

# Ligands Optimization Governed by Solubility Principles for Pure Blue Emission in Mixed-Halide Perovskite LEDs

Dongyu Li,<sup>||</sup> Benzheng Lyu,<sup>||</sup> Jiayun Sun, Qi Xiong, Hanwen Zhu, Zhengyan Jiang, Dezhong Zhang, Chunyu Liu, and Wallace C. H. Choy\*



Cite This: *ACS Energy Lett.* 2024, 9, 3261–3268



Read Online

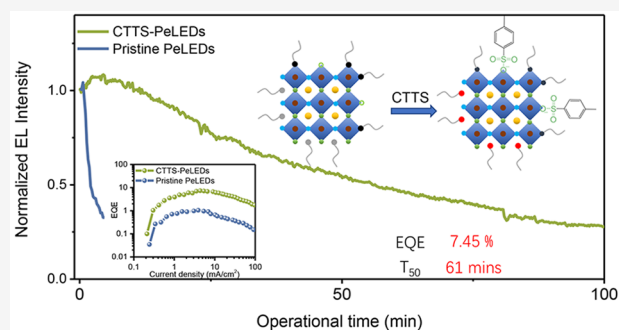
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Mixed-chloride/bromide perovskite nanocrystals (PeNCs) possess unique advantages for pure blue emission but suffer from severe halogen segregation. While ligand exchange is a promising method to improve stability, there are limited studies on comparative evaluation of the ligand ion pair combinations. We conduct a comprehensive investigation of the ligand exchange process by combining different ion pairs. Surprisingly, changes of ligand ion combinations cause a deviation from pure blue emission of  $\text{CsPbBr}_x\text{Cl}_{3-x}$ , even without intentional halogen alteration. This spectral shift is attributed to the halogen redistribution, which is dominated by the solubility principle in a nonpolar environment. With a detailed ligand-exchange study, we demonstrate pure-blue perovskite light-emitting diodes (PeLEDs) with an external quantum efficiency (EQE) of 7.45% and an operational half-lifetime ( $T_{50}$ ) of 61 min at an initial luminance of  $100 \text{ cd m}^{-2}$ . Our findings provide a ligand selection guideline and promote mixed-halide, pure blue PeLEDs for practical applications.



Mixed halide chloride/bromide perovskite nanocrystals (PeNCs) featuring a narrow full-width at half-maximum (fwhm) in emission spectra, and solution process capability, can straightforwardly achieve pure blue emission through modulating the halide anions, making them promising candidates as active layers for pure blue light emitting diodes (LEDs).<sup>1–6</sup> Compared to mixed-halide perovskites, which can modify the energy band by adjusting the chemical composition, the color purity of pure-blue-emitting two-dimensional and small-sized nanocrystals (typically <7 nm) with a strong quantum confinement effect highly depends on the narrowness of the phase and particle size distributions, which presents significant technical challenges and low yields for practical application.<sup>7</sup> In contrast, larger-sized PeNCs with weak quantum confinement effects do not require additional size purification to achieve high color purity.<sup>8</sup> However, mixed-halide PeNCs suffer from spectral instability due to phase segregation, which is very sensitive to the surface defects.<sup>9–13</sup> Furthermore, these localized defect states act as nonradiative recombination centers, reducing the photoluminescence quantum yield (PLQY) of PeNCs and limiting performances of perovskite LEDs (PeLEDs).<sup>14–19</sup> Overall, more effort has to be devoted to constructing high-performance PeNCs and their LED designs.

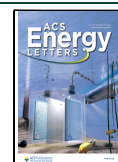
The surface defects are highly related to the dynamic equilibrium of ligands such as oleic acid (OA) and oleylamine (OAm) commonly used in synthesizing PeNCs, whereby ligand post-treatments for the replacing ligands with weak bonding strength and passivation have been extensively studied to eliminate PeNCs vacancies and enhance PeLED performances.<sup>20–24</sup> The charge transfer capability of PeNCs capping ligands is also crucial for efficient carrier injection and thus electroluminescence (EL).<sup>25–29</sup> Among various substitution ligands, the benzenesulfonic group could be an ideal candidate to passivate the PeNCs' surface defects due to the stronger chemical bonding with uncoordinated  $\text{Pb}^{2+}$  than carboxyl and phosphate groups.<sup>30–32</sup> In addition, quaternary ammonium salt can more steadily bind with the surface of PeNCs than  $\text{NH}_4^+$  in OAm, due to the fact that  $\text{OAm}^+$  will easily deprotonate to a neutral molecule, leading to highly dynamic binding.<sup>20,33,34</sup>

Received: March 27, 2024

Revised: May 31, 2024

Accepted: June 4, 2024

Published: June 7, 2024



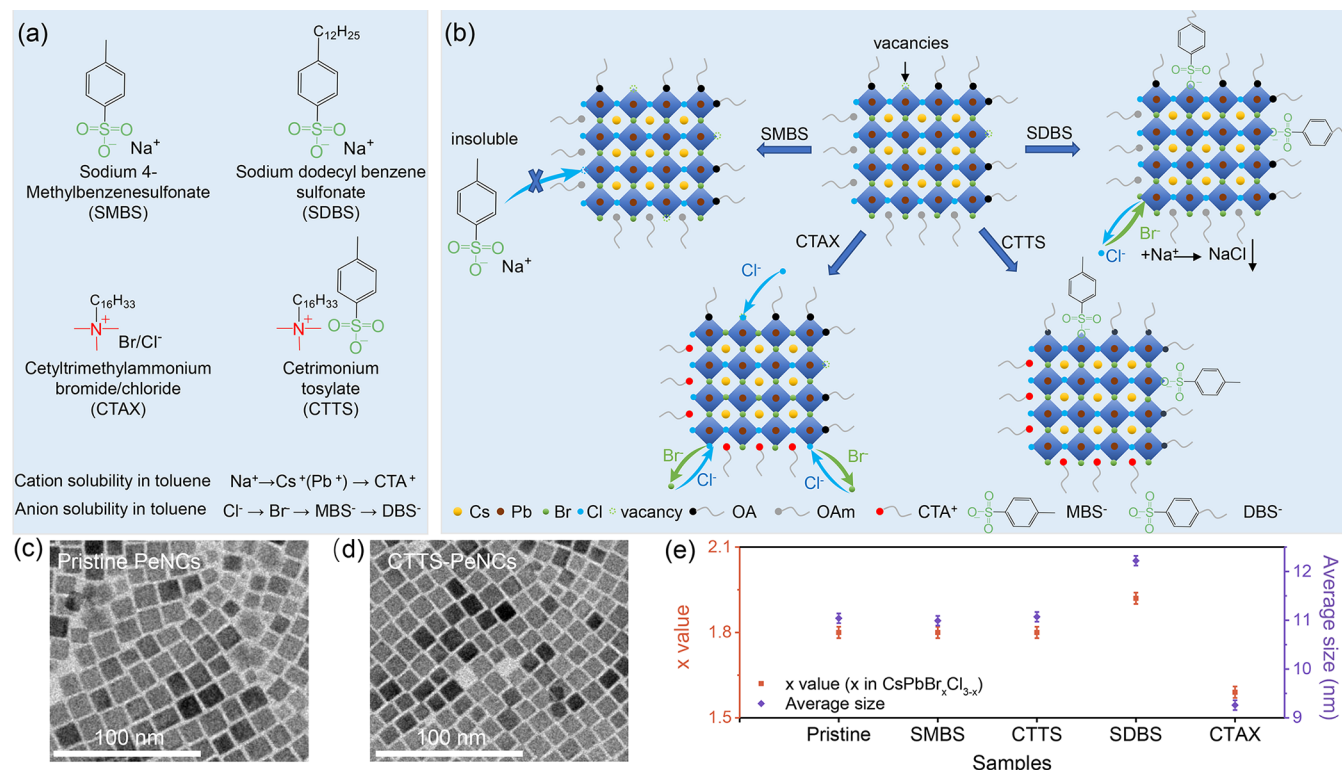


**Figure 1.** (a) The molecular structure and the solubility in toluene of SMBS, SDBS, CTAX, and CTTS ligands. The solubility of  $\text{Cs}^+ (\text{Pb}^+)$  is between  $\text{Na}^+$  and quaternary ammonium salt ( $\text{CTA}^+$ ), while the solubility of anions from low to high is  $\text{Cl}^-$ ,  $\text{Br}^-$ , 4-methylbenzenesulfonate ( $\text{MBS}^-$ ), and dodecyl benzenesulfonate ( $\text{DBS}^-$ ). Here, we categorize ions with a solubility lower than or equal to that of perovskite components as low solubility ions, while those with higher solubility are considered high solubility ions. (b) Illustration of ligand passivation mechanisms of  $\text{CsPbBr}_{1.8}\text{Cl}_{1.2}$  PeNCs. (c,d) TEM image of pristine and CTTS PeNCs. (e) Average size and x value of pristine and ligand-treated PeNCs. The x value is the Br content of  $\text{CsPbBr}_x\text{Cl}_{3-x}$ . Notably, all of the above ligand-treated PeNCs were formed from pristine PeNCs at  $\sim 11$  nm.

Inorganic salts with a good conductivity offer an alternative strategy to passivate PeNCs and improve charge injection/transport in PeLEDs, such as  $\text{NaBr}$ ,<sup>35</sup> thiocyanate salt,<sup>36</sup> tetrafluoroborate salts,<sup>37</sup> and nitrate salts,<sup>38</sup> reducing the turn-on voltage. However, these inorganic ligands usually need to be dissolved in DMF due to their low solubility in nonpolar solvents, leading to PeNCs degradation.<sup>39,40</sup> The combination of inorganic or short carbon chain ligands with longer organic ligands can avoid the use of polar solvents and promote dispersion in nonpolar solvents.<sup>41</sup> To date, the comparative evaluation of the aforementioned exceptional ligands and determination of the optimal ion combination have been limitedly reported, particularly in the case of  $\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs.

In this study, we comprehensively investigate the ligand exchange process involving the combination of different ion pairs. Surprisingly, the combination of inorganic ions with sulfonate or quaternary ammonium results in shifting the blue emission spectrum in  $\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs without adding any halogen or altering of halogen ratios. Further investigation reveals that the spectral shift originates from halogen redistribution caused by the solubility changes of different components in a nonpolar environment. Moreover, the influences of factors such as reaction time, temperature, dispersing solvent, and PeNCs size on the spectral shift have been investigated in detail, showing the complexity in the shift control. As a result, cetrimonium tosylate (CTTS) is identified as a suitable ligand that can ensure pure blue emission of

$\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs, and simultaneously passivate defects as well as enhance charge injection, without the need of any strong polar solvents. Fundamentally, we provide a ligand selection guideline based on solubility principles to prevent the spectral shift of mixed-Cl/Br PeNCs. Finally, pure-blue PeLEDs with Commission Internationale de l'Eclairage (CIE) coordinates of (0.131, 0.046), a peak EQE of 7.45%, and an operational half-lifetime ( $T_{50}$ ) of 61 min are achieved. Consequently, this work highlights the pivotal role of ligands in determining the emission spectrum and provides an effective strategy for significantly enhancing the performance of mixed-halide pure-blue PeLEDs.

The molecular structures of four ligands, including sodium 4-methylbenzenesulfonate (SMBS), sodium dodecyl benzene sulfonate (SDBS), cetyltrimethylammonium bromide/chloride (CTAX), and CTTS, are shown in Figure 1a. At the bottom of Figure 1a, the solubility of ligands and PeNCs in solvents (toluene or octane) is presented based on experimental results. Importantly, based on our results, as will be elaborated later, we provide a guide for selecting ligand ions suitable for  $\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs:

1. The two kinds of ions of the combined ion pairs, both with low solubility, such as  $\text{NaCl}$  and  $\text{NaBr}$ , may potentially serve as effective passivation agents for perovskites without inducing changes in PeNCs composition and spectral shift,<sup>35</sup> but they need to be dissolved in DMF due to their low solubility in nonpolar solvents, which leads to PeNCs degradation. Therefore, low-solubility ion pairs are not

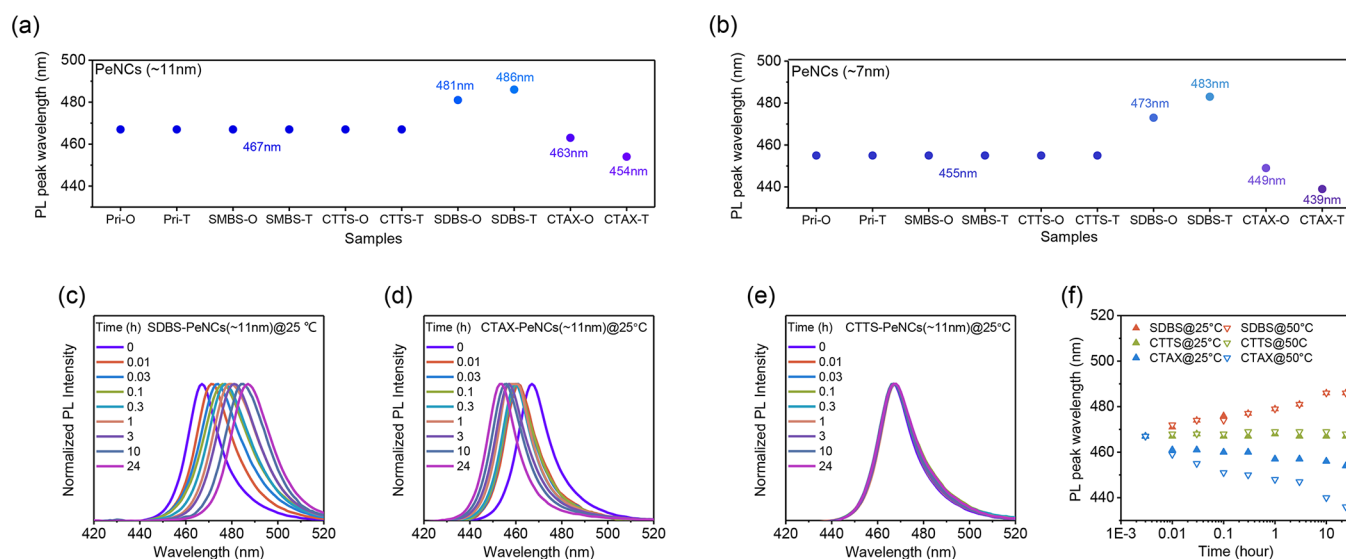


**Figure 2.** (a,b) PL peak position of pristine and ligand-modified PeNCs ( $\sim 11$  nm and  $\sim 7$  nm) in octane/toluene. Pri, O, and T denote pristine, octane, and toluene, respectively. Note that all PLs of ligand-modified samples were measured after 24 h of ligand treatment, and the original PL spectra were presented in Figure S8. (c–e) In situ PL of (c) SDBS-PeNCs, (d) CTAX-PeNCs, and (e) CTTS-PeNCs at 25 °C. (f) PL peak position of SDBS, CTAX, and CTTS PeNCs at 25 and 50 °C as a function of time. To obtain the direct reaction kinetic curve, we used a saturated solution of the ligands instead of solids to eliminate interference from factors such as stirring.

recommended unless the PeNCs degradation has been well addressed.

2. Combinations of the low-solubility and high-solubility ion pairs can facilitate ligand solubility, thereby passivating PeNCs. However, the difference in solubility can result in chemical reactions and halide redistribution, causing changes in perovskite composition and emission spectra, deteriorating the pure blue emission. It should be noted that, although the solubility of  $\text{MBS}^-$  is higher than that of perovskite anions, our experiments show that the solubility is in general still relatively low.

3. Ion pairs with both high solubilities are highly recommended for passivating  $\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs. This combination does not induce halide redistribution, ensuring emission of pure blue light that complies with Rec. 2100 standards. Additionally, it allows for ligand exchange to be completed within a reasonable time frame without the use of hazardous polar solvents, thereby enhancing the performance and stability of pure blue PeLEDs.

Figure 1b illustrates the mechanism of crystal variations governed by the principle of solubility. The mechanism is supported by comprehensive characterizations and spectral analysis in the following sections. For SMBS, the high charge density of the sodium ion and the small organic part result in negligible solubility of the ligand, leading to no changes in the chemical composition of PeNCs or the passivation effect. When the organic chain length is extended to a 12-carbon alkyl chain (SDBS), the solubility significantly increases, and the molecules exist in the form of an ion pair in the solution. Upon interaction with PeNCs, the sulfonate ions exchange with halide ions, preferentially forming NaCl precipitates due to the lower solubility than NaBr. Simultaneously, sulfonate ions form S–Pb bonds on the surface of the perovskite, resulting in an effective passivation. As a result, SDBS exhibits good passivation but leads to an increase in the Br content in PeNCs. For the CTAX ligands with the same chloro-bromine ratio as PeNCs, it provides a halogen-rich environment. The dissolved CTA-Cl and CTA-Br can be considered as the liquid

phase, while PeNCs-Cl and PeNCs-Br are in the solid phase. The solubility of the bromine-based ligand in toluene/octane solution is larger than that of the chlorine-based ligand, making it likely to remain in the solution instead of participating in the crystallization of perovskite. Meanwhile, since the binding energy of  $\text{Cl}^-$  is greater than that of  $\text{Br}^-$  with  $\text{Pb}^{2+}$ , it is easier to participate in the perovskite formation, resulting in an increase in the Cl content in PeNCs. Finally, the combination of  $\text{CTA}^+$  with  $\text{MBS}^-$  does not induce significant spectral changes, as both ions have higher solubility than the ions associated with perovskite. Importantly, both ions exhibit excellent passivation effects, and the presence of short alkyl chains facilitates charge injection in PeLEDs.

To reveal the above halogen redistribution mechanism, we synthesized pristine  $\text{CsPbBr}_x\text{Cl}_{3-x}$  PeNCs using a two-step approach (as detailed in the Methods).<sup>42,43</sup> The crystal structures of various PeNCs were examined by scanning transmission electron microscopy (STEM, Figure 1c,d and Figures S1–S3). SMBS and CTTS ligands did not induce significant changes in the size of PeNCs. However, the size increased from 11.04 to 12.22 nm after SDBS-ligand modification, which is attributed to the lattice expansion caused by the increased  $\text{Br}^-$  ratio. Through the ligand exchange by the CTAX ligand, the size of PeNCs decreases to 9.26 nm due to the substitution of the larger-sized  $\text{Br}^-$  ions by the smaller  $\text{Cl}^-$  ions. The energy dispersive X-ray spectroscopy of STEM shows the chemical composition of PeNCs in Figure S4 and Table S2. Figure 1e summarizes the as-obtained  $x$  values in the chemical formula  $\text{CsPbBr}_x\text{Cl}_{3-x}$ , which exhibit a trend similar to that of the crystal size. Due to the unexpected halide redistribution, the  $x$  values of SDBS and CTAX PeNCs changed to 1.92 and 1.59, respectively, while the  $x$  values of pristine, SMBS, and CTTS PeNCs remained stable at approximately 1.8. From X-ray diffraction (XRD) characterization in Figure S5 and Table S1, the crystal diffraction peaks at  $22.4^\circ$ ,  $31.6^\circ$ , and  $38.8^\circ$  of CTTS-PeNCs were consistent with that of pristine PeNCs corresponding to the (101), (200), and (112) crystal planes of the cubic phase,

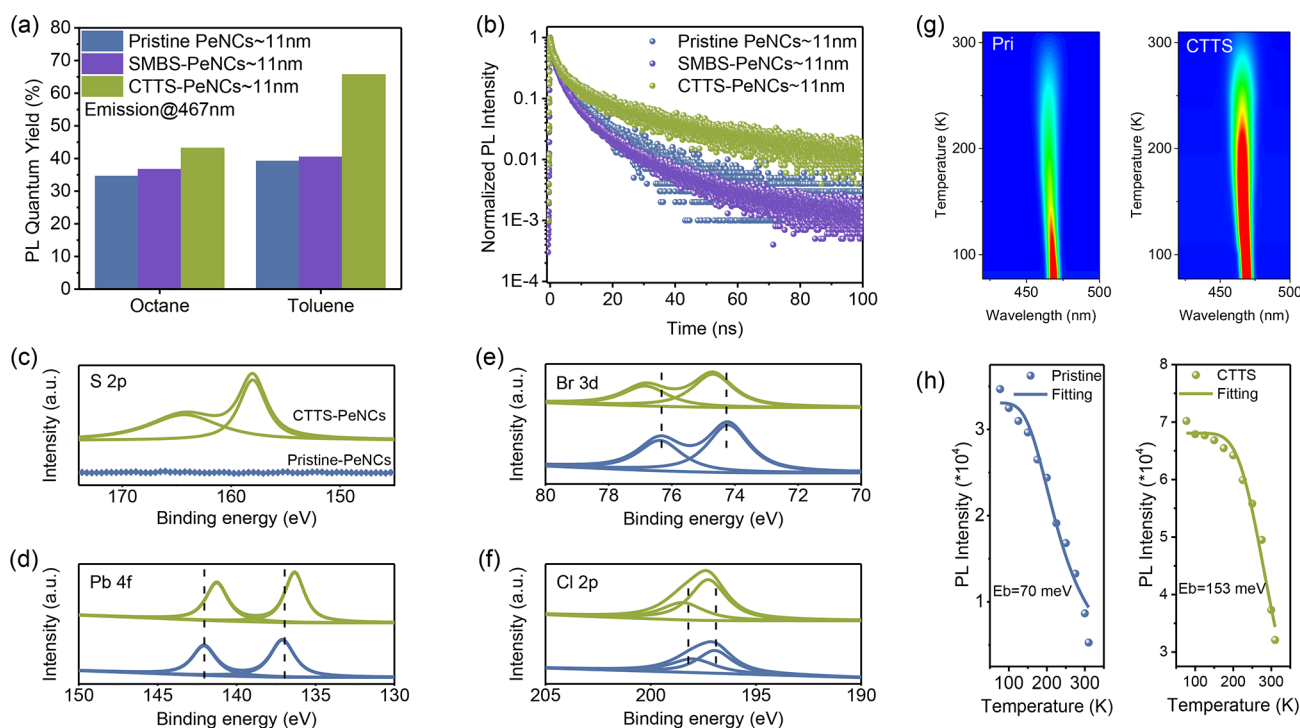


**Figure 3.** (a) PLQY of pristine SMBS and CTTS PeNCs. Since the PL peaks of SDBS and CTAX PeNCs are different from those of pristine PeNCs, we compare the PLQY of pristine, SMBS, and CTTS PeNCs emitting at 467 nm. (b) TRPL of pristine, SMBS, and CTTS PeNCs. (c–f) XPS spectra of pristine and CTTS PeNCs, (c) S, (d) Pb, (e) Br, and (f) Cl. (g) Temperature-dependent PL spectra of pristine and CTTS PeNCs. (h) PL intensity integrated band fitting curve of pristine and CTTS PeNCs.

respectively. To further validate the ligand-solubility-dependent halide composition variation, we also synthesized smaller-sized PeNCs (~7 nm) and subjected them to ligand post-treatment (Figures S6–S7). In all, the above results proved that CTAX and SDBS ligands alter the halide composition of mixed halide PeNCs, while the preferred CTTS ligand does not induce any changes in the crystal structure nor chemical composition of pure-blue PeNCs.

The influence of ligand solubility on the composition of pure blue PeNCs is further investigated by analyzing their photoluminescence (PL) spectra, as the variation in halide composition of PeNCs will directly affect their PL. In addition, a comprehensive investigation is conducted to explore the kinetic factors of halide redistribution driven by ligand solubility, in which the PL peak position serves as the primary indicator. Figure 2a,b and Figure S8 summarize the final PL peak positions of various PeNCs with different sizes (~11 and 7 nm), ligands, and solvents (toluene and octane). For large PeNCs (~11 nm), treatment with SDBS and CTAX ligands resulted in a significant redshift of the PL peak to sky blue (~486 nm) and a blueshift to the deep-blue region (~454 nm), respectively. Additionally, the more polar the solvent (toluene), the more pronounced the spectral changes due to the better ligand dissolution. In contrast, when the CTTS was used, the PL peak remained stable at 467 nm. Moreover, when an equimolar mixture of SDBS and CTAX ligands was employed, the PL peak persisted at 467 nm, as depicted in Figure S9.

Furthermore, an in situ PL system was employed to monitor the effect of the reaction time and temperature on ligand-induced spectral shifts. Figure 2c–e and Figure S10 show the PL changes induced by SDBS, CTAX, and CTTS ligands over a period of 0 to 24 h at 25 and 50 °C. The PL peaks rapidly

shifted after the initial contact with a SDBS or CTAX ligand within the first 30 s, followed by a gradual change with the extension of reaction time. The gradual slowing of spectral shifts is related to the depletion of reactants. Figure 2f summarizes the trend of PL peak change over time under different conditions, showing a nearly linear relationship with log–time. Although these complex reaction kinetics are scientifically intriguing, the precise control of the PL peak is difficult for practical applications. Therefore, based on our results that CTTS-PeNCs maintain a stable emission peak at 467 nm regardless of PeNCs size, solvent, reaction time, and temperature, we can conclude that the CTTS ligand does not cause significant changes in the PeNCs emission peak.

We also explored the effect of ligands on PL intensity. Our results show that the SMBS ligand does not significantly improve PLQY of SMBS PeNCs in both dispersing solvents, while the CTTS ligand enhances PLQY from 39.2% to 65.7% (for 11 nm PeNCs), ascribing to the surface defect reduction (Figure 3a). In addition, the CTTS ligand can improve the PLQY of small size (7 nm) PeNCs from 29.6% to 46.2% (Figure S11). The PLQY of PeNCs in toluene is overall higher than in octane due to the better dispersion in toluene.

Interestingly, after being stored in ambient air for 30 days, PeNCs (11 nm) maintain around 80% of their initial PLQY value, indicating that the CTTS ligand can improve the stability of PeNCs (Figure S12). To elucidate the PL enhancement by CTTS modification, time-resolved PL (TRPL) measurement was conducted to study the exciton dynamics in PeNCs (11 nm) as shown in Figure 3b. The increase in the calculated average lifetime ( $\tau_{\text{avg}}$ ) from 4.6 to 6.1 ns enabled by CTTS modification demonstrates the suppression of the trap-mediated nonradiative recombination loss. X-ray photoelectron spectroscopy (XPS) was performed

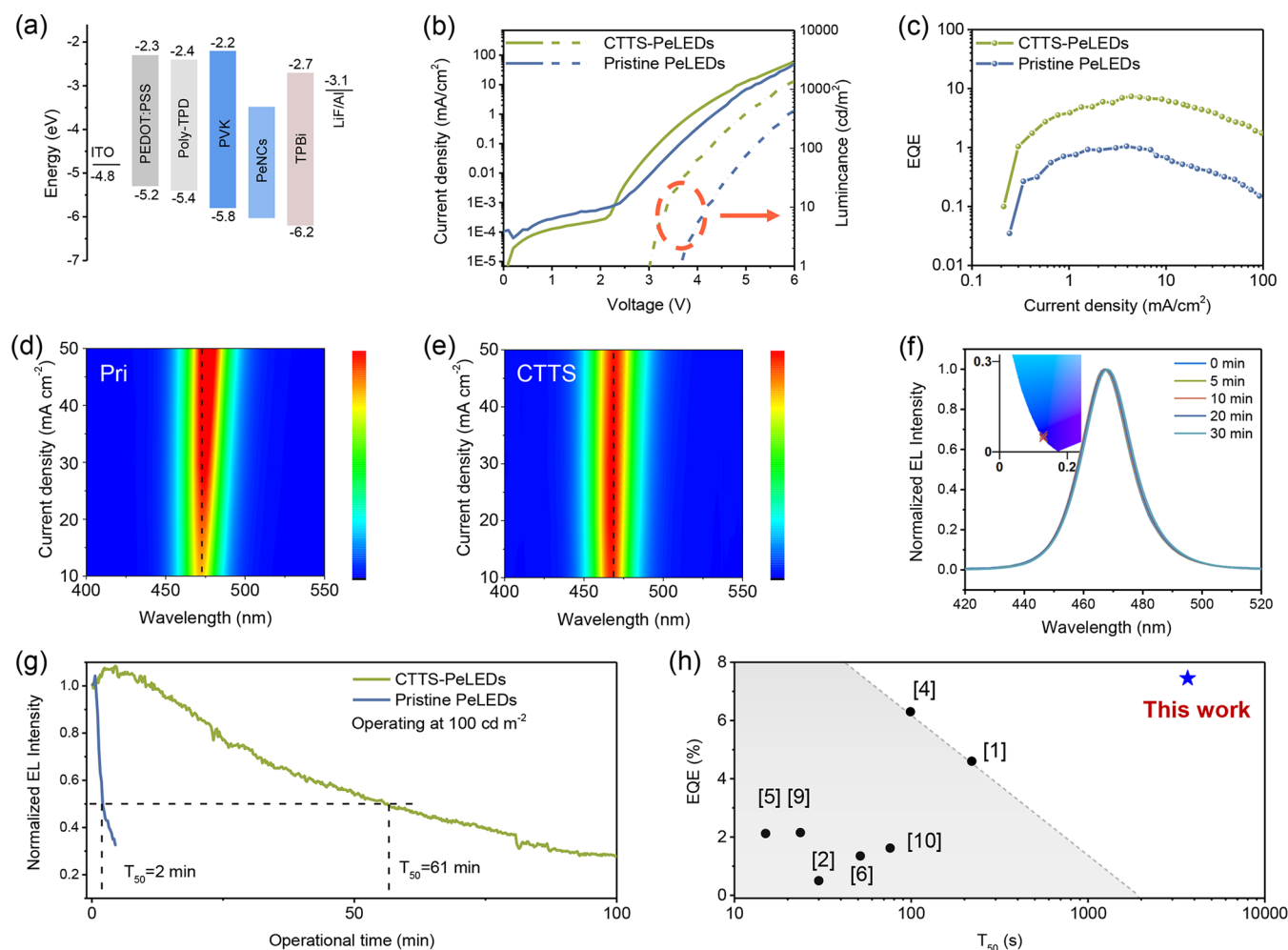


**Figure 4.** (a) Band energy level diagram of the PeLEDs. (b) Current density–luminance–voltage characteristics of pristine and CTTS PeLEDs. (c) EQE curves as a function of current density of pristine and CTTS PeLEDs. (d,e) EL spectral stability as a function of current density for (d) pristine PeLEDs and (e) CTTS-PeLEDs. (f) Normalized EL spectra of the pure blue PeLED based on CTTS-PeNCs. (g) Stability of pristine and CTTS PeLEDs at an initial luminance of 100 cd m<sup>-2</sup>. (h) Summary of the reported PeNCs-based PeLED characteristics on the basis of maximum EQE and estimated or measured half-lifetime. The references in f are listed in Table S3. To ensure the precision and reliability of the data comparison, all of the devices were fabricated in the same batch.

to elucidate the interaction between ligands and PeNCs (Figure 3c–f and Figure S13 and S14). For CTTS PeNCs, the presence of two additional peaks at 164.3 and 158.1 eV from the S 2p indicated successful binding of MBS<sup>-</sup> to the surface of CTTS PeNCs via a strong chemical interaction between benzenesulfonic acid and Pb<sup>2+</sup>. The binding energy of the Pb 4f<sub>5/2</sub> and Pb 4f<sub>7/2</sub> in CTTS-PeNCs decreases compared to that in pristine PeNCs caused by the coordination between benzenesulfonic acid and Pb<sup>2+</sup>. Figure S13 demonstrates the presence of an extra Pb–O bonding peak at 530.4 eV in CTTS PeNCs, providing additional evidence of the bonding between the CTTS ligand and PeNCs. Additionally, the Br 3d<sub>3/2</sub>, Br 3d<sub>5/2</sub>, Cl 2p<sub>1/2</sub>, and Cl 2p<sub>3/2</sub> peaks of CTTS PeNCs shifted toward larger binding energies, which could be due to the interaction between quaternary ammonium salt and incoordination (Cl/Br)<sup>-</sup>. The results are also confirmed by Fourier transform infrared spectroscopy (FTIR) as shown in Figures S15 and S16. Ionic migration is a common issue in perovskite materials due to the nature of their soft ionic species, which is predominantly manifested as phase segregation in mixed halide perovskites.<sup>1–3</sup> Defects, such as halide vacancies, facilitate ion migration by providing “hopping points” for ions, making

surface defect passivation crucial for PeNCs due to their high surface-area-to-volume ratio.<sup>6,7</sup> Extensive theoretical and experimental studies have demonstrated that ligands can passivate the surface defects, thereby suppressing ion migration and phase segregation.<sup>28,31</sup> At the same time, spectroscopic evolution has been considered as a reliable tool to demonstrate the occurrence of phase segregation. Inspired by the surface passivation of the CTTS ligand, we investigated the spectral stability to explore the inhibitory effect of surface passivation on ion migration and phase segregation. After continuous laser irradiation for 10 min, the PL peak of the pristine PeNCs noticeably shifted from 467 to 476 nm, while the PL peak of the CTTS-PeNCs remained unchanged (Figure S17). This confirms the significant role of CTTS in suppressing phase segregation and ion migration.

The temperature-dependent PL of pristine and CTTS PeNCs (~11 nm) in toluene was measured to explore the exciton binding energy, which can also elucidate the PL enhancements. Their PL peak shifted toward blue as the temperature reduced due to the renormalization caused by the longitudinal–optical (LO) phonon<sup>44</sup> (Figure 3g). Figure 3h presents the temperature-dependent integrated PL intensity

that was fitted using the Arrhenius equation.<sup>44</sup> The greater exciton binding energy of CTTS PeNCs (compared with pristine PeNCs) decreases the likelihood of exciton dissociation into free carriers, contributing to their strong light emission/performances.

The PeLED with the configuration of ITO/PEDOT:PSS/Poly-TPD/PVK/PeNCs/TPBi/LiF/Al is shown in Figure 4a. The valence band maximum or Fermi level with respect to the vacuum level was determined using ultraviolet photoelectron spectroscopy (UPS) and Tauc plots (Figures S18 and S19). The cross-section scanning electron microscopy (SEM) image of PeLEDs is revealed in Figure S20, showing thicknesses of 50, 30, and 40 nm for the hole transport layer, active layer, and electron transport layer, respectively. The optimized device based on CTTS-PeNCs exhibits higher current densities after carrier injection, which could be ascribed to the enhancement of the carrier injection through replacing the long chain ligand (OA) by a smaller chain ligand (Figure 4b). In addition, the optimized device based on CTTS-PeNCs has a low current leakage, due to the improving perovskite surface morphology. SEM and atomic force microscopy (AFM) measurements were performed to examine the morphological transition of perovskite films (Figures S21 and S22). The current density–voltage ( $J$ – $V$ ) curves of the electron-only devices (ITO/SnO<sub>2</sub>/CsPb(Cl/Br)<sub>3</sub>PeNCs/TPBi/LiF/Al) were measured under dark conditions (Figure S23).<sup>45</sup> The lower trap-filled limit voltage (VTFL) obtained by employing CTTS and SDBS+CTAX ligands implies the lower concentration of trap states in a perovskite film. As shown in Figure 4b, the CTTS PeLEDs achieve a remarkably improved EQE as compared with that of the pristine one (1.01%), reaching a peak value of 7.45% (more than 7 times). The SDBS+CTAX ligands can reduce trap states, and thus, EQE increases to 2.14%, although the long carbon chain may limit the increment (Figure S24). As shown in Figure S25, the statistical results manifest good reproducibility of the device performances associated with CTTS-ligand modification. In Figure 4d, we show the emission spectra of LEDs against a range of current densities. We observed a redshift of the emission peak for the pristine PeLED at a constant current density of 2 mA cm<sup>-2</sup>. These observations are consistent with halide segregation driven by electrical biasing and/or current injection during LED operation, resulting in lower-energy emission from the bromine-enriched regions. By contrast, the emission spectrum for CTTS PeLEDs is stable at 467 nm under the same operating conditions and duration (Figure 4e). Figure 4f and Figure S27 show the same trend, also indicating that the CTTS ligand can inhibit the ion migration. The pristine PeLEDs drop rapidly and exhibit an operational lifetime of  $T_{50}$  of 2 min. While SDBS+CTAX and CTTS ligands can improve device stability, the stability of CTTS PeLEDs is even better due to its superior electron injection, which offers a lower applied voltage of the emission of 100 cd m<sup>-2</sup> (Figure 4e and Figure S28). It is worth noting that the EQE and  $T_{50}$  of CTTS-PeLEDs exceeded all reported PeLEDs based on PeNCs with the emission peak between 460 and 470 nm (Figure 4f and Table S3). To further explore the effect of the CTTS ligand on ion migration, the hysteretic behavior of the PeLEDs was characterized by forward and reverse scans of current–voltage ( $J$ – $V$ ; Figure S29). No observable hysteresis was recorded for the PeLEDs based on CTTS PeNCs, indicating that CTTS PeNCs are less affected by ion migration.

In conclusion, we demonstrate that the light emission of the ligand-exchanged blue PeNCs would easily shift due to the halogen redistribution in the ligand exchange process. To achieve pure-blue emission, the CTTS ligand is identified to form highly stable CTTS-PeNCs without any spectral shift. This approach reduces surface defects in PeNCs and increases the exciton binding energy, leading to a substantial improvement in PLQY from 31% to 65.7%. With the optimized ligand-exchanged PeNCs, we achieve a highly efficient and stable pure blue LED with a peak EQE of 7.45% and a long  $T_{50}$  of 61 min. Overall, the work not only lays out the pivotal roles of ligands in determining the emission peak position but also provides the strategy/guideline to design the ionic ligands and their combination and improves the performances of pure-blue PeLEDs for promoting their display applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.4c00881>.

Experimental section, STEM, STEM-EDS, XRD, PL spectra, in situ PL, PLQY, XPS, FTIR, UPS, Tauc plots, SEM, AFM, SCLC, J-V-L, EL spectra, and  $T_{50}$  (DOCX)

## ■ AUTHOR INFORMATION

### Corresponding Author

Wallace C. H. Choy – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China; Materials Innovation Institute for Life Sciences and Energy (MILES), The University of Hong Kong Shenzhen Institute of Research and Innovation (HKU-SIRI), Shenzhen 518055, China; [orcid.org/0000-0002-9535-4076](https://orcid.org/0000-0002-9535-4076); Email: [chchoy@eee.hku.hk](mailto:chchoy@eee.hku.hk)

### Authors

Dongyu Li – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Benzheng Lyu – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Jiayun Sun – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China; Department of Electronic and Electrical Engineering, Southern University of Science and Technology, Shenzhen 518055, China

Qi Xiong – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Hanwen Zhu – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Zhengyan Jiang – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China; Department of Electronic and Electrical Engineering, Southern University of Science and Technology, Shenzhen 518055, China

Dezhong Zhang – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Chunyu Liu – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsenerylett.4c00881>

## Author Contributions

<sup>†</sup>D.L. and B.L. contributed equally to this work.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work is supported by the University Grant Council of the University of Hong Kong Grants (grants 202011159254 and 202111159113), General Research Fund (grants 17211220, 7200021, and 17200823) and Collaborative Research Fund (grant no. C7035-20G) from the Research Grants Council (RGC), as well as Innovation and Technology Fund from Innovation and Technology Commission (grant no. ITS/277121FP) of the Hong Kong Special Administrative Region, China.

## REFERENCES

- (1) Hassan, Y.; Park, J. H.; Crawford, M. L.; Sadhanala, A.; Lee, J.; Sadighian, J. C.; Mosconi, E.; Shivanna, R.; Radicchi, E.; Jeong, M.; et al. Ligand-engineered bandgap stability in mixed-halide perovskite LEDs. *Nature* **2021**, *591* (7848), 72–77.
- (2) Karlsson, M.; Yi, Z.; Reichert, S.; Luo, X.; Lin, W.; Zhang, Z.; Bao, C.; Zhang, R.; Bai, S.; Zheng, G.; Teng, P.; Duan, L.; Lu, Y.; Zheng, K.; Pullerits, T.; Deibel, C.; Xu, W.; Friend, R.; Gao, F. Mixed halide perovskites for spectrally stable and high-efficiency blue light-emitting diodes. *Nat. Commun.* **2021**, *12* (1), 361.
- (3) Huang, T.; Tan, S.; Nuryyeva, S.; Yavuz, I.; Babbe, F.; Zhao, Y.; Abdelsamie, M.; Weber, M. H.; Wang, R.; Houk, K. N.; Sutter-Fella, C. M.; Yang, Y. Performance-limiting formation dynamics in mixed-halide perovskites. *Sci. Adv.* **2021**, *7* (46), No. eabj1799.
- (4) Wang, Y.-K.; Singh, K.; Li, J.-Y.; Dong, Y.; Wang, X.-Q.; Pina, J. M.; Yu, Y.-J.; Sabatini, R.; Liu, Y.; Ma, D.; Liu, J.; Liu, Z.; Gao, Y.; Voznyy, O.; Ma, W.; Fung, M.-K.; Liao, L.-S.; Sargent, E. H.; et al. In-situ inorganic ligand replenishment enables bandgap stability in mixed-halide perovskite quantum dot solids. *Adv. Mater.* **2022**, *34*, No. e2200854.
- (5) Chiba, T.; Hayashi, Y.; Ebe, H.; Hoshi, K.; Sato, J.; Sato, S.; Pu, Y.-J.; Ohisa, S.; Kido, J. Anion-exchange red perovskite quantum dots with ammonium iodine salts for highly efficient light-emitting devices. *Nat. Photonics* **2018**, *12* (11), 681–687.
- (6) Zhou, Y.; van Laar, S. C. W.; Meggiolaro, D.; Gregori, L.; Martani, S.; Heng, J.-Y.; Datta, K.; Jimenez-Lopez, J.; Wang, F.; Wong, E. L.; Poli, I.; Treglia, A.; Cortecchia, D.; Prato, M.; Kobera, L.; Gao, F.; Zhao, N.; Janssen, R. A. J.; De Angelis, F.; Petrozza, A. How Photogenerated I(2) Induces I-Rich Phase Formation in Lead Mixed Halide Perovskites. *Adv. Mater.* **2024**, *36* (1), No. e2305567.
- (7) Han, T.-H.; Jang, K. Y.; Dong, Y.; Friend, R. H.; Sargent, E. H.; Lee, T.-W. A roadmap for the commercialization of perovskite light emitters. *Nat. Rev. Mater.* **2022**, *7* (10), 757–777.
- (8) Tong, Y.; Bi, X.; Xu, S.; Min, H.; Cheng, L.; Kuang, Z.; Yuan, L.; Zhou, F.; Chu, Y.; Xu, L.; Zhu, L.; Zhao, N.; Wang, N.; Huang, W.; Wang, J. In-Situ Halide Exchange of Cesium Lead Halide Perovskites for Blue Light-Emitting Diodes. *Adv. Mater.* **2023**, *35*, No. e2207111.
- (9) Mao, W.; Hall, C. R.; Bernardi, S.; Cheng, Y. B.; Widmer-Cooper, A.; Smith, T. A.; Bach, U. Light-induced reversal of ion segregation in mixed-halide perovskites. *Nat. Mater.* **2021**, *20* (1), 55–61.
- (10) Senanayak, S. P.; Dey, K.; Shivanna, R.; Li, W.; Ghosh, D.; Zhang, Y.; Roose, B.; Zelewski, S. J.; Andaji-Garmaroudi, Z.; Wood, W.; et al. Charge transport in mixed metal halide perovskite semiconductors. *Nat. Mater.* **2023**, *22* (2), 216–224.
- (11) Zhao, Y.; Miao, P.; Elia, J.; Hu, H.; Wang, X.; Heummueller, T.; Hou, Y.; Matt, G. J.; Osvet, A.; Chen, Y.-T.; Tarrago, M.; de Ligny, D.; Przybilla, T.; Denninger, P.; Will, J.; Zhang, J.; Tang, X.; Li, N.; He, C.; Pan, A.; Meixner, A. J.; Spiecker, E.; Zhang, D.; Brabec, C. J. Strain-activated light-induced halide segregation in mixed-halide perovskite solids. *Nat. Commun.* **2020**, *11* (1), 2687.
- (12) Chen, Z.; Brocks, G.; Tao, S.; Bobbert, P. A. Unified theory for light-induced halide segregation in mixed halide perovskites. *Nat. Commun.* **2021**, *12* (1), 2687.
- (13) Wang, Z.; Zeng, L.; Zhu, T.; Chen, H.; Chen, B.; Kubicki, D. J.; Balvanz, A.; Li, C.; Maxwell, A.; Ugur, E.; et al. Suppressed phase segregation for triple-junction perovskite solar cells. *Nature* **2023**, *618*, 74–79.
- (14) Zhao, B.; Lian, Y.; Cui, L.; Divitini, G.; Kusch, G.; Ruggeri, E.; Auras, F.; Li, W.; Yang, D.; Zhu, B.; et al. Efficient light-emitting diodes from mixed-dimensional perovskites on a fluoride interface. *Nat. Electron.* **2020**, *3* (11), 704–710.
- (15) Sun, Y.; Ge, L.; Dai, L.; Cho, C.; Ferrer Orri, J.; Ji, K.; Zelewski, S. J.; Liu, Y.; Mirabelli, A. J.; Zhang, Y.; et al. Bright and stable perovskite light-emitting diodes in the near-infrared range. *Nature* **2023**, *615*, 830.
- (16) Lin, R.; Xu, J.; Wei, M.; Wang, Y.; Qin, Z.; Liu, Z.; Wu, J.; Xiao, K.; Chen, B.; Park, S. M.; et al. All-perovskite tandem solar cells with improved grain surface passivation. *Nature* **2022**, *603*, 73–78.
- (17) Kim, J. S.; Heo, J.-M.; Park, G.-S.; Woo, S.-J.; Cho, C.; Yun, H. J.; Kim, D.-H.; Park, J.; Lee, S.-C.; Park, S.-H.; et al. Ultra-bright, efficient and stable perovskite light-emitting diodes. *Nature* **2022**, *611*, 688–694.
- (18) Li, D.; Zhou, D.; Xu, W.; Chen, X.; Pan, G.; Zhou, X.; Ding, N.; Song, H. Plasmonic Photonic Crystals Induced Two-Order Fluorescence Enhancement of Blue Perovskite Nanocrystals and Its Application for High-Performance Flexible Ultraviolet Photo-detectors. *Adv. Funct. Mater.* **2018**, *28* (41), No. 1804429.
- (19) Yuan, F.; Folpini, G.; Liu, T.; Singh, U.; Treglia, A.; Lim, J. W. M.; Klarbring, J.; Simak, S. I.; Abrikosov, I. A.; Sum, T. C.; et al. Bright and stable near-infrared lead-free perovskite light-emitting diodes. *Nat. Photonics* **2024**, *18* (2), 170–176.
- (20) Zheng, X.; Chen, B.; Dai, J.; Fang, Y.; Bai, Y.; Lin, Y.; Wei, H.; Zeng, X. C.; Huang, J. Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations. *Nat. Energy* **2017**, *2* (7), 17102.
- (21) Xie, J.; Yan, K.; Zhu, H.; Li, G.; Wang, H.; Zhu, H.; Hang, P.; Zhao, S.; Guo, W.; Ye, D.; et al. Identifying the functional groups effect on passivating perovskite solar cells. *Sci. Bull.* **2020**, *65* (20), 1726–1734.
- (22) Wang, M.; Zhao, Y.; Jiang, X.; Yin, Y.; Yavuz, I.; Zhu, P.; Zhang, A.; Han, G. S.; Jung, H. S.; Zhou, Y.; et al. Rational selection of the polymeric structure for interface engineering of perovskite solar cells. *Joule* **2022**, *6*, 1032–1048.
- (23) Zhao, H.; Chen, H.; Bai, S.; Kuang, C.; Luo, X.; Teng, P.; Yin, C.; Zeng, P.; Hou, L.; Yang, Y.; et al. High-Brightness Perovskite Light-Emitting Diodes Based on FAPbBr<sub>3</sub> Nanocrystals with Rationally Designed Aromatic Ligands. *ACS Energy Lett.* **2021**, *6* (7), 2395–2403.
- (24) Zhou, Y.; Poli, I.; Meggiolaro, D.; De Angelis, F.; Petrozza, A. Defect activity in metal halide perovskites with wide and narrow bandgap. *Nat. Rev. Mater.* **2021**, *6* (11), 986–1002.
- (25) Calvin, J. J.; Brewer, A. S.; Alivisatos, A. P. The role of organic ligand shell structures in colloidal nanocrystal synthesis. *Nat. Synth.* **2022**, *1* (2), 127–137.
- (26) Bi, C.; Yao, Z.; Hu, J.; Wang, X.; Zhang, M.; Tian, S.; Liu, A.; Lu, Y.; de Leeuw, N. H.; Sui, M.; et al. Suppressing Auger Recombination of Perovskite Quantum Dots for Efficient Pure-Blue-Light-Emitting Diodes. *ACS Energy Lett.* **2023**, *8* (1), 731–739.
- (27) Liu, A.; Bi, C.; Li, J.; Zhang, M.; Cheng, C.; Binks, D.; Tian, J. High Color-Purity and Efficient Pure-Blue Perovskite Light-Emitting

Diodes Based on Strongly Confined Monodispersed Quantum Dots. *Nano Lett.* **2023**, *23*, 2405–2411.

(28) Jiang, Y.; Sun, C.; Xu, J.; Li, S.; Cui, M.; Fu, X.; Liu, Y.; Liu, Y.; Wan, H.; Wei, K.; et al. Synthesis-on- substrate of quantum dot solids. *Nature* **2022**, *612* (7941), 679–684.

(29) Liu, Y.; Wang, S.; Yu, Z.; Chen, G.; Wang, C.; Wang, T.; Ke, W.; Fang, G. A Multifunctional Additive Strategy Enables Efficient Pure-Blue Perovskite Light-Emitting Diodes. *Adv. Mater.* **2023**, *35* (35), No. e2302161.

(30) Yang, D.; Li, X.; Zhou, W.; Zhang, S.; Meng, C.; Wu, Y.; Wang, Y.; Zeng, H. CsPbBr<sub>3</sub> Quantum Dots 2.0: Benzenesulfonic Acid Equivalent Ligand Awakens Complete Purification. *Adv. Mater.* **2019**, *31* (30), No. e1900767.

(31) Guo, B.; Lai, R.; Jiang, S.; Zhou, L.; Ren, Z.; Lian, Y.; Li, P.; Cao, X.; Xing, S.; Wang, Y.; et al. Ultrastable near-infrared perovskite light-emitting diodes. *Nat. Photonics* **2022**, *16*, 637–643.

(32) Zhang, J.; Zhang, T.; Ma, Z.; Yuan, F.; Zhou, X.; Wang, H.; Liu, Z.; Qing, J.; Chen, H.; Li, X.; Su, S.; Xie, J.; Shi, Z.; Hou, L.; Shan, C. A Multifunctional "halide-Equivalent" Anion Enabling Efficient CsPb(Br/I)(3) Nanocrystals Pure-Red Light- Emitting Diodes with External Quantum Efficiency Exceeding 23. *Adv. Mater.* **2023**, *35*, No. e2209002.

(33) Ye, F.; Yan, H.; Liu, S.; Liu, B.; Zhang, Z.; Tian, M.; Zheng, T.; Lan, X.; Huang, J.; Meng, C.; et al. Interface Engineering with Quaternary Ammonium-Based Ionic Liquids toward Efficient Blue Perovskite Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2022**, *14*, 50393–50400.

(34) Naphade, R.; Zhao, B.; Richter, J. M.; Booker, E.; Krishnamurthy, S.; Friend, R. H.; Sadhanala, A.; Ogale, S. High Quality Hybrid Perovskite Semiconductor Thin Films with Remarkably Enhanced Luminescence and Defect Suppression via Quaternary Alkyl Ammonium Salt Based Treatment. *Adv. Mater. Interfaces* **2017**, *4* (19), No. 1700562.

(35) Dong, Y.; Wang, Y. K.; Yuan, F.; Johnston, A.; Liu, Y.; Ma, D.; Choi, M. J.; Chen, B.; Chekini, M.; Baek, S. W.; et al. Bipolar-shell resurfacing for blue LEDs based on strongly confined perovskite quantum dots. *Nat. Nanotechnol.* **2020**, *15* (8), 668–674.

(36) Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P. Essentially Trap-Free CsPbBr<sub>3</sub> Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J. Am. Chem. Soc.* **2017**, *139* (19), 6566–6569.

(37) Ahmed, T.; Seth, S.; Samanta, A. Boosting the Photoluminescence of CsPbX<sub>3</sub> (X = Cl, Br, I) Perovskite Nanocrystals Covering a Wide Wavelength Range by Postsynthetic Treatment with Tetrafluoroborate Salts. *Chem. Mater.* **2018**, *30* (11), 3633–3637.

(38) Wang, S. X.; Wang, Y.; Zhang, Y.; Zhang, X. T.; Shen, X. Y.; Zhuang, X. W.; Lu, P.; Yu, W. W.; Kershaw, S. V.; Rogach, A. L. Cesium Lead Chloride/Bromide Perovskite Quantum Dots with Strong Blue Emission Realized via a Nitrate-Induced Selective Surface Defect Elimination Process. *J. Phys. Chem. Lett.* **2019**, *10* (1), 90–96.

(39) Jiao, H. Y.; Ni, Z. Y.; Shi, Z. F.; Fei, C. B.; Liu, Y.; Dai, X. Z.; Huang, J. S. Perovskite grain wrapping by converting interfaces and grain boundaries into robust and water-insoluble low-dimensional perovskites. *Sci. Adv.* **2022**, *8* (48), No. eabq4524.

(40) Hintermayr, V. A.; Lampe, C.; Low, M.; Roemer, J.; Vanderlinden, W.; Gramlich, M.; Bohm, A. X.; Sattler, C.; Nickel, B.; Lohmuller, T.; et al. Polymer Nanoreactors Shield Perovskite Nanocrystals from Degradation. *Nano Lett.* **2019**, *19* (8), 4928–4933.

(41) Hills-Kimball, K.; Yang, H.; Cai, T.; Wang, J.; Chen, O. Recent Advances in Ligand Design and Engineering in Lead Halide Perovskite Nanocrystals. *Adv. Sci.* **2021**, *8* (12), No. 2100214.

(42) 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<sub>3</sub>, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696.

(43) Akkerman, Q. A. Spheroidal Cesium Lead Chloride-Bromide Quantum Dots and a Fast Determination of Their Size and Halide Content. *Nano Lett.* **2022**, *22* (20), 8168–8173.

(44) Li, H.; Lin, H.; Ouyang, D.; Yao, C.; Li, C.; Sun, J.; Song, Y.; Wang, Y.; Yan, Y.; Wang, Y.; Dong, Q.; Choy, W. C. H. Efficient and Stable Red Perovskite Light-Emitting Diodes with Operational Stability > 300 h. *Adv. Mater.* **2021**, *33*, No. e2008820.

(45) Wang, Y. K.; Yuan, F.; Dong, Y.; Li, J. Y.; Johnston, A.; Chen, B.; Saidaminov, M. I.; Zhou, C.; Zheng, X.; Hou, Y.; et al. All-Inorganic Quantum-Dot LEDs Based on a Phase-Stabilized alpha-CsPbI<sub>3</sub> Perovskite. *Angew. Chem., Int. Ed. Engl.* **2021**, *60* (29), 16164–16170.