

Molecular Engineering of Radialene Catholytes for Redox Flow Battery Applications

Fuead Hasan,^a Sam Paige Macchi,^b Christopher Landes,^a Travis M. Anderson,^b and Christopher M. Bejger^a



UNIVERSITY OF NORTH CAROLINA
CHARLOTTE

^a Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC, 28223

^b Sandia National Laboratories, Albuquerque, NM



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Abstract

Hexasubstituted [3]radialenes remain attractive catholytes for aqueous and nonaqueous redox flow battery (RFB) applications. Here we show the latest investigations into their modification for these purposes. Specifically, we demonstrate that dilithium salts of ester-substituted radialenes exhibit enhanced solubility for neutral pH AORFBs. We also report our latest foray into radialene modification, where sulfone moieties are explored as high redox potential units with favorable solubility. Finally, our exploration of radialene dications as two-electron catholytes in NARFBs is outlined.

Radialenes

- Alicyclic compounds in which all ring atoms are sp²-hybridized
- Exocyclic carbon-carbon double bonds
- π -systems of radialenes are considered cross-conjugated
- Parent, unsubstituted [n]radialenes are unstable
- Substituted radialenes can support multielectron transfer
- Substituted radialenes can be isolated in various oxidation states

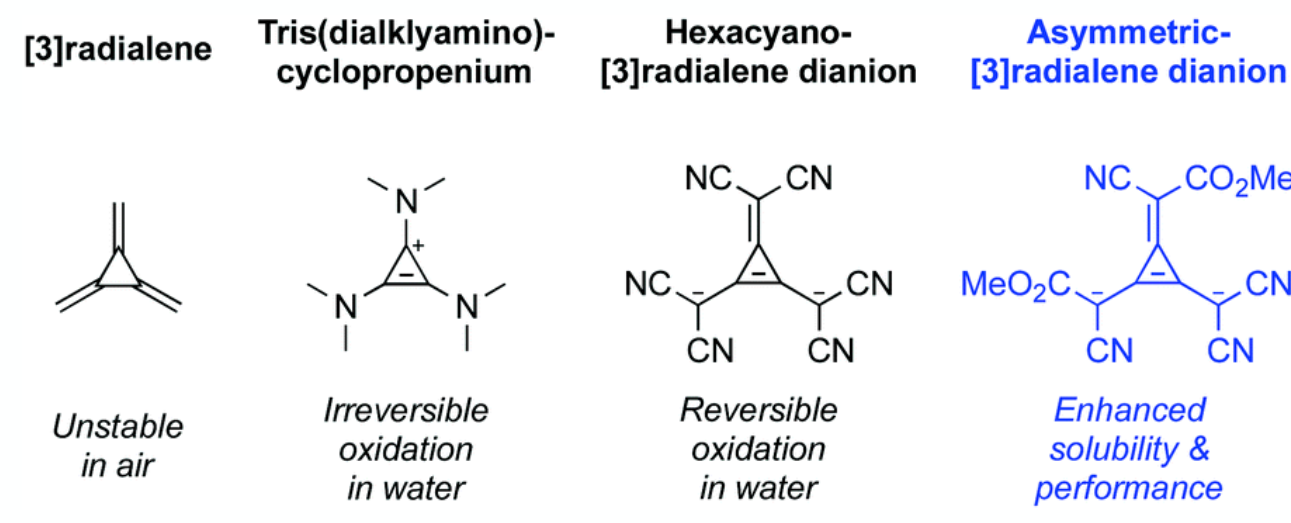
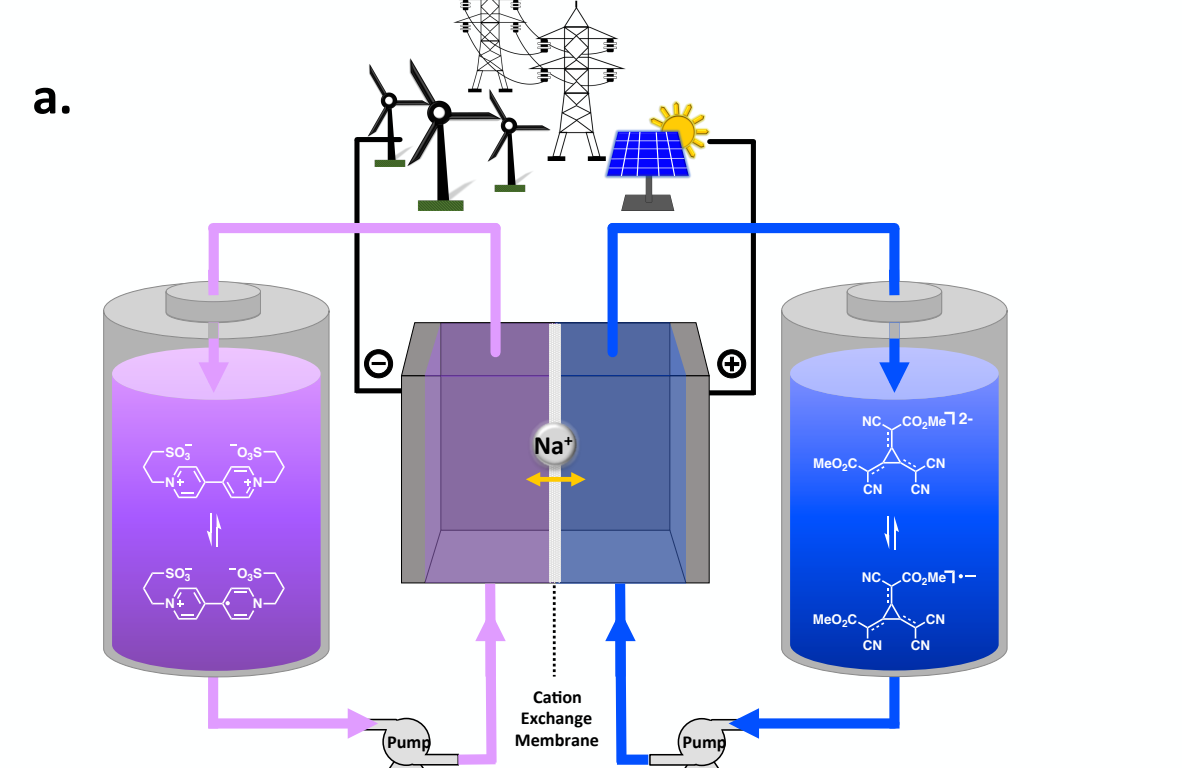


Figure 1. Examples of [3]radialene compounds and their electrochemical properties in aqueous solutions.

First Generation Radialene Catholytes

Table 1	1	2	3	4
Solubility ^a	25 mM	0.19 M	0.5 M	0.85 M
Radical Anion Solubility ^b	< 25 mM	0.08	0.2 M	< 0.1M
E ^{ox} _{1/2} ^c	0.48 V	0.4 V	0.35 V	0.27 V
i _{pa} /i _{pc}	1.03	0.97	1.06	1.15

^aCalculated from saturated aqueous solutions using UV/Vis spectroscopy.
^bMeasured as a Potassium (K⁺) salt
^cRecorded at 100 mV/s using a glassy carbon electrode & Ag/AgCl reference electrode in water.



- 0.1 M electroactive species
- 25 mA charge/discharge rate
- 5 cm² active area
- 2.5 mL/min flow rate
- Serpentine flow field
- SGL GFD carbon felt electrode

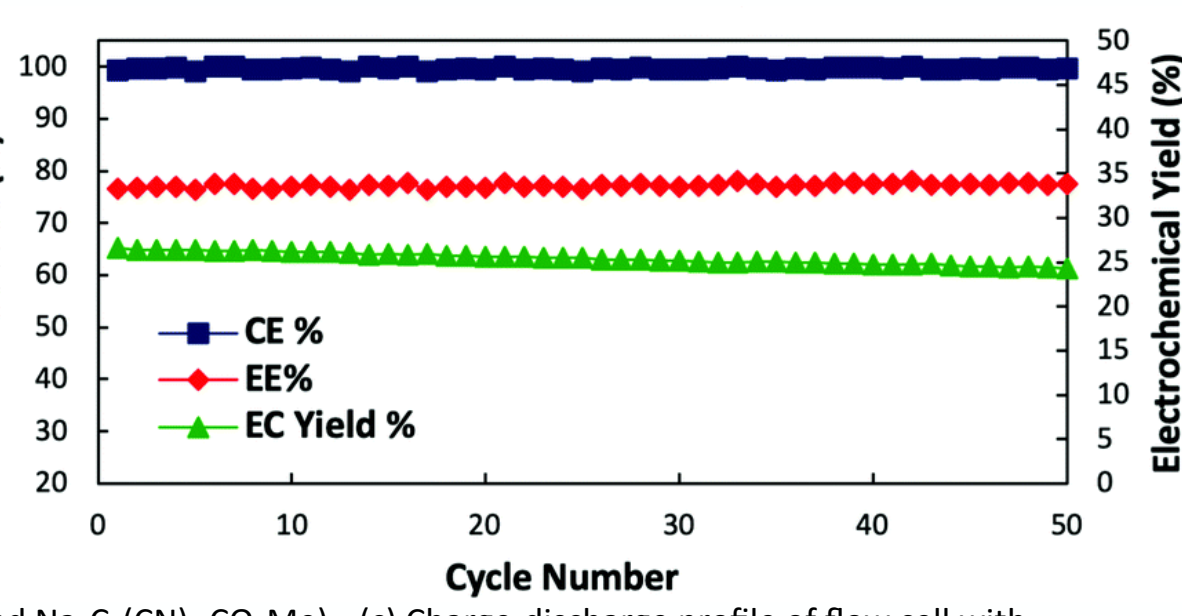


Fig. 2 (a) Schematic of all organic RFB. (b) Cyclic voltammogram of a mixture of MV(SO₃)₂ and Na₂C₆(CN)₄(CO₂Me)₂. (c) Charge-discharge profile of flow cell with electrochemical yield and Coulombic efficiency of the flow cell over 50 cycles.

Turner, N. A.; Freeman, M. B.; Pratt, H. D.; Crockett, A. E.; Jones, D. S.; Anstey, M. R.; Anderson, T. M.; Bejger, C. *Chem. Commun.* 2020, 56, 2739-2742.

Dimerization Contributes to Capacity Fade – But pimerization is stabilizing

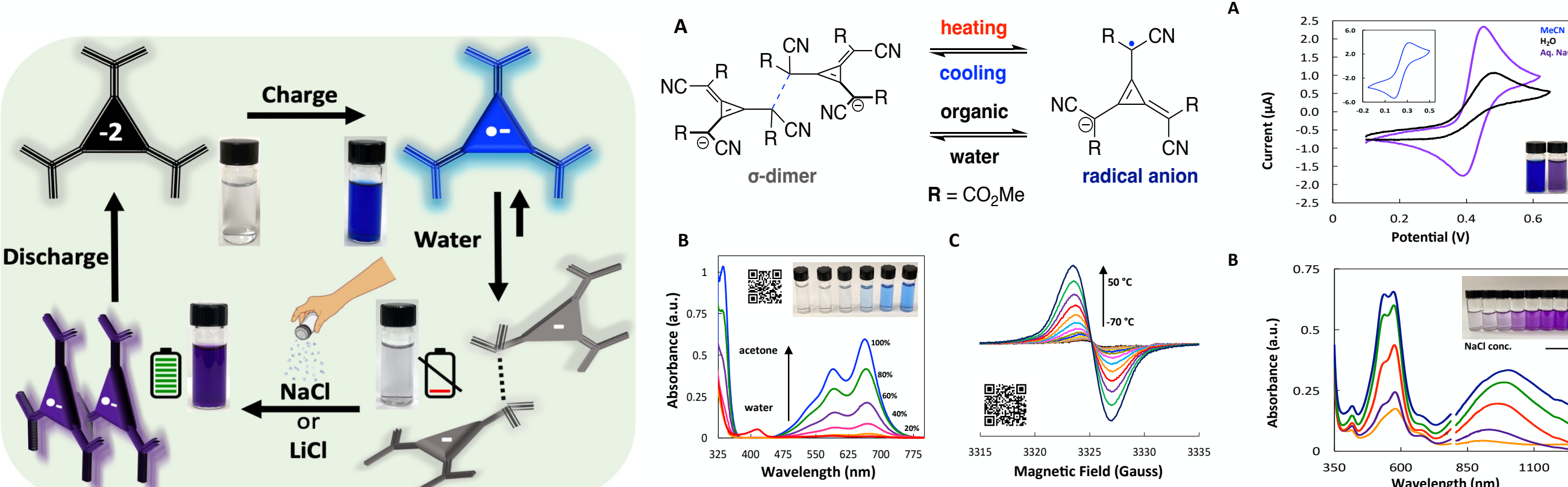


Figure 3. (A) Solvent and temperature dimerization equilibria for triester radical anion. (B) UV-vis spectra (0.5 mM in H₂O) upon addition of acetone. (C) VT-EPR spectra of (1.5 mM) in MeOH.

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Dilithium [3]Radialene Catholytes – Enhanced Solubility

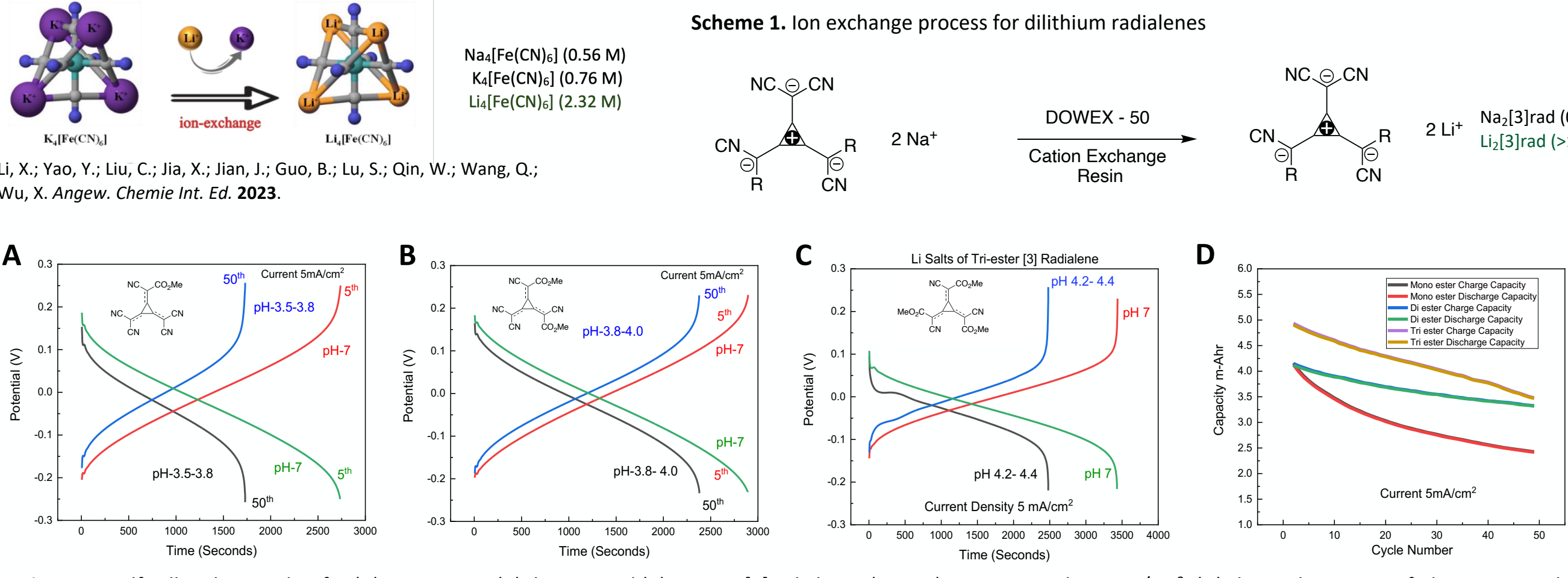


Figure 5. Half cell cycling studies for (A) monoester, (B) diester, and (C) triester [3]radialenes (0.05M) in 0.25 M LiCl at 5mA/cm². (D) shows the capacity fade over 50 cycles.

Higher Concentration Half Cells

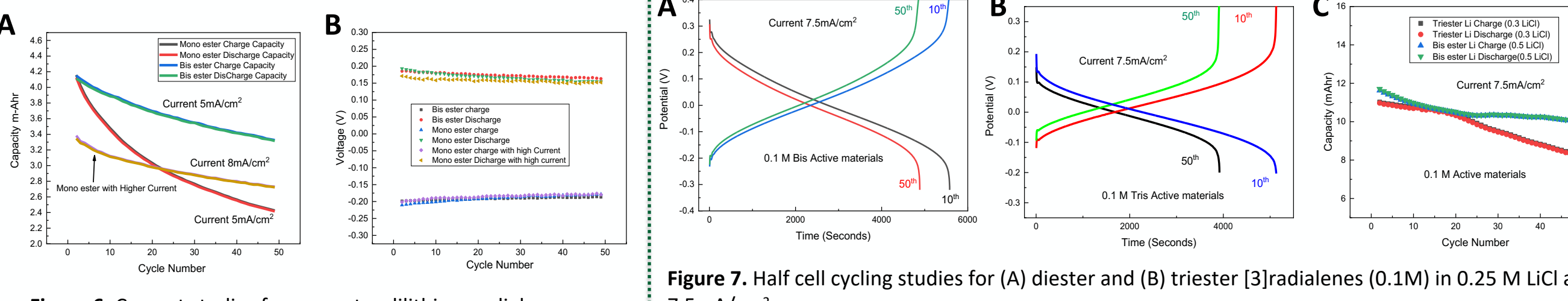


Figure 6. Current studies for monoester dilithium radialene. Figure 7. Half cell cycling studies for (A) diester and (B) triester [3]radialenes (0.1M) in 0.25 M LiCl at 7.5mA/cm².

Sulfone Functionalized [3]Radialenes

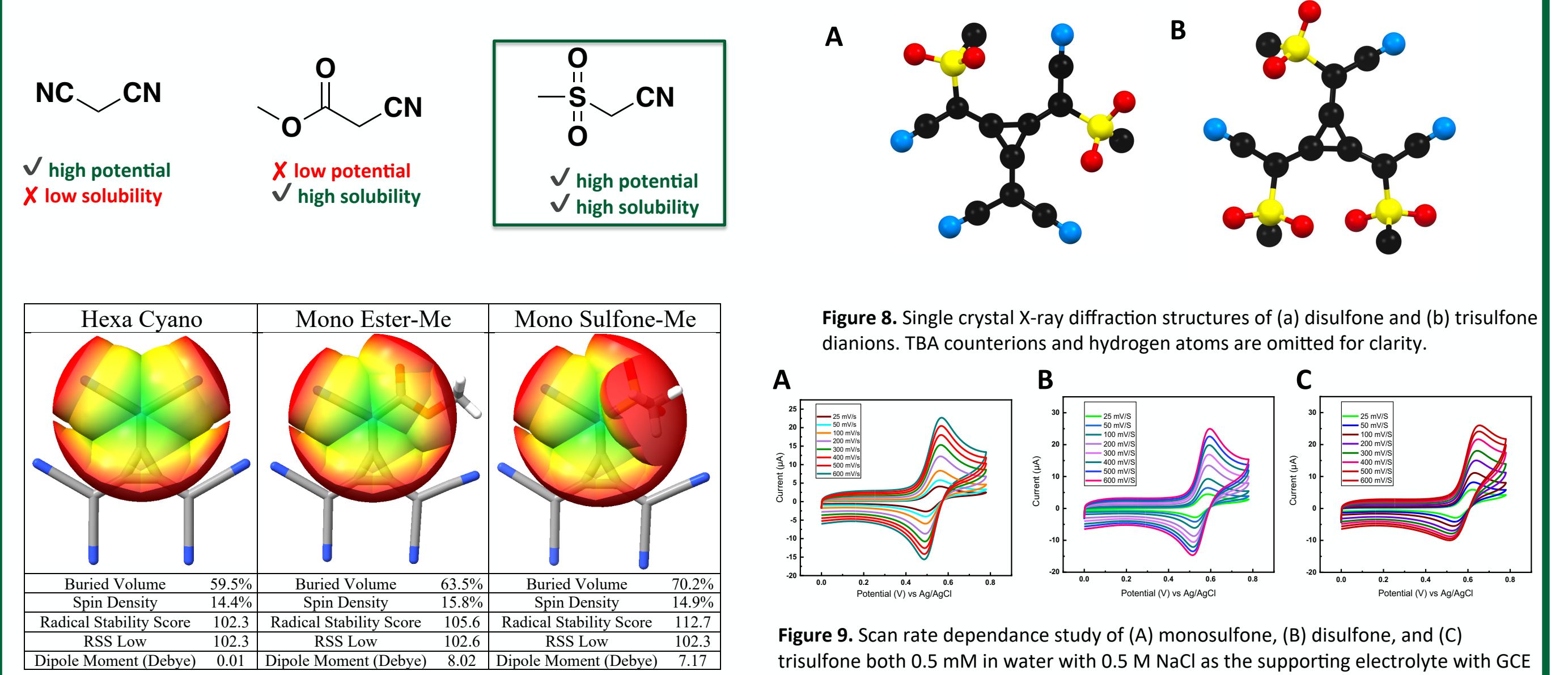


Figure 8. Single crystal X-ray diffraction structures of (a) disulfone and (b) trisulfone dianions. TBA counterions and hydrogen atoms are omitted for clarity.

Figure 9. Scan rate dependence study of (A) monosulfone, (B) disulfone, and (C) trisulfone both 0.5 mM in water with 0.5 M NaCl as the supporting electrolyte with GCE working electrode.

Potential Two Electron Catholytes for NAQRFBs

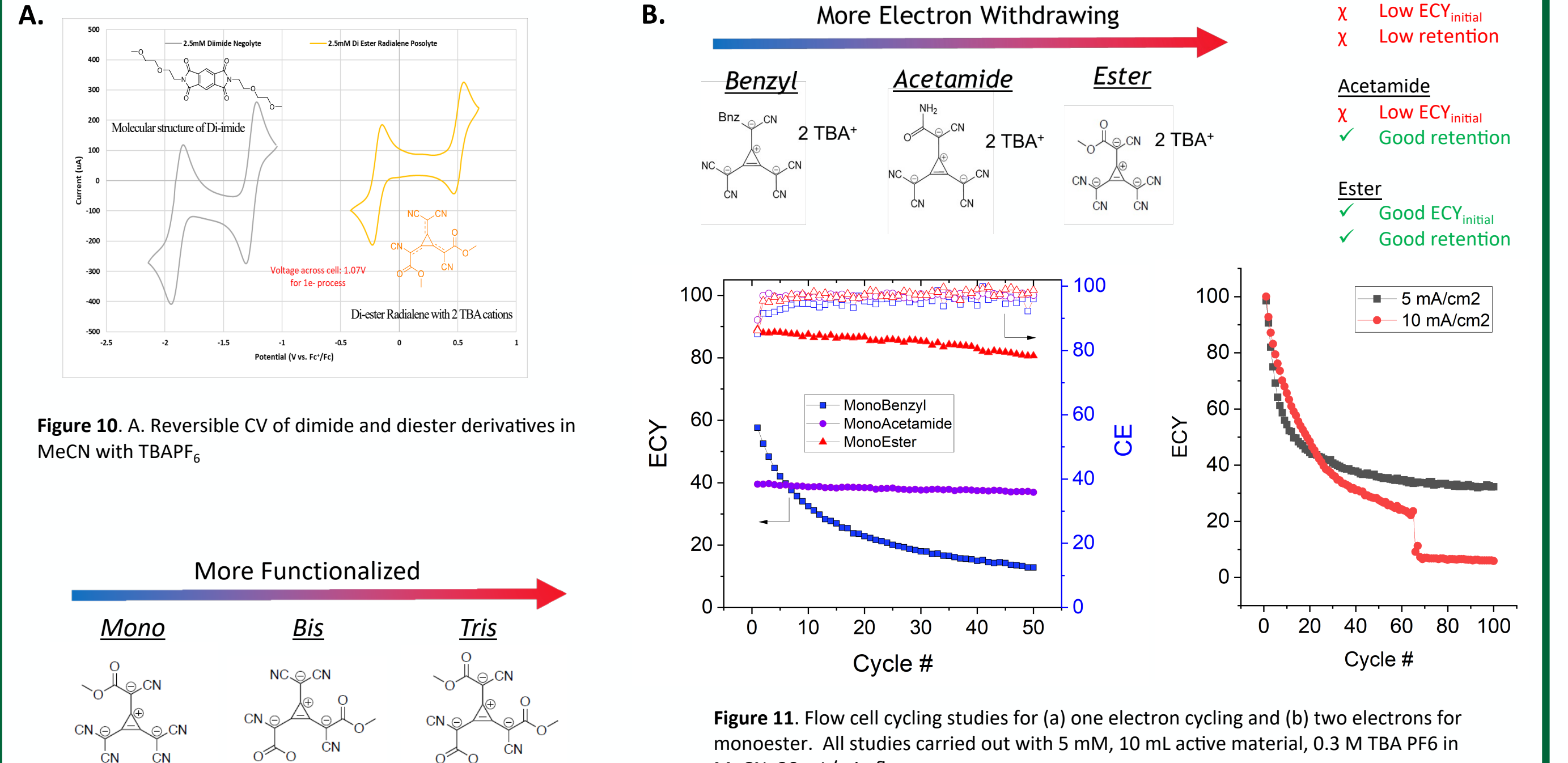


Figure 10. A. Reversible CV of dimide and diester derivatives in MeCN with TBAPF₆. B. Flow cell cycling studies for (a) one electron cycling and (b) two electrons for monoester. All studies carried out with 5 mM, 10 mL active material, 0.3 M TBA PF₆ in MeCN, 20 mL/min flow.

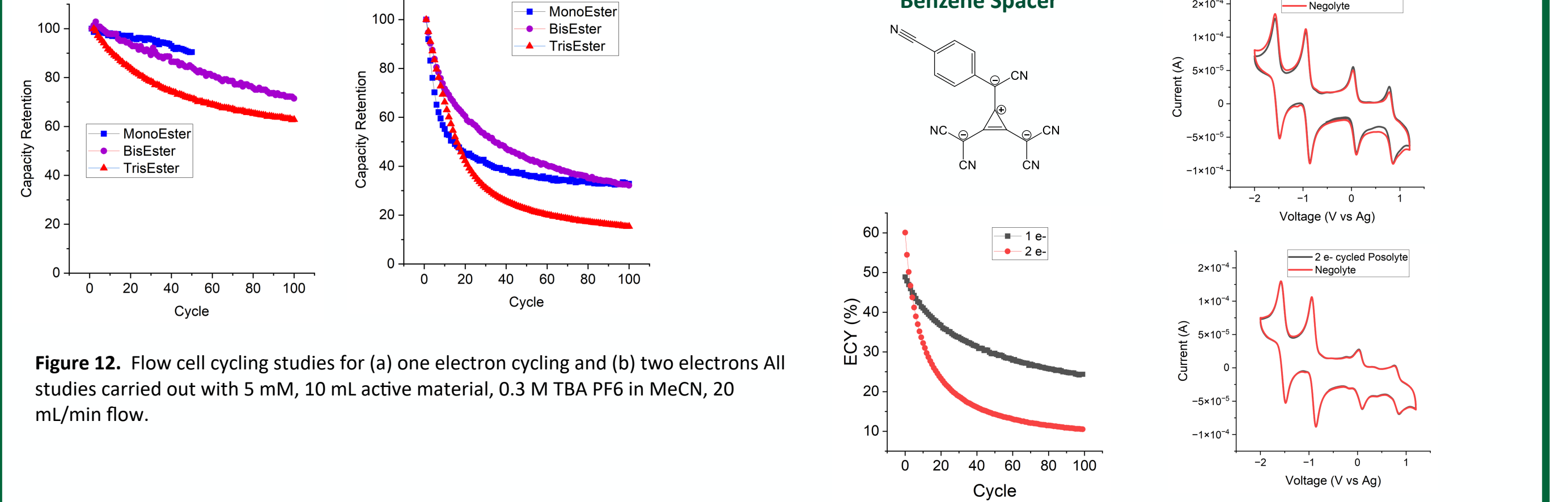


Figure 11. Flow cell cycling studies for (a) one electron cycling and (b) two electrons for monoester. All studies carried out with 5 mM, 10 mL active material, 0.3 M TBA PF₆ in MeCN, 20 mL/min flow.

Future Directions

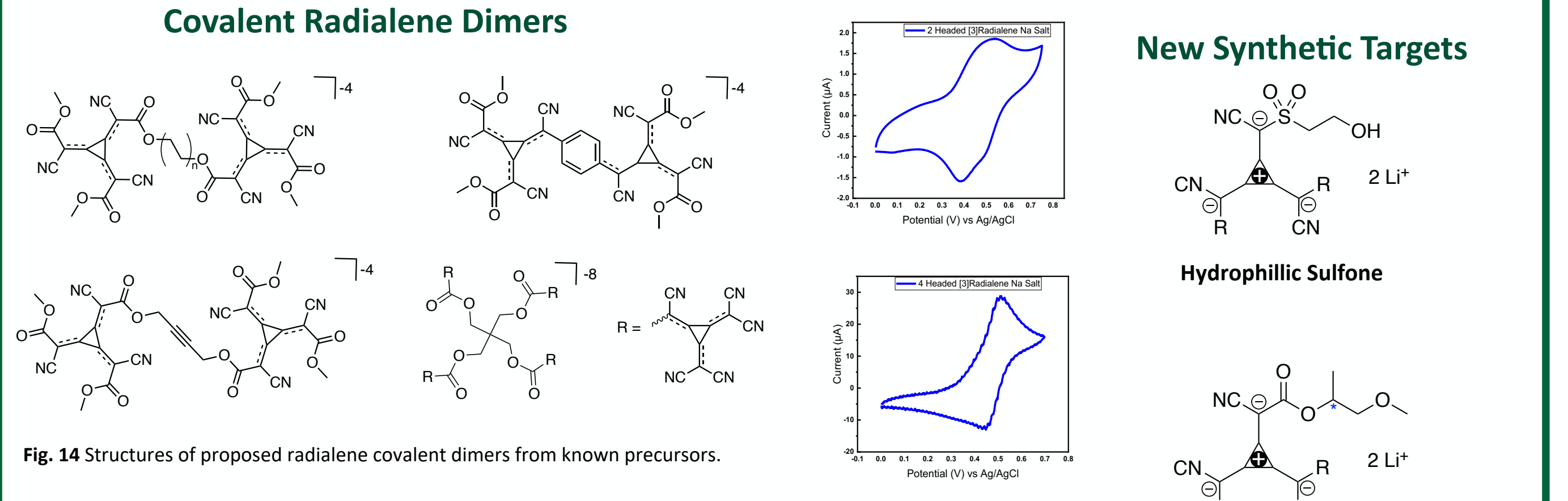


Figure 12. Flow cell cycling studies for (a) one electron cycling and (b) two electrons for benzene spacer derivative. CVs after cycling are also shown. All studies carried out with 5 mM, 10 mL active material, 0.3 M TBA PF₆ in MeCN, 20 mL/min flow.

Conclusions

- Salts protects and promotes pimers and electrochemical reversibility in aqueous solution
- Utilization of Li counterion enhance the solubility of radical and di-anion species.
- Sulfone groups can enhance voltage and solubility – stability is still an open question
- [3]Radialenes do not function as stable 2e- catholyte for NAQRFBs
- New derivatives are being prepared to enhance solubility/voltage and mitigate dimerization

Acknowledgements



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