## ChemComm





**View Article Online** 

Cite this: DOI: 10.1039/c5cc01940k

Received 7th March 2015, Accepted 28th March 2015

DOI: 10.1039/c5cc01940k

www.rsc.org/chemcomm

## Benzofurocarbazole and benzothienocarbazole as donors for improved quantum efficiency in blue thermally activated delayed fluorescent devices†

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Benzofurocarbazole and benzothienocarbazole were used as electron donors of thermally activated delayed fluorescence (TADF) emitters and the performances of the TADF devices were examined. The benzofurocarbazole and benzothienocarbazole donor moieties were better than carbazole as the electron donors of the TADF emitters.

Thermally activated delayed fluorescent (TADF) materials are attractive as third generation organic light-emitting materials because they have the merits of both 1st generation fluorescent emitters and 2nd generation phosphorescent emitters. The TADF materials are similar to fluorescent emitting materials in that single excitons are involved in the light emission and similar to phosphorescent emitters in that both singlet and triplet excitons are harvested for light emission by intersystem crossing process although reverse intersystem crossing process is used in the TADF devices.<sup>1</sup>

The triplet exciton harvesting by reverse intersystem crossing of the TADF devices was dominated by thermal activation of the triplet excitons for light emission in the singlet state, which was induced by small singlet and triplet energy gap of the TADF emitters.<sup>2</sup> Therefore, the TADF material design was based on the donor-acceptor structure to reduce the singlet energy of the emitters, and strong donors and acceptors were introduced in the molecular design of the TADF emitters.<sup>1</sup> Carbazole,<sup>1,4-6</sup> acridine<sup>3,4</sup> and triphenylamine<sup>4,5</sup> were representative donors of the TADF emitters and the singlet-triplet energy gap of the TADF emitters was determined by the electron donating capability of the donors. However, only a few donors were considered as the donor moieties of the TADF emitters and further study about the effect of donor moieties on the photophysical properties and device performances of the TADF emitters is required. In this work, two electron donors, benzofurocarbazole and benzothienocarbazole, were introduced as electron donating moieties of the TADF emitters and they were compared with a common carbazole moiety. It was found that the benzofurocarbazole and benzothienocarbazole work better than carbazole as the electron donors to improve the quantum efficiency of the TADF devices. The replacement of carbazole with benzofurocarbazole and benzothienocarbazole more than doubled the quantum efficiency of the TADF devices.

A synthetic scheme of BFCz-2CN and BTCz-2CN is shown in Scheme 1. The benzofurocarbazole and benzothienocarbazole donors were synthesized by Suzuki coupling and ring closing reactions. The two donor moieties were attached to 4,5-difluorophthalonitrile by NaH mediated coupling reaction to produce 4,5-bis(benzofuro[3,2-c]carbazol-5-yl)phthalonitrile (BFCz-2CN) and 4,5-bis(benzo[4,5]thieno[3,2-c]carbazol-5-yl)phthalonitrile (BTCz-2CN) at a synthetic yield of about 50% after purification by column chromatography and vacuum train sublimation. Chemical analysis



Scheme 1 Synthetic scheme of BFCz-2CN and BTCz-2CN.

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ c5cc01940k

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of the final compounds identified BFCz-2CN and BTCz-2CN as products. The detailed procedure for the synthesis of BFCz-2CN and BTCz-2CN is presented in the ESI.†

As the molecular orbital distribution affects the singlet-triplet energy gap and oscillation strength of the TADF emitters, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the synthesized compounds were calculated using the B3LYP/6-31G\* basis set of Gaussian 09 program (Fig. 1). A small singlet-triplet energy gap is expected from spatial separation of the HOMO and LUMO, and good emission properties are anticipated from a weak HOMO-LUMO overlap in BFCz-2CN and BTCz-2CN. The donor structure had little effect on the HOMO and LUMO distribution. However, the oscillation strength of BFCz-2CN (0.13) and BTCz-2CN (0.13) was higher than that of 2CzPN (0.09) with the carbazole moiety in the molecular structure. The use of the benzofurocarbazole and benzothienocarbazole increased the oscillation strength of the TADF emitters, which may enhance light-emitting properties of the emitters. The HOMO/LUMOs of BFCz-2CN and BTCz-2CN were -6.19/-3.58 eV and -6.17/ -3.58 eV, respectively, from cyclic voltammetry measurements.

Light absorption and light emission of the TADF emitters were analyzed using ultraviolet-visible (UV-vis) and photoluminescence (PL) measurements. Fig. 2 presents the UV-vis absorption and PL emission spectra of BFCz-2CN and BTCz-2CN. The two host materials absorbed UV-vis light strongly at a short wavelength below 310 nm by  $\pi$ - $\pi$ \* transition and weakly at a long wavelength between 310 nm and 430 nm by  $n-\pi^*$ absorption. The introduction of benzofurocarbazole and benzothienocarbazole instead of carbazole extended the UV-vis absorption to 430 nm, which is good for energy transfer from host materials to the dopant materials. UV-vis absorption of BFCz-2CN and BTCz-2CN was well matched with PL emission of 1,3-bis(N-carbazolyl)benzene (mCP) film (Fig. S1, ESI<sup>†</sup>). Singlet energies of BFCz-2CN and BTCz-2CN were 2.59 eV and 2.63 eV from PL emission wavelength in polystyrene. Triplet energy of BFCz-2CN and BTCz-2CN was 2.46 eV from the phosphorescent



emission peak in frozen tetrahydrofuran solution measured at 77 k after applying a delay time of 100 µs. The singlet-triplet energy gaps were 0.13 eV and 0.17 eV for BFCz-2CN and BTCz-2CN, respectively. The donor-acceptor structure of the BFCz-2CN and BTCz-2CN emitters reduced the singlet-triplet energy gap for TADF emission and induced a solvatochromic effect in different solvents. Solution PL spectra in different solvents are presented in Fig. S2 (ESI<sup>†</sup>) and the bathochromic shift of the PL emission spectra in polar solvents was observed, which suggests the charge transfer emission of the TADF emitters. PL quantum yields (PLQY) of BFCz-2CN and BTCz-2CN in toluene were 24.6 and 28.9% before N2 bubbling, and 94.6 and 94.0% after N<sub>2</sub> bubbling for 10 min from absolute PL measurements using an integrating sphere. The PLQY of BFCz-2CN and BTCz-2CN in the mCP host was 85%, which was higher than that of 2CzPN doped mCP film.<sup>1,7</sup> This result confirms that the PL emission of BFCz-2CN and BTCz-2CN is caused by the TADF process and the quantum yields of BFCz-2CN and BTCz-2CN were higher than that of 2CzPN.<sup>1</sup>

Delayed fluorescence emission of BFCz-2CN and BTCz-2CN was investigated using transient PL measurement of BFCz-2CN and BTCz-2CN dispersed in 1,3-bis(*N*-carbazolyl)benzene (mCP). Transient PL decay curves of BFCz-2CN and BTCz-2CN at 297 K are shown in Fig. 3. Both prompt and delayed emissions of BFCz-2CN and BTCz-2CN were observed and emission spectra are shown in Fig. S3 (ESI†). The excited state lifetimes for the delayed emission were 2.60 and 1.98  $\mu$ s, respectively. Compared with 2CzPN which had an excited state lifetime of 166  $\mu$ s,<sup>1</sup> the excited state lifetime of BFCz-2CN and BTCz-2CN was greatly shortened by the benzofurocarbazole and benzothienocarbazole, which restrict the molecular motion of the molecules and reduce the singlet–triplet energy gap, resulting in a short lifetime. Fig. S4 (ESI†) shows transient decay curves at different temperatures. From 100 K to 297 K, the delayed component was increased at high temperature.

Thermal properties of BFCz-2CN and BTCz-2CN were also studied and the glass transition temperatures of BFCz-2CN and BTCz-2CN were 204 and 219  $^{\circ}$ C, respectively. The rigid molecular structure increased the glass transition temperatures of the BFCz-2CN and BTCz-2CN emitters. Thermal decomposition temperatures were 397 and 434  $^{\circ}$ C for BFCz-2CN and BTCz-2CN, respectively. Thermal analysis data are presented in Fig. S5 in the ESI.†





**Fig. 4** (a) Current density-voltage-luminance curves and (b) quantum efficiency-current density curves of BFCz-2CN, BTCz-2CN and 2CzPN devices. (c) EL spectra of BFCz-2CN and BTCz-2CN devices.

The device performances of the BFCz-2CN and BTCz-2CN emitters were collected by doping the emitters in mCP host material. The mCP material was chosen as a matrix material because the high triplet energy of mCP (2.9 eV) can suppress singlet and triplet exciton quenching of the emitters. Device architecture was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl) aniline] (TAPC, 20 nm)/mCP (10 nm)/mCP:BFCz-2CN or BTCz-2CN (25 nm, 1%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 35 nm)/LiF(1 nm)/Al(200 nm). TSPO1 was an electron transport type exciton blocking material and mCP was a hole transport type exciton blocking layer to avoid singlet and triplet exciton quenching of emitters. Device performances at 1% doping concentration were compared since the driving voltage and quantum efficiency were optimized at 1% doping concentration. Fig. 4 displays device characteristics of the BFCz-2CN and BTCz-2CN emitters and device performances at other doping concentrations are summarized in the ESI.<sup>†</sup> Maximum quantum efficiencies of the BFCz-2CN and BTCz-2CN devices were 12.1% and 11.8%, which were higher than 5.0% of the 2CzPN emitter. The higher quantum efficiency of the BFCz-2CN and BTCz-2CN devices than that of the 2CzPN device is caused by high PL quantum yield and short excited state lifetime of the emitters. As explained in the photophysical data, the quantum yield of BFCz-2CN and BTCz-2CN was higher than that of 2CzPN, which more than doubled the quantum efficiency of the BFCz-2CN and BTCz-2CN devices compared to the 2CzPN device. Additionally, efficient up-conversion by a short excited state lifetime for delayed emission contributed to the high quantum efficiency of BFCz-2CN and BTCz-2CN. Electroluminescence (EL) spectra of the BFCz-2CN and BTCz-2CN devices were also similar and a peak wavelength of 486 nm and a full width at half maximum of 73 nm were exhibited by the two emitters.

In conclusion, BFCz-2CN and BTCz-2CN were synthesized as blue TADF emitters and showed high quantum efficiency about 12% at an optimum doping concentration of 1%. The introduction of benzofurocarbazole and benzothienocarbazole increased the PL quantum efficiency and shortened the excited state lifetime of the TADF emitters.

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2013R1A1A2011560, 2013R1A1A2007991) and Ministry of Science, ICT and future Planning (2013R1A2A2A010674).

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