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# Theoretical insights into NH<sub>3</sub> absorption mechanisms with imidazolium-based protic ionic liquids†

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Ionic liquids (ILs) provide a promising way for efficient absorption and separation of ammonia (NH<sub>3</sub>) due to their extremely low vapor pressures and adjustable structures. However, the understanding of absorption mechanisms especially in terms of theoretical insights is still not very clear, which is crucial for designing targeted ILs. In this work, a universal method that integrates density functional theory and molecular dynamic simulations was proposed to study the mechanisms of NH<sub>3</sub> absorption by protic ionic liquids (PILs). The results showed that the NH<sub>3</sub> absorption performance of the imidazolium-based PILs ([BIm][X], X = Tf<sub>2</sub>N, SCN and NO<sub>3</sub>) is determined by not only the hydrogen bonding between the N atom in NH<sub>3</sub> and the protic site (H–N<sup>3</sup>) on the cation but also the cation–anion interaction. With the increase in NH<sub>3</sub> absorption capacity, the hydrogen bonding between [BIm][Tf<sub>2</sub>N] and NH<sub>3</sub> changed from orbital dominated to electrostatic dominated, so 3.0 mol NH<sub>3</sub> per mol IL at 313.15 K and 0.10 MPa was further proved as a threshold for NH<sub>3</sub> capacity of [BIm][Tf<sub>2</sub>N] by the Gibbs free energy results, which agrees well with the experimental results. Furthermore, the anions of [BIm][X] could also compete with NH<sub>3</sub> for interaction with H–N<sup>3</sup> of the cation, which weakens the interaction between the cation and NH<sub>3</sub> and then decreases the NH<sub>3</sub> absorption ability of PILs. This study provides further understanding on NH<sub>3</sub> absorption mechanisms with ILs, which will guide the design of novel functionalized ILs for NH<sub>3</sub> separation and recovery.

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## 1. Introduction

Ammonia (NH<sub>3</sub>) mainly comes from various industrial emissions, such as in synthetic ammonia plants, melamine tail gas, urea granulating tower tail gas, metallurgical tail gas, and so on. The emission of NH<sub>3</sub> into the atmosphere causes serious environmental issues.<sup>1–4</sup> Therefore, the removal and recovery of NH<sub>3</sub> from these gases is significant to satisfy

environmental emission regulations and for resource reuse. Recently, ionic liquids (ILs) have attracted considerable attention as environmentally benign solvents for NH<sub>3</sub> absorption and recovery due to their peculiar properties, such as negligible vapor pressures, tunable properties and high thermal stability.<sup>5–9</sup> Various functionalized ILs, such as hydroxyl ILs,<sup>10–12</sup> metal ILs,<sup>13–16</sup> and protic ILs (PILs)<sup>17,18</sup> were reported for efficient NH<sub>3</sub> absorption. For instance, Shang *et al.* designed a kind of PIL with a strong hydrogen bond donating ability on cations, such as [BIm][Tf<sub>2</sub>N] with a high NH<sub>3</sub> absorption capacity of 2.69 mol NH<sub>3</sub> (mol IL)<sup>–1</sup> at 313.15 K and 0.10 MPa, along with great selectivity and excellent recyclability.<sup>19</sup> Luo *et al.* also designed an efficient PIL, [2PyH][Tf<sub>2</sub>N], by varying the cooperative hydrogen bonding, and the NH<sub>3</sub> absorption capacity was high—up to 3.80 mol NH<sub>3</sub> (mol IL)<sup>–1</sup> at 303.15 K and 0.10 MPa.<sup>18</sup> In addition, the elucidation of the mechanism of gas absorption is crucial for the design of targeted ILs, especially in terms of theoretical perspectives.<sup>20,21</sup>

In 2009, Shi *et al.* published the first work on molecular dynamic (MD) simulations of NH<sub>3</sub> absorption by the IL

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† Electronic supplementary information (ESI) available: The structures and coordinates of each conformer of the ILs studied, NH<sub>3</sub>, ILs combined with NH<sub>3</sub>, isolated cations or anions, and anions combined with NH<sub>3</sub> are provided. See DOI: <https://doi.org/10.1039/d2im00041e>



[EMIm][Tf<sub>2</sub>N]. According to the analysis of the interaction and radial distribution function of NH<sub>3</sub>⋯cation and NH<sub>3</sub>⋯anion, they concluded that the NH<sub>3</sub> absorption capacity of [EMIm][Tf<sub>2</sub>N] is governed by the hydrogen bonding between NH<sub>3</sub> and cations.<sup>22</sup> Inspired by their conclusions, a series of promising ILs, such as hydroxyl ILs and PILs, were designed to absorb NH<sub>3</sub> efficiently by introducing effective sites that interact with NH<sub>3</sub>, and theoretical studies were performed to verify their ideas. For example, Li *et al.* performed density functional theory (DFT) simulations to confirm that the higher NH<sub>3</sub> absorption capacity of a hydroxyl-functionalized IL than that of the analogous IL without the introduction of a hydroxyl group is mainly due to the hydrogen bonding between the hydroxyl group of the cation and the basic N atom of NH<sub>3</sub>.<sup>10</sup> Cai *et al.* also conducted DFT simulations to verify the mechanism of NH<sub>3</sub> absorption in lithium (Li)-triethylene glycol (TEG)-chelated ILs and their results indicated that the high NH<sub>3</sub> capacity of ILs is due to the strong interaction between hydroxyl sites of the cation and NH<sub>3</sub>.<sup>23</sup> Similarly, the DFT calculation results of our previous work<sup>19</sup> also indicated that NH<sub>3</sub> absorption of [BIm][Tf<sub>2</sub>N] may be mainly affected by the protic hydrogen of the cation. Further, MD simulations were conducted to confirm that NH<sub>3</sub> can compete with [Tf<sub>2</sub>N]<sup>−</sup> for interaction with the protic hydrogen of the cation, forming a strong hydrogen bonding.<sup>24</sup> So far, theoretical methods have attracted increasing attention to study the mechanism of NH<sub>3</sub> absorption with ILs.

Our previous work revealed that PILs not only show impressively high NH<sub>3</sub> absorption capacities but also their capacities are considerably affected by anions.<sup>17,19</sup> For instance, the capacities for NH<sub>3</sub> absorption of [BIm][Tf<sub>2</sub>N], [BIm][SCN] and [BIm][NO<sub>3</sub>] were 2.69, 1.96 and 1.30 mol NH<sub>3</sub> (mol IL)<sup>−1</sup> at 313.15 K and 0.10 MPa, respectively, as shown in Table 1. However, the mechanism is not clear. Here, DFT and MD simulations were conducted to further study the NH<sub>3</sub> absorption mechanism by [BIm]<sup>+</sup>-based PILs to reveal the essence of the interaction between ILs and NH<sub>3</sub>, as well as the effect of anions on NH<sub>3</sub> capacity. The comprehensive theoretical studies not only complement deeper understanding on NH<sub>3</sub> absorption mechanisms by the PILs but also provide a guideline to design new efficient ILs.

## 2. Results and discussion

### 2.1 The interaction between NH<sub>3</sub> and [BIm][Tf<sub>2</sub>N]

The optimized structures that illustrate [BIm][Tf<sub>2</sub>N] interacting with one, two, three and four NH<sub>3</sub> molecules are demonstrated in Fig. 2. The results showed that the NH<sub>3</sub>

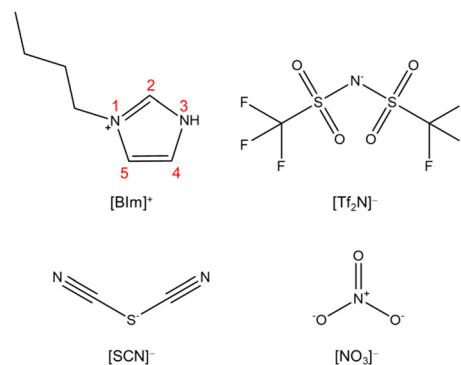


Fig. 1 Structures of the cation and anions studied in this work.

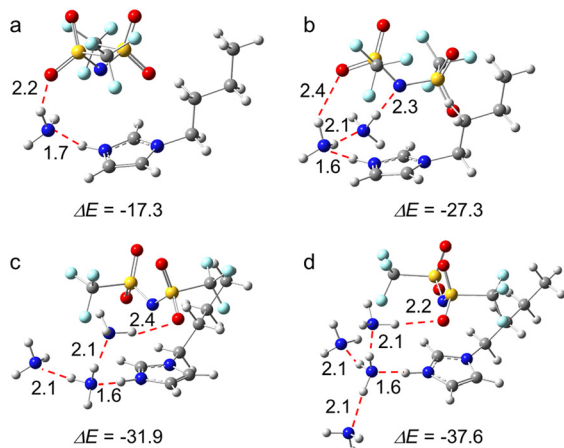
molecule mainly interacts with the site of protic hydrogen (H-N<sup>3</sup>, the atom labels are provided in Fig. 1) of [BIm][Tf<sub>2</sub>N] *via* hydrogen bonding. For example, the distance between N of the 1st NH<sub>3</sub> and H of H-N<sup>3</sup> was 1.7 Å (Fig. 2a), which is less than the sum of the van der Waals radii of N and H atoms.<sup>25</sup> On the other hand, hydrogen bonding was also discovered between NH<sub>3</sub> and the anion [Tf<sub>2</sub>N]<sup>−</sup>, as shown in Fig. 2a–d. For [BIm][Tf<sub>2</sub>N]⋯NH<sub>3</sub>, the interaction energy ( $\Delta E$ ) between the PIL and NH<sub>3</sub> was −17.30 kcal mol<sup>−1</sup> when the NH<sub>3</sub> was located around H-N<sup>3</sup> (Fig. 2a), which is almost twice as those of NH<sub>3</sub> interacting with H-C<sup>2/4/5</sup> (see Fig. S1†). For [BIm][Tf<sub>2</sub>N]⋯2NH<sub>3</sub>, the most stable structure was obtained when the 2nd NH<sub>3</sub> molecule connected to the 1st NH<sub>3</sub> molecule (see Fig. 2b). The  $\Delta E$  between the IL and two NH<sub>3</sub> molecules was −27.30 kcal mol<sup>−1</sup>, implying that the  $\Delta E$  for the 2nd NH<sub>3</sub> molecule was −10.00 kcal mol<sup>−1</sup>. Interestingly, the distance between the N atom of the 1st NH<sub>3</sub> molecule and H-N<sup>3</sup> decreased from 1.7 Å to 1.6 Å while the 2nd NH<sub>3</sub> molecule was absorbed. In other words, the hydrogen bonding formed between the 1st NH<sub>3</sub> molecule and H-N<sup>3</sup> was enhanced. A similar phenomenon was discovered from the interactions between H<sub>2</sub>O molecules and [EMIm][Tf<sub>2</sub>N], which means that the distance between the O atom of the 1st H<sub>2</sub>O molecule and H-N<sup>3</sup> of [EMIm]<sup>+</sup> is shortened when the 2nd H<sub>2</sub>O molecule interacts with the 1st H<sub>2</sub>O molecule.<sup>26</sup>

The structures of [BIm][Tf<sub>2</sub>N] interacting with three and four NH<sub>3</sub> molecules are demonstrated in Fig. 2c and d, respectively. It was found that the rest of NH<sub>3</sub> molecules can interact with the 1st absorbed NH<sub>3</sub> molecule. It is worth noting that the calculated  $\Delta E$  of absorption of the 1st and 2nd NH<sub>3</sub> molecules is much larger than that of the 3rd and 4th NH<sub>3</sub> molecules, *i.e.*, −17.30 and −10.00 kcal mol<sup>−1</sup> *versus* −4.60 and −5.70 kcal mol<sup>−1</sup>. The findings revealed that the 1st and 2nd NH<sub>3</sub> molecules are absorbed *via* different types of interactions compared to the 3rd and 4th NH<sub>3</sub> molecules.

Table 1 The viscosities, densities and NH<sub>3</sub> capacities at 313.15 K and 0.10 MPa of the PILs<sup>17</sup>

ILs	Viscosity (mPa s)	Density (g L <sup>−1</sup> )	NH <sub>3</sub> capacity (mol NH <sub>3</sub> (mol IL) <sup>−1</sup> )
[BIm][Tf <sub>2</sub> N]	47.14	1460.24	2.69
[BIm][SCN]	84.30	1078.66	1.96
[BIm][NO <sub>3</sub> ]	136.95	1165.50	1.30



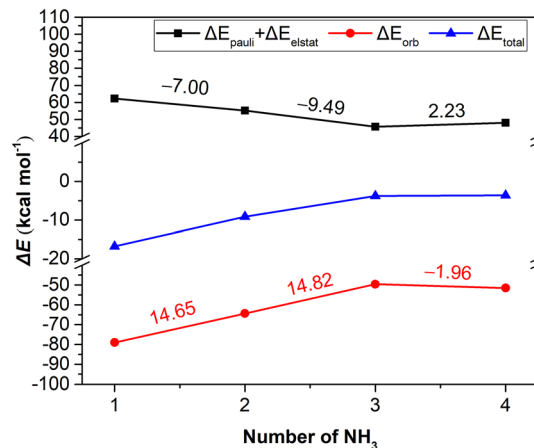


**Fig. 2** The optimized structures of [BIm][Tf<sub>2</sub>N] with (a) one, (b) two, (c) three, and (d) four NH<sub>3</sub> molecules. (Color of ligand: N, blue; H, gray; C, dark gray; S, yellow; O, red; F, pale turquoise). All the distances are given in Å.  $\Delta E = E(\text{IL} \cdots n\text{NH}_3) - E(\text{IL}) - n \times E(\text{NH}_3)$ .

The former two are through strong hydrogen bonding while the latter two are dominated by VdW interactions. The essence of these interactions was further analyzed *via* energy decomposition analysis (EDA), and detailed discussions are given in the next sections.

## 2.2 Energy decomposition analysis of NH<sub>3</sub> absorption with [BIm][Tf<sub>2</sub>N]

In order to present a quantitative interpretation and more details of the interactions between [BIm][Tf<sub>2</sub>N] and NH<sub>3</sub>, EDA was performed. Within the EDA scheme, the total interaction energy consists of three meaningful physical terms, namely, the repulsive exchange (Pauli) interaction  $\Delta E_{\text{Pauli}}$ , the electrostatic interaction  $\Delta E_{\text{elstat}}$  and the orbital interaction  $\Delta E_{\text{orb}}$ , which includes the orbital relaxation and orbital mixing between the fragments.<sup>27,28</sup> In addition, the summation of Pauli repulsion and electrostatic interactions is often defined as the steric interaction  $\Delta E_{\text{steric}}$ , which arises from the fact that each atom in a molecule occupies a certain amount of space. The total and the individual interactions of the process for each NH<sub>3</sub> absorbed by [BIm][Tf<sub>2</sub>N] are given in Table 2 and Fig. 3. The results showed that the interactions between the 1st and 2nd NH<sub>3</sub> molecules with [BIm][Tf<sub>2</sub>N] are considerable, especially for the 1st NH<sub>3</sub>



**Fig. 3** The EDA results at the M062X/TZP level of theory for each step of [BIm][Tf<sub>2</sub>N] to capture one NH<sub>3</sub>. The numbers on the lines indicate the changes of values of adjacent two points, and their colours are consistent with the lines.

molecule, and its total interaction energy is as high as  $-16.79 \text{ kcal mol}^{-1}$ . However, the total interaction energies of the 3rd and 4th NH<sub>3</sub> molecules are much lower than those of the 1st and 2nd NH<sub>3</sub> molecules, which are around  $-3.50 \text{ kcal mol}^{-1}$ . The 3rd NH<sub>3</sub> molecule is favored by electrostatic interactions of  $8.16 \text{ kcal mol}^{-1}$  compared to the 4th NH<sub>3</sub> molecule. This is most likely because the 3rd NH<sub>3</sub> molecule interacts with the anion through hydrogen bonding (see Fig. 2c).

The plots in Fig. 3 demonstrate that the orbital interaction is more likely to decay than the steric interaction. For example, the orbital interaction decreased by  $14.65 \text{ kcal mol}^{-1}$  from the 1st to the 2nd NH<sub>3</sub> molecule, while the corresponding steric interactions only decreased by  $7.00 \text{ kcal mol}^{-1}$ . The results indicated that the orbital interaction makes a great contribution to the total interaction. However, in the case of the 4th NH<sub>3</sub> molecule, the changes of  $\Delta E_{\text{steric}}$  and  $\Delta E_{\text{orb}}$  were small compared to those of the 3rd NH<sub>3</sub> molecule, which is most likely due to physical interaction of the 4th NH<sub>3</sub> molecule. In this case, the electrostatic interaction plays the most important role.

## 2.3 Gibbs free energy of NH<sub>3</sub> absorption with [BIm][Tf<sub>2</sub>N]

Our previous experimental results<sup>16</sup> showed that the NH<sub>3</sub> absorption capacity of [BIm][Tf<sub>2</sub>N] is  $2.69 \text{ mol NH}_3 (\text{mol}$

**Table 2** EDA at the M062X/TZP level for each step ( $[\text{BIm}][\text{Tf}_2\text{N}] \cdots (i-1) \text{NH}_3 + \text{NH}_3 \rightarrow [\text{BIm}][\text{Tf}_2\text{N}] \cdots i\text{NH}_3$ ,  $i = 1-4$ ) of [BIm][Tf<sub>2</sub>N] to capture one NH<sub>3</sub> molecule, and all the energies are expressed in  $\text{kcal mol}^{-1}$

Interaction energies <sup>a</sup>	1st NH <sub>3</sub>	2nd NH <sub>3</sub>	3rd NH <sub>3</sub>	4th NH <sub>3</sub>
$\Delta E_{\text{Pauli}}$	+92.02	+72.05	+61.64	+55.71
$\Delta E_{\text{elstat}}$	-29.76	-16.79	-15.87	-7.71
$\Delta E_{\text{steric}} (\Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}})$	+62.26	+55.26	+45.77	+48.00
$\Delta E_{\text{orb}}$	-79.05	-64.40	-49.58	-51.54
$\Delta E_{\text{total}}$	-16.79	-9.14	-3.81	-3.54

<sup>a</sup>  $\Delta E = E(\text{IL} \cdots n\text{NH}_3) - E(\text{IL}) - n \times E(\text{NH}_3)$ .



$\text{IL}^{-1}$ , which is close to  $3.0 \text{ mol NH}_3 (\text{mol IL})^{-1}$  at  $313.15 \text{ K}$  and  $0.10 \text{ MPa}$ . The high capacity for  $\text{NH}_3$  of  $[\text{BIm}][\text{Tf}_2\text{N}]$  was probably attributed to the strong hydrogen bonding site  $\text{H}-\text{N}^3$  in the  $[\text{BIm}]^+$  cation. Here, we revisited this open question by computing the Gibbs free energy ( $\Delta G$ ) for  $[\text{BIm}][\text{Tf}_2\text{N}]$  absorption of different moles of  $\text{NH}_3$  molecules. The calculated  $\Delta G$  values are shown in Fig. 4, and their values are highlighted in red. The  $\Delta G$  values for  $[\text{BIm}][\text{Tf}_2\text{N}]$  absorbing one and two moles  $\text{NH}_3$  were  $-3.6$  and  $-3.1 \text{ kcal mol}^{-1}$ , respectively. These two negative values indicated that the process of  $[\text{BIm}][\text{Tf}_2\text{N}]$  absorbing one or two moles  $\text{NH}_3$  takes place spontaneously and easily.

The  $\Delta G$  value for  $[\text{BIm}][\text{Tf}_2\text{N}]$  absorbing three moles  $\text{NH}_3$  was  $1.8 \text{ kcal mol}^{-1}$ . This slightly positive value reveals that the absorption of three moles  $\text{NH}_3$  by  $[\text{BIm}][\text{Tf}_2\text{N}]$  is thermodynamically feasible. Moreover, the other conformers of  $[\text{BIm}][\text{Tf}_2\text{N}] \cdots 3\text{NH}_3$  are shown in Fig. S3†. The relative energies ( $E_r$ ),  $\Delta G$  values and Boltzmann distribution weighting factors ( $w_i$ ) are summarized in Table S1†. The results indicated that most of the conformers have comparable  $E_r$  values and their  $\Delta G$  values are close to zero as well. It should be noted that the most stable structure of  $[\text{BIm}][\text{Tf}_2\text{N}] \cdots 3\text{NH}_3$  (Fig. S3a†) is slightly more stable than the structure in Fig. 2c (equal to Fig. S3d†). The energy of the former was  $1.1 \text{ kcal mol}^{-1}$  lower than the latter. Moreover, the most stable structure was dominant among the displayed conformers with a  $w_i$  value of  $0.432$ , and its corresponding  $\Delta G$  value was  $-0.05 \text{ kcal mol}^{-1}$ . The result indicated that  $[\text{BIm}][\text{Tf}_2\text{N}]$  is capable of absorbing close to 3 moles  $\text{NH}_3$  in consideration of thermodynamics. It is also consistent with the experimental fact that the  $\text{NH}_3$  capacity of  $\text{H}-\text{C}^2$  is less than  $1.0 \text{ mol NH}_3 (\text{mol IL})^{-1}$ .<sup>5,6,17</sup>

We also calculated the  $\Delta G$  value for the  $[\text{BIm}][\text{Tf}_2\text{N}] \cdots 4\text{NH}_3$  system. The DFT calculations yielded a large positive value of  $6.7 \text{ kcal mol}^{-1}$  for the hypothetical process, indicating that  $[\text{BIm}][\text{Tf}_2\text{N}]$  failed to absorb 4 moles  $\text{NH}_3$  spontaneously at  $313.15 \text{ K}$  and  $0.10 \text{ MPa}$ . Furthermore, the energy of the most stable structure of  $[\text{BIm}][\text{Tf}_2\text{N}] \cdots 4\text{NH}_3$  (Fig. S4a†) was  $3.8 \text{ kcal mol}^{-1}$  lower than that of the structure shown in Fig. 2d (equal to Fig. S4t†), but the  $\Delta G$  value of  $[\text{BIm}][\text{Tf}_2\text{N}]$  absorbed 4 moles  $\text{NH}_3$  molecules based on the

most stable structure of  $[\text{BIm}][\text{Tf}_2\text{N}] \cdots 4\text{NH}_3$  ( $2.5 \text{ kcal mol}^{-1}$ ), which indicated that this structure is also unfavorable from a thermodynamic point of view.

## 2.4 The interaction between anions and $\text{NH}_3$

Based on the above analysis, it was concluded that  $\text{H}-\text{N}^3$  plays an important role in  $\text{NH}_3$  absorption of  $[\text{BIm}][\text{Tf}_2\text{N}]$ . However, the experimental results (see Table 1) also indicated that the anions have an observable influence on  $\text{NH}_3$  capacity of PILs. To reveal the possible mechanisms, the interactions between anions and  $\text{NH}_3$  were also studied by DFT calculations. As seen in Fig. 5, all the anions interacted with  $\text{NH}_3$  via hydrogen bonding. The interaction energy between  $[\text{NO}_3]^-$  and  $\text{NH}_3$  was the largest one among them, while the difference of interaction energies was less than  $3.0 \text{ kcal mol}^{-1}$ . Although the anion  $[\text{Tf}_2\text{N}]^-$  offered more hydrogen bond acceptors than the other two anions, it seemed impossible to cause such a great difference in  $\text{NH}_3$  capacity of PILs ( $\text{NH}_3$  capacity of  $[\text{BIm}][\text{Tf}_2\text{N}]$  is almost twice that of  $[\text{BIm}][\text{NO}_3]$  in Table 1). Furthermore, in terms of interaction energies,  $[\text{BIm}][\text{NO}_3]$  should show a more likely higher  $\text{NH}_3$  capacity than  $[\text{BIm}][\text{SCN}]$ , which conflicts with experimental results. In sum, the interaction between  $\text{NH}_3$  and anions is not the direct reason that affects  $\text{NH}_3$  absorption capacity of PILs.

## 2.5 The interaction between cations and anions

The  $\text{H}-\text{N}^3$  site is a main hydrogen bond donor that interacts with  $\text{NH}_3$ , and then the anions may also provide hydrogen bond acceptors to form hydrogen bonding with the protic site, therefore influencing the  $\text{NH}_3$  absorption capacity of PILs. In order to verify this assumption, DFT calculations were conducted to study the interactions between cations and anions. The most stable structures for these three “ion pairs” of  $[\text{BIm}][\text{Tf}_2\text{N}]$ ,  $[\text{BIm}][\text{SCN}]$  and  $[\text{BIm}][\text{NO}_3]$  are depicted in Fig. 6. In addition, the interaction energies between cations and anions are indicated as well (the detailed values are in Fig. S10†). It was found that all the anions prefer to interact with  $\text{H}-\text{N}^3$ , meaning that the anions compete against  $\text{NH}_3$  for  $\text{H}-\text{N}^3$ . It was implied that the stronger interaction between cations and anions results in a lower  $\text{NH}_3$  absorption capacity. As seen in Fig. 6, the interaction

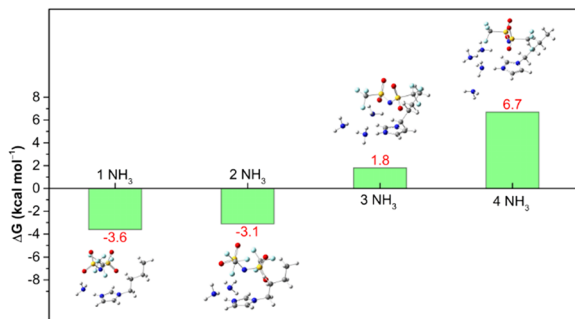


Fig. 4  $\Delta G$  of  $[\text{BIm}][\text{Tf}_2\text{N}] + i\text{NH}_3 \rightarrow [\text{BIm}][\text{Tf}_2\text{N}] \cdots i\text{NH}_3$ , ( $i = 1-4$ ) calculated at the M062X/def2TZVP level, including the B3LYP/6-31 +  $G^*$  thermodynamic correction.

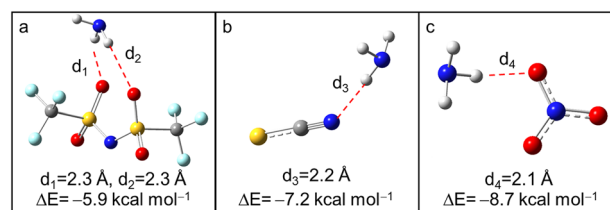
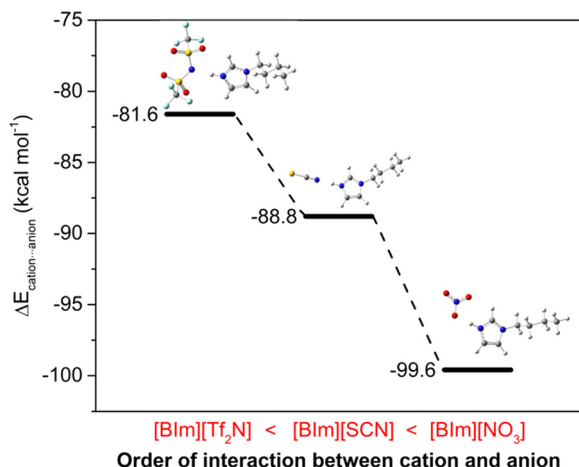


Fig. 5 The optimized structures of  $\text{NH}_3$  interact with (a)  $[\text{Tf}_2\text{N}]^-$ , (b)  $[\text{SCN}]^-$  and (c)  $[\text{NO}_3]^-$  (color of ligand: N, blue; H, gray; C, dark gray; S, yellow; O, red; F, pale turquoise).





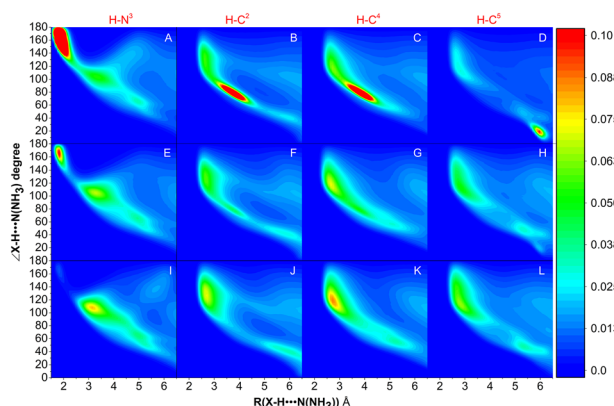


**Fig. 6** The interaction energies between cations and anions of PILs. A more negative value indicates a stronger interaction (color of ligand: N, blue; H, gray; C, dark gray; S, yellow; O, red; F, pale turquoise).

energies between the cations and anions of these PILs followed the order [BIm][Tf<sub>2</sub>N] < [BIm][SCN] < [BIm][NO<sub>3</sub>]. Moreover, the increasing interaction between cations and anions would decrease the free volume in PILs that accommodates NH<sub>3</sub>, decreasing the NH<sub>3</sub> capacity of PILs.<sup>29</sup> Therefore, the reason for the anions influencing NH<sub>3</sub> capacity of PILs originates from the strength of interaction between anions and cations.

## 2.6 The distribution of hydrogen bonding around [BIm]<sup>+</sup>

The MD simulations of NH<sub>3</sub> absorption of ILs were further carried out to study the distribution of NH<sub>3</sub> and anions in PILs. Fig. 7 shows the combined distribution functions of  $\angle X-H\cdots N(NH_3)$  versus the distance between the H atom of the cation and the N atom of NH<sub>3</sub> ( $R_{H\cdots N(NH_3)}$ ). X refers to C

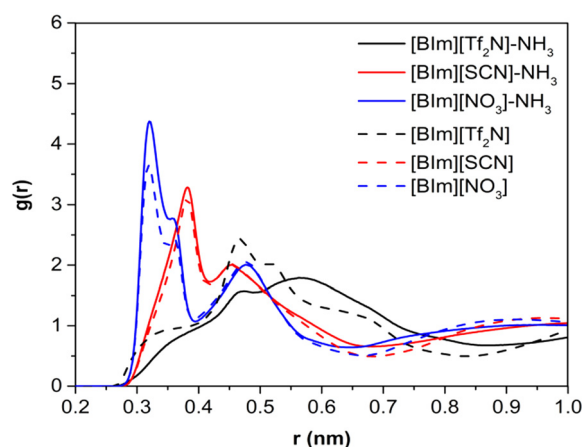


**Fig. 7** Combined distribution functions of  $\angle N/C-H\cdots N(NH_3)$  versus the distance of  $H\cdots N(NH_3)$  between the cation and NH<sub>3</sub>. The first column of panels A, F, and H reflects the distribution of NH<sub>3</sub> around H-N<sup>3</sup>. The 2nd to 4th columns of the panels reflect the distribution of NH<sub>3</sub> around H-C<sup>2</sup>, H-C<sup>4</sup>, and H-C<sup>5</sup>, respectively. Panels A–D, E–H and I–L are combined distribution functions for NH<sub>3</sub> absorption by [BIm][Tf<sub>2</sub>N], [BIm][SCN] and [BIm][NO<sub>3</sub>], respectively.

(i.e., C2-site, C4-site, and C5-site, indicated as C<sup>2</sup>, C<sup>4</sup>, and C<sup>5</sup>, respectively) and N (i.e., N<sup>3</sup>-site, indicated as N<sup>3</sup>) atoms on the imidazolium ring of [BIm]<sup>+</sup>. It was found that NH<sub>3</sub> molecules are mainly distributed around H-N<sup>3</sup> in [BIm][Tf<sub>2</sub>N] (with a large region in red color, panel A). In panel A, the red region represented the range where  $130^\circ < \angle N-H\cdots N(NH_3) < 180^\circ$  and  $1.5 \text{ \AA} < R_{H\cdots N(NH_3)} < 2.0 \text{ \AA}$ , which indicated that most of the NH<sub>3</sub> molecules interact with H-N<sup>3</sup> by strong hydrogen bonding. A similar red region was also found in panel E, but its area was much less than that of [BIm][Tf<sub>2</sub>N]. It was demonstrated that part of NH<sub>3</sub> molecules distribute around H-N<sup>3</sup> in [BIm][SCN] by strong hydrogen bonding. However, it was hard to find any red region in panel I, which means that few NH<sub>3</sub> molecules distribute around H-N<sup>3</sup> in [BIm][NO<sub>3</sub>] by strong hydrogen bonding. In addition, regions with red color were also found in panels B–D. These are possible indications that H-C<sup>2</sup>, H-C<sup>4</sup>, and H-C<sup>5</sup> are sharing part of NH<sub>3</sub> molecules around H-N<sup>3</sup>.

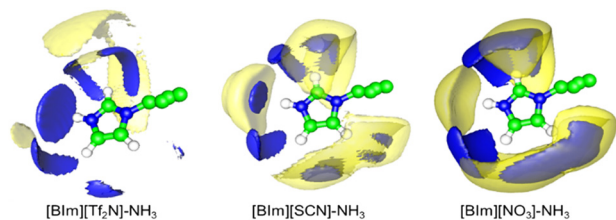
## 2.7 The distribution of anions around the [BIm]<sup>+</sup> cation

To study the distribution of anions around H-N<sup>3</sup> of the cation, the radial distribution functions (RDFs) before and after NH<sub>3</sub> absorption of H-N<sup>3</sup>(cation)⋯N/C(anion) and the three-dimensional probability distribution of NH<sub>3</sub>, and the anions around the [BIm]<sup>+</sup> cation in PILs after NH<sub>3</sub> absorption were calculated as shown in Fig. 8 and 9, respectively. The results showed that the distance of the first evident peak of RDFs for the three PILs follows the order [BIm][NO<sub>3</sub>] < [BIm][SCN] < [BIm][Tf<sub>2</sub>N]. The [NO<sub>3</sub>]<sup>−</sup> anions were organized closer, and more [SCN]<sup>−</sup> anions were around H-N<sup>3</sup>, which leads to a smaller probability for NH<sub>3</sub> molecules interacting with H-N<sup>3</sup> in [BIm][NO<sub>3</sub>] and a lower NH<sub>3</sub> capacity. However, for the [Tf<sub>2</sub>N]<sup>−</sup> anion, it was the most far away from H-N<sup>3</sup> among the three anions.



**Fig. 8** RDF presentation between the H atom of H-N<sup>3</sup> in [BIm]<sup>+</sup> and the central atom in anions (the N atom is assigned as the central atom for [Tf<sub>2</sub>N]<sup>−</sup> and [NO<sub>3</sub>]<sup>−</sup>, and the C atom is assigned as the central atom for [SCN]<sup>−</sup>).





**Fig. 9** Three-dimensional probability distribution of  $\text{NH}_3$  (blue) and anions (yellow) around  $[\text{BIm}]^+$  in the bulk liquid of ILs after  $\text{NH}_3$  absorption. In each case, the blue and yellow surfaces are drawn at 4 times the average density of the corresponding  $\text{NH}_3$  or anions in the bulk region.

Consequently,  $[\text{BIm}][\text{Tf}_2\text{N}]$  provided more opportunities for  $\text{H}-\text{N}^3$  to attract  $\text{NH}_3$  and more free volume to accommodate  $\text{NH}_3$ .<sup>30,31</sup> Interestingly, the RDFs of  $[\text{BIm}][\text{Tf}_2\text{N}]$  before and after  $\text{NH}_3$  absorption exhibited more evident changes than those of the other two PILs. This is likely because the  $[\text{Tf}_2\text{N}]^-$  anion has the largest size among these three anions, so it is vulnerable to be attacked by  $\text{NH}_3$ , resulting in considerable spatial displacement. Fig. 8 also shows that the anion  $[\text{Tf}_2\text{N}]^-$  keeps away from  $\text{H}-\text{N}^3$  in the bulk phase of  $[\text{BIm}][\text{Tf}_2\text{N}]$  with  $\text{NH}_3$  absorption compared to the bulk phase without  $\text{NH}_3$  absorption.

### 3. Conclusions

In this work, both DFT calculations and MD simulations were conducted to deeply understand the mechanisms of  $\text{NH}_3$  absorption with PILs, including  $[\text{BIm}][\text{Tf}_2\text{N}]$ ,  $[\text{BIm}][\text{SCN}]$  and  $[\text{BIm}][\text{NO}_3]$ , in terms of theoretical insights. The interactions between  $[\text{BIm}][\text{Tf}_2\text{N}]$  and  $\text{NH}_3$ , anions and  $\text{NH}_3$ , cations and anions, and the  $\text{NH}_3$  distribution around  $\text{H}-\text{N}^3$  and  $\text{H}-\text{C}^{2/4/5}$  in  $[\text{BIm}]^+$ , as well as the anion organization around  $\text{H}-\text{N}^3$  before and after  $\text{NH}_3$  absorption for the three PILs, were systematically investigated. The results indicated that both the strong hydrogen bonding between  $\text{NH}_3$  and  $\text{H}-\text{N}^3$  of the cation and the weak interaction between cations and anions lead to a high  $\text{NH}_3$  capacity of the PILs. Moreover, the orbital moiety of the total interaction between  $\text{NH}_3$  and  $[\text{BIm}][\text{Tf}_2\text{N}]$  decays dramatically with the increase of  $\text{NH}_3$  absorption, and the major part changed from orbital to electrostatic, which further proved that 3.0 mol  $\text{NH}_3$  (mol IL)<sup>-1</sup> is a threshold for the  $\text{NH}_3$  capacity of  $[\text{BIm}][\text{Tf}_2\text{N}]$ . On the other hand, the anions of the PILs could also compete with  $\text{NH}_3$  for interaction with  $\text{H}-\text{N}^3$  of the cations, when the interaction between the cations and anions became stronger, the corresponding anions would prefer to gather near or around the  $\text{H}-\text{N}^3$  of the cation and decreased the probability of  $\text{H}-\text{N}^3$  to interact with  $\text{NH}_3$ , thus reducing the  $\text{NH}_3$  absorption capacity of the PILs. This study provides a deep understanding of the mechanism of  $\text{NH}_3$  absorption with ILs, which will guide the design of novel functionalized ILs for  $\text{NH}_3$  separation and recovery applications.

## 4. Computational details

### 4.1 Density functional theory (DFT) calculations

The structures of PILs and  $\text{PIL}-\text{NH}_3$  were first optimized at the B3LYP/6-31 + G\* theoretical level in consideration of solvation *via* polarizable continuum mode (PCM),<sup>32</sup> together with the employment of the DFT-D3 approach to consider the interaction of dispersion.<sup>33</sup> Frequency analyses were performed at the same level to confirm the optimized structures: no imaginary frequencies were found for the local minima. Then single point calculations were conducted for optimized structures at the M062X/def2-TZVP level to obtain the energy in the ideal gas phase. The zero point energies (ZPE) were obtained from the frequency calculation at the B3LYP-D3/6-31 + G\* level. When applying PCM, the solvent parameters of ILs are necessary. The dielectric constant and refractive index of the ILs studied were estimated to be 15.0 and 1.43, respectively, based on published works.<sup>34–36</sup> All the above calculations were performed by employing the Gaussian09 package.<sup>37</sup> The Amsterdam density functional (ADF) suite of programs was employed to perform energy decomposition analysis (EDA).<sup>38,39</sup> EDA was conducted *via* single point calculations at the M062X level with an all-electron basis set of TZP quality.<sup>40</sup>

The interaction energy ( $\Delta E$ ), which is the change in energy between the complex and its monomers, was calculated using eqn (1):

$$\Delta E = E(A \cdots B) - E(A) - E(B) \quad (1)$$

where  $E(A)$ ,  $E(B)$  and  $E(A \cdots B)$  are the ideal gas phase electronic energies of  $A$ ,  $B$  and  $A \cdots B$ , respectively.

The final Gibbs energy ( $G$ ) in solution included two parts, *i.e.*, the ideal gas phase electronic energy ( $E$ ) and the gas phase thermostatical contribution ( $G_{\text{RROH}}$ ) (see eqn (2)).

$$G = E + G_{\text{RROH}} \quad (2)$$

The change in Gibbs energy ( $\Delta G$ ) for a process can be calculated by eqn (3):

$$\Delta G = \Delta E + \Delta G_{\text{RROH}} \quad (3)$$

The thermostatical contribution is calculated as follows:

$$G_{\text{RROH}} = \text{ZPE} + E_{\text{therm}} + PV - TS \quad (4)$$

where ZPE is the zero point vibrational energy,  $E_{\text{therm}}$  is the thermal energy, and  $P$ ,  $V$ ,  $T$ , and  $S$  denote the pressure, volume, temperature and entropy, respectively.  $T$  and  $P$  were set to 313.15 K and 0.10 MPa, respectively.

### 4.2 Molecular dynamic (MD) calculations

All the MD simulations were performed using the GROMACS simulation package<sup>41</sup> at 313.15 K and 0.10 MPa. The time step was set to 2 fs and the velocity-Verlet algorithm was used



to integrate the equations of motion. All the covalent bonds were constrained using the LINCS algorithm. A cutoff of 1.2 nm was set for both the LJ and Coulombic interactions. The LJ tail correction was added to the energy and pressure, and long-range electrostatic interactions were calculated using the particle-mesh Ewald (PME) method.<sup>42</sup> Cross interactions between different atom types were computed using standard Lorentz–Berthelot rules. The temperature was controlled using a Nosé–Hoover thermostat with a coupling time constant of 0.2 ps and the pressure was maintained using a Parrinello–Rahman barostat with a coupling time of 2.0 ps. Periodic boundary conditions were applied in all directions.

The initial configurations were built with the PACKMOL package<sup>43</sup> by randomly disposing 1000 ILs for pure IL systems and 1000 ILs +  $m$  NH<sub>3</sub> ( $m = 3000, 2000, 1500$  for [BIm][Tf<sub>2</sub>N], [BIm][SCN] and [BIm][NO<sub>3</sub>], respectively) molecules. The force field values of the ILs were obtained from the literature,<sup>44–47</sup> and the NH<sub>3</sub> molecule was modelled using the OPLS-AA force field.<sup>48</sup> Due to the low-diffusion of ILs, the system was heated up to 500 K for 10 ns to keep the ion mobility. The temperature was gradually decreased to 313.15 K. The production run of 100 ns was carried out in an NPT ensemble, and structure analysis was conducted based on the last 50 ns.

## Abbreviation

[BIm][Tf <sub>2</sub> N]	1-Butyl-imidazolium bis(trifluoromethylsulfonyl)imide
[2PyH][Tf <sub>2</sub> N]	2-Aminopyridinium bis(trifluoromethylsulfonyl)imide
[EMIm][Tf <sub>2</sub> N]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIm][Tf <sub>2</sub> N]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIm][SCN]	1-Butyl-3-methylimidazolium thiocyanide
[BMIm][DCA]	1-Butyl-3-methylimidazolium dicyandiamide
[EIm][Tf <sub>2</sub> N]	1-Ethyl-imidazolium bis(trifluoromethylsulfonyl)imide

## Conflicts of interest

The authors declare no conflict of interest.

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