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## The unseen evidence of Reduced Ionicity: The elephant in (the) room temperature ionic liquids

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(Article begins on next page)

# 1 The unseen evidence of Reduced Ionicity: the elephant in (the) room 2 temperature Ionic Liquids

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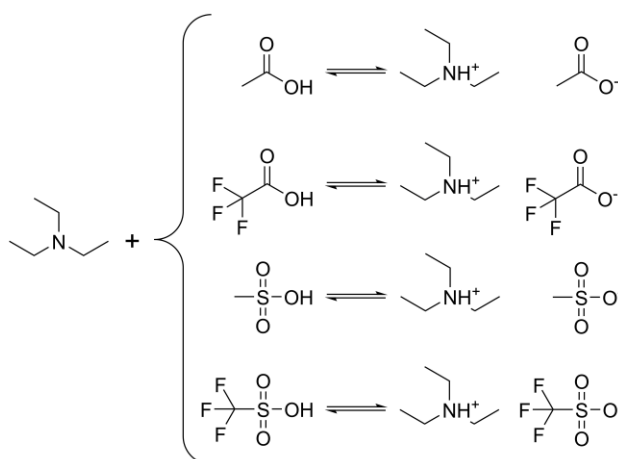
## 14 Abstract

15 The unambiguous quantification of the proton transfer in Protic Ionic Liquids (PILs) and its  
16 differentiation from the concept of ionicity are still unsolved questions. Albeit researchers awfully  
17 quickly treat them as synonyms, the two concepts are intrinsically different and imply a dramatic  
18 modification in the expected chemical and physical properties of a PIL. Some attempts have been  
19 made to shed light on this discrimination, but single-technique-based approaches fail in giving a  
20 clear answer. Aiming at definitively figuring out the differentiation between proton transfer and  
21 ionicity, we performed a multi-technique analysis (NMR, Raman, IR, thermal and electrochemical  
22 analyses, among others). Indeed, thermal and spectroscopic analyses are employed to determine  
23 the acid strength's role in ions' complete formation. To overcome the ambiguity between ionicity  
24 and formation degree, we introduce a new paradigm where Reduced Ionicity accounts for both the  
25 quantities mentioned above. The reduced ionicity directly affects the thermal stability, the phase  
26 behavior, and the spectroscopic observations, resulting in particular features in NMR and vibrational  
27 spectra. The combination of physical-chemical analyses and Pulsed-Gradient Spin-Echo (PGSE) NMR  
28 allows determining the reduced ionicity (and not the ionicity, as reported so far) of the investigated  
29 systems. In this context, being the proton transfer not quantitatively accessible directly, the reduced  
30 ionicity of a reference series of triethylamine-based PILs is investigated through transport properties  
31 as a function of temperature. Our findings point toward a substantial dependence of the reduced  
32 ionicity by the acid strength and the anion's coordination power. Furthermore, some interesting  
33 insights about the proton transfer are obtained, combining all the findings collected.

## 34 Introduction

35 Protic Ionic Liquids (PILs) are a sub-class of the nowadays widely studied ionic liquids[1–5] since they  
36 follow the general definition given by Walden in 1914, *i.e.*, "water-free salts that are in liquid form  
37 below 100 °C" [6]. A more rigorous definition is currently adopted as water-free organic salts  
38 showing a melting point at temperatures below their decomposition. Ionic liquids have been  
39 successfully applied in different fields ranging from sensors to solar cells and batteries, and they can  
40 also be employed as lubricants in technological applications[7–15]. Indeed, interactions leading to

1 PILs formation are constituted by a subtle balance of "weak" forces (*e.g.*, Coulombic interactions,  
 2 hydrogen bonding, cohesion, and dispersion forces). ILs are generally classified into two prominent  
 3 families: protic ionic liquids and aprotic ionic liquids (AILs). The former family results from the proton  
 4 transfer between two neutral species[16], while the AILs are formed by the interaction of two  
 5 preformed ions that, once mixed, give rise to the liquid system. As highlighted in Scheme 1, the  
 6 reaction forming PILs is an equilibrium reaction, meaning that the parent compounds may always  
 7 exist together with the ionic species. This apparent weakness in terms of stability of the ionic species  
 8 can be turned into an advantage. While most AILs have almost zero vapor pressure, PILs precursors  
 9 generally have low boiling points, enabling their distillation thanks to the Le Châtelier's principle[17].  
 10 Their ability to establish extended 3D hydrogen-bonded networks[18] gives rise to a series of  
 11 exciting properties like enhanced proton mobility and peculiar solvation character as observed both  
 12 experimentally[19–24] and by theoretical calculations[21,25,26]. PILs share morphologically similar  
 13 hydrogen bond networks with water[27], although they differ in almost every aspect. The ease of  
 14 preparation and the usually cheap precursors make them appealing materials for a wide range of  
 15 applications[9]. Examples span from electrochemistry[28] to catalysis[29]; the latter also thanks to  
 16 their ability to dissolve a wide variety of compounds[30–35]. As PILs form via an equilibrium  
 17 reaction, "neat" protic ionic liquids are not usually achieved, but some acid and base will be present  
 18 in the system. To minimize the fraction of parent compounds, the use of strong acids and bases  
 19 certainly helps. In this work, we employed triethylamine (TEA) as a Brønsted base in combination  
 20 with a family of acids offering growing Brønsted acidity, *i.e.*, acetic acid (HAc), trifluoroacetic acid  
 21 (HTFA), methanesulfonic acid (mesylic acid, HMS) and trifluoromethanesulfonic acid (triflic acid,  
 22 HTfO), adhering to Scheme 1.  
 23



24 Scheme 1: Compounds discussed in this work. From top to bottom: Triethylammonium acetate; Tri-ethylammonium  
 25 trifluoroacetate; Triethylammonium methanesulfonate; Triethylammonium trifluoro-methanesulfonate.

26  
 27 However, regarding triethylammonium acetate, a two-phase liquid was always obtained  
 28 despite the synthetic route adopted, although previous reports indicated the successful  
 29 synthesis of this compound[36–38]. In particular, we found the lower phase to be a mixture  
 30 of the product and acetic acid in the mole ratio 1:3. Indeed, <sup>1</sup>H-NMR analyses (data not  
 31 shown) of the upper (colorless) and lower (brownish) phases suggest that the former, which

1 has the smallest volume, is almost entirely made up of trimethylamine with the PIL present  
2 only in traces.

3 On the other hand, the lower and most abundant phase contains the final product and a  
4 significant excess of acetic acid. It should be noticed that the preparation protocol followed  
5 in the reports mentioned above [36–38] involved the distillation of the final product to  
6 remove the solvent. We may suggest that the amine-rich phase was lost upon distillation,  
7 resulting in the mixture of acetic acid and IL being misrecognized as a pure ionic liquid. In  
8 fact, in other manuscripts, the formation of two phases has been reported[39]. Recently, it  
9 was shown experimentally[40,41] and computationally[42] that the PIL is, indeed, not  
10 formed when equimolar quantities of triethylamine and acetic acid are mixed.

11 In the following, only the PILs resulting from the reaction of triethylamine (TEA) with either  
12 trifluoroacetic, mesylic, or triflic acid are considered because they form single-phase  
13 products. The determination of the proton transfer is often overlooked and sometimes  
14 confused with the ionicity of the system. The latter does not measure specifically the number  
15 of ionic species in the system, but it is instead a value indicating how many free charge  
16 carriers are present in the system. For an ionic liquid consisting of a cation  $A^+$  and an anion  
17  $B^-$ , the following expression defines the ionicity  $I$ :

$$I = \frac{[A^-] + [B^+]}{[A^-] + [B^+] + [A^-B^+]} \quad (1)$$

19 where the square brackets indicate the concentration of the species comprised, and  $[A^-B^+]$   
20 indicates the concentration of close ion-pairs. In order to be rigorous, the activity of the  
21 species should be used to calculate any thermodynamic quantity, but on first approximation,  
22 the use of concentrations could be accepted. It immediately appears clear how any neutral  
23 molecule is not included in the ionicity definition. In the case of protic ionic liquids, the cation  
24 carries a net charge due to protonation; thus, we will use  $HB^+$  to indicate the cation. The  
25 subtle difference between the proton transfer and ionicity resides in the fact that the  
26 experimentally accessible quantities (*vide infra*) commonly used to determine ionicity can  
27 be decreased by three mostly independent factors: (i) the proton (back)transfer, (ii) the  
28 charge transfer between ions, and (iii) the ion association. Spectroscopic approaches have  
29 been proposed to quantify the proton transfer[43], but the method proposed relies on the  
30 assumption that the solvation shells and dielectric constant of the systems stay unperturbed  
31 upon changing the composition of the system, which is questionable. MacFarlane's group  
32 extensively addressed the proton transfer topic[39,44,45], but always accounting for  $\Delta pK_a$   
33 values, which are strictly meaningful only in aqueous systems. They also pointed to the  
34 proton transfer's qualitative spectroscopic determination [44], but again overlooking the  
35 different chemical environments experienced by the species in the Brønsted precursors and  
36 the ILs. Ionicity and proton transfer cannot be used as synonyms, albeit directly  
37 correlated[46]. The proton transfer (or Formation Degree, FD) is a thermodynamic quantity  
38 indicating the fraction of the Brønsted precursors involved in the proton exchange reaction.  
39 For a Brønsted acid (HA) reaction with a Brønsted base (B) to form the PIL  $HB^+ A^-$ , we have:

1

$$K_{PT} = \frac{[A^-] \cdot [HB^+]}{[HA] \cdot [B]} \quad (2)$$

$$FD = \frac{[A^-] + [HB^+] + [A^-HB^+]}{[A^-] + [HB^+] + [A^-HB^+] + [HA] + [B]} \quad (3)$$

2

3 where  $K_{PT}$  is the equilibrium constant for the proton transfer.

4 The concept of charge transfer refers to the evidence of ions with non-integer electric  
 5 charge[47–50]. Nevertheless, this effect, which is pivotal in aprotic ionic liquids[50,51],  
 6 contributes only marginally to the ionicity value when Protic Ionic Liquids are considered.  
 7 The charge transfer accounts for electron clouds sharing between ions (*i.e.*, negative charges  
 8 moving from one species to another); on the other hand, proton transfer (*i.e.*, positive  
 9 charges moving from one species to another) has a much more marked effect statistically  
 10 and also in absolute value.

11 Strictly speaking, the concept of ionicity refers to the number of "free" ions in solution, as  
 12 defined in Equation 1. Thus, the eventual formation of tight ion-pairs or the occurrence of  
 13 other intermolecular interactions will not directly influence the proton transfer but will have  
 14 a significant impact on system ionicity.

15 Triethylammonium triflate (TEATfO) and triethylammonium mesylate (TEAMS) have already  
 16 been thoroughly investigated by Ludwig *et al.* [23,52–54]. However, they mainly focused on  
 17 the spectroscopic characterization of these materials, simplistically assuming a complete  
 18 formation of the PILs. Albeit they achieved a very in-depth knowledge of the systems,  
 19 whether such systems are neat ILs or mixtures of ILs and their precursors is still undefined.  
 20 Indeed, the second option seems to be the most likely. For example, Davidowsky *et al.*[55]  
 21 investigated the ionicity of very similar systems (*i.e.*, TEA was replaced by diethyl-methyl  
 22 amine, DEMA), finding an interesting correlation between the proton affinity of the acid in  
 23 the gas phase and the PIL proton transfer: the lower the former, the higher the latter,  
 24 resulting in the following order for the proton transfer: HAc < HTFA < HMS < HTfO. However,  
 25 the ionicity of the DEMATfO was found to be as high as 0.61. We reasonably expect a higher  
 26 ionicity in TEATfO, being TEA a stronger Brønsted base than DEMA. A remarkable effort in  
 27 the proton transfer study in PILs has been made recently by Hasani *et al.* [56] employing  $^{15}\text{N}$   
 28 NMR on a series of pyridine-based systems. They find a clear correlation between the  
 29 difference of Brønsted precursors' proton affinities and the chemical shift of TEA nitrogen  
 30 atom. Nevertheless, this approach does not return quantitative results, is limited to  
 31 "ammonium" PILs, and requires  $^{15}\text{N}$  labeled samples, which are substantially expensive.

32 Unfortunately, the proton transfer cannot be directly determined in practice. Many attempts  
 33 have been made to employ potentiometric methods[57–61]. However, albeit the authors  
 34 find reasonable correlations between proton transfer (*i.e.*, the number of neutral species in  
 35 the mixture) with the acid strength of the proton donor precursors, some points prevent us  
 36 from relying on this approach entirely:

37 (i) no matter the IL investigated, two typical trends are evidenced: an almost quantitative  
 38 proton transfer (related to a meager amount of neutral precursor) or an almost null proton

1 transfer (IL not formed), whereas intermediate situations seem not to be detectable with  
2 this approach. (ii) The authors started from the assumption that a superacid (triflic acid,  
3 triflimidic acid (HTFSI)) in an aqueous environment could be used to titrate the unreacted  
4 base quantitatively. However, this assumption is not supported by experimental data  
5 regarding triflic acid strength in pure ionic liquids. For example, Kanzaki *et al.* [57,60] show  
6 how, in an IL, the  $\text{H}_3\text{O}^+$  is a stronger acid than  $\text{HNO}_3$ , whereas the opposite is true in an  
7 aqueous environment. There is no evidence that HTfO or HTFSI are stronger acids than  $\text{HNO}_3$   
8 in the IL environment; thus, the proposed approach seems to be based on not universally  
9 valid assumptions. (iii) Moreover, the employment of triflic acid [60] or triflimidic acid [57]  
10 as a titration agent will lead to the formation of a ternary system in the investigated  
11 environment. Taking as example EAN, when triflic/triflimidic acid is added, the system  
12 becomes a mixture of EAN and EA-TfO/TFSI that could influence the linearity in the response  
13 of the electrochemical measurements. Finally, (iv) The reported approaches neglect the  
14 presence of water traces in the IL entirely. The latter's amount is calculated in the range of  
15 50-100 ppm [57,60] for different ionic liquids corresponding to a mole percent in the range  
16 of 4-8% if we consider EAN. Practically speaking, the contribution of water should be  
17 considered at least when dealing with almost-completely-formed ILs: indeed, in these cases,  
18 the concentration of  $\text{H}_2\text{O}$  is higher than the one of the unreacted ethylamine, and its basicity  
19 could also be comparable if not higher (in IL environment) than the latter. If so, the titration  
20 would involve two different species ( $\text{H}_2\text{O}$  and  $\text{Et-NH}_2$ ), and the quantification of the amine  
21 could be largely overestimated. The pioneering theoretical work of Ingenmey *et al.* [62]  
22 makes use of Quantum Cluster Equilibrium Theory to obtain several thermodynamic  
23 properties from two different PILs computationally. In that work, they find values for the  
24 proton activities in fair agreement with the ones determined with the potentiometric  
25 methods. On this basis, we aim to expand the current work by employing the experimental  
26 and computational techniques abovementioned in a forthcoming paper.

27 For now, we focused on measuring the systems' ionicity but considering the incomplete  
28 formation of the PILs while interpreting the results, *i.e.*, not only referring to ion association.  
29 In this work, we qualitatively prove that a certain degree of the examined PILs is always  
30 formed, no matter which acid is employed, through a spectroscopic approach. A first semi-  
31 quantitative analysis of the PILs ionicity is done by considering the so-called Walden plot,  
32 where the inverse of the viscosity is plotted against the molar conductivity[63]. Studies  
33 [46,64] proposed an empirical factor to derive the ionicity of a solution directly from the  
34 Walden plot:  $\Delta W$ , the vertical distance from the bisector representing the ideal behavior,  
35 and the system's value. Angell's approach has been proven to be trustworthy for simple  
36 mixtures, but it mostly fails to predict the ionicity of more complicated systems such as  
37 molten salts[65]. Concerning PILs, it could be considered a rule of thumb, whose validity  
38 should be further confirmed by additional evidence.

39 Finally, we employ Pulsed-Gradient Spin-Echo (PGSE) NMR as an elegant approach to  
40 measure self-diffusion coefficients ( $D$ ) of the different species existing in a system[66,67].  
41 This technique has been successfully employed in the study of pure ILs[68] and their mixtures  
42 with salts[69,70] and solvents[71,72]. Back in 2007, however, Annat *et al.*[73] proved that

1 PGSE suffers from intrinsic internal gradients and can produce apparent diffusion  
2 coefficients considerably varying (up to 20%) for different protons within a given molecule.  
3 As a matter of fact, most common ILs are constituted by bulky ions. Thus,  $^1\text{H}$  nuclei belonging  
4 to the same species may experience somewhat different environments. Therefore, the  
5 sizeable coupling will be present, and Brownian motion may not be sufficient to average out  
6 the dipolar interactions. Therefore, they resorted to PG stimulated echo (PGSTE)  
7 experiments, minimizing the issue. Currently, that method is the most exploited approach in  
8 the field of ILs[74]. In the present case, however, it should be pointed out that, since both  
9 the anion and the cation are relatively small, the classical PGSE sequence allows to obtain  
10 consistent values (*i.e.*, the difference in the calculation of  $D$  using different  $^1\text{H}$  nuclei of the  
11 same molecule is well below the experimental error). The NMR-derived  $D$  values can be  
12 inserted in the Nernst-Einstein (NE) equation to obtain the related conductivity.

13 By employing a set of the described complementary techniques, such as thermodynamic  
14 measurements, vibrational spectroscopies, NMR spectroscopies, and computational  
15 methods, we found that the usually adopted Nernst-Einstein-based approach is not  
16 associated with the direct determination of the ionicity nor proton transfer. Nevertheless,  
17 considering the diffusion coefficients of anions, cations, and acidic protons, a qualitative  
18 conclusion is achieved. Our results prove out of any doubt that the correct interpretation of  
19 experimental results is of vital importance to account for not-quantitative proton transfer in  
20 protic ionic liquids. Finally, we introduce the new concept of Reduced Ionicity, a quantity  
21 explicitly accounting for both ionicity (defined as non-paired ions in the system) and the  
22 proton transfer extent.

## 23 **Results and discussion**

### 24 **Thermal characterization**

25 The DSC and TGA of the three formed compounds, collected to determine each PIL's  
26 characteristic temperatures, are summarized in Table 1. First, the decomposition  
27 temperature was determined to identify the temperature range in which the stability of the  
28 system was not threatened. All following characterizations were planned accordingly. Figure  
29 1 depicts the obtained results. Although some sources indicate the ILs decomposition to start  
30 at the temperature where the mass loss is 3% ( $T'_d$ ), a better approach consists of taking the  
31 minimum of the TGA derivative curve as the decomposition temperature ( $T_d$ ). For the sake  
32 of comparison with literature data, we report the values obtained with both approaches in  
33 Table 1, but the discussion will be based on the values obtained with the derivative method  
34 (DTGA).

35 TFA anion appears to lead to the least stable PIL (TEATFA), with a  $T_d$  of 478 K. This is due to  
36 the occurrence of the anion decarboxylation as previously reported at considerably higher  
37 temperatures for the pure acid[75]. Such a decomposition path leads to the complete loss  
38 of the sample, as witnessed by the absence of any residual mass.

39 TEAMS is more stable exhibiting  $T_d$  at 485 K. This PIL shows more than a single degradation  
40 process, which can be ascribed to TEAMS' multi-step decomposition and its thermolysis

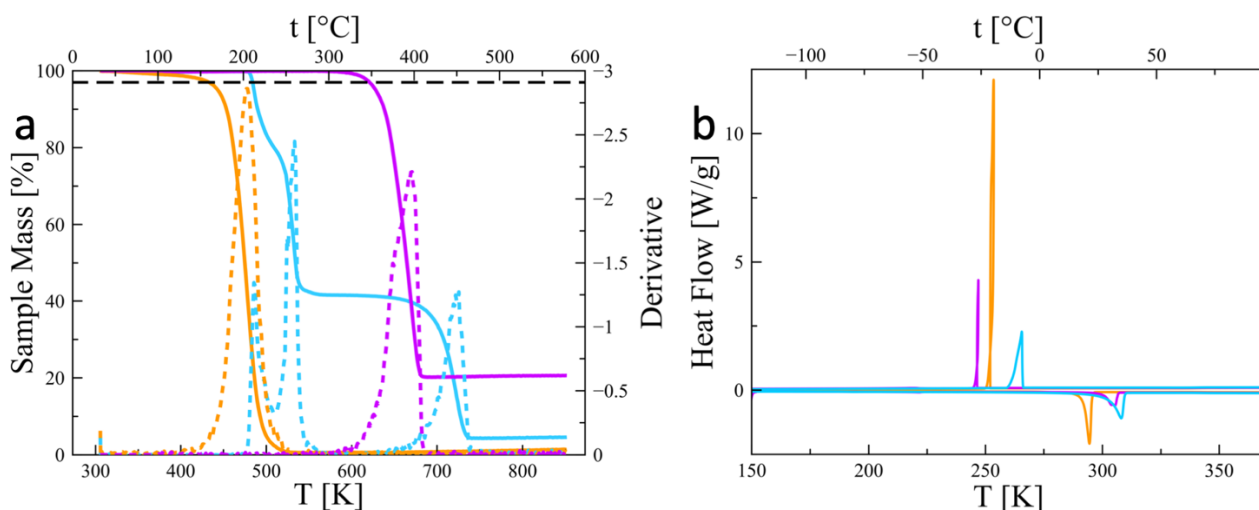
1 residuals. The most stable PIL is certainly TEATfO showing a  $T_d$  of 669 K. The analysis of the  
 2 DTGA curve shows that TEATfO is also decomposing through a multi-step process similar to  
 3 TEAMS. However, fluorination enhances the stability of the whole compound (with a residual  
 4 mass at 800 °C higher than 20%). Indeed, TfO-based ILs are known to be thermally stable  
 5 and are also used in fuel-cells[25,76]. The stability order interestingly follows the parent acid  
 6 strength – TEATfO > TEAMS > TEATFA. Although some sources link the thermal stability to  
 7 the extent of proton transfer[74,77,78], other evidence [79,80] highlighted that there is no  
 8 direct correlation between the two properties, and caution is advised, especially when good  
 9 leaving groups (*e.g.*, CO<sub>2</sub>) are involved.

10 The phase transition temperatures of the PILs were investigated via DSC (Figure 1). At first  
 11 glance, it appears that all three PILs can be extensively super-cooled, showing crystallization  
 12 temperatures ( $T_c$ ) well below their melting temperatures ( $T_m$ ). The same was also observed  
 13 while manipulating the samples for the analysis. All of them appeared solid at room  
 14 temperature, but they melt after heating at 80 °C, remaining liquid upon storage at 20 °C for  
 15 several weeks if left undisturbed in a vacuum desiccator.

16 According to the DSC curves in Figure 1b, TEATFA only shows  $T_c$  at 253 K and  $T_m$  at 294 K,  
 17 with no sign of glass transition ( $T_g$ ) in the examined range. TEAMS shows the  $T_g$  at 188 K in  
 18 addition to the  $T_c$  at 266 K and  $T_m$  at 308 K, while TEATfO shows  $T_g$ ,  $T_c$ , and  $T_m$  at 221 K,  
 19 247 K, and 305 K, respectively.

20 The wide distribution of literature values[16,37,74,79–84] and the discrepancy with our  
 21 findings could be explained considering the different water content in the range 1 ppm[16]  
 22 - 2%<sub>mol</sub>[74] for TEAMS and TEATfO, and 50 ppm[37] - 4200 ppm[79] for TEATFA. Sometimes,  
 23 though, the water content is not even reported. Indeed, it is well known that even small  
 24 differences in water content could have dramatic effects on IL properties, especially in  
 25 PILs[85].

26



27 **Figure 1: (a) TGA (solid lines) and DTGA (dashed lines) collected (heating rate: 5 K min<sup>-1</sup>) of TEAMS (cyan), TEATFA**  
 28 **(orange), TEATfO (purple). The black dashed line corresponds to the 3% mass loss threshold. (b) DSC curves (heating rate:**  
 29 **5 K min<sup>-1</sup>) of TEAMS (cyan), TEATFA (orange), TEATfO (purple)**

30



1 Table 1: Comparison of thermal characterizations of this work (underlined) and literature. All values are expressed in  
 2 Kelvin.

	$T_c$	$T_m$	$T_g$	$T'_d$	$T_d$
<b>TEAMS</b>	<u>265.53</u>	<u>308.03</u>	<u>187.68</u>	<u>484.25</u>	<u>485.52</u>
	241.55[81]	297.45[81]	194.25[81]		578.15[37]
	249.15[37]	306.15[37]	211.05[83]		491.15[74]
	242.15[74]	306.15[82]	176.65[16]		498.15[83]
	250.25[80]	298.15[74]	198.15[82]		542.85[16]
		290.55[83]			476.15[80]
		294.75[16]			563.15[82]
		306.25[80]			
<b>TEATFA</b>	<u>253.50</u>	<u>294.47</u>	--	<u>433.06</u>	<u>478.08</u>
	231.15[37]	275.15[37]	190.15[37]		463.15[37]
	231.75[79]	281.75[79]			459.45[79]
<b>TEATfO</b>	<u>246.97</u>	<u>305.34</u>	<u>221.26</u>	<u>620.56</u>	<u>657.55</u>
	253.15[37]	305.15[37]	215.15[37]		649.15[37]
	260.15[74]	299.15[74]	215.15[84]		595.15[74]
	243.85[80]	307.45[83]			631.15[83]
		306.35[80]			585.65[16]
		307.15[82]			588.55[80]
		309.15[84]			653.15[84]
					663.15[82]

3  
 4 Anyhow, our results fit in the general trend already reported. Shmukler *et al.*[79] proposed a  
 5 correlation between  $T_c$  and  $T_m$  for a series of triethylammonium-based PILs, including the three  
 6 under investigation here, but we do not find anything similar. Again, the samples' different water  
 7 content and thermal history could have a substantial effect on the observed thermal properties.

### 8 Conductivity and Viscosity

9 The study of PILs transport properties offers a deep insight into their nature; therefore,  
 10 conductivity and viscosity measurements were carried out on all samples as a function of  
 11 temperature (Figure 2). The experimental data clearly show Vogel-Tamman-Fulcher (VTF)  
 12 behavior in both cases, markedly deviating from linearity in the Arrhenius plot ( $\log \varphi$  vs.  
 13  $1000/T$ , in Figure S1). Thus, data were fitted with the equation:

$$\varphi(T) = \varphi_{\infty} \exp \left[ -\frac{\xi_a^{\varphi}}{k_B(T - T_0)} \right] \quad (4)$$

14 where  $\varphi$  is either the conductivity ( $\sigma$ ) or the viscosity ( $\eta$ ),  $\varphi_{\infty}$  is the value of that property at  
 15 infinite temperature,  $\xi_a^{\varphi}$  is a parameter which is linked to the activation energy  $E_a^{\varphi}$  by  $E_a^{\varphi} =$   
 16  $|\xi_a^{\varphi}|$ ,  $k_B$  is the Boltzmann constant ( $8.62 \cdot 10^{-5}$  eV K<sup>-1</sup>),  $T$  is the absolute temperature, and  $T_0$   
 17 is the temperature of zero configurational entropy, often referred to as the "ideal glass-  
 18 transition temperature". A comparison with literature data is given in Table 2, while Equation  
 19 4 parameters are listed in Table 3. It is interesting to note how TEATFA is both the least  
 20 viscous and the least conducive PIL. However, such a counter-intuitive behavior is difficult to  
 21 justify only accounting for its low ionicity intended as "pronounced ion-pairing". If this were  
 22 the case, the sample viscosity would have been higher due to the strong coulombic and

1 hydrogen-bonding forces between the ions. A more profound interpretation must consider  
2 the IL's incomplete formation, resulting in a limited amount of charge carriers (explaining  
3 the low conductivity), accompanied by a reduced viscosity coming from the unreacted  
4 precursors (explaining the low viscosity). The presence in the TEATFA system of pure  
5 triethylamine (0.345 mPa s at 25°C) and trifluoroacetic acid (0.813 mPa s at 25°C) is expected  
6 to cause a net decrease in the viscosity, but at the expenses of available charged species  
7 jeopardizing the conductivity. On the other hand, TEAMS appears to be by far the most  
8 viscous PIL but displays higher conductivity than TEATFA. Once more, the degree of IL  
9 formation plays a pivotal role in this PIL, too. Here, the surprisingly high viscosity is  
10 undoubtedly caused by the more pronounced ion formation being mesylic acid stronger than  
11 trifluoroacetic acid (*i.e.*, a higher proton transfer can be confidently assumed). As a  
12 consequence, the conductivity is higher, although the viscosity reduces ion mobility. Finally,  
13 TEATfO is, by a large margin, the most conductive PIL in the explored temperature range.  
14 The low coordinating power of triflate, together with the strength of the triflic acid, makes  
15 this result expected and in line with the literature[25,74,80,86]. Here, we could expect the  
16 PIL to be nearly completely formed. Passing to the VTF space,  $E_a^\sigma$  and  $E_a^\eta$  values for TEATFA  
17 are in excellent agreement with each other, suggesting that the conductivity in this system  
18 is dominated by viscosity, and other effects, such as ion-pairing, are not significant. Once  
19 again, this evidence hints at the incomplete formation of this particular IL. If the unreacted  
20 precursors are in significant excess, then the ion-pairing is statistically limited since the  
21 mixture would be more similar to a dilute salt solution rather than a proper ionic liquid.  
22 Consequently, the activation energies for the viscous and conductive fluxes converge, *i.e.*,  
23 once the charged species start moving, there is no additional energy required to break the  
24 ion pairs activating the conductive flux. For the other two ILs,  $E_a^\sigma$  is lower than  $E_a^\eta$  suggesting  
25 that for higher degrees of formation there is no need to activate the viscous flow to start the  
26 conductivity. In an ion-rich system, there is no need for the ions to move to carry charges, as  
27 they could make the charge "jump" from one site to another by merely changing their  
28 solvation shells, *i.e.*, the hopping mechanism, with no need for viscous flow (As schematically  
29 depicted in Figure S2 in Supporting Information). However, this effect should not be  
30 confused with the Grotthuss mechanism, since no chemical reaction is involved in our case.  
31 It is worth noting that the opposite is observed in AILs, in which stable ion clusters jeopardize  
32 the conductivity. A widespread approach to qualitatively estimate the ionicity of the ionic  
33 liquids is the so-called Walden plot, which correlates the logarithm of the molar conductivity  
34 with the logarithm of the fluidity ( $\eta^{-1}$ ). To obtain the molar conductivity, we extracted the ILs  
35 molarity from density measurements (shown in Figure S3) and applied the relation:

$$\Lambda = \sigma \cdot \frac{\text{MW}}{\rho} \quad (5)$$

36 where  $\Lambda$  is the molar conductivity,  $\rho$  is the density expressed in  $\text{g dm}^{-3}$ , and MW is the sample  
37 molecular weight. In the Walden plot, a reference ideal behavior line is represented by 1M  
38 KCl, which is considered fully dissociated and, thus, 100% ionic. A second reference line is  
39 usually displayed, assuming 10% ionization of the same 1M KCl solution. These references

1 appear to be wholly arbitrary[63,65] and often poorly discussed in the literature, with some  
 2 groups reporting the line being "0.01M KCl", some reporting "0.1M KCl" and others the  
 3 (correct) "1M KCl". Moreover, the aqueous KCl system was selected as a reference only  
 4 because it displays a nice correlation between molar conductivity and fluidity. Here we use  
 5 the unambiguous definition of the ideal behavior line to be "the bisector passing through  
 6 the origin of the Walden plot" (*i.e.*, solution of Equation 6 with  $\alpha=1$ ). For the 10% reference  
 7 line, instead, we simply shift the ideal line down one order of magnitude on the y-axis, thus  
 8 assuming that the conductivity is linearly dependent on the concentration, which might not  
 9 be the case in ILs, but it helps to separate the Walden plot in well-defined regions. Systems  
 10 lying in between these lines are qualitatively defined as "good ionic liquids". Should they fall  
 11 above or below, then they would be considered super-ionic or poorly-ionic, respectively. In  
 12 general, it is expected for any given system to obey the Walden rule[46]:

$$\Lambda\eta^\alpha = C \quad (6)$$

13 C is a temperature-dependent constant, and  $\alpha$  is called the decoupling constant, which  
 14 corresponds to the Walden plot's slope. The vertical distance between the ideal line and the  
 15 examined system is called  $\Delta W$ . Applying[36] the relation:

$$I_W = 10^{-\Delta W} = 10^{-\log(\Lambda/\Lambda_r)} = \frac{\Lambda_r}{\Lambda} \quad (7)$$

16 where  $\Lambda$  and  $\Lambda_r$  are the molar conductivity of the sample and the reference line, respectively,  
 17 it is possible to estimate the Walden ionicity ( $I_W$ ) of the system. From Equations 6 and 7, it  
 18 appears evident that in the ideal case  $\alpha=1$  and  $\Delta W=0$ , therefore we consider this specific  
 19 case as our reference in the Walden plot. The results for the three PILs herein investigated  
 20 are reported in Figure 2 and Table 4. All PILs lie below the ideal line, with TEATFA being just  
 21 under the 10%  $I_W$  reference line, *i.e.*, it is classified as a poor-ionic liquid, which is in complete  
 22 agreement with our previous suggestion of a scarcely formed PIL. The other two PILs lie in  
 23 between the two reference lines, thus behaving as good-ionic liquids, with TEATfO being the  
 24 closest to the reference 100% dissociation line. On a more quantitative analysis, through the  
 25  $\Delta W$  values and Equation 7, the Walden ionicity values are obtained and reported in Table 4.  
 26 As expected,  $I_W$  values follow the order TEATfO>TEAMS>TEATFA. Some groups suggested a  
 27 correlation between the Walden ionicity of protic ionic liquids and the  $\Delta pK_a$  of the Brønsted  
 28 precursors[43,64,77]. While this approach yields consistent results, it must be considered  
 29 contingent because  $pK_a$  values are meaningful only in water (and in a few other solvents).  
 30 Angell, though, has shown[87] how  $\Delta pK_a$  is undoubtedly a valid rule-of-thumb to rationalize  
 31 qualitative results such as  $\Delta W$  values. The  $pK_a$  values for the precursors used in this work  
 32 were found in the literature[88–91] and conveniently reported in Table S1. From a physical  
 33 point of view,  $\Delta pK_a$  is related to the free energy of the proton transfer from the acid to the  
 34 base through:

$$\Delta G^0 = -RT \Delta \ln K_a = -2.303 RT \Delta pK_a \quad (8)$$

1 where  $R$  is the gas constant. It must be clear that Equation 8 is strictly valid only if the proton  
 2 transfer happens in a 1M aqueous solution, as also specified by Angell himself[16]. The  
 3 results obtained for our systems are reported in Table 4. A markedly negative free energy is  
 4 found for all the three systems, hinting at a quantitative proton transfer, in open  
 5 contradiction with all the other experimental results. We can, therefore, conclude that this  
 6 approach is not giving reliable information on the considered PILs. The same is true  
 7 considering the hypothetical protic ionic liquid triethylammonium acetate, with a  $\Delta pK_a$  of  $\sim 6$ .  
 8 By applying Equation 8, a  $\Delta G^0 = -34.3 \text{ kJ mol}^{-1}$  is obtained at room temperature, which points  
 9 toward a quantitative proton transfer. On the other hand, the reaction does not  
 10 quantitatively occur in reality, as mentioned earlier. Yoshizawa *et al.* proposed that a  
 11  $\Delta pK_a > 10$  is required for complete proton transfer[64], which would rule out  
 12 triethylammonium acetate, but would consider TEATFA a completely formed PIL, which is  
 13 also not the case (*vide infra*).

14 As pointed out by Davidowski and coworkers[55], proton affinity differences ( $\Delta PA$ ) are more  
 15 reliable than  $\Delta pK_a$  to discuss Walden ionicity in pure ionic liquids. DFT calculations in the gas  
 16 phase could return the proton affinity value for every protonated/non-protonated pair  
 17 discussed[92]. The proton affinities for the PILs herein investigated are reported in Table S2,  
 18 while the  $\Delta PA$  values are listed in Table 4. Interestingly, the  $\Delta PA$  for triethylammonium  
 19 acetate is  $\sim 500 \text{ kJ mol}^{-1}$ , in agreement with the experimentally observed non-quantitative  
 20 formation of the ionic liquid.

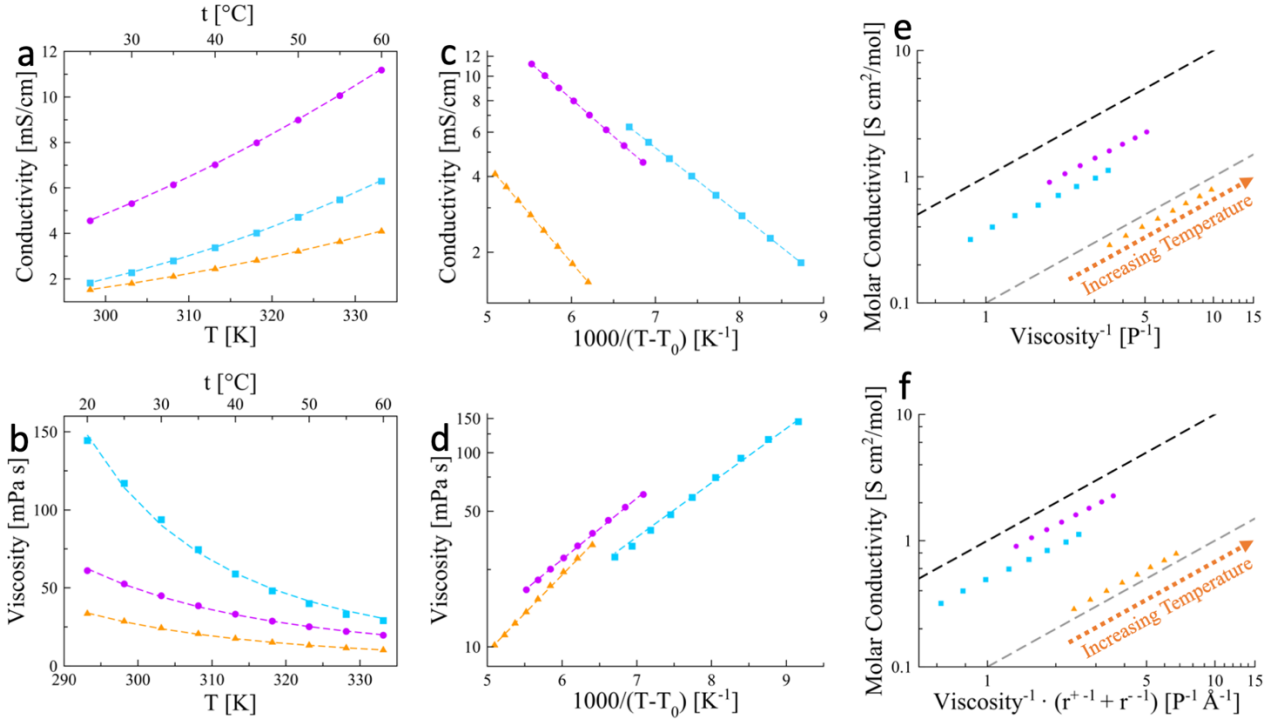
21 A useful correction to the Walden plot was introduced by Bonhôte *et al.* [93] and then re-  
 22 proposed by Abbott and MacFarlane [46,94]. It is based on the role played by the ion size on  
 23 diffusion, clearly highlighted in the Stokes-Einstein equation (Equation 9). They introduced a  
 24 correction factor  $\zeta$  for the viscosity explicitly accounting for the ion sizes (Equation 10), and  
 25 then use  $\log(\zeta \eta^{-1})$  in the Walden plot. Moreover, Equation 6 can be expressed as Equation  
 26 11[46], explicitly showing the ion-size dependency of the Walden rule.

27

28 *Table 2: Conductivity [ $\text{mS cm}^{-1}$ ] and viscosity [ $\text{mPa s}$ ]. Data in this work (underlined) and in literature at 25 °C. Other*  
 29 *temperatures and water content in brackets.*

TEAMS	TEATFA	TEATfo
<b>Conductivity</b>		
<u>1.84 (76 ppm)</u>	<u>1.52 (52 ppm)</u>	<u>4.55 (61 ppm)</u>
1.91 (100 ppm)[81]	2.45 (420 ppm)[79]	27.6 (120 °C) (N/A)[83]
2.03 (2% <sub>mol</sub> )[74]		4.79 (2% <sub>mol</sub> )[74]
16.3 (120 °C) (N/A)[83]		
<b>Viscosity</b>		
<u>117.0 (76 ppm)</u>	<u>28.6 (52 ppm)</u>	<u>52.5 (61 ppm)</u>
94 (810 ppm)[80]		56 (500 ppm)[80]

30



1 **Figure 2: Conductivity (a) and viscosity (b) as a function of temperature. Panels (c) and (d) show the VTF plots of the**  
 2 **same quantities, respectively. Data points (symbols), VTF fit (dashed lines). Walden plot (e) and Rii-corrected Walden**  
 3 **plot (f). Reference lines for 100% dissociation (black) and 10% dissociation (grey). TEAMS (cyan squares), TEATFA (orange**  
 4 **triangles), TEATfO (purple circles).**

5  
 6 **Table 3: VTF fitting derived parameters**

PIL	Conductivity		
	$\sigma_{\infty}$ [mS cm <sup>-1</sup> ]	$E_a^{\sigma}$ [10 <sup>-2</sup> eV]	$T_0^{\sigma}$ [K]
TEAMS	360±1	5.21±0.08	184±1
TEATFA	390±2	7.7±0.2	137±2
TEATfO	470±2	5.8±0.1	152±2
PIL	Viscosity		
	$\eta_{\infty}$ [mPa s]	$E_a^{\eta}$ [10 <sup>-2</sup> eV]	$T_0^{\eta}$ [K]
TEAMS	0.41±0.06	5.6±0.1	184.0±0.2
TEATFA	0.098±0.004	7.87±0.06	137.0±0.1
TEATfO	0.35±0.02	6.27±0.06	152.0±0.1

7

$$D_i = \frac{k_B T}{f \eta r_i} \quad (9)$$

$$\zeta = \frac{1}{r^+} + \frac{1}{r^-} \quad (10)$$

$$\Lambda \eta^{\alpha} = C \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \quad (11)$$

8 In Equation 9,  $D_i$  and  $r_i$  are the diffusion coefficient and the hydrodynamic radius of the  
 9 species  $i$ , respectively. The parameter  $f$  is a constant with a value of  $4\pi$  for entirely slip  
 10 boundaries and  $6\pi$  for perfectly stick boundaries. In Equations 10 and 11,  $r^+$  and  $r^-$  are the

1 hydrodynamic radii of the cation and the anion, respectively. By applying the  $\zeta$  correction  
2 factor, the result is a horizontal shift of the Walden plot points, usually leading to smaller  
3  $\Delta W'$  values[46] compared to the same quantity derived without accounting for ionic radii  
4 correction, as can be seen in Figure 2 and Table 4. The hydrodynamic radius of the ions was  
5 obtained as reported elsewhere[95]. The use of Ångstroms as units for the ion radii is  
6 completely arbitrary, but it should be noted that the same arbitrariness is found in the choice  
7 of centimeters for the molar conductivity and inverse Poise for the fluidity. The Walden plot  
8 is built as an empirical tool and, consequently, the most convenient units are adopted to  
9 return reliable and meaningful information.

10 By choosing the set of units [ $\text{S cm}^2 \text{ mol}^{-1}$ ] vs. [ $\text{P}^{-1} \text{ Å}^{-1}$ ], the  $I_W$  values obtained by Equation 7  
11 are in good agreement with the values obtained with diffusion coefficients and Nernst-  
12 Einstein equation (*vide infra*). The similarities between the systems make the overall relative  
13 order to stay the same for the uncorrected Walden plot. Some critical difference, though,  
14 can be appreciated. Most notably, TEATFA now lies just above the 10%  $I_W$  threshold line,  
15 obtaining the status of good-ionic liquid, with a Walden ionicity of 11.8% obtained by  
16 Equation 7. As it will be more explicit in the following, the correction is capable of returning  
17 more reliable information than the classic approach. The linear fitting of the experimental  
18 data in the Walden plot readily yields  $\alpha$  and  $\log C$  (Equations 6 and 11), which are the slope  
19 and the intercept of the fitted line, respectively. For the three studied PILs, the fitting  
20 parameters are shown in Table 4. The value for  $\alpha$  is the same, being the correction just a  
21 horizontal shift. On the other hand, the intercepts are markedly different for the bare ( $C$ )  
22 and corrected ( $C'$ ) plots.

23 Extrapolating the lines obtained by the fitting to  $\eta^{-1}=0$  (*i.e., infinite viscosity*) when both the axis in  
24 the Walden plot are expressed in linear scale, one obtains the conductivity at *infinite viscosity* ( $\Lambda_{\eta\infty}$   
25 in Table 4), which can be interpreted as resulting from the purely hopping ion movement, being any  
26 diffusion-driven conductivity wholly frozen. TEATFA shows the lowest  $\Lambda_{\eta\infty}$  values by a large margin,  
27 which is explained by the anion's geometry. It is meaningless to define a  $\Lambda'_{\eta\infty}$  including the radii-  
28 correction since the intercept at  $\eta^{-1}=0$  is unaffected by any multiplicative correction on the x-axis.

29 TFA anion can build, in its direct surroundings, a 2D network of hydrogen bonds since the two  
30 carboxylic oxygen atoms lie in the plane. On the other hand, the triflate and mesylate anions have  
31 an additional oxygen atom pointing out of the plane, resulting in a potentially 3D hydrogen-bonded  
32 network. Moreover, the negative charge delocalized on two oxygen atoms makes TFA the most  
33 prone to form firmly bound ion pairs. In this landscape, the potential energy barrier for the hopping  
34 is markedly lower for TEATfO and TEAMS. The observed difference between these two can also be  
35 explained in terms of the coordinating character of the ions. However, the geometry and the  
36 coordination character are not the only properties contributing to the different behaviors. The  
37 proton transfer of the PILs is likely to play a pivotal role in all these observations. The same approach  
38 applied to aprotic ionic liquids would remove the uncertainty on the composition, thus returning a  
39 more solid base for further discussion.

40  
41  
42

1 Table 4: Walden plots-derived parameters and other ionicity indicators. Both  $\Delta W$  and  $\Delta W'$  are the one calculated at 25°  
 2 C (the difference is minimal with other points)

	TEAMS	TEATFA	TEATfO
$\alpha$	0.884	0.975	0.932
$C$ [S cm <sup>2</sup> mol <sup>-1</sup> ]	0.372	0.085	0.499
$C'$ [S cm <sup>2</sup> mol <sup>-1</sup> ]	0.490	0.122	0.693
$\Lambda_{\eta \infty}$ [S cm <sup>2</sup> mol <sup>-1</sup> ]	0.074	0.013	0.107
$\Delta W$	0.426	1.078	0.24
$I_w$ [%]	37.5	8.4	57.5
$\Delta W'$	0.322	0.928	0.183
$I_{w'}$ [%]	47.6	11.8	65.6
$\Delta pK_a$	12.7	10.6	24.8
$\Delta G^0$ [kJ mol <sup>-1</sup> ]	-72.5	-60.5	-141.6
$\Delta PA$ [kJ mol <sup>-1</sup> ]	381.8	388.9	298.3

3

#### 4 Raman Spectroscopy

5 Qualitative insight into the nature of the interactions in bulk PILs is provided by Raman  
 6 spectroscopy. The presence of specific functional groups in the compounds and the different  
 7 symmetry of the precursor Brønsted acid and its anionic conjugated base could shed light on  
 8 the composition of the three PILs. In order to have a reliable set of references, the spectra  
 9 of the pure precursors, the 1M aqueous solutions of each acid potassium salt, and  
 10 triethylammonium chloride were also collected. In this way, it is possible to obtain the  
 11 experimental spectra of the single ions since the monoatomic counter-ions K<sup>+</sup> and Cl<sup>-</sup> have  
 12 no vibrational contribution. The solutions were diluted enough to avoid strong coupling  
 13 between the ions. The collected data are plotted in Figure 3.

14 The band assignment, performed with the aid of DFT calculations, is reported in Supporting  
 15 Information along with the calculated spectra (Figure S4). The spectra of all PILs are very  
 16 well reproduced by the superposition of those from the cation and the anion, as can be  
 17 expected for fully formed ionic liquids. However, some characteristic bands are identified  
 18 (see Table 5), which could differentiate between ions and precursors. It is interesting to note  
 19 that the point group of symmetry changes only for the pairs HMS/MS<sup>-</sup> and HTfO/TfO<sup>-</sup> passing  
 20 from C<sub>s</sub> to the more symmetric C<sub>3v</sub>. The HTFA/TFA<sup>-</sup> pair is always in the C<sub>s</sub> group, while  
 21 TEA/HTEA<sup>+</sup> is in C<sub>3</sub>, regardless of the protonation. These small molecular symmetry changes  
 22 generate little-to-none modifications of the selection rules for the system's active normal  
 23 vibration modes. Nevertheless, for all the anions, a band emerging from the deprotonation  
 24 is easily tracked to witness the IL formation. The proton transfer activates the anti-symmetric  
 25 stretching modes of the carboxylic (~1435 cm<sup>-1</sup>) and sulfonic (~1040 cm<sup>-1</sup>) functional groups.  
 26 Unfortunately, there is no signal coming unambiguously from the Brønsted precursors,  
 27 which would have allowed a quantitative determination of the ILs' proton transfer.

28 Nonetheless, PILs are formed to some extent because of the anions' anti-symmetric stretching peak  
 29 presence in the spectra of the samples. A closer look at the TEA/HTEA<sup>+</sup>  $\delta_{hch}$  mode peak (Figure S5),  
 30 though, hints again to the not complete formation of TEAMS and TEATFA. This feature appears to  
 31 be distinctly asymmetric for these two compounds, clearly showing a shoulder at lower

1 wavenumbers. Comparing the PIL spectra with those of pure triethylamine and the 1M solution of  
2 triethylammonium chloride (Figure S5), it can be concluded that there is a non-negligible amount of  
3 the precursor Brønsted base (and, consequently, the acid) which has not reacted and remained in  
4 the system. These results correlate well with those from Infrared and NMR spectroscopies (*vide*  
5 *infra*). Focusing on TEATFA, the  $\nu_{CC}$  band between  $770\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  is diagnostic of the  
6 formation of the anion for acetate-based systems, as shown by Umebayashi *et al.*[22,24]  
7 Specifically, in the case of dissociation, the signal is substantially red-shifted if compared to the pure  
8 acid one. Figure S6 reports the specific Raman region for the TEATFA system. As reported earlier[22],  
9 the fingerprint of unreacted acid is clearly observed in the spectra.

10 Albeit the signal in TEATFA is red-shifted compared to HTFA, it is at lower frequencies if  
11 compared with the KTFA 1M solution.

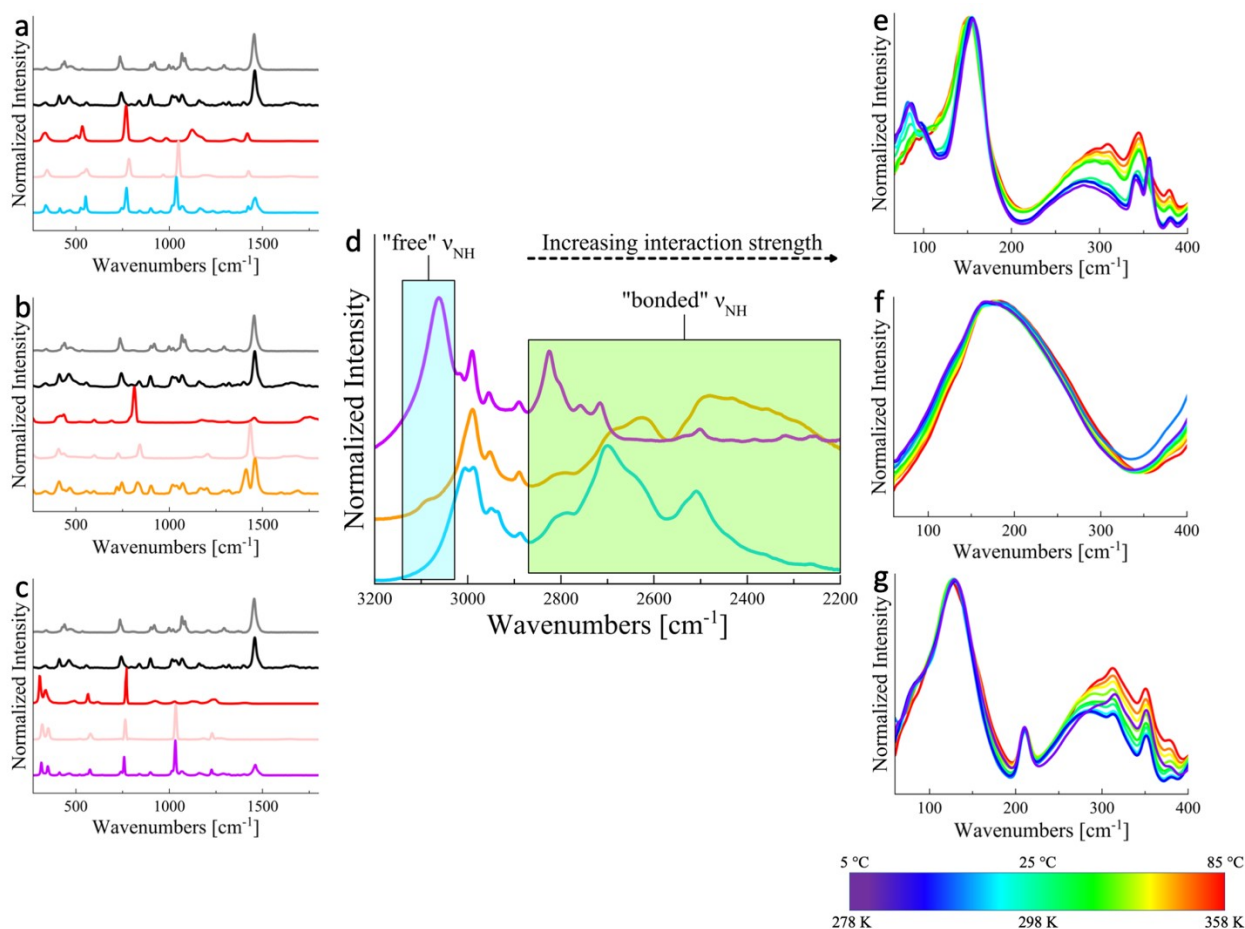
12 In order to exclude the possible influence of different solvation shells and dielectric  
13 constants, a system composed of TEATFA 67%<sub>vol</sub> and HTFA 33%<sub>vol</sub> was prepared, and its  
14 Raman spectrum was collected. The comparison shows that the broad, asymmetric signal at  
15  $\sim 830\text{ cm}^{-1}$  in TEATFA is due to unreacted acid rather than the anion. The pronounced blue-  
16 shift compared to pure HTFA can be explained in terms of different dielectric constants and  
17 solvation shells.

## 18 Far Infrared Spectroscopy

19 The Far Infrared (FIR) region of the vibrational spectra carries essential information regarding  
20 the hydrogen bond features. In particular, the band between  $100$  and  $200\text{ cm}^{-1}$  is  
21 characteristic of the inter-species hydrogen bond stretching in PILs, as widely reported in the  
22 literature[27,52,96–100]. TEAMS and TEATfO have already been studied by Ludwig *et al.*[53]  
23 using FIR along with TEATFSI, including different deuteration degrees. These authors  
24 correlated the interionic peak position with the hydrogen bond binding energy, but they also  
25 state, "However, this relation was obtained by assuming that the full masses of anions and  
26 cations are involved in the vibrational motion. If that is not the case, deviations from the  
27 given relation can be expected", thus assuming that the PILs are completely formed, and the  
28 band originates solely by the interaction between the ions. The evidence herein reported  
29 are, however, point to a different direction, *i.e.*, a more complex system where different  
30 hydrogen-bonding species coexist and potentially contribute to the observed FIR band. DFT  
31 calculations show, indeed, that dimers of all three acids have active normal modes of  
32 vibration in that region, arising from the anti-symmetric HB stretching (see Figure S7). Figure  
33 3 reports the FIR spectra of TEAMS, TEATFA, and TEATfO collected as a function of  
34 temperature.

35 Albeit the signal in TEATFA is red-shifted compared to HTFA, it is at lower frequencies if  
36 compared with the KTFA 1M solution. In order to exclude the possible influence of different  
37 solvation shells and dielectric constants, a system composed of TEATFA 67%<sub>vol</sub> and HTFA  
38 33%<sub>vol</sub> was prepared, and its Raman spectrum was collected. The comparison shows that the  
39 broad, asymmetric signal at  $\sim 830\text{ cm}^{-1}$  in TEATFA is due to unreacted acid rather than the  
40 anion.





1 **Figure 3: (a-c) Raman spectra at 25 °C of (a) TEAMS (cyan), TEATFA (orange), TEATfO (purple). In panels a-c (from top)**  
 2 **pure triethylamine (grey), 1M aqueous triethylammonium chloride (black), pure corresponding acid (red), 1M aqueous**  
 3 **potassium salt of the corresponding acid (pink). (d) X-H stretching region of Mid Infrared spectra at 25 °C. The boxes**  
 4 **highlight specific stretching modes. From top TEATfO (purple), TEATFA (orange), TEAMS (cyan). (e-f) Far Infrared spectra**  
 5 **as a function of temperature. (e) TEAMS, (f) TEATFA, (g) TEATfO. The temperature is indicated by the color bar.**

6  
 7 **Table 5: Normal modes selected as a probe for ionic liquid formation.**

TEA/HTEA <sup>+</sup>		HMS/MS <sup>-</sup>		HTFA/TFA <sup>-</sup>		HTfO/TfO <sup>-</sup>	
cm <sup>-1</sup>	mode	cm <sup>-1</sup>	mode	cm <sup>-1</sup>	mode	cm <sup>-1</sup>	mode
1455	$\delta_{\text{hch}}$	1050	$\nu^{\text{as}}_{\text{so}}$	1435	$\nu^{\text{as}}_{\text{co}}$	1035	$\nu^{\text{as}}_{\text{so}}$
--	--	--	--	830	$\nu_{\text{cc}}$	--	--

8  
 9 As reported above, a shift towards lower frequencies for increasing temperature is observed  
 10 for TEAMS and TEATfO. The explanation given in the literature accounts for the weakening  
 11 of the hydrogen bond as the temperature is increased. On the other hand, TEATFA shows  
 12 the opposite behavior, *i.e.*, its broad band shifts toward higher frequencies upon heating.  
 13 This counter-intuitive trend could find an explanation considering once more the not  
 14 complete formation of this PIL. The trifluoroacetic acid is the weakest among the three  
 15 tested herein. <sup>1</sup>H-NMR spectroscopy investigation of TEATFA (*vide infra*) clearly shows a peak

1 at ~11 ppm, which is more compatible with an acidic proton rather than an ammonium one.  
2 It is reasonable to consider that a non-negligible amount of the acid is still in the system on  
3 these bases. The heating of the IL below its decomposition temperature results in shifting  
4 the equilibrium towards the formation of TEATFA. These results are seemingly in  
5 disagreement with the literature [60,101], where an increased concentration of neutral  
6 species is found in the gas phase upon heating of the ILs. It must be noticed, though, that  
7 gas and liquid phases are intimately different. As a matter of fact, though, in the gas phase  
8 a charged species is vastly less stable than in the liquid phase, being the density of oppositely  
9 charged species (necessary to stabilize the ion) lower. Since the HB interactions in the PIL  
10 are stronger than the one between neutral species, the increased number of ions in the  
11 system explains the counter-intuitive blue-shift of the FIR band of this particular PIL upon  
12 heating. This interpretation would also explain the broadness of the FIR signal for this PIL,  
13 which results in the convolution of several different contributions, all active in a narrow  
14 spectral window. It is also worth noting that for TEAMS and TEATfO, it is possible to recognize  
15 the solid-to-liquid phase transition. Both PILs have a peak at  $<100\text{ cm}^{-1}$  (for TEATfO it is only  
16 a shoulder) at low temperatures, which gradually vanishes upon heating. For TEAMS, also  
17 the peak at  $\sim 360\text{ cm}^{-1}$ , which is visible at lower temperatures, abruptly vanishes as the  
18 system liquefies. These normal modes appear to be IR-active only in the solid-state, which  
19 can be explained with a specific symmetry breaking. We are currently working to determine  
20 the crystal structure of these compounds to clarify this and other observations. Others have  
21 suggested[102] that the hydrogen-bond characteristic signal in PILs may be deconvoluted  
22 into ion-ion mode and precursor-precursor mode. While it is conceptually a valid point,  
23 caution is advised in applying such a simplistic approach. The presence of precursors in non-  
24 negligible amounts would induce a plethora of different hydrogen-bonded pairs. Cation-  
25 anion and acid-base interactions are positively contributing, but one must also consider the  
26 effect of cation-base, cation-acid, anion-acid, and acid-acid even in the simplest case of a  
27 single hydrogen-donor and a single hydrogen-acceptor. Not to mention possible collective  
28 motions and (hindered) rotational modes that could impact this very low-frequency region  
29 of the spectrum.

### 30 **Infrared spectroscopy**

31 We employed infrared spectroscopy to check for the formation of the ammonium functional  
32 group because, in the specific case of triethylammonium cation, the N-H stretching ( $\nu_{NH}$ )  
33 appears to be Raman-inactive[103] in our experiments (Figure S8). In the region around  $3000\text{ cm}^{-1}$ ,  
34 a plethora of active X-H stretching modes are active in the examined systems, but a  
35 general trend is pointing towards a poorly-formed and highly-associated ionic liquid in the  
36 case of TEATFA is emerging. In particular, the  $\nu_{CH_2}$  signal is the highest frequency normal  
37 mode found in pure triethylamine ( $\sim 2975\text{ cm}^{-1}$ ), according to the NIST database[104]. In the  
38 three PILs, the corresponding peak is clearly observed at  $\sim 2988\text{ cm}^{-1}$ ,  $\sim 2990\text{ cm}^{-1}$ , and  $\sim 2990\text{ cm}^{-1}$   
39 for TEAMS, TEATFA, and TEATfO, respectively. Interestingly, an evident band splitting is  
40 found for this vibrational mode for all three samples. The analysis of this feature is beyond  
41 the scope of the present work, but a tentative interpretation is the presence of different

1 triethylammonium conformers in the system. The proton transfer on the nitrogen, though,  
2 generates another additional signal at higher frequencies for TEATfO and, to a much minor  
3 extent, TEATFA. This peak is attributed to poorly-interacting (or "free")  $\nu_{\text{NH}}$ [80], whereas the  
4 complex superposition of signals in the 2200-2850  $\text{cm}^{-1}$  region is also assigned to  $\nu_{\text{NH}}$ , but  
5 with the proton interacting with the surroundings[80]. A strong endorsement for this  
6 assignment comes from the complete absence of signals in both regions in the Raman  
7 spectra. It is known that secondary amines[103] (and, by extension, tertiary ammonium ions)  
8 show no  $\nu_{\text{NH}}$  signals, having the N-H stretching only a very small Raman cross-section due to  
9 the low change in the polarizability ellipsoid during the vibration. The strength of the  
10 interaction is inversely proportional to the wavenumber of the vibrational mode. TEATfO  
11 shows a clear, well-defined, and intense peak at  $\sim 3062 \text{ cm}^{-1}$ , and TEATFA has a low but  
12 recognizable bump at  $\sim 3088 \text{ cm}^{-1}$ . TEAMS seems not to display the "free"  $\nu_{\text{NH}}$  peak,  
13 consistently with our other observations, which point towards strong ion-pairing in this  
14 protic ionic liquid. Considering TEATfO, it is safe to say that the ionic liquid is extensively  
15 formed and that most of it is not engaged in ion-pairing, as expected for the low-coordinating  
16 triflate anion. Conversely, TEAMS appears to be also markedly formed, with most ions  
17 hydrogen-bonded. TEATFA shows a minimum contribution for the "free"  $\nu_{\text{NH}}$ , while a rich  
18 population of vibrational modes is found in the "bonded"  $\nu_{\text{NH}}$  region. It is worth noting that  
19 N-H stretching modes usually have a high IR intensity, more pronounced than C-H modes.  
20 The fact that in TEATFA the  $\nu_{\text{NH}}$  broad signals only barely overcome the  $\nu_{\text{CH}_2}$  points toward a  
21 small ammonium population. These observations advise caution when dealing with protic  
22 ionic liquids in assuming a priori a quantitative proton transfer.

### 23 NMR spectroscopy

24 Albeit NMR spectra could not unambiguously deduce quantitative information on the degree  
25 of PILs' formation, some meaningful conclusions could be drawn. The collected  $^1\text{H}$ ,  $^{13}\text{C}$ , and  
26  $^{19}\text{F}$  NMR spectra are depicted in Figure 4.

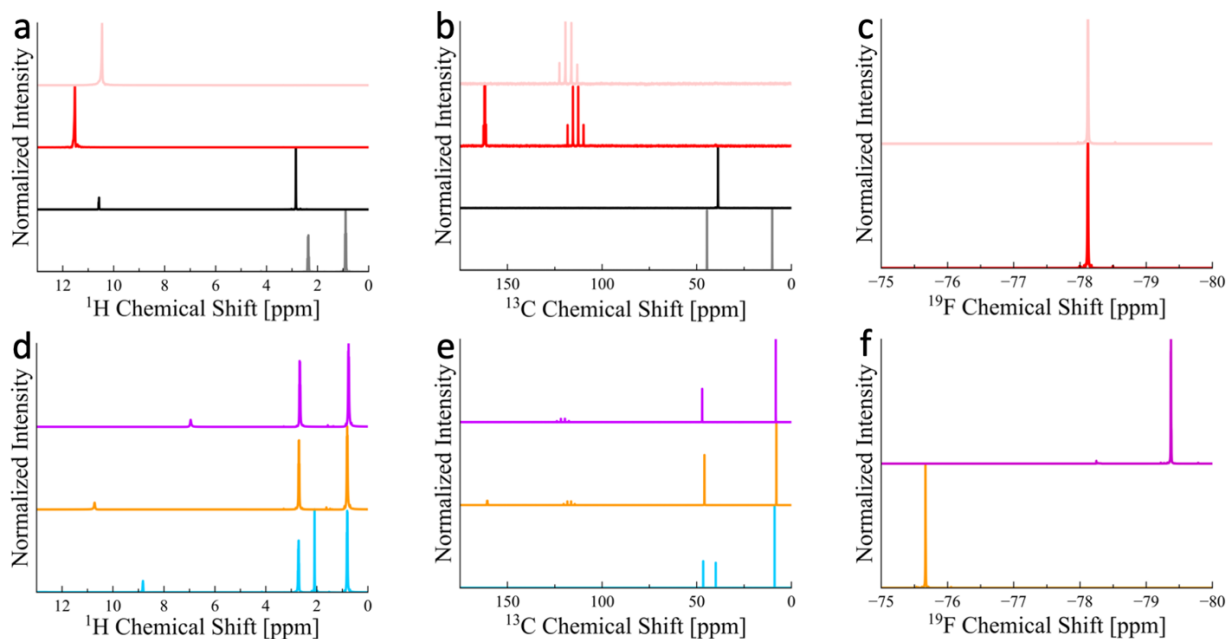
27 Along with the spectra of the prepared PILs, the respective Brønsted precursors were also  
28 investigated to identify differences induced by the proton transfer. Interestingly,  
29 Davidowsky *et al.* [55] analyzed diethyl-methylamine-based PILs correlating the proton  
30 affinity of the acid with the chemical shift of the acidic proton: indeed, the higher the former,  
31 the higher the latter.  $PA$  was preferred to  $pK_a$  since the latter is meaningful only in diluted  
32 environments. The  $^1\text{H}$  NMR spectra reported here show a similar trend: the downfield  
33 shifted values here reported agree with the shielding effect of TEA. **On this basis, we found  
34 an experimental confirmation of the actual proton transfer (*i.e.*, the formation of PILs),  
35 which, unfortunately, does not give us any quantitative hint on the extent of proton transfer.**

36 The acid-to-base proton transfer also influences the chemical shift of  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups  
37 of the formed ammonium cation ( $\text{HTEA}^+$ ) compared to pure TEA. Indeed, a shift at higher  
38 ppm values is evidenced for the  $-\text{CH}_2-$  group, whereas the resonance frequency of the  $-\text{CH}_3$   
39 group is only slightly influenced by the proton transfer, as it could be expected considering  
40 the distance of the terminal methyl groups from the localized net positive charge on the  
41 nitrogen atom. For the methylene group, the chemical shift follows the order TEATFA >

1 TEAMS > TEATfO, according to a previous report[55]. This trend seems to be counter-  
2 intuitive, being the smallest shift brought about by the strongest acid. However, one should  
3 consider that in a neat PIL, the cation is not isolated but rather surrounded (if not closely  
4 paired) by anions, leading to a further modification of the resonance frequency experienced  
5 by the methylene protons. The observed trend is in agreement with the anion coordination  
6 power. The signal related to the methyl group of the anion in TEAMS slightly shifts towards  
7 lower ppm values than pure HMS due to the acid "deprotonation". Regarding  $^{13}\text{C}$  spectra,  
8 the effect of proton transfer is reflected in the de-shielding of methylene carbon (in  $\alpha$   
9 position to the protonation site), following the order TEATfO > TEAMS > TEATFA. The analysis  
10 of  $^{19}\text{F}$  is more puzzling, being the chemical shift is predominantly influenced by the  
11 paramagnetic shielding rather than the diamagnetic one[105] in this case. Very  
12 unexpectedly, the fluorine atom of both HTFA and HTfO resonates at an almost identical  
13 frequency. A tentative explanation considers the sum of two factors: on the one hand, the  
14 sulfonate group has a higher electron-withdrawing character; on the other, the HTFA<sup>+</sup> forms  
15 more persistent dimers implying a larger fraction of the negative charge delocalized on the  
16 fluorine atoms. Once the PIL is formed, the  $^{19}\text{F}$  signal of TEATfO shifts towards more negative  
17 chemical shifts, whereas for the TEATFA the opposite behavior is observed.

18 As stated above, focusing on the mere chemical shift could be misleading; yet, some  
19 interesting information could be extracted by comparing the PILs and the diluted aqueous  
20 solutions of the corresponding acids (see Figure S9). It should be kept in mind that the acids  
21 are entirely deprotonated if their molar fraction in water is lower than 0.4[106] (*i.e.*, 100  
22 times more concentrated than our aqueous solution). Consequently, the obtained spectra  
23 are representative of the anions and not the corresponding acids.  $^{19}\text{F}$  spectrum of TEATfO is  
24 almost entirely superimposed to that of TfO<sup>-</sup>, whereas the spectrum of TEATFA appears  
25 0.8ppm down-shifted compared to TFA<sup>-</sup>. This inconsistency can be tentatively ascribed to  
26 two different factors: (i) an incomplete formation of the PIL, being the  $^{19}\text{F}$  signal a mediated  
27 value between pure TEATFA and HTFA<sup>+</sup>; (ii) the instauration of intermolecular interactions  
28 directly involving F atoms.

29 A verdict on this point (and more generally on NMR analyses) is far beyond the purpose of  
30 the present work, but it will be discussed in the second part of this manuscript, where we  
31 consider NMR to prove the formation of the PILs experimentally.



1 **Figure 4: NMR spectra collected injecting the sample and the deuterated solvent in two separate concentric**  
 2 **tubes at 25 °C. The panels a-c refer to the Brønsted precursors, panels d-f refer to the ionic liquids. <sup>1</sup>H-NMR (a,**  
 3 **d), <sup>13</sup>C-NMR (b, e), <sup>19</sup>F-NMR (c, f). From top triflic acid (pink), trifluoroacetic acid (red), mesylic acid (black),**  
 4 **triethylamine (grey) (a-c); from top TEATfO (purple), TEATFA (orange), TEAMS (cyan) (d-f).**  
 5

## 6 Ionicity vs. Reduced Ionicity

7 PGSE-NMR (Pulsed-Gradient Spin-Echo NMR) is the technique of choice when the  
 8 investigated systems contain NMR-active nuclei. In our case, both the anion and cation of  
 9 TEAMS are easily probed via <sup>1</sup>H-NMR. On the other hand, TEATfO and TEATFA are studied by  
 10 means of <sup>1</sup>H-NMR (cation) and <sup>19</sup>F-NMR (anion). The selected peak decay is fitted with the  
 11 function of Wu *et al.*[67] reported in Equation 12:

$$\ln(I_g) = \ln(I_0) - (\gamma\delta g)^2 D \left( \Delta - \frac{\delta}{3} \right) \quad (12)$$

12 where  $I_g$  is the signal intensity when a field with gradient  $g$  is applied,  $I_0$  is the signal intensity  
 13 for  $g=0$ ,  $\gamma$  is the gyromagnetic constant,  $\Delta$  is the diffusion delay time,  $\delta$  is the duration of the  
 14 gradient pulse, and  $D$  is the desired self-diffusion coefficient.

15 The gradient is calibrated using a pure D<sub>2</sub>O sample, where the diffusivity of HDO in D<sub>2</sub>O is  
 16 calibrated to  $1.9 \cdot 10^5 \text{ cm}^2\text{s}^{-1}$  at 298 K. The diffusion coefficient of the cations and unreacted  
 17 TEA, if present, are measured on both methyl (-CH<sub>3</sub>) and methylene (-CH<sub>2</sub>) peaks. These give  
 18 roughly the same  $D$  value, and the values reported in Table 6 are averages of the two peaks.  
 19 Concerning TEAMS, the  $D$  of the cation (and/or HMS) is measured on the methyl peak.  
 20 Regarding TEATfO and TEATFA, being both the anions proton-free, the  $D$  values are  
 21 measured for the fluorine peak by means of 2D <sup>19</sup>F NMR. The determined self-diffusion  
 22 coefficients as a function of temperature are listed in Table 6 (separated in anion and cation)  
 23 and displayed in Figure 5 (summed).

1 The Stokes-Einstein relationship (SER, Equation 9) is widely employed to relate viscosity and  
 2 diffusion coefficients. It has some severe limitations, though, which prevent its application  
 3 in pure ionic liquids.

4 In particular, for SER to be valid (i) the investigated system must be a solution (*i.e.*, the  
 5 solvent in significant excess of the solute), (ii) the radius of the solute must be substantially  
 6 larger than the radius of the solvent, and (iii) the system must be dynamically homogeneous.  
 7 On these bases, and considering the structural heterogeneity of many  
 8 ILs[2,11,112,113,18,30,99,107–111], it is already clear that pure ionic liquids fail to meet all  
 9 requirements.

10

11 Table 6: PGSE-NMR determined self-diffusion coefficients for the anions and cations as a function of  
 12 temperature

t [K]	TEAMS [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]		TEATFA [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]		TEATfO [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]	
	Cation	Anion	Cation	Anion	Cation	Anion
<b>298</b>	1.11 ±0.01	1.47 ±0.02	2.47 ±0.03	1.63 ±0.02	2.00 ±0.02	1.17 ±0.01
<b>303</b>	1.26 ±0.02	1.59 ±0.06	2.57 ±0.05	2.08 ±0.05	2.14 ±0.02	1.41 ±0.06
<b>308</b>	1.42 ±0.03	1.82 ±0.05	2.99 ±0.06	2.5 ±0.2	2.35 ±0.03	1.8 ±0.1
<b>313</b>	1.68 ±0.04	1.94 ±0.07	3.30 ±0.06	2.8 ±0.4	2.64 ±0.04	2.1 ±0.1
<b>318</b>	1.99 ±0.05	2.26 ±0.09	3.40 ±0.09	3.2 ±0.4	2.71 ±0.05	2.4 ±0.2
<b>323</b>	2.43 ±0.07	2.63 ±0.07	3.70 ±0.09	3.7 ±0.3	2.95 ±0.06	2.7 ±0.2
<b>328</b>	2.70 ±0.08	2.9 ±0.1	3.96 ±0.09	4.1 ±0.4	3.22 ±0.08	3.0 ±0.3
<b>333</b>	2.8 ±0.1	3.0 ±0.1	4.1 ±0.1	4.4 ±0.4	3.49 ±0.08	3.3 ±0.3

13

14 Moreover, in the specific case of protic ionic liquids, one must also consider their different  
 15 proton transfer, which also depends on the temperature. Therefore, an implicit boundary  
 16 condition to the SER exists, *i.e.*, (iv) the ionic strength of the system must be constant with  
 17 temperature. This condition is essential because a change in the PIL proton transfer would  
 18 affect the radius of the moving species and enhance the dynamic heterogeneity by adding  
 19 Coulombic interactions only in some areas of the system. The significant deviation of the  
 20 investigated PILs from SER can be seen in Figure S10. Several corrections for SER have been  
 21 proposed over the years, almost exclusively looking at different ways to define the  
 22 hydrodynamic radius of the charged species[114]. As an example, Cheng-Li[115] correction  
 23 (CLC) was explicitly developed for self-diffusion coefficients to overcome the (i) and (ii)  
 24 limitations of SER. It considers the hydrodynamic radius to be:

$$r_i = \sqrt[3]{\frac{V_m}{N_A}} \quad (13)$$

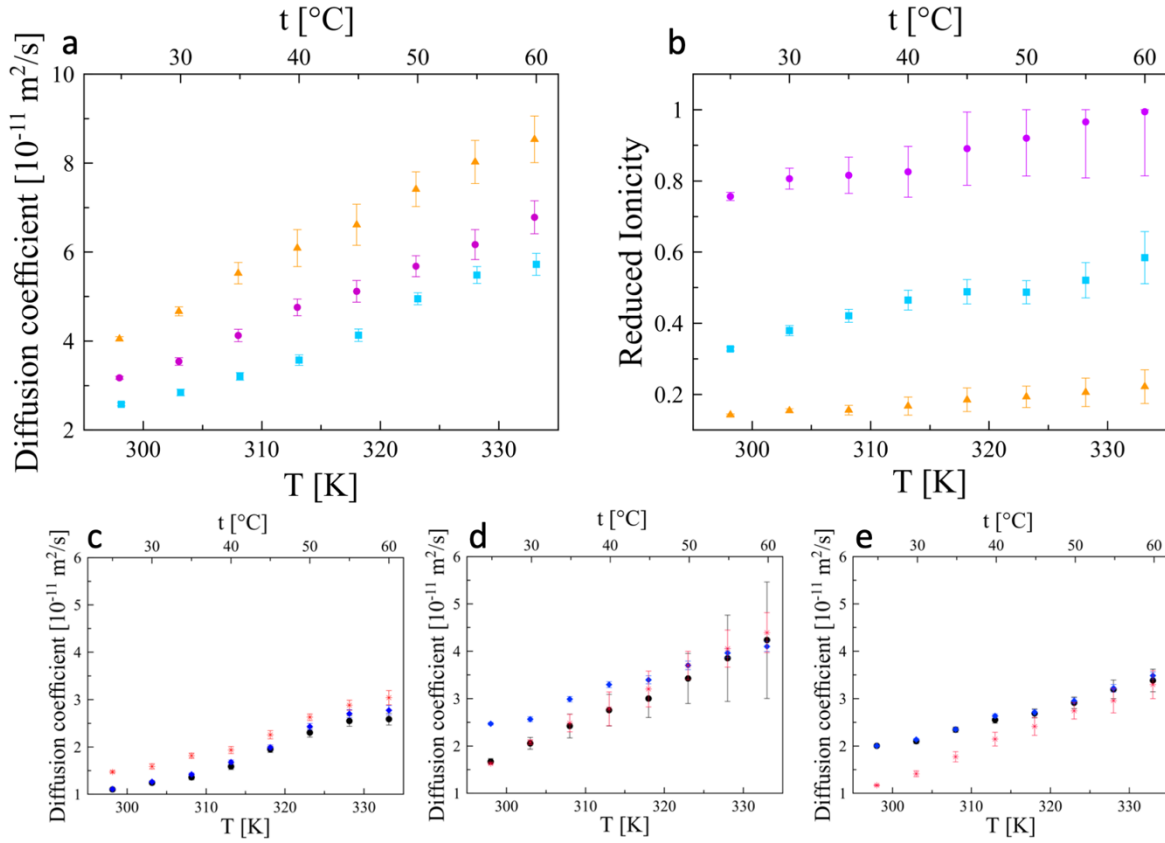
1 where  $V_m$  is the molar volume and  $N_A$  the Avogadro's number. While CLC returns good results  
 2 for molecular liquids (usually within an error of 12%), it does not apply to ionic liquids  
 3 because the molar volume depends on the specific configuration of the ion-pair, thus, in  
 4 principle, being different for each one. Köddermann *et al.*[116] The leading cause for ILs  
 5 deviations from SER is pointed at the dynamic heterogeneity, observing that if the IL is  
 6 heavily diluted in a molecular liquid, the resulting system obeys SER. This finding is, though,  
 7 expected because the system they obtained by dilution approached the requirements for  
 8 SER to hold: (i) the new obtained system is a solution, (ii) the solvent used in their work was  
 9 chloroform, which is markedly smaller than the IL investigated (namely, 1-ethyl-3-methyl-  
 10 imidazolium bis (trifluoromethanesulphonyl) imide), (iii) the system is so diluted that any  
 11 heterogeneity is averaged out. Their use of an aprotic ionic liquid also addressed the implicit  
 12 fourth requirement on the proton transfer of the IL.  
 13 As a different approach, we introduce an empirically derived temperature-dependent  
 14 correction factor ( $\beta$ ) obtained using the PGSE-NMR derived diffusion coefficients in SER.

$$\beta = \frac{k_B T}{6\pi \eta r_i D_{\text{NMR}}} \quad (14)$$

15 The correction factor  $\beta$  accounts for two physical phenomena of crucial importance in PILs:  
 16 (i) the hydrodynamic radius of the diffusing species might significantly differ from those of  
 17 the cations and anions themselves because of the possible aggregation driven by both  
 18 Coulombic and aliphatic forces, and (ii) the partial formation of the ionic liquid generates  
 19 regions with **locally different microscopic viscosity**, with low-viscosity domains where the  
 20 Brønsted precursors are in excess existing along with high-viscosity parts where the IL is  
 21 more concentrated.  $\beta$  values are shown in Table 7. As it appears clear from Equation 14, a  
 22 system ideally follows SER for  $\beta = 1$ . If  $\beta < 1$ , the species in the system show a diffusion  
 23 coefficient, which is larger than the one predicted by SER based on the macroscopic viscosity  
 24 and the single-ion hydrodynamic radius. The opposite is true for  $\beta > 1$ .  
 25 The effect of the correction parameter is then to adjust the quantity  $\eta r_i$  to obtain effective  
 26 viscosity and hydrodynamic radius. It is not possible to separate the two contributions  
 27 because neither  $r_i$  nor the local viscosity are experimentally accessible. The obtained values  
 28 show a marked dependence on the temperature, pointing towards the importance of the  
 29 implicit requirement (iv). Moreover, especially for TEATFA, the higher the temperature, the  
 30 larger than 1 is  $\beta$ , which rules out the hypothesis that changes in the effective  $r_i$  govern the  
 31 deviation. In such a case, in fact,  $\beta$  should progressively become smaller (even smaller than  
 32 one) upon increasing the temperature because clusters are expected to be destroyed at  
 33 higher temperatures. Additionally, also the dynamic heterogeneity should be diminished by  
 34 heating the system, but only if the sample composition remains constant at every  
 35 temperature.

36





1 **Figure 5: (a) PGSE-NMR derived diffusion coefficients. The values are the sum of the anion and cation diffusion**  
 2 **coefficients at the given temperature. TEAMS (cyan squares), TEATFA (orange triangles), TEATfO (purple circles).**  
 3 **(b) Reduced Ionicity derived from the ratio  $\Lambda/\Lambda_{NE}$ . TEAMS (cyan squares), TEATFA (orange triangles), TEATfO**  
 4 **(purple circles). (c-e) Comparison between the diffusion coefficients of the acidic proton (black circles), anions**  
 5 **(red stars), and cations (blue diamonds). TEAMS (c), TEATFA (d), TEATfO (e).**

6

7 **Table 7: Temperature-dependent empirical correction factor for the Stokes-Einstein relationship**

	TEAMS		TEATFA		TEATfO	
<b>t [K]</b>	Cation	Anion	Cation	Anion	Cation	Anion
<b>298</b>	0.409	0.659	0.997	1.952	0.670	1.288
<b>303</b>	0.481	0.734	1.150	1.832	0.747	1.268
<b>308</b>	0.538	0.837	1.183	1.838	0.804	1.198
<b>313</b>	0.649	0.909	1.277	1.952	0.848	1.169
<b>318</b>	0.693	0.956	1.467	2.008	0.966	1.219
<b>323</b>	0.727	0.957	1.561	2.017	1.031	1.246
<b>328</b>	0.815	1.057	1.702	2.149	1.090	1.332
<b>333</b>	0.892	1.189	1.884	2.271	1.149	1.365

8

9 In our case, the proton transfer of the IL likely changes, generating more ions, which are  
 10 responsible for more substantial viscosity variations. By plugging the PGSE-NMR derived  
 11 diffusion coefficients in the Nernst-Einstein relationship (Equation 15), it is possible to



1 calculate the limiting molar conductivity, *i.e.*, the theoretical conductivity that a system  
2 would have if all the moving species were carrying a net electric charge.

$$\Lambda_{NE} = \frac{N_A e_0^2}{k_B T} \cdot (D^+ + D^-) \quad (15)$$

3 In Equation 15,  $\Lambda_{NE}$  is the theoretical molar conductivity.  $D^+$  and  $D^-$  are the diffusion  
4 coefficients of the cation and the anion, respectively. Following the definition of  $\Lambda_{NE}$ , the  
5 ratio  $\Lambda/\Lambda_{NE}$  is a measure of the ionicity of the system. It should be once more clarified that  
6 the term "ionicity" for protic ionic liquids is ambiguous. Indeed, for aprotic ionic liquids, the  
7 term is used to address the degree of dissociation, *i.e.*, is a measure of the ion-pairing  
8 (Equation 1). For PILs, the scenario is more complicated because the proton transfer also  
9 contributes to the "loss" of ion conductivity, resulting in a smaller  $\Lambda/\Lambda_{NE}$  ratio.

10 Based on all the experimental and theoretical evidence above, and to stop the dangerous  
11 confusion between ionicity and proton transfer/formation degree in protic ionic liquids, we  
12 propose the adoption of new terminology, introducing the concept of "Reduced Ionicity" ( $\iota$ )  
13 which is directly linked to both  $I$  and  $FD$ . It is possible to express  $\iota$  as a function of the  
14 concentration of all the species in the system, similarly to Equations 1 and 3:

$$\iota = \frac{[A^-] + [HB^+]}{[A^-] + [HB^+] + [A^-HB^+] + [HA] + [B]} \quad (16)$$

16  
17 By recognizing that  $[A^-]=[HB^+]$  and that  $[HA]=[B]$ , it is possible to combine Equations 1, 2, and  
18 16 to obtain a direct relationship between  $I$  and  $\iota$ :

$$\iota^{-1} = I^{-1} \cdot K_{PT}^{-1/2} \quad (17)$$

20  
21 It directly follows that, in general, for any ionic system regardless of its nature (*e.g.*, aprotic  
22 IL, protic IL, molten salt, aqueous solutions):

$$\frac{\Lambda}{\Lambda_{NE}} = \iota \quad (18)$$

23 contrary to what is usually reported in the literature, where the  $\Lambda/\Lambda_{NE}$  ratio is referred to as  
24 the ionicity of the system. Indeed, it should be clear that Equation 16 holds even if all the  
25 protonated species ( $HB^+$ ,  $A^-HB^+$ , and  $HA$ ) are exchanged with their aprotic counter-parts ( $B^+$ ,  
26  $A^-B^+$ ,  $A$ ). Equation 18 returns the ionicity only if the formation degree of the ionic species is  
27 1, *i.e.*,  $[HA]=[B]=0$ , or  $[A]=[B]=0$ , which is the same for aprotic ionic substances.  
28 Consequently, for PILs the term "ionicity" should not be used as it currently is because of the  
29 possible incomplete proton transfer (*i.e.*, formation degree), and the more general reduced  
30 ionicity should be used instead. By comparing Equations 1, 3, and 16 it is clear that  $FD$  is  
31 always higher than (or, at least, equal to) the reduced ionicity value, but the same is not true  
32 for ionicity. It is important noting the relationships in Equation 19.

33

$$\begin{cases} I \geq \iota \\ FD \geq \iota \end{cases} \quad (19)$$

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The latter expression highlights why we adopted the term “reduced ionicity”, and shows how  $\iota$  is a property fundamentally different from both  $I$  and  $FD$ . For example, in the case of a hypothetical PIL with  $FD \ll 1$  (e.g., TEAAc), it is quite possible that its ionicity (as defined in Equation 1) would be close to 1, because of the high dilution of the ions in the Brønsted precursors. On the other hand, some PILs with strongly coordinating ions (e.g., chloride) could have  $I \ll 1$  but  $FD$  (Equation 3) approaching 1. Both the systems in the examples would have  $\iota \ll 1$  (Equation 16), and a deeper insight on the system is needed to identify the reasons behind the observed value obtained by the  $\Lambda/\Lambda_{NE}$  ratio.

The results of this approach applied to the three PILs studied here are reported in Figure 5. For all the presented PILs, the reduced ionicity increases with the temperature, which is expected considering both the breaking of ion-pairs and the enhanced formation of ions themselves. As mentioned above, these values result from both paired ions and neutral molecules in the system, and a quantification of their relative weight is not possible only based on the obtained reduced ionicity values.

Nevertheless, it is worth pointing to a possible solution to this seemingly insuperable *impasse*. As shown above, MIR spectroscopy shows two distinct signals for “bonded” and “free”  $\nu_{NH}$ , thus offering a chance to obtain the ionicity of the system in line with its standard definition of non-paired ions in the system. In the three proposed examples, though, the “bonded”  $\nu_{NH}$  region is too complex to attempt a reliable quantification. We will give more insight into this direction in a forthcoming paper.

One final insight, and definitive proof of the incomplete formation of TEATFA, is granted by a closer look at the diffusion coefficient trends. PGSE-NMR enables obtaining the diffusion coefficients of whatever has a suitable NMR signal, meaning that any peak can be followed to determine the diffusion coefficient of the associated species. In Table 6, the coefficients for anions and cations are reported for all the PILs herein investigated. These values are compared in Figure 5, with the diffusion coefficient of the acidic proton, which always shows a clear peak in the  $^1H$ -NMR of all the examined PILs. From Figure 5, it appears clear that the acidic proton diffuses bound to the amine in TEAMS and TEATfO, suggesting that the amine is the proton carrier, *i.e.*, the acid is deprotonated. Such a piece of evidence supports the substantial proton transfer in these two PILs. On the other hand, in TEATFA the proton essentially diffused with the  $CF_3$  group, meaning that the acid is still mostly present in the system, confirming the incomplete proton transfer. At higher temperatures, the error bars for the acidic proton in TEATFA become too wide to give a robust interpretation of where the proton is. Such error bars could be seen as a hint to the increasing uncertainty on the proton position, which, at higher temperatures, can jump from the acid to the base more efficiently, increasing the IL proton transfer. All these pieces of evidence point at TEATFA being mainly composed of neutral species, TEATfO being a proper ionic liquid, and TEAMS being half-a-way between these two extremes. In this context, the reader is kindly invited to note how the superimposition of the ionicity concept with the one of proton transfer could

1 be safely done just for TEATfO, whereas other experiments are required to completely rule  
2 out the formation of tough ion-pairs in both TEATFA and TEAMS. However, it is interesting  
3 to note how the reduced ionicity values obtained in this rigorous way are in fair agreement  
4 with those extracted by the radii-corrected Walden plot, suggesting that tool as a reliable  
5 source of reduced ionicity values when PGSE-NMR cannot be used, even if with severe  
6 limitations[65].

## 7 **Conclusions**

8 To summarize, we reported the characterization of thermal, transport, and spectroscopic  
9 properties of three (plus one) triethylammonium-based protic ionic liquids with anions  
10 originated from acids of different strengths. This series was chosen as a proof of concept to  
11 discuss the intricate interplay between ionicity and proton transfer. The latter two concepts  
12 are too often confused with each other, and the effective degree of proton transfer is too  
13 easily overlooked, being considered quantitative. In this context, we aimed to investigate  
14 these PILs by means of different approaches to shed light on the ionicity/proton transfer  
15 interplay. We introduced the innovative concept of Reduced Ionicity for this scope and to  
16 end the ambiguity between ionicity and formation degree, accounting for both the  
17 phenomena. This quantity, and not the properly said ionicity, is what is obtained with the  
18  $\Lambda/\Lambda_{NE}$  ratio (Equation 18).

19 Using several complementary techniques, we have demonstrated how the proton transfer  
20 in PILs is not always quantitative. The thermal stability follows the acid strength, with TEATfO  
21 being the most stable. On the other hand, the relatively low stability of TEATFA is due to the  
22 possible decarboxylation of the acid, which results in rapid evaporation of the whole  
23 compound. All the spectroscopy techniques used hint at the incomplete formation of  
24 TEATFA, but none of them was adequate to quantify the proton transfer. Nevertheless, the  
25 overall picture given by NMR and vibrational spectroscopies returns the information that at  
26 least some ionic liquid is formed in all the cases (Raman), that the degree of formation  
27 follows the order TEATfO>TEAMS>TEATFA (NMR), and that raising the temperature below  
28 the decomposition point increases the number of ionic species (FIR). MIR returns some  
29 (unexpected) concrete direct evidence of (i) the poor proton transfer in TEATFA (displaying  
30 only faint signals for the characteristic  $\nu_{NH}$  vibrational modes), (ii) the sizeable proton transfer  
31 in TEATfO (intense peak of the characteristic  $\nu_{NH}$  vibrational modes) and (iii) the meaningful  
32 aggregation experimented by TEAMS ( $\nu_{NH}$  vibrational modes shifted toward lower  
33 wavenumbers). In order to obtain complementary evidence towards further enlightenment  
34 of proton transfer degree, the Walden plot remains a vital rule-of-thumb to classify these  
35 materials. However, the radii-based correction factor is confirmed to improve the reliability  
36 of Walden ionicity estimation vastly. In this regard, it should be noted how the Walden  
37 ionicity approximates the reduced ionicity and not the ionicity itself. The Walden ionicity  
38 calculated by the radius-corrected Walden Plot reasonably correlates with those measured  
39 by the more conventional and reliable approach based on comparing the experimental and  
40 Nernst-Einstein-derived conductivities. Overall, TEATfO can be considered a wholly-formed  
41 PIL (*i.e.*,  $\iota = I = FD = 1$  in the limit of relatively high temperatures). At the same time, a

1 qualitative consideration can be drawn concerning TEAMS and TEATFA, having reduced  
2 ionicity values close to 0.6 and 0.2, respectively, at room temperature. While the values of  
3 diffusion and viscosity for TEAMS are compatible with a low reduced ionicity solely  
4 determined by ion-pairing, as firmly supported by the MIR spectra, the same is unlikely for  
5 TEATFA, for which we propose a substantial influence of the incomplete proton transfer. This  
6 conclusion is strongly supported by all the spectroscopic techniques used, particularly with  
7 MIR and the 1:2<sub>vol</sub> acid:PIL Raman spectra, and by the fact that the acidic proton clearly  
8 diffuses with the trifluoroacetic species in the PGSE-NMR experiment. Very interestingly, the  
9 diffusion coefficients calculated from the NMR analyses do not obey the Stoke-Einstein  
10 relation nor any of the radii-correction terms proposed over time. Thus, we contextually  
11 proposed an empirical correction factor,  $\beta$ , which accounts for local viscosity fluctuations  
12 and hydrodynamic radii changes. It should be pointed out that, albeit a definitive  
13 determination of ionicity and proton transfer was achieved only for TEATfO, we are  
14 confident that, quoting Agatha Christie, (more than) *three coincidences are a proof*: TEAMS  
15 has an almost quantitative proton transfer, but its reduced ionicity is jeopardized by ion-  
16 pairs formation, while TEATFA experimented a very low proton transfer being also prone to  
17 associating in ion clusters. In general, an IL can be considered pure if it is composed of at  
18 least 99%<sub>w</sub> of ions [117]. In the presented cases, only TEATfO and possibly TEAMS satisfy this  
19 criterion, with TEATFA most probably being a mixture of PIL and Brønsted precursors.  
20 This work clearly shows that more (and different) approaches are required to shed light on  
21 the interplay between ionicity and proton transfer, a key topic in determining PILs' features,  
22 too often overlooked in the literature.

## 23 **Methods**

### 24 **Materials**

25 All materials were purchased at the highest degree of purity available and employed without  
26 further purification. Triethylamine  $\geq 99.8\%$  Merck, Triflic acid  $\geq 99.5\%$  T&J Chemicals, Mesylic  
27 acid  $\geq 99.5\%$  Merck, Trifluoroacetic acid 100% VWR Chemicals, Acetic acid  $\geq 99.99\%$  Sigma  
28 Aldrich.

### 29 **Synthesis of the Ionic Liquids**

30 The three PILs were prepared according to the following procedure. Triethylamine was  
31 poured into an ice-bath cooled, three-neck flask under dry nitrogen flow (1ml/min). A  
32 stoichiometric amount of the acid was then added dropwise under vigorous stirring over  
33 three hours. The flask was then removed from the cooling but left under stirring at room  
34 temperature over 12-16 hours. The final water content, determined by Karl-Fischer  
35 coulometric titration, was found in the range of 50-80 ppm for all three PILs.

### 36 **Characterization**

37 Thermogravimetric analysis (TGA) was performed using the TA Q5000 instrument. The  
38 sample was subject to a temperature ramp of 5 K/min under nitrogen flow.

1 Differential scanning calorimetry (DSC) measurements were performed using a TA Discovery  
2 DSC series with liquid N<sub>2</sub> cooling. First, the samples were heated up from room temperature  
3 to 350 K and then cooled down to 120 K. To allow full crystallization of the samples, *i.e.*, a  
4 more reproducible thermal behavior, sub-ambient annealing was performed by thermal  
5 cycling of the samples from 120 K to their cold crystallization temperature. Finally, the  
6 samples were cycled between 120 K and 373 K two times with a ramp of 5 K/min. For both  
7 TGA and DSC, the samples were filled in aluminum pans.

8 Density measurements were performed with an Anton Paar DMA 4500 M density meter.  
9 Dynamic viscosity was determined with an Anton Paar MCR 102 rheometer, using a cone-  
10 plate geometry with a shear rate of 10 s<sup>-1</sup>. Both the density meter and the rheometer are  
11 placed in a dry-room with a dew-point of 198 K.

12 The conductivity was determined in sealed glass conductivity cells (Materials Mates 192/K1)  
13 equipped with two platinum electrodes (cell constant of (1.0±0.1 cm)) using a thermostatic  
14 Bio-Logic conductivity meter.

15 Raman spectra were collected using the RAM II module of the Bruker Vertex 70v  
16 spectrometer, mounting Nd:YAG laser source (1064 nm) and a high sensitivity InGaAs  
17 detector. The samples were sealed in NMR tubes to prevent contamination. The signal was  
18 accumulated over 500 scans for each sample.

19 Far infrared absorption spectra were acquired using a Michelson interferometer (IFS66 V/S  
20 Bruker) working under low vacuum (2 mbar), equipped with a 6 μm thick mylar beam-splitter  
21 and DTGS detector. A Hg discharge lamp was used as a radiation source. A drop of the sample  
22 (30 μL) was incorporated between the Si windows of a commercial cell. The optical path  
23 length of the radiation was adjusted at 25 μm by a mylar spacer placed between windows.  
24 Reference spectra were collected without a spacer to avoid Fabry-Perot interference effects.  
25 In order to maximize the signal-to-noise ratio, 128 interferograms were accumulated, and  
26 their average was Fourier transformed using the Blackman-Harris apodization function  
27 (actual resolution 4 cm<sup>-1</sup>). The absorption spectra were calculated via the Lambert-Beer law  
28 and pre-processed using the OPUS software.

29 Infrared spectra were collected with a Bruker Vertex 70v using a KBr beam-splitter and a  
30 DLaTGS detector. The samples were collected in the Attenuated Total Reflection (ATR)  
31 configuration on diamond crystals. The sample chamber was kept under vacuum (2 mbar)  
32 during the measurements. To enhance the signal-to-noise ratio the spectra and the  
33 background were collected 256 times and averaged.

34 All NMR spectra (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F) were collected at 298 K with a 600 MHz JEOL ECZR  
35 spectrometer using a 5 mm Royal probe equipped with a z gradient coil producing a  
36 maximum gradient strength of 0.9 T m<sup>-1</sup>. All samples reached thermal equilibrium before  
37 measurement. NMR measurements were made in coaxial tubes. The inner tube contains a  
38 deuterated solvent (required for lock) whereas the outer tube was filled with the  
39 investigated samples, allowing for a good signal-to-noise ratio. The aqueous solution was  
40 directly prepared in the NMR tube by diluting the pure acids (or TEA) to 0.1 mol L<sup>-1</sup> in D<sub>2</sub>O.  
41 The chemical shifts were referenced by setting to zero the standard chemicals, *i.e.*, TMS for  
42 <sup>1</sup>H and <sup>13</sup>C, CCl<sub>3</sub> for <sup>19</sup>F.

1 Diffusion experiments on  $^1\text{H}$  were acquired with a sequence characterized by encoding pulse  
2 duration,  $\Delta$  of 4 ms, a diffusion time of 0.3 s, and 8 nominal gradient amplitudes,  $g$ , ranging  
3 from 80 to 800  $\text{mT m}^{-1}$  chosen to give equal steps in gradient squared. DOSY experiments  
4 were recorded in a range of temperatures within 298 K and 333 K with an interval of 5 K, and  
5 all samples had reached equilibrium before measurement. Before performing DOSY  
6 measurement, for each temperature, the 90-degree pulse has been measured.  
7 Diffusion experiments on  $^{19}\text{F}$  were acquired with a sequence characterized by encoding pulse  
8 duration  $\Delta$  of 5 ms, a diffusion time of 0.1 s, and 8 nominal gradient amplitudes,  $g$ , ranging  
9 from 80 to 800  $\text{mT m}^{-1}$  chosen to give equal steps in gradient squared. DOSY experiments  
10 were recorded in a range of temperatures within 298 K and 333 K with an interval of 5 K, and  
11 all samples had reached temperature equilibrium before measurement. Before performing  
12 DOSY measurement, for each temperature, the 90-degree pulse has been measured.

### 13 **Computational details**

14 All computations were carried out using the Gaussian 09 program package[118] at B3LYP/6-  
15 311++G\*\* level of theory. Starting geometries were built with Avogadro[119]. The geometry  
16 optimization was carried out before computing the intensities of vibrational frequencies. The  
17 calculated frequencies were assigned with the help of the VEDA software[120]. No imaginary  
18 frequencies were observed for any system, indicating the reaching of a real minimum of the  
19 potential energy surface. To account for biases arising from vibrational anharmonicity and  
20 rough treatment of electron correlation, a scale factor of 0.98 was employed to facilitate the  
21 comparison with experimental data[100]. The energetics of the acid deprotonation was  
22 studied through single-point energy at the same level of theory.

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#### 27 **Author Contributions**

28 All authors have given approval to the final version of the manuscript. AM and MB  
29 contributed to the same extent to the manuscript by conceptualization, interpretation of the  
30 results, and writing the manuscript. XG synthesized the PILs and collected DSC, TGA,  
31 conductivity, and viscosity data. AN supervised the FIR experiments. BC and NB performed  
32  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements. RB and AB supervised the NMR experiments and  
33 performed  $^{19}\text{F}$  and PGSE NMR measurements. LG and SP edited the drafts and supervised  
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## 8 **ABBREVIATIONS**

9 <sup>13</sup>C-NMR: carbon-13 nuclear magnetic resonance  
10 <sup>19</sup>F-NMR: fluorine-19 nuclear magnetic resonance  
11 <sup>1</sup>H-NMR: proton nuclear magnetic resonance  
12 AIL: aprotic ionic liquid  
13 ATR: attenuated total reflection  
14 CLC: Cheng-Li correction  
15 DEMA: diethyl methyl amine  
16 DEMATfO: diethyl methyl ammonium triflate  
17 DFT: density functional theory  
18 DOSY: diffusion ordered spectroscopy  
19 DSC: differential scanning calorimetry  
20 DTGA: differential thermal gravimetric analysis  
21 DLaTGS: deuterated lanthanum  $\alpha$  alanine doped triglycine sulfate  
22 DTGS: deuterated triglycine sulfate  
23 FD: formation degree  
24 FIR: far-infrared  
25 HAc: acetic acid  
26 HB: hydrogen bond  
27 HMS: methanesulfonic/mesylic acid  
28 HTEA: triethylammonium  
29 HTFA: trifluoroacetic acid  
30 HTfO: trifluoromethanesulfonic/triflic acid  
31 HTFSI: triflimidic acid  
32 IL: ionic liquid  
33  $k_B$ : Boltzmann constant  
34 KTFA: potassium trifluoroacetate  
35 MIR: mid-infrared  
36 MS: methanesulfonate/mesylate  
37 MW: molecular weight  
38 Nd:YAG: neodymium-doped yttrium aluminum garnet  
39 NE: Nernst Einstein  
40 NMR: nuclear magnetic resonance

1 PA: proton affinity  
2 PGSE: pulsed gradient spin echo  
3 PGSTE: pulse gradient stimulated echo  
4 PIL: protic ionic liquid  
5  $pK_a$ : negative base-10 logarithm of the acid dissociation constant  
6 ppm: parts per million  
7 SER: Stokes-Einstein relationship  
8 TA: thermal analysis  
9 TEA: triethylamine  
10 TEAMS: triethylammonium mesylate  
11 TEATFA: triethylammonium trifluoroacetate  
12 TEATfO: triethylammonium triflate  
13 TEATFSI: triethylammonium bis (trifluoromethylsulfonyl) imide  
14 TFA: trifluoroacetate  
15 TfO: trifluoromethanesulfonate/triflate  
16 TGA: thermal gravimetric analysis  
17 TMS: tetramethyl silane  
18 VEDA: vibrational energy distribution analysis  
19 VTF: Vogel-Tamman-Fulcher

20

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