



Novel spiro-based host materials for application in blue and white phosphorescent organic light-emitting diodes



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ABSTRACT

Two novel spiro-based host materials, namely 3-(9,9'-spiro[fluorene]-6-yl)-9-phenyl-9H-carbazole (**SF3Cz1**) and 9-(3-(9,9'-spiro[fluorene]-6-yl)phenyl)-9H-carbazole (**SF3Cz2**) were designed and synthesized. Due to the *meta*-linkage of spirobifluorene backbone, both **SF3Cz1** and **SF3Cz2** possess triplet energies over 2.70 eV, indicating they could serve as suitable hosts for blue and even white phosphorescent organic light-emitting diodes (PHOLEDs). The fabricated *bis*(4,6-(difluorophenyl)-pyridinato-N,C')picolinate (Flrpic) based PHOLEDs hosted by **SF3Cz1** and **SF3Cz2** exhibited excellent performance with maximum external quantum efficiencies (EQEs) of 18.1% and 19.7%, respectively. Two-color warm white PHOLEDs fabricated by utilizing **SF3Cz1** and **SF3Cz2** as hosts also achieved high EQEs and low efficiency roll-offs. The results demonstrate that **SF3Cz1** and **SF3Cz2** are promising hosts for blue and white PHOLEDs.

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1. Introduction

PHOLEDs have attracted much attention for next-generation displays and lighting technology due to their efficient harvesting of both singlet and triplet excitons with theoretical 100% internal quantum efficiency (IQE) [1–3]. However, phosphorescent emitters usually possess long exciton lifetime in a micro second timescale, which may easily lead to serious triplet–triplet annihilation (TTA) and self-quenching with high emitter concentration. Therefore, to suppress these unfavorable behaviors, the emitter is typically embedded in suitable host materials to form host–guest system which yields a high efficiency with low efficiency roll-off device [4–7]. Therefore, the development of appropriate hosts is as significant as developing efficient phosphors [7,8]. Generally, excellent hosts are required to satisfy several requirements such as high triplet energy (E_T), good charge transport ability, appropriate frontier molecular orbital (FMO) levels and good thermal stability [9–11]. Up to now, effective host–guest systems have been commercialized for green and red emitters, whereas blue

phosphors and suitable hosts are still a challenge [12]. Generally, a wide bandgap is the most demanding criterion for blue host materials because the high E_T hosts can facilitate energy transfer from the host to the emitter and confine the triplet excitons on the emitter [13]. On the other hand, for increasing the operational lifetime of the device, the host materials should possess excellent morphological and chemical stability [14,15]. Various host materials for blue emitting OLEDs which include: carbazole, dibenzothiophene, carboline, oxadiazole, phosphine oxide and cyano groups [16–19] have been reported to date. However, novel host materials with good thermal and chemical stabilities as well as high E_T to afford blue emitters are still desirable.

Recently, spiro compounds with inherent rigid structures are receiving much research attention because their specific physical properties come along with excellent optoelectronic performance [20]. Particularly, Spiro-configured materials show excellent morphological and chemical stabilities. In addition, the 3D configuration of spiro compounds can effectively inhibit excimer formation and keep high E_T in the solid state, which is benefit for improving the performance of OLEDs [21]. Most recently, our group developed *meta*-substituted spirobifluorene derivatives with high E_T for efficient deep blue PHOLEDs [22]. Undoubtedly, the *meta*-substituted spirobifluorene hosts exhibited higher E_T than that of *ortho*- and *para*-analogues due to less conjugation at *meta* position

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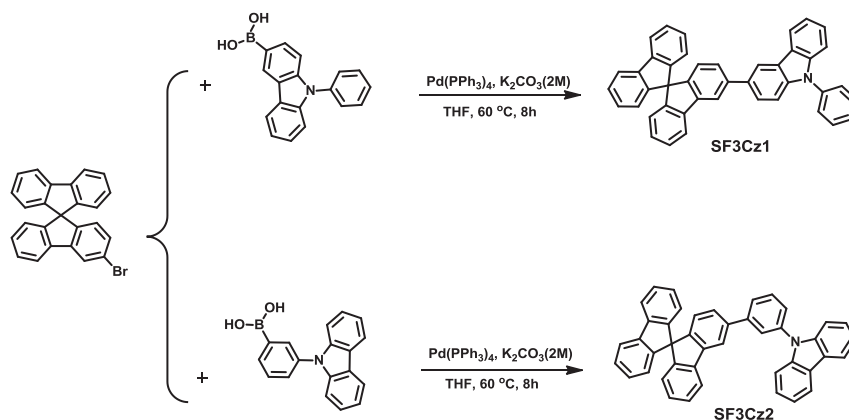
In this contribution, we report the design and syntheses of two spiro-based host materials 3-(9,9'-spiro[fluoren]-6-yl)-9-phenyl-9H-carbazole (**SF3Cz1**) and 9-(3-(9,9'-spiro[fluoren]-6-yl)phenyl)-9H-carbazole (**SF3Cz2**). The two materials are comprised of spirobifluorene and *N*-phenylcarbazole units with different linkage positions. Their photophysical, thermal, and electrical properties were fully investigated. Due to the *meta*-linkage of spirobifluorene unit, the E_{TS} of **SF3Cz1** and **SF3Cz2** are higher than that of the common blue phosphor Irpic. Thus, we anticipate that these two materials might be suitable hosts for blue and even white PHOLEDs. Finally, the Irpic based PHOLEDs hosted by **SF3Cz1** and **SF3Cz2** have been fabricated and exhibited excellent performance with maximum EQEs of 18.1% and 19.7% respectively. Additionally, we also successfully fabricated two-color white PHOLEDs by utilizing **SF3Cz1** and **SF3Cz2** as hosts with maximum EQEs of 18.2% and 19.1% respectively. Especially, the blue and the white devices hosted by **SF3Cz1** and **SF3Cz2** exhibit low efficiency roll-offs while keeping high efficiencies of 14.4%, 15.8% and 14.7%, 16.2% at 5000 cd/m². Thus, **SF3Cz1** and **SF3Cz2** show excellent electroluminescent performance and are potentially useful in the applications of OLED displays and lighting.

2. Results and discussion

2.1. Synthesis and thermal properties

Scheme 1 outlines the synthetic routes for **SF3Cz1** and **SF3Cz2**. **SF3Cz1** and **SF3Cz2** are easily synthesized through a classic Suzuki–Miyaura cross-coupling reaction between 3-bromo-9,9'-spirobifluorene and the corresponding carbazole boric acids. The details of the synthetic procedure and characterization are given in the Experimental section. The target materials were purified by chromatography and repeated temperature gradient vacuum sublimation, yielding a pure white powder. The chemical structure of **SF3Cz1** and **SF3Cz2** was fully characterized by ¹H NMR and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis.

The thermal properties of **SF3Cz1** and **SF3Cz2** were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen atmosphere at a scanning rate of 10 °C/min. As shown in **Fig. 1**, the **SF3Cz1** and **SF3Cz2** exhibited clear glass transition (T_g) at 160 °C and 153 °C, respectively. The decomposition temperatures (T_d) with 5% loss are estimated to be 385 °C and 393 °C for **SF3Cz1** and **SF3Cz2**, respectively. This suggests that **SF3Cz1** and **SF3Cz2** could form homogeneous and stable films by vacuum deposition for OLED fabrication.



Scheme 1. Synthetic routes of **SF3Cz1** and **SF3Cz2**.

2.2. Photophysical properties

The UV–vis absorption and photoluminescence (PL) spectra of **SF3Cz1** and **SF3Cz2** were measured in dilute CH₂Cl₂ solutions. As shown in **Fig. 2a**, the strong absorption peak at 300 nm can be ascribed to the carbazole-centered π – π^* transition, while the absorption shoulder at 315 nm can be assigned to the π – π^* transitions of spirobifluorene. The weaker absorptions around 335 and 365 nm are assigned to the n – π^* transition of the entire molecule. From the onset absorption wavelengths, optical energy gaps (E_g) were estimated as 3.40 eV and 3.54 eV for **SF3Cz1** and **SF3Cz2**, respectively. Upon photoexcitation at the absorption maxima at room temperature, **SF3Cz1** exhibits a structure feature emission spectrum with peaks at 370 nm and 385 nm, whereas **SF3Cz2** reveals a broad PL spectrum with peak at 360 nm. This indicates that **SF3Cz1** and **SF3Cz2** exhibit drastically different molecular geometries in their excited states, which is illustrated in the calculation section. To obtain triplet emission, their low-temperature PL spectrum was measured in a frozen 2-methyltetrahydrofuran matrix at 77 K. As shown in **Fig. 2b**, the E_{TS} of **SF3Cz1** and **SF3Cz2** were determined to be 2.72 and 2.82 eV respectively by the highest energy 0–0 phosphorescent emission, which are higher than that of the widely-used blue phosphor Irpic, implying that they could serve as triplet hosts for blue OLEDs.

2.3. Electrochemical properties and theoretical calculations

The electrochemical properties of **SF3Cz1** and **SF3Cz2** were studied by cyclic voltammetry measurements in deoxygenated DCM and DMF solutions with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu₄NPF₆) as the supporting electrolyte. The cyclic voltammograms are shown in **Fig. 3**. In the anodic scan, **SF3Cz1** and **SF3Cz2** underwent irreversible oxidation processes, which can be assigned to the oxidation of the carbazole unit. The HOMO energies of **SF3Cz1** and **SF3Cz2** were estimated from the onset of the oxidation potentials with regard to the energy level of ferrocene (4.8 eV below the vacuum). The HOMO levels of **SF3Cz1** and **SF3Cz2** were estimated as 5.44 and 5.56 eV respectively. The LUMO energy levels were calculated from the HOMO values and optical band gaps and were about 2.04 and 2.02 eV for **SF3Cz1** and **SF3Cz2** respectively. All the physical property data are summarized in **Table 1**. DFT calculations (B3LYP/6-31g(d)) were carried out to investigate the structure-property relationship of the two compounds. The distribution of HOMOs and LUMOs and optimized geometries for **SF3Cz1** and **SF3Cz2** are shown in **Fig. 4**. Obviously, the HOMO of **SF3Cz2** is mainly located on the electron-donating

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