Tuning the Cation-Anion Interactions by Methylation of the Pyridinium Cation: An X-ray Photoelectron Spectroscopy Study of Picolinium Ionic Liquids

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Abstract

X-ray photoelectron spectroscopy is used to investigate the impact of methylation on the electronic environment of the pyridinium cation. Due to the electron donating effect of the methyl group, there is a significant increase in electron density on the cationic nitrogen. The shift of N 1s binding energy is inversely proportional to the anion basicity. The methylation position on the electronic environment of the cationic nitrogen is investigated. N 1s binding energy follows the trend: 1-octylpyridinium > 1-octyl-3-picolinium > 1-octyl-4-picolinium > 1-octyl-2-picolinium, which is in good agreement with the cation acidity. The increase in inductive effect subsequently weakens the cation-anion interactions through charge-transfer from the anion to the cation, causing subtle change in electronic environment of the anion. Such an effect is noticeably reflected in Br 3d binding energy. It shows that the Br $3d_{5/2}$ binding energy of 1-octyl-2-picolinium bromide is 0.2 eV lower than that of 1-octylpyridinium bromide.

1. Introduction

In general, ionic liquids (ILs) are considered as tuneable solvents, since there are nearly an endless number of combinations of cations and anions, each of which is of distinct physicochemical properties.[1] By simply selecting the cation, the anion and the mixture composition, it is feasible to design ILs with desired properties, such as melting point, viscosity, solubility, hydrophobicity, thermal stability, etc. This tunability has become the most unique advantages of ILs, making them potential materials in a wide range of applications, such as chemical reactions,[2,3] lubrication,[4] phase separation,[5,6] CO_2 capture,[7] desulfurization of fuel[8] and electrochemistry.[9,10]

Over the past decade, there have been many efforts focusing on the tuning of ILs properties. It has concluded that the hydrophobicity and viscosity can be increased with increasing the alkyl substituent length;[11] the solubility of ILs in water can be significantly reduced by switching the anion from halide to $[Tf_2N]^-$ or changing the cation from imidazolium to pyridinium.[12] It is also found that there is a correlation between polarity and thermal stability. For a given cation, when decreasing the coordinating ability of the anion, it significantly decreases the polarity of ILs, which subsequently enhances the thermal stability.[13] From another point of view, the cation seems to have complicated impact on the thermal stability. Imidazolium and pyridinium ILs are usually less stable than their non-aromatic analogues, such as pyrrolidinium.[14] The main problem is the presence of more acidic protons on the cation. To overcome such a problem, proper methylation of the cation would be an effective way. For example, the substitution of a methyl group on C^2 position of imidazolium provides additional thermal stability.[13,15] However, the methyl group on pyridinium cation seems to have only minor influence on thermal stability.[13] Therefore, aiming to design ILs for specific applications, the prediction of the physicochemical properties, which is determined by the cation-anion interactions, needs to be properly understood.

It is well known that X-ray photoelectron spectroscopy (XPS) has been a powerful tool to investigate ILs, focusing on surface composition,[16,17] surface enrichment[18,19] and electronic environment of ILs.[20] XPS is also employed to monitor liquid phase reactions,[21-23] to identify the metal centre in ILs,[24,25] and in particularly to probe the cation-anion interactions.[26-28] It is demonstrated that both the cation acidity and the anion basicity can have noticeable effect on the cation-anion interactions, which are through charge-transfer effect from the anion to the cation.[29,30] In specific for the cation, XPS investigations have provided insights into the impact of C^2-methylation on the electronic environment of imidazolium cation.[26,31] It also inspires the idea to systematically investigate the impact of methylation on the electronic environment of the cation and the anion for pyridinium ILs.
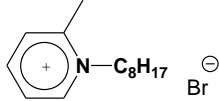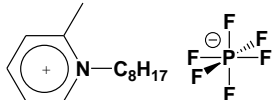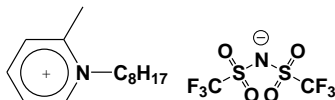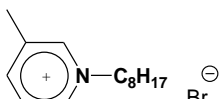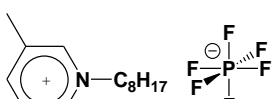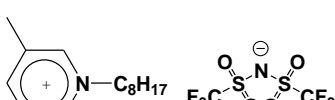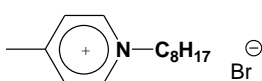
In this work, we extend such a topic to probe the impact of methylation on the cation-anion interactions for pyridinium ILs by XPS for the first time, comparing
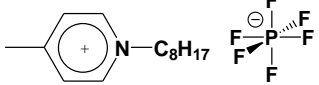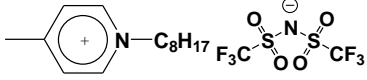
1-octylpyridinium ($[C_8Py]^+$) cation versus three types of 1-octylpicolinium ($[C_8Pic]^+$) cations: 1-octyl-2-picolinium ($[C_8Pic_2]^+$), 1-octyl-3-picolinium ($[C_8Pic_3]^+$) and 1-octyl-4-picolinium ($[C_8Pic_4]^+$), with three commonly used anions. Due to the additional electron donating effect, there is a significant increase in electron density of the cationic nitrogen, which causes the lowering of the N 1s binding energy. The measured cationic N 1s binding energy follows the trend as $[C_8Py]^+ > [C_8Pic_3]^+ > [C_8Pic_4]^+ > [C_8Pic_2]^+$, which is in good agreement with the cation acidity. The additional inductive effect also gives rise to the weakening of the cation-anion interactions. Such an effect is noticeable in the case of Br^- ILs. It concludes that there is a 0.2 eV shift to the lower value for $[C_8Pic_2]Br$, compared to that of $[C_8Py]Br$. These findings are useful to provide a strategy to design ILs by slightly changing the cation structure for specific applications and for the future study aiming to further enhance the thermal stability of pyridinium ILs.

2. Experimental section

2.1 Materials. All chemicals were purchased from Sigma Aldrich and were used as received. All ILs were prepared and purified in our lab using established synthetic protocols. NMR data were recorded on a JEOL 400YH spectrometer as solutions in DMSO-d_6. The structures of all ILs in this study are illustrated in Table 1.

Table 1 Ionic liquids studied in this study

Abbreviation	Structure	Name
$[C_8Pic_2]Br$		1-Octyl-2-picolinium bromide
$[C_8Pic_2][PF_6]$		1-Octyl-2-picolinium hexafluorophosphate
$[C_8Pic_2][Tf_2N]$		1-Octyl-2-picolinium bis (trifluoromethanesulfonyl)imide
$[C_8Pic_3]Br$		1-Octyl-3-picolinium bromide
$[C_8Pic_3][PF_6]$		1-Octyl-3-picolinium hexafluorophosphate
$[C_8Pic_3][Tf_2N]$		1-Octyl-3-picolinium bis (trifluoromethanesulfonyl)imide
$[C_8Pic_4]Br$		1-Octyl-4-picolinium bromide

| [C$_8$Pic$_4$][PF$_6$] | | 1-Octyl-4-picolinium hexafluorophosphate |
| [C$_8$Pic$_4$][Tf$_2$N] | | 1-Octyl-4-picolinium bis (trifluoromethanesulfonyl)imide |

2.2 XPS Data Collection. XPS experiment was conducted using a Thermo Scientific K$_\alpha$ spectrometer employing a focused, monochromated Al K$_\alpha$ source ($h\nu$ = 1486.6 eV), hemispherical analyser charge neutraliser and a 128-channel detector. The instrument employs an oval X-ray spot. The largest spot size (long axis) is 400 microns.

All IL samples were purified at -50 ^{o}C in a freeze dryer (FreeZone 2.5 LABCONOCO) for 72 h prior to use. The liquid sample was firstly transferred into a load-lock of XPS instrument as sample droplet on a piece of Al foil attached to the XPS sample holder. Four solid samples were fixed on the sample hold as thin films. Pumping of samples was conducted to achieve the base pressure of the parking lot, ~10^{-4} mbar. Samples were then transferred to the main analytical chamber.

When analysing liquid samples, charge neutralisation is not necessary, which ensures the maintenance of the pressure to be below 1 × 10^{-8} mbar. When analysing solid samples, the charge neutraliser is switched on. In this case, the pressure is usually below 1 × 10^{-7} mbar. For both cases, it suggests that volatile impurities, such as water and solvents, can be completely removed, leading to high purity samples.[32,33] Therefore, any information derived from XP spectra is reliable.

2.3 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%).[34] Relative sensitive factors for all elements are taken from literature.[34]
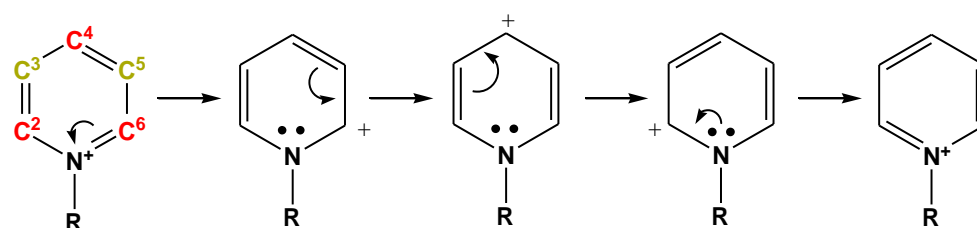
All XP spectra were normalised to the fitted area of cationic N 1s peak for [C$_8$Pic$_2$][Tf$_2$N], in order to aid visual interpretations. This is simply because the cationic nitrogen is present in all ILs in the same amount. The charge correction was conducted by setting the C$_{aliphatic}$ 1s component to 285.0 eV. It must be noted that XP spectra for [C$_8$Py]$^+$ ILs are not measured in this study but can be found in a previous paper published by our group.[28] It must be noted that the experimental error of XPS is ± 0.1 eV. Therefore, any claimed binding energy shift should be no less than 0.2 eV.

3. Results and discussion

3.1 Electronic environment of the carbon regions. A three-component fitting model has been developed for the C 1s region of [C$_n$Py]$^+$ ILs previously in our group,[28] where a systematic calculation of the shake-up deduction has been carried out and confirmed to be 10%. Take [C$_8$Py]$^+$ cation as a representative example. The

C 1s region was fitted using three components: C_{hetero} 1s, C_{inter} 1s and $C_{aliphatic}$ 1s. The C_{hetero} 1s component represents the three carbon atoms bonded directly to the positively charged nitrogen; C_{inter} 1s component refers to the other three carbon atoms present within the pyridinium ring; $C_{aliphatic}$ 1s component represents all other carbon atoms. A detailed demonstration can be found in Ref. 28.

Compared to the $[C_8Py]^+$ cation, the $[C_8Pic]^+$ cation contains an additional methyl group substituted on ortho-, meta- or para-position towards the nitrogen of the pyridinium ring. For all the three cases, according to the ^{13}C NMR data, the signal originated from the methyl group shows the similar upfield shift with those of the aliphatic carbons. Therefore, this carbon signal should be included into the $C_{aliphatic}$ 1s component.

Scheme 1 Resonating structure of the $[C_8Py]^+$ cation.

Furthermore, by carefully considering the resonating structure of the $[C_8Py]^+$ cation, it is found that the positive charge can delocalise on the nitrogen, two ortho-carbons and the para-carbon, as shown in Scheme 1. It concludes that C^2 (or C^6) and C^4 should be much more electropositive than C^3 (or C^5). As a result, the used fitting model can be modified accordingly. Figure 1 demonstrated the newly developed fitting model for the C 1s region of a representative sample, $[C_8Pic_2][PF_6]$. Where C_{hetero} includes C^2, C^4 and C^6; C_{inter} refers to C^3, C^5 and the carbon atom which is bonded directly to the nitrogen but is not within the pyridinium ring, *i.e.* C^7; $C_{aliphatic}$ component corresponds to all other carbons, *i.e.* C^8 to C^{15}. The structure of the cation with detailed atoms numbering is also illustrated in Figure 1.
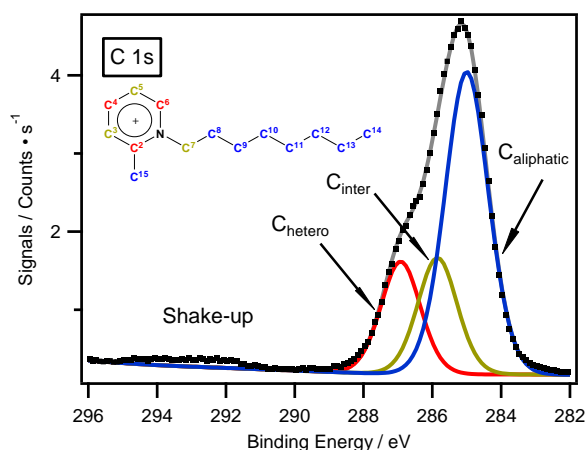

Figure 1 C 1s XP spectrum with fittings for $[C_8Pic_2][PF_6]$, including the structure of the

cation. A three-component model is used for the fitting: C_{hetero} 1s (C^2, C^4 and C^6), C_{inter} 1s (C^3, C^5 and C^7) and $C_{aliphatic}$ 1s (C^8 onwards).

After constraining the area ratio of C_{hetero} : C_{inter} : $C_{aliphatic}$ = 2.7: 2.8: 8, a very satisfactory fitting can be obtained, taking into account of a 10% shake-up deduction for the carbon signals originated from the pyridinium ring,[28] *i.e.* C^2-C^6. For [Tf$_2$N]$^-$ ILs, an additional resolved signal between 292.9 eV and 292.8 eV is also observed, which can be assigned to -CF$_3$ group.[28] However, the model is still applicable for the fitting. Consequently, this model can be used for all picolinium ILs studied herein.

In order to make reliable comparisons, C 1s fitting procedures for [C$_8$Py][Tf$_2$N], [C$_8$Py][PF$_6$] and [C$_8$Py]Br were also conducted according to the newly developed model. It must be noted that the fitting of C 1s region using the two models stated above brings no change for the $C_{aliphatic}$ 1s binding energy. Therefore, binding energies published in the previous work are reliable to be used directly for the data interpretation. Table 2 summaries binding energies of all elements for the twelve ILs studied in this paper.

3.2 Impact of the anion on the electronic environment of the nitrogen.
Figure 2 compares the cationic N 1s binding energy for [C$_8$Pic$_2$]$^+$ ILs, with three commonly used anions. It is found that the N_{cation} 1s binding energies for these three ILs follow the trend: [Tf$_2$N]$^-$ > [PF$_6$]$^-$ > Br$^-$, which is inversely proportional to the anion basicity.[35]
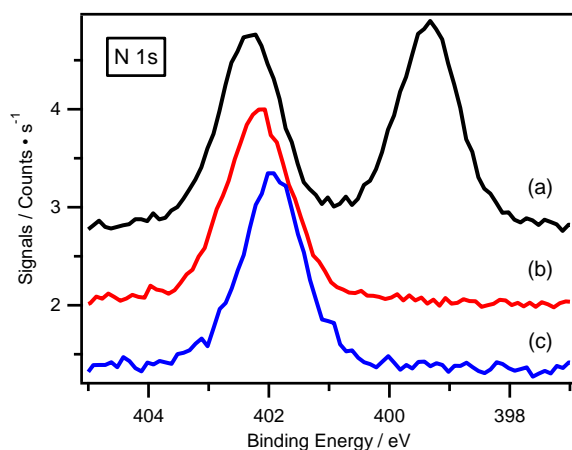

Figure 2 N 1s XP spectra for (a) [C$_8$Pic$_2$][Tf$_2$N], (b) [C$_8$Pic$_2$][PF$_6$] and (c) [C$_8$Pic$_2$]Br.

The less basic anions transfer less negative point charges to the cation, causing the cationic nitrogen centre being more positively charged and thus showing higher binding energy. It is found that the N_{cation} 1s binding energies for [C$_8$Pic$_2$][Tf$_2$N] and [C$_8$Pic$_2$][PF$_6$] are 402.3 eV and 402.2 eV, respectively. The opposite is also true for the more basic anion, *i.e.* Br$^-$. Since the charge-transfer is more intense, the electron density on the cationic nitrogen is effectively increased. As a result, a much lower binding energy at 401.9 eV is measured for [C$_8$Pic$_2$]Br. This trend is in good agreement with those observed for other families of ILs.[27,36]

3.3 Impact of the methylation on the electronic environment of the cation. A comparison of N 1s XP spectra between $[C_8Py][Tf_2N]$[28] and $[C_8Pic_2][Tf_2N]$ is demonstrated in Figure 3. It shows that the N_{cation} 1s binding energy of $[C_8Pic_2][Tf_2N]$ shift 0.3 eV to the lower value, compared to that of $[C_8Py][Tf_2N]$; whilst, the N_{anion} 1s binding energy for these two ILs remains the same. Because of the inductive electron donating effect of the additional methyl group, the electron density on the nitrogen centre is increased, leading to the lowering of the N_{cation} 1s binding energy. It indicates that the electronic environment of the cationic nitrogen has been effectively tuned upon methylation of the pyridinium ring, with the anionic nitrogen staying in an identical electronic environment.
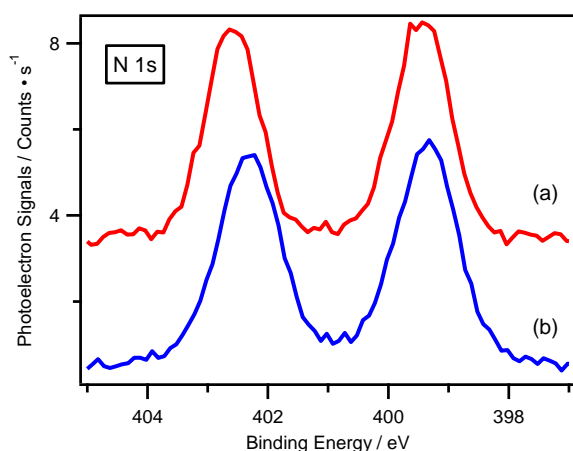

Figure 3 N 1s XP spectra for (a) $[C_8Py][Tf_2N]$ and (b) $[C_8Pic_2][Tf_2N]$.

From another point of view, it is found that the binding energy difference between $[C_8Py]^+$ and $[C_8Pic_2]^+$ ILs for each anion family decreases with increasing the anion basicity. It is well known that cations and anions of ILs interact with each other through charge-transfer from the anion to the cation. For the more basic anion, *i.e.* Br$^-$, the charge-transfer effect is more intense, resulting in a negligible inductive effect from alkyl chain towards cation headgroup. As a result, in the case of Br$^-$, the methylation only causes subtle change in electronic environment of the nitrogen centre, which cannot be reflected on binding energy. The opposite is also true for the two less basic anions, *i.e.* $[Tf_2N]^-$ and $[PF_6]^-$. Since the charge-transfer effect is weak, the inductive effect from alkyl chain towards cation headgroup is significant. The increased electron density of the nitrogen centre upon methylation can thus be measured by XPS. This observation is illustrated in detail in Figure 4. It concludes that the N 1s binding energy differences in the cases of $[Tf_2N]^-$ and $[PF_6]^-$ are 0.3 eV and 0.2 eV, respectively, meaning that both are noticeable by XPS; however, the shift for Br$^-$ is less than 0.2 eV, which is within the experimental error of XPS and considered as negligible.

Meanwhile, the C_{hetero} 1s binding energies for $[C_8Pic_2]^+$ ionic liquids are found identical with those of $[C_8Py]^+$ analogues, for all the three anion-based families. It

explains why there is only subtle influence in stability by methylation on the N-alkylpyridinium cation, as the methylation gives rise to negligible changes in electronic environment of the hetero carbons and more importantly the protons bonded therein.
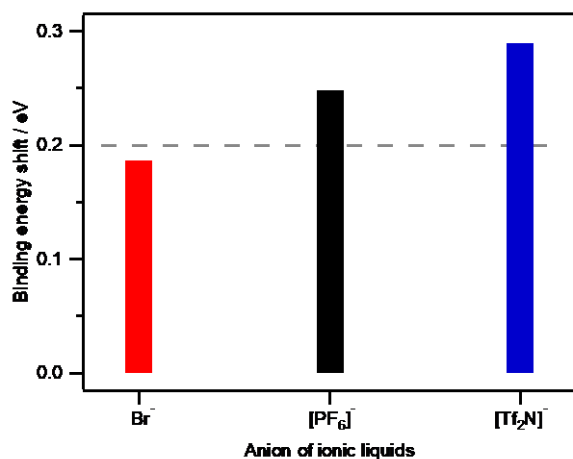

Figure 4 N 1s Binding energy shift between $[C_8Py]^+$ and $[C_8Pic_2]^+$ ionic liquids.

3.4 Impact of methylation position on the electronic environment of the cation. Upon methylation on the $[C_8Py]^+$ cation, there are three types of $[C_8Pic]^+$ cations: $[C_8Pic_2]^+$, $[C_8Pic_3]^+$ and $[C_8Pic_4]^+$. Herein, nine ILs by combinations of these three picolinium cations and three commonly used anions, *i.e.* $[Tf_2N]^-$, $[PF_6]^-$ and Br$^-$, are analysed by XPS.

Figure 5 shows the cationic N 1s binding energy for all picolinium ILs. In order to make visual comparisons, literature data for $[C_8Py]^+$ ILs are also included.[28] It concludes that there is an apparent trend of N_{cation} 1s binding energy for each anion family: $[C_8Py]^+ > [C_8Pic_3]^+ > [C_8Pic_4]^+ > [C_8Pic_2]^+$. This trend is in good agreement with that of the cation acidity,[37] according to Kamlet Taft hydrogen donating ability (α).
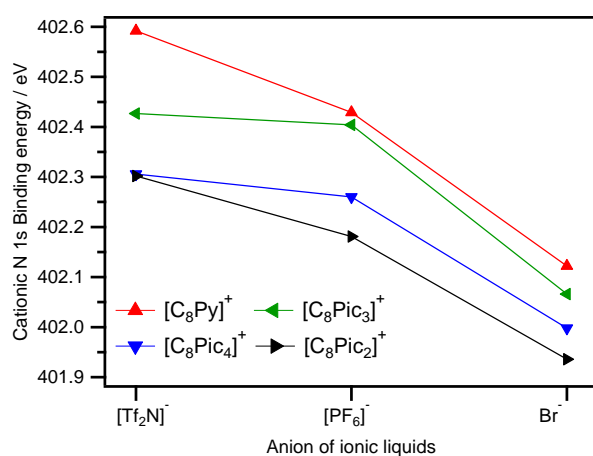

Figure 5 Comparisons of N_{cation} 1s binding energies for all ionic liquids.

Due to the presence of π-π conjugation system, the positive charge is delocalised across the pyridinium ring. However, by carefully considering the resonating structure of

the $[C_8Py]^+$ cation, it is found that the positive charge has more probability delocalising on the nitrogen, two ortho-carbons and the para-carbon within the pyridinium cation, as has been demonstrated in Scheme 1. Therefore, the methylation on 2- (or 6-) and 4-position can surely stabilise the positive charge, reducing the electron density on the nitrogen centre, when compared to that on 3- (or 5-) position. Meanwhile, in the case of $[C_8Pic_2]^+$, the methyl group locates more closed to the nitrogen centre, causing a slightly stronger inductive effect than that of $[C_8Pic_4]^+$, which gives rise to a further subtle decrease of the binding energy.

3.5 Impact of the methylation on the electronic environment of the anion. The methylation of the pyridinium cation not only affects the electronic environment of the nitrogen centre but also decreases the cation acidity. Therefore, the interaction between the anion and the proton present in the pyridinium ring should be shielded. According to α values,[37] $[C_8Pic_2]^+$ is less acidic than the other three cations. Therefore, the charge shielding effect should be more intense in the case of $[C_8Pic_2]^+$. For $[Tf_2N]^-$ and $[PF_6]^-$, since the charge-transfer effect for the less basic anion is weak, for most of the anion-based components, such a shielding effect is not measurable by XPS, as demonstrated in detail in Table 2. For example, the F 1s, O 1s and N_{anion} 1s binding energies for the four $[Tf_2N]^-$ ILs are identical; shifts for C_{anion} 1s and S $2p_{3/2}$ are within the experimental error. For $[PF_6]^-$ ILs, shifts for F 1s and P $2p_{3/2}$ are also within the error. This observation suggests that the mono-methylation of the pyridinium cation only causes subtle change in cation-anion interactions for the less basic anions.
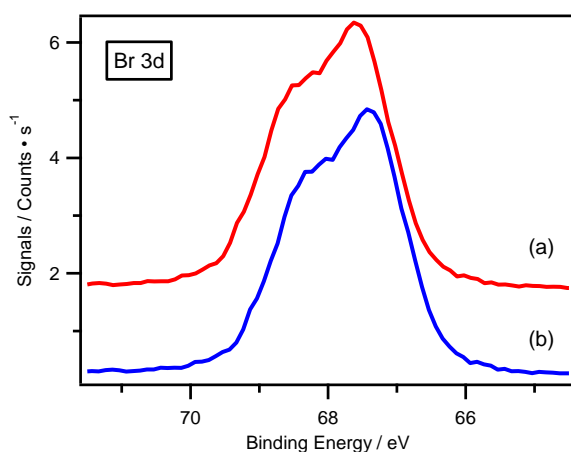

Figure 6 Br 3d XP spectra for (a) $[C_8Py]Br$ and (b) $[C_8Pic_2]Br$.

An extreme case is for the IL with the more basic anion, Br^-. Br^- is one of the most basic anions studied herein, and can transfer large magnitude of negative point charges to the cation. As a result, the methylation of the pyridinium cation can significantly shield the charge-transfer effect from Br^- to the cation, giving rise to a more negatively charged Br^- anion. As shown in Figure 6, it is observed that the Br $3d_{5/2}$ binding energy for $[C_8Pic_2]Br$ is 0.2 eV lower than that of $[C_8Py]Br$. It concludes that the

mono-methylation of the pyridinium cation can also impact the electronic environment of the anion, by shielding the interaction between the anion and the more acidic proton within the cation through charge-transfer effect. This observation may provide a strategy to design ILs with specific physicochemical properties in the future.

4. Conclusions

In conclusion, we use XPS to systematically study $[C_8Pic]^+$ ILs. The fitting model for the carbon region is modified by carefully considering the ^{13}C NMR result, according to an established model published previously. The effect of the anion basicity on the electronic environment of the cationic nitrogen is studied by employing three common anions, $[Tf_2N]^-$, $[PF_6]^-$ and Br^-. It is found that N_{cation} 1s binding energy follows the trend as $[Tf_2N]^- > [PF_6]^- > Br^-$, which is in agreement with other families of ILs. The methylation on $[C_8Py]^+$ cation can significantly affect the electronic environment of the cationic nitrogen centre. It shows that the binding energy gap between $[C_8Py]^+$ and $[C_8Pic_2]^+$ ILs for each anion family decreases with increasing the anion basicity. The shifts for $[Tf_2N]^-$ and $[PF_6]^-$ are 0.3 eV and 0.2 eV, respectively. The shift for Br^- is within the experimental error of XPS. The impact of methylation position on the electronic environment of the cationic nitrogen is also studied. It concludes that the N_{cation} 1s binding energy for the four types of cations follow the trend as $[C_8Py]^+ > [C_8Pic_3]^+ > [C_8Pic_4]^+ > [C_8Pic_2]^+$, which is in agreement with the cation acidity. The methylation also causes the decrease of the cation acidity, which subsequently affects the cation-anion interactions by shielding the charge-transfer effect from the anion to the cation. However, such a shielding effect is only measurable in the case of Br^-, which can transfer large magnitude of negative point charges to the cation. It indicates that the Br $3d_{5/2}$ binding energy of $[C_8Pic_2]Br$ is 0.2 eV lower than that of $[C_8Py]Br$. The results may be helpful for the future design of ionic liquids with specific physicochemical properties.

Table 2 Binding energies in eV of all elements for all ionic liquids in this study. Note that data for [C$_8$Py]$^+$ ionic liquids are not measured herein but can be found in a previous work published by our group.[28]

ILs	Binding energy / eV										
	N$_{cation}$ 1s	C$_{hetero}$ 1s	C$_{inter}$ 1s	C$_{aliphatic}$ 1s	C$_{anion}$ 1s	N$_{anion}$ 1s	F 1s	O$_{anion}$ 1s	S 2p$_{3/2}$	P 2p$_{3/2}$	Br 3d$_{5/2}$
[C$_8$Py][Tf$_2$N][28]	402.6	287.0	286.1	285.0	292.9	399.4	688.8	532.6	169.0		
[C$_8$Pic$_3$][Tf$_2$N]	402.4	287.0	286.1	285.0	292.9	399.4	688.8	532.6	168.9		
[C$_8$Pic$_4$][Tf$_2$N]	402.3	287.0	286.1	285.0	292.8	399.4	688.8	532.6	168.9		
[C$_8$Pic$_2$][Tf$_2$N]	402.3	287.0	286.0	285.0	292.8	399.4	688.8	532.6	168.9		
[C$_8$Py][PF$_6$][28]	402.4	286.9	285.9	285.0			686.7			136.5	
[C$_8$Pic$_3$][PF$_6$]	402.4	286.9	285.9	285.0			686.6			136.5	
[C$_8$Pic$_4$][PF$_6$]	402.3	286.9	285.9	285.0			686.6			136.4	
[C$_8$Pic$_2$][PF$_6$]	402.2	286.9	285.9	285.0			686.6			136.4	
[C$_8$Py]Br[28]	402.1	286.6	285.7	285.0							67.5
[C$_8$Pic$_3$]Br	402.1	286.5	285.7	285.0							67.4
[C$_8$Pic$_4$]Br	402.0	286.6	285.7	285.0							67.4
[C$_8$Pic$_2$]Br	401.9	286.6	285.7	285.0							67.3

Notes

The authors declare no competing financial interest.

Supporting Information

The procedures of synthesis, NMR data and XP spectra for all ILs are provided.

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