White organic light-emitting diodes based on 2,7-bis(2,2-diphenylvinyl)-9, 9 -spirobifluorene: Improvement in operational lifetime

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White organic light-emitting diodes based on 2,7-bis(2,2-diphenylvinyl)-9, 9′-spirobifluorene: Improvement in operational lifetime

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Very bright white organic light-emitting diodes were fabricated using 2,7-bis(2,2-diphenylvinyl)-9, 9′-spirobifluorene (DPVSBF) doped with [4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran)] (DCJTB) as the emission layer. With a device configuration of ITO/NPB(40 nm)/DPVSBF:0.2%DCJTB(11 nm)/Alq(30 nm)/LiF(1 nm)/Al(150 nm), a brightness of 1575 cd/m^2 with an external quantum efficiency of 3.31% and luminous efficiency of 8.00 cd/A, a power efficiency of 5.35 lm/W was achieved at a driving current of 20 mA/cm^2 (4.7 V). The brightness reached 66 000 cd/m^2 at 15 V. The Commission Internationale de l'Eclairage coordinates stayed nearly constant, changed from (0.35, 0.36) to (0.32, 0.34) when the voltage increased from 6 to 12 V. The relative operational lifetime of the device increased by a factor of ~20 compared with a similar device based on 4,4′-bis-(2,2-diphenylvinyl)-1,1′-biphenyl as the source of the blue emission. The much extended half-lifetime was attributed to the higher morphological stability of the DPVSBF. © *2004 American Institute of Physics*.
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White organic light-emitting diode (WOLED) has become the focus of recent efforts in the research of electroluminescent materials and devices, since the electroluminescent device was proven to be a viable technology in fabricating flat panel displays.[1] White light devices will have wide applications, including serving as backlights in liquid crystal displays, as the light source in fabricating full color displays through color filtering technique, or even for general lighting purpose. While the efficiency and brightness required for lighting purposes are yet to be met (compare to incandescent and fluorescent sources), that needed for display purposes ($L \leqslant 300$ cd/m^2) are being fulfilled. Much progress has been made in improving the efficiency and brightness of WOLEDs over the past several years.[2–7] A maximum brightness of $>74\,000$ cd/m^2, efficiencies of 11.0 cd/A and 6.0 lm/W at low driving current (0.6 mA) have been reported for a device based on a layer of 4, 4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl (DPVBi) lightly doped with rubrene as the emission layer.[8] The use of a single emission layer improves the color stability in contrast to those with RGB colors originated from different layers.[3,4] However, the lifetime of the device was not addressed.

For all the display applications, a prime concern is the operational lifetime of the devices. The lifetime of an OLED device is a complicated issue, relating to a number of parameters: the chemical and morphological stability of materials involved in the device, the detailed device structure, the encapsulation process, as well as the device efficiency. A device failure may involve more than one mechanism. Yet in general, the more efficient a device is, the lower voltage is needed to drive the device and a longer lifetime can be expected.

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DPVBi is one of the most efficient blue emitters. Many efficient blue and white devices have been fabricated with this material.[8–11] Nevertheless, the compound has a relative low T_g of 64 °C. A lower T_g has been identified as one of the possible causes of the device failure.[12] In this letter we wish to report a comparative study of the WOLEDs prepared from 2,7-bis(2,2′-diphenylvinyl)spirobifluorene (DPVSBF) and from DPVBi. The DPVSBF is a blue-emitting analogue of DPVBi that uses a spirobifluorene unit, instead of a biphenyl, to link the two diphenylvinyl moieties.[13] The rigid and orthogonally shaped spirobifluorene unit effectively raises the T_g to 115 °C, and thus enhances the morphology stability of the material, yet retains much of the photophysical properties of DPVBi. As a blue emitter in similar device configuration, the DPVSBF gave improved performance characteristics.[13]

The device configuration and materials used in the WOLED device fabrication are shown in Fig. 1. The device was prepared by typical vacuum deposition onto precleaned ITO substrate (resistivity of 30 Ω/□), a layer of 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB) as the hole-transport layer, followed by co-evaporation of DPVSBF (or DPVBi) and [4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethylijulolidyl-9-enyl)-4*H*-pyran)] (DCJTB) as the emission layer, and then the deposition of tris(8-hydroxyquinolinato) aluminum (III) (Alq) as the electron-transport layer. The device was completed by the cathode deposition of LiF(1 nm)/Al(150 nm). In tuning the composite spectrum of the white emission, the concentration of DCJTB in the host DPVSBF can be varied to locate the best concentration for a balanced white color. However, the peak position for DCJTB emission also depends on concentration, giving a significant redshift with increasing concentration. For example, in a film with 0.2% DCJTB in DPVSBF, the photoluminescence measurement has DCJTB emission occurred at 581 nm, whereas with 1% DCJTB, the emission occurred at 599 nm and further shifts to 618 nm with 5%

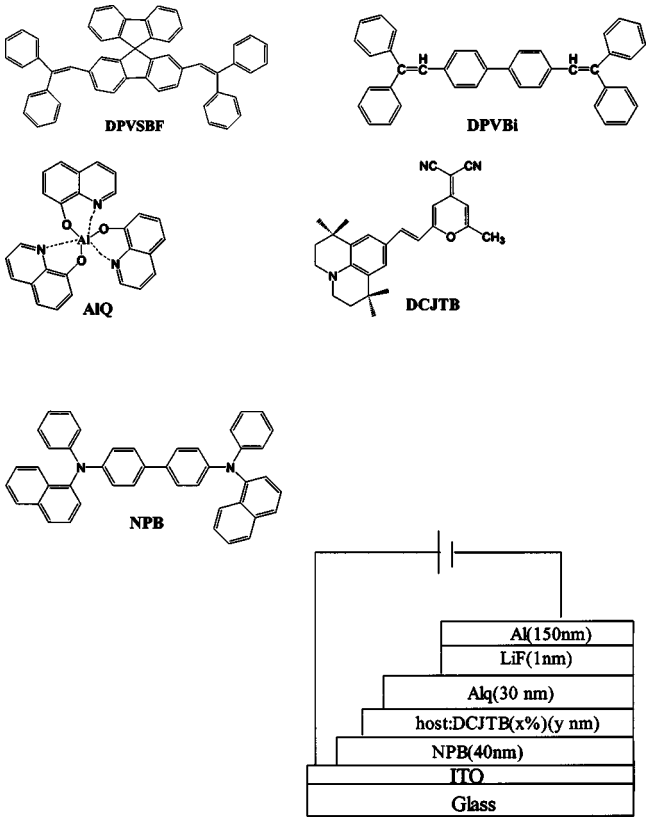

FIG. 1. Structure of devices and materials used in this study.

dopant concentration. This is typical for the polar, donor-acceptor type red dyes. The shift can be attributed to medium effect in a solid state solution.[14] Alternatively, the white color tuning can be achieved with a fixed DCJTB doping concentration while changing the thickness of the doped layer in the device. Figure 2 shows the EL spectra as a function of emission layer thickness in the device structure of ITO/NPB(40 nm)/DPVSBF:0.2%DCJTB(x nm)/Alq(30 nm)/LiF(1 nm)/Al. It is seen that only the relative intensity for DCJTB emission changes but not the peak position, occurring at around 573 nm. The contribution from DCJTB increases with increasing layer thickness. Presumably a thicker emission layer contains more DCJTB sites for light emission.

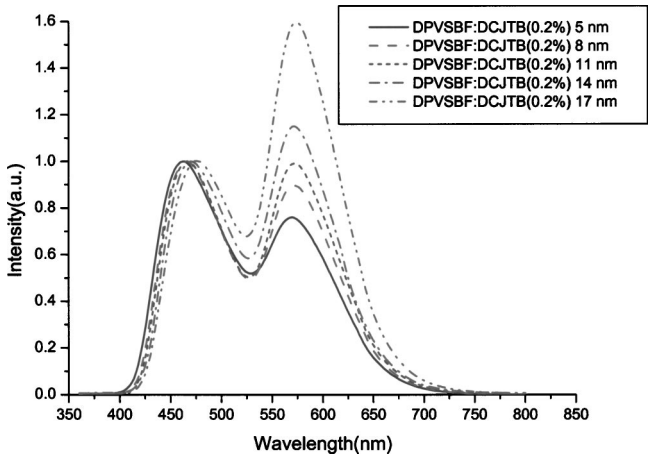

FIG. 2. EL spectra and CIE coordinates as a function of doped layer thickness.

The increasing DCJTB contribution for a thicker film would also imply that there is carrier trap (the DCJTB molecules) mechanism in addition to energy transfer mechanism for the dopant excitation. With an emission layer thickness of 11 nm, the color is closest to white color, giving CIE coordinates of (0.33, 0.34) at 10 V. The device also exhibited a good color stability. At 6 V or ~100 mA, the CIE coordinates are (0.35, 0.36) and changed to (0.33, 0.35) and stay nearly constant to (0.32, 0.34) at 12 V or more than 1000 mA (Fig. 3). The device has a very low turn on voltage (defined as the bias giving 1 cd/m^2) of 2.7 V, and an external quantum efficiency of 3.31%, and luminous efficiencies of 8.00 cd/A, 5.35 lm/W at a driving current of 20 mA (4.71 V) were obtained. The efficiencies decrease with driving current to 6.65 cd/A and 3.37 lm/W at 100 mA. A brightness of ~65 000 cd/m^2 was reached at 15 V.

A similar white device prepared from DPVBi was obtained with a configuration of ITO/NPB(40 nm)/DPVBi:0.4%DCJTB(10 nm)/Alq(30 nm)/LiF(1 nm)/Al(150 nm). The device gave an external quantum efficiency of 2.62%, and efficiencies of 5.52 cd/A, 2.1 lm/W at a driving current of 100 mA/cm^2 (8.3 V). However, a quick drop of the performance was repeatedly noted at bias higher than around 13 V. The performance characteristics of the DPVSBF-based

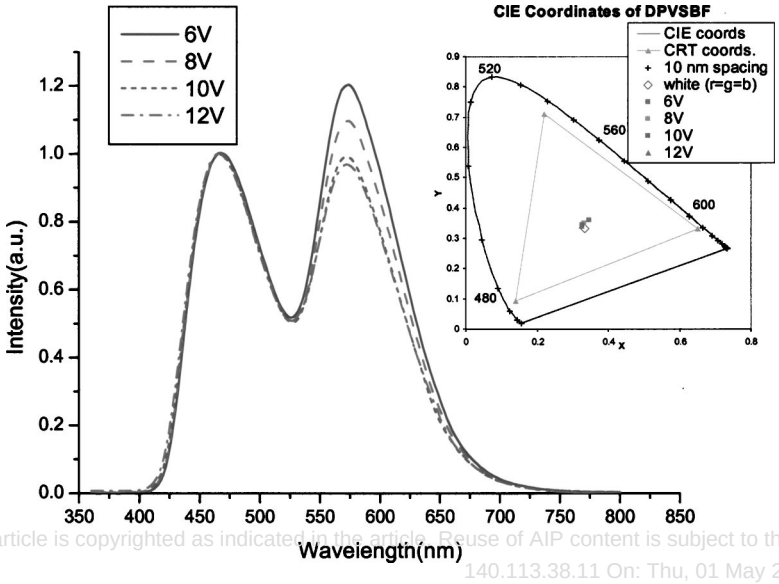

FIG. 3. The EL spectra as a function of bias for the device of ITO/NPB(40 nm)/DPVSBF:0.2%DCJTB(11 nm)/Alq(30 nm)/LiF(1 nm)/Al(150 nm).

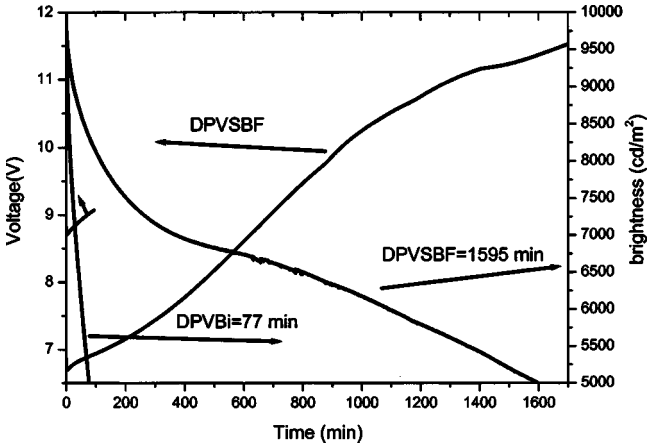

FIG. 4. Relative stability test of the DPVSBF-based and DPVBi-based white devices starting from an initial brightness of 10 000 cd/m^2.

device are better than the DPVBi-based device, even though the two devices have slightly different concentration and emission layer thickness.

The relative operational lifetime of the devices was also measured in an accelerated test. After the devices were prepared, they were taken out of the vacuum chamber and encapsulated with UV-curable epoxy resin and a topping glass slide immediately. Exposure to ambient air was minimized but not totally excluded in our process. At a constant current that yielded a luminance of 10 000 cd/m^2, the decay of luminance with time was followed. After the test, no dark spots[15] can be detected on the devices so that the decay may mainly be due to intrinsic degradation of the materials instead of defects from the substrate or electrode.[15] As shown in Fig. 4, the intensity for the DPVSBF-based device dropped to half of the original value after 1595 min. The driving voltage showed an initial drop and then steadily increased, from 6.8 to 11.5 V over the same period. The decay curve displayed a different shape from that displayed by typical NPB/Alq devices[16] in that a steady decay after 700 min was repeatedly observed. This may signal a different mechanism of degradation, either heat-induced or voltage-induced, after the device is operated for a certain period.[16] The details are yet to be studied. In contrast, the lifetime for the DPVBi-based device reached half of the initial brightness after 77 min. The driving voltage also increased from 8.8 to 9.1 V over that same period. Overall, an improvement by a factor of ~20 was recorded with the DPVSBF-based device. The improvement in the lifetime may due to a more stable morphology and/or more efficient device and thus lower voltage is needed to achieve the same brightness.

In conclusion, with the blue-emitting DPVSBF layer lightly doped with DCJTB as the source of emission and NPB and Alq as the hole-transport, electron-transport layer respectively, a very efficient and color-stable white device can be made in the simple three-layer configuration. The device exhibited luminous efficiencies of 8.00 cd/A, 5.35 lm/W and external quantum efficiency of 3.31% at a driving current of 20 mA (4.71 V). With similar device structure and initial brightness, a significant improvement (by more than 20 fold) in the relative operational stability was achieved compared to a device based on DPVBi.

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