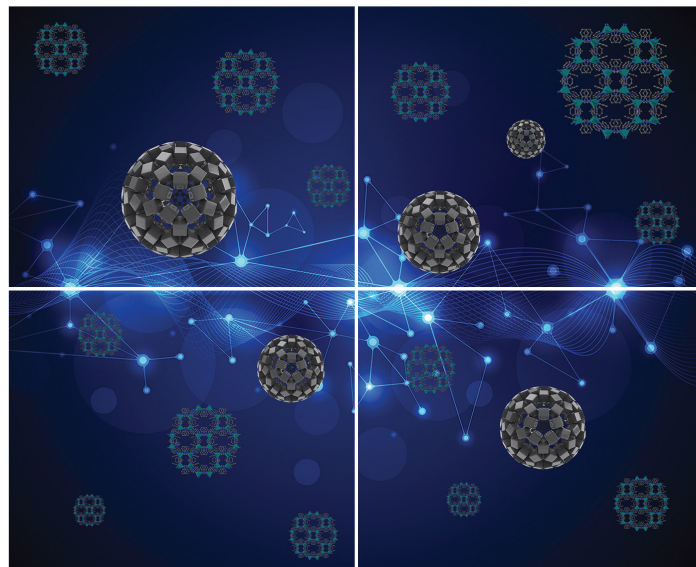


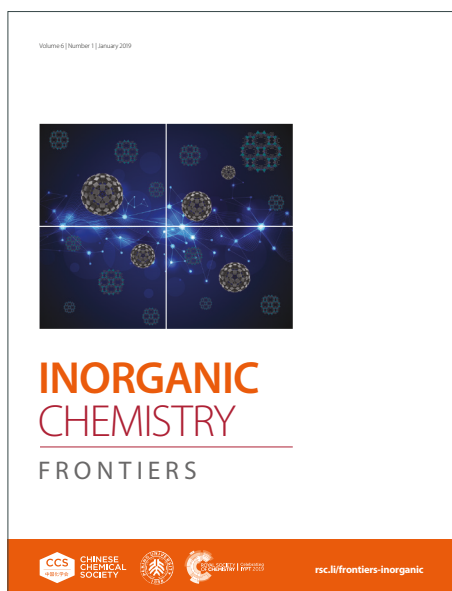
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## ARTICLE

## Aromatic Diamine Constructed Lead-Free Polar Perovskite Towards Stable Self-Driven X-Ray Detection

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The zero-dimensional (0D) bismuth halide perovskites are attractive candidate semiconductors for X-ray detection due to their low biotoxicity and inhibited ionic migration. However, achieving stable X-ray detection applications of 0D perovskites remains challenging. Introducing aromatic diamine cations into perovskites can enhance structural stability and improve charge transport behaviors. Herein, utilizing the strong anchoring effect of the diamine with the inorganic skeleton, stable X-ray detection is obtained by synthesizing novel 0D polar perovskites, namely AP<sub>2</sub>BiI<sub>7</sub> (AP = 4-amidinopyridine). In particular, leveraging intrinsic spontaneous electric polarization that produces a significant 1.15 V photovoltage, the device achieves excellent self-driven X-ray detection at zero electric field, with a high sensitivity of 58  $\mu\text{C Gy}^{-1}\text{cm}^{-2}$  and a low detection limit of 100 nGy s<sup>-1</sup>. Furthermore, the detector exhibits low baseline drift and highly stable X-ray detection, benefiting from the anchoring effect of the aromatic diamine cations in the compound. Our work represents a significant step toward realizing stable, eco-friendly, self-powered X-ray detectors based on perovskite materials.

## Introduction

Direct X-ray detection technology converts X-ray photons directly into electrical signals and is widely used in medical imaging, scientific research, industrial inspection, and other fields.<sup>1-5</sup> Halide perovskites, with their high mobility-lifetime product, strong X-ray absorption, and simple synthesis, show great promise for direct X-ray detection due to these excellent optoelectronic properties.<sup>6-9</sup> MAPbI<sub>3</sub>-based (MA = methylamine) direct X-ray detectors, for instance, achieve sensitivities as high as  $2.2 \times 10^8 \mu\text{C Gy}^{-1}\text{cm}^{-2}$  and detection limits down to 0.1 nGy s<sup>-1</sup>.<sup>10, 11</sup> However, the device instability due to severe ionic migration remains a significant challenge for the real application of perovskite detectors.<sup>12, 13, 14</sup> Furthermore, equipment instability could lead to toxic lead leaking from Pb-based perovskites, resulting in significant contamination of soil and groundwater resources.<sup>15, 16</sup> Therefore, developing “green” lead-free perovskites for stable X-ray detection is urgent.

Bismuth ions (Bi<sup>3+</sup>) share similarities in electronic structure, ionic radius, and electronegativity with lead ions (Pb<sup>2+</sup>). Despite the difference in charge, these similarities make bismuth a promising, less-toxic alternative to lead in many applications.<sup>17, 18</sup> Bismuth halide perovskites (BHPs) have garnered attention for their large

resistivity and low ionic mobility, properties associated with enhanced stability.<sup>19, 20</sup> For example, Liu and his colleagues synthesised a classical 0D BHP, MA<sub>3</sub>BiI<sub>9</sub>, from aliphatic amine cations.<sup>12</sup> Aromatic amine cations are more polar than their aliphatic counterparts, which enhances electronic coupling between inorganic octahedra. This reduces quantum confinement and improves charge transport.<sup>21</sup> More recently, aromatic diamine-constructed BHPs can further effectively enhance the stability of materials and inhibit ionic migration due to the anchoring effect of aromatic diamine cations.<sup>22-24</sup> Yang et al. constructed BHPs (3-(aminomethyl)pyridine)BiI<sub>5</sub> using aromatic diamine cations. The material achieved efficient charge transfer and suppressed ion migration, which ultimately led to stable photodetection performance.<sup>25</sup> However, most currently known BHPs constructed from aromatic diamines lack polar space group symmetry in their crystalline structure. This necessitates the application of an external electric field to achieve efficient charge carrier separation and transport<sup>12, 26</sup>, resulting in complex device architectures and significant energy consumption.<sup>27</sup> Therefore, achieving stable self-powered X-ray detection in BHPs constructed with aromatic diamines is essential.

In this work, by introducing aromatic diamine AP<sup>2+</sup> (AP = 4-amidinopyridine), we have successfully synthesized new polar 0D BHPs, AP<sub>2</sub>BiI<sub>7</sub>. Anchoring aromatic diamines via both termini to an inorganic framework enhances stability and charge carrier mobility in self-driving detection. Moreover, the device based on polar AP<sub>2</sub>BiI<sub>7</sub> exhibits a strong bulk photovoltaic effect (BPVE) with a photovoltage of 1.15 V due to the excellent spontaneous polarization exhibited along the polar *c*-axis of 35.53  $\mu\text{C cm}^{-2}$ . Under zero applied electric field utilizing the BPVE, the detector demonstrates a high sensitivity (58  $\mu\text{C Gy}^{-1}\text{cm}^{-2}$ ) and a low detection limit (100 nGy s<sup>-1</sup>). Moreover, the aromatic diamine cation promotes the stability of the AP<sub>2</sub>BiI<sub>7</sub>; thus, the detector shows a low *I*<sub>drift</sub> of  $3.8 \times 10^{-7} \text{ nA cm}^{-1} \text{ s}^{-1} \text{ V}^{-1}$  at a 500 V cm<sup>-1</sup> and demonstrates excellent environmental stability. Our work provides new insights into

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exploring novel 0D bismuth halide perovskite materials for stable self-driven X-ray detection.

## Results and discussion

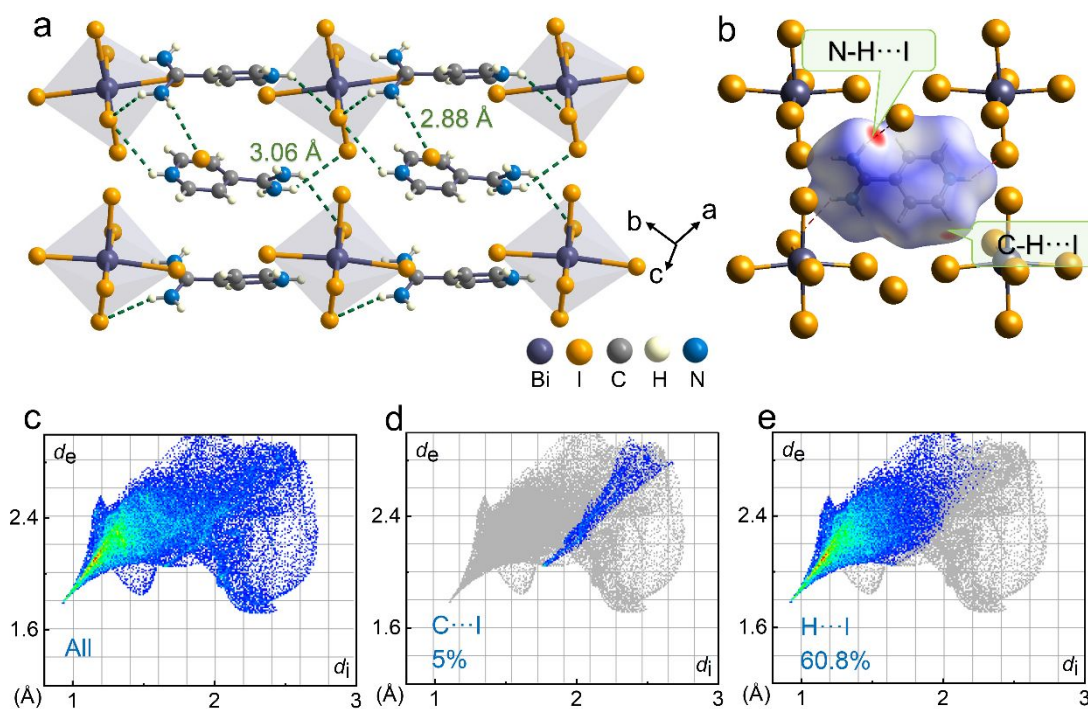
Single-crystal X-ray diffraction (SCXRD) at 300 K confirmed the structure of  $\text{AP}_2\text{BiI}_7$ , which reveals  $\text{AP}_2\text{BiI}_7$  adopts the  $Cc$  polar space group ( $a = 14.2687 \text{ \AA}$ ,  $b = 14.3448 \text{ \AA}$ ,  $c = 15.7364 \text{ \AA}$ ) (Table S1). The polar structure exhibits a significant spontaneous polarization along the  $c$ -axis direction, with calculated polarization values from the point charge model reaching  $35.53 \mu\text{C cm}^{-2}$  (Figure S1 and Table S2). It is therefore promising to observe the obvious bulk photovoltaic effect in the  $c$ -axis direction. The second harmonic generation signal of  $\text{AP}_2\text{BiI}_7$  powders is measured to be about 0.11 times that of  $\text{KH}_2\text{PO}_4$  (KDP), further confirming the non-centrosymmetric structure of  $\text{AP}_2\text{BiI}_7$  (Figure S2). The structure contains the inorganic  $[\text{BiI}_6]^{3-}$  octahedron and isolated  $\text{I}^-$  anion, which are charge-balanced by two independent aromatic diamine  $\text{AP}^{2+}$  cations, forming a 0D structure (Figure 1a). The Bi-I bond lengths in the inorganic skeleton range from  $3.0249(10) \text{ \AA}$  to  $3.1590(10) \text{ \AA}$ , and the I-Bi-I angles from  $83.12(3)$  to  $97.18(3)$  (Tables S3 and S4).

The degree of octahedral distortion of  $\text{AP}_2\text{BiI}_7$  was quantified using the following equation to calculate the distortion index ( $\Delta d$ ) and the bond angle variance ( $\sigma^2$ ):<sup>28</sup>

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

$$\sigma^2 = \frac{1}{11} \sum_{n=1}^{12} (\theta_n - 90^\circ)^2 \quad (2)$$

In which the variable  $d_i$  (or  $\bar{d}$ ) is the individual (or mean) Bi-I bond length, while  $\vartheta_n$  denotes the bond angle between neighboring Bi-Br bonds. The  $\Delta d = 1.64 \times 10^{-4}$ ,  $\sigma^2 = 20.4 \text{ deg}^2$  have been calculated. It indicates that the  $\text{AP}_2\text{BiI}_7$  SC structure has minor structural distortion, which facilitates carrier transport. Furthermore, the  $\text{AP}^{2+}$  molecule bridges and stabilizes the inorganic framework via hydrogen bonds, shortening inter-octahedra distances and suppressing ion migration. The distance between neighboring inorganic skeletons is shorter than that constructed from monoamines. The shortest I-I distance between adjacent  $[\text{BiI}_6]^{3-}$  octahedrons of  $\text{AP}_2\text{BiI}_7$  is  $4.072 \text{ \AA}$ , which is shorter than those in  $(\text{PBA})_4\text{BiI}_7 \cdot \text{H}_2\text{O}$  ( $6.998 \text{ \AA}$ ,  $\text{PBA} = \text{C}_6\text{H}_5(\text{CH}_2)_4\text{NH}_3^+$ ),<sup>29</sup>  $\text{MA}_3\text{BiI}_9$  ( $4.57 \text{ \AA}$ ), and  $\text{BZA}_3\text{BiI}_6$  ( $4.195 \text{ \AA}$ ,  $\text{BZA} = \text{benzylamine}$ ).<sup>30</sup> Furthermore, as demonstrated by the Hirshfeld surface analysis, there is a notable molecular electrostatic interaction between the electron-rich  $\text{I}^-$  anions and the benzene ring ( $\text{I} \cdots \pi$ ). This interaction is attributed to the proximate distance between the  $\text{I}^-$  anion and the neighboring benzene ring, which is approximately  $3.7 \text{ \AA}$  (Figure 1b, c, d, and Figure S3).



**Figure 1.** a) The crystal structure of  $\text{AP}_2\text{BiI}_7$ , in which  $\text{N-H} \cdots \text{I}$  hydrogen bonds between aromatic diamine  $\text{AP}^{2+}$  cations and inorganic skeletons are connected by a dotted line. b) The Hirshfeld  $d_{\text{norm}}$  surfaces (Since the distance between the atoms is less than the sum of their van der Waals radii, the red regions on the Hirshfeld surface indicate a closer interaction between them.) of the aromatic diamine  $\text{AP}^{2+}$  and c-e) corresponding 2D fingerprint plots for  $\text{C} \cdots \text{I}$  and  $\text{H} \cdots \text{I}$  contacts in  $\text{AP}_2\text{BiI}_7$  structure.

The Hirshfeld surface analysis reveals that strong  $\text{N-H} \cdots \text{I}$  hydrogen bonds between the  $\text{AP}^{2+}$  cations and the inorganic

framework account for 60.8% of the total interactions. The account of  $\text{AP}_2\text{BiI}_7$  indicates strong hydrogen bonding between aromatic



diamine cations ( $\text{AP}^{2+}$ ) and the inorganic skeleton. The stronger hydrogen bonding reduces the distance of adjacent  $[\text{BiI}_6]^{3-}$ -octahedra and promotes lattice rigidity and charge transport, resulting in good photoelectric properties.

Red SC of  $\text{AP}_2\text{BiI}_7$  with around  $5.2 \times 4 \times 2 \text{ mm}^3$  was grown from the stoichiometric reaction of  $\text{Bi}_2\text{O}_3$  and AP in a hot hydriodic acid solution via the slow temperature-cooling process (Figure 2a). *PXRD* patterns confirm their phase purity (Figure S4). Meanwhile, the morphology of  $\text{AP}_2\text{BiI}_7$  was simulated by Mercury software, which matched the obtained bulk SCs and determined the *c*-axis orientation (Figure S5). Additionally, a  $d_{33}$  value of  $4.9 \text{ pC N}^{-1}$  characterizes the clear piezoelectric response observed along the *c*-axis in  $\text{AP}_2\text{BiI}_7$  crystals (Figure S6). Thus, it is further verified that the  $\text{AP}_2\text{BiI}_7$  is polar. Furthermore, the *AFM* image of the  $\text{AP}_2\text{BiI}_7$  crystal surface revealed that it was very smooth and flat with few imperfections. The mean roughness and root-mean-square roughness were found to be 0.235 and 0.304 nm, respectively, thereby confirming the exceptional quality of the crystals referring to Figure 2b. The high quality of  $\text{AP}_2\text{BiI}_7$  SCs is conducive to excellent carrier transport. Internal crystal defects were further assessed by measuring trap density ( $n_{\text{trap}}$ ) in  $\text{AP}_2\text{BiI}_7$  SCs with the space-charge-limited current (SCLC) technique.

The current-voltage (*I*-*V*) curve is subdivided into three distinct regions, as illustrated in Figure 2c. These are Trap Filling Limited (TFL) ( $n > 3$ ), Ohmic ( $n = 1$ ), and Child ( $n = 2$ ). The  $n_{\text{trap}}$  value is calculated using the following equation,<sup>31</sup>

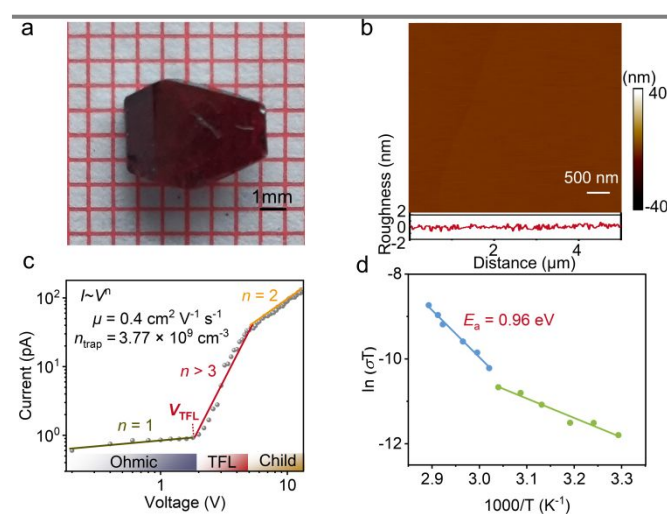
$$n_{\text{trap}} = \frac{2\epsilon\epsilon_0 V_{\text{TFL}}}{eL^2} \quad (3)$$

where  $V_{\text{TFL}}$  is the threshold voltage,  $\epsilon_0$  represents the vacuum dielectric constant,  $e$  denotes the unit charge,  $\epsilon$  designates the relative dielectric constant, and the variable  $L$  indicates the length of the conductive channel. The  $n_{\text{trap}}$  of  $\text{AP}_2\text{BiI}_7$  is calculated as  $3.77 \times 10^9 \text{ cm}^{-3}$ . The value is comparable to high-quality  $\text{MA}_3\text{BiI}_9$  ( $1.2 \times 10^{10} \text{ cm}^{-3}$ )<sup>12</sup> and  $(3\text{-AMP})\text{BiI}_5$  ( $3.53 \times 10^9 \text{ cm}^{-3}$ , 3-AMP = 3-(aminomethyl)pyridine)<sup>32</sup> (for full data, see Table S5). The low  $n_{\text{trap}}$  will favor charge transport and thus improve the mobility-lifetime ( $\mu\tau$ ) product of  $\text{AP}_2\text{BiI}_7$ . Moreover, the hole-only carrier mobility ( $\mu$ ), determined from the Child region using the Mott–Gurney power law:<sup>33, 34</sup>

$$\mu = \frac{8JL^3}{9\epsilon\epsilon_0 V^2}$$

where  $J$ ,  $L$  and  $V$  refer to the dark current density, thickness and applied voltage, respectively. The  $\mu$  value of  $\text{AP}_2\text{BiI}_7$  was calculated to be  $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is higher than that of the bismuth-based perovskites such as  $\text{Cs}_2\text{AgBiBr}_6$  ( $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )<sup>35</sup> and  $\text{FA}_3\text{BiI}_9$  ( $0.0089 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )<sup>26</sup>, indicating that  $\text{AP}_2\text{BiI}_7$  has excellent charge transport properties. Furthermore, the bulk resistivity ( $\rho$ ) of  $\text{AP}_2\text{BiI}_7$  SCs is measured to be  $3.55 \times 10^{10} \Omega \text{ cm}$  by fitting the current-voltage curve along *c*-axis (Figure S7), which is comparable to  $\text{MA}_3\text{BiI}_9$  ( $3.74 \times 10^{10} \Omega \text{ cm}$ )<sup>12</sup>,  $\text{FA}_3\text{BiI}_9$  ( $7.8 \times 10^{10} \Omega \text{ cm}$ , FA = fomaminidinium),<sup>26</sup> and  $\text{AG}_3\text{BiI}_9$  ( $3.78 \times 10^{10} \Omega \text{ cm}$ , AG = aminoguanidinium).<sup>36</sup> Therefore,

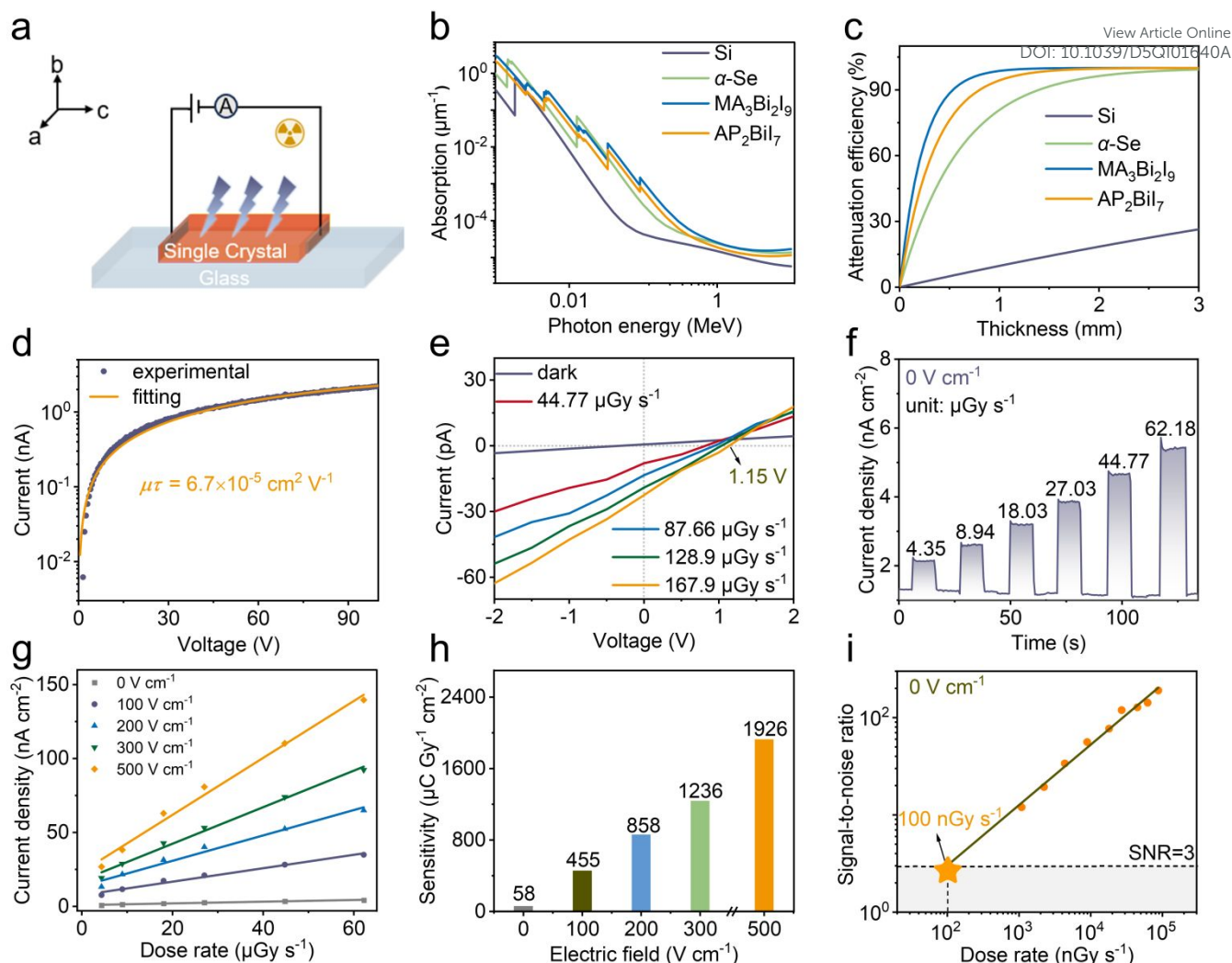
$\text{AP}_2\text{BiI}_7$  with large resistivity is more capable of suppressing dark current, which contributes to improving X-ray detection performance. We have tested the absorption spectra of  $\text{AP}_2\text{BiI}_7$  to illustrate its optical properties (Figure S8). The absorption edge of the material is located at  $\sim 646 \text{ nm}$ , and the optical band gap was further calculated by fitting the Tauc equation to be  $\sim 2.0 \text{ eV}$ . Then, we performed density-functional theory (DFT) calculations on  $\text{AP}_2\text{BiI}_7$  (Figure S9),<sup>37–39</sup> and the results show that the material is characterized by an indirect bandgap. The calculated band gap is  $1.928 \text{ eV}$ , which is in good agreement with the experimental measurements ( $2.0 \text{ eV}$ ) and verifies the accuracy of the calculated model. Partial density of states profiles show that the conduction band minimum (CBM) is mainly contributed by N-2p and C-2p orbitals, while the valence band maximum (VBM) is dominated by I-4p orbitals with contributions from Bi-6p orbitals. Combined with the charge density distributions at VBM and CBM, it can be confirmed that the CBM of the material are dominated by its organic cation, while the VBM is mainly determined by the iodide ions in the inorganic components. To further understand the effect of aromatic diamines on the inhibition of ion migration (as shown in Figure 2d), the activation energy can be obtained from the Nernst–Einstein equation, See support information for more details. The  $E_a$  value of this compound is  $0.96 \text{ eV}$ . This is much larger than that of  $\text{FA}_3\text{BiI}_9$  ( $0.56 \text{ eV}$ )<sup>26</sup> and  $(\text{TMBD})\text{BiBr}_5$  ( $0.64 \text{ eV}$ , *N, N, N', N'*-tetramethyl-1,4-butanediammonium).<sup>40</sup> It implies that the strong contact between the diamine cations and the inorganic skeletons is useful in increasing the energy barrier for ion migration, and ion migration is effectively suppressed.



**Figure 2.** a) An image of a SC of  $\text{AP}_2\text{BiI}_7$ . b) The *AFM* image of the  $\text{AP}_2\text{BiI}_7$  crystal. c) The *I*-*V* curve of the  $\text{AP}_2\text{BiI}_7$  crystal was obtained using the SCLC method. d) The conductivity of  $\text{AP}_2\text{BiI}_7$  is temperature-dependent.







**Figure 3.** a) Diagram of the AP<sub>2</sub>BiI<sub>7</sub> SCs device along the polar *c*-axis direction. b) AP<sub>2</sub>BiI<sub>7</sub>, Si, α-Se, and MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> absorption coefficients as a function of photon energies. c) AP<sub>2</sub>BiI<sub>7</sub>, Si, α-Se, and MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> attenuation efficiency of 50 keV X-ray photons as a function of thickness. d) The voltage-dependent photocurrent of the AP<sub>2</sub>BiI<sub>7</sub> detector yielded a  $\mu\tau$  value of  $6.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1}$  under X-ray irradiation. e) *I*-*V* traces of the AP<sub>2</sub>BiI<sub>7</sub> SC detector in the dark and exposed to X-ray radiation. f) The current density of the AP<sub>2</sub>BiI<sub>7</sub> SC detector at 0 V cm<sup>-1</sup> with increased dose rates. g) The X-ray-induced photocurrent density depends on the dose rate. By fitting the slopes, the sensitivity of the AP<sub>2</sub>BiI<sub>7</sub> detector can be determined. h) The sensitivity of the AP<sub>2</sub>BiI<sub>7</sub> detector at different electric field. i) The X-ray dose rate-dependent SNR for the AP<sub>2</sub>BiI<sub>7</sub> SC detector at 0 V cm<sup>-1</sup>.

The X-ray performance of AP<sub>2</sub>BiI<sub>7</sub> SC was investigated by fabricating it into SC devices. The X-ray device type with an Ag/AP<sub>2</sub>BiI<sub>7</sub> SC/Ag two-terminal structure was adopted in Figure 3a and Figure S10. Through the photon cross-section database,<sup>41</sup> we calculate the X-ray absorption spectra of MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, α-Se, Si, and AP<sub>2</sub>BiI<sub>7</sub> (Figure 3b). The AP<sub>2</sub>BiI<sub>7</sub> demonstrates a markedly greater linear absorption coefficient compared to Si. It approaches that of α-Se, indicating effective X-ray absorption across a wide photon energy range (1 to 1000 keV) for AP<sub>2</sub>BiI<sub>7</sub>. Figure 3c shows the attenuation efficiency of AP<sub>2</sub>BiI<sub>7</sub> for 50 keV X-ray photons. The AP<sub>2</sub>BiI<sub>7</sub> with a thickness of 1 mm can absorb approximately 94% of incident photons, which is considerably higher than the ratio ( $\approx 9.7\%$ ) observed for Si. Excellent X-ray attenuation efficiency and efficient charge collection (quantified by  $\mu\tau$ ) are both essential for high-performance detectors. Here, the voltage-dependent photocurrent of AP<sub>2</sub>BiI<sub>7</sub> SC detectors

can be fitted with the modified Hecht equation to determine the  $\mu\tau$  value.

$$I = \frac{I_0 \mu\tau V}{L^2} \left[ 1 - \exp\left(-\frac{L^2}{\mu\tau V}\right) \right] \quad (4)$$

Where *L* and *V* represent the electrode spacing and the applied voltage, and *I*<sub>0</sub> is the saturated photocurrent. The  $\mu\tau$  value for AP<sub>2</sub>BiI<sub>7</sub>, measured at  $6.7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1}$  (Figure 3d), matches the range observed in some BHPs, such as (R-PPA)<sub>2</sub>BiI<sub>5</sub> ( $5.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1}$ , R-PPA = R-1-phenylpropylamine)<sup>41</sup> and (BAH)BiI<sub>4</sub> ( $1.95 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ , BAH = benzamidinium),<sup>42</sup> and (FA)<sub>3</sub>BiI<sub>2</sub> ( $2.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1}$ ).<sup>26</sup> The AP<sub>2</sub>BiI<sub>7</sub> detector has an enormous potential for X-ray detection, benefiting from its high resistivity, efficient charge collection, and outstanding X-ray absorption. The *I*-*V* traces of the AP<sub>2</sub>BiI<sub>7</sub> detector along the *c*-axis are depicted in Figure 3e, both in the dark and at various X-ray dosage rates. We can observe a significant BPVE of 1.15



V. BPEV originates in the inherent spontaneous polarization of polar crystals. The device is capable of driving the separation and subsequent transport of photogenerated carriers, thereby conferring upon AP<sub>2</sub>BiI<sub>7</sub> the ability to perform self-driven detection. Indeed, even at 0 V cm<sup>-1</sup>, the AP<sub>2</sub>BiI<sub>7</sub> detector shows excellent photoresponse (Figure 3f).

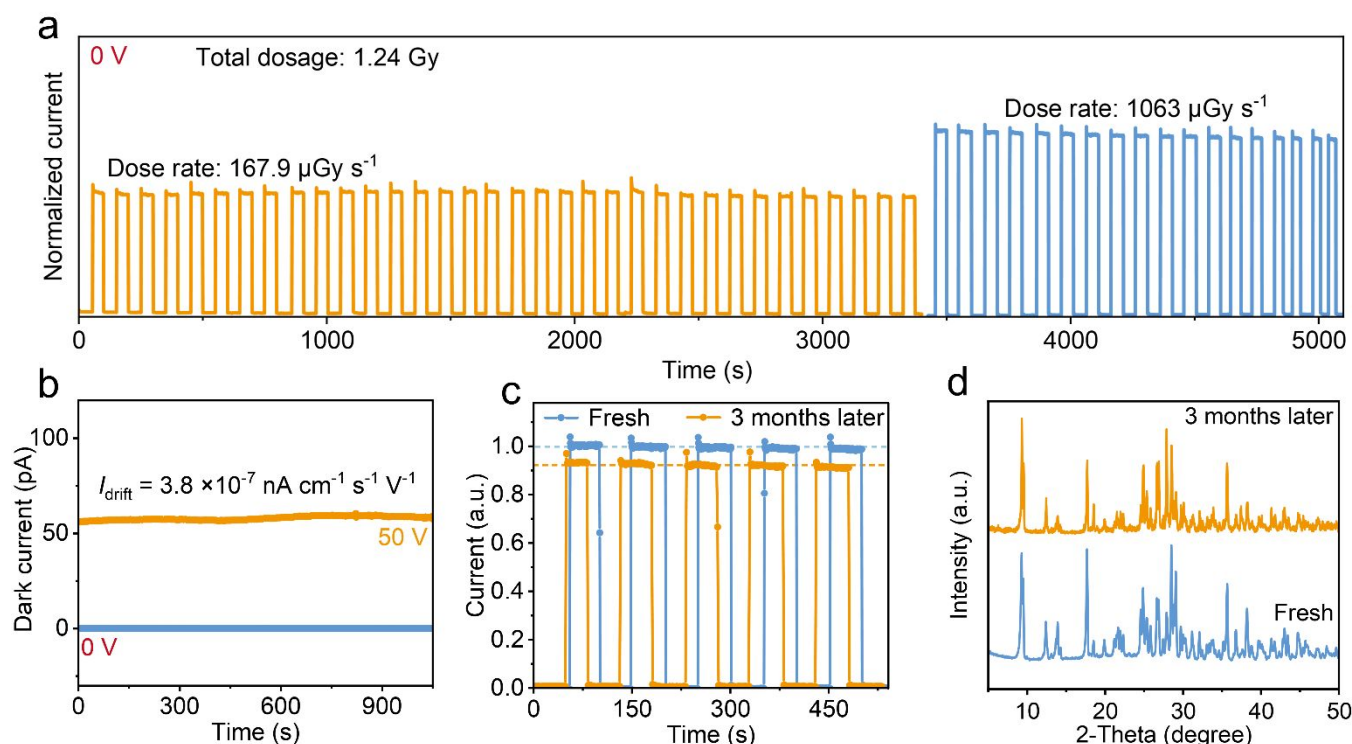
Its exceptional response to X-rays is demonstrated by the current density growing linearly from 4.35 to 62.18 μGy s<sup>-1</sup> as the X-ray dosage rate increases. For comparison, tests were also performed at 100, 200, 300, and 500 V cm<sup>-1</sup> electric field. (Figure S11). As expected, as the external voltage increases, it is more favorable for carrier collection and therefore higher current densities can be obtained. For AP<sub>2</sub>BiI<sub>7</sub> SCs detectors, sensitivity (*S*) is a key performance index, can be determined by the following formula:<sup>43</sup>

$$S = \frac{(J_{ph} - J_d)}{D} (5)$$

where *D* is the X-ray dose rate, *J<sub>ph</sub>* represents the photocurrent density, and *J<sub>d</sub>* denotes the dark current density. Figure 3g shows that the photocurrent density minus the dark current density (*J<sub>ph</sub>* - *J<sub>d</sub>*) is linearly associated with the X-ray dosage rate. By fitting their slopes, the corresponding sensitivities at different electric fields were

calculated in Figure 3h. Even in self-driving mode, the sensitivities of AP<sub>2</sub>BiI<sub>7</sub> SC detector (58 μC Gy<sup>-1</sup> cm<sup>-2</sup>) exceed the commercial a-Se film detector (20 μC Gy<sup>-1</sup> cm<sup>-2</sup> @ 10 V μm<sup>-1</sup>) and OD monovalent cation BHPs of (R-PPA)<sub>2</sub>BiI<sub>5</sub> (31 μC Gy<sup>-1</sup> cm<sup>-2</sup> @ 0 V).<sup>41</sup> Sensitivities reach 1926 μC Gy<sup>-1</sup> cm<sup>-2</sup> at 500 V cm<sup>-1</sup> as the electric field gradually increased. The value exceeds that of many reported BHPs X-ray detectors (for full data, see Table S6).<sup>44</sup>

Furthermore, it should be noted that as the applied electric field increases, the dark current density also increases. For example, the dark current density under 500 V cm<sup>-1</sup> is about 37 times that at 0 V cm<sup>-1</sup>. Self-powered mode reduces dark current, allowing for a lower detection limit. By the definition set forth by the International Union of Pure and Applied Chemistry (IUPAC), the limit of detection (LoD) is defined as a signal-to-noise ratio (SNR) of 3, used to evaluate the detection performance of analytical methods.<sup>45</sup> A LoD of 100 nGy s<sup>-1</sup> at 0 V cm<sup>-1</sup> was acquired by calculating the SNR at various dose rates, as seen in Figure 3i, and then fitting the relationship between the SNR and the dose rates. In addition, LoD values were calculated for different electric field as shown in Figure S12. These values significantly reduce the risk of X-ray injury, which is lower than the conventional medical diagnostic LoD of 5.5 μGy s<sup>-1</sup>.<sup>12, 46</sup>



**Figure 4.** a) X-ray stability test of the unencapsulated AP<sub>2</sub>BiI<sub>7</sub> detectors exposed to X-ray irradiation for more than an hour of continuous operation. b) The dark current was measured. c) Initial radiation photoresponse of the AP<sub>2</sub>BiI<sub>7</sub> detector at a high dose rate of 1063 μGy s<sup>-1</sup> and 0 V cm<sup>-1</sup>, and the radiation photoresponse after three months. d) PXRD patterns of AP<sub>2</sub>BiI<sub>7</sub> powders at preparation and after three months.

The stability of equipment is another important performance indicator for its commercialization. The thermogravimetric decomposition temperature of AP<sub>2</sub>BiI<sub>7</sub> can reach as high as 563 K, indicating its high thermal stability (Figure S13). It is common to quantify this performance in X-ray detection in terms of radiation

stability, *I<sub>drift</sub>*, and environmental stability. To evaluate the radiation stability of the device, it was subjected to prolonged, high-dose-rate X-ray irradiation (167.9 μGy s<sup>-1</sup> and 1063 μGy s<sup>-1</sup>) at 0 V cm<sup>-1</sup>. During 5100 s of continuous operation, the photocurrent of AP<sub>2</sub>BiI<sub>7</sub> remained stable with a slight decline (Figure 4a), demonstrating the



detector's exceptional operational stability in the self-driven mode. In addition, the AP<sub>2</sub>Bil<sub>7</sub> device exhibits excellent radiation stability even at 500 V cm<sup>-1</sup> (Figure S14). Further,  $I_{\text{drift}}$  can be obtained from the following equation:<sup>47</sup>

$$I_{\text{drift}} = \frac{(J_t - J_0)}{Et} (6)$$

where  $J_0$  and  $J_t$  are the dark current density at the subsequent and initial times, respectively, while  $E$  represents the electric field. As is depicted in Figure 4b, the AP<sub>2</sub>Bil<sub>7</sub> SC detector not only obtains a markedly stable dark current at 0 V cm<sup>-1</sup> but also demonstrates an  $I_{\text{drift}}$  value of  $3.8 \times 10^{-7}$  nA cm<sup>-1</sup> s<sup>-1</sup> V<sup>-1</sup> for the AP<sub>2</sub>Bil<sub>7</sub> SC device even under 500 V cm<sup>-1</sup>. The value is considerably lower than that of previously reported BHPs X-ray devices (Table S6).<sup>48</sup> This contrast again emphasizes the stability advantage of aromatic diamine structures. Finally, the stability in resisting ambient air of the device was investigated. As shown in Figure 4c, after 90 days at a temperature of  $(24 \pm 2)$  °C and a humidity of  $(52 \pm 10)$  %, the unencapsulated detector maintains a very high level of operational stability, with only a slight degradation of the X-ray photoresponse (approximately reduced to 92% of the original). In addition, the unencapsulated device retained approximately 90% of its sensitivity after 90 days (Figure S15). The result demonstrates a level of environmental stability in the material system we developed. Furthermore, the AP<sub>2</sub>Bil<sub>7</sub> still maintains excellent phase stability by PXRD after three months (Figure 4d). These indicate the superior environmental stability of the AP<sub>2</sub>Bil<sub>7</sub> SC device. Such stability and exceptional self-driven X-ray detection performance exhibit the great commercial application prospect of AP<sub>2</sub>Bil<sub>7</sub> perovskite devices.

## Conclusions

In summary, a novel OD lead-free polar perovskite, AP<sub>2</sub>Bil<sub>7</sub>, was synthesized by incorporating aromatic diamine AP<sup>2+</sup> cations. High-quality SCs of AP<sub>2</sub>Bil<sub>7</sub> exhibit a lower trap density  $n_{\text{trap}}$  ( $3.77 \times 10^9$  cm<sup>-3</sup>) and a high resistivity ( $3.55 \times 10^{10}$  cm<sup>-3</sup>). Aromatic diamines AP<sup>2+</sup> with anchoring effect can effectively improve stability and charge transport behaviors. Moreover, such a polar structure thus gives them intrinsic spontaneous polarization along the polar axis direction, which further results in a strong BPVE with a photovoltage of 1.15 V under X-ray irradiation. It acts as the driving force for separating and transporting the X-ray-generated charge carriers, thereby endowing AP<sub>2</sub>Bil<sub>7</sub> with the capability for self-driven detection. By leveraging the bulk photovoltage as the driving force, the OD AP<sub>2</sub>Bil<sub>7</sub> detector exhibits a notable sensitivity of 58 μC Gy<sup>-1</sup> cm<sup>-2</sup> and a low LoD of 100 nGy s<sup>-1</sup> at 0 V cm<sup>-1</sup>. Moreover, the aromatic diamine cation through the strong anchoring effect gives AP<sub>2</sub>Bil<sub>7</sub> a stable structure, which makes AP<sub>2</sub>Bil<sub>7</sub> show a low  $I_{\text{drift}}$  of  $3.8 \times 10^{-7}$  nA cm<sup>-1</sup> s<sup>-1</sup> V<sup>-1</sup> under 500 V cm<sup>-1</sup>, as well as excellent radiative stability both under self-drive mode and applied electric field. Impressively, even after three months, the AP<sub>2</sub>Bil<sub>7</sub> shows excellent environmental stability with only a slight decrease in photoresponse. This work demonstrates the first self-driven X-ray detection in OD aromatic diamine-based BHPs, offering new insights for designing "green" and stable self-driven radiation detectors based on hybrid perovskites.

## Author contributions

H. Q. Zhong prepared the samples and wrote the manuscript. C. Qu, G. R. Chen, H. W. Yang, and Y. Wang performed the photoelectric properties. S. H. You, Z. Y. Wu, H. Ye, L. J. Xu, Y. R. Geng, H. Li, and C. S. Zhang provided suggestions for the project. Q. W. Guan and J. H. Luo designed and directed this project. All the authors discussed and commented on the manuscript. CRediT: Haiqing Zhong data curation, formal analysis, investigation, visualization, writing-original draft; Qianwen Guan writing-review & editing; Shihai You data curation, formal analysis; Zhenyue Wu data curation, formal analysis; Huang Ye data curation, formal analysis; Lijun Xu data curation; Yaru Geng data curation, formal analysis; Chengmin Ji data curation; Hang Li data curation; Chengshu Zhang data curation; Chang Qu data curation; Junhua Luo formal analysis, funding acquisition, project administration, supervision, writing-review & editing.

## Conflict of Interest

There are no conflicts to declare.

## Data availability

The data that support the findings of this study are available in the Supporting Information of this article. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2401299. These data can be obtained free of charge from [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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The data supporting this article have been included as part of the Supplementary Information. For example, additional computational details and experimental details, materials, and methods, including crystal morphology, crystal structure data, PXRD patterns, the TG curve, and basic photoelectric properties.

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