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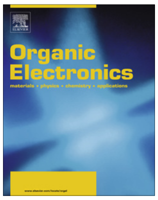

Suppressing molecular aggregation in solution processed small molecule organic light emitting diodes

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ABSTRACT

Solution processing of low-molecular weight organic materials for optoelectronic devices is a challenging task due to often strong molecular aggregation. We present a facile and universal route for suppressing the aggregation of molecules during wet-deposition of emission layers for organic light emitting diodes by incorporating electronically inactive polymers. Moderate polymer concentrations of about 10 wt.% lead to only minor changes of the electrical performance while at the same time improving the film formation and consequently the device luminance significantly. The device performance matches the performance of vacuum processed devices with the same device architecture.

1. Introduction

Organic light emitting diodes (OLEDs) have progressed to consumer electronics products in display technology or low-cost, small-area signage applications. Today, state-of-the-art OLEDs are fabricated by thermal sublimation of low-molecular weight molecules (“small molecules”) in vacuum reaching efficiencies of about 100 cd/A, exceeding the efficiency of most other light sources [1–7]. The key to highly efficient OLEDs was the implementation of phosphorescent emitters such as the green-emitting tris (2-phenylpyridine)iridium(III) ($Ir(ppy)_3$) into host materials such as 4,4′-bis(carbazol-9-yl)biphenyl (CBP) that have a higher triplet energy than the emitter molecule and therefore ensure proper charge carrier confinement on the phosphorescent emitter [8,9].

The prospect of utilizing OLEDs in general lighting in the future is the main driver for large-area fabrication processes. In order to fabricate OLEDs on large-scale while simultaneously reducing production costs, printing and coating processes are widely discussed. Due to their mostly excellent film forming properties upon deposition from solution, conjugated polymers are the materials of choice for printing and other wet-processes. However, polymers usually carry numerous intrinsic defects that result from material impurities during polymer synthesis. In contrast to small molecules, polymers cannot be purified efficiently after synthesis and defects remain within the polymers where they hamper the device performance and stability. Polymeric charge carrier transport layers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) can be replaced effectively by more stable and reliable metal oxide buffer layers such as molybdenum oxide (MoO_3) or tungsten oxide (WO_3) that can be applied via precursor conversion from solution [10–15]. For light emitting layers in solution deposited OLEDs, recently, small molecules have been investigated. Solution processed OLEDs from small molecules utilizing bipolar hosts with efficiencies up to 69 cd/A have been reported by Cai et al. [16]. Multi-layer OLEDs have been realized by applying cross-linkable low-molecular weight transport and

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blocking materials [17,18]. Unfortunately, most small molecules exhibit poor film forming properties in wet processes due to strong molecular aggregation, i.e. the formation of molecular crystalline domains [19,20].

In this work, we present a facile route to suppress aggregation of small molecules in light emitting layers that are deposited from solution. We therefore admix small amounts of the electrically isolating polystyrene (PS) to the emitter material system CBP:Ir(ppy)$_3$ in chlorobenzene solution that accounts for a much better intermixed host–guest system while at the same time hardly affecting the optoelectronic device properties.

2. Experimental

According to the device architecture depicted in Fig. 1a, all OLEDs were fabricated on indium tin oxide (ITO) coated glass substrates ($R_\square \approx 13\ \Omega/\gamma$) that had been structured in hydrochloric acid. The substrates were cleaned with acetone and isopropanol for 15 min in an ultrasonic bath before they were exposed to an oxygen plasma for 2 min in order to remove organic residues and to polarize the ITO surface for better PEDOT:PSS adhesion. After plasma treatment, the samples were moved to a nitrogen glovebox and kept there for the remaining fabrication process and sample characterization. A PEDOT:PSS (VPAI 4083, Heraeus Precious Metals GmbH & Co. KG) hole injection layer was spincast at 4000 rpm for 30 s from a 1:1 water diluted dispersion. Afterwards, the substrates were annealed for 10 min in a vacuum oven at 120 °C. CBP (Sigma–Aldrich Chemie GmbH, purity 99.9%) and PS (Alfa Aesar, $M_w = 100.000$ g/mol) were separately dissolved in chlorobenzene (CB, 20 mg/ml) and then mixed. The mixed host was then doped with 10 wt.% Ir(ppy)$_3$ (Sensient Imaging Technologies GmbH, purity 99.9%) in solution (Fig. 1b). The 30 nm CBP:PS:Ir(ppy)$_3$ emission layer was spincast at 1000 rpm for 60 s and finally annealed at 70 °C for 10 min. The 20 nm bathophenanthroline (BPhen, Luminescence Technologie Corperation, purity > 99.5%) or 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi, Luminescence Technologie Corperation, purity > 99%) hole blocking layers (HBL) and the LiF/Al (0.7 nm/200 nm) counter electrodes were thermally evaporated in high vacuum (10^{-6} mbar).

For reference, devices with the same architecture were thermally evaporated atop an ITO/PEDOT:PSS electrode. CBP was doped with 10 wt.% Ir(ppy)$_3$ in co-evaporation according to literature recommendations [21].

Current density–voltage (J–V) characteristics were recorded with a source measure unit (Keithley 238) at room temperature in nitrogen atmosphere. The device luminance was calculated from the emission spectrum. The spectrometer had been calibrated with a secondary standard calibration halogen lamp (Philips FEL-1000 W). Onset voltages were determined at a luminance of 1 cd/m^2. Current efficiencies (cd/A) and power efficiencies (lm/W) were calculated from the electrical and optical properties assuming Lambertian light distribution.

Atomic force microscopy (AFM) measurements were carried out under inert conditions on a Bruker Dimension Icon atomic force microscope equipped with a Nanoscope V controller. Conductive silicon tips on silicon nitride cantilevers (from Bruker, model ScanAsyst-Air, resonance at ca. 70 kHz, $k = 0.4$ N/m) were used as sensors.

Low-energy scanning transmission electron microscopy (low-keV STEM) imaging was carried out in a FEI Strata 400S dual-beam scanning electron microscope. It is equipped with a 16 bit semiconductor STEM detector which is positioned below the sample holder. The images were taken with the high-angle annular dark-field (HAADF) detector segment, which detects electrons within a scattering-angle range between 0.2 and 0.7 rad for the used working distance of 5 mm. The primary electron energy was 15 keV.

Energy dispersive X-ray (EDX) analyses were carried out in the same microscope, using a Bruker XFlash 5010 detector. The primary electron energy for the analysis was 30 keV, the acquisition time 2 min and the electron current 2.2 nA.

3. Results and discussion

When attempting to deposit neat CBP films from solution atop the ITO/PEDOT:PSS electrode, the molecules immediately aggregate and form distinct CBP structures as depicted in the optical microscope image and the AFM picture in Fig. 2a and b (surface roughness: $R_{\mathrm{rms}} \approx 57.5$ nm), rendering the layer unsuitable for OLED fabrication. Upon incorporation of Ir(ppy)$_3$ molecules into the CBP solution and subsequently into the emission layer, the CBP aggregation is effectively suppressed. Though the CBP:Ir(ppy)$_3$ surface appears much smoother

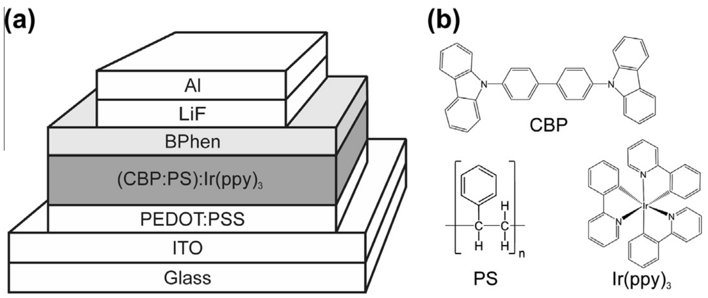

Fig. 1. (a) Device architecture of the solution processed OLEDs and the vacuum fabricated reference devices (without PS). (b) Chemical structure of CBP, PS and the emitter molecule Ir(ppy)$_3$.