Electronic Supplementary Information

Unraveling The Crucial Role of Spacer Ligand in Tuning Contact Properties in Metal–2D Perovskite Interfaces

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METHODS

In this study, the DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP). The projected augmented wave (PAW) pseudopotentials and the PBEsol exchange-correlation functional within the generalized gradient approximation (GGA) were employed. An energy cutoff of 500 eV was set for the plane-wave function’s expansion. The van der Waals (vdW) dispersion correction was found necessary to yield more accurate lattice constants, which are described by the DFT-D3 correction. The optimization of the bulk PEA$_2$PbI$_4$ lattice structure is performed by applying Monkhorst-Pack sampling with a $\Gamma$-centered $5\times5\times3$ k-point grid. The lattice parameters and atomic positions of bulk PEA$_2$PbI$_4$ were relaxed until the total energy changes were less than $1.0\times10^{-5}$ eV and the maximum force component acting on each atom was less than 0.01 eV Å$^{-1}$. Then, the slab models of monolayer PEA$_2$PbI$_4$ are cleaved from the bulk structure along the stacking direction. While the initial unit structure of PEA$_2$MAPb$_2$I$_7$ and PEA$_2$MA$_2$Pb$_3$I$_{10}$ are constructed by appropriately placing the PEA$^+$ ligands at both ends of two and three layers of corner-sharing PbI$_6$ octahedra, respectively, which are obtained by cutting out tetragonal MAPbI$_3$ unit cells along the [001] direction to reduce the number of PbI$_6$ octahedra layers. For the contact simulation, a periodic boundary condition is applied along the in-plane direction, and a vacuum spacing >20 Å is set along the direction perpendicular to the interface to avoid the interaction between periodic cells in the stacking direction. For the construction of metal–PEA$_2$PbI$_4$ interfaces, Al, Ag, Ir, Au, Pd, and Pt substrates that cover a wide range of WFs are used, forming a suitable system for a systematic study of the band level alignment in metal–PEA$_2$PbI$_4$ interfaces. To form better interfacial lattice matching and minimize the interfacial stress, 2×2×1 supercell of PEA$_2$PbI$_4$ is matched with a $3\sqrt{2}\times3\sqrt{2}\times1$ supercell of the metal[001] slab. For consistence, the in-plane lattice constants of all metal–PEA$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ (n = 1, 2, and 3) slabs are fixed in consistence with that of
PEA$_2$PbI$_4$. Thus, maximum tensile strains of 4.7% for Ir and compressive strain of 2.7% for Au are applied among the six metals, as shown in Table 1. A Γ-centered k-point sampling of $2 \times 2 \times 1$ is used for contact calculation. All the contact structures are relaxed until the total energy and maximum force component acting on each atom are $1.0 \times 10^{-5}$ eV and 0.02 eV Å$^{-1}$, respectively.
Fig. S1. Structural configurations of PEA$_2$PbI$_4$. 

Fig. S2. Band structures and corresponding density of states for (a) bulk PEA$_2$PbI$_4$ and (b) monolayer PEA$_2$PbI$_4$. 
Fig. S3. Variation of potential step, $\Delta V$, and Fermi level shift, $\Delta E_F$, with $W_F$ of metals.
Fig. S4. Band structures of (a) PEA$_2$MAPb$_2$I$_7$ and (b) PEA$_2$MA$_2$Pb$_3$I$_{10}$. 
Fig. S5. Projected density of states for I 5p (dark line) and Pb 6p (red line) orbitals in all six metal-PEA$_2$MAPb$_2$I$_7$ contacts.
Fig. S6. Projected density of states for I 5p (dark line) and Pb 6p (red line) orbitals in all six metal-PEA$_2$MA$_2$Pb$_3$I$_{10}$ contacts.
Fig. S7. Schematic illustration of the energy diagram at the interface of metal-PEA$_2$PbI$_4$, -PEA$_2$MAPb$_2$I$_7$, and -PEA$_2$MA$_2$Pb$_3$I$_{10}$, with $\chi_1$, $\chi_2$, and $\chi_3$ the electron affinities of PEA$_2$PbI$_4$, PEA$_2$MAPb$_2$I$_7$, and PEA$_2$MA$_2$Pb$_3$I$_{10}$, respectively.