



Alkyl effects on the optoelectronic properties of bicarbazole/cyanobenzene hybrid host materials: Double delayed fluorescent host/dopant systems in solution-processed OLEDs



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ABSTRACT

Three 3,3'-bicarbazole derivatives, 4,4'-(9*H*,9'*H*-[3,3'-bicarbazole]-9,9'-diyl)bis(2-methylbenzotrile) (*p*CNBCzmMe, **1**), 4,4'-(9*H*,9'*H*-[3,3'-bicarbazole]-9,9'-diyl)bis(3-(trifluoromethyl)benzotrile) (*p*CNBCzoCF₃, **2**) and 4,4'-(9*H*,9'*H*-[3,3'-bicarbazole]-9,9'-diyl)bis(2-(trifluoromethyl)benzotrile) (*p*CNBCzmCF₃, **3**) were designed and synthesized through a simple one-step catalyst-free C–N coupling reaction, by using 9*H*,9'*H*-3,3'-bicarbazole and alkyl substituted fluorocyanobenzene as starting materials. Compounds **1–3** exhibit high thermal stabilities with *T*_d above 400 °C and *T*_g from 134 to 165 °C. They show thermally activated delayed fluorescence (TADF) characteristics with microsecond scale long lifetimes, similar triplet energy of ~2.65 eV whereas different absorption and photoluminescence behavior according to the substitution of CH₃ or CF₃ alkyl units at different *meta*- or *ortho*- positions. Low singlet-triplet band gaps (ΔE_{ST}) of 0.30, 0.19 and 0.14 eV are observed for **1–3**, respectively. By partially blocking the electroactive sites at the 3,3'-position of carbazole to prevent electropolymerization, these 3,3'-bicarbazole derivatives perform favorable electro-oxidative stability. From both experimental and theoretical results, the introduction of electron-withdrawing CF₃ in **2** and **3** lowers both of the HOMO and LUMO levels compared to the weak electron-donating CH₃-substituted **1**. The hole and electron transport properties can also be tuned through different alkyl on different *ortho*- or *meta*-positions. It is interesting that the electron-donating CH₃ *meta*-structured **1** exhibit one order higher electron mobility than the strong electron-withdrawing CF₃ *ortho*-positioned **2** and *meta*-structured **3**, while *ortho*-CF₃ linked compound **2** with more twisted geometry showed the poorest hole-transport properties. By using the three TADF materials as hosts to conduct double host/dopant TADF systems for solution processed green TADF devices, maximum power efficiencies are achieved at 29.9, 22.7 and 30.9 lm/W for **1**, **2** and **3** based devices respectively, in simple structure of ITO/PEDOT:PSS (40 nm)/**1–3**:4CzCNPY (40 nm)/TmPyPB (60 nm)/LiF (0.8 nm)/Al (100 nm).

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1. Introduction

Since the pioneering work of Tang et al., organic light-emitting diodes (OLEDs) have attracted massive attention from both the academic and industry communities [1–3]. Very recently intensive interest has been drawn to the new generation of OLED materials of thermally activated delayed fluorescence (TADF) [4–7]. Compared with the conventional phosphorescent OLEDs (PHOLEDs) involving expensive noble-metal complexes as emitters, the TADF species are

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mostly cost-effective pure organic materials with very small energy gaps (ΔE_{ST}) between their first singlet (S_1) and triplet (T_1) state, which is beneficial for the fast $T_1 \rightarrow S_1$ reverse intersystem crossing (RISC) and ultimately leading to the theoretical 100% internal quantum efficiency upon emission [7a,8].

However, the TADF emitters still face similar problems with the phosphors in PHOLEDs. As the emissive excitons may be self-quenched in the emitting layer (EML) due to the triplet-triplet annihilation and concentration quenching, which finally results in poor device performance [9]. Therefore, the TADF emitters also need to be dispersed into a suitable host matrix at a certain doping concentration [10]. Consequently, the development of host materials favorable for the TADF emitters is of equal importance. In general, requirements for appropriate host materials in both TADF and phosphorescent OLEDs are similar as follows, i) to avoid the energy feedback from the TADF emitters to the host materials, the triplet energy (E_T) of the host is necessary to be higher than that of the doped emitter; ii) the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the host materials should match well with those of materials in the neighboring active layers to facilitate charge injection and reduce the device driving voltage; iii) the hosts are expected to exhibit bipolar characteristics for the balanced hole-/electron-transporting properties; iv) the host materials should have good morphological and thermal stability, which could reduce the possibility of phase separation upon heating and prolong the device operational stability [11–19]. Besides, most TADF materials possess bipolar transport properties as the simultaneous existence of electron donating and withdrawing moiety in their molecular structure which is responsible for the transport of hole and electron, respectively. In addition, host materials with delayed fluorescence characteristics have been proved to achieve highly efficient device performance in conventional fluorescent and phosphorescent OLEDs [20–25]. However, TADF materials as organic hosts for TADF OLEDs have rarely been demonstrated.

It is well known that carbazole is one of the most widely used donor moieties in the design of host materials due to its good hole-transport properties and high E_T of ~ 2.95 eV [12,26,27]. It is noted that organic materials based on its derivative of 9*H*,9'*H*-3,3'-bicarbazole (BCz), which exhibit better donor properties and lower driving voltages compared to carbazole counterparts have been seldom reported in OLEDs [27–32]. The *meta*-linked twisted structure of BCz maintains high E_T of ~ 2.8 eV despite of its enlarged π conjugation. Additionally the small singlet-triplet energy gap (~ 0.46 eV) of BCz is beneficial for energy transfer in PHOLEDs [27–29a]. In addition, BCz derivatives exhibit preferably stable electrochemical properties due to the partial block of active sites at C3 and C3' position, which avoids the electrochemical oxidative polymerization of carbazole and beneficial for the transport of positive charges (holes) in OLEDs [26]. The 9-*N*-positions of BCz hosts are normally blocked by other functional groups instead of the active H atom, to ensure their chemical stability and maintain specific optoelectronic properties [17,29b,30–32].

Herein, we designed and synthesized three simple BCz derivatives, namely *p*CNBCz*m*Me (1), *p*CNBCz*o*CF₃ (2) and *p*CNBCz*m*CF₃ (3) through a cost-effective one-step catalyst-free C–N coupling reaction by using 9*H*,9'*H*-3,3'-bicarbazole and alkyl substituted fluorocyanobenzene as starting materials. The cyanobenzene [33,34] unit was employed to the 9-positions of BCz with the aim of improving solubility and electron-transport capability. Furthermore, methyl (CH₃) and trifluoromethyl (CF₃) moieties were introduced to fine tune their optoelectronic properties. Compounds 1–3 exhibited TADF characteristics, by using them as host materials, and our previously developed green TADF emitter 2,3,5,6-tetra(9*H*-carbazol-9-yl)-4-cyano-pyridine (4CzCNPy) [19] as

dopant in solution-processed OLEDs for double TADF host/dopant system, comparable current efficiencies above 30 cd/A and power efficiencies of 29.9, 22.7 and 30.9 lm/W for 1, 2 and 3 based devices, respectively were achieved due to comprehensive effects of charge injection, carrier transport properties.

2. Experimental section

2.1. General information

¹H NMR and ¹³C NMR spectra were measured on a MECUYRVX300 spectrometer. Mass spectra were measured on a Bruker autoflex matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF). Elemental analyses of carbon, hydrogen and nitrogen were performed on a Vario EL III microanalyzer. Infrared Radiation (IR) was performed on Nicolet 6700. UV–Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The transient lifetime was measured in neat film state and in toluene using the Edinburgh FLS-920 Instruments. The photoluminescence quantum yield (PLQY) was measured in toluene under air or N₂ using the Edinburgh FLS-920 Instruments. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min⁻¹ from 25 to 600 °C. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min⁻¹ from 40 to 300 °C under the nitrogen atmosphere. The glass transition temperature (T_g) was determined from the second heating scan. Cyclic voltammetry (CV) was measured in the nitrogen purged dichloromethane for oxidation scan using a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as a supporting electrolyte. The conventional three-electrode configuration is employed, which consists of a platinum working electrode, a platinum wire auxiliary electrode and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s⁻¹. The onset potential of the new compounds was determined from the intersection of two tangents drawn at rising and background current of the cyclic voltammogram at first circle. The half-wave potential ($E_{1/2}$) value for Fc⁺/Fc is calculated as the average of cyclic voltammetric anodic and cathodic peaks. The HOMO energy levels were calculated from the oxidation curves according to the formula: $- [4.8 \text{ eV} + (E_{\text{onset}} - E_{1/2}(\text{Fc}/\text{Fc}))]$. The LUMO energy level was deduced from the energy band gap (E_g) and HOMO level. The film morphologies of the BCz-based host/4CzCNPy blends were detected by atomic force microscopy (AFM) and the blended films were prepared at the same condition as in OLED devices. AFM was conducted on SPA300HV in tapping mode using an SPI3800 controller, Seiko Instruments Industry, Co., Ltd.

2.2. Computational details

The geometrical and electronic properties of the three compounds were performed using the Gaussian 09 program package [35a]. The calculation was optimized by means of the B3LYP [35b-c] (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the 6-31G(d) [35d] atomic basis sets. Molecular orbitals were visualized using Gauss view.

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