Organic-Inorganic Hybrid Composites as an Electron Injection Layer in Highly Efficient Inverted Green-Emitting Polymer LEDs

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ABSTRACT

Organic-inorganic hybrid light emitting diodes (HyLEDs) consist of an organic emission layer in combination with at least one metal oxide charge injection layer in an inverted structure. Low temperature, solution processing of metal oxide charge injection layers is one of the key factors in reducing the manufacture cost of HyLEDs. Herein, we report the use of composite materials, comprising conjugated polyelectrolytes (CPE) and zinc oxide nanoparticles (ZnO NPs), as the electron injection layer (EIL) in highly-efficient, green-light-emitting poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) polymer LEDs that are carefully optimised for use in an inverted HyLED architecture for the first time. The composite CPE:ZnO EILs are processed via a room temperature, one-step, solution deposition and enable superior device performance relative to ZnO NPs on their own. We find that specifically, they (i) improve EIL morphology, reducing surface roughness as well as pin-hole size and density, (ii) induce a favourable vacuum level shift for electron injection by coordinate bonding between the CPE and ZnO constituents, and (iii) reduce interfacial quenching by passivation of ZnO chemical defects caused by oxygen vacancies. This work is also the first demonstration that blending ZnO NPs and CPE supports much faster electroluminescence turn-on times ($\sim 7.12 \mu\text{s}$) than for traditional ZnO/CPE bilayer devices ($\sim 0.4 \text{ s}$) via ‘locking’ of the CPE mobile ions, as well as higher device performance. This demonstrates good suitability for display applications. After optimisation of the EIL composition and the thickness of the F8BT emissive layer, we achieve promising device efficiencies of 16.5 cd/A and 5.41 lm/W for devices with a $1.1 \mu\text{m}$ thick F8BT layer, which is particularly relevant for potential roll-to-roll fabrication. These results clearly demonstrate the potential that this organic-inorganic composite EIL material has for the realisation of cheap, scalable and highly efficient, printable HyLED devices.

1. Introduction

Polymer and other soluble semiconductor light emitting diodes (LEDs) have been the subject of intense research activity due to their compatibility with high throughput printing-based manufacturing for displays.[1] First commercial inkjet-printed devices have now reached the market but there is still scope for improvement in both device performance and stability. Polymer LEDs (PLEDs) generally comprise a small number of layers due to the constraints of layer-on-layer solution deposition. A critical factor in their performance then becomes the choice of appropriate charge injection layers. For example low workfunction metals such as calcium and barium have traditionally been used as electron injection layers (EILs)[2–6] but these are both oxygen and moisture sensitive, requiring expensive inert-atmosphere processing and encapsulation.[7] Metal complexes like LiF and Cs₂CO₃ have also be utilised and offer somewhat greater stability.[8]

Organic-inorganic hybrid light emitting diodes (HyLEDs) make use of one or more air stable metal oxide charge injection layers to help increase the operational device lifetime.[9] Typically, HyLEDs are fabricated in an inverted architecture with an n-type metal oxide EIL deposited on top of a semi-transparent indium tin oxide (ITO) layer as cathode,[10–13] followed by the emissive layer (EML) and a high workfunction hole injection layer (HIL) plus top anode contact. Titanium (TiO₂), zirconium (ZrO₂) and zinc (ZnO) oxides have all been used as HyLED EILs, with both dense and nanoporous film microstructures.[10,11,14]

ZnO is the focus of the present paper and is studied as an EIL within poly(9,9-dioctylfluorene-co-benzothiadiazole (F8BT) EML devices. Its deep conduction band at 4.1 eV below vacuum (c.f. F8BT lowest unoccupied molecular orbital (LUMO) at -3.5 eV) introduces a significantly larger electron injection barrier than for TiO₂ (-3.8 eV) and ZrO₂ (-3.0 eV),[10,11] correspondingly

reducing device performance. To overcome this limitation, thin interfacial conjugated polyelectrolyte layers (CPEs) have previously been added to improve electron injection.[15–17] However such CPEs can have long, ionic-motion-related, electroluminescence (EL) turn-on times (of order seconds) that make them unsuitable for display applications.[18–20] Additionally, the high temperatures (up to 450 °C) used in the fabrication of ZnO (and other oxides)[10,11] are incompatible with flexible plastic substrates.[21] As an alternative approach, solutions of colloidal ZnO nanoparticles (NPs) fabricated at room temperature have been used to fabricate flexible devices. Issues remain, however, with particle agglomeration, leading to poor surface coverage on ITO and a consequence need for multiple deposition steps to achieve good performance.[22,23] Therefore presently there is a need for solution processed electron injection materials that can be fabricated in one step without the need for high annealing temperatures for the realisation of printable HyLEDs. ZnO nanoparticle/polyelectrolyte composites have been demonstrated as electron injection layers in conventional PLED device structures[24,25], however their use in inverted device structures remains underexplored and are likely to require re-optimisation for peak performance.

In this paper, we elucidate in detail the performance of a ZnO:CPE composite EIL within inverted green-light-emitting F8BT HyLEDs, comparing layers with different weight fractions of CPE and ZnO NPs to compact ZnO (c-ZnO), ZnO NP only and c-ZnO/CPE bilayer EILs. The CPE, namely poly[(9,9-bis((8-(3-methyl-1-imidazolium)octyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene))] dibromide (F8imFO₄-Br) is blended with conventional ZnO NPs, producing an EIL that can be solution processed as a single layer without the need for any additional annealing step and consequently that has great potential for flexible HyLEDs. Optimisation of both the CPE:ZnO NP EIL composition and the F8BT EML thickness enables

excellent PLED performance with a maximum luminous efficiency of 16.5 cd/A (at 19,590 cd/m²) and a maximum luminous power efficiency of 5.4 lm/W (at 258 cd/m²) for 1.1 μ m EML thickness devices. The CPE:ZnO blend EILs offer several further advantages, namely (i) no high temperature annealing required unlike dense ZnO, (ii) fast EL turn-on times ($\approx 7 \mu$ s) compared to ZnO/CPE bilayers and (iii) improved film quality in terms of better surface coverage and reduced roughness relative to ZnO NP only layers. The latter leads to the requirement of only a single deposition step and taken together they offer great potential for the fabrication of cheap, scalable and highly efficient flexible HyLED devices.

2. Results and Discussion

To assess the suitability of CPE:ZnO NP composite materials in HyLEDs, EILs with different CPE weight fractions, specifically 0 (ZnO NP only), 2.25, 4.5, 9 and 18 wt%, were prepared and deployed in ITO/EIL/F8BT/MoO₃/Au PLED structures. The average size (diameter) of the bare ZnO NPs is 5.5 nm, whilst the average feature size for CPE:ZnO NP composite films is 13.4 nm.[24] We also compared the best performing CPE:ZnO NP EIL devices to c-ZnO and c-ZnO/CPE bilayer EIL PLEDs (see below). **Figure 1(a)** shows the device configuration of the HyLEDs with CPE:ZnO NP EILs and **Figure 1(b)** shows the corresponding energy level diagram, whilst **Figure 1(c)** shows the CPE:ZnO NP composite chemical structure.

Figure 1: (a) Schematic diagram of an ITO/EIL (35 nm)/F8BT (75 nm)/MoO₃ (10 nm)/Au (100 nm) HyLED employing a CPE:ZnO NP composite EIL and (b) corresponding energy level diagram (in eV below vacuum). (c) Schematic chemical structure for CPE:ZnO NP composite with coordinate bonding between the CPE ethylene glycol side-chain oxygen atoms and ZnO NP surface (left) and/or the CPE Br⁻ anions and NP Zn²⁺ ions (right). The expanded illustration of the EIL shows the structure of the CPE:ZnO NP composite, with the red and blue protuberances representing co-ordinate bonding between the Zn²⁺ ions and the oxygen moieties and Br ions respectively.

Figure 2: CPE(x wt%):ZnO NP EIL HyLED device performance. (a) current density and luminance vs voltage (J-V-L) and (b) luminous efficiency (cd/A) and luminous power efficiency (lm/W) vs luminance for $x = 0, 2.25, 4.5, 9$ and 18 wt% composite EIL layers.

Figure 2(a) shows the direct current (DC) density-voltage-luminance (J-V-L) characteristics for 75 nm thickness F8BT EML HyLEDs with x wt% CPE:ZnO NP composite EILs. The ZnO NP only ($x = 0$) device shows the lowest luminance turn-on voltage (as required to reach 1 cd/m² luminance), $V_{on} = 2.0$ V. The low turn-on voltage could be associated with the rougher ZnO NP surface causing preferred injection points; however in compact ZnO EIL film devices,[15,26] the low V_{on} values for ZnO only devices have previously been proposed to be due to straightforward injection of holes through MoO₃ into the F8BT resulting in hole accumulation at the F8BT/ZnO interface. This in turn generates an internal electric field that assists injection of electrons. As the

CPE wt% loading increases, the V_{on} values also slightly increase, to 2.2 V for 2.25 wt% CPE and then to 2.4 V for 4.5, 9 and 18 wt% CPE. The latter value is much closer to the average F8BT EML photon emission energy; the EL spectrum (**Figure S1**) peaks at 541 nm and has FWHM linewidth of 80 nm).

The ZnO NP only EIL HyLED shows an initial rapid increase in luminance above V_{on} , up to 2.5 V, however both the DC current density and luminance then saturate more quickly than for the CPE:ZnO NP composite EIL devices, eventually reaching a luminance, $L = 2,257 \text{ cd/m}^2$ at 10 V. This results in relatively low maximum luminous efficiency (LE) and luminous power efficiency (PE) values $LE_{max} = 0.34 \text{ cd/A}$ (at 4.4 V, 962 cd/m^2) and $PE_{max} = 0.30 \text{ lm/W}$ (at 3.2 V, 451 cd/m^2). By contrast, the $x \text{ wt\%}$ CPE:ZnO NP composite EIL devices show much larger increases in luminance above turn-on, reaching $L = 19,260, 27,780, 46,760$ and $44,260 \text{ cd/m}^2$ at 10 V DC for $x = 2.25, 4.5, 9$ and $18 \text{ wt\%}$, respectively. This translates into improved maximum device efficiencies of $LE_{max} = 1.14, 2.49, 4.06$ and 3.45 cd/A and $PE_{max} = 0.62, 2.15, 3.27$ and 2.70 lm/W for $x = 2.25, 4.5, 9$ and $18 \text{ wt\%}$, respectively. The ethylene glycol side-chains F8imFO,-Br have been shown to passivate ZnO NP surface defects by forming coordinate bonds with Zn^{2+} ions, as well as passivation because of bonding between the bromide anions and zinc cations.[24] This also allows the formation of uniform CPE:ZnO NP blends.[24] Passivation reduces F8BT luminescence quenching by the ZnO NPs[24,25]; to demonstrate this transient photoluminescence decay curves of F8BT thin films deposited on top of different CPE:ZnO EILs were recorded via time-correlated single photon counting (TCSPC) spectroscopy and are shown in **Figure S2**. We find that exciton lifetime of F8BT is only 1.62 ns when deposited upon ZnO NP only. However, this lifetime increases to 1.71, 1.73, 1.81 and 1.88 ns for 2.25wt%, 4.5wt%, 9wt% and 18wt% CPE blends respectively showing

the passivating effect of the CPE on the ZnO NPs and reduction in F8BT luminescence quenching via increase in radiative lifetime of F8BT exciton.

Figure S3 shows J-V-L and efficiency data for a HyLED device comprising of only an ITO/CPE electron injection layer with no ZnO NPs present (i.e. a CPE only EIL layer). Here, the luminance turn-on is 2.4 V and a luminance of $L = 1,475 \text{ cd/m}^2$ is reached at 10 V. However, the maximum luminance was found to be $L_{\text{max}} = 4,011 \text{ cd/m}^2$ (at 7.4 V). The device efficiencies are reduced to only $LE_{\text{max}} = 0.70 \text{ cd/A}$ (at $2,450 \text{ cd/m}^2$) and $PE_{\text{max}} = 0.45 \text{ lm/W}$ (at 788.6 cd/m^2). This shows that the presence of ZnO NPs is critical to device performance; electron injection into the F8BT likely occurs from the ZnO CB whilst the CPE induces a vacuum level shift in the ZnO to aid this injection.

To test the universality of the CPE(9wt%):ZnO electron injection layer, F8BT PLED devices were fabricated in a conventional structure consisting of ITO/PEDOT:PSS/Poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB)/F8BT/EIL/Al. Here, we compared our best performing CPE(9wt%):ZnO EIL with Ca, a commonly used low workfunction EIL. **Figure S4** shows the J-V-L and efficiency data for each device; both show a luminance turn-on of $\sim 2.0 \text{ V}$, whilst the luminance at 10 V is $L = 62,790 \text{ cd/m}^2$ for Ca and $L = 95,490 \text{ cd/m}^2$ for CPE(9wt%):ZnO NP devices. The device efficiencies for the Ca device is $LE_{\text{max}} = 7.71 \text{ cd/A}$ (at $4,489 \text{ cd/m}^2$) and $PE_{\text{max}} = 6.71 \text{ lm/W}$ (at 490 cd/m^2) whilst the device efficiencies for the CPE(9wt%):ZnO device were $LE_{\text{max}} = 10.8 \text{ cd/mA}$ (at $13,640 \text{ cd/m}^2$) and $PE_{\text{max}} = 9.31 \text{ lm/W}$ (at $1,410 \text{ cd/m}^2$). This shows that highly efficient conventional-structure PLED devices can be fabricated using the CPE(9wt%):ZnO EIL with superior performance to a standard Ca EIL device. This is likely due to the reduction in interfacial quenching when using CPE:ZnO composite material compared to using a metal.

Figure 3: Atomic force microscope topography images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of EIL films deposited on ITO coated glass substrates, comprising (a) ZnO NPs alone, (b) CPE(2.25 wt%):ZnO NP composite, (c) CPE(4.5 wt%):ZnO NP composite and (d) CPE(9 wt%):ZnO NP composite.

The origin of the improvement in HyLED device efficiency is expected to be twofold. First, the CPE acts as a stabiliser for the ZnO NPs in solution, preventing aggregation.[24] To test this, the surface morphologies of the layers were investigated by atomic force microscopy (AFM). **Figure 3** shows the 2D surface morphologies of EILs comprising ZnO NPs alone and CPE:ZnO NP composites with CPE fractions of 2.25, 4.5 and 9wt%. The ZnO NP layer exhibited a high surface roughness with a root mean square (rms) value of 7.4 nm. The addition of 2.25wt% CPE helped to reduce the rms roughness to 5.9 nm, whilst 4.5 and 9wt% CPE fractions gave further reductions to 5.2 and 3.1 nm, respectively. The 9wt% CPE:ZnO NP EIL has a smooth, dense morphology

with good coverage, facilitating homogeneous electron injection and hole blocking, both of which are desirable for device performance.[25,27]

Secondly, the inclusion of the CPE in composite EILs leads to a desirable shift in workfunction. Kelvin Probe measurements on ZnO NP only and CPE(x wt%):ZnO NP composite films deposited on ITO (**Figure 4**) show that the workfunction, Φ , of the EIL decreases as the CPE fraction increases. For the ZnO NP only EIL $\Phi = 4.73$ eV whilst for composite EILs with 2.25, 4.5, 9 and 18wt% CPE the Φ values are respectively 4.63, 4.37, 4.22 and 4.20 eV, a reduction in workfunction of up to 0.53 eV. The shift in workfunction can be attributed to the formation of interfacial dipoles between the CPE and ZnO NPs due to bonding between the F8imFO₄-Br bromide ions and/or ethylene glycol side-chain oxygen atoms and Zn²⁺ ions.[24] This can be represented by a down shift, Δ , in vacuum level as indicated in **Figure 4**,[28,29] where the electron injection energy barrier, ϕ_e , between the EIL and F8BT EML also then decreases. It is also evident from **Figure 2** that devices with composite EILs show lower DC current densities below EL turn-on, suggestive of better hole blocking when the CPE is present. Increasing the fraction of CPE from 9% to 18% appears to yield only a negligible increase in vacuum level shift, implying that electron injection is not significantly enhanced and additional quenching is likely the reason for the decrease in performance from CPE(9wt%):ZnO to CPE(18wt%):ZnO devices.

Figure 4: Schematic energy level diagram for charge injection processes in HyLEDs with (a) ZnO NP only and (b) composite CPE:ZnO NP EILs on ITO. The CPE component induces a vacuum level shift (Δ) that reduces the electron injection barrier (ϕ_b). The measured workfunction values for ZnO NP only and 2.25, 4.5, 9 and 18wt% CPE fraction composites are compared in (c).

One key advantage of inducing a workfunction shift in this manner is that the mobile ions present in the CPE (the bromide ions) are now fixed due to the coordination bonding with ZnO NP. Early

HyLEDs containing CPE layers used a bilayer of compact zinc oxide (c-ZnO) and CPE deposited on top to aid electron injection *via* modification of the workfunction of the ZnO layer due to the formation of dipoles at the ZnO/CPE interface.[15,16,30] As mentioned, c-ZnO/CPE bilayers are undesirable in HyLEDs due to high processing temperatures required for ZnO layer (making it unsuitable for flexible substrates) and long EL and current turn-on times. To test the performance of 9 wt% CPE:ZnO NP composite EIL against conventional ZnO/CPE devices, c-ZnO and c-ZnO/CPE bilayer EIL F8BT HyLEDs were fabricated and compared. **Figure 5** compares the J-V-L and efficiency characteristics of devices containing c-ZnO, c-ZnO/CPE bilayer and CPE (9 wt%):ZnO NP composite layer as the EIL.

In similar fashion to ZnO NP only EIL devices, c-ZnO devices show a low $V_{on} = 2.0$ V but reach a slightly higher luminance at 10 V, namely $L = 6,453$ cd/m², with $LE_{max} = 0.52$ cd/A (at 4,775 cd/m²) and $PE_{max} = 0.32$ lm/W (at 1,097 cd/m²). Spin-coating F8imFO₄ CPE on top of the c-ZnO layer increases the HyLED luminance up to 36,900 cd/m² at 10V through bromide-Zn and oxygen-Zn bonding allowing passivation of the ZnO surface, reducing ZnO defect EL quenching.[24,31,32] These devices then achieve $LE_{max} = 3.8$ cd/A (at 21,859 cd/m²) and $PE_{max} = 3.0$ lm/W (at 2,593 cd/m²), only slightly lower than for the CPE (9 wt%):ZnO NP EIL devices but with the added requirement of a high temperature processing step.

The EL spectra of the c-ZnO and ZnO/CPE bilayer devices are shown in **Figure S5**. Here, we find that the spectra are slightly red shifted and broadened compared to the CPE:ZnO NP composite devices, peaking at 565 nm with a FWHM of 93 and 89 nm respectively. This difference could be due to scattering or weak microcavity effects caused by the difference in electron injection layers.

Figures 5 (c) and (d) show the normalised transient response curves for current density (J) and EL intensity following application of 5 V amplitude, 1 Hz repetition rate, square wave voltage pulses. This allows the rise time, τ , of the device to be determined by finding the intercept of the EL saturation and the tangent of the rising edge of the signal.³⁶ The current density responses of the c-ZnO alone and CPE:ZnO NP composite devices both closely follow the voltage input signal. The resulting EL signals turn-on just as fast but then show a slow signal drop ($\sim 3\%$) over the course of the 0.5 s pulse. Such behaviour is seen in many polymer LEDs and is often reversible, implicating the effect of charge trapping on internal fields.[33–35] Conversely, for the c-ZnO/F8imFO₄ bilayer devices, both the J and EL signals show an initial rapid rise up to $\sim 75\%$ of peak value, followed by a slower rise with time constant $\tau \sim 0.2$ s. Such a delayed response has previously been observed for other CPE EIL devices due to the rearrangement of mobile ions under the applied electric field.[18–20,36] It is notable, therefore, that the CPE (9 wt%):ZnO NP composite EIL HyLEDs do not show this effect but rather behave the same as c-ZnO EIL devices; their J and EL rise times are fast ($\tau \sim 7 \mu\text{s}$). In comparison the bilayer EIL devices show much longer rise times ($\tau \sim 0.4$ s). The CPE:ZnO NP composite EIL materials thereby yield both (i) high EL efficiency and (ii) fast EL response without any high temperature processing step which makes them attractive for display applications. Another possible advantage of using a CPE:ZnO composite could be improved operational lifetime; previous observations in the literature note longer operational lifetimes when using a polyelectrolyte:ZnO composite EIL as opposed to using only polyelectrolyte EILs.[37]

The otherwise mobile CPE bromide counterions are ‘locked’ in place by the NPs in the CPE (9 wt%):ZnO NP composite EIL.[24] Thermal treatment under an applied bias has also been observed to allow these ions to become locked, resulting in similar reductions in EL rise time.[38] Other

approaches to reducing EL rise time include tailoring the electronic structure of the CPE; for instance using an F8BT based CPE in an F8BT EML PLED can produce fast turn-on times on the order of $\sim 10 \mu s$ by reducing the injection barrier between aluminium and the CPE which in turn prevents the build-up of a local field that acts upon the ions.[36]

Figure 5: Device performance for F8BT HyLEDs with c-ZnO, c-ZnO/CPE bilayer and CPE (9 wt%):ZnO NP composite EIL layers. (a) DC current density and steady state luminance *versus* voltage (J-V-L). (b) Luminous efficiency and luminous power efficiency *versus* luminance. (c) Normalised transient current density (J, upper panel) and electroluminescence (EL, middle panel). The corresponding 5 V amplitude, 1 Hz repetition rate, square wave voltage excitation pulses are also shown (lower panel). (d) Magnified portion of normalised current (upper panel) and EL (lower panel) transients.

As a final characterisation we used the CPE (9 wt%):ZnO composite EIL layer in thicker EML devices to test its potential for more readily scalable, high efficiency, printable LEDs.[39,40] The use of thick ($>1\ \mu\text{m}$) EMLs is especially important in roll-to-roll printing where robust, fault-tolerant and reproducible films are required.[41] **Figure 6** shows the J-V-L and LE and PE device efficiencies for $1.1\ \mu\text{m}$ thickness F8BT EML HyLEDs, with the increase in V_{on} to 5.0 V (from 2.4 V for 75 nm thickness F8BT EML devices) consistent with electric-field dependent charge injection.[42] These devices achieve a notably higher maximum luminance, reaching $L_{\text{max}} = 77,130\ \text{cd/m}^2$ at 25 V (c.f. $L_{\text{max}} = 46,760\ \text{cd/m}^2$ at 10 V for 75 nm EML thickness). The maximum efficiencies obtained also increase significantly to $\text{LE}_{\text{max}} = 16.5\ \text{cd/A}$ (at 18.2 V, $19,590\ \text{cd/m}^2$) and $\text{PE}_{\text{max}} = 5.4\ \text{lm/W}$ (at 7.2 V, $258\ \text{cd/m}^2$) from $\text{LE}_{\text{max}} = 4.10\ \text{cd/A}$ (at 6.4 V, $22,240\ \text{cd/m}^2$) and $\text{PE}_{\text{max}} = 3.3\ \text{lm/W}$ (at 3.2 V, $1,844\ \text{cd/m}^2$) for the thinner EML devices. The LE of the $1.1\ \mu\text{m}$ thick devices remains high ($> 15\ \text{cd/A}$) up to a current density $J = 450\ \text{mA/cm}^2$ (at 21.8 V where $L = 68,350\ \text{cd/m}^2$) but there is then a notable roll-off in efficiency, decreasing to $8.6\ \text{cd/A}$ at $J = 790\ \text{mA/cm}^2$ (for 25 V where $L = 67,630\ \text{cd/m}^2$). The significant increase in device efficiency is attributed to the introduction of a broad recombination zone within the thick F8BT EML layer, as already noted for conventional (non-composite EIL) thick HyLEDs.[42,43] This reduces the fraction of excitons formed near one or other electrode, reducing interfacial quenching and thus improving device efficiency. **Figure S6** also shows the normalised EL emission of the $1.1\ \mu\text{m}$ F8BT device. Here, the emission is slightly red-shifted and broadened compared to the 75 nm F8BT EML devices, peaking at 547 nm with a FWHM of 83 nm. This is likely due to a change in the weak microcavity effect from the large change in EML thickness. The turn-on, luminance, efficiency and CIE (x,y) data for each of the HyLED structures studied in this paper is summarised in **Table 1**.

Figure 6: Device performance for 1.1 μm F8BT EML HyLEDs with CPE (9 wt%):ZnO NP composite EIL layers. (a) Current density and luminance *versus* voltage (J-V-L) and (b) Luminous efficiency and luminous power efficiency *versus* luminance

Table 1: Summary of F8BT EML HyLED devices fabricated with ZnO NP, (x wt%):CPE:ZnO NP composite, c-ZnO and c-ZnO/CPE bilayer EILs. Unless otherwise stated the F8BT EML thickness was 75nm.

^a – Luminance taken at 23.4 V

EIL	Turn-on (V)	Luminance @10 V (cd/m²)	LE_{max} (cd/A) (@ bias, luminance)	PE_{max} (lm/W) (@ bias, luminance)	Max. EQE (%) (@ bias, luminance)	CIE (x,y)
ZnO NP	2.0	2,257	0.34 (@ 4.4 V, 962 cd/m ²)	0.30 (@ 3.2 V, 450 cd/m ²)	0.103 (@ 4.4 V, 962 cd/m ²)	(0.43, 0.56)
CPE(2.25%):ZnO composite	2.2	19,260	1.14 (@ 7.8 V, 13,570 cd/m ²)	0.62 (@ 4.0 V, 2,192 cd/m ²)	0.342 (@ 7.8 V, 13,570 cd/m ²)	(0.43, 0.56)
CPE(4.5%):ZnO composite	2.4	27,780	2.49 (@ 5.4 V, 8,976 cd/m ²)	2.15 (@ 3.2 V, 1,373 cd/m ²)	0.743 (@ 5.4 V, 8,976 cd/m ²)	(0.43, 0.56)
CPE(9%):ZnO composite	2.4	46,760	4.10 (@ 6.4 V, 22,240 cd/m ²)	3.27 (@ 3.2 V, 1,844 cd/m ²)	1.194 (@ 6.4 V, 22,240 cd/m ²)	(0.43, 0.56)
CPE(18%):ZnO composite	2.4	44,260	3.45 (@ 6.0 V, 22,200 cd/m ²)	2.70 (@ 3.4 V, 2,603 cd/m ²)	0.985 (@ 6.0 V, 22,200 cd/m ²)	(0.43, 0.56)
c-ZnO	2.0	6,453	0.52 (@ 7.4 V, 4,259 cd/m ²)	0.32 (@ 4.0 V, 1,097 cd/m ²)	0.156 (@ 7.4 V, 4,259 cd/m ²)	(0.46, 0.53)
c-ZnO/CPE bilayer	2.4	36,900	3.82 (@ 7.0 V, 20,650 cd/m ²)	2.96 (@ 3.6 V, 2,593 cd/m ²)	1.17 (@ 7.0 V, 20,650 cd/m ²)	(0.46, 0.53)
CPE(9%):ZnO composite/1.1 μm F8BT	5.0	77,130	16.5 (@ 18.2 V, 19,590 cd/m ²)	5.4 (@ 7.2 V, 258 cd/m ²)	4.81 (@ 18.2 V, 19,590 cd/m ²)	(0.44, 0.55)

3. Conclusion

In summary, we have demonstrated for the first time use of CPE:ZnO NP composites with varying CPE fraction as effective EILs in inverted F8BT EML HyLEDs. We observe an improvement in EIL film morphology with increasing CPE content, together with an increase in vacuum level shift that supports enhanced electron injection. The 9 wt% CPE:ZnO EIL devices,

in particular, show significantly improved device characteristics compared to c-ZnO/CPE bilayer EIL HyLEDs, with both higher device efficiencies and substantially faster turn-on times, compatible with display application. Increasing the F8BT EML thickness from 75 nm to 1.1 μm then allows demonstration of state-of-the-art efficiencies, $\text{LE}_{\text{max}} = 16.5 \text{ cd/A}$ and $\text{PE}_{\text{max}} = 5.4 \text{ lm/W}$, with $\text{L}_{\text{max}} = 77,130 \text{ cd/m}^2$. The use of such a thick EML layer is particularly relevant to roll-to-roll device fabrication, where thick layers are required for fault-tolerance. This is also the first demonstration that blending CPEs with ZnO NPs causes the ions to ‘lock’ and thus produces fast electron injection, leading to luminance turn-on times on the 10^{-6} s timescale. By contrast, traditional ZnO/CPE bilayer devices showed luminance turn-on times on the 10^{-1} timescale and therefore unsuitable for display applications.

Importantly, these results demonstrate that superior performance for single EML fluorescent PLEDs can be achieved using a simplified device architecture and facile fabrication processes. The CPE:ZnO NP composite EIL films can be formed in a one-step solution deposition process under ambient conditions with no annealing step, making them desirable for use in the high-throughput manufacture of printable LEDs. This approach could further be extended to different F8BT-based polymer EML structures[44] and to flexible optoelectronic devices more generally, including organic photovoltaic cells where the composite would operate as an electron extraction layer.

4. Experimental

PLED Fabrication:

Patterned ITO anode structures on glass substrates (size 12 mm x 8 mm) were cleaned for 15 minutes each in a sequence of ultrasonic baths using acetone, isopropanol and detergent (Hellmanex III, 2% by volume in DI water), followed by oxygen plasma ashing in an Emitech

K1050X plasma cleaner. Compact, ~ 30 nm thickness, ZnO EILs were spin-coated (2000 rpm, 60 s) on top of the ITO from 0.3 M sol-gel solutions of zinc acetate dihydrate and 2-aminoethanol dissolved in 2-methoxyethanol and annealed at 450 °C for 1 hour. For ZnO/CPE bilayer EILs, a ~10 nm thickness F8imFO₄ CPE (synthesised according to previous reports)[24] film was then spin-coated (3000 rpm, 60 s) on top from a 3 mg/ml 2-methoxyethanol solution.

Colloidal zinc oxide nanoparticles were prepared according to previous reports and dispersed in 2-methoxyethanol at a concentration of 40 mg/ml with average particle size = 5.5 nm.[24] F8imFO₄ dissolved in 2-methoxyethanol at different concentrations was then added to a portion of this ZnO NP stock solution and the resulting mixture stirred to obtain a CPE:ZnO NP composite solution. Previous reports have shown that ZnO NPs disperse well when blended with F8imFO₄, with the resulting average cluster size = 13.4 nm. This is believed due to the CPE's ethylene oxide side chains being able to form coordinate bonds with zinc cations on the nanoparticle surface as well as bonds formed between the bromide and zinc cations.[24] ZnO NP and CPE:ZnO NP composite EILs of ~ 30 nm thickness were spin coated (1000 rpm, 30 s) onto pre-cleaned ITO-coated glass substrates.

F8BT EMLs of two thicknesses were next deposited on top of the different EIL layers; 75 nm films were spin coated (2000 rpm, 60 s) from 10 mg/ml and 1.1 μ m films (1500 rpm, 60 s) from 40 mg/ml toluene solutions. To complete the PLEDs an MBraun thermal evaporator was used to deposit a top molybdenum oxide (10 nm) hole injection layer (HIL) and a gold (100 nm) anode.

PLED characterisation:

PLEDs were characterised at room temperature in a sealed sample chamber under nitrogen, using a computer-controlled Keithley Source Measure unit to apply a bias voltage to the chosen

pixel (each substrate comprised 6 PLED pixels) and to measure the resultant current. A Minolta LS100 spot luminance meter measured the corresponding pixel luminance and electroluminescence spectra were recorded using an Ocean Optics USB 2000 CCD spectrometer equipped with a fiber light collection bundle. The PLED EL intensity and current density transient responses were probed using a HP 3325B pulse generator and monitored with a digital oscilloscope (Tektronix DPO 3054); a fast Si-photodiode was used to detect the EL signal.

EIL characterisation:

Atomic force microscopy (AFM) topographic images of the EILs were obtained using a Park NX10 AFM in non-contact mode. Kelvin probe measurements were performed using a KP Technology APS04 system. During the latter measurements the ITO substrate was connected to ground. The workfunction was determined from the contact potential difference measured by the vibrating top Kelvin probe (2mm, gold tip) and from the work function of the tip ($\approx 4.5 - 4.6$ eV), determined using a silver reference. TCSPC measurements of F8BT/EIL bilayers were taken using an Edinburgh Instruments FLS1000 spectrometer, with an excitation wavelength of 405 nm and detection wavelength of 550 nm.

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