Supporting Information: A Doubly Deprotonated Diimine Dioximate Metalloligand as a Synthon for Multimetallic Complex Assembly

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Crystal Structures

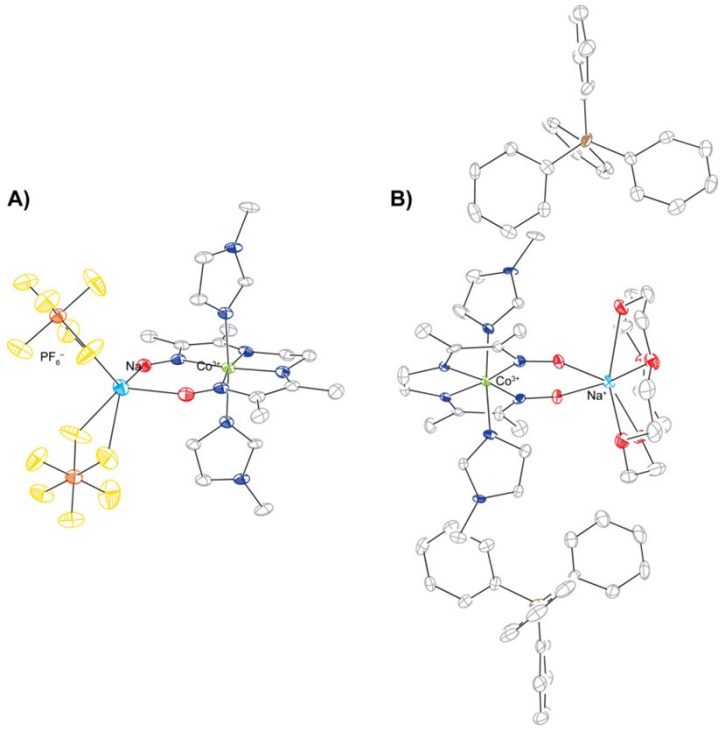

Figure S1: A) Single crystal X-ray diffraction structure of $[(DO)_2en(Im^{Me})_2CoNa][PF_6]_2$ and B) $[(DO)_2en(Im^{Me})_2CoNa\text{-}15crown5][BPh_4]_2$ isolated from treatment of 1 with $NaPF_6$ and $NaBPh_4$ and 15-crown-5, respectively.

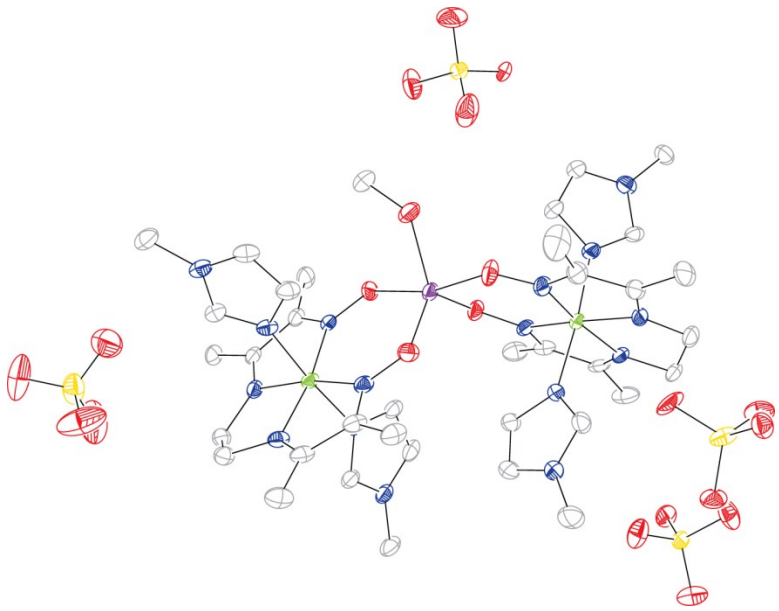

Figure S2: Single crystal X-ray diffraction structure of $[((DO)_2en(Im^{Me})_2Co)_2Zn(HOMe)][ClO_4]_4$.

Complex	O-O interatomic distance (Å)	N-Co-N angle
CoRu	3.24(1)	108.9(4)
CoNa	3.205(4)	109.1(2)
Co_3Cd	3.203(4)	107.9(2)
CoZn	3.197(3)	108.9(1)
OO	3.128(4)	108.5(1)
Co_3Mn	3.071(3)	106.9(1)
Co_3Zn	3.061(4)	106.6(2)
OHO	2.564(1)	104.6(4)

Table S1: Variation in OO interatomic distance for all bimetallic and teterametallic complexes studied.

UV-Vis and Cyclic Voltammetry Data for Titration of 1 with $ZnBr_2$

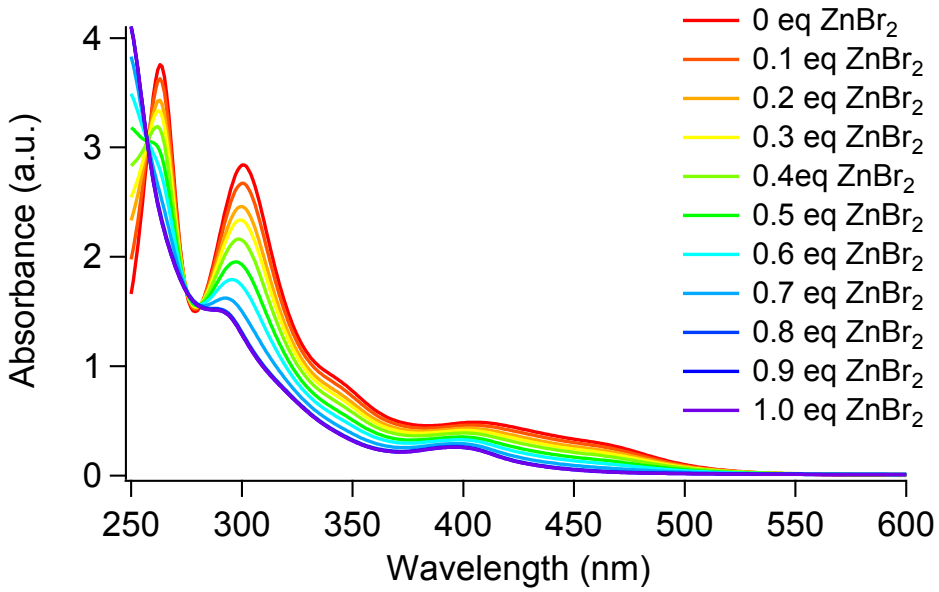

Figure S3: UV-vis titration of **1** with $ZnBr_2$ showing complete conversion to **2** after addition of 1 equivalent of $ZnBr_2$.

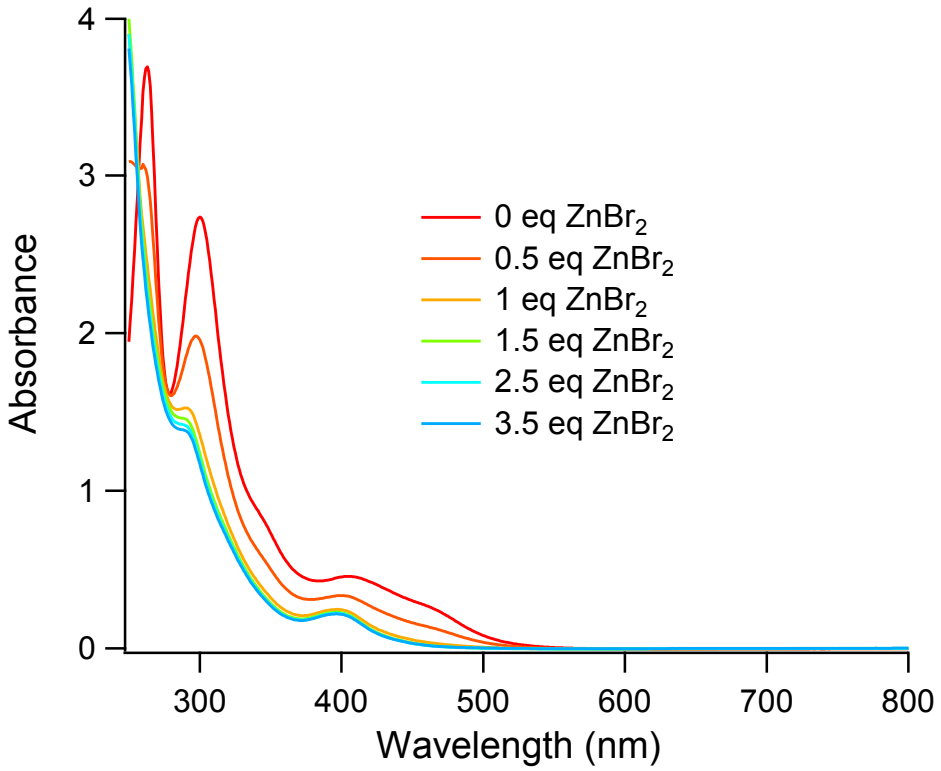

Figure S4: UV-vis titration of **1** with $ZnBr_2$ showing no changes after additional equivalents of $ZnBr_2$

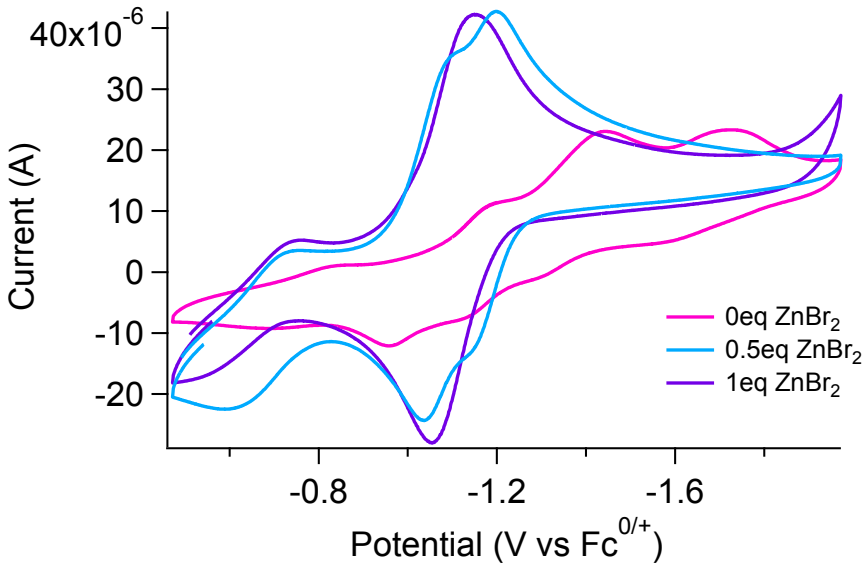

Figure S5: CV titration of 1.5mM **1** with $ZnBr_2$ showing complete conversion to **2** after addition of 1 equivalent of $ZnBr_2$ in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN.

pK_a Determination

The pK_a for Complex **1-H**$^+$ was found using ^{1}H NMR spectroscopy. The exchange between Complex **1** and **1-H**$^+$ was fast on the NMR time scale. Complex **1** was titrated with 2-NO_2-4-CF_3-$C_6H_3P_1H$ (pyrr) PF_6, which has a pK_a of 16.54.[1]

$$1 + HB \rightleftarrows 2 + B$$

The chemical shift was a mole-fraction weighted average of **1** and **1-H**$^+$,

$$\delta_{obs(1)} = N_1\delta_1 + N_{1-H+}\delta_{1-H+}$$

In this expression N represents the mole fraction of Complex **1** or **1-H**$^+$. Expressing this equation in molarity units leads to the following expression. Adapting the method from Drago (Chapter 8)[2], leads to the following expression for $[2]_t$.

$$[2]_t = \frac{(\delta_{obs} - \delta_1)}{(\delta_2 - \delta_1)}[1]_0$$

The following terms, $[1]_t$, $[BH]_t$ and $[B]_t$ can be found from the following expressions,

$$[1]_t = [1]_0 - [2]_t$$

$$[BH]_t = [B]_x - [2]_t$$

$$[B]_t = [2]_t$$

The following equilibrium expression can be plotted to yield the equilibrium constant.

$$K = \frac{[1][BH]}{[B][2]}$$

From the K value determined from Figure S1 below, the pK_a was calculated from the following expression, where pK_a(BH) is the pK_a of the titrated acid, 2-NO_2-4-CF_3-$C_6H_3P_1H$ (pyrr) PF_6.

$$pK_a(2) = pK_a(BH) - \log K$$

A pK_a of 14.9 was found experimentally for Complex **1-H**$^+$.

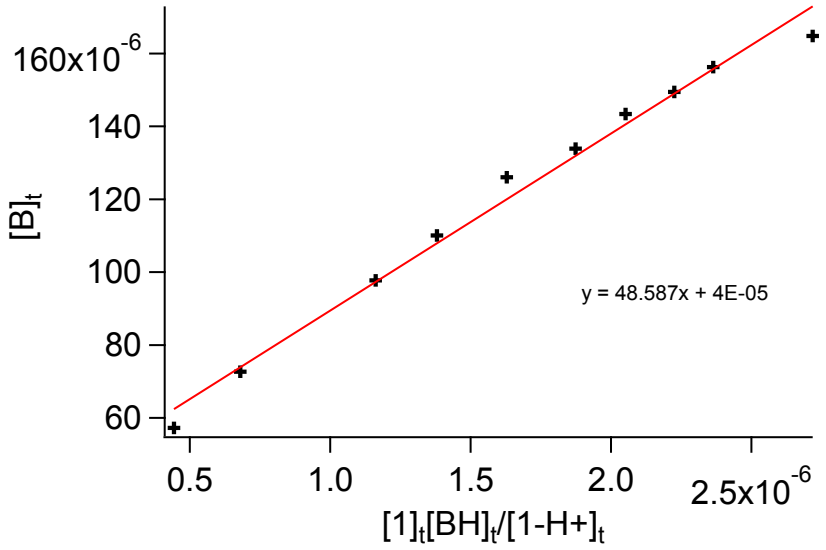

Figure S6: Graph with the necessary parameters to determine pK_a of Complex **1-H**$^+$ by ^{1}H NMR titration, where the slope is the equilibrium constant, K.

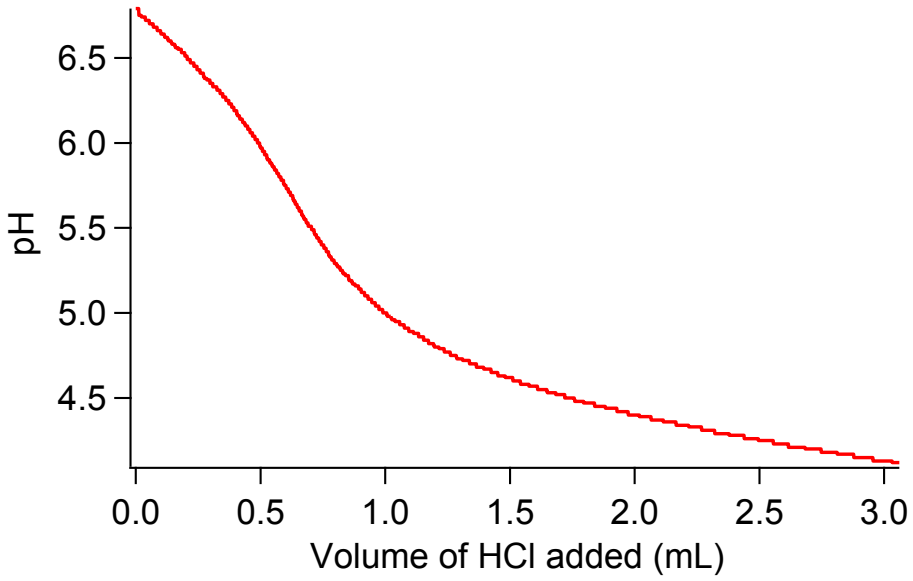

Figure S7: Titration of Complex **1** by HCl in water. Midpoint analysis where pH=pK_a leads to a pK_a for complex **1-H**$^+$ ~6.5. This was determined by approximation of the midpoint.

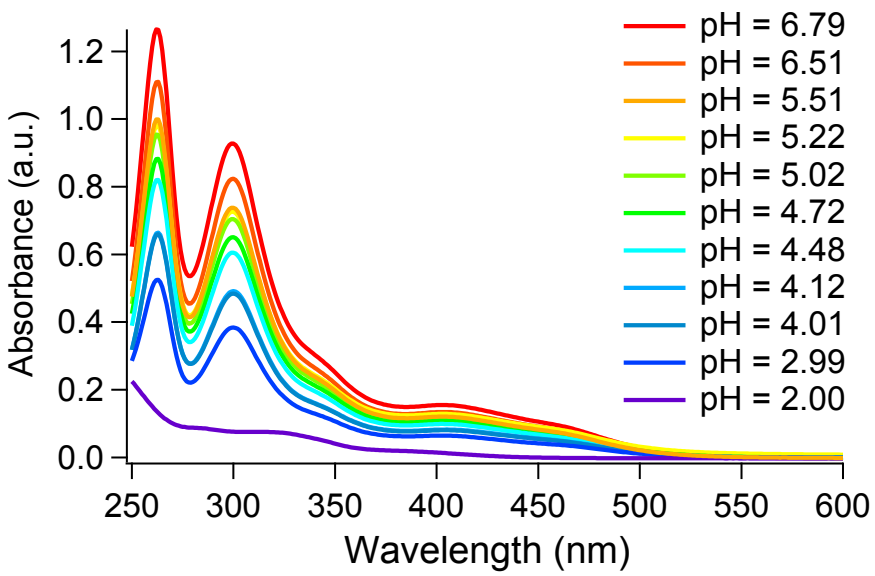

Figure S8: UV-vis in CH_3CN of **1** at various pH aliquots from titration in water. Contains a minimal amount of water. The second protonation occurs between pH 2.00 and 2.99 as seen by the disappearance of most spectral features, which we found to be indicative of the doubly protonated version of Complex 1

Experimental and Computed UV-Vis Data

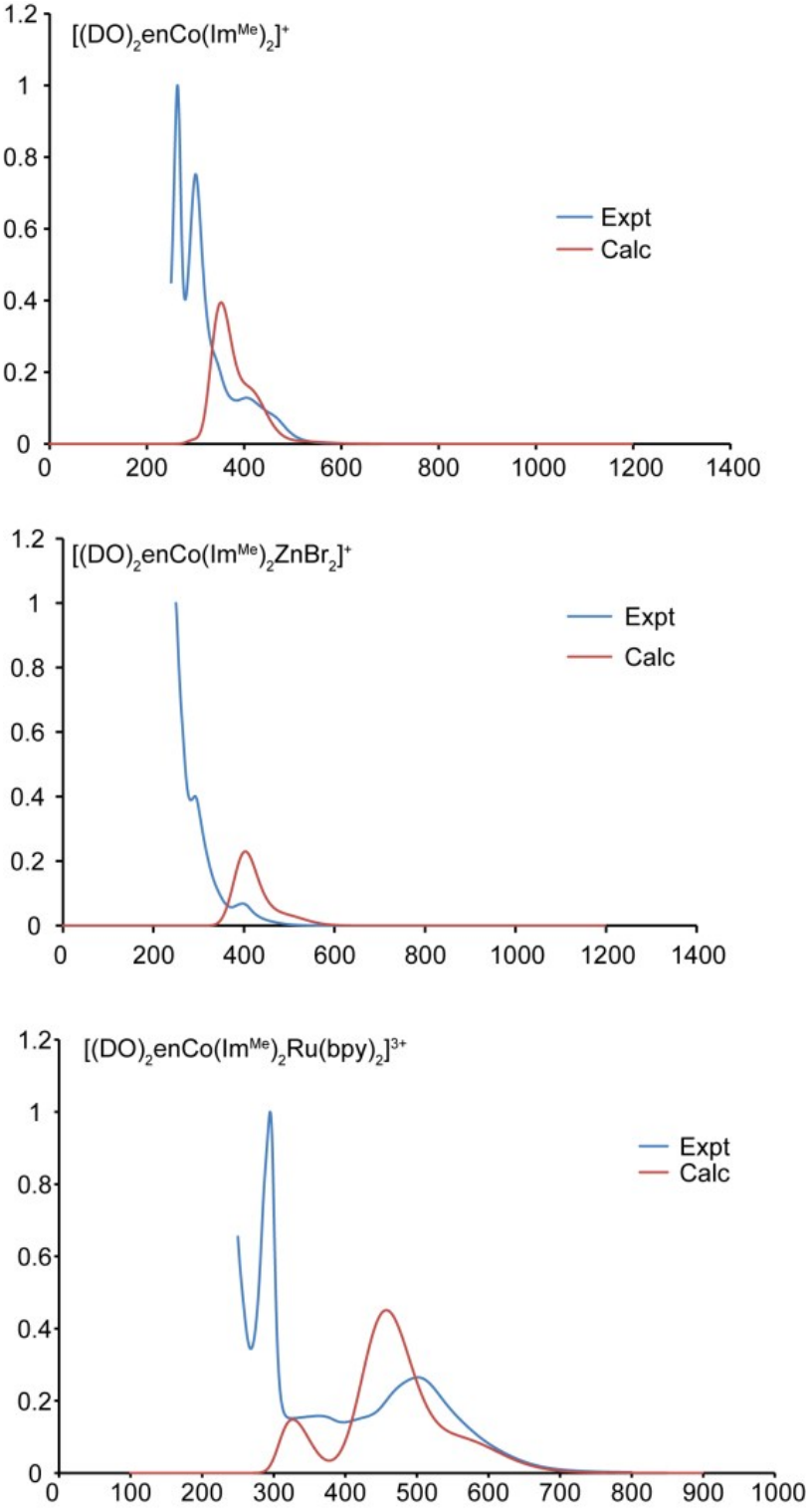

Figure S9: Calculated versus experimental UV-vis spectra for **1**, **2**, and **4**.

CV data

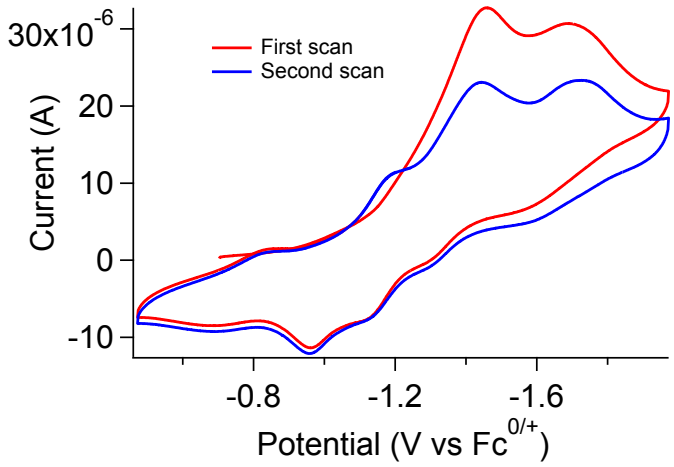

Figure S10: First and second scans at 300mV/s of 1.5mM **1** in 0.2M [$^{n}Bu_4N$][PF_6] in CH_3CN.

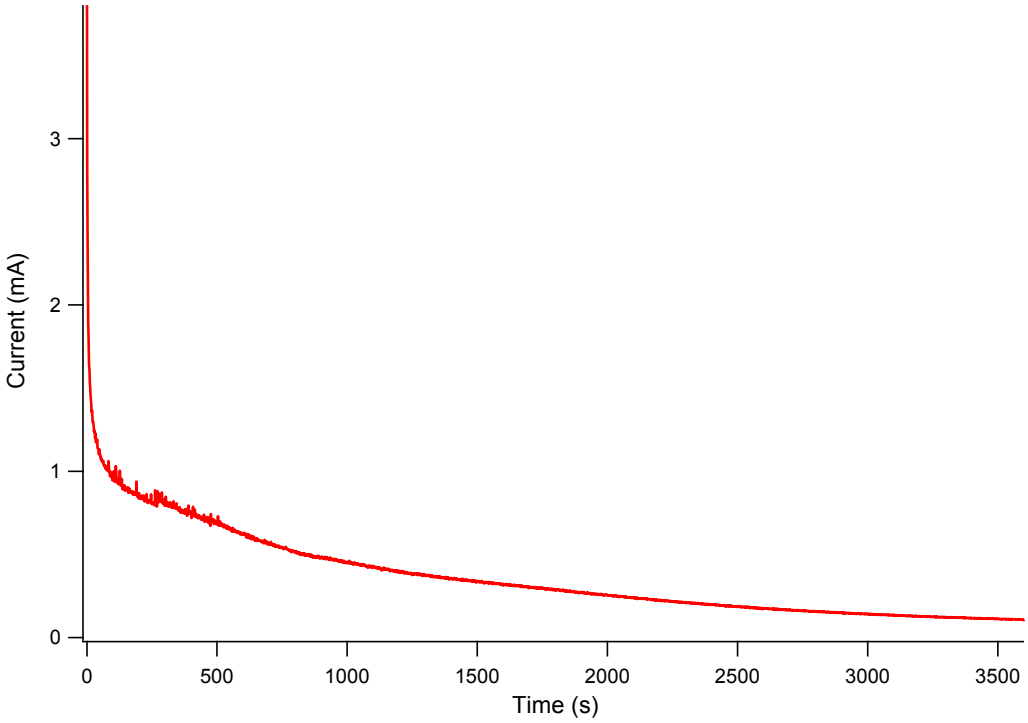

Figure **S11**: Bulk electrolysis of 0.26 mM Complex 2 in 0.15M [$^{n}Bu_4N$][PF_6] in CH_3CN. 1.323 C were passed in this hour experiment.

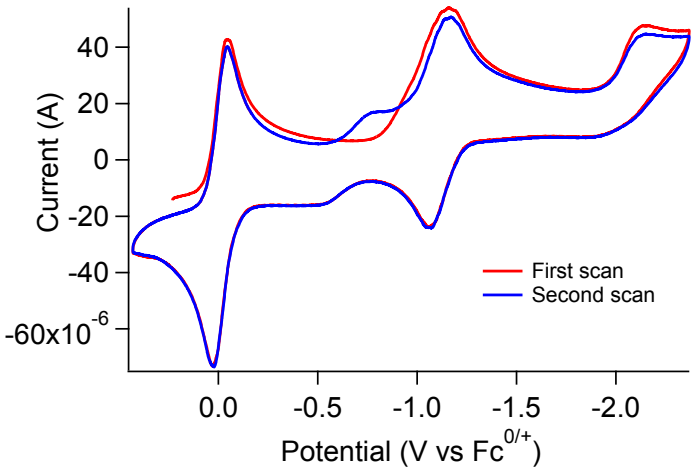

Figure S12: First and second scans at 300mV/s of 1.5mM **2** in 0.2M [$^{n}Bu_4N$][PF_6] in CH_3CN.

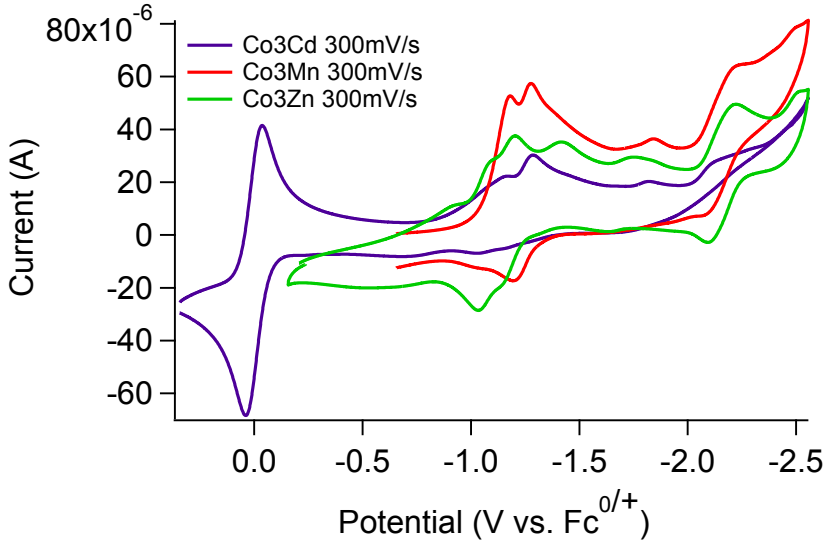

Figure S13: CVs of 0.7mM **3-Mn**, **3-Zn** and **3-Cd** in 0.2M [$^{n}Bu_4N$][PF_6] in CH_3CN.

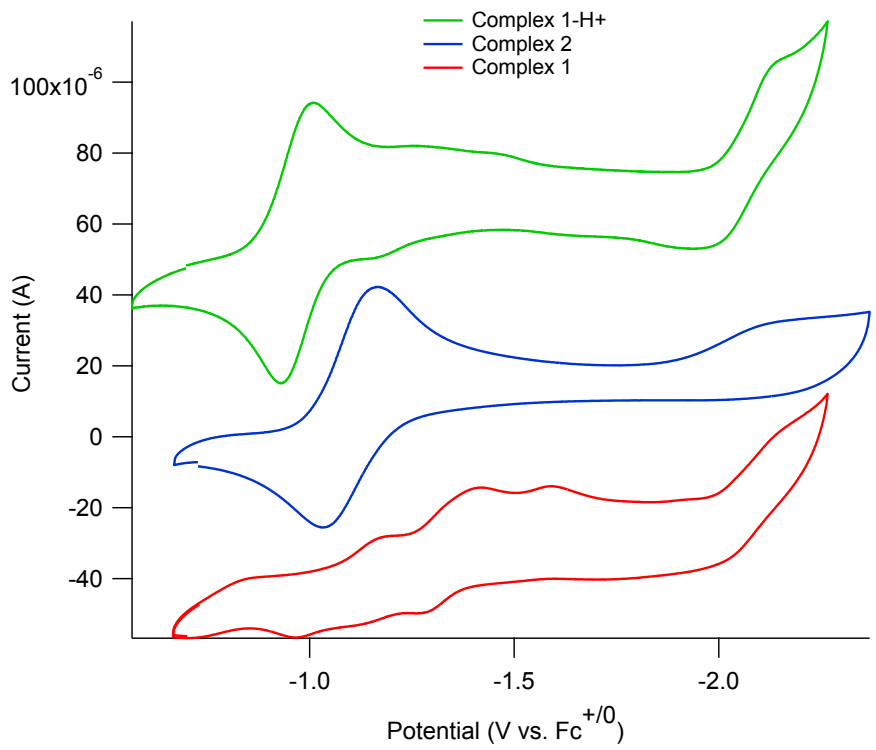

Figure S14: Complexes 1, 1-H+ and 2 scanned to more negative potentials (presumably revealing the Co(I/0) couple; 100mV/s; 0.2 M [$^{n}Bu_4N$][PF_6] in CH_3CN.

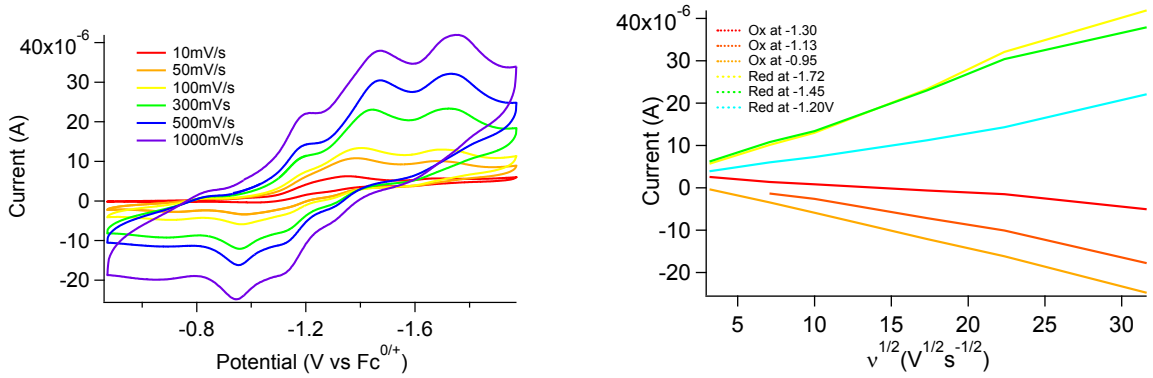

Figure S15: Scan rate dependence (second scan shown) of 1.5mM complex **1** in 0.2M [$^{n}Bu_4N$][PF_6] in CH_3CN.

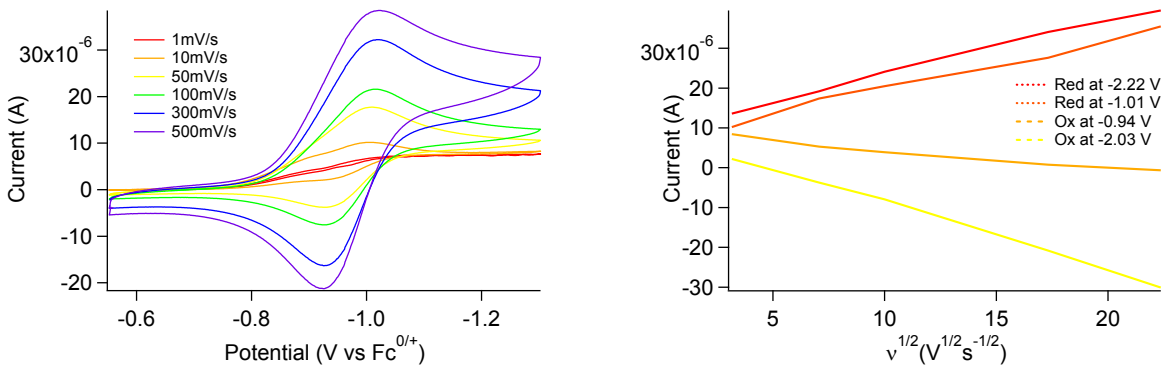

Figure S16: Scan rate dependence of 1.5mM **1-H**$^+$ in 0.2M [^{n}Bu$_4$N][PF$_6$] in CH$_3$CN.

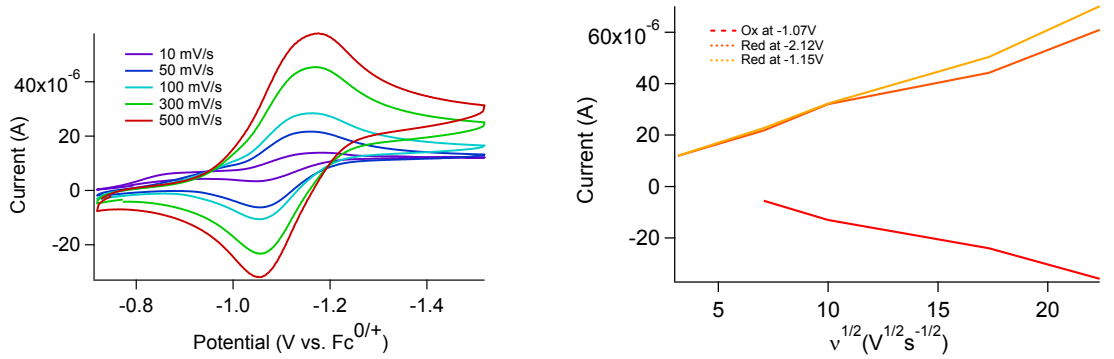

Figure S17: Scan rate dependence of 1.5mM **2** in 0.2M [^{n}Bu$_4$N][PF$_6$] in CH$_3$CN.

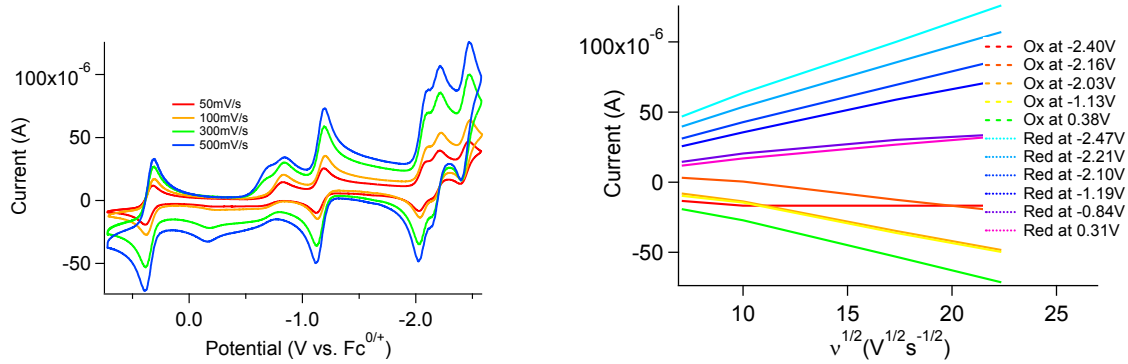

Figure S18: Scan rate dependence of 1.0mM **4** in 0.2M [^{n}Bu$_4$N][PF$_6$] in CH$_3$CN.

Electrocatalysis

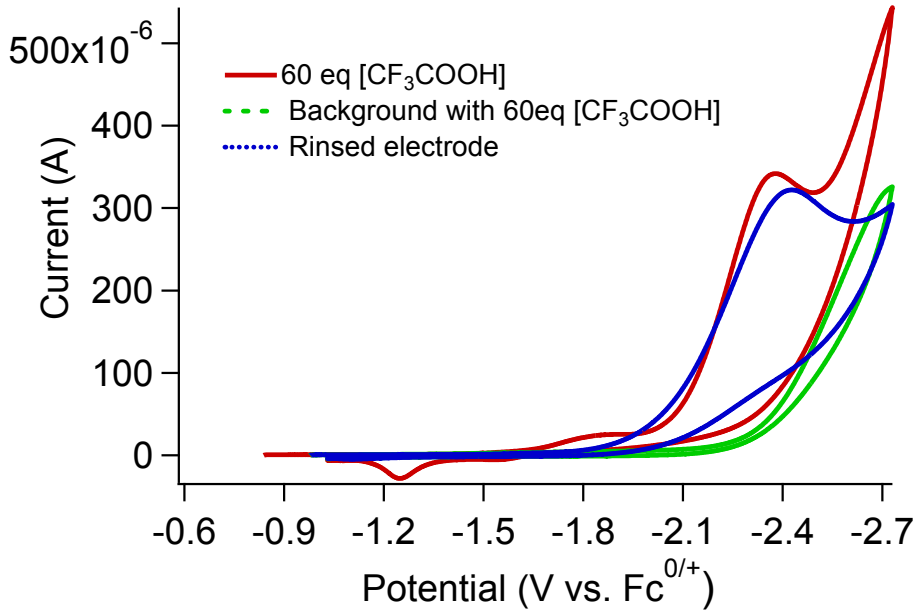

Figure S19: 0.35mM **1** with 60 eq (21mM) [CF_3COOH], scan rate 300mV/s, 0.1M [$^nBu_4N$][PF_6] in CH_3CN. The rinsed electrode was placed in a solution of 21mM [CF_3COOH]. Ferrocene was added before the experiment.

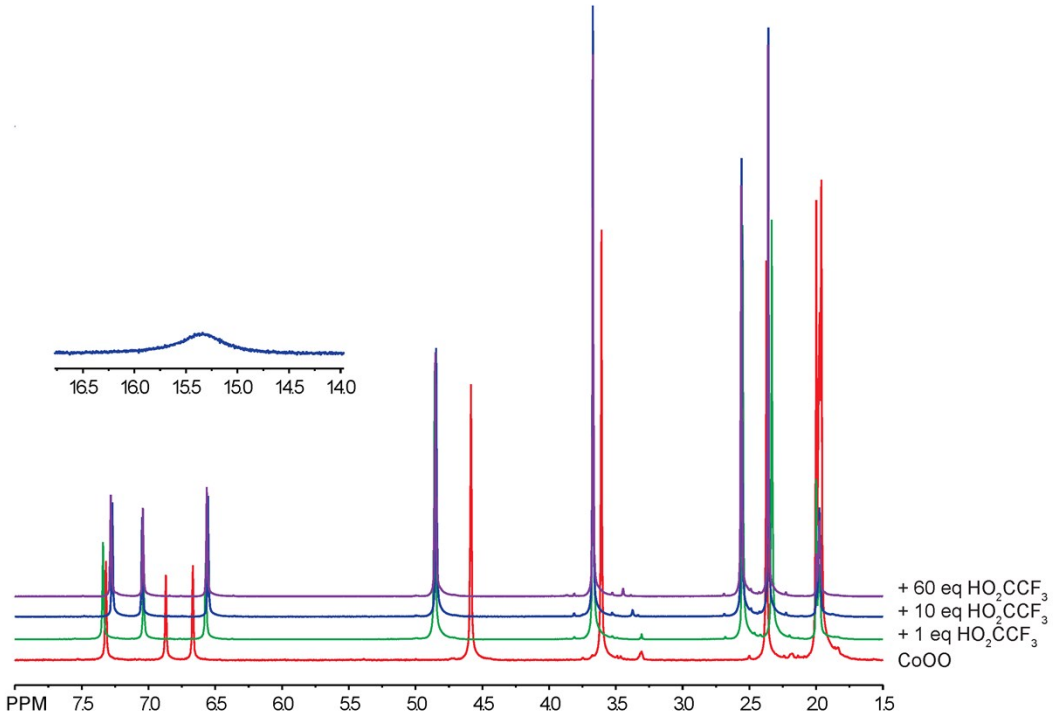

Figure S20: ^{1}H NMR of Complex 1 with equivalents of CF_3COOH in CD_3CN (499MHz)

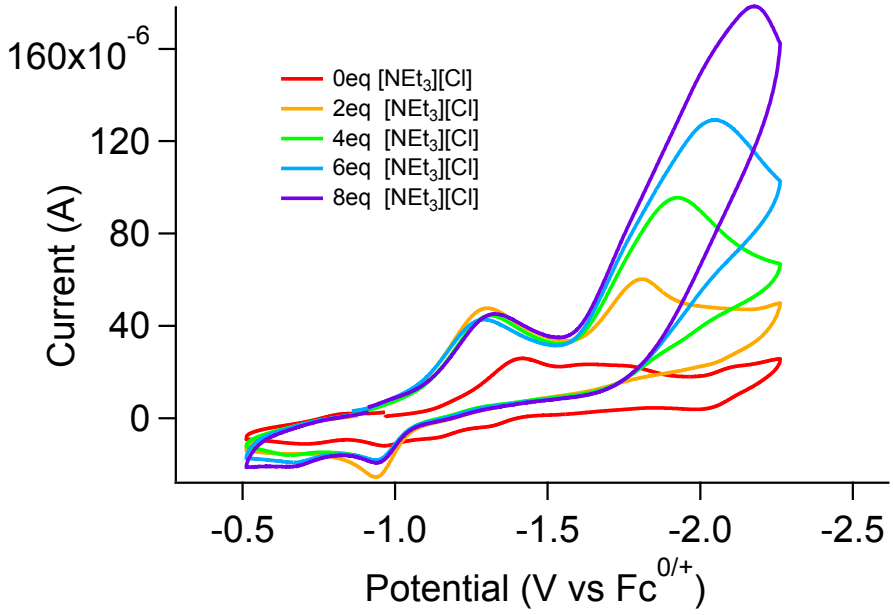

Figure S21: 1.0mM complex **1** with increasing equivalents of $[NEt_3H][Cl]$ (4.0mM to 16mM) at 300mV/s in 0.2M $[^{n}Bu_4N][PF_6]$ in CH_3CN; a shift in the i_{cat} is observed upon additional acid equivalents.

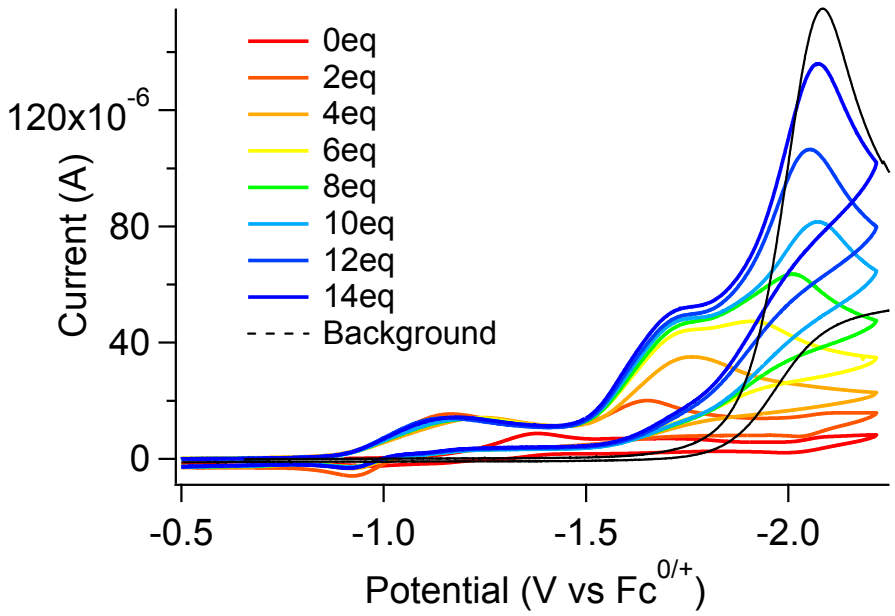

Figure S22: 0.75mM complex **1** with increasing equivalents of $[NEt_3H][BPh_4]$ (2-14 eq or 1.5-10.5mM) at 50mV/s in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN; background with acid at 10.5mM $[NEt_3H][BPh_4]$.

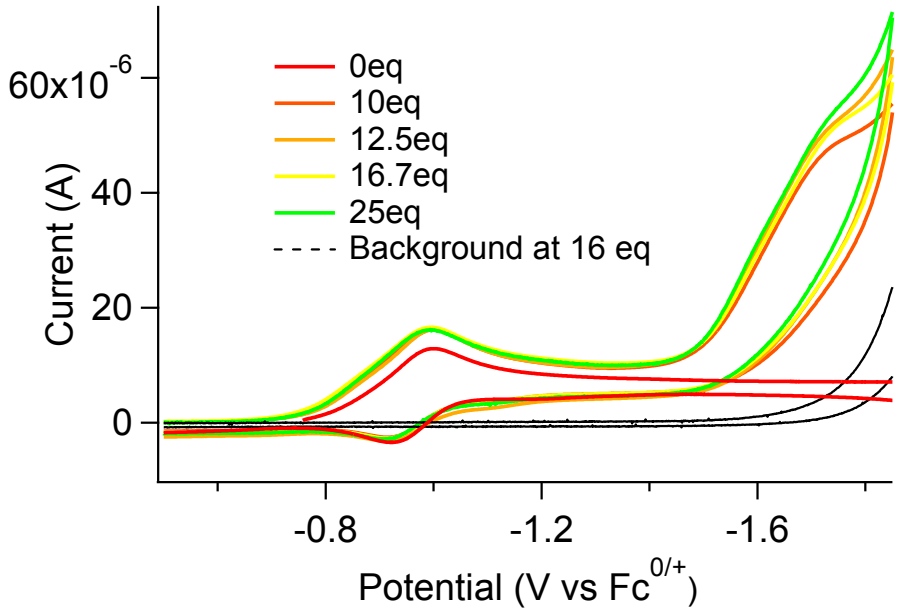

Figure S23: 0.75mM complex **1-H+** with increasing equivalents of $[NEt_3H][BPh_4]$ (10 to 25 eq or 7.5-18.8mM) at 50mV/s in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN; background with acid at 12mM $[NEt_3H][BPh_4]$.

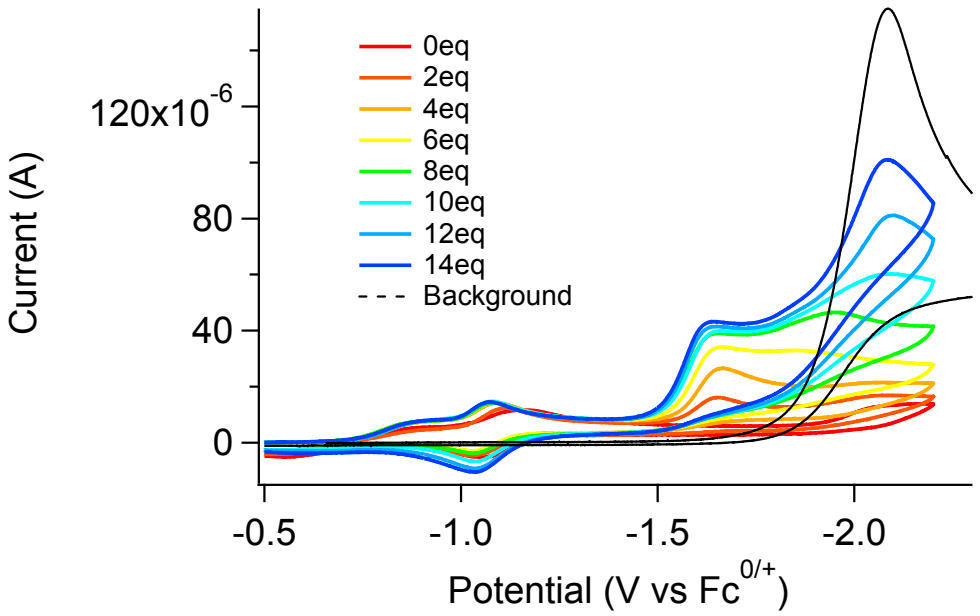

Figure S24: 0.75mM complex **2** with increasing equivalents of $[NEt_3H][BPh_4]$ (2-14 eq or 1.5-10.5mM) at 50mV/s in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN; background with acid at 10.5mM $[NEt_3H][BPh_4]$.

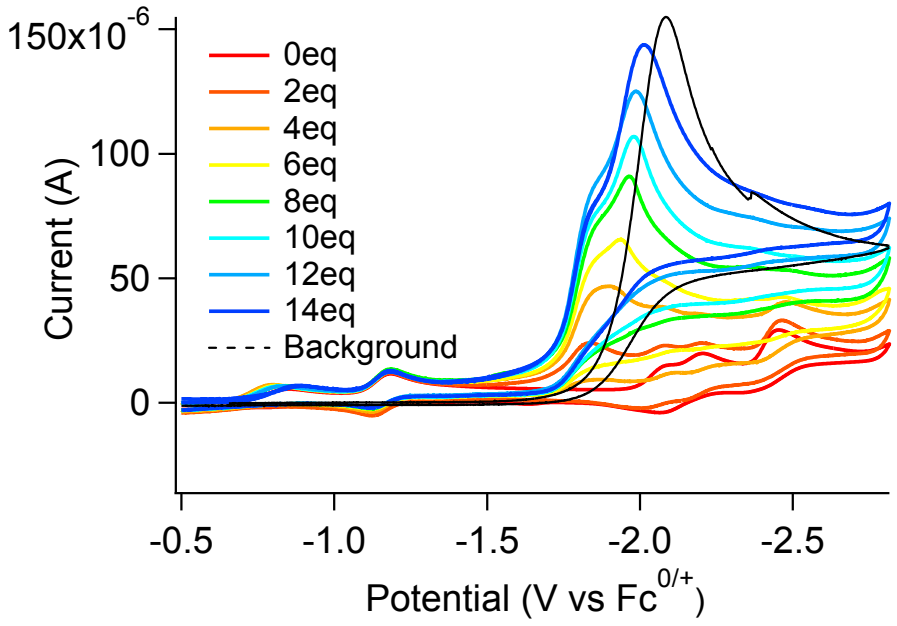

Figure S25: 0.75mM complex **4** with increasing equivalents of $[NEt_3H][BPh_4]$ (2-14 eq or 1.5-10.5mM) at 50mV/s in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN; background with acid at 10.5mM $[NEt_3H][BPh_4]$.

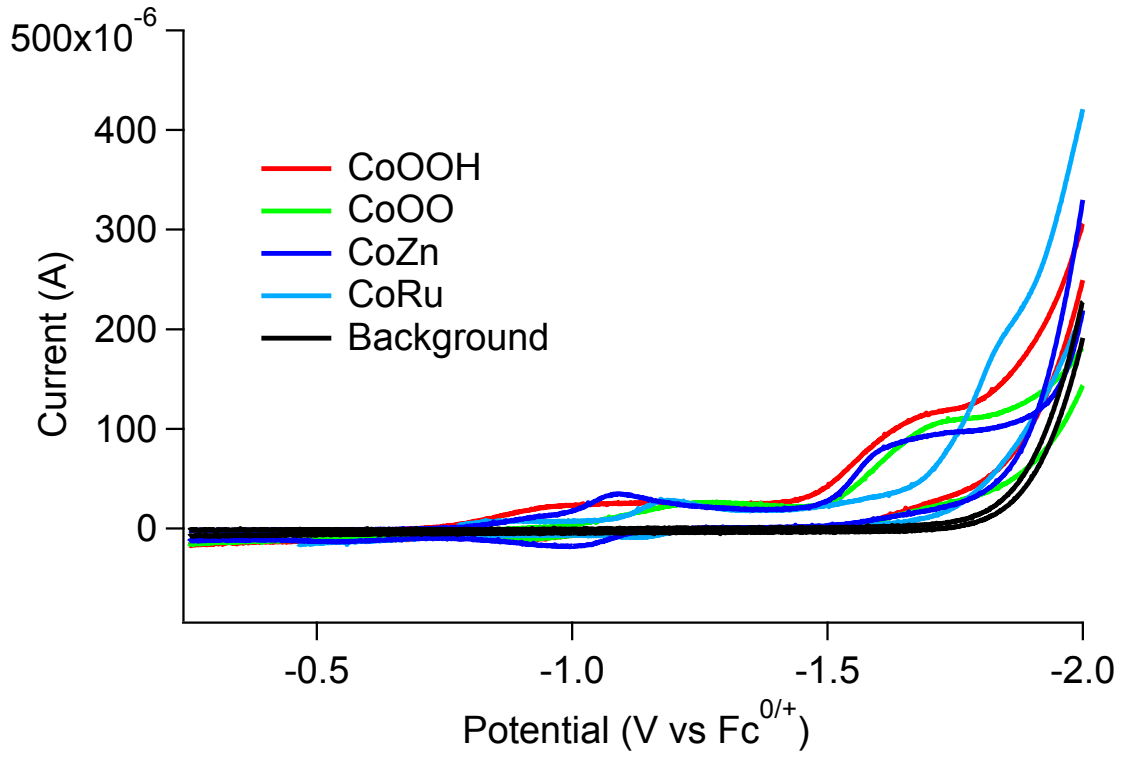

Figure S26: Comparison of 0.75 mM catalyst with 60 equivalents of $[NEt_3H][BPh_4]$ at 300 mV/s in 0.2M $[^nBu_4N][PF_6]$ in CH_3CN.

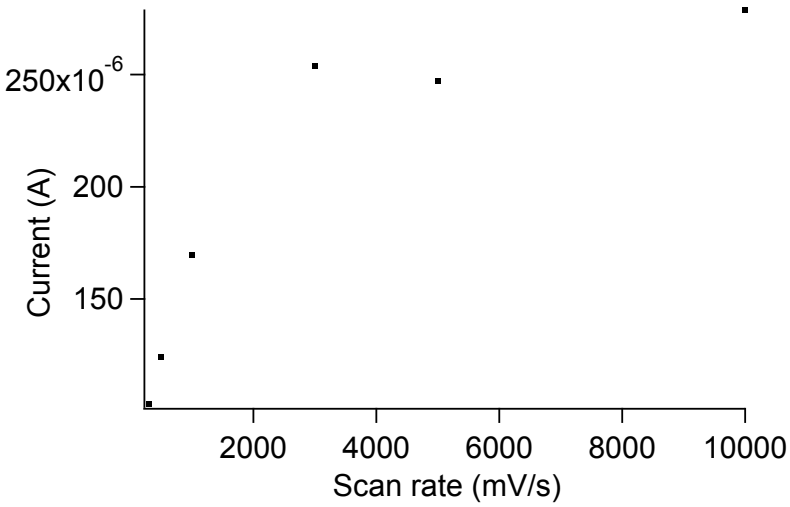

Figure S27: Scan rate dependence on i_{cat} (-1.7 V vs $Fc^{0/+}$) for complex **1** at 60 eq $[NEt_3H][BPh_4]$ (Background acid reduction with 60 eq acid with no catalyst at given scan rate was subtracted).

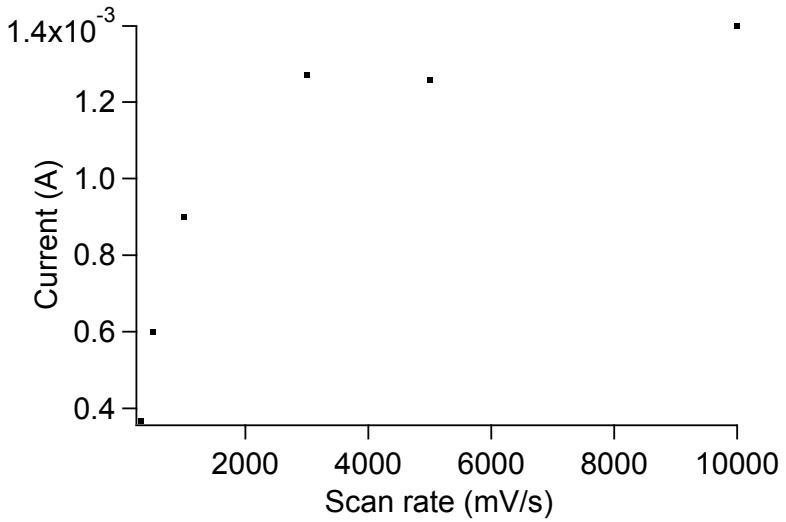

Figure S28: Scan rate dependence on i_{cat} (-1.8 V vs $Fc^{0/+}$) for complex **4** at 60 eq $[NEt_3H][BPh_4]$ (Background acid reduction with 60 eq acid with no catalyst at given scan rate was subtracted).).

Table S2: Diffusion coefficients for complexes **1**, **1-H+**, **2** and **4**.

Complex	Diffusion coefficient (cm^2/s) (determined by ^1H DOSY NMR)
1	1.35 E-5 cm^2/s
1-H+	1.15 E-5 cm^2/s
2	1.20 E-5 cm^2/s
4	9.03 E-5 cm^2/s

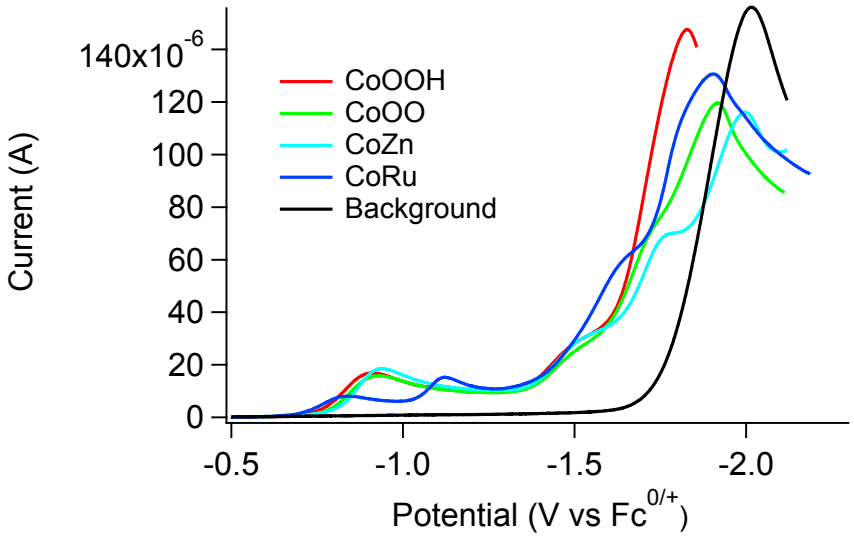

Figure S29: 0.75mM complexes **1**, **1-H**+, **2** and **4** with [^{Me}ImH][BPh$_4$] (10.5 mM) at 50 mV/s in 0.2 M [^{n}Bu$_4$N][PF$_6$] in CH$_3$CN; background with acid at 10.5 mM [^{Me}ImH][BPh$_4$].

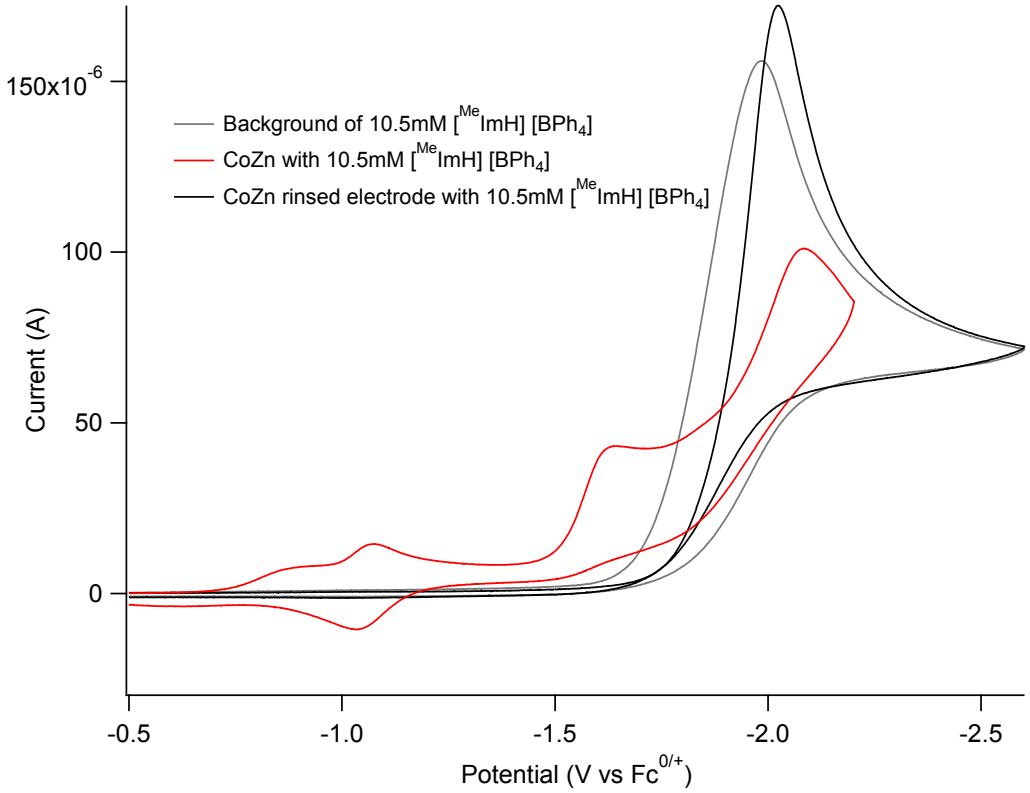

Figure S30: Sample rinse test trace with 0.75mM complex **2** with [^{Me}ImH][BPh$_4$] (10.5 mM) at 50mV/s in 0.2 M [^{n}Bu$_4$N][PF$_6$] in CH$_3$CN; background with acid at 10.5 mM [^{Me}ImH][BPh$_4$].

Bulk Electrolysis

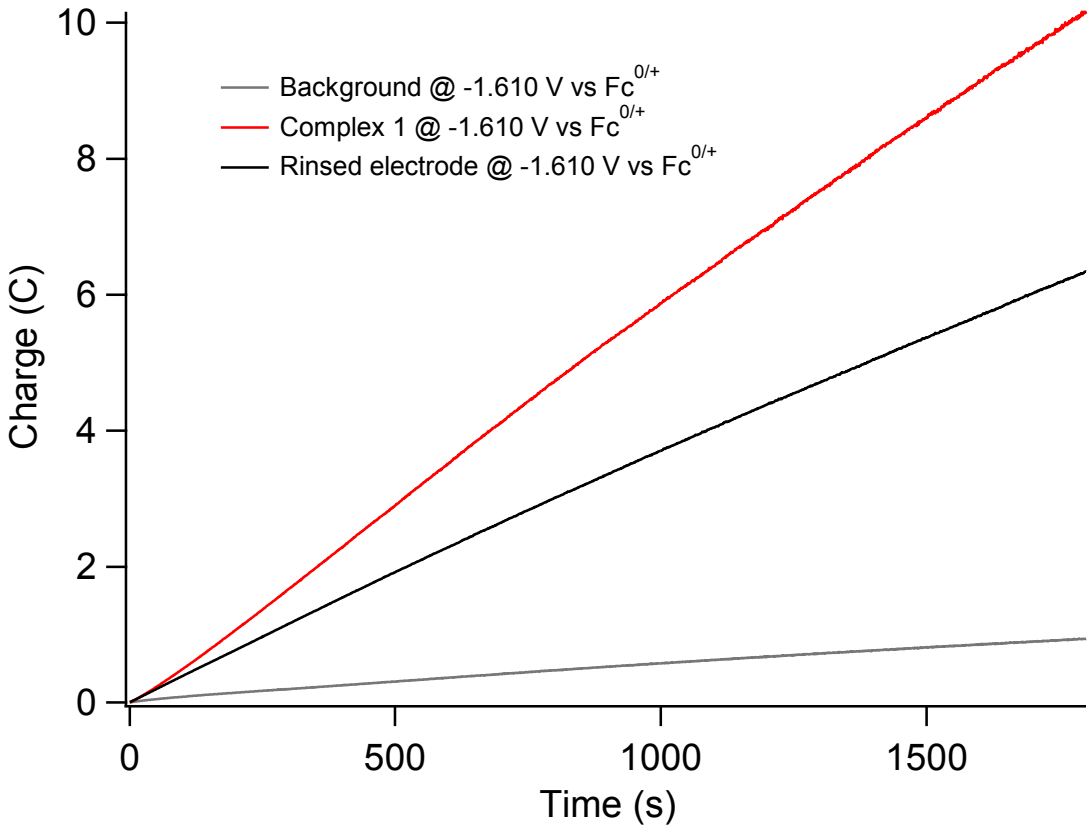

Figure S31: Current versus time from a 30 min electrolysis with 0.25 mM complex **1**, 25 mM $[NEt_3H][BPh_4]$ in 0.1 M $[^nBu_4N][PF_6]$ in CH_3CN.

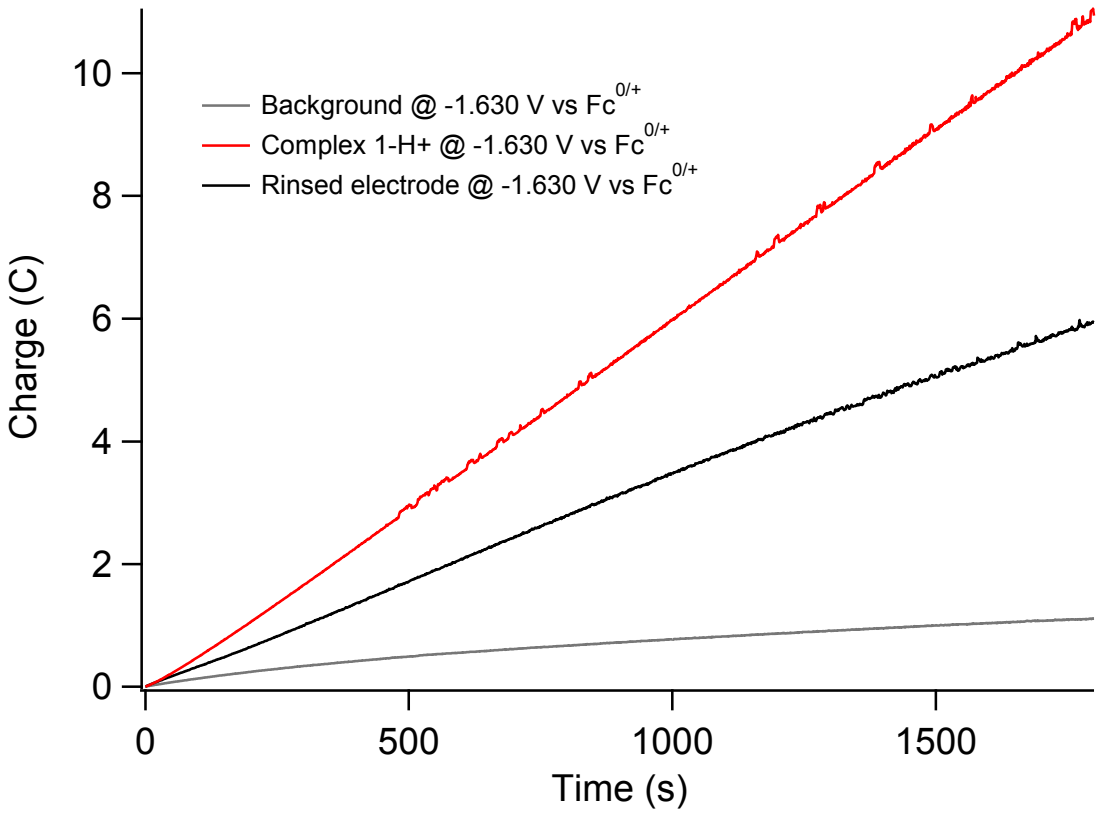

Figure S32: Current versus time from a 30 min electrolysis with 0.25 mM complex **1-H**$^{+}$, 25 mM [NEt_3H][BPh_4] in 0.1 M [$^{n}Bu_4N$][PF_6] in CH_3CN.

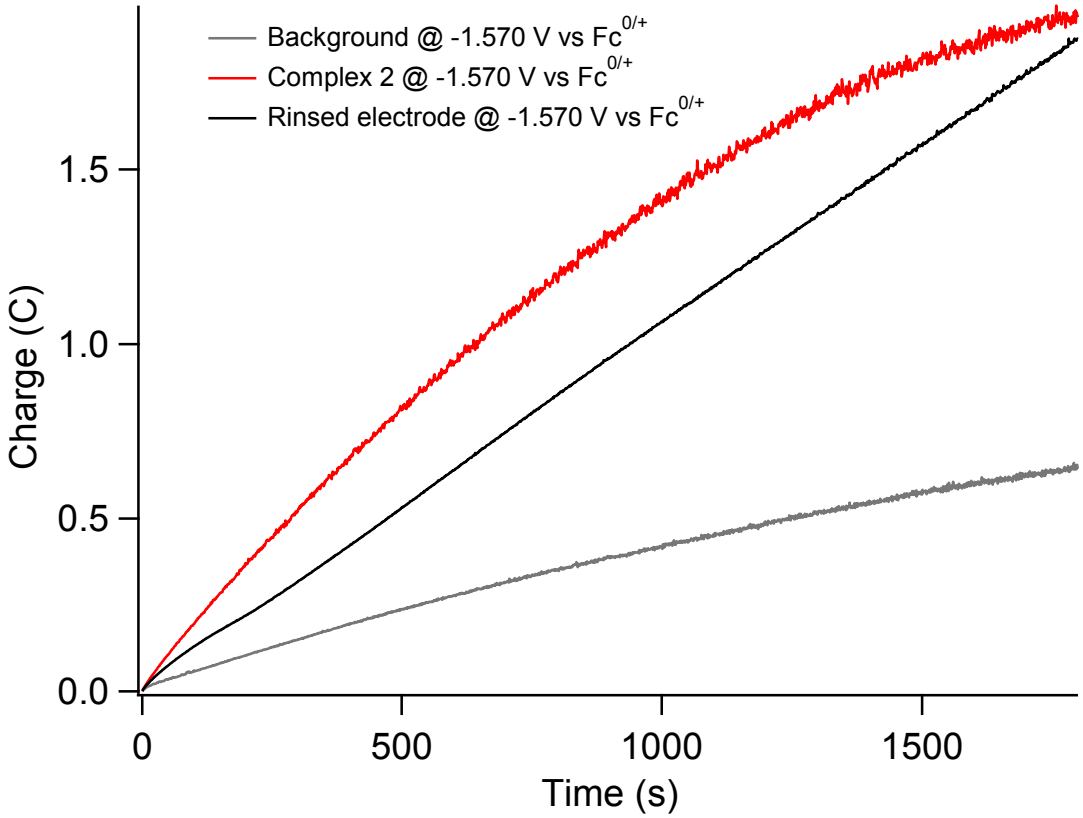

Figure S33: Current versus time from a 30 min electrolysis with 0.25 mM complex **2**, 25 mM $[NEt_3H][BPh_4]$ in 0.1 M $[^nBu_4N][PF_6]$ in CH_3CN.

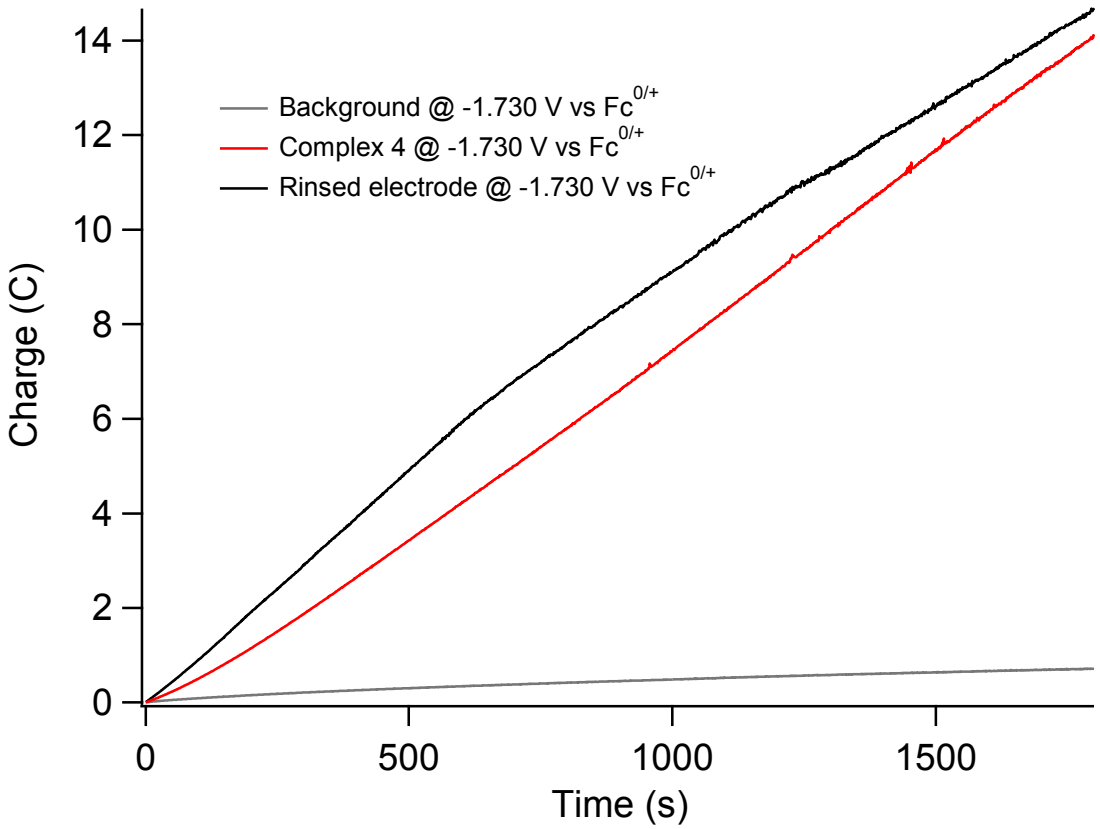

Figure S34: Current versus time from a 30 min electrolysis with 0.25 mM complex **4**, 25 mM $[NEt_3H][BPh_4]$ in 0.1 M $[^nBu_4N][PF_6]$ in CH_3CN.

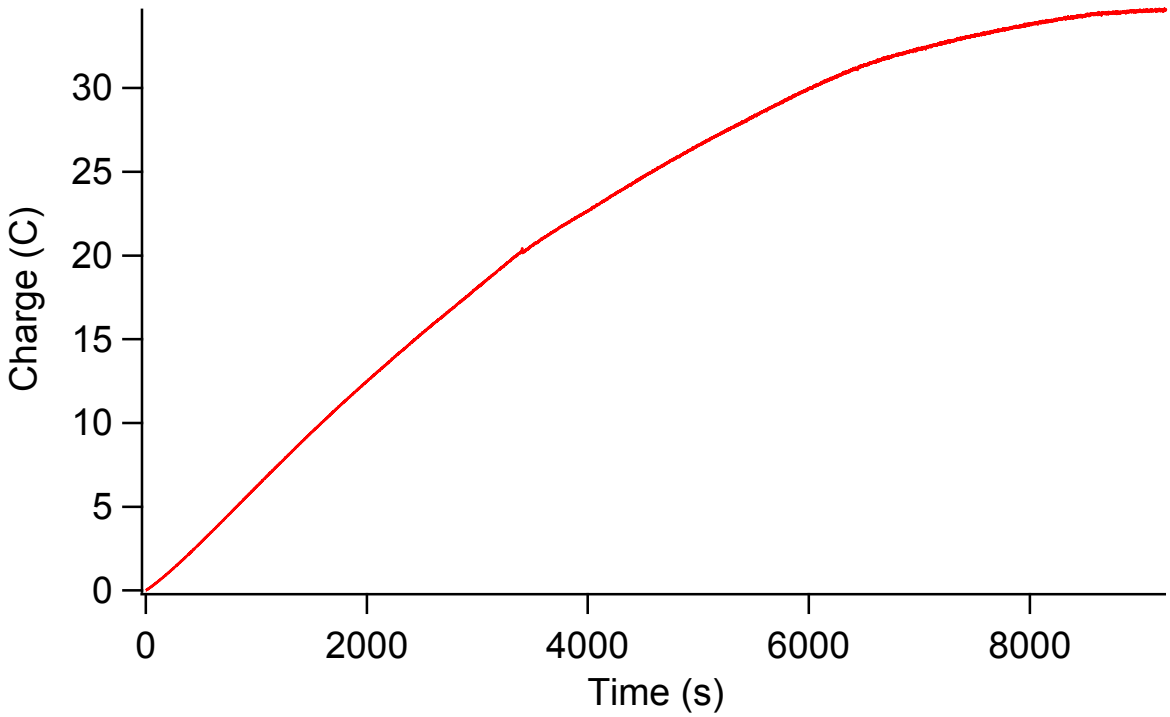

Figure S35: Current versus time from a 2.5 hour electrolysis with 0.25 mM complex **4**, 25 mM $[NEt_3H][BPh_4]$ in 0.1 M $[^nBu_4N][PF_6]$ in CH_3CN.

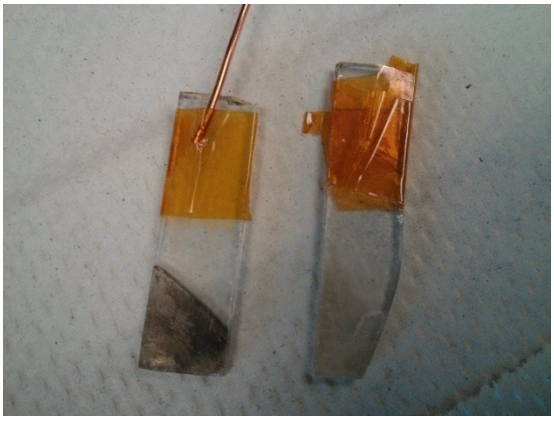

Figure S36: ITO electrodes from a 30 min electrolysis with 0.5mM [cat], 50mM $[NEt_3H][BPh_4]$ in 0.1M $[^nBu_4N][PF_6]$ in CH_3CN; (left) complex **1** at -1.6 V vs $Fc^{0/+}$ (right) complex **4** at -1.9 V vs $Fc^{0/+}$.

Table S3: Champion faradaic efficiencies from a 30 min bulk electrolysis with 0.25 mM [cat], 25 mM $[NEt_3H][BPh_4]$ in 0.1 M $[^nBu_4N][PF_6]$ in CH_3CN.

	Complex **1**	Complex **1-H+**	Complex **2**	Complex **4**
Faradaic Efficiency	63%	72%	21%	80%

Table S4: Moles of hydrogen and charge passed from background with acid, catalysts and rinsed electrode tests from bulk electrolysis experiments. The same electrode was used for the data in each row, however in each row was used a different electrode.

Complex	Charge (C) passed by background with acid	Charge (C) passed by electrolysis with catalyst	Charge (C) passed by rinsed electrode	Moles of hydrogen from background with acid	Moles of hydrogen from catalyst run	Moles of hydrogen from rinsed electrode	Potential (V vs $Fc^{0/+}$)
4	1.04	12.67	16.34	4.5E-6	5.3E-5	7.2E-5	-1.73
1	1.15	10.2	6.70	3.7E-6	3.3E-5	2.9E-5	-1.61
2	0.86	2.7	2.00	1.8E-6	3.8E-6	8.3E-6	-1.57
1-H+	1.61	10.4	6.2	6.3E-6	3.9E-5	1.6E-5	-1.63

Faradaic efficiency was calculated from the following equation:

$$FE = \left[\frac{(moles\ H_2\ from\ catalyst\ run - moles\ of\ H_2\ from\ backgr}{charge\ passed\ by\ electrolysis\ with\ acid - charge\ passed\ by\ bac} \right] * 100$$

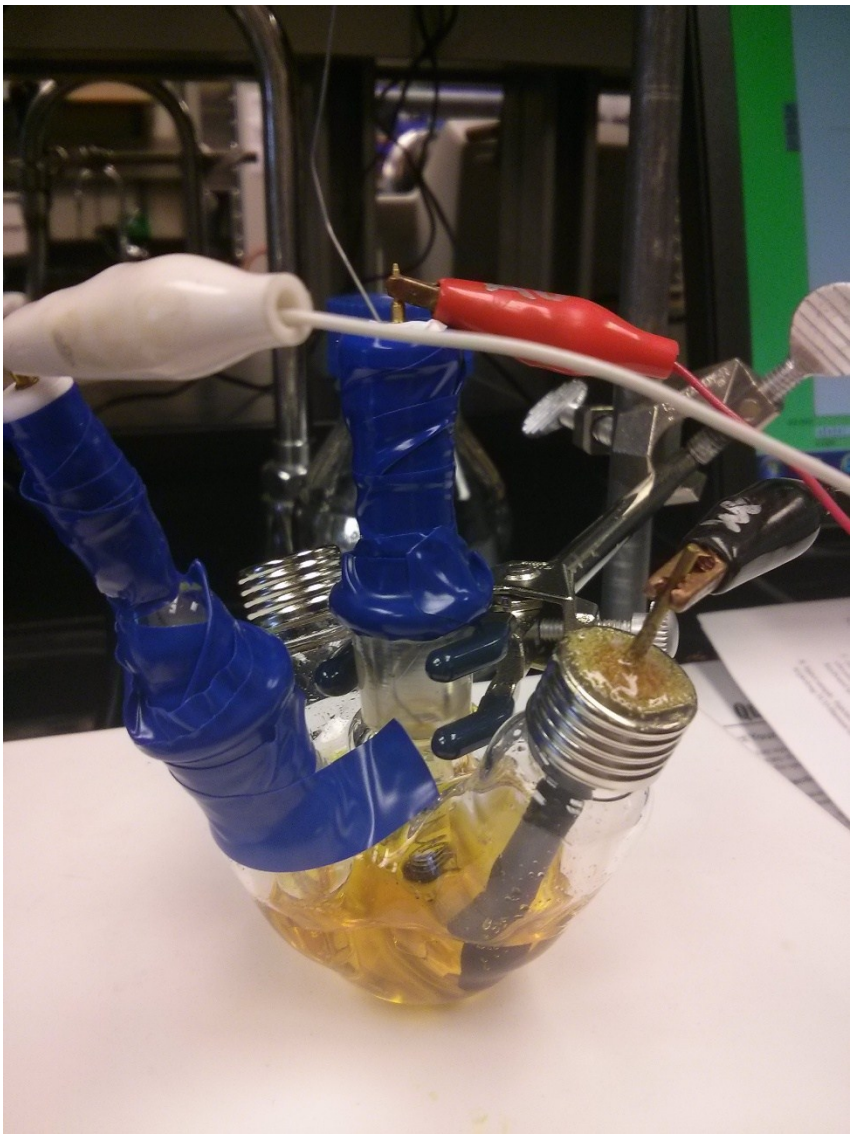

Figure S37: Gas tight custom cell with $Ag/AgNO_3$ reference and Pt auxiliary coil in separated compartment. Another port houses the working electrode and the last port has a gas tight cap with septa for sampling. Seals were reinforced with carbon rim cement glue, parafilm, and electrical tape.

DFT Calculations

The geometry of complexes were optimized using B3LYP[3] level of theory with LAND2Z[4] basis set for the Ru and 6-311+G(d) for all other atoms using Gaussian 09.[5] TD-DFT[6] calculations were carried out from the optimized geometry the first 20 states were calculated for Co and CoZnBr2, the first 50 states were calculated for CoRubpy. The calculated absorption spectra were created on Gausview 5[7] using 0.2 eV fwhm Gaussian functions on each transition. Transitions with oscillator strengths over 0.03 are listed below.

Compound	Orbitals	Wavelength (nm)	Oscillator Strength
1	HOMO-8 -> LUMO+3 (46%) HOMO-2 -> LUMO+3 (36%)	420	0.0125
	HOMO -3 -> LUMO+1 (23%) HOMO-3 -> LUMO+2 (32%) HOMO -> LUMO+1 (22%)	360	0.0337
	HOMO-3 -> LUMO+3 (19%) HOMO-1 -> LUMO+1 (18%) HOMO-1 -> LUMO+2 (10%)	342	0.0214
1-H$^+$	HOMO-3 -> LUMO+1 (41%) HOMO -> LUMO+2 (34%)	357	0.0187
	HOMO -> LUMO+2 (93%)	329	0.0277
	HOMO-9 -> LUMO (79%)	253	0.0310
2	HOMO -> LUMO (98%)	510	0.0029
	HOMO-1 -> LUMO (100%)	504	0.0029
	HOMO-4 -> LUMO (58 %) HOMO-2 -> LUMO+1 (18 %)	407	0.0300
4	HOMO-1 -> LUMO (86%)	572	0.0411

	HOMO-2 -> LUMO+2 (28%) HOMO-1 -> LUMO+3 (20%) HOMO-1 -> LUMO+5 (16%) HOMO -> LUMO+5 (17%)	463	0.0994
	HOMO-2 -> LUMO+2 (81%) HOMO-2 -> LUMO+5 (29%) HOMO-1 -> LUMO+3 (43%)	455	0.0590
	HOMO-2 -> LUMO+3 (81%) HOMO-1 -> LUMO+5 (14%)	433	0.0872
	HOMO-2 -> LUMO+6 (19%) HOMO-1 -> HOMO+7 (62%)	337	0.0274
	HOMO-3 -> LUMO+8 (12%) HOMO-1 -> LUMO+8 (24%) HOMO -> LUMO+8 (41%)	318	0.0200
	HOMO-3 -> LUMO (60%) HOMO -> LUMO+8 (13%)	317	0.0213

Optimized geometry of **1** (+1 singlet)

C	-1.04278100	1.89173400	-3.63324400
C	1.78827800	-3.05664100	-2.33272000
C	1.78075900	2.68432400	-2.61660900
C	-0.44043800	1.30793700	-2.38617300
C	0.68067000	-2.31228600	-2.04223400
C	4.12090100	-3.19914100	-1.34569200
C	0.86137700	1.72426600	-1.92888500
C	-2.39684700	-0.10359800	-1.75891500
C	2.22305600	-1.73386400	-0.62702300
C	-2.53969800	-1.34627600	-0.84384800
C	-2.07363600	1.76885800	1.25285700

C	-3.31020600	3.48831900	2.59948600
C	-1.51790100	-1.94823700	1.34930800
C	-2.54393300	-2.97369700	1.74228400
C	-0.01549100	2.23805500	1.76596700
C	-0.35538900	-1.71505000	2.16824400
C	-0.80878300	3.11583900	2.44597600
C	-0.04832600	-2.36302300	3.48195500
H	-0.41107200	1.68130000	-4.50049500
H	-1.11537200	2.97950000	-3.55152100
H	1.34603000	3.08403800	-3.53226900
H	1.96929000	-3.80427300	-3.08763500
H	-2.03864600	1.50164100	-3.83668500
H	2.03125000	3.52163900	-1.95859800
H	-0.27502400	-2.30885600	-2.53738200
H	-2.65196100	-0.37393600	-2.78793000
H	4.10307000	-4.26729200	-1.12717600
H	4.64409900	-3.02755200	-2.28669200
H	2.73000400	2.20149000	-2.86901600
H	-3.11134100	0.67031500	-1.45272000
H	-2.32376600	-2.25683400	-1.41418000
H	4.64991700	-2.68182000	-0.54762500
H	-3.57442300	-1.43170800	-0.49754800
H	2.75258100	-1.23582800	0.17101900
H	-2.95807900	1.31200300	0.84221100
H	-4.19118200	3.01079500	2.17344500
H	-3.35502500	-3.04880600	1.01996700
H	-3.29712500	4.53685200	2.30026600
H	-2.08207000	-3.96036500	1.83498600
H	-3.36418400	3.42239800	3.68651000
H	1.05751300	2.13307200	1.76360100
H	-2.97609300	-2.73417200	2.71751500
H	-0.56630600	3.91580900	3.12634000
H	-0.84191300	-3.03800900	3.80097800
H	0.88609800	-2.93034200	3.42968800
H	0.09813200	-1.60890100	4.26097100
N	2.75810600	-2.67736700	-1.42681300
N	-1.03456600	0.41391900	-1.64296100
N	0.96303300	-1.49072900	-0.97103400
N	1.23699600	1.16182500	-0.76979500
N	-1.59021500	-1.22798400	0.26205700
N	-0.82098600	1.40115000	1.01848200
N	-2.11292900	2.80888800	2.11268500
N	0.51607400	-0.84061900	1.64083700
O	2.34494100	1.41716900	-0.25324900
O	1.58761100	-0.56475500	2.22014000

Co	-0.09251800	-0.08764400	-0.06089900

Optimized geometry of **1-H**$^{+}$ (+2 singlet)

C	-0.86127	1.93685	-3.56869
C	1.65463	-2.92113	-2.5516
C	1.95322	2.68069	-2.40487
C	-0.32292	1.3329	-2.31072
C	0.64639	-2.0623	-2.22351
C	3.82819	-3.6121	-1.44243
C	0.98802	1.72521	-1.7802
C	-2.31975	-0.09253	-1.70484
C	2.10011	-1.99223	-0.61081
C	-2.45995	-1.34837	-0.78874
C	-2.19011	1.5623	1.37992
C	-3.62245	3.18317	2.66079
C	-1.40348	-1.94468	1.40922
C	-2.3377	-3.02354	1.84943
C	-0.26599	2.57206	1.43692
C	-0.1878	-1.61199	2.23431
C	-1.1551	3.35499	2.1135
C	0.09671	-2.23006	3.56238
H	-0.18934	1.7352	-4.40791
H	-0.9239	3.0246	-3.47186
H	1.56066	3.1187	-3.3211
H	1.79842	-3.55324	-3.41313
H	-1.85104	1.56131	-3.82256
H	2.19814	3.49079	-1.71263
H	-0.23279	-1.82048	-2.79398
H	-2.57184	-0.3627	-2.73318
H	3.62496	-4.6825	-1.43538
H	4.45806	-3.3629	-2.29568
H	2.89598	2.17864	-2.64118
H	-3.03031	0.67956	-1.39496
H	-2.22235	-2.2568	-1.34872
H	4.34709	-3.33912	-0.52572
H	-3.49173	-1.44777	-0.44216
H	2.63355	-1.74293	0.29119
H	-2.98498	0.85688	1.20753
H	-4.40468	2.44623	2.48828
H	-3.22382	-3.08465	1.21971
H	-3.91326	4.12725	2.20105
H	-1.83306	-3.99528	1.81651
H	-3.49407	3.32282	3.73364
H	0.7843	2.73909	1.26855
H	-2.65293	-2.87246	2.88515
H	-1.02838	4.30032	2.61631

H	-0.63858	-1.90236	4.30469
H	0.03674	-3.32015	3.51075
H	1.08489	-1.94957	3.92024
N	2.56701	-2.86433	-1.52179
N	-0.95581	0.44625	-1.59454
N	0.92913	-1.48374	-0.99874
N	1.25653	1.13462	-0.62515
N	-1.50694	-1.24804	0.33048
N	-0.92442	1.4444	0.97502
N	-2.36795	2.70511	2.06838
N	0.56637	-0.73469	1.65185
O	2.30852	1.31491	0.0609
Co	-0.07497	-0.05442	-0.03504
O	1.70812	-0.32773	2.24419
H	2.09626	0.34151	1.61309

Optimized geometry of **2** (+1 singlet)

C	-2.27958400	1.59730100	-2.96594500
C	0.70672300	1.61949600	-2.21561200
C	0.31625700	-2.01531200	-2.01868000
C	2.06229100	1.04141300	-1.73022200
C	-1.65493900	0.90548400	-1.79114900
C	0.45392000	-3.92149400	-0.93308700
C	-3.95176700	-0.01537700	-0.89479000
C	-2.47343800	0.19743800	-0.81687200
C	4.27669600	0.39571100	0.31724600
C	0.40748600	-2.89664100	-0.03431300
C	2.80156300	0.21587500	0.51465100
C	0.58933700	2.97860600	0.98983500
C	2.27738300	-0.37767100	1.73908000
C	-1.05149100	1.99482900	2.02176400
C	0.11472800	3.85713400	1.92021400
C	3.07803200	-0.78517100	2.93436300
C	-1.73636700	3.75143200	3.66087500
H	-2.83168000	0.88574600	-3.58605700
H	-1.54340900	2.09921300	-3.59145100
H	0.64253700	1.54775500	-3.30513300
H	0.23628100	-1.32546000	-2.84088400
H	-3.00216600	2.34450900	-2.62615200
H	2.36448700	0.20586500	-2.37064900
H	0.63568000	2.68123200	-1.95900800
H	-4.38667600	0.44470200	-1.78099300
H	2.84087600	1.80496600	-1.80913100
H	0.49756800	-4.98822500	-0.78622400
H	-4.18735800	-1.08360300	-0.90550500
H	4.79227600	-0.56415100	0.40880900

H	-4.44718400	0.39460800	-0.01018600
H	4.51747800	0.81837200	-0.65661700
H	1.41393000	3.10645500	0.31106000
H	4.69055500	1.05097700	1.08871600
H	0.37821400	-2.96035800	1.03978000
H	-1.76687700	1.27372600	2.38554800
H	0.42062400	4.85859800	2.17558400
H	4.14183000	-0.59446000	2.80076800
H	-2.44506700	4.48729400	3.27931100
H	2.93817600	-1.84873700	3.14751900
H	2.73721400	-0.24923800	3.82488400
H	-1.08750700	4.21721200	4.40168400
H	-2.27308000	2.92769300	4.12798200
N	0.39760800	-3.35022800	-2.18598700
N	-0.37696600	0.89396900	-1.54595200
N	0.32390300	-1.70140000	-0.72474300
N	1.89983500	0.55135600	-0.35923000
N	-1.78108600	-0.26923800	0.21698300
N	-0.15094000	1.81157500	1.05698000
N	0.96135400	-0.54610300	1.72263100
N	-0.91995700	3.21737500	2.56680000
O	-2.38047500	-0.90273300	1.14282000
O	0.37415600	-1.05087000	2.73385300
Co	0.11993600	0.09481900	0.09996400
Zn	-1.67356200	-1.66902000	3.03940100
Br	-1.60049700	-4.00174400	2.89584200
Br	-2.60800600	-0.11552600	4.55387100
C	0.40618300	-4.06726000	-3.45965800
H	1.33196500	-4.63308000	-3.56565800
H	-0.44325600	-4.74864800	-3.50931400
H	0.33336600	-3.35030400	-4.27589700

Optimized geometry of **4** (+3 singlet)

C	-0.49629200	4.81890400	-3.67757900
C	-0.56562300	-1.19624500	-3.96212900
C	-0.17415600	-4.24976400	-3.59688800
C	0.71420300	4.35985800	-3.17288000
C	-1.67549900	4.36636700	-3.09567500
C	-0.27588900	-1.85193600	-2.64962900
C	-0.06330900	-3.28789200	-2.45285500
C	0.72834200	3.46409200	-2.10310300
C	-1.59823600	3.46915400	-2.03937100
C	3.24501200	3.40635500	-1.82506200
C	4.14078400	-1.60712000	-1.54911200
C	2.78481700	-1.45783200	-1.58060000
C	1.96621800	2.96301800	-1.47829800

C	4.35041400	2.94230900	-1.12334500
C	0.32702200	-4.98119300	-0.65725800
C	-4.93942600	-3.92053800	-0.12097400
C	-3.19457000	0.78715100	-0.23362100
C	-2.56166100	-3.12385300	-0.28318000
C	-4.55137300	0.84737800	0.04921300
C	5.77702200	-2.61097300	0.10857600
C	4.15401200	2.03406900	-0.08561700
C	3.27811000	-2.42118900	0.29681100
C	2.86223300	1.61587900	0.19874200
C	0.93889100	-4.88839500	0.76299900
C	-4.98353200	1.67275100	1.08471800
C	-3.58813500	-2.62586600	1.59141900
C	-2.69111900	2.32897800	1.43872800
C	-2.30833100	-2.15521600	1.63872600
C	-4.04206600	2.41637100	1.78445400
C	0.59853600	3.80058800	1.97570300
C	-1.63453500	3.14995400	2.05804800
C	0.90972100	-3.10721900	2.51472200
C	0.75471800	-1.66037800	2.67904700
C	0.43168100	4.68655900	3.03119400
C	-1.86103200	4.01571200	3.12866300
C	1.26810900	-3.98344800	3.67637000
C	-0.82159500	4.79332500	3.62428000
C	0.88543700	-0.92062200	3.97234100
H	-0.51554000	5.51797700	-4.50557000
H	-0.60599500	-1.91350400	-4.77947300
H	0.57916800	-4.02457400	-4.35777800
H	0.19697500	-0.44824400	-4.20026300
H	1.64071000	4.70437000	-3.61269200
H	-1.14694400	-4.16340200	-4.08924200
H	-2.64430200	4.69976400	-3.44741500
H	-1.51694700	-0.65729700	-3.93037900
H	-0.04137700	-5.28432700	-3.28708000
H	3.38093300	4.12787700	-2.61967700
H	4.90323900	-1.33690500	-2.26206000
H	2.18705000	-1.00101100	-2.34738000
H	-2.49437800	3.09456400	-1.56545000
H	5.34365100	3.29816900	-1.37223700
H	-4.78045100	-4.23684700	-1.15017000
H	0.94048500	-5.63163500	-1.28391300
H	-2.40728000	-3.51732500	-1.27224600
H	-2.80750400	0.17161200	-1.03543700
H	-5.25353300	0.27209900	-0.54235700
H	-0.66985000	-5.42998100	-0.60291200

H	6.43420300	-1.74240300	0.12806600
H	-5.79176300	-3.24319400	-0.08506600
H	-5.14501400	-4.79586300	0.49481300
H	6.19186600	-3.36623500	-0.55849400
H	2.01484500	-5.08394300	0.71574300
H	4.98440100	1.66584800	0.50491300
H	5.70390200	-3.02335400	1.11313600
H	0.50085900	-5.65366100	1.40715500
H	-6.03589800	1.75247100	1.33225000
H	3.23104500	-2.88518200	1.26585400
H	2.65065000	0.91995800	1.00024600
H	1.56001700	3.69002400	1.49463600
H	-4.39021400	-2.58045800	2.31058800
H	-1.83288800	-1.60587100	2.43005600
H	-4.36588600	3.07935400	2.57561700
H	1.38328700	-5.02730800	3.39177800
H	1.27225300	5.27753700	3.37415900
H	-2.84336600	4.09058300	3.57583100
H	2.19996200	-3.65186000	4.14338900
H	1.67089800	-0.16168800	3.91209900
H	0.49644400	-3.92620100	4.44979900
H	-0.03750900	-0.38173300	4.20784000
H	-0.99057600	5.47102900	4.45301300
H	1.11479200	-1.58370200	4.80419300
N	-0.43236400	3.01692200	-1.54647100
N	-0.16333300	-1.13676000	-1.53674300
N	0.20422300	-3.63309900	-1.22926400
N	4.43948200	-2.21690200	-0.35179900
N	2.24221700	-1.97761000	-0.41760300
N	1.78768600	2.06282300	-0.47389900
N	-3.73541100	-3.23551900	0.36612400
N	-2.27760600	1.50576000	0.43749100
N	-1.66149400	-2.47524000	0.45746500
N	0.72776300	-3.53757000	1.30214200
N	-0.39926800	3.03966200	1.49348500
N	0.45165300	-1.02407300	1.55387500
O	-0.30555600	0.14230700	-1.60930800
O	0.26900800	0.25062300	1.59664800
Co	0.28845100	-2.21785000	0.02180900
Ru	-0.22051800	1.61460900	-0.01791400

^{1}H NMR Spectra

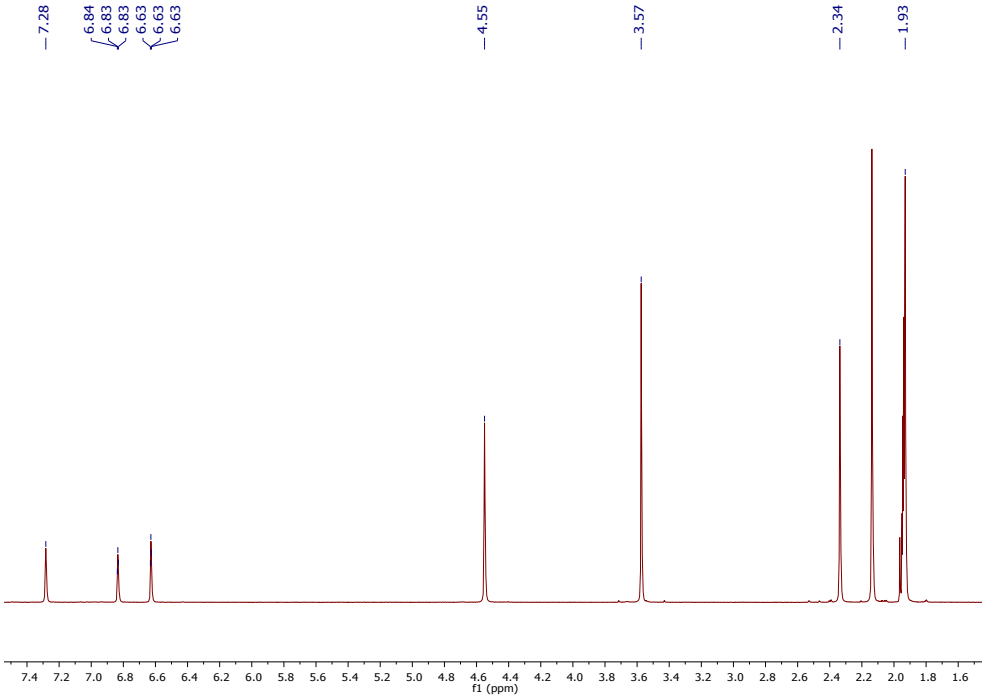

Figure S38: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **1**

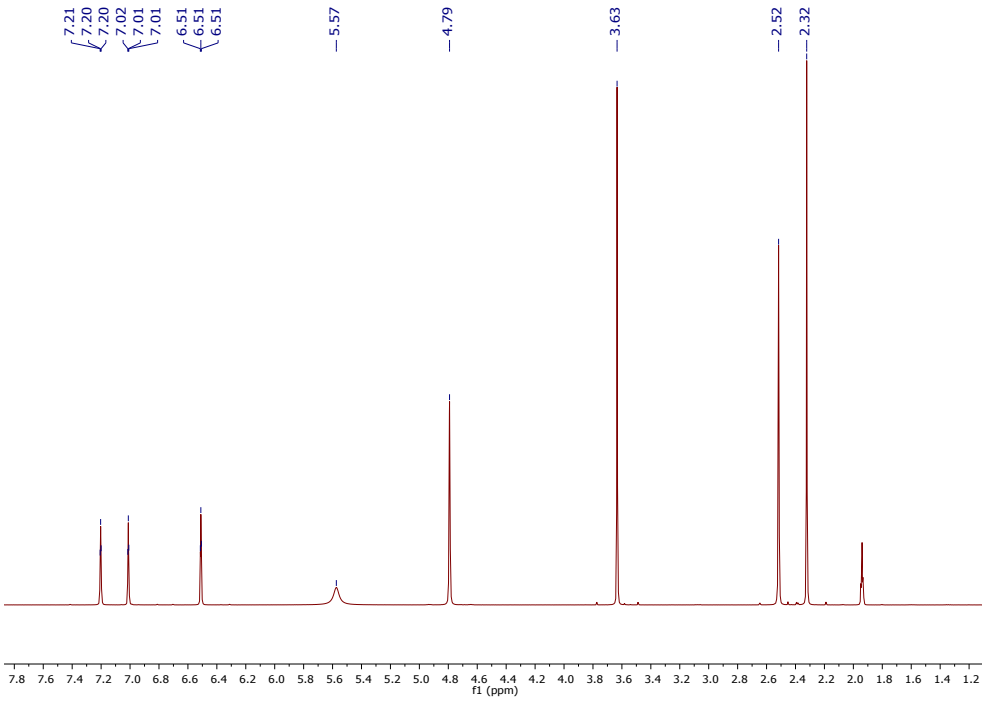

Figure S39: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **1-H+**

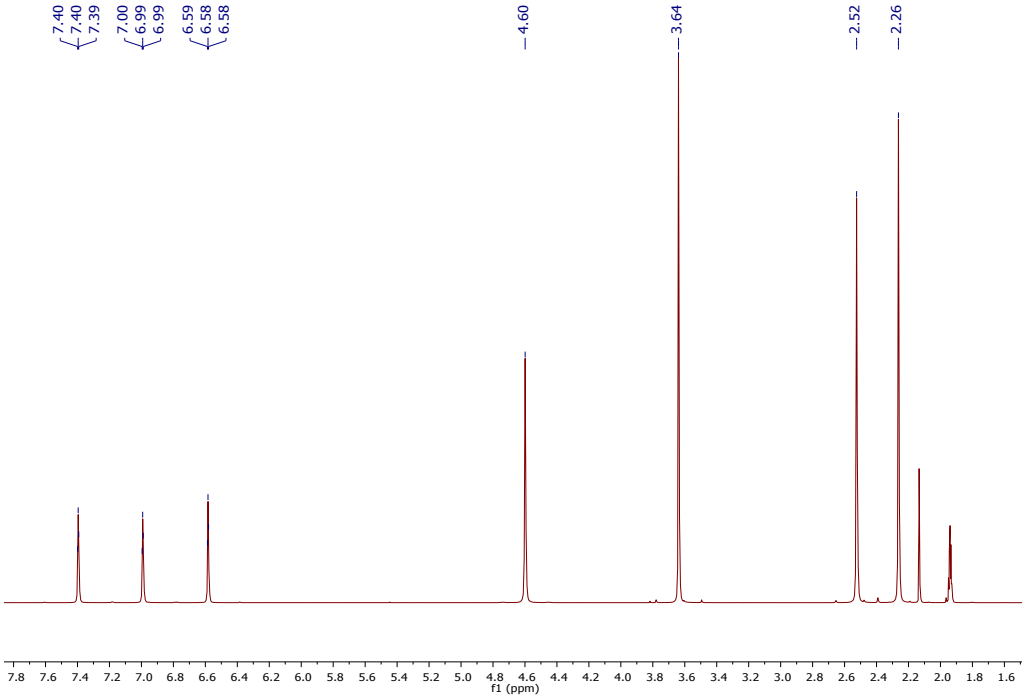

Figure S40: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **2**

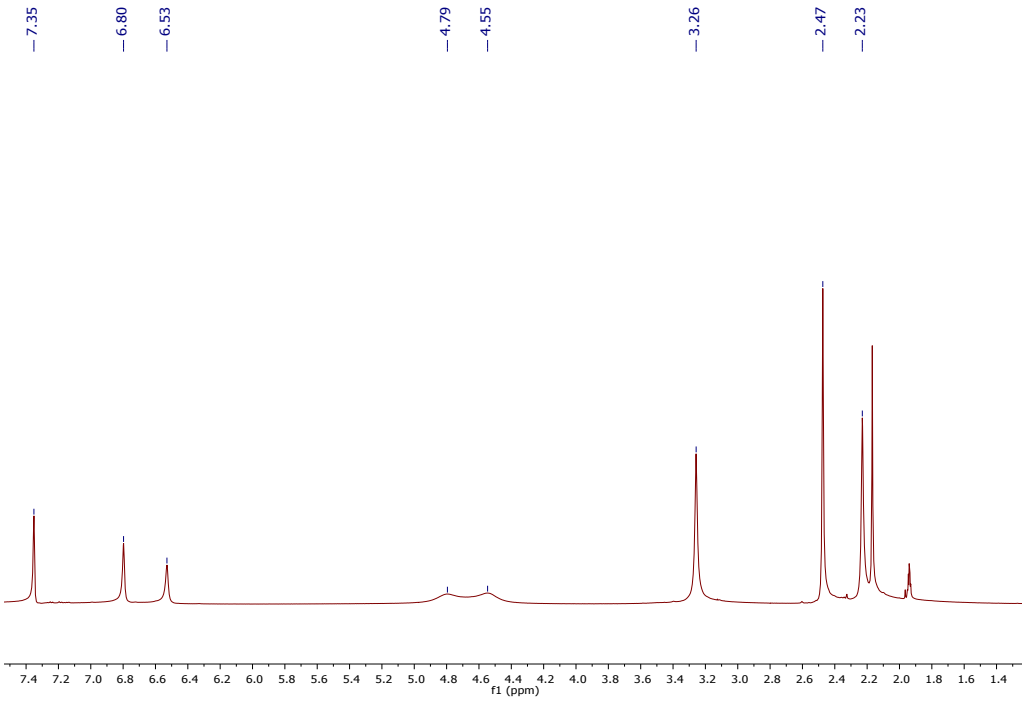

Figure S41: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **3-Cd**

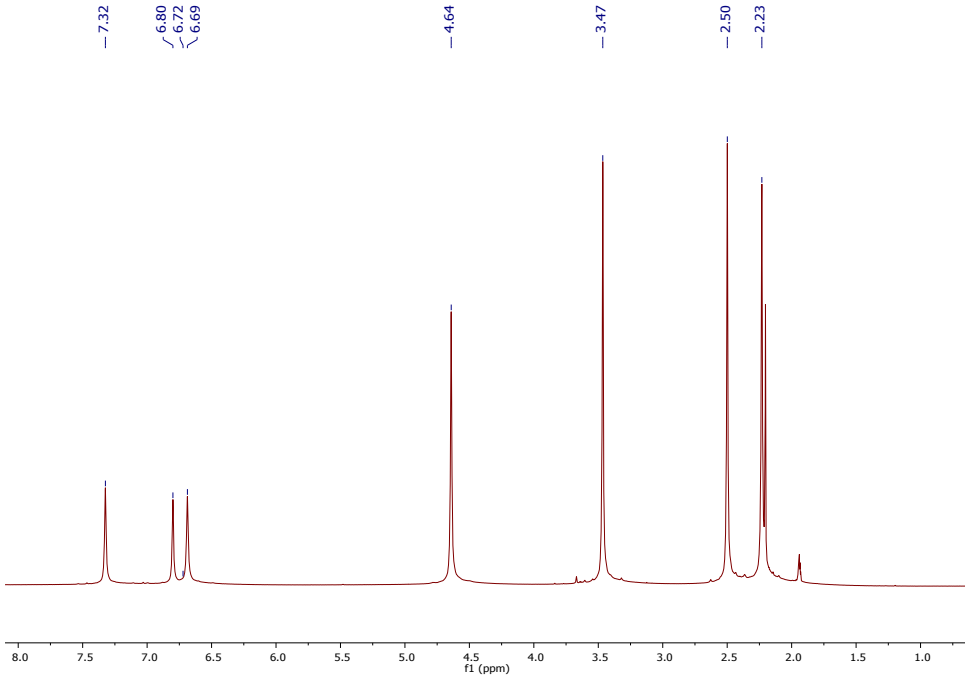

Figure S42: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **3-Zn**

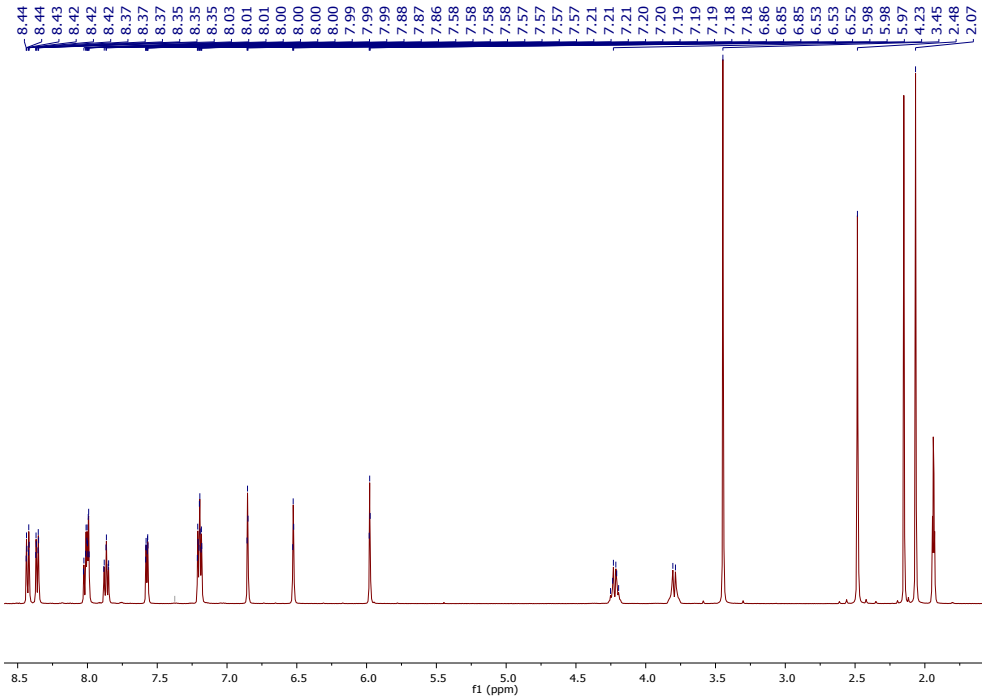

Figure S43: 500 MHz ^{1}H NMR spectrum in CD_3CN of complex **4**

UV-Vis Data for Complexes 3-M

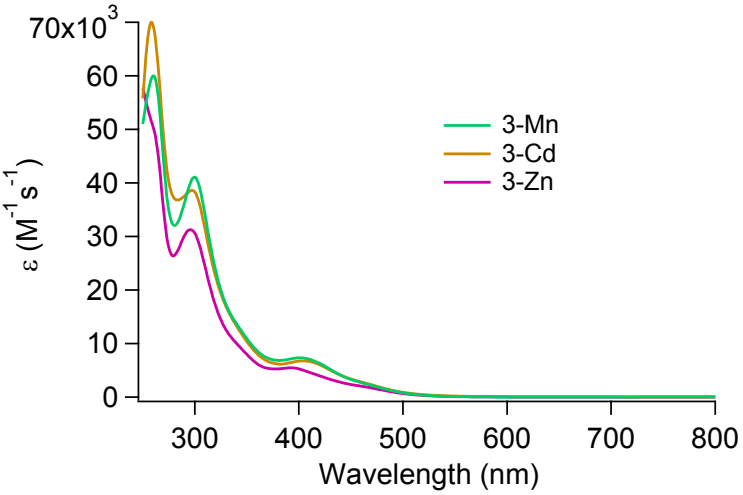

Figure S42: UV-vis spectra of **3-Zn**, **3-Cd**, and **3-Mn** in CH_3CN.

X-ray Data Tables

Table S5: Crystal data and structure refinement for Complex **1**

Identification code	dh_152b_0ma	
Empirical formula	C20 H34 Cl Co N8 O7 S	
Formula weight	624.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P n	
Unit cell dimensions	a = 6.8158(16) Å	α = 90°.
	b = 12.780(3) Å	β = 92.125(14)°.
	c = 15.038(3) Å	γ = 90°.
Volume	1309.0(5) $Å^3$	
Z	2	
Density (calculated)	1.586 Mg/m^3	
Absorption coefficient	0.895 mm^{-1}	
F(000)	652	
Crystal size	0.12 x 0.08 x 0.01 mm^3	
Theta range for data collection	1.59 to 25.42°.	
Index ranges	-8<=h<=8, -15<=k<=15, -18<=l<=18	
Reflections collected	32970	
Independent reflections	4775 [R(int) = 0.1065]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9911 and 0.9002	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4775 / 2 / 351	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0611	
R indices (all data)	R1 = 0.0762, wR2 = 0.0691	
Absolute structure parameter	0.005(15)	
Largest diff. peak and hole	0.350 and -0.415 $e.Å^{-3}$	

Table S6: Crystal data and structure refinement for Complex **1-H**$^{+}$

Identification code	twin5	
Empirical formula	C18 H29 Cl2 Co N8 O10	
Formula weight	647.32	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.714(2) Å	α = 90°.
	b = 11.4270(18) Å	β = 92.610(11)°.
	c = 15.237(3) Å	γ = 90°.
Volume	2559.2(8) Å^3	
Z	4	
Density (calculated)	1.680 Mg/m^3	
Absorption coefficient	0.949 mm^{-1}	
F(000)	1336	
Crystal size	0.20 x 0.10 x 0.07 mm^3	
Theta range for data collection	2.23 to 25.70°.	
Index ranges	-17<=h<=17, -13<=k<=13, 0<=l<=18	
Reflections collected	8597	
Independent reflections	9118 [R(int) = 0.1198]	
Completeness to theta = 25.00°	96.6 %	
Max. and min. transmission	0.9365 and 0.8329	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9118 / 235 / 378	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.1287, wR2 = 0.3120	
R indices (all data)	R1 = 0.1723, wR2 = 0.3501	
Largest diff. peak and hole	2.270 and -1.410 e.Å^{-3}	

Table S7: Crystal data and structure refinement for Complex **2**

Identification code	dh_160_0ma	
Empirical formula	C18 H28 Br2 Cl Co N8 O6 Zn	
Formula weight	772.05	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 17.567(3) Å	α = 90°.
	b = 10.0243(16) Å	β = 102.334(9)°.
	c = 15.749(3) Å	γ = 90°.
Volume	2709.3(8) $Å^3$	
Z	4	
Density (calculated)	1.893 Mg/m^3	
Absorption coefficient	4.595 mm^{-1}	
F(000)	1536	
Crystal size	0.10 x 0.05 x 0.02 mm^3	
Theta range for data collection	2.03 to 28.39°.	
Index ranges	-23<=h<=23, -13<=k<=13, -21<=l<=21	
Reflections collected	123719	
Independent reflections	13533 [R(int) = 0.0536]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9137 and 0.6565	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13533 / 83 / 741	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0621	
R indices (all data)	R1 = 0.0468, wR2 = 0.0666	
Absolute structure parameter	0.102(5)	
Largest diff. peak and hole	1.256 and -1.103 e.$Å^{-3}$	

Table S8: Crystal data and structure refinement for Complex **3-Zn**

Identification code	dh_177_0ma	
Empirical formula	C54 H96 Cl5 Co3 N24 O32 Zn	
Formula weight	2012.96	
Temperature	292(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 c	
Unit cell dimensions	a = 28.732(3) Å	α = 90°.
	b = 28.732(3) Å	β = 90°.
	c = 17.5558(16) Å	γ = 120°.
Volume	12551.0(19) $Å^3$	
Z	6	
Density (calculated)	1.598 Mg/m^3	
Absorption coefficient	1.122 mm^{-1}	
F(000)	6240	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.46 to 25.57°.	
Index ranges	-34<=h<=34, -34<=k<=34, -21<=l<=21	
Reflections collected	133666	
Independent reflections	2588 [R(int) = 0.1365]	
Completeness to theta = 25.00°	98.9 %	
Max. and min. transmission	0.9779 and 0.8961	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2588 / 90 / 260	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1081	
R indices (all data)	R1 = 0.0847, wR2 = 0.1394	
Largest diff. peak and hole	0.338 and -0.349 $e.Å^{-3}$	

Table S9: Crystal data and structure refinement for Complex **3-Mn**

Identification code	dh_183_0ma	
Empirical formula	C54 H96 Cl5 Co3 Mn N24 O32	
Formula weight	2002.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 c	
Unit cell dimensions	a = 28.810(3) Å	α = 90°.
	b = 28.810(3) Å	β = 90°.
	c = 16.9308(19) Å	γ = 120°.
Volume	12170(2) $Å^3$	
Z	6	
Density (calculated)	1.639 Mg/m^3	
Absorption coefficient	1.017 mm^{-1}	
F(000)	6210	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.45 to 28.40°.	
Index ranges	-38<=h<=38, -38<=k<=38, -22<=l<=22	
Reflections collected	141055	
Independent reflections	3409 [R(int) = 0.1074]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9799 and 0.9051	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3409 / 83 / 261	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1252	
R indices (all data)	R1 = 0.0851, wR2 = 0.1417	
Largest diff. peak and hole	0.424 and -0.483 $e.Å^{-3}$	

Table S10: Crystal data and structure refinement for Complex **3-Cd**

Identification code	twin4a	
Empirical formula	C54 H96 Cd Cl5 Co3 N24 O32	
Formula weight	2059.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 c	
Unit cell dimensions	a = 28.981(3) Å	α = 90°.
	b = 28.981(3) Å	β = 90°.
	c = 16.838(4) Å	γ = 120°.
Volume	12247(3) $Å^3$	
Z	6	
Density (calculated)	1.676 Mg/m^3	
Absorption coefficient	1.117 mm^{-1}	
F(000)	6348	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	2.43 to 28.46°.	
Index ranges	-38<=h<=0, -10<=k<=38, -22<=l<=20	
Reflections collected	9984	
Independent reflections	3421 [R(int) = 0.0746]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9780 and 0.8965	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3421 / 83 / 261	
Goodness-of-fit on F^2	1.190	
Final R indices [I>2sigma(I)]	R1 = 0.0789, wR2 = 0.1311	
R indices (all data)	R1 = 0.1306, wR2 = 0.1474	
Largest diff. peak and hole	0.505 and -0.430 $e.Å^{-3}$	

Table S11: Crystal data and structure refinement for Complex **4**

Identification code	dh2_135c_0ma	
Empirical formula	C616 H716 Co16 F288 N196 O32 P48 Ru16	
Formula weight	20896.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$I\,4_1/a$	
Unit cell dimensions	a = 40.556(5) Å	α = 90.000°.
	b = 40.556(5) Å	β = 90.000°.
	c = 12.276(5) Å	γ = 90.000°.
Volume	20191(9) $Å^3$	
Z	1	
Density (calculated)	1.719 Mg/m^3	
Absorption coefficient	0.839 mm^{-1}	
F(000)	10488	
Crystal size	0.10 x 0.03 x 0.03 mm^3	
Theta range for data collection	2.00 to 25.49°.	
Index ranges	-48<=h<=49, -49<=k<=45, -14<=l<=14	
Reflections collected	90430	
Independent reflections	9314 [R(int) = 0.3615]	
Completeness to theta = 25.00°	99.4 %	
Max. and min. transmission	0.9753 and 0.9208	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9314 / 546 / 791	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0861, wR2 = 0.1621	
R indices (all data)	R1 = 0.2700, wR2 = 0.2331	
Largest diff. peak and hole	1.144 and -0.868 $e.Å^{-3}$	

Table S12: Crystal data and structure refinement for $[(DO)_2en(Im^{Me})_2CoNa][PF_6]_2$

Identification code	dh2_73_0ma	
Empirical formula	C18 H28 Co F12 N8 Na O2 P2	
Formula weight	760.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 8.6942(9) Å	α = 90°.
	b = 22.063(2) Å	β = 90°.
	c = 14.9541(15) Å	γ = 90°.
Volume	2868.4(5) $Å^3$	
Z	4	
Density (calculated)	1.761 Mg/m^3	
Absorption coefficient	0.838 mm^{-1}	
F(000)	1536	
Crystal size	0.20 x 0.09 x 0.05 mm^3	
Theta range for data collection	2.29 to 28.51°.	
Index ranges	-11<=h<=11, -29<=k<=29, -20<=l<=19	
Reflections collected	110617	
Independent reflections	3538 [R(int) = 0.1143]	
Completeness to theta = 25.00°	97.3 %	
Max. and min. transmission	0.9593 and 0.8503	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3538 / 0 / 204	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1719	
R indices (all data)	R1 = 0.0859, wR2 = 0.1849	
Extinction coefficient	0.0022(5)	
Largest diff. peak and hole	1.183 and -1.206 $e.Å^{-3}$	

Table S13: Crystal data and structure refinement for $[(DO)_2en(Im^{Me})_2CoNa\text{-}15crown5][BPh_4]_2$

Identification code	twin5	
Empirical formula	C76 H88 B2 Co N8 Na O7	
Formula weight	1329.08	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 11.8905(14) Å	α = 72.344(5)°.
	b = 12.4560(16) Å	β = 66.193(4)°.
	c = 13.6113(17) Å	γ = 73.679(4)°.
Volume	1728.2(4) $Å^3$	
Z	1	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.315 mm^{-1}	
F(000)	704	
Crystal size	0.08 x 0.03 x 0.03 mm^3	
Theta range for data collection	2.05 to 28.37°.	
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18	
Reflections collected	33862	
Independent reflections	33863 [R(int) = 0.1023]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9906 and 0.9752	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33863 / 21 / 865	
Goodness-of-fit on F^2	0.994	
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1102	
R indices (all data)	R1 = 0.1308, wR2 = 0.1303	
Absolute structure parameter	0.036(12)	
Largest diff. peak and hole	0.520 and -0.521 $e.Å^{-3}$	

Table S14: Crystal data and structure refinement for $[((DO)_2en(Im^{Me})_2Co)_2Zn(HOMe)][ClO_4]_4$

Identification code	dh_177b_0m	
Empirical formula	C37 H62 Cl4 Co2 N16 O22 Zn	
Formula weight	1408.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.3205(16) Å	α = 70.715(6)°.
	b = 15.0242(18) Å	β = 76.405(7)°.
	c = 17.218(2) Å	γ = 67.308(6)°.
Volume	2977.7(6) $Å^3$	
Z	2	
Density (calculated)	1.570 Mg/m^3	
Absorption coefficient	1.215 mm^{-1}	
F(000)	1448	
Crystal size	0.22 x 0.12 x 0.05 mm^3	
Theta range for data collection	1.84 to 28.62°.	
Index ranges	-17<=h<=17, -20<=k<=19, -23<=l<=23	
Reflections collected	125072	
Independent reflections	14926 [R(int) = 0.0424]	
Completeness to theta = 25.00°	99.9 %	
Max. and min. transmission	0.9418 and 0.7759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14926 / 87 / 822	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1069	
R indices (all data)	R1 = 0.0649, wR2 = 0.1138	
Largest diff. peak and hole	2.104 and -0.946 $e.Å^{-3}$	

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