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Topological engineering of two-dimensional ionic liquid islands for high structural stability and CO<sub>2</sub> adsorption selectivity

In this work, Yanlei Wang, Hongyan He, and Suojang Zhang *et al.* used theoretical simulations to resolve the quantitative structure-function relations of 2D ionic liquid (IL) islands. Four different subunits are identified first, which can assemble close-packed and sparsely-arranged annular islands. Meanwhile, the island edges are found to be the dominating adsorbing site for CO<sub>2</sub> and better than other pure metal surfaces, showing an ultrahigh adsorption selectivity for CO<sub>2</sub> compared with CH<sub>4</sub>, CO, or N<sub>2</sub>. These results are meaningful for the rational design of ILs-based chemical engineering applications.

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# Topological engineering of two-dimensional ionic liquid islands for high structural stability and CO<sub>2</sub> adsorption selectivity†

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Ionic liquids (ILs) as green solvents and catalysts are highly attractive in the field of chemistry and chemical engineering. Their interfacial assembly structure and function are still far less well understood. Herein, we use coupling first-principles and molecular dynamics simulations to resolve the structure, properties, and function of ILs deposited on the graphite surface. Four different subunits driven by hydrogen bonds are identified first, and can assemble into close-packed and sparsely arranged annular 2D IL islands (2DIIs). Meanwhile, we found that the formation energy and HOMO–LUMO gap decrease exponentially as the island size increases via simulating a series of 2DIIs with different topological features. However, once the size is beyond the critical value, both the structural stability and electrical structure converge. Furthermore, the island edges are found to be dominant adsorption sites for CO<sub>2</sub> and better than other pure metal surfaces, showing an ultrahigh adsorption selectivity (up to 99.7%) for CO<sub>2</sub> compared with CH<sub>4</sub>, CO, or N<sub>2</sub>. Such quantitative structure–function relations of 2DIIs are meaningful for engineering ILs to efficiently promote their applications, such as the capture and conversion of CO<sub>2</sub>.

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## Introduction

Due to the green and environmentally-friendly nature,<sup>1,2</sup> ionic liquids (ILs) have been used in many cutting-edge fields, including green chemistry,<sup>3–5</sup> electrochemistry,<sup>6,7</sup> energy storage,<sup>8,9</sup> gas separation,<sup>10,11</sup> and catalysis.<sup>12,13</sup> In the real application environment, solid-surface supported IL (SSIL) films always exist and show several advantages compared with the bulk ones,<sup>14,15</sup> for example, higher stability, less usage of ILs, faster adsorption kinetics, *etc.* Consequently, SSIL films have attracted broad attention in the academy and industrial community.<sup>16,17</sup> The structure, property, and function of SSILs should be the result of the balance between hydrogen bonding, van der Waals (vdW), Coulomb, and interfacial interactions, which are far more complex than those of simple systems such as water, CO, *etc.* Hence, quantitative understanding of the

structure–function relationship of SSIL films has great significance in the rational design and management of IL-based chemistry.

Recently, plenty of experiments and simulations have been conducted to clarify the correlation between the structure and performance of SSIL films.<sup>18–20</sup> Via using the physical vapor deposition (PVD) technique,<sup>18</sup> Cremer *et al.*<sup>19</sup> demonstrated that an ultrathin IL film consisting of a closed monolayer structure could be produced, which is stable under ambient conditions and should be the sub-structure of SSILs. Moreover, through scanning tunneling microscopy (STM) and theoretical simulations, previous pioneering studies<sup>21–24</sup> identified that ILs could form the so-called ordered checkerboard or disordered glass structure of the monolayer ILs on the metal surface. Considering that the ordered monolayer IL structure should be grown from subunits, Meusel *et al.*<sup>25</sup> studied the subunits within the monolayer ILs on the Au(111) substrate via atomic force microscopy (AFM) and STM, discovering that the striped and hexagonal subunits were composed of two and three cation–anion pairs. Meanwhile, subunits can assemble into different two-dimensional IL islands (2DIIs), for instance, IL islands with branched or quasi-dendritic shapes on the Cu(111) surface.<sup>26</sup> Hence, the 2DIIs can indeed be prepared, and their structure depends greatly on the substrate surface, temperature (*T*), and other external conditions.

Originating from the designable microenvironments and functions, thin IL films or islands have broad application prospects, especially in CO<sub>2</sub> capture and fixation. For example,

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Su *et al.*<sup>27</sup> improved the catalytic activity of ILs in converting CO<sub>2</sub> into cyclic carbonates *via* confining the ILs in the mesoporous silica nanopore, in addition, Xie *et al.*<sup>28,29</sup> and Tang *et al.*<sup>30</sup> substantially strengthened CO<sub>2</sub> adsorption capacity and selectivity by just decreasing the thickness of IL films. These excellent performances of SSIL films suggest that the 2DII should be a preferred candidate in IL-based applications.<sup>31</sup> However, up to now, beyond qualitative understanding of 2DIIs, the quantitative characterization is still a major challenge, for instance, the detailed subunit structure, electronic properties, and gas adsorption performance. Such limitations restrict the theoretical understanding, rational design, and applications of ILs in the field of highly efficient and low-cost gas separation and capture processes.

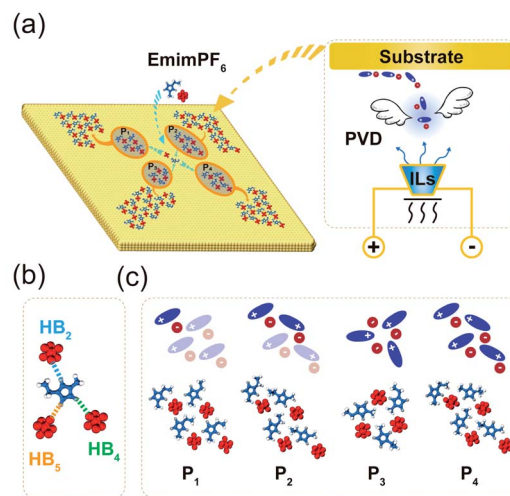
In the present work, the image charge augmented quantum mechanics/molecular mechanics (IC-QM/MM) and full-atomistic molecular dynamics (MD) simulations are performed to reveal the structure and properties of 2DIIs on graphite. We aimed at exploring the potential subunits of the ordered 2DIIs, gaining deeper insights into how the hydrogen bond (HB) network drives subunits and how the topological feature determines the thermodynamic stability, electronic properties, and even the gas adsorption mechanism of 2DIIs. Four different subunits are theoretically proposed, and the critical size ( $N_C$ ) for various 2DIIs is demonstrated, where the thermodynamic stability converges once the size is beyond  $N_C$ . The mechanisms that the subunit and size jointly control the melting behavior and electronic structure of 2DIIs are further revealed, showing the easy-regulating feature of 2DIIs. Finally, the dynamic gas adsorption processes on 2DIIs are conducted, suggesting that the edges of 2DIIs are dominant adsorption sites for CO<sub>2</sub> and possess high selectivity for CO<sub>2</sub>/CO, CO<sub>2</sub>/CH<sub>4</sub>, and CO<sub>2</sub>/N<sub>2</sub>.

## Results and discussion

### Hydrogen bonds driving subunits of 2DIIs

Due to the strong correlation originating from special HBs in ILs,<sup>32</sup> the gaseous particles will be cation-anion pairs in the PVD process (Fig. 1a), which can be deposited on the solid surface and easily assembled into different island structures, especially when IL pairs are few. As illustrated in Fig. 1b, the HBs in 2DIIs mainly include three kinds, C<sub>2</sub>-H<sub>2</sub>...F, C<sub>4</sub>-H<sub>4</sub>...F, and C<sub>5</sub>-H<sub>5</sub>...F, namely HB<sub>2</sub>, HB<sub>4</sub>, and HB<sub>5</sub>. Owing to the unique directional feature of HBs, the cation-anion pair can construct several subunit, as shown in Fig. 1c, namely P<sub>N</sub>, where  $N = 1, 2, 3$ , and 4, representing the number of cation-anion pairs. For P<sub>1</sub>, P<sub>2</sub>, and P<sub>4</sub>, the differences are mainly the combination styles of HBs and relative orientations within the neighboring cations. However, for P<sub>3</sub>, the subunit is composed of three pairs of ILs and is an annular structure. The unique structure of subunits can further dominate the permutation structures of 2DIIs and meanwhile form feature edges.

Based on the formation mechanism of various graphene polycrystals grown on the surface of liquid copper reported by Dong *et al.*,<sup>33</sup> taking subunits as an origin, they can grow into different 2DIIs in the form of parallelograms ( $m, n$ ), where  $m$  and



**Fig. 1** (a) A schematic diagram of 2DIIs on the graphite surface *via* PVD, where red, blue, yellow, white, and silver colors represent [PF<sub>6</sub>]<sup>−</sup>, [Emim]<sup>+</sup>, C atoms in graphite, H<sub>2/4/5</sub> atoms, and H atoms in the alkyl chain, respectively. (b) Three main HBs in the ILs, where HB<sub>2,4,5</sub> represents the HB between F and H in different sites of the imidazole ring. (c) The illustrated diagrams and atomic structures of the P<sub>1</sub>-based 2DII with four subunits, the P<sub>2</sub>-based 2DII with two subunits, the P<sub>3</sub>-based 2DII with one subunit, and the P<sub>4</sub>-based 2DII with one subunit, respectively.

$n$  are the number of cation-anion pairs (P<sub>1/2/4</sub>-based 2DIIs) or subunits (P<sub>3</sub>-based 2DIIs) along two edges (ESI Movie M1†). The size of 2DIIs,  $N_{\text{pairs}}$ , is defined as the total number of cation-anion pairs. To represent the structural feature of 2DIIs, the simulated STM images of P<sub>1/2/3/4</sub>-based 2DIIs with typical combinations of ( $m, n$ ) are displayed in Fig. 2a and b and S4.† For P<sub>1/2/4</sub>-based 2DIIs, two different feature edges exist, namely Z<sub>4</sub> and Z<sub>5</sub>, where Z<sub>4</sub> comprises HB<sub>2</sub> and HB<sub>4</sub> while Z<sub>5</sub> includes HB<sub>2</sub> and HB<sub>5</sub>. Similarly, edges of P<sub>3</sub>-based 2DIIs are defined as E<sub>1</sub> and E<sub>2</sub> (Fig. S5†), where the types of HBs in E<sub>1</sub> are almost the same as E<sub>2</sub>. Moreover, the thermodynamic stability of 2DIIs can be measured by the formation energy ( $E_f$ , see ESI Note†). Comparing  $E_f$  of 2DIIs with the same size but different combinations of ( $m, n$ ), it can be found that P<sub>1/2/4</sub>-based 2DIIs with longer Z<sub>5</sub> are more stable than those with longer Z<sub>4</sub>. For instance,  $E_f$  of P<sub>1</sub>-based 2DIIs with (4,2) and (2,4) is −44.97 and −46.32 kcal mol<sup>−1</sup>, respectively. However, there is no obvious difference between E<sub>1</sub> and E<sub>2</sub>. The anisotropic nature of P<sub>1/2/4</sub>-based 2DIIs and the isotropic nature of P<sub>3</sub>-based 2DIIs coincide well with the styles of HBs in the feature edges, indicating the feasibility of structure and property regulation *via* controlling the HBs within 2DIIs.

### Size-dependent thermodynamic stability and melting process of 2DIIs

To further quantify the influence of size on the structural stability,  $E_f$  for 2DIIs with different  $N_{\text{pairs}}$  is summarized in Fig. 2c, authenticating that  $E_f$  will decline with growing  $N_{\text{pairs}}$  for all 2DIIs. When  $N_{\text{pairs}}$  exceeds the critical value ( $N_C = 18$ ),  $E_f$  for various 2DIIs will only fluctuate in a small range, that means as  $N_{\text{pairs}}$  increases, the thermodynamic stability of 2DIIs will keep





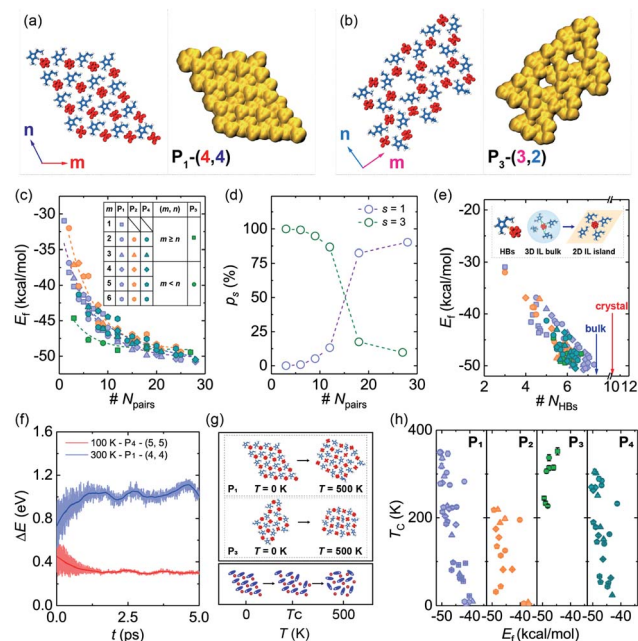


Fig. 2 (a and b) Atomic structures and simulated STM images of the  $P_1$ -based 2DIIIs with (4,4) and the  $P_3$ -based 2DIIIs with (3,2), respectively. The bias energy for the generation of all STM images is 20 eV, and the iso-contour value of all STM images is  $5.0 \times 10^{-5}$  Hartree. (c)  $E_f$  as a function of  $N_{\text{pairs}}$ , where the dashed lines represent exponential decay fitting. (d)  $p_s$  for different 2DIIIs changes with  $N_{\text{pairs}}$ . (e) The correlation between  $E_f$  and  $N_{\text{HBs}}$ , where the inset shows the atomic structures of HBs in the bulk and a 2DII. (f)  $\Delta E$  of two typical 2DIIIs from the AIMD simulations. (g and h)  $T_c$  in the melting process of various 2DIIIs as a function of  $E_f$ .

increasing until convergence. Interestingly,  $E_f$  for  $P_{1/2/4}$ -based 2DIIIs is almost the same, implying that relative orientations within the neighboring cations only have little effect on the thermodynamic stability. Moreover, the tendencies of  $E_f$ - $N_{\text{pairs}}$  for  $P_{1/2/4}$ -based 2DIIIs are fully different from those for  $P_3$ -based 2DIIIs: when the size of 2DIIIs is small ( $N_{\text{pairs}} < N_C$ ), the  $E_f$  of  $P_3$ -based 2DIIIs is the most negative; in contrast, the  $E_f$  of  $P_{1/2/4}$ -based 2DIIIs will be the lowest once the size is beyond  $N_C$ .

Assuming that  $N_{\text{pairs}}$  is fixed, the Boltzmann factor can be used to describe the distribution of  $P_{1/3}$ -based 2DIIIs, that is,  $p_s = \exp(-E_f, p_s/k_B T) / \sum_i \exp(-E_f, p_i/k_B T)$ , where  $s = 1$  and  $3$ ,  $i = 1$  versus  $3$ ,  $k_B$  is the Boltzmann constant, and  $T$  is set as 300 K.<sup>34</sup> As displayed in Fig. 2d, there exist two stages in  $p_s$ - $N_{\text{pairs}}$ . For instance, when  $N_{\text{pairs}} = 12$ ,  $p_1$  and  $p_3$  are respectively 13.18 and 86.82%, while when  $N_{\text{pairs}} = 18$ ,  $p_1$  and  $p_3$  are 82.51 and 17.49%, respectively. Hence,  $P_3$  will be the likeliest subunit if  $N_{\text{pairs}} < 18$ , which is the opposite when  $N_{\text{pairs}} \geq 18$ . The turnover of  $p_s$  implies that the structural transition from  $P_3$  to  $P_1$  may occur during the assembly process. Furthermore, the detailed internal arrangements of many large-sized monolayer IL films from experiments<sup>20,21,25</sup> are almost like those in  $P_{1/2/4}$ -based 2DIIIs rather than those in  $P_3$ -based 2DIIIs, reflecting the rationality of the simulated results herein.

The HBs are further analyzed, as shown in Fig. S6,<sup>†</sup> to understand the correlation between the structure and

thermodynamic stability. The angle and energy of HBs in 2DIIIs are respectively larger and lower than those in the bulk and crystal ILs, showing that graphite strengthens HBs in 2DIIIs and further enhances the structural stability of 2DIIIs. As displayed in Fig. 2e,  $E_f$  almost decreases linearly with the number of HBs per cation-anion pair ( $N_{\text{HBs}}$ ), indicating the dominant role of HBs in constructing 2DIIIs. When  $N_{\text{pairs}} > N_C$ ,  $N_{\text{HBs}}$  will catch up with the bulk value, agreeing well with convergent  $E_f$ . Furthermore, the 5 ps long *ab initio* MD (AIMD) simulations of representative 2DIIIs at  $T = 300$  and 100 K were performed. The energy difference per cation-anion pair ( $\Delta E$ , see ESI Note<sup>†</sup>) with  $N_{\text{pairs}} = 16$  and 25 is only 0.28 and  $-0.15$  eV, respectively (Fig. 2f), and the structures at different simulation times are almost unchanged (Fig. S7<sup>†</sup>). Hence, the AIMD simulations verify the structural stability of the corresponding 2DIIIs.

To further confirm the dynamic stability of 2DIIIs, the melting processes are elucidated *via* classical MD simulations. As  $T$  increases, 2DIIIs first maintain initial structures and then the in-plane transition at the critical temperature ( $T_c$ ) occurs, along with losing the ordered internal arrangements (Fig. 2g). Fig. 2h shows the evolution of  $T_c$  versus  $E_f$ , demonstrating that a negative relation exists in  $P_{1/2/4}$ -based 2DIIIs while a positive relation exists in  $P_3$ -based 2DIIIs. For instance,  $E_f$  of  $P_1$ -based 2DIIIs ( $N_{\text{pairs}} = 28$ ) and  $P_3$ -based 2DIIIs ( $N_{\text{pairs}} = 3$ ) is respectively  $-50.77$  and  $-44.64$  kcal mol<sup>-1</sup>, and  $T_c$  for them is 349.14 and 351.73 K (Fig. S8<sup>†</sup>), respectively. Hence, for some small  $P_3$ -based 2DIIIs and large  $P_{1/2/4}$ -based 2DIIIs,  $T_c$  is above room temperature, indicating their excellent dynamic stability. The different relationships between  $P_{1/2/4}$ -based and  $P_3$ -based 2DIIIs coincide well with two stages of  $p_s$ - $N_{\text{pairs}}$  (Fig. 2d). Combining  $E_f$ - $N_{\text{pairs}}$ ,  $E_f$ - $N_{\text{HBs}}$ ,  $T_c$ - $E_f$ , and  $T_c$ - $N_{\text{pairs}}$ , it can be concluded that HB networks can determine the stability of 2DIIIs.

### The arrangement-size binary control mechanism of the electronic structure in 2DIIIs

Considering the SSILs widely used in electrochemistry and energy storage, where the electronic properties of 2DIIIs can play a dominant role, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and energy gap ( $E_{\text{gap}}$ ) are summarized in Fig. 3a, displaying that the overall trend of the HOMO and the LUMO respectively increases and declines as  $N_{\text{pairs}}$  expands, leading to the reduction of  $E_{\text{gap}}$ . For example, when  $N_{\text{pairs}}$  goes up from 1 to 18,  $E_{\text{gap}}$  of  $P_{1,2,4}$ -based 2DIIIs will drop by 44.87%, 44.06%, and 46.08%, respectively. However,  $E_{\text{gap}}$  of  $P_3$ -based 2DIIIs only drops by 12.07%. Meanwhile,  $E_{\text{gap}}$  of  $P_{1/2/3/4}$ -based 2DIIIs with  $N_{\text{pairs}} > 24$  is 2.74, 2.68, 4.34, and 2.71 eV, respectively, demonstrating that  $P_3$ -based 2DIIIs always possess the largest  $E_{\text{gap}}$ , no matter how big the 2DII is.

Furthermore, the electron distributions of the HOMO and LUMO in 2DIIIs are calculated, as shown in Fig. 3b. Interestingly, the electron of the HOMO and LUMO in  $P_{1/2/4}$ -based 2DIIIs is localized in two different corners, far different from the overlapping distribution of that in  $P_3$ -based 2DIIIs. The localized electron distribution should originate from the anisotropic image charge ( $C_{\text{image}}$ ) distribution of graphite. Taking the  $P_4$ -



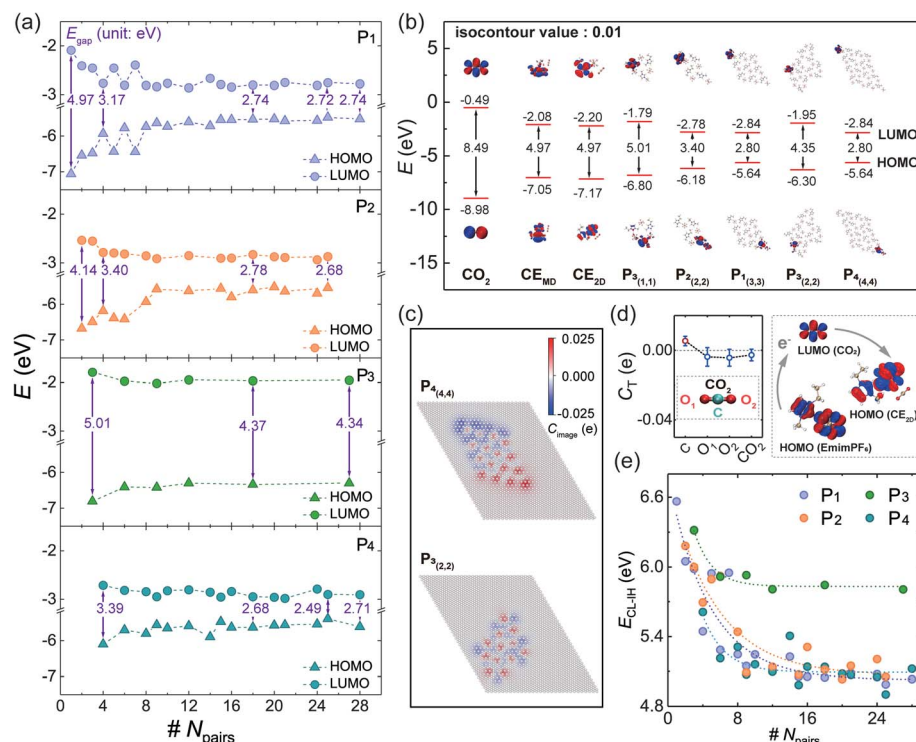


Fig. 3 (a) The HOMO, the LUMO, and  $E_{\text{gap}}$  of 2DIIs change with  $N_{\text{pairs}}$ . (b) Electron distributions of the HOMO and the LUMO in different IL systems. (c) The image charge distributions of first-layer graphite in  $P_4$ -based and  $P_3$ -based 2DIIs. (d) The charge transfer quantity of the  $\text{CO}_2$  molecule before and after adsorption on the 2DII, where the schematic diagram shows electron transfer from ILs to  $\text{CO}_2$ . (e) The energy gap between  $\text{HOMO}_{\text{IL}}$  and  $\text{LUMO}_{\text{CO}_2}$  changes with  $N_{\text{pairs}}$ , where the dotted lines represent exponential decay fitting.

based 2DII with (4,4) as an example, the C atoms at the upper left corner have negative  $C_{\text{image}}$  while those at the lower right corner have positive  $C_{\text{image}}$ , that means graphite will help decouple the electron in the HOMO and LUMO, especially in the ions at the edges of  $P_{1/2/4}$ -based 2DIIs. Thus, for  $P_{1/2/4}$ -based 2DIIs, with more ions at the edge comes more obvious decoupling, enhancing the electrical insulation feature of central ions and the electron transferability between edge ions and the substrate, leading to the plunge of  $E_{\text{gap}}-N_{\text{pairs}}$ . However, for  $P_3$ -based 2DIIs, the  $C_{\text{image}}$  distribution of graphite differs from  $P_{1/2/4}$ -based 2DIIs, and the decoupling effect is extremely weak, producing the largest  $E_{\text{gap}}$ . Thus, the subunit and size can jointly regulate the electronic properties of 2DIIs, the longer edges of  $P_{1/2/4}$ -based 2DIIs, and the stronger electron transferability of 2DIIs.

The SSIL films have been widely used in the process of gas capture and conversion, where the interaction between gas and 2DIIs plays a dominant role. Taking  $\text{CO}_2$  as an example, the charge transfer quantity ( $C_T$ ) between a  $\text{CO}_2$  molecule and the typical 2DII is displayed in Fig. 3d, by statistical averaging from 9 independent adsorption sites. This shows that the  $C_T$  of  $\text{CO}_2$  is negative, demonstrating that  $\text{CO}_2$  will get electrons from the 2DII in the typical chemical process.<sup>35,36</sup> This means electrons may transfer from the HOMO of 2DIIs ( $\text{HOMO}_{\text{IL}}$ ) to the LUMO of  $\text{CO}_2$  ( $\text{LUMO}_{\text{CO}_2}$ ). The difficulty of the electronic transfer process can be quantitatively described by the energy difference:  $E_{\text{CL-IH}} = \text{LUMO}_{\text{CO}_2} - \text{HOMO}_{\text{IL}}$ , as shown in Fig. 3e.

Excitingly,  $E_{\text{CL-IH}}$  will decline exponentially as  $N_{\text{pairs}}$  increases for various 2DIIs, especially for  $P_{1/2/4}$ -based 2DIIs, representing that larger 2DIIs can transfer electrons to  $\text{CO}_2$  more quickly and be effective in the capture and fixation process of  $\text{CO}_2$ .

### Edge selective adsorption of 2DIIs in the $\text{CO}_2$ capture process

During the practical reactive application of gas capture and conversion, the gas adsorption process, especially for  $\text{CO}_2$ , is meaningful for the rational design of the corresponding catalyst. To evaluate the gas adsorption stability, we defined four different adsorption sites of 2DIIs (vertex site –  $R_{\text{vertex}}$ , edge sites –  $R_{Z4}/R_{Z5}/R_{E1}/R_{E2}$ , above site –  $R_{\text{above}}$ , and inside site –  $R_{\text{in}}$ ), as shown in Fig. 4a and S9.† The adsorption energy ( $E_{\text{gas}}$ , see ESI Note†) of different sites is also calculated, as shown in Fig. 4b. For instance,  $E_{\text{gas}}$  of  $\text{CO}_2$  at  $R_{\text{vertex}}$ ,  $R_{Z4}$ ,  $R_{Z5}$ , and  $R_{\text{above}}$  in the  $P_4$ -based 2DII with (4,4) is  $-9.88$ ,  $-10.24$ ,  $-12.08$ , and  $-5.99 \text{ kcal mol}^{-1}$ , respectively, reflecting that the edge site ( $R_{Z5}$ ) provides the strongest adsorption ability (ESI Movie M2 and M3†). The lower  $E_{\text{gas}}$  should originate from the anisotropic  $C_{\text{image}}$  distribution of graphite in Fig. 3c, providing the additional adsorption force to the target gas molecules. However, for the  $P_3$ -based 2DII,  $E_{\text{gas}}$  of  $\text{CO}_2$  at  $R_{\text{in}}$ ,  $R_{E1}$ , and  $R_{E2}$  is close, agreeing well with the isotropic  $C_{\text{image}}$  distribution. In addition, since the position of the  $\text{CO}_2$  molecule at  $R_{\text{above}}$  is so far away from the graphite substrate, this leads to weaker substrate contribution, further resulting in a higher  $E_{\text{gas}}$  compared with that of other sites. Besides,  $E_{\text{gas}}$  of  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{N}_2$  at various



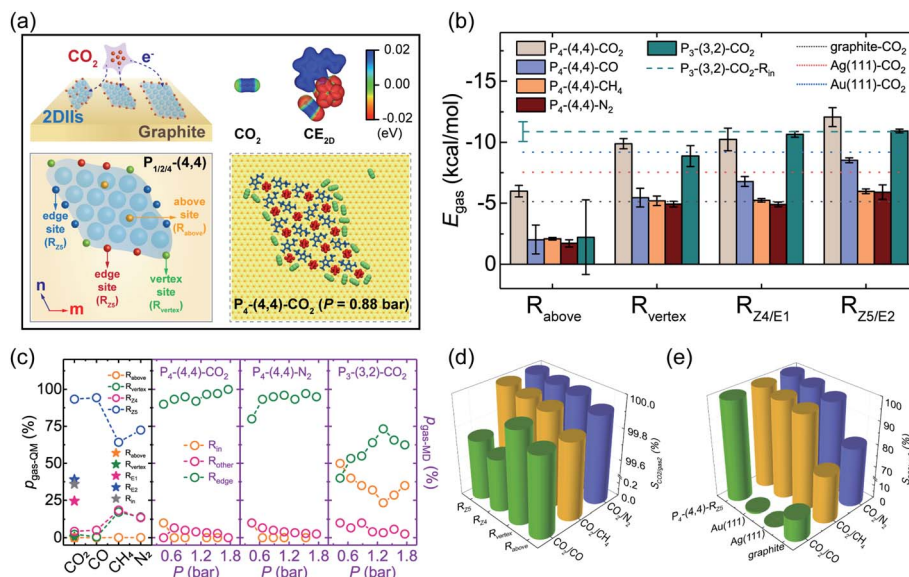


Fig. 4 (a) Schematic diagrams of  $\text{CO}_2$  molecules adsorbed on different sites of 2DIIs, electrostatic potential (ESP) mapped to the van der Waals surface (electron-density isosurface =  $0.01 \text{ e Bohr}^{-3}$ ) of a  $\text{CO}_2$  molecule before (left) and after (right) adsorption on the  $\text{P}_1$ -based 2DII with (1,1), and the illustration in the dotted box shows the atomic structures of  $\text{CO}_2$  molecules adsorbed on the 2DII at  $P = 0.88 \text{ bar}$ . (b)  $E_{\text{gas}}$  for different gases adsorbed on 2DIIs and pure solid surfaces. (c) The  $p_{\text{gas-QM}}$  and  $p_{\text{gas-MD}}$  for gases adsorbed on different sites. (d and e) The  $\text{CO}_2$  adsorption selectivity to other gases on the 2DII and pure solid surfaces.

sites of the  $\text{P}_4$ -based 2DII also shows the same order as that of  $\text{CO}_2$ .

To quantitatively explore the dynamic stability of gases adsorbed on 2DIIs, MD simulations of the adsorption process were further performed at  $T = 300 \text{ K}$  (Fig. 4a and S10†). As the partial pressure of gases ( $P$ ) ranges from 0.44 to 1.76 bar, almost all gas molecules adsorb on the edges of the  $\text{P}_4$ -based 2DII, while some adsorb on the sites inside the  $\text{P}_3$ -based 2DII (ESI Movie M4†). Excitedly, as shown in Fig. 4c, the Boltzmann factor of  $E_{\text{gas}}$  ( $p_{\text{gas-QM}}$ , see ESI Note†) is well consistent with the proportion of gases adsorbed on different sites ( $p_{\text{gas-MD}}$ , see ESI Note†), verifying that the edges of 2DIIs are dominant adsorption sites for different gases.

Furthermore, compared with many pure solids,  $E_{\text{gas}}$  of different gases on edge sites of 2DIIs is even stronger (Fig. 4b and S11†). Taking  $\text{CO}_2$  as an example,  $E_{\text{gas}}$  of  $\text{R}_{25}$  in the  $\text{P}_4$ -based 2DII with (4,4), Au(111), Ag(111), and graphite is  $-12.08$ ,  $-9.20$ ,  $-7.54$ , and  $-5.13 \text{ kcal mol}^{-1}$ , respectively. Considering that  $E_{\text{gas}}$  of  $\text{CO}_2$  is always lower than that of  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{N}_2$  when they adsorb on the  $\text{P}_4$ -based 2DII, we further calculated the  $\text{CO}_2$  adsorption selectivity to other gases ( $S_{\text{CO}_2/\text{gas}_2}$ , see ESI Note†) on different solid surfaces. Fantastically,  $S_{\text{CO}_2/\text{gas}_2}$  for the  $\text{P}_4$ -based 2DII is bigger than 99.70% (Fig. 4d and e), indicating that all adsorption sites of 2DIIs show extremely high  $\text{CO}_2$  selectivity.

Meanwhile,  $S_{\text{CO}_2/\text{CH}_4}$ ,  $S_{\text{CO}_2/\text{CO}}$ , and  $S_{\text{CO}_2/\text{N}_2}$  of the  $\text{P}_4$ -based 2DII can be up to 1.31, 1.52, and 1.23 times higher than those of the pure graphite surface. Moreover,  $S_{\text{CO}_2/\text{CH}_4}$ ,  $S_{\text{CO}_2/\text{CO}}$ , and  $S_{\text{CO}_2/\text{N}_2}$  for Au (111) are 98.59, 1.26, and 98.91%, respectively, lower than those for 2DIIs. The high  $\text{CO}_2$  adsorption selectivity suggests that the 2DII can be viewed as a promising adsorbent or reaction promoter in the process of carbon capture and utilization, which agrees well with recent experiments on the IL-stabilized

single-atom catalysts.<sup>37</sup> Considering that some 2DIIs can maintain stable structures above room temperature, it should be feasible to achieve higher gas adsorption and selectivity by extending the edges of 2DIIs or modulating the ionic micro-environment around the catalyst.

### Additional discussion

Physically, the selective edge adsorption for different gases should originate from the unique  $C_{\text{image}}$  distribution of the graphite supporting  $\text{P}_{1/2/4}$ -based 2DIIs, where the structure, thermodynamic stability, electronic properties, and gas adsorption can also be further enhanced by selecting species of ILs and solid substrates. Moreover, the length of edges can measure the potential effectiveness of 2DIIs adsorbing the gas reactants. The longer side length of the 2DIIs is more conducive to playing the function of 2DIIs in the application of gas adsorption and selectivity. However, the bigger 2DII will lead to the large usage of ILs, which will be a challenge, especially considering the high synthesis cost of ILs.

Excitingly, the optimal size of a  $\text{P}_{1/2/4}$ -based 2DII can be determined from the size-dependent  $E_f$  and  $E_{\text{gap}}$  (Fig. 2c and 4a). A too-small  $\text{P}_{1/2/4}$ -based 2DII ( $N_{\text{pairs}} < N_c$ ) will be thermodynamically unstable and possess a large  $E_{\text{gap}}$ . Meanwhile, a too-large  $\text{P}_{1/2/4}$ -based 2DII ( $N_{\text{pairs}} > N_c$ ) will have almost the same thermodynamic stability and  $E_{\text{gap}}$  as the 2DII of  $N_c$ . Hence, the suitable size of  $\text{P}_{1/2/4}$ -based 2DIIs should exist in practical applications, for instance, highly efficient and low-cost  $\text{CO}_2$  capture and conversion. Hence, multiple  $\text{P}_{1/2/4}$ -based 2DIIs with an optimal size rather than a single large 2DII can provide the best performance, including high electrical conductivity and efficient  $\text{CO}_2$  adsorption and selectivity, and minimize the





usage of ILs to the greatest extent, which is valuable to overcome the economic barrier of the high-price of ILs in real applications.

## Conclusions

In brief, this study set out to better understand the structure, thermodynamic stability, electronic properties, and gas adsorption performance of 2DIIs *via* combined IC-QM/MM calculations and classical MD simulations. We proposed four kinds of subunits, which can assemble into various 2DIIs supported by graphite. Both the formation energy and HOMO–LUMO energy gap decrease as the size of the 2DIIs grow, and they converge once the size is beyond the critical value; some 2DIIs can also maintain their stable structures even above room temperature. Meanwhile, the HOMO–LUMO gap of the sparsely arranged (Table S2†) annular 2DII ( $P_3$ ) is far larger than that of close-packed ones ( $P_{1/2/4}$ ). Furthermore, the edges of 2DIIs are dominant adsorption sites for  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{N}_2$ , and also show high  $\text{CO}_2/\text{CH}_4$ ,  $\text{CO}_2/\text{CO}$ , and  $\text{CO}_2/\text{N}_2$  selectivity, which is up to 1.31, 1.52, and 1.23 times higher than that of the pure graphite surface. The adsorption stability and selectivity are even better than those of some pure metal surfaces. The quantitative structure–function relationship of 2DIIs proves that it is feasible to achieve a higher electronic or gas adsorption performance just by adopting an optimal size of 2DIIs, which is meaningful for the rational design and management of IL-based green chemical engineering applications.

## Computational details

### Atomic structures

The IL considered herein is 1-ethyl-3-methylimidazolium hexafluoro-phosphate, namely  $\text{EmimPF}_6$ , widely used as the electrolyte in supercapacitors and other applications.<sup>38–41</sup> Considering the applications of the  $\text{EmimPF}_6$ –graphite interface in the field of batteries, electrochemical reactions, and other chemical engineering processes,<sup>42,43</sup> graphite was adopted as the solid surface. A three-layer slab models the graphite substrates, and a periodic boundary condition (PBC) was applied in all three dimensions, as shown in Fig. S1.† To properly accommodate the adsorbates on the surface, avoiding spurious interactions with the periodic images, at least  $13 \times 13$  replicas of the unit cell in graphite are used in the lateral dimensions. To decouple the periodic images in the dimension perpendicular to the surface, a vacuum of at least  $\sim 1.7$  nm is added along the  $z$ -direction.

### An IC-QM/MM approach

The optimization of the hybrid IL-graphite system was performed using the CP2K/QUICKSTEP program.<sup>44,45</sup> In order to expand the number of atoms in the hybrid IL-graphite system as much as possible, we employed the IC method<sup>46</sup> within a QM/MM<sup>47,48</sup> framework, where the QM part is treated at the Kohn–Sham (KS) density functional theory (DFT) level within a mixed Gaussian and plane wave<sup>49</sup> (GPW) formalism. The accuracy of

the IC-QM/MM approach is evaluated by comparing the structural and energetic properties to the full DFT results, as shown in Fig. S2.† “Full DFT” in this context means that graphite and the adsorbate are both treated at the DFT level. For QM calculations, double- $\zeta$  valence plus polarization (DZVP) basis sets of the Molopt-type<sup>50</sup> are used to represent the valence electrons. The interactions between valence and core electrons are described by norm-conserving Goedecker, Teter, and Hutter pseudopotentials.<sup>51–53</sup> The Becke–Lee–Yang–Parr (BLYP) functional<sup>54,55</sup> models the exchange and correlation potential. The van der Waals interactions are accounted for by employing the DFT-D3 dispersion correction. The energy cutoff for the auxiliary plane wave expansion of the density is set to 400 Ry. Moreover, The MM-based interactions between  $\text{EmimPF}_6$  and graphite are modeled with the parameters from the MD simulations.

### MD simulations

The parameters of the bond, angle, dihedral, van der Waals interactions, and electrostatic interactions of  $\text{EmimPF}_6$  were described by the all-atom optimized potentials for the liquid simulations (OPLS-AA) force field,<sup>56–58</sup> which has been used to successfully obtain the structures and liquid properties of ILs.<sup>59,60</sup> Previously, Tang *et al.* found that the non-polarizable force field could prophesy a rational interfacial structure at the IL-graphite interface *via* the AIMD simulation.<sup>61,62</sup> Therefore, the non-polarizable OPLS-AA force field employed here commendably described the structure and properties of 2DIIs on graphite. The interactions between  $\text{EmimPF}_6$  and graphite can be divided into electrostatic and van der Waals interactions. The former one, the long-range coulombic interaction, was computed using the particle–particle–particle–mesh (PPPM) algorithm with an accuracy of 0.0001.<sup>63</sup> The latter one was represented by using the 12-6 Lennard-Jones (LJ) potential, which was truncated at 1.2 nm. The Lorentz–Berthelot mixing rules were used to calculate the van der Waals interactions between different atomic species. The SHAKE algorithm<sup>64</sup> was applied to the C–H bonds to reduce high-frequency vibrations. All MD simulations in this work were carried out using a large-scale atomic/molecular massively parallel simulator (LAMMPS).<sup>65</sup> The time step for integrating the Newtonian equations of motion was set as 2.0 fs, which was demonstrated to ensure energy conservation. The in-plane ( $x$ – $y$ ) size of the graphite surface was set as  $3.20 \times 3.20 \text{ nm}^2$  at least, and the height of the PBC box along the  $z$ -direction is 20 nm. The atoms of the graphite substrate were fixed during the MD simulations to maintain the planar structure.  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  were chosen from the equilibrium configuration of monolayer  $\text{EmimPF}_6$  in Fig. S1.† Then,  $P_{1/2/3/4}$ -based 2DIIs with different  $N_{\text{pairs}}$  were placed about 0.3 nm above the graphite substrate, which was relaxed in the NVT ensemble at  $T = 0.01$  K, controlled by using the Berendsen thermostat.<sup>66</sup> After a 10 ns long MD simulation, the initial structure of the hybrid IL-graphite system can be obtained.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.



## Author contributions

H. H., Y. W., and S. Z. designed this research; C. W. performed the simulations; Z. G., Y. L., C. Q., and F. H. discussed the results; C. W., Y. W., H. H., and S. Z. contributed to preparing the final manuscript.

## Conflicts of interest

The authors declare no competing financial interest.

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