# Dicationic disiloxane ionic liquids as heat transfer agents in vacuo

V. G. Krasovskiy,<sup>a\*</sup> G. I. Kapustin,<sup>a</sup> O. B. Gorbatsevich,<sup>b</sup> L. M. Glukhov,<sup>a</sup> E. A. Chernikova,<sup>a</sup> A. A. Koroteev,<sup>c</sup> and L. M. Kustov<sup>a,d</sup>

 <sup>a</sup>N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 137 2935. E-mail: miyusha@mail.ru
 <sup>b</sup>N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation <sup>c</sup>Moscow Aviation Institute, 4 Volokolamskoe shosse, 125993 Moscow, Russian Federation <sup>d</sup>M. V. Lomonosov Moscow State University, Department of Chemistry, Build. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation

Bis(trifluoromethylsulfonyl)imidic dicationic liquids containing a disiloxane linker between the imidazole cations have been synthesized. Their thermal stability was estimated, and their melting points, viscosity, and volatility *in vacuo* were measured. The opportunity to use these ionic liquids as heat transfer agents in a dynamic vacuum has been shown.

**Key words:** dications, ionic liquids, disiloxanes, linkers, bis(trifluoromethylsulfonyl)imides, heat transfer agent, thermal stability, volatility.

Polar ionic liquids (ILs) possessing a wide range of the operating temperatures  $(t_{melt} - t_{decomp})$ , low viscosity, and low volatility are employed in various fields of science and technology. They are used as polar solvents in organic synthesis<sup>1,2</sup> and in the synthesis of metal nanoparticles,<sup>3</sup> as electrolytes in lithium and solar batteries in the electrochemistry,<sup>4,5</sup> and also as a stationary liquid phase in chromatography<sup>6</sup> and extractants in extraction processes.<sup>7</sup> New applied areas arise for applications of the ILs, whereas opportunities to use them in depolymerization processes during the processing of plastic waste,<sup>8,9</sup> as a medium for storage of carbon dioxide,<sup>10</sup> and as a drying agent for industrial gases<sup>11,12</sup> and in air conditioning systems<sup>13,14</sup> are explored. The opportunity to employ ILs as a working fluid in compressors for the oxygen compression has been demonstrated.<sup>15</sup> Results on using ILs as high-energy matrices have been reported.<sup>16</sup>

In the early 2000s, the opportunity to use ILs as classical heat-transfer agents (HTAs) has been evaluated,<sup>17</sup> while this problem still remains crucial.<sup>18–20</sup> Over the recent years, some works revealed the possibility to employ ILs as HTAs for heat removal in solar cells<sup>21,22</sup> and refrigerating units.<sup>23,24</sup> The acquired experimental data indicate higher values of the thermal conductivity and heat capacity for the ILs in comparison with such common HTAs as polyols. An introduction of metallic or metal oxide nanoparticles (nanofluids) into the IL compositions leads to a significant improvement in their thermophysical characteristics.<sup>25–28</sup> At the same time, there are problems

in increasing the density and viscosity of such HTAs, as well as in the dependence of stability of the dispersion of nanoparticles in ILs on the temperature. Some recent reports have revealed the opportunity to employ ILs as HTAs under the conditions of high vacuum due to their low volatility even at high temperatures and low pressures.<sup>29–31</sup>

The present work reports on the synthesis and evaluation of properties of dicationic ILs containing a disiloxane linker, which can be used as HTAs for the removal of lowpotential heat under high vacuum conditions. In this case, necessary requirements for the practical application of ILs include low values of their volatility and viscosity, as well as high hydrolytic and thermal stabilities. Moreover, the ILs have to maintain the liquid aggregation state at room temperature. The properties of ILs are largely dependent on the intermolecular interaction, an increase in which leads to a decrease in their volatility and an increase in the viscosity. The introduction of polar groups into the IL structure, which provide additional interaction between the molecules due to the formation of hydrogen bonds, leads usually to a decrease not only in the volatility, but also in the heat resistance. An addition of the second ion pair contributing to a significant increase in the Coulomb interaction and a decrease in the volatility can lead to an increase in the IL melting point above room temperature. Therefore, obtaining the IL possessing a set of properties required for its application as HTAs is a complex optimization task.

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#### Scheme 1



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	п	Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	n
3a, 4a	Me	Me	Me	1	3d, 4d	Me	Pr <sup>i</sup>	Et	1
3b, 4b	Et	Me	Me	1	3e, 4e	Me	Me	(CH <sub>2</sub> ) <sub>2</sub> OMe	1
3c, 4c	Me	Me	Me	3	3f, 4f	Me	Н	Me	1

Reagents and conditions: i. H<sub>2</sub>O, 1 h, ~20 °C; ii. MeCN, reflux, 72 h; iii. Tf<sub>2</sub>NLi, MeCN, 90 min, ~20 °C.

#### **Results and Discussion**

In this work, we selected bis(trifluoromethylsulfonyl) imidic ILs containing a disiloxane linker between the imidazole cations and a methylene spacer between the silicon atom and the cation. Imidazolium liquids comprising bis(trifluoromethylsulfonyl)imide anion (Tf<sub>2</sub>N<sup>-</sup>) exhibit the thermal stability exceeding 400 °C<sup>32,33</sup> according to the TGA data. Moreover, the bulky fluorine-containing anion reduces associative interactions and consequently, significantly decreases the viscosity of IL and its tendency to crystallize.<sup>34,35</sup> Rotational energy barriers for Si-O and Si–Me bonds (0.8 and 6.7 kJ mol<sup>-1</sup>, respectively) are several times lower than those for C–C and C–Me bonds (11.3 and 15.1 kJ mol<sup>-1</sup>, respectively).<sup>36,37</sup> A dissociation energy<sup>38</sup> for the Si–O bond in hexamethyldisiloxane is 549 kJ mol<sup>-1</sup>, while that for the C–C bond in ethane is  $334 \text{ kJ} \text{ mol}^{-1}$ . The presence of a strong siloxane bond with a high mobility in the linker structure should lead to a decreased probability of the crystallization and an increased thermal stability of the IL.

The common scheme for the synthesis of dicationic liquids comprising a disiloxane linker includes three steps (Scheme 1). At the first step, disiloxane linker reagents  $2\mathbf{a}-\mathbf{c}$  bearing chloroalkyl groups at the each silicon atom were synthesized *via* the hydrolytic condensation of dialkyl(chloroalkyl)chlorosilanes  $1\mathbf{a}-\mathbf{c}$ . Substituted imidazoles were subsequently quaternized with the obtained reagents to give dicationic ILs containing the chlorine anion  $(3\mathbf{a}-\mathbf{f})$ . The target triflate ILs  $(4\mathbf{a}-\mathbf{f})$  were synthesized via the ion exchange reaction of lithium chlorides  $3\mathbf{a}-\mathbf{f}$  with bis (trifluoromethylsulfonyl) imide.

2-Ethyl-1-isopropylimidazole for the synthesis of IL **4d** was obtained *via* the alkylation of 2-isopropylimidazole with bromoethane (Scheme 2). Potassium imidazolate was prepared *via* the exchange reaction of 2-isopropylimidazole with potassium *tert*-butoxide. 1-(2-Methoxyethyl)-2-methylimidazole was obtained similarly from 2-methylimidazole and 1-chloro-2-methoxyethane for the synthesis of IL **4e**.

#### Scheme 2

$$N = \frac{R^2}{N} + \frac{R^2}{-Bu'OK} + \frac{R^2}{N} + \frac{R^2}{-KHal} + \frac{R^2}{N} + \frac{R$$

IL **4d**:  $R^1 = Et$ ,  $R^2 = Pr^i$ ; IL **4e**:  $R^1 = (CH_2)_2OMe$ ,  $R^2 = Me$ 

Disiloxane linker **2b** bearing ethyl substituents at the silicon atom was synthesized similarly to 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane (**1a**) from chloro-(chloromethyl)diethylsilane (**1b**) obtained *via* the Grignard reaction from (chloromethyl)trichlorosilane (Scheme 3).

#### Scheme 3



The synthesis of polymeric dicationic IL 5 (Scheme 4) has been already reported.<sup>39</sup> A polymeric linker,  $\alpha, \omega$ -bis-

### Scheme 4



Reagents and conditions: i. Purolite CT 175/2429 cation exchange resin; ii. 1,2-dimethylimidazole; iii. Tf<sub>2</sub>NLi.

(chloromethyl)polydimethylsiloxane **6**, was obtained *via* the cationic polymerization of octamethylcyclotetrasiloxane (D<sub>4</sub>) using Purolite CT175 cation exchange resin as the catalyst in the presence of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane acting as a regulator of the growth of polymer chain. Quaternization of 1,2-dimethylimidazole with the polymer linker and the exchange of Cl<sup>-</sup> for Tf<sub>2</sub>N<sup>-</sup> were carried out similarly to those in the synthesis of disiloxane dicationic ILs.

All the chloride ILs obtained at the second step of the synthesis, including those containing the polymer linker, are solids at room temperature, which are readily soluble in water.

A DC-705 (Dow Corning)<sup>40</sup> coolant, 1,3,5-trimethyl-1,1,3,5,5-pentaphenyltrisiloxane (7), used in various fields of science and industry was selected as the reference object. The currently produced Russian analog of DC-705, FM-1,<sup>41</sup> is a narrow fraction with a mass content of the target substance  $\geq$ 70% (coolant Penta-410).<sup>42</sup>

$$\begin{array}{ccc} Ph & Me & Ph \\ Ph - Si - O - Si - O - Si - Ph \\ Me & Ph & Me \\ \hline 7 \end{array}$$

Aggregate state of Tf<sub>2</sub>N-IL (according to DSC data). An ionic liquid supposed to be used as a HTA has to be in the liquid state at room temperature. A melting point ( $T_m$ ) of IL 4a is 69 °C (Table 1). The replacement of methyl groups at the silicon atom in the linker moiety with ethyl groups does not lead to any noticeable change in the case of IL 4b. An elongation of the spacer between the silicon atom and imidazole by three times (from methylene to 1,3-propylene) leads to a decrease in  $T_m$  by 10 °C (IL 4c). And finally, only polydimethylsiloxane used as the linker ( $M_n = 502$  amu, D = 1.22, and Si<sub>2</sub>O : D<sub>4</sub> = 2<sup>39</sup>) allows obtaining dicationic IL 5 that remains liquid at room temperature and has  $T_{glass} = -57$  °C (see Table 1).

We also made an attempt to lower the melting point of ILs by introducing polar or bulky nonpolar substituents at the imidazole cation.<sup>40</sup> In the case of 1-ethyl-2-isopropylimidazole bearing substituents with a greater steric effect than that of methyl group, which was used in the synthesis, IL 4d with  $T_m = 61$  °C was obtained. The effect of alkyl substituents at the imidazole on the melting point of IL was comparable to the effect of increasing the length of spacer in the disiloxane linker (see Table 1, IL 4c).

Table 1. Properties of dicationic ILs 4a-f and 5, and organosilicon DC-705 heat transfer agent (7)

Sample	Temperature/	′°C	Volatility <sup>a</sup> /mg h <sup>-1</sup> cm <sup>-2</sup>			
	beginning of destruction	of melting	150 °C	190 °C	220 °C	
4a	437	69	0.00	0.03	0.04	
4b	439	68	0.02	0.05	0.07	
4c	419	59	0.01	0.02	0.17	
4d	417	61	Not evaluated		_	
<b>4</b> e	438	$-43^{b}$	0.07	0.14	0.29	
4f	435	$-52^{b}$	0.02	0.08	0.22	
5	423	$-57^{b}$	0.10	0.25	0.48	
7	317	-25	<i>c</i>			

<sup>a</sup> In vacuo ~0.013 Pa (~10<sup>-4</sup> Torr). <sup>b</sup> Glass transition temperature. <sup>c</sup> B.p. 245 °C (0.5 Torr/67Pa).

A replacement of the weakly polar methyl group by the more polar 2-methoxyethyl group resulted in the production of disiloxane dicationic IL **4e** that is liquid at room temperature ( $T_{\text{glass}} = -43$  °C, see Table 1). The use of 1-methylimidazole containing no any substituent at the position 2 led to IL **4f** that is also in the liquid state at room temperature.

Therefore, the variation of nature of the substituents at the imidazole allowed us to obtain two dicationic disiloxane ILs **4e,f** containing the methylene spacer, which are liquids at room temperature and have  $T_{\text{glass}} = -43$  and  $-52 \,^{\circ}\text{C}$ , respectively. An increase in the size of substituents at the silicon atom in the linker moiety led to a decrease in the  $T_{\text{m}}$  of disiloxane ILs within 10 °C. In the case of  $\alpha, \omega$ -bis(chloromethyl)polydimethylsiloxane **6** used as the linker, it was possible to obtain dicationic IL **5** with a methylene spacer, which is liquid at room temperature and have  $T_{\text{glass}} = -57 \,^{\circ}\text{C}$ .

Kinematic viscosity of the ILs. Dicationic disiloxane ILs 4e,f, and 5, which do not crystallize under the experimental conditions and have a glass transition temperatures below 0 °C, are also characterized by viscosity values ranging from 300 to 700 cSt at 30 °C (Table 2). The lowest viscosity in the case of IL 4f can be explained by the absence of substituent at the position 2 of imidazolium. The presence of acidic proton in the imidazole, capable of forming hydrogen bonds with the anion, may hinder the intermolecular Coulomb interaction, which not only maintain a low viscosity, but also prevents the crystallization of that IL. The presence of polar groups capable of intermolecular interaction in the alkyl substituents at the imidazole (IL 4e) also apparently leads to a manifestation of the steric effect, which reduces the interaction between the anion and cation in the IL. The additional intermolecular interaction (i.e., hydrogen bonds) increases the viscosity of IL 4e in comparison with that of IL 4f and prevents its crystallization. The polymeric nature of siloxane linker explains the low viscosity of IL 5. At a low molecular weight, a high polydispersity of the linker leads to the absence of IL crystallization.

**Table 2.** Viscosities of dicationic disiloxane ILs **4e**,**f** and **5**, and organosilicon DC-705 heat transfer agent (7)

IL	Viscosity at 30 °C/cSt	Constants in the equation of Vogel—Tammann—Fulcher*				
		A	-b	$T_0$		
4e	683	765.7	1.372	206.0		
4f	312	798.0	1.402	191.5		
5	341	703.7	0.729	195.9		
7	175**	—	—	—		

\*  $\ln v = b + a/(T - T_0).$ 

\*\* at 25 °C.



Fig. 1. Kinematic viscosity of ILs 4e,f and 5.

The temperature dependences of viscosity of the dicationic liquids (Fig. 1) clearly show the effect of siloxane nature of the linker, *viz.* the high mobility of polymer chains in a wide temperature range. Viscosity values of disiloxane ILs **4e**,**f** and **5** are significantly different under the normal conditions, but become almost the same (~100 cSt) upon the temperature elevated to 60 °C. Similarly to the most of organic and organosilicon ionic liquids,<sup>43-45</sup> the temperature dependences of kinematic viscosity of the considered ILs are well approximated ( $R^2 > 0.99$ ) by the Vogel—Tammann—Fulcher equation (see Table 2) that describes the temperature dependences for the viscosity of melts.<sup>46</sup>

Thermal stability of the ILs. The inclusion of thermally stable imidazolium cation, bis(trifluoromethylsulfonyl)imide anion, and a siloxane linker into the IL structures ensures their thermal stability up to the temperatures >400 °C. In terms of the thermal stability, the synthesized ILs are divided into two groups: ILs 4a,b,e,f with a decomposition temperature  $(T_{decomp})$  in the range of 435-439 °C and ILs 4c,d and 5 with that of 417-423 °C (see Table 1). The presence in structure of second group of ILs of alkyl substituents  $C_2 - C_3$ , an isopropyl group at the position 2 and an ethyl group at the position 1 in the imidazole cation (IL 4d) or of 1,3-propylene spacer between imidazole and a silicon atom (IL 4c), explains the decrease in the decomposition temperatures by 15-20 °C. The decomposition temperature of IL 5 is decreased down to 423 °C due to the presence of impurity that is a monocationic ionic liquid bearing a silanol terminal group in its cation, which causes the destruction of siloxane chain to give volatile cyclic products (Scheme 5).<sup>39</sup>

Therefore, the dicationic imidazolium ILs containing the disiloxane linker and  $Tf_2N^-$  anion exhibit the thermal stability above 400 °C. An increase in the aliphatic component in the cation structure decreases the thermal stability of ILs by 10 °C. A lower hydrolytic stability of the Si-O-Si bond in comparison with the C-C bond de-





creases the thermal stability of siloxane ILs in the presence of impurities bearing terminal silanol groups in the cation.

Volatility of the ILs. The low volatility of ILs arises due to the strong (Coulomb) intermolecular interaction. An increase in the number of ion pairs in the IL structure results in a significantly decreased volatility.43,45 The introduction of polar substituents (e.g., OH groups) into the cation results in additional intermolecular interactions and consequently, in a decreased volatility of the IL.43,44,47 The classical method to estimate the volatility of liquids, including ILs, is a determination of their enthalpy of vaporization using mass spectrometry<sup>48,49</sup> or calorimetry,<sup>50</sup> as well as a direct measurement of the pressure of saturated vapor according to the Knudsen's method.<sup>51-53</sup> Recently, a significant number of works were aimed at the estimation of IL volatility by thermogravimetry.54,56 Thermogravimetric investigations of the evaporation process, carried out either in an inert gas (nitrogen, argon) or in air, are often complicated by the thermal or thermooxidative destruction of the IL, which accompanies the evaporation of studied object. The evaporation of monocationic ILs in vacuo was also evaluated by the simple distillation on a rotary evaporator, weighing the flasks before and after their distillation for a certain period of time.<sup>57,58</sup> In the case of dicationic ILs, whose volatility values are an order of magnitude lower, this method is not appropriate. In the present work, we measured the volatility of dicationic ILs by the gravimetric method using a McBen balance designed to investigate adsorption and absorption processes and capable of recording a decrease in the weight of sample of dicationic IL at the required temperature under conditions of the given vacuum.<sup>39,43</sup>

The volatility of ILs 4a-c,e,f and 5 was estimated using a McBen balance at the temperatures of 150, 190, and 220 °C and a vacuum of ~0.013 Pa (see Table 1). The value of volatility measured experimentally is a total estimate of both the congruent evaporation of ILs and the processes of thermal destruction releasing volatile products upon heating the IL sample *in vacuo*. All the explored dicationic disiloxane ILs practically do not evaporate at 150 °C. The structural effect on the volatility value of IL begins to manifest itself at the temperatures of  $\geq 190$  °C. The lowest volatility in the explored temperature range  $(<0.2 \text{ mg h}^{-1} \text{ cm}^{-2})$  was observed for ILs **4a**—e, but even for them, the contribution of thermal destruction to volatility was noticeable. The increase in volatility along the series of IL 4a < IL 4b < IL 4c at 220 °C can be explained by an increase in the length of substituents at the silicon atom from  $C_1$  (IL 4a) to  $C_2$  (IL 4b) and  $C_3$  (IL 4c). The highest volatility (IL 5) can be explained by the presence of impurities (monocationic ILs containing terminal silanol groups<sup>39</sup>), which cause decreased thermal and hydrolytic stabilities under the experimental conditions. Ionic liquids **4e**,**f** possessing comparable values of the volatility (see Table 1) contain groups in the cation, which can form hydrogen bonds and participate in intermolecular interactions. In the case of evaporation temperature lower than the temperature of thermal destruction, the presence of additional intermolecular interaction leads to a decrease in the volatility,<sup>43</sup> which explains the low volatility  $(<0.2 \text{ mg h}^{-1} \text{ cm}^{-2})$  of ILs **4e,f** at 150 and 190 °C. The experiment performed at the temperature elevated up to 220 °C promotes thermal destruction processes that are noticeably enhanced in the presence of polar groups in the considered compounds, which leads consequently to the volatility of ILs **4e**,**f** increased 2–3 times (see Table 1).

The values of congruent evaporation of dicationic ILs are very low, *i.e.* they practically do not evaporate under the selected experimental conditions. The elongation of substituents at the silicon atom (an increase in the fraction of organic component in the structure) and the presence of polar groups in the IL cation promote the thermal decomposition and the formation of volatile products.

The synthesized ILs are superior in thermal stability and volatility to the DC-705 siloxane coolant recommended for use *in vacuo* (see Table 1). The significant decrease in the volatility of ILs (~1000 times) is achieved due to an increase in intermolecular interaction, which leads to the viscosities increased to 300 cSt and above as compared to DC-705. In summary, we have synthesized dicationic bis(trifluoromethylsulfonyl)imidic ionic liquids containing the disiloxane linker. Their thermal stability was estimated, and their volatility and viscosity were measured. The ILs possessing the decomposition temperature above 400 °C, viscosity of 300–400 cSt at 30 °C, and volatility of 0.2– 0.5 mg h<sup>-1</sup> cm<sup>-2</sup> at 220 °C and ~0.013 Pa are suitable for use as the heat transfer fluids in dynamic vacuum. The viscosity of synthesized dicationic disiloxane ILs is two times higher than that of DC-705 commercial coolant, while they differ from it by higher (by ~100 °C) thermal stability and significantly lower (by almost three orders of magnitude) volatility in high vacuum.

## **Experimental**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300 spectrometer. Thermogravimetric analysis was performed on a Derivatograph-C instrument (MOM, Hungary) under an argon atmosphere at the heating rate of 10 °C min<sup>-1</sup> (sample weight ~20 mg). Glass transition temperatures were determined by DSC using a DSC-822e differential scanning calorimeter (Mettler—Toledo, Switzerland) working in the temperature range from -100 to 100 °C at the sample heating rate of 10 °C min<sup>-1</sup> under an argon atmosphere. The GLC analysis was performed using a Chromatek—Analytic-5000 chromatograph (Russia) equipped with a 200×3 mm column (stationary phase was 5% SE-30, Chromaton-H-AW); evaporator temperature 350 °C, catharometer temperature 310 °C, and velocity of the helium supply 30 mL min<sup>-1</sup>. Programmed heating of the column was used in the temperature range 150–300 °C at the rate of 20 deg min<sup>-1</sup>.

The kinematic viscosity was measured using an Ostwald viscometer with a capillary diameter of 1.2 mm. The viscometer was calibrated at 25 °C using ethylene glycol (Aldrich, 99.8%, water content <0.01%) as the reference. The density was determined using a pycnometer with a nominal volume of 1 mL. The pycnometer was calibrated using distilled water. The volatility of ILs in vacuo was estimated using a McBen quartz spiral balance. A sample ( $\sim 0.2$  g) was placed in a quartz cuvette mounted on the movable end of spiral of the balance. The surface area of liquid was  $\sim 1.7$  cm<sup>2</sup>. The sleeve containing the sample was placed in a thermostated aluminum block. The spiral extension was determined by changing the position of reference marks using a KM-8 cathetometer within the accuracy of  $\pm 0.02$  mm. The sensitivity of used spiral was 0.3709 mm mg<sup>-1</sup>. The experimental setup was evacuated using a diffusion pump. Prior to the measurements, the samples were dried until a constant weight (~15 h) in a vacuum of at least  $10^{-4}$  Torr at 100 °C in the setup.

Chloro(chloromethyl)dimethylsilane (**1a**, 98%), chloro(3chloropropyl)dimethylsilane (**1c**, 97%), trichloro(chloromethyl)silane (97%), octamethylcyclotetrasiloxane (98%), 1-methylimidazole (99%), 2-methylimidazole (99%), 1,2-dimethylimidazole (98%), bromoethane (98%), 1-chloro-2-methoxyethane (98%), lithium bis(trifluoromethylsulfonyl)imide (99%), metallic magnesium (98%, 20–230 mesh) were purchased from Acros and Sigma—Aldrich. The imidazole derivatives were dried using an azeotropic distillation of absolute acetonitrile. All the organic solvents used were absoluted over CaH<sub>2</sub> and distilled before the synthesis.

General procedure for the synthesis of ionic liquids. Step 1. Synthesis of the siloxane linkers. Linkers for ILs 4a-f, viz. 1,1,3,3-tetralkyl-1,3-bis(chloralkyl)disiloxanes **2a**—**c**, were synthesized *via* the hydrolytic condensation of corresponding dialkyl(chloralkyl)chlorosilane **1a**—**c** in water at the volume ratio of reagents of 1 : 3, respectively. After the addition of chlorosilane to water, the two-phase reaction mixture was stirred at 20 °C for 1 h. Hexane (its volume was equal to the volume of water) was added to the mixture, and the organic layer was separated and washed with water until the neutral pH. The resulting disiloxane solution was dried over Na<sub>2</sub>SO<sub>4</sub> for 2 days. The hexane was evaporated. Yields of the target products were 96—98 wt.% of the theoretical amounts. GLC purity of the products was >97%.

Chloro(chloromethyl)diethylsilane (**1b**) used for the synthesis of disiloxane linker **2b** was obtained *via* the alkylation of trichloro(chloromethyl)silane according to the Grignard reaction with EtMgBr (molar ratio of 1 : 2, respectively) in THF. The target product was isolated by rectification ( $T_{\text{boil}} = 37-38 \text{ °C}/400 \text{ Pa}$ ) in the yield of 42%. The purity of the product was 97% according to GLC.

Polydimethylsiloxane linker for IL 5,  $\alpha, \omega$ -bis(chloromethyl) polydimethylsiloxane 6, was synthesized from 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane and octamethylcyclotetrasiloxane (molar ratio of 2 : 1) in the presence of an acidic catalyst, *viz.* the Purolite CT 175/2429 cation exchange resin (3 wt.%) within 6 h at 60 °C according to the procedure reported previously.<sup>39</sup> The catalyst was removed from the target product by filtration.

Step 2. Synthesis of substituted imidazoles, the objects of quaternization. The objects of quaternization for ILs 4d,e, viz. 1-ethyl-2-isopropylimidazole and 1-(2-methoxyethyl)-2-methylimidazole, were obtained via the alkylation of corresponding 2-alkylimidazoles. First, the corresponding potassium imidazolate in acetonitrile (50% solution) was obtained from equimolar amounts of 2-alkylimidazole and potassium tert-butoxide at 20 °C for 1 h. Then, the corresponding alkyl halide (equimolar amount, ethyl bromide or 1-chloro-2-methoxyethane) was added, and the reaction mixture was stirred for 8 h at 20 °C. The precipitate of potassium halide was filtered off, the solvents were evaporated in vacuo, and the target products were isolated by rectification in the yield of 88 wt.% of the theoretical amount for 1-ethyl-2-isopropylimidazole ( $T_{\rm b} = 69-71 \text{ °C}/10^{-4} \text{ Torr}$ ) and 58 wt.% for 1-(2-methoxyethyl)-2-methylimidazole ( $T_{\rm b} = 89-90$  °C  $/10^{-4}$  Torr). The purity of obtained products was 98% according to GPC data.

Step 3. Synthesis of chloride ILs **3a**–**f**. Alkyl-substituted imidazole was quaternized with 1,1,3,3-tetralkyl-1,3-bis(chloroalkyl)disiloxanes **2a**–**c** or **6** in refluxed acetonitrile (50% solution) at an equimolar ratio of the starting reagents for 72 h. The liquid phase was decanted, and the precipitate was dried *in vacuo*.

Step 4. Synthesis of triflate ILs 4a—f and 5. A mixture of chloride IL 3 prepared at the previous step and a 30% solution of lithium bis(trifluoromethylsulfonyl)imide (10% excess) in acetonitrile was stirred for 90 min. After removal of acetonitrile, the residue was dissolved in dichloromethane (30% solution) and lithium chloride was washed off with water until the rinses were free from chloride ion (test with AgNO<sub>3</sub>). The product was dried by azeotropic distillation of absolute dichloromethane (100 mL of CH<sub>2</sub>Cl<sub>2</sub> per 1 g of IL).

1,3-Bis[(1,2-dimethylimidazolium-3-yl)methyl]-1,1,3,3-tetramethyldisiloxane bis(trifluoromethylsulfonyl)amide (4a). The yield was 93%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz),  $\delta$ : 0.16 (s, 12 H, CH<sub>3</sub>-Si); 2.52 (s, 6 H, CH<sub>3</sub>-C); 3.75 (s, 6 H, CH<sub>3</sub>-N); 3.82 (s, 4 H, CH<sub>2</sub>–N); 7.41 (m, 2 H, =CH); 7.62 (m, 2 H, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz),  $\delta$ : 0.48, 9.74, 35.26, 40.21, 113.45, 117.80, 121.83, 122.07, 122.81, 126.37, 143.97. Found (%): C, 26.23; H, 3.63; N, 9.16; F, 24.94; S, 13.91; Si, 6.26. C<sub>20</sub>H<sub>32</sub>N<sub>6</sub>O<sub>9</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 912.92. Calculated (%): C, 26.31; H, 3.53; N, 9.21; F, 24.97; S, 14.05; Si, 6.15.

**1,3-Bis[(1,2-dimethylimidazolium-3-yl)methyl]-1,1,3,3-tetraethyldisiloxane bis(trifluoromethylsulfonyl)amide (4b).** The yield was 90%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz),  $\delta$ : 0.63 (m, 8 H, CH<sub>2</sub>CH<sub>3</sub>); 0.86 (m, 12 H, CH<sub>2</sub>CH<sub>3</sub>); 2.53 (s, 6 H, C-CH<sub>3</sub>); 3.74 (s, 6 H, N-CH<sub>3</sub>); 3.87 (m, 4 H, N-CH<sub>2</sub>); 7.38 (m, 2 H, =CH); 7.62 (m, 2 H, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz),  $\delta$ : 5.54, 6.25, 9.68, 35.25, 37.80, 113.60, 117.80, 121.90, 121.96, 122.94, 126.40, 144.04. Found (%): C, 29.71; H, 4.22; N, 8.63; F, 23.51; S, 13.27; Si, 5.85. C<sub>24</sub>H<sub>40</sub>N<sub>6</sub>O<sub>9</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 969.03. Calculated (%): C, 29.75; H, 4.16; N, 8.67; F, 23.53; S, 13.23; Si, 5.80.

**1,3-Bis[(1,2-dimethylimidazolium-3-yl)propyl]-1,1,3,3-tetramethyldisiloxane bis(trifluoromethylsulfonyl)amide (4c).** The yield was 95%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz),  $\delta$ : 0.04 (s, 12 H, CH<sub>3</sub>—Si); 0.49 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>C<u>H</u><sub>2</sub>Si); 1.67 (m, 4 H, CH<sub>2</sub>C<u>H</u><sub>2</sub>CH<sub>2</sub>Si); 2.55 (s, 6 H, CH<sub>3</sub>—C); 3.74 (s, 6 H, CH<sub>3</sub>—N); 4.06 (m, 4 H, NC<u>H</u><sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si); 7.61 (m, 4 H, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz),  $\delta$ : 0.33, 9.43, 13.50, 23.90, 34.97, 50.51, 113.52, 117.79, 121.16, 122.05, 122.70, 126.32, 144.54. Found (%): C, 29.66; H, 4.27; N, 8.60; F, 23.50; S, 13.19; Si, 5.87. C<sub>24</sub>H<sub>40</sub>F<sub>12</sub>N<sub>6</sub>O<sub>9</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 969.03. Calculated (%): C, 29.75; H, 4.16; N, 8.67; F, 23.53; S, 13.23; Si, 5.80.

**1,3-Bis**[(1-ethyl-2-isopropylimidazolium-3-yl)methyl]-**1,1,3,3-tetramethyldisiloxane bis(trifluoromethylsulfonyl)amide** (4d). The yield was 95%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz),  $\delta$ : 0.20 (s, 12 H, CH<sub>3</sub>—Si); 1.39 (m, 18 H, CH<sub>3</sub>—CH<sub>2</sub> + CH<sub>3</sub>— CH—CH<sub>3</sub>); 3.62 (m, 2 H, CH<sub>3</sub>—CH—CH<sub>3</sub>); 3.89 (s, 4 H, NCH<sub>2</sub>Si); 4.26 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>—N); 7.44 (m, 2 H, =CH); 7.74 (m, 2 H, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz),  $\delta$ : 0.33, 15.99, 19.18, 24.25, 40.56, 43.86, 113.55, 117.82, 122.08, 123.04, 126.34, 148.47. Found (%): C, 31.27; H, 4.52; N, 8.36; F, 22.85; S, 12.82; Si, 5.59. C<sub>26</sub>H<sub>44</sub>N<sub>6</sub>O<sub>9</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 997.08. Calculated (%): C, 31.32; H, 4.45; N, 8.43; F, 22.87; S, 12.86; Si, 5.63.

**1,3-Bis**[(1-(2-methoxyethyl)-2-methylimidazolium-3-yl)methyl]-1,1,3,3-tetramethyldisiloxane bis(trifluoromethylsulfonyl)amide (4e). The yield was 95%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz),  $\delta$ : 0.14 (s, 12 H, CH<sub>3</sub>—Si); 2.56 (s, 6 H, CH<sub>3</sub>—C); 3.24 (s, 6 H, CH<sub>3</sub>—N); 3.65 (m, 4 H, CH<sub>2</sub>—O); 3.84 (m, 4 H, NCH<sub>2</sub>Si); 4.32 (m, 4 H, CH<sub>2</sub>—N); 7.44 (m, 2 H, =CH); 7.65 (m, 2 H, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz),  $\delta$ : 0.80, 9.89, 40.23, 48.09, 58.53, 70.39, 113.55, 117.81, 122.06, 122.12, 126.34, 144.04. Found (%): C, 28.69; H, 4.10; N, 8.32; F, 22.76; S, 12.77; Si, 5.66. C<sub>24</sub>H<sub>40</sub>F<sub>12</sub>N<sub>6</sub>O<sub>11</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 1001.03. Calculated (%): C, 28.80; H, 4.03; N, 8.39; F, 22.78; S, 12.81; Si, 5.61.

α,ω-Bis{[(1,2-dimethylimidazolium-3-yl)methyl(dimethyl)silyl}polydimethylsiloxane bis(trifluoromethylsulfonyl)amide (5). The yield was 85%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz), δ: 0.05 (m, CH<sub>3</sub>-Si); 0.19 (m, CH<sub>3</sub>-Si); 2.54 (s, C-CH<sub>3</sub>); 3.76 (s, N-CH<sub>3</sub>); 3.83 (m, N-CH<sub>2</sub>Si); 7.42 (m, =CH); 7.62 (m, =CH). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz), δ: -1.11, 0.79, 9.35, 34.54, 40.39, 113.56, 117.82, 121.66, 122.07, 122.50, 126.33, 143.83.

1,1,3,3-Tetramethyl-1,3-bis[(1-methylimidazolium-3-yl)methyl]disiloxane bis(trifluoromethylsulfonyl)amide (4f). The yield was 88%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300.13 MHz), δ: 0.16 (s, 12 H, CH<sub>3</sub>—Si); 3.87 (s, 6 H, CH<sub>3</sub>—N); 3.89 (s, 4 H, CH<sub>2</sub>—N); 7.52 (m, 2 H, =CH); 7.69 (m, 2 H, =CH); 8.90 (s, 2 H, NCHN). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75.47 MHz), δ: 0.96, 36.16, 41.37, 113.42, 117.81, 122.07, 123.54, 124.15, 126.31, 136.25. Found (%): C, 24.33; H, 3.35; N, 9.46; F, 25.73; S, 13.51; Si, 6.45. C<sub>18</sub>H<sub>28</sub>N<sub>6</sub>O<sub>9</sub>F<sub>12</sub>S<sub>4</sub>Si<sub>2</sub>, molecular mass of 884.87. Calculated (%): C, 24.43; H, 3.20; N, 9.50; F, 25.76; S, 14.49; Si, 6.35.

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