Density Functional Theory Studies on Zeolitic Imidazolate Framework-8 and Ionic Liquid-Based Composite Materials

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ABSTRACT: The identification of suitable density functional methods for predicting the properties of nanoporous composite materials is highly significant in the field of chemical and material sciences. The stability of the composite materials depends on the nature of bonding and dispersive interaction at the interface. Thus, we have studied the effect of dispersion correction in the incorporation of hydrophobic and hydrophilic ionic liquids (ILs) into zeolitic imidazolate framework-8 (ZIF-8) nanostructures using the density functional theory (DFT)-based approaches. These structures were analyzed employing selected methods (Becke–Lee–Yang–Parr and Perdew–Burke–Ernzerhof) with dispersion correction (D2 or D3) and different basis sets (such as double-zeta valence polarized (DZVP), triple-zeta valence polarized (TZVP), and triple-zeta valence doubly polarized (TZV2P)) for the understanding of microscopic features of IL@ZIF-8 nanopores. It is found that the result obtained from DFT-D2/TZVP is more reliable for the prediction of the experimental crystal structure as well as stability and spectral information of the complexes. Furthermore, the microscopic analysis of geometries reveals that ILs are highly dispersed and stabilized at the nanopores of ZIF-8, particularly the ZIF-8 structure is highly preferable for the hydrophobic group in ILs. It is found that fluorine-containing anions are highly dispersed on the ZIF-8 surface compared to the nonfluorinated anion (i.e., [BMIM][Cl]). This is confirmed from the adsorption energies (E_ads), charge transfer, electron density analyses, and IR spectral analysis. These findings can provide more insights into the stability of composite materials, which are suitable for applications of catalytic conversion at the confined state, gas storage, and separation techniques.

1. INTRODUCTION

Ionic liquids (ILs) are emerging class of solvents,1 which are liquids below 100 °C and find its application in various fields such as catalysis,2 green solvent,3 clean energy,4 etc. They have widespread applications in many fields, mainly because of their thermal stability, negligible vapor pressure, tunability, and low volatility.5 Imidazolium cation-based ILs form a major class of ILs.6 The high viscosity of ILs is always a limiting factor for the use of it in real-time applications. To avoid this limitation, we can support ILs over different membranes.7 These supporting materials can be either 2D (e.g., graphene or metal surfaces) or 3D nanoporous materials. These are called as supported ionic liquid membranes (SILMs) and form an outstanding category of materials for various applications such as gas storage, separation, and catalysis.8–11

Among 3D supporting materials, metal–organic frameworks (MOFs)12,13 are receiving widespread attention in the fields of catalysis,16 gas storage,17 drug delivery,18,19 etc. These MOFs have several advantages like high surface area, thermal and chemical stability, and tunable pore size.20,21 Zeolitic imidazolate frameworks (ZIFs) are subclass of MOFs, whose structural features are analogous to that of zeolites. ZIF-8 exhibits a cubic sodalite (SOD) structure and is known for its structural flexibility and stability with the larger pore volume and surface area.22 SILMs can be prepared by incorporating ILs into the pores of ZIF-8, thus overcoming their limitation of high viscosity.23,24 SILMs show very high stability in liquid/liquid and gas/gas separations at high temperature and pressure.25 Organic compounds, mixed gases, and metal ions can be easily separated using these ionic liquid membranes.26 Implementation on large scale, cost-effectiveness, reusability, and stability under real-time applications still remains unresolved for SILMs.

Several experimental and theoretical studies have been devoted to realize the properties and applications of various ZIFs and IL-based composites.24,27–31 ILs@MOF composites are used in many applications such as selective separation of CO2/CH4,41 ionic conductor,31 catalysis, etc.27 Recent reports reveal that the ILs@ZIF-8 pore can enhance the properties of ZIF-8 for gas storage and separation.13,34 Kinik et al. reported that incorporation of imidazolium-based IL, [BMIM][PF6], can double the CO2 selectivity of ZIF-8.34 Fujie and co-workers reported that introducing ILs (EMIM-TFSA) into the micropores of ZIF-8 helps to stabilize IL at a lower temperature. This study proves that the incorporation of ILs into ZIFs can provide a novel methodology for the stabilization...
of ILs. This material can also be used as a low-temperature ionic conductor. Even though these methods are also a major approach for treating dispersive interactions. Even though these methods have similar computational cost to DFT-D, this approach increases the computational time by 50% compared to a normal GGA calculation. Galvelis and co-workers studied the relative stability of zinc and lithium–boron ZIFs using DFT methods with different dispersion corrections (DFT-D) and found that DFT-D gives a better description of the framework than DFT. Walker and co-workers studied the effect of dispersion forces on the reversible switching of MIL-53(Al) between large pore (lp) and narrow pore (np). They found that dispersion-corrected DFT (both DFT-D and vdW-DF) can stabilize the low-temperature np phase. They summarized that dispersion can predict different phase transitions and sorption properties of MOF materials. From all these studies, it is clear that incorporation dispersive correction (either D2 or D3) plays an important role in the prediction of structural features of nanoporous materials such as MOFs, ZIFs, and SILMs. For instance, recently, we found that the adsorption properties of CO2 can be tuned by the selection of suitable ILs for the composite materials. Also, we found that the DFT-D3 method is more reliable for the structure and stability of the complexes.

The number of studies based on dispersion-corrected DFT is increasing every year. The vdW density functional (vdW-D) and dispersion-corrected DFT (DFT-D) are two major approaches for treating dispersive interactions. Even though these methods have similar computational cost to DFT-D, this approach increases the computational time by 50% compared to a normal GGA calculation. Galvelis and co-workers studied the relative stability of zinc and lithium–boron ZIFs using DFT methods with different dispersion corrections (DFT-D) and found that DFT-D gives a better description of the framework than DFT. Walker and co-workers studied the effect of dispersion forces on the reversible switching of MIL-53(Al) between large pore (lp) and narrow pore (np). They found that dispersion-corrected DFT (both DFT-D and vdW-DF) can stabilize the low-temperature np phase. They summarized that dispersion can predict different phase transitions and sorption properties of MOF materials. From all these studies, it is clear that incorporation dispersive correction (either D2 or D3) plays an important role in the prediction of structural features of nanoporous materials such as MOFs, ZIFs, and SILMs. For instance, recently, we found that the adsorption properties of CO2 can be tuned by the selection of suitable ILs for the composite materials. Also, we found that the DFT-D3 method is more reliable for the structure and stability of the complexes.

In the present study, the selection of suitable DFT methods for the prediction of the structure and stability of various IL-based SILM materials with the ZIF-8 framework is investigated. Incorporation of dispersion correction is very important to predict the structural flexibility and cell parameters of composite materials. Thus, we have selected well-known DFT methods such as BLYP and PBE with and without dispersion correction. The structure, stability, spectral data (IR), and charge transfer between ILs@ZIF-8 complexes are analyzed using the selected DFT methods. The obtained results were compared with the experimental crystal structure of ZIF-8 and also with results obtained from the Gaussian basis set approach. To the best of our knowledge, this is the first report on the involvement of the DFT method and the effect of dispersion correction for the prediction of the nanoporous structure with and without ILs. This study is helpful to predict the suitable composite materials for the applications in catalysis, ionic conductors, gas storage, separation, sensor, etc.

2. RESULTS AND DISCUSSION

To study the effect of various DFT methods on nanoporous composite materials, we have chosen the ZIF-8 crystal structure with different hydrophilic/hydrophobic ILs. Here, all these ILs are stabilized at nanopores of ZIF-8 and the resulting structure is represented as the composite material (i.e., IL@ZIF-8). The cell optimization was carried out to know the composite stability along with the crystal lattice parameters. These parameters are helpful to study the effect of interaction of ILs with nanopores and corresponding changes in the volume with respect to the original crystal structure. Even though the crystal structure shows exceptional flexibility under various conditions such as temperature, pressure, solvent, host–guest interactions, etc., its effect is found to be negligible in the case of adsorption of gases such as CO2 and CH4. The structural changes in the empty crystal as well as in the composites were analyzed.

In addition, the composite structure and stability are analyzed using DFT functionals (BLYP and PBE) for the study of solid–liquid interfacial materials. It was found from our previous studies that PBE and PBE-D3 methods were able to predict the adsorption of various ILs on the Au(111) surface and also the effect of alkyl groups on the stability ILs@Au(111) surfaces. Another study reveals that PBE with dispersion correction is more efficient for the prediction of the structure and stability of the zinc and lithium–boron-based ZIFs. Thus, the incorporation of dispersion correction is vital for the investigation of composite materials. Thus, we compared the cell parameters obtained from DFT methods with different basis sets and dispersion corrections for all the ILs@ZIF-8. A detailed discussion of the structure, stability, IR spectra, and charge-transfer process of the complexes with suitable methods is given in the following sections.

2.1. Optimization of the Crystal Structure of ZIF-8 at Different DFT Methods

The crystal structure was obtained from the experimental crystallographic data. The cubic sodalite structure of the ZIF-8 unit cell is comprised of 276 (the repeating unit is Zn-(imidazole)₄⁻) framework atoms. The unit cell optimization was carried out using different DFT methods and dispersion correction with the combination of suitable basis sets.

The optimized cell parameters and corresponding changes in volume after optimization of the ZIF-8 structure are provided in Table 1. The table shows that BLYP and PBE methods with the TZVP basis set (for nonmetal atoms) predict significantly larger volume and overestimate the experimental crystal structure, without dispersion correction. The changes in
basis set method using the RPBE/6-31G level of theory. The

have also studied the structural optimization at the Gaussian

less computational cost. In addition, to validate our results, we

is more precise predicting the crystal structure of ZIF-8 with a

method for the general discussion.

higher. Thus, we have considered DFT-D2 with the TZVP

TZV2P method is reliable, the computational cost is slightly

of the structure of ZIF-8. Although the DFT-D3 with the

agreement with the experimental structure and also the

above results, BLYP-D2 and PBE-D2 methods are in excellent

rectangular unit cell with D3 correction is very important for the prediction of the experimental crystal structure of ZIFs with more accuracy.

2.2. Optimization of Different ILs@ZIF-8. A similar methodology is implemented for the investigation of composite materials containing ILs. We have selected the 1-butyl 3-methylimidazolium ([BMIM]+) cation with different hydrophilic (chloride [Cl]− and trifluoroacetate [CF3CO2]−) and hydrophobic (tetrafluoroborate [BF4]− and hexafluoro-

phosphate [PF6]−) anions. These ILs were impregnated within the cavity of ZIF-8 and optimization was carried out without fixing any atomic positions in the cell. These composites were studied using different approaches to analyze the structural changes happening to them.

2.2.1. Hydrophilic ILs@ZIF-8. The hydrophilic ILs chosen are [BMIM][Cl] and [BMIM][CF3CO2], and this is incorporated into the pores of ZIF-8 to make a composite material. After optimization, the lattice parameters and volume changes were noted for both the composites. The optimized crystal cell parameters, volume, and percentage of volume changes are given in Table 2 and Supporting Information Table S1. The percentage of change in volume is calculated with the reference to the experimental crystal structure. In the case of [BMIM][Cl], the BLYP method shows significant changes in the unit cell length values (a, b, and c) and the respective volume also enhances. The cell expansion values for BLYP and PBE methods are 8.9 and 5.7%, respectively. Here onward, the calculated PBE values are shown in parenthesis. When BLYP-D2 is used, the volume is very close to the experimental value and the change in volume is almost negligible, that is, around 0.1% (0.7%). BLYP-D3 is slightly overestimating the experimental crystal structure, and it predicts a volume change of ∼1.9% (1.9%). When BLYP-D3/TZVP is used, it predicts that the lattice parameters are slightly better than that in the BLYP-D3/TZVP method, which corresponds to a change of 1.7% (1.8%), but as mentioned earlier, it is a highly time-consuming process. Among these methods, BLYP-D2/TZVP shows close agreement with the experimental data and the bar diagram of the same is depicted in Figure 2. Table S1 gives all the optimized parameters for [BMIM][CF3CO2]. From the table, it is clear that both BLYP and PBE methods with D2 correction predict the accurate crystal structure, like in the case of [BMIM][Cl].

| ZIF-8b | a (Å) | b (Å) | c (Å) | volume (Å3) | volume change (%) |
|--------|-------|-------|-------|-------------|------------------|
| crystal Structure | 17.25 | 90 | 5135 | 4.69 |
| BLYP | 17.48 | 90 | 5345 | 8.96 |
| BLYP-D2 | 16.98 | 90 | 4891 | −0.28 |
| BLYP-D3 | 17.09 | 90 | 4993 | 1.78 |
| BLYP-D3c | 17.07 | 90 | 4970 | 1.33 |
| PBE | 17.31 | 90 | 5184 | 5.68 |
| PBE-D2 | 16.97 | 90 | 4889 | −0.33 |
| PBE-D3 | 17.12 | 90 | 5014 | 2.23 |
| PBE-D3c | 17.11 | 90 | 5012 | 2.18 |
| RPBE/6-31G | 17.25 | 90 | 5135 | 4.69 |

“DZVP basis set considered for Zn atom and TZVP for all other atoms in ZIF-8. Structures were optimized using the TZV2P basis set except for Zn (DZVP).

Figure 1. (a) Sodalite crystal structure of ZIF-8 cage. (b) The bar diagram represents the volume change in the percentage of ZIF-8 using different DFT methods with and without dispersion correction.

volume at BLYP and PBE methods are 8.9 and 5.7%, respectively. With the incorporation of dispersion correction in above methods, it shows very significant changes in the parameters. Thus, we have added D2 and D3 corrections in the optimization of the framework to study the structure and stability of the composite materials. It is interesting to note that the cell parameters obtained after the incorporation of D2 correction with above methods did not deviate significantly from the crystal structure (i.e., ∼0.3%). The same changes for BLYP-D3 and PBE-D3 corrections are 1.8 and 2.2%, respectively. This reveals that the inclusion of dispersion correction is very important for the prediction of the minimized crystal structure. In addition, the expansion of the basis set for the heteroatom (i.e., TZVP) with D3 dispersion correction further reduces the volume changes. Among the above results, BLYP-D2 and PBE-D2 methods are in excellent agreement with the experimental structure and also the selected basis set (TZVP) is more reliable for the prediction of the structure of ZIF-8. Although the DFT-D3 with the TZVP method is reliable, the computational cost is slightly higher. Thus, we have considered DFT-D2 with the TZVP method for the general discussion.

It is found from Figure 1 that combination of DFT with D2 is more precise predicting the crystal structure of ZIF-8 with a less computational cost. In addition, to validate our results, we have also studied the structural optimization at the Gaussian basis set method using the RPBE/6-31G level of theory. The comparison of cell parameters and corresponding volume changes is provided in Table 1. The calculated volume change obtained from this methods is ∼4.7% and the volume is slightly enhanced when compared to DFT-D calculations. This clearly reveals that the inclusion of dispersion correction is very important for the prediction of the experimental crystal structure of ZIFs with more accuracy.
percentages of volume changes correspond to 0.3 and 0.5, respectively. However, without dispersion correction, these two methods could not predict a reliable crystal structure. With D3 correction and DFT-D3/TZV2P, both the methods show volume changes of \(\sim\) 2%. From all the analyses discussed above, it is clear that for hydrophilic ILs@ZIF-8 complexes, GGA methods such as BLYP and PBE can closely predict the crystal parameters with Grimme’s D2 dispersion correction.

2.2.2. Hydrophobic ILs@ZIF-8.

For making hydrophobic IL-based composites, \([\text{BMIM}]\text{[BF}_4\text{]}\) and \([\text{BMIM}]\text{[PF}_6\text{]}\) were selected. The adsorption properties of hydrophobic ILs at hydrophobic cages are different due to their similar hydrophobicities.\(^6\) Above discussed methodologies are followed for the optimization of the hydrophobic ILs@ZIF-8 complexes, and the corresponding changes are noted. The unit cell parameters and volume changes are given in Table 3 and Supporting Information Table S2 for hydrophobic ILs.

Table 2. Comparison of Unit Cell Parameters and Volume Change of \([\text{BMIM}]\text{[Cl]}\)@ZIF-8 Using Various DFT Methods with and without Dispersion Correction

| \([\text{BMIM}]^+\text{[Cl]}^-\)@ZIF-8 | \(a = b = c\) (Å) | \(\alpha = \beta = \gamma\) (°) | volume (Å\(^3\)) | volume change (%) | adsorption energy \((E_{\text{ads}}, \text{kcal/mol})\) |
|-----------------------------------|------------------|-----------------|-----------------|-----------------|------------------|
| crystal structure                 | 16.99            | 90              | 4905            |                 |                  |
| BLYP                              | 17.48            | 90              | 5338            | 8.82            |                  |
| BLYP-D2                           | 16.99            | 90              | 4902            | -0.07           | -13.28           |
| BLYP-D3                           | 17.10            | 90              | 4999            | 1.90            | 129.33           |
| BLYP-D3\(^b\)                     | 17.09            | 90              | 4987            | 1.67            | 151.31           |
| PBE                               | 17.30            | 90              | 5179            | 5.59            |                  |
| PBE-D2                            | 16.95            | 90              | 4871            | -0.70           | -24.53           |
| PBE-D3                            | 17.10            | 90              | 5000            | 1.93            | -6.66            |
| PBE-D3\(^b\)                      | 17.09            | 90              | 4994            | 1.80            | 3.99             |
| RPBE/6-31G                        | 17.25            | 90              | 5130            | 4.57            | -13.15           |

\(^{a}\)DZVP basis set considered for Zn atom and TZVP for all other atoms in ZIF-8. \(^{b}\)Structures were optimized using the TZV2P basis set except for Zn and B (DZVP).

Table 3. Comparison of Unit Cell Parameters and Volume Change of \([\text{BMIM}]\text{[BF}_4\text{]}\)@ZIF-8 Using Various DFT Methods with and without Dispersion Correction

| \([\text{BMIM}]^+\text{[BF}_4^-\)@ZIF-8 | \(a = b = c\) (Å) | \(\alpha = \beta = \gamma\) (°) | volume (Å\(^3\)) | volume change (%) | adsorption energy \((E_{\text{ads}}, \text{kcal/mol})\) |
|----------------------------------------|------------------|-----------------|-----------------|-----------------|------------------|
| crystal structure                      | 16.99            | 90              | 4905            |                 |                  |
| BLYP                                  | 17.49            | 90              | 5351            | 9.08            |                  |
| BLYP-D2                               | 16.98            | 90              | 4895            | -0.21           | -21.11           |
| BLYP-D3                               | 17.09            | 90              | 4994            | 1.82            | 133.21           |
| BLYP-D3\(^b\)                         | 17.09            | 90              | 4994            | 1.81            | 134.84           |
| PBE                                   | 17.30            | 90              | 5179            | 5.59            |                  |
| PBE-D2                                | 16.96            | 90              | 4874            | -0.64           | -27.18           |
| PBE-D3                                | 17.10            | 90              | 5002            | 1.96            | -9.90            |
| PBE-D3\(^b\)                          | 17.08            | 90              | 4987            | 1.66            | 21.55            |
| RPBE/6-31G                            | 17.24            | 90              | 5127            | 4.51            | -19.54           |

\(^{a}\)DZVP basis set considered for Zn atom and TZVP for all other atoms in ZIF-8. \(^{b}\)Structures were optimized using the TZV2P basis set except for Zn and B (DZVP).

Figure 2. The bar diagram represents the volume change in the percentage of hydrophilic \([\text{BMIM}]\text{[Cl]}\) and hydrophobic \([\text{BMIM}]\text{[BF}_4\text{]}\)@ZIF-8 with different methods.
However, in the present study, with impregnated ZIFs. They found that PBE-D3 correction is good for the ZIF results. The earlier report reveals that dispersion correction is highly varied depending on the selection of dispersion correction and basis sets for the complexes. The comparison of $E_{ads}$ obtained from Gaussian basis with the hybrid basis set formalism approach shows that DFT-D2 correction is more reliable than the DFT-D3/TZVP method. Thus, here onward, we considered $E_{ads}$ obtained from the DFT-D2 method for further discussions. From close analysis, it can be found that DFT with the D2 dispersion approach is very good for the prediction of the structure and energetics of the composite materials. The $E_{ads}$ is in direct relation with the geometrical arrangement of ion pairs of IL at the pores of the ZIF-8 structure. Also, some of the ions are directly adsorbed on the surface of ZIFs. To analyze the microscopic adsorption mechanism of ILs at nanopores, the optimized geometries of all the hydrophilic and hydrophobic IL@ZIF-8 complexes using DFT-D2 are given in Figure 3 and the same geometries for DFT-D3 are given in Supporting Information Figure S1.

Figure 3 shows the adsorption of the IL ion pair in the cavity of ZIF-8 along with the important distances (in Å). The optimized geometries show that the ion pair distances varied depending on the anionic part. For example, [BMIM][Cl]@ZIF-8 shows a stronger hydrogen bond (i.e., $\sim$2.0 Å) in all DFT methods. Also, the anionic part of IL is localized in the cavity with a distance of $\sim$4.21 Å. It is found from the calculations that $E_{ads}$ for [BMIM][Cl]@ZIF-8 predicted by the PBE-D2 method is significantly higher when compared to other methods. This is due to the interaction of the $-\text{CH}_3$ group with the ZIF-8 surface and this leads to enhancement of the binding strength (i.e., $E_{ads}$). The adsorption energies obtained from BLYP-D2 and PBE-D2 are $-13.28$ and $-24.53$ kcal/mol, respectively. The same $E_{ads}$ obtained from the RPBE/6-31G method is $-13.15$ kcal/mol. It is interesting to note that BLYP-D2 is close to the energies obtained from the TZVP basis set show expansion of around $\sim$1.9%. The same values obtained from the DFT-D3/TZVP basis set are close to the TZVP basis set. It is also represented in Figure 2, which shows that DFT-D2 can accurately predict the rigid crystal structure of ZIF-8, after the incorporation of ILs. Similarly, another hydrophobic IL, [BMIM][PF$_6$] was also analyzed using various DFT methods. Its optimized parameters are given in Table S2. Here, also we observed a similar trend in the unit cell parameters with the incorporation of dispersion correction.

Close scrutiny of the above parameters confirms that D2 dispersion-corrected DFT methods are well suited for the prediction of composite materials. In particular, DFT-D2/TZVP predicts the best suitable results, which mimics the experimental crystal structure and already available simulation results. The earlier report reveals that dispersion correction is very important to study the relative stability of Zn and LiB ZIFs. They found that PBE-D3 correction is good for the ZIF structure. However, in the present study, with impregnated ILs inside the 3D pores of the ZIF-8 structure, the experimental values are in good agreement with the DFT-D2 (BLYP and PBE) method. This is the first report on the effect of the involvement of dispersion correction in the structure of the composite material. In the present study, we also optimized the composite structure with the RPBE method and Gaussian basis set approach. The average values of cell parameters and respective volume changes for the composites are mentioned in corresponding tables (Table 2 and 3 and Tables S1 and S2). The calculated unit cell parameters obtained from the RPBE method are varied from the experimental crystal structure ($\sim$4.5%). Meanwhile, the structure prediction from hybrid basis set formalism (i.e., mixing of Gaussian and plane-wave basis (GPW)) is working well for the host–guest interaction between ZIF-8 and ILs. The calculated parameters are in good accordance with earlier reports.

2.3. Geometries and Energetics of ILs@ZIF-8. To validate the adsorption energies ($E_{ads}$) obtained from hybrid formalism, we calculated the same using the Gaussian basis set approach. The $E_{ads}$ values of all the hydrophilic/hydrophobic IL complexes are provided in the respective tables (Table 2 and 3 and Tables S1 and S2). Since the geometry obtained from DFT-D2 and DFT-D3 methods is in excellent agreement with the experimental crystal structure, only their energetics is discussed in this section. The $E_{ads}$ obtained from BLYP-D3 shows more repulsion when compared to the other methods. However, all other methods are predicting an attractive interaction between ZIF-8 and ILs. The calculated $E_{ads}$ is in good agreement with the experimental crystal structure, only their energetics is discussed in this section. The $E_{ads}$ obtained from BLYP-D3/TZVP basis set is working well for the host–guest interaction between ZIF-8 and ILs. The optimized parameters are given in Tables S1 and S2. Here, also we observed a similar trend in the unit cell parameters with the incorporation of dispersion correction.
RPBE method with 6-31G basis. A less $E_{ads}$ ($\sim -13$ kcal/mol) is observed when the butyl group is interacting with the surfaces instead of the $\text{−CH}_3$ group. A similar kind of observation is also found in the host−guest encapsulation of drug molecules in the $p$-sulfonatocalix[4]arene derivatives$^{64}$ In the case of the [$\text{CF}_3\text{CO}_2$]$^-$ anion, the BLYP-D2 method predicts higher $E_{ads}$ (i.e., $-30.37$ kcal/mol) compared to other methods. Also, the stability of the complex is significantly higher due to the stronger interaction of the $\text{−CF}_3$ group in the anion with the ZIF surface. The energies obtained from PBE-D2 and RPBE/6-31G are $-26.17$ and $-20.33$ kcal/mol, respectively. The $E_{ads}$ obtained from the PBE method is very close to Gaussian basis when compared with the BLYP method. Due to the unreliable energies obtained at the DFT methods without dispersion, we have excluded those $E_{ads}$ from the discussions.

In the case of hydrophobic ILs, the calculated $E_{ads}$ by DFT-D ranges from $-21$ to $-52$ kcal/mol. Their optimized geometries at the DFT-D2 level are given in Figure 3. Even though these two anions are strongly adsorbed on the cavity of

Figure 4. IR spectra of the hydrophilic IL@ZIF-8 complexes along with spectra of ZIF-8 and ILs.
ZIF-8, it is interesting to note that the $[\text{PF}_6]^{-}$ anion is strongly adsorbed than the $[\text{BF}_4]^{-}$ anion. PBE-D2 and BLYP-D2 methods predict stronger adsorption for $[\text{BMIM}][\text{BF}_4]$ and $[\text{BMIM}][\text{PF}_6]$, respectively. The $E_{\text{ads}}$ values of $[\text{BMIM}][\text{BF}_4]$ @ZIF-8 at BLYP-D2 and PBE-D2 methods are $-21.11$ and $-27.18$ kcal/mol, respectively. The same values obtained for the $[\text{PF}_6]^{-}$ anion are $-52.72$ and $-35.49$ kcal/mol, respectively. $[\text{BMIM}][\text{PF}_6]$@ZIF-8 has higher adsorption compared to other complexes. This arises from the stronger binding of the fluorinated anion with the metal centers of the ZIF-8 framework. The calculated trends in $E_{\text{ads}}$ are varied depending on the selection of a suitable method and basis set with the dispersion correction term. Here, we limited our discussions to DFT-D2 energies. The order of adsorption strength of ILs@ZIF-8 using the BLYP-D2 method is $[\text{BMIM}][\text{PF}_6] > [\text{BMIM}][\text{CF}_3\text{CO}_2] > [\text{BMIM}][\text{BF}_4] > [\text{BMIM}][\text{Cl}]$, whereas the PBE-D2 method predicts slightly different. The order of strength at the PBE-D2 method is $[\text{BMIM}][\text{PF}_6] > [\text{BMIM}][\text{BF}_4] \sim [\text{BMIM}][\text{CF}_3\text{CO}_2] > [\text{BMIM}][\text{Cl}]$. The order of $E_{\text{ads}}$ obtained from RPBE/6-31G Gaussian basis is well matching with that of the hybrid formalism. The optimized geometries of all ILs@ZIF-8 composites using RPBE/6-31G are given in Supporting Information Figure S2. All three methods predicted the similar trend in the stability of the complexes, interfacial interactions, and charge density.

Figure 5. IR spectra of the hydrophobic IL@ZIF-8 complexes along with spectra of ZIF-8 and ILs.
This confirms the selection of suitable functional for the bulk phase optimization of the ILs@ZIF-8 structure. Since Gaussian basis calculations require more computational power, we have limited the optimization at the RPBE/6-31G level of theory. Also, our results suggest that hybrid formalism is more reliable for the bulk composite materials and predicts the interfacial interactions between ILs and the ZIF-8 structure. In addition, these methods are helpful to analyze the structural flexibility of the ZIF-8 structures. Even though there are previous discussions on the stability of ZIF-8 with different DFT-D methods, this is the first report on the discussion of IL@ZIF-8 complexes for the selection of more reliable DFT-D methods in comparison with the Gaussian basis approach. Through the selection of appropriate DFT methods for IL@ZIF-8 complexes, we can explore the wide range of applications of these complexes in the fields of catalysis, gas storage and separation, ionic conductivity, etc.

2.4. Vibrational Spectral Analysis of IL@ZIF-8 Complexes. The effect of adsorption of ILs on ZIF-8 nanostructures can be studied from the vibrational analysis of the complexes. The calculated IR spectra of the ILs@ZIF-8 complexes and pure components are provided in Figures 4 and 5. The description of respective vibrational frequencies and shift values along with the experimental data is given in Supporting Information Table S3. The important shifts are denoted using blue and red color triangles in Figures 4 and 5. It is found that there is a significant shift in vibrational frequencies of ILs after incorporation into ZIF-8. Depending on the nature of interaction and charge transfer, it may shift toward either a higher frequency (blue shift) or lower frequency (red shift) region. These shifts help to identify the specific interactions and strength of IL@ZIF-8 complexes. All the vibrational frequencies for ZIF-8 and IL@ZIF-8 are calculated at the PBE-D2/TZVP method. The PBE/6-311G* method is used for the IL ion pairs. All the spectra were visualized and analyzed by using the Molden software program.65,66 Figure 4 shows three broad bands (above ν 1600 cm−1) for the ZIF-8 structure and, in these, two peaks were assigned for the symmetric (singlet, νas 2933–2962 cm−1) and asymmetric stretching (singlet, νas 3005–3067 cm−1) of the CH3 group in imidazolium. The third peak was assigned for the asymmetric (νas 3187–3198 cm−1) and asymmetric (νas 3166–3175 cm−1) C–H stretching of C3 and C4 carbons in the imidazolium linker. Furthermore, below 1600 cm−1, three broad bands are observed. They are in-plane C–H bending of C3 and C4 carbons (δ 1084–1165 cm−1), CH3 deformation bending (δ 1366–1475 cm−1), and carbon–carbon double bond stretching between C3 and C4 (ν 1484–1499 cm−1). It is important to note that calculated IR frequencies are in very close agreement with the experimental values of [BMIM][PF6]@ZIF-864 and [BMIM][CF3CO2].65 Our calculations prove that the selected DFT (PBE-D2/TZVP) methodology can predict the properties of composite materials and these results are comparable with the experiment.

In hydrophilic [BMIM][Cl]@ZIF-8, the ion pair interaction in IL (i.e., C2−H...Cl) is slightly weakened after complexation with the ZIF-8 structure. This is observed through blue shifted (~20 cm−1) values of C2−H stretching (~2475 cm−1). At the same time, the [Cl]− anion is strongly H-bonded with the butyl group and the respective red shift is ~126 cm−1. While in the [BMIM][CF3CO2]@ZIF-8 complex, the C2−H stretching is red shifted (~306 cm−1). This proves the enhancement of H-bond (~1.8 Å) strength between the anion and imidazolium ring of the cation in [BMIM][CF3CO2] while incorporating with ZIF-8. This is absent in the case of [BMIM][Cl]@ZIF-8. After incorporation of the [CF3CO2]2− anion, the OCO vibration modes show blue shifts (~18 and 26 cm−1). This indicates the weakening of the C–O bond, which attributes to an electron sharing of the anion between the surface and cation. This leads to direct interaction of the anion with the surface, which contributes to the higher charge transfer observed for this complex (Section 2.5). The observed electrostatic behavior can enhance the binding strength of the IL@ZIF-8. The interaction of [BMIM][Cl] with the ZIF-8 surface is very weak, which corresponds to a low red shift range of 2−4 cm−1 in ring C–H stretching. However, in the [BMIM][CF3CO2]@ZIF-8 complex, the red shift range is 8−10 cm−1. This is good accordance with the calculated Eads values.

In the case of hydrophobic ILs, the ion pair interaction strength is enhanced and the corresponding red shift ranges from 34 to 107 cm−1. This concludes that ion pair interactions are strengthened at the confined environment except for the [Cl]− anion. It is important to note that the C3−H and C4−H symmetric (νs) and asymmetric (νas) vibrational stretching bands are red shifted (~24 cm−1) and the respective peaks are observed at 3228 and 3209 cm−1. The hydrophilic anions ([PF6]− and [BF4]−) directly interact with the surface, and the respective interaction modes are shown in Figure 5. These values are well matching with the available experimental results.28,34 Furthermore, the C–H stretching of the ZIF-8 structure in the complex shows red shift from 2 to 8 cm−1 in both the hydrophobic ILs. This clearly reveals that there is an interaction between ILs and the ZIF-8 structure. Particularly, fluorinated ILs are strongly interacting with the ZIF-8 framework when compared with the nonfluorinated IL (i.e., [BMIM][Cl]). These red shifted values are in good accordance with the calculated Eads values.

2.5. Charge-Transfer Analysis. The adsorption mechanism of ILs at nanoporous materials and stability of the complexes depend on the involvement of charged species. Here, we have computed charge density and partial atomic charges to quantify the charge-transfer ability of the composite materials. For this analysis, we used optimized geometries from hybrid formalism. The Löwdin population scheme has been used to study the charge-transfer analysis between ILs and the surface. The charge density difference Δρ for the different IL@ZIF-8 interfaces can be quantified from the following eq 1.

\[
\Delta \rho = \rho_{\text{ILs@ZIF-8}} - \rho_{\text{ILs}} - \rho_{\text{ZIF-8}}
\]

Where \( \rho_{\text{ILs@ZIF-8}} \) is the total charge density of the complex and \( \rho_{\text{ILs}} \) and \( \rho_{\text{ZIF-8}} \) are the charge densities of ILs and ZIF-8.

| IL@ZIF-8 | [BMIM][Cl]@ZIF-8 | [BMIM][CF3CO2]@ZIF-8 | [BMIM][BF4]@ZIF-8 | [BMIM][PF6]@ZIF-8 |
|---------|-----------------|----------------------|------------------|------------------|
| ZIF-8   | −0.041          | 0.041                | −0.271           | 0.271            |
| ZIF-8   | 0.041           | −0.271               | 0.101            | 0.101            |
| ZIF-8   | −0.246          | 0.246                | −0.246           | 0.246            |

Table 4. Löwdin Population Analysis for ILs@ZIF-8 by Using the PBE-D2 Method with the DZVP for Zinc and TZVP for Other Atoms
units, respectively. The computed charges are given in Table 4, and charge density pictures of all the ILs@ZIF-8 are shown in Figure 6. This charge analysis clearly shows that there is a significant charge transfer between the fluorinated ILs into the ZIF-8 surface when compared to nonfluorinated IL (i.e., [BMIM][Cl]). These results are in good accordance with the calculated $E_{\text{ads}}$, which is discussed in the previous section. The net charge of hydrophilic [BMIM][Cl] is +0.04 a.u. and of ZIF-8 is −0.04 a.u. The less charge transfer observed for this complex can be correlated with the blue shifts observed in the IR spectra. The respective charges for [BMIM][CF$_3$CO$_2$]@ZIF-8 complex are +0.27 a.u. and −0.27 a.u. The large charge transfer shows a strong interaction between the anion and framework, which is responsible for the large red shift observed in the IR band. Similarly, hydrophobic ILs also showed a significant difference in the charges of the IL and ZIF-8 framework (Table 4). The order of magnitude of charge transfer in the composite different anion is [CF$_3$CO$_2$]$^-$ > [PF$_6$]$^-$ > [BF$_4$]$^-$ > [Cl]$^-$. This confirms that the involvement of fluorine atoms in the anion plays a vital role in the stability of the composite materials and more fluorinated composite, [BMIM][PF$_6$]@ZIF-8, is showing better composite stability in accordance to both $E_{\text{ads}}$ and charge transfer. The magnitude order is also closely matching with the vibrational redshift values of ion pair interaction at the confined state.

Furthermore, we have calculated the total electron density and charge density for confirming the interfacial interaction between the confined ILs and ZIF-8 structure, which is given in Figure 6. It can be seen from the total electron density plots that there is no contour density between the ILs and ZIF-8. This clearly indicates that there are only weakly bonded interactions (i.e., dispersive and vdWs) between ILs and the ZIF-8 cage. To understand the charge accumulation and depletion mechanisms, we plotted the charge density difference at this interface. These plots show the charge depletion and accumulation on the anionic part of the IL and ZIF-8, respectively. These plots well correlate with the calculated atomic charges of the complexes. In the case of [BMIM][Cl]@ZIF-8, electron density
accumulates in the IL but not in the ZIF-8. From this, we confirmed the long-range dispersive kind of interaction, which favors the negligible charge transfer in nonfluorinated ILs. While in fluorinated ILs, the charge density is mostly localized on the ZIF-8 surface and a very less dispersion in the anions. The charge-transfer pathway is identified to be from the C2 carbon of imidazole through the anionic part to the ZIF-8 framework. From this analysis, we found that there is a significant charge transfer in fluorinated IL complexes. Thus, we confirmed that the imidazolium-based fluorinated anionic ILs are more suitable for making the composite materials with ZIF-8.

3. CONCLUSIONS

In this study, we have analyzed and compared different DFT methods with and without dispersion correction for the understanding of structural stability of various ILs at ZIF-8 nanopores. It is found from the calculations that both the BLYP and PBE methods with the incorporation of D2 correction in hybrid formalism approaches are more reliably predicting the structure, stability, IR spectra, and charge-transfer process at this interface. These interfacial interactions were also validated by the Gaussian basis approach. Furthermore, the microscopic analysis of geometries reveals that ILs are highly dispersed and stabilized at the nanopores of ZIF-8, particularly the ZIF-8 structure is highly preferable for the hydrophobic ILs. The similar hydrophobicities of ILs and ZIF-8 (like-like pair) lead to the development of better composites as compared to the hydrophilic ILs. It is interesting to note that the involvement of fluorine atom-containing anions (i.e., $\text{CF}_3\text{CO}_2^-$, $\text{BF}_4^-$, and $\text{PF}_6^-$ moieties) plays a significant role in the charge transfer and stability of the complexes. Vibrational analysis reveals that there is a significant shift in frequencies for all the complexes except $\text{[BMIM][Cl]}@\text{ZIF-8}$. The larger red shift value indicates that there is strong adsorption between fluorinated ILs and ZIF-8. These significant findings are well supported by the charge density plots of composite materials. The predicted methodology is helpful to identify suitable DFT methods for the investigation of IL-based composite materials for various applications such as catalysis, carbon capture, and separation.

4. COMPUTATIONAL DETAILS

The cell optimization of the ZIF-8 structure was done using the Quickstep package in CP2K version 5.1. Cell optimization was carried out to optimize both cell vectors

For all the atoms, we considered the triple-zeta basis set (TZVP-MOLOPT-SR-GTH) and double-zeta basis set (DZVP-MOLOPT-GTH) for B and Zn. For all calculations, we used an auxiliary plane wave cutoff of 450 Ry. Vibrational frequencies of all the complexes were obtained from the PBE-D2/TZVP method in the CP2K code.

To validate the structure and stability of the complexes, we did additional quantum calculation with the periodic boundary condition (PBC) module, which is implemented in the Gaussian 16 package. This is the first report on the free optimization of IL@ZIF-8 complexes with the PBC method. Free optimization refers that there are no atoms fixed during the optimization of complexes. Here, also we can compare the changes in the unit cell parameters. This will provide the structural flexibility and expansion of the pore volume. All geometries and $E_{\text{ads}}$ are obtained from the RPBE/6-31G level of theory. RPBE is a revised version of the PBE method, which does not involve fitting of parameters. Adsorption energies ($E_{\text{ads}}$) of all the composites are calculated using the following equation:

$$E_{\text{ads}} = E_{\text{composite}} - (E_{\text{ZIF-8}} + E_{\text{ILs}})$$

Here, $E_{\text{composite}}$ represents the total energy of the composite material and $E_{\text{ZIF-8}}$ and $E_{\text{ILs}}$ represent the total energies of the ZIF-8 and ILs, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03759.

Additional optimized geometries of various ILs@ZIF-8, using BLYP-D3, PBE-D3, and RPBE/6-31G methods; comparison of unit cell parameters, volume change, and $E_{\text{ads}}$ of $\text{[BMIM][CF}_3\text{CO}_2^-$@ZIF-8 and $\text{[BMIM][PF}_6^-$@ZIF-8 complexes; vibrational frequency table for all the complexes (PDF)

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Notes

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