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Synthesis and Properties of Trigeminal Tricationic Ionic Liquids

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Abstract: Novel trigeminal tricationic ionic liquids (TTILs) have been successfully synthesized in high yields by means of Menschutkin quaternization via an S_N1 mechanism. This reaction presents a new convenient method for transforming glycerol into multifunctional compounds. The physical properties of a series of TTILs were characterized by using a variety of techniques. The prepared salts were tested for antimicrobial activity. Electrochemical characterization of TTILs was also performed, which allowed the estimation of the conductivity of these new compounds, to establish their electrochemical stability window and capacitance properties over a wide range of temperatures. A good correlation of the physical properties of TTILs with capacitance values was observed.

Keywords: ammonium salts · biological activity · electrochemistry · green chemistry · ionic liquids

Introduction

Quaternary ammonium salts (quats), the largest group of cationic surfactants, are widely used for many applications, such as in surfactants, biocides, germicides, fabric softeners, antielectrostatics, adhesion promoters in asphalt, corrosion inhibitors, dispersants, and hair conditioners. Therefore, they can be found in a multitude of products, which includes cosmetics, pharmaceuticals, topical antiseptics, sanitizers, mildew preventives, organophilic clays, and algicides. The synthesis of quats through nucleophilic substitution by reacting tertiary amines with an alkyl halide was first reported by Menschutkin in 1890.[1] This substitution reaction, known as the Menschutkin reaction, is still regarded as the best method for the preparation of quats. Most of the cations used are monoquaternized ammonium species with only one quaternary nitrogen atom. Quats containing two hydrophilic and two hydrophobic groups (so-called gemini or dimeric surfactants, Figure 1A) have been the focus of considerable research interest since the early 1990s.[2–5] Comprehensive reviews have documented the solution behavior of these surfactants.[6–8] This type of surfactant is about three orders of magnitude more active than conventional ones.[6] Moreover,

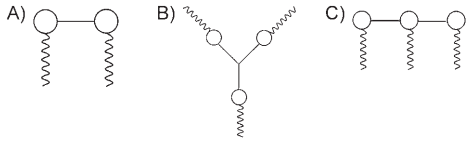

Figure 1. Schematic representations of three types of quats. Structure B represents a novel trigeminal quat.

they exhibit greater potential to act as bactericidal agents than the corresponding monoquats,[7] and as a result are very interesting.[10–12] Trimeric surfactants, which are made up of three amphiphilic moieties connected at the head groups (Figure 1C), have been synthesized in low yields.[13,14]

In this work, we present a new class of quats, namely, trigeminal tricationic salts, that contain three quaternary nitrogen atoms connected to the central carbon atom (Figure 1B).

Recently, new applications for quats have been found through the use of ionic liquids (ILs). ILs open up a wide field for future applications in chemistry, electrochemistry, biology, physics, materials science, and medicine.[15] A number of articles are already available that describe the properties and various applications of ILs.[16–25] Electrochemical applications of ILs, in particular as potential electrolytes for electrical double-layer capacitors, have been widely considered.[26–31]

Dimeric ILs (imidazolium- and pyrrolidinium-based dicationic ILs) have already been described.[32] However, in this paper, a new group of trigeminal tricationic salts is presented for the first time. The synthesis as well as the physical,

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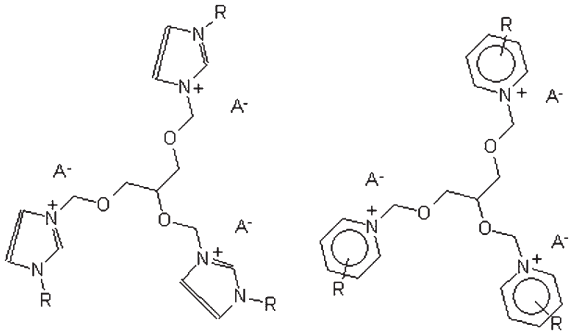
electrochemical, and bactericidal properties of such salts are described herein.

Results and Discussion

Trigeminal tricationic imidazolium (**1**) or pyridinium (**2**) chlorides were prepared by treating 1,2,3-tri(chloromethoxy)propane with 1-alkylimidazole or substituted pyridine, respectively. 1,2,3-Tri(chloromethoxy)propane was obtained



1 **2**

by the chloromethylation of glycerol and is an excellent reagent for quaternization, but it is readily hydrolyzed to form HCl, which in turn gives the amine hydrochloride. The separation of the quaternization product and hydrochloride is practically impossible. For this reason, quaternization with 1,2,3-tri(chloromethoxy)propane should be conducted under strictly anhydrous conditions. This nucleophilic substitution is a specific type of Menschutkin reaction that involves an S_N1 mechanism (Figure 2). The initial rate-determining step involves the formation of the trimeric cation $^{+}CH_2OCH(CH_2OCH_2^{+})_2$. The cation obtained rapidly reacts with tertiary amines giving trigeminal tricationic ammonium chloride with a very high yield. Dry DMF was a convenient solvent from which the product could be isolated as a white powder. The chlorides obtained were very hygroscopic, but they remained stable in air, in aqueous solution, and in common organic solvents. They showed high solubility in common alcohols, DMSO, acetone, and chloroform, but were immiscible with hexane and ethyl acetate.

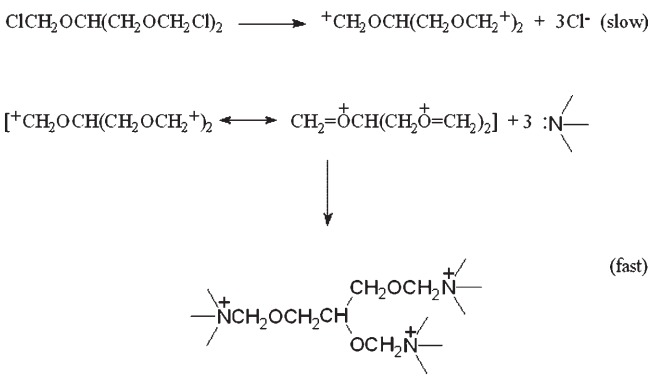


Figure 2. Reactions involving an S_N1 mechanism for the preparation of trigeminal trications.

Imidazolium chloride derivatives **1a** and **1b** were prepared in 94 and 97% yield, respectively, (Table 1), and pyridinium chloride derivatives **2a** (a derivative of niacin (vitamin PP), see Figure 3) and **2b** (a derivative of 4-dimethylaminopyridine (DMAP)) were obtained in 95% yield (Table 2). These derivatives were tested for their antimicrobial activity against rods, cocci, bacillus, and fungi. Minimum inhibitory concentration (MIC) and minimum bactericidal and fungicidal concentration (MBC) values are presented in Table 3.

Table 1. Trigeminal tricationic imidazolium salts (**1**).

Salts	R	A	Yield [%]	T_{onset}[a] [°C]	T_g[b] [°C]
1a	CH_3	Cl	94	–	–
1b	C_8H_{17}	Cl	97	–	–
1c	CH_3	NTf_2	75	300 (450) (550)	−53
1d	$CH_2C_6H_5$	NTf_2	78	300 (445) (550)	−42
1e	$CH_2C_6H_5$	BF_4	90	280 (370) (460) (570)	−4
1f	$CH=CH_2$	NTf_2	75	300 (450) (550)	–

[a] Decomposition temperature determined from onset to 50% mass decrease. [b] Glass transition temperature determined by using differential scanning calorimetry (DSC).

Figure 3. Cation of 1,2,3-propanetri[oxymethyl-1-(3-carbamoylpyridinium)].

Table 2. Trigeminal tricationic pyridinium salts (**2**).

Salts	R	A	Yield [%]	T_{onset}[a] [°C]	T_g[b] [°C]
2a	3-$CONH_2$	Cl	95	–	–
2b	4-$N(CH_3)_2$	Cl	95	–	–
2c	3-$CONH_2$	NTf_2	98	200 (375) (450)	−10.5
2d	3-$CONH_2$	BF_4	89	200 (350) (450)	–
2e	4-$N(CH_3)_2$	NTf_2	88	340 (460)	−30
2f	4-$N(CH_3)_2$	$N(CN)_2$	94	–	–

[a] Decomposition temperature determined from onset to 50% mass decrease. [b] Glass transition temperature determined by using DSC.

Table 3. MIC and MBC values[a] of trigeminal tricationic chlorides.

Strain[b]		Chlorides				
		1a	**1b**	**2a**	**2b**	BAC[c]
M. luteus	MIC	4	<0.1	200	400	1.4
	MBC	64	<0.1	>800	400	11
S. aureus	MIC	125	1.3	200	800	2.8
	MBC	>800	2.6	>800	>800	23
S. epidermidis	MIC	32	<0.1	800	400	1.4
	MBC	32	<0.1	>800	800	5.6
E. faecium	MIC	125	0.26	>800	>800	5.6
	MBC	500	0.52	>800	>800	23
M. catarrhalis	MIC	64	0.26	200	100	0.6
	MBC	64	0.26	>800	400	1.4
E. coli	MIC	1000	2.6	800	>800	2.8
	MBC	1000	2.6	>800	>800	2.8
S. marcescens	MIC	>1000	79.6	>800	>800	175
	MBC	>1000	159	>800	>800	175
P. vulgaris	MIC	>1000	39.8	>800	>800	88
	MBC	>1000	79.6	>800	>800	88
P. aeruginosa	MIC	>1000	39.8	>800	>800	175
	MBC	>1000	79.6	>800	>800	175
B. subtilis	MIC	125	0.26	>800	400	2.8
	MBC	>1000	0.26	>800	400	2.8
C. albicans	MIC	>1000	39.8	>800	>800	11
	MBC	>1000	39.8	>800	>800	88
R. rubra	MIC	>1000	39.8	>800	800	23
	MBC	>1000	39.8	>800	800	88

[a] In μM. [b] For the full names, see the Experimental Section. [c] Benzalkonium chloride.

The pyridinium chloride derivatives tested are inactive against bacteria and fungi. However, the imidazolium chloride derivatives proved to be effective against microbes. The activity depended upon the number of carbon atoms in the alkyl group. Chloride **1b**, which contains an octyl substituent, was strongly active against rods, cocci, bacilli, and fungi, and exhibited a higher efficiency than that of commercially available benzalkonium chloride (BAC, in which the alkyl group represents a mixture of alkyl chains ranging from C_8H_{17} to $C_{18}H_{37}$). Dimeric quats were more active bactericidal agents than the corresponding monoquats.[9] Trigeminal imidazolium chlorides were also more active than the corresponding monoimidazolium chloride derivatives (1-alkoxymethyl-3-methylimidazolium chloride[33]). Trigeminal tricationic salts constitute a new class of quats.

The chloride derivatives prepared were then employed as synthetic precursors of new TTILs. A metathesis reaction was conducted in aqueous solutions by using $LiNTf_2$ (Tf = trifluoromethanesulfonyl), $NaBF_4$, and $NaN(CN)_2$ salts. The final yield of the ion exchange ranged from moderate to high values (75–98%). The chloride derivatives, which were the source of the cation component and the final product salts, are presented in Tables 1 and 2. The $[NTf_2]$ and $[BF_4]$ salts were liquid at room temperature, whereas **2f** was crystalline with a melting point below 100 °C, which indicated that the obtained salts were ILs.

The trigeminal salts synthesized were characterized by means of ^1H and ^{13}C NMR spectroscopic techniques and elemental analysis. The trigeminal tricationic quats prepared were symmetrical with a minor defect. In the ^1H NMR spectra, the signals corresponding to the two $CH_2OCH_2N^+$ branches have identical chemical shift values and the OCH_2N^+ branch has a slightly different chemical shift value.

Anhydrous TTILs were obtained by heating the samples at 70 °C in a vacuum for 24 h. Karl Fisher measurements showed that the water content of these dried compounds was less than 300 ppm. These anhydrous TTILs (colorless liquids) absorbed up to around 0.5% water when they were exposed to air. They were stable under laboratory conditions and manifested a low vapor pressure under standard conditions. The TTILs were also insoluble in water and hexane; slightly miscible with acetone, low-molecular-weight alcohols, and $CHCl_3$; and soluble in acetonitrile. At room temperature, $[NTf_2]$ and $[BF_4]$ salts were very viscous liquids. The differential scanning calorimetry (DSC) thermograms of TTILs exhibited a glass transition temperature (T_g) without melting. $[NTf_2]$ and $[BF_4]$ viscous liquids only formed glasses. The T_g was governed by the strength of the ionic interactions and the ion size. For [imidazolium][NTf_2] T_g was very low, ranging from −42 to −53 °C, and for $[BF_4]$ it amounted to −4 °C.

Thermogravimetric analysis of the [imidazolium][NTf_2] and [imidazolium][BF_4] TTILs showed distinct three-stage decomposition behavior; they started to decompose at 280 or 300 °C. On the other hand, the thermal stability of the pyridinium TTIL strongly depended on the type of cation present. For niacin derivatives **2c** and **2d**, decomposition started at 200 °C and at 340 °C for DMAP derivative **2e**, in which approximately 5–7% weight loss was observed. Only the [imidazolium][BF_4] salt with a benzyl substituent (**1e**) decomposed in a four-stage process starting at 280–300 °C and with 20% weight loss.

Electrochemical measurements: Novel TTILs were electrochemically tested to estimate their suitability for practical applications. One of the most important properties is electrochemical stability, which indicates the oxidation and reduction limits of a salt. Examples of electrochemical stability windows for compounds **1c** and **2e** are shown in Figure 4.

Electrochemical stability investigations performed by means of linear sweep voltammetry showed that **1c** and **2e** were stable over a potential range of 4 V, which allows them to be used as possible electrolytes. Such characteristics pro-

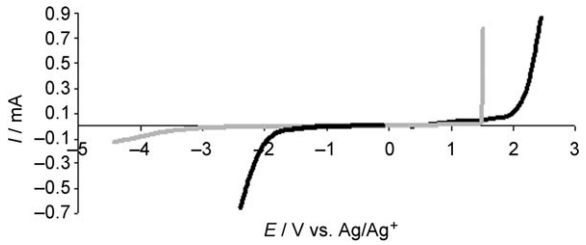


Figure 4. Electrochemical stability windows of TTILs **1c** (——) and **2e** (——) when using a gold electrode. Conditions: scan rate potential = 5 mV s^{-1}; cathodic limits = −1.9 V for **1c** and −3.2 V for **2e**; anodic limits = +2.1 V for **1c** and +1.5 V for **2e**.

vided additional information on the absence of water in TTILs. Both compounds possess the NTf_2 anion; hence, the difference in their stability originated from the cation structure, probably owing to a difference in the π-electron conjugated system of the two ions. However, it is worth noting that generally the cathodic limiting potential is most often affected by the cation but it could be also influenced by the anion stability. Compound **2e** decomposed more rapidly at the anodic limit than at the cathodic one, and a strong oxidation tendency was observed (+1.5 V versus Ag/Ag^+).

Aside from stability towards redox reactions, conductivity represents another very important parameter for practical electrochemical applications. Conductivity values estimated by using impedance measurements in the range from 20 to 70 °C increased significantly with increasing temperatures. It was clear that higher temperatures decreased the viscosity of the TTILs, which accelerated self-diffusion and ionic transport. Figure 5 shows that variable temperature effects

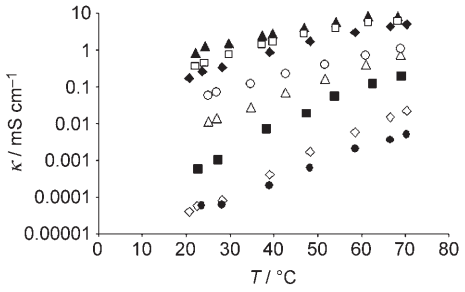


Figure 5. Conductivity versus temperature for TTILs (△=**1a**, ▲=**1c**, ◆=**1d**, ◇=**1e**, ○=**1f**, ■=**2c**, ●=**2d**, and □=**2e**).

were observed for the TTILs investigated. Ionic conduction also depends on the fraction of ion pairs or aggregates. One can assume that in the case of trigeminal tricationic salts an association effect can play an important role.

Subsequent electrochemical investigations of the TTILs were based on capacitance measurements. A linear dependence between capacitance values, estimated from impedance spectroscopy at 1 mHz, and temperature was noted (Figure 6). High capacitance values of 120 $F g^{-1}$ were obtained at approximately 70 °C. Such capacitance values at a high operating voltage are interesting, in particular for the use of capacitors in hybrid vehicles.

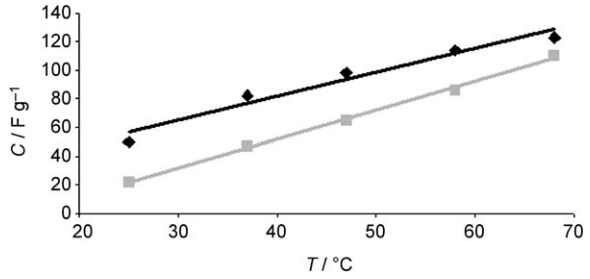


Figure 6. Specific capacitance versus temperature dependence for TTILs **1c** (◆) and **2e** (■).

Charge propagation represents another important parameter to consider for good capacitor performance. The capacitance versus frequency relationship gives the best evidence that compound **1c** supplies limited capacitance at frequencies higher than 100 mHz (Figure 7).

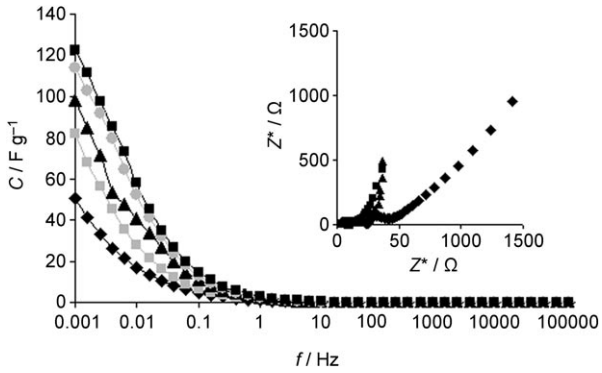


Figure 7. Capacitance versus frequency dependence for TTIL **1c**. Impedance values from 1 mHz to 100 kHz frequency range (the same in the inset). A two-electrode system built from NORIT activated carbon was used (◆=25 °C, ■=37 °C, ▲=47 °C, ●=58 °C, and ■=68 °C).

At low frequencies, the capacitance values ranged from 120 to 20 $F g^{-1}$, which confirmed that this type of electrolyte could not be used for numerous charging/discharging cycles. The same conclusion could be drawn from voltammetry experiments for **1c** (Figure 8) as well as from comparison of

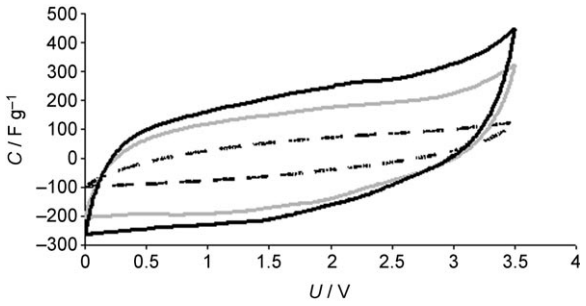


Figure 8. Voltammetry characteristics (1 $mV s^{-1}$) of a carbon electrode in **1c** at a few various temperatures: 25 °C, 43 $F g^{-1}$; 48 °C, 127 $F g^{-1}$; 68 °C, 169 $F g^{-1}$ (– – –=25 °C, ——=48 °C, and ——=68 °C).

1c with **2e** (Figure 9). Particularly at lower temperatures, capacitors demonstrated a remarkable resistance; the shape of the voltammetry curve was far from boxlike and instead was "fishlike". At 68 °C, the experiments gave attractive capacitance values with a high of 169 $F g^{-1}$. On the other hand, at 25 °C, the capacitance values reached only 43 $F g^{-1}$.

Even if the capacitor could reach 3.5 V, good cyclability was obtained by using a smaller voltage range of 3.2 V. In this case, the capacitor performance estimated by cyclic voltammetry showed a good reversibility of charge accumulation, in particular for **1c**. Salt **1c** presents the best electro-

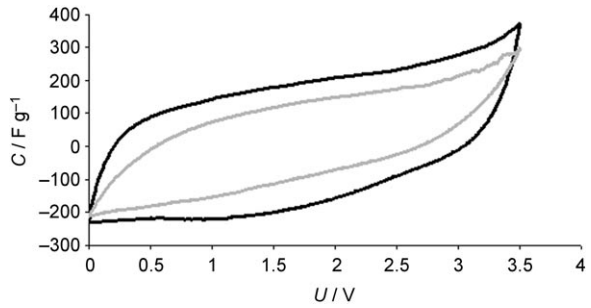


Figure 9. Comparison of voltammetry characteristics (1 mV s^{-1}) for a capacitor carbon electrode operating in **1c** (——, 151 F g^{-1}) and **2e** (——, 86 F g^{-1}) at 58 °C.

chemical properties among all the trigeminal tricationic TTILs investigated. It is worth noting that the conductivity of TTILs are lower than other well-known ILs,[34,35] but their electrochemical window is quite interesting. It can be concluded that a good correlation between the physical and electrochemical properties of the ILs was found. Aside from antimicrobial applications, novel TTILs could be considered as potential electrolytes for electrochemical capacitors.

Conclusion

The high-yielding synthesis of trigeminal tricationic salts was performed by the chloromethylation of glycerol followed by a trimeric cation reaction with tertiary amines. The hygroscopic chlorides synthesized were transformed into ionic liquids by exchanging the anion. The products were stable, but high-viscosity ILs were observed for compounds with three or more oxygen atoms. The presence of oxygen atoms in the molecule decreased its thermal stability. Derivatives of niacin were found to undergo decomposition at 200 °C and the DMAP derivatives maintained their stability up to 340 °C. The trigeminal tricationic imidazolium chloride salt that contained an octyl substituent was strongly active against rods, cocci, bacilli, and fungi. This result not only demonstrates the broad spectrum of antimicrobial activity, but also shows that in this respect, the chloride salts are much more effective than commercially available benzalkonium chloride.

High viscosity, in connection with a strong tendency for the trivalent cation to interact with three anions, appears to be responsible for relatively low conductivity in comparison with other ILs and for moderate charge propagation at room temperature. On the other hand, the high capacitance values obtained at higher temperatures with an operating voltage of approximately 3.5 V (similar to battery values) leads to possible applications for these novel TTILs as high-energy sources; hence, the application of such electrolytes for a special low-current load could be envisaged. Additionally, other applications such as electrodeposition and/or lithium ion batteries could be considered.

The trigeminal tricationic salts synthesized represent a new group of multifunctional compounds. The synthetic technique described allows glycerol to be transformed into ionic liquids, bactericidal and fungicidal compounds, and also into the electrolytic components of a supercapacitor. To the best of our knowledge, TTIL compounds were successfully synthesized and characterized in detail by using physical and electrochemical methods for the first time.

Experimental Section

General: 1,2,3-Tri(chloromethoxy)propane was prepared by passing HCl through a mixture of formaldehyde and glycerol.[36] The purity of 1,2,3-tri(chloromethoxy)propane was determined by using an alkalimetric method in which the crude product (1 g) was added to acetone (10 mL) at −20 °C. The acidified substrate was quickly neutralized with 0.2 M KOH in MeOH before hot water (5 mL) was added. HCl produced from the hydrolysis of 1,2,3-tri(chloromethoxy)propane was neutralized with 0.2 M KOH in MeOH. The water content was determined by using an Aquastar volumetric Karl Fisher titrator with Composite 5 solution as the titrant and anhydrous methanol as the solvent. DSC was carried out by using a Perkin–Elmer instrument calibrated with an indium sample (99.9999 mol % pure).

Preparation of ionic liquids

Menschutkin quaternization: All reactions were performed under anhydrous conditions. A solution of freshly distilled or crystallized tertiary amine (0.03 mol) in dry DMF (30 mL) was prepared before 1,2,3-tri-(chloromethoxy)propane (0.03 mol) in dry DMF (10 mL) was slowly added and the resulting mixture was vigorously stirred for 2 h at 70 °C. The white precipitate was removed by means of filtration and the filter cake was washed with ethyl acetate. The product was dried under reduced pressure overnight.

Metathesis reaction: A saturated aqueous solution of inorganic salt was added to stoichiometric amounts of saturated aqueous solution containing the trigeminal tricationic chloride salts prepared. After phase separation, the aqueous phase was decanted and the product was washed with distilled water until no more chloride ions were detected by using $AgNO_3$. The product was dried for 10 h at 50 °C under vacuum (8 mm Hg).

Characterization

*1,2,3-Propanetri[oxymethyl-1-(3-methylimidazolium)] bis(trifluoromethanesulfonyl)imide (**1c**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.60 (s, 1H), 8.58 (s, 2H), 7.50 (m, 6H), 5.56 (s, 2H), 5.44 (s, 4H), 3.89 (s, 3H), 3.88 (s, 7H), 3.58 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 163.3, 137.1, 127.1, 125.1, 124.9, 122.6, 122.5, 118.2, 114.4, 79.9, 79.2, 78.0, 70.1, 37.1 ppm; elemental analysis calcd (%) for $C_{24}H_{29}O_{15}N_9S_6F_{18}$: C 23.67, H 2.40, N 10.35; found: C 23.85, H 2.18, N 10.03.

*1,2,3-Propanetri[oxymethyl-1-(3-benzylimidazolium)] bis(trifluoromethanesulfonyl)imide (**1d**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.79 (s, 1H), 8.75 (s, 2H), 7.52 (m, 21H), 5.53 (s, 2H), 5.39 (s, 4H), 5.37 (s, 6H), 3.91 (m, 1H), 3.60 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 163.4, 136.6, 134.5, 134.3, 130.3, 130.2, 129.7, 129.6, 127.2, 124.0, 123.7, 123.2, 123.0, 118.7, 80.0, 79.4, 78.0, 70.1, 54.1, 54.0 ppm; elemental analysis calcd (%) for $C_{42}H_{41}O_{15}N_9S_6F_{18}$: C 34.88, H 2.86, N 8.72; found: C 34.62, H 2.68, N 8.55.

*1,2,3-Propanetri[oxymethyl-1-(3-benzylimidazolium)] tetrafluoroborate (**1e**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.79 (s, 1H), 8.75 (s, 2H), 7.52 (m, 21H), 5.53 (s, 2H), 5.39 (s, 4H), 5.37 (s, 6H), 3.91 (m, 1H), 3.60 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 136.8, 136.7, 134.7, 134.5, 130.2, 129.7, 129.6, 123.8, 123.6, 123.2, 123.1, 118.4, 79.9, 79.2, 77.8, 69.9, 53.9, 53.8 ppm; elemental analysis calcd (%) for $C_{36}H_{41}O_3N_6B_3F_{12}$: C 49.92, H 4.77, N 9.70; found: C 49.72, H 4.53, N 9.65.

*1,2,3-Propanetri[oxymethyl-1-(3-vinylimidazolium)] bis(trifluoromethanesulfonyl)imide (**1f**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.88 (m, 3H), 7.79 (m, 3H), 7.62 (m, 3H), 7.21 (m, 3H), 5.88 (m, 4H), 5.63 (s, 2H), 5.50 (m, 6H), 3.99 (m, 1H), 3.68 ppm (m, 4H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 135.6, 135.5, 129.3, 127.2, 123.4, 123.3, 122.9, 121.0, 120.7, 118.7, 118.4, 114.4, 111.1, 111.0, 80.3, 79.7, 78.2, 70.3 ppm; elemental analysis calcd (%) for $C_{27}H_{29}O_{15}N_9S_6F_{18}$: C 25.86, H 2.33, N 10.05; found: C 26.03, H 2.54, N 10.42.

*1,2,3-Propanetri[oxymethyl-1-(3-carbamoylpyridinium)] bis(trifluoromethanesulfonyl)imide (**2c**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 9.42 (s, 1H; arom.), 9.23 (s, 2H; arom.), 8.91 (d, J = 1.5 Hz, 1H; arom.), 8.90 (d, J = 1.5 Hz, 1H; arom.), 8.89 (d, J = 6 Hz, 4H; arom.), 8.23 (t, J = 7 Hz, 3H; arom.), 7.44 (s, 1H; NH), 7.39 (s, 2H; 2NH), 6.82 (s, 1H; NH), 6.80 (s, 2H; 2NH), 6.05 (s, 2H; OCH_2N), 5.84 (q, J = 9.3 Hz, 4H; $2OCH_2N$), 4.19 (m, 1H; *CH*), 3.86 ppm (m, 4H; $2OCH_2CH$); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 164.0, 163.6, 146.3, 146.2, 145.4, 143.9, 135.2, 134.9, 129.3, 129.0, 122.9, 118.6, 118.3, 90.1, 89.3, 79.7, 71.0 ppm; elemental analysis calcd (%) for $C_{30}H_{29}O_{18}N_9S_6F_{18}$: C 26.93, H 2.18, N 9.42; found: C 26.75, H 2.03, N 9.63.

*1,2,3-Propanetri[oxymethyl-1-(3-carbamoylpyridinium)] tetrafluoroborate (**2d**)*: ^{1}H NMR (300 MHz, D_2O, 25 °C, TMS): δ = 9.54 (s, 1H), 9.36 (s, 2H), 9.09 (m, 6H), 8.31 (m, 3H), 6.17 (s, 4H), 5.97 (s, 2H), 4.82 (s, 6H), 4.36 (m, 1H), 3.91 ppm (m, 4H); ^{13}C NMR (75 MHz, D_2O, 25 °C, TMS): δ = 168.1, 148.4, 148.3, 147.8, 147.5, 145.8, 145.5, 136.7, 131.2, 130.9, 92.1, 91.5, 81.8, 72.8 ppm; elemental analysis calcd (%) for $C_{24}H_{29}O_6N_6F_{12}B_3$: C 38.03, H 3.86, N 11.09; found: C 38.24, H 3.65, N 10.95.

*1,2,3-Propanetri[oxymethyl-1-(4-dimethylaminopyridinium)] bis(trifluoromethanesulfonyl)imide (**2e**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.01 (m, 6H), 7.95 (d, J = 9 Hz, 2H), 7.94 (d, J = 8 Hz, 4H), 6.89 (d, J = 8 Hz, 4H), 6.84 (d, J = 9 Hz, 2H), 5.40 (s, 2H), 5.28 (s, 4H), 3.87 (m, 1H), 3.54 (m, 4H), 3.214 (s, 12H), 3.208 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 158.1, 141.7, 141.5, 127.1, 122.9, 118.6, 118.1, 114.4, 108.4, 108.1, 88.6, 86.0, 78.0, 69.8, 40.8 ppm; elemental analysis calcd (%) for $C_{33}H_{41}O_{15}N_9S_6F_{18}$: C 29.61, H 3.09, N 9.42; found: C 29.81, H 3.25, N 9.07.

*1,2,3-Propanetri[oxymethyl-1-(4-dimethylaminopyridinium)] dicyandiamide (**2f**)*: ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.01 (m, 6H), 6.93 (m, 6H), 5.45 (s, 2H), 5.33 (s, 4H), 3.90 (m, 1H), 3.56 (m, 4H), 3.22 (s, 12H), 3.22 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_3CN, 25 °C, TMS): δ = 157.8, 141.7, 141.5, 118.1, 108.2, 108.0, 86.3, 85.6, 77.6, 69.4, 40.7 ppm; elemental analysis calcd (%) for $C_{33}H_{41}O_3N_{15}$: C 56.97, H 5.94, N 30.20; found: C 57.14, H 5.75, N 30.39.

Antimicrobial activities: Standard strains were supplied by the National Collection of Type Cultures (NCTC) London, the American Type Culture Collection (ATCC), and *R. rubra* was obtained from the Department of Pharmaceutical Bacteriology, University of Medical Sciences, Poznań. The following microorganisms were used: *Micrococcus luteus* NCTC 7743, *Staphylococcus aureus* NCTC 4163, *Staphylococcus epidermidis* ATCC 49134, *Enterococcus faecium* ATCC 49474, *Moraxella catarrhalis* ATCC 25238, *Escherichia coli* ATCC 25922, *Serratia marcescens* ATCC 8100, *Proteus vulgaris* NCTC 4635, *Pseudomonas aeruginosa* NCTC 6749, *Bacillus subtilis* ATCC 6633, *Candida albicans* ATCC 10231, and *Rhodotorula rubra* (Demml 1889, Lodder 1934).

Antimicrobial activity was determined by means of tube dilution methods. Bacterial strains were cultured by using a Müller–Hinton broth, and fungi were cultured on Sabouraud agar. The suspensions of standard microorganisms, at a concentration of 10^6 cfu mL^{-1} (cfu = colony forming units), were prepared from each culture. Samples (2 mL) of the compound taken from twofold serial dilutions were inoculated with a standardized suspension of test microorganism to obtain a final concentration of $1–5\times10^5$ cfu mL^{-1}. The growth (or lack thereof) of the microorganism was determined visually after incubation for 24 h at 37 °C (bacteria) or 48 h at 28–30 °C (fungi). The lowest concentration at which there was no visible growth (turbidity) was taken as the MIC. An aliquot was then taken from each tube in a sample loop, was cultured in agar medium with inactivates (lecithin (0.3%), polysorbate 80 (3%), and L-cysteine (0.1%)), and incubated for 48 h at 37 °C (bacteria) or for 5 days at 28–30 °C (fungi). The lowest concentration of the substances that kills 99.9% or more of the test organism was defined as the MBC.

Electrochemical measurements: All the electrochemical investigations were performed by using pure TTILs without any additional solvent. The decomposition potential for all the TTILs was estimated by means of linear sweep voltammetry at 5 mV s^{-1} on two polycrystalline gold electrodes in which an Ag/Ag^+ electrochemical system served as the reference electrode.

Conductivity measurements were based on impedance spectroscopy in which the complex resistivities are generated by using the ac current amplitude. The resistivity of a system, without considering diffusion, was calculated by using Ohm's law. For capacitance measurements, NORIT activated carbon was used, which had a specific surface area of 2070 m^2 g^{-1} and an external surface area of 374 m^2 g^{-1}. Voltammetry, galvanostatic, and impedance spectroscopy experiments were performed with a two-electrode Swagelok system to estimate capacitance values expressed in F g^{-1} per electrode. All the electrochemical measurements were performed by using a potentiostat-galvanostat VMP/2Z instrument (BIOLOGIC, France).

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