

Electronic Supplementary Information

Computational, Electrochemical, and Spectroscopic Studies of two Mononuclear Cobaloximes: The influence of an axial pyridine and solvent on the redox behaviour and evidence for pyridine coordination to cobalt(I) and cobalt(II) metal centres.

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1 Results

1.1 Characterization

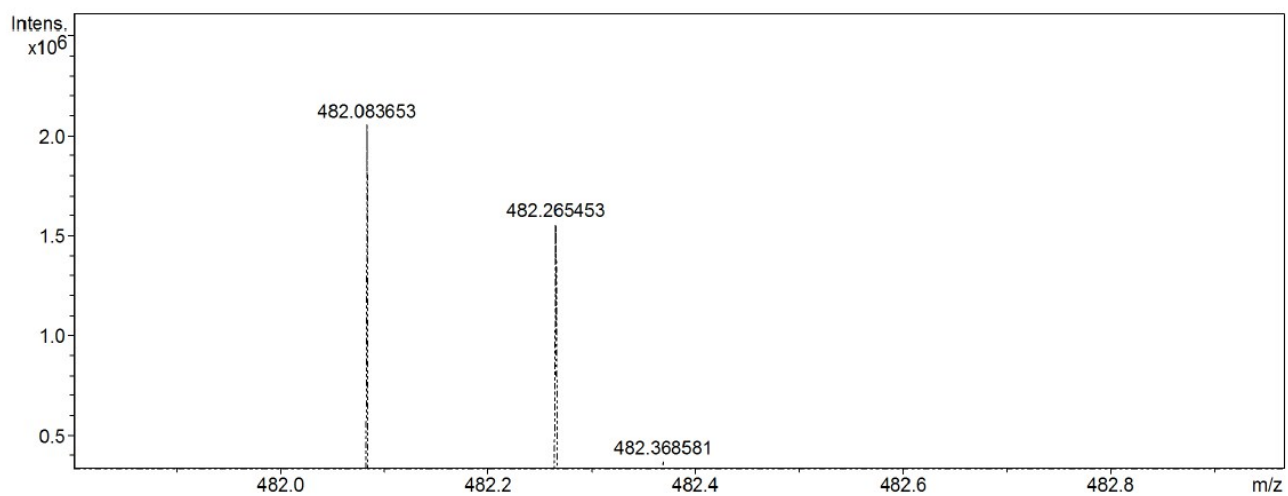
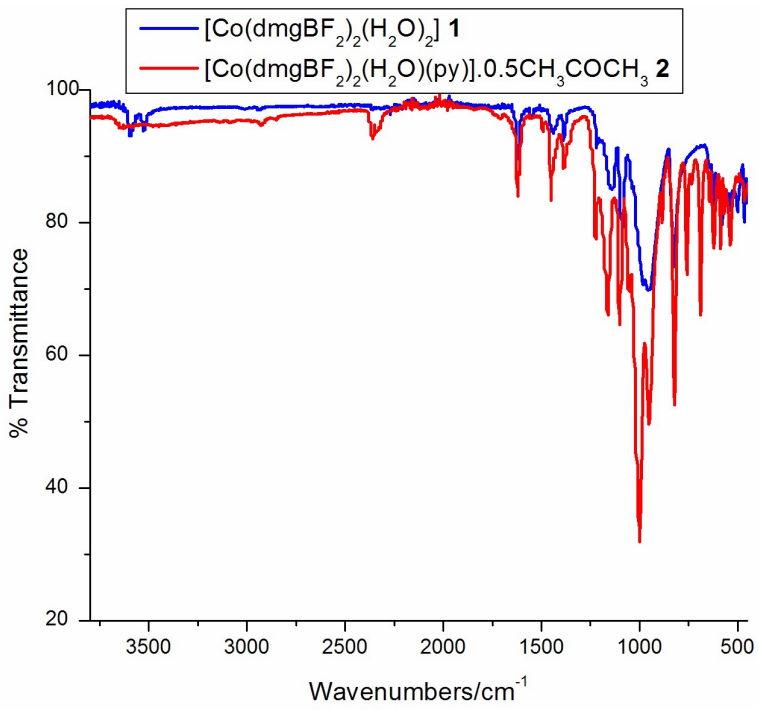


Figure S1. High resolution ESI mass spectrum of $[\text{Co}(\text{dmgbF}_2)_2(\text{H}_2\text{O})(\text{py})]^+$ in the positive mode with CH_3CN as solvent.



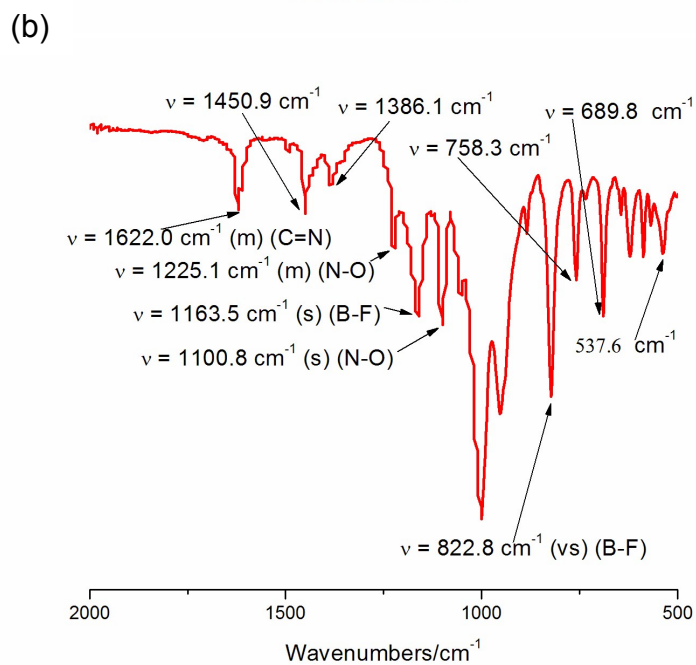
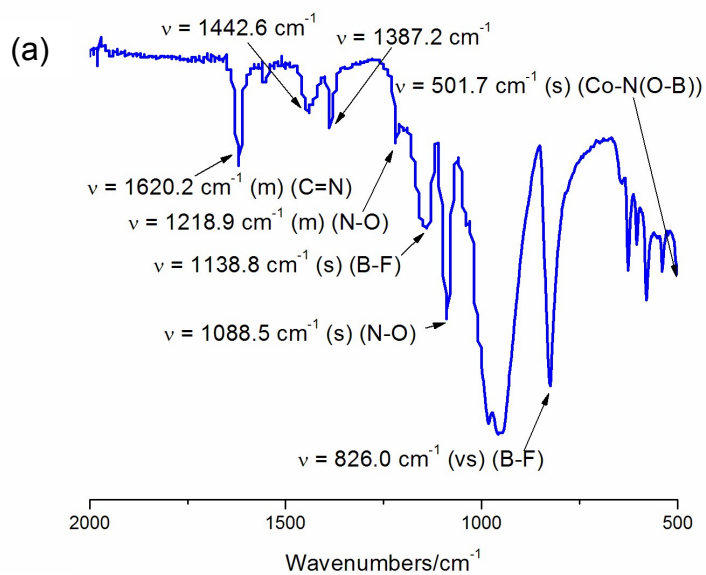


Figure S2. Full FT IR spectra and assignment of selected stretching frequencies of (a) complex **1** and (b) complex **2**.

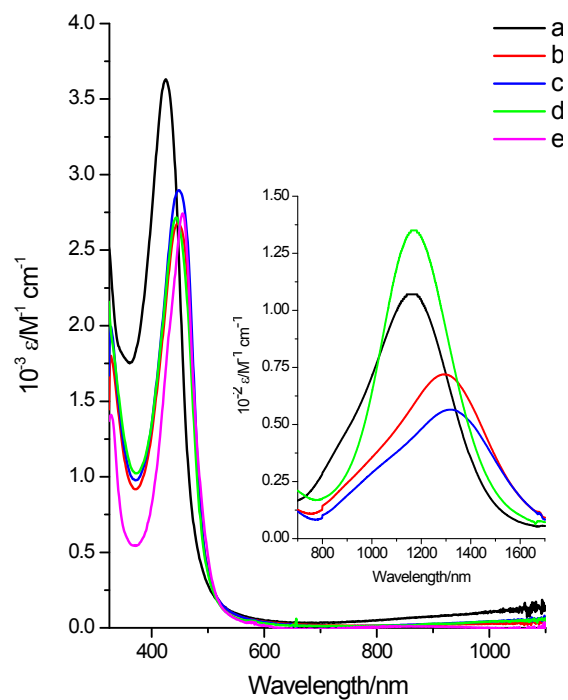


Figure S3. A plot of the molar extinction coefficient versus wavelength of complex **1**. Solvent = acetonitrile (a), acetone (b), 2-butanone (c), 1,2-difluorobenzene/acetone (4:1, v/v) (d), and water (e). NIR spectrum is shown as an inset.

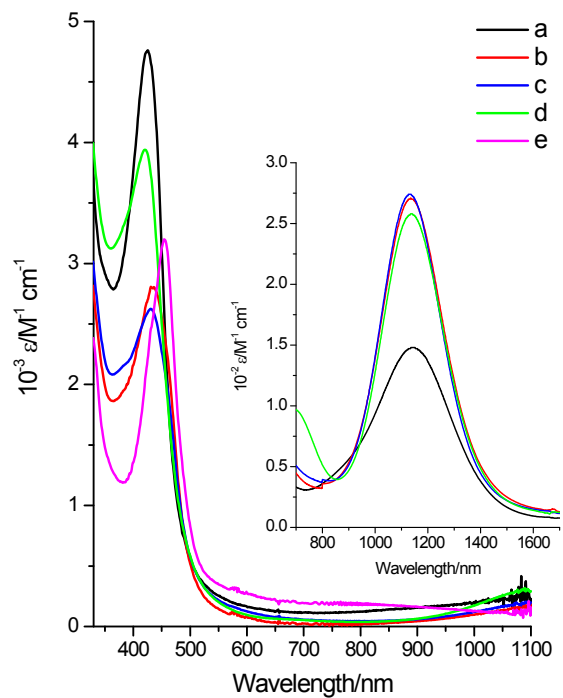


Figure S4. A plot of the molar extinction coefficient versus wavelength of complex **2**. Solvent = acetonitrile (a), acetone (b), 2-butanone (c), 1,2-difluorobenzene/acetone (4:1, v/v) (d), and water (e). NIR spectrum is shown as an inset.

1.2 Mole ratio plots and equilibria studies

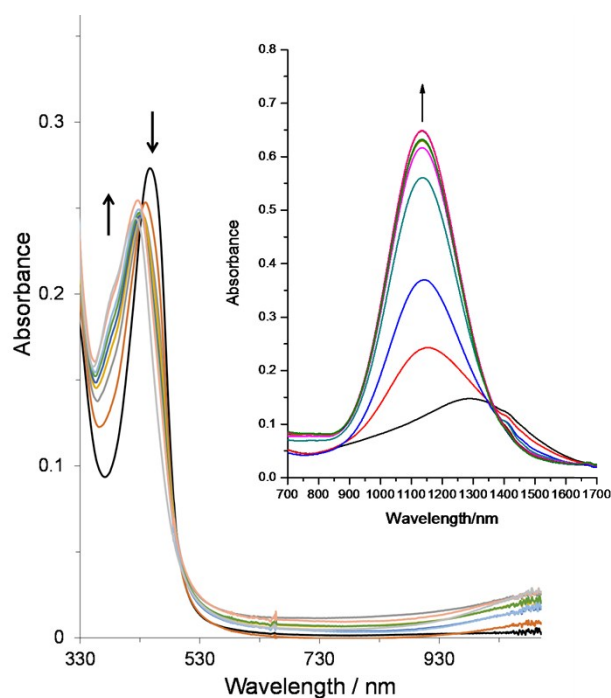


Figure S5. The effect of pyridine addition to complex **1** in the UV-visible spectrum (NIR spectrum is shown as an inset) in acetone. [complex **1**] = 0.1 mM (2.0 mM for NIR spectral studies) and $0.0 \text{ mM} \leq [\text{pyridine}] \leq 4.0 \text{ mM}$ ($0.0 \text{ mM} \leq [\text{pyridine}] \leq 4.0 \text{ mM}$ for NIR spectral studies), and path length = 1.0 cm.

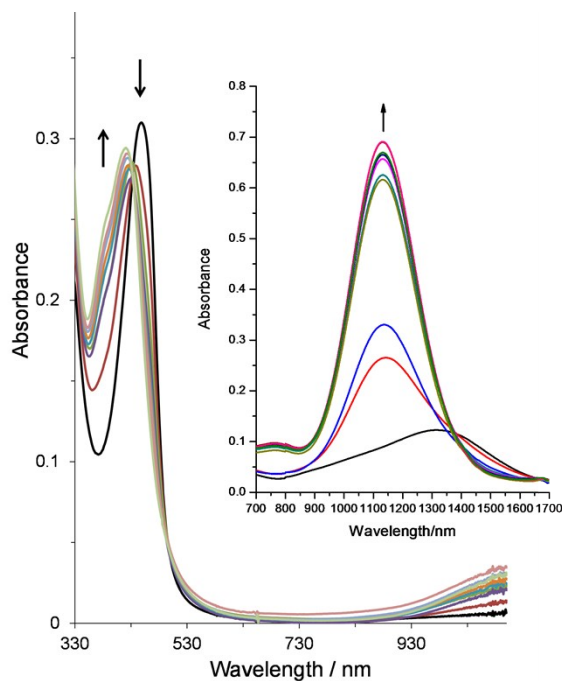


Figure S6. The effect of pyridine addition to complex **1** in the UV-visible spectrum (NIR spectrum is shown as an inset) in 2-butanone. [complex **1**] = 0.1 mM (2.0 mM for NIR spectral studies) and $0.0 \text{ mM} \leq [\text{pyridine}] \leq 4.0 \text{ mM}$ ($0.0 \text{ mM} \leq [\text{pyridine}] \leq 4.0 \text{ mM}$ for NIR spectral studies), and path length = 1.0 cm.

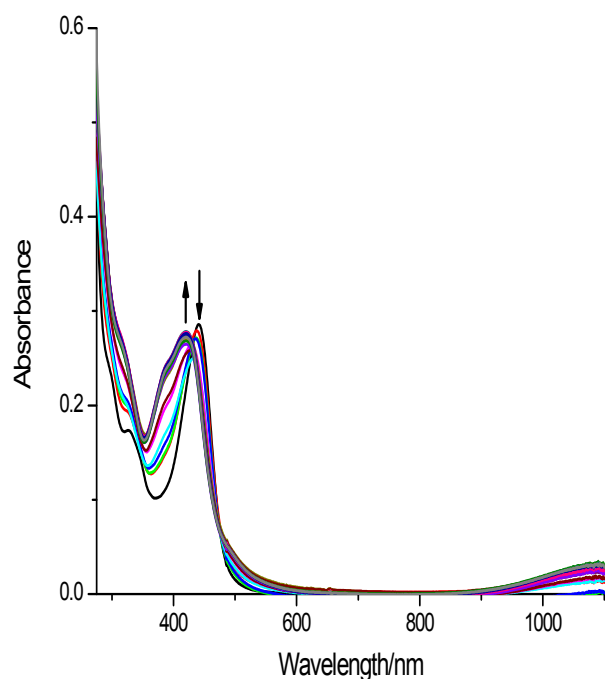


Figure S7. A plot of absorbance versus wavelength for a titration of complex **1** with pyridine in dichloromethane at 20 °C. [Complex **1**] = 0.10 mM and path length = 1.0 cm.

Table S1. NIR spectral data for absorbance at 1162 nm, $\log [(A_0 - A)/(A - A_\infty)]$, and $\log [\text{pyridine}]$ for complex **1** in acetonitrile at 20 °C. [complex **1**] = 2.0 mM and path length = 1.0 cm.

[py]/[complex 1]	Abs _{1162 nm}	$\log [\text{pyridine}]$	$\log [(A_0 - A)/(A - A_\infty)]$
0	0.2474	--	---
0.25	0.2892	-3.572	-0.8823
0.33	0.3059	-3.474	-0.7130
0.40	0.3222	-3.414	-0.5821
0.50	0.3344	-3.286	-0.4977
0.65	0.36315	-3.182	-0.3254
0.75	0.3720	-3.092	-0.2774
0.87	0.3895	-3.021	-0.1870
1.0	0.4062	-2.951	-0.1040
1.12	0.4255	-2.902	-0.0107
1.50	0.4645	-2.746	0.1800
1.75	0.4845	-2.661	0.2831
2.0	0.4949	-2.580	0.3401
2.25	0.5103	-2.517	0.4301
2.75	0.5131	-2.395	0.4473
3.0	0.5258	-2.351	0.5295
4.0	0.5495	-2.199	0.7126
5.0	0.5562	-2.082	0.7756

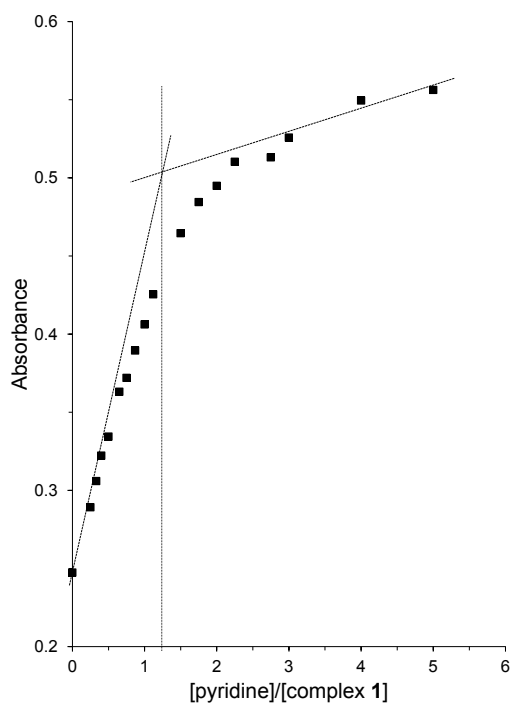


Figure S8. Mole ratio plot for the interaction of pyridine with complex **1** in acetonitrile. [complex **1**] = 2.0 mM, $\lambda = 1162$ nm, temperature = 20 °C, and path length = 1.0 cm.

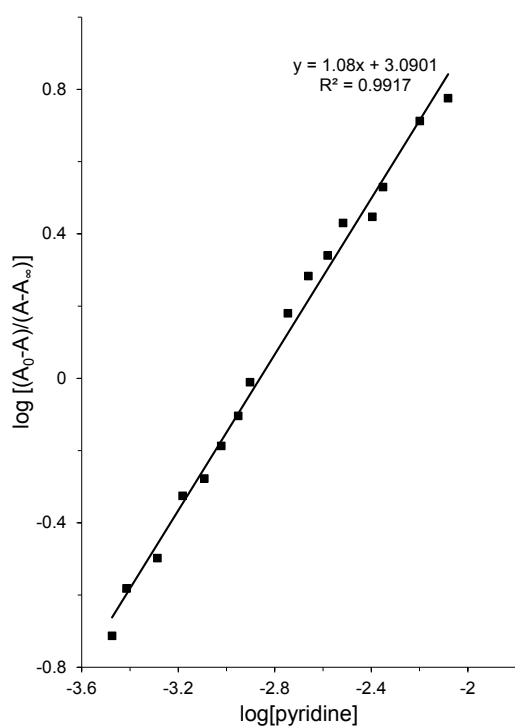


Figure S9. A plot of $\log [(A_0-A)/(A-A_\infty)]$ versus $\log [\text{pyridine}]$ for complex **1** at 1162 nm in acetonitrile at 20 °C.

Table S2. UV-visible spectral data for absorbance at 372 nm, $\log [(A_0-A)/(A-A_\infty)]$, and $\log [\text{pyridine}]$ for complex **1** in acetone at 20 °C. $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$ and path length = 1.0 cm.

$[\text{py}]/[\text{complex } \mathbf{1}]$	$\text{Abs}_{372 \text{ nm}}$	$\log [(A_0-A)/(A-A_\infty)]$	$\log [\text{pyridine}]$
0	0.0922	---	---
0.50	0.1265	-0.2309	-4.886
0.87	0.1444	0.1099	-4.513
1.0	0.1497	0.2128	-4.420
1.25	0.1590	0.4103	-4.276
1.50	0.1618	0.4763	-4.125
1.75	0.1696	0.7018	-4.038
2.0	0.1724	0.8020	-3.945
4.0	0.1796	1.206	-3.514

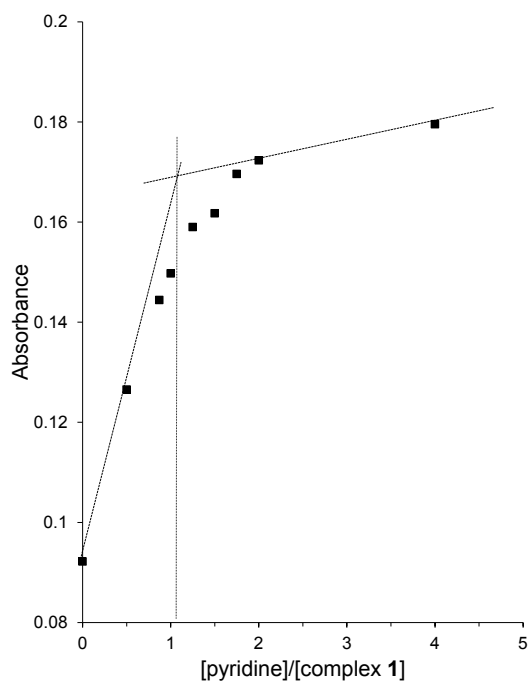


Figure S10. Mole ratio plot for the interaction of pyridine with complex **1** in acetone. $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$, $\lambda = 372 \text{ nm}$, temperature = 20 °C, and path length = 1.0 cm.

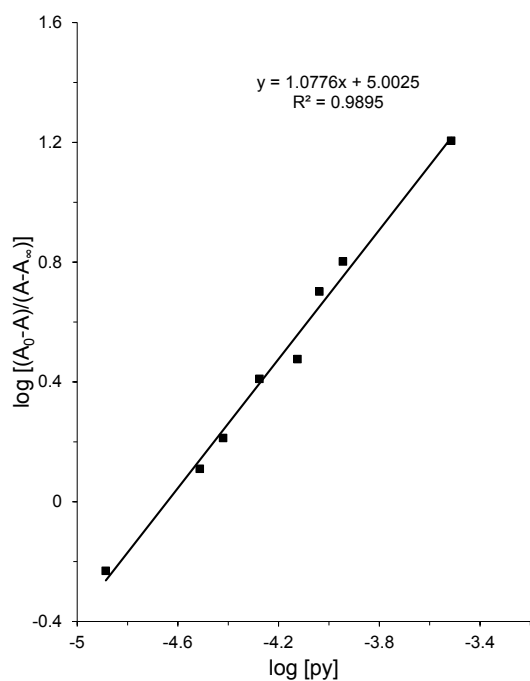


Figure S11. A plot of $\log [(A_0-A)/(A-A_\infty)]$ versus $\log [\text{pyridine}]$ for complex **1** at 371 nm in acetone at 20 °C.

Table S3. UV-visible spectral data for absorbance at 372 nm, $\log [(A_0-A)/(A-A_\infty)]$, and $\log [\text{pyridine}]$ for complex **1** in 2-butanone at 20 °C. $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$, and path length = 1.0 cm.

$[\text{py}]/[\text{complex } \mathbf{1}]$	$\text{Abs}_{372 \text{ nm}}$	$\log [(A_0-A)/(A-A_\infty)]$	$\log [\text{pyridine}]$
0	0.1045	---	---
0.50	0.1498	-4.857	-0.2480
1.0	0.1847	-4.442	0.2479
1.25	0.1973	-4.292	0.4529
1.50	0.2035	-4.148	0.5716
1.75	0.2105	-4.043	0.7357
2.0	0.2150	-3.951	0.8664
4.0	0.2244	-3.516	1.330

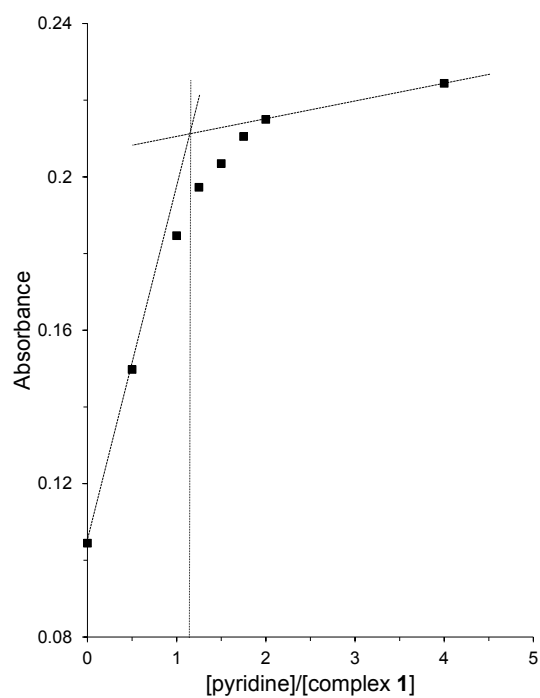


Figure S12. Mole ratio plot for the interaction of pyridine with complex **1** in 2-butanone. [complex **1**] = 0.10 mM, $\lambda = 372$ nm, temperature = 20 °C, path length = 1.0 cm.

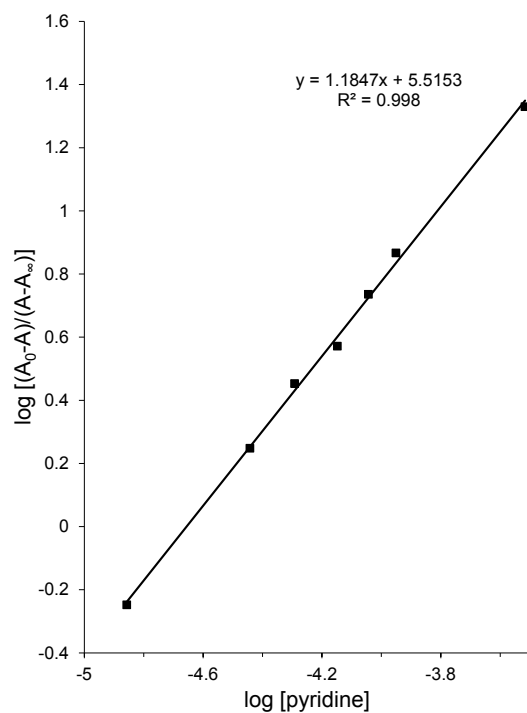


Figure S13. A plot of $\log [(A_0 - A)/(A - A_\infty)]$ versus $\log [\text{pyridine}]$ for complex **1** at 372 nm in 2-butanone at 20 °C.

Table S4. UV-visible spectral data for absorbance at 372 nm, $\log [(A_0-A)/(A-A_\infty)]$, and $\log [\text{pyridine}]$ for complex **1** in 1,2-difluorobenzene/acetone (4:1, v/v) at 20 °C. $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$, and path length = 1.0 cm.

$[\text{py}]/[\text{complex } \mathbf{1}]$	$\text{Abs}_{372 \text{ nm}}$	$\log [\text{pyridine}]$	$\log [(A_0-A)/(A-A_\infty)]$
0	0.1058	---	---
0.33	0.1336	-5.349	-0.3990
0.40	0.1390	-5.231	-0.2858
0.50	0.1444	-4.988	-0.1810
0.65	0.1556	-4.860	0.02092
0.75	0.1593	-4.700	0.08827
1.25	0.1817	-4.329	0.5519
1.50	0.1864	-4.173	0.6848
1.75	0.1874	-4.041	0.7184
2.5	0.1930	-3.795	0.9394
5.0	0.2011	-3.396	1.7048

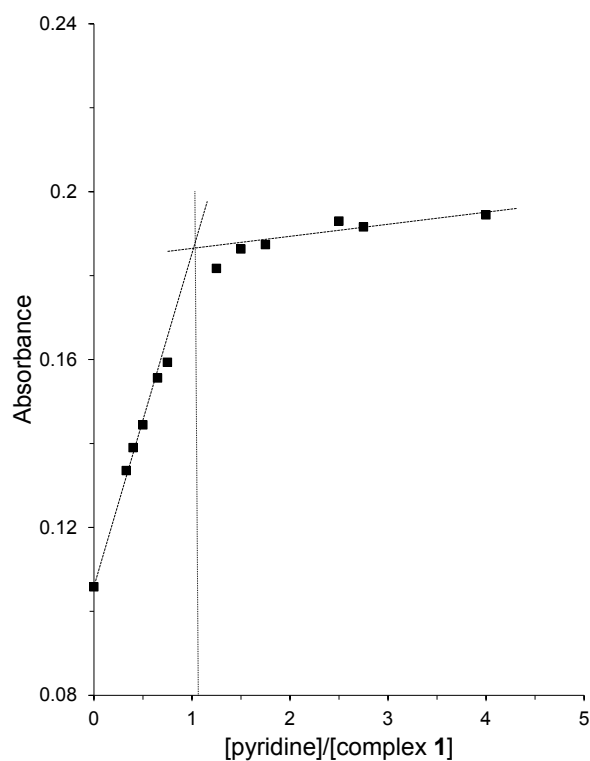


Figure S14. Mole ratio plot for the interaction of pyridine with complex **1** in 1,2-difluorobenzene/acetone (4:1, v/v). $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$, $\lambda = 372 \text{ nm}$, temperature = 20 °C, path length = 1.0 cm.

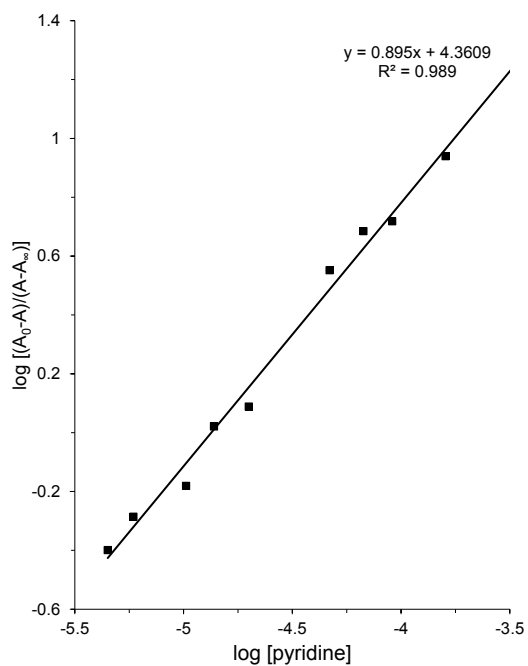


Figure S15. A plot of $\log [(A_0-A)/(A-A_\infty)]$ versus $\log [\text{pyridine}]$ for complex **1** at 372 nm in 1,2-difluorobenzene/acetone (4:1, v/v) at 20 °C.

Table S5. UV-visible spectral data for absorbance at 370 nm, $\log [(A_0-A)/(A-A_\infty)]$ and $\log [\text{pyridine}]$ for complex **1** in dichloromethane at 20 °C. $[\text{complex } \mathbf{1}] = 0.10 \text{ mM}$, and path length = 1.0 cm.

$[\text{py}]/[\text{complex } \mathbf{1}]$	$\text{Abs}_{370 \text{ nm}}$	$\log [\text{pyridine}]$	$\log [(A_0-A)/(A-A_\infty)]$
0	0.1016	--	--
0.33	0.1341	-6.166	-0.3210
0.40	0.1409	-6.068	-0.1916
0.50	0.1506	-5.909	-0.02143
0.75	0.1738	-5.507	0.4077
0.87	0.1843	-5.330	0.6680
1.0	0.1914	-4.977	0.9282
1.12	0.1949	-4.720	1.121
1.25	0.1964	-4.514	1.226
1.5	0.1977	-4.265	1.350
2.0	0.2003	-3.993	1.755
2.25	0.1997	-3.895	1.635
2.5	0.1991	-3.816	1.531
3.0	0.2011	-3.697	2.025

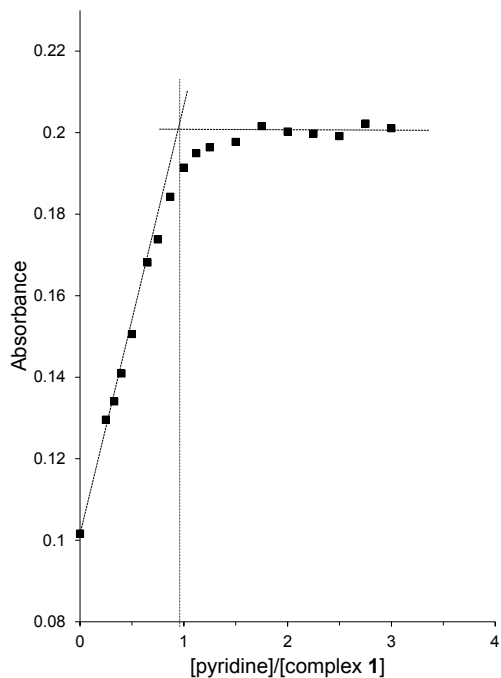


Figure S16. Mole ratio plot for the interaction of pyridine with complex **1** in dichloromethane. [complex **1**] = 0.10 mM, $\lambda = 370$ nm, temperature = 20 °C, and path length = 1.0 cm.

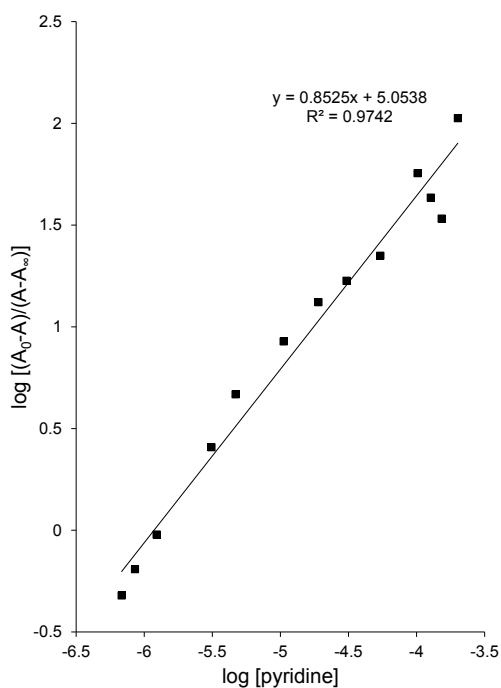


Figure S17. A plot of $\log [(A_0 - A)/(A - A_\infty)]$ versus $\log [\text{pyridine}]$ for complex **1** at 370 nm in dichloromethane at 20 °C.

Table S6. UV-visible spectral data for absorbance at 447 nm, $\log [(A_0-A)/(A-A_\infty)]$, $\log [\text{pyridine}]$ for the $[\text{nBu}_4\text{N}]\text{BH}_4$ reduced form of complex **1** in acetonitrile. $[\text{complex } \mathbf{1}] = 1.0 \text{ mM}$, temperature = 20 °C, and path length = 1.0 mm.

$[\text{py}]/[\text{complex } \mathbf{1}]$	$\text{Abs}_{447 \text{ nm}}$	$\log [(A_0-A)/(A-A_\infty)]$	$\log [\text{py}]$
0	0.1781	---	---
0.5	0.2404	-0.3440	-3.725
1.0	0.2954	0.1524	-3.384
1.5	0.3199	0.3871	-3.102
2.0	0.3433	0.6780	-2.931
2.5	0.3538	0.8610	-2.790
4.0	0.3689	1.322	-2.516

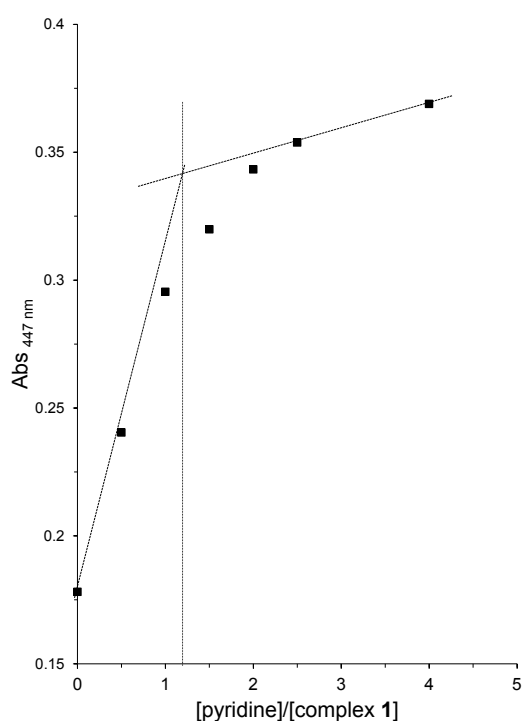


Figure S18. Mole ratio plot for the interaction of pyridine with the $[\text{nBu}_4\text{N}]\text{BH}_4$ reduced form of complex **1** in acetonitrile. $[\text{complex } \mathbf{1}] = 1.0 \text{ mM}$, temperature = 20 °C, and path length = 1.0 mm.

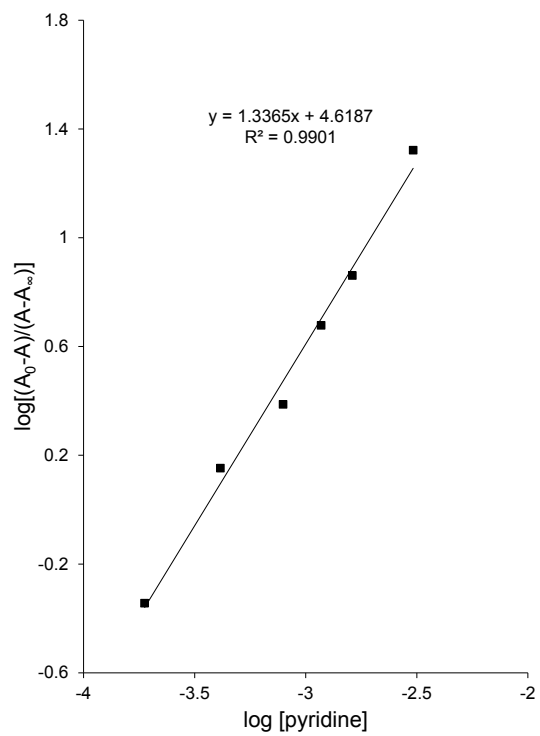


Figure S19. A plot of $\log [(A_0-A)/(A-A_\infty)]$ versus $\log [\text{py}]$ for the $[\text{nBu}_4\text{N}]\text{BH}_4$ reduced form of complex **1** in acetonitrile at 20 °C.

1.3 Electrochemical data

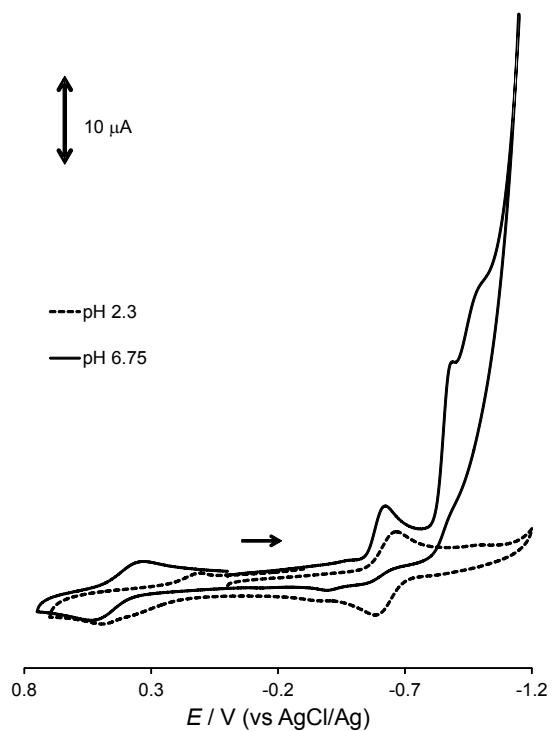


Figure S20. Cyclic voltammograms of complex **1** in water on a glassy carbon working electrode versus AgCl/Ag. [complex **1**] = 0.64 mM, pH = 2.30 (solid lines) and pH = 6.75 (broken lines), supporting electrolyte = 0.10 M NaClO₄, and scan rate = 100 mV s⁻¹.

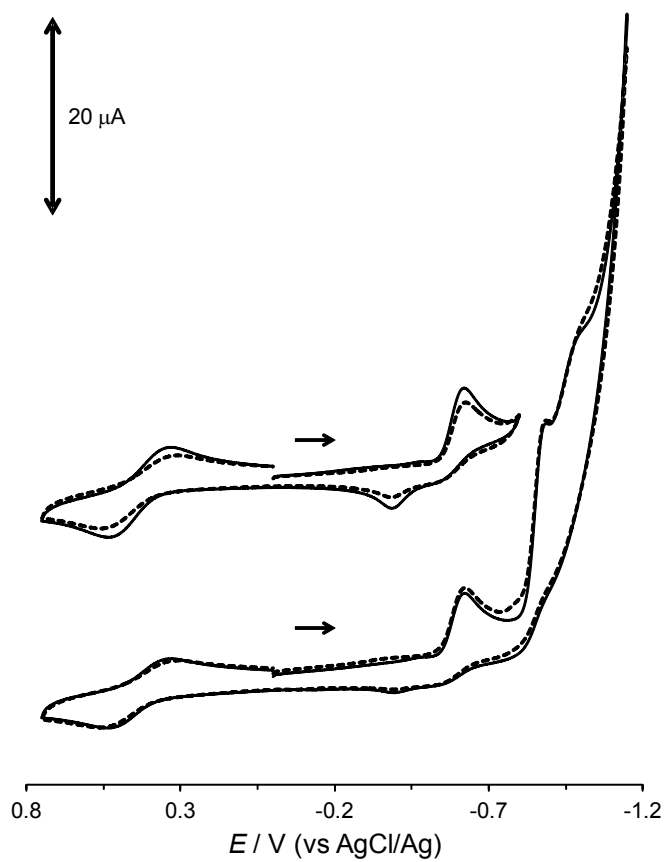


Figure S21. Cyclic voltammograms of complexes **1** and **2** in water on a glassy carbon working electrode versus AgCl/Ag. [complex **1**] = 0.64 mM (solid lines) and [complex **2**] = 0.63 mM (broken lines), pH = 2.30, supporting electrolyte = 0.10 M NaClO₄, and scan rate = 100 mV s⁻¹.

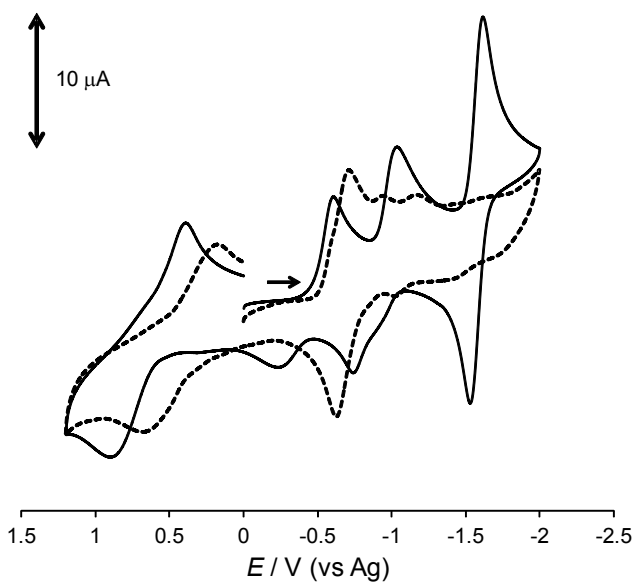


Figure S22. Cyclic voltammograms of complexes **1** and **2** in 2-butanone on a glassy carbon working electrode versus a Ag quasi-reference electrode. [complex **1**] = 1.02 mM (solid lines) and [complex **2**] = 1.08 mM (broken lines), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹.

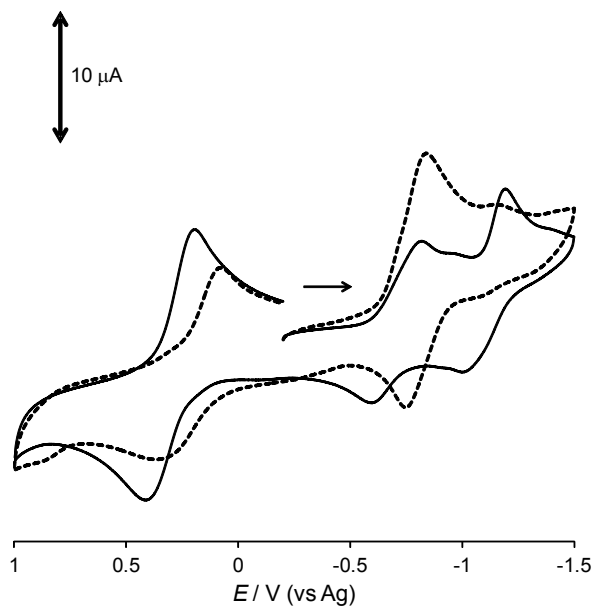


Figure S23. Cyclic voltammograms of complexes **1** and **2** in 1,2-difluorobenzene/acetone (4:1 v/v) on a glassy carbon working electrode versus a Ag quasi-reference electrode. [complex **1**] = 1.05 mM (solid lines) and [complex **2**] = 1.03 mM (broken lines), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹.

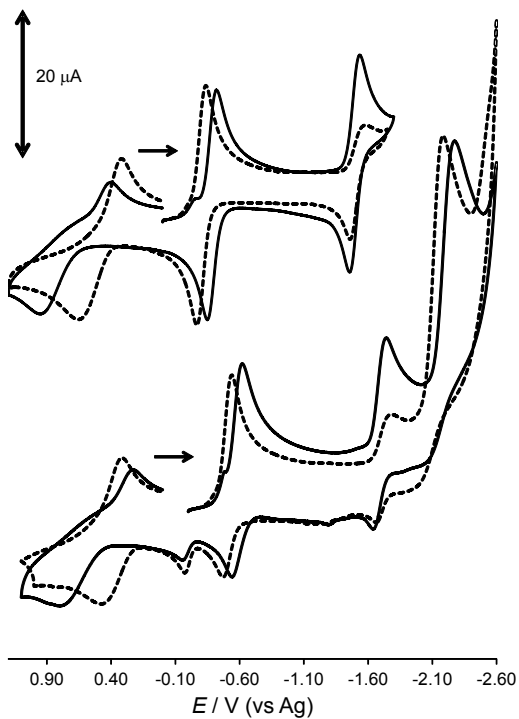


Figure S24. Cyclic voltammograms of complex **1** in CH_3CN on a glassy carbon working electrode versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.04 \text{ mM}$ (solid lines) and $[\text{complex } \mathbf{1}] = 1.04 \text{ mM}$ with 5.09 mM pyridine (broken lines), supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and scan rate = 100 mV s^{-1} .

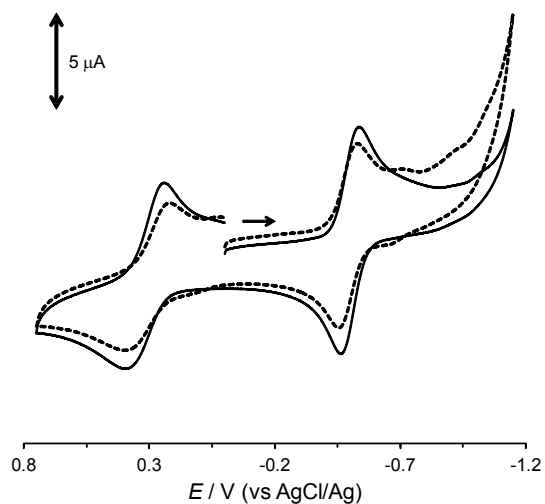


Figure S25. Cyclic voltammograms of complexes **1** and **2** in water with pyridine on a glassy carbon working electrode versus AgCl/Ag. $[\text{complex } \mathbf{1}] = 0.64 \text{ mM}$ with 5.21 mM pyridine (solid lines) and $[\text{complex } \mathbf{2}] = 0.63 \text{ mM}$ with 5.21 mM pyridine (broken lines), supporting electrolyte = 0.10 M NaClO_4 , and scan rate = 100 mV s^{-1} .

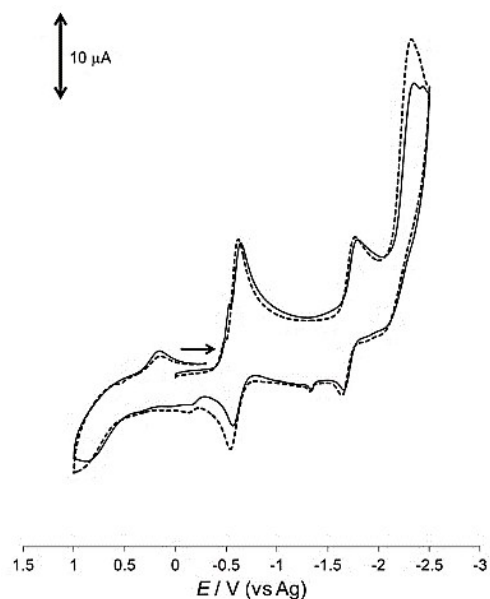


Figure S26. Cyclic voltammograms complex **1** in CH_3CN on a glassy carbon working electrode versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.02 \text{ mM}$ (solid lines) and $[\text{complex } \mathbf{1}] = 1.02 \text{ mM}$ with 15.0 mM 2-methylpyridine (broken lines), supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and scan rate = 100 mV s^{-1} .

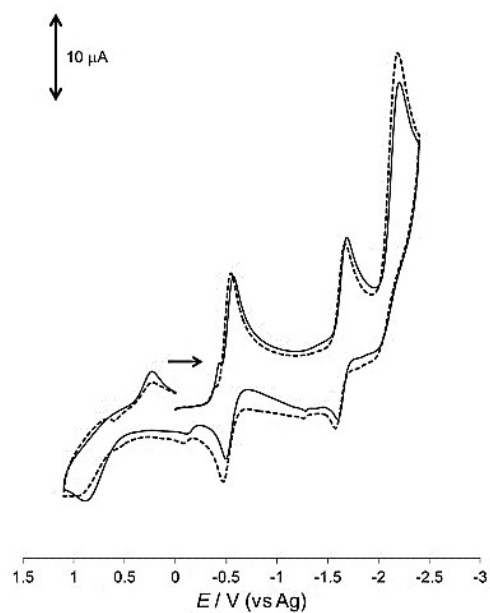


Figure S27. Cyclic voltammograms of complex **1** in CH_3CN on a glassy carbon working electrode versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.02 \text{ mM}$ (solid lines) and $[\text{complex } \mathbf{1}] = 1.02 \text{ mM}$ with 15.1 mM 2,6-dimethylpyridine (broken lines), supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and scan rate = 100 mV s^{-1} .

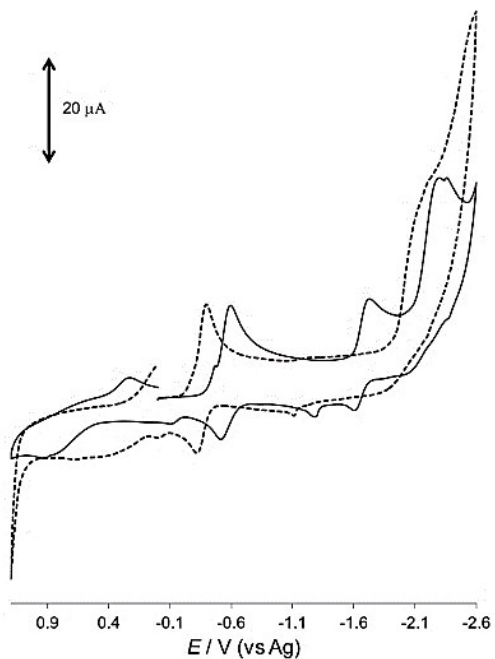


Figure S28. Cyclic voltammograms of complex **1** in acetonitrile on a glassy carbon working electrode versus a Ag quasi-reference electrode. [complex **1**] = 1.05 mM (solid lines) and [complex **1**] = 1.05 mM with [2-aminopyridine] = 5.10 mM (broken lines), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹.

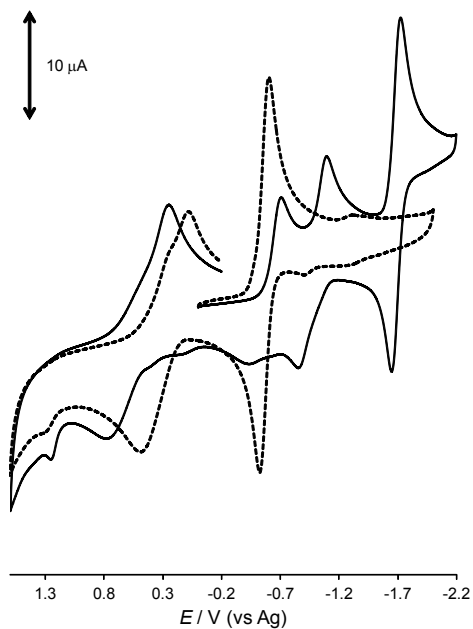


Figure S29. Cyclic voltammograms of complex **1** in acetone on a glassy carbon working electrode versus a Ag quasi-reference electrode. [complex **1**] = 1.04 mM (solid lines) and [complex **1**] = 1.04 mM with 5.09 mM of pyridine (broken lines), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹.

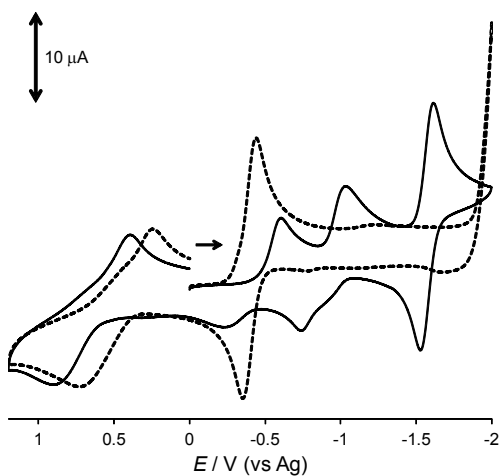


Figure S30. Cyclic voltammograms complex **1** in 2-butanone on a glassy carbon working electrode versus a Ag quasi-reference electrode. [complex **1**] = 1.02 mM (solid lines) and [complex **1**] = 1.02 mM with 5.09 mM of pyridine (broken lines), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹.

1.4 Spectroelectrochemistry

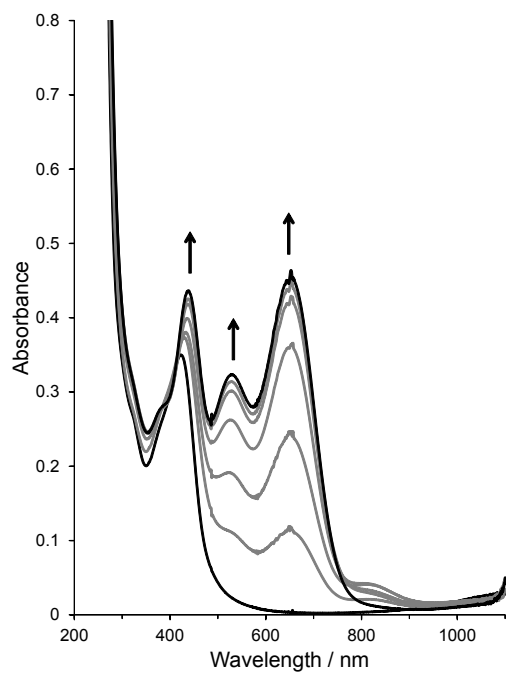


Figure S31. Absorbance changes in the UV-visible spectra of complex **1** with pyridine in acetonitrile at a constant potential of -1.0 V versus a Ag quasi-reference electrode. [complex **1**] = 1.05 mM, [pyridine] = 5.09 mM, supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and path length = 1 mm.

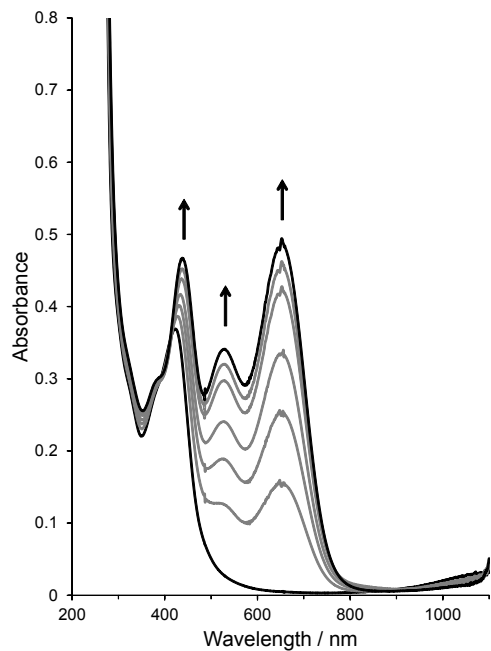


Figure S32. Absorbance changes in the UV-visible spectra of complex **1** with pyridine in acetonitrile at a constant potential of -1.0 V versus a Ag quasi-reference electrode. [complex **1**] = 1.05 mM, [pyridine] = 10.18 mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

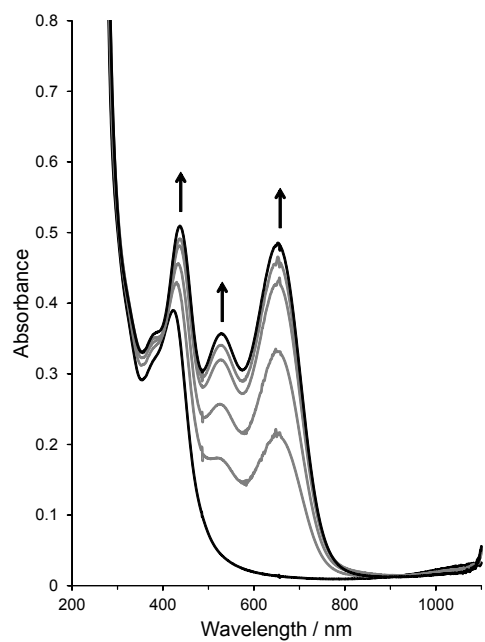


Figure S33. Absorbance changes in the UV-visible spectra of complex **2** with pyridine in acetonitrile at a constant potential of -1.0 V versus a Ag quasi-reference electrode. [complex **2**] = 1.02 mM, [pyridine] = 10.18 mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

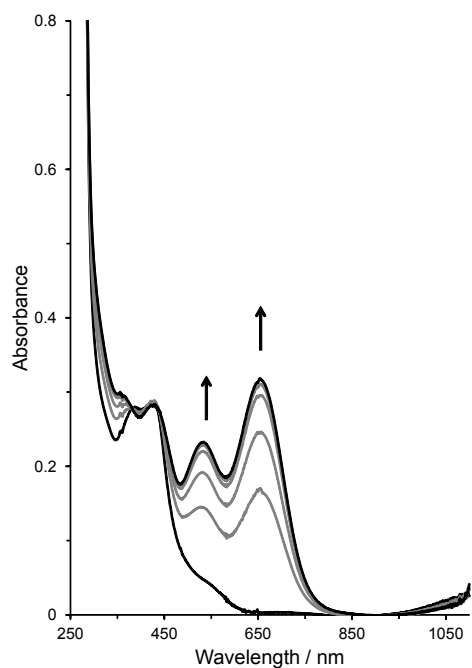


Figure S34. Absorbance changes in the UV-visible spectra of complex **1** with 2-aminopyridine in acetonitrile at a constant potential of -1.0 V versus a Ag quasi-reference electrode. [complex **1**] = 1.05 mM, [2-aminopyridine] = 5.10 mM, supporting electrolyte = 0.10 M [n Bu $_4$ N]ClO $_4$, and path length = 1 mm.

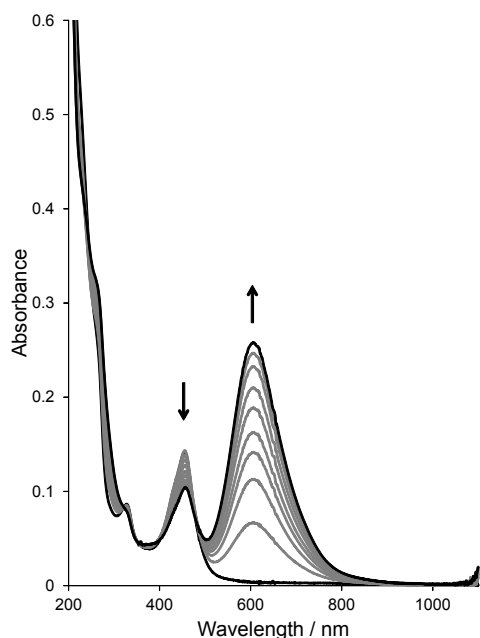


Figure S35. Absorbance changes in the UV-visible spectra of complex **1** in water at a constant potential of -0.75 V versus AgCl/Ag. [complex **1**] = 0.51 mM, supporting electrolyte = 0.10 M NaClO $_4$, pH = 5.79 , and path length = 1 mm. *Note: At low pH (e.g., 2.30) the evolution of hydrogen is observed. The use of a buffer was avoided to eliminate substitution of the axial water ligands in complex **1** via anation.*

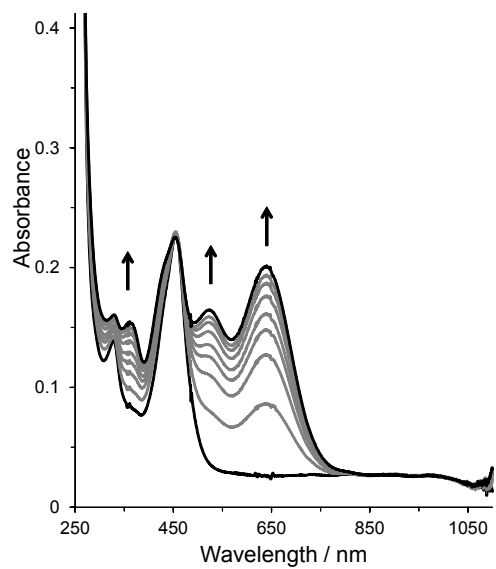


Figure S36. Absorbance changes in the UV-visible spectra of complex **1** in water at a constant potential of -0.70 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 0.60$ mM, $[\text{pyridine}] = 5.21$ mM, supporting electrolyte = 0.10 M NaClO_4 , pH = 4.58, and path length = 1 mm.

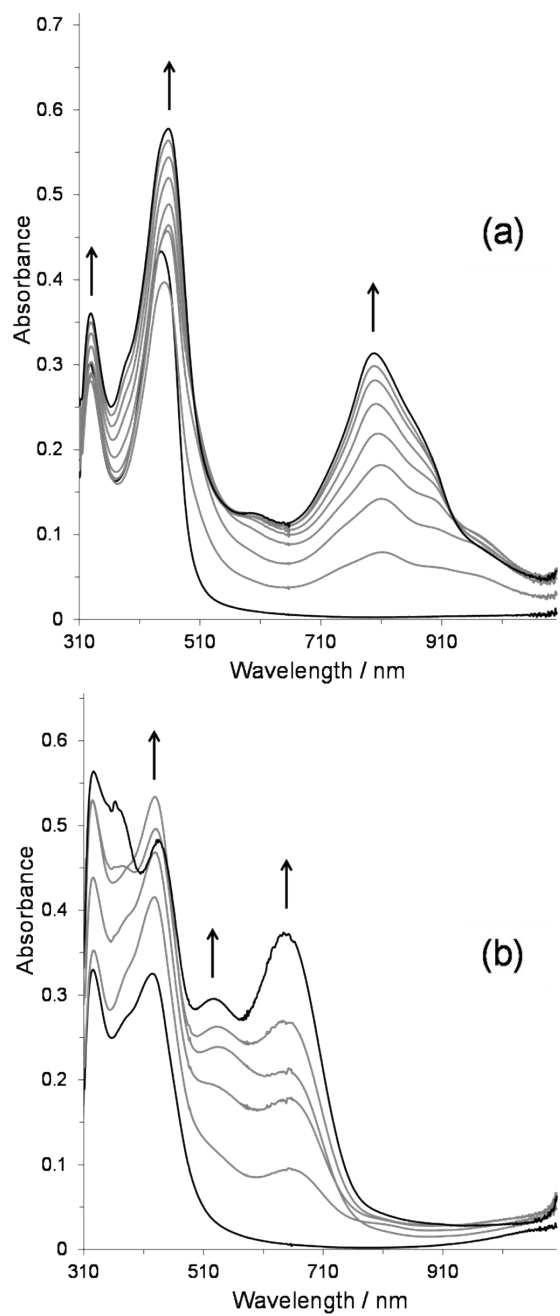


Figure S37. Absorbance changes in the UV-visible spectra of complexes **1** and **2** in acetone at a constant potential of -0.90 V versus a Ag quasi-reference electrode; supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm. (a) $[\text{complex } \mathbf{1}] = 1.14$ mM, (b) $[\text{complex } \mathbf{2}] = 1.08$ mM.

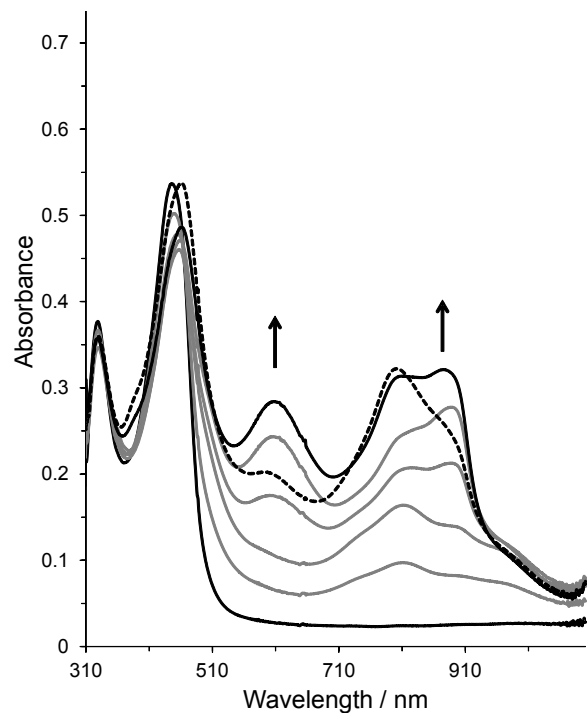


Figure S38. Absorbance changes in the UV-visible spectra of complex **1** in acetone at a constant potential of -1.30 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.14$ mM, supporting electrolyte = 0.10 M $[\text{tBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm. Broken line illustrates the spectrum after an extended time.

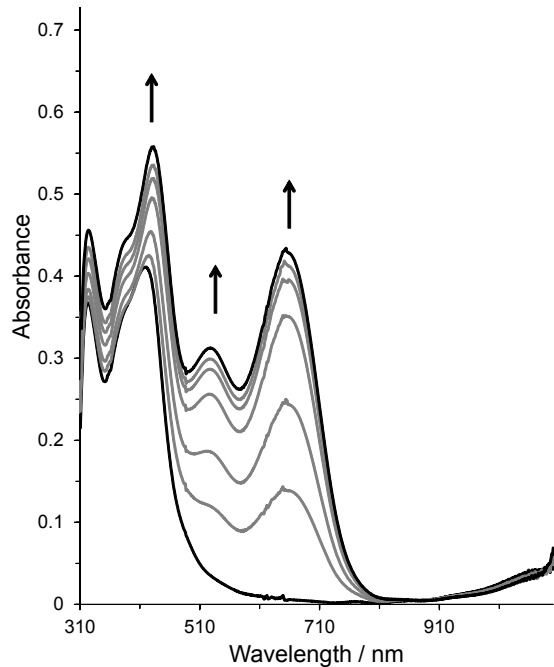


Figure S39. Absorbance changes in the UV-visible spectra of complex **1** with pyridine in acetone at a constant potential of -0.90 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.14$ mM, $[\text{pyridine}] = 5.09$ mM, supporting electrolyte = 0.10 M $[\text{tBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

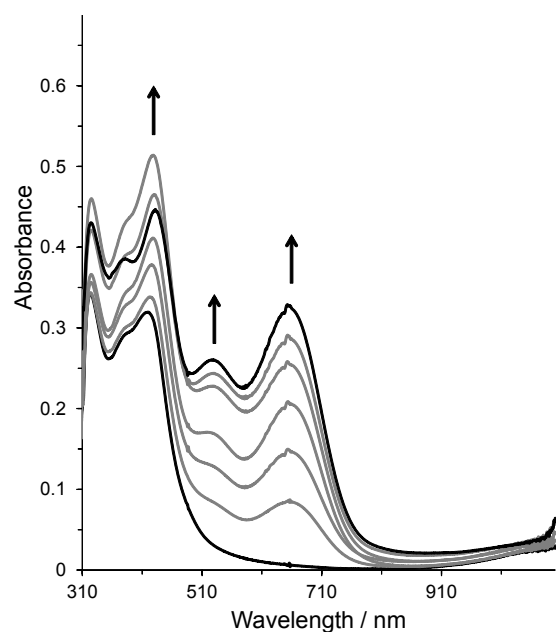


Figure S40. Absorbance changes in the UV-visible spectra of complex **2** with pyridine in acetone at a constant potential of -0.90 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{2}] = 1.08$ mM, $[\text{pyridine}] = 5.09$ mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

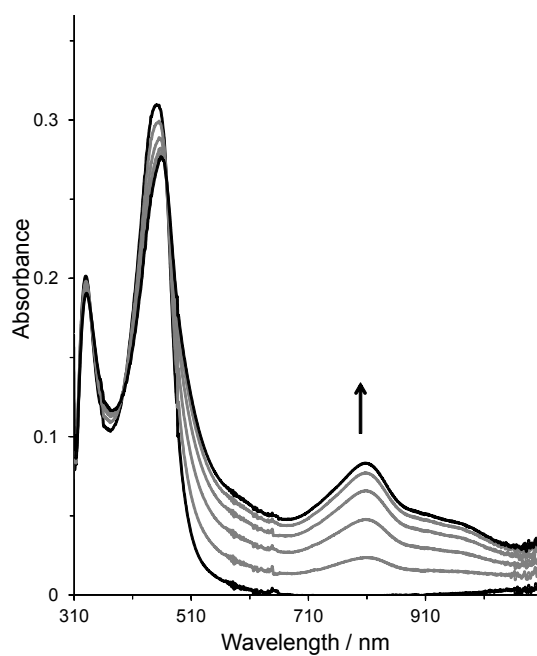


Figure S41. Absorbance changes in the UV-visible spectra of complex **1** in 2-butanone at a constant potential of -0.70 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.04$ mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

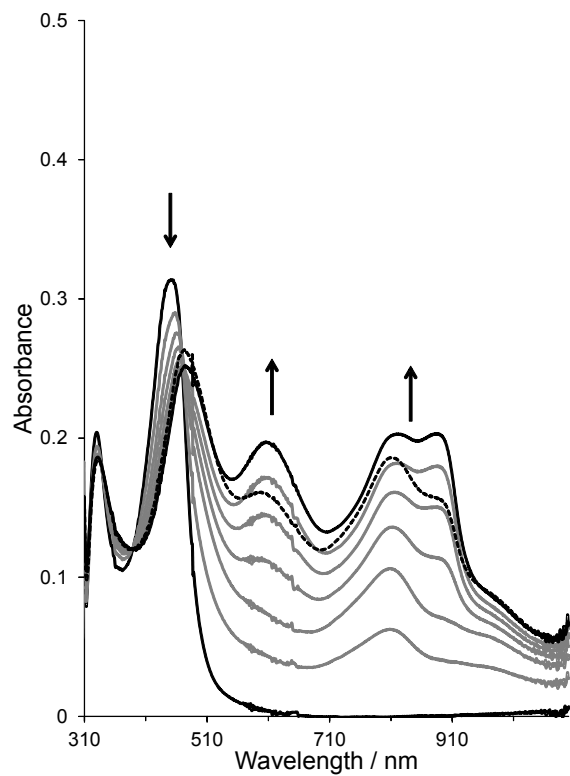


Figure S42. Absorbance changes in the UV-visible spectra of complex **1** in 2-butanone at a constant potential of -1.10 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.04$ mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm. Broken line illustrates the spectrum after an extended time.

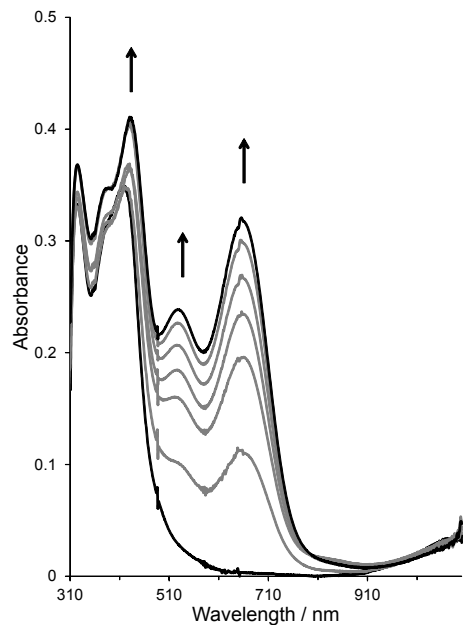


Figure S43. Absorbance changes in the UV-visible spectra of complex **1** with pyridine in 2-butanone at a constant potential of -0.70 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.04$ mM, $[\text{pyridine}] = 5.09$ mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

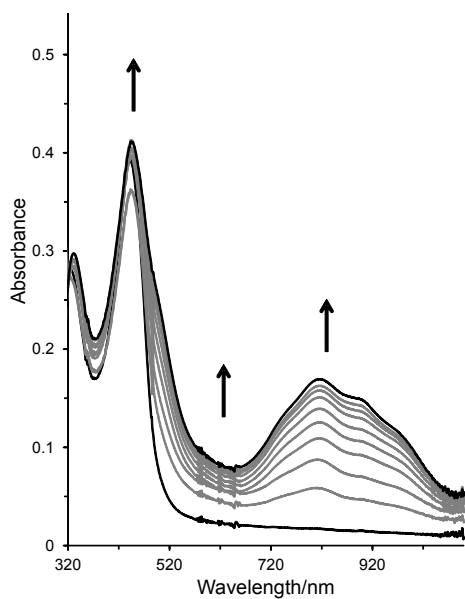


Figure S44. Absorbance changes in the UV-visible spectra of complex **1** in 1,2-difluorobenzene/acetone (4:1, v/v) at a constant potential of -0.90 V versus a Ag quasi-reference electrode. $[\text{complex } \mathbf{1}] = 1.05$ mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

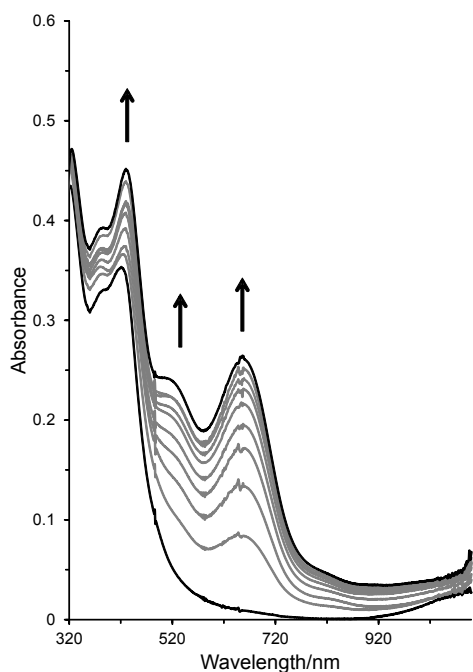


Figure S45. Absorbance changes in the UV-visible spectra of complex **2** in 1,2-difluorobenzene/acetone (4:1, v/v) at a constant potential of -0.90 V versus a **Ag quasi-reference electrode**. [complex **2**] = 1.03 mM, supporting electrolyte = 0.10 M $[\text{nBu}_4\text{N}]\text{ClO}_4$, and path length = 1 mm.

1.5 ^{11}B , ^{19}F , and ^{59}Co NMR spectroscopic studies

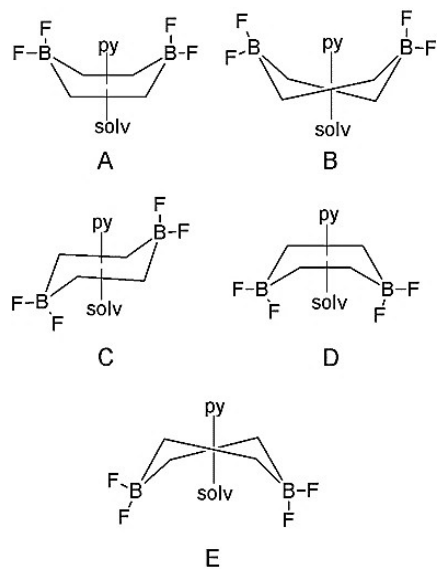


Figure S46. Conformers most likely adopted by the BF_2 caps of complex **2**.

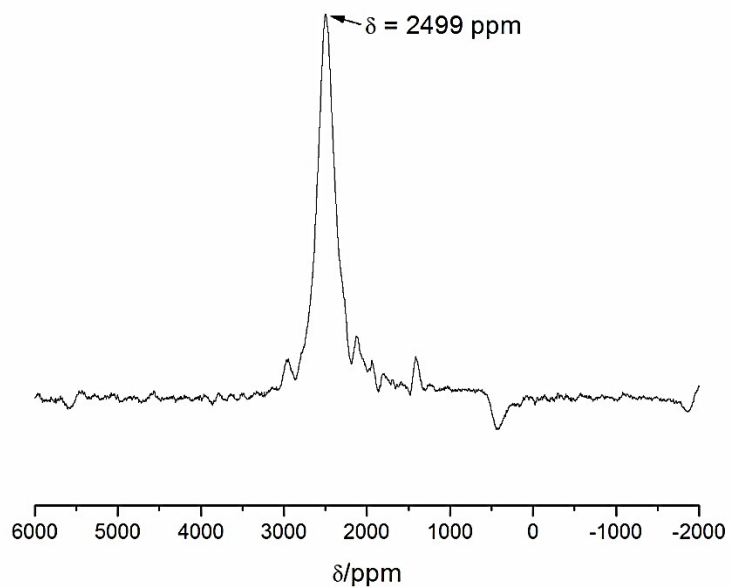


Figure S47. ^{59}Co NMR spectrum of the Co(I) species produced from 50 mM of complex **1**, 500 mM of $[\text{nBu}_4\text{N}]\text{BH}_4$, and 250 mM of 2,3,5,6-tetrafluoropyridine (pyF_4) in CD_3CN .

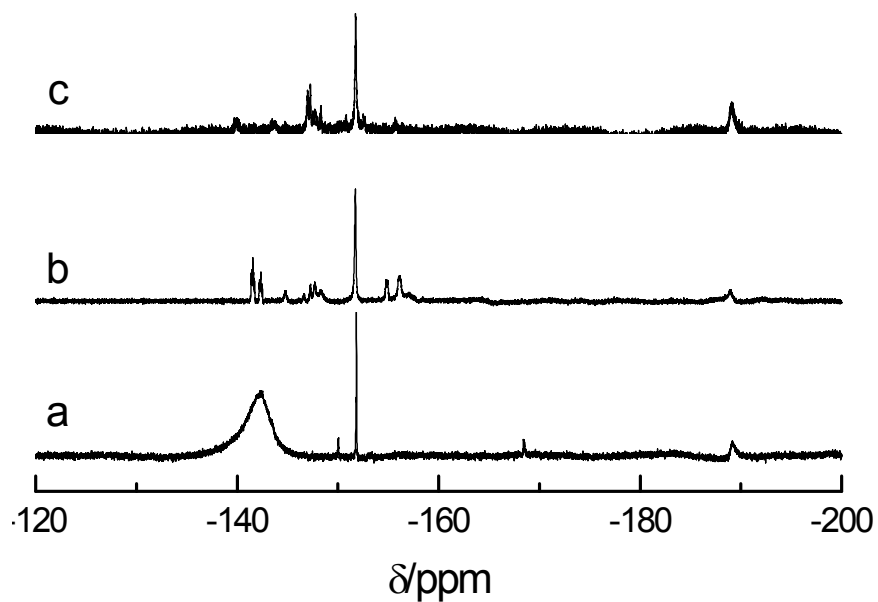


Figure S48. ^{19}F NMR spectra in CD_3CN of (a) 50 mM complex **1**, (b) 50 mM complex **2**, (c) 50 mM complex **1** with 250 mM pyridine.

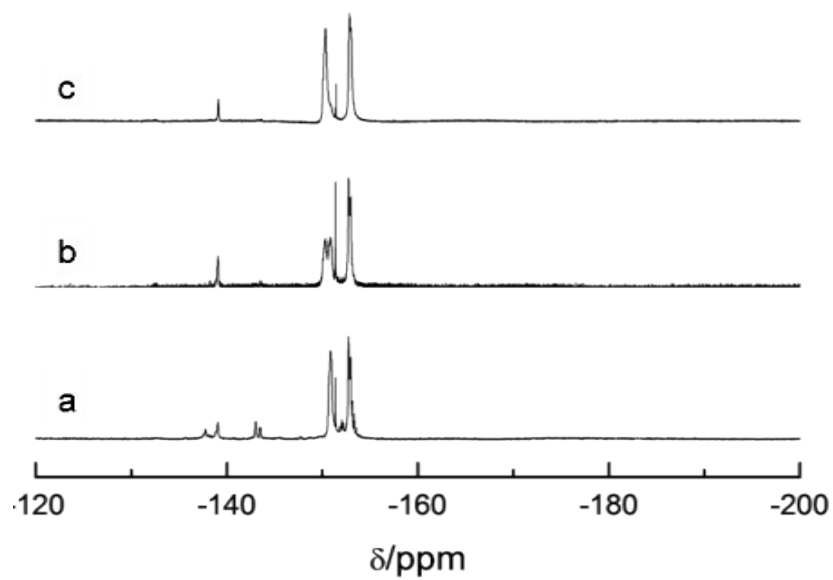


Figure S49. ^{19}F NMR spectra acquired in CD_3CN of (a) 50 mM complex **1** with 500 mM $[\text{Bu}_4\text{N}]\text{BH}_4$; (b) 50 mM complex **2** with 500 mM $[\text{Bu}_4\text{N}]\text{BH}_4$, and (c) 50 mM complex **1** with 250 mM pyridine and 500 mM $[\text{Bu}_4\text{N}]\text{BH}_4$.

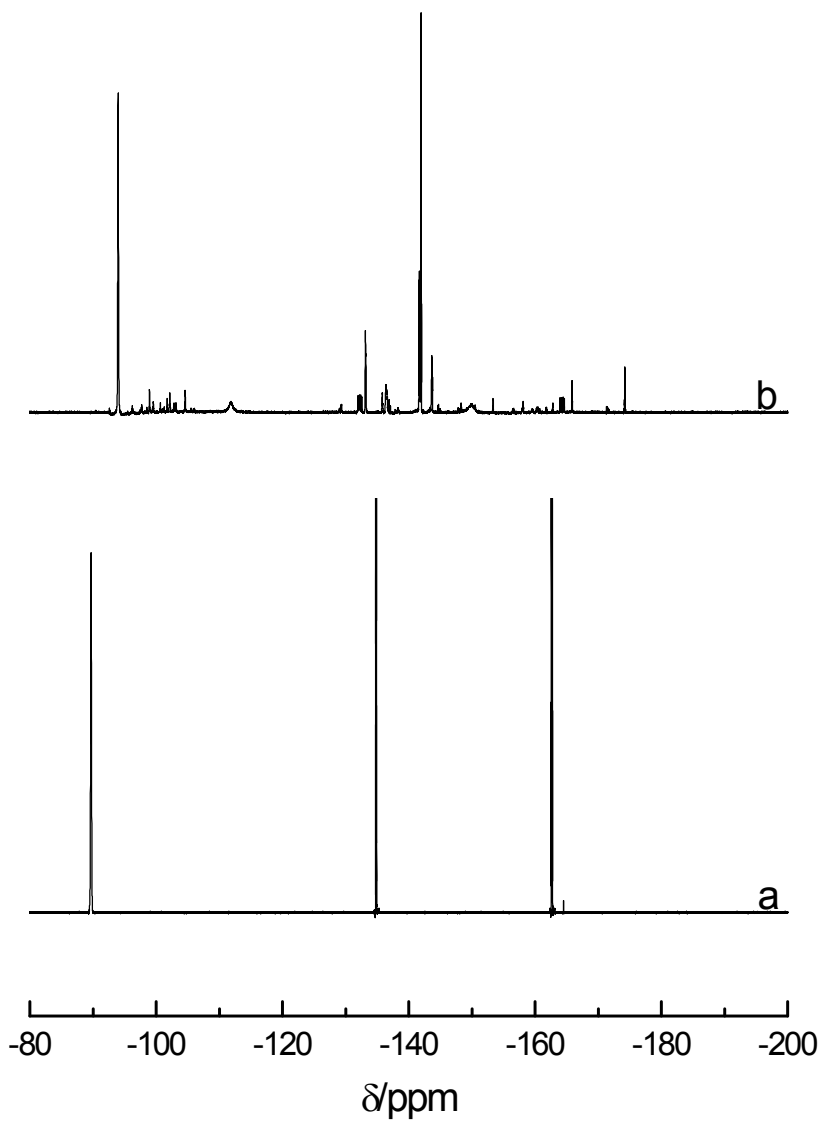


Figure S50. ^{19}F NMR spectra in CD_3CN of (a) 250 mM pentafluoropyridine (pyF_5) and (b) 250 mM pyF_5 with 500 mM $[\text{nBuN}]\text{BH}_4$.

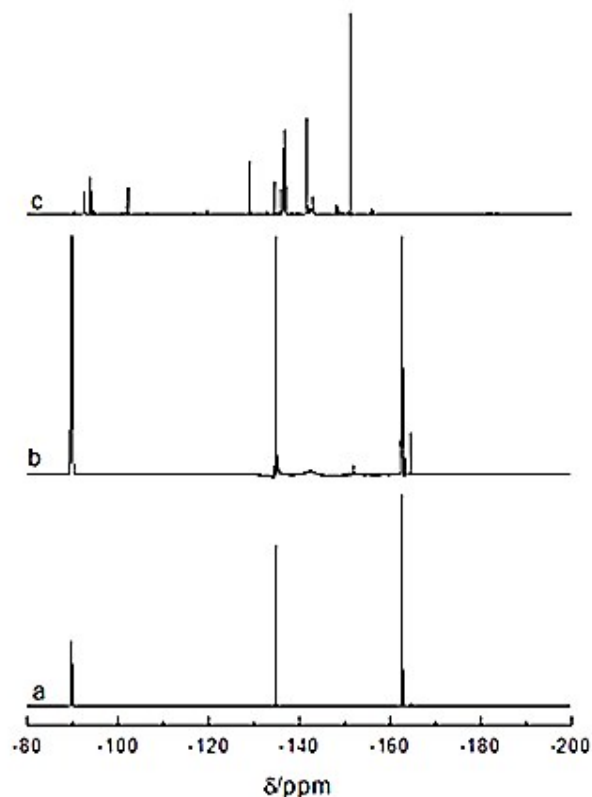
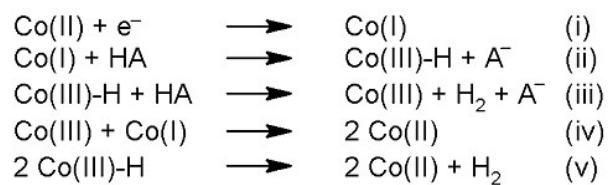


Figure S51. ^{19}F NMR spectra in CD_3CN for (a) 250 mM pyF_5 , (b) 50 mM complex **1** and 250 mM pyF_5 and (c) 50 mM complex **1**, 250 mM pyF_5 and 500 mM $[\text{nBu}_4\text{N}]\text{BH}_4$.

Table S7. ^{19}F and ^{11}B NMR chemical shifts for mixtures of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ (complex **1**), fluorinated pyridines, and tetrabutylammonium tetrafluoroborate in CD_3CN .

Entry	Species/mixture	$\delta_{\text{B}} / \text{ppm}$	$\delta_{\text{F}} / \text{ppm}$
1	Complex 1 + $[\text{nBu}_4\text{N}]\text{BH}_4$ + pyF_5	19.63, 6.11 (t), 3.42, 3.26, 2.06, 1.51, 1.40, 0.95-0.45 (m)	-45.7, -48.4, -49.1, -69.3, -75.1, -89.6, -91.8, -93.2, -95.3, -96.3, -97.5, -98.8, -99.5, -99.9, -100.3, -101.3, -102.0, -103.8, -104.7, -105.4, -105.5, -108.7, -115.8, -118.9, -119.1, -119.9, -122.3, -128.2, -128.5, -130.6, -132.1, -136.0, -137.1, -138.7, -140.9, -141.1, -142.7, -147.4, -147.5, -147.5, -147.65, -147.7, -147.8, -150.6, -164.8, -173.5,
2	Complex 1 + $[\text{nBu}_4\text{N}]\text{BH}_4$ + pyF_4	19.92, 6.09, 3.44, 1.40, 0.79, -1.15, -10.60, -18.99, -19.69	-48.8, -75.1, -89.6, -91.8, -93.2, -95.4, -95.8, -128.2, -128.5, -131.8, -135.0, -135.9, -136.1, -137.2, -138.2, -140.9, -141.1, -142.8, -147.4, -147.5, -147.5, -150.1, -150.6, -150.6, -152.0, -152.2

1.6 Electrocatalytic behavior



Scheme S1. Proposed mechanism for the electrocatalytic reduction of protons (from an acid source, HA) by cobaloximes.¹

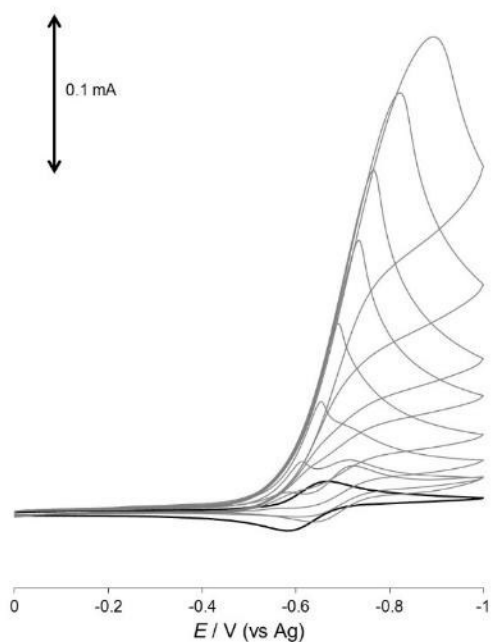


Figure S52. Cyclic voltammograms involving electrocatalysis with complex **2** in CH₃CN. [complex **2**] = 1.08 mM in the absence (black) and presence of aliquots of *p*-cyanoanilinium tetrafluoroborate (3.21, 5.54, 9.52, 13.8, 19.6, 25.3, 34.5, and 44.7 mM), supporting electrolyte = 0.10 M [ⁿBu₄N]ClO₄, and scan rate = 100 mV s⁻¹ at a glassy carbon working electrode versus a Ag quasi-reference electrode.

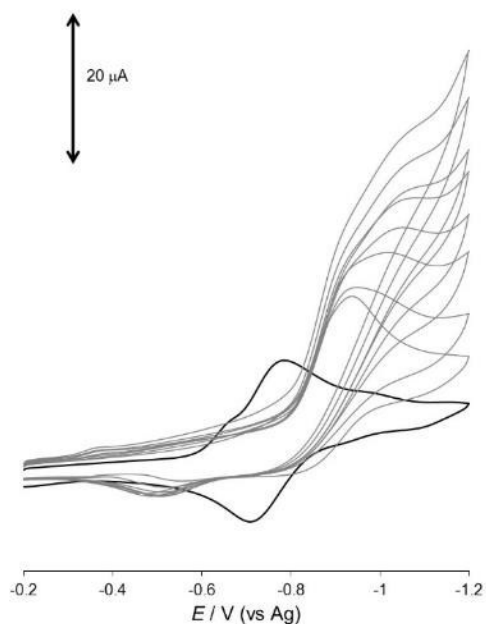


Figure S53. Cyclic voltammograms involving electrocatalysis with complex **1** in acetone. [complex **1**] = 1.08 mM in the absence (black) and presence of aliquots of p -cyanoanilinium tetrafluoroborate (1.80, 3.16, 4.52, 6.17, 8.74, 11.2, 14.9, and 18.6 mM), supporting electrolyte = 0.10 M $[nBu_4N]ClO_4$, and scan rate = 100 mV s^{-1} at a glassy carbon working electrode versus a Ag quasi-reference electrode.

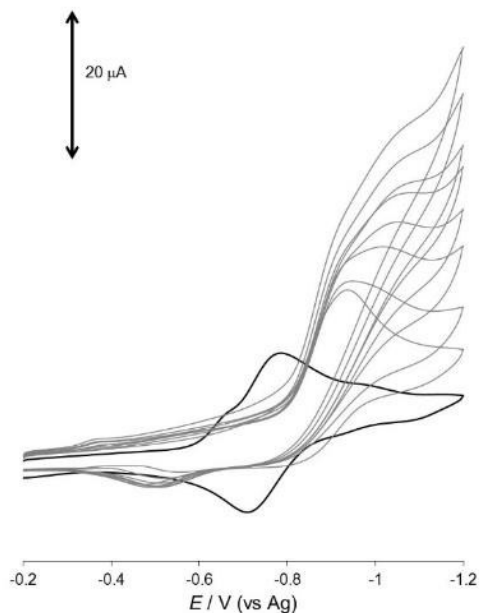


Figure S54. Cyclic voltammograms involving electrocatalysis with complex **2** in acetone. [complex **2**] = 1.08 mM in the absence (black) and presence of aliquots of p -cyanoanilinium tetrafluoroborate (1.70, 3.54, 5.24, 7.28, 9.42, 12.4, 16.1, and 18.7 mM), supporting electrolyte = 0.10 M $[nBu_4N]ClO_4$, and scan rate = 100 mV s^{-1} at a glassy carbon working electrode versus a Ag quasi-reference electrode.

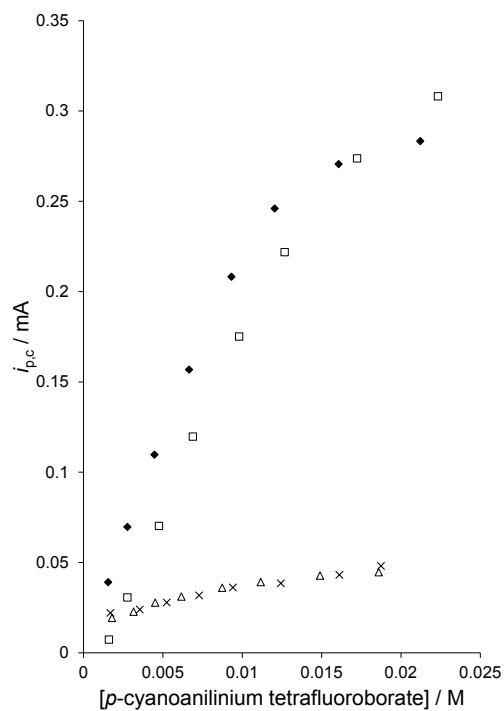


Figure S55. Dependence of the catalytic peak current ($i_{pc,1}$) on the concentration of *p*-cyanoanilinium tetrafluoroborate at a scan rate of 100 mV s⁻¹ for complex **1** (♦: in CH₃CN, Δ: in acetone) and complex **2** (□: in CH₃CN, ×: acetone) in 0.10 M [nBu₄N]ClO₄, at a glassy carbon working electrode versus a Ag quasi-reference electrode.

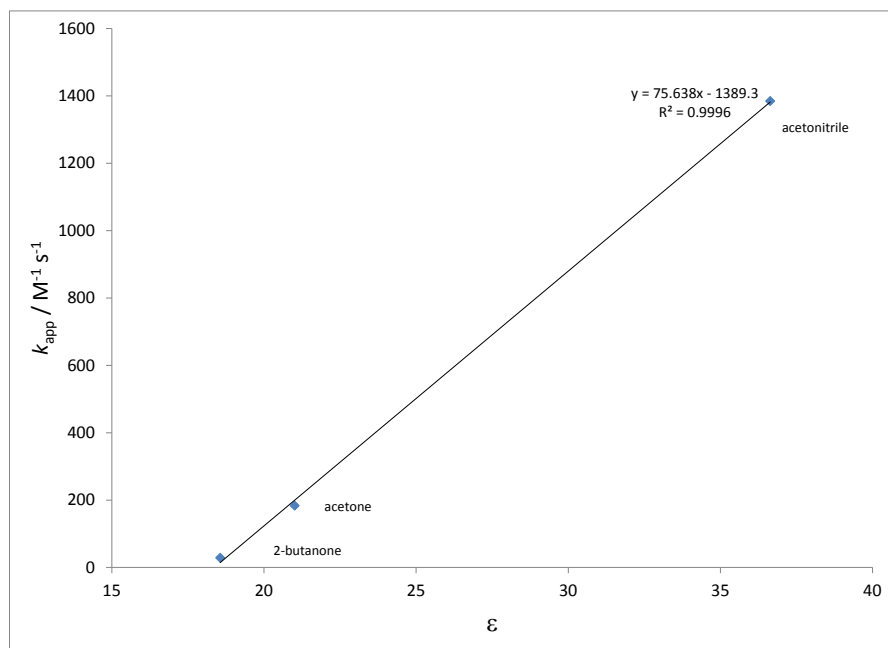


Figure S56. The effect of dielectric constant on k_{app} (from Table 6 of main text) for complex **1**.

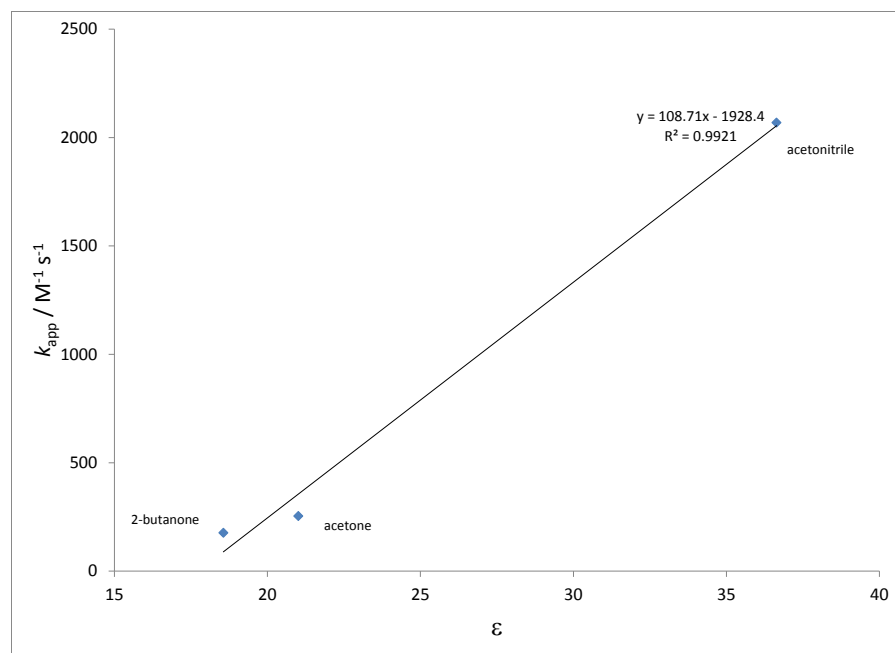


Figure S57. The effect of dielectric constant on k_{app} (from Table 6 of main text) for complex **2**.

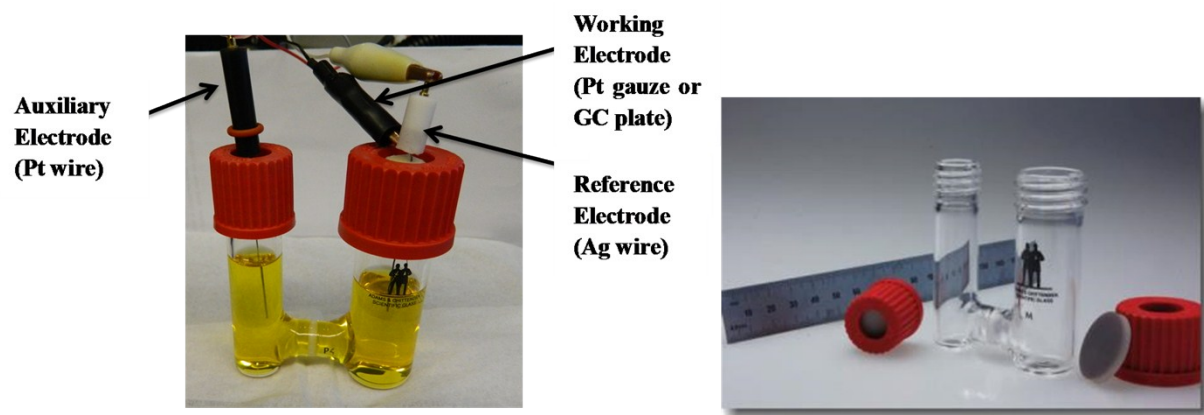


Figure S58. Setup of the H-Cell used for the electrocatalytic generation of hydrogen.

Reference

1. X. Hu, B. S. Brunshwig and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 8988-8998.