

Supporting Information for

“Nickel Complexes of *C*-Substituted Cyclams and Their Activity for CO₂ and H⁺ Reduction”

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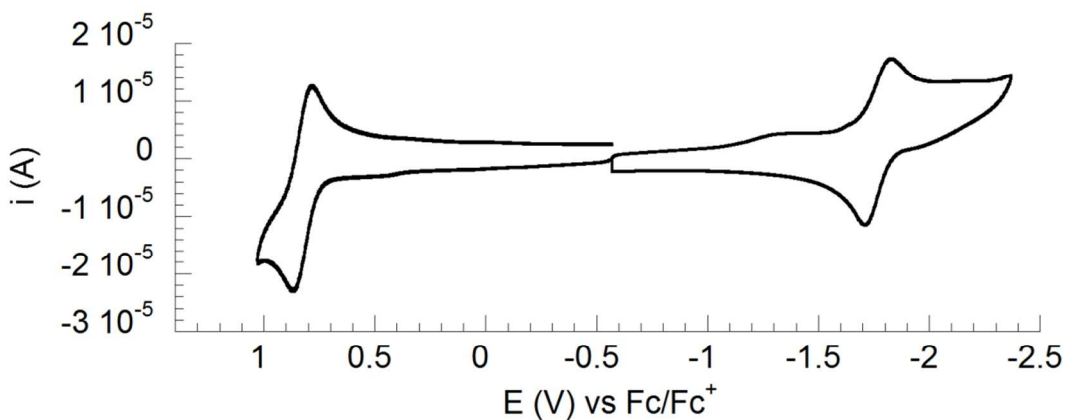


Figure S1: Cyclic voltammogram of **1** in neat MeCN solution of 0.1 M Bu₄NPF₆.

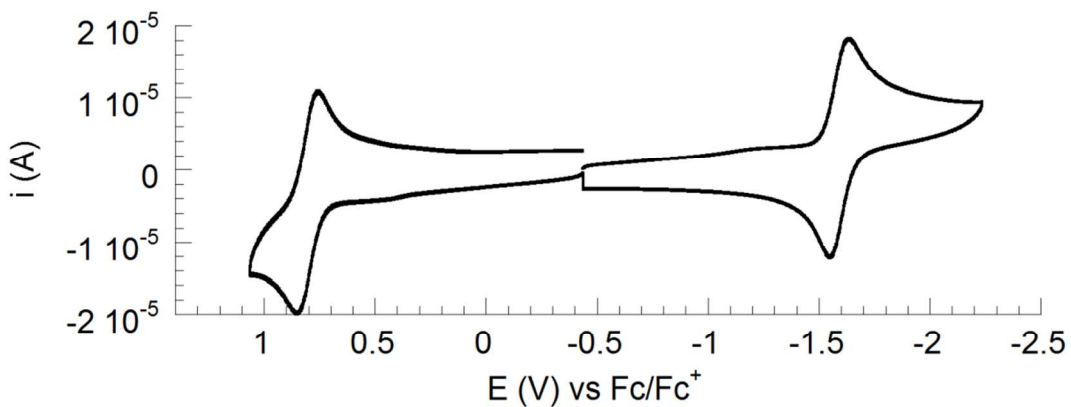


Figure S2: Cyclic voltammogram of **2** in neat MeCN solution of 0.1 M Bu₄NPF₆.

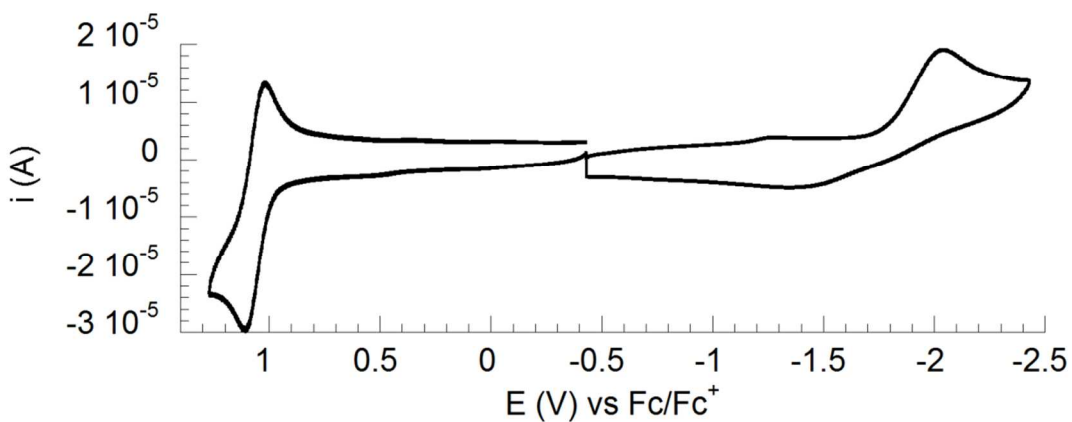


Figure S3: Cyclic voltammogram of **3** in neat MeCN solution of 0.1 M Bu₄NPF₆.

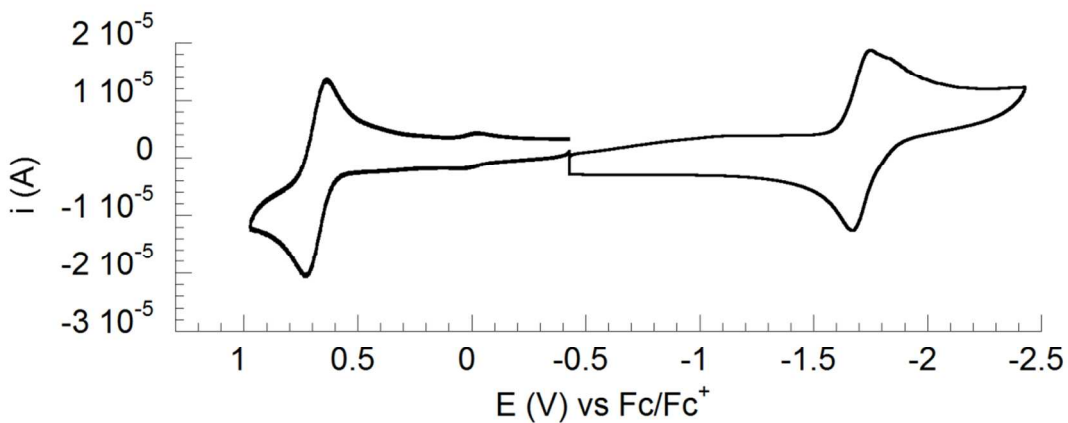


Figure S4: Cyclic voltammogram of **4** in neat MeCN solution of 0.1 M Bu₄NPF₆.

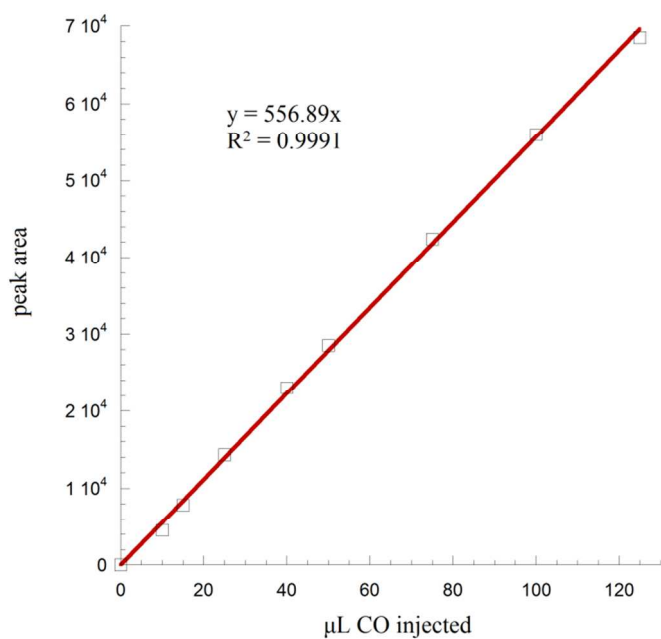


Figure S5: Calibration plot for CO detection using a gas chromatograph with a thermal conductivity detector. Neat samples were injected directly into the chromatograph.

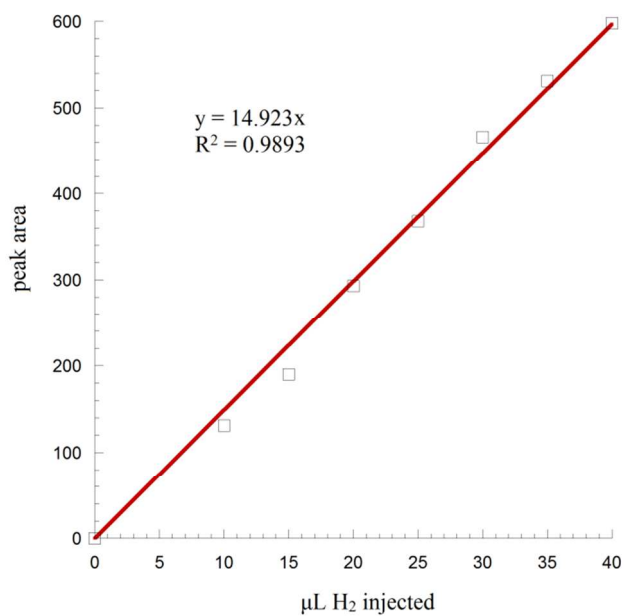


Figure S6: Calibration plot for H₂ detection using a gas chromatograph with a thermal conductivity detector. Neat samples were injected directly into the chromatograph.

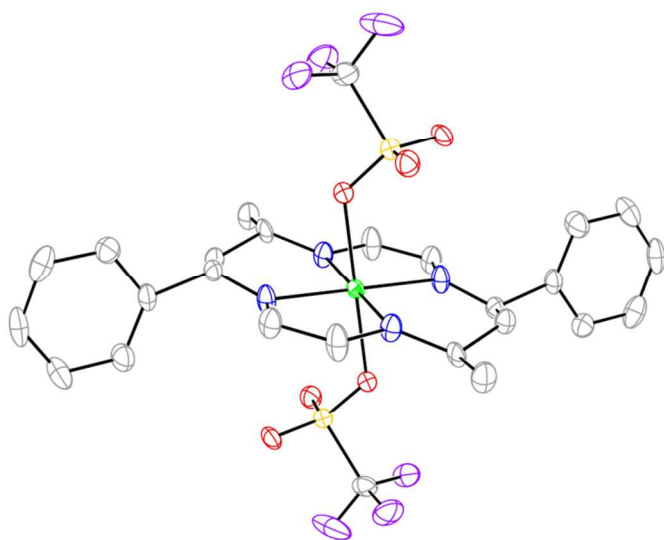


Figure S7: Crystal structure of **1'** at 15% probability level. H atoms have been omitted for clarity. The crystal was grown via slow diffusion of hexanes into a concentrated solution in EtOH.

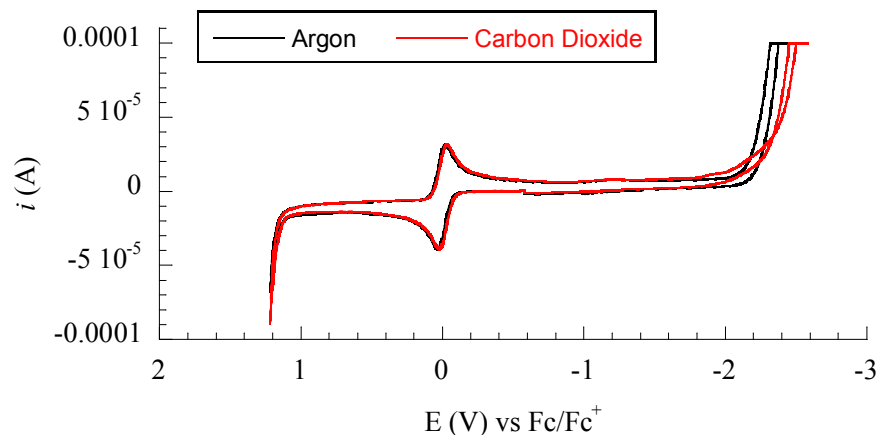


Figure S8: Background scans under both Ar and CO₂ in a 20% aqueous MeCN solution of 0.08 M Bu₄NPF₆. The only peak observed is the added ferrocene as the external reference.

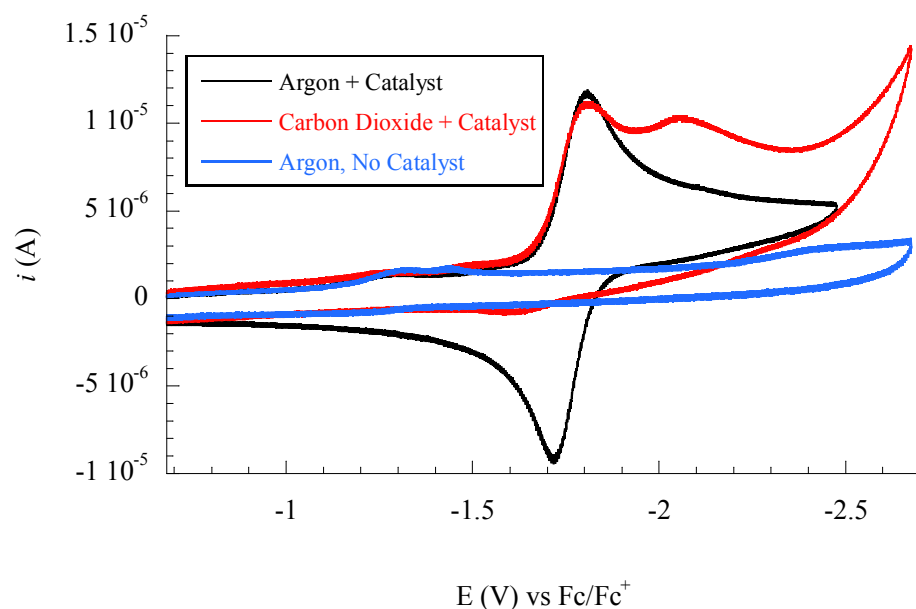


Figure S9: Cyclic voltammograms of **1** (1.0 mM) under Ar and CO₂ in a neat MeCN solution of 0.08 M Bu₄NPF₆.

Table S1: CPE data for **1** compared to the CPE data of Ni(cyclam)Cl₂ using the same set-up.^a

Complex	Q (C)	FE, CO (%)	FE, H ₂ (%)	TON, CO	TON, H ₂
1^b	21.2 ± 0.7	80.0 ± 3.5	7.3 ± 0.5	4.5 ± 0.3	0.4 ± 0.0

Ni(cyclam)Cl₂^c	6.7 ± 1.4	35.3 ± 13	65.7 ± 2.9	0.5 ± 0.1	1.1 ± 0.2
blank	2.9	1	77	-	-

^a Performed in CO₂-saturated solutions of 20% aqueous MeCN with 0.08 M NBu₄PF₆; Solutions were electrolyzed for 30 min and headspace gases were analyzed via GC–TCD. ^bData reported as the averages of 2 trials. ^cData reported as the averages of 3 trials. Q = total charge passed, faradaic efficiency (FE) = $\frac{\text{charge to form product}}{\text{total charge passed}}$, turnover number (TON) = $\frac{\text{mol product}}{\text{mol catalyst}}$

Table S2: Crystal data for **1** (grown via slow diffusion of Et₂O into a concentrated solution in MeCN), **2**, and **3**.

	1	2	3
molecular formula	C ₃₀ H ₄₂ F ₆ N ₆ NiO ₆ S ₂	C ₂₈ H ₄₂ F ₆ N ₄ NiO ₇ S ₂	C ₃₀ H ₃₉ F ₁₂ N ₅ NiO ₇ S ₂
fw, g mol ⁻¹	819.52	783.48	932.49
space group	<i>R</i> $\bar{3}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	32.431	14.792	8.9397
<i>b</i> , Å	32.431	9.055	11.189
<i>c</i> , Å	9.769	26.136	19.998
<i>α</i> , °	90.00	90.00	89.46
<i>β</i> , °	90.00	99.81	78.41
<i>γ</i> , °	120.00	90.00	89.82
<i>V</i> , Å ³	8898.7	3449.9	1959.5
<i>Z</i>	9	4	2
ρ_{calcd} , g cm ⁻³	1.376	1.508	1.580
<i>T</i> , K	200	150	200
final <i>R</i> indicies (<i>I</i> > 2σ(<i>I</i>))	<i>RI</i> = 0.0585 <i>wRI</i> = 0.1343	<i>RI</i> = 0.0426 <i>wRI</i> = 0.1000	<i>RI</i> = 0.0476 <i>wRI</i> = 0.1202
GOF on <i>F</i> ²	1.061	1.022	1.131