

11.2: Degradation of PLEDs and a Way to Improve Device Performances

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Abstract

The most significant degradation problem of PLED has been described and new buffer layer material aimed for use as HTL in PLED to solve this issue has been studied. This approach has enabled the increase of the green device efficiency (~2x) and lifetime (~5-6x).

1. Introduction

Since the discovery of electroluminescence in polymers,¹ over the last few years substantial research has gone into improving the light output, power efficiency, and lifetime of polymer light-emitting diodes (PLEDs). One key component in more advanced multilayer PLED structures is the hole-transport layer (HTL), which is believed to serve two functions:²⁻³ (1) Increases hole injection from the transparent anode, e.g., indium tin oxide (ITO), to the emissive polymer by increasing the work function of the anode; and (2) Planarizes the ITO anode surface, preventing local shorting currents, and thus improves device reproducibility. Typical conducting polymers employed as HTLs include polyaniline and polydioxothiophenes such as PEDOT⁴⁻⁷. These materials can be prepared by polymerizing aniline or dioxothiophene monomers in aqueous solution in the presence of a water soluble polymeric acid, such as poly(styrenesulfonic acid)(PSSA).⁸ A well known

PEDOT/PSS material is Baytron -P, commercially available from H. C. Starck, GmbH. However, these acidic conventional HTLs are not ideal because the undesirable low pH can contribute to decreased stress life of an EL device containing such a buffer layer, and contribute to corrosion within the device. It has also been shown⁹⁻¹⁰ that high acidity of PEDOT:PSSA attacks ITO to cause indium contamination on the light emitting polymer. PEDOT/PSS has a work function of approximately 5.0-5.2 eV which is relatively low. It is difficult to inject holes into some materials and hole injection is a limiting factor in device performance. Thus, the highest occupied molecular orbital (HOMO) of the injection layer is required to be at an energy close to, or even below, that of the π -band of the semiconducting polymer. Therefore, intense efforts in PLED research community have focused on alternative HTLs¹¹⁻¹² and there is a need for new compositions of buffer layers having improved properties.

Understanding of the mechanisms that cause a device to degrade is the first step towards fixing the problem or designing better materials and device structures. Significantly improved device performance is already being realized. Recently DuPont scientists studied light emission degradation to determine ways of improving device operation and developed new HTLs that increased operating lifetime more than 400%. The new HTL is aqueous dispersion made by polymerizing dioxothiophene with a DuPont proprietary

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polymeric sulfonic acid. In this paper, PEDOT doped with the polymeric sulfonic acid, which is called DB1, is used as a hole transporting layer in PLEDs and their film properties and effects on device performances are compared to that of PEDOT:PSSA.

2. Experimental

The detailed synthesis and characterization of DB1 will be published elsewhere.¹³ PEDOT:PSSA was supplied by H. C. Starck under the commercial name of Baytron P (CH8000 and A14083). The PLED devices are made by spin coating DB1 onto patterned ITO to a thickness of 80nm. This layer is then typically baked on a hotplate at 130°C in air for 5 minutes. The LEP (LUMATION 1300 Series Green polymer) is spin coated onto the cured buffer layer films from 1.0 w/w % solution at a speed suitable to achieve 75nm. The films are subsequently baked at 130°C on a hotplate for 10 minutes in a glove box. The substrates were then transferred into a thermal evaporator and cathode deposited under a vacuum of 10^{-6} torr. The cathode consists of 3nm of a low work function metal and then 400nm Al. Devices are then encapsulated using a UV curable epoxy and a glass lid. The PLED characterization was carried out by a Keithley 236 source-measure unit and a calibrated silicon photodiode. The single carrier devices are prepared in an identical manner, except that for hole-only devices Au is used as the cathode material. For electron-only devices Sn onto ITO is used instead of buffer layer.

3. Results

DB1 films are almost totally transparent at 75nm thickness. The transmission spectra of the DB1 films on ITO-coated glass are shown in Figure 1. Over the entire visible spectrum, DB1 film has >90% transmission; essentially no light from the emitting layer is absorbed.

Solid films dried from a commercial PEDOT:PSSA and our DB1 were characterized at room temperature and were tested for re-

dispersibility and acidity with about 10 mL deionized water and also for moisture uptake. Dried films were allowed to equilibrate at ambient conditions before being analyzed for moisture uptake by a TGA (at 20°C/min in nitrogen). The 10 mL water of PEDOT:PSSA turned blue and became very dark as most of the entire film flakes were re-dispersed in the water. The water also became very acidic, having a pH of zero according to a pH paper. The film flakes absorbed 29.4% water at ambient conditions. This result clearly demonstrates that the PEDOT:PSSA films are very hygroscopic and very acidic. It is foreseeable that residual moisture left in the device can be released to cause degradation. In case of DB1, the flakes stayed shiny, indicating that the films were not swollen. Surprisingly, the water was colorless, meaning that DB1 was not re-dispersible in water. Moreover, the water had a pH of 7 according to a pH paper. This clearly shows that the polymeric acid is not mobile. And the film flakes absorbed only 3.3% water, which is far less than commercial PEDOT.

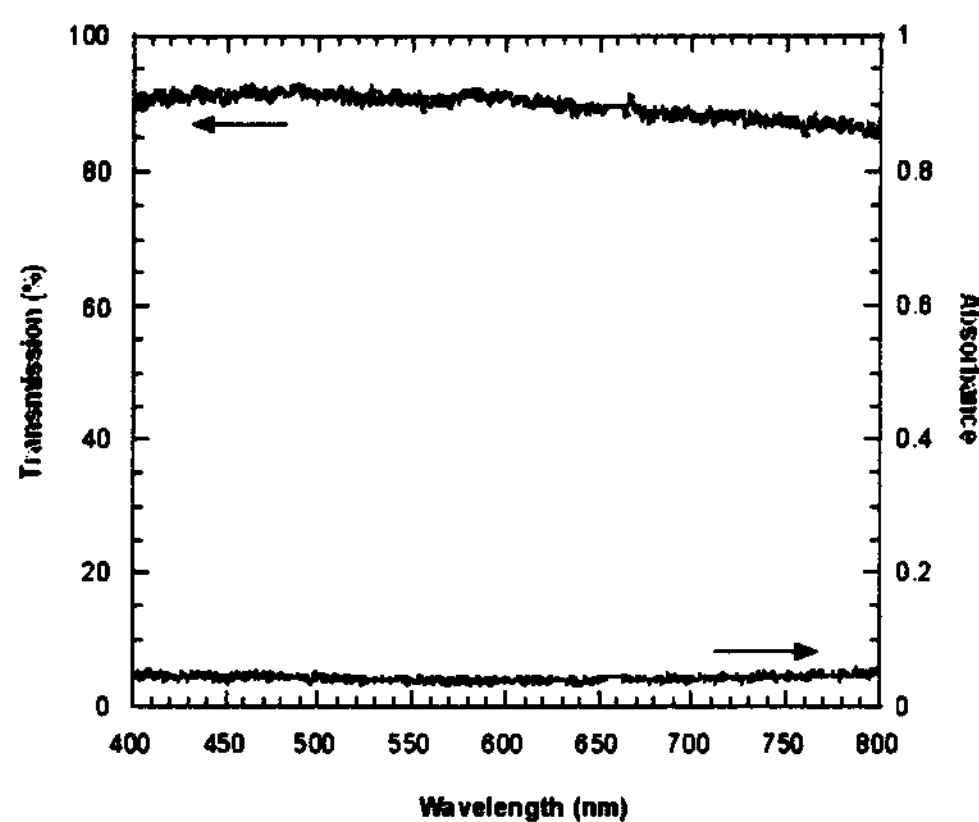


Figure 1. Optical absorption and transmission properties of DB1 films.

The anode/organic interface is of critical importance in determining the lifetime and performance of PLEDs. By using DB1 as hole injecting layer, problems associated with the

acidity of PEDOT:PSSA, namely, etching the ITO surface and with diffusion of indium into the light emitting polymer, was eliminated. The top surfaces of both layers were examined using X-ray photoelectron spectroscopy (XPS). Indium elements were detected in case of PEDOT:PSSA, indicating that ITO was attacked by the aqueous PEDOT:PSSA dispersion, which had a pH of ~ 1.7 .⁹ On the other hand, there was no indium element detected in case of DB1 having pH of 4 or higher, indicating that the ITO was not attacked by DB1.

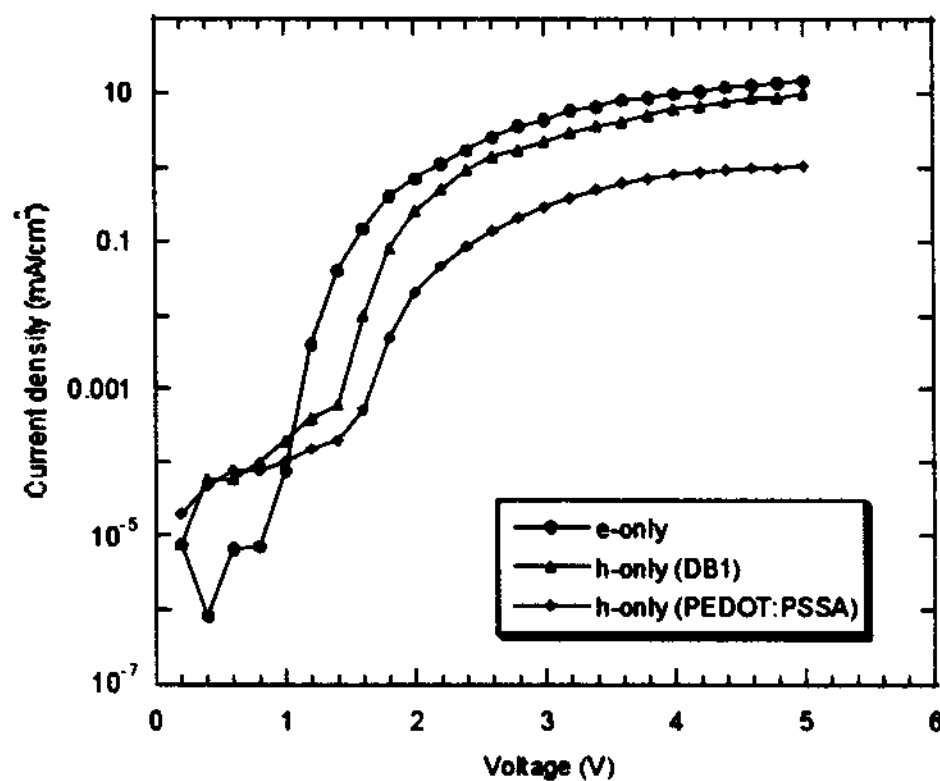


Figure 2. I-V characteristics of electron only and hole only device using green polymer with PEDOT:PSSA and DB-1

For example, a commercially available LEP that seems to benefit from the improved hole injection provided by DB1 is LUMATION Green 1300 Series from Dow Chemical Company. A method used for understanding the charge balance and majority charge carrier in an LEP is to fabricate single carrier devices.¹⁴ A balanced number of holes and electrons is necessary in order to optimize the performance of a device. Detailed experiments using single carrier hole-only and electron-only device have shown that in LUMATION Green 1300 Series doesn't show balanced injection – holes are in short supply in case of using PEDOT:PSSA. By using our DB1, its work function may better match HOMO of LEP, which lead to better balance of electrons and holes.

Figure 2 shows the hole current and electron current from LUMATION Green 1300 Series with PEDOT:PSSA and DB1 as measured by single carrier devices. But the hole and electron flux are strongly dominated by electrons with PEDOT:PSSA. This figure shows a highly improved hole injection by using DB1 compared with PEDOT:PSSA.

Figure 3 shows voltage increase rate (VIR) regarding "hole-only" device data for LUMATION Green 1300 series with both PEDOT:PSSA and DB1 as buffer layer. The VIR is significantly different in the two cases. The only differences are the nature of the buffer layer and the nature of the buffer layer interface. PEDOT-PSSA devices generally have a higher voltage increase rate than DB1 devices. This suggests there is degradation of the PEDOT:PSSA, or at the buffer interface.

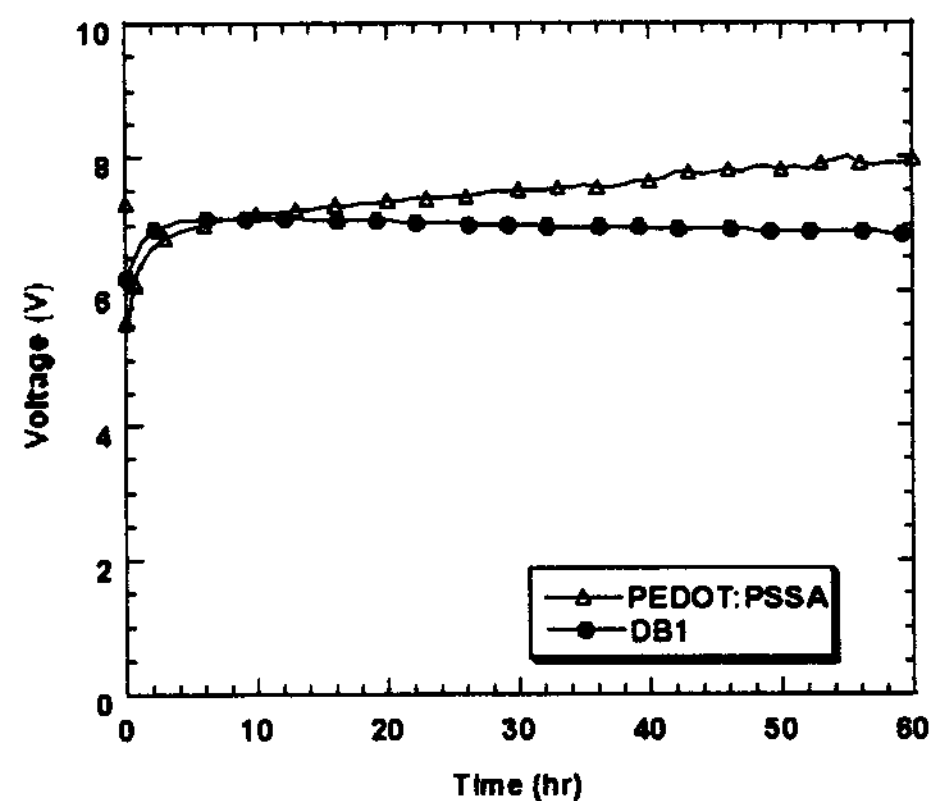


Figure 3. The plot of drive voltage vs time for LUMATION Green 1300 Series LEP hole-only devices with DB1 compared to PEDOT:PSSA.

Recent results with our new buffer layer have shown efficiency enhancements with LUMATION green 1300 Series, reaching values $>20\text{cd/A}$ with the standard device configuration. Furthermore the efficiency stays relatively constant to high luminance levels. Figure 4 shows efficiency difference between two buffer layers. DB1 with much higher efficiencies might simply reflect a better energy level matching with a lower hole

barrier, greater hole injection and hence higher efficiencies.

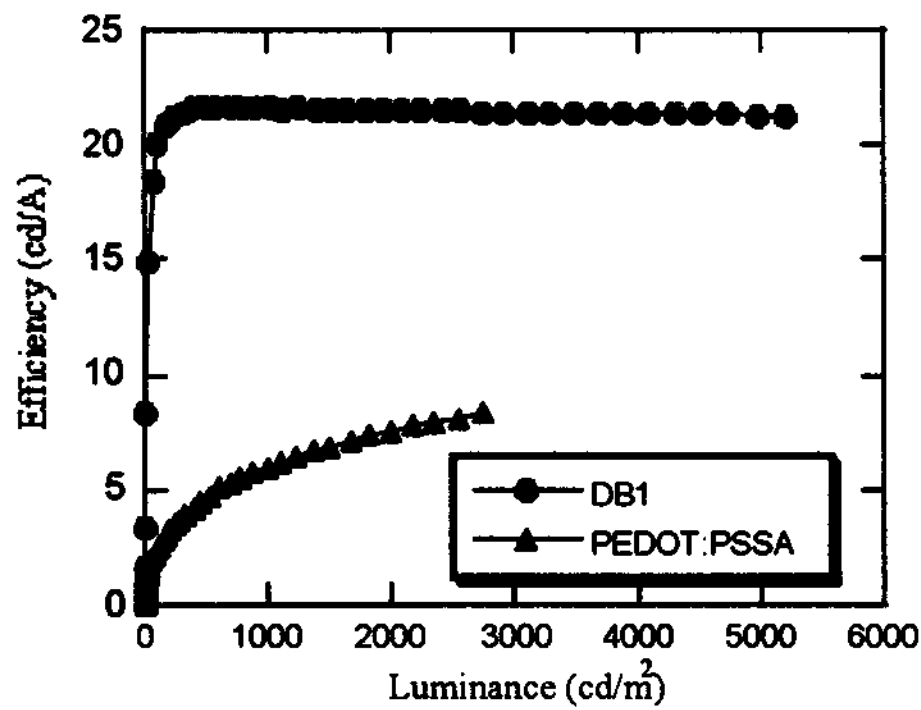


Figure 4. Efficiency-luminance characteristics for LUMATION 1300 Series polymer devices with DB1 compared with PEDOT:PSSA.

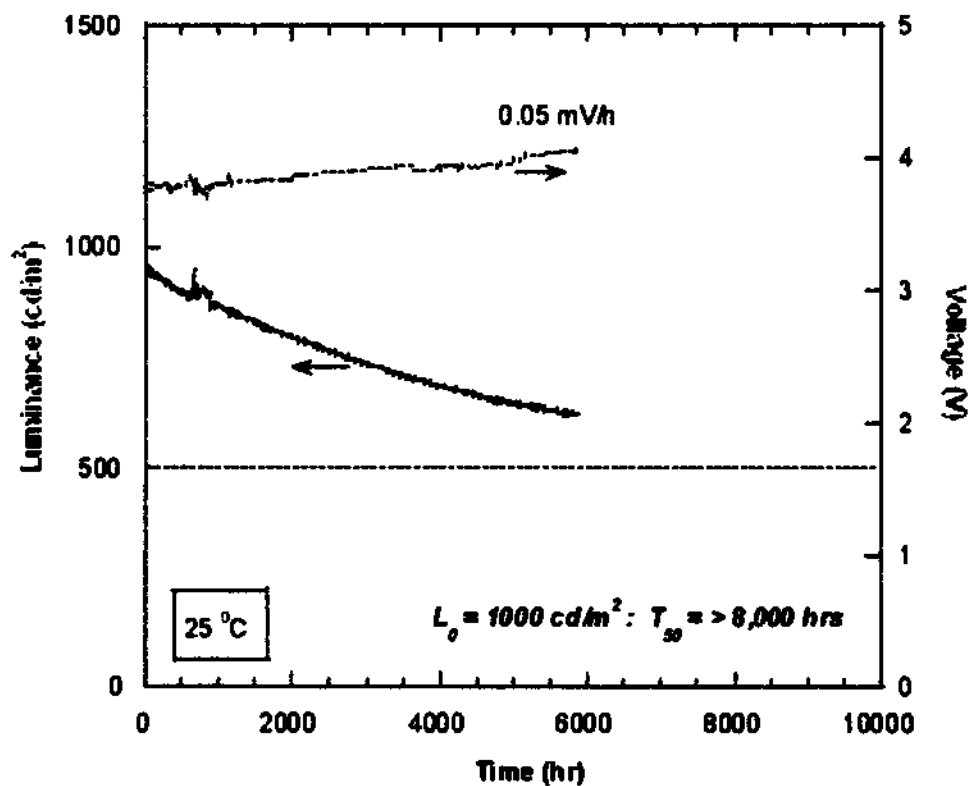


Figure 5. Plot of the luminance and the drive voltage vs time for LUMATION Green 1300 Series LEP device with DB1.

With PEDOT:PSSA the poor hole-injection gets rapidly worse as the device is operated, so the device performance deteriorates. With DB1 the work-function may be more stable, so we retain the benefit of the better alignment – hence lifetime is improved significantly. Figure 5 shows a device half-life of greater than 8,000 hours starting from a

luminance of 1,000 cd/m^2 with DB1. 1,500 hours were exemplified with PEDOT:PSSA.¹⁵ Our new buffer layer enhanced lifetime ~5-6x and efficiency ~2x.

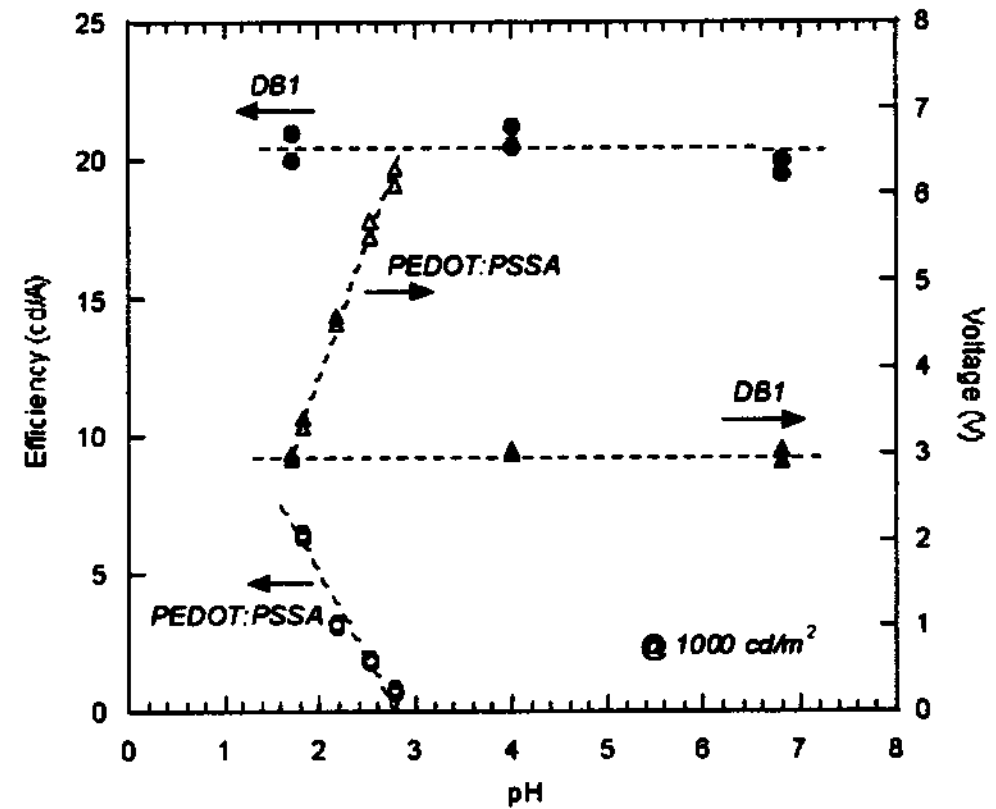


Figure 6. Effect of pH on different buffer layers

Figure 6 shows the initial device performance of LUMATION green 1300 Series that contain a PEDOT:PSSA and DB1 as buffer layers, that has had its pH adjusted. Clearly, increasing the pH of Baytron-P much above 2.5 significantly degrades the performance of PLED devices. Unlike the Baytron-P devices, DB1 devices are not degraded by a high pH DB1 buffer layer.

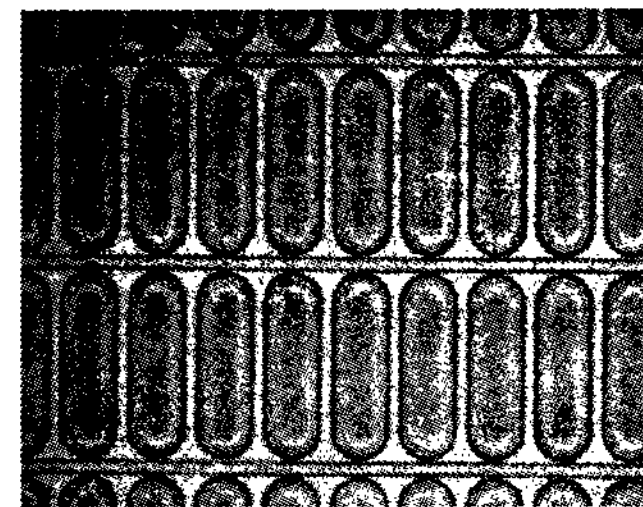


Figure 7. Wells printed with DB1 showing good coverage.

Ink-jetting of DB1 onto ITO proved to be very easy. The liquid jetted at a low head voltage, with

nice spherical drops, free of ligaments. Once on the ITO the liquid spread readily to fill the well structure. Figure 7 shows the result.

4. Conclusions

DuPont has developed a unique buffer material to solve the most significant degradation problem of PLEDs. Using DB1 as a buffer layer the effect of the major degradation mechanism associated with using PEDOT:PSSA buffer was reduced. Our new buffer material can easily be adjusted to give high pH without affecting device performance. This pH neutrality has several benefits: (1) less etching of the ITO, and hence less metallic indium ions in the devices (2) less corrosion of device (3) less attack of certain sensitive LEP functional units (4) less corrosion of manufacturing equipment. DB1 offers additional significant attractions versus conventional PEDOT:PSSA: lower moisture uptake, suspectedly higher work function, better hole injection property and most importantly, a general strategy to achieve ideal HTL/EML energy level alignment in polymer light emitting diodes. This approach has enabled the increase of the green device efficiency (~2x) and lifetime (~5-6x). Currently, we are studying DB1 / LEP devices in fundamental approaches to further refine DB1 as a buffer layer in PLEDs, which will lead to even higher efficiency and longer lifetime. Most RGB materials show a similar 4 - 8x lifetime improvement by using DB1. More details will be published in near future.

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