## Supporting information

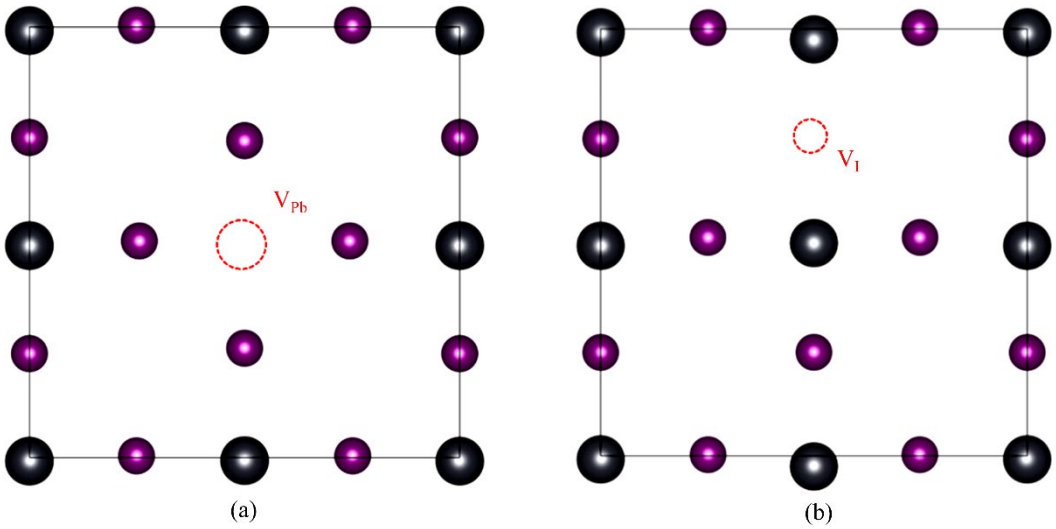


**Figure S1** Top view of the defect model: (a) Location map of lead vacancy defects; (b) Location map of iodine vacancy defects

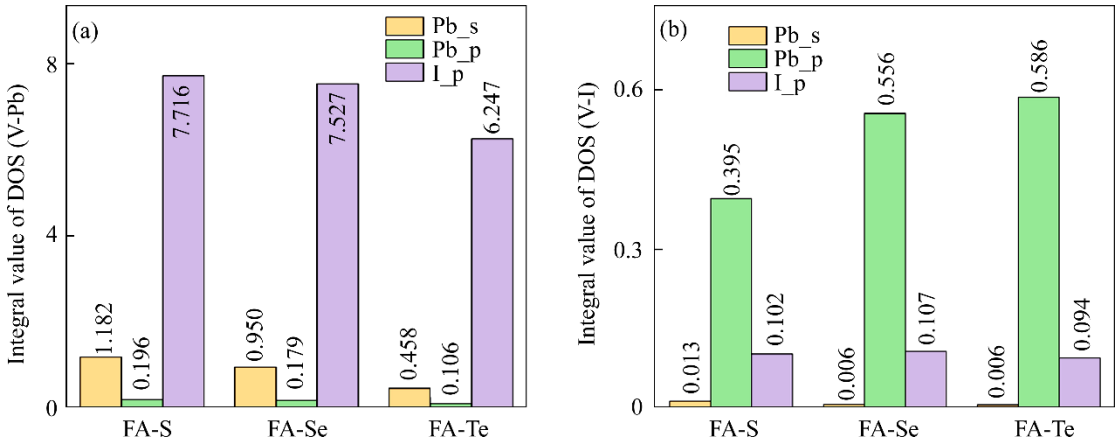


**Figure S2** Histogram of the integral PDOS of the $FAPbI_3$ with PbX covering layer with the integration interval ranges from −0.4 eV to 0.4 eV: (a) Integral value of DOS (V-Pb); (b) Integral value of DOS (V-I)

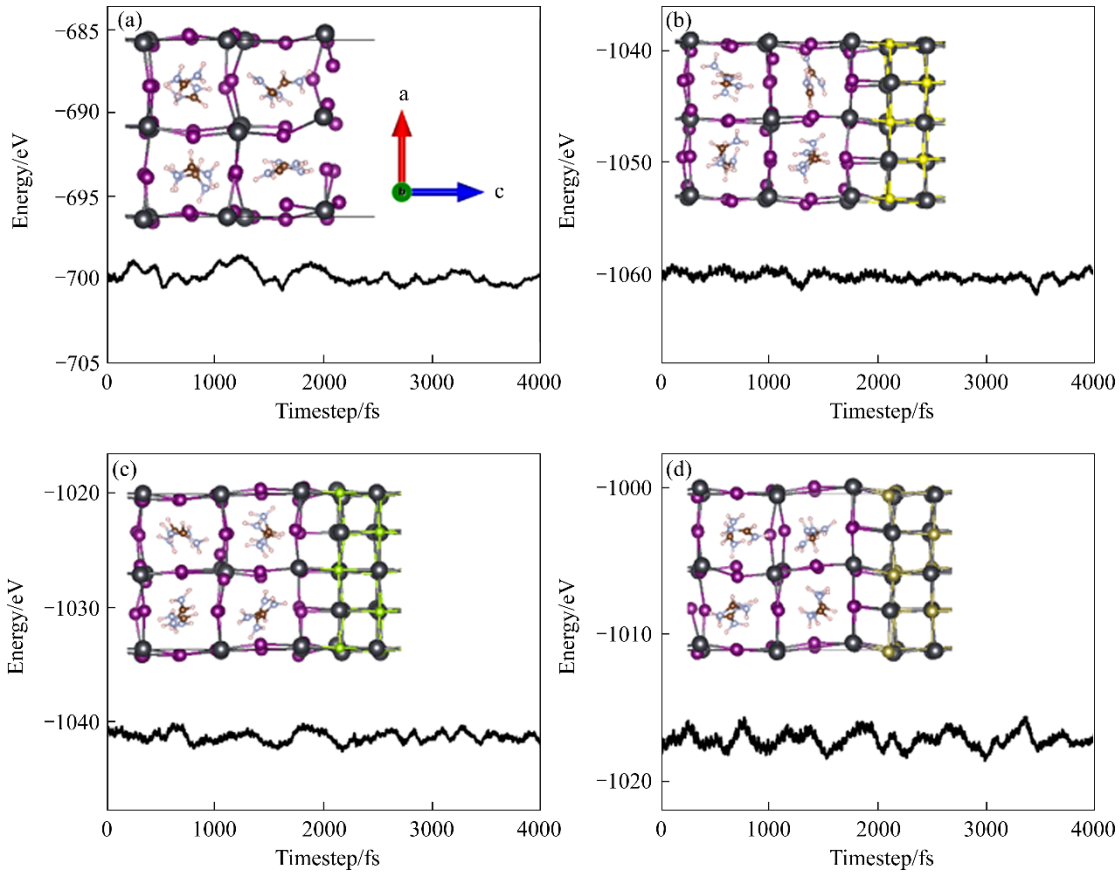


**Figure S3** Energy versus time step curve during AIMD simulation of lead vacancy defect perovskite heterojunction: (a) $FAPbI_3$ (V-Pb); (b) $FAPbI_3$/PbS (V-Pb); (c) $FAPbI_3$/PbSe (V-Pb); (d) $FAPbI_3$/PbS (V-Pb)

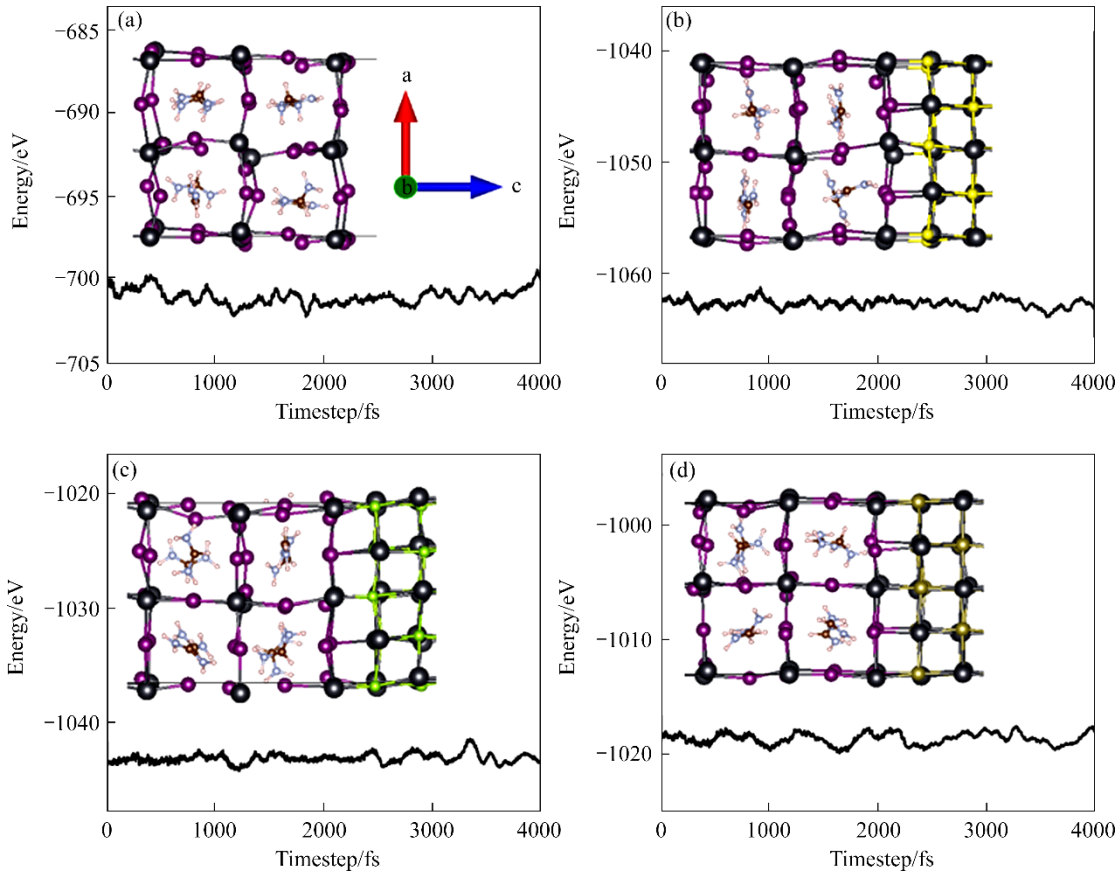


**Figure S4** Energy versus time step curve during AIMD simulation of iodine vacancy defect perovskite heterojunction: (a) $FAPbI_3$ (V-I); (b) $FAPbI_3$/PbS (V-I); (c) $FAPbI_3$/PbSe (V-I); (d) $FAPbI_3$/PbTe (V-I)

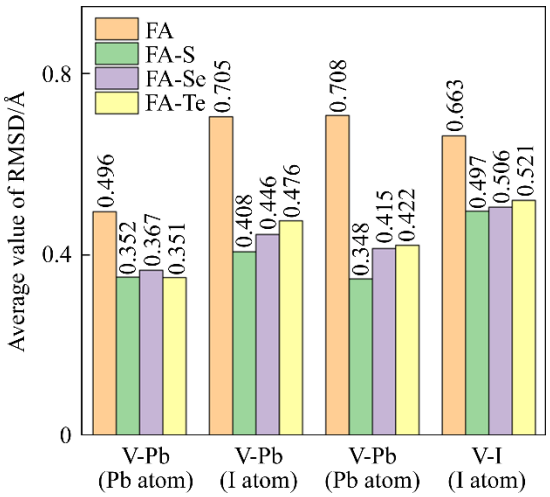


**Figure S5** Histogram of the calculated average values of RMSD for Pb and I atoms of $FAPbI_3$ in $FAPbI_3$/PbX heterostructure

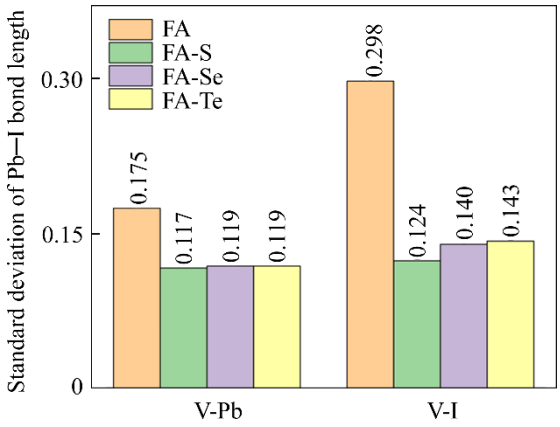


**Figure S6** Histogram of the calculated standard deviation of Pb—I bond length fluctuations of $FAPbI_3$ in $FAPbI_3$/PbX heterostructure

**Table S1** Calculated lattice parameters of $FAPbI_3$ slabs, PbX slabs and lattice parameters and lattice mismatch ratio of $FAPbI_3$/PbX heterostructures

| Lattice parameter | Before | | After | Lattice mismatch ratio/% |
|---|---|---|---|---|
| | $FAPbI_3$ | PbX | $FAPbI_3$-PbX | |
| $FAPbI_3$-PbS | 12.83 | 11.95 | 12.38 | 2.36 |
| $FAPbI_3$-PbSe | 12.83 | 12.36 | 12.59 | 1.24 |
| $FAPbI_3$-PbTe | 12.83 | 13.08 | 12.96 | 0.65 |

**Table S2** Calculated vertical interlayer distances values for the relaxed $FAPbI_3$-PbX at different interface Å

| Interface | $FAPbI_3$/PbS | $FAPbI_3$/PbSe | $FAPbI_3$/PbTe |
|---|---|---|---|
| PbI interface | 2.82 | 2.95 | 3.13 |
| I interface | 3.32 | 3.20 | 3.33 |

**Table S3** Calculated average values of RMSD for Pb and I atoms of $FAPbI_3$ in $FAPbI_3$/PbX heterostructure with different PbX covering layer Å

| Vacancy defect | Atom | FA | FA-S | FA-Se | FA-Te |
|---|---|---|---|---|---|
| V-Pb | Pb | 0.496 | 0.352 | 0.367 | 0.351 |
| | I | 0.705 | 0.408 | 0.446 | 0.476 |
| V-I | Pb | 0.708 | 0.348 | 0.415 | 0.422 |
| | I | 0.663 | 0.497 | 0.506 | 0.521 |