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A Study of Tin Oxide as an Electron Injection Layer in Hybrid Polymer Light-Emitting Diodes

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ABSTRACT

We investigate the n-type metal oxide Tin (IV) oxide (SnO_2), as an electron injection and transport layer in hybrid polymer light-emitting diodes (HyLEDs). SnO_2 is air stable and bio-safe, with high optical transparency and electrical conductivity, and with a deep valence band energy, making it highly suitable for such applications. Results reveal that SnO_2 is effective as an electron injecting cathode material, when a thin hole-blocking interlayer of Cs_2CO_3 or $\text{Ba}(\text{OH})_2$ is coated on it. Devices are optimized with respect to injection-layer thickness and hole-blocking layer configuration, with high performance metrics (current efficiencies of 20 cd/A, external quantum efficiencies of 6.5%) being demonstrated in the device with $\text{Ba}(\text{OH})_2$ as the inorganic interlayer in the hybrid architecture. Also, we characterize thin-films of spray-pyrolysis deposited SnO_2 , as compared with the commonly used interlayer material ZnO , in terms of film morphology and interfacial photophysics.

Keywords; Light-emitting diodes, organic semiconductors, charge injection, metal oxides

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1. INTRODUCTION

In hybrid polymer light emitting diodes (HyLEDs), n-type metal-oxides are employed as electron injecting layers to avoid the use of low work function metals, thus avoiding the requirement for rigorous encapsulation, and thereby simplifying the production process. Amongst the wide range of available n-type transition metal oxides, tin(IV) oxide is air stable, bio-safe, and exhibits both high optical transparency in the visible range and high electrical conductivity, making it an attractive potential electrode material for HyLEDs.^[1,2] Our work reports an innovative use of SnO₂ as an electron injection layer for these devices, which demonstrate high performance metrics, in combination with the other desirable features and properties of this material, as described.

The very first hybrid polymer-LEDs (PLEDs) utilized TiO₂ as the electron injection and transport layer, while molybdenum oxide (MoO₃) was chosen as the hole injection and transport layer, with F8BT (Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)]) as the emissive layer.^[3] This TiO₂/F8BT/MoO₃-based device was the first encapsulation-free device which could be operated in air, and exhibited a lower threshold voltage for current turn-on and similar luminance, compared to conventional PLEDs. The current efficiency was low, however, due to the high current density of holes, which was caused by Ohmic-like injection at the polymer/MoO₃ interface. In this device, the hole current leaked through the n-type metal oxide at the cathode without recombination with electrons, as there was a high barrier for electron injection and also a lack of an effective hole-blocking layer. In the studies which followed, attention has then been paid to finding a more suitable n-type metal-oxide for barrier-free electron injection. Bolink *et al.*^[4] utilized the same HyLED architecture, but used ZnO as the electron injection and transport layer instead of TiO₂, achieving a higher brightness. However, the efficiency of this ZnO-based device was still relatively low (~1.3 cd/A). By inserting of a thin layer of TFB (poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine) in between F8BT and MoO₃, the luminance efficiency was increased to 2.8 cd/A, as shown by Kabra *et al.*^[5] This improvement was attributed to better charge-carrier balance, with TFB acting as a hole trap. However, this use of a double polymer layer makes the fabrication complicated; a more elegant approach is to explore n-type transition metal-oxides, with a high conduction band for electron injection and a deep valence band to block holes at the interface of n-type metal oxide/polymer film. The metal oxide ZrO₂ was used in F8BT-based HyLEDs as both the

electron injection and hole blocking layer, since it has a conduction band edge of -3 eV and deep valence band energy of -8.7 eV.^[6] The device using ZrO₂ as the electron injection layer showed a very high brightness of ~26000 cd/m² and a luminance efficiency of 2.7 cd/A. The study of other two n-type metal oxides with deep valence bands, MgO (-10 eV) and HfO₂ (-8.7 eV),^[7] revealed that the use of these two n-type metal oxides can block holes and reduce the current density. The luminance is increased more in the case of using MgO than HfO₂ as a consequence of MgO having deeper valence band energy. However, the luminance efficiency (2.4 cd/A for HfO₂, and 3.3 cd/A for MgO₂ based HyLEDs) is not significantly increased, suggesting the deep valence band is not necessarily able to ensure highly efficient exciton recombination. The introduction of caesium carbonate (Cs₂CO₃) as an electron injection and hole-blocking layer was a breakthrough in polymer light-emitting diodes.^[8-10] Morii *et al.* showed a high current efficiency of 7 cd/A with Cs₂CO₃ thermally deposited between TiO₂ and F8BT layers.^[11] Bolink *et al.* used a well-known stable polymer, namely “Super yellow” (SY), in the hybrid architecture ITO/ZnO/Cs₂CO₃/SY/MoO₃/Au, and achieved an efficiency of 8 cd/A. Evidently, the device did not show any electroluminescence without the Cs₂CO₃ layer, and this observation emphasizes the importance of the role of a hole-blocking layer in a device with Ohmic injection for holes.^[12] The study of the device with an architecture of ITO/ZnO/Cs₂CO₃/F8BT/MoO₃/Au with a very thick polymer active layer^[13] has achieved the highest efficiency of ~23 cd/A which is one order of magnitude higher than the state of the art PLEDs using F8BT and represents a milestone in single layer polymer light-emitting diodes. The further exploration of hole blocking layers lead to a surprisingly high efficiency of ~28 cd/A with Ba(OH)₂ as inorganic interlayer, instead of Cs₂CO₃.^[14] However, the same study also revealed that there is an imbalance between the opposite charges in this structure (deficiency of electrons), hence leaving scope for further improvement and development of such hybrid devices.

In the present work, spray-pyrolysis coated SnO₂ is studied as a transparent electron injection layer in HyLED structures. The characteristic flat-band energy levels of this material suggest that it should function well in this role; a bandgap energy of 3.7–3.8 eV, with a measured valence band energy reported as being -8.5 eV.^[15] Devices are optimized with respect to injection-layer thickness and hole-blocking layer configuration, with high performance metrics (current efficiencies of 20 cd/A, external quantum efficiencies of 6.5%) being demonstrated. Also, the characteristics of the as-deposited films, in terms of film

morphology and interfacial photophysics, are explored, allowing comparison with the commonly used interlayer material ZnO.

2. EXPERIMENTAL DETAILS

SnO₂ thin films, as produced via spray-deposition methods, have already received some interest and application, particularly in the context of charge transport media in dye-sensitized solar cells.^[16,17] Following similar protocols, the colorless liquid Tin (IV) chloride, SnCl₄, is used as the precursor to prepare Tin (IV) oxide, SnO₂. 250 μl or 300 μl of SnCl₄ is mixed with 5ml ethanol in an amber vial and the solution is deposited by spray pyrolysis onto indium-tin oxide ITO substrates, via a spray gun (atomizer) using oxygen as propellant.^[18] The distance between the atomizer and the substrate is approximately 25 cm and the substrate temperature is controlled at ~ 470-500°C. According to the literature, an SnO₂ film is obtained for temperatures between 420 to 500°C and has high optical transmission in visible range and a high electrical conductivity.^[19] The simple reaction to produce SnO₂ is as follows:



Following the deposition of SnO₂, the substrates are heated for a further 15 minutes and then cooled, with Cs₂CO₃ or Ba(OH)₂ and then F8BT spin-coated sequentially on the surface of SnO₂, followed by annealing at 155°C under nitrogen flow for 45 minutes. The substrates are then transferred to the vacuum chamber and 10nm of MoO₃ and 70nm of gold deposited by thermal evaporation under a vacuum. Then the devices are then encapsulated and dried for 12 hours. The thickness of SnO₂ is ~50 nm when 250 μl precursor of SnCl₄ is used, and 70 nm when 300 μl is used, as confirmed by profilometry; the thickness of the Cs₂CO₃ and Ba(OH)₂ interlayers is ~7 nm. The film thickness of F8BT is between 1000nm and 1200 nm, with the resultant device architecture illustrated in **Figure 1**. In the subsequent device characterizations, the F8BT film thickness was fixed at around 1 μm, which has been found in our previous work to be optimum for the device performance.^[13,20]

3. RESULTS

3.1 LED characteristics with Ba(OH)₂ as inorganic interlayer.

Figure 2(a) shows the characteristics of current density and luminance versus operating voltage (J-V-L) of devices with the structure ITO/SnO₂/ Ba(OH)₂/F8BT/MoO₃/Au where the film thicknesses of SnO₂ are 50nm and 70nm respectively. Both devices show a very low current turn-on voltage and suggest a hole current leakage at sub-voltage as MoO₃ forms an Ohmic contact for hole injection.^[21] For both devices, the electroluminescence turns on at a higher voltages (above 3 V), at which point the current transport changes from unipolar to ambipolar, as is evidenced by the knee in the J-V curve at around 3V. For devices with an SnO₂ thickness of 70 nm, the maximal current efficiency of 20.0 cd/A is achieved and corresponds to an EQE of 6.5%, as indicated in **Table 1**, which is lower than the case with ZnO as electron injection layer (~23 cd/A).^[13] In the case of SnO₂ thickness of 50nm, the current density is much larger than for devices with a 70 nm thick layer and the luminance turn-on voltage is around 3V. The luminance is seen to increase steadily, reaching more than 10000 cd/m² at 16 V, with a maximal current efficiency of 17.4 cd/A corresponding to an EQE of 4.5%. The current turn-on bias is similar in both cases, as is consistent with this current being a unipolar hole current, which is only dependent on the hole-injection and -blocking layer. With the increase of the bias, the current density of the diode with the thinner SnO₂ increases more steeply than the diode with thicker SnO₂. Although the current efficiency of the device with a thinner SnO₂ layer is slightly lower, the absolute luminance is much higher and reaches 1000cd/m² at 9.4V. Both diodes reach maximal efficiency at ~16V.

3.2 LED characteristics with Ba(OH)₂ as inorganic interlayer.

Although the device with SnO₂ as the electron injection layer has a lower current efficiency compared to the device using ZnO as previously reported,^[11] the device efficiency is still significantly improved compared to other n-type metals such as TiO₂, HfO₂, MgO and ZrO₂ etc.^[3,5-7,11] It is well established that Cs₂CO₃ as hole blocking layer plays a decisive role in the enhancement of the device performance in the novel hybrid structure, since Cs₂CO₃ dopes the polymer (to n-type) resulting in improved electron injection.^[22,23] This doping is additionally verified by experiments, when Cs₂CO₃ is annealed prior to the deposition of F8BT there is no electroluminescence at all from the HyLEDs.^[13,24] To compare the relative efficacies of Cs₂CO₃ and Ba(OH)₂ as the inorganic interlayer, we therefore also fabricated devices with Cs₂CO₃ coated on SnO₂.

Figure 2(b) allows a direct comparison of J-V-L characteristics of the devices with Ba(OH)₂ and Cs₂CO₃ as hole blocking layer. It is clear there are two domains of current density versus voltage in both device structures; however, the two domains are more clearly differentiated in the diode using Cs₂CO₃, which also has an earlier current onset without accompanying luminescence. It is likely that the hole-blocking effect is less efficient in the case of Cs₂CO₃ and leads to a hole current leakage at low voltages due to Ohmic injection of holes at the MoO₃/F8BT interface. The luminance turn-on voltage is similar for both devices, ~3V, while the current and luminance in the device with Cs₂CO₃ increases more rapidly than the device with Ba(OH)₂ and reaches a maximum luminance at 12 V. The lower current efficiency of the Cs₂CO₃-based device is likely due to inefficient charge recombination, perhaps related to exciton quenching at the metal-oxide/Cs₂CO₃/F8BT interface. Since Cs₂CO₃ intermixes with F8BT at the interface and consequently causes an improvement of electron injection accompanied by the introduction of defect sites, enhanced exciton quenching may be expected within the interfacial region of the device.^[22,23] The Ba²⁺ ions inherent in Ba(OH)₂ are doubly charged and less easily doped into the polymer. This in turn results in fewer defects at the interface with the F8BT polymer, presumably leading to a better hole blocking effect.^[14,25,26]

Whilst the efficiency of the device using Ba(OH)₂ as hole-blocking layer is much higher than the device using caesium carbonate, the corresponding operating voltage is significantly higher. This might suggest a considerable barrier for electron injection but an improved hole blocking effect with Ba(OH)₂. This mechanism is similar to that presented in reference [13]; the inorganic layer blocks holes at the interface with SnO₂, and the resulting accumulation of holes promotes electron injection. The higher efficiency is also owing to the fact that the recombination zone is expanded into the polymer film, hence further away from the cathode at higher operating voltage, which results in reduced exciton quenching.

3.3 Photophysical Study

To gain a further insight into the role of the caesium carbonate and barium hydroxide interlayers in SnO₂-based devices, measurements of photoluminescence quantum efficiency (PLQE) and fluorescence lifetime (by time correlated single-photon counting, or TCSPC) were carried out. The structure of the samples are quartz/SnO₂/Cs₂CO₃/F8BT and quartz/SnO₂/Ba(OH)₂/F8BT. The polymer film thicknesses are 100nm for PLQE

measurement and 15nm for TCSPC measurements, which are sufficiently thin that photo-generated excitons are in proximity with the SnO₂ interface.

Figure 3 plots the photoluminescence (PL) intensity vs. time revealing the decay lifetime; the time-dependence is well-described by a mono-exponential decay, as summarized in **Table 2**. The fitted decay time for the interface of quartz/SnO₂/Cs₂CO₃/F8BT is 0.91 ns, whilst it is 1.26 ns for that of quartz/Ba(OH)₂/F8BT. These results suggest that both Cs₂CO₃ and Ba(OH)₂ interlayers cause quenching of photoluminescence at the polymer interface, as the decay time of the quartz/F8BT reference sample is measured to be 1.8 ns. However, this quenching is faster for the Cs₂CO₃ interlayer, as compared to Ba(OH)₂. The PLQE of the sample using Cs₂CO₃ is measured to be 41%, which is much lower than the sample with Ba(OH)₂ as interlayer (60%). The low quantum yield for the caesium carbonate-based sample might be due to the quenching effect caused by defects at the Cs₂CO₃/polymer interface, as revealed by X-ray photoelectron spectroscopy (XPS) studies, and the diffusion of Cs⁺ ions onto the benzo[2,1,3]thiadiazol-4,8-diyl (BT) units of F8BT, leading to lower energy states.^[23,27] Although both inorganic interlayers lead to some degree of exciton quenching, this is significantly reduced with Ba(OH)₂ as compared to Cs₂CO₃. This could explain the higher efficiency of devices with the Ba(OH)₂ interlayer. The results from PLQE measurements are summarized in **Table 3**.

3.4 Morphological study of SnO₂ and ZnO thin-films

Whilst the performance of the SnO₂-based devices demonstrated here indicate that it is a suitable n-type metal oxide for electron injection in a HyLED, we note that the device performance is still somewhat lower than that of the device based on ZnO as hole injection layer. It is informative therefore to compare the morphology of ZnO and SnO₂ layers.

Figure 4 shows the morphology of ZnO and SnO₂ surface, as measured by means of atomic force microscopy (AFM); both thin films were made by similar means of spray pyrolysis, as detailed earlier in this report. For comparison, the measured sheet resistance values of the layers on ITO were 0.9 Ω/Sq for ZnO and 2.2 Ω/Sq for SnO₂; i.e. comparable to within an order of magnitude. As shown in figure 4, ZnO apparently forms a microcrystalline morphology, as supported by previous studies.^[6] The morphology of SnO₂ shows an amorphous or grain-like structure, again in agreement with the literature.^[28] Different batches of SnO₂ films with 50nm and 70 nm thickness repeatably show the same morphological

structure, however there is a significant variability in the device performance, especially when Cs_2CO_3 is used as the interfacial layer. The comparison of the fluorescence decay time between the ZnO and SnO_2 based samples (**Table 2**) reveals that ZnO-based samples in general have a longer decay lifetime than SnO_2 -based samples. This may also be related to these differences in morphology.

4. DISCUSSION

The J-V-L curves in **Figure 2** indicates there is a current leakage at the interface of $\text{SnO}_2/\text{Cs}_2\text{CO}_3$, while this effect is less pronounced at the $\text{SnO}_2/\text{Ba}(\text{OH})_2$ interface. Also the photophysical studies reveal that samples based on $\text{Ba}(\text{OH})_2$ have a longer fluorescence decay lifetime and larger PLQE than the one based on Cs_2CO_3 . The reduced PL quenching in the $\text{Ba}(\text{OH})_2$ based samples may be due to the doubly charged Ba^{2+} ions being more difficult to diffuse into polymer film than singly charged Cs^+ ions,^[23] leading to a corresponding reduced defect density at the interface $\text{Ba}(\text{OH})_2/\text{polymer}$. Hence, $\text{Ba}(\text{OH})_2$ provides a better hole-blocking effect, leading to a better device performance. Amongst the large batch of devices, it has been found that devices based on $\text{SnO}_2/\text{Ba}(\text{OH})_2$ show better reproducibility than devices based on $\text{SnO}_2/\text{Cs}_2\text{CO}_3$, and the $\text{Ba}(\text{OH})_2$ based samples also show a reduced exciton quenching effect compared to Cs_2CO_3 based samples, as shown in Table 3. The measured EQE values of devices based on $\text{SnO}_2/\text{Cs}_2\text{CO}_3$ and $\text{SnO}_2/\text{Ba}(\text{OH})_2$ are compared with theoretically estimated ones as shown in Table 2, which are determined as described in equation 1:

$$\eta_{ext} = \gamma R_{st} Q \eta_{outcoupling} \quad (\text{Eq. 1})$$

where γ is the opposite charge balance, R_{st} is the singlet to triplet ratio (taken as 25%), Q is the measured PLQE and $\eta_{outcoupling}$ is the outcoupling factor (which is in the range of $0.75/n^2$ to $1.2/n^2$),^[29] and n is the polymer refractive index being taken as 1.8 for F8BT. The calculated EQE values, using both pre-factors 0.75 and 1.2 for comparison, are given in **table 3**; the results indicate that the measured device efficiency is slightly higher than that theoretically predicted. However, an important caveat is the difference in the F8BT layer thickness between devices (1000 nm) and the theoretical model, which is based on the optical constants with a film thickness of 100 nm.^[13] Furthermore, considering recent evidence that

the singlet-triplet ratio can be greater than 25% and even go beyond 50%, there is indeed scope for a further improvement of device efficiency.^[30]

The morphological study by means of AFM reveals a difference between the ZnO and SnO₂ surfaces. The suggestion is that the ZnO is microcrystalline-like while SnO₂ is amorphous-like; details which may be resolved in the future with a detailed X-ray diffraction study. Also the comparison of fluorescence decay lifetime between the structures of ZnO/inorganic interlayer/F8BT and SnO₂/inorganic interlayer/F8BT reveals that ZnO based samples show a longer fluorescence decay lifetime (see Table 3). This suggests that it might be worthwhile investigating alternative methods of SnO₂ deposition, such as atomic layer deposition (ALD), which delivers a crystalline structure and might allow modification of the interfacial interaction between SnO₂ and the inorganic interlayer, in order to achieve an improved device performance. This method would also have the advantage of lower processing temperatures than those used in spray pyrolysis, where SnO₂ requires annealing at high temperatures, close to where glass starts to bow, and which would obviously be incompatible with plastic substrates. ALD would thus potentially allow compatibility with some of the more niche low-cost flexible substrates. Nevertheless, the reproducibility of devices based on SnO₂/Ba(OH)₂ as electron injection and hole blocking layer is high compared to those based on SnO₂/Cs₂CO₃, in addition to the superior device performance metrics described.

5. CONCLUSIONS

In summary, polymer (F8BT) HyLEDs based on Tin (IV) oxide as an electron injection and transport layer, used in combination with thin hole-blocking interlayers, have been investigated. The device efficiency with Ba(OH)₂ as the interlayer reaches 20.0 cd/A with an EQE of 6.5%, which is significantly higher than that of diodes using Cs₂CO₃ (current efficiency of 12.1 cd/A and corresponding EQE of 4%). The higher efficiency of the devices with Ba(OH)₂ is believed to arise from a better hole-blocking effect, since Ba²⁺ is doubly charged and less readily diffuses into the polymer layer, leading to fewer interfacial defects. Photophysical studies reveal that the fluorescence lifetime of F8BT is longer and PLQE higher for quartz/SnO₂/Ba(OH)₂/F8BT structures compared to quartz/SnO₂/Cs₂CO₃/F8BT. Hence, the interface of SnO₂/Ba(OH)₂ is characterized by reduced exciton quenching, as compared to SnO₂/Cs₂CO₃. A further detailed study of the interface between SnO₂ and interlayer(s) might be helpful for further device optimization. The morphological study of

SnO₂ and ZnO thin films reveals that the surface morphology of SnO₂, as prepared by means of spray pyrolysis, is different from that of ZnO prepared using the same method.

SnO₂ has thus been demonstrated as a highly suitable n-type metal oxide material for electron injection in HyLEDs, in combination with the other desirable features and properties of this material. With suitable improvements of surface morphology in the future, SnO₂ may be exploited in *state-of-the-art* LED devices.

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REFERENCES

- [1] Rao C N R and Raveau B, 1998 *Transition Metal Oxides*, Wiley-VCH, New York.
- [2] Sanon G, Rup R and Mansingh A, 1991 *Phy. Rev. B* **44**, 5672-5680
- [3] Morii K, Ishida M, Takashima T, Shimoda T, Wang Q, Nazeeruddin M K and Grätzel M, 2006 *Appl. Phys. Lett.* **89**, 183510
- [4] Bolink H J, Coronado E, Repetto D and Sessolo M, 2007 *Appl. Phys. Lett.* **91**, 223501
- [5] Kabra D, Song M H, Wenger B, Friend R H and Snaith H J, 2008 *Adv. Mater.* **20**, 3447-3452.
- [6] Tokmoldin N, Griffiths N, Bradley D D C and Haque S A, 2009 *Adv. Mater.* **21**, 3475-3478
- [7] Bolink H J, Brine H, Coronado E and Sessolo M, 2010 *J. Mater. Chem.* **20**, 4047-4049
- [8] Huang J, Li G, Wu E, Xu Q and Yang Y, 2006 *Adv. Mater.* **18**, 114-117
- [9] Wu C, Lin C T, Chen Y, Chen M, Lu Y and Wu C C, 2006 *Appl. Phys. Lett.* **88**, 152104
- [10] Huang J, Watanabe T, Ueno K and Yang Y, 2007 *Adv. Mater.* **19**, 739-743.
- [11] Morii K, Kawase T and Inoue S, 2008 *Appl. Phys. Lett.* **92**, 213304
- [12] Bolink H J, Coronado E, Orozco J and Sessolo M, 2009 *Adv. Mater.* **21**, 79-82.

- [13] Kabra D, Lu L-P, Song M H, Snaith H J and Friend R H, 2010 *Adv. Mater.* **22**, 3194-3198.
- [14] Lu L-P, Kabra D and Friend R H, 2012 *Adv. Funct. Mater.* **22**, 4165-4171.
- [15] Batzill M and Diebold U, 2005 *Prog. Surf. Sci.* **79**, 47-154; Tsuda N, Nasu K, Fujimori A and Siratori K, 2000 *Electronic Conduction in Oxides*, Springer-Verlag, Berlin.
- [16] Green A N M, Palomares E, Haque S A, Kroon J M and Durrant J R J, 2005 *Phys. Chem. B* **109**, 12525
- [17] Snaith H J and Ducati C, 2010 *Nano Lett.* **10**, 1259-1265.
- [18] Gordillo G, Moreno L C, de la Cruz W and Teheran P, 1994 *Thin Solid Films* **252**, 61-66.
- [19] Melsheimer J and Ziegler D, 1985 *Thin Solid Films* **129**, 35-47
- [20] Lu L-P, Finlayson C E and Friend R H, 2014 *Semicond. Sci. Technol.* **29**, 025005
- [21] Kröger M, Hamwi S, Meyer J, Riedl T, Kowalsky W and Kahn A, 2009 *Org. Elec.* **10**, 932-938
- [22] Suhonen R, Krause R, Kozlowski F, Sarfer W, Paezold R and Winnacker A, 2009 *Org. Elec.* **10**, 280-288
- [23] Vaynzof Y, Kabra D, Chua L L and Friend R H, 2011 *Appl. Phys. Lett.* **98**, 113306
- [24] Lu L-P, Kabra D, Johnson K and Friend R H, 2012 *Adv. Funct. Mater.* **22**, 144-150.
- [25] Crispin A, Jonsson A, Fahlman M and Salaneck W R, 2001 *J. Chem. Phys.* **115**, 5252-5257.
- [26] Scheiba F, Benker N, Kunz U, Roth C and Fuess H, 2008 *J. Power Sources* **177**, 273-280.
- [27] Fung M K, Lai S L, Tong S W, Bao S N, Lee C S, Wu W W, Inbasekaran M, O'Brien J J and Lee S T, 2003 *J. Appl. Phys.* **94**, 5763-5770.
- [28] Bueno P R, Varela J A and Longo E, 2008 *J. Eur. Ceram. Soc.* **28**, 505-529.
- [29] Kim J.-S, Ho P K H, Greenham N C and Friend R H, 2000 *J. Appl. Phys.* **88**, 1073-1081.
- [30] Walikewitz B H, Kabra D, Gélinas S and Friend R H, 2012 *Phys. Rev. B* **85**, 045209

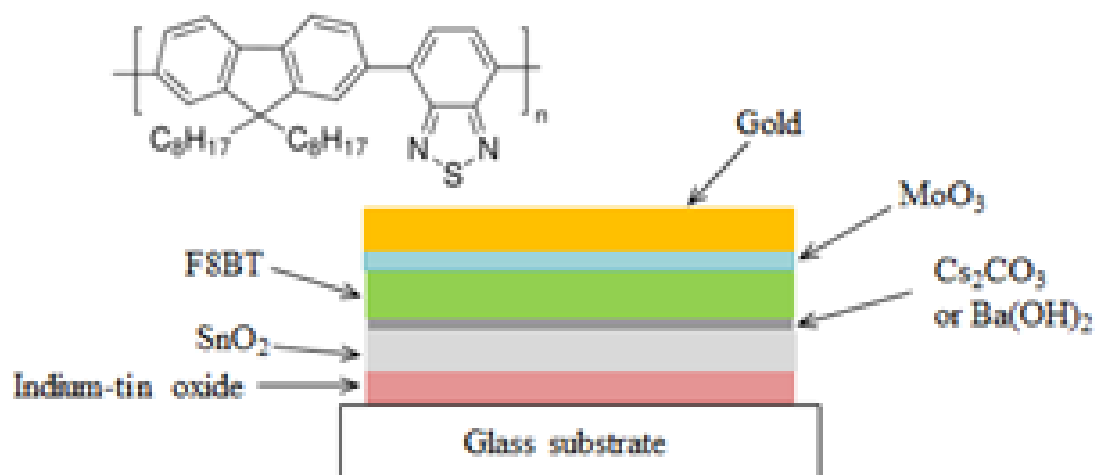


Figure 1 The structure of a hybrid polymer light emitting diode using SnO₂ as the electron injection layer, and Cs₂CO₃ or Ba(OH)₂ as the inorganic interlayer (hole blocking layer). The inset shows the chemical structure of the F8BT active layer.

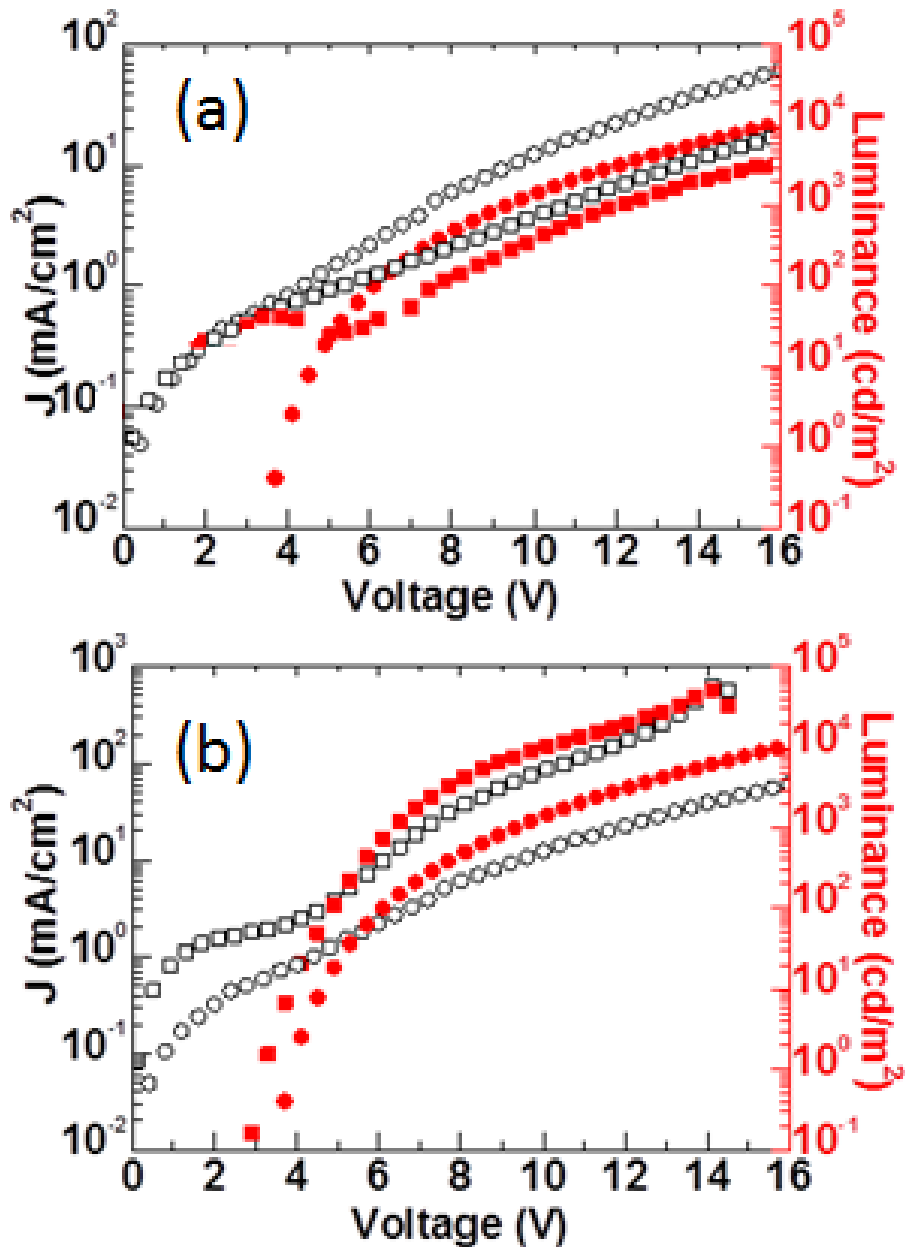


Figure 2 (a) J-V-L curve comparison of the performance of HyLEDs ($\text{Ba}(\text{OH})_2$ hole-blocking layer) with two different SnO_2 layer thicknesses, 50nm (circles) and 70nm (squares). (b) J-V-L curve comparison of diodes based on SnO_2 , using Cs_2CO_3 (squares) and $\text{Ba}(\text{OH})_2$ (circles) as the hole-blocking layer. In both graphs, solid/red symbols represent luminance and empty/black symbols the current density.

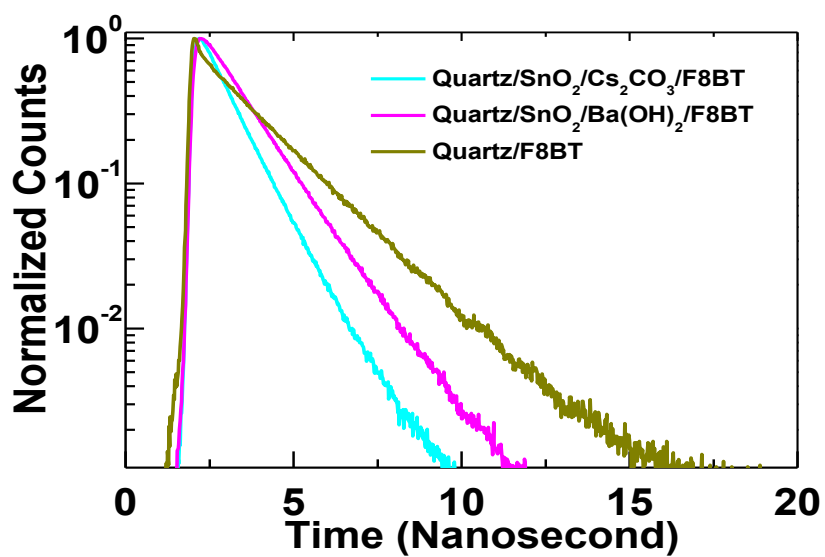


Figure 3 Fluorescence decay-time measurements with F8BT deposited onto three different interfaces, as indicated; quartz/SnO₂/Cs₂CO₃/F8BT, quartz/SnO₂/Ba(OH)₂, and quartz/F8BT. The F8BT film thickness is 15nm, with excitation at $\lambda = 470$ nm, and emission being measured at $\lambda = 555$ nm.

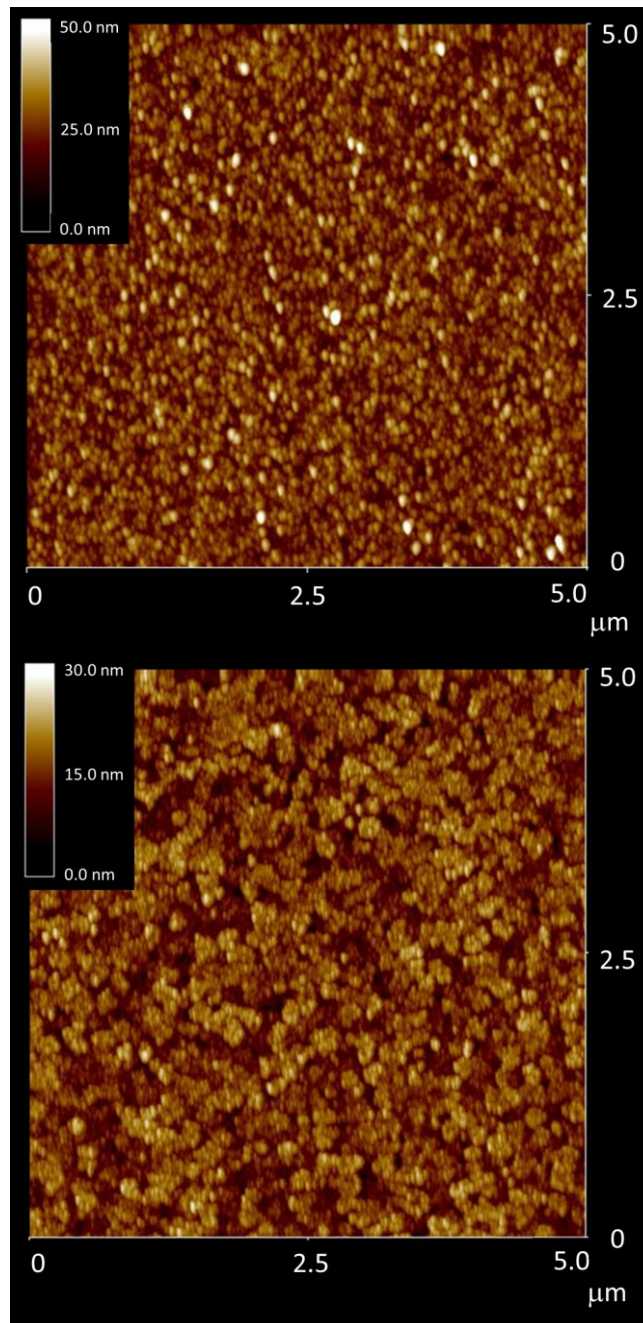


Figure 4. Atomic force microscope (AFM) images of spray deposited ZnO (top) and SnO₂ (bottom). The r.m.s. roughness of both of these films was measured to be below 5 nm. Respective height scales for the two images are shown as insets.

HyLED structure	ITO/SnO ₂ /Cs ₂ CO ₃ /F8BT/MoO ₃ /Au	ITO/SnO ₂ /Ba(OH) ₂ /F8BT/MoO ₃ /Au
Bias@10mA/cm ²	6.2V	10.1V
Bias@1000cd/m ²	6.4V	12.3V
Peak luminance efficiency (cd/A)	12.1@9.4V	20.0@15.6V
Peak EQE (%)	4%	6.5%
Power Efficiency (lm/W)	4.2	4.1

Table 1 HyLED performance parameters using Cs₂CO₃ and Ba(OH)₂ as inorganic interlayers

F8BT (15nm)	Decay time (ns)
Quartz/ZnO/Cs ₂ CO ₃ /F8BT	1.16
Quartz/ZnO/Ba(OH) ₂ /F8BT	1.31
Quartz/SnO ₂ /Cs ₂ CO ₃ /F8BT	0.95
Quartz/SnO ₂ /Ba(OH) ₂ /F8BT	1.26

Table 2 Comparison of fluorescence decay lifetimes between samples based on ZnO and SnO₂ as well as Cs₂CO₃ and Ba(OH)₂. The thickness of ZnO and SnO₂ is ~ 50 nm and that of the thin film of Cs₂CO₃ and Ba(OH)₂ is ~ 7 nm.

	EQE Measured	EQE Predicted	Decay time (ns)	PLQE (%)
SnO ₂ /Cs ₂ CO ₃ /F8BT	4%	2.6-3.7 %	0.95	41
SnO ₂ /Ba(OH) ₂ /F8BT	6.5%	3.8-5.6 %	1.26	60

Table 3 A comparison of EQE values between 1000nm thick devices based on Cs₂CO₃ and Ba(OH)₂, in terms of both measurement and theoretical prediction. The theoretical values account for the full possible range of device *outcoupling factors*. Corresponding F8BT fluorescence decay time and photoluminescence quantum efficiency (PLQE) values are given, where the polymer thickness was set at 15nm.