Supporting Information

Controlled Deuterium Labeling of Imidazolium Ionic Liquids to Probe the Fine Structure of the Electrical Double Layer Using Neutron Reflectometry

Kazuhiro Akutsu-Suyama,[1*] Marina Cagnes,[2] Kazuhisa Tamura,[3] Toshiji Kanaya,[4] and Tamim A. Darwish[2**]

[1] Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), 162-1 Shirakata, Tokai-Mura, Naka-gun, Ibaraki 319-1106, Japan.

[2] Australian Centre for Neutron Scattering and National Deuteration Facility, Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.

[3] Quantum Beam Science Center, Japan Atomic Energy Agency (JAEA), Sayo, Hyogo 679-5148, Japan.

[4] High Energy Accelerator Research Organization (KEK), 203-1 Shirakata, Tokai-Mura, Naka-gun, Ibaraki 319-1106, Japan.

*E-mail: k_akutsu@cross.or.jp (K. Akutsu)
**E-mail: tamim.darwish@ansto.gov.au (T. A. Darwish)

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Synthesis of deuterated ionic liquids

The $C_n$mim cation molecule was deuterated using a single step deuteration reaction. This reaction was performed using a Parr Reactor (600 mL vessel capacity, 3000 psi maximum pressure, 350°C maximum temperature) (Moline, USA).[1] ^{1}H–NMR (400 MHz), ^{13}C–NMR (100.6 MHz), and ^{2}H–NMR (61.4 MHz) spectra were recorded on a Bruker 400 MHz spectrometer at 298 K (Sydney, Australia).[1] Electrospray ionization mass spectra (ESI-MS) (MA, USA) were recorded on a 4000 QTrap AB Sciex spectrometer.[1] Note that since [$C_n$mim][Cl]s are highly hygroscopic, the following synthesis yield, which was treated as an anhydrous ionic liquid, would not be necessarily optimum. All reagents were purchased from Sigma–Aldrich unless otherwise specified.

Synthesis of deuterated [C_2mim][Cl] at 160°C

A mixture of [C_2mim][Cl] (5.32 g), Pt/activated carbon (10% Pt, 0.80 g), and Pd/activated carbon (10% Pd, 0.79 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.83 g (102 %, 91.2 %-*d*). ^{1}H–NMR (400 MHz, D_2O) δ 1.33 (residual signal), 3.74 (residual signal), 4.08 (residual signal), 7.29 (residual signal), 7.36 (residual signal), 8.58 (residual signal). ^{2}H–NMR (61.4 MHz, D_2O) δ 1.33 (s), 3.74 (s), 4.07 (s), 7.33 (s), 7.40 (s), 8.61 (s). ^{13}C{^{1}H}–NMR (101 MHz, D_2O) δ 13.0–13.8 (m), 34.3–35.3 (m), 43.8–44.5 (m), 121.1–121.8 (m), 122.7–123.3 (m), 134.8–135.6 (m). ^{13}C{^{1}H, ^{2}H, d1 = 20 s}–NMR (101 MHz, D_2O) δ 13.4 (s), 34.9 (s), 44.0 (s), 121.4 (s), 123.0 (s), 135.2 (s). ESI-MS, ^{1}H-NMR, and ^{2}H-NMR data are shown in Fig. S3-1-3.

Synthesis of deuterated [C_4mim][Cl] at 100°C

A mixture of [C_4mim][Cl] (5.02 g), Pt/activated carbon (10% Pt, 0.80 g), and Pd/activated carbon (10% Pd, 0.79 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 100°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (44.9 %-*d*). ESI-MS data is shown in Fig. S4.

Synthesis of deuterated [C_4mim][Cl] at 130°C

A mixture of [C_4mim][Cl] (5.02 g), Pt/activated carbon (10% Pt, 0.80 g), and Pd/activated carbon (10% Pd, 0.79 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 130°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (43.8 %-*d*). ESI-MS data is shown in Fig. S5.

Synthesis of deuterated [C_4mim][Cl] at 160°C

A mixture of [C_4mim][Cl] (5.24 g), Pt/activated carbon (10% Pt, 0.80 g), and Pd/activated carbon (10% Pd, 0.77 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.65 g (99.8 %, 93.3 %-*d*). ESI-MS data is shown in Fig. S6.

Synthesis of deuterated [C_4mim][Cl] at 180°C

A mixture of [C_4mim][Cl] (5.12 g), Pt/activated carbon (10% Pt, 0.86 g), and Pd/activated carbon (10% Pd, 0.79 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 180°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.31 g (95.9 %, 94.5 %-*d*). ^{1}H–NMR (400 MHz, D_2O) δ 0.77 (residual signal), 1.15 (residual signal), 1.68 (residual signal), 3.75 (residual signal), 4.05 (residual signal), 7.31 (residual signal), 7.36 (residual signal), 8.59 (residual signal). ^{2}H–NMR (61.4 MHz, D_2O) δ 0.74 (s), 1.13 (s), 1.67 (s), 3.74 (m), 4.04 (s), 7.34 (m), 7.39 (s), 8.61 (s). ^{13}C{^{1}H}–NMR (101 MHz, D_2O) δ 11.3–12.2 (m), 17.3–18.2 (m), 29.7–30.6 (m), 34.7–35.6 (m), 48.1–49.2 (m), 121.6–122.2 (m), 122.8–123.6 (m), 135.2–135.9 (m). ^{13}C{^{1}H, ^{2}H, d1 = 20 s}–NMR (101 MHz, D_2O) δ 11.6 (m), 17.5 (s), 30.0 (s), 34.9 (s), 48.5 (s), 121.8 (s), 123.0 (s), 135.5 (s). ESI-MS, ^{1}H-NMR, and ^{2}H-NMR data are shown in Fig. S7-1-3.

Synthesis of deuterated [C_8mim][Cl] at 160°C

A mixture of [C_8mim][Cl] (4.95 g), Pt/activated carbon (10% Pt, 0.76 g), and Pd/activated

carbon (10% Pd, 0.76 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (64.5 %-*d*). ESI-MS data is shown in Fig. S8.

Synthesis of deuterated [C_8mim][Cl] at 180°C

A mixture of [C_8mim][Cl] (4.90 g), Pt/activated carbon (10% Pt, 0.77 g), and Pd/activated carbon (10% Pd, 0.78 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 180°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (67.7 %-*d*). ESI-MS data is shown in Fig. S9.

Synthesis of deuterated [C_8mim][Cl] at 200°C

A mixture of [C_8mim][Cl] (4.90 g), Pt/activated carbon (10% Pt, 0.77 g), and Pd/activated carbon (10% Pd, 0.78 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 200°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 4.14 g (78.4 %, 78.0 %-*d*). ^{1}H–NMR (400 MHz, D_2O) δ 0.69 (residual signal), 1.10 (residual signal), 1.70 (residual signal), 3.78 (residual signal), 4.07 (residual signal), 7.35 (residual signal), 7.39 (residual signal), 8.70 (residual signal). ^{2}H–NMR (61.4 MHz, D_2O) δ 0.64 (br s), 1.09 (br s), 1.70 (br s), 3.78 (br s), 4.07 (br s), 7.38 (br s), 7.42 (br s), 8.72 (br s). ^{13}C{^{1}H}–NMR (101 MHz, D_2O) δ 12.0–13.6 (m), 20.6–22.2 (m), 24.0–24.9 (m), 26.8–28.8 (m), 29.9–31.2 (m), 34.7–35.8 (m), 48.4–49.3 (m), 121.5–122.2 (m), 122.9–123.6 (m), 135.2–135.9 (m). ^{13}C{^{1}H, ^{2}H, d1 = 20 s}–NMR (101 MHz, D_2O) δ 12.4 (s), 12.7 (s), 13.0 (s), 13.3 (s), 13.6 (s), 20.8 (s), 20.9 (s), 21.0 (s), 21.4 (s), 21.9 (s), 22.0 (s), 22.1 (s), 22.2 (s), 24.3 (s), 24.4 (s), 27.0 (s), 27.2 (s), 27.3 (s), 27.4 (s), 28.2 (s), 28.3 (s), 28.4 (s), 29.9 (s), 31.0 (s), 31.1 (s), 31.2 (s), 34.8 (s), 35.1 (s), 35.3 (s), 48.8 (s), 49.1 (s), 121.8 (s), 123.2 (s), 135.5 (s). ESI-MS, ^{1}H-NMR, and ^{2}H-NMR data are shown in Fig. S10-1-3. Some small extra signals in the ^{1}H-NMR data of deuterated [C_8mim][Cl]

were observed which indicates minor impurities. Note that since 1-methylimidazole is soluble in water, we conclude that these signals in the ^{1}H-NMR data are attributed to the minor impurity of 1-methylimidazole that was generated by the decomposition of C_8mim cation during the hydrothermal reaction.

Synthesis of deuterated [C_{10}mim][Cl] at 160°C

A mixture of [C_{10}mim][Cl] (4.50 g), Pt/activated carbon (10% Pt, 0.79 g), and Pd/activated carbon (10% Pd, 0.78 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (49.0 %-*d*). ESI-MS data is shown in Fig. S11.

Synthesis of deuterated [C_{10}mim][Cl] at 200°C

A mixture of [C_{10}mim][Cl] (4.50 g), Pt/activated carbon (10% Pt, 0.79 g), and Pd/activated carbon (10% Pd, 0.78 g) in D_2O (120 mL) was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 200°C with constant stirring for 24 h. An aliquot of the reaction mixture was taken out from the reactor, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (10 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The deuteration ratio was estimated by ESI-MS (74.7 %-*d*). ESI-MS data is shown in Fig. S12.

Synthesis of 50 % deuterated [C_4mim][Cl]

A mixture of [C_4mim][Cl] (4.83 g), Pt/activated carbon (10% Pt, 0.76 g), and Pd/activated carbon (10% Pd, 0.76 g) in H_2O (60 mL) and D_2O (60 mL) mixture was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.03 g (99.9 %, 48.8 %-*d*). ^{1}H–NMR (400 MHz, D_2O) δ 0.79 (m), 1.18 (m), 1.72 (m), 3.76 (m), 4.07 (m), 7.32 (d), 7.36 (d), 8.60 (s). ^{2}H–NMR (61.4 MHz, D_2O) δ 0.77 (m), 1.16 (br s), 1.67 (br s), 3.78 (m), 4.05 (br s), 7.37 (d), 8.62 (br s). ^{13}C{^{1}H}–NMR (101 MHz, D_2O) δ 11.5–12.7 (m), 17.6–18.7 (m), 30.2–31.2 (m), 34.8–35.7 (m), 48.6–49.3 (m), 121.9–122.3 (m), 123.2–123.5 (m), 135.6–135.9 (m). ^{13}C{^{1}H, ^{2}H, d1 = 20 s}–NMR

(101 MHz, D_2O) δ 12.3 (m), 18.1 (m), 30.7 (t), 35.3 (q), 48.9 (t), 122.0 (t), 123.2 (t), 135.6 (d). ESI-MS and ^{1}H-NMR data are shown in Fig. S13-1-2.

Synthesis of 70 % deuterated [C_4mim][Cl]

A mixture of [C_4mim][Cl] (5.33 g), Pt/activated carbon (10% Pt, 0.77 g), and Pd/activated carbon (10% Pd, 0.80 g) in H_2O (30 mL) and D_2O (70 mL) mixture was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.61 g (99.3 %, 69.9 %-*d*). ESI-MS data is shown in Fig. S14.

Synthesis of position-selective deuterated [C_4mim][Cl]

A mixture of [C_4mim][Cl] (5.07 g), Pt/activated carbon (10% Pt, 0.80 g), and Pd/activated carbon (10% Pd, 0.79 g) in H_2O (55 mL) and D_2O (65 mL) mixture was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 160°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The resulting product (46.6 %-*d*, equally) was used to the next deuteration reaction.

A mixture of [C_4mim][Cl] (46.6 %-*d*, 8.60 g), Pt/activated carbon (10% Pt, 0.82 g), and Pd/activated carbon (10% Pd, 0.81 g) in D_2O (120 mL) mixture was loaded into the Parr Reactor. The contents of the reactor were degassed by purging with N_2 gas and then purged with H_2 gas. After sealing the reactor, the mixture was heated to 120°C with constant stirring for 24 h. The reactor was cooled to room temperature, and the contents were filtered through a short plug of Celite to remove the catalyst, which was further washed with H_2O (100 mL). The aqueous filtrate was evaporated to dryness under reduced pressure, and remaining gel like product was dried at 80°C and reduced pressure (20 mbar) for 10 min. The weight of the resulting product was used to calculate the yield of the deuteration reaction. Yield: 5.51 g (63.1 %, 66.1 %-*d*). ESI-MS, ^{1}H-NMR, ^{2}H-NMR, ^{13}C-NMR data are shown in Fig. S15-1-4.

Starting materials

^{1}H-NMR data of the starting materials are shown in Fig. S15-1-4.

Anion exchange of deuterated ionic liquid

Anion exchange reaction of [C_4mim][Cl] was conducted according to the method of Z. K. Reeder *et al*.[2] with minor change.

An aqueous solution of [C_4mim][Cl] (1.98 g, 30 ml) was mixed with an aqueous solution of lithium bis(trifluoromethanesulfonyl)amide (Li-TFSA) (3.59 g, 30 ml). After 1 min shaking, the upper aqueous phase was removed and remaining IL was washed three times with 30 ml of distilled water. The product was purified by silica gel chromatography eluting with ethyl acetate-chloroform to yield 4.06 g (89.7 %) of [C_4mim][TFSA].

Stability Study of deuterated [$C_n$mim][Cl]

In this study, to reveal the stability of deuterated [$C_n$mim][Cl], neutron irradiation effect was monitored by fluorescence spectrophotometry. Sample solutions (0.1 mM) were prepared using ethanol-d_6 to increase the transmittance of neutron beam, and same sample cells (quartz, total quartz length = 2.0 mm, path length = 1.0 cm) were used in this experiments. The neutron beam size was 10×10 mm^2 and the total neutron exposure times for the experiments was 1.0 h. After the neutron irradiation, the fluorescence spectra were measured to estimate the concentration of $C_n$mim cation. Fluorescence measurements were carried out at the luorescence excitation wavelength of 250 nm. Changes in the fluorescence spectrum can monitor the degradation of $C_n$mim cation. Note that the samples were not shaken to enhance diffusion of the degradated products. All fluorescence measurements were carried out on a FP-8300 (Nihon Bunko Co., Ltd., Tokyo, Japan) spectrofluorophotometer. Fluorescence spectra are shown in Fig. S1.

Although $C_n$mim ILs have high chemical and physical stability, the stability of the C_4mim ILs toward neutron beam irradiation was studied by monitoring of the fluorescence intensity of C_4mim cation to make sure that [C_4mim][Cl] did not undergo decomposition during neutron experiment. Sample solutions (0.1 mM) were prepared using ethanol-d_6, and quartz cell (path length = 1.0 cm) was used in this experiments. The neutron beam size was fixed to 10×10 mm^2, and the total neutron exposure times for the experiments was 1.0 h. After the neutron irradiation, the fluorescence spectra were measured to estimate the concentration of C_4mim cation. Figure 1 shows the fluorescence spectra change of [C_4mim][Cl] and [C_4mim-d_{15}][Cl] by irradiation of neutron beam. The fluorescence peak of C_4mim cation appears at around 310 nm. As shown in Figure 1, the fluorescence intensity of C_4mim cation did not change by neutron beam irradiation even in deuterated C_4mim cation. Therefore, it can be suggested the concentration of C_4mim cation did not change after neutron beam irradiation, that is, the degradation reaction did not occur during neutron beam irradiation. Previous studies indicated that the mean bond length of C-H bond is clearly greater than that of C-D bond,[3] and the C-H bond is thermodynamically more unstable than the corresponding C-D bond.[4] Thus, we can conclude that the deuteration of $C_n$mim ILs do not affect

the neutron experiments in terms of stability of C$_n$mim ILs.

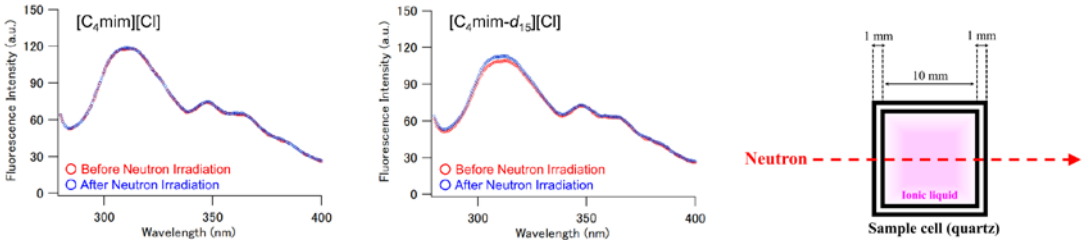

Figure S1 Fluorescence spectra of [C$_4$mim][Cl] and [C$_4$mim-d_{15}][Cl] before and after neutron irradiation, and image of the experimental cell.

Neutron reflectivity measurement

The NR measurements were performed on a BL17 SHARAKU reflectometer installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC.[5] The incident beam power of the proton accelerator was 150 kW for all the measurements. Pulsed neutron beams were generated using a mercury target at 25 Hz, and the NR data were measured using the time-of-flight (TOF) technique. The neutron-source to sample distance was 15.5 m, and the sample to ^{3}He gas point detector distance was 2.5 m. The wavelength (λ) range of the incident neutron beam was tuned to be approximately λ = 1.1–8.8 Å using disk choppers. The covered Q_z range was Q_z = 0.01 – 0.24 Å^{-1}, where $Q_z = (4\pi/\lambda)\sin\theta$ (here, θ represents the incident angle). The incident angle for the samples varied from 0.4° to 1.4°. The total exposure times for the measurements was 9 h. 25 mm beam footprint was maintained on the sample surfaces by using six kinds of incident slits. The samples were placed in a Teflon sample cell on the sample stage, which was installed at the center position of the sample rotator. All the measurements were performed at room temperature.

The data reduction, normalization, and subtraction were performed using a program installed in BL17 SHARAKU that was developed for the TOF data. The Motofit program[6] was used to fit the NR profiles using the least-squares approach to minimize deviations in the fit; the thickness, scattering length density (SLD), and Gaussian roughness were evaluated by the program. Table S1 shows the structural parameters obtained from this analysis.

Table S1. Best-fit parameters for the reflectivity model data shown in Figure 2.

Layer	Molecule	t (Å)	SLD (×10^{-6} Å^{-2})	σ (Å)
Bulk IL Layer	[C$_4$mim][TFSA]	—	5.25	2.26
Diffuse Layer	[TFSA]$^-$ dominant	11.3	4.92	2.80
	[C$_4$mim]$^+$ dominant	11.9	5.51	2.61
Negative Layer	[TFSA]$^-$	13.5	3.57	2.01
Positive Layer	[C$_4$mim]$^+$	7.72	6.53	2.28
Substrate (Negative)	SiO_2	10.5	3.47	2.34
	Si substrate	—	2.07	—

t: thickness (Å), scattering length density (SLD): ρ (×10^{-6} Å^{-2}), σ: surface or interface roughness (Å).

Electrochemical measurement settings for neutron reflectivity measurement

A cell specially designed for NR measurements was used as an electrochemical cell. It is made of Kel-F. The working electrode was a 40 × 40 mm^2 square n-Si(100) single-crystal plate with a height of 5 mm (Nihon Exceed Co., Ltd., Japan). Pt wires were used as the reference and counter electrodes. To minimize the solution resistance effect, the reference and counter electrodes were positioned 3 mm above the working electrode.

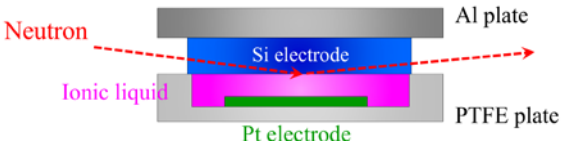

Fig S2. Image of the experimental cell.

The deuterated [C_4mim][TFSA] was dehydrated at 80 °C under vacuum (6×10^0 Pa) for 12 h before use. Before measurement, the working electrode was cleaned with ethanol and acetone in an ultrasonic bath. Finally, it was rinsed with Milli-Q water. All the electrodes, [C_4mim][TFSA] and the electrochemical cell were transferred to a glove box filled with Ar gas and they were assembled in the glove box. During NR measurements, the sample cell was set into a N_2 gas (G3 grade) box and the electrode potential was controlled using a potentiostat (IviumStat, Ivium technologies).

Figures of ESI-MS and NMR data

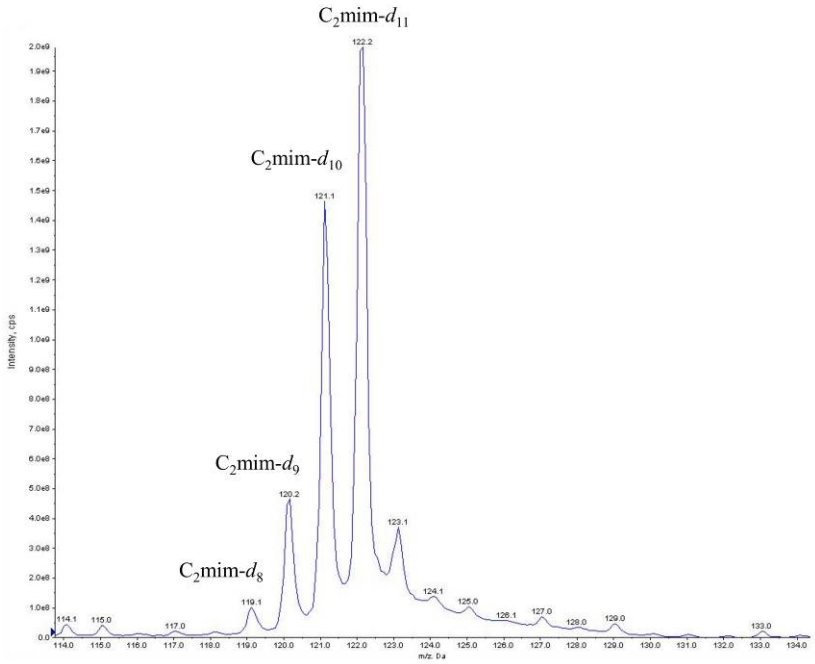

Fig. S3-1. Electrospray ionization mass spectra in positive mode of C_2mim cation showing the mass distribution of the different isotopologues, which ranges from d_8–d_{11}. The distribution of the isotopologues is as follows (M^+): 4.9 %, d_8; 17.8 %, d_9; 33.5 %, d_{10}; 35.0 %, d_{11}.

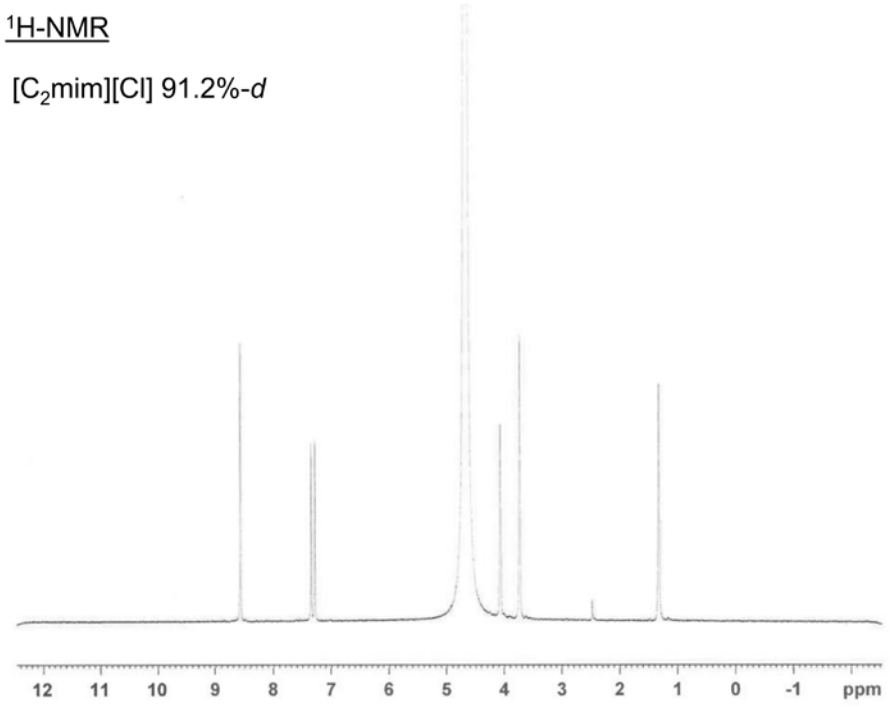

Fig. S3-2. ^{1}H-NMR (D_2O, 400 MHz) of deuterated (91.2%) [C_2mim][Cl].

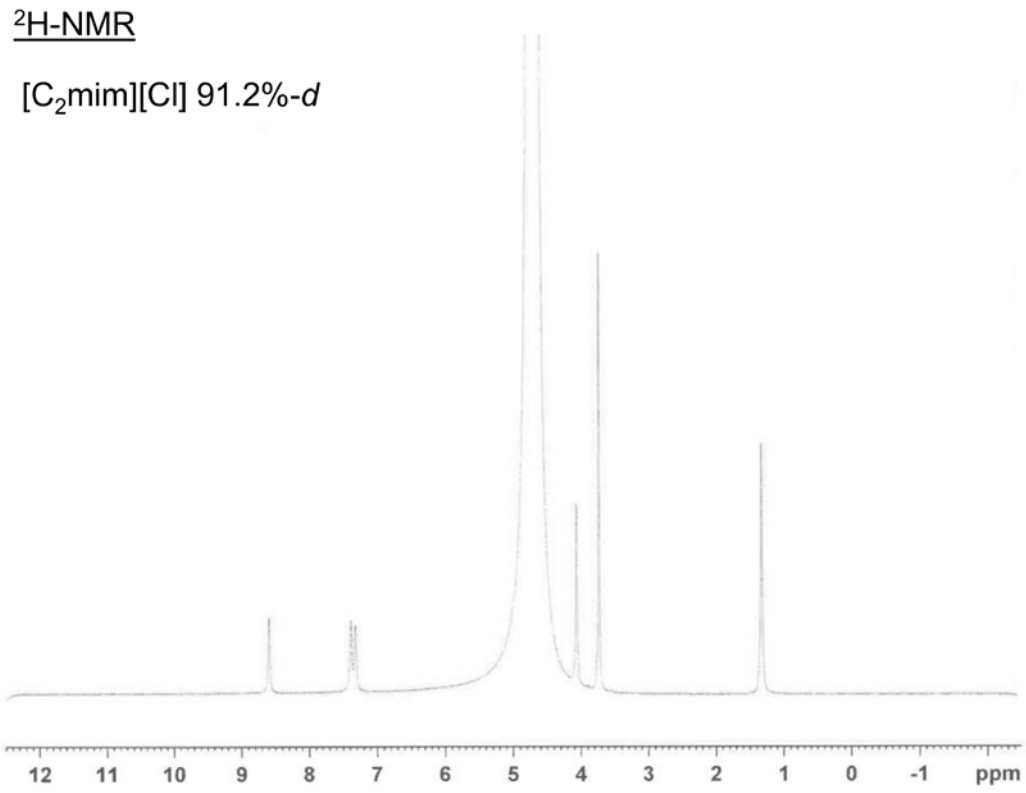

Fig. S3-3. ^{2}H-NMR (D_2O, 61.4 MHz) of deuterated (91.2%) [C_2mim][Cl].

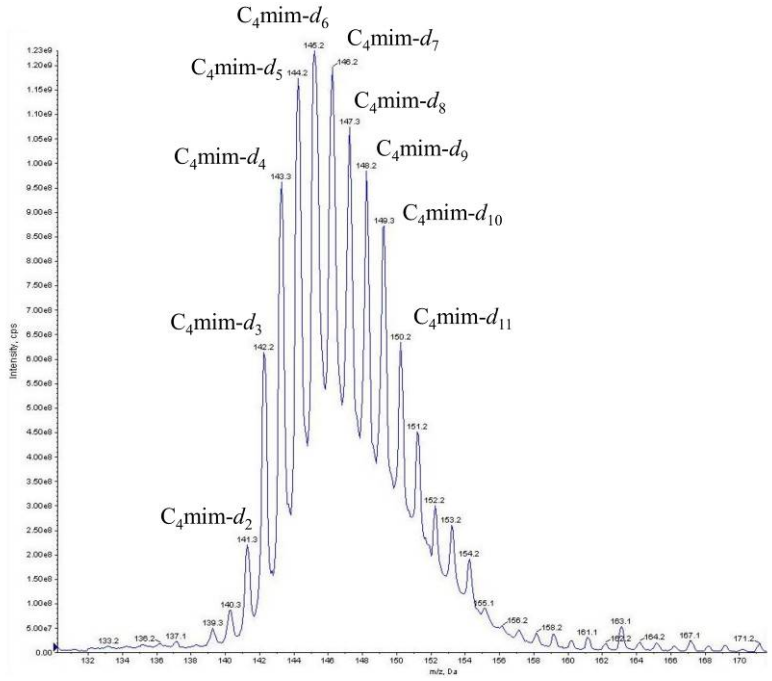

Fig. S4. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_2–d_{11}. The distribution of the isotopologues is as follows (M^+): 2.4 %, d_2; 6.0 %, d_3; 9.3 %, d_4; 12.0 %, d_5; 20.6 %, d_6; 14.6 %, d_7; 10.9 %, d_8; 7.4 %, d_9; 8.4 %, d_{10}; 8.4 %, d_{11}.

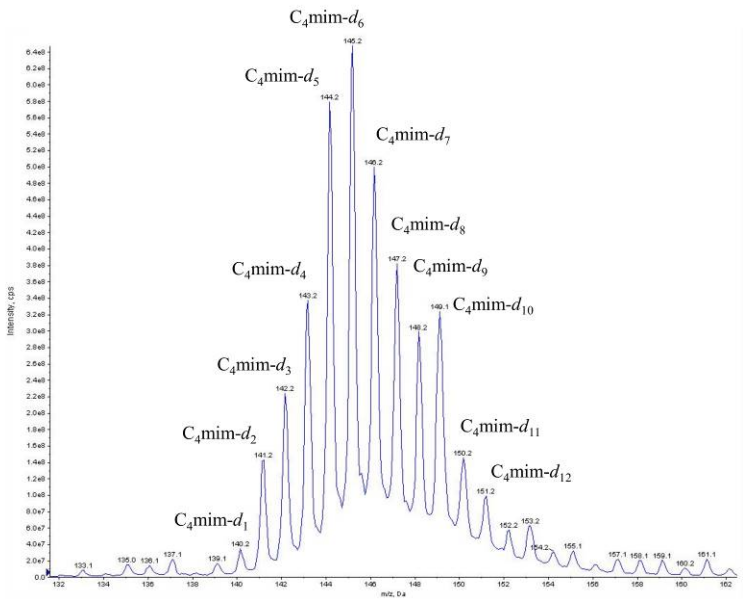

Fig. S5. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_1–d_{12}. The distribution of the isotopologues is as follows (M^+): 1.1 %, d_1; 4.6 %, d_2; 6.2 %, d_3; 9.8 %, d_4; 14.7 %, d_5; 15.7 %, d_6; 13.1 %, d_7; 10.2 %, d_8; 8.5 %, d_9; 8.2 %, d_{10}; 4.7 %, d_{11}; 3.3 %, d_{12}.

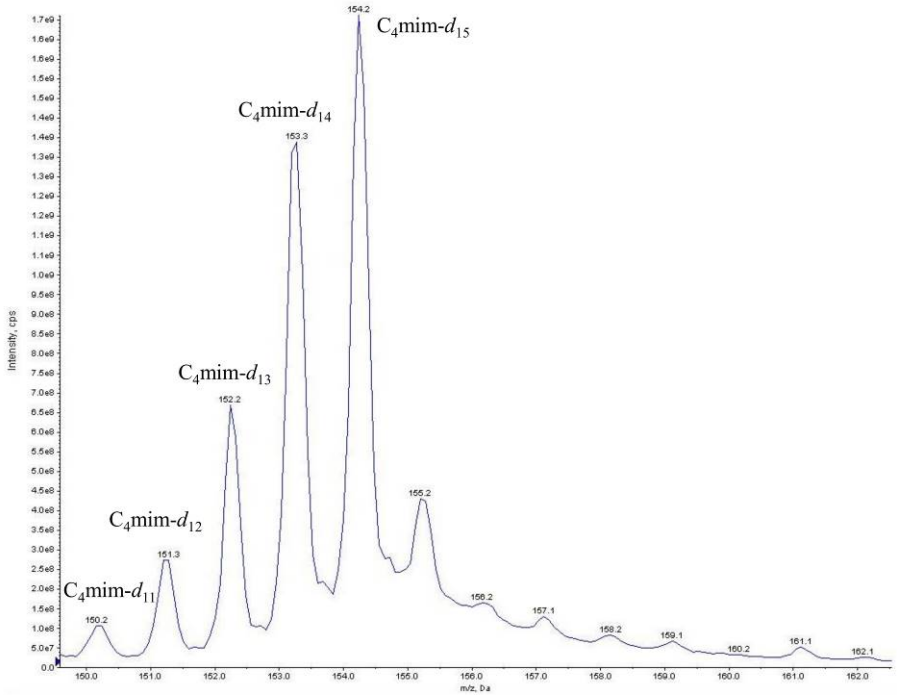

Fig. S6. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_{11}–d_{15}. The distribution of the isotopologues is as follows (M^+): 3.2 %, d_{11}; 7.1 %, d_{12}; 15.6 %, d_{13}; 32.9 %, d_{14}; 41.1 %, d_{15}.

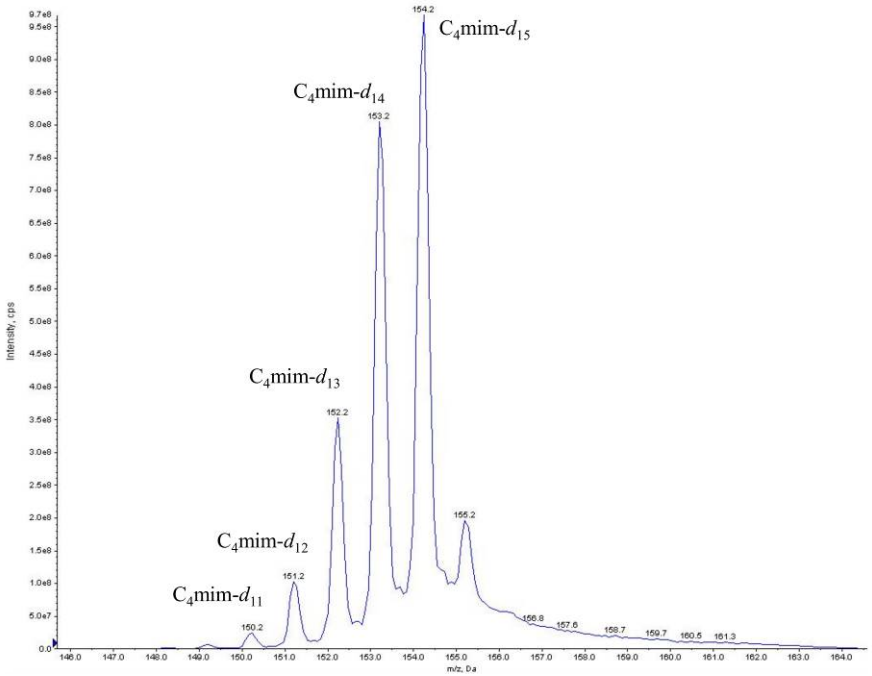

Fig. S7. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_{11}–d_{15}. The distribution of the isotopologues is as follows (M^+): 1.0 %, d_{11}; 4.4 %, d_{12}; 14.8 %, d_{13}; 34.9 %, d_{14}; 44.8 %, d_{15}.

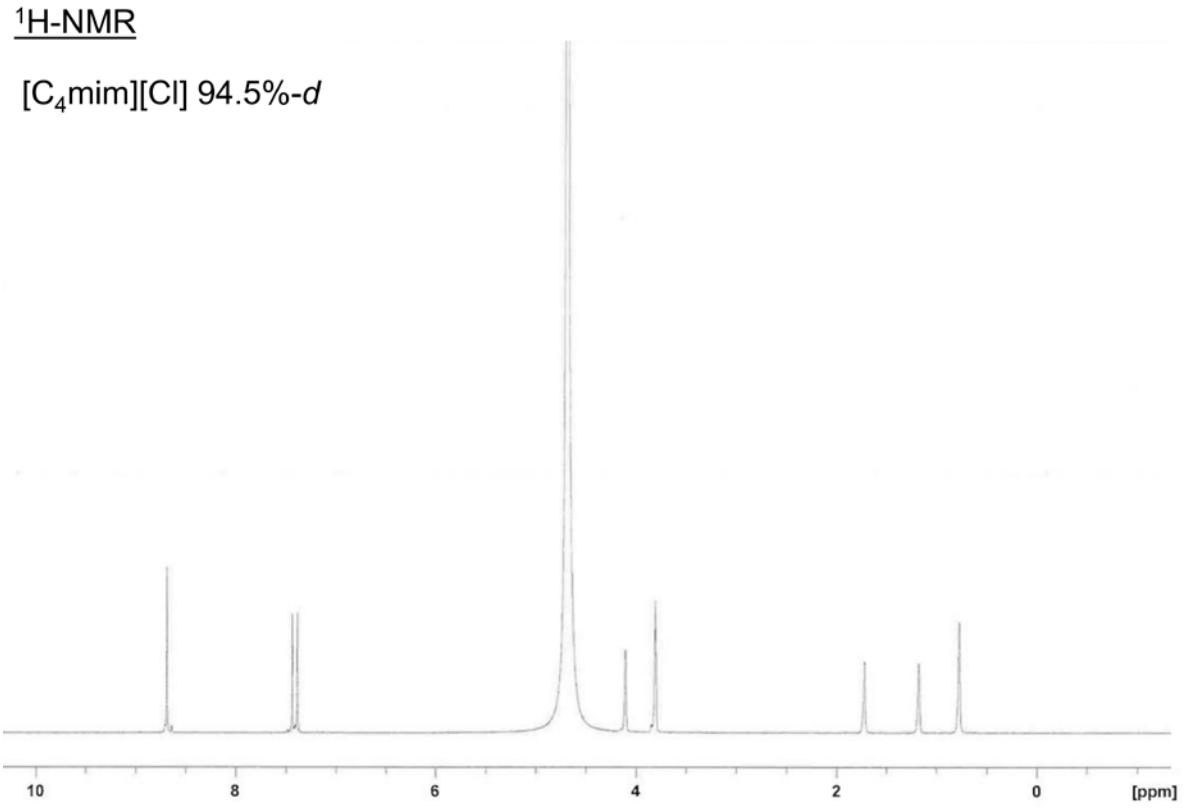

Fig. S7-2. ^{1}H-NMR (D_2O, 400 MHz) of deuterated (94.5%) [C_4mim][Cl].

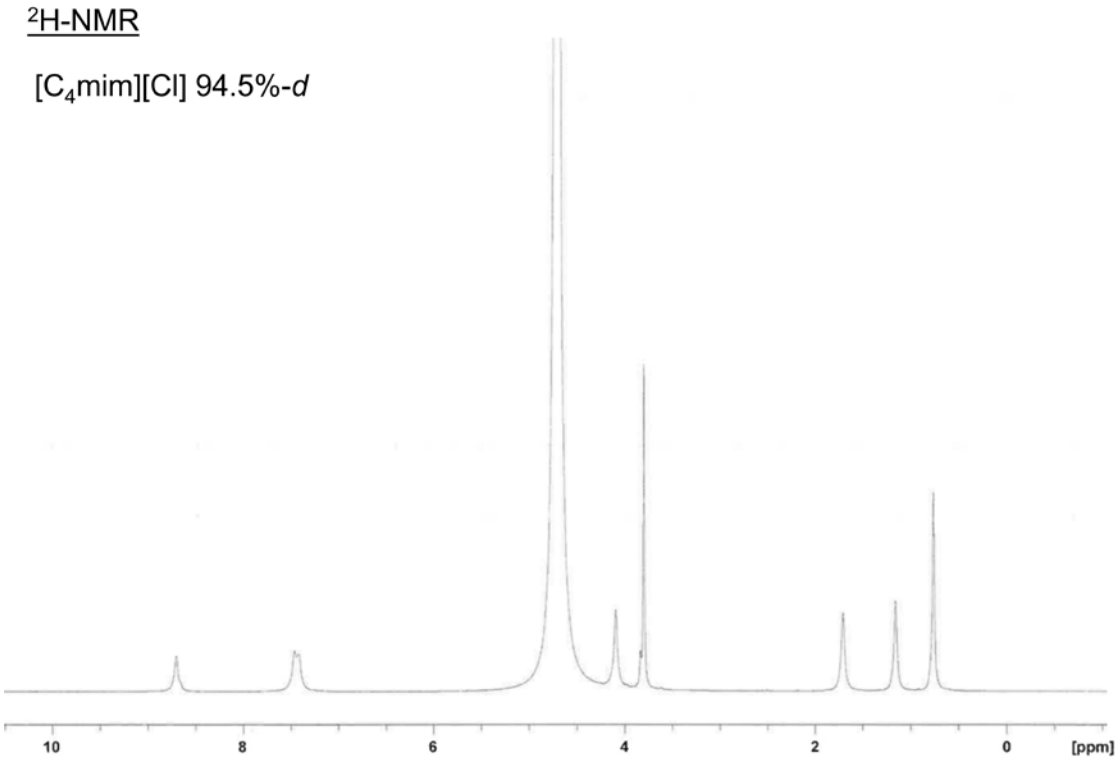

Fig. S7-3. ^{2}H-NMR (D_2O, 61.4 MHz) of deuterated (94.5%) [C_4mim][Cl].

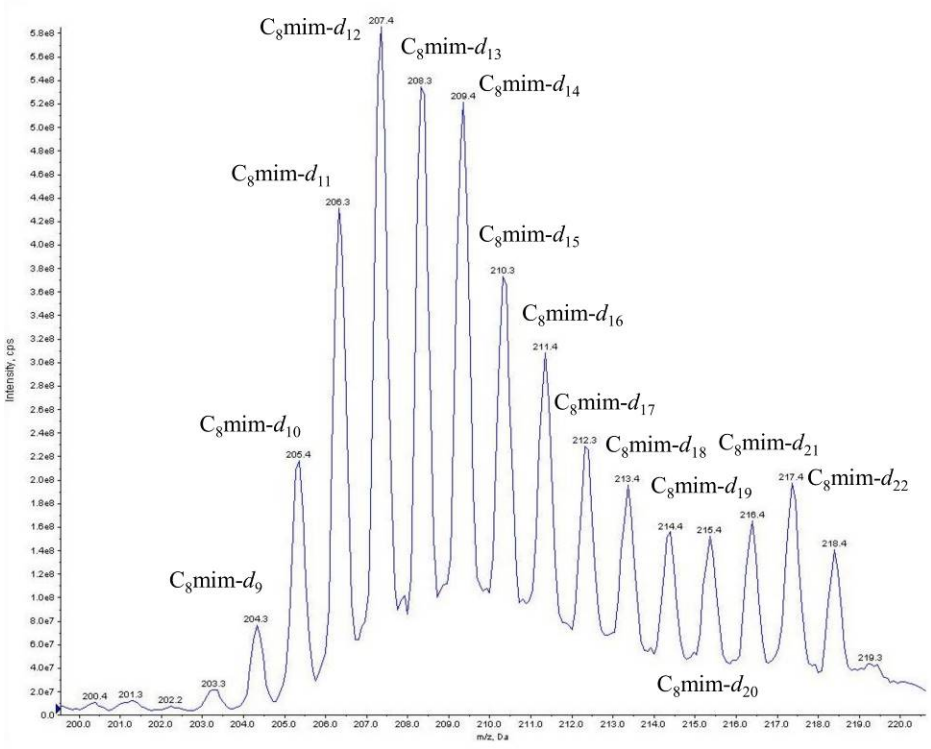

Fig. S8. Electrospray ionization mass spectra in positive mode of C_8mim cation showing the mass distribution of the different isotopologues, which ranges from d_9–d_{22}. The distribution of the isotopologues is as follows (M^+): 1.8 %, d_9; 5.0 %, d_{10}; 9.6 %, d_{11}; 13.6 %, d_{12}; 10.8 %, d_{13}; 13.7 %, d_{14}; 8.6 %, d_{15}; 8.7 %, d_{16}; 5.4 %, d_{17}; 5.6 %, d_{18}; 3.5 %, d_{19}; 4.2 %, d_{20}; 4.1 %, d_{21}; 5.3 %, d_{22}.

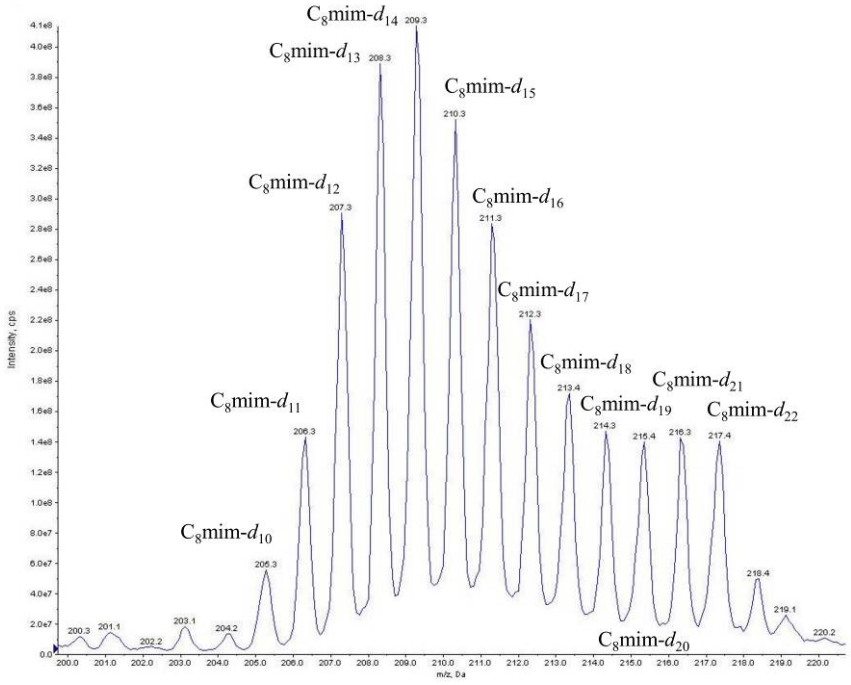

Fig. S9. Electrospray ionization mass spectra in positive mode of C_8mim cation showing the mass distribution of the different isotopologues, which ranges from d_{10}–d_{22}. The distribution of the isotopologues is as follows (M^+): 2.2 %, d_{10}; 4.7 %, d_{11}; 9.8 %, d_{12}; 12.2 %, d_{13}; 14.7 %, d_{14}; 11.6 %, d_{15}; 10.8 %, d_{16}; 7.4 %, d_{17}; 6.3 %, d_{18}; 5.1 %, d_{19}; 5.1 %, d_{20}; 4.6 %, d_{21}; 5.4 %, d_{22}.

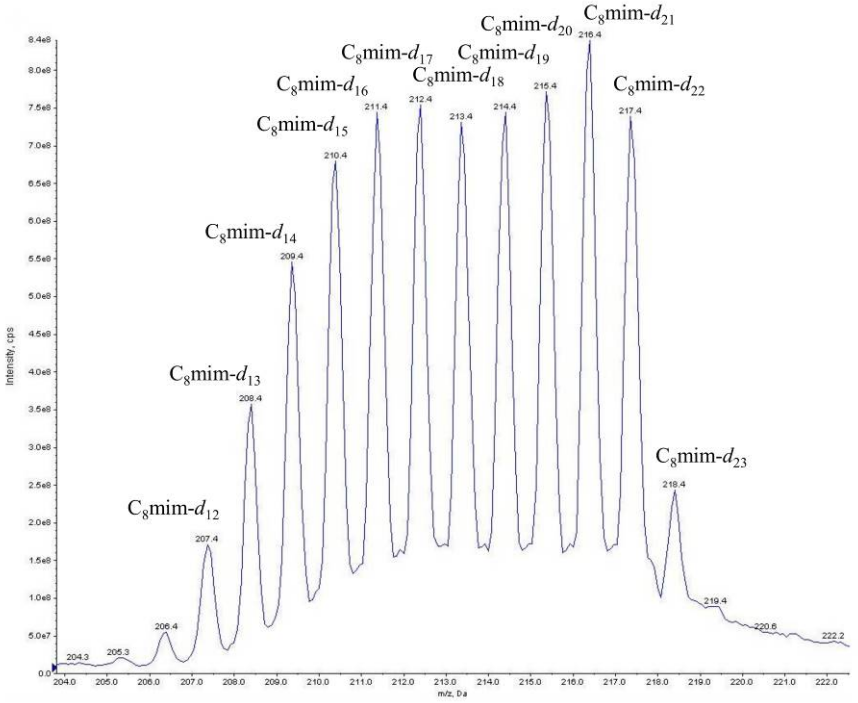

Fig. S10. Electrospray ionization mass spectra in positive mode of C_8mim cation showing the mass distribution of the different isotopologues, which ranges from d_{12}–d_{23}. The distribution of the isotopologues is as follows (M^+): 2.6 %, d_{12}; 4.8 %, d_{13}; 7.5 %, d_{14}; 9.8 %, d_{15}; 10.2 %, d_{16}; 10.6 %, d_{17}; 9.1 %, d_{18}; 10.1 %, d_{19}; 9.7 %, d_{20}; 11.3 %, d_{21}; 10.6 %, d_{22}; 3.6 %, d_{23}.

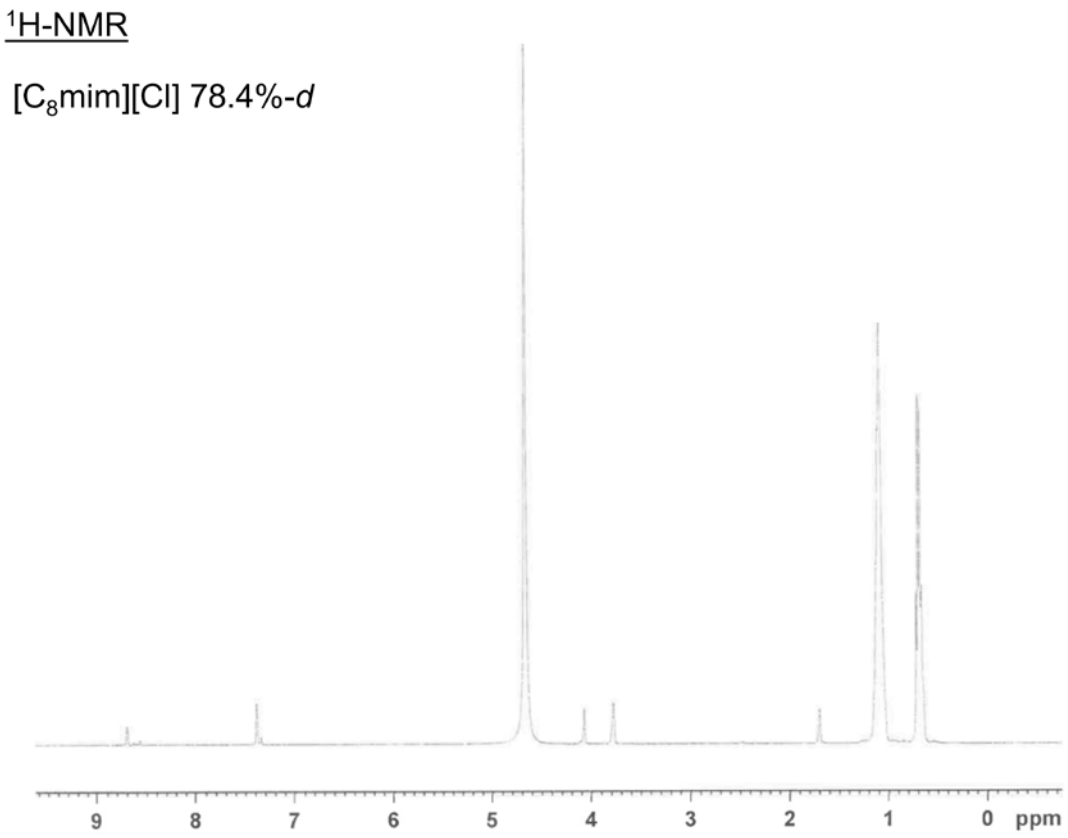

Fig. S10-2. ^{1}H-NMR (D_2O, 400 MHz) of deuterated (78.4%) [C_8mim][Cl].

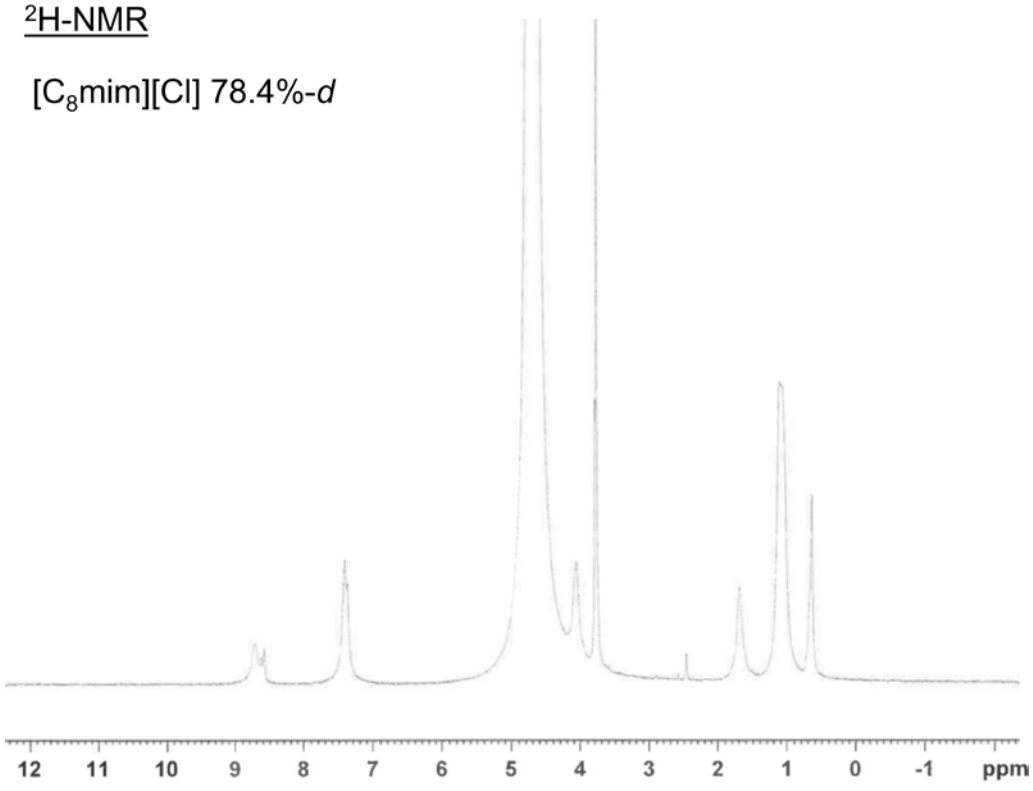

Fig. S10-3. ^{2}H-NMR (D_2O, 61.4 MHz) of deuterated (78.4%) [C_8mim][Cl].

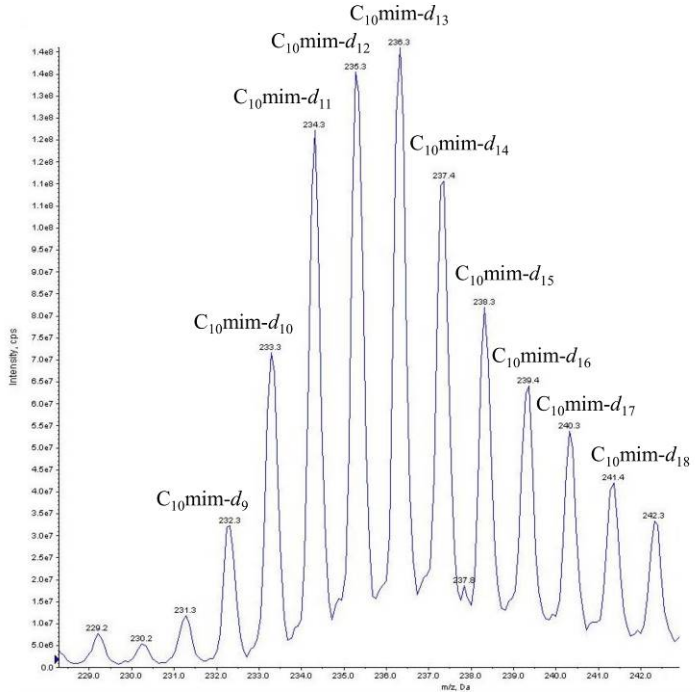

Fig. S11. Electrospray ionization mass spectra in positive mode of C_{10}mim cation showing the mass distribution of the different isotopologues, which ranges from d_9–d_{18}. The distribution of the isotopologues is as follows (M^+): 4.0 %, d_9; 8.3 %, d_{10}; 13.7 %, d_{11}; 15.2 %, d_{12}; 16.6 %, d_{13}; 13.9 %, d_{14}; 8.7 %, d_{15}; 8.7 %, d_{16}; 5.8 %, d_{17}; 5.1 %, d_{18}.

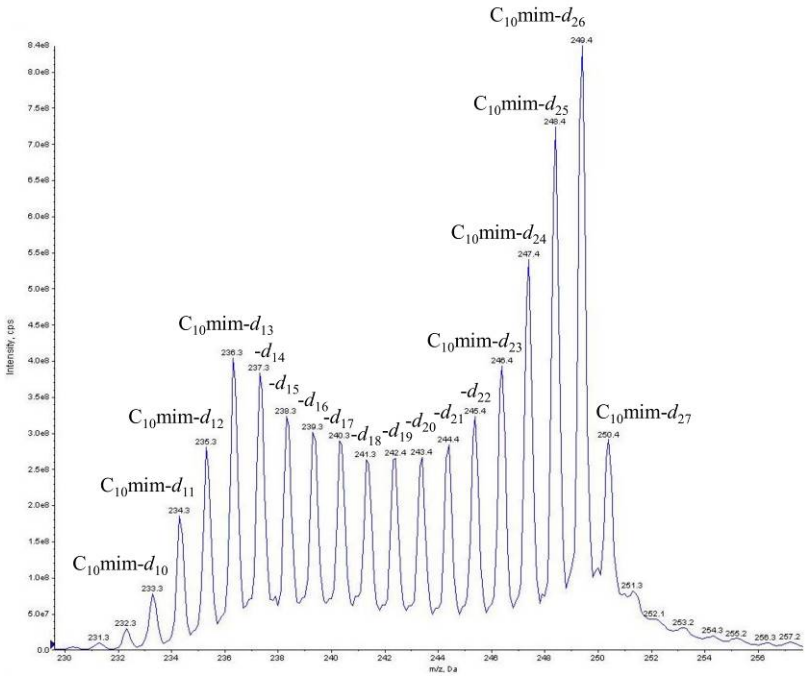

Fig. S12. Electrospray ionization mass spectra in positive mode of C_{10}mim cation showing the mass distribution of the different isotopologues, which ranges from d_{10}–d_{27}. The distribution of the isotopologues is as follows (M^+): 1.2 %, d_{10}; 2.6 %, d_{11}; 4.1 %, d_{12}; 5.8 %, d_{13}; 6.3 %, d_{14}; 4.7 %, d_{15}; 5.3 %, d_{16}; 5.0 %, d_{17}; 4.7 %, d_{18}; 4.1 %, d_{19}; 4.5 %, d_{20}; 4.3 %, d_{21}; 5.2 %, d_{22}; 6.2 %, d_{23};

8.2 %, d_{24}; 10.1 %, d_{25}; 12.3 %, d_{26}; 5.4 %, d_{27}.

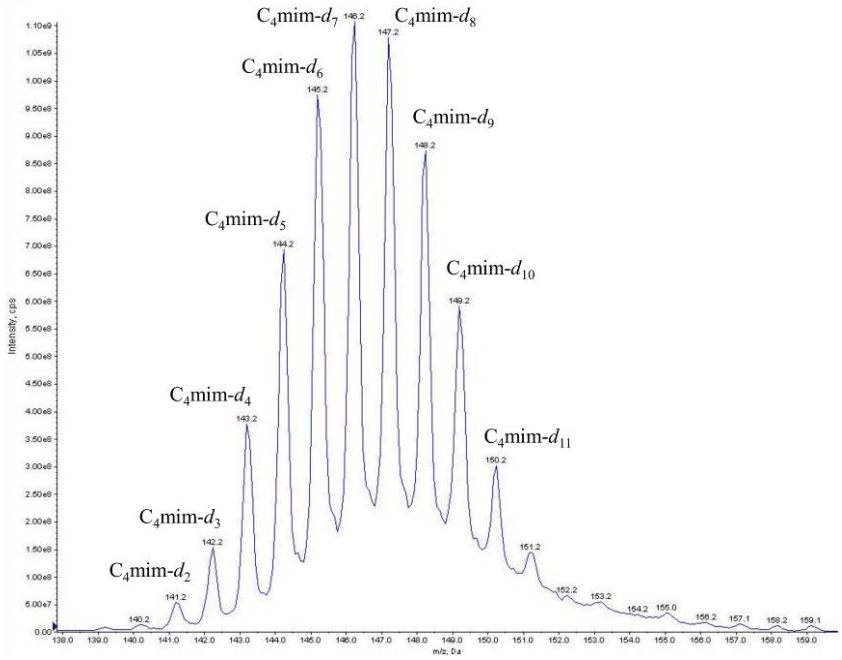

Fig. S13. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_2–d_{11}. The distribution of the isotopologues is as follows (M^+): 1.0 %, d_2; 2.0 %, d_3; 5.7 %, d_4; 9.4 %, d_5; 15.6 %, d_6; 18.6 %, d_7; 17.3 %, d_8; 14.8 %, d_9; 10.2 %, d_{10}; 5.3 %, d_{11}.

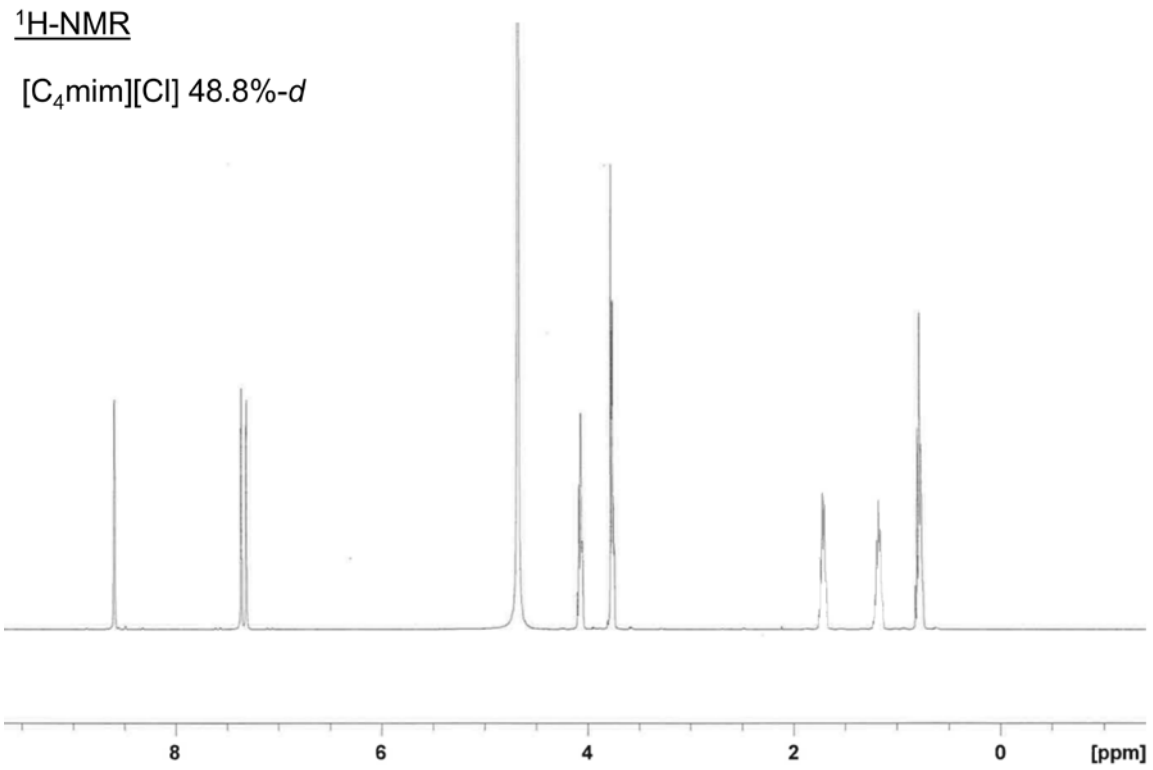

Fig. S13-2. ^{1}H-NMR (D_2O, 400 MHz) of deuterated (48.8%) [C_4mim][Cl].

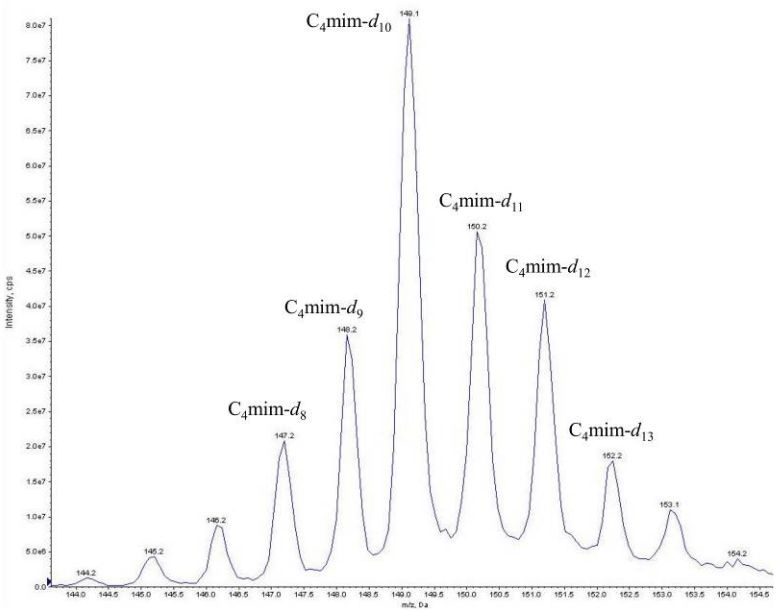

Fig. S14. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_8–d_{13}. The distribution of the isotopologues is as follows (M^+): 7.9 %, d_8; 12.7 %, d_9; 34.7 %, d_{10}; 20.5 %, d_{11}; 16.7 %, d_{12}; 7.5 %, d_{13}.

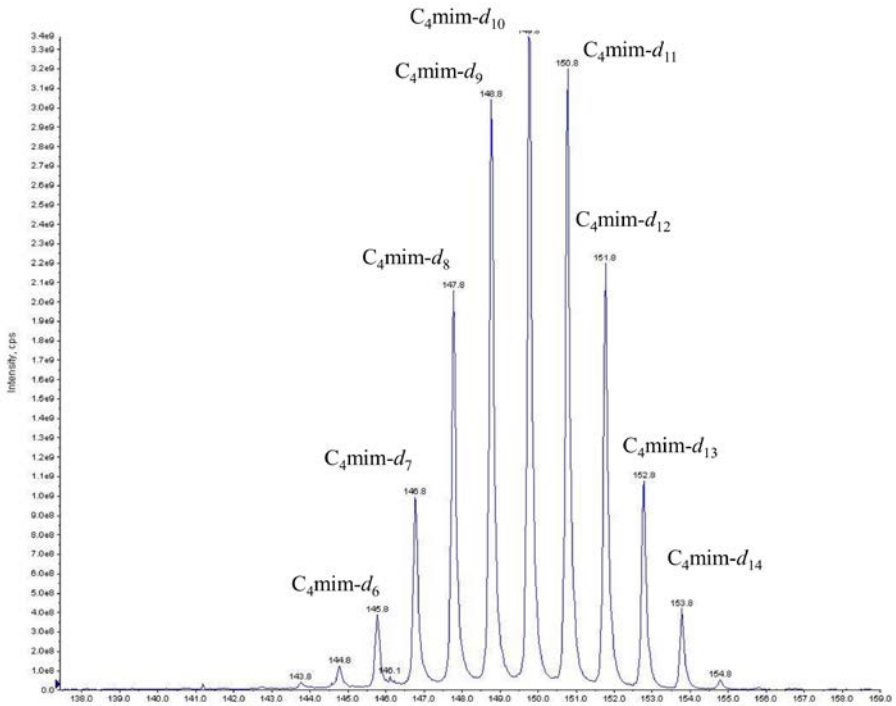

Fig. S15-1. Electrospray ionization mass spectra in positive mode of C_4mim cation showing the mass distribution of the different isotopologues, which ranges from d_6–d_{14}. The distribution of the isotopologues is as follows (M^+): 2.3 %, d_6; 6.4 %, d_7; 12.8 %, d_8; 18.6 %, d_9; 20.6 %, d_{10}; 18.1 %,

d_{11}; 12.6 %, d_{12}; 6.3 %, d_{13}; 2.3 %, d_{14}.

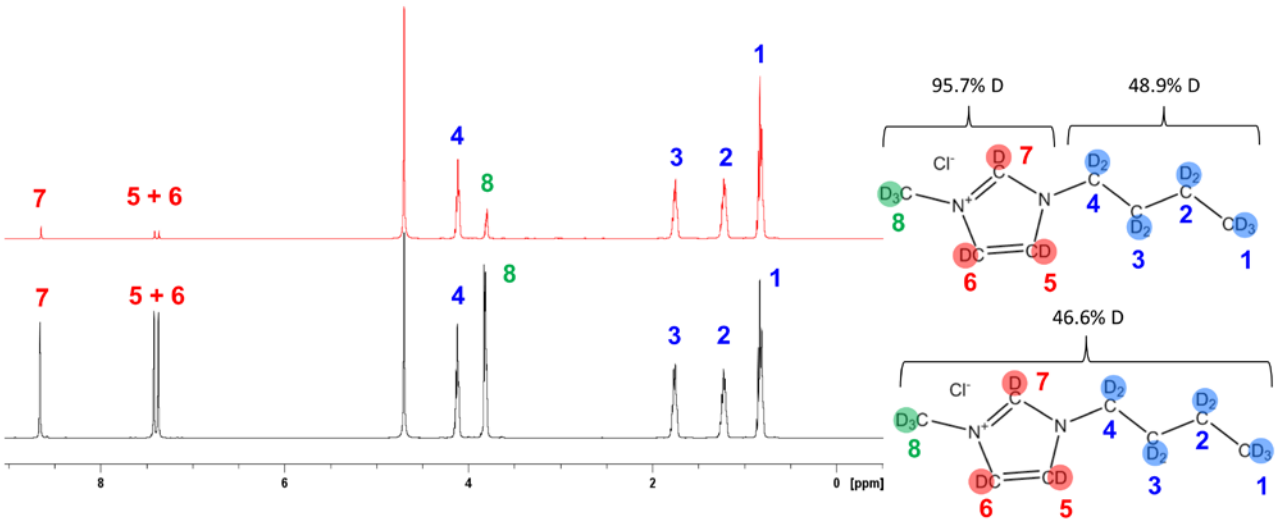

Fig. S15-2. ^{1}H-NMR (D_2O, 400 MHz) of deuteration level controlled (46.6%) [C_4mim][Cl] and position-selective deuterated (head = 95.7 %, tail = 48.9 %) [C_4mim][Cl].

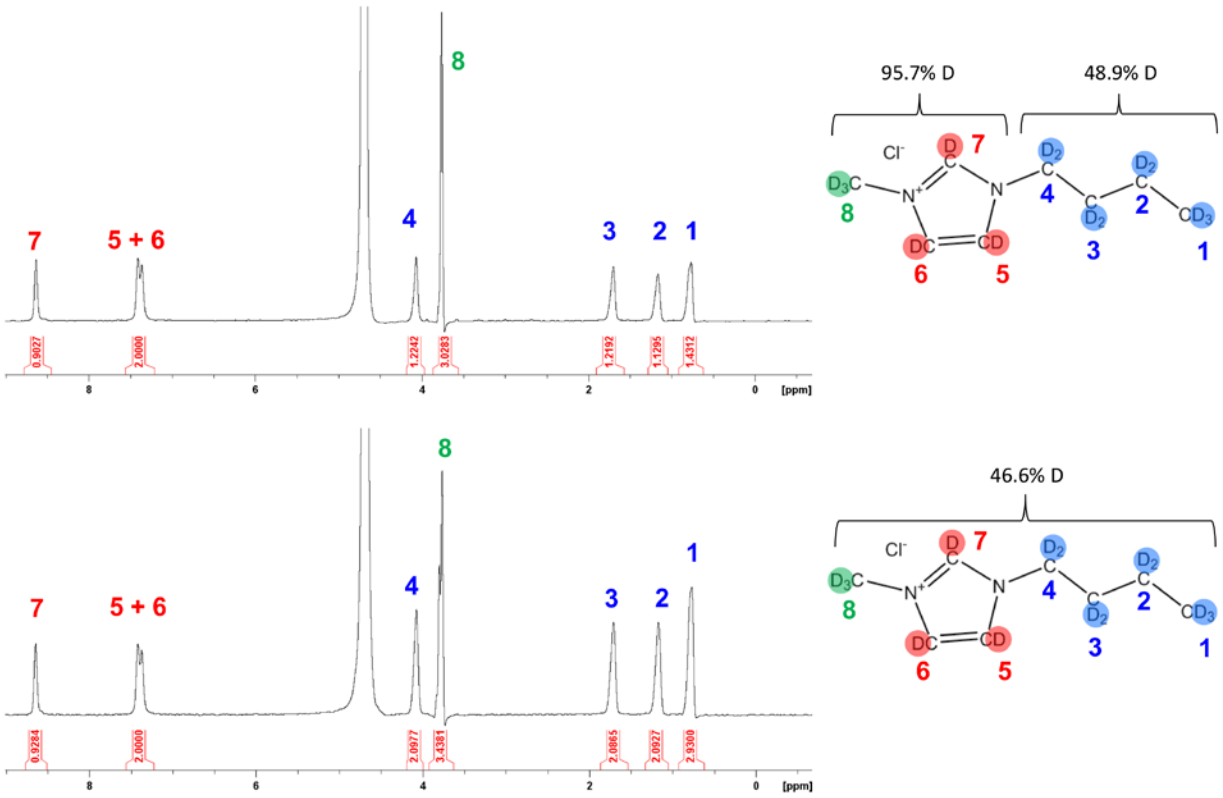

Fig. S15-3. ^{2}H-NMR (D_2O, 61.4 MHz) of deuteration level controlled (46.6%) [C_4mim][Cl] and position-selective deuterated (head = 95.7 %, tail = 48.9 %) [C_4mim][Cl].

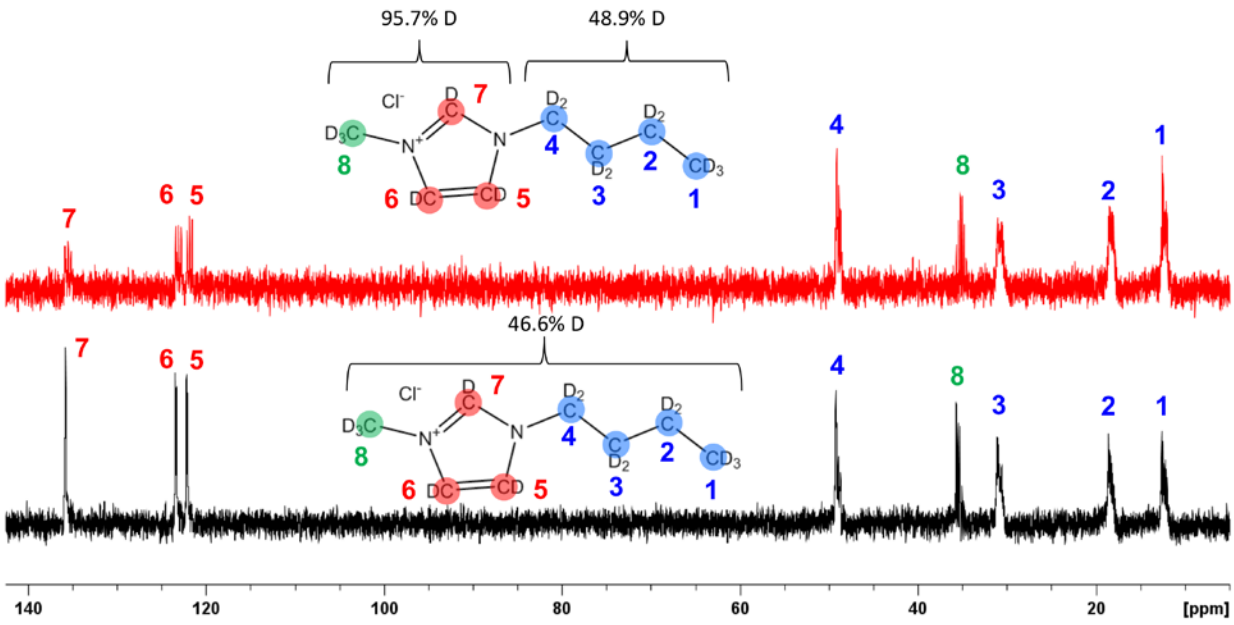

Fig. S15-4. ^{13}C-NMR (D_2O, 400 MHz) of deuteration level controlled (46.6%) [C_4mim][Cl] and position-selective deuterated (head = 95.7 %, tail = 48.9 %) [C_4mim][Cl].

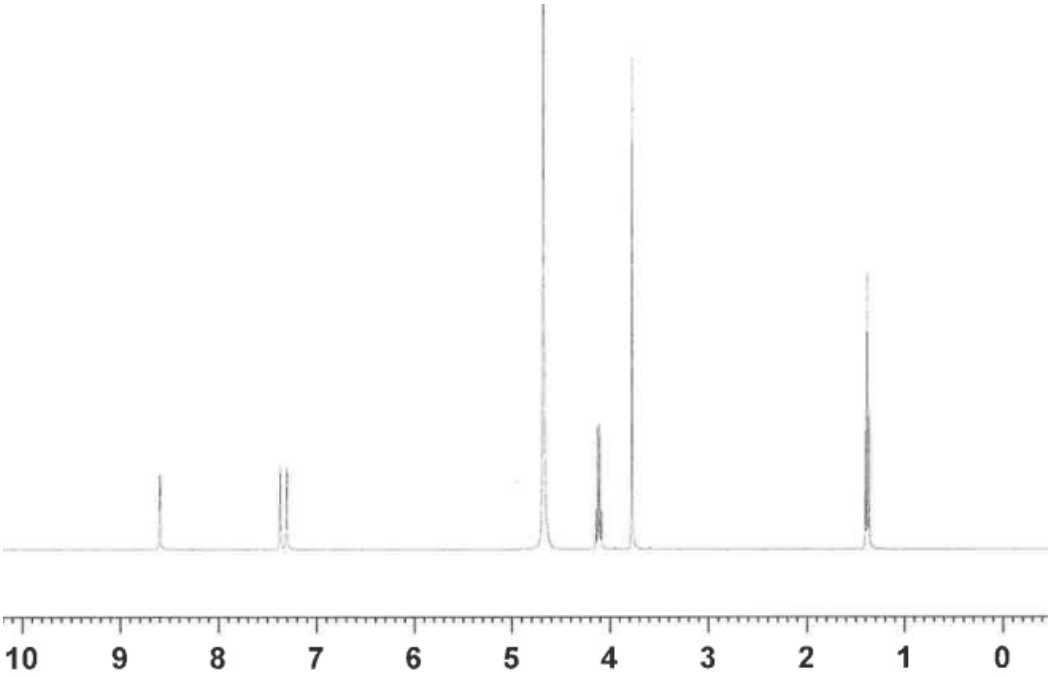

Fig. S16-1. ^{1}H-NMR (D_2O, 400 MHz) of [C_2mim][Cl] (starting material).

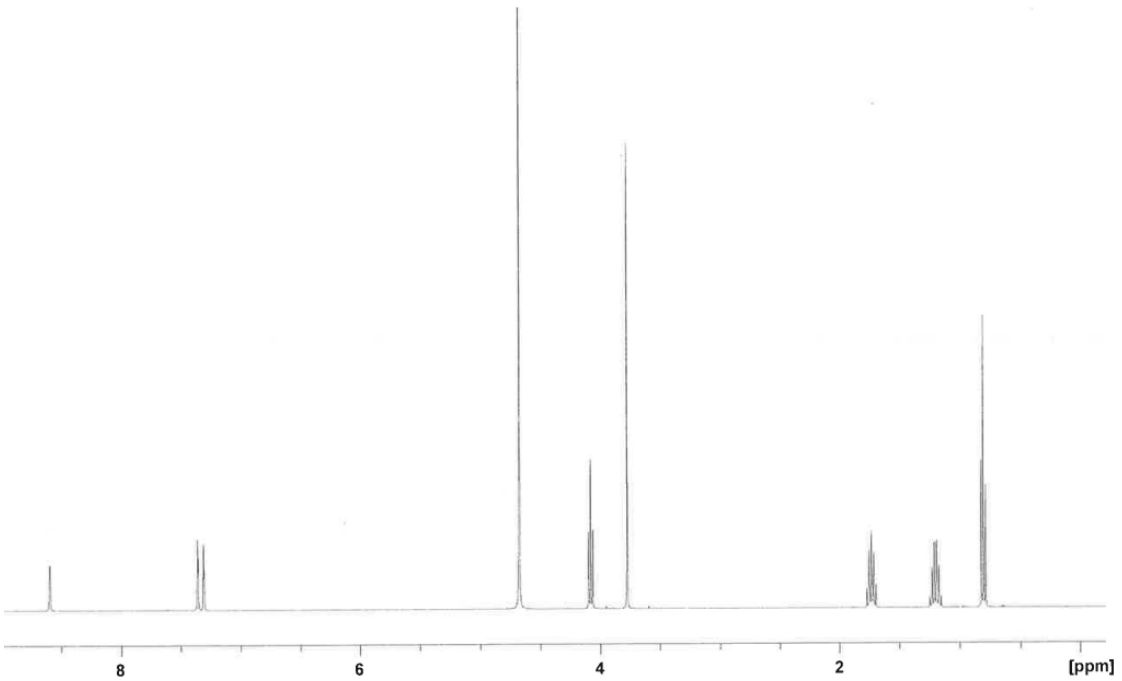

Fig. S16-2. ^{1}H-NMR (D_2O, 400 MHz) of [C_4mim][Cl] (starting material).

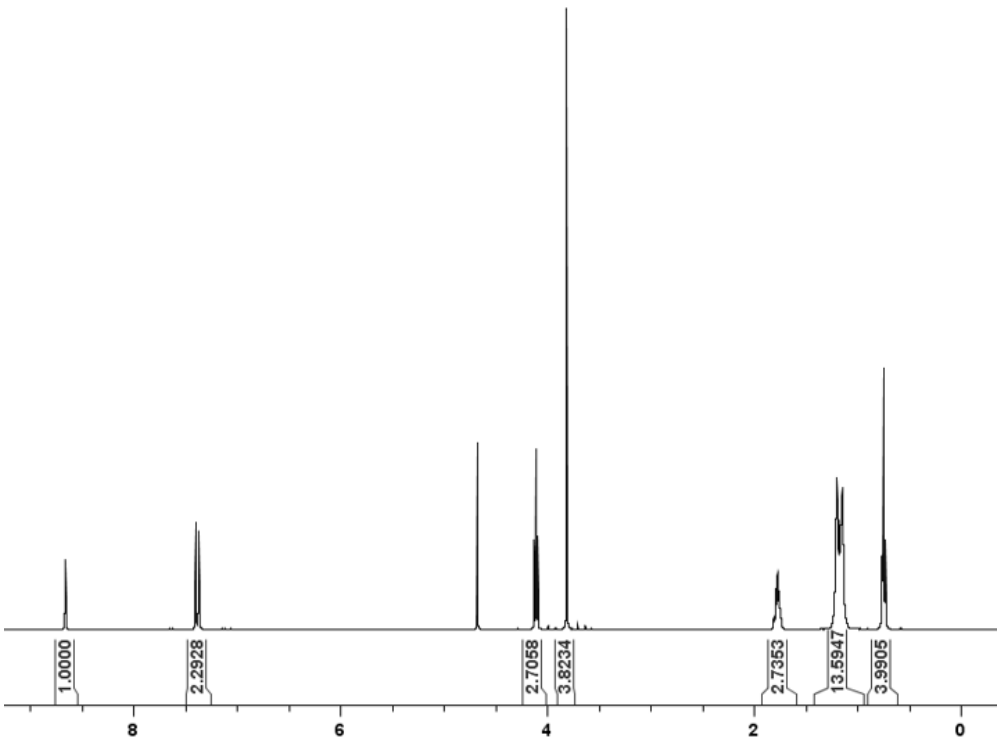

Fig. S16-3. ^{1}H-NMR (D_2O, 400 MHz) of [C_8mim][Cl] (starting material).

Neutron reflectivity analysis for the position-selective deuterated IL

To estimate the SLD value of the position-selective deuterated [C$_4$mim][TFSA], the NR measurements of the partially deuterated [C$_4$mim][TFSA]/SiO$_2$-wafer sample was performed on a BL17 SHARAKU reflectometer. The critical wave vector for the total external reflection (Q_c), which is defined as $Q_c = 4(\pi\rho)^{1/2}$ (ρ represents the difference of the SLD value between the partially deuterated [C$_4$mim][TFSA] and SiO$_2$-wafer sample), was observed around $Q_c = 0.0066$ (Å^{-1}). Using the obtained Q_c value, the SLD value of the partially deuterated [C$_4$mim][TFSA] can be estimated to be 4.34 (×10^{-6} Å^{-2}).

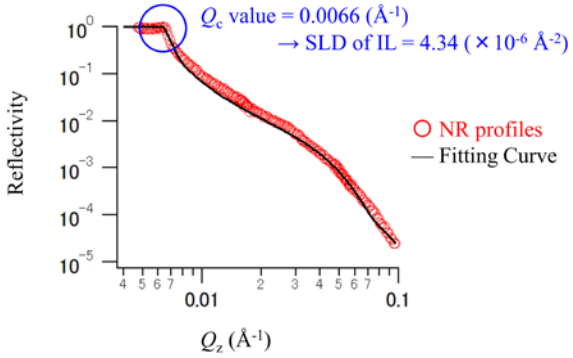

Fig. S16. Neutron reflectivity profiles of the partially deuterated [C$_4$mim][TFSA]/SiO$_2$ sample.

References

1 T. A. Darwish, E. Luks, G. Moraes, N. R. Yepuri, P. J. Holden and M. James, *J. Label. Compd. Radiopharm.*, 2013, **56**, 520–529.

2 Z. K. Reeder, A. M. Adler and K. M. Miller, *Tetrahedron Lett.*, 2016, **57**, 206–209.

3 L. S. Bartell, K. Kuchitsu and R. J. DeNeui, *J. Chem. Phys.*, 1961, **35**, 1211–1218.

4 N. D. Rebuck, A. A. Conte and L. Stallings, *ASLE Trans.*, 1977, **20**, 108–114.

5 K. Akutsu, T. Niizeki, S. Nagayama, N. Miyata, M. Sahara, A. Shimomura, M. Yoshii and Y. Hasegawa, *J. Ceram. Soc. Japan*, 2016, **124**, 172–176.

6 A. Nelson, *J. Appl. Crystallogr.*, 2006, **39**, 273–276.