White electroluminescence from perovskite-organic heterojunction

Nur Fadilah Jamaludin; Natalia Yantara; Giovanni, David; Febriansyah, Benny; Tay, Yeow Boon; Salim, Teddy; Sum, Tze Chien; Mhaisalkar, Subodh; Mathews, Nripan

2020

Nur Fadilah Jamaludin, Natalia Yantara, Giovanni, D., Febriansyah, B., Tay, Y. B., Salim, T., ... Mathews, N. (2020). White electroluminescence from perovskite-organic heterojunction. ACS Energy Letters, 5(8), 2690-2697. doi:10.1021/acsenergylett.0c01176

<https://hdl.handle.net/10356/143322>

<https://doi.org/10.1021/acsenergylett.0c01176>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS Energy Letters, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acsenergylett.0c01176>

Downloaded on 26 Apr 2023 16:39:40 SGT

White electroluminescence from perovskite-organic heterojunction

Nur Fadilah Jamaludin, Natalia Yantara, David Giovanni, Benny Febriansyah, Yeow Boon Tay, Teddy Salim, Tze Chien Sum, Subodh G. Mhaisalkar, and Nripan Mathews

ACS Energy Lett., **Just Accepted Manuscript** • DOI: 10.1021/acsenergylett.0c01176 • Publication Date (Web): 27 Jul 2020

Downloaded from pubs.acs.org on July 28, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

White electroluminescence from perovskite-organic heterojunction

*Nur Fadilah Jamaludin^{a,+}, Natalia Yantara^{a,+}, David Giovanni^c, Benny Febriansyah^a,
Yeow Boon Tay^a, Teddy Salim^d, Tze Chien Sum^c, Subodh Mhaisalkar^{b,*}, and Nripan
Mathews^{b,*}*

^a Energy Research Institute @ NTU, Nanyang Technological University, Research Techno
Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553, Singapore

^b School of Materials Science and Engineering, Nanyang Technological University, 50
Nanyang Avenue, 639798, Singapore

^c Division of Physics and Applied Physics, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, 637371, Singapore

^d Facility for Analysis, Characterisation, Testing and Simulation (FACTS), Nanyang
Technological University, 50 Nanyang Avenue, Singapore 639798

⁺ The authors contribute equally in this article.

Corresponding Authors

* Subodh Mhaisalkar (Email: Subodh@ntu.edu.sg)

* Nripan Mathews (Email: Nripan@ntu.edu.sg)

ABSTRACT

Despite extensive reports on red and green perovskite-based LEDs (PeLEDs), development of white PeLED remains limited by the low photoluminescence quantum yield of white-emitting perovskites and undesired energy transfer (ET) process occurring in multi-domain Ruddlesden-Popper (RP) perovskites. While ET is beneficial for achieving efficient monochromatic emissions, the broadband spectrum required for white electroluminescence, deems this phenomenon undesirable. Processing-induced physical separation of emitters has been proposed as an effective way to curb ET. Here, it is shown that by adopting a bilayered emitter configuration, achieved through a facile antisolvent assisted spincoating process, an increase in spatial separation between the blue perovskite and red organic emitting species employed, can be realized. This, in turn, has allowed for effective reduction of ET efficiency, leading to record efficiency of 1.3%, the highest achieved to date from a perovskite-based white electroluminescent device.

TOC GRAPHICS

The rapid rise in efficiencies of both perovskite (ABX_3 ; where A, B, and X are monovalent cation, divalent cation, and halide anion respectively) based light-emitting diodes (PeLEDs) and photovoltaics, is associated with its superior optoelectronics properties such as high defect tolerance and band gap tunability^{1,2}. From a mere efficiency of 0.1 % in a $CH_3NH_3PbBr_3$ device sandwiched between organic transport layers³, PeLED efficiencies have now exceeded 20%,^{4,5} through the adoption of Ruddlesden-Popper (RP) perovskites ($L_2A_{m-1}B_mX_{3m+1}$; where L and m refer to the bulky spacer cation and the degree of its integration into the perovskite lattice, respectively) as the emitter. This stems from the effectiveness of RP perovskites in encouraging bimolecular recombination through charge localization in the emitting domains^{6, 7} and suppressing undesired non-radiative recombination.^{8,9} The energetic emitter landscape offered by RP perovskite promotes energy transfer (ET) to the energetically favoured lowest bandgap domains¹⁰ and enhances radiative recombination through a process termed as energy funneling. While the introduction of an energy funneling landscape in red⁵ and green^{8, 11} emitters has enabled impressive efficiencies to be achieved, ET becomes a limiting factor for blue¹² and white emissions, owing to the tendency for emission to be dominated by the smallest bandgap domains.

White broadband emission is typically achieved through down conversion luminescence of ultraviolet (UV) light using blue and red phosphors. Alternatively, white electroluminescence from an emissive stack is enabled by the fabrication of either a single emitter or bilayer/tandem LED structure yielding both small and large bandgap emissions. Blending high photoluminescence quantum yield (PLQY) perovskite emitters with molecules such as oligomer¹³, polymer¹⁴, or other organics¹⁵ to obtain a single emitting layer provides a seemingly direct approach to achieve efficient white electroluminescence. However, the undesired ET which arises due to the close proximity of the two emitting species results in blue emission quenching and consequently reduces the probability of white light generation.^{16, 17} Potential of

layered broadband emitting perovskites^{18, 19} as single emitters for white light emission, on the other hand, is shrouded with issues pertaining to low PLQY, spectral instability^{20, 21} and poor charge transport, thus limiting their practical application in LEDs. Moreover with ET process known to be increasingly more efficient with decreasing intermolecular distances,^{14, 22} it is hardly surprising that reports on white electroluminescent devices, particularly those based on perovskites, still remains largely limited (**Table 1**). This highlights the need for control over morphology of multi-emitter systems (i.e. mixing/demixing and aggregation) to suppress ET and achieve white electroluminescence.

Incorporating dual emitter layer or tandem configuration into LEDs are some of the approaches explored to increase spatial separation and reduce ET. Examples include the deposition of perovskite atop ZnCdS nanocrystals²³ or organic layer²⁴ in a dual emitter layer configuration as well as complete tandem LED architecture consisting of red and blue-emitting perovskites,²⁵ both which have been shown to be promising for white emission. However, the increase in processing complexity, which accompanies bilayer film and tandem LED fabrication, disincentivises the adoption of this processing route, necessitating the development of efficient white LEDs through suppression of ET while adopting a simpler LED architecture.

In order to tackle this, a single step processing technique enabling the formation of a graded or bilayer emitter film is proposed. It was previously reported that a graded perovskite emitter with higher organic dopant concentration on top^{26, 27} is attained through an antisolvent assisted spincoating process. Herein, we present an approach to interface highly efficient blue-emitting perovskite film²⁸ with a red-emitting organic through loading of the latter in the antisolvent. We hypothesize that the ET process can be effectively curbed by employing a bilayer emitter configuration in our LEDs. This in turn, enables the retention of both the blue and red emissions, thereby enhancing white light emission (**Figure 1a and 1b**).

The high efficiency blue-emitting perovskite (CsPBA-2) chosen is a Cs-based RP perovskite, which we have recently reported.²⁸ The perovskite precursor solution is prepared with an excess of ligands (phenyl butyl ammonium bromide) and spin coated via antisolvent assisted spincoating process. As discussed previously, excess ligand is used to suppress the formation of higher m domains whereas low solubility A-site cation serves to curb growth of low-conducting $m = 1$ phase. Introduction of antisolvent dripping during the spincoating process ensures the formation of a narrow distribution of m phases about the desired emitting domain, thus yielding a narrow blue emission width. All in all, by exerting fine control over ligand and A-site cation concentrations, solubility limits of A-site cation, as well as the nucleation kinetics, we have been able to template the formation of a narrow distribution of perovskite domains ($m = 2-5$) – essential for facilitating efficient blue emission. By simply tuning the PBA/Pb and PBA/Cs ratios in the precursor solution, we have shown spectral tunability spanning the entire blue region. With the aim of obtaining high efficiency white electroluminescence, we have elected to employ the CsPBA composition (CsPBA-2) yielding the highest external quantum efficiency (EQE) to promote the formation of m domains with emission centered at ~ 490 nm. The red organic material, on the other hand, is a commercially available emitter, Livilux SPR-001.²⁹ It is chosen as the red emitter in our study as the CIE coordinates of its emission (0.66, 0.33) complements those of the CsPBA-2's (0.07, 0.32), thus endowing the possibility of white light creation on interfacing these two emitters. Moreover, the differing degree of solubility of the organic in both the antisolvent and the perovskite precursor solvent (good and poor respectively), serves to not only minimize chemical interactions with the perovskite but also quells ET by increasing the physical distance between the two emitting species¹⁰. The absence of NH_3^+ and OH^- moieties on the organic chain, eliminates the possibility of binding with perovskite, thus ensuring that the latter's crystallization remains unhindered despite the

introduction of the organic emitter.³⁰ This in turn, results in the formation of a red emitter layer on top of the blue, further minimizing parasitic re-absorption.

The energy band characteristics of both CsPBA-2 and SPR-001 were verified using ultraviolet photoelectron spectroscopy (UPS) which reveals the formation of a type I heterojunction (**Figure 1c** and **Figure S1**). This, coupled with the existence of a spectral overlap between the CsPBA-2 photoluminescence and SPR-001 absorbance spectra (**Figure 1d**),^{16, 31} supports the probability of non-radiative ET occurring, which further highlights the importance of spatial separation for effective white emission.

Table 1: Summary of literature works on white emitting electroluminescent devices

Year	Device structure	Emitting layer	V_T (V)	EQE (%)	L_{max} ($cd\ m^{-2}$)	CRI	CCT (K)	Ref
2018	ITO/PEDOT:PSS/PA ₂ CsPb ₂ I ₇ /BIPO:PolyTPD/CsPb(Br, Cl) ₃ /TPBi/LiF/Al	PA ₂ CsPb ₂ I ₇ /CsPb(Br, Cl) ₃	—	0.22	—	—	6000	25
2017	ITO/NiO _x /PEDOT:PSS/HFSO/CsPb(Br _{1.5} I _{1.5})/Ca/Al	HFSO + CsPb(Br _{1.5} I _{1.5})	4.7	—	1200	—	—	13
2017	ITO/NiO _x /CsPb(Br _x /I _{3-x})/MEH:PPV/TPBi/LiF/Al	MEH:PPV + CsPb(Br _x /Cl _{3-x})	3.3	—	105	—	—	14
2019	ITO/ZnO/PEI/ZnCdS/ZnS/CsPb(Br _{1.65} /I _{1.35})/TCTA/MoO ₃ /Au	ZnCdS/ZnS/CsPb(Br _{1.65} /I _{1.35})	2.8	0.015	275	75	5153	23
2019	ITO/PEDOT:PSS/perovskite + organic compound/PBD/LiF/Al	MAPb(Br/Br,Cl) ₃ + compound		0.01 0.001		27.5 -100		15
2019	ITO/PEDOT:PSS/PAN:CsPb(Br _{2.5} I _{0.5})/NPB/CsPbBr ₃ /TPBi/LiQ/Al	CsPb(Br _{2.5} I _{0.5}) + PAN/NPB/CsPbBr ₃		0.2 cd A ⁻¹	360			24

Figure 1: (a) White light emission spectrum achieved through electroluminescence from complementary blue and red emissions. (b) Schematic of ET process' influence on efficient white light generation. (c) Energy band alignment of CsPBA-2 and SPR-001, obtained through UPS. (d) Absorbance and photoluminescence spectra of CsPBA-2 and SPR-001.

The bilayered films are prepared by incorporating various concentrations of SPR-001 into the antisolvent and dripping it onto the sample midway during the spincoating of CsPBA-2 (**Figure 2a**). The difference in solubilities of CsPBA-2 and SPR-001 serves two purposes; (a) facilitate the crystallization of CsPBA-2 without compromising on either of the emitters' emission quality and (b) ensuring segregation of the two emitting species, resulting in the formation of a bilayer emitter with SPR-001 rich region on the surface, necessary for increased spatial separation. Compact films are observed in both pristine CsPBA-2 and the bilayered films, with a thicker film formed on incorporation of SPR-001 (**Figure 2b**). To verify the bilayer

formation, auger electron spectroscopy (AES) depth profiling was employed. Indeed, higher concentration of carbon with low concentrations of Cs and Br are observed on the emitter surface, confirming the formation of SPR-001 rich overlayer atop of CsPBA-2. Increasing the concentration of SPR-001 in the antisolvent (2.5 mg ml^{-1}) simply results in a thicker SPR-001 layer, with minimal effect on CsPBA-2 thickness (**Figure 2c**). The formation is further affirmed by the higher proportion of red PL emission noted on exciting the film from the surface and vice versa (**Figure S2**). The preservation of each emitting phase is evident on assessing the absorbance and photoluminescence spectra of the individually prepared films of CsPBA-2, x SPR (where x is the concentration of SPR-001 used in the antisolvent (mg ml^{-1}) for the preparation of bilayered films) and SPR-001 (**Figure 2d** and **Figure S3**). From the absorbance spectra, it is clear that the excitonic peaks corresponding to the lower dimensional phases of CsPBA-2 remain present as noted by the features at 425 and 452 nm, thereby implying that neither the phase distribution nor the crystallization of the desired domain is significantly affected by the introduction of SPR-001. The low amount of SPR-001 introduced into the bilayered film during spincoating manifests in the form of a slight increase in the absorbance spectra across the scanned range. The PL spectra on the other hand, shows negligible difference in the peak positions of the individual emitters for the bilayered films as compared to that of pristine CsPBA-2 and SPR-001 films. Differences to emitter thickness also contributes towards spectral tunability as demonstrated by the increase in relative contribution of the red emission on varying SPR-001 concentration from $0.7 - 0.85 \text{ mg ml}^{-1}$ in the antisolvent.

Figure 2: (a) Schematic of white emitting film deposition process; where SPR-001 is introduced via antisolvent dripping during the spincoating of CsPBA-2. (b) Top and cross sectional images of CsPBA-2 and 2.5 SPR on PEDOT:PSS coated ITO substrates. (c) AES depth profiling of 0.8 SPR and 2.5 SPR films to assess the incorporation of SPR-001 in CsPBA-2, where R rich and B rich regions refer to regions rich with SPR-001 and CsPBA-2, respectively. (d) The absorbance and photoluminescence spectra of CsPBA-2, SPR-001 and 0.8 SPR indicate negligible difference in emission profiles between the individual and bilayered emitting layers.

In order to verify the efficiency of the ET process, transient absorption (TA) spectroscopy studies were carried out for both CsPBA-2 and 0.8 SPR films (**Figure 3a**). It is interesting to note that although there is minimal difference in the PL and absorbance spectra of CsPBA-2 and 0.8 SPR in the 350 – 500 nm region, the TA spectra reveal a slight difference in domain formation between CsPBA-2 and 0.8 SPR films. A single photo-bleaching peak (485 nm) corresponding to carrier filling upon photoexcitation is noted for the 0.8 SPR film while two photo-bleaching peaks are seen for CsPBA-2 (455 and 475 nm). This suggests that there are localised differences in the phase distribution of the perovskite on introduction of the organic,

detectable due to the spatially resolved manner through which TA is carried out (**Figure S4**). Nevertheless, the absence of significant change in phase distribution in the bulk of the film, confirmed through XRD (**Figure S5**), lends credence to the negligible influence of SPR-001 incorporation on CsPBA-2 crystallization. Formation of higher *m* domains is promoted upon polymer addition, attributed to the slower crystallization rate of the system when less toluene is employed.²⁸ The dynamics of photo-bleaching at 475 and 485 nm peak positions reveal the occurrence of ET in the bilayered film (**Figure 3b**), evidenced by the rapid decay of both the 475 and 485 nm signals for the 0.8 SPR film. Transient PL (TRPL) spectra at 500 nm emission wavelength indicate shorter PL decay of CsPBA-2 in the presence of SPR-001 (0.8 SPR) as compared to pristine CsPBA-2, further confirming the occurrence of ET^{22, 31}. On the other hand, the decay lifetimes are noted to be similar for both SPR-001 and 0.8 SPR films at 625 nm (**Figure 3c**). PL excitation of the red emission peak indicates an enhancement to PL emission on exciting 0.8 SPR film with 425 and 450 nm light, corresponding to the excitonic absorption of CsPBA-2 (**Figure 3d**). Based on the data obtained from TA, TRPL and PL excitation spectra, it is revealed that ET does occur in the bilayered film. Assuming that the ET process in our bilayer system is dominated by Förster Resonance ET, the efficiency of this process,¹⁶ $\eta_{FRET} = 1 - \frac{\tau_{DA}}{\tau_D}$, where τ_D and τ_{AD} refer to the donor and donor-acceptor PL lifetimes, is found to be $\sim 30\%$. The smaller degree to which the ET occurs, accounts for the negligible change in acceptor decay lifetime observed for the 0.8 SPR film.

Figure 3: (a) Transient absorption spectra and kinetics of CsPBA-2 and 0.8 SPR films probed at (b) 475 nm and 485 nm. (c) Transient photoluminescence decay of CsPBA-2 and 0.8 SPR at 500 nm as well as SPR-001 and 0.8 SPR at 625 nm. (d) Photoluminescence excitation spectrum of 0.8 SPR at 630 nm emission, compared against the absorbance spectra of CsPBA-2 and SPR-001.

Figure 4: (a) White PeLED device architecture and the energy band alignment of the various layers in the PeLED device. The (b) normalised electroluminescence spectra, (c) current density and luminance against voltage, (d) EQE as a function of voltage, (e) an example of an electrically driven white PeLED, and (f) (x,y) representation of CsPBA-2, x SPR and SPR-001 PeLEDs electroluminescence profiles on the CIE 1931 plot, where 1, 2 and 3 correspond to different CsPBA compositions; CsPBA-1, CsPBA-2 and CsPBA-3 respectively. The data presented in b-d represent devices characteristics of PeLED fabricated with CsPBA-2 (indicated by 2 in the CIE 1931 plot).

In order to realize white electroluminescence from our films, devices adopting the following architecture: ITO/ PEDOT:PSS/ Emitter/ POT2T/ LiF/ Al were fabricated (**Figure 4a**). The electroluminescence spectra of these devices confirm that not only is there minimal change in emission profiles of the individual emitters in the bilayered films, but the relative intensities of the blue and red emissions are also tunable by varying SPR-001 concentration in the antisolvent (**Figure 4b**), consistent with the observation of the photoluminescence spectra. The difference in the relative intensities of the blue and red emissions observed between the PL and EL spectra of the films prepared with the same SPR-001 concentration range (**Figure S3** and **Figure 4b**) indicate different mechanisms governing the emission process on photo and electrical excitation. On electrical excitation, charge transfer (CT) mechanism may dominate, which changes the balance between the perovskite and organic emissions.³² Higher proportion of red emission in the EL devices signifies that the recombination zone of the device is located close to the perovskite/organic interface,³³ necessitating the use of EL instead of PL, as a yardstick to obtain white light emission. Higher threshold voltage (V_{TH} , voltage at 1 cd m^{-2}) observed for the x SPR devices as compared to that of pristine CsPBA-2 (**Figure 4c**), is associated with the decrease in electric field with increasing emitter thickness. On increasing SPR-001 concentration ($x \text{ mg ml}^{-1}$), the SPR-001 overlayer thickens, resulting in a higher V_{TH} needed to initiate the electroluminescence process. Although the pristine CsPBA-2 device exhibits a maximum EQE of 4.5% (**Figure 4d**), the efficiency of x SPR devices are found to be much lower, limited by the SPR-001 efficiency. This arises due to the shifting of the recombination to the SPR-001 region, leading to the decrease in efficiency noted. Decreasing the SPR-001 thickness (0.7 mg ml^{-1}) on the other hand, moves the recombination zone towards the more efficient CsPBA-2 region leading to higher EQE value. The corresponding luminous power efficiency of these devices as a function of luminance is shown in **Figure S6**. Despite this, our bilayered device exhibits the highest efficiency of 1.3% to date for white electroluminescent

PeLED device, accrued to the suppression of ET from the blue emitter to the red, thus enabling the preservation of dual emission in the *x* SPR PeLEDs. The lower ET efficiency recorded for our bilayered system (30 %), which is significantly lower than those reported in literature,^{14, 16} provide further explanation for the higher efficiency noted.

White light emission (**Figure 4e**) with a CCT value of 8217 is achieved when 0.8 SPR is used, with white electroluminescence maintained on biasing from device turn on, up to 6.5 V (**Figure S7**), indicative of minimal recombination zone shift with bias application. The dependence of overall efficiency on the least efficient emitter in the system is corroborated further by the plateauing of *x* SPR efficiency up to ~ 20 cd m⁻², after which, a noticeable efficiency roll-off is observed after 6.5 V. This coincides with the decline in efficiency of the pristine CsPBA-2 device whereas the pristine SPR-001 device shows a flat efficiency curve up to 8 V. This could be explained by the degradation of CsPBA-2 layer with bias > 6.5 V as observed from the lower blue emission at high bias (**Figure S7**). The *x*, *y* representation of CsPBA-2, *x* SPR and SPR-001 electroluminescence spectra on the CIE 1931 plot are shown in **Figure 4f** (in turquoise), where the electroluminescence of *x* SPR devices are located midway between CsPBA-2 and SPR-001 depending on the SPR-001 concentration used. Through modifications to CsPBA precursor solution composition (CsPBA-1 and CsPBA-3, denoted as 1 and 3 respectively in **Figure 4f**, **Figure S8** and **Figure S9**) as we have previously reported²⁸, blue and red shifting of the blue emission peak is made possible, thus allowing for a wider range of white emissions with varying CCT values, to be achieved (**Table S1**). Moreover, it is worthy to mention that white emission from these devices persists from the onset of device turn on, up to 6.5 V as well as on subjecting the device to constant current measurement (**Figure S10**).

Despite changing the blue emitter source, the device performance trends on increasing organic concentration in the antisolvent remain largely similar. The modulation of red emission contribution to the white electroluminescence spectrum changes linearly with SPR-001

concentration (**Figure S8a-b** and **Figure S9a-b**) and V_{TH} increases (**Figure S8c** and **Figure S9c**) on increasing SPR-001 concentration and, allowing emission spanning the region between the red and blue emissions on the CIE 1931 plot to be achieved. Limitation of white PeLED efficiency by the efficiency of SPR-001 is further confirmed when concentrations across the measured range showed efficiency values with minimal differentiation from that of pristine SPR-001 (**Figure S8d** and **Figure S9d**). The normalized EL spectra of the white PeLED devices obtained from different composition of CsPBA precursor solution (CsPBA-1 and CsPBA-3) and SPR-001 concentrations reveal minimal change in relative intensities of blue and red emissions with different bias application (**Figure S8e** and **Figure S9e**). Upon increasing the voltage from 3.5 V to 4.5 V, the shifting of the recombination zone from SPR-001 towards CsPBA occurs due to the decrease in charge injection imbalance on overcoming electron injection barrier. At higher bias application (> 6.5 V) higher red emission is observed, assigned to the degradation of CsPBA at higher current densities. This is consistent with the decline in performance of pristine CsPBA device at high luminance, emphasizing the need to improve stability of CsPBA to enhance operational lifetime of these bilayered PeLEDs. We further confirm the universality of our processing technique with other red emitter systems by substituting the organic with CdSe/ZnS nanoparticles (CSZ NP), where the emission from CsPBA-2 remains unchanged even with CSZ NP incorporation (**Figure S11**). In doing so, we have shown effective tailoring of the white emission spectrum through variations to both the CsPBA emission profile as well as the relative contributions of the blue and red emissions.

In conclusion, we have shown efficient white PeLEDs with a peak efficiency of 1.3%, the highest recorded to date. This is achieved through interfacing of our reported high efficiency blue perovskite emitter films, CsPBA, with a CIE coordinate matching, complementary red organic emitter, SPR-001. The adoption of a bilayered emitter stack to increase spatial separation, suppresses ET significantly assuming Förster Resonance ET, resulting in efficient

white electroluminescence. The absence of chemical moieties in SPR-001, which are capable of intermolecular interactions with CsPBA ensures that crystallization of CsPBA is unaffected despite the introduction of the red emitter. Compositional engineering of the CsPBA through PBA/Cs and PBA/Pb variations have enabled a wider range of white emissions correlating to CCT values between 5580-8217, to be attained while still employing the same red emitter. We propose that the adoption of various strategies such as the introduction of an interlayer between the two emitters as well as the employment of a high efficiency red emitter will allow for better management of ET in white electroluminescent devices, thus enabling higher efficiency to be attained.

EXPERIMENTAL METHODS

Perovskite film formation. The RP perovskite precursor solution (CsPBA) is prepared by combining CsBr with PbBr₂ and C₆H₅(CH₂)₄NH₃Br in a DMF: DMSO (64:36) cosolvent, as previously reported. Excess C₆H₅(CH₂)₄NH₃Br is mixed with PbBr₂ and CsBr in varying PBA/Pb and PBA/Cs ratios to obtain mixed CsPBA-based precursor solutions. By keeping PbBr₂ concentration constant at 0.11 M, CsPBA-1, CsPBA-2 and CsPBA-3 are obtained by setting the PBA/Pb and PBA/Cs molar ratios to (1.3 and 3), (1.3 and 2.5) and (1.33 and 2) respectively. The pristine CsPBA films were prepared by spincoating the perovskite precursor solution at 5000 rpm for 30s with toluene added as antisolvent 5s from the initiation of each spin coating process. The dual emitting white PeLEDs were fabricated by substituting toluene with varying concentrations of SPR-001 in the antisolvent while the pristine SPR-001 device was prepared by spincoating 5 mg mL⁻¹ of SPR-001. Both the solution preparation and spin coating steps were carried out under inert argon environment with no post deposition annealing done.

Device fabrication. Poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS, Al 4083) film was spin coated at 4000 rpm for 60 s atop of indium tin oxide (ITO) coated glass followed by annealing at 200°C for 40 s to remove excess moisture. The electron transporting material ((1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (PO-T2T) (45 nm) and electrode (i.e. LiF (0.8 nm) and aluminum (100 nm)) were deposited via thermal evaporation after the deposition of the emitter layer. Shadow masks are used during electrode evaporation to define a device area of 8mm².

Physical characterization. Topographical and cross sectional images were captured by employing field effect scanning electron microscope (FE-SEM, JEOL J7600F). Absorption and steady state PL spectra were collected using Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and Horiba Fluoromax-4 respectively.

The transient absorption (TA) measurements were performed using a Helios spectrometer (Ultrafast Systems, LLC). The pump pulse was generated from by a 1 KHz regenerative amplifier [Coherent Libra (150 fs, 1 KHz, 800 nm)] and doubled via second harmonic generation (SHG) by a BBO crystal to obtain 400 nm laser pulses. The regenerative amplifier was seeded by a mode-locked Ti-sapphire oscillator (Coherent Vitesse, 80 MHz). The white light continuum probe beam (in the range from 410 to 750 nm) was generated by focusing a small portion (~10 μJ) of the fundamental 800 nm laser pulses into a 5 mm sapphire crystal, before filtering out the residual by using 750 nm short-pass filter. Both pump and probe beam were focused onto the sample with 1/e² spot diameter of ~510 μm and ~200 μm, respectively. Meanwhile, the funneling time is estimated from the rise time of the bleaching signal ($\Delta R/R > 0$) of the bulk ($m > 3$) phases at 480 nm. Due to its ultrafast nature, this measured rise signal is the convolution between the exciton funneling time with our system response time (i.e., laser pulse width) of ~190 fs.

Time resolved PL spectra were collected with streak camera system (Optronis Optoscope™), with the 400 nm pump pulse obtained by frequency-doubling of 800 nm pulse from the regenerative amplifier (Coherent Libra, pulse width 50 fs, repetition rate 1 kHz) with a BBO crystal.

Device characterization. The current-voltage responses of the devices were recorded using Keithley 2612B. Integrating sphere (OceanOptics FOIS-1) coupled with a calibrated spectrometer (OceanOptics QEPro) was used to collect the light emission output. To collect forward light emission only, devices were placed outside and facing into the opening of the integrating sphere. Absolute irradiance calibration was done by employing 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

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

The Ultraviolet Photoelectron Spectroscopy (UPS) spectra of (a) CsPBA-2 and (b) SPR-001

Photoluminescence (top) and absorbance (bottom) spectra of 5 SPR films excited from the surface (SPR-001 side) and back (CsPBA-2 side)

The absorbance and photoluminescence spectra of CsPBA-2, SPR-001, and x SPR, where $x = 0.7 - 0.85$, indicating negligible difference in emission profile between the dual emitter layer and individual emitter layers

(a) Transient absorption spectra and (b) kinetics of CsPBA-2 and 0.8 SPR films probed at 475 nm and 485 nm, measured on a different spot

XRD patterns for pristine CsPBA-2 and 0.8 SPR films.

The luminous power efficiency of the CsPBA, x SPR and SPR-001 LED devices as a function of luminance

The electroluminescence spectra and the corresponding CIE 1931 plot coordinates on increasing the driving voltage for 0.8 SPR PeLED device fabricated with CsPBA-2 composition.

Device characteristics of PeLEDs fabricated with CsPBA-1 composition and varying SPR-001 concentration. The electroluminescence spectra at 4.5 V (a) as a function of CIE 1931 plot coordinates as well as the (b) relative red and blue contributions to white light emission with increasing SPR-001 concentration, (c) current density and luminance against voltage and (d) EQE against luminance. The (e) electroluminescence spectra and the (f) corresponding CIE 1931 plot coordinates on increasing the driving voltage for 0.7 SPR PeLED device fabricated with CsPBA-1 composition.

Device characteristics of PeLEDs fabricated with CsPBA-3 composition and varying SPR-001 concentration. The electroluminescence spectra at 4.5 V (a) as a function of CIE 1931 plot coordinates as well as the (b) relative red and blue contributions to white light emission with increasing SPR-001 concentration, (c) current density and luminance against voltage and (d) EQE against luminance. The (e) electroluminescence spectra and the (f) corresponding CIE 1931 plot coordinates on increasing the driving voltage for 0.8 SPR PeLED device fabricated with CsPBA-3 composition.

CIE coordinates and CCT values corresponding to white electroluminescence obtained on interfacing different compositions of CsPBA with SPR-001, at 4.5 V bias.

Stability of white PeLED measured under constant current measurements. (a) Change in normalised white electroluminescence as a function of time, with initial luminance of 9.5 cd m⁻². (b) Normalised electroluminescence spectra of white PeLED as a function of time, (c) colour mapping of electroluminescence spectra of white PeLED and (d) the corresponding CIE 1931 plot coordinates of white PeLED as a function of time.

(a) The CIE coordinates representation of CsPBA-2 and CsPBA-2 mixed with CdS/ZnS nanoparticle (CSZ NP) emission profiles. The (b) electroluminescence spectra, (c) current density and luminance against voltage, and (d) EQE as a function of luminance for CsPBA-2 and CSZ NP PeLEDs.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was funded by National Research Foundation, Prime Minister's Office, Singapore under its Competitive Research Programme (CRP Award No. NRF-CRP14-2014-

03) and the Intra-CREATE Collaborative Grant (NRF2018-ITC001-001). T.C.S. and D.G. acknowledge the support from the Ministry of Education AcRF Tier 1 grant (RG91/19) and Tier 2 grant MOE2017-T2-1-001 as well as the NRF Investigatorship NRF-NRFI-2018-04. The authors would like to acknowledge the Facility for Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore, for the X-ray characterization and depth profiling using XRD and AES respectively.

REFERENCES

1. Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal halide perovskite light emitters. *Proceedings of the National Academy of Sciences* **2016**, *113* (42), 11694-11702.
2. Quan, L. N.; Rand, B. P.; Friend, R. H.; Mhaisalkar, S. G.; Lee, T.-W.; Sargent, E. H., Perovskites for Next-Generation Optical Sources. *Chemical Reviews* **2019**, *119* (12), 7444-7477.
3. Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H., Bright light-emitting diodes based on organometal halide perovskite. *Nat Nano* **2014**, *9* (9), 687-692.
4. Lin, K.; Xing, J.; Quan, L. N.; de Arquer, F. P. G.; Gong, X.; Lu, J.; Xie, L.; Zhao, W.; Zhang, D.; Yan, C.; Li, W.; Liu, X.; Lu, Y.; Kirman, J.; Sargent, E. H.; Xiong, Q.; Wei, Z., Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent. *Nature* **2018**, *562* (7726), 245-248.
5. Zhao, B.; Bai, S.; Kim, V.; Lamboll, R.; Shivanna, R.; Auras, F.; Richter, J. M.; Yang, L.; Dai, L.; Alsari, M.; She, X.-J.; Liang, L.; Zhang, J.; Lilliu, S.; Gao, P.; Snaith, H. J.; Wang, J.; Greenham, N. C.; Friend, R. H.; Di, D., High-efficiency perovskite-polymer bulk heterostructure light-emitting diodes. *Nature Photonics* **2018**, *12* (12), 783-789.
6. Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A., The Bright Side of Perovskites. *The Journal of Physical Chemistry Letters* **2016**, *7* (21), 4322-4334.
7. Wang, J.; Wang, N.; Jin, Y.; Si, J.; Tan, Z.-K.; Du, H.; Cheng, L.; Dai, X.; Bai, S.; He, H.; Ye, Z.; Lai, M. L.; Friend, R. H.; Huang, W., Interfacial Control Toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes. *Advanced Materials* **2015**, *27* (14), 2311-2316.
8. 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. *Nature Communications* **2018**, *9* (1), 570.
9. Lee, S.; Kim, D. B.; Yu, J. C.; Jang, C. H.; Park, J. H.; Lee, B. R.; Song, M. H., Versatile Defect Passivation Methods for Metal Halide Perovskite Materials and their Application to Light-Emitting Devices. *Advanced Materials* **2019**, *31* (20), 1805244.
10. Yantara, N.; Bruno, A.; Iqbal, A.; Jamaludin, N. F.; Soci, C.; Mhaisalkar, S.; Mathews, N., Designing Efficient Energy Funneling Kinetics in Ruddlesden-Popper Perovskites for High-Performance Light-Emitting Diodes. *Advanced Materials* **2018**, *30* (33), 1800818.

11. Chin, X. Y.; Perumal, A.; Bruno, A.; Yantara, N.; Veldhuis, S. A.; Martínez-Sarti, L.; Chandran, B.; Chirvony, V.; Lo, A. S.-Z.; So, J.; Soci, C.; Grätzel, M.; Bolink, H. J.; Mathews, N.; Mhaisalkar, S. G., Self-assembled hierarchical nanostructured perovskites enable highly efficient LEDs via an energy cascade. *Energy & Environmental Science* **2018**, *11* (7), 1770-1778.
12. Liu, Y.; Cui, J.; Du, K.; Tian, H.; He, Z.; Zhou, Q.; Yang, Z.; Deng, Y.; Chen, D.; Zuo, X.; Ren, Y.; Wang, L.; Zhu, H.; Zhao, B.; Di, D.; Wang, J.; Friend, R. H.; Jin, Y., Efficient blue light-emitting diodes based on quantum-confined bromide perovskite nanostructures. *Nature Photonics* **2019**, *13* (11), 760-764.
13. Huang, C.-Y.; Huang, S.-J.; Liu, M.-H. M., Hybridization of CsPbBr_{1.5}I_{1.5} perovskite quantum dots with 9,9-dihexylfluorene co-oligomer for white electroluminescence. *Organic Electronics* **2017**, *44*, 6-10.
14. Yao, E.-P.; Yang, Z.; Meng, L.; Sun, P.; Dong, S.; Yang, Y.; Yang, Y., High-Brightness Blue and White LEDs based on Inorganic Perovskite Nanocrystals and their Composites. *Advanced Materials* **2017**, *29* (23), 1606859.
15. Chang, C.-Y.; Solodukhin, A. N.; Liao, S.-Y.; Mahesh, K. P. O.; Hsu, C.-L.; Ponomarenko, S. A.; Luponosov, Y. N.; Chao, Y.-C., Perovskite white light-emitting diodes based on a molecular blend perovskite emissive layer. *Journal of Materials Chemistry C* **2019**, *7* (28), 8634-8642.
16. Singldinger, A.; Gramlich, M.; Gruber, C.; Lampe, C.; Urban, A. S., Nonradiative Energy Transfer between Thickness-Controlled Halide Perovskite Nanoplatelets. *ACS Energy Letters* **2020**, 1380-1385.
17. Hofmann, F. J.; Bodnarchuk, M. I.; Dirin, D. N.; Vogelsang, J.; Kovalenko, M. V.; Lupton, J. M., Energy Transfer from Perovskite Nanocrystals to Dye Molecules Does Not Occur by FRET. *Nano Letters* **2019**, *19* (12), 8896-8902.
18. Smith, M. D.; Connor, B. A.; Karunadasa, H. I., Tuning the Luminescence of Layered Halide Perovskites. *Chemical Reviews* **2019**, *119* (5), 3104-3139.
19. Cortecchia, D.; Yin, J.; Petrozza, A.; Soci, C., White light emission in low-dimensional perovskites. *Journal of Materials Chemistry C* **2019**, *7* (17), 4956-4969.
20. Wang, X.; Meng, W.; Liao, W.; Wang, J.; Xiong, R.-G.; Yan, Y., Atomistic Mechanism of Broadband Emission in Metal Halide Perovskites. *The Journal of Physical Chemistry Letters* **2019**, *10* (3), 501-506.
21. Yangui, A.; Garrot, D.; Lauret, J. S.; Lusson, A.; Bouchez, G.; Deleporte, E.; Pillet, S.; Bendeif, E. E.; Castro, M.; Triki, S.; Abid, Y.; Boukheddaden, K., Optical Investigation of Broadband White-Light Emission in Self-Assembled Organic-Inorganic Perovskite (C₆H₁₁NH₃)₂PbBr₄. *The Journal of Physical Chemistry C* **2015**, *119* (41), 23638-23647.
22. Cho, I.-W.; Ryu, M.-Y., Effect of energy transfer on the optical properties of surface-passivated perovskite films with CdSe/ZnS quantum dots. *Scientific Reports* **2019**, *9* (1), 18433.
23. Wang, C.; Xue, D.; Shen, X.; Wu, H.; Zhang, Y.; Cui, H.; Yu, W. W., White light-emitting devices based on ZnCdS/ZnS and perovskite nanocrystal heterojunction. *Nanotechnology* **2019**, *30* (46), 465201.
24. Chen, S.; Chen, C.; Bao, C.; Mujahid, M.; Li, Y.; Chen, P.; Duan, Y., White Light-Emitting Devices Based on Inorganic Perovskite and Organic Materials. *Molecules* **2019**, *24* (4), 800.
25. Mao, J.; Lin, H.; Ye, F.; Qin, M.; Burkhartsmeyer, J. M.; Zhang, H.; Lu, X.; Wong, K. S.; Choy, W. C. H., All-Perovskite Emission Architecture for White Light-Emitting Diodes. *ACS Nano* **2018**, *12* (10), 10486-10492.
26. Jamaludin, N. F.; Yantara, N.; Ng, Y. F.; Bruno, A.; Chandran, B. K.; Chin, X. Y.; Thirumal, K.; Mathews, N.; Soci, C.; Mhaisalkar, S., Perovskite templating via a bathophenanthroline additive for efficient light-emitting devices. *Journal of Materials Chemistry C* **2018**, *6* (9), 2295-2302.

27. Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T.-W., Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes. *Science* **2015**, *350* (6265), 1222-1225.
28. Yantara, N.; Jamaludin, N. F.; Febriansyah, B.; Giovanni, D.; Bruno, A.; Soci, C.; Sum, T. C.; Mhaisalkar, S.; Mathews, N., Designing the Perovskite Structural Landscape for Efficient Blue Emission. *ACS Energy Letters* **2020**, 1593-1600.
29. Guo, F.; Karl, A.; Xue, Q.-F.; Tam, K. C.; Forberich, K.; Brabec, C. J., The fabrication of color-tunable organic light-emitting diode displays via solution processing. *Light: Science & Applications* **2017**, *6* (11), e17094-e17094.
30. Ng, Y. F.; Kulkarni, S. A.; Parida, S.; Jamaludin, N. F.; Yantara, N.; Bruno, A.; Soci, C.; Mhaisalkar, S.; Mathews, N., Highly efficient Cs-based perovskite light-emitting diodes enabled by energy funnelling. *Chemical Communications* **2017**, *53* (88), 12004-12007.
31. Rossi, A.; Price, M. B.; Hardy, J.; Gorman, J.; Schmidt, T. W.; Davis, N. J. L. K., Energy Transfer between Perylene Diimide Based Ligands and Cesium Lead Bromide Perovskite Nanocrystals. *The Journal of Physical Chemistry C* **2020**, *124* (5), 3306-3313.
32. Chen, P.; Meng, Y.; Ahmadi, M.; Peng, Q.; Gao, C.; Xu, L.; Shao, M.; Xiong, Z.; Hu, B., Charge-transfer versus energy-transfer in quasi-2D perovskite light-emitting diodes. *Nano Energy* **2018**, *50*, 615-622.
33. Li, Z.; Chen, Z.; Yang, Y.; Xue, Q.; Yip, H.-L.; Cao, Y., Modulation of recombination zone position for quasi-two-dimensional blue perovskite light-emitting diodes with efficiency exceeding 5%. *Nature Communications* **2019**, *10* (1), 1027.