Investigation of 1, 10-Phenanthroline based Ionic Liquids using X-ray photoelectron spectroscopy

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ABSTRACT

Ionic liquids—low temperature molten salts composed entirely of mobile ions—are a fascinating class of materials that have experienced an incredible growth in research over recent years. This is because of their immense applications in not only academic but also industrial processes. Ultra high vacuum technique, *i.e.* X-ray photoelectron spectroscopy is now accepted as a reliable method for the study of ionic liquid-based systems. To date, the main focus of research effort employing X-ray photoelectron spectroscopy has been upon imidazolium-based ionic liquids, quite simply because these are the materials most often employed by synthetic chemists. However, X-ray photoelectron spectroscopy data (fitting models) for other than 1, 3-dialkyimidazolium based ionic liquids are required and need to be developed. 1, 10-Phenanthrolinium based ionic liquids are among the new compounds reported recently. However, no attempt is observed to investigate the electronic environments of its component atoms. In this report, therefore, the electronic environments of six N-alkyl-1, 10-Phenathrolinium based ionic liquids, [C_nPhen][Tf₂N] (n=1, 2, 4, 6, 8, 10), were investigated using the X-ray photoelectron spectroscopy and a good fitting is developed for C 1s, and N 1s that applies to each of the compounds studied. This model allows accurate charge correction and the determination of reliable and reproducible binding energies of all the atoms for each compound studied. Hence, this model could be taken as benchmark in investigating any compound containing 1, 10-phenanthroline derivatives.

Keywords: 1, 10-phenanthroline, fitting model, Ionic liquids, X-ray photoelectron spectroscopy DOI: http://dx.doi.org/10.4314/ejst.v9i1.3

INTRODUCTION

Ionic liquids (ILs) are low temperature (below 100 °C) melting salts composed solely of mobile ions. ILs are a fascinating class of materials which have magnetized the research direction of scientists (Plechkova *et al.*, 2008; Wasserscheid and Welton, 2008; Weingartner, 2008;). Unlike molecular solvents, the properties of ILs can be tuned by the structurally diversified cation/anion combination (Coasne *et al.*, 2011). Features such as negligible vapor pressure, non- flammability, widespread liquidus temperature range, high ionic conductivity, excellent dissolving power for many materials, and a wide potential window make ILs the subject of research as alternative solvents in organic synthesis and organometallic catalysis (Dupont *et al.*, 2002), biocatalysis and electrochemistry (van Rantwijk *et al.*, 2007).

To date, the main focus of research effort, particularly in the area of surface characterization and ultra-high vacuum (UHV) characterization of ILs, has been upon imidazolium-based ionic liquids, quite simply because these are the materials most often employed by synthetic chemists (Men *et al.*, 2011). However, this class of ionic liquids have limitations such as poor solubility of simple metal salts. The limited solubility is due to the poor coordinating power of the anions such as tetrafluoroborate, $[BF_4]^-$, hexafluot-

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phosphate, $[PF_6]$, or bis(trifluoromethylsulfonyl) imide, $[Tf_2N]$ (Schaltin *et al.*, 2011). To increase the solubility, either employing new cations and/ or anions or modifications of the traditional ones can be used (Nockemann *et al.*, 2006,; Nockemann *et al.*, 2010). In view of this, a new set of 1, 10-phenanthrolinium cation based ILs were synthesized and their potential applications were reported elsewhere (Villar-Garcia *et al.*, 2012). However, there is no evidence that attempted to investigate the latter class of compounds using ultra-high vacuum (UHV) characterization techniques.

Herein, therefore, we report the investigation of the electronic environment of the component atoms of the N-alkyl-1, 10-phenanthrolinium cations, $[C_n]^+$ n = 1, 2, 4, 6, 8. 10, and the anion, bis(trifluoromethylsulfonyl) imide, $[CF_3SO_2]_2N^-$ (See Table 1) using ultra-high vacuum (UHV) characterization using x-ray photoelectron spectroscopy, XPS.

The electronic environment of each element present in the compounds is discussed. For ionic liquids, the most common, complex and often relevant element is carbon. Therefore, the development of a C 1s fitting model which deconstructs these different electronic

Table 1. Structure and abbreviations of the compounds investigated in this study

Chemical	Structure	Name	
formula			
[C ₁ Phen][Tf ₂ N]		<i>N-Methyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)
[C ₂ Phen][Tf ₂ N]	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	<i>N-ethyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)
[C ₄ Phen][Tf ₂ N]	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	<i>N-butyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)
[C ₆ Phen][Tf ₂ N]	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	<i>N-hexyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)
[C ₈ Phen][Tf ₂ N]	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	<i>N-octyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)
[C ₁₀ Phen][Tf ₂ N]	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	<i>N-decyl-1,10-Phenanthrolinium</i> sulfonyl] imide	bis[(trifluoromethyl)

environments into as small a number of components as possible is a critical goal in all XPS studies (Lovelock *et al.*, 2010; Villar-Garcia *et al.*, 2011). Peak fitting models are developed for C 1s and N 1s regions of $[C_n Phen][Tf_2N]$, This model is believed to be valid for compounds containing 1, 10-phenanthroline as a part. The binding energy data of the component atoms that again illustrate the information about their electronic environment of each atom of every element in the compound is extracted. This can be used to probe the magnitude of cation-anion based interactions.

EXPERIMENTAL

Materials

All compounds presented here were synthesized using established literature methods with minor modifications. Primarily, the compounds with halide anions (I and Br) were synthesized. 1, 10-Phenanthrolinium iodide ([C₁Phen] I) and N-Ethyl-1, 10-Phenanthrolinium iodide ([C,Phen]I) were synthesized using methyl iodide and ethyl iodide as alkylating agents, respectively. And the rest ([C,Phen]Br, n=4, 6, 8 and 10) were synthesized using the corresponding alkyl-1-bromides. In the synthesis of 1, 10-Phenanthrolinium iodide ([C₁Phen] I) and N-Ethyl-1, 10-Phenanthrolinium iodide ([C,Phen]I), 20 g (0.11 mol) 1, 10-Phenanthroline (dried in an oven at 110 °C for 2 hrs.) was dissolved in dried acetonitrile in a 250 ml two necked round bottom flask fitted to a reflux condenser and covered with aluminum foil and guarded from moisture using CaCl₂. 0.12 mol alkyl halide was added drop wise to 1, 10-Phenanthroline while stirring. The mixture was stirred in an oil bath at 30-35 °C for 8 hrs. A yellow precipitate was obtained which was filtered and washed thoroughly with chloroform and dried and put in

a dark vial. Involving alkyl bromides as alkylating agents the quantities of the reagents being the same as above, duration of the reaction time and the temperature were increased from 24 to 72 hrs and 40 to 80 °C, respectively, following the chain length. In all cases, gray precipitates were obtained. The precipitates were filtered and [C₄Phen]Br, [C₅Phen]Br and [C₆Phen]Br were washed thoroughly with acetone while [C_sPhen] Br and $[C_{10}Phen]Br$ were washed with 1, 4-Dioxane. The halide anions were exchanged with $[NTf_2]$ by dissolving 0.050 mol $[C_pPhen]X, X =$ Br⁻, I⁻ n = 1, 2, 4, 6, 8, 10; in deionized water at room temperature to which 0.051 mol of LiNTf₂ dissolved in water was mixed gradually while stirring. White precipitates were obtained. The white powder was filtered, thoroughly washed with deionized water and dried (MacFarlane et al., 1999; Deyko et al., 2009; Papaiconomou et al., 2007;). These compounds were fully characterized at School of Chemistry, University of Nottingham, UK.

All X-ray photoelectron spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al K α source (hv =1486.6 eV), hybrid (magnetic/electrostatic) optics, hemispherical analyzer and a multi-channel plate and delay line detector (DLD) with an X-ray incident angle of 0° (relative to the surface normal).

XPS data collection

Samples were prepared by placing 15-20 mg of the compounds in to a depression on a stainless steel sample stub. The samples were then cast into thin films (approximately to a thickness of 0.5-1 mm), before rapid transfer to the preparative pumping chamber of the XPS instrument. Initial pumping to high vacuum pressure ($p \le 1x10^{-7}$ mbar) was carried out for about 3 hrs in the preparation to insure the complete removal of adsorbed volatiles includ-

ing permanent gases, water vapor and other volatile impurities. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained $\leq 1 \times 10^{-8}$ mbar during XPS measurements of the samples (Men *et al.*, 2011).

XPS data analysis

Relative Sensitivity Factors (RSF) were taken from the Kratos Library (RSF of F 1s = 1) and were used to determine atomic percentages (Wagner et al., 1981; Smith et al, 2006). Peaks were fitted using GL(30) line shapes; a combination of Gaussian (70 %) and Lorenzian (30%) (Briggs et al., 2003; Smith et al., 2006). This line shape has been used consistently in the fitting of XP spectra, and has been found to mach experimental line shapes in ionic liquid systems (Smith et al., 2006; Villar-Garcia et al., 2011). All X-ray photoelectron spectra were charge corrected by setting the binding energy of the aliphatic C 1s photoemission peak $(C_{aliphatic} Is)$ of [C_sPhen][Tf₂N] equal to 285.0 eV. For all other values of n (*i.e.*, when n = 2, 4, 6 and 10) spectra are charge corrected by setting the measured binding energy of the alkylated cationic nitrogen photoemission peak ($N_{cation}Is$) equal to 402.2 eV. This value is the measured binding energy of the cationic alkylated nitrogen photoemission ($N_{cation}Is$) in the standard reference material for this serious of compounds, *i. e.*, [C_nPhen] [Tf₂N]. This method of charge correction is valid because each of the samples in this homologous experimental series has a structurally similar cation and an identical anion, [Tf₂N]⁻.

RESULTS AND DISCUSSION

 $[C_nPhen][Tf_2N]$ composition and purity were established by the measurement of X-ray photoelectron survey and high-resolution spectra for each sample; a representative example of a survey spectrum recorded for N-octyl-1,10-Phenanthrolinium bis[(trifluoromethyl)sulfonyl] imide, $[C_8Phen][Tf_2N]$ is given in Figure 1.

It can be observed that all the expected elements are signaled by their envelopes on their respective position. It can also be seen that no evidence of either Li or halide contamination carried over from ion exchange processes. Experimental stoichiometries were within experimental error



Figure 1. Survey spectrum for [C₈Phen][Tf₂N]

of nominal stoichiometries calculated from the empirical formula of the sample.

Binding energies

In order to obtain absolute binding energies for components within 1, 10-Phenanthrolinium based compounds, it is necessary to charge correct the X-ray photoelectron spectra using an appropriate internal reference. To investigate whether such an internal reference exists for 1, 10-Phenanthrolinium-based compounds, all peaks in the X-ray photoelectron spectra must be identified, and related to the chemical structure of the compounds, *i. e.*, an appropriate multicomponent model must be applied in the deconstruction of the measured photoemission envelopes.

The electronic environment of carbon, the development of a fitting model

To establish a fitting model for our compounds, identification of the different electronic environments for C 1s and then assigning them is vital. For [C, Phen][Tf, N], where n = 2, 4, 6, 8 and 10; (Figure 2) five components were used to fit the C 1s experimental spectrum. However, because the alkyl carbons other than CH₃ are not present, [C,Phen][Tf,N] four component C 1s were employed. The peak at highest binding energy (≈ 293 eV) is assigned to CF₃ group of the anion. This is in good agreement with literature report (Smith et al., 2006; Lovelock et al., 2009). The other values 285.7-286.9 eV and \approx 285 eV assigned for the carbon components within [C, Phen]⁺. Based on this, the first of these four environments is carbon bonded to the alkylated nitrogen; [C Phen]⁺ contains three such atoms labeled as $(C^1 + C^2)$. The second environment is the two carbon atoms bonded to the non-alkylated nitrogen labeled as (C³), the third assignment goes to the other eight carbon atoms in the ring labeled as (C⁴ + C⁵), and finally the alkyl environment labeled as C_{Alkyl} whose magnitude varies depending upon *n*. Regarding [C₁Phen][Tf₂N], the total number of contributions for C 1s is four as the alkyl chain not directly linked to nitrogen is missing.

The constraints used to establish this model was started from [C,Phen][Tf,N] in which there are 14 C atoms whose ratio is given by CF_3 : (C¹+C²) $: C^{1}+C^{2}) : (C^{3}) : (C^{4}+C^{5}) = 1 : 3 : 2 : 8$. However, shake up satellite can be observed as broad features in the spectrum from about 289.12-291.24 eV (Figure 2). Such features are originated from delocalized ring system. Consequently, approximately 20% of the photoelectrons emanated from the ring system are lost to the satellite feature. Therefore, the C 1s peaks should be fitted considering this redistribution of the photoelectrons. In this regard the peak due to C¹, (C^4+C^5) and C^3 is reduced by 20%. As the peak area of aliphatic carbons is not affected by the shakeup phenomenon, the relative peak area ratios for the four cationic components would be 1: 2.6: 1.6: 6.4. While the Full Width at Half Maximum, FWHM, for (C^1+C^2) , (C^3) , and (C^4+C^5) were set to be equal and set to be 1.1, for CF₃ was set from 0.9 to 0.95. In general, for all compounds studied here, similar procedures were followed and the fit shows an excellent agreement to the experimentally acquired signal.

In this regard, the binding energy separation between $(C^{1+}C^{2})1s$ and $(C^{3})1s$ is 0.61 eV, and the separation between $(C^{3})1s$ and $(C^{4+}C^{5})1s$ is 0.70 eV. In the case of $[C_{2}Phen][Tf_{2}N]$, the ratio of the component contributors would be CF_{3} : $(C^{1+}C^{2})$: $(C^{3}) : C^{4+}C^{5})$: $(C^{6}) = 1 : 2.6 : 1.6 : 6.4 : 1$. In this compound (Figure 2), the binding energy separation between $(C^{4} + C^{5})1s$ and $(C^{6})1s$ is also 0.5 eV.



Figure 2. C 1s X-ray photoelectron spectra with component fittings for (a) $[C_1Phen][Tf_2N]$, (b) $[C_2Phen][Tf_2N]$, (c) $[C_4Phen][Tf_2N]$, (d) $[C_6Phen][Tf_2N]$, (e) $[C_8Phen][Tf_2N]$, (f) $[C_{10}Phen][Tf_2N]$

The fitting model of C 1s of CF_3 in $[C_1Phen][Tf_2N]$ is a little different from the rest in that the electron donating CH_3 group significantly influences the electronic environment of the remaining carbons in the compound. However, as the alkyl chain length increases, the influence of the CH_3 group diminishes and thus consistent fittings are observed (Figure 2).

Electronic environment of nitrogen and other anion associated regions

The N 1s X-ray photoelectron spectra for $[C_n$ -Phen][Tf₂N] contain three characteristic peaks (Figure 3). The peak at higher binding energy (402.2 eV) is assigned to the alkylated nitrogen of the cation N_{Cation}. The peak at lower bind-

ing energy (399.52 eV) whose FWHM is nearly twice the former which is assigned to two nitrogen atoms, the unalkylated nitrogen, N_{Cation}^{\prime} , of the cation and that of the anion, Tf_2N^{-} (399.51 eV). This directly leads to the conclusion that the unalkylated N and the Nitrogen in the anion are signaled at around the same binding energy. Even though, the nitrogen in the anion is negatively charged (looks rich in electrons) it is also highly surrounded with large electronegative fluorine atoms which offsets the negative charge that leads it to be nearly neutral and to be signaled nearly at the binding energy of the neutral nitrogen. This binding energy is comparable with that observed for a range of imidazolium based ionic liquids (Smith *et al.*, 2006; Lovelock *et al.*, 2009; Villar-Garcia *et al.*, 2011).

The N 1s fitting model (Figure 3) in [C₁phen]



Figure 3. N 1s X-ray photoelectron spectra with component fittings for (a) $[C_1Phen][Tf_2N]$, (b) $[C_2Phen][Tf_2N]$, (c) $[C_4Phen][Tf_2N]$, (d) $[C_6Phen][Tf_2N]$, (e) $[C_8Phen][Tf_2N]$, (f) $[C_{10}Phen][Tf_2N]$

 $[Tf_2N]$ is a little different from the rest in the same reason as the C 1s of CF₃, which is the proximity of the electron donating CH₃ group created a little discrimination between N_{Anion} and unalkylated nitrogen of 1, 10-phenanthroline, N'_{Cation}.

Fluorine, oxygen and sulfur of these Compounds each show a single electronic environment (Smith *et al.*, 2006; Lovelock *et al.*, 2009; Villar-Garcia *et al.*, 2011). This is because of the obvious reason that the six fluorine atoms are chemically indistinguishable. This fact works the same for the four oxygen atoms and the two sulfur atoms. The doublet due to the region of sulfur does not signify the existence of two electronically different regions. This doublet peak is created because this element acquires two electronic states with respect to its 2p orbitals due to spin-orbit splitting into the S $2p_{1/2}$ and $2p_{3/2}$ levels with area ratio of 1:2 when bombarded and excited by the X-ray photons (Figure 4).



Figure 4. (a) F 1s, (b), O 1s, (c) S 2p X-ray photoelectron spectra for i. $[C_1Phen][Tf_2N]$, ii. $[C_2Phen][Tf_2N]$, iii. $[C_4Phen]$ $[Tf_2N]$, iv. $[C_6Phen][Tf_2N]$, v. $[C_8Phen][Tf_2N]$, and vi. $[C_{10}Phen][Tf_2N]$

It should be noted that the experimental errors associated with the measurement of binding energies in all the above spectra is of the order ± 0.1 ev.

The measurement of accurate binding energies

It is stated earlier that, charge compensation was not carried out consequently the recorded binding energies for these compounds cannot be considered as absolute values. This fact necessitates charge correction by setting the binding energy of aliphatic component of [C,Phen] $[Tf_2N]$ to be 285.0 eV. Subsequently, all the other regions are shifted by the same amount as the CAliphatic 1s component where the binding energy of the alkylated nitrogen, N_{Cation} 1s, shifts to 402.2 eV. Because the electronic environment of the cationic nitrogen is expected to be unaffected by the alkyl chain length, this latter value can then be used to charge correct all other [C, Phen][Tf,N] products. Figures 2-4 show the charge corrected C 1s and N 1s X-ray photoelectron spectra for these products. The binding energy of each element in the six compounds is summarized in Table 2. The binding energy values of alkyl chain C 1s corresponding to lengths shorter than octyl (C_{a}) are greater than 285 eV (285.2, 285.2 and 285.1 eV for C_2 , C_4 and C_6 , respectively). This is because; all the carbons experienced the effect of the high electronegative, alkylated and positively charged nitrogen and the electron deficient ring. C88 and C10, however, are long enough to disseminate the electron withdrawing effect throughout the chain which makes the binding energy smaller (285 eV). Similarly, the carbons(C^{1+2}) directly bonded to the alkylated nitrogen, N^{+}_{Cation} , are experiencing the second highest binding energy next to the C 1s of the CF₃ of the anion and are signaled at 286.9 eV. This is due to the obvious reason that they are

bonded to the positively charged alkylated nitrogen and also they are part of the electron deficient ring. On the other hand, regardless of the alkyl chain length, little or no effect is observed on the binding energies of the remaining parts of the compound including the anion. In general, as the binding energies listed are charge corrected, the data may find future use as a standard list of binding energies for $[C_nPhen][Tf_2N]$ ionic liquids.

In particular, if ionic liquids such as $[C_nPhen]$ $[Tf_2N]$ are studied using XPS, the spectra can be charge corrected to the binding energy of N⁺_{cation} 1s, 402.2 eV, and 399.6 eV for N^o_{cation} (unalkylated nitrogen). It should be noted that the experimental errors associated with the measurement of binding energies of all the elements in all ionic liquids is of the order ±0.1 ev.

CONCLUSIONS

We have successfully measured X-ray photoelectron spectra for six 1, 10-Phenanthrolinium based ionic liquids, varying only the aliphatic chain length of the cation keeping the anion constant. The ionic liquids were demonstrated to be of high purity, allowing conclusions to be drawn on the physicochemical properties of the 1, 10-Phenathrolinium based ionic liquids in particular and any compound containing 1, 10-Phenanthroline in general. The electronic environments of all elements were identified. A reliable fitting model for the C 1s and N 1s regions of 1, 10-Phenanthrolinium-based ionic liquids was produced. The binding energy of the aliphatic carbon (CAlkvl 1s) moiety was determined with high confidence. As reliable binding energies were obtained for CAlkyl 1s, charge corrected binding energies (absolute binding energies) for all components could be obtained. Variation of n was shown to have little or no effect on the electronic

	<u>S 2p3/2</u>	168.9	168.9	168.9	169.0	169.0	169.0
Binding Energy/eV	<u>F1s</u>	688.9	688.7	688.8	688.8	688.8	688.8
	<u>01s</u>	532.5	532.6	532.7	532.6	532.7	532.7
	$\underline{N}^{\mathtt{z}}_{\underline{Anion}}\underline{1s}$	399.4	399.5	399.5	399.6	399.6	399.6
	$\underline{N}^{\pm}_{\underline{Cation}}\underline{1s}$	402.2	402.3	402.2	402.2	402.2	402.2
	$\underline{N}^{\text{-}}_{\underline{\text{Cation}}}1$	399.6	399.6	399.6	399.6	399.6	399.6
	$\overline{\mathrm{CF}}_{\underline{3}}\overline{\mathrm{1s}}$	293.0	292.9	292.9	293.0	292.9	292.9
	$\underline{C}_{\underline{4+5}}\underline{1s}$	285.6	285.6	285.6	285.7	285.7	285.7
	$\underline{C}_{3}\underline{1s}$	286.3	286.8	286.4	286.3	286.3	286.2
	$\underline{C}_{\underline{l+2}}\underline{ls}$	286.9	286.9	286.9	286.9	286.9	286.9
	$\underline{C}_{\underline{alkyl}}\underline{1s}$		285.2	285.2	285.1	285.0	285.0
<u>Ionic Liquid</u>	Cation	[C ₁ Phen]	[C ₂ Phen]	$[C_4Phen]$	[C ₆ Phen]	[C ₈ Phen]	[C ₁₀ Phen]

Table 2. Binding energies in eV for all regions for $[C_nPhen][Tf_2N]$

interaction of the charge-bearing head groups of the ionic liquid. The binding energy data table presented in this paper may find future use as a standard list of binding energies for 1, 10-Phenanthrolinium-based ionic liquids.

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