

Supporting Information

For

Catalytic Dioxygen Activation by Co(II) Complexes Employing a Versatile Ligand Scaffold

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A. General Considerations

All manipulations were carried out using standard Schlenk techniques or conducted in an MBraun Labmaster 130 drybox under a nitrogen atmosphere. All reagents used were purchased from commercial vendors and used as received unless otherwise noted. Anhydrous solvents were purchased from Sigma-Aldrich and further purified by sparging with Ar gas followed by passage through activated alumina columns. Anhydrous $^{16}\text{O}_2$ was purchased from NexAir and passed through a DrieriteTM column before using. $^{18}\text{O}_2$ (99%) was purchased from Icon Isotopes, New Jersey. Elemental analyses were performed by Midwest Microlab, LLC. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Varian Mercury 300 and Inova 400 MHz spectrometers at ambient temperature. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks. ^{31}P chemical shifts were referenced to phosphoric acid. Infrared spectra were recorded as KBr pellets on a Varian Scimitar 800 Series FT-IR spectrophotometer. UV-Visible absorption spectra were recorded on a Cary50 spectrophotometer using 1.0 cm quartz cuvettes. Solution-state magnetic moments were measured using Evans' method.^{1, 2} Mass spectra were recorded in the Mass Spectrometry Center at Emory University on a JEOL JMS-SX102/SX102A/E mass spectrometer. X-ray diffraction studies were carried out in the X-ray Crystallography Laboratory at Emory University on a Bruker Smart 1000 CCD diffractometer. Cyclic voltammetry experiments were carried out using a CH Instruments (Austin, TX) Model 660C potentiostat. All experiments were conducted in CH_2Cl_2 with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Electrochemical experiments were conducted in a three-component cell consisting of a Pt auxiliary electrode, a non-aqueous reference electrode (Ag/AgNO_3), and either a glassy carbon (CV) or reticulated vitreous carbon (bulk electrolysis) working electrode. All electrochemical measurements are referenced and reported versus the ferrocene/ferrocenium couple.

B. Ligand Synthesis

Bis(2-nitrophenyl)amine [$\text{HN}(o\text{-PhNO}_2)_2$]. Prepared using a modified literature procedure.³ A mixture of 2-nitroaniline (2.0 g, 14.1 mmol) and 1-fluoro-2-nitrobenzene (1.5 mL, 14.1 mmol) was stirred in dimethyl sulfoxide (DMSO, 40 mL) at room temperature. KO^tBu (3.3 g, 29.0 mmol) was added slowly and the reaction stirred under N_2 at room temperature for 24 h. The reaction mixture was then diluted with water (200 mL) and filtered to give a bright orange solid. The solid was recrystallized from MeOH (500 mL) and dried under vacuum to afford the product as a bright orange, crystalline solid (63%, 2.30 g). ^1H NMR (δ , CDCl_3 , 300 MHz): 11.02 (s, 1H), 8.21 (dd, 2H, $J = 1.5$), 7.56 (m, 4H), 7.10 (td, 2H, $J = 1.8$ Hz, $J = 1.5$ Hz). ^{13}C NMR (δ , CDCl_3 , 75.5 MHz): 137.40, 134.30, 127.01, 121.32, 119.20. HRMS(ESI): $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_4$ m/z Calcd. 259.0593, Found 260.06584 [$\text{M}+1$]⁺. FTIR (KBr, cm^{-1}): $\nu(\text{NO}_2)$ 1514, 1334, $\nu(\text{NH})$ 3303. UV-vis (CH_2Cl_2) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 430 (14100), 268 (35700).

Bis(2-aminophenyl)amine [$\text{HN}(o\text{-PhNH}_2)_2$]. Prepared using a modified literature procedure.⁴ To a THF (50.0 mL) solution of $\text{HN}(o\text{-PhNO}_2)_2$ (2.0 g, 7.7 mmol) was added 5 wt.% Pd/C (1.0 g, 0.5 mmol, 6 mol%). The reaction mixture was placed in a pressure-safe reaction vessel and shaken under H_2 at 50 psi for 45 min. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo to obtain a thick, colorless oil. Crystalline product can be obtained by layering a concentrated ether solution of the compound with hexanes (1.38 g, 90%). ^1H NMR (δ , CDCl_3 , 300 MHz): 6.93 (m, 4H, ArH), 6.79 (m, 4H, ArH), 5.05 (s, 1H, NH), 3.64 (s, 4H, NH). ^{13}C NMR (δ , CDCl_3 , 75.5 MHz): 138.56, 131.21, 124.12, 122.61, 120.84, 118.78. HRMS(ESI): $\text{C}_{12}\text{H}_{13}\text{N}_3$ m/z Calcd. 199.11095 Found 200.11751 [$\text{M}+1$]⁺. FTIR (KBr, cm^{-1}): $\nu(\text{NH})$ 3413, 3375, and 3344.

2,2'-Bis(isobutyrylamido)diphenylamine ($\text{HN}(o\text{-PhNHC(O)}^i\text{Pr})_2$). A suspension of $\text{HN}(o\text{-PhNH}_2)_2$ (1.32 g, 6.6 mmol) in dichloromethane (CH_2Cl_2 , 50 mL) was lowered to 0 °C under an atmosphere of N_2 . Triethylamine (2.02 mL, 14.5 mmol) was then added, followed by isobutyryl chloride (1.53 mL, 14.5 mmol). The mixture stirred at 0 °C for 1 hour. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 hours. The resulting pale brown solution was extracted with a saturated aqueous NaHCO_3 (3 x 30 mL) solution. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude solid was recrystallised by layering

hexanes onto a concentrated CH_2Cl_2 solution of the product (1.78 g, 80%). ^1H NMR (δ , CDCl_3 , 300 MHz): 7.83 (s, 2H, NH(CO)), 7.67 (d, 2H, $J = 1.6$ Hz, ArH), 7.04 (m, 4H, ArH), 6.88 (d, 2H, $J = 1.2$ Hz, ArH), 5.75 (s, 1H, NH), 2.58 (q, 2H, $J = 6.8$ Hz, CH), 1.16 (d, 12H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (δ , CDCl_3 , 75.5 MHz): 176.48, 136.02, 129.26, 126.27, 124.18, 123.0, 121.11, 36.20, 19.76. HRESI-MS: $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_2$ m/z Calcd. 339.19468 Found 340.20150 $[\text{M}+1]^+$. FTIR (KBr, cm^{-1}): $\nu(\text{NH}_{\text{amide}})$ 3230, $\nu(\text{NH}_{\text{amine}})$ 3367, $\nu(\text{CO})$ 1660.

C. Complex Syntheses

Synthesis of $(\text{Et}_4\text{N})_2[\mathbf{1}]$

To a solution of $\text{HN}(o\text{-PhNHC(O)}^i\text{Pr})_2$ (114.0 mg, 0.34 mmol) in DMF, (10 mL) was added potassium hydride (29.67 mg, 0.74 mmol). When gas evolution ceased, CoBr_2 (36.77 mg, 0.17 mmol) was added as a solid. When the reaction mixture became homogenous, tetraethylammonium bromide (70.67 mg, 0.34 mmol) was added to the red solution. After stirring for 3 h, the DMF was removed under high vacuum and the resulting solid was dissolved in CH_3CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Bulk recrystallization was obtained by diffusing diethylether into a concentrated CH_2Cl_2 solution containing the product. Red, X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated DMF solution of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ (120 mg, 72%). ^1H NMR (δ , CD_3CN , 400 MHz): -70.03 (s), -63.80 (s), -46.48 (s), -37.23 (s), -16.31 (s), -14.7 (s), -4.11 (s), 1.32 (s), 3.60 (s), 4.90 (s), 6.36 (s), 8.56 (s), 9.22 (s), 12.39 (br), 17.67 (br), 23.44 (s), 27.01 (s), 56.50 (s), 60.54 (s). FTIR (KBr, cm^{-1}): $\nu(\text{NH})$ 3388, $\nu(\text{CO})$ 1681. Anal. Calcd (found) for $(\text{Et}_4\text{N})_2[\mathbf{1}]\cdot\text{CH}_2\text{Cl}_2$: C, 63.44 (63.27); H, 8.22 (8.50); N, 10.38(10.02). $\mu_{\text{eff}} = 4.37 \mu_{\text{B}}$ (Evans Method, CD_2Cl_2 , 298K). λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (DMF): 634 (sh), 569 (640), 535 (sh); λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (CH_2Cl_2): 636 (sh), 573 (570), 534 (sh); λ_{max} , nm (solid, silicon oil): 211, 255, 360, 573.

Synthesis of $(\text{Et}_4\text{N})_2[\mathbf{2}]$

To a solution of $\text{HN}(o\text{-PhNHC(O)}^i\text{Pr})_2$ (99.3 mg, 0.29 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (41.11 mg, 1.0 mmol). When gas evolution ceased, CoBr_2 (64.06 mg, 0.29 mmol) was added as a solid and the mixture stirred for 1 h. Tetraethylammonium bromide (61.55 mg, 0.29 mmol) was then added to the deep green solution. After stirring for 3 h, DMF was removed under vacuum and the resulting solid was dissolved in CH_3CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Dark green, X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated DMF solution of the product (70%, 108 mg). ^1H NMR (δ , CD_2Cl_2 , 400 MHz): -46.28 (s), -40.05 (s), -1.12 (s), 0.71 (s), 10.92 (s), 25.99 (s), 28.64 (s), 65.20 (s). FTIR (KBr, cm^{-1}): $\nu(\text{CO})$ 1592. Anal. Calcd (found) for $(\text{Et}_4\text{N})_2[\mathbf{2}]$: C, 63.98 (63.64); H, 8.05 (7.95); N, 10.66 (11.01). $\mu_{\text{eff}} = 4.73 \mu_{\text{B}}$ (Evans Method, CD_2Cl_2 , 298K). λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (DMF): 600 (770), 926 (133); λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (CH_2Cl_2): 609 (749), 926 (106); λ_{max} , nm (solid, silicon oil): 253, 343, 455 (sh), 644.

Synthesis of $(\text{Et}_4\text{N})[\mathbf{1}]$

To a red solution of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ (237.6 mg, 0.239 mmol) in acetonitrile (CH_3CN , 10 mL) was added ferrocenium tetrafluoroborate (FcBF_4) (65.23 mg, 0.239 mmol) as an CH_3CN solution (3 mL). After stirring for 12 h, the solvent was removed under vacuum, and the resulting solid was dissolved in THF and filtered to remove Et_4NBF_4 . The deep blue filtrate was then concentrated to dryness. The deep blue solid that resulted was washed with hexanes (3 x 5 mL) to remove ferrocene, and the crude solid was collected on a frit. Fine blue crystals can be obtained by layering hexanes onto a CH_2Cl_2 solution of the product (149 mg, 72%). ^1H NMR (δ , CD_3CN , 400 MHz): -39.08 (s), -37.15 (d), -26.99 (s), -25.34 (s), -21.74 (s), -18.61 (s), -11.74 (s), -9.59 (s), -9.10 (br), -6.46(s), -2.65 (s), 1.17 (s), 3.16 (s), 5.74 (s), 6.93 (t), 7.31 (s), 7.57 (s), 7.81 (s), 10.16 (br), 12.0 (s), 13.11 (s), 14.27 (s), 16.80 (s), 22.71 (s), 36.98 (s), 38.03 (s), 42.05 (s), 51.23 (s), 54.38 (d). FTIR (KBr, cm^{-1}): $\nu(\text{NH})$ 3378. λ_{max} (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (CH_2Cl_2): 300 (25540), 455 (55030), 582 (6770), 805 (4230). HRESI-MS: for $[\mathbf{1}]^+$ Calcd (m/z): 733.29125, Found 733.29180. $\text{Et}_4\text{N}[\mathbf{1}]$. Anal. Calcd (found) for $(\text{Et}_4\text{N})[\mathbf{1}]\cdot 0.25\text{CH}_2\text{Cl}_2$: C, 65.46 (65.11); H, 7.57 (7.53); N, 11.08 (10.87).

D. Catalytic Oxidation Procedures

Typical procedure for $(\text{Et}_4\text{N})_2[\mathbf{1}]$: Under an inert atmosphere, a 25 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.53 g, 2.0 mmol), $(\text{Et}_4\text{N})_2[\mathbf{1}]$ (0.02 g, 0.020 mmol), and 10 mL of CH_3CN . The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring at room temperature, a constant slow purge of O_2 (1 atm) was then introduced to flask by connecting it, via 18-gauge needles inserted through the septum, to an O_2 line and to a mineral oil gas bubbler. Reactions were monitored by GC (traces compared to authentic samples of PPh_3 and OPPh_3). After 2 hours, 69% of the PPh_3 had been converted to OPPh_3 (1.38 mmol, 0.39 g). Isolate yield of OPPh_3 confirmed by GC and ^{31}P NMR. Catalytic oxidations were run in triplicate and conversion numbers (yields of OPPh_3) in good agreement ($\pm 3\%$).

Typical procedure for $(\text{Et}_4\text{N})_2[\mathbf{2}]$: Under an inert atmosphere, a 25 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.498 g, 1.9 mmol), $(\text{Et}_4\text{N})_2[\mathbf{2}]$ (0.02 g, 0.019 mmol), and 12 mL of CH_3CN . The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring at room temperature, a constant slow purge of O_2 (1 atm) was then introduced to flask by connecting it, via 18-gauge needles inserted through the septum, to an O_2 line and to a mineral oil gas bubbler. Reactions were monitored by GC (traces compared to authentic samples of PPh_3 and OPPh_3). After 2 hours, 95% of the PPh_3 had been converted to OPPh_3 (0.50 g, 1.81 mmol). Isolated yields of OPPh_3 confirmed by GC and ^{31}P NMR. Catalytic oxidations were run in triplicate. Catalytic oxidations were run in triplicate and conversion numbers (yields of OPPh_3) in good agreement ($\pm 3\%$).

Reactions with $^{18}\text{O}_2$: Typical experiment: Under an inert atmosphere, a 10 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.030 g, 0.10 mmol), $(\text{Et}_4\text{N})_2[\mathbf{2}]$ (0.0107 g, 0.010 mmol), and 5 mL of CH_3CN . The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring, $^{18}\text{O}_2$ was then introduced to flask via syringe. Incorporation of ^{18}O from the $^{18}\text{O}_2$ into the oxidized product was confirmed by mass spectrometry.

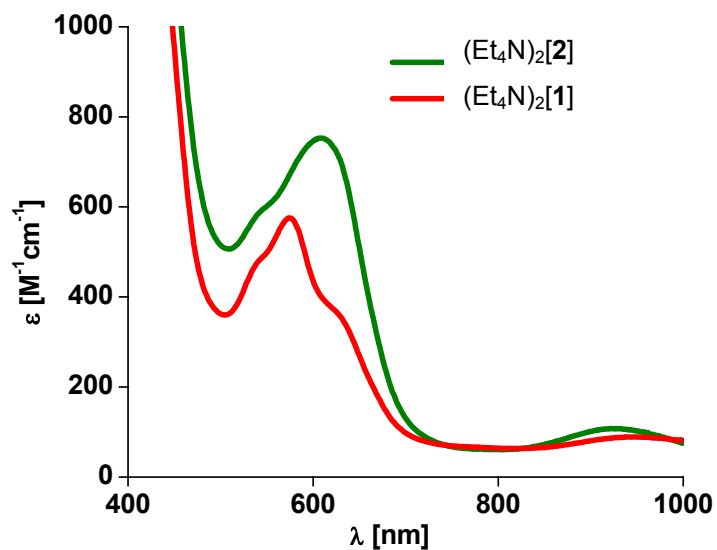


Figure S1: UV-Visible absorption spectra of (Et₄N)₂[2] (green) and (Et₄N)₂[1] (red) in CH₂Cl₂.

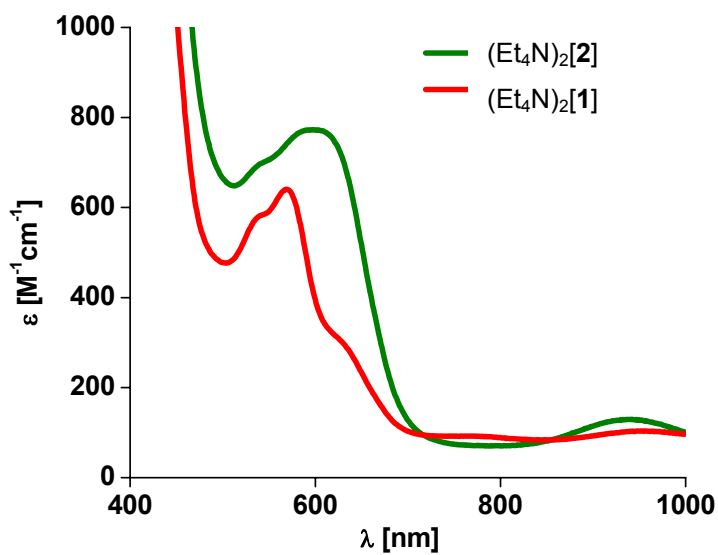


Figure S2: UV-Visible absorption spectra of (Et₄N)₂[2] (green) and (Et₄N)₂[1] (red) in DMF.

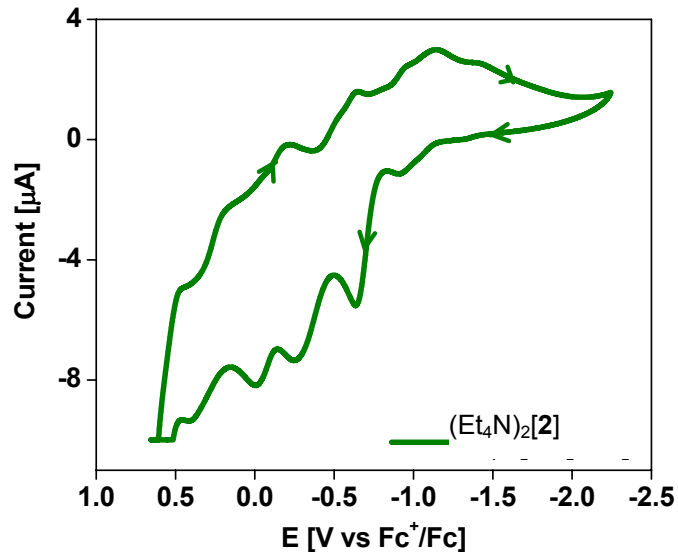


Figure S3: Cyclic voltammogram of $(\text{Et}_4\text{N})_2[2]$ recorded in CH_2Cl_2 (0.10 M $n\text{Bu}_4\text{NPF}_6$) at room temperature at 100 mV/s.

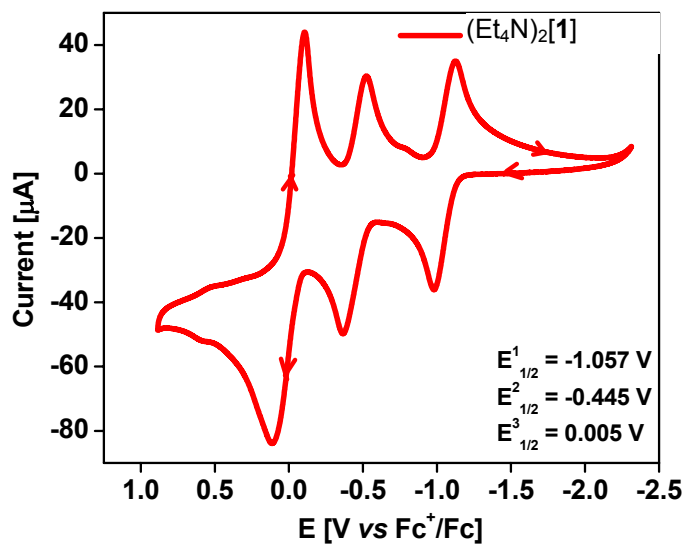


Figure S4: Cyclic voltammogram of $(\text{Et}_4\text{N})_2[1]$ recorded in CH_2Cl_2 (0.10 M $n\text{Bu}_4\text{NPF}_6$) at room temperature at 100 mV/s (ΔE_p for $E^1_{1/2}$, $E^2_{1/2}$ and $E^3_{1/2}$ are 143.5 mV, 170 mV and 216 mV; i_p^a/i_p^c are 1.1, 1.3 and 0.86, respectively).

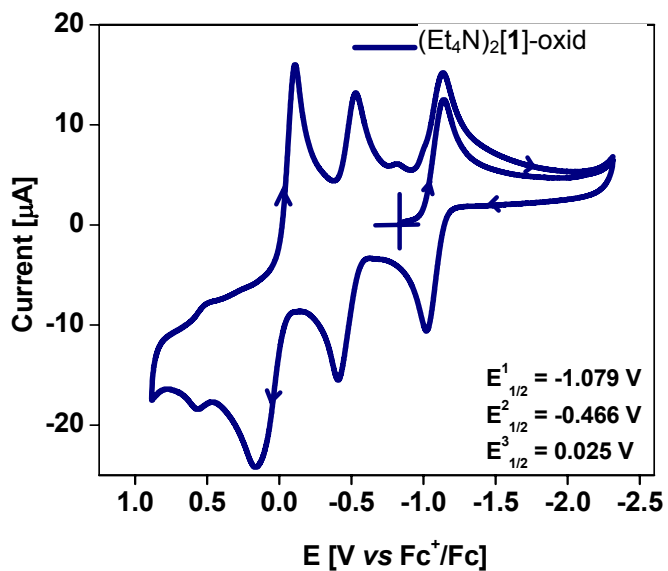


Figure S5: Cyclic voltammogram of electrochemically oxidised (Et₄N)₂[1] after first oxidation in CH₂Cl₂ (0.10 M ^tBu₄NPF₆) at 100 mV/s.

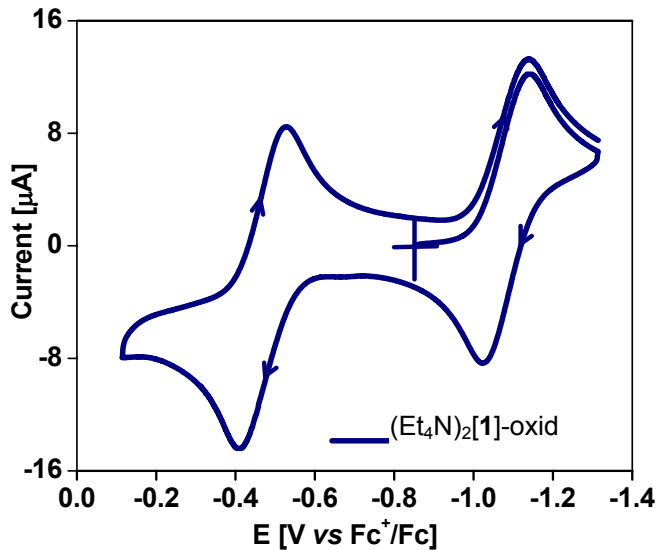


Figure S6: Cyclic voltammogram of electrochemically oxidised (Et₄N)₂[1] after first oxidation in CH₂Cl₂ (0.10 M ^tBu₄NPF₆) at 100mV/s.

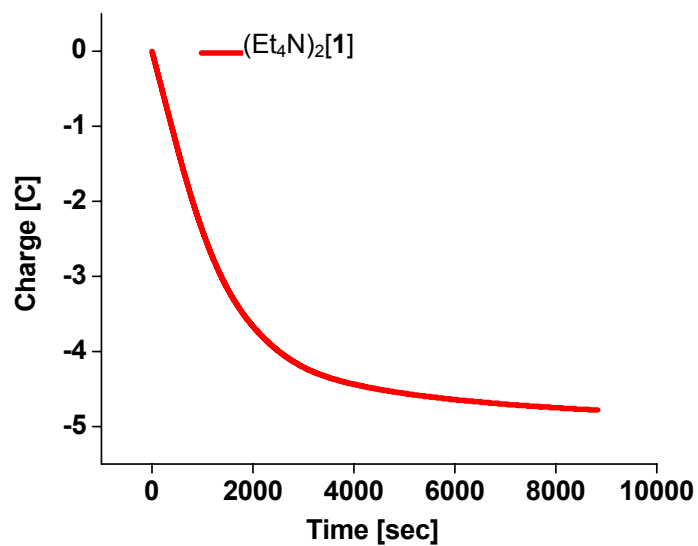


Figure S7: Charge vs. time plot for bulk electrolysis of $(\text{Et}_4\text{N})_2[1]$ in CH_2Cl_2 at room temperature.

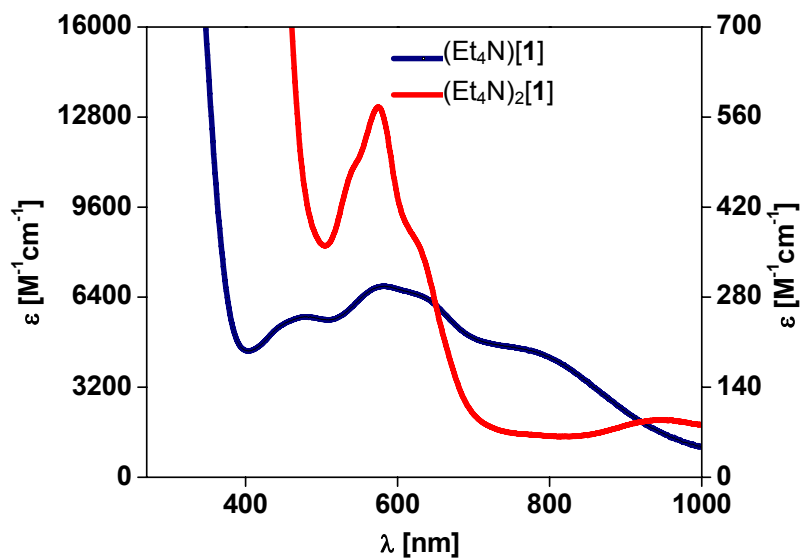


Figure S8: Overlay of UV-Visible absorption spectra of $(\text{Et}_4\text{N})[1]$ (blue) and $(\text{Et}_4\text{N})_2[1]$ (red) in CH_2Cl_2 .

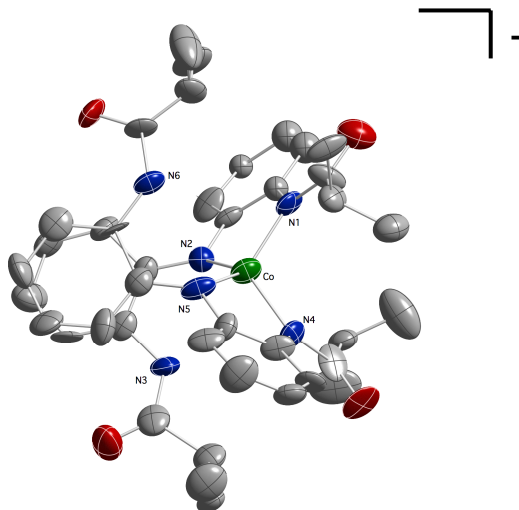


Figure S9. Thermal ellipsoid diagram of (Et₄N)[**1**] drawn at 50% probability. Hydrogen atoms, tetraethylammonium counter cation, and solvent (CH₂Cl₂) have been removed for clarity. Selected bond distances (Å): Co–N1 1.933(14), Co–N2 1.943(14), Co–N4 1.933(13), Co–N5 1.923(15) and angles (°): N1–Co–N5 132.7(6), N1–Co–N2 87.3(6), N5–Co–N4 85.1(6), N1–Co–N4 114.6(4) N5–Co–N2 111.7(5) N4–Co–N2 131.8(6).⁵

References & Notes.

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2. Sur, S. K., *Journal of Magnetic Resonance (1969-1992)* **1989**, 82, (1), 169-173.
3. Gorvin, J. H., *J. Chem. Soc. Perkin Trans. 1* **1988**, 6, 1331-1335.
4. Black, D. S.; Rothnie, N. E., *Australian Journal of Chemistry* **1983**, 36, (6), 1141-1147.
5. Crystal data for (Et₄N)[**1**]: C_{49.47} H_{68.94} Cl_{2.94} CoN₇O₄, *M* = 988.85, 0.29 x 0.18 x 0.07 mm³, Triclinic, space group *P*-1, *a* = 12.264(10) Å, *b* = 14.280(12) Å, *c* = 15.642(13), *V* = 2593(4), *Z* = 2, ρ = 1.266 g cm⁻³, μ = 531 mm⁻¹, *F*(000) = 1047, *T* = 173(2) K, *R*(*F*² > 2 σ) = 0.1377, *wR*₂ = 0.2424, 9133 independent reflections, [θ _{range} = 1.34 – 25.0°] and 560 parameters, GOF on *F*² = 1.096.