Supporting Information

for

Mechanistic Insights into Homogeneous Electrocatalytic and Photocatalytic Hydrogen Evolution Catalyzed by High-Spin Ni(II) Complexes with S_2N_2-Type Tetradentate Ligands

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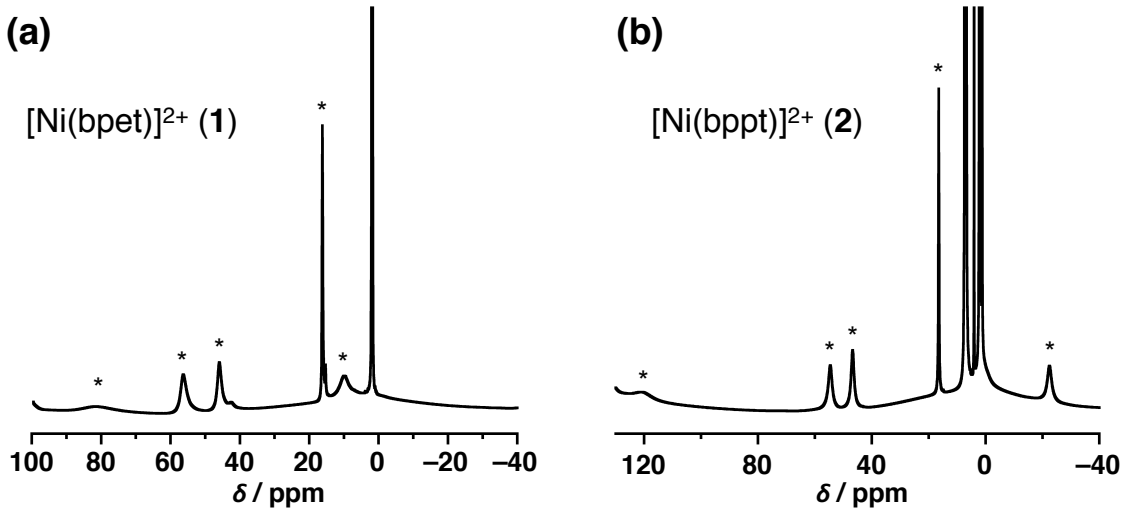

Figure S1. ^{1}H NMR spectra of (a) **1** and (b) **2** in CD_3CN.

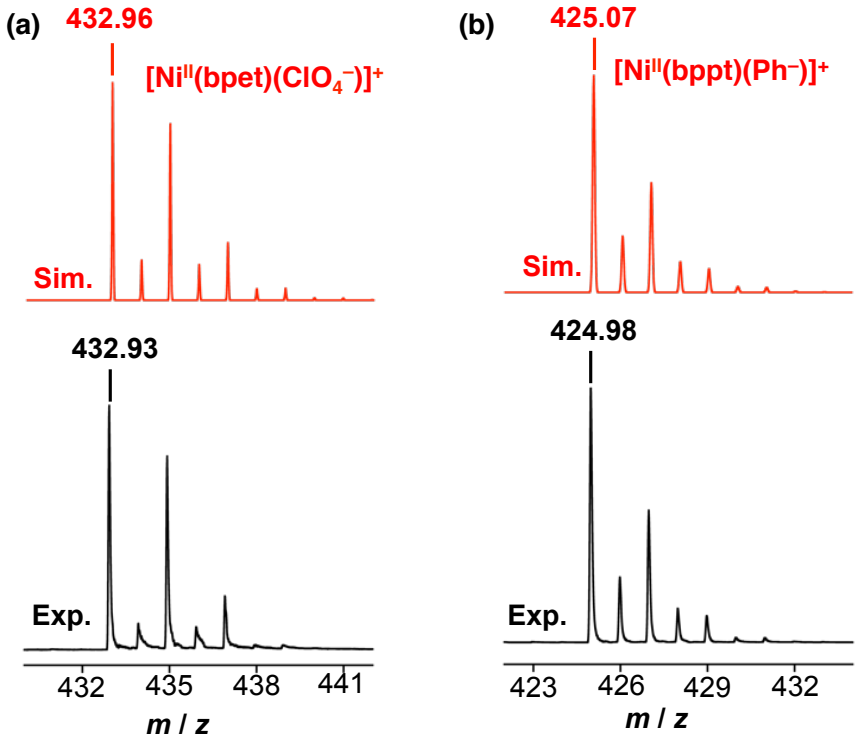

Figure S2. ESI-MS spectra of (a) **1** and (b) **2**. Black traces are experimentally observed spectra and red traces are computer-simulated ones.

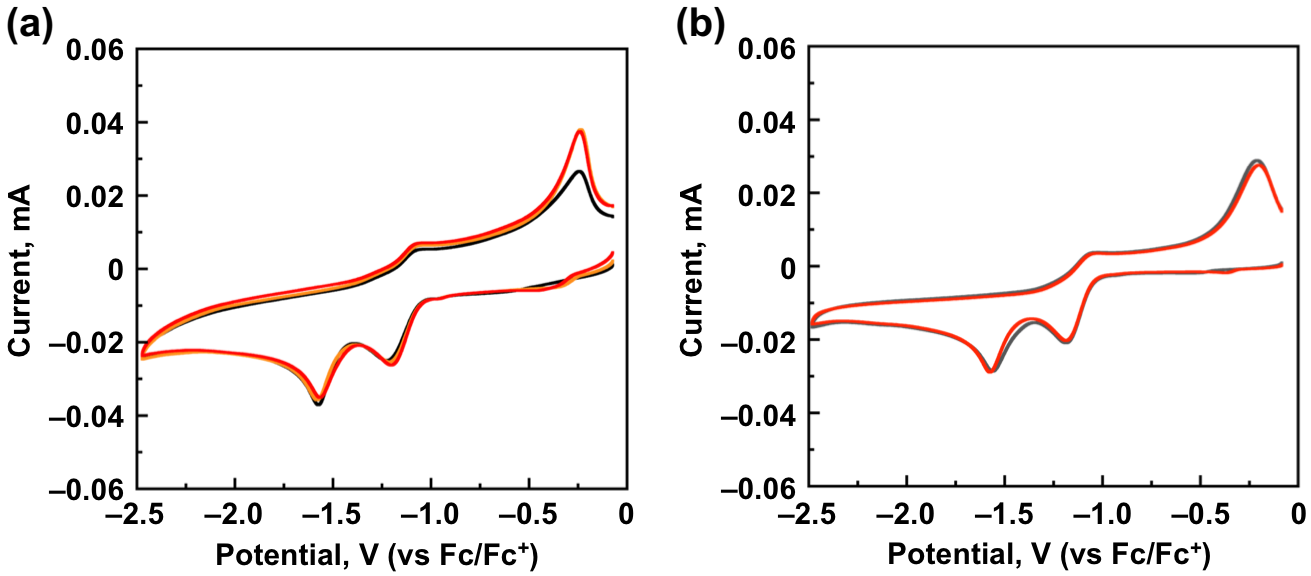

Figure S3. Repeated CV traces of an MeCN solution (2.0 mL) containing (a) **1** (1.0 mM), (b) **2** (1.0 mM), and, in both cases, 0.10 M $TBAPF_6$ as an electrolyte. Conditions: A glassy carbon (A = 0.071 cm^2) as a working electrode; a Pt wire as a counter electrode; an $Ag/AgNO_3$ reference electrode; scan rate, 0.10 V s^{-1}. The working electrode was polished after each scan.

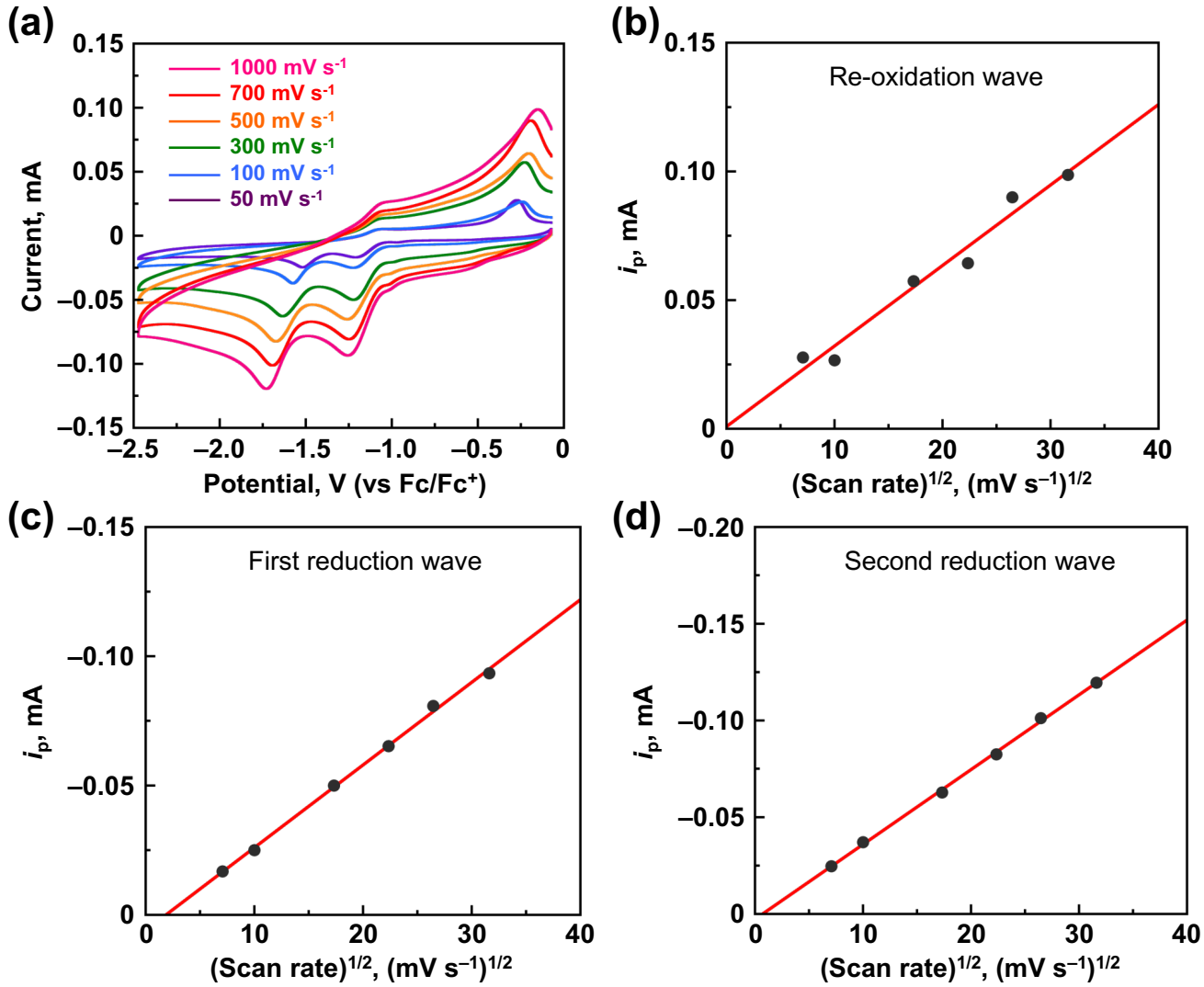

Figure S4. (a) CVs of an MeCN solution (2.0 mL) containing **1** (1.0 mM) and 0.10 M $TBAPF_6$ by using a glassy carbon (A = 0.071 cm^2) as a working electrode, a Pt wire as a counter electrode and an $Ag/AgNO_3$ reference electrode at various scan rates (50 ~ 1000 mV s^{-1}). Plots of the peak currents against (scan rate)$^{1/2}$ for (b) re-oxidation peak, (c) first reduction peak, and (d) second reduction peak.

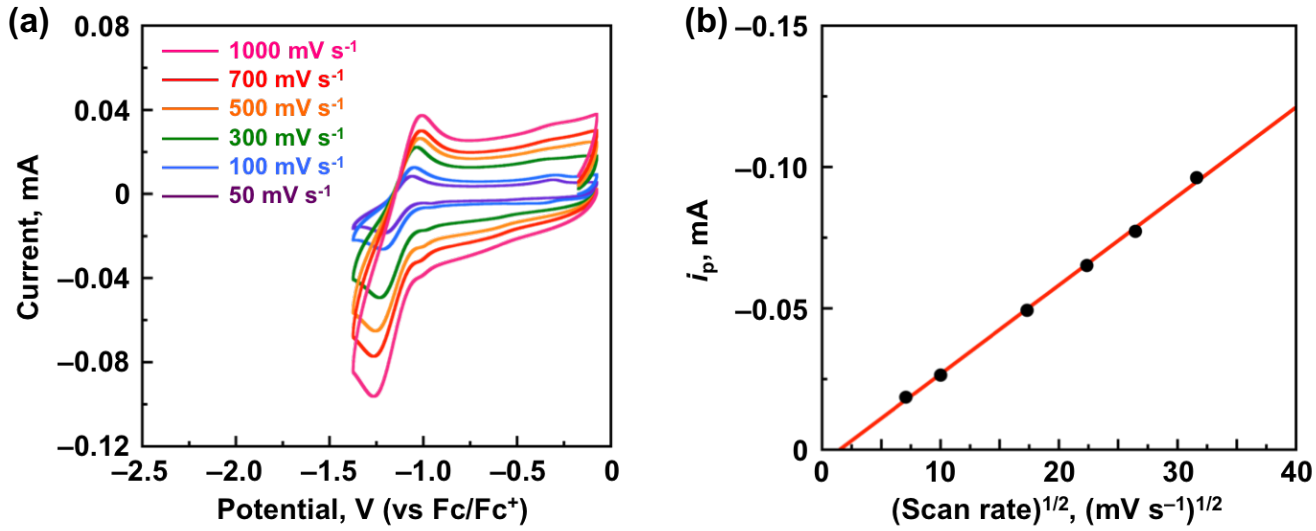

Figure S5. (a) CVs of an MeCN solution (2.0 mL) containing **1** (1.0 mM) and 0.10 M $TBAPF_6$ by using a glassy carbon (A = 0.071 cm^2) as a working electrode, a Pt wire as a counter electrode and an $Ag/AgNO_3$ reference electrode at various scan rates (50 ~ 1000 mV s^{-1}). (b) Plots of the peak currents against (scan rate)$^{1/2}$ for the reduction peak.

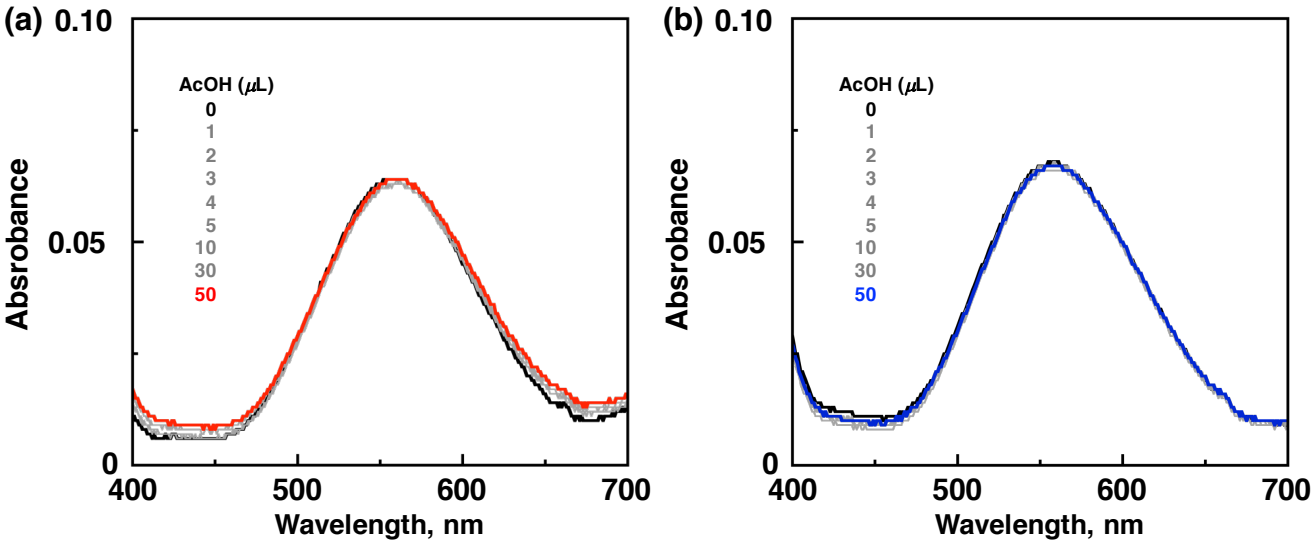

Figure S6. (a) UV-vis spectra of (a) **1** and (b) **2** (5.0 mM) in MeCN (3.0 mL) with the addition of AcOH (0~50 μL (291 mM)).

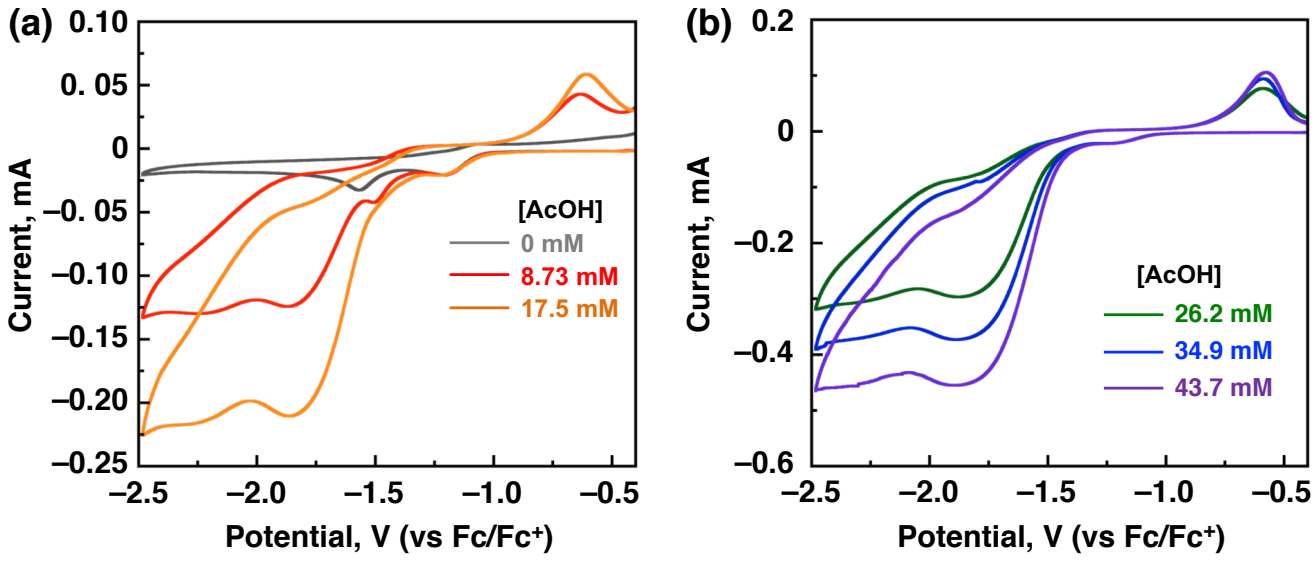

Figure S7. CVs of **1** (1.0 mM) in MeCN solutions (2.0 mL) containing 0.10 M $TBAPF_6$ as an electrolyte in the presence of (a) 0 ~ 17.5 mM and (b) 26.2 ~ 43.7 mM of AcOH by using a glassy carbon (A = 0.071 cm^2) as a working electrode, a Pt wire as a counter electrode and an $Ag/AgNO_3$ reference electrode at the scan rate of 0.10 V s^{-1}.

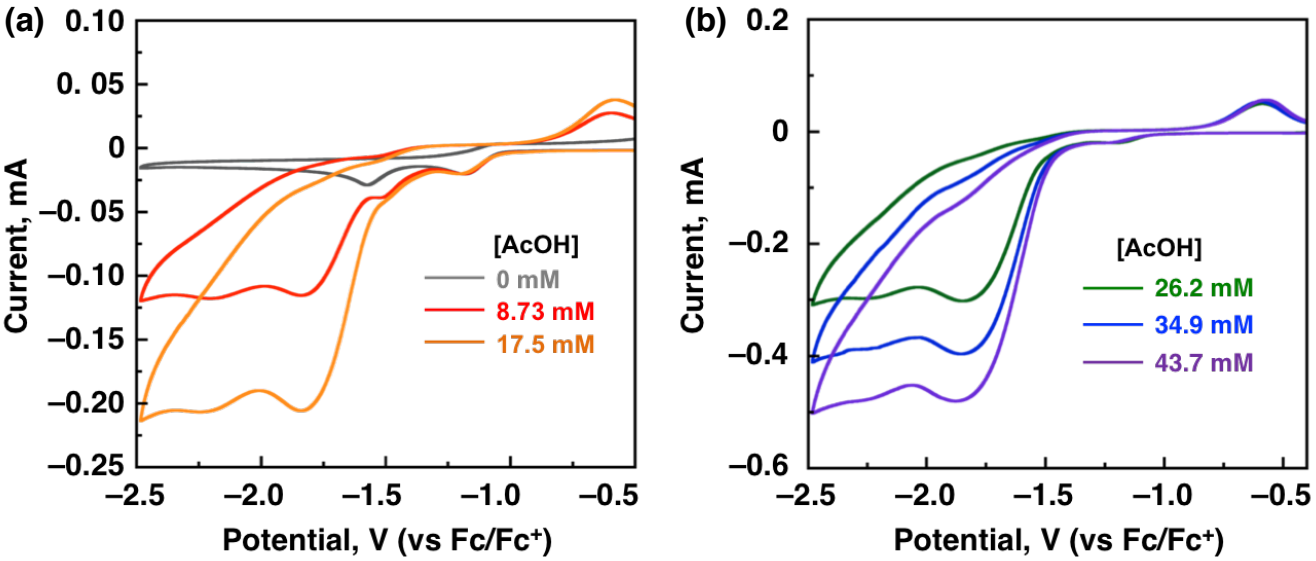

Figure S8. CVs of **2** (1.0 mM) in MeCN solutions (2.0 mL) containing 0.10 M $TBAPF_6$ as an electrolyte in the presence of (a) 0 ~ 17.5 mM and (b) 26.2 ~ 43.7 mM of AcOH by using a glassy carbon (A = 0.071 cm^2) as a working electrode, a Pt wire as a counter electrode and an $Ag/AgNO_3$ reference electrode at the scan rate of 0.10 V s^{-1}.

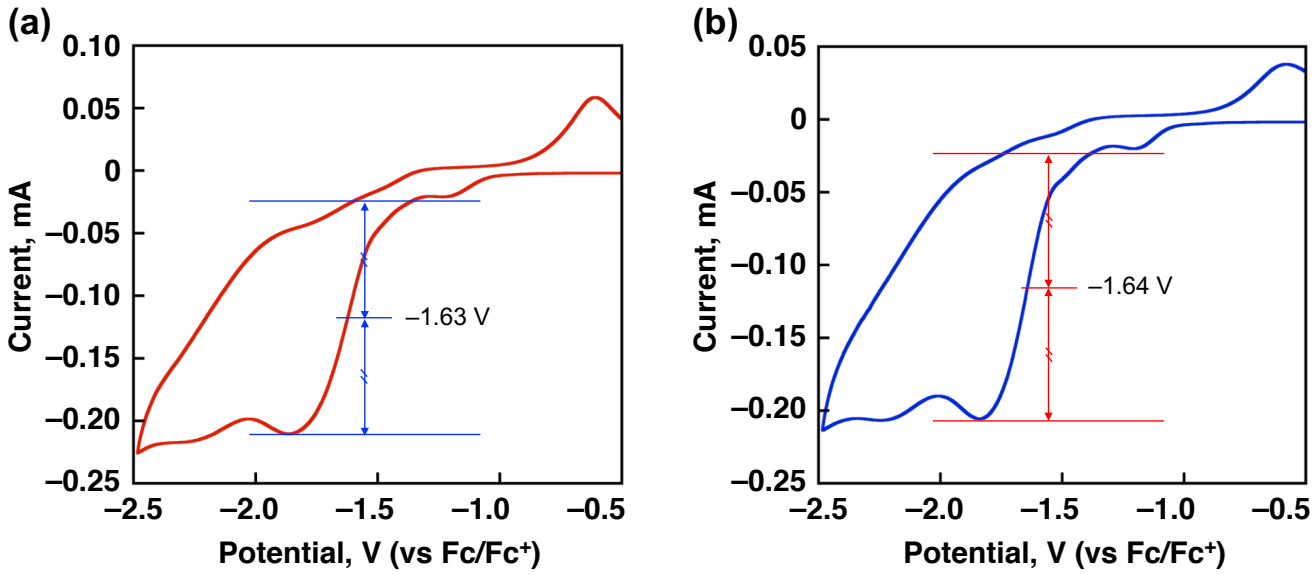

Figure S9. The half-wave potential of **1** and **2** based on the CVs in a MeCN solution containing AcOH (17.5mM). The overpotential (η) is calculated by subtracting theoretical half-wave potential of H_2 in MeCN/AcOH ($E^o_{1/2}$) and systematical error from the observed half-wave potential ($E_{1/2}$): $\eta = |E_{1/2}| - |E^o_{1/2}| + 15$ mV. The value "15mV" is a systematical error to the theoretical potential. $E^o_{1/2}$ is based on the following equation that the homoconjugation of AcOH is not considered.:

$$E^o_{1/2} = -\frac{2.303 \times RT}{F} pK_a + \varepsilon_D - \frac{RT}{2F} \ln \frac{C_0}{C^o{}_{H_2}}$$

where C_0 is the total concentration of acid, $C^o{}_{H_2}$ is hydrogen solubility in MeCN (3.3 mM), ε_D is parameter that depends on diffusion coefficient of H_2 and products (40 ± 5 mV). Please refer the literature (Fourmond et al., *Inorg. Chem.* **2010**, *49*, 10338–10347) for a more detailed calculation and simulation. Base on the equation, $E^o_{1/2}$ is obtained to be –1.23 V in 100 mM acetic acid and the overpotentials (η) for **1** and **2** were calculated to be 0.55 and 0.56 V, respectively.

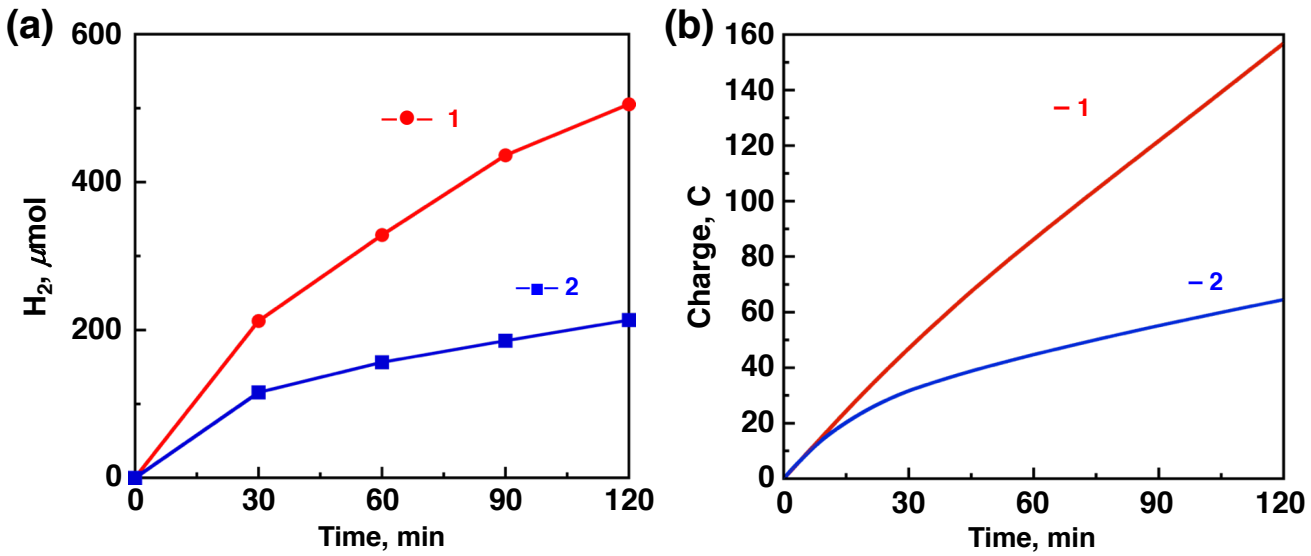

Figure S10. (a) Time courses of H_2 evolution in homogeneous bulk electrolysis of an MeCN/AcOH (40:1 v/v, 15 mL) solution containing **1** or **2** (1.0 mM) at –2.1 V (*vs*. Fc/Fc^+, –1.7 V *vs*. SCE) by using $TPAPF_6$ (0.10 M) as an electrolyte, a pristine CP (A = 2.0 cm^2) as a working electrode, a Pt wire as counter electrode and an $Ag/AgNO_3$ reference electrode. (b) Time courses of the accumulated charge for the bulk electrolysis.

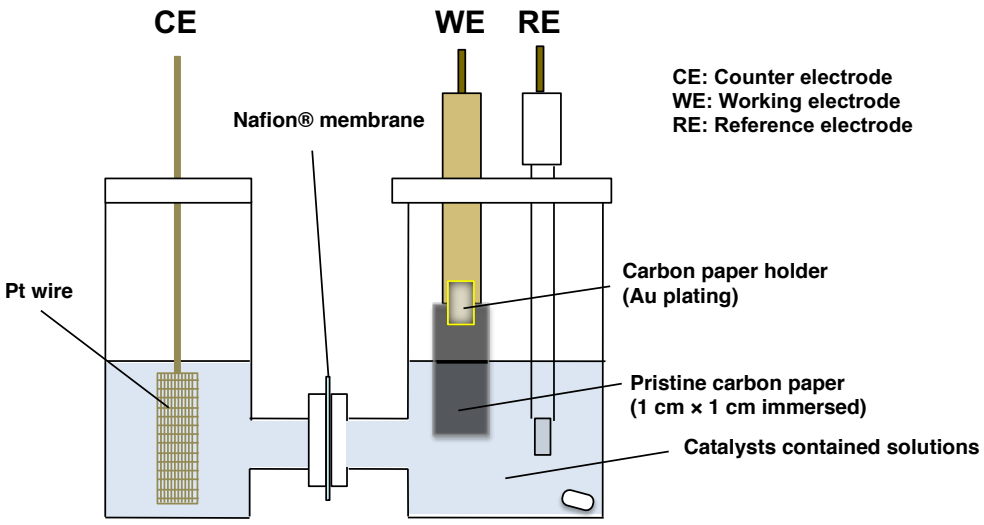

Figure S11. A schematic drawing of the setup for bulk electrolysis.

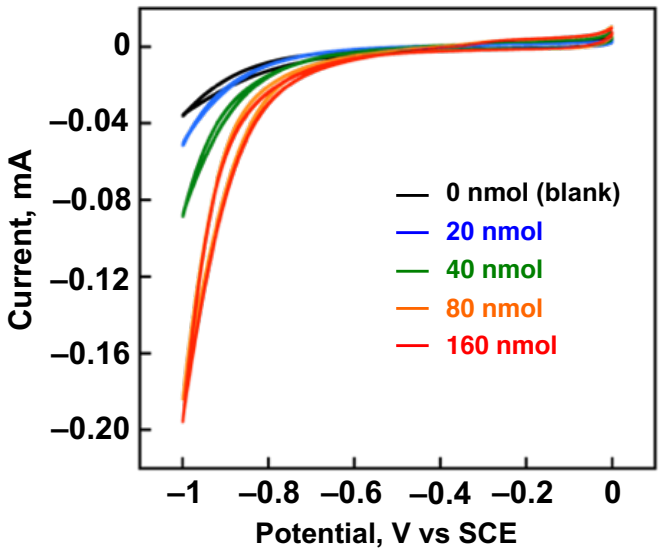

Figure S12. CV traces of **1**-loaded CP electrodes (A = 2.0 cm^2) with various amounts of **1** (0–160 nmol) as working electrodes in an ascorbate buffer solution (pH 4). The scan rate is 0.10 V s^{-1}.

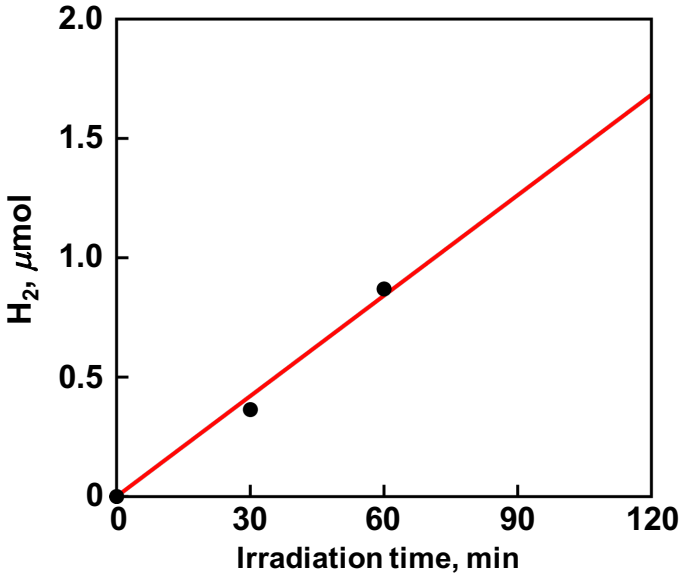

Figure S13. Time course of H_2 evolution under photoirradiation (λ = 450 nm) of a DMA/ascorbate buffer solution (pH 4) (4.0 mL, 1:1 v/v) containing **1** (0.10 mM) and $[Ru(bpy)_3]Cl_2$ (0.25 mM).

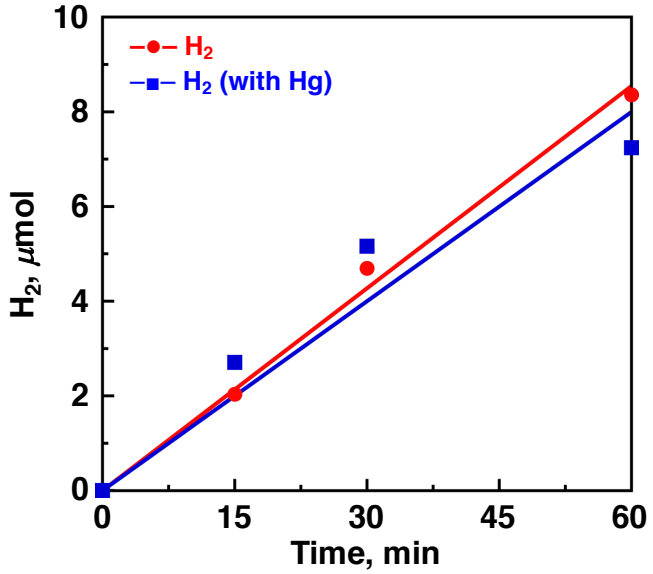

Figure S14. Time course of H_2 evolution under photoirradiation ($\lambda = 450$ nm) of a DMA/ascorbate buffer solution (pH 4) (4.0 mL, 1:1 v/v) containing **1** (0.10 mM) and $[Ru(bpy)_3]Cl_2$ (0.25 mM) in the presence of a drop of Hg (blue line) and in the absence of Hg (red line).

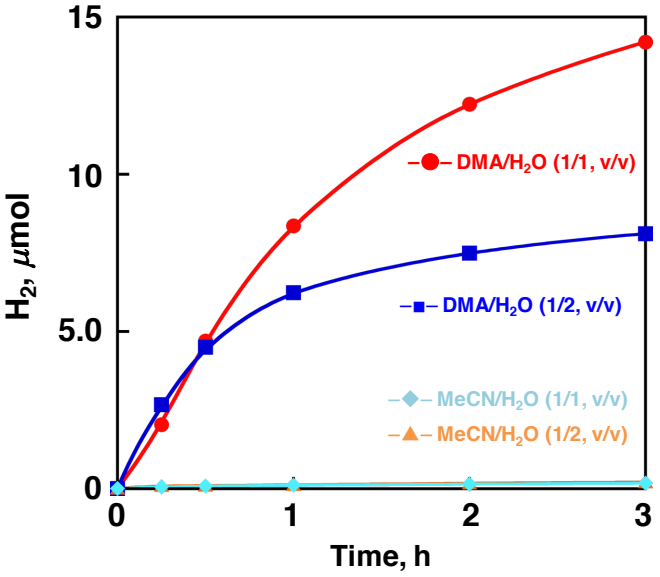

Figure S15. Time courses of H_2 evolution under photoirradiation ($\lambda = 450$ nm) of a DMA/ascorbate buffer (pH 4) or a MeCN/ ascorbate buffer (pH 4) in the ratio of 1:1 and 1:2 (v/v) containing **1** (0.10 mM), $[Ru(bpy)_3]^{2+}$ (0.25 mM), and NaAsc (0.10 M).

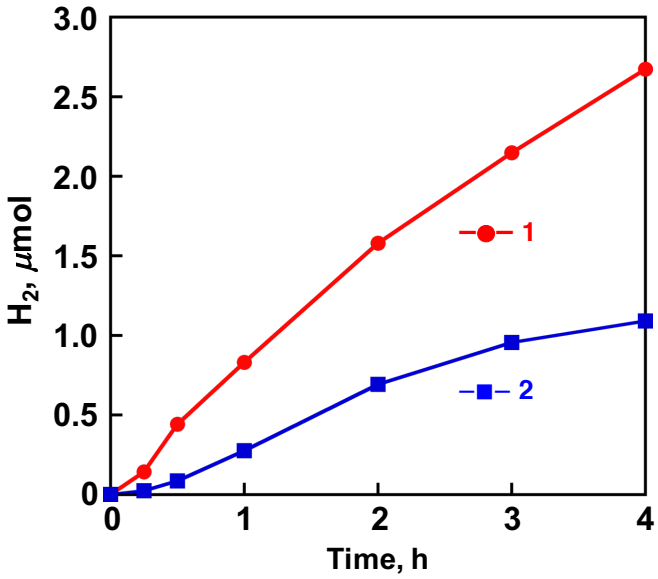

Figure S16. Time courses of H_2 evolution under photoirradiation (λ = 450 nm) of a DMA/H_2O (1:2 v/v) solution containing **1** or **2** (0.10 mM), $[Ru(bpy)_3]^{2+}$ (0.25 mM), and NaAsc (0.10 M).

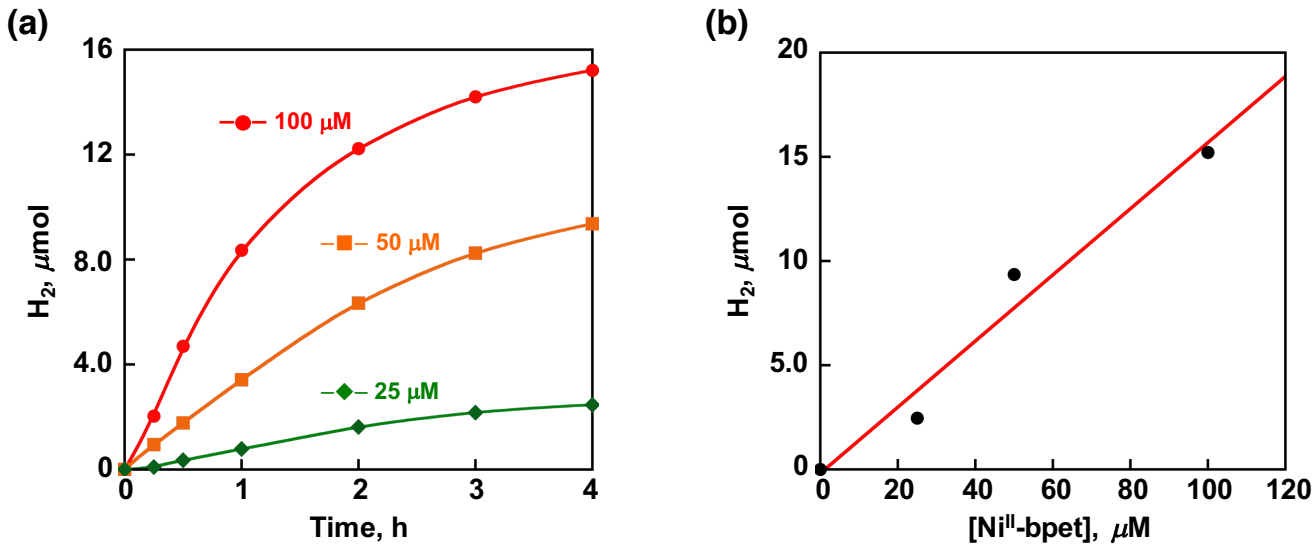

Figure S17. (a) Time courses of H_2 evolution under photoirradiation (λ = 450 nm) in DMA/ascorbate buffer (pH 4) (4.0mL, 1:1 v/v) containing various concentrations of **1** {25 (green diamonds), 50 (yellow squares) and 100 μM (red cycles)}, $[Ru(bpy)_3]^{2+}$ (0.25 mM), and NaAsc (0.10 M). (b) Dependence of the amount of H_2 evolved on the concentration of **1** under the conditions described in (a).

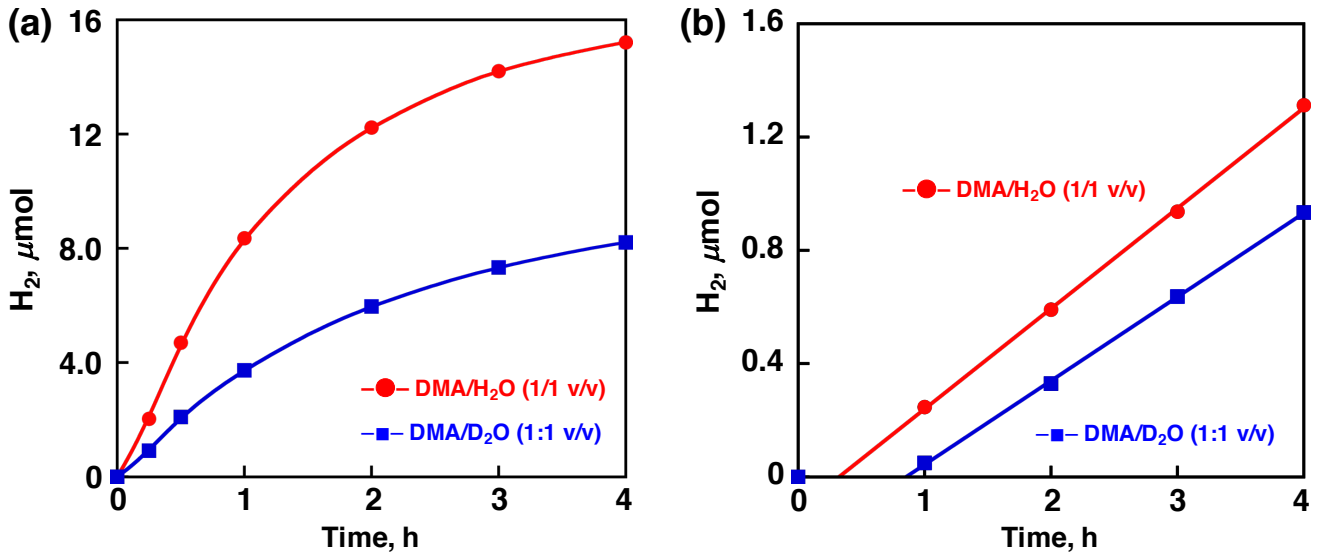

Figure S18. Time courses of H_2 evolution under photoirradiation (λ = 450 nm) in a DMA/ascorbate buffer (H_2O) solution (red cycle) or a DMA/ascorbate buffer (D_2O) solution (blue square) containing (a) **1** (0.10 mM) and (b) **2** (0.10 mM), $[Ru(bpy)_3]^{2+}$ (0.25 mM), and NaAsc (0.10 M).

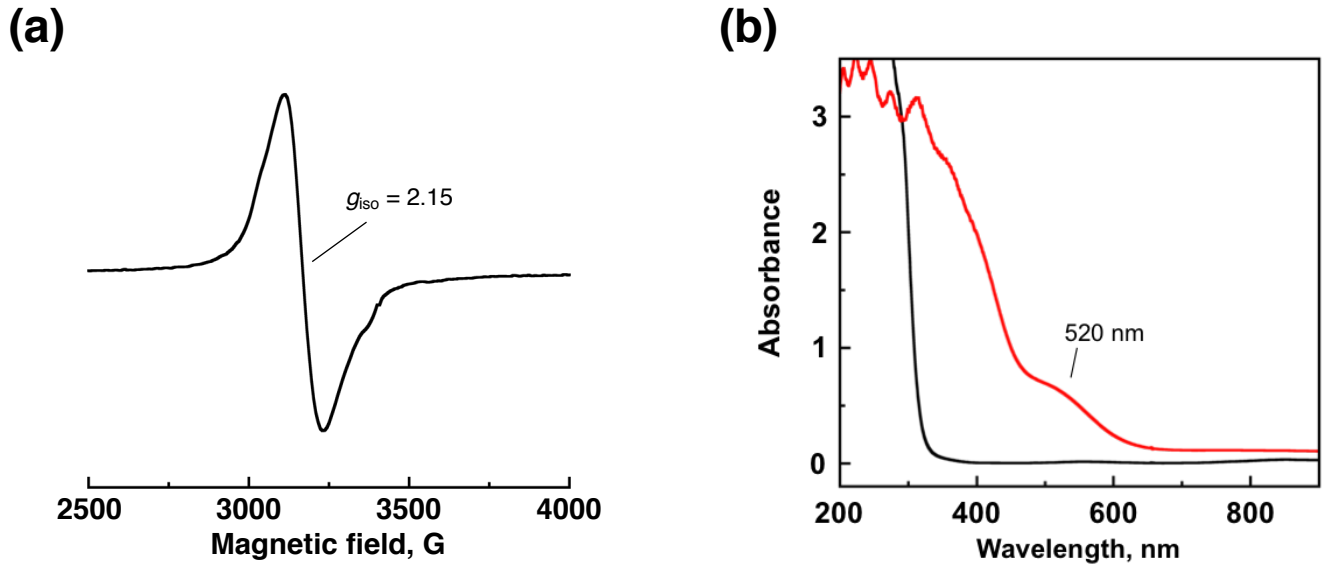

Figure S19. (a) An ESR spectrum of Ni(I) species generated by the reaction of **1** (1.0 mM) with $Co^{II}(Cp)_2$ (1.0 mM) in MeCN at 150K. (b) UV-vis spectra of **1** (1.0 mM, black line) in MeCN and after the addition of one equivalent of $Co^{II}(Cp)_2$ (red line) under Ar at 298K.

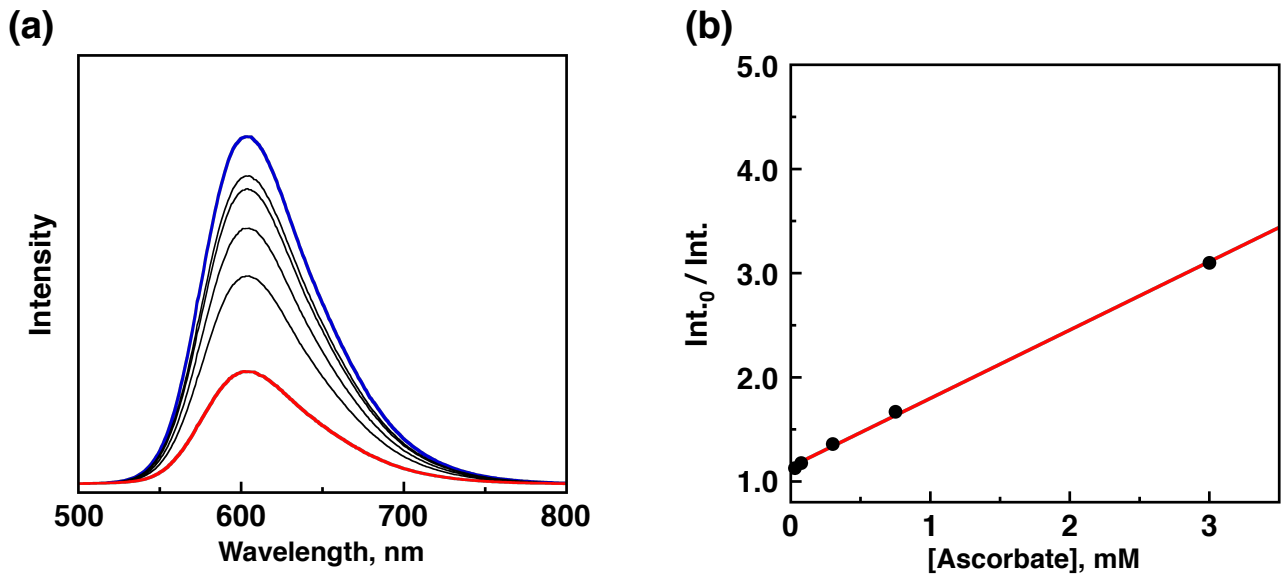

Figure S20. (a) Emission spectra of $^{3}\{[Ru(bpy)_3]^{2+}\}^*$ (15 μM) excited by monochromatic light at 450 nm in DMA/H_2O (1:1 v/v) in the presence of various concentrations of NaAsc at 298 K. (b) A Stern-Volmer plot of the emission quenching monitored at 603 nm. Lifetime of $^{3}\{[Ru(bpy)_3]^{2+}\}^*$ was determined to be 0.80 μs in DMA/H_2O at 298 K.

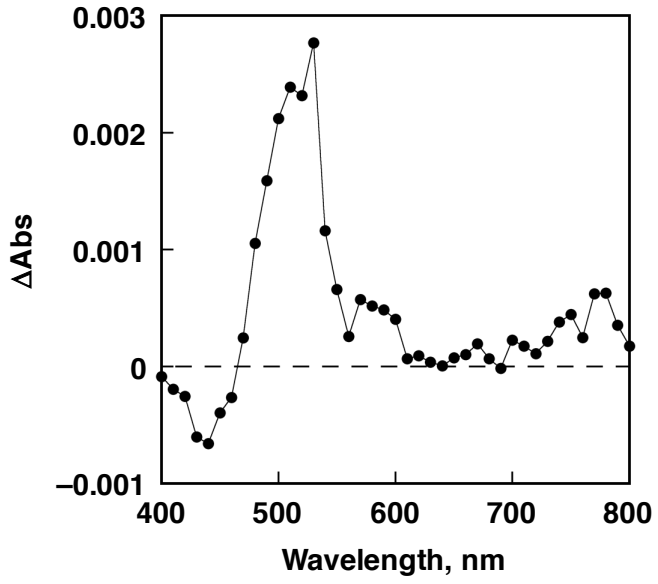

Figure S21. Transient absorption spectrum of $[Ru^{II}(bpy)_3]^{2+}$ (0.10 mM) at 3 μs after laser excitation (λ = 450 nm) in a deaerated DMA/ascorbate buffer (pH4, 1:1 v/v).

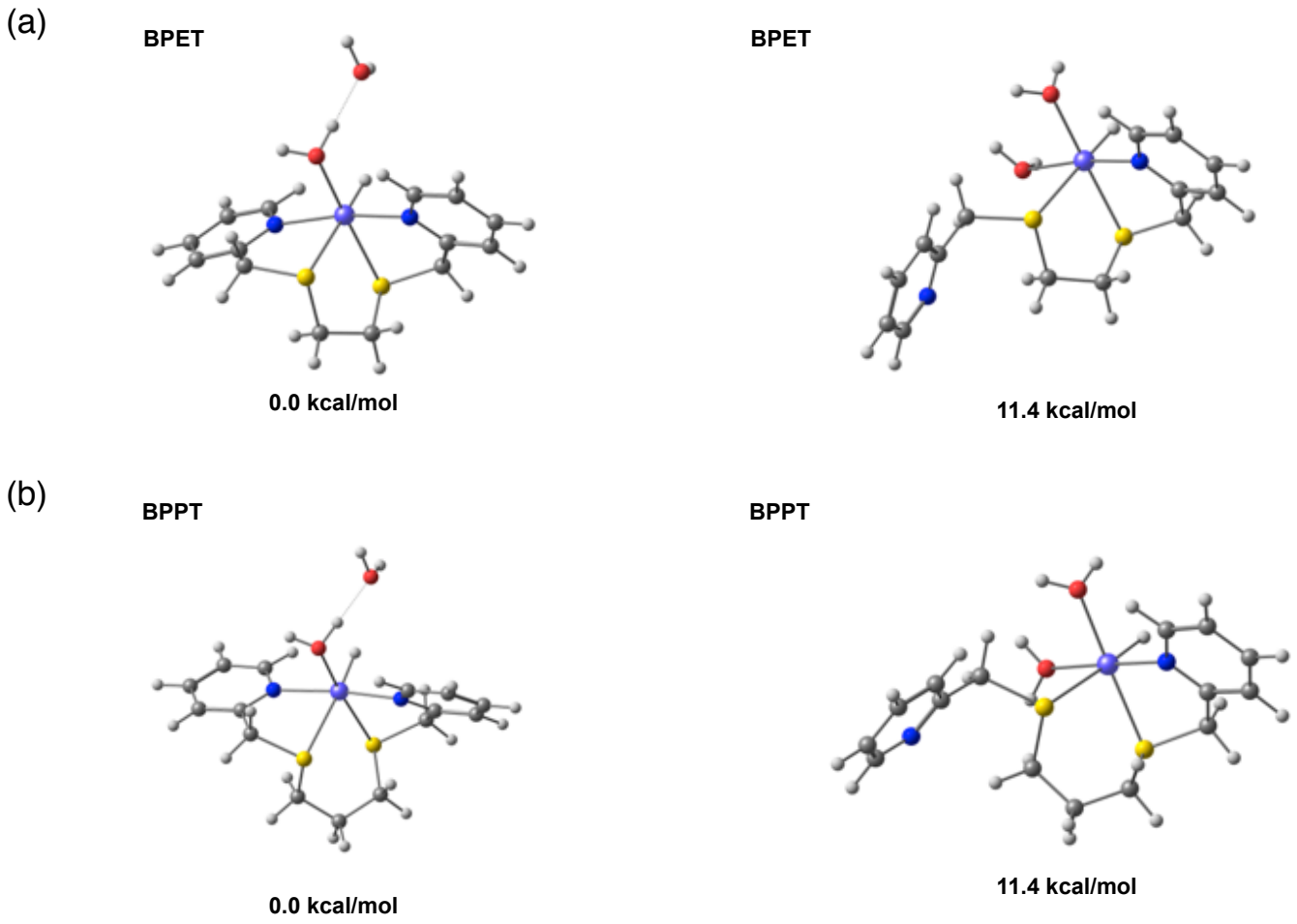

Figure S22. DFT-optimized structures of Ni(II)-hydrido complexes having bpet (a) and bppt (b) as ligands at the UB3LYP/6-311+G** level of theory. In both cases, η^4-structures with one remote water molecule are shown in the left-hand sides and η^3-structures with one aqua ligand are shown in the right-hand sides. The energy levels of the η^3-species are relative to those of the η^4-species as 0.0 kcal mol^{-1}.

Table S1. Cartesian Coordinates of $[Ni(H)(bppt)(H_2O)]^+$

atom	coordinates (Angstroms)		
	X	Y	Z
N	-2.133111	-0.571873	-0.238175
C	-2.856461	0.472826	-0.680622
C	-4.237605	0.536653	-0.497034
C	-4.888518	-0.512025	0.143817
C	-4.137380	-1.594191	0.592565
C	-2.764399	-1.580187	0.385492
C	-2.140178	1.572380	-1.428433
S	-0.412055	1.843970	-0.890589
Ni	-0.001437	-0.563854	-0.534439
N	2.153709	-0.406900	-0.482541
C	2.854186	-0.253493	0.655349
C	4.232414	-0.032923	0.641606
C	4.904015	0.010771	-0.574497
C	4.177387	-0.162046	-1.749246
C	2.807699	-0.363383	-1.656139
C	2.133700	-0.376337	1.980195
S	0.364803	0.082798	1.945468
C	0.465762	1.918801	1.746522
C	-0.639454	2.446769	0.840827
H	2.640631	0.204510	2.750462
H	2.138636	-1.418444	2.311888
H	0.371374	2.366852	2.736056
H	1.452448	2.164639	1.352039
H	-0.611510	3.536776	0.827880
H	-1.623678	2.131986	1.189215
H	-2.691161	2.510344	-1.369323
H	-2.045764	1.306176	-2.484677
H	4.764821	0.098859	1.575399
H	5.973730	0.180191	-0.603600
H	2.190321	-0.493216	-2.536275

Table S2. Cartesian Coordinates of TS(bppt)

atom	coordinates (Angstroms)		
	X	Y	Z
C	4.545280	0.532833	-0.185048
C	3.226772	0.134769	-0.411419
N	2.195542	0.980624	-0.237799
C	2.451771	2.242865	0.146761
C	3.735729	2.715158	0.378458
C	4.804789	1.839258	0.212254
C	2.947752	-1.264567	-0.914361
S	1.302655	-1.929468	-0.475258
Ni	0.126552	0.376451	-0.404502
O	0.154281	0.614447	-2.626943
C	1.492644	-2.200801	1.344062
C	0.205735	-1.886016	2.096009
S	-0.182493	-0.082188	2.002118
C	-2.007892	-0.094802	1.870582
C	-2.532869	-0.713953	0.597205
C	-3.767684	-1.362393	0.590587
C	-4.262040	-1.873349	-0.604735
C	-3.503043	-1.728036	-1.762014
C	-2.276225	-1.083263	-1.674086
N	-1.797334	-0.585573	-0.522200
O	-5.743121	4.535921	0.245488
H	3.717916	-1.957469	-0.576111
H	2.964683	-1.278112	-2.007754
H	1.760404	-3.246188	1.499676
H	2.316915	-1.578742	1.694759
H	0.321345	-2.154966	3.146399
H	-0.639738	-2.441821	1.689206
H	-2.431795	-0.581524	2.748158
H	-2.279098	0.963503	1.910847
H	5.352076	-0.176230	-0.323058
H	5.822360	2.165126	0.391809
H	1.582034	2.876207	0.269881
H	3.886173	3.741102	0.688575
H	-4.328562	-1.461883	1.511536
H	-5.219176	-2.380388	-0.629077
H	-1.644330	-0.950046	-2.542670
H	-3.843445	-2.112727	-2.714692
H	-0.472941	1.867173	-0.288382
H	-0.083236	1.543543	-2.743502
H	0.956645	0.484659	-3.148254
H	-5.122563	3.819245	0.486259
H	-5.975931	4.489990	-0.703367
H	-6.546833	4.500909	0.802162

Table S3. Cartesian Coordinates of Product Complex (bppt)

atom	coordinates (Angstroms)		
	X	Y	Z
C	4.184555	0.097720	0.335848
C	2.809879	0.052681	0.560044
N	1.971952	-0.494904	-0.340936
C	2.475548	-1.027345	-1.470064
C	3.832745	-1.033274	-1.750183
C	4.702596	-0.453488	-0.830413
C	2.235914	0.566448	1.860009
S	0.484792	1.098790	1.758974
Ni	-0.096820	-0.381332	-0.059339
O	-0.101759	-2.230761	0.925258
C	0.628169	2.685581	0.812026
N	-2.172015	-0.251017	0.090195
C	-2.865043	0.528041	-0.764510
C	-4.241634	0.698890	-0.637281
C	-4.919314	0.042497	0.384005
C	-4.199307	-0.760435	1.263221
C	-2.829462	-0.875978	1.085148
C	-2.122233	1.194730	-1.896990
S	-0.366144	1.553266	-1.523607
C	-0.498099	2.837918	-0.199737
O	-1.469616	-4.148397	-0.362035
H	2.828733	1.388339	2.259645
H	2.235668	-0.228711	2.610368
H	0.581253	3.496184	1.538916
H	1.606308	2.706789	0.331465
H	-2.617271	2.114384	-2.205689
H	-2.080312	0.533359	-2.766507
H	-0.427460	3.813733	-0.680102
H	-1.477105	2.751603	0.271347
H	4.834196	0.555637	1.070624
H	5.768810	-0.427268	-1.019206
H	1.756665	-1.450039	-2.161835
H	4.191278	-1.473028	-2.671261
H	-4.769310	1.338888	-1.332714
H	-5.989792	0.164284	0.495575
H	-2.223786	-1.475858	1.750483
H	-4.680887	-1.282771	2.079095
H	11.269918	0.157884	1.242851
H	-0.577115	-2.962352	0.452396
H	0.759732	-2.586784	1.174272
H	11.563936	-0.505314	1.075167
H	-1.914541	-4.810082	0.181534
H	-1.020780	-4.643657	-1.058135

Table S4. Cartesian Coordinates of $[Ni(H)(bpet)(H_2O)]^+$

atom	coordinates (Angstroms)		
	X	Y	Z
C	4.022752	-1.609565	-1.158802
C	4.866855	-0.894236	-0.314864
C	4.306355	-0.097967	0.678568
C	2.919834	-0.048420	0.813325
N	2.106728	-0.748685	-0.000475
C	2.651363	-1.503527	-0.968682
C	2.281488	0.789007	1.894740
S	0.682683	1.526095	1.387364
C	1.254884	2.537920	-0.049630
C	0.099211	3.177070	-0.824233
C	-1.086137	2.263887	-1.146130
S	-0.574985	0.630302	-1.845785
C	-2.221368	-0.159825	-1.951597
C	-2.906907	-0.334869	-0.615047
C	-4.297536	-0.267265	-0.530389
C	-4.916836	-0.468269	0.698132
C	-4.127020	-0.726376	1.814715
C	-2.749323	-0.773908	1.653905
N	-2.146257	-0.581356	0.468410
Ni	0.004083	-0.681671	0.387257
H	-2.853155	0.410918	-2.631944
H	-2.035671	-1.131050	-2.417304
H	-1.737918	2.743152	-1.877197
H	-1.669626	2.062015	-0.247188
H	-0.299504	4.028102	-0.264691
H	2.956824	1.575747	2.229238
H	2.024598	0.164100	2.753506
H	1.922531	3.310571	0.332745
H	1.831172	1.877298	-0.697995
H	0.520910	3.580916	-1.749200
H	-4.880094	-0.058807	-1.419026
H	-5.995928	-0.418934	0.781583
H	-2.085843	-0.972094	2.486431
H	-4.562473	-0.883837	2.792900
H	4.932125	0.484525	1.343114
H	5.942485	-0.945114	-0.433740
H	1.956329	-2.032253	-1.608954
H	4.410704	-2.231091	-1.955291
O	-0.228555	-2.661204	-0.653168
H	0.149929	-1.380694	1.826212
H	0.287212	-3.301255	-0.145285
H	-1.132636	-2.999810	-0.620626

Table S5. Cartesian Coordinates of TS(bpet)

atom	coordinates (Angstroms)		
	X	Y	Z
N	-2.189359	0.073252	0.694434
C	-3.026742	-0.766620	0.056327
C	-4.403984	-0.547576	0.034526
C	-4.929673	0.557650	0.694311
C	-4.061239	1.420955	1.355847
C	-2.702266	1.140239	1.330394
C	-2.443819	-1.985504	-0.622701
S	-0.777505	-1.715194	-1.328002
Ni	-0.053510	-0.226288	0.744076
O	-0.449286	-1.926881	2.162570
C	-1.198257	-0.390552	-2.547129
C	0.025382	0.165485	-3.279954
C	1.234195	0.516297	-2.408838
S	0.778608	1.486882	-0.903264
C	2.400966	1.503374	-0.050895
C	2.907946	0.124931	0.297111
C	4.273521	-0.154819	0.279716
C	4.713213	-1.427274	0.629937
C	3.771644	-2.392954	0.972829
C	2.428258	-2.042497	0.957564
N	2.000928	-0.810078	0.637388
H	-3.113158	-2.343038	-1.404856
H	-2.315055	-2.799906	0.094829
H	-1.900265	-0.817074	-3.264427
H	-1.708548	0.401279	-1.997943
H	-0.308665	1.050498	-3.829124
H	3.125975	2.043859	-0.658443
H	2.216829	2.076729	0.860868
H	1.950252	1.107161	-2.980641
H	1.733734	-0.389700	-2.064356
H	0.371621	-0.554043	-4.027520
H	-5.048939	-1.237561	-0.495026
H	-5.997082	0.743060	0.686612
H	-1.981120	1.775309	1.829507
H	-4.422143	2.297012	1.878853
H	4.977016	0.616477	-0.007758
H	5.770796	-1.662173	0.623689
H	1.659816	-2.764928	1.203083
H	4.063510	-3.400721	1.238294
H	0.189916	0.816855	1.941334
H	0.089453	-1.786816	2.952450
H	-1.358812	-1.922830	2.487867
H	0.832455	4.906145	0.540430
O	1.364923	5.726963	0.567526
H	0.786609	6.515819	0.530907
H	1.925479	5.747981	1.369678

Table S6. Cartesian Coordinates of Product Complex (bpet)

atom	coordinates (Angstroms) X	Y	Z
N	2.065596	-0.118260	-0.657887
C	2.838952	-0.413910	0.407917
C	4.228618	-0.382793	0.323020
C	4.831642	-0.045116	-0.883564
C	4.028896	0.269903	-1.975975
C	2.652490	0.225631	-1.819966
C	2.151530	-0.793283	1.694980
S	0.552108	0.076809	1.932085
C	1.120935	1.838001	1.921750
C	-0.042548	2.833473	1.940374
C	-1.220277	2.531321	1.011858
S	-0.720227	2.114072	-0.722419
Ni	-0.000220	-0.195586	-0.441885
O	-0.134882	-0.955332	-2.443877
C	-2.358855	1.610529	-1.377907
C	-2.911979	0.373570	-0.709751
N	-2.034313	-0.547316	-0.262798
C	-2.490377	-1.680340	0.304595
C	-3.845633	-1.940154	0.445205
C	-4.757921	-0.992198	-0.008750
C	-4.285225	0.180628	-0.588851
H	-3.045478	2.450699	-1.281487
H	-2.196295	1.436309	-2.444277
H	-1.873771	3.400724	0.941117
H	-1.805630	1.690928	1.384546
H	-0.457496	2.900977	2.949650
H	2.792232	-0.605266	2.555281
H	1.867694	-1.849950	1.689189
H	1.748687	1.976216	2.801678
H	1.737613	1.974582	1.033972
H	0.376465	3.815705	1.707047
H	-4.968860	0.940247	-0.945418
H	-5.823458	-1.158569	0.092543
H	-1.736901	-2.379625	0.650925
H	-4.170655	-2.862433	0.908130
H	4.824338	-0.617060	1.195738
H	5.911320	-0.016292	-0.964950
H	1.989971	0.478995	-2.637675
H	4.453177	0.554149	-2.929593
H	1.596673	-6.045087	-0.236054
H	0.544987	-1.580519	-2.729008
H	-0.977201	-1.349912	-2.705811
H	0.888218	-6.196750	-0.410973
O	0.214142	-3.479533	1.395100
H	0.516352	-4.225501	0.862949
H	0.009514	-3.863884	2.256011

Table S7. Cartesian Coordinates of [Ni(η^4-BPPT)(H_2O)]$^+$•H_2O

atom	coordinates (Angstroms)		
	X	Y	Z
C	-2.813672	0.835400	-1.400541
N	-2.176878	0.434142	-0.287001
C	-2.900025	-0.093110	0.717761
C	-4.283422	-0.249641	0.619164
C	-4.936885	0.166818	-0.534904
C	-4.187220	0.726071	-1.565717
Ni	-0.010547	0.501092	-0.283067
O	-0.039128	2.297409	0.980628
C	-2.197170	-0.471808	2.002657
S	-0.452617	-0.984467	1.811730
C	-0.637795	-2.625282	0.979124
C	0.449893	-2.853227	-0.064004
S	0.279172	-1.660778	-1.464479
C	2.026219	-1.299876	-1.875222
C	2.784962	-0.587646	-0.781210
N	2.110365	0.271047	0.004943
C	2.780548	0.943075	0.955085
C	4.146539	0.797966	1.158351
C	4.847233	-0.093283	0.351423
C	4.154903	-0.799187	-0.626687
H	-2.747999	-1.251991	2.527570
H	-2.152775	0.392517	2.671272
H	-0.574065	-3.398947	1.744881
H	-1.631098	-2.668962	0.530968
H	0.364535	-3.864071	-0.464188
H	1.444462	-2.738472	0.368319
H	2.530579	-2.220301	-2.166760
H	1.957372	-0.660484	-2.759398
H	-4.834092	-0.689486	1.441351
H	-6.010392	0.053457	-0.627643
H	-2.178672	1.250107	-2.173552
H	-4.649634	1.064443	-2.483903
H	4.665600	-1.507310	-1.267256
H	5.911832	-0.243370	0.485014
H	2.189065	1.610562	1.568780
H	4.639251	1.363967	1.938284
H	0.117751	1.325361	-1.661588
H	0.345962	3.059437	0.490214
H	-0.929173	2.577977	1.223528
O	1.034924	4.423432	-0.386586
H	0.840538	4.437908	-1.331552
H	0.865977	5.320335	-0.074087

Table S8. Cartesian Coordinates of [Ni(η^3-BPET)(H_2O)$_2$]$^+$

atom	coordinates (Angstroms)		
	X	Y	Z
C	-3.814097	1.920526	-1.118182
C	-3.115246	0.760944	-0.785442
N	-2.445530	0.651862	0.376951
C	-2.467616	1.679645	1.241283
C	-3.154015	2.858901	0.985734
C	-3.837471	2.982508	-0.220373
C	-3.136814	-0.433732	-1.708226
S	-1.621917	-1.460412	-1.641741
Ni	-1.395200	-1.145671	0.777694
H	-2.693925	-2.031003	1.098762
C	-0.348375	-0.319389	-2.350095
C	0.975139	-0.456388	-1.610465
S	0.832294	0.172279	0.116302
C	2.366300	-0.537424	0.868401
C	3.627155	0.122443	0.375025
C	4.105432	1.297106	0.965892
C	5.274112	1.869596	0.476775
C	5.927845	1.254844	-0.588755
C	5.379134	0.088231	-1.113577
N	4.256105	-0.474536	-0.648854
O	-1.189155	-0.668641	2.903363
H	-3.327208	-0.134292	-2.738051
H	-3.931599	-1.121579	-1.407401
H	-0.211073	-0.587583	-3.397719
H	-0.732339	0.700249	-2.303094
H	1.740331	0.123309	-2.126538
H	1.300121	-1.497201	-1.567732
H	2.238631	-0.383735	1.939598
H	2.383487	-1.605685	0.657984
H	-4.332651	1.982668	-2.066671
H	-4.376372	3.890879	-0.461442
H	-1.915223	1.533495	2.160466
H	-3.141400	3.659024	1.714340
H	3.570905	1.746935	1.794266
H	5.669365	2.775862	0.920755
H	5.862689	-0.421692	-1.941463
H	6.841470	1.663544	-1.002312
O	-0.079672	-2.924578	0.997085
H	-1.793376	-1.231319	3.404059
H	-0.360415	-0.655529	3.398682
H	0.335315	-3.036012	1.862378
H	-0.639483	-3.703837	0.884492

Table S9. Cartesian Coordinates of [Ni(η^4-BPPT) (H_2O)]$^+$•H_2O

atom	coordinates (Angstroms) X	Y	Z
N	-2.168482	-0.564553	0.410927
C	-2.952085	-0.286721	-0.648494
C	-4.343499	-0.326078	-0.557000
C	-4.938677	-0.670200	0.651660
C	-4.124995	-0.960361	1.742782
C	-2.748430	-0.894877	1.577113
C	-2.289390	0.045475	-1.967044
S	-0.715465	0.963188	-1.798051
Ni	-0.010040	-0.511079	0.321915
O	-0.106598	-2.347156	-0.890181
C	-1.356740	2.479682	-0.958764
C	-0.247749	3.455607	-0.557178
C	0.963751	2.843483	0.150544
S	0.489311	1.677202	1.502995
C	2.148989	1.035342	1.941453
C	2.844010	0.350671	0.789896
C	4.226686	0.442230	0.638351
C	4.841057	-0.214291	-0.423242
C	4.052027	-0.933978	-1.315157
C	2.680313	-0.974047	-1.102705
N	2.085229	-0.354198	-0.070916
H	-2.970809	0.609271	-2.603888
H	-2.022203	-0.869007	-2.502742
H	-2.052107	2.966181	-1.643491
H	-1.914347	2.150429	-0.081375
H	-0.708003	4.216056	0.080377
H	2.760548	1.843744	2.340512
H	1.953141	0.319302	2.743093
H	1.579685	3.629778	0.588125
H	1.574941	2.280907	-0.556047
H	0.129664	3.975541	-1.442466
H	-4.945918	-0.088539	-1.424874
H	-6.017980	-0.705238	0.739753
H	-2.066272	-1.110668	2.389950
H	-4.541371	-1.227571	2.705372
H	4.807378	1.024317	1.342975
H	5.914561	-0.154297	-0.556635
H	2.025526	-1.513147	-1.775420
H	4.481987	-1.449304	-2.164214
H	0.187834	-1.281702	1.720086
H	0.475851	-3.043513	-0.508169
H	-0.990525	-2.732893	-0.875205
O	1.524868	-4.296273	0.149592
H	1.549468	-4.344737	1.112944
H	1.393554	-5.203878	-0.150054

Table S10. Cartesian Coordinates of a [Ni(η^3-BPPT)(H_2O)$_2$]$^+$

atom	coordinates (Angstroms)		
	X	Y	Z
C	4.170364	-1.277729	-1.425123
C	3.357159	-0.405005	-0.703985
N	2.452599	-0.858881	0.184460
C	2.342230	-2.181861	0.386359
C	3.125178	-3.109911	-0.286627
C	4.056184	-2.647686	-1.212125
C	3.497623	1.089722	-0.867243
S	1.918943	2.001447	-0.682943
Ni	1.310302	0.561458	1.243253
O	-0.021768	2.100172	2.158883
C	1.007384	1.348806	-2.152038
C	-0.468010	1.757091	-2.162183
C	-1.253397	1.508846	-0.870251
S	-0.907258	-0.156440	-0.150273
C	-2.335309	-0.329579	1.015339
C	-3.653492	-0.530186	0.315913
N	-4.419406	0.560133	0.155229
C	-5.599409	0.417273	-0.463101
C	-6.072315	-0.800191	-0.943024
C	-5.275636	-1.930607	-0.772218
C	-4.047456	-1.794809	-0.135718
H	2.543259	1.134277	2.094218
O	0.821882	-0.853669	2.831704
H	3.948175	1.339517	-1.827080
H	4.133416	1.492669	-0.075073
H	1.509191	1.728271	-3.042655
H	1.107934	0.262557	-2.138601
H	-0.935770	1.212335	-2.987575
H	-2.082751	-1.199822	1.621719
H	-2.373640	0.555327	1.648635
H	-2.322589	1.562683	-1.070934
H	-1.010382	2.242132	-0.101732
H	-0.558236	2.821811	-2.396928
H	4.880734	-0.883213	-2.140767
H	4.679843	-3.340990	-1.763554
H	1.603912	-2.489621	1.115697
H	2.997868	-4.166555	-0.090441
H	-3.402213	-2.652244	0.014991
H	-5.607001	-2.900206	-1.125381
H	-6.192679	1.319858	-0.574819
H	-7.037184	-0.857764	-1.431360
H	0.539780	2.865096	2.341217
H	-0.382763	1.848745	3.019036
H	1.403000	-0.692160	3.585927
H	-0.057184	-1.009487	3.199473