Supporting Information for

Topological engineering of two-dimensional ionic liquid islands for high structural stability and CO_2 adsorption selectivity

Chenlu Wang,[a][b] *Yanlei Wang*,*[a][b] *Zhongdong Gan*,[a] *Yumiao Lu*,[a] *Cheng Qian*,[d] *Feng Huo*,[a] *Hongyan He**[a][b][c] *and Suojiang Zhang**[a][b]

[a]Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

[b]University of Chinese Academy of Sciences, Beijing 100049, China.

[c]Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, China.

[d]School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, South Korea.

Corresponding Authors: ylwang17@ipe.ac.cn; hyhe@ipe.ac.cn; sjzhang@ipe.ac.cn

Table of Contents

Supplementary Movies

Supplementary Movie M1

The formation process of two-dimensional ionic liquid islands (2DIIs).

Supplementary Movie M2

The 10-ns long MD simulation of N_2 molecules adsorb on the P_4-based 2DII with (4,4), at T = 300 K and P = 0.88 bar.

Supplementary Movie M3

The 11.5-ns long MD simulation of CO_2 molecules adsorb on the P_4-based 2DII with (4,4), at T = 300 K and P = 0.88 bar.

Supplementary Movie M4

The 3-ns long MD simulation of CO_2 molecules adsorb on the P_3-based 2DII with (3,2), at T = 300 K and P = 0.88 bar.

Supplementary Note

N_{pairs}

For $P_{1/2/4}$-based 2DIIs, $N_{pairs} = m \cdot n$, where m and n are the numbers of cation-anion pairs along Z_4 and Z_5 sides, respectively. For P_3-based 2DIIs, $N_{pairs} = 3 \cdot m \cdot n$, where m and n are the number of P_3 along E_1 and E_2 edges, respectively.

E_f

$E_f = [E_{hyb} - (E_{sub} + N_{pairs}E_{IL})]/N_{pairs}$, where E_{hyb}, $E_{sub,}$ and E_{IL} are total energies of the optimized hybrid IL-graphite system, the optimized graphite substrate, and the optimized isolate $EmimPF_6$ pair, respectively.

ΔE

$\Delta E = (E_{AIMD} - E_{hyb})/N_{pairs}$, where E_{AIMD} is the total energy of the hybrid IL-graphite system after the 5-ps long AIMD.

E_{gas}

$E_{gas} = E_{hyb\&gas} - (E_{hyb} + E_{gas\text{-}only})$, where $E_{hyb\&gas}$, and $E_{gas\text{-}only}$ are total energies of the optimized hybrid gas-IL-graphite system, and the optimized isolate gas molecule, respectively.

$p_{gas\text{-}QM}$

$p_{gas\text{-}QM} = \exp(-E_{gas,\,R_{site}}/k_BT)/\Sigma_i\exp(-E_{gas,\,R_i}/k_BT)$, where k_B is the Boltzmann constant, and T is set as 300 K. For $P_{1/2/4}$-based 2DIIs, R_i is respectively R_{above}, R_{vertex}, R_{Z4}, and R_{Z5}, while R_{site} is the specific R_i. For P_3-based 2DIIs, R_i is respectively R_{above}, R_{vertex}, R_{E1}, R_{E2}, and R_{in}, while R_{site} is the specific R_i.

$p_{gas\text{-}MD}$

$p_{gas\text{-}MD} = N_{gas,\,R_{site}}/N_{gas}$, where $N_{gas,\,R_{site}}$ is the number of gas molecules adsorbed on the R_{site} and N_{gas} is the total number of gas molecules in the hybrid gas-IL-graphite system.

$S_{CO_2/gas2}$

$S_{CO_2/gas2} = \exp(-E_{gas,\,CO_2}/k_BT)/(\exp(-E_{gas,\,CO_2}/k_BT) + \exp(-E_{gas,\,gas2}/k_BT))$, where gas_2 is one of the three gases: CO, N_2, and CH_4.

Supplementary Figures and Captions

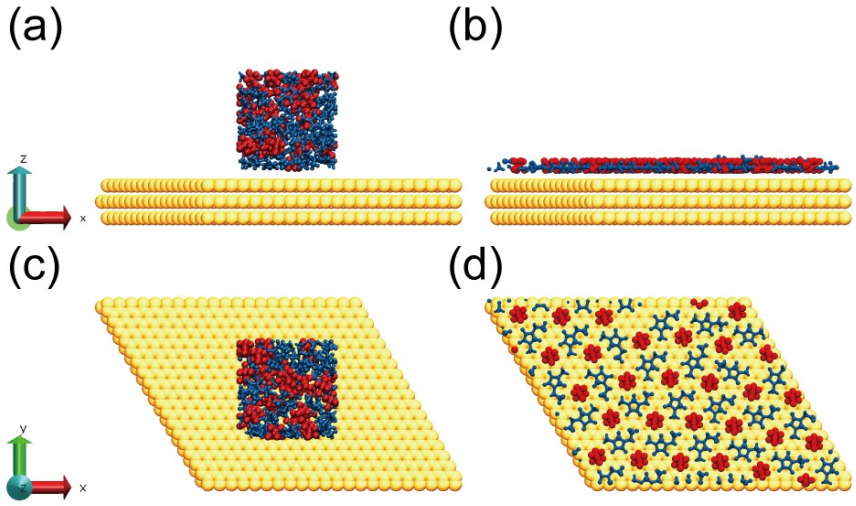

Figure S1. (a) The initial atomic structure of the hybrid IL-graphite system for MD simulations, from the main view, where red, blue, and yellow colors represent $[PF_6]^-$, $[Emim]^+$, C atoms in graphite, respectively. The PBC box has 28 pairs of $EmimPF_6$ and 2376 atoms in graphite. We performed the 20-ns NVT dynamics at 300 K, using temperature and barostat coupling constants of 0.1 ps and 0.1 ps, respectively. (b) The equilibrated atomic structure of the hybrid IL-graphite system, from the main view, with the monolayer $EmimPF_6$. (c) The initial atomic structure of the hybrid IL-graphite system for MD simulations, from the top view. (d) The equilibrated atomic structure of the hybrid IL-graphite system, from the top view.

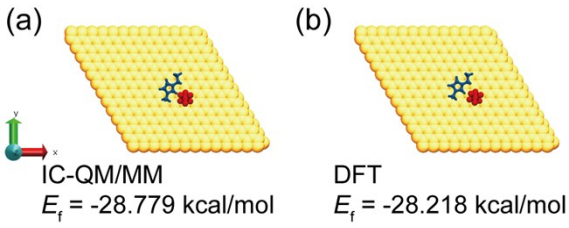

Figure S2. (a) The atomic structure of the hybrid IL-graphite system after geometry optimization by the IC-QM/MM approach, where E_f = -28.779 kcal/mol. (b) The atomic structure of the hybrid IL-graphite system after geometry optimization by the DFT method, where E_f = -28.218 kcal/mol.

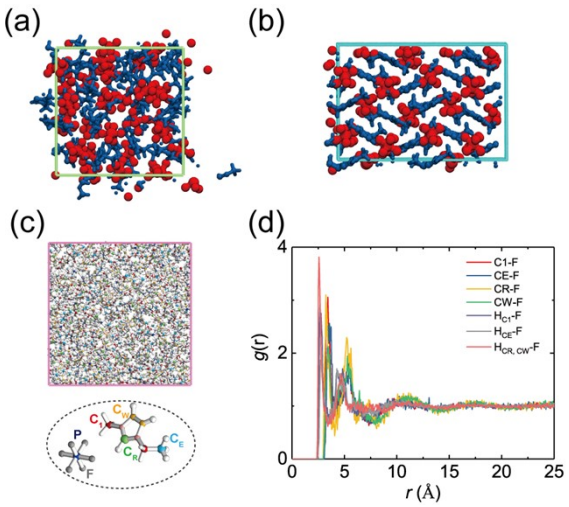

Figure S3. (a-b) Atomic structures of the three-dimensional (3D) ILs after the 5-ps AIMD simulation by the IC-QM/MM approach, consisting of 32 pairs of $EmimPF_6$, where lime, red, blue, and cyan colors represent the PBC box of 3D bulk IL, $[PF_6]^-$, $[Emim]^+$, the PBC box of 3D crystal IL, respectively. (c) Atomic structures of the 3D bulk IL after 10-ns MD simulation with T = 300 K, consisted of 200 pairs of $EmimPF_6$, where mauve, red, yellow, lime, cyan, silver, and blue colors represent the PBC box, C_1 atom, C_W atom, C_R atom, C_E atom, F atom, and P atom, respectively. It should be noted that the C_R atom is a C_2 atom, and C_W atoms include C_4 and C_5 atoms. (d) The radial distribution function (RDF) between C atom and F atom or H atom and F atom.

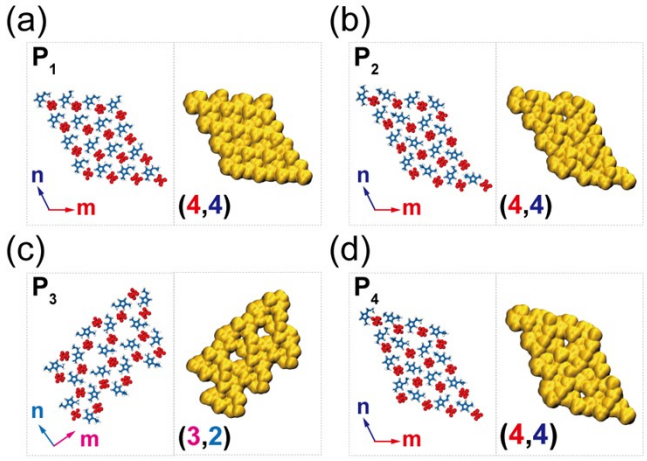

Figure S4. (a-d) Atomic structures and simulated STM images of the $P_{1/2/3/4}$-based 2DIIs with (4,4) or (3,2), respectively. Bias energy for the generation of all STM images is 20 eV, and the iso-contour value of all STM images is 5.0×10^{-5} Hartree.

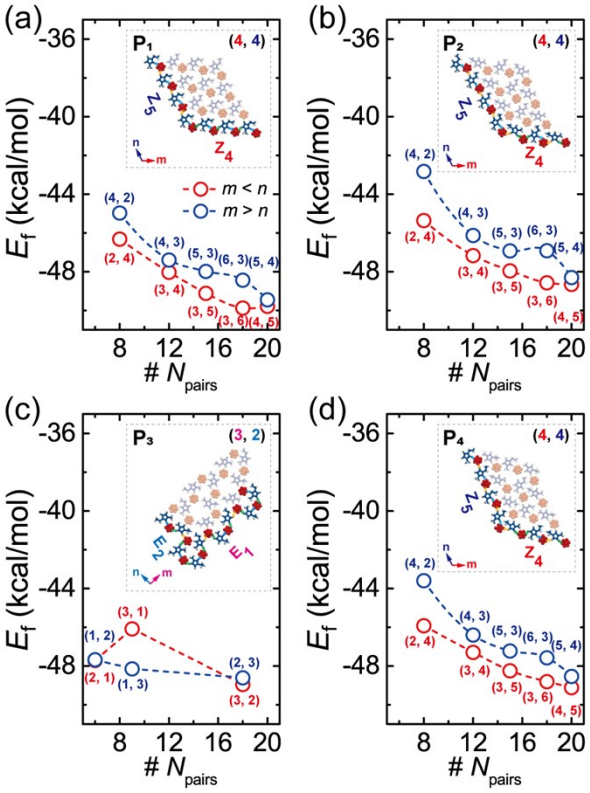

Figure S5. (a-d) E_f changes with N_{pairs} for $P_{1/2/3/4}$-based 2DIIs. The inserts show schematic diagrams of different edge structures, where blue, green, and orange colors represent HB_2, HB_4, and HB_5, respectively.

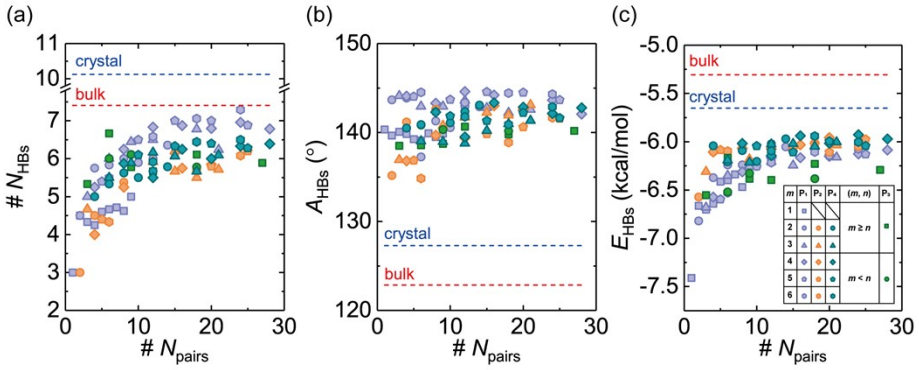

Figure S6. (a-c) The number (N_{HBs}), angle (A_{HBs}), and energy (E_{HBs}) of HBs in 2DIIs and 3D ILs, respectively.

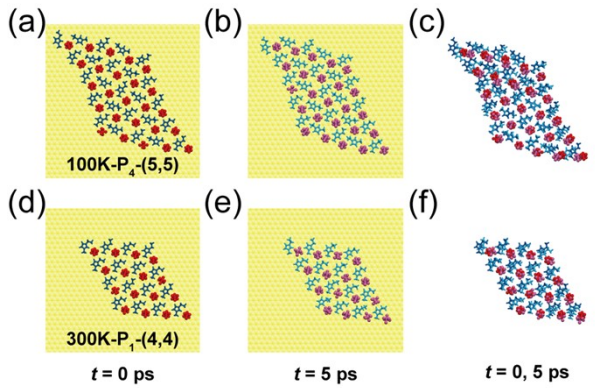

Figure S7. (a-f) Atomic structures of representative 2DIIs at different AIMD simulation time (t) with T = 300 and 100 K, where red, blue, mauve, cyan and yellow colors represent $[PF_6]^-$ at t = 0 ps, $[Emim]^+$ at t = 0 ps, $[PF_6]^-$ at t = 5 ps, $[Emim]^+$ at t = 5 ps, C atoms in graphite, respectively.

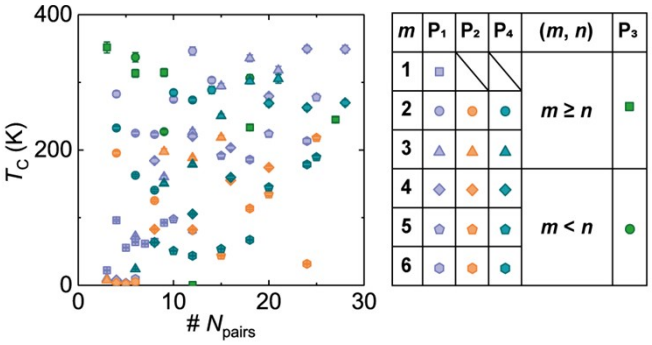

Figure S8. T_c for various 2DIIs as a function of N_{pairs}.

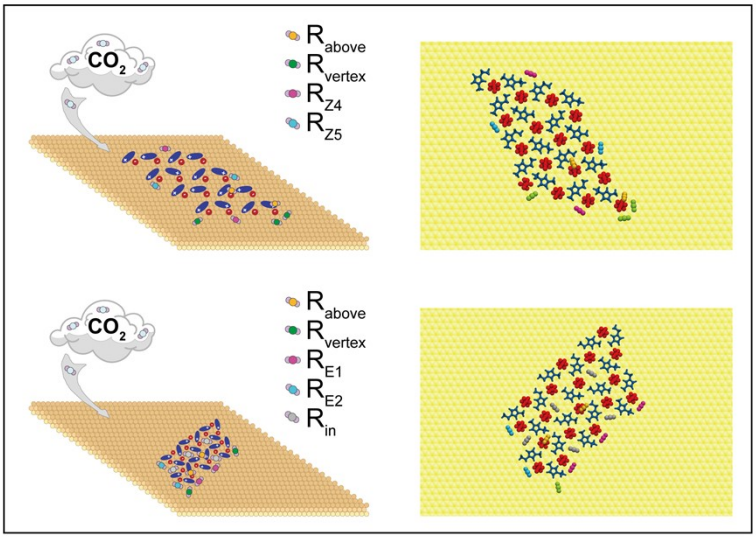

Figure S9. Schematic diagrams and atomic structures of CO_2 molecules adsorbed on different sites of P_4-based and P_3-based 2DIIs. Considering the unique structure of 2DIIs, different adsorbed sites are proposed: the region above the 2DII (R_{above}), the vertex position (R_{vertex}), the edge regions (R_{edge}: R_{Z4}/R_{Z5}, R_{E1}/R_{E2}), inside the 2DII (R_{in}), and the other (R_{other}). In schematic diagrams and atomic structures, orange, olive, magenta, blue, and silver colors represent R_{above}, R_{vertex}, $R_{Z4/E1}$, $R_{Z5/E2}$, and R_{in}, respectively.

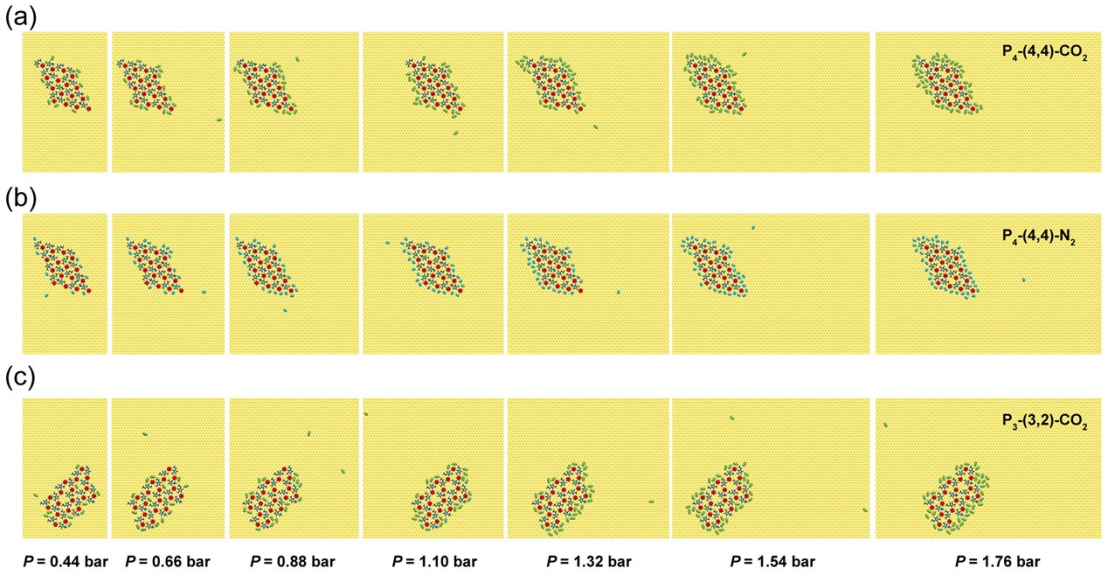

Figure S10. (a-c) Atomic structures of CO_2 and N_2 molecules adsorbed on the representative 2DIIs, as *P* ranges from 0.44 to 1.76 bar, where lime and cyan colors represent CO_2 and N_2, respectively.

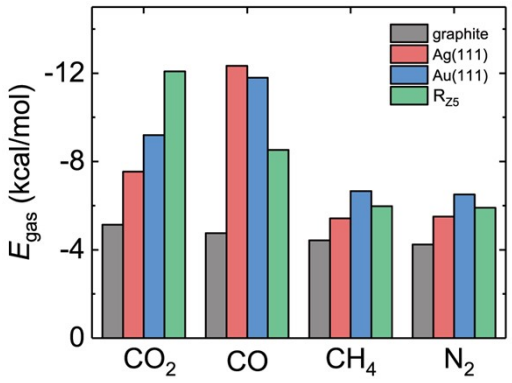

Figure S11. E_{gas} of CO_2, CO, CH_4 and N_2 molecules adsorbed on the P_4-based 2DII with (4,4), Au(111), Ag(111), and graphene.

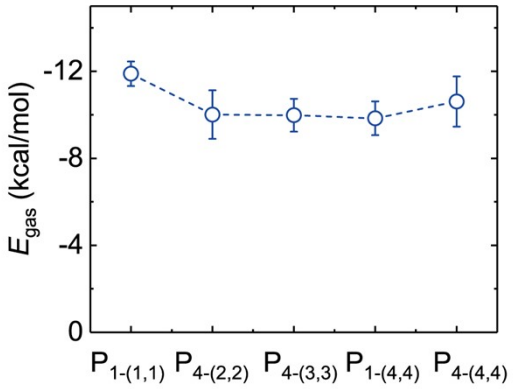

Figure S12. E_{gas} of CO_2 adsorbed on the phase boundaries of various 2DIIs.

Supplementary Tables

Table S1. The E_f of four subunits (P_N, N = 1, 2, 3, 4).

Type	$P_{1\text{-}(1,1)}$	$P_{2\text{-}(2,1)}$	$P_{3\text{-}(1,1)}$	$P_{4\text{-}(2,2)}$
E_f (kcal/mol)	-30.97197	-32.01704	-44.63873	-41.31702

Table S2. The density (ρ) of four 2DIIs and 3D ILs.

Type	$P_{1\text{-}(2,2)}$	$P_{2\text{-}(2,2)}$	$P_{3\text{-}(1,1)}$	$P_{4\text{-}(2,2)}$	bulk	bulk	crystal
T (K)	---	---	---	---	500	300	100
ρ (g/cm^3)	1.47 ± 0.41	1.53 ± 0.46	1.41 ± 0.31	1.47 ± 0.41	1.22	1.42	1.49
					---	---	---