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Designing efficient energy funneling kinetics in Ruddlesden-Popper perovskites for high performance light emitting diodes

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Mixed Ruddlesden Popper (RP) perovskites are of great interest in light emitting diodes (LED), due to the efficient energy transfer (funneling) from high bandgap (donor) domains to low bandgap (acceptor) domains which lead to enhanced photoluminescence (PL) intensity, long PL lifetime, and high efficiency LED. However, the influence of reduced effective emitter centers in the active emissive film as well as the implications of electrical injection into the larger bandgap donor material have not been addressed in the context of an active device. We critically assess and modulate the electrical and optical signatures of the energy cascading mechanisms in a model Ruddlesden Popper perovskite series $((\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1})$. Optimised devices demonstrated a current efficiency of 22.9 cd A^{-1} and 5% external quantum efficiency, more than 5 times higher than systems where funneling was absent. The signature of non-ideal funneling in RP perovskites is

revealed by the appearance of donor electroluminescence from the device, followed by a reduction in the LED performance

1. Introduction

Three dimensional (3D) metal halide perovskites (ABX_3 , where A and B are monovalent and divalent cation respectively while X is the halide anion) with infinite layers of $[BX_6]$ octahedral network have demonstrated favorable traits for optoelectronic applications, such as long carrier diffusion lengths^[1-3], small exciton binding energies^[4,5], low trap densities^[6], low recombination rates^[7], as well as light emission (bandgap) tunability^[8], and high color purity^[9]. Organic or inorganic monovalent cations such as methylammonium, formamidinium, and cesium are typically employed for forming the 3D perovskites. The pedigree of perovskite semiconductors are exemplified in the rapid rise in LED efficiencies from $<1\%$ ^[10] to 11.7% ^[11] within 3 years of first reports of light emission. Though slow bimolecular radiative recombination rates found in 3D perovskite are beneficial for photovoltaic application, they fundamentally limit the LED efficiency improvement in which the emitting states need to compete with non-radiative recombination states. As a consequence, high photoluminescence quantum yield (PLQY) and electroluminescence efficiency could only be achieved if the injected carrier densities are higher than the perovskite trap densities. Since the injected current densities during typical LED operation is comparable to 3D perovskite trap densities, strategies to ensure the dominance of bimolecular radiative emission has to be pursued^[12].

Quasi two dimensional (2D) layered Ruddlesden-Popper (RP, $L_2A_{m-1}B_mX_{3m+1}$) perovskites have been examined for solar cells to enhance the perovskite moisture resistance through the use of hydrophobic organic molecules^[13]. In this structure, the infinite 3D layers of the $[BX_6]$ octahedral network are partially separated with high dielectric constant large aliphatic or aromatic alkylammonium layers (L) which act as spacers. For lead halide

perovskites ($B = \text{Pb}$ and $X = \text{Cl, Br, I}$), the conduction and valence band edges of the perovskite relies solely on the orbital contributions from the inorganic octahedron $[\text{PbX}_6]^{[14]}$, and incorporating 2D cations into the 3D matrix result in a natural multi-quantum well system. With multiple bandgap regions present in RP perovskite films, injected carriers are likely to flow from high band gap “donor” regions to the lower bandgap “acceptor” regions. This results in increased carrier concentrations in the acceptor resulting in enhanced bimolecular radiative rates even at low carrier densities^[12]. Strong carrier concentration have been observed in multi-dimensional / RP perovskite^[15] with alkyl ammonium^[16], phenylethylammonium^[17–20], 1-naphthylmethylammonium^[11,21,22], and phenylbutylammonium^[23] as the 2D spacer which enhances the luminescence properties of the perovskite films. Despite evidence of energy cascading mechanism through optical characterization, no direct measurements utilising electroluminescence (the key process in LEDs) where the contribution of different components are observable, have been reported. Although energy funneling/cascading increases the radiative recombination through carriers localization, efficiency enhancement in the devices could not be directly attributed to the energy cascading phenomena as other parameters such as light out coupling are also perturbed. The implications of electrical injection from the electron and hole transport layers into the larger bandgap donor material and the optimization of the effective emitter centers have also not been addressed in the context of an active device.

In this work, the importance of cascading was demonstrated through both optical and electrical characterization by utilizing a $(\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1}$ RP system. This electrically/optical emissive RP system allows for feedback from both photoluminescence and electroluminescence point of view, enabling an unequivocal comparison. Electrical carrier injection to the donor region was confirmed via the electroluminescence signature that is detected even at turn on voltage of the acceptor poor devices; and energy cascade is verified through charge dynamics as well as device

characterization. An optimized system with complete funneling yielded a high efficiency LED in which current efficiency of 22.9 cd A⁻¹ and EQE of 5% were achieved.

2. Results and Discussion

2.1. Evidence of energy cascading mechanism

Figure 1. Funneling in RP thin film $(\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1}$ perovskite. Schematic crystal structure of 3D $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ (a) and 2D $(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbBr}_4$ (b). Photoluminescence spectra (c) of 3D, 2D, and quasi 2D RP (20% 2D) films. Transient absorption (TA) spectra of 3D (d), 2D (e), and quasi 2D RP (f) films at different delay times as well as the TA kinetics at $\lambda = 425$ nm, 435 nm, and 535 nm for 2D, RP, and 3D films respectively (g).

Mixture of 3D formamidinium lead bromide ($\text{CH}(\text{NH}_2)_2\text{PbBr}_3$, **Figure 1a**) and 2D octylammonium lead bromide ($((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbBr}_4$, **Figure 1b**) perovskite (~20% 2D) were utilized to form electrically emissive quasi 2D RP ($((\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1})$ perovskite (**Figure 1c**). X-ray diffraction (XRD) patterns (**Figure S1**) analysis indicates (00 l) planes interlayer spacing of ~2.1 nm for pure 2D perovskite ($m = 1$, 100%), in agreement with the relationship between alkyl chain length and interlayer spacing ($d(\text{\AA}) = 8.06 + 1.59 \times n$, $n = 8$ for $\text{C}_8\text{H}_{17}\text{NH}_2$) as reported by Takeoka et al^[24]. The XRD spectra of 3D perovskite ($m = \infty$) matched well with reported value^[25], while additional peaks at 10° and 13.3° with no 2D diffraction pattern signature were observed on quasi-2D RP film. Formation of multi-layered RP phases are deduced as the calculated interlayer spacing for the extra peaks does not add up with the spacing of quasi-2D perovskite assuming $m = \text{positive integer}$ ^[24]. Steady state photoluminescence (PL) peak at 540 nm and 400 nm were observed for the pure phases of 3D and 2D perovskite respectively (**Figure 1c**). On the other hand, multiple PL peaks which do not belong to both 3D and 2D perovskite (**Figure 1c**) were present on RP films supporting the formation of multi-layered RP phases in the samples.

The existence of multi-layered RP perovskite phases in the films could potentially drive energy transfer from lower bandgap “donor” domains to higher bandgap “acceptor” domains. Ultrafast transient absorption spectroscopy (TA) (**Figure 1d-g**) reveals the signature of energy cascade from donor to acceptor material within sub-picosecond (ps) timescales. Photo-bleaching signature around 425 nm and 535 nm was observed for 2D and 3D films respectively, indicating carrier filling upon excitation above the bandgap (**Figure 1d** and **1e**). In addition to 535 nm photo-bleaching peak, traces of carrier filling at 435 nm was also observed for quasi-2D RP samples which corresponded to the multi-layered perovskite phase signature (**Figure 1f**). On the other hand, positive signals (photo-induced absorption) were

observed instead for 3D perovskite at 435 nm. The dynamics of photo-bleaching at 435 nm and 535 nm peaks are shown in **Figure 1g** and **Table S1**, for both 3D and quasi-2D RP samples respectively. The rise time of 535 nm bleaching signal is about 0.1 ps for 3D film, while a significant slower kinetic was measured at 535 nm (0.39 ps) for RP films. In addition, TA kinetics at 435 nm shows a fast rising time (0.01 ps), indicating instantaneous buildup of excited state followed by fast decay (2.88 ps) for RP samples. These observations clearly demonstrate funneling and prove the accumulation of excited state in 3D phase (photo-bleaching at 535 nm) that is strongly dominated by the energy transfer from donor (multi-layered RP) to acceptor (3D perovskite) domains in RP films.

2.2. Modulating the efficiency of energy cascading through composition

Figure 2. Time resolved photoluminescence (TRPL) and PL excitation spectra at various 2D concentrations. Steady state absorption and steady state PL spectra (a) of films followed by the PL excitation spectra at 540 nm and 500 nm emission (b), schematic diagram of the proposed energy transfer phenomena in the films (c), TRPL spectra at 440 nm (d), 490 nm (e), and 540 nm (f) emission wavelengths for films at various 2D content.

The efficiency of energy cascading mechanism strongly depends on the overlap between donor photoluminescence and acceptor absorption spectra, the distance between acceptor and donor and the acceptor to donor ratio^[26]. Here, the influence of acceptor and donor concentration on the transfer kinetics was scrutinized by varying the concentration of 2D perovskite (i.e. 0% to 50%) during RP film formation. Multi-layered perovskite RP film formation were observed from the XRD spectra (**Figure S1**) of all films with traces of 2D perovskite. The intensity of 3D perovskite (0%) diffraction pattern signature, which corresponds to the crystallinity of the film, reduced with increasing 2D concentration, with no diffraction peak signature was observed for 50% 2D samples (i.e. $m = 2$). Pinhole free films were attained for all samples, as observed in the topographical field emission scanning electron microscope (FE-SEM) images (**Figure S2**). The roughness of the films was assessed with atomic force microscope (AFM, **Figure S2**), in which additional 10% of 2D resulted in a decrease of the roughness to 5 nm. However, increasing the 2D content above 10% enhances the roughness of the films. Comparable thickness (~300 nm) was observed from the cross sectional images of both 3D and RP films while grain size reduction were visible with all quasi-2D films. This was caused by the strong electrostatic binding of octylammonium ions on the face of perovskite crystals which subsequently confined grain growth and resulted in grain size reduction^[27,28]. Due to huge grain size variation (20 – 120 nm) in the film, grain size reduction could not be confirmed in spite of 2D ratio variation.

An optical absorption signature synonymous with a bandgap of 2.36 eV was observed for all films from the steady state absorption spectra (**Figure 2a**) fitted using Elliot formula (**Figure S3**) attributable to 3D $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ ^[29]. The excitonic peak of the 3D perovskite

diminished upon addition of 2D perovskite, possibly due to perovskite grain size reduction (**Figure 2**)^[30]. While excitonic signature at ~395 nm was detected for 100% 2D perovskite, additional excitonic peak at 431 nm was detected in quasi-2D films, confirming the formation of multi-layered RP perovskite phase, in agreement with the XRD analysis. The 3D absorption signature (i.e. at 529 nm) reduces and the multi-layered RP perovskite absorption signature at 431 nm increases with increasing 2D ratio, pointing to a possible bottleneck of reduced low bandgap emission centers.

Steady state PL intensity was corrected for the number of absorbed photon at the excitation wavelength according to Beer Lambert law and is utilized as a quantitative criterion for comparison. A small Stoke shift between PL and absorption edge were observed, signifying band edge emission of the materials. A single PL peak at 540 nm was detected for 3D and RP films with lower 2D content ($\leq 10\%$). Higher PL intensities were obtained with quasi-2D films as compared to the 3D counterpart with the maximum PL attained with 10% 2D addition. Increasing the 2D ratio above 10% resulted in the appearance of additional broad peaks (resolvable into multiple PL peaks) at smaller wavelength (**Figure S4**), indicative of the multi-layered RP perovskite structure. Increasing the ratio of 2D above 20% enhances the PL peak intensity at lower wavelength ($\lambda < 540\text{nm}$) and decreases the PL peak at 540 nm. Indication of energy transfer in multi-layered RP perovskite is provided by the significant enhancement of 540 nm PL signal for 2D addition up to 20%.

PL excitation spectra (**Figure 2b**) and time resolved PL (TRPL) experiments reveal clearly the energy cascading mechanism in all RP films. After excitation at 405 nm, systematic emission wavelength dependent study ($\lambda = 440, 490, \text{ and } 540 \text{ nm}$) of TRPL reveals energy transfer in the RP film (**Figure 2d-f**) where slower PL decay kinetics are observed with increasing emission wavelength (**Table S2**). Moreover at 540 nm, longer PL lifetimes were observed when RP films were utilized instead of pure 3D perovskite which suggests that energy is cascading to 3D domain which increases the carrier density and subsequently fills in

the available trap states. From the PL intensity vs excitation spectra (**Figure 2b** and **S5**), no signature of energy transfer was visible in 3D perovskite as the PL emission at 500 nm and 540 nm is independent of excitation wavelengths. On the other hand, multiple peaks were detected on the PL excitation spectra of RP films demonstrating that higher PL emission were obtained at certain excitation wavelengths. Excitation spectra peaks at 433 nm and 468 nm were detected when emission was fixed at 500 nm and 540 nm for 10% 2D film, which confirmed the presence of energy transfer from donor to acceptor^[11]. At higher concentration of 2D perovskite ($\geq 20\%$), depression troughs at 400 nm, 433 nm, and 468 nm excitation wavelengths and a bump at 505 nm excitation wavelength were observed when the emission wavelength was fixed at 540 nm. The depression troughs at 433 nm and 468 nm became excitation peaks when the emission wavelength was converted to 500 nm. This behavior indicates incomplete energy transfer from 505 nm emitter center (i.e. RP perovskite / donor) to 540 nm emitter center (i.e. 3D perovskite / acceptor) which subsequently resulted in additional steady state PL peaks (**Figure 2a**). Although XRD, optical absorption, and steady state PL spectra indicated no traces of the pure 2D phase, it was detected in the excitation spectra of RP films, indicating that a small amount of $(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbBr}_4$ exists in the film.

Although a graded donor distribution has been proposed to be favourable for efficient energy transfer^[17], our results contrarily indicate that the system is still hampered by incomplete energy transfer despite the graded domain noted here as well. Energy transfer from 433 nm and 468 nm to 505 nm acceptor material occurs while incomplete energy transfer to 540 nm was observed. Energy transfer can occur as radiative transfer, Förster resonance energy transfer (FRET), or Dexter transfer. In all cases, the efficiency of energy transfer is related to the donor PL and acceptor absorption spectra overlap, the distance between acceptor and donor, and the acceptor concentration, where higher acceptor concentration would increase the energy transfer efficiency^[31–33]. From the absorption spectra, it is evident that the acceptor concentration decreases with increasing quasi-2D percentage in

the film. The average distance between acceptor and donor could also be modulated with varying 2D perovskite concentration. Hence, we postulate that incomplete energy transfer could result from the reduced energy transfer rate (k_{540}) due to low acceptor concentration. The reduction of energy transfer rate could also result in increased recombination (k_{505}) in the donor. The schematic diagram of the proposed mechanism is presented in **Figure 2c**.

2.3. Significance of efficient cascading for high efficiency light emitting device

Figure 3. Device performances and electroluminescence (EL) spectra of RP perovskite. Band diagram of the LED devices (a) followed by the corresponding J-V-L curve (b), EQE and current efficiency curve (c), as well as the electroluminescence spectra (d) of all devices at various bias applications.

To validate the importance of efficient electrical energy cascade behavior, light emitting device stacks were fabricated with Lithium Fluoride (LiF) and ((1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (POT2T) as hole transporting layer (HTL) and electron transporting layer (ETL) respectively. The band energy alignment employed in the devices was presented in **Figure 3a**. The current density – voltage – luminance (J-V-L) characteristics as well as the external quantum efficiency (EQE), current efficiency, and electroluminescence spectra were presented in **Figure 3**. From J-V curves, reduction of the carrier injection to emitter are visible with increasing multi-layered RP concentration as the current turn on voltages (V_{on} , voltage at which $J \sim V^m$) shifted towards higher bias for comparable leakage currents (current at which $J \sim V$) (**Figure 3b**). Efficient carrier injection was observed in the device with higher acceptor content ($\leq 20\%$ 2D) as sub-bandgap light turn on voltage (V_{th} , voltage at 1 cd m^{-2}) $\sim 2.2 \text{ V}$ was observed. Higher V_{th} indicate that carrier injection rate to the emitter is slightly reduced especially when higher donor content ($> 20\%$ 2D) were employed.

The maximum current efficiency, and external quantum efficiency (EQE) of the pure 3D devices were 4.17 cd A^{-1} , and 0.89% respectively. Employing RP films enhance the current efficiency, and EQE by at least 1 order of magnitude depending on the 2D ratio used (**Figure 3c**). A maximum current efficiency of 22.9 cd A^{-1} and EQE of 5% were achieved with 10% 2D films (**Figure 3c**). Enhancing the 2D ratio above 10% resulted in an efficiency drop to approximately half of the EQE obtained with 10% 2D. Higher 2D ratios resulted in greater efficiency at low J regime, consistent with energy cascading resulting in high PLQY at lower power density due to strong carrier concentration at the effective emitter acceptor material^[12,17]. Similar observations were also observed when different ETL (i.e. 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) – TPBi) and HTL (i.e. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate – Pedot:PSS) with lower injection efficiency (i.e. higher V_{th}) to the emitter were used (**Figure S6**).

The electroluminescence spectra of the devices were taken at various bias applications (**Figure 3d**). Electroluminescence peak at 540 nm was observed for pure 3D devices, in agreement with the PL peak of the film. When high acceptor concentration was employed (10% 2D), a single electroluminescence peak was observed at 540 nm regardless of the bias application. With 20% 2D addition, a concurrent presence of the extra donor electroluminescence peak at 505 nm and an efficiency drop were observed for bias application larger than 2.7 V. The consistency between the appearance of the extra donor electroluminescence peak and efficiency drop in the same device rules out light out coupling as a source of variation. This indicates that incomplete energy transfer resulted in low device efficiency, as expected from the optical measurements. Similar to quantum dot based LED, wider carrier generation region at higher currents simultaneously extending distance between donor and acceptor, which could lead to decrease of energy cascade rate and increase probability of donor radiative recombination^[34]. Increasing the current further resulted in significant increase of carrier concentration at the acceptor, which could lead to Auger recombination facilitated quenching of the acceptor emission^[34].

The presence of extra donor electroluminescence peak at 505 nm for RP device with lower acceptor concentration (> 20% 2D) even at V_{th} ($\sim 2.5V$) signifies the capability of the employed ETL and HTL to electrically inject carriers to donor material. As the acceptor concentration is decreased with increasing 2D ratio (> 20%), the energy cascade rate is reduced resulting in high probability of donor radiative emission as evidenced by the appearance of the donor's 505 nm electroluminescence peak. Therefore, it is evident that complete energy cascading behavior is a key factor to gain high efficiency light emitting devices. To the best of our knowledge, we report the first direct evidence of energy cascading in electrical characterization of RP perovskite based LED. The carrier injection to wide bandgap donor material is illustrated together with the importance of well-engineered donor and acceptor regions ratio to device efficiency. While other factors such as surface roughness

and crystallite size of the films would modulate the efficiency of LED devices to a certain extent, we have isolated them to identify the impact of energy transfer within the phases in the film on the LED performances here (**Figure S7**).

3. Conclusion

By using electrically emissive $(\text{C}_8\text{H}_{17}\text{NH}_3)_2(\text{CH}(\text{NH}_2)_2)_{m-1}\text{Pb}_m\text{Br}_{3m+1}$ RP materials, the importance of energy funneling for LED application were presented through optical and electrical characterization. The appearance of extra electroluminescence signature from donor domains even at lower voltage indicates the possibility of carrier injection to the donor domains. It is apparent that energy cascading mechanism could increase the local carrier density which resulted in higher LED efficiency at low carrier injection regime. When the acceptor to donor concentration ratio is low, the rate of the energy transfer becomes slower which resulted in inefficient energy transfer. Subsequently, we successfully identified both photoluminescence and electroluminescence signature of high bandgap RP material and a concurrent drop in both the acceptor PL intensity and LED efficiency. Therefore, a well-engineered acceptor to donor ratio, which could be varied by changing the precursors, is essential to create pathways for high efficiency LED. System with efficient cascading behavior resulted in high efficiency LED at which 5% EQE and 22.9 cd A⁻¹ current efficiency were realized.

4. Experimental Section

Perovskite film formation. Mixture of equimolar (1M) $\text{CH}(\text{NH}_2)_2\text{Br}$ and PbBr_2 in DMF:DMSO (75:25) solvent were used to produce pure 3D perovskite. Pure 2D perovskite solution were synthesized with $\text{C}_8\text{H}_{17}\text{NH}_3\text{Br}$ (2M) and PbBr_2 (1M) in DMF:DMSO (75:25 by volume) solvent. Quasi-2D solutions were produced by mixing both pure 3D and pure 2D perovskite solution in different ratio (i.e. from 0% 2D to 50% 2D). Films were then fabricated

by spin coating from various perovskite solutions where anti-solvent (i.e. toluene) was used to enhance the coverage of the resulting film. The films were then dried in room temperature. Both spin coating and solution mixing were done under argon environment.

Device fabrication. Indium tin oxide (ITO) coated glass was used as the substrates. Depending on the choice of electron and hole transporting layer, two types of devices were used. In Device A, poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (Pedot:PSS, Al 4083) was spun coated on top of ITO at 4000 rpm for 1 min followed by heating at 150°C for 10 mins. Substrates were then transported inside glovebox for perovskite deposition. Approximately 40 nm of 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi) were thermally evaporated. For Device B, 0.5 nm of lithium fluoride (LiF) were thermally evaporated to replace Pedot:PSS, while 40 nm of ((1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (POT2T) were thermally evaporated instead of TPBi. Devices were then completed by thermal evaporation of the electrode (i.e. 10 nm of calcium and 100 nm of aluminum). Device area was fixed at 8mm² by using shadow mask during electrode evaporation.

Physical characterization. The crystallographic information of the films was assessed using Bruker D8 advance diffractometer with 0D LynxEYETM detector. The scans were conducted on perovskite film deposited on top of Pedot:PSS coated glass substrates. Field effect scanning electron microscope (FE-SEM, JEOL J7600F) were employed to capture the topographical and cross sectional images. Atomic Force Microscope (AFM, Asylum Research MFP-3D) with contact modes were used with Ti/Ir coated cantilevers (ASYELEC-01-R2, Asylum Research) for surface roughness measurement. Shimadzu UV-3600 UV-Vis-NIR spectrophotometer was used to collect the absorption spectra while Horiba Fluoromax-4 was utilized to obtain the steady state PL spectra as well as the excitation spectra.

Time resolved PL dynamics were collected using micro-PL setup, employing a Nikon microscope, and using a Picoquant PicoHarp 300 time correlated single photon counting

(TCSPC) system. The excitation source is a picosecond pulsed laser diode (Picoquant P-C-405B, $\lambda = 405\text{nm}$, 40 MHz repetition rate). Output signal were processed through Acton SP-2300i monochromator for spectral selection of the emission light coupled to an avalanche diode synchronized with excitation laser via TCSPC electronic. Overall, the full width at half maximum of the system instrument respond function is around 50 ps.

A home built femtosecond pump-probe setup is used to conduct the transient absorption (TA) measurements. A commercial amplifier, Quantronix Integra-C is externally seeded by a mode-locked Ti:Sapphire oscillator (Ti-Light) that delivers $>200\text{ mW}$ average power up to 100 nm band width. The pulse energy of nJ is amplified to a level of few mJ. The amplifier operates at a repetition rate of 1 KHz with pulse duration of 100 fs. Briefly, the fundamental 800 nm output pulse was split in two beams with a beam splitter. One beam was used to pump the optical parametric amplifier (OPA) and second beam was used to generate pump and probe pulses by using a beam splitter. A pump wavelength of 400 nm was generated by frequency doubling using the type-I BBO crystal. A probe beam of broadband white light with a highest cutoff wavelength 350 nm (3.54 eV) was generated by using 3 mm thick calcium fluoride (CaF_2) crystal via white light continuum generation. In order to avoid the laser induced damage the crystal is continuously spun during the measurements. The delay between the pump and probe pulses was controlled by motorized delay stage. The pump pulses were chopped at 500 Hz by a synchronized chopper and the absorbance changes were calculated with two adjacent probe pulses i.e. pump-blocked and pump-unblocked. Commercial spectrometer, Jobin Yvon CP140 - 104, coupled with a silicon photodiode array was used to record TA spectra (Entwicklungsbüro Stresing). A shortwave pass filter was used to cut off the low energy end of the white light spectrum at 1.77 eV (700 nm) in order to remove higher diffraction orders artefacts in the measurements. To overcome the problem of white light instability artefacts in the measured TA spectra, selected spectra at different time

delays were obtained for 100 measurement cycles at an exposure time of 100 ms. Experiments were conducted at room temperature and samples were kept in nitrogen environment.

Device characterization. Keithley 2612B was employed to measure the current-voltage response of the devices. The forward emission light output was collected by placing the device outside and facing into the opening of an integrating sphere (OceanOptics FOIS-1) connected to a calibrated spectrometer (OceanOptics QEPro). Ocean optics HL-3 Plus vis-NIR light source, which was calibrated using a process and documentation based on ISO 17025, IEC Guide 115 and JCGM100:2008 (GUM) protocols, was used to calibrate the absolute irradiance.

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References

- [1] G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Science*. **2013**, *342*, 344.
- [2] E. Edri, S. Kirmayer, S. Mukhopadhyay, K. Gartsman, G. Hodes, D. Cahen, *Nat. Commun.* **2014**, *5*, 3461.
- [3] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science*. **2013**, *342*, 341.
- [4] T. Ishihara, *J. Lumin.* **1994**, *61*, 269.
- [5] S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum, Y. M. Lam, *Energy Environ. Sci.* **2014**, *7*, 399.
- [6] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* **2014**, *13*, 476.
- [7] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Mater.* **2014**, *26*, 1584.
- [8] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. Il Seok, *Nano Lett.* **2013**, *13*, 1764.
- [9] S. Adjokatse, H. H. Fang, M. A. Loi, *Mater. Today* **2017**, *20*, 413.
- [10] Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, *9*, 687.
- [11] N. Wang, L. Cheng, R. Ge, S. Zhang, Y. Miao, W. Zou, C. Yi, Y. Sun, Y. Cao, R. Yang, Y. Wei, Q. Guo, Y. Ke, M. Yu, Y. Jin, Y. Liu, Q. Ding, D. Di, L. Yang, G. Xing,

- H. Tian, C. Jin, F. Gao, R. H. Friend, J. Wang, W. Huang, *Nat. Photonics* **2016**, *10*, 699.
- [12] G. Xing, B. Wu, X. Wu, M. Li, B. Du, Q. Wei, J. Guo, E. K. L. Yeow, T. C. Sum, W. Huang, *Nat. Commun.* **2017**, *8*, 14558.
- [13] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, H. I. Karunadasa, *Angew. Chemie - Int. Ed.* **2014**, *53*, 11232.
- [14] J. Endres, D. A. Egger, M. Kulbak, R. A. Kerner, L. Zhao, S. H. Silver, G. Hodes, B. P. Rand, D. Cahen, L. Kronik, A. Kahn, *J. Phys. Chem. Lett.* **2016**, *7*, 2722.
- [15] T. M. Koh, K. Thirumal, H. Sen Soo, N. Mathews, *ChemSusChem* **2016**, *9*, 2541.
- [16] X. Y. Chin, A. Perumal, A. Bruno, N. Yantara, S. Veldhuis, L. Martinez-Sarti, B. Chandran, V. S. Chirvony, S.-Z. A. Lo, J. So, C. Soci, M. Grätzel, H. J. Bolink, N. Mathews, S. G. Mhaisalkar, *Energy Environ. Sci.* **2018**, DOI 10.1039/C8EE00293B.
- [17] L. N. Quan, Y. Zhao, F. P. García De Arquer, R. Sabatini, G. Walters, O. Voznyy, R. Comin, Y. Li, J. Z. Fan, H. Tan, J. Pan, M. Yuan, O. M. Bakr, Z. Lu, D. H. Kim, E. H. Sargent, *Nano Lett.* **2017**, *17*, 3701.
- [18] M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim, E. H. Sargent, *Nat. Nanotechnol.* **2016**, *11*, 872.
- [19] Y. F. Ng, S. A. Kulkarni, S. Parida, N. F. Jamaludin, N. Yantara, A. Bruno, C. Soci, S. G. Mhaisalkar, N. Mathews, *Chem. Commun.* **2017**, *53*, DOI 10.1039/C7CC06615E.
- [20] X. Yang, X. Zhang, J. Deng, Z. Chu, Q. Jiang, J. Meng, P. Wang, L. Zhang, Z. Yin, J. You, *Nat. Commun.* **2018**, *9*, 2.
- [21] S. Zhang, C. Yi, N. Wang, Y. Sun, W. Zou, Y. Wei, Y. Cao, Y. Miao, R. Li, Y. Yin, N. Zhao, J. Wang, W. Huang, *Adv. Mater.* **2017**, *29*, 1.
- [22] W. Zou, R. Li, S. Zhang, Y. Liu, N. Wang, Y. Cao, Y. Miao, M. Xu, Q. Guo, D. Di, L. Zhang, C. Yi, F. Gao, R. H. Friend, J. Wang, W. Huang, *Nat. Commun.* **2018**, *9*, 608.
- [23] J. Si, Y. Liu, Z. He, H. Du, K. Du, D. Chen, J. Li, M. Xu, H. Tian, H. He, D. Di, C. Lin, Y. Cheng, J. Wang, Y. Jin, *ACS Nano* **2017**, *11*, 11100.
- [24] Y. Takeoka, K. Asai, M. Rikukawa, K. Sanui, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1607.
- [25] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, H. J. Snaith, *Energy Environ. Sci.* **2014**, *7*, 982.
- [26] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, **2006**.
- [27] Y. Chen, Y. Sun, J. Peng, J. Tang, K. Zheng, Z. Liang, *Adv. Mater.* **2017**, 1703487.
- [28] S. A. Kulkarni, S. Muduli, G. Xing, N. Yantara, M. Li, S. Chen, T. C. Sum, N. Mathews, T. J. White, S. G. Mhaisalkar, *ChemSusChem* **2017**, *10*, 3818.
- [29] S. Chen, A. Nurmikko, *ACS Photonics* **2017**, *4*, 2486.
- [30] A. R. Srimath Kandada, A. Petrozza, *Acc. Chem. Res.* **2016**, *49*, 536.
- [31] C. B. Murphy, Y. Zhang, T. Troxler, V. Ferry, J. J. Martin, W. E. Jones, *J. Phys. Chem. B* **2004**, *108*, 1537.
- [32] A. Govorov, P. L. H. Martínez, H. V. Demir, in *Underst. Model. FRET Förster-Type Reson. Energy Transf. Introd. to Förster-Type Reson. Energy Transf.*, **2016**, pp. 14–15.
- [33] J. B. Hoffman, R. Alam, P. V. Kamat, *ACS Energy Lett.* **2017**, *2*, 391.
- [34] P. O. Anikeeva, C. F. Madigan, J. E. Halpert, M. G. Bawendi, V. Bulović, *Phys. Rev. B* **2008**, *78*, 85434.

Supporting Information

Designing efficient energy funneling kinetics in Ruddlesden-Popper perovskites for high performance light emitting diodes

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Figure S1. The X-Ray Diffraction spectra of all films at various 2D concentrations.

From the X-ray diffraction (XRD) patterns (**Figure S1**) analysis, (00 l) planes interlayer spacing of ~ 2.1 nm were found for pure 2D perovskite ($m = 1$, 100%), while the XRD spectra of pure 3D perovskite ($m = \infty$, 0%) matched well with reported value^[25], in which interlayer spacing of ~ 0.599 nm were found. Incorporation of 10% 2D into 3D perovskite resulted in additional peaks at 12.2° , which does not belong to both pure 3D and 2D perovskite. Increasing the 2D ratio to 20% - 40%, the 12.2° peak disappeared whereas other additional peaks at 10° and 13.3° were observed with no 100% 2D diffraction pattern was visible. The interlayer spacing calculated from 2Θ of 10° and 13.3° was ~ 2.65 nm while ~ 2.89 nm was calculated from 12.2° . As the calculated interlayer spacing does not add up with the spacing of quasi 2D perovskite assuming $m =$ positive integer, formation of multi-layered RP structure are deduced. The intensity of the diffraction pattern signature from 3D perovskite, which corresponds to the crystallinity of the film, reduced with increasing 2D ratio, in which no diffraction peak signature was observed for 50% 2D samples (i.e. $m = 2$). Crystallite size were calculated from the FWHM of the XRD spectra using Scherrer equation and reported in **Figure S7**.

Figure S2. The atomic force microscopy (AFM) images, topographical, and cross sectional images of all films with various 2D content.

Figure S3. Absorption spectra of films with various 2D concentrations fitted using Elliot formula in which x represents excitonic while e-h represents band to band contribution.

Figure S4. The multiple peak fitting of steady state PL spectra for films produced at various 2D concentration.

Figure S5. Magnified PL excitation spectra at 540 nm and 500 nm emission of films with 10% 2D.

Figure S6. Band diagram of the LED devices (a), followed by the corresponding J-V-L curve (b), EQE and current efficiency curve (c), as well as the electroluminescence spectra (d) of all devices at various bias applications.

Figure S7. The crystallite size, surface roughness, and maximum EQE of films with various 2D content.

The crystallite size of the films was reduced with increasing 2D content. The crystallite size for films with 50% 2D content could not be extracted due to the lack of crystallinity of the film itself. From **Figure S7**, it could be seen that while decreasing the crystallite size with 2D addition helps to improve EQE in general, further crystallite size reduction by increasing the 2D content does not yield to continuous EQE enhancement. Therefore, it is concluded that while crystallite size may help to increase the device efficiency, crystallite size alone is not the rate-determining factor of the LED performances here.

The surface roughness calculated using atomic force microscopy (AFM) were presented against the 2D content and the EQE maximum of the devices in **Figure S7**. Though it could be seen that the evolution of EQE maximum of the devices were indeed follows the surface roughness trends in RP films, it still failed to explain the low EQE of the 3D devices as compared to RP devices above 20%. Moreover, surface roughness could itself could not explain the fact that extra electroluminescence peak were observed for RP with 20% 2D at higher voltage. Hence, although surface roughness plays a bigger role for the EQE evolution, it is still not the rate determining factor in the LED performances.

Table S1. Transient absorption (TA) time constants associated for the excitons monitored at 425 nm, 435 nm and 535 nm, following excitation at 400 nm (1.3×10^{13} photons cm⁻²). Here τ_1 represent the rise time of exciton monitored at 535 nm for 20 % mixed sample, while τ_2 and τ_3 represent the decay of all excitons and A1, A2, A3 are the associated coefficients. The lifetimes are the average measurements at three different locations of the films.

2D content [%]	Wavelength [nm]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	A1	A2	A3
0	535	0.1 ± 0.03	3.41 ± 2.34	1053 ± 42	0.15	0.02	0.46
20	435	0.01 ± 0.02	---	2.88 ± 0.07	0.04	---	0.54

	535	0.39 ± 0.09	0.23 ± 0.02	255 ± 11	0.16	0.33	0.34
100	425	0.01 ± 0.1	---	1.07 ± 0.07	0.05	---	0.62

Table S2. The photoluminescence lifetime of films with various 2D contents at different emission wavelengths (i.e. 440, 490, and 540 nm).

2D content [%]	Wavelength [nm]	A1	τ 1 [ns]	A2	τ 2 [ns]	τ ave
0	540	0.75	2.10	0.250	6.61	3.2
	440	1	0.41			0.41
10	490	0.86	0.66	0.14	21.25	3.6
	540	0.42	4.54	0.58	38.38	24.2
	440	1	0.38			0.37
20	490	0.66	1.73	0.34	14.79	6.16
	540	0.19	5.51	0.81	51.71	42.9
	440	1	0.37			0.37
30	490	0.72	1.40	0.28	11.92	4.37
	540	0.23	5.43	0.78	37.85	30.3
	440	1	0.38			0.37
40	490	0.75	1.31	0.25	10.82	3.7
	540	0.48	4.91	0.52	23.67	14.6
	440	1	0.37			0.37
50	490	0.74	1.34	0.26	10.32	3.7
	540	0.39	4.99	0.61	24.01	16.5