

Electronic properties of organic-inorganic perovskites controlled by different diamine long chain organic molecules: first-principles calculations

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Supporting Information

In order to further study the effect of molecular chain length on the properties of perovskites, we also introduced $(\text{NH}_3(\text{CH}_2)_2\text{NH}_3)\text{PbI}_4$ (EDAPbI₄), $(\text{NH}_3(\text{CH}_2)_4\text{NH}_3)\text{PbI}_4$ (HDAPbI₄). We calculated their properties in the same way as in the body part. The optimized structure of EDAPbI₄ and HDAPbI₄ is shown in the Fig. S1. We can see that the Pb-I bond in EDAPbI₄ is significantly distorted. The two Pb-I bonds in the c direction deviate from the same straight line. This is due to the fact that the molecular chains are shorter, the spacing of the inorganic layers is significantly reduced, and the I atoms are mutually exclusive. At the same time, the symmetry of the two Pb-I bonds in the a direction is also seriously degraded, which can be seen from the difference in bond length (3.54 Å and 3.04 Å).

The energy band structure (Fig. S2) of EDAPbI₄ and HDAPbI₄ still has similar band dispersion near VBM and CBM with BDAPbI₄ perovskites. Moreover, EDAPbI₄ has a wider band gap (2.30eV) due to the influence of structural distortion on symmetry. And HDAPbI₄ still has a narrow direct band gap (2.03eV), but slightly larger than that of BDAPbI₄. In particular, the energy band curve of VBM of EDAPbI₄ and HDAPbI₄ appears to be relatively flat and the dispersion is small. The reason is that in EDAPbI₄, the larger position distortion of I atoms in the two adjacent inorganic layers in the c direction, and in DPAPbI₄, the increase of the distance between I atoms in the two adjacent

inorganic layers in the c direction due to the increase of molecular chain length. These all lead to a reduction in the overlap of valence electron functions between I atoms. Therefore, the valence band dispersion of diamino-3D perovskite formed by too short and too long diamino molecules is relatively small, which is not conducive to obtaining the best carrier transport properties.

The results of bader charge analysis (Table S1) and charge density difference (Fig. S3) are consistent with the analysis of the body part. HDAPbI₄ shows better ionicity, but still weaker than BDAPbI₄.

The optical absorption coefficient of EDAPbI₄ and HDAPbI₄ reflects the obvious anisotropy (Fig. S4). Unlike the other materials in which the absorption curves in the lattice vectors a and b directions are very close, the absorption in the a and b directions of EDAPbI₄ shows a significant difference, which is consistent with its structural asymmetry.

In summary, for the diamino-3D perovskite, distortion occurs when the molecular chain length is too short. When the molecular chain is longer, the spacing of the inorganic layers is getting larger and larger, the property gradually tends to 2D perovskite. Therefore, BDAPbI₄ has the most excellent transport properties of carrier due to its suitable molecular chain length and symmetry of even molecular chains.

		EDAPbI ₄		HDAPbI ₄		
Organic	-1.444	C	-1.122	-1.467	C	-1.114
		H	-6.182		H	-6.252
		N	6.013		N	5.899
Inorganic	1.444	Pb	-1.115	1.467	Pb	-1.113
		I	2.559		I	2.579

Table S1 Bader charge analysis. Negative values indicate loss of electrons, positive values indicate that electrons are obtained.

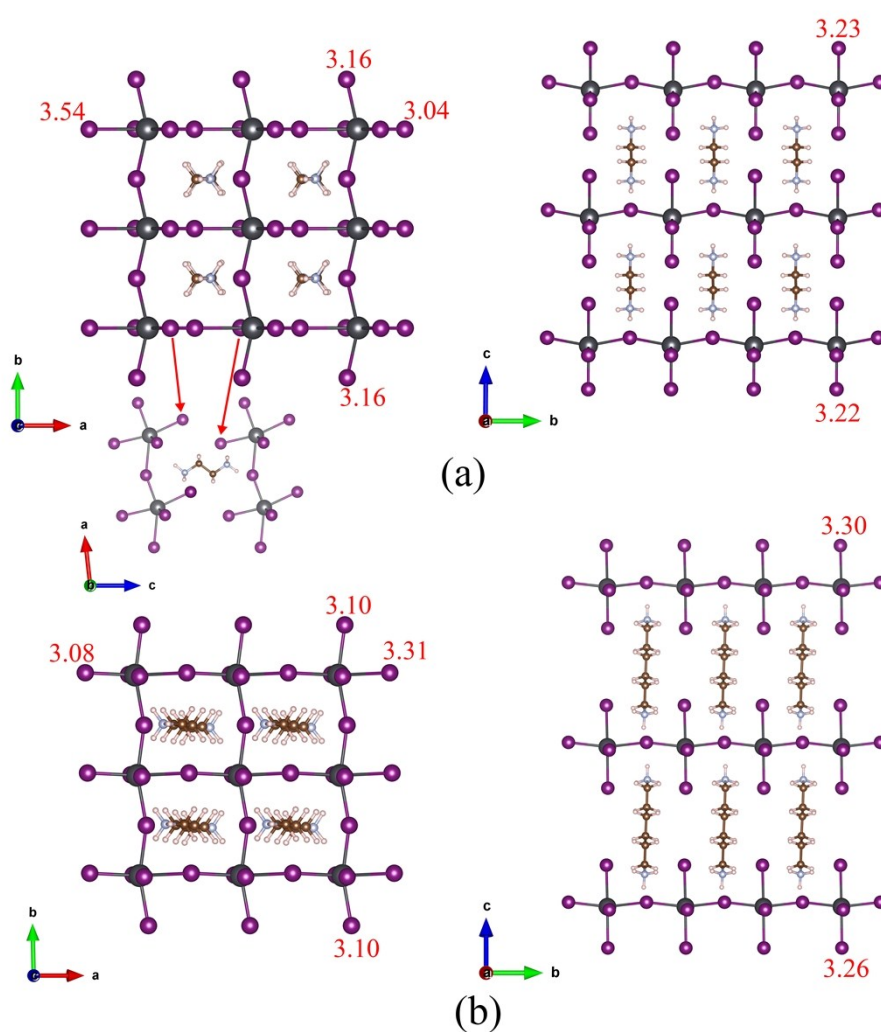


Fig. S1 The optimized geometrical structures of (a) EDAPbI₄, (b) HDAPbI₄ perovskite.

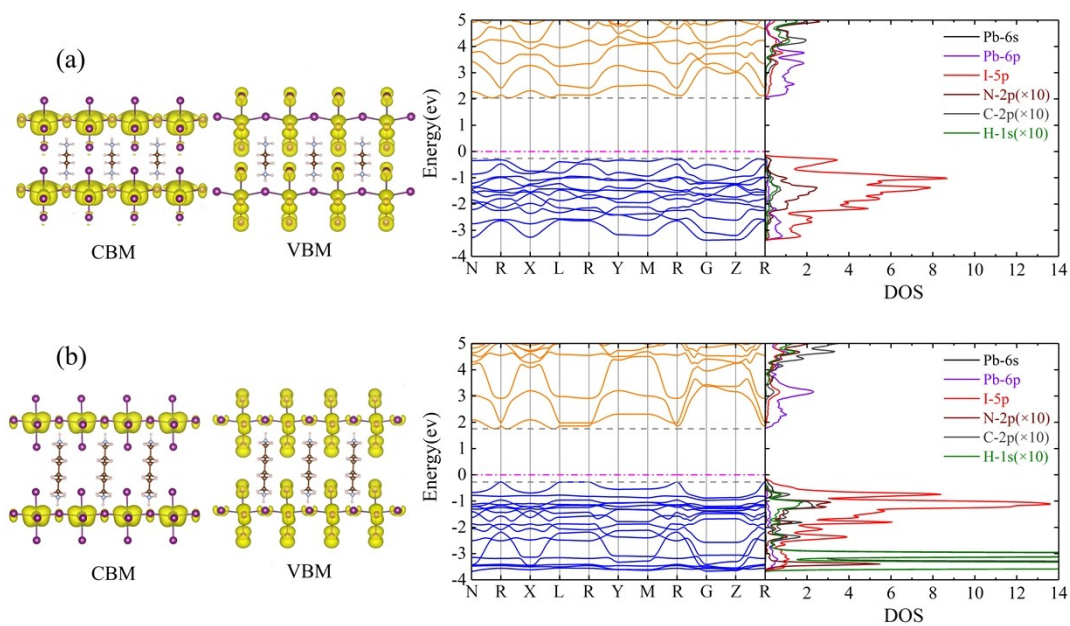


Fig. S2 From left to right, there is densities at the VBM and CBM states (with an isosurface value of $0.0001e/\text{\AA}^3$), energy band structure and density of states (DOS) of (a) EDAPbI₄, (b) HDAPbI₄. And “C-2p”, ”N-2p” and ”H-1s” are increased ten times in the original value.

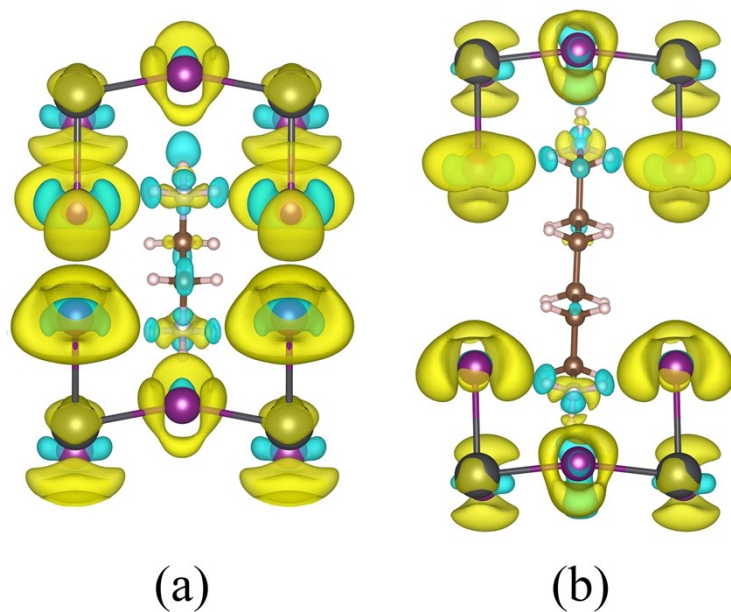


Fig. S3 Charge density difference of (a) EDAPbI₄, (b) HDAPbI₄ with an isosurface value of $0.0015e/\text{\AA}^3$. The yellow part indicates that electrons are obtained, and the blue part indicates electron loss.

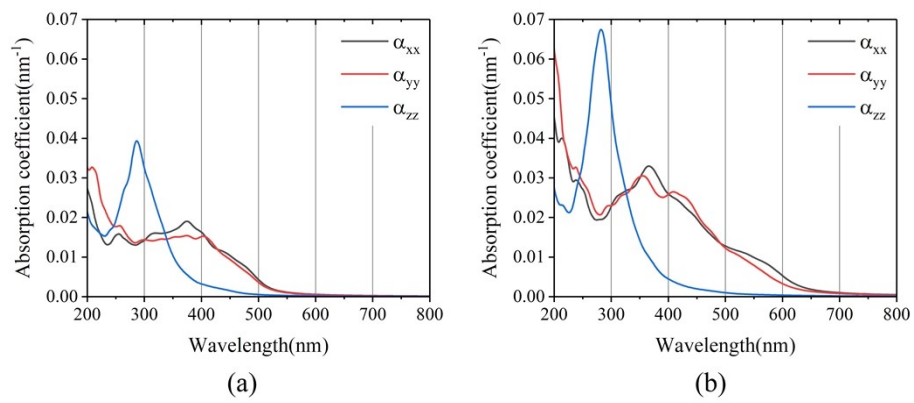


Fig. S4 Absorption coefficients of (a) EDAPbI₄, (b) HDAPbI₄.