Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Monolayer PC_5/PC_6: Promising Anode Materials for Lithium-Ion Batteries

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Table S1. Structural information (lattice constants, bong length, and bond angle) of PC_x systems.

	PC_2	PC_5	PC_6
a(Å)	3.96	4.39	6.69
b(Å)	5.27	7.86	6.69
Rc-c(Å)	1.40, 1.43	1.39, 1.43, 1.46	1.37, 1.42, 1.46
Rc-p(Å)	1.82	1.82	1.81
Rp-p(Å)	2.27	2.12	
α	86.89	88.87	90.00
β	91.70	94.31	90.00
γ	67.95	89.99	120.00

Table S2. Calculated 2D elastic constants for PC_x.

2D elastic constant (N/m)	PC_2	PC_5	PC_6
C_{11}	216.26	226.07	212.61
C_{12}	7.40	27.03	18.67
C_{22}	23.96	212.80	212.48
C_{66}	32.06	99.62	96.89

We calculate the 2D elastic constants in the Voigt notation by multiplying the vacuum layer thickness with the 3D elastic constants obtained from the strain-stress relations (*ACS Nano*, **2015**, 9, 9885). Born criteria ($C_{11}C_{22}$-C_{12}^2>0, C_{66}>0) can be satisfied for all systems, indicating that all systems are mechanical stable.

Table S3. Bader charge transfer from the adsorbed Li atom to PC_x systems.

System	PC_2	PC_5	PC_6
Charge transfer	0.89	0.89	0.91

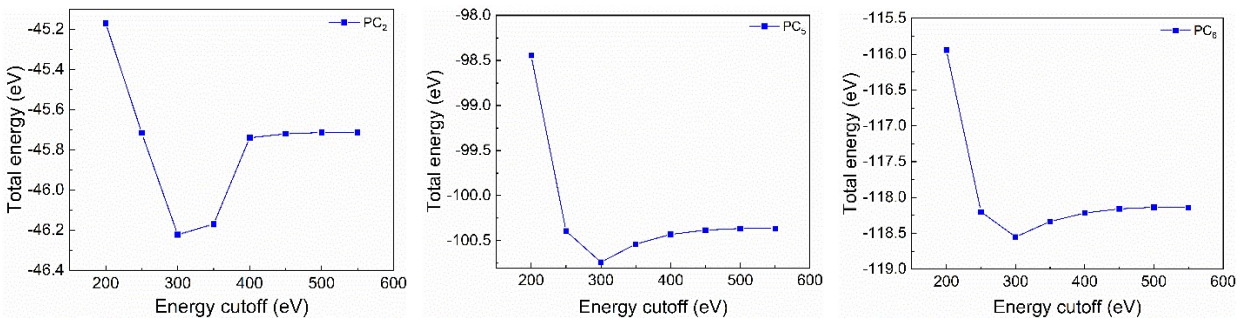


Fig. S1 Convergence test results of total energy as a function of plane-wave cut-off energy for 2D PC_2, PC_5, and PC_6.

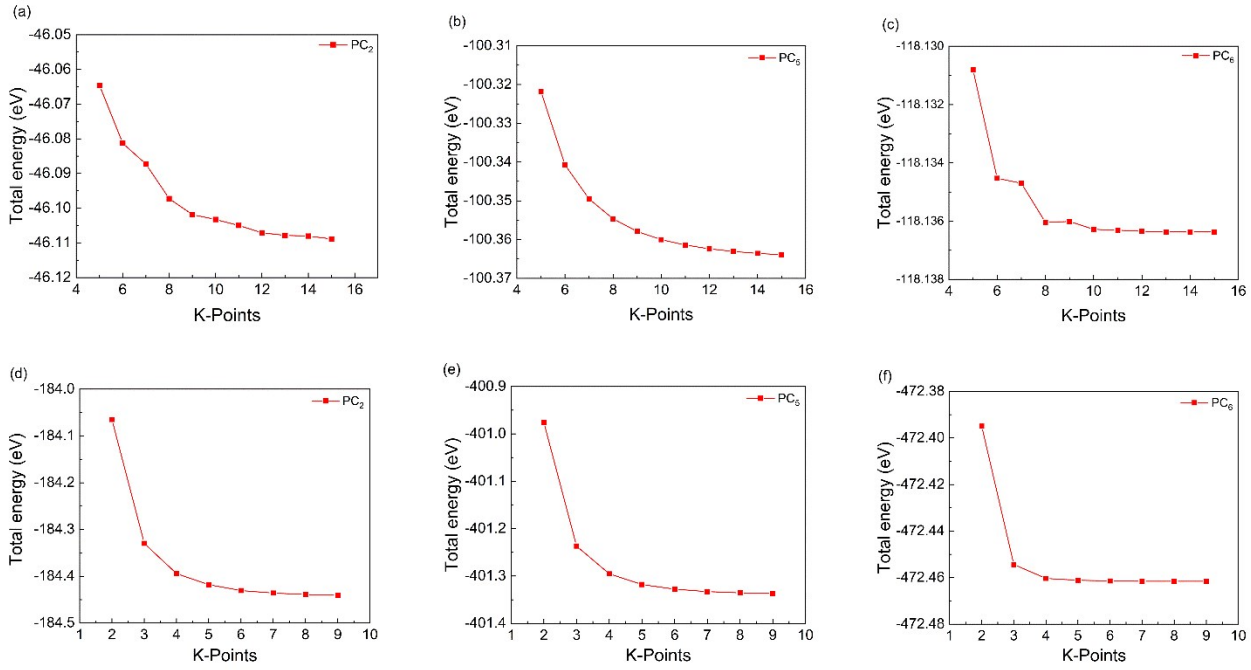


Fig. S2 Convergence test results of total energy as a function of k-points mesh size for 2D (a) PC_2, (b) PC_5, and (c) PC_6 unit cell and (d) PC_2, (e) PC_5, and (f) PC_6 2×2×1 supercell.

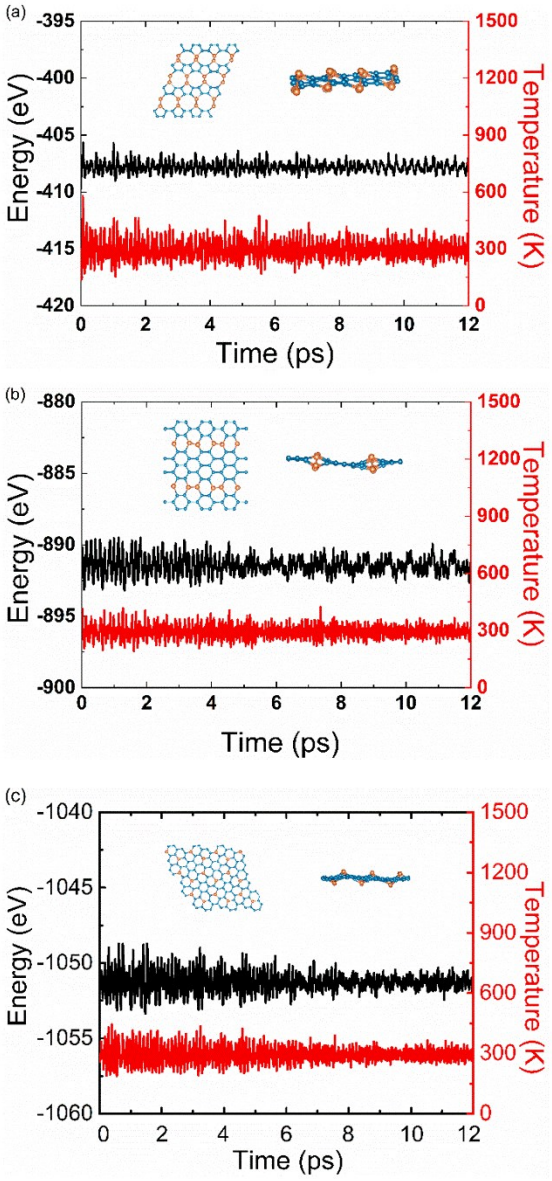


Fig. S3 Total energy and temperature as a function of time (a) PC_2, (b) PC_5, and (c) PC_6 during the AIMD simulation (inset: the structure of after 12 ps AIMD simulation. P and C atoms are distinguished by orange and blue color, respectively).

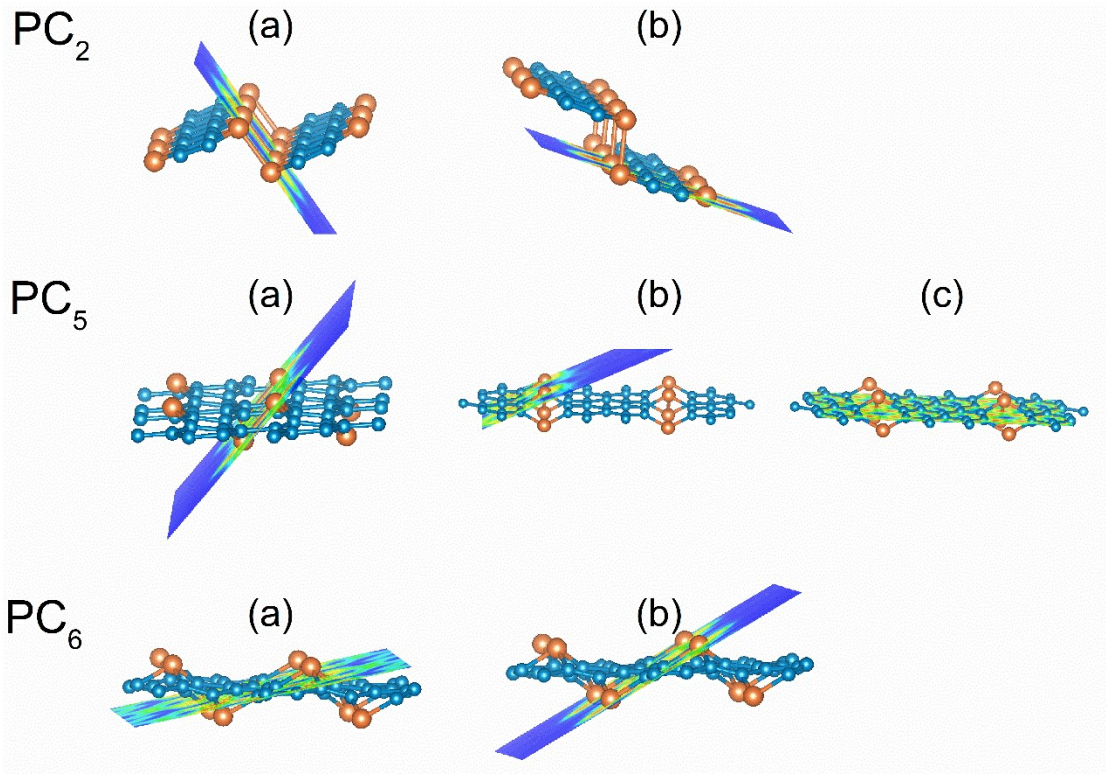
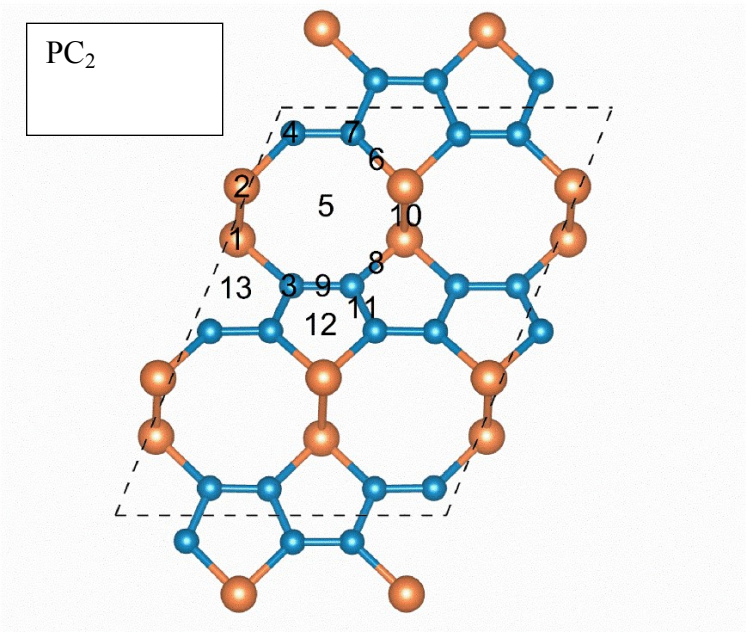
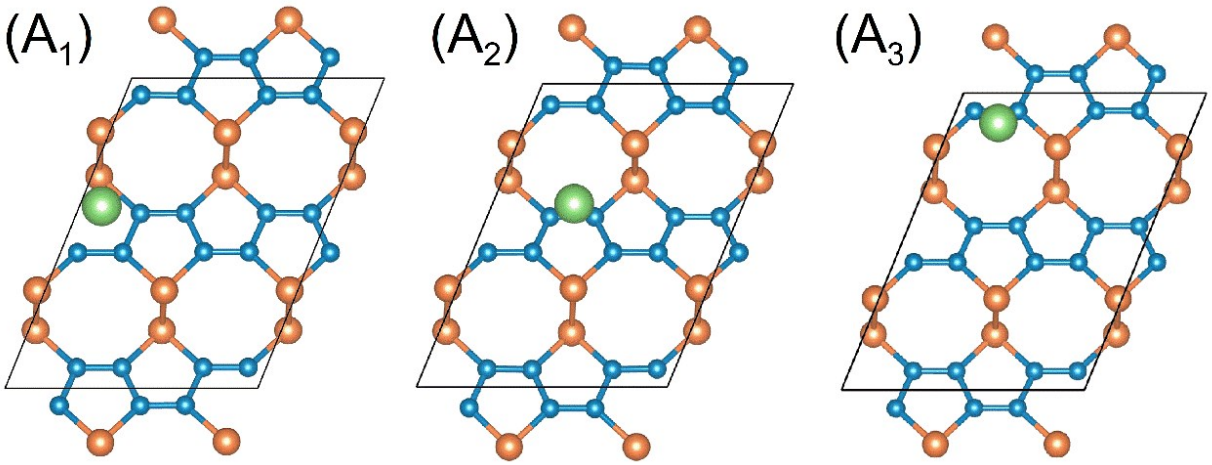


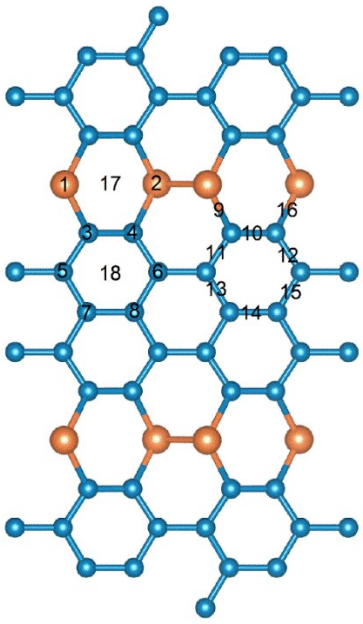
Fig. S4 Schematic illustration of the crystallographic orientation direction along planes containing specified bonding atoms of PC_x system. The P atoms and C atoms are distinguished by orange and blue color, respectively.

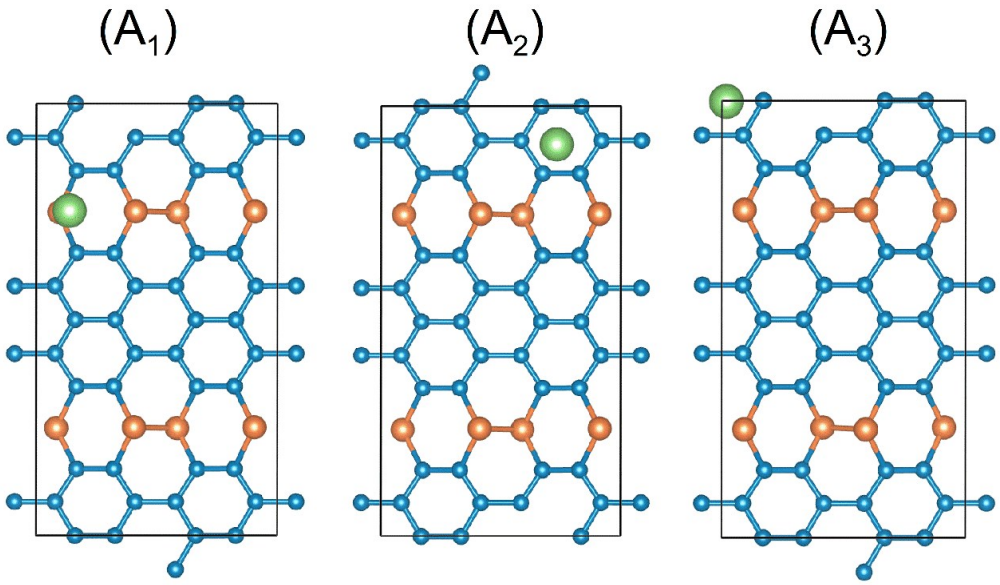




$\Delta E_1 = -0.93eV$ $\Delta E_2 = -0.87eV$ $\Delta E_3 = -0.43eV$

PC_5





$\Delta E_1 = -0.83eV$ $\Delta E_2 = -0.67eV$ $\Delta E_3 = -0.57eV$

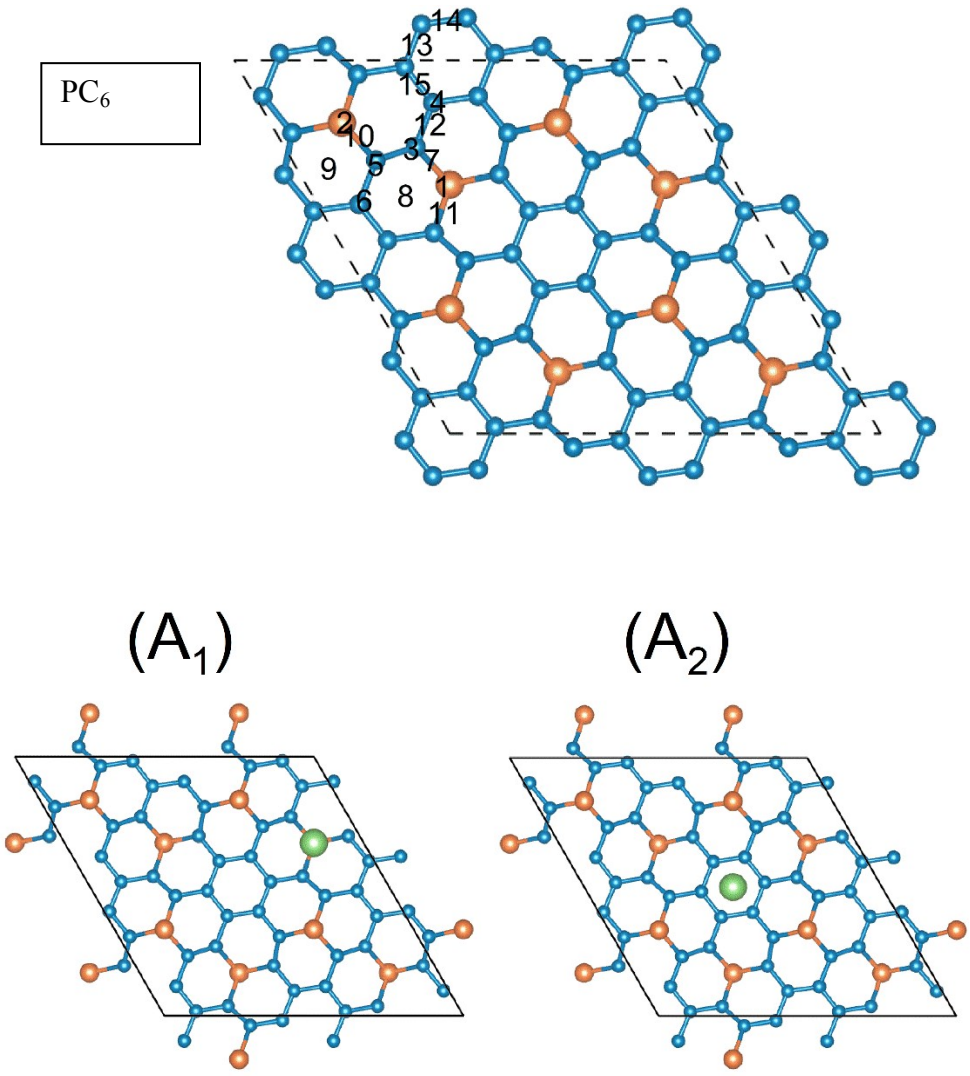
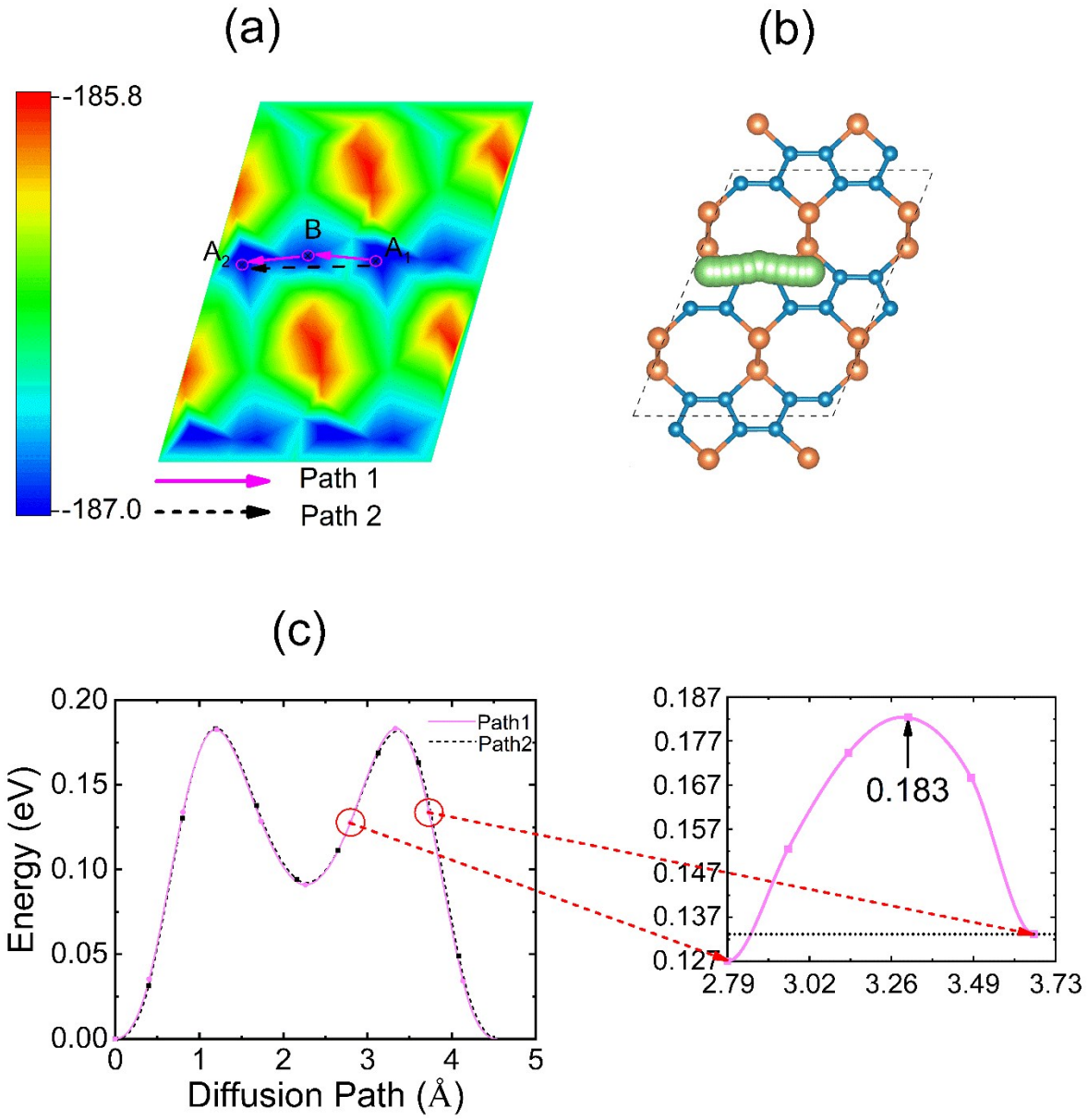


Fig. S5 Geometric structure of possible adsorption sites on PC_2, PC_5, and PC_6 monolayer. The adsorption energy values for Li atom adsorbed on each site are listed below the corresponding figures. The Li, P, and C atoms are distinguished by green, orange, and blue color, respectively.

PC_2


(a)
(b)
-185.8
-187.0
A2
B
A1
Path 1
Path 2
(c)
Energy (eV)
Diffusion Path (Å)
Path1
Path2
0.183

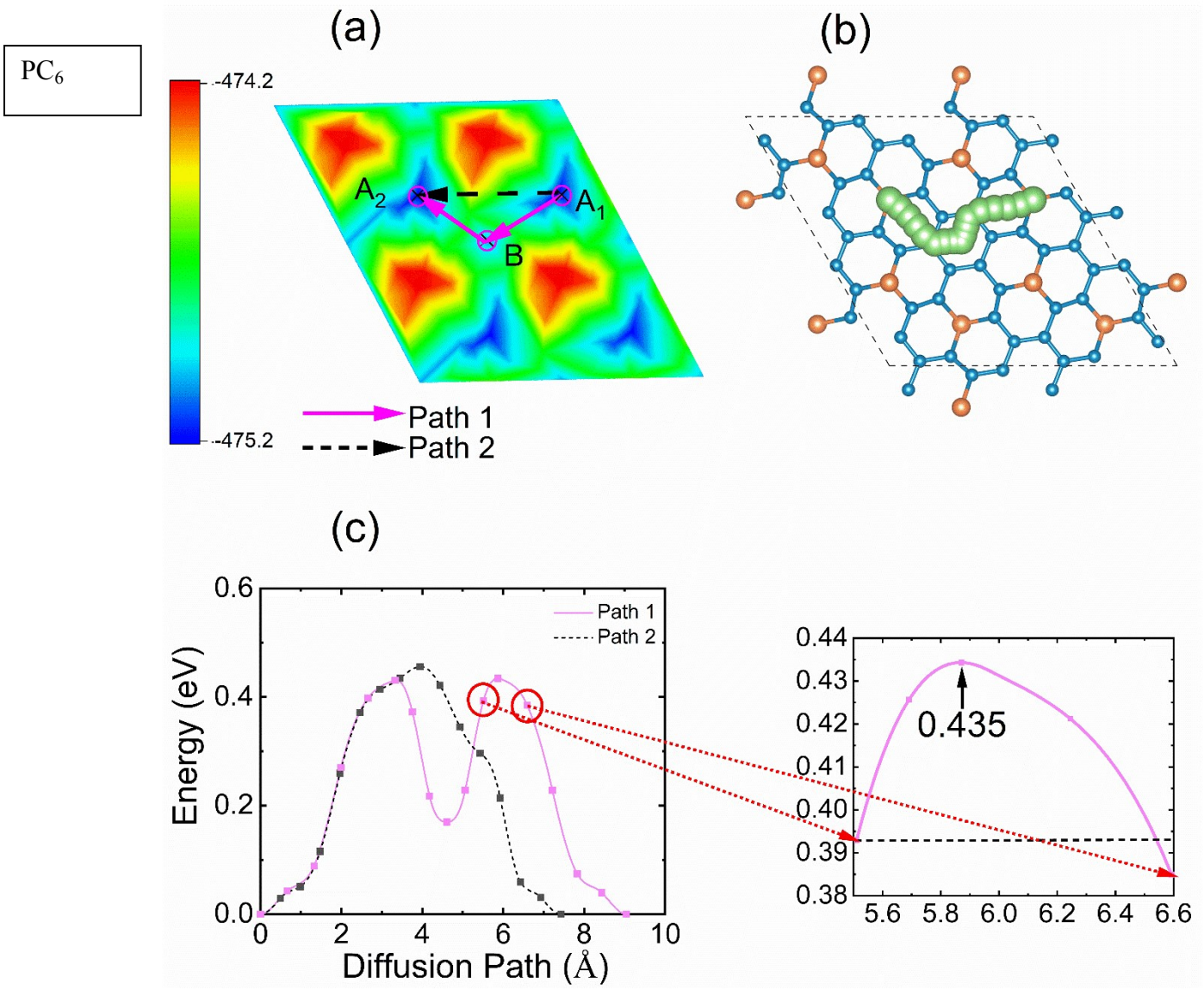


Fig. S6 (a) Schematic illustration of three possible paths for Li diffusion on the PC_2 and PC_6 monolayer based on the color-filled contour plots of adsorption energy of single Li atom on the surface; (b) Diffusion of single adatom over PC_2 and PC_6 monolayer through the more favorable pathways (path 1). (c) The corresponding diffusion barrier diagrams of Li−PC_2 and Li-PC_6 monolayer. Enlarged figures near the maximum energy along Path 1 are also shown. The Li, P, and C atoms are distinguished by green, orange, and blue color, respectively.

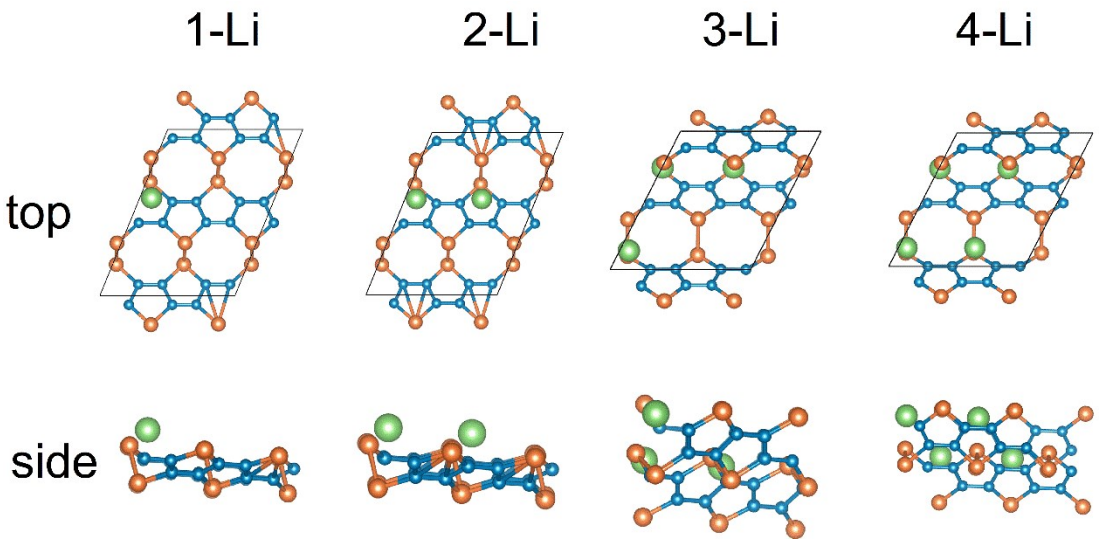


Fig. S7 Optimized structure of different numbers of Li-intercalated PC_2 monolayers ($P_8C_{16}Li$, $P_8C_{16}Li_2$, $P_8C_{16}Li_3$ and $P_8C_{16}Li_4$) from top and side view. The Li, P, and C atoms are distinguished by green, orange, and blue color, respectively.

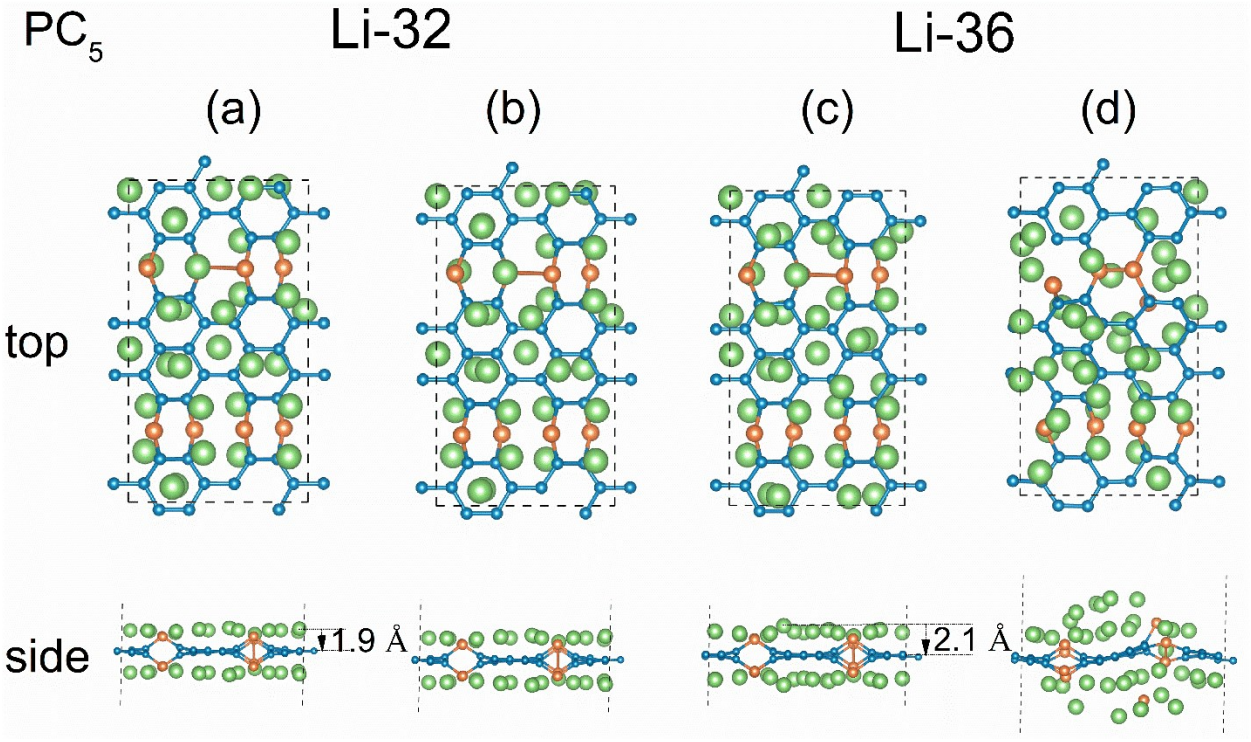


Fig. S8 Optimized structures of different Li-intercalated PC_5 monolayer (2×2 supercell), including $P_8C_{40}Li_{32}$ (a) before and (b) after AIMD simulations, and $P_8C_{40}Li_{36}$ (c) before and (d) after AIMD simulations (300 K). The Li, P, and C atoms are distinguished by green, orange, and blue color, respectively.

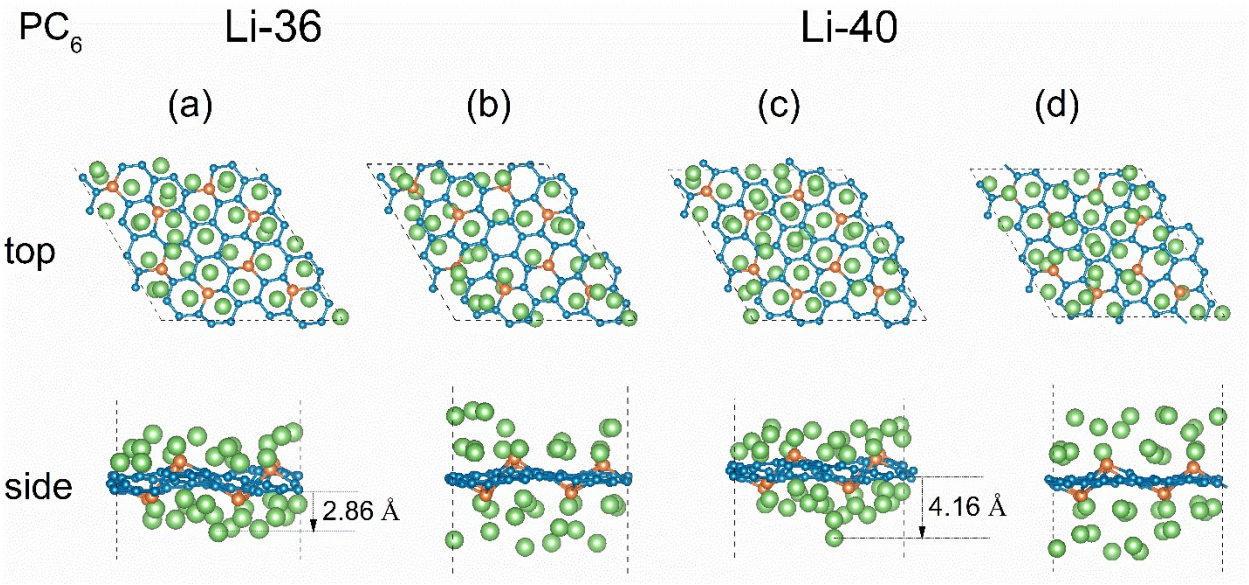


Fig. S9 Optimized structures of different Li-intercalated PC_6 monolayers (2×2 supercell), including $P_8C_{48}Li_{36}$ (a) before and (b) after AIMD simulations, and $P_8C_{48}Li_{40}$ (c) before and (d) after AIMD simulations (300 K). The Li atoms, P atoms and C atoms are distinguished by green, orange, and blue color, respectively.

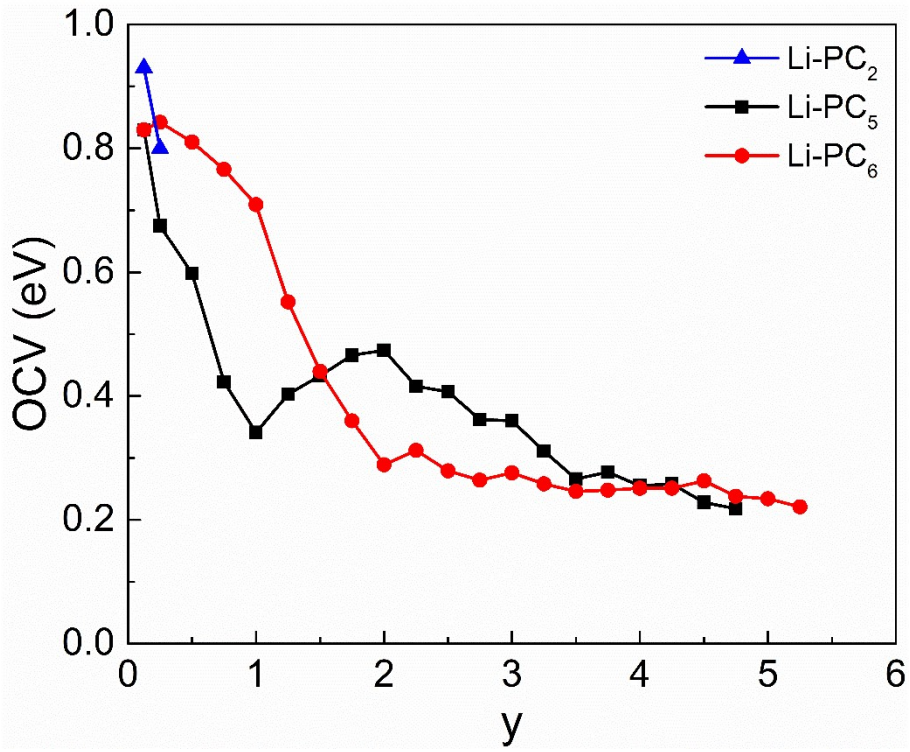


Fig. S10 Open-circuit voltage (OCV) as a function of adatom content y for PC_2, PC_5 and PC_6.