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Supplementary Information for "Theoretical insights into thermal conductivity of 2D hybrid perovskites based on thermal resistance network model"

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1 Details of interfacial binding energy calculation

When considering stacking disorder alone, the range of disordered sliding δx and δy becomes a key parameter influencing $\bar{n}_c$. We employ the COMPASS Lennard-Jones (LJ) force field to compute the binding energy between adjacent HOIP layers [1], allowing us to identify the valid stacking regions, expressed as

$$E(x,y) = \sum_{i}^{N}\sum_{j}^{N} 2\varepsilon\left(\frac{\sigma}{r_{ij}}\right)^{9} - 3\varepsilon\left(\frac{\sigma}{r_{ij}}\right)^{6}. \quad (1)$$

Here, ε denotes the potential well depth, σ is related to the position of the potential energy minimum, and N is the number of atoms in each layer. The interatomic distance is r_{ij}, where the subscripts "i" and "j" refer to atom index in the upper and lower layers, respectively. By continuously translating the layers within the xy plane, we calculated the interfacial binding energy $E(x,y)$ of the system at different sliding distances. The detailed calculation procedure is described below.

Step1 : The initial atomic model was constructed as a $1 \times M \times M$ supercell (where M is the number of unit cells along x- or y-direction), with the lattice parameters and atomic coordinates directly extracted from the CIF file of the 2D-HOIPs to ensure structural consistency with the actual material. This configuration corresponds to the case without any sliding between layers. For atoms fixed in the upper or lower layer, their positions are denoted as r_{ij}. In real material growth processes or after thermal treatment, the stacking disorder varies depending on the ligand type and molecular packing arrangement. According to Eq. 1, when no sliding occurs, we pairwise compute and sum the interactions between atoms in the upper and lower layers, yielding the binding energy corresponding to the E(0,0) point in Fig. 3 in main text.

Step2 : The upper organic layer is shifted by a small displacement (x_1, y_1), and the pairwise interactions between atoms in the upper and lower layers are recalculated and summed to obtain the binding energy corresponding to the point E(x_1, y_1) in Fig. 3 in main text. The procedure is repeated for another small displacement (x_2, y_2), yielding the corresponding E(x_2, y_2) value, and so forth. Due to the periodicity of the material, the range of (x,y) values does not need to exceed the dimensions of a single unit cell.

2 Details of Monte Carlo simulation

We model the material by using a supercell of size $M \times M$ (where $M = 50$ represents the number of unit cells along x- or y-direction). The number of Monte Carlo (MC) simulation times N_{MC} is set to 100000. The vdW contact distances D_{vdW} for determining heat flow between upper and lower organic ligands are set as follows: for carbon atoms 0.34 nm; for hydrogen atoms 0.21 nm.[2] The vibrational degree of atom D_v and distance between clusters δ are set as 1 and 0.4 nm, respectively.[3] We emphasize that a soft-sphere model is used here for carbon and hydrogen atoms, meaning that atoms are considered in contact if the distance between them is less than D_{vdW}, and each atom may contact multiple other atoms simultaneously. Otherwise, they are considered disconnected. The MC process is as follows:

Each ligand and each atom within the ligands of the upper and lower layers are labeled, denoted as $r_k^{i,j}$, where the subscript k represents the layer index, $k = 1$ ($k = 2$) for the upper (lower) layer), the superscript i indicates the ligand index, and j represents the atom index. During each MC simulation, the upper organic layer undergoes a random displacement $\delta r = \delta x + \delta y$, and as a result, each atom in the upper layer is updated with $r_k^{i,j} + \delta r$. The number of ligands in thermal contact N_c is then counted. Here, we define two ligands as being in thermal contact when $\Delta r = |r_1^{i,j} - r_2^{i',j'}| < D_{vdW}$. Here we point out that due to the bottleneck effect in interfacial transport, a ligand in the lower layer contacting two molecules in the upper layer is still considered a single contact.[4] By performing a large number of MC simulations, the final mean value $\bar{n}_c = \sum_{i=1}^{N_{MC}} n_c(i)/N_{MC}$ can be obtained. Meanwhile, large-scale simulations of larger size materials capture the disorder characteristics, yielding a convergent $\bar{n}_c$ result in Fig. 1. From the convergence behavior of the coordination number with respect to the simulated system size, it can be observed that the

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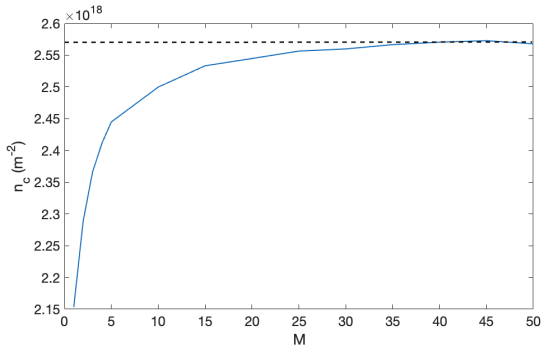

Fig. 1 $\overline{n}_c$ as a function of system size $M \times M$.

results only become convergent when the system size reaches a sufficiently large scale. This highlights the necessity of conducting large-scale simulations for disordered systems and demonstrates the efficiency of the MC method in handling disordered systems without translational symmetry. In contrast, first-principles approaches, when applied to small-scale molecular dynamics simulations, lead to significant fluctuations in the results, preventing the extraction of meaningful statistical insights.

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