Triamine-Based Aromatic Cation as a Novel Stabilizer for Efficient Perovskite Solar Cells

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Operational stability of perovskite solar cells has been a challenge from the beginning of perovskite research. In general, humidity and heat are the most well-known degradation sources for perovskites, requiring ideal design of perovskite chemistry to withstand them. Although triple-cation perovskite \( \text{Cs}_{0.05} \text{(FA}_{0.85} \text{MA}_{0.15})_{0.95} \text{Pb(I}_{0.85} \text{Br}_{0.15})_3 \) has been already introduced as the stable perovskite material, the high reactivity of methylammonium and formamidinium in the cation sites demands further modification. Herein, 1,2,4-triazole is suggested as an effective cation solute to improve the performance and stability of perovskite solar cells. 1,2,4-Triazole is an aromatic cation with low dipole moment that is stable under humidity and heat. It also possesses three nitrogen atoms, forming additional hydrogen bonds in the lattice, stabilizing the material. In this study, the solar cell utilizing 1,2,4-triazole alloying achieves a power conversion efficiency of 20.9% with superior stability under extreme condition (85 °C/85% of relative humidity (RH), encapsulated) for 700 h. The 1,2,4-triazole-alloyed perovskite exhibits reduced trap density and film roughness and enhanced carrier lifetime with electrical conductivity, suggesting an ideal perovskite structure for efficient and stable optoelectronic applications.

1. Introduction

Organometallic perovskites are one of the most popular research areas, and the solar cell application of perovskite materials is gaining enormous attention with the rapid growth. Throughout the extensive work, the power conversion efficiency (PCE) of perovskite solar cells is soaring up to 24.2%, and the stabilities are gradually improving.\(^1\) Even though the PCE of the perovskite solar cell is already comparable to those of commercial materials, the stability is not satisfactory enough to replace the conventional photovoltaics.

Perovskite solar cells are generally designed to have device architectures of either p-i-n or n-i-p type. The perovskite layer (i) plays very important role as the main light absorber, but it is highly reactive under heat, humidity, and light. Although n- or p-type carrier transport layers of metal oxides, polymers, or small molecules also count for device properties,\(^1\) stabilizing the perovskite itself is the most important to realize stable solar-cell device. It is well known that triple-cation perovskite \( \text{Cs}_{0.05} \text{(FA}_{0.85} \text{MA}_{0.15})_{0.95} \text{Pb(I}_{0.85} \text{Br}_{0.15})_3 \), where FA is (NH\(_2\))\(_2\)CH\(^+\) and MA is CH\(_3\)NH\(_3\)\(^+\) is one of the most stable perovskite materials.\(^16\) However, FA and MA are highly reactive under heat, humidity, and light, requiring additional modification to further improve the quality of perovskite.\(^5\) Even though the organic-based p-type materials (the most common one for the perovskite solar cells: spiro-OMeTAD) can have a stability problem,\(^25\) recent researches have revealed that ion doping or alloying of perovskite can largely improve the device stability, compensating the stability issues of spiro-OMeTAD. In more detail, metal-halide doping or organic alloying surely help the device stability by forming a strong bonding within the lattice or passivating the defects.\(^8\) The surface passivation on the perovskite is also introduced as an effective method to reduce the degradation of materials, even though it only stabilizes the interface, and the bulk properties of perovskite may still remain unstable.\(^13\) Therefore, the doping or alloying of perovskite is highly practical and straightforward method to improve the materials stability, and thereby the performance of solar cells.

Herein, we introduce 1,2,4-triazole (C\(_2\)H\(_3\)N\(_3\)) as a cation solute in triple-cation perovskite, since 1,2,4-triazole is an aromatic compound that is extremely stable compared to FA or MA.\(^36\)–\(^40\) 1,2,4-triazole is a triamine-based aromatic compound, having a strong interaction within the perovskite structure, and also improving the charge transport behavior of cation site of the perovskite.\(^5\) However, because of its relatively large size (≈258 pm), 1,2,4-triazole in perovskite is limited to a small amount in order to maintain satisfactory tolerance factor.\(^45\) By optimizing the content of 1,2,4-triazole alloy, the optical and electronic properties are improved boosting the PCE up to 20.9%. Furthermore, the thermal stability of the solar cell is confirmed under the extreme condition (85 °C/85% relative humidity (RH)) for 700 h to address the optimum strategy of perovskite and device stabilization.
2. Results and Discussion

Concerns regarding the perovskite stability are widely discussed in the solar-cell field, and it is realized that the perovskite layer plays a critical role for the degradation of devices. The major degradation sources of the perovskite are organic species of the cations which degrade under humidity, heat and light, and further modification of such species is required to design more practical perovskite materials. 1,2,4-triazole has triamine-based aromatic structure, and it possibly allows a strong interaction within the lattice as well as the energy minimization by the tilting behavior of an organic cation, leading to the structural stabilization. Also, orientation of amine groups in 1,2,4-triazole tends to make them repel one another, resulting in a reduced dipole moment compared with the 1,2,3-triazole or imidazole, obtaining strong advantages over different multiamine-based ring-shaped molecules. The low dipole moment reduces the reactivity with water, guaranteeing the high stability under the humid condition. Furthermore, 1,2,4-triazole is less volatile species than imidazole, MA or FA, making it the ideal stabilizer for the perovskite solute under the operating conditions.

Figure 1 illustrates the schematics of 1,2,4-triazole alloying in triple-cation perovskite. By analyzing the 1,2,4-triazole-alloyed perovskite film, X-ray diffraction (XRD) shows (110) peak shift towards lower angle and (224) and (314) peaks to the opposite direction, due to the transition into tetragonal phase by the 1,2,4-triazole solute in a triple-cation perovskite (Figure 1b). When the solute is added up to 6%, a lead iodide (PbI$_2$) peak is observed with the reduced peak intensities of triple-cation perovskite, indicating the structural instability by excessive alloying (Figure S1a, Supporting Information). In order to advocate the phenomena, tolerance factor is calculated to be ≈1.01 for the 6% alloying (values between 0.9–1.0 as a stable structure). To identify the molecular structure of 1,2,4-triazole solute in the perovskite, Fourier-transform infrared (FTIR) analysis is further conducted for the alloyed perovskite film (Figure 1c), where a clear peak of N=N in ≈1600 cm$^{-1}$ can be seen after the incorporation of aromatic cations (raw data presented in Figure S1b, Supporting Information).

Aside from the lattice change, film morphologies are also analyzed to address the advantages of 1,2,4-triazole alloying. As shown in Figure 2a, 2% and 4% alloys exhibit uniformly sized grains, where 0% and 6% show multiple-size distributions which may be the imperfect grains or PbI$_2$, respectively. In Figure 2b, the root-mean-square (rms) roughnesses and conductivities of perovskite films are addressed, confirming that the proper alloying in perovskite increases the quality of the perovskite films by the lattice stabilization. Topological images from the atomic force microscopy (AFM) and optical images are also presented in Figures S2 and S3 in the Supporting Information. It can be seen that 6% alloy exhibits the highest conductivity, and this value originate from the mixed conductivity of PbI$_2$ and alloyed perovskite (Figure S1a, Supporting Information). However, the improved conductivity of 2% or 4% alloy originates from the substitution of triazole, which contains delocalized aromatic structure to transport the charge efficiently within the perovskite lattice, contributing to the improved optoelectronic properties of perovskite materials.

Defects and traps of materials significantly affect the ion diffusion as well as charge carrier dynamics within the device, and the analyses and understanding of these defect states are undoubtedly important to improve both the device performance and stability. In order to investigate the carrier dynamics and...
recombination behaviors in the perovskite films, time-resolved photoluminescence (TRPL), photoluminescence (PL), and absorptance are measured. As shown in Figure 3a, the alloy with 2% of 1,2,4-triazole exhibits the longest carrier lifetime, with the reduced traps expected. Interestingly, carrier lifetimes of 4% and 6% alloys are observed to be shorter than that of the bare perovskite, indicating the excessive alloying destabilizes the perovskite lattice. To further obtain the insights, absorption coefficients and steady-state PL are measured, with the 2% alloy exhibiting the lowest defects with the highest absorption and PL intensities (evidences for the strong excitation and radiative recombination, respectively). However, the PL of bare and 4% alloys are red shifted, indicating that the shallow traps are reduced in the 2% alloy (with small changes in the bandgap, as illustrated in Figure S4a, Supporting Information). Comparison of PL and bandgap indicates the modified traps at the shallow level, which can be highly influenced by the quality of perovskite and interfaces. Perovskite with 6% alloying forms PbI$_2$ (Figure S1a, Supporting Information), which ruins the proper recombination and weakens the optoelectronic properties. Based on the measured work function and valance band maximum (VBM) with the bandgap energy, the band structure of perovskite with proper 2% alloying is moving towards n-type, thereby enhancing the electron transport (Figure 3b and Figure S4b, Supporting Information). However, excessive alloying is not proper due to the lattice defects, making the light absorber less n-type and leading to an ineffective charge transport for the device performance.

To further explicate the characteristics of charge carriers and electronic structures, the electronic traps of the devices with various 1,2,4-triazole alloy contents are quantitatively analyzed. It is known that various phenomena including carrier accumulation and charging/discharging of electronic traps contribute to the capacitive feature of the device, and therefore a proper interpretation of the device capacitance can elucidate its defective characteristics in a perovskite solar cell.[57–63] The capacitance of a device is obtained from the impedance spectroscopy, and capacitance versus frequency ($C$–$f$) is plotted in Figure 4a. While the capacitances of various alloys are all identical at high-frequency region, the low-frequency capacitances show differences indicating that the electronic trap states change by the addition of 1,2,4-triazole. For further understanding, deep-trap density is calculated from the $C$–$f$ plot, and the distribution of trap states is depicted in Figure 4b.[16,64] The 2%-alloyed device exhibits trap states shifting toward the bandedge plus reduced trap density compared to the bare-, 4%- and 6%- alloyed...
perovskite solar cells, rationalizing its improved carrier transport observed by PL analysis. The shallow traps of 2% alloy possibly reduce the carrier recombination and provide facile charge transfer to the carrier-transport materials (SnO$_2$ and spiro-OMeTAD for electrons and holes, respectively). Schematics for carrier dynamics at the interfaces are drawn in Figure 4c with the considerations of band diagram (from Figure 3 and Figure S4, Supporting Information).

![Figure 3](image1)

**Figure 3.** Carrier and optoelectronic properties of perovskite films. a) Carrier lifetime of 1,2,4-triazole-alloyed perovskite: TRPL, PL data, and bandgap determination by $(\alpha h\nu)^2$ versus $h\nu$. b) Electronic structures of 1,2,4-triazole-alloyed perovskite by UPS: work function and VBM.

![Figure 4](image2)

**Figure 4.** Electronic-trap states of perovskite films. a) Capacitance–frequency plot and b) trap-distribution spectra of solar cells with the 1,2,4-triazole-alloyed perovskite. c) Schematic illustration for the band diagram and trap state in the device.
The photovoltaic performances of solar cells are illustrated in Figure 5a and Table S1, Supporting Information. While devices with 2% alloy exhibits the highest efficiencies with low hysteresis, devices with 4% and 6% alloys result in low reproducibility (Figure S5, Supporting Information) due to the high concentration of deep-level defects and impurities (Figures 2 and 4, and Figure S1, Supporting Information). Steady-state current and external quantum efficiency (EQE) are also shown (Figure 5b,c), where the 2%-alloyed device exhibits stable current up to 1000 s with the highest EQE. TRPL is once more conducted in SnO$_2$/perovskite/spiro-OMeTAD structure (Figure 5d) to confirm how well carriers are transferable. The tendencies are well matched with the performance of perovskite solar cells, exhibiting that the 2%-alloyed perovskite is the optimum light-absorber material for the device efficiency.

Lastly, to evaluate the effect of 1,2,4-triazole on the stability of the device, the alloyed perovskite solar cells are compared with the bare device under the extreme condition (85°C/85% RH). While the perovskite solar cell without alloying sustains 90% of initial PCE for ≈200 h (Figure 6), 2%-alloyed perovskite solar cell sustains 90% PCE for more than 700 h, leading to a potential for the ultrastable perovskite materials. Thermally stable photovoltaic device is enabled thanks to the improved structural stability and passivated defects of 2%-alloyed perovskite, whereas 4%- and 6%- alloyed ones possess structural instability and deteriorative defect/trap characteristics as observed in this study.

3. Conclusions

Obtaining high PCE and stability for the perovskite solar cells are the major bottlenecks for commercialization. Even though the triple-cation perovskite is well known for its stability, reactive species, and weak bonding sites of organic cations (MA and FA) still provide rooms for the further improvement. Herein, we have alloyed 1,2,4-triazole as a cation solute in perovskite to minimize defects and thereby enhance the optoelectronic properties of perovskite, leading to the achievement of superior

![Figure 5](image_url)

**Figure 5.** Photovoltaic performance of perovskite solar cells. a) J–V curves (scan rate: 10 mV s$^{-1}$), b) steady-state current for 1000 s, and c) EQE spectra for the bare and 1,2,4-triazole-alloyed perovskite solar cells. d) TRPL spectra with the bare and 1,2,4-triazole-alloyed perovskite (FTO/SnO$_2$/perovskite/spiro-OMeTAD).

![Figure 6](image_url)

**Figure 6.** Device stability under 85°C/85% RH environment (encapsulated).
performance and stability under extreme conditions. To satisfy the structural stabilization, the addition of 1,2,4-triazole is optimally controlled, and the devices with 2%-alloyed perovskite exhibits the PCE of 20.9% with the superior stability compared with the device without solute. These straightforward and novel strategies can support further development for the perovskite research and practical commercialization.

4. Experimental Section

Synthesis of Triazole-Soluted Perovskite: C$_2$H$_5$N$_3$ (Sigma–Aldrich) was mixed with hydrogen iodide solution (HI, Sigma–Aldrich) with 3:1 molar ratio in a round-bottom flask at 0 °C for 2 h under stirring. After the solvent was evaporated at 70 °C for 12 h, the precipitate was washed with diethyl ether (Daejung) for ten times. The precipitate was dried at 60 °C for 24 h in a vacuum oven to complete the synthesis of triazolium iodide (C$_2$H$_5$N$_3$I).

For the perovskite film, 1.8 M Cs$_0.05$(FA$_{0.85}$MA$_{0.15}$)$_3$Br$_{0.85}$Pb$_{0.15}$ perovskite precursor solution was prepared by dissolving formamidinium iodide (Great Solar Laboratory), methylammonium bromide (Great Solar Laboratory), PbI$_2$ (TCI Chemicals), lead bromide (PbBr$_2$; TCI Chemicals), and cesium iodide (Great Solar Laboratory) into a mixture of N,N-dimethylformamide (DMF; Sigma–Aldrich) and dimethyl sulfoxide (DMSO; Sigma–Aldrich).

To prepare the 1,2,4-triazole-alloyed perovskite, 1.8 M of stock solution of 1,2,4-triazolium perovskite was made by mixing triazolium iodide, PbI$_2$, and PbBr$_2$ into DMF:DMSO mixture solution to make a TAPbI$_0.85$Br$_{0.15}$ (100% of triazole cation, where TA indicates triazolium cation) perovskite precursor solution. The perovskite solution was sonicated for 30 min, and then was spin-coated on a cleaned substrate with the previously developed method. The perovskite solution was sonicated for 30 min, and then spin-coated on the as-prepared SnO$_2$ layer in two steps of spinning program: 500 rpm for 3 s for the first step and 5000 rpm for 20 s for the second step. 1 mL of diethyl ether (Daejung) was dropped 5 s before the second spin-step ended, and the substrate was annealed at 105 °C for 40 min on a hot plate. Hole transporting material was prepared by dissolving 72.3 mg of spiro-OMeTAD (Lumtec) in 1 mL of chlorobenzene (Sigma–Aldrich), and 28.8 μL of 4-tert-butylypyridine (Sigma–Aldrich), and 17.5 μL of bis(trifluoromethane)sulfonimide lithium salt (Sigma–Aldrich) in acetonitrile (520 mg mL$^{-1}$) were added as additives. The solution was spin-coated on the substrate, and finally 100-nm thick Au electrode was thermally evaporated.

Encapsulation: Fabricated device was sealed with encapsulation glass (AMC) by attaching getter (HD-S071313W-48; AD TECH) and dispensing electrode was thermally evaporated.

Characterization: FTIR (Nicolet i550; Thermo Fisher) was conducted to characterize the organic bonding nature of the perovskite. Phases of the synthesized samples were characterized by XRD (D8 Advance; Scientific). The field-emission scanning electron microscopy (Merlin-Compact; Carl Zeiss) was used to observe the morphologies of alloyed perovskite. Work function and VBM of perovskite films were measured via multipurpose X-ray photoelectron spectroscopy (Sigma Probe; Thermo VG Scientific), conducted with argon sputtering and photon energy of $h\nu = 21.22$ eV was used in the ultraviolet photoelectron spectroscopy (UPS) measurement. Optical properties of the perovskite films were measured with UV–vis spectroscopy (V-770; JASCO) with an integrating sphere. PL (FlouTime300; PicoQuant) was conducted to understand the carrier recombination. Incident photon to current efficiency (IPCE) measurements were performed by solar cell IPCE system (K3100; McScience). For impedance analysis, a potentiostat (Zive SP-1; WonAtech) was adopted, and the impedance of photovoltaic device was measured with 10 mV AC perturbation in the frequency range from 10 mHz to 100 kHz under zero bias in dark condition. Photocurrent density–voltage (J–V) curves were achieved via solar cell measurement system (K-3000; McScience) for an active area of 0.09 cm$^2$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

1,2,4-triazole, carrier traps, mixed cations, perovskite solar cells, stability

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