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The Influence of the Nature of Redox-Active Moieties on the Properties of Redox-Active Ionic Liquids and on Their Use as Electrolyte for Supercapacitors

Philipp S. Borchers ^{1,2,†} , Patrick Gerlach ^{2,3,†}, Yihan Liu ^{2,3} , Martin D. Hager ^{1,2,4} , Andrea Balducci ^{2,4,*} and Ulrich S. Schubert ^{1,2,4,*}

- ¹ Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany; philipp.borchers@uni-jena.de (P.S.B.); martin.hager@uni-jena.de (M.D.H.)
- ² Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany; Patrick.Gerlach@uni-jena.de (P.G.); Yihan.Liu@uni-jena.de (Y.L.)
- ³ Institute for Technical Chemistry and Environmental Chemistry, Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany
- ⁴ Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany
- * Correspondence: andrea.balducci@uni-jena.de (A.B.); ulrich.schubert@uni-jena.de (U.S.S.); Tel.: +49-3641-9-48464 (A.B.); +49-3641-9-48201 (U.S.S.)
- † Both authors contributed equally to this work.



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Abstract: In this work, two new redox-active ionic liquids, one based on 2,2,6,6-tetramethylpiperidine-*N*-oxide and the other based on 4,4'-bipyridine, are synthesized and characterized. A ferrocene-based redox-active ionic liquid is used for referencing the results. All ionic liquids are formed via salt-metathesis from halogenate to bis(trifluoromethylsulfonyl)imide. Their fundamental thermal characteristics are assessed with differential scanning calorimetry. While the imidazolium ionic liquids show no melting point, the phase transition is well observable for the viologen-based ionic liquid. The properties of the neat redox-active ionic liquids and of binary mixtures containing these ionic liquids (0.1 M) and 1-butyl-1-methyl pyrrolidinium-bis(trifluoromethylsulfonyl)imide have been investigated. Finally, the use of these binary mixtures in combination with activated carbon-based electrodes has been considered in view of the use of these redox-active electrolytes in supercapacitors.

Keywords: redox-active ionic liquids; task-specific ionic liquids; ionic liquid mixtures; supercapacitors; energy storage

1. Introduction

With the first described ionic liquid ethylammonium nitrate, which was reported as early as 1914 by Walden, ionic liquids (ILs) are a long-known class of molecules [1]. After the initial discovery, there was a lack of further research interest on this class of molecules by the scientific community for nearly half a century before the first reports of bimolecular mixtures with very low melting points, comprising aluminum chloride and ethylpyridinium bromide, were published [1]. The field gained further traction after publications from Wilkes and coworkers in 1982, who reported on dialkylimidazolium chloroaluminate [2], and from Grätzel and coworkers in 1996, who reported dialkylimidazolium-based ionic liquids without any metals [3]. Soon after, the high versatility of ionic liquids was recognized, which arises through manifold combinatorial possibilities of cations and anions and their respective tailorability. In the early 2000s, the term “task-specific ionic liquid” was coined and demonstrated the tuneability of ionic liquids to serve as “designer solvents” for a specific task [4,5]. The subject has been reviewed many times, and the interested reader can rely on great reviews, featuring, e.g., the topic from a general point of view [6], as reaction medium [7] and from the perspective of catalysis in cross-coupling reactions [8].

Ionic liquids are salts with a low melting point below 100 °C and can be realized by combining organic cations and organic or inorganic anions with weak ion–ion interactions. Due to favorable properties such as low flammability, low vapor pressure and a wide thermal and electrochemical stability window, this substance class became attractive for application in electrochemical energy storage devices [9–11]. In the past, ILs have been used as electrolytes in various applications such as supercapacitors, metal-ion-batteries or organic batteries. In the case of supercapacitors, the main advantage associated with the use of ILs as electrolytes lies in the possibility to realize devices with high operating voltage, which can display high energy and power density in a broad range of temperatures [12–15]. In the case of Li-ion-batteries (LIBs), it has been shown that ILs can suppress side reactions, e.g., anodic dissolution of Al current collectors, and to improve the overall safety of these devices [16–19]. In the case of organic batteries, the use of ILs might prevent the dissolution of the active material within the electrolyte, increasing the cycling stability of these systems [20–26].

The results reported above have been obtained utilizing aprotic and protic ionic liquids, which are the two most popular classes of ILs. In the last years, nonetheless, redox-active ionic liquids (RAILs) have also attracted increasing attention. As indicated by the name, in this class of ILs, redox-active moieties are introduced to the cation, the anion or to both of them, making these compounds redox-active. RAILs have been considered as anolyte and catholyte for redox flow batteries [27–30] and as redox shuttle additives to prevent overcharge in LIBs [31]. Furthermore, they have been utilized as redox-active electrolytes in supercapacitors. Fontaine et al. showed that the use of biredox ILs represents an interesting strategy to increase the energy of these devices. In spite of these promising results, however, further investigations are required to better understand the advantages and the limits associated with the use of RAILs in supercapacitors [32–42].

In this study, we investigated three RAILs, two based on imidazolium and containing 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) and ferrocene, and one based on viologen as redox-active moieties and bis(trifluoromethylsulfonyl)imide (TFSI) as anion. Initially, the synthesis of these new RAILs is reported in detail. Afterwards, their chemical-physical properties are investigated. Finally, their use as electrolytes in electrochemical double layer capacitors (EDLCs) is considered.

2. Materials and Methods

2.1. Reagents and Instruments

All chemicals were bought from Sigma Aldrich, TCI, Alfa Aesar, Fischer or Acros Organics and used as received. When dry solvents are mentioned, the corresponding solvent was purified by a solvent purification system.

NMR spectra were recorded on Bruker Avance I and Bruker Avance III spectrometers. The data were processed with the Bruker TopSpin software and were referenced against the solvent residual signal.

DSC was measured on a Netzsch 204 F1 Phoenix device with nitrogen as protective gas. Fourier transform infrared spectra (FTIR) were measured with a Shimadzu IRAffinity.

2.2. Synthesis of the Ionic Liquids

Synthesis of 6-bromohexylferrocene 2

The synthesis was carried out as adapted from a procedure from the literature [43].

Aluminum chloride (14.4 g, 108 mmol) was placed in an argon-purged round bottom flask. Anhydrous dichloromethane (100 mL) was added, and the suspension was stirred. 6-Bromohexanoyl chloride (16 mL, 105 mmol) was diluted with dichloromethane (100 mL). The solution was slowly added to the aluminum chloride suspension and the mixture was stirred for three hours until a slightly cloudy, yellowish solution was formed. Ferrocene (20.09 g, 108 mmol) was dissolved in dichloromethane (200 mL) in an argon atmosphere. The activated acid chloride was subsequently slowly added to the ferrocene solution, which readily changes its color from reddish-brown to purple. After complete addition of the

acyl chloride, the solution was stirred for 24 h. It was then cooled from the outside with crushed ice, and sodium borohydride in diglyme (2 M, 57 mL) was carefully added. The solution was stirred for four hours while warming to ambient temperature. Aqueous hydrochloric acid solution (0.1 M, 50 mL) was added in small portions. The crude product was subsequently extracted with diethyl ether/HCl (0.1 M) three times (50 mL each), and the combined organic phases were dried over anhydrous sodium sulfate. The solvent was removed, and the crude product was subjected to column chromatography (silica, hexane/EtOAc, 98/2 r_F = 0.36). The product (24.4 g, 65%) was received as brown oil. Analytical data are in agreement with the literature [43].

^1H NMR (CD_2Cl_2 , 300 MHz, δ): 4.11–4.06 (m, 9 H, Fc-H), 3.49–3.44 (t, J = 7.8 Hz, 2 H, Br-CH₂), 2.39–2.34 (t, J = 8 Hz, 2 H, Fc-CH₂), 1.94–1.85 (p, J = 7.7 Hz, 2 H, Br-CH₂-CH₂), 1.60–1.33 (m, 6 H, CH₂ + residual water).

Synthesis of *N*-6-ferrocenehexyl-*N'*-methylimidazolium bromide

The bromide (4.7 g, 13.4 mmol) was dissolved in toluene (18 mL), and methylimidazole (2 mL, 25.2 mmol) was added. The solution was stirred at 80 °C overnight. The solvent was removed in vacuo and the residue was dissolved in methanol. After sufficient methanol was added for complete dissolution, the solution was slowly dripped into a stirred tenfold excess of diethyl ether. The mixture was then filtrated, and the brown solid was washed with fresh diethyl ether. Residual solvent was removed and the product (5.77 g, 90%) was received as orange crystals and used as received.

Synthesis of *N*-6-ferrocenehexyl-*N'*-methylimidazolium bis(trifluoromethanesulfon)imide 3

The bromide (5 g, 11.6 mmol) was dissolved in water (5 mL). LiTFSI (6.7 g) was dissolved in water (2 mL), and the solution was then added to the ferrocene solution. Dichloromethane (10 mL) was added, and the mixture was stirred vigorously overnight. Both phases were diluted with 30 mL of the corresponding solvent, and the organic phase was separated and subsequently washed with LiTFSI solution (2 × 50 mL water with each 3 g LiTFSI) and then once with water. The organic phase was dried with anhydrous Na₂SO₄, and the solvent was removed. The product was received after drying the red oil thoroughly in vacuo as a viscous red fluid (7.32 g, 78%).

^1H NMR (CDCl_3 , 300 MHz, δ): 8.81 (s, 1 H, Im-H), 7.57–7.51 (m, 2 H, Im-H), 4.20–4.11 (m, 11 h, Fc-H and Im-CH₂), 3.91 (s, 3 H, Im-CH₃), 2.33–2.28 (t, J = 7.8 Hz, 2 H, Fc-CH₂), 1.92–1.83 (p, J = 6.77 Hz, 2 H, Im-CH₂-CH₂), 1.51–1.36 (m, 6 H, CH₂).

^{13}C NMR (CD_3OD , 75 MHz, δ): 136.3, 126.3, 123.6, 122.3, 122.0, 117.7, 113.5, 89.7, 68.7, 68.3, 67.2, 49.4, 35.1, 30.6, 29.7, 29.0, 28.5, 25.7.

Elemental analysis found (calcd.): C 41.49 (41.85), H 4.28 (4.31), N 6.65 (6.65), S 10.11 (10.15), Br 0.0 (0.00).

FTIR (cm^{-1} , $\bar{\nu}$, 25 °C): 3156, 3098, 2932, 2859, 1570, 1470, 1350, 1331, 1227, 1180, 1134, 1053, 999, 821, 791, 760, 741, 652, 613, 571, 509, 482.

Synthesis of 3-chloropropyl-TEMPO ether 5

The ether was prepared using a method which was adapted from the literature [44].

4-Hydroxy-TEMPO (18 g, 104 mmol) was added to a mixture of toluene (18 mL) and aqueous NaOH (50%, 60 mL) and stirred vigorously. Tetrabutylammonium hydroxide (7.2 mL, 1.5 M) was added. 1-Bromo-3-chloropropane (64 g, 409 mmol) was added, and the mixture was stirred for two days. The crude product was isolated via extraction of the reaction mixture with diethyl ether. It was subsequently purified with column chromatography (EtOAc/Hept 20:80, then EtOAc/Hex 15/85) and received as red oil (9.52 g + mixed fract.). The analytical data are in agreement with the literature [44].

^1H NMR (CDCl_3 , 300 MHz, δ): 3.73–3.54 (m, 5 H, Cl-CH₂ & O-CH₂ & O-CH), 2.07–1.91 (m, 4 H, CH₂), 1.49–1.41 (t, J = 11.7 Hz, 2 H, CH₂), 1.23 (s, 6 H, CH₃), 1.17 (s, 6 H, CH₃).

Synthesis of 1-methyl-3-(3-((2,2,6,6-tetramethylpiperidin-4-yl)oxy)propyl)-1H-imidazol-3-ium bis(trifluoromethanesulfon)imide 6

The ether **5** (3 g, 12.0 mmol) was dissolved in toluene (100 mL), and methylimidazole (1.92 mL, 24 mmol) was added. The mixture was stirred at 80 °C in a round bottom flask for 24 h. Afterwards, the mixture was cooled and poured into diethyl ether. As no precipitate was observed, the solvent was removed, and the remaining mixture was dissolved in toluene (10 mL) and placed in a microwave vial. The reaction was continued in a microwave at 100 °C for 26 h. The reaction solution was cooled, and the precipitate was collected via filtration. Precipitation of the reaction solution in diethyl ether yielded little more precipitate. After removal of the diethyl ether, the remaining compound was again fed into the same reaction route with toluene (3 mL) and subjected to the same purification procedure. The united product (3.5 g, 10.57 mmol, 88%) was received as orange crystals and used as received.

The orange solid (2.5 g) was then dissolved in water (20 mL), and an aqueous LiTFSI solution (2.56 g, 8.92 mmol in 10 mL water) was added. The mixture was vigorously stirred until no more red oil appeared from the aqueous solution. The aqueous phase was discarded, and the red oil was dissolved in dichloromethane (20 mL). The organic phase was washed with aqueous LiTFSI solution (1 g in 50 mL) twice and then with water (20 mL). Afterwards, the remaining water was removed with anhydrous sodium sulfate, and the solvent was removed in vacuo to yield the product (3.12 g, 93%) as viscous red fluid.

¹H NMR (CD₃OD + phenylhydrazine, 400 MHz, δ): 7.60–7.54 (dd, J = 23.2 Hz, 2 H, Im-H), 4.32–4.29 (t, J = 7.0 Hz, 2 H, Im-CH₂), 3.93 (s, 3 H, Im-CH₃), 3.61 (m, 1 H, O-CH), 3.54–3.51 (t, J = 5.8 Hz, 2 H, O-CH₂), 2.15–2.09 (m, 2 H, CH₂), 1.92–1.88 (m, 2 H, CH₂), 1.42–1.00 (m, 14 H, CH₂ + Pip-CH₃).

¹³C NMR (CD₃OD + phenylhydrazine, 100 MHz, δ): 131.2, 131.2, 130.6, 126.1, 125.2, 121.5, 115.1, 73.5, 66.7, 61.3, 46.9, 37.7, 33.9, 32.6, 22.5.

Elemental analysis found (calcd.): C 37.55 (37.56), H 5.09 (5.08), N 9.71 (9.73), S 11.07 (11.14), Cl 0 (0).

FTIR (cm^{−1}, $\bar{\nu}$, 25 °C): 3156, 3117, 2978, 2940, 1573, 1462, 1346, 1331, 1227, 1176, 1134, 1053, 972, 934, 899, 844, 787, 760, 741, 687, 652, 613, 571, 509, 405.

Synthesis of *N*-2-ethylhexyl-4,4'-bipyridinium bromide 8

Exemplary 4,4'-bipyridine (100 g, 640 mmol) was added into acetonitrile (500 mL). 2-Ethylhexylbromide (137 mL, 768 mmol, 1.2 eq.) and sodium iodide (2 g, 13.3 mmol) were added at once, and the stirred suspension was heated to gentle reflux temperature. The clear solution was stirred for 24 h. After cooling, the yellow precipitate was collected on a filter. The solid residue was dissolved in methanol and precipitated in a tenfold excess of diethyl ether at ambient temperature. This step was repeated until no more unreacted bipyridine could be identified via ¹H NMR spectroscopy. The average yield over three reactions was ca. 37% of monosubstituted *N*-(2-ethylhexyl)-4,4'-bipyridinium bromide as orange powder.

¹H NMR (CD₃OD, 300 MHz, δ): 9.21–9.18 (d, J = 7.0 Hz, 2 H, Py-H), 8.86–8.84 (m, 2 H, Py-H), 8.61–8.59 (d, J = 7 Hz, 2 H, Py-H), 8.08–8.06 (m, 2 H, Py-H), 4.70–4.67 (d, J = 7.7 Hz, 2 H, Py-CH₂-CH), 2.19–2.11 (sep, J = 6.2 Hz, 1 H, CH-(CH₂)₃), 1.53–1.34 (m, 8 H, CH₂), 1.02–0.91 (m, 6 H, CH₃).

¹³C NMR (CD₃OD, 75 MHz, δ): 153.7, 150.4, 145.5, 142.2, 125.8, 122.3, 64.7, 41.1, 29.4, 27.9, 22.7, 22.5, 12.9, 9.2.

Elemental analysis bromide/iodide mixed salt found: C 59.97, H 7.08, N 7.86, Halogen (Br[−]/I[−]) 22.39.

Synthesis of *N*-2-ethylhexyl-*N'*-isopentyl-4,4'-bipyridinium bis(di(trifluoromethanesulfon)imide) 9

The monosubstituted bipyridine **8** (5 g, 14.31 mmol) was dissolved in acetonitrile (50 mL) and isopentylbromide (3.44 mL, 28.62 mmol) was added. The reaction mixture

was stirred under heating to reflux for 24 h. After cooling to ambient temperature, the precipitate was collected on a filter and washed with fresh acetonitrile (2×50 mL) and acetone (2×50 mL). After drying in vacuo, the product was received as orange solid (7.16 g, 50.5%).

The bromide (1 g, 2 mmol) was dissolved in water (7 mL) and an aqueous LiTFSI solution (1.26 g, 4.4 mmol in 2 mL water) was added. Immediately a milky, colorless second phase formed, which was readily soluble in CH_2Cl_2 (5 mL). The mixture was stirred overnight and the organic phase was separated and washed with AgNO_3 solution (tip of spatula in 10 mL) and LiTFSI solution (2×20 mL, ca. 0.1 M). The solvent was removed, and the off-white residue was dried in vacuo. The product (1.13 g, 63%) was received as slowly crystallizing, slightly off-white oil.

^1H NMR (CD_3OD , 300 MHz, δ): 9.23–9.19 (dd, $J = 6.9$ Hz, 4 H, Py-H), 8.64–8.61 (t, 6.2 Hz, 4 H, Py-H), 4.79–4.65 (m, 4 H, 2 Py- CH_2), 2.14–1.96 (m, 3 H, Py- CH_2 - CH_2 -CH), 1.84–1.71 (m, 1 H, CH-(CH_2)₃), 1.52–1.26 (m, 8 H, CH_2), 1.08–0.91 (m, 12 H, CH_3).

^{13}C NMR (CD_3OD , 75 MHz, δ): 150.2, 149.9, 145.9, 145.6, 127.0, 126.9, 126.1, 121.8, 117.6, 113.4, 65.3, 60.6, 41.2, 39.8, 29.3, 27.8, 25.6, 22.4, 22.1, 21.1, 12.9, 9.0.

Elemental analysis found (calcd.): C 36.03 (36.00), H 4.10 (4.03), N 6.26 (6.18), S 14.23 (14.24), Br 0 (0).

FTIR (cm^{-1} , $\bar{\nu}$, 25 °C): 3132, 3071, 2967, 2936, 2878, 1640, 1562, 1508, 1451, 1346, 1327, 1227, 1180, 1130, 1057, 849, 829, 787, 764, 737, 718, 644, 617, 594, 571, 509, 409.

2.3. Differential Scanning Calorimetry

For DSC measurements, the sample was initially heated to 120 °C with 5 K min^{-1} and cooled to -110 °C with 5 K min^{-1} . For the second cycle, the sample was heated to 120 °C with 5 K min^{-1} and cooled with 20 K min^{-1} . Lastly, the sample was heated to 200 °C with 10 K min^{-1} .

2.4. Electrochemical Characterization of the Redox Active Ionic Liquids

Electrochemical full-cell tests reported in this study have been carried out utilizing a Swagelok-cell type in a 2-electrode setup with two activated carbon (AC)-based electrodes as positive and negative electrodes and a glass fiber sheet (Whatmann), drenched with 150 μL of electrolyte, as a separator.

Electrochemical half-cell experiments were carried out in a similar setup except that a 3-electrode configuration was used, in which a Ag wire was used as a quasi-reference and an oversized free-standing AC-based electrode was used as a counter electrode.

AC-based electrodes were prepared similar to the procedure following the literature [45]. The mass ratio of active material (AC, DLC50, Norit), conductive agent (Super C55, Imerys) and binder (CMC, Walocel CRT 2000 PPA 12 from Dow Wolff Cellulosis) resulted in 90:5:5. The electrode area was 1.13 cm^2 . The average mass loading yielded to 3.3 mg cm^{-2} .

Oversized free-standing activated carbon-based electrodes have been used as counter electrodes and prepared according to [46].

The electrolytes tested in this study were prepared by mixing a RAIL based on viologen, ferrocene or PTMA in neat $\text{Pyr}_{14}\text{TFSI}$ (purchased from Iolitec, Germany). The concentration of the RAILs in $\text{Pyr}_{14}\text{TFSI}$ resulted in 0.1 M. Pure ILs as well as IL mixtures were stored in a glove box (LabMaster, MBRAUN GmbH) under argon atmosphere with a water and oxygen content below 0.1 ppm.

The viscosity of the electrolytes was measured utilizing a rheometer (Anton Paar, MCR 102) with a shear rate of 1000 1/s , while their conductivity was determined by impedance spectroscopy with an amplitude of 5 mV and frequencies between 300 kHz and 1 Hz using a Modu-Lab XM ECS Electrochemical Test System (AMETEK Scientific Instruments). Both investigations have been carried out from 0 to 80 °C. Cyclic voltammetry (CV) measurements were performed using a scan rate of 0.1 mV s^{-1} .

Galvanostatic charge–discharge cycling was carried out between 0 V and 2 V for full-cell devices using current densities ranging from 0.1 to 5 A g^{−1}.

All electrochemical measurements were carried out using a VMP multichannel potentiostatic-galvanostatic workstation (Biologic Science Instruments, VMP 3) or an Arbin potentiostat-galvanostat workstation (Arbin instruments, LBT21084) at room temperature. Before starting the actual measurements, 3 h of open circuit voltage (OCV) were recorded to set the systems into an equilibrium.

Current densities and specific capacities were calculated based on the total mass of AC of both electrodes in full-cell setup.

3. Results

3.1. Synthesis and Characterization of the Redox Active Ionic Liquids

As imidazolium-based ionic liquids were reported [3] to have very low melting points, this cation was selected for the realization of the RAILs considered in this work. From a synthesis perspective, it seems beneficial to combine a highly polar with a very unpolar domain (Figure 1). Recent discussions in the literature shed light on the existence of nanodomains from the polar and the unpolar groups, and, when fluorine-containing groups are present, a third mixed phase with high fluorine content within the fluid phase [47].

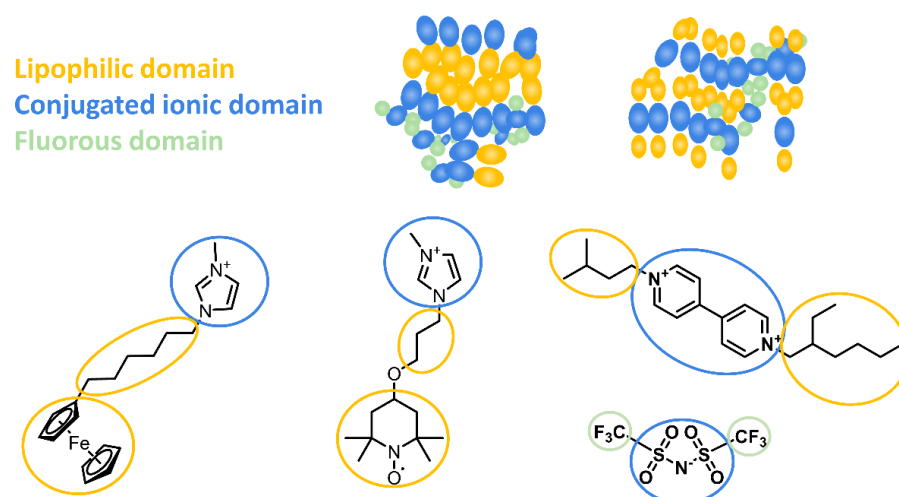
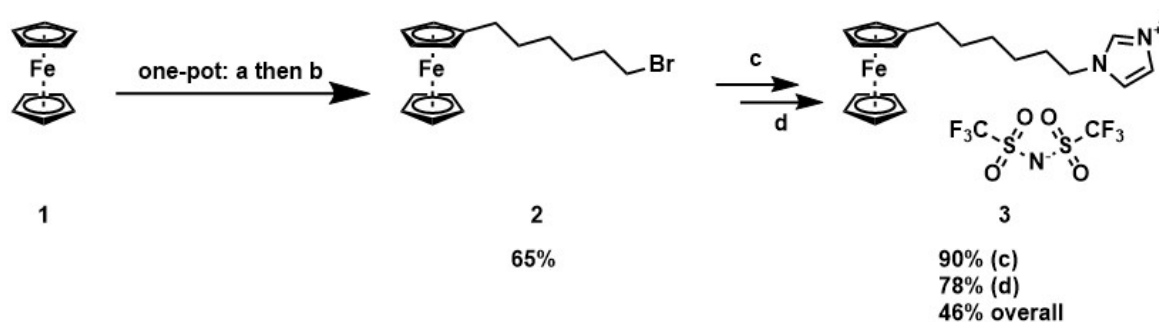


Figure 1. Design principle of the ionic liquids. In the cases of ferrocene and TEMPO as active materials, discrete domains can be postulated in the molecules. The viologen is inherently unable to form similar domains, as the ionic core is surrounded by two lipophilic moieties. The TFSI's CF₃ groups may form further domains, thus resulting in generally low melting points for all three ionic liquids. **Top:** Schematic representation of possible nanodomains [47] within an ionic liquid as made up from the ferrocene and TEMPO RAILs (**left**) and the viologen RAIL (**right**).

In our case, for ferrocene and TEMPO, this was realized by using methylimidazole for the polar domain, while the unpolar domain consisted of the redox-active moiety.

While Gharib and Hirsch presented various ways to synthesize 6-bromohexylferrocene in their publication [48], we adapted [43] a more convenient route, which features a one-pot Friedel–Crafts acylation of the ferrocene with subsequent reduction of the activated carbonyl to a CH₂ group. A substitution–addition reaction with methylimidazole resulted in the final cation for the RAIL. Salt metathesis with lithium TFSI (LiTFSI) from an aqueous organic biphasic mixture yielded the final RAIL (Scheme 1). Overall, we could reduce the number of necessary steps and improve the yield to 46% compared to previous reports. The influence on the conformation of the TFSI counterion onto the melting point of the salt is still a matter of discussion, as it can exist as in two different conformations, i.e., cis- and as trans-form [49], possibly influencing the entropy of the system and thus the melting point of the salt.

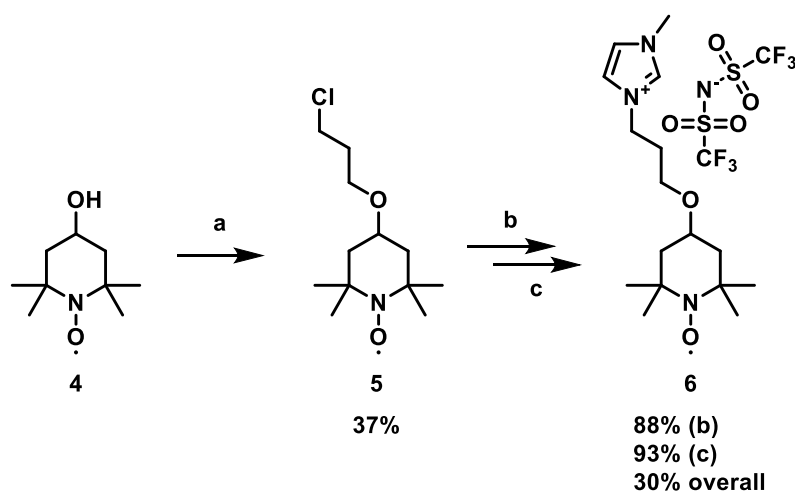


Scheme 1. Schematic representation of the synthesis of a ferrocene-containing redox-active ionic liquid via an optimized synthetic pathway. (a) 6-Bromohexanoyl chloride, AlCl_3 , CH_2Cl_2 , RT, 24 h; (b) NaBH_4 in diglyme, CH_2Cl_2 , 0 °C to RT, 4 h; (c) *N*-methylimidazole, toluene, 80 °C, 18 h; (d) LiTFSI, CH_2Cl_2 /water, RT, 24 h.

The ionic liquid was received as brown oil, which remains liquid since several months already.

Differential scanning calorimetry (DSC) investigations revealed (Figure S14) that the substance **3** features a glass-transition temperature at -50.5 °C (first cooling) or at -51.4 °C during the second heating run (peak values). No melting point was observed. A similar behavior was reported by Gharib and Hirsch, who reported the T_g to be at -52.1 °C [48].

Based on the encouraging results of combining methylimidazole with an active moiety through an alkyl linker, we next focused on the TEMPO moiety. The pre-oxidized TEMPO, i.e., the 4-hydroxy radical, is readily available and offers a versatile attachment point for further substituents with the alcohol group. While previous works used an acetyl linker with the alcohol to form an ester [50], we decided to use an ether linkage, which should be more stable against nucleophiles, e.g., water or amines or even the reduced hydroxylamine-form of TEMPO. Attachment of an imidazole has been demonstrated with a butyl linker in the literature [51]. By using a propyl linker, we could achieve a slight charge-to-weight advantage for the cation. The propyl moiety is introduced (Scheme 2) by a two-phase reaction [44]. We attempted several modifications to the route from the literature, but the yields were, unfortunately, always very low. Furthermore, since BF_4^- and PF_6^- , which were used for the butyl-linked TEMPO RAIL, are readily hydrolyzed [52], we decided to use TFSI as counterion for the ionic liquid. This choice of the anion also enables comparison of the ferrocene **3** and the TEMPO-based **6** RAILS.



Scheme 2. Schematic representation of the synthesis of the TEMPO RAIL. (a) 1-Bromo-3-chloropropane, NaOH, NBu_4OH , toluene/water, RT, 48 h; (b) *N*-methylimidazole, toluene, 100 °C, 26 h; (c) LiTFSI, CH_2Cl_2 /water, RT, 4 h.

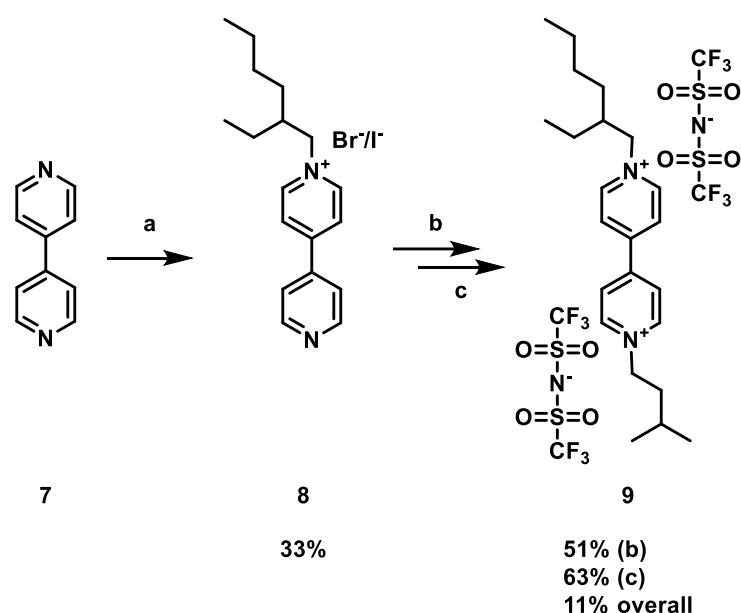
The TEMPO RAIL **6** was liquid at ambient temperature and had remained in that state for several months already. DSC revealed a very similar behavior of the TEMPO RAIL **6**

to the ferrocene RAIL **3** (Figure S15), i.e., a glass transition at $-40.7\text{ }^{\circ}\text{C}$ (compared to the ferrocene RAIL **3** of $-51\text{ }^{\circ}\text{C}$) during the second heating run. Further studies would need to be conducted to judge whether the proximity of the glass transition points for both RAILs is a coincidence or if it is mostly dominated by the methyl-imidazolium. However, due to their nature of being liquid even at low temperature, both RAILs enable construction of electrochemical devices in a very broad temperature range from as low as $-40\text{ }^{\circ}\text{C}$ up to $100\text{ }^{\circ}\text{C}$ and more.

Both ferrocene and TEMPO have a positive potential, when compared to, e.g., a Ag/AgCl reference electrode. To provide an ionic liquid with a molecule that has a negative potential when compared to this reference electrode, we attempted to synthesize ionic liquids from 4,4'-bipyridine. The synthesis principle in this case is different from what was possible for ferrocene and TEMPO. In the latter cases, the ionic domain and the lipophilic domain would be spatially disconnected (Figure 1), thus contributing to the development of the nanodomains within the ionic liquid (v.s.).

Previous studies concerning ionic liquids from viologen indicated that an asymmetric substitution on the 4,4'-bipyridine resulted in the lowest melting points [53]. Promising candidates were *N*-butyl-*N'*-octyl viologen bis-TFSI (C_4VC_8 TFSI) and C_4VC_7 TFSI, with melting points of $52\text{ }^{\circ}\text{C}$ and $57\text{ }^{\circ}\text{C}$, respectively [49]. As, to the best of our knowledge, branched substituents on asymmetrically substituted viologens were not investigated so far by the community, we attempted to synthesize (Scheme 3) a viologen with branched side groups. We chose 2-ethylhexyl bromide for the first functionalization. Even though a slight excess of the bromide was used, and the reaction mixture was heated under reflux conditions, the functionalization of the bipyridine with the 2-ethylhexyl bromide remained difficult. Possibly, elimination reactions and poor steric access to the reaction site cause the reaction to progress very slowly. Since 2-ethylhexane has a chiral carbon, we should find a racemic mixture of *R* and *S* groups on different viologens, which should disturb the formation of crystals when compared to an enantiomerically pure group or achiral groups. Attaching a second chiral group to the viologen would result in diastereomers with distinguished physical characteristics, which might be a promising lead for future investigations. However, we used another branched but achiral group, namely isopentyl bromide, to achieve full substitution on the viologen. This resulted in a viologen with a chiral group and two branched substituents. Anion metathesis to TFSI yielded the final ionic liquid **9**.

The viologen RAIL **9** was not liquid at ambient temperature, but rather a colorless liquid directly after removal of the residual solvent, which slowly crystallized to yield a slightly off-white waxy solid that was particularly distinguished from the halogenates, which are orange (bromide) or red (iodide) powders. DSC (Figure S16) revealed that the molecule **9** has only one endothermal signal at $31\text{ }^{\circ}\text{C}$ during the second heating run, which should correspond to the melting point of the ionic liquid, which is in agreement with the observed behavior during synthesis. Commonly, two signals are reported for viologen in DSC measurements, one being a transition from a crystal to liquid crystal (LC) and one being the transition from an LC phase to an isotropic liquid phase [54,55]. Sometimes, further transitions can be observed [56]. The non-branched analogue octyl-pentyl-viologen was investigated by Causin and Saielli. The authors reported two phase transitions, one at ca. $8\text{ }^{\circ}\text{C}$, where the material enters a mesophase, and one at ca. $61\text{ }^{\circ}\text{C}$, which was described as the clearing point, on which the liquid crystalline phase enters the isotropic liquid phase [57]. Such a behavior was absent until a temperature of $120\text{ }^{\circ}\text{C}$ in our measurements, implying the absence of a mesophase. This might be due to the chiral nature of the ethylhexyl group and the steric demand of both groups, hindering the formation of the otherwise often described nematic phase, which is derived from the rod-like geometry of viologen molecules with (long) linear alkyl chains [57].



Scheme 3. Schematic representation of the synthesis of a RAIL based on 4,4'-bipyridine. (a) 2-Ethylhexyl bromide, potassium iodide, acetonitrile, reflux, 24 h; (b) isopentylbromide, acetonitrile, 110 °C microwave, 24 h; (c) LiTFSI, ethyl acetate (EtOAc)/water, RT, 23 h.

In the following electrochemical characterization, the three selected RAILs are referred to as pure RAILs or pure ferrocene RAIL for **3**, pure TEMPO RAIL for **6** and pure viologen RAIL for **9**. Mixtures of RAILs **3**, **6** and **9** with Pyr₁₄TFSI are referred to as ferrocene, TEMPO and viologen or directly as RAIL based mixtures.

3.2. Electrochemical Characterization of the Redox Active Ionic Liquids

Before the electrochemical investigations, the properties of the three RAILs were investigated. Initially, the viscosity of the pure RAILs was measured in the temperature range from 30 to 80 °C. As shown in Figure 2, all RAILs display a very high viscosity also at elevated temperatures, e.g., >200 mPa s at 60 °C. These values appear too high for use in energy storage devices operating at room temperature. For this reason, binary mixtures of the RAILs and the aprotic ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁₄TFSI) were realized. All three mixtures contained a concentration of 0.1 M RAIL in Pyr₁₄TFSI. This concentration was selected in order to realize mixtures with a relatively low viscosity and, at the same time, provide the electrochemical activity of the RAILs.

Figure 3 compares the viscosity (Figure 3A) and the conductivity (Figure 3B) of the investigated RAIL-based Pyr₁₄TFSI mixtures in the temperature range from 0 to 80 °C. As shown, at 20 °C the mixtures containing the viologen, ferrocene and TEMPO moieties display a viscosity of 76 mPa s, 68 mPa s and 82 mPa s, respectively. At the same temperature, the conductivity of the three mixtures is very similar at 2 mS cm^{−1}. These values, although less favorable compared to those of electrolytes containing organic solvent, appear adequate for the use of the investigated mixtures as electrolytes in energy storage devices operating at room temperature.

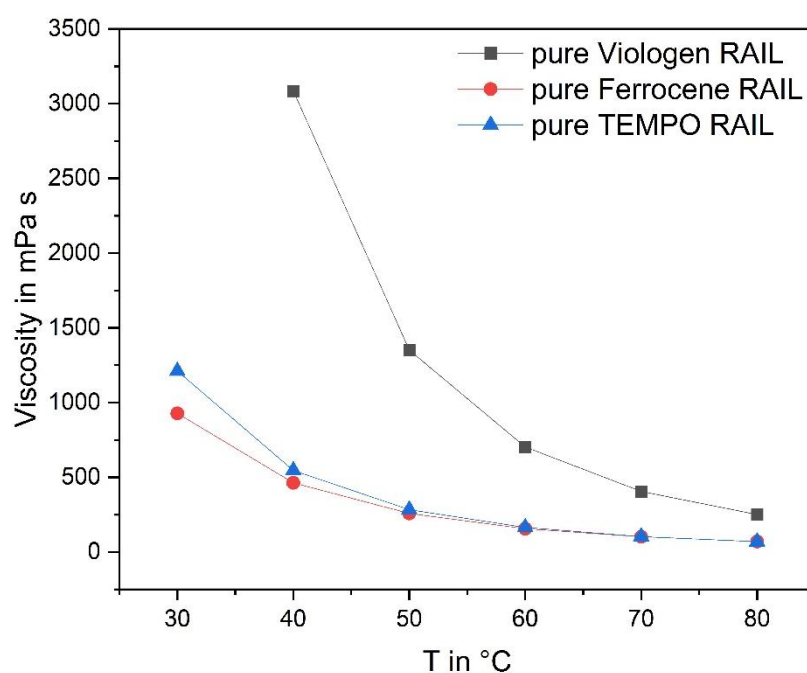


Figure 2. Viscosity of pure RAILs 3, 6, 9 from 30 to 80 °C.

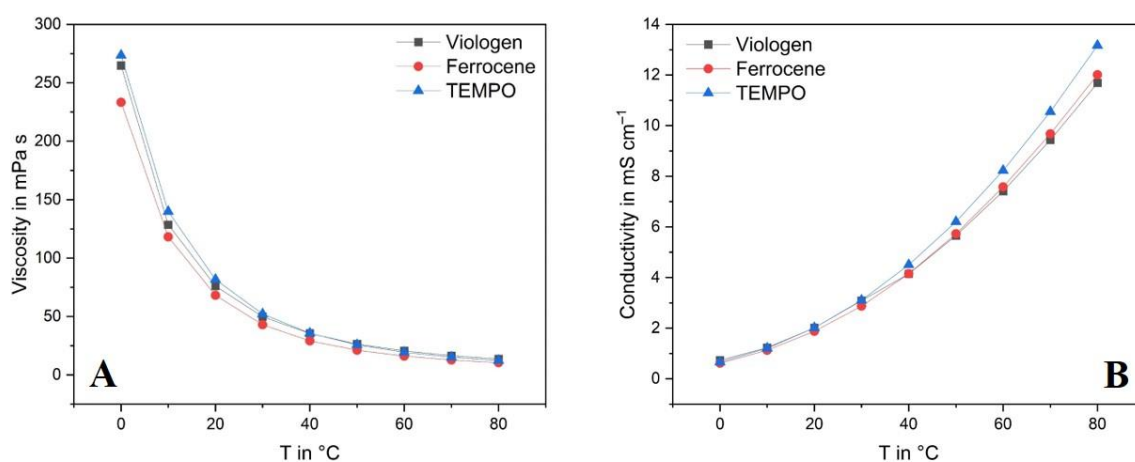


Figure 3. (A) Viscosity and (B) conductivity of 0.1 M RAIL-based electrolytes in Pyr₁₄TFSI from 0 to 80 °C.

Initially, the mixtures were used in combination with AC-based electrodes (half-cell setup), and CV measurements (scan rate of 0.1 mV s^{-1}) were performed in the voltage range between -1 V to 1 V vs. Ag in order to obtain information about the redox behavior of the electrolytes. The results of this investigation are shown in Figure 4. As visible, in the case of the viologen-based Pyr₁₄TFSI electrolyte, two reversible redox peak pairs were observed at -0.52 V and 0.0 V vs. Ag, while for the ferrocene-based Pyr₁₄TFSI mixture, only one redox peak pair at of 0.1 V vs. Ag was obtained. For TEMPO-based Pyr₁₄TFSI electrolyte, a reversible peak at 0.07 V vs. Ag was observed. The intensity of this peak was significantly higher compared to the peaks observed in the electrolytes containing the other two RAILs considered in this work. These results proofed the redox activity of the investigated electrolytes, which is obviously due by the presence of the RAILs. However, it is important to notice that the ferrocene- and TEMPO-based RAILs display unusual potential values, which are shifted toward negative potential, for the redox peaks. As a matter of fact, a peak potential of 0.4 V vs. Ag and 0.8 V vs. Ag were expected for the ferrocene-based and the TEMPO-based RAILs [23,58].

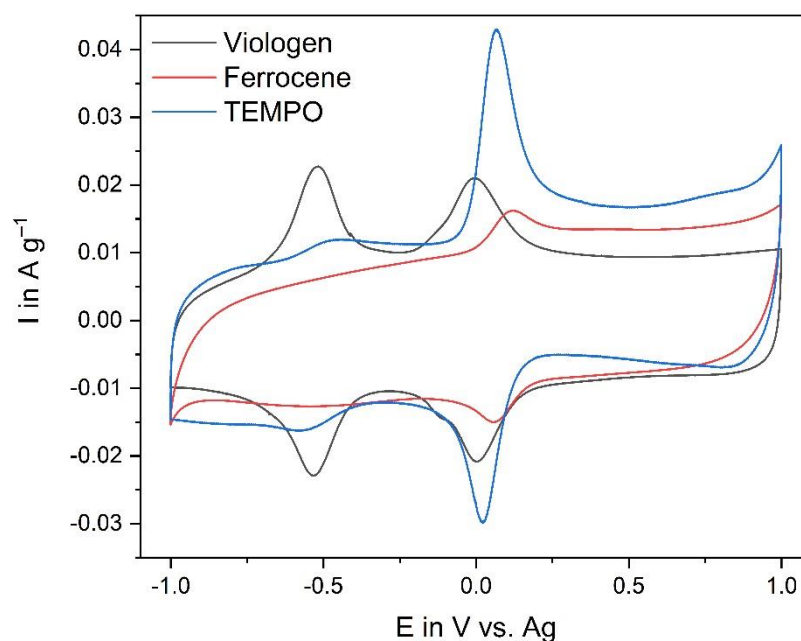


Figure 4. Cyclic voltammograms of 0.1 M RAILs in Pyr₁₄TFSI at 0.1 mV s^{−1} in half-cell setup with an AC working electrode.

The origin of this process is outside of the scope of this study and will therefore not be addressed in the following. In the future, nevertheless, this point should be addressed in order to understand if and how the electrochemical behavior of considered redox moieties is affected by the presence of the activated carbon electrodes.

After this initial investigation, the RAIL-Pyr₁₄TFSI mixtures have been used as electrolytes for EDLCs. Figure 5 displays the CVs (Figure 5A) and voltage profile (Figure 5B) of these devices.

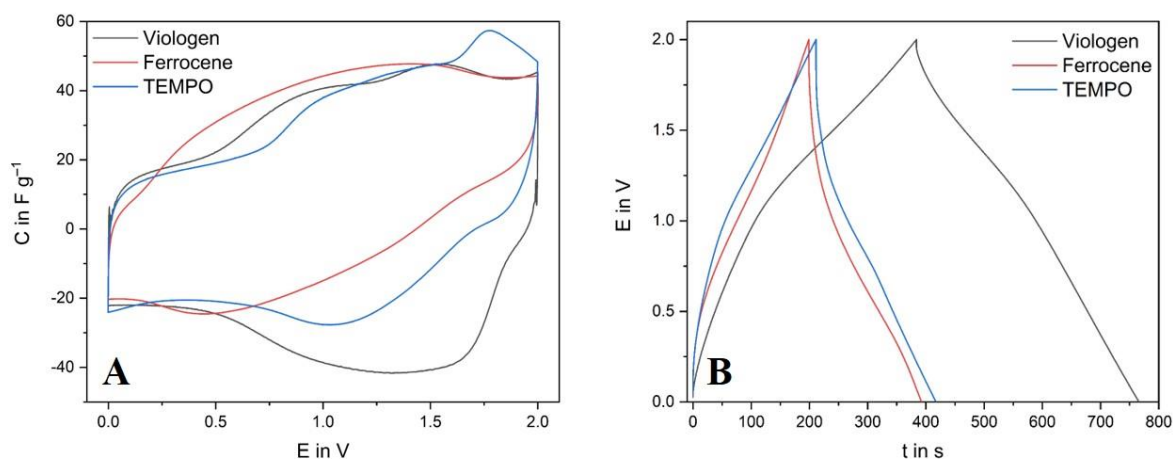


Figure 5. (A) Cyclic voltammograms of 0.1 M RAILs in Pyr₁₄TFSI at 0.1 mV s^{−1} in symmetrical full-cell setup with AC electrodes. (B) Charge/discharge profiles of 0.1 M RAILs in Pyr₁₄TFSI at 0.1 A g^{−1} in symmetrical full-cell setup with AC electrodes.

As expected, all CVs deviate from the classical rectangular shape due to the redox activity of the RAILs within the electrolytes. It has to be mentioned here that we decided to report the capacitance of the electrodes in F g^{−1} even in the presence of these redox peaks. This was done for an easier comparison with the data available in the literature for devices containing Pyr₁₄TFSI. As shown, in the case of the viologen-based electrolyte, cathodic peaks are obtained at 1.0 V and 1.6 V, respectively. The reverse anodic peaks merge in the range of 1.0 to 1.7 V. For the ferrocene-based RAIL mixture, no distinct redox

peaks are visible but a general redox bulk for almost the entire potential range. The most distinct redox peaks are observed in the systems containing the TEMPO-based RAIL, which displays peaks at 1.8 V and 1.1 V. Therewith, redox activity of all RAILs is confirmed also when these electrolytes are used in EDLCs. The occurrence of faradic reactions in the systems is also well visible in the voltage profiles reported in Figure 5. In all investigated systems, the “classical” triangular profiles were not observed, and a mix of faradic (plateau) and capacitive (linear) behavior was present instead. The charge/discharge time indicates the capacitance value for each tested system. Therefore, the highest capacitance should be delivered with the viologen-based RAIL (765 s), followed by the TEMPO-based RAIL (417s) and the ferrocene-based RAIL in Pyr₁₄TFSI (390 s).

To further investigate the electrochemical performance of the RAIL-based EDLCs considered above, the capacitance retention of these devices at different current densities (from 0.1 to 5 A g^{−1}) has also been considered. As show in Figure 6, the EDLCs containing the ferrocene- and TEMPO-based RAILS display a very similar behavior. At a current density of 0.1 A g^{−1}, the devices show capacitances of 12 (ferrocene) and 15 F g^{−1} (TEMPO). These values are comparably low due to the high viscosity of the electrolytes; however, they are comparable with those observed for other Pyr₁₄TFSI-based EDLCs (see Figures S17–S20) [14,59]. When the current density is increased, the capacitance of the devices decreases significantly and already at 1 A g^{−1}, no significant capacitance is displayed. This poor retention is obviously also caused by the high viscosity of these electrolytes. The EDLC containing the viologen-based RAILS displays a different behavior. At 0.1 A g^{−1}, the device shows a capacitance of 21 F g^{−1}, which is significantly higher compared to that observed in the two other devices. Furthermore, the device displays a decent capacitance retention when the current density is increased, and at 2 A g^{−1}, the device is still able to display a capacitance of almost 10 F g^{−1}. Since the conductivity and viscosity of the considered electrolytes are very similar, the higher performance displayed by the EDLCs containing the viologen-based RAILS are very likely related to the presence of the two-electron-exchange reaction, which is indicated in Figure 4. The ability to work at higher current densities can be attributed to the occurrence of more favorable interactions between these redox-active moieties and the carbon electrode compared to ferrocene and TEMPO.

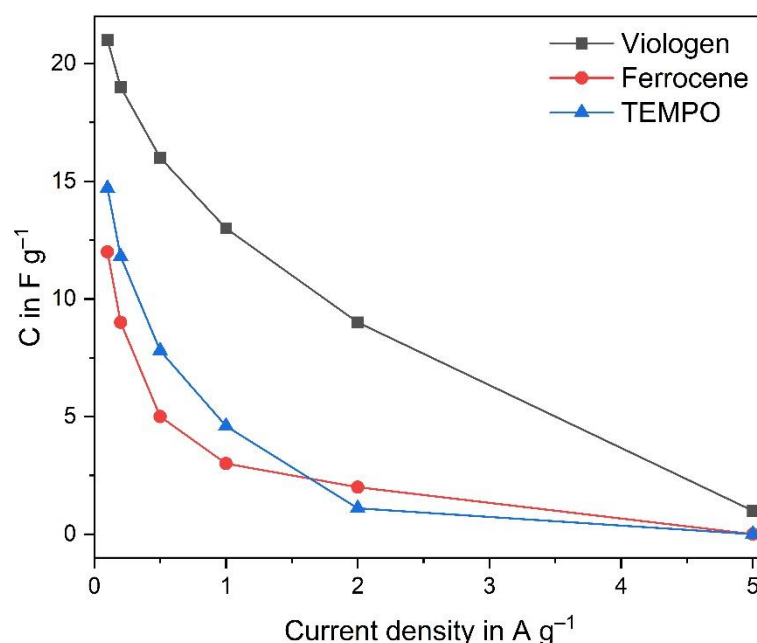


Figure 6. Rate capability of 0.1 M RAILS in Pyr₁₄TFSI from 0.1 to 5 A g^{−1} in symmetrical full-cell setup with AC electrodes.

Finally, the cycling stability of the EDLCs has been considered, and 1000 charge-discharge cycles at 0.1 A g^{-1} have been carried out. As shown in Figure 7, all EDLCs display a stable behavior over the cycling process. The EDLC containing the viologen-based RAIL displays a stable specific capacitance of 19 F g^{-1} , while those containing the ferrocene- and TEMPO-based RAIL reveal a stable capacitance of 10 and 12 F g^{-1} , respectively. Considering these results, it is reasonable to assume that strong parasitic reactions, involving the AC electrode material and RAILs, are not taking place during the investigated cycles.

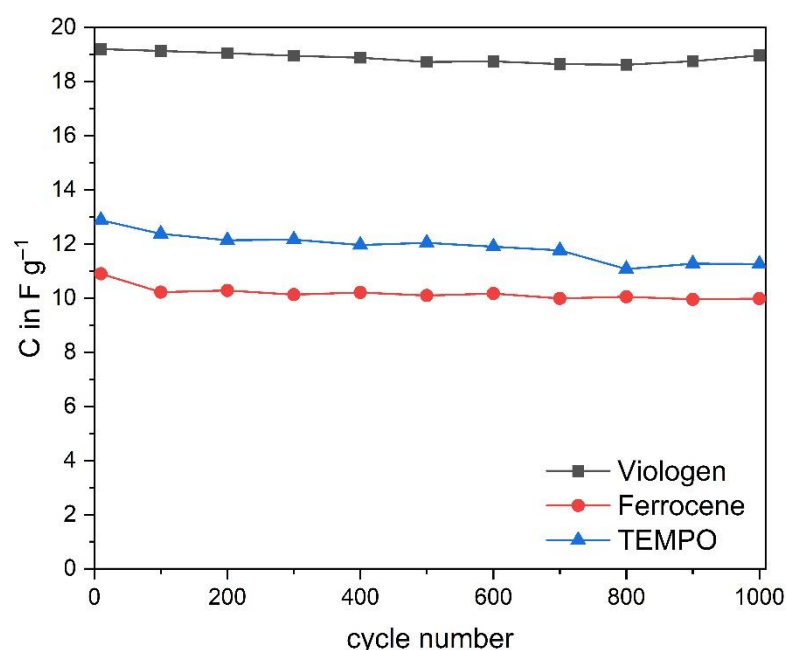


Figure 7. Cycling stability of 0.1 M RAILs in Pyr₁₄TFSI at 0.1 A g^{-1} in symmetrical full-cell setup with AC electrodes over 1000 cycles.

4. Conclusions

In this study, three ionic liquids were synthesized, with two of them being new. Therefore, halogen-alkanes, which were attached to the electroactive molecules ferrocene and TEMPO, were reacted with *N*-methylimidazole to yield the cation. Furthermore, 4,4'-bipyridine was modified by attaching a 2-ethylhexyl and an isopentyl group. In all three cases, the halogen anions were substituted by TFSI. The resulting ionic liquids were analyzed by DSC, which revealed the glass transition points for the ferrocene RAIL to be at -51°C and for the TEMPO RAIL to be at -41°C . No further phase transitions could be observed for these molecules. The viologen RAIL had one solid-liquid transition at 31°C . Viologens are commonly reported in liquid crystal research, and oftentimes two phase transitions are reported [57], which were absent in our case.

After the determination of the physical properties of the pure RAILs as well as 0.1 M binary mixtures of RAILs in Pyr₁₄TFSI, the mixtures were successfully used as electrolytes in EDLCs. There, sufficient redox activity was found in both half-cell and full-cell application with AC electrodes. While the rate capability for the ferrocene- and TEMPO-based electrolytes was limited, a feasible performance has been determined for the viologen-based EDLC. Furthermore, the EDLCs displayed a high cycling stability over 1000 cycles in combination with all RAIL-based electrolytes.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en14196344/s1>, Figures S1–S10: NMR spectra from the synthesis of the materials, Figures S11–S13: Infrared spectra of the RAILs, Figures S14–S16: Schematic representation of the data from DSC measurements, Figures S17–S20: Electrochemical performance of identical full-cell supercapacitor setup in neat Pyr₁₄TFSI.

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