Supporting Information for:

Structural and Electronic Characterization of Multi-Electron Reduced Naphthalene(BIAN)-Cobaloximes

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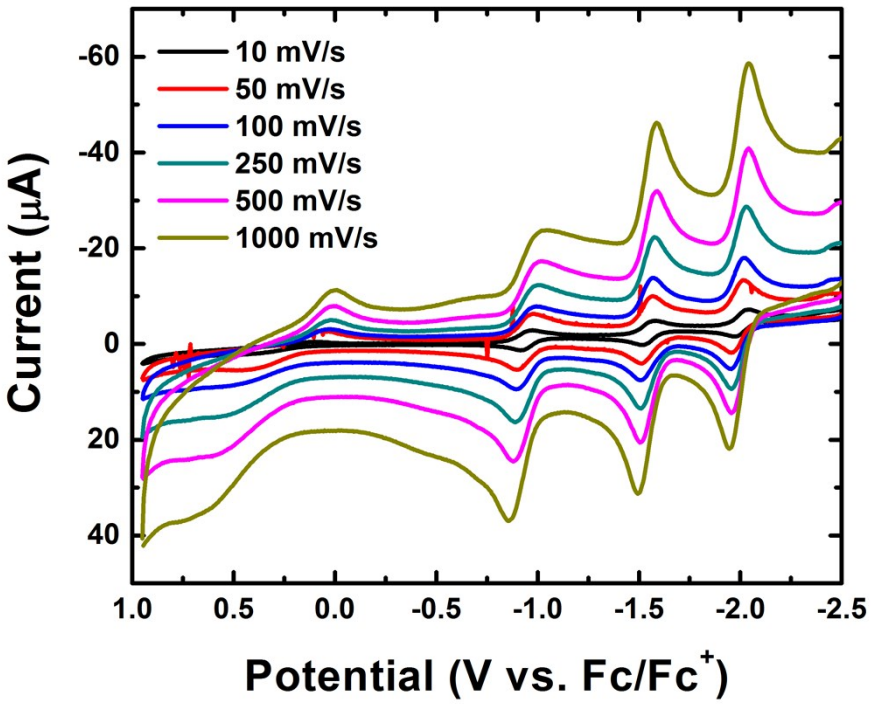

Figure S1. Scan rate dependence of $[Co(aqdBF_2)_2]$ in 0.1 M NBu_4PF_6/DMF.

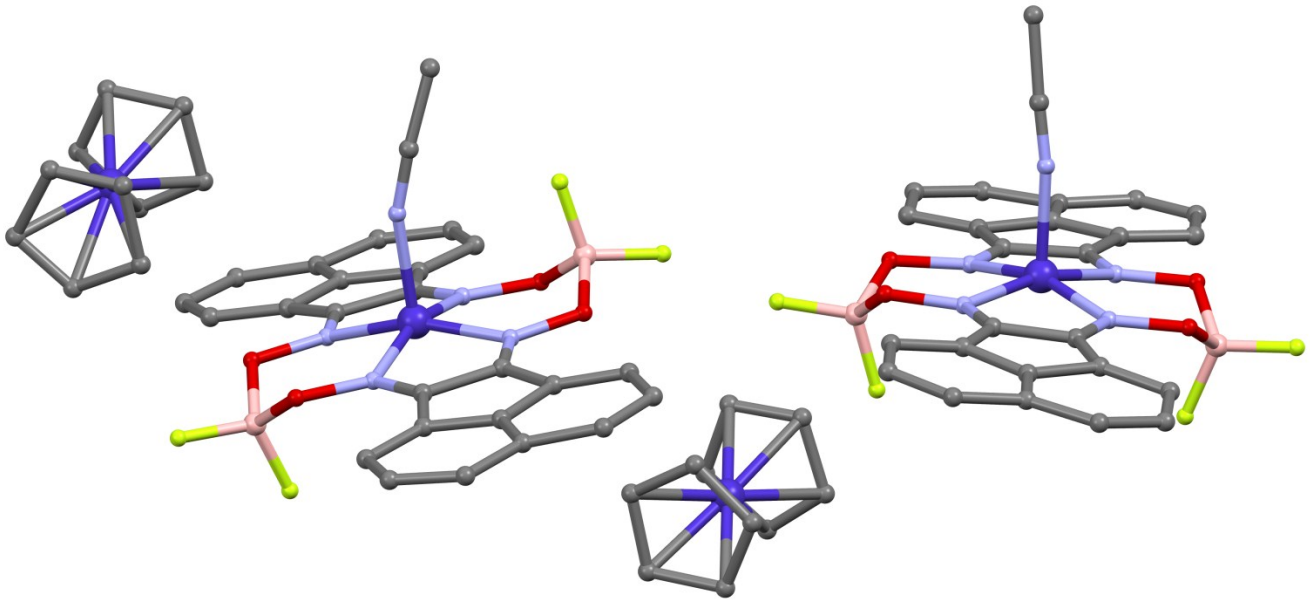

Figure S2. Ball and stick representation of the connectivity structure for the 1-electron reduced complex $[CoCp_2][Co(aqdBF_2)_2(MeCN)]$. The asymmetric unit is shown, and H-atoms have been omitted for the sake of clarity.

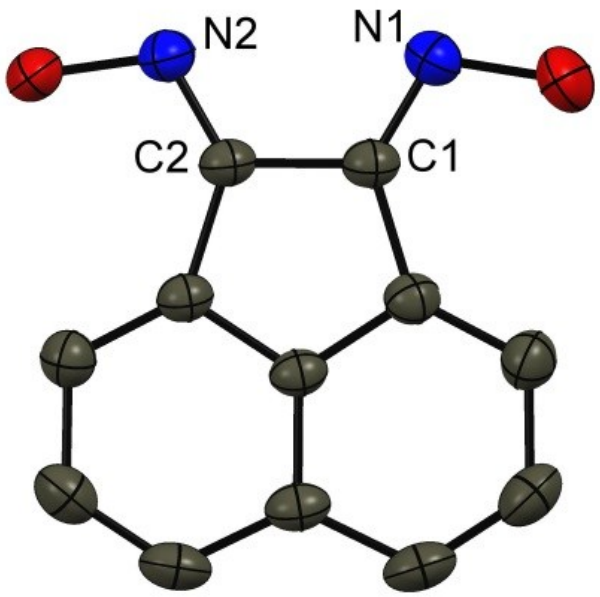

Figure S3. ORTEP diagram (50% thermal ellipsoid plots) of the ligand aqdH$_2$. Hydrogen atoms have been omitted for clarity.

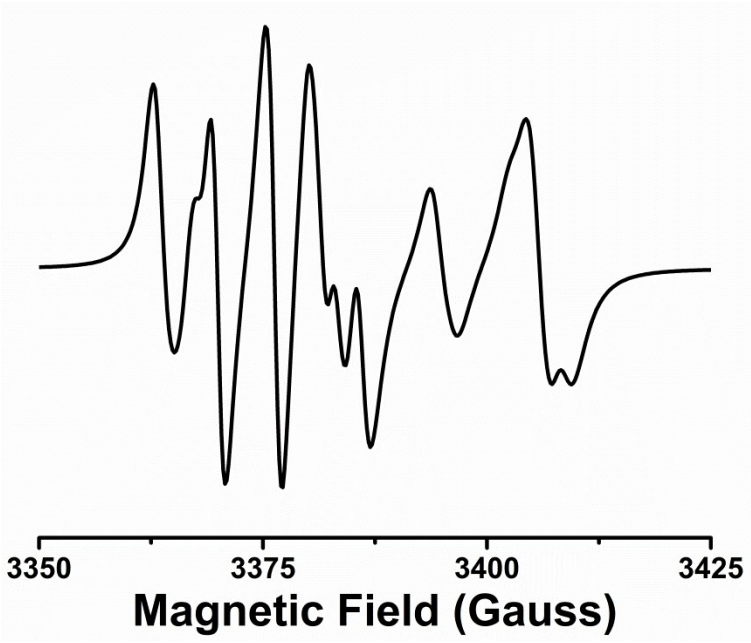

Figure S4. Poly-crystalline EPR of [K(dibenzo-18-crown-6)]$_2$[Co(aqdBF$_2$)$_2$] (**3**) obtained at 85 K. Parameters: frequency, 9.45 GHz; modulation, 100 kHz; power 10 mW; field modulation, 0.1 G.

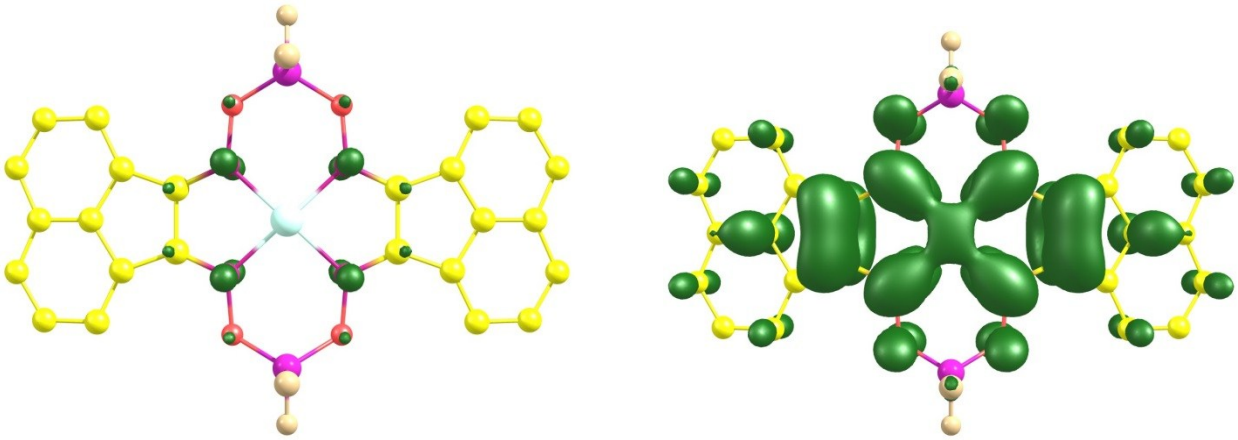

Figure S5. DFT calculated spin density plot for the anion of $[K(dibenzo\text{-}18\text{-}crown\text{-}6)]_2[Co(aqdBF_2)_2]$ (**3**). The spin density surfaces from the *same calculation* are displayed here at two different isosurface values: 0.01 (*left*) and 0.001 (*right*). Note the comparatively small extent of spin density at the cobalt center as compared with the ligand framework.

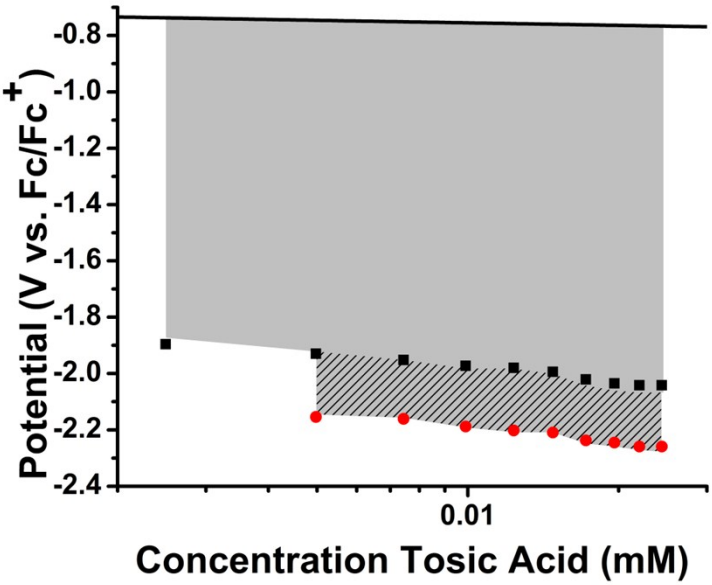

Figure S6. Catalytic reduction "half-wave" potential determined by the derivative technique plotted vs. ln[TsOH]. Overpotentials were determined by comparison with $E_{½}$ (black line). Equations used for the determination of theoretical half wave potential calculation are given below.[1,2]

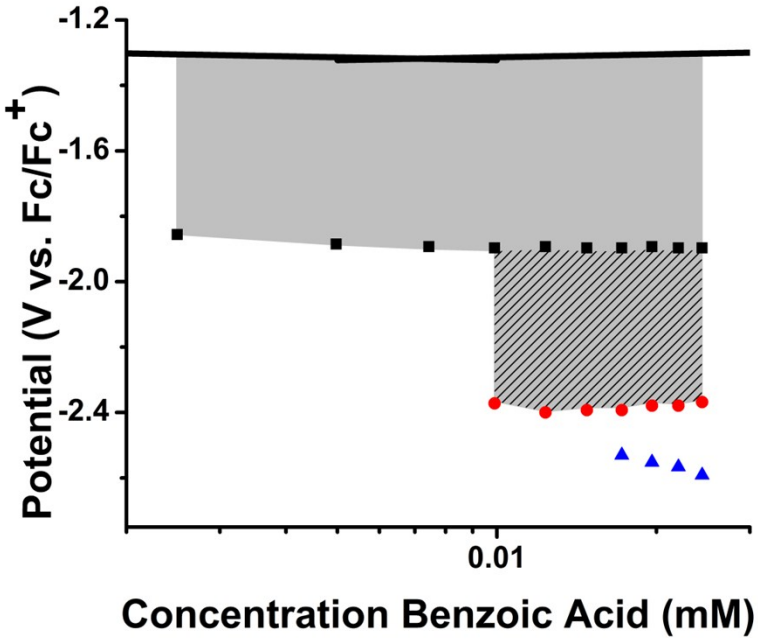

Figure S7. Catalytic reduction 'half-wave' potential determined by the derivative technique plotted vs. ln[$PhCO_2H$]. Overpotentials were determined by comparison with $E_{½}$ (black line), with homoconjugation effects taken into account. Equations used for the determination of theoretical half wave potential calculation are given below.[1,2]

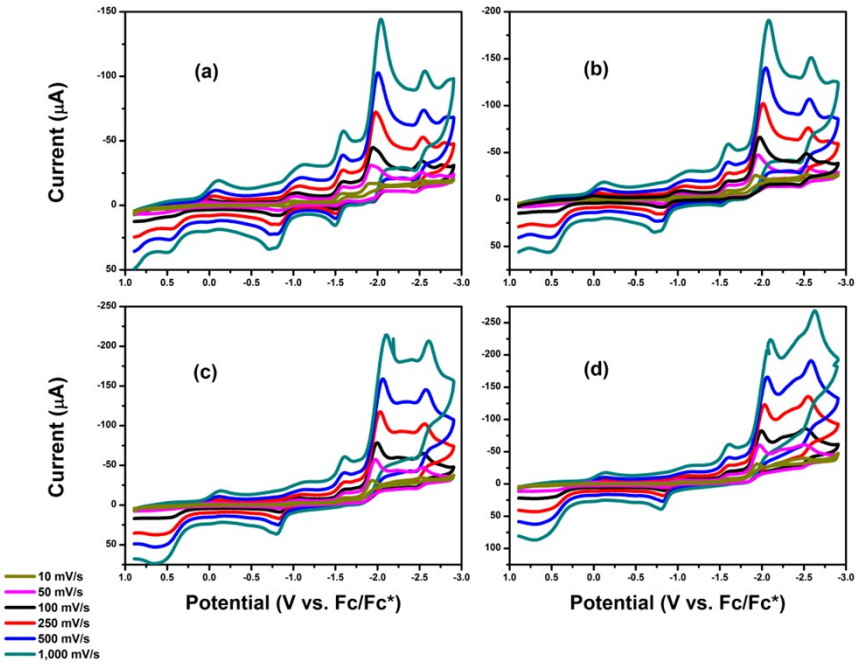

Figure S8. Variation of scan rate (10 - 1,000 mV/s) of $[Co(aqdBF_2)_2(DMF)_2]$ in the presence of (a) 2.5, (b) 5.0, (c) 7.5, and (d) 10 equivalents of benzoic acid.

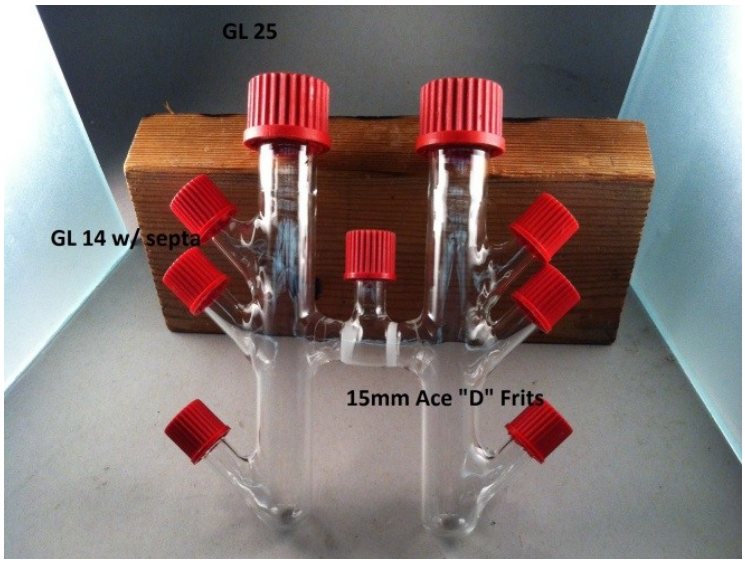

Figure S9. Custom H-cell used in bulk electrolysis experiments.

References

(1) Fourmond, V.; Jacques, P.-A.; Fontecave, M.; Artero, V. *Inorg. Chem.* **2010**, *49*, 10338–10347.

(2)
$$E_{½}^{T} = E_{H^+/H_2}^{0} - \frac{2.303 \times RT}{F} pK_\alpha + \varepsilon_D - \frac{RT}{2F} ln \frac{C_0}{C_{H_2}^{0}}$$

$$E_{½}^{T} = E_{H^+/H_2}^{0} - \frac{2.303 \times RT}{F} pK_\alpha + \varepsilon_D + \frac{RT}{2F} ln (2K_C^2 C_0 C_{H_2}^{0})$$