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High-performance inverted top-emitting green electrophosphorescent organic light-emitting diodes with a modified top Ag anode

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ABSTRACT

Green electrophosphorescent inverted top-emitting organic light-emitting diodes with a Ag/1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) anode are demonstrated. A high current efficacy of 124.7 cd/A is achieved at a luminance of 100 cd/m^2 when an optical outcoupling layer of N,N′-di-[(1-naphthyl)-N,N′-diphenyl]-1,1′-biphenyl-4,4′-diamine (α-NPD) is deposited on the anode. The devices have a low turn-on voltage of 3.0 V and exhibit low current efficacy roll-off through luminance values up to 10,000 cd/m^2. The angle dependent spectra show deviation from Lambertian emission and color change with viewing angle. Hole-dominated devices with Ag/HAT-CN electrodes show current densities up to three orders of magnitude higher than devices without HAT-CN.

1. Introduction

Organic light-emitting diodes (OLEDs) have been intensively researched for their potential use in general lighting and displays [1]. OLEDs can be classified by the position of their electrodes relative to the substrate. Conventional OLEDs [2,3] generally have a bottom-anode directly fabricated on the substrate and a top-cathode, while so-called inverted OLEDs have their relative electrode positions reversed. Despite the fact that inverted OLEDs have better compatibility with the *n*-type transistor driving circuitry used in active-matrix displays, the number of reports on them in the literature have been rather sparse due to the difficulties of creating a bottom-cathode effective at injecting electrons into commonly used electron-transport materials [4].

Recently we showed that an Al/lithium fluoride (LiF) bottom-cathode can be used in high-performance green and blue inverted OLEDs [5,6]. These OLEDs have the additional feature of being top-emitting so that the light exits through the top of the device. In an active matrix display, top-emitting OLEDs can be directly fabricated on their driving electronics allowing the pixel aperture to be maximized. Higher total display brightness can therefore be achieved with a lower individual brightness for each pixel. As a result, the OLEDs can be driven at lower voltages and current densities leading to higher efficiency operation and longer device lifetimes [7]. Top-emitting OLEDs are also compatible with metal foil substrates with efficient heat dissipation leading to improved device lifetimes [8]. Top-emission provides the added benefit of avoiding light trapping and waveguiding losses in the glass and indium tin oxide (ITO) commonly used in conventional OLEDs [9].

Reports on inverted top-emitting OLEDs are especially scarce. Not only do they require a highly reflective bottom-cathode capable of effective electron injection, but they also need a top-anode that is both semitransparent and capable of effective hole injection. Various approaches have been used including anodes consisting of sputtered ITO on PEDOT:PSS [10,11] and pentacene [12] buffer/injection layers, Ag with doped hole-transport layers (HTLs) [13,14], Au [15], and Ag/molybdenum trioxide (MoO_3) [16].

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The highest current efficacy previously reported for inverted top-emitting OLEDs was 96.3 cd/A at a luminance of 1387 cd/m^2 [5]. These OLEDs have a Au/MoO_3 anode which injects holes into an HTL of 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) [3]. The hole-injection process of transparent conducting oxides (TCOs) such as MoO_3 proceeds by the transfer of electrons into the conduction band of the TCO from the highest occupied molecular orbital (HOMO) level of the neighboring HTL. This is the same model used to explain the operation of TCO-containing connecting-units in stacked OLEDs in that the charge-generation process takes place at the TCO/HTL interface [17]. It is for this reason that the material combinations that are used in the charge-generation units of stacked OLEDs can also be used as hole-injection/HTL combinations in single-unit OLEDs.

Like TCOs, 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) has been used in the connecting-units of stacked OLEDs [18,19] and a hole-generating organic interlayer in single-unit OLEDs [20]. HAT-CN is a electron acceptor that has also been used as an *n*-dopant [21] due to its large electron affinity (EA) that has a value comparable to that of the ionization energy (IE) of common HTLs. Chiba et al. reported that a combination of a layer of HAT-CN and a layer of 1,1-bis-(4-bis(4-tolyl)-aminophenyl)cyclohexene (TAPC) could be used in highly efficient stacked electrophosphorescent OLEDs [18]. Under the application of an electric field, electrons are transferred from the highest occupied molecular orbital (HOMO) of TAPC (corresponding to an IE of 5.4 eV) [22] to the lowest unoccupied molecular orbital (LUMO) of HAT-CN (corresponding to an EA which has been reported to range from 4.4 eV [18] to 6.0 eV [23]), resulting in the simultaneous creation of holes. Very recently, a thick layer of HAT-CN has been used as a buffer layer for the sputter deposition of an indium zinc oxide anode on a transparent inverted OLED [24].

Here we present high-performance inverted top-emitting electrophosphorescent OLEDs with a novel Ag/HAT-CN/TAPC anode structure. The use of Ag is more economical than Au and HAT-CN offers the additional benefit of being deposited at a lower temperature (below 350 °C under high vacuum) compared to metal oxides such as MoO_3 [24]. When used in conjunction with a TAPC hole-transporting layer, devices with an outcoupling layer of an N,N′-di-[(1-naphthyl)-N,N′-diphenyl]-1,1′-biphenyl-4,4′-diamine (α-NPD) achieve a high current efficacy of 124.7 cd/A at 100 cd/m^2 in addition to exhibiting a low turn-on voltage of 3.0 V and slight roll-off behavior in current efficacy, yielding an average value of 96.4 cd/A at a luminance of 10,000 cd/m^2.

2. Materials and methods

Substrates of glass micro-slides (VWR International) were cut into 1 × 1 in. squares and then cleaned by ultrasonication (5510, Branson Ultrasonics) in baths of detergent water, distilled water, acetone, and isopropanol. The substrates were treated for 20 min in each solvent and then blown dry with nitrogen gas. They were then exposed to oxygen plasma (Plasma-Preen II, Plasmatic Systems, Inc.) for 2 min. Next, PEDOT:PSS Clevios P VP AI 4083 was dispensed onto the substrates through a 0.45 μm polyvinylidine fluoride filter and spin-coated (WS-400B-6NPP/LITE, Laurell Technologies, Inc.) at a speed of 5000 rpm for 1 min. The substrates were then annealed at 140 °C for 10 min in ambient atmosphere. The thickness of the PEDOT:PSS on glass was measured to be 40 nm-thick by spectroscopic ellipsometry (M-2000UI, J.A. Woollam Co., Inc.). A previous study showed that PEDOT:PSS on glass improves the reliability of electron-dominated organic diodes with bottom metal cathodes [25]. Including this layer also improves the yield and reliability of our inverted top-emitting OLEDs.

The samples were then transferred to a high-vacuum thermal evaporation system (EvoVac, Armstrong Engineering Inc.) and the chamber was pumped down to pressures below 3×10^{-7} Torr. An Al layer of 50 nm thickness was first deposited at a rate of 2 Å/s followed by a LiF electron-injection layer of 2.5 nm thickness at a rate of 0.2 Å/s. All following organic layers were then deposited at a rate of 1 Å/s. A 40 nm-thick electron-transport layer of 1,3,5-tri(p-pyrid-3-yl-phenyl)benzene (TpPyPB) was first deposited. The emissive layer consisting of 6 vol.% tris(2-phenylpyridine)iridium(III) Ir(ppy)$_3$ dopant coevaporated in a 20 nm-thick layer of CBP was then evaporated, followed by a 35 nm-thick HTL of TAPC. A 5 nm-thick layer of HAT-CN was deposited at a rate of 0.1 Å/s as a hole-injection layer. Finally, a 20 nm-thick top Ag anode was deposited at a rate of 2 Å/s. All materials were evaporated through shadow masks. The typical OLED area was 4×5 mm^2. To extract additional light from the devices, an 80 nm-thick layer of α-NPD was deposited on the Ag. All materials were purchased from Sigma–Aldrich with the exception of TpPyPB and Ir(ppy)$_3$, which were obtained from Luminescence Technology Corp. All organic materials were purified by gradient-zone sublimation prior to thermal evaporation.

After fabrication, current–voltage and luminance-voltage characteristics were measured using a digital source meter (2400, Keithley Instruments, Inc.) and a calibrated photodiode (FDS 100, Thorlabs, Inc.). The substrates were mounted on a computer-controlled rotating stage (Thorlabs, Inc.) and a radiometrically calibrated spectrometer (USB4000, Ocean Optics, Inc.) was used to measure the OLEDs' electroluminescent spectra.

3. Results and discussion

The structure and biasing of these inverted top-emitting OLEDs along with a chemical diagram of HAT-CN are displayed in Fig. 1. A plot of the current density versus voltage of the OLEDs is shown in Fig. 2. The luminance versus voltage for the devices is displayed in Fig. 3 with an inset of the current efficacy versus luminance. These devices have a low turn-on voltage (defined here as the voltage required to achieve a luminance of 10 cd/m^2) of about 3.0 V. This low turn-on voltage is comparable to devices incorporating doped transport layers [14,26]. The current efficacy is 124.7 cd/A at a practical luminance of 100 cd/m^2 and shows slight roll-off at luminance levels up to 10,000 cd/m^2. The average performance and standard deviation of multiple OLEDs with the same structure are shown in Table 1.