ZnO Nanorod Arrays as Electron Injection Layers for Efficient Organic Light Emitting Diodes

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Nanostructured oxide arrays have received significant attention as charge injection and collection electrodes in numerous optoelectronic devices. Zinc oxide (ZnO) nanorods have received particular interest owing to the ease of fabrication using scalable, solution processes with a high degree of control of rod dimension and density. Here, vertical ZnO nanorods as electron injection layers in organic light emitting diodes are implemented for display and lighting purposes. Implementing nanorods into devices with an emissive polymer, poly(9,9-dioctyluorene-alt-benzothiadiazole) (F8BT) and poly(9,9-di-*n*-octylfluorene-alt-*N*-(4-butylphenyl)dipheny-lamine) (TFB) as an electron blocking layer, brightness and efficiencies up to 8602 cd m^{-2} and 1.66 cd A^{-1} are achieved. Simple solution processing methodologies combined with postdeposition thermal processing are highlighted to achieve complete wetting of the nanorod arrays with the emissive polymer. The introduction of TFB to minimize charge leakage and nonradiative exciton decay results in dramatic increases to device yields and provides an insight into the operating mechanism of these devices. It is demonstrated that the detected emission originates from within the polymer layers with no evidence of ZnO band edge or defect emission. The work represents a significant development for the ongoing implementation of ZnO nanorod arrays into efficient light emitting devices.

1. Introduction

The development and investigation of ZnO nanostructures for optoelectronic applications is extensive and well-documented, showcasing a variety of morphologies achievable across a wide range of deposition techniques.[1–9] Of particular interest for device applications is the growth of ZnO nanorod arrays (NRAs) from low temperature, aqueous deposition methods[10] which, over the past decade, has seen morphological improvements in alignment and uniformity through the introduction of precursor ZnO seed layers,[11] pH control of the growth environment,[12,13] additive incorporation,[14] as well as manipulation of growth variables including duration and temperature.[15–18] Efforts to implement NRAs into bulk heterojunction hybrid organic–inorganic photovoltaics (hPV) have led to improved devices attributed to more efficient charge collection.[19,20] Consequently, much of the NRA design considerations and postdeposition treatments have been governed by their eventual incorporation into hPV devices.[21–23] In parallel, there has been growing interest in incorporating nanostructured ZnO into light-emitting devices, particularly for UV emission by combining n-type ZnO NRAs with an inorganic p-type materials such as GaN,[24,25] with recent reports of p-type organic materials being studied with the motivation of achieving all solution processed devices.[26] Despite promising initial results with emissive devices the inclusion of ZnO NRAs in light emitting diodes (LEDs) remains less developed than hPVs. For example Yang et al. only recently first reported efficiencies for a UV-emitting diode based on a ZnO NRA/poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) structure[27] almost a decade after Könenkamp et al. first reported UV emission from a diode based on the same materials.[28] Reports of visible light emission from devices of ZnO NRAs and light-emitting polymers, such as polyfluorene[29] or poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV),[30] are given by only electroluminescent (EL) emission spectra.[31–33] Within these reports, white emission is achieved through combined emission from the light emitting polymer together with various emissive defect states present in the NRAs. However, and to the best of our knowledge, the metrics which would further support claims of the potential of these devices for lighting or display applications, such as the luminance (in terms of cd m^{-2}) and lighting efficiency parameters (in terms of cd A^{-1} and lm W^{-1}), have yet to be reported. Comparison between available reports is also complicated by the fact that few devices are grown as standard architectures, leading to different operating mechanisms being discussed between authors.

In this article, we report on a nanorod hybrid LED (NHyLED) device, where vertically aligned ZnO NRAs act as an electron injection/transport layer infiltrated with the green emitting

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polymer poly(9,9-dioctyluorene-alt-benzothiadiazole) (F8BT) in an inverted, top-anode geometry similar to that reported for conventional hPV devices. Through the incorporation of a second polymer layer, poly(9,9-di-*n*-octylfluorene-alt-*N*-(4-butylphenyl)dipheny-lamine) (TFB), as an electron blocker we show that NR HyLEDs can exceed luminance values of 1000 cd m^{-2} thus demonstrating quantitatively for the first time their potential for general lighting applications.

2. Results and Discussion

We present two device structures, one with and one without a TFB layer (herein referred to as Device A and Device B, respectively). The device structures are ITO/ZnO (130 nm)/ZnO NRA (750 nm)/F8BT (450 nm)/TFB (0 or 50 nm)/MoO_x (10 nm)/Au (80 nm), in which approximate layer thicknesses are indicated in parentheses. Both polymers were purchased from American Dye Source while chemicals involved in the NRA growth were purchased from Sigma-Aldrich. All materials were used as received without further purification.

The NRAs were first deposited on clean glass substrates, following the procedure we have previously outlined.[34] To aid nucleation and vertical alignment a 130 nm ZnO seed layer was first cast onto the substrates using sol–gel precursors. The substrates were then suspended in a hydrothermal growth solution of equimolar zinc nitrate hexahydrate and hexamethylenetetramine (HMT), along with potassium chloride (KCl) and polyethyleneimine (PEI) as additives to ensure uniformity and vertical alignment of the rods. Scanning electron microscopy (SEM) images show a highly uniform array with rods approximately 750 nm in length aligned predominantly perpendicular to the substrate (**Figure 1**a,b), with a distribution of diameters around 70 nm (Figure 1c). X-ray diffraction (XRD) measurements show that the rods are highly crystalline and oriented along the *c*-axis (002) of the ZnO wurtzite structure (Figure 1d).

F8BT was dissolved in toluene at a concentration of 30 mg mL^{-1} (yielding 450 nm films on a planar substrate) to ensure effective infiltration of the array whilst still leaving sufficient polymer to separate the tips of the array and the top anode for device fabrication. Cross-sectional SEM showed that the initial spin-coating of the polymer results in a thick overlayer on the rods with little infiltration (**Figure 2**a). Smith et al. have reported on having to cast F8BT from 10 mg mL^{-1} solutions four times via spin coating in order to create a layer thick enough to fully infiltrate their InGaN/GaN NRA,[35] but few experimental details are given in this respect in other published NR HyLED reports and complete infiltration is often presumed. There are extensive reports within hPV literature, however, that show the need for postdeposition thermal treatment to overcome wetting issues between the polymer and the NRA.[20,36,37] From differential scanning calorimetry (DSC) measurements (Figure S1, Supporting Information), our F8BT has glass transition T_g and melting temperatures T_m of 130 and 260 °C, respectively, in line with that reported by others and with no obvious signs of thermal degradation over multiple measurement cycles.[38] Annealing the coated NRAs to temperatures slightly above T_g for 20 min results in some uptake into the NRAs, however complete infiltration can only be achieved by annealing above the T_m giving an intermixed ZnO NRA:F8BT layer of total thickness ≈900 nm (Figure 2b).

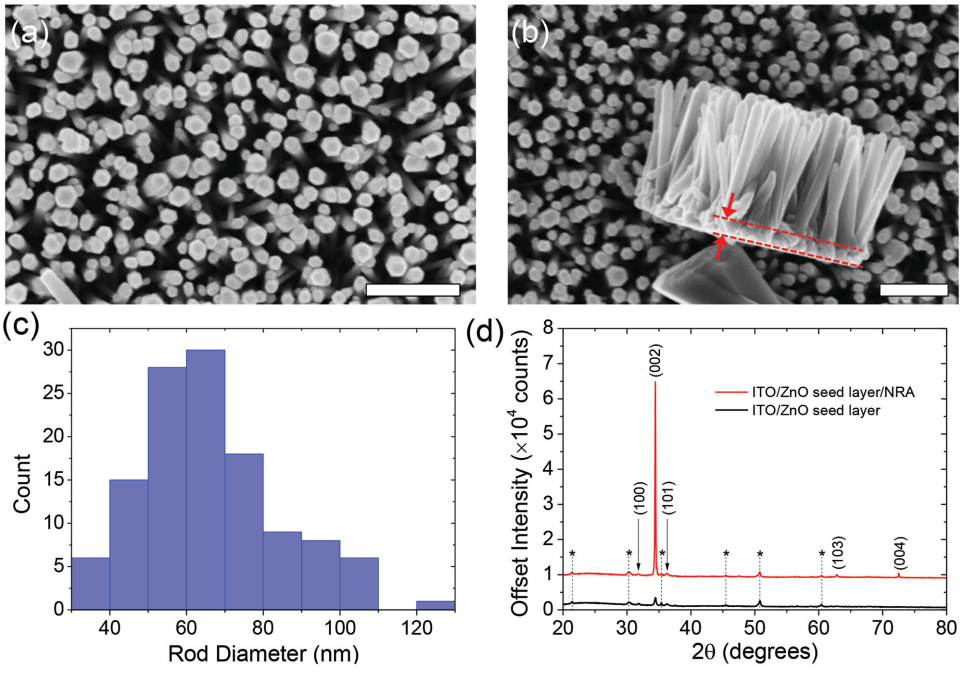

Figure 1. Characterization of ZnO NRAs. SEM images of a) a top view of an NRA and b) a cross-section of the NRA, dashed lines highlight seed layer at base of NRA of thickness ≈130 nm, scale bar: 500 nm. c) The distribution of the rod diameters as measured along the hexagonal axis of greatest extent. d) XRD patterns comparing the crystallinity of the ITO/ZnO seed layer to ITO/ZnO seed layer/NRA. Starred-peaks indicate features of the ITO substrate.

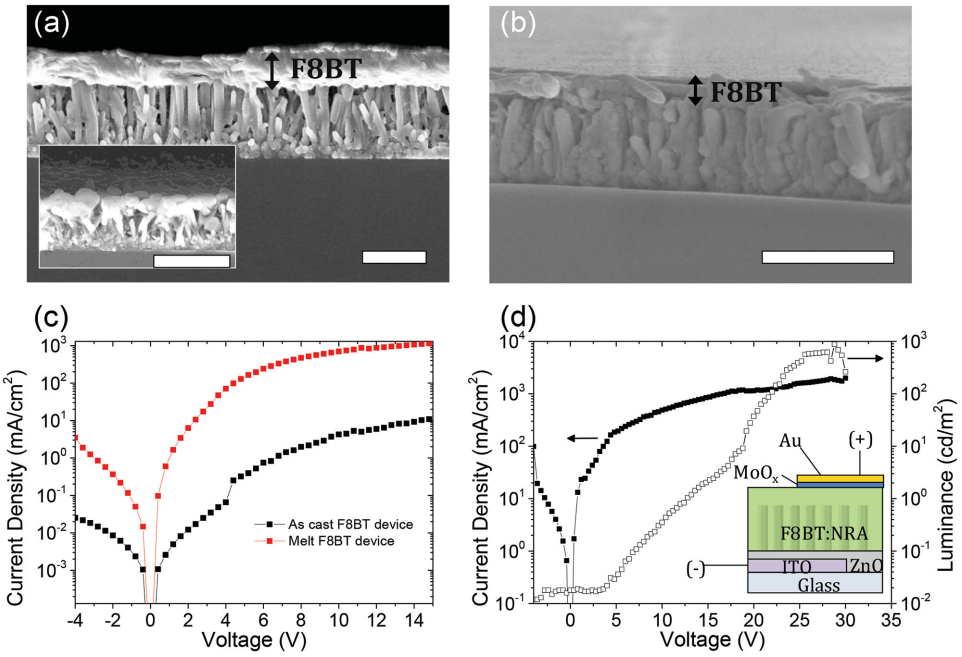

Figure 2. Assessment of polymer infiltration into NRAs. a) SEM cross-section image of as-cast F8BT showing no infiltration into the NRA. Inset: Likewise, little infiltration was observed of T_g annealed polymer. b) SEM cross-section image showing full infiltration once F8BT has been annealed above T_m leaving a ≈150 nm of smooth F8BT on top of the array. Scale bars = 1 μm. c) *J–V* characteristics of ITO/ZnO/ZnO NRA:F8BT/MoO_3/Au devices showing the significant increase in current density as F8BT penetrates the array following the annealing procedure. d) *J–V–L* characteristic of the ITO/ZnO/ZnO NRA:F8BT/MoO_3/Au device (schematic shown inset) which exhibited strong light emission (filled squares represent the current density and open squares.

For device fabrication, the ZnO, NRA, and F8BT depositions were carried out on precleaned glass/ITO substrates. Thermal evaporation of the MoO_x/Au anode contact onto the top F8BT surface device and device characterization was carried out as discussed in the Methods Section.

The effect of annealing the F8BT above T_m compared to a nonheated sample can be clearly observed on the *J–V* characteristics of the diodes fabricated (Figure 2c). Clear diode behavior is observed in both cases with the ratio of forward/reverse currents at ±4 V being 2.60 and 20.3 for the as-cast and melt devices, respectively. Forward current density is almost 1000 times greater (at 10 V) in the heated devices as interfacial contact between the polymer and array is increased. Light emission was observed from the as-cast devices, but driving voltages significantly exceeding 20 V were required to record luminances of <1 cd m^{-2}. Similarly, despite the large current flowing through the melt processed devices there was little light detected. Through repeat measurements we were able to record only one instance of strong EL with a light turn-on voltage (V_L) of 3.2 V and a maximum luminance of 878 cd m^{-2} at 28.8 V (Figure 2d) and a low current efficiency of 0.047 cd A^{-1}. Nonetheless, these results are significant given the luminance values exceeded 100 cd m^{-2}, which is required for display purposes and approaching the general lighting requirement of 1000 cd m^{-2}.

In order to address the undesirably low efficiencies and improve the yield of functional devices, we consider the band energies of the materials studied (**Figure 3**a). It has been reported that the F8BT/MoO_x interface allows for efficient Ohmic hole injection due to the deep work function of MoO_x which pins to the highest occupied molecular orbital at the interface with the organic layer.[39,40] However, there is a large ≈0.7 eV energy barrier to electron injection between the ZnO conduction band (CB) and the F8BT lowest unoccupied molecular orbital (LUMO); it has been suggested that electron injection is achieved due to the potential drop across the oxide/polymer interface as holes accumulate on the polymer side.[41] This mechanism is likely to occur in NR HyLEDs, too, but it is also possible that given the large NRA:F8BT interface that the number of conduction pathways for charge carriers is increased considerably, hence facilitating the overall electron injection. Furthermore, both experimental and theoretical studies show that nanostructured surfaces lead to dramatic enhancements of the internal electric field with a corresponding decrease in the Schottky barrier height for charge injection.[42,43] An theoretical enhancement to the injection current by a factor of 35 was reported even for an injection-limited contact.[42] Once the onset of electron injection is reached, it is likely that the devices become flooded with negative charge carriers. With the reported LUMO of F8BT of ≈3 eV[44] and the CB of MoO_x ≈6.7 eV,[45] a negative barrier ϕ_e to excess electrons exists and so for Device A these electrons will continue to flow out of the device rather than undergo exciton recombination and light emission. Indeed, preliminary results of electron-only ITO/ZnO/ZnO NRA/F8BT/Ca/Al devices show current densities that are approximately twenty times greater than those containing a planar ZnO layer only (Figure S2, Supporting Information). This can be addressed by introducing an electron blocking layer at the F8BT/MoO_x interface. TFB is often used in conjunction with F8BT, to act as an electron blocker and to prevent nonradiative exciton decay at contact interfaces due to

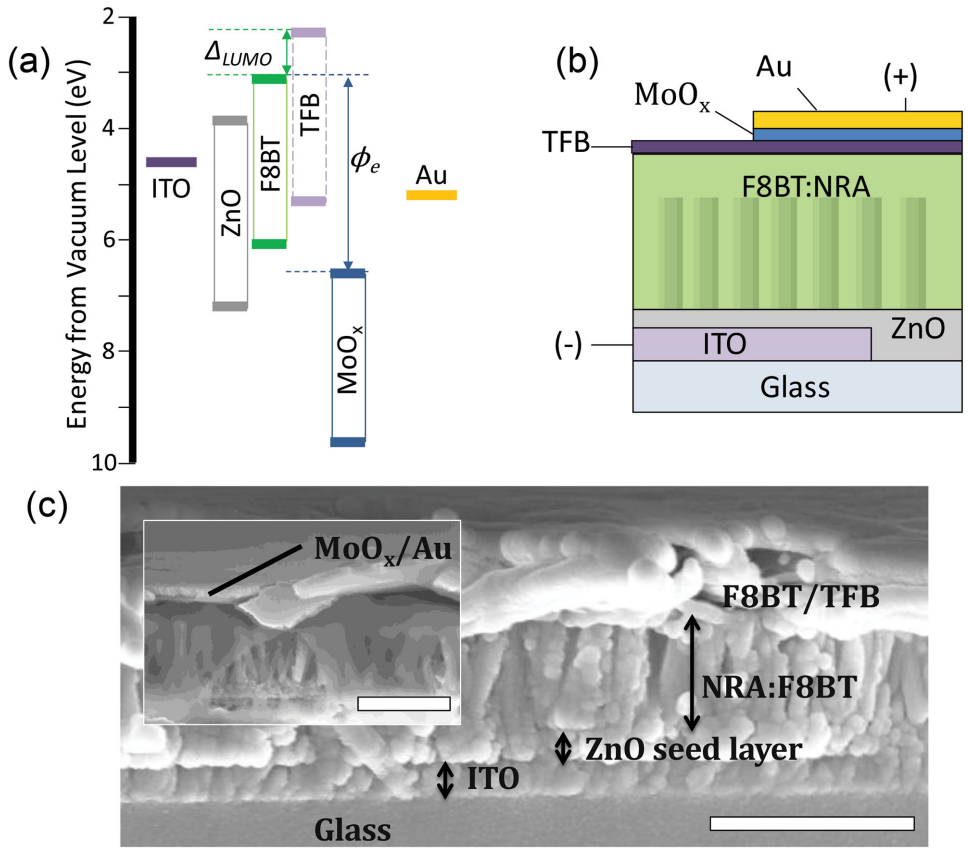

Figure 3. a) Flat-band energy level diagram for all materials discussed in device fabrication. Relevant to Device A is the difference between the F8BT LUMO and the MoO_x CB, ϕ_e, is highlighted. Relevant to Device B is the TFB layer (shown with a dotted outline) and the offset in LUMO energies between the two polymer layers, Δ_{LUMO}. b) Device B schematic. c) Cross-section SEM of Device B highlighting the addition of the TFB layer with a separate cross-section showing the top MoO_x/Au anode contact displayed inset for clarity.

the large LUMO offset Δ_{LUMO} of ≈0.7 eV between the two polymers.[46] Recently we have outlined a methodology that allows TFB to be cast directly onto F8BT with no detectable dissolution of the F8BT.[47] To incorporate the TFB layer, devices were prepared as previously. Following deposition and processing of the F8BT the TFB was cast and dried at 120 °C for 20 min before contact evaporation to create an overall layer structure of ITO/ZnO/ZnO NRA/F8BT/TFB/MoO_x/Au (Device B), Figure 3b. We confirm that the addition of TFB has not impacted the infiltration of F8BT as shown in Figure 3c, which also shows all layers of the device in addition to the top electrode.

With the inclusion of TFB, device yield, luminance, and efficiency all increase markedly, supporting the concept that this interlayer assists in limiting the leakage of electrons and/or nonradiative dissociation of excitons at the contact interface. The spread for the highest recorded performance metrics for a set of 23 devices is illustrated in the frequency diagrams of **Figure 4**a,b. Of these devices, 87% recorded a maximum luminance exceeding 1000 cd m^{-2} with 75% of the set between 1000 and3000 cd m^{-2}. The brightest device had a maximum luminance of 8602 cd m^{-2}. Considering the current efficiency values, ≈22% of devices exceed 1 cd A^{-1} with a maximum of 1.66 cd A^{-1} recorded. Most (56%) of the devices recorded values under 0.3 cd A^{-1}, although in comparison to the TFB free devices all but one pixel recorded higher current efficiencies, similar behavior was observed with respect to power efficiency, with a maximum value of 0.26 lm/W measured in Device B. The observed spread in the recorded data may be attributed to variations in the polymer thickness and individual rod dimensions in our devices. For example the average thickness of F8BT measured on a flat substrate was 450 nm however the absolute values ranged from 410–480 nm, which may lead to a variation in the distance between the nanorod tips and the anode. Additionally, deviations in the length/width and areal spacing of the self-assembled NRAs may further compound this issue. The modest efficiency values can be explained by considering typical Device B current–voltage–luminosity (*J–V–L*) characteristics, Figure 4c. The rapid forward bias increase in current with voltage is accompanied by a slow increase in luminance, despite a low V_L of 4.8 V. Significant light emission (>100 cd m^{-2}) is only achieved at high voltages i.e., those exceeding 15 V. This is consistent with the high current densities, ≈1000 mA cm^{-2}, needed to achieve maximum current efficiencies (Figure 4c inset). The high current-to-light intensity and electrical-to-optical power ratios result in reduced lighting efficiencies. The incorporation of TFB has clearly had a significant impact in improving devices and overcoming some of the inherent limitations related to charge balance and nonradiative exciton dissociation mechanisms although it is apparent that there is scope to address this in the future.

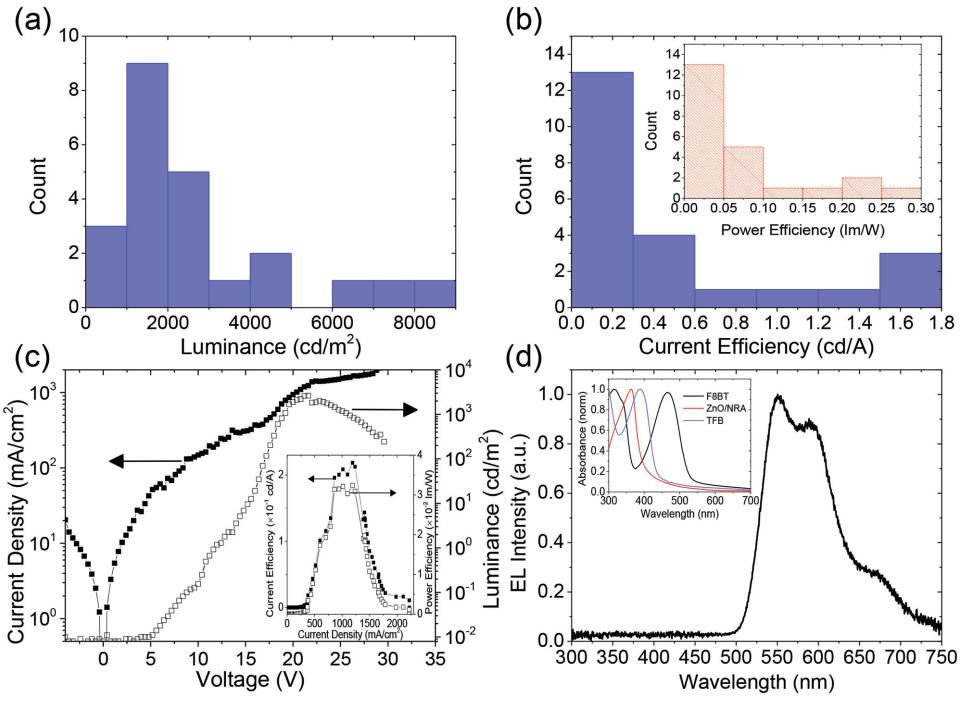

Figure 4. Electrical and optical characterization of ITO/ZnO/NRA:F8BT/TFB/MoO_3/Au devices. Frequency diagrams for a sample of 23 devices showing the maximum recorded a) luminance and b) current efficiencies with the power efficiency shown in inset. c) *J–V–L* characteristics for a typical device with the variation of current and power efficiency values shown inset. Filled squares correspond to the left ordinate axes and open squares to the right axes. d) Device EL spectra with absorbance data for the individual polymer layers as well as for the ZnO NRA shown inset.

Finally, we note the differences in electroluminescence of the Device B architecture (Figure 4d) compared with that reported elsewhere for ZnO NRA HyLEDs, most notably the lack of an emission peak at ≈380 nm associated with ZnO band edge emission.[29,30,48] In NRA-based devices, this is usually the most intense emission peak with weak contributions, attributed to emission from defect states, also reported in the 500–600 nm range. If UV emission from our NRAs is occurring it would overlap with the high absorbance regions of F8BT and TFB (Figure 4d inset). The lack of any observable UV emission evident, allows us to rule out contributions to the detected EL from ZnO band edge and defect state emission, hence all detected EL is attributed to radiative exciton recombination within the F8BT layer. The emission of F8BT normally exhibits a single emission peak at 550 nm with a shoulder at ≈580 nm.[47] It is likely that the three distinct peaks observed here at 550, 590, and 680 nm are interference fringes arising as a result of our inherently thick device structures and changes to the electroluminescence characteristics of emitters due to the variation in thickness of ZnO nanoparticle layers has been previously reported.[49] Transmittance measurements through a device stack (without the evaporated contacts) show distinct Fabry–Perot interference fringes in the optically transparent region >500 nm, (Figure S3a, Supporting Information). This is confirmed by repeat measurements of other devices (Figure S3b, Supporting Information) which again show three distinct peaks, however at different wavelength and relative intensities which would arise due to slight thickness variations between devices. Based on these results, and combined with its transparency over the visible region as well as the ability to be grown into a variety of nanostructures, it is hoped that the ZnO NRA can be further tailored to improve the outcoupling of light from the emissive organic layers.[50–52]

3. Conclusions

In summary, we demonstrate the successful fabrication of hybrid ZnO NRA/polymer LEDs confirming for the first time their potential for display and lighting purposes. We have compared our device characteristics to well-established metrics for lighting performance frequently cited in OLED and PLED literature, namely the luminance, and current and power efficiencies with the majority of devices tested exceeding the luminance requirement for general lighting. Though efficiency values are modest, ongoing optimization should show increases across all metrics as well as a reduction in the spread of device performance. NRAs have been previously highlighted as structures that may improve charge carrier injection or improve light out-coupling when used as external light extraction layers.[42,53,54] Here, the incorporation of an internal NRA, which can simultaneously exploit these potential advantages is presented with our best devices achieving brightness and efficiencies of 8602 cd m^{-2} and 1.66 cd A^{-1}. The potential for further improvements in hybrid LEDs by incorporation of ZnO NRAs is an elegant solution that opens a pathway to improved devices.

4. Experimental Section

Device Preparation and Characterization: ITO-coated glass substrates (PsioTec, sheet resistance ≈ 14 Ω sq^{-1}) were cleaned with successive 10 min ultrasonications in acetone, isopropanol, and deionized water, before undergoing a 10 min UV/Ozone exposure. For the ZnO seed layer, a sol–gel consisting of 0.75 M zinc acetate dihydrate and 2-aminoethanol dissolved in 2-methoxyethanol was prepared and cast onto the cleaned ITO substrates via spin coating. Substrates would then be annealed for 10 min at 300 °C. This spin-anneal step would be repeated three times. The substrates would then undergo a final 450 °C anneal for 1 h. Following this, the substrates were suspended in a solution of equimolar (50×10^{-3} M) zinc nitrate hexahydrate and HMT, 200×10^{-3} M of KCl and 20×10^{-3} M of PEI. The reaction was allowed to proceed for 2 h at 95 °C to reach the serried NR length. Completed substrates were dried and moved into a nitrogen glovebox (H_2O and O_2 <0.01 ppm) for polymer deposition. F8BT (116 kg mol^{-1}, dispersity 3.4) in toluene was cast from 30 mg mL^{-1} solution at 2000 rpm for 40 s and then annealed at 270 °C for 20 min before a slow cool of 5 °C min^{-1} back to room temperature. For Device B substrates, TFB (80 kg mol^{-1}, dispersity 2.4) in cyclohexanone (10 mg mL^{-1}) was spin coated onto the top F8BT surface and the substrates were annealed for 20 min at 120 °C. Thermal evaporation of the top anode contact was carried out through a shadow mask at a base pressure of 1×10^{-6} mbar at rates of 0.1 and 0.5 Å s^{-1} for MoO_x and Au, respectively, producing six 0.45 cm^2 devices per substrate. Both polymers were purchased from American Dye Source, whereas all ZnO precursors were purchased from Sigma-Aldrich. All materials were used without further purification.

Device Characterization: Device testing was carried out under an inert atmosphere using a Keithley 236 Source Measure Unit and a Minolta luminance meter. EL was measured with an Ocean Optics S2000 Fibre Optic Spectrometer.

Materials Characterization: SEM images were carried out on chromium-coated samples using a FEGSEM Leo 1525 microscope. Cross-sections of bare NRA substrates were achieved by scratching the surface with a diamond pen, whereas polymer-coated samples were first submerged into liquid nitrogen and then cleaved. The thicknesses of the polymer and ZnO seed layers were confirmed with the aid of a Dektak 150 surface profilometer. A Panalytical X'Pert Pro diffractometer was used for XRD measurements. Absorbance information of the F8BT, TFB, and ZnO NRA layers was obtained using a Bentham single-beam UV–vis system. Finally, a Toledo DSC 1 was used to measure the thermal transitions of the F8BT using three heating and cooling scans between 50 and 300 °C at a constant scan rate of 10 °C min^{-1}.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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