Effects of the internal dipole alignment on the quantum transport properties of two-dimensional halide perovskite devices

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INTRODUCTION

Ferroelectricity was suggested as a mechanism that contributes to the excellent optoelectronic properties of halide perovskites such as high light absorption rates, long charge carrier diffusion lengths, and strong photoluminescence [1-3]. However, research on the ferroelectricity of halide perovskites has been scarce, and an atomistic understanding remains elusive. In this study, carrying out multi-space constrained-search density functional theory (MS-DFT) calculations [4] for the junction models based on two-dimensional (2D) $MAPbBr_3$, we study effects of the internal dipole alignment on finite-bias quantum transport properties.

COMPUTATIONAL DETAILS

All calculations were performed within SIESTA package, in which MS-DFT is implemented, to describe equilibrium and finite bias non-equilibrium conditions. We used the generalized gradient approximation PBEsol, double ζ-plus-polarization-level numerical atomic orbital basis sets, and the Troullier-Martins type norm-conserving pseudopotentials. The k-point mesh was 3 x 3 x 1 Monkhorst-Pack grid.

RESULT

Here, we consider two different dipole alignments of MA, parallel (P) configurations (4 MA dipoles in the unit cell are aligned in the same direction) and antiparallel (AP) configurations (4 MA dipoles adopt alternating orientations) as shown in Fig. 1. To investigate the influence of dipole moment configurations on transport, we performed MS-DFT calculation. We present current-voltage (I-V) characteristics of each case and analyze their electronic structures. In Fig. 2, the P model exhibits asymmetric transport behavior, whereas the AP model shows no measurable current. To explain this disparity, we obtained projected local density of states and energy-resolved current in Fig. 3. Due to the higher energy level of valence band maximum (VBM) states in the P case, these states (marked by left triangles) in the P case are positioned closer to the bias window than those in the AP case under both bias conditions. Therefore, the VBM states of the P case come into the bias window at +0.8 V compared to those in the AP configuration. This early entry of HOMO states facilitates the flow of charge carriers and contributes to the observed increase in current. Since MA dipoles have the same (opposite) orientation in the P (AP) case, MA alignments enhance (offset) their internal electric field. In Fig. 4, dipole effects can be seen by potential and density of states (DOS). The red box in the left panel indicates that the gradient of Hartree potential within the MA layer, indicating that the MA alignments induce an internal electric field. It results in an upward shift of 0.11 eV in the VBM states for the P-up configuration compared to the AP case, as shown in the right panel of Fig. 4. This shift plays a crucial role in the asymmetric transport behavior, and it can be evidence of ferroelectricity.

REFERENCES

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[4] Lee, J., H.S. Kim, and Y.H. Kim, *Multi-Space Excitation as an Alternative to the Landauer Picture for Nonequilibrium Quantum Transport.* Adv. Sci. **7**(16), 2001038 (2020).

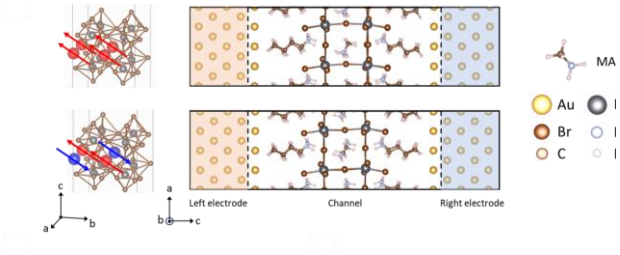

Fig 1. Structures of 2D MAPbBr3 with two different dipole alignment

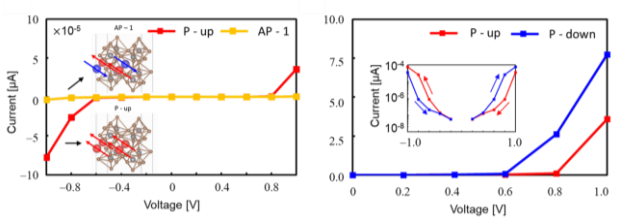

Fig 2. I-V characteristics depending on the dipole moment directions.

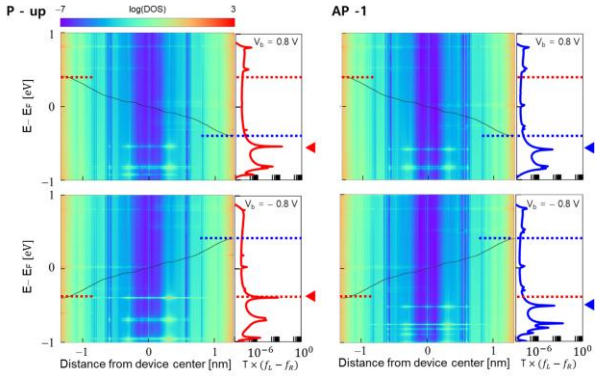

Fig 3. Non-equilibrium projected local density of states and energy-resolved current of P-up and AP-1

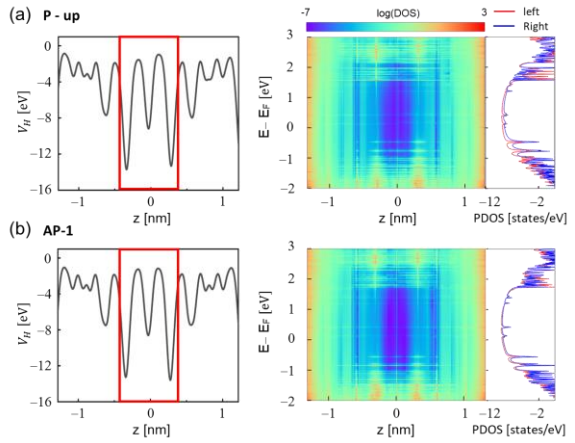

Fig 4. Equilibrium Hartree potential, DOS of (a) P-up and (b) AP-1.