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## Introduction

Halide perovskites (HPs) have attracted significant attention due to their remarkable properties, including ferroelectricity,<sup>1,2</sup> piezoelectricity,<sup>3,4</sup> photoluminescence,<sup>5</sup> and their applications in photodetection and photovoltaics.<sup>6–11</sup> Among them, three-dimensional (3D) HPs are extensively studied for their high absorption coefficients,<sup>12</sup> high defect tolerance,<sup>13</sup> long carrier diffusion lengths,<sup>14–16</sup> and cost-effective solution processing.<sup>17</sup> These characteristics have accelerated advancements in technologies such as solar cells,<sup>18</sup> light-emitting diodes,<sup>19</sup> photodetectors,<sup>20</sup> and lasers.<sup>21</sup> Typically represented by the general formula  $AMX_3$  (Fig. 1a), where A is a monovalent cation, M is a divalent metal, and X is a halide, the phase stability of the 3D perovskites are influenced by the Goldschmidt tolerance factor  $t = (r_A + r_X)/[\sqrt{2}(r_M + r_X)]$ , where  $r_A$ ,  $r_M$ , and  $r_X$  denote the effective ionic radii.<sup>22–24</sup> Perovskite phases typically form effectively when  $0.8 < t < 1$ , with deviations often resulting in non-perovskite structures. Consequently, the choice of A-site cations is restricted to small sizes. Currently, only a few monovalent cations, *i.e.*,  $Cs^+$ ,  $CH_3NH_3^+$ ,  $CH_3NH_2NH_2^+$ ,  $HC(NH_2)_2^+$  and aziridinium, have been identified as capable of maintaining the

# A three-dimensional lead iodide perovskite analog featuring hydrogen-bonded dual monovalent cations†

Wei Wang,<sup>ID</sup> Cheng-Dong Liu,<sup>ID</sup> Chang-Chun Fan<sup>ID</sup> and Wen Zhang<sup>ID</sup>\*

Three-dimensional (3D) halide perovskites have attracted considerable research interest, yet the selection of A-site cations is restricted by the Goldschmidt tolerance factor. To accommodate cations beyond this acceptable range, novel 3D perovskite analog structures with edge- and face-sharing motifs have been developed. Until now, these structures have been limited to divalent cations due to significant electrostatic repulsion when incorporating two monovalent cations. Herein, we employ a supramolecular synthon mechanism to address the issue and an effective hydrogen-bonding pattern is achieved in a novel 3D lead iodide hybrid perovskite, (ammonium)(morpholinium)PbI<sub>6</sub> (**1**). The inorganic framework of **1** consists of two edge-shared [PbI<sub>6</sub>] octahedra connected *via* corner-sharing, thus forming a continuous 3D network. Structural analysis indicates that the spatial separation of N atoms and the existence of N–H...O hydrogen bonds effectively eliminate electrostatic repulsion. This work has demonstrated the potential to mitigate constraints of cation selection on 3D frameworks and could spur the development of novel 3D perovskite materials and related fields.

typical corner-shared 3D perovskite structure.<sup>25–29</sup> Attempts to incorporate larger cations generally lead to lower-dimensional structures that hinder charge transport in at least one direction.<sup>30–32</sup>

Recently, novel 3D perovskite analogs have emerged that can accommodate large diammonium cations.<sup>33–41</sup> The fundamental building blocks consist of edge-shared [M<sub>2</sub>X<sub>10</sub>] units which further link through corner-sharing to form 3D frameworks capable of hosting divalent cations within either parallelepiped-shaped (Type I) or trigonal prism-shaped (Type II) voids (Fig. 1b and c). Synthetically, symmetric cations typically lead to type I voids<sup>39</sup> while less symmetric ones result in type II.<sup>38,40</sup> In essence, these 3D perovskite analogs are composed of edge-sharing octahedral dimers, with voids large enough to accommodate either two monovalent cations (A<sub>2</sub>M<sub>2</sub>X<sub>6</sub>) or one divalent cation (A'M<sub>2</sub>X<sub>6</sub>). The resulting chemical formulas, A<sub>2</sub>M<sub>2</sub>X<sub>6</sub> or A'M<sub>2</sub>X<sub>6</sub>, effectively double the unit cell compared to traditional 3D perovskites. However, the reported structures are presently exclusively limited to A'M<sub>2</sub>X<sub>6</sub> because the presence of significant electrostatic repulsion between two positively charged monocations within the void could make A<sub>2</sub>M<sub>2</sub>X<sub>6</sub> energetically unfavorable and synthetically difficult. Considering the much higher abundance of monocations than dications, it is necessary to overcome this challenge to enrich the 3D perovskite family.

Herein, we employ a supramolecular synthon mechanism to address the issue caused by electrostatic repulsion of two positively charged monocations (Fig. 1d). Through carefully selecting the monocation pair, an effective hydrogen-bonding

Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China. E-mail: zhangwen@seu.edu.cn

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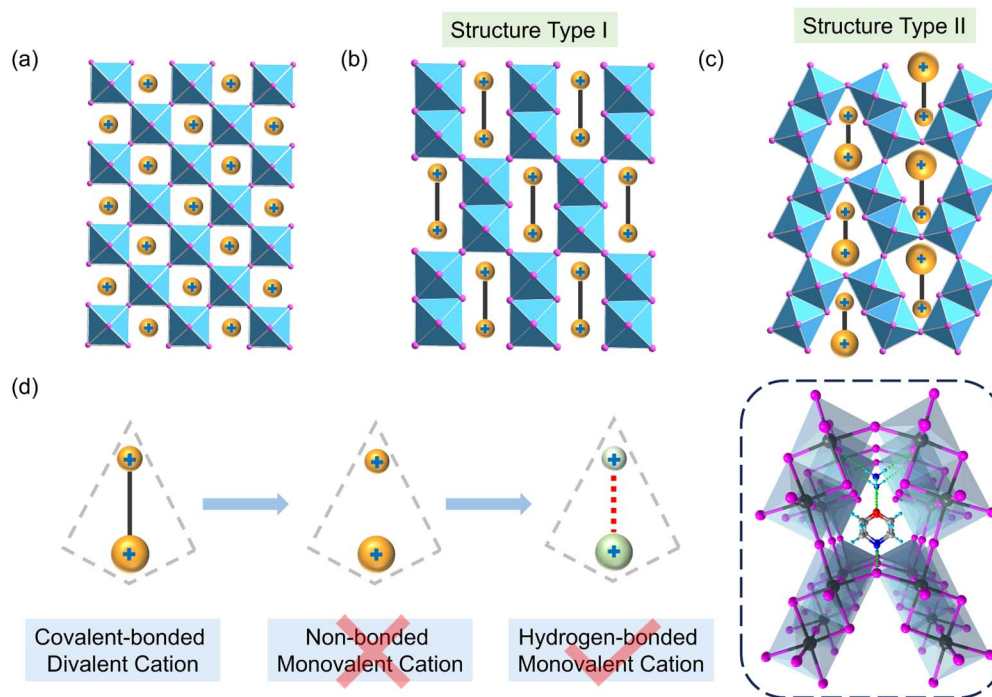


Fig. 1 Octahedra connecting types of reported 3D perovskites: (a) classical  $AMX_3$ ; (b) type I; (c) type II. (d) Type II 3D perovskite analog with hydrogen-bonded monovalent cations reported in this work.

pattern is achieved between them to result in a pseudo-divalent cation and thus favor the formation of the type II framework. A synthesized model 3D perovskite analog (ammonium)(morpholinium) $Pb_2I_6$  (**1**) shows that the ammonium and morpholinium cations occupy the smaller and larger part of the void, respectively, based on their volumes. Structure analysis clarifies that the remote relative position of two positively charged N atoms and intermolecular N-H $\cdots$ O hydrogen bonding interaction helps to diminish the electrostatic repulsion. Compound **1** has an indirect bandgap, akin to the electronic band patterns found in  $AMX_3$  perovskites, featuring notably dispersive valence and conduction bands. And it also exhibits a good photoelectric response, thermal stability up to 250 °C and excellent long-term stability under conditions of 40% relative humidity. This work shows promise in overcoming limitations related to cation selection in 3D frameworks and may inspire the creation of new 3D perovskite materials.

## Results and discussion

### Synthesis

Compound **1** was synthesized using a solution-based method. In contrast to previously reported type I and type II 3D perovskite analogs, which require an excess of  $PbI_2$  to prevent the formation of other phases, **1** was synthesized with a ratio of  $NH_4I$ :morpholine: $PbI_2 = 2:1:1$ . The solution was heated to over 110 °C and then gradually cooled to 90 °C, leading to the precipitation of red crystals within 12 hours (Fig. 2a). More details about crystal synthesis are provided in the ESI.† Phase purity of the sample was verified by powder X-ray diffraction

(PXRD) by comparing experimental and simulated diffraction patterns (Fig. S1†).

### Crystal structure analysis

Single-crystal diffraction analysis of **1** reveals a monoclinic structure within the  $P2_1/m$  space group, characterized by cell parameters of  $a = 6.3366(3)$  Å,  $b = 16.1613(7)$  Å,  $c = 10.1821(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 93.579(4)^\circ$ ,  $\gamma = 90^\circ$ , and volume  $V = 1040.69(8)$  Å<sup>3</sup> (Table S1†). The structure features inorganic dimers composed of two edge-sharing octahedra of adjacent Pb ions. Four dimers, connected *via* corner-sharing, constitute a trigonal prism-shaped void (Fig. 2b). Further corner-sharing of these dimers extends in  $bc$  plane to form a continuous inorganic layer and the layers are stacked along the  $a$ -axis by angle-to-angle connections to result in a 3D inorganic framework (Fig. 2c and d), as classified as type II 3D perovskite. This unique arrangement of the inorganic framework provides ample space to accommodate two monovalent cations, which are anchored to the halide ions of  $PbI_6$  octahedra through N-H $\cdots$ I hydrogen bonding interactions (Fig. 2e, f, Tables S2 and S3†). Specifically, within the trigonal prism-shaped void, the  $NH_4^+$  and morpholinium cations occupy the smaller and larger volume sides, respectively, reflecting their significant volume disparity. Regarding the structure, positively charged N atoms of  $NH_4$  and morpholinium cations are strategically positioned on opposite sides of the void, thereby minimizing electrostatic repulsion. Meanwhile, the N-H $\cdots$ O hydrogen bonding interactions between the  $NH_4^+$  and morpholinium cations further reduce electrostatic repulsion and enhance structural stability. This marks the first successful filling of a void in a 3D perovskite analog structure with mixed



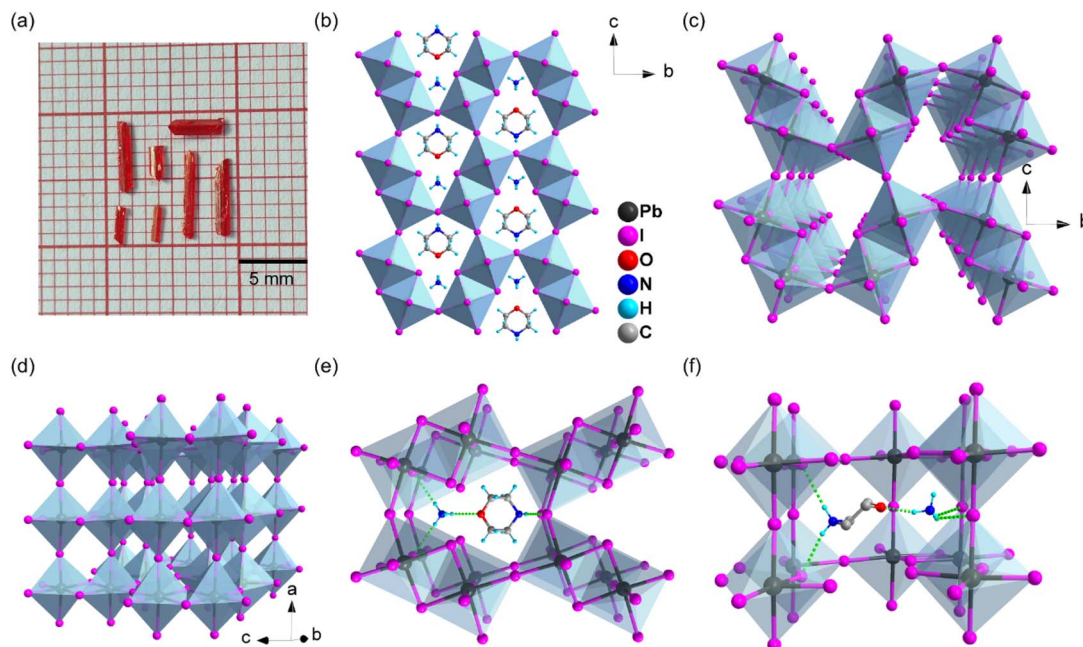


Fig. 2 (a) Crystal image of **1**. (b) basic structure motif of **1** viewed from *a* direction. (c and d) Inorganic framework showing 3D connectivity. Organic parts are omitted for clarity. (e and f) Hydrogen bonding interactions within and between the organic parts and inorganic framework.

monovalent cations *via* intermolecular hydrogen bonds to overcome the electrostatic repulsion between positively charged species.

Given the flexibility of monocations, we aim to identify other cations that could potentially replace morpholinium to form similar 3D frameworks. We selected several cations for calculation based on their comparable volumes and shapes, as well as their potential to form hydrogen bonds with  $\text{NH}_4^+$ . According to Table S4,<sup>†</sup> our calculations suggest that thiomorpholinium, 4-hydroxypiperidinium, and tetrahydro-2*H*-pyran-4-aminium are promising candidates, with volume differences of less than 5%. However, experimental validation is further required to confirm these findings.

Because of the strong links to the electronic properties, it is important to analyze the connectivity types of the metal iodide octahedra in the structure as well as the M–X–M angles and bond distortions. To simplify the discussion, we measure the Pb–I–Pb angles by taking the two edge-shared octahedra as a whole basic unit and only consider the Pb–I–Pb angles of corner-sharing connectivity since they are the special feature in perovskites and most relevant to the charge transport and electronic band dispersion. As shown in Fig. 3, **1** has three different Pb–I–Pb angles. The largest one is  $180^\circ$ , which is slightly higher than that of  $(\text{TMEA})\text{Pb}_2\text{Br}_6$  (Fig. S2,<sup>†</sup> TMEA = *N,N,N*-trimethylethane-1,2-diaminium),<sup>35</sup> indicating the structure is not tilted and very similar to type II structure. In the *a* axial direction where the octahedra are connected by corner-sharing, the Pb–I–Pb angles are  $173.61^\circ$ , closely to  $180^\circ$ . The smallest one is  $146.16^\circ$ , much smaller than  $180^\circ$ . The average Pb–I–Pb angle is calculated to be  $166.59^\circ$ , showing slightly smaller than that of  $(\text{TMEA})\text{Pb}_2\text{Br}_6$ .

We also assess the distortion levels of individual octahedra by using the distortion index ( $\Delta d$ ) and bond angle variance ( $\sigma^2$ ), which are defined based on the variations in Pb–I bond lengths and Pb–I–Pb bond angles as shown in eqn (1) and (2):

$$\Delta d = \left(\frac{1}{6}\right) \sum_{i=1}^6 \left(\frac{d_i - d}{d}\right)^2 \quad (1)$$

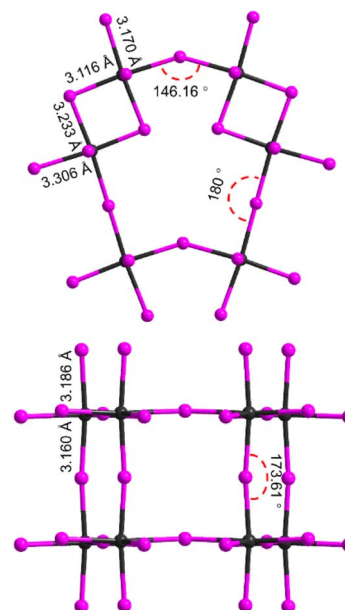


Fig. 3 Summary of bond angles between inter-dimer Pb–I–Pb bonds and bond lengths within each octahedron.



$$\sigma^2 = \left(\frac{1}{11}\right) \sum_{i=1}^{12} (\theta_i - 90)^2 \quad (2)$$

where  $d$  and  $d_i$  are the average and individual bond distance, respectively, and  $\theta_i$  is the individual angle. For **1**, the two octahedra forming the dimer exhibit similar levels of distortion with  $\Delta d$  and  $\sigma^2$  of  $3.58 \times 10^{-4}$  and 12.48, respectively. The values are notably lower than those typically reported for 3D edge-shared HPs,<sup>35,41</sup> suggesting a minimal distortion close resemblance to an ideal structural model.

### Electronic band structure

Density functional theory (DFT) calculations were conducted to analyze the electronic band structures and dimensional properties of **1**. As depicted in Fig. 4a, the valence band maximum (VBM) appears at the A point while the conduction band minimum (CBM) lies at the Y<sub>2</sub> point. The calculated band structure reveals an indirect feature with a bandgap of 1.86 eV, which exceeds that of corner-sharing MAPbI<sub>3</sub> (1.5 eV) and is comparable to 3D lead iodide hybrid perovskite analogs with similar edge-sharing dimers (*e.g.*, 1.93 eV of (M<sub>2</sub>pda)Pb<sub>2</sub>I<sub>6</sub> (M<sub>2</sub>pda = N,N'-dimethylpropane-1,3-diaminium)).<sup>36</sup> Compound **1** exhibits relatively flat valence bands and dispersive conduction bands. This is because the octahedra are connected in a corner-sharing mode along *a* direction while a combination of corner-sharing and edge-sharing is observed in the other two directions. Consequently, the  $\Gamma$ -Y<sub>2</sub> direction in the Brillouin zone, corresponding to *a* direction in real space, exhibits the most energy dispersion for conduction bands. This contrasts sharply with other crystallographic directions where octahedra share edges, resulting in significantly less dispersive electronic bands. This is also evident from the calculated effective masses (Table S5<sup>†</sup>). The effective mass for both electrons and holes along *a* direction is significantly smaller than in the other two

directions, indicating that charge transport is greatly restricted in the edge-sharing plane.<sup>35,41</sup> These results align with our understanding that the corner-shared motif generally results in greater band dispersions compared to the edge-shared one, followed by the face-shared motif.<sup>42–44</sup>

Density of states data indicates that the VBM is formed by overlapping Pb-6s and I-5p orbitals while the CBM results from overlapping Pb-6p orbitals, highlighting that the energy band and semiconductor performance are predominantly governed by the inorganic components, with negligible contributions from organic cations (Fig. 4b). Additionally, partial charge density (PCD) distributions of the CBM and VBM were computed to deepen the understanding of the electronic properties. Analysis of the charge density associated with the VBM and CBM in the *bc* plane also reveals that the VBM is primarily contributed by Pb and I whereas Pb dominates in the CBM (Fig. 4c and d). Contour plots of the PCD for the CBM and VBM within the *bc* plane demonstrate directional differences along the *b* and *c* axes, indicating anisotropic electronic characteristics. Nevertheless, the orbitals contributing to the VBM and CBM maintain continuity across all three crystallographic axes (Fig. S3<sup>†</sup>). Owing to the 3D connectivity of the band edge-determining [PbI<sub>6</sub>] octahedra, **1** showcases a 3D electronic nature, which aligns with the structural connectivity of its inorganic framework.

### Optical properties

Ultraviolet-visible diffuse-reflectance spectra of **1** were recorded and shown in Fig. 5a. There is significant absorption in the ultraviolet region. The edge of the band extends into the visible light region near 600 nm. Based on the Kubelka–Munk equation,<sup>45</sup> the optical bandgap value is estimated to be 2.10 eV (Fig. 5a inset), which is slightly smaller than the bandgap of common 2D lead iodide perovskite semiconductors<sup>42</sup> and is

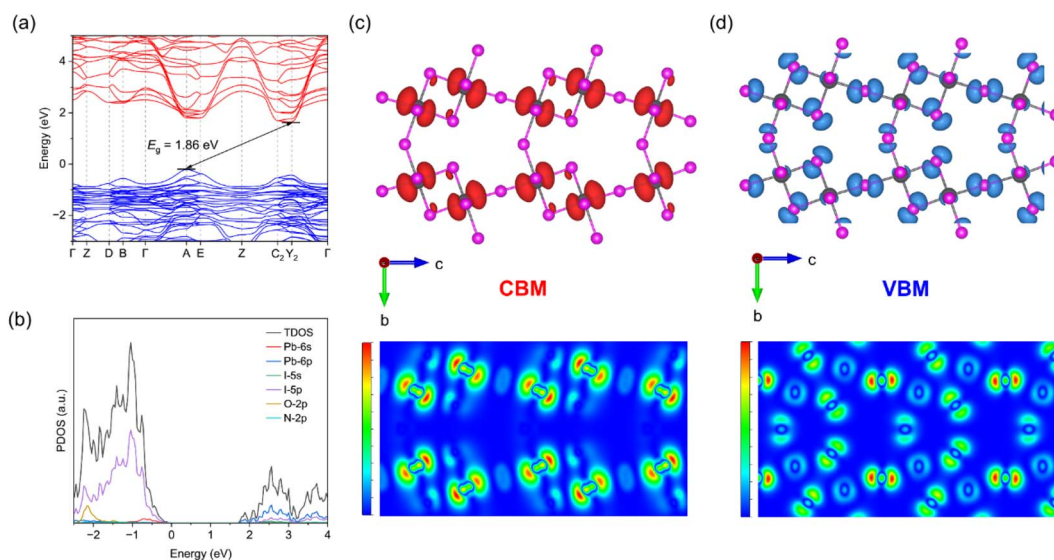


Fig. 4 DFT calculations of the electronic structural features of **1**: (a) band structures and (b) projected density of states (DOS); calculated partial charge densities (PCD) and 2D maps within the (100) plane for (c) VBM and (d) CBM.



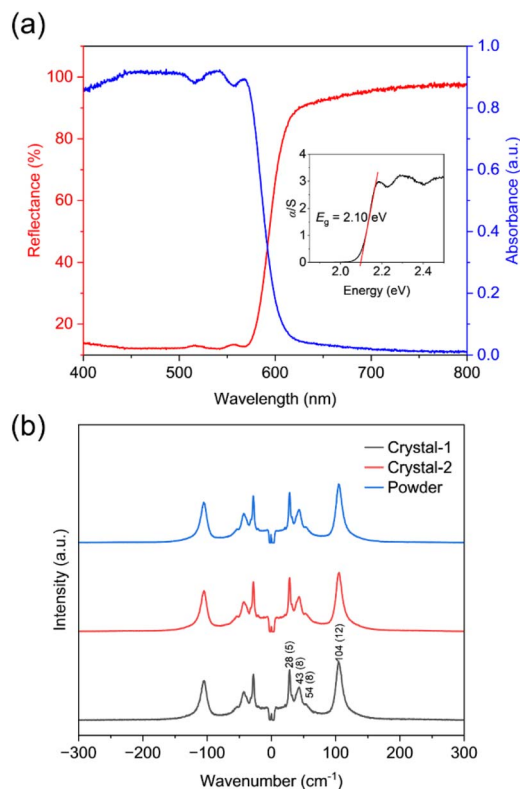


Fig. 5 (a) UV-visible diffuse-reflectance spectra and (b) low-frequency Raman spectra of **1**. The full-width at half-maximum (FWHM) indicated in parentheses.

comparable to 3D lead iodide perovskite ( $M_2\text{pda}$ ) $\text{Pb}_2\text{I}_6$ .<sup>36</sup> A steady-state photoluminescence (PL) spectrum of the powder sample of compound **1** was recorded with 460 nm excitation. At room temperature, **1** exhibits weak emission, similar to many 3D lead perovskite analogs.<sup>35,41</sup> The PL spectrum reveals a relatively narrow peak at 590 nm with a full width at half maximum (FWHM) of approximately 40 nm (Fig. S4a†). This contrasts with previously reported results for (NMPA) $\text{Pb}_2\text{Br}_6$  (NMPA =  $N,N'$ -dimethylpropane-1,3-diaminium) and (DMEA) $\text{Pb}_2\text{Br}_6$  (DMEA =  $N,N'$ -dimethylethane-1,2-diaminium), which display broader emission.<sup>35</sup> And the extracted PL lifetime by fitting the PL decay curves demonstrate a short lifetime of 0.74 ns (Fig. S4b†). Combining with the fact that the emission peak is near the band edge, the PL emission of **1** is likely to be excitonic. However, additional experimental evidence, such as temperature-dependent and power-dependent PL measurements, would be helpful.

Raman spectroscopy of **1** was performed at room temperature to explore the dynamic characteristics (Fig. 5b). It exhibits obvious peaks at 28, 43, and 104  $\text{cm}^{-1}$ , similar to those observed in conventional 3D  $\text{AMX}_3$  structures. Notably, peaks around 105  $\text{cm}^{-1}$  are assigned to the symmetric and asymmetric stretching of  $[\text{PbI}_6]$  octahedra while those below 85  $\text{cm}^{-1}$  correspond to octahedral bending modes.<sup>41,46</sup> The FWHM of these peaks are relatively narrow,<sup>47–49</sup> indicating the absence of disorder at room temperature, which was in agreement with X-ray diffraction result. The Fourier transform infrared (FT-IR)

spectroscopy was conducted to investigate the interaction between the organic molecules and the inorganic framework. The signals around 3570, 3500 and 3130  $\text{cm}^{-1}$ , attributed to N–H vibration of **1**, shift to higher wavenumbers compared to that of the precursor cations, indicating the presence of weak hydrogen bonding interactions between the organic molecular cations and the  $[\text{PbI}_6]$  octahedral frameworks (Fig. S5†). And these signals are sharp than the observed broad peak in  $\text{NH}_4\text{I}$  precursor, which may indicate an order of  $\text{NH}_4^+$  in the lattice. These observation aligns with the structural analysis described above.

### Optoelectronic response

Based on the promising optical and electronic properties of **1**, we conducted an initial evaluation of its photoresponse characteristics. Silver electrodes were utilized with the direction oriented along the  $a$ -axis, where all the octahedra are interconnected by corner-sharing. When subjected to ambient light at a wavelength of 565 nm, the device exhibited a distinct photoresponse, even under low power conditions of 1.6  $\mu\text{W cm}^{-2}$  (Fig. S6a†). The on-off photoresponse increased with the power of the light, and at a light power of 62.9  $\mu\text{W cm}^{-2}$ , the device demonstrated a pronounced photoresponse with a photocurrent that was 10 times higher than the dark current. Furthermore, stability and durability tests under pulsed light revealed that the device maintained excellent photoelectric performance even after more than  $10^3$  cycles (Fig. S6b†). These findings indicate significant potential for photodetection applications at room temperature.

### Structural phase transition and stability

In the context of known 3D perovskites or analogs, many exhibit structural phase transitions.<sup>33,36</sup> However, in the case of **1**, differential scanning calorimetry measurements indicate no phase transition within the measured temperature range (Fig. S7a†). The temperature-dependent dielectric measurements show no anomalies during heating and cooling, which aligns with the DSC results, further confirming that there is no structural phase transition (Fig. S7b†). Thermogravimetric analysis (TGA) evaluated the thermal stability of **1**, demonstrating a good stability up to approximately 250  $^\circ\text{C}$  (Fig. S8†). This stability, while slightly lower than 3D perovskites containing dications, is attributed to the lighter  $\text{NH}_4^+$  and weak N–H $\cdots$ O interactions. Furthermore, after exposure to 40% relative humidity for three months, the powders of **1** maintained a consistent PXRD pattern with fresh one, highlighting its good long-term stability (Fig. S9†).

## Conclusions

In summary, we successfully synthesized a 3D perovskite analogue, (ammonium)(morpholinium) $\text{Pb}_2\text{I}_6$ , by strategically replacing one dication with two hydrogen-bonded monocations in the voids. This innovative approach effectively mitigates issues stemming from electrostatic repulsion between two positively charged monocations. The fundamental 3D inorganic



framework adopts a type II structure with minimal structural distortion, accommodating ammonium and morpholinium cations in regions of varying volume based on their respective sizes. Detailed structural analysis reveals that the spatial arrangement of the two positively charged nitrogen atoms and the N-H...O hydrogen bonding interactions play a crucial role in reducing electrostatic repulsion. Density functional theory calculations indicate that **1** exhibits an indirect bandgap, similar to the electronic band structures observed in AMX<sub>3</sub> perovskites, with relatively dispersive valence and conduction bands. The synthesis of such a 3D perovskite holds promise for alleviating limitations in cation selection and has the potential to catalyze the developments of new 3D perovskite materials and related fields.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Wei Wang: conceptualization, data curation, formal analysis, investigation, methodology, validation and writing original draft; Cheng-Dong Liu: visualization and formal analysis; Chang-Chun Fan: investigation; Wen Zhang: conceptualization, data curation, funding acquisition, resources, supervision, software and writing – review & editing.

## Conflicts of interest

The authors declare no competing financial interest.

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