Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Development and Understanding of Cobaloxime Activity through Electrochemical Molecular Catalyst Screening

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Table S1. Crystal data, structure refinement details and selected bond lengths for [CoCl(dmgH)$_2$(4-methoxypyridine)] (Compound **A**, see Figure 6 for atom labelling scheme).

Parameter	**Value**	**Bond**	**Length (Å)**
Chemical Formula	$C_{32}H_{52}Cl_2N_{10}O_{11}Co_2$	Co–N(1)	1.963(1)
Fw gmol^{-1}	941.60	Co–N(2)	1.903(1)
Space group	$P2_1/n$	Co–N(3)	1.905(1)
a (Å)	8.0000(1)	Co–N(4)	1.895(1)
b (Å)	13.5322(2)	Co–N(5)	1.885(1)
c (Å)	19.2803(3)	Co–Cl	2.2302(4)
α (°)	90		
β (°)	92.183(1)		
γ (°)	90		
V (Å^3)	2085.72		
Z	2		
d_{calcd} (g cm^{-3})	1.499		
μ (cm^{-1})	9.91		
T (K)	180		
R1	0.0387		
wR2	0.1164		

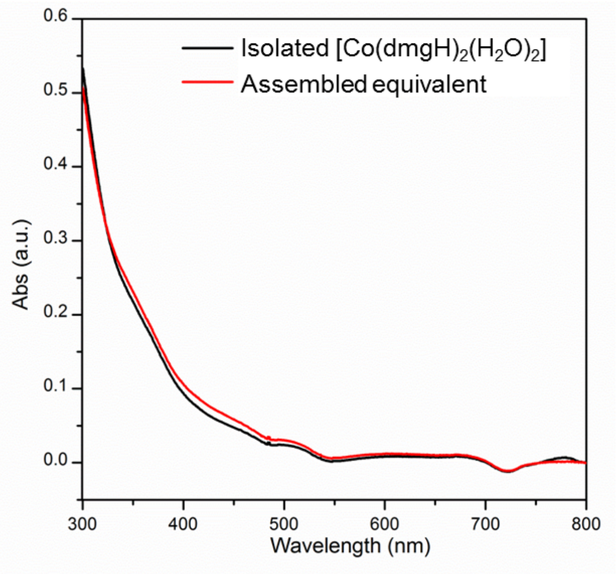

Figure S1. The *in situ* assembly of $[Co(dmgH)_2(H_2O)_2]$ was monitored *via* UV-vis spectroscopy by comparison to an authentic sample of $[Co(dmgH)_2(H_2O)_2]$ synthesised according to a published procedure.[1] The UV-vis spectra show dissolved $[Co(dmgH)_2(H_2O)_2]$ *and* the corresponding *in situ* assembled complex in H_2O (0.08 mM).

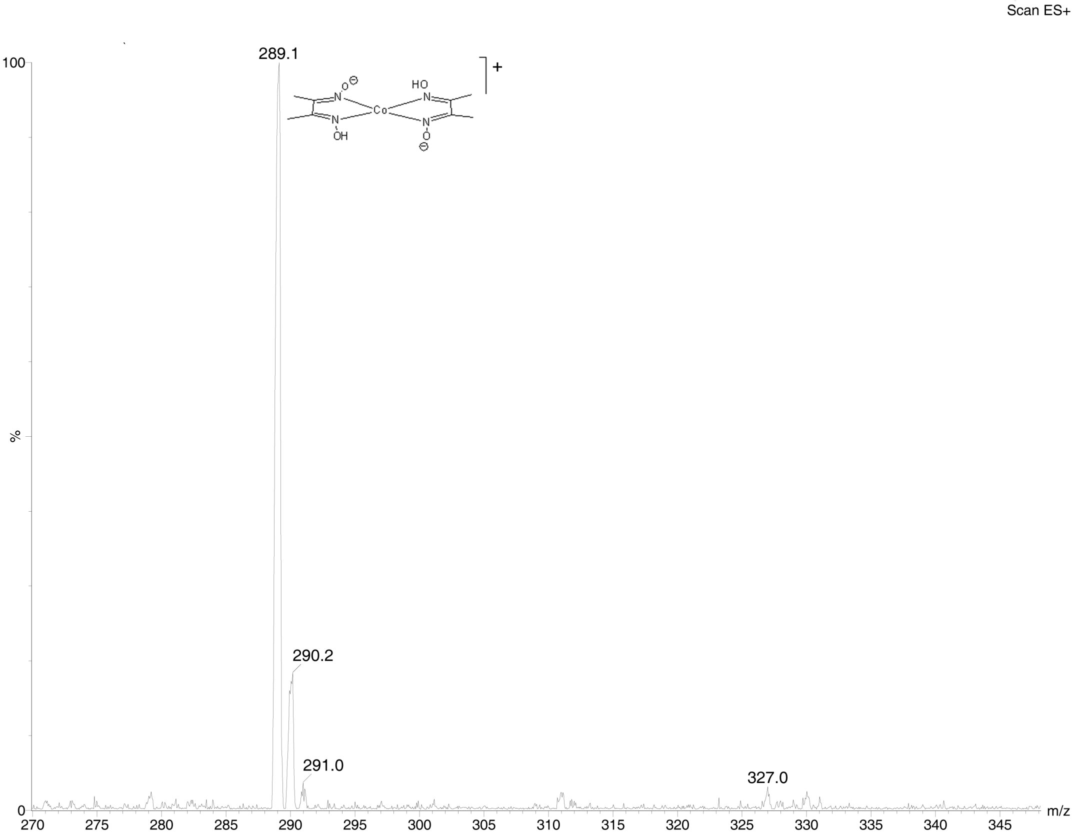

Figure S2. ESI-mass spectrum (+ve mode) of assembled $[Co(dmgH)_2(H_2O)_2]$ in H_2O.

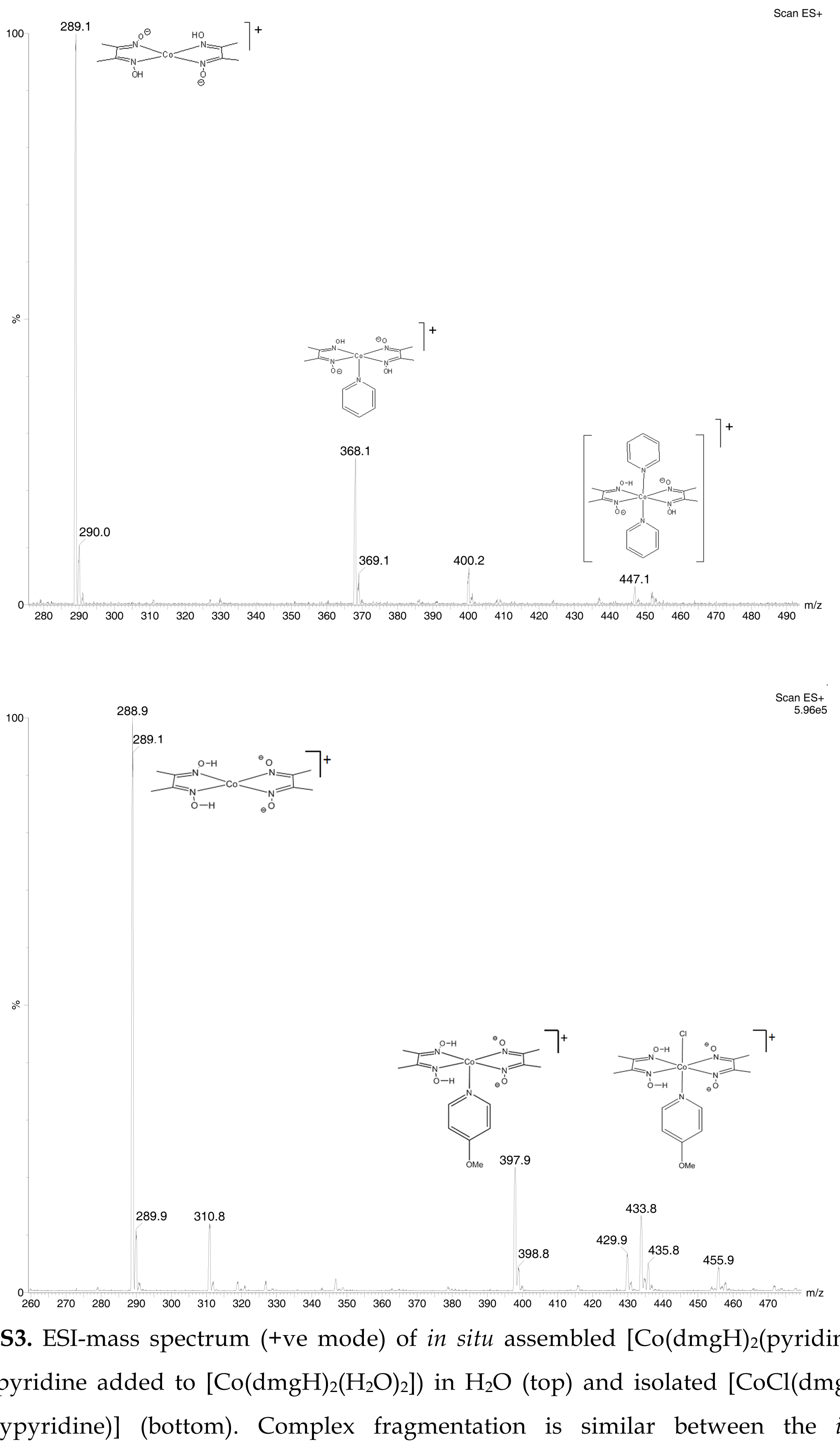

Figure S3. ESI-mass spectrum (+ve mode) of *in situ* assembled [Co(dmgH)$_2$(pyridine)$_2$] (4 equiv. pyridine added to [Co(dmgH)$_2$(H$_2$O)$_2$]) in H$_2$O (top) and isolated [CoCl(dmgH)$_2$(4-methoxypyridine)] (bottom). Complex fragmentation is similar between the *in situ* assembled and isolated cobaloximes.

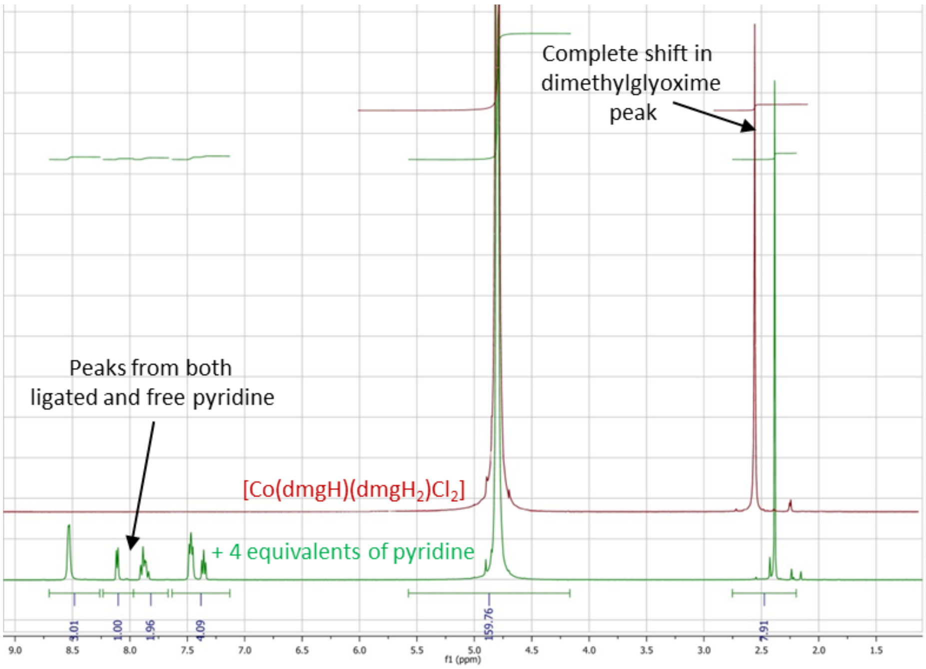

Figure S4. ^{1}H-NMR of [$Co^{III}Cl_2$(dmgH)($dmgH_2$)] in D_2O (titrated with NaOH to pH 7) before and after addition of 4 equiv. of pyridine, showing complete substitution of axial ligands for pyridine.

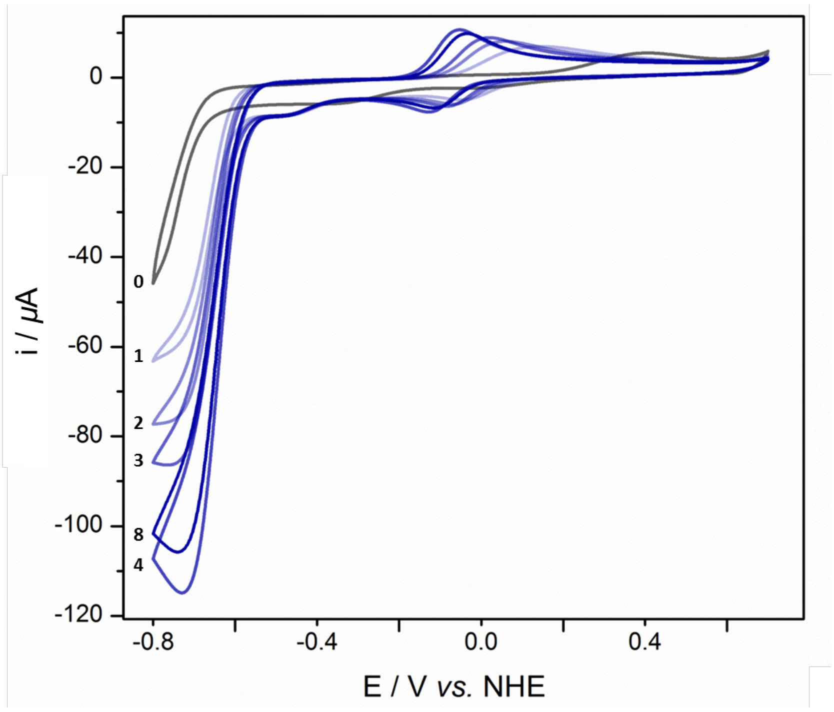

Figure S5. Addition of increasing amounts of pyridine to [$Co(dmgH)_2(H_2O)_2$] (2 mM) in P_i (0.1 M, pH 7) at 100 mV s^{-1}. The numbers left of the catalytic trace indicate the equivalents of pyridine added per Co complex. Enhancement of catalytic current stopped at approximately 4 equiv. of pyridine, after which a slow decrease in catalytic current was observed upon further addition of pyridine.

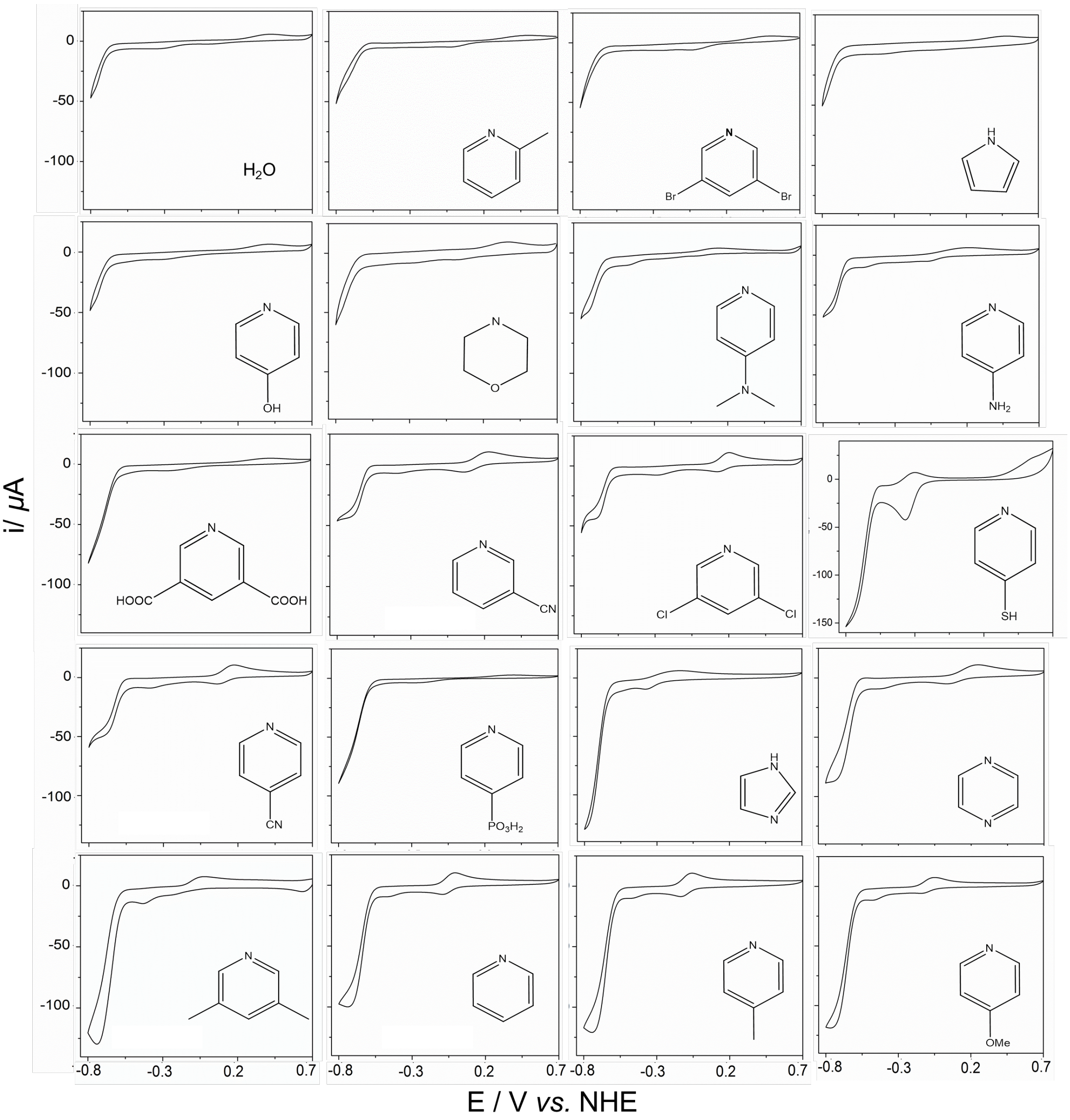

Figure S6. CVs of screened cobaloximes that arose after addition of 4 equiv. of respective axial ligand to $[Co(dmgH)_2(H_2O)_2]$ (2 mM) in Pi (0.1 M, pH 7) at 100 mV s^{-1}. CVs shown are the second consecutive scan with the exception of 3,5-dimethylpyridine (first scan shown), which displays poor stability during catalysis.

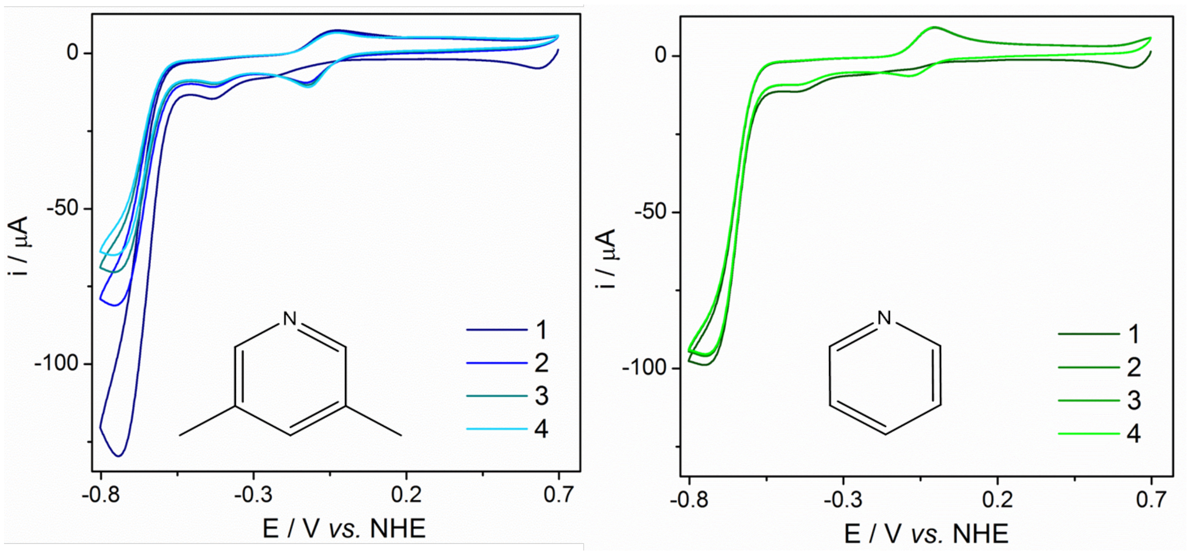

Figure S7. Consecutive CV scans of $[Co(dmgH)_2(H_2O)_2]$ (2 mM) after addition of 4 equiv. of 3,5-dimethylpyridine (left) or pyridine (right) at 100 mV s^{-1} in P_i (0.1 M, pH 7), showing the fast decay of the catalytic current over time when using 3,5-dimethylpyridine.

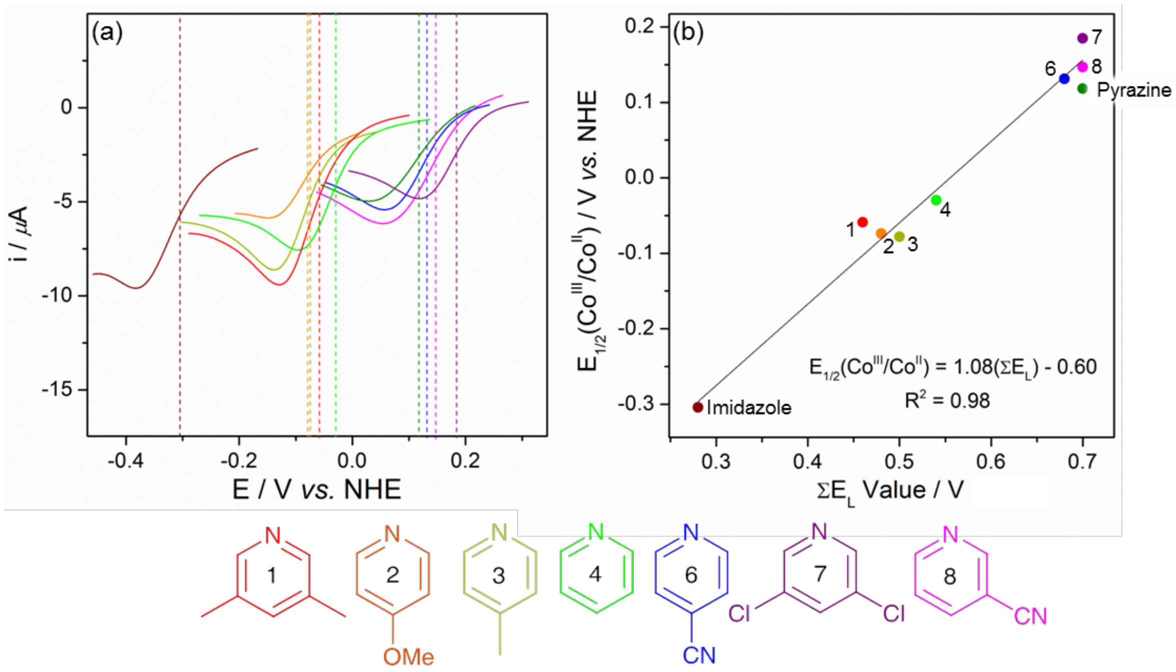

Figure S8. (a) LSVs of the Co^{III}/Co^{II} reduction waves (cathodic sweep) of assembled cobaloximes depicted in Figures 3 and S6 (only cobaloximes with clear Co^{III}/Co^{II} redox waves were used). (b) Correlation between $\sum E_L$ and the $E_{½}$ of the Co^{III}/Co^{II} redox wave. Calculation of $\Sigma E_L = 2\times(Axial\ ligand\ E_L) + 4\times\left(dmgH^-\ E_L\right)$. E_L of $dmgH^-$ was reported as 0.01 V.[2]

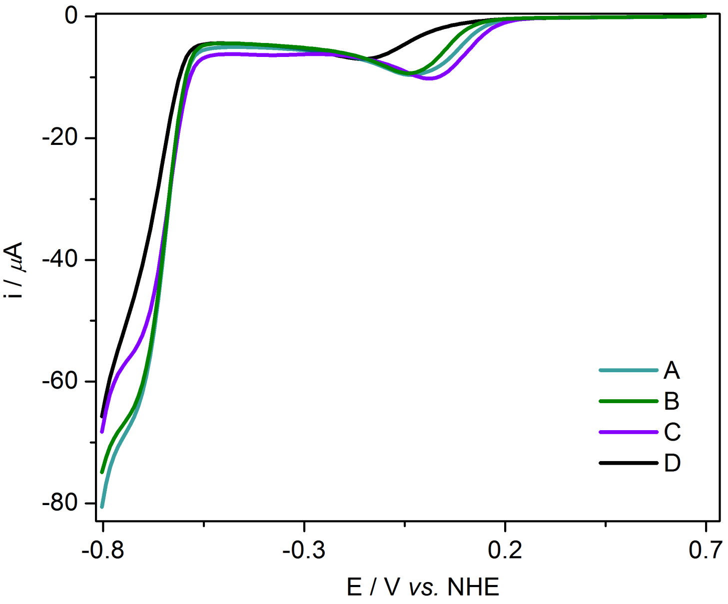

Figure S9. LSVs of the isolated cobaloximes **A** to **D** (1 mM) in an aqueous TEOA/Na_2SO_4 solution (9 mL, 0.1 M each, pH 7) with acetone (1 mL) at 100 mV s^{-1}.

References.

1. G. N. Schrauzer, G. W. Parshall, and E. R. Wonchoba, *Inorganic Syntheses*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 1968, vol. 11.

2. A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1271–1285.