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Introduction

Due to their superior optical and electrical properties, such as high absorption coefficients, long diffusion length, high mobility and tunable bandgaps, metal halide perovskites have gained significant attention in the fields of solar cells,^{1–3} photodetectors,⁴ light emitting diodes (LEDs)^{5,6} and so on. In particular, great and rapid progress has been made in perovskite LEDs with electroluminescent (EL) external quantum efficiency (EQE) outperforming 20%^{7–10} since the first reported room-temperature PeLEDs in 2014,¹¹ enabling them to be promising candidates in displays.

Generally, to fulfill efficient inorganic PeLEDs, tiny crystals as small as possible are expected not only to form uniformly compact films to ensure ultralow current shunt but also to

Synergistic morphology control and non-radiative defect passivation using a crown ether for efficient perovskite light-emitting devices[†]

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Controlling the nucleation process and forming small nanograins, as well as passivating defects at grain boundaries as the grain size becomes smaller, in one-step solution formed polycrystalline halide perovskites are of great importance for achieving efficient perovskite light-emitting diodes (PeLEDs). Here, a crown ether, 2-hydroxymethyl-12-crown-4 (HM12C4), is adopted as an additive and its influence on the photophysical and electroluminescent properties of a PeLED was investigated. It is found that HM12C4 can not only suppress PbBr₆ octahedron agglomeration in the precursor but also improve the wettability of the hole transport layer, resulting in a smoother dense perovskite film with smaller polycrystallites. Moreover, the retained HM12C4 in the perovskite film effectively passivated the defects at the grain boundaries and improved the photophysical and electroluminescent properties. Consequently, significantly enhanced electroluminescent performance was achieved with a low turn-on voltage of 2.3 V, a current efficiency of 17.2 cd A^{-1} , and an external quantum efficiency of 4.52%. Our findings reveal that crown ethers have great potential in exploiting high-performance PeLED, with significant implications for the further development of PeLEDs.

spatially confine the charge carriers to favor exciton formation and radiative recombination with a high photoluminescence quantum yield (PLQY).¹² But, along with the reduced grain size, crystal boundaries are significantly enlarged and more trap sites could appear. Hence, effective passivation tactics are urgently required to achieve high-performance PeLEDs. As a prevalent strategy, the one-step solution method with deposition directly from the precursor solution allows the convenient introduction of additives to ameliorate the film morphology and passivate the generated defects (metallic Pb atoms or halogen vacancies) simultaneously.13-17 Amine-based ionic passivating agents containing both anions and cations have been broadly utilized in perovskite-based optoelectronics due to the dual passivation effect by occupying vacancies from uncoordinated metal cations and halide anions.18 Several amine-based additives with bulky cations, for instance butylammonium halide salts (BAX, X = Br or I),¹⁹ phenethylammonium halide salts (PEAX, X = Br or I)^{20,21} and IPABr (iso-propylammonium bromide),²² have also been adopted to realize efficient quasi-2D/3D hybrid PeLEDs. However, non-environmentally friendly anti-solvents such as toluene and chloroform are very necessary in such amine additive perovskite systems.²⁰⁻²³ Alternatively, some non-ionic passivation agents, such as polyethylene glycol (PEG),²⁴ poly(ethylene oxide),²⁵ lecithin²⁶ and Tween,²⁷ have also been demonstrated as successful additives for delivering high-performance PeLEDs. Recently, several researchers

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combined bulk ammonium halides with non-ionic passivation agents to boost the EQE of PeLEDs to more than 10% by virtue of dimensional engineering and defect passivation.^{28–33} It worth noting that one type of non-ionic organic material, crown ethers (such as dibenzo-21-crown-[7],³⁴ 1,4,7,10,13,16-hexaoxacyclooctadecane³²), have also cooperated with other additives either to facilitate the solubility of the Cs precursor³⁴ or to suppress the crystallization of PEABr *via* forming hydrogen bonding.³² However, whether the crown ether can passivate nonradiative defects is still open to discussion and its sole influence on PeLEDs remains unexplored.

Herein, a facile and plausible method through introducing crown ether into the perovskite precursor was adopted to improve the optoelectrical performance of the PeLEDs. The crown ether facilitates crystallite nucleation in the precursor and improves the wettability of the perovskite on the hole transport layer, resulting in smoother CsPbBr₃ films with smaller crystallites. Moreover, the non-radiative traps were dramatically passivated by the additive with enhanced light-emitting intensity and prolonged exciton decay lifetime. Consequently, the synergistic effect of nucleation and morphology control as well as luminescence quenching suppression significantly enhance the EL performance of the PeLED. The optimized PeLED exhibited a low turn-on voltage of 2.3 V, maximum brightness up to 21700 cd m⁻² and an EQE of 4.52%.

Experimental

Materials

PbBr₂ (99.9%), PEDOT:PSS, TPBi and Bphen were purchased from Xi'an Polymer Light Technology Corp. Dimethyl sulfoxide (DMSO) and CsBr (99.9%) were purchased from Sigma-Aldrich. 2-Hydroxymethyl-12-crown-4 (HM12C4) (97%) was purchased from Alfa Aesar. All materials were used as received without further purification.

Film fabrication and characterization

PbBr₂ and CsBr powders (molar ratio of 1:1.4) were added into a mixed solution of HM12C4 and anhydrous DMSO and then stirred overnight to form a transparent perovskite precursor with a concentration of 174 mg ml⁻¹. The HM12C4 concentrations in DMSO (HM12C4/DMSO weigh ratio) were 5, 10, 20 and 40 mg ml⁻¹. For scanning electron microscopy (SEM, Hitachi S-4800) characterization, the perovskite films were spun on ITO/PEDOT:PSS substrates (3000 rpm, 60 s). Atomic force microscopy (AFM) was performed on

a Shimadzu SPA-9700 instrument for surface roughness analysis. The absorption spectra for the perovskite films fabricated from DMSO and HM12C4/DMSO (on quartz substrates) were performed with a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer. Steady-state PL spectra were measured using a Hitachi fluorescence spectrometer F-7000. Transient PL decay properties and PLQY were performed by an Edinburgh Instruments FLS920 spectrometer. A Malvern Zetasizer Nano ZS was used for DLS (dynamic light scattering) measurement. The contact angles were obtained with a contact angle analyzer JD2000. FTIR spectra were performed with a Thermo-Nicole iS50 FTIR-spectrometer. X-ray diffraction (XRD) was performed on a Rigaku SmartLab.

Device fabrication and characterization

The perovskite device with a configuration of ITO/PEDOT:PSS/Perovskite/TPBi/Bphen/Cs2CO3/Ag is illustrated in Fig. 1a. ITO-coated glass substrates were ultrasonically cleaned with acetone, alcohol, and deionized water in sequence and then treated with UV-ozone for 15 min. The hole transport layer PEDOT:PSS (Clevios P AI 4083) $(\sim 40 \text{ nm})$ was spun coated on the ITO at 2500 rpm and baked at 140 °C for 20 min on a hotplate under air ambience. The perovskite precursor was spun-coated at 3000 rpm for 60 s and annealed at 70 °C for 5 min in an N2 filled glove box. The thickness of the perovskite layer is approximately 30 nm, as measured by a surface profiler Ambios XP-1. Subsequently, electron transport layers TPBi (30 nm) and Bphen (10 nm), electron injection layer Cs₂CO₃ (1 nm) and a cathode electrode Ag (60 nm) were successively thermally evaporated at rates of 1, 1, 0.5, 4 Å s⁻¹, respectively. The work function of the ultrathin Cs2CO3 modified Ag was a good match with the LUMO (lowest unoccupied molecular orbital) of ETL, as shown in Fig. 1c, which will facilitate the electron injection. The active area of the PeLED is 0.015 cm². The brightness and current density of the PeLEDs were measured using a Keithley 2400 source meter and a luminance meter KONICA MINOLTA LS-110. The electroluminescence spectra were recorded with an AvaSpec-ULS2048L fiber spectrometer. EQE was calculated from the brightness, the current and the EL emission spectrum, assuming Lambertian emission. All measurements were carried out in ambient air without encapsulation.

Results and discussion

The electroluminescence characteristics of the PeLED with different HM12C4/DMSO weight ratios are shown in Fig. 2a–c. As the HM12C4



Fig. 1 (a) A schematic diagram of the structure of CsPbBr₃ PeLEDs. (b) The chemical structure of HM12C4. (c) The flat-band energy levels of the active layers.

concentration increases, the achieved maximum brightness gradually increases from 5310 cd m^{-2} (0 mg ml⁻¹) to 12700 cd m^{-2} (5 mg ml^{-1}) , 22300 cd m⁻² (10 mg ml^{-1}) , 21700 cd m⁻² (20 mg ml⁻¹) and 11 800 cd m⁻² (30 mg ml⁻¹). The decrease in the maximum brightness at higher weight ratio probably originated from the insulation properties of HM12C4 that would be residual in the perovskite emission layer. And the turn-on voltages (V_{on}) shows a dramatic decrease from 2.9 V to 2.3 V (as shown in Table 1), which will be of great importance to energy consumption. The optimal V_{on} is very close to its bandgap (\sim 2.4 eV), meaning that the electron and hole injection and transport are balanced, with negligible energy barriers. Together with the enhanced brightness and reduced turn-on voltage, the current efficiency and EOE for the optimized PeLED also performed at more than 1 order of magnitude higher than that without HM12C4 modification, achieving 17.2 cd A^{-1} and 4.52%, respectively. The bright device exhibits stable sharp EL spectra with a peak centered at 522 nm with a full width at half maximum (FWHM) of 18 nm as the voltage varied from 3 V to 6 V with a step of 1 V. The 1931 Commission Internationale de l'Eclairage (CIE) color coordinates are (0.12, 0.79).

To investigate the origins of the enhancement in device performance, SEM and AFM were carried out to study the role of HM12C4 in CsPbBr₃ film formation. As shown in Fig. 3a and b, the rough pristine CsPbBr₃ films (roughness 9.05 nm) are spontaneously

 Table 1
 EL performance of the CsPbBr₃ PeLEDs using different HM12C4/ DMSO precursor solvents

$\begin{array}{c} \rm HM12C4/\\ \rm DMSO\\ (mg\ ml^{-1}) \end{array}$	Max. luminance (cd m^{-2})	$\begin{array}{c} \text{Max. CE} \\ (\text{cd } \text{A}^{-1}) \end{array}$	Max. EQE (%)	Turn-on Voltage (V)
0	5310	1.21	0.32	2.9
5	12700	4.49	1.18	2.5
10	22 300	9.24	2.43	2.5
20	21700	17.20	4.52	2.3
30	11800	15.10	3.97	2.3

composed of many large crystals (hundreds of nanometers) due to the fast crystallization speed and some pin-holes being retained in the film. While the HM12C4/CsPbBr₃ morphology became much more uniform and compact with obviously smaller crystals and a surface roughness of 6.48 nm. The reduced nanocrystals can also be confirmed by the decreased XRD peak intensity (Fig. S1, ESI[†]). In addition, the XRD measurements indicate that HM12C4 does not affect the crystal structure of CsPbBr₃. There were almost no pinholes exhibited after the introduction of HM12C4. A dynamic light scattering (DLS) experiment was conducted to obtain deep insight into the interaction of HM12C4 with the precursor. As displayed in Fig. 3c, there are two types of colloidal particles aggregated from different numbers of PbBr₆ octahedrons in both precursors.³⁰ Without HM12C4, the larger particles with a size of ~2.3 µm dominate in



Fig. 2 (a) Current density-voltage-luminance (J-V-L), (b) current efficiency-voltage (CE-V), and (c) EQE-V curves for PeLEDs with different HM12C4/DMSO weight ratios. (d) EL spectra under different voltages; inset: a photograph of the PeLED under working conditions.



Fig. 3 SEM images of CsPbBr₃ films fabricated from (a) DMSO solvent and (b) HM12C4/DMSO mixed solvent. The insets show the corresponding AFM images with a size of 2 μ m \times 2 μ m. (c) Dynamic light scattering (DLS) spectra of perovskite precursor solutions with and without HM12C4. Contact angles for perovskite precursors on PEDOT:PSS substrates using (d) DMSO and (e) mixed HM12C4/DMSO as solvents. The concentration of HM12C4 or 12C4 in DMSO is 20 mg ml⁻¹ unless otherwise noted.

the mother solution. Whereas in the HM12C4/DMSO precursor, not only the amount of larger colloids reduced but the size also became smaller with a distribution peaking at ~0.7 µm. These results provide direct evidence that HM12C4 can suppress precursor agglomeration. Since HM12C4 has two functional groups, –OH and C–O–C, both of which may affect colloidal dispersion, we chose 12C4 with a C–O–C group alone (depicted in Fig. S2, ESI†) as a reference additive to resolve their influence on colloidal dispersion in the precursor. As evidenced by the DLS results presented in Fig. S3a (ESI†), the introduction of 12C4 did not contribute to the suppression of PbBr₆ aggregation, unlike previous research where 18-crown-6 could increase precursor solubility.^{30,32} Therefore, we deduce that the origin of the decrease in colloid particles was probably the existence of an –OH functional group which can interact with halide atoms *via* hydrogen bonds.^{35,36}

Contact angle measurement further revealed that better wetting was achieved after HM12C4 was added into DMSO, as depicted in Fig. 3d and e. The control DMSO precursor exhibits a contact angle of 20.9°, whereas that of the HM12C4/DMSO precursor decreased to 14.5°. Such a change in contact angle may be attributed to the surfactant properties of HM12C4, which will change the liquid surface tension and consequently affect the interaction between the PEDOT:PSS surface and the precursors, with an important influence on CsPbBr₃ nucleation. According to nucleation theory, crystallization is associated with the contact angle (θ) and can be defined as follows:

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$$\Delta G_{\text{heterogenous}} = \Delta G_{\text{homogenous}} \times f(\theta) \tag{1}$$

$$f(\theta) = (2 - 3\cos\theta + \cos^3\theta)$$
(2)

where $\Delta G_{\text{heterogenous}}$ and $\Delta G_{\text{homogenous}}$ denote the free energy needed for heterogeneous and homogenous nucleation, respectively. From eqn (2), it is obvious that a smaller contact angle will lead to smaller $f(\theta)$ and decrease the nucleation barrier. This essentially means that the nucleation of perovskite crystals will occur more easily for the HM12C4/DMSO precursor compared with the control DMSO solution and result in more crystal nuclei and smaller grain size, which are consistent with the SEM and AFM morphologies. In a word, HM12C4 plays an important role in guiding film formation and morphology.

To confirm whether HM12C4 is retained in the perovskite film, we performed XPS and observed an obvious change in the oxygen atomic percentage. The oxygen atomic percentage accounts for 8.22% in HM12C4/CsPbBr₃ films while it is only 3.86% for pure CsPbBr₃ films, demonstrating the adsorption of HM12C4 in the perovskite films. What is more, the variation in the C 1s spectra (see Fig. S3b, ESI[†]) also confirms the existence of HM12C4 in the perovskite films. The optical properties of the perovskite films were investigated in detail. A pure green photoluminescence was observed with a peak centered at 519 nm and an FWHM of 22 nm for the neat CsPbBr₃ film. The HM12C4 modified CsPbBr₃ film exhibited a red-shifted and notably enhanced light emission with a PL peak at 521 nm and a narrower FWHM of 18 nm in contrast to pure CsPbBr₃ film (Fig. 4a). A similar red-shift phenomenon was also observed in the UV-vis absorption spectra (Fig. 4a). The red-shift may be ascribed to surface composition or assorted changes at the grain boundaries, as reported in previous investigations.27,37,38 Meanwhile, the light-intensity-dependent PLQY was also measured, as displayed in Fig. 4b. Obviously, HM12C4/CsPbBr3 showed a much higher PLQY in comparison with the neat CsPbBr₃ films with a maximum PLQY reaching 17.7%. Even at a low light-intensity of 1 mW cm^{-2} , where non-radiative trap-assisted recombination mainly dominated, the PLQY for the HM12C4/CsPbBr3 film was still higher than 10%, whereas the value for the neat CsPbBr₃ film was extremely low (<1%). The perovskite films were further characterized by time-resolved PL decay measurement to understand the free carrier and exciton kinetics. After the introduction of HM12C4, the PL lifetimes were dramatically prolonged with an average time of 19.9 ns which is 9 times higher than that of pure CsPbBr₃ films (2.2 ns), as fitted by tri-exponential curves. From the following equation:

$$PLQY = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm nr}}$$
(3)

$$\tau_{\rm avg} = \frac{1}{k_{\rm r} + k_{\rm nr}} \tag{4}$$

where $k_{\rm r}$ and $k_{\rm nr}$ are the radiative and non-radiative decay rates, respectively. We can deduce that the nonradiative decay rate $k_{\rm nr}$ can be expressed as: $k_{\rm nr} = \frac{1 - \rm PLQY}{\tau_{\rm avg}}$. Therefore, the higher PLQY and increased $\tau_{\rm avg}$ jointly result in the decreased non-radiative decay rates of the HM12C4/CsPbBr₃ films for the following two reasons:



Fig. 4 Optical characterization of CsPbBr₃ film with and without HM12C4: (a) PL and absorption spectra; (b) excitation-intensity-dependent PLQY data; and (c) time-resolved PL decay profiles. (d) and (e) FTIR spectra of HM12C4 liquid and the HM12C4/CsPbBr₃ complex, respectively.

reduced grain size would actually enhance the exciton spatial confinement and thereby reduce the dissociation and enhance the radiative recombination; HM12C4 could passivate the non-radiative defects at the grain boundaries. The lower non-radiative traps are conducive to lowering the turn-on voltage of a PeLED, as evidenced by the performances of the PeLEDs (Table 1).

To better elucidate how the HM12C4 passivation agent interacts with CsPbBr₃, we performed FTIR (Fourier transform infrared spectroscopy) on an HM12C4/CsPbBr3 mixture (Fig. 4d). From FTIR we observed that the C-O-C stretching vibration frequency at 1097 cm⁻¹ for pure HM12C4 shifted to a lower wavenumber 1089 cm⁻¹ for the HM12C4/CsPbBr₃ mixture, confirming the reduced force constant of C-O-C according to the diatomic harmonic motion model. It has been widely demonstrated that the introduction of Lewis base molecules (such as thiophene, pyridine or thiourea)³⁹⁻⁴² in the perovskite films could efficiently suppress the non-radiative recombination caused by uncoordinated Pb atoms and thus improve optical performance. Actually, HM12C4 is a Lewis base in which the oxygen in C-O-C can serve as an electrondonating atom and could form a complex with the Lewis acid PbBr₂ through weak chemical interaction, just as the FTIR reveals. It has already been demonstrated that the C-O-C functional groups in PEG and Tween 20 can passivate the Pb defects in perovskite films and thus enhance their optical and electrical performance.24,27 Therefore, the Pb²⁺ defect passivation originating from C-O-C may play a key role in the performance enhancement.

Besides the changes in C–O–C stretching vibration, we also observe changes in ν (OH) vibration (from 3430 cm⁻¹ for pure

HM12C4 to 3379 cm⁻¹ for the HM12C4/CsPbBr₃ complex), as shown in Fig. 4e, which could also contribute to the improvement in the device performance. To verify this assumption, we implemented the control 12C4 additive and cautiously optimized the EL performance. Similar to the HM12C4/CsPbBr₃ films, the 12C4/ CsPbBr3 also exhibited enhanced PL intensity with a maximum PLQY of 12.5% and prolonged lifetime of 11.8 ns compared with those of neat CsPbBr₃ films (see Fig. S4, ESI⁺), demonstrating the C-O-C defect-passivation role. Although the PLQY was evidently elevated by 12C4 owing to trap passivation, it is still lower than that of HM12C4/CsPbBr3 films. More importantly, the optimized electrical performance with a maximum brightness of 37 900 cd m^{-2} and CE of 10.6 cd A⁻¹ for the 12C4/CsPbBr3 devices are still inferior to those of HM12C4/CsPbBr3 devices (see Fig. S5, ESI⁺). On the basis of such experimental results, it can safely be deduced that the -OH functional group plays a crucial role in decreasing the non-radiative defects for EL performance amelioration. In addition, thanks to the passivation effect of HM12C4, the device stability without encapsulation under ambient atmosphere was also remarkably improved. As shown in Fig. S6 (ESI⁺), the brightness of the HM12C4/CsPbBr₃ devices dropped to half of the initial value (100 cd m^{-2}) after more than 2000 s, which was significantly prolonged over that of the control device, produced in our laboratory, which only survived for less than ~ 60 s. The performance would be better if the interfacial defects or the energy barriers between the emission layer and charge transport layers were eliminated or if some measures were taken to prevent H₂O corrosion by encapsulation. The combination of HM12C4 with other additives would contribute a further

Conclusions

In summary, we have developed an inorganic PeLED with improved performance through synergistic morphology control and non-radiative defect passivation by incorporating a crown ether. The suppression of PbBr₆ octahedron agglomeration in the precursor and the increased solution wettability between the precursor and the substrate made simultaneous contributions to film amelioration with smaller polycrystallites and flatter morphology. More importantly, FTIR results as well as control experiments revealed that both the C-O-C and -OH functional groups can shield the CsPbBr₃ nanograins to suppress non-radiative traps. As a result, HM12C4/CsPbBr3-based PeLEDs exhibited greatly improved light-emitting efficiency, a decreased turn-on voltage, and a higher working stability, with a maximum brightness of 27300 cd m⁻², CE of 17.2 cd A⁻¹, EQE of 4.52%, and V_{on} of 2.3 V. These results contribute useful information for the development of high-performance PeLEDs with crown ethers.

Conflicts of interest

There are no conflicts to declare.

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