

Supporting Information - Potassium Doping-induced Variations on Geometric and Photoelectric Properties of MAPbI₃ Perovskite and MAPbI₃/TiO₂ Junction[†]

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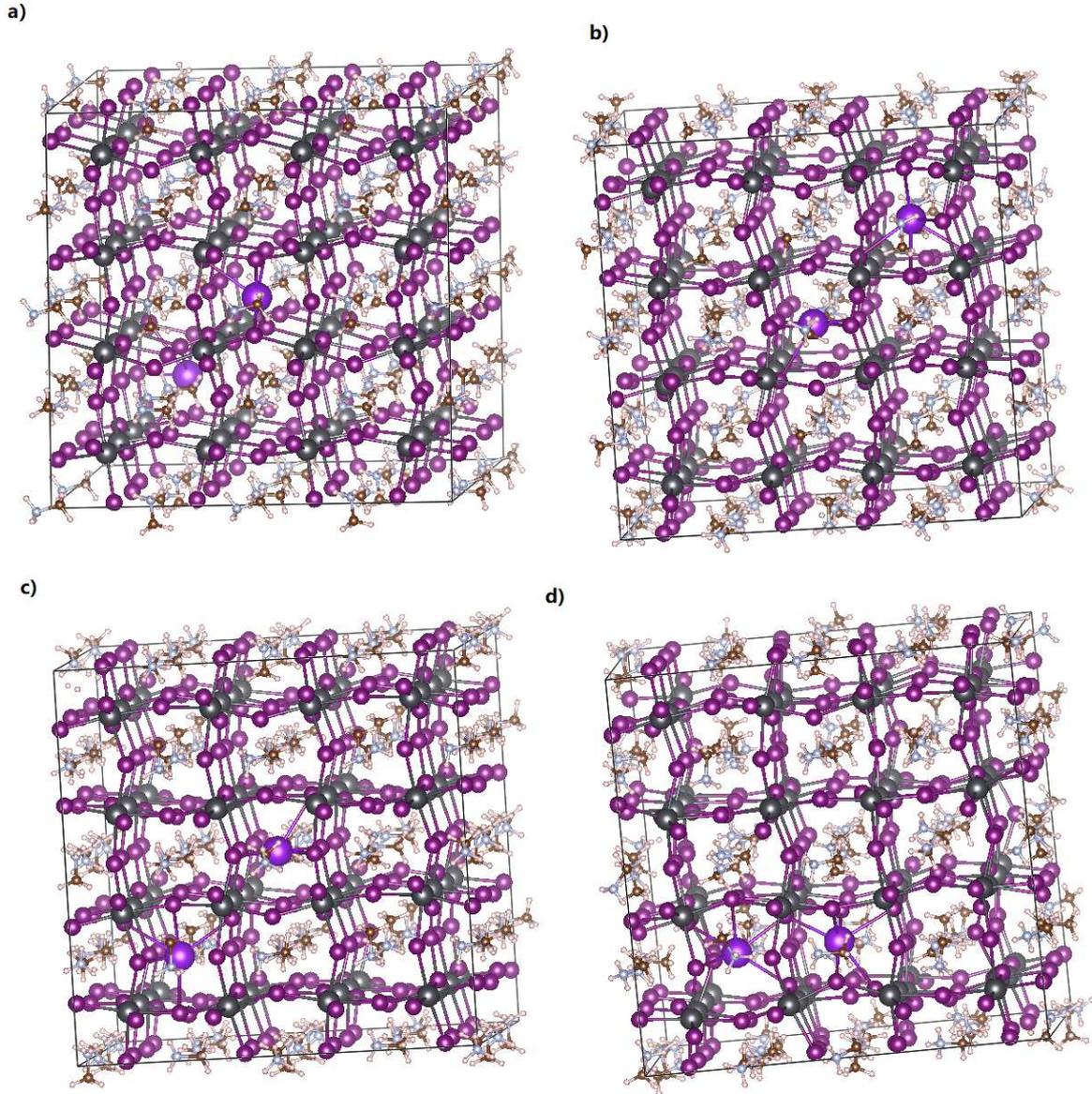


Fig.S 1 Optimized structures of SD-MAPbI₃ slabs: a) two K⁺ located well separately (isolated), b) common-vertexed (vertical), c) common-edged (coplanar) and d) directly face-to-face adjacent

Table 1 Band gaps and conduction band offsets (in eV) for bulk MAPbI₃, TiO₂ and the junction with K⁺ doped inside perovskite layers

Dopants	$E_{cb, don.}$	$E_{cb, acc.}$	ΔV_{mix}	$E_{cb} - V_{don.}$	$E_{cb} - V_{acc.}$	Band Offset
Inside K ⁺	0.932	0.763	8.096	11.621	19.476	0.242

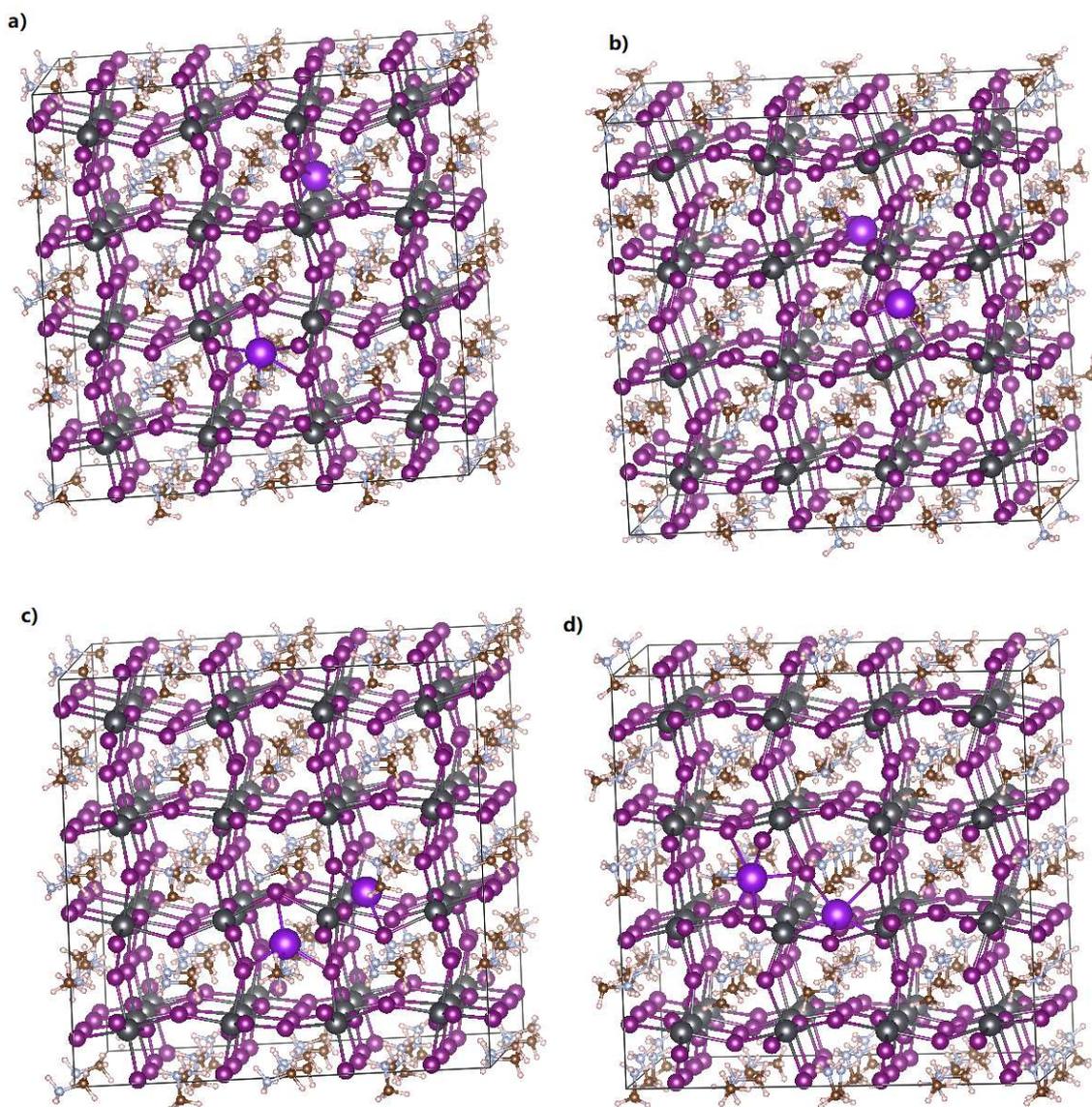


Fig.S 2 Optimized structures of ID-MAPbI₃ slabs: a) two K^+ located well separately (isolated), b) common-vertexed (vertical), c) common-edged (coplanar) and d) directly face-to-face adjacent

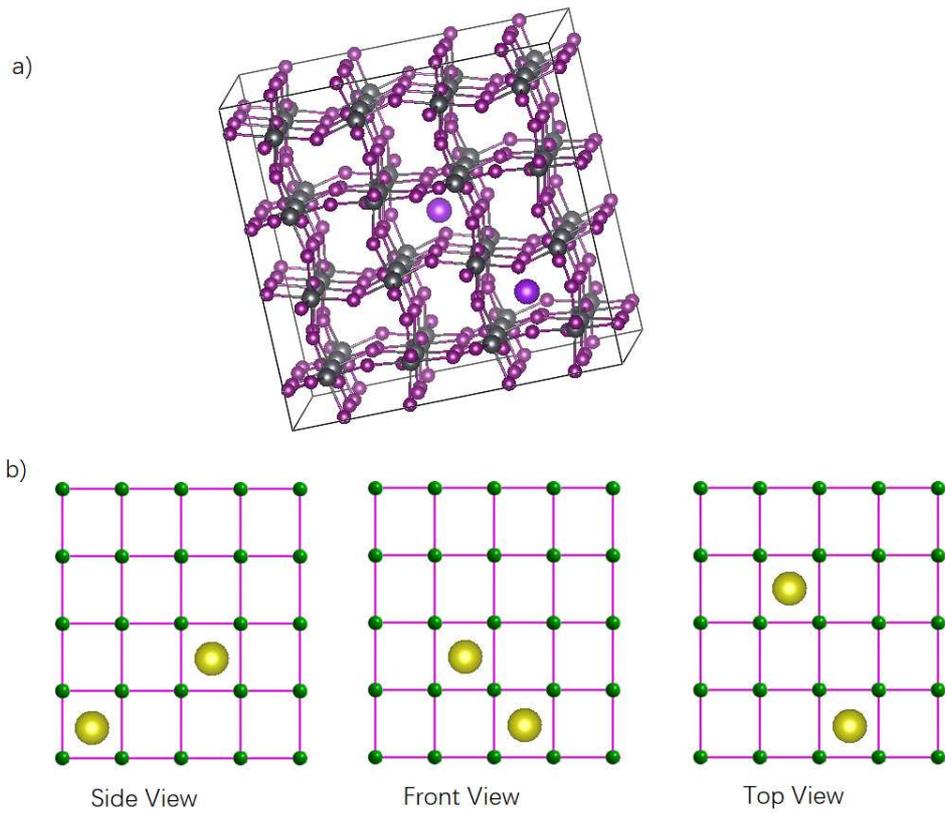


Fig.S 3 The *a*) topological structure and its *b*) three views that make two K^+ doped Pb-I cube neither adjacent directly nor coplanar.

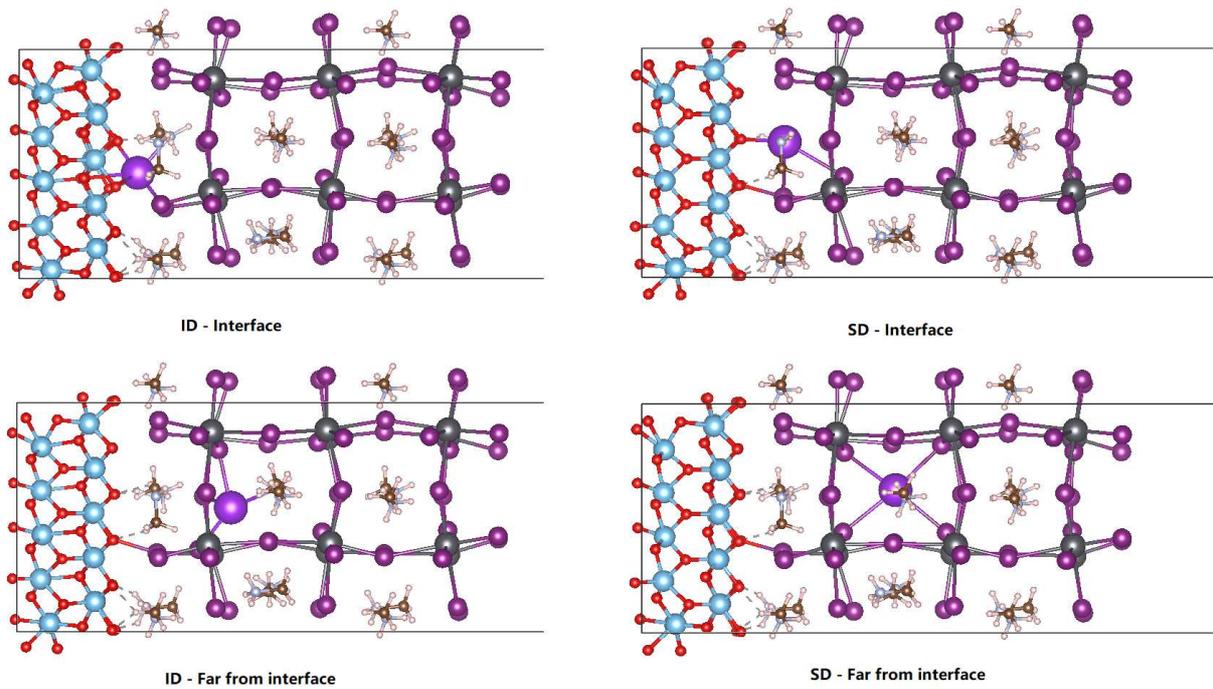


Fig.S 4 Schematic diagram of $MAPbI_3/TiO_2$ heterojunction with different doping manners.

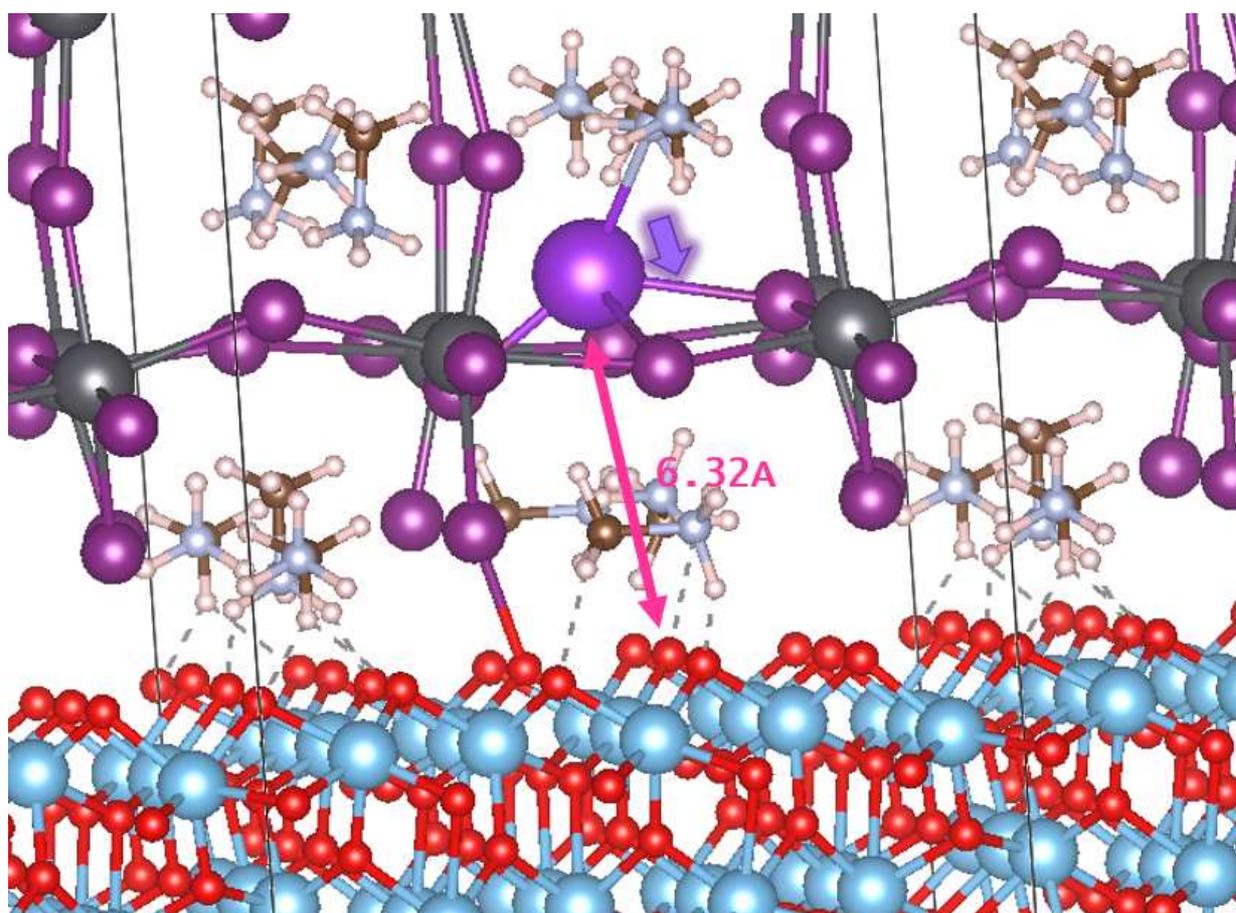


Fig.S 5 Geometric structure for ID-K⁺ set far from MAPbI₃/TiO₂ junction. The purple arrow represents the direction of movement of K⁺ ions during the lattice relaxation.

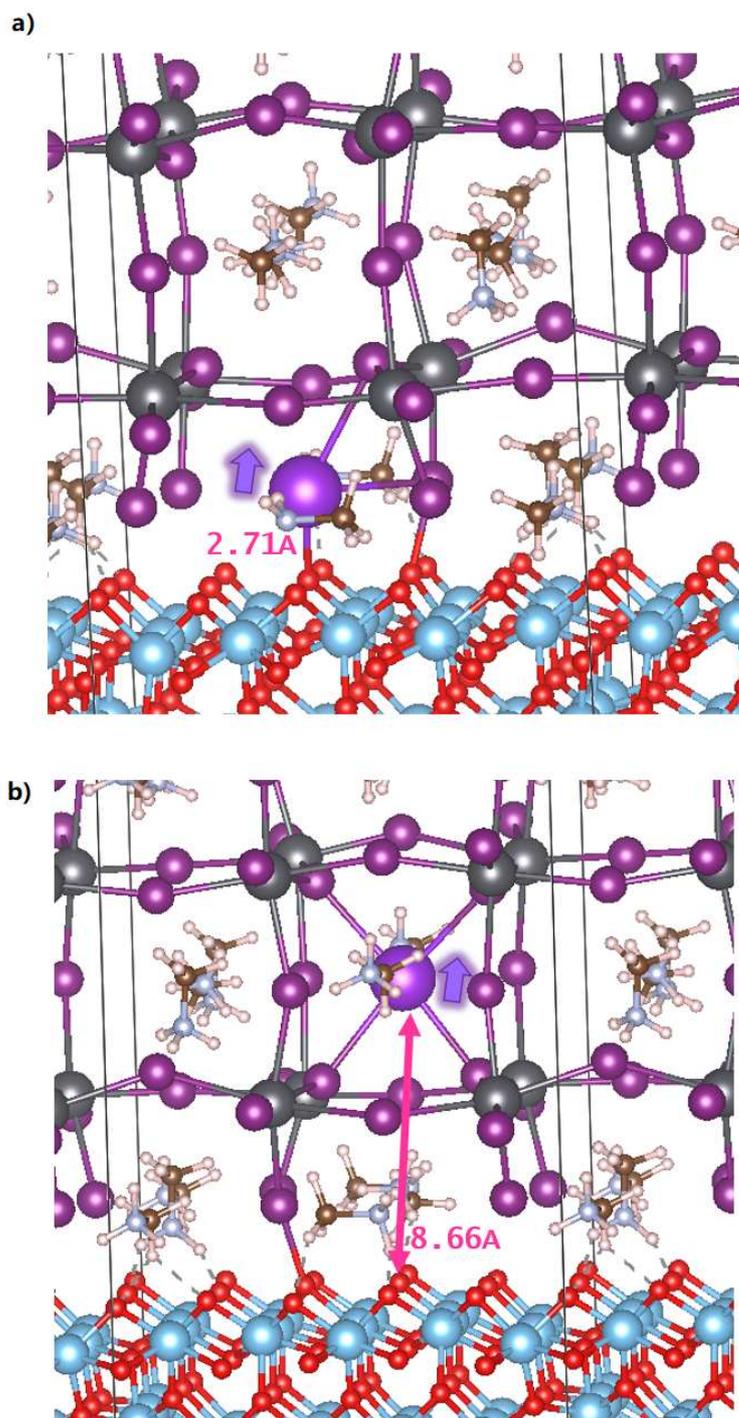


Fig.S 6 Geometric structure for SD-K^+ *a)* near or *b)* far from the $\text{MAPbI}_3/\text{TiO}_2$ junction.

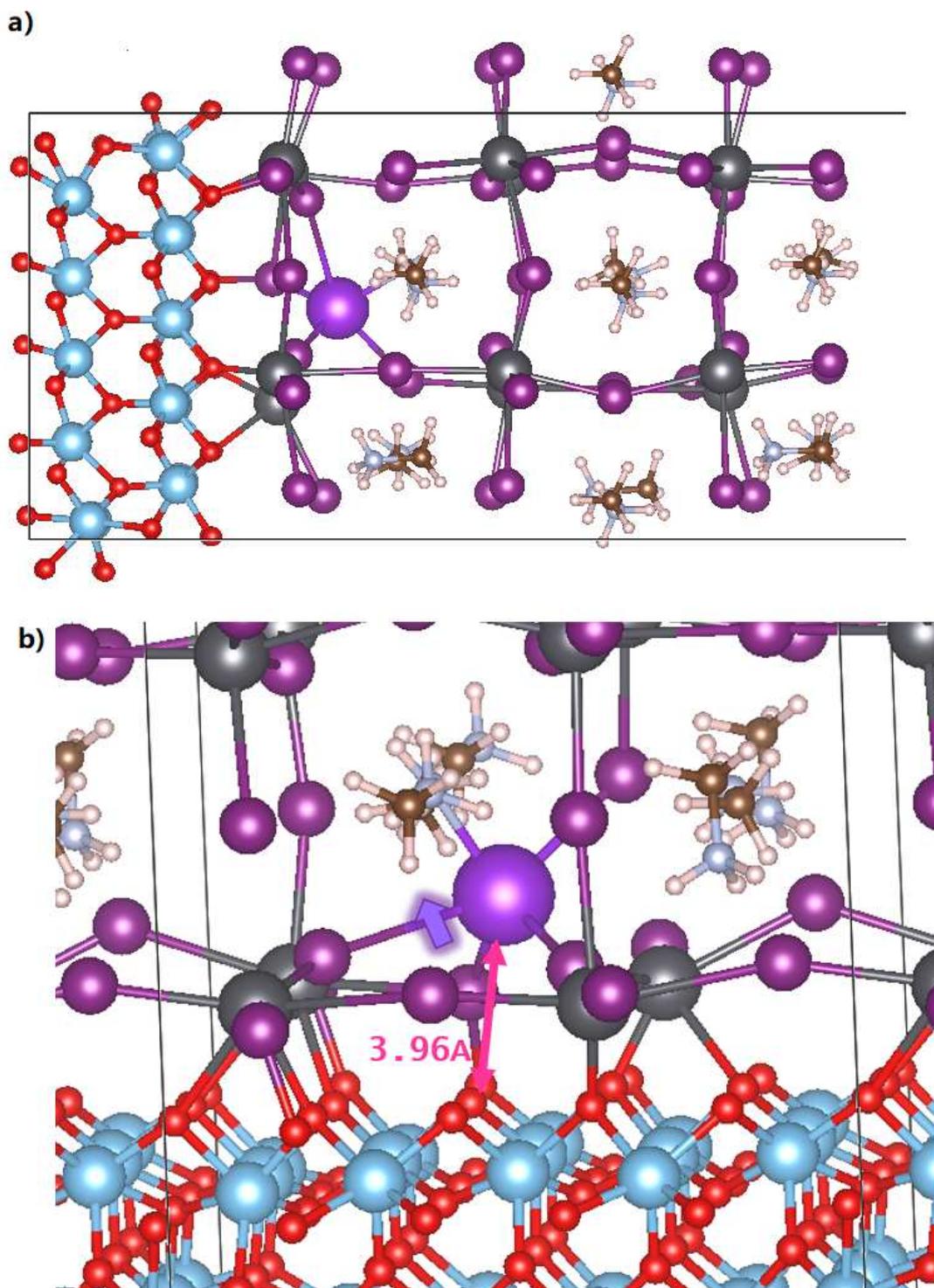


Fig.S 7 Schematic diagram *a*) and optimized geometric structure *b*) of ID-K⁺ in Pbl₂-terminated MAPbI₃/TiO₂ junction.

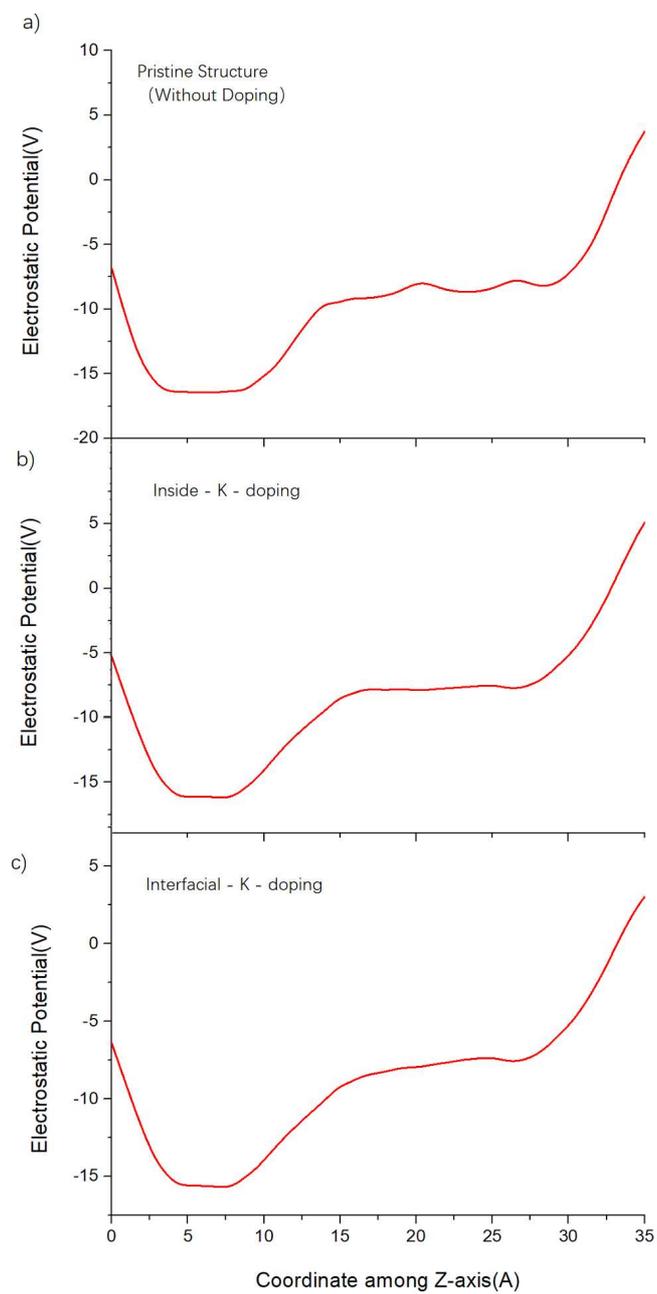


Fig.S 8 Plane-average potentials of pristine and interstitially doped MAPbI₃/TiO₂ heterojunction.

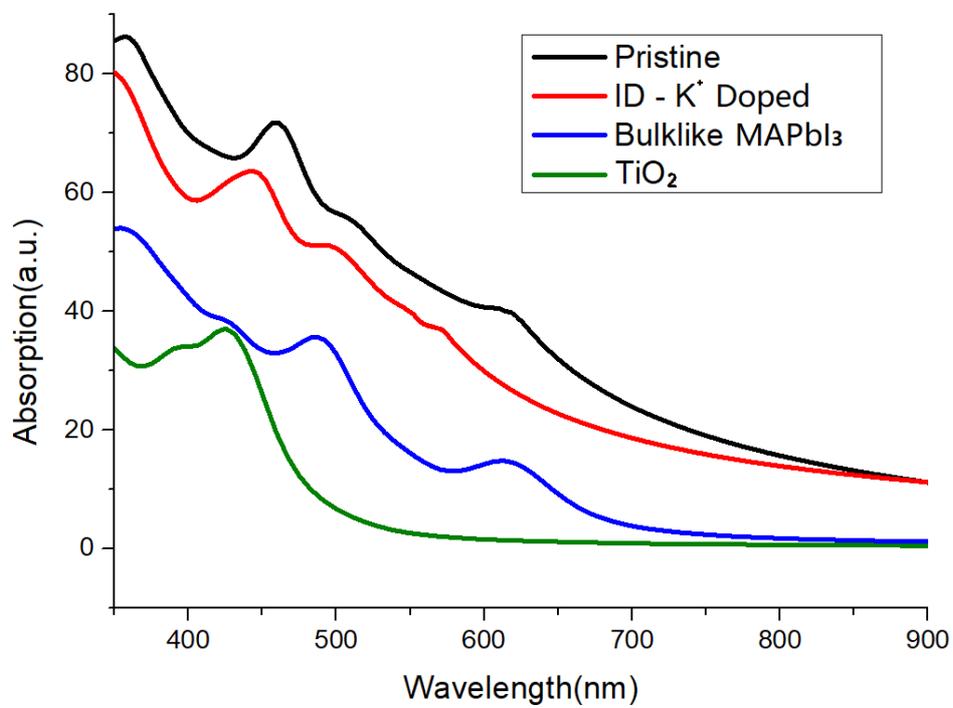


Fig.S 9 Calculated absorption spectra of MAPbI₃/TiO₂ junction with and without ID-K⁺. The bulk-like MAPbI₃ and anatase TiO₂ are shown for reference.

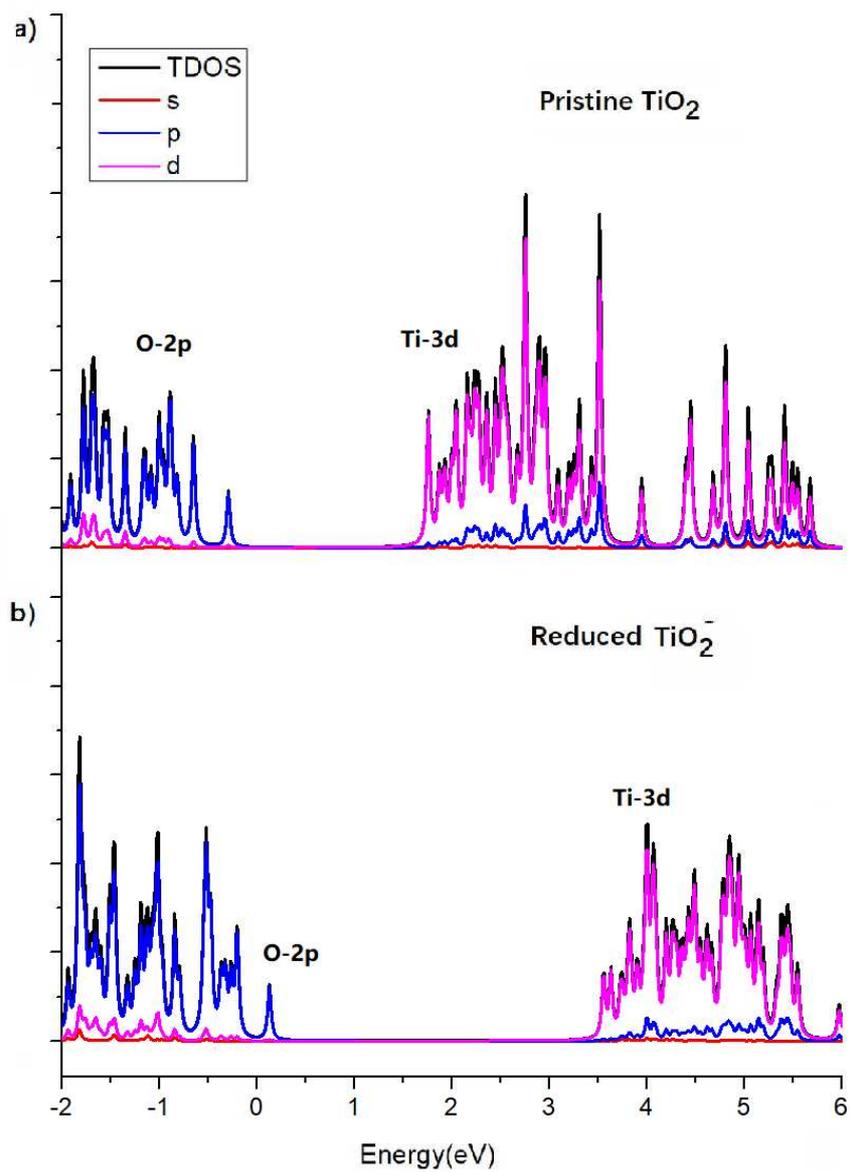


Fig.S 10 pDOSs of a)pristine TiO_2 and b)trivalent TiO_2^- by PBE+SOC.

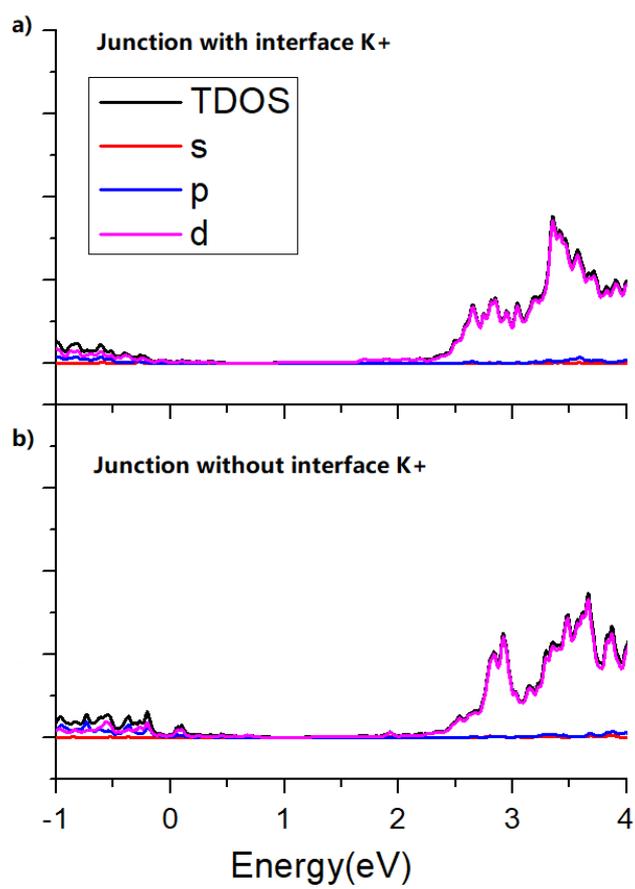


Fig.S 11 pDOS for interfacial Ti cations with *a)* and without *b)* interfacial ID of K⁺ in Pbl₂-terminated MAPbl₃/TiO₂ junction in PBE+SOC.