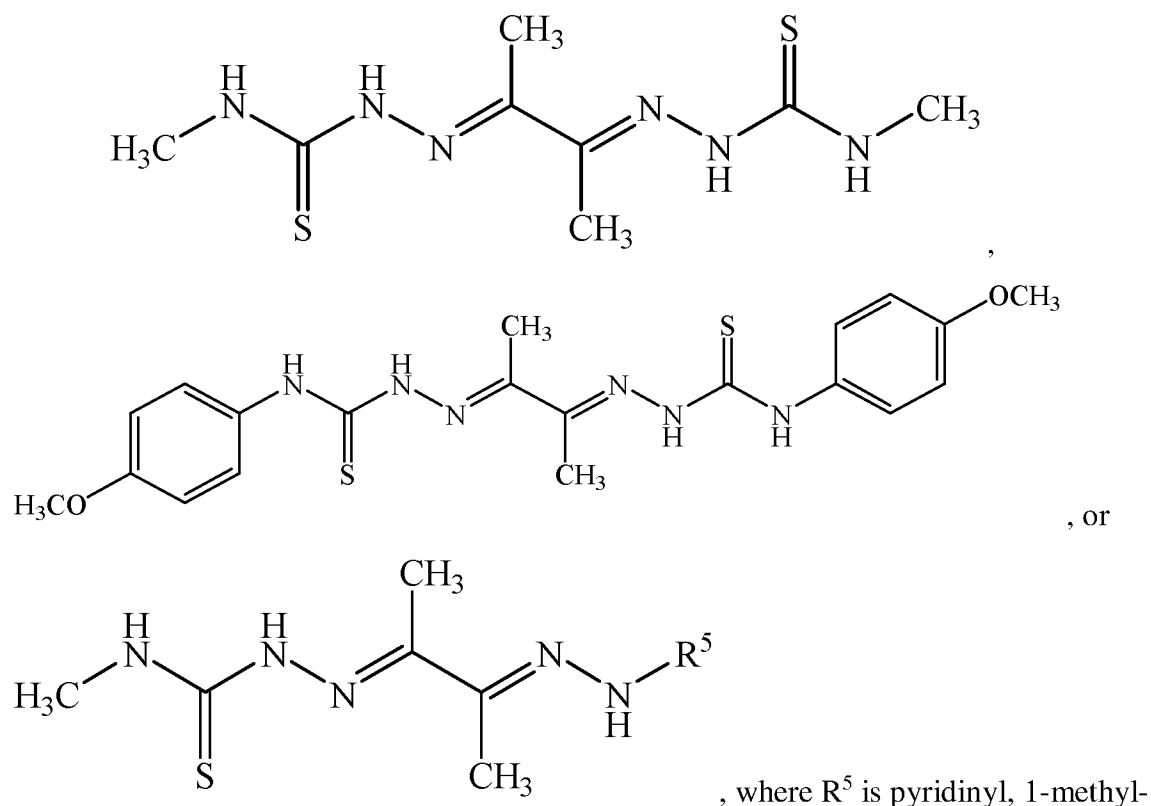
[00128] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

[00129] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

[00130] In some embodiments, Formula (I) further comprises a solvent molecule coordinated with Formula (I). In other embodiments, the solvent molecule can be any suitable solvent. In some embodiments, the solvent molecule is selected from water, methanol, ethanol, propanol, acetonitrile, dimethylformamide, and acetone.

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[00131] In certain embodiments, the compound of Formula (I) is

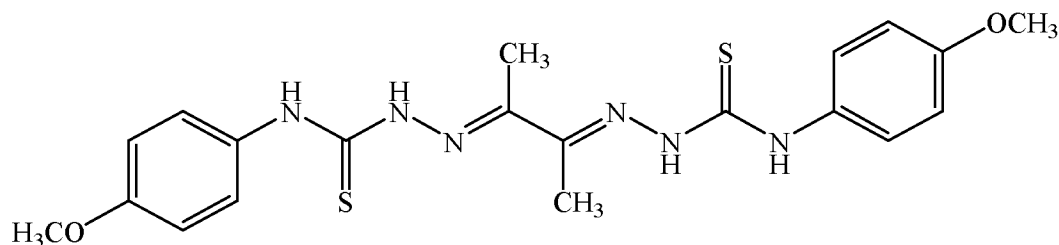


imidazolyl, an N-containing heterocyclyl, or an N-containing heteroaryl.

- 5 [00132] In some embodiments, Formula (I) is one of the molecules described in Example Sets A, B, C, D, or E. In other embodiments, Formula (I) can be symmetric or asymmetric.

[00133] In certain embodiments of Formula (I) (a) X¹ is not -(NH)-, (b) R² is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b). In other embodiments of

- 10 Formula (I) (a) X² is not -(NH)-, (b) R⁶ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b). In yet other embodiments, (a) R³ is not methyl, (b) R⁴ is not methyl, or (c) both (a) and (b). In still other embodiments, Formula (I) is not



[00134] In some embodiments, Formula (I) is part of a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, a heterogeneous aqueous solution, or a glassy carbon electrode. In other embodiments, a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, or a heterogeneous aqueous solution, can each comprise a compound of Formula (I). In certain embodiments, a glassy carbon electrode, a carbon paste (e.g., embedded with one or more of polynuclear catalysts, coordinated polymers, or metal-organic frameworks), covalent modified carbon (e.g., graphene), or non-covalent modified carbon (e.g., graphene), can each comprise or reacted with the compound of Formula (I).

[00135] Some embodiments of the invention include a compound selected from Formula (II),

M·L (II) and

[00136] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein

[00137] - M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe; or

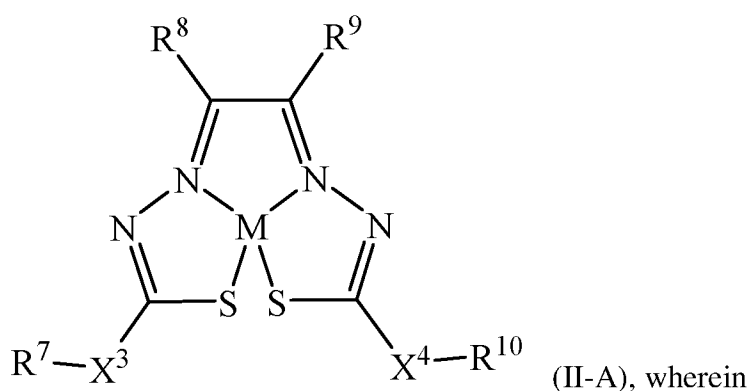
M is Cu²⁺, Cu⁺, Zn²⁺, Co²⁺, Ni²⁺, Cd²⁺, Mn²⁺, Ru²⁺, or Fe²⁺; or M is Cu²⁺, Cu⁺, Zn²⁺,

Co²⁺, Cd²⁺, Mn²⁺, Ru²⁺, or Fe²⁺; or M is Cu²⁺, Zn²⁺, Co²⁺, Cd²⁺, Mn²⁺, or Fe²⁺; or M is

Cu^{2+} , Zn^{2+} , Ni^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Ni^{2+} ; or M is Cu^{2+} or Zn^{2+} ; and

[00138] - L is selected from a compound of Formula (I). In some embodiments, M includes one or more transition metals. In other embodiments, M does not include a transition metal. In certain embodiments, M includes non-transition metals.

[00139] In some embodiments, Formula (II) is a compound of Formula (II-A)



[00140] - R^7 is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro

(-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene),

cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl

(e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇

alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂,

C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl,

heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇

alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4,

5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄,

or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-

CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00141] - X³ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00142] - R⁸ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00143] - R⁹ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇

alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00144] - X⁴ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00145] - R¹⁰ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

[00146] - M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe; or M is Cu²⁺, Cu⁺, Zn²⁺, Co²⁺, Ni²⁺, Cd²⁺, Mn²⁺, Ru²⁺, or Fe²⁺; or M is Cu²⁺, Cu⁺, Zn²⁺,

Co^{2+} , Cd^{2+} , Mn^{2+} , Ru^{2+} , or Fe^{2+} ; or M is Cu^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+} , or Fe^{2+} ; or M is Cu^{2+} , Zn^{2+} , Ni^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Ni^{2+} ; or M is Cu^{2+} or Zn^{2+} .

[00147] In certain embodiments, M is Cu^{2+} , Zn^{2+} , Ni^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Ni^{2+} ; or M is Cu^{2+} or Zn^{2+} . In some embodiments, M includes one or more transition metals. In other embodiments, M does not include a transition metal. In certain embodiments, M includes non-transition metals.

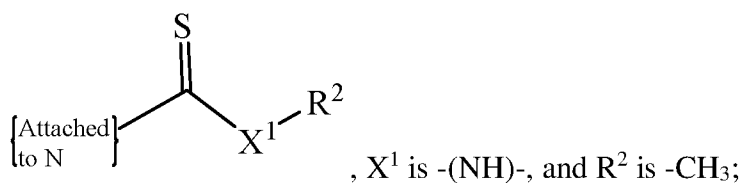
[00148] In some embodiments of Formula (II),

[00149] (a) R^3 is the same as R^4 ;

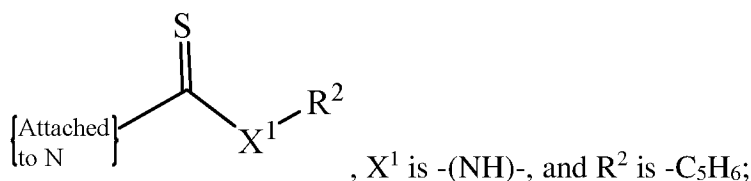
10 [00150] (b) R^3 is the same as R^4 and R^1 is the same as R^5 ;

[00151] (c) R^3 is the same as R^4 , X^1 is $-(\text{NH})-$, X^2 is $-(\text{NH})-$, and R^2 is the same as R^6 ;

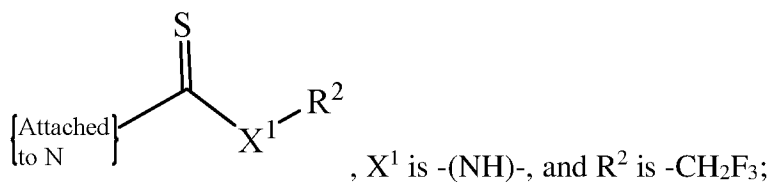
[00152] (d) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



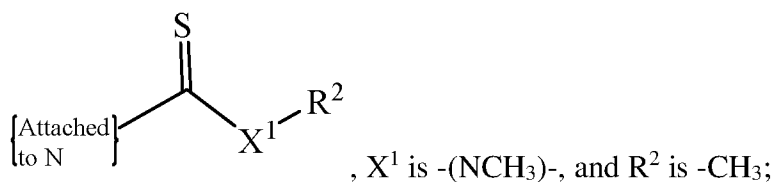
15 [00153] (e) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



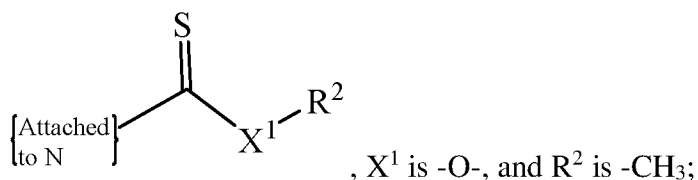
[00154] (f) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



[00155] (g) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



5 [00156] (h) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is

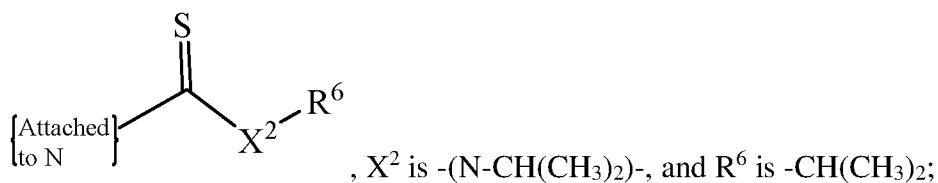


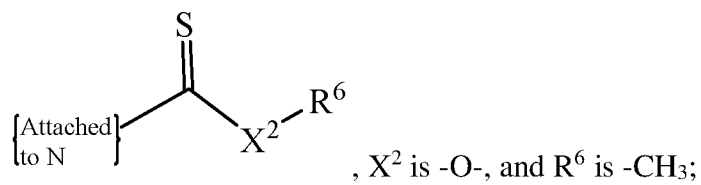
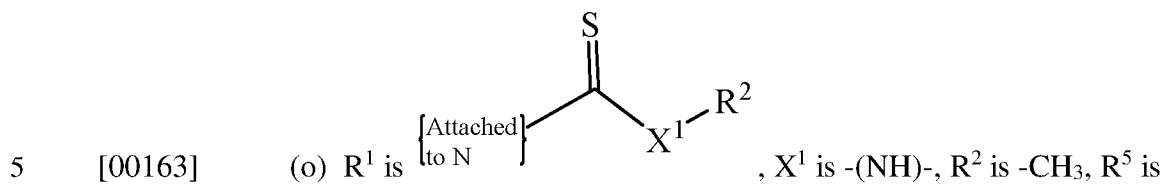
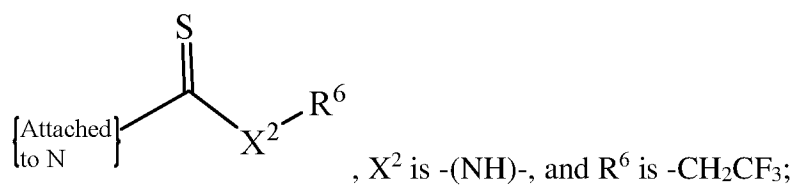
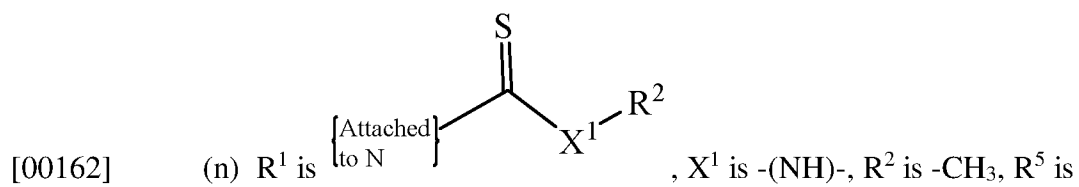
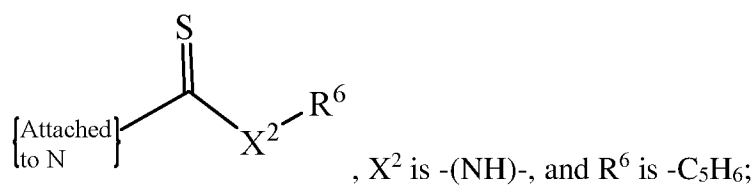
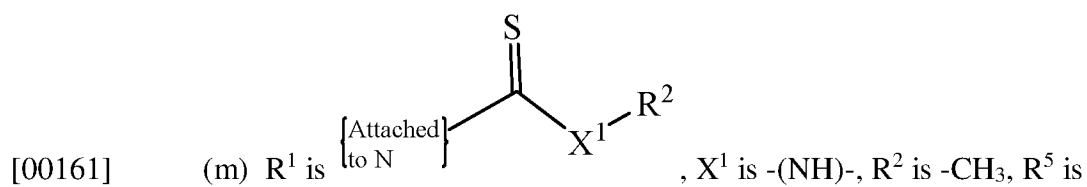
[00157] (i) R^3 is the same as R^4 and R^3 is methyl;

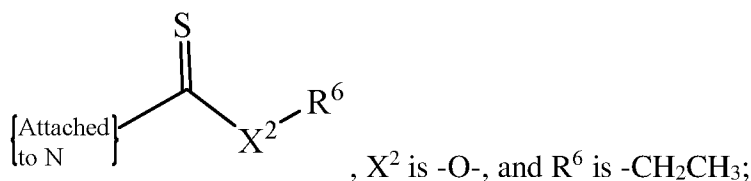
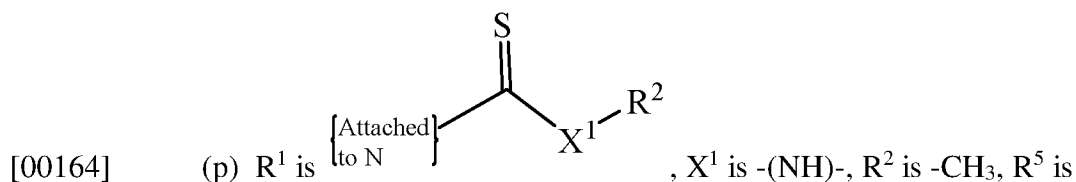
[00158] (j) R^3 is the same as R^4 and R^3 is ethyl;

[00159] (k) R^3 is methyl and R^4 is phenyl;

10 [00160] (l) R^1 is $\left\{ \begin{array}{l} \text{Attached} \\ \text{to N} \end{array} \right\} \text{---} \text{C}(=\text{S})\text{---} \text{X}^1\text{---} \text{R}^2$, X^1 is $-(\text{NH})-$, R^2 is $-\text{CH}_3$, R^5 is







[00165] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

[00166] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

5 [00167] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

[00168] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

[00169] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

[00170] In some embodiments of Formula (II),

[00171] (a) R^8 is the same as R^9 ;

10 [00172] (b) R^8 is the same as R^9 and X^3-R^7 is the same as X^4-R^{10} ;

[00173] (c) R^8 is the same as R^9 , X^3 is $-(\text{NH})-$, X^4 is $-(\text{NH})-$, and R^7 is the same as R^{10} ;

[00174] (d) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is $-(\text{NH})-$, and R^7 is $-\text{CH}_3$;

15 [00175] (e) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is $-(\text{NH})-$, and R^7 is $-\text{C}_5\text{H}_6$;

[00176] (f) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is $-(\text{NH})-$, and R^7 is $-\text{CH}_2\text{F}_3$;

[00177] (g) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is -
(NCH_3)-, and R^7 is $-CH_3$;

[00178] (h) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is -
O-, and R^7 is $-CH_3$;

5 [00179] (i) R^8 is the same as R^9 and R^8 is methyl;

[00180] (j) R^8 is the same as R^9 and R^8 is ethyl;

[00181] (k) R^8 is methyl and R^9 is phenyl;

[00182] (l) X^3 is $-(NH)-$, R^7 is $-CH_3$, X^4 is $-(N-CH(CH_3)_2)-$, and R^{10} is $-CH(CH_3)_2$;

[00183] (m) X^3 is $-(NH)-$, R^7 is $-CH_3$, X^4 is $-(NH)-$, and R^{10} is $-C_5H_6$;

10 [00184] (n) X^3 is $-(NH)-$, R^7 is $-CH_3$, X^4 is $-(NH)-$, and R^{10} is $-CH_2CF_3$;

[00185] (o) X^3 is $-(NH)-$, R^7 is $-CH_3$, X^4 is $-O-$, and R^{10} is $-CH_3$;

[00186] (p) X^3 is $-(NH)-$, R^7 is $-CH_3$, X^4 is $-O-$, and R^{10} is $-CH_2CH_3$;

[00187] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

[00188] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

15 [00189] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

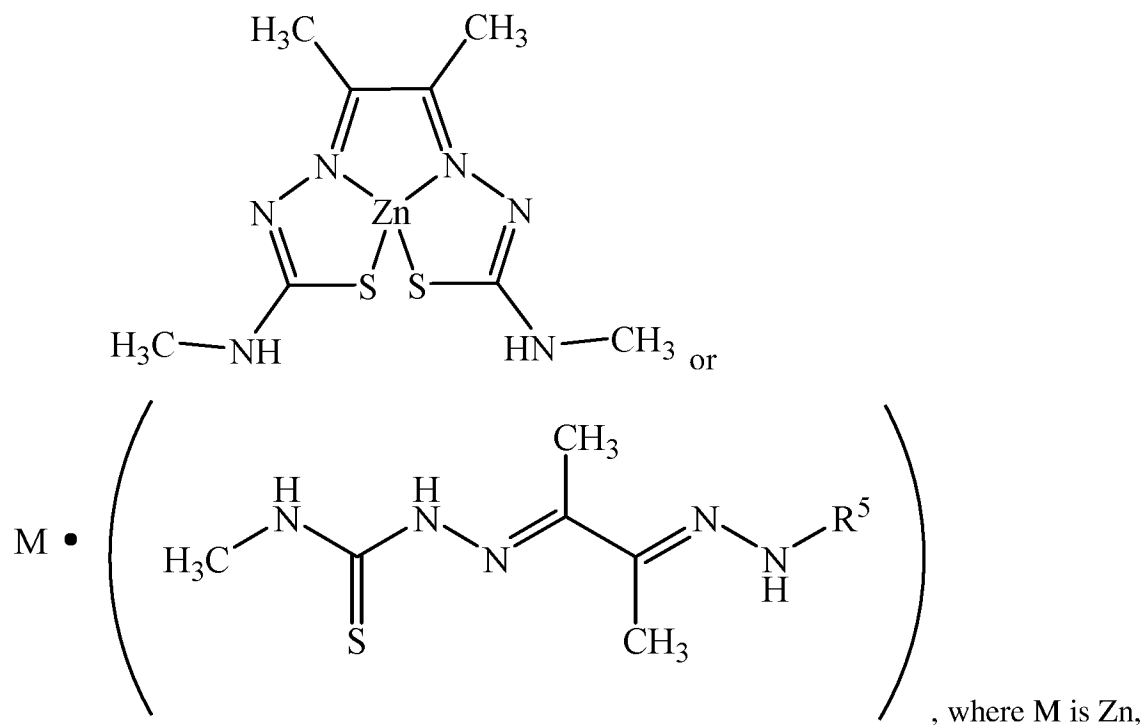
[00190] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

[00191] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

[00192] In some embodiments of Formula (II), M is Zn^{2+} , Co^{2+} , Ni^{2+} or Cu^{2+} , (e.g.,
 M is Zn^{2+} , Ni^{2+} or Cu^{2+} ; or M is Zn^{2+} , Co^{2+} or Cu^{2+} ; or M is Zn^{2+} or Cu^{2+}).

20 [00193] In other embodiments, Formula (II) further comprises a solvent molecule
coordinated with Formula (II). In other embodiments, the solvent molecule can be any
suitable solvent molecule. In certain embodiments, the solvent molecule is selected from
water, ethanol, propanol, acetonitrile, dimethylformamide, and acetone.

[00194] In some embodiments, Formula (II) is

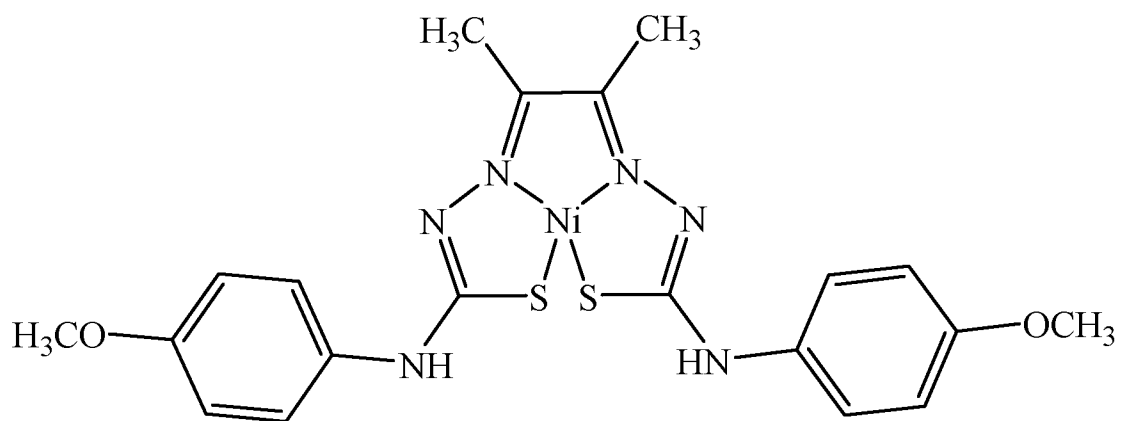


Co, Ni, or Cu (e.g., M is Zn, Ni, or Cu; or M is Zn, Co, or Cu; or M is Zn or Cu) and R⁵ is pyridinyl, 1-methyl-imidazolyl, an N-containing heterocyclyl, or an N-containing heteroaryl.

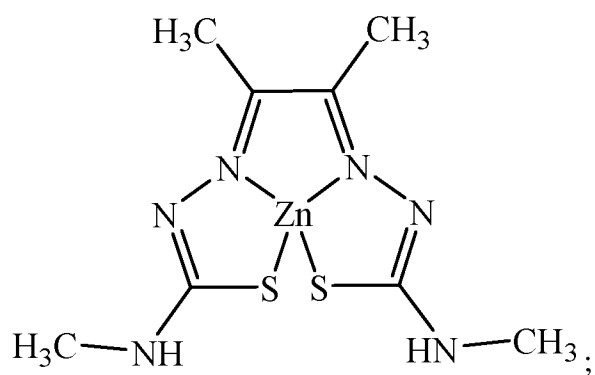
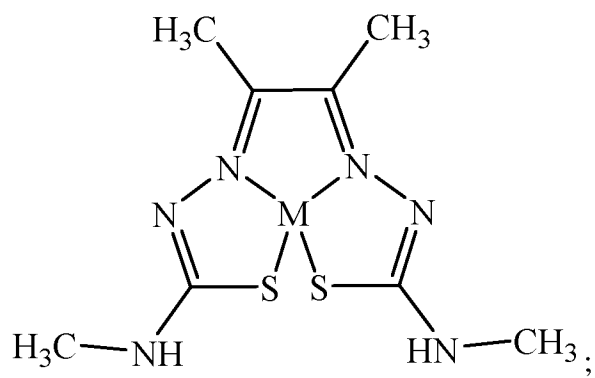
[00195] In certain embodiments, Formula (II) is symmetric or is asymmetric.

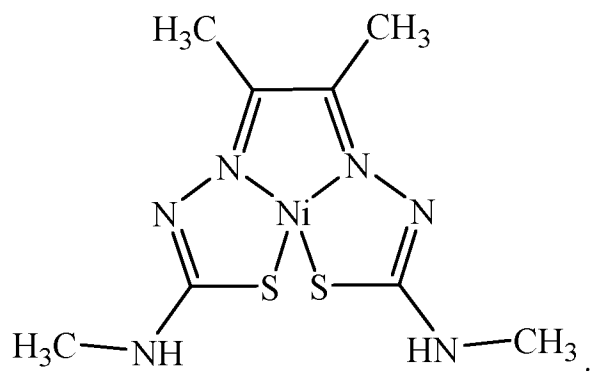
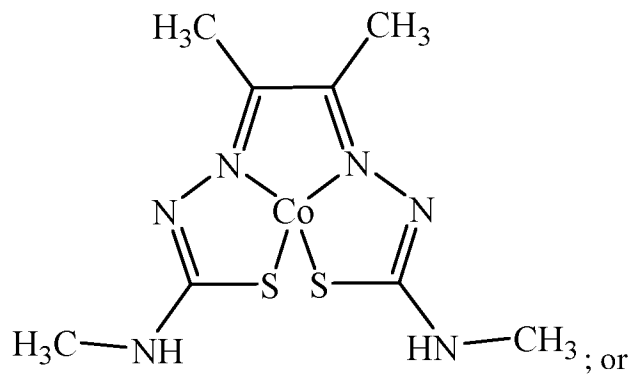
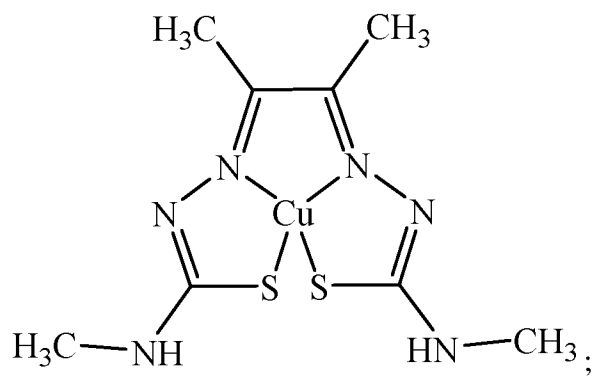
[00196] In other embodiments, (a) X¹ is not -(NH)-, (b) R² is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b). In yet other embodiments, (a) X² is not -(NH)-, (b) R⁶ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b). In certain embodiments, (a) R³ is not methyl, (b) R⁴ is not methyl, or (c) both (a) and (b).

[00197] In some embodiments, Formula (II) is not

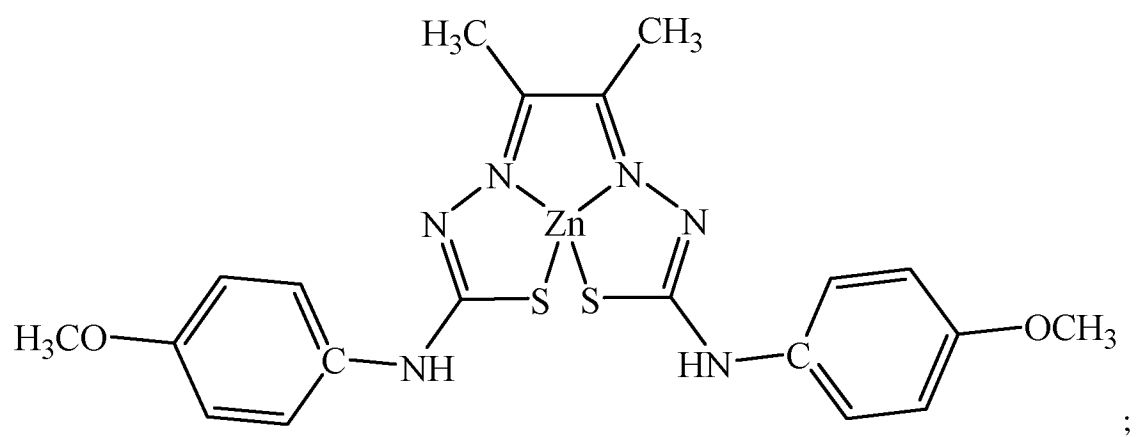
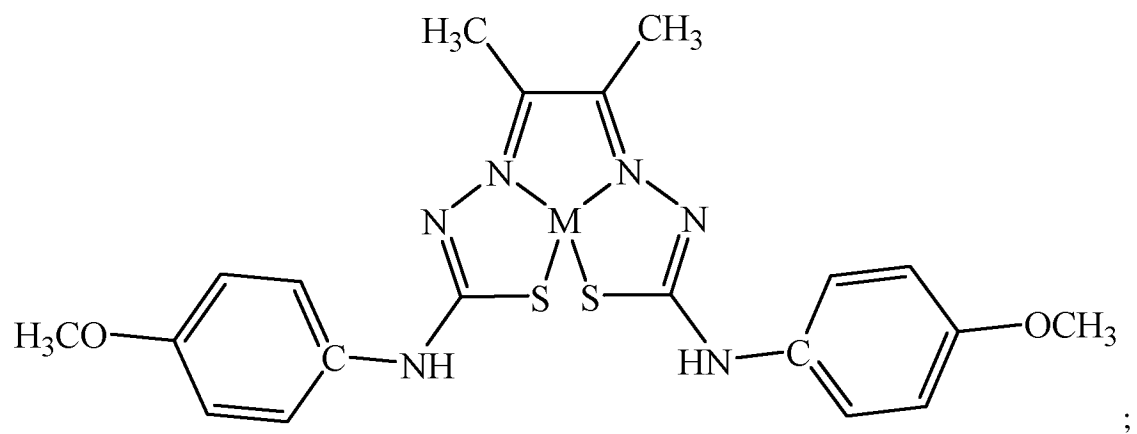


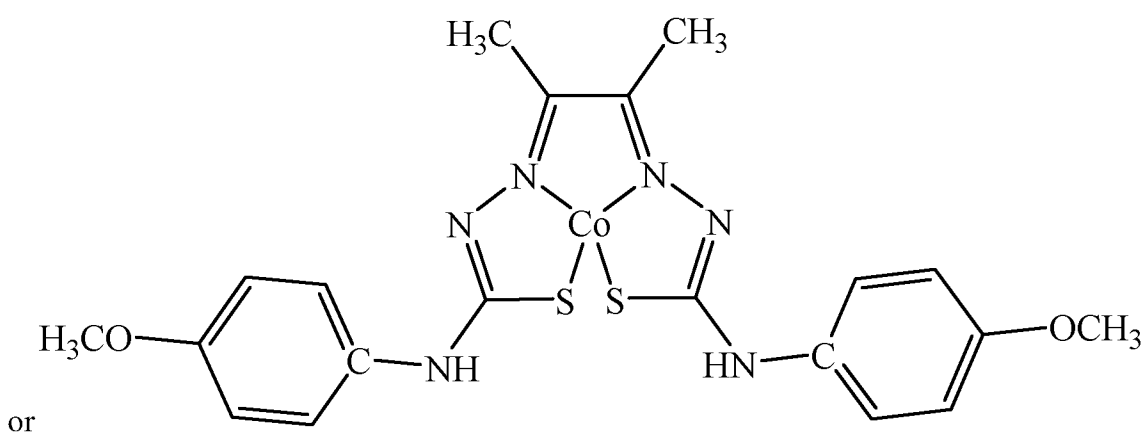
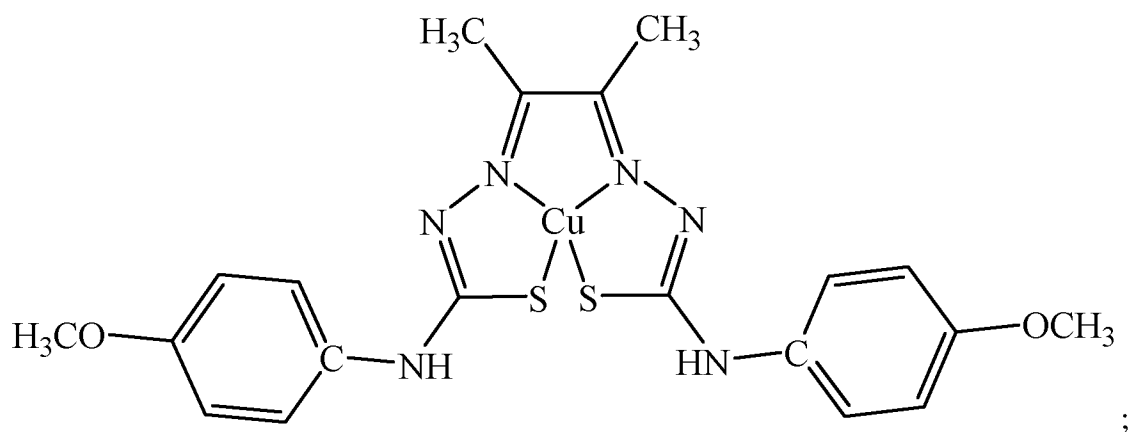
[00198] In some embodiments, Formula (II) is





[00199] In other embodiments, Formula (II) is



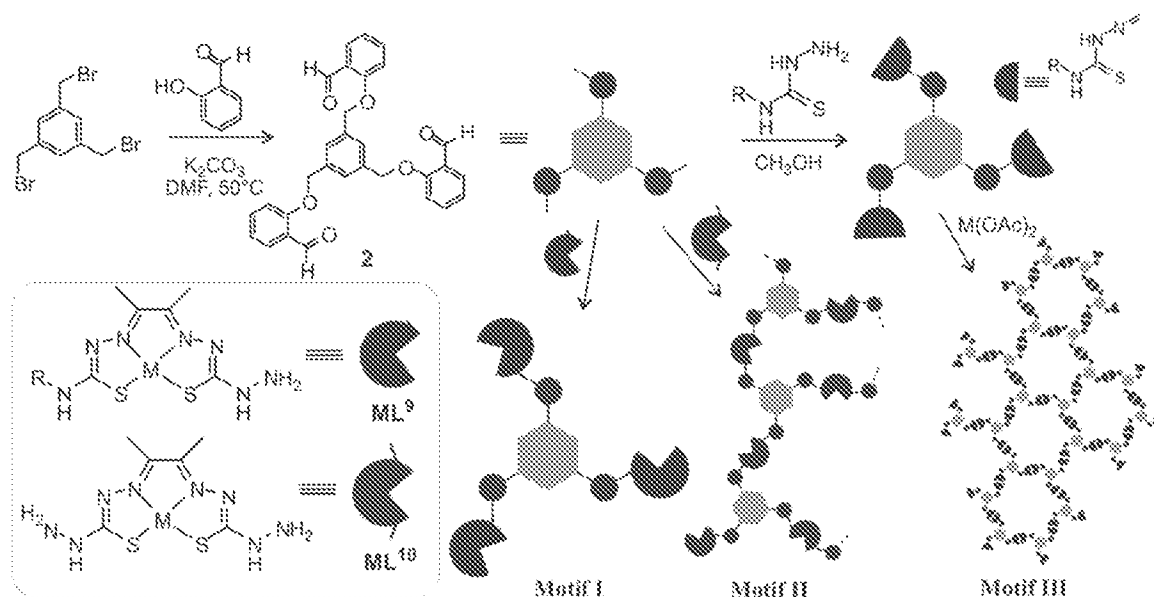


[00200] In some embodiments, Formula (II) is one of the molecules described in Example Sets A, B, C, D, or E.

5 [00201] In some embodiments, a compound of Formula (II) is part of a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, or a heterogeneous aqueous solution. In other embodiments, a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, or a heterogeneous aqueous solution, each comprise a compound of Formula (II).

10 [00202] In other embodiments, a glassy carbon electrode, a carbon paste (e.g., embedded with one or more of polynuclear catalysts, coordinated polymers, or metal-organic frameworks), covalent modified carbon (e.g., graphene), or non-covalent

modified carbon (e.g., graphene), each comprises or is reacted with a compound of Formula (II). In certain embodiments, the carbon paste carbon paste comprises an extended structure motif (e.g., motif I, motif II, or motif III of scheme below).

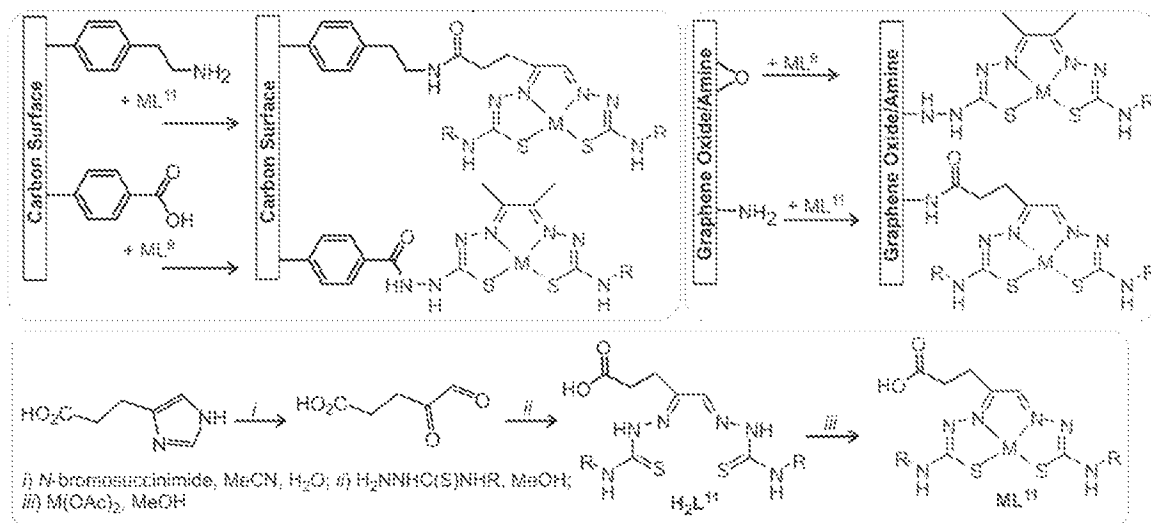


[00203] Certain embodiments of the invention include glassy carbon electrodes (GCE) comprising Formula (I), Formula (II), or both. Glassy carbon electrodes can be used for any suitable purpose including but not limited to use in heterogeneous aqueous solutions. Glassy carbon electrodes can be made using any suitable method including but not limited to dropcast or spray coating. In some instances, contributions to adhesion to the electrode can include but are not limited to π - π interactions, the water-insolubility of Formula (I) or Formula (II), or both. In some instances, asymmetric structures of Formula (I), Formula (II) or both can be used, in that the asymmetric structure is capable (e.g., designed) of linking to the GCE. In other instances, symmetric molecules of Formula (I), Formula (II) or both can be used to make GCEs.

[00204] Other embodiments of the invention include carbon paste electrodes (CPE) embedded with compositions comprising Formula (I), Formula (II), or both. The embedded compositions can be any suitable composition including but not limited to molecular catalysts or related extended structures (e.g., polynuclear catalysts, coordination polymers, metal-organic frameworks, or extended structures as described herein). Extended structures can be made using any suitable technique, including but not limited to those exemplified in the Examples or the scheme above; that technique can be applied to any suitable Formula (I) or Formula (II) and is not limited to the specific molecules used. In some instances, asymmetric structures of Formula (I), Formula (II) or both can be used, in that the asymmetric structure can be capable (e.g., designed) of forming desired extended networks. In other instances, symmetric molecules of Formula (I), Formula (II) or both can be used to make extended structures.

[00205] Still other embodiments of the invention include attachment of Formula (I), Formula (II), or both, to carbon surfaces (e.g., graphene, glassy carbon, graphite, carbon nanotubes, carbon nanospheres, or multiwalled carbon nanotubes). Attachment can include any suitable attachment including but not limited to covalent or enhanced non-covalent attachment (e.g., π - π interactions, insolubility of Formula (I) or Formula (II), or combinations thereof). In certain instances, the carbon surface (e.g., carbon electrode) can be modified with any suitable linker, such as being modified with diazonium compounds, amination chemistry, amide, coupling amines, carboxylic acids, epoxides or any suitable linker so that Formula (I), Formula (II), or an extended structure thereof can be linked to the carbon surface. Linker length, in some embodiments, is chosen to allow catalyst to adopt one or more conformations that occur during catalysis

(e.g., the linker can be used to force drive a desired catalytic mechanism, such as ligand centered reactivity). In yet other embodiments, the linker length is not so long as to diminish electron transfer between catalyst and carbon surface. In certain embodiments, Formula (I), Formula (II) or both can comprise a carboxylic acid or carboxaldehyde to attach to a carbon surface (e.g., modified with amines). In some instances, asymmetric structures of Formula (I), Formula (II) or both can be used, in that the asymmetric structure is capable (e.g., designed) of linking to the modified or unmodified carbon surface. In other instances, symmetric molecules of Formula (I), Formula (II) or both can be used (e.g., designed) to linking to the modified or unmodified carbon surface. In certain embodiments, related extended structures (e.g., polynuclear catalysts, coordination polymers, metal-organic frameworks, or extended structures as described herein) can be attached to the modified or unmodified carbon surface.



[00206] Covalent modification of carbon surfaces can be accomplished using any suitable technique, including but not limited to those exemplified in the scheme above;

that technique can be applied to any suitable Formula (I) or Formula (II) and is not limited to the specific molecules used.

[00207] In some embodiments, the inventive compounds (e.g., Formula (I) or Formula (II), or their embodiments in any of the above GCEs, CPEs, or carbon surfaces) can be used in one or more of the following applications: catalysts (e.g., electrocatalysts) for activation of small molecules (e.g., alcohols, such as, but not limited to, methanol, ethanol, propanol, butanol, and all their isomers), integration into PEM fuel cells; hydrogen evolution for solar energy storage; sustainable hydrogen resource for fertilizer production; solid electrolytes for small battery development; hydrogenation/dehydrogenation catalysts; electrocatalytic CO₂ reduction catalyst; selective olefin binding and functionalization; ethylene and small molecule detection; desulfurization; incorporation into electroactive films or thin films; incorporation into conductive polymers; electroactive, tunable metal-organic-frameworks; water purification; and water desalination.

[00208] In some embodiments, the inventive compounds (e.g., Formula (I) or Formula (II) and their metal (e.g., zinc or copper) complexes) can have one or more of the following uses or properties: use as a substitution for metal-hydride intermediates; capable of being engineered with different functional groups to match a desired application; air and water stable; no special precautions in preparation, storage, or handling; low molecular weights; capable of reducing the mass of catalyst in a particular application; capable of being prepared in high yield (e.g., in 4 - 7 steps from commercially available bulk reagents) and/or inexpensively; does not utilize precious or

semi-precious metals for catalysts; catalysts can be prepared in alcohol solution; and catalysis can be conducted in alcohol or water.

[00209] In certain embodiments, the inventive (e.g., Formula (I) or Formula (II) and their metal (e.g., zinc or copper) complexes) comprise proton relay groups (e.g., as
5 part of the ligand structure). In certain embodiments, the inventive compounds comprise structure(s) or modification(s) that are capable of attaching to an electrode surface, a solid support, or both. In certain instances, light driven evolution of H₂ with the inventive compounds can be accomplished using various photosensitizers and sacrificial redox mediators. In other embodiments, the inventive compounds (e.g., where M is Cu) can be
10 used as a catalyst for the oxidation alcohols to aldehydes using air.

[00210] Some embodiments of the invention include a catalyst (e.g., an electrocatalyst) comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both. Other embodiments include an anode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or
15 both. Other embodiments include a cathode comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both.

[00211] Other embodiments include an electrochemical cell comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both. In some instances, the cathode of the electrochemical cell comprises the
20 composition, the anode of the electrochemical cell comprises the composition, or both.

[00212] Still other embodiments of the invention include a fuel cell comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or

both. In some instances, the cathode of the fuel cell comprises the composition, the anode of the fuel cell comprises the composition, or both.

[00213] Additional embodiments of the invention include a method for producing H₂ comprising contacting, in an electrochemical cell, a first composition comprising a compound of Formula (I), a compound of Formula (II), or both with a second composition comprising water. In some instances, the cathode of the electrochemical cell comprises the first composition. In certain embodiments, the Turn Over Frequency (TOF) is from about 20 s⁻¹ to about 100,000 s⁻¹, about 100 s⁻¹ to about 100,000 s⁻¹, from about 500 s⁻¹ to about 100,000 s⁻¹, from about 500 s⁻¹ to about 50,000 s⁻¹, from about 500 s⁻¹ to about 20,000 s⁻¹, about 20 s⁻¹, about 100 s⁻¹, about 500 s⁻¹, about 1000 s⁻¹, about 5000 s⁻¹, about 10000 s⁻¹, about 12000 s⁻¹, about 16000 s⁻¹, about 20000 s⁻¹, about 50000 s⁻¹, or about 100,000 s⁻¹. In some embodiments, the overpotential is greater than about 0 V, not less than about 0.1 V, not more than about 0.1 V, not more than 0.5 V, not more than 1 V, not more than 10 V, not more than 100 V, from about 0 V to about 2000 V, from about 0 V to about 1000 V, from about 0 V to about 750 V, from about 0 V to about 300 V, from about 0 V to about 350 V, from about 0 V to about 200 V, from about 0 V to about 100 V, from about 0 V to about 20 V, from about 0 V to about 10 V, from about 0 V to about 5 V, from about 0 V to about 2 V, from about 0 V to about 1 V, from about 0.1 V to about 2000 V, from about 0.1 V to about 1000 V, from about 0.1 V to about 750 V, from about 0.1 V to about 300 V, from about 0.1 V to about 350 V, from about 0.1 V to about 200 V, from about 0.1 V to about 100 V, from about 0.1 V to about 20 V, from about 0.1 V to about 10 V, from about 0.1 V to about 5 V, from about 0.1 V to about 2 V,

from about 0.1 V to about 1 V, about 0.1 V, about 0.5 V, about 1 V, about 5 V, about 10 V, about 100 V, about 250 V, about 350 V, about 400 V, about 500 V, or about 1000 V.

[00214] Other instances of the invention include a method for oxidizing an aldehyde, an alcohol, acetonitrile, or water comprising contacting, in an electrochemical cell, a composition comprising a compound of Formula (I), a compound of Formula (II), or both. In some embodiments, the overpotential is greater than about 0 V, not less than about 0.1 V, not more than about 0.1 V, not more than 0.5 V, not more than 1 V, not more than 10 V, not more than 100 V, from about 0 V to about 2000 V, from about 0 V to about 1000 V, from about 0 V to about 750 V, from about 0 V to about 300 V, from about 0 V to about 350 V, from about 0 V to about 200 V, from about 0 V to about 100 V, from about 0 V to about 20 V, from about 0 V to about 10 V, from about 0 V to about 5 V, from about 0 V to about 2 V, from about 0 V to about 1 V, from about 0.1 V to about 2000 V, from about 0.1 V to about 1000 V, from about 0.1 V to about 750 V, from about 0.1 V to about 300 V, from about 0.1 V to about 350 V, from about 0.1 V to about 200 V, from about 0.1 V to about 100 V, from about 0.1 V to about 20 V, from about 0.1 V to about 10 V, from about 0.1 V to about 5 V, from about 0.1 V to about 2 V, from about 0.1 V to about 1 V, about 0.1 V, about 0.5 V, about 1 V, about 5 V, about 10 V, about 100 V, about 250 V, about 350 V, about 400 V, about 500 V, or about 1000 V.

[00215] Some embodiments of the invention include a method for producing electricity comprising contacting, in a fuel cell, a first composition comprising a compound of Formula (I), a compound of Formula (II), or both with a second composition comprising H₂. In some embodiments of this method, the anode of the fuel cell comprises the first composition. In some embodiments of this method, the cathode

of the fuel cell comprises the first composition. In certain instances, the TOF is from about 1 s^{-1} to about 1000 s^{-1} , from about 5 s^{-1} to about 1000 s^{-1} , from about 5 s^{-1} to about 500 s^{-1} , from about 5 s^{-1} to about 200 s^{-1} , about 1 s^{-1} , about 5 s^{-1} , about 10 s^{-1} , about 32 s^{-1} , about 50 s^{-1} , about 76 s^{-1} , about 100 s^{-1} , about 120 s^{-1} , about 200 s^{-1} , about 300 s^{-1} , about 500 s^{-1} , or about 1000 s^{-1} . In yet additional embodiments, the overpotential is greater than about 0 V, not less than about 0.1 V, not more than about 0.1 V, not more than 0.5 V, not more than 1 V, not more than 10 V, not more than 100 V, from about 0 V to about 2000 V, from about 0 V to about 1000 V, from about 0 V to about 750 V, from about 0 V to about 300 V, from about 0 V to about 350 V, from about 0 V to about 200 V, from about 0 V to about 100 V, from about 0 V to about 20 V, from about 0 V to about 10 V, from about 0 V to about 5 V, from about 0 V to about 2 V, from about 0 V to about 1 V, from about 0.1 V to about 2000 V, from about 0.1 V to about 1000 V, from about 0.1 V to about 750 V, from about 0.1 V to about 300 V, from about 0.1 V to about 350 V, from about 0.1 V to about 200 V, from about 0.1 V to about 100 V, from about 0.1 V to about 20 V, from about 0.1 V to about 10 V, from about 0.1 V to about 5 V, from about 0.1 V to about 2 V, from about 0.1 V to about 1 V, about 0.1 V, about 0.5 V, about 1 V, about 5 V, about 10 V, about 100 V, about 250 V, about 350 V, about 400 V, about 500 V, or about 1000 V.

[00216] Other embodiments of the invention include a method for preparing a compound of Formula (I) comprising any suitable method, such as those disclosed herein. In some instances, the compound of Formula (I) is prepared comprising

[00217] (a) reacting a compound of Formula (III) $\text{R}^1\text{-}\overset{\text{H}}{\underset{|}{\text{N}}}\text{-NH}_2$ (III)

[00218] with a compound of Formula (IV) $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}^4 \text{---} \text{C} \text{---} \text{C} \text{---} \text{R}^3 \end{array}$ (IV);

[00219] (b) reacting a compound of Formula (V) $\begin{array}{c} \text{R}^3 \\ | \\ \text{R}^1\text{-}\overset{\text{H}}{\underset{|}{\text{N}}}\text{-N}=\text{C} \text{---} \text{C} \text{---} \text{O} \\ | \\ \text{R}^4 \end{array}$ (V)

5 [00220] with a compound of Formula (VI) $\text{H}_2\text{N}-\overset{\text{H}}{\underset{|}{\text{N}}}-\text{R}^5$ (VI); and

[00221] (c) recovering the compound of Formula (I),

[00222] wherein R^1 , R^3 , R^4 , and R^5 are defined herein. Recovery can occur using any suitable method including but not limited to HPLC (e.g., reverse phase), LC, precipitation, centrifugation, column chromatography (e.g., size exclusion
10 chromatography or ion exchange chromatography), use of silica gel, or combinations thereof.

[00223] Other embodiments of the invention include a method for preparing a compound of Formula (II) comprising any suitable method, such as those disclosed herein. In certain instances, the compound of Formula (II) is prepared comprising

[00224] (a) reacting a compound of Formula (I) with M (e.g., Zn, Co, or Cu) or salt thereof; and

[00225] (b) recovering the compound of Formula (II),

[00226] wherein M is defined herein. Recovery can occur using any suitable

5 method including but not limited to HPLC (e.g., reverse phase), LC, precipitation, centrifugation, column chromatography (e.g., size exclusion chromatography or ion exchange chromatography), use of silica gel, or combinations thereof.

[00227] Additional embodiments include a method for preparing a catalyst (e.g., an electrocatalyst) comprising a composition comprising a compound of Formula (I), a

10 compound of Formula (II), or both, comprising any suitable method, including those

described herein. Additional embodiments include a method for preparing an anode

comprising a composition comprising a compound of Formula (I), a compound of

Formula (II), or both, comprising any suitable method, including those described herein.

Further embodiments include a method for preparing a cathode comprising a composition

15 comprising a compound of Formula (I), a compound of Formula (II), or both, comprising any suitable method, including those described herein.

[00228] The presently-disclosed subject matter is further illustrated by the

following specific but non-limiting examples. The following examples may include

compilations of data that are representative of data gathered at various times during the

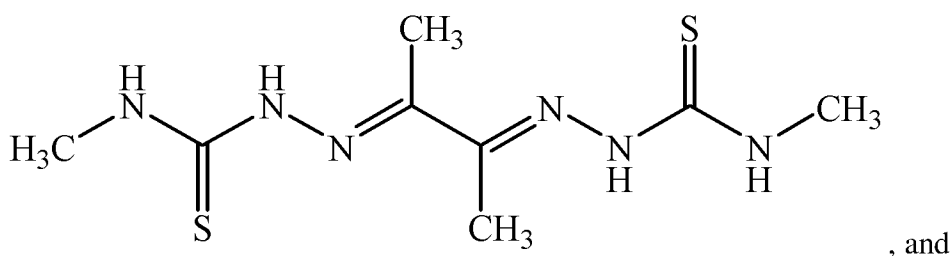
20 course of development and experimentation related to the present invention.

EXAMPLES

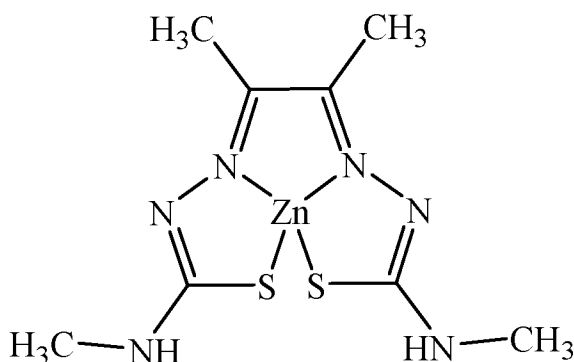
[00229] **Example Set A: HER and HOR of Zn and metal-free complexes**

[00230] The compounds discussed in Example Set A include H₂L and ZnL.

H₂L



ZnL



Materials and Methods for Example Set A

10 [00231] All solvents were purified with an MBraun solvent purification system prior to use.

[00232] Electrochemical Methods

[00233] All cyclic voltammetry (CV) and controlled potential coulometry (CPC) measurements were recorded using a Gamry Interface potentiostat/galvanostat, which
 15 was connected to a glassy carbon working electrode (6.5 mm diameter, surface area = 0.07 cm²), a platinum wire counter electrode, and Ag/AgCl reference electrode. Before use, the working electrode was polished using aqueous alumina slurry. Working and

counter electrodes were cleaned before use by washing with water, ethanol, acetone, isopropanol and methanol, and then sonicated in methanol. CV measurements were conducted using a three-neck electrochemical cell that was washed and dried in oven over night before use. All electrochemical experiments were conducted under a N₂ atmosphere, aside from HOR experiments. All CPC measurements were conducted using a custom built gas tight Parr-electrolysis reactor with a volume of 30 mL washed and dried night before use. The working compartment was fitted with a platinum working electrode (surface area = 0.07 cm²) and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt wire counter electrode. The working compartment contained 12 mM acetic acid added to a 0.1 M Bu₄NPF₆ methanol solution, while the auxiliary compartment was filled with 0.1 M Bu₄NPF₆ methanol solution. Both compartments were purged for 15 min with N₂ and kept under a constant N₂ flow. A control (blank) CPC study was conducted and subtracted from experimental results. Electrolysis was then measured with the addition of the 0.1 mM ZnL. Electrolysis was conducted for 2.5 hours and the samples were subjected to gas chromatographic analysis every 30 minutes. A Gow-Mac series 400 GC-TCD with molecular sieve column was used for product detection. The column was heated to 130 °C under N₂ gas flow with 250 µL injection samples injected onto the column. The integrated area of the H₂ peak was then compared to the pre-made H₂ calibration curve in order to calculate the volume and moles of H₂ generated.

[00234] Statistical Analysis

[00235] Overpotential Determination: Overpotential can be defined as the difference between the thermodynamic and equilibrium potentials for a given reaction

and the potential at which the reaction occurs under a set of specific conditions. Using this method of Appel and Helm (ACS Catal., 2014, Vol. 4, pp. 630-633; DOI: 10.1021/cs401013v), the overpotential (η) for proton reduction or H₂ oxidation by ZnL or H₂L under specific experimental conditions can be estimated as:

$$\eta = |E_{\text{OCP}} - E_{\text{cat}/2}|$$

[00236] E_{OCP} is the measured open circuit potential measured under catalytic conditions specific for each reaction, and $E_{\text{cat}/2}$ is the potential at one-half the maximum of the catalytic current measured for the catalyzed reduction of protons or oxidation of H₂ by ZnL or H₂L.

[00237] Overpotential calculation; ZnL HER:

$$\begin{aligned}\eta &= \text{Overpotential} = |E_{\text{BH}^+(\text{OCP})} - (E_{\text{cat}/2})| \\ \eta &= |[-0.924 - (-1.68\text{V})]| \\ \eta &= \mathbf{0.756\text{ V vs }Fc^+/Fc^0}\end{aligned}$$

[00238] Overpotential calculation; ZnL HOR:

$$\begin{aligned}\eta &= \text{Overpotential} = |E_{\text{BH}^+(\text{OCP})} - (E_{\text{cat}/2})| \\ \eta &= |(0.190 - 0.505)| \\ \eta &= \mathbf{0.315\text{ V vs }Fc^+/Fc^0}\end{aligned}$$

[00239] Overpotential calculation; H₂L HER:

$$\begin{aligned}\eta &= \text{Overpotential} = |E_{\text{BH}^+(\text{OCP})} - (E_{\text{cat}/2})| \\ \eta &= |[-0.37 - (-1.80)]| \\ \eta &= \mathbf{1.43\text{ V vs }Fc^+/Fc^0}\end{aligned}$$

[00240] Overpotential calculation; H₂L HOR:

$$\begin{aligned}\eta &= \text{Overpotential} = |E_{\text{BH}^+(\text{OCP})} - (E_{\text{cat}/2})| \\ \eta &= |(0.177 - 0.505)| \\ \eta &= \mathbf{0.328\text{ V vs }Fc^+/Fc^0}\end{aligned}$$

[00241] Determination of ZnL Diffusion Coefficient (D_0):

[00242] Using the Randles-Sevcik equation (Eq. A2), and plotting peak current vs the square root of the scan rate allows for accurate calculation of the diffusion coefficient, D_0 .

$$\text{Slope (Figs. 10-11)} \equiv 1.94\text{E-}5 = 0.4463FA[\text{cat}][(\text{FD}_0/\text{RT})]^{0.5}$$

$$A = 0.071 \text{ cm}^2$$

$$[\text{cat}] = 3\text{E-}6 \text{ moles/cm}^3$$

$$F = 96485 \text{ C/mole e}^-$$

$$R = \text{ideal gas constant}$$

$$T = 298 \text{ K}$$

$$\mathbf{D_0 = 1.15E-7 \text{ cm}^2/\text{s in MeOH}}$$

[00243] Sample Calculations Electrolysis:

[00244] Theoretical Moles of Hydrogen Made via Total Charge:

$$19.8 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles H}_2$$

theoretical

Moles H₂ theoretical = 0.00011 moles H₂ based on charge from electrolysis

[00245] Faradaic Efficiency Calculations:

$$\text{Faradaic Efficiency} = (\text{Moles H}_2 \text{ Quantified} / \text{Moles of H}_2 \text{ Theoretical}) \times 100\%$$

$$\text{Faradaic Efficiency} = (0.000093 \text{ moles}) / (0.00011 \text{ moles}) \times 100\%$$

$$\mathbf{\text{Faradaic Efficiency} = 85\%}$$

[00246] TON Calculations:

$$\text{TON} = \text{Moles of H}_2 \text{ Produced} / \text{Moles of ZnL Used}$$

$$\text{TON} = (0.00011 \text{ moles H}_2 \text{ produced}) / (0.000003 \text{ moles ZnL used})$$

$$\mathbf{\text{TON} = 36.7}$$

[00247] HER Equations for TOF Calculation:

[00248] Equation A1 details the relationship between the catalytic current i_{cat} , the catalyst concentration $[\text{cat}]$, and the acid concentration $[\text{H}^+]$ for a catalytic reaction that is first-order in acid and first-order in catalyst under scan rate independent conditions. The terms n , F , A , and D are the normal electrochemical terms related to the number of electrons transferred, Faraday's constant, area of the electrode, and diffusion constant, respectively.

$$i_{cat} = nFA[cat]\sqrt{Dk[H^+]} \quad (A1)$$

[00249] Equation A2 (Randle-Sevcik equation) provides the relationship between the peak current i_p , catalyst concentration, and scan rate (v) in the absence of acid. The factor of 0.4463 is related to the diffusion equations, R is the gas constant, and T is temperature in K. The other terms are the same as in equation A1.

$$i_p = 0.4463FA[cat]\sqrt{\frac{FvD}{RT}} \quad (A2)$$

[00250] Thus, the ratio of i_{cat}/i_p (equation A3) is obtained from equations A1 and A2

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk[H^+]}{Fv}} \quad (A3)$$

[00251] Under pseudo first-order conditions where $k_{obs} = k[H^+]$, equation A3 simplifies to A4.

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk_{obs}}{Fv}} \quad (A4)$$

[00252] Equation A4 can further be simplified to equation A5, when $n=1$ for bimolecular processes.

$$k_{obs} = v \times \left[\frac{i_{cat}}{i_p} \right]^2 \quad (A5)$$

[00253] Since no peak current for ZnL was observed in the absence of substrate in methanol, the experimentally determined diffusion coefficient, $1.15E-7$, was used to calculate the value for i_p . This gave an i_p of $43 \mu A$ when run at $5 V/s$ (the scan rate in which catalytic current becomes independent of scan rate). Furthermore, the value of i_p was confirmed through simulations using DigiElch, which agree with the calculated i_p

values. Using equation A5, the TOF or k_{obs} can be calculated using the experimentally determined i_p value as well as the i_{cat} observed at 5 V/s, 230 μ A. This results in a TOF of 1170 s^{-1} .

[00254] We then calculated the TOF using Eq. A6, which is Eq. A1 under pseudo first-order conditions, in order to compare both calculated values, which are in agreement with each other.

$$i_{cat} = nFA[cat]\sqrt{Dk_{obs}} \quad (A6)$$

[00255] Sample Calculations ZnL TOF/ k_{obs} :

10 [00256] Using Eq. A5:

$$i_{cat} = 230 \mu A; i_p = 43 \mu A; v = 5.0 V/s$$

$$= k_{obs}/TOF = 1170 s^{-1}$$

[00257] Using Eq. A6:

15 $i_{cat} = 230 \mu A; n = 1 \text{ mole } e^- / \text{ mole of ZnL}; F = 96485 \text{ C / mole}^-; A = 0.071 \text{ cm}^2; [cat] = 3E-6 \text{ moles / cm}^3; D_{cat} = 1.15E-7 \text{ cm}^2 / s.$

$$= k_{obs} / TOF = 1100 s^{-1}$$

[00258] ZnL HER Kinetic Isotope Effect: Acetic Acid vs d-Acetic Acid:

Scan Rate	k_H	k_D	k_H / k_D
5 V/s	1170	975	1.2

20 [00259] HOR TOF ZnL and H₂L Sample Calculation when $v = 1.0$ V/s:

ZnL:

$$TOF = k_{obs} = v * 1.94(i_{cat}/i_p)^2 \text{ when } i_{cat} = -712 \mu A \text{ and } i_p = -117 \mu A \text{ at } 1.0 V/s$$

$$TOF = 72 s^{-1}$$

H₂L:

25 $TOF = k_{obs} = v * 1.94(i_{cat}/i_p)^2 \text{ when } i_{cat} = -475 \mu A \text{ and } i_p = -117 \mu A \text{ at } 1.0 V/s$

$$TOF = 32 s^{-1}$$

[00260] Computational Methods

[00261] All calculations were performed in the gas phase using density functional theory (DFT) employing the B97-D exchange correlation functional, and the 6-311G(d) basis set for all atoms as implemented in the Gaussian09 suite of programs for electronic structure and ChemCraft was used for graphics visualization. Transition states were determined locally using the Berny algorithm with GEDIIS, and verified by IRC calculations with forward and reverse step sizes of 40. All optimizations were performed under tight constraints, with no symmetry imposed. Several dimeric TS structures in various protonation states were initially investigated by DFT using the berny algorithm for local TS optimization in the gas phase. These structures were constructed manually based on optimized reactants and products, or by modifying previously published semicarbazide dimers. Dimers without ruptured Zn-S and Zn-N bonds were also considered, but precluded based on energetic grounds.

[00262] Supplementary Text

[00263] Blank and control experiments were performed for ZnL and H₂L HER CV studies. Blank runs consisted of 0.1 M Bu₄NPF₆ methanol or acetonitrile, depending on experiment, which had been purged with N₂ gas for 10 minutes. Control CVs run in 0.1 M Bu₄NPF₆ methanol or acetonitrile with 12 mM acetic acid showed minimal currents when compared to currents observed after addition of either ZnL or H₂L electrocatalysts.

[00264] Blank and control experiments were performed for ZnL and H₂L HOR CV studies. Blank runs consisted of 0.1 M Bu₄NPF₆ methanol solutions, which had been purged with N₂ gas for 10 minutes. Control CVs in the absence of ZnL or H₂L were performed. CVs were run under an H₂ atmosphere in solutions of 0.1 M Bu₄NPF₆

methanol with increasing concentrations of triethylamine, added until a concentration of 30 mM. The current observed was significantly lower when compared to the current observed after the addition of the ZnL or H₂L electrocatalysts. Additionally, control experiments were performed with ZnL or H₂L in 0.1 M Bu₄NPF₆ methanol solutions under an N₂ atmosphere. Application of an N₂ atmosphere resulted in no catalytic currents. After introduction of an H₂ atmosphere and purging the solution with H₂ for 15 minutes, catalytic current was observed.

[00265] To quantify H₂ production, the output gas was sampled, 250 μ L, every 30 minutes and analyzed by the GC-TCD described in electrochemical methods section.

After sampling, the chromatographic peak area of hydrogen is obtained. The GC-TCD calibration curve was prepared by sampling known hydrogen concentrations, made with known volumes of hydrogen, from the working compartment, with a constant known N₂ flow rate, and then measured by the same procedure described above. A linear relationship between the chromatographic peak areas of the hydrogen sampled and the specific amounts of hydrogen used was established, defined by $y = mx + b$, where y is the peak area and x is the amount of hydrogen. Using this linear relationship, the amount of hydrogen produced during experimental electrolysis can be calculated from the integrated peak areas obtained.

[00266] Digital simulations of voltammetric data were performed using commercially available DigiElch Pro software package (v.7). Models were fit using an experimentally determined ZnL diffusion coefficient and an experimentally determined value of α and k_s . The consistency of the mechanism over a broad set reaction conditions

was confirmed through models employing multiple scan rates and acid concentrations, all which agree with experimental results

[00267] Examination of the change in bond lengths and bond angles amongst ZnL, [Zn(HL)]⁺, Zn(HL•), and [Zn(H₂L•)]⁺ (Tables A4 – A6) assist to explain structural and electronic changes over the course of the ZnL catalyzed HER mechanism. Initial protonation of ZnL to give [Zn(HL)]⁺ results in a slight puckering of the ligand framework around the Zn center shown by the lengthening of the Zn-S1, Zn-N2, Zn-N3 bonds and a decrease in the Zn-S2 bond as well as an increase in the S1-Zn-S2, N3-Zn-S2 bond angles and decrease of the S1-Zn-N2, N2-Zn-N3 bond angles. Subsequent reduction to the neutral radical species, Zn(HL•), is accompanied by significant contraction of the Zn-N2 and Zn-N3 bonds, 2.118 Å and 2.125 Å to 2.059 Å and 2.045 Å, respectively. Furthermore, moving across the mechanism from protonation to reduction, the C2-C3 bond length always decreases in length moving from an initial length of 1.478 Å to 1.470 Å after protonation, and then decreasing further to 1.427 Å after reduction, in agreement with the spin-density map of Zn(HL•).

Results and Discussion for Example Set A

[00268] Solutions of ZnL in methanol or acetonitrile display catalytic hydrogen evolution upon reduction in the presence of acetic acid. In methanol, the cathodic current at -1.7 V increases with increasing acid concentration indicative of an electrocatalytic process (Fig. 1A). The current plateaus at 12.0 mM acetic acid indicating acid-saturation (Fig. 1B) with a maximum turnover frequency (TOF) of 1170 s⁻¹ at overpotential of 756 mV. No reduction wave for ZnL is observed within the potential limits of methanol in the

absence of acid, signifying that HER might require protonation prior to reduction. In acetonitrile, addition of acetic acid results in catalytic current at -2.3 V, which is near the irreversible ligand-centered reduction of H₂L in the absence of acid (Figs. 4-5) and within the range of reduction potentials previously reported for thiosemicarbizides. Catalytic current becomes independent of acid concentration at 23 mM, yielding a higher TOF of 11700 s⁻¹, but with a larger overpotential of 1074 mV. The lower overpotential in methanol appears consistent with outer-coordination sphere proton shuttling, which facilitates ligand protonation prior to electrochemical reduction. The HER TOF of ZnL is substantially higher than other proposed ligand-centered catalysts suggesting H₂L itself may also demonstrate catalytic activity.

[00269] The metal-free H₂L ligand was subsequently evaluated as a proton reduction catalyst. H₂L displays an irreversible reduction at -2.1 V and an irreversible oxidation at +0.5 V in methanol versus Fc⁺/Fc. Upon addition of acetic acid, the cathodic current at -2.1 V increases steadily (Fig. 6) reaching a maximum at concentrations of 9.8 mM (Fig. 1B). Under acid-saturated conditions, H₂L displays a TOF of 1320 s⁻¹ with an overpotential of 1430 mV. To our knowledge, this is the only reported metal-free, homogeneous electrocatalyst for HER.

[00270] As well as electrocatalytic HER, ZnL and H₂L also catalyze HOR. Introduction of triethylamine to methanol solutions of ZnL or H₂L under one atmosphere of H₂ results in an increase in anodic current near the irreversible oxidation wave of ZnL or H₂L, respectively (Fig. 1C and Fig. 7). For ZnL, the catalytic current shows saturation behavior (Fig. 1D) with near saturation at a base concentration of 30 mM yielding a TOF of 72 s⁻¹ with an overpotential of 315 mV. The HOR activity of H₂L ligand was similarly

assessed reaching saturation at 21 mM base (Fig. 1D) with a TOF of 32 s^{-1} and an overpotential of 328 mV. The HOR TOFs of ZnL and H₂L are among the highest reported of any homogenous electrocatalyst.

[00271] The stability of ZnL as a HER electrocatalyst was further examined by controlled potential coulometry. At an applied potential of -1.7 V versus Fc⁺/Fc, ZnL evolves H₂ from 12 mM acetic acid solutions in methanol with a turnover number (TON) of 37 after 2.5 hours (Fig. 2A) based on a total charge of 19.8 C. The identity of the gaseous product was confirmed as H₂ by gas chromatography thermal conductivity (GC-TCD). The integrated peak areas of headspace samples collected during electrolysis (Fig. 8) indicate a minimum faradaic efficiency of 85%. Throughout the electrolysis, the TOF remained consistent at 15 h^{-1} with no signs of decreasing activity. Spectroelectrochemical experiments were performed on 0.1 M Bu₄NPF₆ methanol solutions of ZnL with an applied potential of -1.7 V in order to identify the absorption characteristics of the one-electron reduced electrocatalyst, [ZnL]⁻. UV-Vis spectra were recorded before electrolysis and then measured every 15 minutes during electrolysis showing the growth of the absorption band near 250 nm and a decrease in the absorption band near 430 nm (Fig. 21). A CV was then recorded with addition of 12 mM acetic acid (Fig. 22). An additional control was performed after prolonged reduction in order to rule out ligand decomposition onto electrode surface as possible source of catalysis. After reduction, the working electrode was removed, washed with DI water, and then placed in fresh solution containing no catalyst, upon which no current was observed.

[00272] To evaluate the HER mechanism of ZnL, we first determined the rate law and measured the H/D kinetic isotope effect. Under acid-dependent conditions, the

catalytic current (i_{cat}) displays a linear dependence on the square root of the scan rate indicating the current appears limited by acid diffusion to the electrode surface (Figs. 9-10). Further, under non-saturating acid conditions i_{cat} appears directly proportional to $[H^+]$ (Fig. 1B) indicating a first-order dependence on acid concentration. Varying the $[ZnL]$ at fixed acid concentrations confirms first-order dependence at catalyst concentrations above 2 mM (Figs. 11-12). Using the deuterated acid CD_3CO_2D , the ZnL catalyst displays a small kinetic isotope effect (KIE) of 1.2.

[00273] Several example simulations and calculations were performed, as described herein. However, the scope of the invention is not limited by the results, pathways, or mechanisms exemplified in the simulations.

[00274] Digital simulations of the cyclic voltammograms (Fig. 2B and Table A1) reveal parallel routes to proton reduction involving homo-coupling of two, neutral $Zn(HL^\bullet)$ radicals and hetero-coupling of a neutral $Zn(HL^\bullet)$ radical with the cationic radical $[Zn(H_2L^\bullet)]^+$. The proposed mechanism (Fig. 2C) begins with protonation of ZnL, $K = 2.4 \times 10^5$, followed by reduction to $Zn(HL^\bullet)$, $E^\circ = -1.81$ V vs. Fc^+/Fc . In the homo-coupling pathway, two $Zn(HL^\bullet)$ rapidly combine, $k_f = 3 \times 10^9$ $M^{-1} s^{-1}$, to evolve H_2 and regenerate two equivalents of ZnL. In the alternate pathway, one equivalent of $Zn(HL^\bullet)$ is further protonated, $K = 8.8$, prior to hetero-coupling. Combination of $[Zn(H_2L^\bullet)]^+$ with the second equivalent of $Zn(HL^\bullet)$, $k_f = 2 \times 10^{10}$ $M^{-1} s^{-1}$, yields H_2 completing the catalytic cycle. The simulated kinetic and thermodynamic parameters reveal that both routes to H_2 evolution are operational across a range of experimental conditions (Figs. 13-15 and Table A2 – A3).

[00275] Density functional theory (DFT) calculations using the B97-D functional and the 6-311G(d) basis set, support the proposed catalytic cycle and elucidate the hydrazino nitrogen as the site of protonation. Each of the metal complexes in Fig. 2C was successfully optimized (Table A4 – A6). Energies (Table A7) reveal that protonation at the hydrazino nitrogen (Fig. 16) is favored by at least 13.0 kcal/mol relative to other potential basic sites within ZnL (Figs. 17-19). Evolution of H₂ through homo-coupling of two Zn(HL•) radicals is exergonic by 42.6 kcal/mol, while the parallel pathway involving hetero-coupling of Zn(HL•) and [Zn(H₂L•)]⁺ releases 28.8 kcal/mol.

[00276] Analyses of the Zn(HL•) and [Zn(H₂L•)]⁺ spin density profiles (Figs. 3A and 3B) show radical character delocalized on both protonated ligand frameworks. H₂ is evolved by radical hetero-coupling, overcoming an 8.1 kcal/mol barrier (Figs. 3C and 3D). The absence of spin density on Zn for all species involved in the HER, is support for ligand based reduction (Table A8). The transition state (TS) can be described as a dimer with H dissociations from each monomer fragment, along their respective N-H coordinates to form H₂ (Fig. 20). This is consistent with N-H bond lengths in the TS of 1.25 Å for Zn(HL•), and 1.36 Å for [Zn(H₂L•)]⁺ compared to respective equilibrium N-H distances, both of 1.02 Å. The longer N-H bond in the TS associated with [Zn(H₂L•)]⁺ may also be attributed to an increased charge density along the forward IRC for both N and H, compared to Zn(HL•) (Fig. 20). The HER from [Zn₂H₃L•₂]⁺ is thus interpreted as dimeric, where the now charge-reorganized Zn(H₂L•) fragment promotes early electron transfer, and is coupled to proton transfer from [Zn(HL•)]⁺ to form H₂.

[00277] In summary, some of the non-transition metal complex ZnL and the metal-free ligand H₂L disclosed herein appear to represent a fundamentally new class of

homogeneous HER and HOR electrocatalysts. Unlike traditional catalysts that employ a metal-hydride as the key intermediate, this new approach facilitates H₂ evolution through ligand-centered radical coupling. The combination of the redox active ligand H₂L with the non-transition metal Zn constrains redox activity to the ligand, in contrast to transition metal complexes where spin-coupling between the ligand radical and unpaired electrons on the metal may reduce reactivity. The confinement of radical character to the ligand is further evidenced by the catalytic activity of H₂L; albeit with higher overpotential than ZnL. The enhanced activity with Zn, in some instances, is understood to be attributed in part to the Lewis acidity of Zn(II), which balances the charge of the anionic ligand, promotes protonation, and lowers the reduction potential. Further, Zn(II) can provide a structural framework for the N₂S₂ chelate that pre-organizes the radical complexes for H₂ evolution.

Table A1. Optimized parameters of data fitting, 12 mM [acid]; $v = 0.2 - 0.5$ V/s vs Fc^+/Fc^0

Charge-transfer Steps	99% Confidence	E^0	α	k_s
$[\text{ZnHL}]^+ + e^- = \text{Zn}(\text{HL}\cdot)$	Optimized	-1.8110	0.3166	0.0070
	Upper Limit	-1.8113	0.3166	0.0070
	Lower Limit	-1.8107	0.3166	0.0070
$[\text{ZnH}_2\text{L}]^{2+} + e^- = [\text{Zn}(\text{H}_2\text{L}\cdot)]^+$	Optimized	-1.5872	0.3166	0.0070
	Upper Limit	-1.5874	0.3166	0.0070
	Lower Limit	-1.5870	0.3166	0.0070
Chemical Steps	99% Confidence	K_{eq}	k_f	
$\text{ZnL} + \text{H}^+ = [\text{ZnHL}]^+$	Optimized	2.42E+05	1.28E+13	
	Upper Limit	3.42E+06	6.40E+13	
	Lower Limit	1.91E+05	1.94E+12	
$[\text{ZnHL}]^+ + \text{H}^+ = [\text{ZnH}_2\text{L}]^{2+}$	Optimized	8.80E+00	4.06E+06	
	Upper Limit	8.93E+00	6.92E+06	

	Lower Limit	8.68E+00	1.20E+06
$\text{Zn}(\text{HL}\cdot) + \text{Zn}(\text{HL}\cdot) = \text{H}_2$	Optimized	4.89E+10	3.09E+09
	Upper Limit	4.96E+10	6.51E+09
	Lower Limit	4.80E+10	6.45E+08
$\text{Zn}(\text{HL}\cdot) + [\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{H}_2$	Optimized	9.07E+07	2.47E+10
	Upper Limit	9.19E+07	3.95E+10
	Lower Limit	8.90E+07	9.94E+09
$[\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{Zn}(\text{HL}\cdot) + \text{H}^+$	Calculated	1.87E-05	8.14E+04
	Upper Limit	1.87E-05	1.07E+05
	Lower Limit	1.87E-05	2.82E+04

Table A2. Optimized parameters of data fitting, 12 mM [acid]; $v = 0.6 - 5.0$ V/s vs Fc^+/Fc^0

Charge-transfer Steps	99% Confidence	E^0	α	k_s
$[\text{ZnHL}]^+ + e^- = \text{Zn}(\text{HL}\cdot)$	Optimized	-1.8004	0.3166	0.007
	Upper Limit	-1.8010	0.3166	0.007
	Lower Limit	-1.8000	0.3166	0.007
$[\text{ZnH}_2\text{L}]^{2+} + e^- = [\text{Zn}(\text{H}_2\text{L}\cdot)]^+$	Optimized	-1.5264	0.3166	0.007
	Upper Limit	-1.5274	0.3166	0.007
	Lower Limit	-1.5254	0.3166	0.007
Chemical Steps	99% Confidence	K_{eq}	k_f	
$\text{ZnL} + \text{H}^+ = [\text{ZnHL}]^+$	Optimized	1364	3.20E+13	
	Upper Limit	1442.8	8.72E+15	
	Lower Limit	1285.2	8.65E+12	
$[\text{ZnHL}]^+ + \text{H}^+ = [\text{ZnH}_2\text{L}]^{2+}$	Optimized	13.438	3.06E+09	
	Upper Limit	13.6	9.83E+10	
	Lower Limit	13.276	9.22E+08	
$\text{Zn}(\text{HL}\cdot) + \text{Zn}(\text{HL}\cdot) = \text{H}_2$	Optimized	3.69E+11	4.57E+08	
	Upper Limit	3.69E+11	5.57E+08	
	Lower Limit	3.68E+11	3.57E+08	
$\text{Zn}(\text{HL}\cdot) + [\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{H}_2$	Optimized	4.44E+08	2.72E+11	
	Upper Limit	4.46E+08	3.84E+11	
	Lower Limit	4.42E+08	1.61E+11	
$[\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{Zn}(\text{HL}\cdot) + \text{H}^+$	Calculated	1.74E-06	2414	
	Upper Limit	1.74E-06	2414	
	Lower Limit	1.74E-06	2414	

Table A3. Optimized parameters of data fitting, 6 mM [acid]; $v = 0.2 - 0.5$ V/s vs Fc^+/Fc^0

Charge-transfer Steps	99% Confidence	E^0	α	k_s
$[\text{ZnHL}]^+ + e^- = \text{Zn}(\text{HL}\cdot)$	Optimized	-1.8431	0.3166	0.007
	Upper Limit	-1.8562	0.3166	0.007
	Lower Limit	-1.8333	0.3166	0.007
$[\text{ZnH}_2\text{L}]^{2+} + e^- = [\text{Zn}(\text{H}_2\text{L}\cdot)]^+$	Optimized	-1.6958	0.3166	0.007
	Upper Limit	-1.7939	0.3166	0.007
	Lower Limit	-1.5977	0.3166	0.007
Chemical Steps	99% Confidence	K_{eq}	k_f	
$\text{ZnL} + \text{H}^+ = [\text{ZnHL}]^+$	Optimized	32000	5.00E+11	
	Upper Limit	6.68E+05	1.43E+12	
	Lower Limit	6.04E+03	1.04E+10	
$[\text{ZnHL}]^+ + \text{H}^+ = [\text{ZnH}_2\text{L}]^{2+}$	Optimized	19.942	2.86E+02	
	Upper Limit	95.717	2.86E+03	
	Lower Limit	0.55833	2.23E+01	
$\text{Zn}(\text{HL}\cdot) + \text{Zn}(\text{HL}\cdot) = \text{H}_2$	Optimized	7.28E+09	2.00E+08	
	Upper Limit	1.05E+11	1.35E+12	
	Lower Limit	9.08E+08	1.35E+06	
$\text{Zn}(\text{HL}\cdot) + [\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{H}_2$	Optimized	8.58E+07	2.00E+12	
	Upper Limit	1.28E+09	1.49E+13	
	Lower Limit	1.11E+06	1.09E+10	
$[\text{Zn}(\text{H}_2\text{L}\cdot)]^+ = \text{Zn}(\text{HL}\cdot) + \text{H}^+$	Calculated	1.55E-04	4000	
	Upper Limit	1.55E-04	4754.6	
	Lower Limit	1.55E-04	3245.4	

5 Table A4. Bond length comparison of calculated HER intermediates

Structures		ZnL	[ZnHL] ⁺	Zn(HL•)	[ZnH ₂ L•] ⁺
Bond Lengths (Å)	Zn-S1	2.368	2.423	2.458	2.386
	Zn-S2	2.368	2.318	2.341	2.386

	Zn-N2	2.116	2.118	2.059	2.061
	Zn-N3	2.116	2.125	2.045	2.061
	S1-C1	1.774	1.719	1.728	1.732
	C1-N5	1.356	1.343	1.373	1.349
	N5-C5	1.460	1.467	1.459	1.463
	C1-N1	1.339	1.373	1.351	1.361
	N1-N2	1.344	1.357	1.368	1.362
	N1-H15	-	1.015	1.016	1.015
	N2-C2	1.312	1.313	1.368	1.348
	C2-C3	1.478	1.470	1.427	1.436
	C3-N3	1.312	1.322	1.345	1.348
	N3-N4	1.344	1.321	1.349	1.362
	N4-C4	1.339	1.361	1.329	1.361
	C4-S2	1.774	1.767	1.792	1.732
	C4-N6	1.356	1.341	1.367	1.349
	N6-C8	1.460	1.469	1.458	1.463

Table A5. Bond angle comparison of calculated HER intermediates

Structures		ZnL	[ZnHL] ⁺	Zn(HL·)	[ZnH ₂ L] ⁺
Bond Angles (°)	S1-Zn-S2	118.02	119.08	116.68	117.56
	S1-Zn-N2	82.78	81.57	82.39	83.80
	N2-Zn-N3	76.43	74.94	77.40	73.34
	N3-Zn-S2	82.78	84.41	85.07	83.30
	C1-S1-Zn	93.70	96.92	95.10	95.54
	N1-N2-C2	121.88	122.99	120.43	122.41
	N1-N2-Zn	122.08	119.62	119.13	118.45
	C2-N2-Zn	116.04	117.39	115.19	118.59
	C3-N3-Zn	116.04	117.76	117.15	118.59
	C3-N3-N4	121.88	122.01	121.05	122.41
	N4-N3-Zn	122.08	120.23	121.44	118.45

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Table A6. Computational Input Coordinates

ZnL

0 1

20	Zn	0.00003000	-0.87035000	-0.00021000
	S	1.99717800	-1.98187000	0.39859600
	C	3.02385700	-0.57568000	0.06312600
	N	2.64126500	0.68182000	-0.11295000
	N	1.29611500	0.83221600	-0.13343000
25	C	0.74221000	2.00306700	-0.01927000
	C	-0.74227000	2.00309000	0.01908300
	N	-1.29622000	0.83222900	0.13305300

	N	-2.64133000	0.68180300	0.11294100
	C	-3.02384000	-0.57582000	-0.06295000
	S	-1.99721000	-1.98199000	-0.39809000
	N	4.35570700	-0.82176000	0.01195100
5	C	5.36070300	0.19708100	-0.24871000
	C	1.51592800	3.28691200	0.08674400
	C	-1.51582000	3.28710900	-0.08627000
	N	-4.35572000	-0.82183000	-0.01172000
	C	-5.36071000	0.19724100	0.24805300
10	H	4.64910400	-1.76944000	0.19775300
	H	-4.64921000	-1.76953000	-0.19732000
	H	6.34217200	-0.28345000	-0.24323000
	H	5.33720300	0.97919000	0.51882200
	H	5.19661500	0.66931400	-1.22332000
15	H	2.57356100	3.10001400	-0.10327000
	H	1.41553600	3.72317600	1.09013800
	H	1.14601100	4.03184200	-0.62751000
	H	-2.57412000	3.09947900	0.09927500
	H	-1.14881000	4.02987600	0.63178900
20	H	-1.41150000	3.72652300	-1.08785000
	H	-6.34227000	-0.28309000	0.24188600
	H	-5.19732000	0.66960500	1.22273300
	H	-5.33643000	0.97923600	-0.51956000
25	<u>[ZnHL]⁺</u>			
	1 1			
	Zn	0.000030000	-0.870350000	-0.000210000
	S	1.997178000	-1.981870000	0.398596000
	C	3.023857000	-0.575680000	0.063126000
30	N	2.641265000	0.681820000	-0.112950000
	N	1.296115000	0.832216000	-0.133430000
	C	0.742210000	2.003067000	-0.019270000
	C	-0.742270000	2.003090000	0.019083000
	N	-1.296220000	0.832229000	0.133053000
35	N	-2.641330000	0.681803000	0.112941000
	C	-3.023840000	-0.575820000	-0.062950000
	S	-1.997210000	-1.981990000	-0.398090000
	N	4.355707000	-0.821760000	0.011951000
	C	5.360703000	0.197081000	-0.248710000
40	C	1.515928000	3.286912000	0.086744000
	C	-1.515820000	3.287109000	-0.086270000
	N	-4.355720000	-0.821830000	-0.011720000
	C	-5.360710000	0.197241000	0.248053000
	H	4.649104000	-1.769440000	0.197753000
45	H	-4.649210000	-1.769530000	-0.197320000

	H	6.342172000	-0.283450000	-0.243230000
	H	5.337203000	0.979190000	0.518822000
	H	5.196615000	0.669314000	-1.223320000
	H	2.573561000	3.100014000	-0.103270000
5	H	1.415536000	3.723176000	1.090138000
	H	1.146011000	4.031842000	-0.627510000
	H	-2.574120000	3.099479000	0.099275000
	H	-1.148810000	4.029876000	0.631789000
	H	-1.411500000	3.726523000	-1.087850000
10	H	-6.342270000	-0.283090000	0.241886000
	H	-5.197320000	0.669605000	1.222733000
	H	-5.336430000	0.979236000	-0.519560000
	H	3.281842792	1.442241206	-0.219812917
15	Zn(HL•)			
	O 2			
	Zn	0.000030000	-0.870350000	-0.000210000
	S	1.997178000	-1.981870000	0.398596000
	C	3.023857000	-0.575680000	0.063126000
20	N	2.641265000	0.681820000	-0.112950000
	N	1.296115000	0.832216000	-0.133430000
	C	0.742210000	2.003067000	-0.019270000
	C	-0.742270000	2.003090000	0.019083000
	N	-1.296220000	0.832229000	0.133053000
25	N	-2.641330000	0.681803000	0.112941000
	C	-3.023840000	-0.575820000	-0.062950000
	S	-1.997210000	-1.981990000	-0.398090000
	N	4.355707000	-0.821760000	0.011951000
	C	5.360703000	0.197081000	-0.248710000
30	C	1.515928000	3.286912000	0.086744000
	C	-1.515820000	3.287109000	-0.086270000
	N	-4.355720000	-0.821830000	-0.011720000
	C	-5.360710000	0.197241000	0.248053000
	H	4.649104000	-1.769440000	0.197753000
35	H	-4.649210000	-1.769530000	-0.197320000
	H	6.342172000	-0.283450000	-0.243230000
	H	5.337203000	0.979190000	0.518822000
	H	5.196615000	0.669314000	-1.223320000
	H	2.573561000	3.100014000	-0.103270000
40	H	1.415536000	3.723176000	1.090138000
	H	1.146011000	4.031842000	-0.627510000
	H	-2.574120000	3.099479000	0.099275000
	H	-1.148810000	4.029876000	0.631789000
	H	-1.411500000	3.726523000	-1.087850000
45	H	-6.342270000	-0.283090000	0.241886000

	H	-5.197320000	0.669605000	1.222733000
	H	-5.336430000	0.979236000	-0.519560000
	H	3.281842792	1.442241206	-0.219812917
5	<u>[ZnH₂L•]⁺</u>			
	1 2			
	Zn	0.000030000	-0.870350000	-0.000210000
	S	1.997178000	-1.981870000	0.398596000
	C	3.023857000	-0.575680000	0.063126000
10	N	2.641265000	0.681820000	-0.112950000
	N	1.296115000	0.832216000	-0.133430000
	C	0.742210000	2.003067000	-0.019270000
	C	-0.742270000	2.003090000	0.019083000
	N	-1.296220000	0.832229000	0.133053000
15	N	-2.641330000	0.681803000	0.112941000
	C	-3.023840000	-0.575820000	-0.062950000
	S	-1.997210000	-1.981990000	-0.398090000
	N	4.355707000	-0.821760000	0.011951000
	C	5.360703000	0.197081000	-0.248710000
20	C	1.515928000	3.286912000	0.086744000
	C	-1.515820000	3.287109000	-0.086270000
	N	-4.355720000	-0.821830000	-0.011720000
	C	-5.360710000	0.197241000	0.248053000
	H	4.649104000	-1.769440000	0.197753000
25	H	-4.649210000	-1.769530000	-0.197320000
	H	6.342172000	-0.283450000	-0.243230000
	H	5.337203000	0.979190000	0.518822000
	H	5.196615000	0.669314000	-1.223320000
	H	2.573561000	3.100014000	-0.103270000
30	H	1.415536000	3.723176000	1.090138000
	H	1.146011000	4.031842000	-0.627510000
	H	-2.574120000	3.099479000	0.099275000
	H	-1.148810000	4.029876000	0.631789000
	H	-1.411500000	3.726523000	-1.087850000
35	H	-6.342270000	-0.283090000	0.241886000
	H	-5.197320000	0.669605000	1.222733000
	H	-5.336430000	0.979236000	-0.519560000
	H	3.281842792	1.442241206	-0.219812917
	H	-3.281933702	1.442187461	0.219910007
40	<u>Protonation of ZnL at sulfur</u>			
	1 1			
	30	0.000030000	-0.870350000	-0.000210000
	16	1.997178000	-1.981870000	0.398596000
45	6	3.023857000	-0.575680000	0.063126000

	7	2.641265000	0.681820000	-0.112950000
	7	1.296115000	0.832216000	-0.133430000
	6	0.742210000	2.003067000	-0.019270000
	6	-0.742270000	2.003090000	0.019083000
5	7	-1.296220000	0.832229000	0.133053000
	7	-2.641330000	0.681803000	0.112941000
	6	-3.023840000	-0.575820000	-0.062950000
	16	-1.997210000	-1.981990000	-0.398090000
	7	4.355707000	-0.821760000	0.011951000
10	6	5.360703000	0.197081000	-0.248710000
	6	1.515928000	3.286912000	0.086744000
	6	-1.515820000	3.287109000	-0.086270000
	7	-4.355720000	-0.821830000	-0.011720000
	6	-5.360710000	0.197241000	0.248053000
15	1	4.649104000	-1.769440000	0.197753000
	1	-4.649210000	-1.769530000	-0.197320000
	1	6.342172000	-0.283450000	-0.243230000
	1	5.337203000	0.979190000	0.518822000
	1	5.196615000	0.669314000	-1.223320000
20	1	2.573561000	3.100014000	-0.103270000
	1	1.415536000	3.723176000	1.090138000
	1	1.146011000	4.031842000	-0.627510000
	1	-2.574120000	3.099479000	0.099275000
	1	-1.148810000	4.029876000	0.631789000
25	1	-1.411500000	3.726523000	-1.087850000
	1	-6.342270000	-0.283090000	0.241886000
	1	-5.197320000	0.669605000	1.222733000
	1	-5.336430000	0.979236000	-0.519560000
	1	2.274340046	-3.233237278	0.753787688

30

Protonation at Amine Nitrogen

1 1

	Zn	0.000030000	-0.870350000	-0.000210000
	S	1.997178000	-1.981870000	0.398596000
35	C	3.023857000	-0.575680000	0.063126000
	N	2.641265000	0.681820000	-0.112950000
	N	1.296115000	0.832216000	-0.133430000
	C	0.742210000	2.003067000	-0.019270000
	C	-0.742270000	2.003090000	0.019083000
40	N	-1.296220000	0.832229000	0.133053000
	N	-2.641330000	0.681803000	0.112941000
	C	-3.023840000	-0.575820000	-0.062950000
	S	-1.997210000	-1.981990000	-0.398090000
	N	4.355707000	-0.821760000	0.011951000
45	C	5.360703000	0.197081000	-0.248710000

	C	1.515928000	3.286912000	0.086744000
	C	-1.515820000	3.287109000	-0.086270000
	N	-4.355720000	-0.821830000	-0.011720000
	C	-5.360710000	0.197241000	0.248053000
5	H	4.649104000	-1.769440000	0.197753000
	H	-4.649210000	-1.769530000	-0.197320000
	H	6.342172000	-0.283450000	-0.243230000
	H	5.337203000	0.979190000	0.518822000
	H	5.196615000	0.669314000	-1.223320000
10	H	2.573561000	3.100014000	-0.103270000
	H	1.415536000	3.723176000	1.090138000
	H	1.146011000	4.031842000	-0.627510000
	H	-2.574120000	3.099479000	0.099275000
	H	-1.148810000	4.029876000	0.631789000
15	H	-1.411500000	3.726523000	-1.087850000
	H	-6.342270000	-0.283090000	0.241886000
	H	-5.197320000	0.669605000	1.222733000
	H	-5.336430000	0.979236000	-0.519560000
	H	4.370833470	-0.021327902	-0.587281548

20

Protonation on Zinc

1 1

	Zn	0.000030000	-0.870350000	-0.000210000
	S	1.997178000	-1.981870000	0.398596000
25	C	3.023857000	-0.575680000	0.063126000
	N	2.641265000	0.681820000	-0.112950000
	N	1.296115000	0.832216000	-0.133430000
	C	0.742210000	2.003067000	-0.019270000
	C	-0.742270000	2.003090000	0.019083000
30	N	-1.296220000	0.832229000	0.133053000
	N	-2.641330000	0.681803000	0.112941000
	C	-3.023840000	-0.575820000	-0.062950000
	S	-1.997210000	-1.981990000	-0.398090000
	N	4.355707000	-0.821760000	0.011951000
35	C	5.360703000	0.197081000	-0.248710000
	C	1.515928000	3.286912000	0.086744000
	C	-1.515820000	3.287109000	-0.086270000
	N	-4.355720000	-0.821830000	-0.011720000
	C	-5.360710000	0.197241000	0.248053000
40	H	4.649104000	-1.769440000	0.197753000
	H	-4.649210000	-1.769530000	-0.197320000
	H	6.342172000	-0.283450000	-0.243230000
	H	5.337203000	0.979190000	0.518822000
	H	5.196615000	0.669314000	-1.223320000
45	H	2.573561000	3.100014000	-0.103270000

H	1.415536000	3.723176000	1.090138000
H	1.146011000	4.031842000	-0.627510000
H	-2.574120000	3.099479000	0.099275000
H	-1.148810000	4.029876000	0.631789000
H	-1.411500000	3.726523000	-1.087850000
H	-6.342270000	-0.283090000	0.241886000
H	-5.197320000	0.669605000	1.222733000
H	-5.336430000	0.979236000	-0.519560000
H	0.000293000	-2.650349596	-0.001380325

Hydrogen

O 1

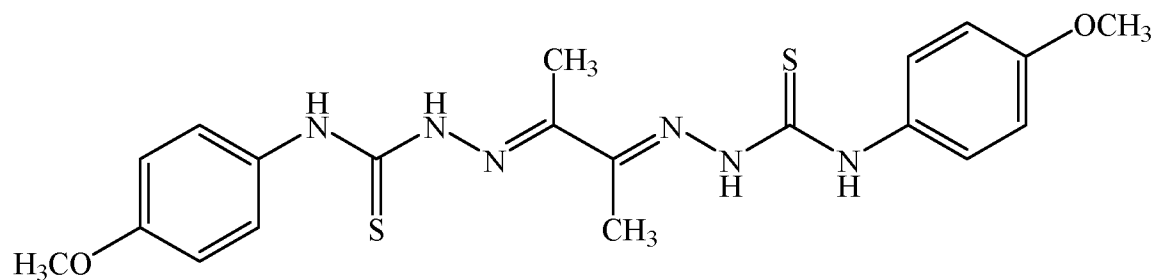
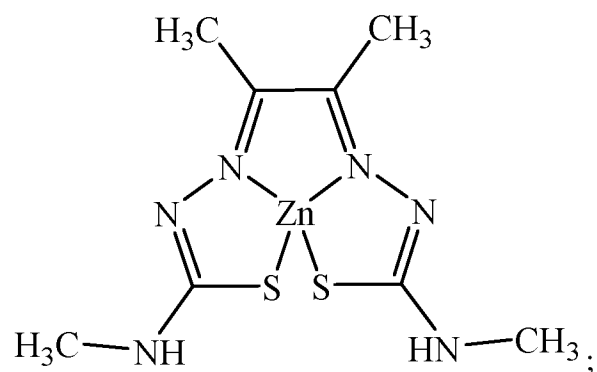
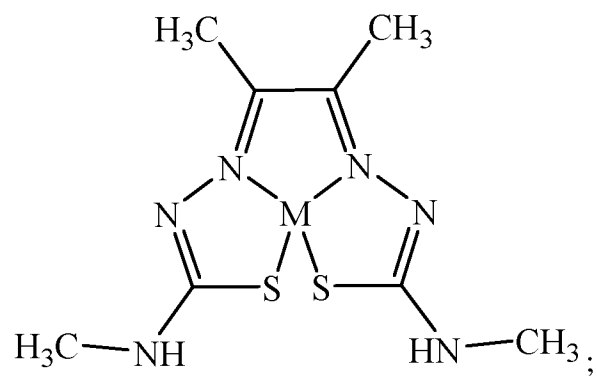
H	3.259348439	4.169555780	-0.124845483
H	3.259348439	4.169555780	-0.864845483

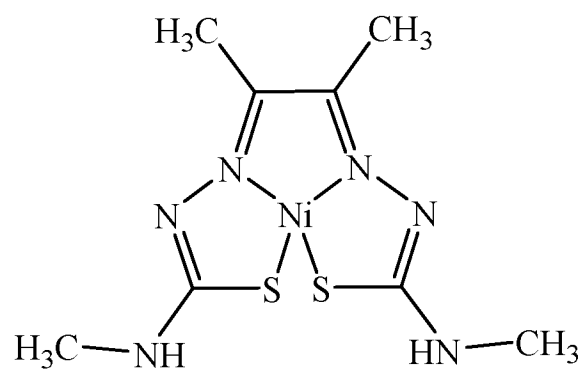
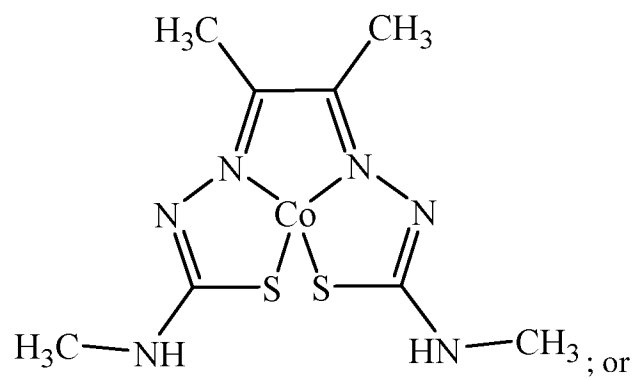
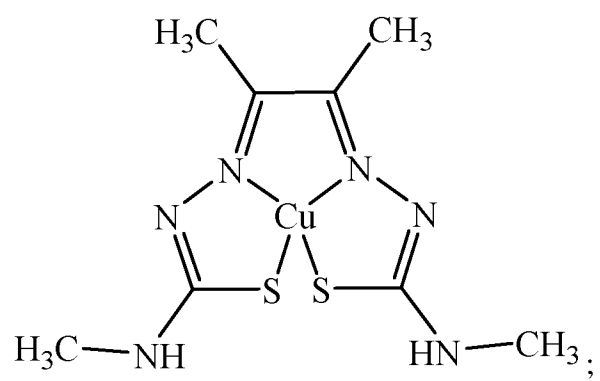
Table A7. Comparison of calculated energies for various protonation sites on ZnL

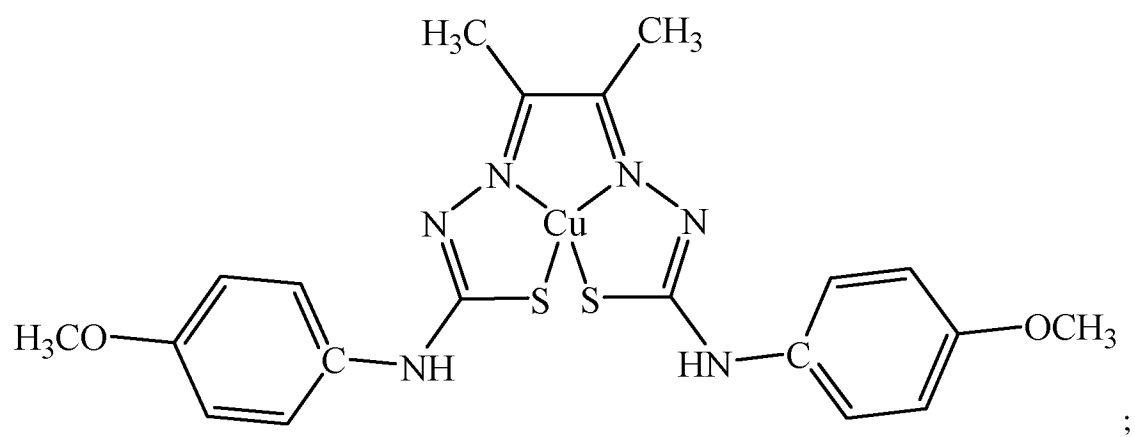
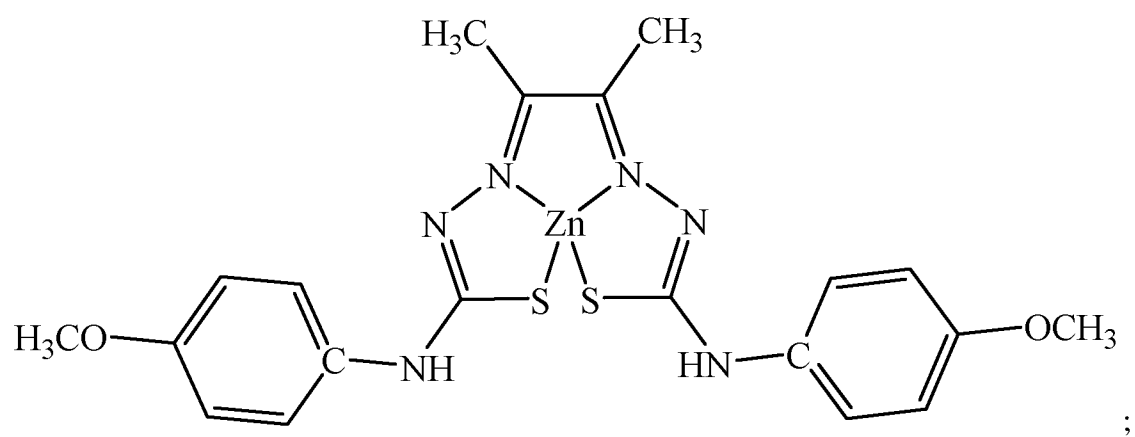
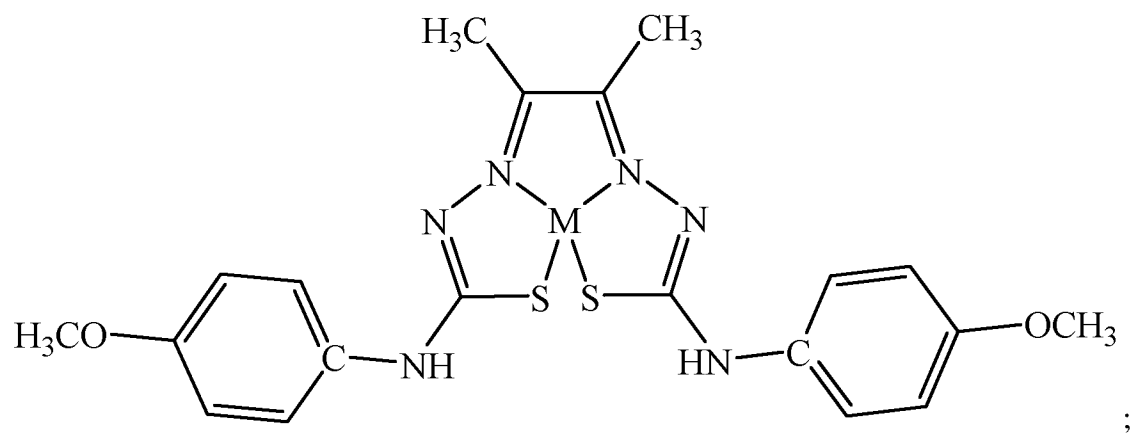
Site of Protonation	Sum of Electronic and Thermal Free Energies (kcal/mole)
S-Protonation	+ 1300
Hydrazino N-Protonation	0
Amine N-Protonation	+ 13
Zn-Protonation	+14

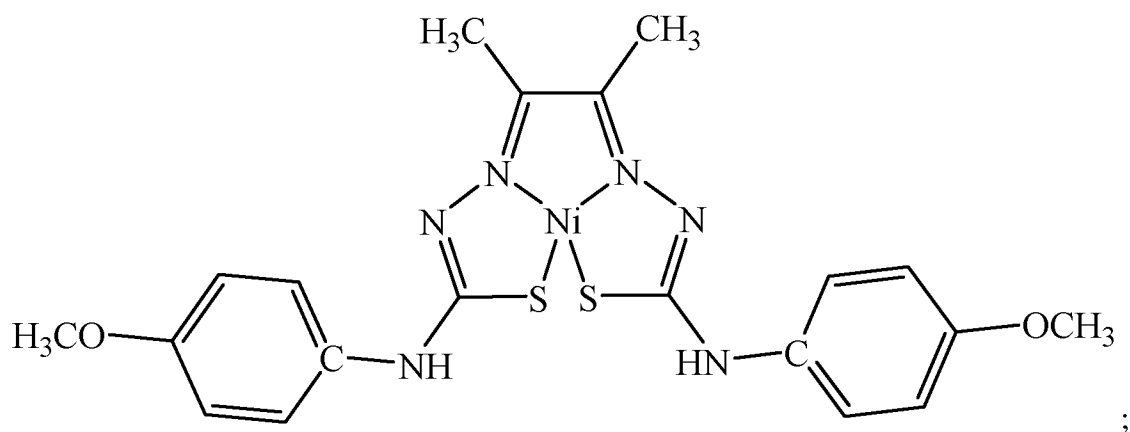
Table A8. α - β spin density comparison for radical species: Zn(HL $\cdot$) and [ZnH₂L $\cdot$]⁺

<i>Spin-Density (α-β)</i>		
Atom	Zn(HL $\cdot$)	[ZnH ₂ L $\cdot$] ⁺
C1	0.096320	0.072671
C2	0.298443	0.211249
C3	-	0.211171
C4	0.094069	0.072688
N2	0.125707	0.192627
N3	0.259371	0.192651
N4	0.022704	-
N5	-	0.033882
N6	0.026308	0.033891
S1	0.014559	-
S2	0.008889	-

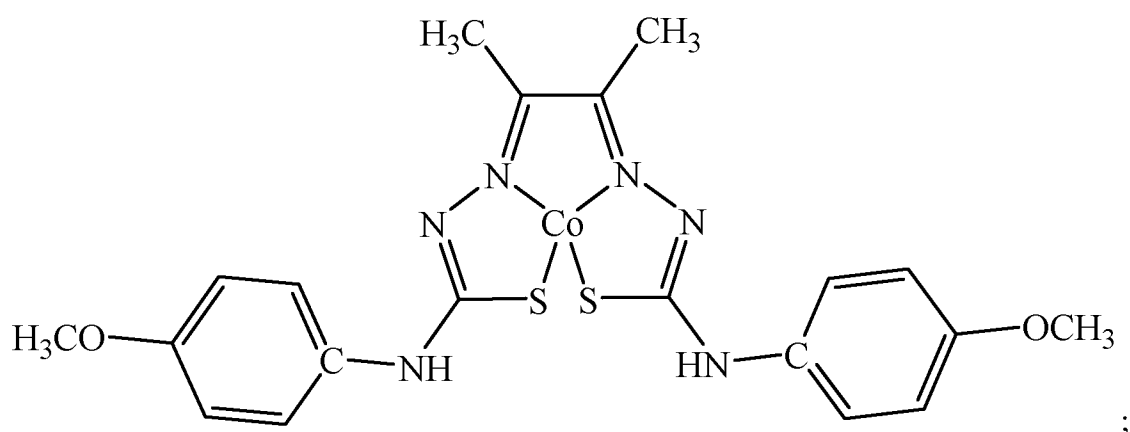
[00278] **Example Set B: HER of Cu complexes**[00279] The compounds discussed in Example Set B include H_2L^2 , ML^1 , and ML^2 .[00280] H_2L^2 5 [00281] ML^1 



[00282] ML²



or



5

Materials and Methods for Example Set B

[00283] Electrochemical Methods

[00284] All cyclic voltammetry (CV) and controlled potential coulometry (CPC) measurements were recorded using a Gamry Interface potentiostat/galvanostat, which

10 was connected to a glassy carbon working electrode (6.5 mm diameter, surface area = 0.07 cm²), a platinum wire counter electrode, and Ag/AgCl reference electrode. Before use, the working electrode was polished using an aqueous alumina slurry. The working

and counter electrodes were cleaned before use by washing with water, ethanol, isopropanol, acetone and then sonication for 10 minutes in acetonitrile. CV measurements were conducted using a three-neck electrochemical cell that was washed and dried in an oven overnight before use. All electrochemical experiments were conducted under a N₂ atmosphere. All CPC measurements were conducted using a two chambered glass electrolysis cell with working and auxiliary compartments separated by a frit, with a volume of 10 mL in each, washed and dried the night before use. The working compartment was fitted with a glassy carbon working electrode and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt wire counter electrode. The working compartment contained 0.292 M acetic acid added to a 0.1 M Bu₄NPF₆ acetonitrile or DMF solution, while the auxiliary compartment was filled with 0.1 M Bu₄NPF₆ acetonitrile or DMF solution. Both compartments were purged for 15 min with N₂ prior to electrolysis. A control (blank) CPC study was conducted and subtracted from experimental results (supporting information). Electrolysis measurements were performed after addition of 0.6 mM CuL¹ to the working compartment for several time durations. The evolved gas was subjected to GC-TCD analysis at the end of the electrolysis using a Gow-Mac series 400 GC-TCD equipped with a molecular sieve column for product detection. The column was heated to 130 °C under N₂ gas flow with 250 µL injection samples injected onto the column to confirm H₂ as the gaseous product.

[00285] Overpotential Determination

[00286] Overpotential can be defined as the difference between the thermodynamic and equilibrium potentials for a given reaction and the potential at which the reaction occurs under a set of specific conditions. In the case of H₂ evolution or

oxidation, when either the equilibrium potential for the standard state H^+/H_2 couple ($E^\circ_{H^+}$) is not known for some particular solvent, or a reliable pKa scale is unavailable, the direct measurement of the equilibrium potential for the reduction of protons (E_{H^+}) can be accomplished through an open circuit potential (OCP) measurements, as described by Appel and Helm (ACS Catal., 2014, Vol. 4, pp. 630-633; DOI: 10.1021/cs401013v).

Using this method provides an accurate determination of the equilibrium potential for the H^+/H_2 couple under a wide range of acids and bases, as well as solvents or mixtures of solvents. This method has proven valuable for the determination of E_{H^+} of protic ionic liquids and various acid base pairs in acetonitrile DMF and/or water. The accurate determination of overpotential can sometimes require an estimation of $E_{cat/2}$ and E_{H^+} , each of which can change, depending on the reaction conditions. The value for the potential for catalysis should be related to the catalytic current, and therefore, we use $E_{cat/2}$. This combined with a value for E_{H^+} , obtained through OCP measurements allows for calculation of the overpotential (η) for proton reduction by CuL^1 under some specific experimental conditions. The overpotential can then be estimated as, $\eta = |E_{OCP} - E_{cat/2}|$, where E_{OCP} is the measured open circuit potential measured under catalytic conditions specific for each reaction, and $E_{cat/2}$ is the potential at one-half the maximum of the catalytic current measured for the catalyzed reduction of protons (see sample calculations).

[00287] Faradaic Efficiency Determination

[00288] Evolved gas from the cathode compartment displaced water in a cylinder with radius 1.12 cm by a height of 2.16 cm. Using the equation for the volume of a cylinder, $V = \pi(r)^2h$, we can calculate the volume displaced. This is calculated to be 8.51

mL. Using the conversion factor of 22.4 L of any ideal gas per one mole of gas allows us to quantify the number of moles of H₂ evolved as 3.80 x 10⁻⁴ moles. This value can then be compared to the theoretical number of moles of H₂ evolved based on charge determined earlier, 4.40 x 10⁻⁴. Faradaic efficiency is defined as moles of H₂ quantified/moles of H₂ theoretical based on charge x 100%. This corresponds with a minimum Faradic efficiency of 86.0%.

[00289] Turnover Frequency Determination

$$i_{cat} = nFA[cat]\sqrt{Dk[H^+]^2} \quad (B1)$$

[00290] Equation B1 details the relationship between the catalytic current i_{cat} , the catalyst concentration [cat], and the acid concentration [H⁺] for a catalytic reaction that is second-order in acid and first-order in catalyst. The terms n, F, A, and D are the normal electrochemical terms related to the number of electrons transferred, Faraday's constant, area of the electrode (0.07 cm²), and diffusion constant, respectively.

[00291] Equation B2 (Randle-Sevcik equation) provides the relationship between the peak current (i_p), catalyst concentration, and scan rate (v) in the absence of acid. The factor of 0.4463 is related to the diffusion equations, R is the gas constant, and T is temperature in K. The other terms are the same as in equation B1.

$$i_p = 0.4463FA[cat]\sqrt{\frac{FvD}{RT}} \quad (B2)$$

[00292] Thus, the ratio of i_{cat}/i_p (equation B3) is obtained from the quotient equations B1 and B2.

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk[H^+]^2}{Fv}} \quad (B3)$$

[00293] Under pseudo first-order conditions where $k_{obs} = k[H^+]^2$, equation B3 simplifies to B4.

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk_{obs}}{Fv}} \quad (B4)$$

[00294] Equation B4 can be simplified further to equation B5, when $n=2$, and
 5 when at scan rate independent conditions can be used to estimate the observed rate constant or turnover frequency (TOF) (see sample calculations).

$$k_{obs} = 1.94 \times v \left[\frac{i_{cat}}{i_p} \right]^2 \quad (B5)$$

[00295] X-ray Photoelectron Spectroscopy of Electrode Adsorbed Films

[00296] CPEs of 0.6 mM CuL¹ with 0.292 M acetic acid added in 0.1 M Bu₄NPF₆

10 DMF and ACN solutions were run for 23.5 and 4.2 hours, respectively. After completion of electrolysis, the working electrode was removed and washed with DI water. A visible red-brown film persisted on the electrode surface. The films were scraped off using a spatula, collected onto wax paper, and transferred to a glass vial, which was sealed and wrapped with parafilm. XPS analysis was conducted by the Nanoscale Characterization
 15 Facility at the University of Indiana (Bloomington, IN) using a PHI VersaProbe II Scanning X-ray Microprobe system.

[00297] Computational Methods

[00298] Initial calculations were performed using M06, B3LYP and B97-D. Based on energetic minima results, B3LYP was chosen for use as the functional for subsequent
 20 calculations. Optimizations were performed in the gas phase using density functional theory (DFT) employing the B3LYP exchange correlation functional, and the 6-

311G(d,p) basis set for all atoms as implemented in the Gaussian09 suite of programs for electronic structure and ChemCraft was used for graphics visualization. All optimizations were performed under tight constraints, with no symmetry imposed. All input coordinates are available below.

5

[00299] Sample Calculations

[00300] Overpotential calculation at the potential of half catalytic current ($E_{cat/2}$);

CuL¹ HER:

$$\eta = \text{Overpotential} = |E_{BH+(OCP)} - (E_{cat/2})|$$

$$\eta = |[-0.50 - (-2.20 \text{ V})]|$$

$$\eta = 1.7 \text{ V vs } Fe^+/Fe^0$$

10

[00301] Determination of CuL¹ Diffusion Coefficient (D_0) (Acetonitrile):

$$\text{Slope} \equiv 3.22E-5 = 0.4463FA[cat][(FD_0/RT)]^{0.5}$$

15

$$A = 0.071 \text{ cm}^2$$

$$[cat] = 6E-7 \text{ moles/cm}^3$$

$$F = 96485 \text{ C/mole } e^-$$

$$R = \text{ideal gas constant}$$

$$T = 298 \text{ K}$$

20

$$D_0 = 7.9E-6 \text{ cm}^2 / \text{s in acetonitrile}$$

[00302] Determination of CuL¹ Diffusion Coefficient (D_0) (DMF):

$$\text{Slope} \equiv 3E-5 = 0.4463FA[cat][(FD_0/RT)]^{0.5}$$

$$A = 0.071 \text{ cm}^2$$

$$[cat] = 6E-7 \text{ moles/cm}^3$$

25

$$F = 96485 \text{ C/mole } e^-$$

$$R = \text{ideal gas constant}$$

$$T = 298 \text{ K}$$

$$D_0 = 9.35E-6 \text{ cm}^2 / \text{s in DMF}$$

[00303] TOF_{max} Sample Calculation for CuL¹ in acetonitrile:

Using equation B5, at scan-rate independent conditions, when $\nu = 0.2$ v/s
and when $i_{cat} = 2250 \mu\text{A}$ and $i_p = 14 \mu\text{A}$

$$\frac{i_{cat}}{i_p} = 160.71$$

$$\text{TOF}_{\max} / k_{obs} = 10000 \text{ s}^{-1}$$

5

[00304] TOF_{max} Sample Calculation for CuL¹ in Dimethylformamide:

Using equation B5, at scan rate independent conditions, when $\nu = 1.0$ v/s,
and when $i_{cat} = 1490 \mu\text{A}$ and $i_p = 29 \mu\text{A}$

$$\frac{i_{cat}}{i_p} = 51.44$$

$$\text{TOF}_{\max} / k_{obs} = 5140 \text{ s}^{-1}$$

10

[00305] Sample Calculations CuL¹ Electrolysis in Acetonitrile:

[00306] *Trial 1:* Total charge = $Q_{\text{with cat}} - Q_{\text{blank}} = Q_{\text{net}}$

$$60.49 \text{ C} - 0.0576 \text{ C} = 60.43$$

15

[00307] Theoretical Moles of Hydrogen Made via Total Charge:

$$60.43 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) =$$

moles H₂ theoretical

$$\text{Moles H}_2 \text{ theoretical} = 0.00031 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

20

[00308] *Trial 1:* CuL¹ TON Calculation:

$$\text{TON} = \text{Moles of H}_2 \text{ Produced} / \text{Moles of CuL}^1 \text{ Used}$$

$$\text{TON} = (0.00031 \text{ moles H}_2 \text{ produced}) / (0.000006 \text{ moles CuL}^1 \text{ used})$$

25

$$\text{TON} = 51.7$$

[00309] *Trial 2:* Total Charge = $Q_{\text{with cat}} - Q_{\text{blank}} = Q_{\text{net}}$

$$84.74 \text{ C} - 0.0576 \text{ C} = 84.68$$

30

[00310] Theoretical moles of Hydrogen made via Total Charge

$$84.68 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) =$$

moles H₂ theoretical

$$\text{Moles H}_2 \text{ Theoretical} = 0.00044 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

35

[00311] *Trial 2:* CuL¹ TON Calculation:

$$\text{TON} = \text{Moles of H}_2 \text{ Produced} / \text{Moles of CuL}^1 \text{ Used}$$

$$\text{TON} = (0.00044 \text{ moles of H}_2 \text{ produced}) / (0.000006 \text{ moles CuL}^1 \text{ used})$$

$$\text{TON} = 73.3$$

[00312] Sample Calculations CuL¹ Electrolysis in DMF

[00313] *Trial 1:* Total charge = $Q_{\text{with cat}} - Q_{\text{blank}} = Q_{\text{net}}$

$$67.03 \text{ C} - 0.0682 \text{ C} = 66.96 \text{ C}$$

[00314] Theoretical Moles of Hydrogen made via total Charge:

$$66.96 \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles of H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ Theoretical} = 0.00035 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

[00315] *Trial 1:* CuL¹ TON Calculation:

$$\text{TON} = \text{Moles of H}_2 \text{ Produced} / \text{Moles of CuL}^1 \text{ Used}$$

$$\text{TON} = (0.00035 \text{ moles of H}_2 \text{ produced}) / (0.000006 \text{ moles CuL}^1 \text{ used})$$

$$\text{TON} = 58.3$$

[00316] *Trial 2:* Total Charge = $Q_{\text{with cat}} - Q_{\text{blank}} = Q_{\text{net}}$

$$85.06 \text{ C} - 0.682 \text{ C} = 85 \text{ C}$$

[00317] Theoretical Moles of Hydrogen made via total Charge:

$$85 \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles of H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ Theoretical} = 0.00044 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

[00318] *Trial 2:* CuL¹ TON Calculation:

$$\text{TON} = \text{Moles of H}_2 \text{ Produced} / \text{Moles of CuL}^1 \text{ Used}$$

$$\text{TON} = (0.00044 \text{ moles of H}_2 \text{ produced}) / (0.000006 \text{ moles CuL}^1 \text{ used})$$

$$\text{TON} = 73.3$$

[00319] *Trial 2:* CuL¹ Faradaic Efficiency Calculation:

$$\begin{aligned}
 \text{Faradaic efficiency} &= (\text{moles of H}_2 \text{ quantified}) / (\text{moles of H}_2 \\
 &\text{theoretical based on charge}) \times 100\% \\
 &= (0.000356 \text{ moles}) / (0.00044 \text{ Moles}) \times 100\% \\
 &= \mathbf{81 \% \text{ Faradaic Efficiency}}
 \end{aligned}$$

5

[00320] Crystallographic Details

[00321] A light-purple plate 0.26 x 0.10 x 0.01 mm³ crystal of **[CuL¹H₂]²⁺**, grown through liquid-liquid diffusion of pentane into methanol/acetonitrile solution of 1 mM CuL¹ with four drops of perchloric acid added, was mounted on a CryoLoop for collection of x-ray data on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer. The CrysAlisPro¹ CCD software package (v 1.171.36.32) was used to acquire a total of 772 forty-five second frame ω -scan exposures of data at 100K to a 2 θ max = 57.42° using monochromated MoK α radiation (0.71073 Å) from a sealed tube.

15 Frame data were processed using CrysAlisPro¹ RED to determine final unit cell parameters: a = 8.7724(3) Å, b = 9.3218(3) Å, c = 12.1476(5) Å, α = 100.149(3), β = 107.682(3)°, γ = 97.493(3)°, V = 913.55(6) Å³, D_{calc} = 1.901 Mg/m³, Z = 2 to produce raw hkl data that were then corrected for absorption (transmission min./max. = 0.848 /1.000; μ = 1.769 mm⁻¹) using SCALE3 ABSPACK. The structure was solved by Direct

20 methods in the space group P-1 using SHELXS and refined by least squares methods on F² using SHELXL. Non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Imine H's were located by difference maps and refined isotropically. Methyl hydrogen atoms were placed in their geometrically generated positions and refined as a riding model and these atoms were assigned U(H) = 1.5 x Ueq.

25 For all 4720 unique reflections (R(int) 0.040) the final anisotropic full matrix least-

squares refinement on F^2 for 264 variables converged at $R1 = 0.044$ and $wR2 = 0.075$

with a GOF of 1.06.

Table B1: Bond lengths (Å) for $[\text{Cu}(\text{L}^1\text{H}_2)(\text{ClO}_4)]\text{ClO}_4$.

Cu(1)-N(1)	1.9579(18)	C(2)-C(4)	1.483(3)
Cu(1)-N(4)	1.9557(18)	C(3)-H(3A)	0.9600
Cu(1)-S(1)	2.2462(6)	C(3)-H(3B)	0.9600
Cu(1)-S(2)	2.2593(6)	C(3)-H(3C)	0.9600
S(1)-C(5)	1.714(2)	C(4)-H(4A)	0.9600
S(2)-C(6)	1.711(2)	C(4)-H(4B)	0.9600
N(1)-C(1)	1.282(3)	C(4)-H(4C)	0.9600
N(1)-N(2)	1.355(3)	C(7)-H(7A)	0.9600
N(2)-C(5)	1.360(3)	C(7)-H(7B)	0.9600
N(2)-H(2N)	0.78(3)	C(7)-H(7C)	0.9600
N(3)-C(5)	1.311(3)	C(8)-H(8A)	0.9600
N(3)-C(7)	1.448(3)	C(8)-H(8B)	0.9600
N(3)-H(3N)	0.76(3)	C(8)-H(8C)	0.9600
N(4)-C(2)	1.287(3)	Cl(1)-O(2)	1.4223(17)
N(4)-N(5)	1.364(2)	Cl(1)-O(4)	1.4274(18)
N(5)-C(6)	1.356(3)	Cl(1)-O(3)	1.4503(17)
N(5)-H(5N)	0.78(2)	Cl(1)-O(1)	1.4541(17)
N(6)-C(6)	1.319(3)	Cl(2)-O(8)	1.4231(19)
N(6)-C(8)	1.465(3)	Cl(2)-O(7)	1.4307(19)
N(6)-H(6N)	0.78(3)	Cl(2)-O(6)	1.430(2)
C(1)-C(3)	1.484(3)	Cl(2)-O(5)	1.4506(18)
C(1)-C(2)	1.501(3)		

5

Table B2: Bond angles (°) for $[\text{Cu}(\text{L}^1\text{H}_2)(\text{ClO}_4)]\text{ClO}_4$.

N(1)-Cu(1)-N(4)	78.80(7)	C(2)-C(4)-H(4A)	109.5
N(1)-Cu(1)-S(1)	86.88(6)	C(2)-C(4)-H(4B)	109.5
N(4)-Cu(1)-S(1)	165.50(5)	H(4A)-C(4)-H(4B)	109.5
N(1)-Cu(1)-S(2)	164.38(6)	C(2)-C(4)-H(4C)	109.5
N(4)-Cu(1)-S(2)	86.08(5)	H(4A)-C(4)-H(4C)	109.5
S(1)-Cu(1)-S(2)	108.02(2)	H(4B)-C(4)-H(4C)	109.5
C(5)-S(1)-Cu(1)	95.64(8)	N(3)-C(5)-N(2)	116.5(2)
C(6)-S(2)-Cu(1)	95.99(7)	N(3)-C(5)-S(1)	121.83(19)
C(1)-N(1)-N(2)	123.56(18)	N(2)-C(5)-S(1)	121.63(17)
C(1)-N(1)-Cu(1)	118.13(15)	N(6)-C(6)-N(5)	117.3(2)
N(2)-N(1)-Cu(1)	118.19(14)	N(6)-C(6)-S(2)	120.89(17)

N(1)-N(2)-C(5)	117.61(19)	N(5)-C(6)-S(2)	121.84(16)
N(1)-N(2)-H(2N)	121(2)	N(3)-C(7)-H(7A)	109.5
C(5)-N(2)-H(2N)	121(2)	N(3)-C(7)-H(7B)	109.5
C(5)-N(3)-C(7)	124.8(2)	H(7A)-C(7)-H(7B)	109.5
C(5)-N(3)-H(3N)	119(2)	N(3)-C(7)-H(7C)	109.5
C(7)-N(3)-H(3N)	116(2)	H(7A)-C(7)-H(7C)	109.5
C(2)-N(4)-N(5)	122.83(19)	H(7B)-C(7)-H(7C)	109.5
C(2)-N(4)-Cu(1)	118.03(15)	N(6)-C(8)-H(8A)	109.5
N(5)-N(4)-Cu(1)	119.13(14)	N(6)-C(8)-H(8B)	109.5
C(6)-N(5)-N(4)	116.86(18)	H(8A)-C(8)-H(8B)	109.5
C(6)-N(5)-H(5N)	120.5(19)	N(6)-C(8)-H(8C)	109.5
N(4)-N(5)-H(5N)	119.9(19)	H(8A)-C(8)-H(8C)	109.5
C(6)-N(6)-C(8)	123.5(2)	H(8B)-C(8)-H(8C)	109.5
C(6)-N(6)-H(6N)	117(2)	O(2)-Cl(1)-O(4)	110.85(12)
C(8)-N(6)-H(6N)	119(2)	O(2)-Cl(1)-O(3)	109.38(11)
N(1)-C(1)-C(3)	125.2(2)	O(4)-Cl(1)-O(3)	110.25(11)
N(1)-C(1)-C(2)	112.56(18)	O(2)-Cl(1)-O(1)	110.29(11)
C(3)-C(1)-C(2)	122.2(2)	O(4)-Cl(1)-O(1)	109.21(10)
N(4)-C(2)-C(4)	124.6(2)	O(3)-Cl(1)-O(1)	106.78(10)
N(4)-C(2)-C(1)	112.47(19)	O(8)-Cl(2)-O(7)	109.28(13)
C(4)-C(2)-C(1)	122.83(19)	O(8)-Cl(2)-O(6)	110.09(14)
C(1)-C(3)-H(3A)	109.5	O(7)-Cl(2)-O(6)	109.35(12)
C(1)-C(3)-H(3B)	109.5	O(8)-Cl(2)-O(5)	109.98(11)
H(3A)-C(3)-H(3B)	109.5	O(7)-Cl(2)-O(5)	109.47(12)
C(1)-C(3)-H(3C)	109.5	O(6)-Cl(2)-O(5)	108.65(11)
H(3A)-C(3)-H(3C)	109.5		
H(3B)-C(3)-H(3C)	109.5		

Table B3. Kinetic Isotope Effect: CH₃COOH vs CD₃COOD

%D-Acid	<i>i</i> _{cat} (uA)	TOF (s ⁻¹)	KIE
0.00	2250	10021.68	1
20.00	1837	6680.269	1.500192
40.00	1257	3127.852	3.204015
60.00	1045	2161.764	4.635883
80.00	910	1639.3	6.113392
100.00	819	1327.833	7.547398

Table B4: Computational Input Coordinates

<u>CuL¹</u>				
0 2				
	Cu	1.431847450	-0.488032580	0.446112510
5	S	2.332615610	-0.119942340	2.552696700
	S	2.858402730	-1.722415690	-0.909505780
	N	-0.257435500	0.971116720	2.468152050
	N	-0.172027540	0.534274340	1.177021620
	N	0.574079220	-1.034389140	-2.391256330
10	N	0.223704470	-0.461096440	-1.204115870
	C	0.866804360	0.696900310	3.160702940
	C	-1.156654600	0.726779040	0.313291070
	C	1.780157800	-1.630949380	-2.329823970
	C	-0.928456430	0.172470660	-1.041194200
15	C	-2.430852170	1.445672040	0.707410510
	C	-1.949721220	0.325466600	-2.151313540
	N	0.905903760	1.099112750	4.470338340
	N	2.249331710	-2.229486700	-3.469048500
	C	1.542073250	-2.300940750	-4.757663730
20	C	-0.256906930	1.621968390	5.210058210
	H	-0.736089590	2.427871470	4.633939270
	H	0.095862870	2.020878310	6.174487110
	H	-1.009760380	0.833110030	5.396764760
	H	-3.052880760	1.693994160	-0.164430810
25	H	-2.187359810	2.369822740	1.257044200
	H	-3.027972700	0.817502200	1.394048690
	H	2.232241150	-2.034661770	-5.577035900
	H	0.709065320	-1.588742850	-4.742827890
	H	1.143750430	-3.316026930	-4.940576080
30	H	-1.595749020	-0.186808630	-3.055724620
	H	-2.117801900	1.390722990	-2.392856600
	H	-2.924379830	-0.103170090	-1.856998090
	H	1.714229460	0.779113230	5.003296850
	H	3.143979070	-2.710111620	-3.380991940

35

[CuL¹H]⁺

1 2

	Cu	1.431847450	-0.488032580	0.446112510
	S	2.332615610	-0.119942340	2.552696700

	S	2.858402730	-1.722415690	-0.909505780
	N	-0.257435500	0.971116720	2.468152050
	N	-0.172027540	0.534274340	1.177021620
	N	0.574079220	-1.034389140	-2.391256330
5	N	0.223704470	-0.461096440	-1.204115870
	C	0.866804360	0.696900310	3.160702940
	C	-1.156654600	0.726779040	0.313291070
	C	1.780157800	-1.630949380	-2.329823970
	C	-0.928456430	0.172470660	-1.041194200
10	C	-2.430852170	1.445672040	0.707410510
	C	-1.949721220	0.325466600	-2.151313540
	N	0.905903760	1.099112750	4.470338340
	N	2.249331710	-2.229486700	-3.469048500
	C	1.542073250	-2.300940750	-4.757663730
15	C	-0.256906930	1.621968390	5.210058210
	H	-0.736089590	2.427871470	4.633939270
	H	0.095862870	2.020878310	6.174487110
	H	-1.009760380	0.833110030	5.396764760
	H	-3.052880760	1.693994160	-0.164430810
20	H	-2.187359810	2.369822740	1.257044200
	H	-3.027972700	0.817502200	1.394048690
	H	2.232241150	-2.034661770	-5.577035900
	H	0.709065320	-1.588742850	-4.742827890
	H	1.143750430	-3.316026930	-4.940576080
25	H	-1.595749020	-0.186808630	-3.055724620
	H	-2.117801900	1.390722990	-2.392856600
	H	-2.924379830	-0.103170090	-1.856998090
	H	1.714229460	0.779113230	5.003296850
	H	3.143979070	-2.710111620	-3.380991940
30	H	0.002279216	-1.014134076	-3.211399298

CuL¹H

0 1

	Cu	1.431847450	-0.488032580	0.446112510
35	S	2.332615610	-0.119942340	2.552696700
	S	2.858402730	-1.722415690	-0.909505780
	N	-0.257435500	0.971116720	2.468152050
	N	-0.172027540	0.534274340	1.177021620
	N	0.574079220	-1.034389140	-2.391256330

	N	0.223704470	-0.461096440	-1.204115870
	C	0.866804360	0.696900310	3.160702940
	C	-1.156654600	0.726779040	0.313291070
	C	1.780157800	-1.630949380	-2.329823970
5	C	-0.928456430	0.172470660	-1.041194200
	C	-2.430852170	1.445672040	0.707410510
	C	-1.949721220	0.325466600	-2.151313540
	N	0.905903760	1.099112750	4.470338340
	N	2.249331710	-2.229486700	-3.469048500
10	C	1.542073250	-2.300940750	-4.757663730
	C	-0.256906930	1.621968390	5.210058210
	H	-0.736089590	2.427871470	4.633939270
	H	0.095862870	2.020878310	6.174487110
	H	-1.009760380	0.833110030	5.396764760
15	H	-3.052880760	1.693994160	-0.164430810
	H	-2.187359810	2.369822740	1.257044200
	H	-3.027972700	0.817502200	1.394048690
	H	2.232241150	-2.034661770	-5.577035900
	H	0.709065320	-1.588742850	-4.742827890
20	H	1.143750430	-3.316026930	-4.940576080
	H	-1.595749020	-0.186808630	-3.055724620
	H	-2.117801900	1.390722990	-2.392856600
	H	-2.924379830	-0.103170090	-1.856998090
	H	1.714229460	0.779113230	5.003296850
25	H	3.143979070	-2.710111620	-3.380991940
	H	0.002279216	-1.014134076	-3.211399298
<u>CuL¹H (Triplet)</u>				
0 3				
	Cu	1.431847450	-0.488032580	0.446112510
30	S	2.332615610	-0.119942340	2.552696700
	S	2.858402730	-1.722415690	-0.909505780
	N	-0.257435500	0.971116720	2.468152050
	N	-0.172027540	0.534274340	1.177021620
	N	0.574079220	-1.034389140	-2.391256330
35	N	0.223704470	-0.461096440	-1.204115870
	C	0.866804360	0.696900310	3.160702940
	C	-1.156654600	0.726779040	0.313291070
	C	1.780157800	-1.630949380	-2.329823970
	C	-0.928456430	0.172470660	-1.041194200

	C	-2.430852170	1.445672040	0.707410510
	C	-1.949721220	0.325466600	-2.151313540
	N	0.905903760	1.099112750	4.470338340
	N	2.249331710	-2.229486700	-3.469048500
5	C	1.542073250	-2.300940750	-4.757663730
	C	-0.256906930	1.621968390	5.210058210
	H	-0.736089590	2.427871470	4.633939270
	H	0.095862870	2.020878310	6.174487110
	H	-1.009760380	0.833110030	5.396764760
10	H	-3.052880760	1.693994160	-0.164430810
	H	-2.187359810	2.369822740	1.257044200
	H	-3.027972700	0.817502200	1.394048690
	H	2.232241150	-2.034661770	-5.577035900
	H	0.709065320	-1.588742850	-4.742827890
15	H	1.143750430	-3.316026930	-4.940576080
	H	-1.595749020	-0.186808630	-3.055724620
	H	-2.117801900	1.390722990	-2.392856600
	H	-2.924379830	-0.103170090	-1.856998090
	H	1.714229460	0.779113230	5.003296850
20	H	3.143979070	-2.710111620	-3.380991940
	H	0.002279216	-1.014134076	-3.211399298
<u>[CuL¹H₂]⁺</u>				
1 1				
	Cu	1.201842280	-0.715405322	0.506889342
25	S	2.102610440	-0.347315082	2.613473532
	S	2.628397560	-1.949788432	-0.848728948
	N	-0.487440670	0.743743978	2.528928882
	N	-0.402032710	0.306901598	1.237798452
	N	0.344074050	-1.261761882	-2.330479498
30	N	-0.006300700	-0.688469182	-1.143339038
	C	0.636799190	0.469527568	3.221479772
	C	-1.386659770	0.499406298	0.374067902
	C	1.550152630	-1.858322122	-2.269047138
	C	-1.158461600	-0.054902082	-0.980417368
35	C	-2.660857340	1.218299298	0.768187342
	C	-2.179726390	0.098093858	-2.090536708
	N	0.675898590	0.871740008	4.531115172
	N	2.019326540	-2.456859442	-3.408271668
	C	1.312068080	-2.528313492	-4.696886898

	C	-0.486912100	1.394595648	5.270835042
	H	-0.966094760	2.200498728	4.694716102
	H	-0.134142300	1.793505568	6.235263942
	H	-1.239765550	0.605737288	5.457541592
5	H	-3.282885930	1.466621418	-0.103653978
	H	-2.417364980	2.142449998	1.317821032
	H	-3.257977870	0.590129458	1.454825522
	H	2.002235980	-2.262034512	-5.516259068
	H	0.479060150	-1.816115592	-4.682051058
10	H	0.913745260	-3.543399672	-4.879799248
	H	-1.825754190	-0.414181372	-2.994947788
	H	-2.347807070	1.163350248	-2.332079768
	H	-3.154385000	-0.330542832	-1.796221258
	H	1.484224290	0.551740488	5.064073682
15	H	2.913973900	-2.937484362	-3.320215108
	H	-0.227725954	-1.241506818	-3.150622466
	H	-1.284747732	1.209226221	2.913152425
<u>CuL·¹H₂-N1H</u>				
0 2				
20	Cu	1.201842280	-0.715405322	0.506889342
	S	2.102610440	-0.347315082	2.613473532
	S	2.628397560	-1.949788432	-0.848728948
	N	-0.487440670	0.743743978	2.528928882
	N	-0.402032710	0.306901598	1.237798452
25	N	0.344074050	-1.261761882	-2.330479498
	N	-0.006300700	-0.688469182	-1.143339038
	C	0.636799190	0.469527568	3.221479772
	C	-1.386659770	0.499406298	0.374067902
	C	1.550152630	-1.858322122	-2.269047138
30	C	-1.158461600	-0.054902082	-0.980417368
	C	-2.660857340	1.218299298	0.768187342
	C	-2.179726390	0.098093858	-2.090536708
	N	0.675898590	0.871740008	4.531115172
	N	2.019326540	-2.456859442	-3.408271668
35	C	1.312068080	-2.528313492	-4.696886898
	C	-0.486912100	1.394595648	5.270835042
	H	-0.966094760	2.200498728	4.694716102
	H	-0.134142300	1.793505568	6.235263942
	H	-1.239765550	0.605737288	5.457541592

	H	-3.282885930	1.466621418	-0.103653978
	H	-2.417364980	2.142449998	1.317821032
	H	-3.257977870	0.590129458	1.454825522
	H	2.002235980	-2.262034512	-5.516259068
5	H	0.479060150	-1.816115592	-4.682051058
	H	0.913745260	-3.543399672	-4.879799248
	H	-1.825754190	-0.414181372	-2.994947788
	H	-2.347807070	1.163350248	-2.332079768
	H	-3.154385000	-0.330542832	-1.796221258
10	H	1.484224290	0.551740488	5.064073682
	H	2.913973900	-2.937484362	-3.320215108
	H	-0.227725954	-1.241506818	-3.150622466
	H	-1.284747732	1.209226221	2.913152425
	<u>CuL·¹H₂-N₄H</u>			
15	0 2			
	Cu	1.431847450	-0.488032580	0.446112510
	S	2.332615610	-0.119942340	2.552696700
	S	2.858402730	-1.722415690	-0.909505780
	N	-0.257435500	0.971116720	2.468152050
20	N	-0.172027540	0.534274340	1.177021620
	N	0.574079220	-1.034389140	-2.391256330
	N	0.223704470	-0.461096440	-1.204115870
	C	0.866804360	0.696900310	3.160702940
	C	-1.156654600	0.726779040	0.313291070
25	C	1.780157800	-1.630949380	-2.329823970
	C	-0.928456430	0.172470660	-1.041194200
	C	-2.430852170	1.445672040	0.707410510
	C	-1.949721220	0.325466600	-2.151313540
	N	0.905903760	1.099112750	4.470338340
30	N	2.249331710	-2.229486700	-3.469048500
	C	1.542073250	-2.300940750	-4.757663730
	C	-0.256906930	1.621968390	5.210058210
	H	-0.736089590	2.427871470	4.633939270
	H	0.095862870	2.020878310	6.174487110
35	H	-1.009760380	0.833110030	5.396764760
	H	-3.052880760	1.693994160	-0.164430810
	H	-2.187359810	2.369822740	1.257044200
	H	-3.027972700	0.817502200	1.394048690
	H	2.232241150	-2.034661770	-5.577035900

	H	0.709065320	-1.588742850	-4.742827890
	H	1.143750430	-3.316026930	-4.940576080
	H	-1.595749020	-0.186808630	-3.055724620
	H	-2.117801900	1.390722990	-2.392856600
5	H	-2.924379830	-0.103170090	-1.856998090
	H	1.714229460	0.779113230	5.003296850
	H	3.143979070	-2.710111620	-3.380991940
	H	0.002279216	-1.014134076	-3.211399298
	H	-0.537578235	-0.345922291	-1.882139314

10

Results and Discussion for Example B

[00322] Synthesis and Electrochemical Characterization

[00323] The CuL^I compound was isolated as an air-stable burgundy solid from

15 H₂L^I and copper(II) acetate as previously reported previously (Betts et al., *Angew. Chem. Int. Ed.* 2008, Vol. 44, pp. 8416-8419 - DOI: 10.1002/anie.200801936; Christlieb et al., *Dalton Trans.* 2007, pp. 5043-5054 – DOI: 10.1039/B705087A). The cyclic voltammogram (CV) of CuL^I in acetonitrile (ACN) or dimethylformamide (DMF) containing 0.1 M Bu₄NPF₆ as supporting electrolyte displays a reversible Cu^{III/I} event at -

20 1.20 V vs. ferrocenium/ferrocene (Fc⁺/Fc) consistent with prior reports. Additional CV data collected at multiple scan rates from 0.1 to 1.0 V/s in ACN (Figure 24) and DMF (data not shown) were used to construct Cottrell plots (Figure 24 inset) establishing that the Cu^{III/I} reduction is diffusion limited and demonstrating the potential of CuL^I as a

25 homogeneous electrocatalyst. The slope of the plot yields a diffusion coefficient of 7.9×10^{-6} cm²/s in ACN and 9.35×10^{-6} cm²/s in DMF. The formal Cu^{III/II} couple was observed at 0.24 V vs Fc⁺/Fc in DMF and ACN in line with prior reports, but this event was not further evaluated in the current study.

[00324] Homogeneous Catalytic Hydrogen Evolution: Cyclic Voltammetry and KIE

[00325] Addition of acetic acid exceeding 24 mM to 0.6 mM ACN solutions of CuL¹ shifts the Cu^{III} reduction potential from -1.20 V to -0.95 V and introduces a catalytic cathodic current at -1.70 V vs Fc⁺/Fc (Figure 25A). The +0.25 V shift is consistent with a single protonation event prior to the initial electrochemical reduction. The ratio of the catalytic current to the peak current displays linear dependence on the acid concentration up to 0.157 M, indicating a second-order dependence of the catalytic rate on the acid concentration. At concentrations greater than 0.157 M the current response begins to plateau, reaching an acid independent region at concentrations of 0.269 M, (Figure 25B). This transition from second-order to zero-order dependence requires a pre-equilibrium step(s) involving two protons that precedes the rate determining step for H₂ elimination. The current becomes scan rate independent at 0.2 V/s. Under these conditions the i_p of the Cu^{III} reduction event, 14.0 μ A, and the i_{cat} max from the acid-independent region, 2.25 mA, correspond with a maximum i_{cat}/i_p value of 161, affording a TOF of 10,000 s⁻¹.

[00326] The electrocatalytic activity of 0.6 mM CuL¹ with acetic acid was also assessed in DMF. An increase in current at -1.9 V vs Fc⁺/Fc is observed upon increasing additions of acetic acid (Figure 26A). At concentrations of acid greater than 0.292 M, the current saturates reaching a maximum i_{cat} of 1.49 mA (Figure 26B). Acid addition results in a shift of the Cu^{III} potential from -1.20 V to -0.95 V, as observed in ACN, attributed to a single protonation event prior to reduction. Catalytic current becomes independent of

scan rate above 1.0 V/s (Figure 26C and 26D). Under these conditions i_{cat} is 1490 μA and i_p is 29 μA giving a TOF of 5140 s^{-1} , which is significantly lower than the TOF in ACN.

[00327] The Tafel plot of the log TOF versus overpotential for CuL^1 (Figure 25C) displays the TOF as a function of the applied overpotential. CuL^1 displays the highest

5 maximum logTOF values reported to date of any homogeneous ligand-centered electrocatalyst, reaching a maximum of 3.99. The CuL^1 electrocatalyst maintains a logTOF value greater than one, with applied overpotentials greater than 1.2 V.

Overpotentials less than 1.2 V result in significantly decreased TOF values, correlating with negative or near zero logTOF values. The local maxima observed near 0.4 V is

10 indicative of the pre-catalytic $\text{Cu}^{\text{III/I}}$ reduction, which has anodic shift of 0.25 V during catalysis. The maximum logTOF for CuL^1 of 3.99 requires a large overpotential of 2.0 V.

[00328] Analysis of the CVs of CuL^1 under catalytic HER conditions appear to reveal a new oxidation event at a potential of -0.65 V Fc^+/Fc during the return anodic scan (Figure 25A inset), which is assigned to the Cu(II/I) couple of the diprotonated copper(I) intermediate, $[\text{CuL}^1\text{H}_2]^+$. This event is 300 mV more positive than the Cu(II/I) couple of the monoprotonated $[\text{CuL}^1\text{H}]^+$, which in turn is 250 mV more positive than the CuL^1 . The intensity of the peak current at -0.65 V demonstrates scan rate dependence typical of diffusion controlled behavior (Figure 26C) confirming it is not due to an adsorbed species.

20 [00329] As noted above, the catalysis is second-order in acid in the acid dependent regime. To determine the order with respect to the catalyst, the concentration of CuL^1 was varied from 0.1 to 1.0 mM in solution containing 0.15 M acetic acid. A plot of

catalyst concentration versus peak current reveals a linear relationship, confirming a first-order dependence on the concentration of the catalyst and an overall third-order process.

[00330] To further evaluate the HER mechanism of CuL^1 , the H/D kinetic isotope effect (KIE) was measured. CuL^1 displays a large KIE of 7.54 using 100 % $\text{CD}_3\text{CO}_2\text{D}$.

5 The high KIE value observed when using 100% $\text{CD}_3\text{CO}_2\text{D}$ is distinct from the inverse KIEs reported for some HER catalysts proceeding through metal-hydrides, but similar to that observed for a ligand-centered Re-thiolate HER catalyst. Since CuL^1 HER catalysis is second-order in $[\text{H}^+]$, a proton inventory study was conducted to determine the number of protons involved in the rate determining step. Cyclic voltammograms collected with
10 variable quantities of $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CD}_3\text{CO}_2\text{D}$ were used to generate plots of KIE versus the percent fraction of $\text{CD}_3\text{CO}_2\text{D}$ (Figures 27A & 27B). The plot yields a linear fit consistent with the involvement of a single proton in the rate determining step.

[00331] Controlled Potential Electrolysis

[00332] A series of controlled potential electrolysis (CPE) experiments were

15 performed using 0.6 mM CuL^1 and 0.292 M acetic acid, with potential held at -1.65 V vs Fc^+/Fc , in both DMF and ACN (Table B5). Electrolysis in 0.1 M Bu_4NPF_6 DMF solutions was allowed to run for 84,400 seconds (23.4 hours) resulting in a total charge passed of 85.0 C, corresponding to 4.4×10^{-4} moles of H_2 produced with a turnover number (TON) of 73.3. Gas analysis of the headspace using gas chromatography thermal
20 conductivity (GC-TCD) confirms H_2 as the gaseous product (Figure 41). The charge increases linearly over time with no signs of degradation or decrease in activity over 23 hours (Figure 28). A second CPE in DMF over 72,120 seconds (20 hours) yielded

comparable results giving a slightly lower charge of 67.0 C, producing 3.5×10^{-4} moles of H_2 corresponding with a TON of 58.3.

Table B5. Summary of CPE Results

<i>Entry</i>	<i>Solvent</i>	<i>Duration (S^{-1})</i>	<i>Charge (C)</i>	<i>Moles of H_2 Produced ($\times 10^{-4}$)</i>	<i>TON</i>
1	ACN	15,000	60.4	3.1	52
2	ACN	13,000	84.7	4.4	73
3	DMF	84,400	67.0	3.5	58
4	DMF	72,120	85.0	4.4	73

5 [00333] The CPEs performed in 0.1 M Bu_4NPF_6 ACN passed similar charge, giving values of 60.4 and 84.7 C corresponding to TON values of 51.7 and 73.3, over shorter electrolysis times of 15,000 and 13,000 seconds, respectively (Figure 28). The current in ACN is higher than in DMF, resulting in a steeper slope in the charge-time plots, consistent with relative TOFs from CV studies. Electrolysis beyond 15,000 seconds
10 in ACN is complicated by diffusion across the frit from the working to auxiliary compartment. This results in the appearance of a brown, cloudy mixture in the auxiliary compartment concurrent with the plateauing of charge. This phenomenon was consistently observed in ACN, but was absent in DMF.

[00334] Control Experiments

15 [00335] A series of control experiments were performed to confirm CuL^1 as the electrocatalyst. First, CVs were recorded on ACN and DMF solutions containing only acetic acid. Addition of 67.2 mM acetic acid to 0.1 M Bu_4NPF_6 ACN solutions resulted

in an observable current of 300 μA (Figure 29A). However, after 2 CV cycles the current drops to a stable value near 100 μA . Upon addition of 0.6 mM CuL^1 , the current increases to 900 μA (Figure 29A). In DMF addition of 22.4 mM acetic acid results in a modest current increase of ~ 5 μA (Figure 29B). Addition of 0.6 mM CuL^1 to this solution
5 resulted in an increase in current, giving a value of 200 μA (Figure 29B). At more cathodic potentials, a substantial change in the CVs of CuL^1 with 22.4 mM acetic acid added is observed with current increase onset potentials near -1.7 V vs Fc^+/Fc (Figure 29B). These control experiments identify CuL^1 as the source of the catalytic activity, but do not exclude the possibility that it may be the precursor to an adsorbed catalyst.

10 [00336] To probe for adsorption of the CuL^1 on the electrode surface *prior* to catalysis, a “soak test” was performed using the methods of Dempsey and co-workers (Lee et al., *Inorg. Chem.* 2017, Vol. 56, pp. 1988-1998 - DOI: 10.1021/acs.inorgchem.6b02586). The working electrode was immersed overnight in a 0.1 M Bu_4NPF_6 ACN solution containing 0.6 mM CuL^1 and 0.292 M acetic acid. It was
15 then removed, washed with DI water, and placed into a fresh solution of 0.1 M Bu_4NPF_6 ACN, with no added acid or catalyst. The resulting CV displayed no redox events indicating no detectable adsorption of CuL^1 derived species under these conditions.

[00337] A second series of controls were performed to evaluate if a catalytically active adsorbed species forms during CV catalysis. These *post-CV* “dip-tests” were
20 conducted after 10 cycles and 50 cycles (See Figures 62 and 63). During the 50 cycles from -0.5 to -2.3 V vs. Fc^+/Fc on 0.6 mM CuL^1 solutions under acid saturated conditions the current reaches a maximum value of ~ 1.5 mA. The working electrode was removed, washed with DI water, and immersed into a fresh solution of 0.1 M Bu_4NPF_6 ACN or

DMF. The resulting CVs showed no significant Faradaic current in the window from -0.5 to -2.3 V. Upon addition of 0.292 M acetic acid, a catalytic current of 1 mA was observed at -1.7 V. After we extended the scan window to include 0.4 V, the catalytic current at -1.7 V is absent. This confirms that at least some of the HER catalysis results from adsorbed CuL^1 species.

[00338] To probe if all of the catalytic activity results from adsorbed catalysts, we repeated the *post-CV* “dip-test” after 10 cycles from -0.5 to -2.5 V vs. Fc^+/Fc on 0.6 mM CuL^1 solutions under acid saturated conditions, again reaching maximum current values of ~ 1.5 mA. The working electrode was removed, washed with DI water, and immersed into a fresh solution of 0.1 M Bu_4NPF_6 DMF. As before, the resulting CVs showed no observable Faradaic current in the window from -0.5 to -2.5 V. CVs following addition of 0.292 M acetic acid that also showed only 400 μA of current -1.7 V. While these results indicate that surface adsorbed CuL^1 is responsible for some of the catalytic current after as few as 10 cycles, they show that the majority of HER activity under homogeneous conditions is due to dissolved CuL^1 complex.

[00339] In addition, a *post-electrolysis* “dip-test” was performed following CPE studies of CuL^1 catalyzed HER. Under these conditions, a substantial amount of surface adsorbed CuL^1 derived complex is expected. After both CPEs in DMF and ACN, the working electrode was removed, washed with DI water, and immersed into a fresh 0.1 M Bu_4NPF_6 DMF/ACN solution. The CV was collected. In contrast to the *post-CV* “dip-tests”, the electrode displays three reduction events at -0.9 V, -1.4 V and -2.1 V vs Fc^+/Fc . The first two events are near the observed Cu(II/I) reductions potentials of $[\text{CuL}^1\text{H}]^+$ and CuL^1 , respectively. The most cathodic event is near the reduction potential

of H_2L^1 . Upon addition of 0.292 M acetic acid to the solution, current increases and catalysis is observed (Figure 30).

[00340] Analysis of the films following electrolysis in DMF and ACN by x-ray photoelectron spectroscopy revealed atomic percentages consistent with CuL^1 , Figure 31.

5 The results are inconsistent with the formation of nanoparticles consisting of metallic Cu, copper oxides, or copper sulfides. The data from the two solvents are indistinguishable. High resolution XPS (see above and Figure 61) confirms the presence of Cu ions and is inconsistent with metallic Cu.

[00341] Protonated Derivatives of CuL^1

10 [00342] A series of protonated derivatives of CuL^1 were evaluated as potential catalytically relevant intermediates. These include the mono- and di-protonated Cu(II) complexes $[\text{CuLH}]^+$ and $[\text{CuLH}_2]^{2+}$ and the Cu(I) analogue CuLH .

[00343] To confirm that $[\text{CuLH}]^+$ is present in solution under catalytic conditions, acid titrations were monitored by UV-visible spectroscopy. The spectrum of 0.6 mM CuL^1 in deoxygenated DMF shows absorbance bands at 310, 375, 475 and 520 nm. The solution was titrated with acetic acid, increasing in concentration from 0.022 M to 0.382 M (Figure 32). The absorbance bands of CuL^1 decrease in intensity, concurrent with increases at 405 and 460 nm consistent with the formation of $[\text{CuL}^1\text{H}]^+$. The proposed protonation site is the hydrazino N, in line with previous reports and density functional theory computations (*vide infra*).

20 [00344] To characterize the monoprotated Cu(I) species, CuL^1H , CuL^1 was first reduced and then protonated. In an Ar filled glove box, CuL^1 was dissolved in DMSO-d_6 . Upon addition of one equivalent of cobaltocene, the solution changed color from red to

light purple. The solution was stirred for 15 minutes to obtain the reduced anionic copper complex, $[\text{CuL}^1]^-$. An aliquot was added to an NMR tube for analysis. The ^1H NMR spectrum of $[\text{CuL}^1]^-$ displays the expected peaks. Chemical shifts at 2.73, 2.89, and 7.95 ppm are assigned to the methyl backbone CH_3 , $\text{NH}(\text{CH}_3)$, and $\text{NH}(\text{CH}_3)$, respectively, and integrate with a ratio of 3:3:1 (Figure 55). Addition of one equivalent of HBF_4 to the $[\text{CuL}^1]^-$ solution results in a color change from light purple to orange. An aliquot was taken and analyzed by ^1H NMR. Each of the peaks observed in $[\text{CuL}^1]^-$ are still present, along with a new peak at 8.27 ppm, which integrates to 1 (Figure 56). The new peak is assigned to the protonation of the hydrazino nitrogen. The chemical shift is inconsistent with metal-centered protonation, which would result in a copper hydride with a negative chemical shift.

[00345] Our CH_3COOH titration studies of diprotonated Cu(II) complex $[\text{CuL}^1\text{H}_2]^{2+}$ show no evidence of a second protonation event under catalytic conditions. Although $[\text{CuL}^1\text{H}_2]^{2+}$ is not catalytically relevant, x-ray quality crystals of $[\text{CuL}^1\text{H}_2]^{2+}$ were obtained from perchloric acid solution. The ORTEP representation shows protonation of both hydrazino nitrogens, axial coordination of one perchlorate, and axial association of the second perchlorate, Figure 33. A complete description of the crystallographic details is provided above.

[00346] Proposed Homogeneous HER Mechanism

[00347] A proposed CECE mechanism for homogenous HER catalyzed by CuL^1 is shown in Figure 34. Step 1 is an initial chemical (C) event involving protonation of the hydrazino nitrogen on CuL^1 to yield $[\text{CuL}^1\text{H}]^+$. This is followed by an electrochemical step (E) assigned as a metal-centered reduction giving the neutral Cu(I) species, CuL^1H .

Step 3 is a chemical step involving protonation on the other hydrazino nitrogen, affording the Cu(I) cation, $[\text{CuL}^1\text{H}_2]^+$. Step 4 is the final electrochemical step, a proposed ligand-centered reduction to give the neutral species, CuL^1H_2 . The CuL^1H_2 complex can be regarded as Cu(I) coordinated by a nitrogen-centered radical. Step 5 shows double bond rearrangement, resulting in an anionic coordinated nitrogen. This anionic nitrogen induces an internal proton transfer, a tautomerism that has been observed in many thiosemicarbazone complexes, leading to formation of the H_2 evolving complex. Finally, in step 6, hydrogen is evolved through hydrogen atom or proton/hydride coupling at the adjacent N-H bonds.

[00348] The proposed mechanism is consistent with the experimentally determined rate law and the KIE study. Both protons are added to a single CuL^1 complex prior to the rate determining step (r.d.s.) consistent with the first-order catalyst and second-order proton dependence on current. The proton inventory study suggests that a single proton is involved in the r.d.s. This favors tautomerization, step 5, over hydrogen evolution, step 6, as the rate limiting event. The solvent dependency of the TOF further supports this interpretation. The TOF in DMF is approximately one-half that in ACN. This is attributed to H-bonding interactions between DMF and ligand N-H groups. These stabilizing interactions retard the rate limiting tautomerization step in DMF relative to ACN. To assess the viability of this mechanism, density functional theory computations on all proposed species were performed.

[00349] Density Functional Theory Investigations

[00350] All proposed complexes in Figure 34 were assessed using density functional theory (DFT) using the B3LYP hybrid functional and the 6-311g(d,p) basis

set. First, we evaluated the protonation event associated with step 1. Calculations on the singly protonated intermediate, $[\text{CuL}^1\text{H}]^+$, support our assignment of the hydrazino nitrogen as the site of protonation. For $[\text{CuL}^1\text{H}]^+$ ($S = 1/2$), the Cu, S, N3 (hydrazino), N4 (coordinated), and N6 (pendant amine) were evaluated as possible protonation sites. In each structure, the geometry and frequencies were optimized and the energies minimized. The hydrazino protonated geometry is energetically preferred, lying 10 kcal/mole lower than the metal-hydride (Figure 35A). Protonation at S is less favored by 12 kcal/mole and attempts to optimize structures with protonation on N4 and N6 resulted in migration of the hydrogen onto the hydrazino nitrogen.

[00351] Next, the one-electron reduced protonated species, CuL^1H ($S = 0$) (Figure 35B), was examined to determine if reduction, step 2, impacts the location of the proton. Computed free energies for structures with protonation at Cu, S, and each N, clearly indicate that protonation on the hydrazino N is still favored. Protonation at S is disfavored by 11 kcal/mole, while protonation at the pendant amine is less favored by 18 kcal/mole. Attempts to optimize CuL^1H with protonation at the coordinated nitrogen again resulted in migration of hydrogen onto the hydrazino nitrogen. We also considered CuL^1H with protonation on the hydrazino nitrogen in its triplet electronic configuration ($S = 1$). However, it is 5.77 kcal/mole higher in energy (see Figure 59), confirming the nature of the first reduction as metal based.

[00352] Step 3 of the proposed mechanism involves addition of a second proton to CuL^1H . Energy minimizations of the doubly protonated, singly reduced intermediate, $[\text{CuL}^1\text{H}_2]^+$ in both the singlet ($S = 0$) and triplet ($S = 1$) electronic states were performed. For each spin state, the copper, the opposing hydrazino nitrogen (N1), sulfur (S2), the

pendant amine (N6) and the coordinated nitrogen (N4) were all considered as the second protonation site. In both electronic states, protonation on the opposing hydrazino nitrogen (N1) is favored over all other protonation sites by at least 8 kcal/mole. Comparison of the singlet and triplet state the energies for protonation on N4 indicate the singlet is more
5 stable by 6.09 kcal/mole (Figure 36).

[00353] The addition of the second electron, step 4, leads to formation of the hydrogen evolving complex CuL^1H_2 through proposed rearrangement, step 5. The geometry and frequencies of CuL^1H_2 were optimized with one proton located on N3 while considering multiple sites for the second proton including the copper, the opposing
10 hydrazino nitrogen (N1), sulfur (S2) the pendant amine (N6) and the coordinated nitrogen (N4). Energy minimizations indicate that placement of the second proton on N1 or N4 nitrogen are most favored, by at least 17 kcal/mole, compared to all other sites (Figure 37A). Notably, energies for protonation at N1 and N4 differ by only 0.39 kcal/mole, indicating that the tautomerization associated with step 5 in the proposed mechanism is
15 viable. Further, examination of the spin-density (SD) shows that the second reduction is primarily ligand based, with 34% on N2, 38% on C4, 14% on N1, 8% on N5, and only 3% on Cu (Figure 37B).

[00354] Discussion

20 [00355] The complexes cited herein present intriguing reactivity as the ligand can participate in electron transfer events, either with or without a transition metal—rendering it “*non-innocent*” in some instances. Additionally, the ligands can be protonated generating various tautomeric forms—rendering it not only non-innocent, but

also “*promiscuous*” in some instances. The combination of these two factors can be dependent on the identity of the metal ion, and, in some instances, can result in three types of HER reactivity: a) ligand-assisted metal reactivity with Ni, b) ligand-centered reactivity with Zn, and c) metal-assisted ligand reactivity with Cu.

5 [00356] In some examples, the impact of the metal is manifested in the initial protonation and initial reduction sites. For both CuL^1 and ZnL^1 , a hydrazino N is protonated prior to the initial reduction. The initial site of reduction can be rationalized based on the relative energies of the metal d-orbitals and an unoccupied ligand centered orbital, Figure 38. The metal d-orbital energies decrease from Ni^{2+} to Cu^{2+} to Zn^{2+} with
10 increasing effective nuclear charge. For Ni^{2+} , a vacant ligand centered orbital lies below the vacant metal d_{z^2} orbital yielding a ligand-centered radical upon reduction. For Cu^{2+} , the stabilized d -orbital manifold falls below the ligand-centered orbital resulting in metal-centered reduction. For Zn^{2+} , the d -orbitals are filled required ligand-centered reduction. Additionally, the site of reduction and the localization of spin-density can impact the site
15 of protonation. For Cu, the proton remains on the hydrazino nitrogen after metal-centered reduction. In contrast, for Ni the ligand-centered reduction favors double bond rearrangement similar to step 5 in Figure 34. As a result, the tautomers with protonation of the hydrazino N and anionic coordinated N have similar energies. For Zn, the tautomer with the proton remaining on the hydrazino N remains favored after ligand-centered
20 reduction.

[00357] In some embodiments, the mechanism for H_2 evolution is a consequence of the initial protonation and reduction sites. For Ni, some has posited that the second reduction is metal-based, generating a nucleophilic d^9 Ni(I) center. Further protonation is

proposed to occur at the metal generating a Ni^{III} -hydride as the catalytically active species for H_2 evolution. In this context, NiL^2 can demonstrate ligand-assisted metal reactivity, in which the ligand serves as an auxiliary redox site to facilitate two-electron chemistry at the metal. This can be a common role for redox active ligands in transition metal catalysis. In contrast, the HER chemistry of ZnL^1 can be ligand-centered. Its HER mechanism can localize all chemical and electrochemical steps on the ligand, with the metal providing structural support. As in the case of NiL^2 , initial protonation and reduction is ligand-centered, however, the d^{10} Zn(II) , in some instances, is incapable of undergoing a second reduction and HER proceeds via a bimolecular process.

[00358] The HER chemistry of CuL^1 displays a less common type of mechanism with redox non-innocent ligands, which we defined as metal-assisted ligand-centered reactivity. The initial metal-centered reduction leads to a d^{10} Cu(I) , which is isoelectronic with ZnL^1 . As such, it can accommodate subsequent ligand-based protonation and reduction events with evolution of H_2 from the ligand-center. In this context, the metal serves as the auxiliary redox site, which can facilitate two-electron chemistry at the ligand.

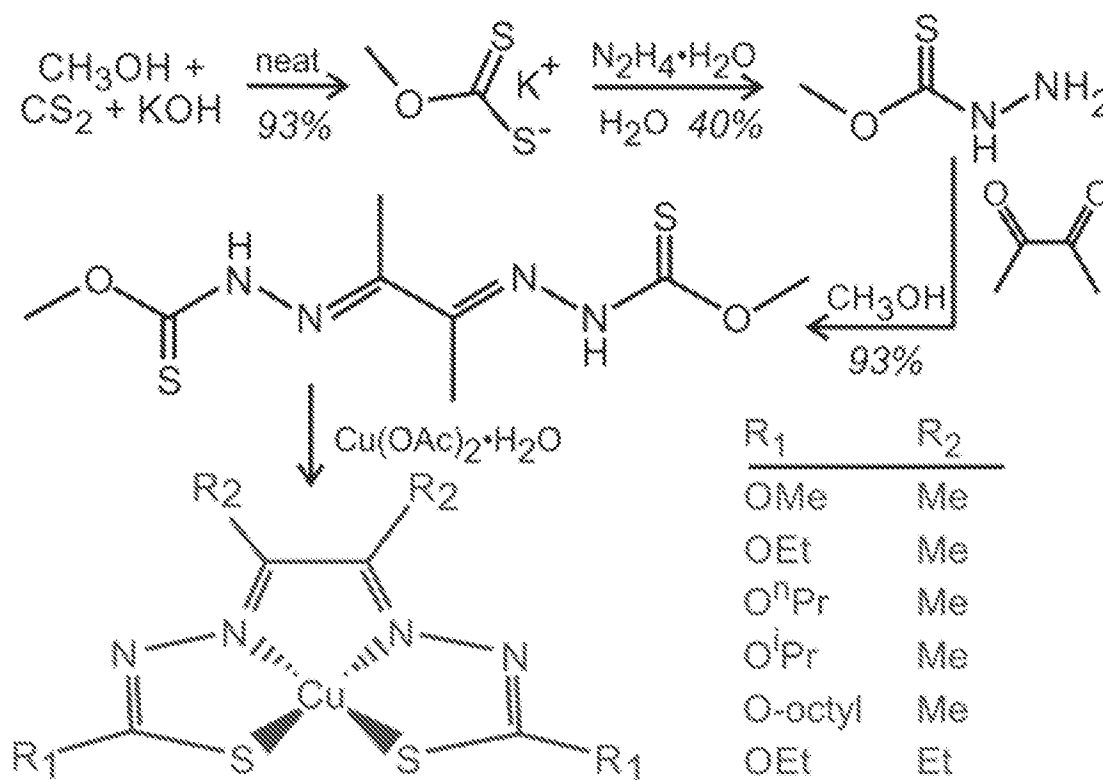
[00359] CuL^1 demonstrates a metal-assisted ligand-centered mechanism, in some instances. The redox non-innocence and protonation promiscuity of the ligand provides for a variety of HER mechanisms, some of which can be dependent on the metal ion. The CuL^1 system exhibits the highest reported TOF of any ligand-centered homogeneous HER catalysts to date. However, its high activity can sometimes require large overpotential. Nonetheless, the metal-assisted ligand reactivity of CuL^1 provides a new template for future HER electrocatalysts that, in some instances, function without the

participation of a metal-hydride. The current study demonstrates that non-innocent ligands can work in conjunction with a redox-active metal to promote ligand-centered reactivity. This represents a new approach to the development of electrocatalysts for HER and, possibly, the activation of other small molecules.

5

[00360] **Example Set C: Example syntheses and electrochemical investigations of alkoxy derivatives**

[00361] Alkoxy derivatives were prepared as shown in the scheme below.



10

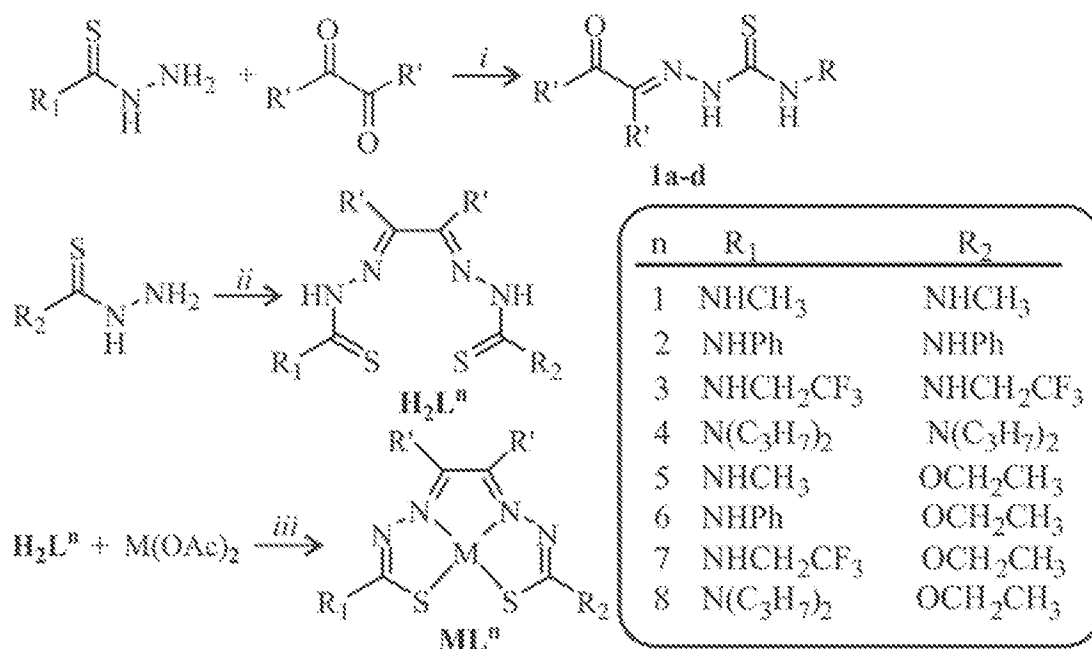
[00362] The hydrazinecarbothioic acid *O*-alkyl esters were prepared and condensed with diones. This was followed by metalation (shown here as Cu acetate).

Characterization of their Cu(II) complexes reveals only small structural and spectroscopic changes relative to their bis-thiosemicarbazone counterparts. However, electro-chemical investigations reveal anodic shifts of ~340 mV in the Cu^{II/I} reduction. The results demonstrate the ability to modulate the potential by variation of the thiosemicarbazone N-termini without imparting large structural changes. The synthetic strategies highlighted in the scheme provide examples of the design of new molecular catalysts, the synthesis of catalysts with extended structures, and the covalent attachment of catalysts to electrode surfaces.

10 [00363] **Example Set D: Example Syntheses**

[00364] A series of compounds can be synthesized containing transition metal- (Cu), non-transition metal- (Zn), and metal-free derivatives of symmetric ($R_1 = R_2$) derivatives (H_2L^{1-4}) and the corresponding asymmetric derivatives (H_2L^{5-8}) in which R_2 is an ethoxy group, as in the scheme below.

15



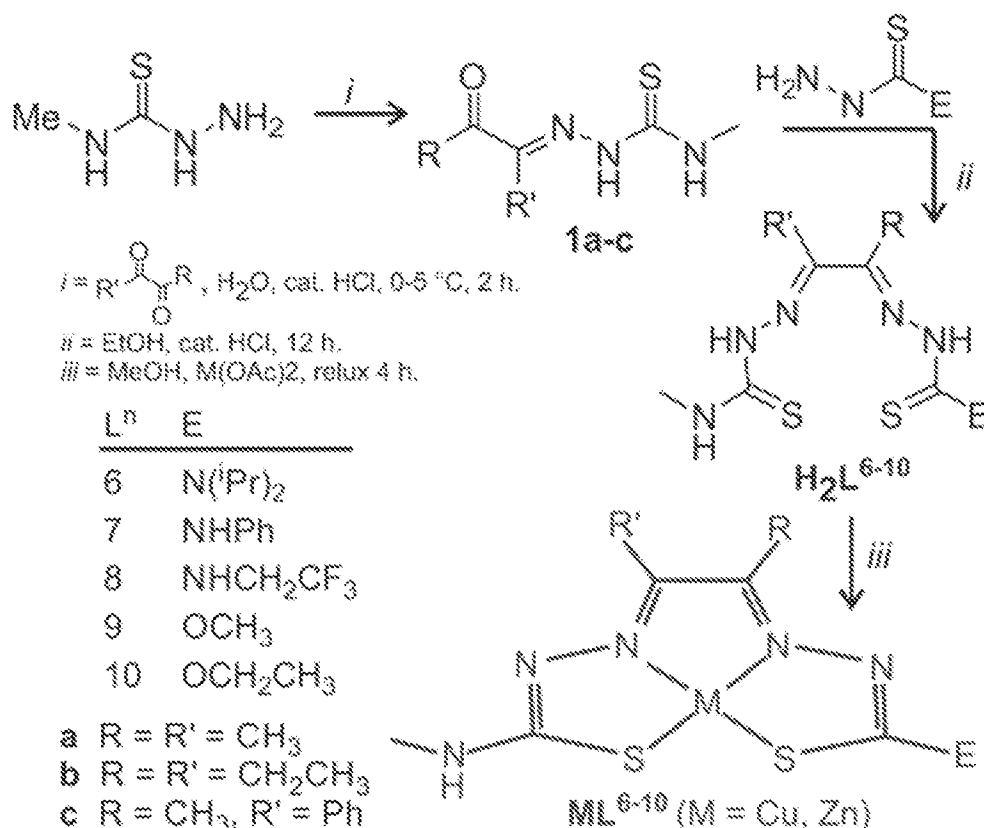
i) H₂O, cat. HCl, 0-5 °C, 2h; ii) **1a-d**, EtOH, cat. HCl, 12 h; iii) MeOH, reflux, 4 h

[00365] The bis-thiosemicarbazone ligands H₂L¹⁻⁴ and their Cu and Zn complexes have been prepared. The asymmetric ligand H₂L⁵, was prepared by condensation of **1a** with the *N*-amino-*O*-ethylthiocarbamate (prepared from ethanol, CS₂, and NH₂NH₂•H₂O) in 50 – 70% yield (see above). Addition of Cu(OAc)₂ in methanol yields CuL⁵ as a dark brown precipitates upon reflux. Spectroscopic characterization reveals a similar ligand environment as CuL¹ and related derivatives. The x-ray structure of CuL⁵, confirms the asymmetric N₂S₂ environment.

10

[00366] **Example Set E: Examples of Asymmetric Formulas**

[00367] A series of asymmetric ligands has been synthesized, according to the scheme below.



[00368] Ligands $\text{H}_2\text{L}^{10a-c}$ have been prepared by condensation of **1a-c** with the *N*-amino-*O*-ethylthiocarbamate (prepared from ethanol, CS_2 , and $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$) in 50 – 70% yield. Addition of Cu(OAc)_2 in methanol yields CuL^{10a-c} as a dark brown precipitates upon reflux. Spectroscopic characterization reveals a similar ligand environment as CuL^1 and related derivatives. The x-ray structure of CuL^{10a} , confirms the asymmetric N_2S_2 environment. H_2L^{8a} and CuL^{8a} were also prepared.

[00369] The CVs of CuL^{10a-c} in acetonitrile (0.1 M TBAHFP) show a quasireversible reduction and oxidation. For CuL^{10a} , the $\text{Cu}^{\text{III/I}}$ reduction occurs at -1010 mV with the formal $\text{Cu}^{\text{III/II}}$ couple observed at +448 mV. These values lie between the respective potentials of the symmetric derivatives CuL^1 and CuL^5 . Substitution of the backbone methyl groups with ethyl results in a small, but measurable cathodic shift to

-1030 mV for the Cu^{III/I}. Incorporation of phenyl substituent in the backbone, CuL^{10c}, yields a larger shift in the Cu^{III/I} potential to -850 mV. Notably, the Cu^{III/I} reduction of CuL^{10c} is more accessible than in the symmetric CuL⁵. This confirms modification of backbone R groups as a viable strategy to tune potential. Also, the CH₂CF₃ group of CuL^{8a} shifts the Cu^{III/I} potential to +70 mV with relative to CuL¹ in DMF.⁴⁰

[00370] Initial CVs confirm the HER activity of CuL^{10b,c} in acetonitrile. Addition of acetic acid to CuL^{10c} increases catalytic current at -1.5 V, Figure 64. The current is first-order in [acid] until it reaches acid independence at [acid] > 0.093 M. The maximum catalytic currents stabilizes at 1.80 mA associated with a maximum i_{cat}/i_p value of 43.8 (v = 1.0 V/s), affording a TOF of 15,600 s⁻¹ assuming the mechanism is bimolecular, as observed for CuL¹. An overpotential of 1.5 V was determined by open circuit potential methods. CuL^{10b} has similar HER electrocatalytic activity.

[00371] **Example Set F: Glassy Carbon Electrode (GCE) Preparation and Results**

[00372] H₂L¹ and its Cu and Zn complexes (See Example Set B) are insoluble in water making them ideal candidates for preparing modified GCEs. GC-H₂L¹, GC-ZnL¹, and GC-CuL¹ were prepared by dropcast of from 20 nmol to 200nmol of the appropriate catalyst on 5 mm GCE disks and curing of the resulting films. Electrodes were thoroughly dried and stored in air prior to use. The Electrochemical Impedance Spectroscopic (EIS) data for GC-CuL¹ is consistent with a contact resistance of 14 Ω. The charge transfer resistance, which has an impact on overpotential, of GC-CuL¹ is 1760 Ω.

This relatively low charge transfer resistance could be attributed to the ease of electron transfer within the planar, conjugated framework of CuL¹. Results for ZnL¹ are similar. Initial CV studies confirm HER activity of the surface confined catalysts. From the polarization curves, the overpotential required to achieve a current density of 10 mA/cm² is 699 mV for GC-CuL¹, Figure 65. GC-ZnL¹ and GC-H₂L¹ have higher overpotential of 940 mV and 1200 mV, respectively.

[00373] **Example Set G: Carbon Paste Electrodes (CPE) – Fabrication and Surface Analysis**

[00374] CPEs modified with H₂L¹, CuL¹ and ZnL¹ (from Example Set B) were prepared by mixing graphite fine powder with and 0.5 wt% of the appropriate catalyst in dichloromethane and sonicating for 15 min. The mixture was dried under an infrared lamp for 30 min. Paraffin oil (20 wt%) was added and the resulting slurry was carefully mixed to form the carbon paste. The paste was pressed into a plastic tube and a Cu wire was inserted to establish electrical contact. The electrode surface was polished with weighing paper and washed with deionized water. Finally, 2 µL of a Nafion (5% in isopropanol) was added to the polished surface and the chemically modified CPE was dried under an infrared heating lamp for 15 min. CPEs were stored in air.

[00375] The CPE-CuL¹ surface was imaged using SEM and the impedance measured by EIS. The SEM images show clear and homogeneous graphite layers with uniformly distributed pores, Figure 66a. The surface porosity should allow for sufficient ion diffusion from the bulk to the catalysts embedded in the electrode film. Resistance

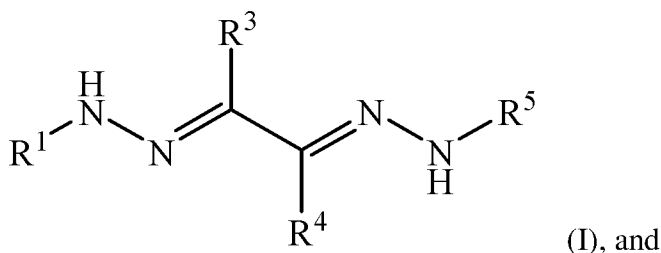
between the CPE-CuL¹ and solution was measured by EIS. Data collected over a frequency range of 10⁻² to 10⁵ Hz at an applied overpotential of 1.3 V were used to construct a Nyquist plot, Figure 66b. Fitting of the data yields a resistance between the electrode surface and electrolyte of 12.3 Ω , a charge transfer resistance within the electrode of 508 Ω , a capacitive component indicative of space charges or electrical dipoles in the sample. Overall, resistance for the CPEs is significantly smaller than the modified GCEs in Example Set F.

[00376] Polarization curves were recorded for the CPE-CuL¹ in 0.5 M H₂SO₄ solution under ambient conditions, Figure 66c. The overpotential required to obtain a current density of 60 mA/cm² is 0.65 V. At lower current densities, the overpotential is below the 0.6 V benchmark for relevant HER catalysts, although the value at the recommended current density of 10 mA/cm² complicated by a series of events attributed to formation of a catalytically active dinuclear species, as seen in homogenous solution. For CPE-ZnL¹ and CPE-H₂L¹, the overpotential required for 60 mA/cm² is 0.94 and 1.04 V, respectively.

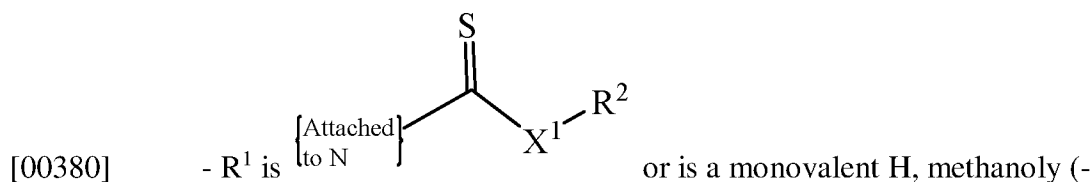
[00377] Initial assessment of the electrode stability of CPE-CuL¹ was investigated by repetitive scanning in 0.5 M H₂SO₄ solution for 500 cycles from 0.0 to -1.7 V at a scan rate of 50 mV/s. The overpotential required for a current density of 100 mA/cm² increased by only 50 mV. The long term stability of CPE-CuL¹ was benchmarked by chronopotentiometry at a fixed catalytic current density of 100 mA/cm² for 24 hours. The overpotential increased by 97 mV over the first 8 hours and remained constant thereafter indicating good stability over long time electrolysis.

Additional Embodiments

[00378] A1. A compound selected from a compound of Formula (I),



[00379] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein



COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

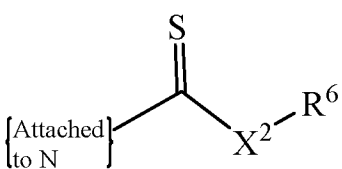
[00381] - X¹ is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more (e.g., 0, 1, or 2) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00382] - R² is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00383] - R³ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇

alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00384] - R⁴ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00385] - R⁵ is  or is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or

pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00386] - X² is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more (e.g., 0, 1, or 2) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

[00387] - R⁶ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl.

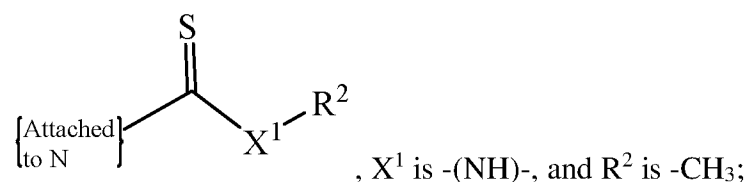
[00388] A2. The compound of embodiment A1, wherein

[00389] (a) R^3 is the same as R^4 ;

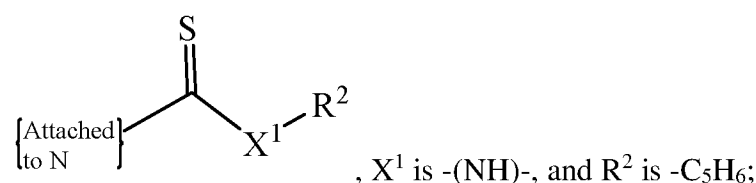
[00390] (b) R^3 is the same as R^4 and R^1 is the same as R^5 ;

[00391] (c) R^3 is the same as R^4 , X^1 is $-(NH)-$, X^2 is $-(NH)-$, and R^2 is the same as R^6 ;

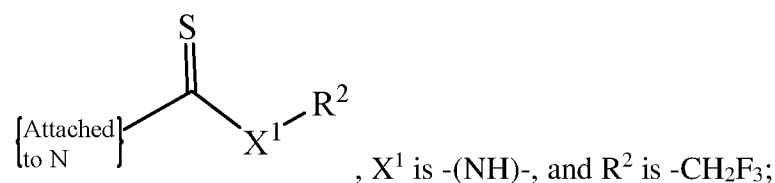
[00392] (d) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



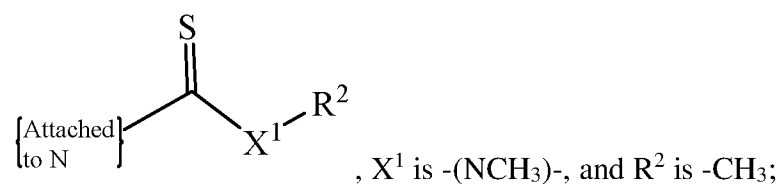
[00393] (e) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



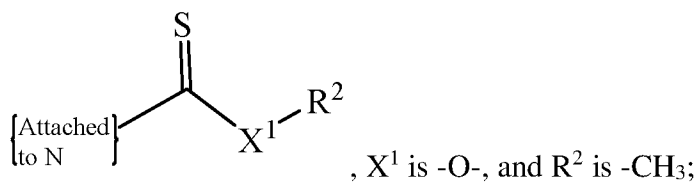
10 [00394] (f) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



[00395] (g) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



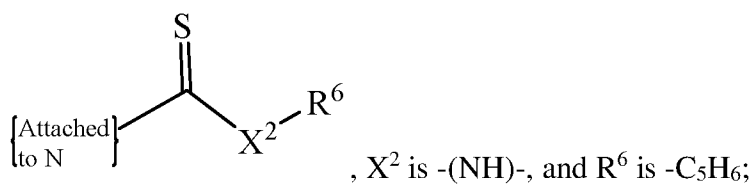
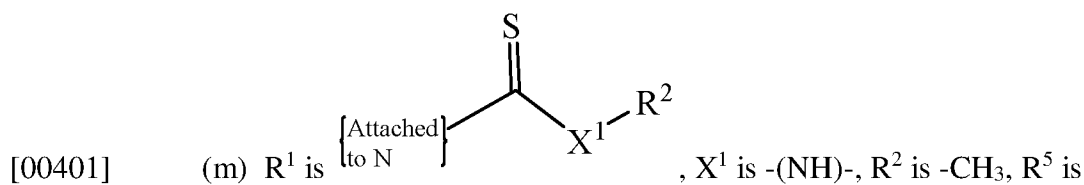
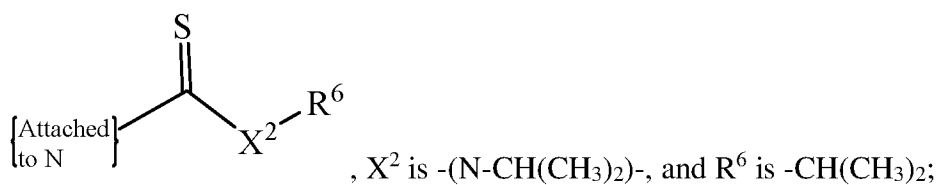
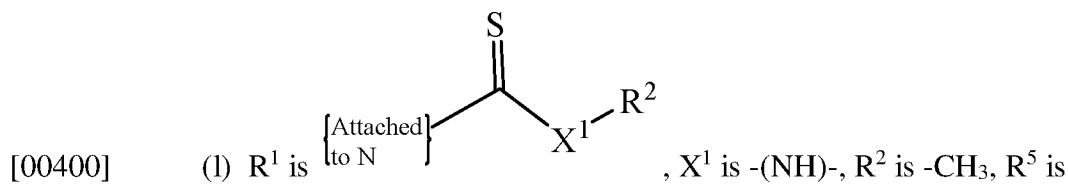
[00396] (h) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is

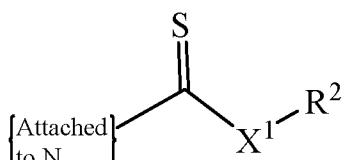


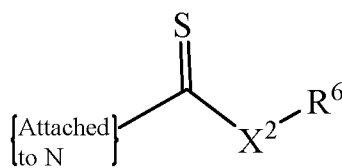
[00397] (i) R^3 is the same as R^4 and R^3 is methyl;

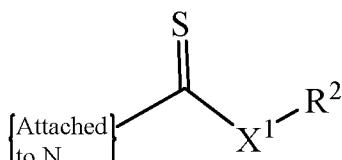
[00398] (j) R^3 is the same as R^4 and R^3 is ethyl;

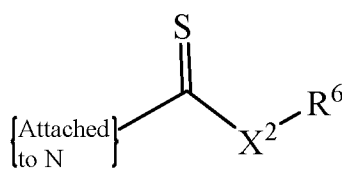
5 [00399] (k) R^3 is methyl and R^4 is phenyl;

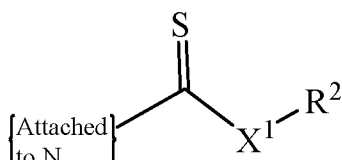


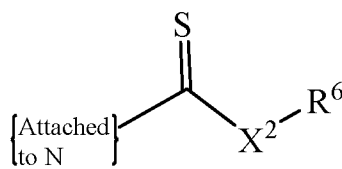
[00402] (n) R^1 is , X^1 is $-(NH)-$, R^2 is $-CH_3$, R^5 is

, X^2 is $-(NH)-$, and R^6 is $-CH_2CF_3$;

[00403] (o) R^1 is , X^1 is $-(NH)-$, R^2 is $-CH_3$, R^5 is

, X^2 is $-O-$, and R^6 is $-CH_3$;

5 [00404] (p) R^1 is , X^1 is $-(NH)-$, R^2 is $-CH_3$, R^5 is

, X^2 is $-O-$, and R^6 is $-CH_2CH_3$;

[00405] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

[00406] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

[00407] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

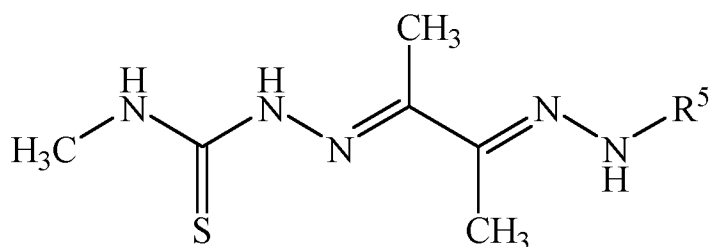
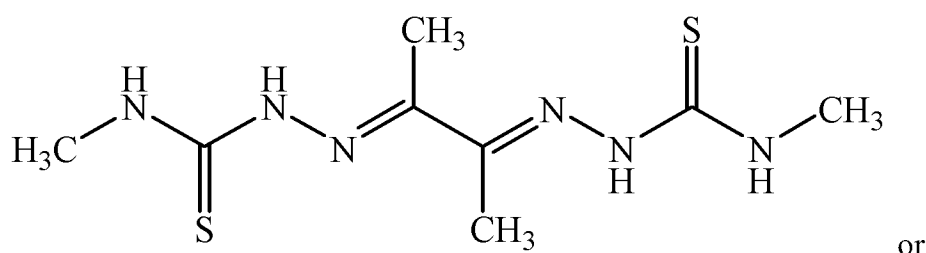
10 [00408] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

[00409] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

[00410] A3. The compound of embodiment A1 or embodiment A2, wherein Formula (I) further comprises a solvent molecule coordinated with Formula (I).

5 [00411] A4. The compound of any of embodiments A1 to A3, wherein Formula (I) further comprises a solvent molecule coordinated with Formula (I) and the solvent molecule is selected from water, methanol, ethanol, propanol, acetonitrile, dimethylformamide, and acetone.

10 [00412] A5. The compound of any of embodiments A1 to A4, wherein the compound is



, where R^5 is pyridinyl, 1-methyl-imidazolyl, an N-containing heterocyclyl, or an N-containing heteroaryl.

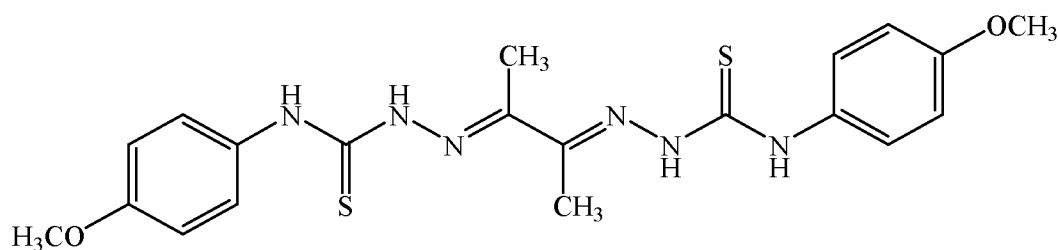
15

[00413] A6. The compound of any of embodiments A1 to A5, wherein (a) X^1 is not $-(NH)-$, (b) R^2 is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

[00414] A7. The compound of any of embodiments A1 to A6, wherein (a) X^2 is not $-(NH)-$, (b) R^6 is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

[00415] A8. The compound of any of embodiments A1 to A7, wherein (a) R^3 is not methyl, (b) R^4 is not methyl, or (c) both (a) and (b).

[00416] A9. The compound of any of embodiments A1 to A8, wherein the compound is not



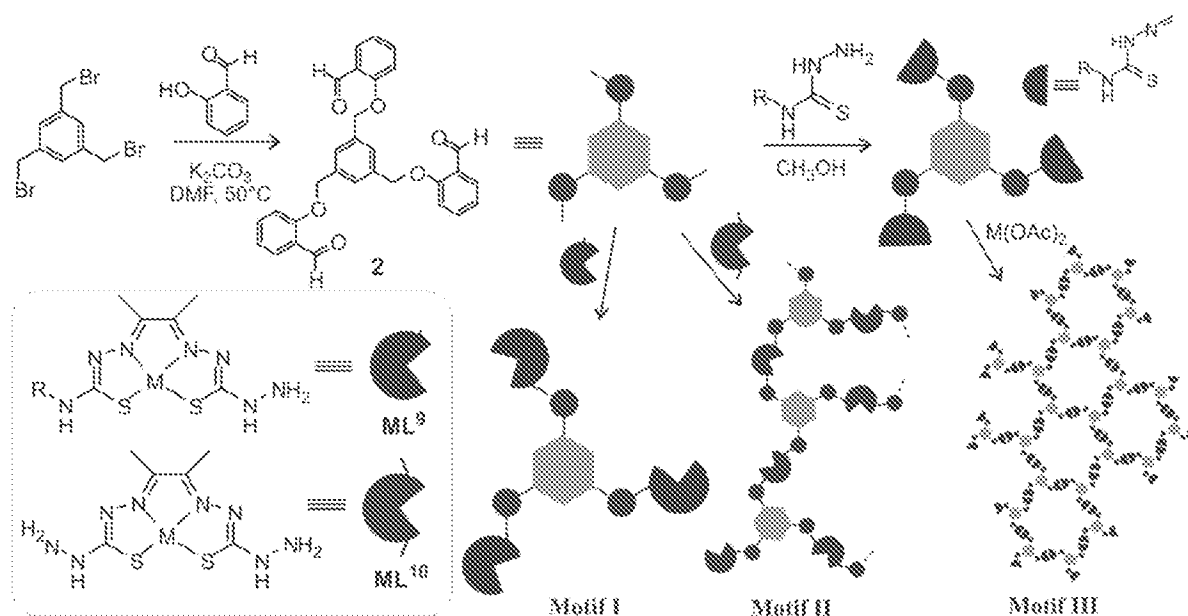
[00417] A10. The compound of any of embodiments A1 to A9, wherein the compound is part of a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, a heterogeneous aqueous solution, or a glassy carbon electrode.

[00418] A11. A homogenous solution, a homogenous aqueous solution, a heterogeneous solution, or a heterogeneous aqueous solution, each comprising the compound of any of embodiments A1 to A9.

[00419] A12. A glassy carbon electrode, a carbon paste (e.g., embedded with one or more of polynuclear catalysts, coordinated polymers, or metal-organic frameworks), covalent modified carbon (e.g., graphene), or non-covalent modified carbon (e.g.,

graphene), each comprising or reacted with the compound of any of embodiments A1 to A9.

[00420] A13. The carbon paste of embodiment A12, wherein the carbon paste
5 comprises an extended structure motif (e.g., motif I, motif II, or motif III of scheme 11).



[00421] B1. A compound selected from Formula (II),

10 [00422] $M \cdot L$ (II) and

[00423] salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein

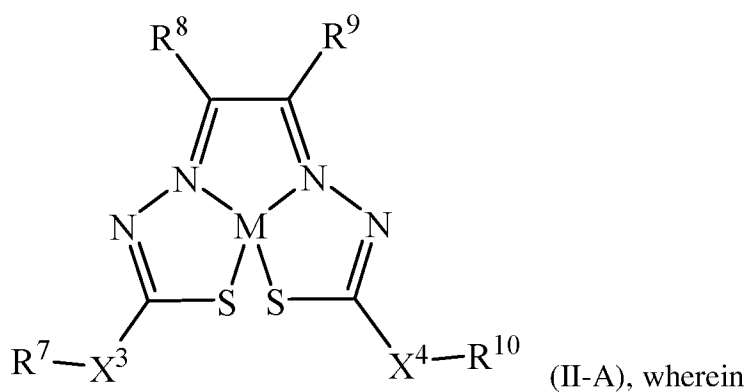
[00424] - M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe (e.g., M is Cu^{2+} , Cu^+ , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Mn^{2+} , Ru^{2+} , or Fe^{2+} ; or M
15 is Cu^{2+} , Cu^+ , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Mn^{2+} , Ru^{2+} , or Fe^{2+} ; or M is Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} ,

Cd^{2+} , Mn^{2+} , or Fe^{2+} ; or M is Cu^{2+} , Zn^{2+} , Ni^{2+} , or Co^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Ni^{2+} ; or M is Cu^{2+} , Zn^{2+} , or Co^{2+} ; or M is Cu^{2+} or Zn^{2+}) and

[00425] - L is selected from a thiosemicarbazone or a compound of Formula (I) of embodiments A1-A9.

5

[00426] B2. The compound of embodiment B1 wherein Formula (II) is a compound of Formula (II-A)



[00427] - R^7 is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro

10 (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄,

15

or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00428] - X³ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be

5 substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl, or , which -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-
10 CCH), sulfo (-SO₃H), methyl, or ethyl;

[00429] - R⁸ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇
15 alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄,
20 or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00430] - R⁹ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene),

cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂, C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl,

heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00431] - X⁴ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl, or, which -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

[00432] - R¹⁰ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen (e.g., F, Cl, Br, or I), aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl (e.g., C₁, C₂, C₃, C₄, C₅, C₆, or C₇ alkyl), C₂-C₇ alkenyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkenyl), C₂-C₇ alkynyl (e.g., C₂, C₃, C₄, C₅, C₆, or C₇ alkynyl), or C₁-C₆ alkoxy (C₁, C₂,

C₃, C₄, C₅, or C₆ alkoxy), which aryl (e.g., benzene or pyrene), cycloalkyl, heterocyclyl, heteroaryl (e.g., pyridinyl and 1-methyl imidazolyl), C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more (e.g., 0, 1, 2, 3, 4, 5, or 6) of halogen (e.g., F, Cl, Br, or I), hydroxy (-OH), C₁-C₅ alkyl (e.g., C₁, C₂, C₃, C₄, or C₅ alkyl), C₁-C₄ alkoxy (C₁, C₂, C₃, or C₄ alkoxy), methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

[00433] - M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe; or M is Cu²⁺, Cu⁺, Zn²⁺, Co²⁺, Ni²⁺, Cd²⁺, Mn²⁺, Ru²⁺, or Fe²⁺; or M is Cu²⁺, Cu⁺, Zn²⁺, Co²⁺, Cd²⁺, Mn²⁺, Ru²⁺, or Fe²⁺; or M is Cu²⁺, Zn²⁺, Co²⁺, Cd²⁺, Mn²⁺, or Fe²⁺; or M is Cu²⁺, Zn²⁺, Ni²⁺, or Co²⁺; or M is Cu²⁺, Zn²⁺, or Ni²⁺; or M is Cu²⁺, Zn²⁺, or Co²⁺; or M is Cu²⁺ or Zn²⁺.

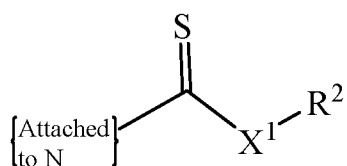
[00434] B3. The compound of embodiment B1 or embodiment B2, wherein

[00435] (a) R³ is the same as R⁴;

[00436] (b) R³ is the same as R⁴ and R¹ is the same as R⁵;

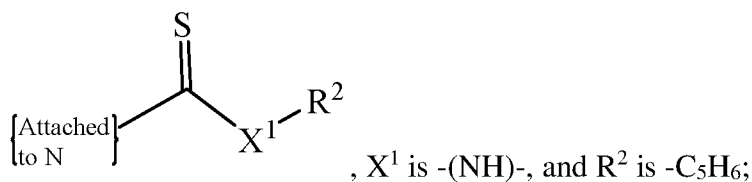
[00437] (c) R³ is the same as R⁴, X¹ is -(NH)-, X² is -(NH)-, and R² is the same as R⁶;

[00438] (d) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is

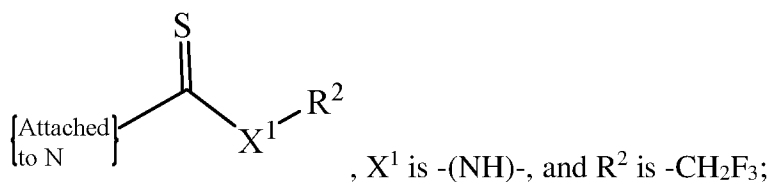


, X¹ is -(NH)-, and R² is -CH₃;

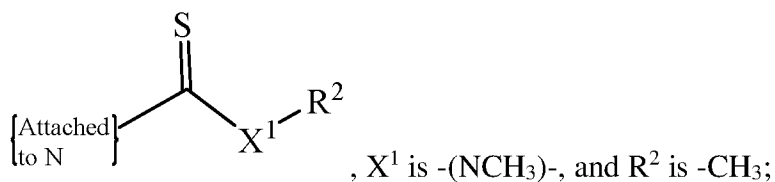
[00439] (e) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



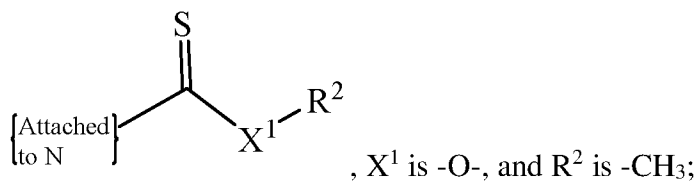
[00440] (f) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



5 [00441] (g) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



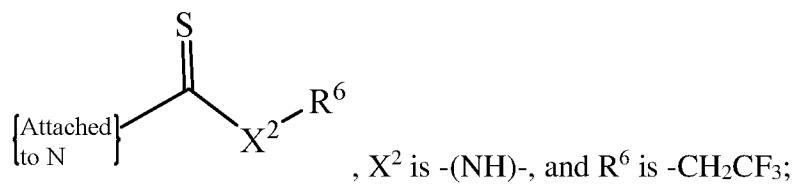
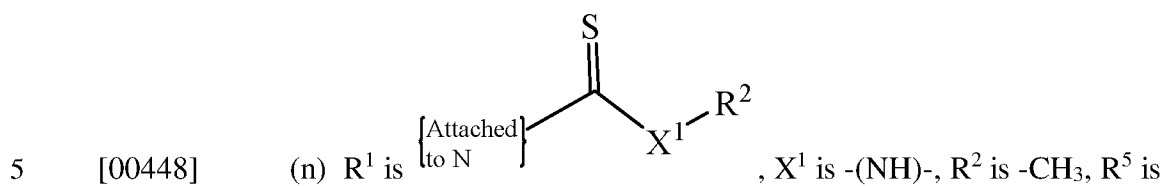
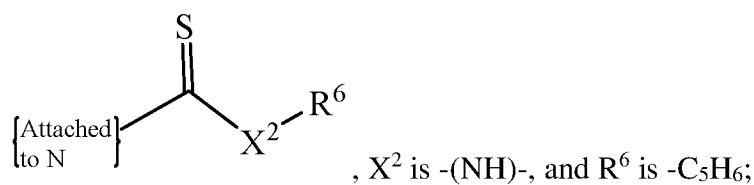
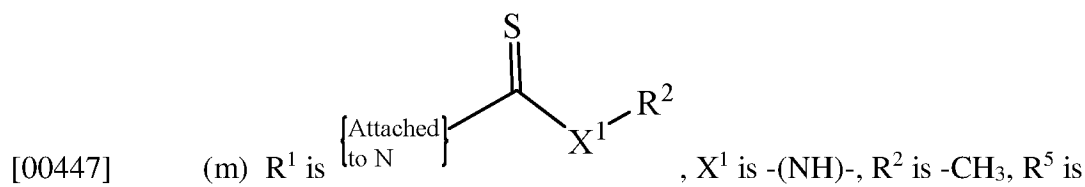
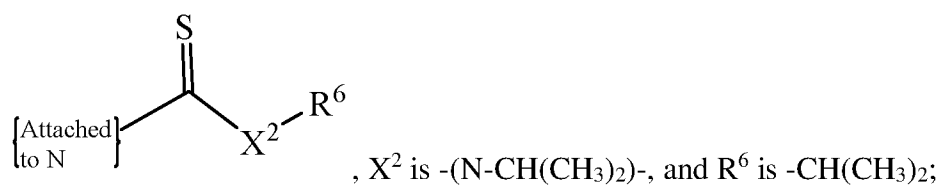
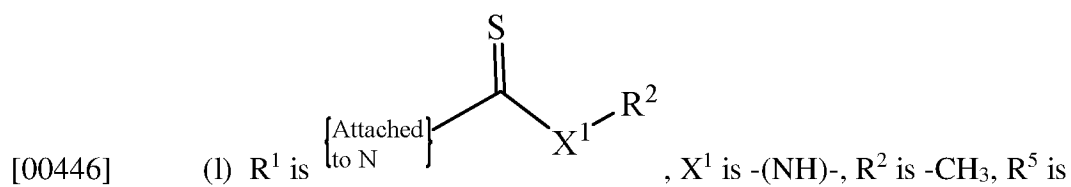
[00442] (h) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is

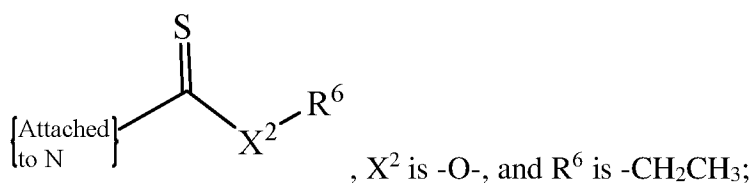
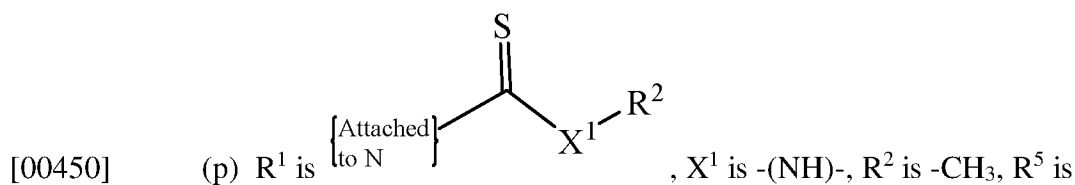
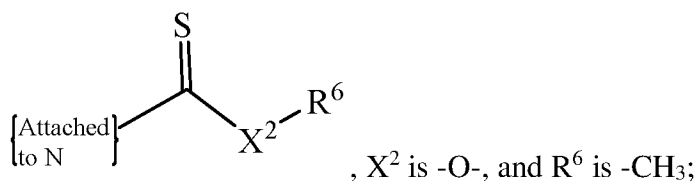
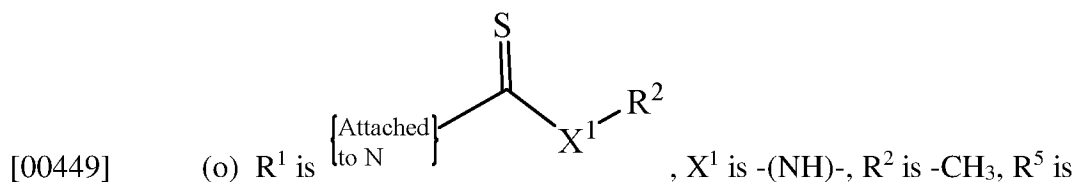


[00443] (i) R^3 is the same as R^4 and R^3 is methyl;

10 [00444] (j) R^3 is the same as R^4 and R^3 is ethyl;

[00445] (k) R^3 is methyl and R^4 is phenyl;





- 5 [00451] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);
- [00452] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);
- [00453] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);
- [00454] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or
- [00455] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

10

[00456] B4. The compound of any of embodiments B1 to B3, wherein

[00457] (a) R^8 is the same as R^9 ;

[00458] (b) R^8 is the same as R^9 and X^3-R^7 is the same as X^4-R^{10} ;

[00459] (c) R^8 is the same as R^9 , X^3 is $-(NH)-$, X^4 is $-(NH)-$, and R^7 is the same as

15 R^{10} ;

[00460] (d) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is - (NH)-, and R^7 is $-CH_3$;

[00461] (e) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is - (NH)-, and R^7 is $-C_5H_6$;

5 [00462] (f) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is - (NH)-, and R^7 is $-CH_2F_3$;

[00463] (g) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is - (NCH₃)-, and R^7 is $-CH_3$;

[00464] (h) R^8 is the same as R^9 , R^8 is methyl, X^3-R^7 is the same as X^4-R^{10} , X^3 is -
10 O-, and R^7 is $-CH_3$;

[00465] (i) R^8 is the same as R^9 and R^8 is methyl;

[00466] (j) R^8 is the same as R^9 and R^8 is ethyl;

[00467] (k) R^8 is methyl and R^9 is phenyl;

[00468] (l) X^3 is - (NH)-, R^7 is $-CH_3$, X^4 is $-(N-CH(CH_3)_2)-$, and R^{10} is $-CH(CH_3)_2$;

15 [00469] (m) X^3 is - (NH)-, R^7 is $-CH_3$, X^4 is - (NH)-, and R^{10} is $-C_5H_6$;

[00470] (n) X^3 is - (NH)-, R^7 is $-CH_3$, X^4 is - (NH)-, and R^{10} is $-CH_2CF_3$;

[00471] (o) X^3 is - (NH)-, R^7 is $-CH_3$, X^4 is - O-, and R^{10} is $-CH_3$;

[00472] (p) X^3 is - (NH)-, R^7 is $-CH_3$, X^4 is - O-, and R^{10} is $-CH_2CH_3$;

[00473] (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

20 [00474] (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

[00475] (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

[00476] (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

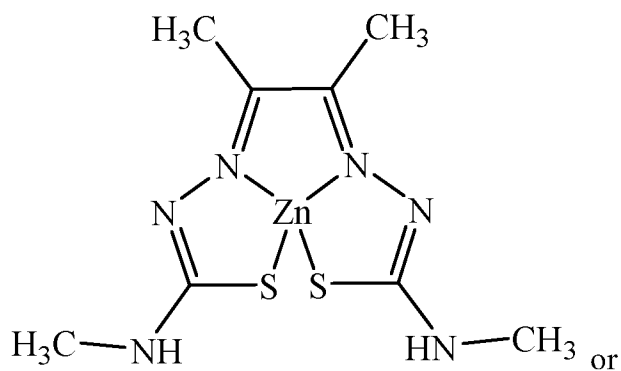
[00477] (u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

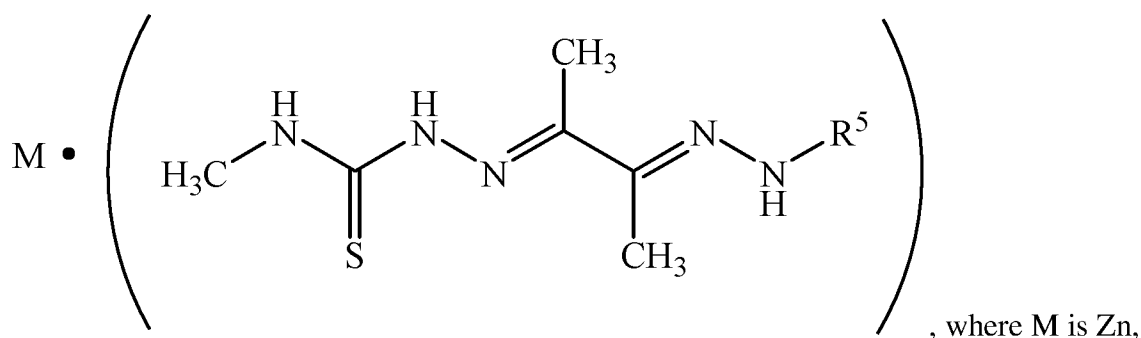
[00478] B5. The compound of any of embodiments B1 to B4, wherein the M is Zn^{2+} , Co^{2+} , Ni^{2+} , or Cu^{2+} (e.g., M is Zn^{2+} , Co^{2+} , or Cu^{2+}).

5 [00479] B6. The compound of any of embodiments B1 to B5, wherein Formula (II) further comprises a solvent molecule coordinated with Formula (II).

[00480] B7. The compound of any of embodiments B1 to B6, wherein Formula (II) further comprises a solvent molecule coordinated with Formula (II) and the solvent molecule is selected from water, ethanol, propanol, acetonitrile, dimethylformamide, and
10 acetone.

[00481] B8. The compound of any of embodiments B1 to B7, wherein the compound is





Co, Ni, or Cu (e.g., M is Zn, Co, or Cu; or M is Zn, Ni, or Cu; or M is Zn or Cu) and R⁵ is pyridinyl, 1-methyl-imidazolyl, an N-containing heterocyclyl, or an N-containing heteroaryl.

5

[00482] B9. The compound of any of embodiments B1 to B8, wherein (a) X¹ is not -(NH)-, (b) R² is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

[00483] B10. The compound of any of embodiments B1 to B9, wherein (a) X² is not -(NH)-, (b) R⁶ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

10

[00484] B11. The compound of any of embodiments B1 to B10, wherein (a) R³ is not methyl, (b) R⁴ is not methyl, or (c) both (a) and (b).

15

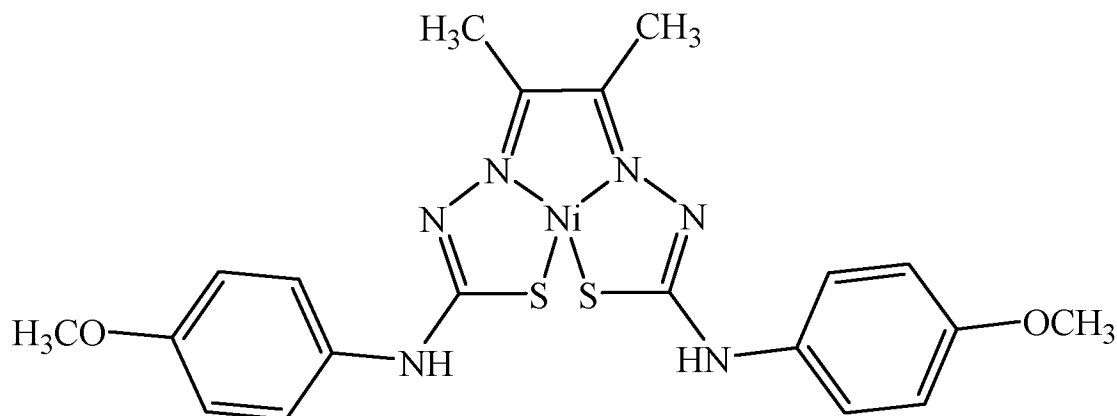
[00485] B12. The compound of any of embodiments B1 to B11, wherein (a) X³ is not -(NH)-, (b) R⁷ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

[00486] B13. The compound of any of embodiments B1 to B12, wherein (a) X⁴ is not -(NH)-, (b) R¹⁰ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

[00487] B14. The compound of any of embodiments B1 to B13, wherein (a) R⁸ is not methyl, (b) R⁹ is not methyl, or (c) both (a) and (b).

20

[00488] B15. The compound of any of embodiments B1 to B14, wherein the compound is not

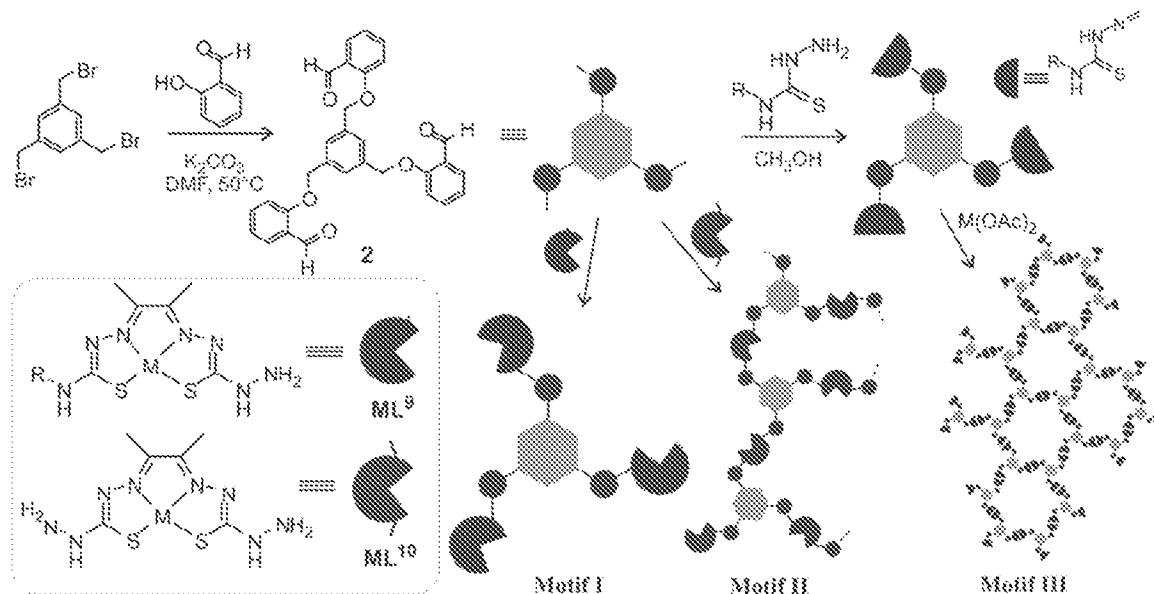


5 [00489] B16. The compound of any of embodiments B1 to B15, wherein the compound is part of a homogenous solution, a homogenous aqueous solution, a heterogeneous solution, or a heterogeneous aqueous solution.

[00490] B17. A homogenous solution, a homogenous aqueous solution, a
10 heterogeneous solution, or a heterogeneous aqueous solution, each comprising the compound of any of embodiments B1 to B16.

[00491] B18. A glassy carbon electrode, a carbon paste (e.g., embedded with one
or more of polynuclear catalysts, coordinated polymers, or metal-organic frameworks),
15 covalent modified carbon (e.g., graphene), or non-covalent modified carbon (e.g.,
graphene), each comprising or reacted with the compound of any of embodiments B1 to
B17.

[00492] B19. The carbon paste of embodiment B18, wherein the carbon paste comprises an extended structure motif (e.g., motif I, motif II, or motif III of scheme 11).



5 [00493] C1. A catalyst (e.g., an electrocatalyst) comprising a composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both.

[00494] D1. An anode comprising a composition comprising a compound of
10 Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both.

[00495] E1. A cathode comprising a composition comprising a compound of
Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g.,
15 embodiments B1-B19), or both.

[00496] F1. An electrochemical cell comprising a composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both.

[00497] F2. The electrochemical cell of embodiment F1, wherein the cathode of
5 the electrochemical cell comprises the composition.

[00498] G1. A fuel cell comprising a composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both.

[00499] G2. The fuel cell of embodiment G1, wherein the anode of the fuel cell
10 comprises the first composition.

[00500] H1. A method for producing H₂ comprising contacting, in an electrochemical cell, a first composition comprising a compound of Formula (I) (e.g.,
15 embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both with a second composition comprising water.

[00501] H2. The method of embodiment H1, wherein the cathode of the electrochemical cell comprises the first composition.

[00502] H3. The method of H1 or H2, wherein the TOF is from about 20 s⁻¹ to
20 about 100,000 s⁻¹, about 100 s⁻¹ to about 100,000 s⁻¹, from about 500 s⁻¹ to about 100,000 s⁻¹, from about 500 s⁻¹ to about 50,000 s⁻¹, from about 500 s⁻¹ to about 20,000 s⁻¹, about 20 s⁻¹, about 100 s⁻¹, about 500 s⁻¹, about 1000 s⁻¹, about 5000 s⁻¹, about 10000 s⁻¹, about 12000 s⁻¹, about 16000 s⁻¹, about 20000 s⁻¹, about 50000 s⁻¹, or about 100,000 s⁻¹.

[00503] H4. A method for oxidizing an aldehyde or an alcohol comprising contacting, in an electrochemical cell, a composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both.

5 [00504] H5. The method of any of H1-H4, wherein the overpotential is greater than about 0 V, not less than about 0.1 V, not more than about 0.1 V, not more than 0.5 V, not more than 1 V, not more than 10 V, not more than 100 V, from about 0 V to about 2000 V, from about 0 V to about 1000 V, from about 0 V to about 750 V, from about 0 V to about 300 V, from about 0 V to about 350 V, from about 0 V to about 200 V, from
10 about 0 V to about 100 V, from about 0 V to about 20 V, from about 0 V to about 10 V, from about 0 V to about 5 V, from about 0 V to about 2 V, from about 0 V to about 1 V, from about 0.1 V to about 2000 V, from about 0.1 V to about 1000 V, from about 0.1 V to about 750 V, from about 0.1 V to about 300 V, from about 0.1 V to about 350 V, from about 0.1 V to about 200 V, from about 0.1 V to about 100 V, from about 0.1 V to about
15 20 V, from about 0.1 V to about 10 V, from about 0.1 V to about 5 V, from about 0.1 V to about 2 V, from about 0.1 V to about 1 V, about 0.1 V, about 0.5 V, about 1 V, about 5 V, about 10 V, about 100 V, about 250 V, about 350 V, about 400 V, about 500 V, or about 1000 V.

20 [00505] I1. A method for producing electricity comprising contacting, in a fuel cell, a first composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of Formula (II) (e.g., embodiments B1-B19), or both with a second composition comprising H₂.

[00506] I2. The method of embodiment I1, wherein the anode of the fuel cell comprises the first composition.

[00507] I3. The method of I1 or I2, wherein the TOF is from about 1 s^{-1} to about 1000 s^{-1} , from about 5 s^{-1} to about 1000 s^{-1} , from about 5 s^{-1} to about 500 s^{-1} , from about 5 s^{-1} to about 200 s^{-1} , about 1 s^{-1} , about 5 s^{-1} , about 10 s^{-1} , about 32 s^{-1} , about 50 s^{-1} , about 76 s^{-1} , about 100 s^{-1} , about 120 s^{-1} , about 200 s^{-1} , about 300 s^{-1} , about 500 s^{-1} , or about 1000 s^{-1} .

[00508] I4. The method of any of I1-I3, wherein the overpotential is greater than about 0 V, not less than about 0.1 V, not more than about 0.1 V, not more than 0.5 V, not more than 1 V, not more than 10 V, not more than 100 V, from about 0 V to about 2000 V, from about 0 V to about 1000 V, from about 0 V to about 750 V, from about 0 V to about 300 V, from about 0 V to about 350 V, from about 0 V to about 200 V, from about 0 V to about 100 V, from about 0 V to about 20 V, from about 0 V to about 10 V, from about 0 V to about 5 V, from about 0 V to about 2 V, from about 0 V to about 1 V, from about 0.1 V to about 2000 V, from about 0.1 V to about 1000 V, from about 0.1 V to about 750 V, from about 0.1 V to about 300 V, from about 0.1 V to about 350 V, from about 0.1 V to about 200 V, from about 0.1 V to about 100 V, from about 0.1 V to about 20 V, from about 0.1 V to about 10 V, from about 0.1 V to about 5 V, from about 0.1 V to about 2 V, from about 0.1 V to about 1 V, about 0.1 V, about 0.5 V, about 1 V, about 5 V, about 10 V, about 100 V, about 250 V, about 350 V, about 400 V, about 500 V, or about 1000 V.

[00509] J1. A method for preparing a compound of Formula (I) (e.g.,
embodiments A1-A13) comprising any suitable method.

[00510] J2. The method of J1, wherein the compound of Formula (I) is prepared
5 comprising

[00511] (a) reacting a compound of Formula (III) $\text{R}^1\text{-}\overset{\text{H}}{\underset{|}{\text{N}}}\text{-NH}_2$ (III)

[00512] with a compound of Formula (IV) $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}^4 \text{---} \text{C} \text{---} \text{C} \text{---} \text{R}^3 \\ \text{(IV)} \end{array}$;

[00513] (b) reacting a compound of Formula (V) $\begin{array}{c} \text{R}^3 \\ | \\ \text{R}^1\text{-}\overset{\text{H}}{\underset{|}{\text{N}}}\text{-N}=\text{C} \text{---} \text{C}=\text{O} \\ | \\ \text{R}^4 \end{array}$

[00513] (b) reacting a compound of Formula (V)
10 (V)

[00514] with a compound of Formula (VI) $\text{H}_2\text{N-}\overset{\text{H}}{\underset{|}{\text{N}}}\text{-R}^5$ (VI); and

[00515] (c) recovering the compound of Formula (I),

[00516] wherein R^1 , R^3 , R^4 , and R^5 are defined as in embodiments A1-A13.

15

[00517] K1. A method for preparing a compound of Formula (II) (e.g.,
embodiments B1-B19) comprising any suitable method.

[00518] K2. The method of K1, wherein the compound of Formula (II) is prepared
comprising

5 [00519] (a) reacting a compound of Formula (I) (e.g., embodiments A1-A13) with
M; and

[00520] (b) recovering the compound of Formula (II),

[00521] wherein M is defined as in embodiments B1-B19.

10 [00522] L1. A method for preparing a catalyst (e.g., an electrocatalyst) comprising
a composition comprising a compound of Formula (I) (e.g., embodiments A1-A13), a
compound of Formula (II) (e.g., embodiments B1-B19), or both, comprising any suitable
method.

15 [00523] M1. A method for preparing an anode comprising a composition
comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of
Formula (II) (e.g., embodiments B1-B19), or both, comprising any suitable method.

[00524] N1. A method for preparing a cathode comprising a composition
20 comprising a compound of Formula (I) (e.g., embodiments A1-A13), a compound of
Formula (II) (e.g., embodiments B1-B19), or both, comprising any suitable method.

[00525] The headings used in the disclosure are not meant to suggest that all disclosure relating to the heading is found within the section that starts with that heading. Disclosure for any subject may be found throughout the specification.

[00526] It is noted that terms like “preferably,” “commonly,” and “typically” are not used herein to limit the scope of the claimed invention or to imply that certain features are critical, essential, or even important to the structure or function of the claimed invention. Rather, these terms are merely intended to highlight alternative or additional features that may or may not be utilized in a particular embodiment of the present invention.

[00527] As used in the disclosure, “a” or “an” means one or more than one, unless otherwise specified. As used in the claims, when used in conjunction with the word “comprising” the words “a” or “an” means one or more than one, unless otherwise specified. As used in the disclosure or claims, “another” means at least a second or more, unless otherwise specified. As used in the disclosure, the phrases “such as”, “for example”, and “e.g.” mean “for example, but not limited to” in that the list following the term (“such as”, “for example”, or “e.g.”) provides some examples but the list is not necessarily a fully inclusive list. The word “comprising” means that the items following the word “comprising” may include additional unrecited elements or steps; that is, “comprising” does not exclude additional unrecited steps or elements.

[00528] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about”.

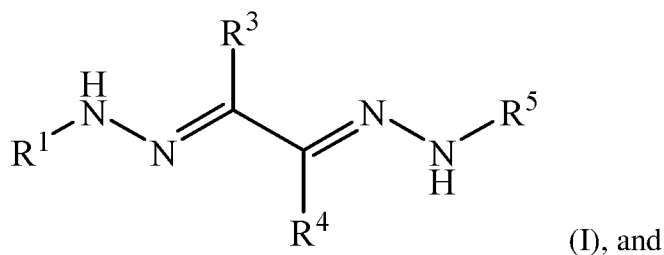
Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and claims are approximations that can vary depending upon the desired properties or functions sought to be obtained by the presently-disclosed subject matter.

[00529] As used herein, the term “about,” when referring to a value or to an amount of mass, weight, time, volume, concentration or percentage is meant to encompass variations of in some embodiments $\pm 20\%$, in some embodiments $\pm 10\%$, in some embodiments $\pm 5\%$, in some embodiments $\pm 1\%$, in some embodiments $\pm 0.5\%$, and in some embodiments $\pm 0.1\%$ from the specified amount, as such variations are appropriate to perform the disclosed method.

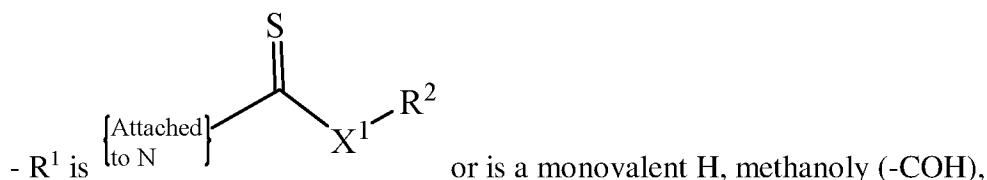
[00530] Detailed descriptions of one or more embodiments are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details disclosed herein (even if designated as preferred or advantageous) are not to be interpreted as limiting, but rather are to be used as an illustrative basis for the claims and as a representative basis for teaching one skilled in the art to employ the present invention in any appropriate manner. Indeed, various modifications of the invention in addition to those described herein will become apparent to those skilled in the art from the foregoing description and the accompanying figures. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

1. A compound selected from a compound of Formula (I),



5 salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein



carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

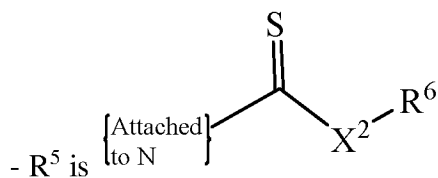
- X¹ is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R² is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH),

carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R³ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R⁴ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;



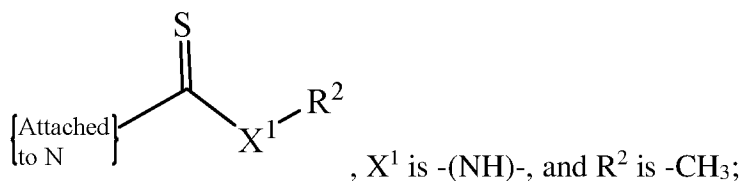
or is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- X² is bivalent -(NH)-, -O-, -(CH₂)-, or -S-, which -(NH)- or -(CH₂)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

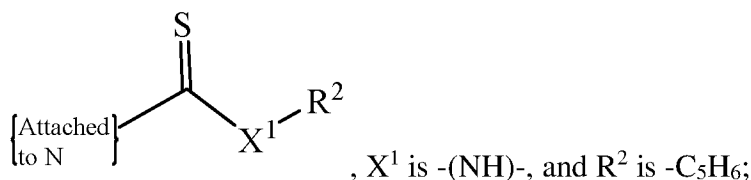
- R⁶ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl.

2. The compound of claim 1, wherein

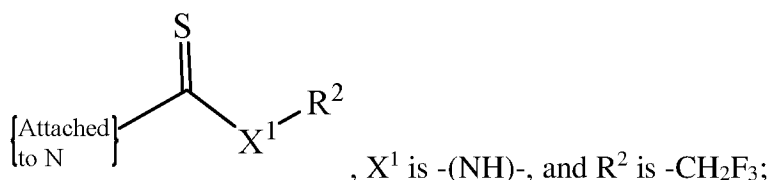
- 10 (a) R³ is the same as R⁴;
 (b) R³ is the same as R⁴ and R¹ is the same as R⁵;
 (c) R³ is the same as R⁴, X¹ is -(NH)-, X² is -(NH)-, and R² is the same as R⁶;
 (d) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is



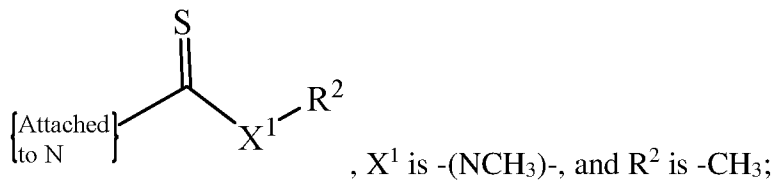
- 15 (e) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is



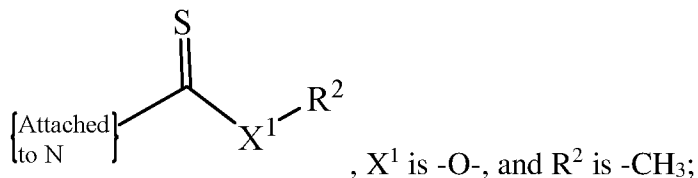
- (f) R³ is the same as R⁴, R³ is methyl, R¹ is the same as R⁵, R¹ is



(g) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is



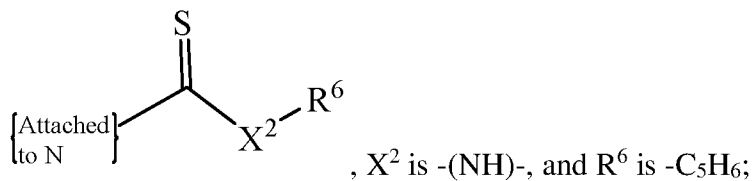
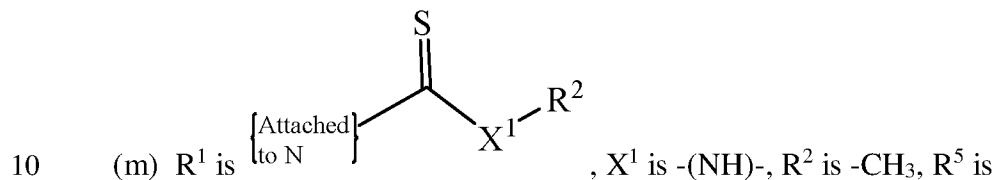
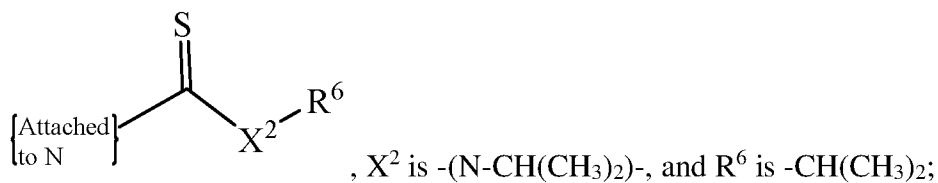
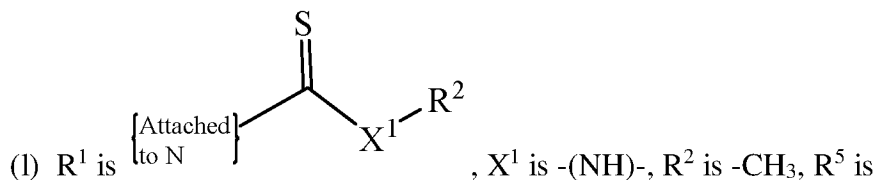
(h) R^3 is the same as R^4 , R^3 is methyl, R^1 is the same as R^5 , R^1 is

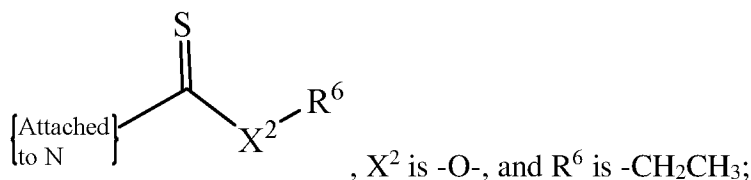
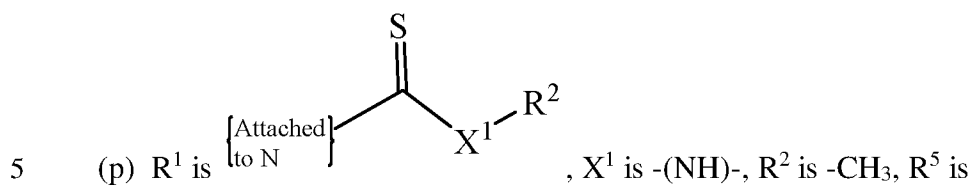
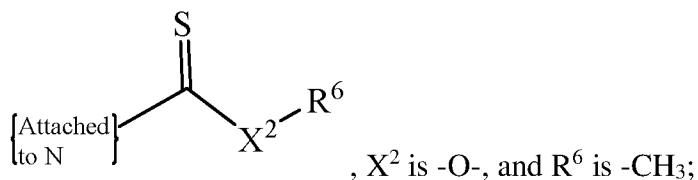
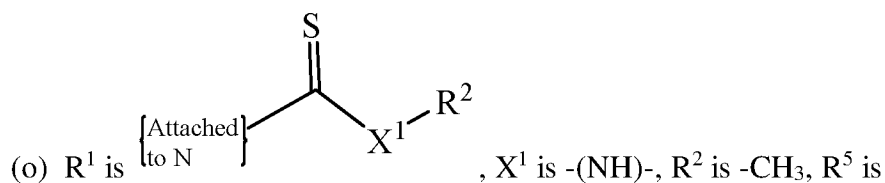
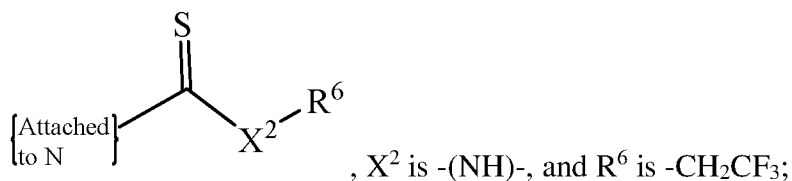
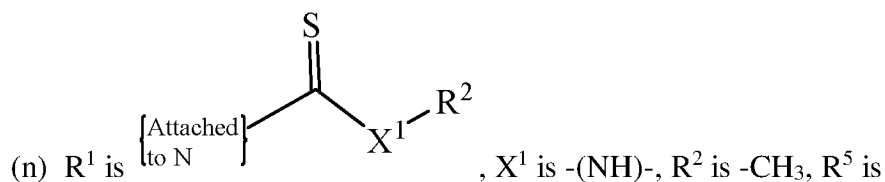


5 (i) R^3 is the same as R^4 and R^3 is methyl;

(j) R^3 is the same as R^4 and R^3 is ethyl;

(k) R^3 is methyl and R^4 is phenyl;





(q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);

(r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);

(s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);

10 (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

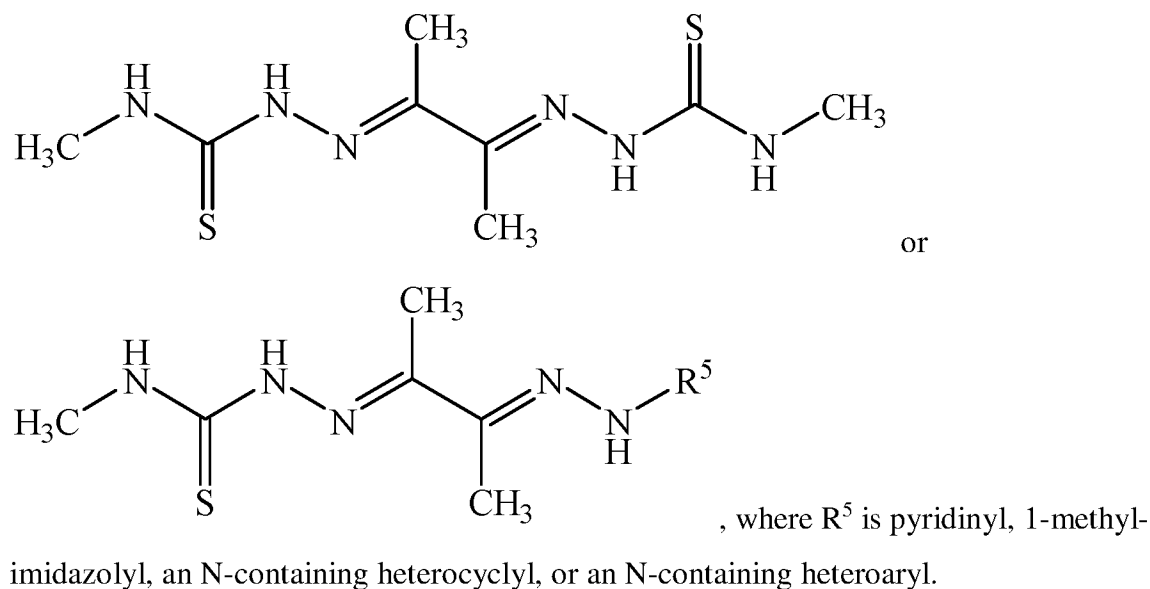
(u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

3. The compound of claim 1 or claim 2, wherein Formula (I) further comprises a solvent molecule coordinated with Formula (I).

4. The compound of any of claims 1-3, wherein Formula (I) further comprises a solvent molecule coordinated with Formula (I) and the solvent molecule is selected from water, methanol, ethanol, propanol, acetonitrile, dimethylformamide, and acetone.

5

5. The compound of any of claims 1-4, wherein the compound is



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6. The compound of any of claims 1-5, wherein (a) X¹ is not -(NH)-, (b) R² is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

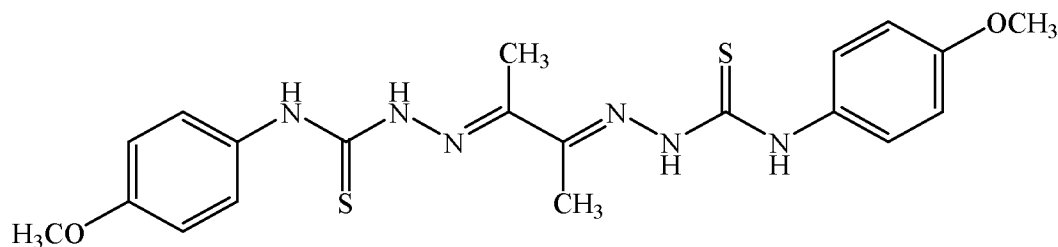
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7. The compound of any of claims 1-6, wherein (a) X² is not -(NH)-, (b) R⁶ is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

8. The compound of any of claims 1-7, wherein (a) R³ is not methyl, (b) R⁴ is not methyl, or (c) both (a) and (b).

20

9. The compound of any of claims 1-8, wherein the compound is not



10. A compound selected from a compound of Formula (II),

M·L (II) and

5 salts, optical isomers, geometric isomers, salts of isomers, and derivatives thereof, wherein

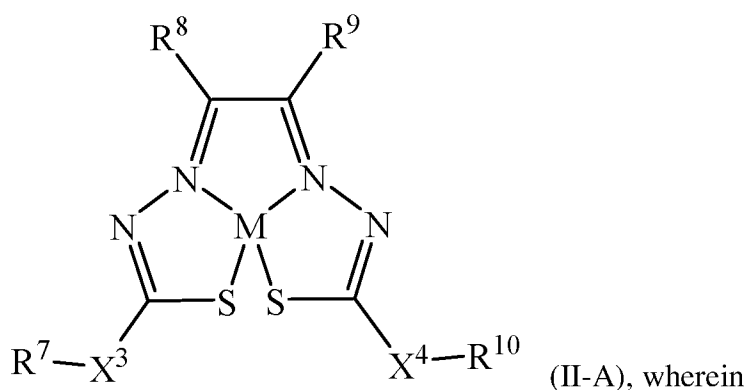
- M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe;

and

- L is a compound of Formula (I) of any of claims 1-9.

10

11. The compound of claim 10, wherein Formula (II) is a compound of Formula (II-A)



- R⁷ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

15

- X³ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R⁸ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R⁹ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- X⁴ is bivalent -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, -(N-CH₃)-, or -O-, which -(NH)-, -(N-CH(CH₃)₂)-, -(N-CH₂CH₃)-, or -(N-CH₃)- can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl;

- R¹⁰ is a monovalent H, methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), sulfo (-SO₃H), halogen, aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy, which aryl, cycloalkyl, heterocyclyl, heteroaryl, C₁-C₇ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, or C₁-C₆ alkoxy can optionally be substituted with one or more of halogen, hydroxy (-OH), C₁-C₅ alkyl, C₁-C₄ alkoxy,

methanoly (-COH), carboxy (-CO₂H), nitro (-NO₂), cyano (-CN), ethynyl (-CCH), sulfo (-SO₃H), methyl, or ethyl; and

- M is Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Co, Rh, Ti, V, Cr, Mn, or Fe.

- 5 12. The compound of claim 10 or claim 11, wherein
 - (a) R⁸ is the same as R⁹;
 - (b) R⁸ is the same as R⁹ and X³-R⁷ is the same as X⁴-R¹⁰;
 - (c) R⁸ is the same as R⁹, X³ is -(NH)-, X⁴ is -(NH)-, and R⁷ is the same as R¹⁰;
 - (d) R⁸ is the same as R⁹, R⁸ is methyl, X³-R⁷ is the same as X⁴-R¹⁰, X³ is -(NH)-,
 - 10 and R⁷ is -CH₃;
 - (e) R⁸ is the same as R⁹, R⁸ is methyl, X³-R⁷ is the same as X⁴-R¹⁰, X³ is -(NH)-, and R⁷ is -C₅H₆;
 - (f) R⁸ is the same as R⁹, R⁸ is methyl, X³-R⁷ is the same as X⁴-R¹⁰, X³ is -(NH)-, and R⁷ is -CH₂F₃;
 - 15 (g) R⁸ is the same as R⁹, R⁸ is methyl, X³-R⁷ is the same as X⁴-R¹⁰, X³ is -(NCH₃)-, and R⁷ is -CH₃;
 - (h) R⁸ is the same as R⁹, R⁸ is methyl, X³-R⁷ is the same as X⁴-R¹⁰, X³ is -O-, and R⁷ is -CH₃;
 - (i) R⁸ is the same as R⁹ and R⁸ is methyl;
 - 20 (j) R⁸ is the same as R⁹ and R⁸ is ethyl;
 - (k) R⁸ is methyl and R⁹ is phenyl;
 - (l) X³ is -(NH)-, R⁷ is -CH₃, X⁴ is -(N-CH(CH₃)₂)-, and R¹⁰ is -CH(CH₃)₂;
 - (m) X³ is -(NH)-, R⁷ is -CH₃, X⁴ is -(NH)-, and R¹⁰ is -C₅H₆;
 - (n) X³ is -(NH)-, R⁷ is -CH₃, X⁴ is -(NH)-, and R¹⁰ is -CH₂CF₃;
 - 25 (o) X³ is -(NH)-, R⁷ is -CH₃, X⁴ is -O-, and R¹⁰ is -CH₃;
 - (p) X³ is -(NH)-, R⁷ is -CH₃, X⁴ is -O-, and R¹⁰ is -CH₂CH₃;
 - (q) (1) the limitations of (l) and (2) the limitations of (i), (j), or (k);
 - (r) (1) the limitations of (m) and (2) the limitations of (i), (j), or (k);
 - (s) (1) the limitations of (n) and (2) the limitations of (i), (j), or (k);
 - 30 (t) (1) the limitations of (o) and (2) the limitations of (i), (j), or (k); or

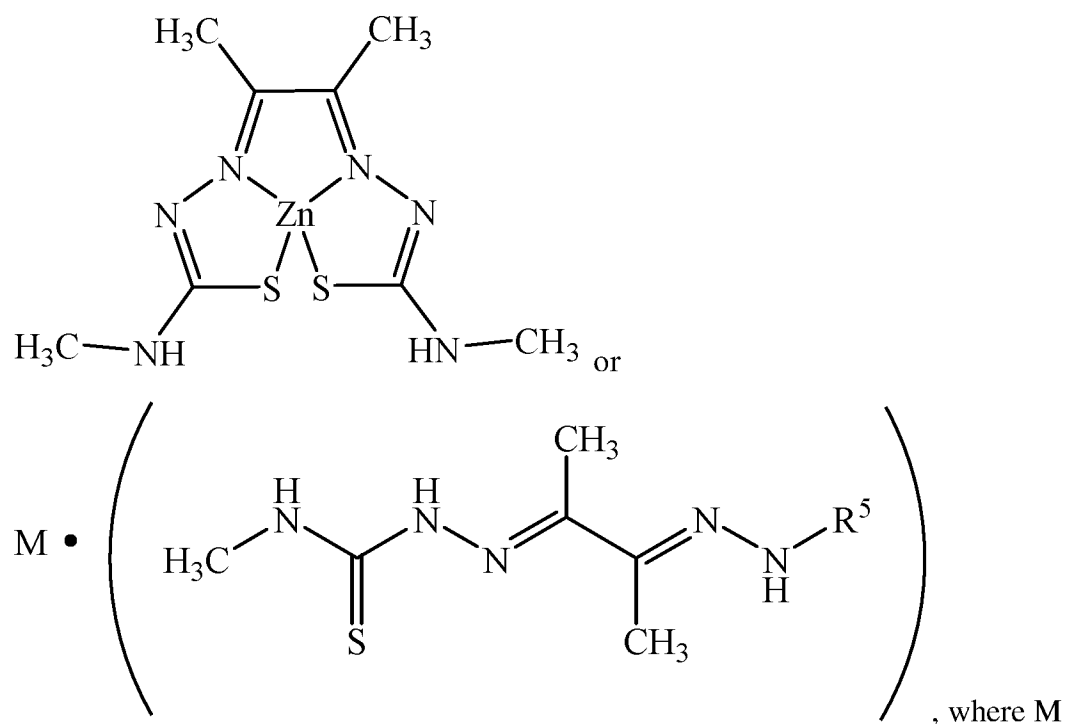
(u) (1) the limitations of (p) and (2) the limitations of (i), (j), or (k).

13. The compound of any of claims 10-12, wherein the M is Zn^{2+} , Co^{2+} , Ni^{2+} , or Cu^{2+} .

5 14. The compound of any of claims 10-13, wherein Formula (II) further comprises a solvent molecule coordinated with Formula (II).

15. The compound of any of claims 10-14, wherein Formula (II) further comprises a solvent molecule coordinated with Formula (II) and the solvent molecule is selected from
10 water, ethanol, propanol, acetonitrile, dimethylformamide, and acetone.

16. The compound of any of claims 10-15, wherein the compound is



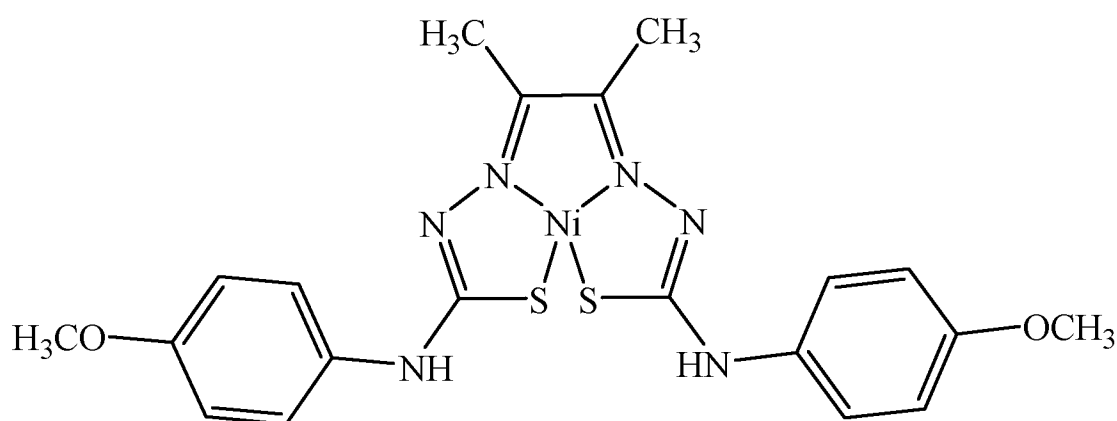
15 is Zn, Co, Ni, or Cu and R^5 is pyridinyl, 1-methyl-imidazolyl, an N-containing heterocyclyl, or an N-containing heteroaryl.

17. The compound of any of claims 10-16, wherein (a) X^3 is not $-(NH)-$, (b) R^7 is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

18. The compound of any of claims 10-17, wherein (a) X^4 is not $-(NH)-$, (b) R^{10} is not methoxyphenyl or p-methoxyphenyl, or (c) both (a) and (b).

19. The compound of any of claims 10-18, wherein (a) R^8 is not methyl, (b) R^9 is not methyl, or (c) both (a) and (b).

20. The compound of any of claims 10-19, wherein the compound is not



21. A catalyst or an electrocatalyst comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both.

22. An electrochemical cell comprising a composition comprising a compound of Formula (I), a compound of Formula (II), or both.

23. The electrochemical cell of claim 22, wherein the cathode of the electrochemical cell comprises the composition.

24. A method for producing H₂ comprising contacting, in an electrochemical cell, a first composition comprising a compound of Formula (I), a compound of Formula (II), or both, with a second composition comprising water.

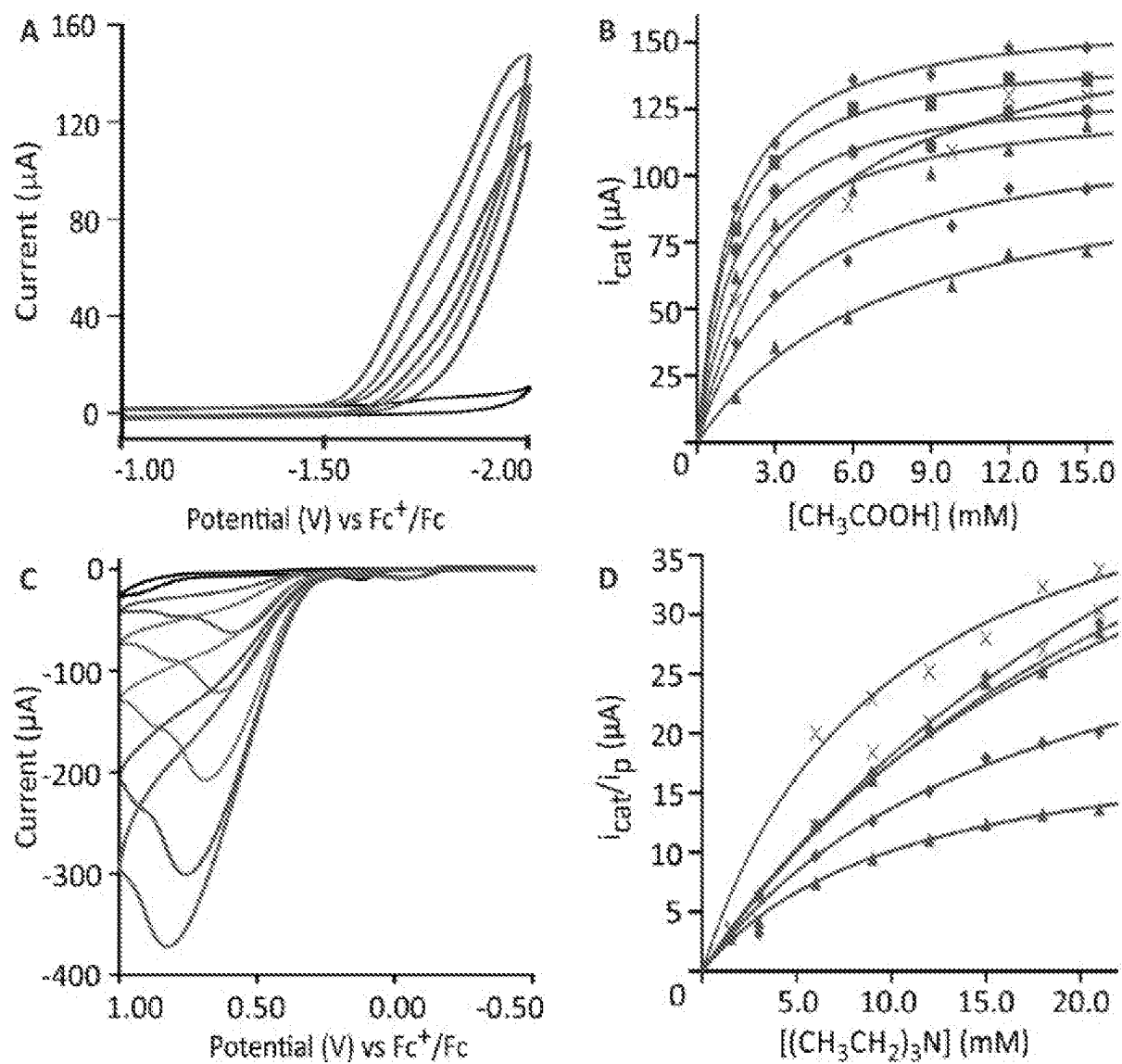
25. The method of claim 24, wherein the cathode of the electrochemical cell comprises the first composition.

- 5 26. The method of claim 24 or claim 25, wherein the TOF is from about 20 s^{-1} to about $100,000 \text{ s}^{-1}$, about 100 s^{-1} to about $100,000 \text{ s}^{-1}$, from about 500 s^{-1} to about $100,000 \text{ s}^{-1}$, from about 500 s^{-1} to about $50,000 \text{ s}^{-1}$, from about 500 s^{-1} to about $20,000 \text{ s}^{-1}$, about 20 s^{-1} , about 100 s^{-1} , about 500 s^{-1} , about 1000 s^{-1} , about 5000 s^{-1} , about 10000 s^{-1} , about 12000 s^{-1} , about 16000 s^{-1} , about 20000 s^{-1} , about 50000 s^{-1} , or about $100,000 \text{ s}^{-1}$.

10

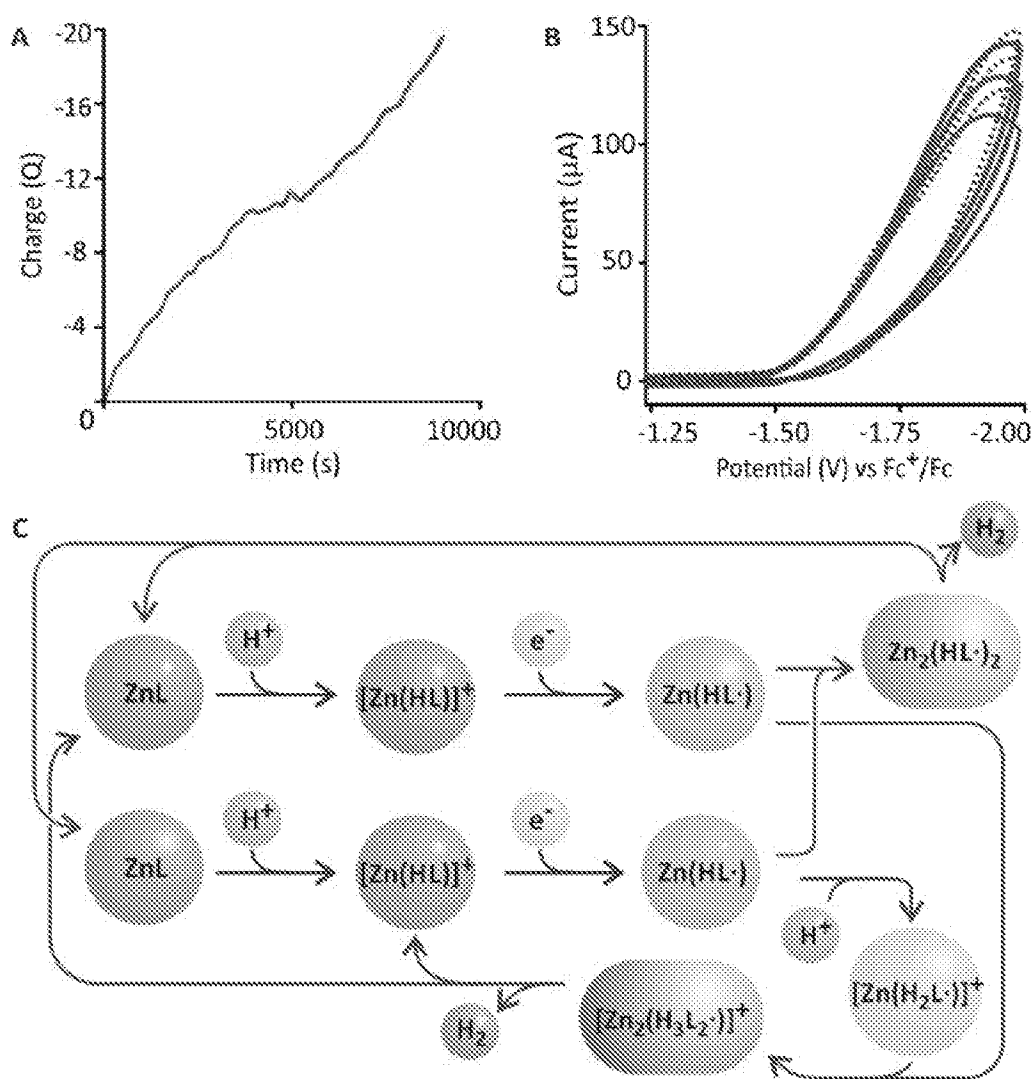
1/66

FIG. 1



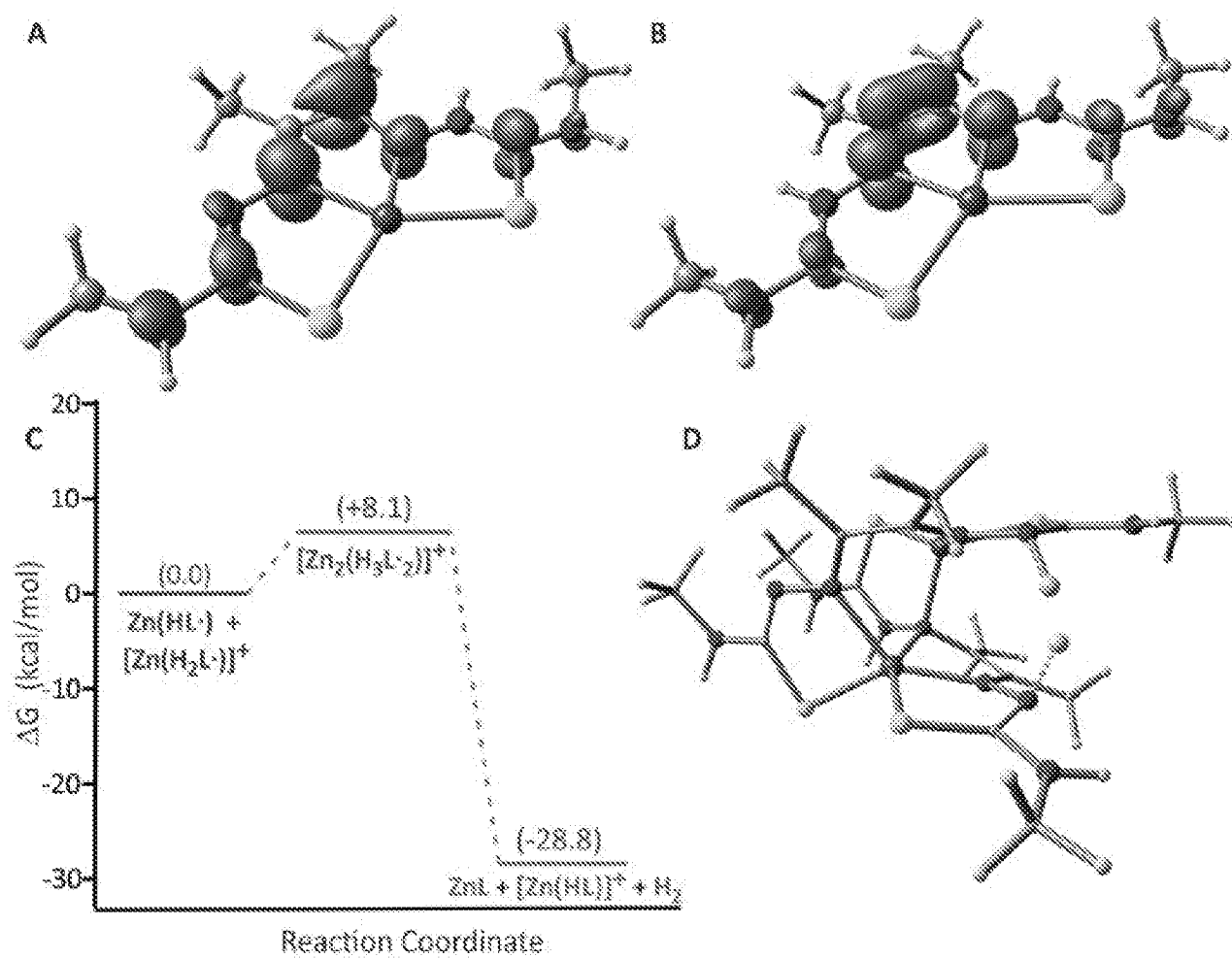
2/66

FIG. 2



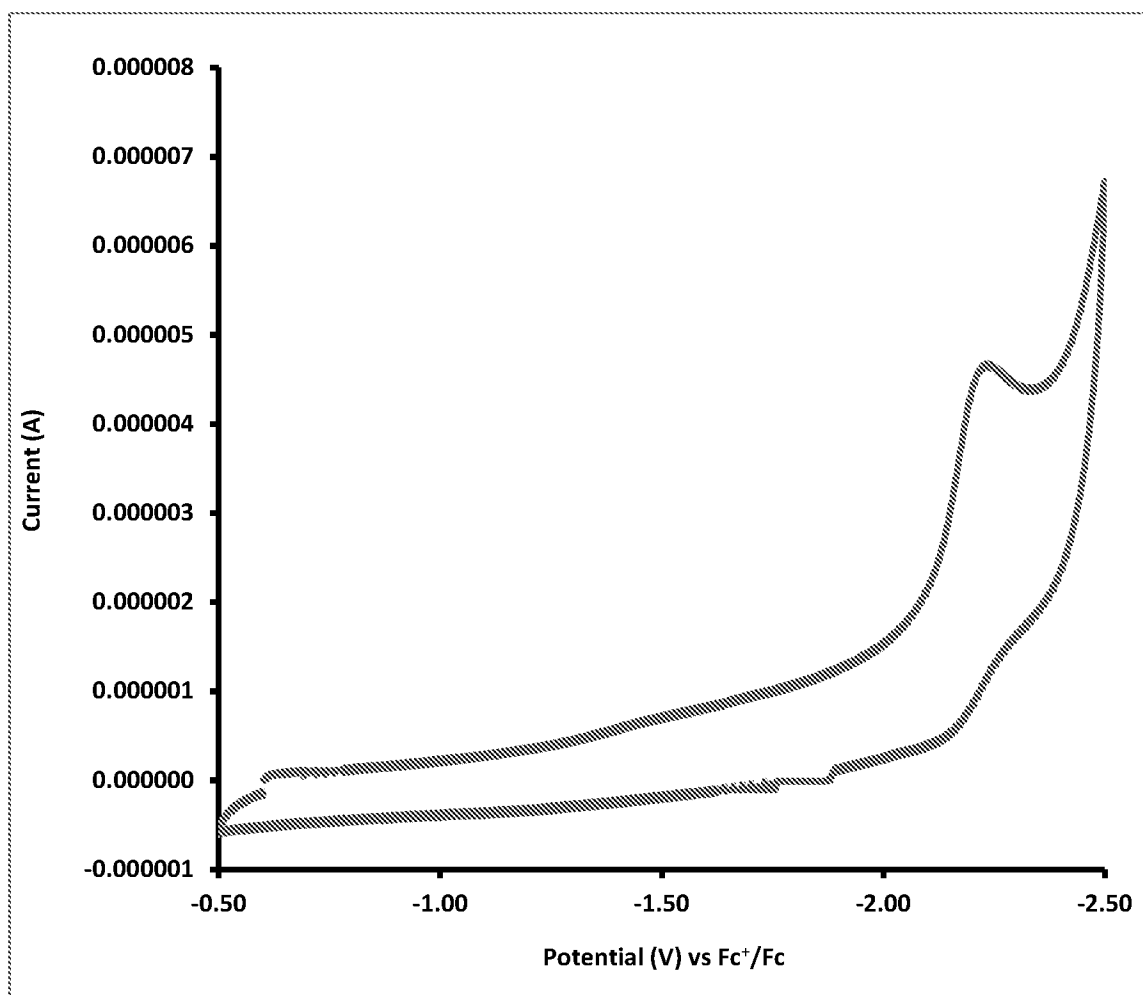
3/66

FIG. 3



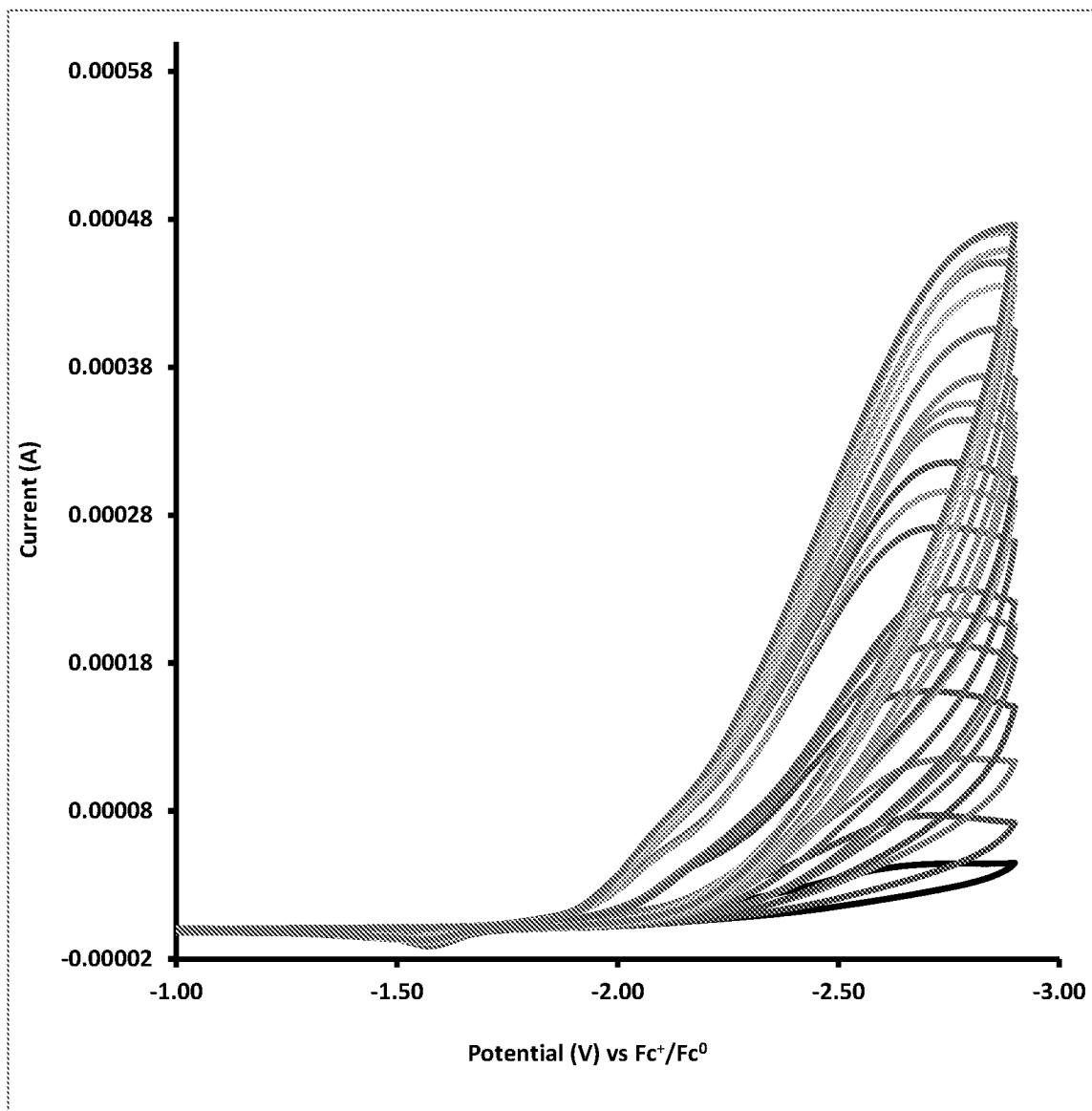
4/66

FIG. 4



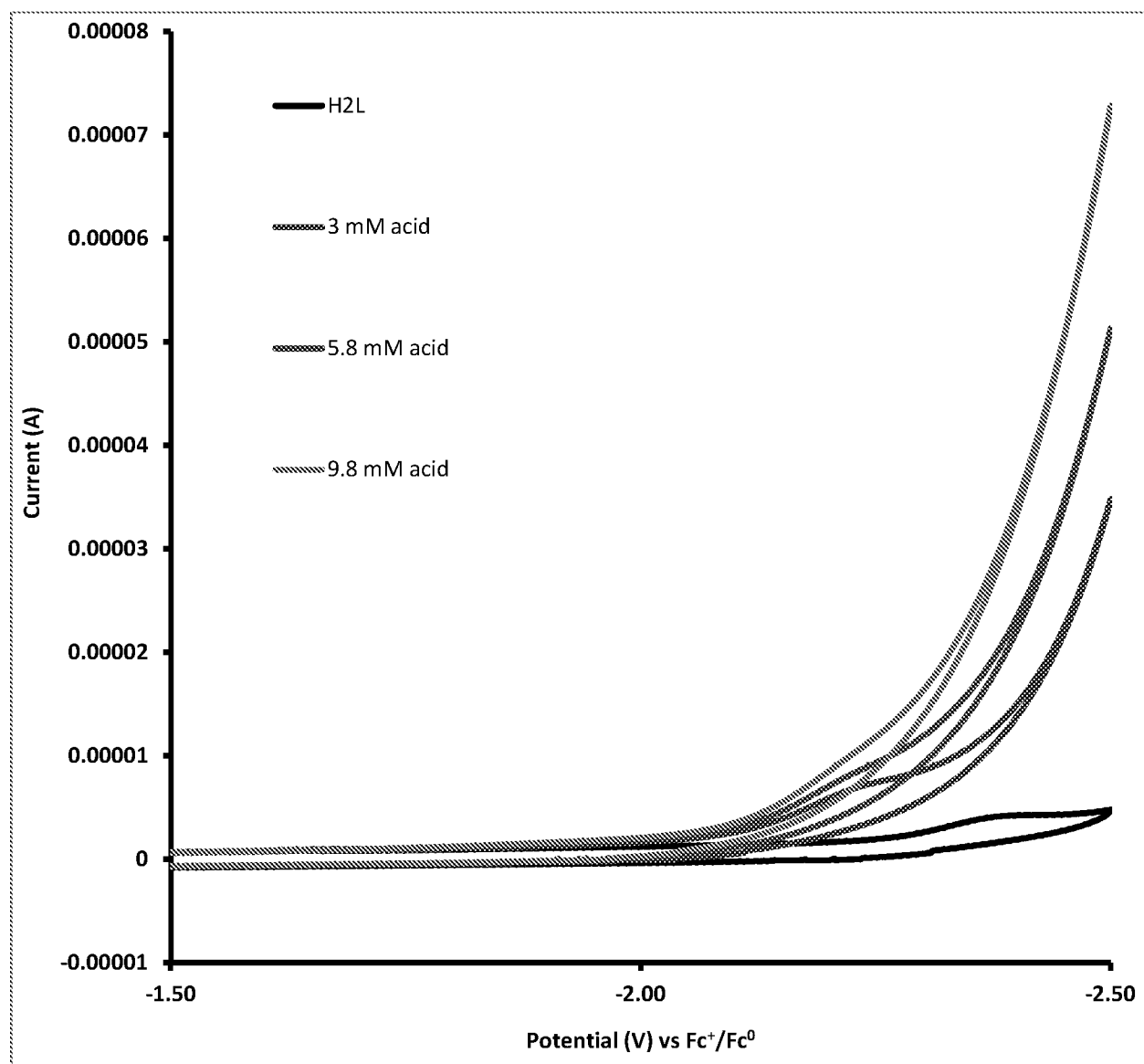
5/66

FIG. 5



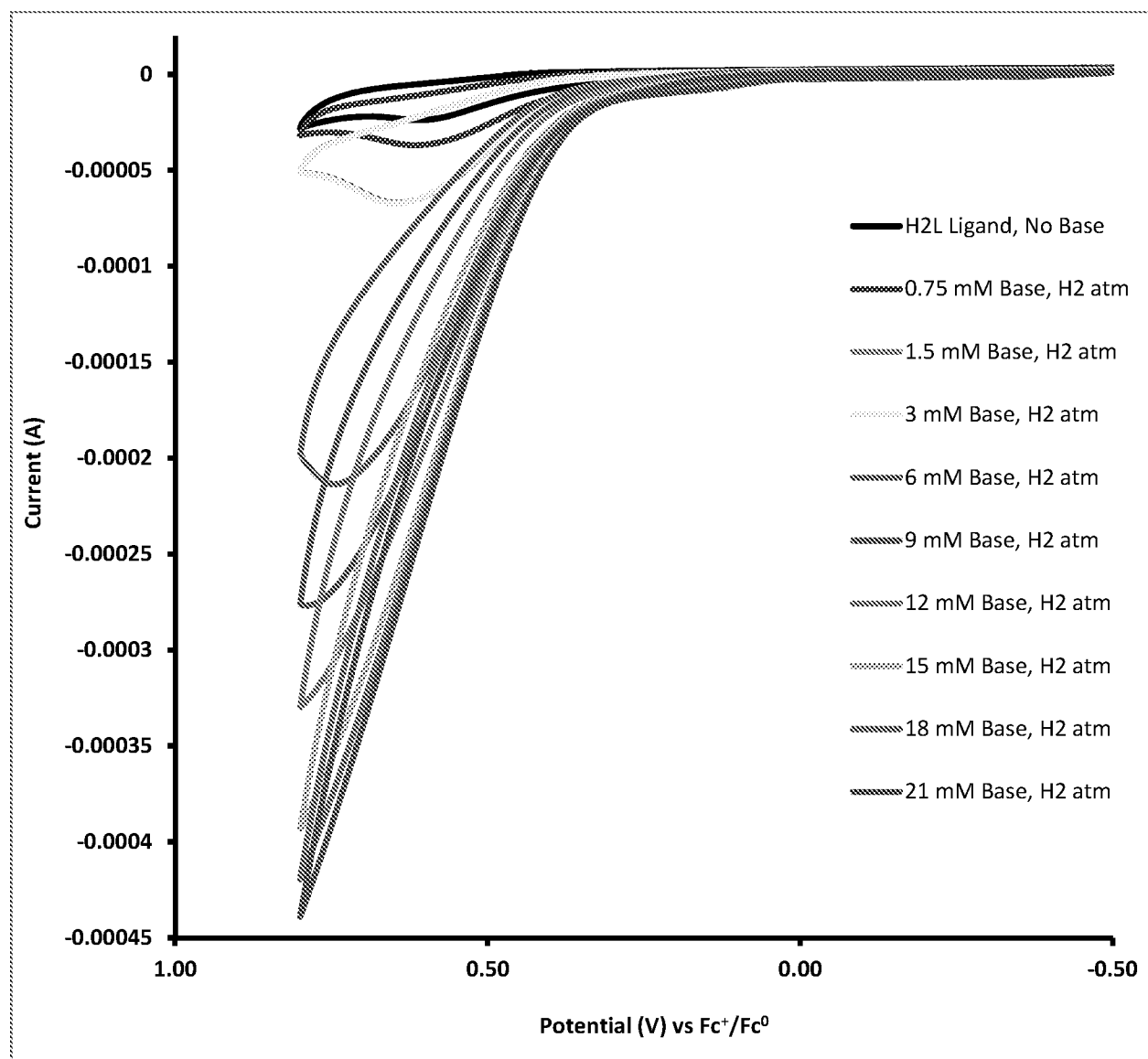
6/66

FIG. 6

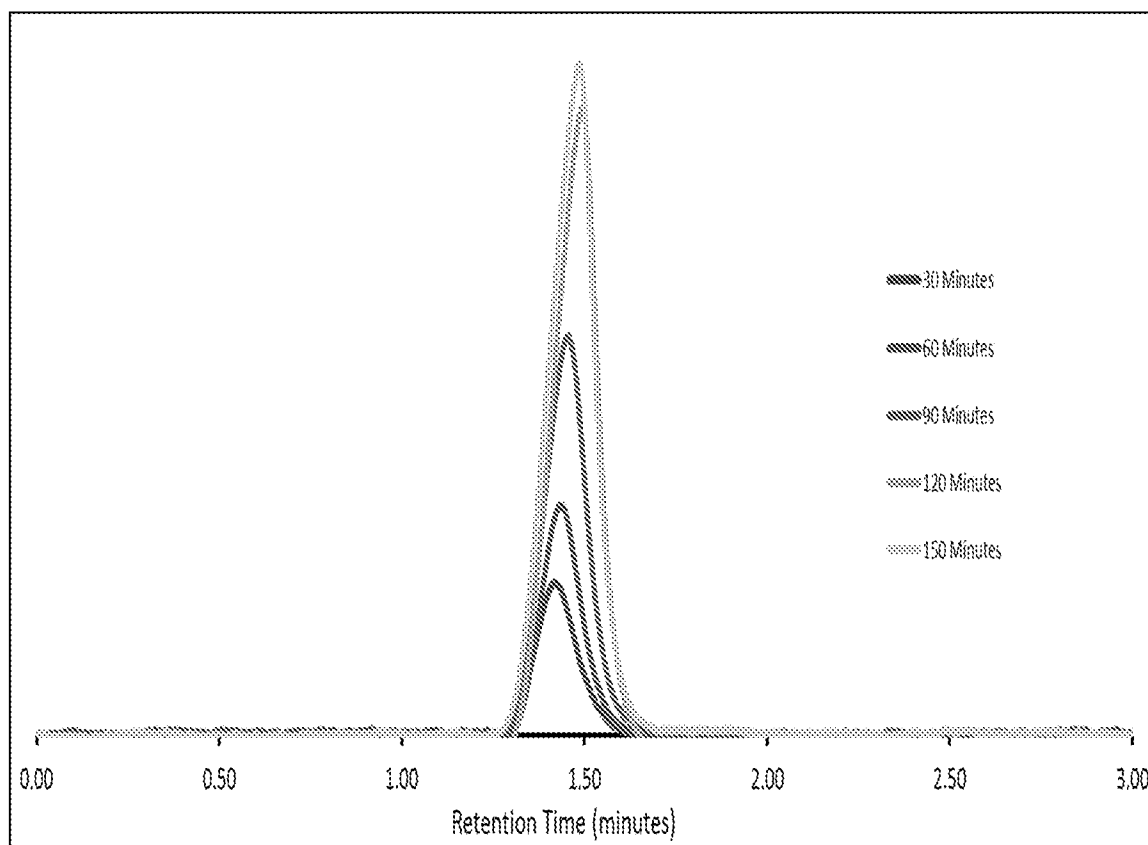


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FIG. 7

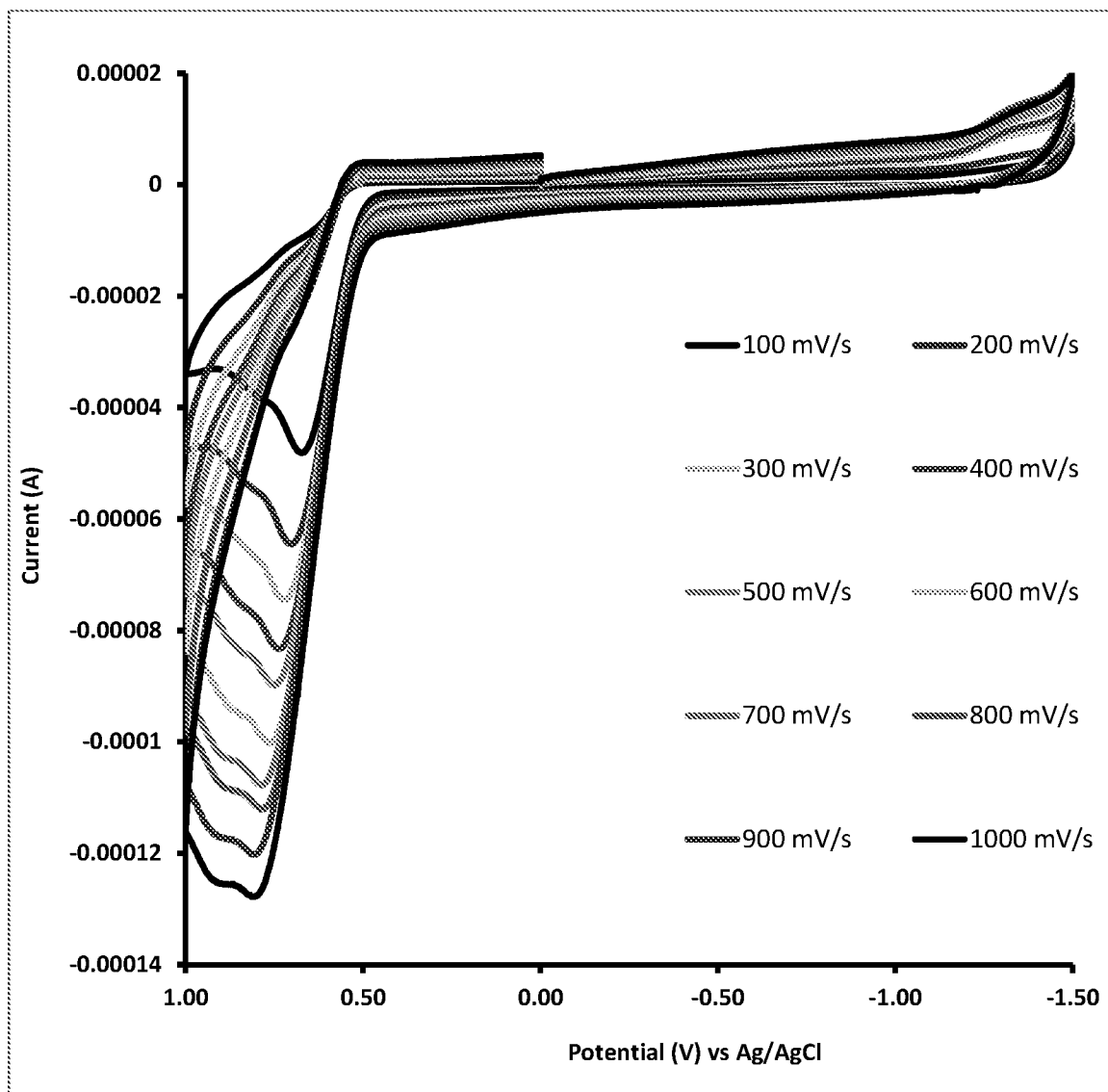


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FIG. 8

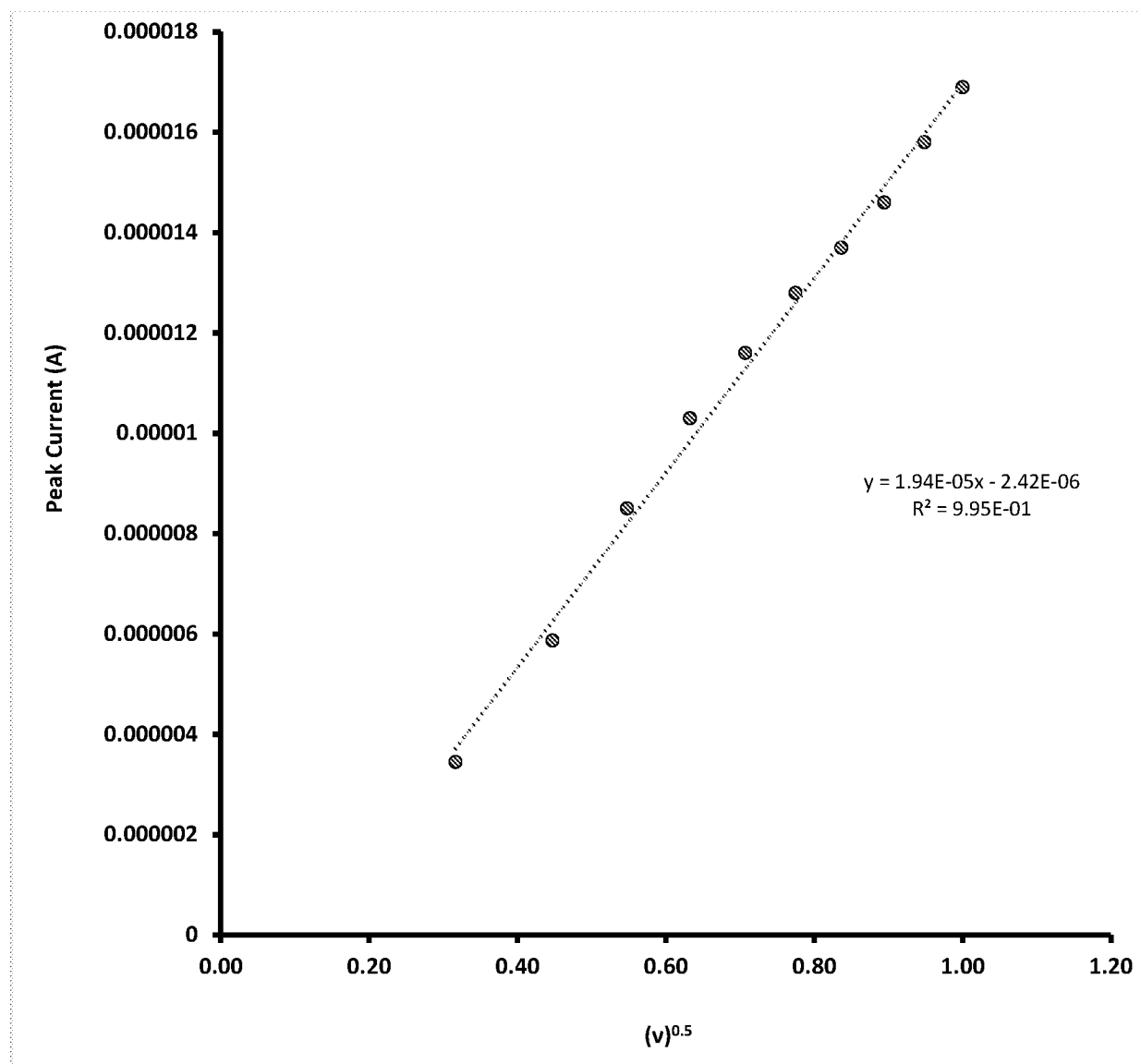
9/66

FIG. 9



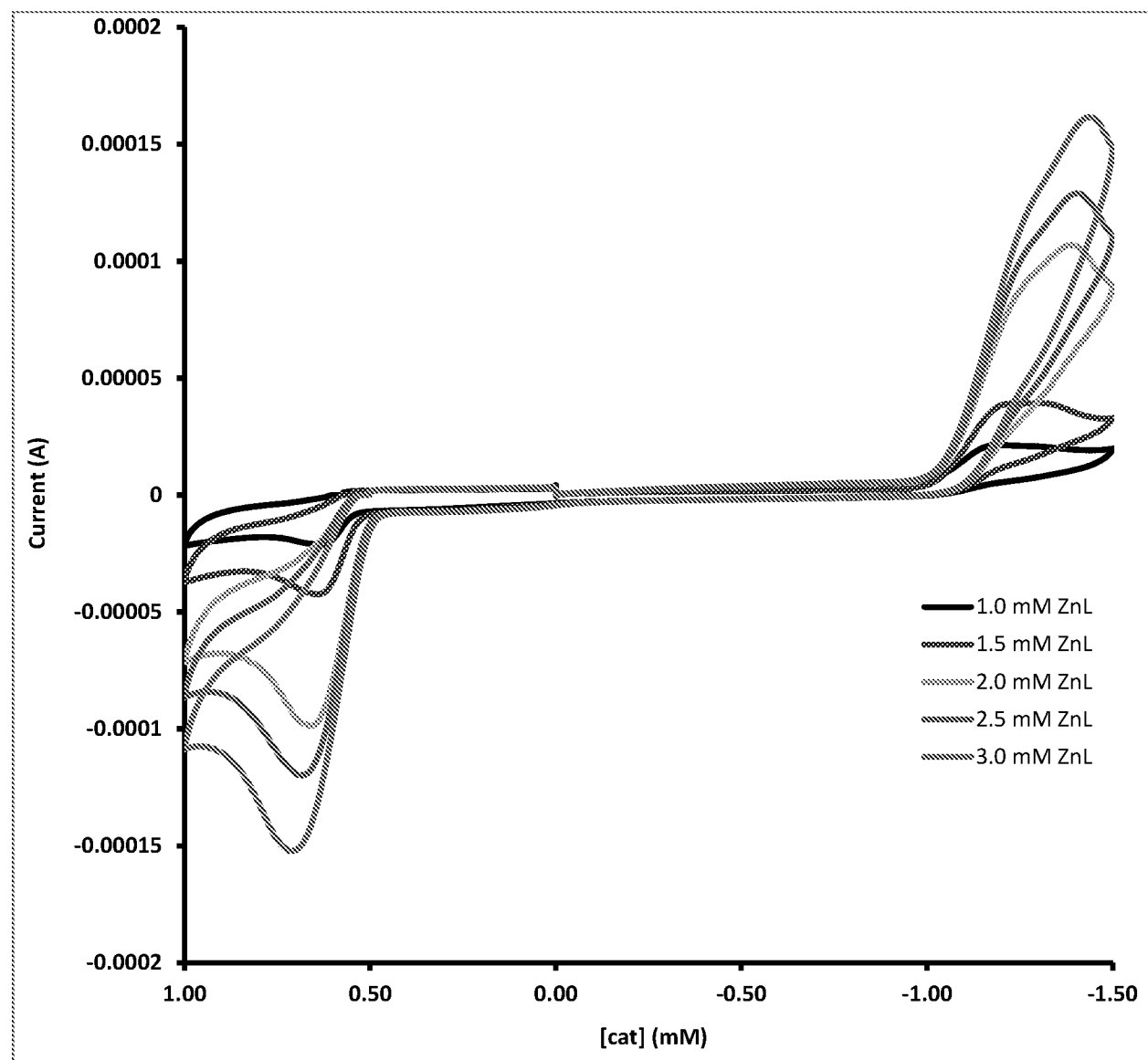
10/66

FIG. 10



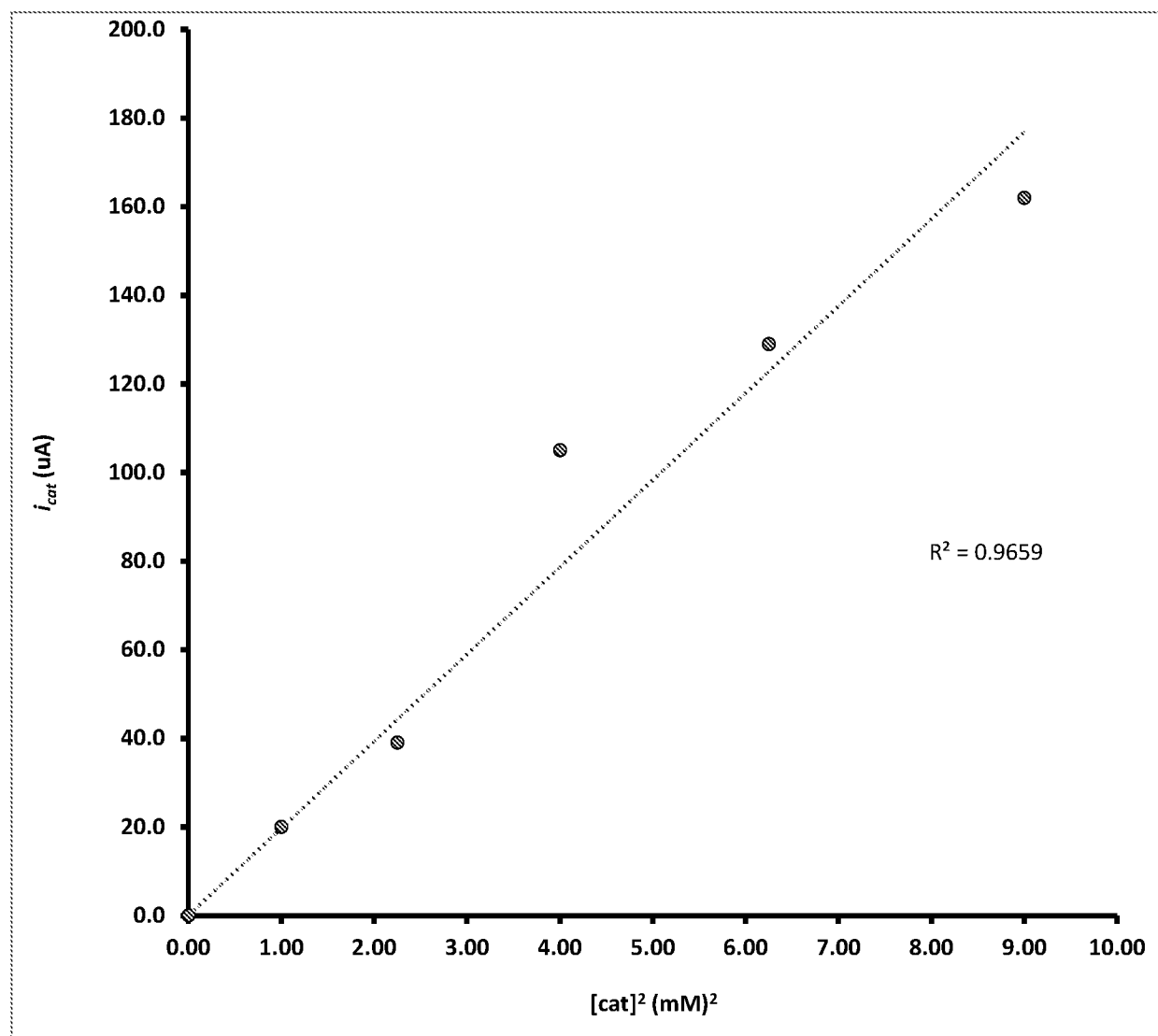
11/66

FIG. 11



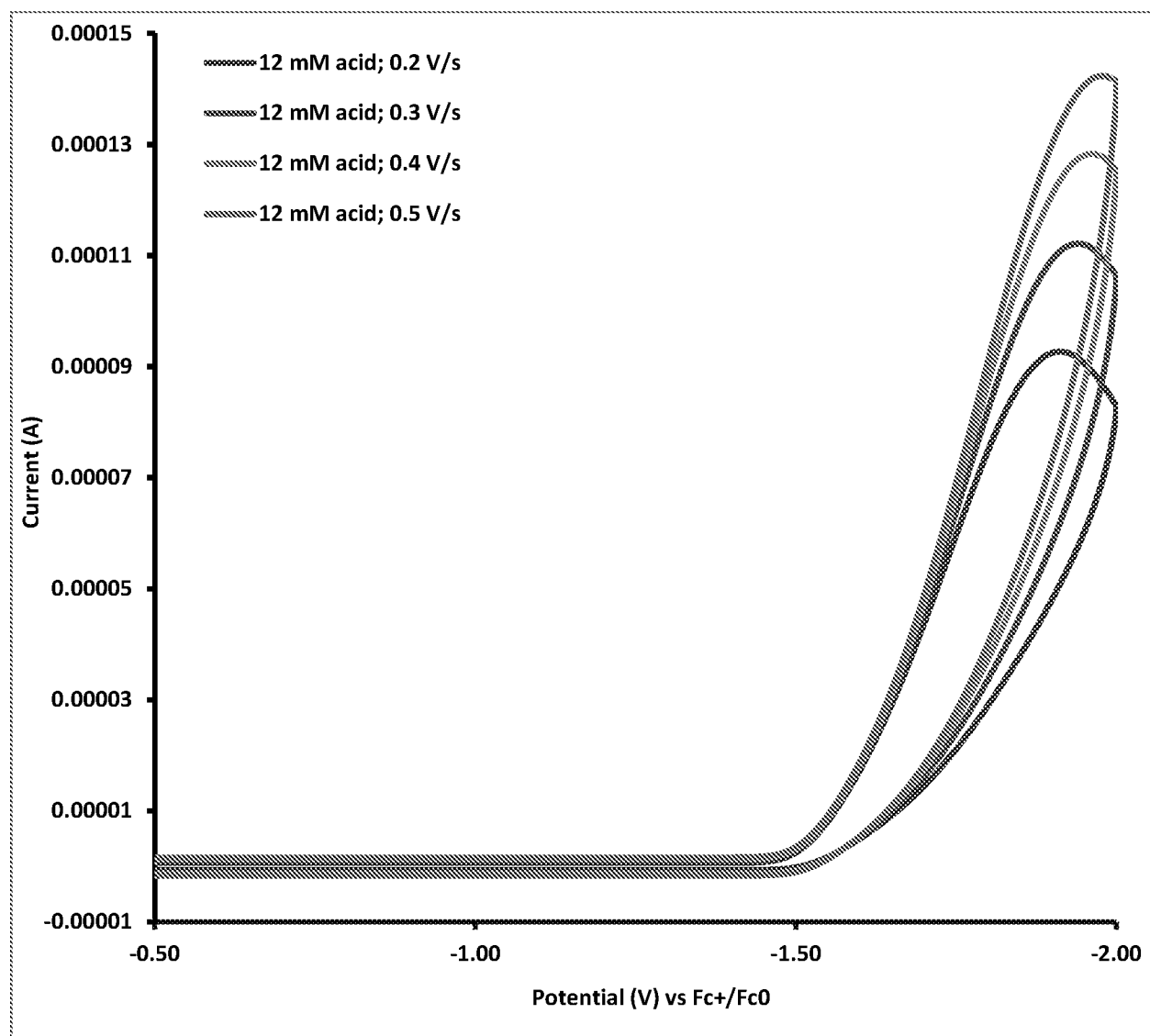
12/66

FIG. 12



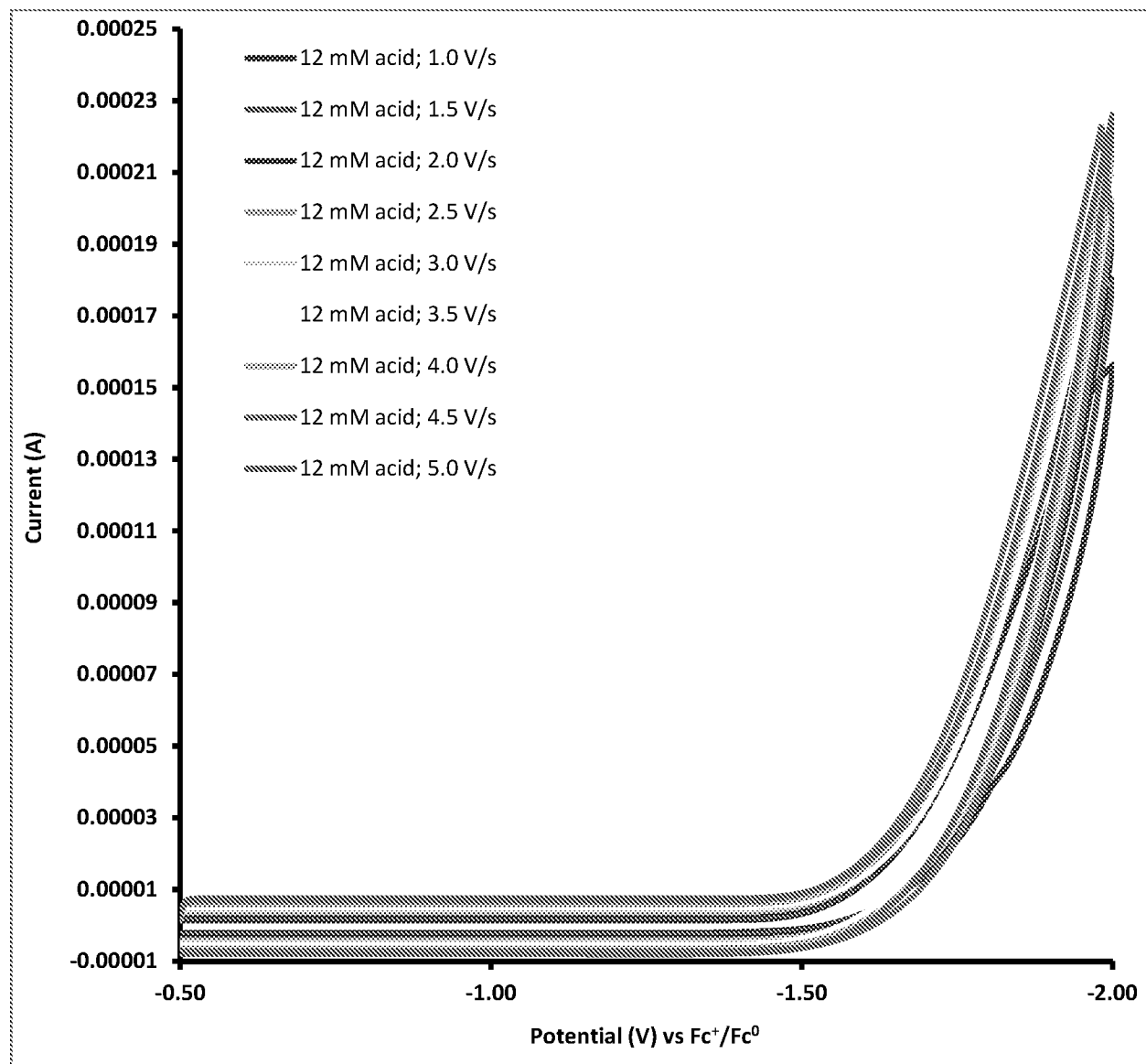
13/66

FIG. 13



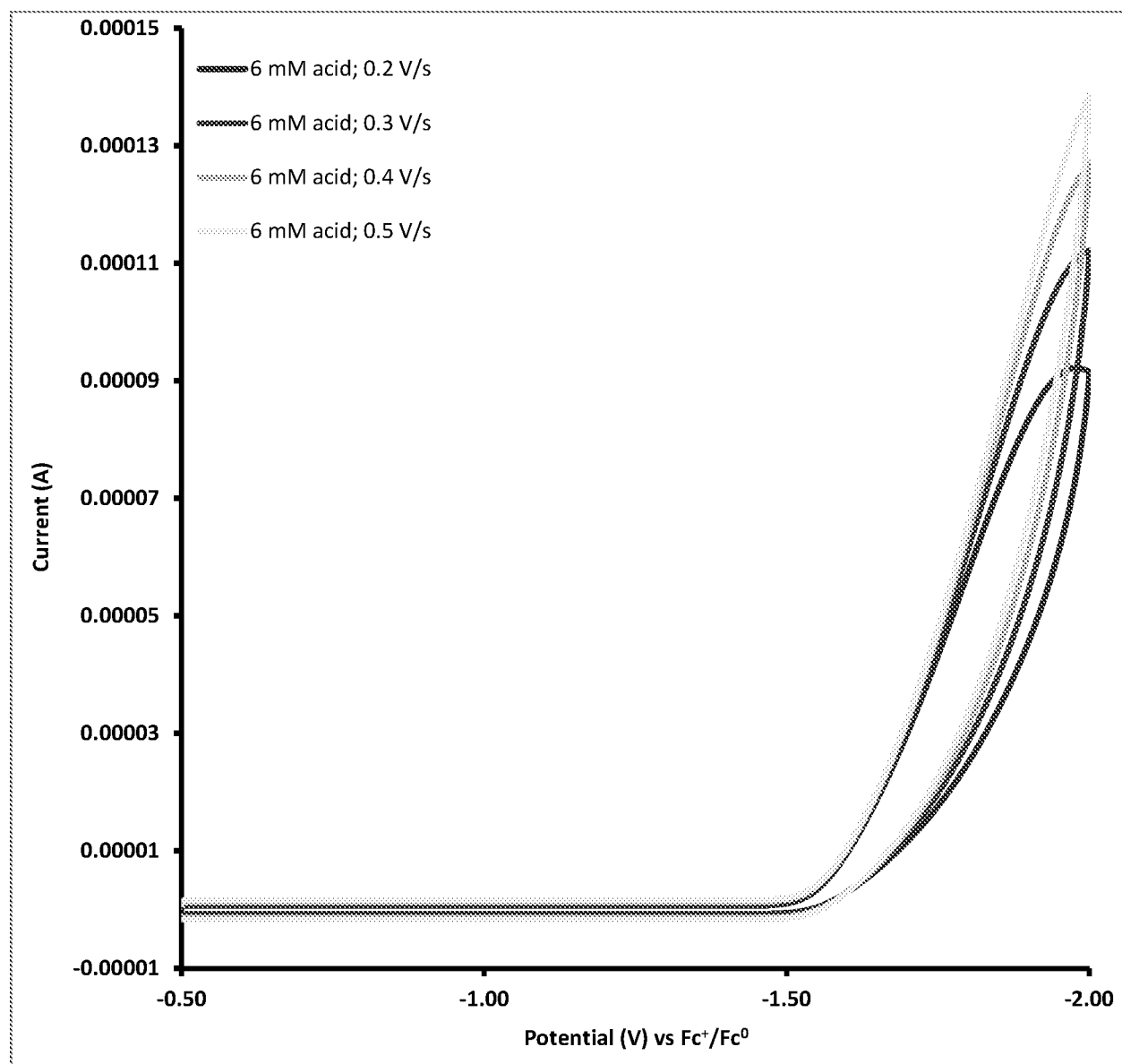
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FIG. 14



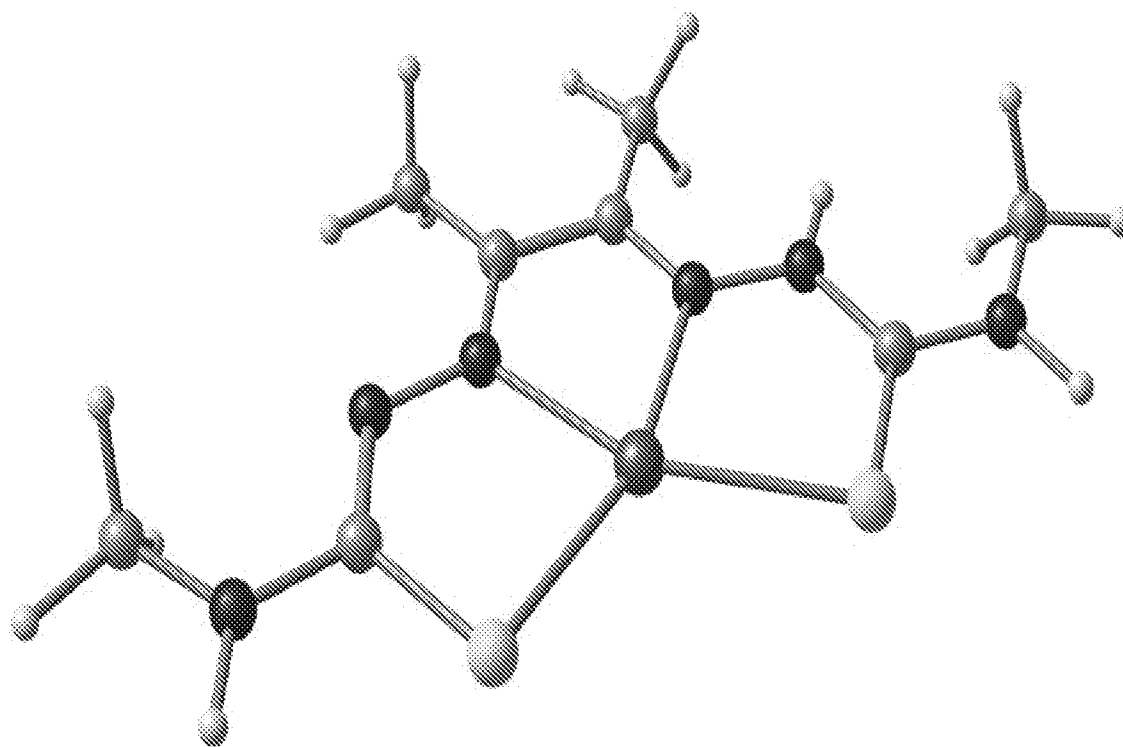
15/66

FIG. 15



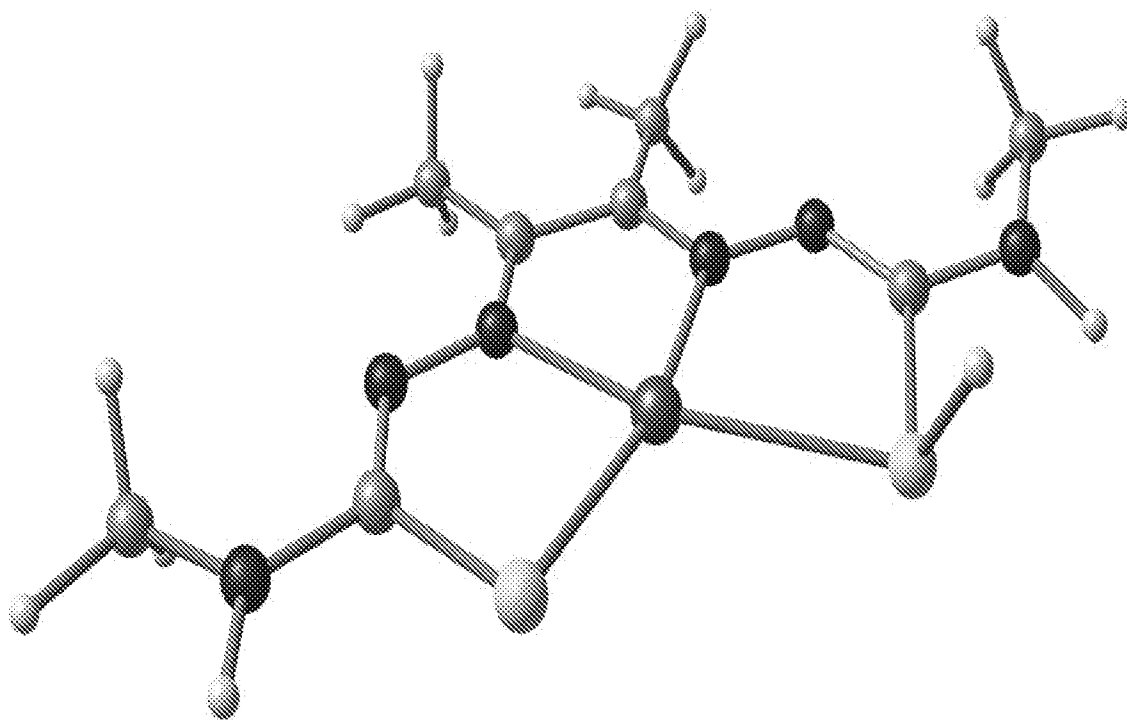
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FIG. 16



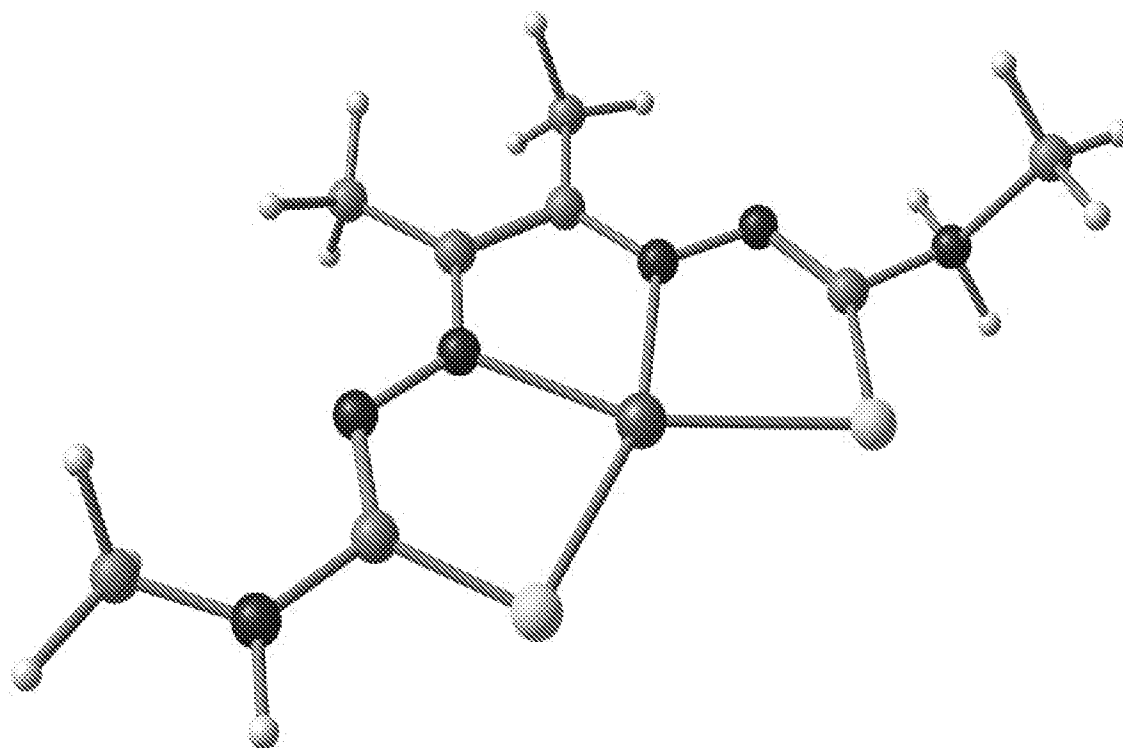
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FIG. 17

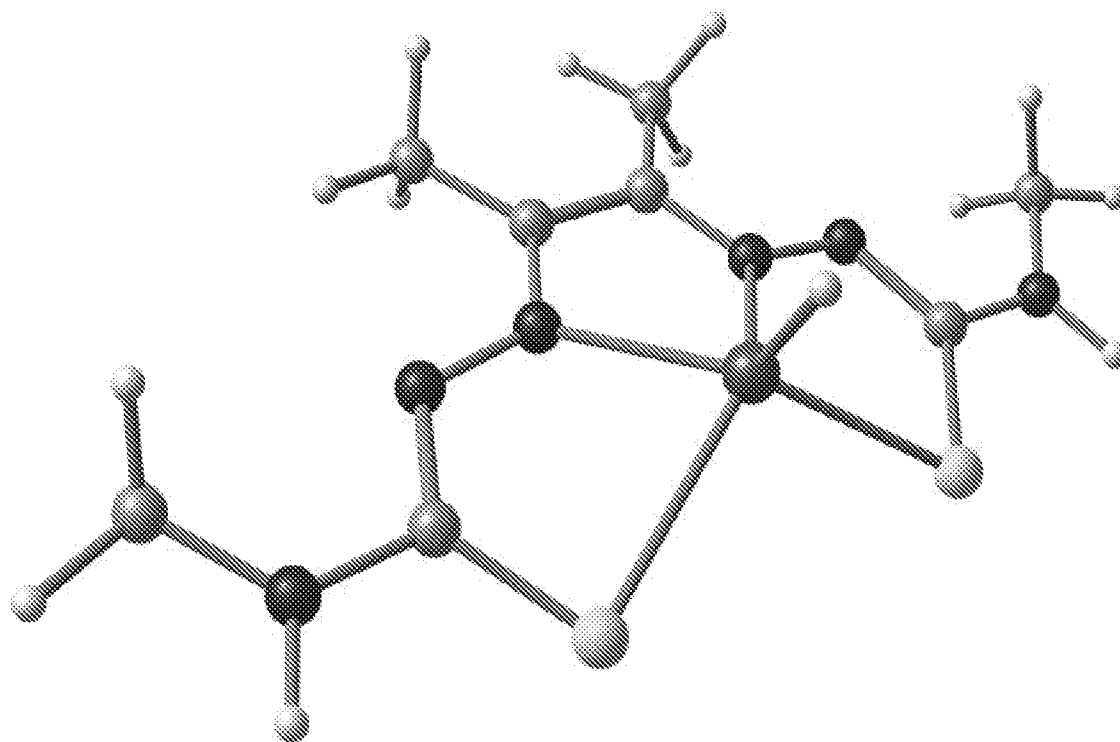


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FIG. 18



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FIG. 19

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FIG. 20

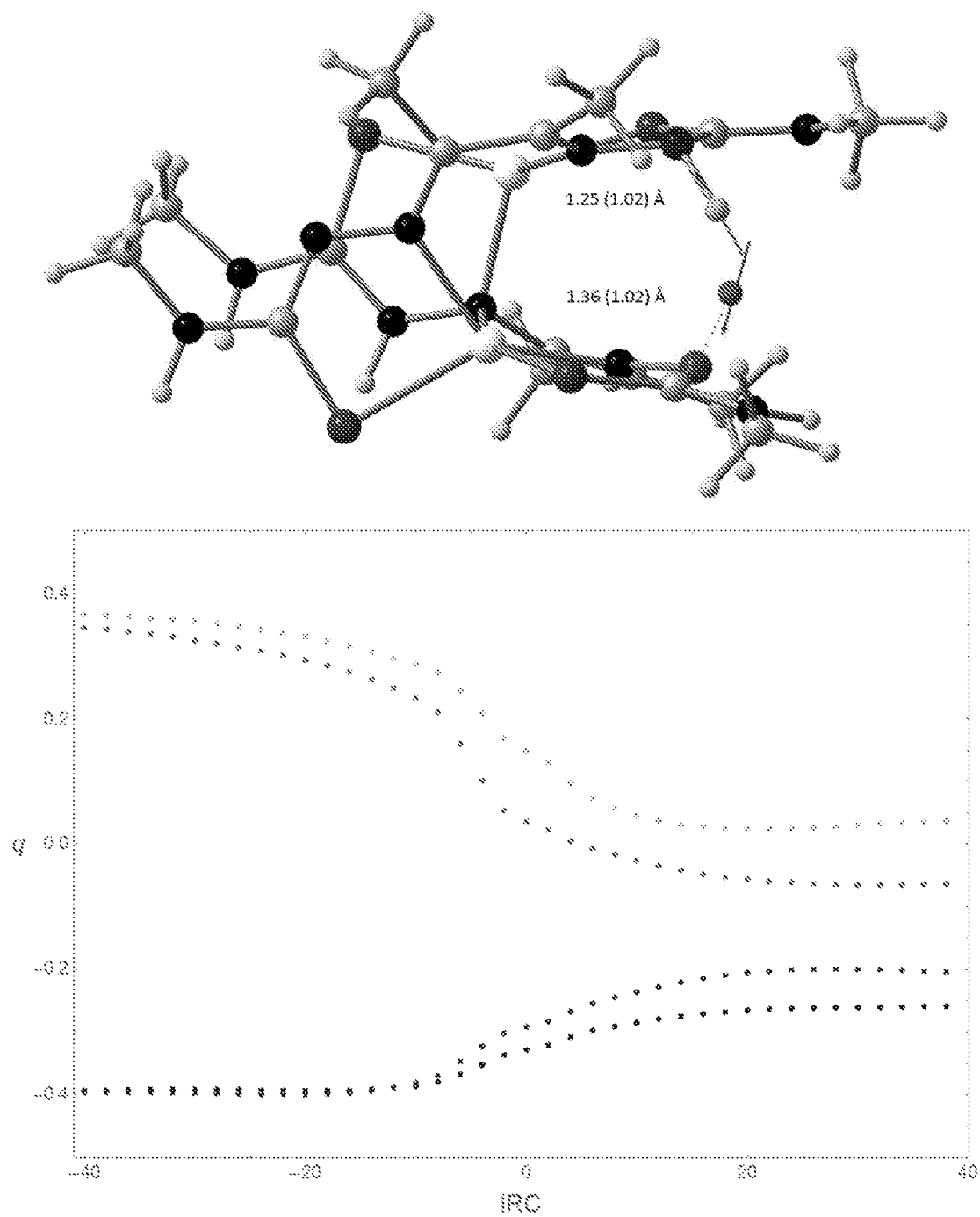
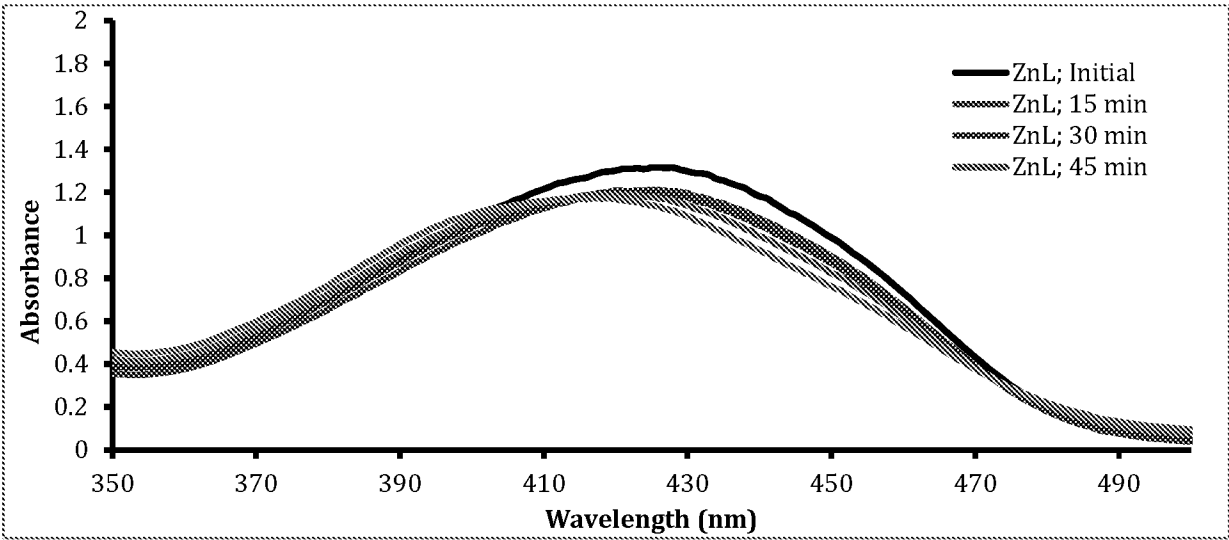
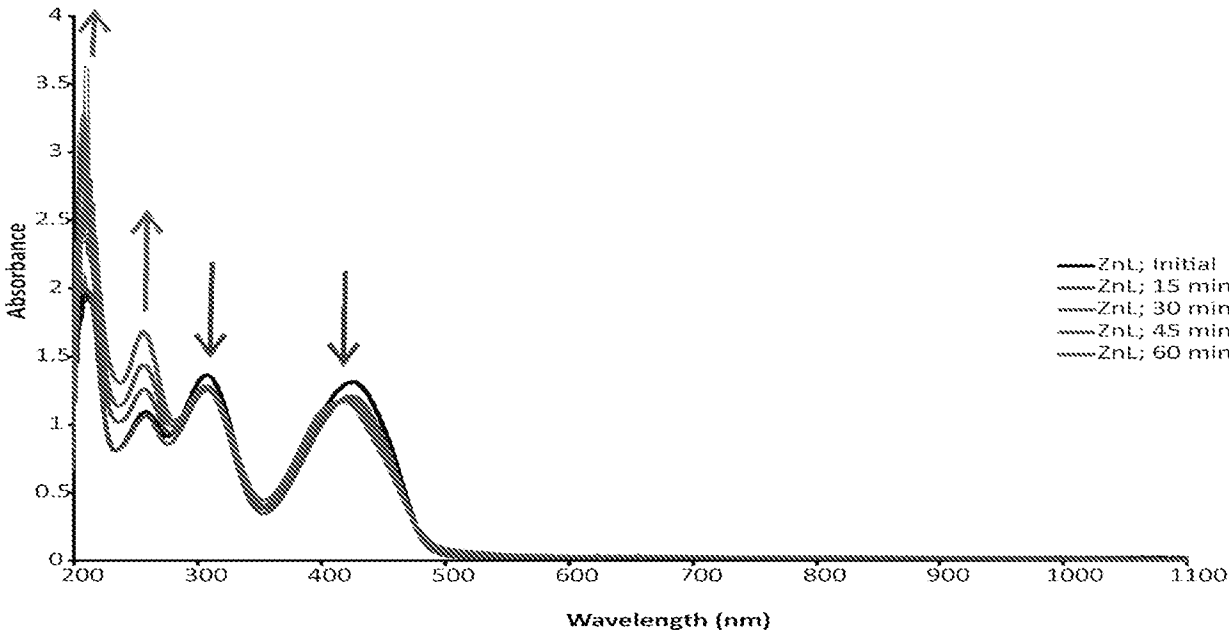
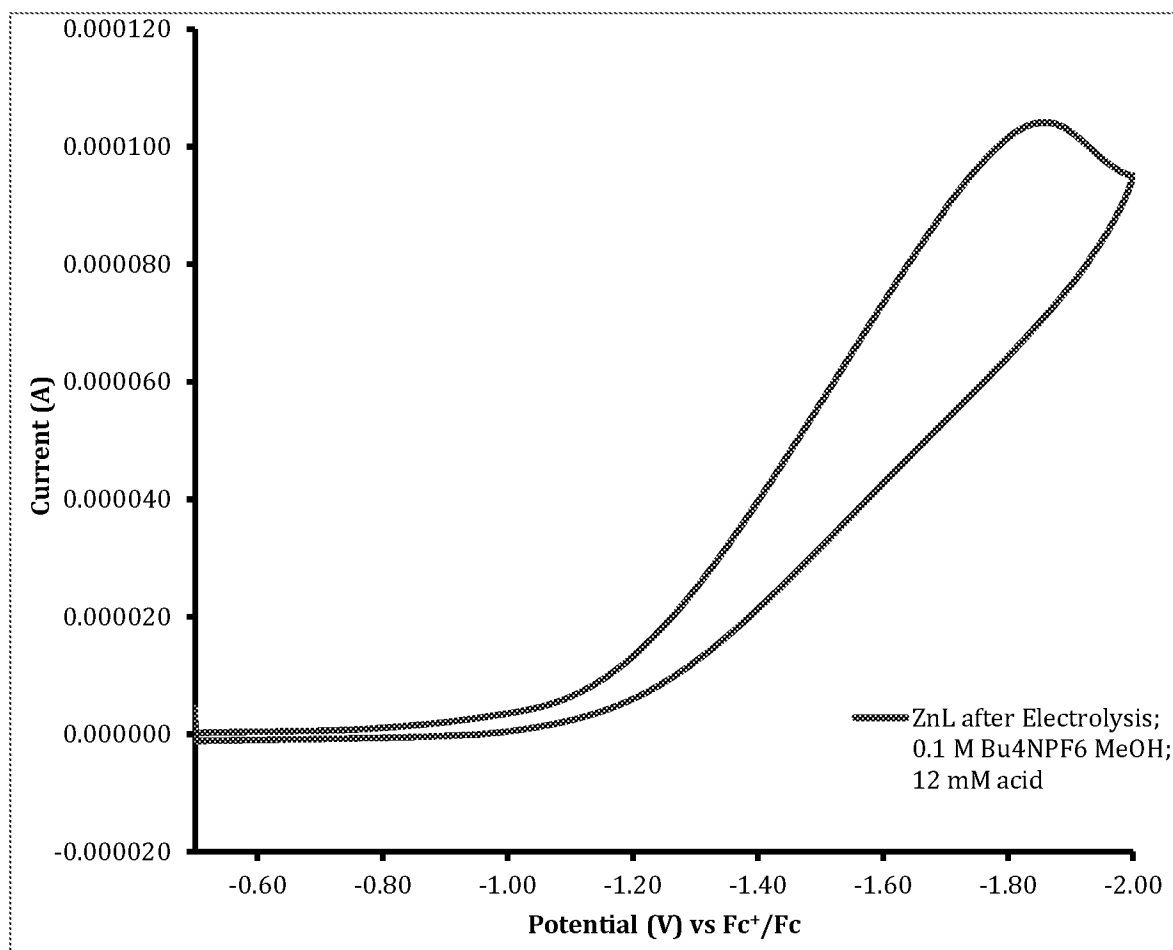


FIG. 21



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FIG. 22

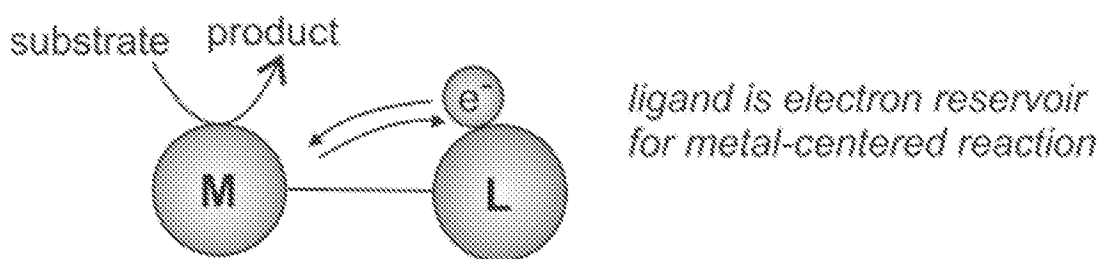


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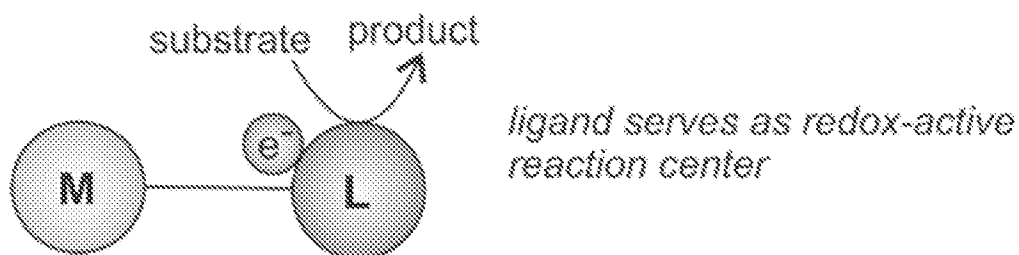
FIG. 23

Ligand Non-Innocence in Catalysis

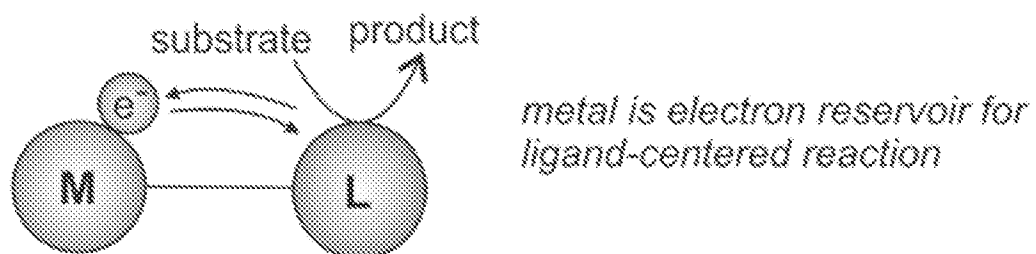
Ligand-Assisted Metal-Centered Reactivity



Ligand-Centered Reactivity

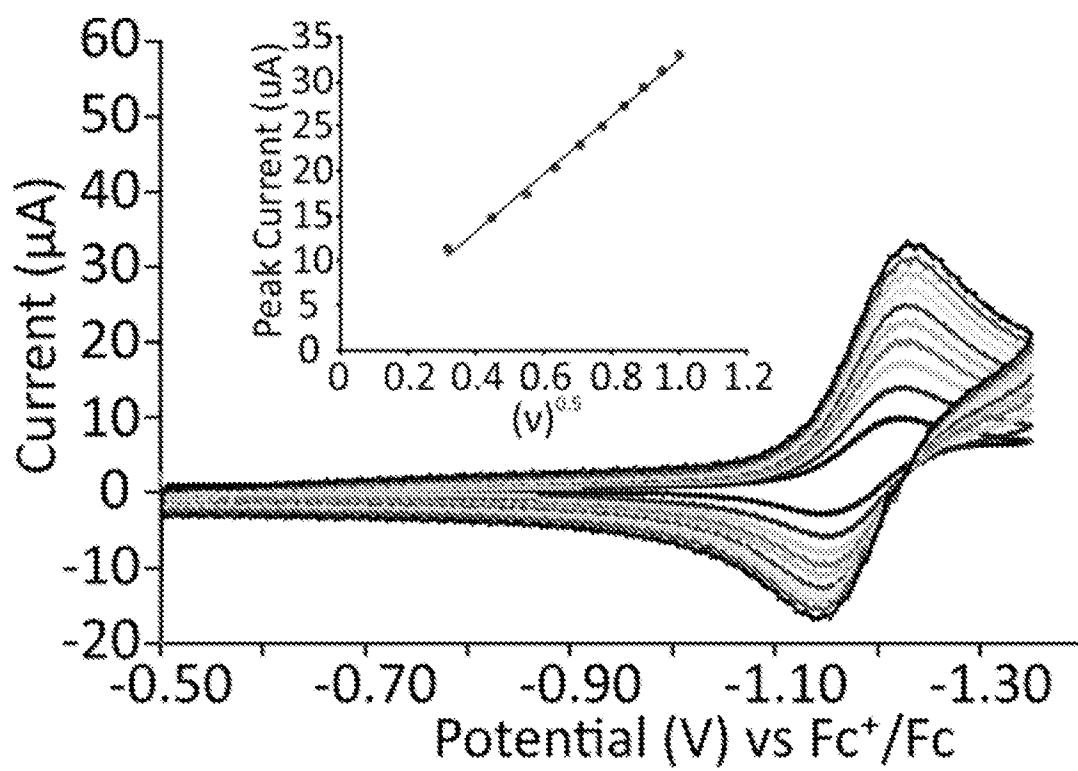


Metal-Assisted Ligand-Centered Reactivity



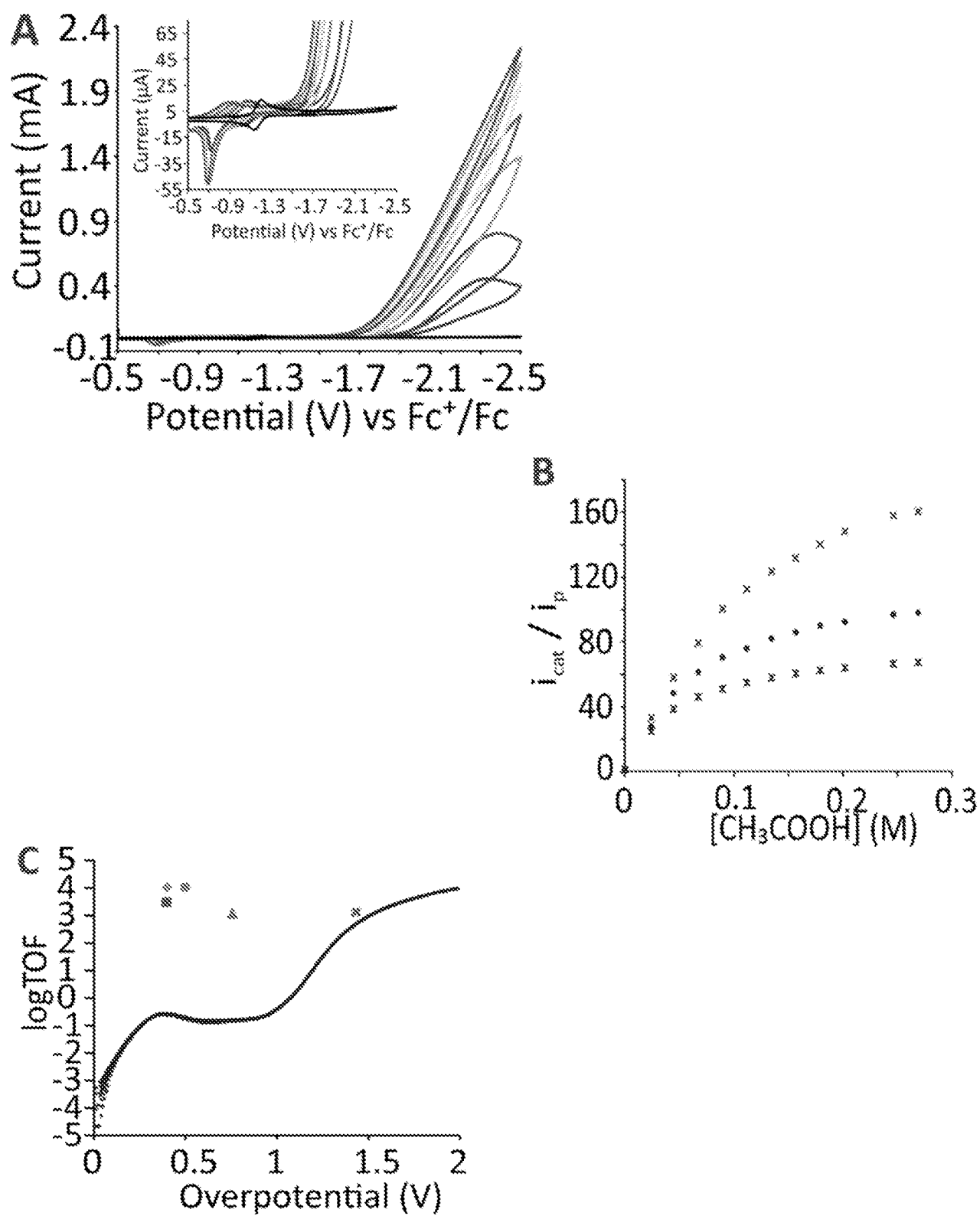
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FIG. 24



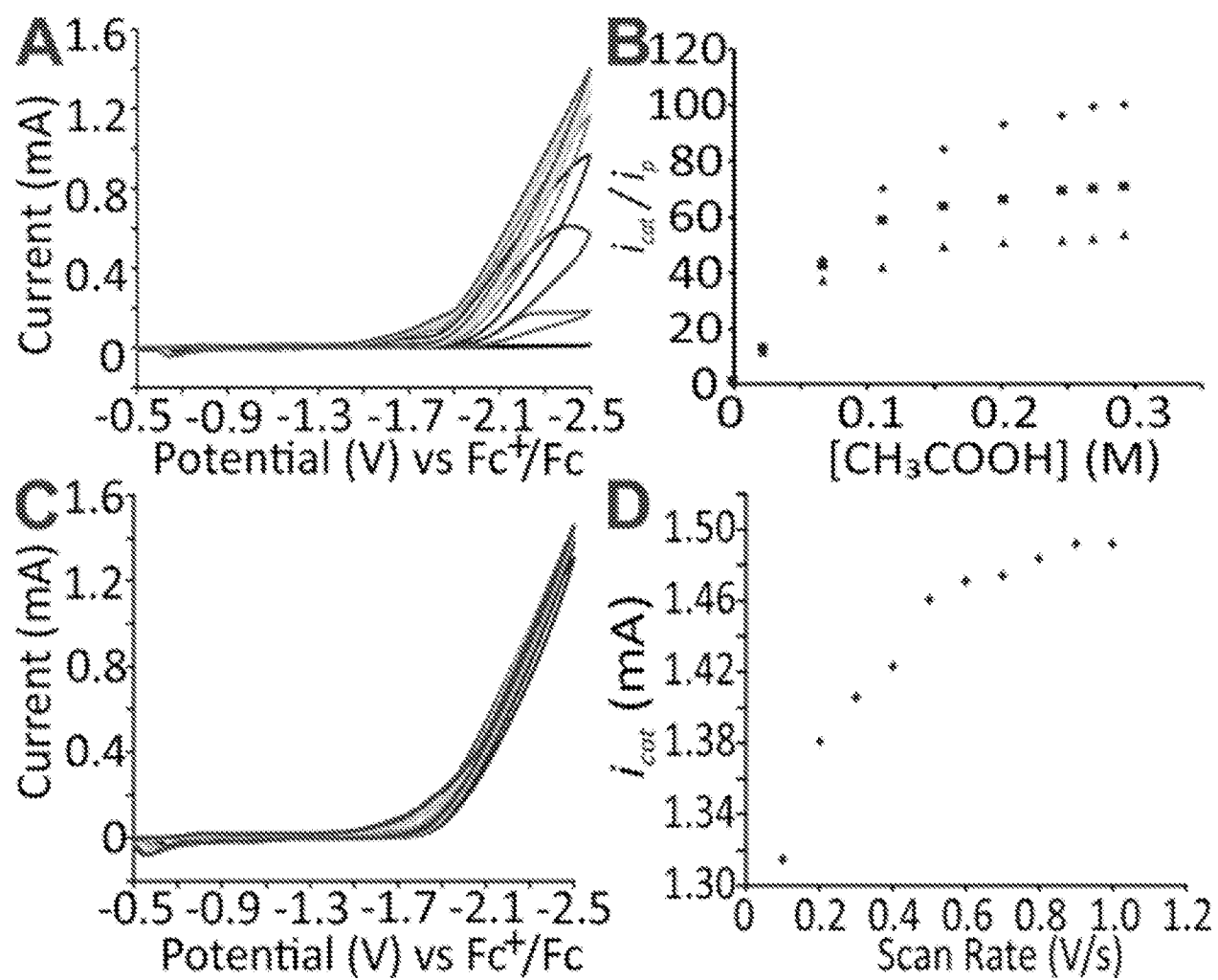
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FIG. 25



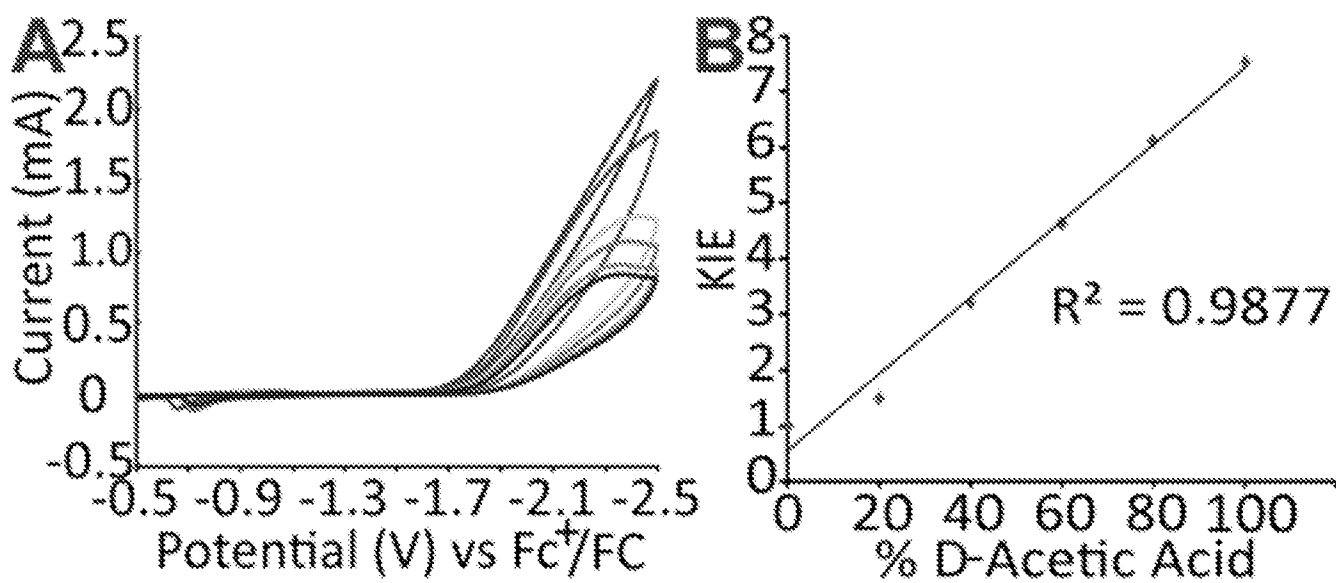
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FIG. 26

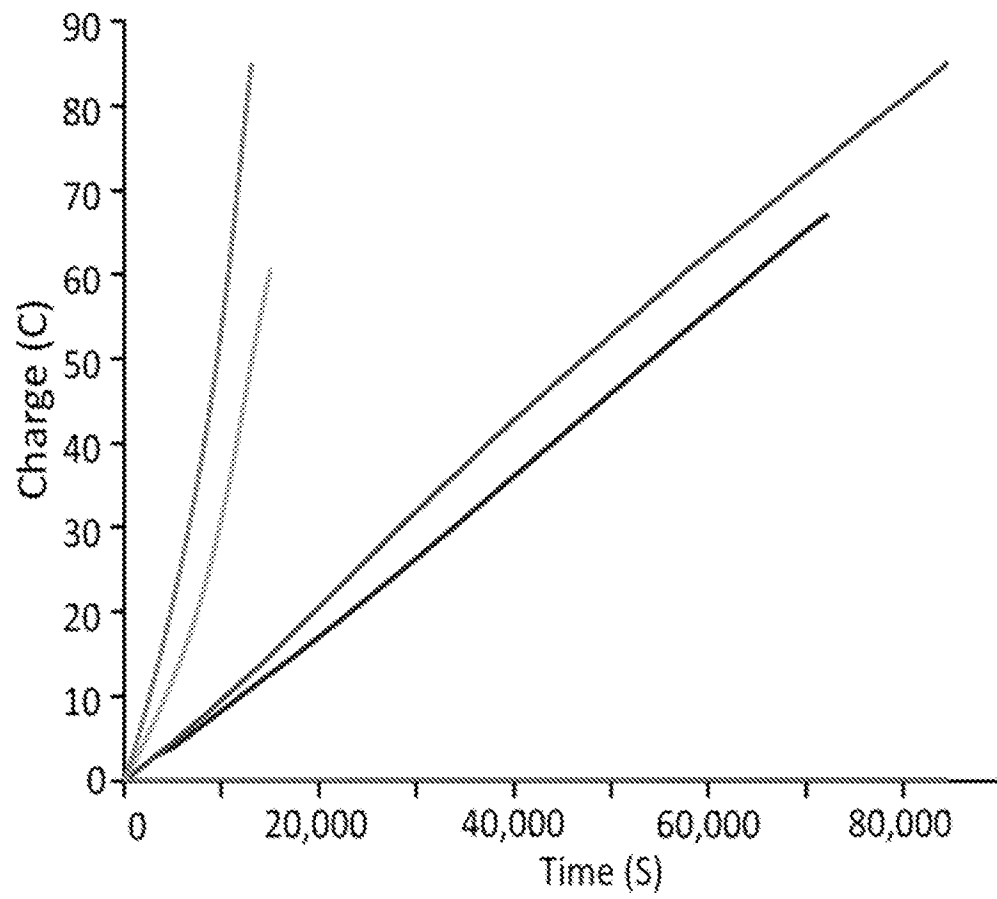


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FIG. 27

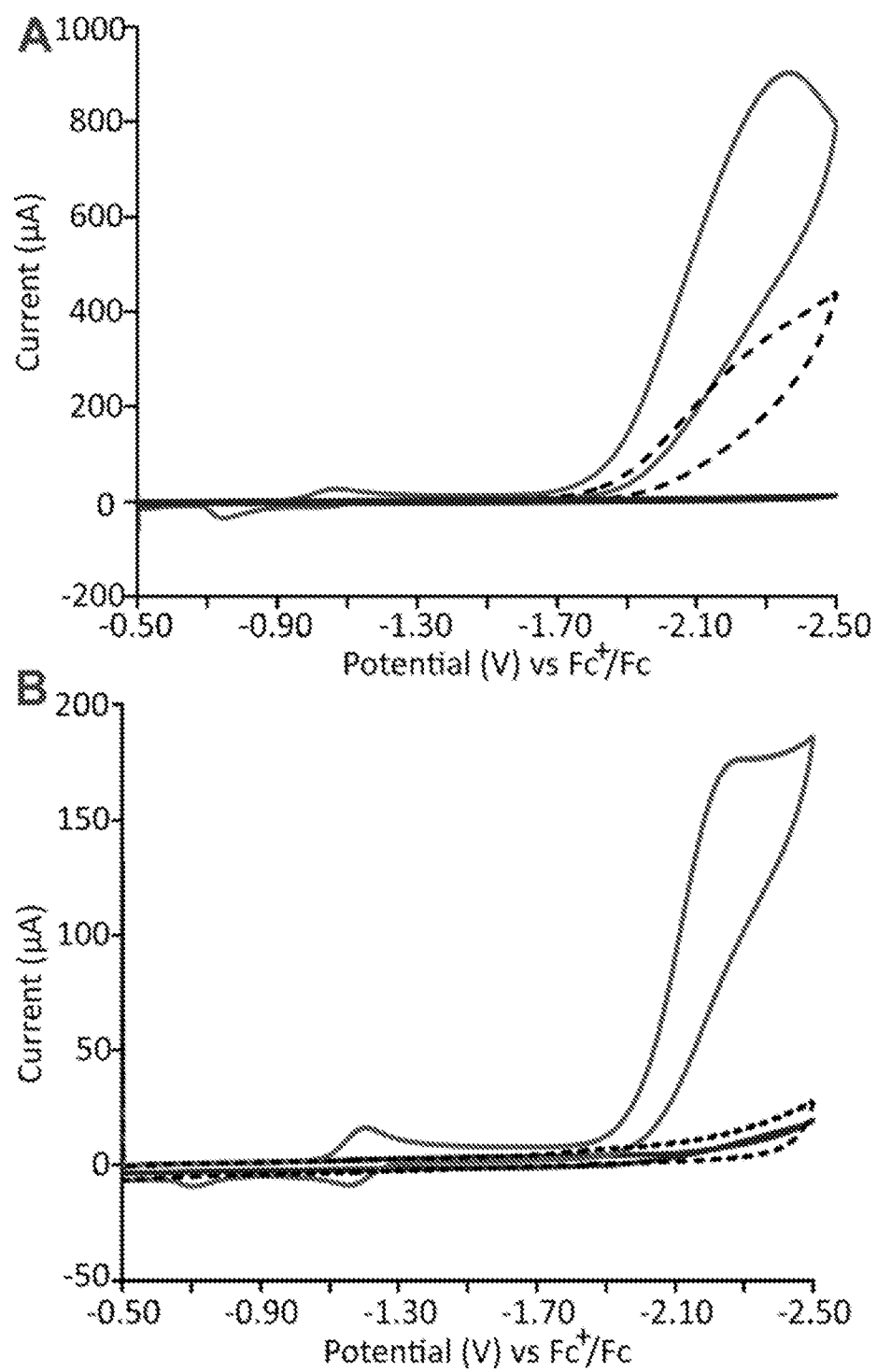


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FIG. 28

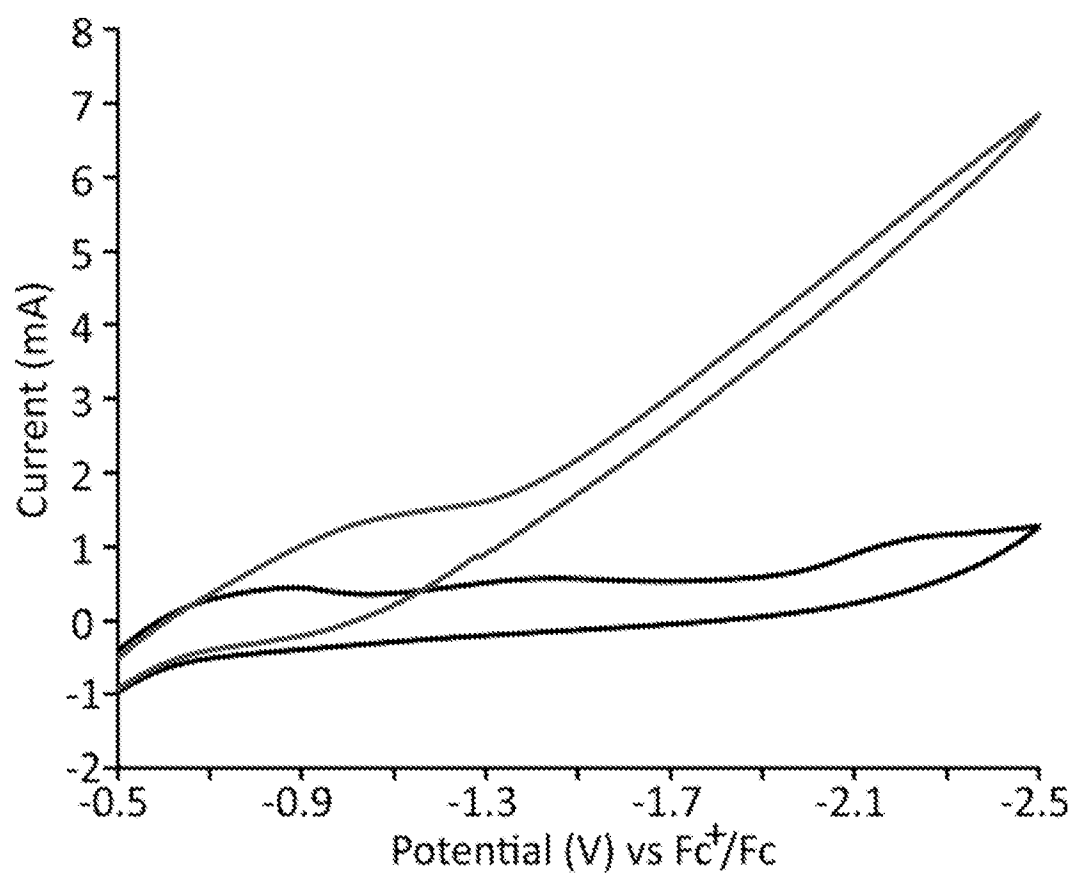
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FIG. 29



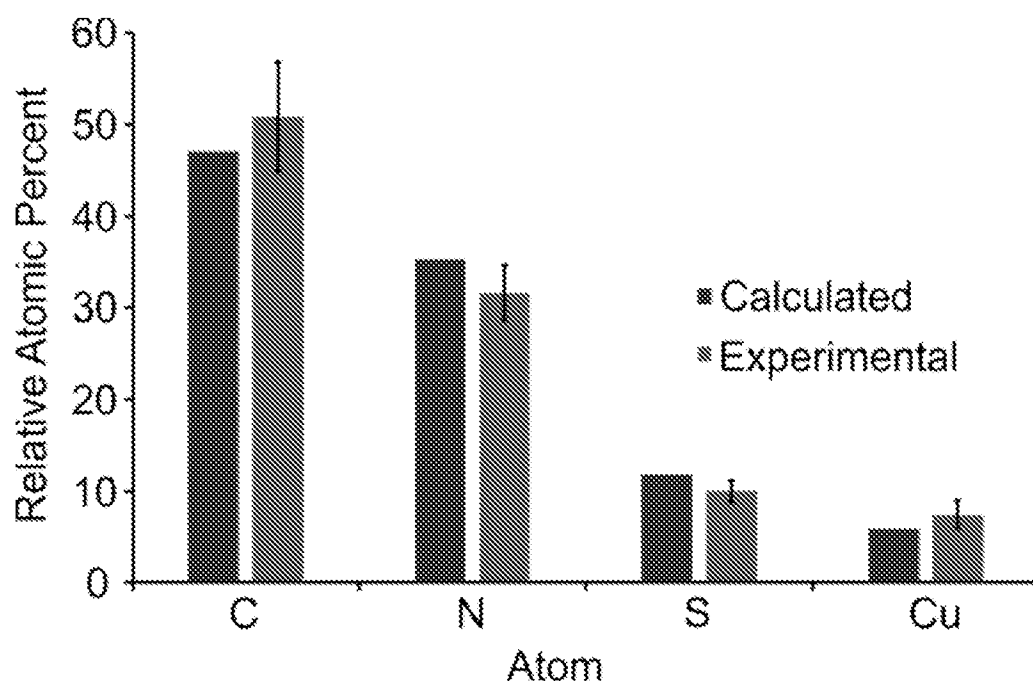
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FIG. 30



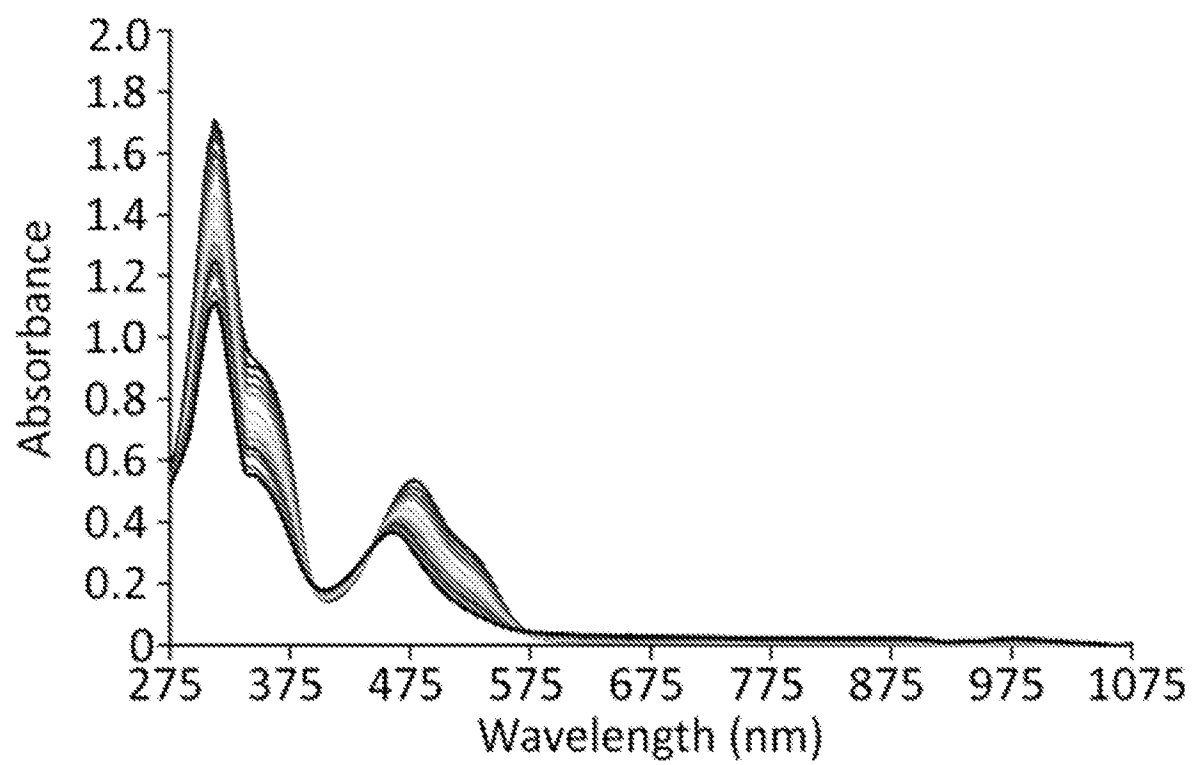
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FIG. 31



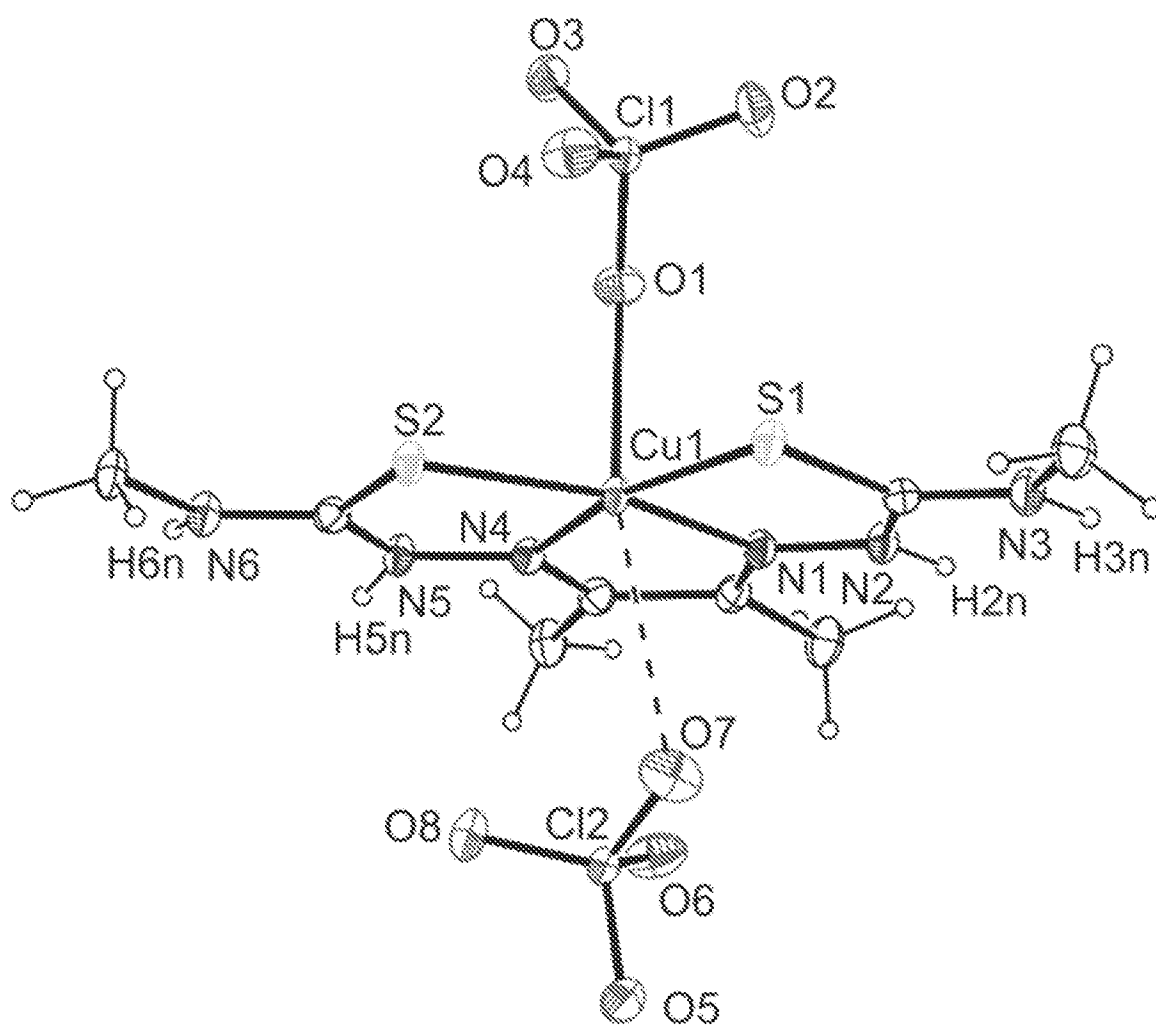
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FIG. 32



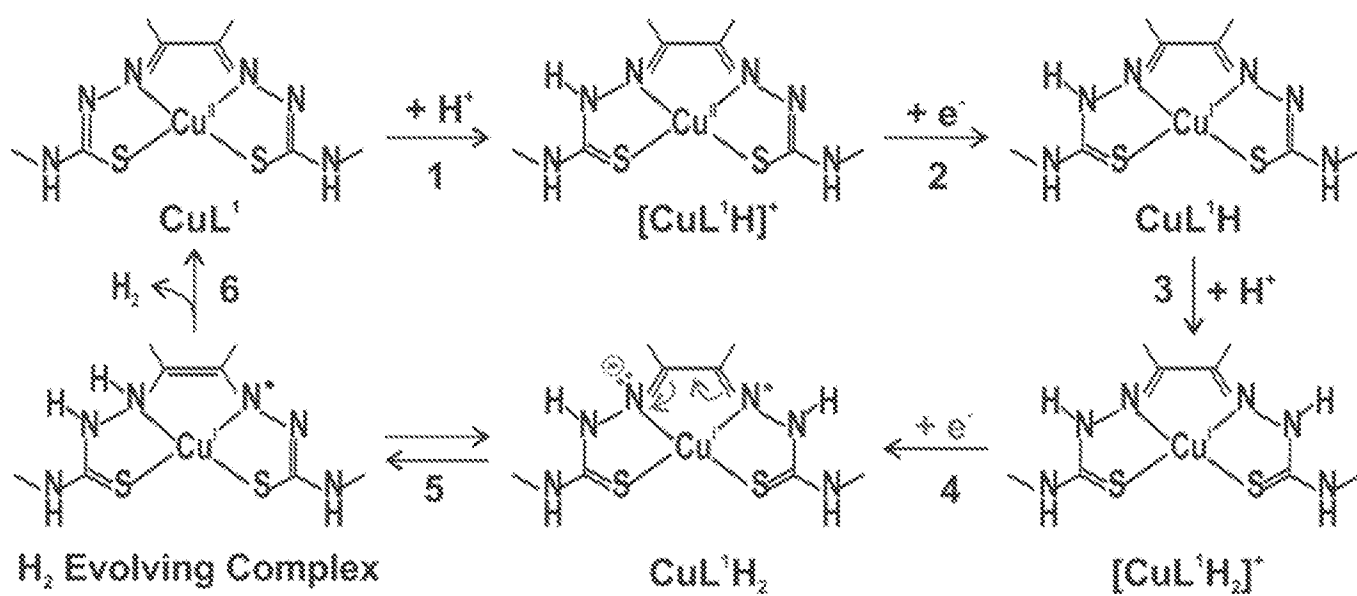
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FIG. 33



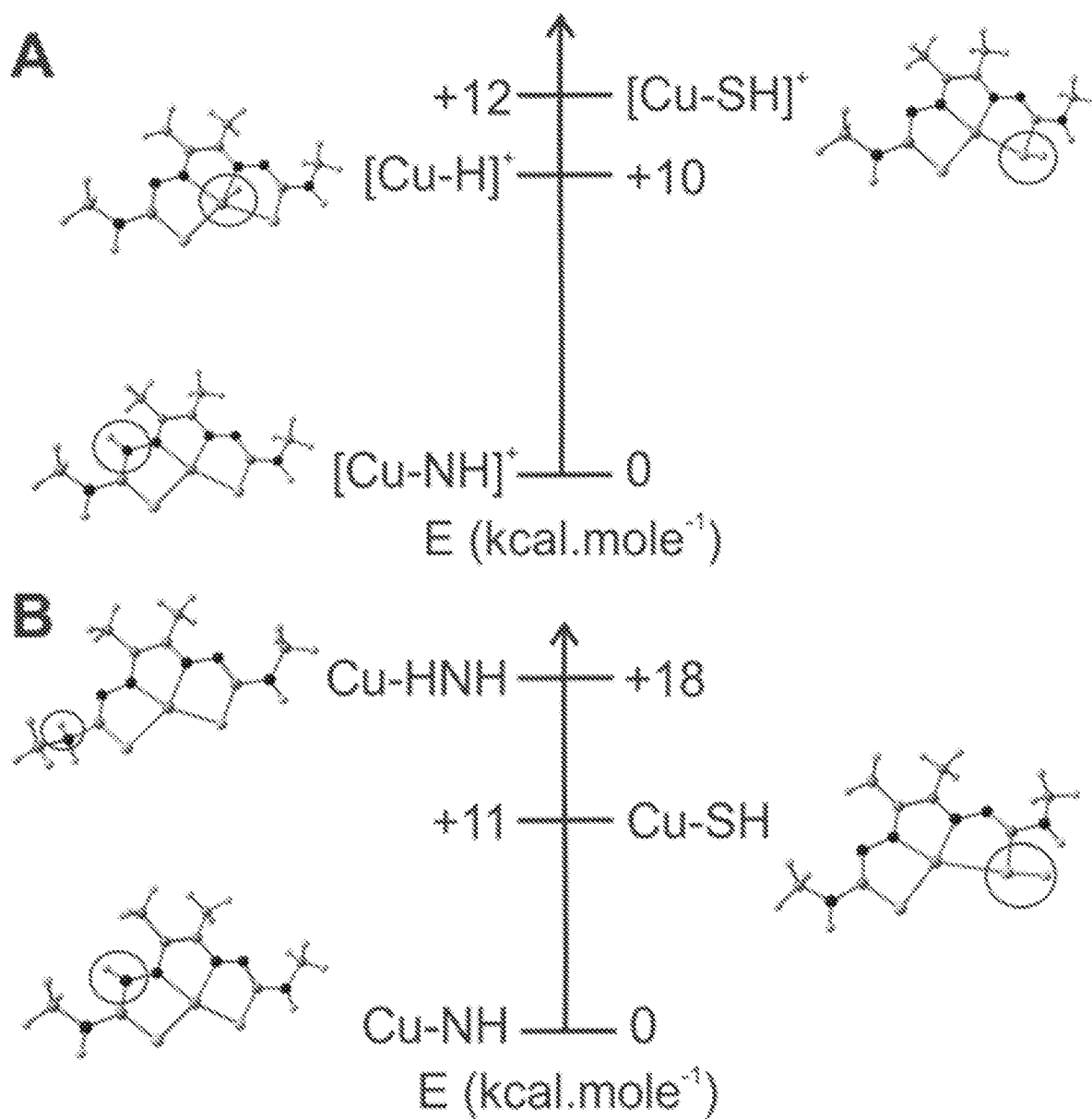
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FIG. 34



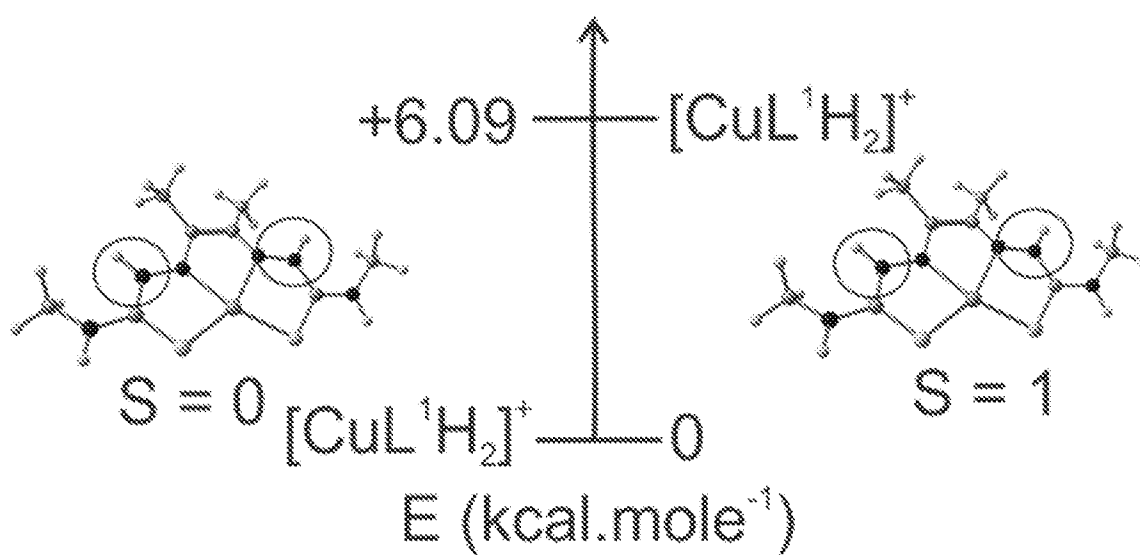
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FIG. 35



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FIG. 36



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FIG. 37

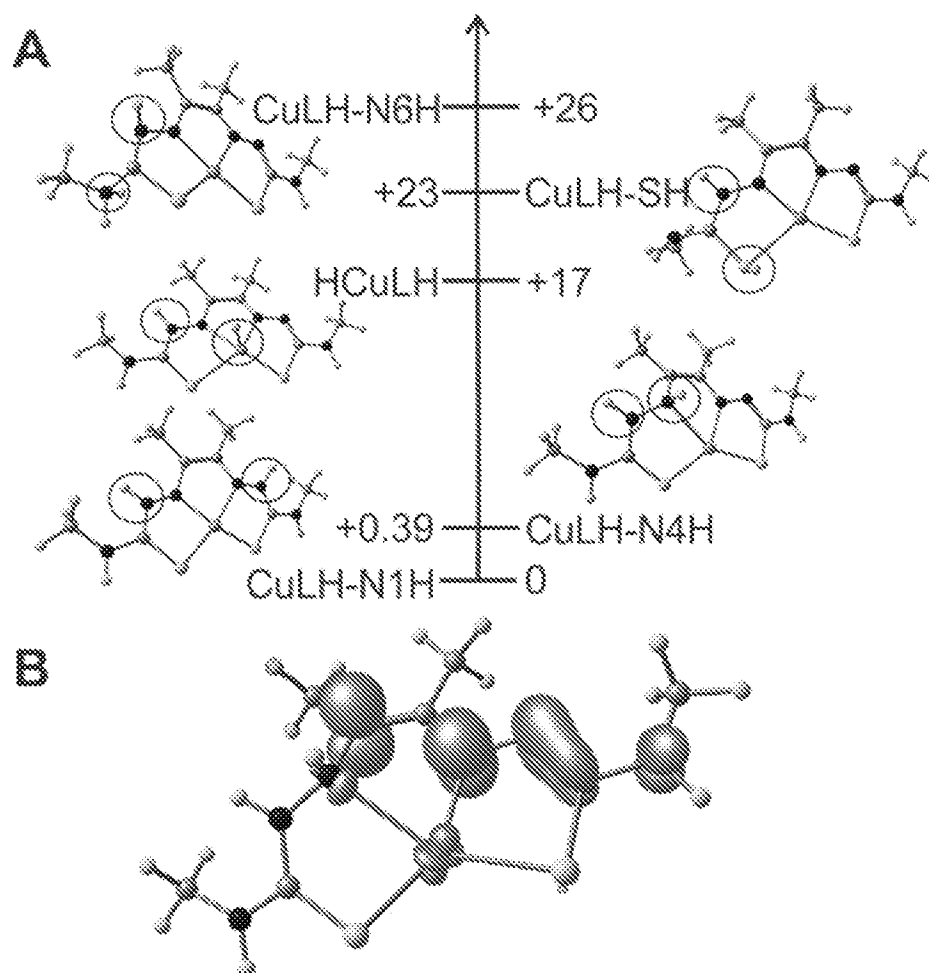
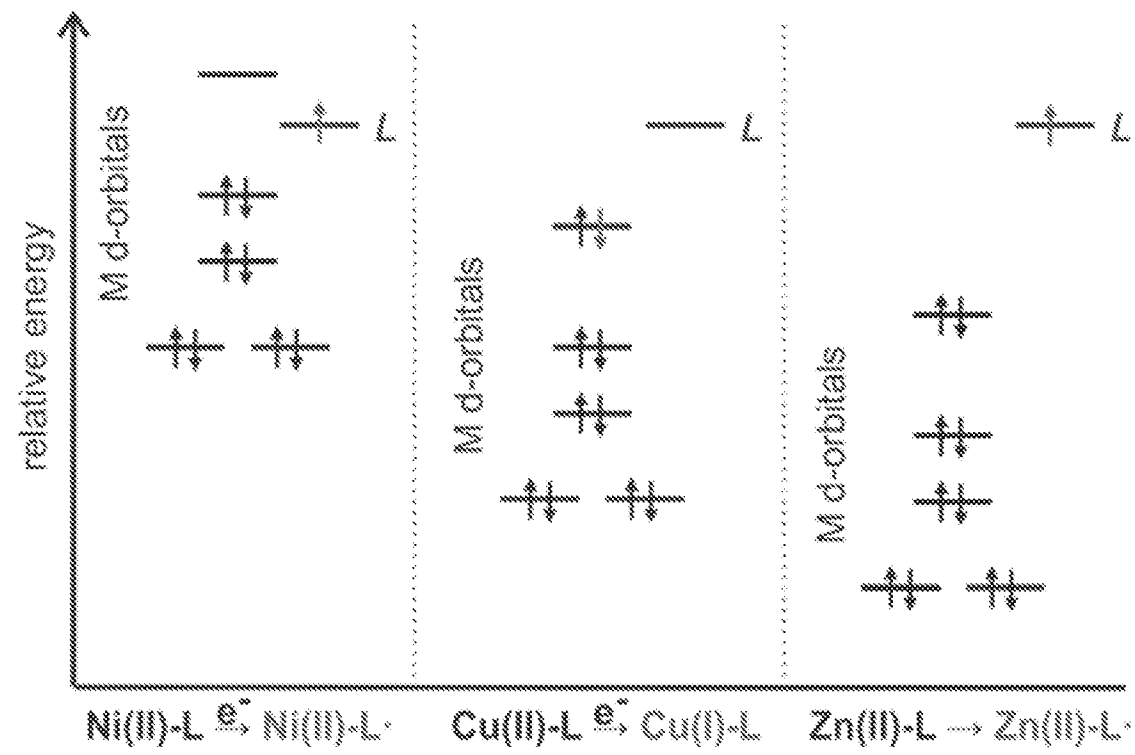
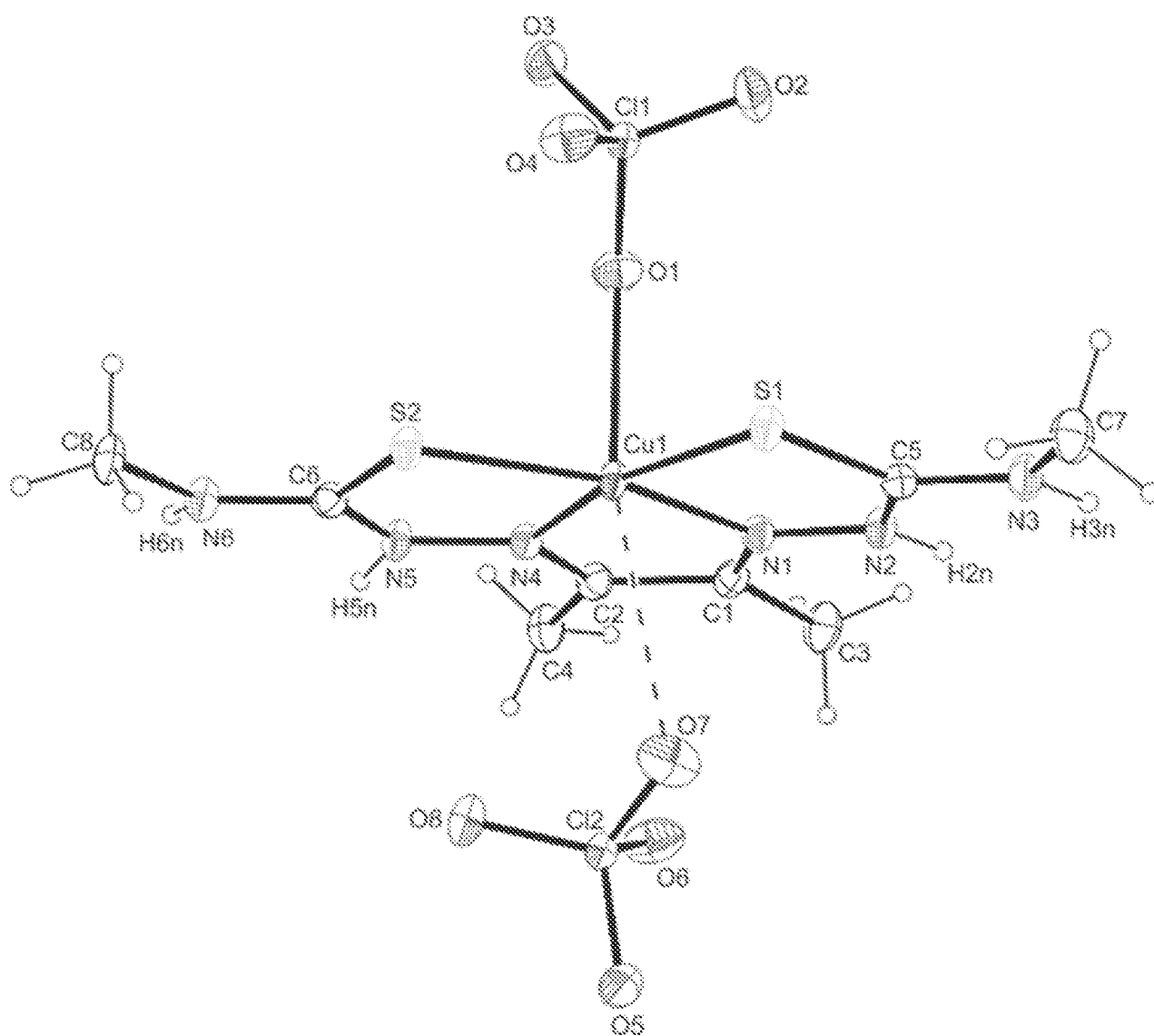


FIG. 38



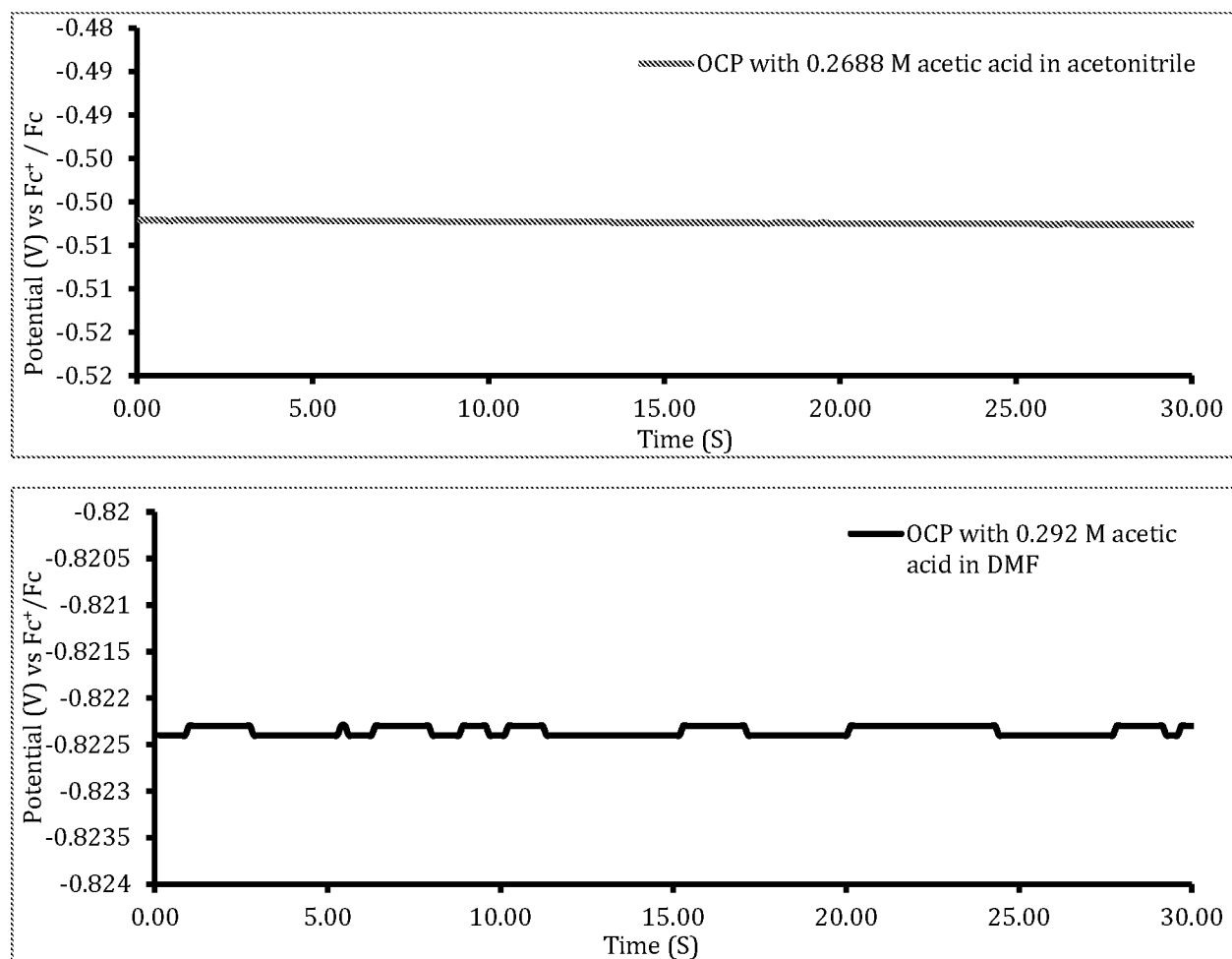
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FIG. 39

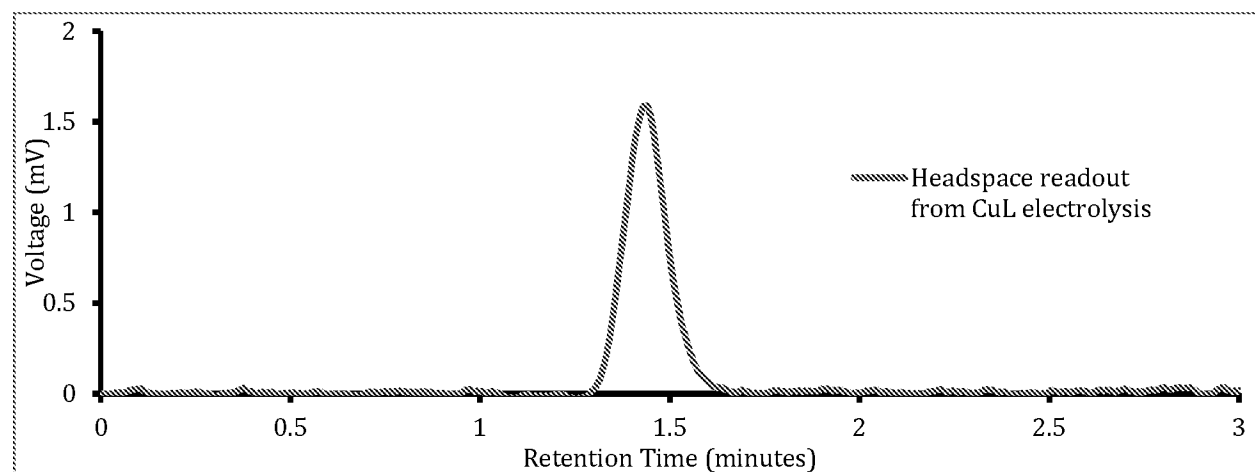


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FIG. 40

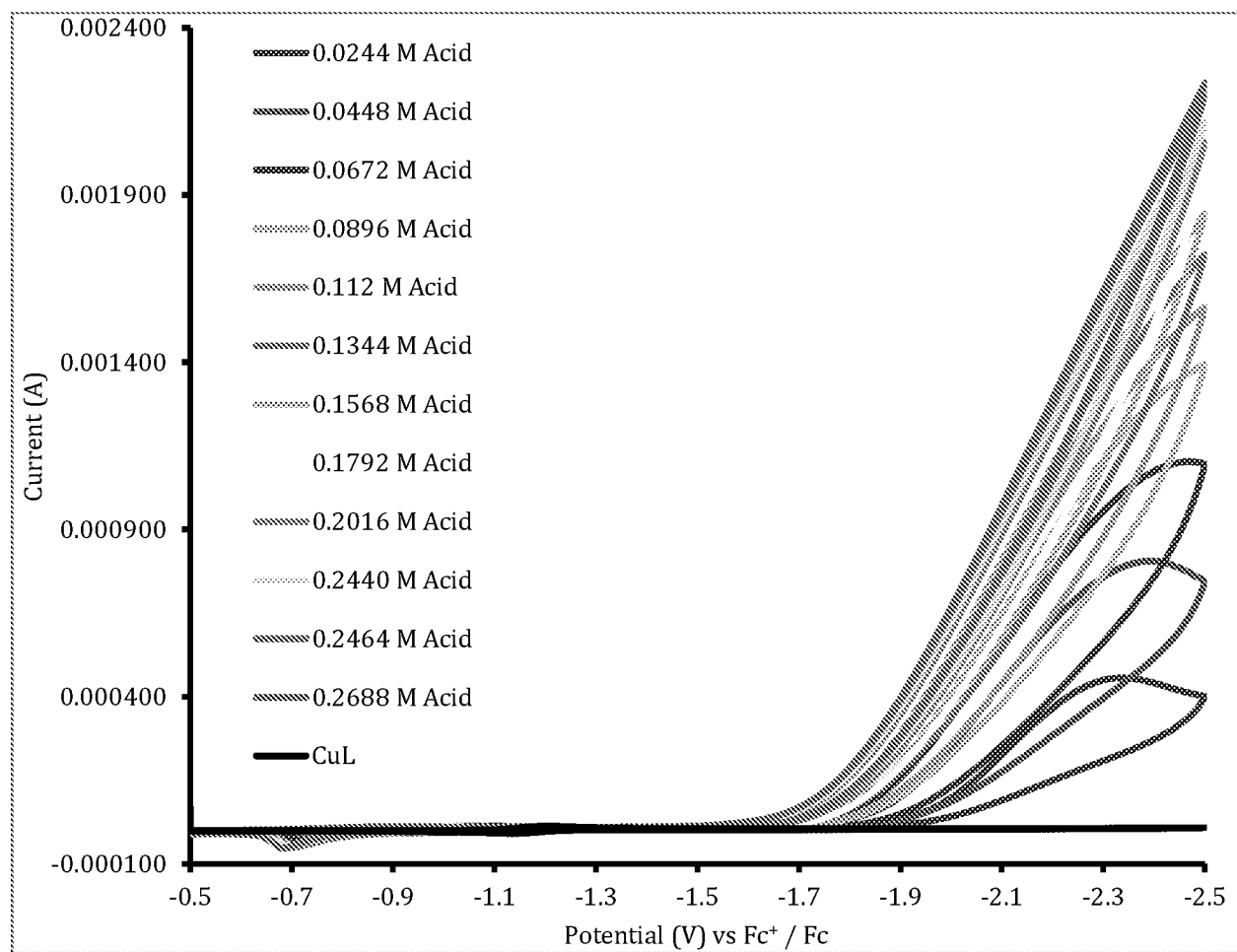


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FIG. 41

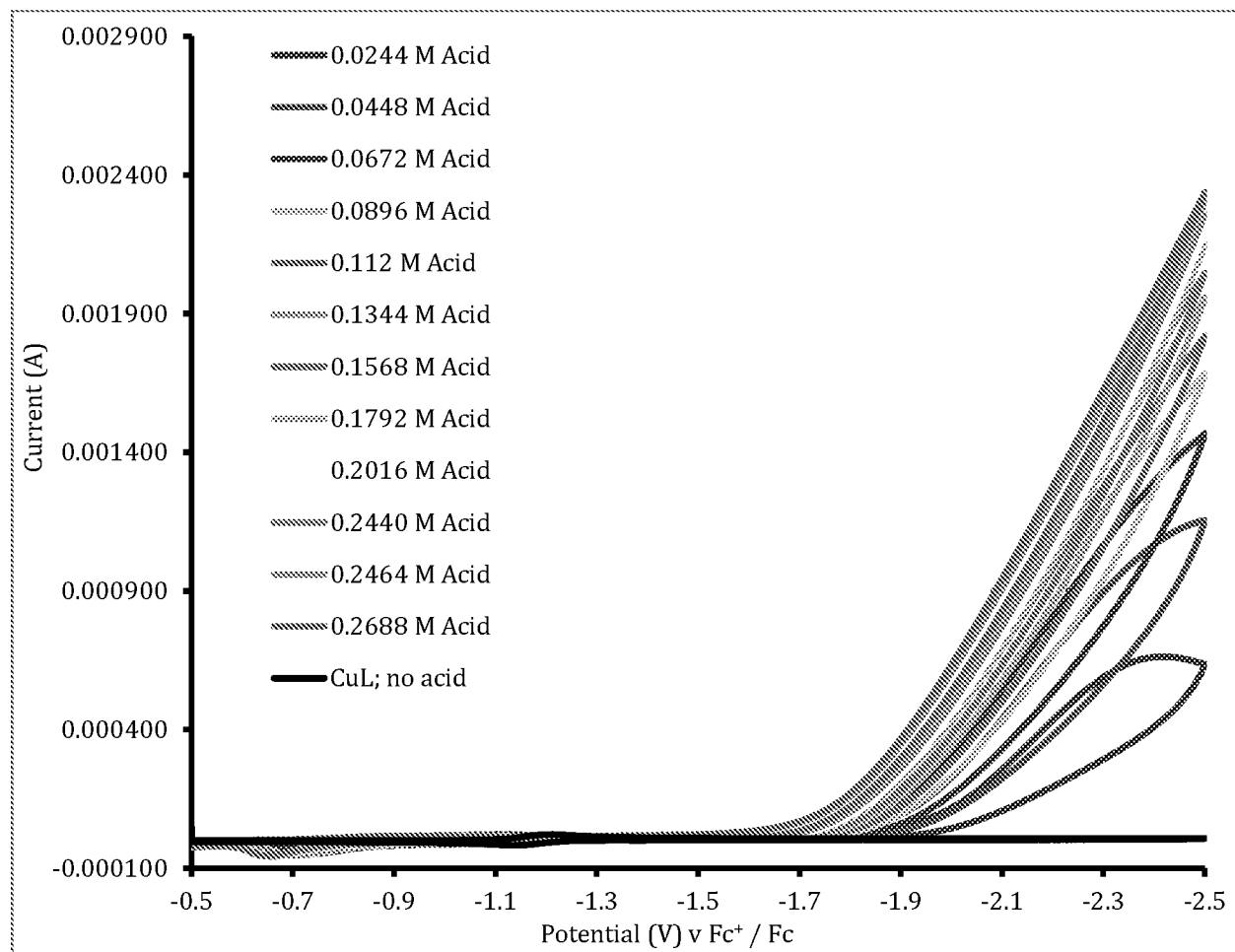
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FIG. 42

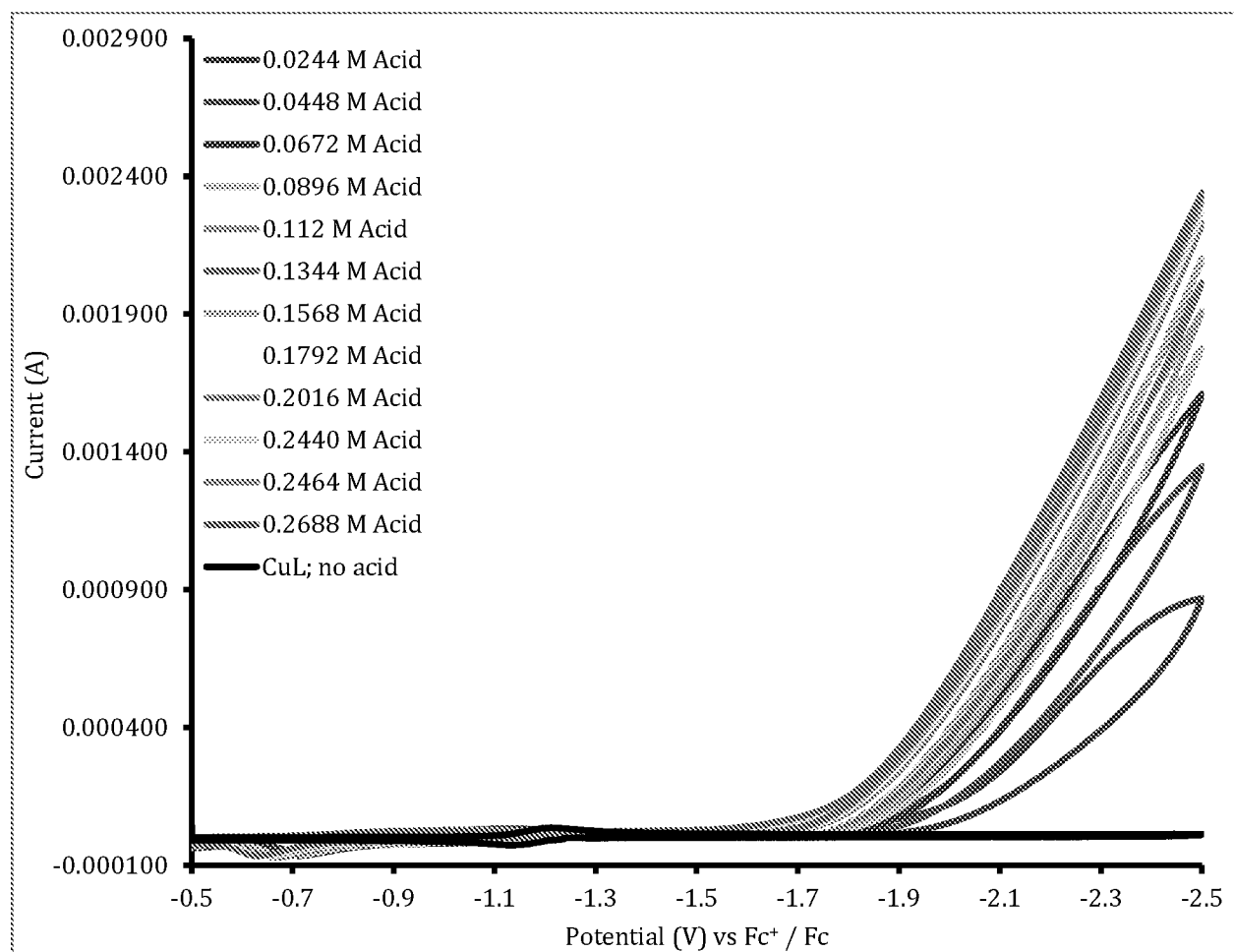


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FIG. 43



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FIG. 44

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FIG. 45

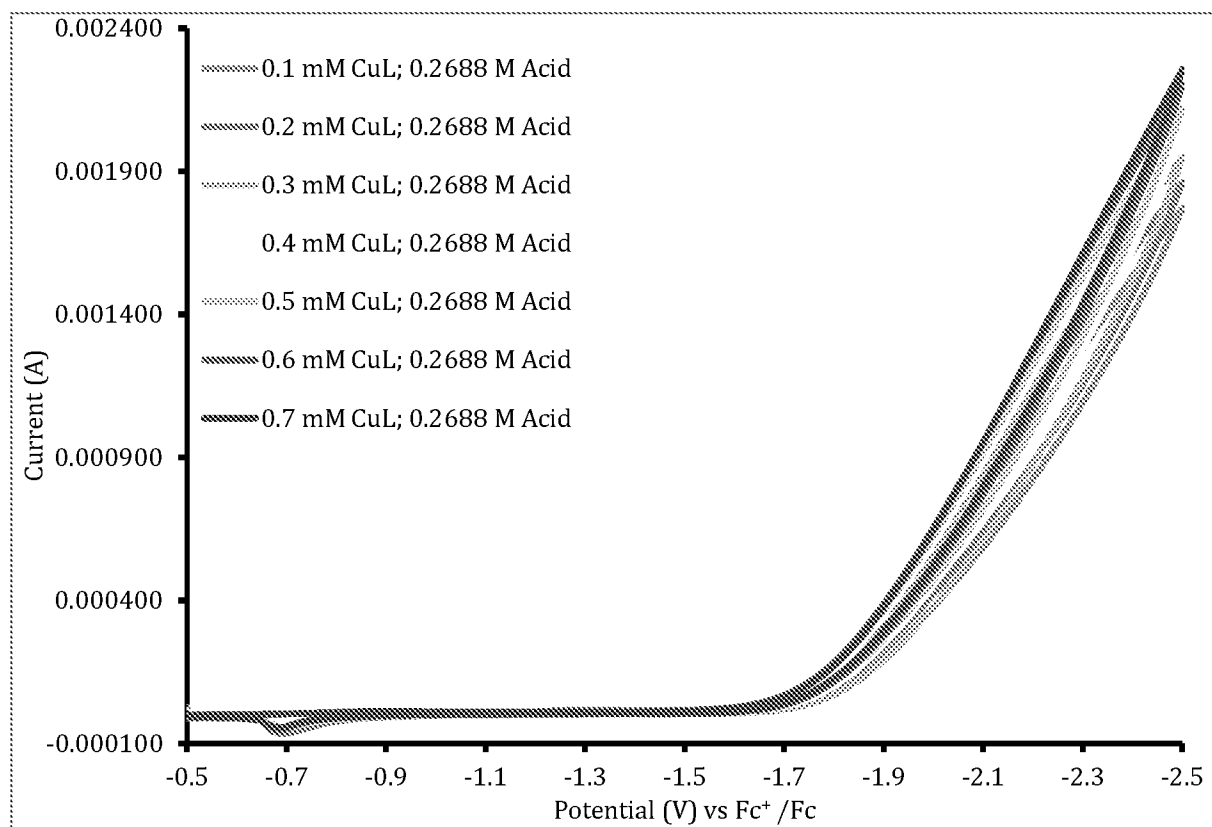
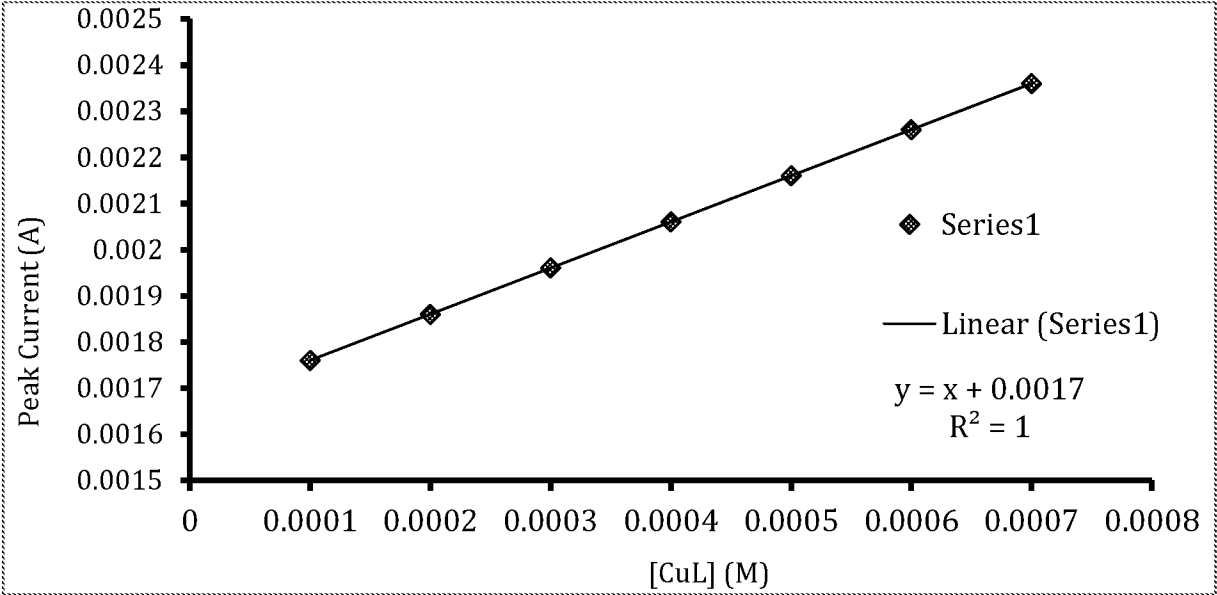
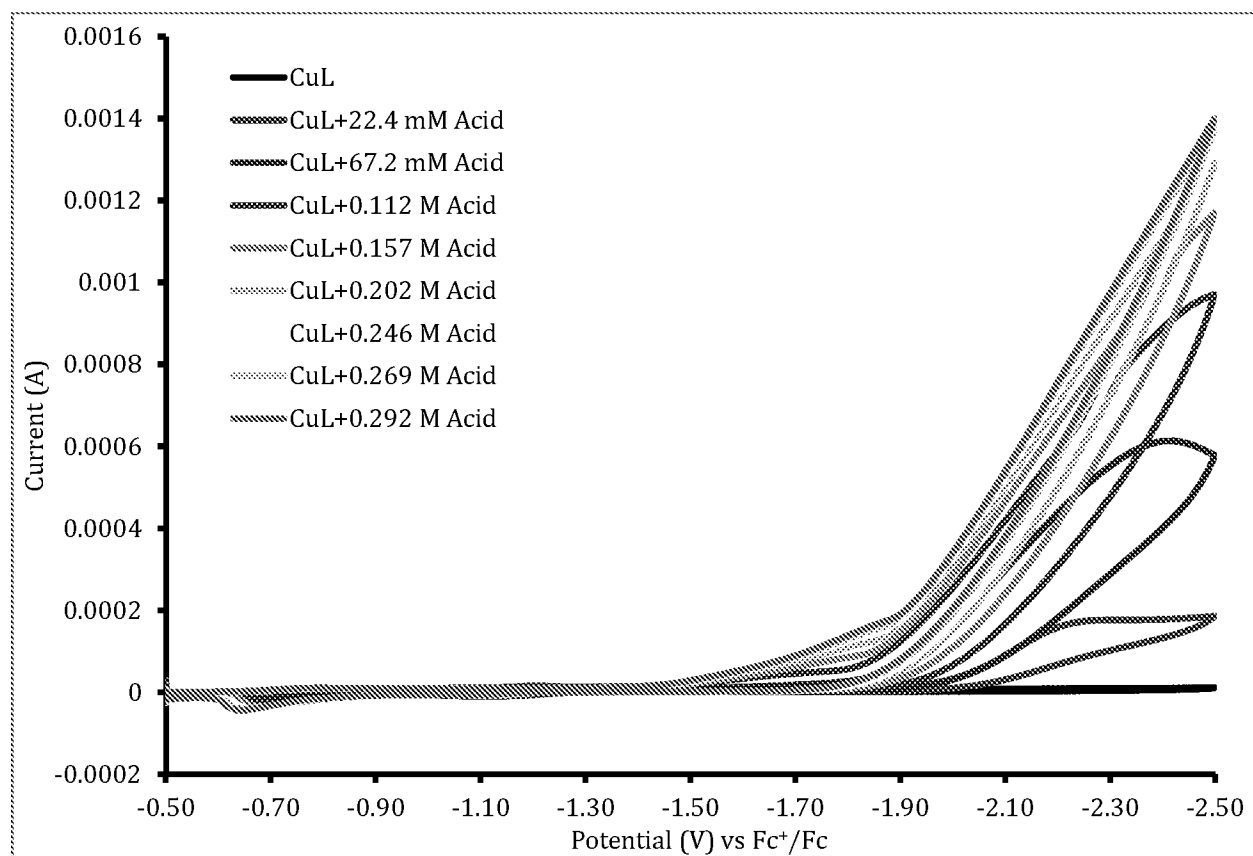


FIG. 46



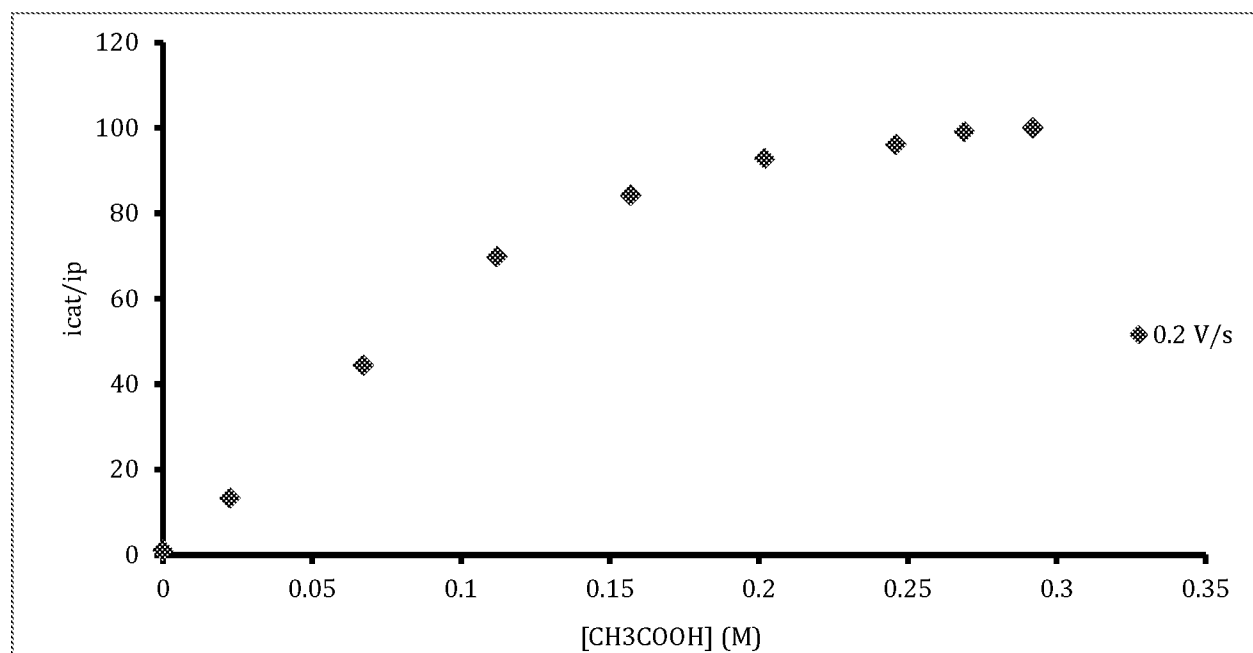
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FIG. 47



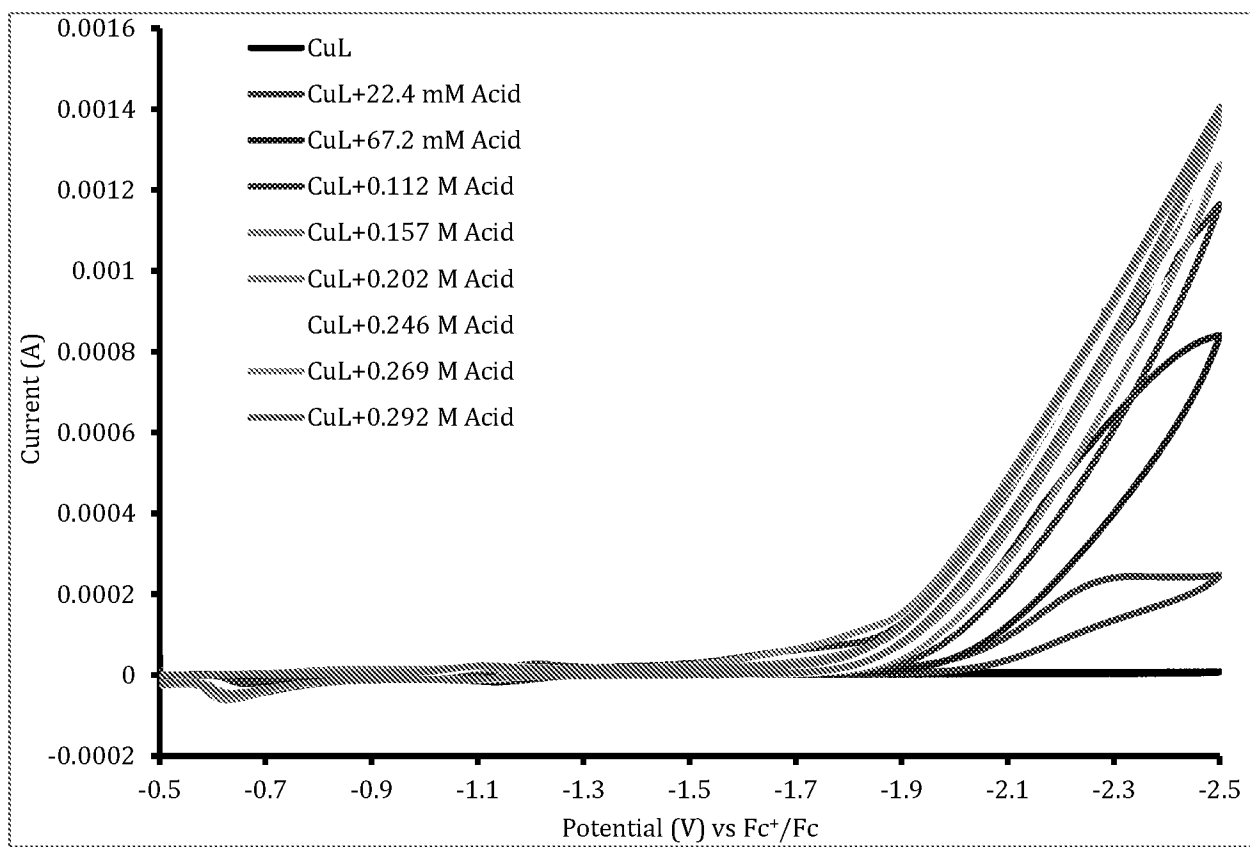
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FIG. 48



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FIG. 49



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FIG. 50

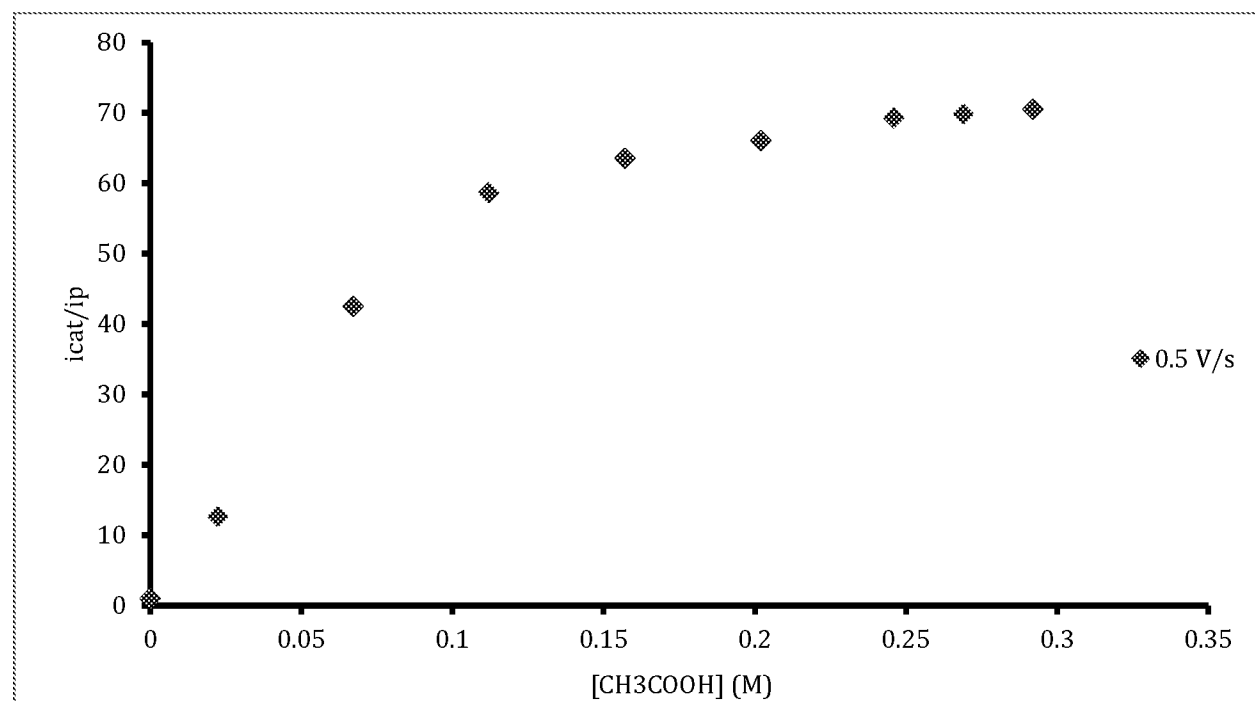
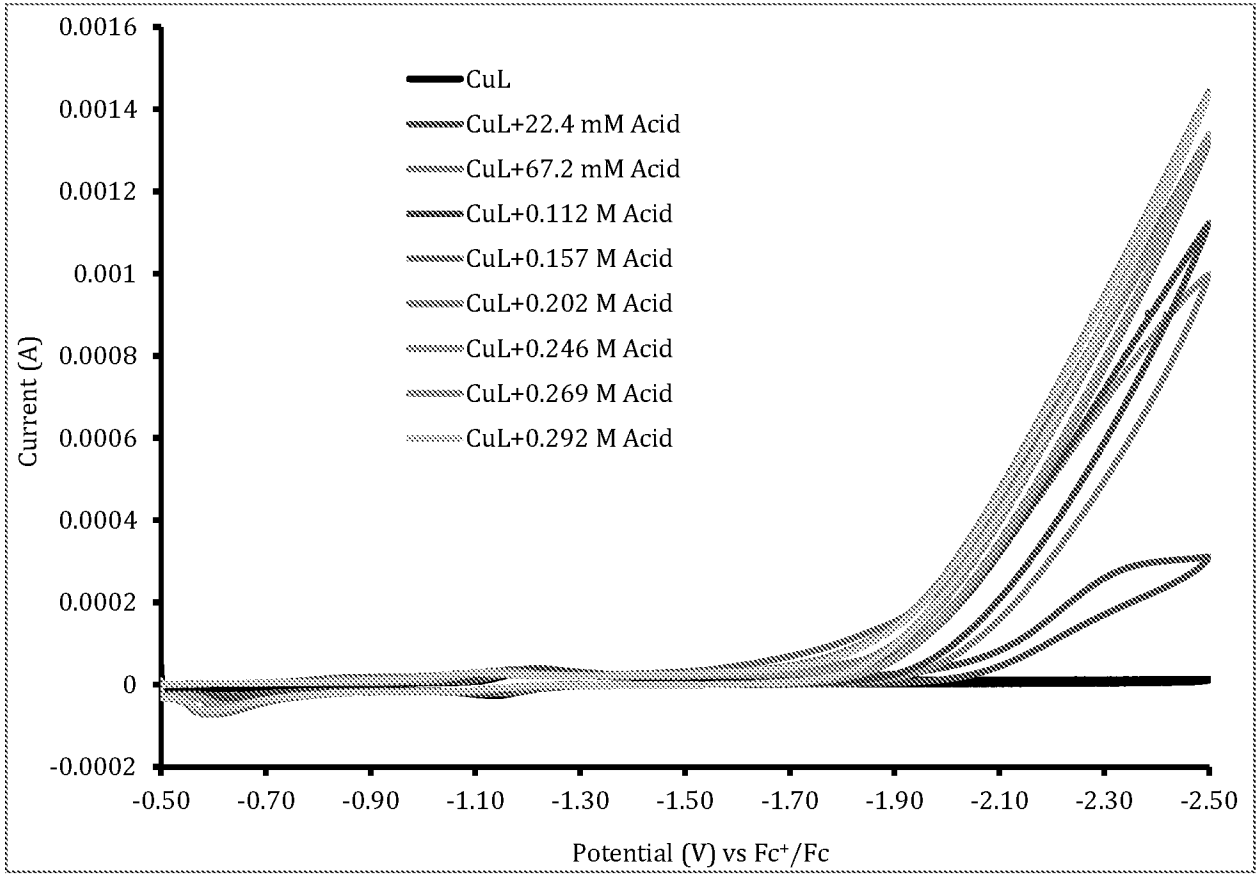
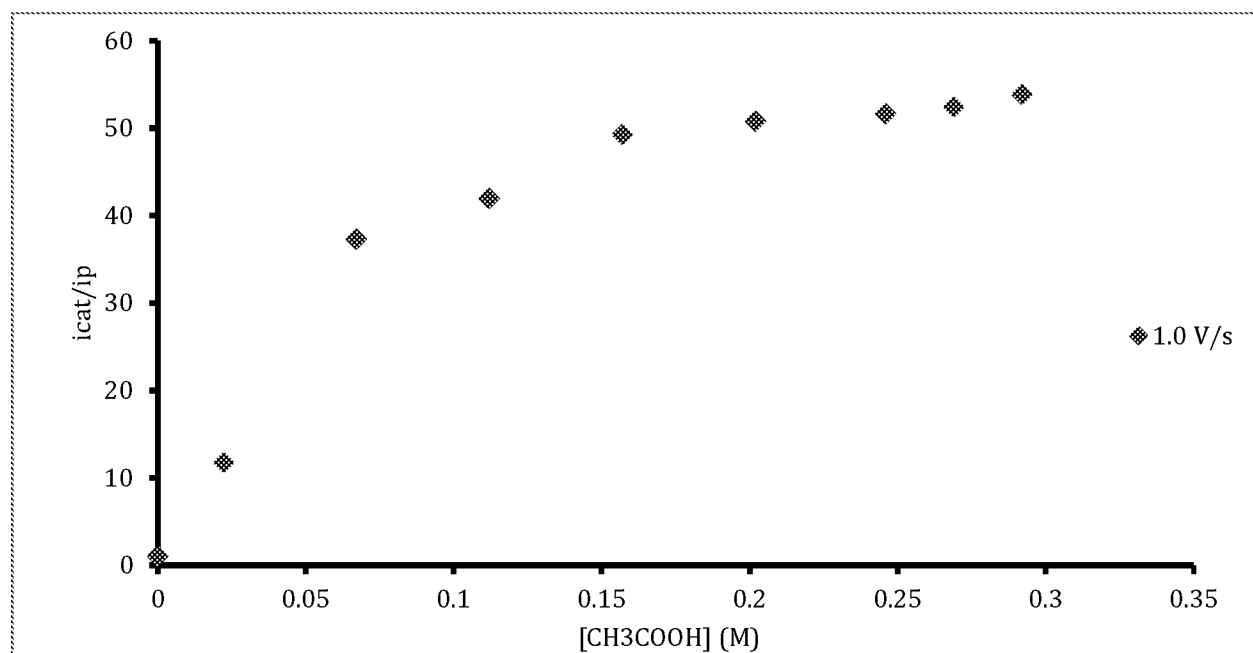


FIG. 51

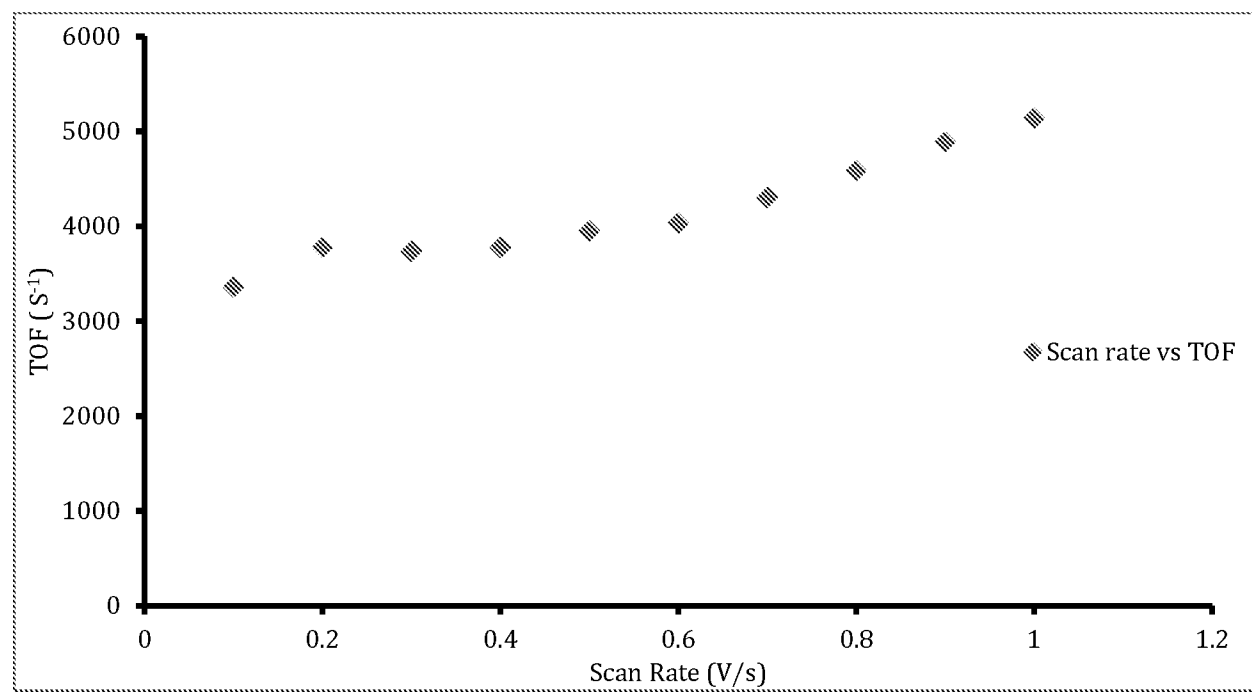


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FIG. 52

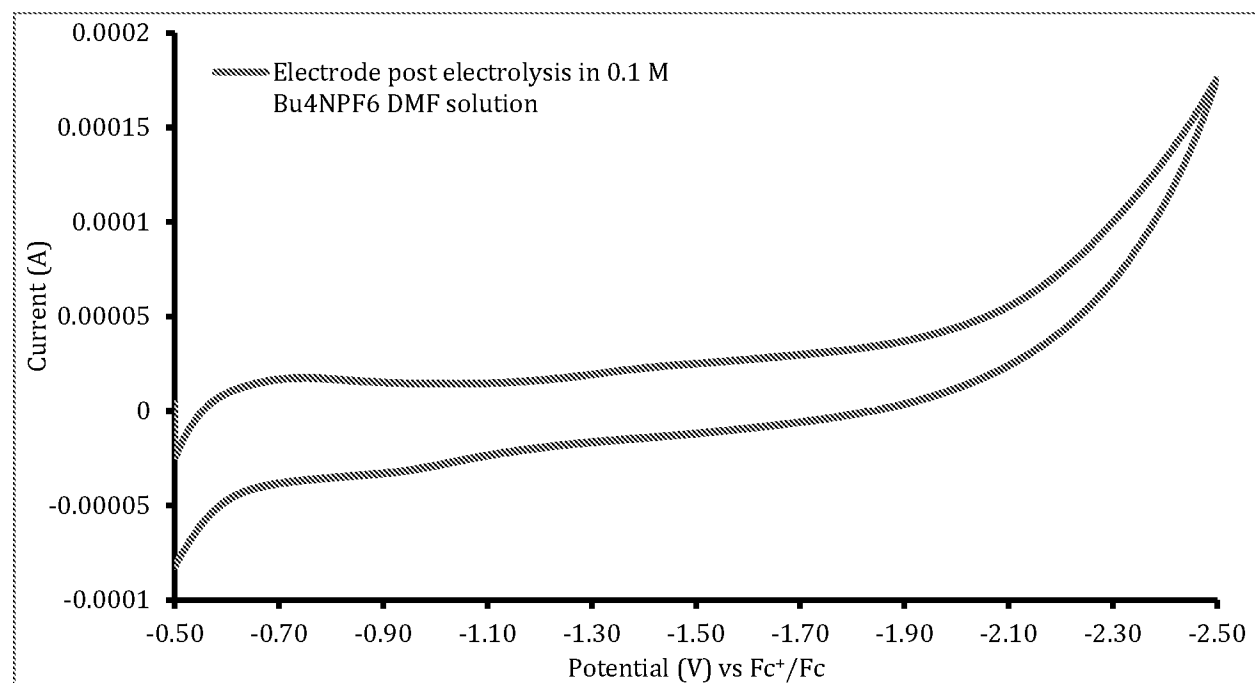


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FIG. 53

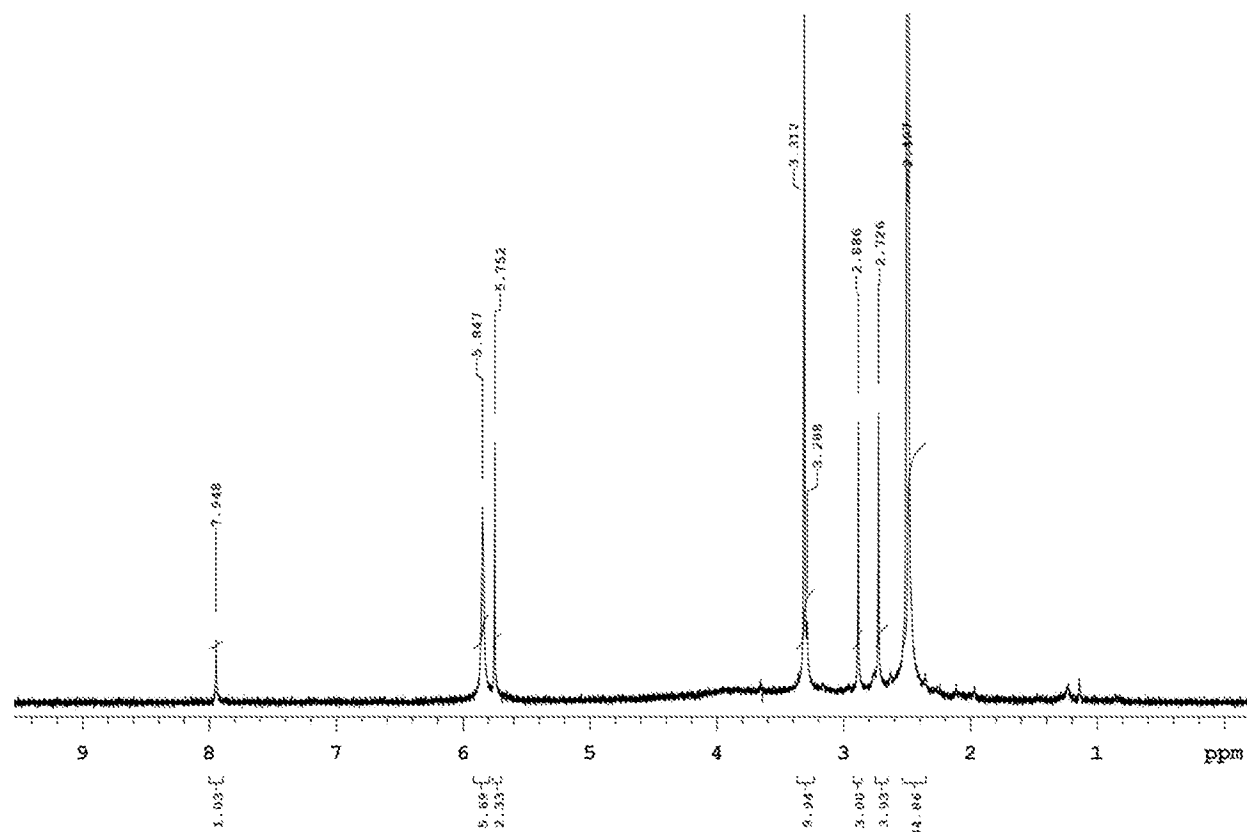
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FIG. 54



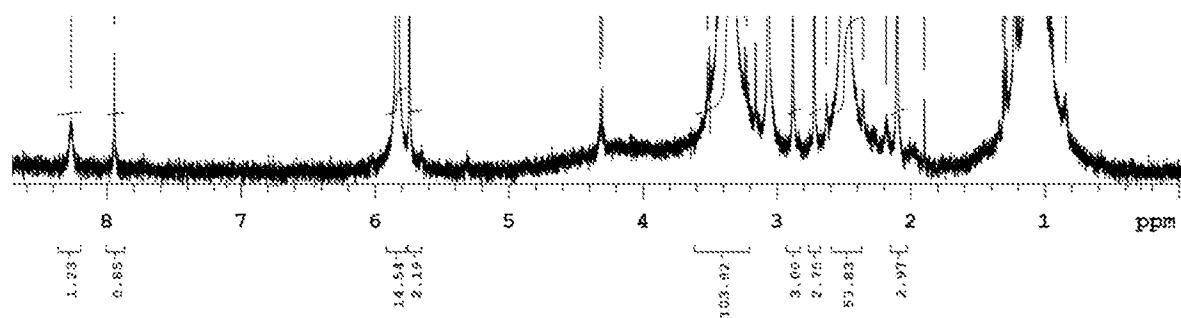
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FIG. 55



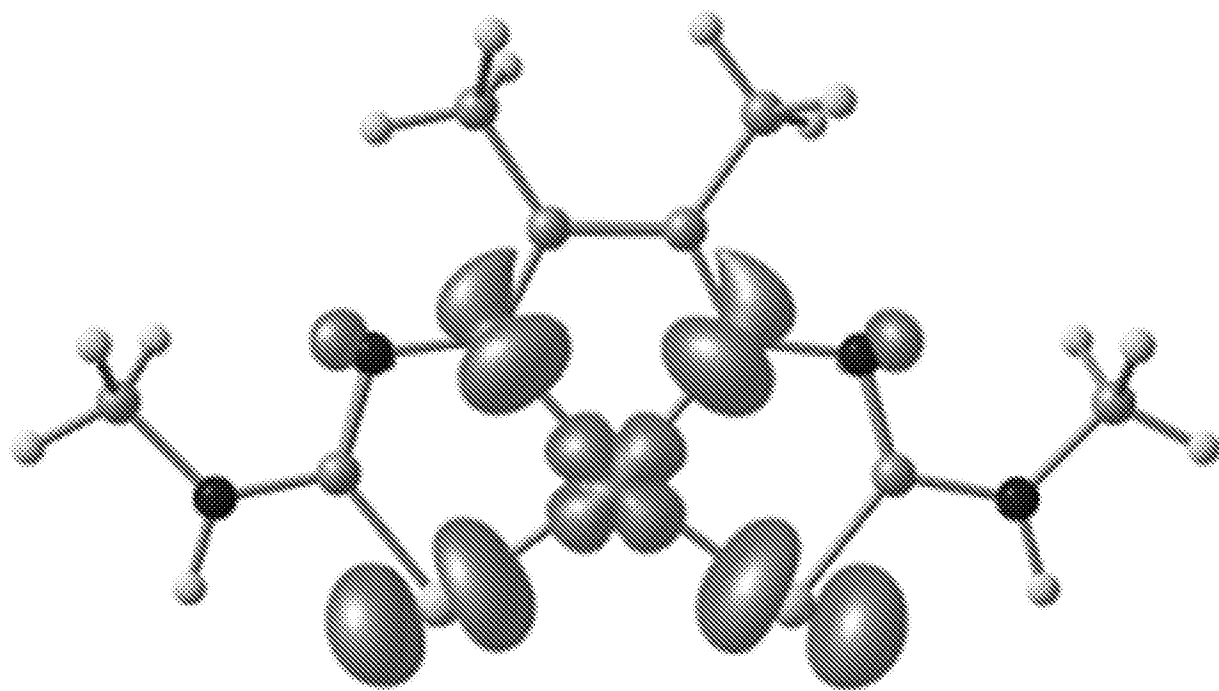
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FIG. 56



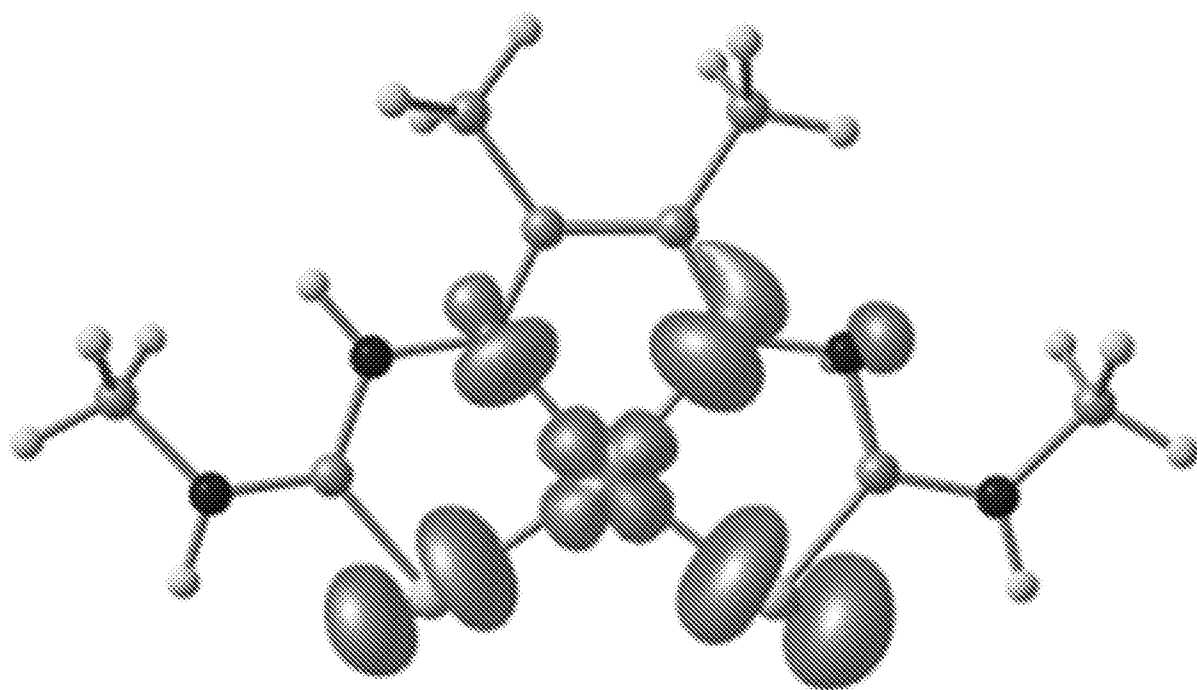
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FIG. 57



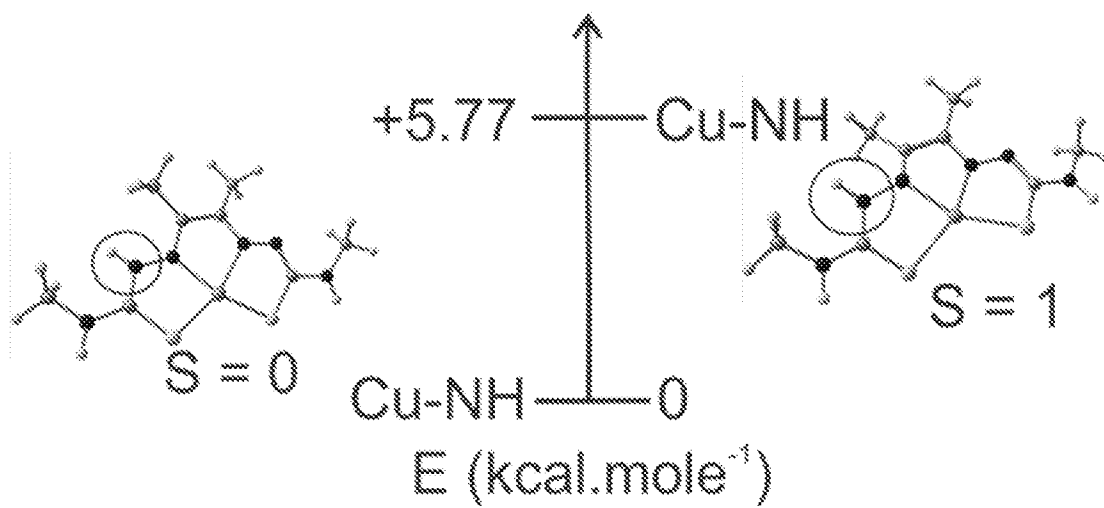
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FIG. 58



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FIG. 59



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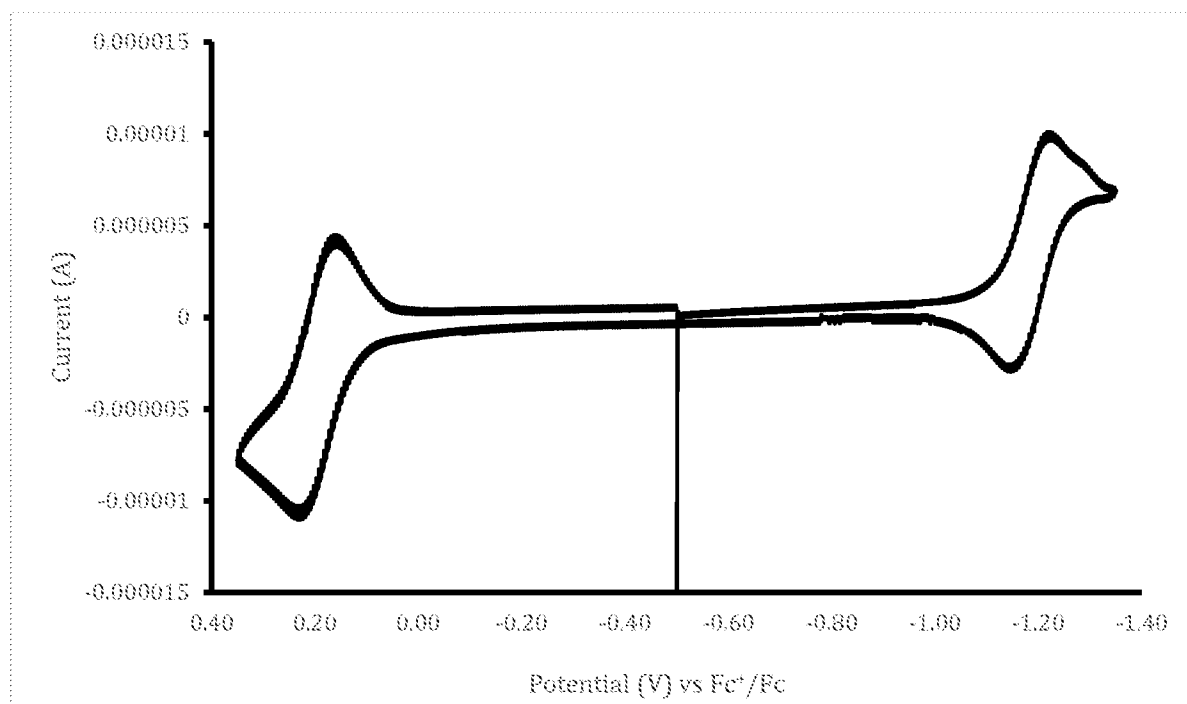
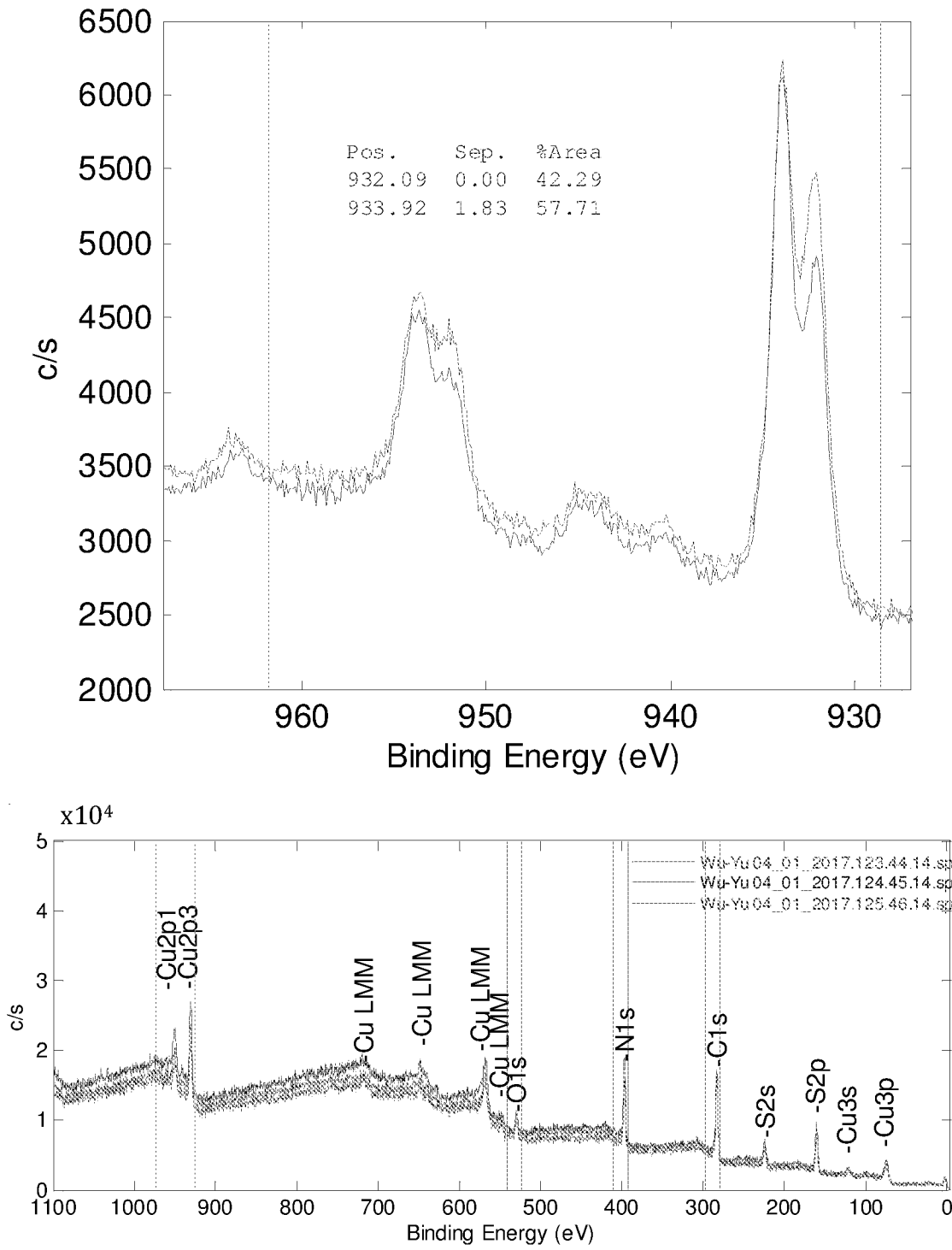
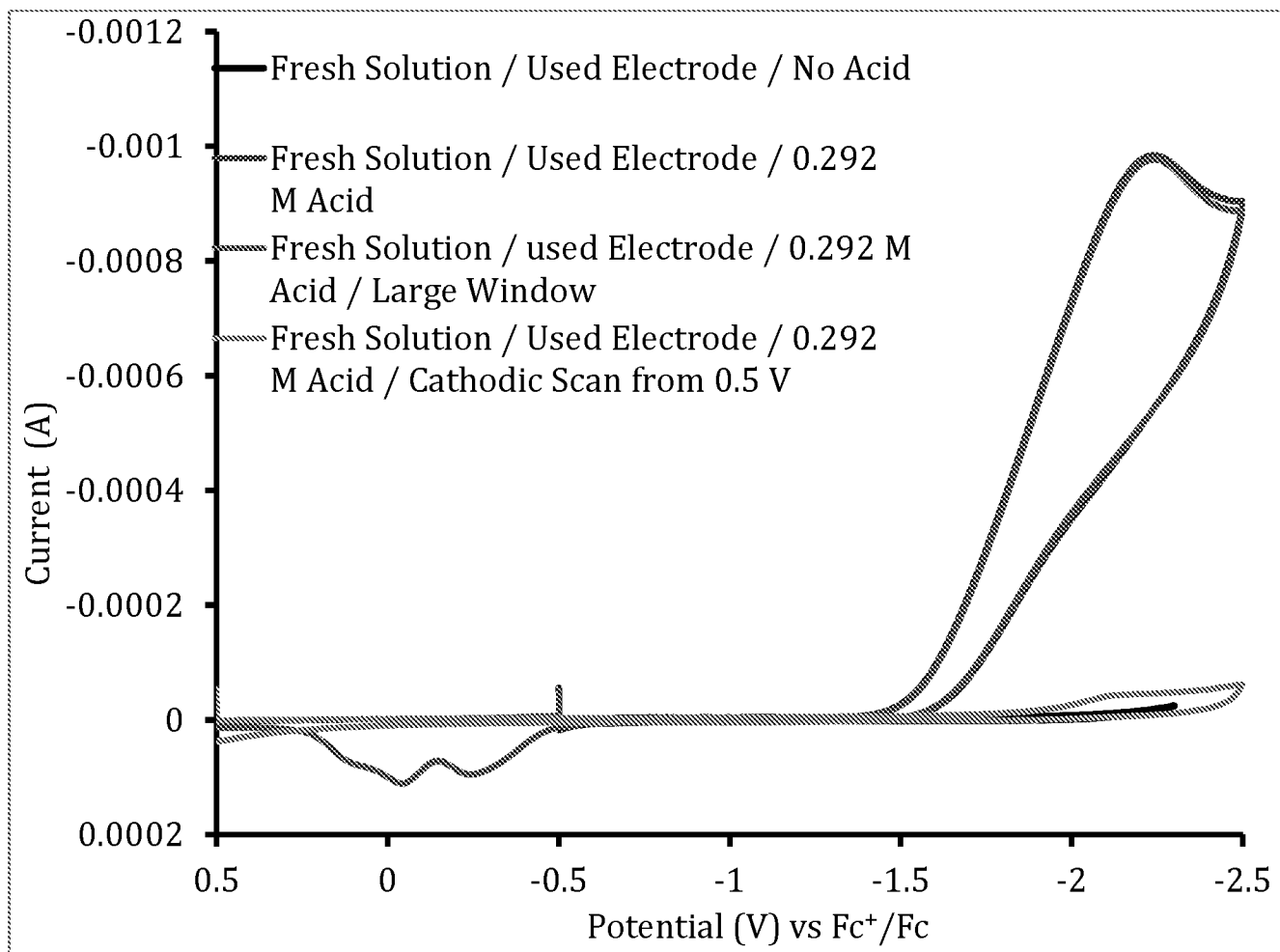
FIG. 60

FIG. 61



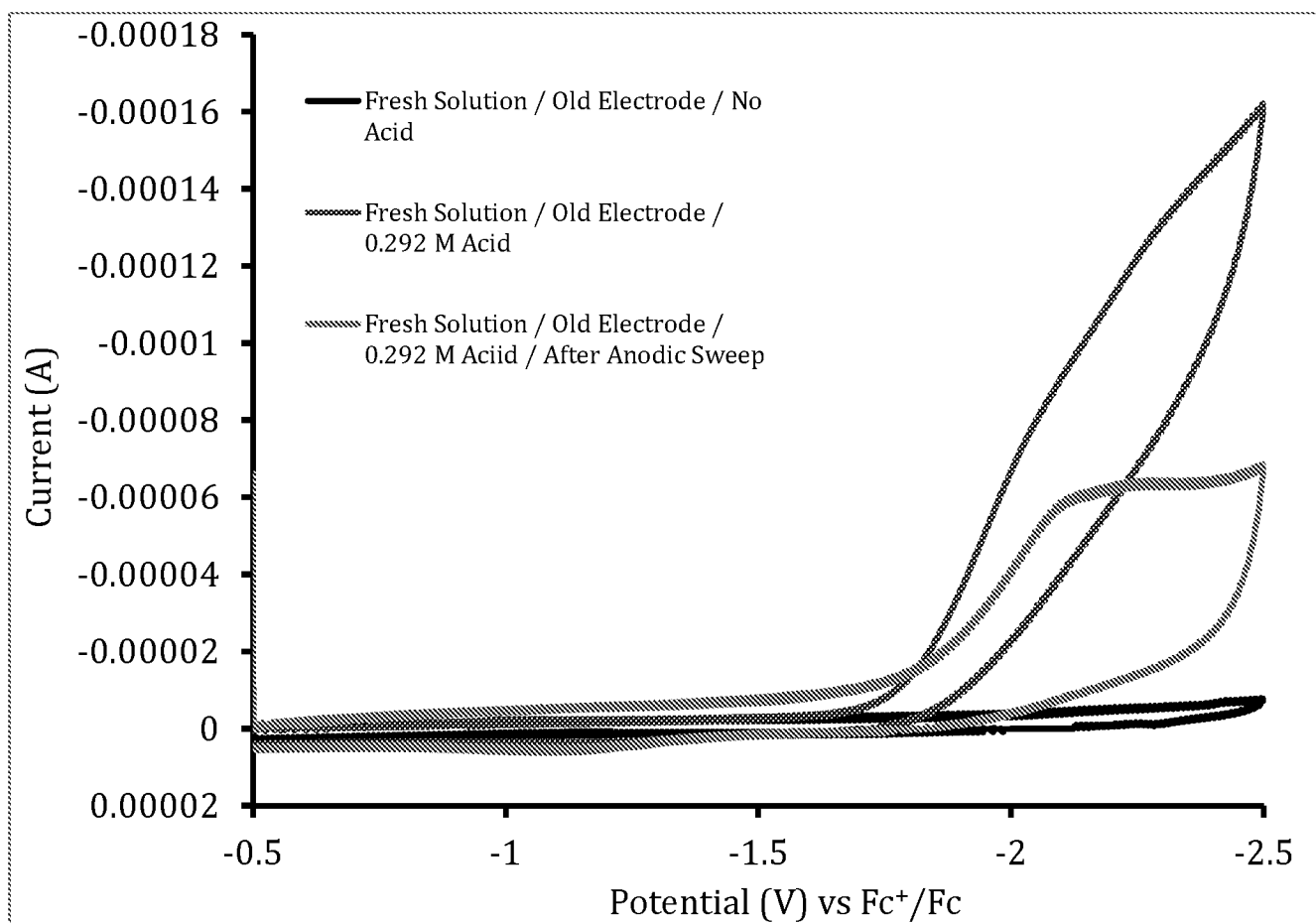
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FIG. 62



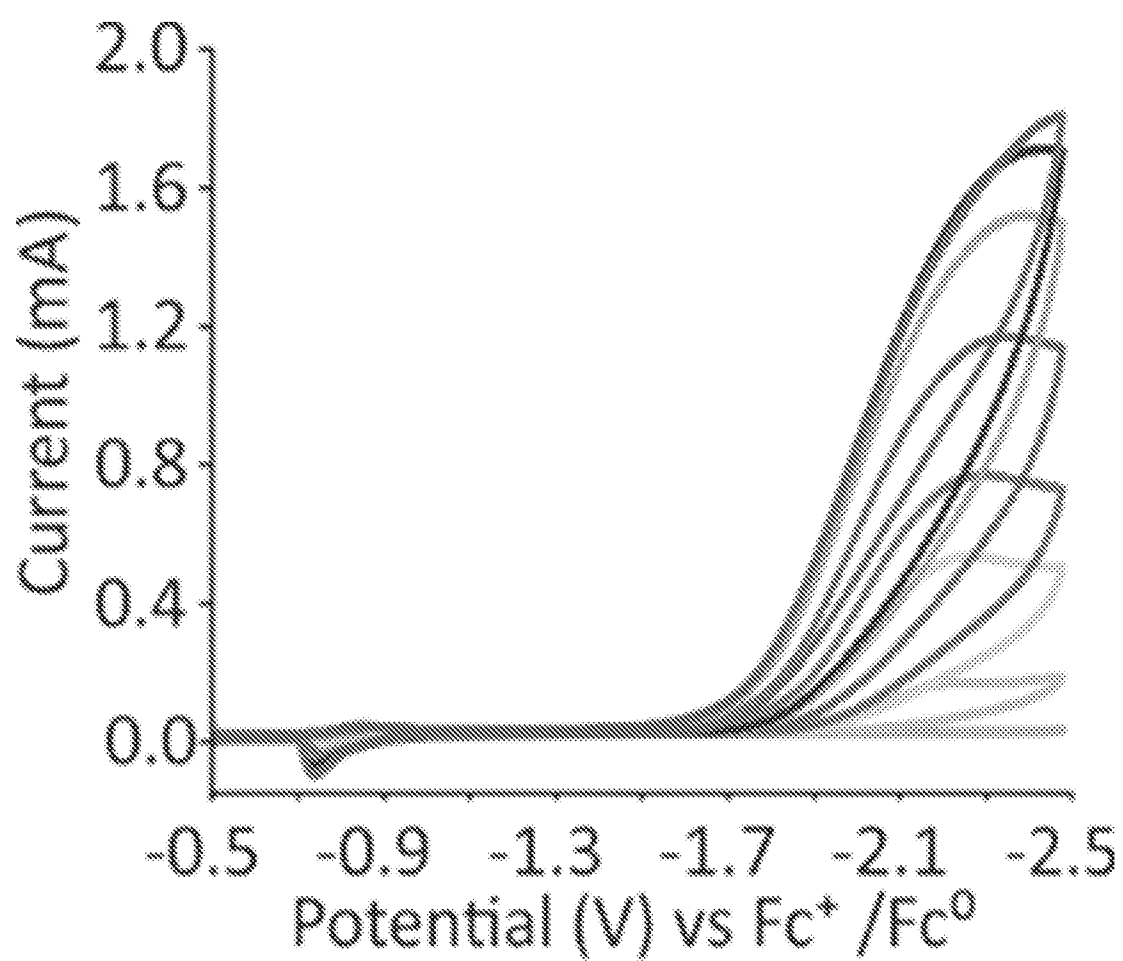
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FIG. 63



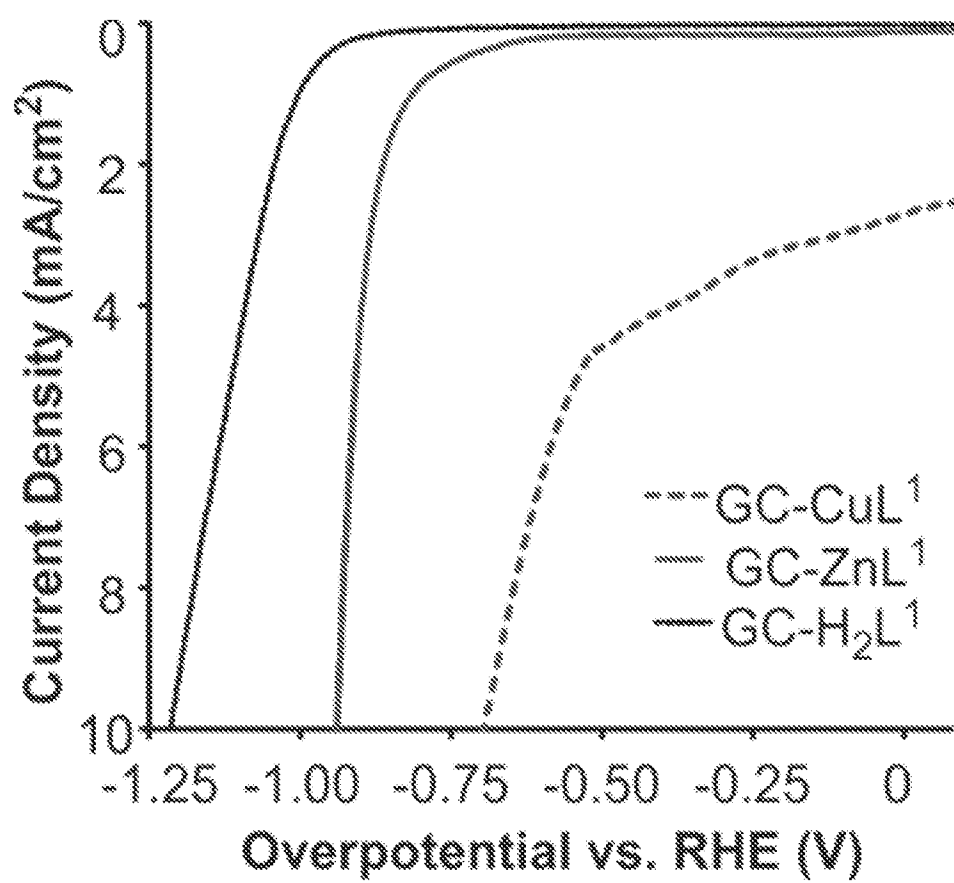
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FIG. 64



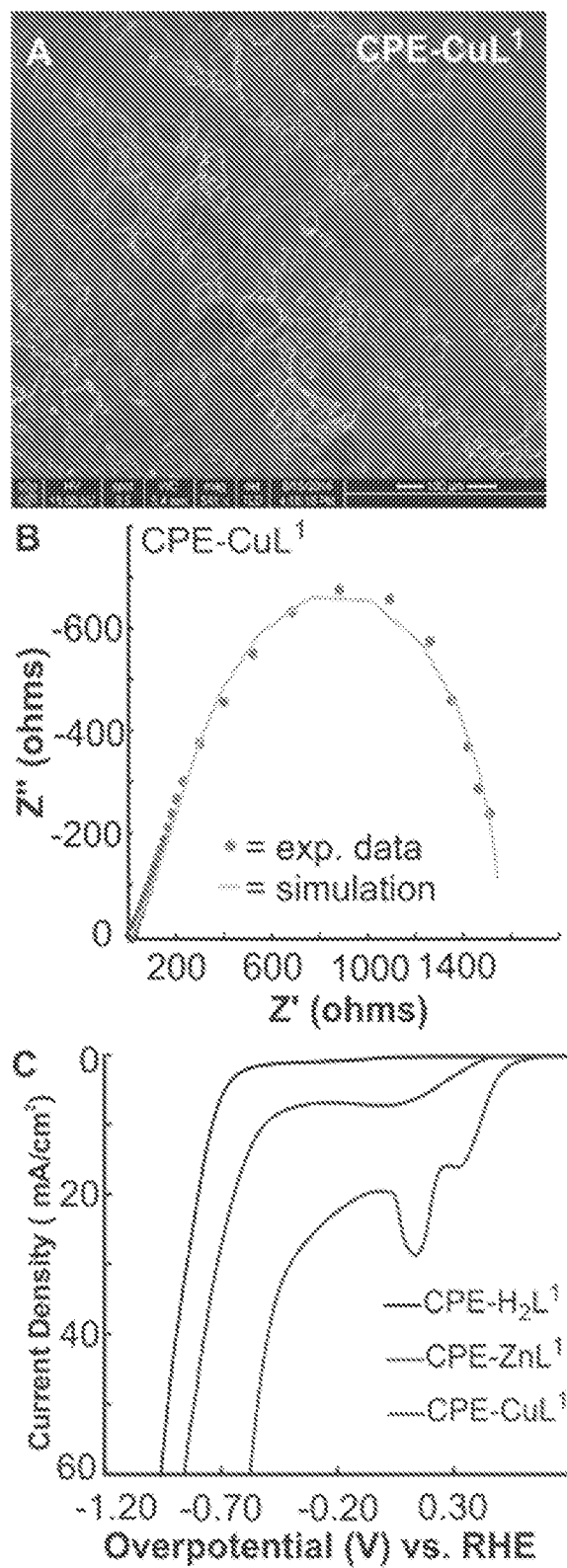
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FIG. 65



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FIG. 66



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/036815

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F3/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STEFANI CHRISTIAN ET AL: "Identification of differential anti-neoplastic activity of copper bis(thiosemicarbazones) that is mediated by intracellular reactive oxygen species generation and lysosomal membrane permeabilization", JOURNAL OF INORGANIC BIOCHEMISTRY, vol. 152, 17 August 2015 (2015-08-17), pages 20-37, XP029338706, ISSN: 0162-0134, DOI: 10.1016/J.JINORGBIO.2015.08.010 figures 1B, 1C ----- -/-	1,2, 5-13, 17-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

25 July 2017

Date of mailing of the international search report

14/08/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bakboord, Joan

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/036815

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/036815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X,P	STRAISTARI T ET AL: "A thiosemicarbazone-Nickel(II) complex as efficient electrocatalyst for hydrogen evolution", CHEMCATCHEM, vol. 9, 22 November 2016 (2016-11-22), pages 2262-2268, XP002772468, the whole document -----	1-26
A	MCKONE ET AL: "Earth-abundant hydrogen evolution electrocatalysts", CHEMICAL SCIENCE, vol. 5, 5 November 2013 (2013-11-05), pages 865-878, XP002772469, figure 1 -----	1-26

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Information on patent family members

International application No

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