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Novel fluorene/carbazole hybrids with steric bulk as host materials for blue organic electrophosphorescent devices

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Abstract—The problem of self-quenching in organic electrophosphorescence devices has been extensively studied and partially solved by using sterically hindered spacers in phosphorescent dopants. This paper attempts to address this problem by using sterically hindered host materials. Novel fluorene/carbazole hybrids with *tert*-butyl substitutions, namely 9,9-bis[4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl]fluorene (TBCPF) and 9,9-bis[4-(carbazol-9-yl)phenyl]-2,7-di-*tert*-butylfluorene (CPTBF), have been synthesized and characterized. The compounds exhibit not only high triplet energy (>2.8 eV), but also high glass transition temperature (>160 °C) and thermal stability. The substitution of inert *tert*-butyl groups to the carbazole/fluorene rings of these host molecules has a remarkable effect on the corresponding properties of the host materials, i.e. enhancing the thermal and electrochemical stability, weakening the intermolecular packing, and tuning the solid-state emission. Blue electrophosphorescent devices with enhanced performance were prepared by utilizing the sterically hindered host materials. The devices based on the four *tert*-butyl substituted material TBCPF exhibit unusual tolerance of high dopant concentration up to 20% and marked reduction of efficiency roll-off at higher current, indicating significant suppression of self-quenching effect in organic electrophosphorescent devices by the substitution of steric bulks.

1. Introduction

Organic light-emitting diodes (OLEDs) have been the focus of both academic research and industrial interest because of their potential application in the flat-panel displays and solid lighting resources in the past two decades. In particular, intensive study has been dedicated to the development of transitional metal complex based phosphorescent OLED (PHOLED) owing to its potential to achieve an internal quantum efficiency of 100% by harvesting both singlet and triplet excitons.[1] Typically, the organometallic phosphorescent dyes are doped as the guest into an organic conductive host matrix to reduce the quenching stemmed from the relative long lifetime of triplet excitons. The triplet energy (E_T) of the host material must be higher than that of the guest in order to favor an exothermic energy transfer and to confine the excitons within the emitting guest molecules.[2] Compared to the very efficient green and red devices,[3] blue PHOLEDs are especially challenging since the difficulty in finding suitable host material with an E_T exceeding that of the commonly used blue phosphorescent dyes, such as bis[(4,6-difluorophenyl)pyridinato-N,C^2]iridium(III)picolinate (FIrpic, E_T=2.62 eV). A few carbazole derivatives[2b,4] and silicon containing compounds[5] can meet the requirement for high energy, but suffer from thermal and morphological instability as a consequence of their extremely limited π conjugation. In our recent work, we designed and synthesized a fluorene/carbazole hybrid 9,9-bis[4-(9-carbazolyl)phenyl]fluorene (CPF),[6] which we believe to be one of the few triplet host materials that successfully combine both large triplet energy and pronounced morphological stability.[7]

In addition to the efficient energy transfer from the host to the guest and the thermal stability of host materials, triplet–triplet annihilation and self-quenching effect are factors of equal importance to the performance of PHOLEDs. Although high efficiency could be achieved, most phosphorescent devices exhibit significant efficiency roll-off on raising either the doping concentration or the operating current density, which is generally attributed to self-quenching of triplet excitons originated from strong bimolecular interaction of phosphorescent dyes.[1] This problem has been addressed through the introduction of sterically hindered spacers to the phosphorescent dye in a few reports.[8] In this work, we proved that using sterically hindered host material is also an efficient way to overcome the self-quenching effect in blue PHOLEDs. By introducing bulky *tert*-butyl groups on

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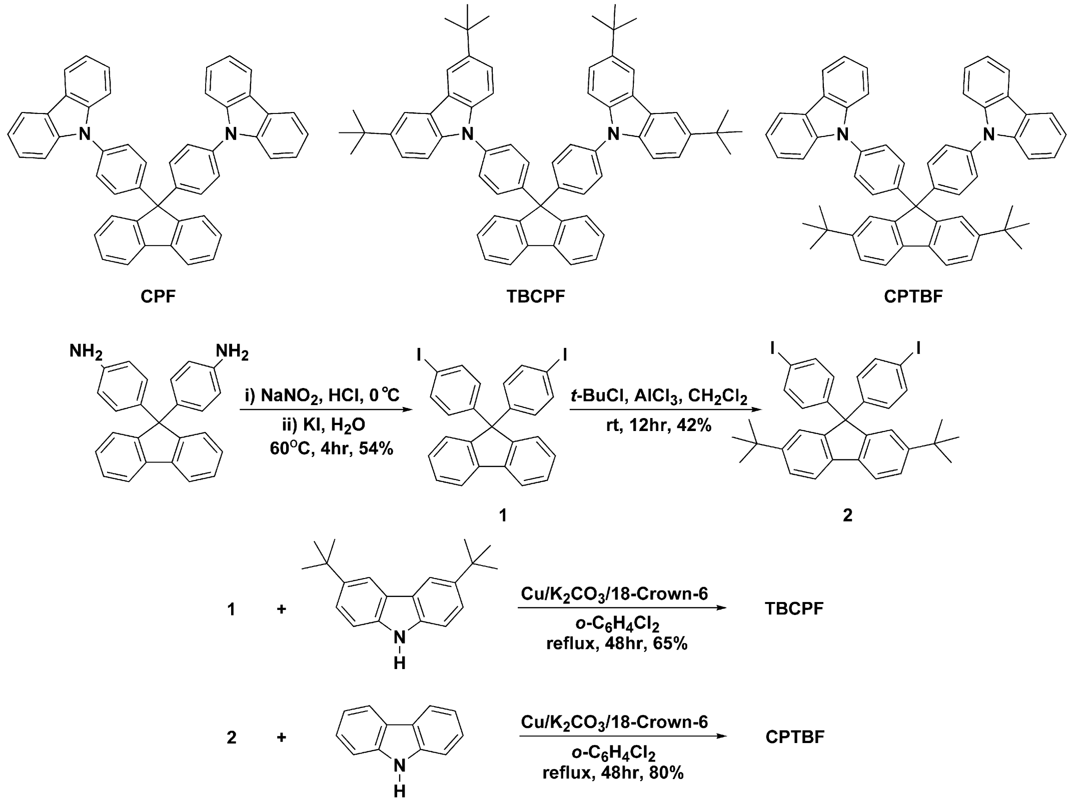
different segments of our previously reported CPF, which possesses both excellent thermal stability and high triplet energy, we synthesized two novel hosts, namely 9,9-bis-[4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl]fluorene (TBCPF) and 9,9-bis[4-(carbazol-9-yl)phenyl]-2,7-di-*tert*-butylfluorene (CPTBF). The compounds were prepared efficiently via copper catalyzed C–N coupling reaction. Several reports of oligomeric and polymeric fluorene and carbazole structures with *tert*-butyl groups have also been reported, which otherwise focused on the effect of molecular aggregation and spectral stability.[9] Herein, a systematic comparative study concerning their physical and electroluminescent properties has been carried out and blue PHOLED devices based on the novel hosts have been demonstrated. It was found that the substitution of inert *tert*-butyl groups to the fluorene/carbazole rings of these host molecules not only affects the photophysical properties but also significantly reduces the self-quenching in blue phosphorescent OLED using the hybrids as the host.

2. Results and discussion

2.1. Synthesis and X-ray crystal structure

The chemical structures of the fluorene/carbazole hybrids and the syntheses of TBCPF and CPTBF are depicted in Scheme 1. 9,9-Bis(4-iodophenyl)fluorene (**1**) was prepared from diazotization of 9,9-bis(4-aminophenyl)fluorene followed by treatment with the water solution of potassium iodide. Compound **1** was further converted to 9,9-bis(4-iodophenyl)-2,7-di-*tert*-butylfluorene (**2**) through Friedel–Crafts alkylation. Finally, Ullman C–N coupling reaction of **1** or **2** with corresponding carbazole derivative using copper/18-crown-6 as the catalyst and potassium carbonate as the base afforded the target fluorene/carbazole hybrids in moderate to good yields. The *tert*-butyl substituted compounds are well soluble in common organic solvents such as CH_2Cl_2 and ethyl acetate so that they can be conveniently purified by column chromatography. The compounds were fully characterized by ^{1}H NMR spectroscopy, mass spectroscopy, and elementary analyses.

Single crystals of CPF and TBCPF suitable for X-ray crystallography were obtained via gradient-temperature sublimation. The crystal data are listed in Table 1. The ORTEP presentations with 35% probability ellipsoids and the packing views of the two compounds are revealed in Figures 1 and 2, respectively. In both CPF and TBCPF crystals, the two phenyl-carbazole moieties are orthogonally arranged and connected to the 9-position of the fluorene bridge and each carbazole ring forms a large torsion angle (85.3° for CPF and 71.8° for TBCPF) with the adjacent phenyl ring, indicating non-planarity and rigidity of the molecules. Notice that the two compounds exhibit large different packing motif in spite of their similar 3D molecular configurations. In CPF, each two adjacent molecules stack closely through short edge-to-face C–H$\cdots\pi$ interaction (2.68 Å) between the 3-position of the fluorene ring and the carbazole moiety, whereas in TBCPF, where the carbazole ring is attached with sterically hindered *tert*-butyl groups, such fluorene-to-carbazole contact becomes unfavorable and another face-to-face $\pi\cdots\pi$ interaction (3.59 Å) occurs between two neighboring fluorene moieties. This $\pi\cdots\pi$



Scheme 1. Chemical structures of the fluorene/carbazole hybrids and synthetic routes to TBCPF and CPTBF.