

Ionic liquids containing the urea moiety for recognition of halides and complex anions

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A series of novel imidazolium based ionic liquids containing the urea moiety were designed and synthesized for anion recognition. 1-Ethylurea-3-methylimidazolium acetate ([Eumim]OAc) was used as the receptor for the halides and complex anions (BF_4^- , PF_6^- , BPh_4^-). ^1H NMR spectra showed that the urea protons and imidazolium C(2) proton of the receptor ([Eumim]OAc) moved upfield on addition of various anions. A Job plot showed that the [Eumim]OAc receptor formed a 1:1 complex with BPh_4^- . X-ray diffraction analysis and the molecular modeling study revealed that the conformations of [Eumim]OAc and [Eumim] BPh_4^- were different. The conformational change of the cation was caused by anion exchange, and may provide an alternative to current methods for recognition of anions.

ionic liquids, anion recognition, anion exchange, conformation, complex anions

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Anions such as fluoride, chloride, tetrafluoroborate, and hexafluorophosphate play a significant role in a wide range of environmental, biological and industrial processes [1–4]. Accordingly, the design and development of receptors for selective sensing or recognition of anions has attracted increasing interest. Most anion receptors have hydrogen bond donating groups, such as amide [5,6], pyrrole [7,8], guanidinium [9], imidazolium [10,11], urea or thiourea [12,13], to recognize anions through the formation of hydrogen bonds. However, recognition of anions like BF_4^- , PF_6^- and BPh_4^- is difficult with this type of receptor because these anions have a poor ability to form hydrogen bonds.

Ionic liquids are widely used as new and designable green chemical materials in organic and inorganic synthesis [14], catalysis [15,16], electrochemical [17] and separation processes [18]. They have high thermal stability and low volatility, and their physicochemical properties can be

finely tuned by selection of the anion and cation. Recently, the interaction between the cations and anions was found to play a major role in controlling the physicochemical properties of ionic liquids [19–21]. The interaction energies of ion pairs of ionic liquids were studied by ab initio calculations, and the magnitude of the interaction energies of ionic liquids with the same cation varied with the counter anion [19]. The cation of the ionic liquid preferentially combines with the anion, which they can form the larger interaction energy. Therefore, anion exchange probably takes place when another anion is added to the ionic liquid, and this changes the specific physicochemical properties of the ionic liquid. These changes could be used to develop a method for anion recognition. In the present study, a series of imidazolium based ionic liquids containing the urea moiety were synthesized. The ionic liquids were used as receptors to recognize halides and complex anions, such as BF_4^- , PF_6^- and BPh_4^- , via the variation in the chemical shifts of the urea and imidazolium C(2) protons.

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1 Experimental

1.1 Materials and methods

2-Chloroethylurea and butyl isocyanate were purchased from Tokyo Chemical Industry (Tokyo, Japan) and *N*-(3-aminopropyl) imidazole was purchased from Alfa Aesar (Ward Hill, MA). *N*-Methylimidazole was fractionally distilled. All other reagents and the anion salts were commercial reagents of AR grade and used without further purification.

¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆, on a Bruker Avance DRX 500 FT NMR spectrometer (Bruker, Billerica, MA) at 500 MHz for ¹H NMR spectra and at 126 MHz for ¹³C NMR spectra. The internal standard was tetramethylsilane. Each anion (1 equiv.) was added to a solution of 10 mg of [Eumim]OAc in 0.6 mL of DMSO-*d*₆. The halides were added as tetrabutylammonium salts. The complex anions, such as BF₄⁻, PF₆⁻ and BPh₄⁻, were added as sodium salts.

The stoichiometry was determined using Job's method. In this method, solutions of [Eumim]OAc and NaBPh₄ (both 6.0×10⁻² mol/L) were prepared in dry DMSO-*d*₆. Then the [Eumim]OAc and NaBPh₄ solutions were mixed in different proportions while maintaining a total volume of 0.6 mL. The ratios of [Eumim]OAc:NaBPh₄ were 1:0, 4:1, 3:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, 1:3, 1:4, and 0:1. All the prepared solutions were kept at room temperature for 5 h, and then their chemical shifts were recorded. The concentration of [HG] was calculated using [HG] = Δδ/δ₀ × [H], where Δδ/δ₀ is the relative chemical shift of the urea NH₂ protons and [H] is the concentration of the pure [Eumim]OAc. The amount-of-substance fraction of the guest (X_G) was plotted against the concentration of HG. The maximum [HG] indicated the stoichiometry of the complex.

The geometries of all species were optimized in the gas phase using B3LYP with Gaussian 03 program on a Pentium (R) Dual-Core E5200 computer. The 6-31+G(d) basis set was used for all atoms. The electronic energies were obtained from the output files of the geometry optimization calculations [22].

1.2 Synthesis of 1-ethylurea-3-methylimidazolium chloride [Eumim]Cl

N-Methylimidazole (4.51 g, 55 mmol) in 50 mL of ethanol was added dropwise to 2-chloroethylurea (6.13 g, 50 mmol) at 40°C. The mixture was stirred under N₂ at 80°C for 3 d. After evaporation of the solvent, the residue was recrystallized from ethanol to give 9.59 g (93.8%) of white solid. ¹H NMR (500 MHz, D₂O, Me₄Si) δ 3.40 (t, *J* = 6 Hz, 2 H), 3.77 (s, 3 H), 4.15 (t, *J* = 6 Hz, 2 H), 7.32 (s, 1 H), 7.36 (s, 1 H), 8.50 (s, 1 H).

1.3 Synthesis of 1-ethylurea-3-methylimidazolium acetate [Eumim]OAc

Silver acetate (3.34 g, 20 mmol) was added to a solution of [Eumim]Cl (4.09 g, 20 mmol) in water (80 mL) and stirred at room temperature for 4 h in the dark. The suspension was filtered to remove silver chloride. The water was removed in vacuo to afford 4.38 g (96%) of colorless oil. ¹H NMR (500 MHz, DMSO-*d*₆, Me₄Si) δ 1.61 (s, 3 H), 3.34–3.38 (m, 2 H), 3.85 (s, 3 H), 4.18 (t, *J* = 6.0 Hz, 2 H), 6.15 (s, 2 H), 7.69 (s, 1 H), 7.76 (s, 1 H), 8.14 (s, 1 H), 9.31 (s, 1 H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 25.6, 35.6, 40.1, 49.3, 122.6, 123.2, 137.2, 159.5, 174.5; ESI-MS *m/z* Calcd for [C₉H₁₆N₄O₂-OAc]: 169.1, found for (M-OAc)⁺: 169.0.

1.4 Synthesis of 1-ethylurea-3-methylimidazolium tetrafluoroborate [Eumim]BF₄

Silver tetrafluoroborate (0.58 g, 3 mmol) was added to a solution of [Eumim]Cl (0.61 g, 3 mmol) in water (30 mL) and stirred at room temperature for 4 h in the dark. The suspension was filtered to remove silver chloride. The water was removed in vacuo to afford 0.61 g (79%) of colorless oil. ¹H NMR (500 MHz, DMSO-*d*₆, Me₄Si) δ 3.37–3.41 (m, 2 H), 3.85 (s, 3 H), 4.17 (t, *J* = 5.75 Hz, 2 H), 5.59 (s, 2 H), 6.16 (t, *J* = 5.5 Hz, 1 H), 7.70 (d, *J* = 0.8 Hz, 2 H), 9.08 (s, 1 H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 35.71, 39.27, 49.57, 122.67, 123.50, 136.87, 158.72; ESI-MS *m/z* Calcd for [C₇H₁₃BF₄N₄O-BF₄]: 169.1, found for (M-BF₄)⁺: 169.0.

1.5 Synthesis of 1-ethylurea-3-methylimidazolium tetraphenylborate [Eumim]BPh₄

Sodium tetraphenylborate (1.03 g, 3 mmol) was added to a solution of [Eumim]Cl (0.61 g, 3 mmol) in water (100 mL) and stirred at room temperature for 5 h. The suspension was filtered to obtain 1.39 g (95%) of white solid. ¹H NMR (500 MHz, DMSO-*d*₆, Me₄Si) δ 3.37–3.40 (m, 2 H), 3.83 (s, 3 H), 4.16 (t, *J* = 5.5 Hz, 2 H), 5.59 (s, 2 H), 6.12 (t, *J* = 5.5 Hz, 1 H), 6.80 (t, *J* = 7.0 Hz, 4 H), 6.93 (t, *J* = 7.0 Hz, 8 H), 7.19 (d, *J* = 1.5 Hz, 8 H), 7.68 (t, *J* = 1.5 Hz, 2 H), 9.04 (t, *J* = 1.5 Hz, 1 H).

1.6 Synthesis of 1-ethylurea-2,3-dimethylimidazolium chloride [Eummim]Cl

1,2-Dimethylimidazole (1.92 g, 20 mmol) in 50 mL of ethanol was added dropwise to 2-chloroethylurea (2.45 g, 20 mmol) at 40°C. The mixture was stirred under N₂ at 80°C for 3 d. After evaporation of the solvent, the residue was recrystallized from ethanol to give 1.69 g (40%) of white solid. ¹H NMR (500 MHz, D₂O, Me₄Si) δ 2.51 (s, 3 H), 3.42 (t, *J* = 5.5 Hz, 2 H), 3.69 (s, 3 H), 4.13 (t, *J* = 5.5 Hz, 2 H), 7.24 (d, *J* = 2.0 Hz, 1 H), 7.26 (d, *J* = 2.0 Hz, 1 H).

1.7 Synthesis of 1-ethylurea-2,3-dimethylimidazolium acetate [Eummim]OAc

Silver acetate (1.29 g, 7.73 mmol) was added to a solution of [Eummim]Cl (1.69 g, 7.73 mmol) in water (70 mL) and stirred at room temperature for 6 h in the dark. The suspension was filtered to remove silver chloride. The water was removed in vacuo to afford 1.48 g (79%) of white solid. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, Me_4Si) δ 1.58 (s, 3 H), 2.57 (s, 3 H), 3.27–3.30 (m, 2 H), 3.74 (s, 3 H), 4.11 (t, $J = 5.5$ Hz, 2 H), 5.74 (s, 1 H), 6.14 (s, 2 H), 7.59 (d, $J = 2.0$ Hz, 1 H), 7.62 (d, $J = 2.0$ Hz, 1 H), 8.08 (s, 1 H); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 9.14, 25.48, 34.56, 39.06, 121.17, 122.16, 144.74, 159.59, 174.26; ESI-MS m/z Calcd for $[\text{C}_{10}\text{H}_{18}\text{N}_4\text{O}_2\text{-OAc}]^+$: 183.1, found for $(\text{M-OAc})^+$: 183.0.

1.8 X-ray crystallographic studies

Diffraction data were collected from a single crystal at 173 K on a Bruker APEX II diffractometer equipped with a charge coupled device detector and graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program [23]. The structure was solved using direct methods and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [24]. Hydrogen atoms attached to the carbon atoms were located geometrically and refined using the riding model, and hydrogen atoms attached to nitrogen atoms were located based on difference maps and refined with isotropic thermal parameters.

2 Results and discussion

2.1 Design and synthesis of ionic liquids

The ionic liquid 1-ethylurea-3-methylimidazolium acetate ([Eummim]OAc) was synthesized by the reaction of *N*-methylimidazole with 2-chloroethylurea followed by ion-exchange with silver acetate in the overall yield of 94%. 1-Ethylurea-3-methylimidazolium tetrafluoroborate ([Eummim] BF_4), 1-ethylurea-3-methylimidazolium tetraphenylborate ([Eummim] BPh_4) and 1-ethylurea-2,3-dimethylimidazolium acetate ([Eummim]OAc) were synthesized using similar procedures. The neutral receptor, 1-butyl-3-propyl-imidazole urea (Bpimu) was synthesized following an established method [25]. The structures of these compounds are shown in Figure 1.

2.2 Halide binding studies

To investigate the binding behavior of [Eummim]OAc, ^1H NMR spectra were recorded in the presence of various halides in deuterated DMSO ($\text{DMSO-}d_6$). Addition of halides as their tetrabutylammonium salts to a solution of

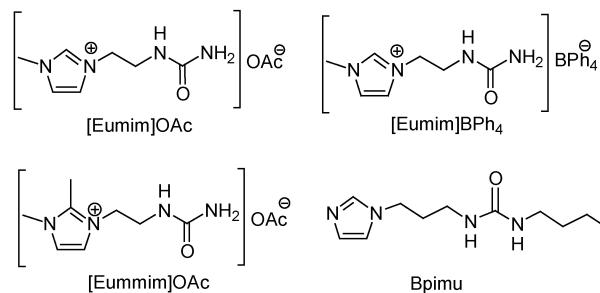


Figure 1 Structures of the ionic and neutral receptors containing the urea moiety.

[Eummim] OAc (1:1) in $\text{DMSO-}d_6$ resulted in upfield shifts of the imidazolium C(2) proton (C(2)–H) and urea protons (NH, NH_2) (Figure 2). The change in the chemical shifts was different for various halides. For example, on addition of F^- , a slight upfield shift of about 0.04 (from 9.33 to 9.29) was observed for the imidazolium C(2)–H. By contrast, the NH and NH_2 protons displayed significant upfield shifts of about 0.34 (from 8.05 to 7.71) and 0.12 (from 6.12 to 6.00), respectively. Addition of Cl^- and Br^- resulted in moderate upfield shifts for the NH and NH_2 protons and a slight downfield shift for the C(2)–H. The largest upfield shifts for C(2)–H (0.05), NH (0.50) and NH_2 (0.13) were observed with the addition of I^- . For comparison, the neutral receptor Bpimu, which has a similar structure to [Eummim]OAc, was also investigated with F^- , Cl^- , Br^- and I^- . These halides all caused downfield shifts of the urea protons. The magnitude of the chemical shift changes decreased in the order of $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (Figure 3), which is consistent with their relative hydrogen-bonding abilities [26,27]. The different trends for the chemical shift changes indicate that the recognition mechanisms for the ionic liquid and neutral receptors are completely different.

2.3 Complex anion binding studies

The unusual upfield shift of the urea protons when [Eummim]-OAc interacted with the halides promoted further investigation

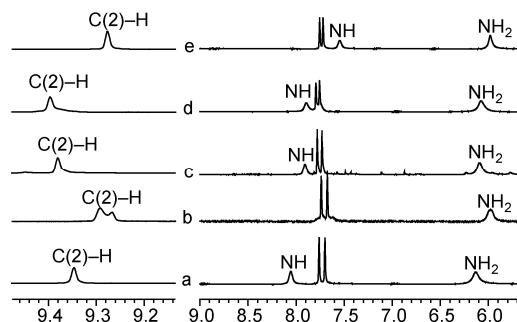


Figure 2 Partial ^1H NMR spectra of [Eummim]OAc ($c = 7.1 \times 10^{-2}$ mol/L) in $\text{DMSO-}d_6$ with different halides. (a) [Eummim]OAc only; (b) [Eummim]-OAc and 1 equiv. of F^- ; (c) [Eummim]OAc and 1 equiv. of Cl^- ; (d) [Eummim]-OAc and 1 equiv. of Br^- ; (e) [Eummim]OAc and 1 equiv. of I^- .

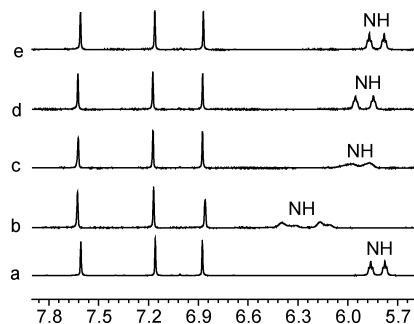


Figure 3 Partial ^1H NMR spectra of Bpimu ($c = 7.1 \times 10^{-2}$ mol/L) in $\text{DMSO-}d_6$ with different halides. (a) Bpimu only; (b) Bpimu and 1 equiv. of F^- ; (c) Bpimu and 1 equiv. of Cl^- ; (d) Bpimu and 1 equiv. of Br^- ; (e) Bpimu and 1 equiv. of I^- .

of the binding behavior between [Eumim]OAc and complex anions such as BF_4^- , PF_6^- and BPh_4^- . The peaks for the imidazolium C(2) proton and urea protons of [Eumim]OAc shifted dramatically in the presence of 1 equiv. of these complex anions (Figure 4). After addition of 1 equiv. of BF_4^- , the C(2)-H, NH and NH_2 protons all showed large upfield shifts of 0.21 (from 9.33 to 9.12), 1.36 (from 8.05 to 6.69), and 0.40 (from 6.12 to 5.72), respectively. Addition of PF_6^- and BPh_4^- also caused upfield shifts as follows: PF_6^- , $\Delta\delta$ C(2)-H = 0.15, $\Delta\delta$ NH = 1.02, $\Delta\delta$ NH_2 = 0.36; and BPh_4^- , $\Delta\delta$ C(2)-H = 0.20, $\Delta\delta$ NH = 0.97, $\Delta\delta$ NH_2 = 0.29 ppm. The change in the chemical shifts of the NH proton decreased in the order of $\text{BF}_4^- > \text{PF}_6^- > \text{BPh}_4^-$. The complex anions also caused upfield shifts of the urea protons of [Eumim]OAc (Figure 5).

It has been reported that the charge densities on the F atoms of BF_4^- and PF_6^- are relative low and they only form weak hydrogen bonds with hydrogen bonding receptors [28]. Furthermore, BPh_4^- does not have an electronegative atom for hydrogen bonding with the receptor. Therefore, both the charge density properties of BF_4^- , PF_6^- and BPh_4^- and the upfield shifts of the urea protons of the ionic liquids indicate that the dominate interaction between the anions and ionic liquid receptors is not hydrogen bonding. The binding behavior of the neutral receptor (Bpimu) with the complex

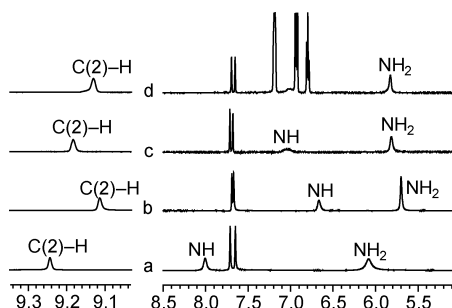


Figure 4 Partial ^1H NMR spectra of [Eumim]OAc ($c = 7.1 \times 10^{-2}$ mol/L) in $\text{DMSO-}d_6$ with different complex anions. (a) [Eumim]OAc only; (b) [Eumim]OAc and 1 equiv. of BF_4^- ; (c) [Eumim]OAc and 1 equiv. of PF_6^- ; (d) [Eumim]OAc and 1 equiv. of BPh_4^- .

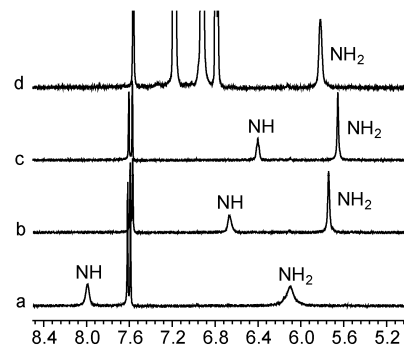


Figure 5 Partial ^1H NMR spectra of [Eummim]OAc ($c = 7.1 \times 10^{-2}$ mol/L) in $\text{DMSO-}d_6$ with different complex anions. (a) [Eummim]OAc only; (b) [Eummim]OAc and 1 equiv. of BF_4^- ; (c) [Eummim]OAc and 1 equiv. of PF_6^- ; (d) [Eummim]OAc and 1 equiv. of BPh_4^- .

anions (BF_4^- , PF_6^- and BPh_4^-) was also investigated by ^1H NMR, and this confirmed that these complex anions could not form hydrogen bonds with the urea moiety (Figure 6).

The stoichiometric ratios of [Eumim]OAc and NaBPh_4 were determined by Job's method. The maximum concentration of the host-guest complex (HG) occurred with an amount-of-substance fraction of the guest (X_G) of 0.5 (Figure 7), which indicates that [Eumim]OAc formed a 1:1 complex with BPh_4^- . On addition of 3 equiv. of BPh_4^- , the chemical shifts of the NH and NH_2 peaks moved to 6.34 and 5.67, which were close to the chemical shifts of NH and

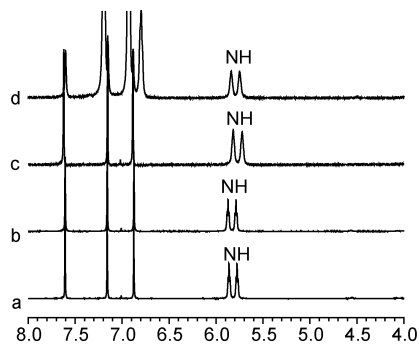


Figure 6 Partial ^1H NMR spectra of Bpimu ($c = 7.1 \times 10^{-2}$ mol/L) in $\text{DMSO-}d_6$ with different complex anions. (a) Bpimu only; (b) Bpimu and 1 equiv. of BF_4^- ; (c) Bpimu and 1 equiv. of PF_6^- ; (d) Bpimu and 1 equiv. of BPh_4^- .

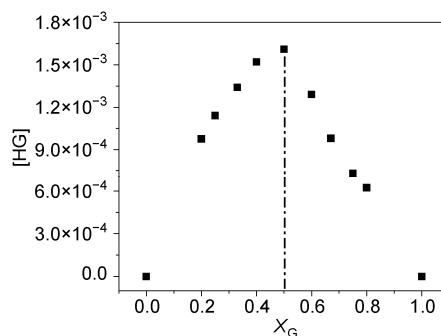
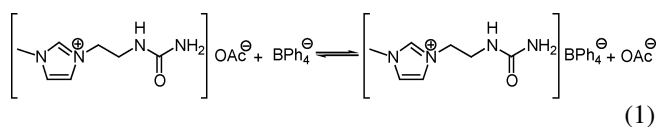


Figure 7 Job plot for formation of a host-guest (HG) complex of [Eumim]OAc with NaBPh_4 with different amount-of-substance fractions of the guest (X_G), $[\text{H}] + [\text{G}] = 6.0 \times 10^{-2}$ mol/L.



NH₂ for [Eumim]BPh₄ (NH = 6.12 and NH₂ = 5.59). These results suggest that anion exchange occurs between [Eumim]OAc and BPh₄⁻ and forms [Eumim]BPh₄ (eq. (1)). Similar results were obtained in binding studies of [Eumim]OAc with BF₄⁻ and PF₆⁻.

2.4 Structures of the imidazolium based ionic liquids

To clarify the mechanism of the upfield shift of the urea protons of [Eumim]OAc on addition of the halides and complex anions, the structures of the ionic liquids were studied by X-ray diffraction analysis and the molecular modeling study. Single crystals of [Eumim]BPh₄ suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution. Crystal data and structure refinements for [Eumim]BPh₄ are listed in Table 1. The crystal structure (Figure 8) indicates that the torsion angle of the imidazolium ring and the urea moiety is 78.1°. The urea

moiety is on the top of the imidazolium ring, and the ring current of the imidazolium ring causes the peak for the urea protons to shift upfield [29]. The interaction between [Eumim]⁺ and BPh₄⁻ is mainly through electrostatic force. The crystal structure also reveals that there are intermolecular hydrogen bonds between the [Eumim]⁺ cations. A urea oxygen atom (O1) of one [Eumim]⁺ cation forms two hydrogen bonds with two urea protons (H3C, H4B) of another [Eumim]⁺ cation, and the N3–H3C···O1 and N4–H4B···O1 bond lengths are 2.919 Å and 3.132 Å, respectively. The bond angles of ∠N3–H3C···O1 and ∠N4–H4B···O1 are 151.85° and 141.23°, respectively. Because the other ionic liquids were liquids at room temperature and it was difficult to obtain single crystals of them, their structures were optimized by Gaussian-03 using the Becke's three-parameter hybrid functional (B3LYP) and the 6-31+G(d) basis set. The optimized geometry of [Eumim]OAc demonstrates that OAc⁻ interacts with the urea moiety through N–H···O hydrogen bonds (Figure 9). The N1–H1···O1 and N2–H2···O1 bond lengths were 2.785 Å and 3.003 Å, respectively. The imidazolium ring and two methylene groups were located in

Table 1 Crystal data and structure refinements for [Eumim]BPh₄

Compound	[Eumim]BPh ₄
Empirical formula	C ₃₁ H ₃₃ BN ₄ O
Formula weight	488.42
Color	Colorless
Shape	Block
Temperature (K)	173(2)
System	Monoclinic
Space group	Cc
<i>a</i> (Å)	9.4084(4)
<i>b</i> (Å)	30.4212(12)
<i>c</i> (Å)	9.4988(4)
<i>α</i> (°)	90.00
<i>β</i> (°)	102.8690(10)
<i>γ</i> (°)	90.00
<i>V</i> (Å ³)	2650.41(19)
<i>Z</i>	4
Crystal size (mm ³)	0.45×0.29×0.22
<i>D_c</i> (g cm ⁻³)	1.224
<i>μ</i> (mm ⁻¹)	0.075
<i>F</i> (000)	1040
<i>θ</i> range (°)	2.32–25.00
Limiting indices	−11 ≤ <i>h</i> ≤ 11, −36 ≤ <i>k</i> ≤ 36, −9 ≤ <i>l</i> ≤ 11
Unique reflections	4188
<i>R</i> (int)	0.0177
GOF on <i>F</i> ²	1.061
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0651
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0258, <i>wR</i> ₂ = 0.0658
Largest diff. peak hole (e Å ⁻³)	1.098 and −0.507

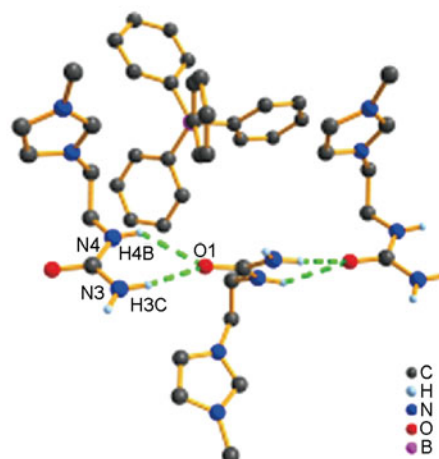


Figure 8 The crystal structure of [Eumim]BPh₄ and intermolecular hydrogen bonds between [Eumim]⁺ cations, some hydrogen atoms are omitted for clarity.

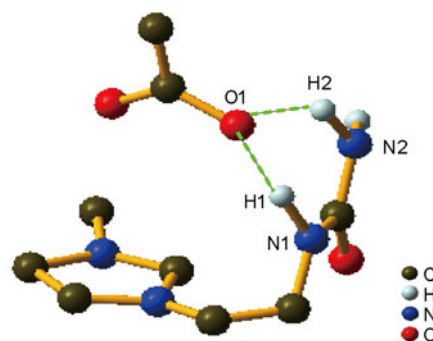


Figure 9 Optimized geometry (B3LYP/6-31+G(d)) of [Eumim]OAc, some hydrogen atoms are omitted for clarity.

almost the same plane, and the torsion angle of the imidazolium ring and the urea moiety was 90.5° . The urea moiety was not on the top of the imidazolium ring, and it would not be affected by the ring current. The different conformations of the [Eumim] cation in [Eumim]OAc and [Eumim]BPh₄ caused distinct chemical shifts for the urea moiety. The simulated structures of the other ionic liquids such as [Eumim]F, [Eumim]Cl, [Eumim]Br, [Eumim]BF₄ and [Eumim]PF₆ showed similar conformations to [Eumim]-BPh₄. The conformational changes of these ionic liquids account for the upfield shift of the urea protons of [Eumim]OAc on addition of anions.

3 Conclusions

A novel imidazolium based ionic liquid containing the urea moiety, [Eumim]OAc, was developed for recognition of halides and complex anions such as BF₄⁻, PF₆⁻ and BPh₄⁻ through anion exchange. ¹H NMR spectra revealed that the peaks for the urea protons and imidazolium C(2) proton of [Eumim]OAc shifted upfield on addition of these anions. These unusual upfield shifts occurred because of the conformational changes in the cation of the ionic liquid on interaction with the different anions. The conformational change of the cation was caused by anion exchange, and this may provide an alternative to current methods for recognition of anions.

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