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# Selection of a suitable ZIF-8/ionic liquid (IL) based composite for selective CO<sub>2</sub> capture: the role of anions at the interface†

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The effective capture of CO<sub>2</sub> from the atmosphere is much needed to reduce its environmental impact. The design and development of CO<sub>2</sub> capturing materials is getting much attention. A zeolitic imidazolate framework (ZIF) can replace many of the conventional materials in gas separation due to its stability and high performance. Here, we analyzed the effect of encapsulation of ionic liquids (ILs) into the pores of ZIF-8 for selective CO<sub>2</sub> capture and separation. The [BMIM]<sup>+</sup> cation with a series of anions was selected to study suitable carbon capture materials using density functional theory (DFT) approaches. Our calculations suggest that the nitrogen containing anions are not well adsorbed on the ZIF-8 surface but their gas separation performance is not affected by these interfacial interactions. This is confirmed from the CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity of these composites, calculated using grand canonical Monte Carlo (GCMC) simulations. A suitable force field for the composites was identified by comparing the available force fields with the experiments. The IL@ZIF-8 composite shows better CO<sub>2</sub> selectivity compared to pristine ZIF-8. Fluorinated hydrophobic anions (such as [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup> and [Tf<sub>2</sub>N]<sup>-</sup>) in the composites show better CO<sub>2</sub> adsorption and significant CO<sub>2</sub> selectivity than pristine ZIF-8, especially at low pressure. The nature of the anion plays an important role in CO<sub>2</sub> separation, rather than its stability at the pores of ZIF-8. Close scrutiny of the results reveal that the CO<sub>2</sub> selectivity of these composite materials depends on the anion of the IL and thus through the selection of a suitable anion we can significantly enhance the CO<sub>2</sub> selectivity for different flue gas mixtures. Our molecular level design shows that the selection of suitable anions in IL based composites is very important in identifying potential carbon capture materials for industrial applications.

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## 1. Introduction

Anthropogenic climate change is the main issue which the scientific community has to address. In these issues, carbon dioxide gas plays a major role.<sup>1</sup> According to the inter-governmental panel on climate change (IPCC), an international climate control forum under the United Nations, there has been a massive increase in CO<sub>2</sub> emission around the world. The recent emission gap report says, in 2018 alone, nearly 55.3 gigatons of CO<sub>2</sub> was pumped into the atmosphere which is 3 gigatons higher than the previous years. Also, to ensure the success of the Kyoto protocol, an agenda was proposed and followed worldwide to reduce CO<sub>2</sub>. It is highly essential to

capture the CO<sub>2</sub> already effluted to the atmosphere as well as to reduce the emissions in the future; therefore it is in the urge to develop novel materials for CO<sub>2</sub> capture.<sup>2</sup> Also, CO<sub>2</sub> freezing have an adverse effect in the cryogenic natural gas processing and the presence of CO<sub>2</sub> will reduce the calorific value of natural gas.<sup>3</sup> The currently available carbon capture materials lack its recyclability and cost-effectiveness also have large energy demand.<sup>4</sup> Thus, the design and development of new carbon capture materials are important in the socio-economic point of view.

Metal-organic frameworks (MOFs) constitute a major class in the micro-mesoporous materials, with exceptional gas storage capacity.<sup>5</sup> MOFs, due to its porous nature and tunability, can store a large amount of gas compared to the available materials.<sup>6,7</sup> Also MOFs exhibit high chemical and thermal stability, with a potential application in CO<sub>2</sub> conversion. The chemical tunability of MOF-based materials make them competitive in the field of gas handling.<sup>8-10</sup> But the selective adsorption is really needed for the separation of definite gases from the flue gas, which remains an unresolved problem for MOFs based separation process. Functionalization and mixed

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matrix membranes (MMMs) helps to overcome this limitation of MOFs by enhancing the selective adsorption.<sup>11–13</sup>

Various reports are available on MOF based materials for efficient and selective CO<sub>2</sub> capture.<sup>14–16</sup> Here, we analyzed the effect of encapsulated ILs and role of their interaction with MOF in selective CO<sub>2</sub> adsorption from flue gas mixtures. It is well known that imidazolium-based ILs have widespread applications in different fields such as gas sensors, separation, energy storage and catalysis.<sup>17,18</sup> ILs can also be incorporated in metal surfaces for electrochemical and various other applications.<sup>19,20</sup> It has a high CO<sub>2</sub> solubility character which results in potential separation techniques.<sup>21</sup> Also the recyclability of ILs helps in making them a better candidate for gas handling applications.<sup>22</sup> Sezginel *et al.* studied CuBTC MOF with the incorporation of ILs for gas separation applications. But the gas separation was inversely affected, which is arisen from the interaction between ILs and open metal sites of MOF.<sup>23</sup> IL encapsulation in MOFs with saturated metal sites can significantly enhance the gas separation performance.<sup>24,25</sup> Recently, Polat and co-workers, analyzed IL/CuBTC composite for the selective CO<sub>2</sub> separation. They found that IL incorporation can enhance the CO<sub>2</sub> selectivity of the material, with the help of experiments and simulations.<sup>26</sup> The high CO<sub>2</sub> selectivity of IL@IRMOF was reported by Gupta *et al.* using atomistic simulations.<sup>27</sup>

Among the MOFs, zeolitic imidazolate framework is a subclass that has a sodalite (SOD) topology with flexible linker and tunable pore size.<sup>28</sup> ZIFs can be used in various applications such as chemical sensors, optical switch, biomedical applications, catalysis *etc.*<sup>29–31</sup> Due to the wide variety of ZIFs and the superior CO<sub>2</sub> solubility of ILs, they can lead to the generation of an energy-efficient carbon capture material as well as these can be used for the membrane-based separation process.<sup>32,33</sup> The modified linkers in these frameworks can also lead to efficient gas mixture separation.<sup>34</sup> Recent experimental and computational approaches show that the hydrophobic/hydrophilic character of ZIFs play a vital role in the efficient binding of guest molecules as well as possible gas storage and separation techniques.<sup>35–37</sup> These studies reveal that the interactions at the interface are playing significant role in the composite stability as well as selective storage of gas molecules at nanopores.

ILs are proven to be efficient CO<sub>2</sub> soluble material, whereas ZIFs are emerged as good storage and separation material. Combining these two novel materials will help us to utilize the unique properties of these materials in one platform. Also, the IL@MOF can provide a good interfacial material for gas separation by combining the advantages of solid adsorption as well as liquid absorption.<sup>38</sup> These IL/MOF composites show better performance in many fields such as ionic conductivity, catalysis, membrane based separation *etc.*<sup>39</sup> Many studies have reported successful encapsulation of ILs into the confinement of porous materials and thus enhancing its CO<sub>2</sub> separation ability. The incorporated IL in ZIFs can avoid freezing up to a much lower temperature and thus can be used as low temperature ionic conductors.<sup>40</sup> Ban *et al.* incorporated IL into ZIF-8 confinement and observed an increasing permeability for CO<sub>2</sub> molecule, compared to CH<sub>4</sub> and N<sub>2</sub>.<sup>32</sup> Keskin and co-workers observed high CO<sub>2</sub>/CH<sub>4</sub> selectivity for core-shell type IL@ZIF-

8 composite.<sup>35</sup> From these studies, it is clear that the modification of ZIFs with specific ILs can enhance the permeability and selectivity of desired gas molecules. Through the combination of ILs and ZIFs, we can design a stable and compatible material for selective gas adsorption from industrial flue gas. There are many experimental and theoretical reports available, which shows the effectiveness of ILs, confined in MOFs, for selective CO<sub>2</sub> adsorption.<sup>41–43</sup> Recent trends show that porous ILs and IL-based composite materials are receiving widespread attention in the fields of gas storage, separation and catalysis.<sup>44–46</sup>

Computational exploration of materials is always valuable because it can give a clear picture of microscopic interfacial interactions in newly designed materials. Thus, in the present study, we have employed computational approaches to screen various ILs at the ZIF-8 nanopores using DFT and GCMC simulations. Also the interfacial interactions between ZIF and ILs and their role in the effective gas separation are analyzed. Cadena *et al.* reported that the anion in the imidazolium ILs has a major part to play in the solubility of CO<sub>2</sub> in the same.<sup>21</sup> So we have selected common 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>) cation with various anions for ILs, to explore its effects in the stability as well as CO<sub>2</sub> separation. Insights into the microscopic interfacial interaction along with macroscopic characteristic features of the composite materials are very important to identify the selective gas adsorption and separation. The structure and stability of the composite materials have been characterized by the DFT with the Grimme's dispersion correction (DFT-D3).<sup>47</sup> Using the results from atomistic simulations, the stable composite materials were analyzed for its selective gas adsorption and storage applications. These computations were done by the force field based GCMC approach. Different force fields were used to compare our results with the available experimental results.<sup>24,25</sup> Based on the observations, new composite materials were reported for the potential CO<sub>2</sub> storage and separation applications. Furthermore, our computational methodology can provide an atomic-scale perception of the interfacial interaction between ILs and ZIFs as well as selective CO<sub>2</sub> adsorption. Even though there are some previous reports on IL@ZIF-8, ours is the first one to analyze the role of anion and influence of interfacial interactions on the selective CO<sub>2</sub> capture. This study provides a systematic computational approach to identify the role of interfacial interactions in the selective CO<sub>2</sub> capture at IL based composites and this can be helpful in experimental/industrial design of such materials.

## 2. Computational methodology

### 2.1. DFT calculations

The geometries of all the ILs were optimized using Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)<sup>48,49</sup> with 6-311++G\*\* basis set in Gaussian16 package.<sup>50</sup> One IL ion-pair is incorporated into the pore of ZIF-8 and optimized using CELLOPT protocol to relax the composite structures. All the DFT periodic calculations are done using Quickstep package in CP2K<sup>51</sup> version 5.1.



CELLOPT method helps in relaxing the structure by adjusting the original lattice parameters.<sup>36</sup> It helps to find the change in the cell volume with the incorporation of ILs in ZIF-8. For this optimization, PBE (Perdew–Burke–Ernzerhof)<sup>52</sup> exchange correlation method is used with Grimme's D3<sup>47</sup> semi-empirical dispersion correction. Inclusion of dispersion correction has great influence on the prediction of properties of composite materials.<sup>36</sup> Also they are found to be effective in predicting the structure of various ZIFs.<sup>53</sup> So we have included D3 dispersion in order to describe the properties of ILs based membranes. A mixed Gaussian plane wave (GPW) basis set scheme was used to represent the pseudo potentials and valence electron density of the elements. All atoms, except B and Zn, were described by the MOLOPT-TZVP (triple-zeta valence polarized) basis set, whereas for zinc and boron atoms, MOLOPT-DZVP (double-zeta valence polarized) was used.<sup>54</sup> GTH (Goedecker–Teter–Hutter)<sup>55</sup> pseudo potentials were used for all atoms. The orbital transformation (OT) was used for the electronic energy minimization and plane wave cut off (450 Ry) was included. The adsorption energies ( $E_{\text{ads}}$ ) for all the complexes are calculated from the optimized geometries using the following equation:

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{ZIF-8}} + E_{\text{IL}}) \quad (1)$$

where  $E_{\text{total}}$ ,  $E_{\text{ZIF-8}}$  and  $E_{\text{IL}}$  are the total energies of the composite, ZIF-8 and IL, respectively.

## 2.2. GCMC simulations

GCMC simulations are carried out at temperature 298 K to study single component adsorption isotherm of  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$  as well as binary mixture ( $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  mixtures) selectivity of these gases in the pure ZIF-8 and composite materials. All calculations were done using RASPA<sup>56</sup> simulation package. Here, the interaction between composite and gas molecules ( $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$ ) were modeled using 12-6 Lennard-Jones (LJ) potential. Cross-atomic force field parameters were defined using Lorentz–Berthelot mixing rule given by,  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$  and  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$  where  $\epsilon_i$  and  $\sigma_i$  are the LJ parameters for the species  $i$ . Validation of different force field was done by comparing the results with the reported experimental isotherm.<sup>24</sup> Universal force field (UFF),<sup>57</sup> Dreiding force field<sup>58</sup> and GenericMOFs force fields<sup>56</sup> (as implemented in RASPA) were compared with the available experimental data. GenericMOFs is a mixed force field where the metal center (Zn) is treated by UFF and other atoms by Dreiding force field. The  $\text{CO}_2$  and  $\text{N}_2$  gas molecules were modeled as three site rigid model and  $\text{CH}_4$  as single site model using TraPPE force field.<sup>59</sup> The force field parameters used for different framework atoms and gas molecules are given in Tables S1 and S2 (in ESI†). Pressure ranges from 0.01 to 10 bar were investigated at 298 K for each isotherm. Each simulation had  $1 \times 10^7$  steps for initialization and  $1 \times 10^6$  steps for equilibration. In single component simulations, four different moves were used, which are translation, rotation, reinsertion and swap. In binary mixture calculations, identity exchange was also considered along with these four moves. Equimolar binary mixtures (50/50) of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  were considered for

selective  $\text{CO}_2$  adsorption. The selectivity ( $S$ ) of these mixtures are calculated using the following equation:

$$S_{a/b} = \left( \frac{N_a}{N_b} \right) / \left( \frac{Y_a}{Y_b} \right) \quad (2)$$

where,  $N$  and  $Y$  are the amount adsorbed in bulk phase and mole fraction of the gas in the mixture respectively, for the gases  $a$  and  $b$ . To know the occupancy of ILs in ZIF-8 pores, we computed helium void fraction and pore-size distribution (PSD) of ILs@ZIF-8, and the same were compared with that of ZIF-8. Also, the heat of adsorption ( $\Delta H_{\text{ads}}$ ) is calculated for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$  at different composites and ZIF-8, at infinite dilution condition.

## 3. Results and discussion

### 3.1. Geometry and energetic of ILs@ZIF-8

A total of eleven ILs, both hydrophilic and hydrophobic, were incorporated to study the effect of anion in the nanopores for the selective  $\text{CO}_2$  capture and separation application. For this, we have chosen  $[\text{BMIM}]^+$  cation with various hydrophilic/hydrophobic anions  $[\text{X}]^-$ , where  $\text{X} =$  trifluoroacetate  $[\text{CF}_3\text{CO}_2]^-$ , tetrafluoroborate  $[\text{BF}_4]^-$ , hexafluorophosphate  $[\text{PF}_6]^-$ , chloride  $[\text{Cl}]^-$ , trifluoromethanesulfonate  $[\text{OTF}]^-$ , dicyanamide  $[\text{DCA}]^-$ , nitrite  $[\text{NO}_2]^-$ , nitrate  $[\text{NO}_3]^-$ , azide  $[\text{N}_3]^-$ , thiocyanate  $[\text{SCN}]^-$  and bis(trifluoromethylsulfonyl)imide  $[\text{Tf}_2\text{N}]^-$ . These anions are experimentally known and can be easily incorporated into ZIF-8 pore. Few of these anions are already reported at the ZIF-8 nanopores to enhance the  $\text{CO}_2$  adsorption.<sup>24,25,32,60</sup> The optimized geometries of various ILs along with the important distance between ion-pairs (in Å) are given in Fig. 1. It is found that all the anions are directly hydrogen bonded (H-bonded) with  $\text{C}_2\text{H}$  group of  $[\text{BMIM}]^+$  cation. The calculated H-bonding distance between IL ion-pair varies from 1.75 to 2.33 Å, irrespective of nature of anions (*i.e.* hydrophobic/hydrophilic). In addition to this some of the anions were weakly H-bonded with alkyl group in  $[\text{BMIM}]^+$ . The optimized geometry of ZIF-8 structure is shown in Fig. 2 along with the pore size ( $\sim 11.95$  Å). ILs are incorporated into this optimized ZIF-8. The geometry of selected IL ion-pairs, ZIF-8 structure, various ILs incorporated ZIF-8 complexes and PSD plots are provided in Fig. S1–S5 (in ESI†).

ILs are impregnated into the nanopores of ZIF-8 and optimized using PBE method with D3 dispersion correction. To find the stability and structural properties of ILs@ZIF-8 composite, we optimized all the complexes using DFT based periodic calculations. This approach can provide a clear picture of microscopic interfacial interaction between ILs and ZIF-8. Also the magnitude of the stability depends on the nature of interfacial charge transfer in the complex.<sup>36</sup> The shortest interacting distances between anion–cation and the framework, observed from the optimized geometries, are given in Table 1. In addition, the optimized geometries along with shortest interaction distances are provided in Fig. S3 (in ESI†). Even at the confined environment, the geometries of ILs are not disturbed and these ion-pairs are stabilized by the electrostatic interactions and H-bond(s). In addition, some of the IL ion-pairs have strongly



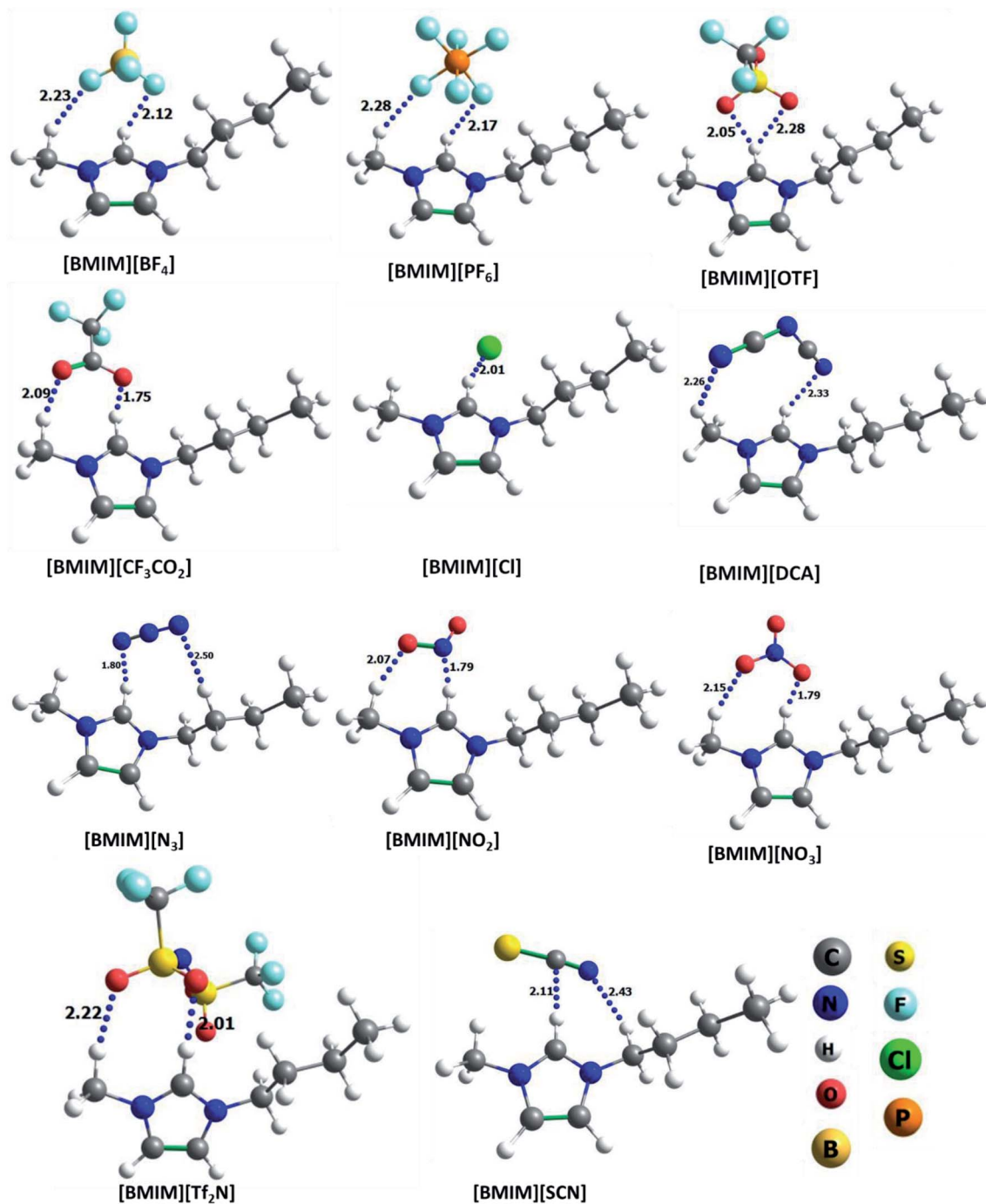


Fig. 1 Optimized geometries of monomers of all the ILs used in this study, along with shortest interaction distances between anion and cation (in Å).

interacted with ZIF-8 surface. The calculated interacting distance of cation-surface and anion-surface are varied from 2.32–2.70 Å and 2.37–4.04 Å, respectively. It is to be noted from the Fig. S3† that both anion and cation of fluorinated ILs are strongly interacting with the surface which significantly influences the calculated adsorption energies.

Also, the change in volume (in percentage) is calculated in comparison with the experimental crystal structure. The changes in unit cell parameters were closely analyzed after the

incorporation of ILs at the ZIF-8 nanopores. These parameters suggest that there are no significant structural changes in the ZIF-8 framework after encapsulation ILs. It can be noted that the average expansion of unit cell is ~1.8% with respect to the experimental crystal structure of ZIF-8. Furthermore, the volume expansion depends on the size of the anion. After optimization of composites, [BMIM]<sup>+</sup> with [PF<sub>6</sub>]<sup>-</sup>, [CF<sub>3</sub>CO<sub>2</sub>]<sup>-</sup> and [OTF]<sup>-</sup> anion containing structures are slightly expanded than the average cell volume (*i.e.* >2%). The significant



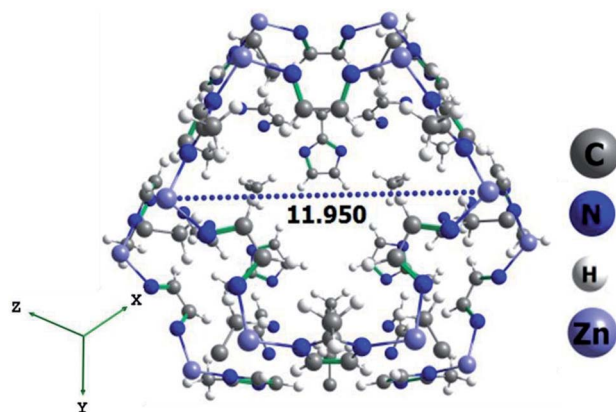


Fig. 2 The optimized geometry of ZIF-8 structure using CELLOPT method. The dotted line shows the pore cavity (in Å).

enhancement in the cell volume may arise from the influence of anions at the confined state. This is also reflected in the calculated adsorption energies of fluorinated anions. Higher adsorption energies of IL leads to more expansion in volume of ZIF-8 crystal structure, which is due to the existence of strong interfacial interaction between ILs and ZIF-8.

The interaction energies of the complexes can be quantified from the calculated  $E_{\text{ads}}$  between ILs and ZIF-8 structure. The dominant interfacial interactions can stabilize the ion-pair at the ZIF-8 nanopore. These interactions can predict the order of stability and the calculated magnitude of strength is provided in Table 1. The obtained results reveal that some of the ILs are not adsorbed on the surface of the ZIF-8. These ILs have a repulsive kind of interaction with the surface, *i.e.*, the ILs are showing positive  $E_{\text{ads}}$ . It is also interesting to note that all the ion pairs with a positive  $E_{\text{ads}}$  contain at least one nitrogen atom in the anion of IL (N-based ILs). The repulsive nature of these ILs may arise from the interaction of non-localized nitrogen lone-pair and the ZIF-8 imidazolate surface. The non-N based anion complexes are well adsorbed on the ZIF-8 surface (shown in ESI Fig. S4†). This is due to the attractive interfacial interaction

between ion-pair and surface (negative value for  $E_{\text{ads}}$ ). Some recent studies investigated the IL@ZIF-8 complexes, but the structure, stability and interfacial interactions of series ILs based composite materials were not reported.<sup>26,60,61</sup> Some of the N-based anions have shown high  $\text{CO}_2$  solubility,<sup>62</sup> but here we observed that they are incompatible and less stable at the ZIF-8 confinement. So in order to find the significance of these interfacial interactions in the gas adsorption/selectivity, we studied these composites using GCMC simulations and discussed in the following sections.

In the present study, we found the anion based selective adsorption of IL@ZIF-8, which is more dominant for gas sensing and separation applications. The stability of complex originates from the well-matched interfacial interaction between IL and ZIF-8. Our previous study showed that hydrophobic ZIFs prefer to stabilize the hydrophobic IL (*i.e.*, like-like pair).<sup>36</sup> Present work shows that not only like-like pair effect but also anionic part of the ILs plays a major role in the composite stability. This infers that anion in the selected ILs play a vital role in identifying the potential composite materials. It is interesting to note that, the fluorine atom(s) in the anion play a significant role in the capture of  $\text{CO}_2$  molecules.<sup>33</sup> All the composites which were screened through DFT method were imposed for the adsorption and selective separation of  $\text{CO}_2$  from  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  binary mixtures using GCMC simulations.

## 3.2. GCMC simulations

**3.2.1 Single component adsorption isotherms.**  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$  gases were selected to analyze the adsorption capacity of the designed composite materials. The charges for framework atoms and ILs were calculated using charge equilibration method as implemented in RASPA and these charges are used in the adsorption studies. The helium void of all the composites are given in Table S3† and PSD of stable ILs@ZIF-8 complexes are provided in Fig. S5 (ESI†). The calculated charges for framework atoms as well as all the ILs considered in this study are given in Tables S4–S6 (in ESI†). PSD and He-void

Table 1 The calculated distances between anion and cation in ILs with the framework (in Å) along with the calculated adsorption energies of IL@ZIF-8 and the respective pore volume changes (in %)

[BMIM][X]@ZIF-8 composites	Shortest interacting distances (Å)			Change in cell volume (%)	$E_{\text{ads}}$ (kcal mol <sup>-1</sup> )
	[BMIM] <sup>+</sup> –[X] <sup>–</sup>	ZIF-8 and [BMIM] <sup>+</sup>	ZIF-8 and [X] <sup>–</sup>		
[BMIM][NO <sub>3</sub> ]	1.78	2.53	2.61	1.49	32.91
[BMIM][TF <sub>2</sub> N]	2.10	2.70	2.53	1.52	27.56
[BMIM][DCA]	2.25	2.44	4.04	1.61	26.94
[BMIM][N <sub>3</sub> ]	1.67	2.36	2.96	1.68	16.79
[BMIM][SCN]	2.13	2.44	3.13	1.81	9.10
[BMIM][NO <sub>2</sub> ]	1.81	2.43	2.70	1.79	4.37
[BMIM][Cl] <sup>36</sup>	2.11	2.34	2.87	1.93	–6.56
[BMIM][BF <sub>4</sub> ] <sup>36</sup>	2.10	2.41	2.68	1.96	–9.90
[BMIM][CF <sub>3</sub> CO <sub>2</sub> ] <sup>36</sup>	1.77	2.49	2.43	2.05	–15.67
[BMIM][PF <sub>6</sub> ] <sup>36</sup>	1.99	2.54	2.37	2.18	–31.72
[BMIM][OTf]	2.02	2.32	2.45	2.31	–43.52



calculations help to analyze the available free space in ZIF-8 with and without encapsulated ILs. They were reduced after IL incorporation in the ZIF-8, which clearly shows that the void space is partially occupied by IL and thus may reduce the uptake of gas molecules. But IL incorporation can enhance the selectivity of particular gas molecules at composites. After these calculations, the loading of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> were calculated at constant temperature (*i.e.* 298 K) with varying pressure conditions.

The selection of suitable force field is important to predict the gas capture ability of the ZIFs.<sup>63</sup> To select suitable force field for molecular simulations and to confirm our results with experimental adsorption isotherm, we studied three different force fields such as UFF, Dreiding force field and GenericMOFs force field for CO<sub>2</sub> and N<sub>2</sub> gas molecules. For these gas molecules, three site rigid TraPPE model was used. The adsorption isotherms for empty ZIF-8 and IL loaded ZIF-8 (*i.e.*, 3[BMIM][PF<sub>6</sub>]) in comparison with available experimental isotherms are shown in Fig. 3a and b, respectively. The previously reported experimental data correspond to 24 wt% of IL in ZIF-8 unit cell.<sup>24</sup> So, here we compared our results with the same wt%, which is equivalent to 3 ion-pairs of ILs per unit cell. It is interesting that among the three different force fields, the Dreiding force field is in very good agreement with the available experimental isotherm for the CO<sub>2</sub> and N<sub>2</sub>@composite. Whereas in the case of pristine ZIF-8, GenericMOFs force field is more closely predicting the experimental results. Even though the GenericMOFs force field shows better agreement with the experiments for empty ZIF-8 crystal, Dreiding force field shows better results for both ZIF-8 and IL based composite materials. The results obtained from UFF were not so promising as compared to other two force fields. Thus, we focused on Dreiding force field to study the adsorption isotherm as well as co-adsorption selectivity of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in the composite materials. A similar result was observed by Polat *et al.* in their recent work on open metal site MOF (CuBTC)/IL composite.<sup>26</sup> Here, we observed analogous results for saturated MOF/IL composite. Using the predicted force field, new stable

composite materials were explored for its gas storage capacity and selectivity.

The comparison of adsorption isotherms of different non-N based stable composite materials is depicted in Fig. 4 for CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>. The designed composite materials show higher gas uptake when compared to ZIF-8 at low pressure ( $\leq 3$  bar) and 298 K. These conditions follow the optimum environment for the flue gas mixture separation.<sup>64</sup> In the plots presented in Fig. 4a, with an increase in the pressure, the isotherm of ZIF-8 are crossing over the isotherms of all composites. This is because of the accommodation of more number of gas molecules in the available ZIF-8 pore at higher pressure ( $\geq 5$  bar). This is absent in ILs@ZIF-8 composite, because of the accumulation of ILs at the pores. In the isotherm plots of N<sub>2</sub> and CH<sub>4</sub> (Fig. 4b and c), there are no intense changes in the adsorption. The individual adsorption isotherms of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> at stable composites are given in Fig. S6 (ESI†).

In order to analyze the effect of interaction energy in the gas storage of the complexes, we also analyzed the CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> gas adsorption isotherms of all N-based composites (Fig. S7 in ESI†). The comparison of isotherms for these composites is given in Fig. S8 in the ESI.† From the figure, it is clear that even though the ILs are not stable inside the ZIF-8 confinement, they still can accommodate large amount of gases, which is no less than the stable composites. The anions in the selected ILs have similar size and they have uniformly occupied the ZIF-8 pore. This is evident from He-void and PSD data. Due to the availability of pores, a large amount of gas (CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>) can be adsorbed on the composites, irrespective of its interaction with ZIF-8. Also, we have added only one IL ion pair/ZIF-8 pore. So this can further enhance the gas adsorption by providing more vacant sites. The amount of gas adsorbed can be slightly varied according to the size of the anion. [BMIM][Tf<sub>2</sub>N]@ZIF-8 has slightly lesser gas storage due to the larger anion size. From this it is clear that the interfacial interaction energies between different ILs and ZIF-8 do not affect the gas adsorption in these composites.

### 3.2.2 Separation of binary gas mixture at the composites.

To understand the CO<sub>2</sub> separation capability of the materials in

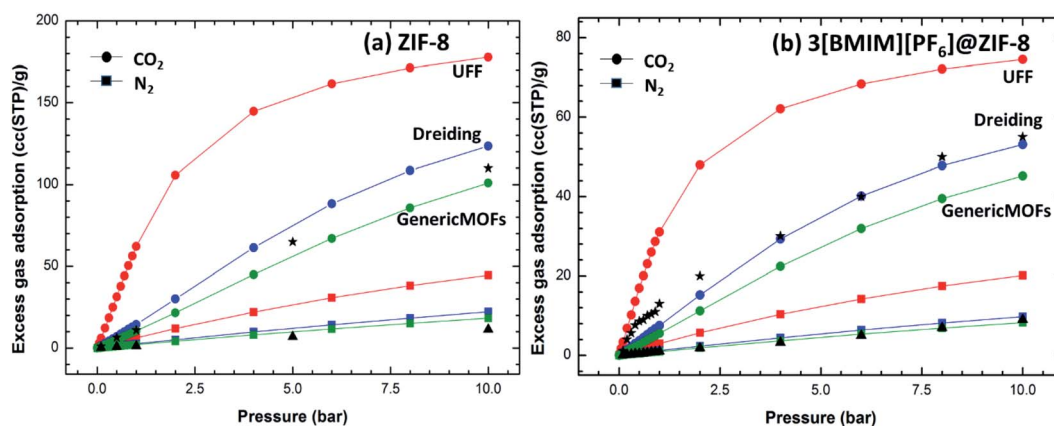


Fig. 3 Adsorption isotherm of (a) ZIF-8 and (b) 3[BMIM][PF<sub>6</sub>]@ZIF-8 computed using different force fields in comparison with available experimental results (▲ and ★ represents experimental N<sub>2</sub> and CO<sub>2</sub> uptakes, respectively).



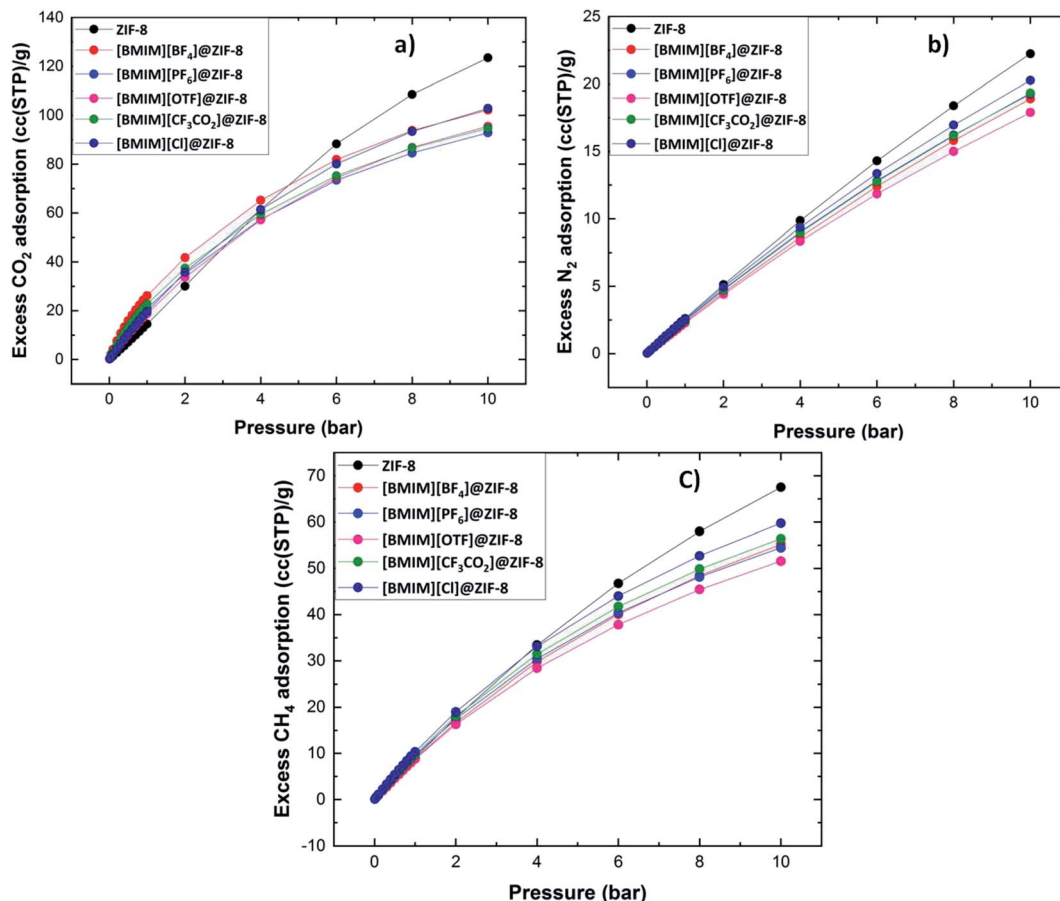


Fig. 4 Comparison of gas adsorption isotherm of ZIF-8 and non-N based anionic ILs@ZIF-8 composites were calculated using Dreiding force field for (a)  $\text{CO}_2$ , (b)  $\text{N}_2$  and (c)  $\text{CH}_4$ .

real-time applications, the  $\text{CO}_2$  selectivity was calculated from the binary mixture adsorption of  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  at equimolar concentrations. The selective separation of  $\text{CO}_2$  was identified from GCMC simulations. Fig. 5 gives a comparison of  $\text{CO}_2$  selectivity from two different gas mixtures, for stable composites. Fig. 5a shows the  $\text{CO}_2/\text{N}_2$  selectivity for different

composites. From the figure, it is clear that the designed composite material has better  $\text{CO}_2$  selectivity compared to pristine ZIF-8. It is found that  $[\text{BMIM}][\text{BF}_4]@\text{ZIF-8}$  complex has high  $\text{CO}_2$  selectivity when compared to others. So our predicted materials show better selective adsorption towards  $\text{CO}_2$  at the optimum experimental condition. The non-fluorinated  $[\text{BMIM}]$

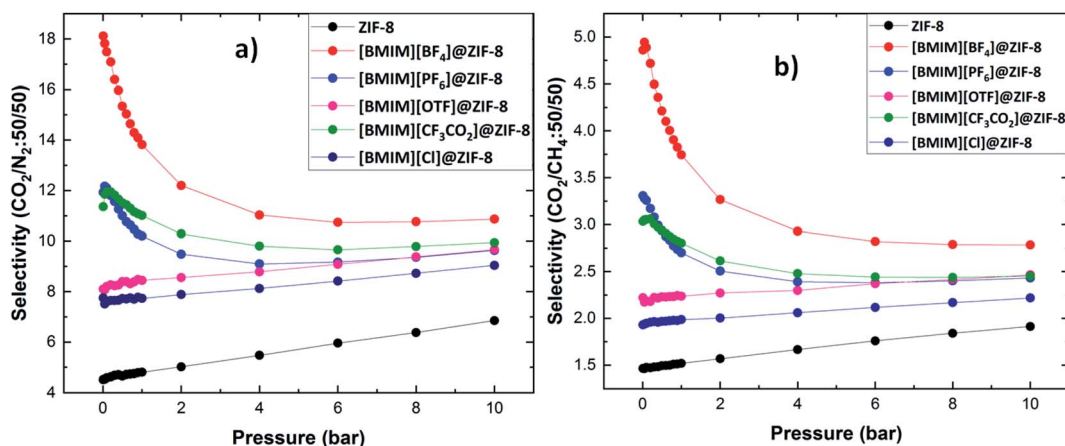


Fig. 5 The binary gas mixture selectivities of ZIF-8 and stable non-N based composite materials (a)  $\text{CO}_2/\text{N}_2$  and (b)  $\text{CO}_2/\text{CH}_4$ .



[Cl]@ZIF-8 has lower selectivity when compared to other materials. Even though  $[\text{Cl}]^-$  anion is polar and has hydrophilic nature, fluorinated anions in IL-based composite shows the better selective adsorption of  $\text{CO}_2$ . This is in well agreement with the calculated  $E_{\text{ads}}$ . These composites show higher selectivity at a lower pressure than higher pressure regions. This can be helpful in industrial flue gas separation. Fig. 5b shows the  $\text{CO}_2/\text{CH}_4$  selectivity of the composites. The selective  $\text{CO}_2$  adsorption is less from this gaseous mixture compared to  $\text{CO}_2/\text{N}_2$  mixture. This mixture follows the similar trend as  $\text{CO}_2/\text{N}_2$  mixture.  $[\text{BMIM}][\text{BF}_4]^-$ @ZIF-8 shows highest selectivity for  $\text{CO}_2$  among the composites. The IL incorporation has enhanced the  $\text{CO}_2$  selectivity of ZIF-8. The fluorinated ILs show better selectivity compared to non-fluorinated  $[\text{Cl}]^-$ . From the interaction strength of ILs@ZIF-8 and selective  $\text{CO}_2$  adsorption, it is clear that fluorinated anions in the IL can efficiently bind to the ZIF-8 surface and they also influence the  $\text{CO}_2$  selective adsorption. It is also interesting that the selectivity of some ILs@ZIF-8 (*i.e.*  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$  and  $[\text{CF}_3\text{CO}_2]^-$ ) reduces with increasing pressure, whereas for other ILs, the selectivity increases with increasing pressure. In these complexes, the selectivity is much higher at lower pressure, *i.e.* the amount of  $\text{CO}_2$  adsorbed compared to other gases is higher at low pressure. But as the pressure increases, the  $\text{CO}_2$  molecules occupy the pores and hence reduces the intake of incoming gas molecules. So the selectivity decreases as the pressure increases. But for the other composites, (*i.e.* pristine ZIF-8,  $[\text{OTf}]^-$  and  $[\text{Cl}]^-$  based complexes) the selectivity is less at low pressure. So the gas molecules adsorbed on the pores are also less. As the pressure increases, the more gas molecules will be accommodated into the pores. Especially  $\text{CO}_2$  molecules, because our interface material has high affinity for  $\text{CO}_2$  molecules. So as the pressure increases, there is a gradual increase in the selectivity for these anions.

In addition, the  $\text{CO}_2$  selectivity for all the N-based ILs@ZIF-8 were analyzed. Fig. S9 in ESI† represents the binary mixture selectivities of different N-based ILs@ZIF-8 for  $\text{CO}_2/\text{N}_2$  and  $\text{CO}_2/\text{CH}_4$  mixtures. All the composites show better selective adsorption than pristine ZIF-8. From Fig. S9,† it is clear that  $[\text{BMIM}][\text{Tf}_2\text{N}]^-$ @ZIF-8 shows comparatively higher selectivity despite of having a repulsive interaction with the surface. Even though they have repulsive interactions, all the N-based complexes show selectivity better than pristine ZIF-8. Compared to  $[\text{BMIM}][\text{Tf}_2\text{N}]^-$ @ZIF-8 complex, other N-based IL complexes show lower selectivity. Recent reports on  $[\text{BMIM}][\text{Tf}_2\text{N}]^-$ @ZIF-8 suggest that IL act as good cavity occupants in ZIF-8 and enhances the  $\text{CO}_2$  selectivity.<sup>65,66</sup>

Close analysis of both type of composites shows that the fluorine containing IL anions in the composites show better  $\text{CO}_2$  adsorption and significant  $\text{CO}_2$  selectivity than pristine ZIF-8, especially at low pressure. Irrespective of the nature of interaction between ILs and ZIF-8, the IL incorporation itself can enhance the  $\text{CO}_2$  selectivity of ZIF-8. Particularly, the fluorine content with the combination of hydrophobic nature plays an important role in enhancing the  $\text{CO}_2$  selectivity. Hydrophobic and fluorinated anions such as  $[\text{BF}_4]^-$ ,  $[\text{Tf}_2\text{N}]^-$  and  $[\text{PF}_6]^-$  can enhance the selective separation of  $\text{CO}_2$  compared to other anions used in this study. We previously reported that

there is an enhanced charge transfer between fluorinated ILs and ZIF-8.<sup>36</sup> This effective charge transfer can be helpful in strong interaction between  $\text{CO}_2$  and ILs@ZIF-8. Even if the composites and pristine ZIF-8 show similar storage capacity, the selectivity is enhanced with the incorporation of ILs. This shows that the composite can store as much more gas molecules as the ZIF-8 with better  $\text{CO}_2$  selectivity.

**3.2.3 Heat of adsorption.** The heat of adsorption indicates the strength of the interaction between adsorbate gas molecules and the adsorbent surface.<sup>67</sup> So quantifying the heat of adsorption can be helpful in the identification of role of IL (anion/cation) in the gas separation. So the heat of adsorption of ZIF-8 and non-N based composites at infinite dilution condition is calculated using the expression,<sup>56</sup>

$$\Delta H_{\text{ads}} = \langle U_{\text{gh}} \rangle - \langle U_{\text{h}} \rangle - \langle U_{\text{g}} \rangle - RT \quad (3)$$

where,  $\langle U_{\text{gh}} \rangle$ ,  $\langle U_{\text{h}} \rangle$  and  $\langle U_{\text{g}} \rangle$  are the average internal energies of the guest–host, host, and guest, respectively.  $R$  is the universal gas constant and  $T$  is the temperature (298 K). The comparison of  $-\Delta H_{\text{ads}}$  for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$  at different composites are given in Fig. 6. From the figure, it is clear that the heat of adsorption increases with IL incorporation. The pristine ZIF-8 has a  $\Delta H_{\text{ads}}$  of  $-15.38$ ,  $-10.19$  and  $-13.43$   $\text{kJ mol}^{-1}$  for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$ , respectively. But, the incorporation of IL into ZIF-8 enhances the  $\Delta H_{\text{ads}}$  of the gas molecules at the composites. For  $\text{CO}_2$  gas molecule, the heat of adsorption follows the order,  $[\text{BF}_4]^- > [\text{PF}_6]^- \sim [\text{CF}_3\text{CO}_2]^- > [\text{OTf}]^- > [\text{Cl}]^- > \text{ZIF-8}$ . After IL incorporation, there is a clear enhancement in the  $\Delta H_{\text{ads}}$  of  $\text{CO}_2$  than  $\text{N}_2$  and  $\text{CH}_4$ . There is only slight enhancement in the  $\Delta H_{\text{ads}}$  of  $\text{CH}_4$  and  $\text{N}_2$ , after IL incorporation. This is due to the strong interaction of  $\text{CO}_2$  with the framework compared to other two gases. This can be favorable in  $\text{CO}_2$  adsorption from different gas mixtures. The non-fluorinated  $[\text{BMIM}][\text{Cl}]^-$ @ZIF-8 has less heat of adsorption when compared to other fluorinated anions. From this, it is evident that fluorine content in the anion has a major role in the affinity of  $\text{CO}_2$  molecules towards composites. The incoming  $\text{CO}_2$  molecules form strong non-covalent interactions with the ion-pair and thus enhancing the heat of adsorption.

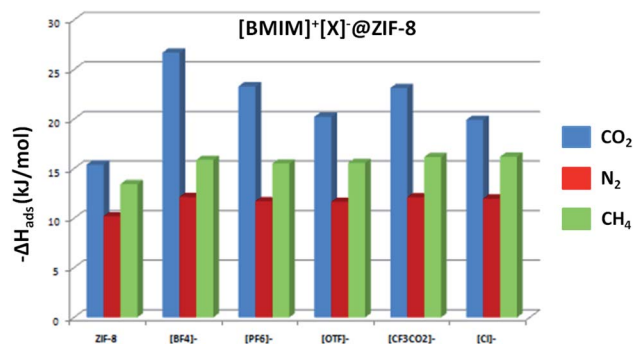


Fig. 6 The heat of adsorption calculated for  $\text{CO}_2$  (blue),  $\text{N}_2$  (red) and  $\text{CH}_4$  (green) at ZIF-8 and different composites, at infinite dilution condition.



Fig. 7 shows the adsorption of CO<sub>2</sub> at ZIF-8 and the site-selective adsorption of CO<sub>2</sub> in the [BMIM][BF<sub>4</sub>]@ZIF-8 complex. From the snapshots of GCMC simulations at different pressure, it is clear that the adsorbed CO<sub>2</sub> molecule is strongly interacting with the fluorine atom in the anion and alkyl chain of the cation. The oxygen in CO<sub>2</sub> interacts with hydrogen atom of alkyl chain in the cation through C–H···O H-bonds. This non-covalent interaction distance is ~3.0 Å. This is the reason for the enhancement in heat of adsorption after IL incorporation, which contributes to the better CO<sub>2</sub> selectivity of these materials. The shortest interaction distance between CO<sub>2</sub> and IL shows the site of adsorption and the role of fluorinated anion in the selective CO<sub>2</sub> capture at the ZIF-8 nanoconfinement. This attributes to the higher CO<sub>2</sub> selectivity of composites at low pressure and ambient temperatures. Also, from the binary mixture adsorption (Fig. S10†), it can be found that the incoming CO<sub>2</sub> forms a strong H-bond (~1.75 Å) with the BMIM<sup>+</sup> cation of IL. This will lead to efficient storage and separation of CO<sub>2</sub> in the IL based composite than the bare ZIF-8. This proves that the designed material show high CO<sub>2</sub> selectivity due to the strong interfacial interactions between gas molecules and composites. Yang and co-workers reported that, at zero pressure, the selectivity depends on the difference in isosteric heats and independent of the material and gas mixtures.<sup>68</sup> By incorporation of ILs to the ZIF-8 nanopore, we can enhance the selective adsorption of CO<sub>2</sub>. Since the heat of adsorption is more for the fluorinated ILs, we can infer that the anion in ILs play a major role in selective CO<sub>2</sub> capture. It is found from our calculations that, the nature of anion and also

the number fluorine atom(s) in the anion plays a vital role in the CO<sub>2</sub> selectivity of the composites, irrespective of their interaction with ZIF-8 framework. The selection of suitable ILs directly leads to the enhancement of CO<sub>2</sub> adsorption as well as selectivity. These findings are observed from the combined DFT based computational screening and GCMC simulations approaches.

## 4. Conclusions

In summary, atomistic simulations were used to identify the interfacial interaction between different ILs and ZIF-8 and also their effect on selective CO<sub>2</sub> capture. We combined both DFT and GCMC approaches to identify better composite material. Adsorption energies quantified from DFT calculations suggest that some of the anions are not well adsorbed on the ZIF-8 surface. These anions contain nitrogen in it and the repulsive nature of lone pair of nitrogen leads to less compatible structure. In order to find out the role of these interfacial interactions in gas adsorption and selective CO<sub>2</sub> separation in these complexes, they were studied using GCMC simulations. Different existing force fields were validated with experimental results and Dreiding force field was found to give a better description of the ILs@ZIF-8. Further analysis of adsorption isotherms proved that the interfacial interaction does not affect the gas storage capacity of the composites. The CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity is enhanced in the IL incorporated ZIF-8. Irrespective of the nature of interaction between ILs and ZIF-8, the IL@ZIF-8 shows improved CO<sub>2</sub> separation. Especially the CO<sub>2</sub>

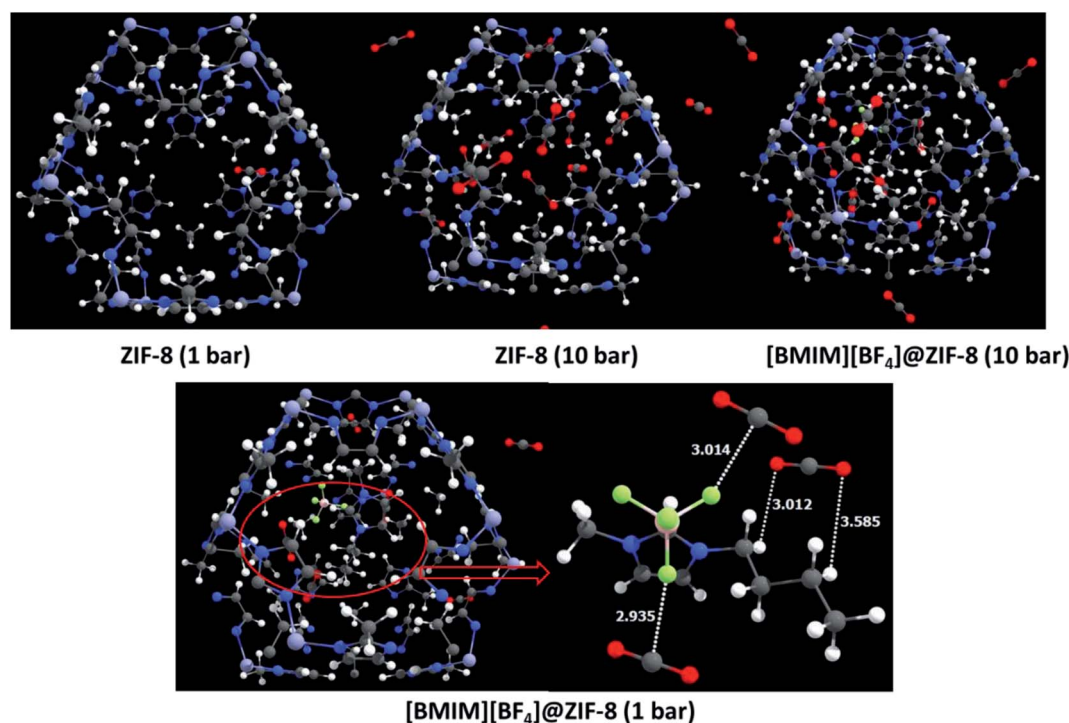


Fig. 7 Snapshots show the adsorption of CO<sub>2</sub> at bare ZIF-8 and [BMIM][BF<sub>4</sub>]@ZIF-8 at different pressure (1 and 10 bar). The bottom figure shows the site selective adsorption of CO<sub>2</sub> at IL@ZIF-8 along with the shortest interacting distances (Å) of CO<sub>2</sub>.



selectivity of hydrophobic fluorinated anions is much better compared to hydrophilic/non-fluorinated anions. Anions such as  $[\text{BF}_4]^-$ ,  $[\text{TF}_2\text{N}]^-$  and  $[\text{PF}_6]^-$  improve the selective  $\text{CO}_2$  separation, which is also confirmed from the enhanced heat of adsorption for  $\text{CO}_2$ . Atomistic simulation based screening and identification of suitable composites for  $\text{CO}_2$  capture can be a useful tool in real-time industrial flue gas separation.

## Conflicts of interest

There are no conflicts of interest to declare.

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