



---

# Steric influence at the 6,6'-positions in Mn(bpy) complexes and the resulting impact on electrochemical CO<sub>2</sub> reduction

Zane Thistleford, Rashi Gupta, Christine A. Caputo

ACS Philadelphia 2020

and

UNH Graduate Research Conference 2020

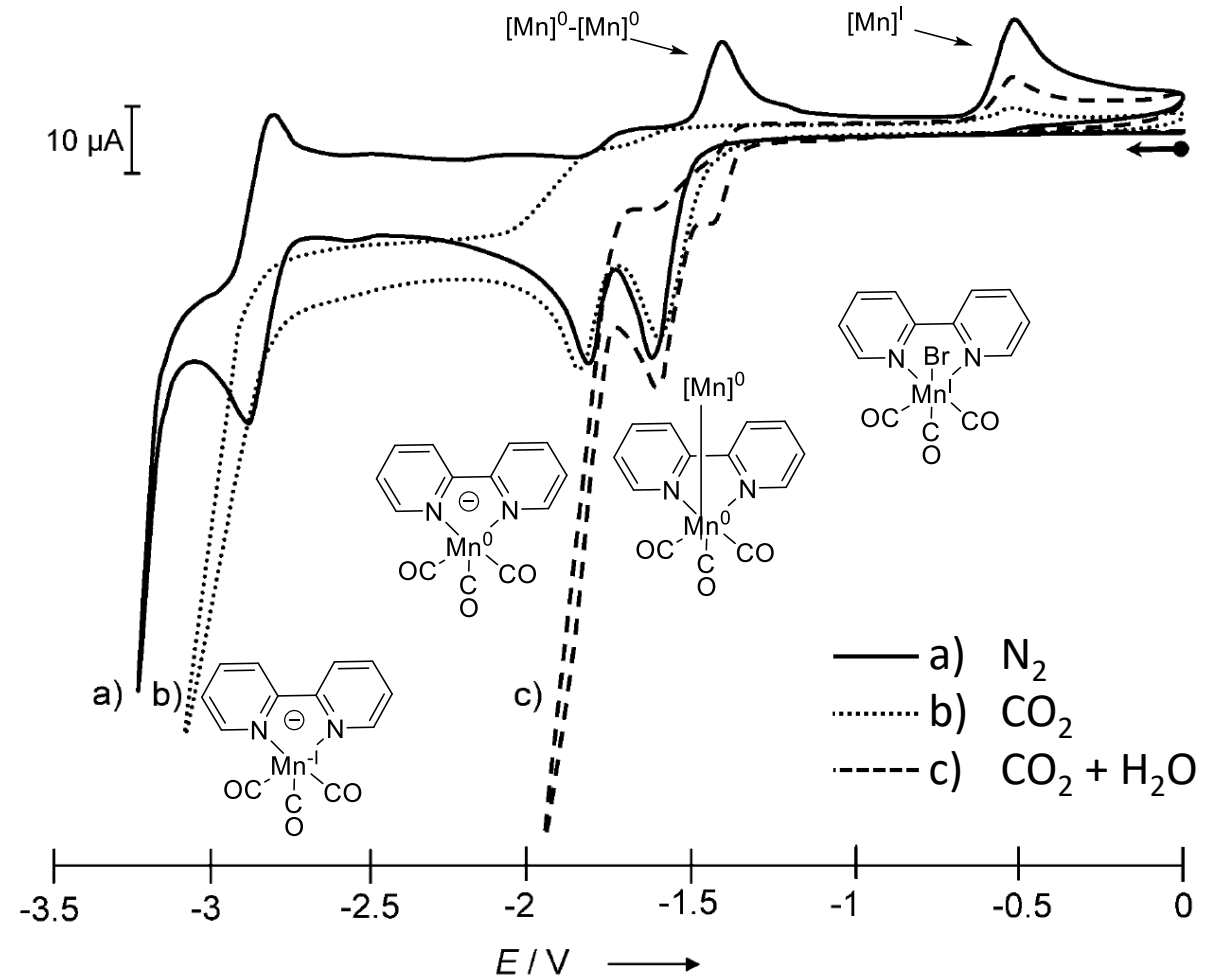
Division of Energy and Fuels

Electrochemistry-Enabled Catalysis for Energy, Chemicals & Materials

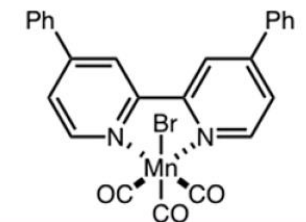
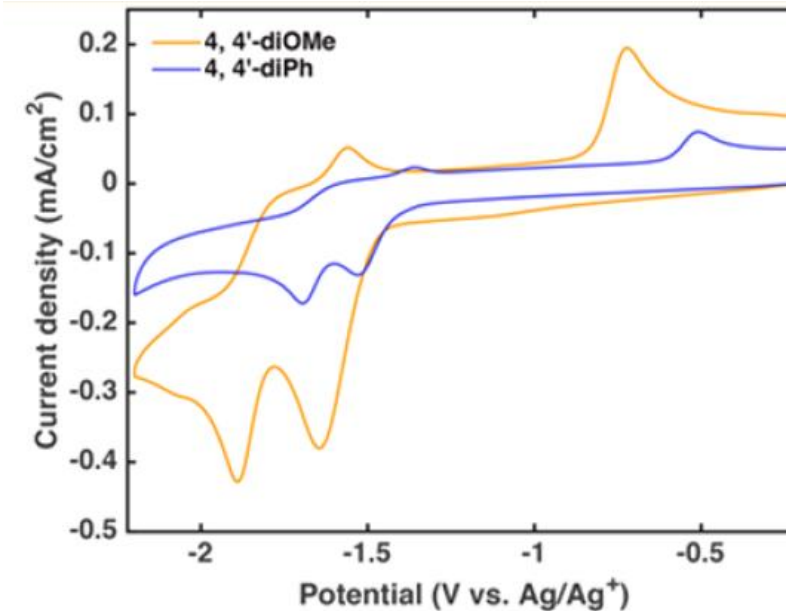
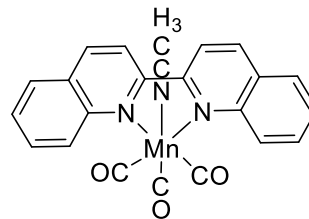
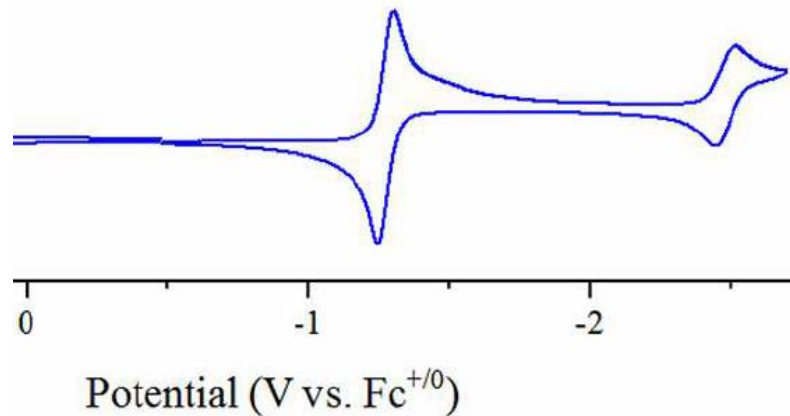
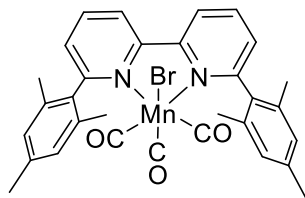
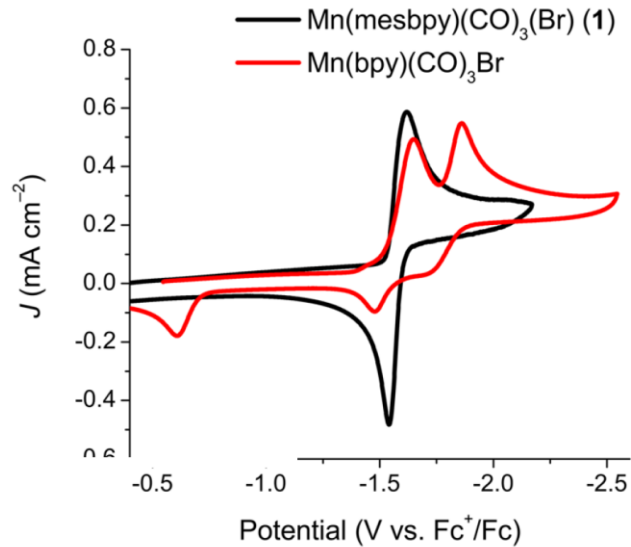


# Catalytic CO<sub>2</sub> Reduction

- $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$
- Catalyst should:
  - Deliver 2 protons and 2 electrons
  - Demonstrate long-term stability and high efficiency
  - Use earth-abundant metals if possible
- $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  demonstrated lower overpotentials than  $\text{Re}(\text{bpy})(\text{CO})_3\text{Br}$ .



# Factors Influencing Dimer Formation



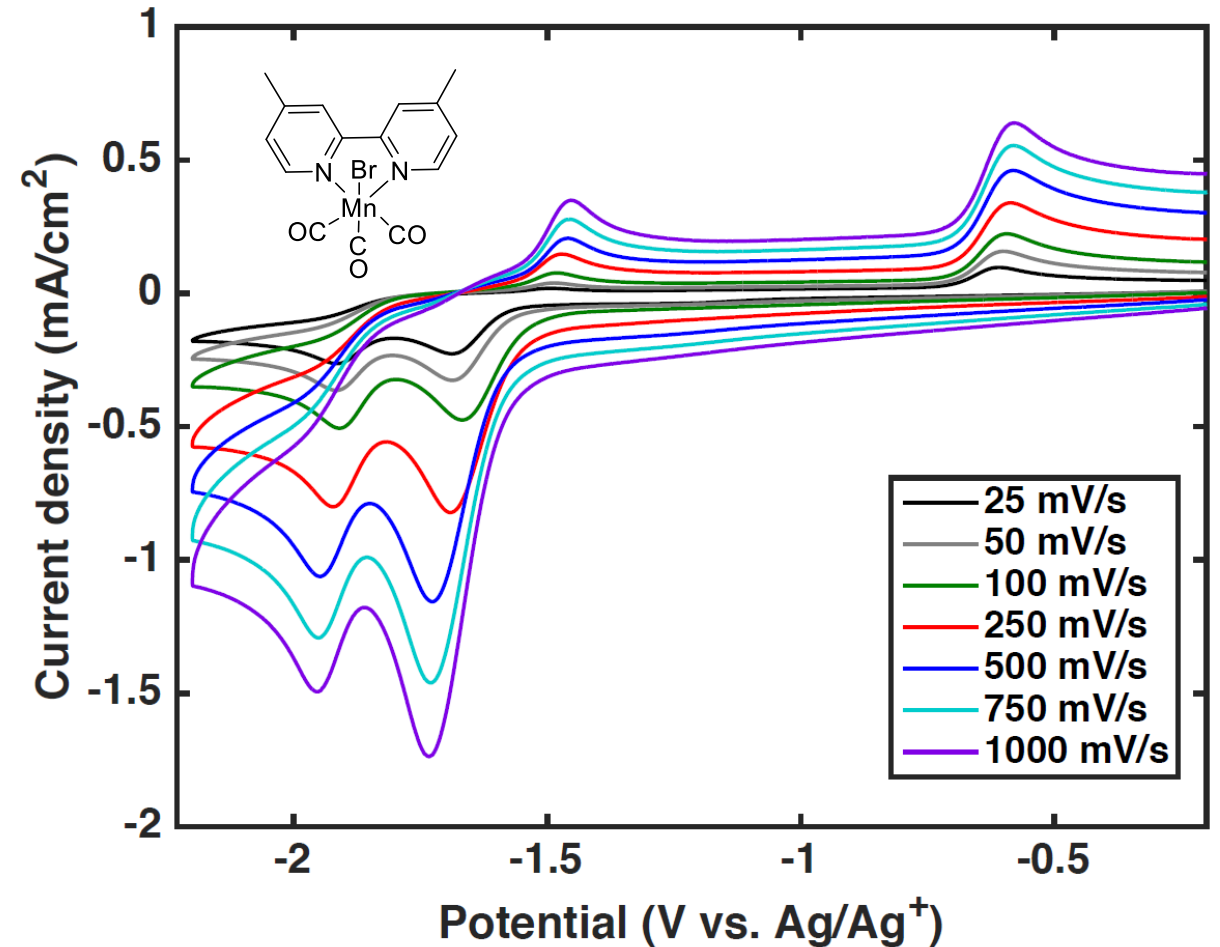
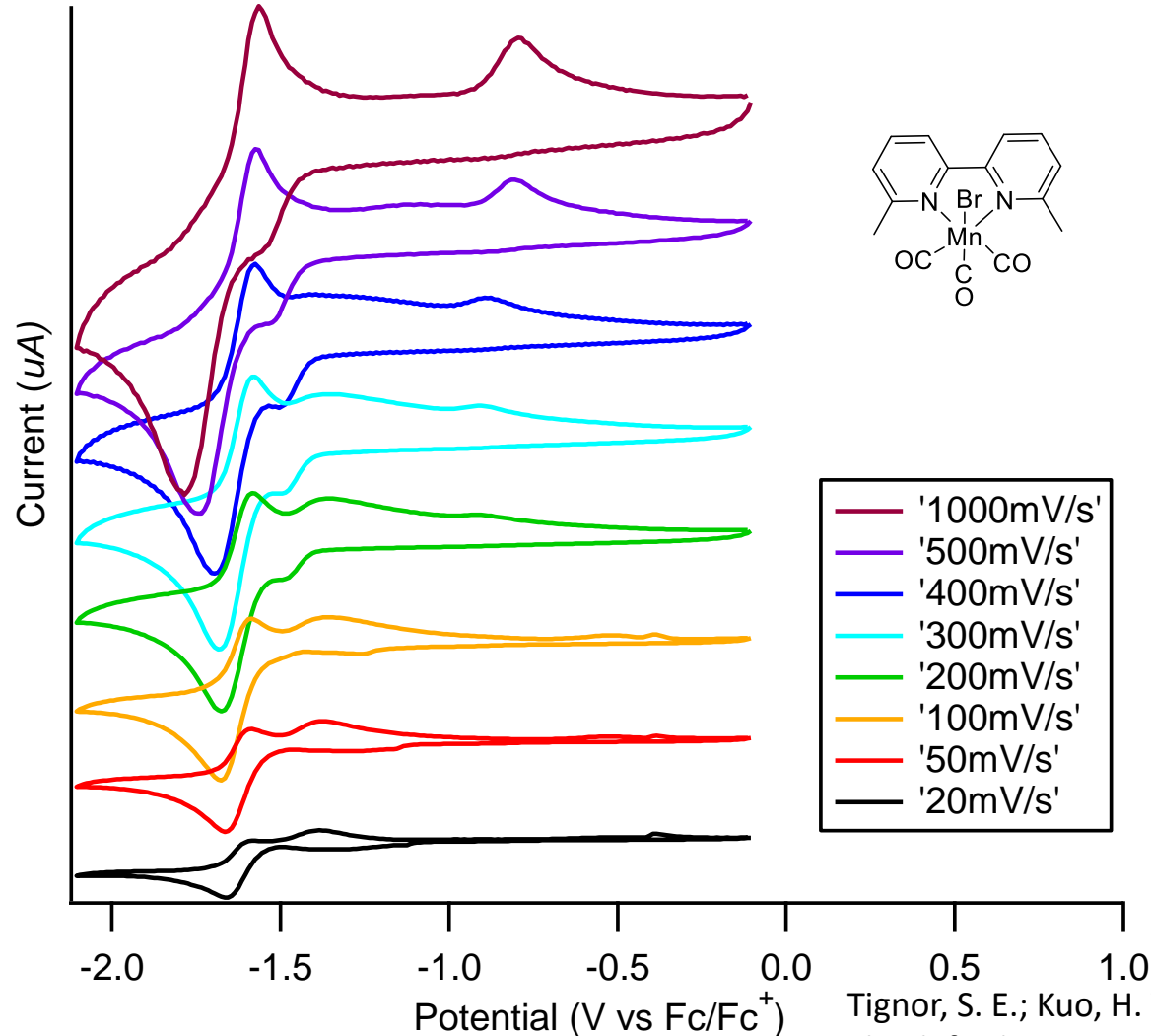
Sampson, M.D.; Nguyen, A.D.; Grice, K.A.; Moore, C.E.; Rheingold, A.L.; Kubiak, C.P. *J. Am. Chem. Soc.*, **2014**, *136*, 5460-5471.

McKinnon, M.; Belkina, V.; Ngo, K.T.; Ertem, M.Z.; Grills, D.C.; Rochford, J. *Front. Chem.* **2019**, *7*:628, 1-14.

Tignor, S. E.; Kuo, H. Y.; Lee, T. S.; Scholes, G. D.; Bocarsly, A. B. *Organometallics* **2019**, *38* (6), 1292-1299.

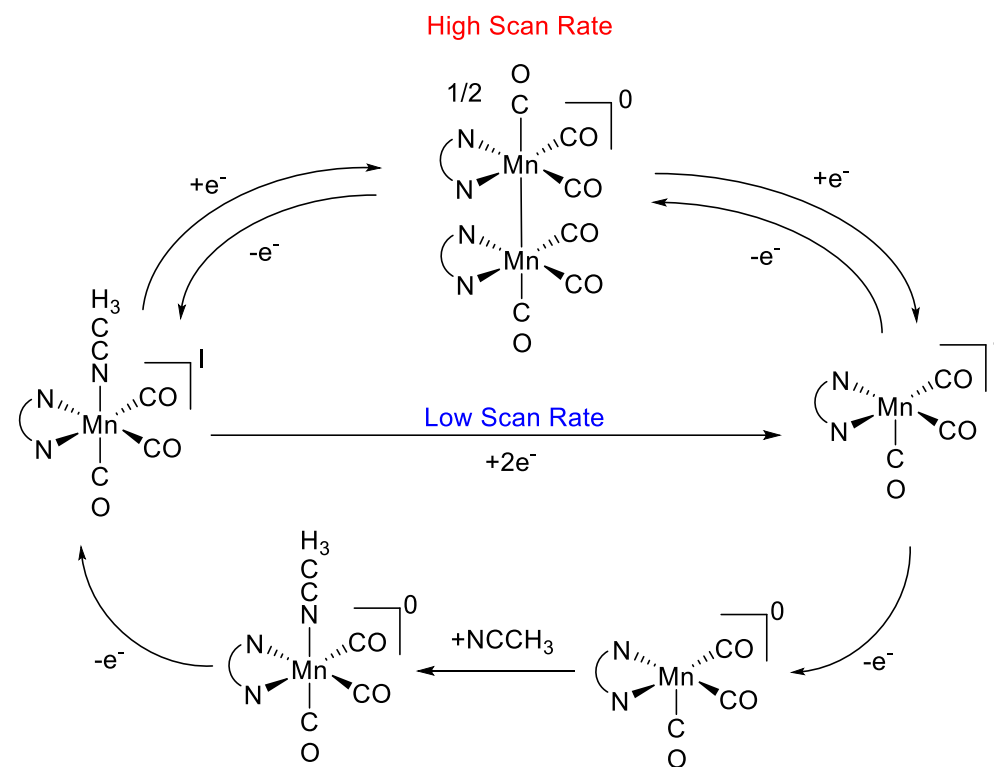
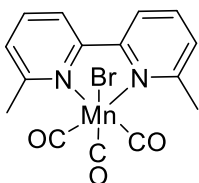
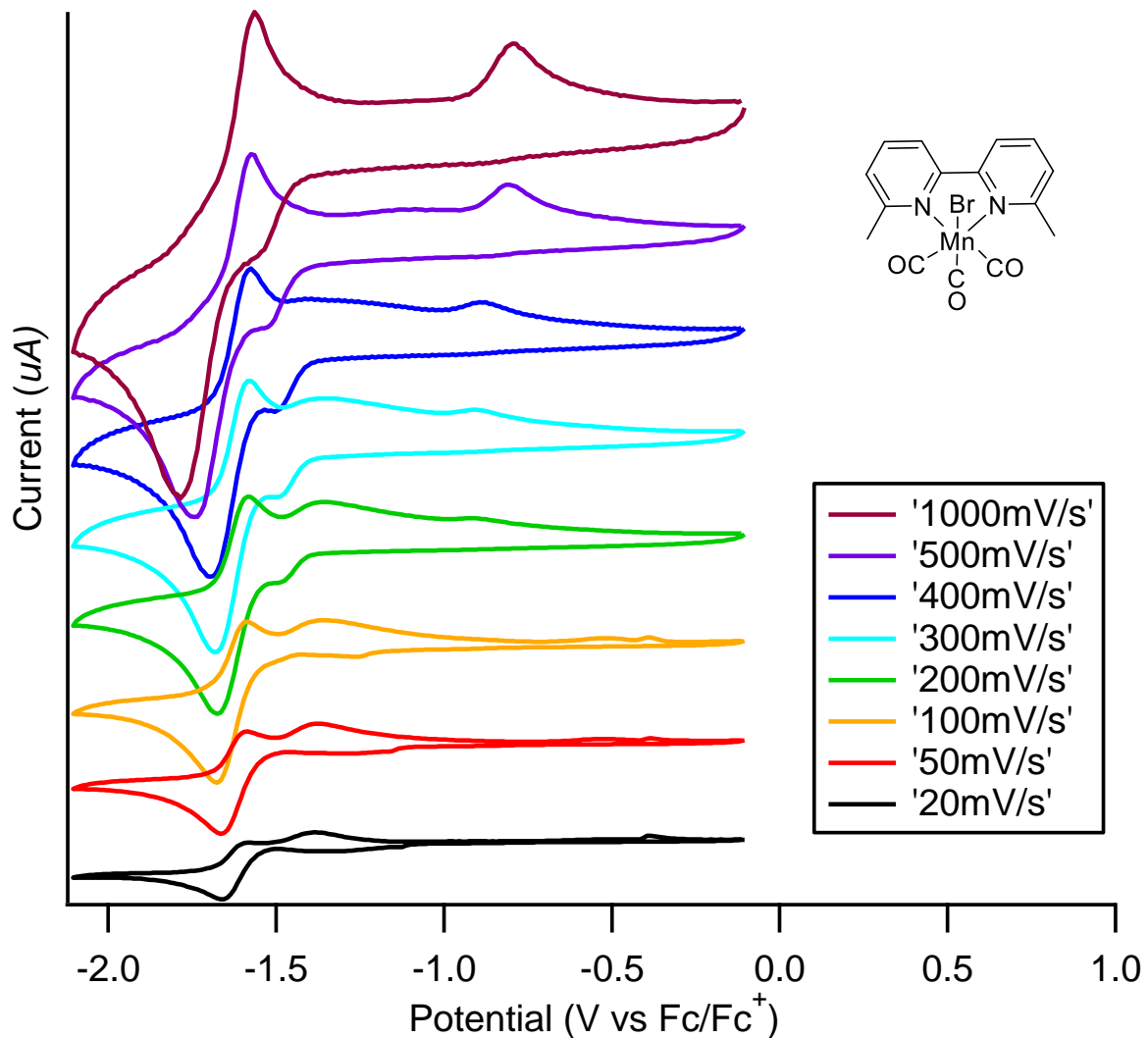


# CV of Mn(6,6'-Me<sub>2</sub>bpy)(CO)<sub>3</sub>Br



Tignor, S. E.; Kuo, H. Y.; Lee, T. S.; Scholes, G. D.; Bocarsly, A. B. *Organometallics* **2019**, *38* (6), 1292–1299.  
 Thistleford, Z.; Gupta, R.; Caputo, C. *In Preparation*.

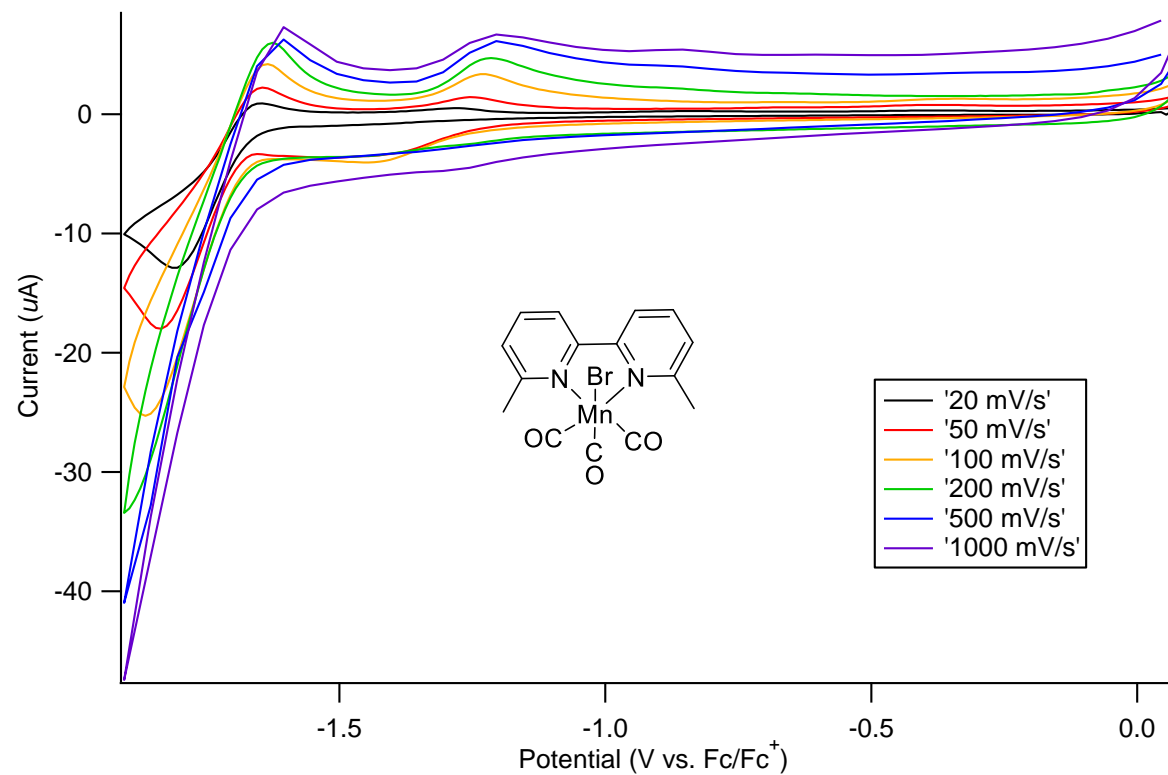
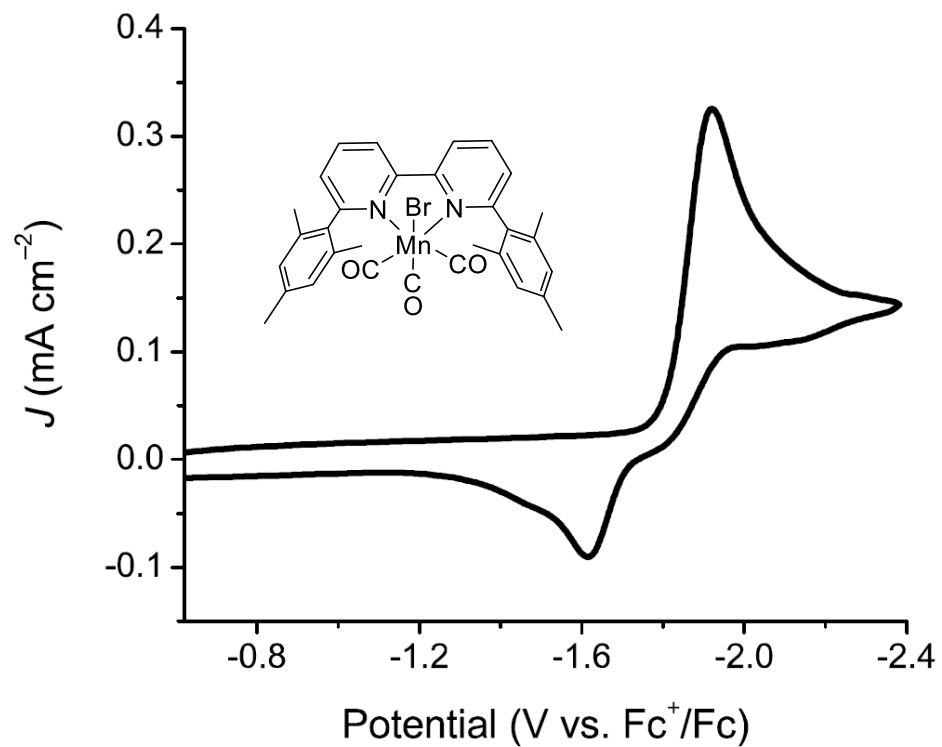
# CV of Mn(6,6'-Me<sub>2</sub>bpy)(CO)<sub>3</sub>Br



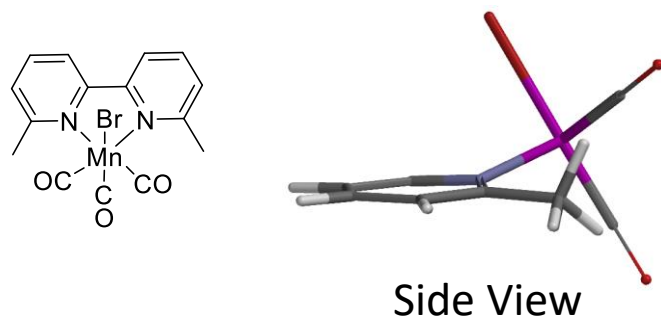
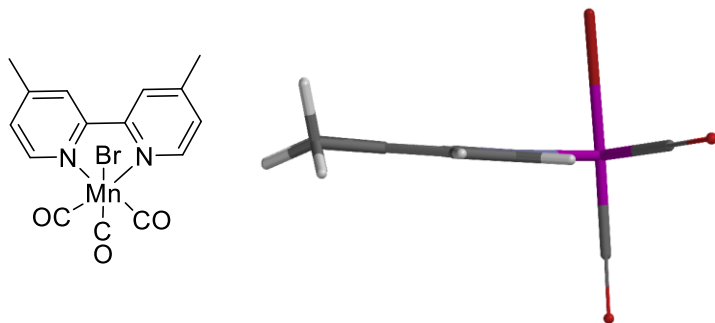
Thistleford, Z.; Gupta, R.; Caputo, C. *In Preparation*.



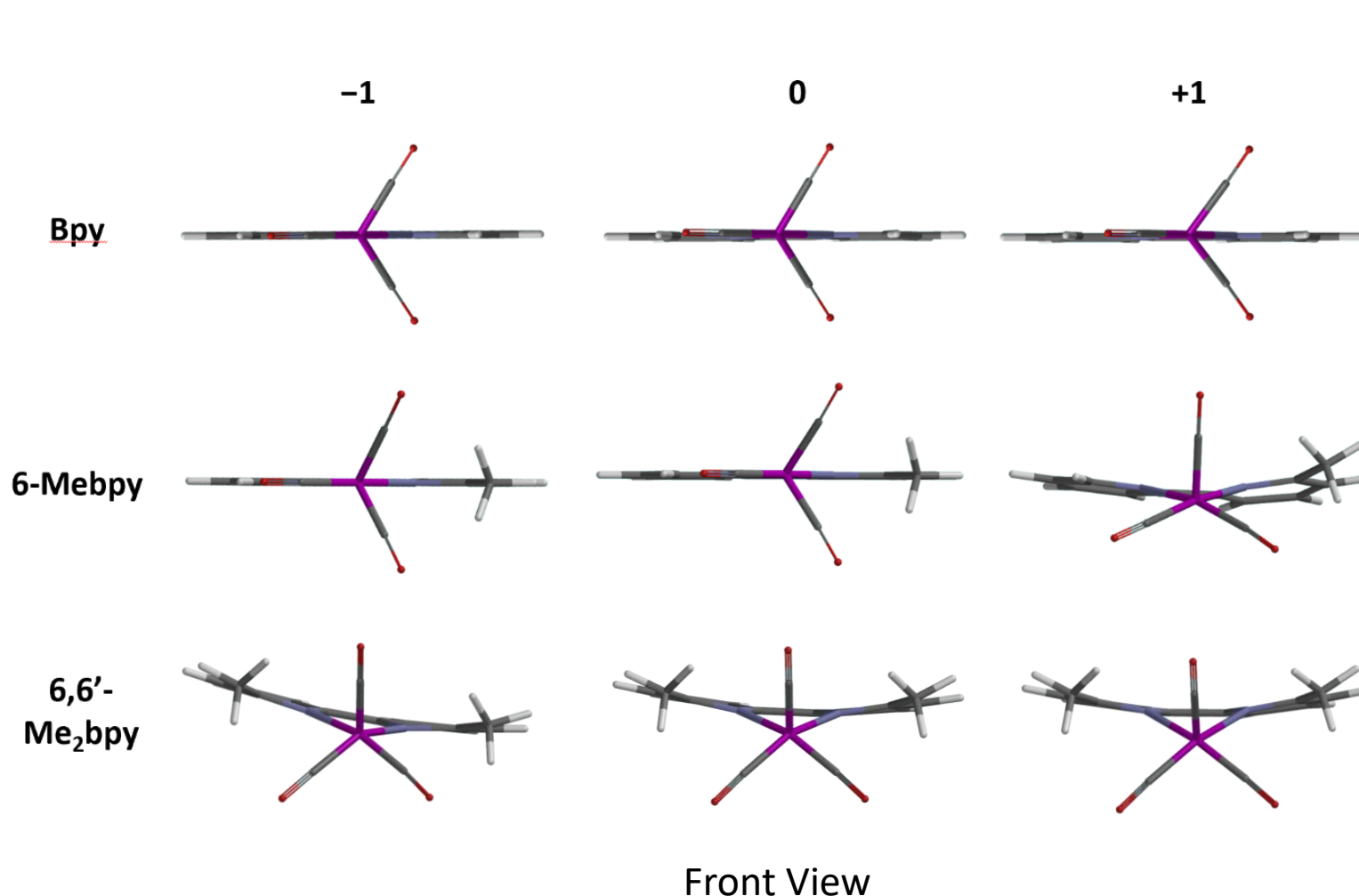
# CV in THF



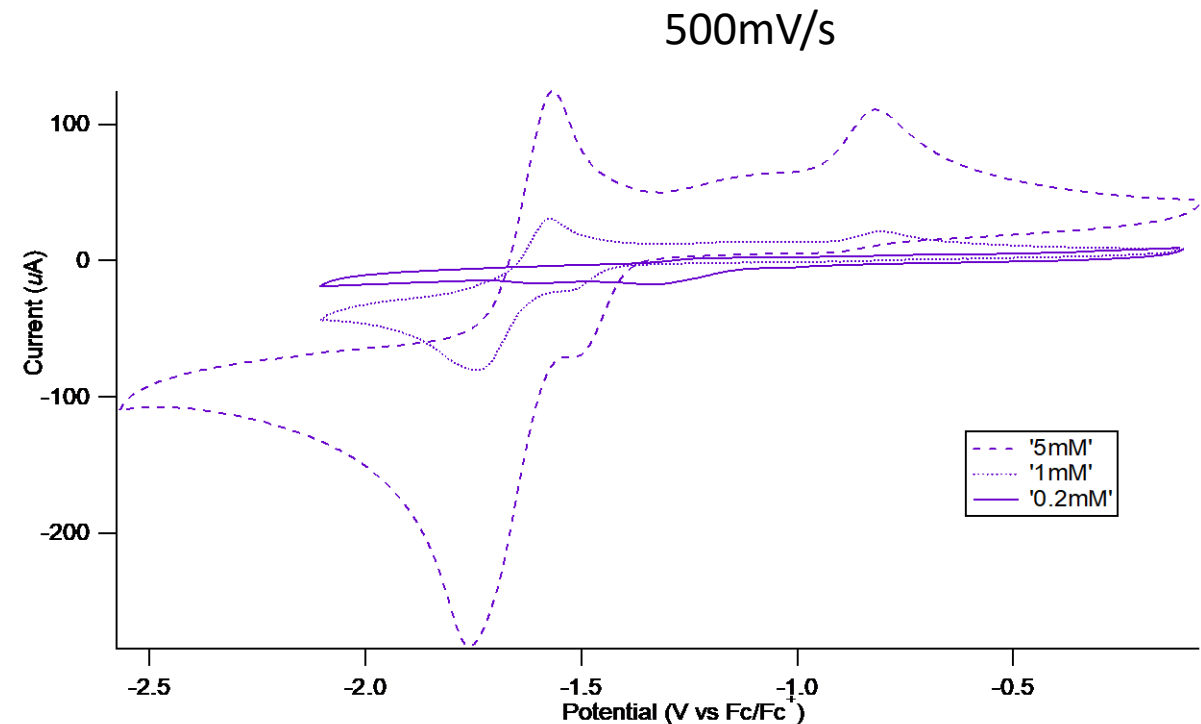
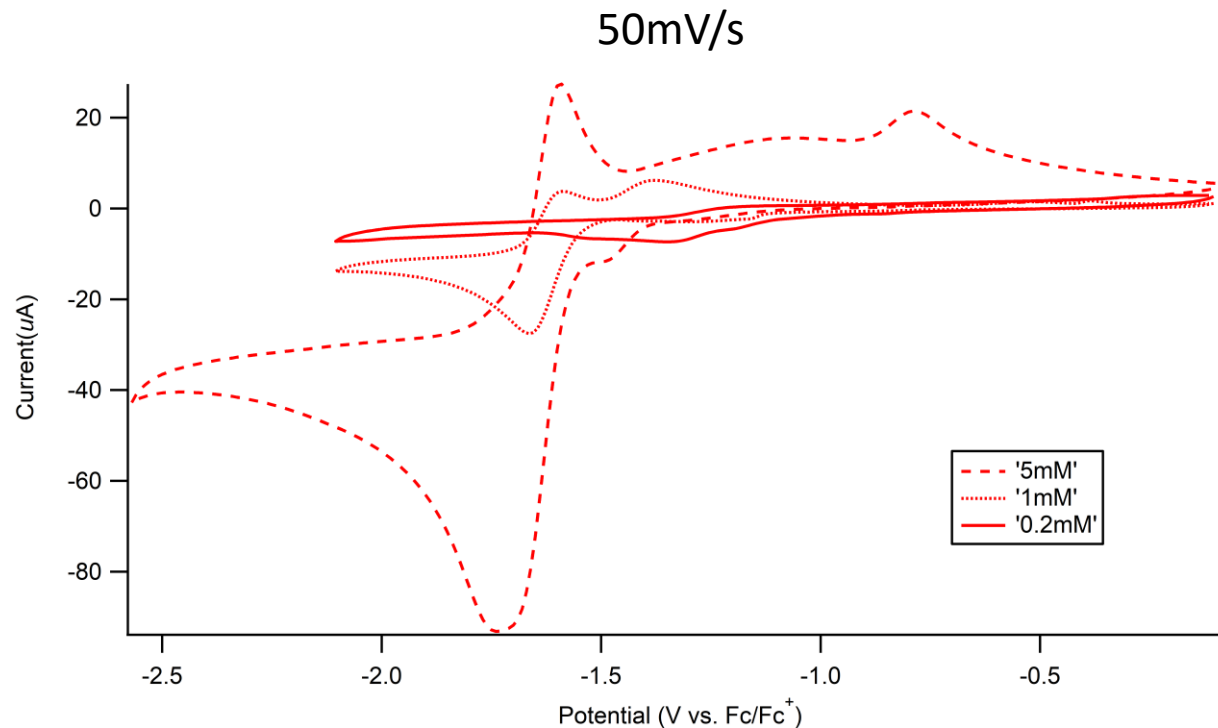
# Mn(bpy)(CO)<sub>3</sub>Br Models



Ligand	MLCT $\lambda_{\max}$ (nm)
bpy	416
4,4'-dmbpy	412
6,6'-dmbpy	397



# Concentration-dependent dimerization

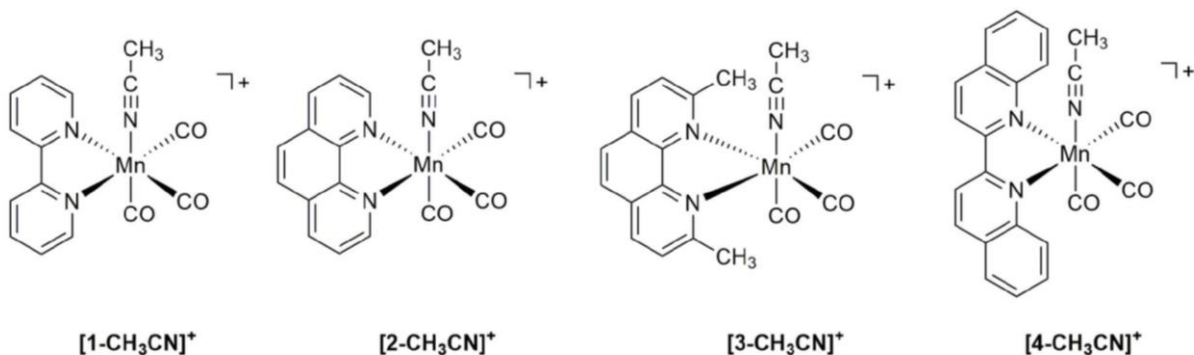


- Dimer formation can be selectively observed in  $\text{Mn}(6,6'\text{-Me}_2\text{bpy})(\text{CO})_3\text{Br}$  by varying scan rate, solvent, and concentration.

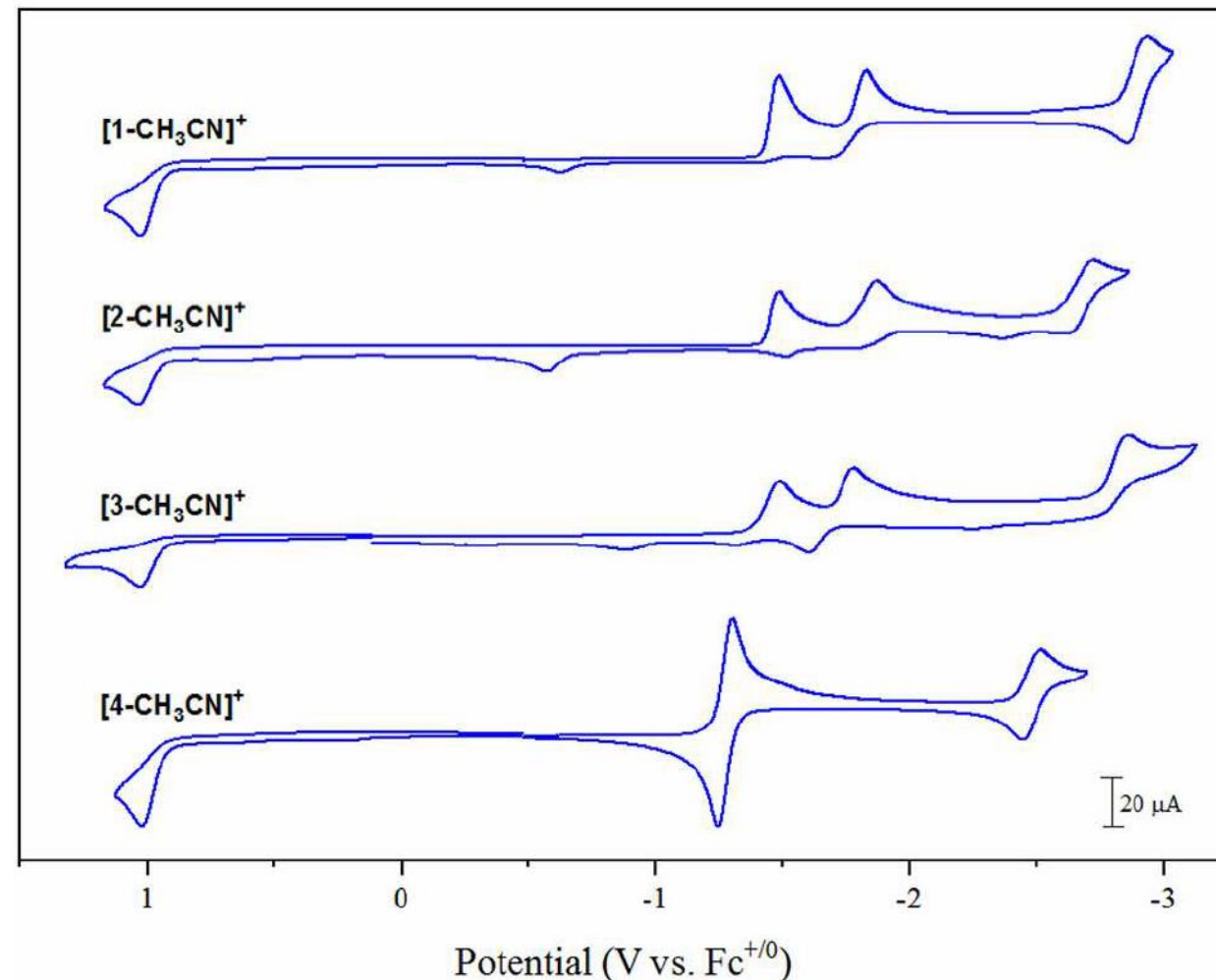




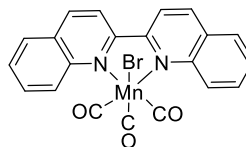
# Analogous Phenanthroline/Biquinoline



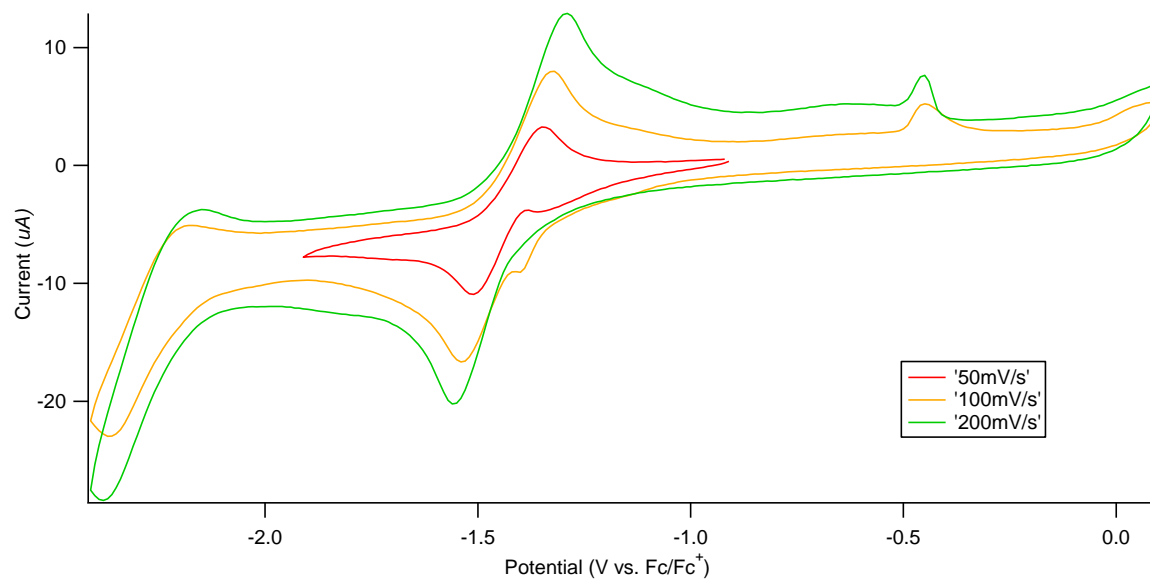
- 6,6'-dimethyl substitution decreased dimer behavior.
- Biquinoline's lack of dimer behavior is attributed to the stability of the acetonitrile-bound complex.



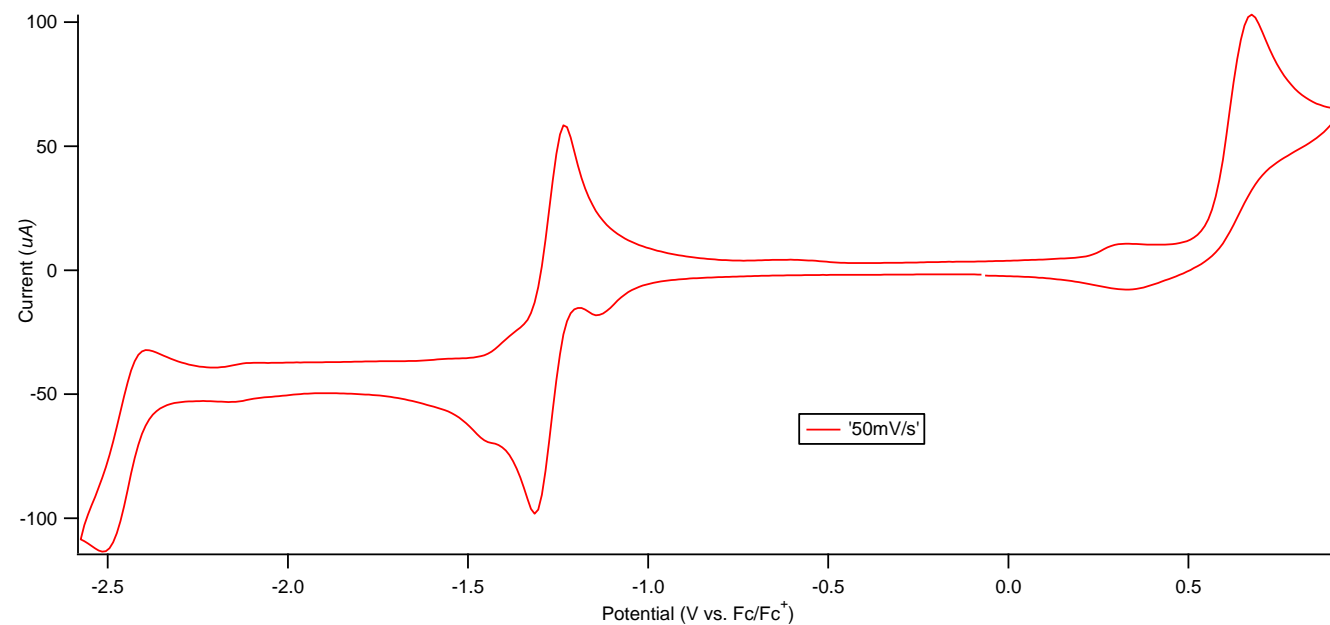
# Biquinoline dimer formation



In THF

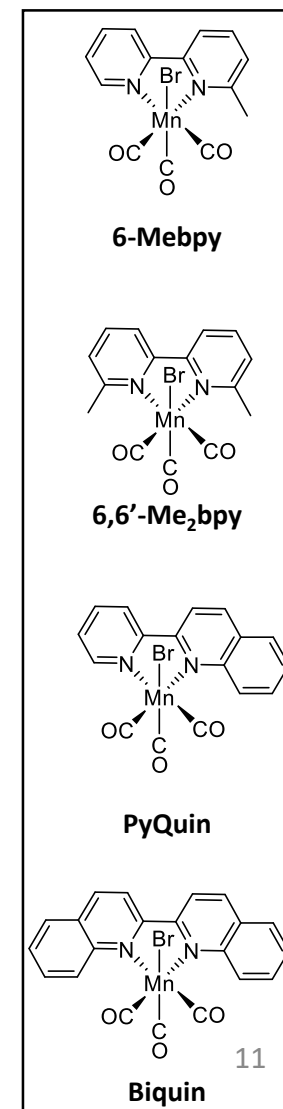
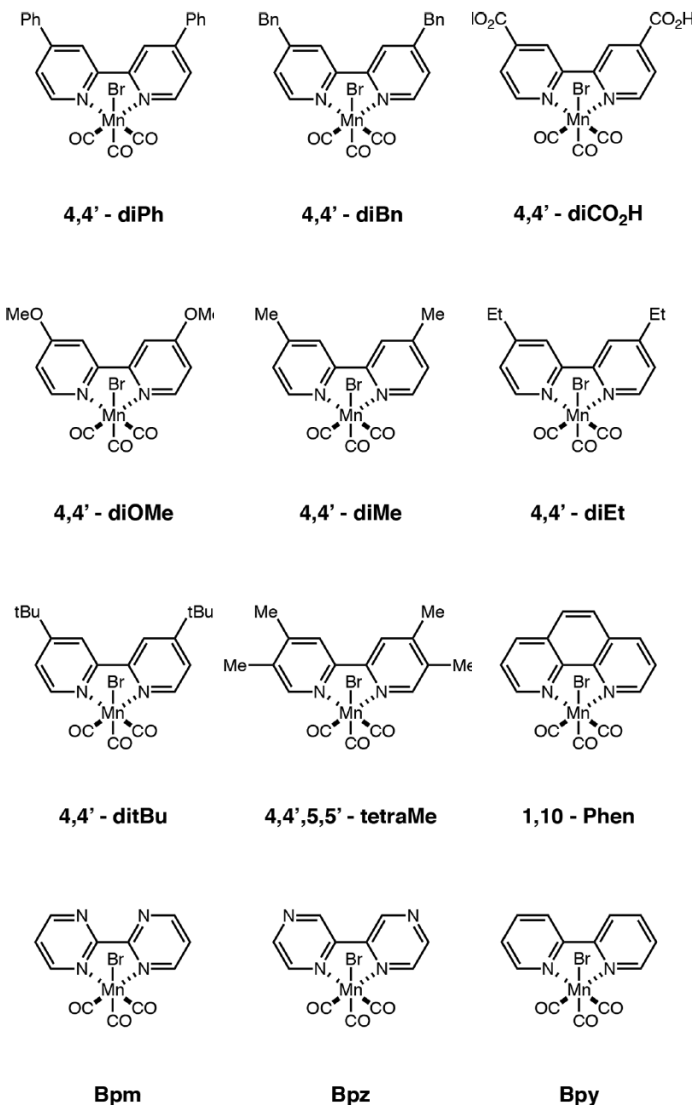
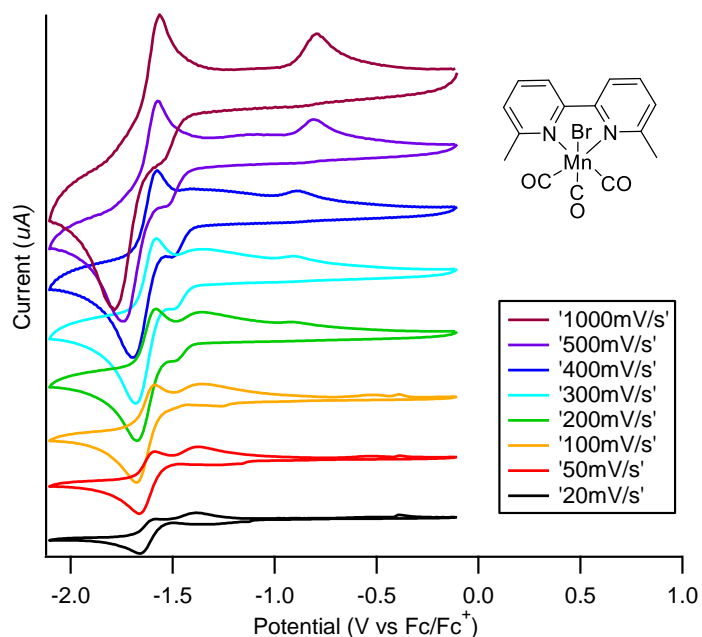


5mM



# Making Predictions based on Trends

- Comparing our complexes against Bocarsly's 4,4'-substituted complexes.
  - HOMO-LUMO gap
  - MLCT  $\lambda_{\max}$
  - Reduction potential to generate anion, 100mV/s

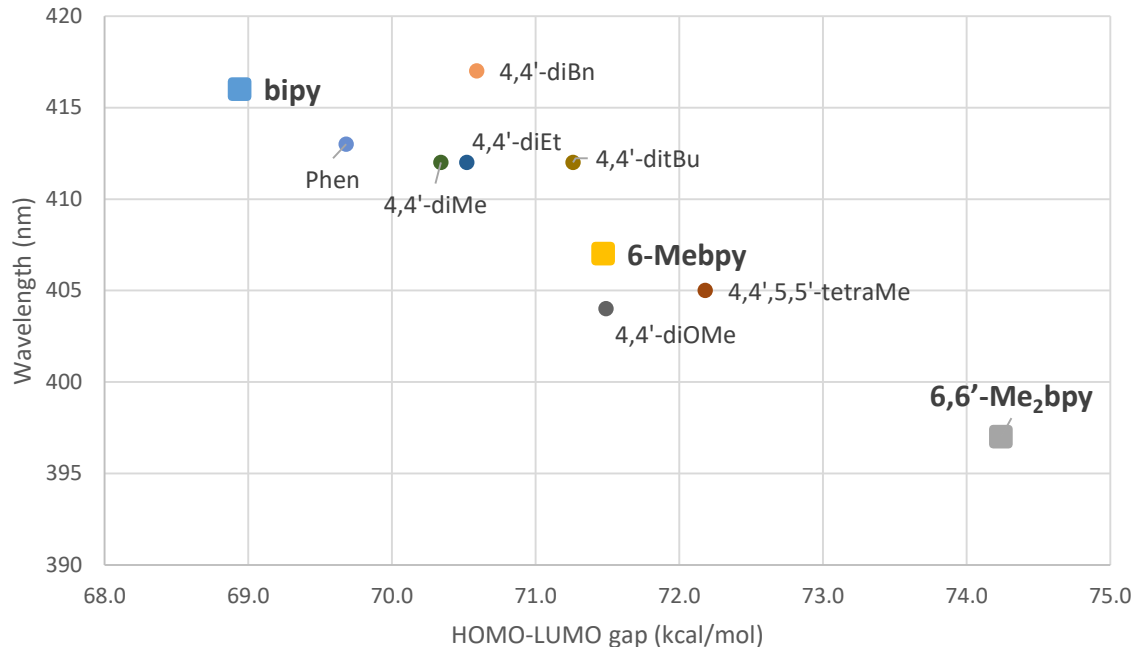


Tignor, S. E.; Kuo, H. Y.; Lee, T. S.; Scholes, G. D.; Bocarsly, A. B. *Organometallics* **2019**, *38* (6), 1292–1299.  
 Thistleford, Z.; Gupta, R.; Caputo, C. *In Preparation*.

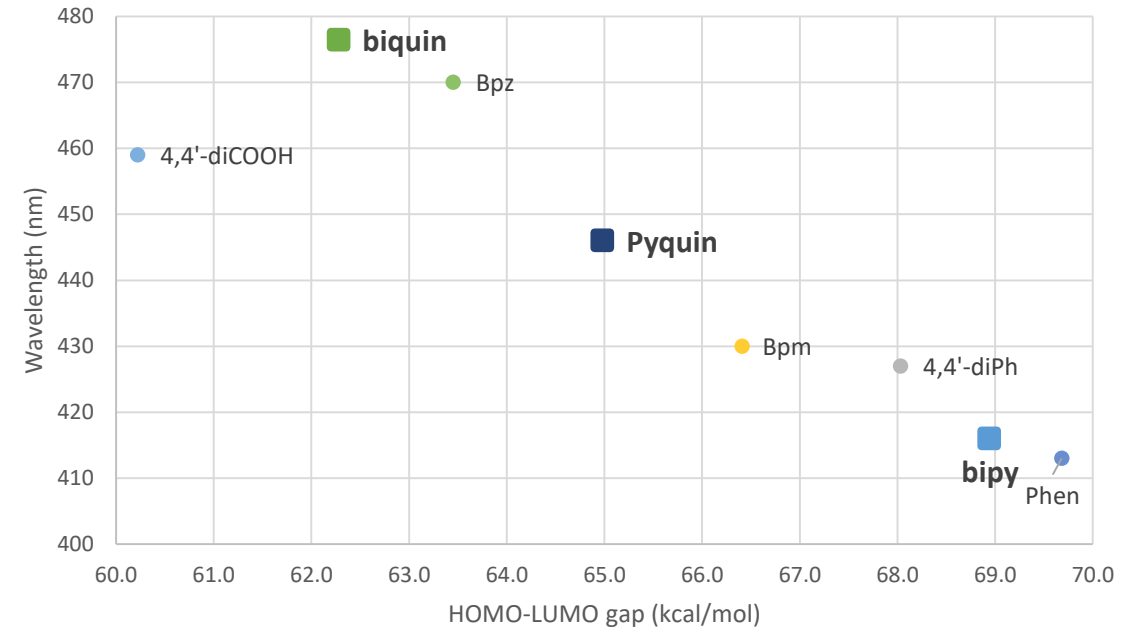


# MLCT $\lambda_{\max}$ vs HOMO-LUMO gap

MLCT vs HOMO-LUMO gap: e-donating



MLCT vs HOMO-LUMO gap: e-withdrawing

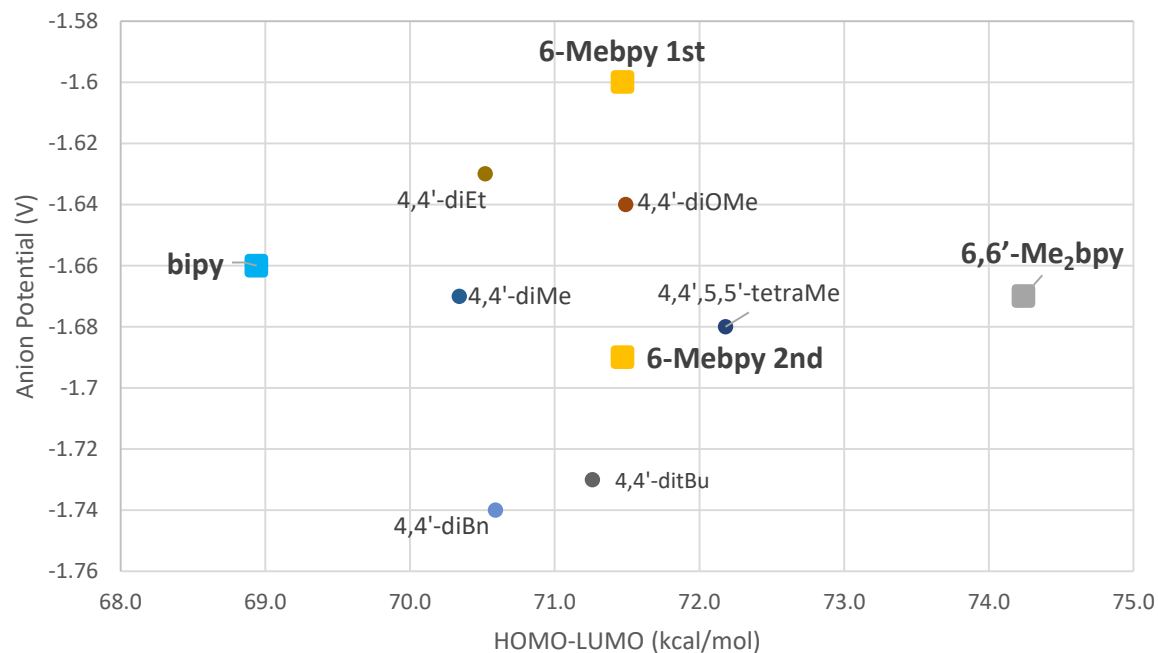


- Substitution at the 6- and 6,6'-positions has a much greater impact on both the HOMO-LUMO gap (mostly by raising the LUMO) as well as wavelength.
- For PyQuin and Biquin, delocalization/e-withdrawing is still more significant.

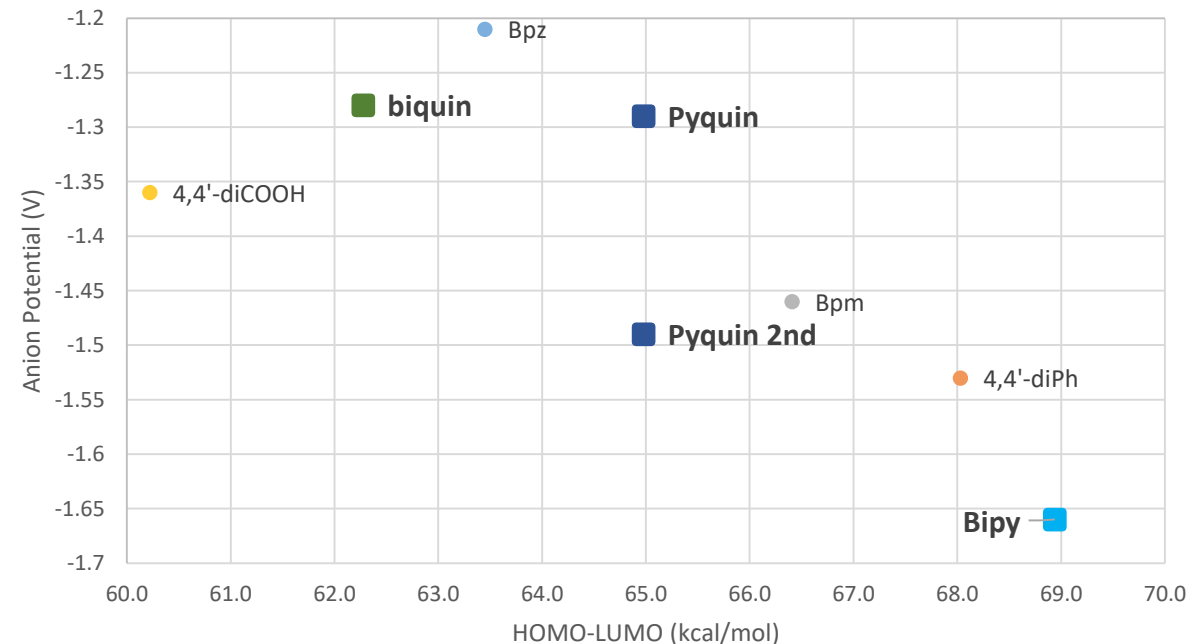


# Reduction Potentials vs HOMO-LUMO gap

Anion-forming potential vs HOMO-LUMO: e-donating



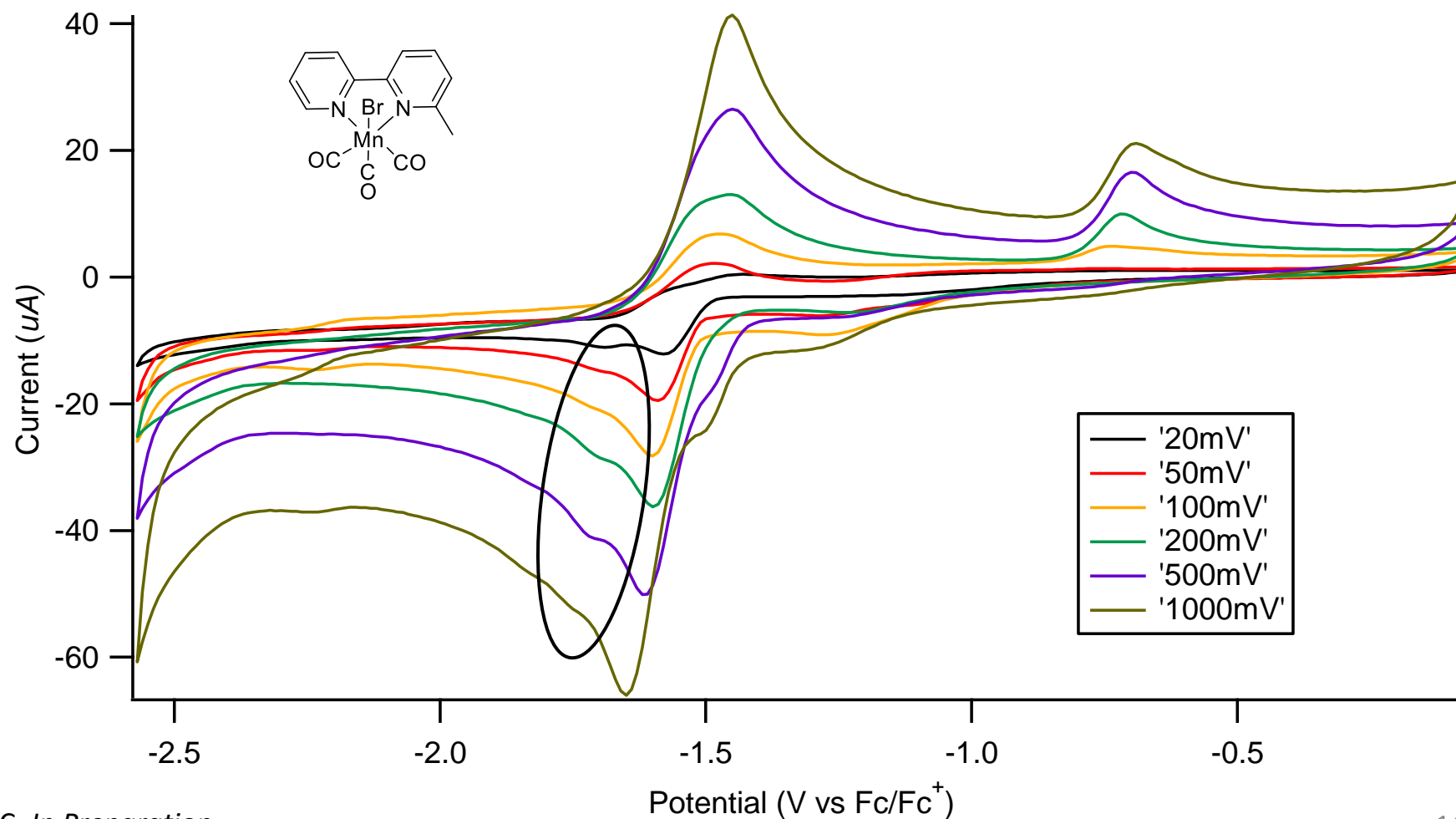
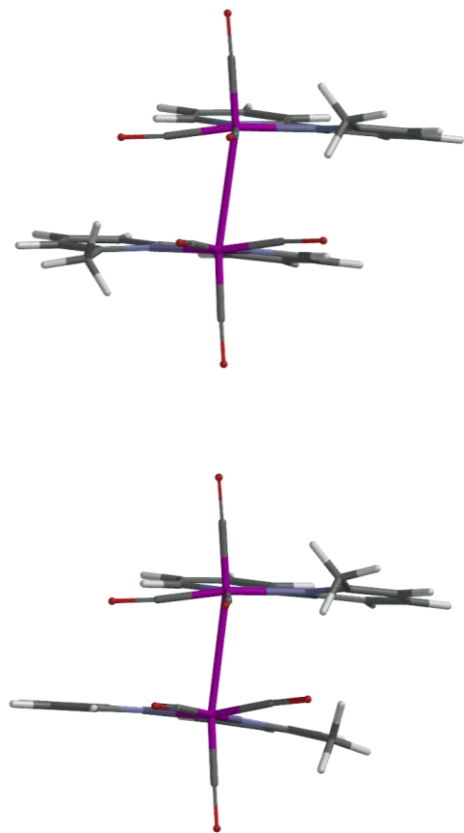
Anion-forming potential vs HOMO-LUMO: e-withdrawing



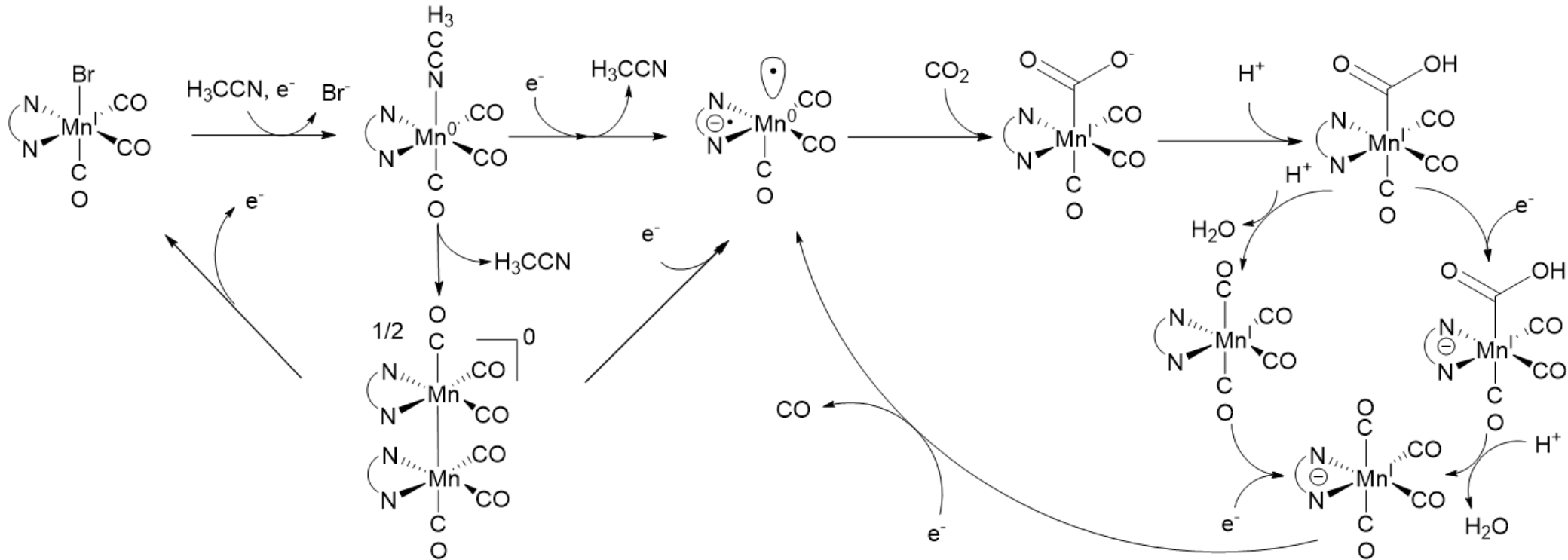
- Electron-withdrawing substituents have less negative reduction potentials.
- Mono-substituted complexes have less negative 1<sup>st</sup> reduction potential than expected.



# Asymmetry leads to 2 anion-formation peaks

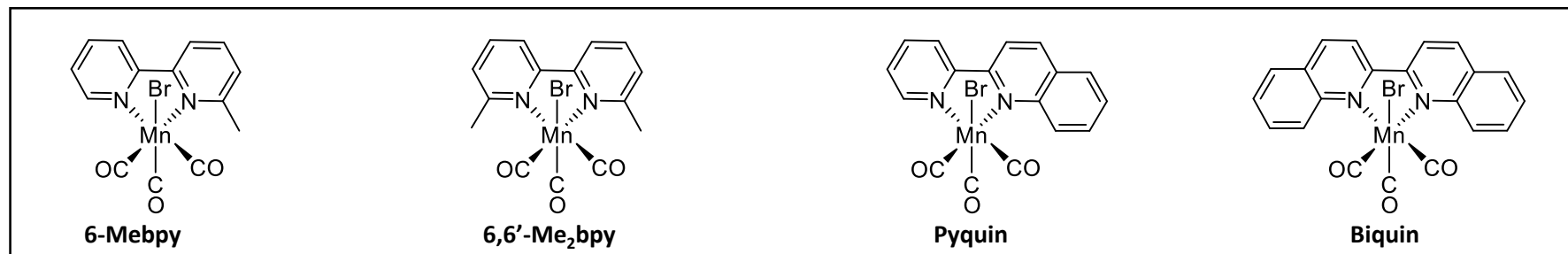


# Mn(bpy)(CO)<sub>3</sub>Br Catalysis



# Summary of Catalysis

Complex	Concentration	Potential vs. Fc/Fc+	Product	1hr TON	1hr FE%	4hr TON	4hr FE%
Mn(6-Mebpy)(CO) <sub>3</sub> Br	1.0mM	-2.1V	CO	0.5	71%	0.9	60%
Mn(6-Mebpy)(CO) <sub>3</sub> Br	1.0mM	-2.1V	H <sub>2</sub>	0.1	19%	0.4	26%
Mn(6,6'-Me <sub>2</sub> bpy)(CO) <sub>3</sub> (OTf)	1.1mM	-2.1V	CO	1.2	59%	3.4	60%
Mn(6,6'-Me <sub>2</sub> bpy)(CO) <sub>3</sub> (OTf)	1.1mM	-2.1V	H <sub>2</sub>	0.5	23%	1.6	29%
Mn(6,6'-Me <sub>2</sub> bpy)(CO) <sub>3</sub> (OTf)	1.1mM	-1.7V	CO	0.3	56%	1.0	54%
Mn(Pyquin)(CO) <sub>3</sub> (OTf)	0.9mM	-2.1V	CO	0.2	15%	0.5	9%
Mn(Pyquin)(CO) <sub>3</sub> (OTf)	0.9mM	-2.1V	H <sub>2</sub>	0.5	39%	2.3	43%
Mn(Biquin)(CO) <sub>3</sub> Br	1.0mM	-1.7V	CO	0.5	80%	1.4	71%

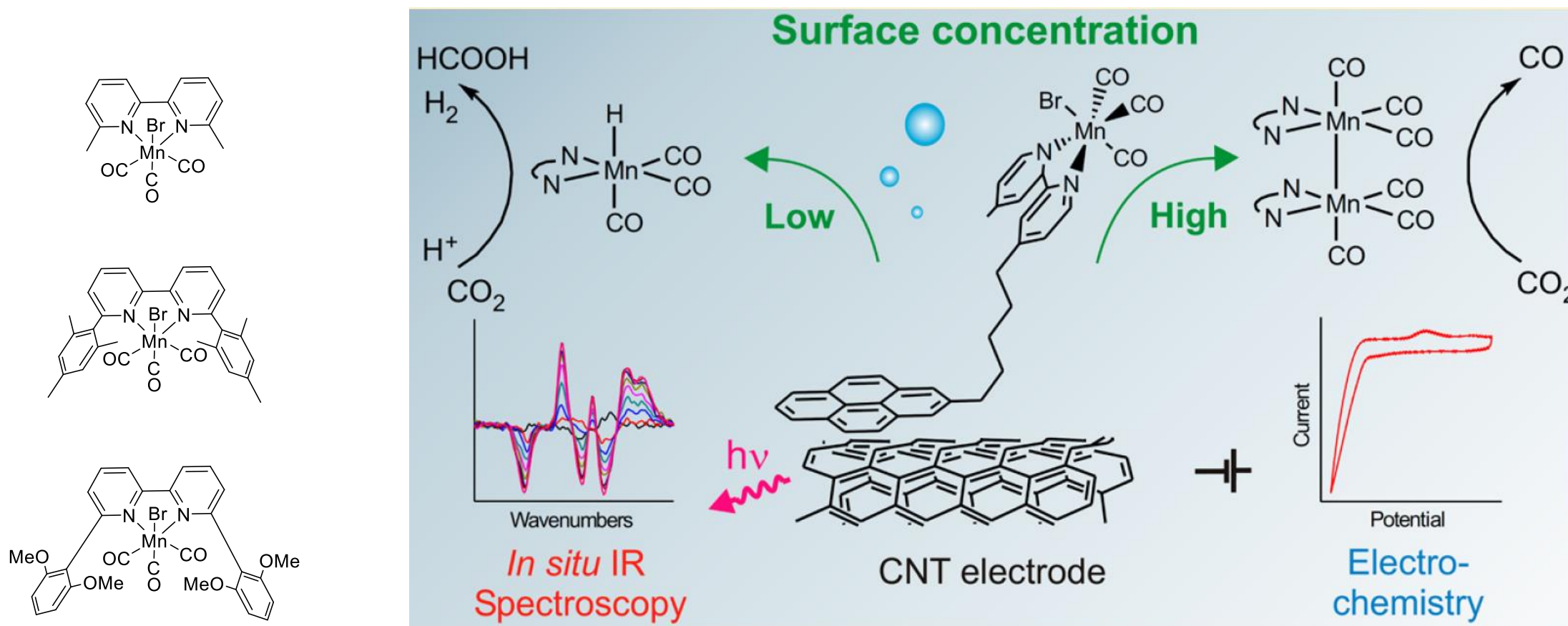


Thistleford, Z.; Gupta, R.; Caputo, C. *In Preparation*.





# Selectivity



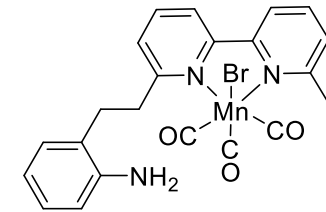
Grills, D.C.; Ertam, M.Z.; McKinnon, M.; Ngo, K.T.; Rochford, J. *Coord. Chem. Rev.* **2018**, 374, 173-217.

Reulliard, B.; Li, K.H.; Rosser, T. E.; Kuehnel, M.F.; Zebger, I.; Reisner, E. *J. Am. Chem. Soc.* **2017**, 139, 14425-14435.



# Future Directions

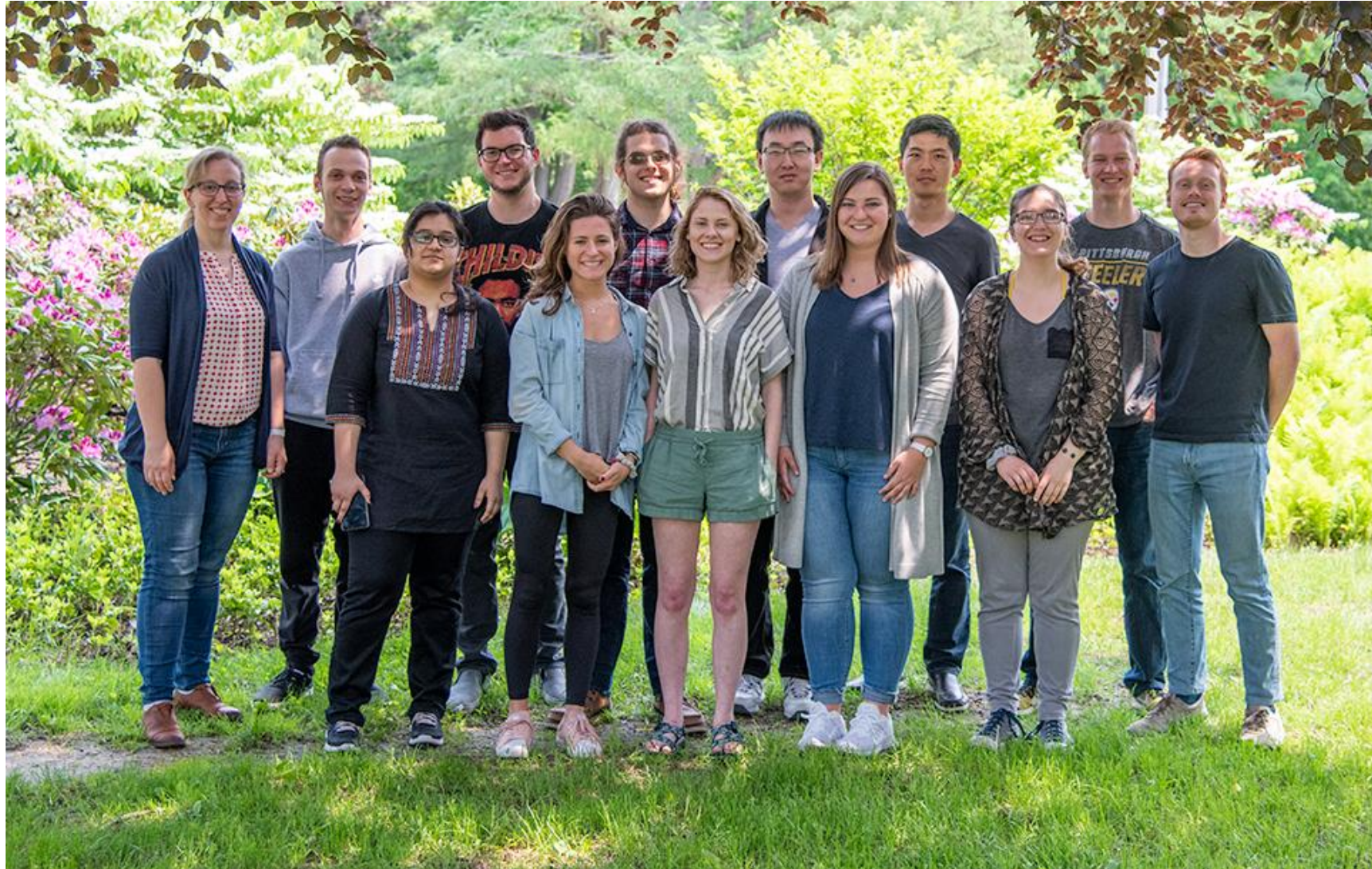
- Adding a pendant proton-transfer group to improve catalysis.
- “bipyridine-aniline” shows similar activity for protonation-first catalysis, but improved reduction-first catalysis.



Complex	Concentration	Potential vs. Fc/Fc <sup>+</sup>	Product	1hr TON	1hr FE%	3hr TON	3hr FE%
Mn(bpy-an)(CO) <sub>3</sub> Br	1mM	-1.7V	CO	0.3	73%	0.5	31%
Mn(bpy-an)(CO) <sub>3</sub> Br	1mM	-2.1V	CO	2.1	85%	4.1	41%
Mn(bpy-an)(CO) <sub>3</sub> Br	1mM	-2.1V	H <sub>2</sub>	0.4	17%	6.6	66%

# Acknowledgments

---



- Caputo Group
  - Dr. Christine Caputo
  - Rashi Gupta

Dr. Jonathan Rochford at  
UMass Boston

UNH CEPS Fellowship



# Energy Computations (values in kcal/mol)

Ligand	H <sub>3</sub> CCN-bound (kcal/mol vs. Dimer)	Monomer (kcal/mol vs. Dimer)
6,6'-dimethylbipyridine	-0.1	3.6
6-methylbipyridine (anti)	1.0	6.3
6-methylbipyridine (syn)	0.9	6.2
Pyridyl-quinoline (anti)	-3.0	5.6
Pyridyl-quinoline (syn)	-3.0	5.6
Pyridyl-isoquinoline (anti)	3.2	9.1
Pyridyl-isoquinoline (syn)	2.9	8.8
Quinoline-isoquinoline (anti)	-2.0	5.7
Quinoline-isoquinoline (syn)	-2.0	5.6
Biisoquinoline	5.7	11.8

Ligand	H <sub>3</sub> CCN-bound (kcal/mol vs. Dimer)	Monomer (kcal/mol vs. Dimer)	Reference
bipyridine	3.3	11.3	Bocarsly
4,4'-dimethylbipyridine	1.7	8.9	Bocarsly
4,4'-diethylbipyridine	2.8	9.2	Bocarsly
4,4'-t-butylbipyridine	3.3	9.0	Bocarsly
4,4',5,5'-tetramethylbipyridine	3.7	9.1	Bocarsly
4,4'-dimethoxybipyridine	2.5	9.3	Bocarsly
4,4'-dicarboxylbipyridine	-10.6	8.8	Bocarsly
4,4'-diphenylbipyridine	0.9	9.4	Bocarsly
4,4'-dibenzylbipyridine	4.5	10.3	Bocarsly
2,2'-bipyramidine	-1.2	23.0	Bocarsly
2,2'-bipyridine	3.7	16.5	Bocarsly
Biquinoline	-7.6	0.8	Rochford
phenanthroline	3.1	8.9	Rochford
6,6'-dimethylphenanthroline	0.0	1.3	Rochford
6,6'-mesbpy	-8.0	-1.9	Sampson

Sampson, M.D.; Nguyen, A.D.; Grice, K.A.; Moore, C.E.; Rheingold, A.L.; Kubiak, C.P. *J. Am. Chem. Soc.*, **2014**, *136*, 5460-5471.

McKinnon, M.; Belkina, V.; Ngo, K.T.; Ertem, M.Z.; Grills, D.C.; Rochford, J. *Front. Chem.* **2019**, *7*:628, 1-14.

Tignor, S. E.; Kuo, H. Y.; Lee, T. S.; Scholes, G. D.; Bocarsly, A. B. *Organometallics* **2019**, *38* (6), 1292–1299.

Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 9903-9906.