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CBP derivatives dendronized self-host TADF dendrimer: Achieving efficient non-doped near-infrared organic light-emitting diodes

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ABSTRACT

A self-host thermally activated delayed fluorescence (TADF) dendrimer, namely MPPA-MCBP, for solution-processed nondoped near-infrared organic light-emitting diodes (OLEDs) was designed and synthesized, in which the bipolar CBP derivatives is introduced to render balanced charge transportation. This structural modification that the dendrons are well-bounded by the flexible alkyl chains, which can efficiently reduce the intermolecular interactions between the emissive cores and ensure the stable operation of the solution-processed device. As a result of the spin-coated OLEDs employing MPPA-MCBP as the host-free near-infrared emitter exhibits a highest external quantum efficiency (EQE) of 0.62% and a peak wavelength at 698 nm, which indicates the design of self-host TADF dendrimers containing bipolar dendrons will be a promising strategy to improve the electroluminescent performance of solution-processed nondoped device.

1. Introduction

Metal-free near-infrared (NIR) materials have aroused fundamentally interesting and practically useful as the extension of organic light emitting diodes (OLEDs) [1–4]. In particular, evaporated NIR OLEDs based small molecules have made a great progress with external quantum efficiencies (EQEs) are dramatic improved [5–9]. Compared with evaporated NIR OLEDs, solution processable NIR OLEDs is of great interest due to the capacity of simplified processing, cost-effective and large-area production [10–13]. Cao et al. reported the polymer light-emitting diodes (PLEDs) based on phosphors have reached EQE of 3.0%, which is among the highest reported for solution-processed OLEDs (s-OLEDs) [14]. However, the efficiencies of fluorescent NIR s-OLEDs are still far behind those of the organometallic phosphors based s-OLEDs due to both the photoluminescence quantum yield (PLQY) and the EQE decrease with decreasing band gap deriving from the internal quantum efficiency (IQE) of 25% and strong vibronic coupling [12]. As a wise alternative, metal-free thermally activated delayed fluorescence (TADF) materials have received considerable attention because they can harvest both singlet and triplet excited states to achieve a theoretical IQE of 100% [15–28]. In solution processable systems, dendrimers have become excellent candidates for the non-doped s-OLEDs due to the characteristics of the well-defined structures and the excellent solution processibility [29,30]. Inspired by this advantage, a series of dendrimers based on transition metal complexes with the emission of blue, green, yellow, and red colors have already been reported for high-performance non-doped phosphorescent OLEDs [31–36]. However, there is a handful of TADF dendrimers with the emission from blue to yellow are reported, rendering the development of red/NIR TADF dendrimers promising and desiring [37–41].

To design high-performance self-host dendrimers, the commendable engineer of dendron is practical and convenient [42,43]. For example, Wang et al. utilized hole-transporting oligocarbazole dendrons to replace the electrically insulating biphenyl dendrons, realizing improved EQE of 15.3% for solution-processed nondoped PhOLEDs [31]. However, the device based on unipolar

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self-host dendrimers still suffer from a severe efficiency roll-off and poor brightness. Subsequently, the bipolar concept was ingenious introduced into self-host dendritic platform, which the device with the low efficiency roll-off and high-brightness is realized [44]. In the same way, the biplor dendrons also introduced into a well-known blue TADF core, the electroluminescent performance of self-host TADF dendrimers is greatly improved [45]. Therefore, the development of bipolar dendron in electrofluoresent and electrophosphorescent dendrimers is promising for the efficient non-doped solution-processed OLEDs. Recently, our group reported a NIR TADF self-host dendrimer MPPA-3Cz utilizing the hole-transporting oligocarbazole as the ambient dendrons, which the EQE of device have achieved 0.25% [46]. Taking into account of the charge unbalance problem results from the strong hole-transporting ability of oligocarbazole, there is still remains considerable room for further improving the device performance. 4,4′-N,N′-dicarbazole-biphenyl (CBP) as the popular and brilliant molecule is likely candidates as singlet/triplet energy transfer and exciton confining media [47]. Employing 4,40-bis(9-carbazolyl) biphenyl (CBP) as hosts for the fluorescent and phosphorescent emitters, a large of highly efficient blue, green, orange and red OLEDs have been reported, deriving from the decent singlet/triplet energy level and bipolar characteristic with extended π-conjugated phenyl bridged [17,24,26,48]. However, CBP has its inevitable flaw in solution-processed devices, which is a faster aggregation quenching compare to evaporated devices under electrical stress and low glass transition temperatures (Tg = 62 °C) in the host/guest doped systems, causing the poor device performance [49,50].

In view of this, we constructed a novel self-host near-infrared (NIR)-emitting TADF dendrimer, namely, MPPA-MCBP, where a bipolar methoxy-CBP (MCBP) is selected as the peripheral dendron instead of the p-type oligocarbazole dendron used in reported unipolar MPPA-3Cz. MPPA-MCBP exhibits its enhanced capability of amorphous film-forming property and good thermal stability. Simultaneously, the dendrons MCBP are well-confined by the flexible alkyl chains, which can effectively reduce the aggregation quenching under electrical stress. The result of hole- and electron-only devices demonstrates that this structural modification can render MPPA-MCBP with more balanced charge transportation relative to that of MPPA-3Cz. Consequently, the nondoped device of MPPA-MCBP gives a considerably high EQE of 0.62%, which is more than doubled electroluminescent performance compared with that of reported unipolar analogue MPPA-3Cz (0.25%), indicative of its great potential in efficient TADF emitter used for a solution-processed nondoped device.

2. Experimental

2.1. General information

All solvents and materials were used as received from commercial sources without further purification. ^{1}H NMR spectra were recorded on a BRUKER AMX 600 MHz instrument relative to $Si(CH_3)_4$ as internal standard. Molecular masses were determined by matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) using a BRUKER DALTONICS instrument, with α-cyano-hydroxycinnamic acid as a matrix. Absorption and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUOROMAX-4 spectrophotometer, respectively. The solid PL quantum efficiency was measured with an integrating sphere. Cyclic voltammetry were performed on a CHI750C voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) (oxidation process) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. AFM (Seiko Instruments, SPA-400) was used to measure the film surface morphology. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409 PC) and DSC 2910 modulated calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min^{-1}.

2.2. Devices measurements and characterization

In general, indium–tin oxide (ITO)-coated glass substrates with a sheet resistance of 30 Ω/cm^{-1} were precleaned with deionized water and treated in an ultraviolet-ozone chamber. The 40 nm-thick poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) film was deposited on the ITO-glass substrates and baked at 150 °C for 10 min. Then, emission layer of MPPA-MCBP or MPPA: MCBP was spin-coated onto the PEDOT:PSS layer to give uniform thin films and annealed at 100 °C for 30 min to remove the residual solvent in N_2 atmosphere. Subsequently, a 40 nm thick TPBI were evaporated as the hole blocking and electron transporting layer, whereas Cs_2CO_3/Al was used as the metal cathode. For hole-only devices, the emission layer was spin-cast on PEDOT-modified ITO glass, and then Al electrode was deposited. For preparing electron-only devices, the emission layer was directly spin-coated on ITO glass, and then Cs_2CO_3/Al electrodes were thermally deposited. The EL spectra and CIE coordinates were measured using a PR655 spectra colorimeter. The current density-voltage and brightness-voltage curves of the devices were measured using a Keithley 2400 source meter calibrated by a silicon photodiode. All the measurements were carried out at room temperature under ambient conditions. The EQE was calculated from the brightness, current density and EL spectrum assuming a Lambertian distribution.

2.3. Materials

2.3.1. Preparation of 9-(4′-(9H-carbazol-9-yl)-[1,1′-biphenyl]-4-yl)-3-methoxy-9H-carbazole (MCBP)

9-(4′-bromo-[1,1′-biphenyl]-4-yl)-9H-carbazole (4 g, 10 mmol), 3-methoxy-9H-carbazole (2.4 g, 12 mmol), potassium carbonate (2.8 g, 20 mmol), copper(I) iodide (0.2 g, 1 mmol), and 1,10-phenanthroline (0.2 g, 1 mmol) were added to 40 mL of dried dimethylformamide (DMF). The mixture was heated at 140 °C for 12 h under nitrogen atmosphere. After this mixture cooled to room temperature, the reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried by anhydrous Na_2SO_4 and filtered. The product was isolated by silica gel column chromatography using petroleum ether/dichloromethane as eluent to afford a white solid (3.1 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.97 (s, 3H), 7.08 (d, J = 9.0 Hz, 1H), 7.29 (t, J = 8.1 Hz, 3H), 7.42–7.52 (m, 7H), 7.64 (s, 1H), 7.69 (d, J = 8.1 Hz, 4H), 7.89 (d, J = 7.2 Hz, 4H), 8.11 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 7.5 Hz, 2H).

2.3.2. Preparation of 9-(4′-(9H-carbazol-9-yl)-[1,1′-biphenyl]-4-yl)-3-((6-bromohexyl)oxy)-9H-carbazole (1)

To a stirred solution of 9-(4′-(9H-carbazol-9-yl)-[1,1′-biphenyl]-4-yl)-3-methoxy-9H-carbazole (1.7 g, 3.3 mmol) in dehydrated dichloromethane at 0 °C was added BBr_3 (1.6 g, 6.4 mmoL). After the addition was completed the mixture was stirred for 24 h. The reaction was quenched by methyl alcohol. The solution was evaporated in vacuo. The crude product was added in a stirred solution of 1,6-dibromohexane (4.8 g, 19.8 mmol) and $CsCO_3$ (2.1 g,