Chemical Analysis of Ionic Liquids Using Photoelectron Spectroscopy

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The feasibility of utilizing X-ray photoelectron spectroscopy (XPS) to analyze room-temperature ionic liquids (RTILs) was investigated in this study. Conventionally, the chemical structure of organic compounds is identified by nuclear magnetic resonance (NMR) spectroscopy. The properties of RTILs, especially their low vapor pressure, make it possible to analyze RTILs by using XPS. The usefulness of XPS on RTILs was confirmed by commercial RTILs. All atoms in RTILs were detected in survey XPS spectra, and the calculated atomic percentages matched well with theoretical values. After the verification of commercial RTILs by XPS, we synthesized three RTILs and investigated them with XPS. The atomic ratio and chemical environment of carbon in RTILs were verified by XPS. By adapting XPS to the investigation of RTILs, carbon atoms in different chemical environments were distinguishable by the binding energy shift, and the atomic ratio of the constituent atoms was identifiable after peak deconvolution. In addition, inorganic constituents were detected by XPS unlike in the case of NMR spectroscopy.

Keywords: X-ray photoelectron spectroscopy, Nuclear magnetic resonance, Room-temperature ionic liquid

Introduction

Room-temperature ionic liquids (RTILs) are remarkable materials due to their unique characteristics including extremely low vapor pressure at room temperature, high ionic mobility, high electrical conductivity, low flammability, low melting point, and superior chemical and thermal stabilities.^{1–3} These properties result from the irregular configuration between organic cations, which generally contain nitrogen or phosphorous atoms, and large organic or inorganic anions.⁴ Because of these properties, RTILs are useful as solvents in organic reactions⁵ and synthesis of metallic particles,⁶ as catalysts in dye-sensitized solar cells,⁷ in tribology,^{8,9} and as electrolytes in batteries or double-layer capacitors.¹⁰

The physicochemical properties of RTILs are dependent on the chemical structures of the cation and anion of RTILs. Many research groups have investigated the effect of different cations with same anions or various anions with same cations on the properties of RTILs.¹¹⁻¹³ To verify the properof RTILs, many techniques such as liquid ties chromatography,⁴ grazing incidence X-ray diffraction,⁹ soft X-ray emission spectroscopy,¹⁴ high-resolution electron energy-loss spectroscopy (HREELS),¹⁵ low-energy ion scattering (LEIS),^{16,17} high-resolution Rutherford backscattering (HRBS),¹³ metastable impact electron spectroscopy (MIES),¹ ultraviolet photoelectron spectroscopy (UPS),^{1,18} and X-ray photoelectron spectroscopy (XPS)^{1,18,19} have been utilized. Among them, photoelectron emission spectroscopy (XPS or UPS) would be a useful technique to confirm the qualitative and semiquantitative properties of solid materials in general. XPS technique is limited to analyzing solid samples because it is performed under ultrahigh vacuum (UHV) conditions. However, the constraint for using XPS to analyze RTILs can be overcome because of their extremely low vapor pressure.

In this study, XPS was used to identify the chemical structure of RTILs. Commercially available RTILs (1-butyl-3methylimidazolium tetrafluoroborate ([BMIM] BF₄), 1butyl-3-methylimidazolium hexafluorophosphate ([BMIM] PF₆), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM] OTf), 1-hexyl-3-methyl imidazolium hexafluorophosphate ([HMIM] PF₆), and 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([EMIM] NTf₂) were qualitatively and semiquantitatively investigated by XPS. In order to confirm whether the results of XPS were correct, nuclear magnetic resonance (NMR) spectroscopy was performed on the commercially available RTILs. After the XPS results were confirmed by NMR spectroscopy, synthesized the RTILs 1-butyl-3-(4-sulfobutyl)-3we imidazolium trifluoromethanesulfonate ([BSBIM] OTf), 1methyl-3-(3-sulfopropyl)-3-imidazolium trifluoromethanesulfonate ([MSPIM] OTf), and 1-butyl-3-(4-sulfopropyl)-3imidazolium trifluoromethanesulfonate ([BSPIM] OTf) and analyzed them with both XPS and NMR spectroscopy.

We used XPS and NMR spectroscopy to analyze commercially available and synthesized RTILs in this work. NMR spectroscopy is a useful tool to analyze organic compounds in the conventional sense. In order to identify the chemical environment of the elements in an RTIL by NMR spectroscopy, ¹H-NMR and ¹³C-NMR analyses should be performed. However, XPS is a useful technique to analyze both organic and inorganic compounds. In addition, NMR spectroscopy

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has to be carried out several times depending on the kinds of constituents of the organic compound, while XPS needs to be performed only once to analyze all constituents in the organic and/or inorganic RTILs.

Experimental

General Methods. Air- and/or moisture-sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. All compounds were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled (1,4-dioxane and toluene over sodium) or dried by passing through an alumina column. Thin-layer chromatography was carried out on glass plates coated with silica gel SiO2 60 F₂₅₄ (Merck: St. Louis, MO, USA), with visualization using a UV lamp (254 nm) or by staining with a panisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO₂ 60 (0.040–0.063 µm, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Proton (¹H) and carbon (¹³C) NMR spectroscopy were performed (JEOL ECP-400 spectrometer: Tokyo, Japan) at 400 MHz (¹H) and 100 MHz (¹³C) at 294 K. Chemical shifts are reported in ppm relative to the residual protiated solvent (CDCl₃: $\delta H =$ 7.26 ppm, $\delta C = 77.16$ ppm). All ¹³C NMR spectra are proton-decoupled. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), and br (broad). The notation and chemical structure of RTILs studied in this work are listed in Table 1.

Synthesis of RTILs

[BSBIM] OTf. 1-(4-Sulfonic acid) butyl-3-butyl-3butylimidazolium was synthesized according to the literature procedure.²⁰ 1-Butylimidazole (1.06 mL, 8.05 mmol) and 1,4-butanesultone (0.824 mL, 8.05 mmol) were dissolved in toluene (2.0 mL), and stirred at 60 °C for 24 h. The mixture was cooled to at 25 °C. The precipitate was washed with ether and toluene to remove non-ionic residues, and dried *in vacuo*. 1-Butyl-3-(butyl-4-sulfonate)imidazolium zwitterion was obtained as a white solid (2.09 g, 99.7%).

Triflic acid (0.710 mL, 8.03 mmol) was added to 1-butyl-3-(butyl-4-sulfonate)imidazolium zwitterions (2.09 g, 8.03 mmol) at 25 °C. The reaction mixture was stirred at 60 °C for 18 h. After cooling to 25 °C, Et_2O (2 mL) was added to the reaction mixture. The ionic liquid– Et_2O mixture was stirred for 2 min, whereupon mixture clearly showed two separate layers. The upper Et_2O layer was carefully removed by decantation. This procedure was repeated five times to remove non-ionic residues. The residue was dried *in vacuo* to afford the title compound as a colorless oil (3.10 g, 94%). Spectral data matched those in the literature.^{20,21}

¹H NMR (400 MHz, DMSO- d_6) δ 9.21 (t, J = 1.7 Hz, 1H), 7.79 (q, J = 1.7 Hz, 2H), 4.17 (dt, J = 8.7, 7.1 Hz, 4H), 2.58 (td, J = 7.4, 1.1 Hz, 2H), 1.89 (p, J = 7.3 Hz, 2H), 1.77 (tt, J = 9.1, 6.8 Hz, 2H), 1.62–1.49 (m, 2H), 1.30–1.19 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, DMSO- d_6)δ137.38, 124.00, 123.84, 120.42 (q, J_{CF} = 324.4 Hz), 51.74, 50.00, 49.87, 32.64, 29.72, 22.73, 20.14, 14.57.

[MSPIM] OTf. 1-Methylimidazole (0.97 mL, 12.2 mmol) and 1,3-propanesultone (1.07 mL, 12.2 mmol) were dissolved in toluene (3.0 mL), and stirred at 60 °C for 24 h. The mixture was cooled to 25 °C. The precipitate was washed with ether and toluene to remove non-ionic residues, and dried *in vacuo.* 3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion was obtained as a white solid (2.41 g, 96.8%).

Triflic acid (1.04 mL, 11.8 mmol) was added to 3-(1methyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion (2.41 g, 11.86 mmol) at 25 °C. The reaction mixture was stirred at 60 °C for 18 h. After cooling to 25 °C, Et₂O (2 mL) was added to the reaction mixture. The ionic liquid– Et₂O mixture was stirred for 2 min, whereupon mixture clearly showed two separate layers. The upper Et₂O layer was carefully removed by decantation. This procedure was repeated five times to remove non-ionic residues. The residue was dried *in vacuo* to afford title compound as a colorless oil (4.12 g, 98.6%). Spectral data matched those in the literature.^{22,23}

¹H NMR (400 MHz, D₂O) δ 8.64 (s, 1H), 7.42 (t, *J* = 1.8 Hz, 1H), 7.35 (q, *J* = 1.6 Hz, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.82 (t, 7.2 Hz, 2H), 2.28–2.15 (m, 2H).

¹³C NMR (101 MHz, D₂O) δ 137.08, 124.86, 123.24, 120.76 (q, J_{CF} = 319.7 Hz), 48.83, 48.35, 36.77, 26.11.

[BSPIM] OTf. 1-Butylimidazole (1.06 mL, 8.05 mmol) and 1,3-propanesultone (0.702 mL, 8.05 mmol) were dissolved in toluene (2.0 mL), and stirred at 60 °C for 24 h. The mixture was cooled to 25 °C. The precipitate was washed with ether and toluene to remove non-ionic residues, and dried *in vacuo*. 3-(1-Butyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion was obtained as a white solid (1.95 g, 98.5%).

Triflic acid (0.699 mL, 7.9 mmol) was added to 3-(1-butyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate zwitterion (1.95 g, 7.9 mmol) at 25 °C. The reaction mixture was stirred at 60 °C for 18 h. After cooling 25 °C , Et₂O (2 mL) was added to the reaction mixture. The ionic liquid–Et₂O mixture was stirred for 2 min, whereupon the mixture clearly showed two separate layers. The upper Et₂O layer was carefully removed by decantation. This procedure was repeated five times to remove non-ionic residues. The residue was dried *in vacuo* to afford title compound as a colorless oil (3.03 g, 96.7%). Spectral data matched those in the literature.²⁴

¹H NMR (400 MHz, D₂O) δ 8.79 (s, 1H), 7.51 (t, *J* = .9, 1H), 7.49 (t, *J* = 1.8 Hz, 1H), 4.34 (t, *J* = 7.1 Hz, 2H), 4.18 (t, *J* = 7.2 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.2 Hz, 2H), 1.82 (q, *J* = 7.4 Hz, 2H), 1.36–1.21 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, D₂O) δ 136.23, 123.55, 123.23, 120.59 (q, J_{CF} = 319.7 Hz), 50.34, 48.71, 48.19, 32.03, 26.00, 19.64, 13.49.

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Table 1. Commercial and synthesized RTILs and their chemical structures.

Chemical Analysis of RTILs

Ionic Liquids	Full name	Structure		
[HMIM] PF ₆	1-Hexyl-3-methyl imidazolium hexafluorophosphate	N [*] F F F F		
[EMIM] NTf ₂	1-Ethyl-3-methyl imidazolium bis((trifluoromethyl)sulfonyl))imide			
[BSBIM] OTf	1- B utyl-3-(4- s ulfo b utyl) im idazolium trifluoromethanesulfonate	$N_{\rm ev}^{\rm ev}$ $N_{\rm ev}^{$		
[BSPIM] OTf	1-Butyl-3-(3-sulfopropyl) imidazolium trifluoromethanesulfonate	N N SO ₃ H F O H F O H O SO ₃ H F O H O SO ₃ H F O H O SO ₃ H F O H O SO		
[MSPIM] OTf	1-Butyl-3-(4-sulfopropyl) imidazolium trifluoromethanesulfonate	N, N, SO ₃ H F O F O - SO ₃ H F O		
[BMIM] OTf	1-Butyl-3-methyl imidazolium trifluoromethanesulfonate	N N F O O F O F O O O F O O O F O		
[BMIM] PF ₆	1-Butyl-3-methyl imidazolium hexafluorophosphate			
[BMIM] BF ₄	1- B utyl-3- m ethyl im idazolium tetrafluoroborate			

X-ray Photoelectron Spectroscopy. The commercially available RTILs ([HMIM] PF₆, [EMIM] NTf₂, [BMIM] BF₄, [BMIM] PF₆, and [BMIM] OTf) were analyzed by an XPS (VG ESCALab 2000: St Leonards-on-Sea, East Sussex, UK) system using the Mg K α source (1253.6 eV) with a high voltage of 15 kV and a beam current of 15 mA. The survey and high-resolution XPS spectra were obtained from a pass energy of 50 and 20 eV and a scan step of 1 and 0.05 eV, respectively. The dwell time for both spectra was 50 ms. The synthesized RTILs, namely [BSBIM] OTf, [MSPIM] OTf, and [BSPIM] OTf, were investigated by a modified XPS (based on the VG ESCALab MKII) system, which consisted of four components: a load-lock chamber, a preparation chamber equipped with two multi-sample carousels, an analysis chamber, and a sputter chamber for deposition of thin films in the UHV environment. The base pressure of the customized electron emission chamber was maintained at below $\sim 1.0 \times 10^{-7}$ Pa using two rotary vane pumps, two turbo molecular pumps, three ion getter pumps, and two Tisublimation pumps. The analysis chamber was equipped with a dual X-ray anode for XPS, a UV lamp for UPS, an electron gun for Auger electron spectroscopy (AES), an Ar ion sputter gun for cleaning the sample and depth profiling, a concentric hemispherical analyzer (CHA), and a channeltron for the detection of the photoemitted electrons. To investigate the chemical property of RTILs using XPS, many researchers have tried to form RTIL films.^{1,19,25,26} This method, however, is cumbersome for analyzing RTILs. To overcome this problem, we designed a customized sample holder made of stainless steel for RTILs. The center region of the sample holder is concave to prevent the spilling of RTILs in the analysis chamber. RTILs in the sample holder were pre-pumped overnight in the load-lock chamber for to evacuate the dissolved gas in the RTILs. RTILs in the preparation chamber were transferred to the analysis chamber by two transfer rods and two wobble sticks. The working pressure of the analysis chamber was maintained below 1×10^{-6} Pa. An Al K α source (1486.6 eV) with an anode voltage of 7.5 kV and a beam current of 20 mA was used in this work. The survey XPS spectra were obtained with a pass energy of 100 eV, a dwell time of 100 ms, and a step size of 0.5 eV. The high-resolution XPS spectra were collected with a pass energy of 50 eV, a dwell time of 100 ms, and a step size of 0.02 eV. The peak-fitting of the XPS spectra was achieved by the XPSPEAK program (version 4.1). The background type applied was Shirley mode, and the Gaussian/Lorentzian ratio was 30:70. The charge accumulation effect was corrected on the basis of the aliphatic carbon at the binding energy of 284.6 eV.

Results and Discussion

RTILs investigated in this work consist of organic cations (imidazolium) and various inorganic anions. In ususal circumstances, organic compounds are investigated by NMR spectroscopy. Therefore, the chemical information of cations is successfully obtained, while information on anions remains unknown because of the inorganic character of the anions. To overcome this limitation, XPS analysis was adapted in this work. The feasibility of using XPS for RTIL analysis was tested on commercially available RTILs. The representative survey XPS spectra and deconvoluted C 1s spectra of [HMIM] PF_6 are shown in Figure 1(a) and (b), respectively. In Figure 1 (a), all characteristic XPS peaks of the constituents of the [HMIM] PF₆ were detected. XPS peaks of P 2p, C 1s, N 1s, and F 1s were observed at the binding energies of 150, 285, 399, and 650 eV, respectively. From the survey spectra of [HMIM] PF₆, the constituent elements in the RTIL were successfully identified. The purity of commercial RTILs was also corroborated by NMR spectroscopy. From the XPS results, all atoms consisting of [HMIM] PF₆ were detected by survey XPS spectra, and the atomic percentages of the RTILs are listed in Table 2. The atomic percentages were calculated by considering the peak areas and atomic sensitivity factors.² It shows that the atomic percentages obtained by XPS match well with the theoretical values of [HMIM] PF₆. This result confirmed the reliability of XPS in the investigation of RTILs. Furthermore, the information about the chemical environment of specific atoms makes XPS a powerful investigating tool for RTILs. In this study, high-resolution C 1s spectra were taken, and deconvolution process was performed to obtain detailed information. The peak-fitting of C 1s was achieved with six singlet peaks, as shown in Table 3. The C1s peak with the lowest binding energy (284.6 eV) is assigned to aliphatic sp^3 carbon (denoted as C1 in the molecular structure of [BSPIM] OTf). The sp³ carbon bonded with sulfonyl group is denoted as C2 at 285.2 eV. The carbon (C3) located at the alkyl chain and bonded with nitrogen is positioned at 285.7 eV. In the imidazolium ring, two carbons with different chemical environments exist. The C4 and C5 peaks are positioned at 286.4 and 287.4 eV, respectively. The C6 is used for denoting the carbon in triflate ions (OTf: CF₃SO₃ or NTf₂: N(SO₂CF₃)₂). Four carbon species were assigned after deconvolution of the C 1s XPS spectra of [HMIM] PF₆ as shown in Figure 1 (b). The atomic ratio of C1:C3:C4:C5 in [HMIM] PF_6 is 5:2:2:1, the obtained experimental value was 5.0:1.6:2.0:1.2. It revealed that the qualification and semiquantitative analysis of RTILs by means of XPS is feasible.

Figure 2 shows the survey XPS spectra of all RTILs analyzed in this work. The characteristic XPS peaks of fluorine centered at 685 eV, oxygen at 531 eV, nitrogen at 400 eV,



Figure 1. (a) Survey XPS spectra and (b) the deconvoluted C 1s spectra of [HMIM] PF₆.

Table 2. Atomic percentage in various RTILs. The numbers in parenthesis are the theoretical values.

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Ionic liquids	С	Ν	F
[HMIM] PF ₆	56.1 (56)	10.2 (11)	33.7 (33)
[EMIM] NTf ₂	48.3 (47)	16.1 (18)	35.6 (35)
[BSBIM] OTf	68.1 (71)	12.0 (12)	19.9 (18)
[BSPIM] OTf	64.4 (69)	12.7 (13)	22.9 (19)
[MSPIM] OTf	65.9 (62)	11.5 (15)	22.6 (23)
[BMIM] OTf	69.1 (64)	11.8 (14)	19.1 (21)
[BMIM] PF ₆	56.7 (50)	9.2 (13)	34.1 (38)
[BMIM] BF ₄	62.5 (57)	10.3 (14)	27.2 (29)

Table 3. Ratio of carbon species in different chemical environments obtained after peak deconvolution of C 1s spectra. The numbers without parentheses indicate the experimental values, and the numbers in parenthesis mean the theoretical value of RTILs

	C4 C4	L .			F 0
C1		V ⁺ C3	SI C2	O₃H	F-C-S-O
•	 				-

Carbon species	C1	C2	C3	C4	C5	C6
Binding energy (eV)	284.6	285.2	285.7	286.4	287.4	292.2
FWHM (eV)	1.6 ± 0.3	1.5 ± 0.1	1.5 ± 0.2	1.5 ± 0.1	1.9 ± 0.2	1.7 ± 0.3
[HMIM] PF ₆	5.0 (5)		1.6 (2)	2.0 (2)	1.2 (1)	
[EMIM] NTf ₂	1.4 (1)		2.2 (2)	2.0 (2)	1.0 (1)	1.6 (2)
[BSBIM] OTf	5.0 (5)	1.0(1)	2.2 (2)	2.0 (2)	1.2 (1)	0.8 (1)
[BSPIM] OTf	3.6 (4)	0.8 (1)	1.6 (2)	2.0 (2)	1.0(1)	0.8 (1)
[MSPIM] OTf	1.0 (1)	1.2 (1)	1.8 (2)	2.0 (2)	1.0 (1)	0.8 (1)
[BMIM] OTf	3.0 (3)		2.0 (2)	2.0 (2)	1.0(1)	0.6 (1)
[BMIM] PF ₆	3.2 (3)		2.0 (2)	2.0 (2)	1.2 (1)	
[BMIM] BF ₄	3.2 (3)		2.0 (2)	2.0 (2)	1.0 (1)	



Figure 2. Survey XPS spectra of RTILs. The star indicates the F KLL Auger lines.

carbon at 285 eV, sulfur at 231 and 167 eV, and phosphorus at 191 eV were detected. It shows that the analysis of RTILs by XPS is simple without any sample preparation processes, such as the formation of RTIL thin films.

Figure 3(a) shows the representative deconvoluted highresolution the C 1s XPS spectra of [BMIM] BF₄ and [BMIM] PF₆ as well as [EMIM] NTf₂ for commercial RTILs and [BSPIM] OTf for synthesized RTILs. The peak profiles of C 1s in [BMIM] BF_4 and [BMIM] PF_6 are similar. This implies that the cation effect on the chemical environment of the anion in RTILs is weak. In order to get detailed chemical information, peak deconvolution of C 1s was performed. The peakfitting for two RTILs containing [BMIM] anion was performed with four singlet peaks (C1, C3, C4, and C5), like for [HMIM] PF₆. The result of peak deconvolution shows that [BMIM] BF₄ and [BMIM] PF₆ have similar parameters, such as a full width at half maximum of each peak and the ratio of peak area. In [BSPIM] OTf, two more peaks (C2 and C6 as shown in Table 3) are added in C 1s spectrum for peak deconvolution. Comparing the carbon species in [BSPIM] OTf with those in [BMIM] BF₄ and [BMIM] PF₆, the carbon bonded with sulfonic acid in cation (C2) and carbon in triflate anions (C6) were detected (285.2 and 292.2 eV) from [BSPIM] OTf. And the other peaks (C1, C3, C4, and C5) are not significantly different from those in [BMIM] BF₄ and [BMIM] PF₆. The carbons in the cation of [EMIM] NTf2 have a similar chemical environment as those in [BMIM] cation. However, the peak position of C3, C4, and C5 are shifted to a higher binding energy region. This phenomenon is caused by the anion effect. The basicity of the anion in [EMIM] NTf₂ is higher than that of other anions. Consequently, electrons in the cation can be dragged to the anion, NTf₂. Therefore, the binding energy of carbons in anion in [EMIM] NTf2 has a higher value than those in [BMIM] BF4 and [BMIM] PF6. The size of [EMIM] cation is smaller than that of [BSPIM] cation which has longer alkyl chains compared to the [EMIM] cation. Thus, the anion effect more strongly influences [EMIM] NTf₂ than [BSPIM] OTf. The carbon (C6) in [EMIM] NTf₂ has also a higher binding





Figure 3. Deconvoluted high-resolution XPS spectra of C 1s (a), N 1s (b), and F 1s (c).

energy than that in [BSPIM] OTf. The ratio of carbon species obtained by peak deconvolution is listed in Table 3. The experimental ratios agree reasonably well with the theoretical values not only for commercial also for synthesized RTILs.

Figure 3(b) shows the high-resolution N 1s XPS spectra after the deconvolution process. Two nitrogen peaks are fitted at 401.5 and 399.3 eV, which correspond to the nitrogen in imidazolium cations (N_{cation}) and the NTf₂ anion (N_{anion}), respectively. Nitrogen in cations is positioned at the imidazolium ring in all cations, and singlet spectra are detected in [BMIM] BF₄, [BMIM] PF₆, and [BSPIM] OTf; however, a shoulder appears in the case of [EMIM] NTf₂. A peak shift to the lower binding energy region in [BSPIM] OTf is observed, which is caused by the charge distribution of imidazolium ring to the long alkyl chain.¹² The theoretical and experimental atomic ratio of N in imidazolium cations to anion N in [EMIM] NTf₂ is 67:33 and 71:29, respectively. The experimental value agrees with the theoretical value within the range of experimental error. The deconvoluted highresolution XPS spectra of F 1s are shown in Figure 3(c). All RTILs contain fluorine atoms, and in this study, the F1s peaks for four RTILs appeared at different binding energies. This is due to the different anions. As the anion basicity is increased, the binding energy of fluorine increases from 685.6 to 688.8 eV. Therefore, we can infer that the basicity of the anion increases in the order BF₄, PF₆, OTf, and the NTf₂ anion. This result is in agreement with the observation of Santos et al. in guanidinium ILs.¹² The atomic percentages of atoms in RTILs, carbon, nitrogen, and fluorine are listed in Table 2. The achieved values match well with the theoretical values for all RTILs. From this study, the application of XPS to the analysis of RTILs was confirmed using commercial RTILs,

were evaluated by XPS and 7 C -T Li C -P Lee

and then the synthesized RTILs were evaluated by XPS and NMR techniques.

Conclusion

We focused on the performance of XPS in terms of the identification of the RTILs. Two types of RTILs were investigated: commercially available and synthesized ones. The commercial RTILs ([HMIM] PF₆, [EMIM] NTf₂, [BMIM] OTf, [BMIM] PF₆, and [BMIM] BF₄) were analyzed by XPS, and the results were cross-checked with NMR techniques. All constituent atoms in the RTILS were detected in the survey XPS spectra. This is an advantage compared to NMR spectroscopy. After deconvolution of the C 1s peak, we could identify the atomic ratio of carbon with different chemical environments in the RTILs. The synthesized RTILs ([BSBIM] OTf, [BSPIM] OTf, and [MSPIM] OTf) were analyzed by XPS, and the experimentally obtained atomic ratios concurred with the theoretical values. XPS was therefore proved to be a useful technique to identify the chemical environment of organic cations and inorganic anions in RTILs as well.

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