

Methylphosphonium Tin Bromide: A 3D Perovskite Molecular Ferroelectric Semiconductor

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3D ABX₃ organic-inorganic halide perovskite (OIHP) semiconductors like [CH₂NH₂]Pbl₃ have received great attention because of their various properties for wide applications. However, although a number of low-dimensional lead-based OIHP ferroelectric semiconductors have been documented. obtaining 3D ABX₃ OIHP ferroelectric semiconductors is challenging. Herein, an A-site cation [CH₃PH₃]⁺ (methylphosphonium, MP) is employed to successfully obtain a lead-free 3D ABX₃ OIHP ferroelectric semiconductor MPSnBr₃, which shows clear above-room-temperature ferroelectricity and a direct bandgap of 2.62 eV. It is emphasized that MPSnBr₃ is a multiaxial molecular ferroelectric with the number of ferroelectric polar axes being as many as 12, which is far more than those of the other OIHP ferroelectric semiconductors and even the classical inorganic perovskite ferroelectric semiconductors BiFeO₃ (4 polar axes) and BaTiO₃ (3 polar axes). MPSnBr₃ is the first MP-based 3D ABX₃ OIHP ferroelectric semiconductor. This finding throws light on the exploration of other excellent 3D ABX₃ OIHP ferroelectric semiconductors with great application prospects.

Organic-inorganic halide perovskite (OIHP) semiconductors exampled by the 3D [CH₃NH₃]PbI₃ have gained tremendous interests in the past decade owing to their intriguing optoelectronic properties for wide applications in solar cells, light emitting diodes, photodetectors, etc.^[1] Among them, the OIHP semiconductors with ferroelectricity, which enables the spontaneous polarization $(P_{\rm s})$ to be switched by electric field, have recently attracted considerable attention as candidates for nextgeneration optoelectronic applications.^[2] In ferroelectric semiconductors, the P_s induced built-in electric field is beneficial for the dissociation of photoexcited carriers.^[3] The incorporation of ferroelectricity also endows ferroelectric semiconductors with some unique features from the ordinary counterparts such as the switchable photovoltaic effect, polarization-induced photovoltaic effect, directionally tunable photovoltaic effect, and polarization-sensitive photodetection.^[4] It has been deemed that

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the superior photovoltaic performance of 3D [CH₃NH₃]PbI₃ might benefit from its ferroelectric polarization.^[5] [CH₃NH₃]PbI₃ has been shown to exhibit a polar crystal structure at room temperature by Breternitz et al.^[6a] and the ferroelectric domain shifting by Röhm et al.[6b] However, 3D OIHP ferroelectric semiconductors remain very rare. To date, OIHP ferroelectric semiconductors are mainly the lowerdimensional lead-based ones,^[2,4,7] such as the 1D [trimethyliodomethylammonium] PbI₃^[7a] and the 2D [4,4-diflorocyclohexyla mmonium]₂PbI₄.^[4b] The 3D OIHP ferroelectric semiconductors are highly desirable for the development of high-performance optoelectronic devices because high structural dimensionality is in favor of excellent optoelectronic properties and device performances.^[8] For instance, in contrast to the low-dimensional counterparts, the 3D OIHP semiconductors represented by

[CH₃NH₃]PbI₃ show lower bandgap, better conductivity, and higher charge carrier mobility, making them promising solarcell absorbers,^[8b] and the solar cells based on 3D OIHPs also show much higher power conversion efficiency.^[8c]

3D OIHP semiconductors like [CH₃NH₃]PbI₃ adopt the ABX₃ perovskite structure, where A is the organic cation, B is the Pb(II), Sn(II), or Ge(II) ion, and X is the halogen ion.^[1a] The A site cation resides in the cavity of the 3D BX₃ framework formed by corner-sharing BX₆ octahedra. To maintain the 3D BX₃ framework, the A site is limited to some small size cations like the classical [CH₃NH₃]⁺ (methylammonium, MA) and [NH₂(CH)NH₂]⁺ (formamidinium, FA) according to the Goldschmidt tolerance factor rule.^[9] Despite great efforts have been made to broad the 3D ABX₃ OIHP family, the resulting fruits were minimal. Recently, the [F-CH₂NH₃]⁺ and [CH₃NH₂NH₂]⁺ cations were utilized to form the 3D ABX₃ lead-based OIHP $[F-CH_2NH_3]PbBr_3^{[10]}$ and $[CH_3NH_2NH_2]PbX_3$ (X = Br or Cl),^[11] respectively, but none of them shows the ferroelectricity. Discovering a new 3D ABX₃ OIHP semiconductor has been a great challenge, while endowing it with ferroelectricity is more arduous. From a structural perspective, in OIHP system, it is the reorientation and ordered alignment of organic cation within an inorganic framework that contributes the possibility of ferroelectricity.^[12] Very recently, we constructed a 3D lead chloride perovskite-related ferroelectric [2-trimethylammonioethylammonium]Pb2Cl6 in which the reorientation of organic cation occurs during the ferroelectric phase transition.^[13] However, the environmental toxicity of lead in [2-trimethylammonioethylammonium]Pb₂Cl₆ and the low-dimensional OIHP ferroelectric semiconductors is an obstacle for future applications. Moreover, [2-trimethylammonioethylammonium]Pb₂Cl₆ is a uniaxial ferroelectric, similar to the cases of most low-dimensional OIHP ferroelectric semiconductors,^[2,4,7] which also impedes the further applications since the polarization in uniaxial ferroelectrics can only be switched between two opposite polarization directions.^[14] The widely used ferroelectrics are mainly the multiaxial ones like BaTiO₃ and Pb(Zr,Ti)O₃, of which the polarization can be switched between multiple directions to obtain high ferroelectric performance.^[14]

[CH₃PH₃]⁺ (methylphosphonium, MP) is a small size cation, which was theoretically predicted to be a choice of A site for constructing 3D ABX₃ OIHPs.^[9b] However, MP-based OIHPs have not been experimentally explored. Here, we successfully synthesized a MP-based lead-free 3D ABX₃ OIHP, MPSnBr₃. We found that MPSnBr3 exhibits two distinct transitions from ferroelectric *m* to ferroelectric *mm*² to paraelectric $m\overline{3}m$ point group at 314 and 357 K, respectively, accompanied by the reorientation of MP cation. MPSnBr3 shows clear above-roomtemperature ferroelectricity and a direct bandgap of 2.62 eV. Very importantly, MPSnBr₃ is a multiaxial molecular ferroelectric with the number of ferroelectric polar axes as many as 12, which is outstanding in molecular ferroelectrics,^[14] and is much more than those of the other OIHP ferroelectric semiconductors (Table S1, Supporting Information),^[2,4,7,13] most of which are uniaxial or biaxial ferroelectrics, and the classical inorganic perovskite ferroelectric semiconductors BiFeO3 (4 polar axes) and BaTiO₃ (3 polar axes).^[14] Strikingly, in terms of the ferroelectric-to-paraelectric phase transition, the mechanism in MPSnBr3 is originated not only from the commonly seen cationic order-disorder dynamics but also from the reorganization of Sn-Br bonds in [SnBr₃]⁻ framework, which is unprecedented in molecular ferroelectrics.^[15] Besides the ferroelectricity and the semiconducting property commonly found in OIHP ferroelectric semiconductors, MPSnBr3 also shows interesting thermochromism. To our knowledge, MPSnBr₃ is the first example of MP-based 3D ABX₃ OIHP ferroelectric semiconductor. This work offers a promising A-site cation for constructing 3D ABX₃ OIHP ferroelectric semiconductors and should inspire further exploration of more excellent 3D ABX₃ OIHP ferroelectric semiconductors.

We first synthesized methylphosphonium bromide (MPBr) through the synthetic route shown in **Scheme 1**. MPBr

crystallizes in the P21/m space group at 223 K (Table S2, Supporting Information), of which the crystal structure is composed of MP cations and Br anions (Scheme 1), MPSnBr₃ was then prepared as crystals from a hydrobromic acid solution with equimolar amounts of MPBr and SnBr₂. Single-crystal structure determinations based on the single-crystal X-ray diffraction data reveal that MPSnBr₃ adopts the 3D ABX₃ OIHP structure, where A, B, and X is MP, Sn (II), and Br⁻, respectively, and the organic MP cation occupies the void of inorganic 3D [SnBr₃]⁻ framework of corner-sharing SnBr₆ octahedron (Figure 1 and Figure S1, Supporting Information), isostructural to the 3D OIHP MASnBr₃.^[16] At 293, 333, and 383 K, MPSnBr3 adopts the polar Pc (m point group), polar *Pna2*₁ (*mm2* point group), and centrosymmetric $Pm\overline{3}m$ ($m\overline{3}m$ point group) space group, respectively (Table S2, Supporting Information), which correspond to the room-temperature ferroelectric phase (RFP), high-temperature ferroelectric phase (HFP), and high-temperature paraelectric phase (HPP), respectively. In the RFP, the MP molecule in the crystal structure occupies a general symmetry position and shows an ordered state. The atomic coordinates of C and P atoms can be clearly identified. The MP molecule thus shows a single orientation (Figure 1a). The [SnBr₃]⁻ framework shows both Sn-Br bonds and $Sn \cdots Br$ interactions with short (average 2.722(3) Å) and long (average 3.361(3) Å) SnBr interatomic distances, respectively (Figure 1a and Table S3, Supporting Information). In the HFP, the MP cation also lies on a general symmetry position and keeps ordered with a single orientation (Figure 1b). For the $[SnBr_3]^-$ framework, the Sn-Br bonds and Sn...Br interactions shows no obvious difference of average SnBr interatomic distances from those in the RFP (Figure 1b and Table S3, Supporting Information), while the average angle of Sn-Br...Sn increases from 156.5° in the RFP to 170.6° (Figure S1, Supporting Information). In the HPP, the MP molecule occupies a special symmetry position of high symmetry $m\overline{3}m$. Consequently, the MP cation becomes highly orientational disorder with many orientations (Figure 1c). In the [SnBr₃]⁻ framework, there are only Sn-Br bonds with SnBr interatomic distance of 3.041(1) Å (Figure 1c). This indicates the reorganization of Sn-Br bonds. Thus, besides the order-disorder transition of MP cation accompanied by its orientation change, the reorganization of Sn-Br bonds in [SnBr₃]⁻ framework also contributes to the ferroelectric-to-paraelectric phase transition from HFP to HPP. We also confirm the structural phase transition of MPSnBr₃ by the variable-temperature powder X-ray diffraction (PXRD) experiments (Figure S2, Supporting Information).



Scheme 1. Synthesis of MPBr.







Figure 1. a-d) The basic structures for MPSnBr₃ at 293 K (a), 333 K (b), and 383 K (c,d) with selected interatomic distances (Å) labeled. The yellow dashed line denotes the Sn…Br interactions.

Differential scanning calorimetry (DSC) curves of MPSnBr₃ present two above-room-temperature phase transitions at $T_{c1} = 314$ K and $T_{c2} = 357$ K, respectively (Figure 2a). It is worth noting that the 3D ABX₃ OIHP analogue MASnBr₃ also show several phase transitions, but the T_c is far below room temperature, with the highest T_c being of 229.4 K.^[17] The higher T_c of MPSnBr₃ than that of the MASnBr₃ is attributed to the larger molecular volume and heavier molecular mass of MP cation, of which the rotational energy barrier is higher than that of MA cation (Figures S3 and S4, Supporting Information). The ferroelectric-to-paraelectric phase transition temperature of 357 K of MPSnBr₃ is also higher than those of some other OIHP ferroelectric semiconductors such as $(C_4H_{11}IN)PbI_3$ (312 K),^[7a] $(C_5H_{14}N)_2(CH_6N)_2Pb_3Br_{10}$ (305 K),^[2a] and (C₄H₁₂N)₂(CH₅N₂)Pb₂Br₇ (322 K),^[7f] and is comparable to that of (C₆H₁₄N)₂PbBr₄ (363 K) (Table S3, Supporting Information).^[7c] We also confirm the phase transitions of MPSnBr₃ by the dielectric anomalies around T_c in the temperature-dependent dielectric real part (ϵ') (Figure 2b). The giant variation of ϵ' around T_{c2} reveals the ferroelectric-to-paraelectric phase transition nature. The AC conductivity of MPSnBr3 also displays anomalies around T_{c1} and T_{c2} , corresponding to the phase transitions (Figure 2c). The conductivity of MPSnBr₃ at room temperature is about $10^{-4.7}$ S m⁻¹, which falls in the range (10^{-8} to 10^{3} S cm⁻¹) of conductivity values of semiconductor materials, revealing the semiconducting characteristic. This conductivity value is larger than that of the 2D OIHP ferroelectric (benzylammonium)₂PbCl₄ (about 10^{-6.8} S m⁻¹).^[7d] Thermogravimetric analysis reveals that MPSnBr₃ is thermally stable up to 450 K, much higher than the T_c (Figure S5, Supporting Information).

We further investigated the phase transitions of MPSnBr₃ by temperature-dependent second harmonic generation (SHG) signal, which is only active in non-centrosymmetric compounds. MPSnBr3 exhibits clear SHG signals with a non-zero intensity in the RFP (Figure 2d), corresponding to the polar m crystal symmetry. The SHG intensity keeps non-zero in the HFP, and becomes almost zero in the HPP (Figure 2d). This coincides with the polar mm2 and centrosymmetric $m\overline{3}m$ crystal symmetry in the HFP and HPP, respectively. The changes of SHG intensity around T_c also verify the phase transitions. We then calculated the number ferroelectric polar axes of MPSnBr₃ based on the change of symmetry elements from paraelectric phase to ferroelectric phase.^[14] For the two sequential phase transition from $m\overline{3}m$ to mm2 to m phase in MPSnBr₃, $m\overline{3}m$ is the paraelectric phase, and mm2 and m are two ferroelectric phase. The number of polar axes for the two ferroelectric phase should be determined based on the $m\overline{3}m$ to mm2 and $m\overline{3}m$ to m phase transitions, similar to the cases







Figure 2. Phase transitions of MPSnBr₃. a) DSC curves. b) Temperature-dependent ε' at 1 MHz. c) Temperature-dependent AC conductivity at 1 MHz. d) Temperature-dependent SHG intensity.

of [quinuclidinium]ReO₄.^[14] The number of total symmetry elements of $m\overline{3}m$ point group in HPP, mm2 point group in HFP, and m point group in RFP is 48, 4, and 2, respectively. Thus, the paraelectric $m\overline{3}m$ to ferroelectric mm^2 phase and paraelectric $m\overline{3}m$ to ferroelectric *m* phase transitions give 12 and 24 polarization directions,^[14] as shown in Figure S6, Supporting Information. Since for both paraelectric-to-ferroelectric phase transition, the polarization vector in ferroelectric phase is reversible, the number of polar axes is half that of the polarization directions, thus the transitions from paraelectric $m\overline{3}m$ to ferroelectric *mm*² phase and paraelectric $m\overline{3}m$ to ferroelectric *m* phase reveals 6 and 12 equivalent ferroelectric polar axes, respectively.^[14,18] This indicates that MPSnBr₃ is a multiaxial molecular ferroelectric, facilitating its future applications.^[14] Such many polar axes are rarely seen in molecular ferroelectrics.^[14] The ferroelectric polar axes of MPSnBr3 are much more than those of the other OIHP ferroelectric semiconductors (Table S3, Supporting Information), most of which are uniaxial or biaxial ferroelectrics, and the classical inorganic perovskite ferroelectric semiconductors BiFeO₃ (4 polar axes) and BaTiO₃ (3 polar axes).^[2,7,13,14]

Piezoresponse force microscopy (PFM) is a powerful tool for the study of ferroelectric and piezoelectric phenomena, which enables non-destructive visualization and control of ferroelectric domains.^[19] **Figure 3** presents the vertical and lateral PFM phase and amplitude images at RFP on the single crystal of MPSnBr₃ without any thermal treatment. The striking 180° vertical phase contrast and the uniform lateral phase signals indicate that the polarizations in two domains have the opposite and same directions in the out-of-plane and in-plane components, respectively. The domain walls emerge as darker lines both in two amplitude images, which should be non-180° ones because the polarization directions in two domains do not intersect at 180°, demonstrating the multiaxial nature of MPSnBr₃. Meanwhile, we also observed the vertical and lateral PFM images in the HFP. As Figure S7, Supporting Information, shows, the vertical and lateral phase images exhibit different patterns, which resemble those in the RFP and thus demonstrate the existence of non-180° domains. As Figure 3f shows, the vertical PFM phase and amplitude signals as a function of the dc voltage at RFP appear as quasi-square hysteretic loops and well-defined butterfly-shaped curves, which are typical for the ferroelectric switching and demonstrate the ferroelectric property of the single crystal of MPSnBr₃.

To visualize the domain switching process, point polarization study was carried out at RFP. First, we scanned the vertical PFM signals of the initial state (Figure 4a), where the phase image shows a clear contrast in the right region. The corresponding lateral phase in Figure S8, Supporting Information, is uniform for the right region, like that in Figure 3, and the striking 180° contrast appears in the left region, which suggests the emergence of another polarization direction and further confirms the multiaxial nature of MPSnBr₃. When a tip under -150 V bias was used to pole the crystal surface for 160 s, the polarization direction of the region marked by a red dashed ellipse is switched (Figure 4b). Once the opposite +150 V bias was applied to the tip for 160 s, the polarization direction of two corresponding regions can also be switched (Figure 4c). Notably, the switched domains can remain unchanged 2 h later (Figure 4d). Moreover, by superimposing the vertical PFM phase and amplitude signals into the 3D topography image, it can be seen that there is no obvious correlation between the piezoelectric signals and the morphology (Figure S9,







Figure 3. a–e) Vertical PFM phase (a) and amplitude (c), lateral phase (b) and amplitude (d), and topography (e) images at RFP for the single crystal of MPSnBr₃. f) Vertical PFM phase and amplitude signals versus the tip voltage at RFP, displaying local piezoelectric hysteresis loops.

Supporting Information). These results provide a solid evidence for the stable and switchable polarization of MPSnBr₃, which is an intrinsic characteristic of ferroelectrics. We then carried out the macroscopic ferroelectric measurements of polarization–electric field (P-E) curves on the compressed pellet samples because of the lack of large-size single crystals of MPSnBr₃ at different phases (Figure S10, Supporting Information). At 303 K, the P-E curve is linear due to the large coercive field, which then opens at 333 K with a certain remnant polarization at zero field because of the contribution of polarization. At 368 K, the P-E curve becomes round owing to the paraelectric nature and the large electric leakage.

We also performed density functional theory (DFT) calculation to evaluate the origin of polarization to gain deep insight into the ferroelectric polarization reversal.^[20] According to the modern theory of polarization,^[21] the necessity of constructing polarization change path lies in selecting polarization quantum properly to avoid the wrong estimation of polarization value. A dynamic path between two ferroelectric states is constructed based on the crystal structure obtained from the single-crystal X-ray diffraction. While the other states are obtained from the matrix transformation of the coordinates considering both the rotational and displacive motion of MP cations in the anionic [SnBr₃]⁻ framework. The variation of polarization as a function of the dynamic path is shown in Figure 5, from which the ferroelectric polarization with 4.5 μ C cm⁻² can be extracted from two equivalent ferroelectric configurations ($\lambda = \pm 1$). During the ferroelectric switching process ($-1 < \lambda < 1$), the polarization value changes smoothly, and turns to zero at $\lambda = 0$, which indicates a reference phase with zero polarization. We also calculated the polarization value of MPSnBr3 by using the point charge model (Figure S11, Supporting Information). The obtained







Figure 4. Topographic (top), vertical PFM amplitude (middle), and phase (bottom) images at RFP of the crystal surface for MPSnBr₃. a) Initial state. b) After the first switching on the red dot in (a) with -150 V for 160 s. The domain inside the red dashed ellipse is switched. c) After the succeeding switching on the blue dots in (b) with +150 V for 160 s. The domains inside the blue dashed ellipses are switched. d) After 2 h.

polarization of 4.28 $\mu C~cm^{-2}$ is comparable to the calculated value (4.5 $\mu C~cm^{-2})$ from DFT calculation.

The optical property of MPSnBr₃ was investigated by the solid-state UV–vis absorbance spectrum (**Figure 6**a), which displays an intense absorption at the band edge onset 500 nm at room temperature, corresponding well with its yellow appearance of bulk crystal. The power law for the variation of absorption coefficient versus photoenergy shows the features of a direct-bandgap semiconductor with optical bandgap of 2.62 eV (Figure S12, Supporting Information), smaller than that of the 2D bromide OIHP ferroelectric $(C_6H_{14}N)_2PbBr_4$ (3.05 eV).^[7c]



Figure 5. Evolution path of polarization with structural distortion of $\mathsf{MPSnBr}_3.$

MPSnBr3 is thus a 3D OIHP ferroelectric semiconductor, having potential applications in future optoelectronics.^[4] Both the conduction band (CB) minimum and the valence band (VB) maximum are localized at the same k-vector in the Brillouin zone (Figure 6b), revealing a direct-bandgap semiconductor as well. The calculated bandgap is 2.58 eV, which agrees well with the experimental value of 2.62 eV. From partial density of states (PDOS) (Figure 6c), it is obvious that for the organic part, the H-1s states overlap fully with the C-2p and P-3p states in the -8 to -5 eV region, indicating the strong covalent interactions in C-H and P-H bonds. For the inorganic part, strong interactions between Sn and Br atoms are also found in almost the whole energy region as Sn-s/p and Br-s/p states overlap obviously. The bands at the VB top originate from the nonbonding states of Br-4p, and those at the CB bottom are mainly from the unoccupied Sn-5p orbitals. Clearly, both VB maximum and CB minimum are from the electronic states of Sn and Br atoms, thus the inorganic [SnBr₃]⁻ framework determines the bandgap of MPSnBr₃. Interestingly, as the temperature increases, the absorption edge of the MPSnBr₃ shows a clear redshift (Figure 6a and Figure S13, Supporting Information), accompanied by the color changes to orange. The absorption edge within each solid phase has almost no obvious change, while the absorption edge between different phases has shifted significantly (Figure S13, Supporting Information). Therefore, the shift of the absorption edge can be attributed to the structural phase transitions rather than thermally induced continuous changes. The bandgaps of HFP and HPP are 2.48 and 2.42 eV, respectively. Therefore, MPSnBr₃ is also a thermochromic ferroelectric semiconductor, having the potential application in smart photovoltaic window.[22]







Figure 6. a) Solid-state variable-temperature UV-vis absorption spectra, b) energy band structure, and c) PDOS of MPSnBr₃.

In summary, we have successfully demonstrated a MP-based 3D ABX₃ OIHP ferroelectric semiconductor MPSnBr₃, which undergoes two phase transitions at 314 and 357 K, respectively, and shows a multiaxial nature with the number of ferroelectric polar axes up to 12. Both the order-disorder transition of MP cation and the reorganization of Sn—Br bonds in [SnBr₃]⁻ framework contribute to the ferroelectric-to-paraelectric phase transition at 357 K. The ferroelectric domains and polarization switching confirm its ferroelectricity. MPSnBr₃ also shows a direct bandgap of 2.62 eV and the interesting thermochromism with the decrease of bandgap upon heating. This work highlights the potential of MP as A site for constructing high-performance 3D ABX₃ OIHP ferroelectric semiconductors with great application prospects. Work on other MP-based OIHPs such as MPPbBr₃, MPSnI₃, and MPPbI₃ is currently underway.

Experimental Section

Synthesis of MPBr: Anhydrous aluminum chloride (0.57 mol) and phosphorus trichloride (0.5 mol) were added into a three-necked flask. Then the mixture was heated at 70 °C for 1 h. After cooling, methyl iodide (0.5 mol) was added dropwise over 0.5 h at -10 °C. The reaction solution solidified gradually over the next 3–5 h. Potassium chloride (0.57 mol) and iron powder (30 g) were added to the above to distill collecting the fraction at 80–165 °C. The mixture was then fractionated to give pure dichloro(methyl)phosphine as a colorless liquid, yield: 30%, b.p. 80–82 °C. Dichloro(methyl)phosphine (4.2 g) was added to 33 mL of dichloromethane. Then, ethylene glycol (3 g) was added to ropwise at room temperature. Colorless crystals continuously appeared on the sublimator, which is methylphosphonium chloride,^[23] which was then dissolved in hydrobromic acid solution and stored in the refrigerator, giving crystals of MPBr, with a yield of 12%.

*Crystals of MPSnBr*₃: Yellow plate crystals of MPSnBr₃ were collected from a hydrobromic acid solution with equimolar amounts of MPBr and SnBr₂ by the temperature cooling method in an inert atmosphere. The results of elemental analysis (Table S4, Supporting Information) and PXRD (Figure S2, Supporting Information), confirm the purity of samples.

CCDC 2019929–2019932 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Measurements: X-ray crystallographic, DSC, dielectric, AC conductivity, SHG, PFM, P-E curve, and UV-vis absorption spectra measurements were described elsewhere previously.^[7e,13]

Calculation Condition: The first-principles calculations were performed within the framework of DFT implemented in the Vienna Ab initio

Simulation Package (VASP).^[24] The energy cut-off for the expansion of the wave functions was fixed to 550 eV and the exchange–correlation interactions were treated within the generalized gradient approximation of the Perdew–Burke–Ernzerhof type.^[25] For the integrations over the k-space we used a 4 × 2 × 2 k-point mesh. The experimental crystal structure was used as the ground state for evaluating the ferroelectric polarization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D hybrid perovskites, methylphosphonium, molecular ferroelectrics, multiaxial ferroelectric nature, semiconductors

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