

Anisotropic Thermal Transport in Quasi-2D Ruddlesden-Popper Hybrid Perovskite Superlattices

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Two-dimensional hybrid metal-halide perovskites (2D-MHPs) have emerged as important solution-processed semiconductors with favorable optical and electronic properties for diverse applications in photovoltaics, optoelectronics, and spintronics. The quasi-2D layered structures, featuring large acoustic impedance mismatches between the organic and inorganic sublattices, are expected to result in distinct and anisotropic thermal transport properties along the cross-plane and in-plane directions. Here, we introduce transducer-free vibrational-pump-visible-probe (VPVP) approaches that enable accurate quantification of anisotropic thermal transport properties in various archetypical single-crystalline 2D-MHPs. Specifically, using VPVP spectroscopy and VPVP microscopy, we measure the anisotropic thermal diffusivities of 2D-MHPs with systematically varied Pb-I octahedral layer thicknesses, as well as organic spacer types and lengths, revealing how these structural parameters alter the cross-plane and in-plane thermal transport properties in distinct ways. While diffuse interface scattering plays an important role in dictating cross-plane thermal transport, in-plane thermal transport is primarily determined by phonon transport within inter-connected inorganic layers. Density functional theory incorporating four-phonon scatterings provides further insight into the low thermal conductivity and modest thermal conduction anisotropy in 2D-MHPs. Our work demonstrates a new all-optical and noncontact method, which requires minimal sample preparation and allows direct visualization of cross-plane and in-plane thermal transport, potentially compatible with *in situ* sample environments. The demonstrated VPVP approaches can advance understanding of thermal transport in 2D-MHPs as well as wide-ranging hybrid and polymeric semiconductors beyond 2D-MHPs.

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I. INTRODUCTION

Organic-inorganic metal halide perovskites (MHPs) have emerged as cornerstone semiconductors for optoelectronic and photovoltaic applications [1,2]. They are distinguished

by solution processability [3], tunable band gaps [4], and high defect tolerance [5]. However, their inherent material instability under environmental stressors such as moisture and oxygen has drawn researchers' attention to their two-dimensional (2D) analogs with enhanced environmental resilience [6,7]. 2D-MHPs, most notably the hybrid Ruddlesden-Popper (RP) phase, $A'_2A_{n-1}B_nX_{3n+1}$, and Dion-Jacobson (DJ) phase, $A'A_{n-1}B_nX_{3n+1}$, where A' and A are organic cations, B is lead, tin or germanium, and X is a halide, feature alternating organic and inorganic sublattices that impart both quantum and dielectric confinement on photoexcited charge carriers [8]. This structural

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motif not only improves material stability but also yields pronounced excitonic effects, rendering 2D-MHPs as attractive candidates for applications beyond photovoltaics such as light emission [9,10] and chiral-induced spin selectivity [11,12]. Despite their versatility, a critical and often overlooked challenge persists: the intrinsically low and anisotropic thermal conductivities (denoted as κ) of 2D-MHPs [13–15] that may lead to thermal transport barriers in devices and hinder their performance and reliability [16,17]. However, researchers have reported conflicting evidence on how factors such as octahedral layer thickness, organic spacer length, and spacer type influence cross-plane thermal transport in these materials [13]. While several studies found that increasing layer thickness [18] or spacer length [19] suppresses the cross-plane thermal transport, others have reported the opposite [20]. Moreover, systematic studies of these effects on in-plane thermal transport are still lacking, largely due to limitations of existing thermometry techniques.

State-of-the-art techniques for nanoscale thermal metrology such as time-domain or frequency-domain thermoreflectance (TDTR or FDTR) require metallic transducers (e.g., aluminum or gold) deposited on sample surfaces [21–23]. However, metallic transducers have κ orders of magnitude greater than those of 2D-MHPs and other low- κ materials. Significant lateral heat spreading in transducers reduces their sensitivity to in-plane thermal conductivity (κ_r) of the underlying material [24]. While alternative measurements such as optothermal Raman thermometry are effective for probing in-plane thermal transport in 2D van der Waals materials [25,26], it is not suitable for MHPs due to their broad Raman peaks at ambient temperature [27], limited material stability, and strong photoluminescence that overwhelms the Raman signals.

Here, we present a vibrational-pump visible-probe (VPVP) platform as a transducer-free technique for rapid and direct tracking of thermal transport in 2D-MHPs with suitable spatiotemporal resolution. The VPVP platform leverages intrinsic thermoreflectance effects of 2D-MHPs around their excitonic resonance and vibrational absorption in the mid-infrared (MIR) region. Utilizing VPVP, we impulsively and thermally excite 2D-MHP lattices with an intense, vibrationally resonant MIR pump, and monitor the spatiotemporal temperature evolution with a time-delayed visible probe in the nanosecond (ns)-to-microsecond (μ s) range. This noncontact and transducer-free approach allows us to accurately measure the anisotropic thermal transport properties of several series of mechanically exfoliated, pristine, and high-quality single-crystalline sheets of 2D-MHPs (Fig. S1) [28], with obtained κ_r as low as $\sim 0.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Compared with existing prevailing thermal metrologies, our VPVP approaches present several advantages. In comparison to transient thermal grating [36] and other spatiotemporal thermometry [37],

our measurements do not involve charge-carrier excitation with above-band gap optical pumping but instead utilize pure thermal excitation, thus providing clear transient optical signals directly informing lattice temperature changes. Moreover, the absence of metallic transducers prevents possible metal penetration into the MHP lattices [38], which could alter their κ . The VPVP methods do not involve pulse accumulation (thus potential thermal degradation) and feature high sensitivity to ultralow in-plane thermal conductivity.

Our VPVP method operates in two configurations (Fig. S2) [28]: VPVP spectroscopy (VPS) with a focused probe to measure cross-plane thermal diffusivity (α_z); VPVP microscopy (VPM) adopting a wide-field probe to measure in-plane thermal diffusivity (α_r) and permit spatiotemporal thermal imaging. We applied these two configurations to a series of RP-phase 2D-MHPs with systematically varied octahedral-layer thicknesses and organic-spacer types and lengths within a unit cell. Specifically, the studied series include $(\text{C}_x\text{H}_{2x+1}\text{NH}_3)_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, where $\text{MA} = \text{CH}_3\text{NH}_3^+$ and $n = 1, 2, 3$ ($x = 4$), denoted as BA- $n1$, BA- $n2$, and BA- $n3$, respectively; $(\text{C}_x\text{H}_{2x+1}\text{NH}_3)_2\text{PbI}_4$ with $x = 6, 8$, corresponding to HA- $n1$ and OA- $n1$; $(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, where $\text{PEA} = \text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+$ and $n = 1, 2, 3$, denoted as PEA- $n1$, PEA- $n2$, and PEA- $n3$, respectively (Supplemental Material note 1) [28].

Our results reveal a monotonic increase in α_z with decreasing organic-inorganic interfacial density, achieved either by thickening the octahedral-layer thickness or lengthening the organic spacer, highlighting the dominant role of diffuse interface scattering (DIS) of phonons in limiting cross-plane thermal transport. This implies superlatticelike thermal behaviors in the cross-plane direction of 2D-MHPs, where a softer but more thermally conductive 2D-MHP can be made using longer and more flexible organic spacers. In contrast, in-plane thermal transport exhibited two opposing trends: thickened octahedral slabs enhance α_r , whereas lengthened alkylammonium chain suppress α_r , indicating that in-plane transport mainly stems from phonon propagation in the interconnected, inorganic octahedral layers. Additionally, 2D-MHPs with a more rigid PEA spacer present larger thermal diffusivities in both cross-plane and in-plane directions due to decreased interfacial density and enhanced lateral intermolecular interactions, respectively. Combining both cross-plane and in-plane data, we reveal that the anisotropic thermal transport behavior remains relatively modest ($\alpha_r/\alpha_z < 2.7$) and progressively decreases with either an increase in the octahedral-layer thickness or an increase in the chain length of aliphatic organic spacers. Our experimental results are corroborated by first-principles calculations, which reveal low sound speeds, high phonon scattering rates, short phonon mean free paths, and strong influence of four-phonon scattering in limiting the thermal conductivity of 2D-MHPs.

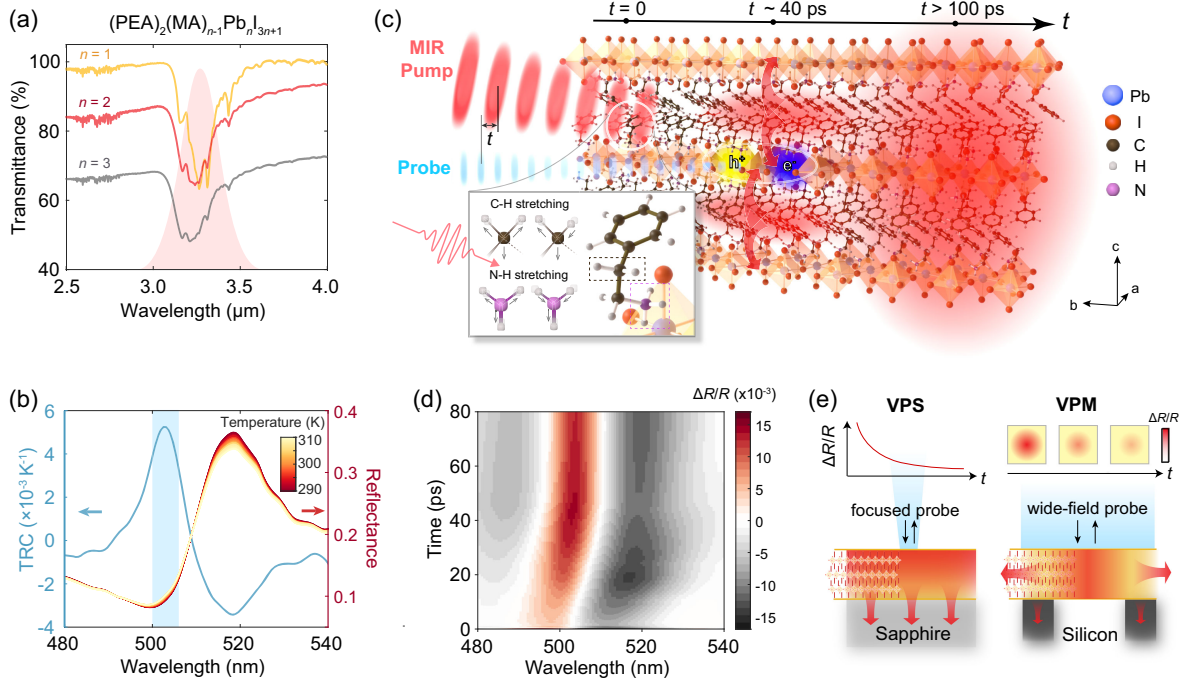


FIG. 1. Working principles of VPVP spectroscopy (VPS) and VPVP microscopy (VPM). (a) FTIR transmittance spectra of thin films of PEA- $n1$ (980-nm thick), PEA- $n2$ (1110-nm thick), and PEA- $n3$ (1060-nm thick). The spectra are vertically shifted for clarity. The absorption peaks centered at $3.2 \sim 3.3 \mu\text{m}$ originate from N-H and C-H stretching vibrations, confirming the feasibility of MIR vibrational excitation of 2D-MHPs (MIR pump represented by the red shaded area). (b) Temperature-dependent reflectance spectra of PEA- $n1$ measured near ambient temperature, along with the calculated thermoreflectance coefficient (TRC) as a function of wavelength (blue shaded area shows the probe wavelength in VPM). (c) Schematic of a PEA- $n1$ single crystal undergoing organic-inorganic sublattice thermal equilibration upon MIR vibrational excitation (0–40 ps), followed by macroscopic, anisotropic thermal transport (>100 ps). In VPS (VPM) experiments, macroscopic thermal transport is measured by time-delayed, ns-pulsed broadband (monochromatic) probe pulses. (d) Transient $\Delta R/R$ spectral map of PEA- $n1$ within the first 80-ps delay time window following vibrational pumping centered at $3.3 \mu\text{m}$. (e) Schematic illustration of VPS (left) for cross-plane thermal transport measurement on samples exfoliated onto sapphire and VPM (right) for in-plane thermal imaging on samples suspended on a holey Si substrate.

II. RESULTS

A. Principles of VPVP techniques

As shown in Fig. 1(a), 2D-MHPs exemplified by the PEA series exhibit pronounced absorption in the MIR region centered at $3.3 \mu\text{m}$, arising from infrared-active asymmetric N-H and C-H stretching vibrations [39]. Such vibrational absorption enables impulsive resonant pump excitation with femtosecond (fs) MIR pulses. Additionally, 2D-MHPs exhibit strong thermoreflectance effects [40], where a lattice temperature rise induces notable changes in optical reflectance (or transmittance), especially around the excitonic resonances [41]. As presented in Fig. 1(b) for PEA- $n1$, the strong exciton oscillator strength leads to a characteristic derivativelike feature in the reflectance spectrum. Temperature dependence of reflectance primarily stems from a variation in the exciton damping factor [42], which manifests as a diminished amplitude of this Lorentzian resonance-type spectral feature with increasing temperature. As a result, we observe a remarkably high thermoreflectance coefficient (TRC), i.e., $(1/R)[(\partial R)/(\partial T)]$, at room temperature, with a peak

positive value ($\sim 5 \times 10^{-3} \text{ K}^{-1}$) an order of magnitude higher than that of metallic transducers ($\sim 10^{-4} \text{ K}^{-1}$) used in TDTR and FDTR (Table S1) [21,28,43,44]. The inherent temperature-dependent reflectance of 2D-MHPs directly serves as a sensitive temperature probe in our VPVP experiments. Thermal transport measurement via VPVP thus includes impulsive heating of the materials by a MIR pulse, and real-time monitoring of temperature change by detecting the change of reflectance (or transmittance).

The sequential process of impulsive lattice heating and temperature sensing is illustrated in Fig. 1(c), using PEA- $n1$ as an example. A MIR pump (~ 200 fs) centered at $3.3 \mu\text{m}$ vibrationally excites the stretching modes of C-H and N-H in the PEA cations [Fig. 1(c) inset]. The subsequent thermal equilibration between the excited organic spacers and the inorganic sublattice unfolds on the tens-of-picoseconds timescale [41,45,46], as revealed in the picosecond transient $\Delta R/R$ spectral map [Fig. 1(d)], where $\Delta R/R = [R(t) - R(0)]/R(0)$ with $R(0)$ denoting the reflectance before pump excitation and $R(t)$ being the reflectance at time t after pump excitation. Following organic-inorganic sublattice phonon equilibration

(30–40 ps), the two sublattices in 2D-MHPs reach a mutual thermal equilibrium, characterized by pure-thermally induced $\Delta R/R$ spectra established at >50 ps (Supplemental Material note 5, Figs. S3 and S4) [28]. The subsequent thermal dissipation from 2D-MHPs to MIR-transparent substrates, driven by pump-induced temperature gradients, proceeds on the hundreds of ns to the μ s timescale. Estimated from our minimum detectable $\Delta R/R$ ($\sim 5 \times 10^{-4}$) in VPVP experiments and the TRCs of 2D-MHPs, our VPVP measurements, with a temporal resolution of one ns [44], detect pump-induced temperature perturbation down to ~ 0.1 K. In the weak perturbative regime in this work, $\Delta R/R$ scales linearly with lattice temperature rise, enabling quantitative readout of small temperature rise (in arbitrary units) based on $\Delta R/R$ [47]. Note that the MIR pump wavelength can match other vibrational modes besides the N-H and C-H stretching modes, as long as the absorption coefficient at the corresponding wavelength is well evaluated.

By selecting different MIR-transparent substrates with relatively high κ , we can establish desired spatial temperature gradient between the thermally excited 2D-MHPs and the unperturbed, MIR-transparent substrates, facilitating the probing of thermal transport in designated directions. As illustrated in Fig. 1(e), exfoliated 2D-MHPs on single-crystalline, *c*-plane sapphire promote a radially uniform pump excitation profile, and a unidirectional heat flow along the cross-plane direction. A visible probe focused on the crystal monitors the real-time reflectance change ($\Delta R/R$) that is proportional to the temperature rise. The $\Delta R/R$ vs time kinetics then allows the extraction of cross-plane thermal diffusivity (denoted as α_z). Placing 2D-MHP sheets onto Si substrates patterned with holes establishes an in-plane temperature gradient between the suspended and supported regions of the samples due to their different heat dissipation rates. A wide-field probe then captures the spatial profile of temperature rise at each delay time, constructing a spatiotemporal image of the in-plane heat flow that informs on the value of in-plane thermal diffusivity (α_r). All thermal measurements presented in Figs. 1–3 were conducted at ambient temperature using freshly exfoliated, single-crystalline sheets of 2D-MHPs.

B. Cross-plane thermal transport

We first measured cross-plane thermal transport using VPS. We selected *c*-plane sapphire as the substrate due to its high κ and suitable refractive index, which ensures a uniform pump absorption profile—and, consequently, a uniform initial temperature rise along the thickness direction, for the investigated range of sample thickness (Supplemental Material note 3) [28]. Figures 2(a) and 2(b) show the crystal structures and representative ns- μ s transient $\Delta R/R$ spectral maps for BA-*n*1, *n*2, and *n*3 sheets with ~ 170 -nm thickness. For each material, the $\Delta R/R$ spectra exhibit a derivativelike profile that

transitions from positive to negative with increasing wavelength, closely resembling the steady-state TRC spectrum shown in Fig. 1(b). As the *n*-number increases from 1 to 3, the $\Delta R/R$ spectral feature undergoes a redshift due to a reduction of the electronic band gap. Figure S5 displays representative $\Delta R/R$ data for HA-*n*1, OA-*n*1, PEA-*n*1, PEA-*n*2, and PEA-*n*3, with similar thicknesses [28]. A stability test is also presented in Fig. S5, where the sample response remained intact over consecutive measurements [28].

The decay kinetics of $\Delta R/R$ in Fig. 2(b) fall within the hundreds-of-ns regime. To ensure high fidelity of results, VPS was performed on ~ 20 flakes per compound across a range of thicknesses. Because of the much larger MIR pump spot size (~ 150 μ m in diameter) than the probe size (~ 5 μ m in diameter) in VPS, and the simple 2D-MHP/sapphire two-layer configuration, cross-plane thermal transport can be described and simulated by a 1D thermal-transport model, governed by $[(\partial T)/(\partial t)] = \alpha_z[(\partial^2 T)/(\partial z^2)]$, where α_z is the cross-plane thermal diffusivity, with prespecified initial and boundary conditions. The kinetics of $\Delta R/R$ extracted at the positive peaks in the transient spectral maps [dashed lines in Fig. 2(b)] are directly proportional to the time-dependent temperature rise (ΔT), averaged over the penetration depth of the probe in the material. Accurate determination of α_z requires knowledge of the 2D-MHP sample thickness, interfacial thermal conductance (G), and additionally, the penetration depths of both pump (δ_{pump}) and probe (δ_{probe}).

The high-quality crystal surfaces support strong Fabry-Perot-type interference due to light reflected at the top (air/2D-MHP) and bottom (2D-MHP/substrate) interfaces, resulting in periodic modulations in the reflectance spectrum below the band gap [Fig. 2(c)]. These interference patterns are directly correlated with sample thickness and the refractive indices of 2D-MHPs and sapphire (see Methods) [51]. The refractive index of sapphire was obtained from literature [52], while the complex refractive indices of 2D-MHPs are experimentally measured (Supplemental Material notes 6 and 7) [28] and presented in Fig. 2(d) for the BA series. Using these refractive indices, the sample thickness can be evaluated *in situ* during the experiments by fitting transfer-matrix-calculated reflectance to the measured reflectance spectrum with single-digit-nm accuracy, as illustrated in Fig. 2(e).

The probe penetration depths at the exciton resonance [dashed lines in Fig. 2(b)], which we used for temperature read out, were calculated from the refractive indices via $\delta_{\text{probe}} = [(4\pi\lambda)/k]$, where λ is the probe wavelength and k is the imaginary part of refractive index (Supplemental Material note 7, Tables S2, S3, and Fig. S6) [28]. The short δ_{probe} indicates that the temperature is mainly probed within the first <100 nm beneath the 2D-MHP surface. The estimated pump penetration depths (Supplemental Material note 3) are much larger than the sample thickness

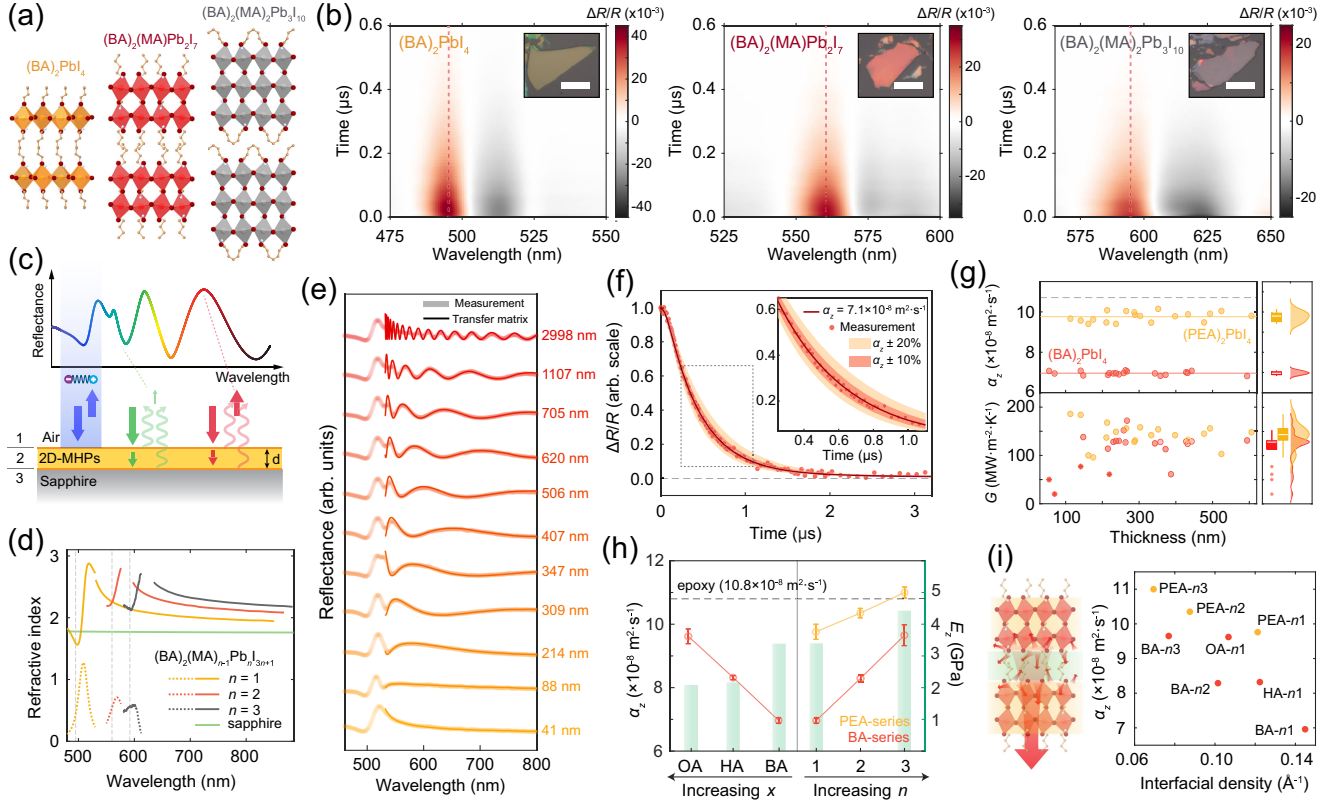


FIG. 2. Cross-plane thermal diffusivities of 2D-MHPs from VPS. (a) Crystal structures and (b) transient $\Delta R/R$ spectral maps of BA- $n1$, $n2$, and $n3$, with the insets showing the optical microscope pictures of the exfoliated crystals on sapphire. The scale bar is 50 μm . (c) Schematic depiction of derivativelike reflectance around the excitonic resonance and alternating constructive or destructive interference fringes in the below-band-gap region of 2D-MHPs. (d) Below-band-gap refractive indices, and refractive indices (real part: solid lines; imaginary part: dashed lines) around the excitonic resonances of BA- $n1$, $n2$, and $n3$. The refractive index of sapphire is also shown. (e) Thickness determination of exfoliated single-crystalline 2D-MHP sheets via transfer-matrix fitting of experimentally measured below-band gap reflectance. (f) Experimental $\Delta R/R$ decay overlaid by the best-fitted temperature decay, alongside calculated temperature decays adopting $\pm 10\%$ or $\pm 20\%$ variations of α_z . (g) Statistical cross-plane thermal diffusivities (α_z) and interfacial thermal conductance (G) extracted by fitting the experimental data for BA- $n1$ and PEA- $n1$. (h) Best-fitted cross-plane thermal diffusivities (α_z , left axis) of all studied 2D-MHPs (marked by circles), along with the cross-plane elastic moduli of OA- $n1$, HA- $n1$, BA- $n1$, and BA- $n3$ (E_z , right axis) presented by the green bars. The values of E_z are referenced from [48]. The thermal diffusivity of epoxy is referenced from [49]. (i) Schematics of diffuse interface scattering (DIS) dominant cross-plane thermal transport and the decreasing trend of α_z with larger interfacial density, defined as the number of organic-inorganic interfaces per unit length in the cross-plane direction.

(hundreds of nm), justifying the assumption of a nearly uniform initial temperature rise along the thickness, and a negligible sensitivity of our results to δ_{pump} under our experimental conditions (Supplemental Material note 8) [28].

With sample thickness, δ_{pump} , and δ_{probe} determined, the two unknown thermal properties, α_z and G , can be subsequently extracted by fitting the finite-element-method (FEM) simulated thermal decays to the measured $\Delta R/R$ kinetics (or, equivalently, the related decay of temperature rise). Sensitivity analysis (Fig. S7 and Supplemental Material note 8) reveals that the measured $\Delta R/R$ kinetics is primarily dependent on α_z [28], while exhibiting significantly lower sensitivity to G , in line with the intrinsically ultralow thermal diffusivities of 2D-MHPs and the relatively large sample thickness compared with the Kapitza length of the interface [14]. Similarly low sensitivity to G has been

reported for 3D-MHP/substrates with comparable thermal transport properties [53]. We note that VPS benefits from a simplified thermal model for its bilayer structure (i.e., no metallic transducers), and the absence of pulse accumulation effects with pump pulses operating at 1 kHz [54,55].

Figure 2(f) presents a representative $\Delta R/R$ decay for BA- $n1$ alongside its optimal fit by FEM-simulated temperature decay (averaged over δ_{probe}), allowing the determination of both α_z and G by minimizing the normalized mean square error between experimental and simulated decay curves [47,53]. Notable discrepancies arise when α_z deviates from its best fit by 10% to 20% [Fig. 2(f) inset]. Repeating this fitting procedure across ~ 20 samples for each compound, with thicknesses spanning sub-100 nm to ~ 600 nm, we obtained statistically robust values for α_z and G as representatively shown in Fig. 2(g) for PEA- $n1$ and

BA-*n*1 (other data in Fig. S8 [28]). The extracted α_z exhibit high consistency and reproducibility across samples—with small error bars (<5% in the most cases, <3% in the best case), defined as the standard deviation of repeated measurements. The fitted G displays larger variability within a reasonable range, likely due to both our low sensitivity to G and differences in sample-substrate adhesion introduced during mechanical exfoliation.

The complete set of extracted α_z values for $(C_xH_{2x+1}NH_3)_2(MA)_{n-1}Pb_nI_{3n+1}$ and $(PEA)_2(MA)_{n-1} \times Pb_nI_{3n+1}$ is summarized in Fig. 2(h), together with the out-of-plane elastic moduli (E_z) of OA-*n*1, HA-*n*1, BA-*n*1, and BA-*n*3 referenced from [48]. Several prominent trends emerge. First, the α_z of all eight materials investigated, except for PEA-*n*3, are lower than that of epoxy, a widely adopted thermal-insulating polymer. Second, for any given n member, the PEA series exhibits higher α_z than the BA series, which we qualitatively attribute to the higher rigidity of PEA cations [56,57], the enhanced interactions between neighboring PEA cations via π - π forces [58–60], as well as a larger distance between neighboring octahedral layers due to the bulkiness of PEA cations (*vide infra*). More importantly, α_z increases monotonically with both n and x , which are attributable to a reduced cross-plane organic-inorganic interfacial density. The monotonically increased α_z with x (i.e., the alkylammonium chain length), despite a $\sim$ 40% reduction in out-of-plane Young's modulus from BA-*n*1 to OA-*n*1 as shown in Fig. 2(h) [48], elucidates the predominant contribution from organic-inorganic interfacial density to cross-plane thermal transport. Analogous enhancement of cross-plane thermal transport with increasing period thickness—or decreasing interfacial density—was observed in other layered materials such as self-assembled monolayers (SAMs) and superlattices, where diffuse interface scattering (DIS) of phonons plays a crucial role in limiting the cross-plane thermal transport [61,62].

The DIS-dominated cross-plane thermal transport is schematically illustrated in Fig. 2(i), together with the overall decreasing trend of α_z with a larger cross-plane interfacial density, defined as the number of organic-inorganic interfaces per unit length along the cross-plane direction. The higher α_z in PEA-*n*1 than that of BA-*n*1 can largely be attributed to the smaller interfacial density. Consistently, OA-*n*1, with a longer alkylammonium spacer, exhibits a similar α_z to PEA-*n*1, despite PEA-*n*1 has a 5 times larger elastic modulus than that of OA-*n*1 [48,58]. The strong dependence of cross-plane thermal transport on interfacial density of 2D-MHPs contradicts with the intuitive positive correlation between rigidity and thermal conductivity, i.e., harder solids should be more thermally conductive [63]. This anomalous property promises a new route to orthogonal design of the mechanical and thermal properties of 2D-MHPs [58], via engineering the rigidity and length of the spacers separately. For example, higher cross-plane thermal conductivity but softer lattice can be

simultaneously achieved by incorporating longer and more flexible spacers.

C. In-plane thermal transport

Having determined α_z , we proceeded to quantify the α_r for these materials via VPM. To enable suspension of 2D-MHPs that facilitates in-plane thermal transport in VPM experiments, we used photolithography and reactive-ion etching to pattern periodic holes on Si wafers (Fig. S9) [28]. The diameter of the holes and the pitch size were 4.5 and 6.5 μ m, respectively—chosen to enable a lateral temperature decay on the tens-of- μ s timescale—with slight fabrication variability across samples accounted for by post-fabrication optical microscopy measurements. Figures 3(a) and 3(b) display a cross-sectional scanning electron microscopy (SEM) image and a top-down optical micrograph of a suspended PEA-*n*1 flake. The flake thickness was extracted based on below-band-gap reflectance interference following the procedure outlined in Fig. 2(e).

Figure 3(c) illustrates the cascading thermal transport processes from the 2D-MHP to the holey Si substrate, alongside representative experimental data obtained for a 480 nm-thick PEA-*n*1 sheet. In all VPM experiments, the probe wavelength was centered at the positive $\Delta R/R$ peak wavelength identified from VPS with a bandwidth of $\sim$ 8 nm in full-width-half-maximum. The data in Fig. 3(c) reveal that immediately following MIR vibrational excitation (0- μ s delay), the entire flake experiences elevated temperature, followed by a rapid, oscillatory “breathing” motion of the suspended membranes within the first few hundred ns (Supplemental Material note 9, Fig. S10) [28]. After the Si-contacted 2D-MHP regions mostly cool down ($\geq$ 3- μ s delay), excess heat in the suspended regions undergoes lateral transfer to the supported 2D-MHP regions, persisting until the entire sample returns to pre-pump-excitation temperature at tens-of- μ s delay time.

Exploiting the axisymmetric symmetry of suspended membranes, we performed an azimuthal averaging of the temperature profiles (Fig. S11) [28], yielding spatiotemporal data shown representatively in Fig. 3(d). Using FEM simulations, which incorporated azimuthal symmetry and measured sample geometry (2D-MHP thickness and hole diameter), we simulated spatiotemporal temperature distribution to fit the experimental data, as shown in Fig. 3(e) for a PEA-*n*1 sample. The α_r value was obtained by matching experimental and simulated temperature profiles over both time and space. To avoid influence from the initial breathing motions and isolate in-plane thermal transport from the cross-plane one, we used VPM data starting from $\sim$ 3 μ s for all the fitting. By this delay time, the breathing mode is fully relaxed, the Si-supported regions have cooled down, while the pronounced in-plane temperature gradient remains, enabling accurate fitting of in-plane thermal transport. More VPM data are shown in Fig. S12 and videos in Supplemental Material [28].

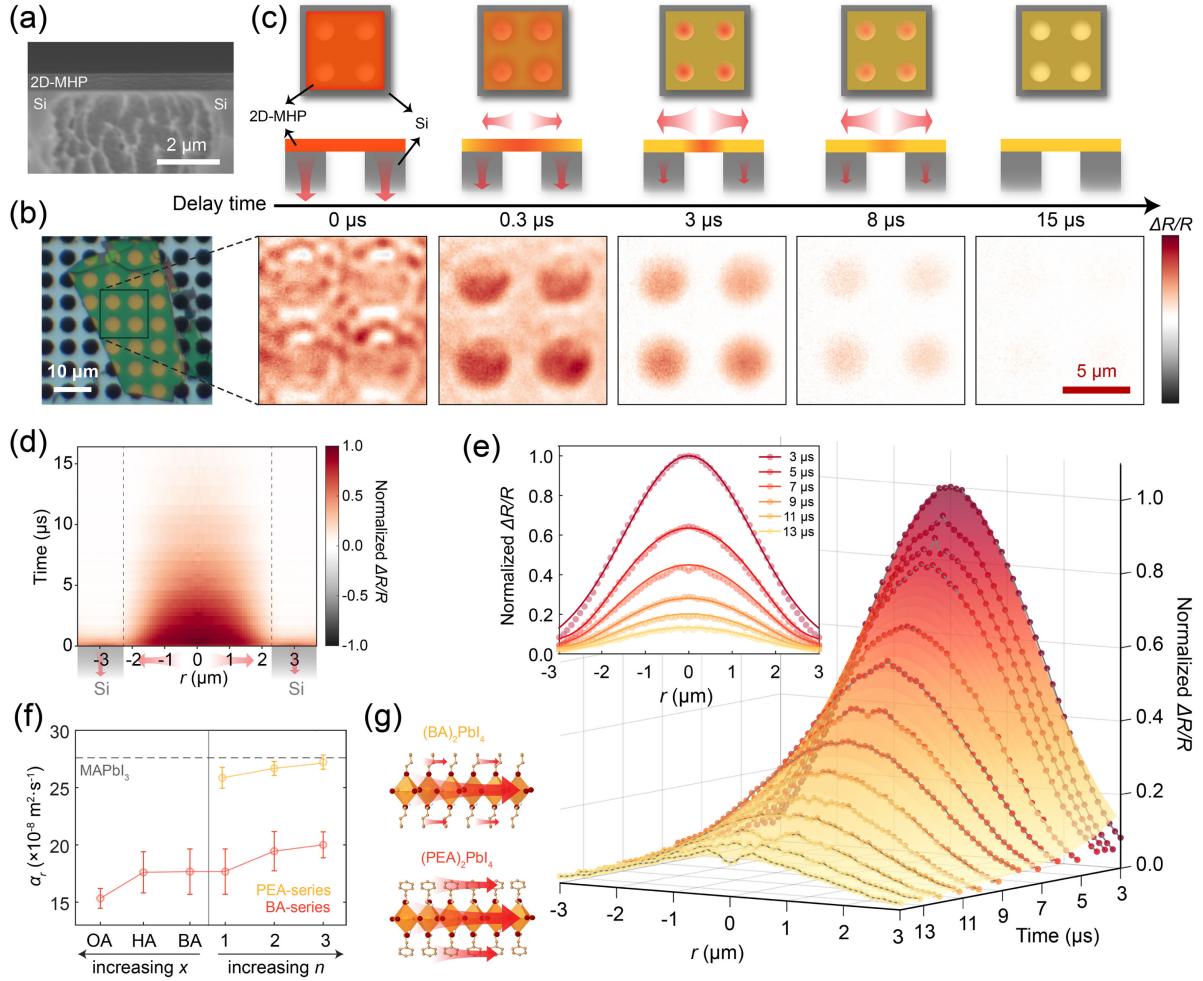


FIG. 3. In-plane thermal diffusivities of 2D-MHPs from VPVP microscopy. (a) Cross-sectional SEM image and (b) optical microscopy image of a PEA-*n*1 sheet exfoliated onto a holey Si substrate. In (b), the black discs correspond to holes in Si substrate. (c) Schematic representation (upper panel) and experimental VPVP microscopy data (lower panel) illustrating cascaded thermal transport from the PEA-*n*1 sheet to the holey Si substrate. At time zero, the entire PEA-*n*1 sheet is uniformly heated by the vibrational pump. Heat then dissipates from the PEA-*n*1 into the Si-supported regions, while the suspended regions retain heat longer. At later times (e.g., 3 μ s), PEA-*n*1 on the Si-supported region are nearly cooled, whereas lateral (in-plane) heat transfer occurs from the suspended region to the Si-supported region of PEA-*n*1. (d) Azimuthally averaged, spatiotemporal evolution of $\Delta R/R$ measured on the suspended region of PEA-*n*1. (e) 3D surface plot of simulated temperature decay profile for a 480 nm-thick PEA-*n*1 sheet, overlaid with experimentally measured data (dotted lines). The figure inset compares experimental data and best simulation fit at selected delay times. All data in (e) are azimuthally averaged. (f) Best-fitted in-plane thermal diffusivities (α_r) of all studied 2D-MHPs. The benchmark value of single-crystal MAPbI₃ (dashed line) is referenced from [50]. (g) Schematics showing octahedral-network dominated in-plane thermal transport in BA-*n*1 and PEA-*n*1.

The extracted α_r values for all eight materials are summarized in Fig. 3(f). Notably, the trend of α_r with varying *n* mirrors that of α_z : both BA- and PEA-based materials have monotonically increased α_r with *n*, with PEA-based materials showing consistently higher α_r than their BA counterparts. Strikingly, PEA-*n*3 exhibits an α_r approaching that of its 3D analog, MAPbI₃ [50,64], where the organic-inorganic interfaces are absent. Furthermore, while the incorporation of longer organic spacers (HA and OA) increases α_z by reducing the organic-inorganic interfacial density, it leads to a decrease in α_r . This opposite trend of α_r and α_z with organic chain length indicates that in-plane thermal transport is governed by distinct

mechanisms and is predominantly enabled by the inorganic sublattice, owing to its continuous octahedral network and interconnected covalent bonding [Fig. 3(g)]. In contrast, the organic sublattice, which comprises a larger volumetric fraction in HA- and OA-based 2D-MHPs, contributes less due to its weak in-plane van der Waals interactions. Meanwhile, despite PEA-*n*1 and OA-*n*1 having similar organic-inorganic volumetric ratios (i.e., similar cross-plane interfacial densities) and sharing the same octahedral network, they exhibit significantly different α_r , i.e., $\alpha_r(\text{PEA-}n1)/\alpha_r(\text{OA-}n1) \approx 1.7$. In the in-plane direction, the benzene rings in PEA⁺ align parallel to their neighbors, featuring a sandwich-type π - π stacking orientation. This

benzene orientation maximizes the interaction strength between the neighboring PEA^+ cations, which in turn boosts the in-plane thermal transport. Another possible factor is that the $[\text{PbI}_6]^{4-}$ octahedra are more distorted in samples with alkyl-ammonium-chain spacers, leading to larger lattice anharmonicity that suppresses heat transfer within the octahedral network.

D. Thermal transport anisotropy and first-principles calculations

With both α_z and α_r determined, we calculate thermal diffusivity anisotropy, defined as α_r/α_z , and present the results in Fig. 4(a). Using the measured specific heat capacities [C_p , Fig. 4(b)], we obtain thermal conductivities (i.e., κ_r and κ_z) using $\kappa = \rho C_p \alpha$ (ρ is mass density determined from crystal structures), as presented in Fig. 4(c). The thermal properties of all studied compounds are summarized in Table I. We note that the thermal transport anisotropy can be fully determined by the thermal diffusivity values and is independent of the measured C_p . From Fig. 4(a), we observe that 2D-MHPs with larger cross-plane period thickness (either by increased n or increase in x) exhibit progressively reduced anisotropy. Additionally, the PEA series show slightly higher anisotropy than the BA series, attributable to their higher α_r . Overall, thermal transport anisotropy in the examined 2D-MHPs is lower than that of other layered 2D materials, as summarized in Fig. S13 [28,65,66].

To further interpret the measured thermal-transport properties and anisotropy, we performed first-principles calculations based on density functional theory (DFT). We adopted a unified thermal transport theory that explicitly includes both the diagonal term—corresponding to the Pierels-Boltzmann treatment of the conventional phonon gas model—and the off-diagonal term, which accounts for heat transport mediated by wavelike tunneling [67]. Because of the prohibitively large unit cells of hybrid 2D-MHPs, we chose a computationally tractable model system: the all-inorganic 2D-MHP Cs_2PbI_4 [Fig. 4(d), inset], constructed by substituting the organic cations in the $n1$ compounds with Cs^+ . This substitutional approach has been widely adopted in previous DFT studies to gain insights into the electronic and excitonic properties of 2D-MHPs [68,69]. The calculated κ_r and κ_z for Cs_2PbI_4 (0.411 and $0.182 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively; Supplemental Material Table S6) [28], incorporating both third-order and fourth-order lattice anharmonicities, yields a thermal transport anisotropy of 2.26. Although the calculated κ_r and κ_z for Cs_2PbI_4 are modestly higher than the measured values for hybrid $n1$ samples, both the magnitude and anisotropy show good agreement with experiments.

As shown in Fig. 4(d), the calculated phonon dispersion diagram at 0 K contains modes with imaginary frequencies, indicating structural instability of the DFT-relaxed structure. However, upon including temperature effects, the

structure is anharmonically stabilized at 300 K (i.e., the measurement temperature), and the phonon spectrum is strongly renormalized for the low-lying optical and acoustic branches [70]. The atom-projected phonon density of states [Fig. 4(d)] reveals that the low-frequency vibrations are primarily associated with iodide and cesium ions, consistent with the strong anharmonic octahedral tilting observed in BA- $n1$ and the large-amplitude motions of Cs^+ in CsPbBr_3 [27,71]. Contributions from the lead cations emerge at frequencies above ~ 1 THz.

Based on the calculated phonon dispersion, we extract the acoustic phonon speeds along both the in-plane and cross-plane directions [Fig. 4(e)]. These values are generally higher than the hybrid counterparts [72] and are in line with the higher calculated thermal conductivities, likely due to stronger interactions between the adjacent Cs^+ layers. To elucidate the effects of three-phonon and four-phonon scatterings, we present in Fig. 4(f) the phonon mode-resolved phonon scattering rates. The results reveal that four-phonon processes significantly enhance the total phonon scattering rates, particularly in the low-frequency range ($0 \sim 1.4$ THz) where heat-carrying acoustic phonons dominate, thereby contributing to reduced thermal conductivity. These high phonon scattering rates, combined with low phonon group velocities, result in short phonon MFPs, as presented in Fig. 4(g). We find that most phonon MFPs lie at or below the nanometer scale, with only a small subset extending beyond 10 nm, consistent with the intrinsically low thermal conductivity of these materials. Notably, the MFPs in Cs_2PbI_4 are also modestly lower than previous estimates of MFPs for 3D-MHPs, which reside in the single-digit nanometer range [50].

Using the mode-resolved phonon MFPs and their associated group velocities, we compute the cumulative κ_r and κ_z , considering only the diagonal term—i.e., the contribution from propagating phonon gas—and neglecting the off-diagonal diffusion channel. As shown in Fig. 4(h), the cumulative κ_r exhibits a steplike rise between 1 to 10 nm, indicating that phonons with MFPs below 10 nm account for the majority of in-plane heat transfer. In contrast, κ_z increases more gradually across the entire MFP range from 0.1 to 100 nm, reflecting contribution from a small number of long-MFP ($10 \sim 100$ nm) phonon modes. However, in hybrid 2D-MHPs, the presence of dynamically disordered organic spacer layers is expected to suppress phonon MFPs along the cross-plane direction, thereby reducing κ_z , as observed in our experimental data. It is worth noting that due to the very small κ_z , the off-diagonal diffusion channel contributes significantly to the total lattice thermal conductivity (43%) along the cross-plane direction, whereas its contribution to the in-plane thermal conductivity is smaller (22%). We did not include the MFP dependence of the diffusion channel because it involves coupling between different phonon modes, leading to ambiguity in choosing an appropriate MFP.

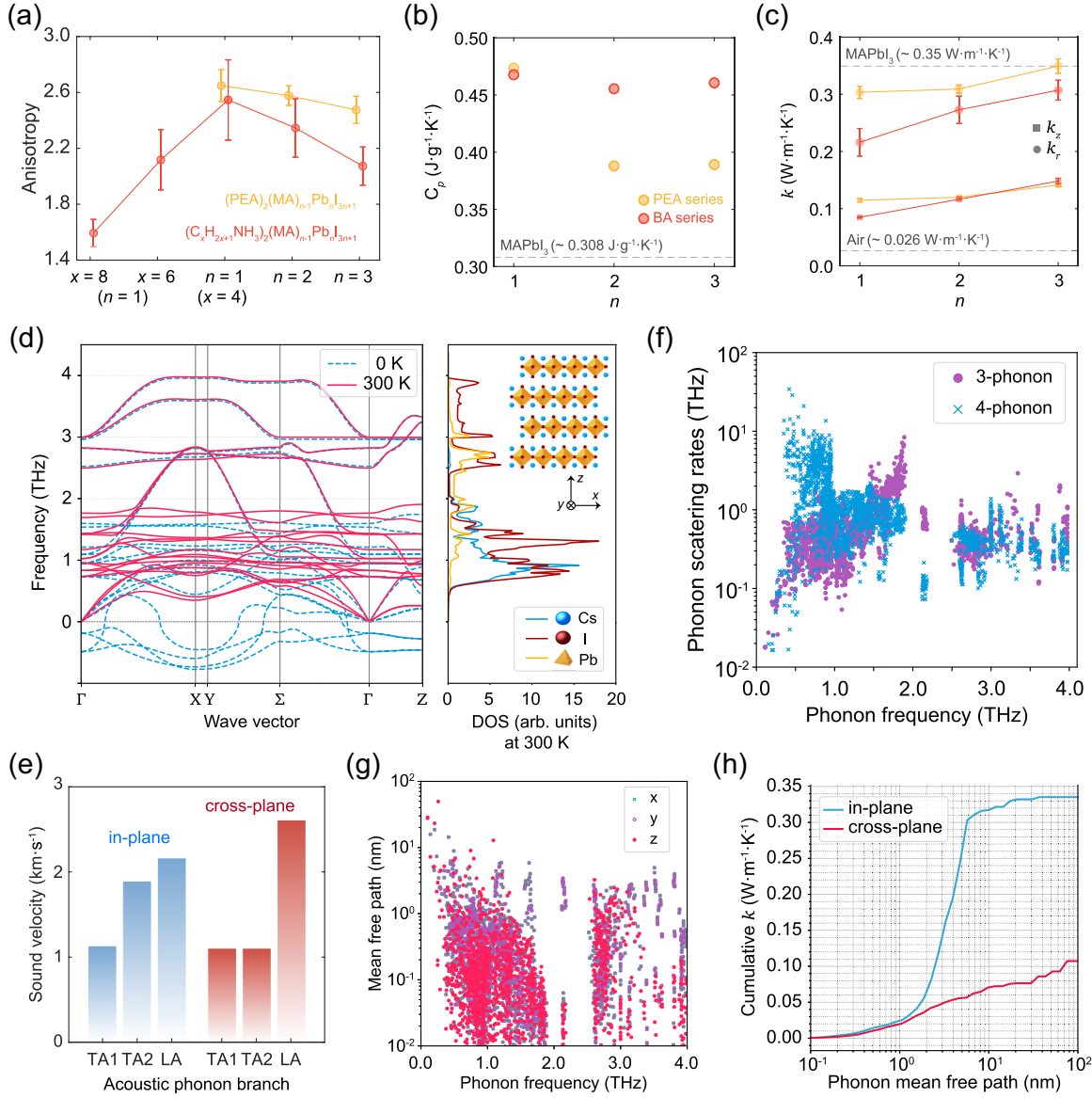


FIG. 4. Anisotropic thermal transport and first-principles thermal transport calculations. (a) Anisotropy of thermal diffusivities for all studied 2D-MHPs. The error bars are calculated as the combined error from both α_z and α_r as $\sqrt{[\text{std}(\alpha_z)/\text{mean}(\alpha_z)]^2 + [\text{std}(\alpha_r)/\text{mean}(\alpha_r)]^2}$, where std and mean indicate standard deviation and arithmetic average of the measured values, respectively. (b) Measured heat capacities for the PEA and BA series. (c) Experimentally determined anisotropic κ for the PEA and BA series. (d) Calculated phonon dispersion diagram (0 K, cyan; 300 K, red) and frequency-dependent phonon density of states of Cs₂PbI₄ (inset: crystal structure of Cs₂PbI₄). (e) Acoustic phonon speeds of Cs₂PbI₄ along the in-plane and cross-plane directions. (f) DFT-calculated phonon mode-resolved scattering rates due to three-phonon scattering and four-phonon scattering. (g) Frequency-dependent phonon MFPs. (h) Calculated cumulative thermal conductivity as a function of phonon MFP (blue: κ_r ; red: κ_z), where only the diagonal, phonon-gas contribution is included.

III. DISCUSSION

In summary, we introduced a transducer-free, all-optical VPVP methodology for quantitatively tracking anisotropic thermal transport in single-crystalline 2D-MHPs. We investigated a series of single-crystalline RP-phase 2D-MHPs, including (BA)₂(MA)_nPbI_{3n+1}, (PEA)₂ × (MA)_nPbI_{3n+1}, (OA)₂PbI₄, and (HA)₂PbI₄, and report their in-plane and cross-plane thermal diffusivities and

most of their conductivities with high fidelity. Our results show superlattice-like anisotropic thermal transport behaviors and how they are influenced by the thickness of octahedral sublattice, as well as the length and rigidity of organic spacers. These findings underscore the important role of DIS and insensitivity to lattice rigidity in the cross-plane thermal transport properties of 2D-MHPs. This enables individual control over the cross-plane mechanical

TABLE I. Summary of thermal properties of 2D-MHPs studied in this work.

Material	ρ (g · cm ⁻³)	C_p (J · g ⁻¹ · K ⁻¹)		α_z (10 ⁻⁸ m ² /s)	α_r (10 ⁻⁸ m ² /s)	Anisotropy	κ_z (W · m ⁻¹ · K ⁻¹)	κ_r (W · m ⁻¹ · K ⁻¹)
		(DSC)						
BA- <i>n</i> 1	2.614	0.4677		6.96 ± 0.09	17.67 ± 1.98	2.55 ± 0.29	0.085 ± 0.001	0.216 ± 0.024
BA- <i>n</i> 2	3.080	0.451		8.29 ± 0.11	19.45 ± 1.71	2.35 ± 0.21	0.116 ± 0.002	0.272 ± 0.024
BA- <i>n</i> 3	3.333	0.354		9.65 ± 0.33	20.01 ± 1.13	2.07 ± 0.14	0.148 ± 0.005	0.307 ± 0.017
PEA- <i>n</i> 1	2.479	0.4785		9.76 ± 0.24	25.85 ± 0.91	2.65 ± 0.11	0.115 ± 0.003	0.303 ± 0.011
PEA- <i>n</i> 2	2.987	0.393		10.35 ± 0.15	26.67 ± 0.61	2.58 ± 0.07	0.120 ± 0.002	0.309 ± 0.007
PEA- <i>n</i> 3	3.299	0.389		11.00 ± 0.17	27.22 ± 0.98	2.47 ± 0.10	0.141 ± 0.002	0.349 ± 0.013
(HA) ₂ PbI ₄	2.319	...		8.32 ± 0.06	17.61 ± 1.79	2.12 ± 0.22	...	...
(OA) ₂ PbI ₄	2.123	...		9.62 ± 0.23	15.33 ± 0.86	1.59 ± 0.10	...	...

and thermal properties via the rigidity and length of the organic spacer, respectively. The in-plane thermal transport, on the other hand, is primarily governed by phonon transport within the inorganic layers and partially influenced by interactions between neighboring organic spacers. These experimental results are rationalized by DFT calculations, showing strong phonon scattering, short phonon MFPs, and pronounced lattice anharmonicity as intrinsic traits of these soft, hybrid semiconductors. Our demonstrated VPVP platforms enable precise characterization of anisotropic thermal diffusivities without the need for invasive sample processing and promise *in situ* measurement of a wide range of hybrid, organic, and polymeric materials.

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P. G. conceived and supervised the project. D.C. conducted optical experiments, COMSOL simulations and anisotropic thermal conductivity fitting. T. T. M. C., S. L., Y. L., L. Dai, X. L., and J. Y. P. synthesized the single crystals. Y. L. and M. Lu fabricated the holey Si substrates. Q. H. and L. Dou performed DSC experiments. T. W. and M. Liu helped with thickness measurements. P. G. assisted with optical measurements and modeling. Y. X. performed DFT calculations. D. C. and P. G. wrote the manuscripts with inputs from co-authors.

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: THERMAL TRANSPORT SIMULATIONS

Both the cross-plane and in-plane thermal transport simulations were performed with COMSOL Multiphysics by solving the Fourier's equation of heat conduction with appropriate initial and boundary conditions. For cross-plane thermal transport, we simplified the simulation to a 1D geometry:

$$\frac{\partial T}{\partial t} = \alpha_z \frac{\partial^2 T}{\partial z^2}$$

$$\frac{\partial T_s}{\partial t} = \alpha_{z,s} \frac{\partial^2 T_s}{\partial z^2},$$

with initial and boundary conditions

$$T(z, t = 0) = T_0 + \Delta T e^{-\frac{z}{\delta_{\text{pump}}}} (0 < z < d)$$

$$Q = -G(T(z = d, t) - T_s(z = d, t)) \text{ at } z = d,$$

where α_z and $\alpha_{z,s}$ are the cross-plane thermal diffusivity of the 2D-MHPs and substrate, respectively, T and T_s are the temperature of the 2D-MHPs and substrate, respectively, d is the thickness of the 2D-MHPs, T_0 is the measurement temperature (room temperature here), ΔT is the maximum temperature rise at the surface of the sample, δ_{pump} is the pump penetration depth, and G is the interfacial thermal conductance between the 2D-MHP and the substrate. An initial temperature rise decaying exponentially from the top surface of the perovskite to its interior was assigned to account for the initial depth-dependent absorption of the MIR pump. The surface temperature averaged from the top surface to the penetration depth of the corresponding probe wavelength (δ_{probe}) is taken to represent the temperature response detected by the probe light. Although analytical solution to the above model exists (Supplemental Material note 10), solving the heat transfer equation using FEM is more numerically stable and efficient.

In the in-plane transport simulation, axial symmetry is used to recover the anisotropic thermal transport occurring in the flake, with the following heat transfer equation in the cylindrical coordinate:

$$\frac{\partial T}{\partial t} = \alpha_z \frac{\partial^2 T}{\partial z^2} + \frac{\alpha_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right)$$

$$T(r, z, t=0) = T_0 + \Delta T e^{-\frac{r^2}{2\sigma^2}} (0 < z < d)$$

$$Q = -G[T(r, z=d, t) - T_s(r, z=d, t)] \text{ at } r \geq R,$$

where r represents the radial distance from the center of the suspended region, σ is the initial temperature distribution extracted from experiments, and R is the radius of the hole.

APPENDIX B: IN SITU EVALUATION OF THICKNESS FROM REFLECTANCE SPECTRA

In the three-layer thin-film structure shown in Fig. 2(c), i.e., air/2D-MHPs/sapphire, the reflection coefficient for transverse-electric-polarized (s -polarized) light incident at an angle of θ_1 is

$$r = \frac{r_{12} + r_{23}e^{2i\beta}}{1 + r_{12}r_{23}e^{2i\beta}},$$

where $r_{nm} = (p_n - p_m)/(p_n + p_m)$, $p_m = \tilde{n}_m \cos \theta_m$, $\beta = [(2\pi)/\lambda] \tilde{n}_2 d \cos \theta_2$, and $\theta_m = \sin^{-1}(\sin \theta_1 / \tilde{n}_m)$. The total reflectance is $R = |r|^2$. For normal incidence ($\theta_1 = 0$) and in the long-wavelength end away from the absorption edge, the reflectance is dependent on the thickness d and refractive indices of 2D-MHPs ($\tilde{n}_2$), and sapphire ($\tilde{n}_3$). With known or predetermined $\tilde{n}_2$ and $\tilde{n}_3$, d was iteratively changed and the corresponding reflectance is calculated with transfer matrix method to fit the measured results. Correct thickness can then be determined from the best

match between the calculated and measured reflectance spectrum, as illustrated in Fig. 2(e).

APPENDIX C: DETERMINATION OF BELOW-BAND-GAP REFRACTIVE INDICES

The below-band-gap refractive indices of 2D-MHPs were determined utilizing optical interference effects exhibited by 2D-MHP single-crystalline sheets on lower-refractive-index substrates [72]. Specifically, below-band-gap light penetrates through the entire crystal and optical interference occurs between reflection at the top (air/2D-MHP) and the bottom (2D-MHP/substrate) interfaces, leading to alternating maxima and minima in its reflectance spectrum. The constructive and destructive interference conditions at the reflectance maxima and minima are shown below.

$$2n(\lambda)d = \left(m - \frac{1}{2}\right)\lambda \quad (\text{maxima})$$

$$2n(\lambda)d = m\lambda \quad (\text{minima}),$$

where λ is the wavelength, $n(\lambda)$ is the wavelength-dependent real refractive index, d is the crystal thickness, and m is a positive integer denoting the mode number. The above two equations permit the calculation of $n(\lambda)$ at wavelengths where reflectance extreme values occur. The thickness can be precisely determined by optical profilometer and the mode number m is determined by a phase-match fitting procedure detailed in Supplemental Material note 6 [28].

APPENDIX D: DETERMINATION OF COMPLEX REFRACTIVE INDICES AROUND EXCITON RESONANCES

Because of the relatively strong quantum confinement and weak dielectric screening, the optical permittivity of $n1$ and $n2$ compounds can be described by a single Lorentzian oscillator model [73]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A_L^2}{\omega_L^2 - \omega^2 - i\omega\gamma},$$

where ε_∞ , A_L , ω_L , and γ are the high-frequency permittivity, exciton oscillator strength, resonance frequency, and damping factor, respectively. We extracted these parameters by fitting the transfer-matrix-calculated reflectance to the experimentally measured one.

For $n3$ compounds, the Lorentzian oscillator model cannot accurately reproduce the reflectance spectra due to a small exciton binding energy and spillover of joint density of states due to band-to-band transitions. To cope with this situation, we used a dielectric-coating method [74,75] to measure the complex refractive index $\tilde{n} = n + ik$ around the exciton resonance. Sheets of $n3$ compounds

were exfoliated onto a thin (265 nm thickness) dielectric Si_3N_4 membrane. The reflectance was collected from the top and bottom sides of the MHP/ Si_3N_4 bilayer structure structure, then n and k were simultaneously determined by cross fitting the two reflectance spectra. More details are available in Supplemental Material note 7 [28].

APPENDIX E: DFT CALCULATIONS OF LATTICE THERMAL CONDUCTIVITY OF Cs_2PbI_4

We conducted first-principles simulations to calculate the vibrational and thermal transport properties of bulk Cs_2PbI_4 using the Vienna *ab initio* simulation package (VASP) [76–79]. Our computational approach encompassed structure relaxation and self-consistent density functional theory (DFT) calculations. We employed the projector-augmented wave (PAW) method [80] in combination with the Perdew-Burke-Ernzerhof revised for solids (PBEsol) [81,82] generalized gradient approximation (GGA) [83] for the exchange-correlation (xc) functional [84]. For structure relaxations of the primitive cell of Cs_2PbI_4 , we utilized Gamma-centered $\mathbf{k}$ -point meshes with a minimum spacing of $0.2 \text{ \AA}^{-1}$ between the $\mathbf{k}$ points. Throughout the study, we maintained a kinetic energy cutoff of 520 eV. To ensure computational accuracy, we set stringent convergence criteria: $10^{-3} \text{ eV} \cdot \text{\AA}^{-1}$ and 10^{-8} eV for the force and energy, respectively. To compute the harmonic phonon dispersion, we employed the Phonopy software package [85] and used a $3 \times 3 \times 3$ supercell containing 189 atoms in total. Compressive sensing lattice dynamics (CSLD) [86] was utilized to extract anharmonic interatomic force constants (IFCs), with the cutoff distances for third- and fourth-order IFCs limited up to 6.0 and 4.5 $\text{\AA}$, respectively. These cutoff distances have been verified to achieve good convergence of lattice thermal conductivity, which was calculated using our own implementation of self-consistent phonon theory [87], three- and four-phonon scatterings [87], and the unified thermal transport theory [67,88,89]. The calculated density of states (DOS) projected to individual atoms at 0 and 300 K, as well as the group velocities along the in-plane (x) and out-of-plane (z) direction are shown in Fig. S26 [28]. The DFT-calculated diagonal and off-diagonal contributions to the thermal conductivities of Cs_2PbI_4 are listed in Supplemental Material Table S6 [28].

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