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Efficient near-infrared light-emitting diodes based on organometallic halide perovskite–poly(2-ethyl-2-oxazoline) nanocomposite thin films†

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Organometallic halide perovskites have recently drawn considerable attention for applications in light emission diodes (LEDs). However, the small exciton binding energy of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite has the concerns of large exciton dissociation and low radiative recombination on its use in near-infrared LEDs (NIR-LEDs). Herein, we propose and demonstrate that the introduction of poly(2-ethyl-2-oxazoline) (PEtOz) into the perovskite can simultaneously improve the recombination rate and radiative decay rate for improving perovskite LED performances. Additionally, our approach results in smooth perovskite films with increased thickness, reduced roughness, and pin-hole free, which facilitates other film deposition on top for practical device fabrication, and reduces current leakage. After optimizing the perovskite–PEtOz nanocomposite emission layer in NIR-LEDs (emission peak at 760 nm), a high radiance of $12.3 \text{ W sr}^{-1} \text{ m}^{-2}$ and 70-fold enhancement of the external quantum efficiency (EQE) compared to that of the pristine perovskite case are achieved. The maximum EQE reaches 0.76%, which is the highest EQE reported so far for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ based NIR-LEDs. The simplicity of our fabrication approach combined with the outstanding device performances further highlights the enormous potential of perovskite-based LEDs.

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Introduction

Organic–inorganic hybrid perovskites have recently emerged as low-cost active materials in photovoltaic devices. Their exceptional electronic and optical characteristics boosted the power conversion efficiency from 3.8% to the present record of 22.1%, exceeding the state-of-the-art performance of crystalline silicon thin film solar cells.^{1–3} Hand-in-hand with their superior photovoltaic performance, perovskite materials exhibit strong photoluminescent (PL) properties; their emission colour can be easily tuned by modifying the precursor solutions and controlling the preparation temperatures, making them desirable candidates in the low-cost light emitting diodes (LEDs) and lasers.^{4–7} In particular, MAPbI_3 (MA =

CH_3NH_3^+) perovskites exhibit near infrared (NIR) emission with narrow spectra in the range of 750–800 nm, which makes them attractive for potential applications in night-vision devices, chemical sensing, and information secured displays.⁸

Just over the last few years, great progress involving optimization of device structures and thin film depositions has been made in perovskite LEDs (PeLEDs), especially for green emitting MAPbBr_3 devices which demonstrated bright electroluminescent (EL) at room temperature.^{9–16} Recently, MAPbBr_3 PeLEDs with high efficiency have been demonstrated through an optimized nanograin engineering process for controlling the perovskite grain size and reducing metallic Pb atoms.¹⁷ The findings of that work show that the small perovskite grain size can limit the exciton diffusion and dissociation in LEDs, which is an opposite requirement to the perovskite solar cells where a large grain size is shown to be crucial to achieve efficient charge carrier diffusion and dissociation.¹⁸ Other reports further validated that higher PL quantum yields can be obtained from nanostructured perovskites (*i.e.* nanoparticles, nanoplatelets, and nanowires) than from their bulk polycrystalline counterparts.^{4,5,19}

As ultrathin (<50 nm) perovskite layers are typically used for PeLEDs, this places a concern of poor film formation which may cause severe current leakage.¹⁰ Although improved film

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quality and improved electrical properties were obtained by introducing dielectric and conductive polymers into perovskite precursors, great reduction of the perovskite crystal size and suppression of exciton dissociation were not demonstrated by polymer blending in previous studies.^{10,13,20} For MAPbI₃ PeLEDs, the exciton binding energy of MAPbI₃ (16 meV) is much smaller than those of MAPbI_{3-x}Cl_x (50 meV) and MAPbBr₃ (60 meV); thus serious luminescence loss will arise from thermal ionization of the bonded excitons.^{21–23} It is more challenging and more desired to reduce the exciton diffusion and dissociation in MAPbI₃ perovskite devices. So far, the highest EQE reported for NIR PeLEDs based on MAPbI₃ bulk films is about 0.04%.^{24,25}

In this work, through introducing the non-ionic and dielectric poly(2-ethyl-2-oxazoline) (PEtOz) polymer into perovskite precursors of methylammonium iodide (MAI) and lead iodide (PbI₂), MAPbI₃ perovskite nanocrystals are obtained with a controllable grain size (20–30 nm) by this simple method. The non-ionic and dielectric PEtOz formed a polymer matrix that wrapped the perovskite nanocrystals and suppressed the exciton diffusion in the perovskite–PEtOz nanocomposite films. Also, the PEtOz matrix passivated the exciton dissociation at grain boundaries that reduced the recombination by trapping sites and improved the emission properties of the MAPbI₃ perovskite. In addition, the perovskite–PEtOz films, which can be easily deposited on different substrates are pin-hole free, thick (up to 160 nm) and cover the whole underneath substrates with low surface roughness (*ca.* 5 nm), which favours the formation of other films on top for fabricating practical devices and ensures low current leakage between the active layer and injection layers. NIR PeLEDs using perovskite–PEtOz nanocomposite emission layers exhibit a high radiance of 12.3 W sr⁻¹ m⁻² and an EQE of 0.76%, which represents a 70-fold increase in the quantum efficiency compared with control devices employing pristine perovskite films. To the best of our knowledge, this is the highest EQE reported so far for MAPbI₃ NIR PeLEDs. The EL spectra of perovskite–PEtOz devices are identical to their corresponding PL spectra and remain stable under various biases, which is important for practical LED applications.

Results and discussion

Formation of perovskite–PEtOz nanocomposite thin films

PEtOz is a well-known polymer compatibilizer which has been widely used for biomedical applications such as drug delivery and biosensors due to its excellent biocompatibility, as well as an effective interface material in polymer solar cells.^{26,27} Its non-ionic and dielectric character offers the prospect of using PEtOz in PeLEDs as it is expected to be free from charge-trapping or exciton-quenching effects. Besides, PEtOz also offers excellent solubility in both water and most popular organic solvents, and possesses excellent thermal-processing capabilities that can be compatible with the process of the perovskite formation *via* thermal annealing.

Perovskite–PEtOz nanocomposite films are formed by incorporating PEtOz, MAI and PbI₂ blends in a binary solvent mixture of gamma-butyrolactone and dimethyl sulfoxide with a concentration of 35 wt%. We vary the mass ratio of PEtOz/PEtOz:MAI:PbI₂ and label the corresponding films and devices by the weight ratio of PEtOz to the perovskite precursors throughout the discussion of this work. For example, the label of 5% stands for the 5% weight ratio of PEtOz in the PEtOz:MAI:PbI₂ blended precursor powder. Perovskite–PEtOz nanocomposite films can be easily deposited by spin-coating on various substrates such as bare glass, ITO coated glass or silicon wafers. Since PEtOz has good shear stability with a high kinematic viscosity of about 7×10^{-5} m² s⁻¹ (in room temperature aqueous solution), the PEtOz in the precursor solution will diminish the diffusion of the perovskite precursors during the solvent evaporation procedure in high-speed spin coating, which results in evenly distributed perovskite precursors in the thin films. In addition, the PEtOz forms a polymer matrix that limits the growth of the perovskite crystal during the annealing procedure. Eventually, by the confinement of the viscous PEtOz polymer, small sized and well-dispersed perovskite nanocrystals are formed within the perovskite–PEtOz thin film after spin coating at 5000 rpm for 50 seconds and thermal annealing at 100 °C for 10 minutes.

Properties of the perovskite–PEtOz nanocomposite thin film

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the films. XRD patterns of perovskite films on glass/PEDOT:PSS substrates are shown in Fig. 1. Both pristine and perovskite–PEtOz films show strong peaks at $2\theta = 14.1^\circ$, 28.4° , and 31.9° , which commensurate with the (110), (220) and (310) planes of the MAPbI₃ perovskite, respectively, and indicate the formation of the tetragonal perovskite structure consistent with the previously reported crystal structure.^{28–30} With increasing the content of PEtOz in the

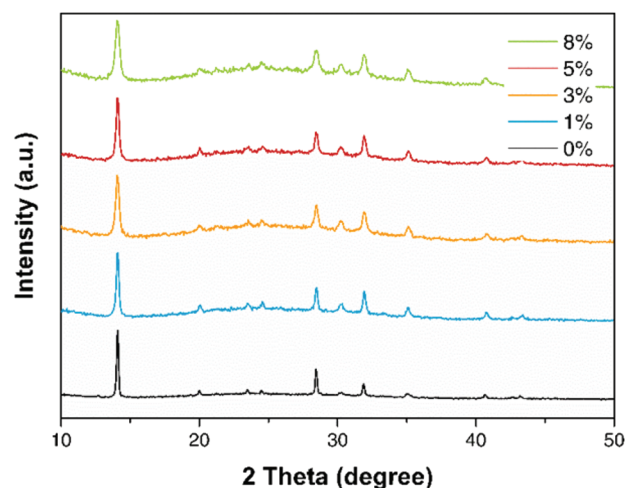


Fig. 1 X-ray diffraction patterns for perovskite–PEtOz nanocomposite thin films with different contents of PEtOz prepared on glass/PEDOT:PSS substrates.

nanocomposite films, the XRD peak slightly broadens, and the intensity slightly decreases. However, the peak positions do not change with the variation of the PEOz ratio, indicating that the perovskite crystal structure is maintained in all films, while the size of the perovskite nanocrystals decreases as the content of PEOz increases. The average sizes of the perovskite nanocrystals estimated from the prominent (110) reflex using the Debye–Scherrer equation on the assumption of spherical perovskite crystals are ~48, ~33, ~28, ~26, and ~21 nm for samples with PEOz weight ratios of 0%, 1%, 3%, 5% and 8%, respectively. These results confirm that our solution processing relying on the mixing of PEOz in the perovskite precursor can effectively reduce the size of the perovskite nanocrystals.

SEM images shown in Fig. 2 manifest the morphology evolution of the perovskite–PEOz nanocomposite films with the increasing PEOz content. In the pristine perovskite films without the PEOz polymer (Fig. 2a), MAPbI₃ perovskite crystals have a relatively large grain size. The apparent grain size (50–200 nm) observed from the planar view SEM image is larger than the size estimated from the XRD pattern as stated above, suggesting that all perovskite domains in the SEM image consist of smaller nanocrystals. As illustrated in Fig. 2b–d, when the PEOz polymer is involved in the film formation, the MAPbI₃ perovskite nanocrystals become noticeably smaller and are distributed uniformly across the whole sample. However, owing to the relatively low electron densities in

perovskite–PEOz nanocomposite films, it is difficult to resolve the sizes of these small nanocrystals from their corresponding SEM images. Besides, it can be found that a number of large pin-holes are distributed in the pristine perovskite film (marked as red dash-line circles in Fig. 2a), that will create electrical shunting paths and increase the leakage current. With increasing the PEOz concentration, these voids are filled by the PEOz polymer which results in pin-hole free thin films where the electrical shunting paths are blocked. The magnitude of the leakage current drops as a result, which is reflected by the shunt resistance (R_{sh}) of photovoltaic devices (Fig. S1†) – the higher the R_{sh} , the lesser the leakage current that travels through the shunt resistor.³¹ For devices with 0%, 1%, 3% and 5% perovskite–PEOz films, the R_{sh} is 459, 1.43×10^3 , 1.92×10^3 and $2.41 \times 10^3 \Omega \text{ cm}^2$, respectively, suggesting that in perovskite–PEOz nanocomposite films, leakage currents can be effectively reduced by filling the pin-holes with the PEOz polymer.

To further evaluate the topography of the perovskite–PEOz nanocomposite films, atomic force microscopy (AFM) study was performed (Fig. S2†). The surface of the perovskite–PEOz nanocomposite films became smoother compared to pristine perovskite films, with an RMS roughness of 8.7, 4.7, 5.1 and 4.8 nm for films with 0%, 1%, 5% and 8% of PEOz, respectively. The smooth surface of the perovskite layer is an important factor for PeLEDs since it ensures the homogeneous depo-

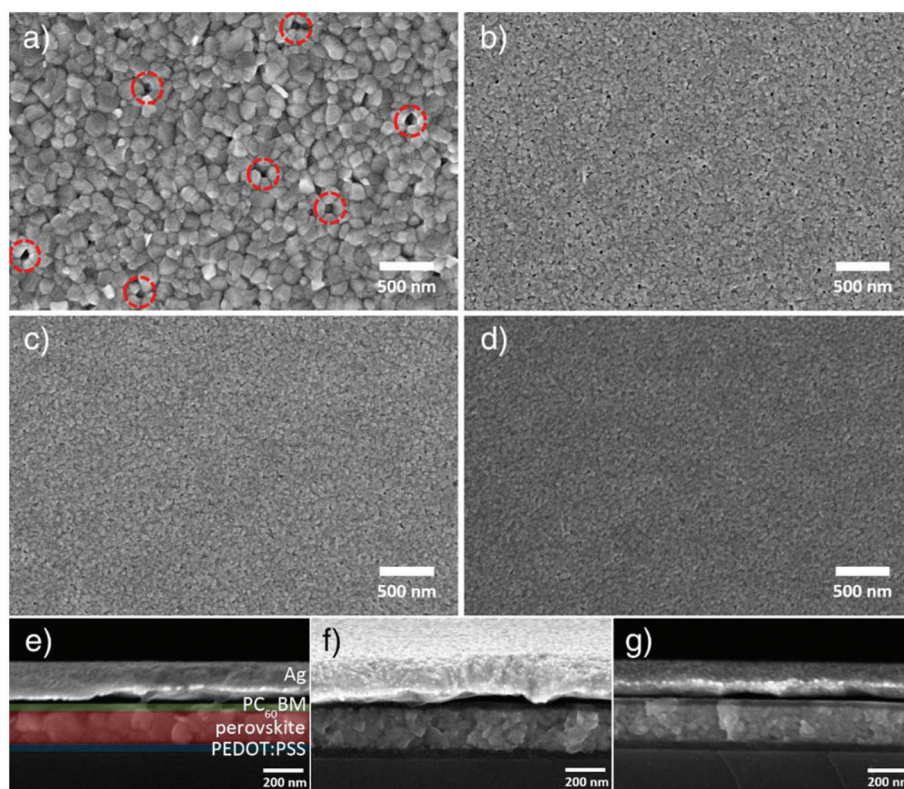


Fig. 2 (a)–(d) Planar view SEM images of perovskite–PEOz films on glass/PEDOT:PSS substrates, with the PEOz content of 0%, 1%, 3% and 5%, respectively. (e)–(g) Cross-sectional SEM images of perovskite–PEOz films deposited between ITO glass/PEDOT:PSS and PC₆₀BM/Ag, with the PEOz content of 0%, 3% and 5%, respectively.

sition of a planar electron injection layer, preventing the undesired electrical shunting path by direct contact of the perovskite layer and Ag cathode. However, excess PETzOz aggregates and forms micrometre-sized polymer particles on top of the nanocomposite films (Fig. S3†), which hinders the carrier injection and is detrimental to the performance of PeLEDs. Hence, we will focus on the nanocomposite films with a lower PETzOz content (<8%) for the discussion below.

From the cross-sectional SEM images shown in Fig. 2e–g, we re-confirm that smaller and densely packed perovskite nanocrystals are formed in perovskite–PETzOz films, and that PC₆₀BM electron injection layers were well coated on top of them. We point out that the thickness of the perovskite layer (~160 nm) in our NIR PeLEDs is larger than that in previous reports where typical values were less than 50 nm.^{9,10} Thinner perovskite layers deposited using a precursor with reduced concentration would give rise to poor film coverage and reduction in the emission intensity. Considering recent reports on efficient PeLEDs with similar or even thicker perovskite layers, the requirement of an ultrathin perovskite layer (<50 nm) proposed by the pioneering works is not a universal guideline for PeLEDs, but should be subjected to material processing processes, conditions and device structures.^{11,17} With the above morphology studies, we confirm that smooth perovskite films are obtained when the PETzOz polymer is mixed in the precursors, so that small perovskite nanocrystals are formed and embedded in the PETzOz matrix resulting in pin-hole free thin films.

Fig. S4† shows the UV-vis absorption spectra of perovskite–PETzOz thin films with different PETzOz contents, and a PL spectrum of the 5% thin film that formed on glass/PEDOT:PSS substrates. Absorption spectra cover the entire visible spectral range with a band edge around 760 nm, which is attributed to the MAPbI₃ perovskite with a direct bandgap of 1.63 eV. Although we observe a slight deviation in the absorption slopes below the band edge that could appear from light scattering, there are no noticeable position alterations among samples with different PETzOz weight ratios, indicating the insignificant change in the bandgap positions of the perovskite semiconductor. Interestingly, as shown in Fig. 3a, when excited by a pulsed 405 nm laser under the same excitation and detection conditions, the PL intensity of the perovskite–PETzOz nanocomposite film increases consistently when the PETzOz content increases. Meanwhile, PL spectra are similar in profile for all nanocomposite films, confirming that the PETzOz matrix does not affect the band edge of MAPbI₃ perovskite semiconductors. More likely, the effect of PETzOz on the MAPbI₃ perovskite is only due to the crystallization and film morphology which will affect the PeLED performances. However, the presence of the PETzOz matrix can also influence free or bound carrier dynamics. Thus, we performed PL decay measurements on films deposited on glass substrates and encapsulated with PMMA (see details in the ESI†). From the estimated PL lifetimes and their relative contributions that are summarized in Table S1,† it is observed that with increasing the amount of PETzOz in the nanocomposite film, τ_{avg} gradually

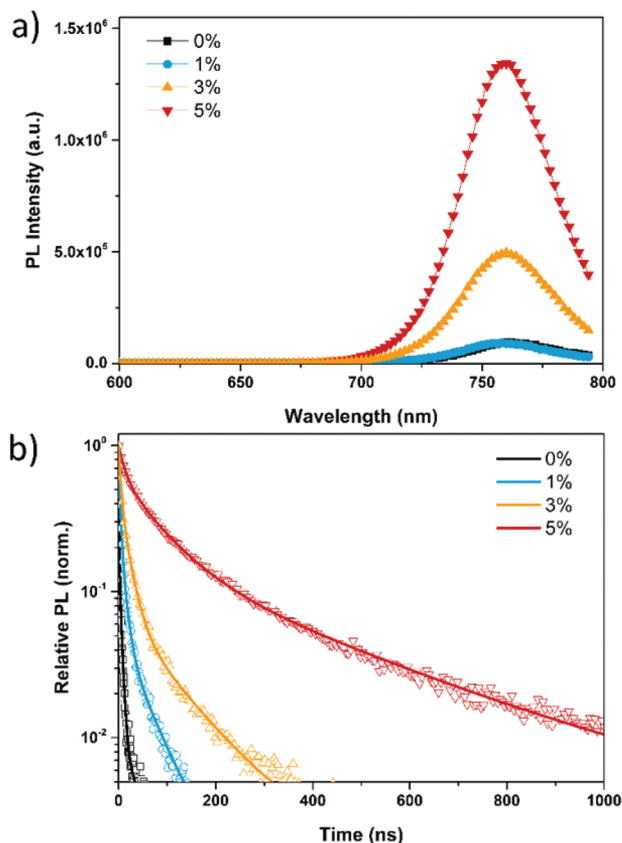


Fig. 3 (a) PL intensities and (b) PL decays of perovskite–PETzOz nanocomposite thin films on glass substrates with different PETzOz contents.

increases from 4.5 to 243 ns. Such a prolonged radiative lifetime and increased PL intensity indicate a gradual reduction of nonradiative recombination rates in perovskite–PETzOz nanocomposite films with the increasing PETzOz content. This also demonstrates that the PETzOz polymer matrix can passivate the perovskite grain boundaries and prevent the excitons from diffusing into trapping sites located between perovskite nanocrystals.

PeLED performance

In NIR PeLEDs, perovskite–PETzOz nanocomposite films were employed as the emission layer with a device configuration as shown in Fig. 4a: ITO/PEDOT:PSS (30 nm)/perovskite–PETzOz (160 nm)/PC₆₀BM (30 nm)/Ag (140 nm). The current density–voltage characteristics and device performance of the NIR PeLEDs are shown in Fig. 4c–e.

With the increase of the PETzOz content in the nanocomposite film, the current density gradually reduces due to the electrically insulating properties of the PETzOz polymer. Particularly, as shown in Fig. 4c, there is a significant reduction in the current density from devices with the pristine perovskite film compared to those with perovskite–PETzOz nanocomposite films. This can be explained by the fact that the PETzOz polymer physically fills the nanocrystal boundaries, forming a dielectric matrix to block the current path between

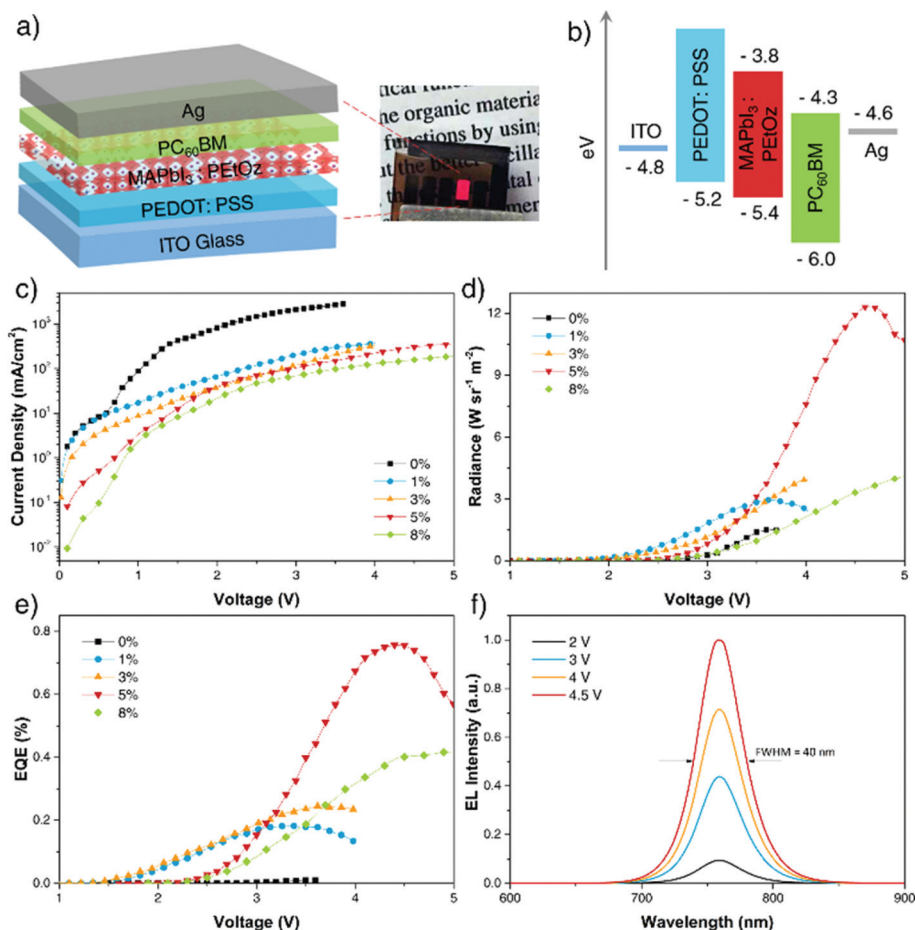


Fig. 4 (a) Device structure of the NIR PeLEDs, along with the respective photograph of an operating device, and (b) energy levels of the device. Characteristics of the NIR PeLEDs with different contents of PEtOz: (c) current density versus voltage; (d) radiance versus voltage; (e) EQE versus voltage; (f) EL spectra of the 5% perovskite-PEtOz device under different biases.

the nanocrystals, resulting in lower current densities for perovskite-PEtOz devices. Moreover, the injected charges are confined within the perovskite nanocrystals by the PEtOz polymer matrix that favours the radiative recombination. As a consequence, lower turn-on voltages and higher radiances are obtained from the nanocomposite perovskite-PEtOz devices (Fig. 4d) compared to the device using the pristine perovskite.

In general, the current density and radiance rise rapidly after the PeLED is turned on, demonstrating favourable electrical and optical properties of our NIR PeLEDs. However, when the PEtOz content increases from 1% to 8%, the charge injection becomes hindered by the insulating polymer matrix, resulting in gradually increased turn-on voltages. The trend of the turn-on voltage change in the device also follows the work function (WF) change in the thin film. When the PEtOz concentration increases from 0 (pristine perovskite) to 1% perovskite-PEtOz, WF decreases from 5.14 eV to 4.69 eV. The WF reduction can be explained by the change of the crystal size in the nanocomposite perovskite films that is also observed in previous work with a reduced perovskite crystal size.¹⁷ Since the optical bandgap of the nanocomposite films did not

change as demonstrated in the PL measurements, this WF reduction favours the hole injection from the PEDOT:PSS layer to the perovskite-PEtOz active layer (Fig. 4b). However, when the PEtOz concentration is further increased towards 8%, owing to the large ionization energy of PEtOz, the WF tends to increase from 4.69 eV (1% case) to 4.96 eV (8% case), which explains the change in the turn-on voltages. As a consequence, by optimizing the concentration of PEtOz in the devices, the reduced injection barrier and improved radiance are achieved in our NIR PeLEDs.

The maximum radiance and EQE of NIR PeLED devices with various PEtOz ratios are given in Table 1. By increasing

Table 1 Device performance for NIR PeLEDs with various PEtOz contents in the active layer

PEtOz ratio	Max. radiance ($\text{W sr}^{-1} \text{m}^{-2}$)	Max. EQE (%)
0%	1.48	0.01
1%	2.96	0.18
3%	4.02	0.25
5%	12.31	0.76
8%	4.21	0.42

the PETz content from 0% to 5% in the perovskite–PETz nanocomposite film, both the radiance and EQE increase. In particular, a peak radiance of $12.31 \text{ W sr}^{-1} \text{ m}^{-2}$ is achieved in the 5% perovskite–PETz device, which possesses a peak EQE of 0.76%. This efficiency represents a ~ 70 -fold increase compared to that of the control pristine perovskite device. To the best of our knowledge, this EQE is the highest value obtained for NIR PeLEDs based on MAPbI₃ thin films in the literature (previous best reported EQE for this kind of devices was 0.04%).²⁵ It should be noted that at higher ratios, the device efficiency drops due to inhibited charge injection, suggesting that the 5% PETz weight ratio provides an optimized electrical environment for our NIR PeLEDs.

For a multi-layered PeLED structure, radiative recombination processes might occur at the interfaces, which often modify the EL spectrum and limit device performances. As observed in Fig. 4f, stable EL spectra from the 5% perovskite–PETz PeLED under different biases prove that undesired radiative recombination pathways are effectively eliminated. Therefore, strong EL signals with a full width at half maximum (FWHM) of 40 nm from the MAPbI₃ perovskite are obtained without any additional emission peaks, which is important for practical LED applications. We also investigate the effects of the PETz concentration on the EL spectra. As shown in Fig. S5,† MAPbI₃ emission centred at 760 nm is observed from devices with different PETz ratios (0% to 5%). There is only a small variation among the EL spectra which can be attributed to the light scattering caused by the PETz polymer matrix. With excess PETz ratio (*i.e.* 8% or higher) in the perovskite–PETz nanocomposite film, the EL spectrum blue shifts compared to lower PETz contents or pristine devices. This can be explained by the quantum confinement of excitons in the perovskite nanocrystals, which is also observed in an earlier report where perovskites are embedded in a small molecular matrix,³² suggesting that with a high PETz concentration in the film, the size of the perovskite nanocrystals tends to become smaller. However, for PeLEDs with higher PETz ratios, the charge injection is inhibited by the dielectrically polymer matrix, limiting the EL radiation efficiencies.

Regarding the dramatic decrease of the current density in the perovskite–PETz devices (Fig. 4c), it implies that the electric properties of the films are significantly changed upon the incorporation of the PETz polymer. We used a structure of Au/perovskite–PETz/Au to investigate the charge mobility of the perovskite–PETz film (see details in the ESI†).³³ The hole mobility of the pristine perovskite film is $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and becomes three orders lower ($3.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the 5% perovskite–PETz nanocomposite film. Therefore, the hole diffusion length (L_{diff}) of the pristine perovskite is estimated to be $L_{\text{diff}} = \sqrt{D\tau} = \sqrt{\mu\tau kT/q} = (0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \times 4.5 \times 10^{-9} \text{ s} \times 0.026 \text{ V})^{0.5} \approx 90 \text{ nm}$. However, L_{diff} of the 5% perovskite–PETz film is $(3.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \times 234 \times 10^{-9} \text{ s} \times 0.026 \text{ V})^{0.5} \approx 45 \text{ nm}$, which is significantly shorter than that for the pristine perovskite film. The shortened L_{diff} ensures that most of the excess carriers recombine in the perovskite–PETz active layer before passing through the entire layer. This is evidenced in the

photovoltaic performance of the devices (Fig. S1†), where the photocurrents of the perovskite–PETz devices are significantly lower than the pristine perovskite device, indicating that most of the photo-generated excess carriers recombine in the active layer and have little chance of traveling out and being collected by the electrode in the perovskite–PETz devices. In consideration of the enhanced PL intensity in the perovskite–PETz thin films, this improved recombination within the nanocomposite active layer contributes more to the radiative recombination, instead of non-radiative pathways. Consequently, the PETz in the perovskite nanocomposite films not only contributes to the formation of small sized perovskite nanocrystals but also offers an excellent charge confinement matrix. As a result, the PL intensity increases and the charge diffusion length decreases in perovskite–PETz films, which boosts the performance of our PeLEDs using the optimized perovskite–PETz nanocomposite films as the emission layers.

Conclusions

In summary, by introducing the PETz polymer into MAPbI₃ perovskite precursors, we propose and demonstrate that the crystal size of the perovskite can be reduced to about 20–30 nm. With the control of the crystal size, we experimentally realised the improvement in the charge recombination in the perovskite–polymer nanocomposite films and enhancement in the radiative rate by suppression of the exciton diffusion. Meanwhile, the pin-hole free perovskite–PETz nanocomposite with the surface roughness considerably reduced by $\sim 40\%$ compared to pristine perovskite films is realized. The reduction of the pin-holes and surface roughness of the nanocomposite films reduces the current leakage and facilitates the formation of films on top that favours the device fabrication. As a result, the optimized NIR PeLEDs with 5% PETz exhibited a high radiance ($12.31 \text{ W sr}^{-1} \text{ m}^{-2}$) and an EQE of 0.76%, which represents a ~ 70 -fold increment in the quantum efficiency compared to the control device using the pristine perovskite film. Besides, EL spectra from the perovskite–PETz based devices retain their shape and peak positions under different biases. The work therefore contributes to the evolution of NIR PeLEDs for their practical applications.

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