Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

A Lipophilic Ionic Liquid Based on Formamidinium Cations and TFSI: The Electric Response and the Effect of CO_2 on Conductivity Mechanism

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Elemental Analysis

The evaluation of the C, H, N and S wt% in the synthesized liquid ionic is carried out by elemental analysis using a Flash 2000 CHNS-O instrument.

Table S1. Chemical Composition of TOFATSFI ionic liquid.

Elemental analyses	C (w/w%)	H (w/w%)	N (w/w%)	S (w/w%)
TOFATFSI	51.12 ± 0.80	9.09 ± 0.17	6.40 ± 0.11	8.22 ± 0.13
Theoretical TOFATFSI	55.29	9.15	4.61	8.20
Theoretical DOFATFSI	43.08	7.05	6.46	11.50
Theoretical dioctyl amine	80.25	14.73	5.02	/

The chemical composition of the TOFATFSI IL is reported in Table S1. The concentrations of H and S are in good agreement with the theoretical values. On the contrary, differences (always <3.5%) in the C and N contents are probably associated with residual nitrogen-based species arising from an

incomplete transamination reaction. However these latters are not ionized and do not contribute to the conductivity in alkane nor in super-critical CO_2.

NMR studies

1D ^{1}H- and ^{13}C-NMR spectroscopy was employed to characterize the ionic liquid. C_7D_8 was used as solvent. The spectra were acquired on a Bruker Avance III 400 spectrometer, operating at 400.13 MHz as ^{1}H resonance frequency, equipped with a 5 mm multinuclear inverse z-field gradient probe-head. Data processing was carried out using the TOPSPIN 3.5 software package. The chemical shifts were referenced to the resonance of the residual proton and to the carbon resonance of the C_7D_8 solvent. The ^{1}H-NMR spectrum was recorded with 8 transients, a spectral width of 10 ppm, a repetition delay of 10 sec and 32K data points. Exponential multiplication with line broadening of 0.3 Hz was applied prior to Fourier transformation. The ^{13}C-NMR spectra were acquired with a spectral width of 210 ppm and 128K data points, both with ^{1}H decoupling with WALTZ16 sequence (4K transients), and without ^{1}H decoupling (6K transients). Exponential multiplication with line broadening of 2 Hz was applied prior to Fourier transformation. The ^{1}H-^{13}C heteronuclear multiple-quantum correlation (HMQC) 2D spectrum[1] was acquired using a repetition delay of 1.5 sec; 256 experiments of 32 scans each were accumulated in TPPI method[2], decoupling of ^{13}C with GARP sequence during acquisition, 3.4 ms evolution delay for $^{1}J_{HC}$ scalar coupling constants; the spectral widths were 10 ppm for ^{1}H and 210 ppm for ^{13}C. Zero-filling in both F1 (^{13}C) and F2 (^{1}H) multiplication with a Gaussian function (in F2) and a square cosine function (in F1) was carried out prior to 2D Fourier transformation.

^{1}H NMR:

Figures S1 shows the ^{1}H NMR spectra of an (aged) sample of the lipophilic ionic liquid TOFATFSI. The multiplets at higher frequency, between 3.3 and 2.5 ppm, are due to the octyl CH_2 groups directly attached to the electron withdrawing nitrogen atoms. The two smaller multiplets at 2.91 and 3.22 ppm are from a dioctyl amine (DOA) group attached to the formamidine. They appear as two peaks of equal size because the chemical structure of the TOFATFSI is planar up to the first CH_2 groups of the dioctyl segment; as a result, one of the N-**CH_2** is in close proximity (CIS) with the formamidine methyl group while the other N-**CH_2** is away from the methyl (TRANS). The other multiplet at 2.59 ppm is from unreacted (DOA). The hydrogen peaks resulting from the N-**CH_2** groups of TOFATFSI appear at higher frequency than the peak from DOA because they are deshielded by the C=N bond.

The broad peak from 3.75 to 6.75 ppm is an indication of the presence of NH protons from DOA. This could be due to unreacted DOA or de-alkylation because the sample tested is aged and has been exposed to CO_2.

The singlets at 2.06 (overlapped by NMR solvent toluene-d_8) and 2.00 ppm are believed to be from the methyl group of the formamidine derivative. The presence of two peaks suggests there is a mixture of mono and di-substituted formamidine and this is supported by the presence of two peaks of similar ratios in carbon NMR for the C=N carbon atom (165.5 and 170.0 ppm). This could also be due to incomplete alkylation or de-alkylation because the sample tested is aged and has been exposed to CO_2.

All the major peaks in proton and carbon NMR are from the DOA, they are sharp and unique peaks unlike the formamidine salt derivative peaks, which appear as multiplets due to conformation and degree of substitution (mono and di).

It is possible to use the integration values in ^{1}H-NMR to establish the predominance of either the mono or the di-substitution product, one or two attached DOA. The integration value of the N-CH_2 peak from "free" DOA was set to 4H which allowed for the complete removal of the integration values due to "free" DOA and resulted in the following integration regions (see ^{1}H-spectrum below): 1.35H (3.8-6.7 ppm), 2.40H (2.8-3.3 ppm), 1.68H (1.94-2.07 ppm) and 19.97H (1.8-0.6 ppm). As seen in the Table S2, these values correspond to mainly mono-substituted, or DOFATFSI, salt:

Table S2. ^{1}H-NMR results

Actual integration values after removal of "free"DOA	**Expected for DOFATFSI**	**Expected for TOFATFSI**
1.35 (NH_2)	1.20	0
2.40 (N-CH_2)	**2.40 (0.60 per H)**	**2.40 (0.30 per H)**
1.68 (-CH_3)	1.80	0.90
19.97 ((-CH_2)$_6$-CH_3)	18.00	18.00

It appears from the ^{1}H-NMR integration values that mono-substituted DOFATFSI is the predominant species.

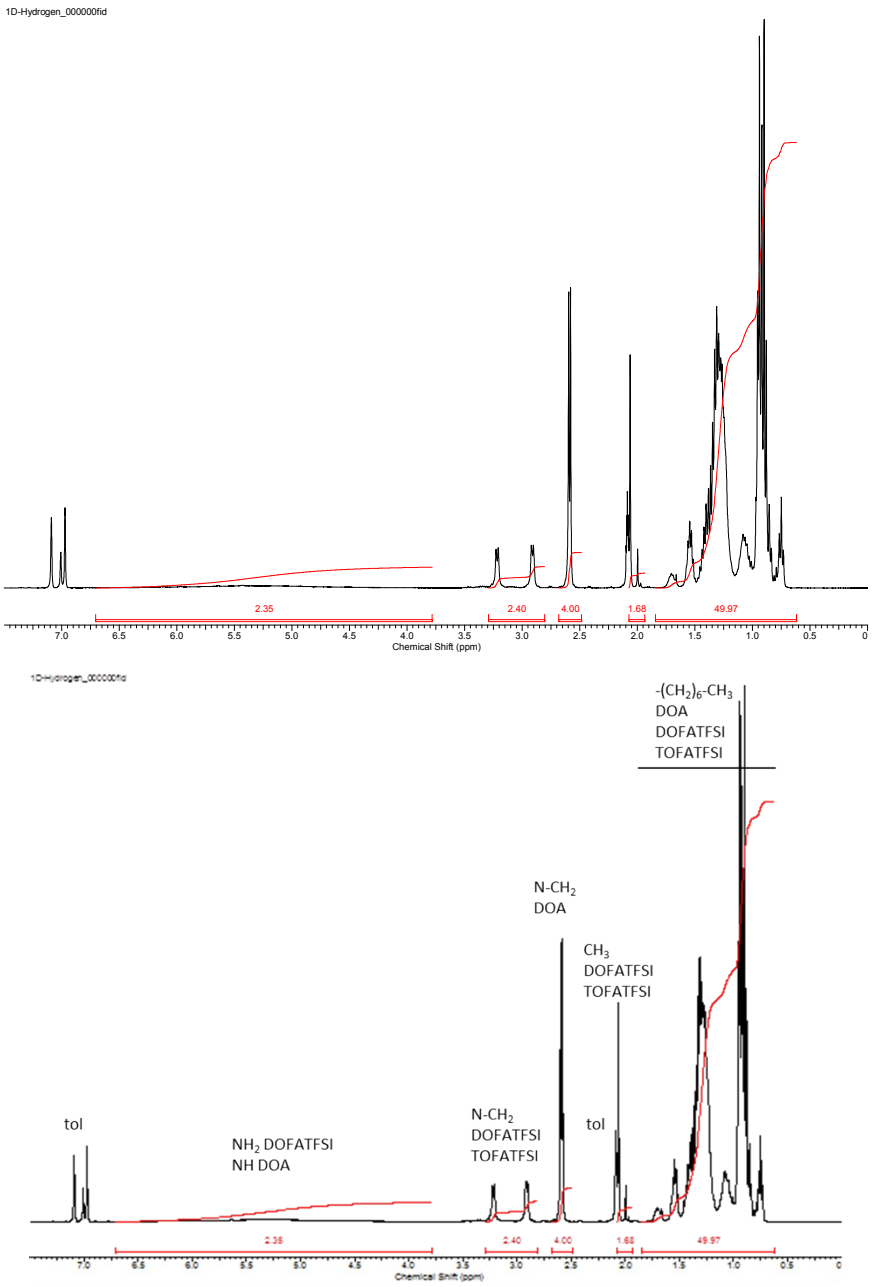

Figure S1. ^{1}H NMR spectra of an (aged) sample of the lipophilic ionic liquid TOFATFSI.

^{13} C NMR:

Figures S2 shows the ^{13}C NMR spectra of an (aged) sample of the lipophilic ionic liquid TOFATFSI. In carbon NMR, the presence of a quartet at 120.5 ppm resulting from the carbon atom of the counter ion's CF_3 group is immediately recognizable due to its large coupling with the three fluorine atoms (321Hz). The C=N carbon also stands out at low frequency, 165.5 ppm with a second smaller peak at 172.0 ppm. All of the "free" DOA carbon signals are sharp intense singlets whereas the "attached" DOA results in multiple peaks due to conformation and degree of substitution.

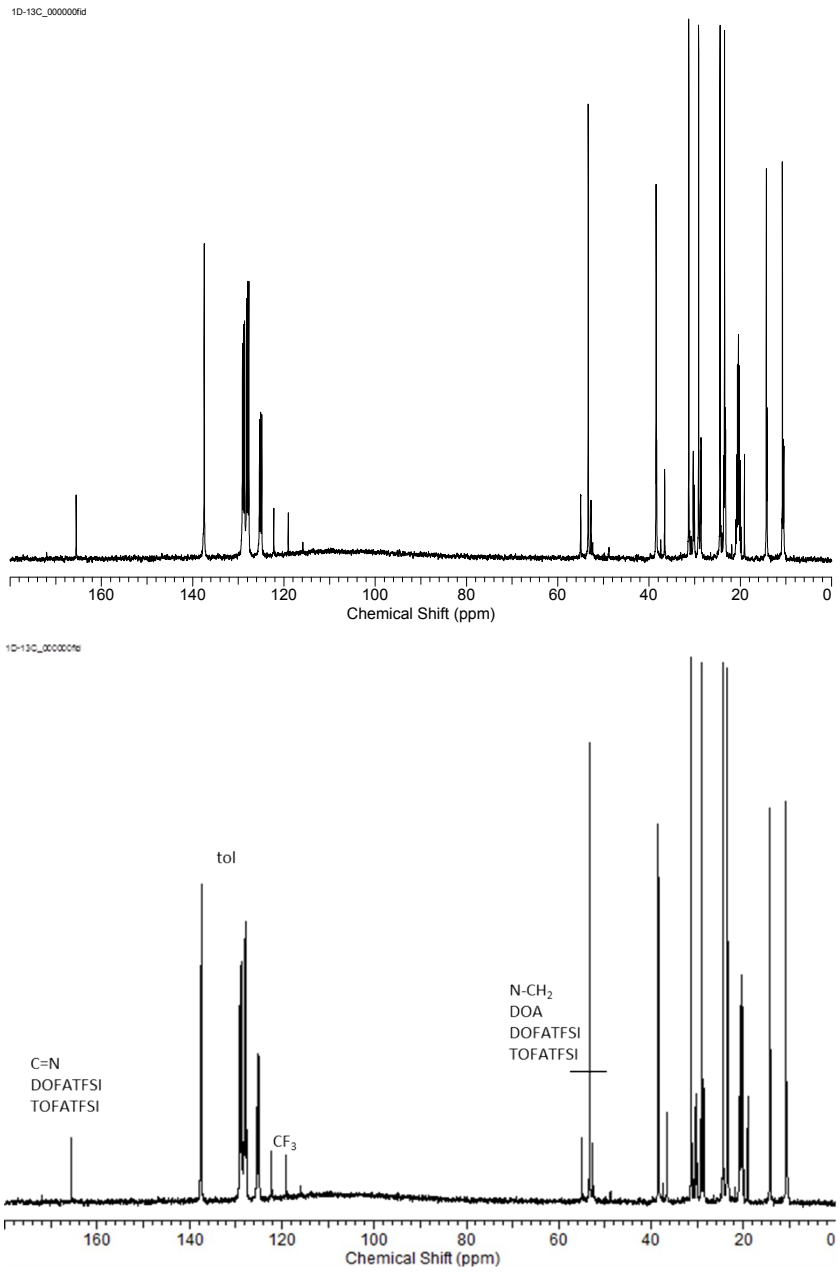

Figure S2. ^{13}C NMR spectra of an (aged) sample of the lipophilic ionic liquid TOFATFSI.

^{1}H-^{13}C heteronuclear multiple-quantum correlation (HMQC) 2D spectrum of an (aged) sample of the lipophilic ionic

Fig. S3 show a good connectivity between the hydrogen and carbon of most of the peaks in the ^{1}H and ^{13}C NMR spectra.

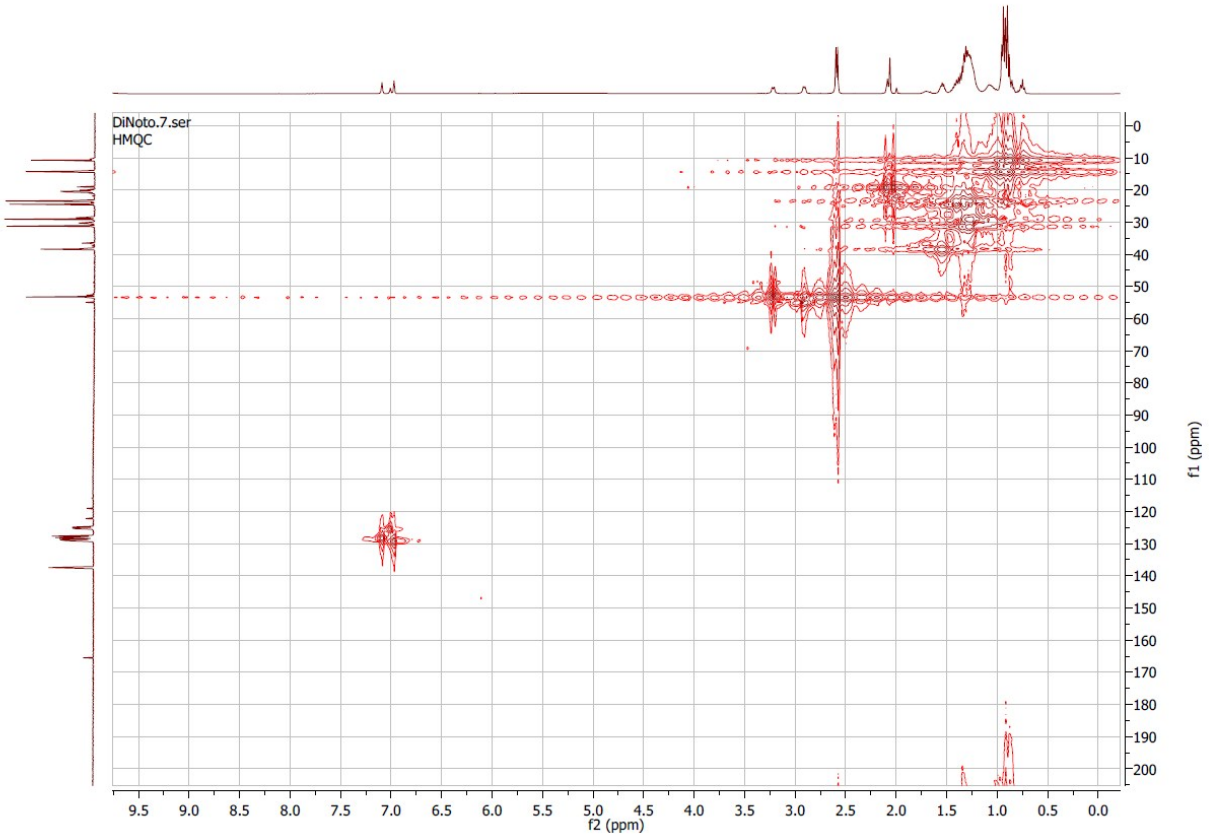

Figure S3. ^{1}H-^{13}C heteronuclear multiple-quantum correlation (HMQC) 2D spectrum of an (aged) sample of the lipophilic ionic liquid TOFATFSI in toluene-d_6.

References

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2. D. Marion and K. Wüthrich, *Biochemical and Biophysical Research Communications*, 1983, **113**, 967-974.