Desymmetrized Hexasubstituted [3]radialene Anions as Aqueous Organic Catholytes for Redox Flow Batteries

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Desymmetrized Hexasubstituted [3]radialene Anions as Aqueous Organic Catholytes for Redox Flow Batteries

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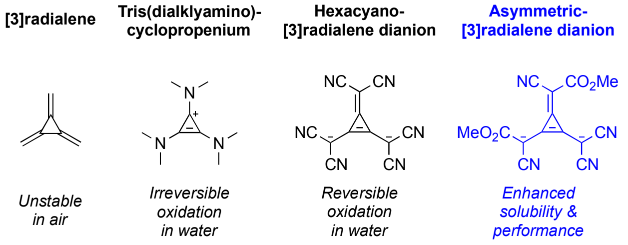
Negatively substituted trimethylenecyclopropane dianions, a subclass of hexasubstituted [3]radialenes, are candidates for use as active species in redox flow batteries (RFBs) due to their stability in water, reversible electrochemistry, and their tailorable synthesis. Hexacyano[3]radialene disodium is investigated as a pH 7 aqueous organic catholyte. The dianion and radical anion are stable in air and aqueous solutions at neutral pH. Systematic introduction of asymmetry via step-wise synthesis leads to enhanced solubility and higher capacity retention during galvanostatic cycling. An aqueous flow cell comprising a disester-tetracyano[3]radialene catholyte, sulfonated-methyl viologen as the anolyte, and a cation exchange membrane provides an operating V_{cell} = 0.9 V, 99.609 % coulombic efficiency, and minimum capacity fade over 50 cycles.

The need for efficient grid-scale energy storage has become crucial as the demand for renewables steadily increases. Redox flow battery (RFB) technologies have emerged as capable electrochemical energy storage devices to mediate the void between power generation and consumption.[1,2] Conventional RFBs use inorganic materials as redox couples (V_2O_5, Zn/Br_2) and corrosive electrolytes such as sulfuric acid.[3–5] Recently, aqueous organic RFBs consisting of light element-based active species have been shown to operate efficiently in laboratory scale devices.[6] Aqueous soluble organic active species offer several advantages over traditional inorganic-based RFBs. Specifically, organic small molecules are earth-abundant compared to traditional vanadium-based active species and are thus more favourable from an economic standpoint.[7] Additionally, organic active species can be tailored synthetically to increase solubility and operating voltage.[8–11] Such modifications translate to RFBs with higher energy densities.

Aqueous organic RFBs that operate at neutral pH are particularly attractive from a technoeconomic and safety standpoint. Specifically, they are non-corrosive, environmentally friendly, and non-flammable. Additionally, they allow for the use of inexpensive electrolytes, such as NaCl, which can be coupled with low-cost ion-exchange membranes.[12,13] It remains a challenge, however, to design soluble and stable organic active species for neutral pH aqueous RFBs. There has been considerable progress in the development of organic anolytes that operate at pH 7, such as anthraquinone[14,15] and methyl viologen[10,12,16] derivatives. However, aqueous organic catholytes are less well studied. While organometallic species, including ferrocyanide[17] and ferrocene derivatives,[12] have been reported as high-performance catholytes, the only all-organic aqueous catholytes are based on derivatives of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl, commonly known as TEMPO.[16,18] Here, we present an initial investigation on a class of radialene dianions for aqueous RFBs and outline a design strategy for developing next-generation radialene-based catholyte materials.

Radialenes are alicyclic compounds in which all ring atoms are sp^2-hybridized and contain cross-conjugated, exocyclic, carbon-carbon double bonds.[19,20] Unsubstituted parent radialenes are difficult to synthesize and polymerize in the presence of oxygen.[21–23] However, many stable substituted radialene derivatives are known and can be prepared efficiently.[24–27] Several radialene derivatives also support multielectron transfer and can be isolated in various oxidation



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

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states.[28] These qualities make such radialene compounds attractive materials for organic RFB applications. Recently, a series of radialene-like imine-cyclopropenium salts have been described as catholytes for non-aqueous RFBs.[29,30] While these salts function as efficient, high voltage, charge-storage species in organic solvents, they are unstable in the presence of even 0.2% water. This precludes their use in aqueous RFBs, the most economical devices for large-scale applications.

Our group has been studying hexacyano[3]radialene disodium ($Na_2C_6(CN)_6$) **1** as a catholyte for aqueous RFBs. This compound, as well as a series of negatively substituted [3]radialene derivatives, were first reported in 1975 by Fukunaga and coworkers.[24,31] The seminal work found that conjugated electronegative functionalities can effectively stabilize the central three-membered cyclopropenium ring and facilitate isolation of [3]radialene derivatives in their dianionic and radical anionic forms. While the neutral radialene $C_6(CN)_6$ is far too reactive for RFB applications, these doubly reduced species fulfill several important prerequisites for use in large-scale energy storage. Specifically, **1** can be synthesized at low temperatures, on a large scale, and in high yield (45g, 91%) using inexpensive precursors. $Na_2C_6(CN)_6$ also exhibits modest solubility in water (< 0.1 M), due to its dianionic nature.[32] Furthermore, **1** is stable in air, and can be sequentially oxidized in two single-electron transfers. The product of the first oxidation, radical anion $\mathbf{1}^{\bullet-}$ is particularly persistent: It can be isolated in high yield via chemical oxidation and stored in air indefinitely. Remarkably, the radical anion is thermally stable to above 180 **°**C.[32] The inherent stability of **1** and persistence of $\mathbf{1}^{\bullet-}$ signifies that the redox couple is favorable for use in a RFB, a device in which long lifespan is required.

The aqueous solubility of **1** is far too low for practical use in RFB applications. Nevertheless, we first used it as a model system to probe the efficacy of hexasubstituted [3]radialenes as redox couples in pH 7 aqueous solutions. Fukunaga, Breslow,[33] and others,[32,34] have reported the electrochemistry of $[C_6(CN)_6]^{2-}$ as a tetrabutylammonium (TBA) salt in organic solvents only. We have determined that both the dianion **1** and radical anion $\mathbf{1}^{\bullet-}$ are stable and exhibit reversible redox activity in aqueous solutions at pH 7. Using cyclic voltammetry (CV), we first established that the one electron oxidation of the dianion to the radical anion occurs at a potential favorable for use as a catholyte for RFBs, 480 mV. This oxidation potential is comparable to that of alkylammonium-functionalized ferrocene[12] (410 mV) and 4-hydroxy-TEMPO[16] (610 mV), two state-of the-art materials recently reported as catholyte components for neutral aqueous RFBs. Plots of the square root of scan rate vs. peak current are linear within the ranges of 0-700 mV/s, which indicates that the redox couple is electrochemically reversible and diffusion- controlled (Fig. 1a). From this data, the Randles-Sevcik equation was used to calculate the diffusion coefficient for the electron transfer process (3.71 x 10^{-6} cm^2/s). This value is almost identical to the diffusion coefficients of hydrophilic ferrocene derivatives in neutral pH solutions of NaCl.[12] Additionally, solutions of both the dianion **1** and radical anion $\mathbf{1}^{\bullet-}$ show no significant changes in peak current height when solutions are left to sit for five days (Fig. S19, ESI†). Such chemical stability is essential for durable RFB electrolytes.

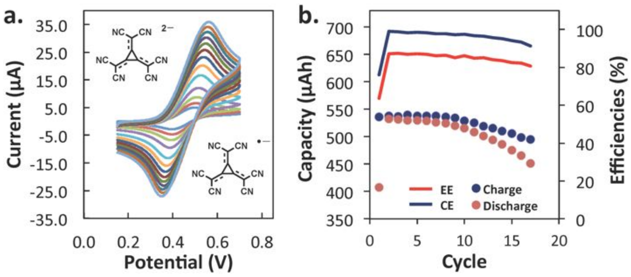
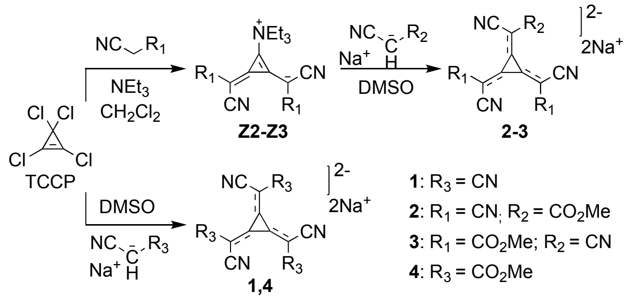


Fig. 1. Cyclic voltammograms (CVs) of **1** (1 mmol) using a glassy carbon (GC) working electrode, Pt auxiliary electrode, and Ag/AgCl reference electrode measured at various scan rates (10-700 mV/s) in water. (b) Plot of capacity, coulombic efficiency (CE), and energy efficiency (EE) for the 1e⁻ cycling experiment of aqueous **1** (10 mM) in an H cell.

We also probed the chemical reversibility of the redox couple in water by performing preliminary galvanostatic charge-discharge measurements using a symmetric H-cell. A Selemion CSO cation-exchange membrane was used to separate the two components of the static H-cell. This membrane has recently been reported as a low-cost alternative to Nafion for neutral aqueous RFBs.[13] We set the voltage cutoffs at 0.8 V and 0.15 V, respectively, to avoid generating the doubly oxidized, neutral, radialene that is unstable in air and insoluble in water. The desired couple exhibits $1e^-$ charge–discharge cycling, with high energy and coulombic efficiencies (Fig. 1b). However, we observed a significant capacity fade after more than ten cycles. We hypothesize that radical dimerization, a common issue in organic radical-based RFB electrolytes, results in the observed drop in capacity.[35] These initial studies encouraged us to make synthetic modifications to **1** in order to both increase solubility and mitigate dimerization.

A logical first step toward higher solubility [3]radialene derivatives is to disrupt symmetry and increase hydrophilicity. Conveniently, a simple synthetic methodology to prepare asymmetric [3]radialene derivatives is well known.[24,31] This route proceeds through a stable zwitterionic intermediate and allows numerous hexasubsitituted [3]radialenes to be prepared. We systematically substituted one nitrile group at a time in an effort to preserve the favorable oxidation potential of the redox couple. To this end, we prepared a series of asymmetric, ester-substituted, [3]radialene species using the zwitterionic prep described above (Scheme 2). The aqueous solubilities of these compounds in both the dianionic and radical anionic states were determined using UV/Vis spectroscopy (Table 1). We prepared the mono-ester (**2**) and found that substituting one nitrile group with a methyl-ester unit improves the aqueous solubility significantly. Encouraged by this marked enhancement, we synthetized the corresponding di- and tri- ester functionalized [3]radialenes (**3** & **4**) for comparison. Increasing the number of methyl ester moieties results in higher solubility for the disodium salts (Table 1). Remarkably, the tri-ester **3** exhibits a solubility of 0.82 M in water. These results demonstrate that even slight molecular modifications of the hexasubstituted [3]radialene scaffold drastically boosts aqueous solubility. It should be noted that we observe a decrease in oxidation potential as a tradeoff for



Scheme 2. Synthesis of zwitterionic intermediates **Z2**-**Z3** and compounds **1-4.**

increased solubility. Desymmetrized derivatives containing more electron deficient esters could address this divergence.

Density functional theory (DFT) calculations were performed to determine the spin density maps of **1-4** as radical anions (Fig. S22, ESI†). Calculations indicate that the spin density is most prominently localized on the methyl ester alpha-carbons in compounds **2-4**. We rationalize this in terms of electron density: the more electron-rich cyanoester sites are easier to ionize than the malononitrile methylene. The spin density maps of $\mathbf{4}^{\bullet-}$ show the radical character to be distributed symmetrically, increasing the likelihood of π-dimerization. These calculations support the observed low solubility of $\mathbf{4}^{\bullet-}$ in water. We also observed distinct differences in the UV-vis spectra of the symmetrical radical anions ($\mathbf{1}^{\bullet-}$ & $\mathbf{4}^{\bullet-}$) vs. the asymmetrical congeners ($\mathbf{2}^{\bullet-}$ & $\mathbf{3}^{\bullet-}$) that corroborate the spin density calculations. Specifically, the single absorption feature centered at 288 nm in aqueous solutions of $\mathbf{1}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$ is split into two peaks in the spectra of $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ (Figs. S6 & S9, ESI†). We attribute this splitting to the break in symmetry, which causes the SOMO orbitals to no longer be degenerate.

Diester **3** was selected for further electrochemical analysis due to its favorable solubility in both redox states and its adequate oxidation potential in water. CV time studies over a period of three days reveal that the diester dianion **3** is stable in water (Fig. S21, ESI†). UV/Vis studies on aqueous solutions of radical $\mathbf{3}^{\bullet-}$ also show minimal changes over a period of 72 hours (Fig. S10, ESI†). Next, a symmetrical H-cell with a cation-exchange membrane separator was used for aqueous galvanostatic charge-discharge experiments (Fig. 2). The compound undergoes steady cycling over a period of 12 days (50 cycles). We observed a high coulombic efficiency (98.2%) and respectable energy efficiency (75.6%) over 50 cycles. Capacity retention in this H-cell experiment is also improved compared to the first generation $Na_2C_6(CN)_6$-based electrolytes. These results are particularly noteworthy considering the cycling studies on **3** were performed under higher concentration conditions that promote dimerization. We ascribe the higher relative capacity retention to the structure of **3**, which was confirmed for the bis(tetrabutylammonium) (TBA) salt of **3** using single crystal X-ray diffraction. The structure clearly shows the asymmetry of the molecule and that the flexible methyl ester groups of **3** force the molecular surface to deviate from planarity (Fig. 2a). These features are expected to inhibit radical dimerization, which is hypothesized to lead to decreases in capacity.

Table 1. Solubility and Electrochemical Properties of **1**-**4**

	1	2	3	4
Solubility[a]	< 0.1 M	0.19 M	0.45 M	0.82 M
Radical Anion Solubility[b]	< 25 mM	0.08 M	0.17 M	< 25 mM
Conductivity (mS/cm)[c]	13.2 (0.147)	15.7 (2.36)	36.7 (23.2)	39 (0.23)
$E^{ox}_{1/2}$[d]	0.48 V	0.4 V	0.35 V	0.27 V[e]
i_{pc}/i_{pa}	1.03	0.97	1.06	1.15

[a] *Calculated from saturated aqueous solutions using UV/Vis spectroscopy.*
[b] *Measured as a potassium (K^+) salt*
[c] *Measured on saturated aqueous solutions. Values for radical species shown in parentheses.*
[d] *Recorded at 100 mV/s using a glassy carbon electrode & Ag/AgCl reference electrode in water.*
[e] *Measured using 0.25 M KCl as supporting electrolyte*

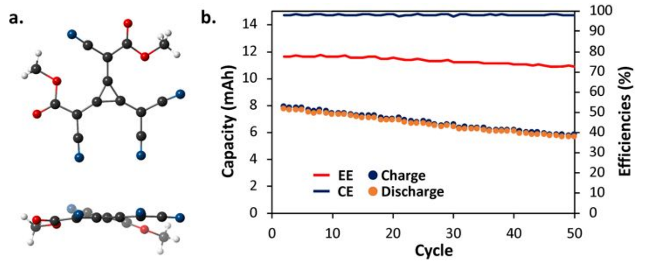


Fig. 2. (a) Top and side ball-and-stick views of single crystal structure of 2TBA•**3** (Carbon, black; hydrogen, white; nitrogen, blue; oxygen, red). TBA counterions omitted for clarity. (b) Plot of capacity, coulombic efficiency, and energy efficiency for the 1e⁻ cycling experiment of aqueous **3** (0.1 M) in an H cell.

Finally, a laboratory scale flow cell was constructed using **3** as the catholyte and 1,1′-bis(3-sulfonatopropyl)-4,4′-bipyridinium [$MV(SO_3)_2$] as the anolyte. This anolyte was selected due to its ability to facilitate cation exchange with **3** during redox cycling. The cell has a theoretical operating voltage of 0.9 V and uses a carbon-felt electrode (SGL GFD / 5 cm^2 active area) with a serpentine flow field (Fig. 3a). The flow rate was set to 2.5 mL/min with a current density of 3 mA/cm^2. We observed high coulombic efficiency (99.609%) over a time period of 50 cycles (Fig. S28, ESI†). The electrochemical yield of the flow cell, which considers the experimental vs. theoretical capacity, was steady around 25 %. This capacity is lower than expected. However, the low observed capacity fade over fifty cycles is noteworthy. We observe a capacity loss of 0.046% per cycle under these flow cell conditions. Additionally, we observed that aqueous solutions **3** are sufficiently conductive at 0.1 M, without the addition of NaCl supporting electrolytes, due to their inherent charge. This is advantageous for further lowering capital costs of future [3]radialene-based RFB implementation.

In summary, we have determined that hexasubstituted [3]radialene dianions are attractive catholytes in neutral pH RFBs. The [3]radialene scaffold was found to be amenable to synthetic modifications that can increase its performance as a catholyte. Significant enhancements in aqueous solubility and cycling stability were obtained by desymmetrization and planarity disruption. A laboratory scale flow cell consisting of a diester-tetracyano [3]radialene catholyte coupled to a viologen anolyte showed steady cycling with high coulombic efficiency over 50 cycles. Finally, the addition of hydrophilic functionalities is expected to further increase the maximum solubility of these promising active species. Such derivatives are currently under

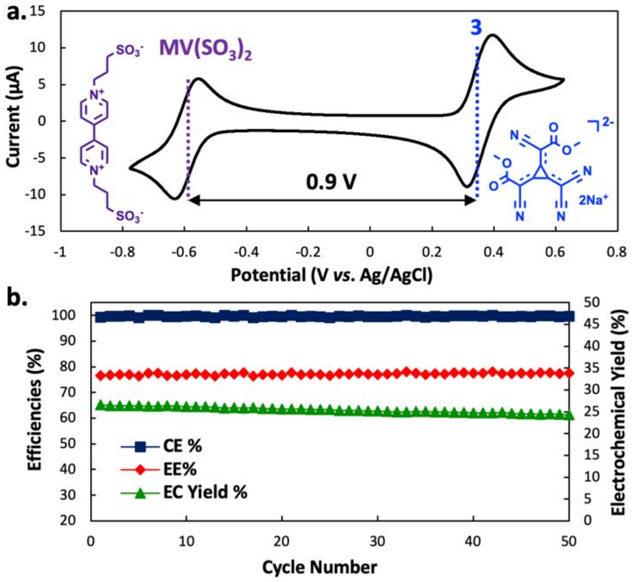


Fig. 3. (a) Cyclic voltammogram of a mixture containing sulfonatopropyl-methyl viologen (MV(SO$_2$)$_2$, 1 mM) as the anolyte (purple) and **3** (1 mM) as the catholyte (blue). (b) Electrochemical yield, coulombic efficiency, and energy efficiency of a 0.1 M flow cell containing MV(SO$_2$)$_2$ and **3** over 50 cycles. The theoretical volumetric capacity and energy density are 2.6 Ah/L and 2.34 Wh/L, respectively.

investigation in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

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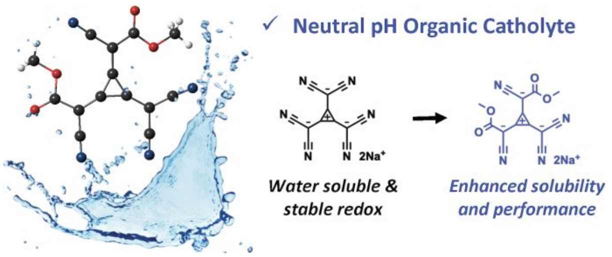
TOC Graphic



Hexasubstituted [3]radialenes can be synthetically tuned to function as catholyte materials for neutral pH aqueous organic redox flow batteries.