Electronic Supplementary Material (ESI) for Dalton Transactions.

The Rigidity of Self-Assembled Cofacial Porphyrins Influences Selectivity and Kinetics of Oxygen Reduction Electrocatalysis

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Supplementary Information

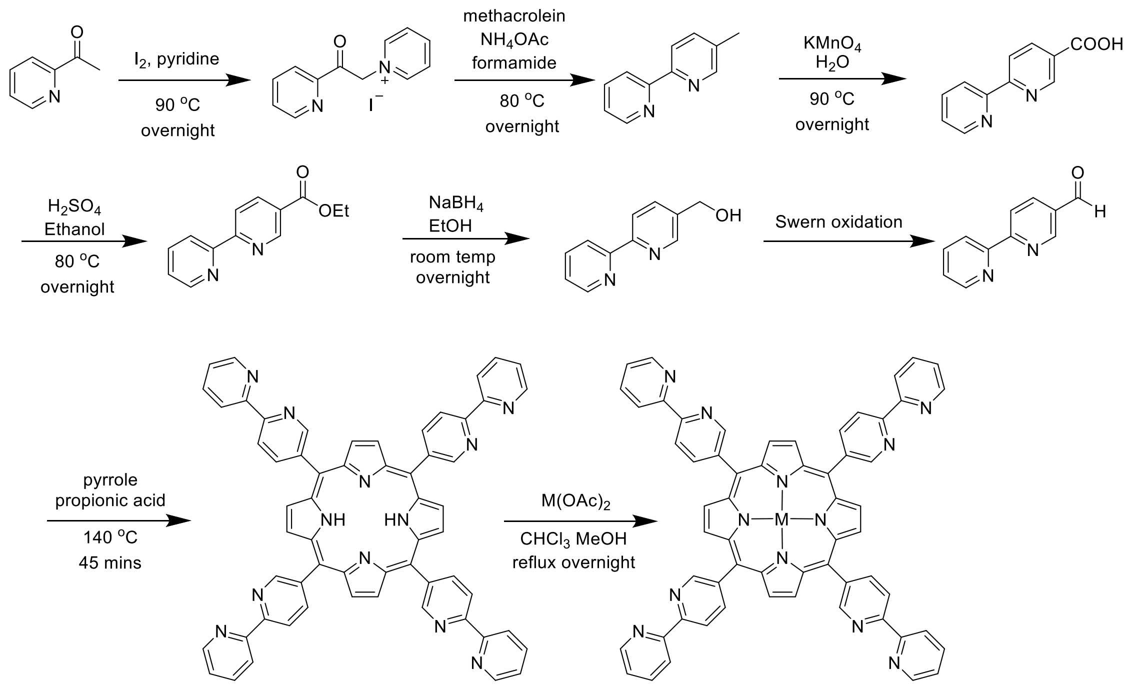
Contents

Experimental Procedures:

Materials:

Chemicals were purchased from commercial sources and used as received unless otherwise noted below. Solvents were purified using a solvent-drying system (Pure Process Technology). ^{1}H NMR spectra were acquired on Varian 300, 400, or 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and referenced against the residual proton resonance of the deuterated solvent. Mass spectra were recorded using the Agilent 6530 Q-TOF mass spectrometer. No precautions were taken to exclude air (O_2 or water) from self-assembly reactions. $Ag(bpy)_2OTf$ was synthesized by following a literature procedure.[1]

Synthesis Procedure for metalloporphyrin:



5-Methyl-2,2'-bipyridine:

A solution of iodine (14.2 g, 56.0 mmol) and 2-acetylpyridine (5.6 mL, 50.0 mmol) in pyridine (60 mL) was prepared in a reaction flask equipped with a condenser and drying tube, and the reaction mixture was stirred for 6 h at 90 °C. At this time, the resulting suspension was filtered as brown solid, the crude product was used without purification. Methacrolein (3.6 mL, 44.0 mmol) and H_4NOAc (18.6 g, 240.0 mmol) were sequentially added to the solution of the brown solid (13.0 g) in formamide (100 mL). The mixture was stirred at 80 °C for 16 h. At this time, the crude mixture was cooled and extracted with diethyl ether (3 × 200 mL). The combined organic layers were washed with brine (200 mL), dried over MgSO4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (5% MeOH in CH2Cl2) to yield 5-Methyl-2,2'-bipyridine (7.0 g, 82.0%) as a brown oil.

2,2'-Bipyridinyl-5-carboxylic acid:

Potassium permanganate (24.6 g, 156 mmol) was added in 7 portions at 1 h intervals to a solution of 5-Methyl-2,2'-bipyridine (6.8 g, 40 mmol) in water (200 mL). The mixture was heated at 70 °C overnight until all the Potassium permanganate turn brown. The brown mixture was then filtered while hot through celite and washed with hot water (2 × 25 mL). The filtrate was concentrated to approximately 10 mL under reduced pressure, and then 1 M HCl was added slowly until a pH of 4 was obtained. The residue was then filtered and dried to obtain pure product (5.8 g, 73.4%) as a white solid.

Ethyl 2,2'-Bipyridinyl-5-carboxylate:
Concentrated sulfuric acid (20 mL) was added to a solution of 2,2'-Bipyridinyl-5-carboxylic acid (5.8 g, 29 mmol) in ethanol (50 mL). The reaction mixture was stirred at 70 °C, the reaction progress was monitored by LTQ-MS, after 48 hours, the mixture was concentrated under reduced pressure, and a NaHCO3 solution was added to the mixture to neutralize the acid. The product was then extracted with ethyl acetate (3 × 100 mL), and the combined organic fractions were washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure to obtain pure product (3.9 g, 59.0%) as a white solid.

2,2'-Bipyridinyl-5-methanol
Sodium borohydride (1.1 g, 30 mmol) was added to ethyl 2,2'-Bipyridinyl-5-carboxylate (1.37 g, 6 mmol) in ethanol (50 mL). The mixture was stirred at room temperature for about 24 hours and monitored by LTQ-MS, then concentrated under reduced pressure. Water (50 mL) was added, and then the crude product was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain as brown oil as product quantitatively.

2,2'-Bipyridinyl-5-carboxaldehyde:
To a solution of $(COCl)_2$ (0.94 mL, 12.0 mmol) in CH_2Cl_2 (14.0 mL) was added dry DMSO (1.70 mL, 24 mmol) at -78 °C. After stirring for 30 min, 2,2'-Bipyridinyl-5-methanol (0.93 g, 10.0 mmol) was added, and the reaction mixture was stirred for 1 h at the same temperature. Then, to the mixture was added triethylamine (6.4 mL, 48 mmol), and the resulting mixture was warmed to room temperature. After stirring for 1 h, the reaction was quenched by addition of water, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness to yield 0.83 g brownish yellow oil as crude product, NMR was acquired to identify the purity and the product was used without further purification.

Tetrakis(bipyridyl) porphyrin:
The purity of aldehyde was obtained by ^{1}H NMR, as shown is Figure S5, the peak at 10.2 ppm was attribute to the aldehyde CHO, and the peak at 4.85 ppm was attributed to the methanol CH_2 peak, based on the peak integration, the aldehyde was around 75% purity, since alcohol group doesn't involve into any reaction during the porphyrin synthesis, the crude product was directly used with further purification.

Pyrrole was distilled under reduced pressure before use. A 1 L round-bottom flask was equipped with a reflux condenser and a magnetic stirring bar. 2,2´-bipyridine-5-carbaldehyde (0.736 g, 3.0 mmol ,1.0 eq, 75% purity) and propionic acid (70 mL) to the flask were added. The mixture was heated at 140 °C. Pyrrole (0.221 g, 3.3 mmol, 1.1 eq) was then dissolved in propionic acid (5 mL) and added to the solution. The reaction mixture was heated at 140 °C for 45 min under aerobic and ambient-light conditions, cooled to room temperature and evaporate the solvent under reduced pressure. The black solid was washed by N,N-dimethylformamide and methanol to obtain the product as purple solid (136 mg, 19.6%).

Zn(II) tetrakis(bipyridyl) porphyrin:

Free-base porphyrin (50 mg, 0.054 mmol, 1.0 eq), $CHCl_3$ (30 mL) and CH_3OH (5 mL) were placed in a 50 mL round-bottom flask. To the clear, red solution was added zinc acetate dihydrate (50 mg 0.27 mmol, 5.0 eq) dissolved in CH_3OH (3 mL). The solution was stirred at room temperature for 16 h under the dark to give clear, purple solution. The solution was transferred to separating funnel, washed with 50 mM EDTA·2Na aqueous solution (20 mL × 3) and with H_2O (20 mL × 3). The combined organic phase was dried over Na_2SO_4, filtered and evaporated to obtain crude 1 as a reddish purple solid (44 mg, 81%).

Zn_2Ag_4 prism:
To a solution of Co-porphyrin (75 mg, 0.076 mmol, 1.0 equiv.) in a mixture of $CHCl_3$ (20 mL) and CH_3OH (20 mL) was added a solution of Ag(OTf) (38.9 mg, 0.15 mmol, 2.0 equiv.) in a round bottom flask, diethyl ether was carefully layered. Let the reaction sited overnight, and the solid was collected by centrifuge, the washed with diethyl ether, (113 mg, quant.).

Elemental Analysis (%) calcd for $C_{124}H_{72}Ag_4Zn_2F_{12}N_{24}O_{12}S_4$•$3CHCl_3$: C 45.31, H 2.25, N 9.99; found: C 44.76, H 2.42, N 9.74.

Co(II) tetrakis(bipyridyl) porphyrin:
Free-base porphyrin (50 mg, 0.054 mmol, 1.0 eq), $CHCl_3$ (30 mL) and CH_3OH (5 mL) were placed in a 50 mL round-bottom flask. To the clear, red solution was added cobalt acetate tetrahydrate (67 mg 0.27 mmol, 5.0 eq) dissolved in CH_3OH (3 mL). The solution was stirred at room temperature for 16 h under the dark to give clear, purple solution. The solution was transferred to separating funnel, washed with 50 mM EDTA·2Na aqueous solution (20 mL × 3) and with H_2O (20 mL × 3). The combined organic phase was dried over Na_2SO_4, filtered and evaporated to obtain crude 1 as a reddish purple solid (48 mg, 89%).

LTQ-MS: m/z = 984.621, corresponding to $[M+H^+]^{1+}$, m/z = 492.995, corresponding to $[M+2H^+]^{2+}$,

Co_2Ag_4 prism:
To a solution of Co-porphyrin (22.4 mg, 0.024 mmol, 1.0 equiv.) in a mixture of CH_2Cl_2 (5.0 mL) and CH_3OH (5.0 mL) was added a solution of Ag(OTf) (12.3 mg, 0.048 mmol, 2.0 equiv.) in a 20 mL vial, diethyl ether was carefully layered. Let the reaction sited overnight, and the solid was collected by centrifuge, the washed with diethyl ether, (34.5 mg, quant.).

Elemental Analysis (%) calcd for $C_{124}H_{72}Ag_4Co_2F_{12}N_{24}O_{12}S_4$•$12CH_2Cl_2$: C 40.69, H 2.41, N 8.37; found: C 40.60, H 2.36, N 8.82.

HR-MS: m/z = 1348.9965, corresponding to $[M-2OTf^-]^{2+}$, m/z = 1369.0182, corresponding to $[M-2OTf^- + ACN]^{2+}$, and m/z = 863.0297, corresponding to $[M-3OTf^- + ACN]^{3+}$

UV-Vis (ACN): soret band λ_{max} = 433 nm, Q bands λ_{max} = 531, 587 nm.

Spectroscopic characterization:

^{1}H NMR spectroscopy

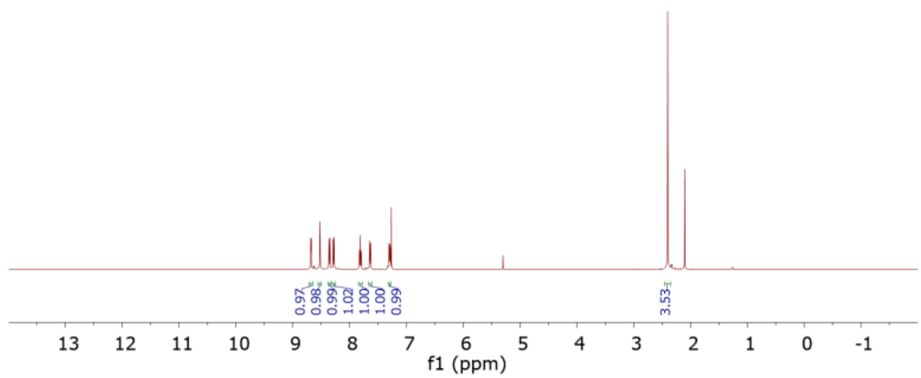


Figure S1 ^{1}H NMR spectrum of 5-Methyl-2,2'-bipyridine ($CDCl_3$, 500 MHz, 298 K).

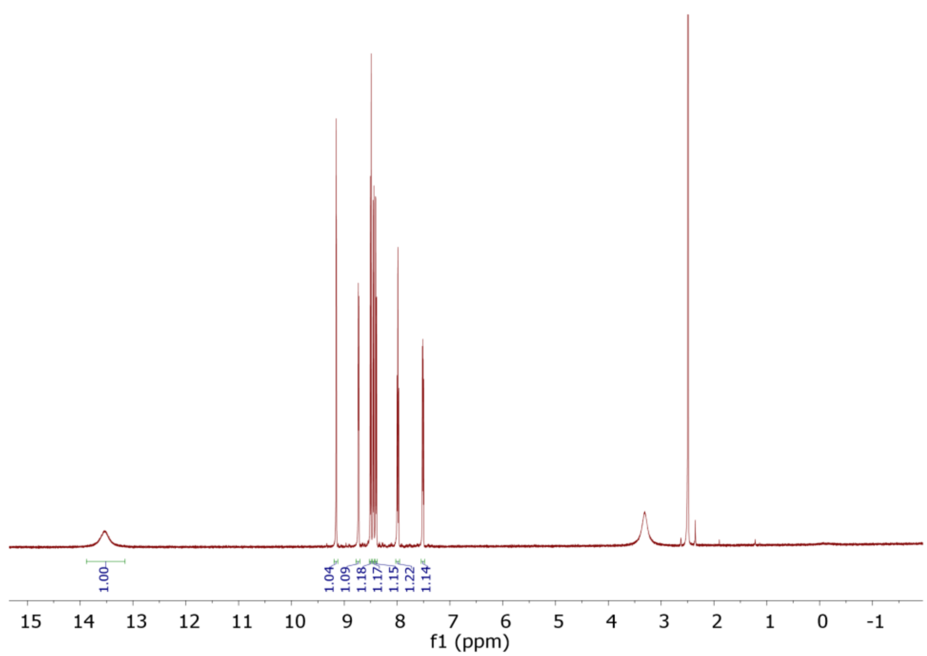


Figure S2. ^{1}H NMR spectrum of 2,2'-Bipyridinyl-5-carboxylic acid (DMSO, 500 MHz, 298 K).

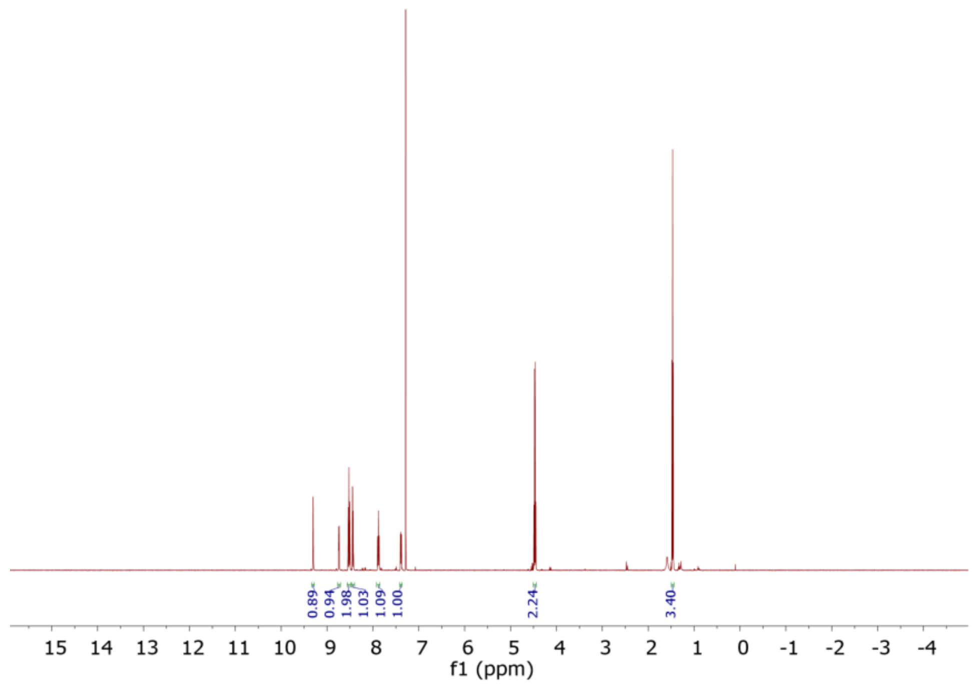


Figure S3. ¹H NMR spectrum of Ethyl 2,2′-Bipyridinyl-5-carboxylate ($CDCl_3$, 500 MHz, 298 K).

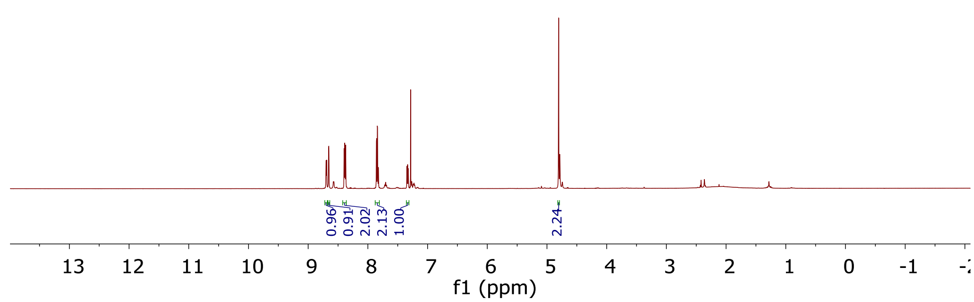


Figure S4. ¹H NMR spectrum of 2,2′-Bipyridinyl-5-methanol ($CDCl_3$, 500 MHz, 298 K).

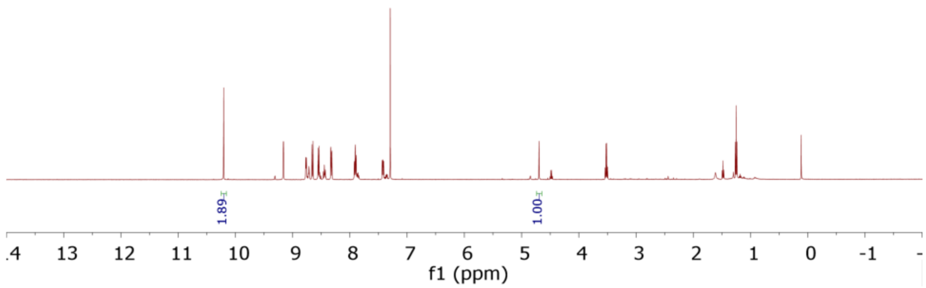


Figure S5. ^{1}H NMR spectrum of 2,2´-bipyridine-5-carbaldehyde ($CDCl_3$, 500 MHz, 298 K).

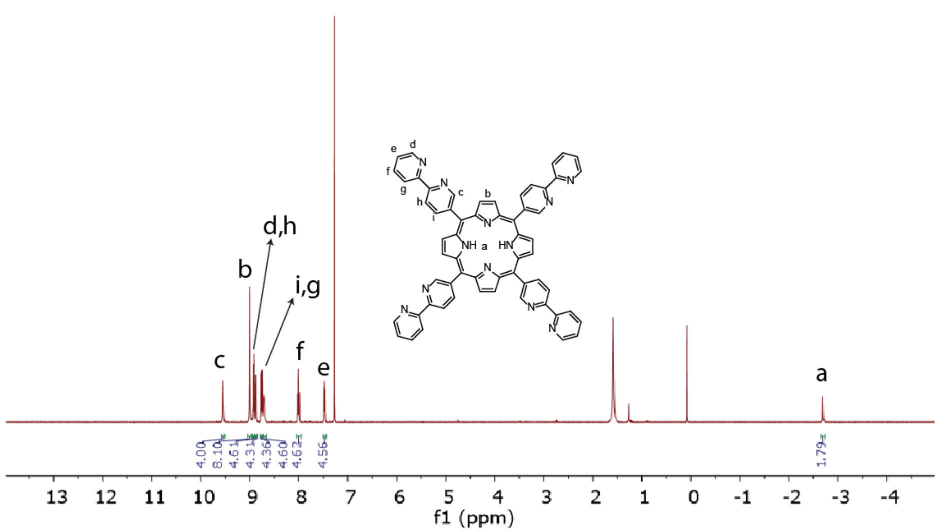


Figure S6. ^{1}H NMR spectrum of tetrakis(bipyridyl) porphyrin ($CDCl_3$, 500 MHz, 298 K).

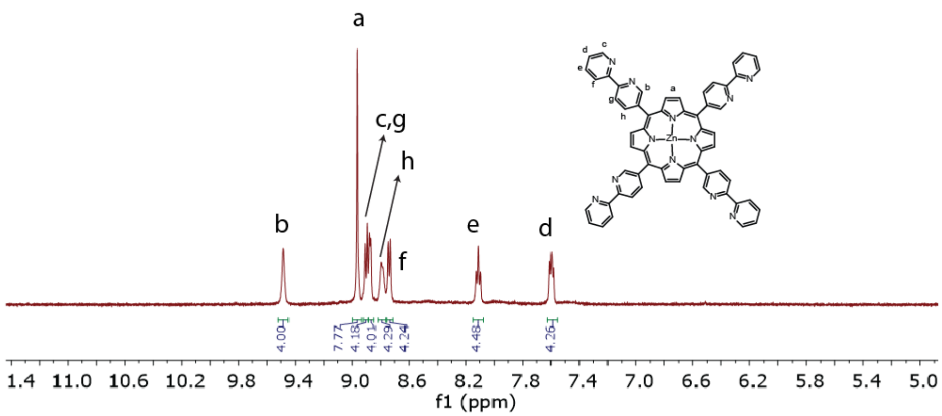


Figure S7. ¹H NMR spectrum of Zn tetrakis(bipyridyl) porphyrin (DMSO, 500 MHz, 298 K).

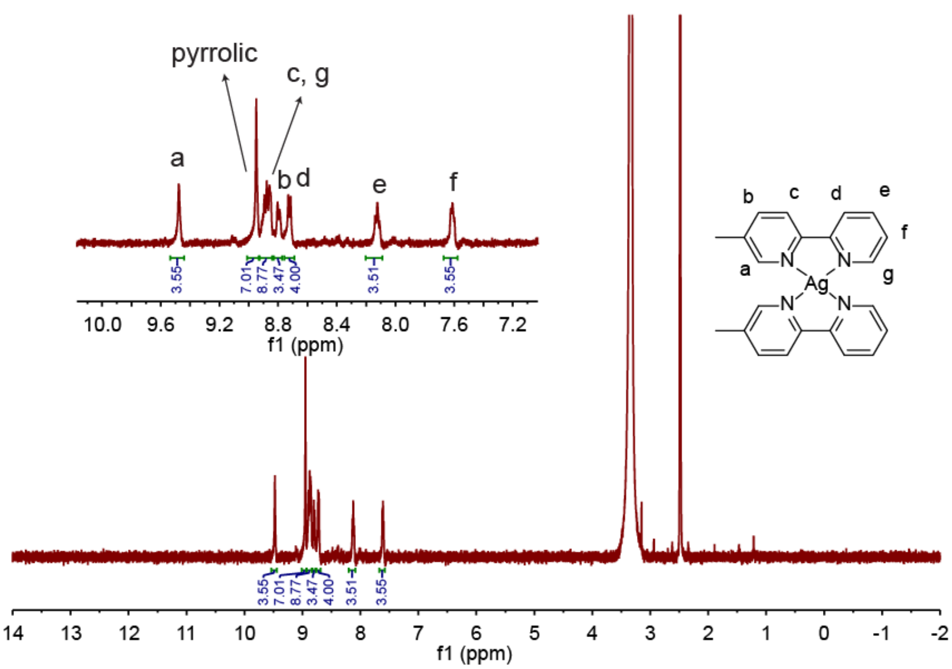


Figure S8. ¹H NMR spectrum of Zn_2Ag_4 prism (DMSO, 500 MHz, 298 K).

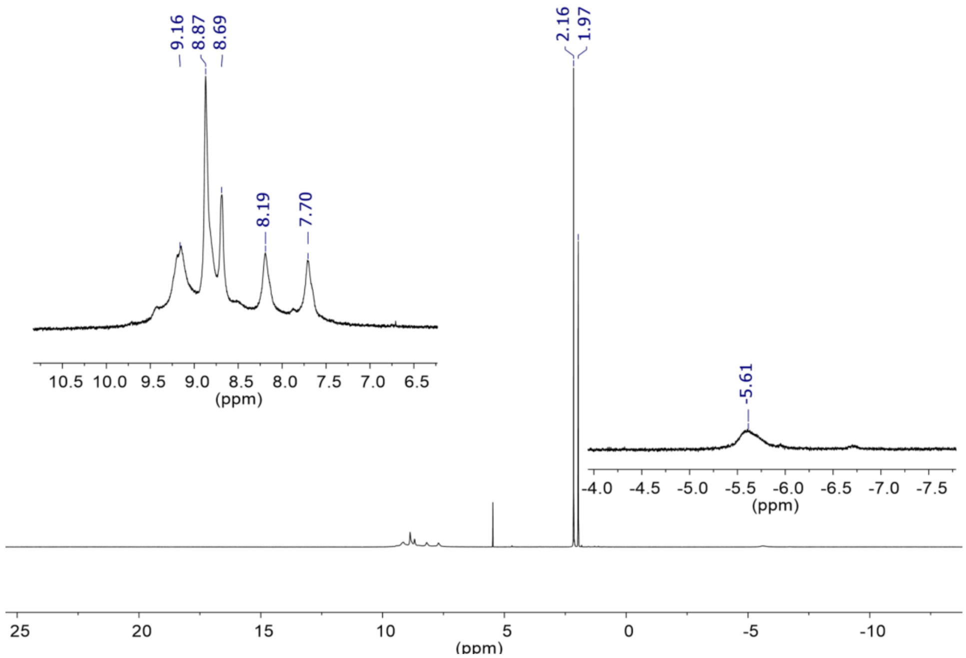


Figure S9. ^1H NMR spectrum of Co_2Ag_4 prism (CD_3CN, 500 MHz, 298 K).

Mass spectrometry:

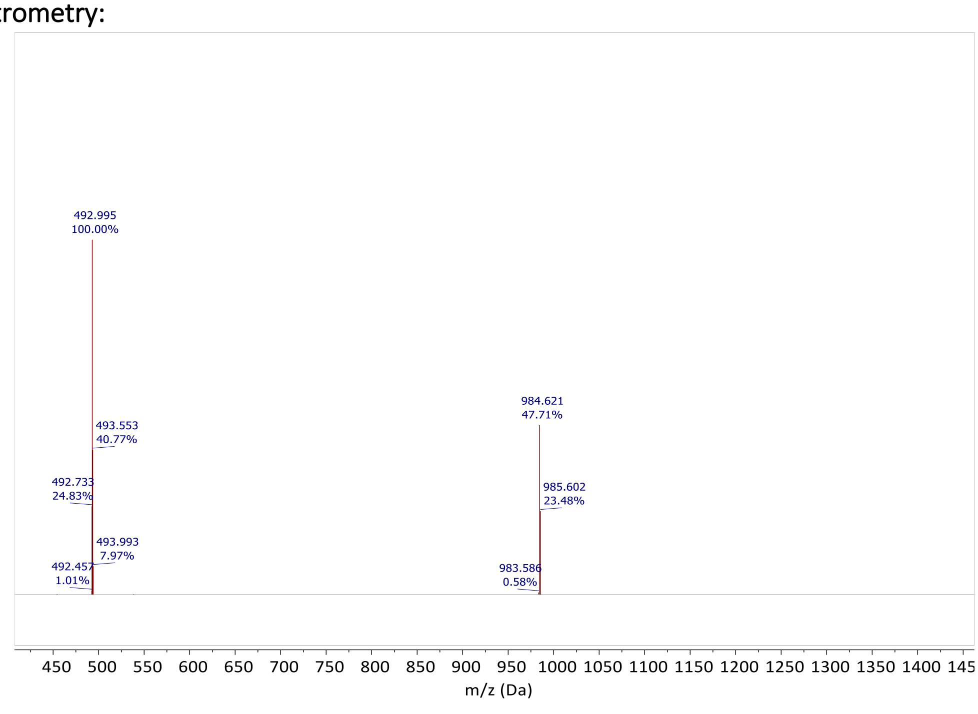


Figure S10. LTQ-MS of Co tetrakis(bipyridyl) porphyrin, m/z =984.621 was attributed to the M+H+.

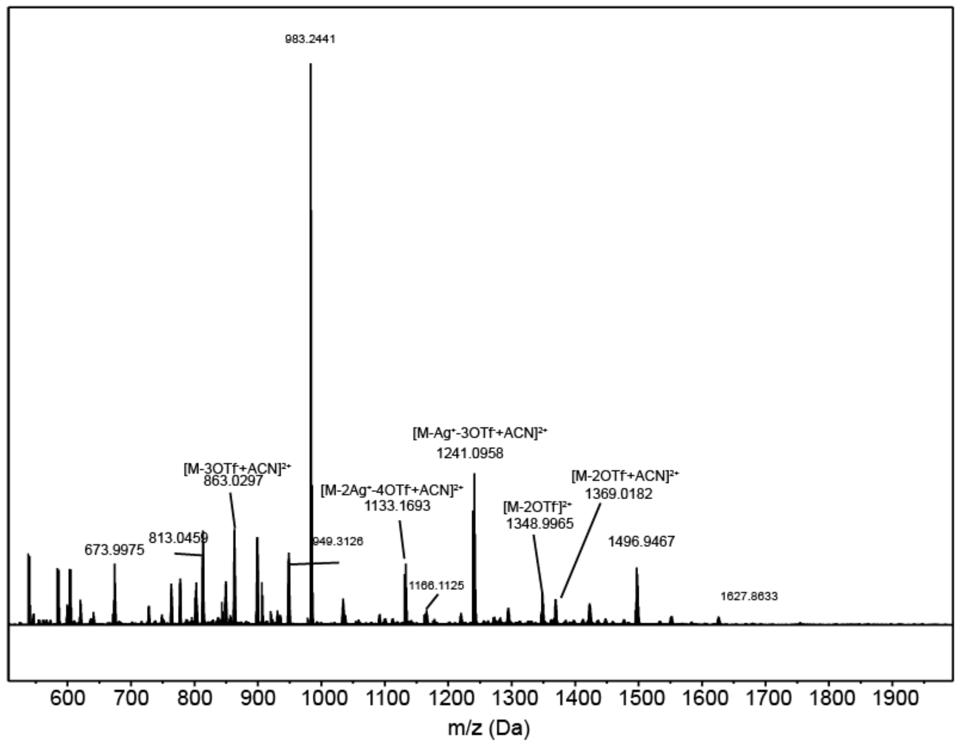


Figure S11. Mass spectrometry of Co_2Ag_4 prism

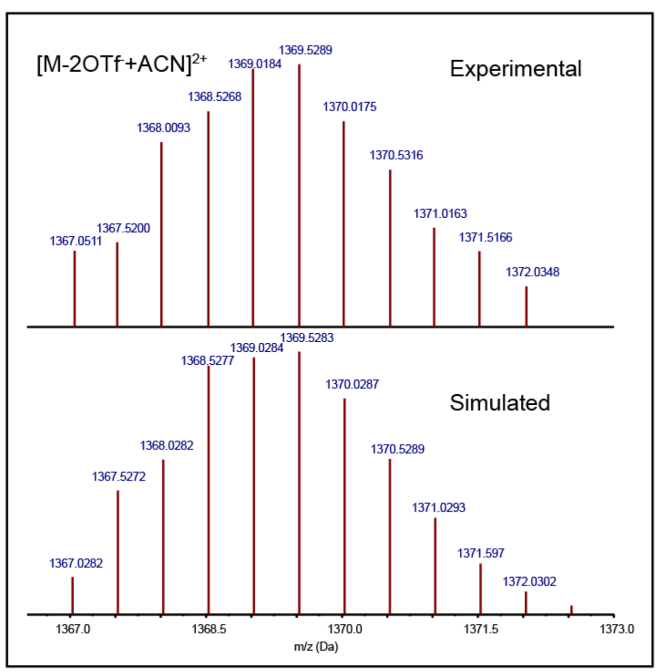


Figure S12. The 2+ base peak for Co_2Ag_4 prism in Figure 11 corresponding (top) Experimental data, (bottom) simulated spectrum with loss of 2 OTf^- counterions and addition of an acetonitrile $[M–2OTf^-+ACN]^{2+}$.

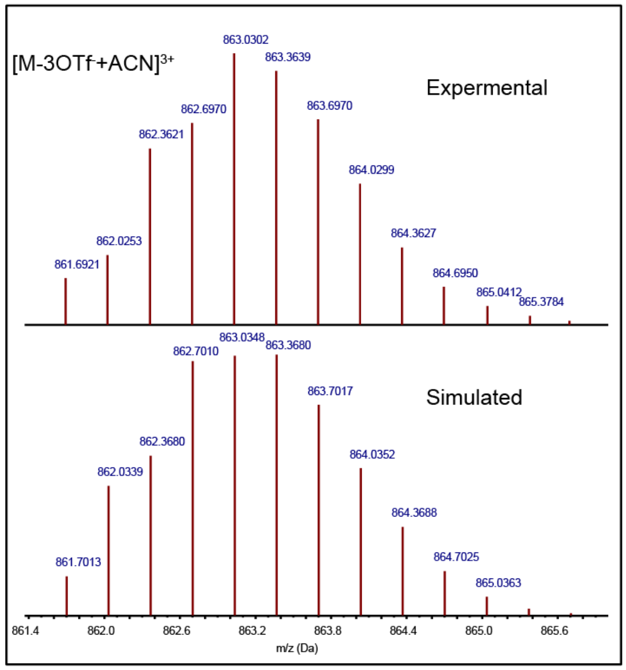


Figure S13. The 3+ base peak Co_2Ag_4 prism in Figure S11 corresponding (top) Experimental data, (bottom) simulated spectrum with loss of 2 OTf– counterions and addition of an acetonitrile $[M–3OTf^{–}+ACN]^{3+}$.

Electrochemical Experiments:

The CVs of **Co_2Ag_4 prism** and **Zn_2Ag_4 prism** show an irreversible oxidization wave at ~0 V vs Fc^+/Fc. The CV of $[Ag(bpy)_2]OTf$ has a similar oxidation feature at the same potential, thus we ascribe this redox event to the Ag nodes. Although the current response is weak, the **Co_2Ag_4 prism** shows a reduction at ca. –1.3 V vs Fc^+/Fc that is not present in the **Zn_2Ag_4 prism** which we attribute to the Co(II)/Co(I) couple. This cobalt centered reduction is seen in our other cofacial porphyrin prisms.[2]

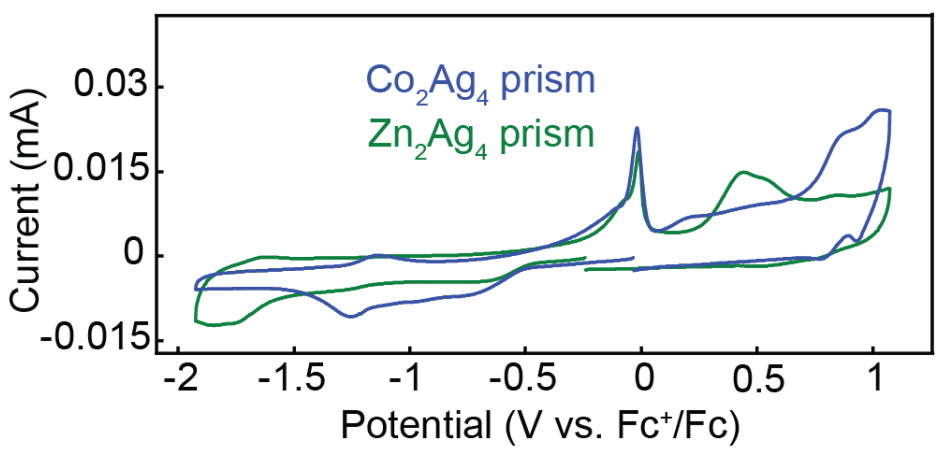


Figure S14. CV of Co_2Ag_4 prism and Zn_2Ag_4 prism under Nitrogen. Conditions: 100 mM $TBAPF_6$ in dry acetonitrile, glassy carbon working electrode, Pt-wire counter electrode, scan rate: 100 mV/sec, scan direction: reduction first.

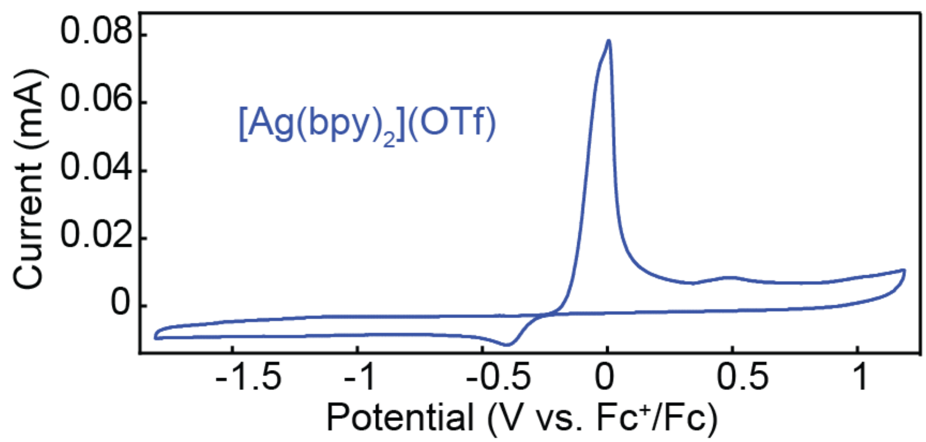


Figure S15. CV of Ag(bpy)$_2$OTf under Nitrogen. Conditions: 100 mM TBAPF$_6$ in dry acetonitrile, glassy carbon working electrode, Pt-wire counter electrode, scan rate: 100 mV/sec, scan direction: reduction first.

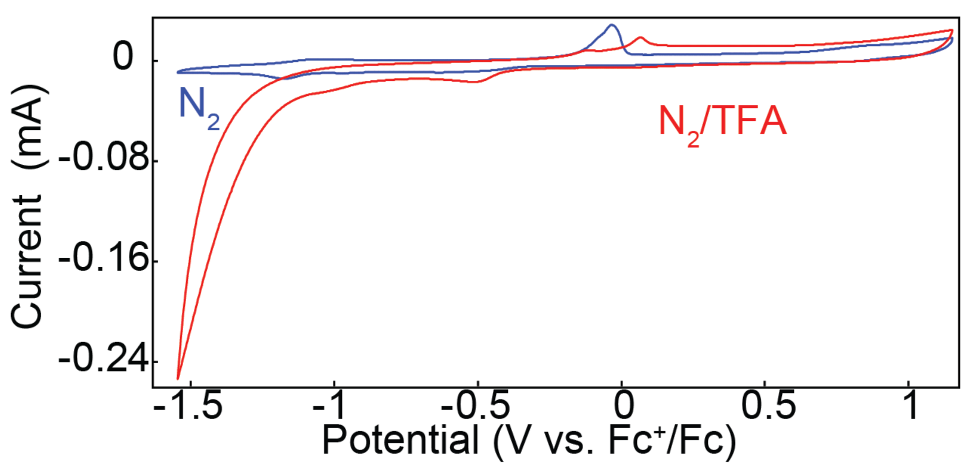


Figure S16. CV of Co$_2$Ag$_4$ Prism under Nitrogen and TFA. Conditions: 100 mM TBAPF$_6$ in dry acetonitrile, glassy carbon working electrode, Pt-wire counter electrode, scan rate: 100 mV/sec, scan direction: reduction first.

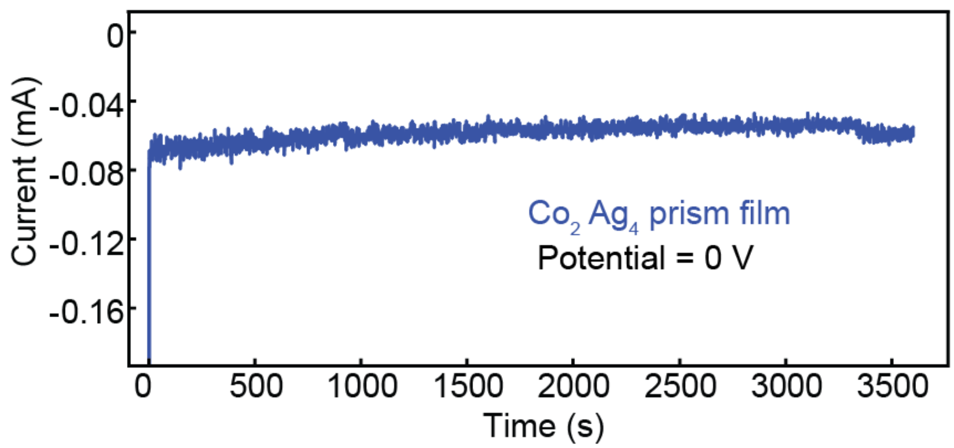


Figure S17. Controlled potential electrolysis (CPE) of Co_2Ag_4 prism under heterogeneous condition. Conditions: potential held at 0 V, in 0.5 M H_2SO_4 aqueous solution, with saturated oxygen, glassy carbon working electrode, Pt-wire counter electrode. Reference electrode: AgCl in 3 M KCl. Plot Current with time.

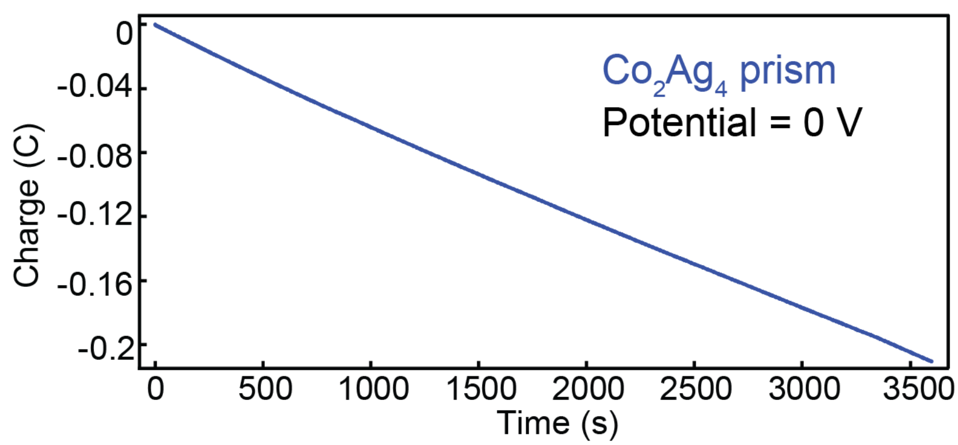


Figure S 18. Controlled potential electrolysis (CPE) of Co_2Ag_4 prism under heterogeneous condition. Conditions potential held at 0 V, in 0.5 M H_2SO_4 aqueous solution, with saturated oxygen, glassy carbon working electrode, Pt-wire counter electrode. Reference electrode: AgCl in 3 M KCl. Plot Charge with time.

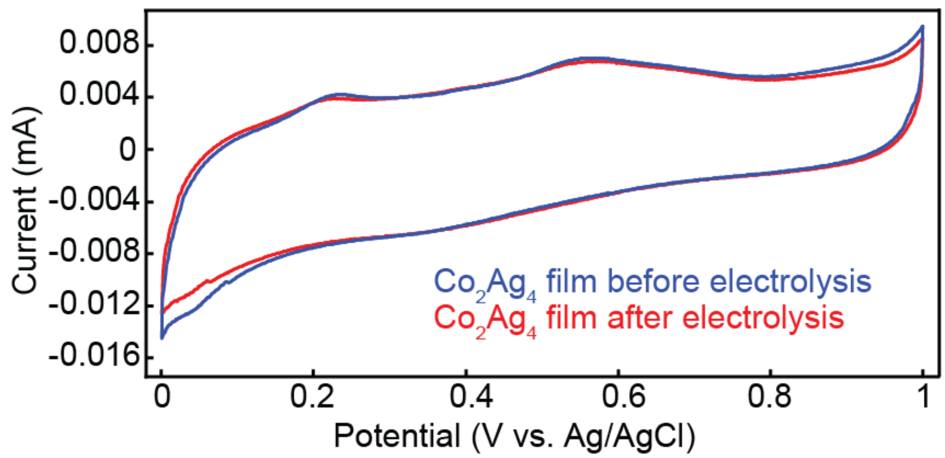


Figure S 19. CV before and after the electrolysis in 0.5 M H_2SO_4, in 0.5 M H_2SO_4 aqueous solution, with saturated oxygen, glassy carbon working electrode, Pt-wire counter electrode. Reference electrode: AgCl in 3 M KCl.

UV-vis study:

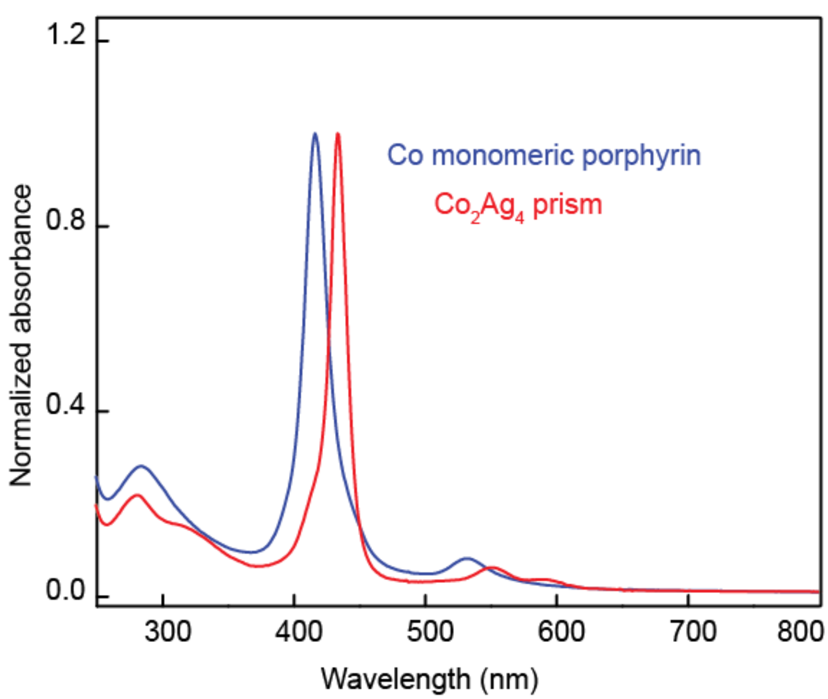


Figure S20. Normalized UV-Vis spectra of monomeric Co porphyrin and Co_2Ag_4 prism.

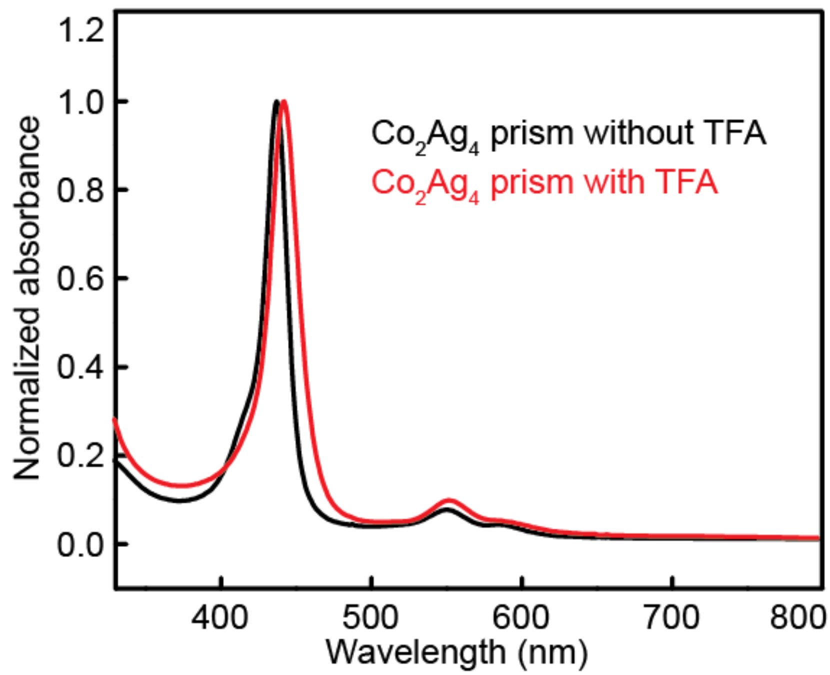


Figure S 21. Normalized UV-Vis spectra of Co_2Ag_4 prism in acetonitrile before and after addition of TFA.

KL-analysis:

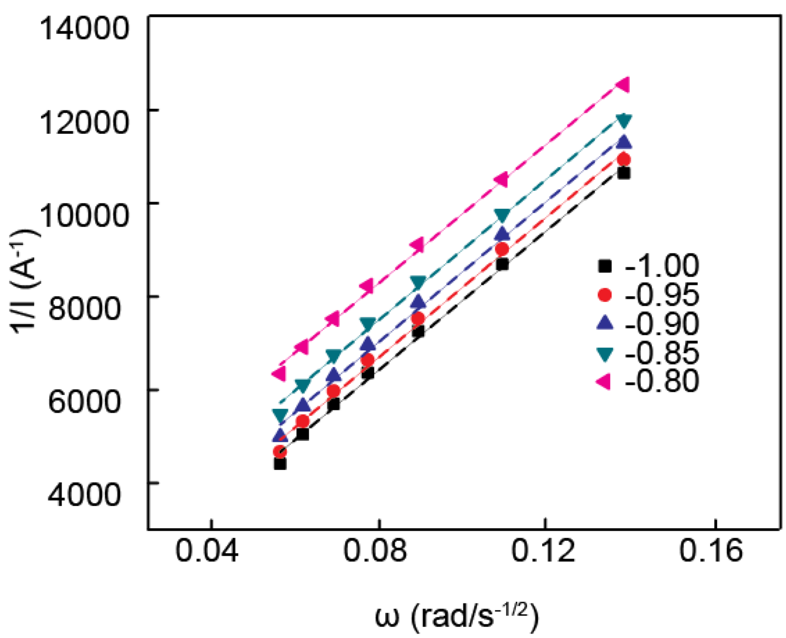


Figure S22. Koutecký-Levich plots of Co_2Ag_4 prism

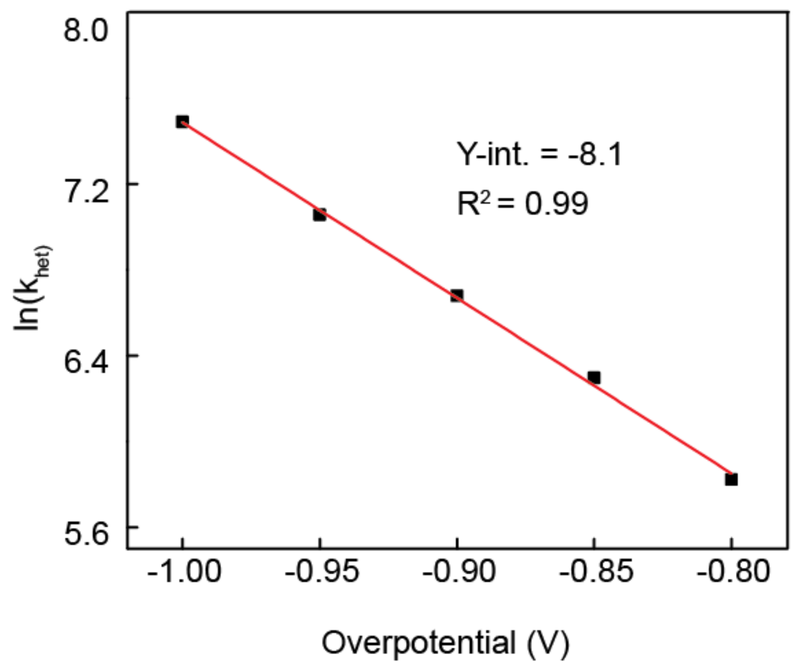


Figure S23. Plot of ln(k_{het}) vs. overpotential for the Co_2Ag_4 prism. The y-intercept of this plot is ln(ks)

KL analysis detail:

The rotating disk data for the catalyst was plotted at various overpotentials using the KL equation in which, i_{lim} is the limiting current (A), B is the Levich constant, ω is the rotation rate (rad/s), and i_K is the kinetically limited current, select five different data at different overpotential from the LSV data (Figure 4.) at different rotation rate, plot ω versus 1/A to obtain KL plot as shown in Figure S22. Koutecký-Levich plots of Co2Ag4 prism. Extracted the Y intercept as $1/i_k$, then use Equation S2 to obtain the value k_{het}. Finally, plot the ln(k_{het}) with overpotential as shown in Figure S23. Plot of ln(khet) vs. overpotential for the Co2Ag4 prism. The y-intercept of this plot is ln(ks)Figure S23. to obtain the y intercept as the standard rate constant values k_s.

$$\frac{1}{i_{lim}} = \omega^{-1/2} + \frac{i}{i_k} \quad \text{Equation S1.}$$

$$i_k = nFAk_{het}[O_2]\Gamma_{cat} \quad \text{Equation S2.}$$

$$k_{het} = k_s e^{\frac{-a\eta}{RT}} \quad \text{Equation S3.}$$

$$n = 4 - a(\frac{\%H_2O_2}{100}) \quad \text{Equation S4.}$$

$$\%H_2O_2 = \frac{\frac{2i_{ring}}{N}}{i_{disk} + \frac{i_{ring}}{N}} \times 100$$

Equation S5.

Computational Details:

The structure of Zn_2Ag_4 and Co_2Ag_4 prisms were optimized using ORCA 5.0.3 with the B97-3c functional and def2-mTZVP basis set. A frequency calculation was performed at the same level of theory/basis set and was analyzed for imaginary frequencies. After several optimizations from various displaced geometries the imaginary frequency remained.

Coordinates of Zn_2Ag_4 Optimized Structure:

Ag	-6.333178000	-6.004808000	2.187593000
Ag	-6.287246000	6.087647000	2.213068000
Zn	-0.022453000	0.014979000	0.005125000
N	2.026159000	0.006493000	0.017918000
N	-0.023513000	2.064481000	-0.009945000
N	-0.039919000	-2.034275000	-0.021071000
N	-2.070251000	0.023544000	-0.052485000
N	-5.647866000	-4.801240000	4.060254000
N	-6.811601000	-7.303241000	4.029590000
N	-7.428269000	-6.409383000	0.248663000
N	-4.939812000	-5.198991000	0.421210000
N	-5.594513000	4.893650000	4.082287000
N	-6.743224000	7.401743000	4.055501000
N	-7.373009000	6.502370000	0.276259000
N	-4.891283000	5.273350000	0.440583000
C	2.832061000	-1.099641000	-0.092941000
C	1.083822000	2.871837000	-0.060777000
C	0.665801000	4.248906000	-0.099543000
C	-1.123196000	2.886907000	-0.061009000
C	-0.690770000	4.256462000	-0.116605000
C	-2.452667000	2.461718000	-0.118074000
C	-2.881623000	1.129919000	-0.066421000
C	-4.257195000	0.710724000	-0.047141000
C	-4.262533000	-0.646494000	-0.050278000
C	-2.890347000	-1.076370000	-0.071218000
C	-2.472082000	-2.411248000	-0.128648000
C	-1.146228000	-2.847519000	-0.073951000
C	-0.725159000	-4.220409000	-0.133826000
C	0.631445000	-4.224000000	-0.117336000
C	1.060766000	-2.850508000	-0.074637000
C	2.394396000	-2.426066000	-0.137209000
C	4.198657000	-0.679656000	-0.254432000
C	4.204087000	0.676698000	-0.250829000
C	2.840914000	1.106752000	-0.087151000
C	2.413916000	2.436801000	-0.125181000
C	-3.882904000	-3.451623000	4.964120000
C	-4.792623000	-3.781565000	3.967376000
C	-3.938915000	-4.193724000	6.142240000
C	-5.679967000	-5.533685000	5.188411000
C	-4.847254000	-5.227200000	6.261130000
C	-6.578273000	-6.703139000	5.211143000
C	-7.140878000	-7.182244000	6.390074000
C	-7.941395000	-8.311010000	6.349758000

C	-7.578181000	-8.396634000	3.999449000
C	-8.157658000	-8.938854000	5.133500000
C	-3.930161000	-4.343567000	0.594161000
C	-3.534159000	-3.419381000	-0.366083000
C	-4.214407000	-3.442893000	-1.582489000
C	-5.240719000	-4.344136000	-1.780885000
C	-5.600216000	-5.208704000	-0.750256000
C	-6.751183000	-6.122857000	-0.878868000
C	-7.139699000	-6.650176000	-2.106701000
C	-8.255650000	-7.466230000	-2.174502000
C	-8.963623000	-7.734616000	-1.013902000
C	-8.510364000	-7.190916000	0.174852000
C	-3.506487000	3.479288000	-0.351466000
C	-4.191238000	3.509070000	-1.565246000
C	-3.889740000	4.407896000	0.609894000
C	-4.749258000	3.866001000	3.986459000
C	-3.839714000	3.527048000	4.980367000
C	-3.884602000	4.270080000	6.158431000
C	-4.782306000	5.312463000	6.279970000
C	-5.616252000	5.626649000	5.210437000
C	-6.505170000	6.803257000	5.236795000
C	-7.502202000	8.500298000	4.028037000
C	-8.069244000	9.049891000	5.164905000
C	-7.848172000	8.423872000	6.381219000
C	-7.055463000	7.289494000	6.418674000
C	-5.556138000	5.288673000	-0.728157000
C	-5.209462000	4.420250000	-1.759973000
C	-6.699152000	6.213269000	-0.852693000
C	-7.084556000	6.746874000	-2.078765000
C	-8.449154000	7.292651000	0.205154000
C	-8.898902000	7.842926000	-0.981816000
C	-8.193927000	7.572030000	-2.143666000
H	1.317214000	5.104481000	-0.120698000
H	-1.333826000	5.117146000	-0.172501000
H	-5.112714000	1.362575000	-0.023350000
H	-5.123081000	-1.291822000	-0.029755000
H	-1.375395000	-5.075594000	-0.191401000
H	1.275889000	-5.084765000	-0.140848000
H	5.043795000	-1.331188000	-0.391716000
H	5.054430000	1.322192000	-0.384458000
H	-4.824795000	-3.209551000	3.049737000
H	-3.258860000	-3.969625000	6.951938000
H	-4.872932000	-5.821471000	7.161959000
H	-6.978072000	-6.667097000	7.325001000

H	-8.392684000	-8.692043000	7.254579000
H	-7.716271000	-8.855959000	3.030187000
H	-8.764017000	-9.829548000	5.060574000
H	-3.418977000	-4.390397000	1.546976000
H	-3.943455000	-2.744408000	-2.361606000
H	-5.785836000	-4.343865000	-2.712606000
H	-6.563313000	-6.447634000	-2.996923000
H	-8.565323000	-7.889272000	-3.119317000
H	-9.847908000	-8.354410000	-1.024703000
H	-9.033142000	-7.370371000	1.104095000
H	-3.930059000	2.807925000	-2.345305000
H	-3.374246000	4.450115000	1.560644000
H	-4.789783000	3.294699000	3.068779000
H	-3.204607000	4.039114000	6.966234000
H	-4.799056000	5.906978000	7.180826000
H	-7.644534000	8.957818000	3.058490000
H	-8.669915000	9.944605000	5.094085000
H	-8.289892000	8.810553000	7.288366000
H	-6.889590000	6.775818000	7.353858000
H	-5.758269000	4.425038000	-2.689533000
H	-6.510448000	6.541706000	-2.969861000
H	-8.969887000	7.473719000	1.135183000
H	-9.778327000	8.469625000	-0.990275000
H	-8.500912000	7.999990000	-3.087141000
Ag	5.905190000	6.030676000	2.453603000
Ag	5.845283000	-6.055052000	2.439629000
Zn	-0.416236000	0.017345000	4.637445000
N	-2.464497000	0.030077000	4.625789000
N	-0.419613000	-2.032360000	4.652350000
N	-0.393775000	2.066298000	4.663581000
N	1.631783000	0.004104000	4.695729000
N	5.203777000	4.839310000	0.580846000
N	6.373146000	7.337869000	0.613847000
N	7.004384000	6.423577000	4.390210000
N	4.510953000	5.222030000	4.222315000
N	5.165613000	-4.850280000	0.566455000
N	6.311557000	-7.359938000	0.599653000
N	6.935743000	-6.465312000	4.378864000
N	4.452840000	-5.241993000	4.205598000
C	-3.267936000	1.137912000	4.737119000
C	-1.528629000	-2.837387000	4.702111000
C	-1.113624000	-4.215455000	4.739318000
C	0.678240000	-2.857206000	4.702913000
C	0.242949000	-4.225929000	4.756476000

C	2.008416000	-2.434887000	4.762052000
C	2.440508000	-1.104161000	4.711553000
C	3.817116000	-0.688315000	4.694892000
C	3.825664000	0.668881000	4.696955000
C	2.454429000	1.102085000	4.715521000
C	2.039186000	2.438028000	4.771907000
C	0.714258000	2.877193000	4.716122000
C	0.296038000	4.251005000	4.775426000
C	-1.060560000	4.257443000	4.758944000
C	-1.492763000	2.884872000	4.716946000
C	-2.827233000	2.463336000	4.780833000
C	-4.635420000	0.720869000	4.898942000
C	-4.643808000	-0.635484000	4.894941000
C	-3.281631000	-1.068442000	4.730869000
C	-2.857645000	-2.399416000	4.767707000
C	3.437131000	3.490933000	-0.321432000
C	4.348834000	3.819512000	0.673967000
C	3.490430000	4.235352000	-1.498261000
C	5.233437000	5.574011000	-0.545892000
C	4.397974000	5.269520000	-1.617076000
C	6.132674000	6.742802000	-0.568787000
C	6.689617000	7.225987000	-1.748770000
C	7.491643000	8.353672000	-1.708190000
C	7.141268000	8.430114000	0.644347000
C	7.715238000	8.976343000	-0.490602000
C	3.498847000	4.369492000	4.050271000
C	3.103344000	3.443838000	5.009402000
C	3.786498000	3.463621000	6.224284000
C	4.815523000	4.361962000	6.421859000
C	5.174677000	5.227441000	5.391853000
C	6.328840000	6.137774000	5.518934000
C	6.722105000	6.661914000	6.746605000
C	7.841161000	7.473785000	6.813130000
C	8.547572000	7.741170000	5.651346000
C	8.089643000	7.200999000	4.462813000
C	3.059900000	-3.454578000	4.997697000
C	3.735557000	-3.490558000	6.216347000
C	3.450894000	-4.377258000	4.033997000
C	4.319344000	-3.823297000	0.659648000
C	3.409352000	-3.487680000	-0.335074000
C	3.456163000	-4.232399000	-1.512007000
C	4.355234000	-5.273920000	-1.631181000
C	5.188246000	-5.585517000	-0.560165000
C	6.076708000	-6.762516000	-0.582946000

C	7.069789000	-8.459065000	0.630257000
C	7.639101000	-9.010273000	-0.504614000
C	7.421280000	-8.385563000	-1.722207000
C	6.629488000	-7.250679000	-1.762838000
C	5.109639000	-5.262934000	5.378902000
C	4.753630000	-4.401415000	6.413284000
C	6.254633000	-6.184795000	5.505531000
C	6.635020000	-6.723311000	6.731024000
C	8.014638000	-7.251519000	4.451879000
C	8.460017000	-7.806183000	5.638522000
C	7.747294000	-7.544440000	6.797762000
H	-1.766973000	-5.069596000	4.759624000
H	0.884394000	-5.087937000	4.811044000
H	4.671124000	-1.342250000	4.673468000
H	4.687793000	1.312096000	4.677205000
H	0.947984000	5.104882000	4.832849000
H	-1.703235000	5.119549000	4.782095000
H	-5.479128000	1.374230000	5.036358000
H	-5.495506000	-1.279282000	5.028208000
H	4.382930000	3.246142000	1.590657000
H	2.809048000	4.012317000	-2.307130000
H	4.421298000	5.865435000	-2.516868000
H	6.521415000	6.714854000	-2.684933000
H	7.938568000	8.737774000	-2.613880000
H	7.285372000	8.885095000	1.614812000
H	8.323129000	9.865966000	-0.417350000
H	2.985109000	4.419702000	3.099010000
H	3.515650000	2.764505000	7.002865000
H	5.362872000	4.358579000	7.352269000
H	6.146989000	6.460064000	7.637802000
H	8.154430000	7.894380000	7.757851000
H	9.434235000	8.357573000	5.661048000
H	8.610928000	7.380036000	3.532675000
H	3.467963000	-2.793879000	6.998245000
H	2.942333000	-4.414954000	3.079369000
H	4.359040000	-3.249838000	1.576090000
H	2.776346000	-4.003725000	-2.320610000
H	4.373422000	-5.869903000	-2.531053000
H	7.209630000	-8.915358000	1.600719000
H	8.239032000	-9.905273000	-0.431280000
H	7.864846000	-8.773635000	-2.627854000
H	6.466101000	-6.737942000	-2.698972000
H	5.295806000	-4.410661000	7.346679000
H	6.055189000	-6.525098000	7.619997000

H	8.541248000	-7.425683000	3.523809000
H	9.342016000	-8.429238000	5.648760000
H	8.050625000	-7.976291000	7.740647000

Coordinates of Co_2Ag_4 Optimized Structure:

Ag	16.91456180061173	9.59836659584698	-2.00383791815975
Ag	13.73659499886531	15.10211732204602	8.30094275718063
Co	10.01769884416324	15.02603145474824	0.06400024188920
N	8.86403184915502	16.26382887937543	-0.95523345406838
N	9.49857195820789	15.92180499321971	1.74548562317373
N	10.53070638980725	14.11801842472820	-1.61231945058434
N	11.14656874696920	13.77588265508424	1.08249071481300
N	17.69732759001080	11.71776898722987	-1.46873318878545
N	18.98121609352717	9.82669543582066	-3.01103108651958
N	16.08766804228183	7.52978122219577	-1.64561845115055
N	14.52367703221657	9.80962501324804	-1.88625658349939
N	15.14550313311387	16.14509705243758	6.79604105317292
N	15.09623486755039	16.52795772715296	9.52393773691167
N	12.67765747678842	13.42297794963509	9.35697461367716
N	11.77073389695818	14.56990706638538	6.99599994337235
C	8.60489841706426	16.24464536204491	-2.31220720801824
C	8.62237261898770	16.97797613460061	1.89469764599916
C	8.48868363424045	17.32633098927931	3.27898386930257
C	9.87369496082214	15.58594892319386	3.03350518868225
C	9.24424354258378	16.45407553290766	3.98200895538617
C	10.70284363109592	14.53840742632977	3.38519488396924
C	11.33392407566265	13.73498570215697	2.45091200166620
C	12.25980535881729	12.70012901064863	2.79804636828763
C	12.61428003135011	12.08283413515191	1.64794352210948
C	11.90836106354731	12.73490413265387	0.58705462392466
C	11.97341983993202	12.32888830229633	-0.73476129759192
C	11.35074645528486	13.01422486635592	-1.76003688634044
C	11.43704640903495	12.63409113495831	-3.13755331519207
C	10.67661595740269	13.50529281081710	-3.83661514916586
C	10.09090569177289	14.40713340722033	-2.88842902047253
C	9.16306575026388	15.37595649934886	-3.23006396154876
C	7.61262671937261	17.22095173673404	-2.64836453602644
C	7.26248904730815	17.84115586242660	-1.49941483283905
C	8.03716486702350	17.24893961936061	-0.45058105872140
C	7.90455471815057	17.58982670092912	0.88163173598832
C	17.09028634223672	14.02802465711520	-1.26767215737977
C	16.88182284018015	12.67678751242740	-1.02752366118612
C	18.25553967155592	14.37979164960329	-1.94499336718441
C	18.80818704793995	12.05769914362623	-2.14728020376749
C	19.12323742669477	13.39469839733459	-2.37471679970731
C	19.63067728870378	10.96098983345477	-2.69129821995187
C	21.00196304548501	11.09069220466058	-2.88764931596333

C	21.71007683929087	10.03789201911153	-3.44167202736755
C	19.66950117738493	8.81833584436079	-3.55260398820463
C	21.03150450225035	8.88150650557063	-3.79168677512678
C	13.87380071920509	10.95818074629182	-1.68476659206507
C	12.65401733807948	11.04336487338316	-1.02371587593271
C	12.08279601841761	9.84678520975804	-0.59484236197808
C	12.73509337373608	8.65187742587649	-0.82182694331850
C	13.97138074018618	8.65913803992121	-1.46297604052990
C	14.74626414742430	7.41726294133403	-1.65045651681507
C	14.12801020179901	6.17982404425287	-1.80236932752101
C	14.90483525310018	5.04110501568166	-1.92785503878709
C	16.28480360627639	5.16178260450002	-1.89385583292758
C	16.83228429993441	6.42497429961480	-1.75790196029360
C	10.85060739798290	14.17283551169774	4.81450886199476
C	10.26759104092382	13.00044004970931	5.29164170311646
C	11.57883942372137	14.93000034164002	5.72520590748233
C	14.87390728222921	16.16965709011768	5.49015030332728
C	15.26404602214506	17.20144739685625	4.64729784121608
C	16.04137751739946	18.21459251586020	5.20343649883264
C	16.35601309015435	18.17886104664753	6.54801757976576
C	15.87029340899699	17.14067578635641	7.33832695955186
C	16.06582539024456	17.11629658311925	8.80009482691516
C	15.19832101736668	16.51878102933744	10.85528984930882
C	16.26819722221542	17.08088268421724	11.53055201867363
C	17.28156302067914	17.66723306312503	10.78935454869440
C	17.17884806879487	17.68774057204356	9.40879705670031
C	11.21234631144558	13.43356255467954	7.44807073641662
C	10.43893487081927	12.63319578263347	6.61090619092833
C	11.49510423646013	13.03784592293230	8.84145817088632
C	10.59664629264774	12.28161443686314	9.58816092888006
C	13.00026794335435	13.04161869981283	10.59749668704898
C	12.16336663153746	12.27528017632626	11.38851899710643
C	10.93269150990622	11.89862051009703	10.87510525581531
H	7.88112742767559	18.12631359885954	3.66227929921897
H	9.36509758369009	16.39799264107424	5.04903256636287
H	12.60067309010664	12.48295739014252	3.79465916261903
H	13.30018775976115	11.26376459769305	1.52451433765390
H	12.00528318421283	11.80380306565248	-3.51723090590805
H	10.51276800962113	13.52846628030625	-4.89897504995801
H	7.21512060177109	17.38609697216654	-3.63395852290124
H	6.52371983936078	18.61104786187454	-1.36469305785402
H	16.01557472264183	12.35099381378475	-0.46760170652129
H	18.46459484452954	15.42005908728753	-2.15148991412582
H	20.01150631312274	13.66191476143223	-2.92680806197924
H	21.51691164312533	11.99142597974293	-2.58852225790387
H	22.77681847552821	10.11840394205185	-3.59374985129376
H	19.09908289073016	7.93748454860024	-3.81396484467053
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H	14.35163069938049	11.85272483425880	-2.06285337231129
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H	12.30704780277028	7.72736994057295	-0.46518029219640
H	13.05173149462879	6.10685557601559	-1.84773526714469
H	14.43899230465261	4.07434889586561	-2.05395038054833
H	16.92758297201000	4.29767306581203	-1.97353401474157
H	17.90351712757812	6.56673358901476	-1.72329224901321
H	9.69429257879866	12.37564008035420	4.62125704749908
H	12.03264767442823	15.86305392880111	5.41680704587375
H	14.30788468495768	15.33423066330981	5.10091770161627
H	16.37639892600987	19.03682021003483	4.58673902402566
H	16.93222560144540	18.97885020603371	6.98753159688124
H	14.38279956281703	16.05459804600055	11.39310787450706
H	16.30330926425402	17.05573220863296	12.60966411566152
H	18.14272323400170	18.09942674001937	11.27838628290667
H	17.96909074843612	18.12128224917555	8.81414537260880
H	10.01041262216762	11.71129773816797	6.97372309581427
H	9.63347509032285	12.01537277848953	9.17941724274862
H	13.97087284309981	13.35583433297288	10.95507239969329
H	12.47129360939724	11.98568185982151	12.38223893692758
H	10.24192636225843	11.31772220039892	11.46917434496050
Ag	7.08835082882222	23.04731893235778	2.00026855176337
Ag	10.24098634677769	17.52795821155846	-8.29740446854255
Co	13.97301876562423	17.60915332152405	-0.06093718365302
N	15.12686743830483	16.37216317315241	0.95909405862566
N	14.49347208653155	16.71361398444561	-1.74210554262475
N	13.46040328254165	18.51835890000257	1.61486568702441
N	12.84519925321666	18.85949132659504	-1.08038398511554
N	6.30392177626342	20.92552065567122	1.46774555950519
N	5.02214834879121	22.82262725179663	3.00452147575317
N	7.91516468445636	25.11635980184337	1.63311244200387
N	9.47634013178269	22.83590523165293	1.88169269168545
N	8.83614788951445	16.48397800186483	-6.79277313636597
N	8.88136285304974	16.09823853457655	-9.52015150175748
N	11.30472829536344	19.20048629297921	-9.35453190407920
N	12.21329350358466	18.05581374916969	-6.99196715264872
C	15.38362567956155	16.39011383331535	2.31652636101918
C	15.37274463059384	15.65999443805242	-1.89099521894066
C	15.50694179008513	15.31109436767736	-3.27509594386825
C	14.11668692247991	17.04737630372037	-3.03020267306646
C	14.74818258621416	16.18036884402186	-3.97837133168160
C	13.28577050180383	18.09331891933525	-3.38244710284567
C	12.65596112902290	18.89822144784432	-2.44864252982415
C	11.73177912719289	19.93438547677269	-2.79639378460658
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