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Synthesis of carbazole-based dendrimer: host material for highly efficient solution-processed blue organic electrophosphorescent diodes

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ABSTRACT

This paper reports the synthesis and physical properties of two novel carbazole-based dendritic host materials Cz-CCP and Cz-mCP for solution-processed blue phosphorescent organic light-emitting devices (PhOLEDs). These dendritic hosts exhibit high triplet energy (≥2.85 eV), excellent film-forming ability (with low root-mean-square (rms) values less than 0.2 nm), high glass-transition temperatures in the range of 242–248 °C, and the appropriate HOMO energy levels (−5.33–−5.35 eV) facilitating the transfer of holes from Poly(3,4-ethylenedioxythiophene):Poly(styrene-4-sulfonate) (PEDOT:PSS) to the emitting layer. The single-layer device using Cz-CCP and Cz-mCP as the host for the phosphorescence emitter iridium(III) bis(4,6-difluorophenylpyridinato)-picolinate (FIrpic) showed the maximum luminance efficiencies of 9.6 and 10.8 cd A^{-1}, respectively. By introducing a thin 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene (TPBI) electron-transporting and exciton-confining layer, the maximum efficiency of the solution-processed double-layer device based on Cz-CCP and Cz-mCP can be further improved to 20.5 and 22.7 cd A^{-1}, and maximum external quantum efficiencies as high as 10.2% and 11.5%, respectively. These results demonstrated that the newly synthesized, carbazole-based dendritic host materials are advantageous for fabrication of highly efficient blue PhOLEDs.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted considerable attention due to their promising applications in highly energy-efficient flat-panel displays, and being potential candidates for the next generation of lighting sources.[1–5] To minimize the triplet–triplet annihilation and concentration quenching effects, the triplet emitters have to be well dispersed into a host matrix at a relatively low concentration. Therefore, the development of efficient host materials is of great importance to achieve the high performance PhOLEDs. Currently, the design of suitable host materials for the efficient and stable blue PhOLEDs still remains a challenge due to the requirement of high triplet energy (>2.75 eV, to confine the electro-generated triplet excitons on the dopant molecules),[6,7] while the search of host for the green and red triplet emitters is relatively easier because of their low triplet energy levels.

Recently, solution-processed PhOLEDs are highly desirable to simplify the fabrication process and achieve the cheaper and larger-area displays.[8–15] Even though polymer-based host materials allow easy access to the solution-processing strategy, the impurities in polymer host materials could result in exciton quenching and the device failure. Compared with polymers, conjugated dendrimers are believed to have a number of advantages including excellent solubility, facilitated formation of good quality film, well-defined structures, and high degree of purity.[6,16–22] These unique features render this kind of dendritic materials rather promising in using as host material for solution-processed PhOLEDs.

Carbazole-based molecules have been widely used as host materials for blue PhOLEDs due to their high triplet energy and excellent hole-transporting properties.[23–30] In this paper, we proposed to modify 1,4-bis(9-carbazolyl)benzene (CCP) and 1,3-bis(9-carbazolyl)benzene (mCP) by linking of two carbazole moieties into the 3, 6 positions of the carbazole units to build novel dendritic host materials. The novel dendrimers are Cz-CCP and Cz-mCP, which possess the following distinct characteristics: (i) the high triplet energy levels (2.85 eV); (ii) the appropriate HOMO energy levels (−5.33–−5.35 eV); (iii) the capability of forming stable amorphous thin films. Additionally, the introduction of the *tert*-butyl groups ensures the good solubility of our novel dendrimers in common solvents. As a result, the solution-processed devices based those new hosts show excellent performances, with

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the luminous efficiency (LE) of 22.7 cd A^{-1} and the external quantum efficiency (EQE) of 11.5% for blue PhOLEDs. These promoted efficiencies of the devices, which are outstanding with respect to other works related to the solution-processed blue PhOLEDs based on dendritic hosts.

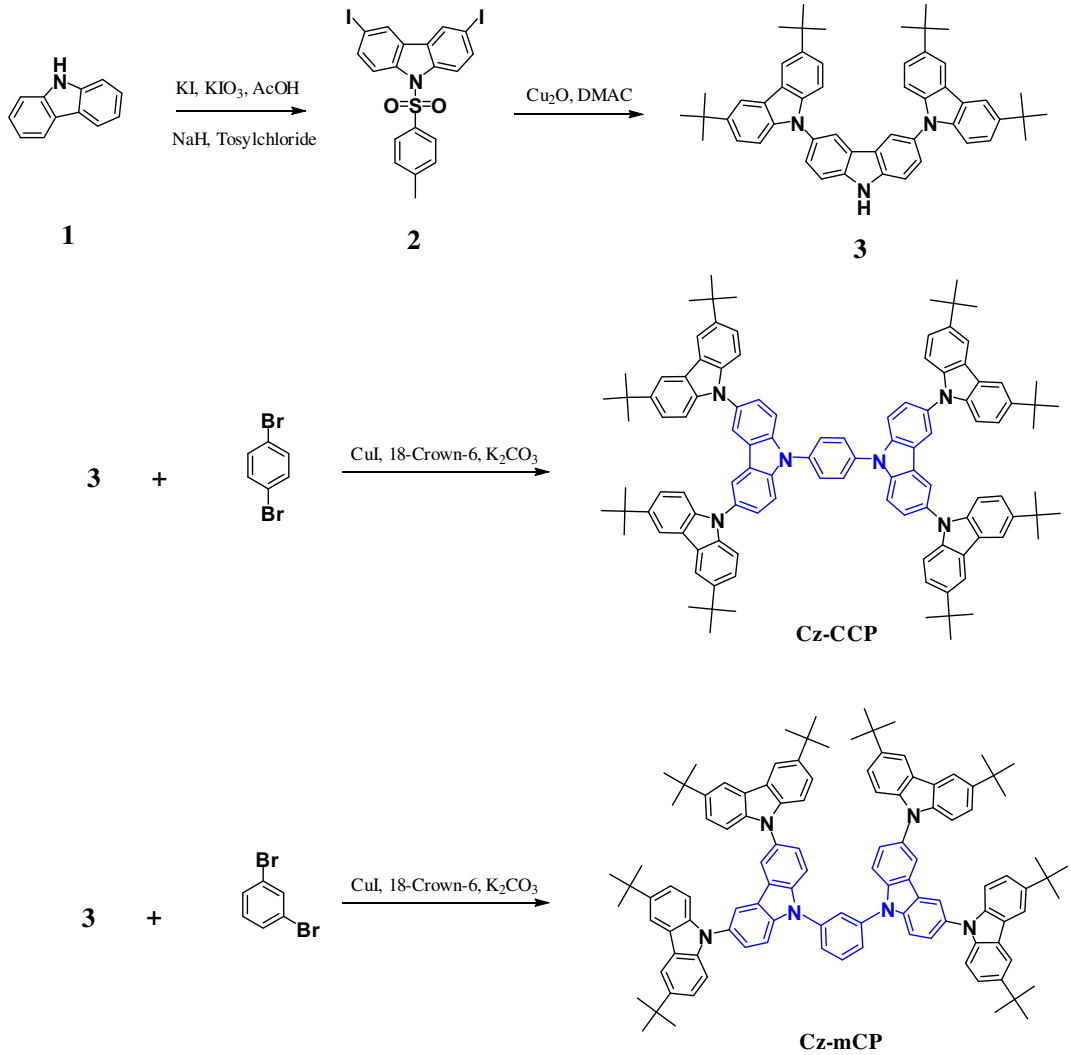
2. Experimental

2.1. General information

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ^{1}H NMR and ^{13}C HMR spectra were measured on a Bruker ARX300 NMR spectrometer with tetramethylsilane as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Mass spectrometry was performed with a Thermo Electron Corporation Finnigan LTQ mass spectrometer. Absorption spectra were recorded with a UV–vis spectrophotometer (Agilent 8453) and PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). TGA was recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) under a dry nitrogen gas flow at a heating rate of 10 °C min^{-1}. Glass-transition temperature was recorded by DSC at a heating rate of 10 °C min^{-1} with a thermal analysis instrument (DSC 2910 modulated calorimeter). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) 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. The solutions were bubbled with a constant argon flow for 10 min before measurements. The film surface morphology was recorded by AFM (Seiko Instruments, SPA-400).

2.2. Device fabrication and performance measurements

In a general procedure, indium-tin oxide (ITO)-coated glass substrates were pre-cleaned carefully and treated by UV ozone for 4 min. An aqueous solution of Poly(3,4-ethylenedioxythiophene) and Poly(styrene-4-sulfonate)(PEDOT:PSS) was spin-coated onto the ITO substrate and the layer thickness was carefully controlled at 40 nm. After being baked at 210 °C for 10 min, the substrate was then transferred into a nitrogen glove box. Then a FIrpic-doped host: 1,3-bis[4-*tert*-butylphenyl0-1,3,4-oxidiazolyl]phenylene (OXD-7) layer was spin-coated onto the PEDOT:PSS layer from 1,2-dichloroethane solution and annealed at 100 °C for 30 min. Finally, the substrate was transferred into an evaporation chamber, where the TPBI was evaporated at an evaporation rate of 1–2 Å/s under a pressure of 4×10^{-4} Pa and the Cs_2CO_3/Al bilayer cathode



Scheme 1. Synthetic routes toward Cz-CCP and Cz-mCP.