

Electronic Supplementary Information

Probing the impact of N3-substituted alkyl chain on the electronic environment of the cation and the anion for 1,3-dialkylimidazolium ionic liquids

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Synthesis of ionic liquids

[C₈C₄Im]Br

1-Butylimidazole was placed in a three necked round-bottomed flask fitted with an air condenser topped with a blue silica tube to avoid introducing of moisture. 0.9 Equivalent of 1-bromooctane was added into the system drop wise with stirring at 70 °C. The reaction was allowed to proceed for 48-72 h. The mixture was then washed with ethyl acetate three times to remove unreacted 1-butylimidazole. The desired product, [C₈C₄Im]Br, was firstly dried using a rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a pale yellow liquid.^{1,2}

¹H NMR δ_H (400Hz, DMSO-*d*₆), 0.88 (m, 6H), 1.22 (m, 12H), 1.77 (m, 4H), 4.17 (m, 4H), 7.84 (s, 2H), 9.35 (s, 1H).

[C₈C₄Im][BF₄]

[C₈C₄Im]Br was firstly dissolved in deionised water and then transferred to a three necked round-bottomed flask fitted with a water condenser topped with a blue silica tube. 1.2 Equivalent of sodium tetrafluoroborate was dissolved in deionised water firstly and then added drop wise into the system. The reaction mixture was then stirred at 70 °C for 72 h. After cooling down, the lower phase was collected and washed with iced deionised water three times. The desired [C₈C₄Im][BF₄] was then dried firstly under rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a colourless liquid.³

¹H NMR δ_H (400Hz, DMSO-*d*₆), 0.90 (m, 6H), 1.24 (m, 12H), 1.77 (m, 4H), 4.15 (m, 4H), 7.79 (s, 2H), 9.19 (s, 1H).

[C₈C₄Im][PF₆]

[C₈C₄Pip]Br was dissolved in deionised water firstly and then placed into a three-neck round bottomed flask. Potassium hexafluorophosphate (1.2 molar equivalents) was dissolved in deionised water and then added into the reaction system by dropping wise. The reaction was conducted under iced bath for 12 h with stirring. Dichloromethane was added into the mixture to aid the collection of the lower phase. After separation, the lower phase was washed with deionised water by at least five times (the solubility of potassium hexafluorophosphate in water is low). The desired [C₈C₄Im][PF₆] was firstly dried under rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a yellow liquid.⁴

¹H NMR δ_H (400Hz, DMSO-*d*₆), 0.90 (m, 6H), 1.24 (m, 12H), 1.78 (m, 4H), 4.15 (m, 4H), 7.76 (s, 2H), 9.16 (s, 1H).

Nomenclature

The correct nomenclature for [C₈C₄Im]⁺ is 1-butyl-3-octylimidazolium, since according to IUPAC, the two alkyl groups should be named in alphabetic order. This is also applicable for [C₈C₁Im]⁺, which is the abbreviation for 1-methyl-3-octylimidazolium.

However, if we focus on the two families of ionic liquids, the nomenclature should be 1-alkyl-3-butylimidazolium for [C_{*n*}C₄Im]⁺ and 1-alkyl-3-methylimidazolium for [C_{*n*}C₁Im]⁺, respectively.

In this study, N1 refers to the nitrogen atom which reacts with alkyl halide during synthesis; N3 represents the nitrogen atom with the original alkyl group from N-alkylimidazole. This assignment aims not to bring ambiguity and to keep consistency with previous works in the field (especially those including 1-butyl-3-methylimidazolium and 1-butyl-3-ethylimidazolium).

Fitting model

A four-component model for C 1s spectrum was developed previously in our group in year of 2011,⁵ including C², C^{4,5}, C^{6,7} and C_{aliphatic}. C² represents the carbon atom bonded directly to two nitrogen; C^{4,5} refers to the other two carbon within the imidazolium ring; C^{6,7} is assigned to the two carbons bonded directly to nitrogen; C_{aliphatic} includes the remaining carbon atoms bonded to carbon and hydrogen only. The area ratio of these four components is constrained to 0.4: 0.8: 1: 3.5, taking into account a 20% of the shake-up deduction for the delocalised imidazolium signals.⁵ A satisfactory fitting can be obtained using the above constraint, as shown in Figure S1, a representative sample in this paper, [C₈C₄Im][PF₆].

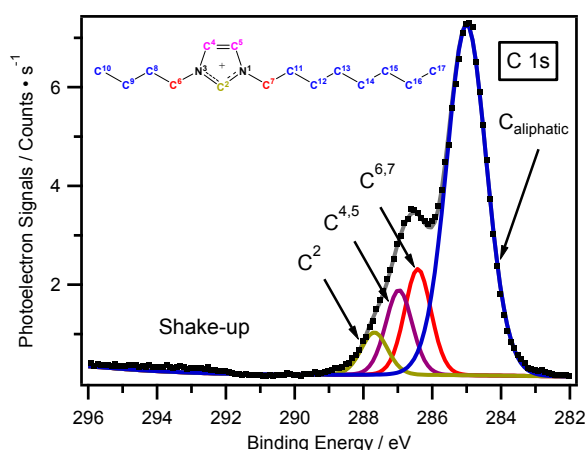


Figure S1 C 1s XP spectrum with fittings for [C₈C₄Im][PF₆]. A four-component model is used for the fitting: C², C^{4,5}, C^{6,7} and C_{aliphatic} 1s (C⁸ onwards).

Later in the year of 2019, our group has modified this model, since we have found evidence that the binding energy of C^{4,5} should be lower than that of C^{6,7}, as demonstrated in Figure 1.⁶

The C 1s spectrum can be also fitted using a five-component model, as illustrated in Figure S2. Apart from C², C^{4,5} and C^{6,7}, the aliphatic carbons can be divided into two components: C_{aliphatic} represents seven aliphatic carbons within the octyl group; C_{butyl} refers to three alkyl carbons present in the butyl group. As the C_{butyl} component is located closer to the cation headgroup, it is expected that this component should show slightly higher binding energy, compared to that of C_{aliphatic}. After doing the similar constraint as stated above, a satisfactory fitting can be obtained.

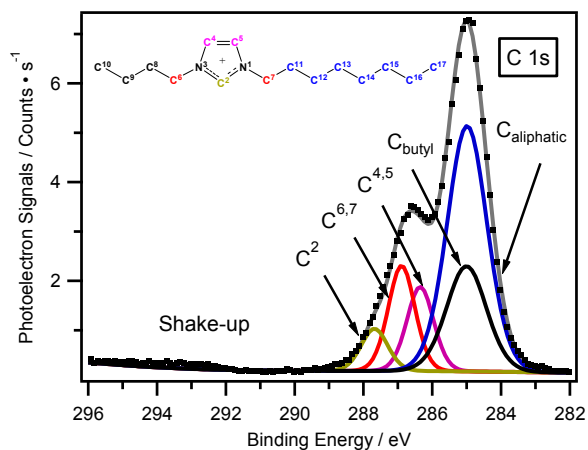


Figure S2 C 1s XP spectrum with fittings for $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$. A five-component model is used for the fitting: C^2 , $\text{C}^{4,5}$, $\text{C}^{6,7}$, $\text{C}_{\text{butyl}} 1\text{s}$ (C^8 to C^{10}) and $\text{C}_{\text{aliphatic}} 1\text{s}$ (C^{11} onwards).

It must be noted that by using these three fitting models, it brings no deviation to $\text{C}_{\text{aliphatic}}$ binding energy.

Survey spectrum

Figure S3a shows the Survey XP spectrum for a representative sample in this study, $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$. Firstly, it is concluded that all signals expected from the structure of this ionic liquid can be observed in the spectrum, including F 1s, N 1s, C 1s, as well as P 2p which is the most sensitive orbital for phosphorus. Apart from those, the P 2s peak is also observed. Paralleled to those photoelectron peaks, C KLL and F KLL auger lines are recorded as well. Meanwhile, there is no signal from oxygen and silicon, which are considered as common impurities present in ionic liquids. It indicates that this ionic liquid is of high purity.

XP spectra

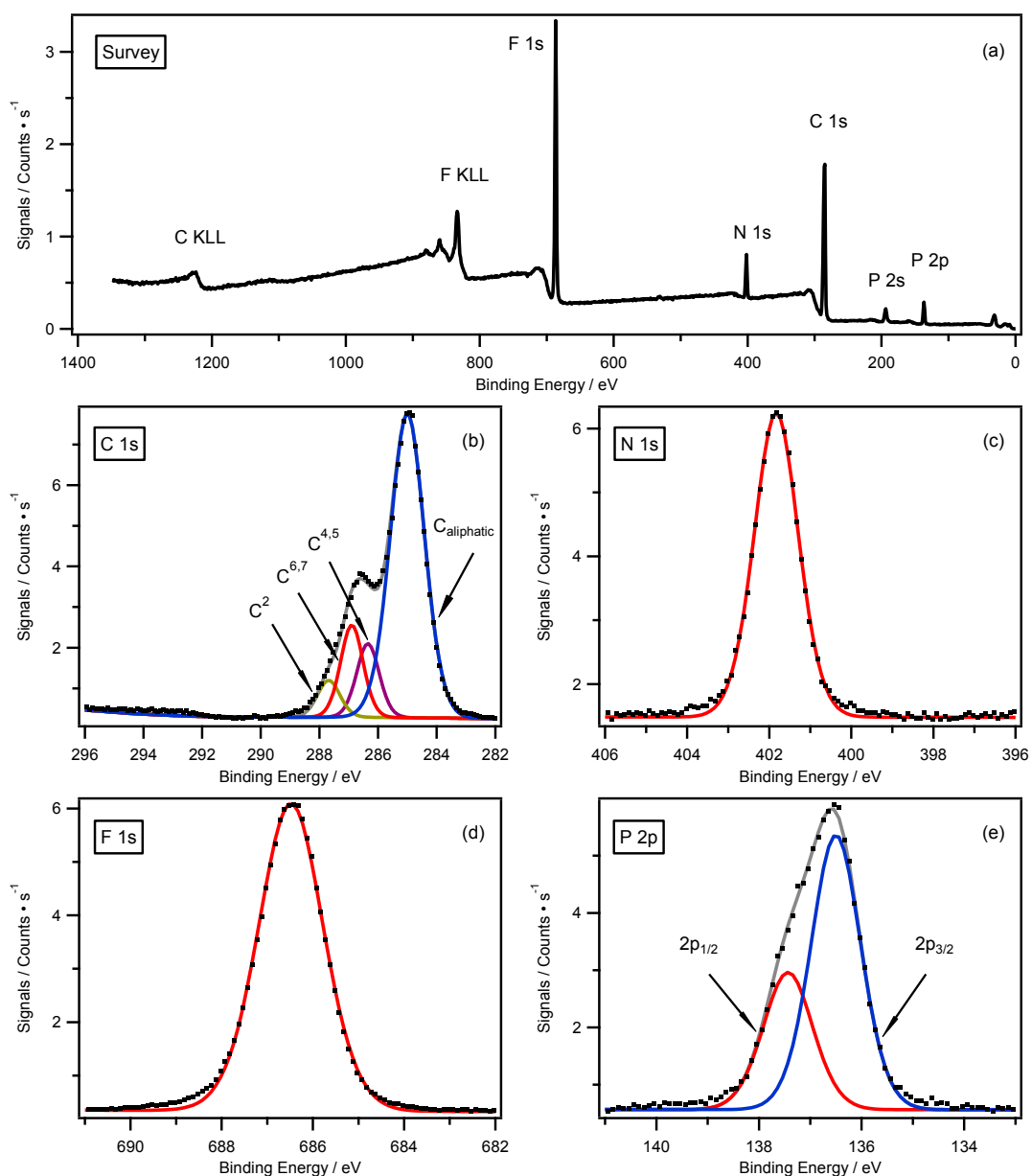


Figure S3 XPS spectra of all elements for $[C_8C_4Im][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) P 2p.

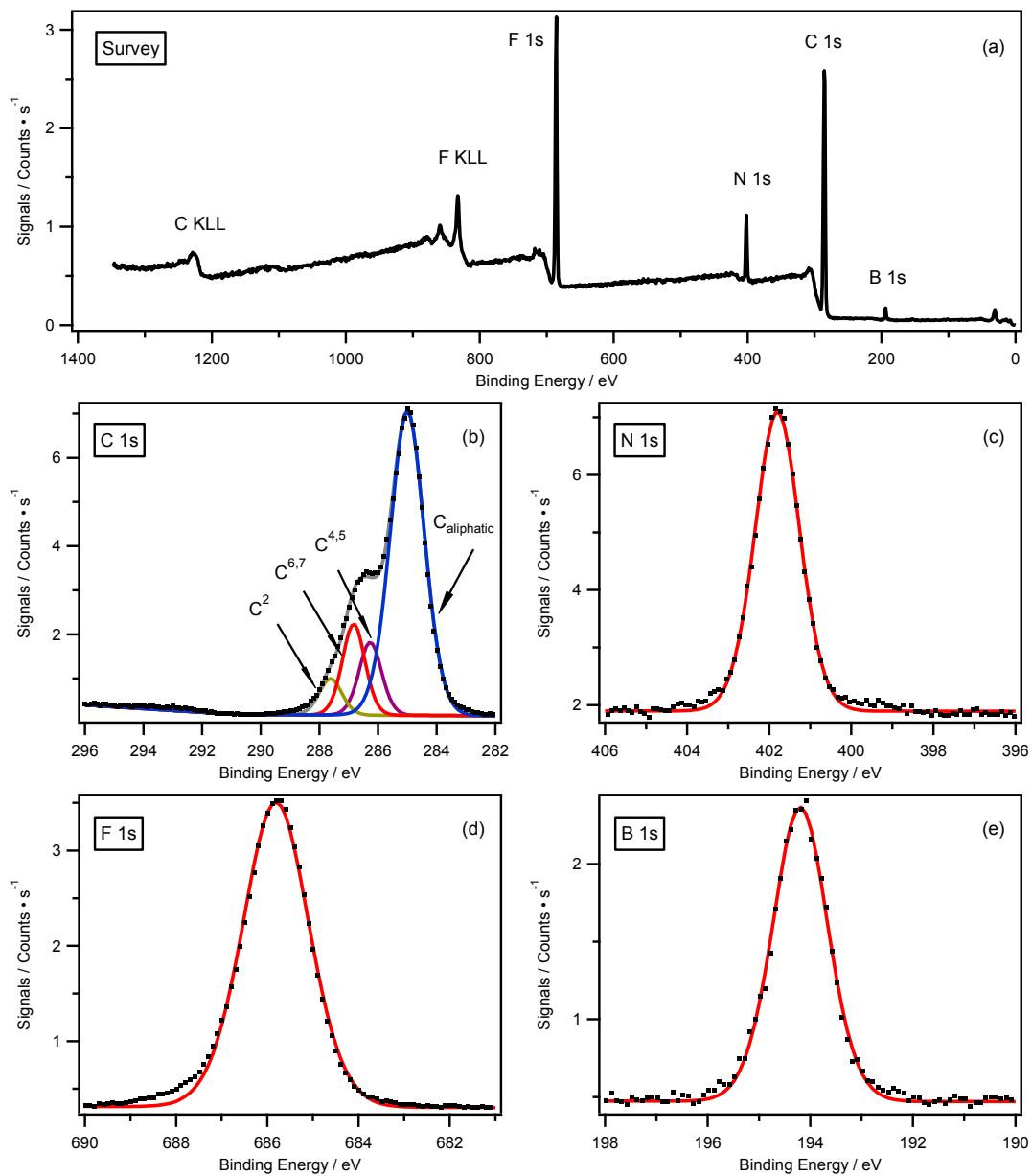


Figure S4 XPS spectra of all elements for $[C_8C_4Im][BF_4]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) B 1s.

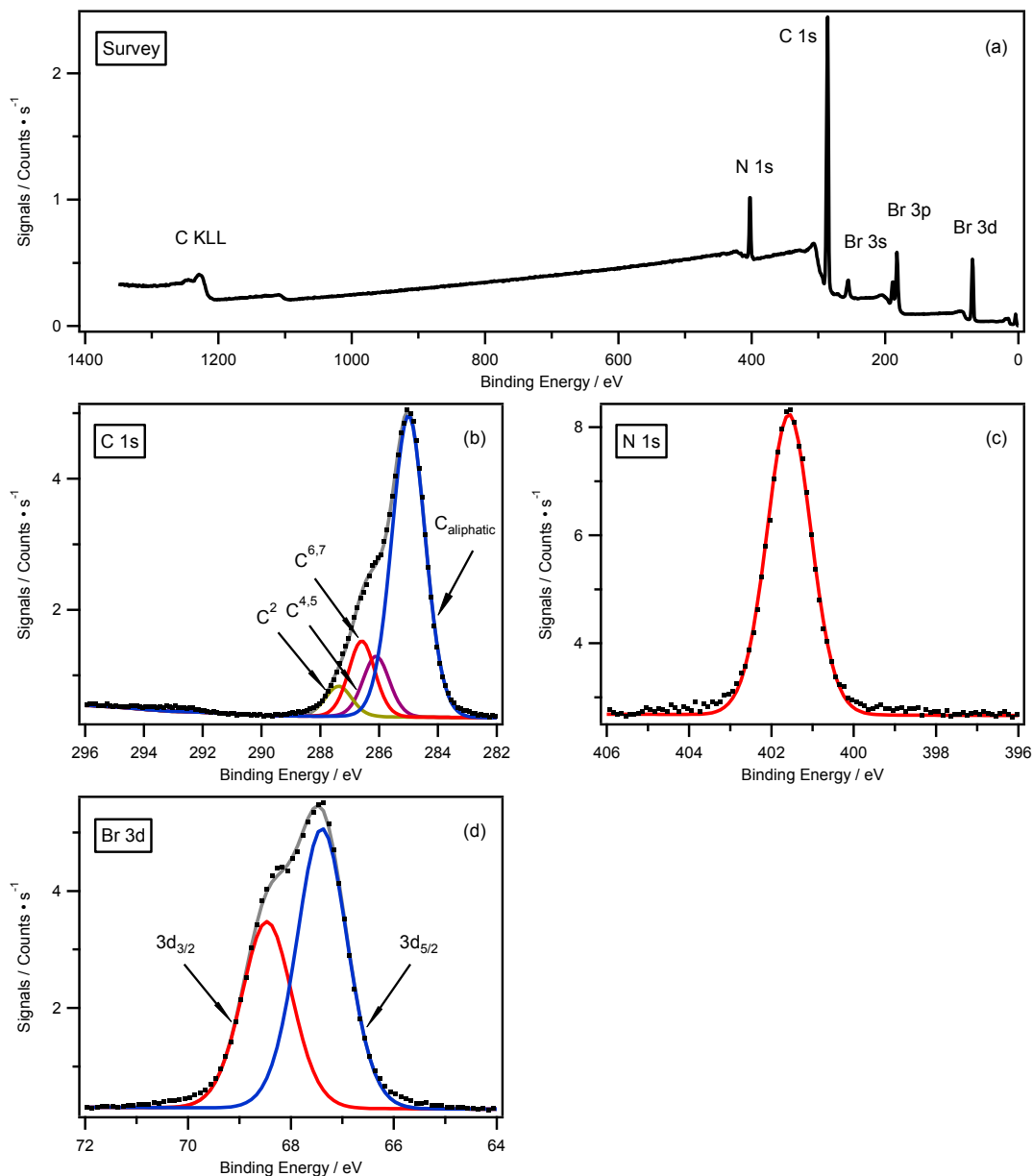


Figure S5 XPS spectra of all elements for $[C_8C_4Im]Br$: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

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