Highly Soluble Imidazolium Ferrocene Bis-sulfonate Salts for Redox Flow Battery Applications

Briana R. Schrage,‡ Baosen Zhang,‡ Stephen C. Petrochko, Zhiling Zhao, ‡ Ariana Frkonja-Kuczín, Aliaksei Boika,* and Christopher J. Ziegler*

Department of Chemistry, University of Akron, Akron, Ohio 44312-3601, United States

KEYWORDS Redox flow batteries, ferrocene bis-sulfonate, imidazolium salts, solubility, aqueous electrochemistry

ABSTRACT: Redox flow batteries (RFBs) are scalable devices that employ solution-based redox active components for scalable energy storage. In order to maximize energy density, new highly soluble catholyte and anolytes need to be synthesized and evaluated for their electrochemical performance. To that end, we have synthesized a series of imidazolium ferrocene bis-sulfonate salts as highly soluble catholytes for RFB applications. Six salts with differing alkyl chain lengths on the imidazolium cation have been synthesized, characterized, and electrochemically analyzed. While aqueous solubility was significantly improved, the reactivity of the imidazolium cation and the increased viscosities of the salt solutions in water (which increase with increasing imidazolium chain length) limit the applicability of these materials to RFB design.
Introduction

The continued research into rechargeable battery systems is the result of a continuing need for energy storage technology. Over the past few decades, redox flow batteries (RFBs) have emerged as possible energy storage solutions. In comparison to solid state batteries like lithium-ion based systems, flow batteries have a high degree of design flexibility. RFBs can be utilized for large scale energy storage needs, the electroactive materials tend to be lower in cost, and the systems can undergo rapid recharging. However, many current RFB designs are known to have moderately low energy densities, usually as a result of low solubility of the electroactive species in solution. The all-vanadium RFB is one of the most well studied systems but can only achieve a maximum energy density of 25-35 W h/ L, compared to the Li-ion battery, which can reach energy densities up to 700 W h/ L.

One way to increase power density is by improving the solubility of the electroactive species in solution. The generation of ionic liquids (ILs) and eutectic mixtures are both potential ways to achieve enhanced solubility, and researchers have already begun to investigate these materials. Ionic liquids have been utilized as eco-friendly solvents for organic transformations, media for catalysts, and applications in pharmaceutical production. Additionally, ILs can conduct electricity and can act as substitutes for traditional solvents in battery systems, since IL solvents often have wider working voltage windows in comparison to traditionally used solvents. Discovered in 1914, ethyl ammonium nitrate was one of the earliest known ionic liquids, melting at 12 °C. Typically, ionic liquids are defined as ionic salts with melting points below 100 °C. IL salts have a large degree of tunability as both the anion and cation can be altered to change the physical properties. The anionic component can contain either organic or inorganic species such
as sulfonates, nitrates, halides, PF$_6^-$, and BF$_4^-$, and cationic components are generally organic molecules such as alkyl ammonium, phosphonium, pyridinium, and imidazolium.

Cations such as imidazolium salts are important precursor molecules for the synthesis of N-heterocyclic carbenes. However, these salts are useful for other applications including the formation of ionic liquids and ionic liquid crystals. Researchers have most recently begun to utilize imidazolium salts as reagents for highly soluble RFB electrolytes. Synthetic efforts either utilize an imidazolium cation paired with an electroactive anion, or systems where the imidazolium N-substituted group is covalently bound to a redox active moiety.

Over the past ten years ferrocene-based electrolytes have been investigated for their use in RFBs. Ferrocene has a highly stable and reversible redox couple making the molecule useful as a scaffold for RFB material designs. Unmodified ferrocene has negligible water solubility, but aqueous battery systems containing cationic tetraalkylammonium modified ferrocenes with varying anions have been widely used in aqueous RFB devices. Liu and coworkers reported the (ferrocenylmethyl)trimethylammonium chloride reaching concentrations up to 4 M in H$_2$O and 3 M in 2 M NaCl.

We have recently successfully designed and implemented an aqueous battery system that pairs the disodium ferrocene-1,1'-bis(sulfonate) salt (1,1'-FcDS) with disodium anthraquinone-2,7-disulfonate salt (2,7-AQDS). Although we varied the electrolyte conditions, we were only able to achieve maximum solubility of ~ 0.3-0.6 M for 1,1'-FcDS. In order to compete with current battery systems, we sought to synthesize highly soluble ferrocene-1,1'-bis(sulfonate)ferrocene dianionic salts with varying imidazolium cations (Figure 1). In this report, we present the synthesis, characterization, and electrochemical properties of a series of imidazolium ferrocene bis
sulfonate salts. Some of these compounds exhibit ionic liquid properties, but all show significantly improved solubility over alkali metal ferrocene bis sulfonate salts. All compounds exhibit reversible redox behavior in cyclic voltammetry experiments, and the RFB performances of these materials are indicative of how ferrocene salts can be further improved as electroactive battery materials.

**Figure 1.** The imidazolium salt cations (left) used in this report, and the ferrocene bis sulfonate anion (right).

**Results and Discussion**

The syntheses of the imidazolium ferrocene sulfonate salts were based on our previous work in which we generated “all-ferrocene” salts via simple ion metatheses.\(^1\) Bis ferrocene sulfonic acid is generated via the reaction of ferrocene and chlorosulfonic acid.\(^2\) Our group has used this reagent in the past to make sulfonamide conjugates containing amino acids, and biomolecules, as well as various electrochemically active sulfonate salts.\(^41\)–\(^45\) The bis ferrocene sulfonic acid was initially reacted with Ag\(_2\)O to generate silver salts *in situ* with subsequent introduction of the imidazolium halide salts to afford pure materials 1–6 (Scheme 1). The preparation of the silver ferrocene salt was completed first to reduce the generation of silver N-heterocyclic carbenes, as they are classically prepared by reacting imidazolium salts with silver(I) oxide.\(^46\)\(^,\)\(^47\)
Scheme 1. Synthetic route for preparation of the compounds 1-6.

All the compounds were fully characterized, and the structures of 1, 2, and 5 were elucidated by single crystal X-ray crystallography as shown in Figure 2. The ferrocene bis sulfonate unit has identical structural features to previously solved structures with varying cations\(^{44,48-51}\). The packing diagrams of 1 and 2 shown in Figure S22-S24, display a tightly packed structure with the cationic imidazolium heads in close proximity to the sulfonate anions. The alkyl chains in compound 2 are tightly folded in an L-shaped conformation. As the alkyl chain increases to \(n = 10\) (compound 5), the packing is less efficient, and the alkyl chains are stretched along the plane of the imidazolium ring. The ferrocene sulfonate and imidazolium core form a hydrophilic domain that is separate from the hydrophobic layer of the alkyl chains. These alternating hydrophilic and hydrophobic layers form a bilayer structure and are seen in other crystal structures of imidazolium salts with long alkyl chains\(^{30,52-54}\).

To evaluate the utility of the imidazolium 1,1’-FcDS salts for RFB applications, we probed their electrochemical activity. The cyclic voltammograms of the 3 and 2,7-AQDS are shown in Figure 3. Cyclic voltammograms of compound 3 at different scan rates (Figure 4a) were also collected to evaluate its diffusion coefficient (D). Figure 4b shows a plot of corresponding peak current versus the square root of scan rates. The diffusion coefficient can be calculated by the Randles-
Sevcik equation \( i_p = 0.4463 \left( \frac{F^3}{RT} \right)^{0.5} n^{1.5} A C_0 v^{0.5} \), where \( i_p \) is peak current (A), \( n \) is the number of electrons in redox process (n=1), \( A \) is the area of glassy carbon electrode, \( C_0 \) is the concentration of the ferrocene salt. Based on this calculation, the resulting diffusion coefficient for imidazolium 1,1’-FcDS compound 3 is \( 1.10 \times 10^{-6} \) cm\(^2\)/s. The obtained diffusion coefficient in water was comparable with the value published previously for ferrocene sulfonate salts.\(^{40,41,44}\) The electrochemical data for imidazolium 1,1’-FcDS compound 3 are summarized in Table 1.

**Figure 2.** Structure of compounds 1, 2 and 5, with 35% probability ellipsoids. Hydrogen atoms have been omitted for clarity.
Figure 3. Cyclic voltammograms of compound 3 and AQDS (orange curve). Dashed line represents the half wave potential of corresponding materials.

The imidazolium 1,1’-FcDS salts are extremely water soluble, resulting in potentially high energy densities for resultant RFBs. The theoretical volumetric capacity (Ah/L) can be calculated by Faraday’s law $Q_v = nFC$, where $n$ is the number of electrons ($n=1$), $F$ is Faraday’s constant (26.8 Ah/mol), and $C$ is the solubility (mol/L). A 2 M solution concentration of an imidazolium FcDS salt would result in an energy density of 34.84 Wh/L, which is comparable to VRFB (25-30 Wh/L). With alternate, more soluble anolytes instead of AQDS, an even higher theoretical energy density could be achieved. Therefore, the highly soluble imidazolium 1,1’-FcDS has the theoretical potential to afford RFB devices with extremely high energy densities.
Table 1. Electrochemical data for compound 3.

<table>
<thead>
<tr>
<th>Compound (supporting electrolyte)</th>
<th>Imidazolium Fc (0.5M H₂SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁/₂ (V) versus SCE</td>
<td>0.605</td>
</tr>
<tr>
<td>D (cm²/s)</td>
<td>1.102E-6</td>
</tr>
<tr>
<td>Solubility (M)</td>
<td>2</td>
</tr>
<tr>
<td>Theoretical capacity (Ah/L)</td>
<td>53.60</td>
</tr>
<tr>
<td>Theoretical energy density (Wh/L)</td>
<td>34.84</td>
</tr>
</tbody>
</table>

Figure 4. (A) CVs for 3 mM of compound 3 in aqueous solution. 0.5 M H₂SO₄ was added as supporting electrolyte. The working electrode is glassy carbon electrode (3 mm diameter). The reference electrode is Ag|AgCl|KCl (2M). The counter electrode is platinum wire. The scan rate varies from 20 mV/s to 65 mV/s. (B) Plot of the corresponding peak current as a function of square root of scan rate.
To initially evaluate our imidazolium salts, we selected compound 3 as a representative example and constructed a low concentration cell (see Figure 3 for CVs of compound 3 and AQDS). A full battery test was performed with 15 mL 20 mM compound 3 as the catholyte and 25 mM AQDS as the anolyte. Both the catholytic and analytic chambers used 0.5 M H₂SO₄ as the supporting electrolyte. A larger concentration of AQDS was used to make sure that the full capacity of the imidazolium 1,1’-FcDS salt could be evaluated. The charge/discharge performance was evaluated at the current density of 3 mA/cm² and the curves are shown in Figure 5a. The trends of the coulombic efficiency (CE) and energy efficiency (EE) of the Fc/AQDS RFB are shown in Figure 5b. The CE stays above 99% for over 80 charge-discharge cycles. The EE is stable at about 56%, which is an acceptable level for a RFB. However, compared to the sodium salt of 1,1’-FcDS, there is a lower energy density, which results from the high viscosity of the solution. A capacity loss is observed the Figure 5b, and since AQDS is quite stable under these conditions with little crossover, we attribute this to the ferrocene side of the RFB device.
Figure 5. RFB experiments on a device comprised of compound 3 and AQDS at a concentration of (20 mM) with 0.5 M H\textsubscript{2}SO\textsubscript{4} as the supporting electrolyte. a) charge and discharge cycles at current density of 3 mA/cm\textsuperscript{2}; b) charge and discharge capacity versus cycle number; c) CE and EE vs cycle number.

Figure 6 shows the CVs of the solutions of compound 3 and AQDS after cycling in the above described RFB. Based on this post-cycling analysis, there is no significant crossover of compound 3 because no redox process is observed in the resultant AQDS solution that could be attributed to a ferrocene derivative. Therefore, we surmise that ferrocene degradation is taking place during the
charge/discharge process. Previously, we have observed some degradation of 1,1’-FCDS in cells under nucleophilic conditions. Imidazolium cations are known to be acidic, forming N-heterocyclic amines that can act as nucleophilic groups.

![Graph](image)

**Figure 6.** Post-cycling CV analysis of catholyte and anolyte solutions. The post-cycling solutions were diluted 2 times. The working electrode is glassy carbon electrode (3 mm diameter). The reference electrode is Ag/AgCl/KCl (2M). The counter electrode is platinum wire. The scan rate is 30 mV/s.

The advantage of the imidazolium 1,1’-FcDS-salt based RFB results from their high solubility in water, thus very high theoretical capacities can potentially be achieved. We therefore evaluated the performance of a higher concentration battery. A 10 mL aliquot of 0.3 M catholyte solution with salt 3 and 30mL of 0.1 M anolyte AQDS were utilized to evaluate the feasibility of a higher concentration battery. The charge/discharge profiles, charge/discharge capacity and efficiency
(CE, EE) are presented in Figure 7. A large capacity loss is observed resulting from the degradation of imidazolium Fc as shown in the post-cycling CV analysis (Figure 8). The EE decreases to 25%, a worse performance compared to the low concentration battery.

**Figure 7.** Performance of imidazolium Fc (3) (0.3M)/AQDS RFB with 0.5 M H₂SO₄ as the supporting electrolyte. (A) charge and discharge cycles at current density of 3 mA/cm²; (B) charge and discharge capacity versus cycle number; (C) CE and EE vs cycle number.
Another factor that affects the performance of the high concentration battery results from the viscosity of the imidazolium salt \( \text{3} \) in water, resulting in significant energy loss. We measured the viscosity of 0.2 M of salt \( \text{3} \) in nanopure water using a falling ball viscometer. The dynamic viscosity (cp) was calculated by the formula \( \mu = K(\rho_s - \rho_f)t \), where \( K \) is viscometer constant, \( \rho_s \) is density of ball (g/mL), \( \rho_f \) is density of fluid (g/mL), \( t \) is time of descent (minutes). The dynamic viscosity is 220 cp, which is higher than reported for VRFB.\(^{55} \)

\[ \text{Figure 8. Post-cycling CV analysis of imidazolium Fc solutions. The working electrode is glassy carbon electrode (3 mm diameter). The reference electrode is Ag|AgCl|KCl (2M). The counter electrode is platinum wire. The scan rate is 30 mV/s.} \]
Conclusions

In conclusion, we have synthesized, characterized, and evaluated a series of imidazolium 1,1’-FcDS salts as potential catholytes for energy storage applications. These compounds are readily produced as pure materials via cation metathesis and, depending on the length of the alkyl chain on the imidazolium cation, are either low melting solids or viscous ionic liquids. All are highly soluble in water and many organic solvents, easily achieving the concentrations needed for a successful RFB device. However, the performance of these materials was limited by decomposition problems as well as issues with viscosity. We are continuing our investigations into the performance of ferrocene-based materials for RFB applications.

Experimental

All reagents and starting materials were purchased from commercial vendors and used without further purification. Bis ferrocene sulfonic acid was prepared according to the previously published procedure.\textsuperscript{51} The imidazolium halide salts were synthesized according to previously published procedures.\textsuperscript{28,56–60} Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Nanopure water was obtained from a Milli-Q Integral 5 water purification system (Millipore, Bedford, MA).

NMR spectra were recorded on 300 MHz and 500 MHz spectrometers and chemical shifts were given in ppm relative to residual solvent resonances (\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra). High-resolution mass spectrometry experiments were performed on a Bruker MicroTOF-III and MicroTOF-qIII instruments. Compounds 1-6 were observed as ion pair clusters, ([Imidazolium\textsuperscript{+}][Imidazolium\textsuperscript{+}](1,1'-FcDS-anion\textsuperscript{-})]; these clusters are commonly seen in the mass spectra of other ionic liquids.\textsuperscript{61–63}
X-ray intensity data were measured on a Bruker CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, $\lambda = 1.54178$ Å, Mo Kα radiation, $\lambda = 0.71073$ Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K (Oxford Cryosystems). The detector was placed at a distance of 5.00 cm from the crystal. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of $F^2$ converged. CCDC 2079830-2079832 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

**Electrochemical characterization.** Cyclic voltammetry electrochemical measurements were conducted with a CHI 920d potentiostat in a standard three-electrode configuration. The working electrode was a glassy carbon disk with a diameter of 3 mm. The reference electrode was a Ag|AgCl|KCl (2M). The counter electrode was platinum wire. The solution used is 3 mM of imidizolium Fc in 0.5 M H$_2$SO$_4$. The electrochemical information of AQDS was reported in our previous paper. The Cyclic voltammograms (CVs) were collected at scan rates varying from 20 to 65 mV/s for the measurement of the diffusion coefficients (D) of imidazolium Fc using Randles-Sevcik equation. The open circuit potential (OCP) under 0.5 H$_2$SO$_4$ is evaluated by comparing the CVs at scan rate of 30 mV/s of imidazolium Fc and AQDS.

**Flow cell tests.** The cation exchange membrane (Nafion 117) was sandwiched with two carbon felt electrodes (G100, AvCarb, USA). Two pieces of silicon foam were used to hold the carbon felt electrodes. Two copper plates were used at the end as current collector. The surface area of the carbon felt is 6.25 cm$^2$. The membrane and carbon felt electrodes were immersed in 0.5M H$_2$SO$_4$.
for 8 hours before cycling tests. The catholytes reservoirs contain 15 mL of 20mM Fc and anolytes reservoirs contain 15mL of 25mM AQDS. Excess of AQDS were used to make Fc side as capacity limiting side. A Masterflex L/S peristaltic pump (Core-Parmer, USA) was used to circulate the electrolytes counter direction at a rate of 40 mL/min. The flow cell was charged/discharged at current density of 3 mA/cm² for 100 cycles in the glovebox filled with Argon.

**Syntheses**

**Synthesis of 1-6.** The procedure for generating 1 is representative for these syntheses except 1-methyl-3-pentylimidazolium bromide (0.34 g, 1.4 mmol) was used in 2, 1-methyl-3-hexylimidazolium bromide (0.36 g, 1.4 mmol) was used in 3, 1-methyl-3-octylimidazolium bromide (0.40 g, 1.4 mmol) was used in 4, 1-methyl-3-decylimidazolium bromide (0.44 g, 1.4 mmol) was used in 5, and 1-methyl-3-dodecylimidazolium bromide (0.48 g, 1.4 mmol) was used in 6. 1,1’-bis ferrocene sulfonic acid (0.25 g, 0.72 mmol), and Ag₂O (0.17 g, 0.72 mmol) in DI water (5.00 mL) were stirred in the dark, at room temperature for 30 min. To this solution, two equivalents of 1,3-dimethylimidazolium iodide (0.32 g, 1.4 mmol) were added, and the solution continued stirring at room temperature overnight. The AgI was filtered, and the filtrate was freeze dried resulting in brown crystalline solids (1, 2, 5, and 6), and brown oils (3 and 4). Crystals of 1, 2 and 5 suitable for X-ray diffraction were taken from the freeze dried solutions of water.

**1:** Yield: 0.37 g (95%). ^1^H NMR (300 MHz, d6-DMSO): δ = 9.03 (s, 2H), 7.67 (s, 4H), 4.26 (s, 4H on C₅H₄), 4.07 (s, 4H on C₅H₄), 3.83 (s, 12H). ^13^C{^1^H} NMR (125 MHz, d6-DMSO): δ = 136.2, 122.5, 69.6, 67.3, 34.8. HRMS (ESI-TOF, positive mode) m/z: calcd for C₂₅H₃₅FeN₆O₆S₂ 635.1403, found 635.1378 [M+C₅H₉N₂]^+.  

16
2: Yield: 0.43 g (92%). $^1$H NMR (300 MHz, d6-DMSO): $\delta = 9.14$ (s, 2H), 7.77 (s, 2H), 7.71 (s, 2H), 4.28 (s, 4H on C$_5$H$_4$), 4.15 (m, 4H), 4.08 (s, 4H on C$_5$H$_4$), 3.84 (m, 6H), 1.78 (m, 4H), 1.32-1.21 (m, 8H), 0.87 (t, 6H, J = 7.3 Hz). $^{13}$C{$^1$H} NMR (125 MHz, d6-DMSO): $\delta = 136.6, 123.6, 122.2, 97.1, 70.3, 67.8, 48.7, 35.7, 30.5, 29.3, 25.1, 21.8, 13.8$.

HRMS (ESI-TOF, positive mode) m/z: calcd for C$_{37}$H$_{59}$FeN$_6$O$_6$S$_2$ 803.3281, found 803.3240 [M+C$_8$H$_{17}$N$_2$]$^+$. 

3: Yield: 0.43 g (87%). $^1$H NMR (300 MHz, d6-DMSO): $\delta = 9.16$ (s, 2H), 7.78 (s, 2H), 7.71 (s, 2H), 4.28 (m, 4H on C$_5$H$_4$), 4.15 (m, 4H), 4.08 (m, 4H on C$_5$H$_4$), 3.85 (m, 6H), 1.77 (m, 4H), 1.26 (m, 12H), 0.86 (t, 6H, J = 6.7 Hz).

$^{13}$C{$^1$H} NMR (125 MHz, d6-DMSO): $\delta = 136.6, 123.6, 122.2, 97.1, 70.3, 67.8, 48.7, 35.7, 30.5, 29.3, 25.1, 21.8, 13.8$.

HRMS (ESI-TOF, positive mode) m/z: calcd for C$_{40}$H$_{65}$FeN$_6$O$_6$S$_2$ 845.3751, found 845.3725 [M+C$_{10}$H$_{19}$N$_2$]$^+$. 

4: Yield: 0.49 g (92%). $^1$H NMR (300 MHz, d6-DMSO): $\delta = 9.15$ (s, 2H), 7.77 (s, 2H), 7.71 (s, 2H), 4.28 (m, 4H on C$_5$H$_4$), 4.14 (m, 4H), 4.08 (m, 4H on C$_5$H$_4$), 3.84 (m, 6H), 1.77 (m, 4H), 1.25 (m, 20H), 0.86 (t, 6H, J = 7.0 Hz).

$^{13}$C{$^1$H} NMR (125 MHz, d6-DMSO): $\delta = 136.7, 123.6, 122.2, 97.1, 70.3, 67.8, 48.7, 35.7, 31.1, 29.3, 28.4, 28.3, 25.4, 22.0, 13.9$.

HRMS (ESI-TOF, positive mode) m/z: calcd for C$_{46}$H$_{77}$FeN$_6$O$_6$S$_2$ 929.4690, found 929.4641 [M+C$_{12}$H$_{23}$N$_2$]$^+$. 

5: Yield: 0.54 g (95%). $^1$H NMR (300 MHz, d6-DMSO): $\delta = 9.12$ (s, 2H), 7.77 (s, 2H), 2.70 (s, 2H), 4.27 (m, 4H on C$_5$H$_4$), 4.14 (m, 4H), 4.08 (m, 4H on C$_5$H$_4$), 3.85 (m, 6H), 1.77 (m, 4H), 1.24 (m, 28H), 0.85 (t, 6H, J = 7.0 Hz).

$^{13}$C{$^1$H} NMR (125 MHz, d6-DMSO): $\delta = 136.5, 123.6, 122.2, 97.1, 70.3, 67.8, 48.7, 35.7, 31.2, 29.3, 28.8, 28.7, 28.6, 28.3, 25.4, 22.0, 13.9$.

HRMS (ESI-TOF, positive mode) m/z: calcd for C$_{52}$H$_{89}$FeN$_6$O$_6$S$_2$ 1013.5629, found 1013.5570 [M+C$_{14}$H$_{27}$N$_2$]$^+$. 

6: Yield: 0.51 g (84%). MP: 46-49 ºC. $^1$H NMR (300 MHz, d6-DMSO): $\delta = 9.12$ (s, 2H), 7.77 (s, 2H), 7.70 (s, 2H), 4.28 (m, 4H on C$_5$H$_4$), 4.14 (m, 4H), 4.08 (m, 4H on C$_5$H$_4$), 3.84 (m, 6H),
1.76 (m, 4H), 1.24 (m, 36H), 0.85 (t, 6H, J = 7.0 Hz). $^{13}$C \{$^1$H$\}$ NMR (125 MHz, d6-DMSO): $\delta =$ 136.5, 123.6, 122.2, 97.1, 70.2, 67.8, 48.7, 35.7, 31.2, 29.3, 29.0, 28.9, 28.8, 28.7, 28.6, 28.3, 25.4, 22.0, 13.9. HRMS (ESI-TOF, positive mode) m/z: calcd for C$^{_{58}}$H$^{_{101}}$FeN$^{_{6}}$O$^{_{6}}$S$^{_{2}}$ 1097.6568, found 1097.6553 [M+C$^{_{16}}$H$^{_{31}}$N$^{_{2}}$]$^{+}$.

ASSOCIATED CONTENT

Electronic supplementary information (ESI) available: Synthetic procedures, spectroscopic data, and X-ray parameters. CCDC 2079830-2079832 contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: XXX

AUTHOR INFORMATION

Corresponding Author

* Co-corresponding authors. E-mails: aboika@uakron.edu (A.B.), ziegler@uakron.edu (C.J.Z.)

Present Addresses

†Present address: Institute for Bioscience and Biotechnology Research, University of Maryland, College Park, Maryland 20742, United States.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

Funding Sources

National Science Foundation (CHE-1665267)
ACKNOWLEDGMENT

The authors are grateful to The University of Akron and the National Science Foundation (CHE-1665267) for support of this research.

ABBREVIATIONS

RFB, Redox flow battery; IL, ionic liquid; 1,1′-FcDS, ferrocene-1,1′-bis(sulfonate); 2,7-AQDS, anthraquinone-2,7-disulfonate

REFERENCES


(6)  Alotto, P.; Guarnieri, M.; Moro, F. Redox Flow Batteries for the Storage of Renewable


(49) Xie, J.; Abrahams, B. F.; Zimmermann, T. J.; Mukherjee, A.; Wedd, A. G. Ferrocene Mono-


Synopsis

The synthesis of new imidazolium ferrocene bis-sulfonate salts result in highly soluble catholytes suitable for redox flow battery (RFB) applications. These salts are soluble in water and many organic solvents, allowing for high concentrations needed for an effective RBF device.

TOC graphic