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X-ray photoelectron spectroscopy of morpholinium ionic liquids: Impact of the long alkyl side substituent on the cation-anion interactions

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Abstract

In this study, X-ray photoelectron spectroscopy is used to analyse nine morpholinium ionic liquids, which are of great interest in green chemistry because of their low toxicity and high recyclability. The effect of alkyl chain length on the aliphatic C 1s binding energies is studied. The impact of the anion basicity on the cationic N 1s and O 1s binding energies is investigated. It is concluded that by changing the basicity of the anion, there is a more noticeable change in the electronic environment of the oxygen centre. The effect of the long alkyl side substituent on the cation-anion interactions is also discussed. It is observed that there is an intense charge shielding effect of the alkyl side chain in the cases of octyl and dodecyl, which is reflected in lowering of the measured Br $3d_{5/2}$ binding energy.

Keywords: Morpholinium; Long alkyl side substituent; Nano-structures

Introduction

Over the past three decades, ionic liquids have seen growing interest in green chemistry, ascribed to their fascinating physicochemical properties. They have shown negligible volatility, high thermal stability, low toxicity and high recyclability,[1] which make them potentially the sustainable replacement to the traditional organic solvents.[2] Furthermore, being composed of cations and anions,[3] there has been a vast number of combinations for ionic liquids, leading to a universe of novel compounds with tuneable physicochemical properties.[1] To date, most ionic liquids investigated in the literature are derived from heterocyclic molecules, such as imidazolium, pyridinium, piperidinium, pyrrolidinium, etc.

Among the cations of all types of ionic liquids, morpholinium has attracted much attention because of its biodegradable and renewable nature.[4] Due to the existence of both oxygen (electronegative centre) and nitrogen (electropositive centre) centres, the morpholinium cation has dipolar structure, which reduces their toxicity.[5] They are literally less toxic than other commonly used ionic liquids, such as imidazolium, pyridinium and ammonium.[6] Apart from that, morpholinium ionic liquids also find applications as a sustainable alternative for cellulose dissolution.[7, 8] As a non-aromatic cation, morpholinium possesses an even higher polarity than its aromatic analogues, *i.e.* imidazolium and pyridinium, which facilitates the interaction between cellulose and ionic liquids.[9] Morpholinium ionic liquids have also shown larger electrochemical windows and reasonable conductivities,[10] and therefore drawn much attention in electrolyte applications[11, 12] for batteries and solar cells. Attributing to their structural properties, morpholinium ionic liquids are also of interest in the research areas of ionic liquid crystals,[13] catalysis[14] as well as heat stabiliser.[15]

Since 2005, X-ray photoelectron spectroscopy (XPS) has been accepted as an effective tool to investigate ionic liquids.[16-19] Binding energies derived from XPS can reflect the cation-anion interactions in an ionic liquid, which are subsequently considered as key factors determining their physicochemical properties.[20] Consequently, the proper understanding of the cation-anion interactions can guide us to tune the properties of ionic liquids for specific uses. Till now, XPS has been employed for the analysis of ionic liquids associated with numerous cations, such as imidazolium,[21, 22] pyridinium,[23] pyrrolidinium,[24, 25] ammounium,[26] guanidinium[27] and phosphonium.[26, 28] However, to the best of our knowledge, there are still insufficient XPS data available for morpholinium ionic liquids.

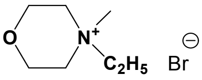
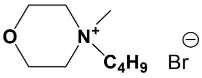
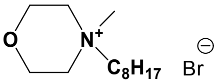
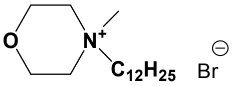
In this study, nine 1-alkyl-1-methylmorpholinium ($[C_nC_1Mor]^+$) ionic liquids are analysed by XPS. A fitting model is developed for the C 1s region. The effect of alkyl chain length on the aliphatic C 1s binding energy is investigated by changing the alkyl substituent from ethyl to dodecyl. It is found that for a less basic anion, $C_{aliphatic}$ 1s binding energy is increased with a decreasing alkyl chain length; for the more basic anion, $C_{aliphatic}$ 1s binding energy is always identical. The impact of anion on the electronic environment of cationic components, *i.e.* N 1s and O 1s, is studied employing three commonly used anions. The anion appears to have more noticeable effect on O 1s binding energies. The impact of the alkyl side chain length on the electronic environment of anion is also discussed when increasing *n* from 2 to 12. It suggests that there is an intense charge shielding effect of the alkyl side chain in the cases of octyl and dodecyl, due to the formation of nano-structures in ionic liquids.

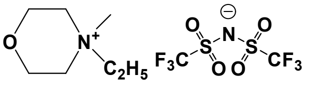
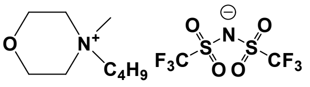
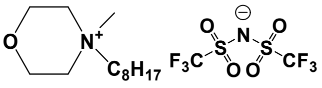
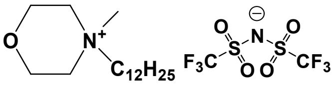
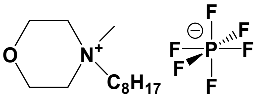
Experimental

Materials

All chemicals purchased from Sigma Aldrich were used as received. Ionic liquids were prepared using established synthetic protocols in our laboratory. The synthesis procedures are described in Electronic Supplementary Information. To confirm the structures of ionic liquids, all samples were characterised by NMR recorded on a JEOL 400YH spectrometer as solutions in $CDCl_3$ or DMSO-d_6. NMR data and XP spectra (including survey spectrum and high resolution spectra for all components) of each ionic liquid can be found in detail in Electronic Supplementary Information.

Table 1 Nine ionic liquids studied in this work

Abbreviation	Structure	Name
$[C_2C_1Mor]Br$		1-Ethyl-1-methylmorpholinium bromide
$[C_4C_1Mor]Br$		1-Butyl-1-methylmorpholinium bromide
$[C_8C_1Mor]Br$		1-Octyl-1-methylmorpholinium bromide
$[C_{12}C_1Mor]Br$		1-Dodecyl-1-methylmorpholinium bromide

$[C_2C_1Mor][Tf_2N]$		1-Ethyl-1-methylmorpholinium bis (trifluoromethanesulfonyl)imide
$[C_4C_1Mor][Tf_2N]$		1-Butyl-1-methylmorpholinium bis (trifluoromethanesulfonyl)imide
$[C_8C_1Mor][Tf_2N]$		1-Octyl-1-methylmorpholinium bis (trifluoromethanesulfonyl)imide
$[C_{12}C_1Mor][Tf_2N]$		1-Dodecyl-1-methylmorpholinium bis (trifluoromethanesulfonyl)imide
$[C_8C_1Mor][PF_6]$		1-Octyl-1-methylmorpholinium hexafluorophosphate

XPS Data Collection

XPS experiment was conducted using a Thermo Scientific K_α spectrometer employing a focused, monochromated Al K_α 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.

Before transferring into XPS instrument, all ionic liquid samples prepared in this work were purified under high vacuum at -50 °C in a freeze dryer (FreeZone 2.5 LABCONOCO) for 72 h. The liquid sample was transferred into the vacuum pumped load-lock of the XPS instrument as sample droplet on a piece of Al foil attached to the XPS sample holder. The solid sample was attached on the sample holder as a thin film. The base pressure for the load-lock is $\sim 10^{-4}$ mbar.

Samples were then transferred to the main analytical chamber, with the base pressure below 1×10^{-9} mbar before analysis. When analysing liquid samples, the pressure is found to be below $\sim 10^{-8}$ mbar. When analysing solid insulating samples, the charge neutraliser is switched on, which increases the pressure in the analytical chamber. In this case, the pressure is usually below $\sim 10^{-7}$ mbar. For both cases, it suggests that all volatile impurities, such as water and solvents, have been removed completely, leading to high purity of the samples.[29] As a result, any information derived from XP spectra should be reliable.

XPS Data Analysis

Data interpretation was carried out using CasaXPS software. A spline linear was employed for background subtraction. Peaks were fitted using GL(30) lineshapes: a combination of a Gaussian (70%) and Lorentzian (30%).[30, 31] The Relative sensitive factor for each element is taken from the literature.[30]

To aid visual comparisons, all XP spectra were normalised to the fitted area of N_{cation} 1s component of $[C_8C_1Mor][Tf_2N]$, simply because the cationic nitrogen atom is present in all morpholinium ionic liquids in the same amount.

The charge correction was carried out by two methods as summarised in our group previously: For *n* = 8, $C_{aliphatic}$ 1s component was set to 285.0 eV; for other *n* values, N_{cation} 1s was charge corrected to the value that obtained for C_8-based analogues within a definite anion family.[21, 24]

Results and discussion

Sample purity

Quantitative analysis derived from XPS is used in this section to confirm the purity of ionic liquid samples. According to the relative sensitivity factor taken from the literature,[30] the surface composition of ionic liquids can be calculated from either the survey or high resolution XP spectra. In this study, in order to reduce the experimental error, high resolution spectra are employed for the surface composition calculation. The results are shown in Table 2. The nominal stoichiometry for each ionic liquid is also given in brackets, so as to give a visual comparison.

It is clearly shown that the experimental surface composition is within the experimental error the same with that calculated from the empirical formulae, as the uncertainty of the quantitative analysis of XPS is ± 20%.

Table 2 Surface composition in terms of atom count for each ionic liquid sample: experimental and nominal (in brackets) stoichiometry.

Ionic Liquids	RSF	C 1s	N 1s	O 1s	F 1s	S 2p	P 2p	Br 3d
		0.278	0.477	0.78	1.000	0.668	0.486	1.055
$[C_8C_1Mor][Tf_2N]$	Measured	15.5	2.0	4.4	6.1	2.0		
	(Nominal)	(15.0)	(2.0)	(5.0)	(6.0)	(2.0)		
$[C_8C_1Mor][PF_6]$	Measured	13.7	0.9	0.9	5.6		0.9	
	(Nominal)	(13.0)	(1.0)	(1.0)	(6.0)		(1.0)	
$[C_8C_1Mor]Br$	Measured	13.6	0.8	0.8				0.8
	(Nominal)	(13.0)	(1.0)	(1.0)				(1.0)
$[C_2C_1Mor][Tf_2N]$	Measured	9.6	2.0	4.5	6.0	1.9		
	(Nominal)	(9.0)	(2.0)	(5.0)	(6.0)	(2.0)		
$[C_4C_1Mor][Tf_2N]$	Measured	11.5	2.0	4.4	6.2	1.9		
	(Nominal)	(11.0)	(2.0)	(5.0)	(6.0)	(2.0)		
$[C_{12}C_1Mor][Tf_2N]$	Measured	19.7	2.0	4.5	5.9	1.9		
	(Nominal)	(19.0)	(2.0)	(5.0)	(6.0)	(2.0)		
$[C_2C_1Mor]Br$	Measured	7.5	0.8	0.9				0.8
	(Nominal)	(7.0)	(1.0)	(1.0)				(1.0)
$[C_4C_1Mor]Br$	Measured	9.4	0.9	0.9				0.8
	(Nominal)	(9.0)	(1.0)	(1.0)				(1.0)
$[C_{12}C_1Mor]Br$	Measured	17.3	0.9	1.0				0.8
	(Nominal)	(17.0)	(1.0)	(1.0)				(1.0)

Electronic environment of carbon regions: Development of the fitting model

A representative sample in this paper, $[C_8C_1Mor][Tf_2N]$, is selected to demonstrate the development of the C 1s fitting model. Apart from cationic carbon signals, a photoelectron peak which can be assigned to $-CF_3$ group within $[Tf_2N]^-$ anion is also observed. This peak shows much higher binding energy and is thus not necessary to be discussed. According to the ^{13}C NMR results that reported in the literature,[32] C^2 and C^6 carbons present in morpholinium cation (see Figure 1, the structure of $[C_8C_1Mor]^+$ cation) show the most downfield shift. Since oxygen atom is more electronegative, the electron density of carbon atoms bonded directly to the oxygen atom is reduced significantly, leading to the increase in binding energy of these two carbons. As a result, a three-component is initially employed for the fitting of C 1s spectrum, as demonstrated in Figure 1. C_{oxy} 1s represents carbon atoms bonded directly to the oxygen atom. C_{hetero} 1s represents the four carbon atoms which are bonded directly to the nitrogen centre. $C_{aliphatic}$ 1s is assigned to the carbon atoms bonded to carbon and hydrogen atoms only. After constraining the area ratio of C_{oxy}: C_{hetero}: $C_{aliphatic}$ = 2: 4: 7, a very satisfactory fitting was obtained.

For other n values, simply changing the constraint of the area ratio of C_{oxy}: C_{hetero}: $C_{aliphatic}$ = 2: 4: (n-1), satisfactory fittings can be obtained.

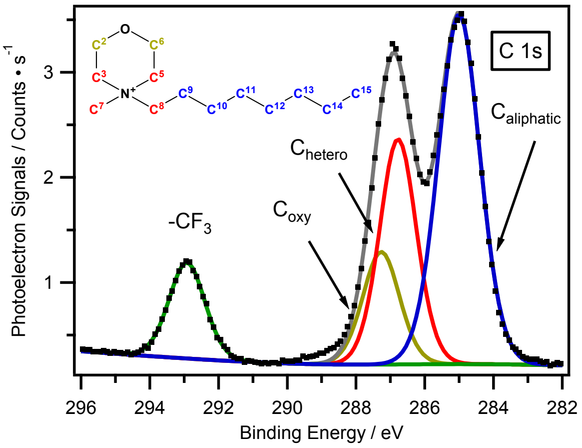


Figure 1 C 1s high resolution spectrum with fittings for $[C_8C_1Mor][Tf_2N]$, with the structure of the cation included. A three-component model is used for the fitting: C_{oxy} 1s (C^2 and C^6), C_{hetero} 1s (C^3, C^5, C^7 and C^8) and $C_{aliphatic}$ 1s (C^9 onwards).

For $[C_8C_1Mor][PF_6]$ and $[C_nC_1Mor]Br$, where n = 2-12, the same model is also applicable; however, there is no $-CF_3$ signal acquired.

Effect of alkyl chain length on the $C_{aliphatic}$ 1s binding energy

In this section, the effect of the alkyl chain length on the electronic environment of $C_{aliphatic}$ 1s component is systematically studied using two representative anions, the more basic anion, Br^-, and the less basic anion, $[Tf_2N]^-$, by varying the alkyl chain from ethyl to dodecyl.

There are two sets of effects determining the electronic environment of the $C_{aliphatic}$

1s component: Cation-anion interactions through charge-transfer from the anion to the cation and the inductive effect from the alkyl substituent. These two sets of effects compete with each other and therefore lead to the distinguishably different observation towards the measured $C_{aliphatic}$ 1s binding energy.

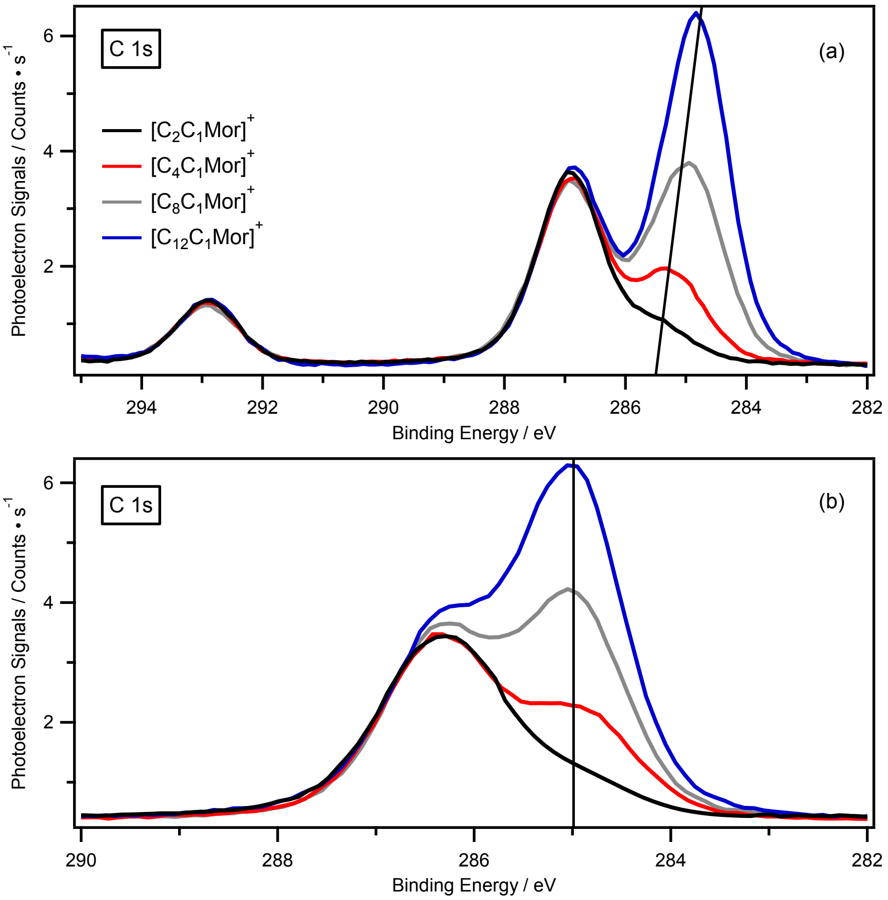


Figure 2 C 1s high resolution XP spectra for (a) $[C_nC_1Mor][Tf_2N]$ and (b) $[C_nC_1Mor]Br$, where n = 2-12.

In the case of Br^-, as the anion is more basic, there has been intense cation-anion interactions, causing the charge transferred from Br^- to the cation significant. The strong cation-anion interactions subsequently weaken the inductive effect of the alkyl chain. As a result, by varying n values from 2 to 12, there is only subtle change in inductive effect, which is not measurable by XPS. As shown in Figure 2b, the $C_{aliphatic}$ 1s binding energies for all Br^--based ionic liquids are identical.

By contrast, in the case of $[Tf_2N]^-$, since the anion is less basic, the cation-anion interactions are weaker, strengthening the inductive effect from the alkyl substituent towards the cation headgroup. Consequently, by increasing the length of the alkyl chain, *i.e.* from 2 to 12, a noticeable binding energy shift for the $C_{aliphatic}$ 1s component can be measured, which is demonstrated in Figure 2a. When decreasing the n value from 8 to 4, the $C_{aliphatic}$ 1s binding energy shifts 0.2 eV towards a higher value, which is more than the experimental error of XPS (of the order ± 0.1 eV). For n = 2, it further increases to

285.4 eV. However, when increasing the *n* value from 8 to 12, the $C_{aliphatic}$ 1s binding energy is found at 284.9 eV, which is within the experimental uncertainty of that measured for $n = 8$. These observations are in good agreement with those for other ionic liquid families.

Impact of anion basicity on the cation-anion interactions: Cationic oxygen and nitrogen regions

Figure 3 shows the cationic N 1s and O 1s XP spectra for $[C_8C_1Mor]^+$ ionic liquids associated with three commonly used anions: $[Tf_2N]^-$, $[PF_6]^-$ and Br^-. At first glance, it indicates that for both the N_{cation} 1s and O_{cation} 1s components, the binding energy follows the trend as $[Tf_2N]^- > [PF_6]^- > Br^-$. Br^- is the most basic among the three anions, and therefore can transfer more point charges to the $[C_8C_1Mor]^+$ cation, leading to less positively charged nitrogen and oxygen atoms. As a result, the cationic N 1s and O 1s binding energies both become smaller. The opposite is also true for the least basic anions, *i.e.* $[Tf_2N]^-$.

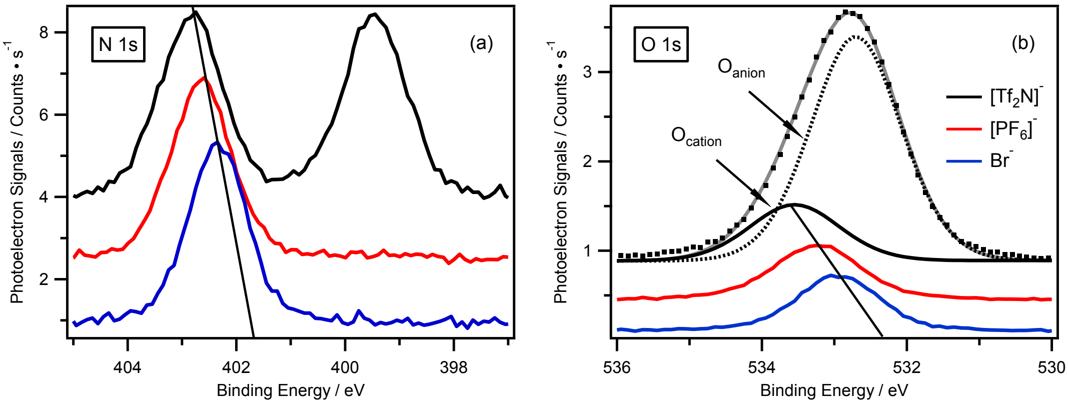


Figure 3 N 1s (a) and O 1s (b) XP spectra for $[C_8C_1Mor][Tf_2N]$, $[C_8C_1Mor][PF_6]$ and $[C_8C_1Mor]Br$.

Furthermore, by carefully considering the measured binding energies of N_{cation} 1s and O_{cation} 1s for the three ionic liquids, it is found that when changing the anion, the shift in electronic environment of O_{cation} centre is more pronounced than that of N_{cation} centre. For example, by switching the anion from $[Tf_2N]^-$ to $[PF_6]^-$, the N_{cation} 1s binding energy shifts 0.2 eV towards lower value; whilst the shift for O_{cation} 1s binding energy is 0.4 eV, which is much more noticeable. Similarly, the shifts of binding energies between $[Tf_2N]^-$ and Br^- are 0.5 eV and 0.7 eV, respectively. According to the ^{13}C NMR result, the C^2 (or C^6) atom is more electropositive than the C^3 (or C^5) atom. Therefore, the predominant interaction between the anion and the proton present in the cation is located on the H-C^2 position (see Figure 1, the structure of the cation).[20] When increasing the anion basicity, the cation-anion interactions become more intense, which leads to a more noticeable increase in electron density of the neighbouring atom of C^2, *i.e.* oxygen. As a result, the measured binding energy of O_{cation} 1s shifted to the lower value by a larger magnitude, compared to that of N_{cation} 1s.

Impact of cation acidity on the cation-anion interactions: Fluorine region

Through the presence of oxygen electron withdrawing effect, morpholine is usually less basic (nucleophilic) than its structural similar piperidine analogue. As a result, the conjugate acid, morpholinium is more acidic than piperidinium. It is known that less acidic cation helps to shield the charge-transfer effect from the anion to the cation, rendering the anion being left more negatively charged. In this section, such an effect is investigated by comparing the binding energy of F 1s between [C_8C_1Mor][Tf_2N] and [C_8C_1Pip][Tf_2N].[33] The synthesis procedure and full characterisation data can be found in a previous published paper in our group.[33]

As shown in Figure 4, the binding energy shift for F 1s is more than 0.2 eV, which is more pronounced than the experimental error of XPS. It concludes that by changing the acidity of the cation, the cation-anion interactions could be tuned in a noticeable magnitude.

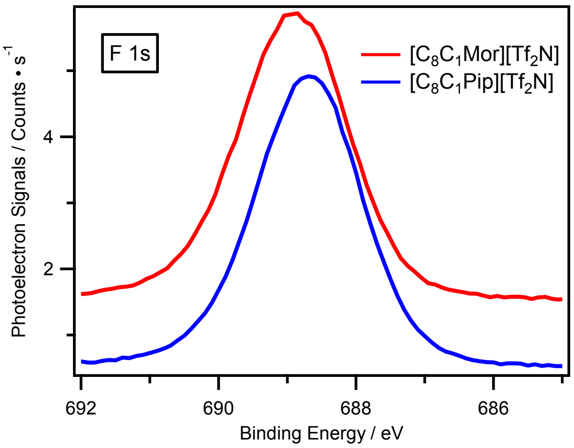


Figure 4 F 1s binding energy for [C_8C_1Mor][Tf_2N] and [C_8C_1Pip][Tf_2N].

Table 3 Binding energies of all elements for all ionic liquids in this work.

Ionic liquids	Binding energy / eV											
	N_{cation} 1s	C_{oxy} 1s	C_{hetero} 1s	$C_{aliphatic}$ 1s	C_{anion} 1s	N_{anion} 1s	F 1s	O_{cation} 1s	O_{anion} 1s	S $2p_{3/2}$	P $2p_{3/2}$	Br $3d_{5/2}$
$[C_2C_1Mor][Tf_2N]$	402.8	287.3	286.8	285.4	292.9	399.5	688.9	533.6	532.7	169.0		
$[C_4C_1Mor][Tf_2N]$	402.8	287.3	286.8	285.2	292.9	399.5	688.9	533.6	532.7	169.0		
$[C_8C_1Mor][Tf_2N]$	402.8	287.3	286.8	285.0	292.9	399.5	688.9	533.6	532.7	169.0		
$[C_{12}C_1Mor][Tf_2N]$	402.8	287.3	286.7	284.9	292.9	399.5	688.9	533.6	532.7	169.0		
$[C_2C_1Mor]Br$	402.3	286.8	286.2	285.0				532.9				67.7
$[C_4C_1Mor]Br$	402.3	286.8	286.2	285.0				532.9				67.6
$[C_8C_1Mor]Br$	402.3	286.8	286.2	285.0				532.9				67.5
$[C_{12}C_1Mor]Br$	402.3	286.8	286.2	285.0				532.9				67.4
$[C_8C_1Mor][PF_6]$	402.6	287.1	286.5	285.0			686.8	533.2			136.6	

Impact of the alkyl side substituent length on the cation-anion interactions: Bromine regions

As shown in Figure 5, it is concluded that the Br $3d_{5/2}$ binding energy decreased with increasing the alkyl side substituent length. The binding energy shift could be as much as 0.3 eV, when changing the side alkyl substituent from ethyl to dodecyl (from 67.7 eV to 67.4 eV).

It has been accepted that long hydrocarbon substituent can significantly shield the charge-transfer effect from the anion to the cation,[34] and subsequently weaken the cation-anion interactions. Due to the more intense electron donating effect from the long alkyl group to the cation headgroup, partial charges transferred from the anion to the cation could be shielded, leading to a more negatively charged anion.

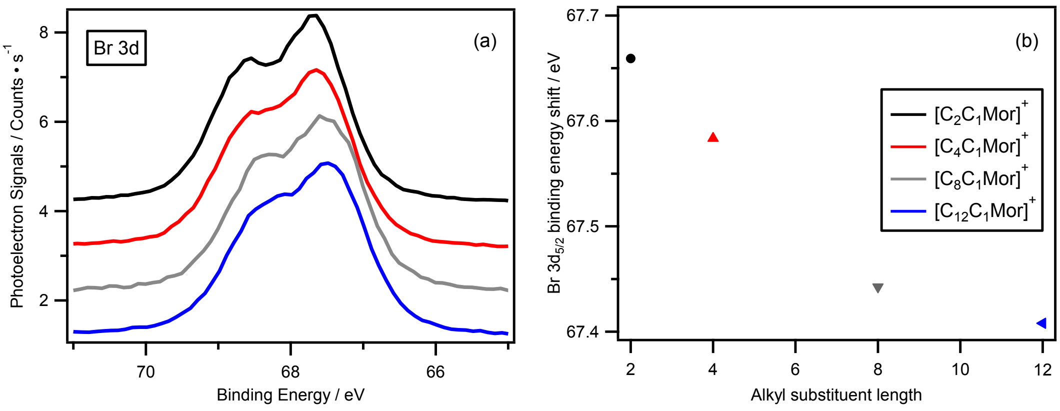


Figure 5 (a) Br 3d XP spectra for $[C_nC_1Mor]Br$; (b) Br $3d_{5/3}$ Binding energies for $[C_nC_1Mor]Br$, where n = 2-12.

From another point of view, ionic liquids can be considered as nano-materials, with the polar region which are composed of the cation headgroup and the anion as the continuous phase and the non-polar region, *e.g.* the alkyl chain, as the isolated phase. When the total number of carbon atoms in the alkyl side substituent is over a certain threshold (usually the number is 6), there might be the percolation of the non-polar isolated phase into the polar continuous phase occurred.[35] It causes the stretching of the polar phases and subsequently the weakening of the interaction between the cation headgroup and the anion. When n=2 or 4, since the total number of carbons is small, the cation-anion interactions cannot be significantly impacted, and thus is not noticeably measured by XPS. The measured Br $3d_{5/2}$ binding energies for $[C_2C_1Mor]Br$ and $[C_4C_1Mor]Br$ are 67.7 eV and 67.6 eV, respectively. In the cases of octyl and dodecyl, the percolation of the non-polar isolated phases into the polar continuous phases gives rise to the stretching of the polar region, which dramatically enlarges the distance of the cation headgroup and the anion. Consequently, the anion is left bearing more negative point charges. It is found that the measured Br $3d_{5/2}$ binding energies for $[C_8C_1Mor]Br$ and $[C_{12}C_1Mor]Br$ are both 67.4 eV, which are 0.3 eV smaller than that for $[C_2C_1Mor]Br$.

It has to be emphasised that when increasing the side alkyl chain length, the change in electronic environment of the cationic components, *i.e.* N_{cation} 1s and O_{cation} 1s, is not measurable by XPS. This might be due to the existence of the dipolar structure of the morpholinium cation. Although less partial negative charge is transferred from Br^- to the cation in the case of long alkyl chains, such an effect can be successfully diluted by the two poles. As a result, for each element, the change in electronic environment is not noticeable.

Conclusions

This study attempts to gain fundamental understanding of the cation-anion interactions for 1-alkyl-1-methylmorpholinium-based ionic liquids using XPS analysis. A reliable three-component fitting model for the carbon region is developed, according to the ^{13}C NMR data. The effect of the alkyl chain length on the measured $C_{aliphatic}$ binding energies is illustrated by varying the substituent length from ethyl to dodecyl and employing two extreme representative anions, Br^- and $[Tf_2N]^-$.

The impact of the anion basicity on the cation-anion interactions is studied. It is found that both N_{cation} 1s and O_{cation} 1s binding energies can be effectively affected. However, the O_{cation} 1s binding energy is found more noticeably shifted. It is concluded that the N_{cation} 1s and O_{cation} 1s binding energies for these three ionic liquids follow the trend: $[Tf_2N]^- > [PF_6]^- > Br^-$. The impact of cation acidity on the cation-anion interactions is also investigated by comparing the F 1s binding energy between $[C_8C_1Mor][Tf_2N]$ and $[C_8C_1Pip][Tf_2N]$. It suggests that the binding energy shift is more than 0.2 eV.

The impact of the long alkyl side substituent on the cation-anion interactions is also investigated by comparing Br $3d_{5/2}$ binding energy, changing the alkyl chain length from ethyl to dodecyl. It indicates that there is an intense charge shielding effect of the alkyl side chain in the cases of octyl and dodecyl. In these two cases, the non-polar isolated phases can significantly percolate into polar continuous phases, and thus cause the weakening of the cation-anion interactions, which can be reflected in the lowering of the measured Br $3d_{5/2}$ binding energy.

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