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Regulating Vertical Domains Distribution in Ruddlesden-Popper Perovskites for Electroluminescence Devices

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ABSTRACT: Efficient perovskite light emitting diodes are designed by employing an ordered vertical domain distribution in quasi 2D perovskites to induce better electron flow to the emitting domains. DMSO is added to the precursor solution to tune the crystallization rate and promote the formation of high m domains near the substrate surface via the one step deposition method. Optimized deposition conditions yielding film with favorable energetic landscape for both carrier injection and confinement results in a fourfold EQE enhancement with maximum EQE of 5.79%. Better carrier injection is further supported by turn on voltage value that is comparable to the bandgap of the emitter material (~ 2.25 eV).

TOC GRAPHICS

Within 5 years, efficiency leap for halide perovskite based light emitting diodes (PeLEDs) has been observed from $<1\%$ ¹ to 20% ^{2,3}. The rapid development has been associated with their favorable optoelectronic properties such as narrow full width half maximum (FWHM)⁴ emission profile, low trap densities⁵, long carrier diffusion lengths⁶⁻⁸, and tunable exciton binding energies^{9,10}. In particular, employing quasi two dimensional (2D) Ruddlesden-Popper (RP)

perovskites with chemical formula of $L_2A_{m-1}B_mX_{3m+1}$ (where L is a large aliphatic or aromatic cation, A is a monovalent cation, B is a divalent metal cation, and X is a halide anion) for PeLEDs has risen to fame as opposed to the three dimensional (3D) counterparts owing to their ability to form multiple domains with various bandgap which promotes energy confinement. Bandgap of the emitter materials can be further expanded by decreasing the m value¹¹ which refers to the degree of L cation incorporation into the crystal structure. PeLEDs emitting at visible region (green) with efficiency as high as 14.36% and stability up to 120 mins were achieved by employing quasi 2D perovskite with surface passivation technology¹². Both spectral and operational stability of PeLEDs can be improved in quasi 2D PeLEDs as the bulky organic cations (L) help to reduce ionic migration in the system^{13–17}. Although depositing phase-pure (single m value) quasi 2D perovskite thin films is challenging due to the thermodynamic stability of the compounds¹⁸, films consisting of multiple m domains have shown considerable success in improving PeLEDs efficiency^{19–22}. This stems from the m domains distribution which governs the energy landscape of the films and subsequently the cascading efficiency^{19,23}. Hence, controlling parameters that greatly affect the m domains distribution during deposition, such as crystallization rate, are important to attain efficient devices.

Polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), are generally used in the preparation of perovskite precursor solution. On the other hand, non-polar solvents that are miscible with the precursor solvent (such as toluene and chlorobenzene) are generally used as anti-solvent. Anti-solvent is introduced during spin coating to promote fast supersaturation and precipitation of perovskite precursors. The interaction between perovskite precursors, solvents, and anti-solvent during deposition will modulate the nucleation and growth rate of perovskite films which ultimately influences the resulting film/grain orientation. For example, the growth

orientation of quasi 2D Sn-based perovskites can be tuned from (010) parallel orientation to (101) perpendicular orientation by simply changing the solvent from DMSO to DMF¹⁸. Better film crystallinity, perpendicular crystal orientation, and bigger grain size can also be achieved with employing a mixture of DMF:DMSO solvent in $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{m-1}\text{Pb}_m\text{I}_{3m+1}$ system due to the strong interaction between metal halide and DMSO molecules, retarding the crystallization process during hot casting of perovskite films²⁴. Those favorable traits result in efficient quasi 2D perovskite solar cells. This revelation points to the need to understand and control the precursor-solvent interaction during crystallization process which will greatly influence the distribution of quasi 2D m domains, the energy landscape, and in turn the PeLEDs efficiency.

We deduced that for PeLEDs adopting the p-i-n structure, an energy landscape that promotes electron flow towards the substrates is beneficial to improve charge injection and efficiency. Therefore, strategies to promote ordered vertical phase distribution with favorable energy landscape are required. Here, the m distribution of the resulting quasi 2D are modulated by the solvent engineering method in which DMSO is added to the perovskite precursors solvent (DMF). Instead of hot casting²⁵ or solvent annealing method²⁶, toluene is selected as anti-solvent here to selectively remove DMF while leaving some DMSO amount in the films after spin coating in order to provide sufficient time for hydrophobic L cation to travel to the film surface. Quasi 2D perovskites based on formamidinium bromide (FABr), 2-(naphthalen-2-yl)ethan-1-aminium bromide (NEABr), and lead bromide (PbBr_2) precursors with m aimed at m = 10 in DMF solvent are used in this study (Figure 1a). In particular, the crystallization rate will be fine-tuned by incorporating various amount of DMSO (from 0 to 30%) into the DMF based precursor solution. The relationship between DMSO content, m domains distribution, and optoelectronic properties

of the film will be discussed in depth which will be used as a building block to make efficient PeLED.

Figure 1. Illustration of quasi 2D perovskite crystal structure (a). Absorbance spectra (b), steady state PL spectra (c) and transient PL data (d) of quasi 2D perovskites prepared with various amount of DMSO indicating traces of phase segregation with DMSO addition.

DMSO addition to the system triggers m domains phase segregation which can be seen from the absorbance spectra. Absorbance onset at 537 nm is observed for the control quasi 2D films (0%). Upon DMSO addition, the absorbance onset is red shifted with increasing DMSO content (inset Figure 1b) to 544 nm with 30% DMSO indicating formation of higher m domain. Additional excitonic absorbance peaks at 427 nm and 462 nm are observed on addition of DMSO with the intensity growing proportionally with the DMSO content (inset Figure 1b) indicating the growth of lower m domains in the films. The prominence of both lower and higher m domains signatures indicates larger phase segregation in films deposited with DMSO additive. Photoluminescence (PL) spectra of the films are in line with the absorption onset where PL peaks are red shifted with increasing DMSO content in the precursor solution (Figure 1c) from 530 nm to 532, 533, and 535 nm for 0%, 10%, 20%, and 30% respectively. Regardless of the PL position, the full width half maximum (FWHM) of the samples is maintained at ~ 25 nm. Although lower m domains signatures are observed from absorbance spectra, single PL peak is observed for all samples which corresponds to the PL of higher m domain. PL decay curves (Figure 1d) are fitted with a bi-exponential decay function, where the fast and slow decay constants correlate to the non-radiative and radiative recombination processes, to extract the amplitude weighted average lifetimes. The decay lifetimes for the measured samples are tabulated in Table S1 and reveal that longer carrier lifetimes are obtained when DMSO is added into the precursor solution, growing from 2ns for 0% to 7ns for 30% system. This indicates lower non-radiative recombination in films with increasing DMSO content.

Figure 2. Topographical and cross-sectional images together with the grain size distribution of quasi 2D perovskites fabricated through solvent engineering method with various amount of DMSO illustrating ordered vertical phase distribution.

Cross-sectional and top morphological images of all the films are presented in Figure 2, which support phase segregation phenomenon observed from spectroscopy. Compact films with thickness of ~ 250 nm are observed for all samples. The grain size of the films was calculated from SEM cross sectional images and uniform grain distribution is observed for samples coated with 0% DMSO. Upon addition of DMSO, bilayer perovskite film formation can be observed from single spin coating method with relatively smaller grains forming on top (T) of larger sized grains. Grain size of the bottom layer (B) increases with increasing DMSO content. Larger grain size formation results in higher surface roughness of the films which increases from 10 nm to 30 nm for 0% and 30% samples respectively (Figure S1). Despite the appearance of lower m domains from the optical characterization, X-Ray Diffraction (XRD) patterns of the films are dominated by 3D FAPbBr_3 spectra (Figure S2a). At 30% DMSO content, low angle peaks at 11.25° and 12.5° which do not correspond to both FAPbBr_3 and PbBr_2 spectra are attributed to signal from the lower m content. The weak signal of lower m domain from XRD of $m = 10$ films are attributed to the relatively small amount of lower m domain found in the film as strong lower m domain signal can be obtained for $m = 3$ films prepared with 30% DMSO content (Figure S2b). Grating incident wide angle X-Ray scattering (GIWAXS) analysis of the quasi 2D ($m = 10$) films indicate formation random crystal orientation in the polycrystalline sample regardless of the solvent used (Figure S2c). The bilayer phase segregation on quasi 2D films induced by DMSO addition is also supported by PL evolution of the films when they are excited from the front and back of the substrates (Figure S3). Low m domains PL signatures (at shorter wavelength) are more dominant than the high m domains (at longer wavelength) when samples are excited from the front and vice

versa when samples are excited from the back of the substrates. This phenomenon is more pronounced in films deposited from low m precursors (Figure S3).

By far, this is the first report indicating tendency to form high m domains at the bottom of the samples from one step deposition of bromide based quasi 2D perovskite. Previous reports on iodide based perovskite have shown that formation of low m domains at the bottom of the surface is preferred from one step deposition methods as low m domains formation are kinetically more favorable^{26–28}. The ordered phase distribution has also been correlated with the sedimentation of bigger colloidal particles (i.e. 2D perovskites) followed by the smaller one (i.e. 3D system)²⁵. On the other hand, two step deposition method promotes the formation of high m domains at the bottom of the films due to decreasing supply of PbI_2 away from the substrates²⁹. By adding anti-solvent to change the growth direction of quasi 2D methyl- and butyl-ammonium lead iodide, formation of high m domains at the bottom of the substrates could be triggered from one step deposition method³⁰. Here, the ordered vertical phase distribution can be explained by the slow evaporation of DMSO which provide ample time for hydrophobic NEABr to re-distribute on the surface. The larger gap between the polarity indexes of anti-solvent (toluene, 2.4) and DMSO (7.2) as compared to DMF (6.4) prevents the anti-solvent from completely displacing DMSO at room temperature¹⁸. The remaining DMSO, trapped in the films, slowly evaporates over time. During the slow evaporation process, DMSO from the surface is replenished by the DMSO closer to the substrate surface. During this process, the hydrophobic NEABr, which may still be present in the DMSO also rises to the top. Hence, a higher volume of DMSO present in the films post spin coating will promote more ordered vertical phase segregation.

Figure 3. The absorbance spectra (a) of quasi 2D films fabricated from precursor solutions with various m values indicating the presence of multi m -domains in quasi 2D films ($1 < m < \infty$) together with the proposed band alignment of the ordered vertical phase distribution (b) calculated from both UPS and absorbance data.

To understand the impact of ordered vertical phase distribution induced by DMSO on the resulting energy landscape, valence bands of the resulting RP films deposited from precursor solutions with various m values are measured using Ultraviolet Photoelectron Spectroscopy (UPS, Figure S4) while the conduction band is calculated from the absorbance spectra of the films (Figure 3a). DMF is used as the solvent during UPS samples preparation to minimize the phase segregation effect. The calculated energy landscape is presented in Figure 3b demonstrating favorable electron flow from higher m to lower m domains. Despite the differences in the conduction band level, similar valence band values are detected regardless of the m value variation. As formation of quasi 2D films with single m value for RP with $m > 1$ and $m < \infty$ is unsuccessful despite utilizing pure DMF

as solvent (Figure 3a), the absolute energy level for RP should be taken cautiously. However, the trend in which conduction band increases with decreasing m is conserved as it can be predicted from the pure 3D ($m = \infty$) and 2D ($m = 1$) systems as well. This result is in line with other reports where favorable electron flow from high m to low m domains has also been observed in other RP systems such as $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ²⁸. Therefore, DMSO induced ordered vertical phase distribution will promote better electron flow towards higher m value domains which are located near to the substrate surface.

Electroluminescence (EL) devices adopting the p-i-n configuration were then fabricated with NiO_x and PO-T2T as the hole transporting layer (HTL) and electron transporting layer (ETL) respectively (Figure 4a). Current density (J) and luminescence (L) response versus voltage (V) of the devices are presented in Figure 4b. Similar diode current turn on voltage (V_{on}) is observed for all devices ($\sim 1.55\text{V}$) while lower light turn on voltage (V_{th} , voltage at 1 cd.m^{-2}) from 2.8 V to 2.15 V is observed with increasing DMSO content from 0% to 30% respectively (table S2). Lower V_{th} with reduced differential resistance (Figure S5) indicates superior charge injection to the emitter while smaller discrepancy between V_{on} and V_{th} suggests better charge balance for devices with higher DMSO content. This is in line with the hypothesis where DMSO induced ordered vertical phase distribution helps to improve electron flow from ETL to HTL. Better charge injection and charge balance result in higher external quantum efficiency (EQE) for the devices with DMSO addition (Figure 4c). Increasing DMSO content further enhances the EQE with saturation point at 20% DMSO content. EQE as high as 5.79% with maximum luminance (L_{max}) of $43,377\text{ cd.m}^{-2}$ are achieved for devices made from precursors with 20% DMSO, which is fourfold higher than control devices (1.38% for 0% DMSO). As balanced carrier injection and carrier confinement in the emitter region must be attained to boost the EQE, it is deduced that better electron flow for devices

with DMSO addition above 20% will fail to effectively confine the charges in the emitter region. As additional carrier flow does not contribute to the radiative process in the emitter region, EQE is therefore reduced. The EL peaks of devices are red shifted from 533 nm to 538 nm with DMSO addition (Figure 4d), in agreement with PL data. The stability of devices was measured under constant current measurement and presented in Figure S6. Regardless of the amount of DMSO being used, device lifetime until the luminance reduced to half (T_{50}) are in the range of 422 – 523 s. Devices with higher EQE demonstrate longer lifetime and vice versa which can be attributed to less joule heating in the system as they convert the input electrical energy to photon more efficiently³¹. Therefore, methods to boost EQE of devices will enhance their stability as well.

In summary, ordered vertical phase distribution with lower m domains segregating on surface of the films can be achieved via single step deposition method by using toluene and DMSO as the anti-solvent and precursor solvent respectively. The ordered vertical phase distribution promotes conducive energy landscape for electron flow from the surface to the bottom of the substrates which is beneficial for PeLEDs application with p-i-n structures. Favorable energy landscape in the film results in at least fourfold EQE and current efficiency enhancement with values up to 5.79% and 26.5 cd/A respectively. In the broader context, the success of creating ordered vertical phase distribution with high m domains located at the bottom of the substrates via simple single step deposition method can also be implemented to improve the efficiency and moisture stability of solar cell with n-i-p structures.

Figure 4. Schematic diagram of PeLEDs with p-i-n configuration (a) together with the J-V-L curves (b), EQE versus J (c), and EL spectra (d) of devices made with various DMSO content in the perovskite precursors.

Experimental Methods

Synthesis of 2-(naphthalen-2-yl)ethan-1-aminium bromide: 2-(naphthalen-2-yl)ethan-1-aminium bromide was prepared via multiple step syntheses, as shown in the following scheme:

Scheme 1. Synthetic route to 2-(naphthalen-2-yl)ethan-1-aminium bromide

2-(naphthalen-2-yl)acetonitrile (2). Under a flow of N₂ gas, 2-(bromomethyl)naphthalene (1) was added in small portions to a two-necked round-bottomed flask containing a stirring suspension of KCN in DMSO. After being stirred at 60 °C for 16 h, plus overnight at room temperature, the reaction mixture was poured into cold H₂O. The beige solid obtained was filtered off, washed with cold H₂O and dried under reduced pressure to afford the desired product (1.52 g; 72%).

2-(naphthalen-2-yl)ethan-1-amine (3). Under an argon gas atmosphere, a solution of AlCl₃ (3.0 eq) in dry THF was added dropwise to a suspension of LiAlH₄ (3.0 eq), also in dry THF. The resulting mixture was stirred for ~10 mins at RT. Subsequently, a solution of 2 (1.0 eq) dissolved in dry THF was added dropwise to it, and the mixture was heated under reflux for at least 12 h. After cooling to room temperature, H₂O was added dropwise with ice bath cooling, followed by 10% aqueous HCl. The resulting mixture was washed with ethyl acetate and the aqueous layer made alkaline using 2 M aqueous NaOH. CHCl₃ was then added and the resultant mixture shaken vigorously. The emulsion obtained was passed through a pad of Celite, after which the organic phase was separated, washed with brine, dried over MgSO₄, filtered, and concentrated to afford 3 as a beige powder (0.63 g; 79%).

2-(naphthalen-2-yl)ethan-1-aminium bromide (4). To a round bottom flask containing ethanol and the amine 3, cooled to 0 °C, was added a stoichiometric amount of concentrated hydrobromic acid.

After stirring the solution for 1 hour, all volatiles were removed using a rotary evaporator. The solids, thereby, obtained were washed with copious amounts of diethyl ether and dried under vacuum at 50°C overnight (1.19 g; 93%).

Perovskites deposition: To make $m = 10$ perovskite precursors, $\text{CH}(\text{NH}_2)_2\text{Br}$ (FABr, 0.7M), PbBr_2 (0.675M), and 2-(naphthalen-2-yl)ethan-1-aminium bromide (NEABr, 0.075M) were dissolved in varied ratio of DMSO:DMF solvent. Films were then deposited by spin coating (5000 rpm, 30s) from 30 ml of various perovskite precursors and 100 ml of anti-solvent (i.e. toluene) was introduced 5s after the start of spin coating session. The films were then dried in room temperature for 30 minutes. Both spin coating and solution mixing were done under argon environment.

Devices fabrication: PeLEDs were fabricated on indium doped tin oxide (ITO, $7 \Omega\cdot\text{cm}^{-2}$) coated glass substrates which are cleaned by sequential sonication in decon soap, distilled water, and isopropanol solution. Substrates were dried and cleaned with oxygen plasma for 15 min. A layer of NiO_x was deposited on the substrates by spin-coating (6000 rpm for 60 s) equimolar solution (0.5M) of nickel nitrate hexahydrate and ethylene diamine in ethylene glycol solvent followed by annealing at 300°C for 1 hour in ambient atmosphere. Samples were then transported into glovebox for perovskite deposition. Approximately 40 nm of ((1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (POT2T) were thermally evaporated on top followed by thermal evaporation of 10 nm Ca and 100 nm Al to complete the device fabrication. Shadow masks were used during electrode deposition to define device active area (8 mm^2). Devices were then encapsulated inside glovebox and tested in ambient atmosphere.

Materials Characterization: X-Ray diffraction spectra was recorded using XRD Bruker D8 Advance. Field effect scanning electron microscope (FE-SEM, JEOL J7600F) were used to

capture topographical and cross sectional images. Surface roughness measurement was done using contact mode Atomic Force Microscope (AFM, Asylum Research MFP-3D) with Ti/Ir coated cantilevers (ASYELEC-01-R2, Asylum Research). Absorption and steady state PL spectra was recorded using Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and Horiba Fluoromax-4 respectively. Transient PL information were recorded using micro-PL setup with a Nikon microscope and a Picoquant PicoHarp 300 time correlated single photon counting (TCSPC) system. A picosecond pulsed laser diode (Picoquant P-C-405B, $\lambda = 405\text{nm}$, 40 MHz repetition rate) was used as excitation source while output signal were processed through Acton SP-2300i monochromator coupled to an avalanche diode synchronized with excitation laser via TCSPC electronic. Overall, the full width half maximum of the system instrument respond function is around 50 ps. Ultraviolet Photoelectron Spectroscopy (UPS, Kratos AXIS Supra) with He plasma at excitation energy of 21.22 eV was used to probe the valence band and work function position of the materials.

Devices Characterization: Current-voltage response of the devices was recorded using Keithley 2612B. Integrating sphere (OceanOptics FOIS-1) connected to a calibrated spectrometer (OceanOptics QEPro) was used to collect the forward emission light output of the devices. The absolute irradiance was calibrated with 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.

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Supporting Information

Regulating Vertical Domains Distribution in Ruddlesden-Popper Perovskites for Electroluminescence Devices

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Figure S1. Atomic force microscopy images of quasi 2D films fabricated with various DMSO content.

Figure S2. X-Ray Diffraction spectra of quasi 2D films ($m = 10$) fabricated using various DMSO content (a) as well as quasi 2D films (30% DMSO) with various m value (b) with grey arrows possibly indicate the signature of lower m domain, pink lines indicate 3D signature (FAPbBr₃), and orange line indicate diffraction of $m = 1$ (NEA₂PbBr₄). In addition, grazing incident wide X-Ray scattering (GIWAXS) measurement of quasi 2D films ($m=10$) prepared with (30%) and without (0%) DMSO in the precursors solution is also presented (c).

Figure S3. Schematic diagram of steady state photoluminescence measurement setup illustrating back and front excitation measurement setup together with the steady state photoluminescence spectra of quasi 2D films deposited from precursors with various m value.

Figure S4. Ultraviolet Photoelectron Spectroscopy spectra of quasi 2D films deposited from precursors with various m value.

Figure S5. Differential resistance curves of perovskite based light emitting devices made from quasi 2D films with various DMSO content.

Figure S6. The stability data of devices made with various DMSO content indicating lifetime (T_{50}) of 422 to 523 s.

Table S1. The photoluminescence decay lifetimes of films made from various DMSO content

<i>DMSO content</i>	τ_1 (ns)	A_1	τ_2 (ns)	A_2	T_{ave} (ns)
0%	0.78	0.75	5.86	0.25	2.05
10%	1.46	0.68	11.37	0.32	4.63
20%	1.8	0.68	14.58	0.32	5.89
30%	1.91	0.64	15	0.36	6.62

Table S2. List of the device names made with various DMSO content and the light emitting diode performances.

<i>DMSO content</i>	V_{on} (V)	V_{th} (V)	L_{max} (cd/m ²)	EQE (%)	$\eta_{A max}$ (cd/A)
0%	1.55	2.8	22,230	1.38	6.05

10%	1.55	2.5	19,702	1.74	7.9
20%	1.55	2.25	43,377	5.79	26.5
30%	1.55	2.15	37,960	4.74	21.6