Azolium-based systems: application of an anion exchange resin (A⁻ form) method and ¹H NMR analysis of the charged-assisted (C–H)⁺⋯anion hydrogen bonds†

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Dedicated to Prof. Rosa M. Claramunt on the occasion of her 65th birthday

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Abstract
The counteranion exchange of quaternary 1,2,3-triazolium salts was examined using a simple method that permitted halide ions to be swap for a variety of anions using an anion exchange resin (A⁻ form). The method was applied to 1,2,3-triazolium-based ionic liquids and the iodide-to-anion exchange proceeded in excellent to quantitative yields, concomitantly removing halide impurities. Additionally, an anion exchange resin (N₃⁻ form) was used to obtain the benzyl azide from benzyl halide under mild reaction. Likewise, following a similar protocol, bis(azidomethyl)arenes were also synthesized in excellent yields. The results of a proton NMR spectroscopic study of simple azolium-based ion pairs are discussed, with attention focused on the significance of the charged-assisted (C–H)⁺⋯anion hydrogen bonds of simple azolium systems such as 1-butyl-3-methylimidazolium and 1-benzyl-3-methyl-1,2,3-triazolium salts.

Keywords: Imidazolium salts, 1,2,3-triazolium salts, anion exchange resin, hydrogen bonds, ionic liquids

Introduction
Azolium systems have gained a place among the anion-binding functional groups, ranging from anion receptors and sensors to transporters,²⁻⁹ and as ionic liquids (ILs) their utility has expanded into domains beyond chemistry.¹⁰⁻¹⁴ The greenness of the most established IL syntheses and purification procedures has been analyzed and evaluated.¹³ Thus, the chemical aspects of imidazolium-based ILs, including their synthesis, counteranion exchange and purity, have been the subject of numerous studies with the aim of obtaining pure IL salts, especially halide-free ion
pairs. However, little attention has been paid to the use of an anion exchange resin (AER).\textsuperscript{1,12-14} Examples of anion exchange resin application to ILs reported in the open literature use either the AER (OH\textsuperscript{−} form) or the AER (A\textsuperscript{−} form) method.\textsuperscript{1,14} We have recently examined the preparation of an AER (A\textsuperscript{−} form) conveniently loaded with a selected anion after treatment with either acids or ammonium salts in water, or hydroalcoholic media, or organic solvents. The halide-to-anion exchange of quaternary imidazolium salts 1·X and their transformation to the corresponding ion pairs 1·A was carried out in methanol or organic solvents providing a pure ionic liquid in excellent to quantitative yields (Figure 1). Moreover, the transformation of both lipophylic quaternary heteroaromatic cations and low hydrophilic anions also proceeded in excellent to quantitative yields.\textsuperscript{1} This simple procedure offers a convenient way to replace halide anions by a broad range of anions in and also eliminates halide impurities and minimizes the formation of toxic by-products with consequent environmental benefits.

A logical extension of our previous studies on imidazolium-based systems was to examine 1,3-dialkyl-1,2,3-triazolium 2·X, which have been described as stable and recyclable solvents.\textsuperscript{15-18} The present study is focused on the application of the AER (A\textsuperscript{−} form) method for the iodide-to-anion exchange of the selected triazolium ion pairs. The reported synthesis of 1-benzyl-3-methyl-1,2,3-triazolium iodide 2b·I ([BnmTr]I) requires benzyl azide 4 for the preparation of the click-derived 1,2,3-triazole 3,\textsuperscript{15} as shown in the retrosynthetic Scheme 1. Thus, an AER (N\textsubscript{3}\textsuperscript{−} form) was prepared and used to obtain azide 4 and bis(azidomethyl)arenes 5 and 6. It should be noted that in the last years theoretical calculations have confronted the question of what is responsible for the anion–cation non-covalent interactions in pure imidazolium-based ILs.
and have challenged the role of (C–H)⁺ hydrogen bonds in explaining IL properties.\textsuperscript{19,20} A relevant part of the present study is focused on the significance of the noncovalent interactions involved between the azolium motifs and a variety of anions, with special attention given to nonclassical charged-assisted (C–H)⁺···anion hydrogen bonds. Thus, the ion pairs prepared provided the opportunity to learn about the hydrogen-bonding interactions of simple azolium systems such as 1-butyl-3-methylimidazolium \textit{1a}·\textit{A} ([\textit{bmin}]\textit{A}) and 1-benzyl-1-methyl-1,2,3-triazolium \textit{2b}·\textit{A} ([\textit{BnmTr}]\textit{A}) salts in solution-phase by proton NMR spectroscopy.

![Scheme 1](image)

\textbf{Scheme 1.} 1,2,3-Triazolium-based ionic liquids \textit{2-X}. (a) Halide-to-anion exchange: the anion exchange resin (A⁻ form) method. (b) Retrosynthetic pathway to the ion pair \textit{2b·I} and to benzylic azides \textit{4}, \textit{5} and \textit{6}.

\textbf{Results and Discussion}

\textit{Preparation of benzylic azides using an anion exchange resin (N₃⁻ form)}

Applications of ion-exchange resins to a variety of chemical reactions have proven to be extremely useful in different chemical fields such as organic synthesis, catalysis and industrial applications\textsuperscript{21,22} as well as chemistry in flow systems.\textsuperscript{23} The anion exchange resin (N₃⁻ form) can be used both for the halide exchange like for nucleophilic substitution reactions.\textsuperscript{24,25} Thus, the benzyl azide component \textit{4} was prepared in excellent yield using a polymeric azide reagent protocol that consists of mixing benzyl bromide or chloride with 12 equivalents of the AER Amberlite IRA-400 (N₃⁻ form) at room temperature in dichloromethane,\textsuperscript{24} and also under
standard reaction conditions between sodium azide and benzyl iodide or bromide at room temperature in a dipolar aprotic solvent, e.g. dimethyl sulfoxide or dimethylformamide, in ≥ 91% yield, since benzylic halides readily undergo nucleophilic substitution reactions.

Following a modified experimental procedure previously reported by Hassner et al., benzyl azide 4 was obtained in 93% yield from both benzyl bromide and chloride using a strong basic AER (N₃⁻ form) in CH₃CN/CH₃OH (1:1) (Scheme 2). Applying our protocol, bis(azidomethyl)arenes 5 and 6 were prepared by stirring the reaction mixture of the corresponding benzylic halides 7 and 8 and the azide-loaded strong basic AER (N₃⁻ form) in organic solvents under mild and safe conditions with a direct work-up. After examining various nucleophilic substitution reaction conditions, the best results were observed when using a solvent mixture of CH₃CN/CH₃OH (1:1) or CH₃CN/CH₂Cl₂ (1:1) to give the diazides 5 and 6, respectively, in 95% yield (Scheme 2 and Supplementary Material).

**Scheme 2.** Preparation of benzyl azide 4 and bis(azidomethyl)arenes 5, 6 using an azide-loaded strong basic AER (N₃⁻ form) in organic solvents.

**Halide-to-anion exchange: AER (A⁻ form) method**

The anion sources used to load the selected anions were mainly via I from acids or via II from the corresponding ammonium salt (Scheme 3 and Table 1). Thus, the AER (OH⁻ form) was
packed in a column and treated with a hydromethanolic solution of the acid or ammonium salt. Following via I, the loading was performed with the hydromethanolic solution of AcOH or MeSO$_3$H and the aqueous inorganic acids HPF$_6$ or HBF$_4$. In via II, anions such as CF$_3$SO$_3$\(^{-}\), PF$_6^-$ and BF$_4^-$ were loaded in the resin using aqueous solutions of their ammonium salts, while the lipophilic BPh$_4^-$ anion required CH$_3$CN/H$_2$O (9:1) solvent mixture. When the anions were loaded in the AER, we examined the efficiency of the counteranion exchange using 1,2,3-triazolium ionic liquids, due to their recent interest as stable and recyclable solvents.\textsuperscript{15-18} A recent study has shown that the key physicochemical aspects of 1,2,3-triazolium-based ILs are their high electrochemical stability and ionic conductivity, which are comparable to their imidazolium counterparts, yet with the advantage that the 1,2,3-triazolium nucleus seems to be more robust under alkaline reaction conditions.\textsuperscript{29}

Scheme 3. AER (A$^-$ form) method applied to 1,2,3-triazolium ionic liquids 2·I. (a) Anion loading and anion source. (b) Iodide-to-anion exchange of 2a·I and 2b·I.

The AER (A$^-$ form) method was then applied to both 1,2,3-triazolium compounds, 1-buthyl-3-methyltriazolium iodide 2a·I and 1-benzyl-3-methyltriazolium iodide 2b·I, and the halide exchange for representative anions proceeded in 90% to quantitative yields when methanol was used (Table 1), improving the results obtained using classical methods.\textsuperscript{15} However, when the recovery of the new ion pairs 2a·A or 2b·A was around 90%, further studies to increase the yield using a less polar solvent, for example acetonitrile, were not carried out.
Table 1. Iodide-to-anion exchange of 1,2,3-triazolium-based ionic liquids in methanol

<table>
<thead>
<tr>
<th>Anion</th>
<th>Loadinga</th>
<th>$2a_b^+$ Yield (%)b</th>
<th>$2a_b^+$ $\Gamma^-(ppm)c$</th>
<th>$2b_b^+$ Yield (%)b</th>
<th>$2b_b^+$ $\Gamma^-(ppm)c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcO$^-$</td>
<td>via I$^d$</td>
<td>100</td>
<td>$&lt;20$</td>
<td>100</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>MeSO$^3$-$ $</td>
<td>via I$^d$</td>
<td>92</td>
<td>$&lt;20$</td>
<td>94</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>via I$^e$ or via II$^e$</td>
<td>90</td>
<td>20-40</td>
<td>97</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>BF$_4^-$</td>
<td>via I$^e$ or via II$^e$</td>
<td>94</td>
<td>20-40</td>
<td>90</td>
<td>20-40</td>
</tr>
<tr>
<td>CF$_3$SO$_3$-$ $</td>
<td>via II$^d$</td>
<td>93</td>
<td>20-40</td>
<td>92</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>BPh$_4^-$</td>
<td>via II$^f$</td>
<td>92</td>
<td>$&lt;20$</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

aAnion source: via I and/or via II (Scheme 3). bIsolated yield. cHalide contents after anion exchange determined by the silver chromate test. dSolvent loading: CH$_3$OH:H$_2$O. eSolvent loading: H$_2$O. fSolvent loading: CH$_3$CN:H$_2$O (9:1).

The prepared ion pairs were dried in a vacuum oven at 60 °C in the presence of desiccant agents and their characterization was confirmed by spectroscopic and spectrometric methods, especially $^1$H NMR, and when necessary unambiguous assignments were made by NOESY experiments at 400 MHz. Moreover, the amount of halide content was determined by a silver chromate test following a similar protocol to that described by Sheldon and co-workers.$^{30}$ Additionally, it should also be considered that the AER used in the exchange can be recycled by treatment with 10% NaOH aqueous solution, and the recovered AER (OH$^-$ form) can be re-utilized for a new anion loading. The chosen strong AER was Amberlyst® A-26 but other similar AERs such Aberlite® IRA-400, which allow the use of aqueous mixtures and non-aqueous solvents, can be used instead.

$^1$H NMR spectroscopy

Imidazolium-based systems form a bridge between the chemistry of ionic liquids (ILs) and anion recognition, notable noncovalent driving forces being a combination of electrostatics and hydrogen bond interactions.$^{6,31}$ Particularly significant is the role of the non-classical (C–H)$^+$⋅⋅⋅anion hydrogen bonds in imidazolium-based anion receptors, sensors and carriers, as well as in ILs, which has sparked a flurry of interest and debate in the last few years. Evidence for hydrogen bonding in the solid phase of the simple 1-ethyl-3-methylimidazolium salt [emim]I was first reported by Seddon and co-workers in 1986,$^{32}$ and later in [emim]A using single-crystal X-ray diffraction analysis,$^{33-35}$ and confirmed in the solution-phase by multinuclear NMR spectroscopy.$^{36}$ Moreover, Ludwig and co-workers reported direct spectroscopic evidence for an enhanced cation-anion interaction driven by (C–H)$^+$⋅⋅⋅anion hydrogen bonds in pure ILs, which gave a stronger the role to hydrogen bonds in imidazolium ILs.$^{19-20}$

Depending on the structure of the imidazolium-based frameworks, other noncovalent intermolecular interactions can also take place between cations and counteranions, a case in point being the usually weaker CH/π noncovalent interactions that can be rather significant for anions
bearing aromatic units, e.g. tetraphenylborate. Thus, the structural study of 1a·BPh₄ ([bmim][BPh₄]) reported by Dupont et al. revealed the presence of (C–H)⁺⋯π hydrogen bonds both in solution phase and solid state. The anion effect has also been examined by Lungwitz and Spange using the representative 1a·A ([bmim]A) ion pairs in dichloromethane as the solvent, which in fact should lower solvation of the ion pairing in favor of contact ion pairs. A hydrogen-bond accepting (HBA) ability scale was then established for varied anions of the (bmim⁺) cation by means of ¹H NMR spectroscopy, at concentrations of 0.02 or 1.8 M, in CD₂Cl₂, and the HBA capacity of anions directly affected chemical shift values in the imidazolium moiety, especially the C(2)-H of the imidazolium ring. As already mentioned, the use of CD₂Cl₂ as a solvent implies minimizing solute-solvent interactions.

The ¹H NMR data obtained from the routine checking of the quaternary heteroaromatic salts [ILs]A provide useful information about the noncovalent interactions between the cations and the counteranions. Following with our work, the ¹H NMR spectral data of 1a·A ([bmim]A) in a selected 0.02 M concentration were registered in CDCl₃ and CD₃CN and the chemical shift values of C(2)-H of the imidazolium ring were compared, as shown in Figure 2. Standard reference values were obtained from samples whose purity had been confirmed by other techniques. As expected, chemical shift values of C(2)-H varied according to the anion, with higher deshielding when a strong hydrogen bond anion binding interaction was established. Excluding 1a·BPh₄ ([bmim][BPh₄]), the proton chemical shift differences were greater in CDCl₃, reaching more than 2 ppm when comparing e.g. AcO⁻ and PF₆⁻, while the differences decreased when using a solvent that enhances the solvation effect such as the nonhydroxylic dipolar CD₃CN (see figure 2).

In contrast, the observed proton NMR chemical shift of 1a·BPh₄ ([bmim][BPh₄]) showed a greater shielding in CDCl₃ for C(2)-H (δH = 4.54 ppm) due to the CH/π interactions with the aromatic units of the anion, while in a dipolar-aprotic solvent such as CD₃CN, this interaction was weakened by solvation (δH = 8.19 ppm). These results are in accordance with the abovementioned in-depth structural study of 1a·BPh₄ ([bmim][BPh₄]) reported by Dupont et al.

The data obtained allowed us to establish a pattern of proton chemical shift values, which was then used to check the effectiveness of halide-for-anion exchange, especially useful for inorganic anions.

In addition, it is well established that the chemical shifts of the acidic C(2)–H protons in the imidazolium motifs are the most sensitive to the nature of the counteranion, solvent polarity and structural factors of imidazolium-based systems such as anion receptors and sensors as well as ILs. In order to compare imidazolium and triazolium cation behaviour, ionic liquids 1a·A and 2b·A were further examined by ¹H NMR in CDCl₃ and CD₃CN at concentrations of 0.002 and 0.02 M to ascertain the influence of the counteranion and the solvent polarity on the heteroaromatic proton chemical shifts of imidazolium and 1,2,3-triazolium cations (see Figure 3 and Table 2). As the counteranion, the basic oxoanion AcO⁻, the halide Cl⁻ and the weakly-
coordinating and charge diffuse PF$_6^-$ anion were selected as representative examples,\textsuperscript{42,43} the results being summarized in Table 2.

![Chemical structure of Bu$^+$ N$^+$ N$^-$ Me$^-\cdot$A$^-$](image)

\textbf{Figure 2.} 1-butyl-1-methylimidazolium salts 1a$\cdot$A ([bmim]A): $^1$H NMR C(2)-H chemical shift at 300MHz of a 0.02 M solution in CDCl$_3$ (●) or CD$_3$CN (■).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
\multicolumn{2}{|c|}{[bmim]$^+$} & \multicolumn{4}{c|}{0.002 M} & \multicolumn{4}{c|}{0.02 M} \\
\hline
$\text{A}^-$ & Solvent & H-2 & H-4 & H-5 & H-2 & H-4 & H-5 & H-2 & H-4 & H-5 \\
\hline
AcO$^-$ & CDCl$_3$ & 11.81 & 7.08 & 7.07 & 11.35 & 7.09 & 7.08 & AcO$^-$ & CDCl$_3$ & 9.91 & 9.60 & 9.60$^a$ & 9.44$^a$ \\
 & CD$_3$CN & 8.93 & 7.34 & 7.31 & 9.25 & 7.35 & 7.32 & CD$_3$CN & 8.61 & 8.43 & 8.89 & 8.61 \\
PF$_6^-$ & CDCl$_3$ & 8.97 & 7.23 & 7.21 & 9.07 & 7.26 & 7.23 & PF$_6^-$ & CDCl$_3$ & 8.71 & 8.59 & 8.84 & 8.74 \\
 & CD$_3$CN & 8.38 & 7.34 & 7.31 & 8.42 & 7.35 & 7.31 & CD$_3$CN & 8.31 & 8.26 & 8.32 & 8.27 \\
\hline
\end{tabular}
\caption{Selected $^1$H NMR (300 MHz) chemical shift values of 1a$\cdot$A ([bmim]A) and 2b$\cdot$A ([BnmTr]A) in CDCl$_3$ and CD$_3$CN at concentrations of 0.02 M and 0.002 M.}
\end{table}

\textsuperscript{a}Unambiguous assignments were made by NOESY-1D (400 MHz).
The tendency of the imidazolium molecular motif in current 1a·A ([bmim]A) ion pairs to form non-classical (C–H)+···anion hydrogen bonds was then qualitatively examined by 1H NMR and the greatest deshielding effect corresponded to the acidic C(2)-H when comparing 1a·AcO or 1a·Cl with 1a·PF$_6$, in both CDCl$_3$ ($\Delta\delta \geq 2$ ppm ) and CD$_3$CN ($\Delta\delta \geq 0.3$ ppm), while differences in proton chemical shifts of C(4)-H and C(5)-H were negligible. In contrast, in quaternary 1,2,3-triazolium salts 2b·A ([BnmTr]A) a significant deshielding of C(4)-H and C(5)-H was observed, although the $\Delta\delta$ (H-4 or H-5) was lower than $\Delta\delta$ (H-2) in the imidazolium cation (see Figure 3 and Table 2).

**Figure 3.** Differences in heterocyclic proton chemical shifts between AcO$^-$ or Cl$^-$ and PF$_6^-$ salts at concentrations of 0.02 and 0.002 M in (a) CDCl$_3$ or (b) CD$_3$CN.

In relation to the solvent and concentration, in CDCl$_3$ we verified that by increasing the dilution the cation-anion interaction was enhanced and consequently higher chemical shift values were obtained at 0.002M than 0.02M, whereas the contrary was observed in CD$_3$CN due to the competitive solvating effect (see Figure 3 and Table 2).
Regarding the anion, both quaternary azolium salts displayed hydrogen-bonding interaction with AcO−, but in CD3CN the triazolium cation showed poor Cl− binding affinity (see Figure 3). It should be noted that the basicity of the AcO− anion could result in the formation of carbene species,44,45 although this was not observed in the experiments carried out.

The results of the present work are in concordance with the anion affinity profile of the azolium units as recognition moieties in abiotic anion receptors. They also confirm that the hydrogen bonding ability and acidity of azolium based ILs should be considered when they are used as solvents, since the interactions with reactants and intermediates could affect the course of the reaction.

Conclusions

Against a pool of quaternary heteroaromatic ionic liquids, the azolium salts 2a·I and 2b·I were chosen to validate the utility of the AER (A− form) method in non-aqueous media for a halide exchanged by assorted anions. It was then confirmed that this simple method is efficient with 1,2,3-triazolium-based ionic liquids 2·X, improving the currently operative procedures of classical counteranion exchange, e.g. 2a·BF4, 2a·PF6 and 2a·CF3SO3 prepared from 2a·I. Recapping the results, the anion loading of the AER (OH− form) with acids, ammonium salts and sodium azide was carried out in water or a hydromethanolic or CH3CN/H2O (9:1) solvent mixture according to the lipophilic nature of the anion source. Then, the anion exchange using the AER (A− form) method in organic solvents was easily applied to the 1,2,3-triazolium salts and the halide-to-anion exchange progressed in excellent to quantitative yields.

On the whole, the AER (A− form) method in organic solvents is a method of choice for exchanging halide anions for a variety of anions in quaternary heteroaromatic salts, simultaneously removing halide impurities, which is often a troublesome task, and minimizing the formation of toxic by-products. In addition, the preparation of a few benzylic azides and diazides was carried out using an AER (N3− form) in organic solvent mixtures such as CH3CN/CH3OH (1:1) and CH3CN/CH2Cl2 (1:1), resulting in a clean and mild protocol with easy work-up. The results of the 1H NMR spectroscopic analysis focus attention on the significance of the charged-assisted (C–H)···anion hydrogen bonds. Thus, a qualitative 1H NMR comparison between 1-butyl-3-methylimidazolium salts and 1-benzyl-3-methyl-1,2,3-triazolium salts has shown that the nature of the azolium motifs modulated their 1H NMR response.

Experimental Section

General. Ion exchanger resin Amberlyst A-26 (Aldrich, OH− form), benzylbromide and benzylchloride together with all acids, ammonium salts, reagents and solvents were purchased from commercial suppliers, unless mentioned otherwise, and used without further purification.
All solvents were reagent grade and methanol and THF were distilled prior to use. 1-butyl-3-methylimidazolium salts 1a·A,1 1-buthyl-3-methyltriazolium iodide 2a·I,15 1-benzyl-3-methyltriazolium iodide 2b·I,15 1,3-bis(bromomethyl)-4-tert-butylbenzene 7,46 and 9,10-bis(chloromethyl)anthracene 847 were prepared according with the literature. 1H NMR spectra were recorded on a Varian Gemini 300 (300 MHz) or Mercury 400 (400 MHz) spectrometers at 298 K. Chemical shifts were referenced and expressed in ppm (δ) relative to the central peak of DMSO-d$_6$ (2.49 ppm), CD$_3$CN (1.94 ppm) and TMS for CDCl$_3$. 13C NMR spectra were recorded on a Varian Gemini 300 (75.4 MHz) or Mercury 400 (100.6 MHz) spectrometer at 298 K. IR spectra were recorded on a Thermo Nicolet Avatar 320 FTIR apparatus. Mass spectrometric analyses were performed by using EI at 70 eV in a Hewlett-Packard spectrometer (HP-5989A model) or by using CI at 120 eV in a Thermo Finnigan TRACE DSQ spectrometer. ESI(+-)MS and ESI(-)-MS mass spectra were obtained on a LC/MSD-TOF (2006) mass spectrometer with a pumping system HPLC Agilent 1100 from Agilent Technologies at Serveis Científico-Tècnics of universitat de Barcelona. Melting points was measured in a Gallenkamp Melting Point Apparatus MPD350.BM2.5 with digital thermoter and are uncorrected. The pH was measured with benchmeter pH1100 (Eutech Instruments), using Hamilton Flushtrode pH electrode for hydroalcoholic solutions.

The amount of halide contents was determined by a silver chromate test following a similar protocol to that described by Sheldon and co-workers.30 An aqueous solution (5 mL) of potassium chromate (5 % p/v in Milli-Q water, 0.257 M) was added to the sample (5-10 mg). To 1 mL of the resulting dark yellow solution was added a minimum amount of silver nitrate aqueous solution (0.24 % p/v in Milli-Q water, 0.014 M). A persistent red suspension of silver chromate would be observed if the sample was free of halide. The minimum measurable amount of silver nitrate aqueous solution was 0.011 mL; consequently, the detection limit is approx. 6 ppm for Cl⁻, 13 ppm for Br⁻ or 20 ppm for I⁻. The halide content was determined at least twice for each sample.

Additionally, the use of alumina and silica columns can leave a low level of residual particulate contamination in ILs1,14 and then, nano-particulates may also be an issue when using strongly basic anion exchange resins (A⁻ form). However, the analysis of possible particulate contamination was beyond the scope of the present study.

**Preparation of the AER (N³⁻ form).** 12 g of wet Amberlyst® A-26 (OH⁻ form) were packed in a glass column and washed with H$_2$O (100 mL). A 10% NaN$_3$ aqueous solution (160 mL, 246 mmol) was passed slowly through the AER (OH⁻ form) until the pH of eluates reached the same value than the original solution (pH~10.25). Then, AER (N$_3$⁻ form) was washed with H$_2$O (50 mL), H$_2$O:CH$_3$OH progressive mixtures (9:1, 7:3, 5:5, 3:7, 1:9; 50 mL of each mixture) and CH$_3$OH:CH$_3$CN progressive mixtures (9:1, 7:3, 5:5; 50 mL of each mixture). The calculated amount of N$_3$⁻ loaded in the resin is 5.8 mmol/g.1

**Benzylazide (4). (a) From benzylchloride.** The AER (N$_3$⁻ form) (12 g, 69.4 mmol of N$_3$⁻) was added to a solution of benzylchloride (1.099 g, 1 mL, 8.68 mmol) in 30 mL of CH$_3$CN:CH$_3$OH
(1:1) solvent mixture, and the suspension was heated under stirring at 40 °C for 2.5 h. The AER was filtered and the solvent was eliminated under vacuum providing the oily pure benzylazide \(4\) (1.069 g, 93% yield). As a caution the product was stored in the freezer until further use.

(b) From benzylbromide. The AER (N\(3^-\) form) (8.7 g , 50.3 mmol of N\(3^-\)) was added to a solution of benzylbromide (1.438 g, 1 mL, 8.40 mmol) in 30 mL of CH\(_3\)CN:CH\(_3\)OH (1:1) solvent mixture, and the suspension was stirred at room temperature for 1.5 h. The AER was filtered and the solvent was eliminated under vacuum, providing the oily pure benzylazide \(4\) (1.040 g, 93% yield). As a caution, the product was stored in the freezer until further use.

IR (NaCl): 3031, 2967, 2860, 1739, 1600, 1323, 1269, 690 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 4.35 (s, 2H), 7.34–7.40 (m, 5H). \(^13\)C NMR (CDCl\(_3\), 75.4 MHz): \(\delta\) 54.85, 128.1, 128.2, 128.8, 135.4.

1,3-bis(Azidomethyl)-4-tert-butylbenzene (5). The AER (N\(3^-\) form) (3.45 g, 20 mmol of N\(3^-\)) was added to a solution of 1,3-bis(bromomethyl)-4-tert-butylbenzene \(7\) (0.400 g, 1.250 mmol) in 25 mL of CH\(_3\)CN:CH\(_3\)OH (1:1) solvent mixture and the suspension was stirred at room temperature for 2 h. Then, the AER was filtered, washed with CH\(_3\)CN:CH\(_3\)OH (1:1) (25 mL) and the solvent was removed under vacuum, to afford the pure diazide \(5\) (0.290 g, 95%) as orange oil. As a caution, the product was stored in the freezer until further use. IR (NaCl): 2967, 2111 (N\(_3\)), 1600, 1323, 1269, 690 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.35 (s, 9H), 4.37 (s, 4H), 7.10 (s, 1H), 7.30 (s, 2H). \(^13\)C NMR (CDCl\(_3\), 75.4 MHz): \(\delta\) 31.2, 34.8, 54.9, 125.0, 125.1, 135.8, 152.7. CIMS \(m/z\) (%): 263 (75) [M+NH\(_4^+\)], 217 (100) [M+H−N\(_2\)]; 189 (74) [M+H−2N\(_2\)].

9,10-bis(Azidomethyl)antracene (6). The AER (N\(3^-\) form) (3.14 g , 18.18 mmol of N\(3^-\)) was added to a solution of 9,10-bis(chloromethyl)antracene \(8\) (0.250 g, 0.909 mmol) in 40 mL of CH\(_3\)CN:CH\(_2\)Cl\(_2\) (1:1) solvent mixture and the suspension was heated under stirring at 40 °C for 7.5 h. The AER was filtered, washed with CH\(_3\)CN:CH\(_2\)Cl\(_2\) (1:1) (25 mL) and the solvent was removed under vacuum, to afford the pure diazide \(6\) (0.290 g, 95%) as orange solid. As a caution, the product was stored in the freezer until further use. mp 107–108 °C. IR (KBr): 3065, 2922, 2075 (N\(_3\)), 1445, 1088, 750 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 5.36 (s, 4H), 7.65 (m, 4H), 8.37 (m, 8H). \(^13\)C NMR (CDCl\(_3\), 75.4 MHz): \(\delta\) 46.4, 124.5, 126.6, 128.1, 130.4.

**Anion loading in the AER (OH\(^-\) form)**

(via I) **Acids as anion source.** 2.5 g (~ 3 cm\(^3\)) of commercial wet strongly basic anion exchange Amberlyst A-26 (OH\(^-\) form) was packed in a glass column (1 cm diameter ) and washed with water, and the column bed was equilibrated progressively with water-methanol mixtures until reaching the selected solvent media used afterwards for anion loading (~ 25 mL of each solvent mixture). A 1% acid solution in the appropriate solvent was passed slowly through the resin until the eluates had the same pH value as the original selected acid solution, and then the resin was washed with solvent until constant pH. The process was carried out at room temperature, using gravity as the driving force.

(via II) **Ammonium salts as anion source.** 2.5 g (~ 3 cm\(^3\)) of commercial wet strongly basic anion exchange Amberlyst A-26 (OH\(^-\) form) was packed in a glass column (1 cm diameter) and washed with water (~ 25 mL). A 1% ammonium salt aqueous solution was passed slowly through the resin until the eluates had the same pH value as the original selected acid solution,
and then the resin was washed with water until constant pH. The process was carried out at room temperature, using gravity as the driving force. In order to load BPh₄⁻ anion, a CH₃CN:H₂O (9:1) solvent mixture was used and the process involves to wash the AER (OH⁻ form) with the same solvent mixture previously to pass the ammonium salt solution.

**Anion exchange: general procedure.** A solution of the triazolium salt (0.5-0.6 mmol) in 10 mL of methanol was passed slowly through a column packed with ~ 3 cm³ of AER (A⁻ form), and then washed with 25 mL of solvent. The combined eluates were evaporated, and the residue obtained was dried in a vacuum oven at 60 °C with P₂O₅ and KOH pellets.

1-Buthyl-3-methyltriazolium acetate (2a·AcO). Iodide exchange of 2a·I (0.110 g, 0.412 mmol) was carried out with AER (AcO⁻ form) following the general procedure described above, and using CH₃OH as solvent. Brown oil (0.081 g, 92% yield). ¹H NMR (300 MHz, CDCl₃): δ 0.96 (t, 3H), 1.38 (m, 2H), 1.94 (s, 3H, AcO), 1.98 (m, 2H), 4.42 (t, 2H), 9.66 (s, 1H), 9.92 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.3, 19.3, 31.1, 40.1, 53.4, 53.6, 131.0, 132.0, 133.5. Iodide content < 20 ppm according silver chromate test.

1-Buthyl-3-methyltriazolium methylsulphonate (2a·MeSO₃). Iodide exchange of 2a·I (0.100 g, 0.374 mmol) was carried out with AER (MeSO₃⁻ form) following the general procedure described above, and using CH₃OH as solvent. Yellow oil (0.081 g, 92% yield). ¹H NMR (300 MHz, CDCl₃): δ 0.97 (t, 3H), 1.40 (m, 2H), 1.99 (m, 2H), 2.76 (s, 3H, MeSO₃), 4.45 (s, 3H), 4.68 (t, 2H), 9.22 (s, 1H), 9.32 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.2, 19.3, 31.2, 39.4, 40.1, 53.5, 131.5, 132.4. Iodide content < 20 ppm according silver chromate test.

1-Buthyl-3-methyltriazolium terephenylborate (2a·BPh₄). Iodide exchange of 2a·I (0.110 g, 0.412 mmol) was carried out with AER (BPh₄⁻ form) following the general procedure described above, and using CH₃OH as solvent. Light brown solid (0.175 g, 92% yield), mp 149-50 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.98 (t, 3H), 1.13 (m, 2H), 1.50 (m, 2H), 3.00 (s, 3H), 3.49 (t, 2H), 5.48 (s, 1H), 5.50 (s, 1H), 6.78 (d, 8H), 6.95 (t, 4H), 7.51 (t, 8H). ¹³C NMR (CDCl₃, 100.6 MHz): δ 13.2, 19.2, 30.8, 38.9, 52.9, 122.0, 125.9, 129.3, 130.3, 135.9, 164.1 (m, C-B). Iodide content < 20 ppm according silver chromate test.

1-Buthyl-3-methyltriazolium hexafluorophosphate (2a·PF₆). Iodide exchange of 2a·I (0.100 g, 0.374 mmol) was carried out with AER (PF₆⁻ form) following the general procedure described above, and using CH₃OH as solvent. Yellow oil (0.096 g, 90% yield). ¹H NMR (300 MHz, CDCl₃): δ 0.98 (t, 3H), 1.40 (m, 2H), 2.00 (m, 2H), 4.38 (s, 3H), 4.60 (t, 2H), 8.59 (s, 1H), 8.63 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.2, 19.3, 31.1, 40.0, 53.8, 130.4, 131.5. NMR spectral data were according with those reported in the literature.¹⁵ Iodide content < 20 ppm according silver chromate test.

1-Buthyl-3-methyltriazolium triflate (2a·CF₃SO₃). Iodide exchange of 2a·I (0.100 g, 0.374 mmol) was carried out with AER (CF₃SO₃⁻ form) following the general procedure described above, and using CH₃OH as solvent. Yellow oil (0.100 g, 93% yield). ¹H NMR (300 MHz, CDCl₃): δ 0.94 (t, 3H), 1.37 (m, 2H), 1.96 (m, 2H), 4.36 (s, 3H), 4.59 (t, 2H), 8.74 (s, 1H), 8.76 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.2, 19.2, 31.2, 40.5, 53.9, 130.9, 131.9, 120.6 (m, C-
F). NMR spectral data were according with those reported in the literature. Iodide content < 20 ppm according silver chromate test.

1-Buthyl-3-methyltriazolium tetrafluoroborate (2a·BF₄). Iodide exchange of 2a·I (0.110 g, 0.412 mmol) was carried out with AER (BF₄⁻ form) following the general procedure described above, and using CH₂OH as solvent. Yellow oil (0.088 g, 94% yield). ¹H NMR (300 MHz, CDCl₃): δ 0.98 (t, 3H), 1.40 (m, 2H), 2.00 (m, 2H), 4.39 (s, 3H), 4.14 (t, 2H), 8.66 (s, 1H), 8.73 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 13.2, 19.3, 31.1, 40.0, 53.7, 130.7, 131.8. NMR spectral data were according with those reported in the literature. Iodide content < 20 ppm according silver chromate test.

1-Benzyl-3-methyltriazolium acetate (2b·AcO). Iodide exchange of 2b·I (0.100 g, 0.332 mmol) was carried out with AER (AcO⁻ form) following the general procedure described above, and using CH₂OH as solvent. Colorless oil (0.077 g, quantitative yield). ¹H NMR (300 MHz, CDCl₃): δ 1.98 (s, 3H, AcO), 4.40 (s, 3H), 5.82 (s, 2H), 7.42 (m, 3H), 7.47 (m, 2H), 9.44 (s, 1H), 9.60 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 39.9, 56.6, 57.3, 129.0, 129.1, 129.5, 130.9, 132.0, 132.5, 133.5. Iodide content < 20 ppm according silver chromate test.

1-Benzyl-3-methyltriazolium methylsulphonate (2b·MeSO₃). Iodide exchange of 2b·I (0.100 g, 0.332 mmol) was carried out with AER (MeSO₃⁻ form) following the general procedure described above, and using CH₂OH as solvent. Colorless oil (0.084 g, 94% yield). ¹H NMR (300 MHz, CDCl₃): δ 2.78 (s, 3H, MeSO₃), 4.43 (s, 3H), 5.87 (s, 2H), 7.40 (m, 3H), 7.52 (m, 2H), 9.25 (s, 1H), 9.29 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 39.5, 40.2, 57.1, 129.2, 129.3, 129.7, 131.4, 131.8, 132.6. Iodide content < 20 ppm according silver chromate test.

1-Benzyl-3-methyltriazolium hexafluorophosphate (2b·PF₆). Iodide exchange of 2b·I (0.100 g, 0.332 mmol) was carried out with AER (PF₆⁻ form) following the general procedure described above, and using CH₂OH as solvent. White solid (0.103 g, 97% yield). mp 89-90 ºC. ¹H NMR (300 MHz, CDCl₃): δ 3.37 (s, 3H), 5.75 (s, 2H), 7.44 (m, 5H), 8.74 (s, 1H), 8.84 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 40.1, 57.2, 129.3, 129.4, 129.7, 130.5, 131.4, 131.8, 132.6. Iodide content < 20 ppm according silver chromate test.

1-Benzyl-3-methyltriazolium triflate (2b·CF₃SO₃). Iodide exchange of 2b·I (0.100 g, 0.332 mmol) was carried out with AER (CF₃SO₃⁻ form) following the general procedure described above, and using CH₂OH as solvent. Colorless oil (0.099 g, 92% yield). ¹H NMR (300 MHz, CDCl₃): δ 4.37 (s, 3H), 5.75 (s, 2H), 7.43 (m, 3H), 7.48 (m, 2H), 8.71 (s, 1H), 8.78 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 40.5, 57.5, 129.4, 129.5, 130.0, 130.8, 131.2, 132.2, 120.5 (m, C-F). NMR spectral data were according with those reported in the literature. Iodide content < 20 ppm according silver chromate test.

1-Benzyl-3-methyltriazolium tetrafluoroborate (2b·BF₄). Iodide exchange of 2b·I (0.100 g, 0.332 mmol) was carried out with AER (BF₄⁻ form) following the general procedure described above, and using CH₂OH as solvent. White solid (0.078 g, 90% yield). mp 74-5 ºC. ¹H NMR (300 MHz, CDCl₃): δ 4.33 (s, 3H), 5.72 (s, 2H), 7.40 (m, 3H), 7.46 (m, 2H), 8.51 (s, 1H), 8.55 (s, 1H). ¹³C NMR (CDCl₃, 75.4 MHz): δ 40.1, 57.3, 129.3, 129.4, 129.8, 130.7, 131.5, 132.0.
NMR spectral data were according with those reported in the literature.\textsuperscript{15} Iodide content < 20 ppm according silver chromate test.

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