

Article

Concentration-Dependent Precursor Engineering with Butylammonium Acetate for Inverted Triple-Cation Perovskite Solar Cells

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Abstract

Butylammonium acetate (BAAc) was investigated as a concentration-dependent precursor additive for inverted triple-cation perovskite solar cells based on $\text{FA}_{0.80}\text{Cs}_{0.07}\text{MA}_{0.13}\text{PbI}_{2.64}\text{Br}_{0.39}$. BAAc loadings ranging from 0 to 7 mol% were systematically compared to determine how moderate and excessive additive concentrations influence film formation, defect behavior, and device operation. At 3 mol% BAAc, the mean equivalent-circle grain diameter increased from 0.508 to 0.719 μm , and the median increased from 0.495 to 0.688 μm , while cross-sectional SEM confirmed a comparable absorber thickness of 500 ± 20 nm across the series. The PbI_2 -to-perovskite diffraction peak height ratio decreased from 0.2691 to 0.0427, and the intensity-weighted photoluminescence lifetime increased from 230.2 to 350.0 ns. Light-intensity-dependent open-circuit voltage, impedance spectroscopy, thermal admittance spectroscopy, and space-charge-limited current measurements consistently indicated reduced trap-assisted recombination and transport loss at this concentration. In the EIS analysis, BAAc-3 showed the lowest transport resistance ($222.17 \pm 9.52 \Omega$) and the highest recombination resistance ($8.211 \pm 0.061 \text{ k}\Omega$); all principal resistance parameters had relative standard errors below 10%, although systematic high-frequency residuals limit quantitative interpretation of the transport CPE. The champion BAAc-3 device reached 23.37% efficiency, compared with 20.42% for the control, and the 50-device mean increased from $19.63 \pm 0.45\%$ to $22.77 \pm 0.30\%$. At 7 mol%, the morphological and electrical trends reversed and the champion efficiency decreased to 19.34%, which defines an over-treatment boundary. The 30-day dry-dark storage and 120 min maximum-power-point tests provide comparative, short-duration stability evidence. The concentration dependence is consistent with a literature-supported working model of precursor coordination and ammonium-halide interactions, without constituting direct spectroscopic identification of a specific complex.



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1. Introduction

Since the first use of an organometal-halide perovskite as a visible-light sensitizer in 2009 [1], perovskite solar cells (PSCs) have developed rapidly as solution-processed thin-film photovoltaics [2]. Perovskite absorbers are part of a wider photovoltaic materials landscape that includes crystalline silicon wafers, oxide ceramic photoelectrodes and

transport layers, and III–V semiconductor nanowire heterostructures [3–6]. Silicon remains the dominant commercial platform, whereas oxide and nanostructured semiconductor systems provide complementary routes to chemical robustness, light management, and band-structure engineering. Against this background, metal-halide perovskites are distinguished by low-temperature solution processing and compositionally tunable optoelectronic properties, although their defect-sensitive crystallization remains a central limitation. Compositional engineering has been central to this progress. Mixed formamidinium (FA), methylammonium (MA), and cesium (Cs) A-site compositions improve phase stability and processing reproducibility compared to many single-cation absorbers [7]. The inverted p–i–n architecture is attractive for its low-temperature fabrication, compatibility with tandem integration, and low current–voltage hysteresis. Buried-interface molecular hybrids, interfacial bond-strength regulation, and coordinated bulk/surface defect control have recently produced efficient inverted devices with improved operational robustness [8–11].

The photovoltaic performance of mixed-cation, mixed-halide perovskites remains sensitive to film-formation kinetics and the resulting defect landscape. Energy-level offsets and recombination at the perovskite/charge transport layer interfaces can dominate the open-circuit-voltage loss [12]. Grain boundaries provide ion-migration pathways [13], while undercoordinated Pb^{2+} , halide vacancies, residual precursor phases, strain, and compositional heterogeneity create nonradiative recombination sites and accelerate degradation [14]. Stability data also require a clear definition of illumination, temperature, atmosphere, encapsulation, electrical bias, and test duration, as specified by the ISOS consensus framework [15].

Precursor-intermediate control offers a direct route to address these limitations. Hydrogen-bond-bridged intermediates can regulate nucleation and crystallization [16], the homogenization of out-of-plane cation distributions can suppress local compositional fluctuations [17], and the bidirectional control of nucleation and crystal growth can improve crystallinity and interfacial contact [18]. These studies show that the coordination environment before and during antisolvent extraction determines the final grain structure and defect distribution.

Ionic liquids and related protic organic salts are useful precursor modifiers because their cations and anions can be varied independently. Ionic-liquid additives have extended the stability of planar PSCs [19], and polymeric room-temperature molten salts have provided simultaneous crystallization regulation and defect passivation in inverted devices [20]. Ionic-liquid solvent engineering [21], pseudo-halide-mediated strain regulation [22], rational ionic-liquid solvent design [23], and protic ionic liquids for stable metal-halide perovskite colloids [24] further demonstrate the broad chemical space available for precursor control. Spectroscopic and computational analyses indicate that passivation depends on specific coordination and hydrogen-bonding interactions between the ionic species and undercoordinated lattice sites [25].

The size and structure of the organic cation therefore influence film formation. A systematic ionic-liquid comparison identified a size-dependent balance among precursor complexation, steric effects, and crystallization kinetics [26]. Alkylammonium passivators with different chain lengths also change molecular packing, steric hindrance, interfacial orientation, and charge extraction [27]. Moderate alkylammonium loading can support crystallization and defect passivation, whereas excessive loading favors organic-rich accumulation and electronically resistive low-dimensional motifs.

Acetate-based protic salts are especially relevant because acetate (Ac^-) can coordinate Pb^{2+} through its carboxylate oxygen atoms, while an alkylammonium cation can interact with I^- and Br^- through $\text{N-H} \cdots \text{X}$ hydrogen bonds. Methylammonium acetate (MAAc) has passivated defects in CsPbIBr_2 absorbers [28] and regulated crystallization in inverted

triple-cation mixed-halide devices [29]. Butylammonium acetate has also served as a multifunctional modifier in flexible PSCs [30]. The anion provides a Pb coordination site, and the alkylammonium chain controls steric demand, interfacial residence, and the risk of transport barriers.

Butylammonium acetate (BAAc) occupies an intermediate steric and hydrophobic range between MAAc and longer-chain ammonium acetates. BAAc-mediated interfacial-energy regulation has been associated with shallower grain-junction grooves and improved nanoscale cross-grain cation homogeneity in FA–Cs perovskites [31]. BAAc has also been incorporated into FAPbI₃ precursors to regulate film growth and passivate defects [32]. These reports establish the chemical relevance of BAAc and indicate that its optimum concentration depends on absorber composition, substrate interface, solvent coordination, antisolvent kinetics, and thermal history.

The FA_{0.80}Cs_{0.07}MA_{0.13}PbI_{2.64}Br_{0.39} absorber was selected as a reproducible MA/Br-containing triple-cation baseline that allows direct comparison with the previously reported MAAc strategy in an inverted device [29]. The retained MA fraction provides a defined reference for evaluating how the longer butylammonium cation changes the useful additive window, while the FA-rich composition preserves the absorption and phase-stability advantages of mixed A-site formulations. Related studies further show that antisolvent processing and the PTAA-based buried interface strongly influence crystallization and optical coupling [33,34]; these parameters were therefore kept unchanged throughout the concentration series.

The present work does not claim the first use of BAAc or a record device efficiency. Its specific contribution is the concentration-resolved identification of a beneficial window and an over-treatment boundary for BAAc in an inverted, mixed-halide triple-cation architecture. In contrast to the earlier FAPbI₃ study, six BAAc loadings are correlated with morphology, diffraction, optical decay, device-level recombination, energetic trap response, 50-device statistics, and short-term stability. The comparison with MAAc is used only as a literature benchmark. Because this study resolves the BAAc concentration window rather than screening ammonium-cation identity, no cation-size or steric superiority over MAAc is claimed.

Accordingly, Ac[−]–Pb²⁺ coordination and BA⁺–halide hydrogen bonding are treated below as a literature-supported working hypothesis. The experimental conclusions are based on the observed concentration-dependent structural, optical, electrical, and photovoltaic trends rather than on a claim that a specific coordination complex was directly identified.

Here, BAAc loadings of 0, 1, 2, 3, 5, and 7 mol% relative to the methylammonium content were evaluated in inverted FA_{0.80}Cs_{0.07}MA_{0.13}PbI_{2.64}Br_{0.39} devices. The samples are denoted control, BAAc-1, BAAc-2, BAAc-3, BAAc-5, and BAAc-7. Section 2 describes materials, precursor preparation, device fabrication, and characterization. Section 3.1 discusses the proposed interactions and concentration-dependent film formation; Section 3.2 analyzes optical and electrical defect indicators; and Section 3.3 presents photovoltaic statistics, EQE, and stability. Section 4 summarizes the effective concentration window, limitations, and future directions.

2. Materials and Methods

2.1. Materials and Precursor Preparation

Formamidinium iodide (FAI, 99.99%), cesium iodide (CsI, 99.99%), methylammonium bromide (MABr, 99.99%), lead (II) bromide (PbBr₂, 99.99%), and lead (II) iodide (PbI₂, 99.99%) were obtained from Advanced Electron Technology (Dongguan, China). Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ),

and 4,7-diphenyl-1,10-phenanthroline (Bphen) were obtained from Nichem Fine Technology Co., Ltd. (Taiwan, China). Polymethyl methacrylate (PMMA, 2.0–4.0 mPa s) was obtained from TCI (Tokyo, Japan). BAAC (99.5%) was supplied by Xi'an Bailete (Xi'an, China). N,N-Dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), 2-butanol, chlorobenzene, ethyl acetate, ethanol, acetone, and isopropanol were purchased from Sigma-Aldrich (Shanghai, China).

The perovskite precursor was prepared by dissolving FAI (285.5 mg), CsI (36.4 mg), MABr (29.1 mg), PbI_2 (802.1 mg), and PbBr_2 (95.42 mg) in 0.87 mL DMF and 0.13 mL NMP. The mixture contained approximately 2.00 mmol total Pb and had the molar ratios $\text{FAI}:\text{CsI}:\text{MABr}:\text{PbI}_2:\text{PbBr}_2 = 0.830:0.070:0.130:0.870:0.130$ relative to total Pb. The total Pb concentration was 2.0 M. The slight excess of organic/alkali halides was retained for all formulations. The preparation process of the battery components is detailed in Table 1.

BAAC was added at 0, 1, 2, 3, 5, and 7 mol% relative to the methylammonium content. A calibrated BAAC stock solution in DMF/NMP was used to maintain the same final precursor volume, solvent ratio, and Pb concentration across the series. BAAC was treated as a processing additive and was not included in the nominal A-site stoichiometry.

Table 1. Preparation and processing parameters used for the BAAC concentration series.

Process	Parameter	Value
Perovskite ink	Total Pb concentration/solvent	2.0 M; DMF/NMP = 0.87/0.13 (v/v)
Perovskite ink	Solute masses per 1 mL	FAI 285.5 mg; CsI 36.4 mg; MABr 29.1 mg; PbI_2 802.1 mg; PbBr_2 95.42 mg
BAAC series	Loading relative to MA	0, 1, 2, 3, 5, and 7 mol%
ITO treatment	Cleaning/activation	Water, acetone, and isopropanol; UV-ozone, 15 min
Hole-selective layer	PTAA:F4-TCNQ	PTAA 5.0 mg mL^{-1} and F4-TCNQ 0.25 mg mL^{-1} in chlorobenzene; 4000 rpm, 30 s; 100 °C, 2 min
Buried interlayer	PMMA	0.2 mg mL^{-1} in ethyl acetate; 4000 rpm, 20 s; 100 °C, 1 min
Perovskite coating	Spin/antisolvent/anneal	6000 rpm, 20 s; 300 μL 2-butanol at 5–6 s; 100 °C, 15 min
Electron-selective layer	PC_{61}BM	20 mg mL^{-1} in chlorobenzene; 2500 rpm, 20 s
Buffer layer	Bphen	0.7 mg mL^{-1} in ethanol; 6000 rpm, 20 s
Electrode	Ag	100 nm; thermal evaporation

2.2. Device Fabrication

Inverted devices were fabricated with the architecture glass/ITO/PTAA:F4-TCNQ/PMMA/perovskite/ PC_{61}BM /Bphen/Ag. Patterned ITO-coated glass substrates were sequentially ultrasonicated in deionized water, acetone, and isopropanol; dried with compressed gas; and treated with UV-ozone for 15 min. PTAA:F4-TCNQ solution, prepared by dissolving 20 mg PTAA and 1 mg F4-TCNQ in 4 mL chlorobenzene, was spin-coated at 4000 rpm for 30 s and annealed at 100 °C for 2 min. PMMA (0.2 mg mL^{-1} in ethyl acetate) was then spin-coated at 4000 rpm for 20 s and annealed at 100 °C for 1 min. The ultrathin PMMA layer was used as a fixed buried-interface modifier to improve wetting of the hydrophobic PTAA surface and suppress interfacial defect-assisted recombination [35]. The cross-sectional SEM did not resolve PMMA as a separately measurable stratum; therefore, no absolute thickness is assigned. Its solution composition and deposition conditions were

identical for all BAAC concentrations, and no concentration-dependent effect is attributed to PMMA thickness.

The perovskite precursor was dispensed onto the PTAA:F4-TCNQ/PMMA substrate and spin-coated at 6000 rpm for 20 s. During spinning, 300 μL of 2-butanol was dropped onto the wet film at 5–6 s. The films were annealed at 100 $^{\circ}\text{C}$ for 15 min. All concentration groups were processed with the same precursor volume, antisolvent volume and timing, substrate temperature, and annealing history. After cooling, PC₆₁BM (20 mg mL^{-1} in chlorobenzene) was spin-coated at 2500 rpm for 20 s, followed by Bphen (0.7 mg mL^{-1} in ethanol) at 6000 rpm for 20 s. A 100 nm Ag electrode was deposited by thermal evaporation through a shadow mask.

2.3. Characterization

Top-view and cross-sectional morphologies were examined using a field-emission scanning electron microscope (FEI Quanta FEG 250, Thermo Fisher Scientific, Shenzhen, China). The top-view micrographs were acquired at an accelerating voltage of 20 kV and a working distance of 9.0 mm, as recorded in the image metadata. For grain-size analysis, the 5 μm scale bar of each image was calibrated independently. The annotation and instrument-footer regions were excluded; the analysis region was converted to grayscale, Gaussian-smoothed, enhanced using a local ridge/gradient score, and segmented by a marker-controlled watershed procedure. Objects intersecting the analysis boundary and objects with equivalent-circle diameters below 0.18 μm or above 2.20 μm were excluded to suppress texture noise and abnormal merged regions. The projected area A of each retained grain was converted to an equivalent-circle diameter using $D = 2(A/\pi)^{1/2}$. The displayed fields yielded $n = 627, 340, 353, 278, 524$, and 393 grains for control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively. Mean $\pm$ standard deviation, median, interquartile range, and coefficient of variation were calculated from the individual grain distributions.

Crystal structure was characterized using an Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Patterns were collected over $2\theta = 5\text{--}40^{\circ}$ with a step interval of 0.02° . Peak positions, full widths at half maximum (FWHMs), integrated areas, and the PbI₂/perovskite peak height ratio were compared using the same baseline and normalization procedure. The $5\text{--}12^{\circ}$ region was examined for crystalline BA-containing reduced-dimensional phases. Considering the 0.02° acquisition interval and instrument repeatability, peak-position differences smaller than approximately 0.02° were not interpreted as lattice changes.

UV-visible absorption spectra were recorded from 400 to 900 nm using a Shimadzu UV-1780 spectrophotometer (Kyoto, Japan). The six cross-sectional SEM images show absorber thicknesses within approximately 480–520 nm; the common thickness used for optical and SCLC calculations was $500 \pm 20 \text{ nm}$. Direct-transition Tauc plots, $(\alpha h\nu)^2$ versus $h\nu$, were fitted over the steep fundamental-absorption region immediately above the onset (approximately 1.64–1.72 eV); the sub-bandgap tail and visibly curved regions were excluded. Variation in the fitting window gave an uncertainty of approximately $\pm 0.005 \text{ eV}$. Steady-state PL spectra were collected from glass/perovskite films from the air side using an OmniPL fluorescence spectrometer (Raleigh, NC, USA) under 600 nm excitation with a 1 nm spectral interval. The incident power, spot position, integration time, and collection geometry were unchanged for all samples, and the spectra were normalized to the absorbed excitation fraction obtained from the corresponding UV-visible spectrum. TRPL decays and fluorescence-lifetime maps were acquired from the same glass/perovskite configuration using a Leica TCS SP8 STED 3X confocal system (Shanghai, China) equipped with a PicoHarp 300 time-correlated single-photon-counting module and a HyD SMD detector. A 600 nm pulsed laser (pulse width $< 5 \text{ ps}$; repetition rate 2.16 MHz)

was used. The same decay model, instrument response, acquisition window, and fitting procedure were applied to all samples, and the intensity-weighted average lifetime was used for comparison.

Electrochemical impedance spectroscopy (EIS) was performed with a CHI760E electrochemical workstation (Shanghai, China) in the dark at a DC bias of 1.0 V, using a 10 mV AC perturbation over 1 MHz–0.1 Hz (61 frequency points). The complex spectra were fitted simultaneously in Z' and $-Z''$ using the common circuit $R_s + (R_{tr} || CPE_{tr}) + (R_{rec} || CPE_{rec})$, with modulus weighting by $|Z|$. The CPE impedance was defined as $Z_{CPE} = 1/[Q(j\omega)^n]$. Seven free parameters were fitted to 122 real residual components, giving 115 degrees of freedom. Parameter standard errors were obtained from the Jacobian-based asymptotic covariance matrix, and 95% confidence intervals used the corresponding t-critical value. The reduced χ^2 was calculated as $\Sigma[(\Delta Z' / |Z|)^2 + (\Delta(-Z'') / |Z|)^2] / (2N - p)$; fit quality was assessed jointly from this statistic and the frequency-dependent normalized residuals. The high-frequency branch is assigned to transport/contact response and the low-frequency branch to recombination response. Light-intensity-dependent V_{oc} measurements were carried out from 0.1 to 100 mW cm⁻² using calibrated neutral-density filters, and the ideality factor n was obtained from $V_{oc} = (nkBT/q)\ln(I) + C$. Thermal admittance spectroscopy was performed at 0 V DC bias with a 20 mV AC amplitude over 100 Hz–1 MHz.

Space-charge-limited current (SCLC) measurements were conducted in the dark using electron-only devices with the structure glass/ITO/SnO₂/perovskite/PC₆₁BM/Bphen/Ag. The trap-filled-limit voltage (V_{tFL}) was determined from the intersection of the linear fits to the ohmic and trap-filled regimes. The effective trap density was calculated using $N_t = 2\epsilon_r\epsilon_0 V_{tFL} / (qL^2)$, with $\epsilon_r = 25$ and the measured perovskite thickness $L = 500 \pm 20$ nm. These values are reported as model-dependent effective trap densities because mobile ions, contact injection, film thickness, and the selected transition point can affect the absolute SCLC result [36,37].

Photovoltaic measurements were performed under simulated AM 1.5G irradiation at 100 mW cm⁻² using a class-AAA Sirius-SS solar simulator (Zolix Instrument Co., Ltd., Beijing, China) calibrated with a certified silicon reference photodiode (ABET Technologies, Baltimore, MD, USA). J–V curves were recorded with a Keithley 2400 source meter over 0–1.2 V at 50 mV s⁻¹ in both forward and reverse directions. The metal overlap and non-reflective aperture both defined an active area of 0.09 cm². Reverse scans were used for the reported statistical and champion values after a 5 s stabilization at open circuit; The corresponding reverse- and forward-scan curves acquired under the same conditions as a hysteresis check. No light soaking or voltage pre-bias was applied before acquisition. EQE spectra were measured using a Sirius-SS source, an Omni- λ -300 monochromator (Beijing, China), and a Keithley 2400 (Shanghai, China). Device reproducibility was evaluated using 50 functional devices per composition. MPP output was tracked under continuous one-sun illumination in N₂ at 25 ± 2 °C for 120 min. Dry-dark shelf stability was measured using unencapsulated devices stored for 30 days at 25 ± 2 °C and $15 \pm 5\%$ relative humidity. These tests are described as short-duration operational and shelf-stability comparisons rather than standardized lifetime certification.

3. Results

3.1. Analysis of Crystallization Performance

Figure 1a presents a literature-supported working model for the precursor interactions. BAAC dissociates into butylammonium (BA⁺) and acetate (Ac⁻) in the polar DMF/NMP medium. Related acetate and ionic-liquid systems support Lewis-basic Ac⁻–Pb²⁺ coordination and N–H ··· I/Br interactions involving alkylammonium species [25,29,32,38]. In the present formulation, these specific interactions were not directly resolved by vibrational or

photoelectron spectroscopy; the scheme therefore illustrates chemically plausible precursor associations rather than an experimentally identified coordination complex.

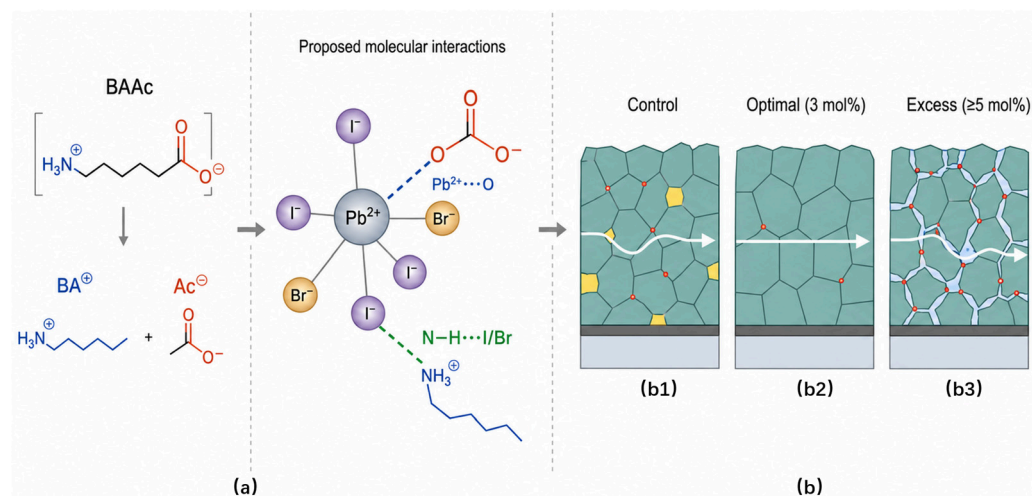


Figure 1. Literature-supported working model of BAAC-mediated precursor regulation: the arrows indicate the sequence of the process of action. (a) BAAC dissociation and proposed Ac[−]–Pb²⁺/BA⁺–halide interactions; (b) concentration-dependent film response comprising (b1) control, (b2) moderate loading (1–3 mol%), and (b3) excess loading (5–7 mol%).

The phenomenological concentration response is summarized in Figure 1b. Figure 1(b1) represents the control condition, Figure 1(b2) the beneficial 1–3 mol% range, and Figure 1(b3) the excess 5–7 mol% range. Moderate loading is consistent with regulated nucleation/growth and fewer electronically active defects. At 5–7 mol%, the favorable morphology and transport response is lost. Butylammonium can support 2D–3D motifs under suitable conditions [26,27,31,32,39]; however, no additional crystalline reflection attributable to such a phase was resolved between 5° and 12°. The high-loading response is therefore described as possible BA-rich or organic-rich interfacial accumulation, without assigning a specific reduced-dimensional phase.

The top-view SEM images (Figure 2a–f), cross-sectional images (Figure 2g–l), and individual grain distributions (Figure 2m and Table 2) provide complementary measures of morphology, the black line in Figure 2m represents the mean value, and the red line represents the median value. The mean equivalent-circle diameters were 0.508 ± 0.179 , 0.653 ± 0.270 , 0.643 ± 0.248 , 0.719 ± 0.296 , 0.540 ± 0.203 , and 0.609 ± 0.251 μm for the control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively. BAAC-3 therefore had the largest mean diameter, which represented a 41.5% increase over the control. The corresponding medians were 0.495, 0.623, 0.627, 0.688, 0.504, and 0.577 μm , respectively, which confirms that the trend was not produced solely by a small number of large grains.

Table 2. Descriptive statistics of the individual grain equivalent-circle-diameter distributions.

Sample	n	Mean $\pm$ SD (μm)	Median (μm)	IQR (μm)	CV (%)
Control	627	0.508 ± 0.179	0.495	0.267	35.18
BAAC-1	340	0.653 ± 0.270	0.623	0.365	41.41
BAAC-2	353	0.643 ± 0.248	0.627	0.366	38.63
BAAC-3	278	0.719 ± 0.296	0.688	0.420	41.18
BAAC-5	524	0.540 ± 0.203	0.504	0.292	37.58
BAAC-7	393	0.609 ± 0.251	0.577	0.322	41.15

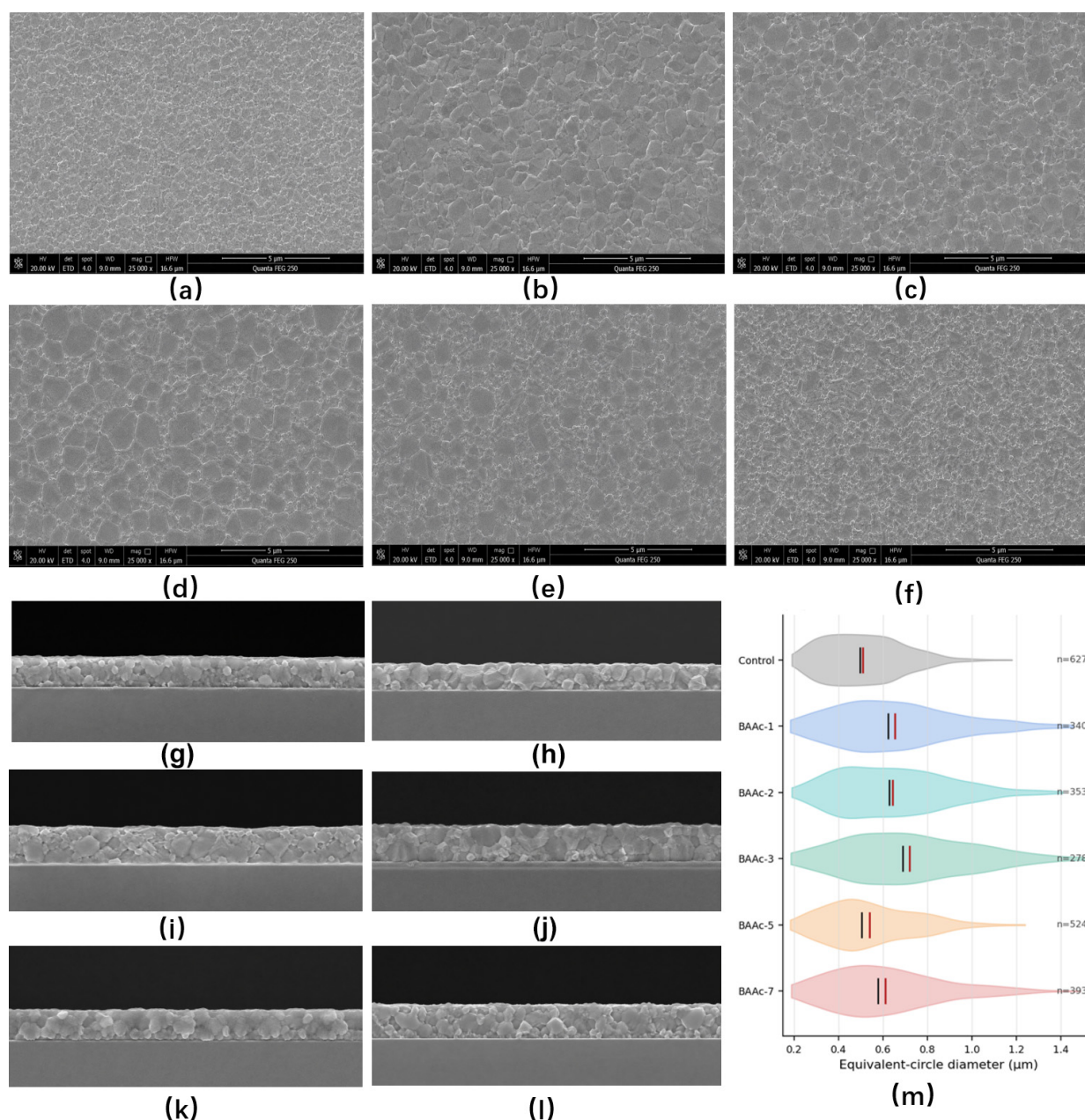


Figure 2. Morphology and grain-size distributions of the BAAC series: top-view SEM images of (a) control, (b) BAAC-1, (c) BAAC-2, (d) BAAC-3, (e) BAAC-5, and (f) BAAC-7; corresponding cross-sectional SEM images (g–l); and (m) individual grain equivalent-circle-diameter distributions. Top-view scale bars: 5 µm. Cross-sectional absorber thickness: approximately 500 ± 20 nm.

The IQR values ranged from 0.267 to 0.420 µm and the coefficients of variation from 35.18% to 41.41%. Thus, BAAC-3 increased the characteristic grain size but did not narrow the relative grain-size distribution; the earlier claim of reduced morphological heterogeneity has been removed. The cross-sectional images show continuous absorber layers with comparable thicknesses of approximately 480–520 nm, supporting the use of a common 500 ± 20 nm thickness in the optical and SCLC calculations. Because neither projected diameter nor a limited set of cross-sections provides a statistically independent pinhole-density measurement, the morphological conclusion is restricted to grain-size distribution, layer continuity, and thickness.

The XRD patterns in Figure 3a retained the characteristic perovskite reflections at approximately 14.1° , 28.4° , and 31.8° for every composition. The fitted principal-peak

positions for the control and BAAC-3 were 14.06° and 14.08° , respectively; this difference is comparable to the acquisition interval and is not interpreted as a measurable change in the average bulk lattice. The peak height increased from 4.46×10^3 to 1.172×10^4 counts, the FWHM narrowed from 0.156° to 0.142° , and the apparent coherent-domain size increased from 51.3 to 56.4 nm. The PbI_2 /perovskite peak height ratio decreased from 0.2691 for the control to 0.1259, 0.0674, and 0.0427 for BAAC-1, BAAC-2, and BAAC-3, respectively, which indicates more complete conversion under the selected processing conditions. No additional diffraction peak was resolved in the $5\text{--}12^\circ$ region. BAAC-7 showed a broader main peak (0.175°) and a PbI_2 /perovskite ratio of 0.3317. Residual PbI_2 can improve or impair performance depending on its amount and location [40–42].

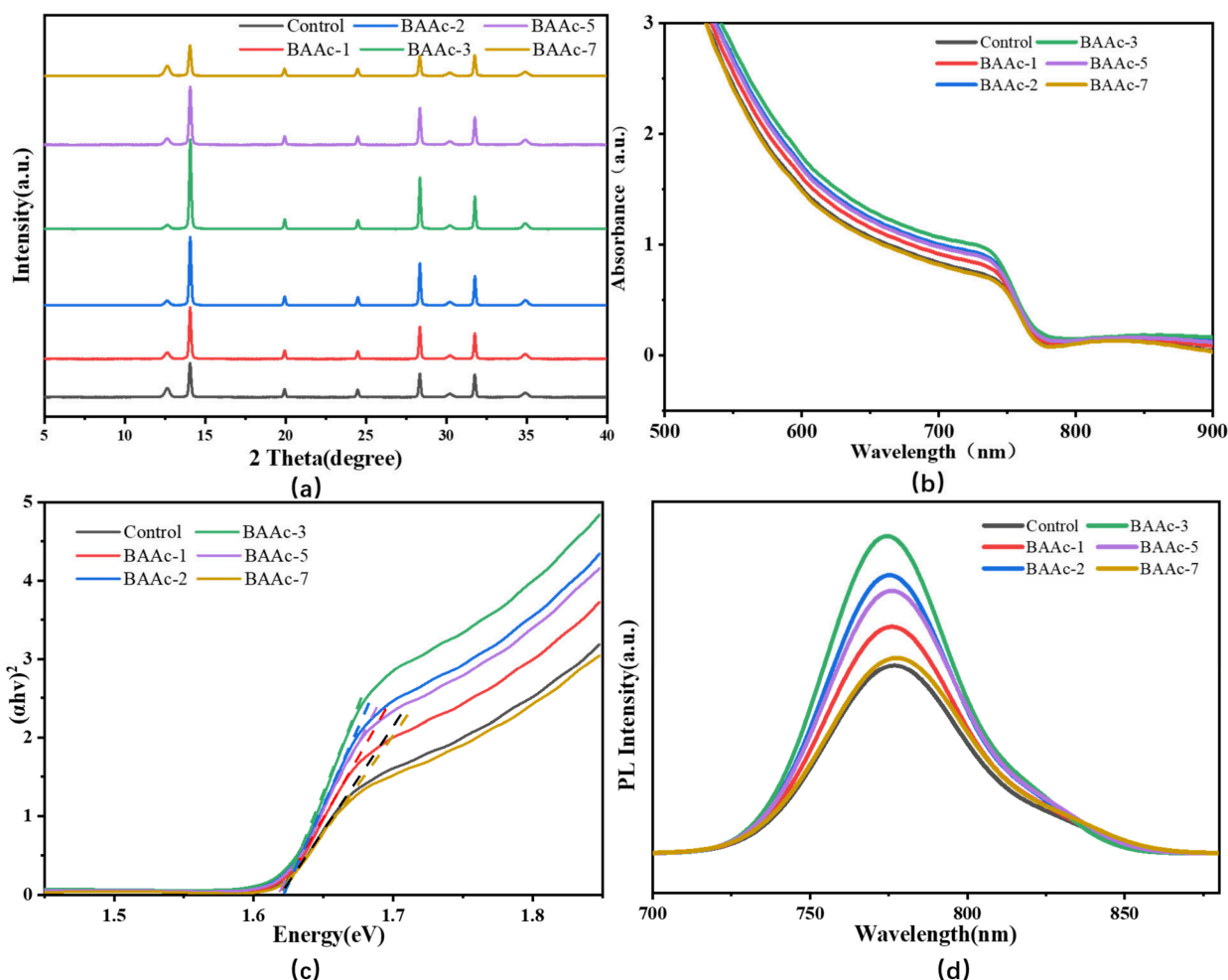


Figure 3. Concentration-dependent structural and steady-state optical properties: (a) XRD patterns, (b) UV–visible absorption spectra, (c) direct-bandgap Tauc plots with linear extrapolations, and (d) steady-state PL spectra of control and BAAC-treated perovskite films.

The UV–visible spectra in Figure 3b displayed similar long-wavelength onsets and no concentration-dependent displacement of the band edge. BAAC-2 and BAAC-3 showed slightly higher absorbance through the visible region. Direct-transition Tauc fits (Figure 3c) were restricted to the steep fundamental-absorption region described in Section 2.3, in which the dashed lines represent the tangents of the PL curve. The intersection points of these tangents with the coordinate axes indicate the bandgap energy, avoiding the sub-bandgap tail and visibly curved region in accordance with established cautions on Tauc analysis [43]. The fitted values were 1.619, 1.622, 1.624, 1.624, 1.623, and 1.618 eV for the control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively, with an estimated

fitting uncertainty of ± 0.005 eV. The 5.9 meV total variation is therefore not interpreted as a composition-induced bandgap shift.

The dominant steady-state PL band in Figure 3d occurs at 775–780 nm and is assigned to near-band-edge radiative recombination in the mixed-cation, mixed-halide absorber [44,45]. The control film emitted at 778 nm with an FWHM of approximately 47 nm. BAAC-3 showed a peak at 775 nm, a 2.6-fold intensity enhancement, and an FWHM of approximately 38 nm, whereas BAAC-7 emitted near 780 nm, with an FWHM of approximately 54 nm. The comparison was corrected using the absorbed 600 nm excitation fraction obtained from the corresponding UV–visible spectra. The enhanced and narrowed BAAC-3 emission, together with the TRPL response, is consistent with reduced nonradiative loss and energetic disorder.

3.2. Optical and Electrical Performance Analysis

The TRPL curves in Figure 4a follow the steady-state PL ordering. The intensity-weighted average lifetime increased from 230.2 ns for the control to 280.0, 330.0, and 350.0 ns for BAAC-1, BAAC-2, and BAAC-3, respectively, and then decreased to 310.0 and 245.0 ns for BAAC-5 and BAAC-7, respectively. All decays were measured on glass/perovskite films from the air side under the common 600 nm TCSPC conditions specified in Section 2.3, so the comparison does not include extraction by a charge transport layer. The 52.0% increase between the control and BAAC-3 is therefore consistent with the suppression of effective nonradiative decay channels [44–46], although TRPL alone does not identify a specific defect species.

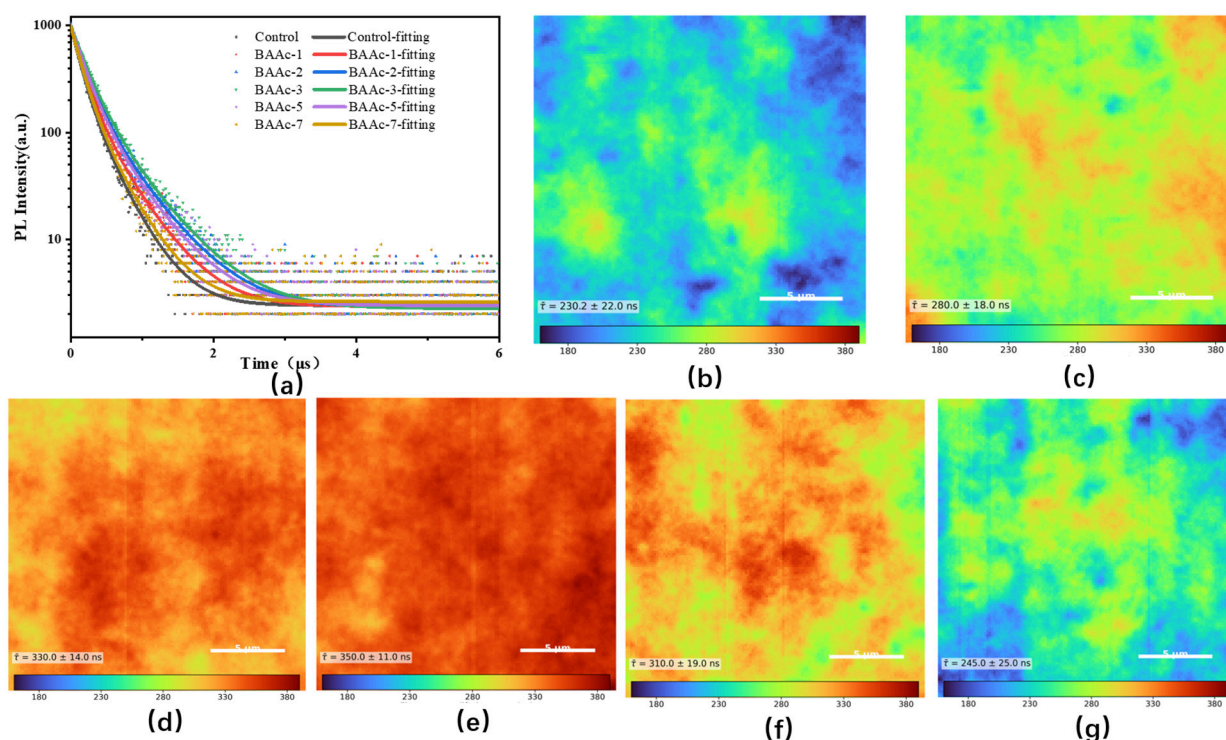


Figure 4. (a) TRPL decay curves and fitted decays of the concentration series. Spatial fluorescence-lifetime maps for (b) control, (c) BAAC-1, (d) BAAC-2, (e) BAAC-3, (f) BAAC-5, and (g) BAAC-7. All maps use the same lifetime scale; scale bars: 5 μ m.

The spatial lifetime maps in Figure 4b–g resolved the same concentration dependence. Mean lifetimes of 230.2 ± 22.0 , 280.0 ± 18.0 , 330.0 ± 14.0 , 350.0 ± 11.0 , 310.0 ± 19.0 , and 245.0 ± 25.0 ns were obtained for the control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively. The coefficient of variation decreased from 9.56% for the control

to 3.14% for BAAC-3, showing that the optimized film combined a longer lifetime with a more uniform spatial response. BAAC-7 had the widest distribution (10.20% coefficient of variation), consistent with renewed local heterogeneity.

The light-intensity-dependent V_{oc} data in Figure 5a yielded ideality factors of 1.364, 1.290, 1.230, 1.210, 1.280, and 1.380 for the control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively. The corresponding fitted V_{oc} values at 100 mW cm^{-2} were 1.092, 1.145, 1.176, 1.188, 1.164, and 1.105 V, respectively. The decrease to 1.210 at 3 mol% is consistent with a reduced contribution from trap-mediated Shockley–Read–Hall recombination, while the increase at 7 mol% indicates renewed defect-assisted loss. Ideality factors in PSCs can contain contributions from bulk, interfacial, and transport-layer recombination; the interpretation was therefore made in combination with TRPL, EIS, tDOS, and SCLC [47,48].

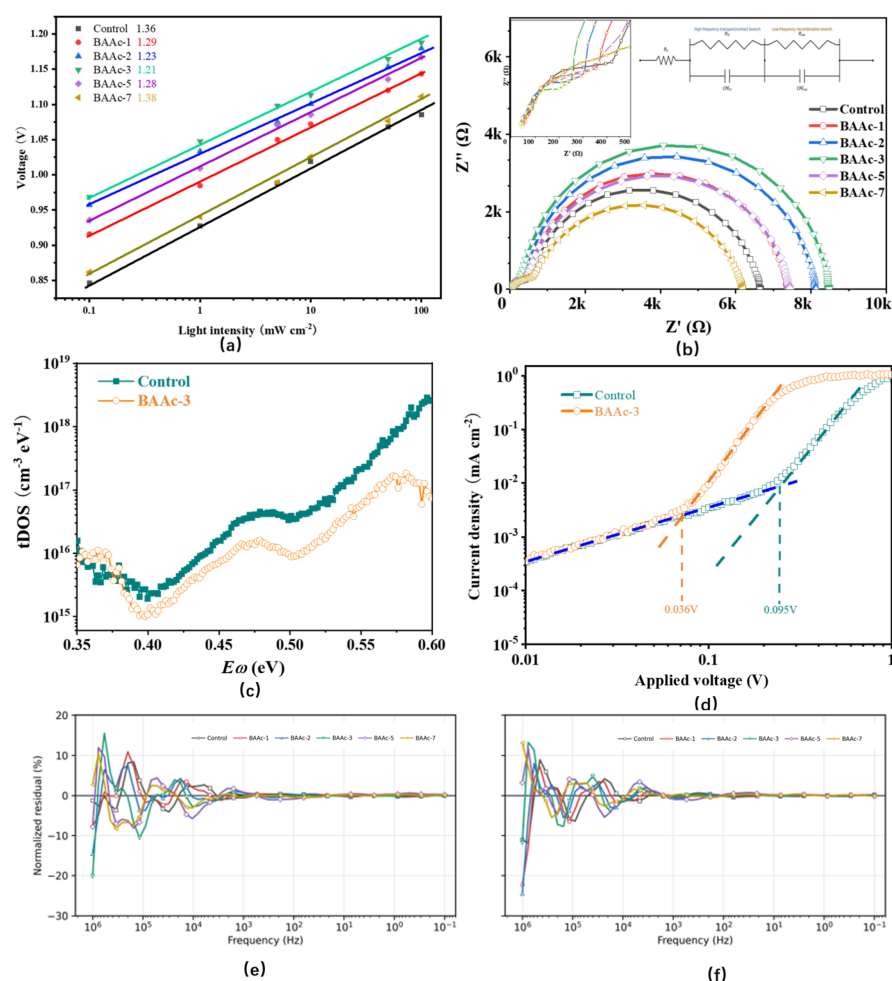


Figure 5. Electrical characterization of the BAAC series: (a) light-intensity-dependent V_{oc} measurements and linear fits; (b) Nyquist plots and common equivalent-circuit fits; (c) energetic tDOS of control and BAAC-3; (d) SCLC characteristics of control and BAAC-3 electron-only devices; and normalized (e) real and (f) imaginary EIS residuals for all six concentrations.

The Nyquist plots in Figure 5b and the common equivalent-circuit analysis in the Figure 5b inset and Table 3a show a clear concentration dependence. R_{tr} decreased from $453.38 \pm 14.89 \Omega$ for the control to 343.33 ± 13.39 , 258.69 ± 9.53 , and $222.17 \pm 9.52 \Omega$ for BAAC-1, BAAC-2, and BAAC-3, respectively, while R_{rec} increased from 6.155 ± 0.039 to 6.993 ± 0.050 , 7.825 ± 0.054 , and $8.211 \pm 0.061 \text{ k}\Omega$, respectively. At higher loading, R_{tr} increased to $327.34 \pm 9.57 \Omega$ for BAAC-5 and $527.66 \pm 14.65 \Omega$ for BAAC-7, whereas R_{rec} decreased to 7.087 ± 0.046 and $5.644 \pm 0.039 \text{ k}\Omega$, respectively. The principal resistance

trends therefore support improved transport and reduced device-level recombination near 3 mol% BAAc, followed by an over-treatment response.

Table 3. (a) Main EIS parameters. Values are estimate $\pm$ standard error; square brackets give the 95% confidence interval, followed by RSE for the three resistance parameters. (b) CPE parameters. Values are estimate $\pm$ standard error; square brackets give the 95% confidence interval.

(a)				
Sample	R_s (Ω)	R_{tr} (Ω)	R_{rec} (k Ω)	Reduced χ^2
Control	29.45 ± 2.10 [25.56, 33.92]; 7.14%	453.38 ± 14.89 [424.83, 483.86]; 3.28%	6.155 ± 0.039 [6.078, 6.233]; 0.63%	6.628×10^{-4}
BAAc-1	41.71 ± 2.18 [37.61, 46.25]; 5.22%	343.33 ± 13.39 [317.81, 370.90]; 3.90%	6.993 ± 0.050 [6.895, 7.093]; 0.71%	1.042×10^{-3}
BAAc-2	45.93 ± 1.79 [42.52, 49.61]; 3.89%	258.69 ± 9.53 [240.49, 278.27]; 3.68%	7.825 ± 0.054 [7.720, 7.932]; 0.68%	1.107×10^{-3}
BAAc-3	37.85 ± 1.75 [34.54, 41.48]; 4.62%	222.17 ± 9.52 [204.08, 241.86]; 4.29%	8.211 ± 0.061 [8.091, 8.334]; 0.75%	1.413×10^{-3}
BAAc-5	39.67 ± 1.49 [36.83, 42.72]; 3.75%	327.34 ± 9.57 [308.92, 346.87]; 2.92%	7.087 ± 0.046 [6.997, 7.179]; 0.65%	8.774×10^{-4}
BAAc-7	36.83 ± 1.77 [33.49, 40.50]; 4.80%	527.66 ± 14.65 [499.43, 557.48]; 2.78%	5.644 ± 0.039 [5.566, 5.722]; 0.70%	6.863×10^{-4}
(b)				
Sample	Q_{tr} ($S \cdot s^n$)	ntr	Q_{rec} ($S \cdot s^n$)	nrec
Control	$6.330 \times 10^{-8} \pm 1.196 \times 10^{-8}$ [4.354 $\times 10^{-8}$, 9.202 $\times 10^{-8}$]	0.811 ± 0.014 [0.783, 0.839]	$1.709 \times 10^{-7} \pm 1.041 \times 10^{-8}$ [1.514 $\times 10^{-7}$, 1.928 $\times 10^{-7}$]	0.890 ± 0.007 [0.875, 0.904]
BAAc-1	$2.159 \times 10^{-8} \pm 5.375 \times 10^{-9}$ [1.319 $\times 10^{-8}$, 3.536 $\times 10^{-8}$]	0.900 ± 0.019 [0.864, 0.937]	$1.232 \times 10^{-7} \pm 8.580 \times 10^{-9}$ [1.074 $\times 10^{-7}$, 1.415 $\times 10^{-7}$]	0.902 ± 0.008 [0.886, 0.917]
BAAc-2	$6.145 \times 10^{-9} \pm 1.596 \times 10^{-9}$ [3.674 $\times 10^{-9}$, 1.028 $\times 10^{-8}$]	0.999 ± 0.019 [0.961, 1.037]	$9.066 \times 10^{-8} \pm 5.917 \times 10^{-9}$ [7.967 $\times 10^{-8}$, 1.032 $\times 10^{-7}$]	0.914 ± 0.007 [0.900, 0.929]
BAAc-3	$6.553 \times 10^{-9} \pm 1.991 \times 10^{-9}$ [3.589 $\times 10^{-9}$, 1.196 $\times 10^{-8}$]	0.999 ± 0.022 [0.955, 1.043]	$6.360 \times 10^{-8} \pm 4.555 \times 10^{-9}$ [5.519 $\times 10^{-8}$, 7.330 $\times 10^{-8}$]	0.939 ± 0.008 [0.924, 0.954]
BAAc-5	$6.034 \times 10^{-9} \pm 1.199 \times 10^{-9}$ [4.071 $\times 10^{-9}$, 8.945 $\times 10^{-9}$]	0.986 ± 0.015 [0.958, 1.015]	$1.675 \times 10^{-7} \pm 1.019 \times 10^{-8}$ [1.485 $\times 10^{-7}$, 1.889 $\times 10^{-7}$]	0.870 ± 0.007 [0.856, 0.883]
BAAc-7	$3.023 \times 10^{-8} \pm 4.865 \times 10^{-9}$ [2.197 $\times 10^{-8}$, 4.158 $\times 10^{-8}$]	0.858 ± 0.012 [0.835, 0.882]	$3.716 \times 10^{-7} \pm 2.350 \times 10^{-8}$ [3.278 $\times 10^{-7}$, 4.212 $\times 10^{-7}$]	0.831 ± 0.008 [0.815, 0.847]

All R_s , R_{tr} , and R_{rec} estimates had relative standard errors below 7.14%, 4.29%, and 0.75%, respectively. The reduced χ^2 values ranged from 6.63×10^{-4} to 1.41×10^{-3} , which is within or close to the commonly targeted 10^{-4} – 10^{-3} range under the present weighting definition. However, the normalized residuals in Figure 5e,f show systematic high-frequency oscillations near 10^4 – 10^6 Hz. In addition, Q_{tr} had relative standard errors of 16.10–30.39%, and ntr reached the upper fitting bound of 0.999 for BAAc-2 and BAAc-3 (Table 3b). Consequently, the major resistance trend is used for comparison, whereas the high-frequency CPE parameters are treated as descriptive fit quantities and are not assigned an independent mechanistic meaning.

Thermal admittance spectroscopy, as shown in Figure 5c, resolved the energetic trap distribution. At 0.47 eV, the tDOS values were 3.71×10^{16} and 1.41×10^{16} cm $^{-3}$ eV $^{-1}$ for the control and BAAc-3, respectively, corresponding to a 62.0% reduction. The integrated density over 0.20–0.50 eV decreased from 5.14×10^{15} to 1.94×10^{15} cm $^{-3}$. The conversion followed the derivative-admittance method for extracting defect-energy distributions from junction capacitance [49].

The electron-only SCLC curves in Figure 5d give V_{tFL} values of 0.095 V for the control and 0.036 V for BAAc-3. Using $\epsilon_r = 25$ and $L = 500 \pm 20$ nm, the corresponding model-dependent effective trap densities were 1.05×10^{15} and $3.96 \times 10^{14} \text{ cm}^{-3}$, respectively. The relative decrease is 62.3%; varying the common film thickness within its measured uncertainty changes the absolute values but not this ratio. The SCLC and tDOS magnitudes are not expected to coincide because tDOS is an energy-resolved junction-admittance quantity, whereas SCLC integrates the traps accessed under carrier injection, the specific data can be found in Table 4. Their common direction, together with a longer TRPL lifetime, higher R_{rec} , and lower ideality factor, supports reduced trap-assisted recombination at 3 mol% BAAc [36,37].

Table 4. Electrical and defect-related parameters extracted using the common analysis protocol.

Sample	Ideality Factor	tDOS at 0.47 eV ($\text{cm}^{-3} \text{ eV}^{-1}$)	V_{tFL} (V)	Effective N_t (cm^{-3})
Control	1.364	3.71×10^{16}	0.095	1.05×10^{15}
BAAc-3	1.210	1.41×10^{16}	0.036	3.96×10^{14}

3.3. Photovoltaic Performance Analysis

The 50-device distributions in Figure 6 follow the concentration trend established by the film and electrical measurements. Mean V_{oc} values were 1.08 ± 0.0086 , 1.13 ± 0.0069 , 1.16 ± 0.0056 , 1.18 ± 0.0057 , 1.15 ± 0.0079 , and 1.08 ± 0.0127 V for the control, BAAc-1, BAAc-2, BAAc-3, BAAc-5, and BAAc-7, respectively. The mean J_{sc} changed within a narrower range: 23.091 ± 0.150 , 23.170 ± 0.154 , 23.261 ± 0.133 , 23.260 ± 0.119 , 23.030 ± 0.164 , and $22.533 \pm 0.232 \text{ mA cm}^{-2}$, respectively.

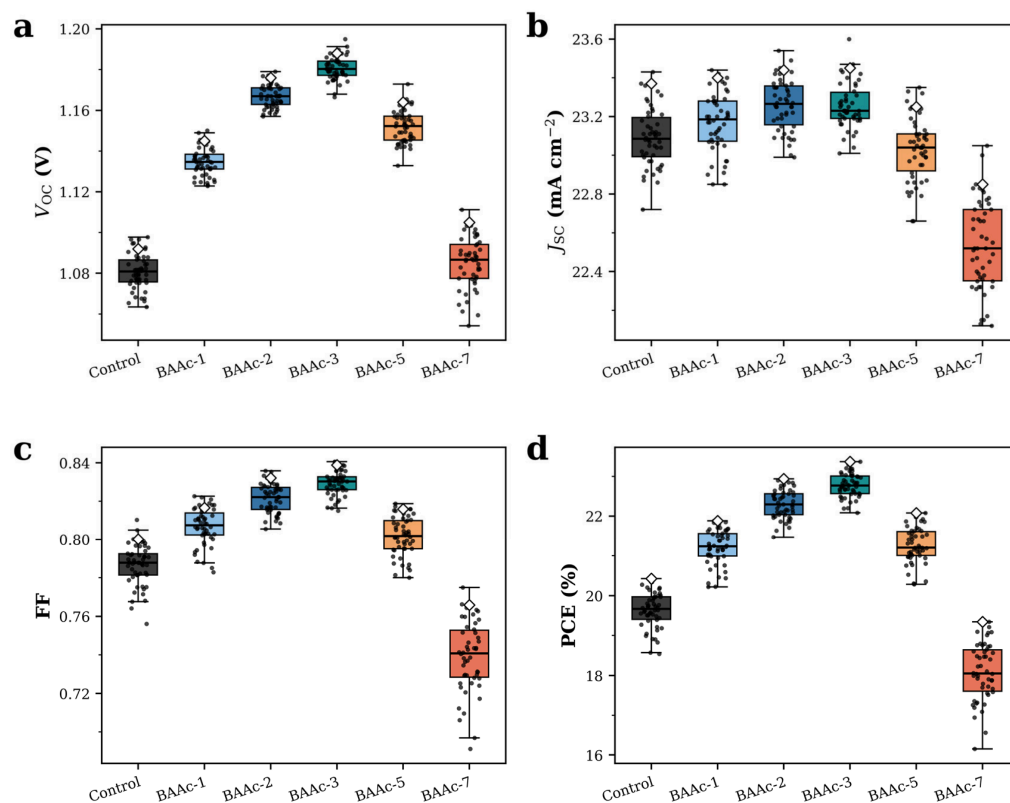


Figure 6. Statistical distributions from 50 devices per composition: (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE for control, BAAc-1, BAAc-2, BAAc-3, BAAc-5, and BAAc-7.

The FF distributions gave 0.7864 ± 0.0107 , 0.8067 ± 0.0098 , 0.8215 ± 0.0075 , 0.8292 ± 0.0063 , 0.8017 ± 0.0101 , and 0.7392 ± 0.0185 . The corresponding mean PCEs were $19.63 \pm 0.45\%$, $21.21 \pm 0.44\%$, $22.30 \pm 0.36\%$, $22.77 \pm 0.30\%$, $21.27 \pm 0.44\%$, and $18.08 \pm 0.71\%$, respectively. The coefficient of variation of PCE decreased from 2.29% for the control to 1.31% for BAAC-3 and increased to 3.94% for BAAC-7. The BAAC-3 group therefore combined the highest mean output with the narrowest efficiency distribution. The improvement is concentrated in V_{oc} and FF, matching the lower recombination and transport losses in Figure 5.

Figure 7a shows the inverted device architecture, while Figure 7b,c compares the reverse- and forward-scan J–V curves of the control and BAAC-3 acquired at 50 mV s^{-1} . The paired traces preserve the performance ranking between the two compositions and show limited scan-direction separation over the measured voltage range. Reverse scans remain the basis of the champion and statistical values to maintain a single reporting convention; the bidirectional comparison is used only as a hysteresis check. The concentration-dependent champion PCEs were 20.42%, 21.88%, 22.94%, 23.37%, 22.08%, and 19.34% for the control, BAAC-1, BAAC-2, BAAC-3, BAAC-5, and BAAC-7, respectively (Table 5). The 2.95 percentage-point gain from the control to BAAC-3 arose mainly from a 96 mV increase in V_{oc} and a 0.039 increase in FF, whereas J_{sc} increased by only 0.08 mA cm^{-2} . This partition is consistent with lower nonradiative recombination and improved extraction. The present dataset does not separate these contributions from a possible change in surface potential or energy alignment because no UPS or Kelvin probe measurement was performed. The EQE-integrated current densities in Figure 7d are 22.65 and 22.91 mA cm^{-2} for the control and BAAC-3, respectively, 3.08% and 2.30% below the J–V-derived values and the dotted line represents the integrated current. The mismatch is attributed to spectral mismatch, aperture alignment, monochromator bandwidth, and the different acquisition geometries; neither dataset was rescaled.

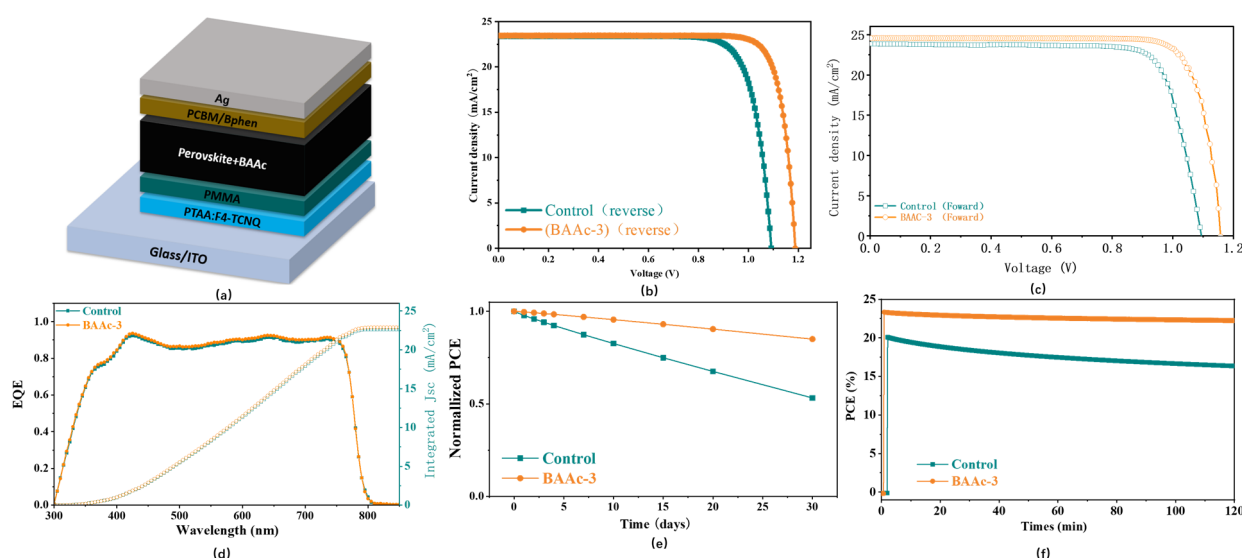


Figure 7. Device architecture, photovoltaic performance, and stability: (a) inverted device structure glass/ITO/PTAA:F4-TCNQ/PMMA/perovskite/PC₆₁BM/Bphen/Ag; (b) representative reverse-scan J–V curves of control and BAAC-3 devices; (c) corresponding forward-scan J–V curves; (d) EQE spectra with integrated current densities; (e) normalized PCE during 30 days of dry–dark shelf storage; and (f) PCE during 120 min of continuous MPP tracking under one-sun illumination.

Table 5. Statistical and champion photovoltaic parameters of the six BAAC concentrations.

Sample	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)	Champion $V_{oc}/J_{sc}/FF$	Champion PCE (%)
Control	1.080 ± 0.0086	23.091 ± 0.150	0.7864 ± 0.0107	19.63 ± 0.45	1.092/23.37/0.800	20.42
BAAC-1	1.130 ± 0.0069	23.170 ± 0.154	0.8067 ± 0.0098	21.21 ± 0.44	1.145/23.40/0.817	21.88
BAAC-2	1.160 ± 0.0056	23.261 ± 0.133	0.8215 ± 0.0075	22.30 ± 0.36	1.176/23.44/0.832	22.94
BAAC-3	1.180 ± 0.0057	23.260 ± 0.119	0.8292 ± 0.0063	22.77 ± 0.30	1.188/23.45/0.839	23.37
BAAC-5	1.150 ± 0.0079	23.030 ± 0.164	0.8017 ± 0.0101	21.27 ± 0.44	1.164/23.25/0.816	22.08
BAAC-7	1.080 ± 0.0127	22.533 ± 0.232	0.7392 ± 0.0185	18.08 ± 0.71	1.105/22.85/0.766	19.34

Dry–dark shelf stability is shown in Figure 7e. Unencapsulated devices were stored at 25 ± 2 °C and 15 ± 5% relative humidity. After 30 days, the control and BAAC-3 retained 53.2% and 85.0% of their initial efficiencies, respectively. The improved retention is consistent with the reduced grain-boundary and recombination indicators, but no specific moisture-barrier mechanism is assigned. In accordance with ISOS reporting principles [15], this result is described as a preliminary dry–dark shelf comparison rather than a standardized operational lifetime.

The 120 min MPP traces in Figure 7f provide a short-duration check of the swept J–V values. At 5.04 min, the control and BAAC-3 delivered 19.80% and 23.20%, respectively; after 120 min, the outputs were 16.35% and 22.25%, respectively. The initial relaxation can include light soaking, thermal equilibration, and ion redistribution in addition to irreversible degradation, so it is described as burn-in/relaxation rather than assigned to a single process. From the measured traces, the control device reached T_{95} and T_{90} at approximately 16.1 and 39.4 min, respectively, whereas BAAC-3 remained above both thresholds throughout the 120 min window (T_{95} and T_{90} > 120 min). These values quantify the short measurement window and are not extrapolated to long-term lifetime.

Table 6 places the optimized BAAC-3 device in the context of related acetate- and alkylammonium-based strategies. The 23.37% champion PCE is lower than the 25.62% and 26.12% reported for the BAAC systems in references [31,32], respectively; however, direct efficiency ranking is not used because the absorber composition, device architecture, additive definition, and stability protocol differ among the studies. The closest MAAC benchmark reached 23.68% [29]. In the absence of a same-batch MAAC control, this comparison does not establish a cation-size or steric advantage. The distinguishing result of the present work is the six-point concentration window in an MA/Br-containing inverted triple-cation system, including the reversal of the morphological, electrical, and photovoltaic trends at excessive loading.

Table 6. Comparison with selected acetate-, alkylammonium-, and ionic-liquid-modified perovskite solar cells.

Additive/ Study	Absorber/Architecture	Loading	PCE/ V_{oc}/FF	Stability Condition	Distinguishing Point
MAAC [29]	Triple-cation mixed-halide; inverted	MAAC-2M	23.68%/1.208 V/0.829	73.2% after 30 d dry storage	Closest composition; shorter cation
PenAAC [30]	Flexible inverted PSC	Optimized in source	23.68% (23.35% certified)/1.17 V/—	>91% after 5000 bends	Flexible interfacial modification

Table 6. Cont.

Additive/ Study	Absorber/Architecture	Loading	PCE/V _{oc} /FF	Stability Condition	Distinguishing Point
BAAc [31]	FA–Cs perovskite	Optimized in source	25.62%/—/—	Improved stability under multiple standardized protocols	Cross-grain cation homogenization
BAAc [32]	FAPbI ₃ ; n–i–p	2 $\mu\text{L mL}^{-1}$ optimum	26.12%/—/—	90% after 1000 h continuous ambient operation	Prior BAAc crystallization/ passivation
This work	FA _{0.80} Cs _{0.07} MA _{0.13} PbI _{2.64} Br _{0.39} ; inverted	0–7 mol% relative to MA; 3 mol% optimum	23.37%/1.188 V/0.839	85.0% after 30 d dry–dark; 120 min MPP	Six-point dose window and over-treatment boundary

4. Conclusions

The systematic BAAc series revealed a non-monotonic relationship among additive loading, grain-size distribution, defect response, and photovoltaic performance. The mean equivalent-circle diameter increased from 0.508 μm for the control to 0.719 μm for BAAc-3, while the median increased from 0.495 to 0.688 μm , respectively. The CV remained broad (35.18–41.41%), so the morphological result is grain coarsening rather than a demonstrated narrowing of the size distribution. Cross-sectional SEM confirmed continuous absorber layers with comparable thicknesses of approximately 500 ± 20 nm. BAAc-3 also showed the lowest R_{tr} ($222.17 \pm 9.52 \Omega$), the highest R_{rec} ($8.211 \pm 0.061 \text{ k}\Omega$), a longer PL lifetime, a lower ideality factor, and lower tDOS/SCLC estimates, without a resolvable bandgap shift. The agreement of these independent measurements supports reduced nonradiative recombination and transport loss as the immediate device-level explanation.

The BAAc-3 champion device reached 23.37%, and the 50-device mean increased to $22.77 \pm 0.30\%$, compared with 20.42% and $19.63 \pm 0.45\%$, respectively, for the control. At 7 mol%, the favorable electrical trend reversed and the champion PCE decreased to 19.34%, which defines an over-treatment boundary. This study does not directly identify an Ac^- – Pb^{2+} complex or a BA-rich reduced-dimensional phase, and the absence of UPS/Kelvin probe data prevents the separation of defect passivation from possible energy-level changes. The EIS resistance parameters are well constrained, but the systematic high-frequency residuals and the Q_{tr}/n_{tr} correlation limit detailed interpretation of the high-frequency CPE branch. The 30-day shelf and 120 min MPP tests establish comparative trends under the stated conditions but do not constitute long-term lifetime certification. Future work should prioritize direct coordination spectroscopy, work-function analysis, multi-area quantitative morphology, and longer standardized MPP testing. Within these limitations, the robust conclusion is that BAAc acts as a strongly concentration-sensitive precursor additive in this inverted triple-cation process.

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