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Boosting CsSnI$_3$-based near-infrared perovskite light-emitting diodes performance via solvent coordination engineering

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Abstract
Due to their unique photoelectric properties, nontoxic tin-based perovskites are emerging candidates for efficient near-infrared LEDs. However, the facile oxidation of Sn$^{2+}$ and the rapid crystallization rate of tin-based perovskites result in suboptimal film quality, leading to inferior efficiencies of tin-based perovskite light-emitting diodes (Pero-LEDs). In this study, we investigate the influence of commonly used solvents on the quality of the CsSnI$_3$ films. Remarkably, DMSO exhibits a stronger interaction with SnI$_2$, forming a stable intermediate phase of SnI$_2$/C$_3$DMSO. This intermediate effectively inhibits the oxidation of Sn$^{2+}$ and slows down the crystallization rate, bringing in lower defect state density and higher photoluminescence quantum yield of the prepared perovskite films. Consequently, the corresponding Pero-LEDs achieve a maximum external quantum efficiency (EQE) of 5.6%, among the most efficient near-infrared Pero-LEDs. In addition, the device processes ultra-low efficiency roll-off and high reproducibility. Our research underscores the crucial role of solvent-perovskite coordination in determining film quality. These findings offer valuable guidance for screening solvents to prepare highly efficient and stable tin-based perovskites.

KEYWORDS
intermolecular interaction, light-emitting diodes, solvent engineering, tin-based perovskites
1 | INTRODUCTION

As an emerging semiconductor material, metal halide perovskites exhibit immense potential for applications in next-generation flat panel displays and solid-state lighting, owing to their low cost, high color purity, remarkable photoluminescence quantum yields (PLQYs), tunable luminous wavelength, and facile solution processing.\(^1\)–\(^3\) Notably, since the first room temperature operative perovskite light-emitting diodes (Pero-LEDs) were reported in 2014,\(^4\) substantial advancements have been achieved, propelling external quantum efficiency (EQE) of Pero-LEDs to more than 20%.\(^5\)–\(^9\) However, it is crucial to note that high-performance Pero-LED devices predominantly utilize lead-based perovskites, and the issue of toxicity significantly hampers their widespread commercial adoption.\(^10\)–\(^12\)

Recently, tin-based perovskites have emerged as one of the most promising alternatives due to the similarity in the outer electronic configurations to Pb.\(^12\)–\(^14\) However, the efficiency and stability of tin-based Pero-LEDs lag behind those of lead-based ones, primarily attributed to the facile oxidation and rapid crystallization process of tin-based perovskites.\(^15\)–\(^17\) The absence of the inert electron pair effect in tin atoms, characteristic of lanthanide contraction, renders its two 5s electrons highly reactive, making tin-based perovskites prone to oxidation. Additionally, the distinctive properties exhibited by electrons in the s orbital lead to elevated Lewis acidity in Sn\(^{2+}\), resulting in its rapid reaction with halide ions (X\(^-)\) and thus causing extremely fast crystallization.\(^18\),\(^19\) Furthermore, tin-based perovskites have higher energy levels and sharper band edges than lead-based ones. As a consequence, the reduction in ionization energy facilitates the formation of weaker Sn–X bonds, accelerating reactions with H\(_2\)O and O\(_2\) molecules and leading to faster oxidation.\(^20\),\(^21\) To further advance the development of tin-based Pero-LED technology, these issues urgently need to be addressed. Given a limited number of studies addressing these challenges in Pero-LEDs, it is noteworthy to consider the analogous situation faced by tin-based perovskite solar cells. By leveraging insights from the latter, which confront similar predicaments, we can potentially shed light on effective solutions for the former.

To address the issue of Sn\(^{2+}\) oxidation, reducing agents or bulky organic cations were used as passivation into the precursor solution.\(^22\)–\(^24\) For instance, Zhu et al.\(^25\) demonstrated that the addition of SnF\(_2\) not only mitigates the oxidation of Sn\(^{2+}\) but also serves as a hetero-phase nucleation site, effectively regulating the nucleation and growth of MASnBr\(_3\) perovskite films. Tai et al.\(^26\) achieved the synthesis of highly efficient and stable FASnI\(_3\) solar cells by incorporating SnCl\(_2\)-hydroxy benzene sulfonic acid into the precursor solution. The addition of these additives facilitated the in-situ encapsulation of FASnI\(_3\), effectively mitigating the oxidation of Sn\(^{2+}\) and obtaining perovskite solar cells (PSCs) with a power conversion efficiency (PCE) of 6.76%. Guan et al.\(^27\) introduced formamidine thiocyanate (FASCN) into the precursor and took advantage of the strong chemical interaction between Sn\(^{2+}\) and SCN\(^-\). This approach effectively enhanced the stability of Sn\(^{2+}\) and mitigated the heat-induced disproportionation decomposition during annealing, ultimately obtaining efficient Pero-LEDs with a maximum EQE (EQEmax) of 5.3%, accompanied by an extremely low roll-off.

Moreover, to address the challenge of rapid crystallization in tin-based perovskites, researchers have employed techniques such as incorporating Lewis basic molecules, solvent engineering, and precise spin-coating technology.\(^28\)–\(^30\) Deng et al.\(^31\) incorporated polyvinyl alcohol (PVA) molecules into FASnI\(_3\) perovskite precursors, establishing hydrogen bond interactions with I\(^-\) ions, which effectively retards the crystallization of perovskite and facilitates uniform film formation. Liu et al.\(^32\) added polyvinyl-vinyl acetate (EVA) to the antisolvent, which interacts with SnI\(_2\) to form Lewis acid–base complexes during nucleation. This slows the perovskite crystallization rate and regulates the growth direction of FASnI\(_3\) films. Additionally, the introduction of EVA can effectively prevent water and oxygen from penetrating the grain boundaries of the perovskite layer, leading to optimal PSCs with a PCE of 7.7%. More recently, Nasti et al.\(^33\) successfully formed a stable mesophase with SnI\(_2\) by replacing DMSO with 4-(tert-butyl) pyridine, resulting in the production of perovskite thin films with low defect density and PSC devices exhibiting high PCE up to 7.3%.

Although these efforts have made some progress in mitigating the oxidation and rapid crystallization of tin-based perovskites, it is notable that they heavily rely on foreign additives to address these issues. Moreover, the composition and chemical properties of solvent molecules are frequently overlooked. The selection of solvents directly impacts the quality and performance of perovskite films. Therefore, a comprehensive investigation into the interaction mechanism between solvents and perovskites is crucial for understanding their influence on film formation processes, providing systematic theoretical guidance to enhance film quality and enable high-performance device fabrication.

Herein, we investigated the interaction between solvent molecules and tin-based CsSnI\(_3\) perovskites, analyzed the underlying causes of their rapid oxidation and crystallization rates, and proposed a systematic solution. Our focus centered on four commonly used solvents, namely dimethyl sulfoxide (DMSO),...
N,N-dimethylformamide (DMF), N-methylpyrrolidine (NMP), and gamma-butyrolactone (GBL). Through a series of experiments, we demonstrated that the coordination ability between the solvent molecule and CsSnI₃ perovskite plays a crucial role in determining the quality of perovskite films. Based on the infrared analysis and calculations, we inferred that DMSO exhibits strong coordination with Sn²⁺, leading to their mainly existing as an intermediate phase of SnI₂·3DMSO in the perovskite precursor. By employing x-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV–vis absorption testing, we found that the strong coordination between DMSO and Sn²⁺ effectively inhibited the oxidation of Sn²⁺ and delayed perovskite crystallization. Leveraging these superior photoelectric properties, Pero-LED devices based on DMSO achieved an EQE of 5.6%, surpassing other solvents-based devices by 2–3 times. Additionally, these devices exhibited excellent electroluminescence (EL) stability and reproducibility. We believe that this research provides a systematic approach to effectively suppress oxidation and rapid crystallization of tin-based perovskite, offering valuable insights for the development and fabrication of highly efficient and stable tin-based Pero-LEDs.

2 | RESULTS AND DISCUSSION

2.1 | Characterization of molecular interactions

In theory, the majority of solvents utilized in perovskite film deposition are polar solvents containing robust electronegative polar groups (e.g., C=O, S=O, or P=O) within their molecular structure, exhibiting Lewis basicity. In solution and wet film, solvent molecules coordinate with Lewis acid perovskite precursor lattice to form intermediate phases, serving as protective barriers against oxidation and delaying crystallization.③ Fig. S1A depicts a schematic diagram illustrating the process of CsSnI₃ perovskite film preparation via mesophase generation, where X represents solvent molecules possessing Lewis alkaline properties. In this study, we employed four common polar solvents (DMSO, DMF, NMP, and GBL) to prepare the CsSnI₃ perovskite precursor. Their molecular structures are shown in Fig. S1B. To better understand the coordination capabilities of these solvents, we investigated their donor numbers (DNs), which measure the Lewis basicity of a molecule or its ability to donate a lone pair to Lewis acids.④ Among them, DMSO exhibited a relatively high DN value of 29.8 kcal mol⁻¹, while the DN values of NMP, DMF, and GBL decreased successively to 27.3, 26.6, and 18.0 kcal mol⁻¹, respectively (Fig. S1C). Therefore, we inferred that DMSO, with its high DN value, has stronger coordination with perovskite precursor substances.

To test this conjecture, we conducted Fourier transform infrared (FTIR) spectroscopy to investigate the interactions between different solvent molecules and perovskite precursor components. Fig. 1A and Fig. S2A showed the FTIR spectra of pure DMSO, DMSO + CsI, DMSO + SnI₂, and DMSO + CsI + SnI₂ solutions. The S=O stretching vibration peak of pure DMSO molecule is observed at 1042 cm⁻¹. The introduction of CsI has little effect on the vibration frequency of S=O, indicating a weak interaction between DMSO and CsI. However, when SnI₂ is added, the characteristic peak shifts to around 925 cm⁻¹, which signifies a strong interaction between SnI₂ and DMSO molecules due to the formation of a SnI₂·3DMSO adduct.⑤ This phenomenon can be attributed to the coordination bond formation between SnI₂ and the lone pair electrons of oxygen in the S=O bond, weakening the S=O bond strength and causing the shift toward lower frequencies in the stretching vibration. The FTIR spectra of pure DMF, DMF + CsI, DMF + SnI₂, and DMF + CsI + SnI₂ are presented in Fig. 1B and Fig. S2B. The C=O stretching vibration frequency of pure DMF is observed at 1660 cm⁻¹, and upon adding CsI, the stretching vibration frequency remains relatively unaffected. However, upon introducing SnI₂, a splitting peak at 1631 cm⁻¹ appears in the C=O region, indicating successful coordination between Sn²⁺ and DMF. The FTIR spectra of the four NMP-related solutions are presented in Fig. 1C and Fig. S2C, under identical experimental conditions. When only CsI is added, the vibration stretching peak of C=O is around 1668 cm⁻¹, almost consistent with the vibration stretching frequency of pure NMP at 1673 cm⁻¹. In contrast, SnI₂ + NMP shows a C=O splitting peak at 1616 cm⁻¹, which indicates that SnI₂ interacts with NMP. The FTIR spectra of the four GBL-related solutions are presented in Fig. 1D and Fig. S2D. Unlike the previous three solvents, the stretching vibration frequency of C=O remained almost unchanged (1760 cm⁻¹) when CsI and SnI₂ were dissolved separately in GBL. Only when both CsI and SnI₂ coexist can they be dissolved completely in GBL (Fig. S3).⑥ This indicated a very weak interaction between these two molecules and GBL solvent molecules.

It is essential to highlight the noteworthy observation that the stretching vibration frequency of S=O is nearly identical to that of SnI₂ + DMSO when CsI and SnI₂ are co-dissolved in DMSO. In contrast, the C=O stretching vibration frequency in DMF, NMP, and GBL remains almost the same as that of the corresponding pure solvent when CsI and SnI₂ coexist. This discrepancy makes us guess that the two solute molecules exist in different states within the solution. In the CsI + SnI₂ + DMSO
solution, a strong interaction force exists between Sn$^{2+}$ and DMSO molecules, favoring the existence of Sn$^{2+}$ as a stable intermediate phase SnI$_2$$\cdot$DMSO. In the other three solvents, the interaction force between SnI$_2$ and solvent molecules is lower than the ionic binding energy with CsI. As a result, SnI$_2$ is more likely to exist in the solvent as a free ion state.

To further investigate the interaction between the solvents and perovskite components, we employed density functional theory (DFT) to calculate the binding energies between CsI, SnI$_2$, and the four solvent molecules, respectively. The most stable molecular structures of SnI$_2$ and the four solvent molecules are depicted in Figure 1E–H. In parallel, Figure S4 showcases the most stable molecular structures of CsI along with the four solvent molecules. The corresponding interaction energies are comprehensively summarized in Table S1 and visually presented in Figure S5. The interaction energies of SnI$_2$ with DMSO, DMF, NMP, and GBL are −2.29, −2.10, −1.79, and −1.89 eV, respectively. Consistent with the FTIR results, our calculations reveal a robust interaction force between SnI$_2$ and DMSO molecules, forming a stable intermediate phase of SnI$_2$$\cdot$DMSO. This stable intermediate phase is promising to inhibit the oxidation of Sn$^{2+}$ and concurrently delay the perovskite crystallization process.

### 2.2 Effect of solvent on perovskite oxidation

To investigate the impact of various solvents on the oxidation of perovskite, we initially examined the oxidation of precursor solutions using different solvents. In previous experiments concerning tin-based perovskite precursor oxidation, changes in solution color have been conventionally employed to assess the degree of precursor oxidation. In the air, the precursor solution
undergoes a color change from yellow to brown over time due to the generation and accumulation of Sn^{4+}. It has been widely observed that Sn^{2+} is oxidized by oxygen in the air to form SnO_2 and SnI_4. The possible oxidation reaction is represented by Formula (1).

\[
2\text{SnI}_2 + O_2 = \text{SnI}_4 + \text{SnO}_2
\]  

(1)

Based on this, we prepared a 0.2 M CsSnI_3 precursor solution using DMSO, DMF, NMP, and GBL as solvents in sequence. Subsequently, the four solutions were simultaneously exposed to air with a humidity of approximately 50% for 40 min while monitoring their changes. As depicted in Figure 2A, extending the exposure time to ambient air leads to a noticeable outcome. In all four solutions, gradual oxidation initiates at the air/solution interface, resulting in a gradual darkening of their colors. Notably, the perovskite precursor solution with DMSO as the solvent exhibited remarkable antioxidant properties, with its surface color remaining almost unchanged even after 40 min of air exposure. In contrast, when the solutions prepared using the other three solvents were exposed to air for only 1 min, their yellow hue rapidly turned brown and darkened over time, indicating a significant amount of oxidation. We attributed this result to the strong interaction between SnI_2 and DMSO, which generates a stable mesophase that effectively inhibits the oxidation of Sn^{2+}. In contrast, the weak interaction force between DMF, NMP, and GBL molecules and SnI_2 results in a higher proportion of unprotected Sn^{2+} in the solution, rapidly oxidizing to Sn^{4+} in the presence of oxygen.

To further validate the conclusions, we utilized four types of CsSnI_3 solutions to fabricate thin films, and their oxidation properties were examined via XPS analysis. The XPS spectra of the four distinct perovskite films are depicted in Figure 2B–E. The figure illustrates that the Sn 3d_5/2 of CsSnI_3 perovskite films have two peak signals at
Effect of different solvents on crystallization rate of CsSnI$_3$. Ultraviolet–visible absorbance spectra of unannealed CsSnI$_3$ films with solvents of (A) DMSO, (B) DMF, (C) NMP, and (D) GBL at different times in the nitrogen-filled glovebox. Photoluminescence (PL) spectra of unannealed CsSnI$_3$ films with solvents of (E) DMSO, (F) DMF, (G) NMP, and (H) GBL at different times in the N$_2$-filled glovebox.

486.2 and 489.1 eV, corresponding to Sn$^{2+}$ and Sn$^{4+}$, respectively. We examined the influence of different solvents on perovskite oxidation by analyzing the Sn chemical states in the various films. It is evident that the concentration of Sn$^{2+}$ in the DMSO solvent is significantly higher, accounting for 70.89%. However, when perovskite films are prepared using DMF, NMP, and GBL solvents, the content of Sn$^{2+}$ is lower than that of Sn$^{4+}$, with percentages of 15.75%, 26.46%, and 25.82%, respectively. This finding aligns with the previously observed experimental results on solution oxidation. When used as a solvent, DMSO can effectively form a stable intermediate phase with Sn$^{2+}$, thereby inhibiting the oxidation of Sn$^{2+}$ and enhancing the quality of the film.

2.3 Effect of solvent on perovskite crystallization rate

The strength of the solvent-perovskite interaction has a significant impact on the crystallization rate of perovskite. Generally, a stronger interaction between solvent molecules and perovskite components leads to slower crystallization, as the formation of a stable intermediate phase retards perovskite crystallization. To test this hypothesis, we fabricated perovskite films using four different solvents and subjected them to unannealed conditions in a nitrogen-filled glove box for 25 min. The crystallization of the films was monitored through in-situ UV–vis absorption and fluorescence tests. Figure 3A–D show the ultraviolet absorption spectra of the perovskite film prepared using four solvents after being placed for 9 min. The absence of absorption and fluorescence peaks in the DMSO-based perovskite film after the spin coating is evident in Figure 3A,E. However, after 20 min, absorption and fluorescence peaks gradually emerged. Over time, the film’s absorption and fluorescence intensities increased, with a gradual redshift observed in the fluorescence peak, indicating the crystallization of CsSnI$_3$. Under identical conditions, the film prepared using DMF as the solvent showed the appearance of absorption and fluorescence peaks at the end of the spin coating (Figure 3D,F), and as time elapsed, the fluorescence intensity of CsSnI$_3$ gradually increased, accompanied by peak red shifting, indicating crystal growth. In contrast to DMF, the fluorescence intensity of CsSnI$_3$ films prepared using NMP did not change significantly (Figure 3C,G), suggesting that the perovskite film prepared with NMP as the solvent had essentially completed crystallized during the spin coating process. Under the condition of GBL as the solvent, the freshly coated perovskite film exhibited fluorescence and absorption at approximately 918 nm. As the placement time increased, the fluorescence intensity significantly increased, indicating rapid
crystal growth. Figure S6 depicts the film under unannealed conditions. It can be observed that at the end of the spin coating, the film prepared with DMSO as the solvent is transparent, while the other three films appear brown, which aligns with the above results.

We attribute this result to the difference in interphase stability. When DMSO is used as the solvent, the presence of a stable intermediate phase SnI2·3DMSO delays perovskite crystallization. As the placement time increases, the solvent gradually volatilizes, allowing CsSnI3 to begin crystallizing. In contrast, when using the other three solvents, the weak interaction between solvent and perovskite leads to rapid crystal growth during film preparation.

2.4 | Characterization of perovskite films

We initially characterized the optical properties of perovskite films prepared using various solvents. Figure 4A illustrates the steady-state fluorescence spectra of perovskite films prepared with four different solvents. It is evident that the photoluminescent peak of perovskite films prepared using these solvents is consistently located at 934 nm. Among these solvents, DMSO yields the highest luminous intensity, followed by DMF, GBL, and NMP, in decreasing order. The PLQVs of the films were also evaluated, showing a high consistency with the steady-state fluorescence results. The DMSO-based films exhibited the highest PLQV value of 10.4%, while those prepared using DMF, NMP, and GBL solvents showed lower values of 5.9%, 6.4%, and 5.4%, respectively. (Table S2)

This suggests that using DMSO as a solvent in film preparation leads to fewer defect states and inhibits nonradiative defect-assisted recombination. Figure S7 shows the SEM images of four kinds of perovskite films, and it can be seen that all four films exhibit dendritic structures. As reported previously, the dendritic structure facilitates balanced charge injection, which plays an important role in manufacturing efficient Pero-LEDs.43
Additionally, the perovskite films prepared using DMF, NMP, and GBL solvents exhibit larger grain sizes and higher coverage. This phenomenon is primarily attributed to the crystallization rate of perovskite during film formation. The faster the crystallization rate, the more likely it is to form a larger grain size. X-ray diffraction (XRD) data further support this conclusion. As shown in Figure 4B, CsSnI₃ films prepared with the four solvents show the same main peaks at 14.4° and 29.1°, corresponding to the (110) and (220) crystal faces of B-γ-CsSnI₃ (PDF#43–1162), respectively. In contrast to the film prepared with DMSO, the diffraction peaks in the other three thin films are more pronounced. This can be attributed to the smaller grain size of perovskite when DMSO is used as the solvent, as compared to the use of other solvents. The absorption spectra of DMSO, DMF, NMP, and GBL films display distinct absorption peaks at around 899 nm (Figure 4C). The absorption strength of DMSO-based films is lower than that of DMF, which is related to grain size and film coverage. Figure 8B shows the picture after the annealing of the four films. It can be observed that all four films appear brown, with the films prepared based on DMF having the deepest color, which is also consistent with the measured absorption spectra.

To further validate the impact of different solvent coordination capabilities on the quality of CsSnI₃ film, we conducted quantitative evaluations of defect state density within the films using space charge limited current (SCLC) tests. For this purpose, we fabricated electron-only devices with the following structure: indium tin oxide (ITO)/SnO₂/perovskite/B3PYMPM/LiF/Al. According to the device dark current density–voltage (J–V) curve, the corresponding voltage is defined as the defect-filling limit voltage (V_{TFL}) when the current density increases rapidly. The electron defect density of perovskite films can be calculated according to Formula (2):

\[ N_{\text{defects}} = 2\varepsilon_0 V_{\text{TFL}}/eL^2. \]  

Here, \( N_{\text{defects}} \) represents the defect state density of the film, \( \varepsilon \) denotes the relative dielectric constant of perovskite material, \( \varepsilon_0 \) is the dielectric constant of vacuum, \( V_{\text{TFL}} \) represents the defect filling limit voltage, \( e \) stands for elementary charge, \( L \) indicates the thickness of the perovskite film. From Figure 4D, it can be observed that the \( V_{\text{TFL}} \) of perovskite film prepared using DMSO as the solvent is 1.15 V, whereas the \( V_{\text{TFL}} \) of DMF, NMP, and GBL films successively increase to 1.75, 2.10, and 2.48 V, respectively. Correspondingly, the defect densities of the perovskite films are \( 3.68 \times 10^{17} \), \( 5.59 \times 10^{17} \), \( 6.71 \times 10^{17} \), and \( 7.93 \times 10^{17} \) cm\(^{-3} \), respectively. These results indicate that the density of defect states in perovskite films prepared with DMSO as the solvent is significantly reduced due to the strong interaction between Sn\(^{2+} \) and DMSO, which inhibits the formation of Sn vacancies and the oxidation of Sn\(^{2+} \). Consequently, the film exhibits a high PL and PLQY. These findings suggest that the defect state density in perovskite films prepared using DMSO as the solvent is significantly reduced due to the strong interaction between Sn\(^{2+} \) and DMSO within the films, which hinders the formation of Sn vacancies and oxidation of Sn\(^{2+} \). As a result, the film exhibits a strong PL peak and a high PLQY.

2.5 | Performance evaluation of Pero-LED devices

Pero-LED devices were fabricated using CsSnI₃ films prepared in different solvents, and their effects on device performance were investigated, with the device structure shown in Figure 5A. The corresponding energy level structure of the functional layer is depicted in Figure 5B, whose values were extracted from the literature. To accurately evaluate device performance, we conducted current density–voltage (J–V) and radiance–voltage (R–V) curve tests. As illustrated in Figure 5D,E, the DMSO-based device exhibits a higher current density, indicating more efficient carrier injection within the device. Furthermore, the radiation intensity of the DMSO-based device is significantly higher than that of DMF, NMP, and GBL-based devices due to the low defect density and high crystal quality of CsSnI₃ films. Conversely, the lower emission observed in DMF, NMP, and GBL devices may be attributed to the richer defect state density in CsSnI₃ film caused by the fast crystallization rate and oxidation of Sn\(^{2+} \) during the preparation process. Figure 5F presents the EQE–current density (EQE–J) curve of the devices, it can be seen that the DMSO-based device exhibits the highest EQE of 5.6%, 2–3 times higher than that of other samples in the same batch, along with a low-efficiency roll-off, remaining 91% of the EQE_{max} under a high current density of 190 mA cm\(^{-2} \). Moreover, the normalized EL spectra of devices prepared using the four solvents and driven by a 4 V are recorded in Figure 5C. It is evident from the experimental result that the primary emission peaks of all four devices are situated at 931 nm, accompanied by a subtle satellite peak at 951 nm, which remains unchanged despite variations in solvent. The appearance of the satellite peak may be attributed to slight differences in the lattice structures between the surface and bulk regions of the CsSnI₃ crystalline film. Furthermore, we also evaluated the EL stability of Pero-LEDs fabricated using DMSO, and the results are presented in Figure S9. As the driving voltage...
is increased from 1.6 to 4 V, the primary emission peak of the EL spectrum remains constant at 931 nm, indicating excellent EL stability.

We prepared several batches of Pero-LEDs based on four different solvents to evaluate the device’s reproducibility. As shown in the statistical results in Figure S10A–D, the average EQEs of Pero-LEDs prepared using DMSO, DMF, NMP, and GBL were 5.0%, 2.47%, 1.71%, and 1.73%, respectively. In addition, we attempted the utilization of mixed solvents containing DMSO and DMF for the fabrication of Pero-LEDs. However, as shown in Figure S11, the obtained performance was found to be inferior compared to Pero-LEDs fabricated using the pure DMSO solvent. This result demonstrates the excellent reproducibility and high EQE of Pero-LEDs fabricated using DMSO, achieving up to 5.6%. Meanwhile, we tested the lifetime (T_{50}) of Pero-LEDs prepared with various solvents at a constant current density of 20 mA cm^{-2}. The results are shown in Figure S12, where the Pero-LED devices based on DMSO exhibited an impressive lifetime of 1475 minutes (T_{50}), surpassing other devices by 2–7 times. Our CsSnI_{3}-based devices, with an emission peak at 931 nm, successfully avoid the “red burst” phenomenon in lead-based NIR Pero-LEDs. (“Red burst” phenomenon refers to the undesired presence of visible red light in NIR LEDs.) This is crucial for applications like night vision cameras, facial recognition, iris recognition, communications, and biomedical devices. As summarized in Table S3, our work stands out as it represents one of the most efficient NIR Pero-LEDs without the presence of “red burst”. This achievement underscores the potential of our research and the promising direction it represents in the field of lead-free Pero-LEDs.

3 | CONCLUSION

In summary, our study has highlighted the critical role of solvent coordination in determining the quality of perovskite films. Through a series of experiments, we have uncovered that DMSO, as a solvent with strong coordination ability, formed a stable intermediate phase SnI_{2}·3DMSO with SnI_{2} in the perovskite precursor solution. This effectively inhibited the oxidation of Sn^{2+} and delayed the crystallization process of perovskite, resulting in improved crystal quality. Compared to films with DMF, NMP, and GBL solvents, CsSnI_{3} films produced
using DMSO exhibit a higher Sn\(^{2+}/Sn^{4+}\) ratio and slower crystallization rate. Consequently, the film possesses superior photoelectric properties, indicated by increased PLQY values and lower defect state density. Due to its superior photoelectric properties, the Pero-LED devices based on DMSO films exhibited an EQE of 5.6%, which surpassed that of other solvents-based devices by 2-3 times. Furthermore, these devices exhibited excellent EL stability and reproducibility. The results indicate that solvents with strong Lewis's alkalinity are anticipated to establish a stable mesophase with perovskite components, facilitating the production of high-quality perovskite films. We firmly believe that our research provides a methodological foundation for the development and preparation of highly efficient and stable tin-based Pero-LEDs. The insights gained from this work have the potential to pave the way for the advancement of environmentally friendly and commercially viable LED technologies using lead-free perovskite materials.

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CONFLICT OF INTEREST STATEMENT
The authors declare no conflicts of interest.

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REFERENCES


**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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