Polymerized Hybrid Perovskites with Enhanced Stability, Flexibility, and Lattice Rigidity

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The intrinsic soft lattice nature of organometal halide perovskites (OHPs) makes them very tolerant to defects and ideal candidates for solution-processed optoelectronic devices. However, the soft lattice results in low stability towards external stresses such as heating and humidity, high density of phonons and strong electron–phonon coupling (EPC). Here, it is demonstrated that the OHPs with unsaturated 4-vinylbenzylammonium (VBA) as organoammonium cations can be polymerized without damaging the perovskite structure and its tolerance to defects. The polymerized perovskites show enhanced stability and flexibility compared to regular three-dimensional and two-dimensional (2D) perovskites. Furthermore, the polymerized 4-vinylbenzylammonium group improves perovskite lattice rigidity substantially, resulting in a reduced non-radiative recombination rate because of suppressed electron–phonon coupling, and enhanced carrier mobility because of suppressed phonon scattering. 2D polymerized perovskite light-emitting diodes (PeLEDs) with strong electroluminescence at room temperature, and quasi-2D PeLEDs with an external quantum efficiency (EQE) of 23.2% and enhanced operation stability are demonstrated. The work has opened a new way of enhancing the intrinsic stability and optoelectronic properties of OHPs.

1. Introduction

Organometal halide perovskites (OHPs), including three-dimensional (3D) and two-dimensional (2D) perovskite (Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phases), have become a new generation of semiconducting materials for electronic and optoelectronic devices. An intrinsic nature of OHPs is its soft lattice due to weak ionic bonding between metal and halide, and non-covalent bonding between organic cations and the inorganic framework.[2] The soft lattice nature enables OHPs to be very tolerant to defects compared to conventional inorganic semiconductors such as silicon and III–V compounds,[3,4] making OHPs ideal candidates for solution-processed optoelectronic devices. However, the soft lattice results in low stability towards external stresses such as heat and humidity.[4,5] In addition, it induces a high density of phonons, causing strong electron–phonon coupling (EPC) in OHPs,[6] particularly in the 2D RP phase with weak Van der Waals force between adjacent organic layers.[7,8] The strong EPC results in rapid non-radiative exciton quenching, and low photoluminescence quantum yield (PLQY),[8–10] which is detrimental to devices working at high temperatures or under high current density. For example, perovskite light-emitting diodes (PeLEDs) based on 2D OHPs, such as phenethylammonium lead iodide, has electroluminescence only at liquid nitrogen temperature.[11]

There are many small ligands and polymer ligands explored to improve the stability and/or optoelectronic properties of OHPs, such as those containing the C=O group[12–14] and hydrophobic group.[15] Their functions include trap passivation,[13,14] making the film more hydrophobic,[14] improving the film quality,[14,16] and/or suppression of ion migration,[12] etc. (Table S1, Supporting Information). In general, the polymer ligands work as additives located at the grain boundary (Figure S1, Supporting Information), and form a polymer–perovskite mixture, rather than in the perovskite lattice.[12–16] A limitation of those approaches is that the polymer additives cannot change the intrinsic properties of OHPs, such as their strong EPC, although they can form coordinate bonding with the metallic lead or dangling bonds of halides at the crystal surface.

In this work, we report solid-state polymerization (SSP) of perovskite lattice using unsaturated organoammonium cations 4-vinylbenzylammonium (VBA) without damaging the perovskite structure. The polymerized perovskite with a polymerization degree above fifty, a new phase of OHPs which is different from the RP or DJ phase with monoamine...
and diamines respectively, shows polymer-like behavior such as enhanced water/thermal stability and flexibility, resulting from the high molecular weight of the polymerized-VBA (PVBA) ligands and strong covalent C–C bonding between adjacent organoammonium groups. More excitingly, as an organic component of the perovskite structure which is superior to regular polymer additives, the PVBA ligands increase the rigidity of the perovskite lattice without sacrificing its tolerance to defects, resulting in less activated optical phonon modes and weakened EPC, suppressed non-radiative exciton recombination rate, as well as increased electron/hole mobility due to less phonon scattering. Benefitted from the above advantages of polymerized perovskite, PeLEDs based on 2D (PVBA)PbI$_4$ show bright electroluminescence at room temperature. In addition, the PeLEDs based on quasi-2D perovskite (PVBA)$_2$(FA$_{0.83}$Cs$_{0.17}$)$_9$Pb$_{10}$(I$_{0.9}$Br$_{0.1}$)$_{31}$ (FA: formamidinium) show a record external quantum efficiency (EQE) of 23.2% and improved operation stability.

2. Results and Discussion

2.1. Theoretical Prediction of the Formation of Polymerized Perovskite

SSP within the organic component of the perovskite structure depends highly on the molecular structure of organoammonium ligands.$^{[17,18]}$ Firstly, the distance between two adjacent C=C functional groups in the perovskite lattice before polymerization should be less than 5 Å to activate SSP.$^{[18]}$ Secondly, the distance between two adjacent ammonium ligands ($d_{N-N}$) after polymerization should match the distance between two adjacent metal-halide octahedral ($d_{M-M}$). Lastly, ammonium ligands should be susceptible to polymerization without additional initiators. VBA has a similar structure to phenymethylammonium (PMA), a very popular ligand in 2D perovskites, but has an unsaturated vinyl group in the para position of the aromatic phenyl ring (Figure 1a). The styrene group in the VBA

![Figure 1](image_url)
monomer enables easy polymerization under UV irradiation or low-temperature heating.[10,20] Therefore, we selected VBA monomer as the organoammonium for SSP. As shown in Figure 1a, the styrene groups are first excited into a singlet state by UV irradiation or heating,[10] followed by intersystem crossing to a triplet state and formation of radicals on the vinyl carbons. The radicals then form new covalent bonds with other nearby vinyl groups,[19] forming PVBA ligands.

We first estimated the feasibility of forming a polymerized perovskite phase with VBA monomer using density functional theory (DFT) (see Experimental Section). Figure 1b and Figure S2a (Supporting Information) show the calculated molecule structure of (VBA)2PbI4 perovskite with VBA before polymerization, which is similar to that of (PMA)2PbI4.[21] The distances between adjacent unsaturated C=C bonds are 3.8 and 4.1 Å (Figure 1c), satisfying the criteria for the SSP. Our calculation shows that the Gibbs free energy of (VBA)2PbI4 decreases by 3.6 eV per unit cell after SSP, indicating stabilization of polymerized-(VBA)2PbI4 (noted as (PVBA)2PbI4). Figure 1d and Figure S2b (Supporting Information) show a molecular structure of (PVBA)2PbI4, which has the lowest Gibbs free energy. The d_{N\rightarrow C} in the (PVBA)2PbI4 structure varies from 5.3 to 7.7 Å depending on the tilting angle of the aromatic phenyl ring (Figure 1e), matching d_{M\rightarrow M} of methylammonium lead iodide/chloride (6.3 Å, 5.9 Å, 5.7 Å, respectively).[22]

It should be noted that the SSP process causes minor structural changes in the perovskite lattice, as predicted by DFT calculation. For example, the distance between two inorganic layers reduces from 18.3 to 17.2 Å due to the formation of strong covalent bonding between two adjacent VBA layers (Figure 1b,d). The orientations of phenyl rings become vertical to the carbon chain to minimize the repulsion interaction of hydrogen atoms between the carbon chain and phenyl rings. The average Pb–I–Pb angles also slightly increased from 148.1° to 152.7° to adapt to the configuration of PVBA (Figure 1f). As a result of the greater Pb s and p orbital overlap, the bandgap of (VBA)2PbI4 is reduced by 0.06 eV after SSP (Figure S2, Supporting Information). Nevertheless, regardless of those above minor configuration changes, the (VBA)2PbI4 retains its perovskite structure after SSP.

2.2. Experimental Evidence for Polymerized Perovskite

We first synthesized VBAI monomer (see Experimental Section), and then mixed it with PbI2 in dimethylformamide (DMF) to prepare perovskite films. Interestingly, the mixed VBAI-PbI2 (2:1 molar ratio) solution (1 M) changes from liquid before polymerization to viscous colloidal after polymerization under UV irradiation (Figure S3, Supporting Information), suggesting polymerization of VBA monomers in the solution. Perovskite-like absorption, PL, and X-ray diffraction (XRD) patterns of the films (Figure 2a,b), similar to 2D (PMA)2PbI4 perovskite (Figure S4, Supporting Information), suggest that 2D (VBA)2PbI4 perovskite with VBA monomer in the lattice is formed. As expected, the 2D (VBA)2PbI4 film maintains its perovskite structure after polymerization under UV irradiation, evidenced by its sustained perovskite-like characteristics. Interestingly, the minor structural and bandgap changes after SSP, as predicted by DFT calculation, were also experimentally observed. As shown in Figure 2a,b, the PL peak slightly redshifts, and d-spacing of (002) plane (d_{002}) gradually decreases from 18.1 Å to 17.2 Å. In contrast, the PL and d-spacing of (PMA)2PbI4 remain unchanged. Those results suggest that the VBA monomers polymerized in the perovskite lattice, rather than at the grain surface only.

Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (1H NMR) were used to track the polymerization process of VBA monomers in the perovskite structure. As shown in Figure 2c, the C=C stretching, and =CH2 and =CH wagging vibration peaks from the vinyl group gradually disappear with UV exposure time, indicating the polymerization of VBA monomers in the (VBA)2PbI4 films. The 1H NMR peaks assigned to the vinyl group decrease obviously with the appearance of new peaks in the sp3 carbon region at 2.5 ppm, resulted from polymerization of the vinyl group (Figure 2d). In addition, the peaks coming from aromatic protons are partially shifted to around 7.0 ppm due to the shielding effect caused by polymerization.

We further examine if the polymerization of VBA happens in the perovskite lattice or grain boundary. By normalizing the known quantity of tetramethylsilane (TMS, as the internal standard material), the percentage of polymerized VBA monomers can be calculated by comparing the integral areas of a, b, and c peaks before and after polymerization. It is shown that around 65% of VBA monomers are polymerized after UV for 60 min. This high percentage of polymerized VBA monomers suggests the polymerization process happens not only at the grain boundary but also in the perovskite lattice inside the grains. Gel permeation chromatography (GPC) was conducted to investigate the degree of polymerization (DP) of VBA monomers in (PVBA)2PbI4 films. As shown in Figure 2e, the average molecular weight (Mw) of PVBA is positively correlated with the UV exposure time with DP ranging from 4 to 75. We further grow single crystals by slow drying of precursors on a Si wafer substrate using pre-polymerized VBA as the organic component. Micrometer-sized crystals were obtained with strong PL emission (Figure 2f), further demonstrating that PVBA ligands are in the 2D perovskite lattice.

In addition to the (PVBA)2PbI4 perovskite, a series of quasi-2D perovskite films with different dimensions (PVBA)2MA1–xPbxI3+x films were also successfully prepared. They all show characteristics of quasi-2D perovskites in absorption, PL, as well as XRD (Figure S5, Supporting Information). The d-spacing of (PVBA)2MA1–xPbxI3+x films calculated from (00l) peak of XRD matches well with the high-resolution transmission electron microscopy (HRTEM) images and DFT calculations (Figure S6, Supporting Information), demonstrating the formation of the (PVBA)2MA1–xPbxI3+x perovskite structure.

2.3. The Polymerized Perovskite with Enhanced Stability

A very attractive property of polymerized perovskite is its enhanced intrinsic stability towards heat and humidity. Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the (PVBA)2PbI4 film. As shown in Figure 2g, three stages of TGA curves are observed, which can be attributed to loss of VBA capping layer at the surface, organic amine salt in the perovskite framework, and PbI2, respectively.[23] An obvious
delay is observed in the organic species of (VBA)\textsubscript{2}PbI\textsubscript{4} after UV treatment, suggesting better thermal stability after polymerization. In order to examine humid stability, we directly soaked both (VBA)\textsubscript{2}PbI\textsubscript{4} and (PVBA)\textsubscript{2}PbI\textsubscript{4} films in water without any encapsulation (Movie S1, Supporting Information). Figure 2h shows the photographs of the films immersed in water for different times. The control film degrades rapidly in seconds, while the polymerized perovskite (PVBA)\textsubscript{2}PbI\textsubscript{4} film remains unchanged for 30 s. The improved thermal stability can be attributed to the strong covalent bond between organoammonium ligands and the higher molecular weight of PVBA than VBA monomer. Benefited from its polymer-like behavior, the polymerized perovskite shows greatly enhanced flexibility. Figure 2i shows scanning electron microscopy (SEM) images of the (VBA)\textsubscript{2}PbI\textsubscript{4} and (PVBA)\textsubscript{2}PbI\textsubscript{4} films (thickness 500 nm) after 500 bending cycles with a bending radius of 3 mm.

2.4. The Polymerized Perovskite with Enhanced Lattice Rigidity

Another exciting property of polymerized perovskite is its enhanced lattice rigidity because of the polymerized carbon chains in the lattice. This is in direct contrast with the polymer-perovskite mixture film with polymers at the gain boundary.\cite{12,14}

We first calculated the average atomic displacement of (PVBA)\textsubscript{2}PbI\textsubscript{4} and (PMA)\textsubscript{2}PbI\textsubscript{4} as control, at different temperatures using DFT (see Experimental Section). As shown in Figure 3a, the root mean square displacement (RMSD) of carbon atoms in (PVBA)\textsubscript{2}PbI\textsubscript{4} is half of that of the control (PMA)\textsubscript{2}PbI\textsubscript{4} structure due to the restricted motions of carbon atoms after polymerization. Notably, resulting from the interaction between organic and inorganic components in the perovskite structure, the RMSD of both Pb and I atoms are also smaller in (PVBA)\textsubscript{2}PbI\textsubscript{4} as temperature increases from 80 K to 380 K. Figure 3b shows the DFT calculated real-space displacement of both (PVBA)\textsubscript{2}PbI\textsubscript{4} and (PMA)\textsubscript{2}PbI\textsubscript{4} structures. It is clear that the displacement of the I atom, whose orbitals form the valence band maximum (VBM) and conduction band minimum (CBM), is suppressed in (PVBA)\textsubscript{2}PbI\textsubscript{4}. The displacement of heavy Pb atoms is much smaller than the I atoms. The atom displacement causes fluctuations in the electronic bandstructure. Obviously, the time variation of both VBM and CBM in (PVBA)\textsubscript{2}PbI\textsubscript{4} is much smaller than that of (PMA)\textsubscript{2}PbI\textsubscript{4} structure (Figure 3c).

The higher rigidity results in less activated optical phonon modes and weaker EPC in (PVBA)\textsubscript{2}PbI\textsubscript{4} perovskite.\cite{8} Temperature-dependent steady-state PL was conducted to investigate the strength of EPC in the perovskite films (Figure S7, Supporting Information).
Information). It has been demonstrated that EPC dominates the line broadening in various 2D perovskites, and the contribution from impurities can be neglected. As shown in Figure 3d,e, the (PVBA)2PbI4 film has obviously smaller full-width at half-maximum (FWHM) than the control (PMA)2PbI4 film, particularly at high temperatures. The deformation potential (D) defined as the shift in energy band per unit strain, which can be used to quantify the EPC strength, is reduced from 1.3 × 10^9 eV cm^{-1} in (PMA)2PbI4 to 8.7 × 10^8 eV cm^{-1} in (PVBA)2PbI4 (see Experimental Section).

Weak EPC is expected to reduce non-radiative recombination rates of excitons in perovskite. Both temperature-dependent PLQY and carrier lifetime (τ_{average}) were measured to examine the recombination dynamics of the polymerized perovskite (Figure S7, Supporting Information). Radiative and non-radiative recombination rates (k_{rad} and k_{non}, respectively) are calculated using equations 1/τ_{average} = k_{rad} + k_{non} and PLQY = k_{rad}/(k_{rad} + k_{non}). As shown in Figure 3f,g, the k_{non} of (PMA)2PbI4 increase dramatically with temperature up to 380 K, in contrast to the slight increase of (PVBA)2PbI4 films. Considering that the trap densities of (PVBA)2PbI4 and (PMA)2PbI4 calculated by space-charge limited current (SCLC) measurement are similar (Figure S8, Supporting Information), the dramatic difference in the k_{non} of (PVBA)2PbI4 and (PMA)2PbI4 therefore results from the EPC difference (Figure 3f,g).

In addition to charge recombination dynamics, EPC also influences charge transportation due to phonon scattering. Temperature-dependent SCLC was measured to examine the influence of EPC on carrier mobility (Figure S9, Supporting Information). As shown in Figure 3h,i, two regimes are identified corresponding to orthorhombic and tetragonal phases. Both regimes can be fitted by a power law, \( \mu \propto T^{-m} \), where \( m \) is a co-efficient indicating strength of the EPC. In both regimes, the exponent (m) of (PVBA)2PbI4 is smaller than that of (PMA)2PbI4 for both electron and hole mobility, indicating that weaker EPC in the polymerized perovskite.
2.5. The Polymerized PeLEDs

As an application of polymerized perovskite, we first fabricated PeLEDs using 2D (PVBA)$_2$PbI$_4$ films, and (PMA)$_2$PbI$_4$ as control, with a structure of ITO/HTL/perovskite/TPBi/LiF/Al (ITO: indium tin oxide, HTL: hole transporting layer, TPBi: 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) (Figure 4a). It should be noted that the conduction band (CB) energy of the (PVBA)$_2$PbI$_4$ perovskite reaches a low value of 1.9 eV (Figure S10, Supporting Information), consistent with many other 2D RP phase perovskites.[28] Therefore, the injection barrier of electrons is relatively high compared with the holes. In order to balance the carrier injection, we made devices without HTL, and used an insulating PMMA (polymethyl methacrylate) as a hole blocking layer. The optimized UV treatment time was found to be around 60 min (Figure S11, Supporting Information), which should result from the trade-off between polymerization and possibly decomposition of the UV effect. As shown in Figure 4b,c, the (PVBA)$_2$PbI$_4$ based PeLED with a PMMA blocking layer shows a maximum EQE of 0.01%, bright electroluminescence (EL), and a narrow FWHM of 14 nm at room temperature (Figure 4d). In contrast, the control device using (PMA)$_2$PbI$_4$ does not work at room temperature due to strong EPC, consistent with previous reports.[11] We further conducted temperature-dependent measurements to examine the effect of EPC on the performance of 2D PeLEDs (Figure S12, Supporting Information). The EQE of the (PMA)$_2$PbI$_4$ based PeLEDs decreases dramatically with temperature compared to that of (PVBA)$_2$PbI$_4$ based PeLEDs (Figure 4d). The maximum EQE is much lower than the theoretical limit given their PLQY values. This should be due to the carrier injection imbalance. Further improvement is expected with better electron injection.

We further fabricated PeLEDs using quasi-2D perovskite (PVBA)$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$. It should be noted that the quasi-2D perovskite films consist several phases with different $n$ values. Figure 5a shows the energy level diagram of the devices, and the carriers transfer from large bandgap perovskite (small $n$ phases) to small bandgap ones (large $n$ phases).[29] The strong EPC in small $n$ phases causes non-radiative recombination and thus charge loss during the energy transfer process (Figure 5a). The polymerized perovskite with weak EPC suppresses this loss and results in higher PLQY. For example, the PLQY increases from 32.8% for control (PMA)$_2$(MA)$_9$Pb$_{10}$I$_{31}$ film to 45.7% for (PVBA)$_2$(MA)$_9$Pb$_{10}$I$_{31}$ film, which should be attributed to their different EPC as both films have similar trap density (Figure S8, Supporting Information). The EQE of the PeLEDs increases from 12.5% to a decent value of 17.6% accordingly (Figure 5b). The EQEs of polymerized perovskite (PVBA)$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ ($n=2, 5, 7, 10, 20$) based PeLEDs are much higher than that of control PeLEDs, particularly for devices with small $<n>$ films ($<n>$ is the value for stoichiometric quasi-2D perovskite in solution) (Figure 5c). The EQE was further improved to a record value of 23.2%, approaching the out-coupling limit of 24.7% (Figure S13, Supporting Information), using popular mixed-cations and mixed-halides perovskite (PVBA)$_2$(FA$_{0.83}$Cs$_{0.17}$)$_9$Pb$_{10}$(I$_{0.9}$Br$_{0.1}$)$_{31}$. The higher EQE should be due to their better film crystallinity of mixed-cation perovskites,[30] evidenced by its higher external PLQY value of 56.8%. The internal quantum yield reaches 93.5% assuming both charge carrier balance and radiative excitons.

![Figure 4. Device performances of 2D PeLEDs. a) Energy diagram of 2D PeLEDs. b,c) J–V–L curves (b) and EQE curves (c) of the 2D PeLEDs with hole transporting layers. d) Temperature-dependent PLQY and EQE of (PVBA)$_2$PbI$_4$ and (PMA)$_2$PbI$_4$ based PeLEDs. Inset: EL spectrum and a photograph of the (PVBA)$_2$PbI$_4$ PeLEDs at 5 V at room temperature.](image-url)
are unity. This value is slightly different from that calculated from the PLQY values (91.2%, as the escape probability of photons is 12.7%) due to their different carrier concentrations. The current density–voltage–radiance (J–V–R), angular spectra and intensity profiles, and EQE curves of the devices are shown in Figures S14 and S15 (Supporting Information). The EQE roll-off of our polymerized PeLEDs should be due to the charge injection imbalance because of the different charge injection efficiency between polyTPD and TPBi.[32] This imbalance is exaggerated for FA0.83Cs0.17 based PeLEDs due to its lower carrier mobility.[32] Notably, the electroluminescence (EL) spectra of polymerized perovskite based PeLEDs are generally sharper than that of (PVBA)2MA2Pb2I7 PeLEDs (Figure 5d), further demonstrating weaker EPC in the emissive low-bandgap domains in the PeLEDs.

We further conducted temperature-dependent measurements to examine the effect of EPC on device performance using \( <n> = 2 \) perovskites (Figure S16, Supporting Information). As shown in Figure 5e, the EQE of the control PeLEDs decreases dramatically with temperature compared to that of (PVBA)2MAPb2I7 based PeLEDs. The EQE change of quasi-2D PeLEDs with temperature is smaller than that of 2D PeLEDs, indicating the stronger EPC in the smaller \( n \) phase.

We finally measured the operation stability (T50, time to half of the initial luminance) under a constant current density of 5 mA cm\(^{-2}\) in a N2 glove-box without encapsulation. The T50 of (PVBA)2MAPb2I7 based PeLEDs reached 20.8 h, much longer than the control PeLEDs (Figure 5f). The better operation stability can be ascribed to the more stable structure of polymerized perovskite than (PMA)2MAPb2I7.

## 3. Conclusion

We have demonstrated the formation of polymerized perovskite using unsaturated organoammonium ligands. The polymerized perovskites show polymer-like behavior such as improved film stability and flexibility, in contrast to regular RP and DJ phases with ammonium functional monomers. Compared to various polymer additives reported previously (Table S1, Supporting Information), a unique advantage for polymerized perovskite is that PVBA ligands are in the perovskite lattice and form a perovskite structure with metal-halide octahedron. Benefitted from the polymerized perovskite structure, the strong C–C covalent bond in PVBA can reduce ion vibration of the metal-halide octahedron and increase lattice rigidity. The increased lattice rigidity further suppresses EPC of OHPs, leading to a suppressed nonradiative recombination rate, small PL/EL FWHM, as well as increased carrier mobility without sacrificing its tolerance to defects. As a result, PeLEDs made from 2D polymerized perovskite (PVBA)2PbI4 have bright EL at room temperature. In addition, the quasi-2D (PVBA)2(FA0.83Cs0.17)9Pb10I31 based PeLEDs showed a decent EQE of 23.2% with improved operation stability. Our discovery of polymer perovskite opens up a new way to design perovskites to improve their intrinsic stability, and tune the physical properties of perovskites.

## 4. Experimental Section

**Materials:** Chemicals used in the experiments include lead iodide (PbI2; 99.999%, Alfa-Aesar), cesium iodide (CsI; 99.999%, Alfa-Aesar),
formamidinium iodide (FAI; 99%, Xi’an Polymer Light Technology Corp), lead bromide (PbBr2; 99.999%, Alfa-Aesar), poly[N,N′-bis (4-butylphenyl)-N,N′-bis(phenyl)benzidine] (poly-TDP; American Dye Source Inc.), 2,2′-′-((1,3,5-Benzinetril)-tris(1-phenyl-1-H-benzimidazole) (TPBi; Lumtect Inc.), lithium fluoride (LiF; 98.5%, Alfa-Aesar), N,N-dimethylformamide (DMF; 99.8%, Sigma-Aldrich), chlorobenzene (CB; 99.8%, Sigma-Aldrich), toluene (99.8%, Sigma-Aldrich), acetonitrile (99.8%, Sigma-Aldrich).

Methylammonium iodide (MAI) or (phenylmethylammonium iodide, PMAI) was synthesized by mixing methylamine (40 wt.% in H2O, Sigma-Aldrich) or (phenylmethylamine, 99%, Sigma-Aldrich) with equimolar amounts of aqueous hydrochloric acid (HI; 57. wt.% in H2O, Sigma-Dyke) at 0 °C with constant stirring for 2 h. The solvent was then evaporated under reduced pressure at 65 °C. The remaining white solid product was purified by recrystallization in ethanol, and the recrystallized solid was dried in the N2 glove-box at 60 °C for 24 h. VBAI was synthesized using a similar procedure with PMAI. 4-vinylbenzylammonium (92%, stabilized with 4-methoxyphenol, TCI) was first dissolved in cold ethanol (cooled in an ice bath), and then mixed with an equal molar amount of HI solution and stirred at 0 °C for 2 h. VBAI solids were obtained by adding diethyl ether in the mixed solution, followed by filtration and washing with diethyl ether. The VBAI solids were finally dried in the N2 glove-box at 50 °C for 24 h.

Perovskite Nanocrystal Growth: Pre-polymerized VBAI was obtained by heating the VBAI in the presence of UV at 100 °C under N2 atmosphere for 24 h. The synthesis of nanocrystals was referred to in the reported literature.[3] Pre-polymerized VBAI (20 μmol) and PbI2 (10 μmol) were dissolved in 2 ml of mixed solvent of DMF and CB (1:1 volume ratio). The solution was then diluted 60 times using mixed acetonitrile/CB (1:3 volume ratio). The diluted solution was further diluted 5 times with pure CB and cleaned Si wafer was used as the substrate for the 2D perovskite growth. The substrates were preheated at 80 °C on a hot plate. 10 μl of the diluted solution was dropped onto the preheated substrate surface and dried at 80 °C for 2 h. VBAI solids were obtained by adding diethyl ether in the mixed solution, followed by filtration and washing with diethyl ether. The VBAI solids were finally dried in the N2 glove-box at 50 °C for 24 h.

Perovskite Film Preparation and Characterization: Quasi-2D perovskite (VBA)2(FA0.83Cs0.17)I3 (or (PMA)2(MA)n-1PbnI3n+1) solution was prepared by dissolving stoichiometric quantities of PbI2, MAI and VBAI (or PMAI) mixture in DMF with a concentration of 0.3 M, and stirred for overnight before use. Quasi-2D perovskite (VBA)(FA0.83Cs0.17)2PbI5(FA0.83Cs0.17)3nm solution was prepared using a similar method. The perovskite solutions were spin coated on clean glass substrates at 5000 rpm for 60 s, followed by thermal annealing at 150 °C for 20 min. The poly-TDP or PMMA layer were treated by O2 plasma for 10 min before use. Poly-TDP solution (6 mg ml−1 in CB) or PMMA solution (0.05 mg ml−1 in CB) were spin-coated on the ITO substrates at 1000 rpm for 60 s, followed by thermal annealing at 150 °C for 20 min. The poly-TDP or PMMA layer were treated by O2 plasma for 5 s to improve wetting. TPBi, LiF, and Al layers were sequentially evaporated on top of the perovskite film with thicknesses of 40, 1.2, and 100 nm, respectively. The device area was 0.04 cm2.

The performance of PeLEDs was measured in an N2 glove-box using a homemade motorized goniometer setup consisting of a Keithley 2400 sourcemeter unit, a calibrated Si photodiode (FDS-100-CAL, Thorlabs), a picomammeter (4140B, Agilent), and a calibrated fiber optic spectrophotometer (UVN-SR, StellarNet Inc.). The current–voltage (J–V) curve was obtained by scanning the voltage from −0.5 to 5 V (forward scan) with a step of 0.05 V. Temperature-dependent PeLED and SCLC measurements were conducted using N2 cryostat mentioned above. Si photodiode and fiber probe were attached to the quartz window of the cryostat. The EQEs values at different temperatures were calibrated using the EQE value at room temperature.

Computational Method: Ab initio molecular dynamics (AIMD) simulations and electronic structure calculations were performed using the Vienna ab initio simulation package (VASP).[36] Projector-augmented wave pseudopotentials were employed to describe the electron-nuclei interactions.[38] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were used in all calculations.[39] The Kohn-Sham wave functions were expanded in plane waves up to 400 eV. We used a 3 × 3 × 1 mesh grid to sample the k-space uniformly. The convergence threshold of energy in the self-consistent step was set to 10−5 eV with Gaussian smearing of 0.01 eV Å−1. Moreover, the force threshold of geometry optimization is 0.02 eV Å−1 for each dimension of all atoms in the supercell. The elastic tensor was determined by performing six finite lattice distortions, and the elastic constants were derived from the strain-stress relationship.[37] The effective masses of free carriers were derived by fitting the E-k diagram near the band extremum by a parabola. Ion-clamped dielectric constants of anionic and organic layers were estimated in frozen configurations using density functional perturbation theory.[36] AIMD was used to reveal atomic displacement at specific temperatures (80, 300, and 380 K after geometry optimization). Then, a 5 ps microcanonical AIMD trajectory was then generated with a time step of 1 fs. Finally, the root mean square displacement (RMSD) was evaluated by comparing it to the optimum configuration. The phonons at Γ point were calculated by the finite-displacement method implemented in the PHONOPY package with a step of 0.01 Å.[36] Here, we took VASP as the force-constant calculator with a high plane wave cutoff at 500 eV, and the force evolutions were performed on 1 × 1 × 1 supercells using k-point sampling meshes 2 × 2 × 2.
Deformation Potential Calculation: Deformation potential (D) is defined as the change in the bandgap energy per unit strain due to phonon scattering, which has been used to describe the electron-phonon interaction.\[25\] To estimate D, the temperature-dependent FWHM of (PVBA)$_2$Pbl$_4$ and (PMA)$_2$Pbl$_4$ were fitted by the following model:\[26\]

$$\Gamma (T) = \Gamma_0 + \gamma_0 T + \frac{\Gamma_{LO}}{\epsilon_{LO} k_B T} + \Gamma_{imp} \epsilon_{LO}/k_B T$$

(1)

where $\Gamma_0$ is the temperature-independent inhomogeneous broadening due to scattering from disorder and/or crystallographic defects, $\gamma_0$ is the acoustic phonon interaction constant, $\Gamma_{LO}$ is the optical phonon interaction constant, $E_{LO}$ represents the optical phonon energy, $\Gamma_{imp}$ is the PL broadening from the completely ionized impurity states, $E_{imp}$ is the average energy of the impurities ionizing, and $k_B$ and $T$ correspond to the Boltzmann constant and the temperature, respectively.

The homopolar optical phonon scattering has been proved to be the main source of scattering by the relaxation mechanism at high temperatures.\[27\] Thus, the charged impurities and acoustic phonons to the broadening can be ignored.\[28,29\]

FWHM = $\Gamma_0 + \frac{\Gamma_{LO}}{\epsilon_{LO} k_B T} + \frac{\Gamma_{imp} \epsilon}{k_B T}$

(2)

where the value of $\Gamma_{LO}$ and $E_{LO}$ can be obtained by fitting the experimental data about temperature and FWHM by the above formula.

At high temperatures, $\Gamma_{LO}$ is approximated as:

$$\Gamma_{LO} = \frac{M E_{LO}}{\rho L} \left( \frac{D}{E_{LO}} \right)^{\gamma}$$

(3)

where $M = m_e^* + m_h^*$ is the sum of electron and hole effective masses (Table S2, Supporting Information), $\rho$ is the mass density (2.7 g cm$^{-3}$ for both materials), $L$ is the thickness of the quantum well where the excitation is confined ($L = 0.64$ nm for Pb-I-Pb inorganic layer).

Trap Density and Carrier Mobility Calculation: The trap density and carrier mobility were calculated using SCLC results. The hole-only device structure is ITO/poly-TPD (40 nm)/2D perovskite (100 nm)/poly-TPD (40 nm)/MoO$_3$ (10 nm)/Ag (100 nm) (ITO: indium tin oxide, poly-TPD: poly[N,N″-bis (4-butylphenyl)-N,N″-bis(phenyl)benzidine]). The electron-only device structure is ITO/SnO$_2$ (20 nm)/2D perovskite (100 nm)/TPBi (40 nm)/LiF (1.2 nm)/Al (100 nm) (TPBi: 2,2′,2″-(1,3,5-Benzinetriyl)-tris(1-phenyl-1H-benzimidazole)). Three distinct regions could be identified from the I-V curves including Ohmic, trap-filled limited (TFL) as well as SCLC regions. The hole and electron trap density were extracted from hole and electron only devices, respectively, using equation:\[30\]

$$N_{trap} = 2\epsilon_0\epsilon_r V_{TFL} / (qL^2)$$

(4)

where $\epsilon_0$, $\epsilon_r$, $V_{TFL}$, $q$, and $L$ are the vacuum permittivity, the relative dielectric constant, the onset voltage of the TFL region, elementary charge and the thickness of the perovskite films, respectively.

The charge carrier mobility was extracted from the SCLC regions using the Mott-Gurney Law:\[31\]

$$J = \frac{9\epsilon_0\epsilon_rV^2}{8L}$$

(5)

where $\mu$ is the charge mobility, $J$ and $V$ are current density and applied voltage, respectively.

Optical Modeling: The light outcoupling calculations were based on a classical dipole emission model.\[32\] The power ratio radiated to each in-plane wavevector range (outcoupled, substrate, waveguided, surface plasmon polariton) was simulated by using the experimentally obtained optical constants (refractive index) of each layer to construct the model device. The refractive indexes of perovskite were obtained by ellipsometry. The dipole position was assumed to be at the center of the perovskite layer.

Internal Quantum Yield Calculation: The refractive index of perovskite at the band edge is higher than air and glass, leading to an escape cone for emitted photons at the perovskite-air interface. By considering the existence of photon-recycling, the external PLQY value is lower than the internal quantum yield (IQE). The external PLQY and the IQE have the following relationship:\[33\]

$$PLQY = \frac{IQE \times n_{esc}}{1 - IQE + IQE \times n_{esc}}$$

(6)

where $n_{esc}$ is the probability that an emitted photon will leave the film before re-absorption.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electron–phonon coupling, light-emitting diodes, organometal halide perovskite, solid-state polymerization

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