

Dibenzothiophene derived hosts with CN substituted carbazole for blue thermally activated delayed fluorescent organic light-emitting diodes



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ABSTRACT

In this work, dibenzothiophene type host materials modified with 9H-carbazole, 9H-carbazole-3-carbonitrile and 9-phenylcarbazole were synthesized for high quantum efficiency and elongated lifetime in blue thermally activated delayed fluorescent (TADF) organic light-emitting diodes. Three host materials having one or two CN modified carbazole units were prepared for strengthened chemical bond as well as improved electron transport properties. The host materials designed using the carbazole and CN modified carbazole units built on the dibenzothiophene core showed low driving voltage, high quantum efficiency and elongated lifetime at the same time without any sacrifice of device performances in the blue TADF devices.

1. Introduction

Organic light-emitting diodes (OLEDs) have played an important role as light-emitting devices both in popular electronic display panels and lighting applications. As is well known, OLEDs have two emission processes, which are fluorescence and phosphorescence [1–3]. These processes make photons using singlet and triplet excitons generated in the ratio of 1:3 in emitting layer by electroluminescence (EL) [4,5]. In 2012, Adachi et al. discovered a new fluorescent process that is called thermally activated delayed fluorescence (TADF) in OLEDs as a high efficiency emitting process. TADF process enables harvesting both singlet and triplet excitons using a reverse intersystem crossing (RISC) mechanism which is effectively induced using small energy gap between the singlet and triplet excited states [6]. Therefore, the TADF and phosphorescent OLEDs can achieve a theoretical maximum 100% internal quantum efficiency. Recently, many devices with external quantum efficiency (EQE) exceeding 20% have been developed with TADF and phosphorescent OLED [7–16].

Typically, in order to obtain high EQE in the TADF system, the role of host materials is very important in the emitting layer. The requirements of the host materials are higher singlet and triplet energy than dopant material, efficient charge injection from the hole and electron transport layers, and stability. Although many researchers have lots of interest in high efficiency [17–19] and long lifetime [20–22] host materials for blue TADF OLEDs, only limited number of host materials are available. In fact, a well-known 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) material has been widely used as the host in blue TADF OLEDs due to high triplet energy and moderate stability [23–25], but mCBP is

not compatible with high efficiency and long lifetime TADF OLEDs due to strong electron trapping [26,27]. Furthermore, mCBP has weak bond strength of C–N bond under negative polarons. Therefore, it is required to develop bipolar host materials to improve these demerits [28–31].

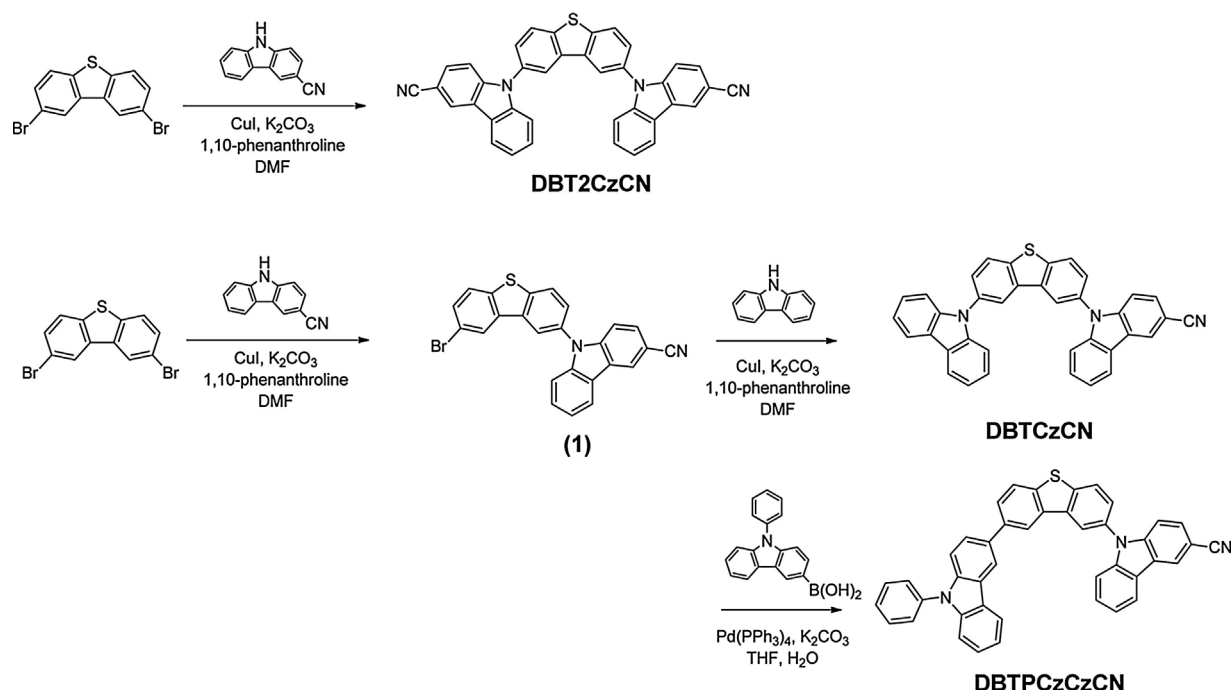
In this work, three host materials based on a dibenzothiophene moiety, 9,9'-(dibenzo[b,d]thiophene-2,8-diyl)bis(9H-carbazole-3-carbonitrile) (DBT2CzCN), 9-(8-(9H-carbazol-9-yl)dibenzo[b,d]thiophen-2-yl)-9H-carbazole-3-carbonitrile (DBTCzCzCN), and 9-(8-(9-phenyl-9H-carbazol-3-yl)dibenzo[b,d]thiophen-2-yl)-9H-carbazole-3-carbonitrile (DBTPCzCzCN), were developed for both high quantum efficiency and long lifetime in blue TADF OLEDs. The host materials showed low driving voltage and improved EQE above 15% in as the host material of blue TADF devices. Among the three materials, The DBTCzCzCN showed higher EQE and longer lifetime than other host materials because the DBTCzCzCN host had balanced carrier mobility, proper energy levels and high C–N bond dissociation energy.

2. Results and discussion

In previous study, we designed host materials using 2,8-dibromodibenzo[b,d]thiophene and 9-phenylcarbazole moieties by changing the substitution position of 9-phenylcarbazole [32]. The synthesized host materials showed high quantum efficiency and long lifetime in blue phosphorescent OLEDs. In particular, a 3-position modified phenylcarbazole based host material showed high efficiency and long lifetime relative to other host materials. Utilizing these features, the molecular design in this work was intended to improve electron injection and transport by introducing bipolar structure in the

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Scheme 1. Synthetic scheme of DBT2CzCN, DBTCzCzCN and DBTPCzCzCN.

molecule based on the previous approach to use 2,8-dibromodibenzo[*b,d*]thiophene. We utilized CN modified carbazole instead of carbazole for electron transport and high bond dissociation energy of C–N chemical bond.

All three host materials were synthesized by Ullmann amination and Suzuki coupling reactions using a 2,8-dibromodibenzo[*b,d*]thiophene starting material. Synthetic scheme of blue TADF host materials is presented in Scheme 1. DBT2CzCN, DBTCzCzCN, and DBTPCzCzCN were three host materials with a chemical platform of 2- and 8-position modified dibenzo[*b,d*]thiophene and carbazole-3-carbonitrile. DBT2CzCN had two carbazole-3-carbonitrile units, DBTCzCzCN had one carbazole and one carbazole-3-carbonitrile, and DBTPCzCzCN had one phenylcarbazole and one carbazole-3-carbonitrile.

The molecular orbital of the three host materials was simulated by density functional theory (DFT) calculations (B3LYP/6–31 g(d)) to confirm the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distribution (Fig. 1). The HOMO of DBTCzCzCN and DBTPCzCzCN were mainly distributed on the carbazole and 9-phenylcarbazole moieties. However, the HOMO of DBT2CzCN was widely distributed on the whole molecular structure due to weak electron donating attribute of the carbazole-3-carbonitrile unit. The dibenzothiophene moiety and carbazole-3-carbonitrile moiety had moderate electron donating character and shared the HOMO. The LUMO of the three host materials were only distributed on the dibenzothiophene moiety due to electron poor character of dibenzothiophene moiety relative to carbazole, 9-phenylcarbazole and carbazole-3-carbonitrile moieties.

Photophysical analysis of the host materials was carried out by measuring ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) (Fig. 2). In the UV-vis absorption spectra, main absorption peaks were detected below 320 nm by π – π^* transition and additional absorption peaks at 320 ~ 370 nm were weakly observed in the three host materials caused by the n – π^* transitions of carbazole, 9H-phenylcarbazole and CzCN moieties. The bandgap energies were 3.51, 3.51 and 3.46 eV from the absorption edges of DBT2CzCN, DBTCzCzCN and DBTPCzCzCN. Slight reduction of the bandgap by 0.05 eV was noted in the DBTPCzCzCN because of extended π – π conjugation by connecting the phenylcarbazole via 3- position. Peak positions of the solution PL emission spectra in toluene were detected at 368, 382 and

394 nm for DBT2CzCN, DBTCzCzCN and DBTPCzCzCN, respectively. Therefore, the singlet energy of three host materials was estimated to be 3.37, 3.24 and 3.15 eV for DBT2CzCN, DBTCzCzCN and DBTPCzCzCN, respectively. The singlet energy was also low in the DBTPCzCzCN by the extension of conjugation and weak donor-acceptor character decreased the singlet energy of DBTCzCzCN compared to that of DBT2CzCN. Phosphorescent emission spectra of DBT2CzCN, DBTCzCzCN and DBTPCzCzCN were observed at 429, 428 and 450 nm (Fig. 2). The triplet energies of three host materials were revealed to be 2.89, 2.90 and 2.75 eV, respectively. The DBTPCzCzCN host material had low triplet energy compared with other host materials due to extended degree of conjugation through 3- position of carbazole moiety. However, the three host materials showed high triplet energy to suppress exciton leakage in blue emitting 2,3,4,5,6-penta(9H-carbazol-9-yl)benzonitrile (5CzCN) TADF device and the triplet energies of DBT2CzCN and DBTCzCzCN outstripped 2.80 eV of a well known carbazole based mCBP host material. Cyclic voltammetry (CV) characterization results of the host materials are shown in Fig. 3. As shown in the graph, the HOMO and LUMO of DBT2CzCN, DBTCzCzCN and DBTPCzCzCN were -6.28 eV/ -2.80 eV, -6.09 eV/ -2.61 eV and -6.01 eV/ -2.62 eV, respectively. The HOMO of DBTPCzCzCN was shallower than that of other host materials due to the HOMO localization in the carbazole moiety and HOMO/LUMO of DBT2CzCN was deeper than that of other host materials due to contribution of carbazole-3-carbonitrile to the molecular orbital.

In order to investigate device performances, we fabricated blue TADF devices using the 2,3,4,5,6-penta(9H-carbazol-9-yl)benzonitrile (5CzCN) as a blue dopant material. The device structure was indium tin oxide (ITO, 120 nm)/DNTPD (60 nm)/BPBPA (20 nm)/PCzAc (10 nm)/emitting layer (30 nm)/DBFTz (5 nm)/ZADN (30 nm)/LiF (1.5 nm)/Al (200 nm) designed for long-term stability rather than high efficiency. Where DNTPD is *N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine, BPBPA is *N,N,N',N'*-tetra[(1,10-biphenyl)-4-yl]-(1,10-biphenyl)-4,4'-diamine, PCzAc is 9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10-dihydroacridine, DBFTz is 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan, and ZADN is 2-(4-(9,10-di(naphthalen-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1H-benzo[*d*]imidazole. The emitting layer was 30% 5CzCN doped DBT2CzCN, DBTCzCzCN and DBTPCzCzCN in the TADF devices. Current density

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