

Side-Chain-Promoted Polymer Architecture Enabling Stable Mixed-Halide Perovskite Light-Emitting Diodes

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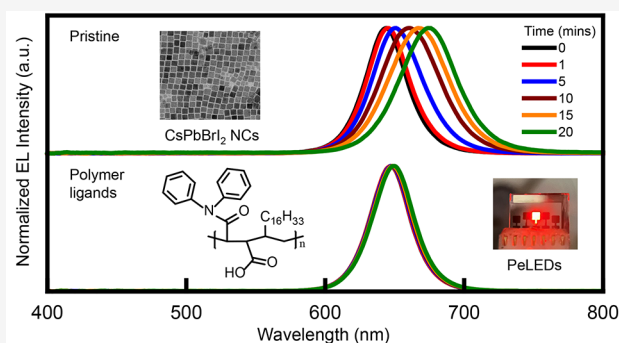


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ABSTRACT: Mixed-halide perovskite nanocrystals (PeNCs) featuring bandgap-tunable luminescence with narrow bandwidth have emerged as promising electroluminescent materials for light-emitting diodes (LEDs) to satisfy the color standard of Rec. 2100. However, the phase segregation of mixed-halide perovskites severely restricts the spectral stability and lifetime of perovskite LEDs (PeLEDs). Here, we report that the introduction of multifunctional side-chain-promoted polymer architectures in the synthesis of I/Br-mixed PeNCs to suppress halide segregation and enable electroluminescent stability of the PeLEDs up to ~2500 min, which is the longest to our knowledge. Meanwhile, the PeLEDs exhibit the pure-red electroluminescence spectrum with Commission Internationale de l'Eclairage coordinates (0.705, 0.292) at one of the highest external quantum efficiencies reported to date, 23.6%. Fundamentally, the as-proposed polymer ligand architecture simultaneously offers long-term nanocrystal dispersion, good charge transport, defect elimination, and phase segregation suppression. Overall, the work demonstrates the potential of the multifunctionalized polymer ligands for developing high-performance PeLEDs toward practical applications.



Mixed-halide perovskite nanocrystals (PeNCs) have emerged as promising next-generation electroluminescent materials for the ever more demanding lighting and display applications due to their tunable emission wavelength with narrow full-width at half-maximum (fwhm), high photoluminescence quantum yield (PLQY), and low-cost solution production.^{1–5} In contrast to other materials that rely on reducing particle size to achieve a strong quantum confinement effect and thereby regulate the emission wavelength, such as traditional CdSe or single-halide perovskite quantum dots with sizes smaller than the Bohr radius, the emission peak and bandgap of mixed-halide PeNCs can be easily adjusted by varying the mixed-halide ratio, enabling the production of high-purity colors across the visible light spectrum.^{4,6–8} This unique feature of mixed-halide PeNCs allows them to fundamentally address the strong correlation between color purity and particle size, making them the materials with the most potential to meet the latest Rec. 2100 standard for visual displays.^{4,9,10} However, the major challenge hindering the application of mixed-halide PeNC-based light-emitting diodes (PeLEDs) is halide-migration-induced phase segregation. During operation, halide ions undergo directional

migration, which causes composition changes (i.e., phase segregation). The migrating ions can even penetrate through the adjacent transport layer and react with electrodes.¹¹ Consequently, mixed-halide PeLEDs will suffer from spectrum shifts (i.e., spectral instability) and intensity degradation (i.e., operational instability).

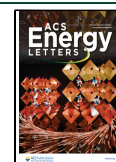
Numerous experimental and theoretical studies have attempted to elucidate the mechanisms and channels of halide-migration-induced phase segregation. The ion migration of lead halide perovskite originating from the soft ionic bonding nature of lead halide perovskite has been confirmed to affect photoluminescence (PL) and electroluminescence (EL) spectral stability.^{12,13} While ion migration is ubiquitous in all halide perovskite devices, stabilizing mixed-halide red PeNCs is

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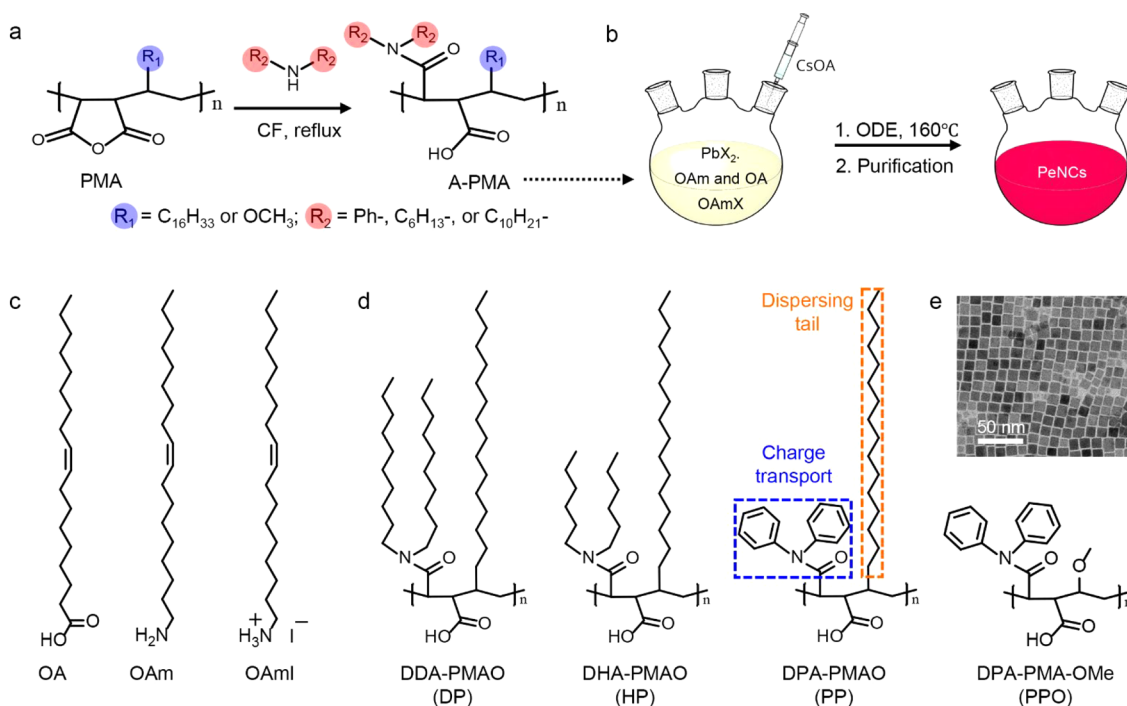


Figure 1. Synthesis reaction of polymer ligands (a) and PeNCs (b). The molecular structure of (c) OA, OAm, and OAmI and (d) DP, HP, PP, and PPO. (e) Typical STEM image of the PeNCs.

particularly challenging due to the lower activation energy for ion migration in red Br/I mixed perovskite (~ 28 kJ/mol for MAPbBr_{0.5}I_{0.5}) compared to Cl/Br-mixed perovskites (~ 38 kJ/mol for MAPbBr_{0.5}Cl_{0.5}).^{14,15} As a result, the record spectral stability of pure-red Br/I mixed PeLEDs to date is only ~ 20 min and ~ 30 min based on PeNCs and quasi-2D perovskite, respectively.^{1,16} Consequently, it is highly desirable to further suppress phase segregation for realizing both spectral and operational stabilities.

Here, we demonstrate the multifunctional side chain-promoted polymer architectures for suppressing the phase segregation of Br/I mixed PeNCs and improving the PeLED spectral and operational stabilities. The polymer ligands are well designed to meet the requirements of PeLEDs, including the proper combination of long alkyl and short aromatic groups to address the contradiction between the nanocrystal dispersibility and carrier injection and the establishment of the ordered repeating structure with the amide groups in the side-chain and carboxylic groups on the main-chain for the passivation of the PeNC surface. The PeLEDs achieve pure-red ELs with Commission Internationale de l'Eclairage (CIE) coordinates of (0.705, 0.292) and one of the highest external quantum efficiency (EQE) of 23.6% and demonstrate exceptional operational stability against time, with a recorded T_{50} of over 2500 min. Additionally, the role of side-chain in the phase segregation process is experimentally confirmed by the altering of side-chains, which enhances the stability of the EL spectrum under different currents and during continuous operation and also the PL spectrum stability under laser soaking. Theoretical calculations also reveal that the polymers with carboxyl and amide groups are lattice-matched to PeNCs, which is beneficial for eliminating defects and minimizing phase segregation. Finally, the use of polymer ligands significantly improves the material and colloidal stability of Br/I mixed-halide PeNCs, extending their storage stability to

over a year. Consequently, the pronounced phase segregation suppression and decent EL properties establish the contributions of the multifunctionalized polymer architecture on developing high-performance mixed-halide PeLEDs toward practical applications.

Previous studies have shown that eliminating surface defects is one of the effective methods to suppress the segregation of halogens in PeNCs,¹ while the migration of halogens between nanocrystals is significantly influenced by ligand shells.¹⁷ Ligand shells with appropriate thickness and density are expected to hinder halogen segregation and are also necessary for long-term stable dispersion of nanocrystals in practical applications.¹⁸ Aiming to simultaneously meet the requirements of long-term dispersion, charge transport, defect elimination, and phase segregation suppression, a kind of polymer ligand architecture is proposed through designing the strategic combinations of functionalized side-chains and functional groups in order. The side-chain-promoted polymers are synthesized by introducing a series of dihydrocarbyl-amines to react with poly maleic-anhydride derivative as shown in Figure 1a (see also Methods). Subsequently, the dihydrocarbylamine amidated polymaleic-anhydride ligands are directly incorporated by a hot-injection method into the precursor for synthesizing CsPbBr_xI_{3-x} PeNCs (Figure 1b), and the pristine PeNCs are synthesized with typical oleic acid (OA), oleylamine (OAm), and oleylamine iodide (OAmI) as control samples. The chemical structures of the three small molecule ligands, as well as four synthetic polymer ligands including didecylamine-polymaleic-anhydride (DP), dihexylamine-polymaleic-anhydride (HP), diphenylamine-polymaleic-anhydride (PP), and diphenylamine-polymaleic-anhydride-OMe (PPO), are presented in Figure 1c,d, respectively. The annotated dispersing tail (C₁₆H₃₃-) is very important for polymer ligands to dissolve in the nonpolar PeNC synthesis environment and impart dispersion stability to the final product PeNCs. Without

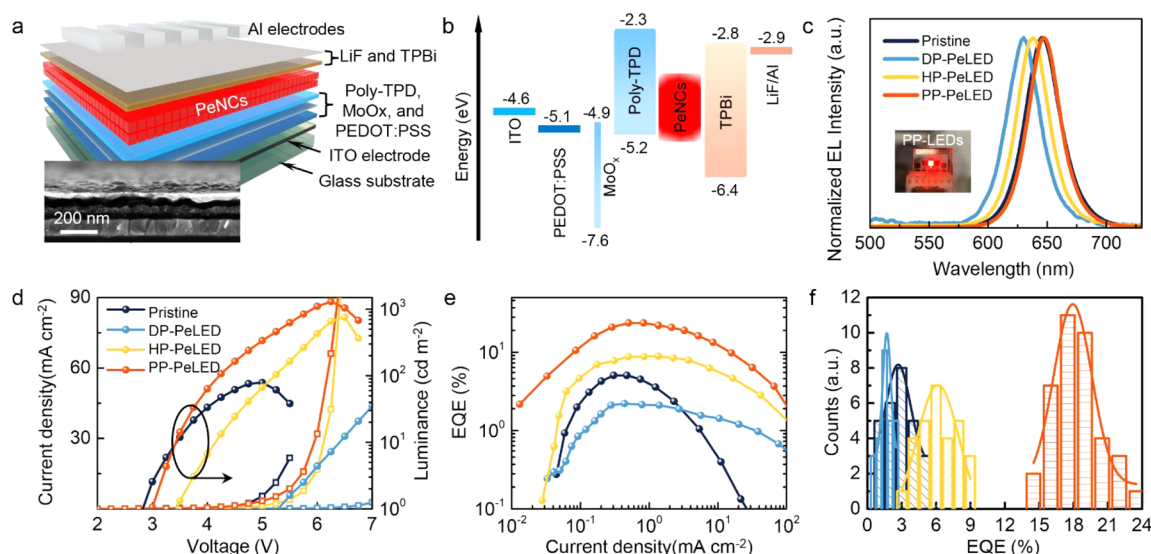


Figure 2. Characterization of PeLED performance. (a) Schematic LEDs structure and SEM images (inset). (b) Energy alignment of the device. (c) EL spectrum of the PeLEDs; inset, optical image of pure-red LEDs during continuous use. (d) J - V - L curves and (e) EQE curves as a function of current density. (f) Statistical EQE of 30 devices.

the dispersing alkyl tail like the case of PPO, it cannot be used and studied in the PeNC synthesis due to the poor solubility of PPO. Meanwhile, the conjugated aromatic amide group of polymer ligands which favors the charge transport is crucial for achieving high performance, as will be discussed in detail later.

The successful synthesis of the multifunctionalized polymer ligand was confirmed by total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements (Figure S1). Typically, the original poly maleic-anhydride shows two characteristic bands of anhydride, including a weak absorption band around 1858 cm⁻¹ and strong band near 1773 cm⁻¹ assigned to symmetric and asymmetric C=O stretching.^{19,20} After amidation, the anhydride signal significantly decreases and three intensive amide I, II, and III bands are exhibited at around 1705, 1590, and 1236 cm⁻¹, respectively.^{21,22} Nuclear magnetic resonance (NMR) spectroscopy was also utilized to characterize the amination reactions (Figure S2), demonstrating distinct proton signals of the carboxyl group (~12.12 ppm), amide α -H (2.9–3.6 ppm), and phenyl ring (7.15–7.42 ppm).^{23–25} Figure S3 illustrates the comparison of ATR-FTIR spectra between pristine and PP-NCs. It is observed that no amide I peak is detected in the pristine NCs. However, in the PP-NCs, the amide I peak is observed at a lower frequency of 1696 cm⁻¹, indicating the presence of polymer ligands in the purified NCs and a possible C=O–Pb interaction.²⁶ Further investigation was conducted to determine the presence and the density of PP in the purified sample using quantitative NMR (Figure S4) and ICP-OES (inductively coupled plasma-optical emission spectrometry).^{27–29} The concentration of NCs was determined to be approximately 47.3 μ M by an ICP-OES analysis. By comparing the ¹H spectra of the reference compound ferrocene and PP, the concentration of PP was calculated to be 1.05 μ M, and the final ligand density (LD) of PP was determined to be 0.19 nm⁻² (detailed calculation are described in Methods). The as-synthesized PeNCs exhibited typical cubic morphologies in scanning transmission electron microscopy (STEM) images (Figure 1e and Figure S5). The high-resolution STEM (HR-STEM, inset of Figure S5) shows the lattice spacing of the (110) plane with 0.612, 0.607, 0.608,

and 0.612 nm for pristine, DP-, HP-, and PP-NCs, respectively, and the space differences originate from changes in the halogen composition, as will be discussed later. The corresponding size distributions and Gaussian fits, as shown in Figure S6, demonstrate the negative correlation between PeNC size and the side-chain length of the polymer, implying the hindering effect of side-chains on ion movement during crystal growth.

The as-synthesized PeNCs were applied as the active layer materials in the PeLEDs. The p-i-n device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS)/molybdenum oxide/poly-TPD/PeNCs/tris(1-phenyl-1H-benzimidazole) (TPBi)/lithium fluoride (LiF)/Al is presented in Figure 2a, together with a cross-sectional scanning electron microscopy (SEM) image (inset of Figure 2a) and the energy diagram of the device (Figure 2b). The band structure of the synthesized PeNCs was comprehensively investigated through ultraviolet photoelectron spectroscopy (UPS, Figure S7), and the bandgap was determined by PL spectrum (presented later) and is summarized in Figure S8, which includes the conduction band, work function, and valence band. Atomic force microscopy (AFM) was used to characterize the surface roughness of the spin-coated PeNCs films (Figure S9a–d), and the trend of the root-mean-square (RMS) follows the change in particle size. Narrow EL spectra with peaks at 646, 630, 638, and 647 nm were obtained (Figure 2c; the inset shows an optical photograph of the working PP-PeLED). No luminescence from hole and electron transport layers was observed in pristine, HP-, and PP-PeLEDs, suggesting excellent carrier injection from the transport layers to PeNCs, while the energy barrier generated by the long alkyl chain of DP makes the exciton partially recombine in the transport layer.^{30,31} Meanwhile, as shown in the current density–voltage–luminance (J - V - L) curves (Figure 2d), the DP-PeLEDs exhibited much lower current density and higher turn-on voltage (V_{ON} , 5.3 V) compared to the other devices. With the shortening of the side-chain, V_{ON} is gradually reduced to 3.4 and 3 V for HP- and PP-PeLEDs, respectively. The space-charge limited current (SCLC) method was applied to analyze both the trap density

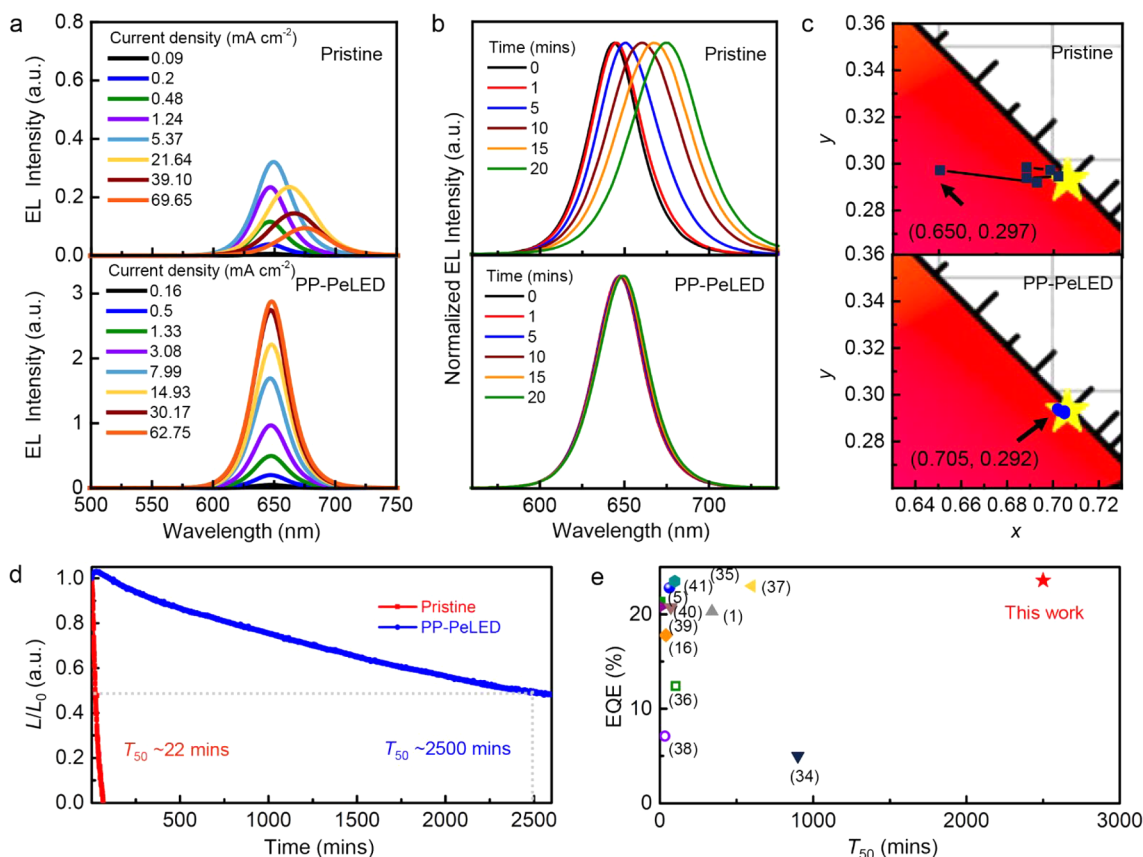


Figure 3. The influence of polymer ligands on spectral and operational stability of PeLEDs. (a) EL spectrum at different current density, (b) EL spectra during continuous operation, and (c) CIE coordination of pristine (upper panel) and PP-PeLED (bottom panel). (d) T_{50} of the pristine and PP-PeLEDs. (e) Summarized EL performance of representing pure-red PeLEDs with CIE coordinates close to the Rec. 2100 pure-red color of (0.708, 0.292).

(N_{trap}) and carrier transport characteristics by fabricating electron-only devices (Figure S10).³² By fitting the current density–voltage curves of the double-exponential form into three regions of Ohmic ($n = 1$), trap-filled limited (TFL, $n > 3$), and Child ($n = 2$), the trap density was extracted as 4.26×10^{17} , 8.35×10^{16} , 8.16×10^{16} , and 6.89×10^{16} , respectively, and the electron mobility was calculated as 2.30×10^{-4} , 1.27×10^{-6} , 1.03×10^{-5} , and 1.15×10^{-4} for pristine, DP-, HP-, and PP-NCs. The obtained results indicate that the pristine PeNCs exhibit a high defect density and high mobility due to the detachment of OA and OAm ligands.³³ However, the synthesized multifunctional polymer ligand effectively passivates the surface of PeNCs, while the aromatic side chains ensure charge injection at a magnitude similar to that in pristine PeNCs. Overall, the champion EQE of 23.6% is achieved in PP-PeLEDs under a current density of 0.5 mA cm⁻² (Figure 2e), which is almost the ideal EQE of planar PeLEDs without a deliberate light out-coupling design.^{34,35} In contrast, pristine PeLEDs present a weak EQE of only 5.1% because of the abundant trap sites, and the insufficient EQEs of 2.3 and 8.9% for DP- and HP-PeLED, respectively, are attributed to lack of carrier transport side-chains. The statistical EQE of 30 devices is summarized in Figure 2f.

Moreover, we have investigated the effects of the different polymer ligands on the spectral stability against applied current and operational time, as well as operational (intensity) stability of PeLEDs which are currently the most severe challenges in mixed-halide PeLEDs. Regarding the spectral stability against

applied current, Figure 3a and Figure S11 present the EL evolution as the current density increases. For pristine PeLEDs, The EL spectra start to shift at a current density as low as 5.37 mA cm⁻². The spectral peak considerably moves from 646 to ~680 nm (69.65 mA cm⁻²), which becomes almost the same EL spectrum of pure-iodine CsPbI₃ PeLEDs.³⁶ Remarkably, neither peak shift nor spectral broadening are observed in DP-, HP-, and PP-PeLEDs even though the applied current density reached 140.87, 84.49, and 62.75 mA cm⁻², respectively, which is more than an order higher than that of pristine PeLEDs.

Encouraged by the above results, we have explored the spectral stability against the operation time of PP-PeLEDs (which showed the highest EQE over 20% with an initial luminance of 150 cd m⁻²). As shown in Figure 3b,c, the EL spectra of pristine PeLEDs obviously broaden (fwhm up to 49 nm), and the peak positions shifted from 646 to 676 nm by ~30 nm within a very short initial time of 20 min, and the Commission Internationale de l'Eclairage (CIE) coordinates finally moved to (0.650, 0.297). Negligible changes of fwhm and peak positions were observed in the case of PP-PeLEDs, and the CIE coordinates were maintained as (0.705, 0.292), close to the standard (0.708, 0.292) denoted by the yellow star. The EL spectra of pristine LEDs with a logarithmic y-axis (Figure S12) clearly explained the shift of the CIE coordinates. In the case of PP-PeLEDs, only a slight phase segregation occurred within 200 min, as indicated by spectral shifts per 1 nm occurring at 13, 23, 38, 52, 75, 100, 133, and 200 min,

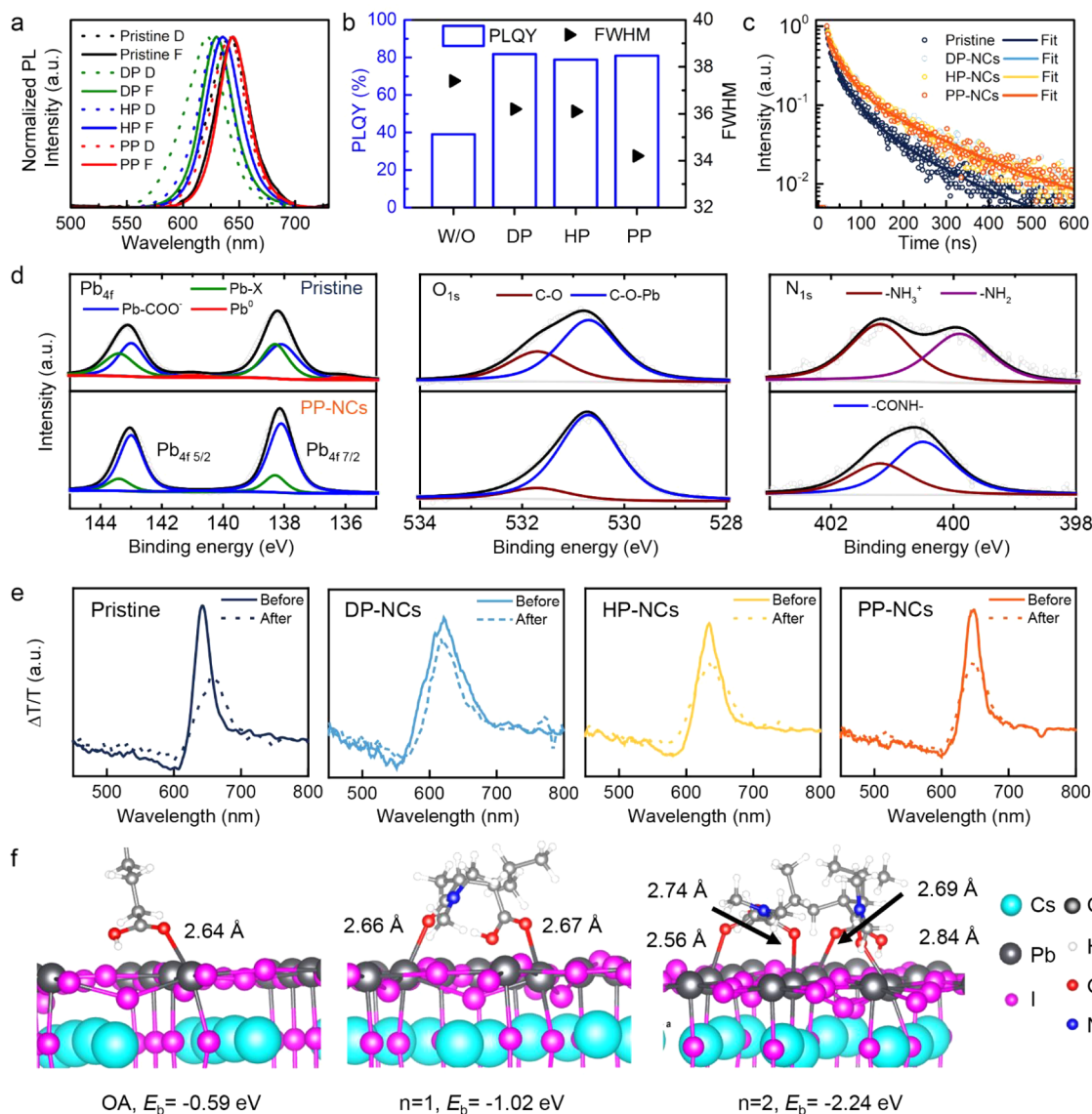


Figure 4. Characterization, photoluminescence property, and DFT calculation. (a) The PL spectrum of PeNC dispersion (D) and films (F). (b) The summarized PLQY and fwhm of PeNC films extracted from PL spectrum. (c) TRPL spectra and triexponential fitting for pristine, DP-, HP-, and PP-NCs. (d) XPS spectra of Pb 4f, O 1s, and N 1s spectra of pristine and PP-NCs. (e) TAS measured at 250–300 ps delay time range after photoexcitation for pristine, DP-, HP-, and PP-NCs. (f) Configuration structure of the ligands interacting with PeNCs with the corresponding bond length and binding energy (E_b).

respectively. A video of the device operation for 1 h was recorded, during which there was no obvious spectral shift nor intensity decay (to be discussed in detail later) of the EL (Movie S1). The EL spectral peaks' positions versus time over the entire T_{50} period are plotted in Figure S13a, and the phenomenon of EL spectral recovery is illustrated in Figure S13b, resembling the previously reported recovery of light- and electro-induced phase segregation.^{1,13}

For the operational (EL intensity) stability against time, the pristine PeLEDs degrade fast to 50% of its initial intensity value with a short lifetime T_{50} of ~22 min (Figure 3d), which is comparable with that of the newest reported mixed-halide pure-red PeLEDs.¹⁶ With PP, the T_{50} is dramatically increased by more than 2 orders of magnitude up to ~2500 min, which is the longest record in mixed-halide pure-red PeLEDs. Figure 3e and Table S1 further summarize the representative mixed-

halide and single-halide PeLEDs that meet the Rec. 2100 pure-red coordinate of (0.708, 0.292), i.e., the EQE as a function of T_{50} , clearly demonstrating the superior stability of the PP-PeLEDs.^{5,16,37–44}

To fully understand how the polymer ligands enable the excellent spectral and operational stabilities of PeNCs, comprehensive characterizations and photophysical studies are conducted. Similar to the EL spectrum, as-synthesized PeNCs emitted a tunable PL spectrum peak from 620 to 644 nm in the pure-red range (Figure 4a and Figure S14a,b). The fwhm of PeNCs films reduces (Figure 4b and Table S2), indicating that the quality of PeNCs improved. The incorporation of polymer ligands significantly improves the PLQY of the PeNC film from 39.1% up to ~80%, confirming the excellent passivation effect of the polymer ligands (Figure 4b and Figure S15). We also study the time-resolved PL

(TRPL) decays of the as-synthesized PeNCs (Figure 4c) and fit the plots with a triexponential function.⁴⁵ The average (τ_{avg}), nonradiative (τ_{nr}), radiative (τ_r), and lifetimes are extracted as shown in Table S3, together with the nonradiative (decay) rate (k_{nr}) and radiative rate (k_r). Interestingly, the incorporation of DP, HP, and PP dramatically reduces the k_{nr} from $1.9 \times 10^7 \text{ s}^{-1}$ to $\sim 3 \times 10^6 \text{ s}^{-1}$, indicating that polymer ligands effectively suppressed defect-assisted nonradiative recombination. Meanwhile, the polymer ligands slightly improve k_r from $1.2 \times 10^7 \text{ s}^{-1}$ to about $1.3\text{--}1.4 \times 10^7 \text{ s}^{-1}$. The energy dispersive X-ray spectroscopy (EDS) in STEM was conducted to analyze the chemical composition of all the samples (Figure S16 and Table S4). The pristine PeNCs without polymer ligands show a chemical composition similar to $\text{CsPbBr}_{1.3}$, probably due to the breakdown of the Pb–I bond that occurred during purification, while DP, HP, and PP have a standard elemental ratio of $\text{CsPb}(\text{Br/I})_3$ within atomic error, demonstrating the effective protection of PeNCs by all of the polymer ligands. Interestingly, the side-chains showed selectivity for halogen species; that is, DP with the longest side-chain contains the largest proportion of Br ($\text{Br/I} = 1.23/1.77$), and the shortest PP has the lowest Br/I ratio ($0.97/2.03$). Considering that the crystal growth of PeNCs is completed within 5 s and is mainly controlled by kinetics rather than thermodynamics in the hot-injection method, regular halogen selection illustrates the stronger blocking effect of side-chains on large-sized I^- than on small-sized Br^- ions. Consistent with HR-STEM, X-ray diffraction (XRD) patterns showed clear difference in the intense peaks positioning at $\sim 14.5^\circ$, 20.7° , and 29.5° , which are assigned to the (110), (111), and (220) crystal planes of tetragonal phase PeNCs (Figure S17 and Table S5).^{45,46} The lower-intensity peak at 12.7° observed in pristine PeNCs was attributed to the PbI_2 produced by the perovskite degradation.⁴⁷ The XRD results provided further evidence that the side-chain-promoted polymer ligands affect the crystal structure and crystal stability. Furthermore, the chemical environment of the Pb and O elements is studied by high-resolution X-ray photoelectron spectroscopy (XPS) (Figure 4d). The Pb 4f spectra were fitted to Pb–X, Pb– COO^- , and Pb^0 peaks, and the much larger proportion of Pb– COO^- in polymer ligands–PeNCs than the pristine samples proved the existence of abundant polymer ligands in the purified PeNCs (Figure S18).^{48,49} Note that without polymer ligands about 4.7% of lead decomposes into metal Pb^0 due to the instability of perovskite, again proving the protective effect of polymer ligands on PeNCs. For the O 1s peaks, the percentage of O bonded to Pb (C–O–Pb) increased from 53.5% for pristine PeNCs to 84.97%, 81.25%, and 83% in DP-, HP-, and PP-NCs respectively, confirming the strong interaction between polymer ligands and PeNCs.⁵⁰ Due to the incorporation of the acidic polymer ligands with the amide N–C=O group, the N 1s peak of PP was clearly shifted to the higher binding energy compared to that of the pristine PeNCs,⁵¹ while the other elements did not show obvious differences (Figure S19).

Transient absorption spectroscopy (TAS) was conducted to explore the effect of polymer ligands on photoinduced PeNCs phase segregation (Figure 4e and Figure S20). The initial stages of TAS are dominated by the cooling process of hot carriers and bandgap renormalization, thus we mainly analyzed the ground-state bleach (GSB) signal at 250–300 ps time range which is the reflection of the bandgap.⁵² After laser soaking, the pristine sample shows an obvious redshift of GSB

maximum equal to $\Delta\lambda = 16.1 \text{ nm}$ ($\Delta h\nu = 46.6 \text{ meV}$, Figure 4e), which can be contributed to the phase segregation resulting in the I-rich phase. As for all the three polymer ligand-capped PNCs, the GSB maximum does not shift after UV exposure, and only slight broadening is observed. In particular, DP with the longest side-chain stabilized PeNCs show comparable peaks before and after irradiation, indicating that DP completely inhibits photoinduced phase segregation. The strong interaction between PeNCs and ligands was essential to suppress defects and improve luminescence performance. We have also conducted density functional theory (DFT) calculations to understand the interaction between polymer ligands and the PbI_2 -terminated PeNCs surfaces, and traditional OA is used as the control ligands due to the same carboxylic acid groups in all polymer ligands (Figure 4f and Figure S21). When the repeating unit of the polymer is one, the carboxyl and amide groups of PP synergistically coordinate with the adjacent Pb atoms on the PeNCs surface with a binding energy (E_b) of -1.02 eV , which is significantly higher than that of OA (-0.59 eV). Importantly, when the number of repeat units is increased to two, the conformation of PP perfectly matches the surface of PeNCs without obvious steric hindrance, and the E_b also increases to -2.24 eV greater than that of two single repeat units, demonstrating the cooperative coordination between repeat units. Therefore, polymer ligands with multiple repeating units is more stable on PeNCs than traditional small molecule ligands, which is not only beneficial to passivate NCs but also provides a platform to systematically reveal the profound effect of polymer side-chains on NCs and PeLEDs. Figure S22 presents a schematic diagram depicting the possible interaction between the surface of PeNCs and different ligands, including OA, OAm, and PP. Based on the above studies, the side-chains of polymer ligands demonstrate profound effects on the crystal growth, defect passivation, and phase segregation.

Notably, the PeNCs have prolonged storage stability, which not only further supports their spectral and operational stabilities but also is important for massive practical applications. Our results show that even after 12 months of storage in octane, the encapsulated PP–PeNCs still maintained their initial color and bright photoluminescence, while pristine PeNCs became colorless materials (i.e., decomposed into nonperovskite materials) and lost their luminescence (Figure S23). Figure S24 reports the continuous monitoring of PLQY during long-term storage as a function of time. The PLQY of pristine PeNCs films gradually declines to 9.5% of the initial value within six months and approaches to the extinction of its luminescence. The PLQY of PP–PeNCs retains 78.6% even after 1 year of storage, demonstrating excellent storage stability. STEM and EDS (Figures S25 and 26, Table S6) suggest that the supernatant fraction of pristine PeNCs lost a large amount of Pb and I that can be attributed to the decomposition of weak Pb–I bond,⁵³ and finally formed a nonperovskite Cs_4PbI_6 phase, although the samples were kept in brown bottles to avoid high-energy UV light. PP–PeNCs still maintained the initial morphology and lattice structure with a little bit of Pb and I loss.

In summary, we demonstrate the multifunctional side-chain-promoted polymer architecture enabling stable pure-red PeLEDs. The polymer architectures are established from alternating arrangements of long alkyl and short aromatic side-chains to solve the contradiction between dispersibility and

carrier injection as well as introducing the amide groups in the side-chain to form the ordered repeating structure with the carboxylic groups on the main-chain for the passivation of the PeNC surface. The polymer ligands are directly applied to the solution synthesis of PeNCs without involving a complicated ligand exchange process. The optimized polymeric ligand enabled spectrographically stable pure-red PeLEDs with near standard CIE coordinate of (0.705, 0.292) and one of the highest EQE values of 23.6%. Remarkably, the polymer ligands not only prolong the storage stability of PeNCs to a year but also enable the mixed-halide pure-red PeLEDs' multiple stabilities, including the spectral stability against applied current (the current density more than an order of magnitude higher than that of the pristine sample without any clear peak shift nor broadening), the spectral stability against operation time (only 1 nm peak shift as compared to 30 nm for the pristine sample in 20 min), and operational (intensity) stability against time (recorded T_{50} reaches 2500 min and over 100 times longer than that of the pristine sample). Fundamentally, the polymer ligands simultaneously address the needs of long-term nanomaterial dispersion, decent charge transport, defect elimination, and phase segregation suppression for enabling high-performance PeLEDs. This work contributes to formulating a powerful guide for the design of polymeric ligands in the future to achieve the practical application of PeNCs or other materials such as quantum dots.

METHODS

Synthesis of Polymer Ligands. To synthesize DP, HP, and PP, 0.692 g (1.97 mM) of Poly(maleic anhydride-*alt*-1-octadecene) (Sigma-Aldrich, high viscosity) was slowly added to 30 mL of anhydrous chloroform in a 100 mL three-necked round-bottom flask under vigorous stirring with a Teflon stirring bar. The flask is filled with inert N_2 and stirred continuously until the Poly(maleic anhydride-*alt*-1-octadecene) is completely dissolved. Then temperature is increased to reflux and 586 mg of didecylamine (TCI, >97%), 459 μ L of dihexylamine (TCI, >98%), or 333 mg of diphenylamine (TCI, >99%) is added drop-wise. Subsequently, the reaction was continued for $\sim$ 7 days. The product was directly used in the next step. In the case of PPO, 15 mL of acetonitrile was used to dissolve Poly(methyl vinyl ether-*alt*-maleic anhydride) (1.97 mM, Macklin, average $M_n \approx 80,000$) instead of chloroform, and 30 mL of anhydrous chloroform was added after the addition of 333 mg of diphenylamine.

Synthesis of PeNCs. To synthesize PeNCs, CsOA was presynthesized by mixing Cs_2CO_3 (0.814 g, Solarbio, 99.90%), OA (3 mL, Aladdin, 85%), and octadecene (ODE, 30 mL, TCI, >90%) at 100 $^{\circ}C$ under vacuum for 2 h. OAmI was synthesized by adding 0.95 mL of HI solution (Acros, 57%) into the mixed ODE (40 mL) and OAm (8 mL, Aladdin, 80–90%) under inert atmosphere, and then the temperature was raised from room temperature to 60 $^{\circ}C$. After 2 h, the excess H_2O was removed by vacuum to obtain the OAmI contained product. The as-synthesized polymer ligands were added into the 100 mL flask containing ODE (16 mL), OA (2 mL), and OAm (2 mL), and the low boiling point component was removed by vacuum at 60 $^{\circ}C$ for 1 h. Then PbI_2 (0.233 g, TCI, >98%) and $PbBr_2$ (0.093 g, TCI, >98%) were added, and the mixture was degassed at 100 $^{\circ}C$ for 1 h. Finally, 2 mL of CsOA was injected into the flask at 160 $^{\circ}C$, and the PeNC growth kinetics was terminated after 5 s by quenching with an ice bath. The PeNCs were washed with methyl acetate (2:1 vol %) by

centrifugation (2 cycles, at 6000 rpm) and manual shaking. The purified PeNCs were redispersed in 3 mL of octane.

Device Fabrication and Measurement. The 1.5 cm $\times$ 1.5 cm ITO/glass was sequentially cleaned with detergent, deionized water, acetone, and ethanol in a sonication bath. After UV-Ozone treatment, the PEDOT:PSS (Clevios PVP AI4083) was fabricated on ITO by spin-coating and thermal annealing at 130 $^{\circ}C$ for 20 min. Then a 2 nm thick molybdenum oxide layer was evaporated. Poly-TPD (4 mg mL^{-1}) was spin-coated on the molybdenum oxide as hole transport layer. The PeNCs were diluted twice with octane and subsequently spin-coated to fabricate the active layer. At last, TPBi (35 nm), LiF (1 nm), and Al (100 nm) were thermally evaporated and served as the electron transport layer and electrodes, respectively. A Keithley 2635 sourcemeter and a fiber optic integration sphere (Ocean Optics FOIS-1) coupled to a spectrometer (Ocean Optics QE 65 000) were used for the LED measurements.

Characterization. The STEM, HRSTEM, and EDS was obtained by Thermo Scientific Talos F200X. The ATR-FTIR spectra were recorded using a JASCO FT/IR-6600 spectrometer. All NMR data were obtained using a Bruker AVANCE III HD. ICP-OES analysis was performed using a PerkinElmer Optima 8300 instrument. The cross-sectional SEM images were captured by a Hitachi S-4800. The XRD patterns were acquired by a Bruker D8 ADVANCE Powder X-ray Diffractometer, and the X-ray source is a Siemens copper sealed tube which has a Cu $K\alpha$ wavelength ($\lambda = 1.54178 \text{ \AA}$) with maximum power of 40 kV and 40 mA while the detector is a scintillation counter. The XPS (Thermo Scientific ESCALAB 250Xi) was used for analyzing the chemical environment of elements. Steady-state PL spectra, PLQY, and TRPL were measured by a PicoQuant FluoTime 300 spectrometer, and a laser diode with a peak wavelength of 375 nm was used as the excitation source. The PeNC films were fabricated by a spin-coating method in an N_2 filled glovebox and encapsulated in two sheets of quartz sheets. The roughness of the PeNC film was measured using AFM (NT-MDT NTEGRA). TAS was carried out on a home-built pump-probe setup with a Ti: Sapphire regenerative amplifier (Coherent Legend Elite) was seeded by a titanium sapphire oscillator (Coherent Mira 900) as a light source.

LD Calculation. For LD calculation, the following equations were used:

$$LD = n_{pp}/S_A,$$

$$S_A = 6L^2n_{pb}/(L/a)^3$$

$$n_{pb} = C_{pb}VN_A$$

where n_{pp} and n_{pb} represent the number of PP units and Pb atoms, respectively. S_A denotes the surface area of NCs, L refers to the size of NCs, and a represents the lattice constant of NCs; C_{pb} represents the concentration of Pb^{2+} obtained through ICP-OES analysis of the further purified NCs sample, V represents the sample volume, and N_A denotes Avogadro's constant.

Trap Density and Mobility Calculation. For calculating trap density and mobility, the following equations were used:

$$N_{trap} = 2\epsilon_0\epsilon V_{TFL}/eL^2,$$

$$\mu = 8L^3J/9\epsilon_0eV^2$$

where N_{trap} is the trap density; μ is the mobility; and ϵ_0 and ϵ (~ 4.1) are the vacuum and relative permittivity, respectively. V_{TFL} is the trap-filled limit voltage. e is the elementary charge. L is the thickness of PeNCs film; J and V are the current density (J) and voltage (V) in the Child region, respectively.^{54–56}

PLQY Calculation. The PLQY is calculated according to the following equations:

$$\text{PLQY} = \frac{P_c - (1 - A)P_b}{L_a A}$$

$$A = 1 - \frac{L_c}{L_b}$$

where L_a is the initial excitation and L_b and P_b present the excited and emitted photon indirect illumination on the sample, respectively. L_c and P_c mean the excited and emitted photons in the case of direct illumination.

DFT Calculation. The interactions of OA and polymer ligands on perovskite surfaces were investigated by using state-of-the-art DFT calculations, including dispersion interactions, to mimic the surface chemistry of perovskite nanocrystals. In this work, we focus on CsPbI₃, for which we have a reliable surface picture. All of our results are obtained considering a PbI₂-terminated surface, which is representative of the extreme situation of a fully unpassivated perovskite surface exposing undercoordinated surface Pb.

All simulations were carried out with the VASP package.^{57–59} DFT calculations were carried out on the (001) CsPbI₃ surface within the supercell approach by the Perdew–Burke–Ernzerhof functional using PAW potentials and a cutoff on the wave functions of 400 eV. Slab models were built starting from the tetragonal phase of CsPbI₃ by fixing cell parameters to the experimental values and generating a 2×2 supercell in the a and b directions. Along the nonperiodic direction perpendicular to the slabs, 20 Å of vacuum was added in all cases. Since traditional DFT calculations at the Perdew–Burke–Ernzerhof level cannot correctly include the nonlocal van der Waals interactions, the calculations with dispersion corrections may affect the adsorption energies of small molecules. In this regard, the DFT-D3 method was adopted for dispersion corrections here.⁶⁰ During the geometry optimizations, the bottom two layers were fixed at the bulk position, whereas the top two atomic layers and the adsorbents were fully relaxed with the energy and force convergences 10^{-5} eV and 0.01 eV/Å, respectively. The adsorption energy of each adsorbate [E_b (eV)] was calculated as follows:

$$E_b = E_{\text{ad/surf}} - E_{\text{ad}} - E_{\text{surf}}$$

where E_{ad} , E_{surf} , and $E_{\text{ad/surf}}$ are the energies of an adsorbate, the clean (001) surface, and the surface with adsorbates, respectively.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.4c00355>.

Video of PP-PeLED stable operation for 1 h (MOV)

ATR-FTIR and NMR of polymer ligands and PeNCs; STEM, EDS, XPS, UPS, AFM, and XRD of PeNCs; digital photographs; PL and EL performance and

stability; PLQY and TRPL; electron-only device; TAS; DFT calculation (PDF)

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Notes

The authors declare no competing financial interest.

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