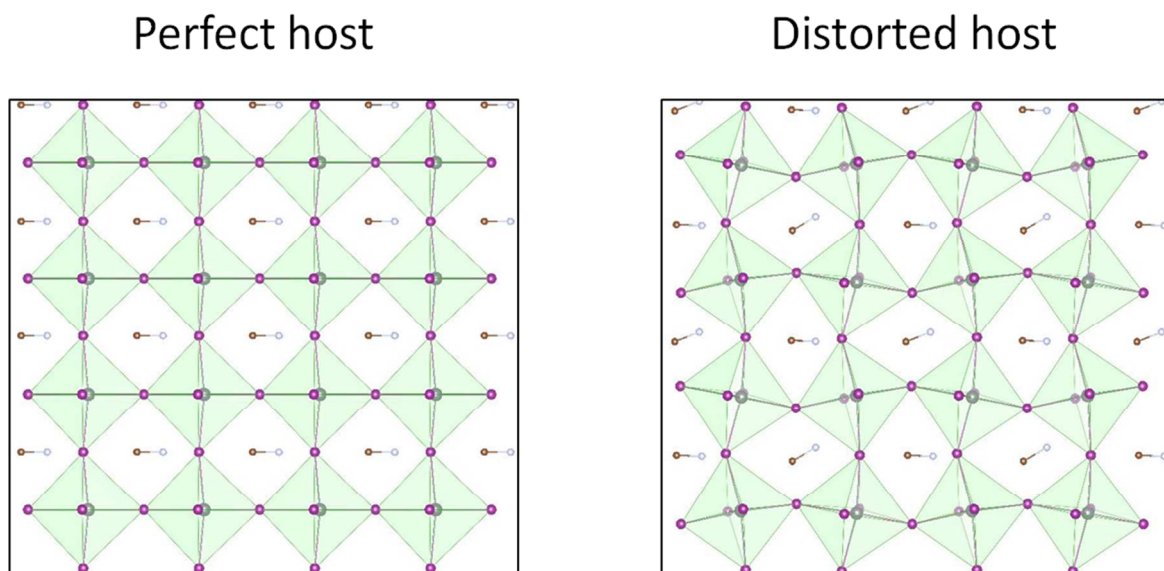


# SUPPORTING INFORMATION

## Preferential $\text{CH}_3\text{NH}_3^+$ Alignment and Octahedral Tilting Affect Charge Localization in Cubic Phase $\text{CH}_3\text{NH}_3\text{PbI}_3$

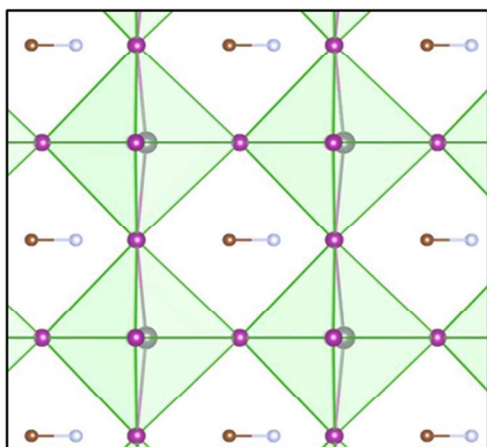
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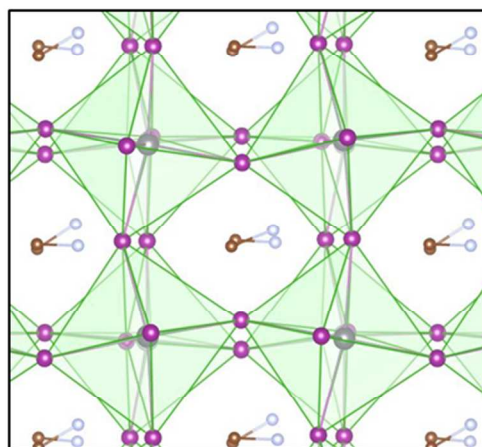
**Figure S1.** Optimized perfect and distorted host structures of cubic  $\text{MAPbI}_3$ . All  $\text{MA}^+$  ions are aligned to  $[100]$  direction in the perfect host. Sizeable MA reorientation (along  $[110]$  and  $[111]$ ) along with octahedral tilt appear in distorted host. Notice the anisotropies in MA cavity brought about by the reoriented organic cations and octahedral tilting.

## Perfect host



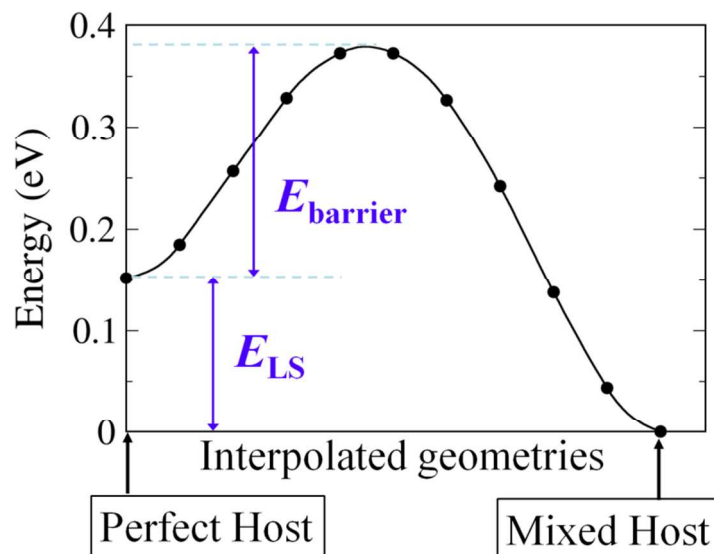
$a=12.768, b=12.63, c=12.79 \text{ \AA}$   
 $\alpha=90.00, \beta=89.62, \gamma=90.00^\circ$   
Volume= $2062.38 \text{ \AA}^3$   
Relative Energy =  $0.37 \text{ eV}$

## Distorted host



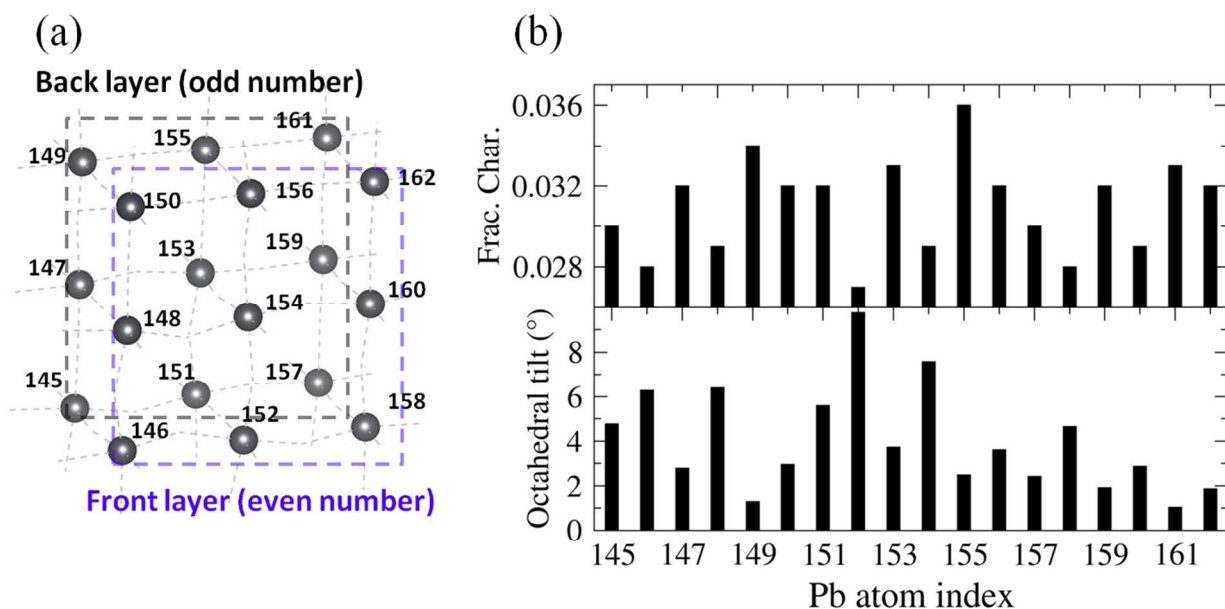
$a= b=12.62, c=12.63 \text{ \AA}$   
 $\alpha=90.00, \beta=90.00, \gamma=90.00^\circ$   
Volume= $2012.82 \text{ \AA}^3$   
Relative Energy =  $0 \text{ eV}$

**Figure S2.** Fully relaxed 96-atom supercells (including volume and shape) of perfect and distorted host performed at the PBE0-SOC level. The total energy of the perfect host is higher than the distorted structure by about 0.37 eV.



**Figure S3.** Relative energy of interpolated geometries between 216-atom perfect and mixed host.

In order to estimate the energy barrier between a 216-atom perfect supercell with [100]  $\text{MA}^+$  alignment and the mixed host, we generated several interpolated geometries between the two. Figure S3 provides an approximate estimate about the barrier height starting from the perfect supercell, passing through intermediate geometries and finally reaching the mixed host structure shown as the ground state along the energy landscape. The calculated barrier ( $E_{\text{barrier}}$ ) is about 0.22 eV which amounts to  $\sim 12$  meV/ $\text{MA}^+$ , similar to those reported from neutron scattering measurements and density functional calculations.<sup>1,2</sup> The energy difference between perfect and mixed host is given as the lattice stabilization energy,  $E_{\text{LS}} = 0.15$  eV. Note that more accurate barrier heights may be obtained from nudged elastic band calculations and the values given here are meant only as a guidance.



**Figure S4.** Additional electron distribution in 216-atom mixed host structure containing four reoriented  $\text{MA}^+$  (see main text for details). The presented data are obtained from relaxed mixed host with one excess electron. (a) Pb atom index in back layer (odd numbered ions) and front layer (even numbered ions). (b) Fractional orbital character of each Pb 6p orbital carrying the additional electron and the corresponding Pb-centered octahedral tilt angle. There is a correlation between additional electron distribution and octahedral tilting. The degree of tilting is also influenced by proximity to the four reoriented  $\text{MA}^+$  ions. Hence, the extra charge distribution is not isotropic. Individual octahedral tilts are on average larger in the front layer than those in the back layer. Overall electronic charge localization is greater in the back layer.

## REFERENCES

- (1) Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; Schilfgaarde, M. V.; Walsh A. Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14*, 2584-2590.
- (2) Leguy, A. M. A.; Frost, J. M.; McMahon, A. P.; Sakai, V. G.; Kockelmann, W.; Law, C.; Li, X.; Foglia, F.; Walsh, A.; O'Regan, B. C.; et al. The Dynamics of Methylammonium Ions in Hybrid Organic-inorganic Perovskite Solar Cells. *Nat. Commun.* **2015**, *6*, 7124.