

RESEARCH ARTICLE OPEN ACCESS

Stability of $\text{PEA}_2\text{PbBr}_4$ Thin-Film Photodetectors under Thermal and Moisture StressSara Cepić¹ | Andrea Ciavatti^{1,2}  | Enrico Gianfranco Campari¹ | Beatrice Fraboni^{1,2}¹Department of Physics and Astronomy, University of Bologna, Bologna, Italy | ²INFN, Sezione di Bologna, Bologna, Italy**Correspondence:** Andrea Ciavatti (andrea.ciavatti2@unibo.it)**Received:** 24 March 2026 | **Revised:** 9 June 2026 | **Accepted:** 15 July 2026**Keywords:** environmental stability | halogen bond passivation | perovskites | photodetectors

ABSTRACT

Low-dimensional perovskite photodetectors attract significant attention due to their tunable optoelectronic properties, quantum confinement effects and solution processability. Among them, phenethylammonium lead bromide ($\text{PEA}_2\text{PbBr}_4$) is more stable than its 3D counterparts. However, degradation under environmental stress remains an obstacle to practical applications, particularly with prolonged exposure to temperature and humidity. This study systematically evaluates the impact of these stressors on the morphology, crystallinity, and optoelectronic performance of $\text{PEA}_2\text{PbBr}_4$ photodetectors. The impact of the halogen-bonding additive 1,4-TFIB (1,4-diiodotetrafluorobenzene) on the stability of the devices is also considered. Here, the devices were subjected to an increase in temperature (20°C–120°C) and humidity (40%RH–98%RH) in five steps, with each condition maintained for two days. Morphological and structural analyses are performed, as well as optoelectronic analyses under UV light and X-ray irradiation. The results show that, while pristine films undergo significant physical degradation and material loss at elevated temperature and humidity, the incorporation of 1,4-TFIB significantly enhances material endurance. Although the additive reduces the photocurrent signal of the device under UV and X-ray irradiation, it mitigates physical loss of the material and maintains structural integrity in harsh conditions, thereby enhancing device longevity in optoelectronic sensing applications.

1 | Introduction

Low-dimensional hybrid perovskites are promising materials for optoelectronic applications due to their high absorption coefficients, excellent charge carrier mobility, large carrier diffusion lengths, and high photoelectric conversion efficiency and low-cost solution processability at low temperatures [1–3]. Their structures can be finely tuned using chemical modifications, allowing for bandgap engineering and multifunctionality [4]. Thanks to these advantages, perovskites have emerged as a major research focus for various applications, such as solar cells [5, 6], high-efficiency radiation photodetectors [7, 8], personal dosimeters and medical devices [9, 10], space applications [11, 12], light-emitting diodes (LEDs)

[13], low-power transistors [14] and many others. However, ensuring their stability and durability under diverse environmental conditions remains a critical challenge, limiting their commercialization.

Compared to traditional metal halide perovskites, characterized by an isotropic crystalline structure over three dimensions (so-called 3D perovskites), low-dimensional halide perovskites could offer enhanced environmental stability, greater hydrophobicity, and superior resistance to temperature- and light-induced degradation. These advantages arise because 2D layered perovskites incorporate hydrophobic organic spacer layers that block moisture, while their reduced dimensionality provides natural encapsulation and improved surface passivation. In

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *Advanced Electronic Materials* published by Wiley-VCH GmbH

addition, compositional engineering (e.g., incorporation of Cs⁺ or FA⁺ cations) can further enhance their intrinsic stability [15, 16]. They consist of 2D sheets composed of corner-sharing [MX₆] octahedra, where M²⁺ is usually Pb or another metal cation, and X⁻ is a halide anion. Connected through electrostatic forces to octahedral [MX₆] units are large-sized organic cations [17], which contribute to their hydrophobic nature and moisture resistance [18, 19]. Despite these advantages, excessive moisture can still degrade lead halide perovskites, either by initiating perovskite decomposition into precursor salts or by forming hydrated phases that disrupt device performance [20, 21]. In contrast, small amounts of water can facilitate perovskite crystallization, improving film quality and device performance [22–26].

Another major factor affecting perovskite stability is thermal degradation. This challenge is particularly critical for practical applications in solar cells or other electronic sensing, as degradation processes typically begin close to about 85°C, a temperature commonly reached during the day under full sunlight or in the space environment under direct sun AM0 exposure [27, 28]. Moreover, humidity accelerates thermal decomposition, exacerbating material instability [29].

Several strategies have been explored to improve perovskite durability under environmental stress. These include encapsulation techniques [30], compositional engineering like doping [31] or incorporation of additives for surface and grain boundaries passivation [32, 33], or environmental control during the fabrication process [34]. Encapsulation is effective in isolating the material from external agents such as oxygen and moisture. However, it increases fabrication complexity and cost, specifically for flexible or large-area devices. Additionally, encapsulation layers can introduce optical absorption, signal losses, and increase device thickness or mass [35, 36]. Encapsulated devices may also experience internal mechanical stress during thermal cycling due to the mismatch between the relatively high thermal expansion coefficients of perovskites and those of typical encapsulation materials. Compositional engineering, including cation substitution or the formation of mixed-dimensional structures, can enhance intrinsic stability, but it often modifies the electronic structure and bandgap of the material [36]. Furthermore, it frequently introduces lattice strain, phase segregation, and carrier recombination centers, increasing overall carrier losses [37–39]. Additive-based passivation has emerged as a versatile approach to reduce defect density, yet many commonly used additives rely on relatively weak interactions, such as hydrogen bonding or electrostatic interactions.

In this work, we couple the intrinsic stability of low-dimensional perovskite with the employment of a halogen bond (XB) as a passivation strategy to bind free ions on the perovskite surface, potentially enhancing its stability. XB is a noncovalent electrostatic interaction between the electropositive region of a halogen atom (the sigma hole) and a nucleophilic site, such as a lone pair of a Lewis base or π -electrons. This highly directional interaction allows precise molecular engineering and controlled self-assembly by selecting an appropriate halogen atom [40]. Additionally, fluorine atoms, frequently present in XB donor molecules, enhance material hydrophobicity and increase bond strength, improving resistance to moisture degradation

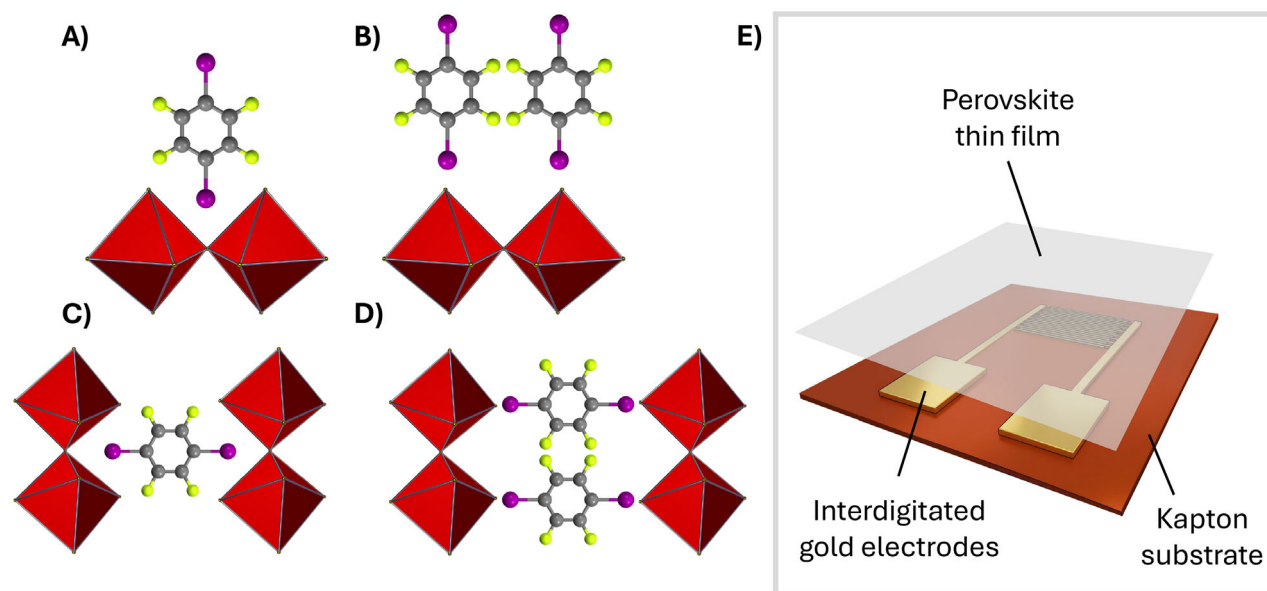
[41]. Moreover, XB has been shown to enhance charge transport by lowering the HOMO-LUMO gap due to the presence of halogen atoms [42–44]. Previous research on XB-mediated surface passivation has yielded promising results, suggesting its potential for improving perovskite stability [40, 45–48]. This approach represents a surface-level chemical treatment that differs fundamentally from bulk compositional modification or encapsulation. Rather than altering the crystal lattice or introducing a thick physical barrier, XB exploits supramolecular interactions to selectively target and neutralize surface defects without inducing additional mechanical stress. A landmark study by Abate et al. demonstrated that supramolecular halogen-bond complexation effectively passivates undercoordinated halide defects, enabling solar cells to maintain stable power output under continuous operation [49]. Recent progress has shown that XB interactions can form supramolecular networks at the perovskite surface and grain boundaries, reducing defect density and limiting moisture ingress. Devices incorporating fluorinated XB donors exhibit improved environmental stability, with reduced performance degradation under prolonged humidity exposure and extended operational lifetimes compared to non-passivated counterparts. Such approaches aim to provide intrinsic stabilization of the perovskite lattice by addressing degradation pathways that persist even in encapsulated devices [49, 50].

While standard perovskite degradation, like methylammonium lead iodide (MAPbI₃) films, under humidity and thermal stress has been extensively studied for solar cell applications [51–54], the assessment of phenethylammonium lead bromide (PEA₂PbBr₄) thin-film photodetectors under similar conditions remains less explored, even if low-dimensional lead halide perovskites are becoming widely used as an interlayer in solar cells [16, 55, 56] as well as in UV-vis and ionizing radiation sensing [9, 57, 58]. Furthermore, most XB studies have focused on 3D perovskites in photovoltaic applications [59], while investigations on photodetectors and sensing devices, particularly those based on 2D perovskites, remain limited. This is a critical gap, as photodetectors operate under fundamentally different conditions compared to solar cells, involving continuous electrical bias and, in the case of ionizing radiation detection, exposure to high-energy photons that can accelerate defect formation and material degradation. In addition, due to the required low dark current noise in photodetectors, their device performance is highly sensitive to trap states, making defect passivation and long-term stability even more crucial. The literature comparison between different strategies for mitigating environmental impact is summarized in Table S1.

This study systematically investigates XB passivation in 2D layered thin-film photodetectors under thermal and humidity stress. It provides insights into the degradation mechanisms of 2D lead-halide perovskite PEA₂PbBr₄, evaluates device stability under extreme humidity conditions up to 98% RH, exceeding typical laboratory testing ranges, and directly compares the impact of environmental stress on UV responsivity and morphology. Furthermore, by correlating optoelectronic performance with morphological and structural evolution, we identify the onset of irreversible degradation in pristine films and demonstrate the role of XB in mitigating material loss and enhancing device robustness.

TABLE 1 | Short names of the investigated samples and corresponding recipe descriptions.

Short name	Perovskite solution	Antisolvent
PEA+CB	Phenethylammonium lead bromide	Chlorobenzene
PEA+CB_A	Phenethylammonium lead bromide	Chlorobenzene containing 1,4-diiodotetrafluorobenzene
PEA_A+CB	Phenethylammonium lead bromide containing 1,4-diiodotetrafluorobenzene	Chlorobenzene

**FIGURE 1** | Schematic representation of 1,4-TFIB interacting with perovskite in an asymmetric way (A,B) or symmetric (cross-linking) (C,D), attacking two binding sites, a cation vacancy (A,C) or halide anions (B,D). Schematic representation of the device with patterned electrodes (E).

2 | Results and Discussion

PEA₂PbBr₄ thin films were fabricated by spin-coating onto interdigitated metal electrodes deposited on a flexible plastic substrate, as described in detail in the Experimental Section. Three different deposition recipes were investigated across three batches (of 3 samples each) for each recipe, labeled PEA+CB, PEA+CB_A and PEA_A+CB, respectively. A summary of the three compositions and short name labels used throughout this manuscript can be found in Table 1. The first batch was used for the humidity-stress study, the second for the temperature-stress study, and the third served as the reference batch.

The PEA+CB recipe consists of a consolidated PEA₂PbBr₄ solution (see Experimental methods) with the addition of chlorobenzene as an antisolvent during deposition to enhance crystallization [60]. The other two recipes incorporate the XB donor 1,4-diiodotetrafluorobenzene (1,4-TFIB), either dissolved in the antisolvent (PEA+CB_A) or directly in the PEA₂PbBr₄ solution (PEA_A+CB). The XB donor (1,4-TFIB) is expected to interact with the perovskite structure through XB, targeting electron-rich halide anions or monovalent cation (A-site) vacancies. Researchers have studied various configurations for how XB donors bind, particularly using bifunctional modulators like 1,4-TFIB. The envisaged modes of XB donor interaction with the

perovskite surface are classified based on their symmetry and the binding site, as shown in Figure 1A–D. The asymmetric mode involves XB donor binding to the A-site vacancy (Figure 1A) or halide anion (Figure 1B) on the perovskite surface. The two sites on the bifunctional modulator are chemically distinct. The symmetric mode (or cross-linking) involves the bifunctional XB donor linking two sites in a configuration that maintains chemical equivalence between the reactive groups on the modulator. It can bridge two A-site vacancies (Figure 1C) or two halide anions (Figure 1D). Bifunctional modulators, which are capable of halogen bonding on two sites, have shown promise as structure-directing agents. We expect that 1,4-TFIB forms an ordered self-assembled monolayer at the perovskite surface, where the iodine atoms engage in XB with surface halides or vacancies. This interaction can strengthen surface passivation, reduce defect density, and enhance hydrophobicity, as previously reported [61]. The schematic representation of the device structure is shown in Figure 1E.

The study was conducted using a Binder climatic chamber to precisely control the environmental conditions. The experimental procedure consisted of three sets of experiments. In the first, the temperature was kept constant at 20°C, while relative humidity (RH) was increased every 48 h, starting from 40%RH and progressing through 60%RH, 70%RH, 80%RH,

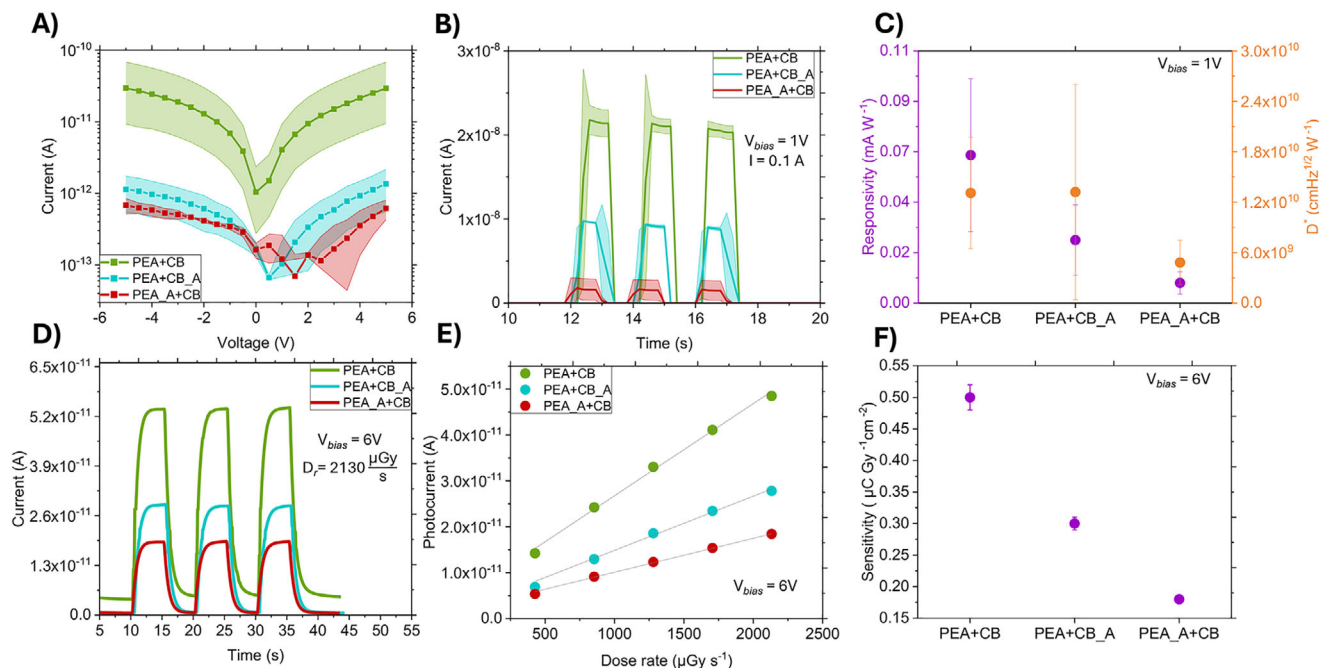


FIGURE 2 | Electrical characterization of the devices of the three recipes at 20°C and 40%RH. Dark current vs. voltage, where the shaded area represents the variability of the samples (A). Photocurrent dynamic signal for three ON/OFF cycles of UV-LED ($\lambda = 385$ nm, 100 mA) with 1 V of applied bias at room conditions. The shaded area represents variability in samples (three samples for each recipe) (B). Responsivity and specific detectivity of the samples for three different recipes measured under UV-LED ($\lambda = 385$ nm, 100 mA) with 1 V of applied bias, for each sample measured at room conditions (C). Dynamic response at a dose rate of $2130 \mu\text{Gy s}^{-1}$ for three different samples (D). Photocurrent dependence on dose rate (E), and sensitivity (F) to X-ray irradiation (40 kVp, $D_r = 2130 \mu\text{Gy s}^{-1}$) for each sample measured at room conditions.

90%RH, and 98%RH. In the second study, the humidity was held constant at 40%RH, representative of standard indoor conditions, while the temperature was increased every 48 h, covering the range of 20°C, 40°C, 60°C, 80°C, 95°C, and 120°C. Electrical parameters, resistivity in the dark, and responsivity under UV light, at standard room conditions, were evaluated at every step. A third set of measurements has been performed on a reference batch, which was kept constantly at 20°C and 40%RH for the same amount of time. Each study lasted 12 days.

To establish a baseline for comparison, the performance of the samples before any treatment was characterized under X-ray and UV-LED exposure, allowing for a direct assessment of sensitivity and responsivity across the three different formulations. Figure 2 presents the results for the three deposition recipes under the initial conditions (20°C and 40% RH), prior to any temperature or humidity treatment. Figure 2A shows the dark current–voltage (I – V) characteristics, where curves represent the average current values obtained from samples of two independent batches. The results clearly indicate that incorporating the XB donor leads to a reduction in conductivity, as evidenced by the lower dark current values ($\sim 10^{-12}$ A) and an increase in sheet resistance ($\sim 8 \times 10^{15} \Omega$) compared to those of the PEA+CB devices without any additive (with dark current value 4×10^{-11} A and sheet resistance $\sim 3.2 \times 10^{14}$).

To evaluate responsivity, devices were irradiated using a UV-LED ($\lambda = 385$ nm) operated at 100 mA in three ON/OFF cycles. The LED was placed 3 cm above the samples. A 1 V bias voltage was

applied to collect the photogenerated charges. Responsivity was calculated using the following formula:

$$R = \frac{I_{ph}}{E \cdot A}$$

where I_{ph} is the photocurrent (i.e., $I_{ph} = I_{LED\ ON} - I_{dark}$), E is the irradiance (5.36 mW cm^{-2}) of the LED, and A is the active area of the device (0.04 cm^2). The specific detectivity (D^*) was then obtained using:

$$D^* = \frac{R}{\sqrt{2eJ_{dark}}}$$

where J_{dark} is the dark current density under a 1 V bias, and e is the elementary charge. Figure 2B shows the typical dynamic response to UV light ON/OFF cycles for the three formulations. Averaged responsivity and specific detectivity values for each recipe across two batches are shown in Figure 2C.

Sheet resistance ($\rho_{\square}$) was calculated using the formula:

$$\rho_{\square} = \frac{R \cdot W}{L}$$

where R is the Resistance extracted from the slope of the linear I – V response, W is the length of the finger multiplied by the number of fingers, and L is the channel length ($30 \mu\text{m}$).

For X-ray testing, the devices were irradiated using a tungsten-target X-ray tube operating at 40 kVp. The tube current was

varied from 100 to 500 μA , corresponding to a dose rate range of 430–2130 $\mu\text{Gy s}^{-1}$. Samples were positioned 30 cm from the source. A 6 V bias voltage was applied across the devices to enable charge collection, generating a measurable photocurrent upon X-ray exposure. Each sample was subjected to three ON/OFF cycles at five different dose rates. Photocurrent was calculated as:

$$I_{\text{XR-ph}} = I_{\text{XR ON}} - I_{\text{dark}}$$

Figure 2D presents the dynamic response to X-ray ON/OFF cycles for the three formulations. A linear relationship between dose rate and photocurrent was observed, as illustrated in Figure 2E. The slope of the linear fit represents the device sensitivity. By normalizing this sensitivity to the device's active area (0.04 cm^2), sensitivity per unit area was obtained and is reported in Figure 2F.

The pristine PEA+CB samples exhibited the highest responsivity values among all tested configurations, comparable to expected values under similar bias and irradiance conditions [8]. Notably, the recipe with the additive directly dissolved in the solutions (PEA_A+CB) has the lowest responsivity and the lowest specific detectivity. Further, the X-ray sensitivity follows the same trend of responsivity under UV light for all the recipes. This behavior was expected, as both UV and X-ray detection in these devices rely on the same fundamental charge transport and collection principles, although the primary carrier generation mechanisms differing (non-ionizing optical excitation versus ionizing radiation).

2.1 | Stability under Increased Humidity

The results from the humidity stress study, the first experiment, are reported in Figure 3. Dark current–voltage (I - V) and responsivity measurements were performed at standard environmental conditions, after two days of exposure to each stress: at 20°C and for six different relative humidity (RH) conditions. Figure 3A displays the I - V characteristics in the dark for the pristine PEA+CB samples across varying humidity levels. A clear trend is observed: as humidity increases, the sample's conductivity increases until 98%RH, where a notable drop in conductivity occurs.

Figure 3B shows the relationship between sheet resistance and relative humidity for all the recipes. Sheet resistance increases for the samples with additives. For all additive recipes, an increase in resistivity up to 60%RH, followed by a decrease with further %RH content, is observed. The non-additive sample shows a constant, gradual decrease in sheet resistance value with %RH.

The dynamic response of the typical PEA+CB samples to LED ON/OFF cycles across different humidity levels is shown in Figure 3C. The photocurrent increases with humidity, peaking before sharply declining at 98%RH. Responsivity for all recipes is plotted as a function of humidity in Figure 3D. While the pristine PEA+CB exhibits the highest responsivity overall, it shows a marked drop at the highest humidity level. In contrast, the recipes containing XB additives appear more stable under extreme moisture conditions, maintaining or gradually increasing responsivity throughout exposure up to 98%RH. Calculated absolute deviation for the PEA+CB sample is 8.8×10^{-3} while for the sample with the

additive, this value is reduced by 45% across the humidity range (4.8×10^{-3}).

The progressive decrease in sheet resistance of PEA+CB with increasing relative humidity (Figure 3B, green) is attributed to water-assisted ion migration. At moderate humidity, water molecule adsorption through grain boundaries and defect sites facilitates halide ion mobility, leading to increased ionic conductivity without immediate structural degradation [62]. At 98% RH, both the partial recovery in sheet resistance (Figure 3B) and the sharp drop in responsivity (Figure 3D) indicate a transition from reversible hydration to irreversible degradation. At near-saturation humidity, water penetration leads to the formation of hydrated intermediate phases, which are poorly conductive and optically inactive [62, 63]. The apparent increase in sheet resistance is therefore attributed to material degradation and loss of conductive pathways, rather than recovery of the pristine structure. This interpretation is supported by optical microscopy and AFM (Figures 5B and 6), which show clear evidence of grain dissolution and morphological redistribution after exposure to 98% RH. In contrast, XB-treated samples (PEA+CB_A and PEA_A+CB) exhibit a significantly attenuated response to humidity. The smaller variation in sheet resistance and the absence of responsivity loss at 98% RH indicate that moisture-induced degradation is effectively suppressed. This behavior is attributed to halogen bonding at grain boundaries, which passivates defect sites and limits water interaction, thereby reducing ion migration and preventing the dissolution–recrystallization processes observed in pristine films.

2.2 | Stability under Increased Temperature

The results from the temperature stress study, the second experiment, are shown in Figure 4. Under thermal stress, pristine PEA+CB films exhibit a continuous decrease in both dark current and photocurrent (Figure 4A,C), indicating progressive degradation. This behavior is consistent with thermally induced material loss and structural disruption, as supported by macroscopic observations (Figure S4A) and XRD analysis showing an increased relative contribution from the Kapton substrate (Figure 7B). The reduction in active material directly decreases the effective charge generation and transport pathways, resulting in degraded device performance.

In contrast, PEA+CB_A maintains nearly constant responsivity across the 20–95°C range, while pristine PEA+CB shows a significant decline ($\sim 51\%$, Figure 4D). The reduced variation in performance (83% lower standard deviation) indicates enhanced thermal stability. This improvement is attributed to XB passivation, where directional interactions between iodine atoms in 1,4-TFIB and surface Br^- ions reduce defect formation and suppress ion migration under thermal activation. As a result, charge transport pathways remain more stable. Supporting this interpretation, white-light interferometry (Figure S4A) shows a substantially smaller increase in surface roughness for XB-treated films (38%) compared to pristine films (138%), indicating reduced thermally induced morphological degradation.

For PEA_A+CB (additive incorporated in the precursor solution), the continuous increase in sheet resistance with temperature

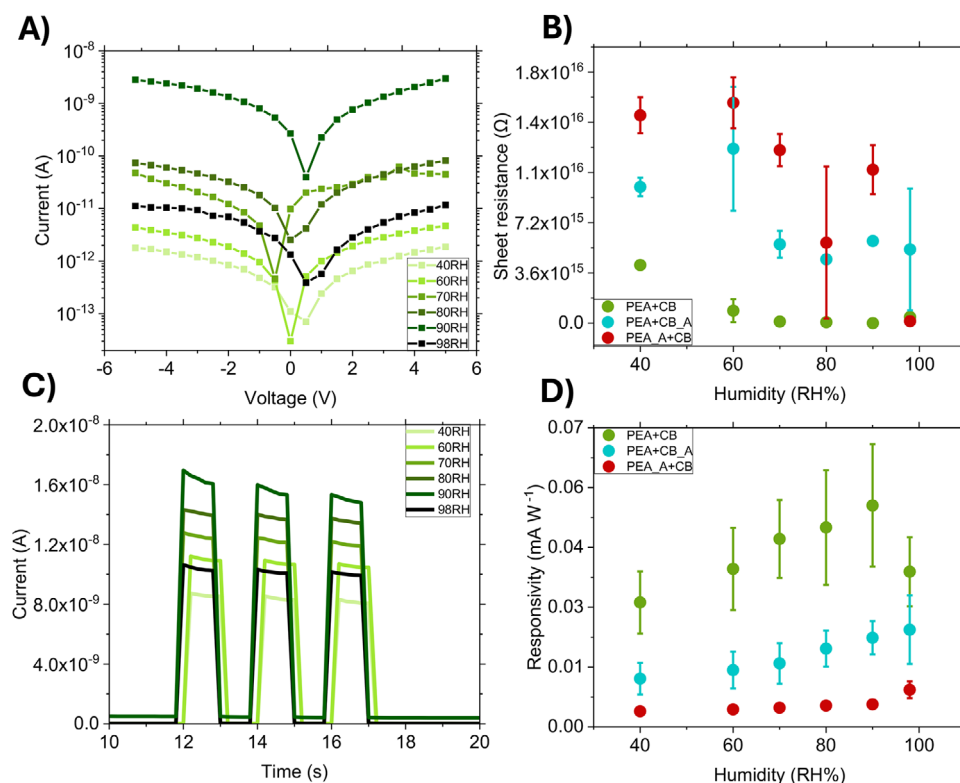


FIGURE 3 | Humidity stress effects: Dark Current variation as a function of humidity for pristine PEA₂PbBr₄ (PEA+CB) samples (A). UV LED response variation as a function of humidity for pristine PEA₂PbBr₄ (PEA+CB) samples (C). Sheet resistance (B) and responsivity (D) variations as a function of relative humidity for all 3 types of tested samples (green: pristine sample—PEA+CB, cyan: recipe with additive dissolved in antisolvent—PEA+CB_A, red: recipe with additive dissolved in perovskite solution—PEA_A+CB).

(Figure 4B, red) suggests that bulk incorporation of 1,4-TFIB disrupts charge transport. This likely arises from structural disorder or increased scattering within the lattice. The differing behavior compared to PEA+CB_A samples highlights that effective passivation is achieved when the XB donor is localized at grain boundaries and surfaces, rather than distributed throughout the bulk.

Full *I*-*V* characteristics for all three sample types, along with their responses under UV-LED exposure, are presented in the Supplementary Information (Figures S1 and S2).

To better explain the opto-electronic behavior, the morphologies of the films are analyzed. Figure 5A,B illustrates the effects of increasing temperature and humidity on the standard PEA+CB sample and on the most promising additive-based sample, PEA+CB_A, respectively. A concerning observation is the significant degradation of the active material, which visibly disappears from the substrate under environmental stress. For temperature stress, this deterioration becomes evident after just three days (i.e., two days at 20°C and two at 60°C), as shown in Figure S3.

Morphological transformations under thermal stress suggest recrystallization of the material into distinct crystal morphologies—round and needle-shaped structures (Figure 5A). While the additives did not prevent degradation at 120°C, a noticeable enhancement in thermal endurance is observed up to 80°C. The difference in surface roughness between 20°C and 80°C was quantified using white-light interferometry (Figure S4).

The film without additive (PEA+CB) exhibited a 138% increase in roughness, whereas the sample containing the additive in the antisolvent (PEA+CB_A) showed only a 38% change. Enhanced resistance to humidity-induced degradation is also evident for the additive-containing films, as shown in Figure 5B.

The AFM analysis (Figure 6) reveals significant differences in degradation behavior between pristine and XB-treated samples after humidity exposure. For the PEA+CB films, the original elongated grain morphology is largely lost, with clear evidence of grain dissolution and recrystallization into more irregular, squared crystallites. This morphological evolution is accompanied by a substantial increase in surface roughness, increasing by approximately 56% compared to the initial condition, indicating severe surface degradation and material redistribution. In contrast, the XB-treated PEA+CB_A films exhibit a more preserved grain structure, with more clearly defined grain shapes and recognizable boundaries. The increase in surface roughness is significantly smaller (approximately 29%), indicating improved structural stability. Although degradation is still present, it appears more localized at the grain level, rather than resulting in large-scale morphological disruption. Roughness values were obtained from measurements on three samples for each recipe. These observations are further supported by crystallite size estimates obtained from the Scherrer equation using the (001) diffraction peak. For the pristine PEA+CB sample, the calculated crystallite size decreases from 64.07 nm to 22.51 nm after humidity treatment, consistent with a reduction in coherent crystalline domain size caused by structural degradation. In contrast, the

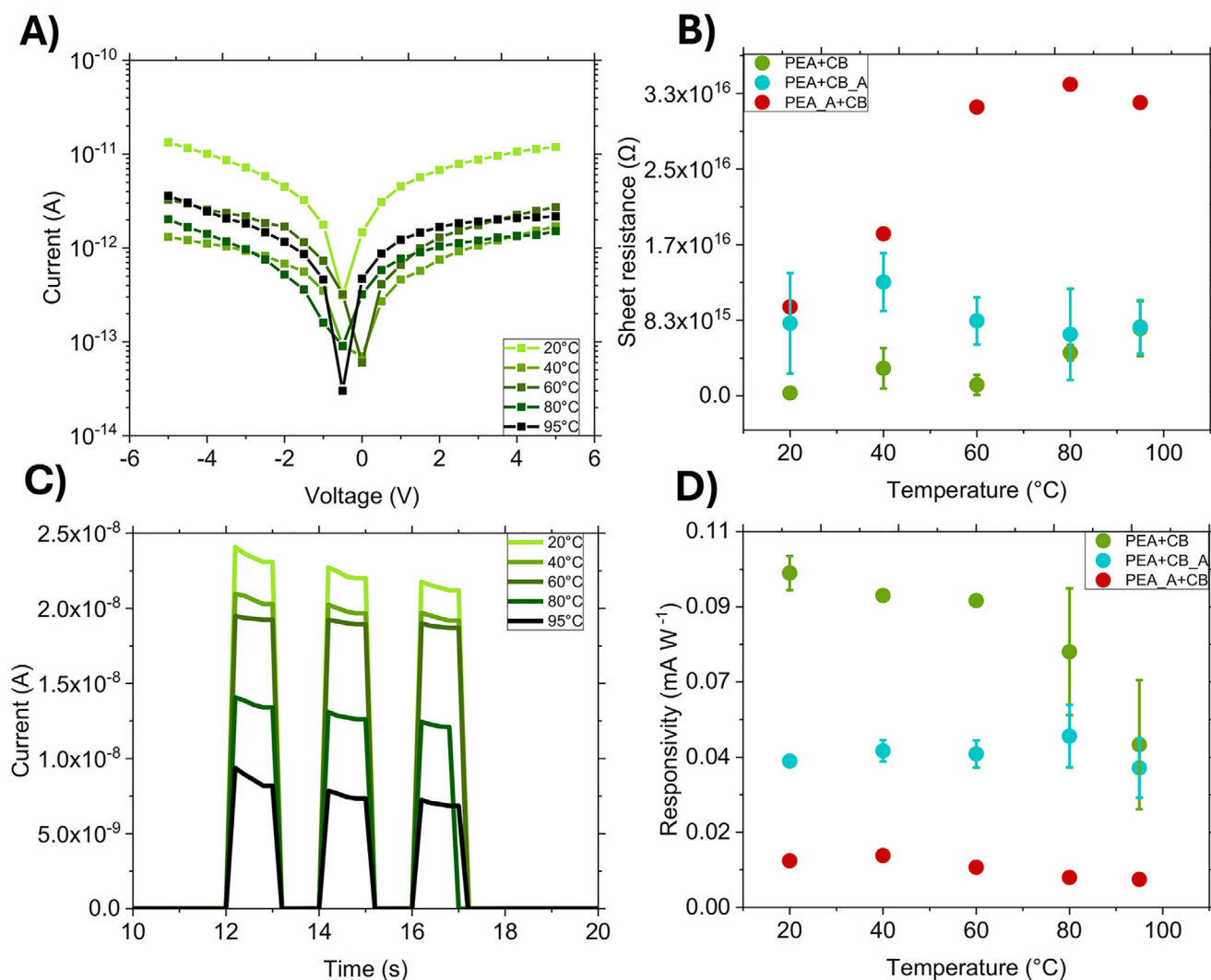


FIGURE 4 | Temperature stress effects: Dark Current variation as a function of temperature for pristine $\text{PEA}_2\text{PbBr}_4$ (PEA+CB) samples (A). UV LED response variation as a function of temperature for pristine $\text{PEA}_2\text{PbBr}_4$ (PEA+CB) samples (C). Sheet resistance (B) and responsivity (D) variations as a function of temperature for all 3 types of tested samples (green: pristine sample—PEA+CB, cyan: recipe with additive dissolved in antisolvent—PEA+CB_A, red: recipe with additive dissolved in perovskite solution—PEA_A+CB).

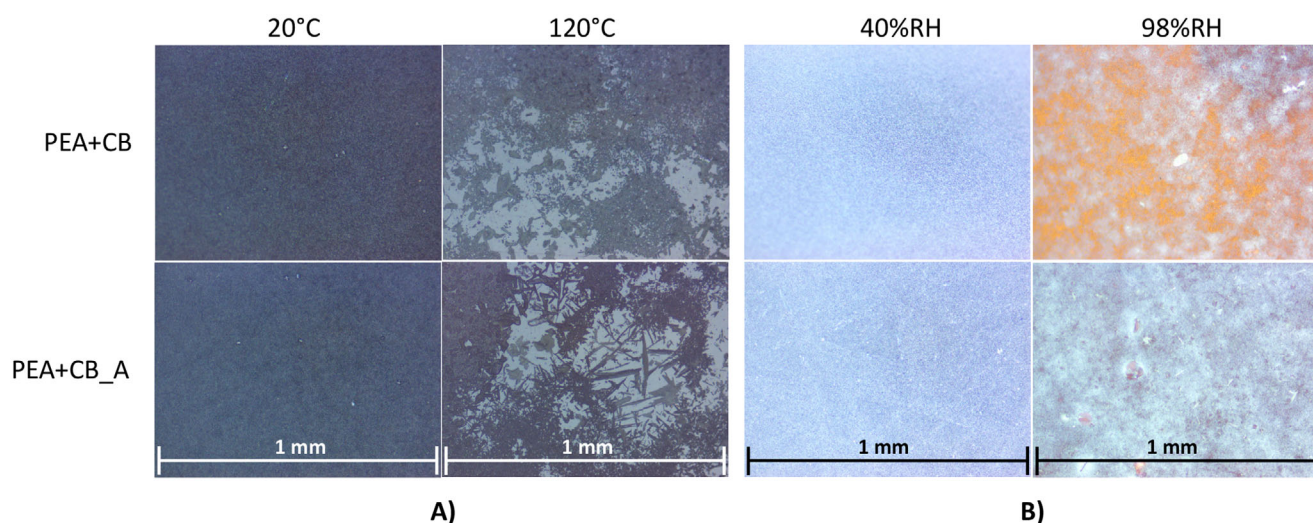


FIGURE 5 | Optical microscopy images in reflection mode, showing the morphological changes in samples fabricated with different recipes exposed to temperature (A) and humidity (B) treatment.

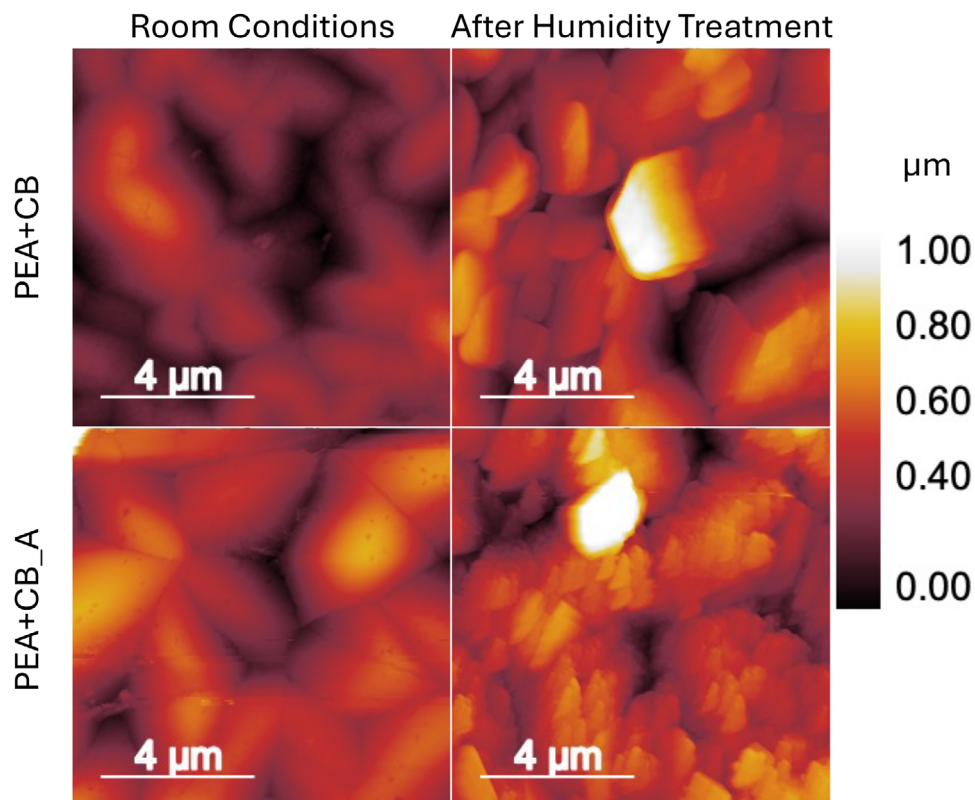


FIGURE 6 | AFM images of film morphology for pristine (PEA+CB) and XB-treated (PEA+CB_A) samples, comparing the initial state at room conditions with the morphology after humidity treatment. The color scale represents the relative surface height (μm), with darker colors corresponding to lower topographical regions and lighter colors corresponding to higher surface features.

calculated crystallite size for the XB-treated sample increases from 85.97 to 211.02 nm after humidity exposure. Since the AFM images do not show a corresponding increase in lateral grain dimensions, this result likely reflects an increase in coherent domain size along the out-of-plane direction associated with the (001) reflection, rather than physical grain growth. The preservation of grain boundaries observed by AFM suggests that the layered structure remains largely intact and that degradation is primarily localized near the film surface, sheltering the bulk and bottom interfaces connected to the collection electrodes. It should be noted that Scherrer analysis should be considered a relative indicator of structural changes rather than an absolute measure of grain size.

For the temperature stress case, both film types undergo extensive degradation, leading to large height variations and partial material loss. Under these conditions, reliable roughness quantification was not feasible, and high-quality AFM imaging could not be consistently obtained.

The degradation of halide perovskites under humidity typically proceeds through the following pathways. In 2D perovskites, the hydrophobic organic spacer (such as PEA in $\text{PEA}_2\text{PbBr}_4$) initially hinders water penetration by forming a van der Waals barrier between inorganic layers, which contributes to their enhanced stability compared to 3D systems. However, at high humidity levels, water molecules can penetrate through grain boundaries and surface defects. Then, the water interacts with undercoordinated Pb^{2+} sites and forms hydrogen bonds with halide

ions and organic cations, leading to the formation of hydrated intermediate phases and ultimately to irreversible decomposition into PbBr_2 and organic salts, as widely reported in the literature [21, 62–64]. At intermediate humidity levels, adsorbed water molecules partially solvate halide ions and lower the activation energy for ion migration, resulting in increased ionic conductivity and a corresponding decrease in sheet resistance. However, when the humidity approaches saturation, water penetration becomes sufficient to induce the formation of hydrated intermediate phases and initiate dissolution of the perovskite grains. These processes are consistent with the experimentally observed increase in conductivity at intermediate humidity and the subsequent performance loss at high RH, visible in Figure 3.

The incorporation of 1,4-TFIB addresses these degradation pathways at the molecular level through halogen bonding interactions. The electrophilic σ -hole on the iodine atoms forms directional noncovalent interactions with electron-rich halide ions or vacancy sites at the perovskite surface and grain boundaries. This results in effective passivation of defect sites, reducing trap-assisted recombination and limiting the accumulation of charge that can trigger degradation reactions [45]. In addition, the fluorinated nature of the XB donor introduces local hydrophobicity, which reduces moisture adsorption and slows water ingress into the film. XB interactions also contribute to stabilizing halide ions, thereby increasing the energetic barrier for ion migration and suppressing thermally activated degradation processes [65–67]. As a result, XB passivation acts simultaneously on

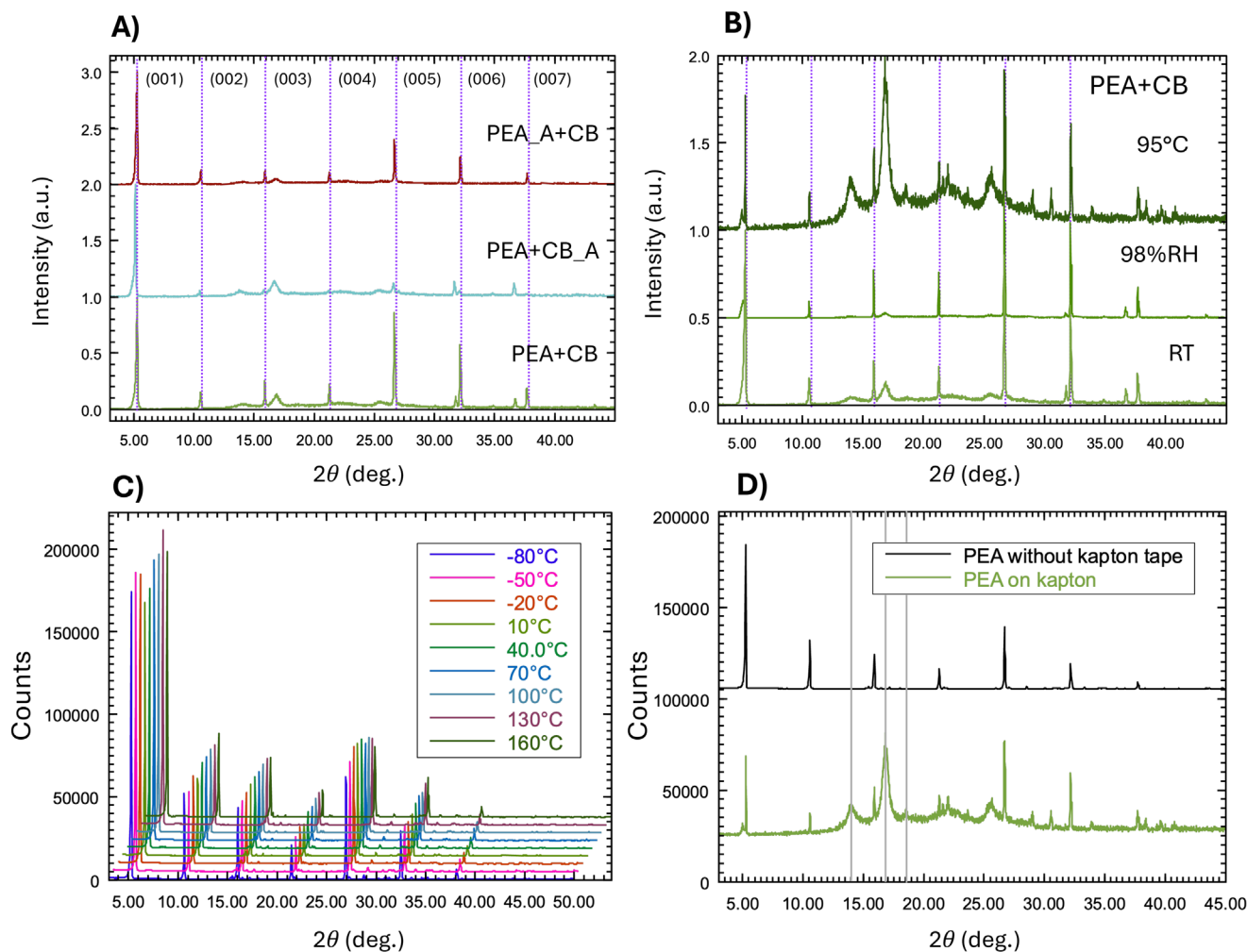


FIGURE 7 | X-ray diffraction (XRD) patterns for three samples with different fabrication recipes at room conditions (A). X-ray diffraction (XRD) patterns for the pristine PEA+CB sample in the room condition, after humidity treatment, and after temperature treatment (B). Temperature-dependent XRD patterns for PEA₂PbBr₄ measured over the range from -80°C to 160°C (C). Comparison of XRD patterns acquired with and without a Kapton substrate beneath the material (D). The intensities in panels (A) and (B) are normalized, and the diffractograms are vertically offset for clarity.

multiple degradation pathways, including defect passivation, moisture resistance, and ionic stabilization. Importantly, XB interactions are sufficiently robust to persist under the harsh conditions explored in this work. Halogen bond strengths for iodinated perfluoroarenes typically lie in the range of tens of kJ/mol [68], comparable to or exceeding many hydrogen bonds, while benefiting from high directionality. Fluorination enhances the σ -hole on iodine, strengthening the interaction and reducing competition from water molecules. Previous studies have shown that XB interactions remain effective in polar and even aqueous environments [69, 70], and can stabilize interfaces under thermal stress. Moreover, because XB is a reversible, non-covalent interaction, it can dynamically reform if temporarily disrupted by thermal fluctuations, contributing to sustained passivation over time. While a direct calorimetric measurement of the binding energy is beyond the scope of this study, the observed stability enhancement is quantitatively consistent with established XB-mediated suppression of ion migration and defect activity reported in similar halide perovskite systems. Finally, the AFM results presented in Figure 6 provide indirect experimental support for these mechanisms. The significantly reduced roughness

increase and better preservation of grain morphology in XB-treated films indicate suppressed dissolution–recrystallization processes and reduced mass transport under humidity stress, confirming the stabilizing effect of XB at the grain boundaries.

Figure 7A presents the X-Ray diffraction (XRD) patterns of the three film recipes measured at 20°C and 40% RH. The diffractograms show that all samples exhibit reflections characteristic of the layered perovskite phase PEA₂PbBr₄, with major peaks at $2\theta = 5.12^{\circ}, 10.64^{\circ}, 15.88^{\circ}, 21.25^{\circ}, 26.73^{\circ}, 32.23^{\circ}$, and 37.70° , corresponding to the (001)–(007) planes, respectively [71]. Additional reflections originating from the Kapton substrate are observed at $2\theta = 14.01^{\circ}, 16.83^{\circ}, 18.58^{\circ}$, and 25.53° [72]. Purple dashed lines represent the pattern calculated from the reported crystal structure, which shows a good correlation with our experimental peak positions (FoM = 0.998). Among the three recipes, PEA_A+CB samples exhibit the sharpest and most intense diffraction peaks, suggesting a higher degree of crystallinity and larger coherent domain size compared with the other films. In contrast, PEA+CB_A samples show broader and less intense peaks, indicative of smaller crystalline domains or

TABLE 2 | Averaged values for thickness, roughness, dark current, resistivity, and responsivity for the samples that went through humidity treatment.

		PEA+CB	PEA+CB_A	PEA_A+CB
Thickness [μm]		2.33 ± 0.69	2.27 ± 0.49	2.04 ± 0.26
Roughness Sq [μm]		0.38 ± 0.03	0.78 ± 0.10	0.75 ± 0.20
Dark current at -5 V [A]	40%RH	$(-2.6 \pm 0.1) \times 10^{-12}$	$(-1.3 \pm 1.9) \times 10^{-12}$	$(-1.1 \pm 0.1) \times 10^{-12}$
	60%RH	$(-8.3 \pm 7.8) \times 10^{-11}$	$(-1.1 \pm 0.3) \times 10^{-12}$	$(-8.5 \pm 1.0) \times 10^{-13}$
	70%RH	$(-2.4 \pm 1.9) \times 10^{-10}$	$(-1.9 \pm 0.8) \times 10^{-12}$	$(-1.3 \pm 0.2) \times 10^{-12}$
	80%RH	$(-2.0 \pm 0.1) \times 10^{-10}$	$(-3.1 \pm 1.0) \times 10^{-12}$	$(-3.8 \pm 3.5) \times 10^{-11}$
	90%RH	$(-5.4 \pm 1.4) \times 10^{-9}$	$(-2.8 \pm 0.6) \times 10^{-12}$	$(-1.9 \pm 0.1) \times 10^{-12}$
	98%RH	$(-4.6 \pm 3.1) \times 10^{-11}$	$(-1.7 \pm 0.2) \times 10^{-12}$	$(-1.2 \pm 0.4) \times 10^{-10}$
Sheet resistance [Ω]	40%RH	$(4.2 \pm 0.1) \times 10^{15}$	$(1.0 \pm 0.7) \times 10^{16}$	$(1.5 \pm 0.1) \times 10^{16}$
	60%RH	$(9.0 \pm 8.3) \times 10^{14}$	$(1.3 \pm 0.4) \times 10^{16}$	$(1.6 \pm 0.2) \times 10^{16}$
	70%RH	$(1.1 \pm 0.8) \times 10^{14}$	$(5.7 \pm 1.0) \times 10^{15}$	$(1.2 \pm 0.1) \times 10^{16}$
	80%RH	$(7.0 \pm 3.2) \times 10^{13}$	$(4.6 \pm 0.1) \times 10^{15}$	$(5.8 \pm 5.5) \times 10^{15}$
	90%RH	$(2.4 \pm 0.3) \times 10^{12}$	$(5.9 \pm 0.2) \times 10^{15}$	$(1.1 \pm 0.2) \times 10^{16}$
	98%RH	$(4.4 \pm 2.5) \times 10^{14}$	$(5.3 \pm 4.4) \times 10^{15}$	$(1.4 \pm 0.5) \times 10^{14}$
Responsivity [$\mu\text{A W}^{-1}$]	40%RH	31 ± 8	12 ± 3	4 ± 1
	60%RH	40 ± 10	14 ± 5	4 ± 1
	70%RH	47 ± 10	16 ± 5	5 ± 1
	80%RH	50 ± 14	20 ± 5	5 ± 1
	90%RH	56 ± 15	22 ± 4	6 ± 1
	98%RH	39 ± 9	24 ± 9	9 ± 2

increased structural disorder. PEA+CB and PEA_A+CB samples display comparable crystallinity, with only minor variations in relative peak intensities. The similar positions of the main diffraction peaks across all recipes indicate that the underlying crystal structure remains consistent, as expected when the additives predominantly influence the film surface while the XRD measurement primarily probes the bulk.

As shown in Figure 7B, neither thermal nor humidity stress treatments introduce significant structural changes, confirming the phase stability of $\text{PEA}_2\text{PbBr}_4$ under these conditions. This conclusion is further supported by temperature-dependent XRD measurements (Figure 7C), performed between -80°C and 160°C , which reveal no evidence of phase transitions. However, films subjected to thermal treatment exhibit increased intensity of the Kapton-related peaks and a corresponding decrease in the perovskite reflections. The apparent increase in the relative intensity of the Kapton-related broad feature after environmental stress is attributed to degradation-induced loss of perovskite material. As the perovskite layer partially dissolves, redistributes, or detaches from the substrate during prolonged humidity or thermal exposure, the diffracting volume of the crystalline perovskite decreases. Consequently, the contribution of the underlying

Kapton substrate becomes more pronounced in the measured diffraction pattern. This interpretation is consistent with the optical microscopy and white-light interferometry observations, which show significant material redistribution and surface degradation after environmental stress.

The Kapton-derived features are highlighted in Figure 7D. Comparative diffractograms for the remaining recipes are provided in the Supporting Information (Figure S5).

Tables 2 and 3 summarize all observed figures of merit. Sample thickness and surface roughness were measured using white light interferometry, with profiles provided in Figure S4. Reported values represent averages from multiple samples of each recipe exposed to identical conditions, ensuring statistical relevance.

Figure 8 presents the change in specific detectivity under UV irradiation, expressed as the metric $(D^*_{\text{max}} - D^*_{\text{min}})/D^*_{\text{avg}}$, to quantify the stability and fluctuations of the devices. The values are shown for all three formulations across the reference, humidity-treated, and temperature-treated batches. Error bars present the coefficient of variance for each group. As expected, the reference samples exhibit the smallest variation.

TABLE 3 | Averaged values for thickness, roughness, dark current, resistivity, and responsivity for the samples that went through temperature treatment.

		PEA+CB	PEA+CB_A	PEA_A+CB
Thickness [μm]		1.66 ± 0.24	2.22 ± 0.26	3.55 ± 0.59
Roughness Sq [μm]		0.65 ± 0.05	0.73 ± 0.07	0.53 ± 0.05
Dark current at -5 V [A]	20°C	$(-6.4 \pm 5.9) \times 10^{-11}$	$(-2.2 \pm 1.7) \times 10^{-12}$	$(-1.2 \pm 0.1) \times 10^{-12}$
	40°C	$(-6.8 \pm 9.8) \times 10^{-11}$	$(-1.3 \pm 0.8) \times 10^{-12}$	$(-6.3 \pm 0.1) \times 10^{-13}$
	60°C	$(-2.3 \pm 2.6) \times 10^{-11}$	$(-1.6 \pm 0.5) \times 10^{-12}$	$(-2.0 \pm 0.1) \times 10^{-13}$
	80°C	$(-2.0 \pm 0.1) \times 10^{-12}$	$(-2.7 \pm 1.3) \times 10^{-12}$	$(-3.6 \pm 0.1) \times 10^{-13}$
	95°C	$(-2.1 \pm 1.2) \times 10^{-12}$	$(-2.1 \pm 0.9) \times 10^{-12}$	$(-3.4 \pm 0.1) \times 10^{-13}$
Sheet resistance [Ω]	20°C	$(3.2 \pm 3.2) \times 10^{14}$	$(8.0 \pm 5.5) \times 10^{15}$	$(9.8 \pm 0.5) \times 10^{15}$
	40°C	$(3.0 \pm 2.2) \times 10^{15}$	$(1.3 \pm 0.3) \times 10^{16}$	$(1.8 \pm 0.1) \times 10^{16}$
	60°C	$(1.2 \pm 1.1) \times 10^{15}$	$(8.2 \pm 2.6) \times 10^{15}$	$(3.2 \pm 0.2) \times 10^{16}$
	80°C	$(4.7 \pm 0.9) \times 10^{15}$	$(6.8 \pm 5.0) \times 10^{15}$	$(3.4 \pm 0.2) \times 10^{16}$
	95°C	$(7.4 \pm 3.0) \times 10^{15}$	$(7.6 \pm 3.0) \times 10^{15}$	$(3.2 \pm 0.2) \times 10^{16}$
Responsivity [$\mu\text{A W}^{-1}$]	20°C	98 ± 5	43 ± 1	14 ± 0.1
	40°C	91 ± 1	46 ± 3	15 ± 0.2
	60°C	90 ± 1	45 ± 4	12 ± 0.2
	80°C	75 ± 19	50 ± 10	8.8 ± 0.2
	95°C	48 ± 19	41 ± 10	8.2 ± 0.2

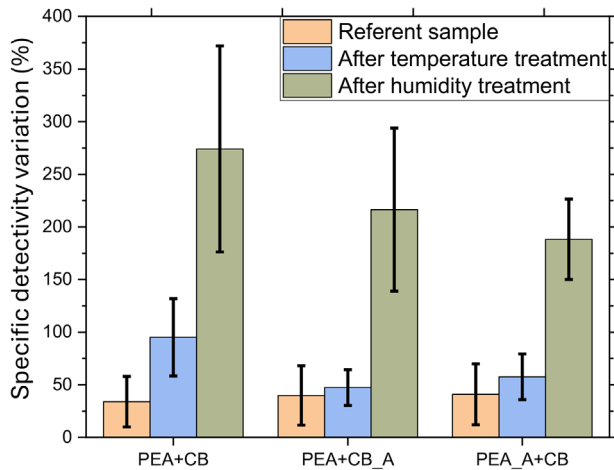


FIGURE 8 | Comparison of variations in specific detectivity under UV irradiation for reference samples (one sample per recipe) and samples after temperature (average of samples from the first batch) and humidity (average of samples from the second batch) stress treatments.

3 | Conclusion

In this study, we investigated the impact of humidity and temperature on the performance and morphology of 2D perovskite $\text{PEA}_2\text{PbBr}_4$ thin-film photodetectors. The collected data suggest

that the degradation in photocurrent and dark current, particularly at elevated temperatures and prolonged exposure to high relative humidity, is due to the physical degradation and loss of the active material.

As observed in previous studies, low humidity levels can enhance crystallization and improve the performance of perovskite films. While $\text{PEA}_2\text{PbBr}_4$ shows good resistance to humidity in moderate conditions, temperature-induced degradation becomes evident within two days at 60°C. In addition to performance loss, powder X-ray diffraction analysis confirmed structural changes.

The incorporation of 1,4-TFIB, an XB donor, was found to enhance the material's resistance to humidity, effectively preventing the perovskite layer from physically disappearing. However, this additive also resulted in a decrease in photocurrent, sensitivity, and responsivity, suggesting that its integration into the perovskite matrix may introduce structural defects that negatively impact device performance. Overall, the surface passivation through the inclusion of an XB additive in the antisolvent (PEA+CB_A) has been demonstrated to offer the best balance between performance and stability to humidity and temperature stressing agents. Such stability studies are particularly important for assessing the potential applicability of these materials in harsh operating environments, such as space technologies, where devices face extreme temperature fluctuations, and solar cell

applications, where combined thermal and moisture stress often exceeds 85°C.

Further work should explore varying the additive concentrations to avoid excess XB incorporation into the crystal lattice, which lowers electronic performance. This would help to balance stability and functionality.

4 | Experimental Methods

4.1 | Device Fabrication

Equimolar amounts of $C_6H_5C_2H_4NH_3Br$ (PEABr, Sigma-Aldrich > 98%) and $PbBr_2$ (Sigma-Aldrich > 98%) were dissolved in *N,N*-dimethylformamide (DMF, Sigma-Aldrich 99.8% anhydrous) to prepare 1 M and 0.7 M solutions. The solution was stirred overnight to ensure complete dissolution of the precursors. Before the deposition, Kapton substrates (75 μm) were ultrasonicated with acetone, IPA, and water (for 10 min each). After that, they were dried under a nitrogen blow. A Cr/Au (6.2 ± 3.2 nm Cr and 32.6 ± 11.3 nm Au) interdigitated electrode pattern was fabricated on a substrate using photolithography. S1818 positive photoresist was employed, and the electrodes were deposited via evaporation. The area of the electrodes was 4 mm². Post-lift-off, the Cr/Au patterns were sonicated in water (for 10 min) and then cleaned with air plasma (for 5 min) before perovskite deposition. The perovskite material was deposited by spin-coating at 2000 rpm (for 60 s), with the addition of antisolvent chlorobenzene C_6H_5Cl (Merck > 99.5%) in the last 10 s. After the deposition, samples are annealed at 50°C (for 10 min). As an additive, XB donor $C_6F_4I_2$ (1,2,4,5-Tetrafluoro-3,6-diiodobenzene, Sigma-Aldrich 98%) is used with PEA_2PbBr_4 in a stoichiometric ratio of 1:1, dissolved either in chlorobenzene or PEA_2PbBr_4 solution.

4.2 | Electrical Characterization

I–*V* characteristics were obtained using a Keithley 6517A electrometer. All the electrical measurements were carried out in a probe station at lab atmosphere.

The dynamic response under UV, LED with wavelength 385 nm, is used, powered by a Keithley 2614B precision Source/Measure Unit driven in current mode at 0.1 A. Measurements were conducted outside the climatic chamber. Samples were temporarily removed for a few hours to perform the necessary measurements and then returned to the chamber

4.3 | X-Ray Irradiation

Electrical response under X-ray irradiation was acquired by a Keithley 6517A electrometer. The fabricated devices were placed in a Faraday box with an aluminum window for the X-ray measurement. The radiation source was a Hamamatsu L12161 Microfocus X-ray tube with a W target used at 40 kVp accelerating voltages and filament currents ranging from 100 μA to 500 μA . A lead mechanical shutter was employed to control the ON/OFF

beam switching. The dose rates were previously calibrated by a Barracuda radiation detector (RTI Group).

4.4 | X-Ray Diffraction

X-ray diffraction (XRD) measurements were performed using a Malvern Panalytical Empyrean diffractometer operating in Bragg–Brentano geometry (reflection mode) over a 2θ range of 3° to 50°. The diffractometer was equipped with a scintillation detector and a monochromator. Data acquisition followed a θ – 2θ scan method using Cu $K\alpha$ radiation with a weighted average wavelength of 1.5406 Å ($K\alpha_1 = 1.5406$ Å, $K\alpha_2 = 1.5445$ Å, intensity ratio $K\alpha_1 : K\alpha_2 = 2 : 1$).

Temperature-dependent measurements were carried out using an Anton Paar TTK 600 chamber, enabling precise thermal control from –80°C to 160°C, maintained in an air atmosphere and cooled with liquid nitrogen.

4.5 | Atomic Force Microscopy

The surface morphology and grain structure of the perovskite films were characterized using a NX-10 Atomic Force Microscope (Park Systems, South Korea). All measurements were performed in Non-Contact Mode (NCM) using an NCHR cantilever (Nanosensors) with a nominal resonance frequency of ~320 kHz and force constant of 42 N/m. Images were acquired with a resolution of 256 × 256 pixels. Topographic data were processed and analyzed using the Gwyddion software package.

Acknowledgements

S.C. acknowledges the funding by the EU—NextGenerationEU with funds made available by the National Recovery and Resilience Plan (NRRP) Mission 4, Component 2, Investment 3.1 “IR ETIC” project (CUP: I53C21000420006). A.C. and B.F. acknowledge funding from INFN through the CSN5 “PROVIDE” experiment. A.C. and B.F. acknowledge funding from the European Union - NextGenerationEU under the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 3.1 | Project Code: IR0000027 - CUP: B33C22000710006 - iENTRANCE@ENL: Infrastructure for Energy TRAnSition aNd Circular Economy @ EuroNanoLab.

Open access publishing facilitated by Universita di Bologna, as part of the Wiley - CRUI-CARE agreement.

Funding

The study was supported by the Italian Ministry (PNRR) under the project IR ETIC (CUP: I53C21000420006). Italian Ministry - PNRR under the project iENTRANCE@ENL CUP B33C22000710006.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. H. J. Snaith, "Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells," *The Journal of Physical Chemistry Letters* 4, no. 21 (2013): 3623–3630, <https://doi.org/10.1021/jz4020162>.
2. S. D. Stranks, G. E. Eperon, G. Grancini, et al., "Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber," *Science* (1979) 342, no. 6156 (2013): 341–344, <https://doi.org/10.1126/science.1243982>.
3. S. De Wolf, J. Holovsky, S. J. Moon, et al., "Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance," *Journal of Physical Chemistry Letters* 5, no. 6 (2014): 1035–1039, <https://doi.org/10.1021/jz500279b>.
4. R. J. Sutton, G. E. Eperon, L. Miranda, et al., "Bandgap-Tunable Cesium Lead Halide Perovskites With High Thermal Stability for Efficient Solar Cells," *Advanced Energy Materials* 6, no. 8 (2016): 1502458, <https://doi.org/10.1002/aenm.201502458>.
5. F. Zhang, D. H. Kim, and K. Zhu, "3D/2D multidimensional Perovskites: Balance of High Performance and Stability for Perovskite Solar Cells," *Current Opinion in Electrochemistry* 11 (2018): 105–113, <https://doi.org/10.1016/j.coelec.2018.10.001>.
6. A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells," *Journal of the American Chemical Society* 131, no. 17 (2009): 6050–6051, <https://doi.org/10.1021/ja809598r>.
7. X. Hu, X. Zhang, L. Liang, et al., "High-Performance Flexible Broadband Photodetector Based on Organolead Halide Perovskite," *Advanced Functional Materials* 24, no. 46 (2014): 7373–7380, <https://doi.org/10.1002/adfm.201402020>.
8. F. Lédée, A. Ciavatti, M. Verdi, L. Basiricò, and B. Fraboni, "Ultra-Stable and Robust Response to X-Rays in 2D Layered Perovskite Microcrystalline Films Directly Deposited on Flexible Substrate," *Advanced Optical Materials* 10, no. 1 (2022): 2101145, <https://doi.org/10.1002/adom.202101145>.
9. I. Fratelli, L. Basiricò, A. Ciavatti, et al., "Real-Time Radiation Beam Monitoring by Flexible Perovskite Thin Film Arrays," *Advanced Science* 11, no. 40 (2024): 2401124, <https://doi.org/10.1002/adv.202401124>.
10. L. Basiricò, I. Fratelli, M. Verdi, et al., "Mixed 3D–2D Perovskite Flexible Films for the Direct Detection of 5 MeV Protons," *Advanced Science* 10, no. 1 (2023): 2204815, <https://doi.org/10.1002/adv.202204815>.
11. V. Romano, A. Agresti, R. Verduci, and G. D'Angelo, "Advances in Perovskites for Photovoltaic Applications in Space," *ACS Energy Letters* 7, no. 8 (2022): 2490–2514, <https://doi.org/10.1021/acsenenergylett.2c01099>.
12. Y. Tu, J. Wu, G. Xu, et al., "Perovskite Solar Cells for Space Applications: Progress and Challenges," *Advanced Materials* 33, no. 21 (2021): 2006545, <https://doi.org/10.1002/adma.202006545>.
13. A. B. Wong, M. Lai, S. W. Eaton, et al., "Growth and Anion Exchange Conversion of $\text{CH}_3\text{NH}_3\text{PbX}_3$ Nanorod Arrays for Light-Emitting Diodes," *Nano Letters* 15, no. 8 (2015): 5519–5524, <https://doi.org/10.1021/acs.nanolett.5b02082>.
14. Y. Lin, P. Pattanasattayavong, and A. TD, "Metal-Halide Perovskite Transistors for Printed Electronics: Challenges and Opportunities," *Advanced Materials* 29, no. 46 (2017): 1702838, <https://doi.org/10.1002/adma.201702838>.
15. W. Chi and S. K. Banerjee, "Engineering Strategies for Two-Dimensional Perovskite Solar Cells," *Trends in Chemistry* 4, no. 11 (2022): 1005–1020, <https://doi.org/10.1016/j.trechm.2022.08.009>.
16. J. Zhang, X. Yang, H. Deng, et al., "Low-Dimensional Halide Perovskites and Their Advanced Optoelectronic Applications," *Nanomicro Lett* 9, no. 3 (2017): 36, <https://doi.org/10.1007/s40820-017-0137-5>.
17. E. B. Kim, M. S. Akhtar, H. S. Shin, S. Ameen, and M. K. Nazeeruddin, "A Review on Two-Dimensional (2D) and 2D-3D Multidimensional Perovskite Solar Cells: Perovskites Structures, Stability, and Photovoltaic Performances," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 48 (2021): 100405, <https://doi.org/10.1016/j.jphotochemrev.2021.100405>.
18. W. Fu, H. Liu, X. Shi, L. Zuo, X. Li, and A. K.-Y. Jen, "Tailoring the Functionality of Organic Spacer Cations for Efficient and Stable Quasi-2D Perovskite Solar Cells," *Advanced Functional Materials* 29, no. 25 (2019): 1900221, <https://doi.org/10.1002/adfm.201900221>.
19. G. Grancini and M. K. Nazeeruddin, "Dimensional Tailoring of Hybrid Perovskites for Photovoltaics," *Nature Reviews Materials* 4, no. 1 (2018): 4–22, <https://doi.org/10.1038/s41578-018-0065-0>.
20. A. M. A. Leguy, Y. Hu, M. Campoy-Quiles, et al., "Reversible Hydration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in Films, Single Crystals, and Solar Cells," *Chemistry of Materials* 27, no. 9 (2015): 3397–3407, <https://doi.org/10.1021/acs.chemmater.5b00660>.
21. J. Huang, S. Tan, P. D. Lund, and H. Zhou, "Impact of H_2O on Organic-Inorganic Hybrid Perovskite Solar Cells," *Energy & Environmental Science* 10, no. 11 (2017): 2284–2311, <https://doi.org/10.1039/C7EE01674C>.
22. A. García-Fernández, Z. Moradi, J. M. Bermúdez-García, et al., "Effect of Environmental Humidity on the Electrical Properties of Lead Halide Perovskites," *The Journal of Physical Chemistry C* 123, no. 4 (2019): 2011–2018, <https://doi.org/10.1021/acs.jpcc.8b03915>.
23. G. E. Eperon, S. N. Habisreutinger, T. Leijtens, et al., "The Importance of Moisture in Hybrid Lead Halide Perovskite Thin Film Fabrication," *ACS Nano* 9, no. 9 (2015): 9380–9393, <https://doi.org/10.1021/acsnano.5b03626>.
24. K. K. Bass, R. E. McAnally, S. Zhou, P. I. Djurovich, M. E. Thompson, and B. C. Melot, "Influence of Moisture on the Preparation, Crystal Structure, and Photophysical Properties of Organohalide Perovskites," *Chemical Communications* 50, no. 99 (2014): 15819–15822, <https://doi.org/10.1039/C4CC05231E>.
25. C. H. Chiang, M. K. Nazeeruddin, M. Grätzel, and C. G. Wu, "The Synergistic Effect of H_2O and DMF towards Stable and 20% Efficiency Inverted Perovskite Solar Cells," *Energy & Environmental Science* 10, no. 3 (2017): 808–817, <https://doi.org/10.1039/C6EE03586H>.
26. J. You, Y. (Michael) Yang, Z. Hong, et al., "Moisture Assisted Perovskite Film Growth for High Performance Solar Cells," *Applied Physics Letters* 105, no. 18 (2014): 183902, <https://doi.org/10.1063/1.4901510>.
27. Y. Han, S. Meyer, Y. Dkhissi, et al., "Degradation Observations of Encapsulated Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells at High Temperatures and Humidity NH_3PbI_3 Perovskite Solar Cells at High Temperatures and Humidity," *Journal of Materials Chemistry A* 3, no. 15 (2015): 8139–8147, <https://doi.org/10.1039/C5TA00358J>.
28. S. Bailey and R. Raffaele, "Operation of Solar Cells in a Space Environment," in *Practical Handbook of Photovoltaics* (Elsevier, 2012), 863–880, <https://doi.org/10.1016/B978-0-12-385934-1.00027-1>.
29. S. D. Stranks and H. J. Snaith, "Metal-Halide Perovskites for Photovoltaic and Light-Emitting Devices," *Nature Nanotechnology* 10, no. 5 (2015): 391–402, <https://doi.org/10.1038/nnano.2015.90>.
30. Q.-Q. Chu, Z. Sun, D. Wang, et al., "Encapsulation: The Path to Commercialization of Stable Perovskite Solar Cells," *Matter* 6, no. 11 (2023): 3838–3863, <https://doi.org/10.1016/j.matt.2023.08.016>.
31. M. Saliba, T. Matsui, J.-Y. Seo, et al., "Cesium-containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency," *Energy & Environmental Science* 9, no. 6 (2016): 1989–1997, <https://doi.org/10.1039/C5EE03874J>.
32. F. Wang, W. Geng, Y. Zhou, et al., "Phenylalkylamine Passivation of Organolead Halide Perovskites Enabling High-Efficiency and Air-Stable Photovoltaic Cells," *Advanced Materials* 28, no. 45 (2016): 9986–9992, <https://doi.org/10.1002/adma.201603062>.

33. C. Park, H. Ko, D. H. Sin, K. C. Song, and K. Cho, "Organometal Halide Perovskite Solar Cells With Improved Thermal Stability via Grain Boundary Passivation Using a Molecular Additive," *Advanced Functional Materials* 27, no. 42 (2017): 1703546, <https://doi.org/10.1002/adfm.201703546>.
34. H. Wang, F. Ye, J. Liang, et al., "Pre-annealing Treatment for High-efficiency Perovskite Solar Cells via Sequential Deposition," *Joule* 6, no. 12 (2022): 2869–2884, <https://doi.org/10.1016/j.joule.2022.10.001>.
35. Y. Wang, I. Ahmad, T. Leung, et al., "Encapsulation and Stability Testing of Perovskite Solar Cells for Real Life Applications," *ACS Materials Au* 2, no. 3 (2022): 215–236, <https://doi.org/10.1021/acsmaterialsau.1c00045>.
36. W. Kim, B. Koo, and M. J. Ko, "Perovskite Solar Cells for Extreme Environments: Tailoring Material Design and Exploring New Opportunities," *Nanomicro Lett* 18, no. 1 (2026): 329, <https://doi.org/10.1007/s40820-026-02173-0>.
37. F. P. Sabino, A. Zunger, and G. M. Dalpian, "Intrinsic Doping Limitations in Inorganic Lead Halide Perovskites," *Materials Horizons* 9, no. 2 (2022): 791–803, <https://doi.org/10.1039/D1MH01371H>.
38. L. Hu, X. Guan, T. Wan, et al., "Valence-Regulated Metal Doping of Mixed-Halide Perovskites to Modulate Phase Segregation and Solar Cell Performance," *ACS Energy Letters* 7, no. 12 (2022): 4150–4160, <https://doi.org/10.1021/acsenergylett.2c02040>.
39. L. Li, Z.-X. Yang, T. Huang, et al., "Doping-free Janus Homo Junction Solar Cell With Efficiency Exceeding 23%," *Applied Physics Letters*, no. 22 (2024): 223904, <https://doi.org/10.1063/5.0232498>.
40. P. Politzer, J. S. Murray, and T. Clark, "Halogen Bonding: An Electrostatically-Driven Highly Directional Noncovalent Interaction," *Physical Chemistry Chemical Physics* 12, no. 28 (2010): 7748, <https://doi.org/10.1039/c004189k>.
41. A. Priimagi, G. Cavallo, P. Metrangolo, and G. Resnati, "The Halogen Bond in the Design of Functional Supramolecular Materials: Recent Advances," *Accounts of Chemical Research* 46, no. 11 (2013): 2686–2695, <https://doi.org/10.1021/ar400103r>.
42. M. Chu, J.-X. Fan, S. Yang, et al., "Halogenated Tetraazapentacenes With Electron Mobility as High as $27.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in Solution-Processed n-Channel Organic Thin-Film Transistors," *Advanced Materials* 30, no. 38 (2018): 1803467, <https://doi.org/10.1002/adma.201803467>.
43. M.-P. Zhuo, Y.-C. Tao, X.-D. Wang, et al., "2D Organic Photonics: An Asymmetric Optical Waveguide in Self-Assembled Halogen-Bonded Cocrystals," *Angewandte Chemie International Edition* 57, no. 35 (2018): 11300–11304, <https://doi.org/10.1002/anie.201806149>.
44. Y. Wang, C. Zheng, W. Hao, et al., "Impact of Stoichiometry and Fluorine Atoms on the Charge Transport of Perylene- F_4 TCNQ," *The Journal of Physical Chemistry Letters* 10, no. 12 (2019): 3376–3380, <https://doi.org/10.1021/acs.jpclett.9b01299>.
45. P. Metrangolo, L. Canil, A. Abate, G. Terraneo, and G. Cavallo, "Halogen Bonding in Perovskite Solar Cells: A New Tool for Improving Solar Energy Conversion," *Angewandte Chemie International Edition* 61, no. 11 (2022): e202114793, <https://doi.org/10.1002/anie.202114793>.
46. S. Zhang, J. Cheng, H. Cao, et al., "Halogen-Bond-Mediated Inhibition of Ion Migration for Stable Sn–Pb Perovskite Solar Cells," *Chemical Communications* 61, no. 12 (2025): 2500–2503, <https://doi.org/10.1039/D4CC06741J>.
47. S. Bi, H. Wang, J. Zhou, et al., "Halogen Bonding Reduces Intrinsic Traps and Enhances Charge Mobilities in Halide Perovskite Solar Cells," *Journal of Materials Chemistry A* 7, no. 12 (2019): 6840–6848, <https://doi.org/10.1039/C8TA11835C>.
48. X. Fu, T. He, S. Zhang, et al., "Halogen-Halogen Bonds Enable Improved Long-Term Operational Stability of Mixed-Halide Perovskite Photovoltaics," *Chemistry* 7, no. 11 (2021): 3131–3143, <https://doi.org/10.1016/j.chempr.2021.08.009>.
49. A. Abate, M. Saliba, D. J. Hollman, et al., "Supramolecular Halogen Bond Passivation of Organic–Inorganic Halide Perovskite Solar Cells," *Nano Letters* 14, no. 6 (2014): 3247–3254, <https://doi.org/10.1021/nl500627x>.
50. E. Aydin, M. De Bastiani, and S. De Wolf, "Defect and Contact Passivation for Perovskite Solar Cells," *Advanced Materials*, no. 25 (2019): e1900428, <https://doi.org/10.1002/adma.201900428>.
51. Z. Zhu, V. G. Hadjiev, Y. Rong, et al., "Interaction of Organic Cation with Water Molecule in Perovskite MAPbI_3 : From Dynamic Orientational Disorder to Hydrogen Bonding," *Chemistry of Materials* 28, no. 20 (2016): 7385–7393, <https://doi.org/10.1021/acs.chemmater.6b02883>.
52. M. T. Mbumba, D. M. Malouangou, J. M. Tsiba, L. Bai, Y. Yang, and M. Guli, "Degradation Mechanism and Addressing Techniques of Thermal Instability in Halide Perovskite Solar Cells," *Solar Energy* 230 (2021): 954–978, <https://doi.org/10.1016/j.solener.2021.10.070>.
53. G. Divitini, S. Cacovich, F. Matteocci, L. Cinà, A. Di Carlo, and C. Ducati, "In Situ Observation of Heat-induced Degradation of Perovskite Solar Cells," *Nature Energy* 1, no. 2 (2016): 15012, <https://doi.org/10.1038/nenergy.2015.12>.
54. A. Alberti, I. Deretzis, G. Mannino, et al., "Revealing a Discontinuity in the Degradation Behavior of $\text{CH}_3\text{NH}_3 \text{PbI}_3$ During Thermal Operation," *The Journal of Physical Chemistry C* 121, no. 25 (2017): 13577–13585, <https://doi.org/10.1021/acs.jpcc.7b04196>.
55. C. Ma, D. Shen, B. Huang, et al., "High Performance Low-Dimensional Perovskite Solar Cells Based on a One Dimensional Lead Iodide Perovskite," *Journal of Materials Chemistry A* 7, no. 15 (2019): 8811–8817, <https://doi.org/10.1039/C9TA01859J>.
56. J. Chen, Y. Yang, H. Dong, et al., "Highly Efficient and Stable Perovskite Solar Cells Enabled by Low-Dimensional Perovskitoids," *Science Advances* 8, no. 4 (2022): eabk2722, <https://doi.org/10.1126/sciadv.abk2722>.
57. I. Fratelli, F. Pino, L. Basiricò, et al., "Fast Neutron Detector Based on Hybrid 2D Perovskite Thin Films," *Advanced Functional Materials* 35, no. 46 (2025): 2502530, <https://doi.org/10.1002/adfm.202502530>.
58. A. Ciavatti, V. Foderà, G. Armaroli, et al., "Radiation Hardness and Defects Activity in $\text{PEA}_2 \text{PbBr}_4$ Single Crystals," *Advanced Functional Materials* 34, no. 46 (2024): 2405291, <https://doi.org/10.1002/adfm.202405291>.
59. J. N. Lukić, W. Luo, S. Kim, et al., "Interfacial Halogen Bonding with Charge-Transport Layers for Operational Stability of Hybrid Perovskite Solar Cells," *Energy Advances* 4, no. 12 (2025): 1432–1437, <https://doi.org/10.1039/D5YA00166H>.
60. M. Konstantakou, D. Perganti, P. Falaras, and T. Stergiopoulos, "Anti-Solvent Crystallization Strategies for Highly Efficient Perovskite Solar Cells," *Crystals* 7, no. 10 (2017): 291, <https://doi.org/10.3390/cryst7100291>.
61. M. L. Ball, J. V. Milić, and Y. L. Loo, "The Emerging Role of Halogen Bonding in Hybrid Perovskite Photovoltaics," *Chemistry of Materials* 34, no. 6 (2022): 2495–2502, <https://doi.org/10.1021/acs.chemmater.1c03117>.
62. J. Cao, X. Zhang, Y. Miao, et al., "Interactions Between H_2O and Lead Halide Perovskites: Recent Progress and Applications," *Matter* 7, no. 11 (2024): 3728–3755, <https://doi.org/10.1016/j.matt.2024.08.001>.
63. J. Zhuang, J. Wang, and F. Yan, "Review on Chemical Stability of Lead Halide Perovskite Solar Cells," *Nanomicro Lett* 15, no. 1 (2023): 84, <https://doi.org/10.1007/s40820-023-01046-0>.
64. R. Wang, M. Mujahid, Y. Duan, Z. Wang, J. Xue, and Y. Yang, "A Review of Perovskites Solar Cell Stability," *Advanced Functional Materials* 29, no. 47 (2019): 1808843, <https://doi.org/10.1002/adfm.201808843>.
65. M. Yusoff AbdR bin, M. Vasilopoulou, D. G. Georgiadou, L. C. Palilis, A. Abate, and M. K. Nazeeruddin, "Passivation and Process Engineering Approaches of Halide Perovskite Films for High Efficiency and Stability Perovskite Solar Cells," *Energy & Environmental Science* 14, no. 5 (2021): 2906–2953, <https://doi.org/10.1039/D1EE00062D>.
66. F. Wang, S. Bai, W. Tress, A. Hagfeldt, and F. Gao, "Defects Engineering for High-Performance Perovskite Solar Cells," *npj Flexible Electronics* 2, no. 1 (2018): 22, <https://doi.org/10.1038/s41528-018-0035-z>.
67. L. K. Ono, S. (Frank) Liu, and Y. Qi, "Reducing Detrimental Defects for High-Performance Metal Halide Perovskite Solar Cells," *Angewandte*

Chemie International Edition 59, no. 17 (2020): 6676–6698, <https://doi.org/10.1002/anie.201905521>.

68. G. Cavallo, P. Metrangolo, R. Milani, et al., “The Halogen Bond,” *Chemical Reviews* 116, no. 4 (2016): 2478–2601, <https://doi.org/10.1021/acs.chemrev.5b00484>.

69. M. J. Langton, C. J. Serpell, and P. D. Beer, “Anion Recognition in Water: Recent Advances From a Supramolecular and Macromolecular Perspective,” *Angewandte Chemie International Edition* 55, no. 6 (2016): 1974–1987, <https://doi.org/10.1002/anie.201506589>.

70. R. Hein and P. D. Beer, “Halogen Bonding and Chalcogen Bonding Mediated Sensing,” *Chemical Science* 13, no. 24 (2022): 7098–7125, <https://doi.org/10.1039/D2SC01800D>.

71. B. Yang, X. Ouyang, X. Zhao, et al., “Inch-Sized 2D Perovskite Single-Crystal Scintillators for High-Resolution Neutron and X-ray Imaging,” *InfoMat* 7, no. 4 (2025): 12648, <https://doi.org/10.1002/inf2.12648>.

72. C. Wei, Z. Guo, H. Wang, S. Zhang, D. Hao, and J. Huang, “Recent Progress of Gas Sensors Based on Perovskites,” *Materials Horizons* 12, no. 2 (2025): 317–342, <https://doi.org/10.1039/D4MH01306A>.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: aelm70505-sup-0001-SuppMat.docx.