REVIEW PAPER

Carbazole based bipolar host materials for organic electroluminescent devices -recent advances

Abdul Bais[1] and Zaman Ashraf[1]*

Abstract Organic light-emitting diode (OLED) is an emerging technology for flat panel displays and lighting applications because they are highly efficient, ultrathin, lightweight, flexible and exhibit multicolor emission. A typical OLED is constructed by sandwiching an emissive layer between anode and cathode surrounded by additional layers for improved performance. These layers can employ host material doped with suitable guest material to accomplish the required effect of the layers such as hole transport effect, electron transport effect, or an emissive effect. The resulting guest-host system for phosphor-based OLEDs gives better performance over the traditional neat phosphor films because of low quenching concentration and triplet-triplet annihilation. Bipolar host materials containing both electron-donating and electron-accepting moieties in the same molecule provides balance charge carrier mobility which results in higher quantum efficiency, pure emission of luminance layer, and high stability. The selection of appropriate host material is a challenging task as the non-emissive triplet excited state of host material must ordinarily be higher than the emissive triplet excited state of the guest phosphor. Carbazole based bipolar molecules are more important as host materials for OLEDs due to advantageous properties of cabazole group to form stable radical cations (holes) along with high charge carrier mobilities. This mini review is a selection from recent advances in the design and synthesis of carbazole based bipolar host materials for OLEDs.

Keywords: Organic light-emitting diode (OLED), Carbazole, Bipolar host material

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INTRODUCTION

Organic electroluminescence (i.e. light production by electrical excitation of an organic compound) based technology is evolved as an essential contestant to liquid crystal display (Pope et al., 1963). The principal work of Tang and VanSlyke brought about overall activity in various research groups making progress in the field of device science, device fabrication and also in the fields of physical and material science of OLEDs (C. W. Tang & VanSlyke, 1987). The enormous enthusiasm for OLEDs and the devices produced from them is particularly determined by technological viewpoints, for example, low costs, simplicity of fabrication (Shuai et al., 2000; Wohlgenannt et al., 2001; Köhler et al., 2002; Blom et al., 2005; Weiner, 2005) the likelihood of producing large sized and flexible displays, their lighting applications and the range of organic materials showing emission wavelengths from near infrared to the ultraviolet.

A typical OLED is constructed by sandwiching an emissive layer between anode and cathode surrounded by additional layers for improved performance. These layers can employ host material doped with suitable guest material to accomplish the required effect of the layers such as hole transport effect, electron transport effect, or an emissive effect. Heavy-metal complexes showing phosphorescence are frequently doped into appropriate host material to devise exceedingly proficient electrophosphorescence and detrimental impacts, for example, aggregation quenching and triplet-triplet destruction of phosphors can be decreased. Hence the host material and dopant synthesis are both essential for the formation of effective PhOLEDs (Su et al., 2008).

The selection of appropriate host material is a challenging task as the non-emissive triplet excited state of host material must ordinarily be higher than the emissive triplet excited state of the guest phosphor. The level of difficulties is added by the fact that as the emissive wavelength of guest material gets shorter, the emissive triplet excited state becomes higher. Most of the host materials are better hole carrier, while at the same time, they provide comparatively little electron transport and electron injection into the emissive layer (Thoms, 2003).

Four types of host materials are recognized i.e., hole transport type, electron transport type, dipolar transport host materials and the host material based on pure-hydrocarbon compounds. Among these bipolar molecules containing electron-donating and electron-accepting moieties can accomplish higher quantum efficiency than others as a result of carrier balance property (Tao et al., 2008). Carbazole based bipolar molecules have drawn much attention as OLEDs host materials because of the advantageous properties of cabazole group to form stable radical cations (holes) from Carbazolyl groups, comparatively high charge carrier mobilities, high thermal and photochemical stability, substitution ease and its accessibility as cheap starting material (Partridge, 1983).

The advantageous properties possess by carbazole based bipolar material have triggered immense research activity in this field with aim to synthesize better material to meet the future technological demands. This mini review is aims to highlight recent advances in material design and synthesis of carbazole based bipolar host material for electroluminescent devices application.

Carbazole–pyridine based material

Tang et al. (2015) designed a single step methodology for carbazole–pyridine hybrid molecules (Fig. 1) starting from several fluorine substituted pyridines and carbazole to produce exceedingly proficient host materials for blue phosphorescent. Pyridine derivative having bi-, tri- and tetra- carbazoles were claimed to display expanded temperature stabilities and likewise high triplet energy levels of ~3.0 eV. Maximal current productivities ranging from 32–42 cd A^{-1} are reported to achieved by using them as host materials for blue phosphorescent OLEDs (C. Tang et al., 2015).

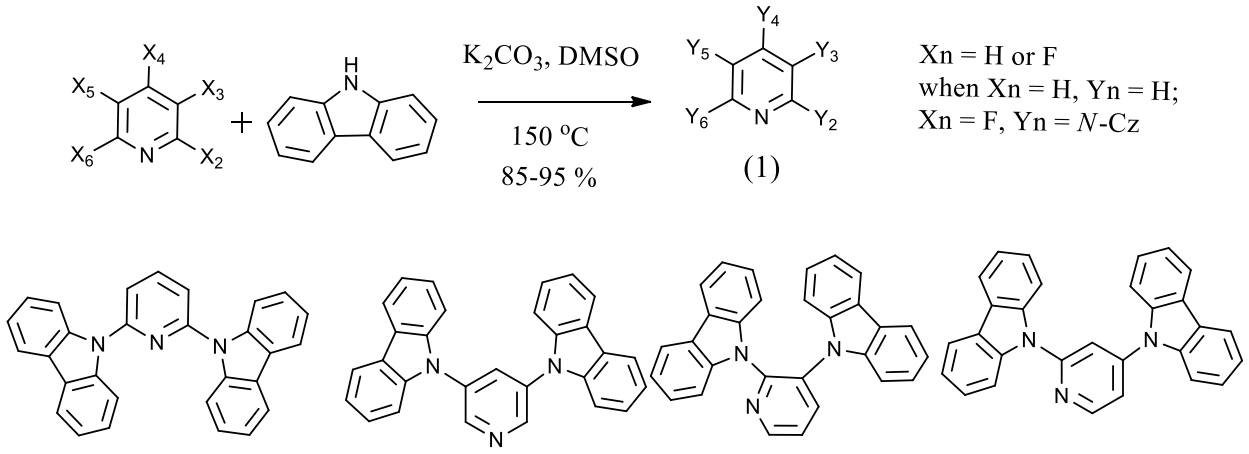


Fig. 1 Scheme for different carbazole/pyridine hybrid compounds.

Carbazole-pyrene based materials

Carbazole substituted pyrene based electroluminescent organic semiconductors (Fig. 2) for OLED devices were invented by (Salunke et al., 2016). The reaction involves conversion of 1,3,6,8-tetrabromo pyrene into its corresponding tetra-substituted carbazole derivatives by employing the Suzuki reaction. These newly devised materials were investigated for their utilization as active light-emitting layer in OLEDs which produces blue and green emission with tremendous device performance. Maximum brightness at about 2500 cd m^{-2} was reported by compound (2a) and was asserted to show t[he power efficiency of 1.5 lm W^{-1}.

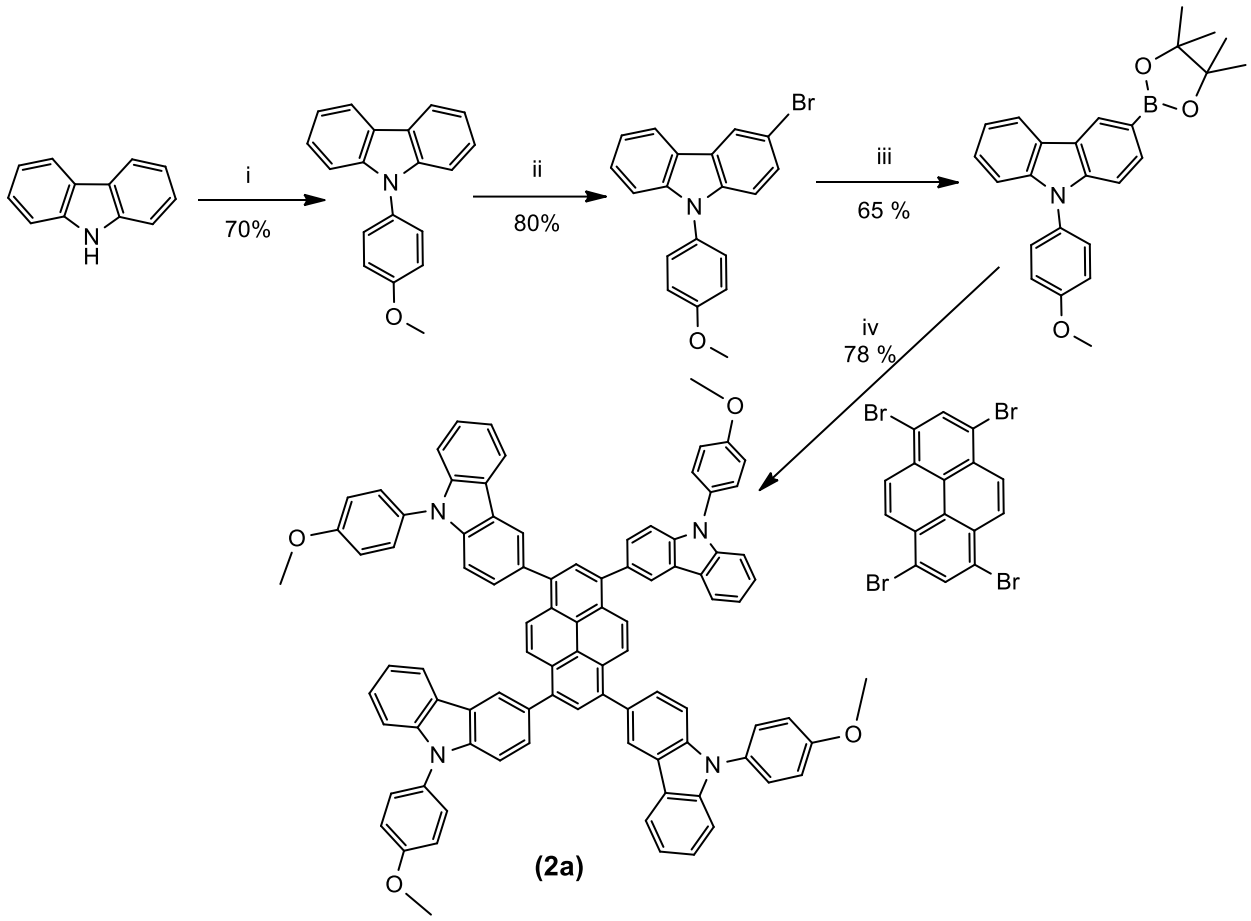


Fig. 2 Scheme for various carbazole/pyrene based hybrid compounds

Pyrene-functionalized carbazole derivatives (Fig. 3) as non-doped blue emitters for highly efficient blue organic light-emitting diodes OLEDs were devised by Kotchapradist et al. (2013) The substitution of various pyrenes on the carbazole ring causes improved stability and solubility while retaining the emissive ability of pyrene in solid (Kotchapradist et al., 2013). These materials reveal high solution fluorescence quantum efficiencies (up to 94%) and form morphologically stable amorphous thin films with T_g as high as 170 °C.

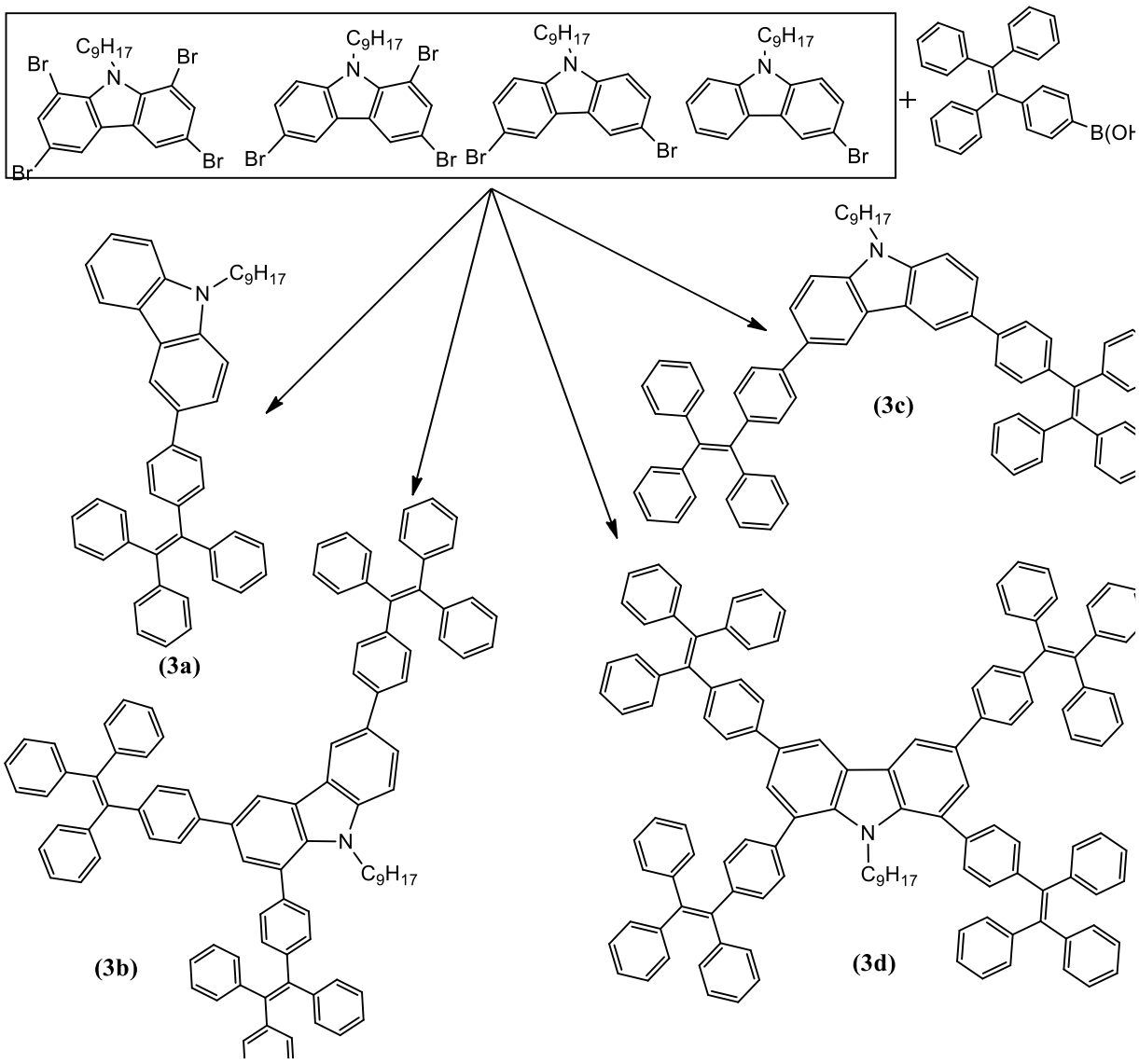


Fig. 3 Synthesis of pyrene substituted carbazoles

Oligofluorene-cored carbazole based material

Moonsin et al. (2014) reported solution-processable oligofluorene-based dendrimers (G*n*F*m*, *n* =1-2, *m* = 2-3) by utilizing a number of difunctional oligofluorene-centered carbazole dendrimers containing third generation carbazole dendrons as end-caps and evaluated them as nondoped solution-processed blue-light emitters and hole transporters for organic light-emitting diodes (OLEDs) (Moonsin et al., 2014). These novel material displays a prominent dark-blue fluorescence with solution fluorescence quantum yields (Φ_F)of about 0.91–0.99 and makes morphologically stable amorphous thin films with glass transition temperatures as high as 273 °C.

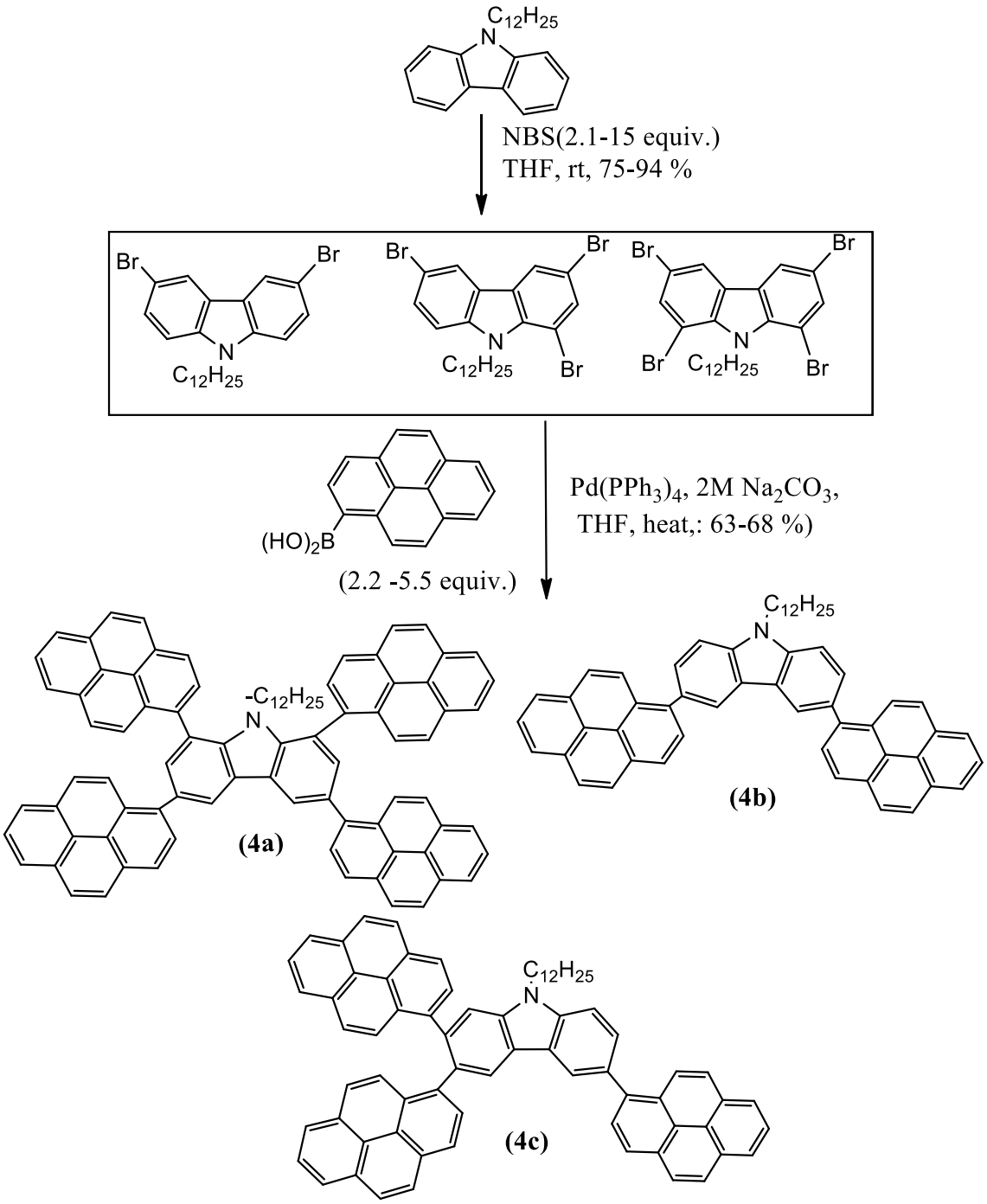
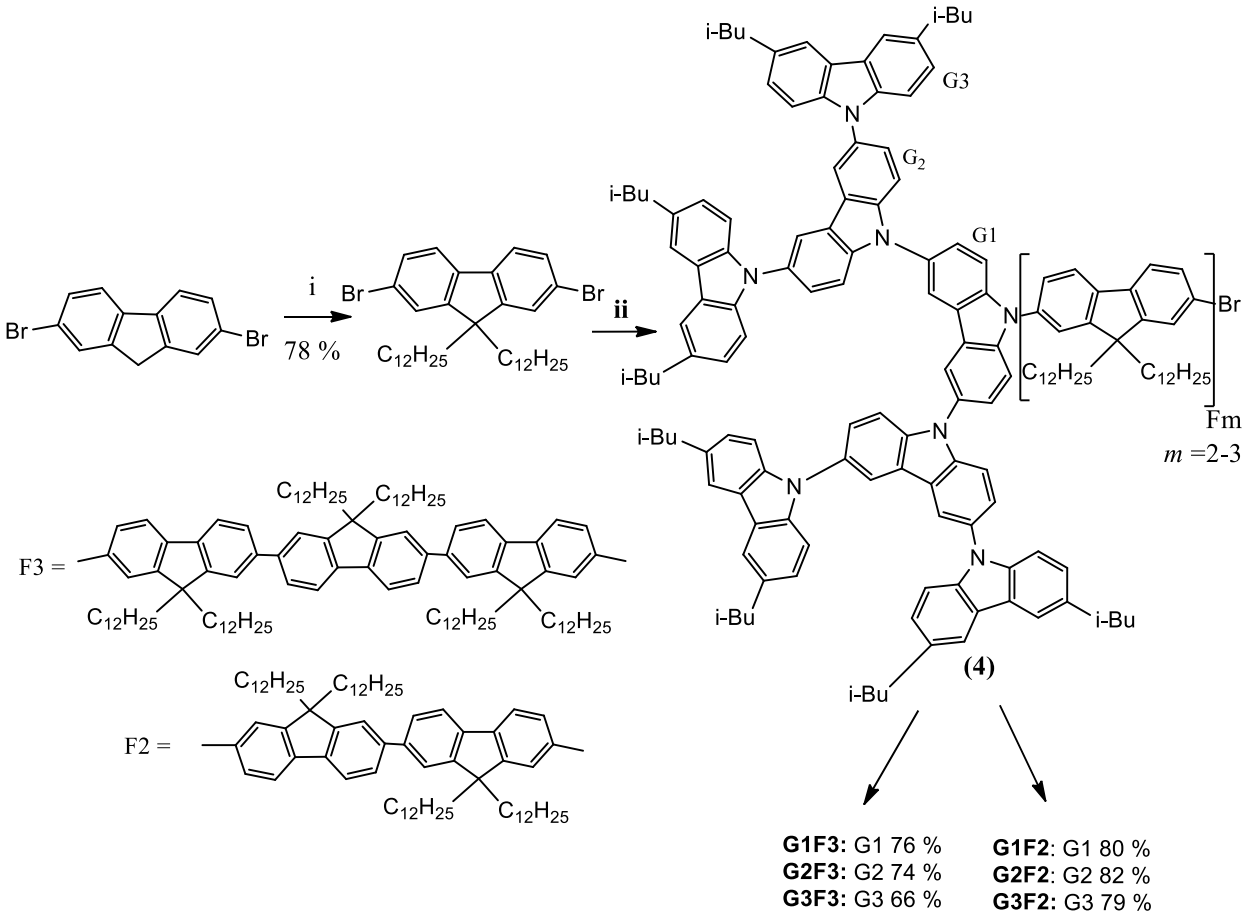


Fig. 4 Synthesis of oligofluorene-cored/carbazole based hybrid material

Carbazole-tetraphenylethene based materials

Gong et al. (2014) reported a controlled bromination of carbazole (Cz) for subsequent mono, di, tri and tetrabromocarbazoles synthesis utilizing Suzuki cross-coupling to form various carbazole-tetraphenylethene (TPE) **(5a-c)** derivatives having different quantities of peripheral TPE groups (Gong et al., 2014). All these Cz-TPEs in THF radiate dark blue fluorescence after UV light with more TPE groups indicating fluorescence upgrade at moderate level. The maximum blue shift reduces and become non-emissive when exposed to UV

illumination for 1.5 hr in nearly all Cz-TPEs thin films (40 nm). The author attributed these optical properties to photo-induced non-reversible changes of TPE to diphenylphenanthrene derivatives.



(i) n-CNBr, DMSO
(ii) GnNH, ± trans-1,2-diaminocyclohexane,CuI, $K_{12}H_{25}Br$, 50% NaOH, n-Bu_3PO_4,toluene, heat
(iii) hexabutylditin, Pd(PPh_3), toluene, heat
(iv) 9,9-dihexyl?uorene-2,7-diboronic acid Pd(PPh_3)$_4$, 2M Na_2CO_3, THF, heat

Fig. 5 Synthesis of carbazole/tetraphenylethene based hybrid material

Carbazole-benzimadazole based material

Two isomeric bipolar molecules (6a & 6b) made from two benzimidazoles as peripheral acceptors and carbazole as core donor and are bridged by phenylene groups with different connection topologies have been reported by Shu-Hua Chou et al. The authors observe the physical properties to be quietly administered by the linkage topology, counting promising properties for the two isomers to serve in as general bipolar PhOLEDs with a common device configuration (Chou et al., 2013).

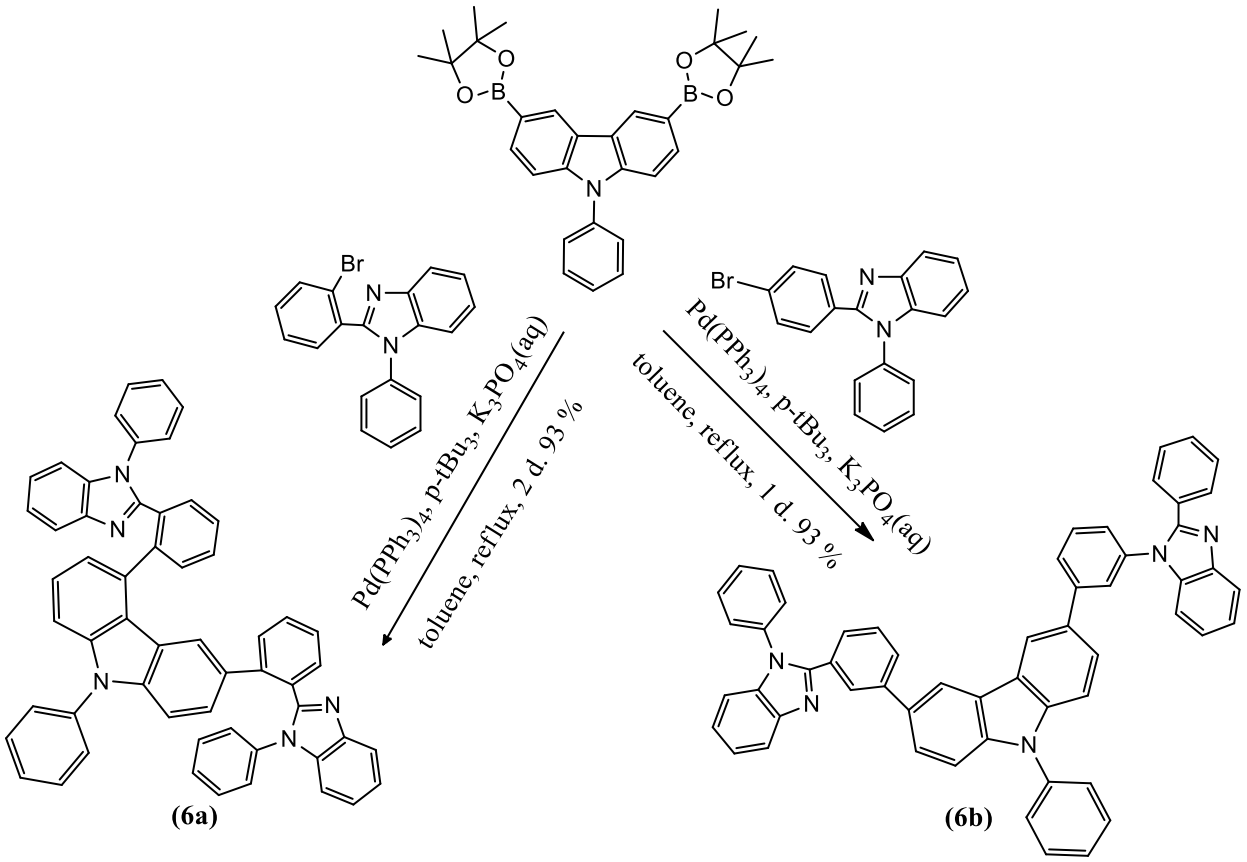


Fig. 6 Synthesis of Carbazole-benzimadazole based material

***N*-Alkylsubstituted carbazole based material**

Gong et al. (2012) reported tri-and tetra-bromination of carbazole (Fig. 7) for subsequent synthesis of novel carbazole oligomers **(Cz a-d)** with substitution at 1-and 8-position (Gong et al., 2012). The glass transition temperature was found to increase as the carbazole central core is enlarged (0 ^{o}C to 54 ^{o}C) with all oligomers shows excellent thermal stability with high thermal decomposition temperatures at about 442 ^{o}C to 494 ^{o}C. These carbazole materials were found to emanate dark blue photoluminescence ranging from 416 to 432 nm in the solid-state.

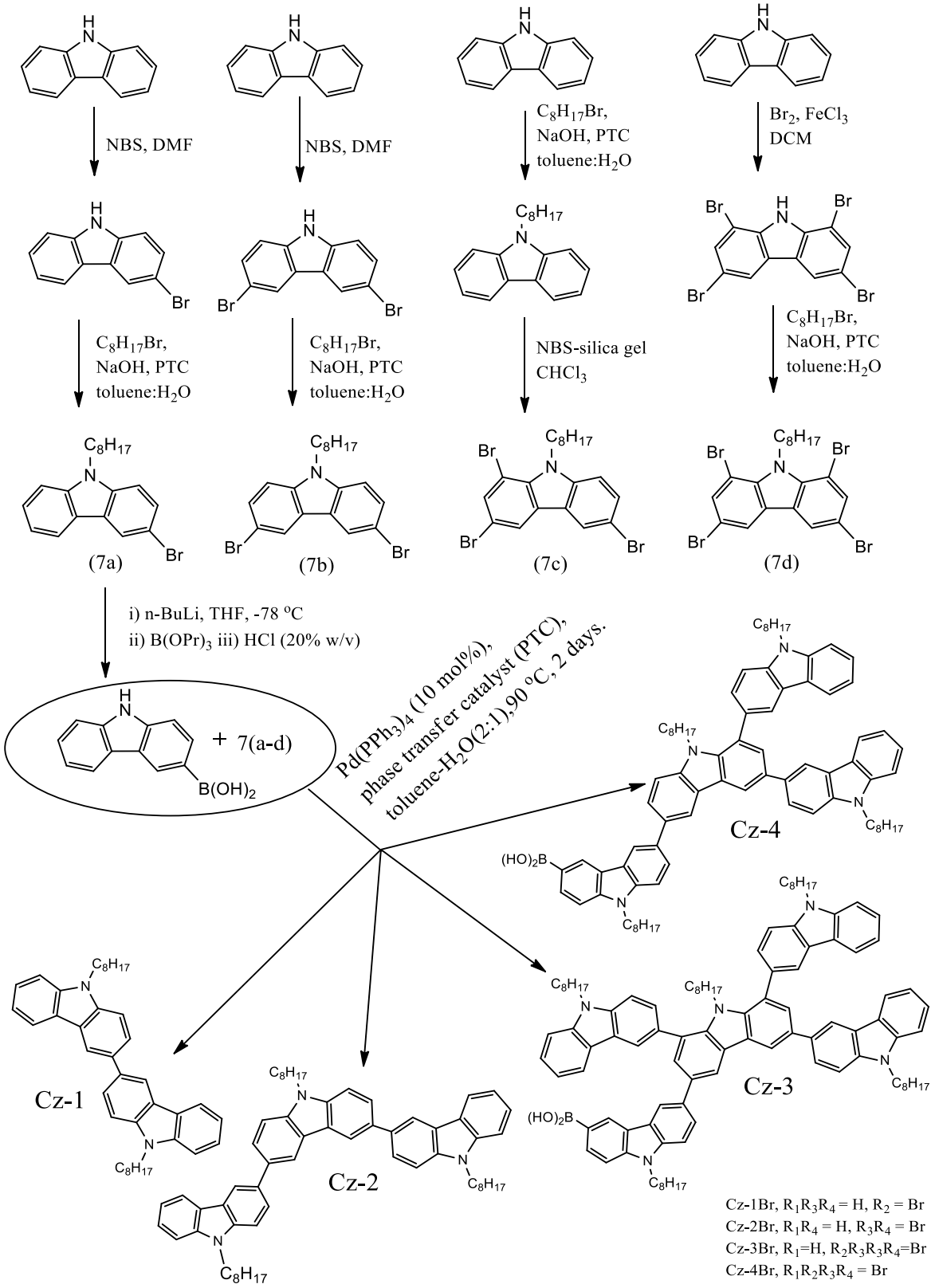


Fig. 7 N-alkylsubstituted carbazole based material

Carbazole-triazine based materials

Hu et al. (2017) devised and synthesized two novel triazine-carbazole based host-material **(BFTC & BTTC)** to fabricate green phosphorescent organic light emitting devices (PhOLEDs). These two compounds were asserted to demonstrate exceptional physical properties and high thermal stabilities with sensible HOMO–LUMO energy levels. Among these two material, BTTC based device perform exceptional electroluminescence performance with remarkable current efficiency, higher power efficiency and external quantum efficiency of 63.5 cd A^{-1}, 52.4 lm W^{-1} and 21.5 %, respectively thus proving BTTC as promising material for green PhOLEDs (Hu et al., 2017).

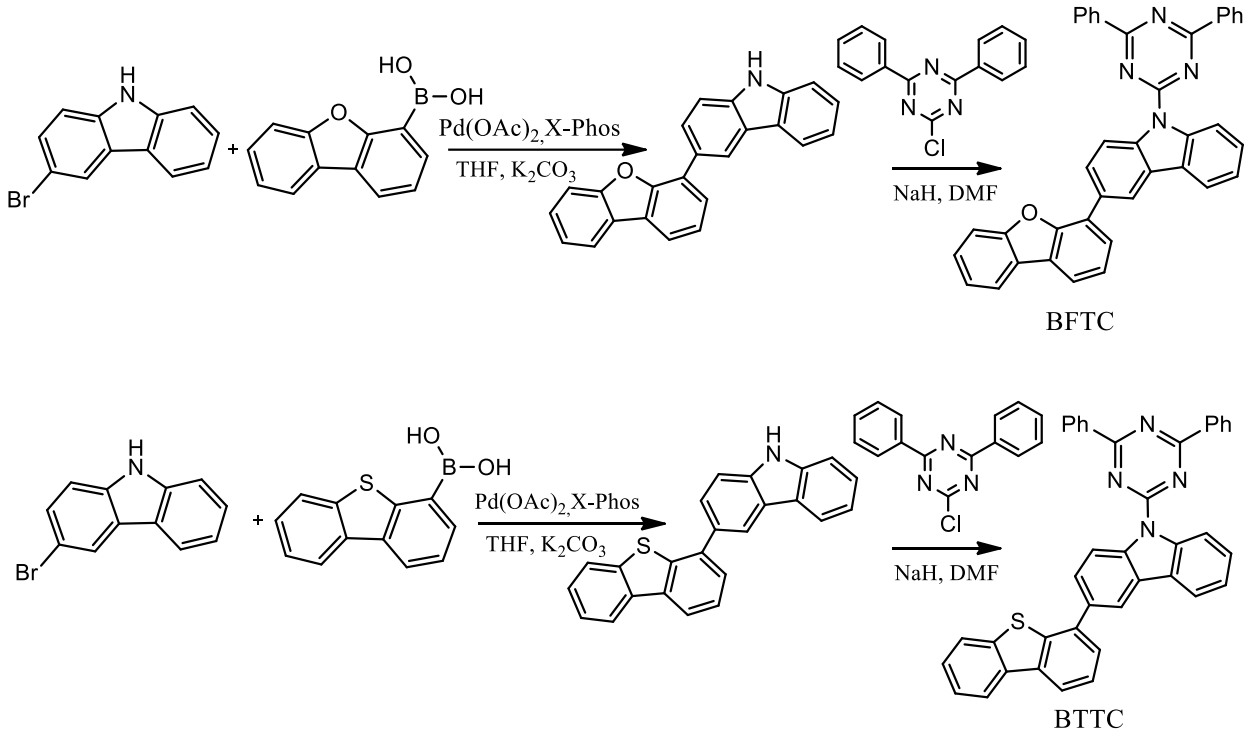


Fig. 8 Synthetic scheme for carbazole-triazine based host material

CONCLUSION

Organic light emitting diodes (OLEDs) attract significant consideration because of their superior device properties which are superbly suitable for flat panel display and solid state lightening. However, OLEDs at present is considered as non-competitive to liquid crystal display (LCDs) because of their short life span and as well as a low efficiency of blue emitting materials. Hence, materials for blue phosphorescent organic light-emitting diodes (PhOLEDs) have turned exceptionally important to overcome such issues. Carbazole derivatives containing peripheral electron donating functionalities are found to be a good host system for guest emitter having short emission wavelength. These compounds bring significantly large band gap along with sufficiently high T1 to S1 energy states which permit emission from the guest well into the blue spectrum. Additionally they are less inclined to crystallization which makes it easy for them to adopt robust morphology. Accordingly, hole and electron injection gets improved throughout the emissive layer by the combination of both electron donating and accepting moieties on host molecular structure.

Author Contribution Statement Zaman Ashraf conceived the idea. Zaman Ashraf and Abdul Bais wrote the manuscript.

Conflict of Interest The authors declare that there is no conflict of interest regarding the publication of this article.

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