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Electronic Effects of *para*-Substitution on the Melting Points of TAAILs

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Abstract: Owing to numerous new applications, the interest in "task-specific" ionic liquids increased significantly over the last decade. But, unfortunately, the imidazolium-based ionic liquids (by far the most frequently used cations) have serious limitations when it comes to modifications of their properties. The new generation of ionic liquids, called tunable aryl–alkyl ionic liquids (TAAILs), replaces one of the two alkyl chains on the imidazolium ring with an aryl ring which allows a large degree of functionalization. Inductive, mesomeric, and steric effects as well as potentially also π–π and π–π$^+$ interactions provide a wide range of possibilities to tune this new class of ILs. We investigated the influence of electron-withdrawing and -donating substituents at the *para*-position of the aryl ring (NO_2, Cl, Br, EtO(CO), H, Me, OEt, OMe) by studying the changes in the melting points of the corresponding bromide and bis(trifluoromethanesulfonyl)imide, ($N(Tf)_2^-$), salts. In addition, we calculated (B3LYP/6-311++G(d,p)) the different charge distributions of substituted 1-aryl-3-propyl-imidazolium cations to understand the experimentally observed effects. The results indicated that the presence of electron-donating and -withdrawing groups leads to strong polarization effects in the cations.

Keywords: computational chemistry · electronic effects · electrostatic interactions · ionic liquids · taail

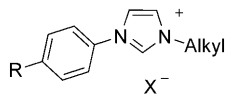
Introduction

Since their discovery at the beginning of the 20th century, ionic liquids have come a long way to become a class of high performance materials with huge potential for various applications.[1] In the middle of the 20th century, up to the 1970s, first-generation ionic liquids were investigated in aluminium-plating processes.[2–5]

The next steps towards a wide applicability of ionic liquids were the development of water- and air-stable ionic liquids with, for example, BF_4^- and PF_6^- counterions and task-specific ionic liquids (TSILs), which were developed individually with specific problems in mind, for example, in organic synthesis.[6–8]

Right now, there are many special applications that demand new tunable ionic liquids, like the electrodeposition of semiconducting materials and metals,[9–13] catalytic and stoichiometric reactions,[14–21] or even wood processing and pharmaceutical applications.[22–25]

Lately, research efforts have concentrated more on the development of new anions and only very few new cations have been published.[8,26–28] Recently, we introduced a new class of imidazolium-based cations and their salts, the aryl–alkyl imidazolium salts (TAAILs, Scheme 1).[29] Owing to the combination of sp^2 and sp^3 carbon substituents in TAAILs and the interaction of the phenyl π-system with the imidazolium core, the possibilities for variations and fine-tuning are far greater than in the common TSILs. In addition, they might allow the study of π–π and π–π$^+$ interactions as recently discussed for similar systems,[30,31] or function as an anion receptor.[32,33]



Scheme 1. Tunable Aryl-Alkyl Ionic Liquids (TAAILs)

In our previous work concerning TAAILs, we kept the aryl part constant (2,4,6-trimethylphenyl, mesityl) and studied the influence of different alkyl chains (C_1–C_8, C_{11}, C_{14})

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and anions (Br^-, BF_4^-, PF_6^-, $N(Tf)_2^-$) on their melting points and properties.[34]

For the mesityl system, we observed a large anion effect, which in some cases turned out to be as much as a melting point difference of more than 150 °C. It was remarkable that, with increasing alkyl chain length, a nearly linear decrease in the melting points of the bromide salts was observed. The decomposition temperatures of the mesityl TAAILs were found to be dominated by anion effects and to be nearly independent of the alkyl chain length. Those with bromide anions decomposed at lower temperatures compared to the bis(trifluoromethylsulfonyl)imide ($N(Tf)_2^-$) salts, which decompose at significantly higher temperatures than the conventional ionic liquids.

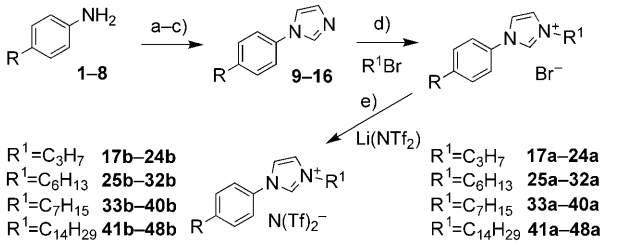
Calculations of the charge distribution in TAAILs indicated that compared to conventional imidazolium-based cations like ethylmethylimidazolium (EMIM) or butylmethyl imidazolium (BMIM), the new TAAILs exhibit a higher positive charge on the imidazolium core. Therefore, we were interested in finding out how much the electronic effects of the substituents on the phenyl ring will influence the charge distribution in the imidazolium ring as well as the general properties of the resulting ionic liquids.

Results and Discussion

Herein, we report the results for electron-withdrawing- and electron-donating groups in the *para*-position of the phenyl ring, but restricted the length of the linear alkyl chains to a propyl, hexyl, heptyl, and tetradecyl chain, and the anions to bromide and ($N(Tf)_2^-$).

The synthesis is described in Scheme 2. To evaluate the substituent effect we looked at the melting point and the ^1H and ^{13}C NMR shifts, and we calculated the electrostatic surface potentials (ESPs) to assess the electronic structure.

As shown in Scheme 2, the synthesis starts from substituted anilines leading to the corresponding 1-phenyl-1H-imidazoles. Then the 1-phenyl-1H-imidazole derivatives are alkylated by alkyl bromides and the resulting bromide salts are converted into the ($N(Tf)_2^-$) salts by anion metathesis.



Scheme 2. Scheme of the synthetic approach, a) glyoxal, MeOH (60 mL), RT; b) NH_4Cl, CH_2O, MeOH (400 mL), 1 h reflux; c) H_3PO_4, 4 h reflux; d) THF, 80-110 °C; e) H_2O/CH_2Cl_2 RT. R = NO_2 (**1**; **9**; **17a,b**; **25a,b**; **33a,b**; **41a,b**), R = Cl (**2**; **10**; **18a,b**; **26a,b**; **34a,b**; **42a,b**), R = Br (**3**; **11**; **19a,b**; **27a,b**; **35a,b**; **43a,b**), R = EtO(CO) (**4**; **12**; **20a,b**; **28a,b**; **36a,b**; **44a,b**), H (**5**; **13**; **21a,b**; **29a,b**; **37a,b**; **45a,b**), R = Me (**6**; **14**; **22a,b**; **30a**; **38a**; **46a,b**), R = OEt (**7**; **15**; **23a,b**; **31a,b**; **39a**; **47a,b**), R = OMe (**8**; **16**; **24a,b**; **32a,b**; **40a**; **48a,b**). THF = tetrahydrofuran.

The influence of the substituents can be clearly shown by comparing the melting points and phase transitions of salts with the same alkyl chain length, but different *para*-substitution. According to Figure 1 and Table 1, electron-withdrawing groups lead to higher melting points, whilst electron-donating groups lead to room-temperature ionic liquids (RT-TAAILs), even for the bromide salts.

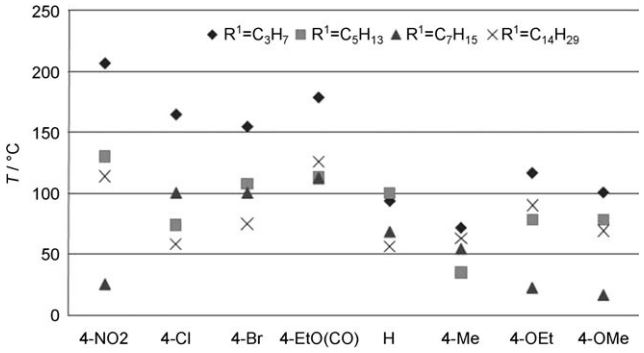


Figure 1. Melting points of the bromide salts.

Table 1. Phase transition temperatures of the ($N(Tf)_2^-$) salts.

R	$R^1 = C_3H_7$	$R^1 = C_6H_{13}$	$R^1 = C_7H_{15}$	$R^1 = C_{14}H_{29}$
NO_2	67	[a]	−45	35
Cl	22	[a]	21	36
Br	20	30	26	36
EtO(CO)	21	[a]	22	−28
H	23	27	[a]	13
Me	42		–	30
OEt	−51[b]	−53[b]; 27	–	34
OMe	56	[a]	–	21

[a] liquid at room temperature. [b] glass transition.

There is little difference between the *para*-chloro- and *para*-bromo-substituted imidazolium salts for both anions. This is also true for the alkoxy-substituted salts, which show nearly the same behavior with the only exception being the ($N(Tf)_2^-$) salt with a propyl chain. The methoxy-substituted compound shows an unexpectedly high melting point whereas the ethoxy-substituted salt exhibits only a glass-transition point, no melting point could be found. With respect to the bromide salts, the ester, nitro, and halo substituents lead to ILs with higher melting points. The melting points for the bromide salts with propyl and tetradecyl chains show similar trends with a typical melting point difference of circa 100 °C. In contrast, the alkyl chains of intermediate chain lengths show a different behavior; there, one can find almost the same melting points (Br, EtO(CO), Me) or differences of 60–90 °C (NO_2, OMe).

Although the melting points are strikingly different, the NMR spectra do not show remarkable differences. It is well

known that the hydrogen atom at the C2 carbon atom in imidazolium ions is the most-acidic proton, and this fact is widely exploited in metal–organic chemistry. Deprotonation at the C2 carbon leads to the formation of N-heterocyclic carbenes which are frequently used ligands in many complexes.[35–37] It is also easily identifiable in the ^{1}H- and ^{13}C NMR spectra. Therefore, we chose these signals to probe the change in the electronic structure of the imidazolium core and observed changes of up to 0.3 ppm in the ^{1}H NMR shifts, and, in most cases, less than $\Delta\delta = 1$ ppm for the ^{13}C NMR shifts. In addition, there is virtually no influence of the alkyl chain on the observed NMR shifts, which is in agreement with the results of the previous study on the mesityl-substituted system, where we did not observe any changes in the NMR spectrum in the presence of different chain lengths and anions.

In conclusion, the melting points show a considerable substituent influence as well as the ^{1}H and ^{13}C NMR shifts (see the Supporting Information) of the C2 imidazolium position. Therefore, we started to investigate the nature of the substituent effect using density functional theory calculations. As we did not observe a significant effect of the different alkyl chains on the NMR spectra, we chose to restrict the calculations to the shortest chain, the 1-phenyl-3-propylimidazolium cations.

To visualize the electronic effects, we calculated the electrostatic surface potentials (ESP) of all of the substituted 1-aryl-3-propyl-imidazolium cations. In Figure 2, only the ESPs for the *para*-nitro- and *para*-methoxy-substituted cations are compared, all other ESPs are given in the Supporting Information. The ESPs are plotted for two different potentials, a wide range (0.05–0.235; Figure 2a, b) and a smaller one (0.135–0.175; Figure 2c, d).

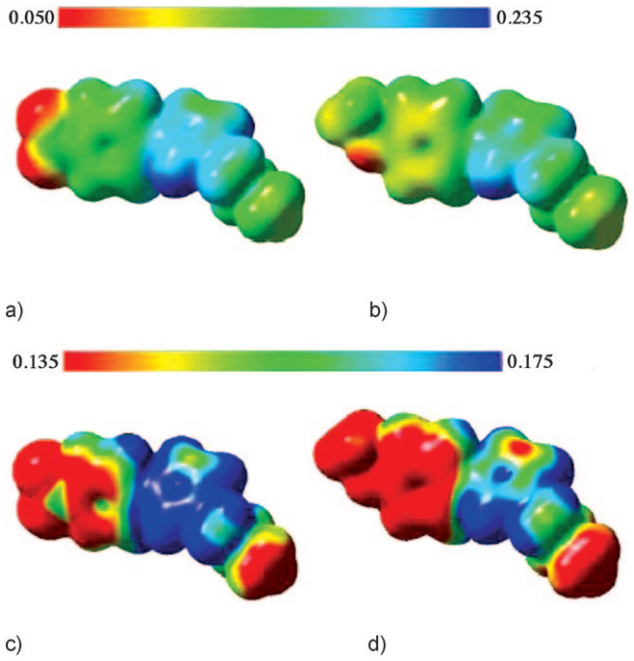


Figure 2. ESP representations for 1-(4-nitrophenyl)-3-propyl-1*H*-imidazolium (a, c) and 1-(4-methoxyphenyl)-3-propyl-1*H*-imidazolium (b, d)

The ESP representation of the *para*-nitro-substituted cation (Figure 2a) visualizes the negative polarization (red) of the electron-withdrawing nitro group and the positive polarization (blue) of the imidazolium C2 position. The *para*-methoxy-substituted compound (Figure 2b) exhibits visible differences in the polarization of the phenyl ring, as can be seen by the color coding of the ring ("green" vs. "yellow"). In accordance with our expectations, the phenyl ring of the *para*-nitro-substituted compound shows a larger positive potential (Figure 2a, "green") and the donating methoxy group results in a smaller potential (Figure 2b, "yellow") on the phenyl ring.

Figures 2c and d demonstrate the different polarization of the imidazolium cores and that the electronic effect of the substituent is not restricted to the aryl ring, but also influences the conjugated π-system of the imidazolium core. From the ESP representations, it becomes clear that the cation is polarized along the aromatic rings. Although we were aware of the potential problems involved, we decided to calculate the dipole moments to check whether they also show a substituent effect (for these results, see Supporting Information).

Conclusions

We synthesized and characterized substituted 1-phenyl-3-alkyl-1*H*-imidazolium bromide and ($N(Tf)_2^-$) salts and investigated their melting points. There is a significant substituent influence on the melting point, which can be best explained by polarization effects. In addition, we were able to calculate the electron distribution in the different substituted 1-phenyl-3-propyl-1*H*-imidazolium cations. We can conclude that the considered macroscopic properties of the new TAAIL*s* are predominantly determined by the electronic character of the substituent on the phenyl ring.

Experimental Section

General

NMR spectra were recorded at 20 °C on a Bruker-AC-300P NMR spectrometer operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C. [D$_6$]DMSO was used as solvent and special care was taken to measure at the same concentration to be able to compare the chemical shifts. These shifts are reported relative to $Si(CH_3)_4$ (= 0 ppm) for ^{1}H- and ^{13}C NMR spectra. Elemental analysis was performed on a EUROVEKTOR Hekatech EA3000, for DSC measurements a Setaram DSC121 was used (scan rate 5 K min^{-1}). A more detailed description of the syntheses and the analytical characterization is presented in the Supporting Information. Owing to the large number of synthesized compounds, we chose to report only one example of each class here, all other syntheses are described in the Supporting Information.

Preparation of the Phenyl Imidazoles

The aniline derivative (0.3 mol) is dissolved in 50–60 mL methanol, slowly mixed with 34.2 mL aqueous glyoxal solution (40%), and stirred at room temperature overnight. This reaction leads to a solid precipitate

or a highly viscous substance. After diluting the reaction mixture with 400 mL methanol, 32.1 g ammonium chloride and 48 mL formaldehyde solution (37% in water) are added. The reaction mixture is heated under reflux for 1 h and the resulting dark solution is allowed to cool down and is mixed with 14 mL phosphoric acid. Finally, the reaction mixture is heated for 4 h under reflux. 2/3 of the solvent is removed by evaporation under reduced pressure, and the resulting crude solution is mixed with 200–300 mL ice water. Potassium hydroxide solution (40%) is added until pH 9 is reached. The aqueous phase is extracted 4 times with dichloromethane and the combined organic phases are washed with water, saturated sodium chloride solution, and dried over magnesium sulphate. To isolate the crude product, the solvent is removed under reduced pressure after filtration. The product is either purified by Kugelrohr distillation or recrystallization from ethyl acetate.

Ethyl 4-(1H-imidazol-1-yl)benzoate **12**

Following the general synthetic procedure, 0.1 mol ethyl-4-aminobenzoate is used. The resulting product is recrystallized from 20 mL ethyl acetate to give a solid product. Yield: 15.93 g (74%); ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.37 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, CH$_3$), 4.36 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, CH$_2$), 7.18 (s, 1H, NCHCHN), 7.31 (s, 1H, NCHCHN), 7.42 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH), 7.90 (s, 1H, NCHN), 8.11 ppm (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 14.2, 61.1, 117.6, 120.4, 129.2, 130.9, 131.2, 135.3, 140.5, 165.3 ppm; elemental analysis: calcd (%) for $C_{12}H_{12}N_2O_2$ (216.24): C 66.65, H 5.59, N 12.96; found: C 66.42, H 5.54, N 12.57.

The synthetic procedures and analytical characterizations of compounds **9**–**16** are given in the Supporting Information.

Preparation of the Imidazolium Bromides

Alkylation of the 1-*N*-substituted imidazoles is carried out in an ACE pressure tube, within a temperature range of 80–110 °C. 1 Equivalent of the substituted imidazole derivative is dissolved in 10 mL tetrahydrofuran and a slight excess (1.1 equiv) of the bromoalkane is added. The reaction mixture is heated for 8 to 10 hours. By washing with tetrahydrofuran the resulting crude product is purified and dried under vacuum.

*1-(4-(Ethoxycarbonyl)phenyl)-3-propyl-1H-imidazolium bromide **20a***

Following the general synthetic procedure, 4.6 mmol (1.00 g) ethyl 4-(1H-imidazol-1-yl)benzoate, and 5.5 mmol (0.68 g) 1-bromopropane are dissolved in THF and heated for 20 h at 95 °C. Yield: 0.838 g (52%); m.p.: 179 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.97 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH$_2$CH$_2$C*H*$_3$), 1.42 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, OCH$_2$C*H*$_3$), 1.99 (hept, $^3J_{H,H}$ = 7.3 Hz, 2H, NCH$_2$C*H*$_2$), 4.25 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, NC*H*$_2$), 4.72 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, OCH$_2$), 8.00 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.12 (s, 1H, NCHCHN), 8.25 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.48 (s, 1H, NCHCHN), 10.02 ppm (s, 1H, NC*H*N); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 10.5, 14.1, 22.6, 51.0, 61.3, 121.0, 121.9, 123.5, 130.7, 131.0, 135.8, 138.1, 164.6 ppm; elemental analysis: calcd (%) for $C_{15}H_{19}BrN_2O_2$·0.35H$_2$O: C 52.14, H 5.75, N 8.11; found: C 52.19, H 5.79, N 8.11.

*1-(4-(Ethoxycarbonyl)phenyl)-3-hexyl-1H-imidazolium bromide **28a***

Following the general synthetic procedure, 1.62 mmol (0.35 g) ethyl 4-(1H-imidazol-1-yl)benzoate, and 1.78 mmol (0.294 g) 1-bromohexane are dissolved in THF and heated for 20 h at 95 °C. Yield: 0.417 g (68%); m.p.: 113 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.89 (m, 3H, CH$_3$), 1.32 (m, 6H, 3xCH$_2$), 1.37 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH$_3$), 1.90 (m, 2H, CH$_2$), 4.26 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, N-CH$_2$), 4.38 (q, $^3J_{H,H}$ = 7.4 Hz, 2H, OCH$_2$), 7.97 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH), 8.10 (s, 1H, NCHCHN), 8.22 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH), 8.44 (s, 1H, NCHCHN), 9.97 ppm (s, 1H, NCHCHN); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 13.9, 14.1, 21.9, 25.2, 29.0, 30.6, 49.5, 61.3, 120.9, 121.9, 123.5, 130.7, 130.9, 135.8, 138.1, 164.6 ppm; elemental analysis: calcd. (%) for $C_{18}H_{25}BrN_2O_2$: C 56.70, H 6.61, N 7.35; found: C 56.48, H 6.67, N 7.25.

*1-(4-(ethoxycarbonyl)phenyl)-3-heptyl-1H-imidazolium bromide **36a***

Following the general synthetic procedure, 4.60 mmol (1.00 g) ethyl 4-(1H-imidazol-1-yl)benzoate, and 5.50 mmol (0.99 g) 1-bromoheptane are dissolved in THF and heated for 20 h at 95 °C. Yield: 1.14 g (62%); m.p.: 112 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.89 (m, 3H; CH$_3$), 1.32 (m, 8H, 4xCH$_2$), 1.37 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH$_3$), 1.90 (m, 2H, CH$_2$), 4.26 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, NCH$_2$), 4.38 (q, 2H, $^3J_{H,H}$ = 7.4 Hz, OCH$_2$), 7.97 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH), 8.10 (s, 1H, NCHCHN), 8.22 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, ArH), 8.44 (s, 1H, NCHCHN), 9.96 ppm (s, 1H, NCHN); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 13.9, 14.1, 21.9, 25.5, 28.1, 29. 1, 31.0, 49.5, 61.3, 120.9, 121.9, 123.5, 130.7, 130.9, 135.8, 138.1, 164.6 ppm; elemental analysis: calcd. (%) for $C_{19}H_{27}BrN_2O_2$: C 57.72, H 6.88, N 7.09; found: C 57.37, H 6.96, N 7.06.

*1-(4-(ethoxycarbonyl)phenyl)-3-tetradecyl-1H-imidazolium bromide **44a***

Following the general synthetic procedure, 4.60 mmol (1.00 g) ethyl 4-(1H-imidazol-1-yl)benzoate, and 5.50 mmol (1.50 g) 1-bromotetradecane are dissolved in tetrahydrofuran and heated for 20 h at 95 °C. Yield: 1.40 g (61%); m.p.: 126 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.85 (t, $^3J_{H,H}$ = 6.9 Hz, 3H, CH$_2$CH$_2$C*H*$_3$), 1.27 (m, 22H, alkyl−C*H*$_2$), 1.40 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 1.93 (m, 2H, NCH$_2$C*H*$_2$), 4.25 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, NC*H*$_2$), 4.39 (q, $^3J_{H,H}$ = 7.1 Hz, 2H; OC*H*$_2$), 7.97 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.10 (s, 1H, NCHCHN), 8.23 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.45 (s, 1H, NCHCHN), 9.96 ppm (s, 1H, NC*H*N); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 13.9, 14.1, 22.1, 25.5, 28.4, 28.7, 28.8, 28.9, 29.0, 29.0, 31.3, 49.5, 61.3, 120.9, 121.9, 123.5, 130.7, 131.0, 135.8, 138.1, 164.6 ppm; elemental analysis: calcd. (%) for $C_{26}H_{41}BrN_2O_2$: C 63.28, H 8.37, N 5.68; found: C 63.28, H 8.42, N 5.76.

A detailed description of the preparation and analytical characterization for all bromide salts **17a**–**48a** is given in the Supporting Information.

Preparation of the Corresponding Bis(trifluoromethanesulfonyl)imides

After completely dissolving 1 equivalent of imidazolium bromide in water, or, for the longer alkyl chains, a water/methanol mixture, 1.1 equivalents of lithium bis(trifluoromethansulfonyl)imide is added. This leads to a biphasic system where dichloromethane is added for better phase separation. The organic phase is separated from the aqueous phase by a separatory funnel and the aqueous phase is washed twice with dichloromethane. The combined organic phases are dried over MgSO$_4$, filtered, and evaporated in a rotary evaporator under vacuum. The resulting ionic liquid is dried under vacuum.

*1-(4-(Ethoxycarbonyl)phenyl)-3-propyl-1H-imidazolium bis(trifluoromethanesulfonyl) imide **20b***

Following the general synthetic procedure, 1.47 mmol (0.50 g) 1-(4-ethoxycarbonyl-phenyl)-3-propyl-1*H*-imidazolium bromide and 1.64 mmol (0.47 g) lithium bis(trifluoromethane-sulfonyl)imide are dissolved in a biphasic system consisting of 50 mL water/20 mL dichloromethane and stirred at room temperature. Yield: 0.73 g (92%); m.p.: 67 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 0.98 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, C*H*$_3$), 1.98 (hept, 2H, C*H*$_2$), 4.23 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, NC*H*$_2$), 4.48 (q, $^3J_{H,H}$ = 7.1 Hz, 2H, CH$_2$), 8.00 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, ArH), 8.11 (s, 1H, NCHCHN), 8.27 (d, $^3J_{H,H}$ = 8.8 Hz, 2H; ArH), 8.48 (s, 1H, NCHCHN), 9.99 ppm (s, 1H, NCHCHN), ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): δ = 10.5, 14.1, 22.6, 51.0, 61.3, 119.5, 121.0, 121.6, 123.5, 130.7, 131.0, 135.8, 164.6 ppm; elemental analysis: calcd (%) for $C_{17}H_{19}F_6N_3O_6S_2$: C 37.85, H 3.55, N 7.79, S 11.89; found C 38.07, H 3.20, N 7.92, S 11.74.

A detailed description of the preparation and analytical characterization for all bis(trifluoromethanesulfonyl)imide salts **17b**–**48b** is given in the Supporting Information.

Computational Details

Density functional (DFT) calculations were carried out on the 1-aryl-3-propyl-imidazolium cations of the prepared imidazolium salts. Geometry optimizations of the structures were performed using the B3LYP hybrid density functional combined with the split valence triple-ζ (TZ) basis set 6–311++G(d,p).[38–42] No symmetry or internal coordinate constraints

were applied during optimizations. Vibrational frequency calculations were carried out for all structures to verify them as true minima by the absence of imaginary frequencies. Charges were computed using the CHELP-G procedure using Breneman radii, except for Br, where the Van der Waals radius of 1.85 Å was employed.[43–44] As molecular electronic dipole moments for cations are origin dependant, they were calculated with the origin placed at the centre of nuclear charge. We are aware of the problems associated with this approach to the description of ionic liquids (see the Supporting Information).[45] Electrostatic surface potentials were calculated from the SCF density and plotted on an isodensity surface of 0.004 using GaussView3.[46] All calculations were carried out using the GAUSSIAN 03 program package.[47]

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