

Supplementary information for
Modulating the Band Gaps, Binding Energetics, and Diffusion Kinetics of Black and Blue Phosphorene via K⁺ Adsorption: A DFT Study

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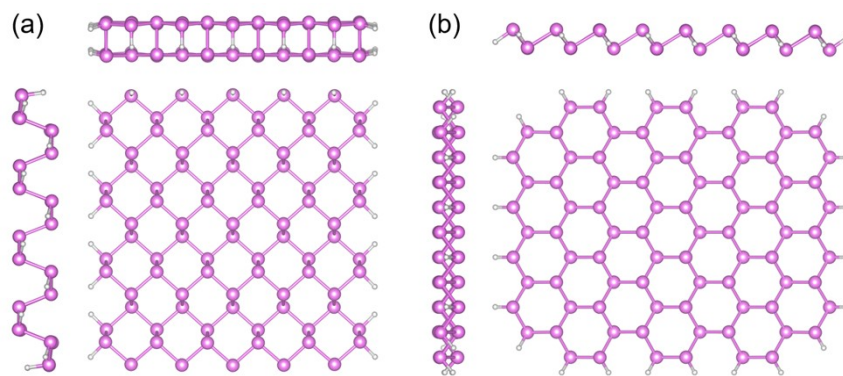


Figure S1. The H-terminated (a) 2D-BlackP and (b) 2D-BlueP models used in this study. Spheres in violet, pink, and white represent K^+ , phosphorus, and hydrogen, respectively. The image illustrates that both armchair and zigzag edges are fully passivated with hydrogen atoms (white spheres) to ensure a chemically stable and representative cluster for non-periodic calculations.

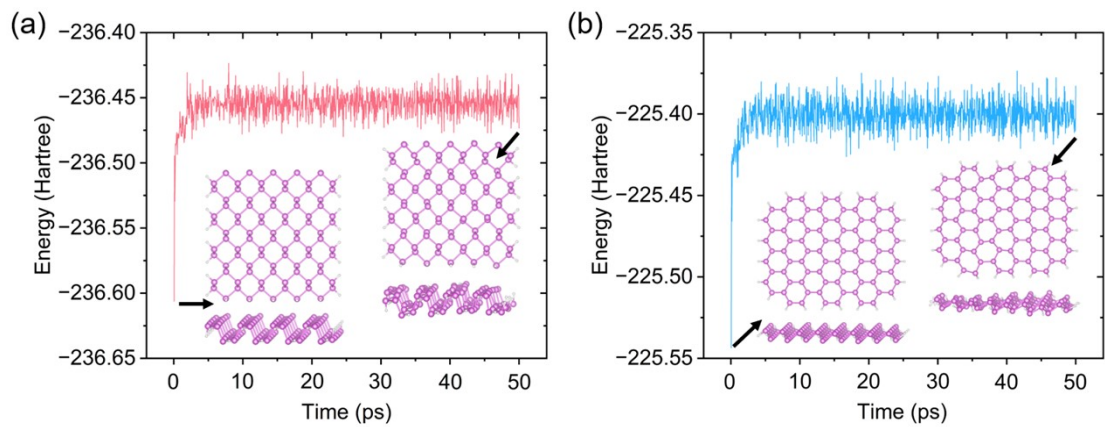


Figure S2. Total energy profiles of the (a) 2D-BlackP and (b) 2D-BlueP nanosheets as a function of simulation time obtained from AIMD simulations. The initial configurations at 0 ps and the final configurations at 50 ps are embedded in each panel.

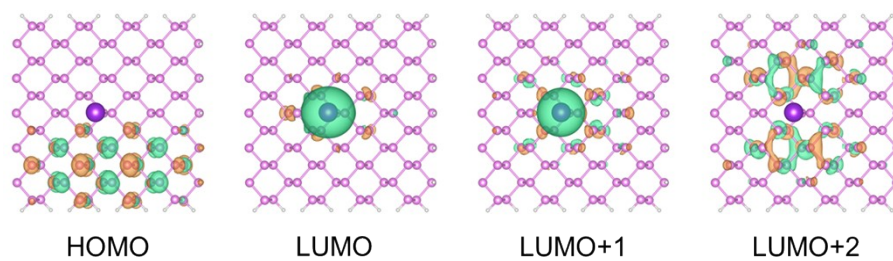


Figure S3. Spatial localization of frontier molecular orbitals in $\text{K}^+@2\text{D-BlackP}$ complex at larger separation distances: $H = 0.4$ nm. All orbitals predominantly localized on the ion correspond to the p-orbitals of K^+ . The molecular orbital is plotted for iso-values of ± 0.02 atomic units, with orange and green denoting opposite signs. Spheres in violet, pink, and white represent K^+ , phosphorus, and hydrogen, respectively.

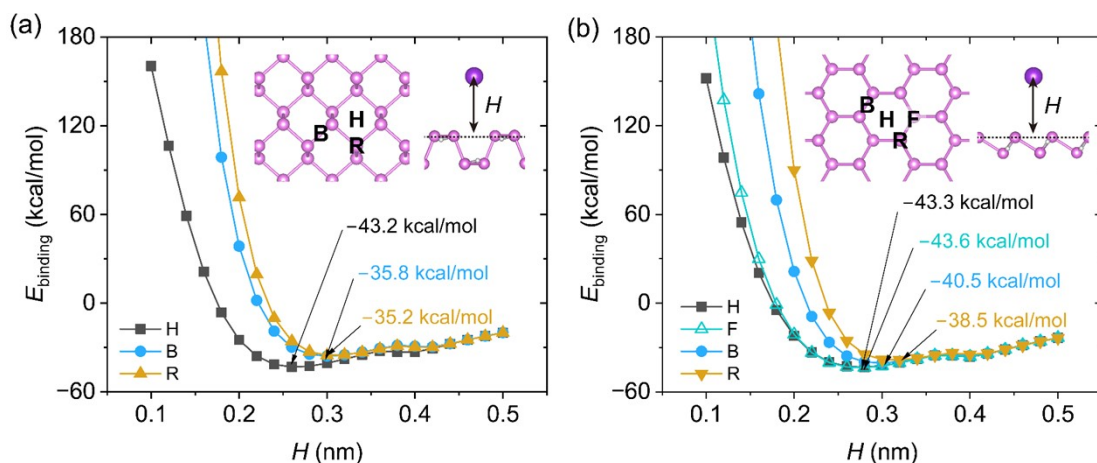


Figure S4. Binding energies of (a) K^+ @2D-BlackP and (b) K^+ @2D-BlueP complexes at different adsorption sites. For both K^+ @2D-BlackP and K^+ @2D-BlueP, three geometrically distinct adsorption sites were considered: (1) above the center of a P hexagon (H site), (2) above the midpoint of a P–P bond (B site), and (3) above a ridge P atom (R site). In addition, for the K^+ @2D-BlueP complex, a fourth adsorption site was examined, corresponding to K^+ positioned above a P atom along the furrow (F site).

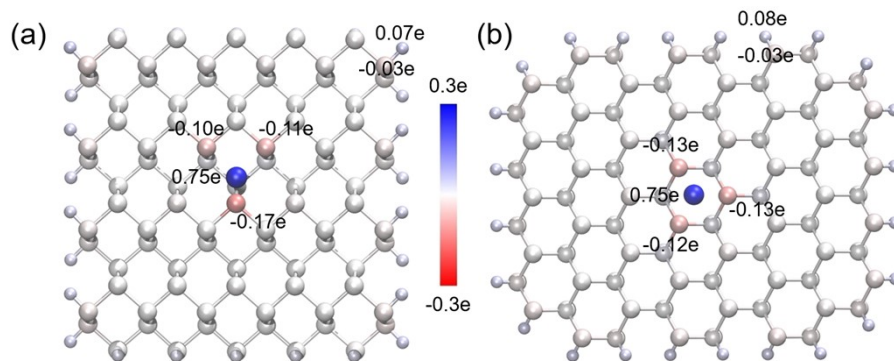


Figure S5. Charge distributions of (a) $K^+@2D\text{-BlackP}$ and (b) $K^+@2D\text{-BlueP}$ complexes at the minimum relative energy point.

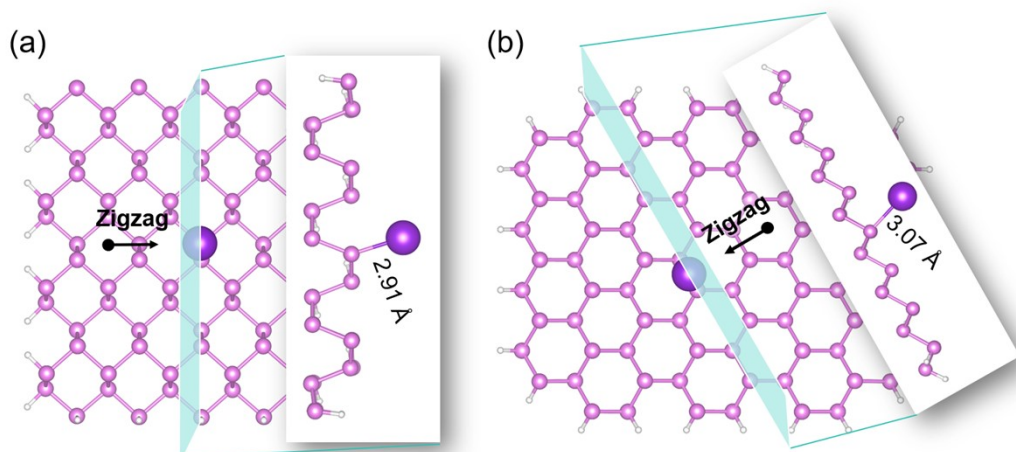


Figure S6. Structural configurations at the maximum relative energy point for K^+ ion on the (a) 2D-BlackP and (b) 2D-BlueP sheets along the Zigzag diffusion path. The cross-sectional views highlight the distance between the K^+ cation and the nearest-neighbor phosphorus (P) atoms, illustrating the structural basis for the differing migration barriers.

Table S1. Energetics of various ions adsorbed on black phosphorene.

Cations	Binding energy at hollow site (kcal/mol)	Lowest diffusion energy barrier (eV)
K ⁺ (Current study)	-43.2	0.09
Li ⁺ ^{a)}	-67.9	0.31
Na ⁺ ^{a)}	-54.6	0.12
Mg ²⁺ ^{a)}	-250.6	0.68
Ca ²⁺ ^{a)}	-187.2	0.35

^{a)} data taken from reference [*Int. J. Mol. Sci.* 2024, 25, 11841].