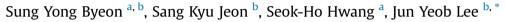
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# Carbazole-carboline core as a backbone structure of high triplet energy host materials



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## 1. Introduction

The carbazole moiety has been widely used as a building unit of triplet host materials because of high triplet energy of 3.02 eV, good hole transport properties, good thermal stability and facile modification by coupling reaction with various functional groups [1–12]. In particular, the high triplet energy and expandability of the molecular structure make the carbazole moiety attractive as the building block of high triplet energy host materials for blue phosphorescent organic light-emitting diodes (PHOLEDs).

The high triplet energy of the carbazole moiety can be maintained by introducing substituents at the 3-,6-positions or 9position of carbazole to minimize the extension of conjugation. Triplet host materials possessing a triplet energy above 2.80 eV could be easily realized by substituting various functional groups to control the charge transport properties of the host materials. Generally, electron deficient moieties were selected as the functional group to compensate for the poor electron transport properties of the carbazole moiety [7–12]. The other option to keep the high triplet energy of the carbazole moiety was to link two carbazole moieties via 3-position of carbazole to produce a bicarbazole

# ABSTRACT

A carbazole-carboline core was developed as a backbone structure of high triplet energy host materials and three derivatives of the carbazole-carboline core were synthesized. The carbazole and carboline units were linked via the 3-position of the carbazole and the 6-position of the carboline, and the carbazole-carboline core was modified with cyanophenyl, phenyl and 9-carbazolylphenyl moieties to control the charge transport properties of the host materials. Triplet energy of the carbazole-carboline core derived host materials were above 2.85 eV irrespective of the substituent of the carbazolecarboline core. The new materials were tested as the host materials for blue phosphorescent organic light-emitting diodes and the quantum efficiency of the blue devices reached 23.4%.

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moiety [13–19]. The bicarbazole moiety could limit the reduction of the triplet energy and show high triplet energy above 2.80 eV. Typically, the bicarbazole core was also modified with electron deficient functional groups for charge balance in the emitting layer because of the strong hole transport properties of the bicarbazole core [13–15]. However, the number of electron deficient units useful for the modification of carbazole or bicarbazole is rather limited because of low triplet energy of the electron deficient moieties. Therefore, it is necessary to develop a carbazole derived bipolar core structure for high triplet energy and bipolar charge transport properties.

Recently, carboline has been reported as a weak electron transport type moiety with a high triplet energy and was effective to improve the quantum efficiency of blue PHOLEDs because of better charge balance in the emitting layer [20-26]. However, not many derivatives of carboline moiety were synthesized in spite of versatility of the carboline moiety for substitution. Only the nitrogen unit at the 9-position of the carboline was modified with various functional groups although the carboline can be modified at the 6-position by halogenation. Therefore, it is very interesting to develop carboline derivatives with other functional units at the 6-position of carboline.

In this work, a carbazole-carboline core was developed as a high triplet energy backbone structure for blue triplet host materials. Functionalization of carboline using an electrophilic halogenation





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and preparation of the carbazole-carboline core were studied and three high triplet energy host materials were synthesized from the carbazole-carboline core. A high triplet energy above 2.80 eV, bipolar charge transport properties and high quantum efficiency above 20% were demonstrated in the blue PHOLEDs using the carbazole-carboline based host materials.

## 2. Experimental

## 2.1. General information

Potassium iodide, potassium iodate, copper iodide,  $(\pm)$ -trans-1,2diaminocyclohexane, 3-bromobenzonitrile and bromobenezene were purchased from Aldrich Chem. Co. (9-Phenyl-9H-carbazol-3yl)boronic acid, tetrakis(triphenylphosphane) palladium(0) and 9-(3-bromophenyl)-9H-carbazole were provided from P&H tech Co. Acetic acid, sodium bicarbonate, potassium carbonate, and potassium phosphate tribasic from Duksan Sci. Co. was used without further purification. Tetrahydrofuran (Duksan Sci. Co.) was distilled with calcium hydride and sodium. Chemical analysis of the synthesized materials was carried out according to the method described in other work [25]. The energy levels were measured with a cyclic voltammetry (CV) using Ferrocene as a standard material. Oxidation and reduction scans were carried out separately, and oxidation/reduction potentials were determined from the onset voltage of the oxidation/reduction scans. Acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration was used to gather the CV data. Ag and Pt were used as the reference electrode and counter electrode, respectively and carbon electrode was a working electrode.

#### 2.2. Synthesis

The route used to synthesis the CzCbCN, CzCbPh and CzCbCz compounds is described in Scheme 1.

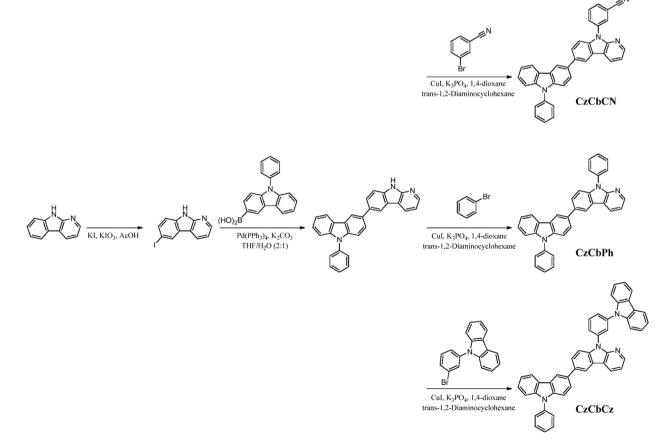
### 2.2.1. 6-Iodo-9H-pyrido[2,3-b]indole

9*H*-pyrido[2,3-*b*]indole (7.00 g, 4.16 mmol) and potassium iodide (4.56 g, 2.75 mmol) were dissolved in acetic acid. The mixture was stirred and refluxed for 1 h under a nitrogen atmosphere. Potassium iodate (4.45 g, 2.08 mmol) was slowly added into the solution and refluxed for another 2 h. The solution was cooled down and neutralized with sodium bicarbonate aqueous solution. The white solid was obtained after the precipitate was filtered and washed with distilled water and n-hexane.

Yield 85% (10.40 g),  $T_m$  280 °C,  $^1H$  NMR (400 MHz, DMSO):  $\delta$  11.95 (s, 1H), 8.58–8.43 (m, 3H), 7.71 (d, 1H, J = 8.8 Hz), 7.35 (d, 1H, J = 8.8 Hz), 7.22 (t, 1H, J = 6.4 Hz),  $^{13}$ C NMR (125 MHz, DMSO):  $\delta$  151.66, 146.77, 137.82, 134.35, 129.53, 128.92, 122.99, 115.30, 113.92, 113.57, 82.12 MS (HR) m/z 294.97 [(M + H)<sup>+</sup>].

#### 2.2.2. 6-(9-Phenyl-9H-carbazol-3-yl)-9H-pyrido[2,3-b]indole

6-lodo-9*H*-pyrido[2,3-*b*]indole (1.50 g, 0.51 mmol) and (9phenyl-9*H*-carbazol-3-yl)boronic acid(1.90 g, 0.66 mmol) were dissolved in THF and 2 M potassium carbonate aqueous solution was poured into the mixture. Tetrakis(triphenylphosphane)palladium(0) (0.18 g, 0.02 mmol) was added into the solution and refluxed for 36 h. The reaction was extracted with ethyl acetate and distilled water, and organic layer was dehydrated with magnesium sulfate. White solid was taken by purification with column chromatography using silica gel with ethyl acetate and n-hexane (1:2).



Scheme 1. Synthetic scheme of CzCbCN, CzCbPh and CzCbCz.

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