

Supporting Information

Electronic Effects on a Mononuclear Co Complex with a Pentadentate Ligand for Catalytic H₂ Evolution

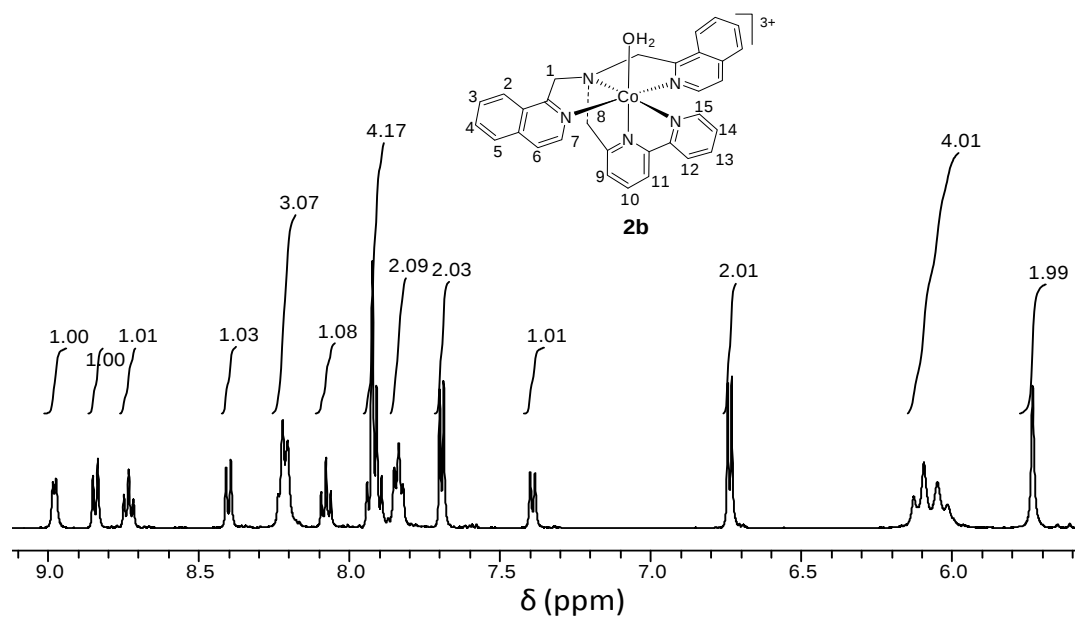
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(a) ^1H NMR



(b) gCOSY

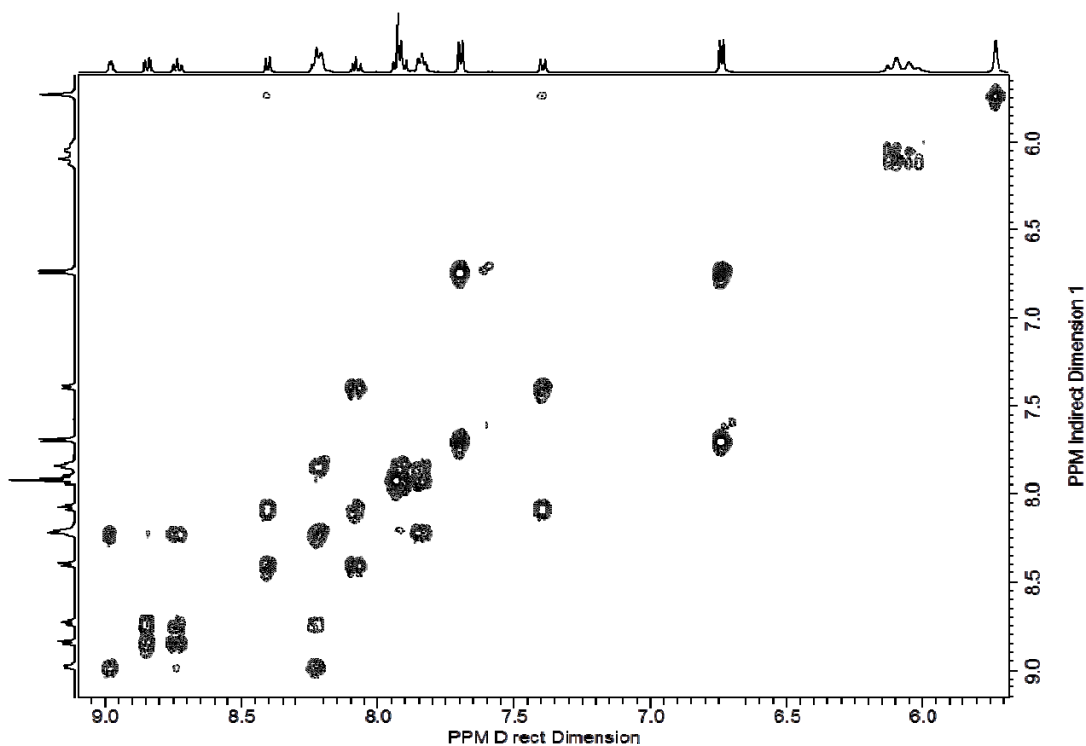


Figure S1. 1D and 2D NMR Spectra (500 MHz, 298 K, D_2O) for $[\text{Co}(\text{DIQ-Bpy})(\text{H}_2\text{O})](\text{PF}_6)_3$ (**2b**): (a) ^1H NMR; (b) gCOSY.

Table S1. ^1H NMR data for DIQ-Bpy (**L**) and $[\text{Co}(\text{DIQ-Bpy})(\text{H}_2\text{O})](\text{PF}_6)_3$ (**2b**) (Chemical Shift, ppm)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
L	4.41	7.89	7.1	7.56	7.75	7.54	8.45	3.99	7.08	7.64	8.23	8.39	7.78	7.29	8.66
2b	6.03	7.90	8.21	7.84	7.94	6.74	7.70	5.72	7.39	8.08	8.40	8.84	8.73	8.22	8.98
	6.11														

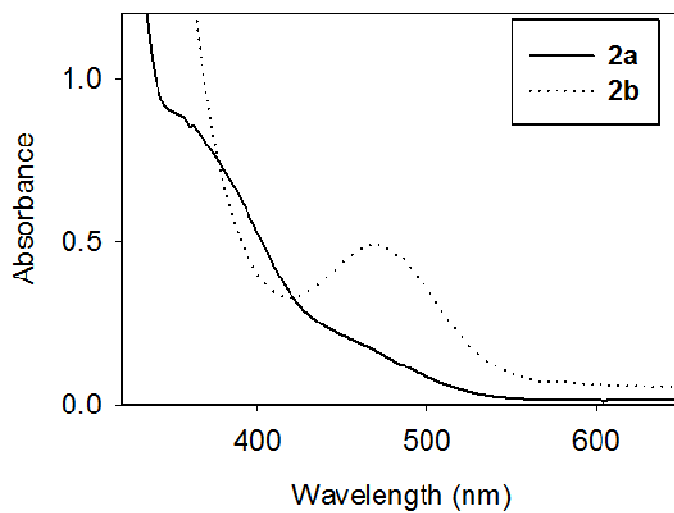


Figure S2. UV-vis spectra of **2a** and **2b** in water.

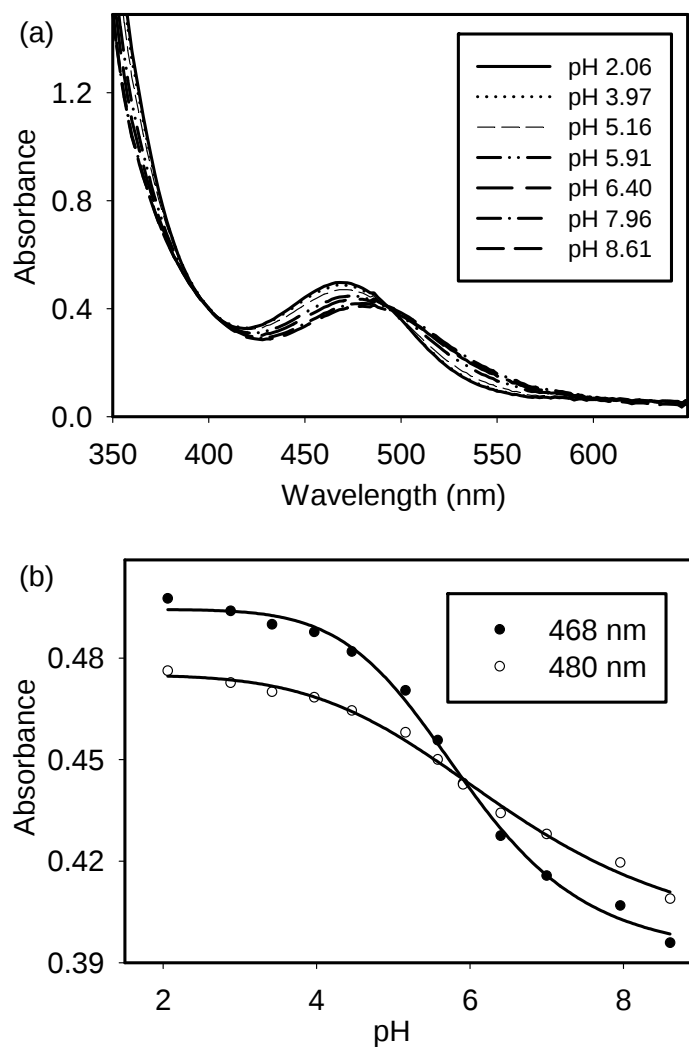


Figure S3. (a) UV-vis spectra change of **2b** at varying pHs. (b) Absorbance change vs pH at 468 and 480 nm for complex **2b**. The best-fit lines from both 468 (solid circles) and 480 nm (open circles) yield a pK_a of 5.9.

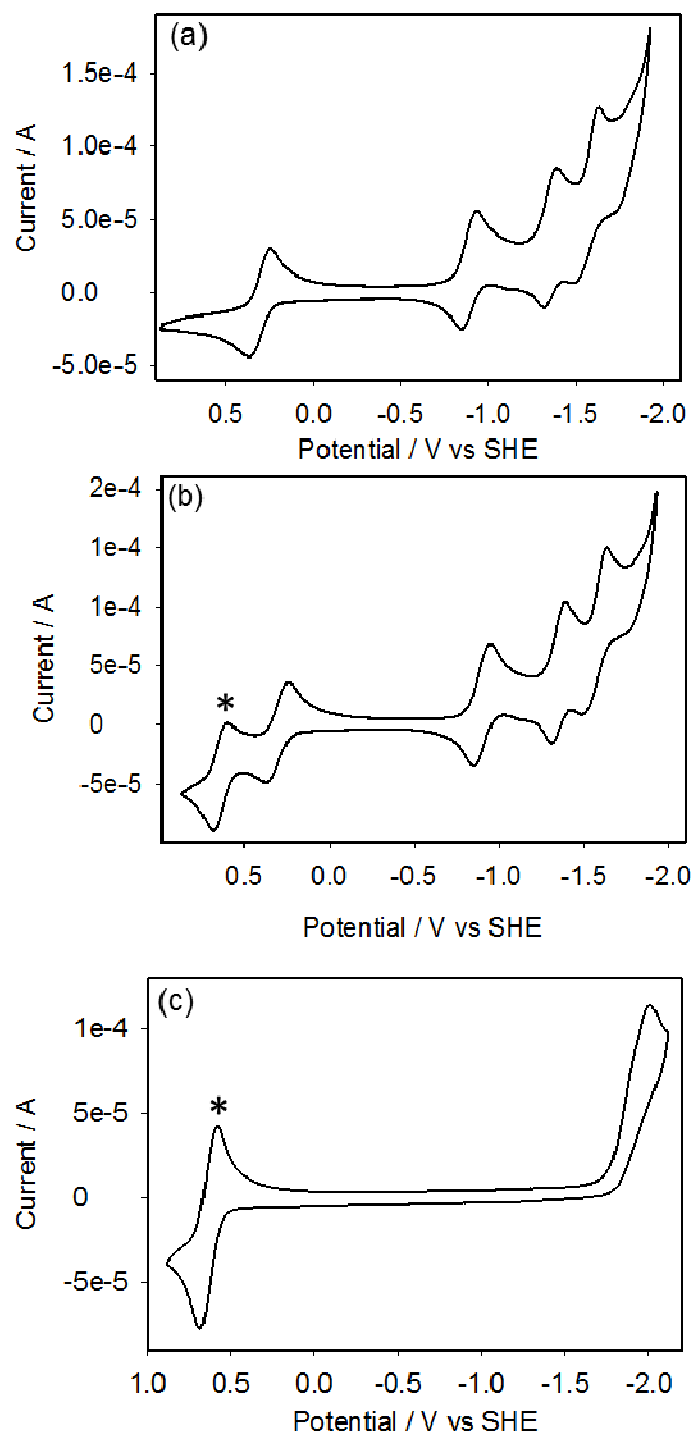


Figure S4. Cyclic voltammograms of (a) **2a**, (b) **2a**, and (c) DIQ-Bpy ligand in the presence of ferrocene in CH₃CN solution, 0.1 M Bu₄NPF₆ buffer. Scan rate, 100 mV/s; working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, Pt wire. Ferrocene (*) was included as an internal reference ($E_{1/2} = 0.64$ V vs SHE).

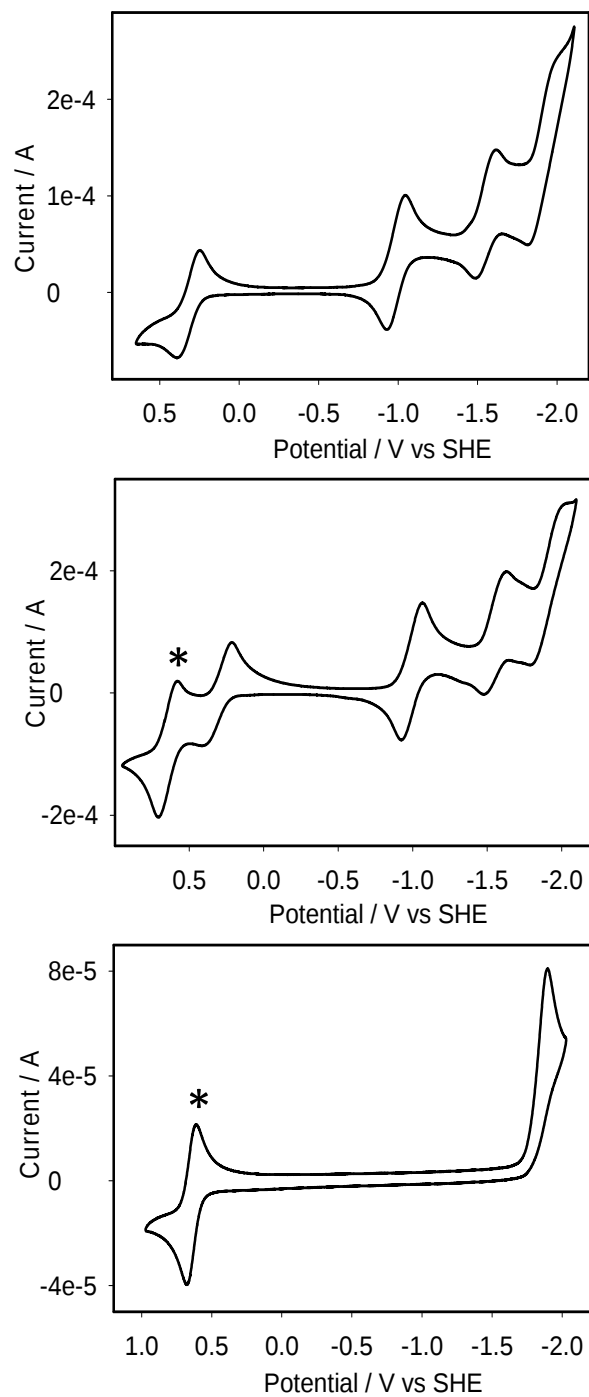


Figure S5. Cyclic voltammograms of (a) **1a**, (b) **1a** and (c) DPA-Bpy ligand in the presence of ferrocene in CH₃CN solution, 0.1 M Bu₄NPF₆ buffer. Scan rate, 100 mV/s; working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, Pt wire. Ferrocene (*) was included as an internal reference ($E_{1/2} = 0.64$ V vs SHE).

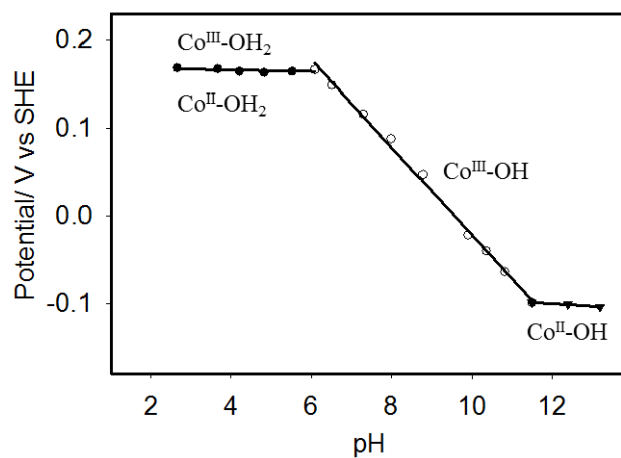


Figure S6. Pourbaix diagram for the $\text{Co}^{\text{III/II}}$ redox couples of complex **2b** ($E_{1/2}$ vs SHE, slope = 49.9 mV/pH), in aqueous universal buffer, Scan rate, 100 mV/s; working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, Pt wire.

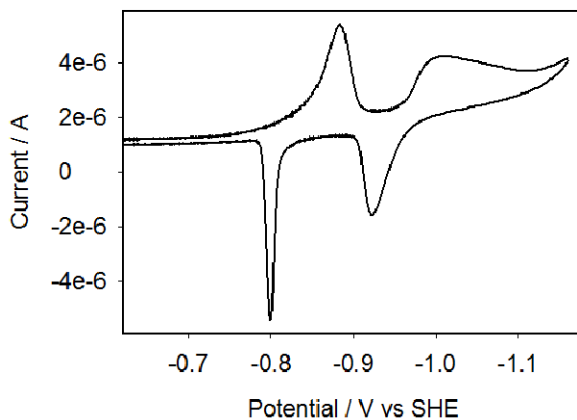


Figure S7. Cyclic voltammogram of **1b** in 1.0 M phosphate buffer at pH 7.0. Scan rate, 100 mV/s; working electrode, mercury drop; reference electrode, Ag/AgCl; counter electrode, Pt wire.

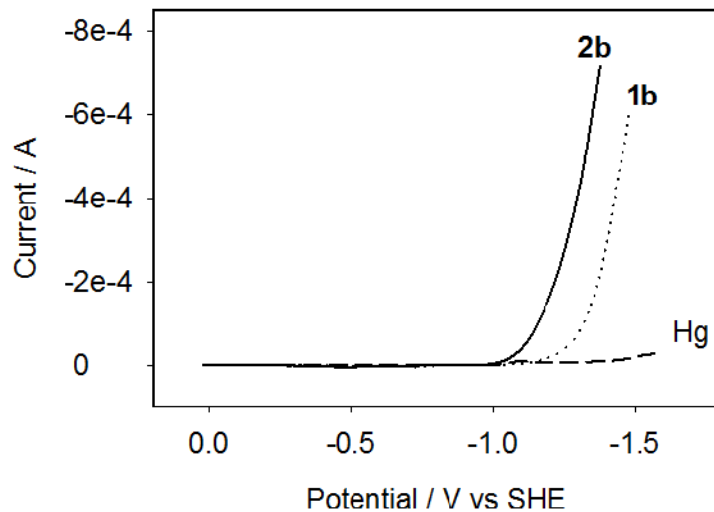


Figure S8. Cyclic voltammograms of 1.0 M sodium phosphate buffer solution at pH 7.0 in the presence of 1 mM **1b** (dotted line), **2b** (solid line), and in the absence of catalyst (long dashed line). Scan rate, 100 mV/s; working electrode, mercury drop; counter electrode, Pt wire; reference electrode, aqueous Ag/AgCl.

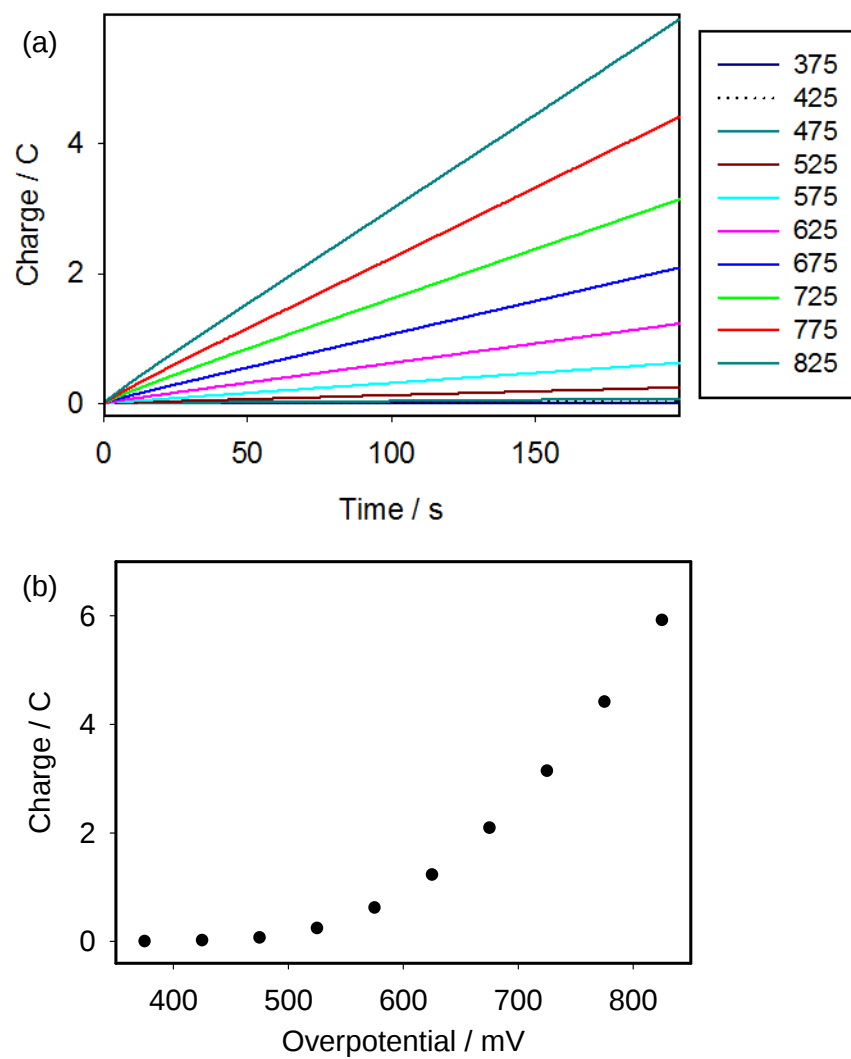


Figure S9. (a) Charge build-up over time (200 s) and (b) overpotential for the controlled potential electrolysis of 50 μM **2b** in 1.0 M sodium phosphate buffer at pH 7.0.

Table S2. Experimental results from controlled-potential electrolysis on **2b** in 1.0 M phosphatebuffer at pH 7 at applied potential of -1.3 and -1.4 V (vs SHE).

Sample Number	1	2	3	4	5	6	7	8	9	10
Applied Potential, (V vs SHE)	-1.40	-1.40	-1.40	-1.40	-1.40	-1.30	-1.30	-1.30	-1.30	-1.30
Coulombs	28.04	26.79	24.25	19.6	31.42	21.51	18.32	23.31	20.1	21.0
Calc Volume of H ₂ (mL)	3.494	3.338	3.022	2.442	3.915	2.680	2.283	2.904	2.504	2.617
Obs'd Volume Change (mL)	3.6	3.4	3.1	2.5	4.0	2.7	2.3	2.9	2.5	2.6
Expt H ₂ Volume (mL)	3.51	3.315	3.023	2.438	3.90	2.633	2.243	2.828	2.438	2.535
Current Efficiency (%)	100.4	99.3	100.0	100.0	99.8	98.22	98.24	97.35	97.33	96.88

Table S3. Experimental results from controlled-potential electrolysis on **1b** and **2b** in 1.0 M phosphate buffer at pH 7 at applied potential of -1.2 V (vs SHE).

	Complex 1b				Complex 2b				
Sample number	1	2	3	4	1	2	3	4	5
Coulombs	11	16.92	23	22.8	10.6	12.21	15.65	20.22	17.5
Calc Volume of H ₂ (mL)	1.371	2.108	2.866	2.841	1.321	1.521	1.950	2.519	2.181
Obs'd Volume Change (mL)	1.2	1.8	2.5	2.4	1.3	1.5	1.9	2.5	2.1
Expt H ₂ Volume (mL)	1.17	1.755	2.438	2.34	1.268	1.463	1.853	2.438	2.048
Current Efficiency (%)	85.36	83.24	85.05	82.36	95.96	96.13	95.0	96.74	93.90

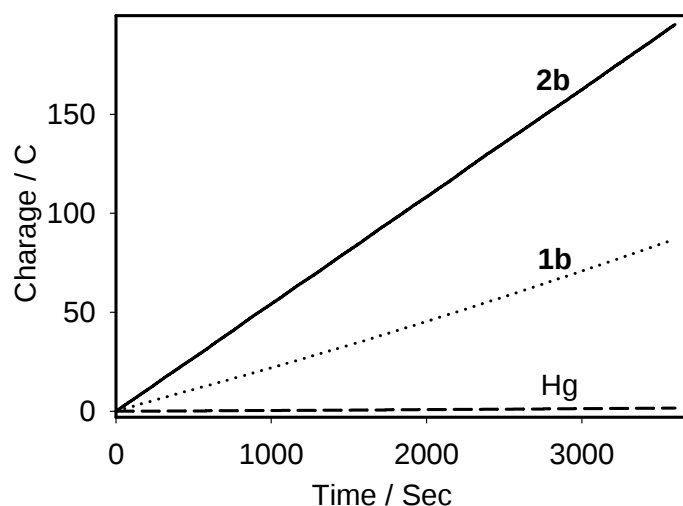


Figure S10. Controlled potential electrolysis at -1.4 V (vs SHE) in the presence of $50\ \mu\text{M}$ of **1b** (dotted line) or **2b** (solid line) and in the absence of catalyst (long dashed line) in 1.0 M sodium phosphate buffer solution at pH 7.0. Working electrode, mercury pool; counter electrode, Pt mesh; reference electrode, aqueous Ag/AgCl.

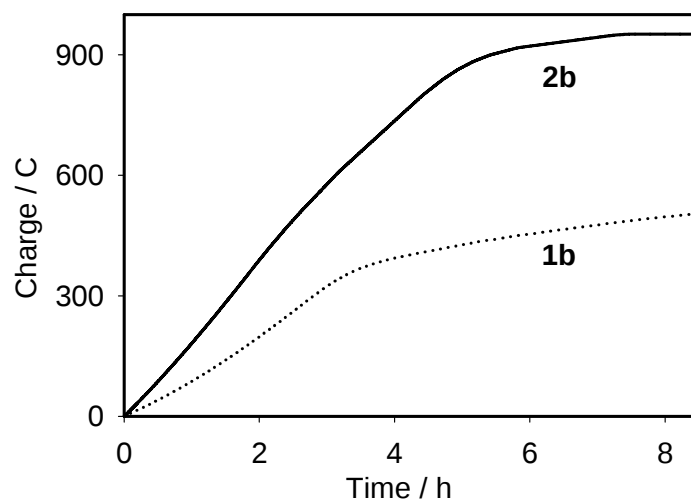


Figure S11. Stability test of $50\ \mu\text{M}$ **1b** (dotted line) and **2b** (solid line) at -1.4 V (vs SHE) in 1.0 M sodium phosphate buffer solution at pH 7.0. Working electrode, mercury pool; counter electrode, Pt mesh; reference electrode, aqueous Ag/AgCl.

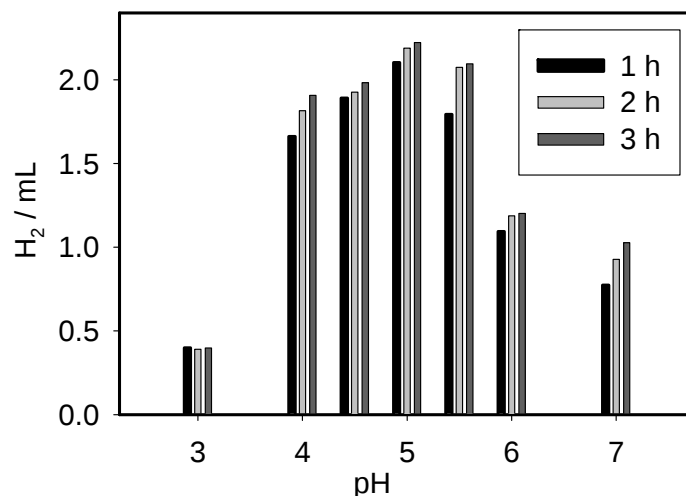


Figure S12. Photocatalytic H₂ evolution at various pH values. Conditions: 10 mL 1.0 M buffer solutions with [ascorbic acid] = 0.1 M, [Ru(bpy)₃]²⁺ = 0.5 mM, [**2b**] = 5.0 μM, LED light: 450 nm.

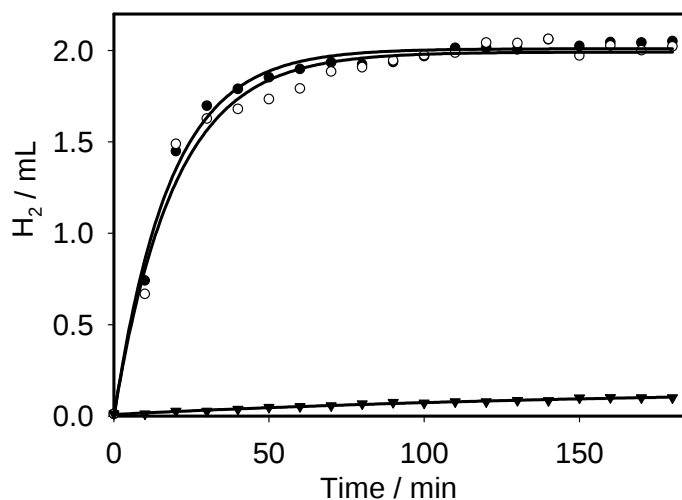


Figure S13. Photocatalytic H₂ production over time in the presence (open circles) and absence (closed circles) of Hg (1 mL), control without catalyst (closed triangles). Conditions: 10 mL 1.0 M acetate buffer at pH 5.0, [ascorbic acid] = 0.1 M, [Ru(bpy)₃]²⁺ = 0.5 mM, [**2b**] = 5.0 μM, LED light: 450 nm.

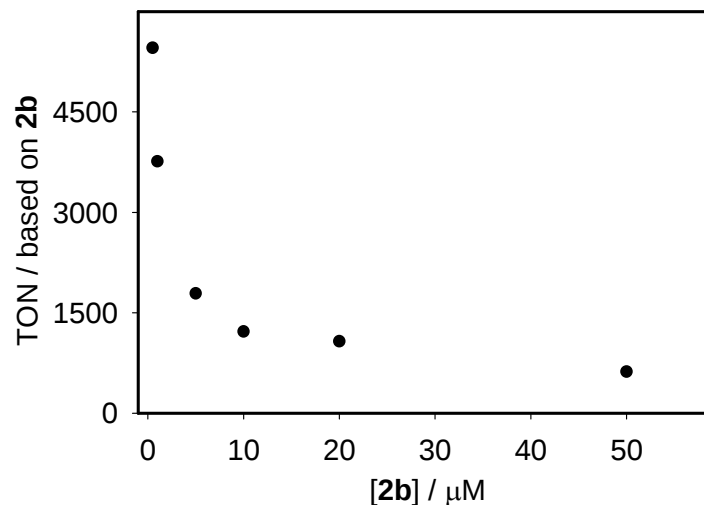


Figure S14. Photocatalytic H_2 evolution at various concentrations of **2b**. Conditions: 10 mL 1.0 M acetate buffer at pH 5.0, [ascorbic acid] = 0.1 M, $[\text{Ru}(\text{bpy})_3]^{2+}$ = 0.5 mM, LED light: 450 nm.

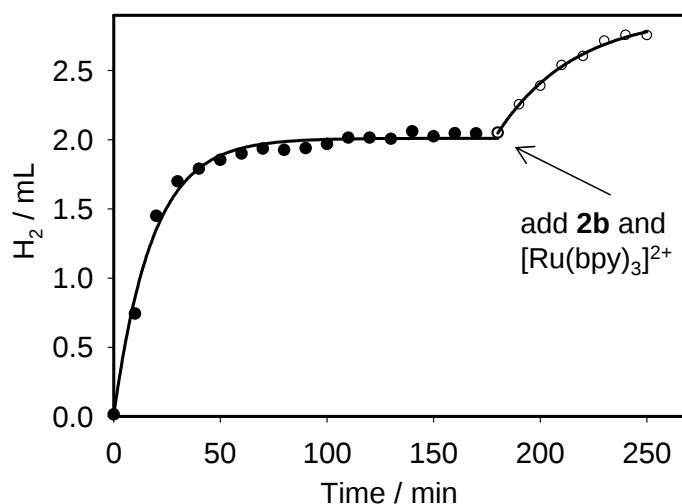


Figure S15. Photocatalytic H_2 production over time. Conditions: 10 mL 1.0 M acetate buffer at pH 5.0, [ascorbic acid] = 0.1 M, $[\text{Ru}(\text{bpy})_3]^{2+}$ = 0.5 mM, **2b** = 5.0 μM , LED light: 450 nm. The arrow indicates addition of **2b** (5.0 μM) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.5 mM) after H_2 evolution stopped at indicated time.

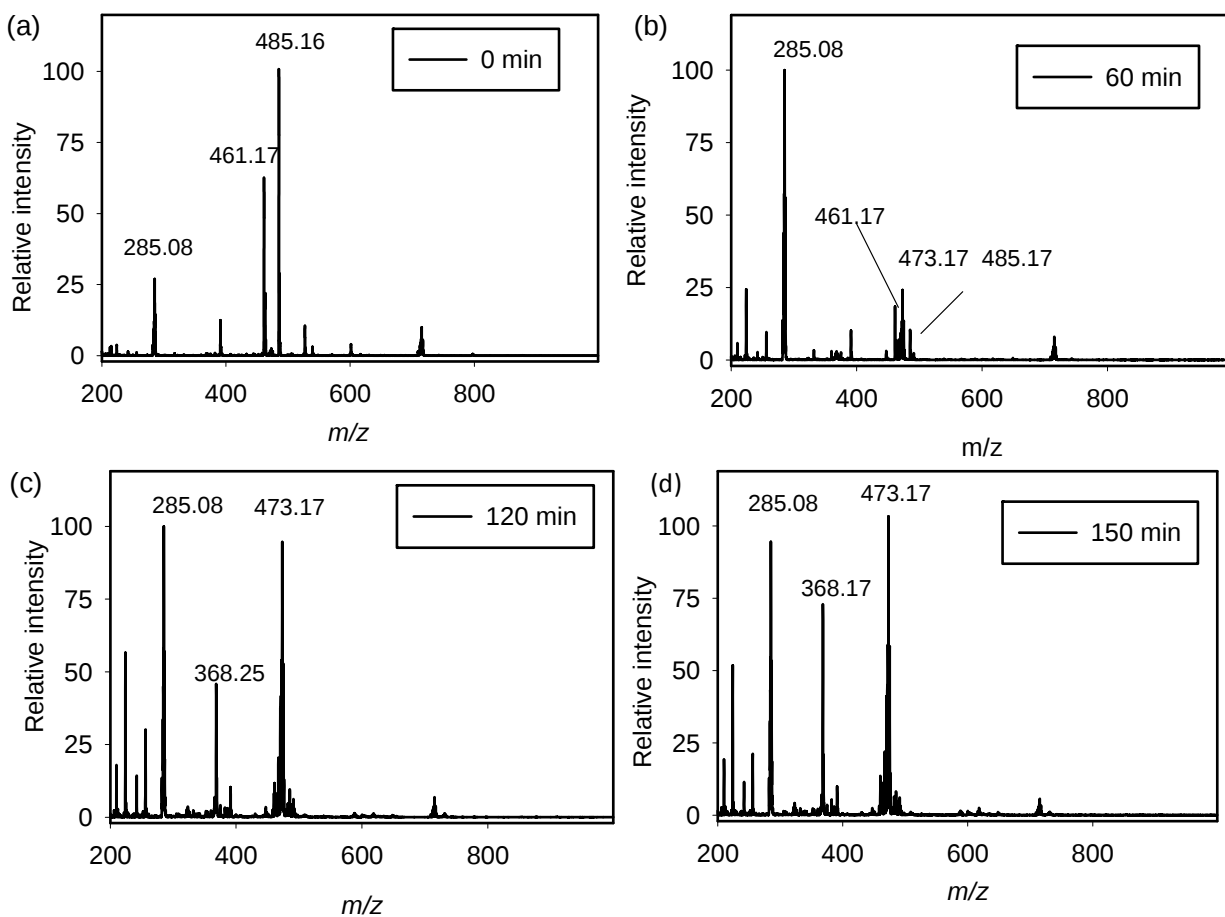
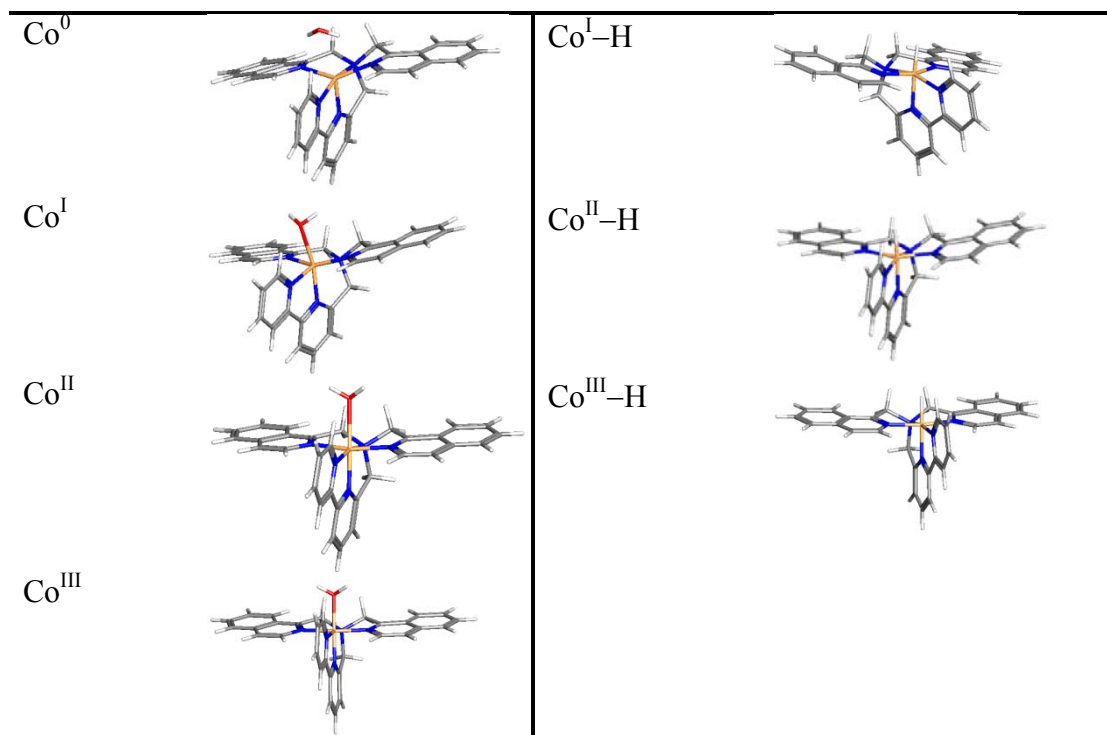


Figure S16. ESI-MS spectra of showing photo decomposition of photo sensitizer and catalyst **1b** (a) before photolysis, (b) 30 min, (c) 60 min and (d) 150 min of photolysis.

Table S4. DFT optimized structures of the possible intermediates during H₂ evolution by **2b****Table S5.** DFT computed relative energies (in Hartrees) of the possible intermediates during H₂ evolution by **2b**

	E	E ₀	G _(gas)	E _(soln)
Co ⁰	-1689.75841	-1689.256683	-1689.321454	-1689.778598
Co ^I	-1689.62072	-1689.115446	-1689.181121	-1689.684053
Co ^{II}	-1689.35526	-1688.846242	-1688.909327	-1689.564314
Co ^{III}	-1688.95502	-1688.442630	-1688.502327	-1689.424442
Co ^I -H	-1613.99038	-1613.504421	-1613.565783	-1614.005265
Co ^{II} -H	-1613.85810	-1613.367282	-1613.428439	-1613.917065
Co ^{III} -H	-1613.59547	-1613.100170	-1613.158618	-1613.803319

Table S6. Cartesian coordinates of optimized structures and absolute energies (in Hartrees) of the possible intermediates during H₂ evolution by **2b**

Co^I-H (Triplet)

Co	-0.141796	0.388741	-0.674331
N	-2.122311	0.125869	-0.495516
C	-2.569483	-1.143554	-0.341015
C	-3.962256	-1.461890	-0.242213
C	-4.909201	-0.370994	-0.258857
C	-4.391418	0.950249	-0.403202
C	-3.028991	1.145122	-0.531123
H	-2.596641	2.142032	-0.665593
C	0.571857	2.076006	1.527407
N	0.227359	0.782105	1.192507
C	0.375188	-0.224839	2.083255
C	0.895882	-0.010161	3.360524
H	1.003351	-0.843571	4.063712
C	1.252801	1.311070	3.729591
H	1.663212	1.513396	4.724951
C	1.088620	2.350711	2.813794
H	1.378254	3.372230	3.083562
C	0.007068	4.654575	-1.784847
H	-0.151797	5.257388	-2.684922
C	-0.151148	3.267183	-1.833881
H	-0.431481	2.753060	-2.761301
N	0.025241	2.449498	-0.769478
C	0.387190	3.027176	0.443076
C	0.565734	4.427131	0.556638
H	0.843187	4.862317	1.523401
C	0.375931	5.246629	-0.553296
H	0.506732	6.331403	-0.469527
C	4.545768	-0.83428	-0.745989
C	3.515075	-1.815832	-0.497279
C	2.150614	-1.390504	-0.573336
N	1.799377	-0.119609	-0.881555
C	2.783942	0.794852	-1.126865
H	2.428666	1.799663	-1.375443
C	4.129634	0.491148	-1.069415
N	-0.207991	-1.692475	0.134586
C	0.985945	-2.351625	-0.424817
H	-0.330193	0.114914	-2.160714

C	5.911272	-1.214022	-0.674786
C	6.272877	-2.525557	-0.376974
C	5.268866	-3.495970	-0.145025
C	3.921553	-3.155032	-0.205742
C	-6.296791	-0.644910	-0.137467
C	-6.757839	-1.953634	-0.012460
C	-5.837201	-3.027809	-0.011650
C	-4.469975	-2.792202	-0.128011
H	0.707912	-2.713329	-1.435784
H	6.678360	-0.452679	-0.864006
H	7.330575	-2.808453	-0.327280
H	5.554286	-4.530132	0.081779
H	3.169582	-3.931897	-0.032492
H	-7.001149	0.196271	-0.146978
H	-7.831603	-2.152551	0.081742
H	-6.202466	-4.057679	0.078986
H	-3.782078	-3.644106	-0.138926
H	1.269802	-3.242757	0.173878
H	-5.073319	1.808400	-0.415482
H	4.877090	1.264644	-1.280861
C	-1.492971	-2.214707	-0.368196
H	-1.813533	-3.121844	0.187259
H	-1.325168	-2.518125	-1.421498
C	-0.178578	-1.560893	1.612284
H	-1.227392	-1.628641	1.963388
H	0.372765	-2.404291	2.080559

el energy = -1613.99038271

zpe = -1613.504421

th energy = -1613.474603

th enthalpy = -1613.473658

free energy = -1613.565783

Co^{II}-H (Doublet)

Co	0.082801	0.374702	-0.569526
N	-1.858220	-0.150385	-0.737790
C	-2.210649	-1.388585	-0.366762
C	-3.570503	-1.842193	-0.391116
C	-4.584251	-0.912138	-0.820455
C	-4.165602	0.390936	-1.207646
C	-2.828680	0.723309	-1.158515
H	-2.467058	1.709225	-1.462449
C	-0.407480	2.227899	1.545727
N	-0.145651	0.914839	1.278606
C	-0.151537	-0.006925	2.266621
C	-0.453882	0.345506	3.587986
H	-0.463174	-0.415756	4.376015
C	-0.734587	1.691067	3.881281
H	-0.974766	1.993628	4.905957
C	-0.705053	2.644088	2.855373
H	-0.919939	3.694727	3.073400
C	-0.164760	4.509376	-2.019715
H	-0.085603	5.031277	-2.978972
C	0.010723	3.122639	-1.964866
H	0.224977	2.530643	-2.861574
N	-0.072895	2.409433	-0.815544
C	-0.342856	3.089701	0.349347
C	-0.530476	4.483366	0.365425
H	-0.741142	5.001115	1.306895
C	-0.441672	5.204704	-0.830501
H	-0.584522	6.290387	-0.834426
C	4.849471	-0.470852	-0.486566
C	3.888675	-1.531633	-0.306820
C	2.499461	-1.183471	-0.318214
N	2.073373	0.075427	-0.507256
C	2.993605	1.076831	-0.676701
H	2.572432	2.075255	-0.826475
C	4.354157	0.850019	-0.668107
N	0.167626	-1.643020	0.382284
C	1.400619	-2.229097	-0.185347
H	0.203602	0.009907	-2.032260
C	6.239572	-0.773975	-0.483989
C	6.673315	-2.080049	-0.318358
C	5.731418	-3.129672	-0.148824
C	4.369974	-2.865686	-0.141735

C	-5.945737	-1.322811	-0.857066
C	-6.300405	-2.612283	-0.491851
C	-5.304738	-3.536263	-0.077655
C	-3.969420	-3.163598	-0.027103
H	1.158257	-2.594131	-1.201200
H	6.959219	0.041942	-0.619986
H	7.744947	-2.307825	-0.319772
H	6.085170	-4.159064	-0.02393
H	3.667623	-3.696651	-0.020698
H	-6.706551	-0.604371	-1.184412
H	-7.350192	-2.923992	-0.524531
H	-5.594839	-4.554666	0.203626
H	-3.224457	-3.901581	0.287336
H	1.746654	-3.100553	0.407064
H	-4.901610	1.126003	-1.552341
H	5.050997	1.684141	-0.807623
C	-1.072483	-2.337786	-0.009213
H	-1.391359	-3.046030	0.782079
H	-0.859083	-2.949228	-0.907050
C	0.275930	-1.405292	1.845625
H	-0.286819	-2.171704	2.417430
H	1.339076	-1.526491	2.131453

el energy = -1613.85810130

zpe = -1613.367282

th energy = -1613.337803

th enthalpy = -1613.336859

free energy = -1613.428439

Co^{III}–H (Singlet)

Co	-0.000223	0.246328	-0.535483
N	-1.938927	0.036323	-0.575712
C	-2.361577	-1.233817	-0.407110
C	-3.741864	-1.587806	-0.361079
C	-4.710261	-0.524941	-0.496366
C	-4.221806	0.797937	-0.670609
C	-2.863496	1.041779	-0.704879
H	-2.467063	2.048341	-0.846245
C	0.001156	2.129954	1.556371
N	0.000685	0.801371	1.293401
C	0.000566	-0.141517	2.245329
C	0.001094	0.230051	3.599441
H	0.001014	-0.522485	4.395042
C	0.001703	1.602024	3.907711
H	0.002124	1.920581	4.955589
C	0.001706	2.571141	2.888854
H	0.002112	3.636501	3.139279
C	0.000061	4.173426	-2.170406
H	-0.000286	4.626640	-3.166638
C	-0.000347	2.777524	-2.047381
H	-0.000996	2.115740	-2.918184
N	0.000061	2.161252	-0.843079
C	0.000873	2.924181	0.308655
C	0.001323	4.325222	0.242847
H	0.001988	4.915713	1.164686
C	0.000923	4.958446	-1.008383
H	0.001277	6.051751	-1.072418
C	4.709654	-0.525880	-0.497410
C	3.741082	-1.588503	-0.361450
C	2.360854	-1.234296	-0.407650
N	1.938417	0.035819	-0.576990
C	2.863156	1.041012	-0.706899
H	2.466905	2.047538	-0.849015
C	4.221427	0.796954	-0.672547
N	-0.000363	-1.588688	0.159490
C	1.242130	-2.243917	-0.37128
H	-0.00092	-0.172385	-1.971232
C	6.097466	-0.833549	-0.462681
C	6.516289	-2.146105	-0.306023
C	5.565562	-3.195698	-0.178110
C	4.205159	-2.929141	-0.203584

C	-6.098120	-0.832409	-0.461834
C	-6.517148	-2.145002	-0.306004
C	-5.566590	-3.194824	-0.178744
C	-4.206147	-2.928467	-0.204041
H	1.027832	-2.566543	-1.407184
H	6.826431	-0.021841	-0.566326
H	7.585860	-2.381167	-0.282493
H	5.914077	-4.227393	-0.060442
H	3.497493	-3.759986	-0.115004
H	-6.826953	-0.020518	-0.564960
H	-7.586754	-2.379912	-0.282623
H	-5.915260	-4.226539	-0.061723
H	-3.498606	-3.759473	-0.115978
H	1.483761	-3.146437	0.218346
H	-4.922307	1.632275	-0.786004
H	4.922074	1.631080	-0.788579
C	-1.243036	-2.243661	-0.371199
H	-1.484718	-3.146222	0.218358
H	-1.028970	-2.566180	-1.407180
C	-0.000377	-1.555161	1.692563
H	-0.887248	-2.105404	2.056228
H	0.885564	-2.106810	2.056354

el energy = -1613.59547102

zpe = -1613.100170

th energy = -1613.071830

th enthalpy = -1613.070886

free energy = -1613.158618

Co⁰ (Doublet)

Co	0.152288	0.451809	-0.511685
N	-1.707692	-0.168995	-1.080114
C	-2.086485	-1.416937	-0.675928
C	-3.456028	-1.802344	-0.523871
C	-4.475935	-0.821337	-0.817134
C	-4.042203	0.471699	-1.247459
C	-2.697254	0.745673	-1.356322
H	-2.339213	1.732411	-1.669561
C	-0.716168	1.813213	1.849299
N	-0.267550	0.604702	1.383820
C	-0.369792	-0.514181	2.143994
C	-0.948694	-0.482491	3.412540
H	-1.024942	-1.397507	4.011283
C	-1.423077	0.754108	3.910600
H	-1.891085	0.805999	4.899576
C	-1.301969	1.907142	3.128816
H	-1.683213	2.866020	3.496548
C	-0.184814	4.788434	-1.124536
H	-0.039948	5.500132	-1.944467
C	0.032749	3.427159	-1.340252
H	0.328711	3.026013	-2.320038
N	-0.129839	2.481771	-0.375969
C	-0.548050	2.897413	0.876518
C	-0.780803	4.259419	1.154868
H	-1.095586	4.562031	2.159828
C	-0.597910	5.217163	0.155249
H	-0.772399	6.278352	0.364239
C	4.896901	-0.277955	-0.221909
C	3.972658	-1.390484	-0.192004
C	2.599880	-1.134716	-0.496978
N	2.126764	0.116061	-0.806403
C	3.027064	1.156500	-0.827413
H	2.597246	2.134165	-1.073179
C	4.368827	1.009765	-0.557144
N	0.269464	-1.730180	0.043099
C	1.542425	-2.209520	-0.561402
O	0.467357	0.872552	-3.460850
H	1.158762	0.552553	-2.841112
C	6.265076	-0.488414	0.072468
C	6.744034	-1.759620	0.391164
C	5.850047	-2.854678	0.417060

C	4.498978	-2.680782	0.130554
C	-5.843751	-1.162140	-0.678504
C	-6.225941	-2.437365	-0.265074
C	-5.235097	-3.407068	0.015773
C	-3.883287	-3.103113	-0.113181
H	1.306986	-2.426047	-1.625580
H	6.945856	0.371852	0.044103
H	7.805897	-1.910180	0.616112
H	6.223592	-3.856479	0.661132
H	3.838580	-3.554315	0.146957
H	-6.599956	-0.399898	-0.905113
H	-7.287332	-2.689967	-0.162009
H	-5.533229	-4.412965	0.334917
H	-3.143763	-3.881554	0.102105
H	1.884313	-3.161478	-0.107280
H	-4.781107	1.243883	-1.491520
H	5.034936	1.879330	-0.599222
C	-0.935998	-2.384923	-0.516857
H	-1.221958	-3.274692	0.079771
H	-0.649726	-2.757220	-1.524622
C	0.308086	-1.729158	1.527443
H	-0.101463	-2.672264	1.949203
H	1.378466	-1.683817	1.811943
H	-0.347893	0.480089	-3.085047

el energy = -1689.75840993

zpe = -1689.256683

th energy = -1689.223733

th enthalpy = -1689.222789

free energy = -1689.321454

Co^I (Triplet)

Co	0.138438	0.490778	-0.513087
N	-1.791690	-0.257979	-0.853495
C	-2.107713	-1.484447	-0.406487
C	-3.449494	-1.989064	-0.413917
C	-4.492886	-1.123970	-0.907975
C	-4.119883	0.171876	-1.364577
C	-2.795848	0.554571	-1.323845
H	-2.469939	1.544709	-1.659860
C	-0.755570	2.170073	1.686651
N	-0.297691	0.918405	1.398661
C	-0.370848	-0.068708	2.318445
C	-0.940799	0.138177	3.577167
H	-0.997959	-0.678696	4.305460
C	-1.425097	1.424840	3.891118
H	-1.879237	1.619843	4.868273
C	-1.325505	2.450495	2.944475
H	-1.703849	3.451006	3.177103
C	-0.231287	4.751678	-1.637949
H	-0.075863	5.358220	-2.536308
C	0.003218	3.375382	-1.677435
H	0.333268	2.871790	-2.593723
N	-0.165403	2.554726	-0.608607
C	-0.598463	3.120738	0.571515
C	-0.851448	4.501393	0.679049
H	-1.180197	4.925221	1.633683
C	-0.667262	5.330446	-0.431206
H	-0.856091	6.406625	-0.358279
C	4.970754	-0.402153	-0.313356
C	4.011118	-1.464891	-0.126644
C	2.620813	-1.130821	-0.209256
N	2.187422	0.117596	-0.465304
C	3.111558	1.119650	-0.633776
H	2.687705	2.111815	-0.822553
C	4.472711	0.907207	-0.566082
N	0.262319	-1.603584	0.428731
C	1.528168	-2.187778	-0.063597
O	0.389179	0.434750	-2.855865
H	1.216206	-0.027072	-3.088262
C	6.361618	-0.689514	-0.243200
C	6.802073	-1.982973	-0.006006
C	5.863791	-3.034335	0.170344

C	4.500402	-2.785636	0.113091
C	-5.837549	-1.585870	-0.932102
C	-6.150766	-2.864202	-0.494502
C	-5.127127	-3.724693	-0.017665
C	-3.806636	-3.300718	0.023402
H	1.332375	-2.629462	-1.060244
H	7.077970	0.128775	-0.382782
H	7.875023	-2.198117	0.045469
H	6.221734	-4.053516	0.353911
H	3.802649	-3.618915	0.244913
H	-6.620216	-0.915340	-1.306475
H	-7.188425	-3.214828	-0.517653
H	-5.383283	-4.734707	0.321175
H	-3.039581	-3.990881	0.389190
H	1.871225	-3.019592	0.585852
H	-4.881746	0.859902	-1.748562
H	5.168967	1.741642	-0.707846
C	-0.941111	-2.364205	0.034063
H	-1.258908	-3.039228	0.854357
H	-0.676183	-3.025344	-0.814902
C	0.320389	-1.354314	1.895530
H	-0.070279	-2.223654	2.465722
H	1.389018	-1.252955	2.166646
H	-0.338259	-0.099805	-3.225577

el energy = -1689.62072482

zpe = -1689.115446

th energy = -1689.082475

th enthalpy = -1689.081531

free energy = -1689.181121

Co^{II} (Doublet)

Co	0.069250	0.297761	-0.488731
N	-1.890724	-0.021923	-0.633528
C	-2.266609	-1.289204	-0.356524
C	-3.633451	-1.697702	-0.305834
C	-4.642570	-0.693873	-0.552110
C	-4.207065	0.629630	-0.835175
C	-2.859312	0.924655	-0.865460
H	-2.49932	1.932666	-1.083166
C	-0.339575	2.173831	1.635400
N	-0.113683	0.866487	1.387849
C	-0.187267	-0.086389	2.323440
C	-0.507402	0.249965	3.647562
H	-0.573857	-0.512446	4.431251
C	-0.735994	1.607548	3.943676
H	-0.986894	1.902126	4.968224
C	-0.654053	2.589567	2.940868
H	-0.843623	3.640466	3.181543
C	0.013904	4.291394	-2.039054
H	0.112146	4.766898	-3.019964
C	0.094050	2.898152	-1.930681
H	0.248872	2.260931	-2.807628
N	-0.018739	2.245689	-0.750468
C	-0.225491	2.982811	0.399516
C	-0.314702	4.382925	0.352327
H	-0.472810	4.949067	1.275846
C	-0.193974	5.047233	-0.875401
H	-0.260208	6.139344	-0.921672
C	4.821132	-0.422058	-0.259417
C	3.860114	-1.498936	-0.182138
C	2.478600	-1.160564	-0.292665
N	2.048194	0.107921	-0.476190
C	2.968675	1.124031	-0.539527
H	2.560326	2.128510	-0.674718
C	4.327061	0.898854	-0.439943
N	0.117800	-1.543244	0.260706
C	1.365712	-2.184801	-0.276358
O	0.177577	-0.531914	-2.721449
H	0.965397	-0.400237	-3.282555
C	6.209220	-0.712203	-0.154094
C	6.638220	-2.019870	0.015428
C	5.696748	-3.083070	0.085396

C	4.336142	-2.834354	-0.010015
C	-6.017039	-1.055945	-0.514272
C	-6.386692	-2.366254	-0.250679
C	-5.396993	-3.359399	-0.015564
C	-4.048311	-3.038033	-0.040754
H	1.149821	-2.497939	-1.313431
H	6.931058	0.110500	-0.211264
H	7.708256	-2.240041	0.095082
H	6.052675	-4.110861	0.214779
H	3.636327	-3.675212	0.035383
H	-6.775590	-0.287118	-0.700607
H	-7.446290	-2.642647	-0.224595
H	-5.705318	-4.390823	0.186633
H	-3.310113	-3.827659	0.133877
H	1.617372	-3.090333	0.305609
H	-4.940522	1.418400	-1.036078
H	5.023772	1.742029	-0.503323
C	-1.116513	-2.258017	-0.206016
H	-1.352009	-3.098888	0.471025
H	-0.891358	-2.691371	-1.198008
C	0.184710	-1.459605	1.786105
H	-0.438334	-2.258340	2.227711
H	1.230240	-1.670326	2.078357
H	-0.597974	-0.447388	-3.307810

el energy = -1689.35525591

zpe = -1688.846242

th energy = -1688.814215

th enthalpy = -1688.813271

free energy = -1688.909327

Co^{III} (Singlet)

Co	0.000441	0.261390	-0.465648
N	-1.955307	0.053409	-0.451795
C	-2.368100	-1.231167	-0.315030
C	-3.744671	-1.588476	-0.262984
C	-4.720211	-0.518242	-0.331590
C	-4.239026	0.813170	-0.454465
C	-2.882019	1.067394	-0.509866
H	-2.493202	2.082040	-0.610188
C	-0.002306	2.148928	1.553304
N	-0.000860	0.810154	1.295428
C	-0.001426	-0.127492	2.261827
C	-0.003786	0.261102	3.610213
H	-0.004330	-0.493559	4.404394
C	-0.005297	1.631650	3.914662
H	-0.007121	1.958231	4.960483
C	-0.004470	2.588018	2.885170
H	-0.005605	3.656877	3.120904
C	0.000486	4.206961	-2.150881
H	0.001279	4.660245	-3.147667
C	0.000979	2.811255	-2.026061
H	0.002133	2.166366	-2.909579
N	0.000041	2.194307	-0.823588
C	-0.001442	2.955178	0.324134
C	-0.001986	4.356850	0.263901
H	-0.003144	4.948413	1.185278
C	-0.001010	4.991547	-0.987507
H	-0.001423	6.085350	-1.051493
C	4.721285	-0.516548	-0.329277
C	3.746080	-1.587205	-0.262288
C	2.369430	-1.230333	-0.314740
N	1.956265	0.054277	-0.450369
C	2.882631	1.068642	-0.506830
H	2.493493	2.083267	-0.606193
C	4.239700	0.814825	-0.450964
N	0.000832	-1.589696	0.221613
C	1.249334	-2.243691	-0.303493
O	0.001198	-0.397219	-2.391971
H	0.795564	-0.226551	-2.936980
C	6.106518	-0.826148	-0.275983
C	6.519128	-2.147490	-0.168437
C	5.564887	-3.201965	-0.110553

C	4.204412	-2.935521	-0.155389
C	-6.105359	-0.828281	-0.278738
C	-6.517555	-2.149661	-0.170107
C	-5.562975	-3.203737	-0.110659
C	-4.202570	-2.936848	-0.155004
H	1.041564	-2.588746	-1.332481
H	6.840509	-0.013934	-0.325265
H	7.587783	-2.385953	-0.130426
H	5.912267	-4.237967	-0.032209
H	3.498010	-3.771654	-0.122750
H	-6.839614	-0.016379	-0.329243
H	-7.586147	-2.388463	-0.132445
H	-5.910032	-4.239783	-0.031482
H	-3.495877	-3.772688	-0.121124
H	1.485277	-3.139219	0.2984930
H	-4.943547	1.650412	-0.513790
H	4.943951	1.652386	-0.509002
C	-1.247795	-2.244258	-0.302460
H	-1.483676	-3.139034	0.300648
H	-1.040192	-2.590651	-1.331039
C	0.001885	-1.544462	1.747580
H	-0.883058	-2.08950	2.123439
H	0.891163	-2.083776	2.121557
H	-0.792828	-0.226628	-2.937489

el energy = -1688.95502196

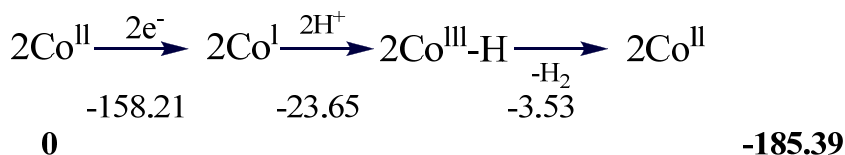
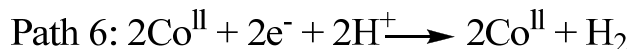
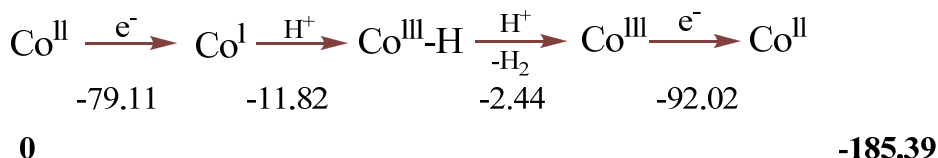
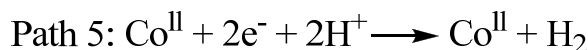
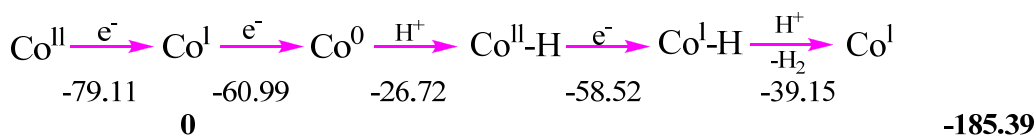
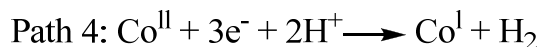
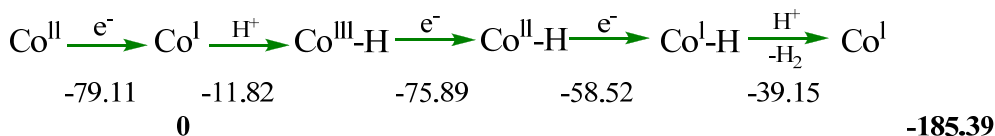
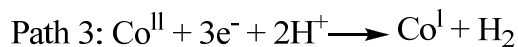
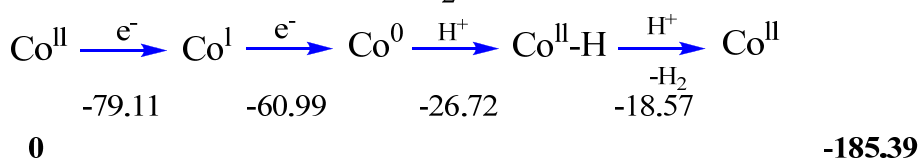
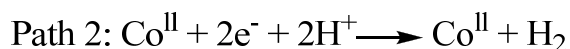
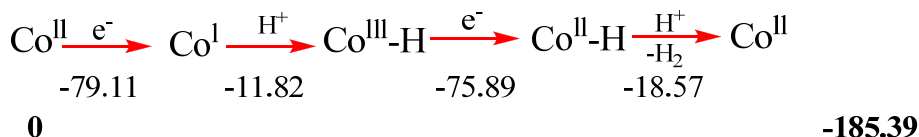
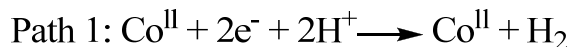
zpe = -1688.442630

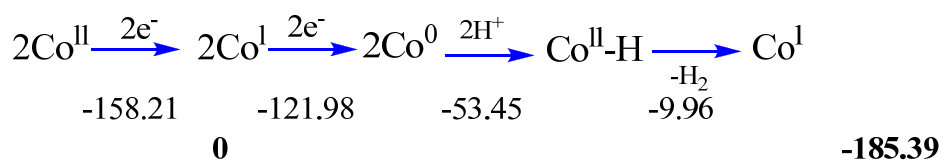
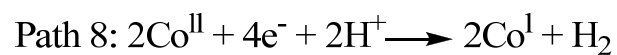
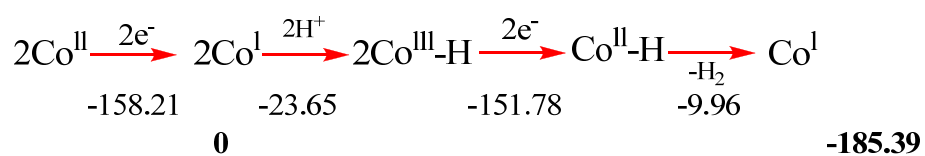
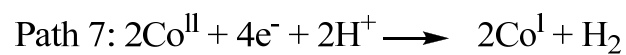
th energy = -1688.412060

th enthalpy = -1688.411116

free energy = -1688.502327

Scheme S1. Postulated intermediates (with computed relative free energies) for H₂ evolution by **2b** in water. Units for mononuclear and dinuclear reactions are kcal mole of cobalt and kcal/2 moles of cobalt, respectively. Values below reaction arrows are free energy changes of each step and the relative free energies of catalytic H₂ production are in bold font.





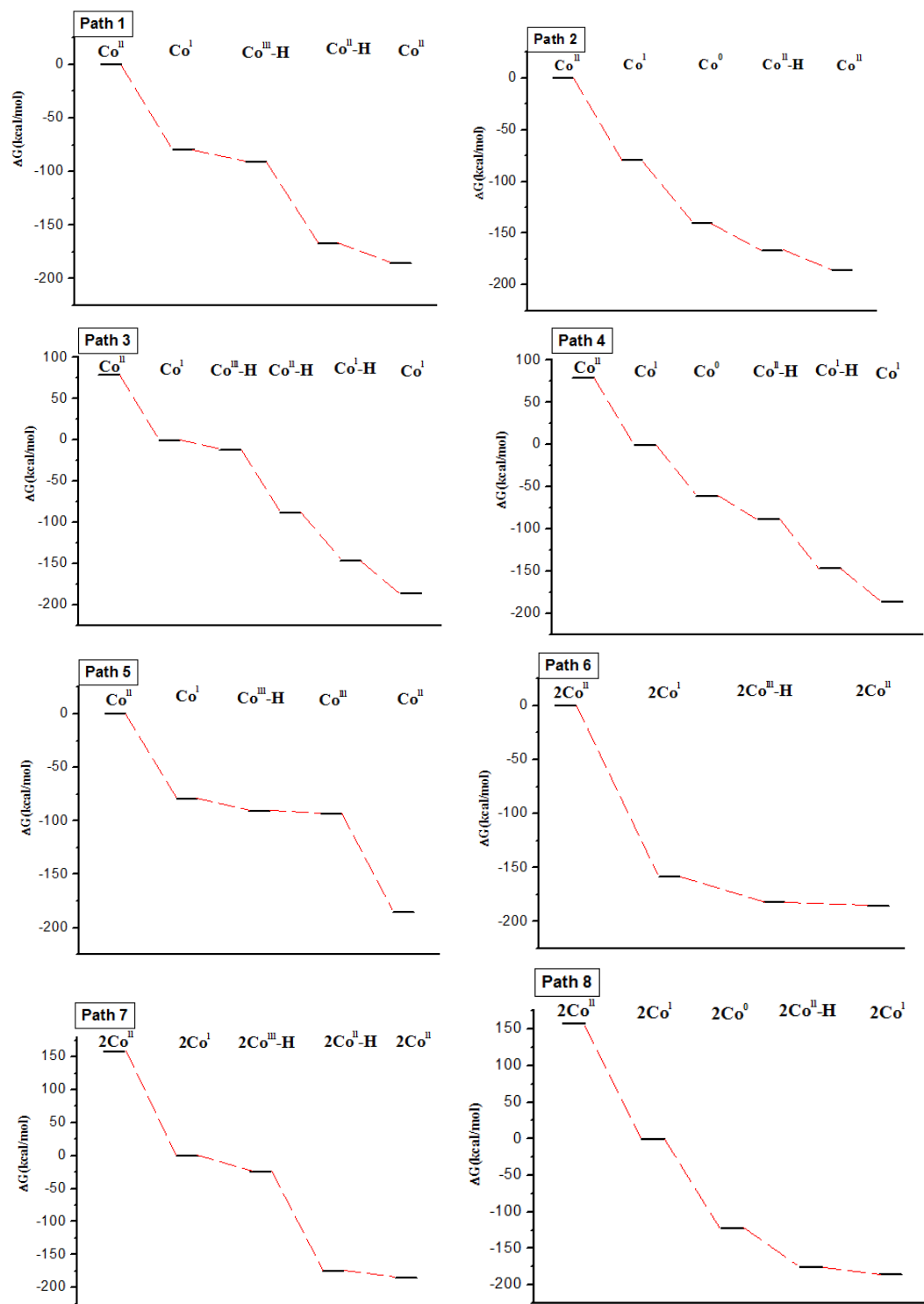


Figure S17. Relative reaction free energy changes diagrams of postulated catalytic cycles of H_2 evolution by **2b** in water.