

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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Abstract

In this study, X-ray photoelectron spectroscopy is used to probe the impact of the N3-substituted alkyl group on the electronic environment of the cation and the anion by comparing two types of imidazolium cations, 1-alkyl-3-butyliimidazolium and 1-alkyl-3-methyliimidazolium. Due to the more intense inductive effect changing from methyl to butyl, the electronic environment of the cationic nitrogen can be significantly affected, which is reflected on a shift of N 1s binding energy. The magnitude of the binding energy shift is found more pronounced in the case of the less basic anion and inversely proportional to the basicity of the anion. The increase of the N3-substituted alkyl chain length can also influence the charge-transfer effect from the anion to the cation. It gives rise to a change in electronic environment of the anion. Such an impact is found concentrated on the anion-based component bearing more negative point charges.

Keywords: N3-substituent; Interactions; Inductive effect; Cation-anion distance

Introduction

Over the past two decades, attentions to imidazolium ionic liquids have been mainly focused on 1-alkyl-3-methyliimidazolium ($[C_nC_1Im]^+$) cation.¹⁻³ By changing either the N1-substituted alkyl chain length or the type of the anion, it is feasible to tune the physicochemical properties of ionic liquids.^{4, 5} It allows 'design' of ionic liquids for specific functions.⁶ To achieve this final goal, it always requires the prediction of ionic liquids properties. Hence, the interaction between the cation and the anion, which has been considered as a key factor determining the physicochemical properties of ionic liquids,⁴ must be properly understood. On the other hand, the cation symmetry has also been probed to impact the physicochemical properties of 1,3-dialkylimidazolium ionic liquids. Given the total carbon number of the substituent, by increasing the N3-substituted alkyl chain length, it causes slight lowering of the viscosity and density of ionic liquids.⁷ To date, many works have been conducted in the field, indicating the effect of N1-bonded alkyl chain length on the cation-anion interactions. However, few studies have focused on the impact of the N3-substituted alkyl group. It raises an open question: How does the N3-substituted alkyl chain impact the electronic environment of the cation and the anion?

X-ray photoelectron spectroscopy (XPS) has been accepted as an effective method able to investigate ionic liquids,⁸⁻¹⁰ in particularly to illustrate surface composition,^{9, 10} surface enrichment^{11, 12} and electronic environment of ionic liquids.¹³ The anion basicity can significantly impact the electronic environment of the cationic component;¹⁴ whilst the cation may also influence the electronic environment of the anion-based component.¹⁵ The subtle change in electronic environment of a component contained in ionic liquids may be reflected on the shift of binding energy. In specific for imidazolium ionic liquids, XPS investigations have provided insights into the effect N1-substituted alkyl chain length on the electronic environment of both cations and anions.¹⁶

Unfortunately, it only causes subtle binding energy shift, which is within the error of XPS. However, as has been reported in literature, variation of alkyl chain length on both sides should have a significant effect on the magnitude of charge-transfer.¹⁷ As a result, we extended such a scope herein, aiming to probe the effect of the N3-substituted alkyl chain length upon the cation-anion interactions, by comparing two types of cations, 1-alkyl-3-butylimidazolium ($[C_nC_4Im]^+$) and $[C_nC_1Im]^+$.

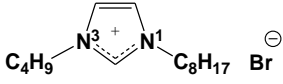
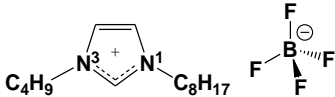
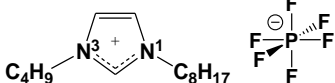
In this work, XPS is used to probe the impact of N3-substituted alkyl group on the cation-anion interactions by comparing two cations, $[C_8C_4Im]^+$ versus $[C_8C_1Im]^+$, with three commonly used anions. The impact of the N3-substituted alkyl group on the electronic environment of the cationic nitrogen is compared. It shows that by varying the alkyl group from methyl to butyl, significant effect on the electronic environment of the cationic nitrogen can be observed. The magnitude of binding energy shift for the three anion families follows a trend, which is inversely proportional to the basicity of the anion. On the other hand, the increase of alkyl chain length on N3 position may also affect the electronic environment of the anion. Such an effect is found concentrated on the anionic component bearing more point charges. However, the impact magnitude is also inversely proportional to the basicity of the anion.

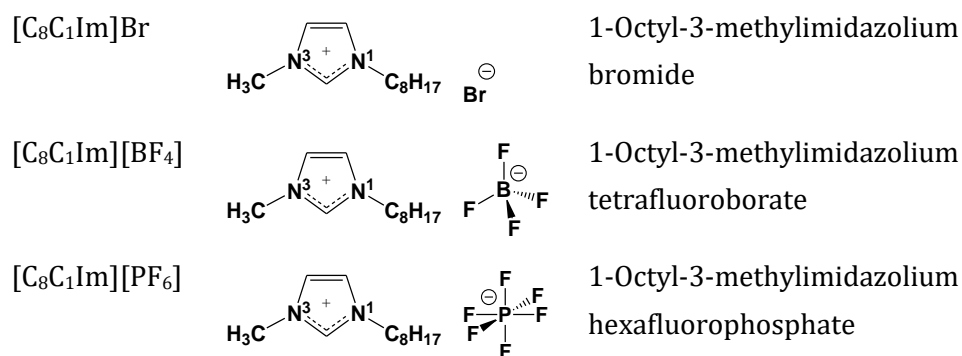
Experimental

Materials

All chemicals were purchased from Sigma Aldrich and were used as received. The three $[C_8C_4Im]^+$ ionic liquids were prepared in our laboratory using established synthetic protocols. NMR data were recorded on a JEOL 400YH spectrometer as solutions in DMSO- d_6 . The synthesis procedures and the results including NMR data, survey and high resolution XP spectra for all the three ionic liquids can be found in detail in Electronic Supplementary Information. It should be emphasised that the synthesis and XPS characterisation of $[C_8C_1Im]^+$ ionic liquids, *i.e.* $[C_8C_1Im]Br$, $[C_8C_1Im][BF_4]$ and $[C_8C_1Im][PF_6]$, were not conducted herein but can be found in a previous work in our group.¹⁸ Table 1 lists the structures of all six ionic liquids.

Table 1 Ionic liquids studied in this paper.

Abbreviation	Structure	Name
$[C_8C_4Im]Br$		1-Octyl-3-butylimidazolium bromide
$[C_8C_4Im][BF_4]$		1-Octyl-3-butylimidazolium tetrafluoroborate
$[C_8C_4Im][PF_6]$		1-Octyl-3-butylimidazolium hexafluorophosphate



Note: The discussion on the nomenclature of $[\text{C}_8\text{C}_4\text{Im}]^+$ and $[\text{C}_8\text{C}_1\text{Im}]^+$ can be found in detail in Electronic Supplementary Information.

XPS Data Collection

XPS experiment was conducted using a PHI Quantera II spectrometer employing a focused, monochromated Al K_α source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD) with an X-ray incident angle of 30° (relative to the surface normal).

All ionic liquids were purified under schlinkline at 60°C for at least 12 h. The ionic liquid sample was placed as a droplet on a stainless sample holder and then transferred into a load-lock of XPS instrument. Pumping was carried out to achieve the pressure at approximately 10^{-4} mbar and maintained overnight before transferring to the main analytical chamber. For all the three liquid samples, charge neutralisation is not necessary. When analysing ionic liquid samples, the pressure is found to be below 1×10^{-8} mbar. It ensures the removal of all volatile impurities,^{19, 20} such as water. Consequently, data derived from XPS are reliable to give comparable information.

XPS Data Analysis

CasaXPS software was used for data interpretation. A spline linear background subtraction was used. Peaks were fitted using GL (30) lineshapes: a combination of a Gaussian (70%) and Lorentzian (30%).^{21, 22} The relative sensitive factors for all elements are taken from literature.²¹

All XP spectra were normalised to the fitted area of cationic N 1s peak for $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$, in order to aid visual interpretations, simply because all ionic liquids studied in this paper contain two nitrogen atoms. Charge corrections for all XP spectra were conducted by referencing the aliphatic C 1s component to 285.0 eV.¹⁶ It must be noted that the experimental error associated with XPS is of the order ± 0.1 eV; therefore, any claimed binding energy shift should be no less than 0.2 eV.

Results and discussion

Surface composition

In order to confirm the purity of the three $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids, surface composition has been calculated based upon **quantitative** analysis from XPS. Table 2 lists the surface composition for all three ionic liquids. In order to give comparable

information, the nominal stoichiometry is also calculated from the empirical formulae and included. It concludes that the surface composition is the same with the nominal stoichiometry, for each of the ionic liquid, taking into account the error of the **quantitative** analysis of XPS.

Table 2 Surface composition and nominal stoichiometry for all $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids.

Ionic Liquids	RSF ²¹	C 1s	N 1s	F 1s	B 1s	P 2p	Br 3d
		0.278	0.477	1.000	0.159	0.486	1.055
$[\text{C}_8\text{C}_4\text{Im}]\text{Br}$	Measured	15.3	1.8				0.9
	(Nominal)	(15.0)	(2.0)				(1.0)
$[\text{C}_8\text{C}_4\text{Im}][\text{BF}_4]$	Measured	15.3	1.8	3.9	1.0		
	(Nominal)	(15.0)	(2.0)	(4.0)	(1.0)		
$[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$	Measured	15.2	1.8	6.0		1.0	
	(Nominal)	(15.0)	(2.0)	(6.0)		(1.0)	

Electronic environment of the C 1s region: Fitting model

An established four-component fitting model has been **recently modified** for the C 1s region of $[\text{C}_8\text{C}_1\text{Im}]^+$ ionic liquids.²³ By simply amending the appropriate weighting of the four components, it is also found applicable for $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids. Figure 1 shows the C 1s spectrum with fittings for $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$, as well as the structure with atom-numbering of the cation. The four components are named as 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.¹⁶ A satisfactory fitting can be obtained using the above constraint. This fitting model is also applicable for $[\text{C}_8\text{C}_4\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_4\text{Im}]\text{Br}$. **A more detailed discussion about C 1s fitting can be found in Electronic Supplementary Information.**

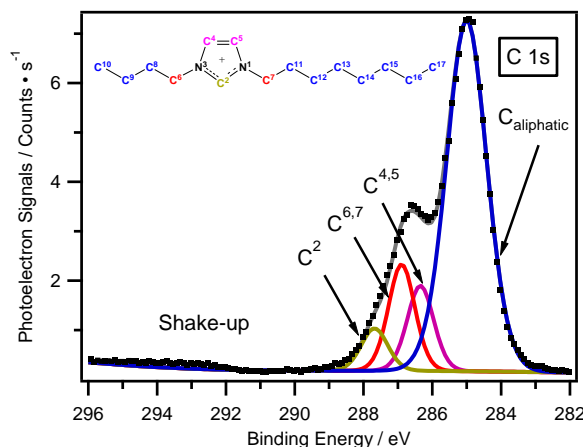


Figure 1 C 1s XP spectrum with fittings for $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$. A four-component model is

used for the fitting: C², C^{4,5}, C^{6,7} and C_{aliphatic} 1s (C⁸ onwards).

Impact of N3-substituted alkyl chain on the electronic environment of the cation

Cation-anion interactions in 1,3-dialkylimidazolium ionic liquids may be affected by the type¹¹ and/or the length^{24, 25} of the substituent bonded to the imidazolium cation. Previous XPS investigations have concluded that by varying the length of N1-substituted alkyl chain, the change in electronic environment of the cationic nitrogen and all anion-based components may not be noticeably measured by XPS.^{16, 26} **However, the variation of alkyl chain length on both sides may have a more noticeable impact on the magnitude of charge-transfer.**

Figure 2 shows a comparison of the N 1s high resolution spectra between [C₈C₄Im][PF₆] and [C₈C₁Im][PF₆]. At first glance, a more than 0.2 eV shift to lower binding energy is observed for the N 1s peak of [C₈C₄Im][PF₆], which is larger than the experimental error of XPS,²² indicating that there has been a noticeable change in electronic environment of the cationic nitrogen by increasing the N3-substituted alkyl chain length. The decrease in N 1s binding energy of [C₈C₄Im][PF₆] suggests that the nitrogen centre is less positively charged, compared to that of [C₈C₁Im][PF₆]. It indicates that by switching the methyl group to the butyl group on N3 position, a significant increase in electron density on the nitrogen centre is caused. The larger magnitude of binding energy shift is ascribed to the fact that for the less basic anion, *i.e.* [PF₆]⁻,^{27, 28} there is a more intense inductive effect from the alkyl substituent towards the cation headgroup, due to the weak charge-transfer effect from the anion to the cation.²⁹ Consequently, when increasing the N3-substituted alkyl chain length, a more significant change in N 1s binding energy can be observed. Apparently, increasing the N3-substituted alkyl chain length can affect the electronic environment of the cationic nitrogen.

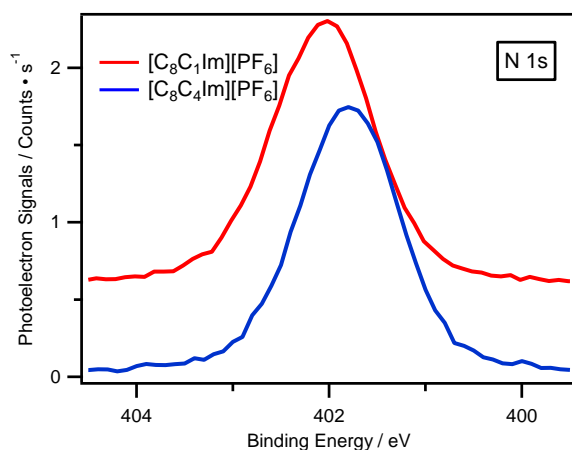


Figure 2 N 1s XP spectra for [C₈C₁Im][PF₆] and [C₈C₄Im][PF₆].

A similar trend is also observed for a moderate basic anion, *i.e.* [BF₄]⁻, when comparing N 1s XP spectra of [C₈C₄Im][BF₄] and [C₈C₁Im][BF₄], as illustrated in Figure 3a.

However, the magnitude of binding energy shift is smaller. It has been reported that there is a linear relationship between charge-transfer and the Kamlet-Taft hydrogen bond accepting ability (β) of the anion.^{26, 30, 31} The less basic anion such as $[\text{PF}_6]^-$ transfers less charge to the cation; the opposite is also true for more basic anions such as halides. This can be also used to explain the smaller binding energy shift observed in the case of $[\text{BF}_4]^-$ ionic liquids. $[\text{BF}_4]^-$ transfers more negative charges to the cation than $[\text{PF}_6]^-$, leading to a less intense inductive effect from alkyl chain to the cation headgroup. As a result, a smaller magnitude of binding energy shift is observed.

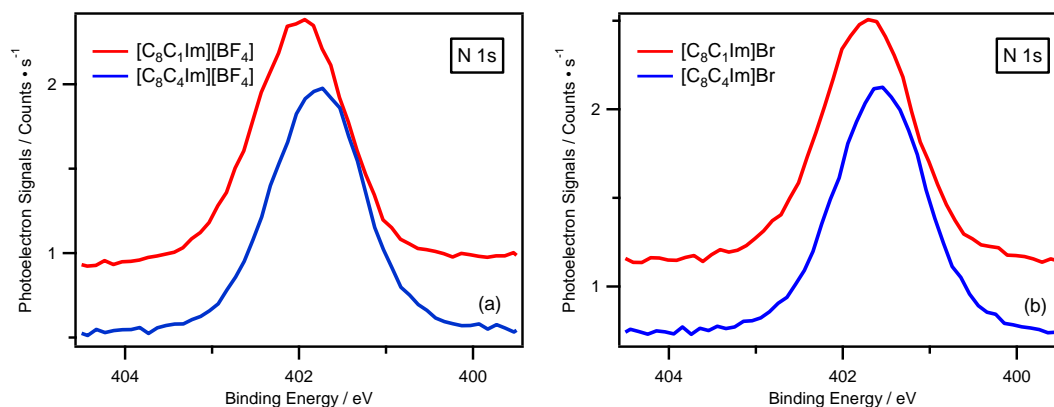


Figure 3 N 1s XPS spectra for $[\text{C}_8\text{C}_1\text{Im}]^+$ and $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids: (a) $[\text{BF}_4]^-$ and (b) Br^- .

For a more basic anion, *i.e.* Br^- , since cations and anions are tightly paired, it leads to a negligible inductive effect from the alkyl substituent to the cation headgroup. Therefore, when increasing the length of alkyl chain on N3 position, it only causes subtle change in electronic environment to the cation. As shown in Figure 3b, the binding energies of N 1s of $[\text{C}_8\text{C}_4\text{Im}]\text{Br}$ is only 0.1 eV smaller than that of $[\text{C}_8\text{C}_1\text{Im}]\text{Br}$. However, such a 0.1 eV shift falls into the experimental error of XPS.

Impact of N3-substituted alkyl chain on the electronic environment of the anion

From another point of view, when increasing the alkyl chain length on N3 position, the inductive effect becomes more intense, which can increase of electron density of the nitrogen centre. It may subsequently influence the electronic environment of the C2 atom, which is bonded directly to the two nitrogen atoms. Since the predominant interaction between the anion and the imidazolium cation are located on H-C2 position,²⁹ the charge-transfer effect from the anion to the cation may be subsequently weakened, giving rise to a more negatively charged anion.

As shown in Figure 4a, a 0.3 eV shift to lower value is measured, when comparing F 1s spectra between $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$. It must be noted that the P $2p_{3/2}$ binding energy also shifts slightly towards lower value. However, the shift is found within the experimental error, as illustrated in Figure 4b. By carefully considering the point charges calculated by other research groups,^{32,33} it

indicates that the six fluorine atoms bear more negative point charges than the central phosphorus atom. It explains the fact that the weakening in charge-transfer effect is more noticeably reflected on F 1s spectrum than P 2p spectrum. It suggests that the N3-substituted alkyl chain length can also affect the electronic environment of the anion.

The weakening of the charge-transfer may be also due to the increase of the distance between the cation and the anion. When increasing the alkyl chain length on N3 position, it significantly increases the cation-anion distance,¹⁷ which can surely shield the negative point charges transferred from the anion to the cation, leaving the anion being more negatively charged.

Meanwhile, over a certain critical alkyl length threshold, ionic liquids can be considered as nano-structured materials, forming polar and nonpolar regions through hydrogen bonds.³⁴ It has been reported that imidazolium ionic liquids could be described as supramolecules in which polar network (the cation headgroup and the anion) was permeated by nonpolar domains (alkyl side chains). When switching from $[\text{C}_8\text{C}_1\text{Im}]^+$ to $[\text{C}_8\text{C}_4\text{Im}]^+$, the increase in size of the nonpolar domain gives rise to the disorder/stretching of the polar network, leading to a weak interaction between the anion and the cation headgroup.¹⁷ As a result, the anion should be left with higher electron density.

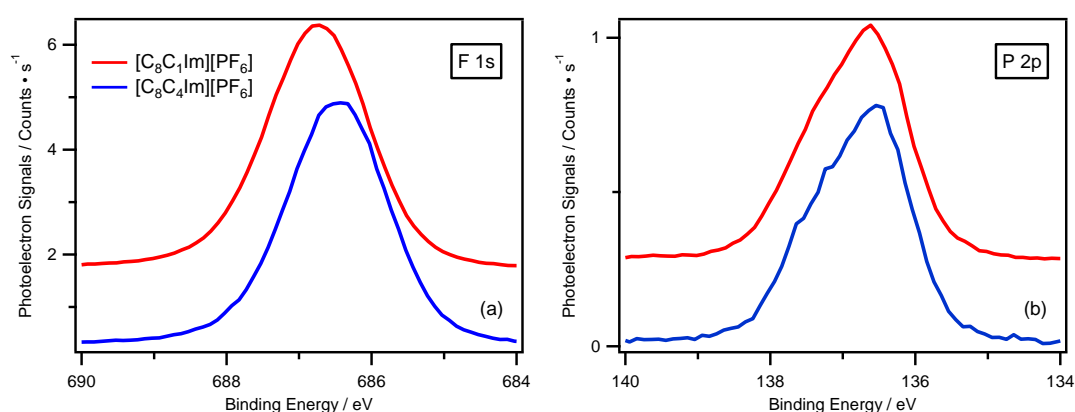


Figure 4 XP spectra for $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$ and $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$: (a) F 1s and (b) P 2p.

A similar trend can also be observed for $[\text{BF}_4]^-$, as demonstrated in Figure 5. The impact upon the anion is also concentrated on F 1s component, with a 0.2 eV binding energy shift, as the negative point charges are distributed over four fluorine atoms.^{35,36}

The reason for the smaller magnitude of the binding energy shift may lie in that in the case of $[\text{BF}_4]^-$, the charge-transfer effect is relative strong, causing a less intense inductive effect from the alkyl chain towards the cation headgroup. When changing from $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ to $[\text{C}_8\text{C}_4\text{Im}][\text{BF}_4]$, the shielding on the interaction between the cation and the anion is less pronounced than that in the case of $[\text{PF}_6]^-$. As a result, the magnitude of the change in electronic environment for the anion is smaller.

From another point of view, it is proposed that the strength and directionality of

the hydrogen-bonding may also impact the charge-transfer effect. For fluorinated anions, the predominant cation-anion interactions lie in the hydrogen bond between -F and C2-proton. Therefore, the distance of these two atoms can significantly affect the strength of the hydrogen bonding. Due to the relative short distance between the above two atoms,^{37, 38} the charge-transfer effect in the case of $[\text{BF}_4]^-$ should be more intense, leading to the stronger cation-anion interactions.

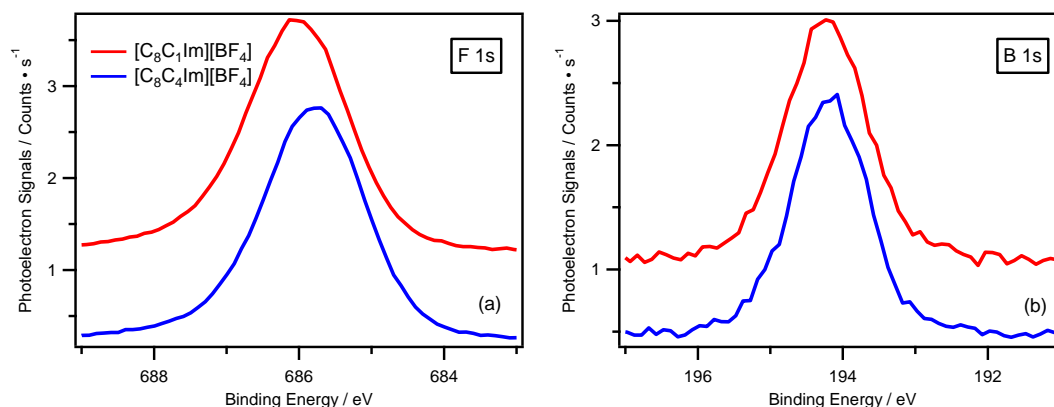


Figure 5 XP spectra for $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ and $[\text{C}_8\text{C}_4\text{Im}][\text{BF}_4]$: (a) F 1s and (b) B 1s.

For Br^- , the magnitude of the change is further weakened. It is found that the change in N3-substituted alkyl chain cannot noticeably affect the electronic environment of the anion. As shown in Table 3, the Br $3d_{5/2}$ binding energy of $[\text{C}_8\text{C}_4\text{Im}]\text{Br}$ is **only** 0.1 eV lower than that of $[\text{C}_8\text{C}_1\text{Im}]\text{Br}$. Considering the experimental error of XPS, these two binding energies are identical.

Figure 6 summarises the shift in binding energy for cationic N 1s and each anion-based component between $[\text{C}_8\text{C}_1\text{Im}]^+$ and $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids for all the three employed anions. It concludes that the length of the N3-substituted alkyl chain can significantly impact the electronic environment of both the cation and the anion. Such an effect is more pronounced in the case of the less basic anion. The magnitude of the impact is found inversely proportional to the basicity of the anion, following the trend as $[\text{PF}_6]^- > [\text{BF}_4]^- > \text{Br}^-$.

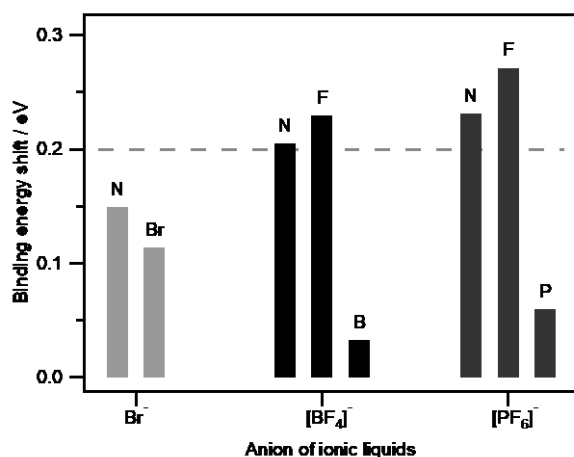


Figure 6 Binding energy shift between $[\text{C}_8\text{C}_1\text{Im}]^+$ and $[\text{C}_8\text{C}_4\text{Im}]^+$ ionic liquids for cationic nitrogen and each anion-based component.

Conclusions

In this study, XPS is used to probe the impact of the N3-substituted alkyl chain length upon the electronic environment of the cation and the anion. The established fitting model used for $[\text{C}_8\text{C}_1\text{Im}]^+$ ionic liquids is used after amending the appropriate weighting of the four components.

The impact of the N3-substituted alkyl chain length on the electronic environment of the cationic nitrogen is discussed based on the comparisons of N 1s spectra between $[\text{C}_8\text{C}_4\text{Im}]^+$ and $[\text{C}_8\text{C}_1\text{Im}]^+$ ionic liquids. For the less basic anion, *i.e.* $[\text{PF}_6]^-$, due the weak charge-transfer effect between the cation and the anion, the inductive effect is more intense. Therefore, when increasing the length of the N3-substituted alkyl chain, it causes a significant increase in electron density on cationic nitrogen centres. The change in electronic environment is perfectly reflected on the N 1s binding energy shift. It is found that the N 1s binding energy for $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$ is more than 0.2 eV lower than that of $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$. For the moderate basic anion, *i.e.* $[\text{BF}_4]^-$, the impact is slightly weakened. However, the shift for N 1s binding energy is still more than 0.2 eV. For the more basic anion such as Br^- , such an effect is negligible.

On the other hand, the increase of the inductive effect can increase the electron density of the nitrogen centre, and the C2 atom, which is bonded directly to the two nitrogen atoms. It subsequently shields the predominant interaction between the anion and H-C2 within the cation, leading to a more negatively charged anion. Such an impact is more concentrated on the anion-based component bearing more negative point charges. It shows that the F 1s binding energy of $[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$ shifts 0.3 eV to the lower value, compared to that of $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$. **Such a binding energy shift could also be due to the longer distance between the cation and the anion. Furthermore, this observation may also be explained by the supramolecular structures of ionic liquids. With the increasing of the size of nonpolar domains, the polar network becomes more disordered, leading to the weak cation-anion interactions.** For $[\text{BF}_4]^-$, the shift is 0.2 eV. For Br^- , the shift falls into the experimental error of XPS. It concludes that the magnitude of the impact on both the cation and the anion is inversely proportional to the basicity of the anion: $[\text{PF}_6]^- > [\text{BF}_4]^- > \text{Br}^-$.

Table 3 Binding energies of all elements for all ionic liquids in this paper. Note: XP spectra of $[\text{C}_8\text{C}_1\text{Im}]^+$ ionic liquids are not measured in this study but are available in a previous work.¹⁸

Ionic liquids	Binding energy / eV								
	N 1s	C ² 1s	C ^{4,5} 1s	C ^{6,7} 1s	C _{aliphatic} 1s	F 1s	P 2p _{3/2}	B 1s	Br 3d _{5/2}
$[\text{C}_8\text{C}_4\text{Im}][\text{PF}_6]$	401.8	287.7	286.3	286.9	285.0	686.5	136.5		
$[\text{C}_8\text{C}_4\text{Im}][\text{BF}_4]$	401.8	287.6	286.3	286.8	285.0	685.8		194.2	
$[\text{C}_8\text{C}_4\text{Im}]\text{Br}$	401.6	287.4	286.1	286.6	285.0				67.4
$[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$	402.1	287.8	286.4	287.0	285.0	686.8	136.6		
$[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$	402.0	287.7	286.4	286.8	285.0	686.0		194.2	
$[\text{C}_8\text{C}_1\text{Im}]\text{Br}$	401.7	287.4	286.1	286.6	285.0				67.5

Acknowledgements

The authors thank Liaoning Provincial Foundation of Science and Technology (20180550482) for financial support. SM acknowledges Beijing Key Laboratory of Quality Evaluation Technology for Hygiene and Safety of Plastics (Beijing Technology and Business University, Beijing 100048, China) for the award of an Open Fund (QETHSP2019004). Drs. Jun Qu (Oak Ridge National Laboratory) and Coby Clarke (University of Nottingham) are acknowledged for helpful discussions.

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