

Investigation of Multi-Electron Bispyridinylidenes for Symmetric Organic Non-Aqueous Redox Flow Batteries

by

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ABSTRACT

Redox flow batteries (RFBs) present a promising solution for large-scale energy storage, facilitating the proper utilization of renewable energies like solar and wind energy. Their unique advantage lies in the flexibility to separately scale up both power and energy capacity. Within the realm of RFBs, those employing organic molecules as active species are particularly promising. Most organic RFBs feature an asymmetric design, where distinct active species are used for the two electrodes. However, these systems suffer from active material crossover, reducing their lifetime. In an effort to eliminate such irreversible crossover issues, researchers have recently focused on developing bipolar molecules amenable to a symmetric RFB design. Symmetric systems utilize a single redox-active molecule (bipolar molecule) capable of existing in multiple oxidation states, enabling the incorporation of two distinct redox couples for the anolyte and catholyte. This work introduces ester-substituted bispyridinylidene bipolar molecules for non-aqueous RFBs, demonstrating the first effectively concerted two-electron oxidation and reduction processes for an organic active material. Symmetric static and flowing tests, utilizing cost-effective polypropylene separators, revealed capacity fade rates of 0.025% and 0.23% per cycle for static (2000 cycles) and flow (70 cycles) cells, respectively, signify commendable overall performance in comparison to the current state of the art. Considering the practical limits on active material solubility, this achievement represents a milestone towards the development of high energy density ORFBs. Furthermore, this study systematically categorizes five distinct classes of organic bipolar molecules utilized in both aqueous and non-aqueous solvent systems, providing a thorough exploration of their performance characteristics. Through the observation of diverse types of bipolar molecules, the study

concludes by outlining the potential for designing new multi-electron redox-active molecules, which hold promise for achieving energy-dense ORFBs. Overall, the findings contribute valuable insights to the development of sustainable and efficient energy storage technologies, and pave the way for large-scale energy storage solutions in the future.

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List of Symbols, Nomenclature or Abbreviations

AEM	Anion exchange membrane
AgNO ₃	Silver nitrate
AORFB	Aqueous organic redox flow battery
BPY	Bispyridinylidene
NAORFB	Non-aqueous organic redox flow battery
CE	Coulombic efficiency
CV	Cyclic voltammetry
d	Doublet
RFBs	Redox flow batteries
ORFBs	Organic redox flow batteries
dd	Doublet of doublets
MeCN	Acetonitrile
ppm	Parts per million
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
E_{cell}	Cell potential
SOC	State of charge
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
J	Coupling constant
DCM	Dichloromethane
CD ₃ CN	Deuterated acetonitrile
C ₆ D ₆	Deuterated benzene
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
MeCN	Acetonitrile
NaBF ₄	Sodium tetrafluoroborate

TBAPF ₆	Tetrabutylammonium hexafluorophosphate
NG	Not given
NMR	Nuclear magnetic resonance
PC	Propylene carbonate
RFBs	Redox flow batteries
s	Singlet
SCE	Saturated calomel electrode
t	Triplet
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
THF	Tetrahydrofuran
VE	Voltage efficiency
EE	Energy Efficiency
δ	Chemical shift
ROMs	Redox active organic molecules
TEAPF ₆	Tetraethylammonium hexafluorophosphate

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Chapter 1: Introduction

1.1 Background of large-scale energy storage systems

Global warming is one of the biggest challenges in the 21st century.¹ The burning of fossil fuels releases pollutants into the atmosphere, trapping heat and leading to temperature rise, unpredictable weather patterns, and rising sea levels.² Renewable energy has emerged as an essential solution in addressing the pressing challenges posed by climate change, and environmental degradation. Unlike fossil fuels, which are finite and emit harmful greenhouse gases (i.e. carbon dioxide, methane, and nitrous oxide) upon combustion,³ renewable energy sources offer a sustainable and cleaner alternative to power our societies. By harnessing energy from renewable sources like sunlight and wind, no greenhouse gases are emitted. This mitigates the impact of climate change and contributes to a healthier planet for current and future generations. Another key advantage of renewable energy lies in its potential to reduce our dependence on finite and often geopolitically unstable fossil fuel reserves. Renewable sources are abundant and naturally replenished, ensuring a consistent and reliable energy supply. This diversification of energy sources enhances energy security, reduces vulnerability to price fluctuations, and promotes a more resilient energy infrastructure; however, the production of energy from sunlight and wind sources largely depends on seasons and weather conditions resulting in discontinuous energy production.⁴ The stable and consistent energy supply is the prerequisite for smooth industrial and household operation. Therefore, the regular energy demand is not addressable with this intermittent nature of renewable energy supplies. Hence, the development of an efficient energy storage system is essential to balance the temporal deviations in energy production and consumption.

The major technologies available for grid-scale energy storage are pump hydropower, thermal, and compressed air systems.^{5,6} Pumped storage hydropower stands out as the leading technology for large-scale energy storage, utilizing gravitational force to produce electricity.⁶ It involves pumping water to a higher elevation during periods of low-cost energy and high renewable energy production. When electrical demand arises, the stored water is released back to a lower reservoir, driving turbines to generate power.⁷ However, there are certain constraints related to geology and the environment, along with the substantial initial capital investment associated with this technology.⁸

Thermal energy storage systems offer a viable solution to overcome the geographic constraints typically associated with pumped hydro storage systems. They function by storing heat or cold in diverse media like natural rocks, oils, molten salts, and organic liquids, which can subsequently be harnessed to produce thermal energy or electricity.⁹ While these systems are already employed for commercial and industrial cooling purposes, their full potential as energy storage solutions remains untapped due to challenges such as significant heat loss during storage and discharge, along with the high installation cost of the system.^{10,11}

In compressed air storage systems, air is compressed and stored within an underground cavity, often a salt cavern, using energy from renewable sources.¹² When energy demand arises, the pressurized air is released from the underground reservoir, brought back to the facility, and utilized to turn an electricity generator through controlled expansion. The selection of a suitable site for a compressed air energy storage system is constrained by the necessity for the presence of mines, caverns, and specific geological formations.¹³

Site-selectivity and specific geographical constraints could be avoided by developing an efficient, inexpensive, and scalable electrochemical energy storage (EES) system. Lithium-ion batteries are the most commercially available and effective EES system for small scale and portable applications, making them a unique choice for small electronics such as laptops and cell phones.¹⁴ However, the prospects for their incorporation into long-term grid-scale storage brings some issues including the scarcity of lithium, rapid heat generation in operation, costs, safety, and toxicity.¹⁵

The latest technology to emerge as large-scale energy storage is the vanadium redox flow battery.¹⁶ These batteries are nonflammable, compact, reusable over semi-infinite cycles, and comparatively longer lifetime. Although vanadium redox flow battery possesses remarkable prospects, sustainability is greatly affected by the cost-effectiveness, toxicity of vanadium metal and other environmental issues.¹⁶ Organic redox flow batteries, a leading cost-effective alternative, could eliminate the major shortcomings of existing technologies.¹⁷ It is one of the most promising EES system over others because of its cost-effectiveness, safety aspects, modularity, scalability, and operational flexibility;¹⁸ however their development is still in the early stages, and systems are comparatively far from commercialization.

1.2 General operating principle of a redox flow battery (RFB)

The RFB (Figure 1.1) is a technology designed for grid-scale energy storage. The fundamental principle of RFBs involves the conversion of chemical energy into electrical energy through reversible oxidation and reduction reactions of electroactive species. In RFBs, the anode and cathode active species, along with supporting salt, are dissolved in aqueous or organic solvents, stored in separate tanks named anolyte and catholyte tanks (see Figure 1.1).^{19–21} During cell operation, the stored catholyte and anolyte are simultaneously pumped through the cell, where the active species accept or give up electrons based on whether it is charging or discharging. The cell is equipped with a membrane as a separator to segregate the two electrodes and prevent the catholyte and anolyte from mixing, while allowing supporting ions to diffuse through during the charge and discharge process to maintain charge balance. RFBs offer a distinct advantage in their ability to separate power and energy components, providing scalable and flexible energy storage capabilities. Power capabilities depend on the active electrode surface area in the cell, the reaction kinetics, and electrolyte conductivity. Furthermore, the energy storage capacity is determined by factors such as the concentration of active materials, the number of electrons participating in the cell reaction, the cell voltage, and the size of the storage tanks. The ability to decouple power and energy capacity in RFBs enables cost-effective solutions for large-scale energy storage, contributing to the integration of renewable energy sources into the power grid.²² Overall, the versatility, scalability, and efficiency of redox flow batteries position them as promising candidates for addressing the challenges of modern energy storage needs.

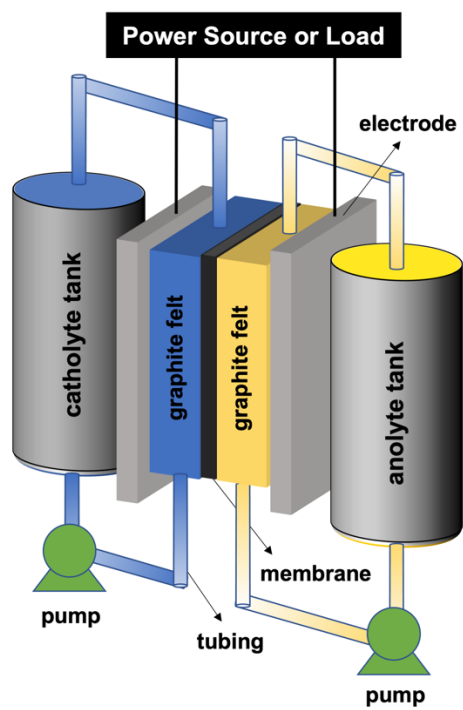


Figure 1.1 Schematic diagram of a redox flow battery.

1.3 Thesis objectives and motivation

Exploring the use of organic active materials in RFBs for large-scale renewable energy storage holds promise, but there are some significant challenges to overcome (Figure 1.2). These include dealing with the lower energy density of organic systems, managing active material crossover in asymmetric systems where the anolyte and catholyte are distinct chemical entities, and ensuring the solubility and stability of organic active species.¹⁷ One of the primary goals of this thesis is to develop a bipolar molecule (a molecule with at least three redox states that can serve as both an anolyte and a catholyte)²³ capable of multi-electron transfer while fine-tuning its molecular structure to enhance solubility. This project explores the use of non-aqueous solvents to take advantages of the extended electrochemical window of various organic solvents (up to 5 V).²⁴ This approach provides design flexibility for the development of bipolar molecules, aiming to address challenges and enhance the overall effectiveness of organic redox flow batteries.

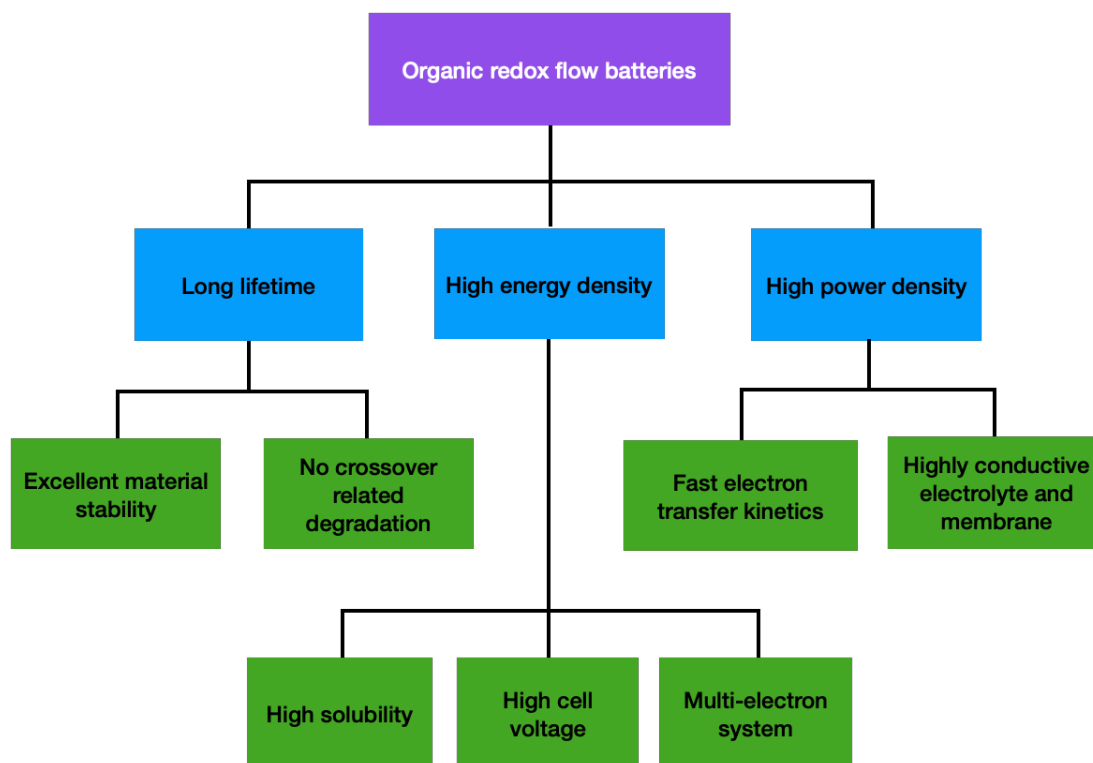


Figure 1.2 Consideration for optimizing organic active materials in flow batteries

1.4 Thesis outline

In Chapter 2, a comprehensive review is presented, outlining the diverse classes of bipolar molecules for symmetric ORFBs. This chapter also presents a detailed comparison of the performance exhibited by existing symmetric ORFBs. The aim is to provide a comprehensive summary that enhances our understanding of the prospects and potential advancements in this field.

In Chapter 3, the synthesis and characteristics of a specially designed bipolar double concerted two-electron organic molecule for use in symmetric non-aqueous ORFBs have been discussed. The chapter covers the stability, solubility, and performance of the bipolar molecule in both static and flow cells.

In Chapter 4, a summary and future works derived from Chapters 2 and 3 are presented. These observations are used to outline recommendations for the future study of symmetric ORFBs.

I, along with my supervisor Dr. Dyker, have co-authored a paper published in ACS Energy Letters, 2023, **8**, 3314–3322.²⁵ I served as the first and sole student author, responsible for conducting all experiments reported in the paper. Additionally, I am currently in the process of submitting a comprehensive review on symmetric ORFBs, where I am the sole student author. These two manuscripts, for which I collected and compiled all data, produced all figures and tables, and drafted, reviewed, and edited the text in collaboration with my supervisor, form the core content of Chapters 3 and Chapter 2 in this thesis, respectively.

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Chapter 2: Status and Prospects for Symmetric Organic Redox Flow Batteries

2.1 Abstract

This review explores the growing field of symmetric organic redox flow batteries (ORFBs) within the context of the escalating global shift to renewable energy sources. As environmental concerns from fossil fuel consumption intensify, large-scale energy storage becomes imperative for the integration of renewable sources like wind, hydro, and solar into the electrical grid. Redox flow batteries, particularly those employing organic molecules, are positioned as a potential technology for this purpose. Unlike traditional asymmetric designs, which suffer from crossover issues and reduced lifetime, recent research emphasizes the development of bipolar organic molecules to enable a symmetric ORFB design. This review categorizes and discusses five distinct classes of organic bipolar molecules used in both aqueous and non-aqueous solvent systems, providing a comprehensive overview of their performance characteristics. Despite data variations, the manuscript offers a thorough summary, highlighting the strengths and weaknesses of diverse bipolar molecule categories. The aim of this review is to inspire new research directions and advance the commercialization of symmetric ORFBs.

2.2 Introduction

The world is shifting toward renewable energy sources such as wind, hydro, and solar because of catastrophic environmental issues created by fossil fuel consumption. In order to make proper utilization of these energy sources and integrate them with the electrical grid, large scale energy storage is required, and redox flow batteries (RFBs) are regarded as a leading technology for this application.^{1,2} Unlike traditional batteries, RFBs feature active materials that are dissolved in liquid electrolytes that are stored in the external tanks, and that are pumped to the cell stacks for charging or discharging as needed. Therefore, the capacity of the battery can independently be scaled up by the size of the storage tanks without the need for costly large surface area electrodes, which makes it unique from conventional rechargeable batteries (e.g. Li-ion, Ni-Cd, and Pb-acid).³

The first RFB ($\text{TiCl}_4/\text{FeCl}_2$ or $\text{Ti}(\text{SO}_4)_2/\text{FeSO}_4$) was introduced by Kangro and Pieper in 1962, where $\text{Ti}^{3+}/\text{Ti}^{4+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ were used as catholyte and anolyte, respectively.⁴ However, commercialization of this systems was not economically viable due to the low cell potential (0.8 V) and low concentration of active materials. Later, in 1974, NASA scientist L. H. Thaller reported a $\text{Cr}^{3+}/\text{Cr}^{+2}$ (anolyte) and $\text{Fe}^{2+}/\text{Fe}^{3+}$ (catholyte) redox pair for a flow battery system. Although the iron/chromium redox couples provided a large cell voltage 1.19 V at a potentially low cost, this system suffered from cross-contamination issues.⁵ In 1986, Australian scientist Maria Skyllas-Kazacos came up with an idea of a “symmetric” vanadium redox flow battery (VRFB) with a cell voltage 1.25 V, employing the redox couple $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ as the catholyte and anolyte, respectively.⁶ Interestingly, Kangro and NASA both studied vanadium redox couples but they ruled out the possibility of commercialization because of the high cost and poor kinetics of vanadium

redox pairs.⁷ The poor kinetics were mostly resulting from electrode materials rather than that of active vanadium redox couple.^{7,8} The term “symmetric” is used for VRFB because the crossover of any vanadium species through the membrane results only in reversible capacity loss, rather than permanent cross-contamination issues as when the anolyte and catholyte are based on completely separate active species (asymmetric), and the original state can be regenerated.^{9,10} The VRFB has been the most successful commercially available system to date. Nevertheless, the high cost of vanadium metal, expensive ion-exchange membrane, corrosive acidic electrolytes, narrow voltage window and the temperature dependent solubility of the redox-active species leave room for the development of a cost-effective, next-generation, and sustainable flow battery energy storage system.¹¹ Along these lines, much recent effort has been focused on developing RFBs based on organic active materials, which are advantageous based on abundant elements, and are amenable to molecular tuning to alter redox properties, solubility and stability.^{12–15}

This review will provide a comprehensive overview of all the advancements in symmetric ORFBs. After defining general performance characteristics for RFBs and distinctions between symmetric and asymmetric systems, five general categories of organic bipolar molecules used in RFBs are described. Symmetric RFBs based on metals or organometallic active species^{16–20} are excluded except in cases where the system features at least one organic active material. Based on these general categories, specific compounds used in symmetric ORFB systems are described.^{21–26} These compounds are presented with abbreviated names used in other literature, as well as a numerical identifier followed by an “a” or “b” to denote it as an active material for a non-aqueous or aqueous RFB,

respectively. Finally, their performance is compared and analyzed. Despite the early stages of this field and gaps in data between studies (such as variations in testing conditions, absence of data on solubility and stability of all redox states, etc), the goal is to provide a comprehensive discussion of existing knowledge, summarize the progress within this field, and hopefully inform and inspire new directions and advancements.

2.3 Performance parameters of RFBs

In assessing the performance of RFBs, several key parameters are volumetric energy density, power density, calendar life stability of active materials, coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE).^{27,28} These factors play a crucial role in understanding and evaluating the effectiveness of RFBs.

The volumetric energy density in a flow battery refers to the amount of electrical energy that the battery can store per unit volume. It is a critical performance metric used to assess the cost efficiency and practicality of flow battery technology for real-life applications. The unit of volumetric energy density is Wh L⁻¹ and can be expressed by the following equation²⁹:

$$\text{Volumetric energy density (E)} = n \cdot C \cdot F \cdot V / \mu_v \quad \dots\dots\dots (1)$$

Where n is the number of electrons being transferred during the reaction, C is the lower concentration of either the catholyte or anolyte (mol L⁻¹), F is Faraday's constant (26.801 Ah mol⁻¹), V is the theoretical cell voltage (discharge voltage is used to calculate the real volumetric energy density), and μ_v is the volume factor ($\mu_v = 1 + (\text{lower electrolyte concentration}) / (\text{higher electrolyte concentration})$).

According to the equation, the volumetric energy density of a flow battery depends on three main variables such as the molar concentration of active materials in the electrolyte, the

number of electrons transferred per molecule during the charge/discharge cycling processes, and the cell voltage. A key approach to significantly improve the volumetric energy density of RFBs is therefore by using active materials with larger differences in redox potentials, thereby increasing the cell voltage of the battery. Major increases can only be achieved by utilizing non-aqueous solvents since aqueous systems have limited electrochemical windows (1.23 V in water vs >4 V in non-aqueous solvents).³⁰ The use of such non-aqueous solvents offers several benefits, including wide electrochemical potential windows and a broad range of operating temperatures, but comes at increased cost compared to aqueous systems. Increasing the concentration of redox active species indeed leads to higher energy density, but compelling evidence suggests that concentrations exceeding 2 M are impractical for most non-aqueous RFBs due to significant reductions in ionic conductivity and increased viscosity beyond this limit.³¹ Given this limitation, enhancing energy density through active materials involved in multi-electron redox processes will likely become crucial for advancing the field.

Another essential aspect of battery performance is power density (W m^{-2}), which indicates the amount of power a battery can deliver per unit area. It can be expressed using the equation²⁹:

$$\text{Power density (P)} = I \times V_{\text{discharge}} / S \quad \dots\dots\dots (2)$$

Where $V_{\text{discharge}}$ is the average discharge voltage (V), I is the discharge current (A), and S is the contacting area of electrode with the separator (m^2).

Flow batteries with higher power density can efficiently deliver electrical power when needed, especially for specific applications like grid stabilization or providing backup power during sudden surges in demand. However, the operating current required to deliver

electrical energy depends on various factors, including the ionic conductivities of the electrolytes, membrane properties, electrode materials, as well as the diffusion coefficient and electron transfer kinetics of the redox-active species. Additionally, other factors such as operating temperature, flow field design, and the operating flow rate also play a significant role in affecting the power density of a flow battery.³² Given the relatively early stage of development of non-aqueous and aqueous symmetric organic RFBs, research endeavors have thus far largely neglected the examination of power density within these systems, with emphasis being primarily directed toward the investigation of energy density and cycle and/or calendar life.

The calendar life stability of active materials is one of the most crucial performance metrics for developing sustainable grid-scale energy storage system.¹² In assessing the longevity of flow batteries, both their calendar life and cycle life are of paramount significance. The cycle life of a battery is determined through the systematic monitoring of capacity retention during a series of consecutive charge and discharge cycles, and is measured on a per cycle basis. On the other hand, calendar life is determined by evaluating capacity retention per unit of time. Researchers have typically evaluated calendar life stability through the method of dividing the total capacity lost by time (decay rate per unit time). This particular approach, while effective at providing an average assessment of the calendar life stability across various oxidation states, has certain limitations when it comes to assessing the stability of individual oxidation states. Alternatively, calendar life stability can be probed by intermittent pauses during cycling at different states of charge on the capacity-limiting side.³³ In this way calendar life analysis is a valuable method for assessing the stability of various oxidation states within the electrolyte and cell components.³⁴ Several factors can

affect the calendar and cycle life stability of active materials in ORFBs such as proper selection of solvents, supporting salt, temperature, purity of active materials and moisture in non-aqueous systems.³⁴

The Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) are the key performance indicators that assess the effectiveness and reliability of flow batteries. High values for these metrics are essential to ensure efficient energy conversion, reduced losses, and long-term stability, making flow batteries more competitive and suitable for energy storage applications. CE is obtained as the ratio between the discharge capacity and the charge capacity, and can be affected by several factors including the crossover of redox species through the membrane, irreversible side reaction, felt compression, and current density.^{35,36} The membrane, especially ion exchange membranes, can improve CE by reducing material crossover but may lower voltage efficiency compared to charge-free microporous separators owing to their lower porosity and ionic conductivity.³⁷

VE is defined as the ratio between the average discharge and charge voltages in a system. This efficiency metric is susceptible to reduction due to various losses, including ohmic resistances, activation overpotential, and concentration overpotential, all of which have an adverse impact on the voltage efficiency.^{38,39} In addition, elevating the current density within the system serves to decrease the voltage efficiency.⁴⁰ To maximize the voltage efficiency, it is essential to minimize the resistance within all components of the electrochemical cell and employ electrode materials characterized by high electrical conductivity, excellent electroactivity, and a substantial surface area. In flow batteries, utilizing flow-through graphite felt electrodes is beneficial for efficient electron transfer reactions, and pre-treatment techniques have been demonstrated to enhance the wettability

of graphite felts.⁴¹ This improvement is achieved by introducing surface functional groups that act as active sites, thereby increasing electrochemical activity. Finally, EE is obtained as the product of CE and VE, reflecting the ratio between discharge energy and charge energy.

2.4 Classification of ORFBs

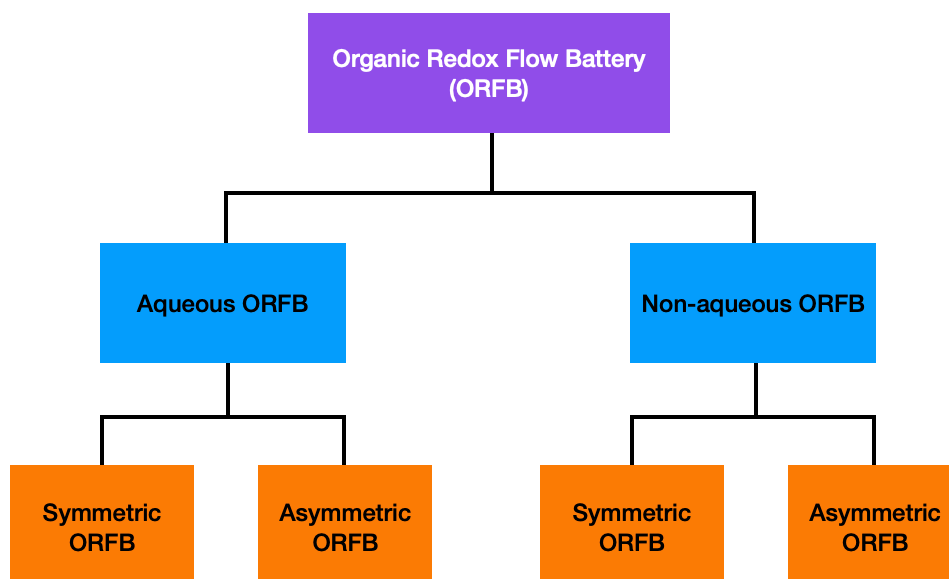


Figure 2.1 Classification of ORFBs

In ORFB systems, the active charge-storage materials are dissolved in a solvent in order to make the active solution flowable and for facilitating the charge/discharge process. Based on the nature of solvents, the ORFB can be classified in two main categories (i) Nonaqueous ORFBs (NAORFBs), and (ii) Aqueous ORFBs (AORFBs) (Figure 2.1). It should be mentioned that unique symmetric ORFBs based on non-miscible solvents (i.e. aqueous and non-aqueous) have also been developed.⁴²

2.5 Nonaqueous ORFBs (NAORFBs)

Non-aqueous organic redox flow batteries (NAORFBs) represent an energy storage system that uses non-aqueous solvents such as acetonitrile, dimethylformamide, dichloromethane, propylene carbonate, ethylene carbonate, or dimethyl sulfoxide to dissolve organic redox-active molecules and the supporting electrolyte salts such as LiBF_4 , LiTFSI , NaBF_4 , KPF_6 , TBAPF_6 etc. to facilitate the storage and release of energy via reversible redox reactions. Due to the narrow electrochemical window of water, a wide array of active materials cannot be integrated for the aqueous battery system. On the other hand, these non-aqueous solvents exhibit a wider electrochemical window ($> 4\text{V}$) that facilitates the utilization of active materials with larger separations of redox potentials and therefore higher cell potentials.³⁰ Another notable advantage is the ability to operate the flow cell in low-temperature environments, leveraging the wider operating temperature range of organic solvents.³⁰ Nonetheless, non-aqueous system poses challenges, particularly when the active materials possess very positive or negative redox potentials as these are often more reactive and prone to cause unwanted side reactions that ultimately make the systems vulnerable to decay over time. Furthermore, organic solvents also come with safety concerns due to flammability and toxicity, they require careful selection of cell components to be compatible with these solvents, and, of course, they involve higher costs than aqueous systems.

2.6 Aqueous ORFBs (AORFBs)

Aqueous organic redox flow batteries (AORFBs) represent an energy storage system that employs water, the most abundant solvent, to dissolve the charge-storage species, along with a supporting electrolyte (e.g., HCl, H₂SO₄, NaCl, NaOH and KOH, etc.). Aqueous systems offer several advantages, such as higher ionic conductivity, lower cost, improved safety, and the promise of eco-friendly energy storage. A significant number of aqueous asymmetric flow batteries have been studied recent years.^{43–45} However, water poses several challenges such as a limited electrochemical potential window of 1.23 V (thermodynamic), and operating temperature limitations.³⁰

Aqueous and non-aqueous organic redox flow batteries (ORFBs) can each be further categorized into symmetric and asymmetric configurations based on the active materials employed for electrochemical energy storage (Figure 2.1). In an asymmetric system, two separate and distinct molecular entities, represented by neutral molecules B and C (Figure 2.2), are employed as the anolyte and catholyte, respectively. Upon the initiation of the charging process, molecule B undergoes reduction to form B⁻, while molecule C undergoes oxidation to form C⁺. With distinct chemical origins for the anolyte and catholyte, there is no common oxidation state between B and C. In practice, this is easily recognized for organic systems because B and C have unique molecular formulas, but for metal-based systems, this distinction is not precise enough. For example, the VRFB employs VO²⁺/VO₂⁺ as catholyte and V(II)/V(III) as anolyte, with distinct molecular formulas for the two electrodes; however, since all oxidation states of the vanadium species can be interconverted electrochemically, the system can be regarded as symmetric (described in more detail below). Asymmetric AORFBs frequently employ anolytes such as quinones,^{46–}

⁴⁹ viologens,^{47,50–53} and phenazines,^{54–58} and catholytes are predominantly sourced from TEMPO,^{50,59} ferrocene,^{52,60} and ferrocyanide.^{61,62} Similarly, there are number of ROMs that have been investigated for non-aqueous ORFBs as anolytes (viologens,⁶³ quinoxalines,^{64,65} anthraquinone,⁶⁶ benzophenones,⁶⁷ and fluorenones⁶⁸) and catholytes (nitroxide radicals,⁶⁹ alkoxybenzenes,^{65,70} phenothizines⁷¹ and cyclopropenium ions^{72,73}). In an asymmetric system, active material crossover through the membrane remains a major issue for cell lifetime, leading to self-discharge and irreversible capacity loss.^{10,74,75}

In contrast, within a symmetric system, a single active species that can exist in at least three redox states (i.e. a bipolar species) serves as the active species in both the anolyte and catholyte. For the symmetric VRFB system, this encompasses four redox states total, but for organic systems, three total redox states are more typical. As illustrated in Figure 2.2, compound A represents the discharged state of the cell, present in both halves. During the charging phase, molecule A is reduced to form A⁻ at the anode, and A simultaneously oxidized to A⁺ at the cathode. In this system, the crossover of charged active species negatively affects Coulombic efficiency for a given charge/discharge cycle as energy is lost through chemical reaction (i.e. A⁻ + A⁺ → 2 A). Unlike the asymmetric case however, this does not lead to a permanent loss of capacity as the original state can be regenerated. At some level this can be managed by polarity reversals (switching of cathode and anode poles during cycling) or by mixing the discharged electrolyte and redividing to two equal portions.^{9,10} This design can facilitate the use of low-cost porous separators instead of expensive ion selective membranes, and avoids special modifications to the active material aimed at preventing crossover in asymmetric systems (such as oligomerization for size selectivity,⁷⁶ or appending fixed charges to impede diffusion through ion exchange

membranes⁷⁷). Additionally, symmetric systems can simplify cell design and potentially enhance the overall cost-effectiveness of the energy storage system.

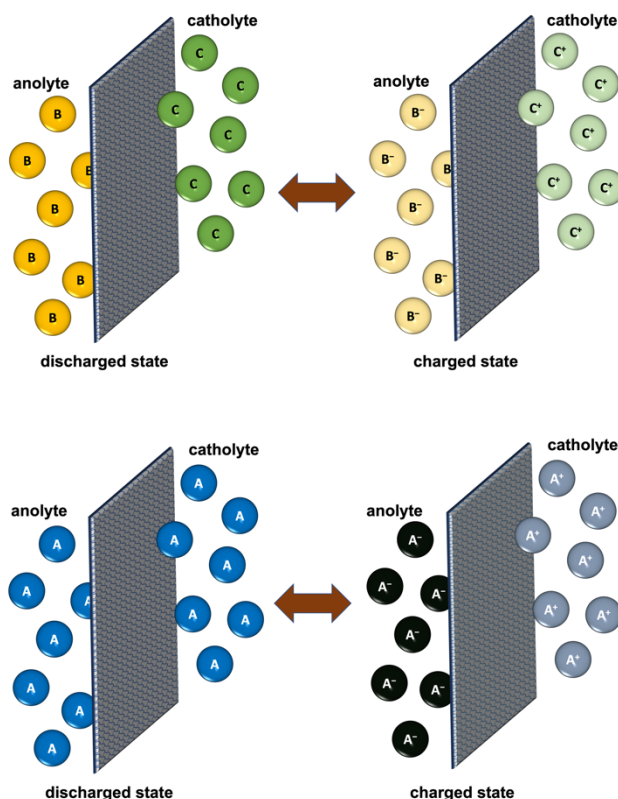


Figure 2.2 Representation of asymmetric (top) and symmetric (bottom) configurations in ORFBs. In the asymmetric system, anolyte B and catholyte C are distinct chemical entities, while in the symmetric system, bipolar molecule A functions as both an anolyte and a catholyte.

A previous mini-review has proposed five categories of active species.⁷⁸ It is also proposed here that there are five different types of bipolar organic molecules for symmetric RFBs, but two of the originally proposed systems would fall under the same more broadly defined category here (type I), while another category is unique to this review (type V). Further

oligomers of any of these molecule classes can be proposed, but these are representative of what has been studied to date. The first category encompasses tethered bipolar molecules (also called artificial bipolar molecules), wherein separate anolyte and catholyte materials are covalently connected through an inert linker chain like methylene or glycol (I, Figure 2.3).^{25,79} These active species are mostly derived from the typical catholytes and anolytes from asymmetric ORFBs. The linker adds molecular weight but can enhance active material solubility compared to the alternative of employing 50:50 mixtures of both active materials as anolyte and catholyte. Additionally, strategically incorporating the linker chain into vulnerable sites of the distinct anolyte or catholyte materials, or employing steric hindrance to shield chemically reactive functional groups, enables the design of chemically robust bipolar molecules.^{80,81} Upon charging the cell, the cathode-active moiety undergoes oxidation within the catholyte, while simultaneously, the anode-active moiety undergoes reduction in the anolyte, meaning that the other species serves only as a spectator at the opposing electrode. To date, all studied type I systems are one-electron systems ($n = 1$, Figure 2.3), meaning they undergo only single electron redox processes, but a variety of two-electron (or even multi-electron) cathode- and anode-active species are known and so systems with $n = 2$ or more can be envisioned. In this case, each the two-electron redox processes may be concerted or sequential.

The second category (II, Figure 2.3) pertains to intrinsic bipolar molecules characterized by a conjugated framework that fosters electronic communication between atoms involved in reduction and oxidation, including instances where these atoms are predominantly identical (as shown, for example, by the frontier orbitals).^{69,82} This intrinsic category offers inherent benefits in terms of atom efficiency, yet devising such molecules is more intricate

compared to artificial counterparts. Certain systems in this category have been developed through the direct conjugation of established anode and cathode components, and this conjugation results in an advantageous elevation in cell potential when compared to individual components or tethered derivatives.^{83–85} These may also be one-electron ($n = 1$) or two-electron ($n = 2$). Most systems described thus far are one-electron systems, and of the two-electron intrinsic bipolar molecules, only one⁸² has shown double concerted two-electron behaviour rather than sequential electron transfers.

The third category encompasses ion-paired bipolar compounds,^{78,86} where the cation and anion of an ionic organic salt are each redox active and one serves as the anolyte and the other as the catholyte (III, Figure 2.3). Remarkably, this class of compound also fulfills the role of a supporting electrolyte, reducing or eliminating the requirement for adding additional inactive charged species as charge carriers and consequently contributing to reduced costs and increased energy density.

The remaining two bipolar molecule classes are always multi-electron systems. The fourth category exhibits similarities with the first category. In this case, rather than tethering a catholyte and anolyte, two intrinsic bipolar molecules are joined by an inert linker, leading to the creation of a double bipolar molecule (IV, Figure 2.3).⁸⁷ This type of molecule shares analogous advantages to those discussed earlier for type I, but because the bipolar active units are insulated from each other both fragments will be oxidized or reduced simultaneously at their respective redox potentials. Therefore these molecules advantageously undergo concerted two-electron oxidation and concerted two-electron reduction as shown. Similar strategies can be extended to systems with three or more

electrons, involving the tethering of three bipolar molecules for a three-electron system, and so forth.

The final category is referred to as double-tethered bipolar molecules. These are similar to type-I molecules, but feature one two-electron anolyte (or catholyte) covalently connected to two one-electron catholyte (or anolyte) units (V, Figure 2.3, represented with a two-electron anolyte in the center, but other combinations and connectivity is possible). The redox process for the two-electron active unit may be concerted or sequential.

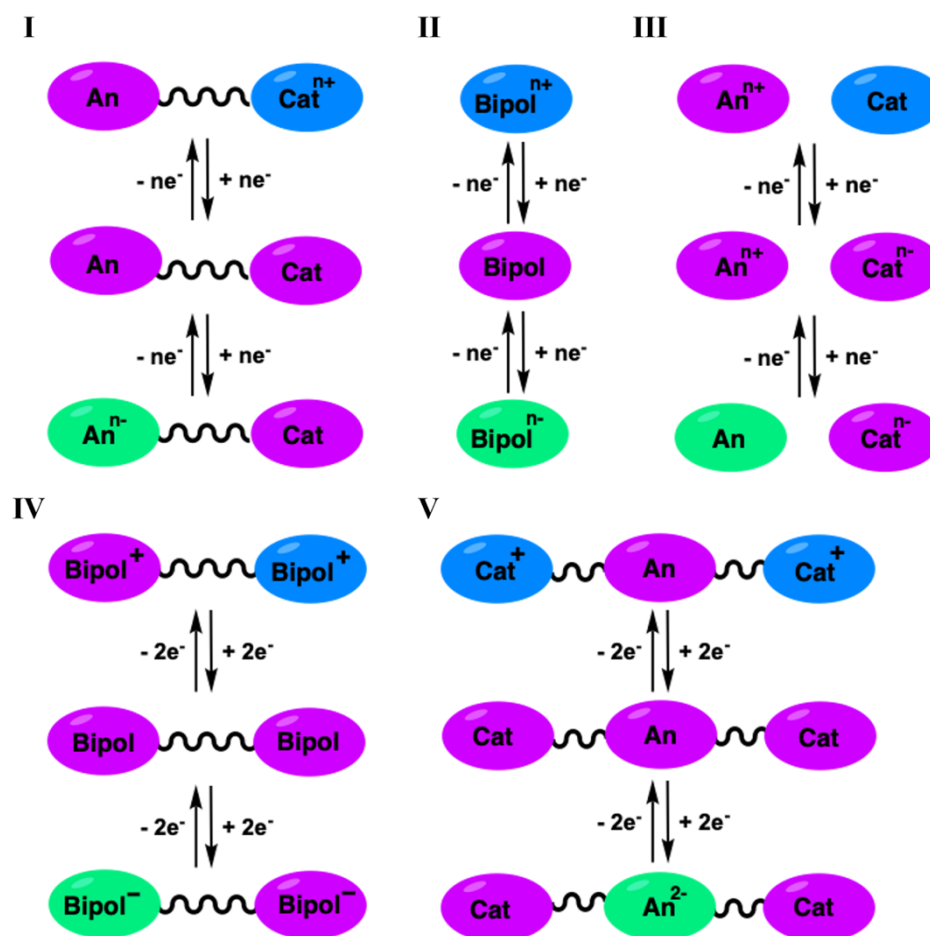


Figure 2.3 Schematic representation of different types of bipolar molecules (I) Tethered (II) Intrinsic (III) Ion-paired (IV) Double bipolar (V) Double-tethered (An or Cat may be switched). (An = anode-active species; Cat = cathode-active species; Bipol = intrinsic bipolar species; $n = 1$ or 2 ; Purple = discharged state; Blue is charged state for cathode-active species; Green is charged state for anion-active species)

In the context of two-electron systems, the majority of reported compounds exhibit sequential electron transfer mechanisms. However, it is worth noting that concerted two-electron systems offer distinct advantages in terms of achieving enhanced voltage

efficiency.⁸⁸ A detailed exploration of this aspect is provided in the subsequent sections of the review.

2.7 Symmetric NAORFBs

Compared to aqueous chemistries, a wider array of bipolar compounds has been tested in non-aqueous solvents. In this section, all the different class of symmetric NAORFBs are elaborately discussed.

2.7.1 Tethered bipolar molecules (type I)

Liu *et al.* synthesized a tethered bipolar (also referred to as artificial bipolar) compound, **VIODAMB (1a)**, employing 2,5-dimethyl-1,4-dialkoxybenzene (DAMB) as the cathode component and a viologen (VIO) moiety as the anode component.⁷⁹ **VIODAMB** displayed three reversible redox couples at half-wave potentials of -1.18 (VIO/VIO⁺), -0.76 (VIO⁺/VIO²⁺), and $+0.82$ V (DAMP/DAMP⁺) (vs Ag/Ag⁺), with the catholyte component at more positive potential than commonly used ferrocene. However, the authors favored a cell with only a one-electron oxidation and one-electron reduction of the bipolar compound, as the VIO/VIO⁺ couple demonstrated poor stability. This resulted in a cell voltage of 1.58 V. The solubility was reported at 0.66 M in acetonitrile without supporting electrolyte. Employing 0.01 M **VIODAMB** in 1 M LiTFSI/MeCN as both anolyte and catholyte, a stable Coulombic efficiency (CE) of approximately 93%, voltage efficiency (VE) of 94%, and energy efficiency (EE) of 88% were achieved. The flow cell demonstrated 80% capacity retention (0.57% per cycle) and an energy efficiency of 85% over 35 cycles at a current density of 1.5 mA cm^{-2} in cycling tests. The cycling performance of the symmetric flow cell was further evaluated using **VIODAMB** concentrations of 0.05

and 0.1 M. Higher concentrations showed a slight reduction in Coulombic efficiency (CE), likely due to increased active material crossover during extended cycling. Cycling rate tests at 0.05 M **VIODAMB** exhibited improved CE, from 85% at 5 mA cm⁻² to 98% at 20 mA cm⁻². At an electrolyte concentration of 0.1 M, initial 10-cycle averages indicated CE of 90% and EE of 75% at 10 mA cm⁻². However, extended cycling revealed significant capacity decay, with a loss of around 60% by the 20th cycle. To understand the reasons of capacity fade, postmortem cyclic voltammetry and UV–vis spectra were gathered from the anolyte solution after 20 cycles. The CV curves remained mostly unaltered, and negligible impurities were detected, indicating chemical stability during cycling. Decomposition of the redox-active species is therefore an unlikely major contributor to the capacity fade, which was instead attributed to crossover (which was faster at higher concentrations) and incomplete active material utilization.

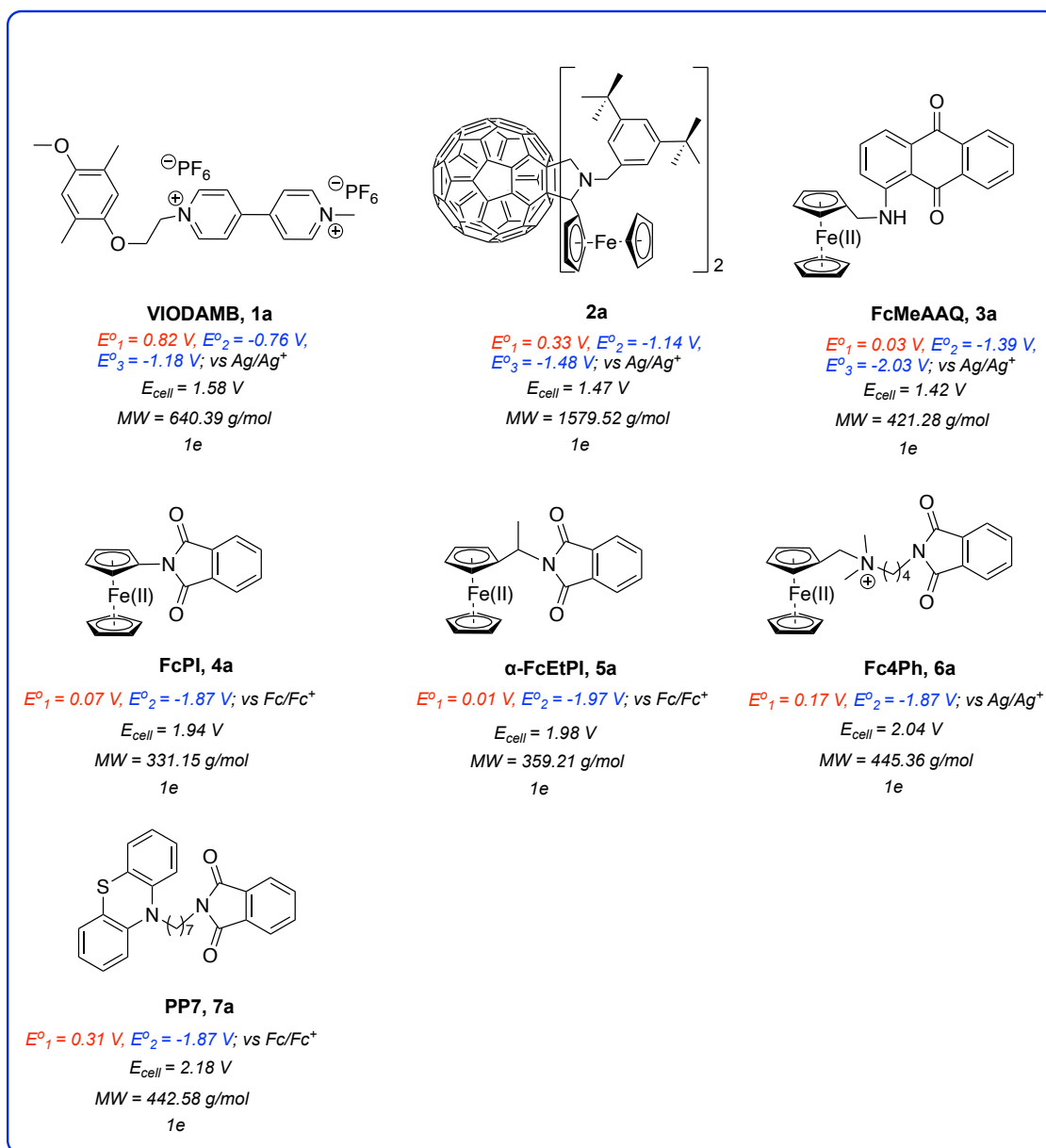


Figure 2.4 Structure, redox potentials, cell potential, molecular weight and number of electrons transferred during cycling for tethered bipolar redox-active molecules (type I) used in symmetric NAORFBs (designated by the **a**). Structures represent the discharged state, and redox potentials in red and blue relate to the cathode and anode active substructures, respectively.

In another study, a compound was synthesized by attaching two ferrocene units with a fullerene molecule to form a bipolar molecule **2a** (Figure 2.4).⁸⁹ Fullerenes are renowned for their intricate sequential multi-electron redox processes.⁹⁰ However, for **2a** the investigation primarily considered two more positive sequential one-electron processes. The electrochemical analysis of **2a** revealed a reversible oxidation peak at 0.33 V (vs Ag/Ag⁺), originating from the two ferrocene units. In contrast, the reduction peaks arising from the fullerene component were characterized as quasi-reversible, occurring at -1.14 V and -1.48 V (vs Ag/Ag⁺). The authors conducted a static cell investigation involving 100 charge/discharge cycles for the bipolar molecule, employing *ortho*-dichlorobenzene and a 0.1 M NBu₄BF₄ electrolyte. This study investigated a one-electron reduction process originating from the fullerene component and a two-electron oxidation process due to the presence of two ferrocene units, resulting in a cell voltage of 1.47 V. However, the system experienced a relatively elevated rate of capacity fade (>30% over 100 cycles) during cycling.

In 2020, Y. Zhen *et al.* explored an artificial bipolar molecule where they covalently tethered an anthraquinone (anolyte) and ferrocene (catholyte) moiety to obtain a well separated redox couples for symmetric battery application (**FcMeAAQ**, **3a**, Figure 2.4).⁹¹ They found three single electron redox couples in 0.1 M TEATFSI/DMF supporting electrolyte, two originating from sequential reduction of the quinone functionality (at -1.39 V and -2.03 V, versus Ag/Ag⁺) and one from ferrocene oxidation (at +0.03 V versus Ag/Ag⁺), but CV cycling revealed that redox event at -2.03 V was not stable over time. Therefore, authors limited the battery performance testing to the redox events at -1.39 V and +0.03 V, resulting a theoretical cell voltage of 1.42 V. The flow cell performance was

studied by symmetrically loading equal amounts of **FcMeAAQ** (0.01 M) in both compartment with 0.1 M TEAPF₆ in DMF as supporting electrolyte. At a current density of 2 mA cm⁻² over 100 cycles, it exhibited an average CE of 90.8%, VE 90.1% and EE 81.8% with 66.8% material utilization. The battery underwent substantial capacity degradation attributed to flow cell leakage and the occurrence of side reactions involving the negatively charged phenolate oxygen in **FcMeAAQ**⁻, based on post cycling CV studies that revealed new redox peaks on the anode side of the cell.

Hwang *et al.* studied another artificial bipolar molecule by combining ferrocene and phthalimide units.⁸⁰ When ferrocene and phthalimide were directly conjoined to form **FcPI** (**4a**), two reversible redox peaks were observed by CV. The first occurred at $E_{1/2} = 0.07$ V (versus Fc/Fc⁺), corresponding to the one-electron oxidation of the ferrocene unit which is only slightly positive compared to ferrocene itself. The second peak appeared at $E_{1/2} = -1.87$ V (versus Fc/Fc⁺), corresponding to the one-electron reduction of the phthalimide unit, which was found to occur only 0.03 V more positive than the parent phthalimide in the same electrolyte. Notably, phthalimide itself (featuring an N-H bond) undergoes an irreversible reduction around -1.90 V (vs. Fc/Fc⁺), with the oxidation peak missing due to the chemical instability of the reduced ketyl anion radical species. The direct bonding of ferrocene to phthalimide resulted in stable electrochemical behavior similar to when various alkyl groups are placed at N.^{92,93} The charge/discharge cyclic performance of the coin-cell was investigated using a 0.1 M **FcPI** solution in 1.0 M TBABF₄ in 1,3-dioxolane, over 30-50 cycles, including C-rates of 1.0 C, 2.0 C, and 3.0 C. At these rates, the coulombic efficiency remained between 95.9% and 98.7%, while the voltage efficiency maintained a range of 96.5% to 90.1%.

The maximal solubility of **FcPI** at room temperature was found to be 0.3 M in a solution of 1.0 M TBABF₄ in 1,3-dioxolane; however, the solubility of the oxidized and reduced forms of **FcPI** were not reported. The moderate solubility of **FcPI** is attributed to its dense packing in the solid state, facilitated by its planar and rigid phthalimide moiety and the cyclopentadienyl ligand in the ferrocenyl group.^{94–96} The well-organized packing promotes strong intermolecular interactions which, unfortunately, leads to reduced solubility.⁹⁷ Therefore, Hwang *et al.* modified **FcPI** by introducing an α -methyl group between the ferrocenyl and phthalimide groups, resulting in N-(α -ferrocenyl)ethylphthalimide (**α -FcEtPI**, **5a**, Figure 2.4).⁹⁸ The α -methyl group is known to impede molecular packing in solid materials,⁹⁵ and in this case, analysis conducted using differential scanning calorimetry (DSC) indicates it leads to a decrease in inter-molecular interactions. Experimental data reveals that the maximum solubility of **α -FcEtPI** is measured at 0.81 M, which is nearly three times higher than the solubility of **FcPI** at 0.30 M. Cyclic voltammetry of **α -FcEtPI** reveals two redox processes: positive region ($E_{1/2} = 0.01$ V vs. Fc/Fc⁺) and negative region ($E_{1/2} = -1.97$ V vs. Fc/Fc⁺), with a cell voltage of 1.98 V. Notably, these reactions take place within a voltage range similar to that observed for **FcPI**, indicating that the molecular modification of the inter-connecting link between the ferrocenyl and phthalimide moieties does not affect the electrochemical characteristics. This result also suggests that while there is no inert linker between the ferrocene and phthalimide units in **FcPI**, it can behave more similarly to an artificial bipolar system rather than an intrinsic one, perhaps because of twisting between phthalimide and cyclopentadienyl rings or a node at the nitrogen⁹⁵ which inhibits electronic communication between the fragments. The authors investigated the coin cell performance of **α -FcEtPI** at

concentrations of 0.1 M and 0.6 M, dissolved in an electrolyte consisting of 1 M TBABF₄ in 1,3-dioxolane. The results indicate that both concentrations exhibit stable charging and discharging within a similar voltage range of 1.98 V, as observed in the cyclic voltammograms. The study did not explore the flow cell performance or assess the capacity fade rate over cycles or time, similar to the investigation of **FcPI**.

In a related study, Xu *et al.* synthesized **FcnPh** compounds with a fixed tetraalkylammonium ion and different carbon chain lengths ($n = 2, 4$, and 6 ; Figure 2.4, only $n=4$ (**Fc4Ph**, **6a**) is shown) tethering the redox active ferrocene and phthalimide units.⁹⁹ A comprehensive cyclic voltammetry (CV) analysis was conducted on the three ionic bipolar redox-active organic molecules. The results showcased promising characteristics, including relatively high open circuit voltages (1.96–2.04 V) and efficient mass- and charge-transfer kinetics. Flow cell cycling tests were conducted on all three bipolar redox-active molecules using 10 mM **FcnPh** (where $n = 2, 4$, or 6) in 0.5 M TEATFSI/DMF, with Daramic-250 as the porous separator. The flow cells were evaluated for 50 cycles at a current density of 7.5 mA cm^{-2} . **Fc2Ph** showed rapid capacity decay, while extending the linker to **Fc4Ph** and **Fc6Ph** produced significantly improved cycling stability. The reduced stability of **Fc2Ph** was attributed to spin density being transferred from the reduced phthalimide unit to the ammonium and ferrocene units owing to the small separation between them, as supported by DFT studies. After 50 cycles, capacity retention was measured at 84.1% for **Fc4Ph** and 83.8% for **Fc6Ph**-based NARFBs. Given the relatively high cycling stability of **Fc4Ph**, a high-concentration flow cell was employed. The charge/discharge cycling properties were examined using 0.5 M **Fc4Ph** in 1.0 M TEATFSI/DMF at a current density of 40 mA cm^{-2} . The average Coulombic efficiency

(CE), voltage efficiency (VE), and energy efficiency (EE) were measured at 87.3%, 57.9%, and 50.3% respectively. The initial charge and discharge capacities were recorded as 9.4 and 6.8 Ah L⁻¹, with the material utilization reaching 70.2% of the theoretical capacity of 13.4 Ah L⁻¹. However, the high-concentration system exhibited significant cycling degradation with a capacity loss of approximately 50% after 20 cycles. This capacity degradation is attributed to factors such as crossover, electrolyte leakage, and in particular parasitic reactions, as post cycling CVs showed loss of signals for the active species as well as new species. The authors hypothesized that the presence of free radical anions at the anode side contributed to the parasitic reactions via protonation with the solvent. To validate their hypothesis, the authors conducted a flow battery test of 10 mM **Fc4Ph** using three solvents with varying acidity levels: propylene carbonate (PC)>MeCN>DMF. The DMF-based battery demonstrated superior performance, maintaining 84.1% of its initial capacity after 50 cycles. In contrast, the MeCN-based battery retained only 59.8% capacity, while the PC-based battery exhibited a mere 12.8% capacity retention.

Phenothiazine as catholyte^{71,100} and phthalimide as anolyte⁹² are well studied in asymmetric RFBs.⁸⁴ Li *et al.* investigated covalently connected phenothiazine and phthalimide as a bipolar redox active molecule and described the stability and solubility of bipolar molecules (**PPn**) with different chain lengths (methylene linker, n=1, 3, 5, 7 and 9; Figure 2.4, only n = 7 (**PP7**, **7a**) shown).⁸¹ Though both the cathode-active (phenothiazine) and anode-active (phthalimide) units are able to undergo sequential two-electron oxidation and reduction processes, respectively, the authors focused on the one-electron redox processes for both units (~0.3 V and ~-1.87 V vs Fc/Fc⁺ for phenothiazine and phthalimide, respectively, in 0.5 M TBAPF₆ in acetonitrile), with relatively high cell voltages of ~2.2

V. The study revealed that trends in charge transfer, solubility, and stability upon selectively cycling the anode or cathode portions of the molecule are not monotonic with chain length. Controlled cycling tests of H-cells (5 mM active materials in 0.5 M TBAPF₆ in acetonitrile), revealed that the cathode-active phenothiazine retained capacity (94-99%) over 100 cycles better than the phthalimide unit. The decay of this anolyte unit was more sensitive to the linker chain length, ranging from 83% to 95 % as *n* increased from 1 to 7, but *n* = 1, and 9 exhibited the most rapid capacity fade that was similar to N-methylphthalimide itself (~20% capacity loss after 20 cycles). Most decomposition was shown to be from the phthalimide radical anion reacting with the acetonitrile solvent,⁶⁸ while the intermediate chain lengths resulted in greater stability via inter- and intramolecular interactions including the formation of clusters. This study demonstrates that the choice of tether can have important but hard to predict effects on the solubility, stability and electrochemical performance of these artificial bipolar molecules relative to mixtures of the same untethered active materials.

2.7.2 Intrinsic bipolar molecules (type II)

In a departure from previous works on tethering anolyte and catholyte active species together by insulating linkers, Tracy *et al.* conducted a study in which they synthesized various derivatives featuring electronically coupled phenothiazine and phthalimide moieties (see **N-MEEtBuPhePhth-1**, **8a**, Figure 2.5), which yielded open circuit voltages ranging from 2.31 to 2.49 V depending on the solubilizing group present in the backbone.⁸⁴ These cell voltages are improved over the 2.13 V for the asymmetric cell involving similarly substituted phenothiazine and phthalimide as catholyte and anolyte components, respectively, demonstrating a beneficial synergistic effect of the electronic conjugation over the asymmetric or tethered designs. Indeed, the electron rich neutral phenothiazine (catholyte) fragment raises the energy of the LUMO of **8a** relative to phthalimide itself, while at the same time the electron accepting phthalimide unit lowers the energy of the HOMO of **8a** compared to that of the phenothiazine, so **8a** is harder to oxidize and reduce, and the cell voltage is increased. DFT studies show that the HOMO and LUMO are mostly based on the phenothiazine and phthalimide fragments, respectively, as expected, but with minor contributions from the atoms belonging to the other unit.

In a parallel cycling study between the asymmetric system and a symmetric system based on a similarly substituted bipolar active material, it was shown that while using polarity reversals every 50 cycles, the bipolar system had much better capacity retention (64% and 42% for the symmetric and asymmetric cases, respectively) and post cycling CV analysis showed homogenization of catholyte and anolyte via crossover in the asymmetric case, demonstrating tangible benefits of a symmetric design.

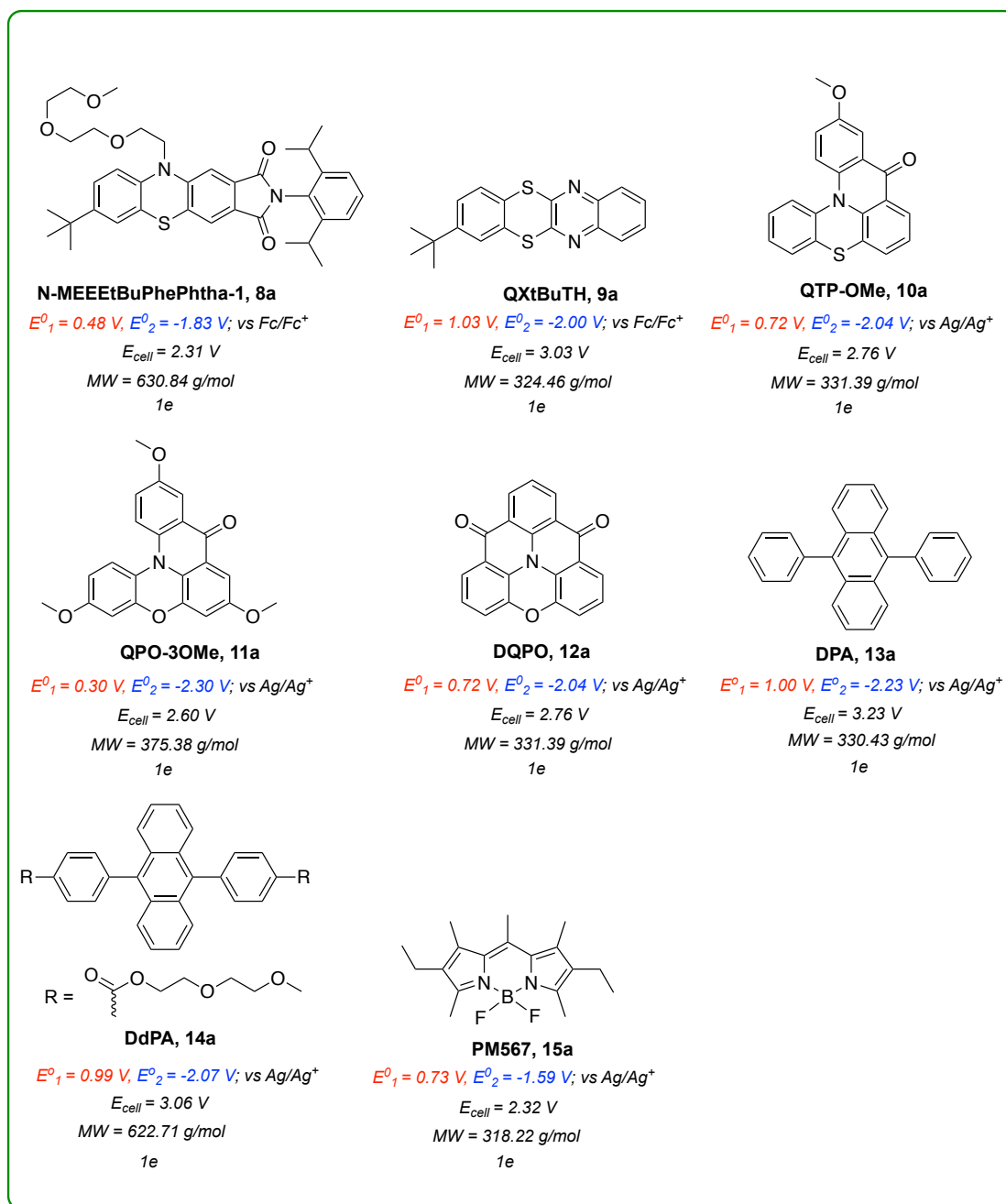


Figure 2.5 Structure, redox potentials, cell potential, molecular weight and number of electrons transferred during cycling for one-electron intrinsic bipolar redox-active molecules (type II) used in symmetric NAORFBs. Structures represent the discharged state, and redox potentials in red and blue relate to the cathode and anode active substructures, respectively.

After that, they focused on a particular bipolar molecule, **8a**, which exhibited higher solubility in pure MeCN (1.8 M) compared to other derivatives. During H-cell cycling, **8a** was tested at a low concentration of 5 mM in 0.5 M TBAPF₆/MeCN at a current density of 5 mAcm⁻², resulting in capacity fade rates of 3.12% per day for oxidative cycling and 8.88% per day for reductive cycling, based on discharge capacity. In flow cell cycling, **8a** showed an average energy efficiency of 86.8%, an average coulombic efficiency of 93.6%, and a capacity retention of 68.6% over 275 cycles, with a capacity fade rate of 0.11% per cycle or 13.2% per day. The post-cycling CV analysis revealed a loss of just 17% in the concentration of the redox molecule based on a comparison of peak currents before and after cycling. However, they also noted a higher capacity loss of 31.4% over the same period, which could be attributed to small leaks during operation of the flow cell and the formation of insoluble deposits on/within the electrodes and separator. The solubility limits of the cationic and anionic oxidation states of this compound were not investigated and no cell tests were conducted at concentrations closer to the limit of **8a** itself, which ultimately resulted in a low theoretical energy density of the tested system. Overall, this study underscores the significance of electronically coupling phenothiazine and phthalimide moieties to mitigate crossover issues in asymmetric NAORFBs and achieve a high cell voltage cell.

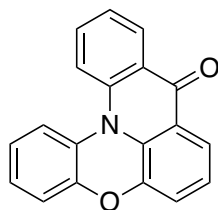
Similarly, the Swager research group investigated a conjugated bipolar molecule known as **QXtBuTH (9a)**, Figure 2.5), featuring fused sulfur- (electron-donating) and nitrogen- (electron-withdrawing) containing heterocycles.⁸⁵ A similar molecule had previously been explored by Kim *et al.* in the context of symmetric solid-state batteries.¹⁰¹ Cyclic voltammetry analysis of **QXtBuTH** revealed a one-electron oxidation peak at 1.03 V vs

Fc/Fc⁺ and a one-electron reduction peak at -2.00 V vs Fc/Fc⁺, resulting in a cell voltage of 3.03 V. In a 1:4 MeCN:MB solvent with 1 M TBATFSI, **QXtBuTH** exhibited a solubility of 0.61 ± 0.01 M. However, during static cell cycling, **QXtBuTH** displayed significant capacity degradation over successive cycles.

Around the same time and independent of the works by Toste and Swager, Zhao's group applied a similar conjugation strategy in the development of a bipolar molecule called **QTP-OMe (10a)**, Figure 2.5). This molecule consists of fused conjugation of redox active quaternary N (phenothiazine unit) and ketone (anthracene-9(10H)-one) units, resulting in a high open circuit voltage of 2.76 V, and frontier orbitals show a high degree of delocalization over the conjugated molecular core.⁸³ The researchers tested the molecule in a static cell with a current of 5 mA cm⁻², using a concentration of 25 mM in 0.5 M TBATFSI/MeCN. They cycled the cell 900 times and achieved a capacity retention of approximately 63.5% with a decay rate of around 0.04% per cycle. The CE and energy EE were both around 97% and 84%, respectively. In a flow cell, using the same material concentration, the charge/discharge cycling resulted in a higher capacity fade of 0.52% per cycle over 50 cycles; however, the CE and EE were similar to the static cell, reaching approximately 95% and 87%, respectively. The authors proposed that the capacity fade observed during the flow cell cycling of the **QTP-OMe** bipolar molecule could be due to the reaction of a carbonyl-based radical with acetonitrile through nucleophilic substitution, surface oxidation of carbon felt at a high oxidation potential leading to increased internal resistance, and the possibility of precipitation and deactivation of trapped active materials in the porous graphite plate due to solvent evaporation. Additionally, the low solubility of the compound limited testing to low concentrations. To address this issue, the authors

substituted the methoxy group with a long oligoether and the resulting derivative (**QPT-TEG**, not shown)⁸³ was found to be a viscous liquid that was miscible with various solvents. The performance of this derivative was assessed in a static cell at 0.5 M active material concentration, which resulted in a capacity fade rate of 0.19% per cycle over 200 cycles. Capacity retention and active material utilization were lower compared to the lower concentration cell, which was attributed to increased viscosity and mass transfer polarization at higher concentrations.

In a subsequent study, the fused conjugation strategy was applied to a phenoxazine core to design new high voltage (~2.5 V) redox-active intrinsically bipolar molecules **QPO** (Scheme 2.1), its trimethoxy derivative **QPO-3OMe (11a)**, Figure 2.5), and related dione **DQPO (12a)**, Figure 2.5).¹⁰² The three derivatives had similar HOMO-LUMO gaps (and E_{cell}) but functionalization was important in keeping both the oxidation and reduction within the electrochemical window of the solvent, showcasing the important of redox potential modulation by molecular tuning. In acetonitrile **QPO** demonstrated reversible redox behavior at -2.20 V (vs. Ag^+/Ag) associated with the one electron reduction involving the ketone moiety, but oxidation exceeded the upper limit of the electrochemical window. In a similar manner, in dichloromethane, the reduction process for **QPO** exhibited irreversibility, primarily because it fell below the limit of the electrochemical window for the dichloromethane solvent; however, the one electron oxidation demonstrated good reversibility.



QPO

CV in Acetonitrile: *irreversible oxidation, reversible reduction*

CV in Dichloromethane: *reversible oxidation, irreversible reduction*

Scheme 2.1 Structure of **QPO** and summary of its electrochemical properties in acetonitrile and dichloromethane.

By introducing electron-donating groups (EDGs) to the **QPO** molecule, the redox potentials of both oxidation and reduction were lowered and the modified **QPO-3OMe** exhibited redox potentials that fell within the electrochemical window of the acetonitrile electrolyte. Conversely, the additional ketone functionality in **DQPO** can be viewed as adding an electron withdrawing group to **QPO** and both the redox processes for **DQPO** were increased, enabling them to fall within the electrochemical window of the dichloromethane electrolyte. The electrochemical performances of bipolar **QPO-3OMe** and **DQPO** were evaluated using galvanostatic charge and discharge measurements in symmetric H-cells in these respective solvents. In the case of **QPO-3OMe**, a solution comprising 1.0 mM **QPO-3OMe** and 20 mM TBAPF₆ in acetonitrile was utilized as both the catholyte and anolyte. During charge/discharge cycling at a current density of 1 mA cm⁻², the discharge voltage plateau remained consistently around 2.5 V. Over the course of 200 cycles, the cell exhibited a capacity retention of 43%, reflecting a capacity fade rate of 0.29% per cycle. The **DQPO** based cell employed a solution comprising 1.0 mM **DQPO** and 20 mM TBAPF₆ in dichloromethane as its catholyte and anolyte. Remarkably, the charge/discharge profiles in this cell demonstrated notable similarities to the **QPO-3OMe**

based cell, featuring a discharge voltage plateau at approximately 2.4 V and exhibited similar efficiencies and capacity fading during cycling.

In 2020, the Monroe research group demonstrated that heteroatom-free aromatics can display promising characteristics for symmetric RFBs, with 9,10-diphenylanthracene (**DPA**, **13a**, Figure 2.5) based systems that offered very high cell voltages (>3 V).¹⁰³ Several solvents were investigated to assay the electrochemical stability of **DPA** and its functionalized analogues. Among them, the active species exhibited good reversibility in MeCN and DME. **DPA** exhibited two distinct one-electron redox couples for its oxidation and reduction with a separation of 3.09 V in MeCN and 3.23 V in DME, which represent the highest cell voltages among existing NAORFBs; however, the active material is sparingly soluble in acetonitrile (0.6 mM) and DME (44 mM), severely limiting the energy density of a flow battery system. Therefore, the **DPA** was functionalized by appending various groups at the 4- positions of the phenyl groups. It was found that diethyleneglycoxy esters improve the solubility by 5 and 20 times for DME and acetonitrile, respectively. Although the diethyleneglycoxy ester functionalized **DdPA** (**14a**, Figure 2.5) showed improved solubility, the CV analysis revealed poor electrochemical reversibility, and cells based on active molecules **DPA** and **DdPA** showed poor stability over cycling.

The Cook group investigated the potential of a commercially available boron-dipyrromethene dye known as **PM567** (**15a**, Figure 2.5) as a bipolar molecule for symmetric ORFBs.¹⁰⁴ The cyclic voltammetry (CV) analysis of **PM567**, when dissolved in 0.1 M TBAPF₆ in anhydrous acetonitrile, revealed two distinct one-electron redox events occurring at approximately 0.73 V and -1.59 V versus Ag/Ag⁺, representing a theoretical cell voltage of 2.32 V. Though the solution of **PM567** was stable to 30 CV cycles, bulk

electrolysis revealed that both the radical cation and radical anion of the dye decomposed over time. Remarkably, within one week, UV/Vis and CV monitoring revealed that a steady state was achieved within one week, and the resulting solutions remained electrochemically active at potentials similar to those of the initial **PM567** solution (though with multiple irreversible signals in the voltammograms). This prompted the authors to test non-flowing symmetric cells where **PM567** acts as a precursor to the active materials. The cell was observed to charge at ~ 2.2 V and discharge at ~ 1.6 V, with poor initial Coulombic efficiency ($\sim 22\%$) which stabilized at 78% after 40 cycles, but cell capacity suffered major decay ($>50\%$) within this number of cycles. This work represents an interesting case where electrochemically active decay products, and not the initially targeted molecule, can potentially lead to useful active materials for ORFBs.

Not all bipolar active species are charge neutral when discharged. C.G. Armstrong *et al.* studied another carbonyl containing active species, croconate violet dye, that exhibits five different oxidation states: **Croc**⁴⁻, **Croc**^{•3-}, **Croc**²⁻ (**16a**, Figure 2.6), **Croc**^{•-} and **Croc**.¹⁰⁵ However, the tetraanionic **Croc**⁴⁻ and neutral **Croc** species were found to be unstable and not suitable for RFB applications. Therefore, authors assembled a symmetric system with a theoretical cell potential of 1.82 V, where the radical anions **Croc**^{•3-} and **Croc**^{•-} represent the charged state of anode and cathode side, respectively, and dianion **16a** acts as the discharged state for both.¹⁰⁵ The system, which is unusual in having anionic species in all charged states, underwent flow cell cycling at 10 mM concentration of **16a** with TEABF₄ electrolyte and a Fumapem® F-930 cationic-exchange membrane and achieved 100% of the theoretical capacity at first charge, but 90% of the capacity degraded after only 11 cycles. The post-cycling analysis, and independent cycling of the **Croc**^{•3-}/**Croc**²⁻ and

Croc²⁻ /**Croc**^{•-} redox couples, revealed that **Croc**^{•3-} had dramatically lower lifetime compared to **Croc**^{•-} radical anion, but both sides experienced uncharacterized decomposition. Although the active material **16a** showed reasonably high solubility as a tetrabutylammonium salt (1 M in MeCN), the authors studied the flow cell at low concentration 10 mM. Though the overall battery performance is relatively poor, this work encourages the investigation of related low molecular weight molecules with several oxidation states separated by a large potential difference for high energy density symmetric batteries.

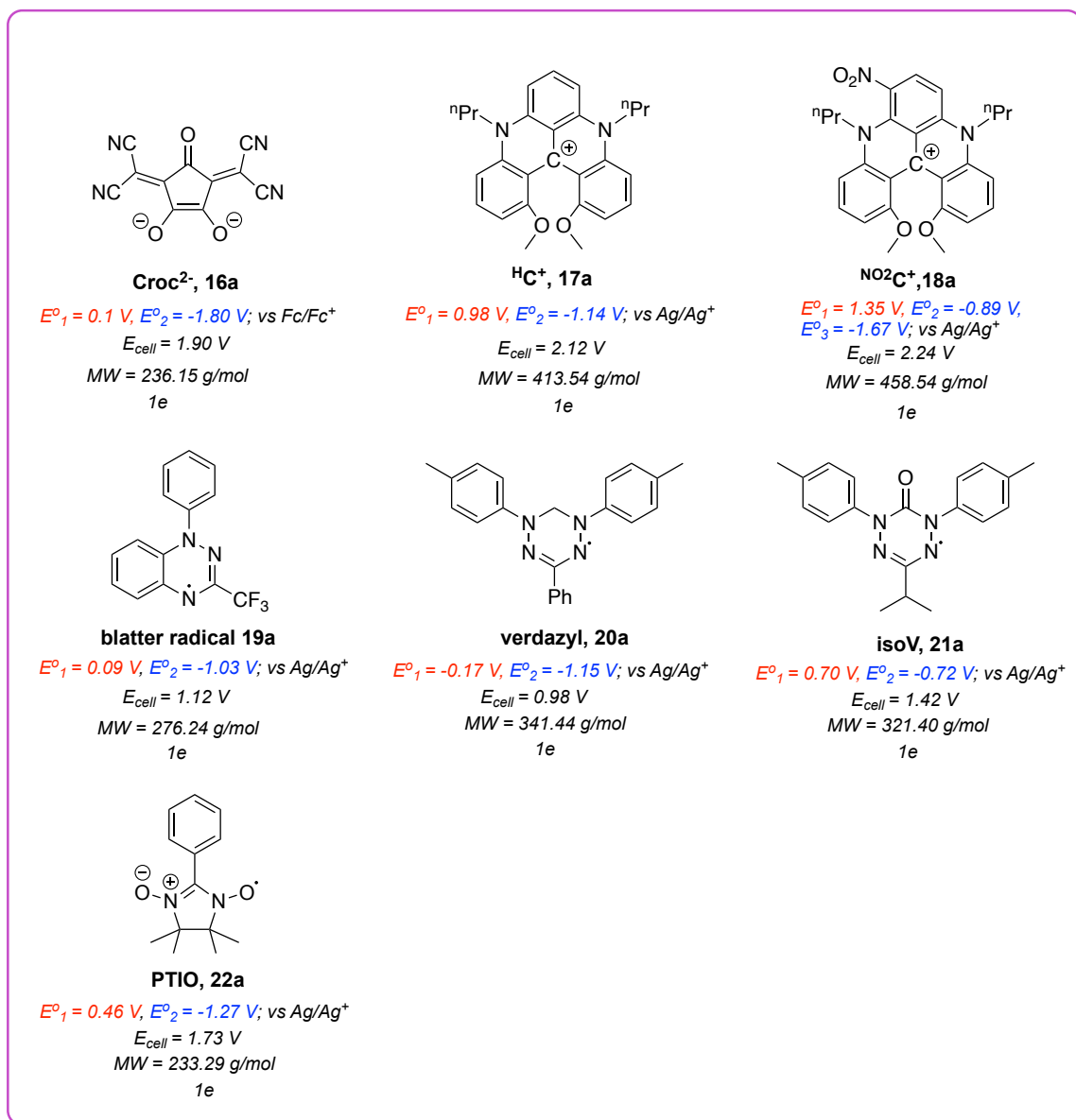


Figure 2.6 Structure, redox potentials, cell potential, molecular weight and number of electrons transferred during cycling for one-electron intrinsic bipolar redox-active molecules (charged or radical type II species) used in symmetric NAORFBs. Structures represent the discharged state, and redox potentials in red and blue relate to the cathode and anode active substructures, respectively.

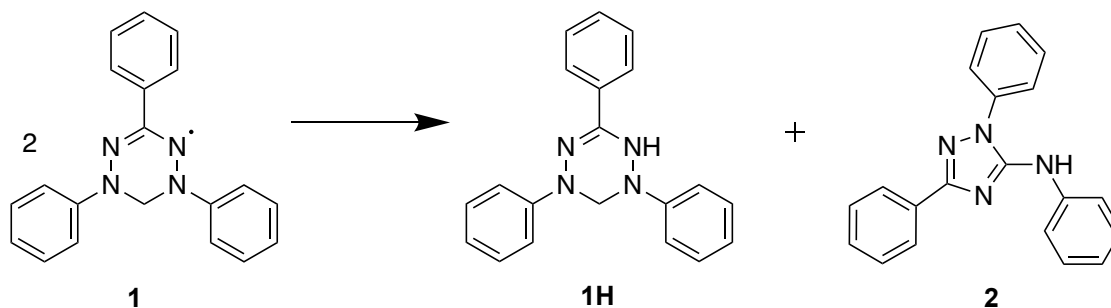
Helical carbenium ions have become a subject of growing interest because of their unique characteristics in photophysics, electrochemistry, and biology.¹⁰⁶ Moutet *et al.* for the first time studied helical carbenium ion H^+C^+ (**17a**, Figure 2.6) as an active material for symmetric NAORFBs.¹⁰⁷ The compound exhibited good reversibility, with an open circuit voltage of 2.12 V, based on the potentials for the one-electron oxidation and reduction as determined by cyclic voltammetry in acetonitrile 0.1 M TBAPF₆/MeCN. The solubility of H^+C^+ and $\text{H}^+\text{C}^\bullet$ in acetonitrile (without a supporting salt) was determined through UV-visible spectroscopy, with reported solubility values of 32.4 mM and 149.1 mM, respectively. To evaluate the performance of H^+C^+ as an active material, the authors conducted a static H-cell cyclic performance test with a current density of $\pm 5 \text{ mA cm}^{-2}$, using 1.2 mM solution of H^+C^+ (0.1 M TBAPF₆/MeCN) in both compartments. The cell was run for 800 cycles (88.7 hours), and the columbic efficiency was maintained at nearly 100%. The capacity fade rate was 0.05% per cycle (11.35% per day). However, postmortem CV analysis revealed that while the concentration of active material remained the same on the anolyte side, significant changes in concentration were observed on the catholyte side, likely due to the precipitation of H^+C^{2+} or some decomposition. In a subsequent study, the same research group synthesized the nitro-derivative of H^+C^+ namely NO_2^+C^+ (**18a**, Figure 2.6) to investigate its battery performance.¹⁰⁸ Though the authors were unsuccessful in preparing salts of the H^+C^{2+} and $\text{NO}_2^+\text{C}^{2+}$ oxidation states, it was found that the introduction of a nitro group onto the helical carbenium scaffold increased the open circuit voltage from 2.12 V to 2.24 V, and also significantly enhanced its solubility. While H^+C^+ showed a solubility of 32 mM in pure acetonitrile, NO_2^+C^+ exhibited a solubility of 154 mM. As a result of this increased solubility and cell voltage, the theoretical energy density of NO_2^+C^+ was found to

be approximately 5 times higher than that of ${}^{\text{H}}\text{C}^+$, increasing from 0.97 WhL^{-1} to 4.76 WhL^{-1} .¹ The charge/discharge cycling of 1.0 mM of ${}^{\text{NO}_2}\text{C}^+$ in $0.1 \text{ M TBAPF}_6/\text{MeCN}$ was conducted for 400 cycles at a current density of $\pm 5 \text{ mA cm}^{-2}$. The coulombic efficiency was very high throughout the experiment, but the capacity fade rate was higher than that of the ${}^{\text{H}}\text{C}^+$ derivative at 0.17% per cycle. Postmortem CV analysis revealed some decomposition in both the anolyte and catholyte compartments, suggesting that the introduction of the NO_2 group may have a negative effect on the stability of helical carbenium scaffold.

Whereas the intrinsic compounds discussed so far are diamagnetic species in the discharged state, there have been a few NAORFB studies of stable bipolar radicals (**19a-22a**, Figure 2.6) that can undergo one-electron oxidation and reduction. Blatter radicals, which are well-known for their excellent chemical stability,¹⁰⁹ were studied by the Otten research group for their suitability in symmetric ORFBs.¹¹⁰ One of the compounds, a CF_3 -substituted Blatter radical (**19a**), exhibited excellent stability in a static H-cell test, with a cell voltage of 1.12 V . The static cell was operated for 277 cycles (20 days) at a current density of 1 mA cm^{-2} , with 12 mM of **19a** in $0.3 \text{ M TBAPF}_6/\text{MeCN}$. The average capacity fade rate was only 0.02% per charge/discharge cycle or 0.3% per day. Based on these promising results, the material was further tested in a flow cell, at a concentration of 0.1 M in $0.3 \text{ M TBAPF}_6/\text{MeCN}$, with a current density of 35 mA cm^{-2} . The flow experiments showed encouraging results, with an overall capacity retention of 98% after 100 cycles (equivalent to 0.02% capacity fade per cycle, or 1.5% capacity fade per day), and average coulombic, voltage, and energy efficiencies of 89% , 67% , and 60% , respectively. The cycling stability of the battery is superior to that of other symmetric NAORFBs, probably

in large part due to the water-stability of the active material; nonetheless, the theoretical energy density of 9.60 WhL^{-1} is limited due to the low cell voltage.

A bipolar verdazyl radical (**20a**, Figure 2.6) symmetric system was reported by the Dyker and Gilroy groups in 2019 with a cell voltage of 0.98 V.¹¹¹ The active molecule **20a** shows good reversibility by cyclic voltammetry analysis. Using an anion exchange membrane at a current density of 0.12 mA cm^{-2} , the charge/discharge cycle of the static cell was studied with active material concentration 0.04 M in acetonitrile and 0.5 M TBAPF₆ supporting electrolyte. The active materials reached 93% of the theoretical discharge capacity but the capacity faded to 35% after 50 consecutive cycles. The coulombic efficiencies maintained between 94% to 97% throughout the experiment, and the voltage and energy efficiencies were 68% and 65%, respectively. Analysis of the post-cycle electrolyte revealed that decomposition of the anionic species was predominant and was suggested to be the major cause of performance degradation. Subsequent kinetic and theoretical work by Otten's group showed that while the anion is susceptible to protonation, this process is reversible, and instead a bimolecular disproportionation involving the radical itself is responsible for capacity fade (Scheme 2.2), with both products detected in NMR studies of post-cycled electrolyte.¹¹² This suggests that high concentration cells based on verdazyl radicals would require a means to prevent this process, perhaps by steric preclusion of the dimeric transition state.



Scheme 2.2 Disproportionation of **1** to **1H** and **2**

In a separate study, Korshunov *et al.* investigated the use of oxo-verdazyl (**isoV**, **21a**, Figure 2.6) in a symmetric ORFBs.¹¹³ Compared to the verdazyl radical, **isoV** exhibited a higher cell voltage of 1.42 V. To assess the flow cell performance, a 10 mM solution of **isoV** in 0.3 M TBAP in acetonitrile was subjected to continuous galvanostatic charge/discharge cycles at a current density of 2.2 mA cm⁻², employing a FAP-375-PP anion exchange membrane. After 80 cycles, the flow cell capacity reduced to 36%, indicating a capacity fade rate of 0.8% per cycle. The authors suggested that the redox electrolyte instability primarily arises from an intrinsic flaw of ion exchange membranes, where one of the active material charge states matches the type of ion permeable to the membrane (i.e., anion) and hence fouling of the membrane can be promoted, which causes resistance to increase and incomplete use of active material within the set voltage limits. A detailed experimental study of the decomposition products was not provided.

In 2016, Duan *et al.* investigated a nitronyl nitroxide radical, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (**22a**, **PTIO**, Figure 2.6), as a potential bipolar organic redox-active molecule for symmetric NAORFB.⁶⁹ Compound **22a** is commercially available, and showed excellent reversibility under CV scan conditions with distinct redox couples for its one-electron oxidation and reduction processes at potentials of -1.27 V and

0.46 V (vs Ag/Ag⁺), respectively, resulting in a theoretical cell voltage of 1.73 V. Although the redox-active molecule **22a** is highly soluble in acetonitrile (up to 2.5 M), the solubility of the oxidized and reduced forms was not investigated. The charge/discharge cyclic performance of the system was studied at 0.1 M and 0.5 M concentration using Daramic® porous separator with 1.0 M TBAPF₆ as the supporting electrolyte. The battery cycling performance at lower concentration was better than that of higher concentration. For example, at a current density of 20 mA cm⁻², the coulombic and voltage efficiency at 0.1 M concentration was 96% and 75% (35 cycles), respectively, while at 0.5 M concentration the values were 90% and 67% (15 cycles). The authors described the decrease in coulombic efficiency at higher concentration to the increased crossover during longer charge/discharge times. At the same time, concentration is proportional to the viscosity, and high viscosity contributes to the lower ionic conductivity of the system that ultimately results lower the voltage efficiency.⁶⁹ It is noteworthy that the flow cell experienced continuous capacity degradation, which the authors suggested was probably due to an electrolyte imbalance and/or the decomposition of redox-active materials.

2.7.3 Two-electron intrinsic symmetric systems (type II, IV, V)

In addition to maximizing cell voltages and concentration of active materials, a complementary strategy to increasing energy density involves bipolar active materials that engage in multi-electron oxidations and reductions. One approach to this is to end is by the tethering of two intrinsically bipolar subunits (type IV, Figure 2.3). To date, this has only been adopted in one study by the Schubert group where two subunits of nitronyl nitroxide radical were connected by a tetraethylene glycol chain.⁸⁷ As a result, the solubility of the compound **23a** (Figure 2.7) increased (3.8 M in acetonitrile) compared to the single unit nitronyl nitroxide radical (**PTIO**) at the expense of increasing the molecular weight and decreasing the overall cell voltage slightly to 1.62 V (vs 1.73 V for **PTIO**).⁶⁹ The two discreet radical units were observed to interact via EPR, but because of the insulating linker chain, the CV results showed that both units underwent redox processes at the same potential, with a single quasi-reversible wave at 0.37 V (vs Ag/Ag⁺) for the one electron oxidation of both units (two-electrons total) and a single quasi-reversible wave at -1.25 V (vs Ag/Ag⁺) for the one-electron reduction of both units (two-electrons total). Since precipitation of charged species was observed at concentrations of 0.5 M, cell testing was conducted at lower concentrations. In a static cell, the cycling performance of the compound **23a** was investigated using an anion-exchange membrane at low concentration (0.016 M in 0.5 M TBAPF₆/acetonitrile). Only 27% of the theoretical discharge capacity was achieved during the first cycle at a current density of 1 mA cm⁻², and after 75 cycles, 20% of the initial capacity was lost. The coulombic efficiencies of the system reached up to 95%, a voltage efficiency of 86% and an energy efficiency of 82%. A higher

concentration active material (0.1 M) was used for investigating flow cell performance, but 50% capacity fade was observed only after 11 cycles at a current density of 6 mAcm⁻².

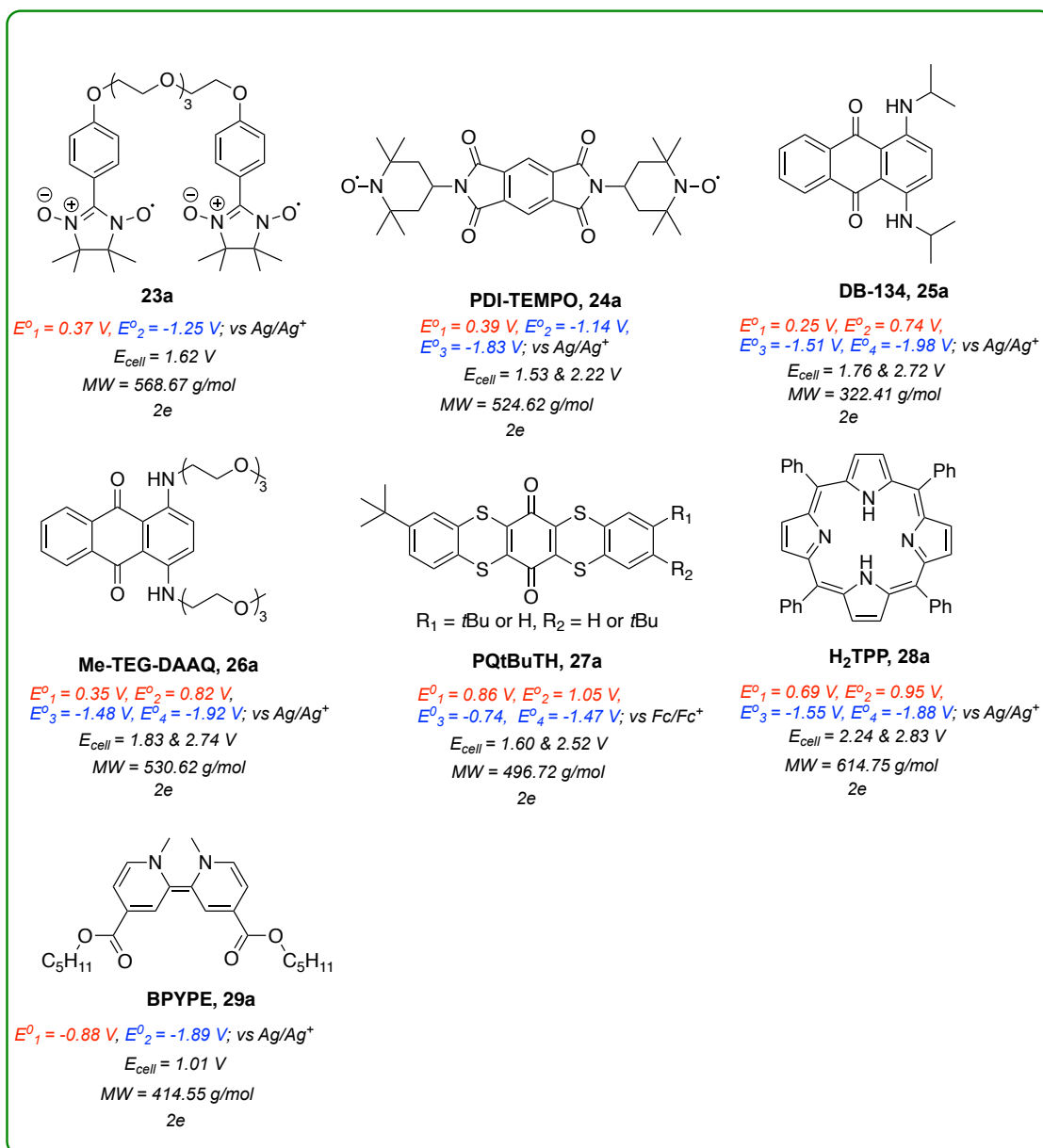


Figure 2.7 Structure, redox potentials, cell potential, molecular weight and number of electrons transferred during cycling for two-electron bipolar redox-active molecules [type II (25a–29a), IV (23a), and V (24a)] used in symmetric NAORFBs. Structures represent

the discharged state, and redox potentials in red and blue relate to the cathode and anode active substructures, respectively.

In a different approach (type V, Figure 2.3) to forming a multi-electron bipolar molecule, Nambafu *et al.* introduced **PDI-TEMPO (24a)**, Figure 2.7), by tethering two one-electron TEMPO units (cathode active) to a central two-electron pyromellitic diimide core (anode active)¹¹⁴. In a TBAPF₆/DMF supporting electrolyte, **PDI-TEMPO** displayed three distinct redox couples at -1.83 V, -1.14 V (attributed to two single-electron reductions of the pyromellitic diimide), and 0.39 V (two-electron process associated with the simultaneous oxidation of both discrete TEMPO units) vs Ag/Ag⁺. In a TBAPF₆/MeCN supporting electrolyte, these redox couples occurred at -1.72 V, -1.17 V, and 0.45 V vs Ag/Ag⁺. **PDI-TEMPO** exhibited good solubility, reaching 1.3 M in 0.1 M TBAPF₆/MeCN but displaying lower solubility of 0.2 M in 0.1 M TBAPF₆/DMF. For acetonitrile this translates to theoretical cell voltages of 2.22 V (involving the dianion/radical anion couple of PDI) and 1.53 V (radical anion/neutral PDI couple) in acetonitrile. During flow cell cycling at a **PDI-TEMPO** concentration of 1 mM, a faster capacity decay was observed when using MeCN as the solvent (0.6% per cycle) compared to DMF (0.2% per cycle), potentially due to side reactions with MeCN, but better capacity utilization was seen in MeCN (80%) over DMF (~30%). The authors conducted a high-concentration flow cell cycling experiments at a 0.5 M active material concentration in MeCN over 100 consecutive cycles. This yielded a columbic efficiency of 90% and an average capacity retention of 99.4% per cycle. Post cycling analysis by UV vis, CV, and NMR spectroscopy suggested that the anode active diimide was primarily responsible for cell degradation due

to decomposition which was proposed to involve deprotonation of MeCN by the radical anion.

Not all multi-electron bipolar compounds are tethered. In 2015, Potash *et al.* reported multi-electron intrinsic bipolar (type II, Figure 2.3) diaminoanthraquinones (DAAQs) as the active material for symmetric NAORFB systems.⁹ Cyclic voltammetry analysis revealed that out of three commercially available diaminoanthraquinones (DAAQs) only **DB-134 (25a)**, Figure 2.7) exhibited good electrochemical reversibility in 0.1 M TBAP acetonitrile solution. **DB-134** exhibits four different one-electron transfer redox couples at -1.98 V, -1.51 V, $+0.25$ V, and $+0.74$ V versus Ag/Ag⁺ that allows theoretical cell voltage of 2.72V and 1.76V for the outer and inner redox couples, respectively. Interestingly, the theoretical molar energy density of **DB-134** surpasses the value of commercial VRFB electrolytes (34 Wh mol^{-1}) for both single electron transfer inner (47 Wh mol^{-1}) and double electron transfer outer (120 Wh mol^{-1}) redox couples, but the sparingly soluble nature of the active materials (50 mM in MeCN) limits the achievable energy density. Moreover, the system demonstrated capacity fade after the first few cycles, which may be due to the degradation of the redox-active species. In 2020, Pieter *et al.* reported an improvement to Potash's work in terms of solubility. Functionalizing the amino groups of **DB-134** structure with triethylene glycol monomethyl ether (**26a, Me-TEG-DAAQ**, Figure 2.7) resulted in significantly increased solubility to $\sim 1.0 \text{ M}$ of the active materials in the presence of supporting electrolyte 1 M TEATf₂N, in both MeCN and DME solvents.¹¹⁵ When they tested battery performance using Nafion™ XL cation-exchange membrane in those two solvents with a concentration of active materials 0.1 M, noticeably greater capacity fade was observed in MeCN (44% and 61% in catholyte and anolyte mode, respectively)

compared to DME (7% and 18% in catholyte and anolyte mode, respectively) after 100 cycles. Notably, the DME cell exhibited higher coulombic efficiency compared to that in MeCN. Although MeCN-based electrolytes (1 M TEATf₂N) exhibited enhanced conductivity and reduced voltage drop, the poorer capacity retention may be influenced by assumed side reactions involving reduced/oxidized DAAQ species and C≡N triple bond. DME shows better capacity retention for cells limited to the inner redox couples over 100 cycles, while outer redox couples displayed lower reversibility with substantial capacity decline in both DME and MeCN electrolytes.

The Swager group conducted a study on a series of thianthrene-based bipolar redox-active molecules to evaluate their potential for use in all organic symmetric RFBs.⁸⁵ The researchers assessed the solubility and stability of various derivatives and tested the performance of **PQtBuTH** (**27a**, Figure 2.7) using a zeolite/PTFE separator in a static cell. In the MeCN:MB (1:4) solvent mixture, with a supporting electrolyte of 0.1 M TBATFSI, **PQtBuTH** exhibits two distinct single-electron oxidation events at 0.86 V and 1.07 V vs Fc/Fc⁺, and two single-electron reductions at -0.72 V and -1.42 V vs Fc/Fc⁺. These electrochemical processes result in an inner couple cell voltage of 1.58 V and an outer couple voltage of 2.49 V. Interestingly, when the supporting electrolyte was changed to LiTFSI, the two sequential one-electron reductions of **PQtBuTH** merged into a concerted two-electron reduction event occurring at -0.53 V vs Fc/Fc⁺. This observation suggests significant interactions between the reduced **PQtBuTH** and Li⁺ ions; however, the limited solubility of Li⁺-coordinated **PQtBuTH** dianion restricts its application in RFBs. Consequently, the authors conducted static cell performance testing using a 0.1 M TBATFSI supporting electrolyte. After 450 charge/discharge cycles, the cell exhibited a

capacity fade rate of 0.12% per cycle or 3.4% per day, resulting in a 64% total capacity fade. Postmortem CV analysis indicated the formation of unknown decomposition products, which the authors were unable to identify using NMR spectroscopy. Due to the brittleness of the zeolite/PTFE separator under pressure, the authors could not test the material in a flow cell condition, and other commercial separators such as polyethylene (PE, Celgard), poly(vinylidene fluoride) (PVDF), or poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) were incompatible with the solvent methyl benzoate. Overall, the study presents a strategic approach to designing intrinsic multi-electron bipolar redox-active molecules; however, the poor material solubility in common non-aqueous solvents and its limited performance restrict its use.

In 2018 S. Ma *et al.* reported a porphyrin-based symmetric ORFB for the purpose storing energy in cold regions,¹¹⁶ with functionality in the temperature range between 20 and -40°C . The CV of the active material **H₂TPP (28a)**, Figure 2.7) shows four reversible one-electron redox couples at potentials of -1.88 , -1.55 , 0.69 , and 0.95V (*vs* Ag/Ag⁺) that allows theoretical cell voltage of 2.83 V and 2.24 V for outer and inner redox couples, respectively. Due to the low solubility of active molecule **28a** in common organic solvents (such as 10 mM in DCM) the authors used Ketjen Black additives with different weight ratios to form **H₂TPP@KB** composites that help to increase the conductivity when suspended in a DCM based electrolyte. The authors used a specially prepared Y-zeolite–poly(vinylidene fluoride) ion-selective membrane for battery cycling. The system was safely charged and discharged within the voltage window of -3.2 to 3.2 V (cycling with polarity reversals) at a current density of 1 mA cm^{-2} . The active materials utilization and resistance of the system varies with temperature. While the internal resistance is high at

low temperature, the material utilization significantly decreases. For example, initial state of charge was around 92, 83, 69, and 63%, at 20, 0, -20, and -40 °C, respectively. The capacity retention maintains 99.98%/cycle and coulombic efficiencies remains over 99% at all the tested temperatures over a total of 800 cycles. The voltage efficiencies were always less than 50% due to the high viscosity and ohmic resistance of the electrolyte; however, the stability of active species is very good at the different temperatures based on the excellent cycling performance.

While multi-electron molecules have an advantage in terms of energy storage capacity over single electron bipolar molecules, the sequential nature of the two-electron oxidation and/or reduction steps in **24a-28a** creates a major inherent disadvantage in terms of voltage efficiency (and therefore energy efficiency). Indeed, such systems show a “step-up” voltage during charging and “step-down” voltage during discharge, and because of comproportionation processes, such cells will spend more time charging at the higher voltage and more time discharging at the lower voltage.¹¹⁷ Brushett has shown that the voltage efficiency drops significantly as the spacing between the sequential reduction (and/or oxidation) steps increases,⁸⁸ and makes a case for systems where multi-electron transfers occur in a concerted fashion, or with an inverted potential.⁸² Recently, the Dyker research group introduced a novel double concerted two-electron redox-active molecules for symmetric ORFBs.⁸² Molecule **BPYPE** (**29a**, Figure 2.7), and the related methylester **BPYME** (not shown), exhibit distinct and well-separated two-electron oxidation and two-electron reduction processes, which are dependent on the electrolyte. In acetonitrile with a non-coordinating cation (tetrabutylammonium) the CV of **BPYME** showed four distinct one electron redox processes, while using a salt based on a coordinating lithium cation in

DMF resulted in nearly concerted two-electron reduction and two-electron oxidation, with an open circuit voltage of 1.01 V. Though the cell voltage is low, the concerted nature of the two-electron reduction and oxidation eliminates the inherently poor efficiency of systems with sequential multielectron transfers.⁸⁸ **BPYME** was found to have solubility issues, but the more soluble **BPYPE** (with solubilities of at least 0.41 M for the dianionic species, and > 2 M for the neutral and dicationic oxidation states) was tested in cells. In addition, the stability of all three oxidation states of **BPYPE** was evaluated using cyclic voltammetry, which demonstrated no decay over a period of 7 days. The active material, **BPYPE**, was also evaluated in a flow cell configuration with an active material concentration of 0.04 M using the same 1.2 M LiTFSI/DMF electrolyte. Under galvanostatic cycling with potentiostatic holds, a material utilization of approximately 88.5% was attained. After 70 cycles, a capacity retention of around 71% was observed, with a decay rate of approximately 0.41% per cycle (equivalent to 0.58% per hour). While post-cycling CV data indicated that cell cycling may overstate degradation, a comprehensive understanding of the mechanisms leading to the loss of active species requires further exploration. Aside from membrane and electrode fouling, which can elevate cell resistance, other potential factors such as decomposition into electrochemically inactive species or active material absorption onto cell components could contribute to capacity decline. Overall, though cell voltages need to be improved, this study introduces a promising avenue for designing concerted multi-electron bipolar molecule for energy-dense ORFBs.

It is worth noting that both **BPYPE** and **23a** exhibit concerted multielectron bipolar character but via different molecular designs (type II and type IV, respectively, Figure 2.3).

BPYPE is a completely conjugated molecule with frontier orbitals involving the whole scaffold, while **23a** features two distinct one-electron bipolar units. Such concerted multi-electron bipolar systems could be key to achieving viable energy densities in symmetric RFBs considering the evidence for a limit of $\sim 2\text{M}$ for active material concentrations.³¹

2.8 Symmetric AORFBs

Relatively few symmetric ORFBs have been developed in aqueous media, with most belonging to the artificial type (type I, Figure 2.3) of bipolar active material. Nambafu *et al.* introduced bipolar redox molecule, **RIBOTEMPO** (**1b**, Figure 2.8), which combines riboflavin and a TEMPO radical.¹¹⁸ This molecule exhibited electrochemically reversible reactions at -0.72 V (two-electron/two-proton reduction of the riboflavin unit) and 0.51 V (one electron TEMPO/TEMPO⁺ unit) vs Ag/Ag⁺, resulting in a theoretical cell voltage of 1.23 V . Using UV-vis spectroscopy, the solubility of the **RIBOTEMPO** molecule in a 0.1 M NaCl supporting electrolyte was investigated, revealing a molecular solubility of 0.32 M . Interestingly, by introducing nicotinamide into the supporting electrolyte, solubility of up to 1.22 M could be achieved, elevating the energy density to 26.81 Wh L^{-1} . During flow battery cycling at a concentration of 0.003 M and a current density of 2.5 mA cm^{-2} , **RIBOTEMPO** retained only 44.7% of its capacity over 100 cycles and exhibited an 80% coulombic efficiency. Further testing employing up to 0.5 M **RIBOTEMPO** and 1.5 M nicotinamide at a relatively high current density of 40 mA cm^{-2} showed 90% coulombic efficiency over 120 consecutive charge and discharge cycles but only about 10% of the original charge capacity was retained. Various studies, including NMR and UV/Vis spectroscopy, mass spectrometry and CV analysis, as well as systematically replacing catholyte or anolyte after 100 cycles, showed that the capacity fade, was primarily

attributed to the decomposition of the catholyte (TEMPO) part of the combined molecule, while the anolyte (riboflavin part) experienced less significant decomposition. The research suggests a need for further investigation into the decomposition mechanisms of these organic molecules to address stability issues, a crucial step in advancing ORFBs.

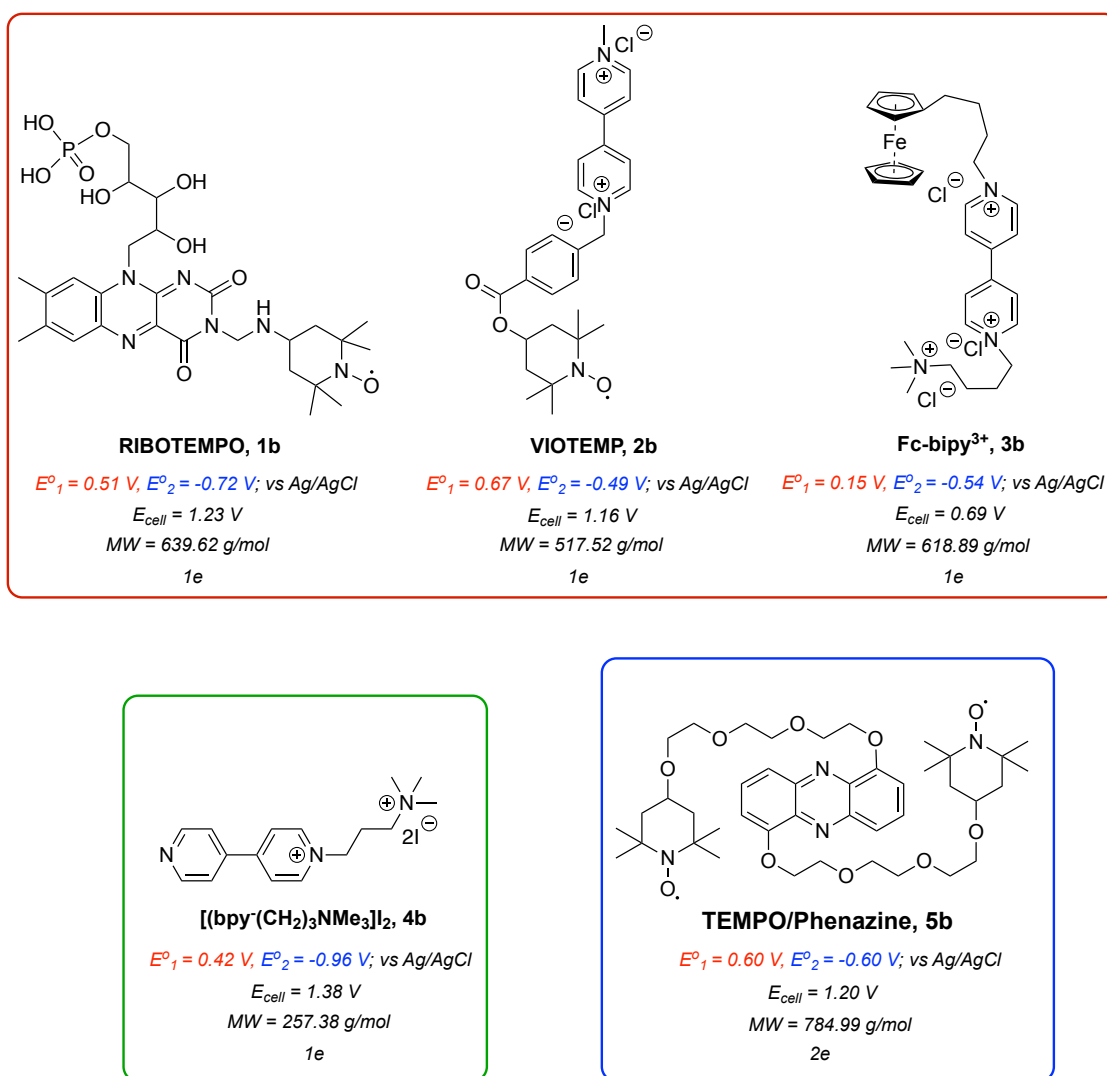
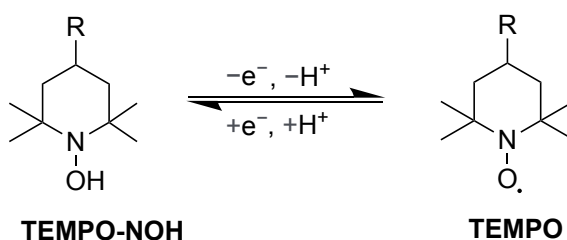


Figure 2.8 Structure, redox potentials, cell potential, molecular weight and number of electrons transferred during cycling for bipolar redox-active molecules [type I (**1b–3b**), type III (**4b**), type V (**5b**)] used in symmetric AORFBs. Structures represent the discharged

state, and redox potentials in red and blue relate to the cathode and anode active substructures, respectively.

The Schubert research group reported another bipolar molecule **VIOTEMP (2b)**, Figure 2.8) in 2017, containing the redox-active subunits viologen, an anode material, and a TEMPO based cathode material, covalently bonded by a benzyl linker.¹¹⁹ In 0.5 M NaCl aqueous solution, CV analysis of **VIOTEMP** revealed that viologen and TEMPO subunits exhibit quasi-reversible one-electron redox event at -0.49 V and 0.67 V (vs. Ag/AgCl), respectively, corresponding to an open current voltage of 1.16 V. Additionally, a small shoulder at about -0.35 V observed due to the reduction of the TEMPO radical to its protonated hydroxylamine form **TEMPO-NOH** (Scheme 2.3), resulting the considerable changes of proton concentration in the electrolyte solution. Therefore, the authors added an acetate or phosphate buffer solution to maintain the pH value between 2.5 and 7. Moreover, an additional 20 vol% ethylene carbonate organic solvent was also added because of the low solubility of radical cationic form of **VIOTEMP** in pure aqueous solution. Overall, the unwanted side reaction and presence of additives made the system vulnerable to degradation. Consequently, significant capacity loss was observed within 5-10 cycles during testing at VIOTEMP concentrations of 0.1 M.



Scheme 2.3 Schematic representation of the conversion of **TEMPO** radical to its hydroxylamine form (**TEMPO-NOH**).

Recently, Zhu *et al.* reported another bipolar molecule that featured covalently tethered ferrocene and bipyridinium moieties (**3b**, **Fc-bipy**³⁺, Figure 2.8) and tested its performance in a symmetric static cell with an anion exchange membrane at a concentration of 0.5 M **Fc-bipy**³⁺ in 1 M NaCl solution and a current density of 1 mA cm⁻².¹²⁰ The maximum solubility of **Fc-bipy**³⁺ is 1.2 M in water but the limiting solubility of its oxidized and reduced forms was not reported. The bipolar molecule **Fc-bipy**³⁺ shows good electrochemical stability with an open circuit voltage of 0.69 V. This bipolar redox active molecule exhibited good cycling performances over 4000 cycles with a capacity retention of 75%. The anion-conductive membrane is particularly well suited to this system and helps to prevent electrolyte crossover due the presence of positive charge in all three-oxidation states (**Fc-bipy**^{2+/3+/4+}) resulting in the high coulombic efficiency >99.8% and cycle life of the system.

Apart from the above mentioned one-electron artificial bipolar molecules, Liu *et al.* introduced an interesting ion-pair bipolar compound (type III, Figure 2.3) in which a single ionic salt **4b** (Figure 2.8) serves the three functions of anolyte, catholyte and supporting electrolyte.⁸⁶ Unlike other aqueous bipolar molecules in which anolyte and catholyte fragments are covalently tethered, the cationic (mono-N-substituted bipyridinium) and anionic (iodide) moieties of this ionic compound functions as anolyte and catholyte, respectively. The presence of a permanent charge group -NMe₃⁺ in molecule **4b** helps to increase solubility and charge transport properties that ultimately reduce the need of supporting electrolyte. The CV spectra of **4b** exhibit two pairs of reversible redox peaks at -0.96 V ([bpy-(CH₂)₃NMe₃]²⁺/[bpy-(CH₂)₃NMe₃]^{•+}) and +0.42 V (3I⁻/I₃⁻, 2e⁻) (vs. Ag/AgCl), resulting a theoretical open circuit voltage of 1.38 V. Although the maximum

solubility of the ionic compound is 1.76 M in water, the authors studied the battery cycling performance at 0.8 M concentration in a pH neutral condition with supporting NaCl electrolyte. They determined an optimal current density of 10 mA cm⁻² in terms of material utilization, and used a low-cost microporous membrane for charge/discharge cycling. After 100 consecutive cycles, the cell lost about 50% of its initial capacity. The post-cycling analysis revealed that the capacity fade is not related to material decomposition but the deposition of iodine on the electrode surface. The capacity fade can be recovered almost completely by refreshing the electrode or by replacing it with new one. Overall, this study opens a new motif for designing symmetric ORFBs.

In 2016, the Schubert group introduced a two-electron double-tethered (type V, Figure 2.3) bipolar redox-active molecule that can be oxidized and reduced within the potential window of water. They chemically tethered phenazine (anolyte) and two TEMPO (catholyte) electroactive species by triethylene glycol (TEG) linkers. The **TEMPO/Phenazine** combi-molecule (**5b**, Figure 2.8), features an open circuit voltage of 1.20 V.¹²¹ Cyclic voltammetry (CV) measurements of combi-molecule **5b** showed a quasi-reversible two-electron redox process for phenazine²⁻/phenazine (-0.60 V vs Ag/AgCl) and a reversible process for the TEMPO subunits, with both TEMPO/TEMPO⁺ redox process occurring at the same potential (0.60 V vs Ag/AgCl). The authors performed flow battery tests by using 10 mM **5b** as both catholyte and anolyte, in 0.5 M NaCl as the supporting electrolyte, with 10 vol % diglyme as an additive. Only 60% of the theoretical capacity was achieved in this experiment with current densities of 1–5 mA cm⁻², however; no capacity degradation was observed after over 1800 consecutive charge–discharge cycles. The coulombic efficiency reached up to 98.3% but energy efficiency was only 50% due to a

voltage drop between charging and discharging attributed to the slow two-electron redox kinetics of the phenazine unit. Polarity reversals were shown to effect electrolyte rebalancing through improved capacity utilization. The combi-molecule demonstrated durable bipolar redox activity over multiple cycles without capacity loss, representing progress towards a potential bipolar organic alternative for all-vanadium RFBs.

To the best of our knowledge there has been no intrinsic bipolar molecule (type II, Figure 2.3) for symmetric AORFB reported so far, likely because soluble and stable active species with two redox couples within the electrochemical window of water (-0.83 V to 0.4 V at $\text{pH} = 14$, and 0 V to 1.23 V at $\text{pH} = 0$ vs. SHE)³⁰ are hard to find. We do note that in 2016, Armand *et al.* investigated the electrochemical properties, specifically through cyclic voltammetry, of significantly water-soluble derivatives of alizarin (1,2-dihydroxy-9,10-anthraquinone), quinizarin (1,4-dihydroxy-9,10-anthraquinone), and indigo dyes. These compounds exhibited two-proton/two-electron reduction and oxidation processes compatible within the electrochemical window of water which promotes high energy density; however, their study did not extend to examining the battery performance of these intrinsic multi-electron bipolar compounds.¹²²

2.9 Performance comparisons and outlook

2.9.1 Stability of bipolar redox-active molecules

Within the field of symmetric ORFBs, a notable disparity emerges when comparing cycle life of non-aqueous system to their aqueous counterparts. Symmetric non-aqueous ORFBs generally display lower cycle life stability when compared to their aqueous counterparts. An exception to this trend is the non-aqueous blatter radical **19a** compound (Table 2.1), which stands out for its commendable cycle life performance at 0.02% degradation per cycle. However, it is important to note that even though it exhibits improved cycle life, its decomposition rate remains relatively high when compared to some of the aqueous systems. For example, materials employed in symmetric aqueous ORFBs (Table 2.3), such as **TEMPO/Phenazine, 5b** (reported to have no capacity degradation after 1800 cycles), **Fc-bipy³⁺, 3b** (capacity fade of 0.0063% per cycle), and **[(bpy-(CH₂)₃NMe₃)]I₂, 4b** (which shows a 0.5% capacity fade per cycle, attributed to the deposition of iodine on the electrode surface; this capacity is regained when the surface is polished), have demonstrated commendable cycle life stability.

On the other hand, it is essential to underscore that research on the calendar life stability (decay rate per unit time) of materials employed in non-aqueous ORFBs has been relatively constrained, with only a select set of compounds (Table 2.1 & 2.2), such as **N-MEEtBuPhePhtha, 8a** (degradation rate: 13.2% per day), **⁺Pr-DMQA, 17a** (11.36% per day), **blatter radical, 19a** (1.5% per day), **PQtBuTH, 27a** (3.4% per day), and **BPYPE, 29a** (13.9% per day), having a reported calendar life. Unfortunately, the calendar life of the aqueous bipolar redox-active molecules has not been reported but the lifetimes are likely much closer to the requirements for commercialization based on the cycle life

data highlighted above. This understanding of material stability, encompassing both cycle and calendar life metrics, are pivotal in ongoing efforts toward the development and optimization of symmetric ORFBs, but the current data demonstrates stability as a significant hurdle in non-aqueous systems. Indeed, the targeted operational lifetimes for RFBs should exceed 10 years and entail over 10,000 cycles, with a capacity fade not exceeding 20%.^{23,123,124} We note that a number of reports realize an overestimate of capacity fade during cycling caused by increased cell resistance, leading to unused active material within the voltage limits. Potentiostatic holds³³ during cycling is highlighted as an effective way to minimize these errors and to decouple the increased ohmic resistance (which is another problem requiring solving) from the decay caused by active material decomposition. Nevertheless, none of the symmetric NAORFBs currently approach viable lifetimes while aqueous systems such as **3b** and **5b** show promise that long term stability may be achievable for aqueous systems, but calendar life assessments are needed.

2.9.2 Coulombic, Voltage, Energy Efficiencies

Evaluating overall battery performance relies significantly on key parameters such as Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE). However, a direct comparison across various reported ORFBs proves to be challenging due to the inherent differences among these systems. Factors like the choice of solvents, operational current densities, cell resistance, electrochemical kinetics, and the influence of static and flow cell configurations all contribute to the complexity.

Coulombic efficiency in flow batteries is influenced by membrane crossover, self-discharge of active materials, and molecular degradation.¹²⁵ As previously noted, capacity fade rates are generally elevated in non-aqueous ORFBs. Nonetheless, certain systems,

namely **4a**, **5a**, **8a**, **10a**, **17a**, **18a**, **27a**, **28a**, and **29a**, stand out by exhibiting good average Coulombic efficiencies (over 97%) (Figure 2.9) while **1a**, **3a**, **4a**, **8a**, **10a**, **11a**, and **23a**, demonstrate favorable voltage efficiencies exceeding 85% (Figure 2.9). Notably, compounds **4a** (in a static cell configuration), **8a**, and **10a** achieve high Coulombic and voltage efficiencies, resulting in outstanding overall energy efficiencies consistently surpassing 85%. Within aqueous systems, **3b** and **5b** demonstrate remarkable Coulombic efficiencies of 99.9% and 98.3%, respectively, highlighting their exceptional stability. There is a lack of efficiency data in these aqueous studies, but we note that **4b** and **5b** exhibit relatively low energy efficiencies of 72% and 50%, respectively, in comparison to some of their non-aqueous counterparts. This disparity is primarily attributed to the notably reduced voltage efficiency observed in **4b** (80%) and **5b** (50.9%). The reduced voltage efficiency observed in **4b** is attributed to cell polarization,⁸⁶ whereas in **5b**, it is associated with sluggish redox kinetics of phenazine subunits,¹²¹ and may be influenced by the use of an anion exchange membrane.³⁷

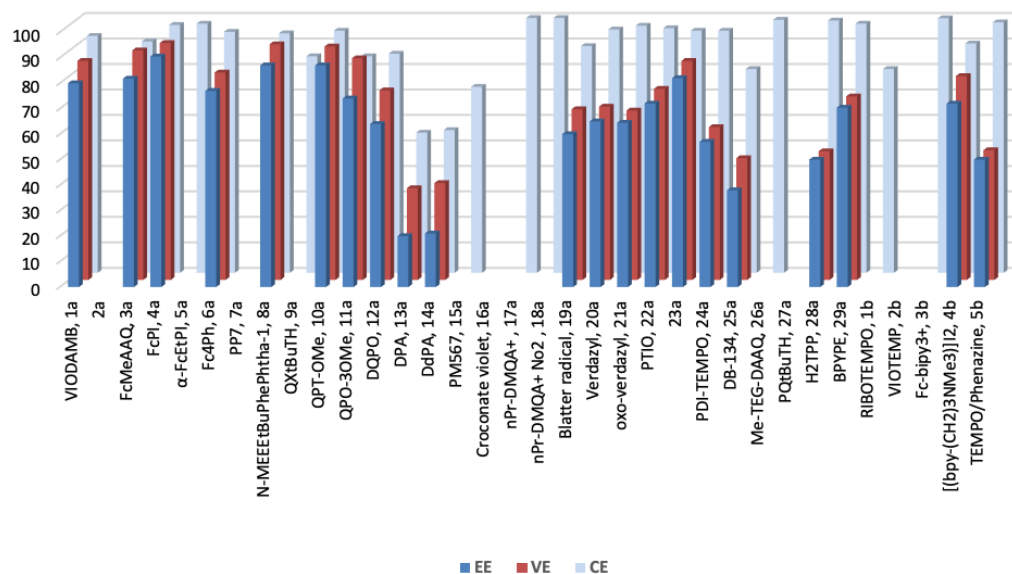


Figure 2.9 Comparison of Coulombic, voltage, and energy efficiencies for all reported symmetric ORFBs. Entries **1a–29a** represent non-aqueous systems, while entries **1b–5b** denote aqueous systems. Some entries remain blank, indicating unreported data in the literature. The dataset comprises both flow cells and static cells, and in cases where both flow and static cell data are available, the flow cell data are included. See also Tables 2.1, 2.2, and 2.3.

2.9.3 Energy Density

Volumetric energy density stands as a pivotal parameter for assessing the economic feasibility of ORFBs. In accordance with a technoeconomic study conducted in 2014, it was suggested that for a non-aqueous ORFB system to be economically viable, it should involve active materials in the solubility range of 4-5 M, with a cell voltage of 3 V for a one-electron system.¹²⁶ In the case of an aqueous system, economic viability is projected

at a lower solubility of 1-2 M, with an associated cell voltage of approximately 1.5 V for a one-electron system.¹²⁶ In both solvent systems, cost estimates related to the active materials and supporting electrolytes were key factors in deriving these numbers. Meeting the active material cost targets remains a key challenge, but acknowledging that symmetric ORFBs are in the early stages of development where costs are often neglected in favor of fundamental investigations, the implied energy densities from these values can be used as a benchmark for making comparisons among systems and to measure progress in the field. Considering two equal volumes for a symmetric ORFB, this translates to a volumetric energy density of 180 Wh/L for non-aqueous systems (based on a solubility of 4.5 M) and a volumetric energy density of 30 Wh/L for aqueous systems (based on a solubility of 1.5 M). For symmetric ORFBs reported to date, the tested energy densities fall considerably below these benchmarks for both symmetric non-aqueous and aqueous systems (Table 2.1, 2.2, & 2.3). For instance, the highest reported volumetric energy densities for one-electron non-aqueous system compounds are **5a** (15.92 Wh/L in a static cell), **6a** (13.67 Wh/L), **22a** (11.59 Wh/L), and for a sequential two-electron system, **28a** (22.12 Wh/L, although this value is an overestimate based on average voltage). All other compounds fall within the range of 0.025-6.11 Wh/L (Table 2.1, 2.2). Similarly, for one-electron aqueous systems, the highest reported volumetric energy densities are **1b** (8.24 Wh/L) and **4b** (14.79 Wh/L), with all other compounds falling within the range of 0.33-4.62 Wh/L (Table 2.3). These observations underline the considerable gap between the reported energy densities in the literature and targets for economic viability, highlighting the need for further research and development to enhance the energy density of symmetric ORFB systems.

As discussed previously, the volumetric energy density relies on three critical factors: cell voltage, solubility, and the number of electrons stored per molecule. Therefore, it is crucial to explore the traits of molecules with high cell voltages and exceptional solubility. Within the realm of non-aqueous symmetric systems, three specific intrinsic bipolar molecules have surpassed the expected 3 V threshold, demonstrating impressive cell voltages: compound **9a** (3.03 V), **13a** (3.23 V), and **14a** (3.06 V) (Figure 2.10). Similarly, within the aqueous systems, the ion paired type compound **4b** has produced the highest cell voltage of 1.38 V (Figure 2.10), just below the benchmark 1.5 V mark.

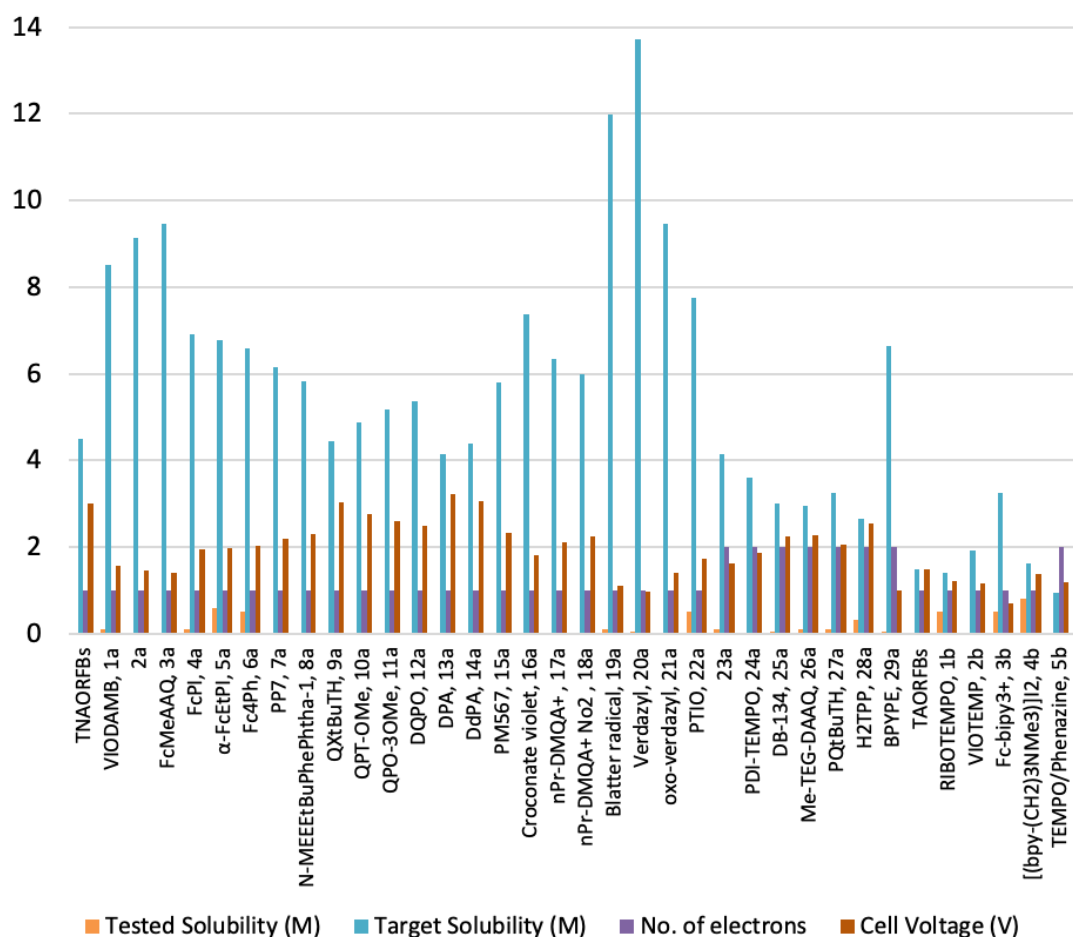


Figure 2.10 Volumetric energy density variables for bipolar systems, including solubility, the number of electrons, and cell voltage, as compared to the Targeted Solubility, which is that needed to achieve 180 Wh/L and 30 Wh/L in non-aqueous and aqueous systems, respectively. The entries “TNAORFBs” and “TAORFBs” represent the suggested parameters to achieve these energy densities. The tested solubilities for compounds **2a** and **7a** are not reported, and several systems reported low solubilities (ranging from 0.001 to 0.025 M) that are challenging to discern in the graph; detailed values are available in Tables 2.1, 2.2, and 2.3.

In the context of non-aqueous symmetric systems, the available literature predominantly focuses on examining active compounds at very low concentrations. Notably, tethered compound **5a** (0.6 M), **6a** (0.5 M), and intrinsic compound **22a** (0.5 M) have been tested at concentrations notably higher than other compounds, which typically fall within the range of 0.001-0.325 M (Table 2.1 & 2.2). An intriguing observation is the case of nitronyl-nitroxide **22a** (**PTIO**), where tethering two of these units to form **23a** increases the theoretical solubility of the middle (bipolar) oxidation state from 2.6 M to 3.8 M, although cell testing is conducted at 0.1 M. Similarly, within the aqueous system, tethered compounds **1b** (0.5 M) and **3b** (0.5 M), along with ion-paired compound **4b** (0.8 M) (Table 2.3), exhibit favorable tested solubility but still fall short of what is required to achieve 30 Wh L⁻¹ with these active materials (1.42 M for **1b**, 3.24 M for **3b**, and 1.62 M for **4b**). These observations highlight the potential of tethered compounds in enhancing the solubility of both non-aqueous and aqueous symmetric systems, contingent upon the selection of an appropriate linker chain.

The solubility of all distinct oxidation states plays a pivotal role in the effective operation of a flow cell since the least soluble oxidation state within the system serves as a limiting factor. Unfortunately, most of the reported literature has focused on the solubility of the middle (bipolar) oxidation state, which in most cases is probably not the state with the lowest solubility. The maximum theoretical energy densities in Table 2.1, 2.2, 2.3 are primarily based on these imperfect maximum solubilities, but a few systems have reported solubilities for all oxidation states. It is worth noting that in some small-scale static cells tests (such as coin cell experiments), poor solubility of one charge state sometimes does not significantly reduce cycling performance because precipitation can occur directly on

the electrode surface and can therefore be electrochemically accessible during cyclic operation. However, the scenario shifts significantly in flow cells. In this context, if an oxidation state exhibits low solubility and precipitates during the charging or discharging process, it can potentially accumulate in the external tanks where it is separated from the electrode and is therefore electrochemically inaccessible. As tested solubilities lag far behind what is required to achieve benchmark energy densities in most cases (see Targeted Solubility, Figure 2.10), more detailed solubility studies on all redox states of the active materials are needed areas are more cell tests at concentrations closer to the maximum solubilities.

In our assessment of non-aqueous systems with a targeted volumetric energy density of 180 Wh/L, it becomes apparent that only a limited subset of these systems can achieve this energy density at solubilities at or below the 4-5 M range (Figure 2.10), with others requiring unrealistically high solubilities (for example, >13 M for verdazyl **20a**). Specifically, this subset includes one-electron systems **9a**, **13a**, and **14a**, as well as all the two-electron systems **23a-28a**, except **29a**. In cases where a compound exhibits a two-electron transfer mechanism, achieving the target volumetric energy density criteria can be technically achieved by either halving the cell voltage or the active material solubility (the latter is reflected in Figure 2.10). Undesirably, compounds **25a-28a** exhibit a notable voltage separation between their two sequential reduction and oxidation processes. Specifically, these compounds suffer from voltage drop issues during discharging, thereby adversely affecting their overall voltage and energy efficiency.⁸⁸ While **29a** shows more promising concerted two-electron reduction and oxidation, its cell voltage (1.01 V) limits energy density. Importantly, compelling evidence highlights the impracticality of

surpassing organic active material concentrations beyond 2 M in non-aqueous solvents.³¹ This is primarily attributed to the severe reduction in ionic conductivity and the concurrent increase in system viscosity that occurs when attempting to exceed this concentration threshold. Given this more stringent constraint of a 2 M concentration limit, it becomes evident that none of the non-aqueous systems effectively meet practical expectations in terms of solubility. Nevertheless, the two-electron systems clearly stand out as advantageous when compared to their one-electron counterparts, as visually represented in Figure 2.10, demonstrating greater potential to meet the desired objectives.

In the context of an aqueous system with a targeted volumetric energy density of 30 Wh/L, it can be seen (Figure 2.10) that one-electron systems VIOTEMP **2b** and ion pair type compound **4b** can accomplish this at concentration below 2 M, but the tested solubilities are still less than half of this value. In the case of the two-electron system, double-tethered compound **5b** requires only a solubility of 0.93 M to achieve the target energy density. Though the tested solubility was much lower (0.01 M), reaching 0.89 M or higher could potentially be achieved through functionalization. Further in its favor is the fact that **5b** undergoes concerted, rather than sequential, two-electron redox processes. Though fewer aqueous systems have been studied, this analysis suggests that, in terms of energy density, they are much closer than the non-aqueous counterparts to meeting targets. Moreover, the inherent benefit of two-electron systems is underlined for the development of economically sustainable symmetric ORFBs in both solvents.

For symmetric NAORFBs, the above analysis shows that major hurdles remain in terms of active material stability, and energy density. To make major advances in terms of energy density, and considering the likelihood of a 2 M solubility limit,³¹ bipolar active materials

should ideally be designed to engage in two-electron reduction and oxidation processes, with a separation (E_{cell}) of 3 V or more. To achieve acceptable energy efficiencies, each two-electron event should be concerted or nearly-concerted.⁸⁸ Stability is a harder target to design for, and it remains to be seen if stability targets can be met while meeting these requirements, but more detailed studies on material decomposition, and electrode and membrane fouling should help guide progress in this area. Among the five distinct categories of bipolar molecules explored, intrinsic bipolar molecules (type II, Figure 2.3) exhibit promise for designing atom-economical systems; however, the design of a double concerted two-electron system operating a high voltage presents a formidable challenge that will likely require predictive computational studies to meet. Consequently, the design of double bipolar and double-tethered (type IV and V, respectively; Figure 2.3) molecules emerge as alternate promising strategies. Indeed, bipolar systems of type II have reached cell voltages of 3 V (see Figure 2.5) and tethering two such units will naturally enable double concerted behavior, while judicious choice of catholyte and anolyte units from asymmetric ORFBs should enable similar features in molecules of type V. In both cases the tethers should be chosen to enable desirably high solubility, but also to enhance stability, over the related untethered redox active molecules. It is imperative to balance these benefits with the potential challenges associated with the impaired kinetics of larger molecules in pursuing the tethered, double bipolar and double-tethered strategies.

Concerning symmetric AORFBs, though fewer bipolar systems for aqueous solvents have been studied, the reported cycle life and cell voltages shows that the field is more on track to reach viable systems for energy storage. Even tethered one-electron molecules (type I) appear promising, as reasonable energy densities can be achieved at cell voltages of 1.5 V

and concentrations of 1.5 M, but further work is needed to get the tested concentrations closer to this limit, and to improve efficiencies. Nonetheless, double-tethered (type V) molecules, exemplified by the single reported example **5b**,¹²¹ emerge as more promising systems for symmetric AORFBs, capitalizing on the advantages of storing two electrons such that high energy densities can be achieved even at low concentrations. To the best of our knowledge, there are no intrinsic bipolar molecules (type II) that have been tested in aqueous RFB cells, but double concerted two-electron compounds operating in the potential window of water have been demonstrated.¹²² As such, there is much promise in further studies to develop these and other new type II species for AORFB applications. Overall, the noteworthy advantage of symmetric ORFBs is their potential to replace the costly ion exchange membranes commonly employed in asymmetric systems. This cost reduction associated with membrane choice may introduce additional benefits and offer flexibility in lowering the solubility and voltage parameters required for viable energy storage systems based on organic active materials in aqueous and non-aqueous electrolytes.

Table 2.1 Comparison of reported bipolar molecules for symmetric NAORFBs (flow cells)

Bipolar Active Materials	Electron storage per molecule (ox, red)	Cell voltage (V)	Tested and [Limiting] Molar solubility (M)	Tested energy density (Wh/L)	Theoret. energy density (Wh/L)	Capacity fade (%/cycle, %/day)	No. of cycles	CE, EE, VE (%) ^f
VIODAM B, 1a ⁷⁹	1, 1	1.58	0.01 ^f 0.1 ^f [0.53] ^{d, g}	0.21 ^f 2.12 ^f	[11.22] ^g	0.57, NR 3.00, NR	35 ^f 20 ^f	93.0, 80.0, 86.0 NR, NR, NR
FcMeAA Q, 3a ⁹¹	1, 1	1.42	0.01 ^f [0.016] ^{d, g}	0.19 ^f	[0.30] ^g	NR	100 ^f	90.8, 81.8, 90.1
Fc4Ph, 6a ⁹⁹	1, 1	2.04	0.01 ^f 0.05 ^f 0.50 ^f [2.27] ^{c, g}	0.27 ^f 1.37 ^f 13.67 ^f	[62.05] ^g	0.32, NR 0.20, NR NR, NR	NR 50 ^f 20 ^f	NR 94.6, 77.0, 81.4 87.3, 50.3, 57.9
N-MEEEtBu PhePhtha-1, 8a ⁸⁴	1, 1	2.31	0.005 ^e 0.025 ^f [1.8] ^{c, g}	0.15 ^e 0.77 ^f	[55.72] ^g	0.11, 13.2	100 ^e , 275 ^f	94.0, 87.0, 92.5
QPT-OMe, 10a ⁸³	1, 1	2.76	0.025 ^e 0.025 ^f [NR]	0.92 ^e 0.92 ^f	NR	0.52, NR	900 ^e , 50 ^f	95.0, 87.0, 91.6
Croconate violet, 16a ¹⁰⁵	1, 1	1.82	0.01 ^f [1.0] ^{c, g}	0.24 ^f	[24.39] ^g	9, NR	10 ^f	NR, NR, NR

Blatter radical, 19a¹¹⁰	1, 1	1.12	0.012 ^e 0.10 ^f [0.64] ^{c, g}	0.18 ^e 1.50 ^f	[9.60] ^g	0.02, 1.5	277 ^e , 100 ^f	89.0, 60.0, 67.0
oxo-verdazyl, 21a¹¹³	1, 1	1.42	0.01 ^f [2.4] ^{c, g}	0.19 ^f	[45.67] ^g	0.8, NR	80 ^f	~97.0 , ~64.5 (average), ~66.5
PTIO, 22a⁶⁹	1, 1	1.73	0.1 ^f 0.5 ^f [2.6] ^c	2.32 ^f 11.59 ^f	[60.27] ^g	NR	35 ^f 15 ^f	96.0, 72.0, 75.0 90.0, 60.0, 66.7
23a⁸⁷	2 ^b , 2 ^b	1.62	0.016 ^e 0.1 ^f [3.8] ^{c, g}	0.69 ^e 4.34 ^f	[164.98] ^g	0.27, NR 0.5, NR	75 ^e 20 ^f	95.0, 82.0, 86.0 NR, 79, NR
PDI-TEMPO, 24a¹¹⁴	2 ^a , 2 ^b	1.87 ⁱ (2.22/1.53)	0.001 ^f [0.2] ^{d, g}	0.025 ^{f, j}	[10.05] ^{g, j}	0.2, NR	100 ^f	95.0, 57.0, 60.0
H₂TPP, 28a¹¹⁶	2 ^a , 2 ^a	2.54 (2.83/2.24)	0.325 ^f [NR]	22.12 ^{f, j}	[NR]	0.02, NR	200	99.0, 50.0, 50.5
BPYPE, 29a⁸²	2 ^b , 2 ^b	1.01	0.015 ^e 0.04 ^f [2.5] ^{d, g} [0.41] ^{d, h}	0.20 ^e 1.08 ^f	[67.67] ^g 11.10 ^h	0.35, 13.9	2000 ^e , 70 ^f	~99.0 , ~72.0 , ~72.0

^aSequential two-electron; ^bConcerted two-electron; ^cHighest molar solubility without supporting electrolyte; ^dHighest molar solubility with supporting electrolyte; ^eStatic cell; ^fFlow cell; ^gBased only on the bipolar (middle) oxidation state; ^hBased on minimum measured solubility of all three oxidation states; ⁱAverage voltage with outer and inner voltages given in parenthesis; ^jOverestimated energy density calculated based on average voltage; the cell predominantly discharges at inner couple voltage⁸⁸; NR = Not reported

Table 2.2 Comparison of reported bipolar molecules for symmetric NAORFBs (static cells)

Bipolar Active Materials	Electron storage per molecule (ox, red)	Cell voltage (V)	Tested and [Limiting] Molar solubility (M)	Tested energy density (Wh/L)	Theoret. energy density (Wh/L)	Capacity fade (%/cycle, %/day)	No. of cycles	CE, EE, VE (%)
2a ⁸⁹	1,1	1.47	NR NR	NR	NR	NR	100	NR, NR, NR
FcPI, 4a ⁸⁰	1, 1	1.94	0.1 [0.3] ^{d,f}	2.6	[7.80] ^f	NR	50	95.9– 98.7, 88.3– 92.7, 93.0
α-FcEtPI, 5a ⁹⁸	1, 1	1.98	0.6 [0.81] ^{d,f}	15.92	[21.50] ^f	NR	50	97.8, NR, NR
PP7, 7a ⁸¹	1, 1	2.18	NR [NR]	NR	NR	0.54	100	NR, NR, NR
QXtBuTH, 9a ⁸⁵	1,1	3.03	0.02 [0.61 $\pm$ 0.0] ^d	0.81	[24.8] ^f	NR	100	85.0, NR, NR
QPO-3OMe, 11a ¹⁰²	1,1	2.60	0.001 [NR]	0.03	NR	0.29, NR	200	85.0, 74.0, 87.0
DQPO, 12a ¹⁰²	1,1	~2.50	0.001 [NR]	0.03	NR	0.29, NR	200	86.0, 64.0, 74.4
DPA, 13a ¹⁰³	1,1	3.23	0.01 [0.044] ^{c,f}	0.43	[1.90] ^f	NR	25	55.0, 20.0, 36.0

DdPA, 14a¹⁰³	1, 1	3.06	0.01 [0.012] ^{c,f}	0.41	[0.49] ^f	NR	20	54.0– 58.0, 21.0, 38.0
PM567, 15a¹⁰⁴	1, 1	2.32	0.001 [0.2] ^{c,f}	0.031	[6.22] ^f	NR	100	73, NR, NR
ⁿPr- DMQA⁺, 17a¹⁰⁷	1, 1	2.12	0.0012 [0.032] ^{c,f}	0.03	[0.91] ^f	0.05, 11.36	800	~100, NR, NR
ⁿPr- DMQA⁺ No2, 18a¹⁰⁸	1, 1	2.24	0.001 [0.154] ^{c,f}	0.03	[4.62] ^f	0.17, NR	400	~100, NR, NR
Verdazyl, 20a¹¹¹	1, 1	0.98	0.04 [NR]	0.52	NR	1.3, NR	50	94.0– 97.0, 65.0, 68.0
DB-134, 25a⁹	2 ^a , 2 ^a	2.24 ^b (2.72, 1.76)	0.05 [0.2] ^{c,f}	3.00 ^e	[12.00] ^{e,f}	NR	6	~80.0 , ~38.0 , ~47.8
Me-TEG- DAAQ, 26a¹¹⁵	2 ^a , 2 ^a	2.28 ^b (2.74, 1.83)	0.1 [1.0] ^{d,f}	6.11 ^e	[61.10] ^{e,f}	0.18, NR	100	99.3, NR, NR
PQtBuTH, 27a⁸⁵	2 ^a , 2 ^a	2.06 ^b (2.52, 1.60)	0.1 [0.48] ^{c,f}	5.52 ^e	[26.50] ^{e,f}	0.12, 3.40	450	NR, NR, NR

^aSequential two-electron; ^bAverage voltage with outer and inner voltages given in parenthesis; ^cHighest molar solubility without supporting electrolyte; ^dHighest molar solubility with supporting electrolyte; ^eOverestimated energy density calculated based on average voltage; the cell predominantly discharges at inner couple voltage⁸⁸; ^fBased only on the bipolar (middle) oxidation state; NR = Not reported

Table 2.3 Comparison of all reported bipolar molecules for symmetric AORFBs (flow and static cells)

Bipolar Active Materials	Electron storage per molecule (ox, red)	Cell voltage (V)	Tested and [Limiting] Molar solubility (M)	Tested energy density (Wh/L)	Theoret. energy density (Wh/L)	Capacity fade (%/cycle, %/day)	No. of cycles	CE, EE, VE (%)
RIBOTE MPO, 1b ¹¹⁸	1,1	1.23	0.02 ^f [0.32] ^{b,g} 0.5 ^f [1.22] ^{c,g}	0.33 ^f 8.24 ^f	[5.27] ^g [20.11] ^g	NR, NR	1000 120	80.0, NR, NR 90.0, NR, NR
VIOTEM P, 2b ¹¹⁹	1,1	1.16	0.025 ^f [NR]	0.39 ^f	NR	NR, NR	5-10	NR, NR, NR
Fe-bipy³⁺, 3b ¹²⁰	1,1	0.69	0.5 ^e [1.20] ^{d,g}	4.62 ^e	[11.09] ^g	0.00625, NR	4000	99.8–100%, NR, NR
[(bpy-(CH₂)₃NMe₃)]I₂, 4b ⁸⁶	1,1	1.38	0.8 ^f [1.76] ^{d,g}	14.79 ^f	[32.55] ^g	0.5, NR	100	90.0, 72.0, 80.0
TEMPO/Phenazine, 5b ¹²¹	2 ^a , 2 ^a	1.20	0.01 ^f [NR]	0.64 ^f	NR	NR, NR	1800	98.3, 50.0, 50.90

^aConcerted two-electron; ^bHighest molar solubility with supporting electrolyte; ^cHighest molar solubility with supporting electrolyte and additive; ^dHighest molar solubility without supporting electrolyte; ^eStatic cell; ^fFlow cell; ^gBased only on the bipolar (middle) oxidation state; NR = Not reported

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Chapter 3: Ester-Substituted Bipyridinylienes: Double Concerted Two-Electron Bipolar Molecules for Symmetric Organic Redox Flow Batteries

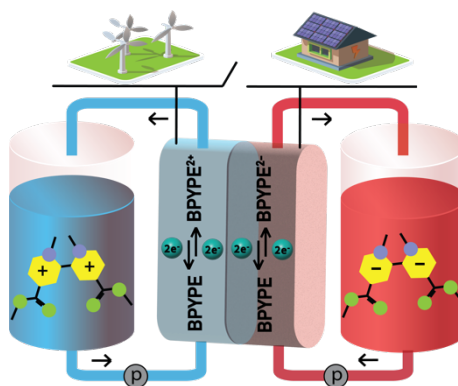
This document is reprinted with permission from Raihan, M. A.; Dyker, C. A. Ester-Substituted Bipyridinylienes: Double Concerted Two-Electron Bipolar Molecules for Symmetric Organic Redox Flow Batteries. *ACS Energy Lett.* **2023**, 8 (8), 3314–3322, copyright © 2023, American Chemical Society. To access the final, edited, and published work, please visit [<https://doi.org/10.1021/acsenerylett.3c00969>]. A few grammatical changes and adjustments in figure numbers differentiate this chapter from the published paper.

3.1 Abstract

Organic redox-active molecules are promising materials for charge storage in redox-flow batteries (RFBs); however, the development of all-organic RFBs is hindered by material crossover, limited energy density and poor stability of active materials. Here, ester-substituted bipyridinylienes are reported as the first examples of intrinsic bipolar molecules that exhibit basically concerted double two-electron redox activity at a potential difference of 1.01V. All three oxidation states of the pentylester derivative exhibited excellent temporal stability and good solubility in the electrolyte. Testing this active material in symmetric cells, which alleviates crossover issues, revealed good cyclability (fade of 0.025% and 0.35% per cycle for static and flow cells, respectively), capacities of up to 89% of the theoretical value, and coulombic efficiencies above 99%. Considering previous evidence for active material solubility limits of ~2 M, and the benefits of a

symmetric design, such double concerted multielectron bipolar active materials will be key to developing energy dense organic RFBs.

TOC GRAPHICS



3.2 Introduction

Redox flow batteries (RFBs) have emerged as a leading grid-scale stationary energy storage technology.¹ Unlike traditional rechargeable solid-state batteries, RFBs store energy in solutions of active materials that are pumped through the cell stack from external tanks, allowing capacity and power density of the battery to be independently scaled.² The vanadium redox flow battery has been the most successful commercial RFB to date.³ Nevertheless, the high cost of vanadium metal, expensive ion-exchange membranes, corrosive acidic electrolytes, and the narrow voltage window of water (1.23 V) leave room for the development of a cost-effective, sustainable next-generation energy storage system.⁴ Redox-active organic molecules (ROMs) dissolved in non-aqueous solvents (such as acetonitrile, DMF, DME, PC, etc.) with a wider electrochemical window (>5 V) are being actively studied for this purpose, but issues with solubility, stability, and energy density remain.⁵

A number of ROMs have been investigated as anolytes and catholytes for non-aqueous RFBs, but when paired in an RFB (an asymmetric design), active material crossover through the membrane remains a major issue for cell lifetime, leading to self-discharge and irreversible capacity loss.⁶⁻⁸ Strategies to minimize this have included pairing expensive ion selective membranes with active materials that incorporate an appropriate permanent charge,⁹ or the use of porous membranes (Celgard, Daramic, etc) paired with macromolecular active materials (oligomers, polymers, etc) such that size exclusion becomes possible but at the cost of increased active material complexity.^{10,11}

As an alternate strategy to resolve this crossover issue, symmetric organic redox flow batteries based on bipolar ROMs have received much recent interest.¹²⁻¹⁶ A symmetric RFB uses a single redox-active parent molecule capable of existing in at least three different oxidation states such that two different redox couples can be used for the anolyte and catholyte, respectively. Often this means both compartments have the identical composition in the discharged state, resulting in no electrical or chemical gradients across the membrane.^{17,18} Crossover of charged species in symmetric systems only causes loss of coulombic efficiency through self-discharge, but no long-term capacity fade as the original charged state can be restored.^{7,19} These symmetric systems therefore have the advantage that low-cost porous separators can be used without special modification of the active material.

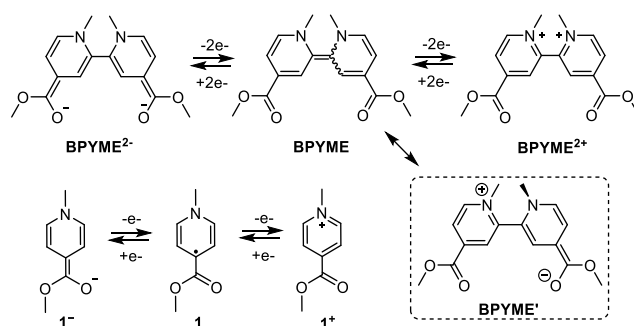
Broadly speaking, there are two different kinds of bipolar molecule that have previously been studied for organic redox flow batteries. One is artificial,²⁰⁻²⁵ where independent anolyte and catholyte materials are connected together by an inert linker chain (such as methylene, glycol, etc.), such that the low and high redox potential units are discreet and

largely have the properties of their respective unbridged parent structures. The other are intrinsic bipolar molecules, which feature a conjugated framework with electronic communication between atoms associated with reduction and those associated with oxidation (including cases where those atoms are largely identical).^{17,18, 26–41} Intrinsically bipolar molecules therefore offer advantages in term of atom economy, but are more challenging to design than artificial alternatives. One promising recent design strategy involves the direct π -conjugation of typical anode and cathode active species,^{29–31,42} where such electronic coupling causes synergistic benefits in cell potentials compared to the parent molecules.^{29,30}

Most intrinsically bipolar molecules are based on one-electron redox events (one-electron oxidation and one-electron reduction),^{14,18,26–35,38,39} which severely limits energy densities (the product of cell voltage, active material concentration, and number of electrons transferred). Indeed, a previous analysis has suggested that for non-aqueous organic RFBs to be cost effective, active material concentrations as high as 4-5 M would be needed (assuming one-electron processes and cell voltages of 3 V).⁴³ Not only have tested concentrations typically been much lower than this, but there is convincing evidence that concentrations above 2 M are not viable for most non-aqueous RFBs because of severely decreasing ionic conductivity and increasing viscosity above this limit.⁴⁴ In this light, increasing energy density via active materials that are involved in multi-electron redox processes will be key to progressing the field. A few two-electron intrinsic bipolar systems are known,^{15,17,31,36,37} but in all cases the redox events are a series of single electron couples (i.e. sequential first and second oxidations and reductions at four distinct potentials). While this theoretically improves energy density, it has been shown that such sequential electron

transfers result in detrimental voltaic and energy efficiency, and therefore ROMs with concerted (or more nearly concerted) multielectron events are more desirable.⁴⁵ Here we identify [2,2']bispyridinylidene-4,4'-dialkyl esters as the first examples of intrinsic, two-electron bipolar molecules that exhibits twofold, basically concerted, two-electron redox activity at potentials suitable for a symmetric organic redox flow battery (ORFB), and demonstrate their energy storage behavior in static and flowing cells.

The inspiration to investigate dialkylester substituted bispyridinylidenes came from our extensive experience with bispyridinylidenes,^{46–50} and previous electrochemical studies on pyridinium ions substituted with electron withdrawing groups.⁵¹ Indeed, a closely-spaced sequential two-electron redox process for the **BPYME**²⁺/**BPYME** couple (Scheme 3.1) has already been established,⁵² and though the low potential electrochemical activity of this scaffold was not reported, we were optimistic that a two-electron couple for **BPYME**/**BPYME**²⁻ could also be accessible owing to the electron withdrawing ester groups. This idea was supported by the fact that pyridiniums such as 4-(methoxycarbonyl)-1-methylpyridinium (**1**⁺) can be reduced sequentially to the neutral radical (**1**) and then the anion (**1**⁻) (Scheme 3.1) with a separation of 0.73 V,⁵¹ but we supposed that directly conjugating two such units as in **BPYME**²⁺**BPYME**²⁺ should lead to a desirable multi-electron reduction where radicals could be avoided, which should be beneficial for stability.



Scheme 3.1 Redox processes for **BPYME** and related monopyridine derivative **1**.

3.3 Result and discussion

The air-stable, oxidized form of the active material was prepared as a BF_4^- salt by the alkylation of 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine using trimethyloxonium tetrafluoroborate ($\text{Me}_3\text{O}^+\text{BF}_4^-$), according to the literature report by Clennan and co-workers.⁵² Initial cyclic voltammetry analysis of **BPYME**²⁺-2 BF_4^- was conducted in MeCN solvent with TBAPF₆ supporting electrolyte, which shows four sequential reversible one-electron redox couples at -0.66 V, -0.84 V, -1.95 V, and -2.10 V vs Ag/Ag⁺ (Figure 3.1a). The separation between first-second and third-fourth redox pairs are 0.18 and 0.15 V, respectively. For battery applications, this would translate to a theoretical cell voltage of 1.44 V initially that drops off to 1.11 V, with the majority of the discharge occurring at the lower voltage owing to disproportionation.⁴⁵ This kind of step-down in voltage is therefore inefficient and undesirable; however, this initial CV screening establishes that **BPYME** is indeed able to accept two electrons and form a dianion (**BPYME**²⁻), which was not reported earlier.

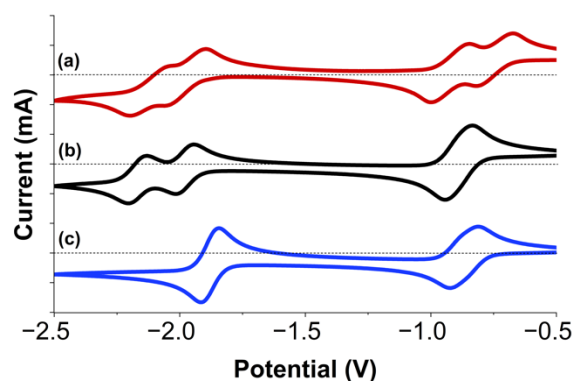


Figure 3.1 Cyclic voltammograms for 0.01M **BPYME**²⁺-**2BF**₄⁻, at scan rate of 50 mVs⁻¹, vs Ag/Ag⁺: (a) in 0.1 M TBAPF₆ in MeCN (b) in 1.0 M TBAPF₆ in DMF; (c) in 1.0 M LiTFSI in DMF. Dashed line represents 0 mA and each increment on the y-axis is 0.05 mA. WE: 3.0 mm diameter glassy carbon disk, CE: Pt wire, RE: Ag wire (pseudoreference).

Redox processes can depend strongly on the choice of electrolyte solvent and salt, and modulation from two sequential one-electron redox processes to a concerted two-electron process can be achieved.^{31,53–55} We therefore investigated DMF as an alternate solvent, which has been shown to promote concerted two-electron oxidation of other BPYs,^{48,50} and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as a supporting salt, which features the more strongly coordinating Li⁺ cation. This cation has been shown to enable concerted two-electron reduction processes for carbonyl containing compounds such as quinones while at the same time causing a positive shift of the redox process because of stabilization provided by strong ionic interactions between ions.^{31,55} When the TBAPF₆/DMF supporting electrolyte was used (Figure 3.1b), the reduction from **BPYME** to **BPYME**²⁻ is observed as two sequential one-electron processes (−1.98 V and −2.17 V vs Ag/Ag⁺) similar to what occurred in MeCN/TBAPF₆, but the oxidation to **BPYME**²⁺-**2BF**₄⁻ occurs

as an effectively concerted two-electron process at a single potential (-0.89 V vs Ag/Ag⁺, with a peak-to-peak separation (ΔE_p) of 100 mV; $i_{pc}/i_{pa} = 0.98$). On the other hand, with LiTFSI supporting salt in DMF, the compound maintained a concerted two-electron **BPYME**²⁺/**BPYME** couple at -0.87 V vs Ag/Ag⁺ (with $\Delta E_p = 110$ mV; $i_{pc}/i_{pa} = 0.98$), but also demonstrated a single two-electron wave at -1.88 V vs Ag/Ag⁺ (with $\Delta E_p = 70$ mV; $i_{pc}/i_{pa} = 0.96$) for the **BPYME**/ **BPYME**²⁻ couple (Figure 3.1c), which is expectedly more positive than with the less coordinating ammonium cation. Under similar conditions, the one-electron couple for ferrocene oxidation was observed to have $\Delta E_p = 80$ mV (Figure S3.1), suggesting that the smaller observed peak separation of 70 mV for the **BPYME**/ **BPYME**²⁻ couple may represent an inverted potential⁵⁶ redox process, while the 110 mV peak separation of the **BPYME**²⁺/**BPYME** couple suggests two single-electron processes that occur at nearly the same potential (ΔE approaching 0 V). RFB modelling has shown that an inverted potential has small efficiency advantages over two overlapping single-electron processes ($\Delta E = 0$ V),⁴⁵ but these CV results ultimately establish **BPYME** as the first basically concerted two-electron bipolar system. Though the theoretical cell voltage of 1.01 V leaves room for improvement, it has the Faradaic equivalency of a one-electron bipolar system with a cell voltage of 2.02 V which has been rarely achieved.³⁰ Further CV studies are reported in the Supporting Information, including a DMF/NaBF₄ electrolyte, where intermediately coordinating Na⁺ results in sequential two-electron reduction of **BPYME** with a separation of only 0.14 V (Figure S3.2a) between the two couples (compared to 0.21 V for TBA⁺, and 0 V for Li⁺), and MeCN/LiTFSI, which showed two sequential one-electron redox process for the oxidation processes (at -0.82 , and -0.66 V,

respectively), but an irreversible redox event appeared at -1.59 V vs Ag/Ag⁺ for the reduction of the **BPYME** (Figure S3.2b).

To gain insight in the electronic structure of this bipolar molecule, DFT optimization was carried out on **BPYME**²⁺, **BPYME** and **BPYME**²⁻ (Table 3.1, Figure S3.3). While the neutral and cationic forms (including the monocation radical) were previously subjected to a detailed conformational analysis by Clennan,⁵⁷ no theoretical studies were previously conducted on the dianion. Major structural features are summarized in Table 3.1. Our results for **BPYME**²⁺ and **BPYME** were in very good agreement with the lowest energy structures determined previously, and readers are referred to this work for an detailed description of the structural changes.⁵⁷ In summary, long (single) C2-C2' bond between nearly perpendicular pyridal rings and planar N atoms of the **BPYME**²⁺ shift to a shorter C-C bond between pyridyl rings, with sterics inducing pyramidalization of the N atoms and twisting of the olefinic linkage between rings in **BPYME**. Though the results are consistent with the structures depicted for **BPYME**²⁺, and **BPYME** in Scheme 3.1, Clennan previously noted that the C2-C2' distance in **BPYME** (1.415 Å) is longer than in bispyridinylidenes where the CO₂Me group is substituted by H, Cl, OMe, and NMe₂ functionalities, and **BPYME** was the only derivative observed to have a low energy “push-pull” conformation, suggesting significant contributions from resonance form **BPYME**' (Scheme 3.1).⁵⁷ Therefore substantial single bond character may be involved for this particular compound, enabled by the electron withdrawing ester groups which were found to be co-planar with the pyridyl rings in this compound and all other compounds studies, as reflected by the near 0 ° torsional angles (O=CCC, Table 3.1).

In going from **BPYME** to the dianion, the N atoms prefer an *anti* conformation, the C-C bond between rings lengthens to 1.472 Å (but does not reach the value for the dication of 1.500 Å), while the C-CO₂Me interactions shorten (Table 3.1). Within the rings, the C-C bonds show a high degree of π bond localization (Figure S3.3), with long (~1.45 Å, adjacent to the ester group) and short (1.36 Å) distances, and the N atoms are highly pyramidalized (sum of angles at N of 339.25°). All data is consistent with the quinoidal resonance structure for **BPYME**²⁻ given in Scheme 3.1. Unlike in **BPYME**²⁺, where rings are basically perpendicular with an NCCN torsional angle of 108.50°, the two rings in **BPYME**²⁻ attempt to maintain some level of co-planarity with an NCCN torsional angle of 164.40° (only 15.60° deviation from 180°).

Table 3.1 Averaged structural parameters of DFT optimized (B3LYP/cc-PVDZ) BPYME in various redox states.

	C2-C2' (Å)	NCCN (τ , °) ^a	H ₂ CNCC (τ , °) ^a	$\Sigma < N$ (°) ^b	C-CO ₂ Me (Å)	O=CCC (τ , °) ^a
BPYME ²⁺	1.500	108.50	3.77	360.00	1.517	1.64
BPYME ^c	1.417	24.72	41.07	354.15	1.478	1.44
BPYME ^{2-d}	1.472	164.40	72.42	339.25	1.409	3.52

^a Torsional angles. ^b Averaged sum of angles around the N atoms. ^c *Z* isomer. ^d *anti* isomer

The frontier orbitals for the series of compounds (Figure 3.2) show significant delocalization in all oxidation states. Particularly, the HOMO for **BPYME** (from which electrons are removed during oxidation) shows significant π conjugation between the two rings (C2-C2') and includes some C-CO₂Me π interaction as well. The characteristics of this MO are largely preserved in the LUMO of **BPYME**²⁺, though the significant twisting

between the two pyridyl rings (see NCCN in Table 3.1) inhibits significant C2-C2' π conjugation. The LUMO for **BPYME** (to which electrons are added upon reduction) represents a quinoidal type electron distribution, with significant C-CO₂Me conjugation, lone-pair character on N, and a node between the pyridyl rings. These features are mirrored in the HOMO for **BPYME**²⁻, except that the N atoms are *anti* to each other. Overall, the frontier orbitals for the series of compounds show significant conjugation involving the CO₂Me group and the pyridyl rings, as well as varying degrees of conjugation between rings, indicating that oxidation and reduction is not localized to a particular functional group in this intrinsically bipolar system.

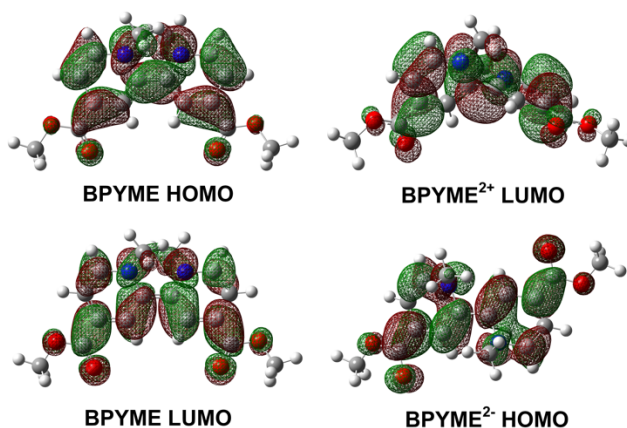
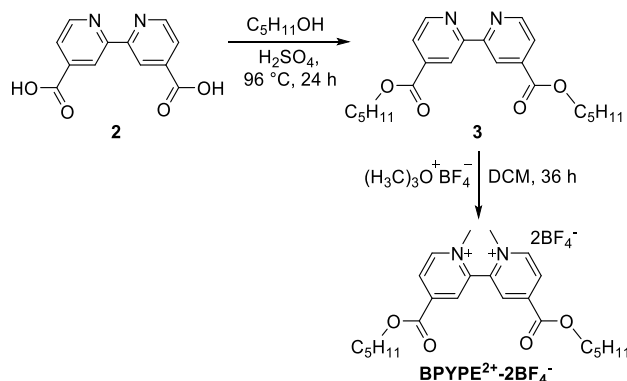


Figure 3.2. Selected frontier molecular orbitals for **BPYME**²⁺, **BPYME**, and **BPYME**²⁻

Our next efforts focused on chemically generating **BPYME**, which has not previously been isolated, as a straightforward entry point to preliminary symmetric RFB studies. The addition of sodium metal to a suspension of colorless **BPYME**²⁺-**2BF**₄⁻ in dry THF under inert atmosphere at room temperature resulted in the formation of a blue solution within 45 min. After filtration, the air-sensitive blue solution was concentrated to yield **BPYME** as a sticky blue solid. This solid demonstrated CV behavior (Figure S3.4) that matched that

of **BPYME**²⁺-**2BF**₄⁻, but also showed a small signal at -1.06 V and a small cathodic shoulder peak at -1.68 V vs Ag/Ag⁺ for unidentified species. In further experiments, we found that these signals for an unidentified byproduct appear in minor amounts during the reductive formation of **BPYME** with sodium metal, but they do not appear to grow over time. Analysis of the blue solid by ¹H, ¹³C, ¹H-¹H COSY NMR spectroscopy in C₆D₆ (Figure S3.5, S3.6 & S3.7) was consistent with the formation of the neutral compound **BPYME**, but we noted that the ¹H and ¹³C NMR spectra showed only broad signals for a single isomer, instead of sharp peaks for both *E* and *Z* isomers as found for most other N-Me bispyridinylidenes.^{48–50,58,59} Based on the earlier discussion of the longer C2-C2' bond in **BPYME**, and the likely involvement of “push-pull” resonance structures (**BPYME'**), it is believed that the CO₂Me group induces a low barrier to *E/Z* isomerization via C2-C2' bond rotation, which combines with the rotation of the ester functional group to give rise to the broad resonances we observe by NMR spectroscopy.

With bipolar **BPYME** in hand, preliminary symmetric cell cycling performance was studied in a coin cell and a flow cell (Figure S3.8), but the poor performance of the latter combined with the observation of precipitate made it clear that the **BPYME**²⁻-**2Li**⁺ suffered solubility issues. To increase the solubility of the dianion of the bipolar molecule, we modified the ester functionality by replacing -CH₃ with a long alkyl -C₅H₁₁ group. This was accomplished by the reaction of 2,2'-bipyridine-4,4'-dicarboxylic acid (**2**) with pentanol followed by methylation of bipyridine **3** as shown in Scheme 3.2.



Scheme 3.2 Synthesis of **BPYPE²⁺-2BF₄⁻**

The CV analysis of new derivative **BPYPE²⁺-2BF₄⁻** shows expected similarities to **BPYME²⁺-2BF₄⁻**, with two separate two-electron redox couples appearing at -0.88 V (with $\Delta E_p = 110$ mV for **BPYPE²⁺/BPYPE**; $i_{pa}/i_{pc} = 0.98$) and -1.89 V (with $\Delta E_p = 70$ mV for **BPYPE/BPYPE²⁻**; $i_{pa}/i_{pc} = 0.97$) vs Ag^+/Ag in 1.2 M LiTFSI/DMF, corresponding to a cell voltage of 1.01 V (Figure S3.9). The neutral compound **BPYPE** was generated by two-electron reduction of **BPYPE²⁺-2BF₄⁻** by excess Na metal and the sticky blue solid was characterized by ^1H , ^{13}C NMR, and 2D NMR (Figure S3.10 – S3.15). Spectral features were in line with those of **BPYME**, including broad resonances and no indication of a pair of *E/Z* isomers. NMR studies of **BPYPE** in DMF were less resolved than in benzene and did not improve on decreasing the temperature to -38 °C (Figure S3.16), while temperatures as high as 60 °C in C_6D_6 (Figure S3.17) only showed further broadening of the signals at 1.9 and 5.5 ppm for the N-CH₃ and -CH (singlet) groups, respectively. The addition of TEMPO as a radical trapping agent to NMR samples in C_6D_6 did not affect the NMR spectra (Figure S3.18), nor did exposing the C_6D_6 solution to a small piece of freshly cut sodium (Figure S3.19), suggesting that the broad signals are caused by dynamics and not an indication of paramagnetic compounds or oxidized impurities.

Attempts to chemically generate the lithium salt of dianion (**BPYPE²⁻-2Li⁺**) from **BPYPE²⁺-2BF₄⁻** using stoichiometric amount of Li as reductant in THF under inert atmosphere resulted in the formation of an unidentified insoluble brown precipitate. Instead, the dianion **BPYPE²⁻-2Li⁺** could be electrochemically generated in a coin cell by using a lithium disc on the anode side (excess Li) and 0.3 ml of 0.021 M **BPYPE²⁺-2BF₄⁻** in 1.2 M LiTFSI/DMF as catholyte. Upon discharging the cell, **BPYPE²⁺-2BF₄⁻** was converted to red dianion **BPYPE²⁻-2Li⁺** with good faradaic efficiency (97% conversion based on measured current), and two voltage plateaus separated by ~1 V were observed (Figure S3.20), consistent with the separation between the **BPYPE²⁺/BPYPE** and **BPYPE/BPYPE²⁻** redox couples. The red solution containing the dianion was collected from the carbon felt by pipette and analysis by CV (Figure S3.9) was similar to that of **BPYPE²⁺-2BF₄⁻**, with slight differences in redox processes and peak shapes attributed to the different concentrations studied. We attempted to conduct ¹H NMR spectroscopic analysis of this solution, but even with the addition of TEMPO as a radical trapping agent (Figure S3.21) or at low temperature (-38 °C, Figure S3.22), only broad resonances for the n-pentyl functionality could be observed, suggesting a dynamic system on the NMR timescale. Evidence of formation of dianion **BPYPE²⁻-2Li⁺** was further supported by coin cell testing. After electrochemically generating **BPYPE²⁻-2Li⁺** in 1.2 M LiTFSI/DMF as described above, the excess lithium disc was carefully removed from the cell and replaced with carbon felt soaked with 0.4 ml of 0.021 M **BPYPE²⁺-2BF₄⁻** in 1.2 M LiTFSI/DMF yielding a charged-state cell with a capacity of 0.33 mAh (based on limiting **BPYPE²⁻** from the Li cell at 97% conversion). The first cycle shows 91% (0.30 mAh) of the expected discharge capacity, followed by a charge of 94% (0.31 mAh) and a second discharge of 88% (0.29

mAh) capacity at an E_{cell} of 0.96 V (Figure S3.20). The observed cell voltage, and high percent utilization matches the expected result considering the likelihood of some self-discharge via crossover, and supports the formation of the dianion. Moreover, the reaction of equimolar amounts of **BPYPE**²⁻-2Li⁺ and **BPYPE**²⁺-2BF₄⁻ in 1.2 M LiTFSI/DMF results cleanly in the formation of **BPYPE** as evidenced by ¹H NMR in this solvent and in C₆D₆ (Figure S3.23 and S3.24), supporting that crossover does not lead to unwanted side reactions.

With a method to form all three redox states, we sought to individually test their solubility limits and stability in the electrolyte. In terms of solubility, CV analysis of **BPYPE**²⁺-2BF₄⁻ solutions of known concentrations (0.0005 – 0.0035 M) in 1.2 M LiTFSI/DMF were used to develop a linear correlation between concentration and peak height (the cathodic peak at -1.89 V vs Ag/Ag⁺ was used) (Figure S3.25). Subsequent CV analysis of saturated, filtered and carefully diluted solutions of **BPYPE**²⁺-2BF₄⁻ and **BPYPE** in 1.2 M LiTFSI in DMF allowed us to determine the saturated concentrations to be 2.10 M and 2.50 M, respectively, based on the height of the same peak in the CV of the diluted solutions. Because of the challenges associated with preparing larger amounts of **BPYPE**²⁻-2Li⁺, we were unable to determine a concentration for a saturated solution of this active species. Instead, by concentrating the as-prepared 0.15 M **BPYPE**²⁻-2Li⁺ solution and carefully diluting a known volume of precipitate-free solution and subsequent analysis by CV, we were able to use the calibration curve to determine that concentrations of at least 0.41 M are achievable for this species. This corresponds to a theoretical minimum capacity of 22.0 Ah L⁻¹ (for a single electrolyte volume) and a minimum energy density of 11.10 Wh L⁻¹ for a symmetric **BPYPE** RFB operating at 1.01 V. We note that if the solubility **BPYPE**²⁻

can approach the proposed limit of 2 M,⁴⁴ then up to 107 Ah L⁻¹ and 54.10 Wh L⁻¹ is achievable. This represents a very high theoretical capacity for the electrolyte solution, owing to the two-electron redox process, and the theoretical energy density surpasses that of vanadium RFBs (20-33 Wh L⁻¹).⁶⁰

Next, we examined the stability of all the three different oxidation states in 1.2M LiTFSI/DMF supporting electrolyte. The stability of 0.1 M **BPYPE**²⁺-**2BF**₄⁻ in 1.2 M LiTFSI/DMF electrolyte was monitored by means of ¹H NMR spectroscopy over a period of 30 days, and showed no new signals or loss of signal, indicating excellent stability (Figure S3.26). The stability of **BPYPE** and **BPYPE**²⁺-**2Li**⁺ could not be studied by this method owing to their poorly resolved ¹H NMR spectra. We therefore monitored the temporal stability of these species by CV, along with a solution of **BPYPE**²⁺-**2BF**₄⁻ for comparison. Freshly prepared 3 mM **BPYPE**²⁺-**2BF**₄⁻, **BPYPE**, and **BPYPE**²⁺-**2Li**⁺ in 1.2 M LiTFSI/DMF were monitored by periodic CV analysis over the course of 7 days, and the measured peak currents were plotted vs time (Figure 3.3).⁴⁶ Linear regression of the peak current data for the active material signals over time gave small negative slopes of -6.50×10^{-5} mA d⁻¹ to -1.05×10^{-4} mA d⁻¹, corresponding to a loss of approximately 0.38%–0.61% per day for **BPYPE** and -5.50×10^{-5} mA d⁻¹ to -7.00×10^{-5} mA d⁻¹, corresponding to a loss of around 0.26%–0.34% per day for **BPYPE**²⁺-**2Li**⁺ (from *i*_{pa} and *i*_{pc} respectively, based on the respective intercepts as original values); however, the same experiment conducted on **BPYPE**²⁺-**2BF**₄⁻ in the electrolyte (Figure 3.3a), gave similar small negative slopes (-3.50×10^{-5} to -7.00×10^{-5} mA d⁻¹, corresponding to 0.18%–0.37% per day). Considering no decay of **BPYPE**²⁺-**2BF**₄⁻ was observed by NMR spectroscopy over 30 days of monitoring, the negative slopes are attributed to the experimental method,

and the data indicate that the decay rates for **BPYPE**²⁺-2BF₄⁻, **BPYPE**, and **BPYPE**²⁻-2Li⁺ in the electrolyte are very similar and very small. We note that the previously observed signals for impurities (at -1.06 V and -1.68 V vs Ag⁺/Ag), formed from reduction of **BPYPE**²⁺-2BF₄⁻ with sodium, are present in the CVs of **BPYPE** and **BPYPE**²⁻-2Li⁺ but show no observable change over time, suggesting they are a byproduct of the formation of **BPYPE** and not a decomposition product.

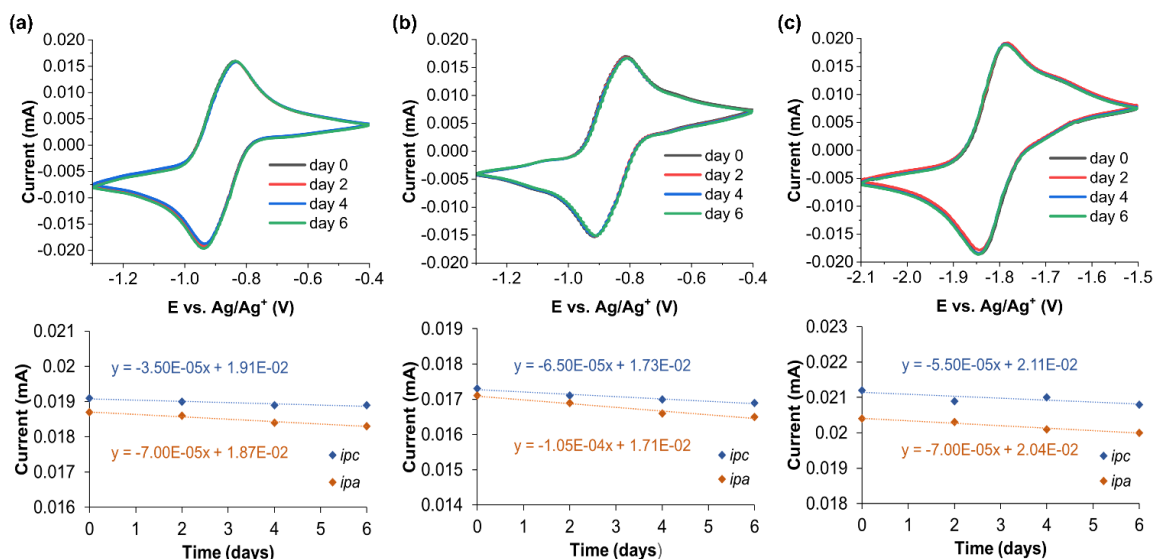


Figure 3.3 CVs over a period of 7 days (top) and plots of anodic (*i_{pa}*) and cathodic (*i_{pc}*) peak currents vs time (bottom) of 3 mM (a) **BPYPE**²⁺, (b) **BPYPE**, and (c) **BPYPE**²⁻ in 1.2 M LiTFSI/DMF, respectively.

Having determined that the three oxidation states of **BPYPE** display excellent stability in 1.2 M LiTFSI/DMF supporting electrolyte, we determined the diffusion coefficients based on CV data at different scan rates and found *D* values of 2 to 4 × 10⁻⁷ cm² s⁻¹ (see Figure S3.27), which are slightly low but on the order of other organic active materials in non-aqueous electrolytes.^{46,47} Subsequently, charge/discharge cycling was conducted in a static

symmetric coin cell with **BPYPE** as active material featuring carbon felt electrodes and Tokuyama Neosepta AHA anion exchange membrane (see Figure S3.28), with results that were very similar to the analogous **BPYME** test (Figure S3.8a), including single charging/discharging plateaus consistent with concerted two-electron utilization. Since the AEM necessitated the use of a low operating current (0.34 mA cm^{-2}), we also investigated a similar cell that employed a polypropylene separator. This allowed for a current density of 10 mA cm^{-2} to be used (corresponding to a theoretical charge/discharge time of around 33 seconds), and cycling was conducted with upper and lower cut-off voltages of 1.65 and 0.25 V, respectively, for 2000 cycles (Figure 3.4a). This coin cell achieved a material utilization of $\sim 70\%$ (based on first discharge, double two-electron) and a gradually increased of CE from 98.6% to 99.8% throughout the cycles. This cell exhibits around 50% capacity loss after 2000 cycles, corresponding to a 0.025% capacity loss per cycle (3.4% per hour). Interestingly, replacing the membrane with a fresh one after 2000 cycles leads to a 12.8% capacity recovery (Figure 3.4a), despite the inevitable losses of absorbed active material upon removing the original membrane. This suggests that the capacity fade upon cycling is partially a limitation of the membrane, which likely becomes fouled over time and more resistive.

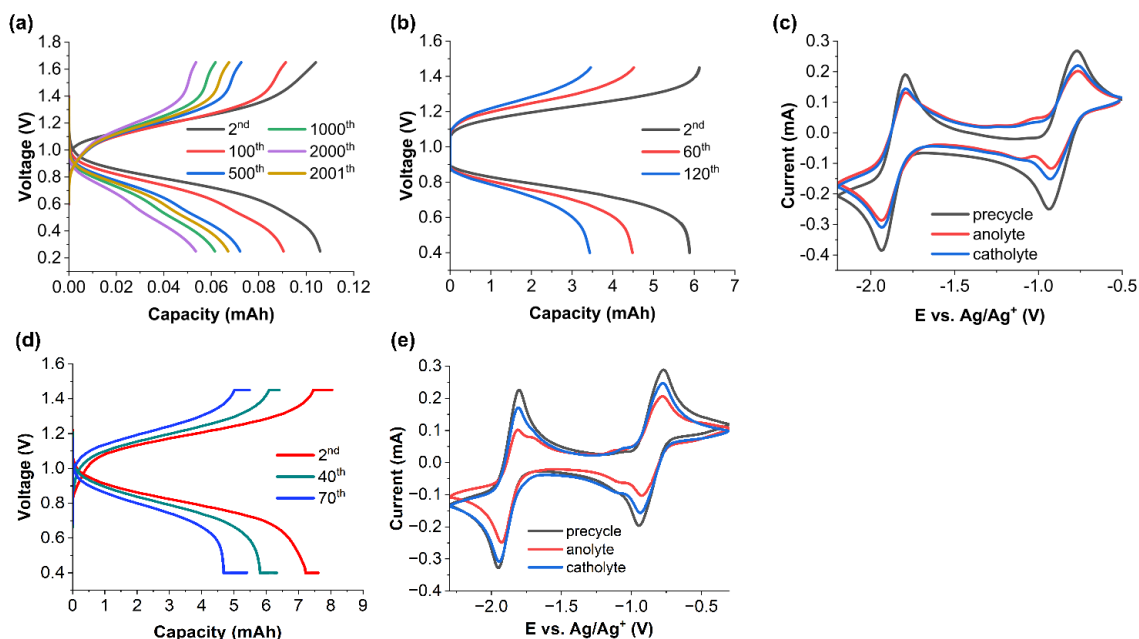


Figure 3.4 Galvanostatic symmetrical charge–discharge cycling of bipolar **BPYE** in 1.2 M LiTFSI/DMF with polypropylene separator (a) Coin cell cycling performance of 0.2 mL 0.015 M **BPYE**. The 2000 cycles represent 14.8 h of cycling (b) Flow cell cycling performance of 3.5 mL 0.04 M **BPYE**. The 120 cycles represent 48.8 h of cycling (c) CV analysis before and after flow cell cycling. (d) Flow cell cycling performance of 4.0 mL 0.04 M **BPYE** using potentiostatic holds. The 70 cycles represent 49.6 h of cycling (e) CV analysis before and after flow cell cycling with potentiostatic holds.

The cycling behavior of **BPYE** was also assessed using a zero-gap flow cell⁶¹ with a polypropylene separator. The catholyte and anolyte reservoirs were filled with 3.5 mL of 0.04 M **BPYE** in a 1.2 M LiTFSI/DMF electrolyte solution. Galvanostatic charge-discharge cycling was performed using currents of $\pm 10 \text{ mA cm}^{-2}$ with a voltage cutoff at 1.45 V and 0.40 V (Figure 3.4b). The theoretical capacity was 7.50 mAh, and the flow cell

accessed around 79% (5.93 mAh) of this capacity during the first discharge. The charge/discharge cycling was continued for 120 cycles (~48.8 h) and the coulombic efficiency increased from 96.10% to 99.35% during cycling. The final discharge capacity was 3.40 mAh indicating the cell lost 42.70% of its initial discharge capacity, and resulting in a capacity fade rate of 0.35% per cycle (0.88% per hour), which was much higher than observed in the coin cell experiments. The quantitative postmortem CV analysis of the electrolytes revealed the concentration of anolyte and catholyte are 0.029 and 0.031 M (based on peak heights before (0.04 M) and after cycling), which correspond to 72.5% and 77.5% of active materials in the anolyte and catholyte compartment, respectively (Figure 3.4c). The CV results therefore show that only up to 27.5% of active material is actually lost (equating to a capacity loss of 0.23% per cycle, 0.56% per hour), which contrasts the cell cycling data (Figure 3.4b) where 42.7% of the initial capacity was lost. The poorer performance observed upon cycling must arise from factors other than decomposition, such as leakage (which would lower capacity but not impact active material concentration) or membrane/electrode fouling which leads to increased resistance and causes an apparent loss of capacity within the imposed voltage limits because these limits are reached before all viable active material is used.⁶² Experiments involving galvanostatic cycling with potentiostatic holds supports this (Figure 3.4d). Indeed, higher initial capacities are achieved (88.5% of the theoretical 8.58 mAh on second discharge), and after similar cycling duration of 49.6 hours (70 cycles) a more modest loss of 29% discharge capacity is observed (fade rate of 0.41 % per cycle, 0.58% hour), which better matches the loss observed by post cycling CV analysis of this cell (loss of up to 27.5 %, Figure 3.4e)

The post cycling CVs in Figure 3.4c and 4e do not show any new electrochemically active species, but rather the same impurity signals at -1.7 and -1.0 V, that can be observed as

shoulder peaks in the formation of **BPYPE** from sodium, are more apparent. It is not obvious whether the molecule(s) behind these signals is growing slightly over cycling or simply appear more resolved owing to the lower intensity of the **BPYPE** signals. In comparing these two sets of CV data, it appears that there is fairly even signal loss in the catholyte and anolyte when galvanostatic cycling is used, while the potentiostatic holds cause greater decay to the anolyte over the catholyte. Surprisingly, post cycling ^1H NMR analysis of the electrolyte from this cell (Figure S3.30) showed poorly resolved signals for the catholyte while the anolyte was consistent with **BPYPE**. No new species could be identified by ^1H NMR though some new broad signals of low intensity at 1.2, 1.4 and 3.5 ppm could be seen in the anolyte. While the data shows that cell cycling seems to overestimate decay, mechanistic details behind the loss of active species require further investigation. In addition to membrane/electrode fouling causing increased resistance in the cell, decomposition into electrochemically inactive species, or absorption of active materials on the cell components (which would lower active material concentration) may be responsible for capacity loss.

Comparison of theoretical energy densities is not meaningful in the case of symmetric organic RFBs, as to the best of our knowledge, no other study of bipolar organic molecules has investigated the limiting solubility of all oxidation states. The cells tested here were well below the achievable concentrations (between 0.41 M and 2 M), largely because of synthetic challenges in scaling up the preparation of **BPYPE**. The cycling performance and tested energy density (1.08 WhL^{-1}) for **BPYPE** cells are similar to many other symmetric RFB systems (see supporting information Table S3.1, S3.2), and clearly show a limiting performance metric for this emerging research area.

3.4 Summary

In conclusion, we have demonstrated that ester-substituted bispyridinylidenes are intrinsic, double two-electron materials for symmetric organic RFBs. By careful choice of electrolyte salt (LiTFSI) and solvent (DMF), we showed that effectively concerted two-electron bipolar character can be achieved. Though solubility issues were encountered for the dianionic form of the methylester **BPYME**, the pentyl derivative showed good solubility (≥ 0.41 M) in all oxidation states, and monitoring studies by ^1H NMR spectroscopy and/or CV revealed excellent temporal stability of all charge states in the electrolyte. Nevertheless, static and flowing cell tests reveal capacity loss which was shown to be related to increased internal resistance as well as some possible decomposition on cycling. While it is clear that higher energy densities among symmetric organic RFBs must be established, we note recent progress in achieving systems operating at higher cell potentials (>2 V).^{29,30} The present work complements these efforts and demonstrates for the first time that intrinsic double concerted two-electron bipolar systems are viable targets for increasing energy density, setting the stage for the development of such bipolar compounds that can operate at higher cell voltages. Considering the support for active material solubility limits of ~ 2 M,⁴⁴ such molecules will likely play a major role in achieving viable energy densities among symmetric ORFBs.

Notes

The authors declare no competing financial interest.

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3.6 Supporting information

3.7 General Information

3.7.1 Chemicals

All commercial chemicals were used as received unless stated otherwise. 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine (Combi-blocks), 2,2'-bipyridine-4,4'-dicarboxylic acid (Combi-blocks), trimethyloxonium tetrafluoroborate (Oakwood Chemical), 1-pentanol (Alfa Aesar), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Novalyte), sodium tetrafluoroborate salt (NaBF₄, Alfa Aesar), tetrabutylammonium hexafluorophosphate (Sigma-Aldrich). Dimethylformamide (DMF, Sigma-Aldrich, anhydrous 99.8%) solvent was dried over molecular sieves (Fisher Chemical, 4 Å) prior to use, anhydrous tetrahydrofuran (THF, Fisher Chemical), anhydrous benzene (Fisher Chemical), and anhydrous CH₂Cl₂ (Fisher Chemical) were obtained from a solvent purification system.

3.7.2 Cyclic voltammetry

CV was carried out in an argon filled glovebox using a potentiostat/galvanostat (BioLogic SP-150) with a cell consisting of a working electrode (platinum disk, 0.07cm²), counter electrode (platinum wire, 5cm) and Ag/Ag⁺ reference electrode (0.01 M AgNO₃ in 0.1 M NBu₄PF₆ in DMF). A sample of **BPYPE** was also referenced to ferrocene (Fig S23). The working electrode was polished using an alumina slurry and a polishing disk prior to CV analysis. All CV's were recorded with *iR* correction except for those in Figure 1a, 4 (stability), S2, S4 (**BPYPE**), S4 (**BPYPE**²⁻), and S18 (solubility).

3.7.3 CV lifetime monitoring studies

A special setup for calendar life assessments was designed to maintain a fixed distance between the working and the reference electrodes to minimize i_{pa}/i_{pc} fluctuations.¹ 20 mL glass vials with a Teflon-lined screw caps were used. Periodic CV analysis (over 7 days) was carried out by replacing the vial lid with a custom cap, in which three holes were made to tightly accommodate the three electrodes (counter, working and reference) and hold them in place. A Teflon holder was placed midway along the height working and reference electrodes keep a minimum and fixed distance in between. After each CV test, the sample was recapped with the Teflon-lined screw cap.

3.7.4 DFT calculation

The computational calculations were based on Gaussian09 program². All structures were optimized in the gas-phase with the B3LYP density functional and the cc-PVDZ basis set. The optimized geometries were verified by frequency computations as minima (zero imaginary frequencies). Mercury³ was used to measure the bond lengths, torsion angles and bond angles in the structure.

3.7.5 Coin cell design and testing

The coin cell^{1,4} was assembled, and charge-discharge cycling experiments were conducted in an argon filled glove box with H₂O level 0.5 ppm and O₂ 0.1 ppm. The active material solutions and cell components were placed within two 2032-coin cell halves (MTI, two negative caps were used). In each half was placed a stainless-steel spacer (diameter = 15.5 mm, MTI), and a circular piece of electrically conductive graphite felt (thickness = 2.10 mm, surface area = 1.77 cm², SGL Group, G334-01, dried under vacuum at 100 °C overnight).

prior to use). The active materials (dissolved in 0.100-0.400 mL of 1.2 M LiTFSI/DMF) were injected to each graphite felt. A punched-out circular disc of 2.20 cm diameter (wider than the 2032 cell casings) of Tokuyama Neosepta AHA (0.20 mm thick) anionic exchange membrane (AEM, purchased from Electrolytica, USA, stored in 0.5 M aqueous NaCl), or a polypropylene film (0.025 mm thick, MTI corp.) was used to separate the two half cells. The AEM or polypropylene film was preconditioned by being soaked in electrolyte (1.2 M LiTFSI/DMF) in the presence of molecular sieves at least 24 h prior to use. The whole cell was held together with a plastic-coated pinch clamp, oriented vertically, and connected to the potentiostat/galvanostat (BioLogic SP-150).

3.7.6 Flow cell design and testing

The flow cell⁵ was assembled inside the glovebox. A combination of a polypropylene flow field, a graphite plate current collector and a carbon felt electrode with an area of 2.24 cm² (1.4 × 1.6 cm) was put on either side of the flow cell. A 25% compression of the graphite felt (thickness = 2.10 mm, SGL Group, G334-01, dried under vacuum at 100 torr overnight prior to use) was achieved using Gore-tex ePTFF gaskets (thickness 1.5875 mm or 1/16"). The two half cells were separated by a preconditioned AEM (purchased from Electrolytica, USA, stored in 0.50 M aqueous NaCl) or polypropylene film (0.025 mm thick, MTI corp.). The gasket window provided for an exposed area (2.24 cm²; 1.4 × 1.6 cm) of the membrane which was used as the active area of the flow cell. The cell was connected to a peristaltic pump (Cole-Parmer) by a hard PFA tubing (1/16" ID x 1/8" OD) and a Versilon™ 2001 L/S 14 high performance precision tubing using a flow rate of 10-20 mL min⁻¹. Before starting the charge-discharge cycling, the cell was pretreated by flowing the solution through the cell for 60-90 minutes. When galvanostatic cycling with potentiostatic holds

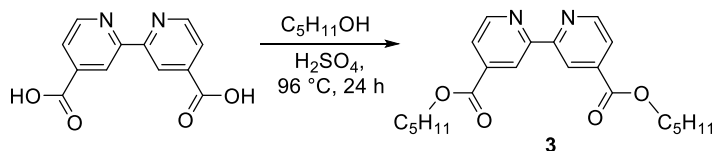
was used, the potential hold at the cut-off voltage was applied until the current reached 5% of the value used during the galvanostatic phase.

3.7.7 NMR studies

NMR was carried out on an Agilent 400 MR and INOVA 300 NMR spectrometer at 25 °C. Deuterated solvents were referenced internally (C_6D_6 : ^1H , $\delta = 7.16$, ^{13}C , $\delta = 128.06$; CDCl_3 : ^1H , $\delta = 7.26$; ^{13}C , $\delta = 77.16$; CD_3CN : ^1H , $\delta = 1.96$; ^{13}C , $\delta = 1.32$ and 118.26). Chemical shifts are reported in parts per million (ppm), and multiplicities were abbreviated to: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), multiplet (m) and broad (br). All coupling constants were reported in Hz. J. Young NMR tube used for air sensitive compounds. All ^1H NMR in non-deuterated DMF were referenced by setting the singlet for DMF to 7.60 ppm.

3.8 Synthetic procedures

3.8.1 4,4'-dipentyl ester-2,2'-bipyridine, 3



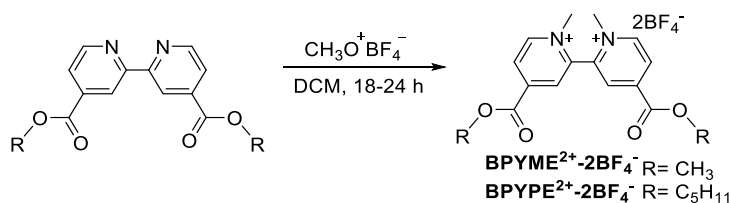
In a round-bottom flask (50 mL) equipped with a stir bar, 2,2'-bipyridine-4,4'-dicarboxylic acid (1.28 g, 5.24 mmol) stirred with pentanol (20 mL), then sulfuric acid (1.4 mL) was slowly added. The reaction mixture was heated at $96\text{ }^\circ\text{C}$ for 24 hours until it appeared as a clear pink colored solution. After cooling, 20 mL of water was added followed by 20 mL of chloroform. The organic phase was separated and then dried over MgSO_4 . The chloroform was removed using a rotary evaporator. The pink-colored solution, which

contained the compound with pentanol, was placed in a freezer at -5°C for 24-36 hours, which yielded a white, amorphous solid. The solids were filtered and washed three times with diethyl ether to obtain 4,4'-dipentyl ester-2,2'-bipyridine, **3** (1.61 g, 79.50 %).

^1H NMR (400 MHz, CD_3CN): δ 8.85 – 8.86 (m, 4H), 7.88 (dd, $J = 2.5, 1.6$ Hz, 2H), 4.36 (t, $J = 6.7$ Hz, 4H), 1.87 – 1.68 (m, 4H), 1.55 – 1.31 (m, 8H), 1.15 – 0.81 (m, 6H). ^{13}C NMR (400 MHz, CD_3CN) δ 165.95, 157.13, 151.40, 140.08, 124.14, 120.63, 66.82, 28.98, 28.84, 23.04, 14.26. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{NaO}_4^+$, **3-Na** $^+$: 407.1941, found: 407.1939. Melting point: 69.7-71.6 $^{\circ}\text{C}$.

3.8.2 General synthetic procedure for bipyridinium tetrafluoroborate derivatives

(BPYME²⁺-2BF₄⁻, BPYPE²⁺-2BF₄⁻)



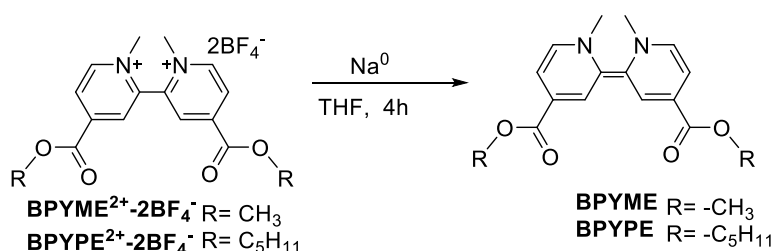
In a glovebox, 2,2'-bipyridine (1.0 equiv) was dissolved in anhydrous dichloromethane and then slowly added trimethyloxonium tetrafluoroborate (2.1 equiv) at rt. The reaction mixture was stirred for 18-24 hrs. A colorless solid was precipitated by adding diethyl ether, collected by filtration, and washed again with diethyl ether. A saturated solution of colorless solid was made with acetonitrile, and ethyl acetate was added dropwise until the solution became cloudy. The mixture was then put in freezer (−5 °C) overnight to obtain white crystals.

BPYME²⁺-2BF₄⁻: The general procedure was followed using 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine (1 g, 3.67 mmol) as the substrate. Compound **BPYME²⁺-2BF₄⁻** : 1.26 g, 72% yield. ¹H NMR (300 MHz, CD₃CN): δ 9.21 (d, *J* = 6.3 Hz, 2H), 8.72 (dd, *J* = 6.3, 1.9 Hz, 2H), 8.67 (d, *J* = 1.8 Hz, 2H), 4.16 (s, 6H), 4.04 (s, 6H). ¹³C NMR (400 MHz, CD₃CN): δ 162.34, 151.95, 147.10, 144.18, 131.35, 130.87, 54.81, 49.06. HRMS (ESI) *m/z* calcd for C₁₆H₁₈BF₄N₂O₄⁺, **BPYME²⁺-BF₄⁻**: 389.1290, found: 389.1293. Melting point: 177.6-178.1 °C.

BPYPE²⁺-2BF₄⁻: Using 4,4'-bis(pentoxycarbonyl)-2,2'-bipyridine (1.33g, 3.46 mmol) as the substrate. **BPYPE²⁺-2BF₄⁻** was isolated as a white solid (1.39 g, 68% yield). ¹H NMR (300 MHz, CD₃CN): δ 9.21 (d, *J* = 6.3 Hz, 2H), 8.74 (dd, *J* = 6.3, 1.8 Hz, 2H), 8.67 (d, *J*

= 1.7 Hz, 2H), 4.46 (t, J = 6.6 Hz, 4H), 4.16 (s, 6H), 1.89 – 1.69 (m, 4H), 1.55 – 1.29 (m, 8H), 0.93 (t, J = 7.1 Hz, 6H). ^{13}C NMR (400 MHz, CD_3CN): δ 161.76, 151.78, 147.36, 144.11, 131.27, 130.79, 68.49, 48.98, 28.40, 28.26, 22.63, 13.87. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{34}\text{BF}_4\text{N}_2\text{O}_4^+$, **BPYME** $^{2+}$ -**BF** $_4^-$: 501.2542, found: 501.2545. Melting point: 104.3-105.5 °C.

3.8.3 General synthetic procedure for bispyridinylidenes



In a glovebox, a 20 mL vial was charged with bispyridinium ester tetrafluoroborate (1 equiv.) and anhydrous THF. To this heterogeneous mixture was added 8-9 small pieces of sodium metal (7-8 equiv.). The reaction mixture was stirred for 3-4 hours to obtain a blue color solution. The resulting blue solution was filtered through syringe filter. The solution was collected, and solvent was removed under vacuum in the dry box. The compound was collected as a blue sticky solid.

BPYME: The general procedure was followed using **BPYME** $^{2+}$ -**2BF** $_4^-$ (0.051g, 0.107 mmol) dication as substrate. Compound **BPYME** was isolated as a sticky blue product (0.026 g, 81% yield). ^1H NMR (400 MHz, C_6D_6): 7.45 (d, J = 1.4 Hz, 2H, -CH), 5.94 (dd, J = 7.2, 1.6 Hz, 2H, -CH), 5.39 (br s, 2H, -CH), 3.42 (s, 6H, O- CH_3), 1.83 (br s, 6H, N- CH_3). ^{13}C NMR (400 MHz, C_6D_6): δ 136.59, 131.60, 129.30, 106.18, 67.83, 51.16, 38.65, 25.83.

BPYPE: The general procedure was followed using **BPYPE**²⁺-**2BF₄⁻** (0.097 g, 0.164 mmol) dication as substrate. Compound **BPYPE** was isolated as a sticky blue product (0.057 g, 83% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.54 (d, *J* = 2.5 Hz, 2H, -CH), 5.98 (dd, *J* = 7.3, 1.8 Hz, 2H, -CH), 5.42 (br s, 2H, -CH), 4.11 (t, *J* = 6.7 Hz, 4H, O-CH₂), 1.86 (br s, 6H, N-CH₃), 1.46 (m, 4H), 1.16 (m, 8H), 0.80 (m, 6H). ¹³C NMR (400 MHz, C₆D₆): δ 164.21, 136.19, 131.12, 128.90, 119.61, 105.87, 64.02, 38.24, 28.49, 28.05, 22.25, 13.75.

3.8.4 Electrochemical generation of **BPYPE²⁻**

To produce the red dianion **BPYPE²⁻-2Li⁺**, an electrochemical process was employed in a coin cell with a polypropylene separator. The process involved using two negative caps of a 2032-coin cell (MTI). One of the negative caps was loaded with a stainless-steel spacer ($\varnothing=15.5$ mm, MTI), a stainless-steel spring ($\varnothing=15.4$ mm, 1.2 ± 0.03 mm height, 0.2 mm thick, MTI), another stainless-steel spacer, and a lithium metal disc ($\varnothing=16$ mm, 0.6 mm thick, MTI) inserted sequentially. The other negative cap had a stainless-steel spacer and a piece of electrically conductive graphite felt ($\varnothing=15$ mm, SGL Group, G334-01) inserted, which was dried under vacuum at 100 °C overnight before use. The solution of 0.3 ml of 0.021 M **BPYPE²⁺-2BF₄⁻** in 1.2 M LiTFSI/DMF was then injected into the graphite felt. A polypropylene separator was placed between the two negative caps and they were held together with a plastic-coated pinch clamp, with the cell oriented vertically, and connected to the BioLogic SP-150 potentiostat/galvanostat. The cell was discharged to 0.5 V at a current density of 5 mA cm⁻², and during the discharge process, two voltage plateaus, separated by approximately 1.0 V, were observed (refer to Fig S16a). For the solubility measurement experiment on **BPYPE²⁻-2Li⁺**, 0.3 mL of 0.15 M **BPYPE²⁺-2BF₄⁻** was used instead, with a Faradic efficiency of 98%.

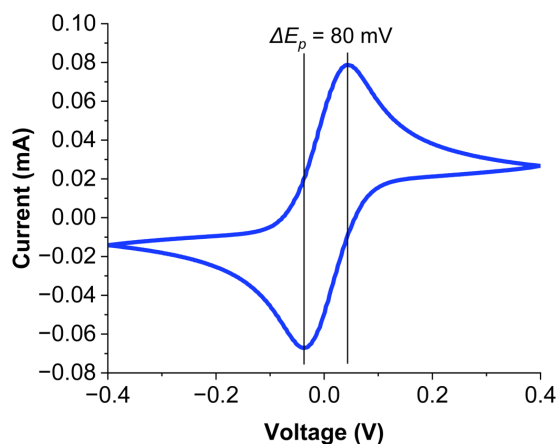


Figure S3.1 CV profile of ferrocene (Fc) (with iR correction) in 1.2 M LiTFSI/DMF at scan rate of 50 mVs^{-1}

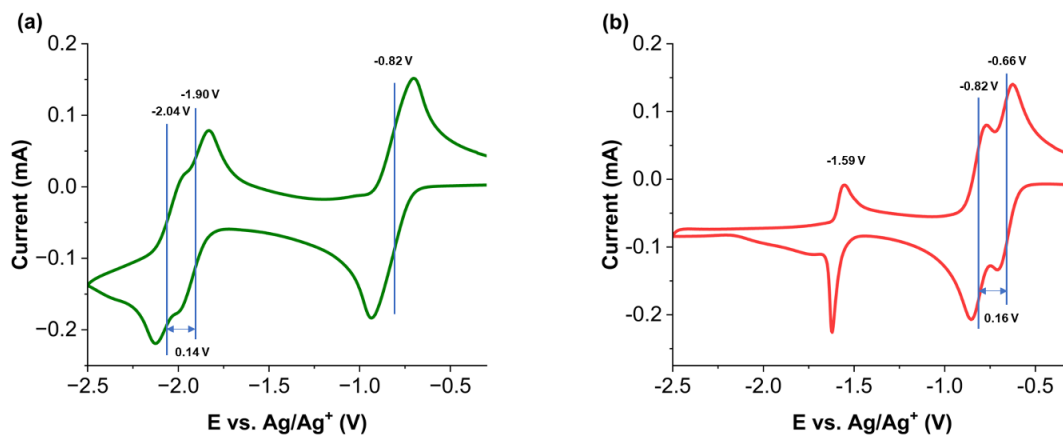


Figure S3.2 CV profile of $\text{BPYME}^{2+}\text{-}2\text{BF}_4^{-}$ (without iR correction) in (a) 0.1 M NaBF_4/DMF and (b) 0.1 M LiTFSI/ CH_3CN at scan rate of 50 mVs^{-1}

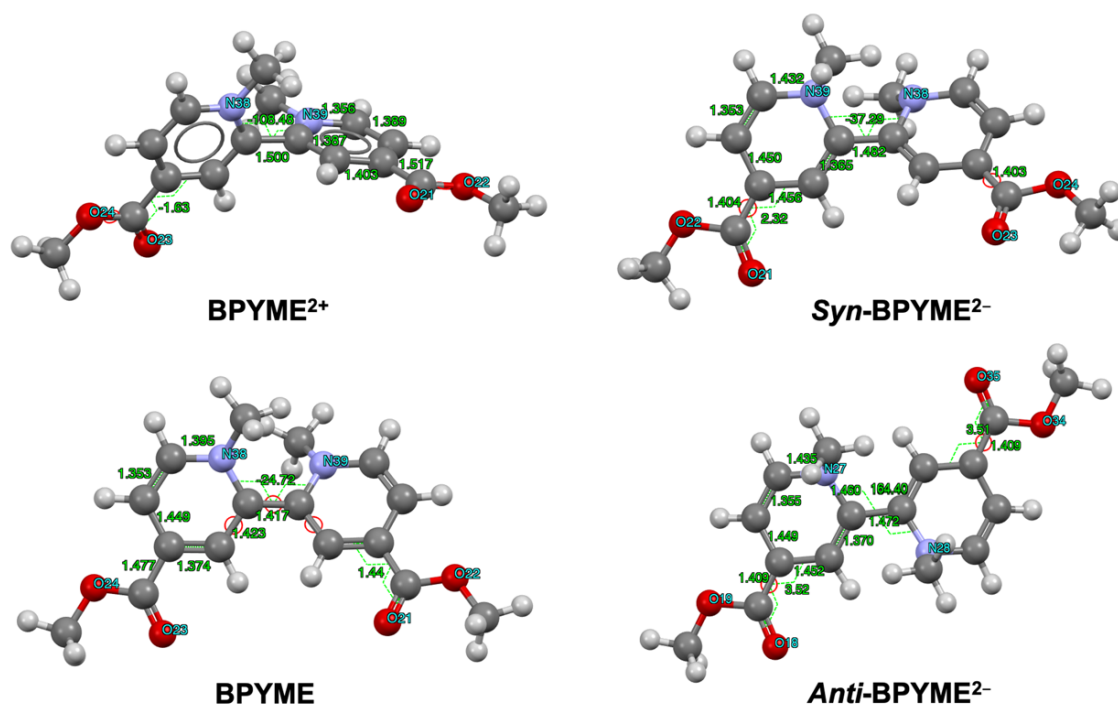


Figure S3.3 Optimized structure of **BPYME²⁺**, **BPYME**, and **BPYME²⁻** showing select representative bond distance and torsion angles. The relative energy of **Z-BPYME** isomer is 1.59 kcal/mol lower than that of lowest energy **E-BPYME⁶**; the **syn-BPYME²⁻** is 1.82 kcal/mol higher in energy than **anti-BPYME²⁻**, so only the *anti* conformer is discussed in the text.

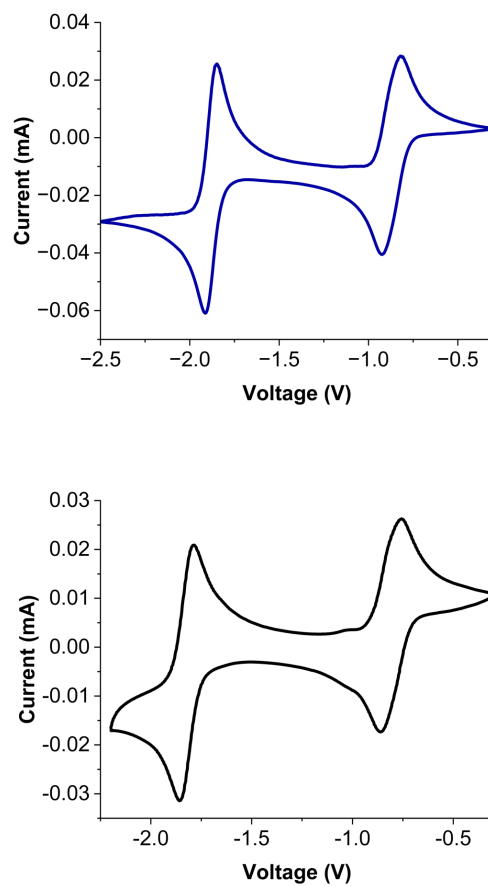


Figure S3.4 CV profile of **BPYME²⁺** (left blue, with *iR* correction) and **BPYME** (right black, no *iR* correction) in 1.2 M LiTFSI/DMF at scan rate of 50 mVs⁻¹. There is a slight shift of redox potential between two figures due to changes within the reference electrode (0.01 M AgNO₃ in 0.1 M NBu₄PF₆ in DMF).

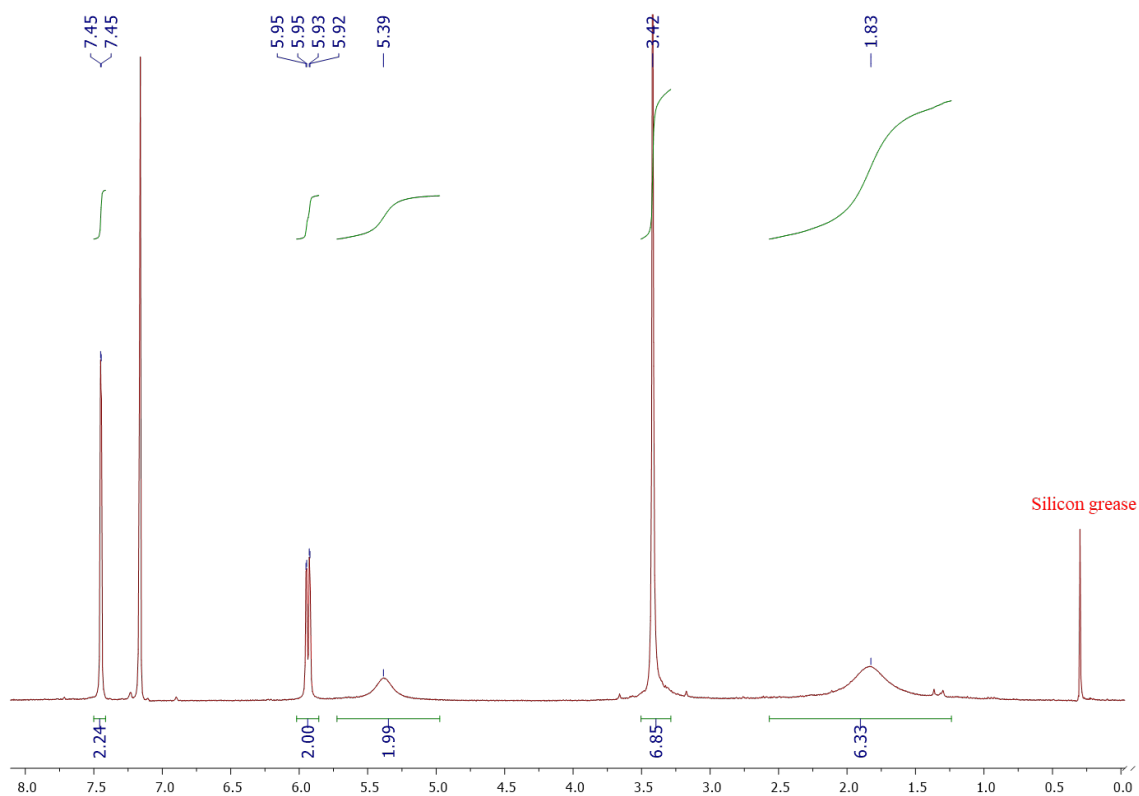


Figure S3.5 ¹H NMR spectrum of **BPYME** (C₆D₆, 25 °C, 400 MHz).

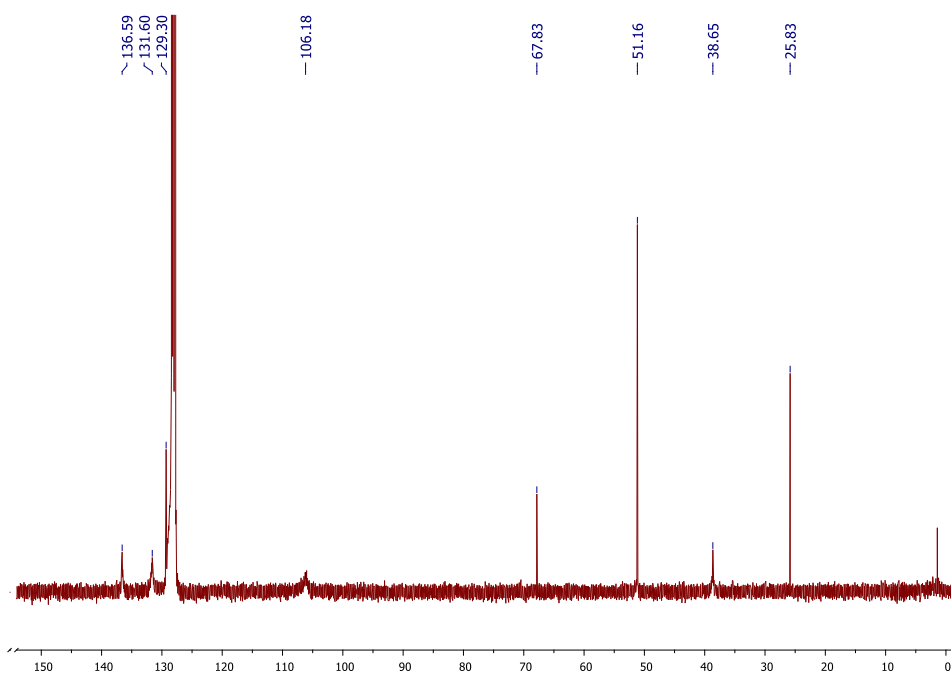


Figure S3.6 ¹³C NMR spectrum of **BPYME** (C₆D₆, 25 °C, 100 MHz).

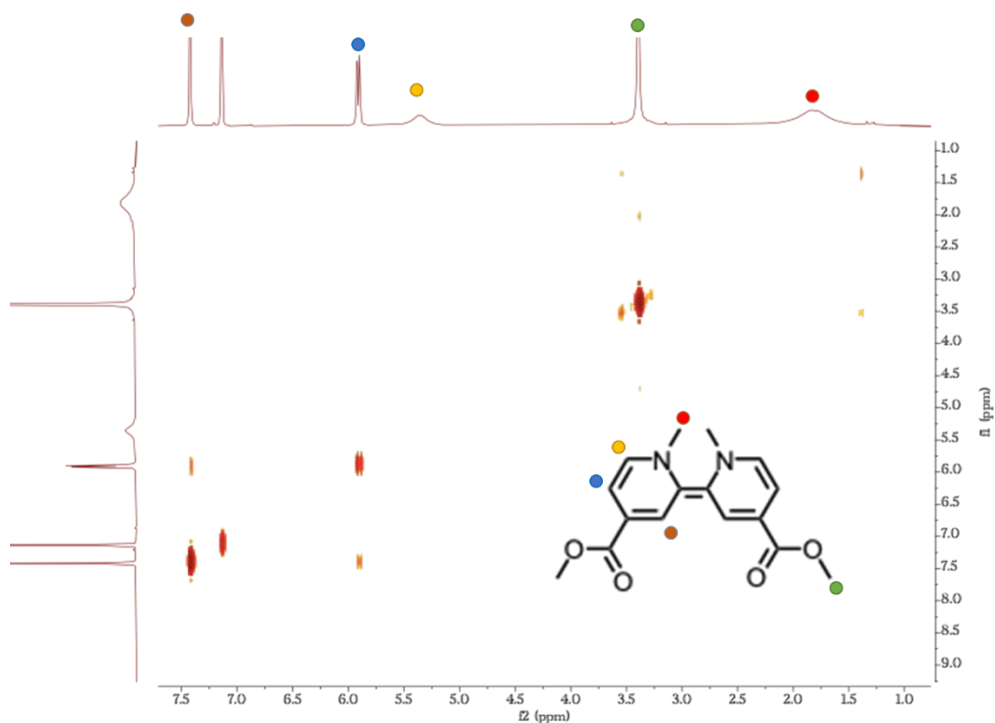


Figure S3.7 ^1H - ^1H COSY spectrum of **BPYME** (C_6D_6 , 25 °C, 400 MHz). Assignments based on comparison to the 2D NMR data for related **BPYE**.

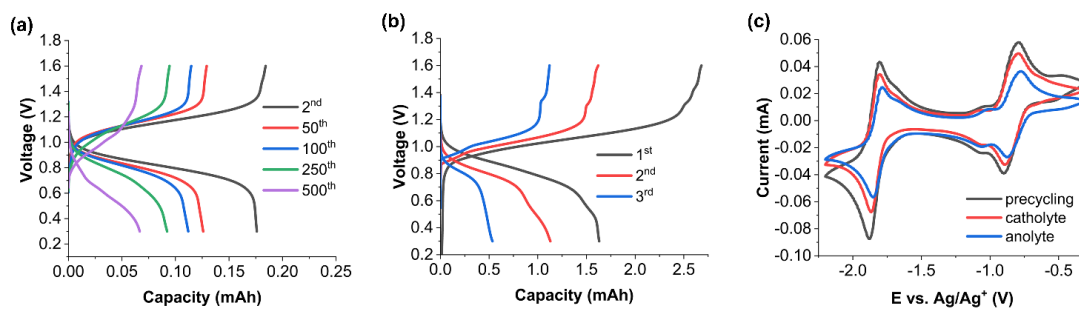


Figure S3.8 Galvanostatic charge–discharge cycling ($\pm 0.32 \text{ mA cm}^{-2}$) of 0.02 M bipolar **BPYME** in 1.2 M LiTFSI/DMF as catholyte and anolyte with a Tokuyama Neosepta AHA anion exchange membrane.

Figure S3.8a, coin cell cycling performance (0.2 mL of **BPYME**). The cell lost around 63% of its initial capacity after 500 cycles (162 h) resulting in an average fade rate of 0.13% per cycle (0.39% per hour). The coulombic efficiency maintained over 96% throughout the cycles.

Figure S3.8b, flow cell cycling performance (4.0 mL of **BPYME** per reservoir). The 3 cycles represent 14.5 h of cycling. The theoretical capacity was 4.28 mAh, of which 2.72 mAh (64%) could be accessed on the first charge, but the cell demonstrated a discharge capacity of only 40.7%, and poor cycling thereafter

Figure S3.8c, CV analysis before and after flow cell cycling of **BPYME** shows a loss of active material on catholyte side of the cell (80.5 % remaining), but a greater loss on the anolyte side associated with the **BPYME**/ **BPYME2⁻2Li⁺** couple (64.5% remaining), and no sign of the formation of any new electrochemically active species during this cycling experiment. Dark precipitate was also observed in the glass storage tank on the anolyte side of the cell. We concluded that the rapid capacity degradation observed upon cycling is primarily attributed to the low solubility of the **BPYME2⁻2Li⁺** and not from material decomposition. The problem of poor solubility is amplified in the flowing cell because the precipitates are free flowing and have only brief and poor contact with the electrodes, while in the static cell, precipitation will occur primarily on the surface of the porous carbon felt electrodes which makes it possible to recover more of the charge on cycling.

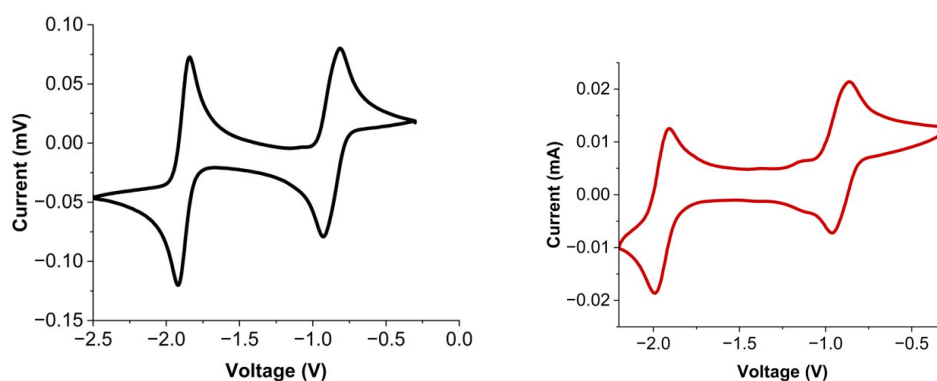


Figure S3.9 CV profile of BPYE^{2+} (left black, with iR correction) and BPYE^{2-} (right red, no iR correction) in 1.2 M LiTFSI/DMF at scan rate of 50 mVs^{-1} . There is a slight shift of redox potential between two figures due to changes within the reference electrode (0.01 M AgNO_3 in 0.1 M NBu_4PF_6 in DMF).

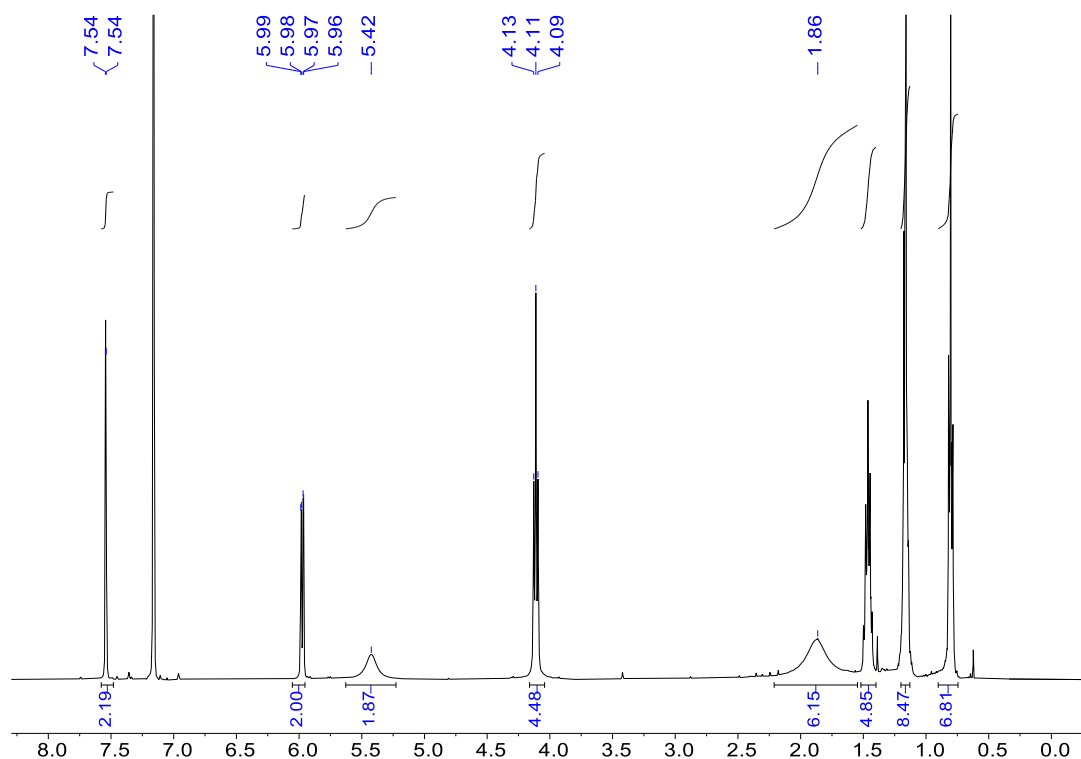


Figure S3.10 ^1H NMR spectrum of BPYE (C_6D_6 , 25°C , 400 MHz).

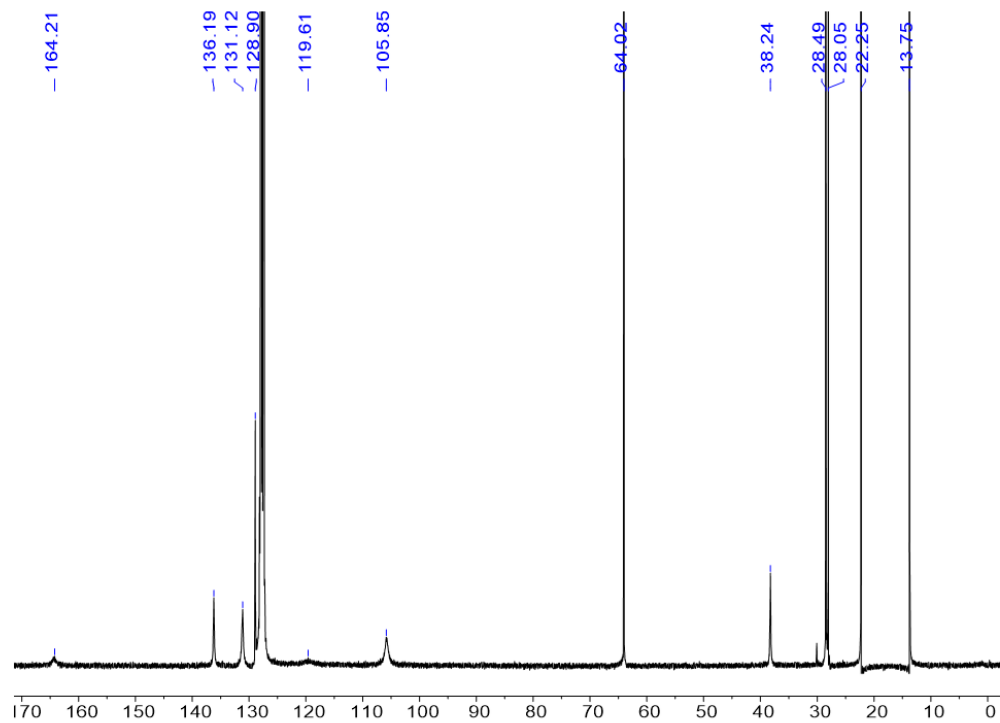


Figure S3.11 ¹³C NMR spectrum of **BPYPE** (C₆D₆, 25 °C, 100 MHz).

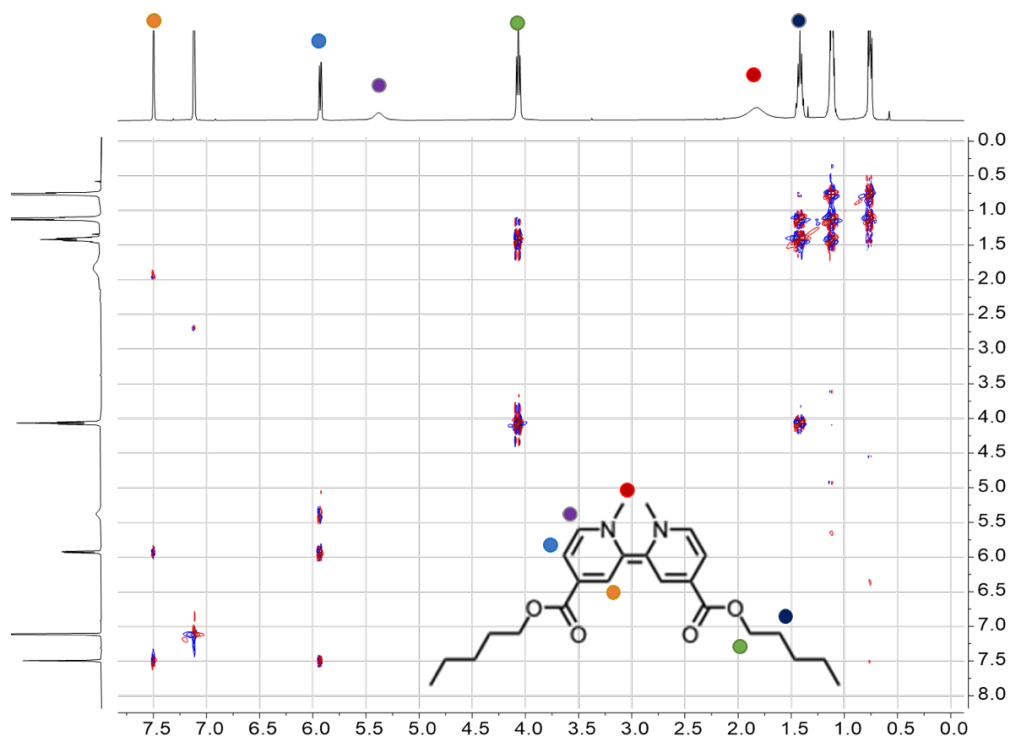


Figure S3.12 ¹H-¹H COSY spectrum of **BPYPE** (C₆D₆, 25 °C, 400 MHz).

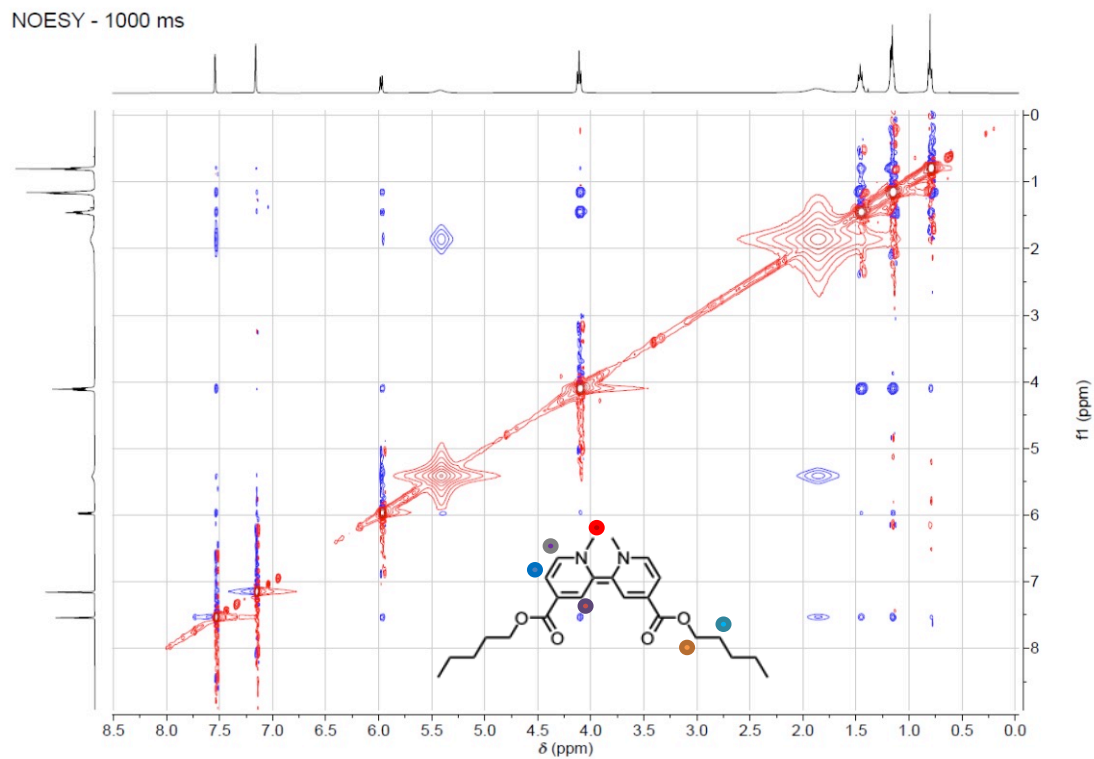


Figure S3.13 NOESY spectrum of **BPYPE** (C_6D_6 , 25 °C, 400 MHz), showing correlations between the NCH_3 (1.9 ppm) and the pyridyl $-\text{CH}'\text{s}$ (purple, 5.4 ppm and yellow, 7.5 ppm) suggesting *E/Z* interconversion.

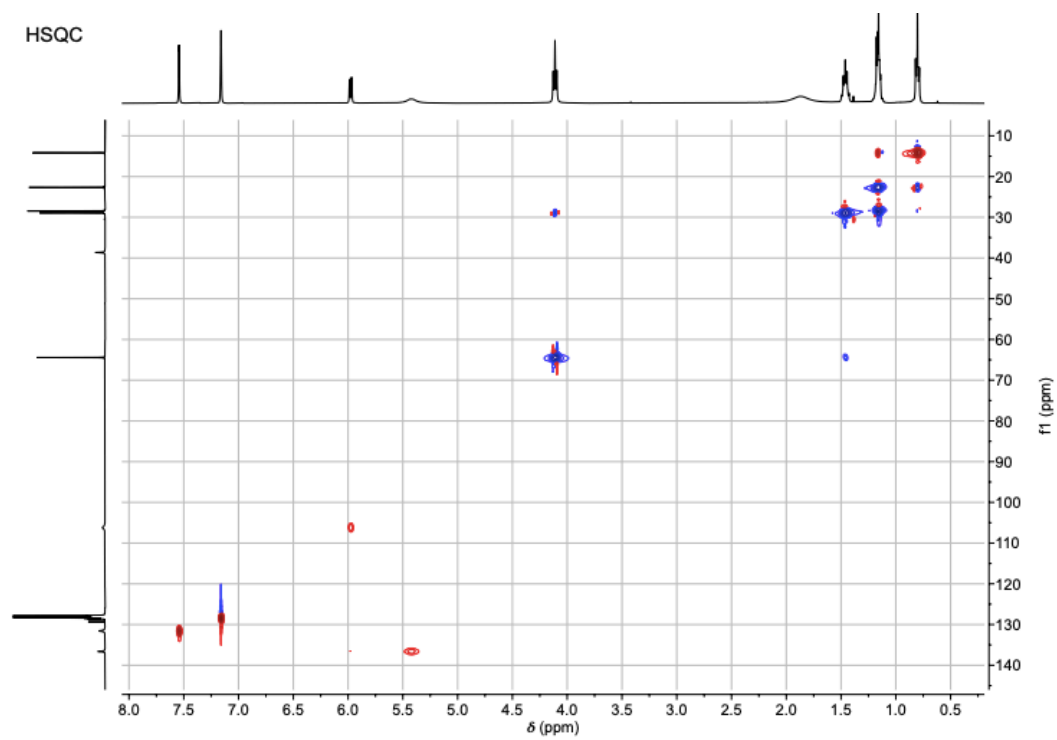


Figure S3.14 HSQC spectrum of **BPYPE** (C_6D_6 , 25 °C, 400 MHz).

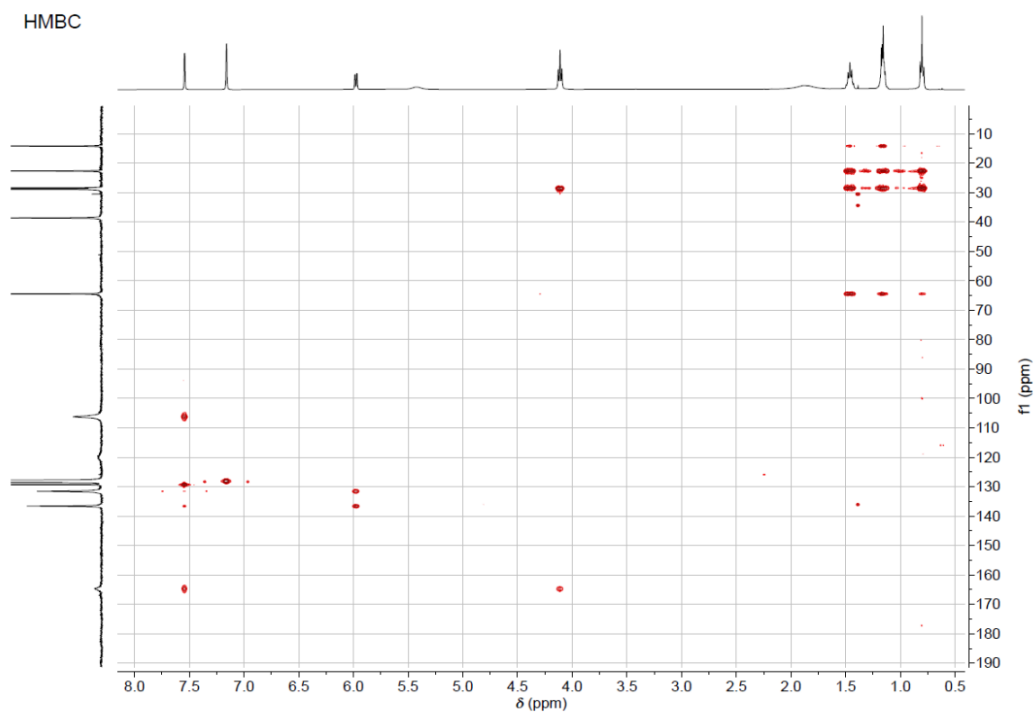


Figure S3.15 HMBC spectrum of **BPYPE** (C_6D_6 , 25 °C, 400 MHz).

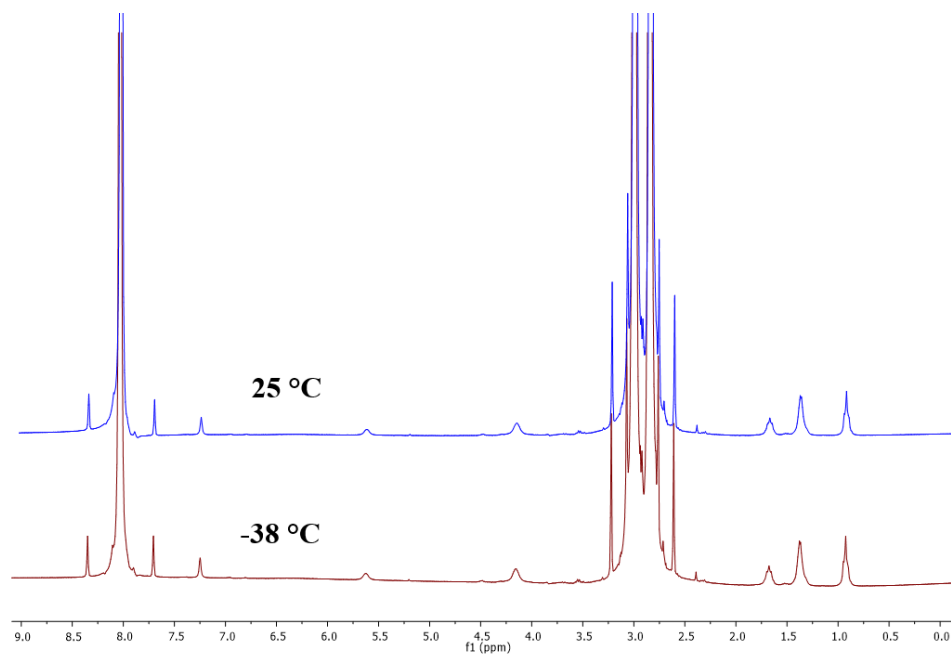


Figure S3.16 Variable temperature ^1H NMR spectrum of **BPYPE** (DMF, 400 MHz).

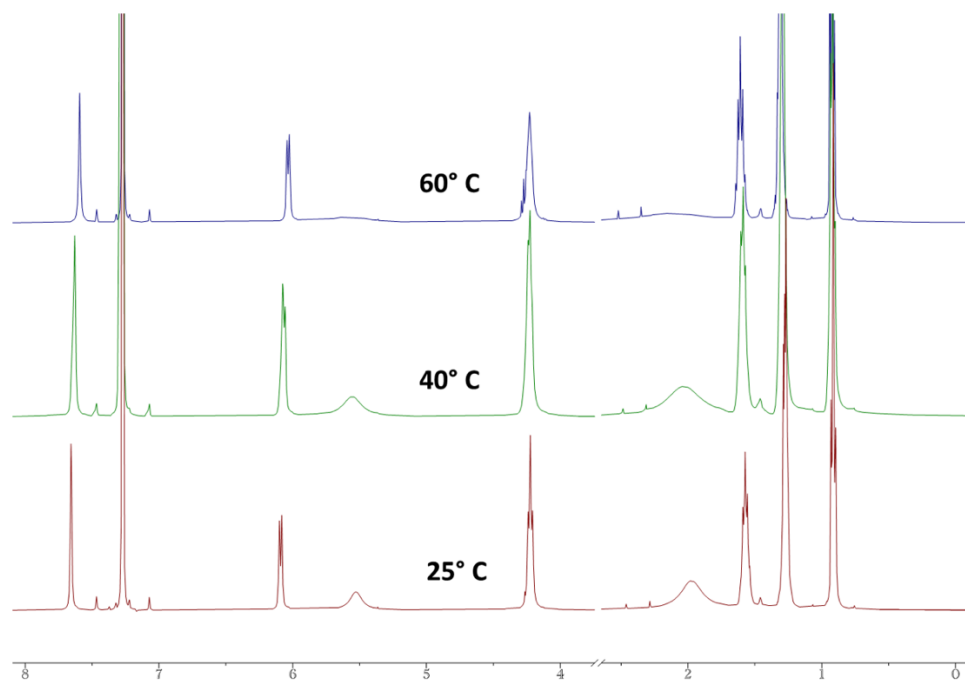


Figure S3.17 Variable temperature ^1H NMR spectrum of **BPYPE** (C_6D_6 , 400 MHz).

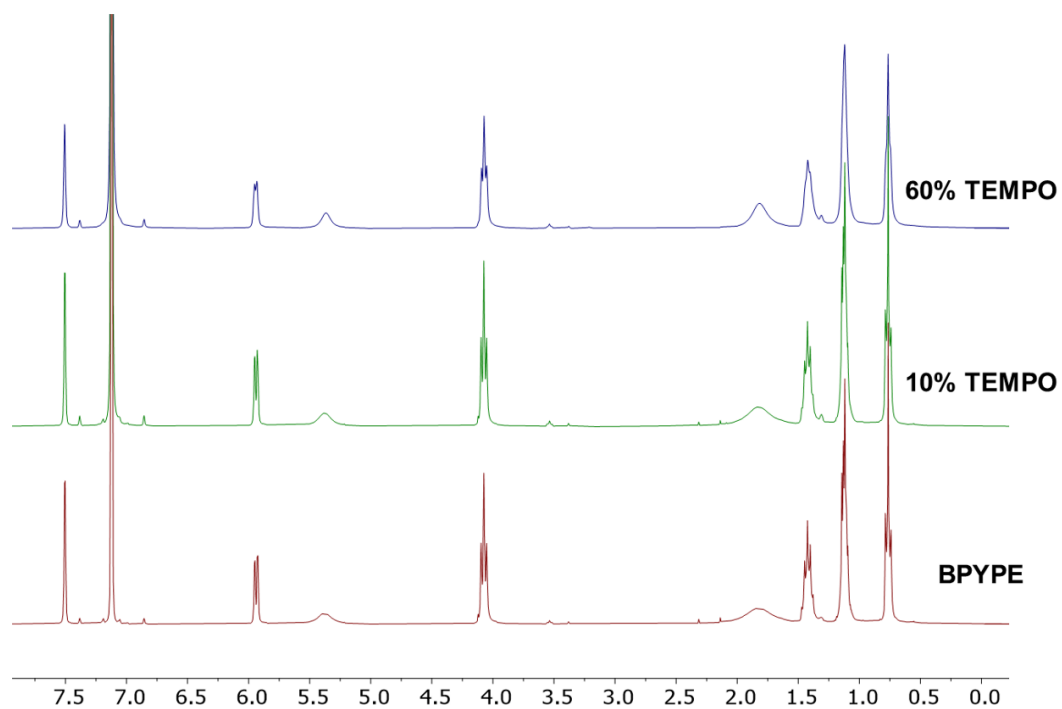


Figure S3.18 ^1H NMR spectrum of **BPYE** with varying amounts of radical trapping agent TEMPO (C_6D_6 , 25 $^\circ\text{C}$, 300 MHz).

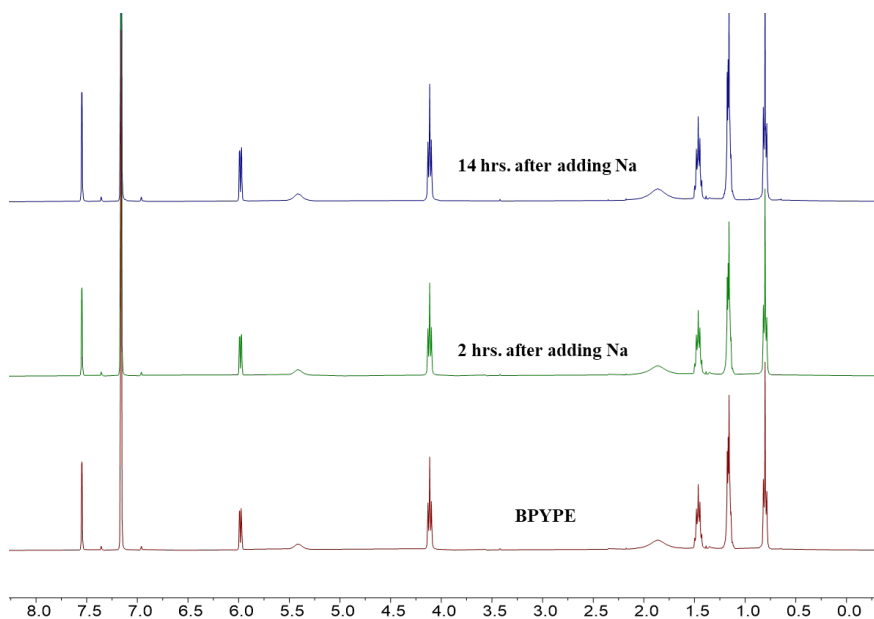


Figure S3.19 ^1H NMR spectrum of **BPYE** in the presence of a small piece of freshly cut Na metal over 14 hours (C_6D_6 , 25 $^\circ\text{C}$, 300 MHz).

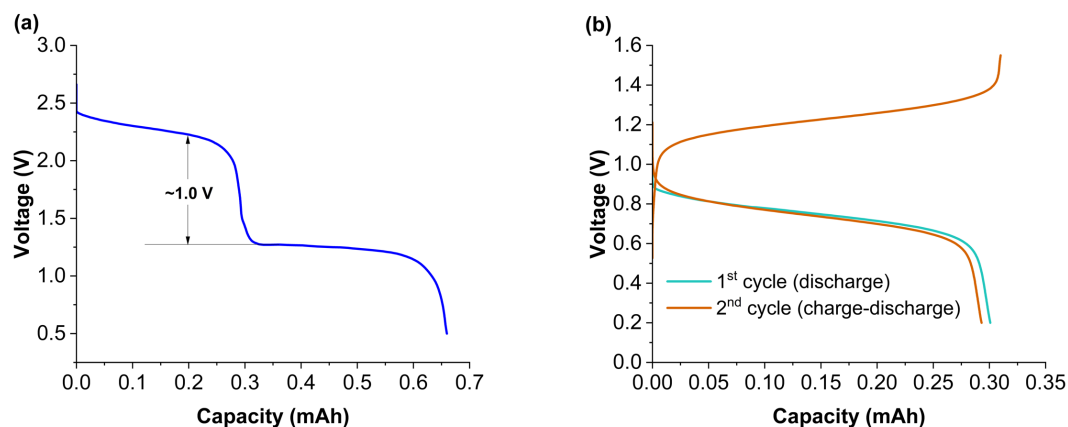


Figure S3.20 (a) Coin cell discharge profile (excess Li anode side and 0.3 ml 0.021M **BPYPE²⁺-2BF₄** in 1.2M LiTFSI/DMF cathode side) (b) Coin cell charge-discharge profile for electrochemically generated 0.3 ml 0.021M **BPYPE²⁺-2Li⁺** vs 0.4 ml 0.021M **BPYPE²⁺-2BF₄** in 1.2M LiTFSI/DMF.

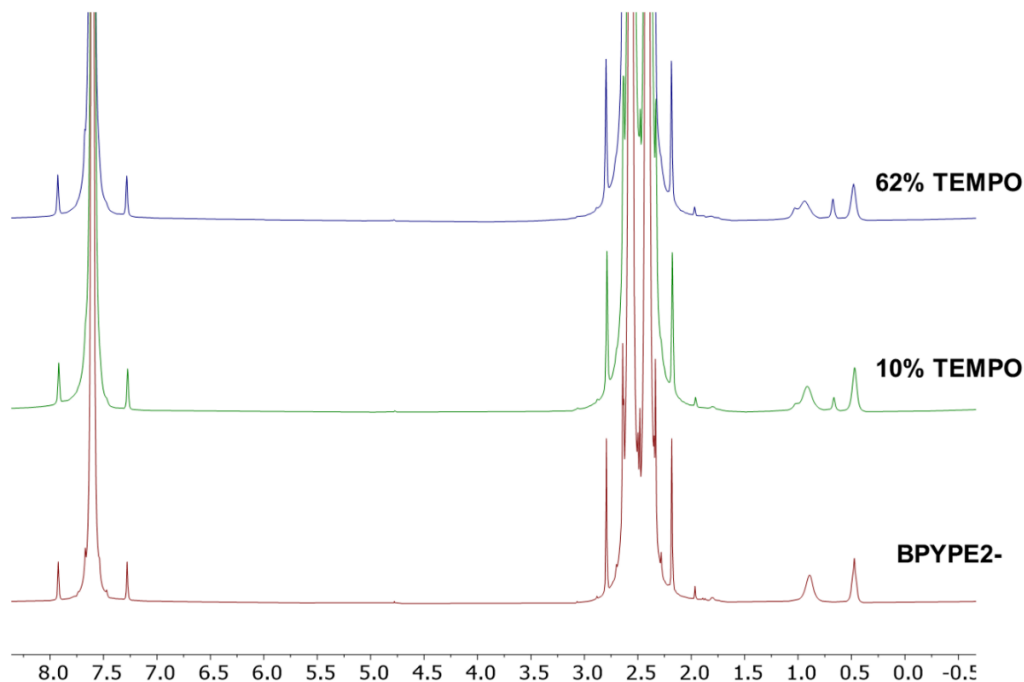


Figure S3.21 ¹H NMR spectrum of **BPYPE²⁺-2Li⁺** in 1.2 M LiTFSI/DMF with radical trapping agent TEMPO (DMF, 25 °C, 300 MHz).

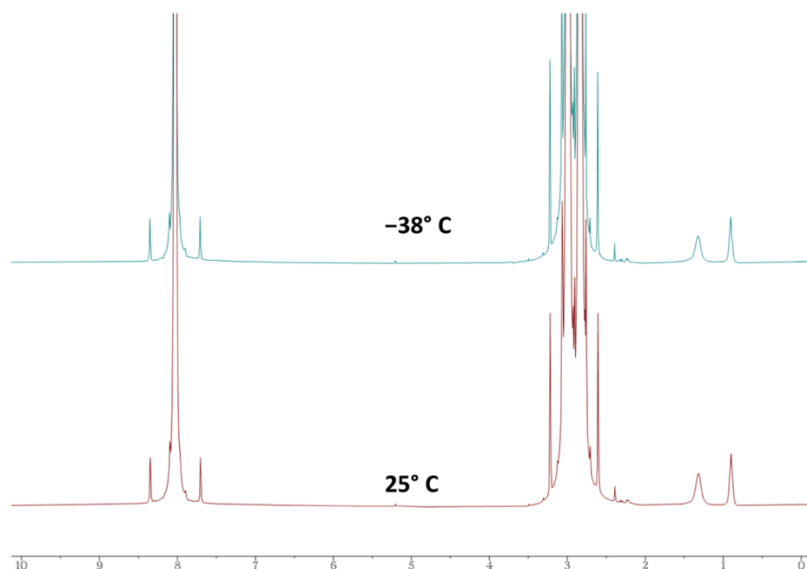


Figure S3.22 Variable temperature ^1H NMR spectrum of **BPYPE $^{2+}$ -2Li $^+$** in 1.2 M LiTFSI/DMF (DMF, 25 °C, 400 MHz).

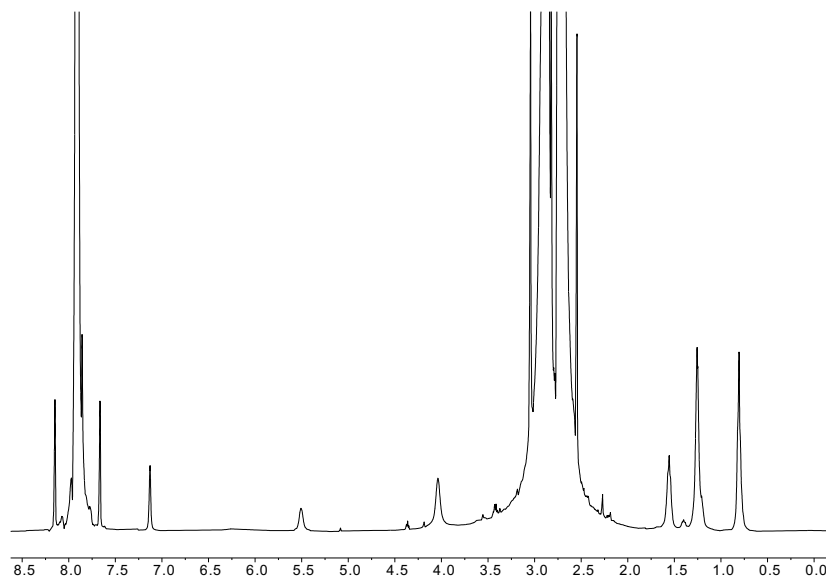


Figure S3.23 ^1H NMR spectrum after the addition of 0.4 mL of 0.04 M **BPYPE $^{2+}$ -2BF $_4^-$** in 1.2 M LiTFSI/DMF to 0.4 mL of 0.04 M of **BPYPE $^{2+}$ -2Li $^+$** (electrochemically generated from a Li cell, in the same electrolyte) showing the formation of **BPYPE** (DMF, 25 °C, 400 MHz).

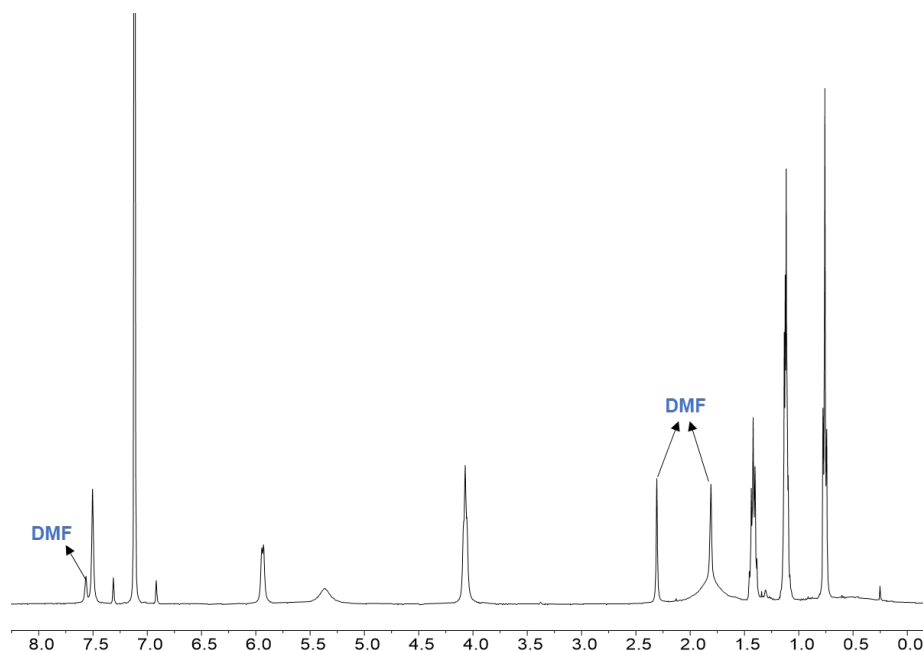


Figure S3.24 ^1H NMR spectrum after concentrating the sample from Figure S3.23 and dissolving the residue in C_6D_6 . (C_6D_6 , 25 $^\circ\text{C}$, 400 MHz).

3.9 Solubility

The solubility of three different oxidation state was measured by CV. A calibration curve was made based on seven solutions of **BPYPE** $^{2+}$ -**2BF** $_4^-$ (at known concentration of 0.0005 M, 0.001 M, 0.0015 M, 0.002 M, 0.0025 M, 0.003 M, 0.0035 M) in 1.2 M LiTFSI/DMF electrolyte. The values of cathodic peak current intensity at a potential of -1.89 V and corresponding values of concentration were plotted to obtain a linear correlation equation (Figure S3.18b). Subsequently, **BPYPE** $^{2+}$ -**2BF** $_4^-$ and **BPYPE** were individually added to 50 μL 1.2 M LiTFSI/DMF electrolyte solution inside the glovebox until solids no longer dissolved. After that, the suspensions were filtered by a micro syringe filter to remove the solid precipitate. 10 μL of these saturated solutions were each dispensed in 9.0 ml of 1.2 M LiTFSI/DMF electrolyte solution. A CV spectrum was recorded of this diluted sample

to obtain cathodic peak current intensity. Using the correlation equation, a concentration was determined for these samples, and subsequently by accounting for dilution the maximum solubility of **BPYPE**²⁺-**2BF**₄⁻ and **BPYPE** in 1.2 M LiTFSI/DMF electrolyte was determined to be 2.10 M and 2.50 M, respectively. Next, 0.6 ml electrochemically generated 0.15 M **BPYPE**²⁻-**2Li**⁺ was concentrated to 0.2 ml of 0.45 M **BPYPE**²⁻-**2Li**⁺. 10 μ L of this solution was dispensed in 1.5 ml of 1.2 M LiTFSI/DMF electrolyte solution and the CV spectrum was recorded. The cathodic peak current value was used as described above and a solubility of 0.41 M was determined.

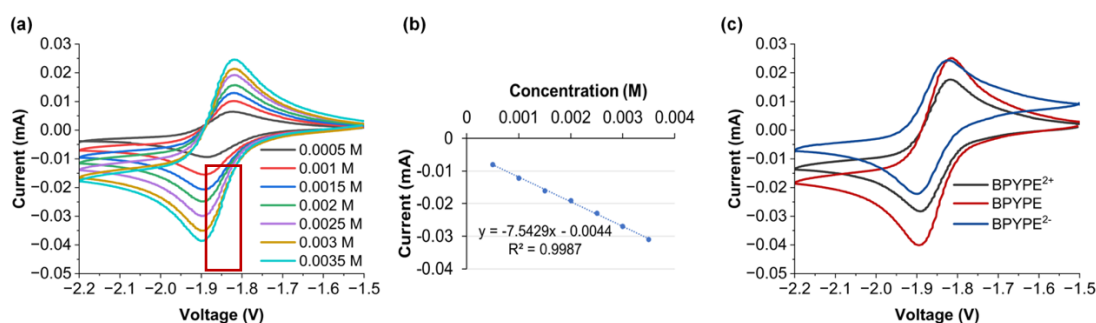


Figure S3.25 (a) CV of **BPYPE**²⁺-**2BF**₄⁻ in 1.2 M LiTFSI/DMF at various concentration 0.0005 M, 0.001 M, 0.0015 M, 0.002 M, 0.0025 M, 0.003 M, 0.0035 M (only the **BPYPE**/**BPYPE**²⁻ redox couple was measured) (b) The relationship between cathodic peak current (mA) and concentration (M) (c) The CVs were obtained for **BPYPE**²⁺-**2BF**₄⁻, **BPYPE** samples diluted 900 times, and for **BPYPE**²⁻-**2Li**⁺ sample diluted 150 times, all in a 1.2 M LiTFSI/DMF solution.

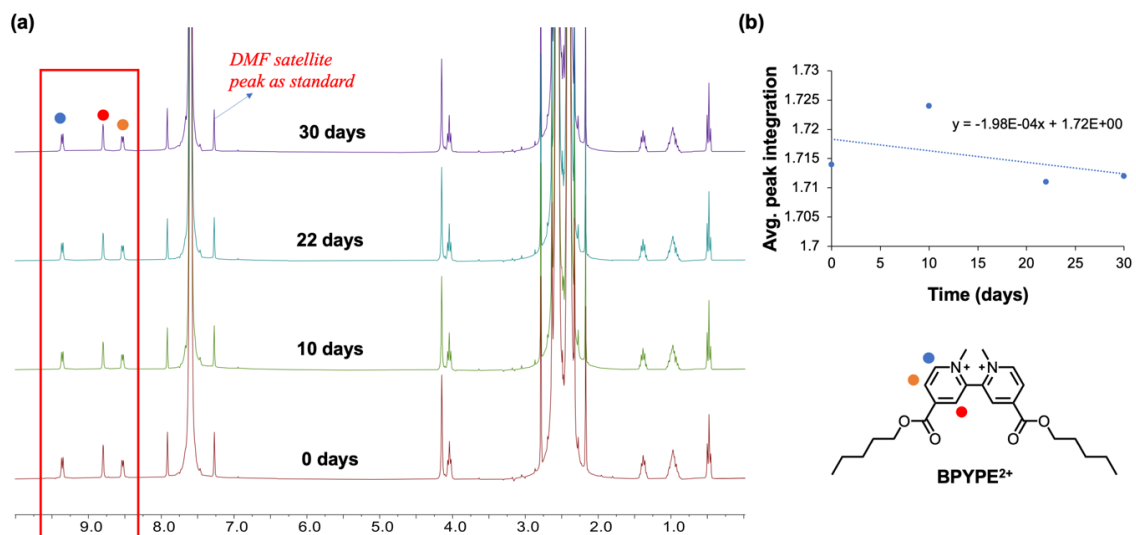


Figure S3.26 (a) ^1H NMR spectra of $\text{BPYPE}^{2+}\text{-}2\text{BF}_4^-$ in 1.2 M LiTFSI/DMF electrolyte in a j-young NMR tube under argon atmosphere (DMF , 25°C , 300 MHz) over a period of 30 days. No new peaks appear over the monitoring period (b) A graph was plotted with the average of all the $-\text{CH}$ pyridium proton (highlighted in red, DMF satellite peak as a standard) vs time, shows a negligible 0.012% decay per day.

3.10 Diffusion coefficients

The diffusion coefficients of **BPYPE**, **BPYPE^{2+}** and **BPYPE^{2-}** were calculated from peak intensities of CV curves (Figure S3.20) using the Randles-Sevcik Eq.1

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C^* \nu^{1/2}$$

Where i_p is the peak current in amperes, n is the number of electrons involved in the half-reaction for the redox couple (2 electrons), C^* is the initial concentration of active materials in mol L^{-1} (0.01 M), ν is scan rate in V s^{-1} , A is electrode area in cm^2 (0.07 cm^2), and D is the diffusion coefficient in $\text{cm}^2\text{ s}^{-1}$. The CV scan rate varied from 10 to 160 mV s^{-1} resulting changes the intensity of peak currents i_p (peak height in mA). Cathodic (i_{pc} , lower) and anodic (i_{pa} , upper) peak currents were plotted against the square root of different scan rates

($v^{1/2}$) to obtain a straight line with slope. The D values were calculated from slopes of the straight lines. For **BPYPE**²⁺/ **BPYPE** redox couple, D values $2.19 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (corresponding to **BPYPE**²⁺) and $2.25 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (corresponding to **BPYPE**) are obtained using i_{pa} and i_{pc} values, respectively. Similar analysis for the **BPYPE**²⁻/**BPYPE** couple leads to D values of $3.64 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (anodic peaks, corresponding to **BPYPE**) and $3.76 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (cathodic peaks, corresponding to **BPYPE**²⁻), respectively.

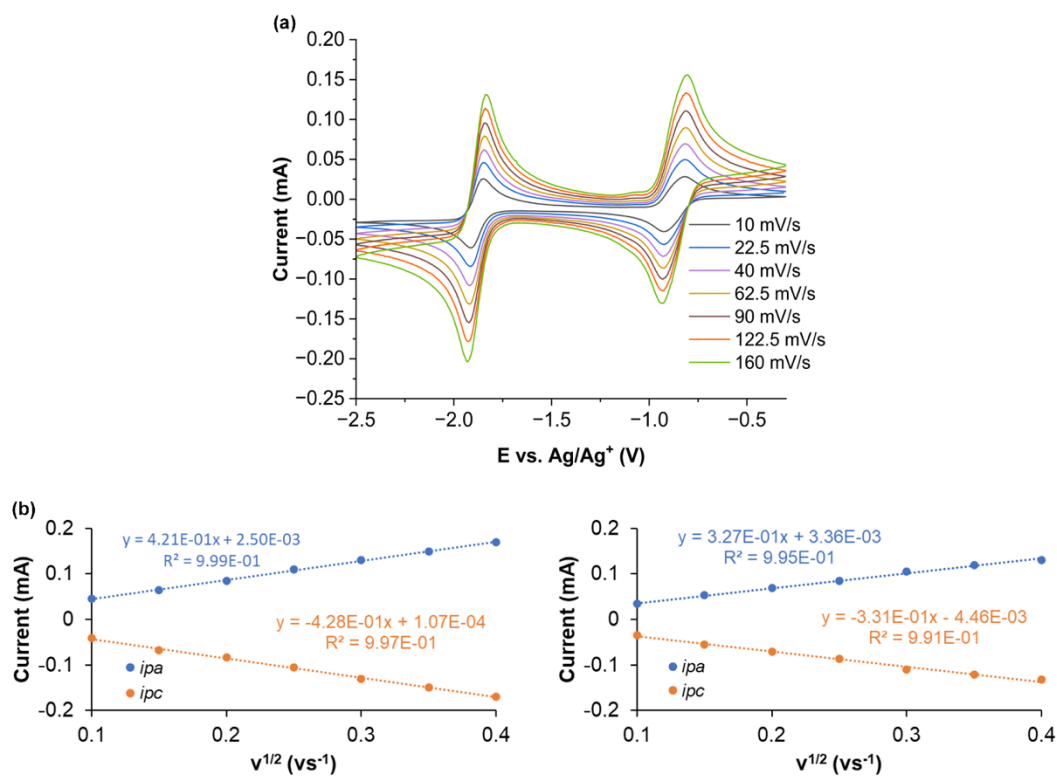


Figure S3.27 (a) Cyclic voltammograms of 0.013 M BPYE²⁺-2BF₄⁻ in 1.2 M LiTFSI/DMF and (b) the relationship between peak current and $v^{1/2}$, obtained at scan rates of 10, 22.5, 40, 62.5, 90, 122.5 and 160 mV s⁻¹ (BPYE²⁺/BPYE left, BPYE/BPYE²⁺ right). WE: 3.0 mm diameter glassy carbon disk, CE: Pt wire, RE: Ag wire (pseudoreference).

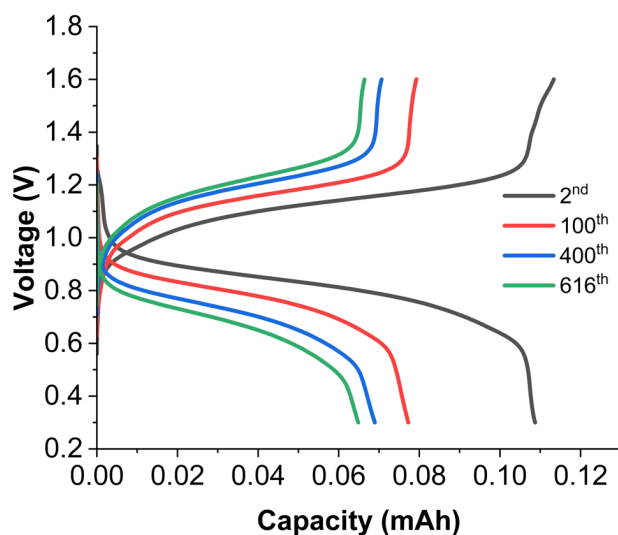


Figure S3.28 Coin cell charge–discharge cycling (0.34 mA cm^{-2}) of bipolar 0.2 ml of 0.015 M **BPYPE** in 1.2 M LiTFSI/DMF with a Tokuyama Neosepta AHA anion exchange membrane. Theoretical capacity 0.16 mAh, SOC 73.5% on first charge; average of 0.08% capacity fade per cycle or 0.26% per hour.

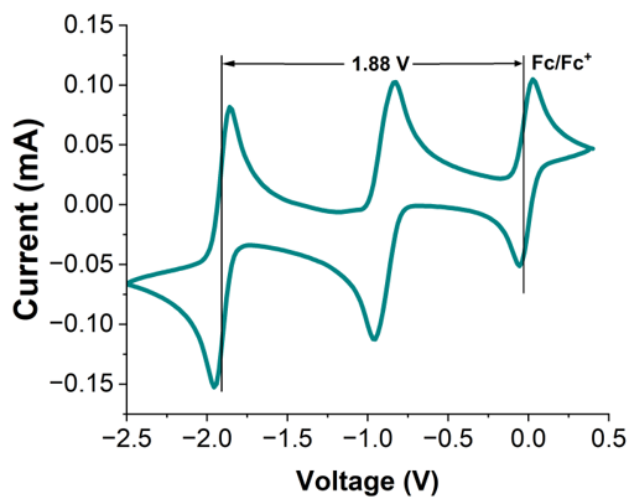


Figure S3.29 CV of **BPYPE**²⁺ (with iR correction) in 1.2 LiTFSI/DMF with an internal reference Fc/Fc⁺

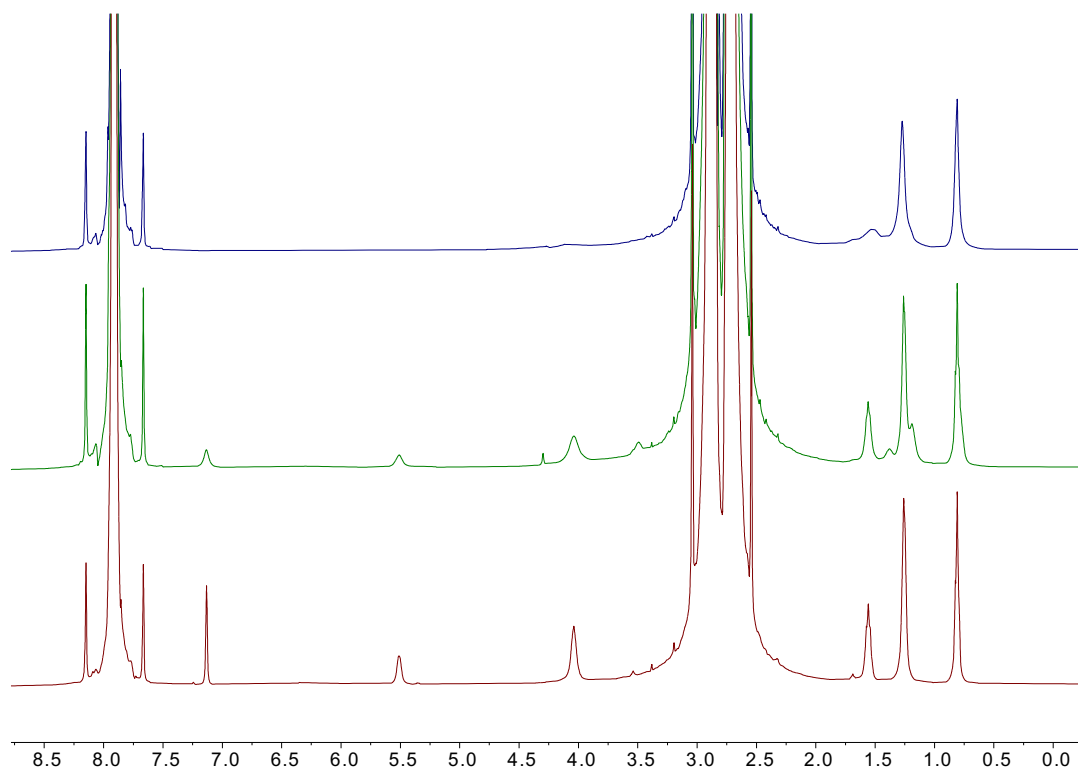


Figure S3.30 ^1H NMR of **0.04 M** BPYPE in 1.2 LiTFSI/DMF (400 MHz) before (red/bottom) and after flow cell cycling with potentiostatic holds (green/middle: anolyte after cycling; blue/top: catholyte after cycling) (see Figure 4d for cell cycling data).

Table S3.1 Comparison of reported all-organic non-aqueous symmetrical RFBs

Bipolar Active Materials	Electron storage per molecule (ox, red)	Cell voltage (V)	Tested and [Limiting] Molar solubility (M)	Tested energy density (Wh/L)	Theoret. energy density (Wh/L)	Flow cell capacity fade (%/cycle, %/day)	No. of cycles	CE, EE (%) (flow cell)
PTIO ⁷	1, 1	1.73	0.1 ^f 0.5 ^f [2.6] ^c	2.32 ^f 11.59 ^f	[60.27] ^g	NR	35 ^f 15 ^f	96, 72 90, 60
VIODAM B ⁸	1, 1	1.58	0.01 ^f 0.1 ^f [0.53] ^{d, g}	0.21 ^f 2.12 ^f	[11.22] ^g	0.57, NR 3.00, NR	35 ^f 20 ^f	93, 80 NR
Croconate violet ⁹	1, 1	1.82	0.01 ^f [1.0] ^{c, g}	0.24 ^f	[24.39] ^g	9, NR	10 ^f	NR
oxo-verdazyl ¹⁰	1, 1	1.42	0.01 ^f [2.4] ^{c, g}	0.19 ^f	[45.67] ^g	0.8, NR	150 ^f	97, NR
Blatter radical ¹¹	1, 1	1.12	0.012 ^e 0.10 ^f [0.64] ^{c, g}	0.18 ^e 1.50 ^f	[9.60] ^g	0.02, 1.5	277 ^e , 100 ^f	89, 60
QPT-OMe ¹²	1, 1	2.76	0.025 ^e 0.025 ^f [NR]	0.92 ^e 0.92 ^f	NR	0.52, NR	900 ^e , 50 ^f	95, 87
D (N-MEEEtBu PhePhtha-1) ¹³	1, 1	2.31	0.005 ^e 0.025 ^f [1.8] ^{c, g}	0.15 ^e 0.77 ^f	[55.72] ^g	0.11, 13.2	100 ^e , 275 ^f	~94, ~87
PDI-TEMPO ¹⁴	2 ^a , 2 ^b	1.87 ⁱ (2.22/1.53)	0.5 ^f [1.3] ^{d, g}	25.13 ^{f, j}	[65.33] ^{g, j}	0.6, NR	100	90, NR
BPYPE (This work)	2 ^b , 2 ^b	1.01	0.015 ^e 0.04 ^f [2.5] ^{d, g} [0.41] ^{d, h}	0.20 ^e 1.08 ^f	[67.67] ^g 11.10 ^h	0.35, 13.9	2000 ^e , 120 ^f	~99, ~72

^aSequential two-electron; ^bConcerted two-electron; ^cHighest molar solubility without supporting electrolyte; ^dHighest molar solubility with supporting electrolyte; ^eStatic cell; ^fFlow cell; ^gBased only on the bipolar (middle) oxidation state; ^hBased on minimum measured solubility of all three oxidation states; ⁱAverage voltage with outer and inner voltages given in parenthesis; ^jOverestimated energy density calculated based on average voltage; the cell predominantly discharges at inner couple voltage¹⁵; NR = Not reported

Table S3.2 Comparison of reported all-organic non-aqueous static symmetrical cells

Bipolar Active Materials	Electron storage per molecule (ox, red)	Cell voltage (V)	Tested and [Limiting] Molar solubility (M)	Tested energy density (Wh/L)	Theoret. energy density (Wh/L)	Static cell capacity fade (%/cycle, %/day)	No. of cycles	CE, EE (%)
DB-134 ¹⁶	2 ^a , 2 ^a	2.24 ^b (2.72, 1.76)	0.05 [0.2] ^{c,f}	3.00 ^e	[12.00] ^{e,f}	NR	6	<80, <50
Me-TEG-DAAQ ¹⁷	2 ^a , 2 ^a	2.28 ^b (2.74, 1.83)	0.1 [1.0] ^{d,f}	6.11 ^e	[61.10] ^{e,f}	0.18, NR	100	99.3, NR
PQTBuTH ¹⁸	2 ^a , 2 ^a	2.06 ^b (2.52, 1.60)	0.1 [0.48] ^{c,f}	5.52 ^e	[26.50] ^{e,f}	0.12, 3.40	450	>95, <40
DMQA ⁺¹⁹	1, 1	2.12	0.0012 [0.032] ^{c,f}	0.03	[0.91] ^f	0.05, 11.36	800	~100, NR
verdazyl ²⁰	1, 1	0.97	0.04 [NR]	0.52	NR	1.3, NR	50	94– 97, 65

^aSequential two-electron; ^bAverage voltage with outer and inner voltages given in parenthesis; ^cHighest molar solubility without supporting electrolyte; ^dHighest molar solubility with supporting electrolyte; ^eOverestimated energy density calculated based on average voltage; the cell predominantly discharges at inner couple voltage¹⁵; ^fBased only on the bipolar (middle) oxidation state; NR = Not reported

$$\text{Volumetric Energy Density } \left(\frac{\text{Wh}}{\text{L}} \right) = \frac{\text{Number of electrons (n)} * \text{Molar solubility of active material (M)} * \text{Cell voltage(V)} * 26.8 \left(\frac{\text{Ah}}{\text{mol}} \right)}{2 \text{ (electrolyte volume)}}$$

3.11 NMR spectroscopy

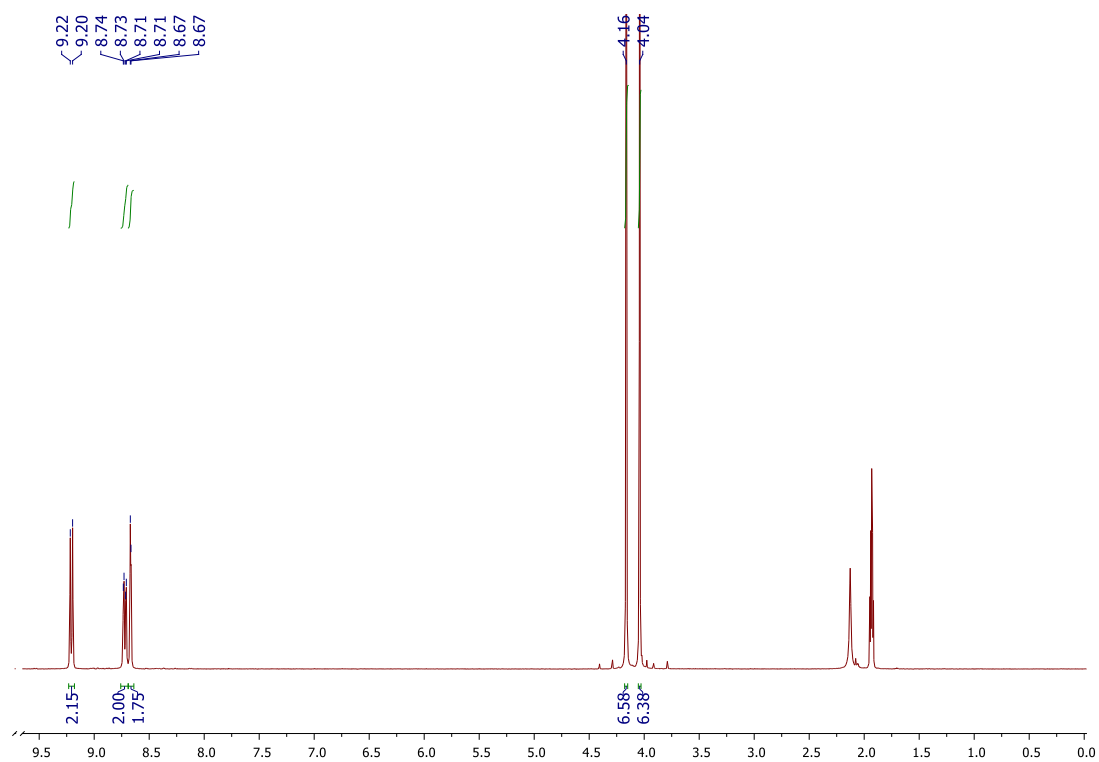


Figure S3.31 ^1H NMR spectrum of $\text{BPYME}^{2+}\cdot 2\text{BF}_4^-$ (CD_3CN , 25°C , 300 MHz).

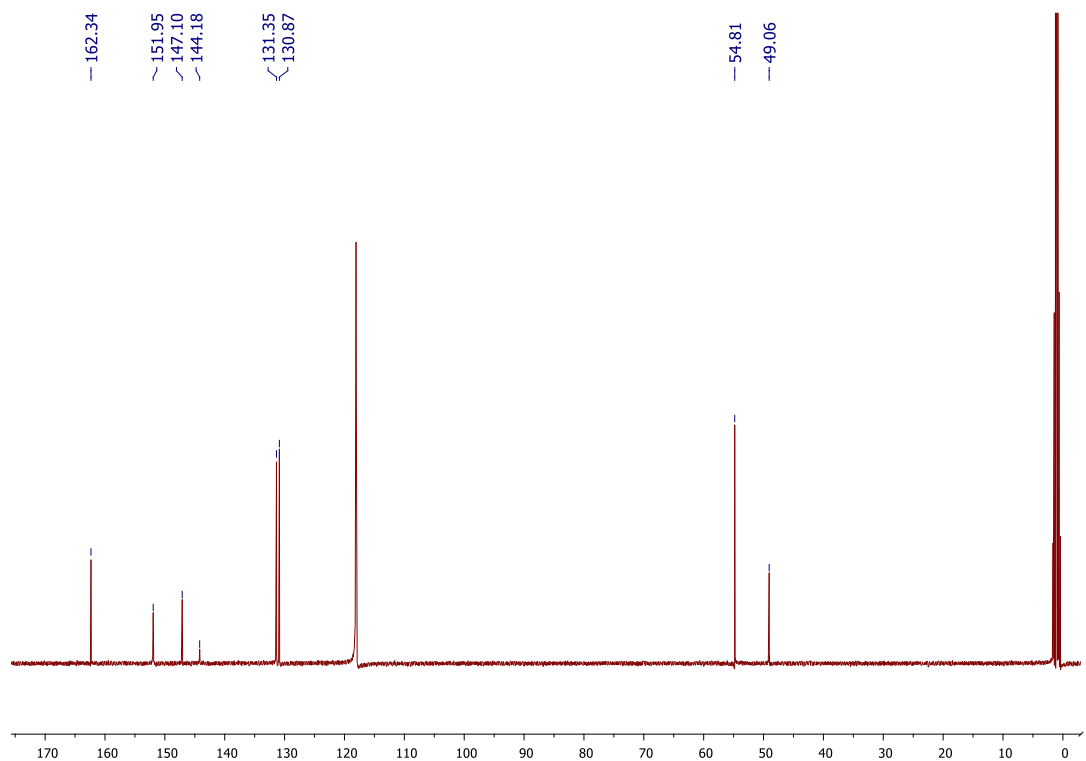


Figure S3.32 ^{13}C NMR spectrum of **BPYME** $^{2+}$ -**2BF** $_4^-$ (CD_3CN , 25 °C, 100 MHz).

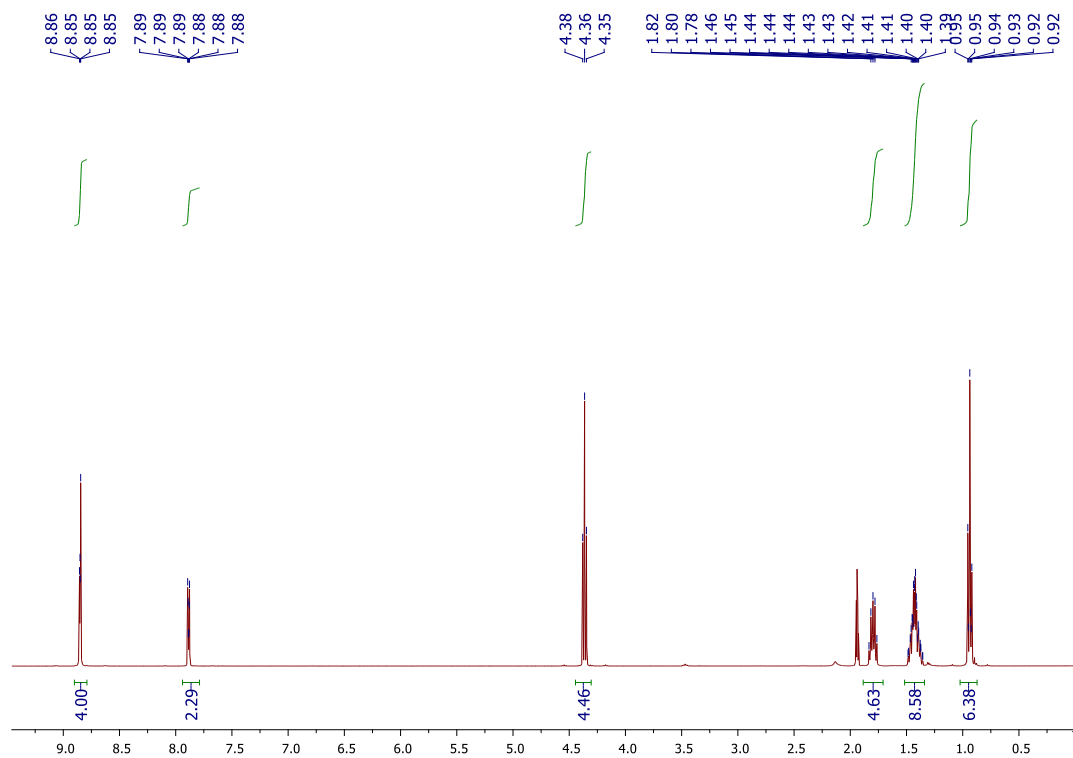


Figure S3.33 ^1H NMR spectrum of **3** (CD_3CN , 25 °C, 400 MHz).

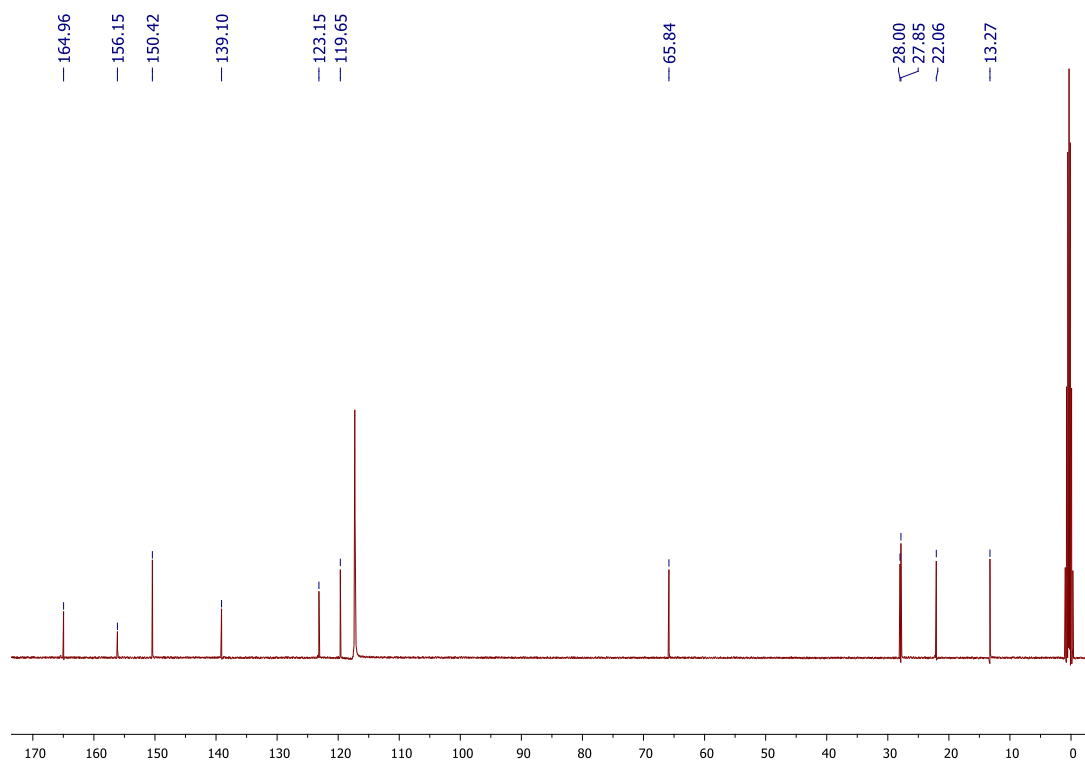


Figure S3.34 ^{13}C NMR spectrum of **3** (CD_3CN , 25 °C, 100 MHz).

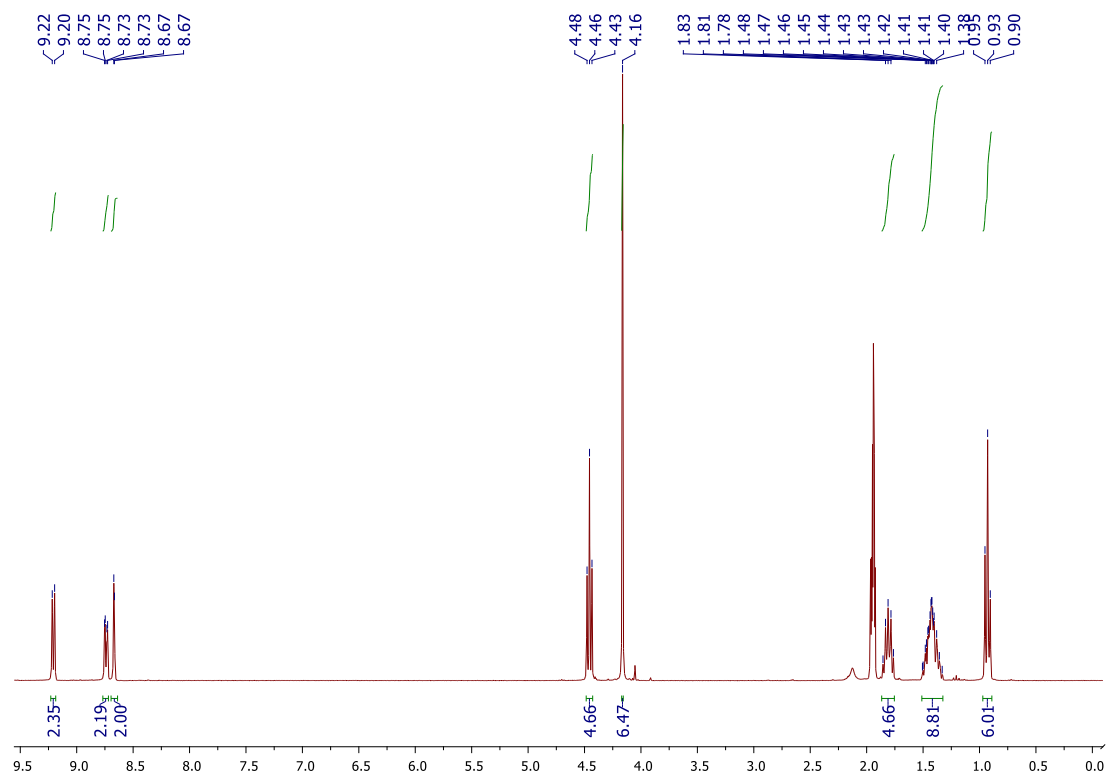


Figure S3.35 ^1H NMR spectrum of **BPYPE** $^{2+}$ -**2BF** $_4^-$ (CD_3CN , 25 °C, 300 MHz).

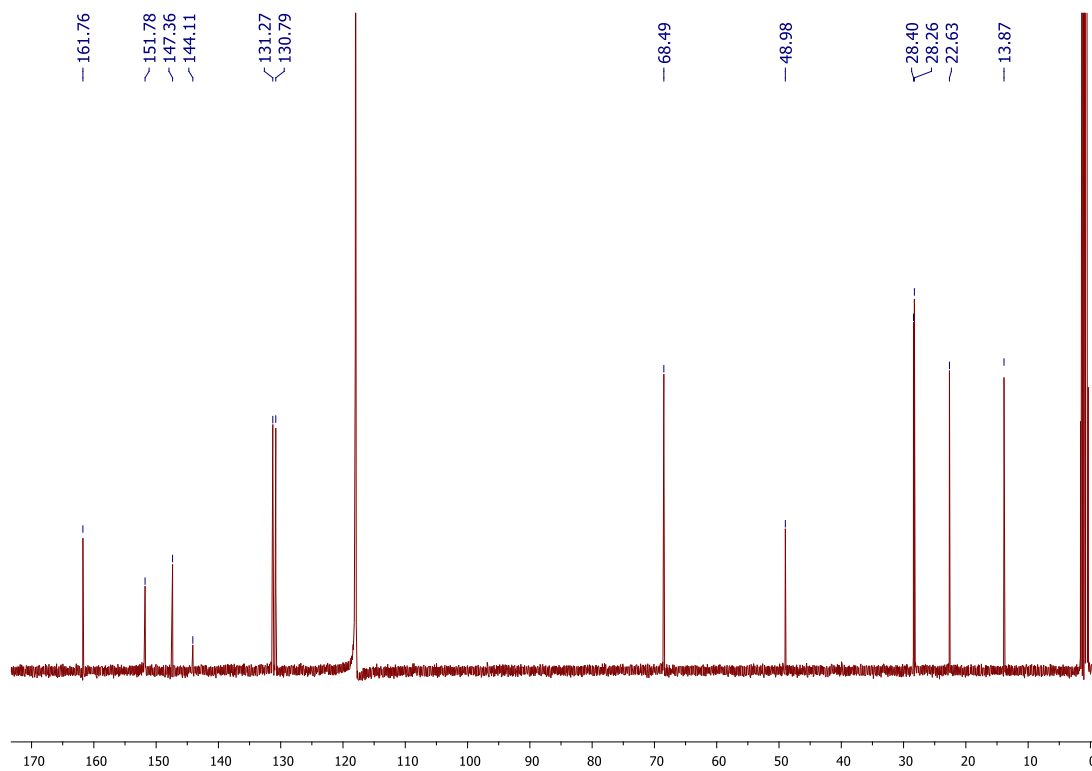


Figure S3.36 ^{13}C NMR spectrum of **BPYPE** $^{2+}$ -**2BF** $_4^-$ (CD_3CN , 25 °C, 100 MHz).

3.12 Cartesian coordinates

BPYME²⁺

Charge = 2, Multiplicity = 1

b3lyp/cc-pvdz				O	3.69556 -1.77769 1.42297
C	-2.96203	-0.19363	0.20712	O	5.15742 -1.02224 -0.13475
C	-1.66635	-0.15297	-0.32152	O	-3.69559 -1.77758 -1.42308
C	-0.70181	0.656	0.25916	O	-5.15743 -1.02224 0.13471
C	-2.26181	1.37651	1.87625	C	-6.20618 -1.8475 -0.42927
C	-3.25961	0.58686	1.32241	C	6.20617 -1.84751 0.42921
H	-1.42033	-0.7692	-1.18565	H	5.91973 -2.90658 0.37244
H	-2.43668	2.00179	2.74948	H	7.09106 -1.64814 -0.18338
H	-4.25219	0.58916	1.76781	H	6.38114 -1.56547 1.47643
C	2.96201	-0.19364	-0.20715	H	-5.91972 -2.90656 -0.37255
C	3.25961	0.58693	-1.32239	H	-7.09106 -1.64817 0.18334
C	2.26182	1.37663	-1.87617	H	-6.38116 -1.56542 -1.47647
C	0.7018	0.65601	-0.25915	H	-0.63834 2.74327 -1.29312
C	1.66634	-0.15301	0.32148	H	-0.61846 1.61087 -2.69001
H	4.2522	0.58925	-1.76778	H	0.63844 2.74308 1.29332
H	2.43671	2.00197	-2.74935	H	-0.51279 3.00226 2.63442
H	1.42031	-0.76929	1.18557	H	0.51285 3.00245 -2.63425
C	0.00725	2.24746	2.03759	N	-1.014 1.40812 1.35859
C	-0.00721	2.24765	-2.03744	N	1.01402 1.40822 -1.35852
C	3.97139	-1.09228	0.462	H	0.61844 1.61062 2.69015
C	-3.97141	-1.09222	-0.46208		

BPYME

Charge = 0, Multiplicity = 1

b3lyp/cc-pvdz

C	-2.80197	-0.28262	-0.38199	O	4.01906	-2.04876	-1.55861
C	-1.45006	-0.34363	-0.3029	O	3.84288	-2.48571	0.57647
C	-0.64607	0.84299	0.00825	O	-3.90349	-1.79574	-1.9144
C	-2.78562	1.9996	0.37917	O	-4.09985	-2.3009	0.20625
C	-3.50419	0.93622	-0.0887	C	-3.81254	-1.99483	1.59027
H	-0.90692	-1.26999	-0.5038	C	3.33397	-2.13302	1.88279
H	-3.27254	2.93262	0.68748	H	2.24206	-2.08237	1.86413
H	-4.57716	0.99413	-0.24234	H	3.681	-2.97095	2.50162
C	2.77781	-0.42645	-0.26318	H	3.7733	-1.18846	2.21612
C	3.49888	0.75346	0.18366	H	-4.22261	-1.01594	1.85518
C	2.87247	1.9512	0.13642	H	-4.33977	-2.80019	2.11951
C	0.7076	0.86761	-0.24792	H	-2.73553	-2.04531	1.77192
C	1.45113	-0.36362	-0.51745	H	0.14394	3.12423	-1.47292
H	4.53276	0.64952	0.49918	H	1.69221	2.69244	-2.23079
H	3.37852	2.89623	0.35217	H	-0.39169	3.83332	0.75242
H	0.89855	-1.21407	-0.92274	H	-1.45982	3.3652	2.11525
C	-0.75842	2.98425	1.35679	H	1.6221	4.02956	-1.04356
C	1.22698	3.0328	-1.29085	N	-1.3958	1.96176	0.49198
C	3.57049	-1.66432	-0.50807	N	1.47532	2.10046	-0.14311
C	-3.61359	-1.47262	-0.79109	H	0.11521	2.56124	1.89021

Syn-BPYME²⁻

Charge = -2, Multiplicity = 1

b3lyp/cc-pvdz

C	-0.59843	0.84252	0.	O	5.36623	-1.50028	0.3411
C	0.77389	0.81203	-0.06913	O	7.21788	-0.23173	0.0469
C	1.57382	1.97804	0.08802	O	-0.83178	-1.50019	-0.45635
C	-0.49094	3.19833	0.50049	O	-2.6834	-0.23175	-0.16186
C	-1.25414	2.11089	0.24671	C	-3.46954	-1.41111	-0.37389
H	1.24996	-0.13571	-0.32047	C	8.00399	-1.41113	0.25893
H	-0.92372	4.17417	0.72847	H	7.76725	-2.17952	-0.49274
H	-2.33854	2.18856	0.22513	H	9.04978	-1.09218	0.16722
C	5.13291	0.84248	-0.11508	H	7.81549	-1.83301	1.25803
C	5.78868	2.11081	-0.36179	H	-3.2319	-2.18012	0.37684
C	5.02549	3.19825	-0.61568	H	-4.51529	-1.0924	-0.28088
C	2.96069	1.97804	-0.20333	H	-3.28209	-1.83223	-1.37354
C	3.7606	0.81201	-0.0461	H	2.00015	4.4294	-1.13006
H	6.87308	2.18843	-0.34021	H	2.69772	3.51015	-2.48528
H	5.45829	4.17406	-0.84371	H	2.53477	4.4286	1.01586
H	3.28446	-0.13571	0.20521	H	0.93786	4.89768	1.67721
C	1.59284	4.04913	1.43697	H	3.597	4.89779	-1.79215
C	2.9417	4.04957	-1.55168	N	0.90413	3.16831	0.49524
C	5.87173	-0.41611	0.11575	N	3.63045	3.16821	-0.6105
C	-1.33724	-0.41605	-0.23083	H	1.83605	3.50949	2.37064

Anti-BPYME²⁻

Charge = -2, Multiplicity = 1

b3lyp/cc-pvdz

C	-2.35254	0.62414	0.	H	4.60567	2.60479	-1.8849
C	-3.26185	-0.10339	0.69174	H	5.7812	1.66498	-0.99723
C	-5.08455	0.80957	-0.91626	H	4.58006	0.86018	-1.97837
C	-4.15688	1.66553	-1.40757	H	-2.47189	-0.81672	1.94589
H	-6.07667	0.79852	-1.31685	H	-1.55554	0.36956	2.84373
H	-4.48713	2.43566	-2.07296	H	-1.28919	-1.33455	3.12323
C	1.51892	1.06313	0.06036	N	-0.4861	-0.60563	1.3405
C	1.82322	0.32973	1.35915	N	-2.70791	1.61574	-1.05631
C	0.82848	-0.34567	1.98604	H	-2.94016	3.20959	0.27038
C	-0.86062	0.39389	0.30457	H	-1.32449	3.0175	-0.36664
C	0.06543	1.0995	-0.39058	H	-2.58966	3.67426	-1.37713
H	2.80814	0.35396	1.77656	C	-4.71038	-0.11016	0.23362
H	0.99906	-0.7145	2.97587	C	-5.66431	-0.93275	0.84787
H	-0.2232	1.68152	-1.24078	O	-7.02037	-0.91698	0.39429
C	-1.52109	-0.59619	2.38435	O	-5.32755	-1.68528	1.79859
C	2.52937	1.69554	-0.67652	C	-7.19008	-1.89492	-0.63514
C	-2.36739	2.9715	-0.60149	H	-6.95459	-2.8644	-0.24842
O	2.24537	2.30251	-1.74165	H	-8.20476	-1.88312	-0.97453
O	3.88316	1.6511	-0.21807	H	-6.53787	-1.66899	-1.45274
C	4.76823	1.69823	-1.34027	H	-2.95902	-0.68624	1.5364

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Chapter 4: Summary and Future works

4.1 Summary

The research presented in Chapter 3 of this thesis focuses on the development of symmetric NORFBs based on ester-substituted bispyridinylidenes. This study showed it was possible to optimize the redox behavior of the bispyridinylidene active materials by selecting the appropriate electrolyte salt and solvent. The cyclic voltammetry of the bipolar molecule **BPYME** was examined employing various supporting salts, including TBAPF₆, NaBF₄, and LiTFSI, in combination with MeCN or DMF solvent. Remarkably, the combination of the electrolyte salt LiTFSI and the solvent DMF resulted in effectively concerted two-electron oxidation and reduction processes at 0.88 V and -1.89 V vs Ag/Ag⁺, respectively—a characteristic not previously observed in symmetric ORFB active materials. Molecular derivatization of **BPYME** was employed to form **BPYPE** to enhance solubility, a crucial factor in the practical application of these materials. The solubility of all three different oxidation states, **BPYPE**²⁺-2BF₄⁻, **BPYPE**, and **BPYPE**²⁻-2Li⁺, was determined to be 2.1 M, 2.5 M, and at least 0.41 M, respectively, in the electrolyte 1.2 M LiTFSI/DMF.

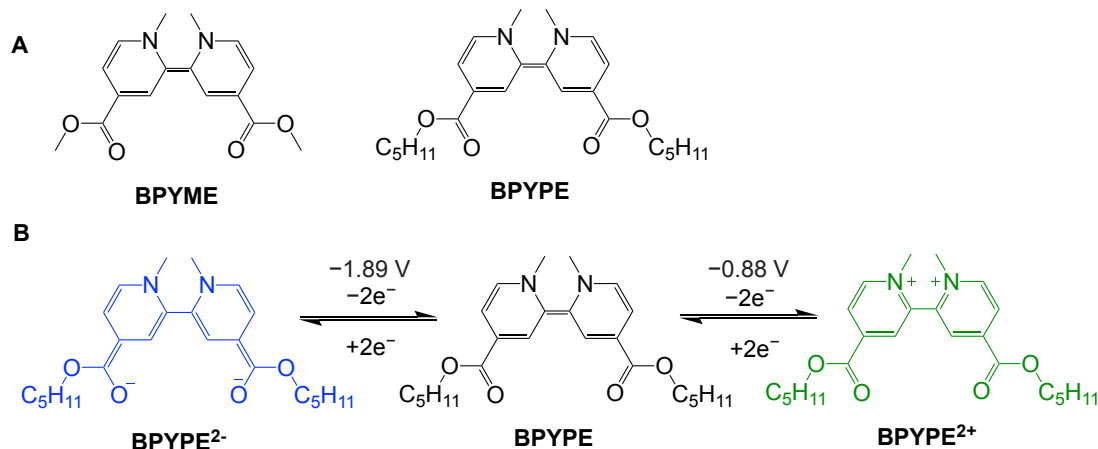


Figure 4.1 Structure of **BPYME**, **BPYPE**, **BPYPE²⁺**, and **BPYPE²⁻**

Lifetime studies of all three oxidation states of the active material in the electrolyte revealed remarkable stability over time, with negligible decay observed by periodic CV sampling over a one-week period. The assessment of the active material, employing a cost-effective polypropylene separator, demonstrated commendable cyclability with fade rates of 0.025% and 0.35% per cycle for static and flow cells, respectively. These cells exhibited capacities reaching up to 89% of the theoretical value, accompanied by Coulombic efficiencies surpassing 99%.

Despite the drawback of a low cell voltage at 1.01 V associated with the bipolar molecule **BPYPE**, this is the first reported double concerted two-electron bipolar system. Considering recent studies indicating that the likely maximum concentration of organic active materials in RFB applications is 2 M,¹ the utilization of such concerted two-electron bipolar molecules becomes crucial for achieving viable energy densities in organic RFBs. **BPYPE** is therefore a landmark in the multi-electron energy storage strategy for symmetric ORFBs, and will inspire new designs with higher cell voltages. Overall, the findings should

contribute significantly to advancing the feasibility and efficiency of symmetric organic RFBs towards their application into large-scale energy storage solutions.

Chapter 2 of this thesis comprehensively overviewed all symmetric ORFBs in the literature, excluding those solely based on metals or organometallic active species. It categorizes organic bipolar molecules into five distinct groups, namely tethered, intrinsic, ion-paired, double bipolar, and double-tethered molecules (see Figure 4.2 for all categories except ion-paired, which can be found in Figure 2.3 of Chapter 2), providing a detailed and insightful description of each category. The chapter concludes with a comparative analysis of the performance of these organic bipolar molecules. Key parameters such as Coulombic efficiency, voltage efficiency, energy efficiency, and energy density are thoroughly examined and discussed. Acknowledging the early stage of this field and data gaps among studies, which include variations in testing conditions and a lack of information on the solubility and stability of all redox states, the objective of the chapter is to present a comprehensive discussion of existing knowledge, offering a summarized overview of the progress within the field of symmetric ORFBs. This chapter also emphasizes active material stability and energy density in the existing literature for symmetric NAORFBs and AORFBs.

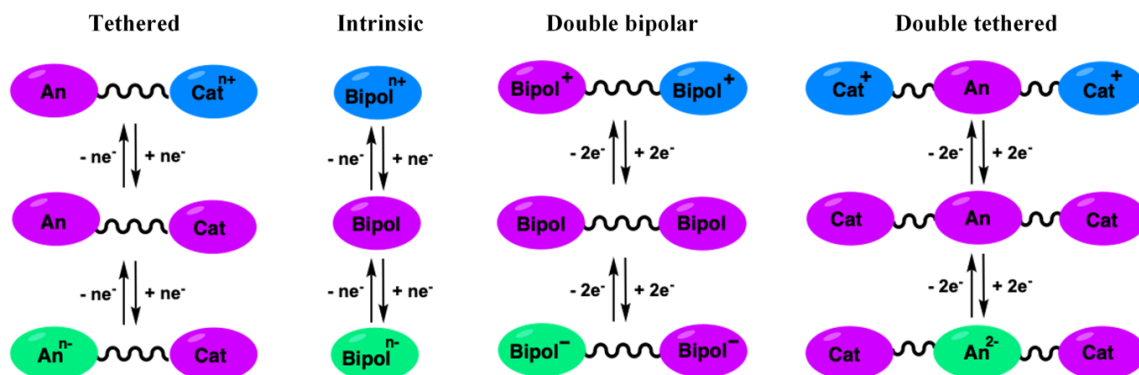


Figure 4.2 Schematic representation of different types of bipolar molecules (An = anode-active species; Cat = cathode-active species; Bipol = intrinsic bipolar species; $n = 1$ or 2 ; Purple = discharged state; Blue is charged state for cathode-active species; Green is charged state for anion-active species)

For symmetric NAORFBs, it is evident that enhancing energy density requires bipolar active materials engaging in two two-electron processes with a separation (E_{cell}) of 3 V or more, necessitating concerted or nearly-concerted two-electron events for favourable energy efficiencies. Intrinsic bipolar molecules show promise for atom-economical systems, but the design of double concerted two-electron systems with high E_{cell} remains a formidable challenge. Double bipolar and double-tethered molecules emerge as promising alternatives, potentially achieving high cell voltages and double concerted behaviour in a more straightforward way. Attaining stability is complex, with in-depth studies on material decomposition needed for progress. The right balance between benefits and challenges, encompassing solubility, stability, and kinetics, is imperative for future advancements in this field. Section 4.2 details some specific avenues of research that follows these recommendations for new active materials for non-aqueous ORFBs.

For symmetric AORFBs, despite limited studies on bipolar systems for aqueous solvents, reported cycle life and cell voltages suggest progress towards viable energy storage. Tethered one-electron molecules show promise, achieving reasonable energy densities at 1.5 V and concentrations of 1.5 M. However, further optimization is needed to bring the tested concentrations closer to this limit and improve efficiency. Double-tethered molecules are more promising, offering high energy densities even at low concentrations. In conclusion, by carefully studying the existing literature, this review aims to serve as a guiding resource, inspiring new directions and advancements in the promising field of symmetric ORFBs for energy storage. Specific targets for aqueous active materials are detailed in section 4.2.

4.2 Future works

4.2.1 Design bispyridinylidene derivatives for higher cell voltage bipolar molecules

In Chapter 2, the compound **BPYPE** has been revealed to undergo a reversible, simultaneous two-electron oxidation and a reversible, simultaneous two-electron reduction, albeit with a relatively low cell voltage of approximately 1.01 V in a non-aqueous (LiTFSI/DMF) electrolyte. This observation prompted further investigation by our group (Sydney Crain, PhD candidate, and Eve Lavers, BSc candidate) to synthesize two additional derivatives, **BPYA₆** and **BPYA₅** (see Figure 4.3A). In these derivatives, electron-donating groups (EDGs) piperidyl and pyrrolidyl groups are attached to the carbonyl of the BPY. Notably, **BPYA₆** and **BPYA₅** exhibit a slight increase in the overall cell potential, measuring 1.06 V and 1.17 V, respectively, when using LiTFSI/DMF electrolyte. Interestingly, when employing TBAPF₆/DMF electrolyte, these cell potentials further rise to 1.26 V and 1.31 V, while still maintaining the characteristic double concerted two-electron oxidations and reductions. This is in contrast to **BPYPE**, which displayed concerted two-electron oxidation but a sequential two-electron reduction in TBAPF₆/DMF electrolyte. It is noteworthy that the enhanced cell voltage is attributed to the shift of the neutral/dianion redox couple towards the negative direction with the incorporation of more EDGs onto the carbonyl group, while the redox couple for dication/neutral remains relatively unchanged. Notably, the order of effectiveness in increasing cell potential is observed as alkyl ester < piperidyl amide < pyrrolidyl amide.

This study encourages introducing more electron-donating groups to the carbonyl group of the BPY scaffold to achieve a more favorable cell potential. Consequently, the exploration

of other electron-donating groups, such as -N=PPh_3 or -N=PCy_3 ,² attached to the carbonyl group, holds promise for further enhancing the cell potential. A proposed synthetic scheme is shown in Figure 4.3B.

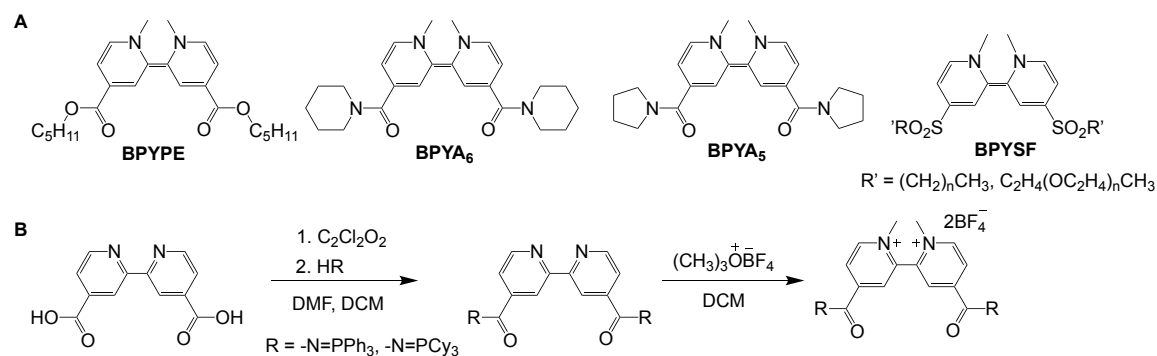


Figure 4.3 (A) Structure of **BPYPE**, **BPYA₆**, **BPYA₅**, and **BPYSF** (B) Proposed synthetic scheme of bipolar BPY derivatives featuring iminophosphorano substituents.

Additionally, introducing alternate electron-withdrawing substituents, such as $\text{-SO}_2\text{R}'$, at the 4,4' positions (**BPYSF**) (see Figure 4.3A) of the BPY framework presents an interesting avenue for exploring the redox properties and stability across various supporting electrolytes. It would be interesting to computationally calculate the redox potential of this modified scaffold and ascertain whether the compound resides within the potential window of the solvent and to predict the E_{cell} .³ This computational determination is beneficial for predicting the of the most promising experimental studies. Moreover, the maintenance of concerted two-electron behaviour in this newly designed molecule would need to be established through experimental validation.

4.2.2 Double bipolar molecules for symmetric non-aqueous system

The impact of low temperatures on aqueous ORFBs presents a significant challenge, particularly in cold regions like Canada. In such environments, water-based electrolytes are prone to freezing, leading to solidification of the electrolyte, posing a substantial operational hurdle for flow cells by requiring energy intensive thermal management. In contrast, numerous organic solvents offer a promising solution due to their considerably lower freezing points. For example, widely utilized solvents in non-aqueous systems, such as acetonitrile and DMF, exhibit freezing points of -44°C and -60°C , respectively.⁴ Consequently, the utilization of non-aqueous solvents emerges as a promising solution for ORFBs in cold climates, ensuring the continued functionality of flow cells despite extreme temperature conditions.

The literature survey in Chapter 2 on non-aqueous ORFBs developments reveals a clear need for systems capable of achieving the targeted energy density of 180 Wh/L, a requirement for competitive performance with their aqueous counterparts. To achieve the targeted energy density, the system must feature a cell voltage of at least 3 V, a solubility not exceeding 2 M to uphold favourable ionic conductivity and viscosity, and operate with a double two-electron mechanism. While there are existing systems demonstrating a cell voltage of around 3 V, they operate as single-electron systems.⁵⁻⁷ In Chapter 2, various design strategies for bipolar molecules are discussed. Among these, the double bipolar system emerges as a promising choice to achieve the desirable properties. Tethering two one-electron bipolar molecules with an appropriate linker not only aids in increasing solubility but also naturally enables a double concerted behaviour. Hence, two units of the one-electron bipolar molecule (**QXtBuTH**),⁷ as reported by the Swager research group,

have been considered for tethering using an ethylene glycol linker to form **(QXTH)₂** (see Figure 4.4A). This choice is motivated by the observed increase in solubility in MeCN associated with the ethylene glycol linker.⁸ **QXtBuTH** exhibits a cell voltage of 3.03 V and a moderate solubility of 0.61 ± 0.01 M in a solvent mixture of MeCN and methyl benzoate (1:4). Despite **QXtBuTH** demonstrating poor cycling performance, it is crucial to investigate the reasons for this performance limitation, given the potential of this molecule for high energy density batteries. For example, incorporation of the greater solubility of the linker chain may enable other solvents (DMF, polycarbonates etc) that lead to improved stability.⁹ In summary, this proposed study aims to provide insights into the detailed molecular properties of sulfur and nitrogen-containing heterocycle.

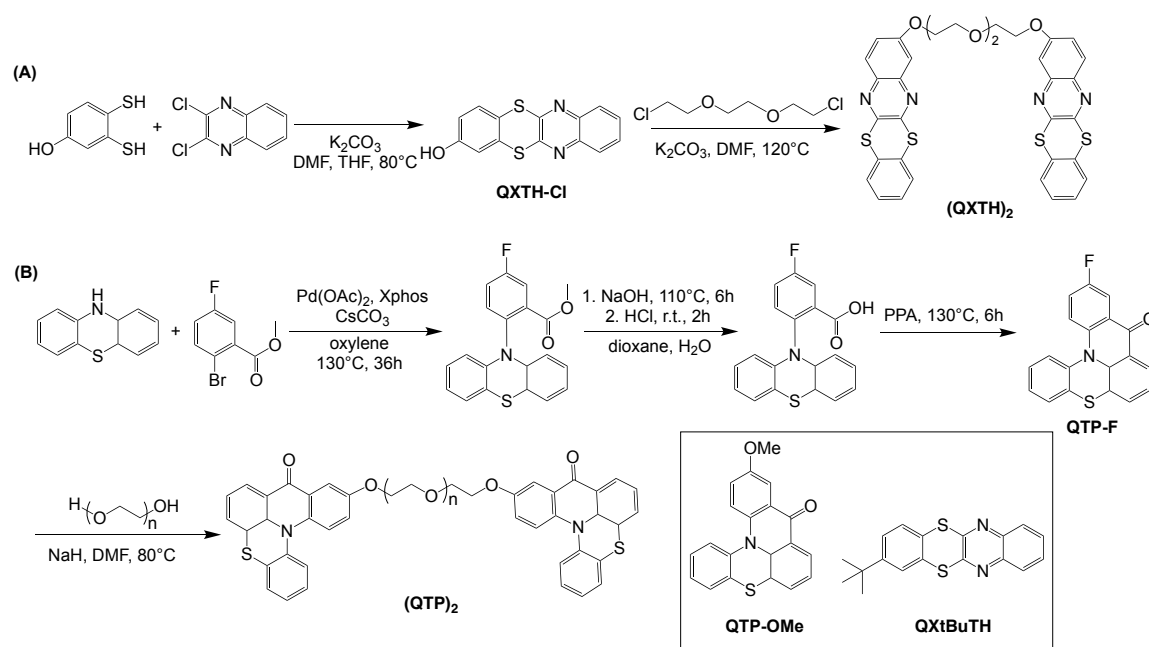


Figure 4.4 (A) Proposed synthetic scheme of **(QXTH)₂** (B) Proposed synthetic scheme of **(QTP)₂**

Similarly, two units of the one-electron bipolar molecule (**QTP-OMe**),⁶ as documented by the Zhao research group, are under consideration for tethering through an ethylene glycol linker to form (**QTP**)₂. The scheme is proposed according to the literature report by Liu and co-workers (see Figure 4.4B).⁶ The bipolar molecule **QTP-OMe** exhibits a cell voltage of 2.76 V, but its solubility in a 0.5 M TBATFSI/MeCN supporting electrolyte is significantly low. This limitation could potentially be addressed by the incorporation of an ethylene glycol linker in (**QTP**)₂. While the compound **QTP-OMe** displays capacity degradation over cycling, the causes may include the reaction of a carbonyl-based radical with acetonitrile through nucleophilic substitution, surface oxidation of carbon felt at a high oxidation potential resulting in increased internal resistance, and the potential for precipitation and deactivation of trapped active materials in the porous graphite plate due to solvent evaporation.⁶ Therefore, it would be interesting to investigate the stability of the suggested molecule, (**QTP**)₂, in various electrolyte solvents such as DMF, which may potentially enhance its stability.⁹ If the newly proposed molecule exhibits decomposition similar to **QTP-OMe**, it would be beneficial to elucidate the decomposition pathways through the analysis of spent liquor, utilizing techniques such as NMR spectroscopy or liquid chromatography–mass spectrometry (LC-MS). Such analyses would contribute to the design of new, more stable derivatives.

4.2.3 Double tethered molecule for a symmetric aqueous system

Aqueous ORFBs show significant promise in terms of cost-effectiveness, particularly under ambient temperature conditions. According to the literature survey in Chapter 2, double tethered bipolar molecule shows great potential to develop energy-dense system. Therefore, a concerted two-electron π -conjugation extended viologen (as anolyte) and two one-electron TEMPO units (as catholyte) are tethered by alkoxy groups to form a proposed double tethered bipolar molecule **3**. The utilization of an extended viologen as the anolyte and TEMPO as the catholyte has been reported in asymmetric systems; however, concerns persist regarding the crossover of active materials.¹⁰ Cyclic voltammetry analysis reveals that the π -conjugation extended viologen exhibits a concerted two-electron redox couple at -0.75 V, while TEMPO displays a single electron redox couple at 0.81 V in a 0.5 M NaCl/water electrolyte versus SHE. By implementing the double-tethered strategy, a two-electron bipolar molecule with a cell voltage of 1.56 V can be achieved, which is higher than traditional aqueous RFBs. This strategy not only addresses the challenge of crossover but also holds the potential to replace costly membranes and facilitate the development of an energy-dense system, thereby presenting a solution for the development of cost-effective aqueous ORFBs.

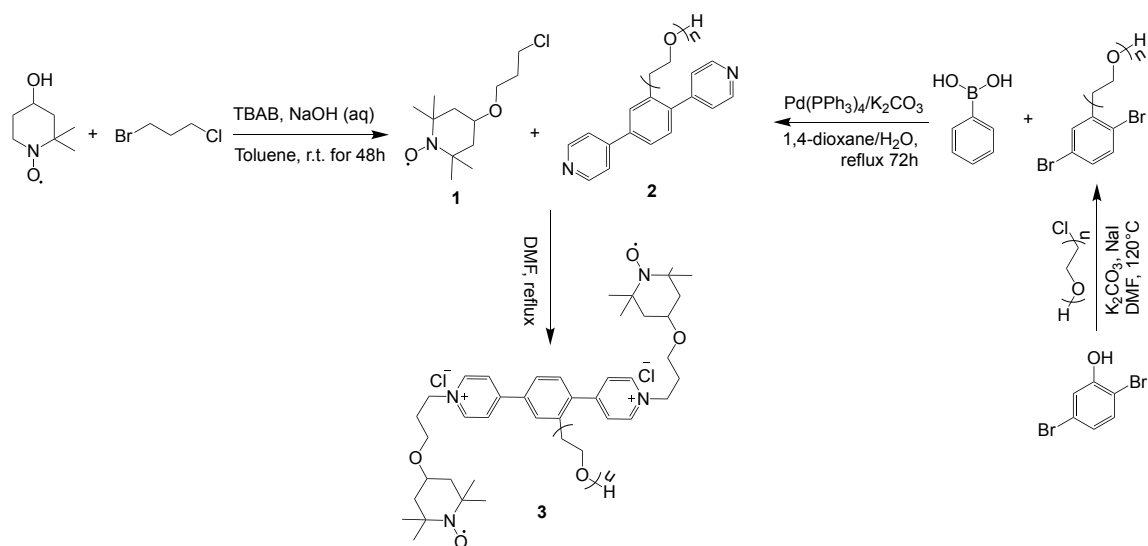


Figure 4.5 Proposed synthetic routes of compound **3**

4.3 Characterization and assessment of bipolar molecules

After synthesizing the proposed compounds, assessment of their redox properties, including redox potentials, electrochemical reversibility, and diffusion coefficients/kinetics, using cyclic voltammetry will be conducted. The stability of all three oxidation states will be determined through proton NMR spectroscopy, cyclic voltammetry, or UV-vis analysis of solutions over time. Solubility will be evaluated by combining these techniques with standardized calibration curves.

Charge-discharge cycling of the synthesized compounds will be carried out in both small-scale static and small-scale flowing cells. Static cells, with a simpler design and fewer variables, offer advantages for initial assessments, while flowing cells provide a more representative view of larger-scale flow cell performance. Various concentrations and current densities will be explored to understand the material properties.

4.4 Investigation of capacity fade

Achieving high stability of redox-active species poses a formidable challenge. This challenge is exacerbated by the inherent complexity introduced when these redox-active species are actively engaged in electrochemical processes. Beyond their intrinsic stability within the chosen supporting salt and solvent, the overall stability of active materials is intricately influenced by their interactions with various cell components. These components, encompassing flow tubing, peristaltic tubing, membrane or separator, and graphite or carbon felt, can individually impart unique effects on the stability of diverse oxidation states. For instance, as demonstrated in Chapter 3, ester-substituted bipyridinylidene exhibits excellent stability in all three different oxidation states when exposed to the supporting salt and solvent. However, when tested in a coin cell, it manifests a capacity decay of 0.025% per cycle, and in a flow cell, the deterioration worsens (0.35% per cycle), suggesting that the cell components themselves may be playing a significant role in the overall decay of the active materials.

To discern the reasons behind the high capacity fade rate, active materials in different oxidation states can be circulated through the cell without undergoing charge/discharge cycling. The observation of potential decomposition can be facilitated through techniques such as NMR, CV, or UV-vis spectroscopy, where peak height/integration changes can be monitored over time. Alternatively, to identify the cell components contributing most to active material decomposition, the individual cell components can be immersed in the electrolyte with the active materials, and any subsequent decomposition can be monitored over time using the same spectroscopic techniques. Conducting such experiments is

imperative for gaining insights into the influence of cell components on decomposition, aiding in the informed selection of appropriate materials for constructing flow cells.

Furthermore, cell performance failures may arise from the degradation of membranes and graphite felts. Evaluating the chemical stability of the membrane in the electrolyte and during cycling is essential for ensuring prolonged cyclability. To address this, membrane and graphite felt electrode characterization, involving X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) before and after cycling, can elucidate alterations in chemical composition or morphology. For instance, SEM can discern changes in surface morphology, such as the peel-off of the active surface layer of fibres or variations in the surface area of the fibres during cycling, which can impact cell performance.¹¹ Monitoring alterations in surface functionalization through XPS, including changes in carbon, oxygen, nitrogen, fluorine, etc., before and after cycling, can help in tracing back any source of these atoms (solvent, salt, active material) and help identify incompatibilities.¹² Therefore, surface analysis of graphite felts and the membrane before and after cycling could give us a clue of how they contributed, if at all, to the poor cyclability observed.

4.5 References

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1. A. R. Aguilera, B. Balcom, C. A. Dyker, F. Marica, G. R. Goward, K. J. Sanders, M. A. Raihan “Multinuclear MR and MRI Study of Lithium-Ion Cells Using a Variable Field Magnet and a Fixed Frequency RF Probe” 2023 CAP Congress, UNB, Canada, **Jun 2023** (oral)
2. **M. A. Raihan**, S. A. Crain, C. Adam Dyker “Concerted Two-electron Bipolar Bispyridinylidenes for Symmetric, Organic Redox Flow Batteries” Canadian Chemistry Conference and Exhibition, Vancouver, **Jun 2023** (oral)
3. **M. A. Raihan**, C. A. Dyker “A Multi-electron Transfer Neutral Bipolar Bispyridinylidene Molecule for a Symmetric Organic Redox Flow Battery” Intl. Conf. on Nano-bio and Advanced Materials Engineering in Bangladesh, **Jan 2023** (oral)
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5. **M. A. Raihan**, C. A. Dyker “Two-electron, Low Molecular Weight Bipyridinium-based Symmetric Organic Non-aqueous Redox Flow Battery” UNB Graduate Research Conference, **Feb 2021** (Oral)
6. **M. A. Raihan**, T. Naota “Synthesis and properties of highly strained *cis*-bis(π -extended-salicylaldiminato)platinum(II) complexes” Chemical Society of Japan, **Mar 2018** (Poster)