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White-electrophosphorescent devices based on copper complexes using 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole as chromaticity-tuning layer

Zisheng Su, Guangbo Che, Wenlian Li,[a] Wenming Su, Mingtao Li, Bei Chu, and Bin Li
Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China and Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Zhiqiang Zhang and Zhizhi Hu
Optic Photo-electronic Materials and Research Development Center, Anshan University of Science and Technology, Anshan 114044, People's Republic of China

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Efficient white organic light-emitting diodes based on copper complex, [Cu(bis[2-(diphenylphosphino)phenyl]ether)(6,7-dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline)]BF_4 [Cu(I) complex], in which the white emission composed of yellow emission from Cu(I) complex doped 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) layer and blue emission from *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-(1,1′-benzidine)-4,4′-diamine layer, were fabricated. A thin 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (Bu-PBD) layer sandwiched between the two emission layers acts as a chromaticity-tuning layer. The white device with 10 nm, 2 wt % Cu(I) complex doped CBP layer and 2 nm Bu-PBD layer shows CIE coordinates of (0.33,0.36) at applied bias of 10 V, a maximum luminance of 2466 cd/m^2, and a maximum current efficiency of 6.76 cd/A, corresponding to the power efficiency of 3.85 lm/W. The efficient white emission is attributed to the simultaneous exciton formation in both emission layer. The working mechanism of the thin Bu-PBD layer for achieving white emission was also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2207489]

White organic light-emitting diodes (WOLEDs) have drawn particular attention due to their potential applications as full color displays, backlights for liquid-crystal displays, and even next generation paper-thin lighting sources.[1–4] Unlike fluorescent materials that can only make use of singlet excitons, phosphorescent materials can harvest both singlet and triplet excitons and make the potential of reaching a maximum internal efficiency of 100%.[5] Since efficient electrophosphorescent devices were reported by Baldo *et al.*,[6] WOLEDs based on phosphorescence complexes, e.g., iridium,[7–9] platinum,[10] and rhenium[11] complexes, have attracted more and more attention. However, the costliness of these complexes made them unsuitable for practical applications. In the past few years, efficient organic light-emitting diodes (OLEDs) based on cheaper Cu(I) complexes were demonstrated.[12–14] Thus, WOLEDs based on cheaper but efficient Cu(I) complexes provide an alternative for practical applications to cut down the cost.

In a previous work, we demonstrated an efficient yellow emission device based on [Cu(bis[2-(diphenylphosphino)phenyl]ether)(6,7-dicyanodipyrido[2,2-*d*:2′,3′-*f*]quinoxaline)]BF_4 [Cu(I) complex]; this result will be published in a separate letter. In this letter, we focus on the WOLEDs in which yellow emission comes from Cu(I) complex doped 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) layer and blue emission from *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-(1,1′-benzidine)-4,4′-diamine (NPB) layer. Among the two emission layers, sandwiched a thin 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (Bu-PBD) layer which acts as a chromaticity-tuning layer. We obtained an efficient white light emission from the device with 10 nm, 2 wt % Cu(I) complex doped CBP layer and 2 nm Bu-PBD layer, which shows the Commission Internationale de l'Eclairage (CIE) coordinates of (0.33,0.36) at applied bias of 10 V and the maximum luminance, current efficiency, and power efficiency of 2466 cd/m^2, 6.76 cd/A, and 3.85 lm/W, respectively.

The WOLEDs have the structure of ITO/2-TNATA (10 nm)/NPB (60−*d* nm)/Bu-PBD (*x* nm)/CBP:Cu(I) complex (*c* wt %, *d* nm)/TPBI (20 nm)/Alq_3 (20 nm)/LiF (0.5 nm)/Al (120 nm), where 4,4′,4″-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA), NPB, 2,2′,2″-(1,3,5-benzenetriyl)tris-[1-phenyl-1*H*-benzimidazole] (TPBI), and tris(8-hydroxyquinoline) aluminum (Alq_3) act as hole-injection layer, hole-transporting layer, exciton-blocking layer, and electron-transporting layer, respectively. Figure 1 shows the chemical structure of the Cu(I) complex and the structure of the WOLEDs. A series of devices with different thicknesses of Bu-PBD layer, different doping concentrations of Cu(I) complex in CBP layer, and/or different thicknesses of doping layer were fabricated. Organic layers were deposited onto a precleaned indium tin oxide (ITO) glass substrate (10 Ω/sq) by thermal evaporation in vacuum chamber at 3×10^{-4} Pa, followed by a LiF buffer layer, and an Al cathode in the same vacuum run. Deposition rates and thickness of the layers were monitored *in situ* using an oscillating quartz monitor. The evaporating rates were kept at 2–3 Å/s for organic layers and LiF layer and 10 Å/s for Al cathode, respectively.

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[a] Author to whom correspondence should be addressed; electronic mail: wllioel@yahoo.com.cn

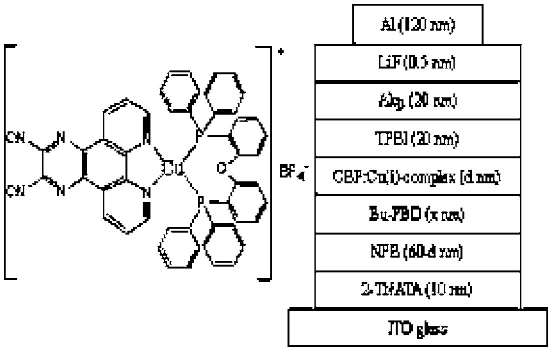

FIG. 1. Chemical structure of Cu(I) complex and the structure of WOLEDs.

Electroluminescent (EL) spectra and CIE coordinates of these devices were measured by a Hitachi F-4500 fluorescence spectrophotometer. The dates of luminance-current-voltage (*L-I-V*) were measured with a 3645 dc power supply combined with a 1980a spot photometer and were recorded simultaneously with measurements. All the measurements were carried out at room temperature under ambient conditions.

Figure 2(a) shows the normalized EL spectra at applied bias of 10 V of the devices with various thicknesses of Bu-PBD layer (x=0, 2, 5, or 8 nm) when the doping concentration of Cu(I) complex and the thickness of the doping layer were fixed at 2 wt % and 10 nm, respectively. It can be seen that the emission intensity of NPB with the peak at about 440 nm and the shoulder at about 490 nm increases relatively to the emission of Cu(I) complex with the peak at about 562 nm as the thickness of Bu-PBD layer increases from 0 to 8 nm. Correspondingly, the CIE coordinates vary from (0.36,0.39) to (0.27,0.31). It indicates that the inserted Bu-PBD layer plays a role of chromaticity tuning without changing the thickness of the emission layers. The lowest unoccupied molecular orbital (LUMO) of NPB at 2.2 eV (Ref. 15) is only 0.4 eV higher than that of Bu-PBD at 2.6 eV (Ref. 15) thus electrons can transport through the Bu-PBD/NPB interface easily. In contrast, the offset between the highest occupied molecular orbital (HOMO) of NPB at 5.2 eV (Ref. 15) and Bu-PBD at 6.2 eV (Ref. 15) acts as an efficient barrier to retard the flow of holes from the NPB layer to doped CBP layer. However, when the Bu-PBD layer is thin enough, parts of holes can transport through it to CBP layer, thus excitons can be formed at both NPB/Bu-PBD and Bu-PBD/CPB interfaces. As the thickness of Bu-PBD layer increases, the number of holes reaching CBP layer will decrease dramatically, leading to the increase emission of NPB relatively to the emission of Cu(I) complex. Figure 2(b) describes the EL spectra of the device with 10 nm CBP layer doped with 2 wt % Cu(I) complex and 2 nm Bu-PBD layer at applied biases from 9 to 15 V. Obviously, the EL spectra of the device shows an apparent dependence on the applied bias: the blue emission band gradually grows relatively to the yellow emission band with the applied bias. Correspondingly, the CIE coordinates of the device shift from (0.39, 0.35) at 9 V to (0.26, 0.27) at 15 V, but all of them are in white light region. The shift of the coordinates indicates that the recombination zone is field dependent. The increased applied bias would increase the number of carriers injected from the anode and cathode and hence formatted excitons, the emission sites of Cu(I) complex may reach saturation and the effect of triplet-triplet annihilation may become remarkable with further increase of applied bias,[16] which leads to the increase of the NPB emission relatively to the Cu(I) complex emission.

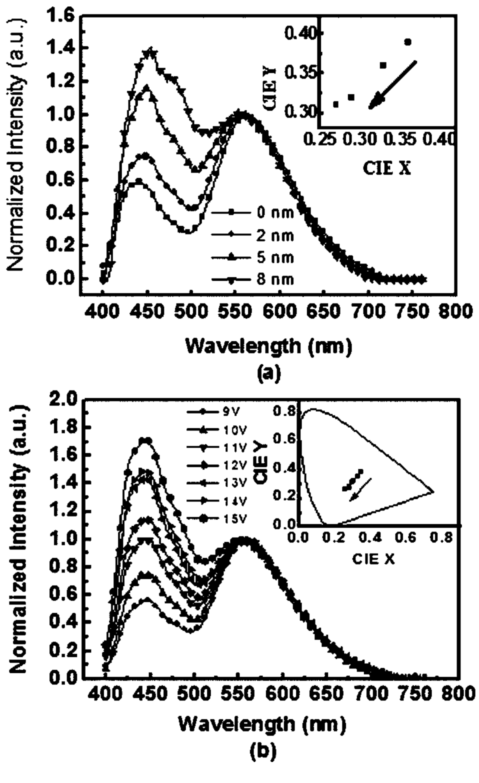

FIG. 2. (a) EL spectra at applied bias of 10 V of the devices with various thickness of Bu-PBD layer when the doping concentration of Cu(I) complex and the thickness of the doping layer were fixed at 2 wt % and 10 nm. Inset: CIE coordinates of these devices, arrow denotes the increase of the thickness of Bu-PBD layer. (b) EL spectra of the device with 2 nm Bu-PBD layer and 10 nm, 2 wt % Cu(I) complex doped CBP layer at applied biases from 9 to 15 V. Inset: CIE coordinates of different applied biases, arrow denotes the increase of the applied bias.

The effects of the doping concentration of Cu(I) complex in CBP layer and the thickness of doping layer on the emission color were also investigated. Figure 3(a) shows the normalized EL spectra at applied bias of 10 V of the devices with various doping concentration of Cu(I) complex (c=1, 2, 3, or 6 wt %) when the thickness of the doping layer and the Bu-PBD layer were fixed at 10 and 2 nm, respectively. As can be seen, the relative emission intensity of the Cu(I) complex to the NPB increases with the concentration of Cu(I) complex, thus the CIE coordinates change from (0.18,0.19) to (0.49,0.50). The energy transfer from CBP to Cu(I) complex increases as the doping concentration of Cu(I) complex increases from 1 to 6 wt %, which results in dramatically increased emission of Cu(I) complex relatively to the emission of NPB. Note that the emission of Cu(I) complex slightly redshifts with the doping concentration in CBP, this is identical to our previous work due to the dipole-dipole interaction between Cu(I) complex molecules. Figure 3(b) describes the EL spectra at applied bias of 10 V of the devices with various thickness of the doping layer (d=5, 10, 15, or 20 nm) when the doping concentration of the Cu(I) complex and the thickness of the Bu-PBD layer were fixed at 2 wt % and 2 nm, respectively. It can be found that when the thickness of doping layer increases from 5 to 20 nm corresponding to the thickness of NPB layer decreases from 55 to 40 nm, the emission intensity of Cu(I) complex in-

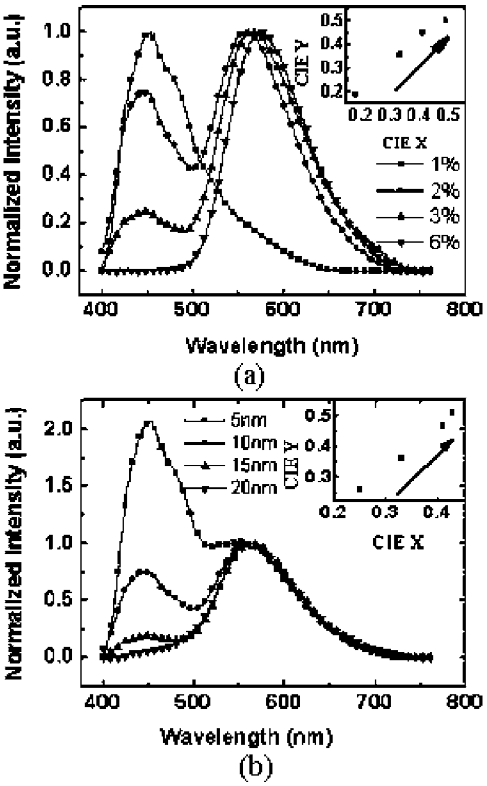

FIG. 3. (a) EL spectra at applied bias of 10 V of the devices with various doping concentration of Cu(I) complex when the thickness of the doping layer and the Bu-PBD layer were fixed at 10 and 2 nm. Inset: CIE coordinates of these devices, the arrow denotes the increase of doping concentration. (b) EL spectra at applied bias of 10 V of the devices with various thicknesses of the doping layer when the doping concentration of the Cu(I) complex and the thickness of the Bu-PBD layer were fixed at 2 wt % and 2 nm. Inset: CIE coordinates of these devices, arrow denotes the increase of the thickness of doping layer.

creases relatively to the emission of NPB, thus the CIE coordinate changes from (0.25,0.26) to (0.43,0.51). This may be attributed to the fact that the number of the Cu(I) complex molecules participating in the light emission increased. When the thickness of the doping layer is 10 nm corresponding to the thickness of NPB layer is 50 nm, we obtained a better white emission with the CIE coordinates of (0.33,0.36) at bias of 10 V.

Figure 4 plots the current efficiency and power efficiency as a function of current density of the device with 10 nm CBP layer doped with 2 wt % Cu(I) complex and 2 nm Bu-PBD layer. As shown before, the number of the injected holes could be distributed moderately at the two emission layers, so it gives practically white light with the CIE coordinates of (0.33,0.36), which is very close to the ideal white color with the coordinates of (0.33,0.33). The maximum current efficiency and power efficiency of 6.76 cd/A and 3.85 lm/W were obtained at current density of 0.13 mA/cm^2, a gradual efficiency decrease is found at high current density, which has been due to triplet-triplet annihilation observed in all electrophosphorescent.[17] The WOLED has a turn on voltage of about 4.5 V and a maximum luminance 2466 cd/m^2 which was achieved at applied bias of about 12 V.

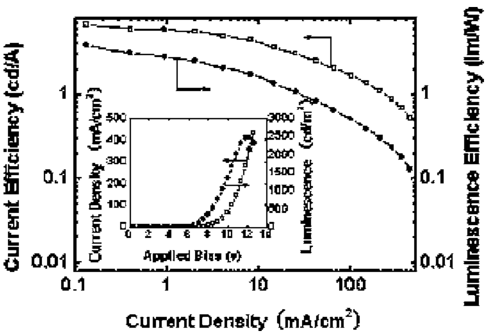

FIG. 4. Current efficiency and power efficiency vs current density of the device. Inset: the current density-voltage-luminance characteristics of the device.

In summary, we demonstrated an efficient WOLED based on yellow emission from Cu(I) complex doped CBP layer and blue emission from NPB layer. The maximum luminance, current efficiency, and power efficiency were 2466 cd/m^2, 6.76 cd/A, and 3.85 lm/W, respectively. The CIE coordinates of the WOLED were in white region from 9 to 15 V. The efficient white light emission is attributed to the simultaneous exciton formation in both emission layers due to a thin Bu-PBD layer, which acts as a chromaticity-tuning layer, sandwiched between them. Although the properties of the device should be further improved for commercial applications, this work develops another process to design WOLEDs. Using the Cu(I) complex for constructing phosphorescent WOLEDs has a potential interesting for reducing the cost. The EL mechanism will be further understood to improve the performances of the WOLEDs.

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