Supporting Information

Organic Cation Steered Interfacial Electron Transfer within Organic-Inorganic Perovskite Solar Cell

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S1. Construction of supercell

The experimental lattice parameters of (001) surfaces of $MAPbI_3$ and TiO_2 are ~6.31 Å and 4.59 Å, respectively. Therefore, to obtain a reasonable lattice mismatch, we use the $\sqrt{2} \times \sqrt{2}$ R45 unit cell of TiO_2 (001) surface (dashed lines in Fig. S3) having the experimental lattice parameter of 6.50 Å. Thus lattice mismatch is reduced to a much reliable value (~3 %).

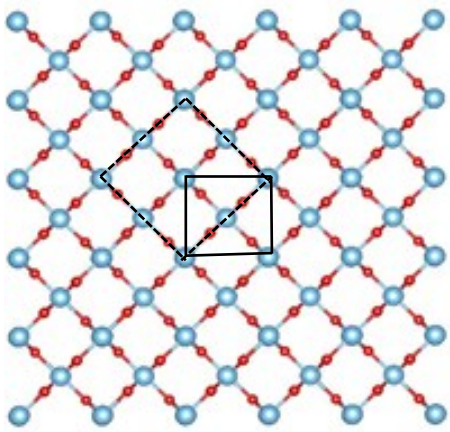

Fig. S1. Construction of TiO_2 (001) surface unit cell; Solid lines represent the standard cell, while the dashed lines depict the $\sqrt{2} \times \sqrt{2}$ R45 unit cell adopted for $TiO_2/MAPbI_3$ interface.

S2. Structural properties from MD simulations

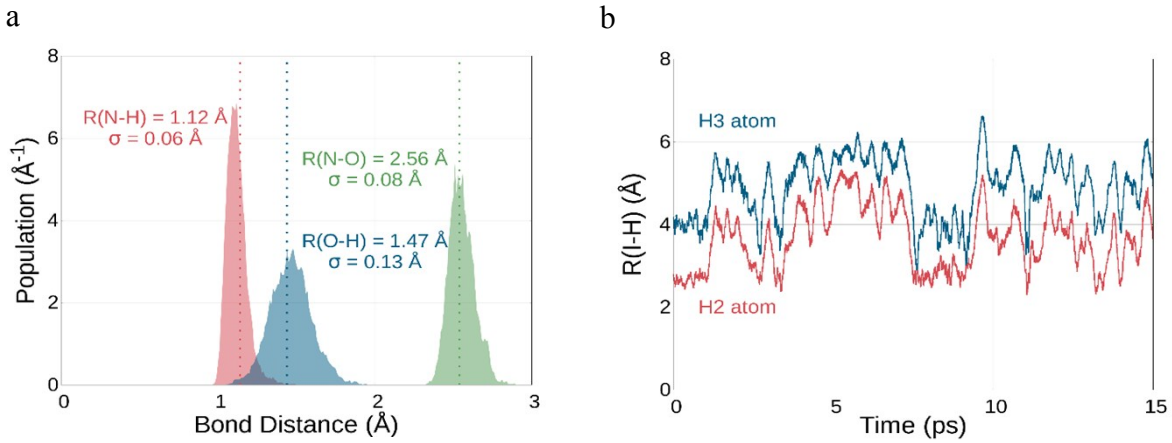

Fig. S2. Bond distances from MD simulation. (A) The average and standard deviation of bond length of N-H, O-H, and N-O of NH_3^+-O_2Ti interface calculated from MD simulations. (B) The time evolution of R(I-H) between I and H2/H3 (H1 is not shown which is attached to O).

S3. Interface electronic structure with GGA

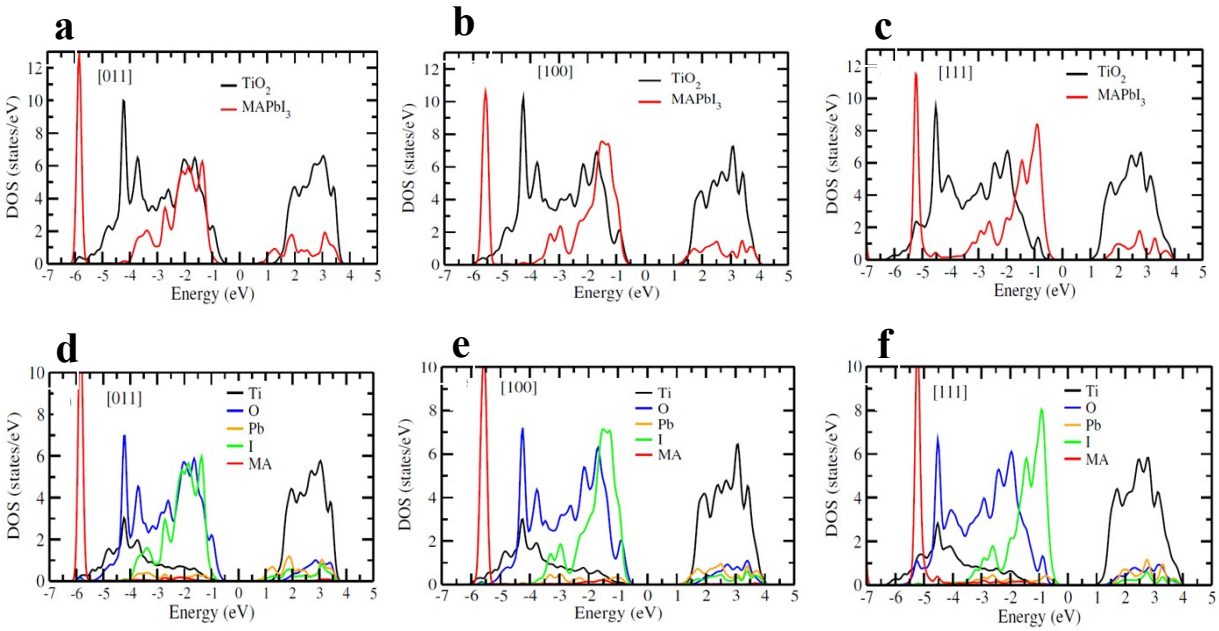

Fig. S3. DOS for TiO_2/$MAPbI_3$ interface for three different MA orientations calculated with GGA. In comparison to results with HSE06 functional presented in main text (Fig. 3), we observe some quantitative differences. For example, valence bands of $MAPbI_3$ are shifted to lower energies with GGA as compared with HSE06. Nevertheless, the overall GGA results follow a similar trend to that of HSE06: TiO_2 bands are shifted to lower energies as the MA orienation is changed from [011] to [111]. As discussed in the manuscirpt, such changes arise due to proximity of H^+ to TiO_2 surface for energetically optimum interface configuration. This effect is also captured by GGA+vdW calculations in this figure.

S4. Impact of spin-orbit coupling

Here we discuss the impact of Spin-orbit coupling (SOC) on the interface electronic structure. As previous studies suggest, inclusion of SOC generally reduces the bandgap of $MAPbI_3$, though the general features of CBM/VBM remain unchanged.[1, 2] Fig. S4 shows PDOS for [011] and [111] orientation, calculated with GGA+SOC. As expected, inclusion of SOC reduces the band gap of $MAPbI_3$ in comparison to GGA (Fig. S3). Impact on conduction bands is relatively stronger than that of valence band since former is dominated by heavier Pb atoms. Moreover, interface with [011] MA orienation seems to more strongly impacted by SOC since interface interactions are relatively weak as compared to the [111] case. Overall, we observe a similar downward shift of TiO_2 states for (111) case as observed with HSE06 (Fig. 3) and GGA (Fig. 3S), arising due to H^+ proximity. Thus, the conduction band offset reduces and becomes more favorable for electron transfer with optimum (111) case as compared to energetically unfavorable (011) MA orientation. Therefore, overall, GGA+SOC provides qualitatively similar description of interface electronic structure as without SOC.

Calculations of SOC within VASP is done without symmetry. As a results, both the number of k-points and eigenstates increase considerably with DFT+SOC. Thus, hybrid HSE06+SOC calculations are computationally prohibitive for such large system with sizeable vacuum. In order to qualitatively assess the impact of SOC on electron transfer process, we calculated the shifts of CBM/VBM of $MAPbI_3$ relative to those of TiO_2 due to the inclusion of SOC in GGA for each interface. As discussed earlier, such shifts are relatively larger for CBM (~ 0.4-0.6 eV) as compared to the VBM (~ 0.1-0.2 eV). Finally, these shifts are added to corresponding $MAPbI_3$ CBM/VBM as calculated by HSE06 to get a more realisitic estimate of electron transfer barrier. These results are presented in of main text (Fig. 4).

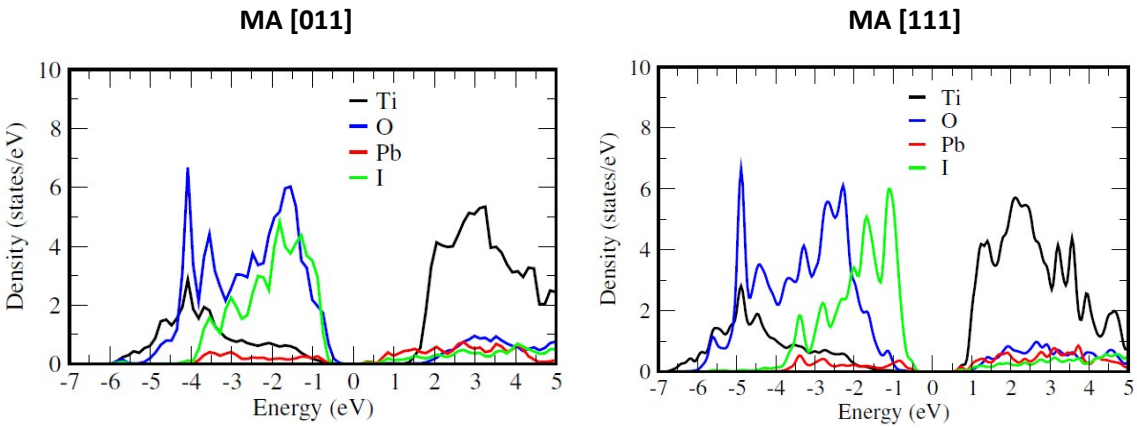

Fig. S4. PDOS of TiO_2/$MAPbI_3$ interface after the inclusion of SOC for MA orientation of left) [011] and right) [111].

References

1- S. Teunis. A. G. Melissen, F. Labat, P. Sautet, T. Le Bahers, *Phys.Chem.Chem.Phys*., 2015, 17, 2199.

2- W.-J. Yin, J.-H. Yang, J. Kang, Y. Yanb, S.-H. Wei, *J. Mater. Chem. A*, 2015, 3, 8926.