

# Bicarbazole based donor–acceptor compound as a host for thermally activated delayed fluorescent emitter



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## ABSTRACT

A bicarbazole based donor–acceptor compound, 4,4'-([3,4'-bicarbazole]-9,9'-diyl)dibenzonitrile (4CN34BCz), was synthesized as a host material for thermally activated delayed fluorescent emitter and the device performances of the green devices with the synthesized host and (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) delayed fluorescent emitter were investigated. 4CN34BCz with CN unit at *para*-position could effectively assist delayed fluorescent emission of 4CzIPN and achieved a high external quantum efficiency of 20.8% compared to 13.8% of the similar host with CN unit at *meta*-position because the orientation of the CN functional group at *para* position of the benzonitrile was favourable for charge balance in the emitting layer.

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## 1. Introduction

Thermally activated delayed fluorescent (TADF) devices have been actively studied for the last couple of years [1–5]. Especially, the study from the first report of high external quantum efficiency close to 20% by Adachi and co-workers using (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) as a TADF emitter has been widely performed [6–9]. The 4CzIPN dopant was suitable as the TADF emitting material due to high PL quantum efficiency above 90%, excited state lifetime around 5 μs and small singlet–triplet energy difference of 0.10 eV [10]. Therefore, 4CzIPN has been widely used as the TADF emitter of green TADF devices and the best quantum efficiency of the 4CzIPN TADF device is 29.6% [11].

The progress of quantum efficiency of the TADF devices was made by engineering the host materials of the 4CzIPN TADF emitter. Common carbazole based host materials such as 4,4'-bis(carbazol-9-yl)biphenyl and 3,3'-bis(carbazol-9-yl)biphenyl were generally used as the host materials for 4CzIPN, but the quantum efficiency of the TADF devices could not reach above 20% external quantum efficiency because of poor electron transport properties of the carbazole based host materials [10]. Therefore, mixed hosts were used as the host materials of the 4CzIPN emitter. Several hole transport type host materials were mixed with electron transport type host materials to develop the mixed hosts for 4CzIPN emitter.

1,3-Bis(*N*-carbazolyl)benzene (mCP):1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBI) and mCP:1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (BmPyPb) were effective to enhance the quantum efficiency of the 4CzIPN device and high quantum efficiency of 28.6% was reported using the mCP:BmPyPb mixed host [12]. An even higher quantum efficiency of 29.6% was obtained by employing mCP:bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine as the mixed host [11].

The other way to compensate for the poor electron transport properties of the carbazole based host materials was to apply host materials with both hole transport and electron transport moieties for bipolar charge transport properties. 3',5'-Di(carbazol-9-yl)-[1,1'-biphenyl]-3,5-dicarbonitrile was proven to be effective as the bipolar host material for 4CzIPN by providing high quantum efficiency of 26.7% [13]. Additionally, bipolar host materials derived from aromatic amine modified benzofuroppyridine and phosphine oxide modified phenylcarbazole were applied as the host materials of 4CzIPN [14,15]. However, only a few bipolar host materials were studied as the host materials of 4CzIPN and further development of bipolar host materials for 4CzIPN is necessary. Our group reported 3,3'-(9H,9'H-[3,4'-bicarbazole]-9,9'-diyl)dibenzonitrile (3CN34BCz) as the host material of green and blue triplet emitters and the 3CN34BCz host could demonstrate excellent device performances [16]. Therefore, the 3CN34BCz type compound can also work as the host material of 4CzIPN.

Herein, we demonstrate the synthesis of a bicarbazole based bipolar host material, 4,4'-([3,4'-bicarbazole]-9,9'-diyl)dibenzonitrile (4CN34BCz), as the host of 4CzIPN and high quantum

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efficiency above 20% in green TADF devices by managing device parameters. The comparison of 4CN34BCz with 3CN33BCz host revealed that the combination of bicarbazole and benzonitrile with CN at *para* position rather than at *meta* position is a useful way of improving the device performances of the TADF devices.

## 2. Experimental

### 2.1. General information

Characterization and analysis of 4CN34BCz are explained in supporting information.

### 2.2. Synthesis of 4,4'-(3,4'-bicarbazole)-9,9'-diyl)dibenzonitrile (4CN34BCz)

9H,9'H-3,4'-bicarbazole (1.00 g, 3.0 mmol), 4-bromobenzonitrile (1.37 g, 7.5 mmol), copper iodide (0.34 g, 1.8 mmol) and  $K_3PO_4$  (1.66 g, 12.0 mmol) were dissolved in 1,4-dioxane (40 mL) and ( $\pm$ )-*trans*-1,2-diaminocyclohexane (0.21 g, 1.8 mmol) was added to the solution. The mixture was refluxed for 48 h and then cooled to room temperature. The solution was extracted with ethyl acetate and water. The combined organic layer was dried over  $MgSO_4$  and concentrated by evaporation of solvent. Purification by silica gel chromatography using ethyl acetate: *n*-hexane (1:4) eluent gave a white powder as a product (0.9 g, yield 56%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.40(s, 1H), 8.13(d, 1H,  $J=8.0$  Hz), 7.99–7.94(m, 4H), 8.87(d, 2H,  $J=8.0$  Hz), 7.72(d, 1H,  $J=8.0$  Hz), 7.63(d, 1H,  $J=8.0$  Hz), 7.56–7.29(m, 9H), 6.98(t, 1H,  $J=16.0$  Hz).  $^{13}C$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  206.9, 142.1, 140.6, 140.5, 140.4, 139.6, 138.4, 134.1, 133.9, 127.8, 127.7, 127.3, 126.8, 126.2, 126.1, 124.4, 124.2, 123.8, 123.2, 122.7, 121.8, 121.3, 121.2, 120.8, 120.6, 118.4, 111.0, 110.8, 109.8, 109.6, 109.3, 108.4. MS (FAB)  $m/z$  534[(M + H) $^+$ ]. Anal. Calcd for  $C_{38}H_{22}N_4$ : C, 85.37; H, 4.15; N, 10.48. Found: C, 85.05; H, 4.39; N, 10.10.  $T_g$  149 °C,  $T_d$  381 °C.

### 2.3. Device fabrication and measurements

Device growth of the TADF devices was carried out on patterned indium tin oxide (ITO, 50 nm) substrate. Hole injection layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS, 60 nm), was spin coated on the ultraviolet/ozone treated ITO substrate. Hole transport and exciton blocking materials, 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC, 20 nm) and mCP (10 nm), were deposited by thermal evaporation at a deposition rate of 0.1 nm/s. 4CN34BCz and 4CzIPN were co-deposited by thermal evaporation and the doping concentration

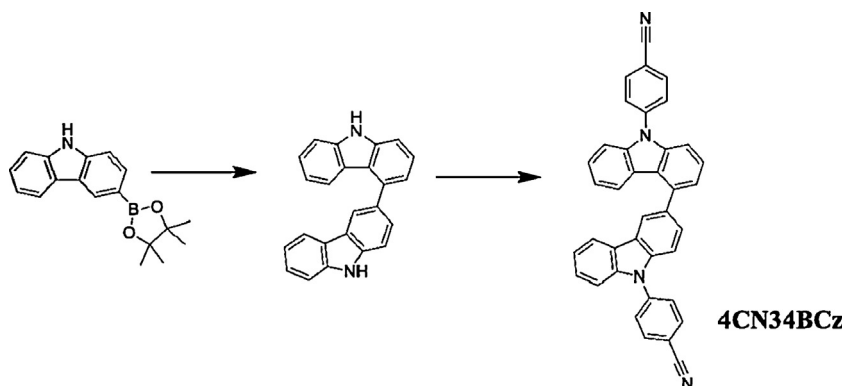
was changed by controlling the relative deposition rate of 4CN34BCz and 4CzIPN. Doping concentration of 4CzIPN was 1%. Exciton blocking layer and electron transport layer, diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 5 nm) and TPBI (30 nm), were thermally evaporated on the 4CN34BCz:4CzIPN emitting layer and LiF (1 nm)/Al (200 nm) was deposited as a cathode. 3CN34BCz device was also prepared by using the same device structure and device fabrication method. Hole only device fabrication was carried out using a device structure of ITO/PEDOT: PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/host (25 nm)/TAPC (5 nm)/Al (200 nm) and electron only device was fabricated using a device structure of ITO/Ca (10 nm)/host (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm). The fabricated devices were encapsulated inside glove box for device performance measurement. Keithley 2400 source measurement unit and CS 2000 spectroradiometer were used for the device characterization.

## 3. Results and discussion

The design of 4CN34BCz was motivated by good hole transport properties of bicarbazole and good electron accepting character of benzonitrile by a strong electron withdrawing CN unit. The modification of the bicarbazole backbone with the benzonitrile unit can compensate for the poor electron accepting properties of the bicarbazole moiety and make the 4CN34BCz host have bipolar charge transport characteristics. In addition, the bicarbazole backbone structure can secure high triplet energy to harvest triplet excitons of 4CzIPN TADF emitter. Therefore, the 4CN34BCz host can play a role of bipolar host to balance holes and electrons in the emitting layer and to harvest triplet excitons of 4CzIPN. Additionally, the CN unit was attached at *para* position rather than *meta* position of 3CN34BCz because the orientation of CN unit may affect charge transport properties of the host materials.

Scheme 1 shows the synthetic scheme of 4CN34BCz. The synthesis of 4CN34BCz was performed by CuI mediated coupling of 4-bromobenzonitrile with 9H,9'H-3,4'-bicarbazole. The 9H,9'H-3,4'-bicarbazole intermediate was prepared according to the synthetic method of previous report [16]. Synthetic yield of the coupling reaction was 56% after wet purification by column chromatography. Final product for characterization and device evaluation was purified by vacuum sublimation and high purity level above 99% was obtained.

As the bipolar host materials with both hole transport and electron transport moieties should have separated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the HOMO and LUMO calculation of the 4CN34BCz was carried out. The HOMO and LUMO distribution



Scheme 1. The synthetic scheme of 4CN34BCz.

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