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Highly efficient white organic light-emitting diodes with single small molecular emitting material

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We demonstrate a highly efficient white organic light emitting device with fluorescent small molecule 4,4′-bis(9-(1-naphthyl)anthracene-10-yl)biphenyl (BUBH-3). With a simple device architecture of indium tin oxide/tris 4,4′,4″-tris-N-naphthyl-N-phenylamino-triphenylamine (60 nm)/*N*,*N*′-bis-(1–naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (10 nm)/BUBH-3 (45 nm)/Alq_3 (15 nm)/LiF (1 nm)/Al (150 nm), a white light with $CIE_{x,y}$ color of (0.31,0.36) was generated. The device achieved one of the best single-emitting-material electroluminescence performance of white organic light-emitting devices with efficiencies of 7.0 cd/A and 3.17 lm/W at 6.9 V. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2804003]

White light organic light-emitting devices (WOLEDs) have attracted much current interest because of their potential applications for large area solid-state lightings, maskless full color OLED fabrication with color filter, as well as backlights for liquid crystal display.[1] Many methods of developing WOLEDs have been reported, such as using a multilayer structure in which each layer emits a complimentary color of light to generate white-light emission,[2–6] or using single-layer structure into which different luminescent red-green-blue dyes are doped.[7–10] In the case of multilayer white devices, charge blockers are usually needed to confine the carriers and excitons within the desired regions for improved emission, but the usage of blockers often causes high driving voltages and, consequently, low power efficiencies. In the method using multiple dopants to tune the emission to generate WOLED, precise control of individual dopant concentration within the emissive layer is very critical as it usually requires very low doping concentration of yellow or orange dye to which the resulting color can be very sensitive. Nonetheless, good result could be obtained, such as that of Williams *et al.* who reported a WOLED with the nearly 100% internal quantum efficiency with efficiencies of 42.5 cd/A and 29 lm/W using phosphorescent material platinum(II)[2-(4′,6′-difluorophenyl)pyridinato-N,C^2)](2,4-pentanedionato).[8] In certain cases, white-light emission can also be obtained from a single emissive layer: WOLEDs such as polymeric chromophores,[11–15] or the formation of electromer,[16,17] excimers,[18] exciplexes,[19] and aggregation.[20] Compared to WOLEDs with multiemitting component, those with a single-emitting material is advantageous in terms of stability, reproducibility, and a much simplified fabrication process. There have been many reports about polymeric materials, but their color instability due to phase separation of various emissive components, color variation upon driving voltage, and undesired Förster-type energy transfer between chromophores remain to be key issues that need to be resolved.[17]

Recently, Lee *et al.* reported a single-emitting-component small molecule WOLED derived from the electromer formation of 1,3,5-tris(2-(9-ethylcarbazyl-3)ethylene) benzene with a maximum brightness of 1200 cd/m^2 and a current efficiency of 1.1 cd/A.[17] Liu *et al.* group obtained a single-emitting-component white electroluminescence (EL) with blue emission originated from an isolated molecule and orange emission from its excimers. The maximum brightness was 1395 cd/m^2 and the current efficiency was 2.07 cd/A at the drive voltage of 16 V with $CIE_{x,y}$ of (0.32,0.33).[18] However, the current efficiency of both single-emitting-component WOLEDs are low. Until now, few small molecular materials have been reported to emit satisfactory white emission with both good color and luminous efficiency.

Recently, we have developed a highly efficient and stable white OLED with fluorescent dopant BUBD (Ref. 21) which achieved an efficiency of 17.1 cd/A with $CIE_{x,y}$ (0.29,0.41) and a long half lifetime of 40 000 h at an initial luminance of 300 cd/m^2. In this letter, we report highly efficient WOLEDs with a single-emitting-fluorescent material of 4,4′-bis(9-(1-naphthyl)anthracene-10-yl) biphenyl (BUBH-3) in a trilayer device structure. The device achieved an EL efficiencies of 7.0 cd/A and 3.17 lm/W at 6.9 V with $CIE_{x,y}$ (0.31,0.36). According to the previously published literatures, the current efficiency of this trilayer device is among the best ever reported for any WOLEDs based on a single-emitting-small molecular material without the use of a dopant.

Prior to the deposition of organic materials, the indium tin oxide (ITO)/glass was cleaned with a routine cleaning procedure and pretreated with UV ozone.[22] Devices were

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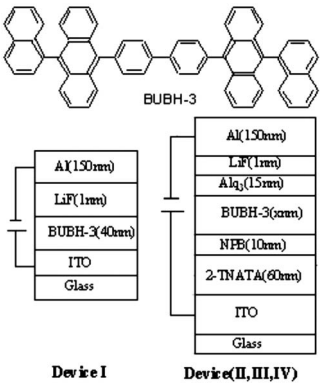
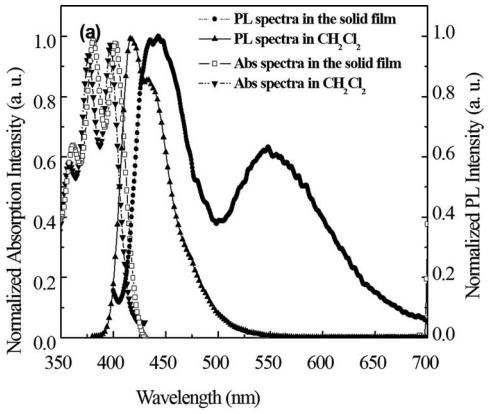


FIG. 1. Molecular structure of BUBH-3 and the structure of devices (I, II, III, and IV); the thicknesses of the BUBH-3 in devices II, III, and IV are 40, 45, and 50 nm, respectively.

fabricated under a base vacuum of about 10^{-6} Torr in a thin-film evaporation coater following a published protocol.[22] In devices II, III, and IV, 4,4′,4″-tris-N-naphthyl-N-phenylamino-triphenylamine (2–TNATA) was used as hole-injection layer, *N*,*N*′-bis(1-naphtyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) served as hole-transporting layer; tris(8-hydroxyquinoline) aluminum (Alq_3) was used as electron-transporting layer. The current-voltage-luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled, programable, direct-current source.

The structure of BUBH-3 is composed of two 9-(1-naphthyl)-anthracene moieties, chemically bridged by biphenyl, as depicted in Fig. 1. It was purified by train sublimation in vacuum (10^{-6} Torr) at about 375 °C prior to device fabrication. It is interesting to note that BUBH-3 has no detectable T_g after quick cooling and repeated scan up to 450 °C but it melts with decomposition at 487 °C directly as determined by differential scanning calorimetry. Figure 2(a) shows the absorption and fluorescence spectra of BUBH-3 in dilute dichloromethane solution and as vacuum-evaporated thin film on quartz substrate. On irradiation at 376 nm in CH_2Cl_2, BUBH-3 exhibits intense blue fluorescence, with an emission peak centered at λ_{max}417 nm. In solid state thin film, the blue emission of BUBH-3 is redshifted to 444 nm and an additional broad band emission at 530–570 nm tailing to 670 nm is also observed. The redshifted emission observed in solid photoluminiscence (PL) has been observed for organic and polymer materials probably due to intermolecular interactions or exciton hopping in the solid state,[23] but the appearance of the orange emission is interesting and requires further investigation.

Usually, an appearance of additional band gap in the solid may be caused by aggregation, phosphorescence, or excimer. To probe the origins of the long-wavelength broad emissions at about 545 nm, PL excitation spectra, absorption and solid state thin-film spectra of BUBH-3 were studied first. As shown in Fig. 2(a), this broad emission band stems from species that appears to exist only in the excited state since no absorption is detected in this spectral region. Therefore, we can rule out aggregate state between subunits of the solid as the source of the additional luminescence band.[24] In order to further verify this conclusion, the PL of BUBH-3 in polymethyl methacrylate (PMMA) were measured [Fig. 2(b)]. In the PMMA sample, BUBH-3 did not form any



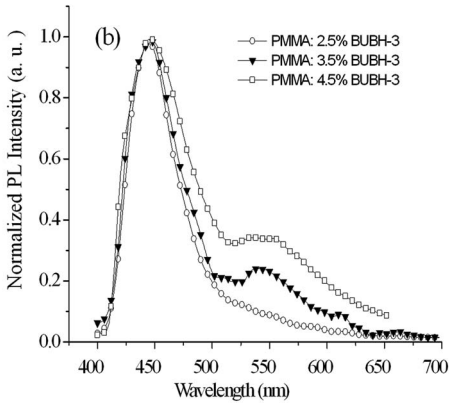


FIG. 2. (a) Photoluminescence (PL) (λ_{ex}=376 nm) and absorption spectra of BUBH-3. (b) PL spectra of solid films with 2.5%, 3.5%, and 4.5% of BUBH-3 dispersed in polymethyl methacrylate (PMMA) (λ_{ex}=376 nm).

aggregates, but the green emission band was observed again and the relative intensity of this band was found to increase-with the concentration of BUBH-3. As supported by this experimental result, we assign the additional green band to the formation of excimer, for the efficient formation of excimer process goes within microcrystallites which is formed only in high concentrated solid solution of BUBH-3 in PMMA.[23] Secondly, low temperature photoexcition of BUBH-3 at −78 °C in liquid nitrogen was investigated and the absence of phosphorescence suggests that it could not have been the origin of this broad emission band. Further, our results (Table I) on time-resolved PL decay dynamics of BUBH-3 films show that the radiative lifetime which increases as the spectrally selected band shifts toward the long wavelength emission threshold, suggesting the formation of at least one more well-defined BUBH-3 excimer (around λ=545 nm). We also note that the nanosecond scale of the decay times could rule out the involvement of possible triplet excitons and their excimers as a possible source of the long-wavelength emission band. As a result, it is reasonable to assign the additional broad orange emission band to singlet excimeric states formed by BUBH-3 in the solid state.

To investigate the EL properties of this molecule, a single-layer device with a structure of ITO/BUBH-3(60 nm)/LiF/Al (device I) was fabricated by vacuum deposition. Compared to the PL spectrum of the BUBH-3 film,

TABLE I. Excited states lifetime of BUBH-3 at different wavelengths.

Wavelength (nm)	430	460	490	530
Lifetime (τ) (ns)	0.31	0.45	0.49	1.13

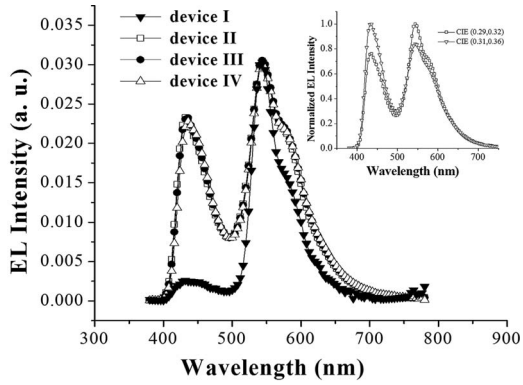


FIG. 3. Electroluminescence (EL) spectra of BUBH-3 based devices I, II, III, and IV. Inset: EL spectra of device III driven at 20 and 200 mA/cm^2.

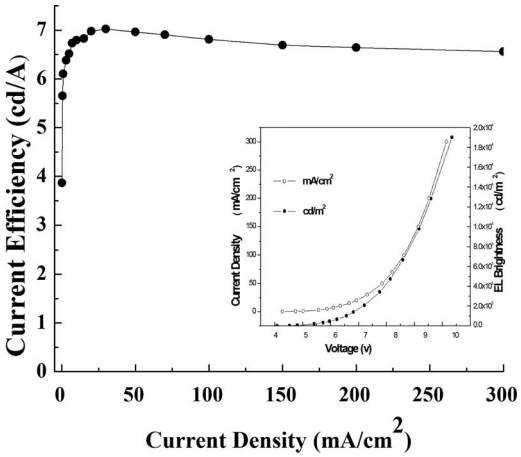


FIG. 4. Dependence of the EL efficiency on the drive current density for BUBH-3 based device III (inset: current density–voltage–brightness characteristics).

the long wavelength emissions found around 545 nm of the EL spectrum became stronger (Fig. 3). The difference in line shape (or emission intensity) between the EL and the PL spectra might be due to electron injection which can sometimes generate excitations that cannot be induced by optical excitation.[18,25] Since the overall EL pattern of the BUBH-3 trilayer devices (II, III, and IV) was similar to that of the single-layer device I (Fig. 3), we conclude that the longer-wavelength EL emissions (545 nm) of these devices should have similar origins of excimer. It also rules out the possibility of formation of a species such as an exciplex at the NPB/BUBH-3 interface (or Alq_3/BUBH-3 interface) in the case of devices II, III, and IV).[18] In device III, the emission is close to white with Commission Internationate de'Eclairage ($CIE_{x,y}$) coordinates of (0.31, 0.36) and (0.29, 0.32) when the drive current increased from 20 to 200 mA/cm^2 (see the inset of Fig. 4). As shown in Fig. 3, in devices II, III, and IV, the EL spectra change a little when the thickness of the BUBH-3 was increased from 40 to 50 nm, thus demonstrating also that the $CIE_{x,y}$ of the device is not dependent on the thickness of the BUBH-3 emitting layer.

The current efficiency versus current density characteristics of device III is shown in Fig. 4, which shows maximum efficiencies of 7.0 cd/A at 20 mA/cm^2 and 3.17 lm/W at 6.9 V with its current density–voltage–brightness characteristics of device III shown in the inset. The brightness of device III is 1396 cd/m^2 driven at 6.9 V, which is among the lowest drive voltages ever reported for a single-emitting-component fluorescent device. For benchmark, a single-component WOLED device which exhibited a maximum brightness of 1200 cd/m^2 at 18 V was reported in 2004,[17] and more recently, in 2006, another device of 1395 cd/m^2 at a drive voltage of 16 V was disclosed.[18]

In summary, the present results demonstrate that the blue fluorescent small molecular material BUBH-3 without the addition of any dopant is capable of producing white light in the single-emitting-component EL devices with white-light emission consisting of two fluorescence and one excimer components. The three-layer EL devices fabricated with BUBH-3 exhibit bright and efficient white light with a good luminance of 1396 cd/m^2 and a current efficiency of 7.0 cd/A obtained at a low drive voltage of 6.9 V. The $CIE_{x,y}$ color is (0.31,0.36), which does not change significantly with drive current densities. The EL performance is among the best reported for most WOLEDs based on a single-emitting material without dopant.

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