1. Introduction

Metal halide perovskites (MHPs) have emerged as a novel class of revolutionary semiconductor arisen from their amazing optoelectrical properties including long carrier diffusion length and high defect tolerance. The successive breakthroughs in perovskite solar cells have promoted the progress of MHPs in other optoelectronic applications, such as light-emitting diodes (LEDs), photodetectors, field-effect transistors, and lasers. In particular, halide perovskite LEDs (PeLEDs) have exhibited unprecedented performances. Since the first report of room temperature PeLEDs in 2014, the external quantum efficiency (EQE) of green and red/infrared PeLEDs devices has risen from <1% to >20% and the late-developed blue PeLEDs also exceeds 12.3%. In addition to high EQEs, light-emitting MHPs offer numerous advantages, such as tunable emission wavelength from ultraviolet to near-infrared, narrow emission linewidth, and intrinsically high photoluminescence quantum yields (PLQYs). These features indicate that MHPs have the potential to become one of the most promising candidates in next-generation display and lighting. Currently, different halide perovskite materials such as perovskite nanocrystals (NCs), quasi-2D perovskite, and perovskite embedded polymer composite films have been used as emissive layers. CsPbI$_3$ NCs which emit red light are an essential part of the family of perovskite NCs to cover the entire visible spectrum. While there are advances in the EQEs and PLQYs, the grand challenge of red-color PeLEDs is the operational stability because of the easy transformation from cubic to orthorhombic structure and the weak bond energy between inorganic surface and long-chain capping ligands. Several strategies have been reported to improve CsPbI$_3$ NC’s stability, such as doping, small-molecule ligands, and core–shell structure. The stability of LED is generally evaluated by $T_{50}$, that is, the elapsed time for devices decaying to 50% of their initial electroluminescence (EL) intensity. Currently, the $T_{50}$ values of most of reported red PeLEDs are less than 10 h, which is far behind the commercialized organic LEDs with over 6 × 10$^6$ h. The long-term operational stability of perovskite light-emitting diodes (PeLEDs), especially red PeLEDs with only several hours typically, has always faced great challenges. Stable β-CsPbI$_3$ nanocrystals (NCs) are demonstrated for highly efficient and stable red-emitting PeLEDs through incorporation of poly(maleic anhydride-alt-1-octadecene) (PMA) in synthesizing the NCs. The PMA can chemically interact with PbI$_2$ in the precursors via the coupling effect between O groups in PMA and Pb$^{2+}$ to favor crystallization of stable β-CsPbI$_3$ NCs. Meanwhile, the cross-linked PMA significantly reduces the PbCs anti-site defect on the surface of the β-CsPbI$_3$ NCs. Benefiting from the improved crystal phase quality, the photoluminescence quantum yield for β-CsPbI$_3$ NCs films remarkably increases from 34% to 89%. The corresponding red-emitting PeLEDs achieves a high external quantum efficiency of 17.8% and superior operational stability with the lifetime, the time to half the initial electroluminescence intensity ($T_{50}$) reaching 317 h at a constant current density of 30 mA cm$^{-2}$.
In this work, we demonstrated highly efficient deep red-emitting PeLEDs with EQE of 17.8% and excellent operational stability of 317 h by adopting thermodynamically stable tetragonal phase CsPbI₃ (β-CsPbI₃) NCs as the emitting layer. The stable β-CsPbI₃ was successfully synthesized via incorporating the poly(maleic anhydride-alt-1-octadecene) (PMA) into the precursor. The PMA can interact with PbI₂ in the precursors to regulate the crystalization kinetics of β-CsPbI₃ NCs and finally adsorb on the surface of β-CsPbI₃ NCs through strong Pb-O bond to significantly stabilize the β-CsPbI₃ NCs without any crystalline deformation on the NCs crystal structure. Additionally, these chemically crosslinked PMA also significantly reduces deep defects of PbCs via increasing the formation energy and passivating the PbCs deep defects. Moreover, the PMA-incorporating β-CsPbI₃ NCs exhibit increasing exciton binding energy and reducing longitudinal-optical (LO) phonon energy. Benefiting from the improved crystal phase quality with PMA incorporation, the PLQY of β-CsPbI₃ NCs yields an increase from 34% to 89%. The corresponding PeLEDs achieve a high EQE of 17.8% and exhibited superior operational stability with $T_{50}$ of 317 h.

2. Results and Discussion

2.1. Crystal Structure Characterization of Thermodynamically Stable Colloidal β-CsPbI₃ NCs

The PMA was used to chemically interact with PbI₂ in the precursor solution and help to crystallize thermodynamically stable β-CsPbI₃ NCs (hereafter denoted as PMA-NCs), as shown in Figure 1a. The detailed synthesis route and purification processes are illustrated in Figure S1, Supporting Information and Section 4. With PMA incorporation, the as-synthesized β-CsPbI₃ NCs solution exhibits improved phase stability, which does not show any signs related to the phase transition after storing in octane solution for a month (Figure 1b). The powders can even be kept in water for a few minutes (Figure S2, Supporting Information). However, the β-CsPbI₃ NCs without PMA incorporation (hereafter denoted as pristine NCs) begin to transform to the non-photoactive yellow phase within 2 days under the same conditions and completely turn to δ-CsPbI₃ in a week.

X-ray diffraction (XRD) was performed on as-synthesized β-CsPbI₃ NCs to confirm their crystal structures. Both pristine NCs and PMA-NCs exhibit strong peaks at 14.2° and 28.6° (Figure 1c), which are assigned to the (110) and (220) reflections of tetragonal phase CsPbI₃, respectively. The obvious (111) reflection is observed for the PMA-NCs sample, suggesting that the incorporated PMA can regulate the crystallization and growth of β-CsPbI₃ NCs. Meanwhile, the incorporated PMA has a negligible effect on UV–vis absorption. Both pristine NCs and PMA-NCs show an absorbance edge ≈690 nm (Figure S3, Supporting Information) and a bandgap of 1.79 eV as determined from a Tauc plot (Figure S4, Supporting Information). The full width at half maximum (FWHM) values obtained from the Gaussian fitting of the PL spectra are 38.6 and 38.2 nm with corresponding PL peak of 690 and 689 nm for pristine- and PMA-NCs, respectively.

![Figure 1. Crystal structure of thermodynamically stable β-CsPbI₃ NCs. a) Schematic diagram of the PMA-incorporating β-CsPbI₃ NCs, OA: oleic acid, OAm: oleylamine. b) Comparison of the aged colloidal β-CsPbI₃ NCs with and without PMA incorporation. c) XRD spectra of pristine NCs and PMA-NCs films; the standard α-, β-, γ-CsPbI₃ XRD pattern calculated for Cu Ka radiation determined by Marronnier et al. a.u., arbitrary units. d,e) TEM images of twice-washed NCs: d) pristine NCs, e) PMA-NCs. The scale bars denote 20 nm. The insets are the corresponding enlarged HRTEM images, the scale bars in the inset image represent 5 nm.](https://www.advancedsciencenews.com/content/2100882)
The transmission electron microscopy (TEM) was further used to investigate the detailed microstructure of these \( \beta\)-CsPbI\(_3\) NCs (Figure 1d,e and Figure S5, Supporting Information). The average particle size of pristine NCs is 21.3 nm. The incorporated PMA confines the NCs’ growth. With PMA incorporation, all \( \beta\)-CsPbI\(_3\) NCs exhibits significantly reduced grain size (Figure S5, Supporting Information). Moreover, the particle size of those \( \beta\)-CsPbI\(_3\) NCs also strongly depends on the contents of incorporated PMA. Here, according to PLQY results in Figure S6, Supporting Information, the optimal quality ratio of PMA to Pbl\(_2\) is two and the corresponding grain size is 13.5 ± 2.7 nm. The reduced NC size favors quantum confinement, which is beneficial to LEDs with high EL performance.[28]

The high-resolution TEM (HRTEM) images indicate that the pristine-NCs exhibit the lattice fringes with \( \approx 0.63 \text{nm} \), assigned to the (110) plane of \( \beta\)-CsPbI\(_3\), while there are 0.63 and 0.44nm for the PMA-NCs sample related to (110) and (111) planes for the \( \beta\)-CsPbI\(_3\) (Figure S7, Supporting Information). These results are well consistent with the above XRD results. The blurring edge of pristine NCs in Figure 1d indicates that, although the crystalline structures form, the pristine NCs surfaces are obviously deformed originating from the weak bond energy between the CsPbI\(_3\) NCs surface and the long-chain capping ligands (OA and OAm).[29] We also provide the TEM of once-washed pristine NCs which shows better morphology to confirm the loss of ligands and its influence on the pristine NCs surfaces, as shown in Figure S8, Supporting Information. In contrast, the PMA-NCs maintain high-quality tetragonal morphology (Figure 1e) even with a twice-washed process, implying that PMA can stabilize the tetragonal phase CsPbI\(_3\) NCs without any crystalline deformation on the NCs crystal structure. Overall, we have successfully synthesized highly thermodynamically stable \( \beta\)-CsPbI\(_3\) NCs with smaller NCs’ size through the incorporation of PMA.

### 2.2. Device Performances

Scanning electron microscopy (SEM) was used to investigate the NCs thin films prepared by spin-coating as-synthesized NCs on the poly(4-butylphenyldiphenylamine) (poly-TPD) substrate. Because of the aggregation of pristine NCs, some obvious holes/voids are observed on the pristine \( \beta\)-CsPbI\(_3\) NCs thin films (Figure 2a). In contrast, the PMA-NCs thin films show compact morphology without any clear pin-holes (Figure 2b) because of the better dispersion arisen from PMA surface ligand. To further overcome the film coverage issue, \( \beta\)-CsPbI\(_3\) NCs thin films are sequentially spin-coated twice for both pristine NCs and PMA-NCs in device fabrication to reduce the possible current leakage. As shown from the atomic force microscopy (AFM) images in Figure S9, Supporting Information, both the final NCs films without and with PMA incorporation can fully cover the underlayer after twice spin-coating.

We fabricated PeLEDs with device configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PS)/poly-TPD/\( \beta\)-CsPbI\(_3\) NCs/tris-(1-phenyl-1H-benzimidazole) (TPBi)/lithium fluoride (LiF)/Al, as shown in Figure S10, Supporting Information. Figure 2c shows the champion devices’ normalized EL spectra at 5 V. The peak wavelengths are 690 nm for pristine NCs and 689 nm for PMA-NCs devices. Under different applied voltages, both PeLEDs exhibit stable spectra (Figure S11, Supporting Information), and no emission can be observed from the carrier transport layers of poly-TPD or TPBi, indicating that the injected carriers are effectively recombined in the \( \beta\)-CsPbI\(_3\) NCs emission layer rather than in the carrier transport layers. Because of the narrow FWHM of the EL spectra of \( \approx 37 \text{nm} \) for both pristine and PMA-NCs based PeLEDs, high color purities can be obtained from these PeLEDs, with CIE coordinates of (0.17, 0.276) for pristine NCs and (0.721, 0.275) for PMA-NCs based PeLEDs, which exceeds the ITU-R Recommendation BT.2020 color space recommended for ultra HD TVs (Figure S12, Supporting Information).

Figure 2d shows the current density–voltage–luminance curves. The PMA-NCs red LEDs exhibited lower turn-on voltages compared to pristine NCs LEDs, which is attributed to the highly efficient, reduced-barrier-charge injection[30] and the decreased surface traps in PMA-NCs, which will be discussed later.[31] The maximum luminance is 58 cd m\(^{-2}\) for pristine NCs based PeLEDs and 618 cd m\(^{-2}\) for PMA-NCs based PeLEDs. Compared to the pristine-NCs with a peak EQE of 3.2%, the PMA-NCs device shows a peak EQE of 17.8%, which is highest in the currently reported phase pure CsPbI\(_3\) based PeLEDs (Figure 2e and Table S1, Supporting Information). Such significantly improved performance for the PMA-NCs based PeLEDs can be attributed to the combined effects of higher-quality film, unspoiled emission properties, and improved carrier balance.

The poor EL performance in the pristine NCs based PeLEDs may be attributed to the poor NCs films quality, as shown in Figure S13, Supporting Information.

The operational emission stability for unencapsulated pristine-NCs and PMA-NCs based PeLEDs is further investigated inside a nitrogen-filled glove box, as shown in Figure 2g. The pristine-NCs based PeLEDs drops rapidly and exhibits an operational lifetime \( L_{50} \) of 5.1 h, which is comparable to previously reported stable CsPbI\(_3\) based PeLED.[32] Remarkably, the PMA-NCs based PeLEDs show superior operational stability with a greatly extended \( T_{50} \) of 317 h at a constant current density of 30 mA cm\(^{-2}\), which is much longer than the red PeLEDs currently reported (Table S2, Supporting Information). It should be noted that there is a gradual increment in the first 10 h. Such increasing performance can be attributed to the defect self-healing behavior under electric fields.[33] In the beginning, the defects in the device will decrease because of the self-healing under electric fields, leading to the gradual increment of performance.[34,35] Figure 2f further shows the time dependence of EL spectra. The PMA-NCs based PeLEDs exhibits stable spectra throughout the stability testing. We also record a video clip about half an hour for an emitting PMA-NCs based PeLEDs, as shown in the Movie S1, Supporting Information.

### 2.3. Effects of the Incorporated PMA on the \( \beta\)-CsPbI\(_3\) NCs

The PeLEDs with PMA-incorporating \( \beta\)-CsPbI\(_3\) NCs as emissive layer achieves significantly improved EL performance and operational stability. Fourier-transform infrared spectroscopy (FTIR) was first performed on pristine-NCs and PMA-NCs thin films to investigate the interaction effect between PMA
and β-CsPbI₃ NCs. Figure 3a shows the molecular structure of OAm, OA, and PMA ligands used during NCs’ synthesis. Compared to pristine NCs, a distinctive peak related to C=O stretching vibration was observed at 1700 cm⁻¹ for PMA-NCs samples (Figure 3b and Figure S14, Supporting Information). We further investigated the precursor solutions step-by-step to confirm the formation and origin of C=O stretching and the bonding of the ligands with the β-CsPbI₃ NCs. After PbI₂ and OAm were dispersed in octadecene (ODE) (Figure S15, Supporting Information), both N–H stretching (3400–3300 cm⁻¹) and bending (1650–1580 cm⁻¹) vibration peaks from pristine OAm disappeared in the FTIR spectrum because of the acid–base interaction between OAm and iodides. The OA was subsequently added to the previous PbI₂ and OAm mixture solution and a clean precursor solution was obtained in which the PbI₂ was fully dissolved (Figure S16, Supporting Information). Interestingly, there are no signs related to the C=O vibration peak at 1700 cm⁻¹ of OA (red line in Figure S14, Supporting Information) in the mixture PbI₂–OAm–OA precursor. A similar feature can be also observed in the pure OA–OAm mixture, as the purple line shown in Figure S14, Supporting Information. These results imply the potential facile coordination between OA and OAm through their headgroup interactions. However, after adding PMA into the precursor, the solution always retains...
clean and exhibits a yellowish color (Figure S16, Supporting Information), indicating a strong interaction/reaction between PMA and PbI₂ in the precursor. The calculation results on bond energy between OA, OAm, PMA, and Pb²⁺ in Figure S17, Supporting Information show that there is stronger bond energy between PMA and Pb²⁺ in comparison with OA and OAm. Furthermore, the C=O stretching peak was observed in the FTIR spectrum of the PMA-added precursor, as the red line shown in Figure S18, Supporting Information. All of these results indicate that the C=O peak in the initial PMA-NCs thin film is from the PMA interacting with β-CsPbI₃ NCs. Interestingly, even though all these samples were washed twice, the distinctive vibration peak still presents, indicating a strong interaction between the PMA and β-CsPbI₃ NCs through a strong Pb=O bond. This was also confirmed by X-ray photoelectron spectroscopy. Figure S19, Supporting Information shows that Pb 4f and N 1s both shift to lower binding energies while the O 1s shifts to higher binding energy compared to pristine NCs, indicating that the electron density around Pb and N atom increases and that around the O atom decreases. This reveals that the electron lone pairs on the O of PMA can replace that on N of OAm and donate to Pb forming stronger coordination bonds.

The ¹H nuclear magnetic resonance (¹H NMR) measurement was further carried out on the dry NCs sample to identify the interaction between the PMA and NCs surface, as shown in Figure 3c, Figures S20 and S21, Supporting Information. All test samples have gone through twice purification processes and then re-dispersed in the toluene-d₈ solvent. The chemical shift region of the alkene resonance peaks ranges from 5.4 to 5.7 ppm (Figure 3c; Figure S20, Supporting Information). Compared to the pure OAm and OA corresponding to 5.30 and 5.29 ppm, respectively (Figure S21, Supporting Information), the alkene resonance peaks in the pristine NCs has an obvious chemical shift toward lower-field, that is, higher ppm at about 5.5. Such alkene resonance can be attributed to the formed oleylammonium oleate ligands by deprotonation reaction between OAm and OA adsorbed on the NCs' surface.[38,39] Furthermore, the doublet signals of pristine NCs can be deconvoluted into two well-resolved regions. One is the weaker and broadened peak at 5.51 ppm originating from the bound ligands of oleylammonium oleate (from OA and OAm) with NCs; the other sharp peak located at 5.50 ppm can be related to the unbound free OAm and/or OA ligands.[39,40] However, in the case of PMA-NCs, the alkene resonance features the shift of singlet peak to low-field (5.55 ppm), indicating the lower electronic cloud density of octadecene chains on PMA-NCs than that on pristine-NCs. It further confirms that PMA strongly interacts with β-CsPbI₃ NCs. The much-broadened peak at high-fields (1–2 ppm) in the ¹H NMR spectrum of PMA-NCs should arise from the functional groups in polymerized PMA (Figure 3c; Figure S21, Supporting Information).

The comprehensive results evidenced that, after incorporating the PMA into the precursors, the PMA can preferentially interact with PbI₂ to regulate the crystallization kinetic and further realize the desired growth of β-CsPbI₃ NCs. Because of the strong bonding energy of the Pb=O bond, the PMA would eventually be retained on the NCs' surface to stabilize β-CsPbI₃ (Figure 1a). In fact, the amphiphilic nature and large steric
hindrance of PMA lead to the formation hydrophobicity layer, which can prevent direct attacking of polar solvents during the purification process.

Interestingly, the incorporated PMA can significantly improve the absolute PLQYs of NCs thin films (deposited on quartz substrates). The PMA-NCs thin film exhibits almost three-fold enhancement in QY with a value reaching 89% as compared to the pristine NCs thin film with QY of 34% (Figure S6, Supporting Information). To further investigate the radiative mechanism of the improved PLQY of PMA-NC thin films, time-resolved PL (TRPL) was performed on the pristine- and PMA-NCs thin films. The TRPL decay curves are well described by a tri-exponential decay fitting with one fast and two slower components, the detailed parameters are listed in Table S3, Supporting Information. The fast decay component (τ₁) is related to the carrier trapping by defects at the NCs' surface,[41] τ₂ is related to the radiative recombination of free carriers, and τ₃ is related to the polycrystallinity of thin films.[42,43] The fraction of the trapping-related component (f₁; Table S3, Supporting Information) in PMA-NCs (7.7%) is only about half of the pristine NCs (14.1%), indicating that the incorporated PMA offers a significant inhibition/healing effect on the defects in CsPbI₃ NCs.

Considering that PMA can interact with Pb²⁺, we then investigate three Pb-related surface defects in the β-CsPbI₃ NCs, two anti-sites (PbCs and PbI) and one interstitial (Pb int) (Figure 3e,f; Figure S22, Supporting Information), which are recognized as non-radiative recombination centers.[44,45] Compared to the Pb int, the two anti-sites (Pb Cs and Pb I) are found to have deep defect levels in the bandgap, which can trap charge carriers (Figure 3e; Figures S23 and S25, Supporting Information). Under Pb rich conditions, the formation energy of PbCs is 1.38 eV in comparison with 2.02 eV of PbI and 2.18 eV of Pb int, while the formation energies are 2.39, 5.02, and 4.19 eV for PbCs, PbI, and Pb int, respectively, under I rich condition. These results show that detrimental Pb Cs are the dominant Pb-related defects on β-CsPbI₃ NCs surface. However, the incorporated PMA not only increases the formation energy of PbCs from 1.38 to 1.75 eV but also passivates the defect levels of Pb Cs in the bandgap (Figure 3f). The effect of PMA on the defect levels of PbI and Pb int defects can be found in the Supporting Information (Figures S24 and S26, Supporting Information).

Overall, these results reveal that both CsPbI₃ NCs synthesized with and without PMA incorporation could exhibit strong emission properties. Very differently, the incorporated PMA not only improves the stability of β-CsPbI₃ NCs but also reduce the deep defect levels of PbCs in NCs. The enhanced stable β-CsPbI₃ with reduced defects would be beneficial to the significantly improved EL performance.

We further investigated the exciton binding energy and electron-phonon interaction to explain the improvement in EL performance and operational stability for the PeLEDs. The PL peak wavelength shift in Figure 4a,b indicates that the bandgap energy of the β-CsPbI₃ NCs increases as temperature.
increases, possibly originating from band renormalization by LO phonon. The PL peak intensity gradually decreases and the spectral linewidth broadens when the temperature increases from 77 to 300K (Figure 4a). The decreased PL intensity for both pristine NCs and PMA-NCs should be attributed to the thermal quenching originated from non-radiative traps. However, the pristine NCs exhibits noticeable thermal quenching even at lower temperatures (Figure 4a). This can be explained that the hot carriers are not only thermalized to the band-edge state but also trapped in deep defect states.

These results further confirm that the PMA incorporation can efficiently suppress the defects in PMA-NCs, therefore lead to high PLQY in PMA-NCs.

Considering that the decrease in PL intensity is caused by thermal quenching from non-radiative traps, the temperature-dependent integrated PL intensity \( I(T) \) in Figure 3c can be fitted with the Arrhenius equation:\[^{48}\]

\[
I(T) = \frac{I_0}{1 + A e^{-E_b/k_B T}}
\]

where \( I_0 \) is the PL intensity at 0 K, \( E_b \) is the exciton binding energy, \( A \) is the pre-exponential coefficient, and \( k_B \) is the Boltzmann constant. The extracted binding energy \( E_b \) is 32.6 ± 5.4 and 59.6 ± 8.8 meV for pristine NCs and PMA-NCs thin films, respectively. The higher binding energy of PMA-NCs indicates a probability reduction for excitons dissociation into free carriers without radiation, which makes it a very excellent candidate for LEDs.

The variation of full-width-half-maximum PL linewidth as functions of temperature are displayed in Figure 4d and fitted using the independent Boson model:\[^{49}\]

\[
\Gamma(T) = \Gamma_{inh} + \sigma T + \frac{\Gamma_{LO}}{e^{E_{LO}/k_B T} - 1}
\]

in which the \( \Gamma_{inh} \) is the inhomogeneous broadening coefficient that related to the size, shape, and composition of the perovskite NCs, \( \sigma \) is the exciton-acoustic phonon coupling coefficient, \( \Gamma_{LO} \) denotes the exciton-LO phonon coupling coefficient, and \( E_{LO} \) represents the LO phonon energy. Since exciton–phonon interaction is dominated by the acoustic phonons in the low-temperature range (<100 K) and dominated by high energy LO phonons in the high-temperature region, the measured FWHM data was fitted, which was represented by the solid lines shown in Figure 4e. It is found that \( \Gamma_{inh} = 47.7 ± 1.3 \) meV, \( \Gamma_{LO} = 166.4 ± 36.3 \) meV, and \( E_{LO} = 378 ± 4.5 \) meV for pristine NCs. Accordingly, \( \Gamma_{inh} = 39.3 ± 2.9 \) meV, \( \Gamma_{LO} = 52.7 ± 16.9 \) meV, and \( E_{LO} = 16.9 ± 4.4 \) meV were extracted for PMA-NCs. In the same temperature range, as the temperature continues to increase, the smaller variation in PL intensity of PMA-NCs indicates that the excitons in PMA-NCs are less affected by lattice vibrations. Compared to pristine NCs, both exciton-LO phonon coupling coefficient \( \Gamma_{LO} \) and LO phonon energy \( E_{LO} \) in PMA-NCs are significantly reduced, indicating that the vibration of the PbI\(_6\) octahedra cage in PMA-NCs is associated with much smaller energies. Theoretically, the \( E_{LO} \) is expected to be negligibly small due to the near-identical spatial dependence of electron and hole wavefunctions in a confined NCs system.

Meanwhile, at elevated temperatures above 150 K, the phonon-assisted thermal escape of excited carriers out of luminescing states plays an important role, as illustrated in Figure S27, Supporting Information. The reduced LO phonon energy \( E_{LO} \) of PMA-NCs predicts that the placement of non-luminescing energy state above the lowest radiative excitonic state is lower as compared to pristine NCs. Subsequently, thermal assisted exciton–phonon scattering reduces in PMA-NCs. This result can reflect that the PL intensity is less sensitive to temperature increment in PMA-NCs (Figure 4c), therefore contributing to the excellent operational stability in PMA-NCs PeLEDs. Overall, along with the colloidal stability improvement, the increased exciton binding energy and reduced LO phonon energy confirm that the incorporated PMA on the surface of \( \beta \)-CsPbI\(_3\) NCs can significantly increase the population of excitation generated electron–hole pairs in the luminescing states and prevent them from quenching through exciton–phonon scatterings.

### 3. Conclusion

In summary, we have successfully synthesized highly thermodynamic stable \( \beta \)-CsPbI\(_3\) NCs via introducing the PMA into the precursor. The incorporated PMA regulates the crystallization kinetics of \( \beta \)-CsPbI\(_3\) NCs via interacting with PbI\(_2\) in the precursors, confines the NCs grain morphology and size, and enhances the colloidal and phase stability of NCs. Moreover, the incorporated PMA reduces the deep defect levels of PbCs in NCs. Meanwhile, the \( \beta \)-CsPbI\(_3\) NCs with PMA incorporation exhibited significantly increased exciton binding energy and reduced LO phonon energy. Benefit from these improvements, the PLQYs for \( \beta \)-CsPbI\(_3\) NCs yield increases from 34% to 89%. Moreover, we achieve highly efficient and stable red-emitting CsPbI\(_3\) PeLEDs with a high peak EQE of 128% and a long operational lifetime of 317 h.

### 4. Experimental Section

**Materials:** Cesium carbonate (Cs\(_2\)CO\(_3\), 99.9%), 1-octadecene (ODE, 90%), n-octane (99%), methyl acetate (MeOAc, 99%), and oleylamine (OAm) were purchased from J&K Scientific. Poly(maleic anhydride-alt-1-octadecene) (PMA) and oleic acid (OA, 90%) were purchased from Sigma Aldrich. PbI\(_2\) (99.9%) was purchased from TCI.

**Synthesis of Cs-Oleate:** Cs\(_2\)CO\(_3\) (0.814 g), OA (3 mL), and ODE (30 mL) were loaded to a 100 mL three-necked flask with slow heating from room temperature to 100 °C under vacuum for 30 min. The mixture was heated to about 150 °C until the Cs\(_2\)CO\(_3\) was fully dissolved under a continuous flow of N\(_2\).

**Synthesis of Pristine and PMA CsPbI\(_3\) Nanocrystals:** PbI\(_2\) (0.173 g), ODE (10 mL) were added to a 50 mL three-necked flask. For CsPbI\(_3\) NCs with PMA incorporation, 0.346 g PMA (2:1 weight ratio to PbI\(_2\)) was added to the flask at this step. The mixture was heated to 120 °C under vacuum for 1 h. The reaction was then cooled to 15 °C under vacuum. The mixture was then cooled to 15 °C and aged for 1 h. The aged mixture was centrifuged, and the supernatant was removed. The precipitate was washed with ethanol (3 mL) and acetone (3 mL) to remove any remaining surfactant and PbI\(_2\).

**Synthesis of PMA Incorporation:** A solution of PbI\(_2\) (0.173 g) and Cs\(_2\)CO\(_3\) (0.814 g) in ODE (30 mL) was prepared. The solution was heated to 160 °C under vacuum for 1 h. The mixture was then cooled to 15 °C and aged for 1 h. The aged mixture was centrifuged, and the supernatant was removed. The precipitate was washed with ethanol (3 mL) and acetone (3 mL) to remove any remaining surfactant and PbI\(_2\).
Purification of Pristine and PMA CsPbI₃ Nanocrystals: 10 mL MeOAc was first added to the crude solution. The mixture was then transferred to centrifuge tubes and centrifuged at 16,000 rpm for 10 min. The as-prepared precipitate was re-dispersed in 2 mL n-octane. 6 mL MeOAc was further added to the solution. The mixture was centrifuged at 6000 rpm for another 10 min. The as-achieved precipitate was dispersed in 1.5 mL n-octane for characterization and device fabrication.

Characterizations: XRD patterns were obtained from a Bruker D2 PHASER X-ray diffractometer equipped with a copper X-ray source (λ = 1.5406 Å). Scanning transmission electron microscope was performed on an FEI Tecnai G2 20 S-TWIN that was equipped with energy-dispersive X-ray spectroscopy. Samples were prepared by dropping the tenfold diluted CsPbI₃ NCs solution on the copper mesh grids followed by slow evaporation of the octane solvents in the air. Steady-state and TRPL were recorded with a PicoQuant Fluotime 300 spectrometer and a laser diode with a peak wavelength of 510 nm was used as the excitation source. Thin films deposited on cleaned quartz substrates were used for these PL measurements. PLQYs were also determined from the thin films using the Fluotime 300 spectrometer coupled with an integrating sphere. The UV–vis absorption spectra were measured using a home-built system with a Newport Xe-lamp light source and Ocean Optics QE Pro spectrometer. FTIR spectra were measured by a JASCO FT/IR-6600 spectrometer. FTIR of the CsPbI₃ NCs was measured using condensed thick films while FTIR of precursors was measured using the solution. The ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz Ultrashield NMR spectrometer. CsPbI₃ NCs were purified twice and dried for 2 days in the glove box before dispersing in 1.5 mL n-octane. 6 mL MeOAc was then added to the crude solution. The mixture was then transferred to a home-built system with a Newport Xe-lamp light source and Ocean Optics QE Pro spectrometer. FTIR of the CsPbI₃ NCs was measured using condensed thick films while FTIR of precursors was measured using the solution. The ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz Ultrashield NMR spectrometer. CsPbI₃ NCs were purified twice and dried for 2 days in the glove box before dispersing in the toluene-d₄ (with a concentration of about 10 mg mL⁻¹) for ¹H NMR measurements. OA, OAam, and PMA were directly diluted in toluene-d₄ for ¹H NMR measurements. Temperature-dependent PL was performed with a Bruker D2 PHASER X-ray diffractometer equipped with a copper X-ray source -octane for characterization and device fabrication.

PeLED Fabrication and Characterization: The indium tin oxide (ITO) coated glass substrates were sequentially cleaned with detergent, deionized water, acetone, and ethanol by ultrasonic spin cleaning. The cleaned substrates were dried with N₂ flow and then treated by UV–ozone. Subsequently, TPBi (35 nm), LiF (1 nm), and Al (120 nm) were deposited by thermal evaporation under high vacuum (≈ 10⁻⁵ Pa). The active area of the PeLED was 4.25 mm², defined by the intersection of ITO and Al strips. The PeLEDs were characterized in the ITO and Al strips.

Computational Methods: All the geometric optimization and static calculation were performed with gamma point only, semi-local PBE functional was implemented in CP2K[P7,P8]. The basis set was a double zeta valence polarization basis set optimized on molecular geometries (shorter range)[P9,P10] and the energy cutoff was 600 Ry. 4-layer 3 × 3 tetragonal β-phase perovskite slab model was used for the simulation, the vacuum length was 30 Å, and surface dipole correction was applied.

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.

Data Availability Statement
Research data are not shared.

Keywords
nanocrystals, operational stability, perovskite light-emitting diodes, β-CsPbI₃

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