Electronic Supporting Information (ESI)

Key factor governing the physicochemical properties and extent of proton transfer in protic ionic liquids: ΔpK_a or chemical structure?

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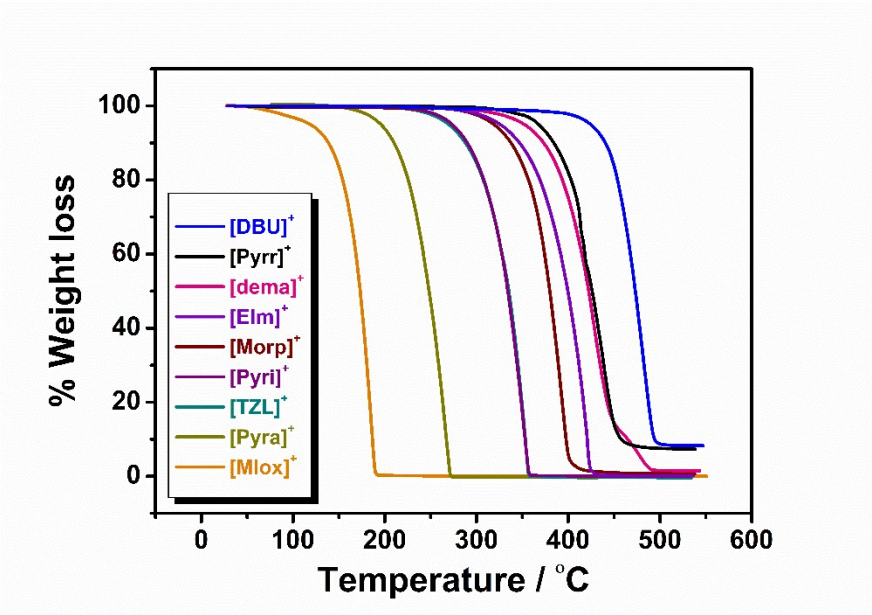

Fig. S1. TGA curves of [NTf_2]-based PILs.

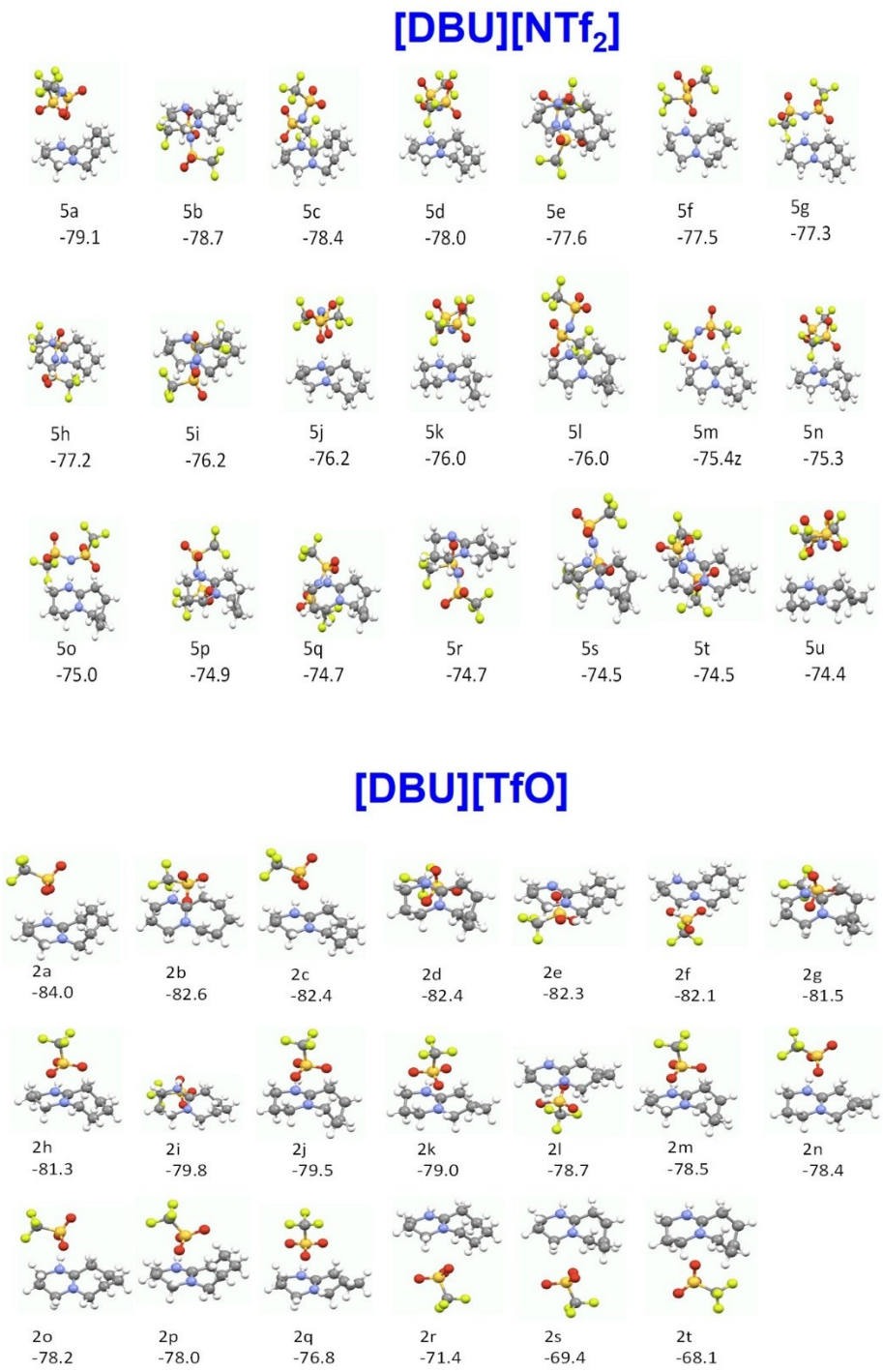

Fig. S2. Optimised geometries and stabilisation energies (E_{form}) calculated for the [DBU][NTf_2] and [DBU][TfO] complexes.

The number of geometries for [DBU]$(CF_3SO_2)_2N$ is almost twice that for [DBU][TfO] due to the special structure of the $(CF_3SO_2)_2N$ anion. Comparison of the geometries and stabilisation energies for the most stable structures suggests that the most stable geometries of the five complexes are those where an oxygen atom of the anion interacts with the N–H bond of DBU; in contrast, the geometries with no interaction between the N–H bond and oxygen atoms are significantly less stable.

Viscosity

$$\eta = \eta 0\, e^{\frac{B}{T - T0}} \quad (1)$$

where η^0, B, and T^0 were obtained via non-linear regression of the measured η vs T data. Furthermore, the activation energy, E_a (expressed in kJ mol^{-1}), for the viscosity provided by the VTF model is given by

$$\mathrm{E}a = RB\left(\frac{T}{T - T0}\right)^2 \quad (2)$$

For VTF fluids, E_a is temperature-dependent and thus, when $T >> T^0$, **eq. (2)** becomes

$$\mathrm{Ea} = RB \quad (3)$$

Therefore, **eq. (2)** can also be written in the following form to represent the VTF behaviour of the viscosity with the temperature,

$$\frac{dE\mathrm{a}}{dT} = -\frac{2RBTT0}{(T - T0)3} \quad (4)$$

Equation (4) indicates that, at a certain temperature, the decreasing rate of E_a with respect to the temperature is directly proportional to B. The best-fit VTF parameters and estimated E_a based on **eq. (3)** are provided in **Table S1.**

Table S1. VTF fitting parameters from **Fig. 6**

$$\eta = \eta 0\, e^{\frac{B}{T - T0}}$$

PILs	η_0 / mPa s	B / 10^2 K	T_0 / 10^2 K	E_a / kJ mol^{-1}	R^2
[DBU][NTf_2]	0.20±0.01	8.89±0.08	1.83±0.07	7.39	1.00
[Pyrr][NTf_2]	0.20±0.01	7.31±0.09	1.74±0.06	6.08	1.00
[dema][NTf_2]	0.14±0.00	7.89±0.05	1.62±0.05	6.56	1.00
[EIm][NTf_2]	0.25±0.00	7.47±0.11	1.64±0.01	6.21	1.00
[Morp][NTf_2]	0.17±0.01	8.62±0.14	2.06±0.01	7.17	1.00
[Pyri][NTf_2]	0.30±0.14	7.07±0.16	1.80±0.02	5.88	0.99
[TZL][NTf_2]	0.21±0.01	8.56±0.11	2.05±0.07	7.12	1.00
[Pyra][NTf_2]	0.40±0.04	5.77±0.03	2.18±0.03	4.80	0.99

Conductivity

$$\sigma = \sigma 0\, e^{-\frac{B}{T - T0}} \qquad (5)$$

where σ^0, B, and T^0 were obtained via non-linear regression of the measured σ vs T data. The fitted parameters are given in **Table S2**. For VTF fluids, the E_a of the conductivity is temperature-dependent and thus, when $T >> T^0$, **eq. (5)** becomes

$$\mathrm{Ea} = -RB \qquad (6)$$

Table S2. VTF fitting parameters from **Fig. 8**

$$\sigma = \sigma 0 e^{-\frac{B}{T - T0}}$$

PILs	σ_0 / S cm^{-1}	B / 10^{2}K	T_0 / 10^{2}K	E_a / kJ mol^{-1}	R^2
[DBU][NTf$_2$]	0.37±0.03	6.08±0.32	1.99±0.04	5.06	0.99
[Pyrr][NTf$_2$]	0.49±0.06	6.03±0.47	1.79±0.07	5.01	0.99
[dema][NTf$_2$]	0.50±0.01	5.36±0.78	1.75±0.14	4.45	0.99
[EIm][NTf$_2$]	0.76±0.08	7.93±0.48	1.49±0.07	6.59	0.99
[Morp][NTf$_2$]	0.39±0.04	5.88±0.34	2.24±0.05	4.89	0.99
[Pyri][NTf$_2$]	0.38±0.03	5.20±0.25	1.98±0.04	4.32	0.99
[TZL][NTf$_2$]	0.38±0.01	5.57±0.15	2.25±0.02	4.63	0.99
[Pyra][NTf$_2$]	0.29±0.04	4.48±0.43	2.25±0.08	3.72	0.99

Density

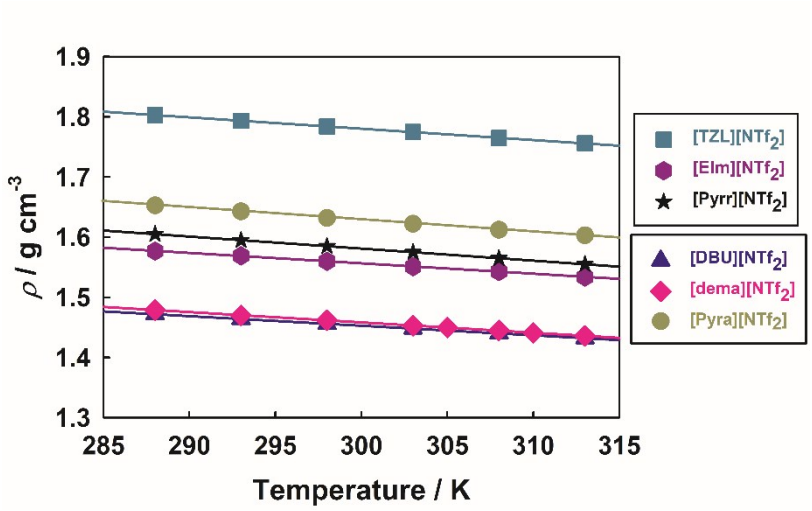

Fig. S3. Temperature dependence of the density for [NTf_2]-based PILs.

Table S3. Fitting parameters for the density equation from **Fig. S3** and M_{30} values for [NTf_2]-based PILs

$\rho = b - aT$						
PILs	ρ / g cm^{-3} at 30 °C	FW / g mol^{-1}	M_{30} / 10^{-3} mol cm^{-3}	a / 10^{-4} g cm^{-3} K^{-1}	b / g cm^{-3}	R^2
[DBU][NTf_2]	1.46	433.4	3.34	16.0	1.95	1.00
[Pyrr][NTf_2]	1.58	352.2	4.47	20.0	2.18	1.00
[dema][NTf_2]	1.45	368.3	3.95	17.1	1.97	0.99
[EIm][NTf_2]	1.55	377.2	4.11	17.2	2.07	0.99
[TZL][NTf_2]	1.78	350.2	5.07	18.8	2.34	0.99
[Pyra][NTf_2]	1.63	361.24	4.51	20.0	2.23	1.00

Molar Conductivity

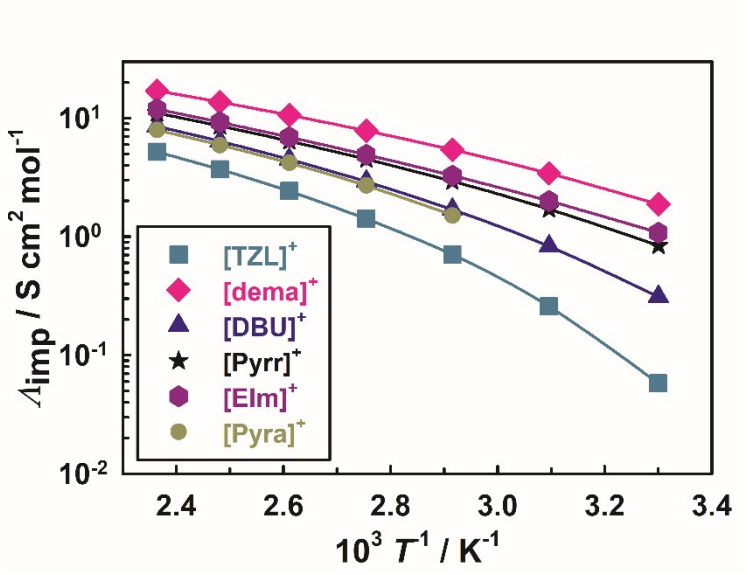

Fig. S4. Molar conductivity as a function of the temperature for [NTf_2]-based PILs.

Table S4. VTF fitting parameters from **Fig. S4**

$$\Lambda = \Lambda 0 e^{-\frac{B}{T - T0}}$$

PILs	Λ^0 / mS cm² mol^{-1}	B / 10²K	T_o / 10²K	R^2
[DBU][NTf_2]	0.19±0.05	7.30±0.09	1.89±0.01	1.00
[EIm][NTf_2]	0.36±0.01	10.00±0.14	1.31±0.02	1.00
[Pyrr][NTf_2]	0.22±0.07	7.82±0.14	1.62±0.02	1.00
[dema][NTf_2]	0.24±0.07	7.03±0.12	1.57±0.02	1.00
[TZL][NTf_2]	0.12±0.05	6.57±0.15	2.16±0.02	1.00
[Pyra][NTf_2]	0.13±0.02	6.16±0.42	2.05±0.06	1.00