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Supramolecular Virtual Crystal: A fast and accurate guideline for molecular passivation of perovskite materials

Suppl. Info.

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1 Methodology

First-principles density functional theory (DFT) based calculations were performed by the Vienna ab Initio Simulation Package (VASP) [1]. The exchange-correlation potential was treated within the generalized gradient approximation (GGA) with the PBEsol parametrization [2]. The projected augmented wave (PAW) method [3], with a kinetic energy cutoff for the plane-wave expansion of 910 eV was used to solve the Kohn-Sham equations. The (001) surface was cleaved from an optimized bulk orthorhombic phase which is the most stable $MAPbI_3$ perovskite configuration, and the a and b lattice parameters were fixed to those optimized values. The surface considered on this study contains three layers of octahedra which is enough to reproduce experimental properties of the surface of the 3D system [4]. Passivation is performed at both sides of the surface to avoid the creation of dipole moment across the structure. The optimization of atomic positions was performed using a conjugate gradient algorithm until the Hellmann-Feynman forces reached a threshold of 1×10^{-4} eV/Å. A vacuum of at least 10Å was employed to avoid undesired interactions between periodic layers. The Brillouin zone was sampled with a $6\times6\times1$ k-point mesh. To calculate binding energies, the isolated molecule was optimized in a $20 \times 20 \times 20 \text{Å}^3$ cell. Dipole calculations of the ionized molecules were calculated by solving the restricted Kohn-Sham equations with the Psi4 code [5] and using B3LYP [6] and the aug-cc-pVTZ basis.

2 Charge Density Difference

To further analyse the molecule-surface bonding mechanism, we calculated the charge density difference ($\Delta\rho$) between the passivated perovskite surface and the sum of isolated surface and molecules sub-systems as:

$$\Delta\rho = \rho_{\mathrm{T}} - (\rho_{\mathrm{S}} + \rho_{\mathrm{A}}^{\mathrm{T}})$$

where ρ_{T}, ρ_{S} and $\rho_{\mathrm{A}}^{\mathrm{T}}$ represent the total charge density and of the unpassivated surface and total organic passivator subsystems respectively. Figures 1(a)-(c) present $\Delta\rho$ for the calculated structures. It shows charge redistribution only located at the molecule-surface bonding region for most of the structures. Furthermore, there is electron loss (yellow surface) on the ammonium group mainly at the most inserted H atom and electronic re-accommodation on the N atom. It is also observed electron loss on the axial external I atoms. Besides, the main gain is observed along the Ammonium H - I bonds ($l < 2.74$Å) as indicated by the blue lobes located in between these atoms and being distributed in the perpendicular direction to the bond.Additional charge redistribution is observed in phenyl with $m = 0$ and $m = 1$ on the ring C atoms due to the interaction of it with the surface.

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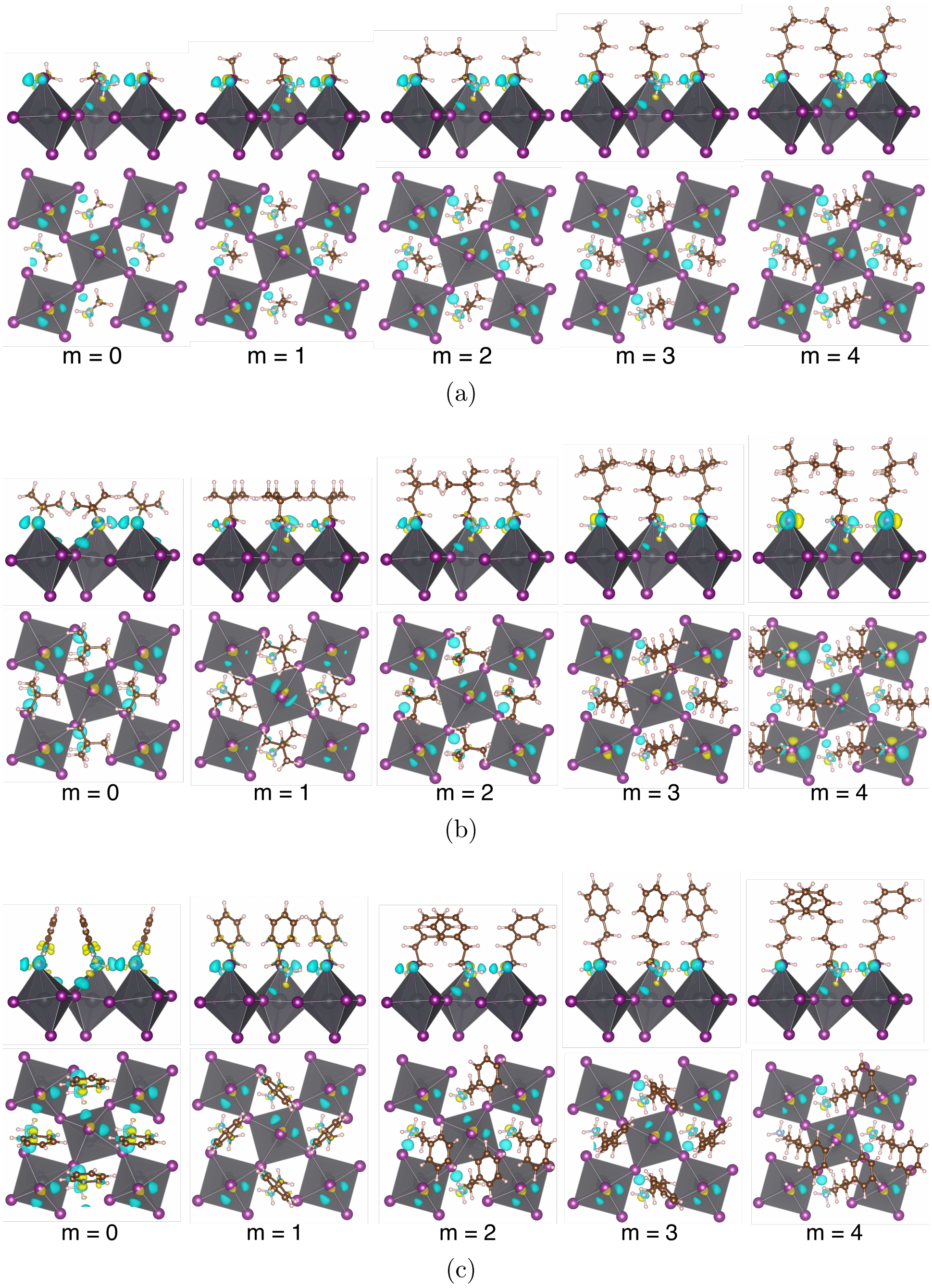

Figure 1: Charge density difference ($\Delta\rho$) between the between the passivated perovskite surface and the sum of isolated surface and passivating molecules sub-systems for each m of value and (a) R=Methyl, $m = 2$. (b) R=tert-butyl, $m = 4$. (c) R=Phenyl.

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