

All-Perovskite Emission Architecture for White Light-Emitting Diodes

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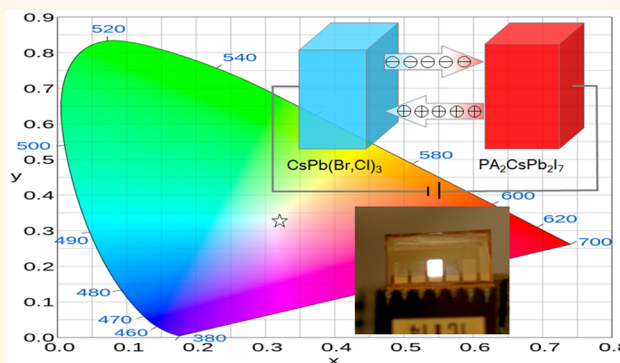
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Supporting Information

ABSTRACT: We demonstrate all-perovskite light-emitting diodes (PeLEDs) with white emission on the basis of simultaneously solving a couple of issues including the ion exchanges between different perovskites, solvent incompatibility in the solution process of stacking different perovskites and carrier transport layers, as well as the energy level matching between each layer in the whole device. The PeLEDs are built with a two-dimensional $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CsPb}_2\text{I}_7$ perovskite that emits red light, $\text{CsPb}(\text{Br},\text{Cl})_3$ quantum dots that emit a cyan color, and an interlayer composed of bis(1-phenyl-1H-benzo[d]imidazole)phenylphosphine oxide (BIPO) and poly(4-butylphenyl-diphenyl-amine) (Poly-TPD). The interlayer is designed to realize desirable white electroluminescence by tuning the electron and hole transportation and distribution in-between multilayers. With this PeLED configuration, we achieve the typical white light with chromaticity coordinates of (0.32, 0.32) in Commission Internationale de L'Eclairage (CIE) 1931 color space diagram and steady CIE coordinates in a wide range of driving current densities (from 2.94 to 59.29 mA/cm^2). Consequently, our work, as the starting point for future research of all-perovskite white PeLEDs, will contribute to the future applications of PeLEDs in lighting and display. In addition, we believe that the proposed material and all-perovskite concept will leverage the design and development of more perovskite-based devices.

KEYWORDS: white light-emitting diode, all-perovskite, 2D perovskite, quantum dots, carrier transportation and distribution



As one of the promising photonic sources, perovskite has attracted extensive attention from worldwide researchers due to its advantages of high quantum efficiency,¹ high color purity,² and easy wavelength tunability.^{3,4} Near-infrared, red, green, and blue electroluminescence (EL) has been demonstrated with perovskite thin films,^{5–8} perovskite quantum wells,⁹ perovskite quantum dots (QDs),^{10–12} and perovskite nanogratings.¹³ Perovskite light-emitting diodes (PeLEDs) with white color EL are highly desirable for practical applications in display and lighting.

Recently, some low-dimensional perovskites, such as $(\text{N-MEDA})\text{PbBr}_4$,¹⁴ $(\text{DMEN})\text{PbBr}_4$,¹⁵ $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$,¹⁶ and $\text{C}_4\text{N}_2\text{H}_{14}\text{PbBr}_4$ ¹⁷ have been reported to show white light photoluminescence (PL) through the formation of self-trapped excitons by the coupling of photogenerated electrons/holes and phonons, but white EL based on these materials has not yet been reported, probably due to temperature-sensitive phonons involved in the luminescence process that lead to varying spectra change with temperature. Alternatively,

forming perovskites on a commercial inorganic LED chip (e.g., blue InGaN chip) as phosphor^{18–21} or blending perovskites with organic emitting materials as emission layers aiming for white light emitting has been reported.^{22,23} Blending different kinds of perovskite for white light emission was also carried out; however, this approach faces the grand challenge of ion exchange reactions (especially between halides), which leads to the emission of unexpected color rather than white color.^{24,25} Nevertheless, no white light PeLEDs have been demonstrated merely using perovskite active emission layer(s).

Herein, we propose an all-perovskite emission architecture of $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CsPb}_2\text{I}_7$ ($\text{PA}_2\text{CsPb}_2\text{I}_7$) two-dimensional (2D) perovskite/interlayer/ $\text{CsPb}(\text{Br},\text{Cl})_3$ QD for white emission PeLEDs. The white color is expected when the red light emitted from $\text{PA}_2\text{CsPb}_2\text{I}_7$ superimposed onto the

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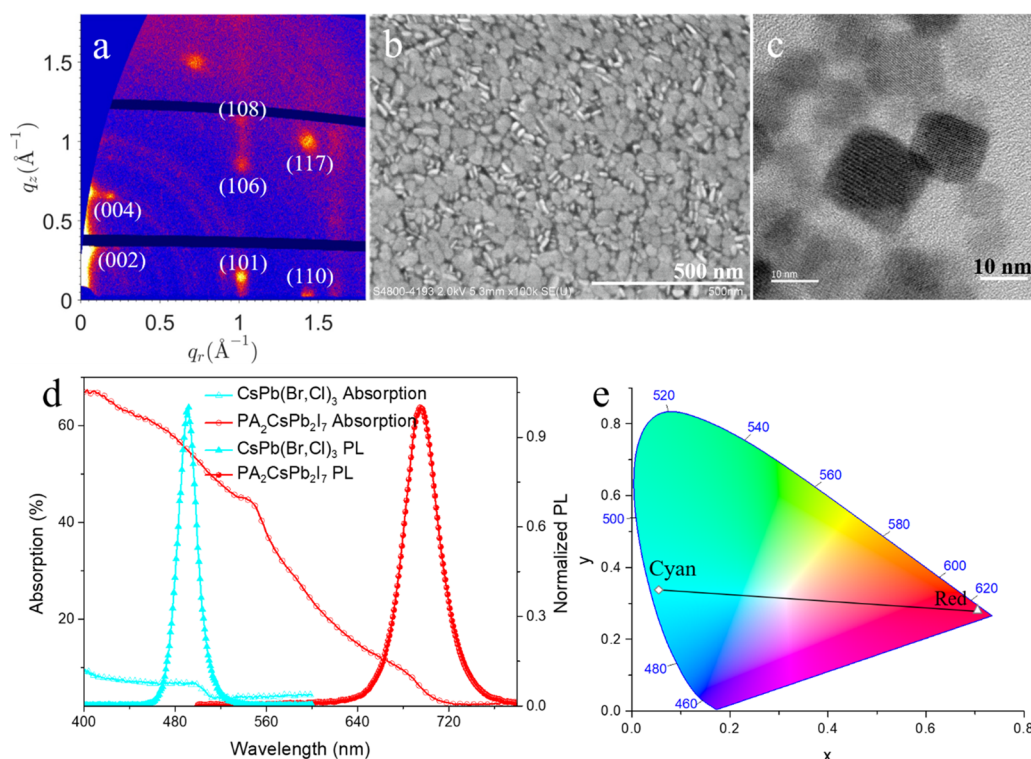


Figure 1. (a) GIWAXS pattern and (b) SEM image of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film, (c) TEM image of $\text{CsPb}(\text{Br},\text{Cl})_3$ QDs, (d) absorption and PL spectrum of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ thin films, and (e) CIE 1931 chromaticity diagram with red and cyan colors.

cyan light emitted from $\text{CsPb}(\text{Br},\text{Cl})_3$ QDs. By carefully choosing the mixture of bis(1-phenyl-1H-benzo[d]imidazole)-phenylphosphine oxide (BIPO) and poly(4-butylphenyl-diphenyl-amine) (Poly-TPD) as the interlayer to avoid the ion exchange between these two perovskites and to facilitate carrier transportation and distribution in the architecture, we successfully demonstrate white PeLEDs with a Commission Internationale de L'Eclairage (CIE) coordinates of (0.32, 0.32), peak radiance of $0.17 \text{ W}/(\text{sr}\cdot\text{m}^2)$, and correlated color temperature (CCT) of $\sim 6000 \text{ K}$. Besides, the PeLEDs exhibit steady CIE coordinates in a wide range of driving current density from 2.94 to $56.29 \text{ mA}/\text{cm}^2$. We believe that our work contributes to the understanding and controlling of carrier distribution in multilayer perovskite emission architecture for all-perovskite white PeLEDs as well as the evolution of PeLEDs toward practical applications in lighting and display.

RESULTS AND DISCUSSION

Owing to the large volume of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$ (PA) group, red emitting $\text{PA}_2\text{CsPb}_2\text{I}_7$ is formed as a layered 2D perovskite, as evidenced by the discrete peaks in grazing incidence wide-angle X-ray scattering (GIWAXS) pattern in Figure 1a. The 2D $\text{PA}_2\text{CsPb}_2\text{I}_7$ possesses good phase stability, as compared with bulk CsPbI_3 which tends to become orthorhombic phase with large band gap ($E_g = 2.82 \text{ eV}$) at room temperature.^{26,27} Besides, $\text{PA}_2\text{CsPb}_2\text{I}_7$ also has good film formability, as shown in the scanning electron microscope (SEM) image in Figure 1b, which is similar to reported 2D perovskites.^{9,28–30} The cyan emitting $\text{CsPb}(\text{Br},\text{Cl})_3$ is an inorganic perovskite QD with sizes around 10 nm , as shown in Figure 1c (and Figure S1). Its electron diffraction pattern (Figure S2) reveals d -spacings of 0.5847 , 0.4095 , 0.3330 , 0.2911 , and 0.2599 nm , corresponding to its (100), (110), (111), (200), and (210)

planes, respectively, which are in accordance with refs 31 and 32. As shown by the PL and absorption spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ in Figure 1d, $\text{PA}_2\text{CsPb}_2\text{I}_7$ emits red color at 695 nm with a full width at half-maximum (fwhm) of 37 nm , and $\text{CsPb}(\text{Br},\text{Cl})_3$ emits cyan color at 492 nm with a fwhm of 20 nm . Guided by the CIE 1931 chromaticity diagram shown in Figure 1e, we expected to achieve white light after combining these two perovskites because the line connecting their CIE coordinates passes through the white emission region.

However, we do not simply mix these two perovskites to obtain white light because the rapid ion exchange between them will generate an unintended color. As shown in the PL spectrum and time-resolved fluorescence lifetime of directly mixed $\text{PA}_2\text{CsPb}_2\text{I}_7$ - $\text{CsPb}(\text{Br},\text{Cl})_3$ thin film (Figure S3), a new peak is found at 637 nm with a shortened lifetime, which is neither the emission of $\text{PA}_2\text{CsPb}_2\text{I}_7$ (695 nm) nor that of $\text{CsPb}(\text{Br},\text{Cl})_3$ (492 nm). Instead, we stack these two perovskites layer-by-layer by carefully selecting appropriate solvents (where n -octane solvent is used for QD to minimize the side-effect on underneath 2D perovskite layer) together with an in-between interlayer. This interlayer is designed to simultaneously function as (i) a spacer to isolate $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ for eliminating ion exchange reaction and (ii) carrier distributors/transporters in the multilayered emission structure. To facilitate the interlayer optimization, we first determined the energy level of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ from their optical absorption and ultraviolet photoelectron spectroscopy (UPS), as shown in Figures S4 and S5, respectively. The optical band gap (E_g) of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ is calculated to be 1.76 and 2.46 eV , respectively. The valence band (VB) is derived to be -5.52 and -6.12 eV , and thus the conduction band (CB) is calculated to be -3.76 and -3.66 eV for $\text{PA}_2\text{CsPb}_2\text{I}_7$ and

CsPb(Br,Cl)₃, respectively. Taking these results into account, we adopt the mixture of BIPO and Poly-TPD as the interlayer since their energy level aligns well with the two perovskites, as shown in Figure 2.

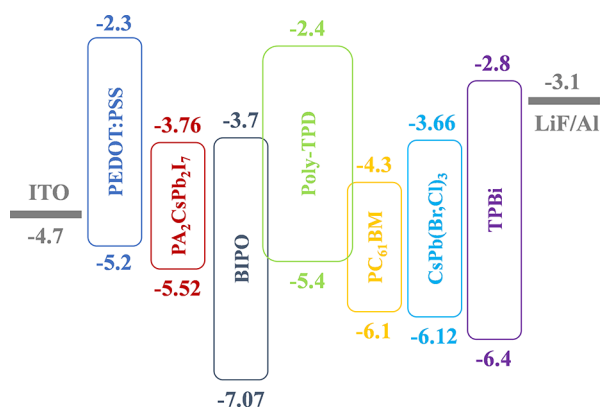


Figure 2. Energy level (units in eV) diagram of PA₂CsPb₂I₇/interlayer/CsPb(Br,Cl)₃ emission architecture based PeLEDs. The interlayer is formed by blending either BIPO:Poly-TPD or PC₆₁BM:Poly-TPD.

Functioning as an efficient interlayer, BIPO serves for electron transport and Poly-TPD for hole transport.^{12,33,34} Also, Poly-TPD exhibits a good cross-linkable property so as to protect the underneath perovskite from damage during the fabrication of the upper perovskite.³⁵ The molecular structures of BIPO and Poly-TPD are shown in Figure S6. In order to prove the effectiveness of the interlayer, we fabricated PeLEDs with the structure of ITO/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃/2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-

1-H-benzimidazole) (TPBi)/lithium fluoride/aluminum (LiF/Al). The multilayer structure of the PeLEDs can be observed from its cross-sectional SEM image in Figure S7. We also prepared red PA₂CsPb₂I₇ PeLED with the structure of ITO/PEDOT:PSS/PA₂CsPb₂I₇/TPBi/LiF/Al and cyan CsPb(Br,Cl)₃ PeLED with the structure of ITO/PEDOT:PSS/Poly-TPD/CsPb(Br,Cl)₃/TPBi/LiF/Al as control devices. The EL spectra of PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLEDs are plotted in Figure 3a. The emission peaks at 493 and 693 nm match well with the PL peaks of red PA₂CsPb₂I₇ PeLED and cyan CsPb(Br,Cl)₃ PeLED, which confirms the effective spacing and carrier transport capabilities of the interlayer. We note that the red light is not caused by blue light excitation of CsPb(Br,Cl)₃ because no red light can be detected when a PA₂CsPb₂I₇ thin film is probed by a 470 nm blue LED with various incident light intensities, as shown in Figure S8. Besides, this emission structure also has the advantage of eliminating the use of insulating capping agents (such as PMMA and silica) for preventing the chemical ion exchange reaction between different perovskites and thus the degradation of electrical conduction in PeLEDs.^{18–20,36} We have carried out the device stability measurement in the glovebox for our PeLEDs, as shown in Figure S9. Owing to the common issue of delocalization of surface ions of perovskite QDs,³⁷ the stability of CsPb(Br,Cl)₃ PeLED is not as good as 2D PeLEDs. Here, the CsPb(Br,Cl)₃ PeLED possesses a L₅₀ (time taken for the electroluminescence decay to 50% from its initial value) of about 25 s and works continuously for a 100 s under an applied current density of 50 mA/cm². Nevertheless, after stacking the cyan CsPb(Br,Cl)₃ QDs with 2D PA₂CsPb₂I₇, the operation lifetime of all-perovskite white PeLED (measured under fixed current density of 30 mA/cm²) is improved, and its L₅₀ prolongs to ~150 s, that is, 5 times longer than that of cyan PeLEDs. This indicates the 2D

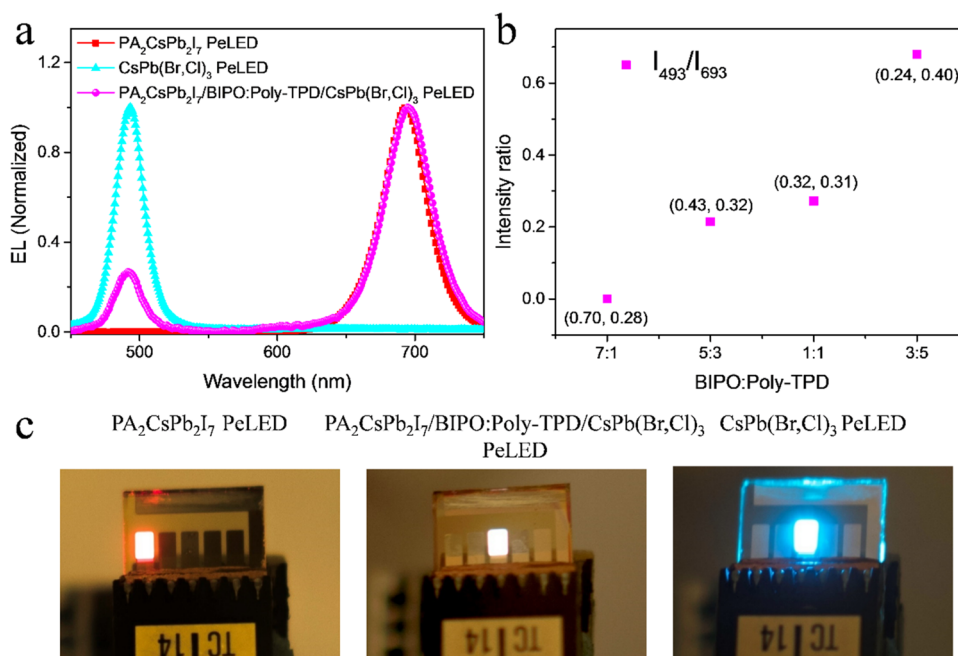


Figure 3. (a) Normalized EL spectra of PA₂CsPb₂I₇ PeLED, PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLED (BIPO:Poly-TPD = 1:1), and CsPb(Br,Cl)₃ PeLED. (b) Influence of BIPO:Poly-TPD ratio on the intensity ratio of EL peak at 493 nm to the peak at 693 nm (I_{493}/I_{693}) as well as the CIE coordinates in PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLEDs. (c) Photographs of PA₂CsPb₂I₇ PeLED, PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLED (BIPO:Poly-TPD = 1:1), and CsPb(Br,Cl)₃ PeLED.

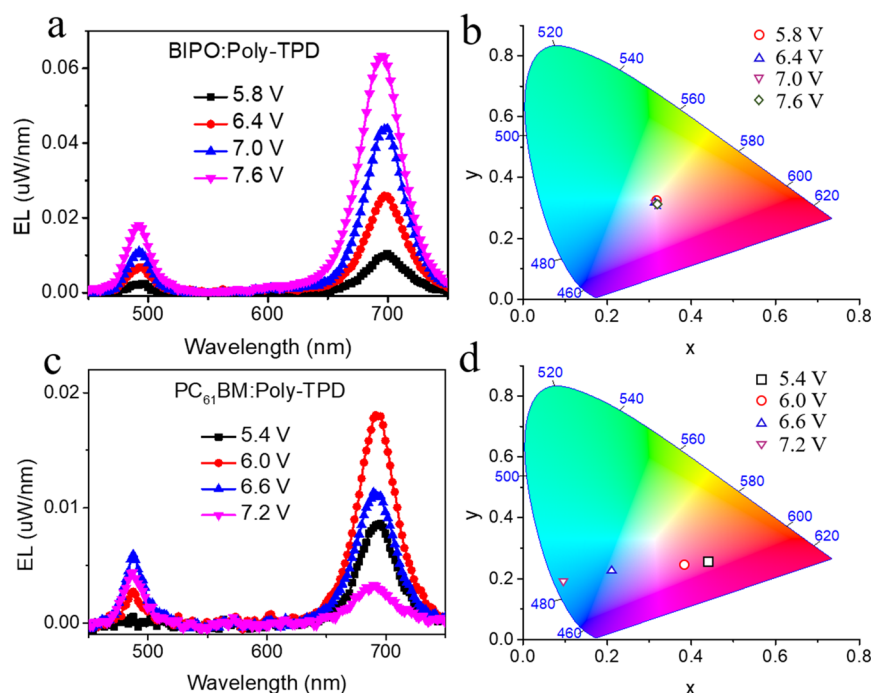


Figure 4. (a) EL spectra and (b) CIE coordinates against voltage change of PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLED. (c) EL spectra and (d) CIE coordinates against voltage change of PA₂CsPb₂I₇/PC₆₁BM:Poly-TPD/CsPb(Br,Cl)₃ PeLED.

PA₂CsPb₂I₇ is beneficial to improve the stability of the white PeLEDs. Future improvement in the stability of all-perovskite white PeLED will focus on the improvement of the stability for the cyan light component.

Moreover, we discovered that the intensity ratio of EL peak at 493 nm to the peak at 693 nm, defined as I_{493}/I_{693} , is tunable by controlling the weight ratio of BIPO to Poly-TPD in the interlayer. Decreasing the ratio of BIPO:Poly-TPD interlayer gradually from 7:1 to 3:5 leads to the increase of I_{493}/I_{693} from 0 to 0.68, allowing us to achieve tunable CIE coordinates from the red region (0.70, 0.28) through the white region (0.32, 0.32; used for our white PeLED) to the cyan region (0.24, 0.40), as shown in Figure 3b. The EL spectra are plotted in Figure S10a–d. We attribute this EL tunability to the carrier distribution in PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLEDs controlled by the interlayer. During the operation of PeLEDs, electrons will pass through the Al cathode, the lowest unoccupied molecular orbital (LUMO) of TPBi, the CB of CsPb(Br,Cl)₃, the LUMO of BIPO, and finally the CB of PA₂CsPb₂I₇.³⁸ At the same time, holes will follow the path of ITO anode, the highest occupied molecular orbital (HOMO) of PEDOT:PSS, the VB of PA₂CsPb₂I₇, the HOMO of Poly-TPD, and finally the VB of CsPb(Br,Cl)₃. When the interlayer is dominated by the electron transport material (ETM) (BIPO:Poly-TPD = 7:1), electrons can easily transport through the interlayer and reach underneath PA₂CsPb₂I₇ layer. However, holes are difficult to pass through the interlayer and reach upper CsPb(Br,Cl)₃ layer because of the limited hole transport channel, resulting in dominate red emission but negligible cyan. If their components are comparable at BIPO:Poly-TPD = 1:1, both electrons and holes can transport through the interlayer and reach two perovskites, leading to the appropriate emission of red and cyan colors for white color. It should be noted that we also found similar EL tunability in PA₂CsPb₂I₇/phenyl-C61-butyric acid methyl ester (PC₆₁BM):Poly-TPD/CsPb(Br,Cl)₃ Pe-

LEDs, where PC₆₁BM functions as ETM, as shown in Figure S10e–h.

The tunability of the emission spectra allows us to find the protocol of BIPO:Poly-TPD = 1:1 in PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLED for white light emission with a CIE coordinates of (0.32, 0.32) and correlated color temperature (CCT) of ~6000 K. A photograph of the white PeLED is given in Figure 3c, and its video clip is provided in Video S1. The peak radiance and peak EQE of the white PeLED reach 0.17 W/(sr·m²) and 0.22%, respectively, as shown in Figure S11a,d, which are significantly higher than the PeLED using PC₆₁BM:Poly-TPD as the interlayer in device structure of PA₂CsPb₂I₇/PC₆₁BM:Poly-TPD/CsPb(Br,Cl)₃ (e.g., 0.065 W/(sr·m²) and 0.058% for PC₆₁BM:Poly-TPD = 5:3 that optimized for white light emitting). The higher performance of the BIPO:Poly-TPD based PeLED can be explained by the matched energy level configurations among BIPO (LUMO: −3.7 eV), PA₂CsPb₂I₇ (CB: −3.76 eV), and CsPb(Br,Cl)₃ (CB: −3.66 eV). While for PC₆₁BM:Poly-TPD-based PeLED, the LUMO (−4.3 eV) of PC₆₁BM is much lower than the CB of PA₂CsPb₂I₇ and CsPb(Br,Cl)₃, leading to inefficient electron transport between two perovskites and thus low radiance and poor EQE. The overall EQE value in white PA₂CsPb₂I₇/BIPO:Poly-TPD/CsPb(Br,Cl)₃ PeLED should be affected by the PA₂CsPb₂I₇ and CsPb(Br,Cl)₃ emission layers, as shown in Figure S12, as well as the interlayer. It should be noted that improving EQE of PeLED (especially blue PeLED) is one of the widespread problems and part of our ongoing research.^{22,39,40}

Importantly, we found that the PeLED configuration of PA₂CsPb₂I₇/BIPO:Poly-TPD (1:1)/CsPb(Br,Cl)₃ is vital for maintaining steady white emission in a wide range of driving current density from 2.94 mA/cm² (5.4 V) to 56.29 mA/cm² (8.4 V), with very small CIE coordinates fluctuation (0.322 ± 0.002 , 0.316 ± 0.007), as shown in Figure 4a,b. Detailed CIE data under different voltage are tabulated in Table S1. Steady

white emission LED is valuable for practical application. We attribute the steady white emission to the large energy barrier (1.55 eV) between the VB of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and the HOMO of BIPO for holes transport as well as the large barrier (1.26 eV) between the CB of $\text{CsPb}(\text{Br},\text{Cl})_3$ and the LUMO of Poly-TPD for electrons transport. These large energy barriers contribute to good hole and electron blocking properties, respectively. In this case, the transport of holes and electrons is determined by the HOMO of Poly-TPD and the LUMO of BIPO, respectively, resulting in a balanced carrier distribution in the two perovskite layers in a wide range of driving current densities. In comparison, CIE coordinates of PC_{61}BM :Poly-TPD based PeLEDs show a small bias tolerance, with the EL spectra shifting from red region at a low voltage of 5.4 V to cyan region at a high voltage of 7.2 V, as shown in Figure 4d,e. This behavior is attributed to the small barrier (0.58 eV) between the VB of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and the HOMO of PC_{61}BM since holes should be able to overcome the small barrier at high voltage, leading to a color shifting.

CONCLUSIONS

In conclusion, all-perovskite white PeLEDs concept and architecture have been demonstrated using a $\text{PA}_2\text{CsPb}_2\text{I}_7$ /BIPO:Poly-TPD/ $\text{CsPb}(\text{Br},\text{Cl})_3$ emission architecture. With the proposed architecture, we address the challenges of the ion exchanges between different perovskites, solvent incompatibility in stacking different perovskite, and carrier transport layers during the solution process. The matched energy level configuration between perovskites and interlayer and the effective spacing through interlayer contribute to the realization of high performance and color-stable all-perovskite white PeLEDs. Future research will focus on perfecting the emission architecture by exploring new perovskites and interlayers to further improve the EQE of white PeLEDs. We believe that our work will contribute to the practical applications of PeLEDs in lighting and display, and the proposed perovskite material and all-perovskite concept will provide ideas for the design and development of more perovskite-based devices.

METHODS

Chemical Synthesis. $\text{PA}_2\text{CsPb}_2\text{I}_7$ 2D perovskite was prepared by dissolving *n*-propylammonium iodide (PAI, 0.2 mmol, Dyesol), cesium iodide (CsI, 0.1 mmol, Aladdin, 99.999%), and lead iodide (PbI_2 , 0.2 mmol, TCI) in dimethylformamide (DMF, 1 mL, Acros, extra dry). $\text{CsPb}(\text{Br},\text{Cl})_3$ QD was fabricated using a modified hot injection method. In detail, cesium carbonate (Cs_2CO_3 , 407 mg, J&K Scientific, 99.9%), oleic acid (OA, 1.4 mL, International Lab, 98%), and octadecene (ODE, 20 mL, Acros, 90%) were mixed in a three-necked flask. The mixture was heated at 150 °C with nitrogen flow until Cs_2CO_3 was completely dissolved. The obtained Cs-oleate solution was kept at 130 °C. On the other hand, lead bromide (PbBr_2 , 0.305 mmol, TCI), lead chloride (PbCl_2 , 0.072 mmol, Sigma-Aldrich, 99.9%), OA (1 mL), oleylamine (OLA, 1 mL, J&K Scientific, 97.5%), and ODE (10 mL) were added to another three-necked flask. The lead halide was dissolved after heating it at 110 °C with nitrogen flow for 1 h. After increasing the temperature of the lead halide solution to 180 °C, as-prepared Cs-oleate solution (0.75 mL) was swiftly injected into the lead halide solution. Less than 5 s after injection, the lead halide solution was cooled down using an ice bath. The color became yellowish during cooling, indicating the formation of $\text{CsPb}(\text{Br},\text{Cl})_3$ QDs. The crude product was centrifuged at 6000 rpm for 10 min after adding ethyl acetate (EA, 30 mL, Acros). The obtained precipitate was dissolved in octane (2 mL, J&K Scientific) and precipitated again after adding EA (5 mL). Centrifugation at 12,000

rpm for 8 min was used to obtain a purified $\text{CsPb}(\text{Br},\text{Cl})_3$ QD. The $\text{CsPb}(\text{Br},\text{Cl})_3$ QD was eventually dispersed in octane (6 mL).

PeLEDs Fabrication. We have fabricated a number of PeLEDs, namely red $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLED, cyan $\text{CsPb}(\text{Br},\text{Cl})_3$ PeLED, and $\text{PA}_2\text{CsPb}_2\text{I}_7$ -interlayer- $\text{CsPb}(\text{Br},\text{Cl})_3$ PeLED. In $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLED, the PEDOT:PSS (Heraeus Clevis 4083) was spin coated at 4000 rpm and annealed at 150 °C for 10 min. The $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film was prepared by spin coating its precursor (dissolved in DMF) at 6000 rpm on PEDOT:PSS and annealing at 120 °C for 10 min. Subsequently, TPBi (30 nm, Nichem), LiF (0.5 nm), and Al (120 nm) were thermally evaporated under a vacuum of $<5 \times 10^{-6}$ Torr. In $\text{CsPb}(\text{Br},\text{Cl})_3$ PeLED, PEDOT:PSS, TPBi, LiF, and Al were deposited under the same condition in $\text{PA}_2\text{CsPb}_2\text{I}_7$ PeLED. Poly-TPD (5 mg/mL, 1-material) was dissolved in chlorobenzene (Acros, extra dry), spin coated at 4000 rpm on PEDOT:PSS, and then annealed at 120 °C for 20 min. $\text{CsPb}(\text{Br},\text{Cl})_3$ QDs (dispersed in octane) were spin coated at 4000 rpm. In red-interlayer-cyan PeLEDs, PEDOT:PSS, $\text{PA}_2\text{CsPb}_2\text{I}_7$, $\text{CsPb}(\text{Br},\text{Cl})_3$, TPBi, LiF, and Al were deposited under the same conditions in $\text{PA}_2\text{CsPb}_2\text{I}_7$ (or $\text{CsPb}(\text{Br},\text{Cl})_3$) PeLED. The mixture interlayer (8 mg/mL) with weight ratios of 7:1, 5:3, 1:1, 3:5 was prepared by dissolving BIPO (Lumtec) (or PC_{61}BM (Solarmer)) and Poly-TPD in chlorobenzene and spin coated at 4000 rpm. Annealing at 120 °C for 10 min was performed to crystallize the interlayer.

Characterization. The morphology of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film was measured with SEM (Hitachi S-4800 FEG) with an accelerating voltage of 2 kV. The GIWAXS of $\text{PA}_2\text{CsPb}_2\text{I}_7$ thin film was measured with an in-house device Xeuss2.0 manufactured by Xenocs. The X-ray source was copper (Cu), and its wavelength was 1.54 Å. The incidence angle was 0.2°. The $\text{CsPb}(\text{Br},\text{Cl})_3$ QD was characterized with transmission electron microscope (TEM) (Philips CM100). The absorption spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ thin films were obtained from a home-built system with a xenon lamp as the light source and an integrated sphere associated with a charge-coupled device (CCD, Ocean Optics QE Pro) as the detector. The PL spectra of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ thin films were measured with a 375 nm ps pulse laser (PicoQuant LDH-P-C-375) and a photomultiplier (PMA-C 192-M) detector. The UPS of $\text{PA}_2\text{CsPb}_2\text{I}_7$ and $\text{CsPb}(\text{Br},\text{Cl})_3$ thin films was conducted with Axis Ultra DLD (Kratos). He (I) with 21.22 eV was used to obtain the spectra. The performance of PeLEDs was measured in the glovebox using a Keithley 2635 SourceMeter, and the EL spectra and radiance were recorded using an integrating sphere which was connected to an Ocean Optics QE65000 spectrometer. The integrating sphere was calibrated with an Ocean Optics HL-3P-CAL radiometric calibration light source. The CIE coordinates and CCT of PeLEDs were calculated using software LED ColorCalculator (OSRAM).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b06196.

Tabulated performance data of white emission PeLED and additional figures characterizing the materials and devices (Table S1 and Figures S1–S12) (PDF)

Video S1: Electroluminescence of white, red and blue PeLEDs under continuously applied voltages (AVI)

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Author Contributions

^{||}Jian Mao and Hong Lin contributed equally to this work.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Wang, N. N.; Cheng, L.; Ge, R.; Zhang, S. T.; Miao, Y. F.; Zou, W.; Yi, C.; Sun, Y.; Cao, Y.; Yang, R.; Wei, Y. Q.; Guo, Q.; Ke, Y.; Yu, M. T.; Jin, Y. Z.; Liu, Y.; Ding, Q. Q.; Di, D. W.; Yang, L.; Xing, G. C.; Tian, H.; Jin, C. H.; Gao, F.; Friend, R. H.; Wang, J. P.; Huang, W. Perovskite Light-Emitting Diodes Based on Solution-processed Self-organized Multiple Quantum Wells. *Nat. Photonics* **2016**, *10*, 699–704.
- (2) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission With Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
- (3) Kim, Y. H.; Cho, H.; Lee, T. W. Metal Halide Perovskite Light Emitters. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 11694–11702.
- (4) deQuilettes, D. W.; Zhang, W.; Burlakov, V. M.; Graham, D. J.; Leijtens, T.; Osherov, A.; Bulović, V.; Snaith, H. J.; Ginger, D. S.; Stranks, S. D. Photo-induced Halide Redistribution in Organic–inorganic Perovskite Films. *Nat. Commun.* **2016**, *7*, 11683.
- (5) Tan, Z. K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9*, 687–692.
- (6) Lin, H.; Zhu, L.; Huang, H.; Reckmeier, C. J.; Liang, C.; Rogach, A. L.; Choy, W. C. Efficient Near-infrared Light-Emitting Diodes Based on Organometallic Halide Perovskite-poly(2-ethyl-2-oxazoline) Nanocomposite Thin Films. *Nanoscale* **2016**, *8*, 19846–19852.
- (7) Cho, H.; Jeong, S. H.; Park, M. H.; Kim, Y. H.; Wolf, C.; Lee, C. L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T. W. Overcoming the Electroluminescence Efficiency Limitations of Perovskite Light-Emitting Diodes. *Science* **2015**, *350*, 1222–1225.
- (8) Zhang, L.; Yang, X.; Jiang, Q.; Wang, P.; Yin, Z.; Zhang, X.; Tan, H.; Yang, Y. M.; Wei, M.; Sutherland, B. R.; Sargent, E. H.; You, J. Ultra-bright and Highly Efficient Inorganic Based Perovskite Light-Emitting Diodes. *Nat. Commun.* **2017**, *8*, 15640.
- (9) Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H. Perovskite Energy Funnels for Efficient Light-Emitting Diodes. *Nat. Nanotechnol.* **2016**, *11*, 872–877.
- (10) Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H. 50-fold EQE Improvement Up to 6.27% of Solution-processed All-inorganic Perovskite CsPbBr_3 QLEDs via Surface Ligand Density Control. *Adv. Mater.* **2017**, *29*, 1603885.
- (11) Li, G.; Rivalora, F. W.; Davis, N. J.; Bai, S.; Jellicoe, T. C.; de la Pena, F.; Hou, S.; Ducati, C.; Gao, F.; Friend, R. H.; Greenham, N. C.; Tan, Z. K. Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method. *Adv. Mater.* **2016**, *28*, 3528–3534.
- (12) Zhang, X.; Lin, H.; Huang, H.; Reckmeier, C.; Zhang, Y.; Choy, W. C.; Rogach, A. L. Enhancing the Brightness of Cesium Lead Halide Perovskite Nanocrystal Based Green Light-Emitting Devices Through the Interface Engineering with Perfluorinated Ionomer. *Nano Lett.* **2016**, *16*, 1415–1420.
- (13) Mao, J.; Sha, W. E. I.; Zhang, H.; Ren, X. G.; Zhuang, J. Q.; Roy, V. A. L.; Wong, K. S.; Choy, W. C. H. Novel Direct Nanopatterning Approach to Fabricate Periodically Nanostructured Perovskite for Optoelectronic Applications. *Adv. Funct. Mater.* **2017**, *27*, 1606525.
- (14) Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. Self-assembly of Broadband White-light Emitters. *J. Am. Chem. Soc.* **2014**, *136*, 1718–1721.
- (15) Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G. White-light Emission and Structural Distortion in New Corrugated Two-dimensional Lead Bromide Perovskites. *J. Am. Chem. Soc.* **2017**, *139*, 5210–5215.
- (16) Thirumal, K.; Chong, W. K.; Xie, W.; Ganguly, R.; Muduli, S. K.; Sherburne, M.; Asta, M.; Mhaisalkar, S.; Sum, T. C.; Soo, H. S.; Mathews, N. Morphology-independent Stable White-light Emission from Self-assembled Two-dimensional Perovskites Driven by Strong Exciton–phonon Coupling to the Organic Framework. *Chem. Mater.* **2017**, *29*, 3947–3953.
- (17) Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. One-dimensional Organic Lead Halide Perovskites with Efficient Bluish White-light Emission. *Nat. Commun.* **2017**, *8*, 14051.
- (18) Li, X.; Wu, Y.; Zhang, S.; Cai, B.; Gu, Y.; Song, J.; Zeng, H. CsPbX_3 Quantum Dots for Lighting and Displays: Room-temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes. *Adv. Funct. Mater.* **2016**, *26*, 2435–2445.
- (19) Sun, C.; Zhang, Y.; Ruan, C.; Yin, C.; Wang, X.; Wang, Y.; Yu, W. W. Efficient and Stable White LEDs with Silica-coated Inorganic Perovskite Quantum Dots. *Adv. Mater.* **2016**, *28*, 10088–10094.
- (20) Pathak, S.; Sakai, N.; Rivalora, F. W. R.; Stranks, S. D.; Liu, J. W.; Eperon, G. E.; Ducati, C.; Wojciechowski, K.; Griffiths, J. T.; Haghighirad, A. A.; Pellaroque, A.; Friend, R. H.; Snaith, H. J. Perovskite Crystals for Tunable White Light Emission. *Chem. Mater.* **2015**, *27*, 8066–8075.
- (21) Huang, H.; Chen, B. K.; Wang, Z. G.; Hung, T. F.; Susa, A. S.; Zhong, H. Z.; Rogach, A. L. Water Resistant CsPbX_3 Nanocrystals Coated with Polyhedral Oligomeric Silsesquioxane and Their Use as Solid State Luminescences in All-perovskite White light-Emitting Devices. *Chem. Sci.* **2016**, *7*, 5699–5703.
- (22) Yao, E. P.; Yang, Z.; Meng, L.; Sun, P.; Dong, S.; Yang, Y.; Yang, Y. High-brightness Blue and White LEDs Based on Inorganic Perovskite Nanocrystals and Their Composites. *Adv. Mater.* **2017**, *29*, 1606859.
- (23) Huang, C. Y.; Huang, S. J.; Liu, M. H. M. Hybridization of $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ Perovskite Quantum Dots with 9,9-dihexylfluorene Co-oligomer for White Electroluminescence. *Org. Electron.* **2017**, *44*, 6–10.
- (24) Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V. Fast Anion-exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, I). *Nano Lett.* **2015**, *15*, 5635–5640.
- (25) Li, G. J.; Ho, J. Y. L.; Wong, M.; Kwok, H. S. Reversible Anion Exchange Reaction in Solid Halide Perovskites and Its Implication in Photovoltaics. *J. Phys. Chem. C* **2015**, *119*, 26883–26888.
- (26) Swarnkar, A.; Marshall, A. R.; Sanhira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum Dot-induced Phase Stabilization of Alpha- CsPbI_3 Perovskite for High-efficiency Photovoltaics. *Science* **2016**, *354*, 92–95.
- (27) Eperon, G. E.; Paterno, G. M.; Sutton, R. J.; Zampetti, A.; Haghighirad, A. A.; Cacialli, F.; Snaith, H. J. Inorganic Caesium Lead Iodide Perovskite Solar Cells. *J. Mater. Chem. A* **2015**, *3*, 19688–19695.
- (28) Chen, Z.; Zhang, C.; Jiang, X. F.; Liu, M.; Xia, R.; Shi, T.; Chen, D.; Xue, Q.; Zhao, Y. J.; Su, S.; Yip, H. L.; Cao, Y. High-

performance Color-tunable Perovskite Light Emitting Devices Through Structural Modulation from Bulk to Layered Film. *Adv. Mater.* **2017**, *29*, 1603157.

(29) Wang, Z.; Lin, Q.; Chmiel, F. P.; Sakai, N.; Herz, L. M.; Snaith, H. J. Efficient Ambient-air-stable Solar Cells with 2D–3D Heterostructured Butylammonium-caesium-formamidinium Lead Halide Perovskites. *Nature Energy* **2017**, *2*, 17135.

(30) Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. 2D Homologous Perovskites as Light-absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, *137*, 7843–7850.

(31) Song, J.; Li, J.; Li, X.; Xu, L.; Dong, Y.; Zeng, H. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX_3). *Adv. Mater.* **2015**, *27*, 7162–7167.

(32) Wang, S.; Bi, C.; Yuan, J.; Zhang, L.; Tian, J. Original Core-shell Structure of Cubic CsPbBr_3 @amorphous CsPbBr_x Perovskite Quantum Dots With a High Blue Photoluminescence Quantum Yield of Over 80%. *ACS Energy Lett.* **2018**, *3*, 245–251.

(33) Yoo, S. J.; Yun, H. J.; Kang, I.; Thangaraju, K.; Kwon, S. K.; Kim, Y. H. A New Electron Transporting Material for Effective Hole-blocking and Improved Charge Balance in Highly Efficient Phosphorescent Organic Light Emitting Diodes. *J. Mater. Chem. C* **2013**, *1*, 2217–2223.

(34) Malinkiewicz, O.; Yella, A.; Lee, Y. H.; Espallargas, G. M.; Graetzel, M.; Nazeeruddin, M. K.; Bolink, H. J. Perovskite Solar Cells Employing Organic Charge-transport Layers. *Nat. Photonics* **2014**, *8*, 128–132.

(35) Haverinen, H. M.; Myllyla, R. A.; Jabbour, G. E. Inkjet Printing of Light Emitting Quantum Dots. *Appl. Phys. Lett.* **2009**, *94*, 073108.

(36) Wang, H. C.; Lin, S. Y.; Tang, A. C.; Singh, B. P.; Tong, H. C.; Chen, C. Y.; Lee, Y. C.; Tsai, T. L.; Liu, R. S. Mesoporous Silica Particles Integrated with All-inorganic CsPbBr_3 Perovskite Quantum-dot Nanocomposites (MP-PQDs) with High Stability and Wide Color Gamut Used for Backlight Display. *Angew. Chem., Int. Ed.* **2016**, *55*, 7924–7929.

(37) Zhang, M.; Tian, Z. Q.; Zhu, D. L.; He, H.; Guo, S. W.; Chen, Z. L.; Pang, D. W. Stable CsPbBr_3 Perovskite Quantum Dots with High Fluorescence Quantum Yields. *New J. Chem.* **2018**, *42*, 9496–9500.

(38) Reineke, S.; Thomschke, M.; Lussem, B.; Leo, K. White Organic Light-Emitting Diodes: Status and Perspective. *Rev. Mod. Phys.* **2013**, *85*, 1245–1293.

(39) Gangishetty, M. K.; Hou, S.; Quan, Q.; Congreve, D. N. Reducing Architecture Limitations for Efficient Blue Perovskite Light-Emitting Diodes. *Adv. Mater.* **2018**, *30*, 1706226.

(40) Tsai, H.; Nie, W.; et al. Stable Light-Emitting Diodes Using Phase-pure Ruddlesden-popper Layered Perovskites. *Adv. Mater.* **2018**, *30*, 1704217.