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Supporting information for:

Chelated $[Zn(cyclam)]^{2+}$ Lewis Acid Improves the Reactivity of the Electrochemical Reduction of CO_2 by Mn Catalysts with Bulky Bipyridine Ligands.

Almagul Zhanaidarova, Han Steger,[a] Mark H. Reineke and Clifford. P. Kubiak*

Contribution from the Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, Mail Code 0358, La Jolla, California 92093-0358

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I. Synthesis of Mn complex and $[ZnCyclam][BF_4]_2$

$Mn(Mesbpy)(CO)_3Br$ (1) and $[Mn(Mesbpy)(CO)_3MeCN][OTf]$ (2): Compounds **1** and **2** were synthesized as described in previous work. [1]

$[ZnCyclam][BF_4]_2$: 0.41 g of 1,4,8,11-tetraazacyclotertradecane (2.05 mmol) was dissolved in 15 mL of ethanol (**solution 1**) and 0.48 g of zinc tetrafluoroborate (2.01 mmol) was dissolved in 20 mL of ethanol (**solution 2**). Solution 2 was added to the solution 1 dropwise and the combined solution was stirred overnight under reflux. Ethanol was removed under rotary evaporation. The white solid was then dissolved in acetonitrile and filtered. Diethyl either was added to the filtrate until the white precipitate crashed out. The resulting white solid (74% yield) was then dried under vacuum overnight.

	Experimental composition (wt%)	Theoretical composition (wt%)
C	27.37	27.34
H	5.56	5.51
N	12.77	12.75

Table S1. Elemental analysis comparison between theoretically determined concentration and experimental determined concentration of [ZnCyclam][BF_4]$_2$ without the observation of ACN coordination.

II. Physical measurement

Electrochemistry (CV): Electrochemical experiments were carried out using a BASi Epsilon potentiostat. A glassy carbon electrode was used as a working electrode (3 mm in diameter), with a Pt wire as a counter electrode and Ag/AgCl wire with the vycor tip as a reference electrode. Ferrocene was added as an internal reference. All electrochemical experiments were performed with 0.1 M $TBAPF_6$ electrolyte solution in MeCN. Cell was shielded from light with aluminum foil during all the electrochemical experiments and the solutions were degassed with Ar or CO_2. CO_2 electrocatalysis experiments were carried out with CO_2 at gas saturation, 0.28M. All electrochemical data were compensated for the iR drop.

Control potential electrolysis (CPE): CPE experiments were carried out in a 64 mL 4 neck electro cell designed by Gamry. A carbon rod electrode was used as a working electrode, a Pt wire in a form of a spool with high surface area was used as a counter electrode and was separated from the solution by a porous glass frit and Ag/AgCl reference electrode was separated from the solution by a Vycor tip. The electrocatalyst and the Lewis acid were dissolved in 30 mL of 0.1 M $TBAPF_6$ solution in dry acetonitrile, and purged with CO_2 for at least 20 min. The cell was wrapped with aluminum foil and stirred throughout the entire experiment. A Hewlett-Packard 7890A series gas chromatograph and 1 ml glass syringe were used for gas analysis for all CPE experiments.

III. Crystallography

Experimental:

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with molybdenum Kα radiation (λ = 0.710 73 Å). The crystals were mounted on a Cryoloop with Paratone oil and data were collected under a nitrogen gas stream at 100 K using ω and φ scans. Data were integrated and scaled using the Bruker SAINT software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Crystallographic data and structure refinement parameters are summarized in the supporting information.

Table S2. Crystallographic Data and Refinement Information

Compound	$[Zn(cyalam)](BF_4)_2$	**pcalc (g/cm³)**	1.519
empirical formula	$C_{14}H_{30}B_2F_8N_6Zn$	**μ (Mo Kα) (mm-1)**	2.223
Formula weight	521.42	**temperature (K)**	100 (2)
Crystal system	Monoclinic	**2Θ max (deg)**	68.19
a	17.4835(5)	**no. obs. (I > 2α(I))**	4171
b	7.9463(5)	**no. parameters**	310
c	18.0503(5)	**goodness of fit**	1.101
α (deg)	90	**max. shift in cycle**	0.001
β (deg)	114.592(1)	**residuals: R1; wR2**	0.0298; 0.0764
γ (deg)	90	**largest peak**	0.478

V (Å3)	2280.25(11)	**deepest hole**	-0.470
space group	$P2_1/n$		
Z value	4		

Table S3. Selected bond lengths and angles for $(ACN)_2[Zn(cyclam)](BF_4)_2$

Atoms	**Bond Angle**	**Atoms**	**Bond Length**
N1-Zn-N3	179.27(6)	**Zn-N1**	2.0980(14)
N2-Zn-N4	179.48(6)	**Zn-N2**	2.0963(15)
N5-Zn-N6	179.18(5)	**Zn-N3**	2.0965(15)
N1-Zn-N2	90.73(5)	**Zn-N4**	2.0987(14)
N4-Zn-N3	90.81(6)	**Zn-N5**	2.2973(15)
N1-Zn-N5	87.99(6)	**Zn-N6**	2.3314(15)
N3-Zn-N6	88.59(6)		

Single Crystal X-ray structural data for $[Zn(cyclam)](BF_4)_2$ is deposited under CCDC number **CCDC 1562780.**

IV. Figures and tables

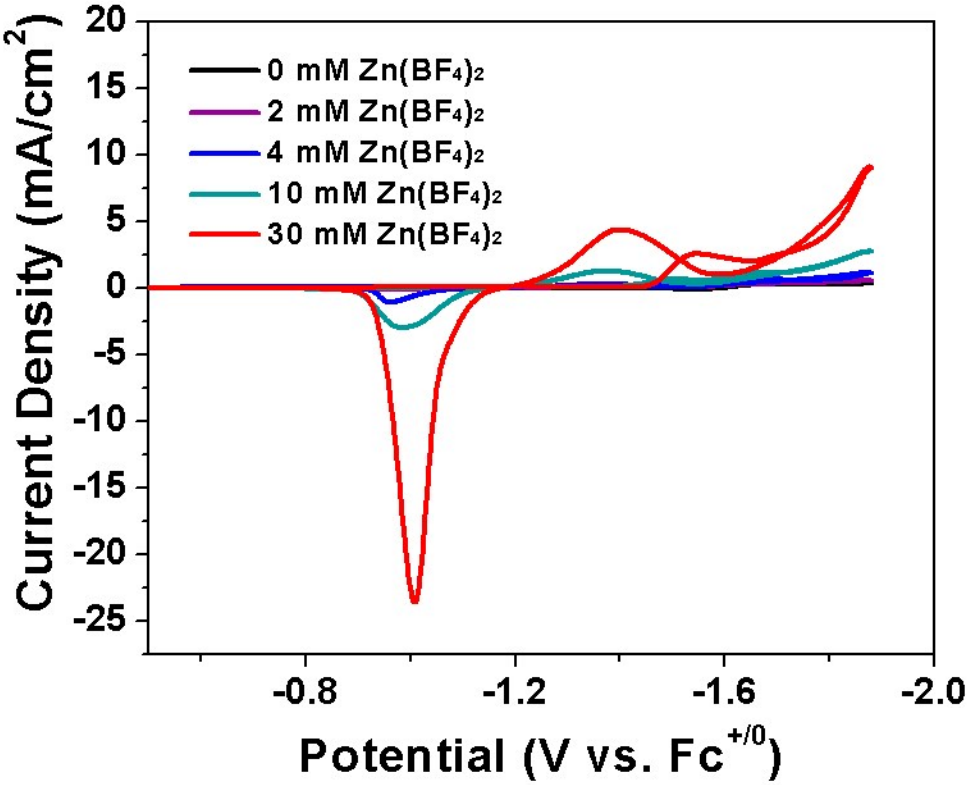


Figure S1. CVs of 1 mM **2** under CO_2 with free Zn^{2+} ($Zn(BF_4)_2$). Conditions: 0.1 M $TBAPF_6$/MeCN; v = 0.1 V/s; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl; ferrocene (Fc) added as an internal reference.

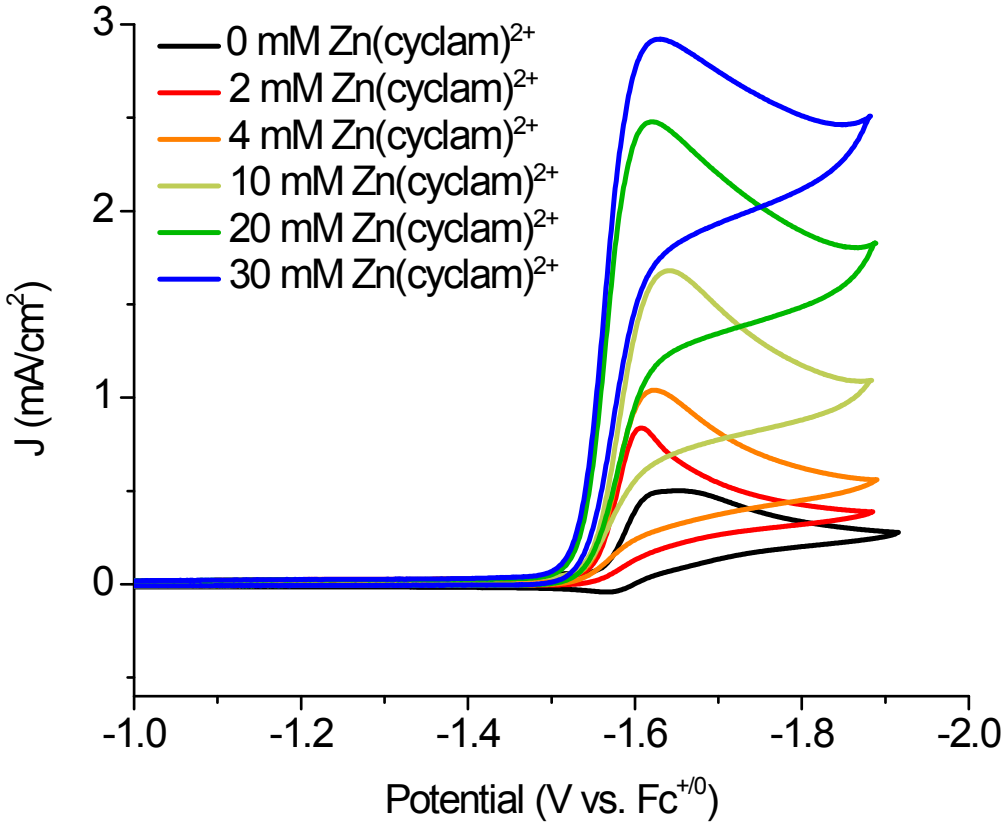
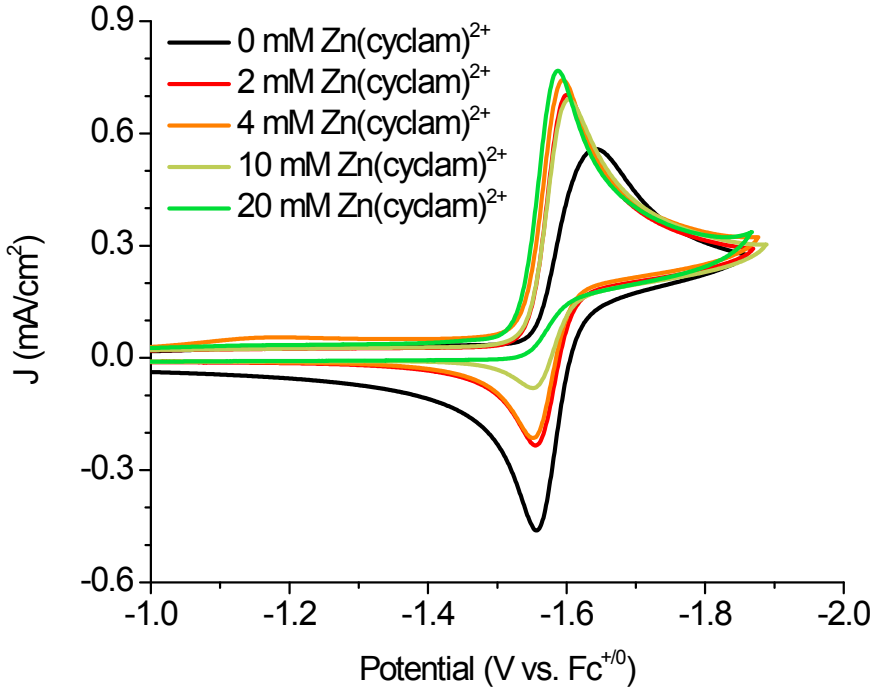


Figure S2. CVs of 1 mM **1** under CO_2 with varying concentrations of ZnCyclam, showing electrocatalytic reduction of CO_2. Conditions: 0.1 M $TBAPF_6$/MeCN; v = 0.1 V/s; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl; ferrocene (Fc) added as an internal reference

a



b

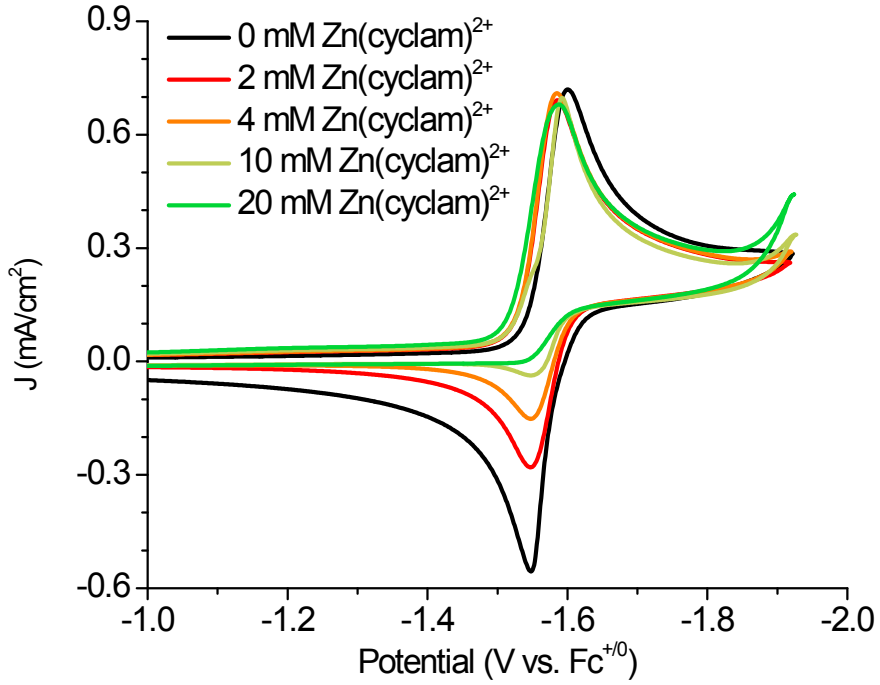


Figure S3. CVs of 1 mM **1 (a)** and **2 (b)** under Ar with varying concentrations of ZnCyclam. Conditions: 0.1 M $TBAPF_6$/MeCN; v = 0.1 V/s; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl; ferrocene (Fc) added as an internal reference.

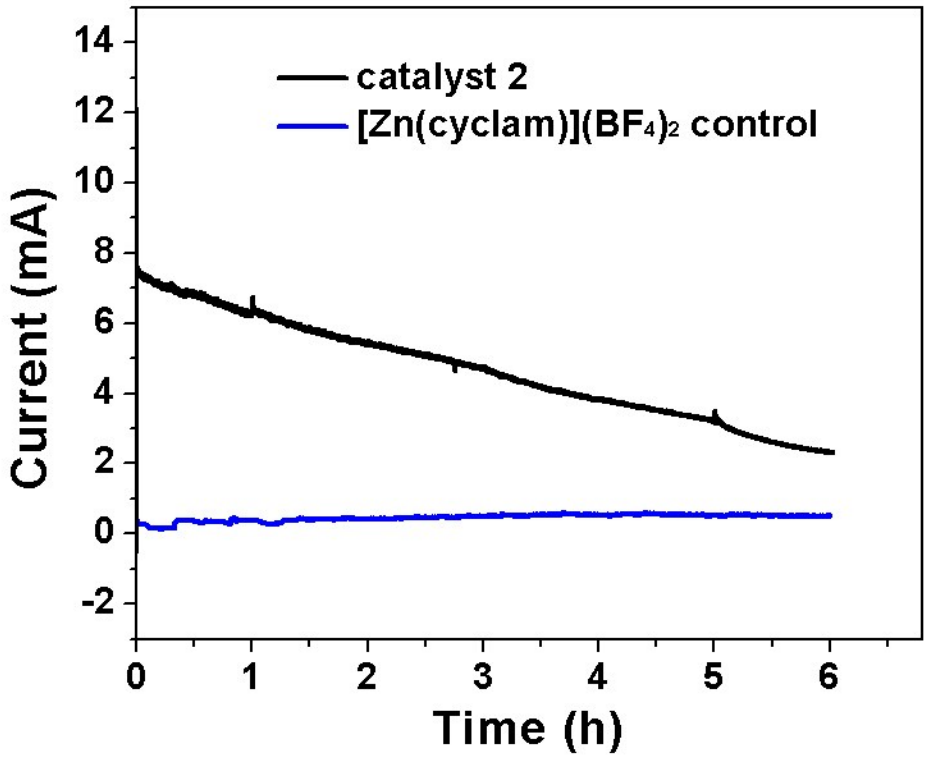


Figure S4. CPE current density over time for 0.5 mM of **2** under CO_2 with 30 mM of $[Zn(cyclam)]^{2+}$. Conditions: potential = −1.6 V versus Ferrocene; 0.1 M TBAPF6/MeCN; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl

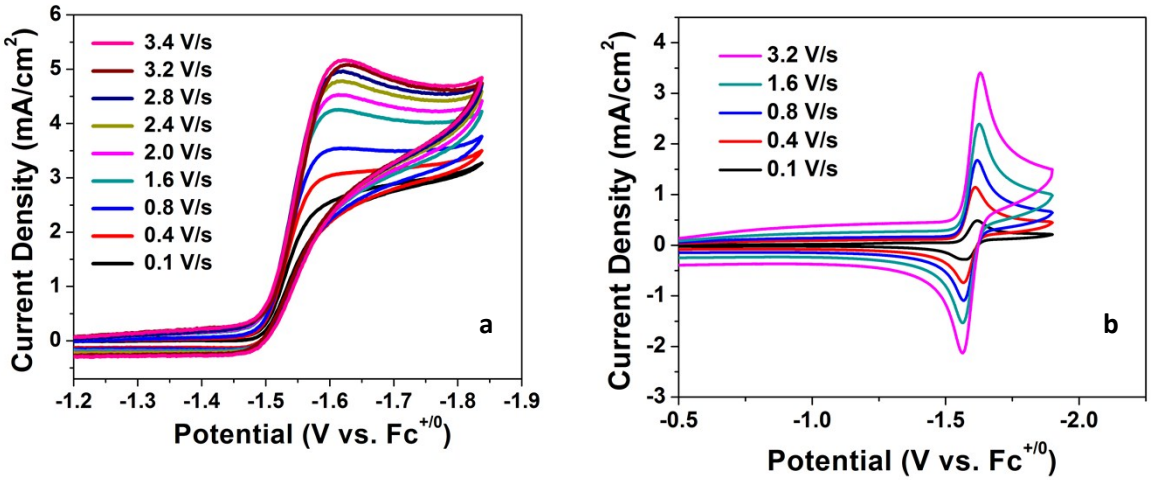


Figure S5. CV of 1 mM of **2** with 30 mM of $[Zn(cyclam)]^{2+}$ under CO_2 **(a)** and under N_2 without a substrate **(b)** In 0.1 M $TBAPF_6$/MeCN at various scan rates (0.1 – 3.4 V/s) ; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl.

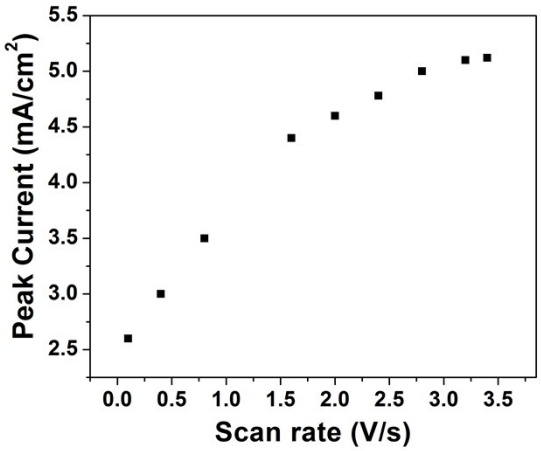


Figure S6. Scan rate dependence of peak current recorder for 1 mM of **2** with 30 mM of $[Zn(cyclam)]^{2+}$ In 0.1 M $TBAPF_6$/MeCN; working electrode = glassy carbon; counter electrode = Pt; reference electrode = Ag/AgCl.

Steady state was reached at scan rate of 3.2 V/s.

TOF of 105 s^{-1} was calculated from CV using i_{cat}/i_p = 1.5 at a scan rate 3.2 V/s.

TOF was calculated using the formula TOF = 0.1992 $(Fv/RT)(n^3_p/n^2_{cat})(i_{cat}/i_p)^2$

V. References

1. Sampson, D. M.; Nguyen, D. A.; Grice, A. K.; Moore, E, C.; Rheingold, A. L.; Kubiak, C. P. *J. Am. Chem. Soc.* **2014**, 136, 5460-5471.
2. Ngo T. K., McKinnon M., Mahanti B., Narayanan R., Grills C. D., Ertem Z. M., Rochford J. *J. Am. Chem. Soc*. **2017**, 139, 2604−2618