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Organic-Inorganic Hybrid Ruddlesden-Popper Perovskites: An Emerging Paradigm for High- Performance Light-Emitting Diodes

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ABSTRACT: Recently, lead halide perovskite materials have attracted extensive interest, in particular, in the research field of solar cells. These materials are fascinating “soft” materials with semiconducting properties comparable to the best inorganic semiconductors like silicon and gallium arsenide. As one of the most promising perovskite family members, organic-inorganic hybrid Ruddlesden-Popper perovskites (HRPPs) offer rich chemical and structural flexibility for exploring excellent properties for optoelectronic devices, such as solar cells and light-emitting diodes (LEDs). In this perspective, we present an overview of HRPPs on their structural characteristics, synthesis of pure HRPP compounds and thin films, control of their preferential orientations and investigations of heterogeneous HRPP thin films. Based on these recent advances, future directions and prospects have been proposed. HRPPs are promising to open up a new paradigm for high performance LEDs.

TOC GRAPHICS

KEYWORDS: layered perovskites, solar cells, LEDs, two dimensional, orientation

Perovskites refer to the materials with the same crystal structure as calcium titanate (CaTiO_3), with a general formula of ABX_3 , where A and B are cations and X is an anion. The perovskite structure can be predicted by using an empirical index – Goldschmidt tolerance factor (t)¹, which is expressed as

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1),$$

where r_A , r_B , and r_X are the atom radius of the constituting atoms A, B and X, respectively. In general, a t value between 0.8 and 1 would give a stable cubic structure, whereas $t < 0.8$ and $t > 1$ would lead to non-perovskite structures.²

Recently, lead halide perovskite materials have attracted extensive interest, in particular, in the research field of solar cells. Lead halide perovskites have a perovskite structure with the formula of APbX_3 , where A are monovalent cations, in most case CH_3NH_3^+ (MA^+), $[\text{H}_2\text{N}=\text{CHNH}_2]^+$ (FA^+), Cs^+ , Rb^+ or their mixture, and X are halide anions (I^- , Br^- , Cl^- or their mixture). Lead halide perovskites show excellent semiconducting properties, such as high absorption coefficient, easily tunable bandgaps, small exciton binding energy, long carrier diffusion length, strong photoluminescence and high color purity, which are comparable to the best inorganic semiconductors such as silicon and gallium arsenide.³⁻⁵ Beyond their excellent optoelectronic properties, these materials are easily obtained by depositing from solutions containing raw materials at low temperature ($< 200\text{ }^\circ\text{C}$), showing promising applications in low-cost optoelectronic devices, such as solar cells, light-emitting diodes, photodetectors, lasers and transistors.^{6,7} In the last 9 years, we have witnessed the rapid development of solar cells based on lead halide perovskites, of which the power conversion efficiency (PCE) has reached over 22%, towards that of high-quality crystalline silicon (26%).⁸ State-of-the-art light-emitting diodes

(LEDs) based on lead halide perovskites deliver external quantum efficiencies (EQEs) up to 14.4%, catching up with other LED technologies, *e.g.* quantum-dot and organic LEDs.⁹

In addition, the perovskite family offers rich chemical and structural opportunities to explore new properties and applications.¹⁰ In this perspective, we present an overview on an emerging perovskite family member – organic-inorganic hybrid Ruddlesden-Popper perovskites (HRPPs), in understanding of their structural characteristics, synthesis of pure HRPPs, investigations of heterogeneous HRPP thin films, control of preferential orientations and characterizations of their optoelectronic properties. Recent advances in this field, combined with the rich chemical and structural flexibility of HRPPs, indicate that HRPPs are promising to be a new paradigm for high performance LEDs.

Organic-inorganic hybrid Ruddlesden-Popper perovskites offer rich chemical and structural flexibility for exploring excellent properties for optoelectronic devices

Structural characteristics of Ruddlesden-Popper perovskites (RPPs). RPPs are named after S. N. Ruddlesden and P. Popper, who first reported such structures in 1957.¹¹ By sintering mixtures of SrCO_3 and TiO_2 (by molar ratio of 3:2) to 1400 °C, they obtained a new compound $\text{Sr}_3\text{Ti}_2\text{O}_7$ other than perovskite SrTiO_3 in spite of suitable tolerance factor.¹² The $\text{Sr}_3\text{Ti}_2\text{O}_7$ exhibits a structure similar to Sr_2TiO_4 (K_2NiF_4 -type), whose unit cell is tetragonal and body-centered with $a = 3.88$ Å and $c = 12.60$ Å.¹¹ The $\text{Sr}_3\text{Ti}_2\text{O}_7$ is considered as the intermediate phase between those of Sr_2TiO_4 and SrTiO_3 (perovskite), consisting of alternated SrTiO_3 and SrO layers. As a result, the formula of oxide-based RPPs is written as $\text{AO}(\text{ABO}_3)_n$ or $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ ($n = 1, 2, \dots$), where n is the number of stack layers of perovskite unit cells in a RPP unit cell (Figure 1). In addition to

oxide-based RPPs, very recently, lead-halide-based RPPs $\text{Cs}_{n+1}\text{Pb}_n\text{Br}_{3n+1}$ ($n = 1, 2, \dots$) were reported based on the observations of atomic-level aberration-corrected scanning transmission electron microscopy (STEM).¹³ In general, the formula of RPP phases can be extended to $\text{A}_{n-1}\text{A}'_2\text{B}_n\text{X}_{3n+1}$ ($n = 1, 2, \dots$), whose crystal structures are shown in Figure 1.¹⁴ The A' cations, which are located in the boundaries between the perovskite stack layers and block layers, form spacing layers. It is worthwhile to note that A' cations can be as small as those A cations in ABX_3 perovskite phases (*e.g.*, Cs and Sr). However, they cannot be incorporated into the perovskite lattice to form RPPs if they contain steric hindrance groups.¹⁵ In spite of chapped perovskite crystal lattice, RPPs containing numerous perovskite unit stacks are the closet successors of their 3D perovskite counterparts. As a result, RPPs keep perovskite features to some extent, depending on the n value and the A' cation that prevents electronic coupling between two adjacent perovskite layers.

Figure 1. Unit cell structures of RPPs with n values of 1, 2, 3, and 4.¹⁴ A unit cell contains two formula units. Copyright © 2000, Springer Nature.

Organic-inorganic hybrid RPPs (HRPPs). The A' cation of RPPs can be organic monoammonium or diammonium cation, resulting in formulas of $(\text{RNH}_3)_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ ($n = 1, 2, \dots$) and

$R(\text{NH}_3)_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ ($n = 1, 2, \dots$), respectively, where R is an organic unit, for example, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($\text{BA}^+ = \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$, $n = 1, 2, \dots$).¹⁶ In HRPPs, the organic cations are organized via hydrogen bonds between their ammonium groups and the halogens of the inorganic octahedrons at the boundaries of the perovskite layers. These organics are also self-organized via van der Waals interactions between each other, forming organic spacing layers.

In principle, the organic spacing layers have relative larger electronic band gaps and lower dielectric constants than the perovskite layers. As a result, the HRPPs exhibit heterostructures where the perovskite layers are sandwiched between the organic layers. Strong excitonic effect with exciton binding energy of several hundreds of milli-electronvolts (meV) was observed in monolayer HRPPs, which was assigned to dielectric confinement effect.¹⁷ As a result, the HRPPs are dielectric quantum wells, where the dielectric confinement effect is dominated.¹⁸ Besides the dielectric confinement, conventional size-related electronic confinement was also observed.¹⁸ In the HRPPs with very thin perovskite layers (< 4 nm in consideration of the Bohr radius of ~ 2 nm), tailoring the thickness of the perovskite layers will alter the optoelectronic properties of the HRPPs.¹⁸ On the basis of the dielectric confinement effect and the size-related quantum confinement effect, the optical and electronic properties of the HRPPs can be tuned by tailoring the perovskite ‘wells’ and organic ‘barriers’, such as the width of the ‘wells’ and ‘barriers’, composition of the ‘wells’, and dielectric constants of the ‘barriers’.^{18–21} The organics have a huge materials library, offering a wide range of opportunities of substituents for exploring HRPPs with excellent optoelectronic properties.

Exploring new HRPPs. As shown in Figure 2, three main strategies are considered to explore new HRPPs: 1) changing the composition of the perovskite layers, including constituting atoms and feed ratios, 2) incorporating selected organic ammonium cations that could affect the bonding

feature or electronic structure of the perovskite layers, 3) tailoring dimensionality of the HRPPs, *e.g.* atomically thin HRPPs. Though HRPPs, which can self-assemble into nanoplates, are believed to be two-dimensional (2D) or quasi-2D materials, their dimensionality can still be tailored by controlling the processing conditions.²²

Figure 2. Strategies for exploring new HRPPs.

Electronic coupling between adjacent perovskite layers will be avoided when the organic spacing layer is wide enough, for example, if the organic chain is longer than propyl amine.²⁰ Reducing the thickness of the organic spacing layer will provide moderate interaction between the adjacent perovskite layers, and may lead to new distinctive properties.¹³ Extended Hückel tight-binding band structure calculations suggest that the X-B-X bond angle and B-X bond distance are dominant factors affecting the electronic structure of the perovskites.²³ Short and small organic units will lead to halogen-halogen contact and distortion of the perovskite lattice. Short-distance iodine-iodine contact (4.19Å , larger than van der Waals distance of 4.0Å) was reported in a

monolayer HRPP employing an organic dication ($((\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{NH}_3^+)$ with high charge density and small size, causing significant red-shifted excitonic peak.²⁴ Halogen substituents in the organic units were reported to strongly affect the steric interaction between the organic units and the inorganic framework, causing notable perovskite lattice distortions.²⁵ However, employing bifunctional ammonium cations $\text{X}(\text{CH}_2)_2\text{NH}_3^+$ ($\text{X} = \text{Br}, \text{Cl}$) into PbI_4 -based HRPPs will form $\text{N-H}\dots\text{X}$ - hydrogen bonding and $\text{C-X}\dots\text{I}$ - halogen bonding, leading to the formation of undistorted PbI_4 perovskite layers and distinct properties, as compared with other salts such as $(\text{I}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$.²⁶ In addition, broad emissions with spectra covering the entire visible range were observed in monolayer HRPPs with corrugated perovskite layers.^{27,28} These HRPPs employ N^1 -methylethane-1,2-diammonium (N-MEDA) or (ethylenedioxy)bis(ethylammonium) (EDBE) as the organic cations, which cause lattice distortions and therefore electron-phonon coupling in a deformable lattice.

In principle, electronic coupling between adjacent perovskite layers will be avoided in HRPPs with large organic spacing layer, suggesting that the properties of atomically thin HRPPs will be the same as that of the bulk crystals.²⁹ However, it is reported that several-unit-thick HRPPs (< 8 units), which are obtained by a micromechanical exfoliation technique, show different properties from bulk HRPPs (> 15 units) due to structural rearrangement of organic molecules around the inorganic sheets.³⁰ In 2015, Dou et al. obtained single- and few-unit-cell-thick single-crystalline HRPPs through solution-phase growth.²⁹ These atomically thin HRPPs show unusual structural relaxation, leading to band gap shift as compared to the bulk crystal. In addition, recent reports on perovskite nanoplates with a thickness from dozens to several hundred nanometers show much longer diffusion lengths³¹ and the feature of built-in whispering gallery mode microresonator^{32,33}. Similar properties can be anticipated in HRPP nanoplates.

Heterogeneous multilayer HRPPs open up new opportunities for high-performance optoelectronic devices

Synthesis of pure HRPPs. In 1980s, monolayer HRPP single-crystals were synthesized using stoichiometric PbX_2 and RNH_3X .¹⁷ A bilayer HRPP $\text{PEA}_2\text{MAPb}_2\text{I}_7$ ($\text{PEA}^+ = \text{Ph}(\text{CH}_2)_2\text{NH}_3^+$) was synthesized in 1991 using a similar approach. However, attempts for preparing multilayer and bromine- and chlorine-based HRPP single crystals were unsuccessful.³⁴ In addition, thin films of multilayer HRPPs prepared using nominal compositions show absorption features of monolayer HRPP phase and perovskite phase, indicating that these films are imperfectly self-assembly and heterogeneous.³⁴ In 1994, pure phase multilayer HRPPs $\text{BA}_2\text{MA}_{n-1}\text{Sn}_n\text{I}_{3n+1}$ ($n = 1 \sim 4$) were obtained based on stoichiometric feed ratios of SnI_2 , BAI, and MAI.³⁵ In 2002, a self-assembly method was developed to grow ultra-thin monolayer HRPPs.³⁶ Till 2015, homogenous multilayer lead-based HRPP powders $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1 \sim 4$) were synthesized using PbO , aqueous HI solution, aqueous H_3PO_2 solution, MAI, and BA as the raw materials.³⁷ In 2016, a series of pure HRPPs $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1 \sim 4$) were synthesized using a scalable method by Stoumpos *et al.*, who demonstrated that the use of BA as the reaction limiting reagent is essential in obtaining the pure compounds.¹⁶ However, efforts for synthesizing higher- n HRPPs ($n > 4$) were unsuccessful. Very recently, pure Sn-based HRPPs $(\text{BA})_2(\text{MA})_{n-1}\text{Sn}_n\text{I}_{3n+1}$ ($n = 1 \sim 5$) were reported by Cao *et al.*, and stoichiometric BAI was claimed to be necessary for obtaining pure compounds.³⁸ In addition, they demonstrated that homogenous HRPP thin films could be obtained with the use of pure bulk crystals as precursor solutions, whereas precursor solutions prepared by mixing stoichiometric metal halide and ammonium halide salts will lead to heterogeneous HRPP films.

Heterogeneous multilayer HRPP thin films with enhanced optoelectronic properties. As mentioned in the above section, it is very difficult to obtain pure multilayer HRPP thin films. However, recent studies demonstrate that heterogeneous multilayer HRPP thin films are favorable to form energy funnels for high-efficiency LEDs³⁹ and self-driven charge separation for efficient solar cells⁴⁰. The monolayer HRPP thin films show stable excitons with large exciton binding energy and photoluminescence (PL) with narrow bandwidth from the exciton band. However, these films suffer severe exciton-phonon coupling, which quenches their PL efficiency at room temperature. Although intense electroluminescence (EL) from monolayer HRPPs can be observed at liquid-nitrogen temperature⁴¹, their room-temperature EL is quite weak⁴². It was reported that the use of stoichiometric feed ratios of multilayer HRPPs results in graded distribution of multilayer HRPP phases, leading to efficient energy transfer from small-*n* HRPPs to large-*n* HRPPs and therefore efficient HRPP films.^{39,43} As shown in Figure 3, the HRPP thin film prepared from nominal NMA₂FAPb₂I₇ (NMA = 1-naphthylmethylamine) is heterogeneous, which exhibits absorption and PL peaks from several HRPPs, such as NMA₂PbI₄, NMA₂FAPb₂I₇, and NMA₂FA₃Pb₄I₁₃.⁴³ The energy-dispersive X-ray spectroscopy (EDX) elemental mapping clearly demonstrates that large-*n* HRPPs and small-*n* HRPPs are located close to TFB and ZnO layers, respectively. Based on such heterogeneous HRPP thin films, LEDs are achieved with EQEs approaching and beyond 10%.⁴³ Interestingly, tuning the feed ratios and compositions of the nominal multilayer HRPPs will lead to heterogeneous HRPP thin films with different optoelectronic properties.^{9,43–47} Table 1 briefly summarizes device performance of the recently reported LEDs based on HRPPs.

Figure 3. Heterogeneous HRPP thin film prepared from nominal $\text{NMA}_2\text{FAPb}_2\text{I}_7$.⁴³ (a) Absorption and PL spectra of this film. (b) EDX elemental mapping. Colour-mixed EDX mapping images (scale bar, 50 nm) present the element distribution of Pb, I and Zn. The normalized EDX count distribution of Pb and I across the HRPP film are also presented. (c) Flat-band energy level diagram showing the graded distribution of multilayer HRPP phases. Reproduced with permission. Copyright © 2016, Springer Nature.

Table 1. Summary of device performance of the recently reported LEDs based on HRPPs.

Nominal HRPP	V_{on} (V) ^a	EQE_{max} (%)	EL peak (nm)	Ref.
$\text{NMA}_2\text{FAPb}_2\text{I}_{7-x}\text{Br}_x$ ($x = 0, 1, 2, 3, 4, 5, 7$)	1.3-2.2	0.01-11.7	518-786	43
$\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 3, 5, 10, 40$)	2.9-4.4	0.3-8.8	735-770	39
$\text{NMA}_2\text{CsPb}_2\text{I}_{7-x}\text{Cl}_x$ ($x = 0, 1$)	2.3, 2.0	2.4, 3.7	688	45
$\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ ($n = 3, 5$)	3.5, 3.0	4.8, 7.4	520, 526	48
$\text{NMA}_2\text{Cs}_{n-1}\text{Pb}_n\text{I}_{3n+1}$	1.9	7.3	694	49
$\text{PEA}_2\text{FA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ ($n = 2, 3, 4, 5, 6$)	2.8-3.4	1.5-14.4	532	9
PEA_2PbI_4	2.8	0.005	526	42
$\text{PEA}_2\text{PbBr}_4$	4.0	0.04	410	22
$(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$	2.7	2.3	700	44
$(\text{BA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16}$	3.3	1.0	523	44
$(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{Br}_7\text{Cl}_3$	5.2	0.01	468	44
$\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 4, 5$)	1.3, 1.0	0.2, 1.0	733, 744	50

^aTurn-on voltage.

HRPP thin films with preferential orientation. One of the major drawbacks of lead halide perovskites is the instability of the material to atmospheric moisture, in spite of their fascinating PCEs in solar cells. One possible way to solving this problem is to use HRPPs, which are more resistant to humidity than their 3D perovskite counterparts.⁵¹ However, monolayer HRPPs have unsuitable bandgaps for light absorption, and their tightly bound excitons are difficult to dissociate into free charges at room temperature.⁵² Fortunately, multilayer HRPPs show appropriate bandgaps for light absorbers as well as good moisture stability.^{37,51} Furthermore, it was found that the HRPPs exhibit enhanced moisture stability with decreasing n values, whereas the efficiency of their solar cells drops remarkably, which is mainly attributed to the inhibition of out-of-plane charge transport by the organic cations.⁵³ By using a hot-casting technique, Tsai *et al.* demonstrated that highly oriented HRPPs, whose perovskite layers are vertically aligned with respect to the contacts in planar solar cells to facilitate efficient charge transport, can be obtained.⁵⁴ The solar cells based on these films exhibit largely improved PCE while maintaining good stability. The preferential orientation of the HRPPs is definitely important for realizing high-efficiency solar cells. Cao *et al.* demonstrated that monolayer HRPP thin film strongly favors the growth of its perovskite layers along the substrate, resulting in horizontally oriented (001) plane.³⁷ Nevertheless, this tendency is changed in multilayer HRPP thin films, where the perovskite layers tend to vertically grow.³⁷ Studies on Tin-based HRPP thin films show that their preferential orientation can be switched using different precursor solvents.³⁸ Specifically, the perovskite layers of the HRPPs are parallel to the substrate when dimethyl sulfoxide (DMSO) is used as the precursor solvent, and the preferential orientation is flipped to perpendicular when N, N-dimethylformamide (DMF) is used. Similar results are found in lead-based HRPP thin films, whose n values are also inherently correlated with the preferential orientation.⁵⁵ In addition, the change of linear-chain

organic spacer BA into short-branched-chain *iso*-BA will significantly improve the crystallinity and out-of-plane preferential orientation.⁵⁶ Our recent work revealed that high-quality HRPP thin films with vertically oriented perovskite layers can be obtained by using DMSO and MACl as additives in precursor solutions, which have a synergistic effect on crystal growth.⁵⁷ More interestingly, these highly oriented HRPP films show type-II heterostructures, which facilitate self-driven charge separation.⁵⁷

Future directions and prospects are likely to push the HRPPs towards a new paradigm for high-performance LEDs.

In-situ HRPP nanocrystals for monochrome emission. The development of green and infrared perovskite LEDs is very fast, of which EQEs have exceeded 10%.^{9,47,58} However, perovskite LEDs with other colors (*e.g.* blue, orange, and red) are much less efficient.^{59–61} The green-emitting bromide perovskites and infrared-emitting iodide perovskites show high PL quantum efficiency (PLQE) in thin films. However, mixed-halide perovskite films show severely descending PLQEs compared with their pure counterparts, although they have been demonstrated monochrome emission with various colors.⁴³ In addition, the mixed-halide perovskites have the tendency for phase segregation, leading to unstable emission.⁶² One possible way is to use size-related quantum confinement effect of HRPPs to tune the emission colors.⁶³ In addition, recent report demonstrated that atomically thin HRPPs show higher crystal quality, leading to much higher PLQE (~ 26%) than that of the bulk crystal (< 1%).²⁹ A solvent-vapor-annealing technique was demonstrated for converting as-deposited polycrystalline HRPP thin films into high-quality HRPP nanoplates with enhanced optoelectronic properties.²² Based on these nanoplates, a color-pure, room-temperature violet LED was successfully achieved, though with low efficiency. Very recently, efficient green

and red LEDs were reported based on *in-situ* HRPP nanoplates, showing high EQEs of 10.4% and 7.3%, respectively.⁶⁴ *In-situ* HRPP nanocrystals open up a new approach to tune the emission colors and at the same time get rid of problems of low efficiency and instability caused by mixed halides.

Heterogeneous HRPP films for tunable white emission. White light emission was observed in HRPPs because of strong electron-phonon coupling in a deformable lattice and a distribution of intrinsic trap states.^{27,28} These HRPPs show stable white light emission under light excitation, with a PLQE up to 9%.²⁸ Unfortunately, white EL from perovskites has not been reported yet. Heterogeneous HRPP thin films exhibit PL peaks from several multilayer HRPPs⁴³, which can be considered as a host-guest system where large- n ($n > 4$) HRPPs are doped into small- n ($n = 1$ or 2) RPP matrix. It is interesting to note that the spectra of heterogeneous RPP films can cover a wide range of > 200 nm (Figure 3a), suggesting that white emission ranging from ~ 450 nm to ~ 650 nm could be realized by tuning the precursor composition. In addition, similar to other host-guest white-emitting material systems, such white emission can be easily tuned by changing the ratio of emitting components.⁶⁵ Specifically, tunable white light emission could be realized by optimizing the feed ratio and composition of the nominal HRPPs.

Promoting internal quantum efficiency. The EQE of an LED is a production of internal quantum efficiency (IQE) and light out-coupling efficiency, which is expressed as

$$EQE = IQE \cdot \eta_c = \gamma \cdot \chi \cdot \eta_{PL} \cdot \eta_c \quad (2),$$

where η_c is the light out-coupling efficiency that describes the fraction of photons extracted out of the device in the viewing direction (usually forward view) over the total electrically generated photons. The IQE describes the capability of converting electrons into photons of the emitting

layer. The IQE can be estimated by the charge carrier balance factor (γ), the fraction of excitons for radiative decay (χ), and the effective radiative quantum yield (η_{PL}) (Equation 2). Device engineering, such as optimization of the charge transport layers of the LEDs, could promote the charge balance factor towards its maximum ($\gamma = 1$). In addition, the use of electron- and hole-blocking layers can confine the charge carriers in the emitting layer and thus lead to enhanced charge balance.⁶⁶ HRPPs show obvious excitonic characteristics, and electroluminescence is mainly from excitonic recombination (assuming typical charge densities $< 10^{15} \text{ cm}^{-3}$ under electrical excitation).⁶⁷ The emission characteristics of perovskites (*e.g.* MAPbI₃) are predominately singlet excitons in nature, whereas triplet properties are found in monolayer (MA)₂Pb(SCN)₂I₂, whose phosphorescence was > 47 times more intense compared to its bandgap fluorescence.⁶⁸ It is likely that the HRPPs have similar properties. It seems that the χ should be taken into consideration to further improve the EQE. The η_{PL} can be roughly referred to the PLQE of the HRPP films, which is a key factor determining the IQE. Possible ways to achieve HRPP films with high PLQEs are to carefully tune the doping concentration of the large-*n* HRRPs and to reduce exciton-phonon coupling by using rigid organic cations. Although the excitons in the perovskite layers are dielectrically confined by the organic layers in HRPPs, energy leakage from the perovskite layers to the triplet states of the organic cations should also be taken into consideration to design high-efficiency HRPPs, in particular, for those employing large π -conjugated organic cations.⁶⁹ In addition, passivation on the HRPP nanocrystals can promote the PLQE and consequently the device performance.⁹

Improving light out-coupling efficiency. Equation 2 shows that the EQE of an LED is largely influenced by the η_c besides the IQE. A major concern on the η_c of perovskite LEDs is that perovskite materials have much higher refractive index (~ 2.6) than organic molecules (~ 1.7),

based on which a maximum η_c of 7.4% is predicted using the ray-optics theory⁷⁰. However, we simulated the optical energy losses in perovskite LEDs and found that perovskite LEDs can still reach a high η_c more than 20% in spite of their high refractive index.⁷¹ In addition, as mentioned above, the HRPPs could be anisotropic oriented. Further improvement of the η_c is to control the orientation of the emitting HRPP components. It is widely reported that high EQEs approaching or even beyond 40% can be achieved when the transition dipole moments of organic emitters parallel to the substrate.⁷² Heteroepitaxy⁷³ – atomically aligned growth of a crystalline film atop a different crystalline substrate – could be a possible way to grow horizontally oriented HRPP films, which could be favorable to promoting the η_c in LEDs.

In conclusion, the HRPPs offer rich chemical and structural flexibility for exploring new and excellent optoelectronic properties, including tailoring the perovskite layers, the organics, and the dimensionality. In addition, their mixtures and preferential orientations provide more opportunities. Their mixtures – heterogeneous HRPP thin films show enhanced optoelectronic properties in both LEDs and solar cells, and provide chances for white LEDs. Controlling the preferential orientations of the HRPPs can further promote their performance in solar cells as well as LEDs. Future directions and strategies on developing high-performance HRPP LEDs are proposed. It is likely that HRPPs will open up a new paradigm for high-performance LEDs.

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Notes

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REFERENCES

- (1) Goldschmidt, V. M. Die Gesetze der Krystallochemie. *Naturwissenschaften* **1926**, *14*, 477–485.
- (2) Li, Z.; Yang, M.; Park, J.-S.; Wei, S.-H.; Berry, J. J.; Zhu, K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chem. Mater.* **2016**, *28*, 284–292.
- (3) Manser, J. S.; Christians, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116*, 12956–13008.
- (4) Docampo, P.; Bein, T. A Long-Term View on Perovskite Optoelectronics. *Acc. Chem. Res.* **2016**, *49*, 339–346.
- (5) Peng, J.; Chen, Y.; Zheng, K.; Pullerits, T.; Liang, Z. Insights into Charge Carrier Dynamics in Organo-Metal Halide Perovskites: From Neat Films to Solar Cells. *Chem. Soc. Rev.* **2017**, *46*, 5714–5729.

- (6) Chen, Q.; De Marco, N.; Yang, Y. (Michael); Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. Under the Spotlight: The Organic–inorganic Hybrid Halide Perovskite for Optoelectronic Applications. *Nano Today* **2015**, *10*, 355–396.
- (7) Sun, Y.; Peng, J.; Chen, Y.; Yao, Y.; Liang, Z. Triple-Cation Mixed-Halide Perovskites: Towards Efficient, Annealing-Free and Air-Stable Solar Cells Enabled by Pb(SCN)₂ Additive. *Sci. Rep.* **2017**, *7*, 46193.
- (8) Correa-Baena, J.-P.; Saliba, M.; Buonassisi, T.; Grätzel, M.; Abate, A.; Tress, W.; Hagfeldt, A. Promises and Challenges of Perovskite Solar Cells. *Science* **2017**, *358*, 739–744.
- (9) Yang, X.; Zhang, X.; Deng, J.; Chu, Z.; Jiang, Q.; Meng, J.; Wang, P.; Zhang, L.; Yin, Z.; You, J. Efficient Green Light-Emitting Diodes Based on Quasi-Two-Dimensional Composition and Phase Engineered Perovskite with Surface Passivation. *Nat. Commun.* **2018**, *9*, 570.
- (10) Saparov, B.; Mitzi, D. B. Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design. *Chem. Rev.* **2016**, *116*, 4558–4596.
- (11) Ruddlesden, S. N.; Popper, P. New Compounds of the K₂NiF₄ Type. *Acta Crystallogr.* **1957**, *10*, 538–539.
- (12) Ruddlesden, S. N.; Popper, P. The Compound Sr₃Ti₂O₇ and Its Structure. *Acta Crystallogr.* **1958**, *11*, 54–55.
- (13) Yu, Y.; Zhang, D.; Yang, P. Ruddlesden–Popper Phase in Two-Dimensional Inorganic Halide Perovskites: A Plausible Model and the Supporting Observations. *Nano Lett.* **2017**, *17*, 5489–5494.

- (14) Beznosikov, B. V.; Aleksandrov, K. S. Perovskite-like Crystals of the Ruddlesden-Popper Series. *Crystallogr. Rep.* **2000**, *45*, 792–798.
- (15) Jemli, K.; Audebert, P.; Galmiche, L.; Trippé-Allard, G.; Garrot, D.; Lauret, J.-S.; Deleporte, E. Two-Dimensional Perovskite Activation with an Organic Luminophore. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21763–21769.
- (16) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden–Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chem. Mater.* **2016**, *28*, 2852–2867.
- (17) Ishihara, T.; Takahashi, J.; Goto, T. Exciton State in Two-Dimensional Perovskite Semiconductor $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$. *Solid State Commun.* **1989**, *69*, 933–936.
- (18) Hong, X.; Ishihara, T.; Nurmikko, A. V. Dielectric Confinement Effect on Excitons in PbI_4 -Based Layered Semiconductors. *Phys. Rev. B* **1992**, *45*, 6961–6964.
- (19) Ishihara, T.; Takahashi, J.; Goto, T. Optical Properties Due to Electronic Transitions in Two-Dimensional Semiconductors $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$. *Phys. Rev. B* **1990**, *42*, 11099–11107.
- (20) Takeoka, Y.; Asai, K.; Rikukawa, M.; Sanui, K. Systematic Studies on Chain Lengths, Halide Species, and Well Thicknesses for Lead Halide Layered Perovskite Thin Films. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1607–1613.
- (21) Chen, Y.; Sun, Y.; Peng, J.; Tang, J.; Zheng, K.; Liang, Z. 2D Ruddlesden–Popper Perovskites for Optoelectronics. *Adv. Mater.* **2018**, *30*, 1703487.

- (22) Liang, D.; Peng, Y.; Fu, Y.; Shearer, M. J.; Zhang, J.; Zhai, J.; Zhang, Y.; Hamers, R. J.; Andrew, T. L.; Jin, S. Color-Pure Violet-Light-Emitting Diodes Based on Layered Lead Halide Perovskite Nanoplates. *ACS Nano* **2016**, *10*, 6897–6904.
- (23) Knutson, J. L.; Martin, J. D.; Mitzi, D. B. Tuning the Band Gap in Hybrid Tin Iodide Perovskite Semiconductors Using Structural Templating. *Inorg. Chem.* **2005**, *44*, 4699–4705.
- (24) Xu, Z.; Mitzi, D. B.; Medeiros, D. R. $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{NH}_3]\text{SnI}_4$: A Layered Perovskite with Quaternary/Primary Ammonium Dications and Short Interlayer Iodine–Iodine Contacts. *Inorg. Chem.* **2003**, *42*, 1400–1402.
- (25) Xu, Z.; Mitzi, D. B.; Dimitrakopoulos, C. D.; Maxcy, K. R. Semiconducting Perovskites $(2\text{-XC}_6\text{H}_4\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ (X = F, Cl, Br): Steric Interaction between the Organic and Inorganic Layers. *Inorg. Chem.* **2003**, *42*, 2031–2039.
- (26) Sourisseau, S.; Louvain, N.; Bi, W.; Mercier, N.; Rondeau, D.; Boucher, F.; Buzaré, J.-Y.; Legein, C. Reduced Band Gap Hybrid Perovskites Resulting from Combined Hydrogen and Halogen Bonding at the Organic–Inorganic Interface. *Chem. Mater.* **2007**, *19*, 600–607.
- (27) Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. Self-Assembly of Broadband White-Light Emitters. *J. Am. Chem. Soc.* **2014**, *136*, 1718–1721.
- (28) Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. Intrinsic White-Light Emission from Layered Hybrid Perovskites. *J. Am. Chem. Soc.* **2014**, *136*, 13154–13157.
- (29) Dou, L.; Wong, A. B.; Yu, Y.; Lai, M.; Kornienko, N.; Eaton, S. W.; Fu, A.; Bischak, C. G.; Ma, J.; Ding, T.; et al. Atomically Thin Two-Dimensional Organic-Inorganic Hybrid Perovskites. *Science* **2015**, *349*, 1518–1521.

- (30) Niu, W.; Eiden, A.; Vijaya Prakash, G.; Baumberg, J. J. Exfoliation of Self-Assembled 2D Organic-Inorganic Perovskite Semiconductors. *Appl. Phys. Lett.* **2014**, *104*, 171111.
- (31) Ha, S. T.; Liu, X.; Zhang, Q.; Giovanni, D.; Sum, T. C.; Xiong, Q. Synthesis of Organic-Inorganic Lead Halide Perovskite Nanoplatelets: Towards High-Performance Perovskite Solar Cells and Optoelectronic Devices. *Adv. Opt. Mater.* **2014**, *2*, 838–844.
- (32) Liao, Q.; Hu, K.; Zhang, H.; Wang, X.; Yao, J.; Fu, H. Perovskite Microdisk Microlasers Self-Assembled from Solution. *Adv. Mater.* **2015**, *27*, 3405–3410.
- (33) Zhang, Q.; Ha, S. T.; Liu, X.; Sum, T. C.; Xiong, Q. Room-Temperature Near-Infrared High-Q Perovskite Whispering-Gallery Planar Nanolasers. *Nano Lett.* **2014**, *14*, 5995–6001.
- (34) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. Preparation and Characterization of Layered Lead Halide Compounds. *J. Am. Chem. Soc.* **1991**, *113*, 2328–2330.
- (35) Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. Conducting Tin Halides with a Layered Organic-Based Perovskite Structure. *Nature* **1994**, *369*, 467–469.
- (36) Matsui, T.; Yamaguchi, A.; Takeoka, Y.; Rikukawa, M.; Sanui, K. Fabrication of Two-Dimensional Layered Perovskite $[\text{NH}_3(\text{CH}_2)_{12}\text{NH}_3]\text{PbX}_4$ Thin Films Using a Self-Assembly Method. *Chem. Commun.* **2002**, *0*, 1094–1095.
- (37) Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, *137*, 7843–7850.

- (38) Cao, D. H.; Stoumpos, C. C.; Yokoyama, T.; Logsdon, J. L.; Song, T.-B.; Farha, O. K.; Wasielewski, M. R.; Hupp, J. T.; Kanatzidis, M. G. Thin Films and Solar Cells Based on Semiconducting Two-Dimensional Ruddlesden–Popper $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ Perovskites. *ACS Energy Lett.* **2017**, *2*, 982–990.
- (39) Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; et al. Perovskite Energy Funnel for Efficient Light-Emitting Diodes. *Nat. Nanotechnol.* **2016**, *11*, 872–877.
- (40) Liu, J.; Leng, J.; Wu, K.; Zhang, J.; Jin, S. Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimensional Perovskite Films. *J. Am. Chem. Soc.* **2017**, *139*, 1432–1435.
- (41) Era, M.; Morimoto, S.; Tsutsui, T.; Saito, S. Organic-inorganic Heterostructure Electroluminescent Device Using a Layered Perovskite Semiconductor $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$. *Appl. Phys. Lett.* **1994**, *65*, 676–678.
- (42) Li, R.; Yi, C.; Ge, R.; Zou, W.; Cheng, L.; Wang, N.; Wang, J.; Huang, W. Room-Temperature Electroluminescence from Two-Dimensional Lead Halide Perovskites. *Appl. Phys. Lett.* **2016**, *109*, 151101.
- (43) Wang, N.; Cheng, L.; Ge, R.; Zhang, S.; Miao, Y.; Zou, W.; Yi, C.; Sun, Y.; Cao, Y.; Yang, R.; et al. Perovskite Light-Emitting Diodes Based on Solution-Processed Self-Organized Multiple Quantum Wells. *Nat. Photonics* **2016**, *10*, 699–704.

- (44) Hu, H.; Salim, T.; Chen, B.; Lam, Y. M. Molecularly Engineered Organic-Inorganic Hybrid Perovskite with Multiple Quantum Well Structure for Multicolored Light-Emitting Diodes. *Sci. Rep.* **2016**, *6*, 33546.
- (45) Zhang, S.; Yi, C.; Wang, N.; Sun, Y.; Zou, W.; Wei, Y.; Cao, Y.; Miao, Y.; Li, R.; Yin, Y.; et al. Efficient Red Perovskite Light-Emitting Diodes Based on Solution-Processed Multiple Quantum Wells. *Adv. Mater.* **2017**, *29*, 1606600.
- (46) Byun, J.; Cho, H.; Wolf, C.; Jang, M.; Sadhanala, A.; Friend, R. H.; Yang, H.; Lee, T.-W. Efficient Visible Quasi-2D Perovskite Light-Emitting Diodes. *Adv. Mater.* **2016**, *28*, 7515–7520.
- (47) Zou, W.; Li, R.; Zhang, S.; Liu, Y.; Wang, N.; Cao, Y.; Miao, Y.; Xu, M.; Guo, Q.; Di, D.; et al. Minimising Efficiency Roll-off in High-Brightness Perovskite Light-Emitting Diodes. *Nat. Commun.* **2018**, *9*, 608.
- (48) Quan, L. N.; Zhao, Y.; García de Arquer, F. P.; Sabatini, R.; Walters, G.; Voznyy, O.; Comin, R.; Li, Y.; Fan, J. Z.; Tan, H.; et al. Tailoring the Energy Landscape in Quasi-2D Halide Perovskites Enables Efficient Green-Light Emission. *Nano Lett.* **2017**, *17*, 3701–3709.
- (49) Chang, J.; Zhang, S.; Wang, N.; Sun, Y.; Wei, Y.; Li, R.; Yi, C.; Wang, J.; Huang, W. Enhanced Performance of Red Perovskite Light-Emitting Diodes through the Dimensional Tailoring of Perovskite Multiple Quantum Wells. *J. Phys. Chem. Lett.* **2018**, *9*, 881–886.
- (50) Tsai H.; Nie W.; Blancon J. - C.; Stoumpos C. C.; Soe C. M.; Yoo J.; Crochet J.; Tretiak S.; Even J.; Sadhanala A.; et al. Stable Light-Emitting Diodes Using Phase-Pure Ruddlesden–Popper Layered Perovskites. *Adv. Mater.* **2018**, *30*, 1704217.

- (51) Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem.* **2014**, *126*, 11414–11417.
- (52) Safdari, M.; H. Svensson, P.; Tam Hoang, M.; Oh, I.; Kloo, L.; M. Gardner, J. Layered 2D Alkyldiammonium Lead Iodide Perovskites: Synthesis, Characterization, and Use in Solar Cells. *J. Mater. Chem. A* **2016**, *4*, 15638–15646.
- (53) Quan, L. N.; Yuan, M.; Comin, R.; Voznyy, O.; Beauregard, E. M.; Hoogland, S.; Buin, A.; Kirmani, A. R.; Zhao, K.; Amassian, A.; et al. Ligand-Stabilized Reduced-Dimensionality Perovskites. *J. Am. Chem. Soc.* **2016**, *138*, 2649–2655.
- (54) Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; et al. High-Efficiency Two-Dimensional Ruddlesden–Popper Perovskite Solar Cells. *Nature* **2016**, *536*, 312–316.
- (55) Soe, C. M. M.; Nie, W.; Stoumpos, C. C.; Tsai, H.; Blancon, J.-C.; Liu, F.; Even, J.; Marks, T. J.; Mohite, A. D.; Kanatzidis, M. G. Understanding Film Formation Morphology and Orientation in High Member 2D Ruddlesden–Popper Perovskites for High-Efficiency Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1700979.
- (56) Chen, Y.; Sun, Y.; Peng, J.; Zhang, W.; Su, X.; Zheng, K.; Pullerits, T.; Liang, Z. Tailoring Organic Cation of 2D Air-Stable Organometal Halide Perovskites for Highly Efficient Planar Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1700162.

- (57) Qing, J.; Liu, X.-K.; Li, M.; Liu, F.; Yuan, Z.; Tiukalova, E.; Yan, Z.; Duchamp, M.; Chen, S.; Wang, Y.; et al. Aligned and Graded Type-II Ruddlesden-Popper Perovskite Films for Efficient Solar Cells. *Adv. Energy Mater.* **2018**, DOI: 10.1002/aenm.201800185.
- (58) Xiao, Z.; Kerner, R. A.; Zhao, L.; Tran, N. L.; Lee, K. M.; Koh, T.-W.; Scholes, G. D.; Rand, B. P. Efficient Perovskite Light-Emitting Diodes Featuring Nanometre-Sized Crystallites. *Nat. Photonics* **2017**, *11*, 108–115.
- (59) Wang, Q.; Ren, J.; Peng, X.-F.; Ji, X.-X.; Yang, X.-H. Efficient Sky-Blue Perovskite Light-Emitting Devices Based on Ethylammonium Bromide Induced Layered Perovskites. *ACS Appl. Mater. Interfaces* **2017**, *9*, 29901–29906.
- (60) Li, G.; Rivarola, F. W. R.; Davis, N. J. L. K.; Bai, S.; Jellicoe, T. C.; de la Peña, F.; Hou, S.; Ducati, C.; Gao, F.; Friend, R. H.; et al. Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method. *Adv. Mater.* **2016**, *28*, 3528–3534.
- (61) Chen, Z.; Zhang, C.; Jiang, X.-F.; Liu, M.; Xia, R.; Shi, T.; Chen, D.; Xue, Q.; Zhao, Y.-J.; Su, S.; et al. High-Performance Color-Tunable Perovskite Light Emitting Devices through Structural Modulation from Bulk to Layered Film. *Adv. Mater.* **2017**, *29*, 1603157.
- (62) Slotcavage, D. J.; Karunadasa, H. I.; McGehee, M. D. Light-Induced Phase Segregation in Halide-Perovskite Absorbers. *ACS Energy Lett.* **2016**, *1*, 1199–1205.
- (63) Kumar, S.; Jagielski, J.; Yakunin, S.; Rice, P.; Chiu, Y.-C.; Wang, M.; Nedelcu, G.; Kim, Y.; Lin, S.; Santos, E. J. G.; et al. Efficient Blue Electroluminescence Using Quantum-Confined Two-Dimensional Perovskites. *ACS Nano* **2016**, *10*, 9720–9729.

- (64) Si, J.; Liu, Y.; He, Z.; Du, H.; Du, K.; Chen, D.; Li, J.; Xu, M.; Tian, H.; He, H.; et al. Efficient and High-Color-Purity Light-Emitting Diodes Based on In Situ Grown Films of CsPbX₃ (X = Br, I) Nanoplates with Controlled Thicknesses. *ACS Nano* **2017**, *11*, 11100–11107.
- (65) Liu, X.-K.; Chen, Z.; Qing, J.; Zhang, W.-J.; Wu, B.; Tam, H. L.; Zhu, F.; Zhang, X.-H.; Lee, C.-S. Remanagement of Singlet and Triplet Excitons in Single-Emissive-Layer Hybrid White Organic Light-Emitting Devices Using Thermally Activated Delayed Fluorescent Blue Exciplex. *Adv. Mater.* **2015**, *27*, 7079–7085.
- (66) Adamovich, V. I.; Cordero, S. R.; Djurovich, P. I.; Tamayo, A.; Thompson, M. E.; D'Andrade, B. W.; Forrest, S. R. New Charge-Carrier Blocking Materials for High Efficiency OLEDs. *Org. Electron.* **2003**, *4*, 77–87.
- (67) Xing, G.; Wu, B.; Wu, X.; Li, M.; Du, B.; Wei, Q.; Guo, J.; Yeow, E. K. L.; Sum, T. C.; Huang, W. Transcending the Slow Bimolecular Recombination in Lead-Halide Perovskites for Electroluminescence. *Nat. Commun.* **2017**, *8*, 14558.
- (68) Younts, R.; Duan, H.-S.; Gautam, B.; Saparov, B.; Liu, J.; Mongin, C.; Castellano, F. N.; Mitzi, D. B.; Gundogdu, K. Efficient Generation of Long-Lived Triplet Excitons in 2D Hybrid Perovskite. *Adv. Mater.* **2017**, *29*, 1604278.
- (69) Braun, M.; Tuffentsammer, W.; Wachtel, H.; Wolf, H. C. Tailoring of Energy Levels in Lead Chloride Based Layered Perovskites and Energy Transfer between the Organic and Inorganic Planes. *Chem. Phys. Lett.* **1999**, *303*, 157–164.

(70) Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. Angular Dependence of the Emission from a Conjugated Polymer Light-Emitting Diode: Implications for Efficiency Calculations. *Adv. Mater.* **1994**, *6*, 491–494.

(71) Shi, X.-B.; Liu, Y.; Yuan, Z.; Liu, X.-K.; Miao, Y.; Wang, J.; Lenk, S.; Reineke, S.; Gao, F. Optical Energy Losses in Organic-Inorganic Hybrid Perovskite Light-Emitting Diodes. *Adv. Opt. Mater.* **2018**, DOI:10.1002/adom.201800667.

(72) Kim, S.-Y.; Jeong, W.-I.; Mayr, C.; Park, Y.-S.; Kim, K.-H.; Lee, J.-H.; Moon, C.-K.; Brütting, W.; Kim, J.-J. Organic Light-Emitting Diodes with 30% External Quantum Efficiency Based on a Horizontally Oriented Emitter. *Adv. Funct. Mater.* **2013**, *23*, 3896–3900.

(73) Vispute, R. D.; Talyansky, V.; Choopun, S.; Sharma, R. P.; Venkatesan, T.; He, M.; Tang, X.; Halpern, J. B.; Spencer, M. G.; Li, Y. X.; et al. Heteroepitaxy of ZnO on GaN and Its Implications for Fabrication of Hybrid Optoelectronic Devices. *Appl. Phys. Lett.* **1998**, *73*, 348–350.