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High thermal stability 3, 6-fluorene-carbazole-dendrimers as host materials for efficient solution-processed blue phosphorescent devices

Yinbo Qian [a,*], Feng Cao [a], Wenping Guo [b]

[a] School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, PR China
[b] Wuhan National Laboratory for Optoelectronics, Wuhan 430074, PR China

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ABSTRACT

A novel series of solution-processable 3,6-disubstituted-fluorene-carbazole based host materials 36FCzG1 and 36FCzG2 are designed and synthesized. Owing to the highly asymmetry tetrahedral configuration, these hosts exhibit high glass transition temperatures (T_g) (161 and 162 °C, respectively), high triplet energy levels (2.80 and 2.80 eV, respectively), excellent film forming capabilities, and chemical miscibility. Phosphorescent organic lighting-emitting diodes (OLEDs), which base on these host materials doped with the guests of iridium(III) bis(4,6-difluorophenylpyridinato)-picolinate (FIrpic) by spin coating, possesses a low turn-on voltage of 4.0 V, a maximum efficiency of 18.5 cd/A (8.1 lm/W), and a maximum external quantum efficiency of 10.3%. These results show that the devices are among the excellent solution processable blue phosphorescent OLEDs based on dendrimers. Furthermore, a novel way is developed to construct solution processable small molecules based on 3,6-disubstituted fluorene and carbazole dendrimers combined in a highly rigid configuration.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention as it has been recognized as the next-generation high-quality full color displays.[1–5] The efficiencies of OLEDs have been improved dramatically because of the development of efficient phosphorescent hosts & dopants containing transition metals that can harvest both singlet and triplet excitons for emission, providing the opportunity to realize internal quantum efficiency reach to 100% theoretically.[6–10] To date, most of the efficient PhOLEDs have been fabricated through vacuum thermal evaporation in multilayer configurations.[11–14] But it requires complex technological processes and a large amount of organic materials are wasted, leading to relatively high fabrication costs, at the same time, pixilation limits large-size scalabilities, and high-resolution applications.[15] Solution processes offers an attractive alternative to vacuum deposition techniques, mainly due to their better compatibility with low-cost production techniques and large substrates. Compared with success of developing the red and green PhOLEDs fabricated by solution processing,[16,17] high performance solution-processed blue PhOLEDs are still scarce, owing to the lack of appropriate host materials. Generally, for high efficient solution-processed blue PhOLEDs, the hosts would possess the following properties: (i) A high triplet energy gap (>2.70 eV), which prevents the reverse energy transfer from the dopant to the host; (ii) Suitable highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels matching those of the adjacent layers are required to reduce the operational voltage; (iii) Good solubility and film formation ability.

Recently, solution-processed blue PhOLEDs using small organic molecules and conjugated polymers as host materials have been reported.[18–22] For polymer host materials, impurities, especially the metal catalyst used in polymer synthesis would dramatically influence the performance of OLEDs. In contrast to the polymer hosts, the small molecule hosts can be easily synthesized and purified, but the configuration isn't rigid enough so that the material would be recrystallized easily. Dendrimer hosts combine the advantages of both the polymers and the small molecules. As far as we know, almost all of them incorporates a solubilizing group such as an alkyl or alkoxy chain to overcome their poor solubilities and film-forming abilities. It is well known that alkyl or alkoxy groups are electrically insulating, and introducing such groups into a molecule to affect its conductivity. Even worse, by attaching alkyl or alkoxy chains to a molecule, its glass-transition temperature (T_g) drops rapidly, which reduces morphological stability, especially when the molecule is small.[23,24] Thus it is very difficult for dendrimers to possess both morphological stability and

* Corresponding author. E-mail address: purse@smail.hust.edu.cn (Y. Qian).

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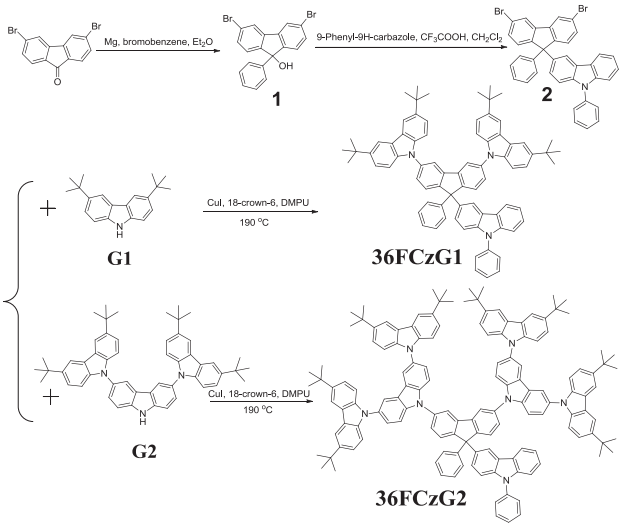
solution processability, especially for blue phosphorescent host materials whose effective conjugation length must be very short to encompass the phosphor emitter. Kakimoto et al. reported that solution-processed green PhOLEDs hosted by triphenylamine/benzimidazole hybrids, and a maximum current efficiency of 27.3 cd/A was realized by using *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$) as a guest, but this host material couldn't be used as the blue phosphorescent for the low triplet energy level.[25] Usluer et al. designed a series of compounds including the 2,7-disubstituted fluorene derivatives and carbazole dendrimers, a maximum current efficiency of 7.7 cd/A was harvested by using the Alq_3 as emitter layer and these compounds as hole transport layer (HTL).[26] Qiu et al. also reported a series of carbazole dendrimer hosts, a maximum current efficiency of 11.5 cd/A was achieved based on the deep-blue phosphorescent emitter FIr6, but the electron transporting material OXD-7 was also added for the double hosts.[27]

As we all know, 2,7-disubstituted fluorene is often used as common groups in the fluorescence emitters for both high quantum yield and excellent film formation ability, but it isn't suitable for blue PhOLED materials for the low triplet energy levels. Recently, 3,6-substituted fluorene derivatives were reported as the promising blue hosts for polymer PhOLEDs.[28] However, blue PhOLEDs using 3,6-substituted fluorene derivatives as dendrimer host materials have not been explored. In this study, we design and synthesis a series of 3,6-substituted fluorene derivatives including carbazole dendrimers 9,9′-(9-phenyl-9-(9-phenyl-9*H*-carbazol-3-yl)-9*H*-fluorene-3,6-diyl)bis(3,6-di-*tert*-butyl-9*H*-carbazole) (36FCzG1), 9,9′-(9-phenyl-9-(9-phenyl-9*H*-carbazol-3-yl)-9*H*-fluorene-3,6-diyl)bis(3,6-bis(3,6-di-*tert*-butyl-9*H*-fluoren-9-yl)-9*H*-carbazole) (36FCzG2), using a 3,6-substituted fluorene derivatives as the rigid core with two carbazole dendrimer groups linked to the core part through the 3,6-positions. Additionally, *tert*-butyl groups are introduced into the molecular structure to ensure good solubility and to form high-quality films. As a result, the newly synthesized compounds possess three important characteristics: (I) relative high triplet energy levels (2.80 eV) because of the non-conjugated linkage; (II) appropriate HOMO energy levels (−5.21 to −5.36 eV), thereby facilitating the transfer of holes from poly(3,4-ethyle-nedioxy-thiophene): poly(styrene-4-sulfonate) (PEDOT:PSS) to the emitting layer; (III) the high thermal stability of forming stable amorphous thin films as a result of the highly twisted configuration of the molecules. In our work, with the newly synthesized hosts and the blue phosphorescent emitter FIrpic, the device performance reaches a maximum efficiency value of 18.5 cd/A. This series of molecules exhibits excellent thermal and morphological stability, good film-forming ability, and solubility making them very promising candidates for optoelectronics.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes and chemical structures of 36FCzG1 and 36FCzG2, are shown in Scheme 1. The carbazole dendrimers G1 and G2, and 3,6-dibromo-9*H*-fluoren-9-one were synthesized according to a literature method.[28,29] 3,6-Dibromo-9-phenyl-9*H*-fluoren-9-ol (**1**) was synthesized by using Grignard Reagent with a high yield (70%). The following reaction of the compound **1** and *N*-phenylcarbazole losses a H_2O molecule through the strong acid to form 3-(3,6-dibromo-9-phenyl-9*H*-fluoren-9-yl)-9-phenyl-9*H*-carbazole (**2**), and the final products are prepared by the classic Ullmann reaction of the compound **2** and the compounds G1 and G2 in the presence of a catalytic amount of copper(I) iodide and 18-crown-6 in 1,3-dimethyltetra-hydropyrimidin-2(1*H*)-one (DMPU) with high yield 85% and 88%, respectively.



Scheme 1. Synthetic routes toward the compounds 36FCzG1 and 36FCzG2.

All compounds were purified using the silica gel column method, producing very pure powders. ^1H, ^{13}C NMR, mass spectrometry, and elemental analysis were employed to confirm the chemical structures of above mentioned compounds as described in the Experimental section. This result matches the 3D model of the two compounds optimized by the Amsterdam Density Functional 2009.01 (ADF2009.01) program, which is to be discussed in the following section.

3. Thermal analysis

For a better insight into the structure–property relationship, thermal properties were measured. Fig. 1 shows high thermal stability as determined by thermogravimetric analysis (TGA), and the decomposition temperature (T_d), corresponding to 5%-weight-loss, is 464 and 461 °C for the compounds 36FCzG1 and 36FCzG2, respectively. The T_g explored by differential scanning calorimetry (DSC) reached 161 °C for 36FCzG1, and 162 °C for 36FCzG2, compared with *N*,*N*′-di(naphthalen-1-yl)-*N*,*N*′-diphenylbiphenyl-4,4′-diamine (NPB) (T_g=98 °C), a commonly used material in OLEDs, our compounds show greatly improved thermal resistance.[30] It is obviously related to their increased molecular sizes by the introduction of *tert*-butyl groups in their structures.

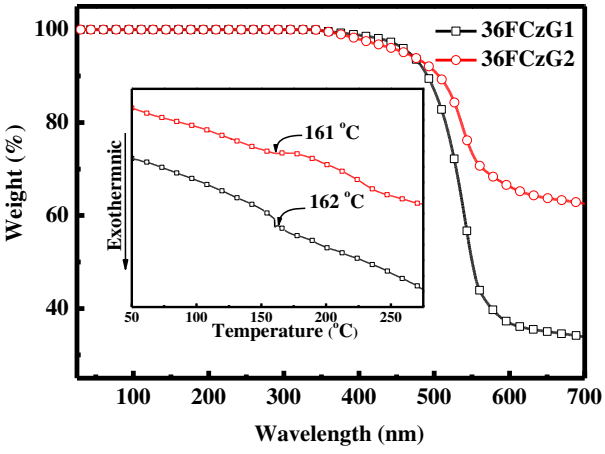


Fig. 1. TGA traces of 36FCzG1 and 36FCzG2 recorded at a heating rate of 10 °C/min. Inset: DSC measurement recorded at a heating rate of 10 °C/min.