Supplementary Information

Controlling the phase behavior and ion mobility of trialkylammonium-based protic ionic liquids: The role of asymmetry

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Synthesis and characterization

^{19}F and ^{1}H NMR spectra were recorded on a QONE AS400 spectrometer (Zhongke Niujin Magnetic Resonance Technology Company Co. Ltd) 400 MHz at an operating frequency of 376.25 (^{19}F), 399.86 (^{1}H) MHz. Chemical shifts were measured relative to CCl_3F, using C_6F_6 (-162.9 ppm, ^{19}F) as a secondary standard and TMS and residual solvent protons (^{1}H) as a secondary standard.

DSC measurements were performed using DSC 204 F1 (NETZSCH) equipment in an argon atmosphere (flow rate 30 ml/min). Samples were placed in the closed and pressed alumina melting pot with 25 µl volume. Setup calibration was done using indium (99,999%) and zinc (99.8+%) purchased from Sigma Aldrich.

First, the samples were heated to 150° C and held at this temperature for 5 minutes. After this, the samples were quickly (40° C/min) cooled to a temperature of -60° C, then the cooling went down to -100 C at a rate of 20° C/min, and, after holding for 5 minutes at the lowest *T*, the sample was heated at a rate of 1° C/min to -60° C and then to the room temperature (25° C) at a speed of 10° C/min.

1-bromooctane (99 %, Aldrich), diethylamine (99%, Chimmed, RUS), D_2O (99,9 %, Aldrich and all standard chemicals were obtained from commercial sources

CF_3SO_3Na was synthesized by neutralizing a solution of trifluoromethylsulfonic acid with sodium hydroxide followed by evaporation

Preparation of N-octyl-N,N-diethylamine

N-octyl-N,N-diethylamine was prepared by reacting diethylamine with octyl bromide by boiling in an aqueous medium followed by treatment with alkali by analogy with the literature method [S1]. The reaction equation is shown in Figure S1.

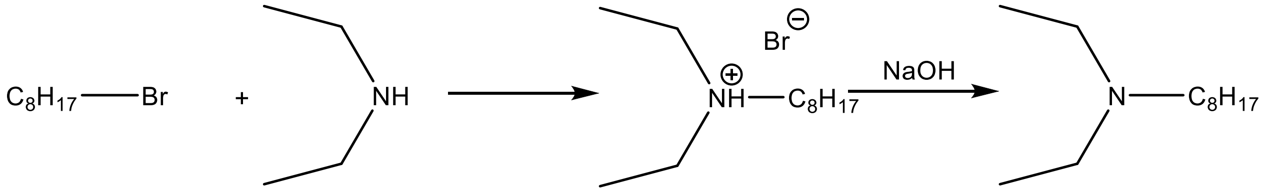

Figure S1. Preparation of N-octyl-N,N-diethylamine

In a 1 L round-bottomed flask equipped with a reflux condenser, 44.25 g (40 mL, 0.229 mol) of octyl bromide, 67.58 g (95 mL, 0.916 mol) of diethylamine and 500 mL of water were mixed. The mixture was refluxed for 10 h. After the end of the process, the mixture was cooled and treated with excess of sodium hydroxide (about 500 g). The organic layer (upper) was separated, the aqueous layer was extracted with diethyl ether. The extract was dried over magnesium sulfate. The drying agent was filtered off, diethyl ether and excess of diethylamine were distilled off, the product was isolated by distillation in a vacuum (Bp 89-92 °C/13 mbar). 34.75 g of product (82%) was obtained.

The structure and purity of the product were confirmed by NMR spectroscopy, the results are consistent with the literature data.

Preparation of N-octyl-N,N-diethylammonium hydrochloride

N-octyl-N,N-diethylammonium hydrochloride was obtained by reacting of N-octyl-N,N-diethylamine (6.5 g, 0.0350 mol) with an equimolar amount of hydrochloric acid in an aqueous emulsion (50 ml of water). The water was evaporated, and the residue was dried in a high vacuum. The yield of the product was quantitative.

Preparation of N-octyl-N,N-diethylammonium trifluoromethanesulfonate (D)

N-octyl-N,N-diethylammonium trifluoromethanesulfonate was obtained by reacting of N-octyl-N,N-diethylammonium hydrochloride with sodium triflate in acetonitrile solution. The exchange of hydrogen for deuterium was carried out by stirring with an excess of a D_2O/CH_3CN mixture (acetonitrile was added since the ionic liquid is hydrophobic) (Figure S2).

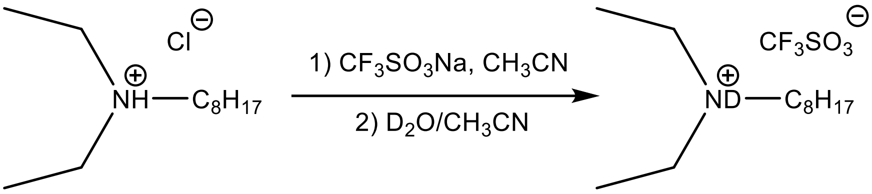

Figure S2. Preparation of N-octyl-N,N-diethylammonium trifluoromethanesulfonate (D)

A 100 ml round-bottomed flask fitted with magnetic stirrer bar was charged by 860 mg (3.88 mmol) of N-octyl-N,N-diethylammonium hydrochloride, 1.0 g (5.81 mmol) of CF_3SO_3Na and 80 ml of acetonitrile. The mixture was stirred for 4 hours at 40 °C. The solid was filtered and washed by 10 ml of acetonitrile. The filtrate was evaporated in vacuum. The residue was solved in 30 ml of dry dichloromethane (to remove excess of starting salt) and filtered. The filtrate was evaporated and product was dried in high vacuum (10^{-2} mbar) at 80 °C for 6 hours. The reaction of sample of ionic liquid with $AgNO_3$ was negative, that demonstrates the absence of Cl^- ions in the ionic liquid media. A mixture of 1 ml of D_2O and 0.2 ml of acetonitrile was added to the flask, the mixture was stirred for 1 hour, after which the volatile components were evaporated in a vacuum. The procedure was repeated three times. The product was dried in high vacuum (10^{-2} mbar) at 80 °C for 6 hours. 1.12 g of product (86%) was obtained.

NMR data for $C_{228}ND^+CF_3SO_3^-$ ($CDCl_3$):

^{1}H NMR: δ 3.17 (q, 4H, CH_2 – ethyl); 3.01 (m, 2H, α-CH_2 – octyl); 1.72 (m, 2H, β-CH_2 – octyl); 1.37 (t, 6H, CH_3 – ethyl); 1.21-1.31 (m, 10H, 3-7-CH_2 – octyl); 0.87 (t, 3H, CH_3 – octyl) (Figure S3).

^{19}F NMR: δ -79.45 (s, 3F, CF_3SO_3) (Figure S4).

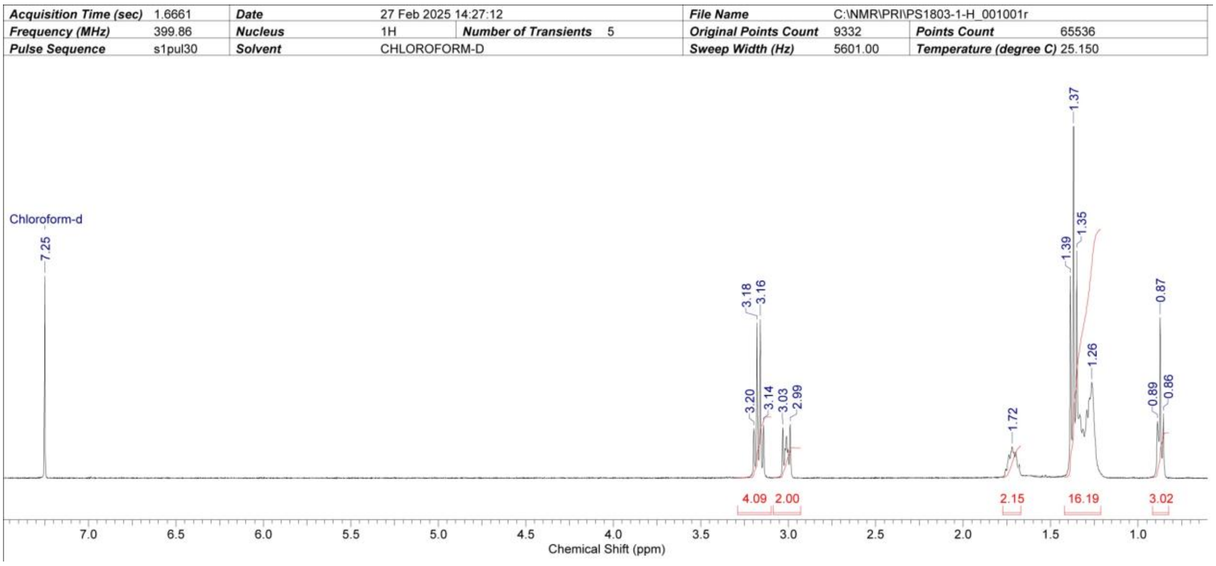

Figure S3. ^{1}H NMR of N-octyl-N,N-diethylammonium trifluoromethanesulfonate (D)

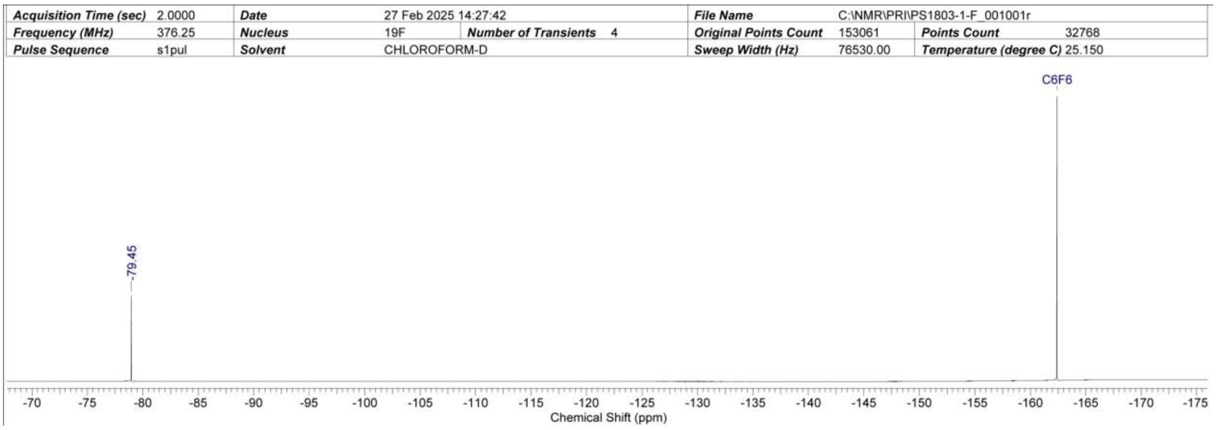

Figure S4. ^{19}F NMR of N-octyl-N,N-diethylammonium trifluoromethanesulfonate (D)

DSC measurements

First, the samples were heated to 150° C and held at this temperature for 5 minutes. After this, the samples were quickly (40° C/min) cooled to a temperature of -60° C, then the cooling went down to -100 C at a rate of 20° C/min, and, after holding for 5 minutes at the lowest *T*, the sample was heated at a rate of 1° C/min to -60° C.

[1] – the inflection point between the beginning and end of the glass transition

[2] – maximum of the phase transition peak in the glass transition and heating region

№	**Sample**	**T_g onset, °C**	**Inflection1), °C**	**$T_{phas.trans}$2), °C**	
				Endo	**Exo**
1	**N822D-CF_3SO_3**	**-93.5**	**-92.5**	**-9.6**	**-64.8/-55.2**
2	**N888D-CF_3SO_3**	**-**	**-**	**20.6 / -47**	**-**

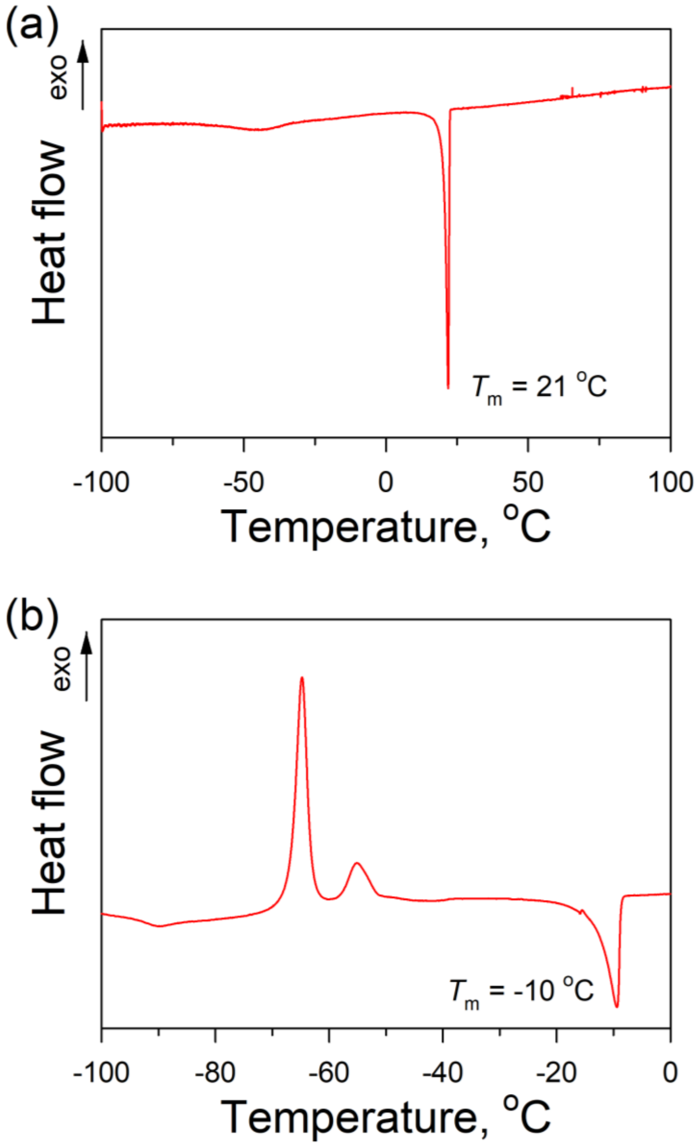

Figure S5. The DSC traces for the ILs [N888D][OTf] (a) and [N822D][OTf] (b). For the sake of clarity, we only show the heating scans with similar heating rate of 1 Kmin^{-1}.

Table S1: Phase transition temperatures measured by DSC and ^{2}H NMR together with the thermodynamic parameters describing the mobile/static transition observed in PILs [N222D][OTf], [N888D][OTf], and [N822D][OTf]) using first and second order expansions of the molar standard Gibbs free energy difference according to ΔG^{o}=$-$RT ln K_{eq}.

Cation type	T_{SS},^{DSC} K	T_m,^{DSC} K	T_{SS}^{nmr}, K	T_m^{nmr}, K	ΔH^{Θ}, kJ mol^{-1}	ΔS^{Θ}, J mol^{-1}K^{-1}	$\Delta S°_{Tt}$ J mol^{-1}	ΔC_p kJ mol^{-1}K^{-1}	T_t K
[N222D]$^{+}$	227*	302*	228*	304*	-	-	195 ± 18	0,84 ± 0,15	307 ± 2,2
[N888D]$^{+}$	226	294	263	294	72 ± 4	232 ± 14	-	-	310 ± 20
[N822D]$^{+}$	217	263	223	263	-	-	600 ± 50	4,8 ± 0,8	262 ± 1

* - data adapted from Ref. [9]

^{2}H NMR experiments

In order to prepare sample for the NMR experiments, the NH-deuterated ionic liquid was loaded into a glass tube (5 mm o.d.; 20 mm long), connected to a high vacuum grade valve (HI-VAC). All manipulations were performed in argon atmosphere. The sample was then attached to a vacuum line and the argon was pumped off under vacuum to a final pressure above the sample of 10^{-2} Pa. To fully degas the material, the sample was slowly introduced into liquid nitrogen 2-3 times, while being connected to vacuum line. After degassing, the neck of the tube was sealed off, while the material sample was maintained in liquid nitrogen in order to prevent its heating by the flame. The sealed sample was then transferred into an NMR probe for analysis with ^{2}H NMR spectroscopy. The temperature of the samples was controlled with a flow of nitrogen gas by a variable-temperature unit BVT-3000 with a precision of about 1 K.

To ensure reproducibility, the spectra acquisition was preceded by melting, cooling by liquid N_2, rapid transfer to the pre-cooled to 133 K NMR probe and then heating it up to the required temperature. Such procedure allowed a perfect reproducibility of the experimental results in the solid phase.

^{2}H NMR experiments were performed at Larmor frequency $\omega_z / 2\pi$ = 61.42 MHz on a Bruker Avance-400 spectrometer, using a high power probe with 5 mm horizontal solenoid coil. All ^{2}H NMR spectra were obtained by Fourier transformation of quadrature-detected phase-cycled quadrupole echo arising in the pulse sequence ($90°_x - \tau_1 - 90°_y - \tau_2$ – acquisition – t), where τ_1 = 20 μs, τ_2 = 21 μs and t is a repetition time of the sequence during the accumulation of the NMR signal. The duration of the $\pi/2$ pulse was 1.6-1.7 μs. Spectra were typically obtained with 50 - 20000 scans with repetition time ranging from 0.5 to 15 seconds.

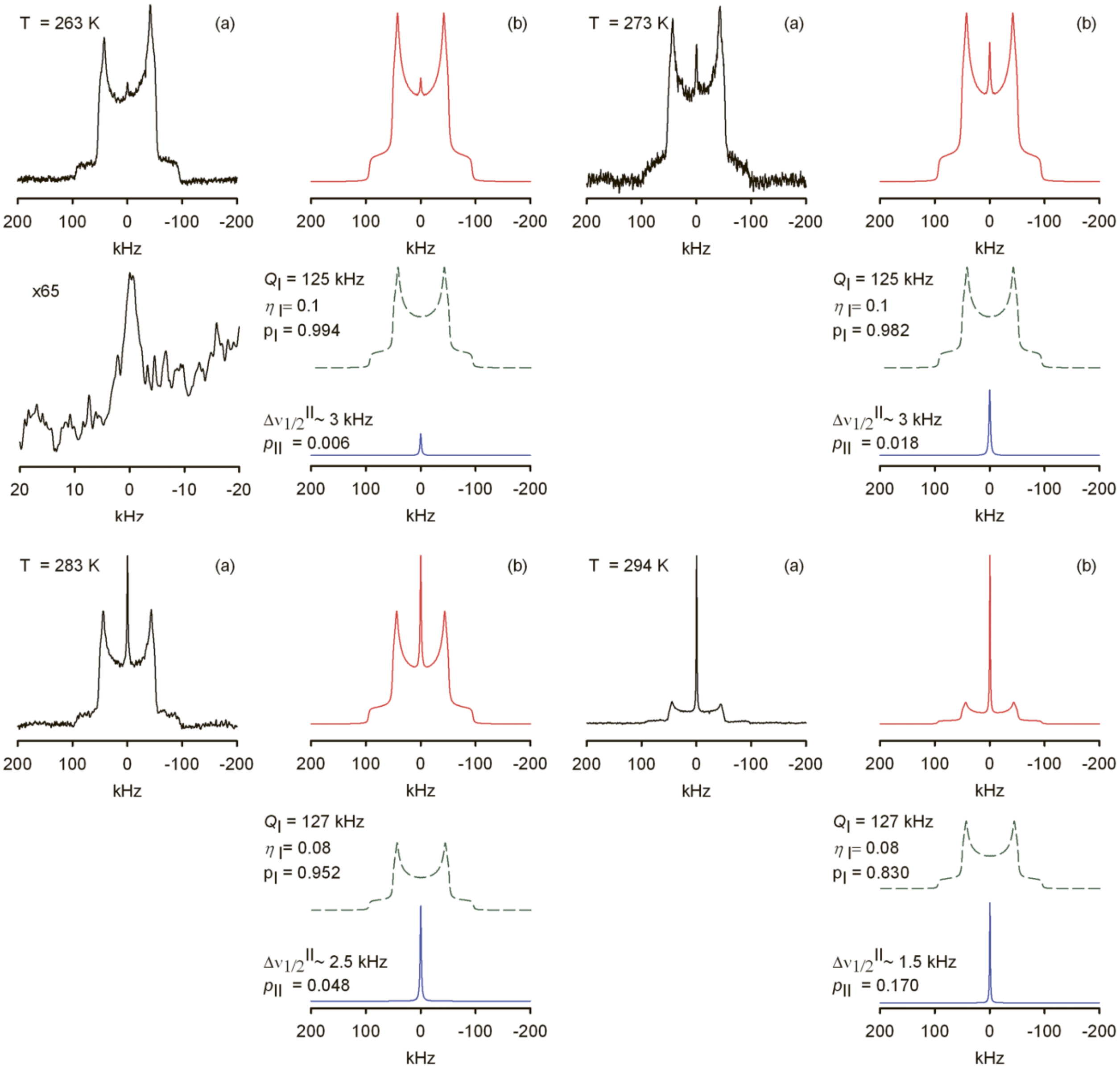

Figure S6. ^{2}H NMR spectra with deconvolution of [N888D][OTf].

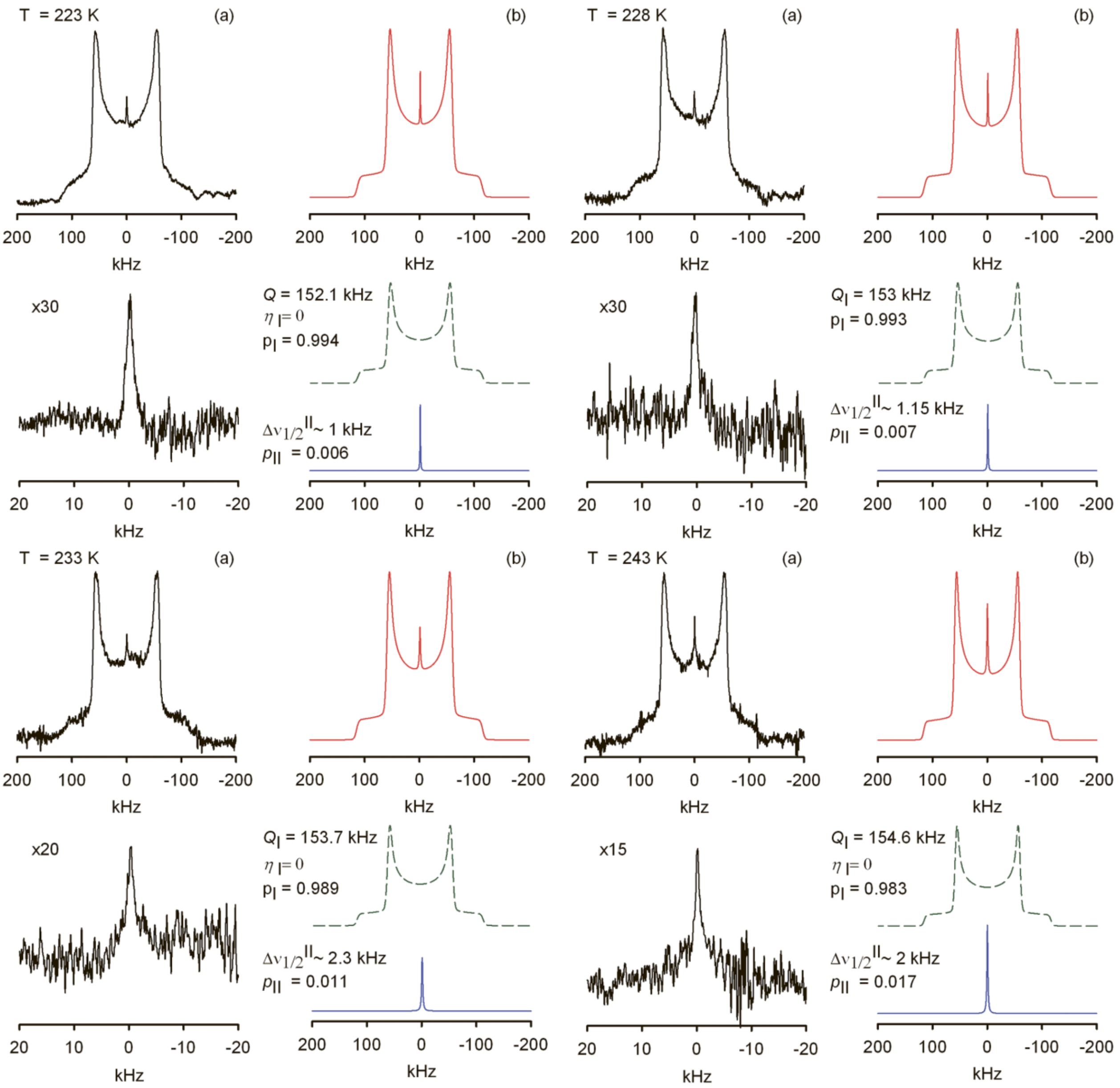

Figure S7. ^{2}H NMR spectra with deconvolution of [N822D][OTf].

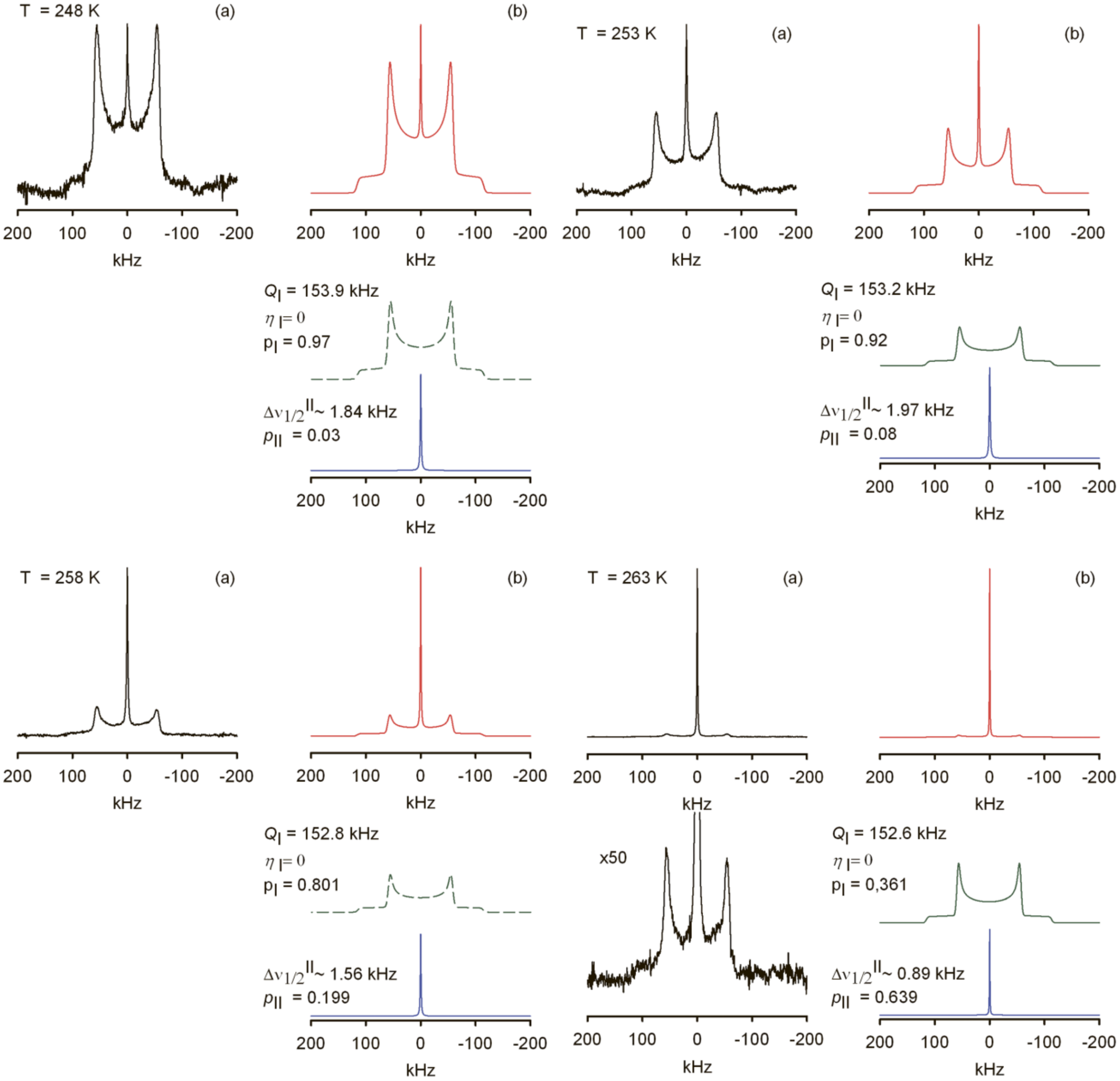

Figure S8. ^{2}H NMR spectra with deconvolution of [N822D][OTf].

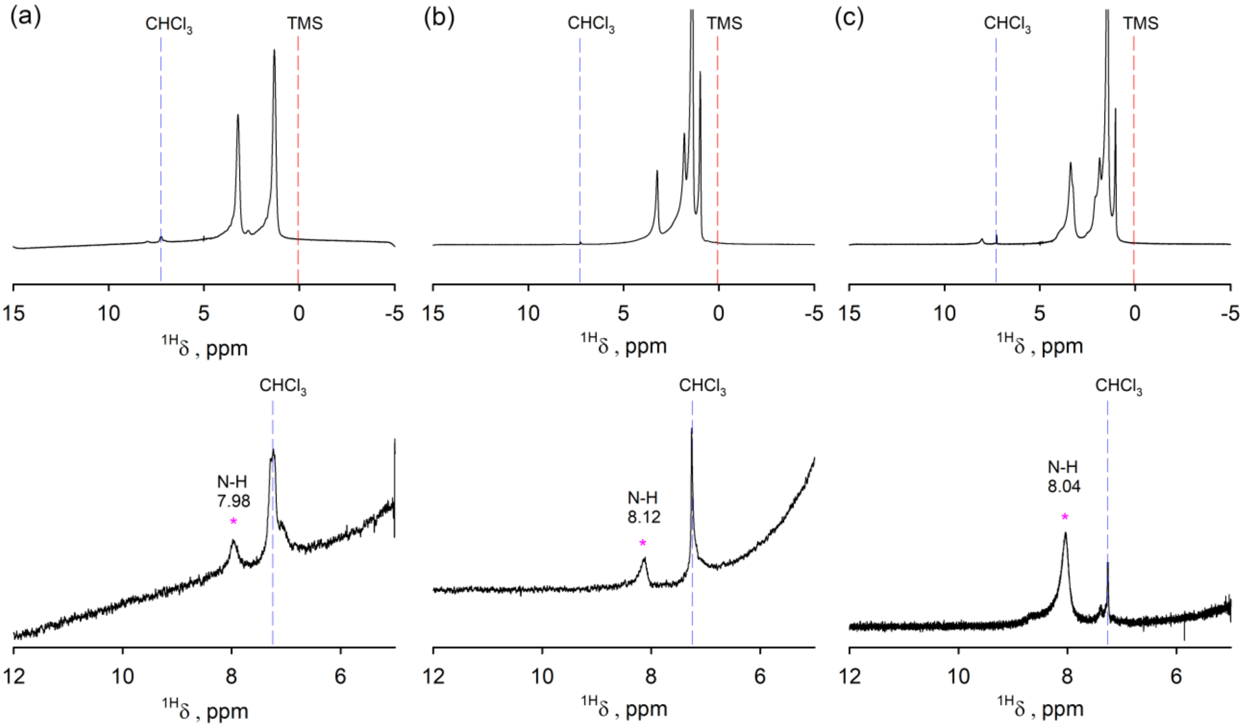

Figure S9. 1H NMR spectra with internal standard of (a) [N222D][OTf], (b) [N888D][OTf], (c) [N822D][OTf] referenced to TMS. Upper plots are spectra with the full spectra width, downward plots are scaled to show the region of the N-H groups vibrations.

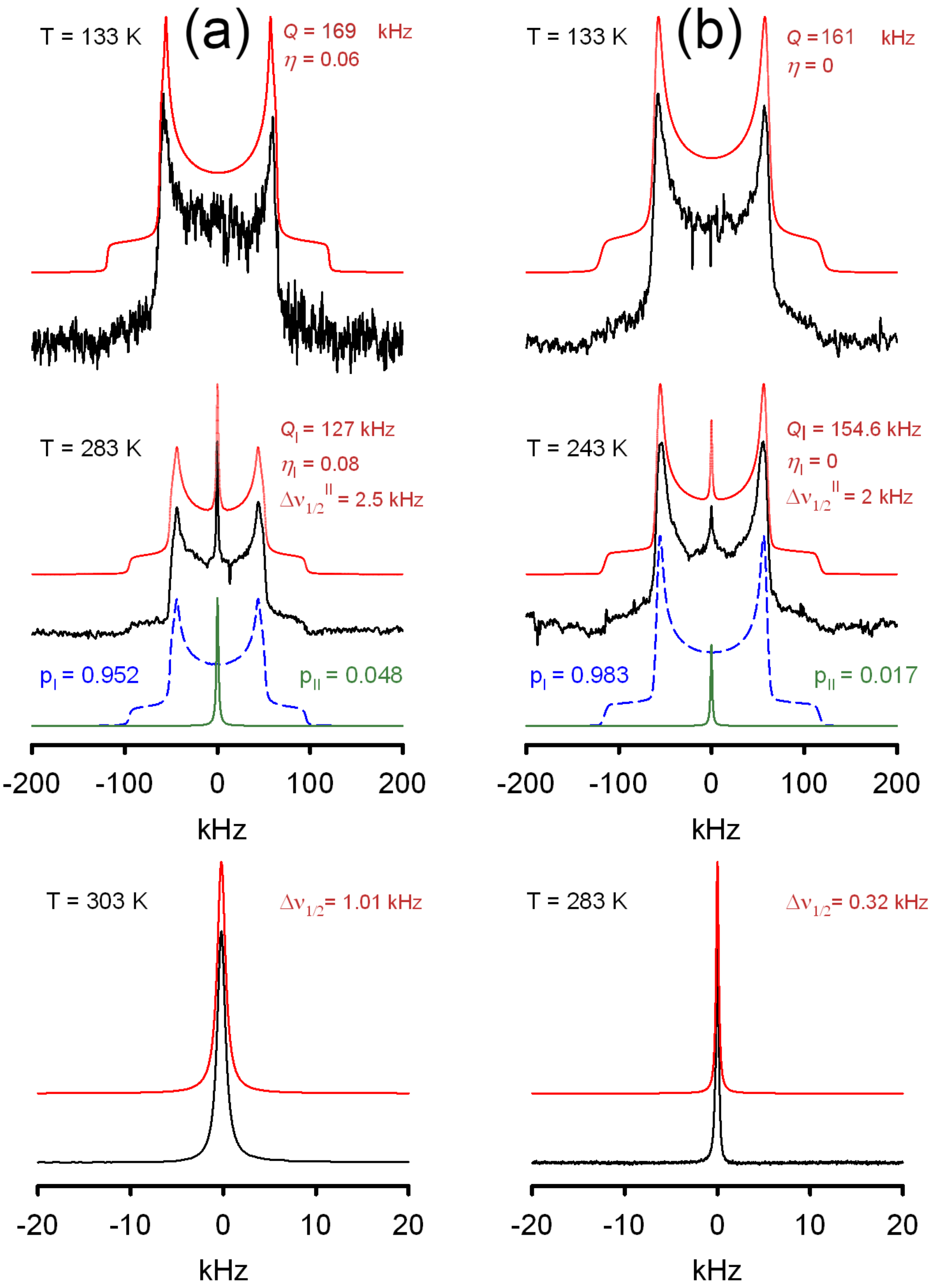

Figure S10. Measured ^{2}H NMR spectra (black lines) and simulated line shapes (red lines) as a function of temperature of (a) [N888D][OTf] and (b) [N822D][OTf], ranging from fully static at 133 K up to fully dynamically melted at 303 K. The ^{2}H NMR spectra in the heterogenous phase between 243 K and 283 K were deconvo-luted and provided the static and mobile fractions p_{I} and p_{II}.

The ^{2}H NMR spin relaxation times are given by the following equations:

$$\left(\frac{1}{T_1}\right)_{\mathrm{D}} = \frac{3}{16}\left(\frac{eQeq_{zz}}{h}\right)_{\mathrm{D}}^2 \{J_1(\omega_0) + \ 4J_2(2\omega_0)\}\,, \qquad (1)$$

$$\left(\frac{1}{T_2}\right)_{\mathrm{D}} = \frac{3}{32}\left(\frac{eQeq_{zz}}{h}\right)_{\mathrm{D}}^2 \{(3J_0(0) + 5J_1(\omega_0) + 2J_2(2\omega_0))\}\,, \quad (2)$$

where $\chi_{\mathrm{D}}=(eQeq_{zz}/h)$ is the deuteron nuclear quadrupole coupling constant, the unaveraged DQCC and the $J_1(\omega_0)$ and $J_2(2\omega_0)$ are spectral densities referenced to the Zeeman frequency.

References

[S1] A. Talybov et al. Green and Sustainable Chemistry, 2013, 3, 31-35, http://dx.doi.org/10.4236/gsc.2013.31006