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Stability of a high-voltage ionic liquid with a substituted piperidinium cation and a TFSI anion, promising for electrochemical applications

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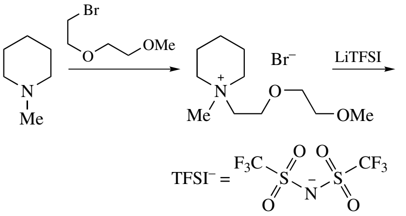
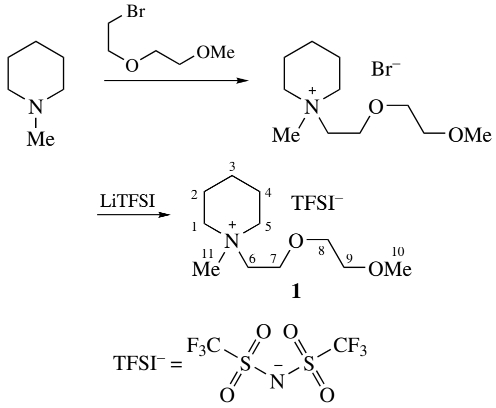
The novel ionic liquid *N*-methyl-*N*-[2-(2-methoxyethoxy)ethyl]piperidinium bis(trifluoromethylsulfonyl)imide was synthesized from *N*-methylpiperidine by a sequence of nucleophilic substitution and anion exchange reactions and characterized by physico-chemical and electrochemical methods.



The development of supercapacitors as an alternative to well-known batteries is a problem of considerable current interest. Nowadays, the supercapacitors exceed other energy storage devices in parameters such as lifetime and efficiency.[1] The supercapacitors can be manufactured from eco-friendly materials. A search for a suitable electrolyte for electrochemical reactions in supercapacitors is a serious problem.[2] As minimal requirements, a good electrolyte should fully dissociate into ions, which can be used as charge carriers in an electrically conductive medium possessing a wide-range electrochemical stability, low crystallization point, high decomposition point, low viscosity and high electroconductivity.[3] Electrolyte can be used in aqueous or organic salt solutions, including ionic liquids.

Due to practical applications in different fields of chemical industry, ionic liquids are of great interest to researchers. Depending on properties, the ionic liquids can be used as green solvents,[4,5] promoters[5] or/and catalysts[6] in organic synthesis[7] and in fuel cells.[8] In particular, they can serve as suitable media for electrochemical processes in supercapacitors[9] and Li–ion batteries.[10] Synthesis of target ionic liquids with predetermined properties such as viscosity, thermal and electrochemical stability and conductivity can be of interest for the manufacture of high efficiency electrochemical energy storage devices.

Here, we report the synthesis of *N*-methyl-*N*-[2-(2-methoxyethoxy)ethyl]piperidinium bis(trifluoromethylsulfonyl)imide **1** *via* a two-stage procedure (Scheme 1).[†] The product was characterized by thermal analysis, NMR spectroscopy and cyclic voltammetry. Because of the low electrical conductivity and high viscosity of this ionic liquid, its solution in dry acetonitrile was also investigated. Acetonitrile was chosen as a solvent in view of its high electrochemical stability and affinity to other ionic liquids.[11,12] To the best of our knowledge, this ionic liquid has not been reported so far.



Scheme 1

[†] *Synthesis of* N-*methyl*-N-*[2-(2-methoxyethoxy)ethyl]piperidinium bromide*. *N*-methylpiperidine (0.2 mol) was placed in a three-neck flask of dark glass with dropping funnel with counter flow and capillary for passing argon, then, 1-bromo-2-(2-methoxyethoxy)ethane (0.2 mol) was added dropwise with stirring for 30 min. The reaction mixture was left at room temperature for a day. Remains of unreacted materials were removed *in vacuo*.

Synthesis of N-*methyl*-N-*[2-(2-methoxyethoxy)ethyl]piperidinium bis(trifluoromethylsulfonyl)imide* **1**. To *N*-methyl-*N*-[2-(2-methoxyethoxy)ethyl]piperidinium bromide (0.2 mol), which was dissolved in three-fold excess redistilled water, a solution equal to the volume of 0.22 mol of lithium bis(trifluoromethylsulfonyl)imide was poured with stirring. After that, the lower layer of the reaction mixture was separated and washed twice with distilled water, the residual water was removed *in vacuo*. Further purification of the halide-ion admixture was carried out by column chromatography using silica gel combined with aluminum oxide and acetonitrile as an eluent. The yield of product **1** was 68%. ^{1}H NMR, δ: 1.54 (m, 2H, 3-Me), 1.79 (m, 4H, 2-Me, 4-Me), 3.05 (s, 3H, 10-Me), 3.25 (s, 3H, 11-Me), 3.34 (m, 4H, 8-CH$_2$, 9-CH$_2$), 3.47 (m, 2H, 7-CH$_2$), 3.55 (m, 4H, 1-CH$_2$, 5-CH$_2$), 3.84 (m, 2H, 6-CH$_2$). ^{13}C NMR, δ: 19.59 (2-C, 4-C), 20.68 (3-C), 48.48 (11-C), 58.08 (10-C), 61.37 (1-C, 5-C), 62.00 (6-C), 63.82 (7-C), 68.72 (8-C), 71.24 (9-C), 115.04, 118.20, 121.44, 124.62 (2-CF$_3$, J_{CF_3} 321 Hz).

Under normal conditions, compound **1** is a viscous, non-volatile, light yellow odorless liquid, d = 1.415 g cm^{-3} (25 °C), n_D^{21} = 1.4327.

When the ionic liquid was heated in an argon atmosphere, the evident weight loss began at 413.4 °C. There are three weight loss steps in the TG curve for the sample: the initial (320–410 °C), the main (410–460 °C) and the end (460–500 °C) sections. At the end of the heating process at 599.8 °C, the weight of the residue was 2.5%.

Using DSC to study the heating and cooling of compound **1** at low temperatures, the temperature ranges of melting the glassy ionic liquid and glass transition were detected. It was found that the ionic liquid vitrifies in a temperature range of –81 to –74 °C, and melts in a range of –77 to –73 °C.

From the viewpoint of utilization in energy storage devices, it is important to study the temperature dependence of electroconductivity and degradation products. The analysis was performed using mass spectroscopy of outgoing gases during thermal treatment (see Online Supplementary Materials).

The electrochemical window of ionic liquid **1** was measured in a three-electrode cell. A glass-carbon working electrode with a diameter of 3 mm and platinum counter and reference electrodes were used. The measurements were performed in a voltage range from –3.5 to 2.5 V using a gradually increasing voltage method with a scanning rate of 2 mV s^{-1}. Electrochemical window was measured at current density less than 50 μA cm^{-2}.[11] It was revealed that compound **1** was electrochemically stable in a range from –2.46 to 2.36 V (Figure 1) Therefore, the electrochemical window was 4.82 V for the ionic liquid, and for its solution in acetonitrile at a concentration of 1.1 mol dm^{-3} with maximum conductivity, it was 4.8 V in a range from –3.35 to 1.45 V. Note that the symmetry of the electrochemical window loses upon the dilution of the ionic liquid with acetonitrile (Figure 2).

Electrical conductivity upon dilution of the ionic liquid with polar solvents is expected to increase. Thus, the conductivity of the solutions of compound **1** in acetonitrile in a range from 0 to 100% ionic liquid (concentrations from 0 to 2.935 mol dm^{-3}) was measured by electrochemical impedance spectroscopy in a two platinum electrode cell using a Biologic VSP-219 potentiostat-galvanostat, which was calibrated using three standard solutions with known conductivity (0.084, 1.413 and 12.880 mS cm^{-1}) at 25 °C. The two electrode cell constant was 2.1504. The maximum electrical conductivity of 5.6 S m^{-1} was observed at a 1.1 mol dm^{-3} concentration of the ionic liquid (Figure 3).

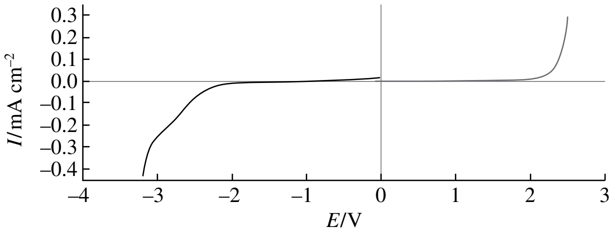


Figure 1 Cyclic voltammetry (–3.5 to 2.5 V) of ionic liquid **1**.

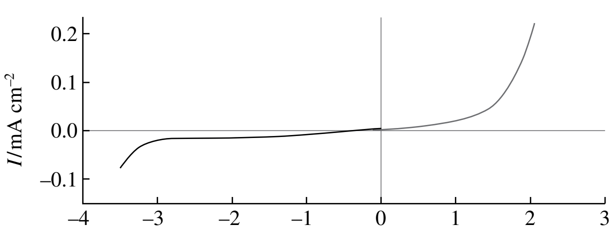


Figure 2 Cyclic voltammetry (–3.5 to 2.5 V) of the solution of ionic liquid **1** in acetonitrile.

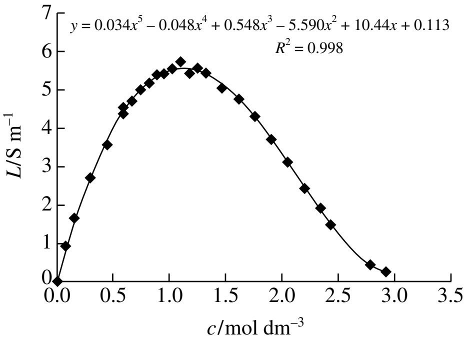


Figure 3 Dependence of the specific electrical conductivity of the solution of compound **1** in acetonitrile on concentration.

Then, the dissociation constant of the solution of ionic liquid **1** in acetonitrile was calculated by the Bartel model.[13]

$$K_d^0 = \frac{\alpha^2 c \gamma_\pm^2}{1-\alpha}, \quad \gamma_\pm = \exp\left(-\frac{k_D q}{1+k_D R}\right),$$

$$k_D^2 = 16\pi N_A q \alpha c, \quad q = \frac{e^2}{8\pi\varepsilon_0 \varepsilon k_B T},$$

where e is the electron charge, ε_0 is the dielectric constant, ε is the dielectric permittivity of the medium, k_D is the Debye parameter, R is the minimum distance at which the oppositely charged ions move freely, and α is the extent of dissociation of the ionic liquid: $\alpha = \lambda/\lambda_0 = 0.929$.

The value of R was calculated from the formula $R = 2a + a_+ + a_-$, where a is the radius of the solvent molecules, and a_+ and a_- are the radii of the ionic liquid cation and anion, respectively, which were theoretically calculated in the model of rigid-chain molecules with fixed angles and ties; a_+ = 5.8615 Å, a_- = 3.5243 Å, and a = 1.5775 Å.

The dissociation constant of the ionic liquid solution with a minimum concentration (0.0009 mol dm^{-3}) was 0.0089 mol dm^{-3}.

It is known that supercapacitors may work at relatively higher temperatures; thus, the temperature dependence of the conductivity for compound **1** was measured in a range from 25 to 95 °C (Figure 4). The experiment showed that the electrical conductivity of the ionic liquid increased with temperature. Therefore, it is possible to achieve a maximum effectiveness of the supercapacitors by changing the operating temperature of the device.

This dependence could be linearized in the $\ln L - T^{-1}$ coordinates according to the equation

$$L = L_0 \exp(E_a/RT),$$

where E_a is the activation energy of electrical, and L_0 is the maximum electrical conductivity[14] (Figure 5). From the slope, the activation energy of electrical conductivity was found to be 27.1 kJ mol^{-1}.

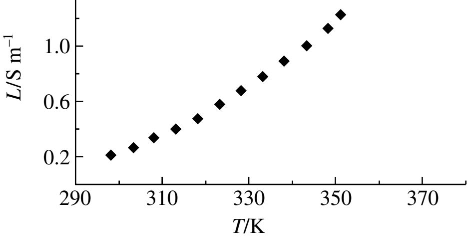


Figure 4 The temperature dependence of the electrical conductivity of ionic liquid **1**.

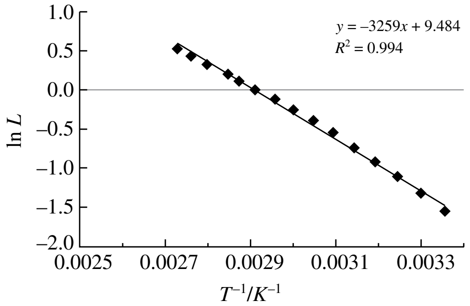


Figure 5 Linearized temperature dependence of conductivity to find the activation energy of electrical conductivity.

Thus, the ionic liquid *N*-methyl-*N*-[2-(2-methoxyethoxy)-ethyl]piperidinium bis(trifluoromethylsulfonyl)imide was successfully synthesized *via* a two-step procedure, and characterized by ^{1}H and ^{13}C NMR spectroscopy, simultaneous thermal analysis, low-temperature DSC, measurements of electrical conductivity of acetonitrile solutions using impedance spectroscopy and cyclic voltammetry. The broad and symmetrical electrochemical windows of the ionic liquid provide wide prospects for its use in the energy storage devices, such as supercapacitors, as component of electrolyte. The results of the study of the temperature dependence of the electrical conductivity will allow us to find the optimal working conditions for electrochemical devices based on it.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.05.006.

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