

Additive and interfacial control for efficient perovskite light-emitting diodes with reduced trap densities

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Metal halide perovskite semiconductors show excellent optoelectronic properties including tunable bandgaps^[1, 2], narrow emission bandwidths^[3] and high luminescence quantum efficiencies^[4], making them an ideal candidate for light-emitting diode (LED) applications. Perovskite LEDs (PeLEDs) have attracted considerable attention since the initial report of room-temperature electroluminescence (EL) from halide perovskites in 2014^[5]. In recent years, great efforts have been made to raise the EQEs of PeLEDs to 20% and beyond^[6–13]. Emissive layer compositional engineering and device architecture design were key strategies for improving the performance of PeLEDs^[6–13]. To obtain high-quality perovskite emissive layers for LEDs, a wide range of additives, including polymer^[8, 14] organic small molecules^[7, 15–17], ionic compounds^[18, 19], and Lewis acid/base^[20–23], were developed. These additives are known to function as passivating agents for the perovskite materials, improving the photoluminescence quantum efficiencies (PLQEs). In PeLEDs where multiple functional layers and interfaces are present, interfacial non-radiative losses become more significant, limiting the luminescence performance. A number of methods, including interfacial chemical reactions^[24], anti-solvent treatments^[9, 21, 25], and interfacial layers at the charge-transport interfaces^[3, 26], were reported to improve device EQEs. As stated, additives and interfacial control are known to be effective in suppressing non-radiative losses, leading to enhanced PeLED performance. However, the densities of traps directly related to the luminescence properties of PeLEDs were rarely investigated, limiting the pace of development in this area. In this work, we report the effects of crown additive and LiF interface on the densities of traps in lead bromide perovskites using space-charge-limited current (SCLC) analysis, complemented by steady-state and transient optical studies. The density of defects in the perovskite emissive material was reduced from 7.02×10^{17} to $5.10 \times 10^{17} \text{ cm}^{-3}$. This allowed an EQE improvement from 5.0% to 19.0% in PeLEDs. Optical modeling was performed for the perovskite device structure, presenting directions for further improvements.

To prepare the emissive layers for perovskite light-emitting diodes (PeLEDs), quasi-2D perovskite films, $(\text{MOPEA})_2(\text{Cs}_x\text{FA}_{1-x})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ (MCFPB), were formed by spin-coating perovskite precursor solution comprising cesium bromide (CsBr), formamidinium bromide (FABr), lead bromide (PbBr_2)

and 2-(4-methoxyphenyl)ethylammonium bromide (MOPEABr) (Supplementary Information), n represents the number of layers of the $[\text{PbBr}_6]$ octahedra. The $(\text{MOPEA})_2(\text{Cs}_x\text{FA}_{1-x})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ -crown (MCFPB-C) films were spin-coated from precursor solution prepared by introducing crown (Fig. S1)^[17] as an additive into the MCFPB solution. The morphologies of the MCFPB and MCFPB-C samples were measured using scanning electron microscope (SEM) and atomic force microscope (AFM) on bare quartz substrates. MCFPB films showed rough surfaces with island-like structures (Fig. S2(a)). The root-mean-square (RMS) roughness of MCFPB sample was 5.90 nm (Fig. S2(c)). In contrast, the morphology of MCFPB-C was improved significantly. It was reported that crown additive could inhibit MOPEABr crystallization^[17] (Fig. S2(b)), resulting in smaller crystal sizes and smoother film morphology. The RMS roughness of MCFPB-C sample was reduced to 4.05 nm (Fig. S2(d)). LiF was found to be an effective interlayer for PeLEDs^[3], allowing the integration of high quality perovskite with high-performance charge-transport layers. The LiF interface has negligible influence on the morphology and crystal structures of the perovskite films (Figs. S2–S4).

The optical absorption and normalized PL spectra of the MCFPB and MCFPB-C films are shown in Fig. S5(a). Three pronounced absorption peaks are present at 405, 435 and 465 nm for MCFPB samples. For MCFPB-C samples, similar peaks are located at 407, 437 and 462 nm. These peaks could be attributed to quasi-2D perovskite phases^[27]. However, no PL emission from these phases was observed. The differences in the relative peak intensities in the absorption spectra indicate that additive crown modulates the phase distribution in the quasi-2D perovskite composition. This may facilitate efficient energy transfer^[8, 15] between the phases with different bandgaps, resulting in high PLQEs. The MCFPB and MCFPB-C films show identical PL spectra peaked at 511 nm with full-width at half-maximum (FWHM) of ~ 22 nm. The PL intensity of MCFPB-C films was considerably enhanced compared to the MCFPB films (Fig. S5(b)), along with the improvement of film uniformity, indicating possible reduction of non-radiative losses in these films.

We found that the LiF layer plays an important role in reducing the density of defects at the interface between the hole-transport layers and the perovskite emissive layers^[26]. From the TCSPC results (Fig. S5(c)), the effective PL lifetime increased from 7.8 ns for samples on bare quartz substrates to 9.6 ns for samples on quartz/LiF substrates, consistent with a PLQE enhancement from 52% to 67%. Further, we carried out transient absorption (TA) measurements for MCFPB-C samples on bare quartz and on quartz/LiF substrates (Fig.

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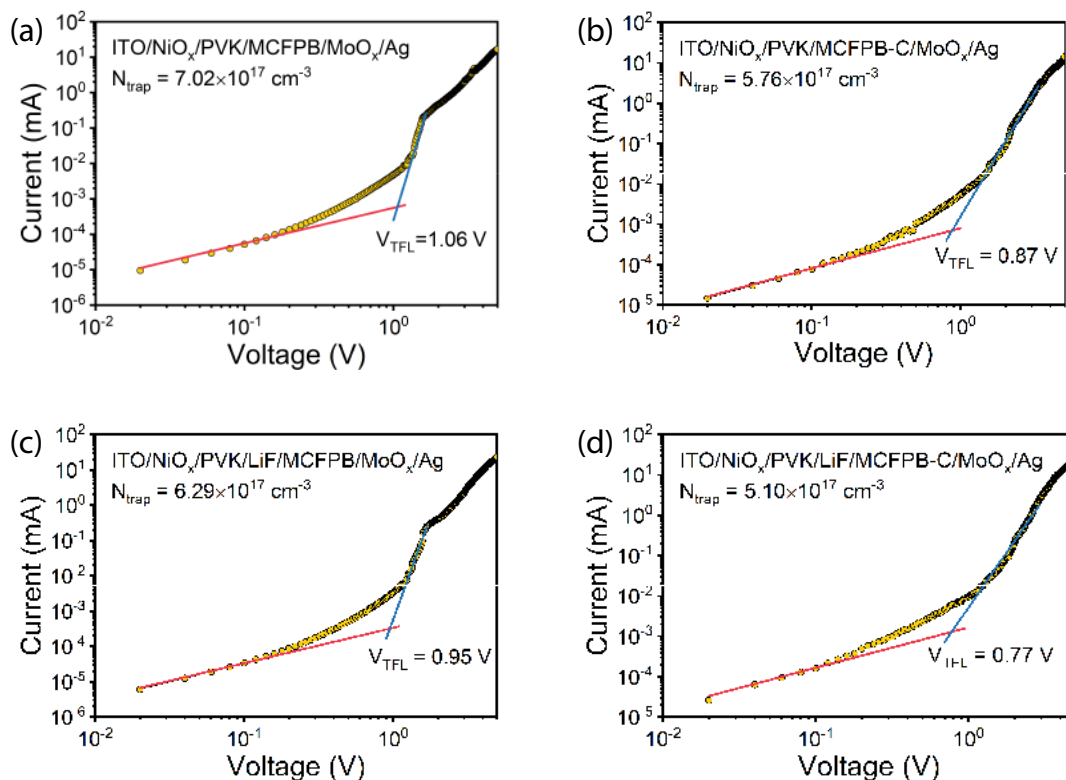


Fig. 1. (Color online) SCLC analyses for MCFPB and MCFPB-C perovskite films. Current–voltage characteristics of devices with structures of (a) ITO/NiO_x/PVK/MCFPB/MoO_x/Ag, (b) ITO/NiO_x/PVK/MCFPB-C/MoO_x/Ag, (c) ITO/NiO_x/PVK/LiF/MCFPB/MoO_x/Ag and (d) ITO/NiO_x/PVK/LiF/MCFPB-C/MoO_x/Ag.

S5(d)). Both the TCSPC and TA kinetic traces showed that the LiF interface has a positive effect on the carrier lifetime, pointing to reduced density of defects in these samples.

To quantitatively study the densities of defects in perovskite films with and without the crown additives and the LiF interface, we employed the space-charge limited current (SCLC) method^[28]. In the SCLC model, the density of traps (N_{trap}) are calculated using $N_{\text{trap}} = 2\epsilon_0\epsilon_r V_{\text{TFL}}/ql^2$, where V_{TFL} is the trap-filled limit (TFL) voltage, q is the elementary charge, l is the film thickness, ϵ_r is the dielectric constant, and ϵ_0 is the vacuum permittivity. q and ϵ_0 are 1.6×10^{-19} C and 8.85×10^{-12} F/m, respectively. ϵ_r of CsPbBr₃ is 29.37^[29].

Based on hole-only devices with a structure of ITO/NiO_x/PVK/perovskite/MoO_x/Ag, the N_{trap} in the MCFPB samples was determined to be 7.02×10^{17} cm⁻³ (Fig. 1(a)). For the MCFPB-C samples, N_{trap} was determined to be 5.76×10^{17} cm⁻³ (Fig. 1(b)). The reduced trap density is consistent with the view that the crown additive passivates defects in the perovskite films. Similarly, we fabricated electron-only devices based on the structure of ITO/TPBi/perovskite/TPBi/LiF/Al, and found that the density of traps was similarly reduced (Figs. S6(a) and S6(b)). These results are in agreement with the enhanced PL intensity and lifetime (Figs. S5(b) and S5(c)). By introducing the LiF interface into the hole-only devices, ITO/NiO_x/PVK/LiF/perovskite/MoO_x/Ag, the N_{trap} in MCFPB and MCFPB-C samples were further reduced to 6.29×10^{17} cm⁻³ (Fig. 1(c)) and 5.10×10^{17} cm⁻³ (Fig. 1(d)), respectively. These results support the view that the LiF interface suppresses defect formation at the interface between the PVK and the perovskite emissive layer.

We fabricated PeLEDs based on the device structure of

ITO/NiO_x (~20 nm)/PVK (~30 nm)/perovskite (~75 nm)/TPBi (~45 nm)/LiF (1 nm)/Al (100 nm) with or without the LiF interfacial layer (Fig. 2(a) & Supplementary Information). The layer thicknesses of our PeLEDs were determined from Fig. S7. NiO_x and PVK are hole-injection and hole-transport layers respectively. TPBi was the electron-transport layer. The energy level diagram of the PeLEDs is illustrated in Fig. 2(b). The valence band maximum (VBM) and conduction band minimum (CBM) values of MCFPB and MCFPB-C perovskite films were calculated based on UV photoelectron spectroscopy (UPS) and UV-Vis absorption spectra (Fig. S8 & Table S1). The VBM and CBM values of other functional layers are obtained from the literature^[30]. The current density–voltage–luminance (J - V - L) curves of PeLEDs based on MCFPB and MCFPB-C showed typical diode behaviors (Figs. 2(c) and 2(d)). The turn-on voltages of PeLEDs based on MCFPB and MCFPB-C perovskite films were 2.8 and 2.6 V (Figs. 2(c) and 2(d)), respectively. The lower turn-on voltage of MCFPB-C device may be attributed to the reduced charge-injection barriers (Fig. S8). For MCFPB-C PeLEDs without and with the LiF interface, the maximum brightness values were 3459 and 3771 cd/m² (Fig. 2(d)), respectively. The leakage current (at < 2 V) for devices without LiF interface was large (about 10⁻² mA/cm²) due to the poor morphology of MCFPB films (Fig. S2(a)), while the leakage current of devices with the LiF interfaces was reduced, in line with the improved film morphology (Fig. S2(b)). Similar results for devices based on MCFPB-C films were shown in Fig. 2(d). The leakage currents in these devices were reduced to ~10⁻⁴ mA/cm² (Fig. 2(d)), likely resulting from the improved uniformity of the perovskite films. The introduction of LiF interface leads to improved PeLEDs, with

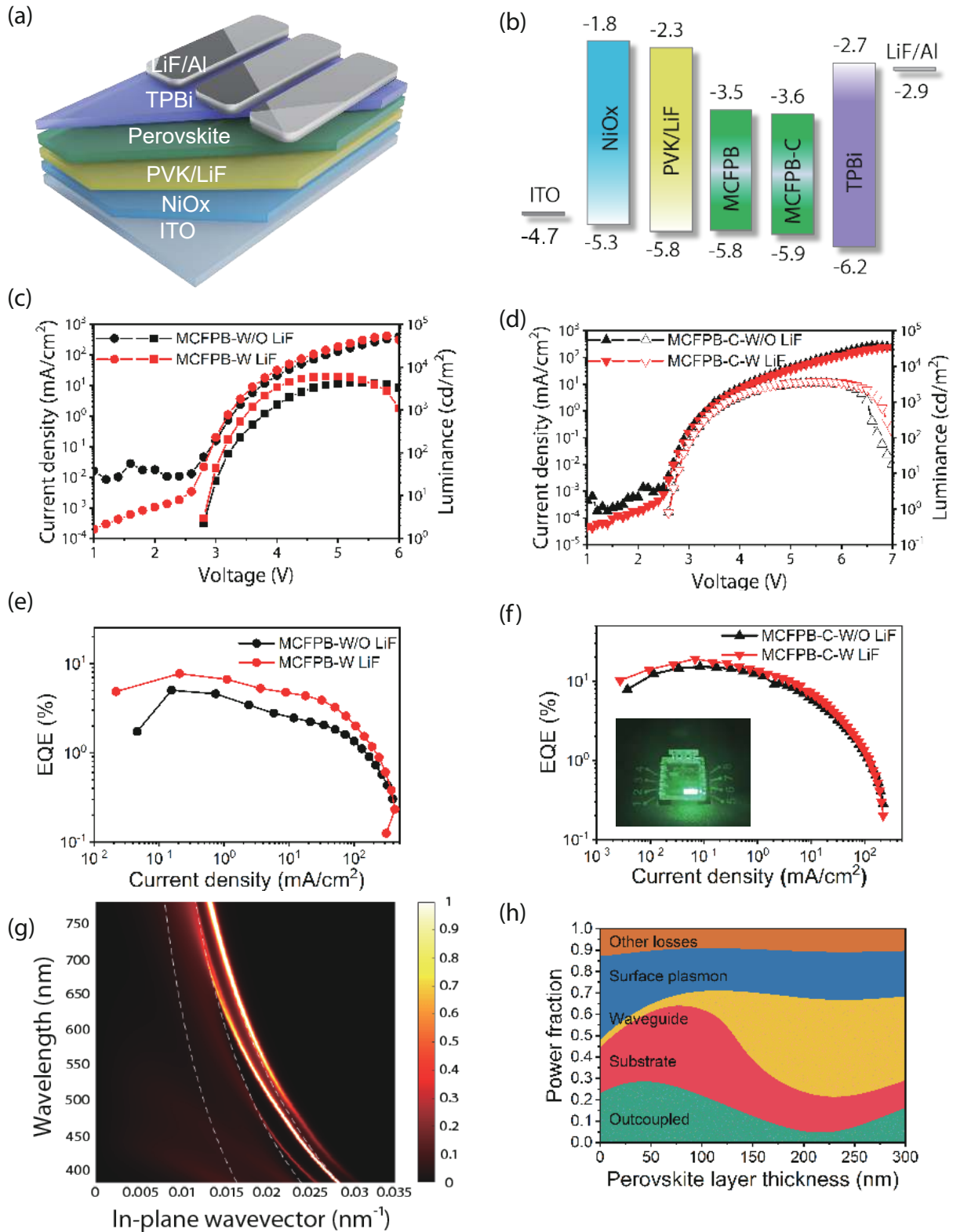


Fig. 2. (Color online) Characterization of PeLEDs. (a) Device structure. (b) The energy levels of the device functional layer materials. (c) J - V - L and (e) EQE- J curves of devices based on ITO/NiO_x/PVK/(with or without)LiF/MCFPB/TPBi/LiF/Al. (d) J - V - L and (f) EQE- J curves of devices based on ITO/NiO_x/PVK/(with or without)LiF/MCFPB-C/TPBi/LiF/Al. Inset: a photograph of a working device. (g) Simulated power distribution of a PeLED with isotropic emitter orientation. The dashed lines divide the graph into four regions: (1) direction emission, (2) substrate mode, (3) waveguide mode, and (4) surface plasmon mode. (h) Fractional power distribution of different optical modes in PeLEDs as a function of perovskite layer thickness.

EQEs improved from 5% to 7.6% for devices based on MCFPB (Fig. 2(e)), and from 15.1% to 19.0% for devices based on MCFPB-C (Fig. 2(f)). The EL spectra of the PeLEDs are shown

in Fig. S9. The devices show no observable shifts in EL regardless of the presence of crown and LiF.

We employed an optical simulation method based on a

classical dipole model (Supplementary Information) to calculate the optical outcoupling efficiency of our PeLEDs⁸, 31–34]. From our simulation results (Figs. 2(g) and 2(h)), the maximum outcoupling efficiency (equivalent to the highest achievable EQE) is 28.2%. Further improvements in EQE is possible by eliminating optical and non-radiative loss channels.

In summary, we explored a combinatory approach employing molecular additive crown and LiF interfaces for the preparation of efficient PeLEDs with reduced trap densities. We demonstrated through SCLC analysis that the trap densities in the MCFPB-C perovskite on LiF were reduced by 27.4% (from $7.02 \times 10^{17} \text{ cm}^{-3}$ for the control sample, to $5.10 \times 10^{17} \text{ cm}^{-3}$). The PLQEs of the emissive perovskites were improved from 29% (for the control sample) to 67% (for the MCFPB-C sample on LiF), consistent with the improved carrier lifetimes from transient optical measurements. As a result, efficient PeLEDs with peak EQEs of 19.0% were obtained. Optical modelling for the devices revealed that further improvements are possible through functional layer thickness optimization and the elimination of non-radiative recombination pathways. Our work serves as a case study for how trap densities in halide perovskites are reduced through a combination of molecular additive and interfacial control, paving a path for improving the performance of perovskite light-emitting devices, such as blue PeLEDs and micro-PeLEDs.

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at <https://doi.org/10.1088/1674-4926/43/5/050502>.

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