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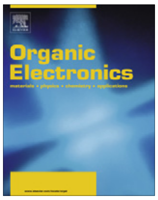

# Synthesis of 2- and 4-substituted carbazole derivatives and correlation of substitution position with photophysical properties and device performances of host materials

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ABSTRACT

A synthetic method to synthesize 4-substituted carbazole derivative was developed to study the effect of substitution position of carbazole on photophysical properties and device performances of host materials. Two high triplet energy host materials with substituents at 2- and 4-positions of carbazole were synthesized by the new synthetic approach. Substitution of electron withdrawing group at 2-position was better than the substitution at 4-position to stabilize energy levels and to improve hole transport properties. However, high glass transition temperature and high quantum efficiency were obtained in the carbazole based host material with substituent at 4-position.

## 1. Introduction

A carbazole unit has been widely used as a building block of host and charge transport materials for phosphorescent organic light-emitting diodes (PHOLEDs) because of good hole transport properties and high triplet energy [1–5]. In particular, the high triplet energy of carbazole (3.02 eV) enabled the development of various high triplet energy host and hole transport materials for PHOLEDs.

In general, 9H-carbazole was used as a basic unit for carbazole based organic materials for PHOLEDs. 9H-carbazole could be easily modified at 9-position using various aromatic units by a simple amination reaction. It could also be substituted with a lot of aromatic moieties or functional groups at 3- and 6-positions [2,6,7]. The most common reaction of 9H-carbazole was the bromination of carbazole at 3- and 6-positions, yielding 3-bromo-9H-carbazole or 3,6-dibromo-9H-carbazole [8,9]. The two carbazole intermediates have been widely used as the building units of host and hole transport materials. In addition to 3-bromo-9H-carbazole and 3,6-dibromo-9H-carbazole, 2,7-dibromo-9H-carbazole was also used as the intermediate of organic materials for PHOLEDs and organic solar cells [10–19].

As 2,7-dibromo-9H-carbazole could not be prepared by direct bromination of 9H-carbazole, it was synthesized by ring closing reaction from brominated aromatic intermediate [20,21]. It was reported that 2,7-substitution reduced the bandgap and triplet energy of host materials due to extended conjugation through para linkage. Several compounds were synthesized from 2,7,-dibromo-9H-carbazole. However, there was no work reporting 4-bromo-9H-carbazole as the intermediate of host materials and no material with a substituent at 4-position of carbazole was reported. Therefore, it was difficult to fully correlate the substitution position of carbazole with photophysical properties and device performances of host materials. The synthesis of carbazole derivative with substituents at 4-position of carbazole may enable the study of effect of substitution position of carbazole on photophysical properties and device performances of carbazole derivatives.

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In this work, a synthetic method to prepare 4-bromo-9H-carbazole intermediate was developed and a host material derived from the intermediate, phenylbis(9-phenyl-9H-carbazol-2-yl)phosphine oxide (4DCPO), was synthesized. In addition, a host material derived from 2-bromo-9H-carbazole, phenylbis(9-phenyl-9H-carbazol-2-yl)phosphine oxide (2DCPO), was also synthesized to study the effect of substitution position of carbazole on the photophysical properties and device performances of host materials. It was demonstrated that substitution of 2-position of carbazole with electron withdrawing phosphine oxide stabilizes energy levels, while substitution of 4-position of carbazole enhances quantum efficiency of blue PHOLEDs.

## 2. Experimental

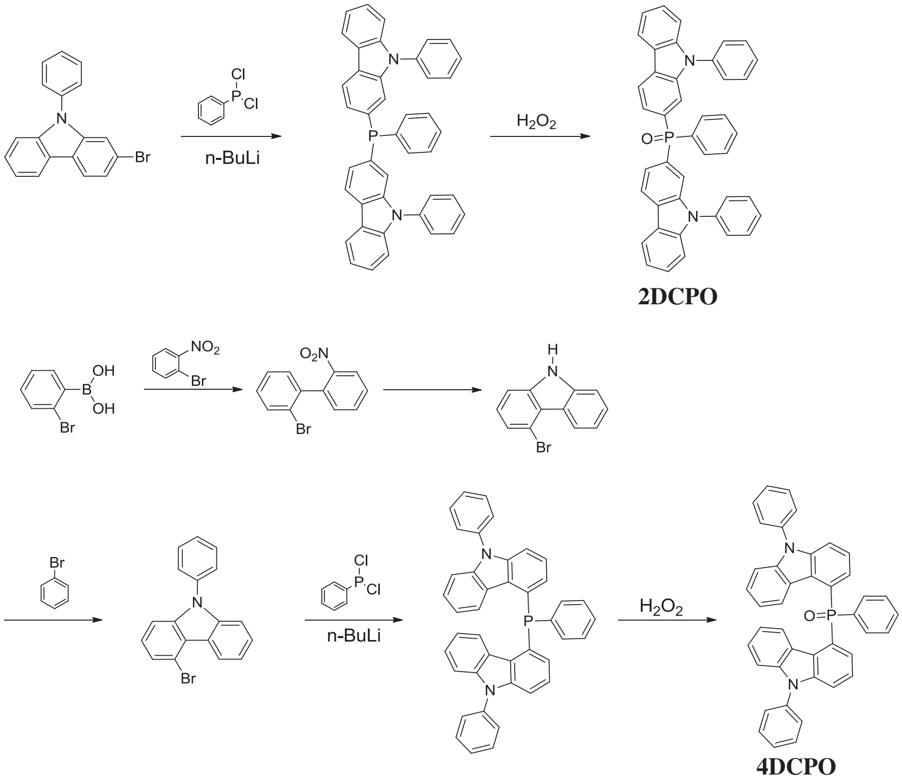
Synthetic scheme of DCPO compounds is described in Scheme 1.

### 2.1. Synthesis of phenylbis(9-phenyl-9H-carbazol-2-yl)phosphine oxide (2DCPO)

2-Bromo-9-phenyl-9H-carbazole (3.5 g, 10.86 mmol) was dissolved in tetrahydrofuran (35 ml) under argon atmosphere at −78 °C and n-butyllithium (5 ml, 2.5 M) was added. After 1 h, dichlorophenylphosphine (0.81 ml, 5.98 mmol) was added slowly. The mixture was stirred for 2 h at −78 °C, and allowed to warm to room temperature. After overnight stirring, the reaction mixture was added to methanol (10 ml) for 2 h and extracted with water and methylene chloride. The combined organic layer was dried over $MgSO_4$ and concentrated. Purification by column chromatography using methylene chloride : n-hexane (1:4) eluent gave a white powder. After vacuum drying for 2 h, the white powder was dissolved in methylene chloride (10 ml) and hydrogen peroxide (2 ml) was added followed by stirring for 2 h. The reaction mixture was extracted with water and methylene chloride. The combined organic layer was dried over $MgSO_4$ and concentrated. The product was obtained to 1.2 g (yield 19%). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ 8.16 (d, 2H, $J$ = 12.0 Hz), 8.14 (s, 2H), 8.01 (d, 2H, $J$ = 12.0 Hz), 7.66(d, 2H, $J$ = 18.0 Hz), 7.52–7.49 (m, 5H), 7.48–7.45 (m, 6H), 7.44–7.34 (m, 8H), 7.32 (t, 2H, $J$ = 6.0 Hz). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ 142.0, 137.0, 132.4, 132.3, 130.2, 128.6, 128.5, 128.0, 127.5, 127.3, 126.3, 123.4, 122.6, 121.1, 120.6, 120.3, 120.2, 114.4, 110.4. MS (FAB) $m/z$ 609[$(M + H)^+$]. Anal. Calcd for $C_{42}H_{29}N_2OP$ : C, 82.88; H, 4.80; N, 4.60. Found: C, 82.81; H, 4.70; N, 4.59.

### 2.2. Synthesis of 2-bromo-2′-nitro-1,1′-biphenyl

2-Bromophenylboronic acid (5.03 g, 25.05 mmol), 1-bromo-2-nitrobenzene (4.60 g, 22.77 mmol), and tetrakis(triphenylphosphine)palladium(0) (1.32 g, 1.14 mmol) were dissolved in tetrahydrofuran (60 ml) followed by addition of $K_2CO_3$ (8.29 g, 2 M) in water (30 ml). The mixture was refluxed for 12 h and cooled to room temperature



**Scheme 1.** Synthetic scheme of 2DCPO and 4DCPO.