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High performance organic light-emitting diodes with tunable color range from orange to warm white based on single thermally activated delayed fluorescence emitter

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ABSTRACT

In this work, we reported the highly efficient organic light-emitting diodes based on orange-emitting thermally activated delayed fluorescence emitter 1,4-dicyano- 2,3,5,6-tetrakis(3,6-diphenyl-carbazol-9-yl)benzene (4CzTPN-Ph). By utilizing the bipolar material 2,6-bis(3-(9H-carbazol-9-yl)phenyl)-pyridine (26DCzPPy) and hole type material 4,4′,4″-Tri(9-carbazoyl)triphenylamine (TcTa) as host and ladder materials, respectively, the optimized single light-emitting layer (EML) orange device obtained the maximum brightness, external quantum efficiency, current efficiency and power efficiency up to 41791 cd/m^2, 13.1%, 42.97 cd/A and 44.98 lm/W, respectively. Except for the 570 nm characteristic emission, interestingly, there is another emission peak at about 475 nm, which increases rapidly with decreasing doping concentration. Therefore, device color shifts gradually from orange to warm white with decreasing doping concentration due to the increasing relative intensity of exciplex emission. Finally, warm white device (Commission Internationale de L'Eclairage (CIE) Coordinates at (0.337, 0.476)) based on single TADF emitter with the maximum brightness, external quantum efficiency, current efficiency and power efficiency up to 23560 cd/m^2, 10.2%, 32.33 cd/A and 32.75 lm/W, respectively, was also obtained.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great interest throughout the world because of their potential applications in solid-state lighting and full-color flat panel displays [1–4]. According to spin statistics, 25% singlet (S_1) and 75% triplet (T_1) excitons are formed by numerous couples of holes and electrons under electrical excitation. Traditional fluorescent material can only utilize the S_1 excitons energy, thus only 25% internal quantum efficiency (IQE) could be expected. A variety of methods have been attempted to break the limitation of fluorescent material such as triplet-triplet annihilation (TTA) [5], hybridized local and charge-transfer (HLCT) [6–8] and thermally activated delayed fluorescence (TADF) [9–14]. In recent years, electro-luminescent (EL) devices based on TADF emitters have acquired great breakthrough in utilizing the T_1 excitons energy via reverse intersystem crossing (RISC) [15–18]. For these TADF emitters, the small energy difference (ΔE_{ST}) between S_1 and T_1 ($\Delta E_{ST} < 0.1$ eV) makes it possible for electrons to up-convert from T_1 to S_1 by absorbing environmental thermal energy and then radiatively decay from the S_1. Therefore, 100% IQE could be achieved by these devices based on TADF emitters.

Since the first report in 1930 [19], many groups have devoted their effort to the design of new TADF emitters and the optimization of device structures. Until 2012, Adachi and co-workers made a significant breakthrough in realizing the TADF OLEDs with high external quantum efficiency (EQE) above 30%, which broke the efficiency limitation of fluorescent OLEDs [20]. More importantly, these remarkable discoveries have revolutionized our understanding of organic semiconductors and optoelectronics. For commercial application, three primary colors of red, green and blue are required [21]. Up to now, the efficiency and brightness of green and blue TADF OLEDs have been rapidly developed. For example, Seino et al. reported a green TADF OLEDs with turn-on voltage, EQE and power efficiency of 2.33 V, 25.7%

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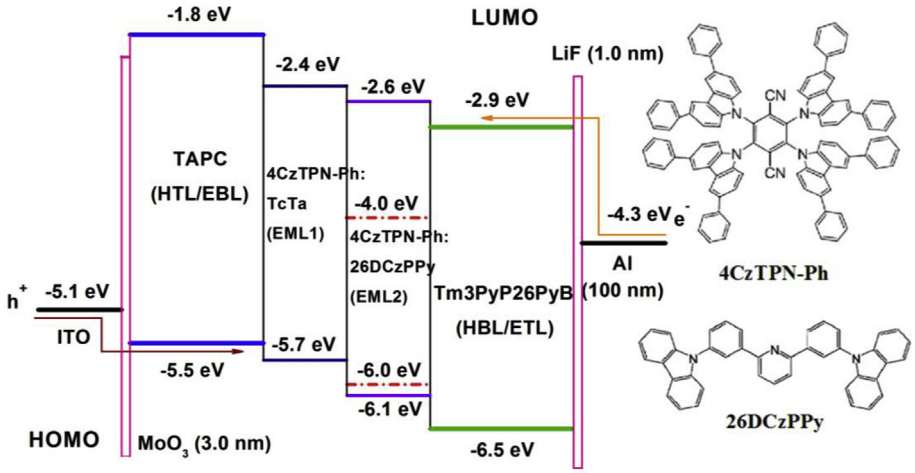

Fig. 1. Proposed energy level diagram of the OLEDs used in this work and the molecular structures of 4CzTPN-Ph and 26DCzPPy.

and 107 lm/W, respectively, and this device realized the record power efficiency as high as 79.4 lm/W at the brightness of 1000 cd/m^2 [22]. Shizu et al. fabricated a sky-blue TADF emitter 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9′- phenyl-9H, 9′H-3,3′-bicarba-zole (BCzT), and the device with BCzT as emitter exhibited a maximum EQE of 21.7% [23]. On the other hand, performances of red TADF OLEDs remain to be optimized in the context of color purity, efficiency and brightness although many red organic compounds have been synthesized [24–28]. Recently, Zhang et al. fabricated the TADF OLEDs with the orange TADF emitter 4CzTPN-Ph with EQE of 4.79% [29]. Uoyama et al. also obtained 4CzTPN-Ph based TADF OLEDs with EQE of 11.2% by using the high triplet energy host material N, N′-dicarbazolyl-4-4′-biphenyl (CBP) [20].

In this work, we aim to improve the EL performance of orange TADF emitter 4CzTPN-Ph by designing the device structure with stepwise energy levels. The widely used hole transport material TcTa and bipolar material 26DCzPPy were chosen as the host materials to broaden recombination zone, which could suppress the annihilation of triplet excitons. Based on these materials, a series of single-EML or double-EMLs devices were fabricated and compared. Finally, single-EML device with TcTa as ladder layer between hole transport layer and EML obtained the maximum brightness, external quantum efficiency, current efficiency and power efficiency up to 41791 cd/m^2, 13.1%, 42.97 cd/A and 44.98 lm/W, respectively, which were even higher than those of the optimized double-EMLs devices. Interestingly, based on only one TADF emitter, single-EML device displayed warm white light emission (CIE coordinates at (0.337, 0.476)) and obtained the maximum brightness, external quantum efficiency, current efficiency and power efficiency up to 23560 cd/m^2, 10.2%, 32.33 cd/A and 32.75 lm/W, respectively.

2. Experimental

All the organic materials used in this work were obtained commercially and used as received without further purification. Indium tin oxide (ITO) coated glass with the sheet resistance of 10 Ω/sq was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned with detergent, rinsed in de-ionized water, and finally dried in an oven. All organic layers were evaporated with the rate of 0.1 nm/s under high vacuum ($\leq 3.0 \times 10^{-5}$ Pa). The doped EMLs were prepared by co-evaporating the dopant and host material from two individual sources, and the doping concentration was modulated by controlling the evaporation rate of dopant. LiF and Al were evaporated in another vacuum chamber ($\leq 8.0 \times 10^{-5}$ Pa) with the rates of 0.02 and 1.0 nm/s, respectively, without being exposed to the atmosphere. The thicknesses of these deposited layers and the evaporation rate of individual materials were monitored in vacuum with quartz crystal monitors. A shadow mask was used to define the cathode and to make eight emitting dots with the active area of 9 mm^2 on each substrate. Current density-brightness-voltage (*J-B-V*) characteristics were measured by using a programmable Keithley source measurement unit (Keithley 2400 and Keithley, 2000) with a silicon photodiode. The EL spectra were measured with a calibrated Hitachi F−7000 fluorescence spectrophotometer. The external quantum efficiency of EL device was calculated based on the photo energy measured by the photodiode, the EL spectrum and the current pass through the device.

3. Results and discussion

In this work, 4CzTPN-Ph was chosen as the orange TADF emitter because of its high efficiency and good film-forming property. Owing to the high hole mobility (1×10^{-2} cm^2 V^{-1} s^{-1}) and high-lying LUMO level (−1.8 eV), di-[4-(N,N- ditolyl-amino)-phenyl]cyclohexane (TAPC) was chosen as hole transport layer (HTL) and electron block layer (EBL) material. Simultaneously, 1,3,5-tri(6-(3-(pyridin- 3-yl)pyridin-2-yl)benzene (Tm3PyP26PyB) was selected as hole block layer (HBL) and electron transport layer (ETL) material due to its low-lying HOMO level and high electron mobility. The hole transport material TcTa and bipolar material 26DCzPPy were used as host materials. Fig. 1 depicted the device structure and the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) levels diagram of the designed TADF OLEDs. In addition, the molecular structures of 4CzTPN-Ph and 26DCzPPy were also shown in Fig. 1. In this case, the stepwise LUMO levels of Tm3PyP26PyB (−2.9 eV), 26DCzPPy (−2.6 eV) and TcTa (−2.4 eV) are helpful for the injection and transport of electrons [30], while the stepwise HOMO levels of TAPC (−5.5 eV), TcTa (−5.7 eV) and 26DCzPPy (−6.1 eV) are beneficial for the injection and transport of holes [31]. Hence, balanced carriers' distribution could be expected in these devices.

Firstly, to determine the optimal doping concentration of 4CzTPN-Ph, several single-EML devices with the structure of ITO/MoO_3 (3 nm)/TAPC (50 nm)/4CzTPN-Ph (**a** wt%):26DCzPPy (10 nm)/Tm3PyP26PyB (50 nm)/LiF (1 nm)/Al (100 nm) and several double-EMLs devices with the structure of ITO/MoO_3 (3 nm)/TAPC (50 nm)/4CzTPN-Ph (**b** wt %):TcTa (5 nm)/4CzTPN-Ph (**b** wt%): 26DCzPPy (10 nm)/Tm3PyP26PyB (50 nm)/LiF (1 nm)/Al (100 nm) were fabricated and measured by controlling doping concentration from 0.2 wt% to 3.0 wt %. The doping concentration dependence of EL efficiency-current density characteristics of the single-EML devices were depicted in Fig. 2, while the current density-brightness-voltage characteristics of these devices were given in the insert of Fig. 2. With increasing doping concentration of 4CzTPN-Ph, EL performances of single-EML devices