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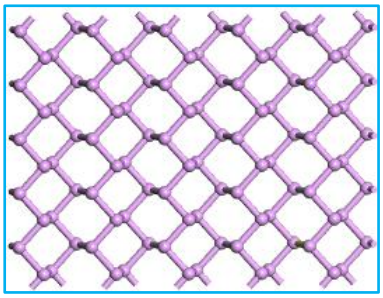
A first-principles study of the mechanism for the ionic liquid s-exfoliation of black phosphorus

Wenbo Huai, Aiping Fu*,Hao Li, Fengna Guo, Yue Yu, Zonghua Wang

Collaborative Innovation Center for Marine Biomass Fiber, Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, China

Abstract: **Ionic liquids (ILs) play an important role in the exfoliation of two-dimensional(2D) materials. In this study, first-principles calculations have been performed to investigate the mechanism for the dispersion of black phosphorus (BP) by imidazolium-based ILs. The adsorption parameters of different ILs on single-layer phosphorene, such as the magnitude of the interaction energy and charge transfer between phosphorene and ILs, were used to analyze the efficiency of ILs in the BP- exfoliation process. The adsorption energies (ranging from -0.670 eV to -1.299 eV) and the charge transfer number (ranging from -0.003e to -0.110e) demonstrate that the physisorption of the ILs on the BP, and the obtained phosphorene through ILs-exfoliation of BP can maintain its electronic properties because the weak van der Waals interaction dominates between the ILs and surface.**



Keywords: Adsorption; First-principles calculations;Ionic liquids(ILs); Black phosphorus(BP)

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*Corresponding Author:Aiping Fu, apfu@qdu.edu.cn

1. Introduction

Because of the unique electrical and optical properties, two-dimensional (2D) materials quickly became the new-star in the field of materials science in recent years[1-4]. Since in 2004, Konstantin Novoselov, Andre Geim and co-workers used a simple mechanical exfoliation technique to obtain the freestanding single layer graphene[5], many other attractive 2D monolayer or few-layer materials such as layered transition metal dichalcogenides (MoS_2,$MoSe_2$, $MoTe_2$, WS_2, WTe_2)[6], boron-nitride(BN)[7] nanosheets and silicene[8-10] have been isolated successfully by mechanical exfoliation from their 2D crystals. With many promising applications in exfoliation or dispersion the 2D materials, the ionic liquids are stripped to these stuffs for a relatively new and exciting area.

Recently, a new 2D semiconducting material (black phosphorus) has been isolated successfully by mechanical exfoliation from black phosphorus crystals[11,12]. Black phosphorus is a layered material that is clustered together through a van der Waals interaction among the single atomic layers. Within a single layer, each phosphorus atom is covalently bonded to three adjacent phosphorus atoms to form a pleated honeycomb structure[13-16]. As a new type of two-dimensional semiconductor material, it draws widespread attention in various fields since it has significant potential applications in electronic thin films and infrared photoelectrons. There are many ways to peel off and disperse black phosphorus. Very recently, Zhao[17] have reported that the ionic liquids could be used as the green liquid for the large-scale, highly efficient exfoliation of black phosphorus. As the ionic liquids have its unique physical and chemical properties, it possesses many practical applications. If it is suitable for the exfoliation of the layer materials, what is the mechanism for this process and how to understand the efficiency of different ILs in dispersion the materials? Shakourian-Fard[18] have investigated the ILs adsorption on the graphene surface using the density functional theory (DFT) at the M06-2X/cc-pVDZ level. They have proposed that the process of adsorption is dominated by the non-covalent weak interactions between ILs and the graphene surface. Ghatee[19] have also studied the physisorption of hydrophobic and hydrophilic ionic liquids on the graphene and analyzed the effect of the properties of ILs on the adsorption parameters. Very recently, Garcia[20] reported the in silico rational design of ionic liquids for the exfoliation and dispersion of boron nitride nanosheets. DFT simulations have provided a detailed picture of the interaction mechanism and useful structure-property relationships in the search of a new ionic liquid for BN exfoliation. This work, because the black phosphorus can be successfully exfoliated by the ionic liquids, we think to investigate the dispersion mechanism during this process at the molecular level following previous literatures. Quantum mechanical calculations have been performed to investigate the interaction nature between ILs and BP, where the single layer phosphorene is used to model the BP surface, and the ILs are composed of 1-butyl-3-methylimidazolium $[BMIM]^+$, 1-ethyl-3-methylimidazolium $[EMIM]^+$, 1-hexyl-3-methylimidazolium $[HMIM]^+$, 1-octyl-3-methylimidazolium $[OMIM]^+$ and 1-hydroxyethyl-3-methylimidazolium $[HOEMIM]^+$ cations paired to tetrafluoroborate $[BF_4]^-$, bis ((trifluoromethyl)sulfonyl)-imide $[Tf_2N]^-$ and

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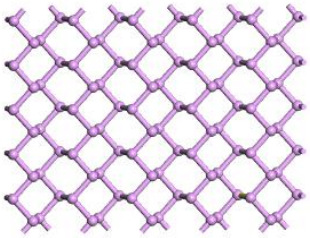
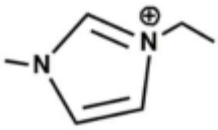
trifluoromethansulfonate $[TfO]^-$ anions (Figure 1).

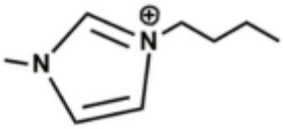


Black Phosphorus(BP)-top view

Black Phosphorus(BP)-side view



$[EMIM]^+$



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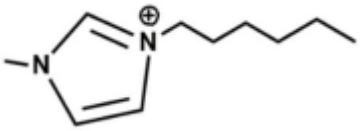

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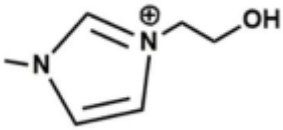
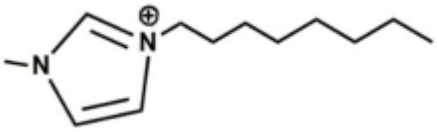
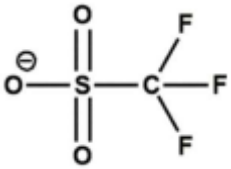


$[HOEMIM]^+$

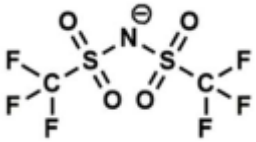


$[OMIM]^+$

$[BF_4]^-$



$[TFO]^-$



$[TF_2N]^-$

Figure 1.Structures of Black phosphorus(BP), cations and anions for various IL combinations studied in this work

2. Computational details

The first-principles calculations are based on the density functional theory (DFT) implemented in the DMol3 code in Material Studio[21,22]. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)[23,24] and the double-numerical-quality basis set with polarization functions (DNP) [25] was adopted. Because the weak interactions are not well described by the standard PBE functional, the DFT-D (D stands for dispersion) approach within the Grimme scheme was employed for the vdW corrections[26]. The k-point was set to 5×5×1 for the structural optimizations and the electronic properties calculations. Initial structure of phosphorene used in our simulation is obtained from black phosphorus. Our calculated lattice constants for bulk black phosphorus are a = 3.31 Å, b =4.38 Å, and c=10.5 Å, in good agreement with experimental values and other theoretical calculations. To study the adsorption of ILs on the single-layer phosphorene, we adopt a 5×5×1 super cell containing 100 P atoms. A large vacuum of 20 Å was used to prevent the interaction and artificial dipole moment effects from neighboring cells in the direction normal to the BP surface. The plane-averaged electron density and electron density difference were calculated using CASTEP code[27] with a plane-wave kinetic energy cutoff of 330 eV.

The adsorption energy Eads is calculated as following:

$$E_a=E_{BP\text{-}IL}-(E_{BP}+E_{IL}) \quad (1)$$

where EBP-IL, EBP and EIL are the energies of the composite, the free-standing Black phosphorus (BP), the ionic liquids (IL) and the BP-IL complexes respectively.

3. Results and discussion

3.1 Structures and energetics of ionic liquids adsorpted on the BP

The most stable geometries, together with the shortest distances between various ILs and the BP surface are illustrated in Figure 2. The distances are 3.87 Å, 3.74 Å, 3.51 Å, 3.84 Å, 3.85 Å, 3.69 Å, 3.71 Å, 3.57 Å, 3.90 Å and 3.85 Å for $[BMIM][BF_4]$, $[BMIM][TF_2N]$, [BMIM][TFO], $[EMIM][BF_4]$,

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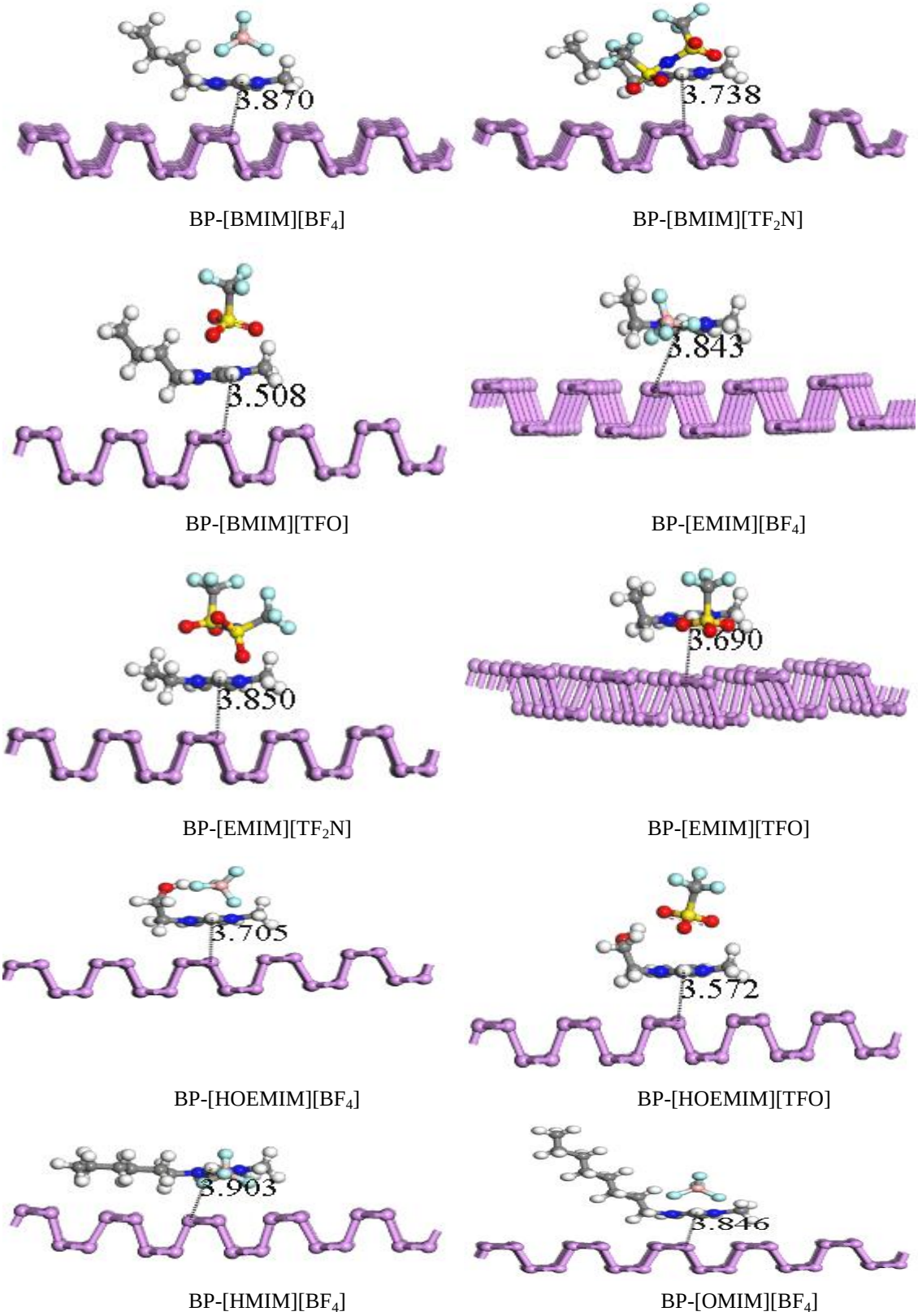
[EMIM][TF_2N], [EMIM][TFO], [HOEMIM][BF_4], [HOEMIM][TFO], [HMIM][BF_4] and [OMIM][BF_4] adsorbed on the surface. The large distance (3.5-3.90 Å) suggests the weak interaction force between the ILs and surface. Moreover, the imidazolium rings of the [BMIM], [HOEMIM], [EMIM], [HMIM] and [OMIM] are paralleled to the BP surface, and the [BF_4], [TFO] and [TF_2N] anions interact with the cations or the surface by three fluoride atoms or the sulfur atoms.



BP-[BMIM][BF_4] BP-[BMIM][TF_2N]

BP-[BMIM][TFO] BP-[EMIM][BF_4]

BP-[EMIM][TF_2N] BP-[EMIM][TFO]

BP-[HOEMIM][BF_4] BP-[HOEMIM][TFO]

BP-[HMIM][BF_4] BP-[OMIM][BF_4]

Figure 2.Most stable geometries of ionic liquids adsorption on BP.

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The stability of BP⋯IL complexes can be evaluated by comparing the adsorption energies (Ea) of various ionic liquids on the surface. Table 1 presented the adsorption energies (Ea), shortest IL- BP distance (D) and Mulliken charge transfer values (Q) for the most stable configurations of IL on BP. As seen from the table, the Eas based on [BMIM], [HOEMIM], [EMIM], [HMIM] and [OMIM] cations follow the order : BP-[HMIM][BF_4] (-1.299eV) > BP-[BMIM][TF_2N] (-1.124eV) > BP-[EMIM][TFO] (-1.088eV) > BP-[BMIM][BF_4] (-0.835eV) > BP-[BMIM][TFO] (-0.803eV) >BP-[EMIM][TF_2N] (-0.720eV) > BP-[OMIM][BF_4] (-0.684eV) > BP-[HOEMIM][BF_4] (-0.679eV) > BP-[EMIM][BF_4] (-0.675eV) > BP-[HOEMIM][TFO] (-0.670eV), respectively. This order indicates that the cation and anion type, the arrangement of the cation and anion in ILs, and the adsorption behavior of ILs on the surface could be the most important factors influencing the adsorption energy values.

Table1. Adsorption energy(Ea), shortest IL-BP atom distance(D) and Mulliken charge (Q) for the most stable configurations of IL on BP. Q is defined as the total Mulliken charge on the substrates and a negative number means charge transfer from IL to BP

Model	Ea(eV)	d(Å)	Q(e)
[BMIM][BF_4]	-2.147	\	\
[BMIM][TF_2N]	-1.938	\	\
[BMIM][TFO]	-2.096	\	\
[EMIM][BF_4]	-2.267	\	\
[EMIM][TF_2N]	-2.033	\	\
[EMIM][TFO]	-2.154	\	\
[HOEMIM][BF_4]	-2.366	\	\
[HOEMIM][TFO]	-2.407	\	\
[HMIM][BF_4]	-2.312	\	\
[OMIM][BF_4]	-2.341	\	\
BP-[BMIM][BF_4]	-0.835	3.87	-0.011
BP-[BMIM][TF_2N]	-1.124	3.74	-0.050
BP-[BMIM][TFO]	-0.803	3.51	-0.048
BP-[EMIM][BF_4]	-0.675	3.84	-0.074
BP-[EMIM][TF_2N]	-0.720	3.85	-0.007
BP-[EMIM][TFO]	-1.088	3.69	-0.092
BP-[HOEMIM][BF_4]	-0.679	3.71	-0.003
BP-[HOEMIM][TFO]	-0.670	3.57	-0.013
BP-[HMIM][BF_4]	-1.299	3.90	-0.110
BP-[OMIM][BF_4]	-0.684	3.85	-0.005

3.2. Valence Band maximum (VBM), conduction band minimum (CBM) and density of states (DOS)

We calculated the valence band maximum (VBM), conduction band minimum (CBM) of the ionic liquids, BP-IL respectively. And the energy gap was defined as VBM-CBM. The VBM, CBM, VBM-CBM energy gaps of IL, BP, BP-IL complexes are shown in Table 2. As shown in the table, the VBM-CBM energy gaps of different ionic liquids fall between 3.15 and 4.80 eV. The energy gaps of BP-IL complexes change from 0.57 to 0.59 eV. Then it can be seen that the energy gaps decrease when the ionic liquids adsorbed on the BP surface.

Table 2. Valence band maximum (VBM in a.u), conduction band minimum (CBM in a.u), and VBM-CBM energy gap (△E in eV) of BP, IL and BP⋯IL Complexes

structure	VBM	CBM	∆ E
BP	-0.1819	-0.1606	0.58
[BMIM][BF_4]	-0.2443	-0.0784	4.51
[BMIM][TF_2N]	-0.2409	-0.0913	4.07

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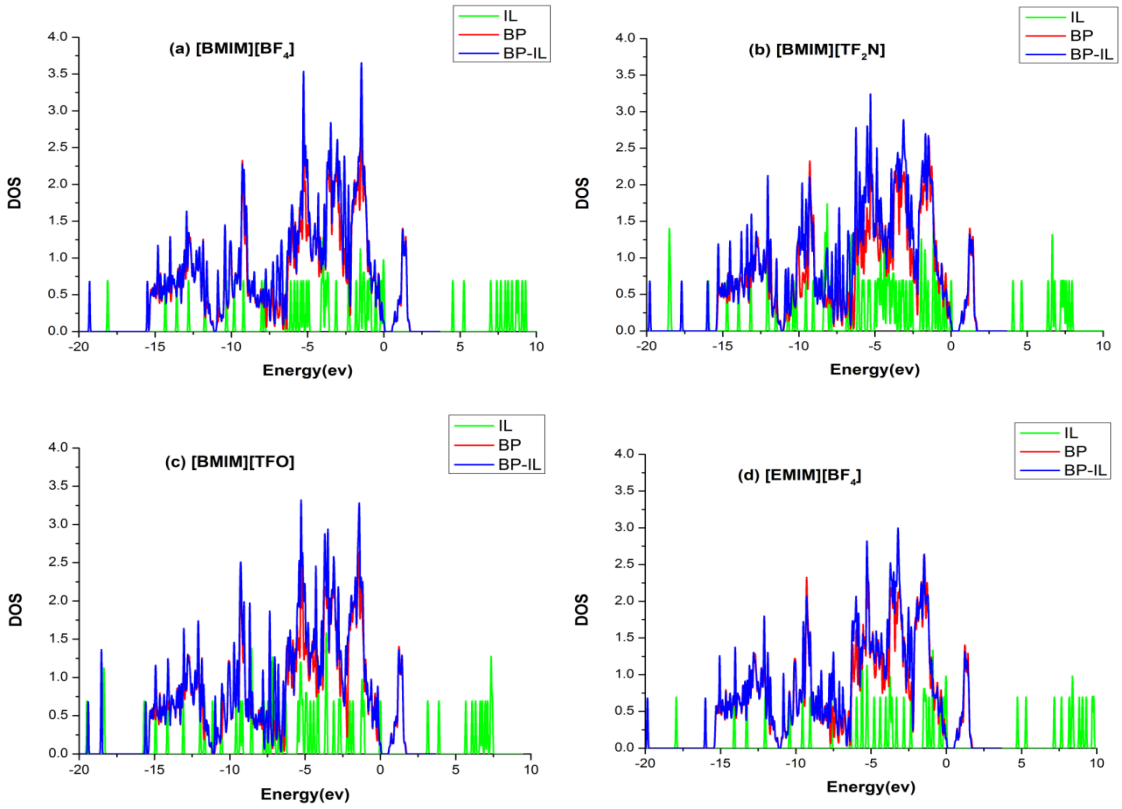
[BMIM][TFO]	-0.1953	-0.0796	3.15
[EMIM][BF_4]	-0.2510	-0.0773	4.73
[EMIM][TF_2N]	-0.2333	-0.0828	4.10
[EMIM][TFO]	-0.2023	-0.0795	3.34
[HOEMIM][BF_4]	-0.2329	-0.0855	4.01
[HOEMIM][TFO]	-0.2113	-0.0807	3.55
[HMIM][BF_4]	-0.2522	-0.0765	4.78
[OMIM][BF_4]	-0.2533	-0.0768	4.80
BP-[BMIM][BF_4]	-0.1898	-0.1682	0.59
BP-[BMIM][TF_2N]	-0.1831	-0.1620	0.57
BP-[BMIM][TFO]	-0.1889	-0.1675	0.58
BP-[EMIM][BF_4]	-0.1816	-0.1603	0.58
BP-[EMIM][TF_2N]	-0.1897	-0.1681	0.59
BP-[EMIM][TFO]	-0.1799	-0.1589	0.57
BP-[HOEMIM][BF_4]	-0.1897	-0.1682	0.59
BP-[HOEMIM][TFO]	-0.1901	-0.1686	0.59
BP-[HMIM][BF_4]	-0.1811	-0.1599	0.58
BP-[OMIM][BF_4]	-0.1893	-0.1677	0.59

Figure 3 shows the density of states (DOSs) for ionic liquids, isolated BP and BP-IL complexes. The energy gaps of ionic liquids adsorbed on the surface are 0.59, 0.57, 0.58, 0.58, 0.59, 0.57, 0.59, 0.59, 0.58 and 0.59 eV, respectively. And the gaps of the [BMIM][BF_4], [BMIM][TF_2N], [BMIM][TFO], [EMIM][BF_4], [EMIM][TF_2N], [EMIM]TFO], [HOEMIM][BF_4], [HOEMIM][TFO], [HMIM][BF_4] and [OMIM][BF_4] are 4.51, 4.07, 3.15, 4.73, 4.10, 3.34, 4.01, 3.55,4.78 and 4.80 eV, respectively. It can be seen that the band gap width of the ion pair is much larger than that of BP. Considering the fact that the gap of BP is 0.58 eV, the adsorption of ILs has little effect on the electronic properties of BP.



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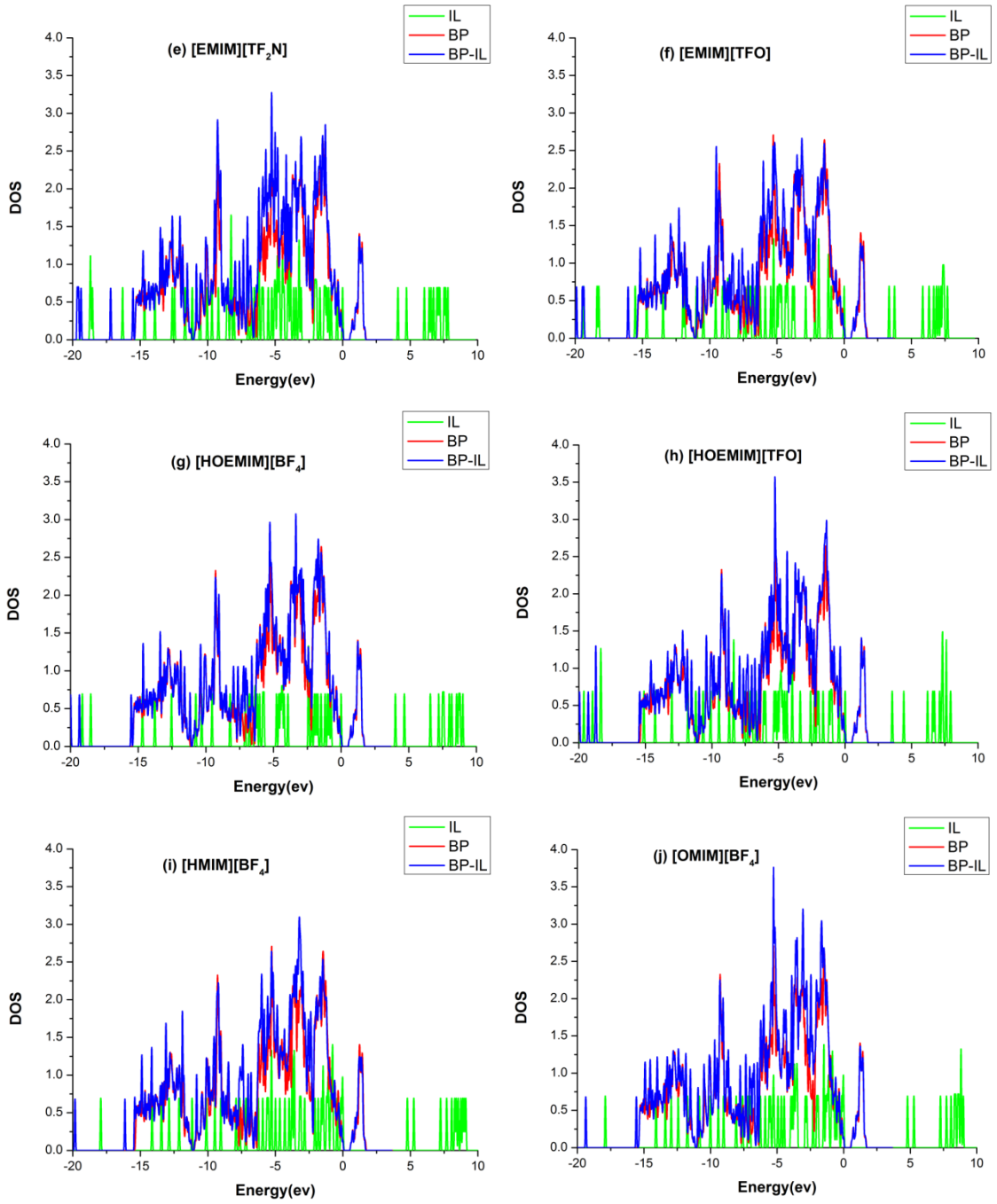

Figure 3. Density of states (DOSs) before and after adsorption of ionic liquids on BP.

3.3. Charge Transfer between Ionic Liquids and the Black phosphorus (BP)

Mulliken charge analysis was used to investigate the atomic charge redistributions of ILs adsorption on surface and Table 3 provides the related results. As shown in the table 3, the adsorption of [BMIM][BF_4], [BMIM][TF_2N], [BMIM][TFO],[EMIM][BF_4], [EMIM][TF_2N], [EMIM]TFO], [HOEMIM][BF_4], [HOEMIM][TFO] and [OMIM][BF_4] on the BP surface cause the cation to become less positive by -0.015, -0.250, -0.027, -0.004, -0.014, -0.011, -0.007, -0.008 and -0.009e, and the anion to become less negative by 0.004, -0.025, -0.021, -0.070, 0.007, -0.081, 0.004, -0.0005 and 0.004e, respectively. This has induced a charge of -0.011, -0.050, -0.048, -0.074, -0.007, -0.092, -0.003, -0.013 and -0.005e on the surface. The sign of induced charges on the surface indicates that charge transfer occurs from [BMIM][BF_4], [BMIM][TF_2N], [BMIM][TFO], [EMIM][BF_4], [EMIM][TF_2N], [EMIM]TFO], [HOEMIM][BF_4], [HOEMIM][TFO] and [OMIM][BF_4] to the BP. Meanwhile, the plots of charge density differences of the ILs adsorption on BP (shown in Figure 4) are made using CASTEP code[27] to clearly show the charge redistribution induced by the adsorption of ILs on BP.

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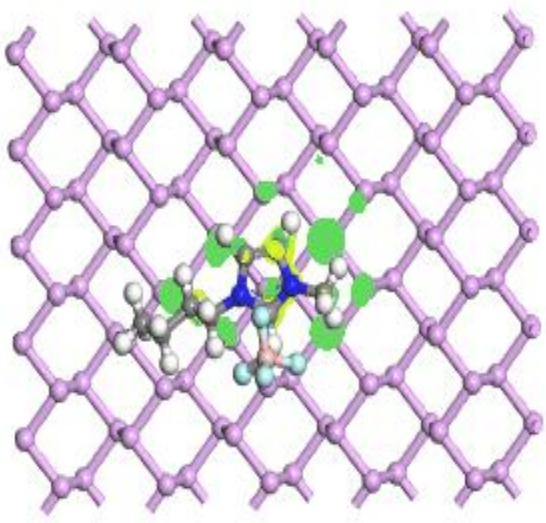
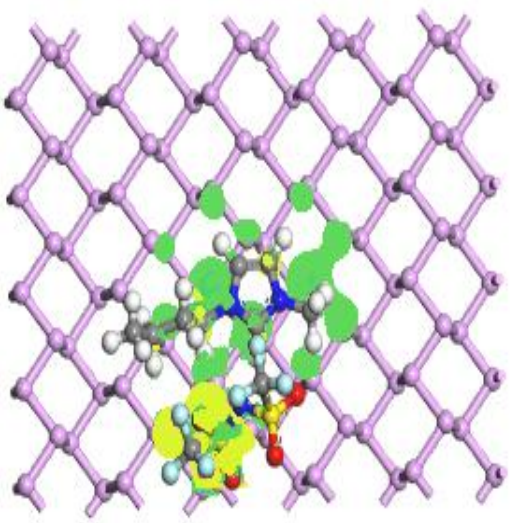
Table 3. Charge difference of cation, anion, and BP after adsorption (values in e)[a]

structure	△q(+)b	△q(-)c	▵ q(BP)
[BMIM][BF_4]	-0.015	0.004	-0.011
[BMIM][TF_2N]	-0.025	-0.025	-0.050
[BMIM][TFO]	-0.027	-0.021	-0.048
[EMIM][BF_4]	-0.004	-0.070	-0.074
[EMIM][TF_2N]	-0.014	0.007	-0.007
[EMIM][TFO]	-0.011	-0.081	-0.092
[HOEMIM][BF_4]	-0.007	0.004	-0.003
[HOEMIM][TFO]	-0.008	-0.005	-0.013
[HMIM][BF_4]	-0.046	-0.064	-0.110
[OMIM][BF_4]	-0.009	0.004	-0.005



BP-[BMIM][BF_4]-top view



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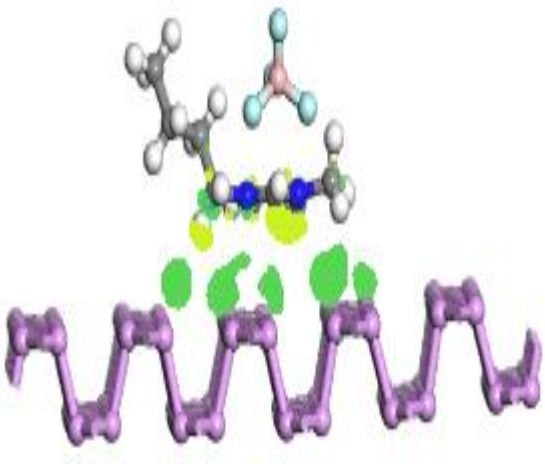
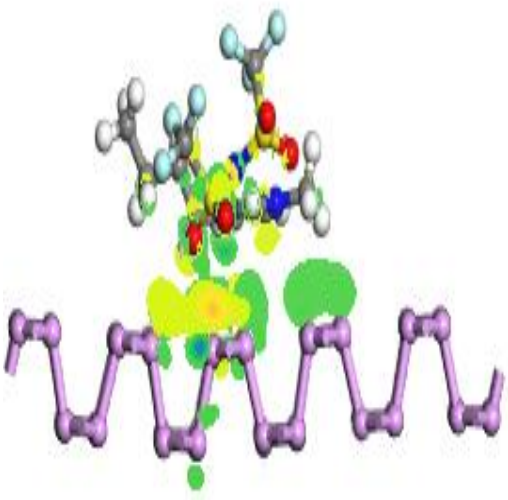


BP-[BMIM][BF_4]-side view



BP-[BMIM][TF_2N]-side view

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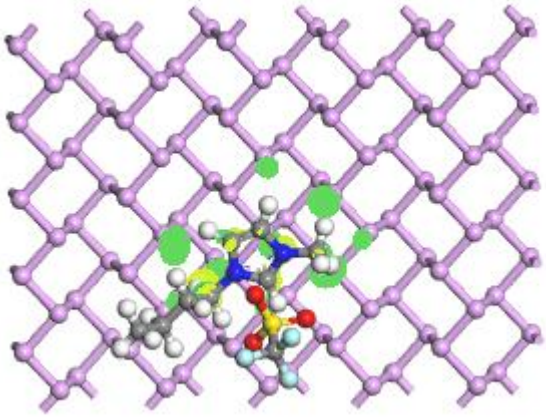
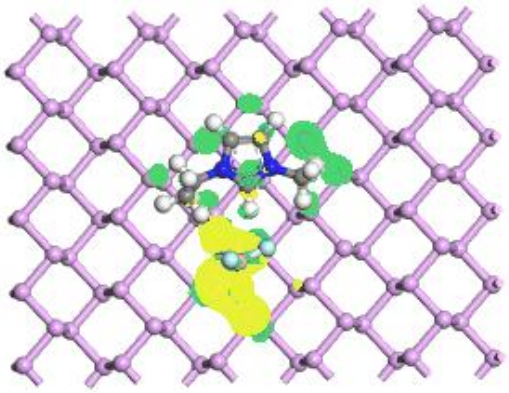
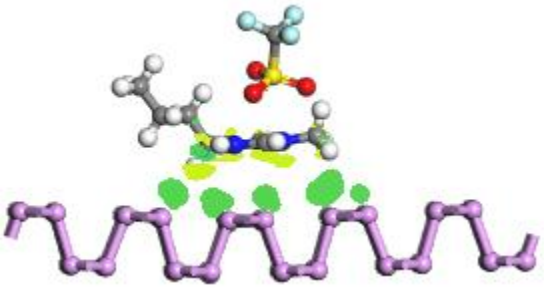


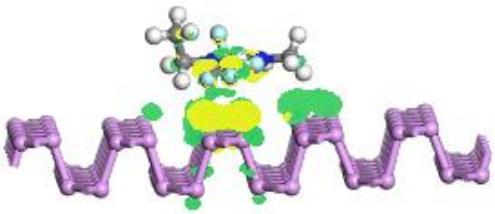
BP-[BMIM][TFO]-top view



BP-[EMIM][BF_4]-top view



BP-[BMIM][TFO]-side view



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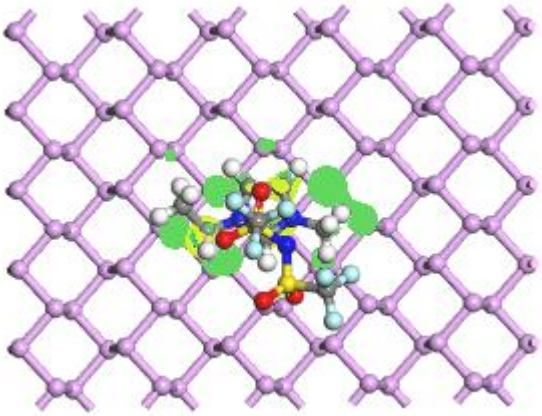
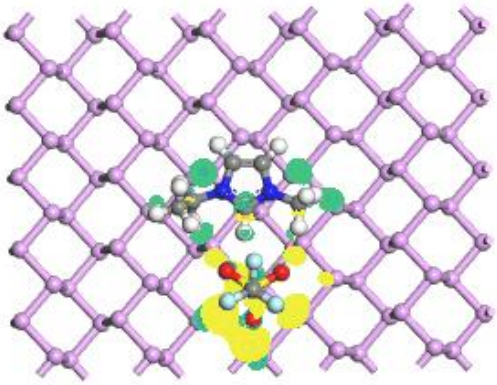
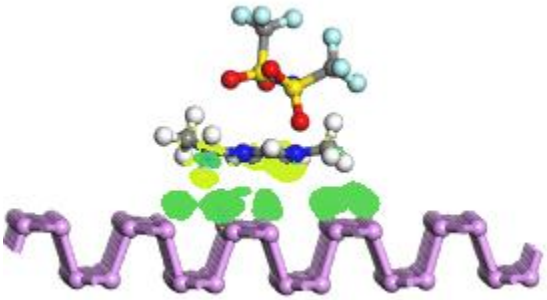


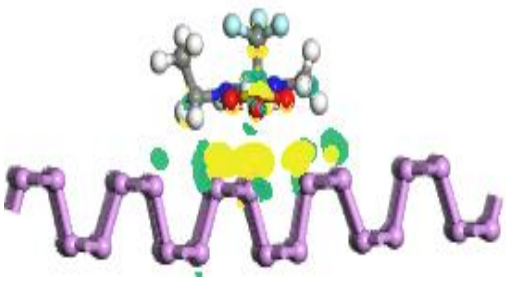
BP-[EMIM][TF_2N]-top view



BP-[EMIM][TFO]-top view



BP-[EMIM][TF_2N]-side view



BP-[EMIM][TFO]-side view

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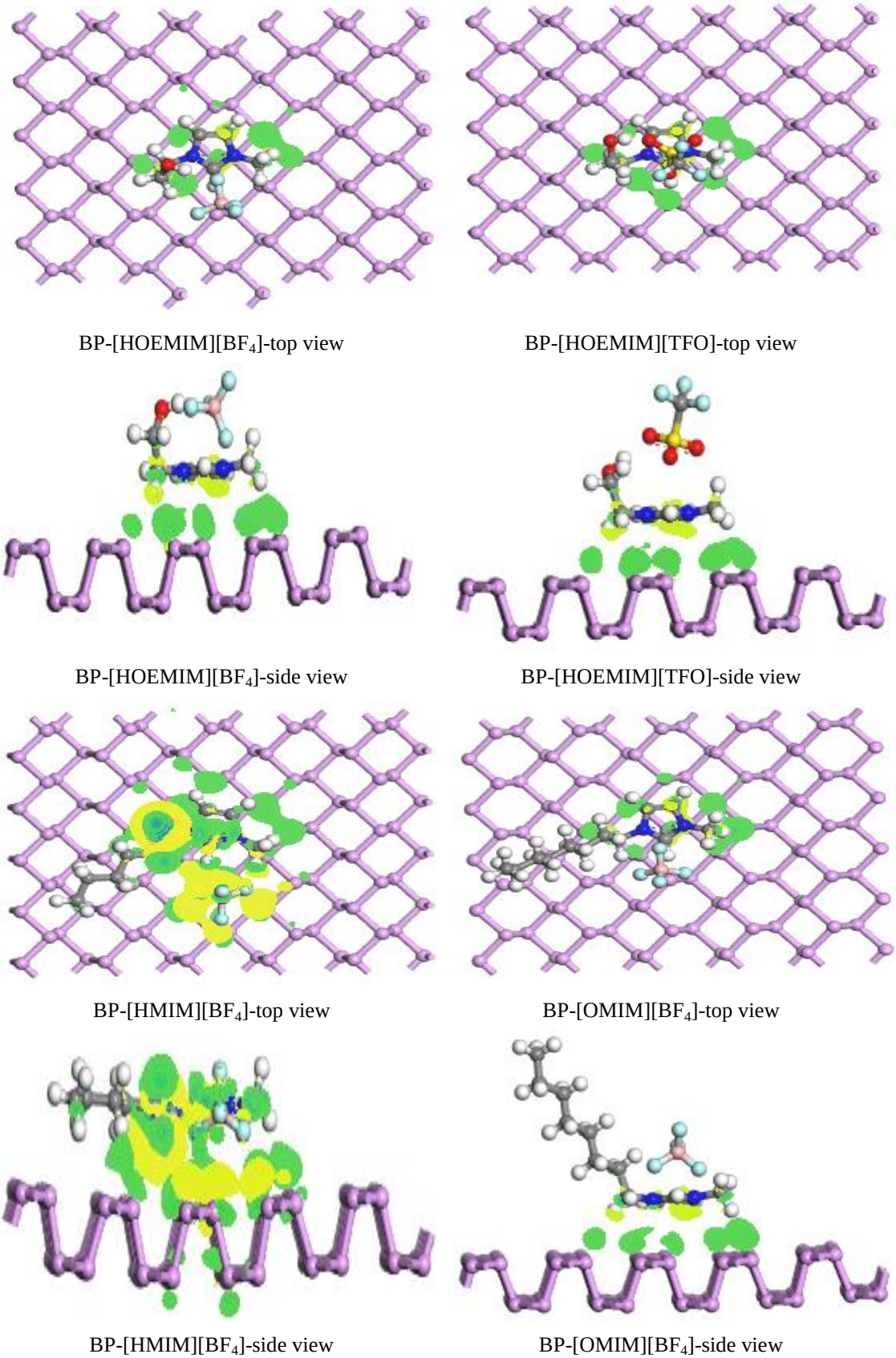

Figure 4. Charge density differences of [BMIM][BF_4], [BMIM][TF_2N], [BMIM][TFO], [EMIM][BF_4], [EMIM][TF_2N], [EMIM][TFO], [HOEMIM][BF_4], [HOEMIM][TFO], [HMIM][BF_4] and [OMIM][BF_4] adsorption on BP with the isosurface value of 0.0003e/Å^3. The green region shows electron accumulation, while the yellow region shows electrons loss.

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4. Conclusions

In summary, we have performed a comprehensive first-principles study on the adsorption of ionic liquids based on 1-butyl-3-methylimidazolium[BMIM]$^+$,1-ethyl-3-methylimidazolium[EMIM]$^+$,1-hexyl-3-methylimidazolium[HMIM]$^+$, 1-octyl-3-methylimidazolium [OMIM]$^+$and1-hydroxyethyl-3-methylimidazolium [HOEMIM]$^+$ cations paired to tetrafluoroborate [BF_4]$^-$, bis((trifluoromethyl)sulfonyl)-imide[Tf_2N]$^-$ and trifluoromethansulfonate [TfO]$^-$ anions. Our results indicated that the cation and anion type, the arrangement of the cation and anion in ILs, and the adsorption behavior of ILs on the BP surface could be the most important factors influencing the adsorption behavior. The magnitude of adsorption energy values for follows the order: BP-[HMIM][BF_4] (-1.299eV) >BP-[BMIM][TF_2N] (-1.124eV) > BP-[EMIM][TFO] (-1.088eV) > BP-[BMIM][BF_4] (-0.835eV) > BP-[BMIM][TFO] (-0.803eV) > BP-[EMIM][TF_2N] (-0.720eV) > BP-[OMIM][BF_4] (-0.684eV) > BP-[HOEMIM][BF_4] (-0.679eV) > BP-[EMIM][BF_4] (-0.675eV) >BP-[HOEMIM][TFO] (-0.670eV), respectively. VBM-CBM energy gaps and the density of states (DOSs) of the ionic liquids adsorption the BP surface demonstrate that the electronic properties of BP can be preserved after the adsorption of ILs. The order for the magnitude of charge transfer between different ILs and BP surface is follows:[HMIM][BF4](-0.110e) >[EMIM][TFO](-0.092e) > [EMIM][BF_4] (-0.074e) > [BMIM][Tf_2N] (-0.050e) > [BMIM][TFO] (-0.048e) > [HOEMIM][TFO] (-0.013e) > [BMIM][BF_4] (-0.011e) > [EMIM][TF_2N] (-0.007e) > [OMIM][BF_4] (-0.005e) > [HOEMIM][BF_4] (-0.003e), respectively. This order demonstrated that the type of IL distinctively determines the charge modification of surface. Our study offers fundamental insights into the structure and energetics of adsorption of ionic liquids on 2D materials. The results of this work could be the foundation for the study of the interaction of ionic liquids with other 2D materials.

Conflict of interest

No conflict of interest have been declared in this paper.

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