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NMR study on the possible interactions between imidazolium based ionic liquids and widely applied in solvent extraction and separation of f-ions extractants --Manuscript Draft--

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NMR study on the possible interactions between imidazolium based ionic liquids and widely applied in solvent extraction and separation of f-ions extractants

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Abstract

A detailed NMR study on the possible interactions between a series of imidazolium based ionic liquids (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, RmimTf₂N, n=4, 6, 8, 10) and commonly applied in solvent extraction and separation science of 4f and 5f-ions acidic chelating and neutral extractants is presented. Analytical techniques applied are ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra and NOESY experiments. Investigation of the types and strengths of the solvent-solute interactions is necessary for a knowledge-based features concerning chemical solubility, reactivity and selectivity as ILs have a strong influence on the solvent extraction mechanism of metallic species in comparison with traditional molecular solvents used. The goal of the scientific research is to gain insight on the role of ILs as a perspective efficient “green” medium in the solvent extraction processes with more pro-ecological aspect. Experimental results do not evidence any specific interactions between the IL components and the ligands.

Key-words Ionic liquids • Chelating extractants • Neutral ligands • Interactions • NMR

1. Introduction

Ionic liquids (ILs) are a class of remarkable diluents with unusual solvation properties that consist entirely of ions. Today, ILs represent a key instrument of the green chemistry converting numerous processes in environmentally friendly procedures [1-2] with comprehensive industrial applications [3, 4] and undoubtedly unquestionable future in critical

1 technological areas such as nuclear fuel cycles. The main advantages of ILs over molecular
2 organic solvents are the unique ionic character, extremely wide liquid diapason (up to 800°C),
3 non-volatility, no vapour pressure, non-flammability, negligible toxicity but not always [5],
4 capability to dissolve a wide spectrum of organic and inorganic compounds, an excellent
5 solution behaviour, adjustable miscibility and polarity, multiple reusability etc. ILs can be used
6 as design solvents or the so-called task specific ionic liquids, due to the ability to adjust their
7 physicochemical properties in a variety of applications. Imidazolium based ILs are among the
8 most widely applied in synthesis, catalysis, separation science and continue to attract
9 increasing interest due to their low melting points and viscosity, no complicated synthesis, and
10 good stability to oxidative/reductive conditions [6-11]. Their properties are strongly dependent
11 on the length of the alkyl chain and on the anion component. Most often fluorinated anions are
12 chosen in solvent extraction systems because of their hydrophobicity, low viscosity and low
13 coordination ability. Some of them are not so “green” as diluents due to their degradation in the
14 aqueous phase; for instance $[\text{PF}_6]^-$ is hydrolytically unstable: $[\text{PF}_6]^- + 4\text{H}_2\text{O} \leftrightarrow 5\text{HF} + \text{F}^- +$
15 H_3PO_4 . So, the selection of the anion $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (Tf_2N^-) is preferable, although some loss to
16 the aqueous phase also occurs by solubilisation [12]. In general, it can be summarized that
17 imidazolium cations are responsible for the air-, water-, temperature-, and radiation-stability of
18 ILs, while their hydrophobicity is controlled by the anions. These properties, among many
19 others, make them so attractive for science, technology and engineering and their application in
20 the separation technology can be considered as a “hot” research topic. ILs are the obvious
21 replacements for currently used organic noxious molecular solvents in all developing areas of
22 chemistry.

23
24 The interactions between anionic part of ILs and metal ions are widely studied mainly in
25 respect for their solvation [10, 13-15]. On the other hand, it has been found in the extraction of
26 natural compounds [16-19] that the interactions between the extracted species and ILs are
27 crucial for efficient processes. It has also been demonstrated [20] that the interactions between
28 ILs and radicals play an important role in the radical reactions in ionic liquids. Therefore, two
29 reasonable questions arise: Are the extractant/IL interactions important in metal extractions?
30 Are the structural changes occurring during equilibrium process and how this will affect the
31 deviation from the ideal mixing behaviour solvent-solute?

32
33 Recently, we found that the new synthesized complexing agent 3-methyl-1-phenyl-4-(4-
34 trifluoromethylbenzoyl)-pyrazol-5-one extracts efficiently Ln^{3+} ions in 1-butyl-3-
35 methylimidazolium bis(trifluoromethylsulfonyl)amide [21] and, using NMR experiments, that
36 no interactions occur between IL and the pyrazolone compound, independently on the solvent
37 nature (benzene, acetonitrile or chloroform). For that reason, we decided to extend this study

1 towards a variety of acidic chelating agents and neutral oxygen-donor ligands and ILs as a first
2 step to exploit the potential offered by such systems. It is worthwhile to mention that the well-
3 known principle “like-dissolves-like” cannot be attributed in these investigations as the IL
4 diluent possesses different chemical nature (i.e. ionic) from the solute (extractant molecule,
5 neutral). On the other hand, the mutual solubility in aqueous-ionic liquid biphasic systems by
6 Q-NMR technique was investigated applying five ILs of the imidazolium family with
7 hydrophobic anion (CF₃SO₂)₂N⁻ and chloride, nitrate and perchlorate-based aqueous phases
8 [12]. An unavoidable and so intricate ionic exchange was established with remarkable
9 solubility of IL’s anion under some of the chemical conditions [12]. The aim of the current
10 study is to examine the possible interactions between a homologous series of hydrophobic
11 imidazolium based ILs and commonly applied in separation science of f-ions extractants in
12 order to detect some changes in the organic IL phase that may occur upon ligand addition,
13 which, to the best of our knowledge, has never been discussed in the literature, by solution
14 NMR spectroscopy.

25 **2. Materials and methods**

26 The acidic chelating and neutral extractants (E) were purchased from Fluka and Chemos
27 GmbH, respectively, and were used without further purification (purity >98%). The
28 deuteriochloroform is from Aldrich, 99.8 atom % D. The ionic liquids were supplied by
29 Solvionic (all with purity of 99.5%, Toulouse, France) and were dried in *vacuo* prior to sample
30 preparation following a previously published procedure [22]. The individual NMR spectra of
31 ILs, E (0.1 M concentrations) and their mixture were recorded as CDCl₃ solutions on Bruker
32 Avance 500 at 20°C and ¹⁹F at 25°C. Various ratio i.e. 4:1, 2:1 and 1:1 of IL–E mixtures were
33 recorded as 0.1 M IL and 0.025 M, 0.05 M and 0.1 M concentration of E, respectively. The
34 concentration 0.1 M and 1:1 ratio of IL–E mixtures were applied for deriving NOESY spectra.
35 The chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an
36 internal standard and against CF₃COOH and H₃PO₄ as external standards in ¹⁹F and ³¹P
37 spectra, respectively. The coupling constants were calculated in Hz. The spectra were
38 processed with Topspin 2.1 program.

51 **3. Results**

52 Modern high-resolution NMR spectroscopy in neat ILs is not applicable in this particular study
53 due to serious drawbacks as emphasized in a recent paper [23]. First, only the changes in the IL
54 signals can be followed due to the absence of reference extractants spectra. Second, only a
55 small part of the IL entities equal to the molar concentration of the extractant, can interact and
56

if such moieties exist, their signals are commensurable with the noise. For that reason, the explicit and easy applicable way to examine the possible IL–E interactions is served by the solution NMR.

The interactions between four hydrophobic ILs and five commonly used in liquid-liquid extraction processes of f-ions ligands were studied by NMR spectra in CDCl₃ solution. The latter was chosen due to the limited solubility of ILs in hydrocarbons combined with the already observed by us fact [21] that the spectra of 4-trifluoromethylbenzoyl pyrazolone/bmimTf₂N mixture in benzene, acetonitrile and chloroform showed identical results; no interactions between the two species dissolved. The selected ILs of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide group differing in their miscibility with water are 1-butyl- (**bmimTf₂N**), 1-hexyl- (**hmimTf₂N**), 1-octyl- (**omimTf₂N**), and 1-decyl- (**dmimTf₂N**) presented on Figure 1. Furthermore, viscosity at 25°C increases continuously with the length of the alkyl chain bound at the nitrogen atom of the imidazolium ring (cP: 61.14÷104, for comparison the viscosity of conventional VOCs diluents is about 1cP).

Fig. 1 The chemical structures of ionic liquids and extractant molecules studied.

The ligands under study could be divided in two main groups: acidic and neutral. The first series consists of commonly applied in extraction processes β-dicarbonyl compounds: thenoyltrifluoroacetone (**HTTA**), 4-benzoyl-3-methyl-1-phenyl-pyrazol-5-one (**HP**) and 4-benzoyl-3-phenyl-isoxazol-5-one (**HPBI**), drawn in their predominant keto-enol form in solution, Figure 1. The second group of neutral molecules includes two acetamides: N,N-diisobutyl-2-(octyl(phenyl)phosphoryl)acetamide (**CMPO**) and 2,2'-oxybis(N,N-diethylacetamide) (**TODGA**).

The spectra of acidic chelating extractants showed sharp and well defined signals compatible with pure keto-enol forms. As demonstrated for the typical β-diketone compound **HTTA** on Figure 2, the tautomeric CH appears as singlet at 6.48 ppm in the proton spectrum and at 93.7 ppm in the carbon as quartet due to a coupling with the three fluorine atoms. No CH₂ signals are registered both in proton and carbon spectra. The same pattern was observed for 4-acylpyrazolone, **HP**, and isoxazolone molecule, **HPBI**.

Fig. 2 ¹H (a) and ¹³C (b) spectra of **HTTA** in CDCl₃.

The interactions between the chosen four ILs and the acidic chelating extractants were studied by proton, carbon and fluorine spectra in different molar ratios, i.e. IL:E 4:1, 2:1 and 1:1. The

spectra of **dmimTf₂N**, **HTTA** and their mixtures are shown on Figure 3 and selected signals in the spectra of **ILs**, **HTTA** and all **IL/HTTA** mixtures are listed on Table 1. As it can be seen, proton, carbon and fluorine resonances as well as J_{CF} coupling constants have practically the same values in the spectra of the individual compounds and in those of their mixtures. The same pattern was observed in all cases, which is an indication that no interactions between the ionic liquid and acidic extractant occur in chloroform solution independently on their proportions. Some of the original spectra are given in the Supplementary Material (Fig. 9-20).

Fig. 3 Spectra of **dmimTf₂N** (blue), **dmimTf₂N:HTTA** 4:1 (brown), **dmimTf₂N:HTTA** 2:1 (green), **dmimTf₂N:HTTA** 1:1 (red), and **HTTA** (violet): a) 1H ; b) ^{13}C ; c) ^{19}F .

Table 1. Selected signals in the spectra of **ILs**, **HTTA** and **IL/HTTA** mixtures.

	^{19}F -IL	^{19}F -E	CH , E	CH , J_{CF} , E	C_q -OH, E	C_q =O, J_{CF} , E	CF_3 , J_{CF} , E	CF_3 , J_{CF} , IL
bmim Tf₂N	-80.06	-	-	-	-	-	-	119.90, 320.2
4:1	-80.07	-76.71	6.452	93.70 2.7	182.96	171.27 36.7	117.73 280.3	119.90 320.8
2:1	-80.09	-76.71	6.451	93.70 2.7	182.93	171.23 36.5	117.73 280.3	119.89 320.6
1:1	-80.09	-76.71	6.452	93.69 2.7	182.97	171.24 36.7	117.73 280.6	119.89 320.4
HTTA	-	-76.70	6.452	93.70 2.7	182.93	171.32 36.7	117.79 280.6	-
hmim Tf₂N	-80.06	-	-	-	-	-	-	119.89 320.1
4:1	-80.07	-76.71	6.452	93.69 2.7	182.97	171.31 36.7	117.73 280.3	119.89 320.1
2:1	-80.06	-76.71	6.452	93.69 2.7	182.97	171.24 36.5	117.73 280.5	119.89 320.1
1:1	-80.08	-76.72	6.451	93.68 2.7	182.98	171.22 36.7	117.72 280.6	119.89 320.2
HTTA	-	-76.70	6.452	93.70 2.7	182.93	171.32 36.7	117.79 280.6	-
omim Tf₂N	-80.04	-	-	-	-	-	-	119.89 320.1
4:1	-80.04	-76.71	6.453	93.69 2.7	182.97	171.26 36.6	117.72 280.7	119.89 320.4
2:1	-80.05	-76.71	6.452	93.69 2.7	182.97	171.24 36.6	117.72 280.4	119.89 320.3
1:1	-80.05	-76.72	6.451	93.68 2.7	182.97	171.23 36.6	117.73 280.7	119.89 320.3
HTTA	-	-76.70	6.452	93.70 2.7	182.93	171.32 36.7	117.79 280.6	-
dmim	-80.03	-	-	-	-	-	-	119.89

Tf₂N								320.4
4:1	-80.03	-76.71	6.453	93.69 2.7	182.96	171.26 36.6	117.72 280.3	119.89 320.3
2:1	-80.04	-76.71	6.452	93.69 2.7	182.97	171.24 36.6	117.72 280.5	119.89 320.4
1:1	-80.04	-76.71	6.451	93.68 2.7	182.97	171.24 36.5	117.73 280.6	119.90 320.2
HTTA	-	-76.70	6.452	93.70 2.7	182.93	171.32 36.7	117.79 280.6	-

The possible interactions were additionally investigated by analyzing the cross peaks in NOESY experiments recorded for 1:1 IL/E mixtures in 0.1 M concentrations. As illustrated on the example of **dmimTf₂N/HTTA** (Fig. 4), only intramolecular interactions are registered. Despite the relatively high concentration for such experiment, no intermolecular cross peaks were observed. The same pattern is valid for other systems including **HP** and **HPBI** as target compounds and butyl-, hexyl- octyl- and decyl forms of RmimTf₂N.

Fig. 4 Partial ¹H-¹H NOESY spectrum of **dmimTf₂N:HTTA** 1:1 mixture.

The two neutral ligands under study, **CMPO** and **TODGA**, showed the same model of behavior in the NMR spectra (SM, Fig. 21-29). No chemical shift changes were registered in the spectra upon mixing with ILs. As illustrated on the example of **dmimTf₂N/CMPO** mixture (Fig. 5), both proton and carbon resonances are identical in the spectra of the individual compounds and their mixtures independently on the IL/E ratio. Even the changes in the signals, which have to be the most significantly influences in case of interactions, those neighbouring to IL's nitrogens and extractant's carbonyls, are negligible (Table 2).

Fig. 5 Spectra of **dmimTf₂N** (blue), **dmimTf₂N:CMPO** 4:1 (brown), **dmimTf₂N:CMPO** 2:1 (green), **dmimTf₂N:CMPO** 1:1 (red), and **CMPO** (violet): a) ¹H; b) ¹³C.

Table 2. Selected signals in the spectra of **CMPO**, **ILs** and **IL:CMPO** 1:1 mixtures.

	³¹ P-E	¹⁹ F-IL	CH ₃ -3,IL	CH-2, IL	C _q =O, J _{CP} , E	CF ₃ , J _{CF} , IL
CMPO	37.83	-	-	-	166.29, 3.7	-
1:1	37.85	-80.05	3.903	8.733	166.19, 3.7	119.87, 321.1
bmim Tf₂N	-	-80.06	3.926	8.724	-	119.90, 320.2
1:1	37.84	-80.08	3.894	8.733	166.24, 3.8	119.88, 320.6
hmim Tf₂N	-	-80.06	3.922	8.715	-	119.89, 320.1
1:1	37.86	-80.06	3.892	8.734	166.23, 3.8	119.83, 321.1

omim Tf₂N	-	-80.04	3.924	8.719	-	119.89, 320.1
1:1 dmim Tf₂N	37.84	-80.04	3.899	8.747	166.25, 3.8	119.87, 321.3
dmim Tf₂N	-	-80.03	3.926	8.723	-	119.89, 320.4

The fluorine spectra (Fig. 6, Table 2) show that no changes in IL anion environment occur in the presence of the extractant. Both chemical shifts and carbon-fluorine constants possess practically the same values; 0.1-0.6 ppm and 0.5-0.9 Hz differences, respectively.

Fig. 6 ¹⁹F NMR spectra of **dmimTf₂N** (blue), **dmimTf₂N:CMPO** 1:1 (red), **dmimTf₂N:CMPO** 2:1 (green), and **dmimTf₂N:CMPO** 4:1 (brown).

The ligand **CMPO** presents a special example in the series studied as it offers additional important technique to examine the interactions with ILs; phosphorus spectra, which are very sensitive to structural or conformational changes in general. As seen (Fig. 7, Table 2), phosphorus **CMPO** signals underwent negligible downfielding, 0.01-0.03 ppm, and carbon-phosphorus constants remain practically the same in the spectra of **RmimTf₂N/CMPO** 1:1 mixture in respect to that of the individual ligand.

Fig. 7 ³¹P NMR spectra of **CMPO** (blue), **dmimTf₂N:CMPO** 4:1 (red), **dmimTf₂N:CMPO** 2:1 (green), and **dmimTf₂N:CMPO** 1:1 (brown).

As in the case of the acidic extractants studied, no intermolecular interactions were detected in NOESY spectra of the IL/neutral ligand combinations. The latter is illustrated on Figure 8 on the example of **dmimTf₂N:CMPO** 1:1 mixture.

Fig. 8 Partial ¹H-¹H NOESY spectrum of **dmimTf₂N:CMPO** 1:1 mixture.

4. Discussion

The unique solvation environments in the bulk of IL are the results of the forces exhibited by the **RmimTf₂N** on the solute including Coulomb, van der Waals and hydrogen bonding interactions [24, 25], which are already present to some degree in the pure ILs. The IL can act not only as a pure solvent and water scavenger [12, 25], but also as a reagent in particular by hydrogen bonding interaction of its anion and the organic molecules [25]. The strength of the

ion-ion interaction depends on the IL structure and may strongly affect the ability of anions and/or cations to interact with dissolved species [26].

As already stressed above, molecular diluents and ILs display totally different structures and, therefore, offer very specific features for metal liquid/liquid extraction. ILs play a more active role not only in the partitioning process as a receiving phase but represent an important mode of metal ion extraction taking part in the formation of metallic species. It has been shown that aqueous/IL biphasic systems are significantly more complicated than that with VOCs and the presence of an acidic extractant as well as the length of the 1-alkyl chain of the IL cation, Rmim⁺, strongly influence mutual solubilities of all ions (H₂O, H⁺, Rmim⁺ and Tf₂N⁻, etc.) [27]. Addition of an acidic ligand to the IL phase has no significant effect onto the water solubility. The pK_{aIL} values of ligands with different acidity **HTTA**, **HP** and **HPBI** have been measured in bmimTf₂N (pH range 1-3.5). The obtained three values of pK_{aIL} corresponding to the ligand dissociation in a water saturated bmimTf₂N phase (12 200 ppm average H₂O amount) are very similar, 2.0-3.5, in comparison with the large difference observed for their pK_{aW} values of 1.12-6.23 [27]. A clear effect of IL's nature is also observed during these measurements.

When considering the mechanism of lanthanoid(III) extraction towards IL or molecular solvent phases by use of β-dicarbonyl compounds, two very different situations can be found: in molecular solvents, the extracted species are always neutral, while in ILs, extracted species are predominantly charged, owing to the ionic nature of the solvent. In particular, the extraction of anionic complexes by **HTTA** has been shown to proceed by the exchange of the Tf₂N⁻ anions into the aqueous phase:

However, other mechanisms are possible, such as cationic exchange or extraction of neutral species, in a way rather similar to that occurring in molecular solvents [21]. In principle, the anionic exchange mechanism can be assessed by following the amount of Tf₂N⁻ anions transferring to the aqueous phase during the extraction process but such a determination is difficult; even in the absence of metallic ions, some Tf₂N⁻ anions transfer to the aqueous phase in amounts that are in the range of 2-70 mM depending on IL nature and aqueous phase composition (Cl⁻, NO₃⁻, ClO₄⁻) [12], while the amount of Tf₂N⁻ transferred due to the extraction mechanism itself is in the order of the metallic ion concentration, which, most of the time, is very low as compared to the above mentioned mM range. Very efficient and simple way to determine the stoichiometry of the extracted species in the organic phase during liquid-liquid extraction is by use of the classical slope analysis method [28] but it is sometimes difficult to perform, either because it requests large solubility of the ligand or because slopes are quite

often far from integer values in ILs, again because of the IL cation and anion solubilities in the aqueous phase, which sometimes distort the expected linear trends. This method gives good insight into the first coordination sphere of the metal ion in solvent extraction using molecular diluents. The method is based on an examination of the variation of the distribution ratio (D) with the relevant experimental variables. A plot of the logarithm of D vs the logarithm of one of the variables (the concentration of the two extractants and of H^+), keeping the other two constant, indicates the stoichiometry of the extractable complex and a suitable equilibrium expression can be obtained, and consequently, the equilibrium constant can be computed [21, 29, 30]. The method will not give good results if some impurities are presented in the organic phase that is likely to form addition compounds with extractants. The antagonistic effect found for the extraction of Pd(II) with mixtures of 3-methyl-1-phenyl-4-propinoyl-pyrazol-5-one and a tertiary alkylamine, established by Zhang, was expressed by a decrease of the pyrazolone concentration in the organic phase ($CHCl_3$ medium) due to the formation of an associated species $HPMPP \cdot NR_1R_2R_3$ through hydrogen bonding [31]. So, it is of great importance to investigate through the present NMR experiments, the interaction between some ligands and ILs, which could reduce the concentration of the free extractants; especially of co-extractant in synergistic solvent extraction usually used at lower concentration.

5. Conclusion

The possible interactions between a series of imidazolium based ionic liquids and acidic chelating and neutral extractants were studied by proton, carbon, fluorine, and phosphorus NMR spectra and it was shown that no interactions occurred in chloroform solution independently on the length of the imidazolium alkyl chain and on the structure and acidity of the ligand. NOESY technique provides valuable information and gives “insight” into the bulk liquid phase widely applied today as innovative medium in solvent extraction and separation chemistry. The absence of interactions, whatever the relative proportions of IL and ligand in chloroform is a strong indication that no interaction occurs in the bulk IL either. This could be a hint to explain the dramatic increase in extraction efficiencies observed for various ligands (among which those studied here) dissolved in IL media, as compared to organic molecular solvents.

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Supplementary Material

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Graphical Abstract

Fig. 1

Fig 2a

Fig 2b

Fig 3a

Fig 3b

Fig 3c

Fig 4

Fig 5a

Fig 5b

Fig 6

Fig 7

Fig 8

SUPPLEMENTARY MATERIAL

NMR study on the possible interactions between imidazolium based ionic liquids and widely applied in solvent extraction and separation of f-ions extractants

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The NMR spectra of ILs, E and their mixture were recorded in CDCl₃ on Bruker Avance 500 at 20°C and ¹⁹F at 25°C. The signals were calibrated against tetramethylsilane (TMS) as an internal standard in ¹H and ¹³C and against CF₃COOH and H₃PO₄ as external standards in ¹⁹F and ³¹P spectra, respectively. The spectra were processed with Topspin 2.1 program.

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I) NMR spectra of **IL/HTTA** mixtures

Fig. 9 ^1H NMR spectra of **bmimTf₂N** (blue), **bmimTf₂N:HTTA** 4:1 (brown), **bmimTf₂N:HTTA** 2:1 (green), **bmimTf₂N:HTTA** 1:1 (red), and **HTTA** (violet).

Fig. 10 ^{13}C NMR spectra of **bmimTf₂N** (blue), **bmimTf₂N:HTTA** 4:1 (brown), **bmimTf₂N:HTTA** 2:1 (green), **bmimTf₂N:HTTA** 1:1 (red), and **HTTA** (violet).

Fig. 11 ^{19}F NMR spectra of **omimTf₂N** (blue), **omimTf₂N:HTTA** 4:1 (brown), **omimTf₂N:HTTA** 2:1 (green), **omimTf₂N:HTTA** 1:1 (red), and **HTTA** (violet).

Fig. 12 ^1H - ^1H NOESY spectrum of **dmimTf₂N:HTTA** 1:1.

II) NMR spectra of **IL/HP** mixtures

Fig. 13 ^1H NMR spectra of **hmimTf₂N** (blue), **hmimTf₂N:HP 4:1** (brown), **hmimTf₂N:HP 2:1** (green), **hmimTf₂N:HP 1:1** (red), and **HP** (violet).

Fig. 14 ^{13}C NMR spectra of **omimTf₂N** (blue), **omimTf₂N:HP 4:1** (brown), **omimTf₂N:HP 2:1** (green), **omimTf₂N:HP 1:1** (red), and **HP** (violet).

Fig. 15 ^{19}F NMR spectra of **dmimTf₂N** (blue), **dmimTf₂N:HP** 4:1 (brown), **dmimTf₂N:HP** 2:1 (green), and **dmimTf₂N:HP** 1:1 (red).

Fig. 16 ^1H - ^1H NOESY spectrum of **bmimTf₂N:HP** 1:1.

III) NMR spectra of **IL/HPBI** mixtures

Fig. 17 ^1H NMR spectra of **omimTf₂N** (blue), **omimTf₂N:HPBI 4:1** (brown), **omimTf₂N:HPBI 2:1** (green), **omimTf₂N:HPBI 1:1** (red), and **HPBI** (violet).

Fig. 18 ^{13}C NMR spectra of **dmimTf₂N** (blue), **dmimTf₂N:HPBI 4:1** (brown), **dmimTf₂N:HPBI 2:1** (green), **dmimTf₂N:HPBI 1:1** (red), and **HPBI** (violet).

Fig. 19 ^{19}F NMR spectra of **bmimTf₂N** (blue), **bmimTf₂N:HPBI 4:1** (brown), **bmimTf₂N:HPBI 2:1** (green), and **bmimTf₂N:HPBI 1:1** (red).

Fig. S20 ^1H - ^1H NOESY spectrum of **bmimTf₂N:HPBI 1:1**.

IV) NMR spectra of **IL/CMPO** mixtures

Fig. 21 ^1H NMR spectra of **dmimTf₂N** (blue), **dmimTf₂N:CMPO** 4:1 (brown), **dmimTf₂N:CMPO** 2:1 (green), **dmimTf₂N:CMPO** 1:1 (red), and **CMPO** (violet).

Fig. 22 ^{13}C NMR spectra of **bmimTf₂N** (blue), **bmimTf₂N:CMPO** 4:1 (brown), **bmimTf₂N:CMPO** 2:1 (green), **bmimTf₂N:CMPO** 1:1 (red), and **CMPO** (violet).

Fig. 23 ^{19}F NMR spectra of **hmimTf₂N** (blue), **hmimTf₂N:CMPO** 4:1 (brown), **hmimTf₂N:CMPO** 2:1 (green), and **hmimTf₂N:CMPO** 1:1 (red).

Fig. 24 ^1H - ^1H NOESY spectrum of **omimTf₂N:CMPO** 1:1.

Fig. 25 ^{31}P NMR spectra of **CMPO** (blue), **dmimTf₂N:CMPO** 1:1 (brown), and **dmimTf₂N:CMPO** 2:1 (green).

V) NMR spectra of **IL/TODGA** mixtures

Fig. 26 ^1H NMR spectra of **bmimTf₂N** (blue), **bmimTf₂N:TODGA** 4:1 (brown), **bmimTf₂N:TODGA** 2:1 (green), **bmimTf₂N:TODGA** 1:1 (red), and **TODGA** (violet).

Fig. 27 ^{13}C NMR spectra of **hmimTf₂N** (blue), **hmimTf₂N:TODGA** 4:1 (brown), **hmimTf₂N:TODGA** 2:1 (green), **hmimTf₂N:TODGA** 1:1 (red), and **TODGA** (violet).

Fig. 28 ^{19}F NMR spectra of **omimTf₂N** (blue), **omimTf₂N:TODGA** 4:1 (brown), **omimTf₂N:TODGA** 2:1 (green), and **omimTf₂N:TODGA** 1:1 (red).

Fig. 29 ^1H - ^1H NOESY spectrum of **dmimTf₂N:TODGA** 1:1.

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