Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

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

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Experimental Section

General information

Sodium hydride (Alfa asear), 1-bromo-2-nitrobenzene (Aldrich Chem Co.), 4,5-difluorophthalonitrile (TCI Chem. Co.), dibenzofuran-4-boronic acid and dibenzothiophene-4-boronic acid (P&H Tech. Co) were used without further purification. Tetrahydrofuran (Duksan Sci. Co.) was distilled over sodium and calcium hydride. General chemical analysis was described in our previous paper[1].

Synthesis

4-(2-nitrophenyl)dibenzo[b,d]furan

1-bromo-2-nitrobenzene (15.00 g, 74.25 mmol), dibenzofuran-4-boronic acid (18.89 g, 89.10 mmol) and potassium carbonate (20.53 g, 148.51 mmol) were dissolved in tetrahydrofuran (450 ml) and

distilled water (150 ml) and then bubbled with nitrogen (N_2) gas. After 30min of N_2 bubbling, tetrakis(triphenylphosphine)palladium(0) (3.00 g, 2.60 mmol) and refluxed for 24 hours under N_2 atmosphere. The reaction mixture was cooled down to room temperature and extracted with ethyl acetate and distilled water 3 times. The organic layer was treated with anhydrous magnesium sulfate, and the solvent was removed by rotary evaporator. Impurities were removed by column chromatography on silica gel using n-hexane/ethylene acetate (1:4). As a result, the title compound was obtained as a yellow gel.

Yield : 18.39, 85 %. MS(FAB) m/z 289[$(M+H)^+$]. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.34 (t, J= 7.6 Hz, 1H), 7.40~7.49 (m, 4H), 7.56~7.63 (m, 2H), 7.72 (t, J=10.4 Hz, 1H), 7.95~8.01 (m, 2H), 8.09 (d, J=9.6 Hz, 2H).

4-(2-nitrophenyl)dibenzo[b,d]thiophene

Synthetic method of 4-(2-nitrophenyl)dibenzo[b,d]thiophene was the same as that of 4-(2-nitrophenyl)dibenzo[b,d]furan except that dibenzothiophene-4-boronic acid (20.32 g, 89.104 mmol) was used instead of dibenzofuran-4-boronic acid.

Yield : 18.72, 83 %. MS(FAB) m/z 305[$(M+H)^+$]. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.32 (d, J=8.0 Hz, 1H), 7.43~7.49 (m, 2H), 7.54 (t, J=7.6 Hz, 1H), 7.59~7.63 (m, 2H), 7.72 (t, J=8.2 Hz, 1H), 7.78 (d, J=9.2 Hz, 1H), 8.09 (d, J=8.0 Hz, 1H), 8.19 (d, J=9.6 Hz, 2H).

5H-benzofuro[3,2-c]carbazole

4-(2-nitrophenyl)dibenzo[b,d]furan (20.00g, 69.14 mmol) and triphenylphosphine (45.33 g, 172.84 mmol) were dissolved in 1,2-dichlorobenzene (136 ml) and refluxed 36 hours. Solvent was removed by distillation and washed with toluene. Residue was purified by sublimation under vacuum. As a result the title compound was obtained as a white powder.

Yield : 16.88 g, 95 %. MS(FAB) m/z 257[$(M+H)^+$]. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.35~7.52 (m, 6H), 7.72 (d, J=8.4 Hz, 1H), 7.95~7.99 (m, 2H), 8.31 (s, 1H), 8.50 (d, J=7.6 Hz, 1H).

5H-benzo[4,5]thieno[3,2-c]carbazole

Synthetic method of 5H-benzo[4,5]thieno[3,2-c]carbazole was the same as that of 5H-benzofuro[3,2-c]carbazole except that 4-(2-nitrophenyl)dibenzo[b,d]thiophene (20.00 g, 65.50 mmol) was used instead of dibenzofuran-4-boronic acid.

Yield : 16.40 g, 92 %. MS(FAB) m/z 273[$(M+H)^+$]. ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.38~7.54 (m, 6H), 7.97 (d, J=8.0 Hz, 1H), 8.19 (d, J=8.4 Hz, 2H), 8.24 (d, J=8.4 Hz, 1H), 8.29 (s, 1H).

4,5-Bis(5*H*-benzofuro[3,2-*c*]carbazol-5-yl)phthalonitrile (BFCz-2CN)

Sodium hydride (0.22 g, 5.48 mmol) was washed with hexane three times and dried in vacuo. 5*H*-benzofuro[3,2-*c*]carbazole (1.18 g, 4.57 mmol) was dissolved in tetrahydrofuran (30 ml) and then was added to the flask. After stirring for 30 min at room temperature under a nitrogen atmosphere, a solution of 4,5-difluorophthalonitrile (0.30 g, 1.83 mmol) in tetrahydrofuran (10 ml) was added. The reaction mixture was stirred for 12 h at room temperature and the reaction was quenched with distilled water (10 ml). The solvent was removed by rotary evaporator and crude product was washed with water. Impurities were removed by column chromatography on silica gel using n-hexane/methylene chloride (1:2). Additionally, BFCz-2CN was purified by sublimation under vacuum. As a result, the title compound was obtained as a yellow powder.

Yield : 0.61 g, 52 %. T_g 204 ℃. MS(FAB) m/z 638[$(M+H)^+$]. ^{1}H NMR (400 MHz, DMSO) : δ 7.17~7.27 (m, 5H), 7.32~7.51 (m, 7H), 7,68 (t, J=10.0 Hz, 2H), 7.81 (d, J=8.0 Hz, 1H), 7.85 (d, J=8.0 Hz, 1H), 7.93 (d, J=8.0 Hz, 1H), 8.02 (d, J=8.0 Hz, 1H), 8.06 (d, J=8.0 Hz, 2H), 8.99 (s, 2H). ^{13}C NMR (100 MHz, DMSO) : δ 106.03, 108.14, 110.34, 111.58, 115.33, 115.82, 118.58, 120.39, 121.61,

121.86, 123.23, 123.33, 123.86, 125.94, 126.05, 136,89, 138.03, 138.17, 138.48, 139.11, 149.42, 155.36. Elemental analysis Calcd for $C_{44}H_{22}N_4O_2$: C,82.75; H,3.47; N,8.77; O,5.01. Found : C,82.52; H,3.46; N,8.78; O,4.92.

4,5-Bis(5*H*-benzo[4,5]thieno[3,2-*c*]carbazol-5-yl)phthalonitrile (BTCz-2CN)

Synthetic method of BTCz-2CN was the same as that of BFCz-2CN except that 5*H*-benzo[4,5]thieno[3,2-*c*]carbazole (1.17 g, 6.09 mmol) was used instead of 5*H*-benzofuro[3,2-*c*]carbazole.

Yield : 0.80g, 49%. T_g 219 ℃. MS(FAB) m/z 670[$(M+H)^+$]. ^{1}H NMR (400 MHz, DMSO) : δ 7.21~7.32 (m, 6H), 7.39~7.42 (m, 2H), 7.55 (d, J=8.0 Hz, 3H), 7.62 (d, J=8.0 Hz, 1H), 7.80~7.86 (m, 3H), 7.95~7.97 (m, 3H), 8.11 (d, J=8.0 Hz, 1H), 8.19~8.23 (m, 1H), 8.97 (d, J=4.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) : δ 108.41, 110.94, 115.88, 116.33, 117.81, 120.40, 121.23, 121.88, 122.37, 122.51, 123.40, 125.20, 126.25, 126.49, 129.30, 131.69, 135.35, 137.44, 138.01, 138.53, 138.74, 139.28. Elemental analysis Calcd for $C_{44}H_{22}N_4S_2$: C,78.78; H,3.31; N,8.35; S,9.56. Found : C,78.74; H,3.30; N,8.34; SS,9.57.

Device fabrication and measurements

Device structure 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)/1,3-bis(*N*-carbazolyl)benzene (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). Electrical and optical data of the devices were collected using Keithley 2400 source measurement unit and CS1000 spectroradiometer.

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References

Y. J. Cho, K. S. Yook, J. Y. Lee, *Adv. Mater.* 2014, **26**, 4050-4055.

List of figures

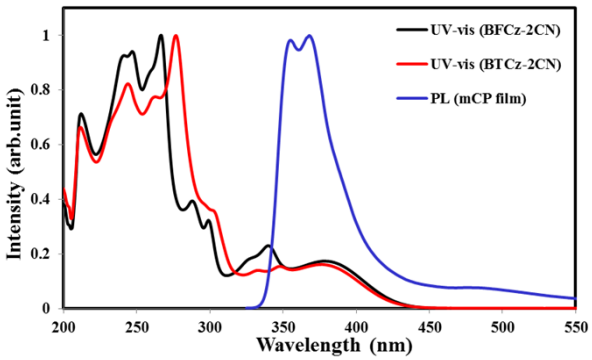

Figure S1. UV-vis absorption spectra of BFCz-2CN and BTCz-2CN with PL emission of mCP film.

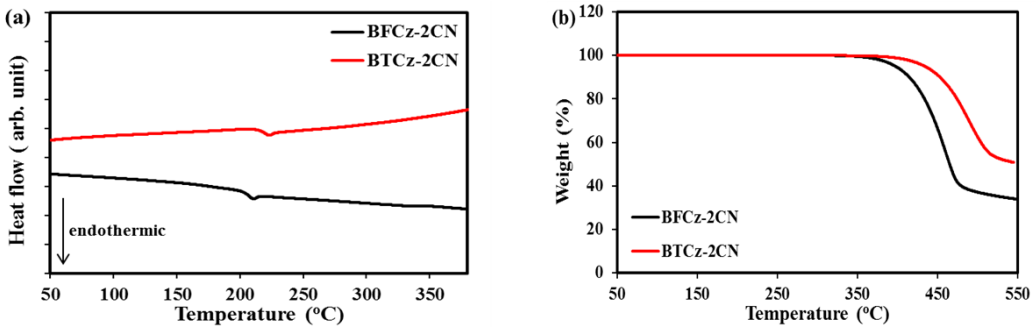

Figure S5. (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) spectra of BFCz-2CN and BTCz-2CN.

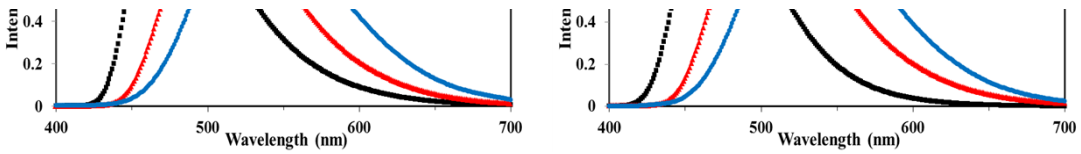

Figure S2. Solution PL spectra of (a) BFCz-2CN and (b) BTCz-2CN in cyclohexane, toluene and tetrahydrofuran.

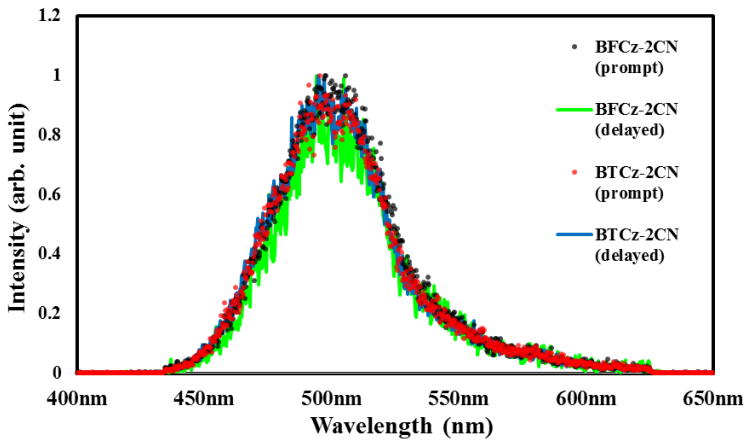

Figure S3. Prompt and delayed emission spectra of BFCz-2CN and BTCz-2CN in toluene solution.

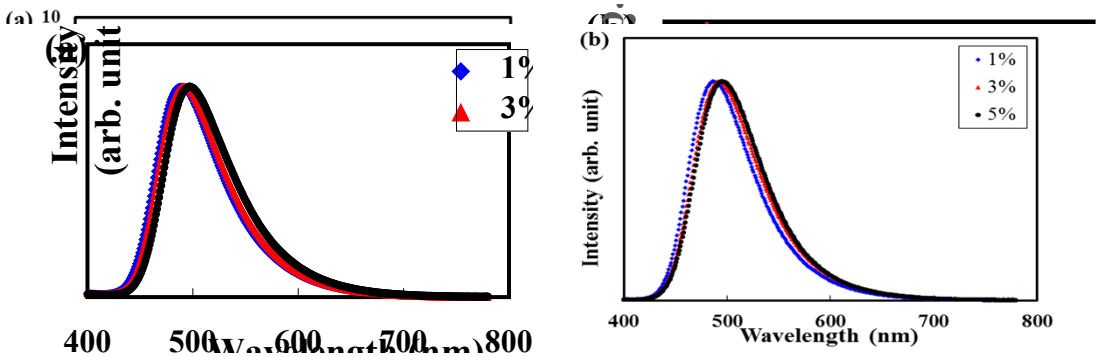

Figure S7. EL spectra of (a) BFCz-2CN and (b) BTCz-2CN at different doping concentrations.

Figure S4. Transient decay curves spectra of (a) BFCz-2CN and (b) BTCz-2CN at different temperature.

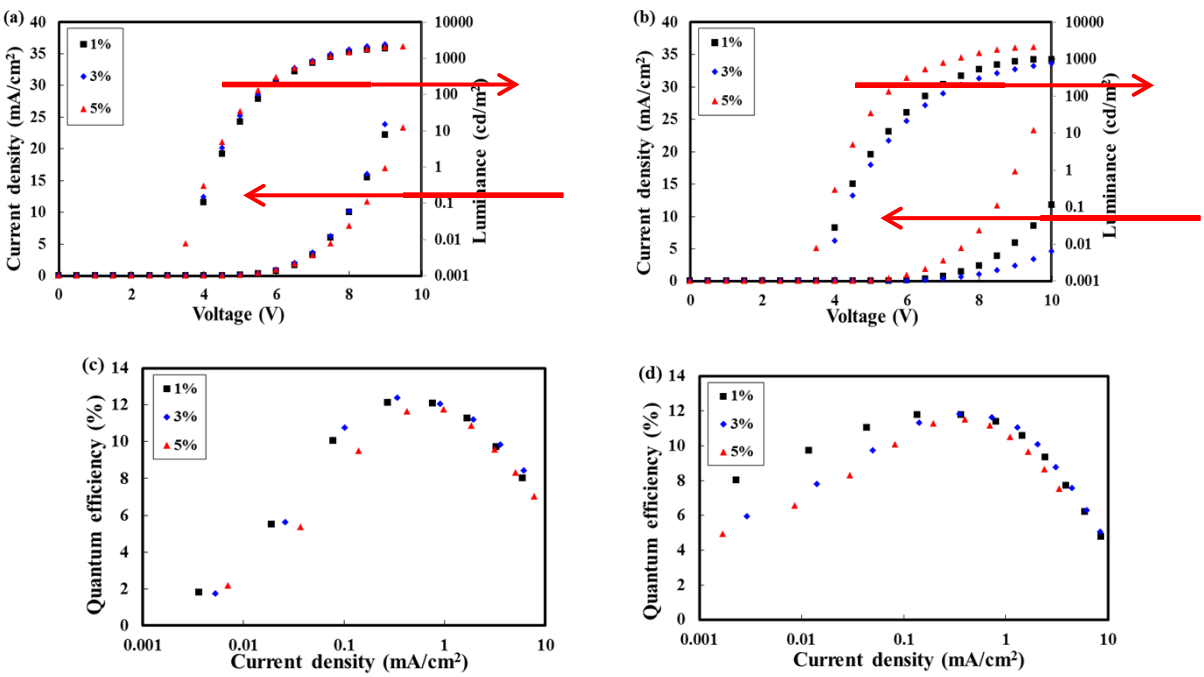

Figure S6. Current density–voltage-luminance curves of (a) BFCz-2CN and (b) BTCz-2CN at different doping concentrations. Quantum efficiency-current density curves of (c) BFCz-2CN and (d) BTCz-2CN at different concentrations.

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