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Centimeter-sized single crystals of 3D perovskitoid (4-AP)Pb₂X₆ (X = Br, I) for efficient and stable X-ray detection

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Three-dimensional (3D) metal halide perovskites (MHPs) have been widely studied in the field of X-ray detection, due to their easy synthesis, strong X-ray absorption and high carrier transport capability. However, the conventional 3D ABX₃ MHPs have fatal problems of large dark current drift, severe ion migration and poor environmental stability, which calls for extensive research on the design and modulation of novel 3D perovskitoids to address these issues. In this study, two AB₂X₆-type 3D perovskitoids (4-AP)Pb₂X₆ (4-AP = 4-amidinopyridinium, X = Br, I) with centimeter-sized single crystals have been synthesized for X-ray detection. Thorough studies disclose unique inorganic frameworks composed of both corner-sharing and edge-sharing octahedra, while multi-ammonium aromatic 4-AP²⁺ cations are situated within the expansive cavities of the inorganic network. Strikingly, both of these compounds are characterized by elevated activation energy (*E_a*) of ionic conductivity, reduced dark current drift, and superior stability compared to the conventional 3D perovskite MAPbI₃. In particular, (4-AP)Pb₂I₆ with a flatter framework achieves a high sensitivity of 2512 μC Gy⁻¹ cm⁻² and a low detection limit of 0.72 μGy s⁻¹, due to the better carrier transmission channels and stronger X-ray absorption. This work highlights the potential of the 3D AB₂X₆ perovskitoid family in high-performance optoelectronics.

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Introduction

Direct X-ray detection, transforming X-ray photons directly into an electrical signal, has great potential for the development of security screening, medical diagnosis, nondestructive determination, computed tomography imaging, *etc.*^{1–3} The performance of X-ray detectors is primarily determined by the semiconductors that convert the X-rays into electrical signals. Recent studies show that metal-halide hybrid perovskites offer unique properties including large atomic number (*Z*), high mobility–lifetime product (*μτ*), large resistivity, and fast photo-response, making them promising candidates for high-performance direct X-ray detectors.^{4–6} Additionally, the low-cost solution processability makes them attractive for large-scale and disposable applications such as personal dosimetry and medical imaging. Due to the spatial connectivity of the inorganic framework in all three directions, the conventional 3D ABX₃ (A = +1 cations; B = Ge²⁺, Pb²⁺, Sn²⁺; X = Cl⁻, Br⁻, I⁻)

perovskite structure (formed by the corner-sharing motif of the BX₆ octahedra) is preferred because of its fast charge carrier transport, high density and quick response.^{7,8} For example, X-ray detectors utilizing MAPbI₃ (MA = CH₃NH₃⁺) have demonstrated remarkable performance, achieving a sensitivity of 2.2 × 10⁸ μC Gy⁻¹ cm⁻² and an exceptionally low detection limit of 1.5 nGy s⁻¹.⁹ Typically, the conventional 3D perovskite structure has defined cages which are stabilized by the so-called Goldschmidt tolerance factor, a geometrical constraint that the A cations in the general formula ABX₃ must satisfy.^{10–12} So far, only three +1 A-site cations have been found capable of stabilizing the 3D perovskite frameworks: Cs⁺, MA, and HC(NH₂)₂⁺ (FA).^{13,14} In addition to the limited variety of structures, conventional 3D perovskites also have the widespread problems of high dark current drift (~10⁻⁴–10⁻³ nA cm⁻¹ s⁻¹ V⁻¹), high noise and environmental instability,^{15–18} which are not conducive to the realization of practical X-ray detection applications. While significant progress has been made in improving the stability and reducing ion migration in conventional 3D perovskites through surface passivation and compositional engineering,^{19,20} structural modification offers an equally effective and fundamentally distinct approach to enhance material performance. Rationally designing the inorganic framework and tailoring the organic–inorganic interactions at the molecular level provides a promising platform to achieve these improvements intrinsically, bypassing the need for post-synthetic treatments or complex device engineering.

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It is possible to use a dimensionality reduction strategy to construct 2D/1D/0D perovskite detectors with lower dark currents drift and higher stability. This also reduces X-ray absorption and carrier transport efficiency, leading to lower sensitivity, *e.g.* (BA)₂PbBr₄:²¹ 726.18 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$; (BDA)PbI₄:²² 242 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$; (MPC)₂PbX₄:²³ 185 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$; (R/S-PPA)₂BiI₅:²⁴ 150 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$. Thus, the development of novel 3D perovskitoids capable of accommodating larger organic molecules, which not only inherit the high performance of conventional 3D structures but also exhibit better application stability, is therefore in great demand. Fortunately, substituting the B–X octahedral unit in AB₂X₆ perovskites with a pair of edge-sharing B–X octahedra enables the creation of expanded perovskitoid structures: AB₂X₆.^{25–27} In 2020, Umeyama *et al.*¹³ reported seven members of this new family of materials by synthesizing derivatives with dication pyridinium and ammonium. In the same year, Li *et al.*¹⁴ synthesized four aminomethylpyridinium (AMPY) templated AB₂X₆ compounds and studied the X-ray detection capability of (3AMPY)Pb₂I₆, gaining an X-ray detection sensitivity of 207 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$. Nevertheless, the impact of halide-modulated molecular assembly on their structure and properties remains largely unexplored. In addition, how to further improve X-ray detection capability through structural modification also remains challenging. As a multi-ammonium aromatic cation, 4-amidinopyridinium (4-AP²⁺) can provide enhanced interactions with the inorganic framework through multiple N–H⋯X hydrogen binding sites, resulting in improved carrier transport and structural stability.^{10,28,29} Moreover, the aromatic structure of 4-AP²⁺ has a higher dielectric constant than its aliphatic counterparts, which has been considered as an excellent characteristic to improve the optoelectronic performance, *i.e.* better carrier transport and enhanced light absorption.^{30–33} In this context, the construction of such 3D perovskitoids using functional 4-AP²⁺ is expected to achieve better detection performance.

Herein, templated by 4-AP²⁺, we synthesised two AB₂X₆-type 3D perovskitoids (4-AP)Pb₂Br/I₆ to gain a systematic understanding of their structure–property relationships. Both of them achieved high qualities with centimeter-size single crystals (SC) by a simple solution cooling method. Notably, compared to the conventional MAPbI₃, they were characterized by elevated activation energy (E_a) of ionic conductivity, reduced dark current drift, and superior stability. In particular, the lead iodine counterpart with a flatter inorganic framework and enhanced hydrogen binding has better carrier transmission channels and stronger X-ray absorption, resulting in excellent X-ray detection performance with high sensitivity (2512 $\mu\text{C Gy}^{-1} \text{cm}^{-2}$), low detection limit (0.72 $\mu\text{Gy s}^{-1}$), and high operational stability. This work provides a deep insight into the potential of the AB₂X₆ perovskitoid family in high-performance optoelectronics.

Results and discussion

To avoid the 2D perovskite (4-AP)PbBr/I₄ structures (formed when the ratio of Pb and 4-AP starting materials is 1 : 1), we used a 4 : 1 ratio to obtain the new compounds. All compounds crystallize in the orthorhombic space groups *Pnna*, with the

crystallographic data shown in Table S1. The powder X-ray diffraction (PXRD) results indicate that both (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ are pure phases (Fig. S1 and S2). As Fig. 1a shows, for (4-AP)Pb₂Br₆ (the structure of (4-AP)Pb₂I₆ is similar), two octahedra are linked through edge-sharing to create dimers, which subsequently connect *via* corner-sharing with other dimers, forming continuous layers that extend along the *bc* crystallographic plane. Four edge-sharing dimers are corner-connected across these layers, generating triangular or rectangular voids. These layers, featuring alternating voids, stack along the *a*-axis (stacking direction) through corner connections, ultimately building the anionic inorganic 3D framework (Fig. 1b). An insight into the crystal structure shows that the inorganic framework is formed by two crystallographically independent Pb atoms (Fig. 1c, Pb1 and Pb2). To further investigate the structural difference between (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆, the structural distortion was examined by calculating the distortion index (Δd , eqn (1)) and bond angle variance (σ^2 , eqn (2)), through the variance of the Pb–X bond length and Pb–X–Pb bond angle of the different Pb atoms.

$$D = \frac{1}{6} \sum_i^6 \frac{|l_i - l_{av}|}{l_{av}} \quad (1)$$

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

where l_i is the individual bond length, l_{av} is the average B–X bond distance, and θ_i is the individual bond angle. As Fig. 1d indicates, the Δd and σ^2 of both Pb1 and Pb2 are significantly higher in (4-AP)Pb₂I₆ than those in (4-AP)Pb₂Br₆, revealing less structural distortion of (4-AP)Pb₂I₆. In addition, the protonated 4-AP provides three N atoms that are directly connected to the inorganic sheets by multiple hydrogen bonds (Fig. 1e). The corresponding 2D fingerprint plot of 4-AP²⁺ further shows that the strong N–H⋯I contacts of (4-AP)Pb₂Br₆ (Fig. 1f) and (4-AP)Pb₂I₆ (Fig. S3) are distributed over 70.7% and 72.5% of the surface area, respectively. This smoother inorganic framework and enhanced hydrogen interaction of (4-AP)Pb₂I₆ are likely to result in more favorable charge transport, improved phase stability, and hence improved X-ray detection performance.

The thermogravimetric curves (Fig. 2a) show that (4-AP)Pb₂Br₆ has high thermal stability up to 246 °C, while (4-AP)Pb₂I₆ is much more stable up to 278 °C, both of which are superior to the 3D MAPbI₃ (240 °C, Fig. S4). To further investigate the structural stability of the new 3D perovskitoids, the ion migration rate was characterized by the activation energy (E_a) of ionic conductivity, which is calculated from its temperature-dependent conductivity curve according to the Nernst–Einstein equation³⁴ (eqn (3)):

$$\sigma(T) = \left(\frac{\sigma_0}{T}\right) \exp\left(\frac{-E_a}{k_B T}\right) \quad (3)$$

where σ is the conductivity at a given temperature T , σ_0 is a constant, and k_B is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$). The conductivities of the SC devices were extracted by fitting the *I*–*V* curves in the high-temperature region (Fig. 2b).



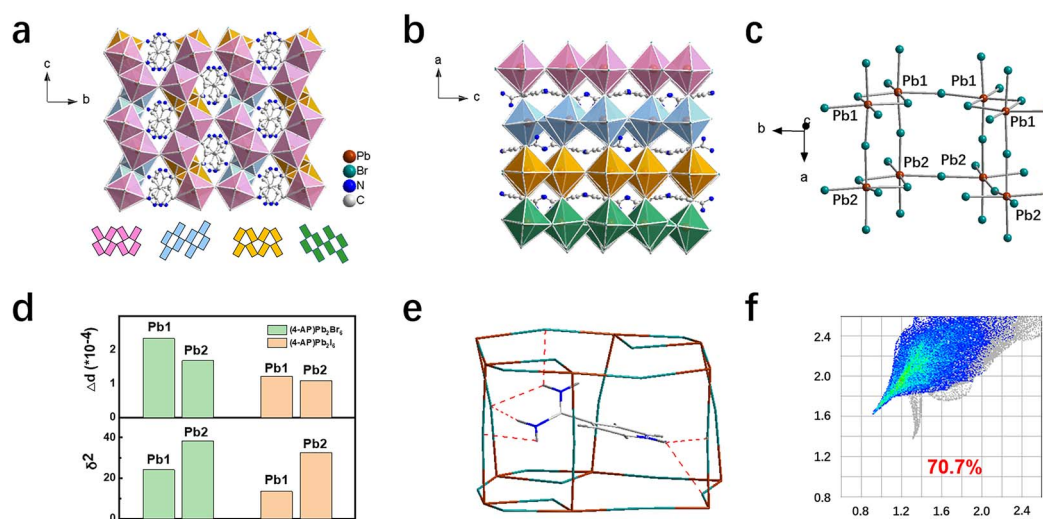


Fig. 1 (a) The crystal structure of (4-AP)Pb₂Br₆ viewed from the *a*-axis. The different colors indicate the different inorganic layers. H atoms are omitted for clarity. (b) The crystal structure of (4-AP)Pb₂Br₆ viewed from the *b*-axis. (c) Fragment of the (4-AP)Pb₂Br₆ structure showing the coordination environment and connectivity of octahedra. (d) Distortion index (Δd) and bond-angle variance (σ^2) of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆. (e) Multiple hydrogen bonding between the 4-AP²⁺ cation and inorganic framework in (4-AP)Pb₂Br₆. (f) 2D fingerprint plots for 4-AP²⁺ cations in (4-AP)Pb₂Br₆.

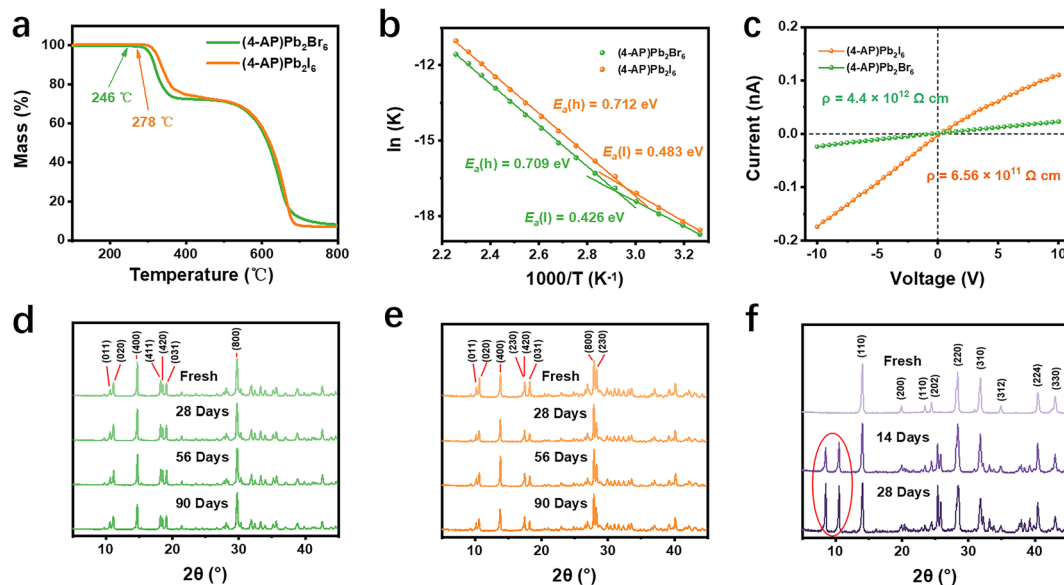


Fig. 2 (a) The thermogravimetric curves of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆. (b) Temperature-dependent conductivities of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ SCs. (c) Resistivities of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ SCs. (d–f) Experimental powder X-ray diffraction patterns of (4-AP)Pb₂Br₆ (d), (4-AP)Pb₂I₆ (e) and MAPbI₃ (f) powder crystals, before and after exposure to the ambient environment (20 ± 10 °C, 70 ± 10% RH).

The ionic conductivity (ion migration) activation energy at high temperature $E_a(h)$ is calculated to be 0.709 eV for the (4-AP)Pb₂Br₆ SC, while a slightly higher value of 0.712 eV is observed for the (4-AP)Pb₂I₆ SC. In contrast, the ion migration is relatively more severe for the MAPbI₃ SC with a lower value of 0.419 eV (Fig. S5), suggesting that by constructing new 3D frameworks, the migration energies become higher and the ion migration is actually inhibited. The low-temperature activation energy $E_a(l)$ was calculated to be 0.426 eV for (4-AP)Pb₂Br₆ and 0.483 eV for

(4-AP)Pb₂I₆. These values are notably lower than their high-temperature counterparts, which is consistent with previously reported behaviors in hybrid perovskites where low-temperature ion migration is often associated with defect-assisted processes or shallow trap-mediated conduction. The slightly higher $E_a(h)$ and $E_a(l)$ observed in (4-AP)Pb₂I₆ suggests that the flatter inorganic framework and enhanced hydrogen bonding in this compound also effectively suppress ion migration. This dual-regime analysis further corroborates the



superior ion-migration inhibition capability of the 3D perovskitoid structure, particularly in the iodide analogue. Additionally, high resistivity helps minimize dark current and current noise, which are essential for achieving stable and high-performance X-ray detection. Fig. 2c shows the current density–voltage curve, which gives a high bulk resistivity (ρ) of $4.4 \times 10^{12} \Omega \text{ cm}$ for (4-AP)Pb₂Br₆ and $6.56 \times 10^{11} \Omega \text{ cm}$ for (4-AP)Pb₂I₆. These values are superior to that of commercial CdZnTe ($10^{10} \Omega \text{ cm}$), and over three orders of magnitude higher than that of 3D MAPbI₃ perovskite SCs ($3.2 \times 10^8 \Omega \text{ cm}$, Fig. S6). Noteworthily, compared with the MAPbI₃ SCs, the new 3D SCs are phase stable even when exposed to the ambient environment ($20 \pm 10^\circ \text{C}$, $70 \pm 10\% \text{ RH}$) for 90 days. As presented in Fig. 2d and e, the powder X-ray diffraction (XRD) patterns of the ground single-crystal powders of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ show no detectable non-perovskitoid diffraction peaks throughout the 90-day ambient exposure period. In contrast, the powder XRD patterns of ground MAPbI₃ single-crystal powders (Fig. 2f) exhibit pronounced new diffraction peaks within just a few days (indicated by red circles), which progressively intensify with prolonged exposure. The additional diffraction peaks correspond to the formation of PbI₂, which is the final degradation product of MAPbI₃ under ambient conditions.^{35,36}

Given the above-mentioned advantages, large SCs were grown through a simple slow temperature cooling process, as shown in the schematic diagram (Fig. 3a and S7). Fig. 3b shows the photographs of the resulting centimeter-scale (4-AP)Pb₂Br₆ (top, bright yellow crystal) and (4-AP)Pb₂I₆ SCs (bottom, dark red crystal), with dimensions of $11 \times 4 \times 3 \text{ mm}^3$ and $13 \times 4 \times 2 \text{ mm}^3$, respectively. The SCXRD diffraction spots exhibit strong intensity and precise alignment (Fig. 3c and S8), highlighting the superior crystal quality of these SCs. Additionally, the SEM image in Fig. 3d reveals a remarkably flat and smooth surface for (4-AP)Pb₂Br₆, further demonstrating its high crystal quality. The UV-vis absorption spectrum (Fig. S9) displays absorption cutoffs at 470 nm ((4-AP)Pb₂Br₆) and 638 nm ((4-AP)Pb₂I₆), from

which their optical bandgap can be derived to be 2.75 and 2.04 eV, respectively, according to their corresponding Tauc plots.

Due to the high stability, large bulk resistivity and high quality of these new 3D perovskitoids, two-terminal structures of Ag/SC/Ag X-ray detectors (Fig. 4a, electrode thickness: 2 nm; electrode spacing: $\sim 5 \text{ mm}$) based on SCs were fabricated to further study their X-ray detection performance. The absorption spectra of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ and some typical X-ray detection materials ($\alpha\text{-Se}$, Si and MAPbI₃) over a wide range of photon energies (10–1000 keV) were simulated based on the photon cross section database, as shown in Fig. 4b. Obviously, the linear absorption coefficients of the new 3D perovskitoids are significantly higher than those of Si and $\alpha\text{-se}$, indicating their good X-ray attenuation capability. In particular, the linear absorption coefficient of (4-AP)Pb₂I₆ is even comparable to that of MAPbI₃, due to its high crystal density and compositional high Z elements, making it well suited for high-performance X-ray detectors. The mobility–lifetime product ($\mu\tau$, Fig. 4c) used to evaluate the effectiveness of X-ray detectors is calculated to be $1.074 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ ((4-AP)Pb₂Br₆) and $1.179 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ ((4-AP)Pb₂I₆). These values are comparable to the reported (3AMPY)Pb₂I₆ device ($1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$), demonstrating a promising charge collection performance for X-ray detection applications. Under a bias of 100 V, both detectors show an increased current density with a gradual increase in the X-ray dose rates from 4.35 to 87.66 $\mu\text{Gy s}^{-1}$ (Fig. 4d), while the (4-AP)Pb₂I₆ detector has a higher current density than that of the (4-AP)Pb₂Br₆ detector. By fitting their slopes (Fig. S10 and 11), the sensitivity under 100 V is calculated to be $633 \mu\text{C Gy}^{-1} \text{ cm}^{-2}$ ((4-AP)Pb₂Br₆) and $2512 \mu\text{C Gy}^{-1} \text{ cm}^{-2}$ ((4-AP)Pb₂I₆). This result of (4-AP)Pb₂I₆ is more than 10 times higher than that reported for (3AMPY)Pb₂I₆ with a value of $207 \mu\text{C Gy}^{-1} \text{ cm}^{-2}$, demonstrating the successful performance enhancement by the functional 4-AP²⁺. Furthermore, this result also outperforms most low-dimensional perovskite-based detectors, indicating the superiority of three-dimensional structures.^{37–39} The detection ability was then tested under different external bias voltages (e.g. 10, 20, and 50 V), as illustrated in Fig. 4e, where it is evident that sensitivity increases with increasing voltage. We also examined the detection limit, which measures the smallest X-ray dose rate that can be accurately identified. As defined by IUPAC, the limit of detection (LoD) corresponds to the dose rate where the signal-to-noise ratio (SNR) equals 3.⁴⁰ By fitting SNRs as a function of dose rates (Fig. 4f), the LoD of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ at 100 V is determined to be $1.49 \mu\text{Gy s}^{-1}$ and $0.72 \mu\text{Gy s}^{-1}$, respectively. Both these values are much lower than that of commercial $\alpha\text{-Se}$ film detectors ($5.5 \mu\text{Gy s}^{-1}$, with X-ray energy around 20 keV), fully demonstrating their excellent detection capability. Notably, the high sensitivity and low LoD of (4-AP)Pb₂I₆ are primarily attributable to its higher crystal density (stronger X-ray absorption) and flatter framework (better carrier transmission channels).

Dark current drift (I_{drift}) is another vital parameter of X-ray detectors, where a high value can increase the scattering noise and result in a poor SNR.^{18,24} As shown in Fig. 4g, there is a slight dark current drift of $3.1 \times 10^{-6} \text{ nA cm}^{-1} \text{ s}^{-1} \text{ V}^{-1}$ for (4-AP)Pb₂Br₆ and $1.48 \times 10^{-5} \text{ nA cm}^{-1} \text{ s}^{-1} \text{ V}^{-1}$ for (4-AP)Pb₂I₆ under

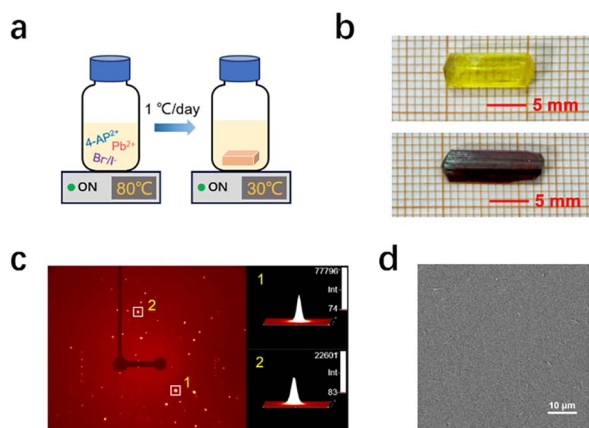


Fig. 3 (a) A schematic showing the growth of SCs. (b) The photos of centimeter-sized SCs of (4-AP)Pb₂Br₆ (top) and (4-AP)Pb₂I₆ (bottom). (c) SCXRD diffraction spots of (4-AP)Pb₂Br₆. (d) The SEM image of the crystal surface of (4-AP)Pb₂Br₆.



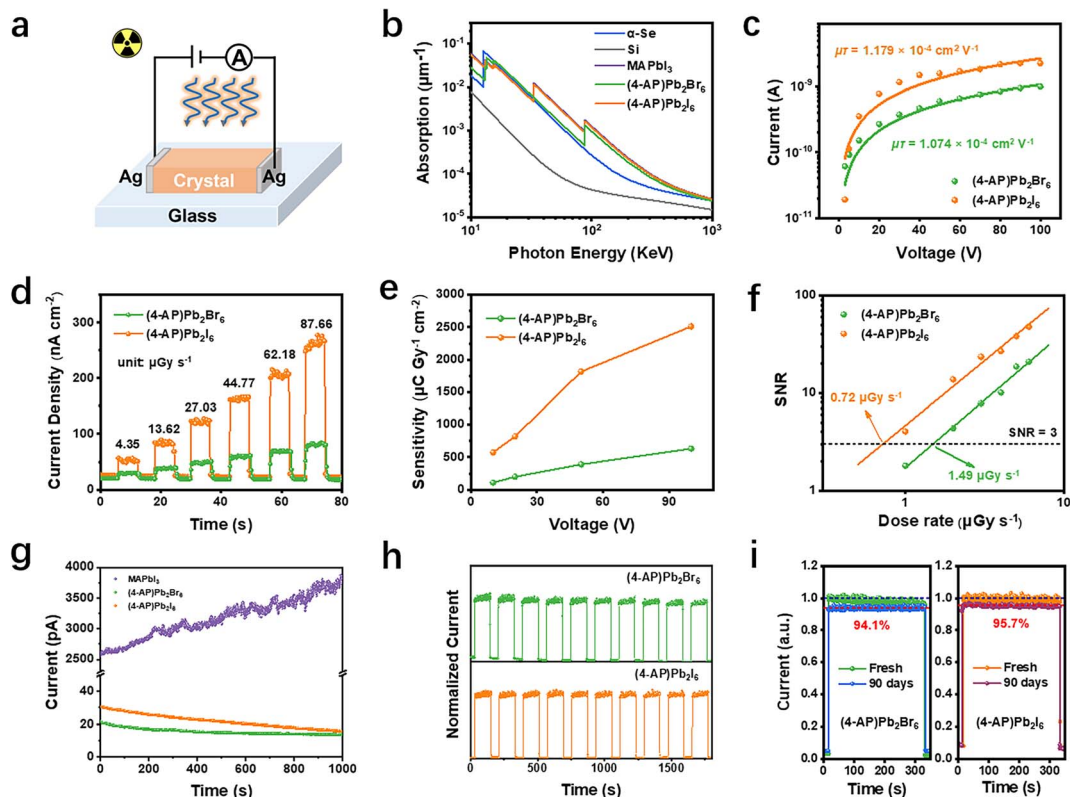


Fig. 4 (a) Schematic diagram of the X-ray photodetector based on single crystals (electrode thickness: 1 mm, electrode spacing: ~ 1 mm). (b) Absorption coefficients of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ in comparison to α -Se, Si and MAPbI₃. (c) The voltage-dependent photoconductivity of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ under X-ray irradiation. (d) Photocurrent response of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors to X-ray with increasing dose rates under a bias voltage of 100 V. (e) Sensitivity of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors at different bias voltages. (f) Signal-to-noise ratio (SNR) of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors at 100 V. (g) Dark current measurements of MAPbI₃, (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors under 10 V. (h) Stability results of (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors exposed to on-off X-ray irradiation in a test period of 10 times under 100 V and 167.9 $\mu\text{Gy s}^{-1}$ doses. (i) Stability measurement of the (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ detectors in the ambient environment (20 ± 10 °C, $70 \pm 10\%$ RH).

10 V. Both are much lower than the that of conventional 3D perovskite SC X-ray detectors, including MAPbI₃ (1.18×10^{-3} nA cm⁻¹ s⁻¹ V⁻¹), MAPbBr₃ (4.9×10^{-3} nA cm⁻¹ s⁻¹ V⁻¹), MAPbCl₃ (5.8×10^{-3} nA cm⁻¹ s⁻¹ V⁻¹) and CsPbBr₃ (1.9×10^{-4} nA cm⁻¹ s⁻¹ V⁻¹).^{17,18} Such a low I_{drift} can be attributed to the effectively suppressed ion migration resulting from the unique framework in the novel 3D perovskitoids.⁴¹ In addition, both the detectors show excellent on-off and long-term irradiation stability, as shown in Fig. 4h, where we applied ten times cycles of “on/off” X-ray irradiation switching over a long period of time under high external bias of 100 V and 167.9 $\mu\text{Gy s}^{-1}$ doses. Storage stability measurement was performed on the detectors under ambient conditions (20 ± 10 °C, $70 \pm 10\%$ RH) without any encapsulation. The result shows that the response current of the (4-AP)Pb₂Br₆ SC detector was still 94.1% of the initial value after 3 months, while the (4-AP)Pb₂I₆ SC detector retained 95.7% of the response current (Fig. 4i). The above stability test results illustrate the great practical application prospects of these 3D perovskitoid SC-based devices. Table S2 shows a comparison of the performance of the detector (in terms of sensitivity, detection limit, and dark current drift) with a few of

the most representative MHP-based X-ray detectors reported in the literature.

Conclusions

In summary, by using 4-AP²⁺, we have constructed two AB₂X₆-type 3D perovskitoids with centimeter-size single crystals for X-ray detection, which not only inherit the high performance of 3D structures, but also exhibit better stability. Notably, both (4-AP)Pb₂Br₆ and (4-AP)Pb₂I₆ exhibit reduced ion migration, reduced dark current drift and enhanced stability compared to the conventional 3D MAPbI₃ analogue, making them excellent candidates for X-ray detection. Changing the halide from Br to I results in higher crystal density, reduced structural distortion and stronger hydrogen bonding in crystal structures and therefore better X-ray absorption and more efficient charge transport. As a result, an efficient X-ray photoresponse was achieved by (4-AP)Pb₂I₆ with a sensitivity up to 2512 $\mu\text{C Gy}^{-1}$ cm⁻² and a low detection limit of 0.72 $\mu\text{Gy s}^{-1}$. This work demonstrates that the large single crystals of 3D AB₂X₆ perovskitoids provide a promising platform for high performance optoelectronics. Although carrier transport pathways in single



crystals are more ordered, making it easier to achieve high-performance X-ray detection, growing single crystals of large dimensions remains extremely challenging. Looking forward, the future development of thin-film or flexible configurations based on these perovskitoids holds promise for expanding their utility into large-area and wearable X-ray detectors.

Author contributions

H. Dai prepared the samples and wrote the manuscript. Z.-K. Zhu and S. You provided suggestions for the project. J. Luo designed and directed this project. All the authors discussed and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2312099 and 2312100 contain the supplementary crystallographic data for this paper.^{42a,b}

Additional synthetic, analytical, and crystal data are available in the supplementary information (SI) of this article. Supplementary information is available. See DOI: <https://doi.org/10.1039/d6sc00616g>.

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