

Supplementary material for

**A DFT Study of Band Gap Tuning in 2D Black Phosphorus via Li⁺,
Na⁺, Mg²⁺, Ca²⁺ Ions**

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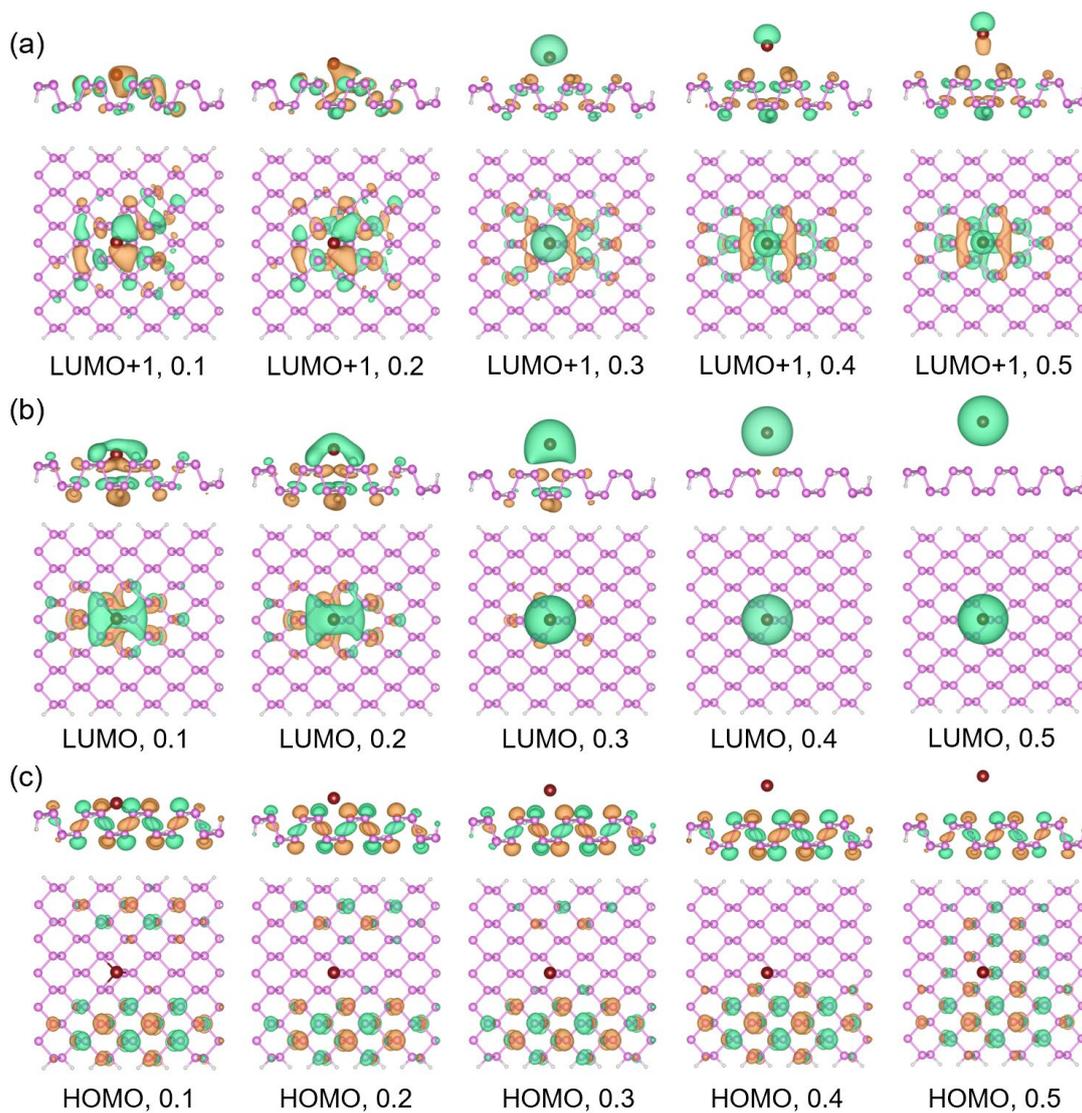


Figure S1. Spatial localization of frontier molecular orbitals for (a) LUMO+1 (b) LUMO, and (c) HOMO in Li^+ @2D-BP complex at varying separation distances (H , in nm). The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in red, pink, and white represent Li^+ , phosphorus, and hydrogen respectively.

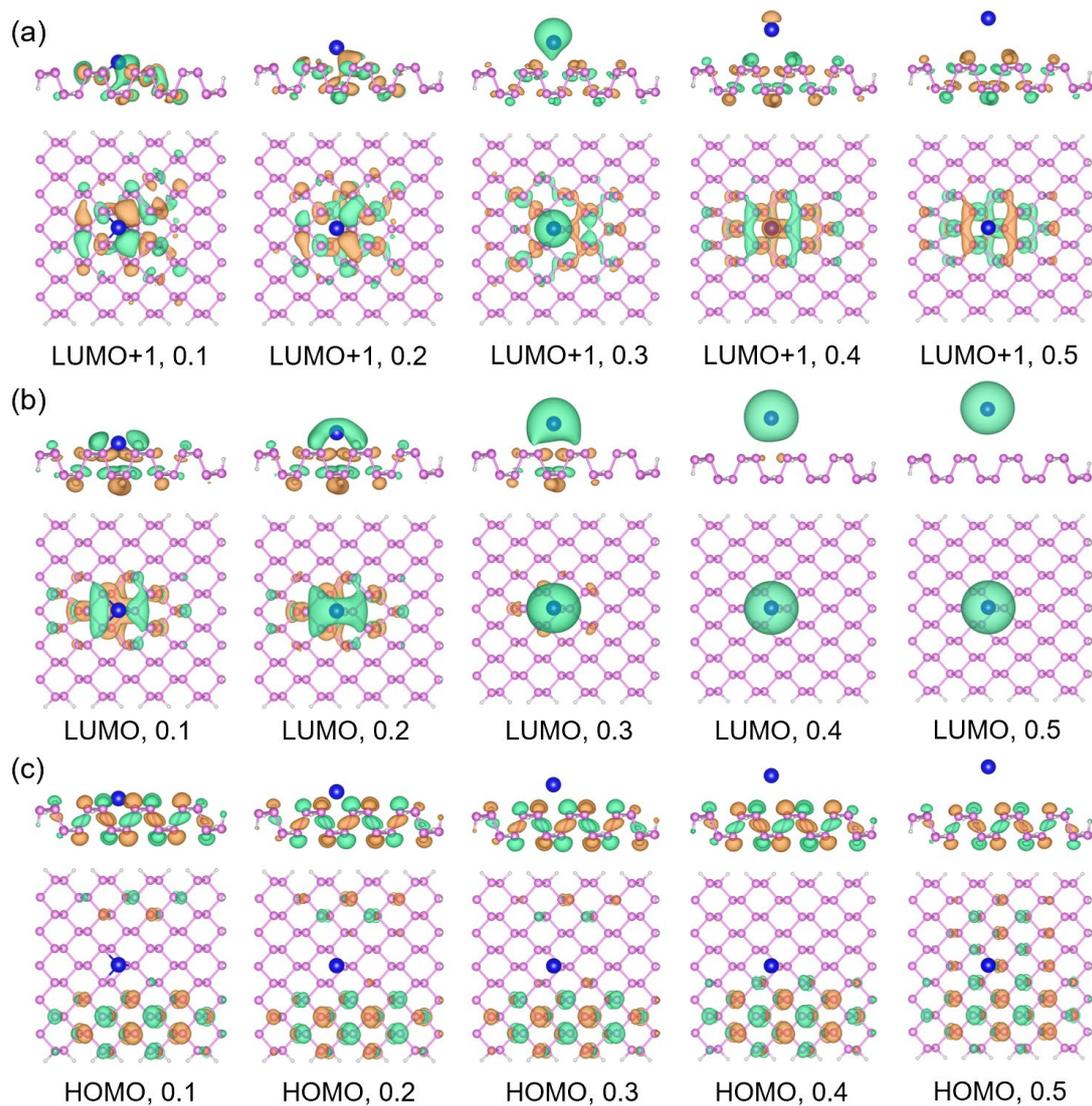


Figure S2. Spatial localization of frontier molecular orbitals for (a) LUMO+1 (b) LUMO, and (c) HOMO in $\text{Na}^+@2\text{D-BP}$ complex at varying separation distances (H , in nm). The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in blue, pink, and white represent Na^+ , phosphorus, and hydrogen respectively.

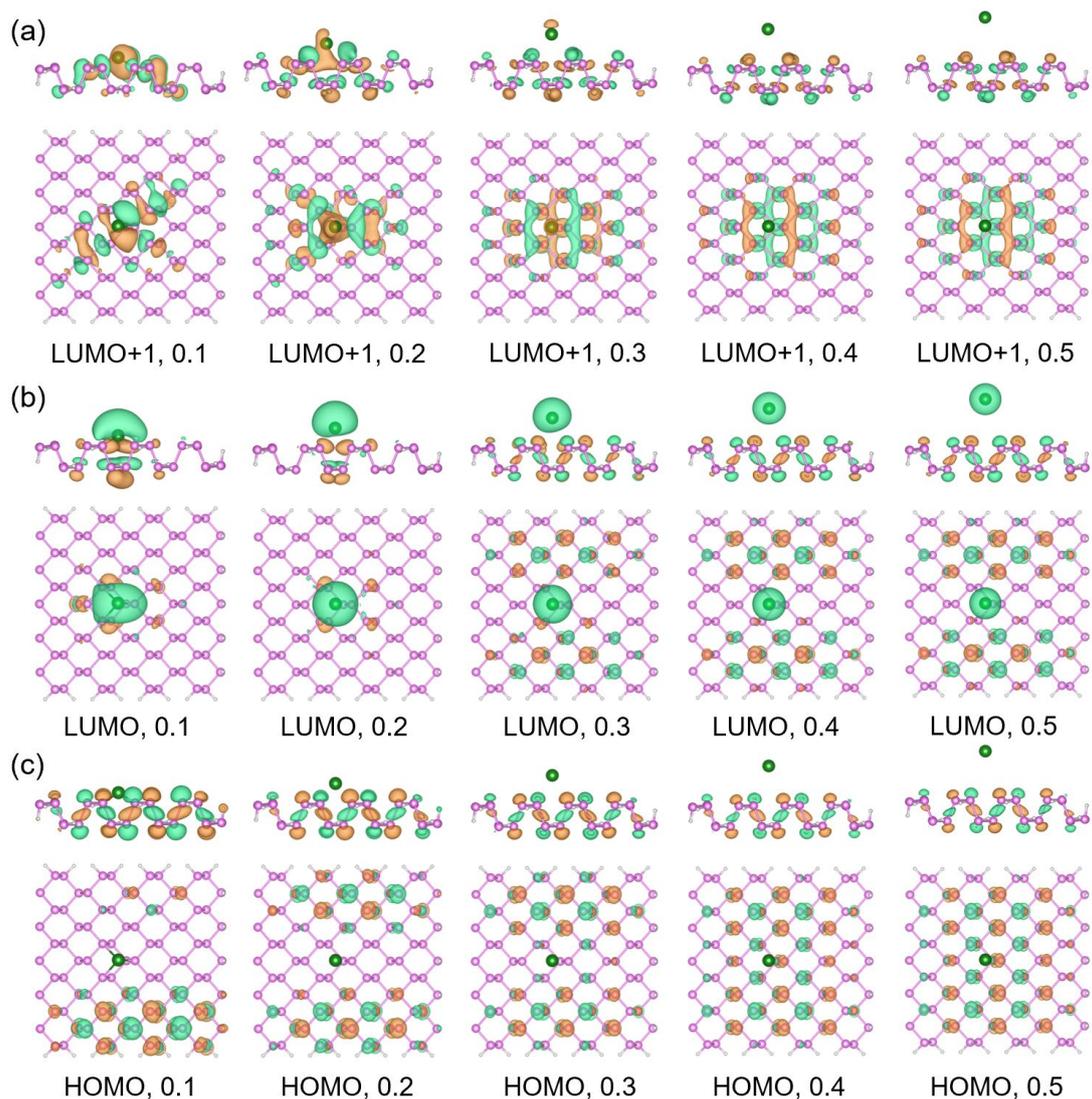


Figure S3. Spatial localization of frontier molecular orbitals for (a) LUMO+1 (b) LUMO, and (c) HOMO in $\text{Mg}^{2+}@2\text{D-BP}$ complex at varying separation distances (H , in nm). The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in green, pink, and white represent Mg^{2+} , phosphorus, and hydrogen respectively.

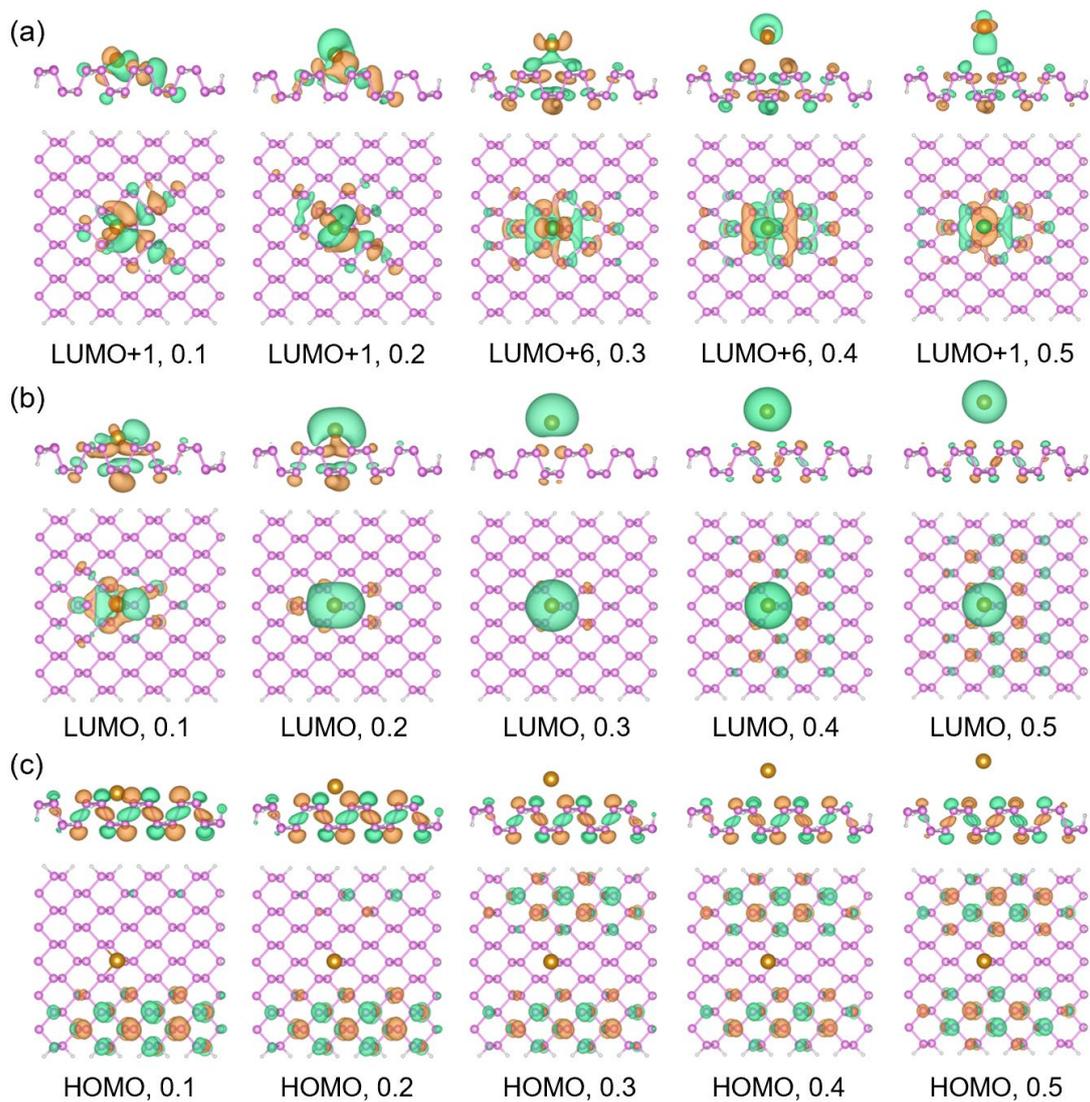


Figure S4. Spatial localization of frontier molecular orbitals for (a) LUMO+1/LUMO+6 (b) LUMO, and (c) HOMO in $\text{Ca}^{2+}@2\text{D-BP}$ complex at varying separation distances (H , in nm). The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in orange, pink, and white represent Ca^{2+} , phosphorus, and hydrogen respectively.

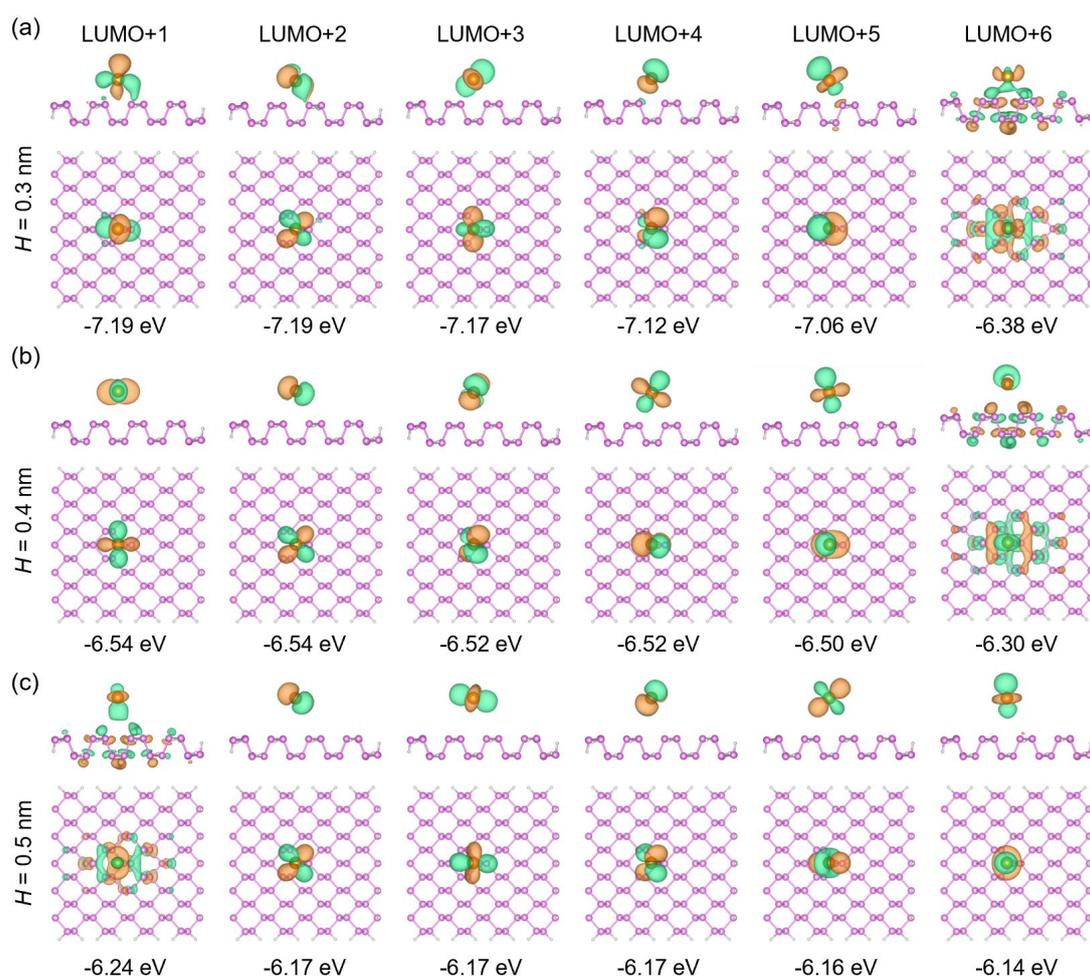


Figure S5. Spatial localization of frontier molecular orbitals in $\text{Ca}^{2+}@2\text{D-BP}$ complex at larger separation distances: (a) $H = 0.3$ nm, (b) $H = 0.4$ nm and (c) $H = 0.5$ nm. Corresponding energy levels are provided below each image. All orbitals predominantly localized on the ion correspond to the d-orbitals of Ca^{2+} . The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in orange, pink, and white represent Ca^{2+} , phosphorus, and hydrogen respectively.

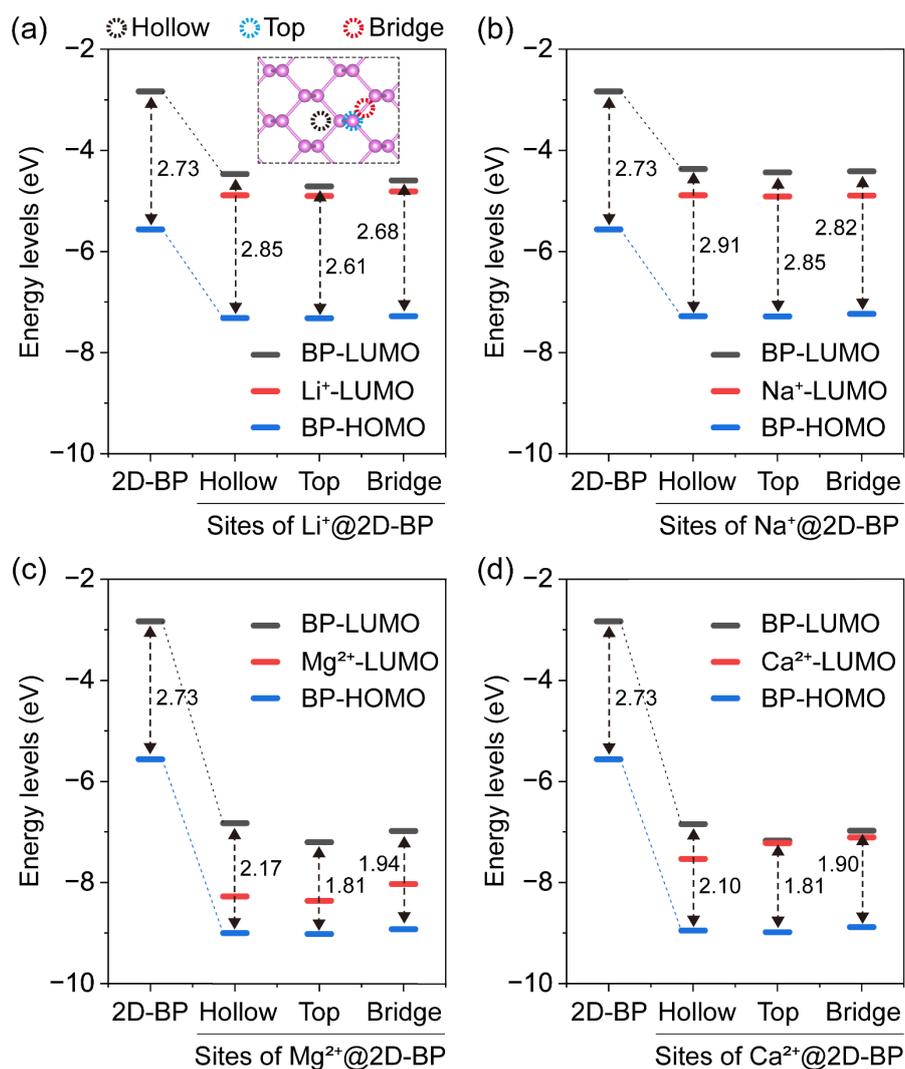


Figure S6. Evolution of frontier molecular orbital energy levels in (a) $\text{Li}^+@2\text{D-BP}$, (b) $\text{Na}^+@2\text{D-BP}$, (c) $\text{Mg}^{2+}@2\text{D-BP}$, and (d) $\text{Ca}^{2+}@2\text{D-BP}$ complexes at the potential energy minimum across different adsorption sites (hollow, top, and bridge, as illustrated in (a)). Upon the adsorption of a cation into the system, the energy levels of both the HOMO and LUMO of 2D-BP (denoted as BP-HOMO and BP-LUMO) undergo a significant decrease.

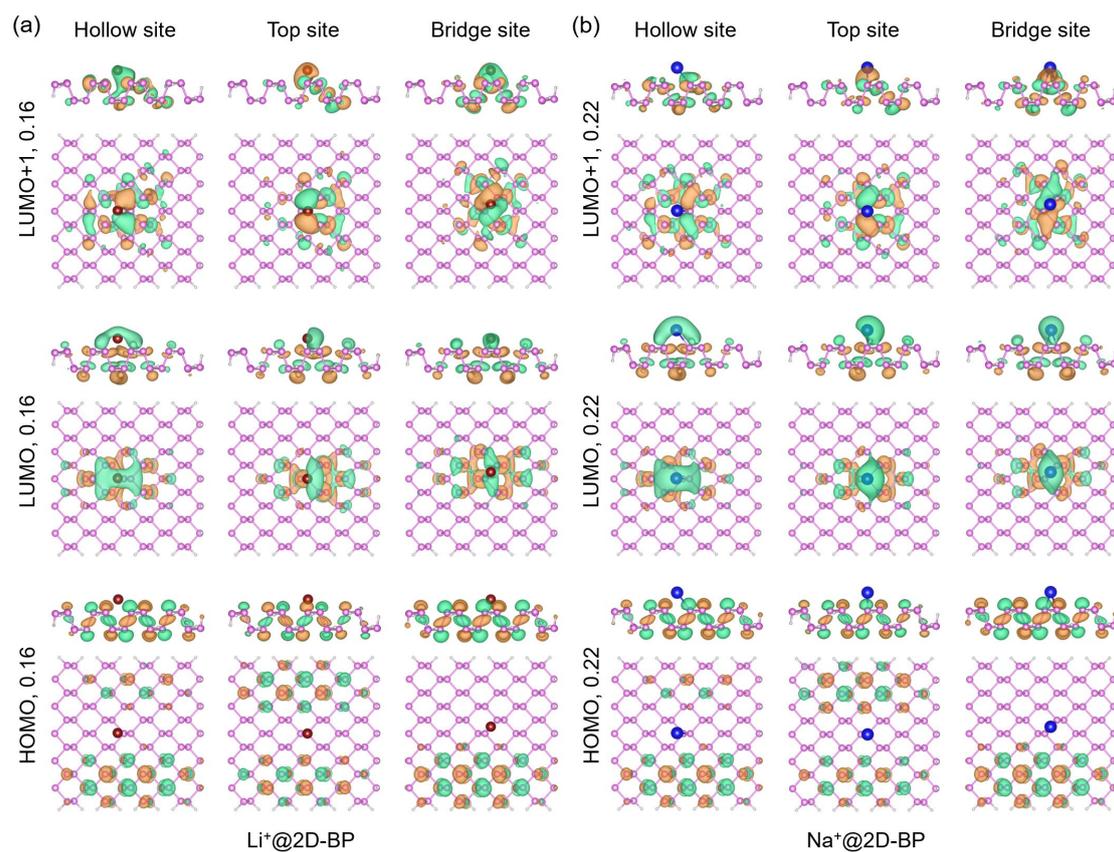


Figure S7. Spatial localization of frontier molecular orbitals in (a) $\text{Li}^+@2\text{D-BP}$ and (b) $\text{Na}^+@2\text{D-BP}$ complexes at the potential energy minimum across different adsorption sites (hollow, top, and bridge). Corresponding separation distances (H , in nm) are provided to the left of each image. The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in red, blue, pink, and white represent Li^+ , Na^+ , phosphorus, and hydrogen respectively.

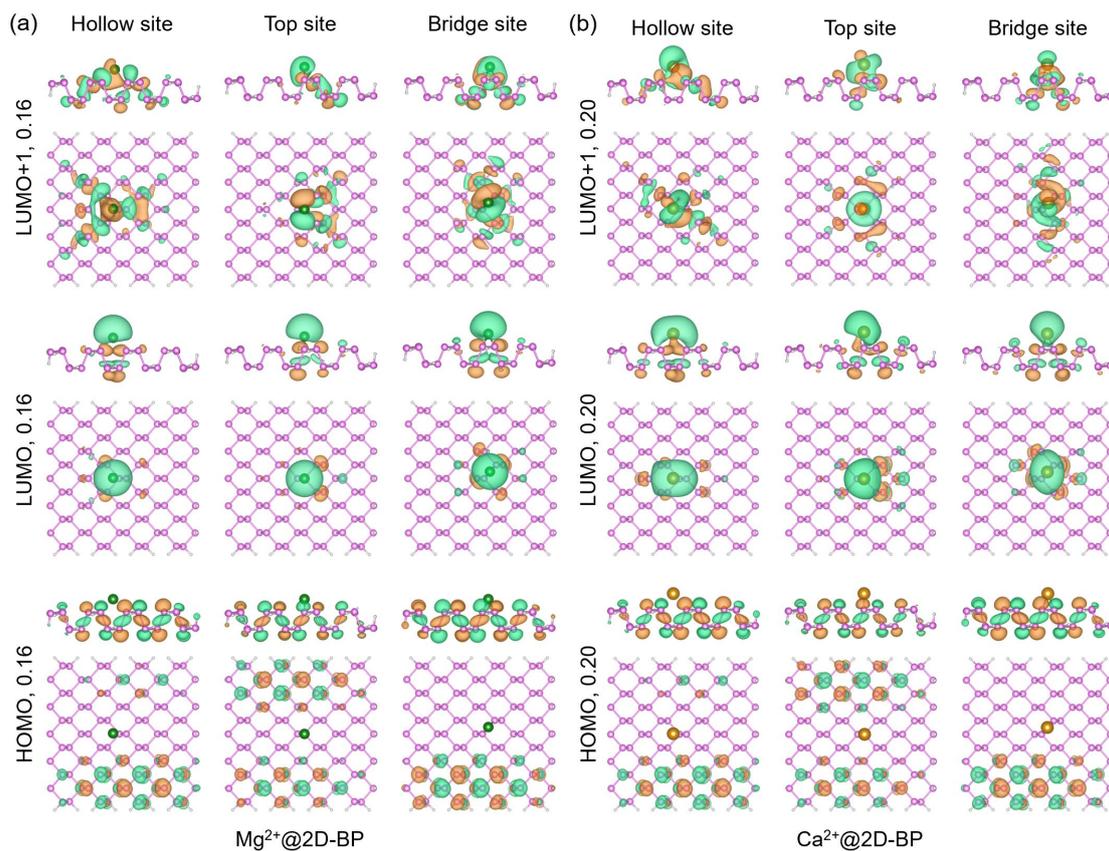


Figure S8. Spatial localization of frontier molecular orbitals in (a) $\text{Mg}^{2+}@2\text{D-BP}$ and (b) $\text{Ca}^{2+}@2\text{D-BP}$ complexes at the potential energy minimum across different adsorption sites (hollow, top, and bridge). Corresponding separation distances (H , in nm) are provided to the left of each image. The molecular orbital is plotted for iso-values of ± 0.02 atomic units with orange and green denoting opposite signs. Spheres in green, orange, pink, and white represent Mg^{2+} , Ca^{2+} , phosphorus, and hydrogen respectively.