Electronic Supporting Information (ESI)

ESI-1:

Analysis and spectroscopic measurements

^{1}H NMR, ^{13}C NMR, and ^{19}F spectra were recorded on a Bruker ARX 300 spectrometer. Spectra were calibrated with respect to the solvent signal ($CDCl_3$: ^{1}H $\delta = 7.27$; ^{13}C $\delta = 77.0$; CD_3CN: ^{1}H $\delta = 1.94$; ^{13}C $\delta = 1.32$; CD_3OD: ^{1}H $\delta = 3.31$; ^{13}C $\delta = 49.0$). Elemental analyses for C, H, and N were obtained with a Flash EA 1112 NC Analyzer from CE Instruments. Melting points were determined by DSC measurements using a Mettler Toledo DSC823^{e} in the range of -100 - 300 °C with a heating rate of 10 K·min^{-1} (N_2 atmosphere, Al crucible). All melting points are endothermic peak temperatures.

Materials

Lithium bis(trifluoromethane)sulfonimide (Li[NTf_2]) (IoLiTec GmbH Denzlingen, 99 %), potassium carbonate (Aldrich, 99 %), 2,4-dimethylimidazole (DMIm, ABCR, 97 %), and 1,2,4,5-tetramethylimidazole (1,2,4,5-TeMIm, ABCR, 95 %) were used without further purification. Iodomethane (Aldrich, 99 %) was distilled over CaH_2 prior to use. 2,4,5-trimethylimidazole (TMIm) [1], and 4,5-dimethylimidazolium chloride [4] were prepared as reported in the literature.

Syntheses

Synthesis of 1,2,3,4,5-pentamethylimidazolium iodide – PeMImI

TMIm (1.0 g, 9.1 mmol), K_2CO_3 (3.8 g, 27.2 mmol) and 50 mL of iodomethane were refluxed in 150 mL acetonitrile overnight. Excess iodomethane and the solvent were evaporated and the residue was extracted with dichloromethane. The combined dichloromethane solutions were concentrated to a volume of 50 mL and 100 mL Et_2O were added under constant stirring until a white precipitate was formed. The solid was removed by means of filtration and dried in vacuum overnight, yielding PeMImI as a white solid. Yield 2.3 g (98 %). mp. 210 °C (lit. 213 °C [2]). Elemental analysis for $C_8H_{15}N_2I$ % (calc.): C 36.27 (36.11); H 5.53 (5.68); N 10.25 (10.53). ^{1}H NMR ($CDCl_3$): $\delta = 2.23$ (s, 6H, Me-C=C-Me), 2.82 (s, 3H, C-Me), 3.73 (s, 6H, N-Me); ^{13}C NMR ($CDCl_3$): δ = 9.1 (Me-C=C-Me), 12.7 (C-Me), 33.2 (N-Me), 125.7 (Me-C=C-Me), 142.8 (C-Me).

Synthesis of 1,2,3,4,5-pentamethylimidazolium bis(trifluoromethane)sulfonimide – PeMIm[NTf$_2$] - I

PeMImI (2.0 g, 7.5 mmol) was dissolved in 50 mL water, followed by the addition of Li[NTf$_2$] (2.4 g, 8.3 mmol). Immediately, the solution became cloudy and a fine precipitate formed after a few minutes. The suspension was stirred for additional 30 min and then extracted three times with 100 mL portions of dichloromethane. The combined organic phases were dried over $MgSO_4$ and the filtrate was evaporated in vacuum yielding **I** as a white solid. The solid was finally dried in vacuum overnight. Yield 2.2 g (70 %). mp. 118 °C (lit. 118 °C [2]). Elemental analysis for $C_{10}H_{15}N_3S_2F_6O_4$ % (calc.): C 28.75 (28.64); H 3.74 (3.61); N 9.94 (10.02). ^{1}H NMR ($CDCl_3$): δ = 2.19 (s, 6H, Me-C=C-Me), 2.54 (s, 3H, C-Me), 3.58 (s, 6H, N-Me); ^{13}C NMR ($CDCl_3$): δ = 8.4 (Me-C=C-Me), 10.0 (C-Me), 31.8 (N-Me), 125.6 (Me-C=C-Me), 142.2 (C-Me), 119.7 ([NTf$_2$]$^-$; J^{C-F} = 321.3 Hz); ^{19}F NMR ($CDCl_3$): δ = -79.1 ([NTf$_2$]$^-$).

Synthesis of 1,2,3,4-tetramethylimidazolium iodide – 1,2,3,4-TeMImI

DMIm (3.0 g, 31.2 mmol), K_2CO_3 (12.9 g, 93.6 mmol), and 50 mL iodomethane were refluxed in 150 ml acetonitrile overnight. Excess iodomethane and the solvent were evaporated and the residue was extracted with dichloromethane. The combined dichloromethane solutions were concentrated to a volume of 50 mL and 100 mL Et_2O were added under constant stirring until a white precipitate was formed. The solid was removed by means of filtration and dried in vacuum, yielding 1,2,3,4-TeMImI as a white solid. Yield 6.7 g (85 %). mp. 141 °C. Elemental analysis for $C_7H_{13}N_2I$ % (calc.): C 33.15 (33.35); H 5.21 (5.20); N 10.63 (11.11). ^{1}H NMR (CD_3CN): δ = 2.24 (s, 3H, H-C=C-Me), 2.51 (s, 3H, C-Me), 3.58 (s, 3H, H-C-N-Me), 3.68 (s, 3H, N-Me), 7.08 (s, 1H, C-H); ^{13}C NMR (CD_3CN): δ = 9.6 (H-C=C-Me), 10.8 (C-Me), 32.9 (H-C-N-Me), 35.7 (N-Me), 119.7 (C-H), 131.0 (H-C=C-Me), 145.1 (C-Me).

Synthesis of 1,2,3,4-tetramethylimidazolium bis(trifluoromethane)sulfonimide – 1,2,3,4-TeMIm[NTf_2] - II

Li[NTf_2] (6.3 g, 21.8 mmol) was added in one portion to 150 mL of a stirred aqueous solution of 1,2,3,4-TeMImI (5.0 g, 19.8 mmol). The suspension is concentrated to a volume of 50 mL and extracted three times with 100 mL portions of dichloromethane. The combined organic phases were filtered over $MgSO_4$, evaporated to dryness, yielding **II** as a white solid. Yield 7.4 g (92 %). mp. 83 °C. Elemental analysis for $C_9H_{13}N_3S_2F_6O_4$ % (calc.): C 26.49 (26.67); H 3.12 (3.23); N 9.74 (10.37). ^1H NMR (CD_3CN): δ = 2.23 (s, 3H, H-C=C-$\underline{\text{Me}}$), 2.47 (s, 3H, C-Me), 3.56 (s, 3H, H-C-N-$\underline{\text{Me}}$), 3.65 (s, 3H, N-Me), 6.98 (s, 1H, C-H); ^{13}C NMR (CD_3CN): δ = 9.5 (H-C=C-$\underline{\text{Me}}$), 10.4 (C-$\underline{\text{Me}}$), 32.6 (H-C-N-$\underline{\text{Me}}$), 35.5 (N-Me), 119.8 (C-H), 131.2 (H-C=$\underline{\text{C}}$-Me), 145.2 ($\underline{\text{C}}$-Me), 121.0 ([NTf_2]$^-$; $J^{C\text{-}F}$ = 320.8 Hz); ^{19}F NMR (CD_3CN): δ = -80.2 ([NTf_2]$^-$).

Synthesis of 1,3,4,5-tetramethylimidazolium iodide – 1,3,4,5-TeMImI

4,5-Dimethylimidazolium chloride (5.0 g, 37.7 mmol), K_2CO_3 (15.6 g, 113.1 mmol), and 50 mL iodomethane were refluxed in 150 ml acetonitrile overnight. Excess iodomethane and the solvent were evaporated and the residue was extracted with dichloromethane. The combined dichloromethane solutions were concentrated to a volume of 50 mL and 100 mL Et_2O were added under constant stirring until a white precipitate was formed. The solid was removed by means of filtration and dried in vacuum, yielding 1,3,4,5-TeMImI as a white solid. Yield 9.1 g (96 %). mp. 159 °C (lit. 158 °C [3]). Elemental analysis for $C_7H_{13}N_2I{\cdot}0.25H_2O$ % (calc.): C 32.80 (32.76); H 5.36 (5.30); N 10.41 (10.92). ^1H NMR (CD_3CN): δ = 2.20 (s, 6H, C-Me), 3.70 (s, 6H, N-Me), 8.65 (s, 1H, C-H); ^{13}C NMR (CD_3CN): δ = 8.5 (C-$\underline{\text{Me}}$), 34.3 (N-Me), 128.3 (Me-$\underline{\text{C}}$=$\underline{\text{C}}$-Me), 135.3 ($\underline{\text{C}}$-H).

Synthesis of 1,3,4,5-tetramethylimidazolium bis(trifluoromethane)sulfonimide – 1,3,4,5-TeMIm[NTf_2] - III

Li[NTf_2] (6.3 g, 21.8 mmol) was added in one portion to 150 mL of a stirred aqueous solution of 1,3,4,5-TeMImI (5.0 g, 19.8 mmol). The suspension is concentrated to a volume of 50 mL and extracted three times with 100 mL portions of dichloromethane. The combined organic phases were filtered over $MgSO_4$, evaporated to dryness, yielding **III** as a white solid. Yield 7.6 g (94 %). mp. 32 °C. Elemental analysis for $C_9H_{13}N_3S_2F_6O_4$ % (calc.): C 27.15 (26.67); H 3.43 (3.23); N 10.00 (10.37). ^1H NMR (CD_3CN): δ = 2.19 (s, 6H, C-Me), 3.66 (s, 6H, N-Me), 8.23 (s, 1H, C-H); ^{13}C NMR (CD_3CN): δ = 8.4 (C-<u>Me</u>), 34.2 (N-Me), 128.3 (Me-<u>C</u>=<u>C</u>-Me), 135.3 (<u>C</u>-H), 119.7 ($[NTf_2]^-$; $J^{C\text{-}F}$ = 320.8 Hz); ^{19}F NMR (CD_3CN): δ = -80.2 ($[NTf_2]^-$).

Synthesis of 1,2,4,5-tetramethylimidazolium chloride – 1,2,4,5-TeMImCl

Hydrochloric acid (37 %, 4.0 g, 40.3 mmol) was added slowly with stirring to 50 mL of an aqueous solution of 1,2,4,5-TeMIm (5.0 g, 40.3 mmol). The resulting solution was evaporated to dryness leaving 1,2,4,5-TeMImCl as a white solid. Yield 6.4 g (99 %). mp. 221 °C. Elemental analysis for $C_7H_{13}N_2Cl\cdot 0.2H_3OCl$ % (calc.): C 49.16 (49.01); H 8.24 (7.99); N 16.00 (16.33). ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3H, C-Me), 2.18 (s, 3H, C-Me), 2.61 (s, 3H, C-Me), 3.56 (s, 3H, N-Me), 15.14 (br, 1H, N-H); ^{1}H NMR (CD_3OD): δ = 2.24 (s, 6H, C-Me), 2.59 (s, 3H, C-Me), 3.65 (s, 3H, N-Me); ^{13}C NMR ($CDCl_3$): δ = 8.2 (C-<u>Me</u>), 8.9 (C-<u>Me</u>), 10.7 (C-<u>Me</u>), 31.2 (N-Me), 123.9 (Me-<u>C</u>=<u>C</u>-Me), 124.7 (Me-<u>C</u>=<u>C</u>-Me), 141.3 (<u>C</u>-Me); ^{13}C NMR (CD_3OD): δ = 8.3 (C-<u>Me</u>), 9.1 (C-<u>Me</u>), 11.0 (C-<u>Me</u>), 31.9 (N-Me), 124.5 (Me-<u>C</u>=<u>C</u>-Me), 127.6 (Me-<u>C</u>=<u>C</u>-Me), 143.6 (<u>C</u>-Me).

Synthesis of 1,2,4,5-tetramethylimidazolium bis(trifluoromethane)sulfonimide – 1,2,4,5-TeMIm[NTf$_2$] - IV

Li[NTf$_2$] (2.0 g, 6.9 mmol) was added in one portion to 50 mL of a stirred aqueous solution of 1,2,4,5-TeMImCl (1.0 g, 6.2 mmol). The suspension is concentrated to a volume of 10 mL and extracted three times with 50 mL portions of dichloromethane. The combined organic phases were filtered over $MgSO_4$, evaporated to dryness, yielding **IV** as a white solid. Yield 2.3 g (91 %). mp. 40 °C. Elemental analysis for $C_9H_{13}N_3S_2F_6O_4$ % (calc.): C 26.85 (26.67); H 3.39 (3.23); N 10.23 (10.37). ^{1}H NMR ($CDCl_3$): δ = 2.19 (s, 6H, C-Me), 2.56 (s, 3H, C-Me), 3.59 (s, 3H, N-Me), 11.25 (br, 1H, N-H); ^{13}C NMR ($CDCl_3$): δ = 8.1 (C-<u>Me</u>), 8.7 (C-<u>Me</u>), 10.5 (C-<u>Me</u>), 31.4 (N-Me), 124.0 (Me-<u>C</u>=<u>C</u>-Me), 125.9 (Me-<u>C</u>=<u>C</u>-Me), 141.8 (<u>C</u>-Me), 119.7 ($[NTf_2]^-$; $J^{C\text{-}F}$ = 320.8 Hz); ^{19}F NMR ($CDCl_3$): δ = -79.1 ($[NTf_2]^-$).

References:

[1] N. Kuhn, G. Henkel, J. Kreutzberg, *Z. Naturforsch.*, 1991, **46b**, 1706-1712.

[2] H. L. Ngo, K. LeCompte, L. Hargens, Alan B. McEwen, *Thermochimica Acta*, 2000, **357-358**, 97-102.

[3] H. A. D. Jowett, *J. Chem. Soc.*, 1905, **87**, 405-409.

[4] Patent, GB 2 068 362 A.

ESI-2:

Deconvoluted FIR spectra of ionic liquids I-IV

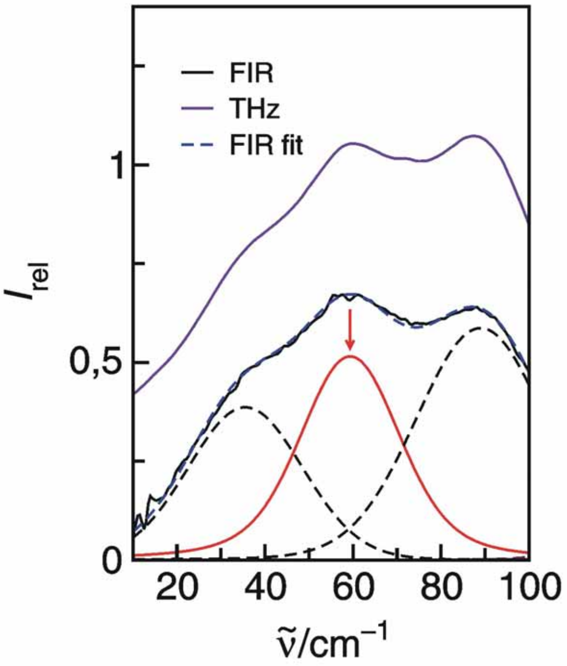

Figure ESI-2a:
FIR, THz and deconvoluted FIR spectra of **I**.

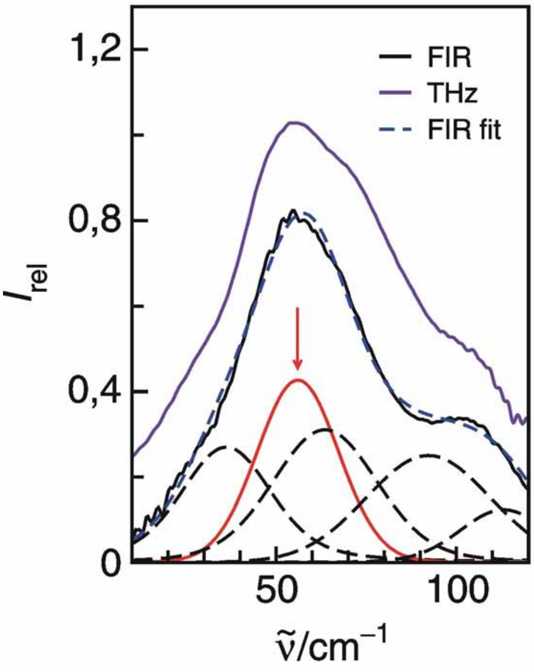

Figure ESI-2b:
FIR, THz and deconvoluted FIR spectra of **II**.

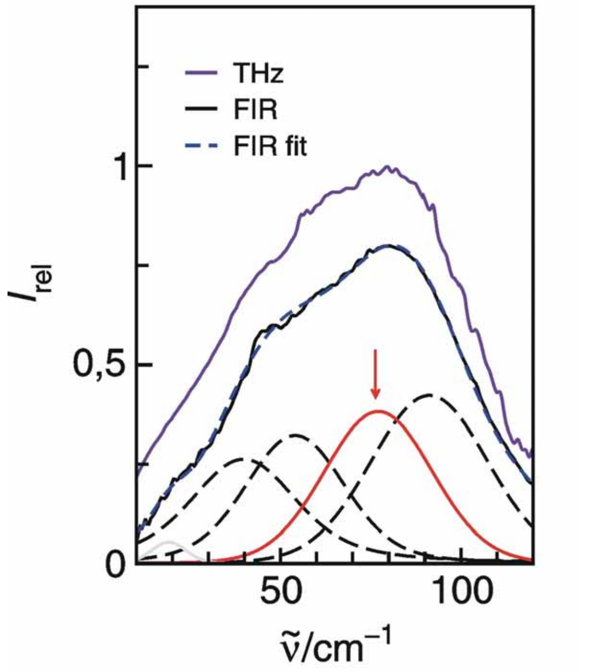

Figure ESI-2c:
FIR, THz and deconvoluted FIR spectra of **III**.

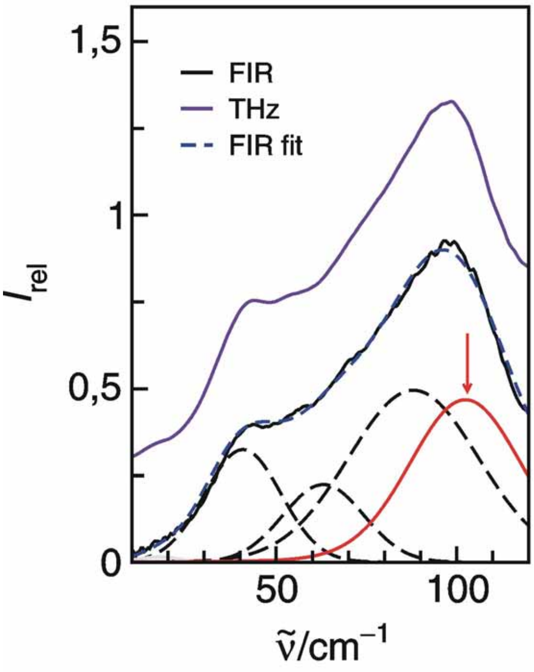

Figure ESI-2d:
FIR, THz and deconvoluted FIR spectra of **IV**.

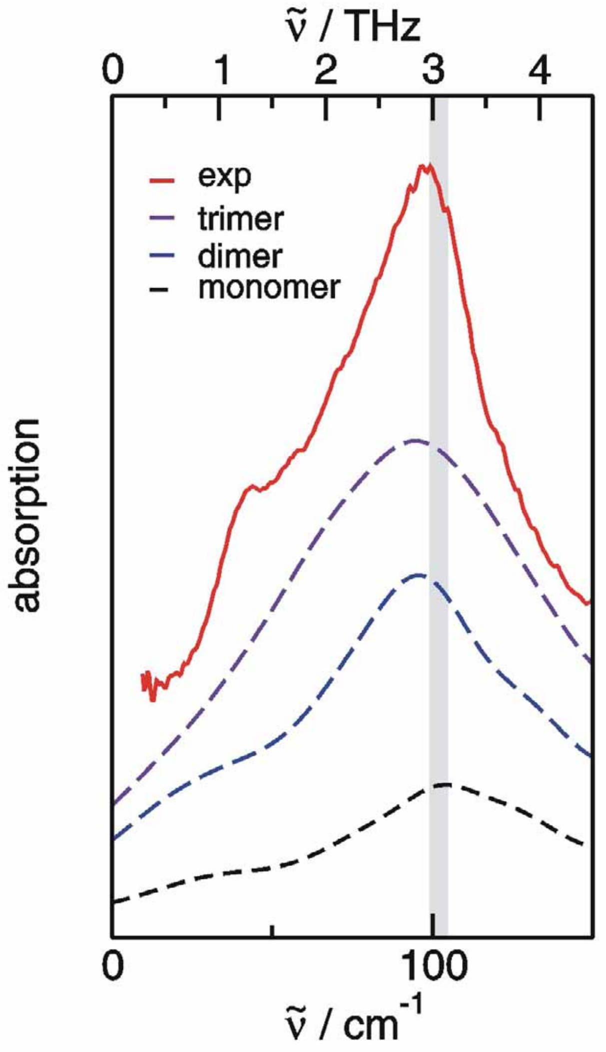

Figure ESI-2e Measured low vibrational frequencies for 1,2,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide compared to calculated frequencies of monomers, dimers and trimers of ion-pairs for this IL. The contributions at about 100 cm^{-1} can be mainly assigned to hydrogen bonding.

ESI-3:

Viscosity measurements

The measurements of the kinematic viscosity ν has been carried out at atmospheric pressure with commercial Ubbelohde viscometers (Labor-Therm/Jena, Cappilary No. II, Schott geräte GmbH/Germany, Capillaray No. Ic and No. III), inserted in a thermostated bath (LAUDA Proline PV 24).[1] The thermostat fluid was LAUDA THERM 180 silicon oil, suitable in the temperature range from 273 K to 353 K. The flow-time in the viscometer was measured using an electronic stopwatch having a precision of ±0.01 s. The temperature was measured with a precision thermometer with an accuracy of ±0.01 K. The Hagenbach-correction was carried out by subtracting a correction value y from each time interval determined for the effluence, according to $v=k(t-y)$. The correction value y was interpolated from the data given in the instruction manuals by Schott Geräte and JENAer Glaswerk.[2,3] At least five sets of readings for the flow times were taken for the liquid and the arithmetic mean was taken for the calculation of the viscosity. The scattering of the experimental values of the viscosity measurement runs was less than 1 mPa s, the coefficient of vairation of the measurements less than 0.1% for the given temperatures. The relative error of the viscosity measurement is estimated to be less than ±0.5% below 323 K and ±1% for temperatures above. The measured values for temperature between 303 and 343 K could be fitted to an Arrhenius equation. The extrapolated value for ν at 293 K was then converted to dynamic viscosity η, applying the measured density ρ according to $\eta=\nu\rho$.

[1] LAUDA DR. R. WOBSER GmbH & Co. KG Betriebanleitung LAUDA Proline Wärmethermostate.

[2] Schott Geräte GmbH Hofheim (Germany) Operation INstruction Ubbelohde-Viscometer

[3] JENAer GLASWERK SCHOTT & GEN., Jena (Germany) Korrekturtafel für Bewegungsenergie

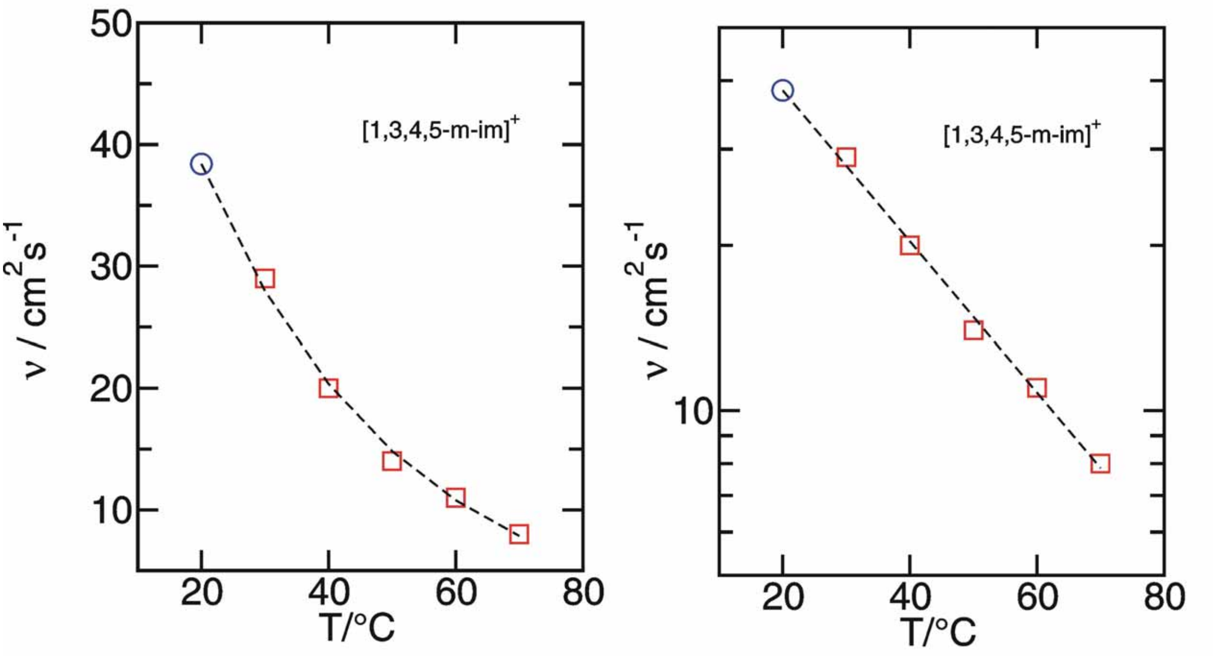

Figure ESI-3 Measured kinematic viscosities of 1,3,4,5-tetramethyl-imidazolium bis(trifluoromethylsulfonyl) imide in the temperature range between 30 and 70 °C. The extrapolated value at 20 °C is indicated by the blue circle.

ESI-4: Enthalpies of Vaporization

Enthalpies of vaporization of ILs have been measured using the quartz-crystal-microbalance (QCM) technique.

Table ESI-4a. The results of the temperature dependence of mass uptake in QCM-measurements for 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

T / K	f / Hz·s^{-1}	T^{-1} / K^{-1}	R·ln($fT^{1/2}$)
392.24	0.2723	0.00255	14.01
387.24	0.1718	0.00258	10.13
382.23	0.1069	0.00262	6.130
377.24	0.06569	0.00265	2.025
372.24	0.03977	0.00269	-2.202
367.24	0.02374	0.00272	-6.548
362.25	0.01399	0.00276	-11.00

Table ESI-4b. The results of the temperature dependence of mass uptake in QCM measurements for 1,2,3-trimethylimidazolium bis(trifluoromethanesulfonyl)imide.

T / K	f / Hz·s^{-1}	T^{-1} / K^{-1}	R·ln($fT^{1/2}$)
409.37	0.8977	0.002443	24.11
404.36	0.5456	0.002473	19.92
399.36	0.3530	0.002504	16.24
394.38	0.2268	0.002536	12.51
389.38	0.1421	0.002568	8.575
384.38	0.08799	0.002602	4.534
380.38	0.05946	0.002629	1.232

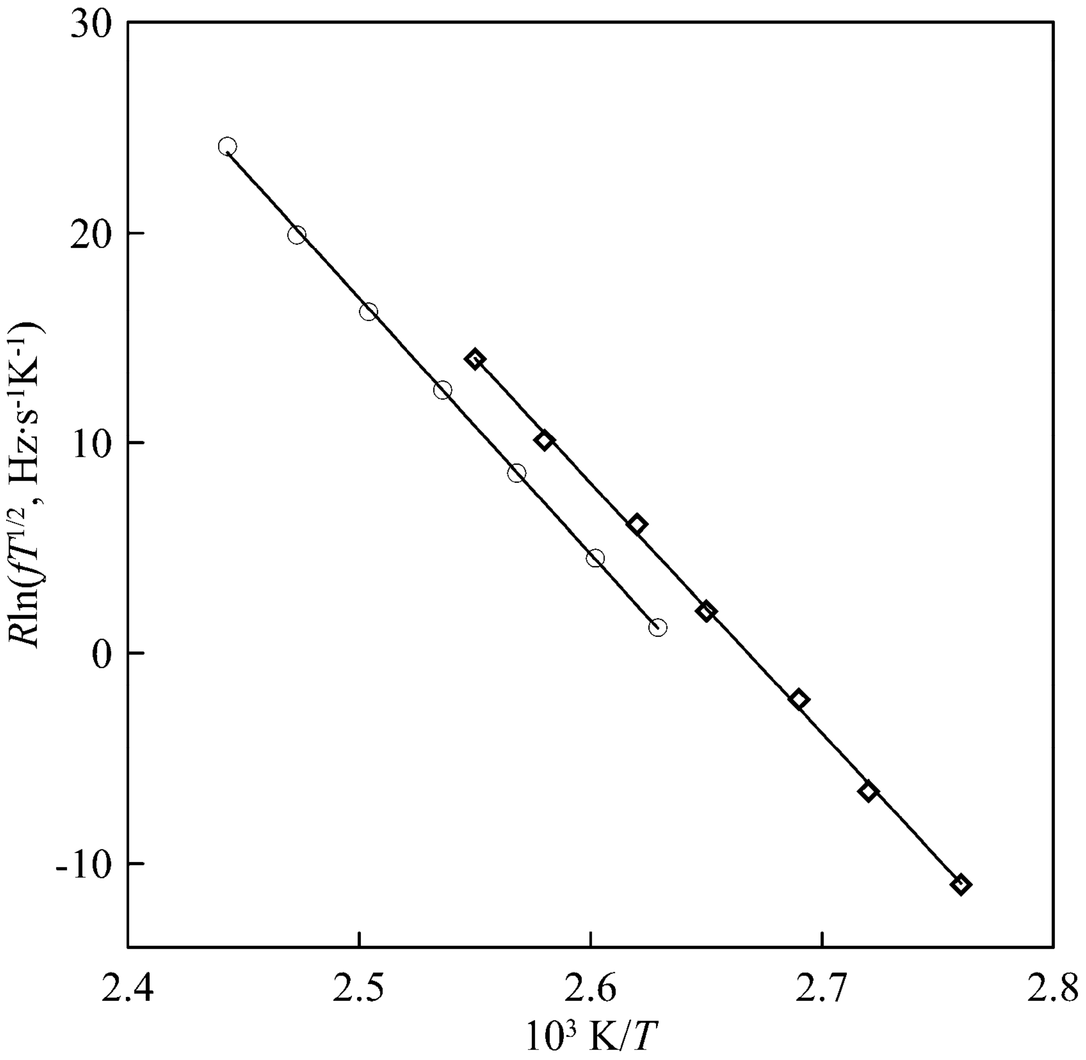

Figure ESI-4 The temperature dependence of mass uptake for 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (◊) and 1,2,3-trimethylimidazolium bis(trifluoromethanesulfonyl)imide (○) obtained in QCM-Langmuir method.