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Tunable Ferroelectricity in Ruddlesden–Popper Halide Perovskites

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Supporting Information

ABSTRACT: Ruddlesden–Popper (RP) halide perovskites are the new kids on the block for high-performance perovskite photovoltaics with excellent ambient stability. The layered nature of these perovskites offers an exciting possibility of harnessing their ferroelectric property for photovoltaics. Adjacent polar domains in a ferroelectric material allow the spatial separation of electrons and holes. Presently, the structure–function properties governing the ferroelectric behavior of RP perovskites are an open question. Herein, we realize tunable ferroelectricity in 2-phenylethylammonium (PEA) and methylammonium (MA) RP perovskite $(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_{n+1}\text{I}_{3n+1}$. Second harmonic generation (SHG) confirms the noncentrosymmetric nature of these polycrystalline thin films, whereas piezoresponse force microscopy and polarization–electric field measurements validate the microscopic and macroscopic ferroelectric properties. Temperature-dependent SHG and dielectric constant measurements uncover a phase transition temperature at around 170 °C in these films. Extensive molecular dynamics simulations support the experimental results and identified the correlated reorientation of MA molecules and ion translations as the source of ferroelectricity. Current–voltage characteristics in the dark reveal the persistence of hysteresis in these devices, which has profound implications for light-harvesting and light-emitting applications. Importantly, our findings disclose a viable approach for engineering the ferroelectric properties of RP perovskites that may unlock new functionalities for perovskite optoelectronics.

KEYWORDS: Ruddlesden–Popper perovskites, ferroelectricity, second harmonic generation, polarization–electric field, and molecular simulation

INTRODUCTION

Organic–inorganic halide perovskites have garnered tremendous attention because of their potential for facile low-cost high-efficiency photovoltaic technology. Their outstanding properties such as large absorption coefficient,¹ tunable band gap,² long charge carrier diffusion lengths,^{3,4} high charge carrier mobility,⁵ and low exciton binding energy⁶ also make them suitable for a broad range of optoelectronic applications apart from photovoltaics.⁷ These include light-emitting devices,⁸ transistors,⁹ memory devices,¹⁰ lasers,² and photo-detectors.¹¹ Amidst the intense debate over the origin(s) of hysteresis (i.e., defects,¹² ion migration,¹³ and ferroelectricity¹⁴) in perovskite solar cells, the ferroelectric nature of halide perovskites was thrown into the spotlight. This triggered a controversy as mixed findings over the ferroelectric behavior in three-dimensional (3D) $\text{CH}_3\text{NH}_3\text{PbI}_3$ were reported.^{15–18} Although recent measurements¹⁶ seem to have established ferroelectricity in tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$, its origin and the very existence still remain under strong debate. As for the two-dimensional (2D) systems, Liao et al. discovered ferroelectricity in a layered (benzylammonium)₂PbCl₄ crystal that

exhibits strong polarization at a higher Curie temperature.¹⁹ However, the large band gap of 3.65 eV (i.e., absorption below 367 nm) makes this system unsuitable for most optoelectronic devices. Ye et al. tuned the band gap between 3.05 and 2.74 eV in cyclohexylammonium-based layered perovskite through composition engineering.²⁰ Though these materials exhibited excellent ferroelectric properties, such a band gap range is still undesirable for optoelectrical applications. Apart from these reports, Sun et al. also reported ferroelectric polarization in layered single bis(cyclohexylammonium)tetrabromo lead where the corner-sharing PbBr_6 octahedra are interleaved by the bilayers of organic ammonium cations.²¹ A remarkable photoconductivity with $>10^4$ on/off current ratio is achieved, which is comparable to that of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Nonetheless, there is no concerted effort to systematically tune the ferroelectricity.

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Figure 1. RP perovskites and SHG. (a) Structural orientation of RP perovskites $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{PbI}_{3\bar{n}+1}$ (where $\bar{n} = 2$ to ∞) on a conducting substrate. (b) Samples excited by a p-polarized beam at an incident angle $\theta = 60^\circ$ to the normal of the sample surface. (c) SHG intensity and the out-of-plane component of $\chi^{(2)}$ as a function of $\bar{n}$. The error bars represent the uncertainties in the determination of SHG intensities.

Ferroelectricity is the characteristic of a dielectric material to spontaneously switch its polarization under an external electric field, and the polarization persists even after the electric field is removed. Ferroelectricity has a strong influence on spatial charge separation and carrier transfer,²² thus affecting the performance of perovskite devices. To further improve the performance and stability of electronic devices, it is essential to understand how to enhance or suppress the ferroelectricity in halide perovskites for specific applications. For instance, ferroelectricity in Ruddlesden–Popper (RP) perovskite can lead to the formation of distinct electron and hole diffusion pathways toward the respective electrodes, thereby avoiding the chance encounters of opposite charges and suppressing recombination losses in solar cell devices. These diffusion pathways are mainly located at the boundaries of the ferroelectric domains inside the bulk film.^{23–25} The spontaneous spatial charge separation and suppression of the recombination losses yield a higher open-circuit voltage and thus better efficiency in photovoltaics.²⁴ On the other hand, such avoidance is undesirable for light-emitting diodes (LEDs) as it could lead to reduced emission efficiency as well as decreased emission color purity under sustained operations.²⁶

Recently, RP halide perovskites are found to exhibit favorable photovoltaic efficiency (power conversion efficiency (PCE) = 20.6%)²⁷ and LED performance (EQE = 14.4%)²⁸ with excellent moisture stability. RP perovskites have a general formula $(\text{RNH}_3)_2\text{A}_{\bar{n}-1}\text{M}_{\bar{n}}\text{X}_{3\bar{n}+1}$ ($\bar{n} = 1, 2, 3, 4, \dots$), where RNH_3 is a large organic ammonium-insulating spacer cation [e.g., 2-phenylethylammonium (PEA), *n*-butylammonium (*n*-BA), etc.], and A represents a monovalent organic cation [e.g., CH_3NH_3^+ (MA^+), $\text{HC}(\text{NH}_2)_2^+$ (FA^+), etc.]. M is a divalent metal cation such as Pb and Sn, whereas X represents a halide anion and $\bar{n}$ is the number of $[\text{MX}_6]^{4-}$ octahedral layers within

each organic spacer. Essentially, RP halide perovskites can be considered as $\bar{n}$ layers of $[\text{MX}_6]^{4-}$ octahedral sheets sandwiched by two layers of large organic spacer cations that are held together by weak van der Waals forces (Figure 1a). Here, we posit that the “soft nature” of layered RP halide perovskites and its rich chemistry could be leveraged to engineer the ferroelectric properties. Different organic species can be accommodated in the intervening organic layers to induce distortions of the $[\text{PbI}_6]^{4-}$ octahedral and the interplay of dipole–dipole interactions between methylammonium (MA) molecules to influence the ferroelectric properties. Although the generation of the second harmonic signal evidences the presence of noncentrosymmetry in the structures, dipole–dipole interactions offer an unprecedented degree of freedom to maximize ferroelectric polarization. Furthermore, the coercive electric field and remnant polarization are well-captured by molecular dynamics (MD) simulations proving the orchestrated origin of the ferroelectricity. Temperature-dependent SHG and dielectric constant measurements of the phase transition temperature around 170 °C in these films provide unequivocal proof of the existence of ferroelectricity.

RESULTS AND DISCUSSION

Our samples are a family of RP perovskites based on PEA and MA with the general formula $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{PbI}_{3\bar{n}+1}$ (Figure 1a). Note that $\bar{n}$ represents the dominant *n* component for each sample, though other phases may be present in smaller proportions. It is extremely challenging to synthesize and fabricate single-phase polycrystalline thin films. Yang et al. and Han et al. reported that a dominant phase can be achieved through composition and phase engineering in quasi-two-

Figure 2. Piezoresponse force micrographs and ferroelectric polarization switching in RP perovskites. PFM images of the $\bar{n} = 5$ sample after (a) -4 V dc poling and (c) $+4$ V dc poling. (b,d) Dipole directions (depicted by red/blue arrows) in the sample after -4 V dc or $+4$ V dc poling with the tip. The regions in phase with the reference external ac sinusoidal electric field (inset) are represented by the red arrows and the regions in random phase by blue arrows. The direction of the poling electric field is shown by the black arrows. In relation to the PFM images in (a,c), the regions with the same color exhibit a 180° phase difference (i.e., dipoles had flipped) after poling with an opposite polarity (i.e., from -4 to $+4$ V poling). (e,f) Local phase and amplitude remnant hysteresis loops for the RP perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{PbI}_{3\bar{n}+1}$ (where $\bar{n} = 2-5$) and MAPbI_3 thin films under a scan speed of 0.112 V/s/nm.

dimensional perovskites.^{28,29} In this work, thin films with different dominant $\bar{n}$ phases were fabricated by the interplay between the careful selection of PEA to MAI ratio in the perovskite precursors and temperature control. It is probable that the different halide (i.e., iodide in the present work instead of bromide) leads to a dominant higher $\bar{n}$ phase (for the $\bar{n} \geq 2$ sample), whereas a mixed phase is still observed in the bromide-based samples. UV-vis absorption measurements (Figure S1) confirm the $\bar{n}$ values of the samples (from $\bar{n} = 1-5$), which are in agreement with the previous reports.³⁰ X-ray diffraction shows that the PEA planes (004) are aligned parallel to the quartz substrate for $\bar{n} = 1$ (Figure S2a), whereas the PEA planes ($\bar{1}10$) are predominantly aligned normal³¹ to the substrate for samples of $\bar{n} > 1$ (Figures 1a and S2c).

Grazing incidence wide-angle X-ray scattering patterns for $\bar{n} = 2$ show inhomogeneous rings (Figure S2c), which indicate high crystallinity of the samples and the different orientations for the in-plane and out-of-plane directions. For MAPbI_3 , the uniform ring indicates a more random orientation of crystals compared to the $\bar{n} = 2$ sample. Increasing q_x position for the strongest in-plane scattering spot (circled in red) provides evidence for the increase in the spacing of the planes perpendicular to the substrate $d_\perp$ with a larger $\bar{n}$ value.³² Correlating with the energy barriers for the charge transport, PbI_6 octahedral layers with a lower energy barrier act as a quantum well between two adjacent PEA layers of a higher potential barrier. On the basis of the X-ray diffraction and scattering patterns, we confirm that the PbI_6 octahedral layers or quantum wells are aligned perpendicular to the substrates, and thus vertically standing wells are obtained for $\bar{n} > 2$. Sargent et al. also recently reported that the in-plane and out-of-plane geometries in an RP perovskite system can be controlled by the number of $\bar{n}$ layers, width of the inorganic spacer (i.e., spacing between the adjacent octahedral cages), and sample preparation methods.³³

Second harmonic generation (SHG) provides a litmus test for materials with a noncentrosymmetric space group—one of the key criteria for ferroelectricity.¹⁶ Checking the symmetry breaking for any potential ferroelectric material should be the

first step to ensure that we are heading in the right direction. Figure 1b shows a schematic of the transmission setup to probe the SHG properties in the RP samples and the purely 3D MAPbI_3 reference sample. The samples (~ 300 nm coated on quartz substrates) were excited by an 800 nm p-polarized pulsed laser beam, and the SHG signal (at 400 nm) was monitored. The quadratic dependence of the SHG signal with the excitation power confirms the presence of SHG (Figure S3).

The total SHG signal I_{SHG} exhibits a quadratic dependence with the second-order susceptibility $\chi^{(2)}$ (i.e., $I_{\text{SHG}} \propto \chi^{(2)2}$). As the polarization of the SHG signal is parallel to the fundamental (Figure S4d), we are only interested in the diagonal elements of the third-rank $\chi^{(2)}$ tensor. For our highly oriented polycrystalline sample, the diagonal elements of the $\chi^{(2)}$ tensor could be described by the in-plane $\chi_{\text{in}}^{(2)}$ and out-of-plane $\chi_{\text{out}}^{(2)}$ components, with the sample plane as the reference—Figure 1b. On the basis of our setup geometry, the SHG signal would have contributions from $\sqrt{3}/2\chi_{\text{out}}^{(2)} + 1/2\chi_{\text{in}}^{(2)}$ —see Supporting Information for details. Further measurements show that the $\chi_{\text{in}}^{(2)}$ components in the $\bar{n} > 1$ RP perovskites are negligible—see Figure S4 for details. Figure 1c shows the variation in the SHG signal intensity and $\chi_{\text{out}}^{(2)}$ for various $\bar{n}$ RP samples. The SHG intensity increases with the number of octahedral layers to a maximum around $\bar{n} = 5$ or $\bar{n} = 6$, followed by a drastic drop upon further increase of the layers to $\bar{n} = \infty$. This indicates the varying degrees of noncentrosymmetry in these samples with different octahedral cage thicknesses between the two consecutive PEA layers. The presence of the SHG signal in $\bar{n} = 2$ confirms that a small width of the 3D octahedral cage (~ 15.3 Å)²⁵ is sufficient to lift the inversion symmetry. We attribute this to the interplay between the $\bar{n}$ layers and the organic spacer cations that give rise to nonpolar structural distortions (from rotation or tilt) of the octahedral cage, thus maximizing the SHG signal.

Having established the structural orientations and noncentrosymmetric nature of the samples, because of the dipolar nature of constituents, we envisaged the ferroelectric nature of

Figure 3. Temperature-dependent ferroelectric–paraelectric phase transition behavior in the $\bar{n} = 5$ sample. (a) DSC in the $\bar{n} = 5$ sample confirms that the phase transition temperature is ~ 172 °C. (b) Intensity of the SHG peak at 400 nm for the $\bar{n} = 5$ sample on amorphous quartz shows a sharp decrease around the phase transition temperature. (c) SHG peak intensity extracted from figure (b) by fitting. (d) Temperature-dependent (quasi-static) dielectric constant under an electric field of $1.67 \text{ V}/\mu\text{m}$ showing a dramatic variation which confirms the ferroelectric–paraelectric phase transition in these films. (a.u. represents arbitrary units).

the RP perovskites. In this case, we turned to piezoresponse force microscopy (PFM) to prove and visualize the existence of ferroelectric domains and local polarization switching at the nanoscale and thus the noncentrosymmetry and switchable polarity to verify the existence of ferroelectricity. PFM is one of the best tools as the amplitude and phase information provide direct evidence of polarization intensity and orientation.³⁴ Generally, the ferroelectric domains exhibit a switching ability under the influence of external electric fields larger than their coercive magnitude. Herein, we demonstrate the electric field-controlled polarization switching of the RP perovskite ferroelectric domain using PFM. Figure 2a shows the PFM measurement for an $\bar{n} = 5$ sample obtained with the dual ac resonance tracking PFM mode. A $1 \times 1 \mu\text{m}^2$ area of the thin film was first polarized by applying a dc bias of $V = -4 \text{ V}$ on the conductive tip with the conducting substrate [indium tin oxide (ITO)] grounded (Figure 2a). With respect to the dc voltage polarity, the red regions (Figure 2a) represent the ferroelectric domains oriented out-of-plane in the sample (and along the applied dc field direction of the tip), whereas the blue regions represent the domains with random orientations, as illustrated in Figure 2b. The phase image (Figure 2a) shows that most of the domains in this region of the RP perovskite film are readily polarized by the -4 V bias and are oriented in the direction of the applied field.

To demonstrate the switching of the ferroelectric domains, we flipped the poling polarity. Conversely, Figure 2c shows the PFM image of the same region following an opposite dc poling of $V = +4 \text{ V}$. To avoid any phase-wrapping effects (i.e., the PFM phase lower than -180° or higher than $+180^\circ$), the phase offset was manually changed to 180° just after positive poling and before the acquisition of PFM images. The red regions (Figure 2c) represent the ferroelectric domains oriented into the plane of the sample (and along the applied

dc field direction of the tip), whereas the blue regions still represent the domains oriented randomly, as illustrated in Figure 2d. Likewise, the domains in the same region of the RP perovskite film (Figure 2c) are readily polarized by the $+4 \text{ V}$ bias and are oriented in the direction of the applied field. Therefore, the regions with the same color (the majority) in the PFM images in Figure 2a,c exhibit a 180° phase difference (i.e., dipoles had flipped) under opposite polarity-poling conditions (black arrows), clearly demonstrating a switchable spontaneous polarization in the RP perovskites, which is a fundamental property of the ferroelectric materials.

Figure 2e,f shows the local phase remnant and amplitude hysteresis loops for the $\bar{n} = 2\text{--}5$ RP perovskites and the reference MAPbI_3 ($\bar{n} = \infty$) films on random sample spots (see Supporting Information for details). To eliminate the electrostatic interactions from the tip and sample which may originate from hysteretic surface charging, pulsed voltage³⁵ with a maximum of 7 V was applied, and only the remnant signal was used for analysis in this study. Furthermore, an inert argon environment was employed to avoid any dielectric layer formation because of surface oxidation. The pure 2D perovskite ($\bar{n} = 1$) is excluded from the comparison here because of its different crystalline plane orientations (see Figure S2). These phase hysteresis loops provide the first evidence of the ferroelectric polarization reversal in the RP perovskite films. The ferroelectric coercivity under the phase loops and the displacement under the amplitude loops increase from $\bar{n} = 2\text{--}5$ and subsequently drop for larger $\bar{n}$ values (Figure 2e), consistent with the observations from the SHG of the samples (Figure 1c). Note, however, that in general, it does not suffice to demonstrate the phase loops alone to claim the ferroelectric behavior. Accumulation of the surface charges could also lead to the phase contrast under the influence of an external field which can further mislead the existence of

Figure 4. *P*–*E* hysteresis and macroscopic ferroelectric behavior in RP perovskites. (a) Device configuration where a thin layer of PCBM (<10 nm) was inserted to prevent Ag migration into the perovskite film. (b) Macroscopic polarization–electric field hysteresis loops of the $\bar{n} = 5$ RP device measured at 0.3 V. Average variation in (c) experimental coercive electric field (E_c) in the RP perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{PbI}_{3\bar{n}+1}$ for $\bar{n} = 2, 3, 4$, and 5 and MAPbI₃ (based on 10 devices each) and (d) calculated coercive electric field (E_c).

ferroelectricity.³⁶ Therefore, PFM amplitude hysteresis loop (i.e., butterfly loop) must also be presented, which is the robust evidence of the polarization switching. As shown in Figures 2f and S5, the well-defined butterfly loops of the PFM amplitude signals and the 180° phase switching at room temperature show the ferroelectric polarization in these RP films.^{37,38} These average local switching behaviors are consistently reproducible on different batches of thin-film samples with average $\bar{n}$ values (see Figure S5 in the Supporting Information). If thin single crystals with pure n phases can be prepared, even larger differences in both PFM amplitude and coercivity can be expected.

Differential scanning calorimetry (DSC) is used to detect the phase transition Curie temperature by measuring the variation of heat flow because of the specific heat change during the structural phase transition of samples. In Figure 3a, the main peak between 171 and 176 °C for $\bar{n} = 5$ (Figure S6 for the other samples) is the first-order reversible phase transition peak with latent heat hysteresis during the heating and cooling processes. These dominant peaks represent the ferroelectric-to-paraelectric phase transition temperature. (Paraelectric refers to the phase at which the ferroelectric phase transforms above T_c and which does not bear spontaneous polarization³⁹ and is also commonly known as dielectric.) The RP perovskite films show higher T_c than the recently reported organic-based ferroelectric materials.^{40,41} On the other hand, no phase transition is observed in RP perovskites at room temperature accordingly.

For a ferroelectric material, a significant change of the SHG signal around the ferroelectric–paraelectric phase transition temperature is another key signature. Figure 3b shows the SHG signal as a function of temperature for the $\bar{n} = 5$ RP film. Over the phase transition temperature, the SHG signal decreases around 140–180 °C (see Figure S7 for SHG versus temperature for the $\bar{n} = 2, 3$, and 4 perovskite films). This shows the noncentrosymmetry present in the RP films below

the phase transition temperature, which breaks down upon transitioning to the paraelectric phase at higher temperatures.

Furthermore, the temperature dependence of the dielectric constants for different RP perovskite films is established by measuring the device capacitance at different temperatures. These devices were prepared by depositing 300 ± 20 nm perovskite films on cleaned ITO glass substrates, followed by gold on top as the second electrode (see the Experimental Section). The capacitances of these devices at 54 kHz were measured from room temperature to 180 °C. Figures 3d and S8 show the dielectric constant ϵ_0 ($\epsilon = \epsilon_0 + i\epsilon_i$, where ϵ_0 is the real part and ϵ_i is the imaginary part) as a function of temperature. At room temperature, the $\bar{n} = 5$ perovskite thin film shows the highest dielectric constant among these RP perovskite films (Figure S8 inset) consistent with the SHG and PFM measurements, indicating the strongest ferroelectric properties among these RP perovskite films. The value of the dielectric constant remains almost invariant up to 100 °C and increases drastically and peaking around 170–180 °C for all these perovskite films. The small variation of the phase transition temperature obtained from the SHG and dielectric constant measurements is probably because of the differences in the experimental setups. Higher peak values of the dielectric constant, that is >300, are much larger than the value at room temperature, which is the fundamental property of the ferroelectric phase transition. This dependence in the dielectric constant confirms the ferroelectric–paraelectric phase transition in these films, which is consistent with the DSC and SHG findings. The trend is similar to that for traditional ferroelectric materials such as PZT,⁴² which follows the Curie–Weiss law. These results validate the existence and the tunability of ferroelectricity from the $\bar{n} = 2$ to $\bar{n} = 5$ RP perovskite films.

Ferroelectricity has a strong influence on spatial charge separation and carrier transfer in semiconductor materials,²² which could enhance or detract the performance of perovskite

light-harvesting and light-emitting devices. In perovskite optoelectronic devices, defects, ion migration, and ferroelectricity are proposed as origins of the current–voltage (I – V) hysteresis.⁴³ Most reports highlight ion migration as the main origin for the I – V hysteresis,⁴⁴ although the ferroelectric nature of the material cannot be discounted. Ion migration in halide perovskites is rather severe under the influence of the electric field and could influence the ferroelectric polarization through the distortion of the $[\text{PbI}_6]^{4-}$ octahedral. The I – V hysteresis measurements now constitute a routine characterization procedure in any perovskite solar cell study. Although strategies have been formulated to mitigate the I – V hysteresis issue in perovskite solar cells, the exact origin remains controversial because of the complex interplay of the factors discussed here. The RP perovskites under investigation here are not immune to the I – V hysteresis effects. Figure S9 shows an I – V scan and the unmistakable hysteresis loop for an $\bar{n} = 5$ RP sample with the device configuration (see Figure 4a) glass/ITO/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (~ 30 nm)/perovskite (~ 300 nm)/6,6-phenyl-C61-butyric acid methyl (PCBM) ester (< 10 nm)/Ag (~ 100 nm) measured under dark conditions. The I – V characteristics were measured by applying a controlled sweep voltage on the Ag electrode as $0 \text{ V} \rightarrow +0.85 \text{ V} \rightarrow 0 \text{ V} \rightarrow -0.85 \text{ V} \rightarrow 0 \text{ V}$, whereas the bottom electrode (ITO) was grounded. The non-Ohmic I – V characteristic loop (Figure S9) and switching under 0.1 mA compliance current confirm the nonleaky characteristics of the device.⁴⁵ Figure 4b shows the room-temperature P – E (polarization–electric field) loops for the $\bar{n} = 5$ RP device measured using a varying electric field and Figure S10 shows the P – E loops for the $\bar{n} = 2, 3, 4$ and 3D perovskite devices. The stability of the ferroelectric phase at room temperature during measurements is confirmed by DSC measurements (Figure S6). The perovskite film is sufficiently thick to prevent any leakage as the measured dark current (even at 0.3 V) is still lower than the set compliance value (0.1 mA), as shown in Figure S9. The measured P – E hysteresis loops of different RP films measured at 0.3 V (Figure 4b) reveal the nonlinear dependence of polarization on an external electric field.⁴⁶ Coercivity (E_c) is a common figure of merit that shows the field needed to switch the system polarization back to zero. Our experimental E_c data (Figure 4c) are compared very favorably with the calculated values (Figure 4d). Generally, linear lossy dielectrics, shorted circuits, or any artifacts in the measurements might show a closed banana-shaped P – E loop, which can be mistaken for ferroelectricity. However, the P – E loop in the RP perovskites close to 10 kV/cm shows a concave region which indicates the onset of saturation behavior (typically observed in ferroelectric materials^{46,47}) and thus confirms the ferroelectricity in the RP perovskites.⁴⁸ In traditional ceramic-based ferroelectric materials (typically insulating in nature), the P – E loop prominently saturates with the increase of electric field.⁴⁹ However, we observe the resistive behavior at a higher electric field likely because of the dominant ion migration over ferroelectricity, indicated by the circle-shaped P – E loop. Such a P – E loop shape has also been widely observed in various ferroelectric reports.^{23,50,51}

Finally, we performed MD simulations in a bid to gain deeper insights into the polarization switching behavior in these RP perovskites. Unlike the pure 2D perovskite (i.e., $\bar{n} = 1$), which only consists of the weakly polar PEA molecule, the polarity of $\bar{n} = 2$ to $\bar{n} = 5$ can be enhanced by the highly polar

MA⁺ molecule (2.3 Debye). The calculated polarization hysteresis loops (Figure S12) excellently reproduce their experimental counterparts (Figures 4b and S10). Their analysis reveals that the collective reorientation and displacement of the MA ions provide $\sim 50\%$ to the effect, whereas the ionic rearrangements around lead account for $\sim 45\%$; the remaining 5% come from the PEA molecules. The contribution from the pure rotation of MA around the molecular center of mass accounts for 20%. The limited contribution of the PEA molecules is due to their bulky size and limited motion (Figure S12d).

The calculated magnitudes of the coercive electric field (Figure 4d) are also close to the experimental values. However, the coercive electric field generally increases with the thickness of the MA layers, in contrast to the experimental data, which tend to decrease. The most likely sources of this discrepancy originate in the employed force field with the dipole magnitude of the MA molecules, or too small dielectric screening from the ion polarizabilities, but the low-frequency nuclear motion may contribute to the dielectric screening as well. It should also be noted that although the bulk simulation formally describes a bulk sample, in reality, the $6 \times 6 \times 6 \text{ PbI}_3$ MA unit size and the periodic boundary conditions lead to indirect self-interactions resulting in a corresponding effective layer thickness in the order of the size of the simulation box. For instance, the control simulations of a $12 \times 12 \times 12$ bulk system do show a lower overall polarization (Figure S12c); larger systems are computationally not tractable. Nonetheless, it is clear that the correlation length of the ferroelectric order must be overestimated in the bulk simulations.

Alternatively, impurities and dislocations (i.e., defects) in experiments may lower the observed correlation length. Correlating with the film morphology, the perovskite grain size also increases with a decrease in the amount of defects in the $\bar{n} = 3$ to $\bar{n} = 5$ thin films. On the other hand, for MAPbI₃ (no PEA molecules), perovskite grains with plenty of grain boundaries are observed. This suggests that the PEA molecules could have a role in tuning the morphology and function as defect-passivating agents. The authors would like to highlight here that a flat morphology is generally observed in PEA-based RP films compared to a grainy structure in the most commonly used butylammonium (BA)-based RP perovskite films. PEA is well-documented to show such a morphology which is also recently observed by Yang et al.²⁸ On the other hand, the grain size in 3D perovskite films varies depending on one or more organic–inorganic cations involved. The $\bar{n} = 5$ samples appear to yield the minimum amount of grain boundaries and voids (i.e., defect regions), whereas these are higher in the MAPbI₃ films (Figure S14). Conversely, polarization switching in the defect regions is easier compared to switching in a crystallized domain.⁵² The presence of such defects in real samples would account for the lowering of the correlation length and the ferroelectric switching in the MAPbI₃ films. An interplay of defects, the morphology effects affecting the collective and correlated reorientation of MA molecules, is at work in the real samples. Nonetheless, the calculations point to the collective and correlated reorientation of MA molecules as a likely dominant origin.

CONCLUSIONS

In summary, our findings reveal the ferroelectric nature of the RP halide perovskites $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}-3\bar{n}+1}$ and a strategy to tune the ferroelectric properties in this class of materials.

SHG confirms the noncentrosymmetric nature of these RP perovskites. A clear observation of the ferroelectric polarization switching domains and the existence of macroscopic ferroelectric polarization—electric field nonlinear hysteresis loops in thin films and temperature-dependent phase transition measurements backed by extensive MD studies incontrovertibly prove the ferroelectric nature of the RP perovskites, which originates from the collective and correlated motions of both MA, lead ions, and the surrounding iodine cages. Macroscopic observations of the ferroelectricity from the P – E hysteresis characteristics show the tunability of coercivity and remnant polarization by varying the number of inorganic layers and tuning the correlation length of the ferroelectric order. Our findings present fresh insights into the theory behind the origin of the ferroelectric properties in the RP perovskites essential for developing new functionalities in perovskite optoelectronics.

■ EXPERIMENTAL SECTION

Sample Preparation. The formula of the RP perovskite we study is $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}-3\bar{n}+1}\text{I}_{3\bar{n}+1}$, with $\bar{n}$ equal to 1, 2, ...7. Note that here average $\bar{n}$ is used instead of n because the multiphase nature cannot be ruled out except for the pure 2D sample. $\bar{n}$ represents the dominated n component for each sample. To be consistent, a pure 2D sample also uses the expression of $\bar{n}$. Different precursor solutions for different RP and 3D perovskite films (Table S1 in the [Supporting Information](#)) were prepared by dissolving PEA, MAI (both from Dyesol), and PbI_2 (from Acros Organics) by different concentrations in 1 mL dimethylformamide (from Sigma-Aldrich) on a hot plate at 50 °C for 2 h. ITO-coated glass substrates (from Xin Yan Technology Ltd.) were cleaned by soap solution followed by ultrasonication in deionized water, acetone, and isopropanol. To make the ITO surface hydrophilic, the substrates were cleaned with air plasma for 8 min just before spin-coating the solution. All the precursor solutions were filtered through a 0.45 μm poly(tetrafluoroethylene) filter before spin-coating. The RP perovskite hot solutions (i.e., $n = 1$ –5) were spin-coated on these cleaned substrates at 4000 rpm for 30 s in a nitrogen-filled glovebox and subsequently annealed at 70 °C for 10 min to remove the solvent residue. For 3D films, the MAPbI_3 solution was spin-coated at 5000 rpm for 12 s, and 100 μL of chlorobenzene (Sigma-Aldrich) was dripped onto the film at the third second. These films were further annealed at 100 °C for 30 min. The thickness of these films was measured to be 300 ± 20 nm by a surface profilometer and used for subsequent PFM studies. The X-ray diffraction patterns were collected using a Bruker-AXS (D8 ADVANCE) X-ray diffractometer equipped with a $\text{Cu K}\alpha$ ($\lambda = 1.5418$ Å) X-ray source. A UV–vis–NIR spectrophotometer (Shimadzu UV-3600) was employed to collect the absorption spectra of the perovskite films.

SHG Signal Measurements. SHG anisotropy patterns were obtained in transmission mode with an 800 nm pulsed laser and collected at 400 nm by a monochromator with proper filters. As the depth of focus for the lens we use is larger than the thin-film thickness, we confirm that the signals are generated from the bulk thin film instead of the surface. In this paper, we use SHG transmission mode to collect the signal with a fixed 60° angle between the incident p-polarized laser beam and the thin-film surface. It is important to exclude the filter-generated false signals in the measurement. The power of the incident laser source was carefully controlled to avoid damaging the thin-film samples. A linear polarizer was placed before the samples to generate a p-polarized beam only. Then a lens was used to focus the beam in the samples. Another polarizer was placed after the samples, which was used to collect signals at p-polarization. For out-of-plane nonlinear susceptibility measurements, the incident beam was at 60° to the sample's normal, whereas for in-plane nonlinear susceptibility measurements, the laser beam was at normal incidence on the samples. For temperature-dependent SHG signal measurements, the rotational sample stage was replaced by a hot plate. The sample temperature was monitored by a noncontact

infrared thermometer at a 1 cm distance away from the sample surface. At the same time, the incident beam was carefully aligned at 60° to the sample's normal.

PFM Measurements. All PFM measurements were conducted with the sample and its holder in a dry nitrogen environment to minimize any humidity effects on the samples. Furthermore, to eliminate any possible light-induced effects, the measurements were conducted under dark conditions. An ac electric field was applied to the scanning probe which was in contact with the grounded sample surface and induced mechanical vibration within the sample surface because of the local piezoresponse. According to the detected signal difference from the ac input and sample surface by a lock-in amplifier, the phase images reveal the ferroelectric domain polarization, whereas the amplitude shows the ferroelectric domain walls.

Dielectric Constant Measurements. A simple device configuration glass/ITO/perovskite/Au was prepared to measure the capacitance of these materials under an electric field of 1.67 V/ μm . Different perovskite films were prepared using the same conditions as described above on clean ITO substrates. A thin layer of ~80 nm of gold was thermally deposited on these films under high vacuum through a metal mask, with the device area of approximately 7×10^{-3} cm^2 . The capacitance of these devices was measured using an Agilent 4294A precision impedance analyzer.

Device Fabrication and Measurements. Devices with an inverted structure glass/ITO/PEDOT:PSS/perovskite/PCBM/Ag were fabricated for macroscopic ferroelectric measurements. PEDOT:PSS (Al4083 Clevios from Heraeus) was first spin-coated on cleaned ITO glass substrates at 3000 rpm for 30 s followed by heating at 130 °C for 15 min. Subsequently, the perovskite films on substrates were prepared using the same coating conditions as mentioned above. A solution of PCBM (from nano-C) in chlorobenzene as 2 mg/mL was prepared and spin-coated at 4000 rpm for 30 s on these perovskite films. Finally, a 100 nm thick silver electrode was thermally evaporated onto the top of PCBM under high vacuum conditions with a device area of approximately 7×10^{-3} cm^2 . The presence of a very thin layer of PCBM (<10 nm) was used to prevent Ag migration into the perovskite. The current–voltage characteristics of these devices were measured using a source meter of Keithley model 2400. These measurements were conducted inside the glovebox under dark conditions. The Precision Premier II from radiant technology was employed to measure the polarization–electric field loop of these devices in a vacuum.

Computational Descriptions. MD simulations were performed using the GROMACS MD package (version 4.6.7).⁵³ We constructed simulation boxes for the $\bar{n} = 3$ and $\bar{n} = 5$ structures using lattices with one square 6×6 PEA double layer as well as a bulk-like simulation box with the cubic dimensions of $6 \times 6 \times 6$ PbI_3MA units. The inorganic ions were described using an existing polarizable force field,⁵⁴ MA was treated using an existing optimized potential for liquid simulations—all atom (OPLS/AA)-based force field,⁵⁴ whereas a new OPLS/AA⁵⁵-based force field was developed for PEA; the bonded force field parameters were taken from the OPLS/AA⁵⁵ force field using the mktop script.⁵⁶ The point charges were guided by DFT-based calculations with the ORCA package⁵⁷ using the CHELPG scheme⁵⁸ for determining the point charges. For these calculations, the RPBE exchange correlation functional⁵⁹ was employed together with the Ahlrichs-VDZ basis set.⁶⁰ The ionic response was determined by applying external electric fields during the calculations and scanning the field strength in a direction parallel to the layers. The response was analyzed by partitioning the system into neutral units centered around the cations, which allows for the determination of local dipole moments as well as determining the overall polarization response. More details and results are provided in the [Supporting Information](#).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b21579.

Linear absorption spectra of RP and 3D perovskites; X-ray diffraction patterns of RP perovskites; power dependence of SHG signals on RP perovskites; SHG spectra and schematic crystalline structure of RP perovskites; local switching behavior of RP perovskite; polarization electric field hysteresis loops; DSC, temperature-dependent SHG and dielectric constant measurements of RP perovskites; illustration of the three simulation boxes; calculated switching dynamics for bulk MAPbI₃; calculated polarization electric field hysteresis loops; relation between the coercive electric field E_c , remnant polarization P_r and $\bar{n}$; and surface morphology of RP perovskites (PDF)

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Author Contributions

Q.Z. and A.S. contributed equally to this work. T.C.S., A.S., and M.S.P. conceived the idea for the manuscript and designed the experiments. Q.Z. and A.S. prepared and characterized the samples. Q.Z. conducted the microscopic electrical characterization. A.S. and K.P. conducted the macroscopic electrical characterization. Q.Z., M.L., and D.G. conducted the spectroscopic measurement. T.L.C.J. conducted the calculation of MD. T.C.S., A.S., Q.Z., M.S.P., and T.L.C.J. analyzed the data and wrote the paper. All authors discussed the results and commented on the manuscript at all stages. T.C.S. and M.S.P. led this project.

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Notes

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