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Derivatization and Optimization of Iron Bipyridine Complexes for Non-Aqueous Flow Batteries

PRESENTED BY

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Non-aqueous Flow Battery Chemistries

Why non-aqueous?

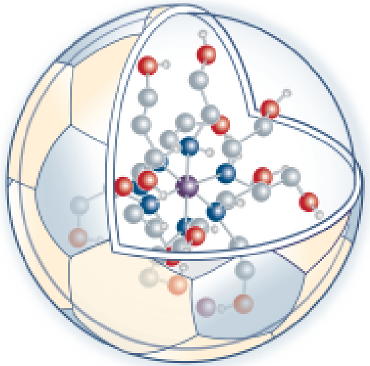
- Wider voltage window
- Higher charge cycle efficiency
- Decreased temperature sensitivity
- Increased cycle life
- Degradation mechanisms well understood

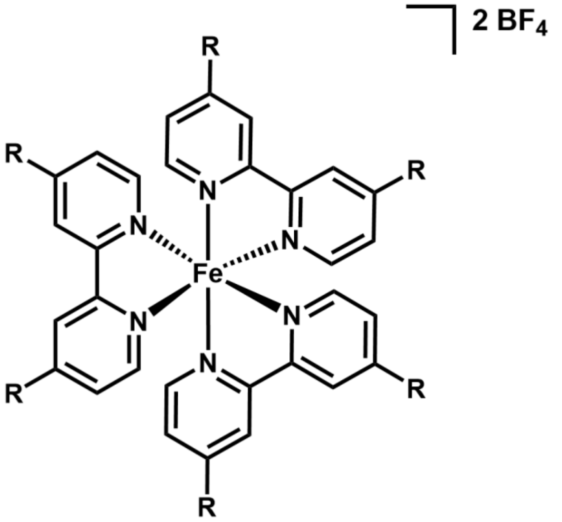
Why not?

- Low concentration of electroactive species
- Viscosity
- Expensive and toxic solvents
- Poorly performing membrane/separators

Examples of non-aqueous flow battery chemistries

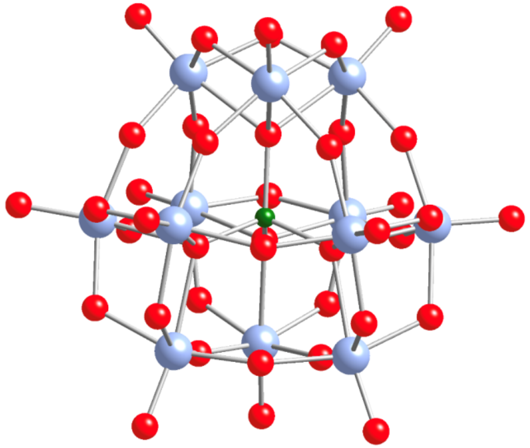
Metal Ionic Liquids (MetILs)





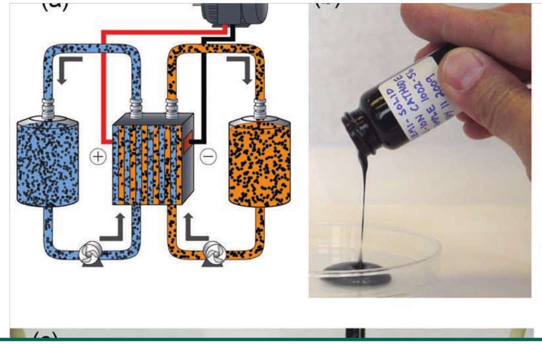
R = CF_3
CO_2Me
Br
H
Me
^tBu
OMe
NH_2

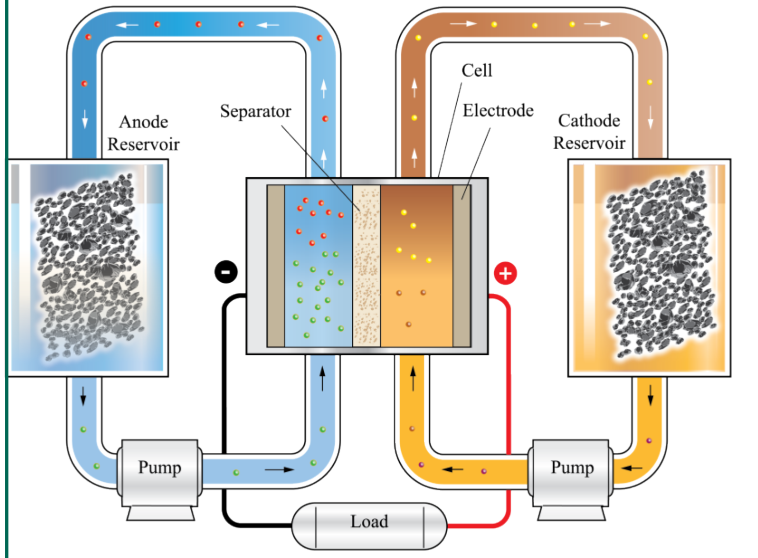
Metal Coordination Complexes (MCCs)



Polyoxometalates (macromolecule)

Semi-solid lithium ion





Hybrid Systems

T. A. Palmer *et al*. *ChemSusChem*, **2021**, *14*, 1214-1228.

Non-aqueous Flow Batteries

Project Goal: Build a better flow battery* by targeting (1) Energy Density (2) Materials Cost (3) Mechanisms of Capacity Fade

$$\boxed{\textbf{Energy Density}_{RFB} = \tfrac{1}{2}nFV_{cell}c_{active}}$$

$ED_{AQ} = \tfrac{1}{2}1F1.5_{cell}2_{active} = \mathbf{1.5F}$

$ED_{MetIL} = \tfrac{1}{2}2F2_{cell}3_{active} = \mathbf{6.0F}$ **Low-Cost Materials** **Viscosity** ☠

$ED_{MacM} = \tfrac{1}{2}2F2_{cell}0.1_{active} = \mathbf{0.2F}$

$ED_{RedTarg} = \tfrac{1}{2}1F3_{cell}5_{active} = \mathbf{7.5F}$ **High Energy Density**

Surface Area Kinetics ☠

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*>4.4 mol e^-/L according to Darling *et al.*, *Energy Environ. Sci.*, **2014**, *7*, 3459-3477.

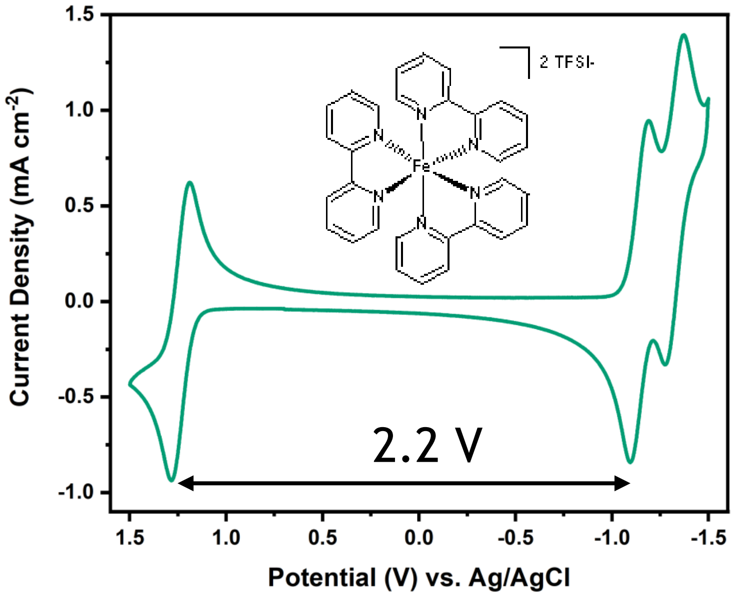
Non-aqueous Iron-Organic Flow Batteries

$ED_{MCC} = \frac{1}{2}2F2.2_{cell}0.2_{active} = \mathbf{0.4F}$ **Low-Cost Materials** **Crossover ☠**

First Generation redox reactions (2.26 V)

Posolyte: $Fe(bpy)_3(BF_4)_2 \rightarrow Fe(bpy)_3(BF_4)_3 + e^-$

Negolyte: $Ni(bpy)_3(BF_4)_2 + 2\ e^- \rightarrow Ni(bpy)_3(BF_4)_2$



Second Generation (symmetric) all-iron battery minimizes issues with crossover and utilizes *non-innocent* ligands.

Next Generation

$ED_{MCC} = \frac{1}{2}2F2.6_{cell}1_{active} = \mathbf{2.6F}$

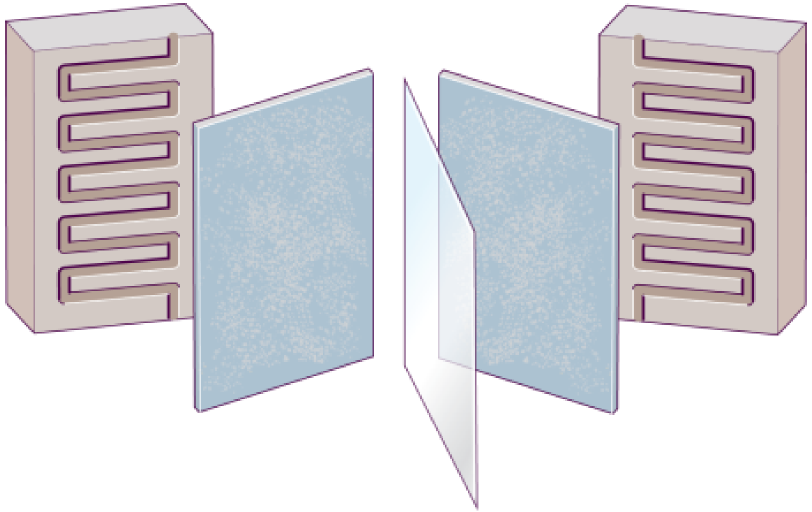
Lower Symmetry, Higher Solubility

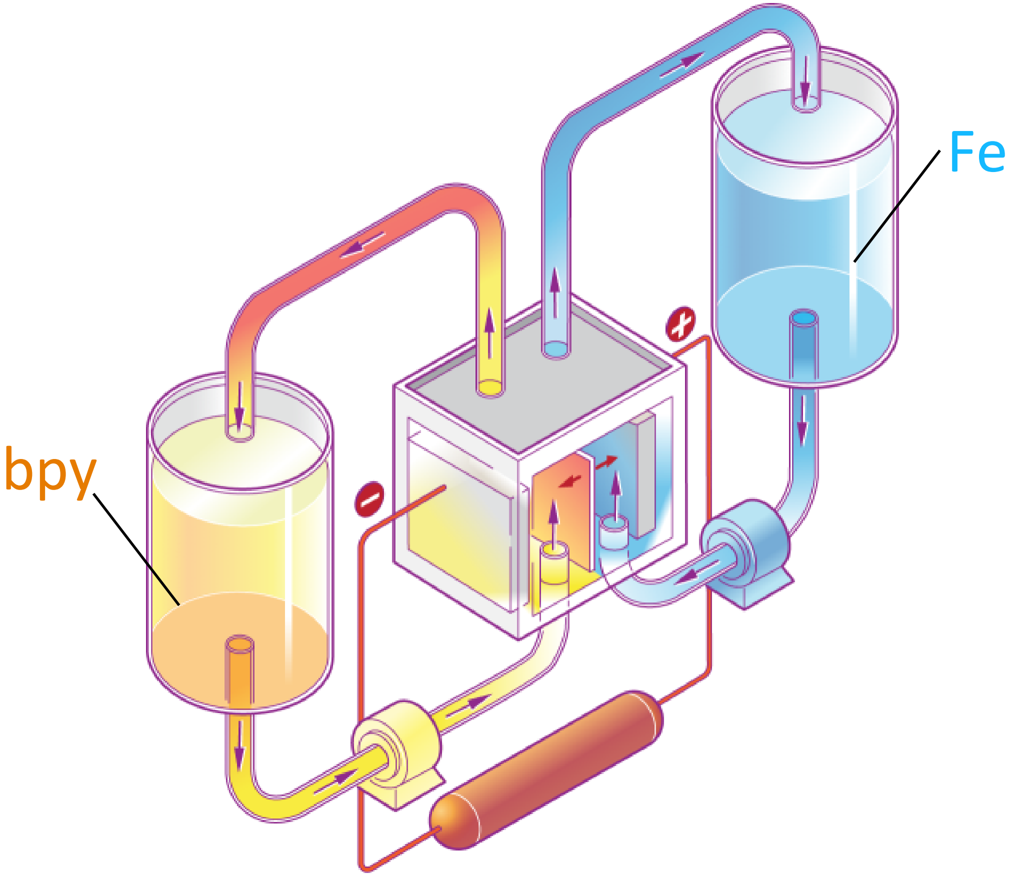
Tunable Ligands, Wider Voltage

(1) Mun, Lee, Park, Oh, Lee, & Doo, *Electrochem. Solid-State Lett.*, **2012**, *6*, A80-A82 (2) Mn, Oh, Park, Kwon, Kim, Jeong, Kim, & Lee, *J. Electrochem. Soc.*, **2018**, *165*, A215-A219 (3) Hogue & Toghill, *Curr. Op. Electrochem.*, **2019**, *18*, 37-45.

$Fe(bpy)_3(BF_4)_2$ Optimization

- Test materials and parameters
  - Membrane: Fumasep FAP-450 anion exchange membrane
  - Solvents: propylene carbonate and acetonitrile
  - Electrolyte Salts: TEA-BF_4 , TBA-OTf, TBA-TFSI, TBA-BF_4 , and TBA-PF_6
  - 0.5 M electrolyte salt + 0.2 M $Fe(Bipy)_3(BF_4)_2$
  - Argon glovebox
  - Graphite blocks/carbon felt
  - 3 mL/min flow rate
  - 20 cycles at ±10 mA cm^{-2}

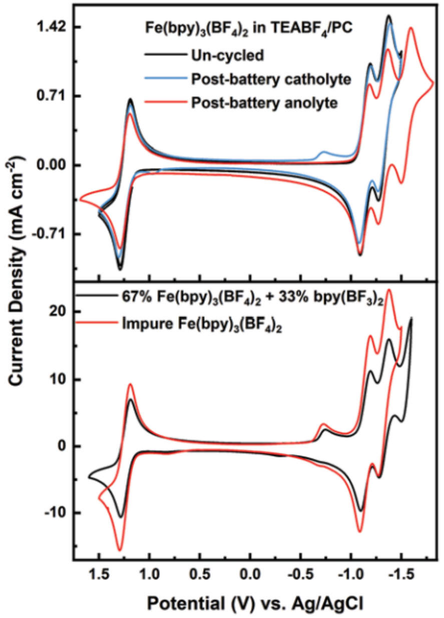


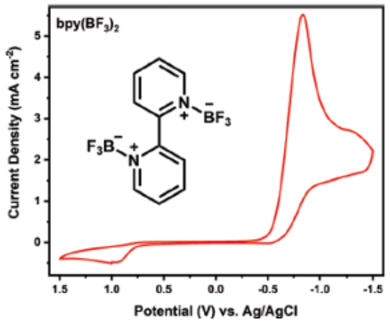


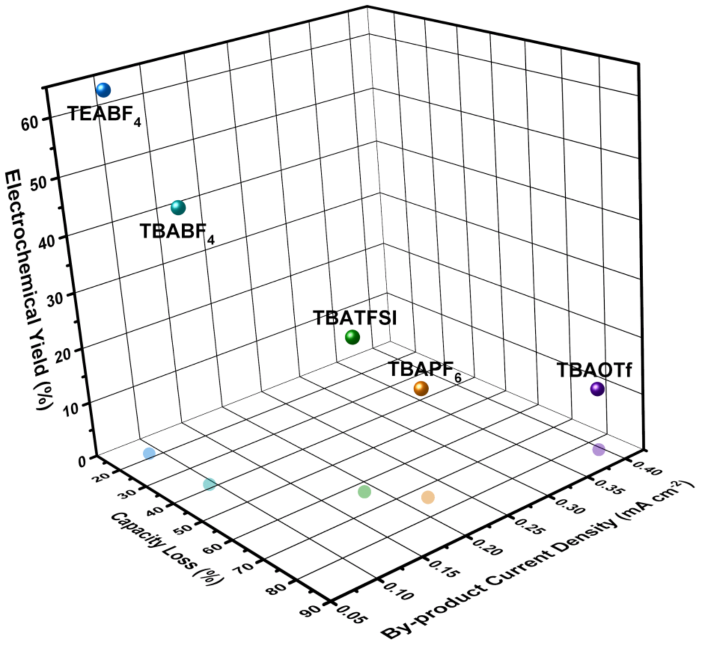
$Fe(bpy)_3(BF_4)_2$ Optimization

Varied supporting electrolyte to observe performance

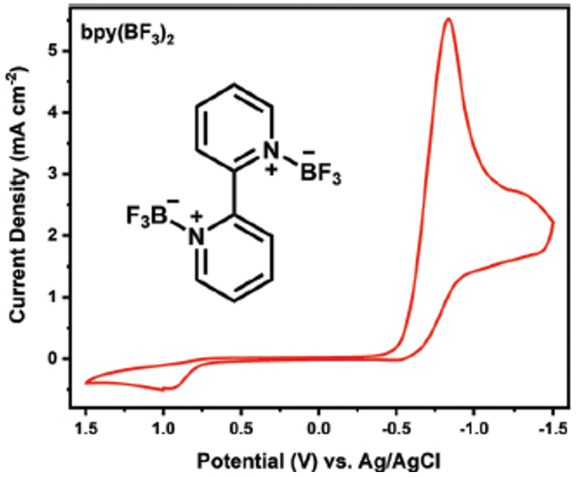
- TEA^+ is superior to TBA^+
- BF_4^- is a superior anion
- Little crossover observed, but a common by-product forms upon cycling
- Found a relationship between capacity fade and by-product formation
- Negolyte ligand shedding, crossover, BF_4^- hydrolysis, followed by nucleophilic attack
- 15-20% improvement in performance when extra drying measures and higher purity precursors were used

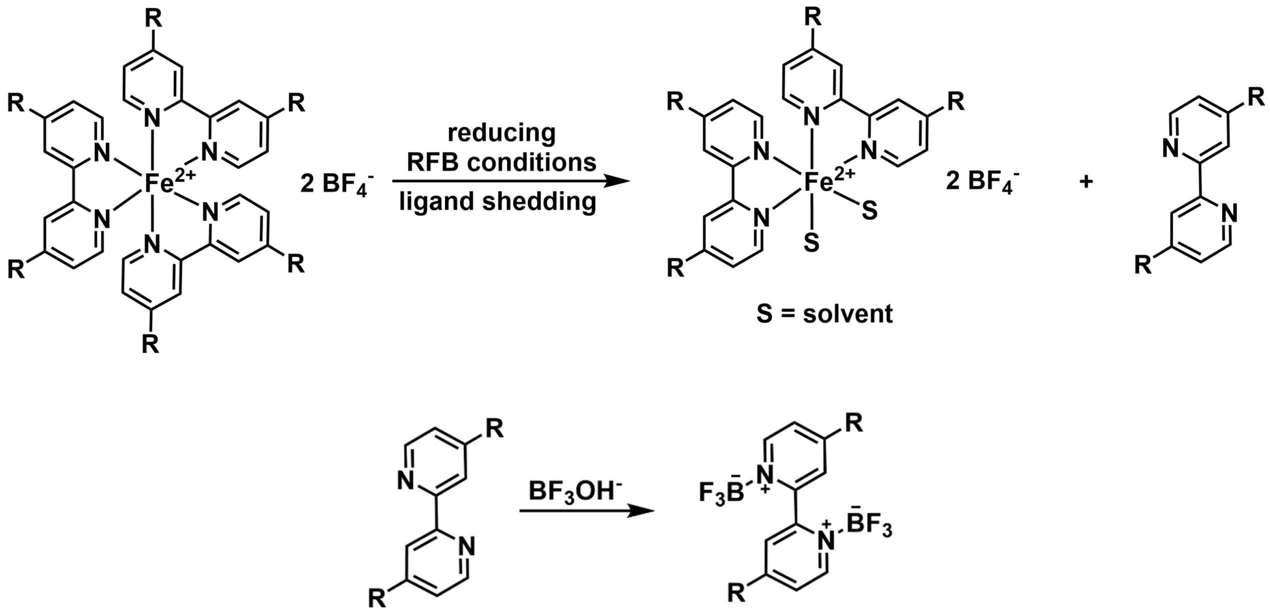






Mechanism of Symmetric Fe(bpy)$_3$(BF$_4$)$_2$ Capacity Fade



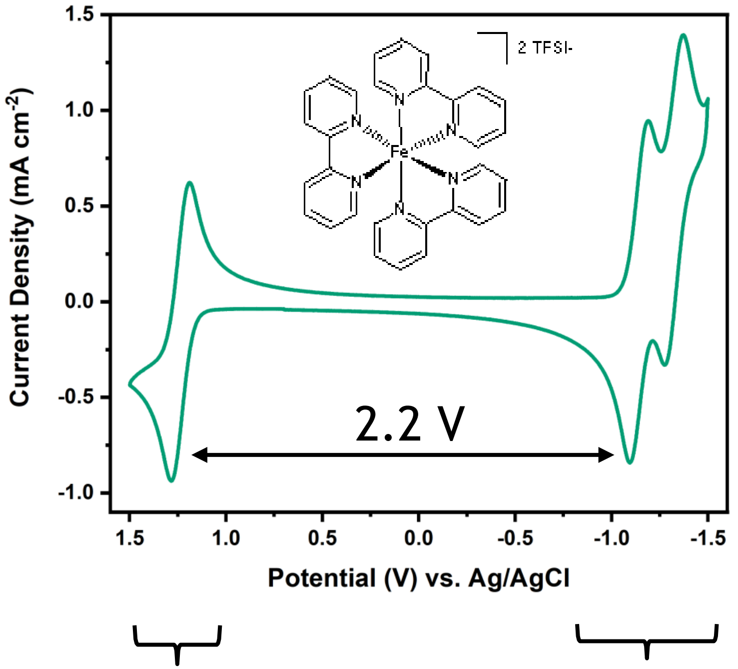


- Ligand shedding, posilyte BF$_4^-$ crossover and hydrolysis, followed by nucleophilic attack.
- Final product was confirmed by MS
- “Mechanistic studies (e.g., molecular dynamics, decompositions, and electrode-solution interface) are essential as they can gain insights into this complex battery system and may inspire crucial factors that revolutionize control of key physicochemical properties.”

Tuning Bipyridine Ligands

Goal: produce a higher voltage symmetric RFB using inorganic synthesis and fundamentals of coordination complex chemistry

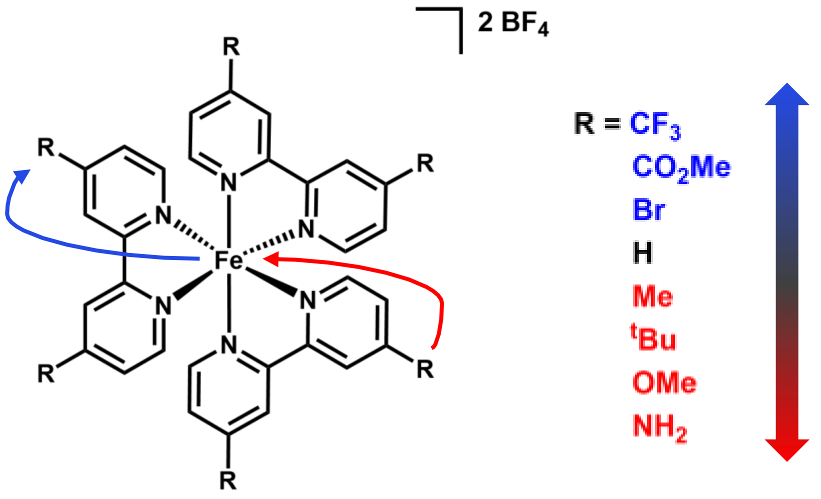
Samsung RFB



Fe(II)/(III)

Bpy redox

Our complexes



Movement of e- density with substituents

Substituent inductive effects

Electron-withdrawing (EWG)

More positive $E_{1/2}$

More difficult to oxidize Fe(II)

Electron-donating (EDG)

More negative $E_{1/2}$

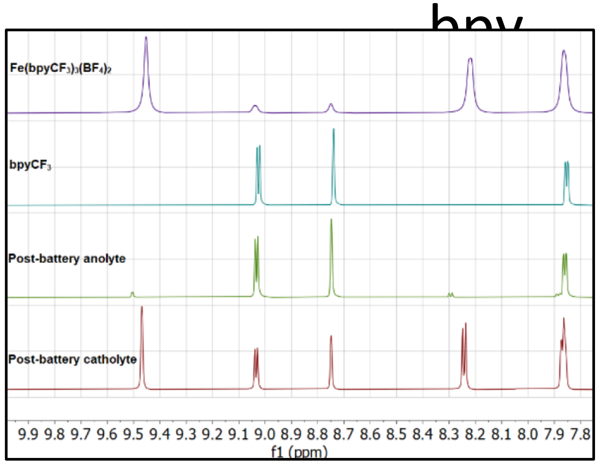
Easier to oxidize Fe(II)

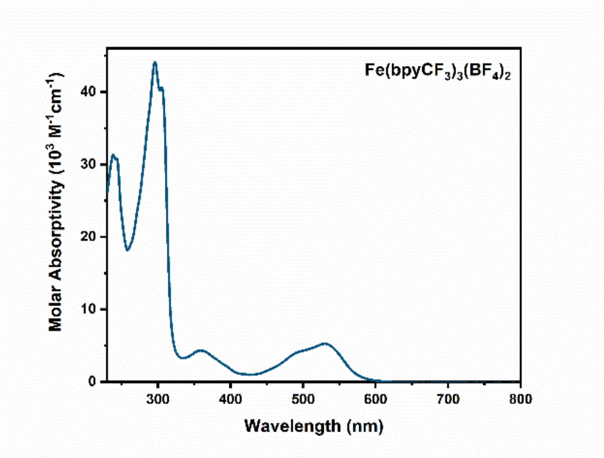
bipyridine: traditional π-acceptor ligand

C. X. Cammack *et al*. *Dalton Trans*., **2021**, *50*, 858-868.

Synthesis of the Substituted Bipyridine Ligands

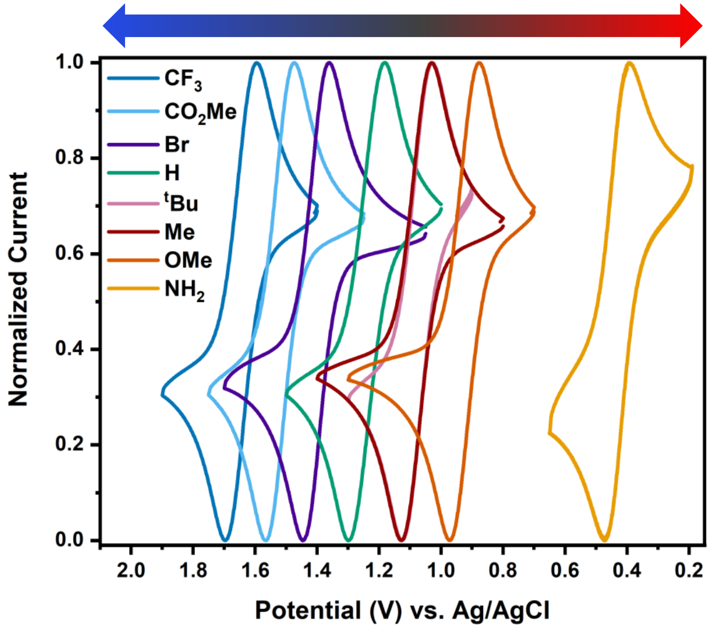
$$\mathrm{Fe(BF_4)_2 \cdot 6H_2O} \quad + \quad \mathrm{3\ R\text{-}bpy} \xrightarrow{\text{methanol}} \mathrm{Fe(bpyR)_3(BF_4)_2}$$

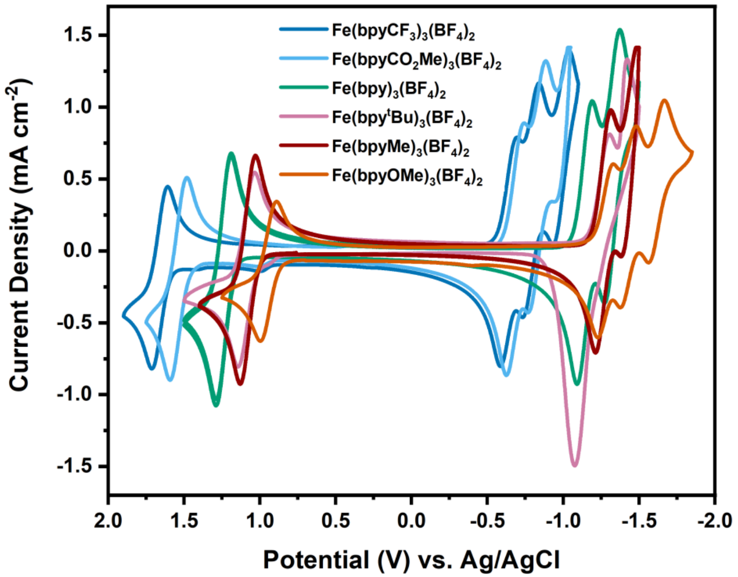




- High yields using earth abundant precursors
- Purity was confirmed by proton NMR (also provides information about structural integrity during battery cycling)
- EWGs shift resonances downfield as expected (and vice-versa EDGs shift resonances upfield)
- UV-Vis data suggest the bpy ligands maintain their highly conjugated electronic structure (required for the voltage separation needed for the symmetric RFB)

Ligand Effects on Redox Potentials





	Fe$^{3+/2+}$ E$_{1/2}$ (V)	Fe$^{2+/+}$ E$_{1/2}$ (V)	ΔE$_{1/2}$ (V)
Fe(bpyCF$_3$)$_3$(BF$_4$)$_2$	1.65	-0.63	2.28
Fe(bpyCO$_2$Me)$_3$(BF$_4$)$_2$	1.53	-0.68	2.21
Fe(bpyBr)$_3$(BF$_4$)$_2$	1.43	-	-
Fe(bpy)$_3$(BF$_4$)$_2$	1.25	-1.12	2.37
Fe(bpy^{t}Bu)$_3$(BF$_4$)$_2$	1.09	-1.19	2.28
Fe(bpyMe)$_3$(BF$_4$)$_2$	1.07	-1.25	2.32
Fe(bpyOMe)$_3$(BF$_4$)$_2$	0.94	1.27	2.21
Fe(bpyNH$_2$)$_3$(BF$_4$)$_2$	0.43	-	-

Fe(II)/(III)

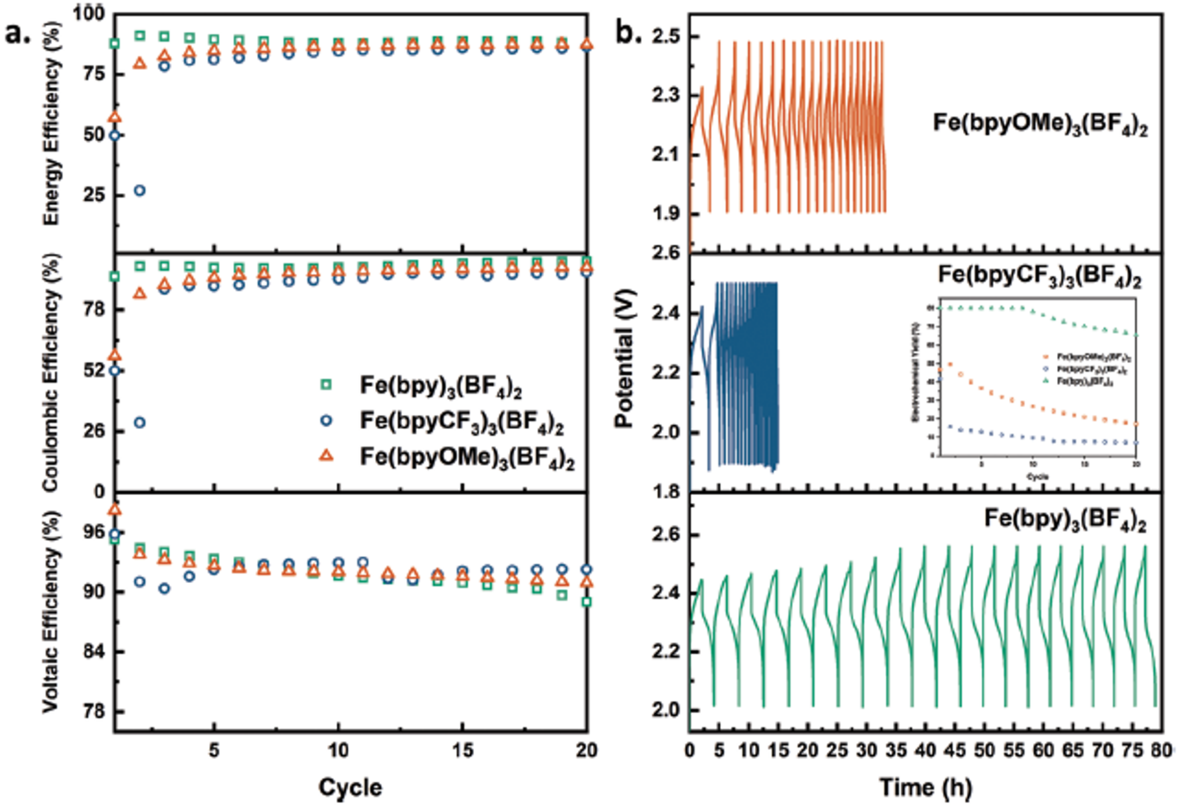
ligand

voltage gap

Inductive effects change ease oxidation of Fe(II)
EWGs shifted positively by up to 0.4 V
EDGs shifted negatively by up to 0.8 V
Fe(II) and ligand-centered redox shifted together

Substituted $Fe(bpyR)_3(BF_4)_2$ in Symmetric RFBs

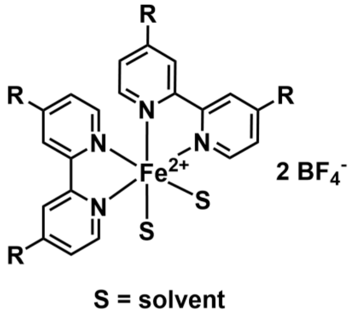
- Analyzed the effect substituents on bpy have on cycling in a RFB
- The most EWG and EDG were compared to the unsubstituted $Fe(bpy)_3$
- The unsubstituted showed greatest cycling stability, followed by the EDG (-OMe), then the EWG ($-CF_3$)
    - Capacity fade (& electrochemical yield inset)
    - Negolyte degradation due to ligand shedding



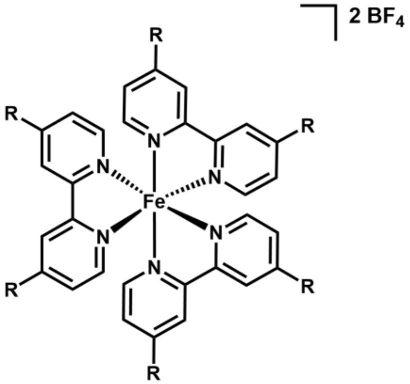
The **negolyte is unstable**. How can we fix it? Pseudo-symmetric flow batteries!

Why Pseudo-Symmetric?

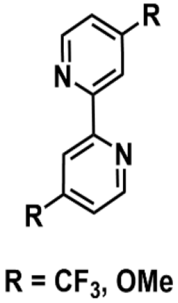
1. More stable under highly reducing conditions
2. Coordinatively unsaturated complex can catalyze unwanted reactions
3. Free ligand is more tunable (synthetically)
4. Improve atom economy



This entire portion of the molecule is not being used in the anode.



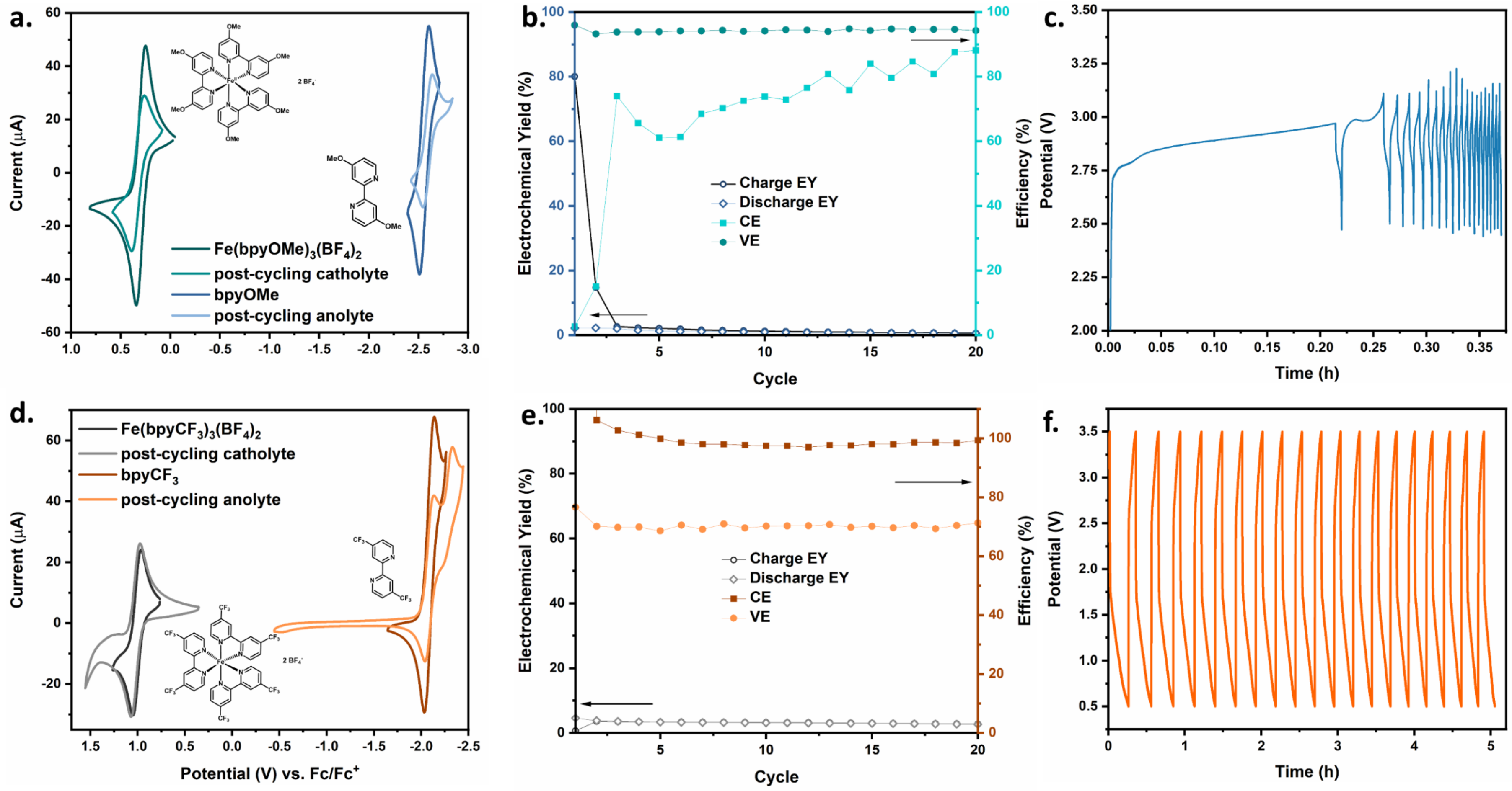
Posolyte

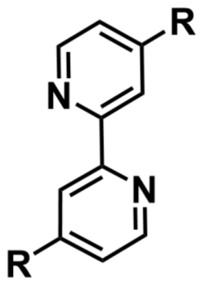


Negolyte

Pseudo-symmetric flow batteries will have **metal-free negolytes**.

First Generation Pseudo-Symmetric Flow Cell Studies





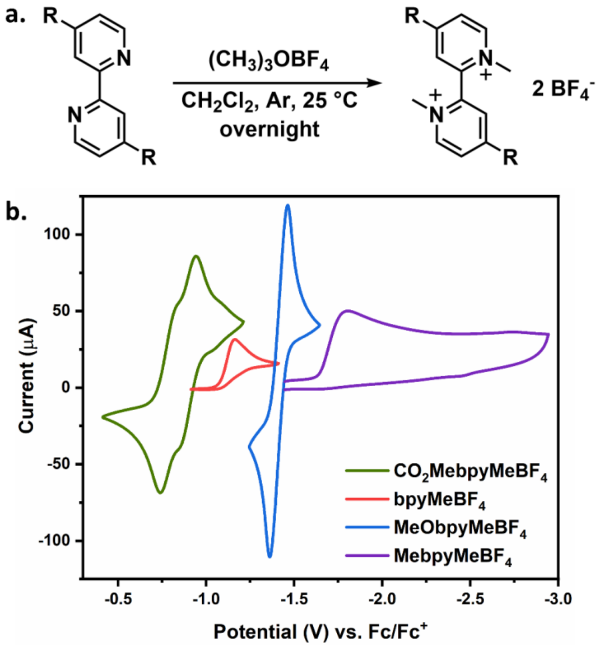
R = CF_3, OMe

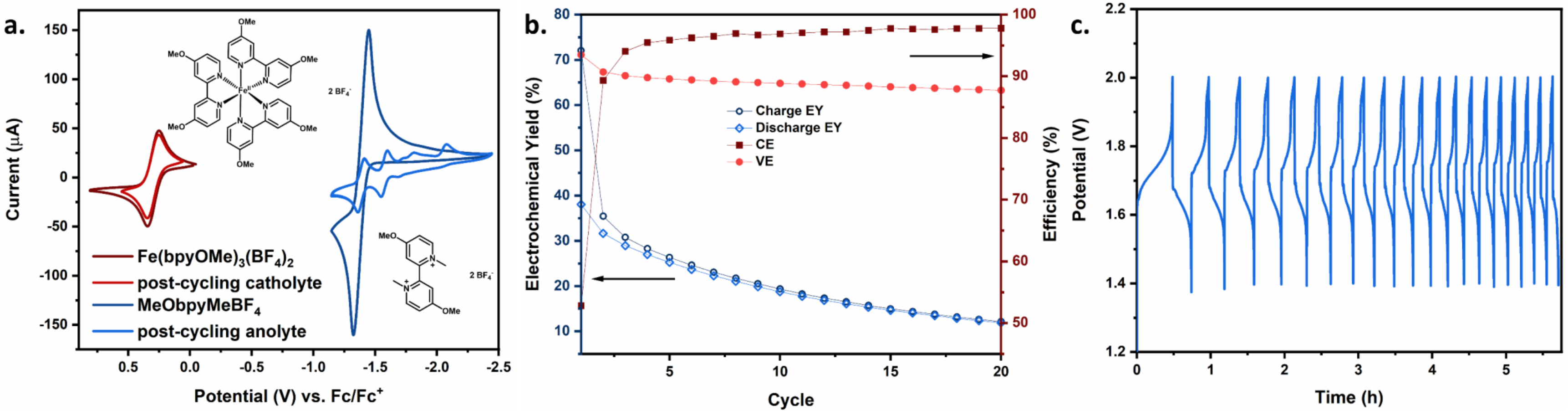
No discharge!

C. X. Kolesnichenko *et al*. *ChemElectroChem*, **2022**, e202101490.

Second Generation Pseudo-Symmetric Flow Cell Studies

The second generation negolyte has a **methylated** nitrogen. The literature shows this significantly improves the electrochemistry.

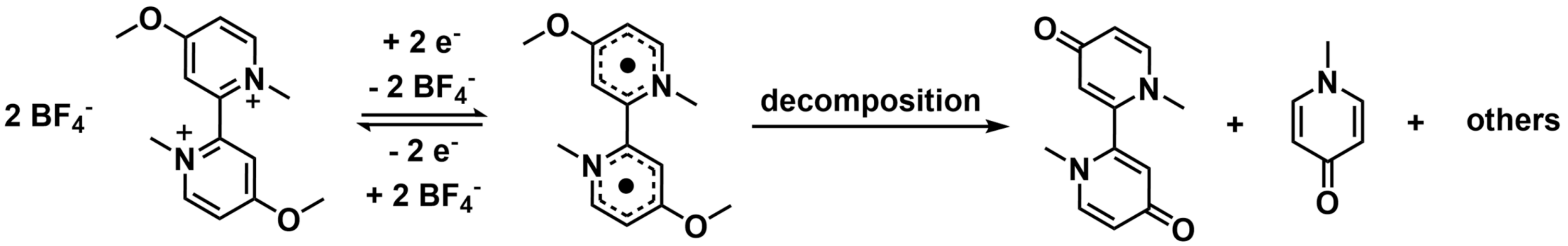


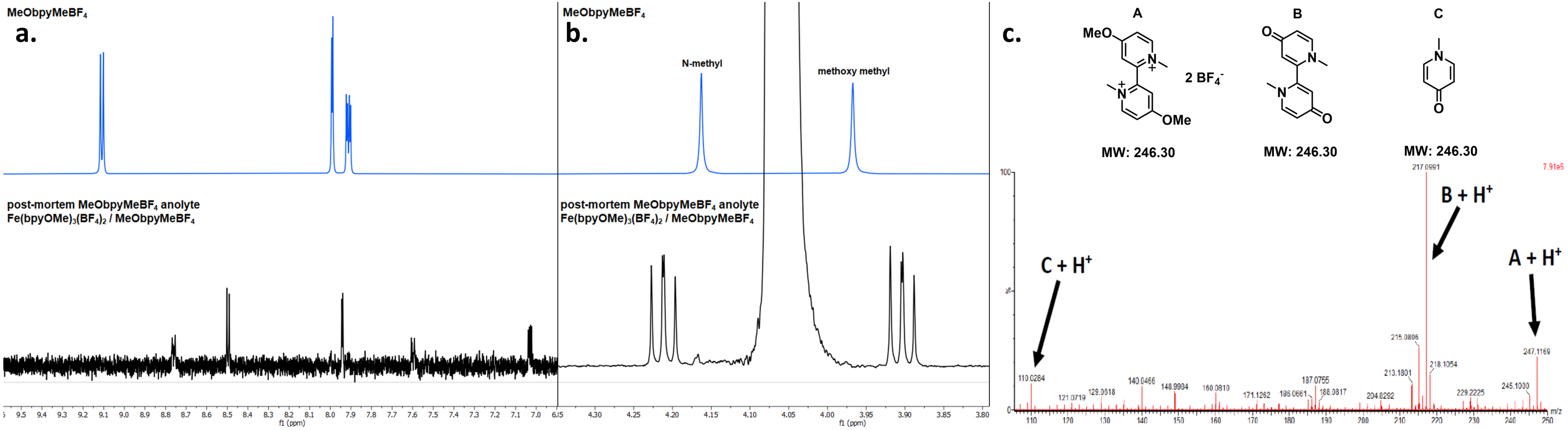


The methylated, OMe derivative showed **improved cycling** over first generation but poor material utilization.

Mechanism of Second Generation Capacity Fade

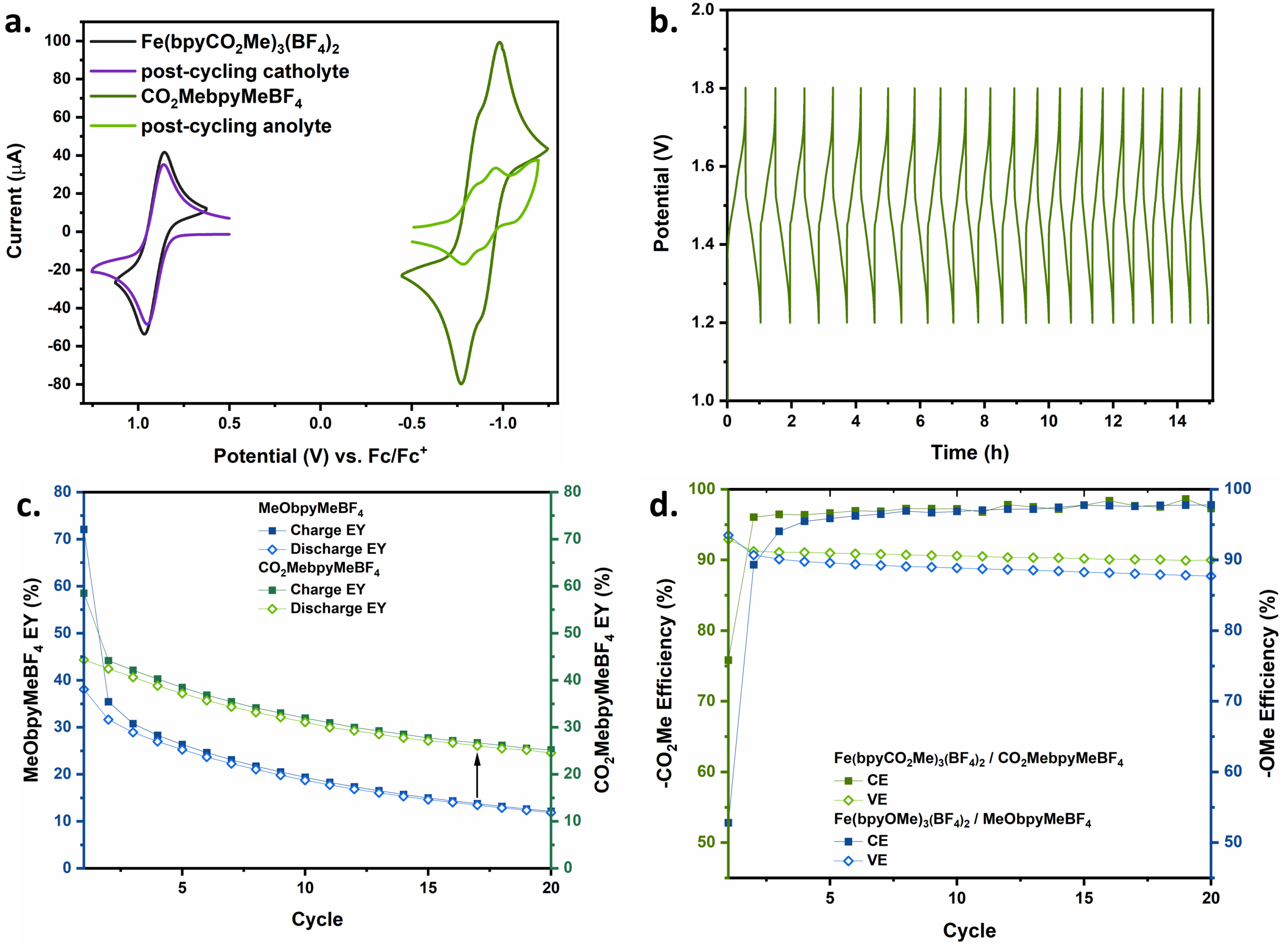
Significant degradation was observed in the first cycle, forming various by-products.

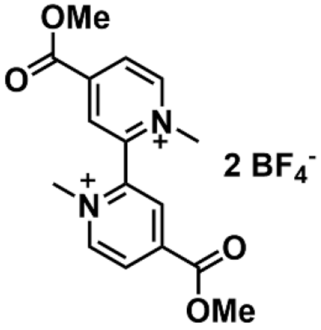




Third Generation Pseudo-Symmetric Flow Cell Studies

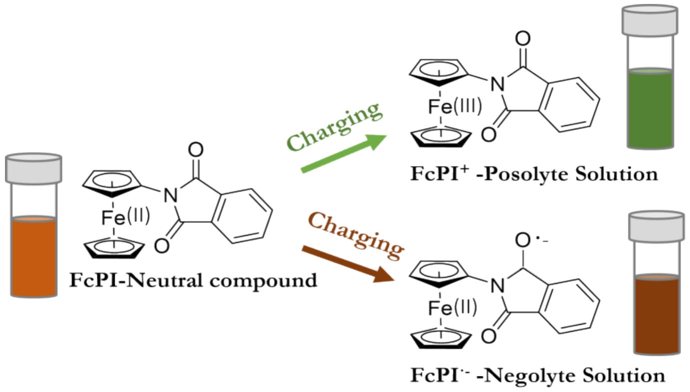
The methylated, CO_2 derivative showed an **18% improvement** of material utilization over second generation.

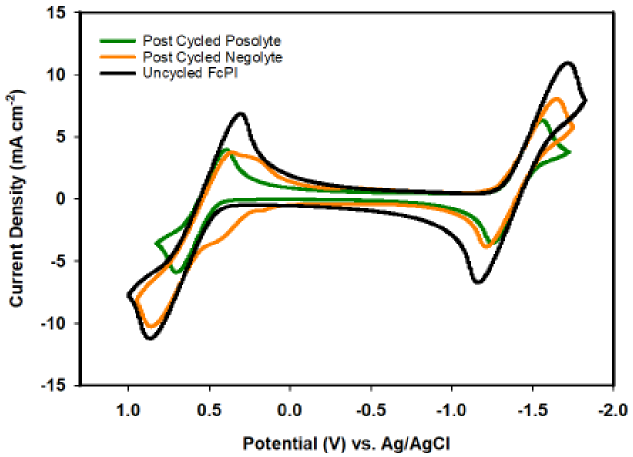


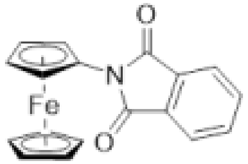


Bipolar Redox Molecules (BRMs)

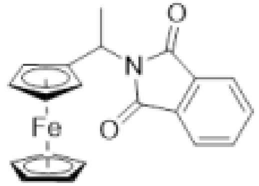
N-ferrocenylphthalimides



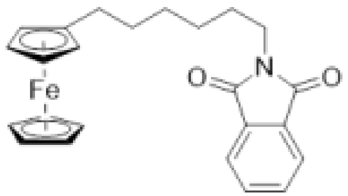




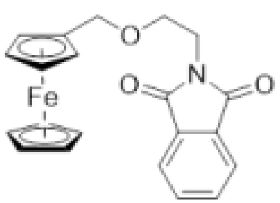
No spacer



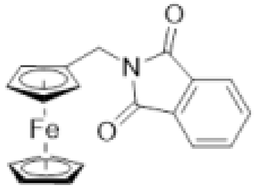
Branched methylene spacer



Hexyl spacer



Ether Spacer



Methylene spacer

(1) Li, Case, and Minteer, *ChemElectroChem*, **2021**, *8*, 1215-1232 (2) Hwang, Kim, Ryu, and Oh, *J. Power Sources*, **2018**, *395*, 60-65 (3) Hwang, Kim, Ryu, and Oh, *J. Power Sources*, **2019**, *421*, 1-5

Conclusions

- We have identified (and mitigated) the mechanism for capacity fade in the symmetric iron-bipyridine flow battery.
- We have determined that chemical substitutions can be made in MCCs to increase voltage, but this can decrease the overall stability of the system.
- We have determined that this stability is primarily centered around the negolyte and identified (and executed) a path forward involving a pseudo-symmetric system.
- The negolytes of pseudo-symmetric flow batteries can be stabilized with chemical modifications.

Acknowledgements and Project Contacts

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