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Ultra-simple two color WOLEDs with CRI exceeding 90 based on electron-transporting $Bepp_2$ simultaneously as blue emitter and exciplex acceptor

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ABSTRACT

In this work, a series of two color white organic light-emitting diodes (WOLEDs) with color rendering index (CRI) exceeding 90 were demonstrated via an ultra-simple novel device structure. The proposed WOLEDs were structured by simply doping exciplex donor of m-MTDATA in the $Bepp_2$ side of bilayer structure TAPC (HTL)/ $Bepp_2$ (ETL), where the $Bepp_2$:m-MTDATA layer is away from HTL/ETL interface for a certain distance. And white emission was realized by combining yellow emission of $Bepp_2$:m-MTDATA forming exciplex and blue emission of $Bepp_2$ spacer layer between HTL and $Bepp_2$: m-MTDATA layer. The optimized WOLED exhibits a low driving voltage of 2.7 V, and also achieves the high maximum luminance and power efficiency of 5561 cd/m^2 and 11.08 lm/W, and an ultra-high CRI of 93 at a practical luminance of 5000 cd/m^2. To the best of our knowledge, the CRI is by far the highest value for two-color WOLEDs with exciplex emission. The detailed working mechanism was unveiled by checking the influence of the thickness of $Bepp_2$ space layer and the mixing ratio and thickness of $Bepp_2$:m-MTDATA layer on the device performance. It was found that in addition to yellow emission, the exciplex emitting layer of $Bepp_2$: m-MTDATA in the proposed devices is also served as a feasible carrier adjusting layer, which was realized by changing its mixing ratio between donor and accepter to affect the distribution of charges, contributing to high CRI white emission.

1. Introduction

White organic light-emitting diodes (WOLEDs) have been extensively investigated for their potential applications in solid-state lighting and flat-panel displays fields owing to their superior characteristics, such as surface-emitting, high efficiency, flexibility, transparent, and low cost, etc. [1–7]. For general lighting, WOLEDs are typically required to provide not only high efficiency and low cost but also high color rendering index (CRI) [4,5]. As we all know, CRI is a numerical measure of how "true" a color appears when viewed with the light source. The CRI ranges from 0 to 100, with 100 representing true color reproduction [6]. For universal lighting applications, the CRI needs to be higher than 80. But for some special lighting places such as hospitals, art galleries, and museums, etc. the CRI needs to be higher than 90 to meet the basic requirement [7].

For achieving ideal white emission with very-high CRI of > 90, the commonly used approach is combining several complementary emitters through the reasonable design of device structure, i. e. blue-yellow emitters, blue-green-red emitters, blue-green-yellow-red emitters, and so on [8–19]. Intuitively, the high CRI can be obtained by increasing the number of complementary emitters to extend the spectral range of the electroluminescence (EL). Typically, in previous work, we developed a series of highly efficient four-color hybrid WOLEDs, achieving the maximum CRIs of 94–96 [13]. Jou et al. even employed five organic dyes to fabricate WOLEDs, demonstrating the maximum CRIs of 93–98 [14]. Obviously, the adoption of more emitters inevitably brought about a complicated device structure, high cost as well as low device reproducibility, limiting the commercial development of very-high-CRI WOLEDs used for special illumination places [10,18,19].

Another method for realizing high CRI white emission is to take the advantage of excited state complexes known as exciplex/excimer, which, to our knowledge, have the obviously red-shifted and broad emission spectra relative to the individual molecules, which is conducive to simplify the device structure of high CRI WOLEDs [17–27]. To date, numerous efforts have been made to obtain ultra-high CRI WOLEDs based on the emission of exciplex/excimer. For example,

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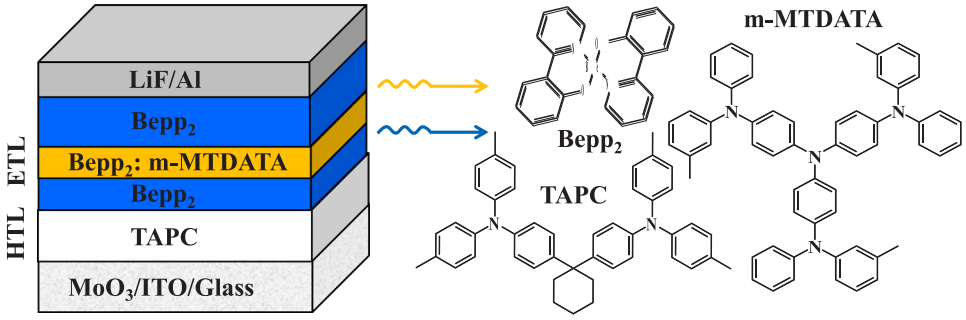

Fig. 1. Schematic structure diagram for the proposed two color WOLEDs and molecular structure for organic materials involved in device fabrication.

Kalinowski et al. developed a simple-structured white device with CRI of 90 by combining emissions of excimer and exciplex simultaneously [17]. Recently, Han et al. fabricated a device structure with a red exciplex formed between two blue emitters in a single emitting layer, demonstrating a two-color WOLED with an ultra-high CRI of 90.8 [21]. Very recently, we used yellow exciplex formed between 4,4′,4″-Tris [phenyl(m-tolyl)amino] triphenylamine (m-MTDATA) and bis[2-(2-hydroxyphenyl)-pyridine]beryllium ($Bepp_2$) to demonstrate an ultra-simple WOLED with CRI as high as 92 by combining blue emission of $Bepp_2$ and exciplex yellow emission, and the proposed WOLED using only three organic functional materials, opens up a new avenue for achieving simple-structured, but ultra-high CRI WOLEDs. However, the above-mentioned WOLEDs generally suffer from a relatively low efficiency and luminance ($< 5000\ cd/m^2$), which further restrains their various applications in the lighting field [10,11,23]. Thus, to develop a simple but high performance ultra-high CRI WOLEDs is still an urgent task.

In this work, we employed di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexan (TAPC) as an suitable hole transporting layer (HTL) and electron blocking layer and $Bepp_2$ as an efficient electron transporting layer (ETL) and blue emitting layer, by simply doping exciplex donor m-MTDATA in exciplex acceptor $Bepp_2$ of bilayer structure TAPC (HTL)/$Bepp_2$ (ETL) away from HTL/ETL interface for different distance, to demonstrate a series of efficient and highly simple two-color WOLEDs. White emission was realized by combining yellow emission of $Bepp_2$: m-MTDATA forming exciplex and blue emission of $Bepp_2$ spacer layer between HTL and $Bepp_2$: m-MTDATA layer. The optimized white device shows a low turn-on voltage of 2.7 V, high luminance of 5561 cd/m^2, high power efficiency (PE) of 11.08 lm/W, and ultra-high CRI of 93 at a luminance of 5000 cd/m^2. To the best of our knowledge, the CRI is by far the CRI is by far the highest value for two-color WOLEDs with the emission of exciplex [25–27].

2. Experimental

In this work, all materials involved in device fabrication were purchased through commercial sources and used without further purification. The energy levels for all materials were obtained from the published literatures [11,28–30]. All the devices were fabricated on the pre-patterned indium tinoxide (ITO) glass substrate with sheet resistance of 15 Ω/□ by vacuum deposition. The detailed fabrication and testing process for all OLEDs in this work were shown in Section S1 in Supporting information, which is consistent with the previously reported work by our group [10,11].

3. Results and discussion

3.1. The proposed novel device structure for WOLEDS

In our previous work, the exciplex formed between m-MTDATA and $Bepp_2$ has been clearly demonstrated by the normalized photoluminescence (PL) spectra of m-MTDATA, $Bepp_2$ and m-MTDATA:$Bepp_2$ mixed films (see Fig. S1 in Supporting information) as well as the EL spectra for the device of ITO/m-MTDATA (20 nm)/m-MTDATA:$Bepp_2$ (1:1, 5 nm)/$Bepp_2$ (45 nm)/LiF (1 nm)/Al (100 nm) [11]. It was found the emission peak of m-MTDATA:$Bepp_2$ exciplex is located at around 560 nm, and the EL spectra is very wide with a full width at half maximum of over 100 nm, which proves its great potentials in term of constructing high CRI WOLEDs using less emitters.

On the basic of above analysis, combining broad spectra characteristic of m-MTDATA:$Bepp_2$ exciplex, a simple device structure for two color WOLEDs was proposed, and the schematic structure diagram of two color WOLEDs as well as molecular structure of organic materials involved in device fabrication were displayed in Fig. 1 [24,25]. In proposed WOLEDs, TAPC was selected as HTL for its superior hole transporting capacity and intrinsic higher lowest unoccupied molecular orbital (LUMO), and $Bepp_2$ was utilized as ETL and highly efficient blue emitter because of its high photoluminescence quantum efficiency (PLQY) (> 80%) and excellent electron transporting capacity [31,32]. Clearly, the proposed WOLEDs can be fabricated by simply doping exciplex donor of m-MTDATA in the exciplex acceptor $Bepp_2$ of bilayer structure TAPC (HTL)/$Bepp_2$ (ETL), where the $Bepp_2$:m-MTDATA layer is away from HTL/ETL interface for a certain distance. The white emission can be realized by combining yellow emission of $Bepp_2$ and m-MTDATA forming exciplex and blue emission of $Bepp_2$ spacer layer between HTL and $Bepp_2$: m-MTDATA layer.

3.2. EL performance and working mechanism for proposed WOLEDs

To verify our design and further explore the working mechanism of the proposed two color WOLEDs, a series of two color WOLEDs, having the structure of ITO/MoO_3 (3 nm)/TAPC (40 nm)/$Bepp_2$ (x nm)/$Bepp_2$:m-MTDATA (1:1 10 nm)/$Bepp_2$ (40 nm)/LiF (1 nm)/Al (100 nm), were fabricated, where x was set as 5, 7, and 9, corresponding to the devices W1, W2, and W3, respectively.

Fig. 2 shows the normalized EL spectra, CIE and CRI of the devices W1-W3 at different luminance, and the inset is the photograph of the corresponding white device under a practical luminance of 5000 cd/m^2. It can be seen that the EL spectra for the devices W1-W3 exhibit two obvious emission peaks at about 440 nm and 560 nm, well corresponding to the emissions of $Bepp_2$ and m-MTDATA:$Bepp_2$ exciplex, respectively [11]. And with the voltage increases (corresponding to increasing luminance), all white devices W1-W3 showed an enhanced relative intensity of blue light emission, which may be caused by more excitons be used by $Bepp_2$ spacer layer for blue light emission under a high voltage. As shown in Fig. 2(a), corresponding to the device W1, with the increasing blue light intensity, the value of CRI greatly improved with the maximum CRI reaching 83 at a luminance of 5000 cd/m^2, which meets the basic requirement for commercial lighting applications (CRI > 80), and is superior to the majority of reported complementary WOLEDs [10,27].

From Fig. 2**(b)**, with the thickness of $Bepp_2$ spacer layer increases to 7 nm, the corresponding device W2 exhibits a stronger blue emission intensity at the same luminance compared to the device W1,