Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Benzonitrile and dicyanocarbazole derived electron transport type host materials for improved device lifetime in blue thermally activated delayed fluorescent organic light-emitting diodes

Sung Yong Byeon, Kyung Hyung Lee, ***and*** **Jun Yeob Lee ***

School of Chemical Engineering, Sungkyunkwan University

2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Korea

E-mail : leej17@skku.edu

Experimental

General information

1-Bromodibenzo[*b*,*d*]furan, dibenzo[*b*,*d*]furan-2-ylboronic acid, dibenzo[*b*,*d*]furan-4-ylboronic acid, palladium(II) acetate, tetrakis(triphenylphosphine)palladium(0), bis(pinacolato)diboron, 3-bromo-2-fluorobenzonitrile, 9*H*-carbazole-3,6-dicarbonitrile (P&H tech), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-phos), dimethylsulfoxide-d_6 (Sigma-Aldrich Co. LLC.), potassium acetate, cesium carbonate, potassium carbonate, and *N*,*N*-dimethylformamide (DMF) (Duksan Sci. Co.) were used without further purification. Tetrahydrofuran (THF) (Samchun pure chemical Co. Ltd.) was distilled over sodium and calcium hydride.

The final compounds were confirmed using ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra recorded on a Avance-500(Bruker, 500MHz) spectrometer. The ultraviolet-visible (UV-vis) spectra were obtained using UV-vis spectrophotometer (JASCO, V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, LS-55). The energy levels of highest occupied molecular orbital and lowest unoccupied molecular orbital were estimated using a cyclic voltammetry (Ivium Tech., Iviumstat). The mass spectra were recorded using a Advion, Expresion^L CMS spectrometer in APCI mode.

Synthesis

2-(Dibenzo[*b*,*d*]furan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

1-Bromodibenzo[*b*,*d*]furan (3.0 g, 12.14 mmol), bis(pinacolato)dibron(4.6 g, 18.21 mmol), palladium(II) acetate (0.3 g, 1.21 mmol), X-phos (1.2 g, 2.43 mmol) and potassium acetate (3.6 g, 36.42 mmol) were poured into a round bottom flask (RB) and dissolved in 60 ml of toluene. The reaction mixture was stirred for 12 h at a reflux temperature. Then the reaction mixture was cooled to room temperature and extracted using methylene chloride (MC)/water. The organic layer was collected and dehydrated using magnesium sulfide ($MgSO_4$). A white powder was obtained after further purification using column chromatography with an eluent of MC and n-hexane (HEX).

Yield 90%. ^{1}H NMR (300 MHz, DMSO-*d6*): δ 8.79 (d, 1H, J=7.8H_Z), 7.81 (d, 1H, J=8.1H_Z), 7.75 (d, 1H, J=7.2H_Z), 7.50 (t, 1H, J=7.8 H_Z), 7.39 (t, 1H, J=7.7 H_Z), 1.38 (s, 12H), MS (APCI) m/z 294.3 [$(M+H)^+$].

3-(Dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile

2-(Dibenzo[*b*,*d*]furan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.5 g, 8.50 mmol) and 3-bromo-2-fluorobenzonitrile (1.9 g, 9.35 mmol) were poured into RB and dissolved in THF (50 ml). The 20 ml aqueous solution of potassium carbonate (3.5 g, 25.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.25 mmol) were poured into the RB and the reaction mixture was heated up with stirring to reflux temperature for 12 h. Then the reaction mixture was cooled to room temperature and extracted using MC/water. The organic layer was collected and dehydrated using $MgSO_4$. A white solid was obtained after further purification using column chromatography with an eleuenet of MC:HEX.

Yield 75 %. ^{1}H NMR (300 MHz, DMSO-*d6*): δ 8.15 (t, 1H, J=6.9H_Z), 8.01 (t, 1H, J=7.7H_Z), 7.86 (d, 1H, J=8.4H_Z), 7.76 (d, 1H, J=8.1H_Z), 7.69-7.62 (m, 2H), 7.53 (t, 1H, J=7.8H_Z), 7.40 (d, 1H, J=7.2H_Z), 7.28 (t, 1H, J=7.7H_Z), 7.17 (d, 1H, J=7.8H_Z), MS (APCI) m/z 287.5 [$(M+H)^+$].

3-(Dibenzo[*b*,*d*]furan-2-yl)-2-fluorobenzonitrile

The same synthetic procedure for 3-(dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile was used except that 2-(dibenzo[*b*,*d*]furan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was replaced by dibenzo[*b*,*d*]furan-2-ylboronic acid (1.8 g, 8.49 mmol).

Yield 70 %. ^{1}H NMR (300 MHz, DMSO-*d6*): δ 8.40 (s, 1H), 8.20 (d, 1H, J=7.5H$_Z$), 8.04-7.94 (m, 2H), 7.83 (d, 1H, J=8.7H$_Z$), 7.75-7.70 (m, 2H), 7.58-7.51 (m, 2H), 7.43 (t, 1H, J=7.5H$_Z$), MS (APCI) m/z 287.2 [(M+H)$^+$].

3-(Dibenzo[*b*,*d*]furan-4-yl)-2-fluorobenzonitrile

The same synthetic procedure for 3-(dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile was used except that 2-(dibenzo[*b*,*d*]furan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was replaced by dibenzo[*b*,*d*]furan-4-ylboronic acid (1.8 g, 8.49 mmol).

Yield 80 %. ^{1}H NMR (300 MHz, DMSO-*d6*): δ 8.29 (d, 1H, J=7.5H$_Z$), 8.23 (d, 1H, J=7.8H$_Z$), 8.13-8.06 (m, 2H), 7.74 (d, 1H, J=8.1H$_Z$), 7.66-7.53 (m, 4H), 7.45 (t, 1H, J=7.5H$_Z$), MS (APCI) m/z 287.3 [(M+H)$^+$].

9-(2-Cyano-6-(dibenzo[*b*,*d*]furan-1-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (1DBF-2CNCZ)

3-(Dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile (0.9 g, 3.13 mmol) and 9*H*-carbazole-3,6-dicarbonitrile (0.7 g, 3.13 mmol) were poured into a pressure tube and dissolved in DMF (12 ml). The cesium carbonate (1.5 g, 4.70 mmol) were poured into the pressure tube and the reaction mixture was heated to 130 ℃ with stirring for 12 h. The reaction mixture was cooled to room temperature and precipitated with excess amount of water. The obtained precipitate through the filter was dissolved in MC and dehydrated using $MgSO_4$. A white solid was obtained after further purification using column chromatography with an eleuenet of MC:HEX. The white solid was recrystallized in toluene and vacuum sublimated to obtain highly pure product.

Yield 75 %. ^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.86 (s, 1H), 8.68 (s, 1H), 8.47 (d, 1H, J=7.5H$_Z$), 8.29 (d, 1H, J=7.5H$_Z$), 8.12 (t, 1H, J=8.0H$_Z$), 8.05 (d, 1H, J=8.5H$_Z$), 7.80 (d, 1H, J=8.5H$_Z$), 7.70 (d, 1H, J=8.5H$_Z$), 7.56 (t, 1H, J=8.5H$_Z$), 7.47 (d, 1H, J=7.5H$_Z$), 7.42 (d, 1H, J=8.0H$_Z$), 7.35 (t, 1H, J=7.8 H$_Z$), 7.21 (d, 1H, J=8.5H$_Z$), 7.00-6.96 (m, 2H), 6.59 (d, 1H, J=7.5H$_Z$) ^{13}C NMR (125MHz, DMSO-*d6*): δ 155.4, 155.2, 143.9, 142.1, 140.1, 137.2, 135.4, 135.0, 131.5, 131.3, 130.2, 129.8, 128.1, 126.8, 126.7, 126.5, 123.4, 122.3, 122.0, 121.8, 121.8, 121.7, 121.1, 119.4, 119.0, 115.5, 114.0, 112.2, 111.9, 111.8, 111.0, 103.9, 103.5. HRMS (FAB+) m/z 484.1318 [(M+H)+]; Calcd. For $C_{33}H_{16}N_4O$, 484.1324.

9-(2-Cyano-6-(dibenzo[*b*,*d*]furan-2-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (2DBF-2CNCZ)

The same synthetic procedure for 1DBF-2CNCZ compound was used except that 3-(dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile was replaced by 3-(dibenzo[*b*,*d*]furan-2-yl)-2-fluorobenzonitrile (0.9 g, 3.13 mmol).

Yield 70 %. ^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.83 (s, 2H), 8.31 (d, 1H, J=7.5H$_Z$), 8.22 (d, 2H, J=8.0H$_Z$), 8.05 (t, 1H, J=7.8H$_Z$), 7.92 (s, 1H), 7.87 (d, 1H, J=8.5H$_Z$), 7.78 (d, 1H, J=7.5H$_Z$), 7.61 (d, 1H, J=8.0H$_Z$), 7.48 (t, 3H, J=8.3H$_Z$), 7.36 (d, 1H, J=7.0H$_Z$), 7.33 (d, 1H, J=8.5H$_Z$), 6.97 (d, 1H, J=8.5H$_Z$) ^{13}C NMR (125MHz, DMSO-*d6*): δ 155.6, 154.9, 142.8, 142.5, 137.2, 134.3, 134.2, 131.5, 130.9, 128.1, 126.7, 126.5, 123.6, 123.4, 122.7, 121.9, 120.8, 120.6, 119.3, 115.6, 113.2, 111.8, 111.7, 111.5, 103.8. HRMS (FAB+) m/z 484.1326 [(M+H)+]; Calcd. For $C_{33}H_{16}N_4O$, 484.1324.

9-(2-Cyano-6-(dibenzo[*b*,*d*]furan-4-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (4DBF-2CNCZ)

The same synthetic procedure for 1DBF-2CNCZ compound was used except that 3-(dibenzo[*b*,*d*]furan-1-yl)-2-fluorobenzonitrile was replaced by 3-(dibenzo[*b*,*d*]furan-4-yl)-2-fluorobenzonitrile (0.9 g, 3.13 mmol).

Yield 75 %. ^{1}H NMR (500 MHz, DMSO-*d6*): δ 8.64 (s, 2H), 8.40 (d, 1H, J=7.5H$_Z$), 8.27 (d, 1H, J=8.0H$_Z$), 8.10 (t, 1H, J=7.8H$_Z$), 7.91 (d, 1H, J=7.5H$_Z$), 7.87 (d, 1H, J=7.5H$_Z$), 7.83 (d, 2H, J=8.5H$_Z$), 7.50 (d, 2H, J=8.5H$_Z$), 7.39-7.34 (m, 2H), 7.25 (t, 1H, J=7.5H$_Z$), 7.21 (t, 1H, J=7.8H$_Z$), 6.96 (d, 1H, J=8.0H$_Z$) ^{13}C NMR (125MHz, DMSO-*d6*): δ 154.7, 151.9, 142.3, 137.8, 137.2, 135.4, 135.1, 131.4, 130.4, 127.8, 127.7, 126.4, 123.3, 123.2, 123.2, 122.6, 121.7, 121.6, 121.2, 120.2, 119.3, 115.7, 113.0, 112.2, 110.7, 103.5. HRMS (FAB+) m/z 484.1324 [(M+H)+]; Calcd. For $C_{33}H_{16}N_4O$, 484.1324.

Device fabrication and measurements

Blue TADF devices were fabricated based on the device structure of indium tin oxide (50 nm)/DNTPD (40 nm)/BPBPA (10 nm)/PCZAc (10 nm)/host:5CzCN (30 nm : 20 wt%)/DBFTrz (5 nm)/NAPIm (20 nm)/LiF (1.5 nm)/Al (200 nm), 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-9*H*-carbazol-3-yl)-9,10-dihydroacridine, DBFTrz is 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b*,*d*]thiophene, and NAPIm is 9,10-di(naphthalene-2-yl)anthracen-2-yl-(4,1-phenylene)(1-phenyl-1*H*benzo[*d*]imidazole and LiF is lithium fluoride. The host of blue TADF device was the mixed host system that was composed of hole transport type 3,3'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (mCBP) and newly synthesized electron transporting host with different host compositions of 75:25, 50:50 and 25:75. The electron only device structure was ITO (50 nm)/PEDOT:PSS (60 nm)/TSPO1 (10 nm)/host (25 nm)/TSPO1 (5 nm)/TPBi (40 nm)/LiF (1.5 nm)/Al (200 nm), where PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and TSPO1 is diphenylphosphine oxide-4-(triphenylsilyl)phenyl.

Vacuum thermal evaporation process was used in the device fabrication, and the devices were encapsulated for the device test. Device performance analysis was carried out using measurement system of Keithley 2400 and CS 1000 (Konica Minolta Inc.) spectroradiometer. Lifetime test was carried out in dark condition using Polaronix (McScience Co.) lifetime measurement system equipped with electrical source and photodiode as a detecting unit.

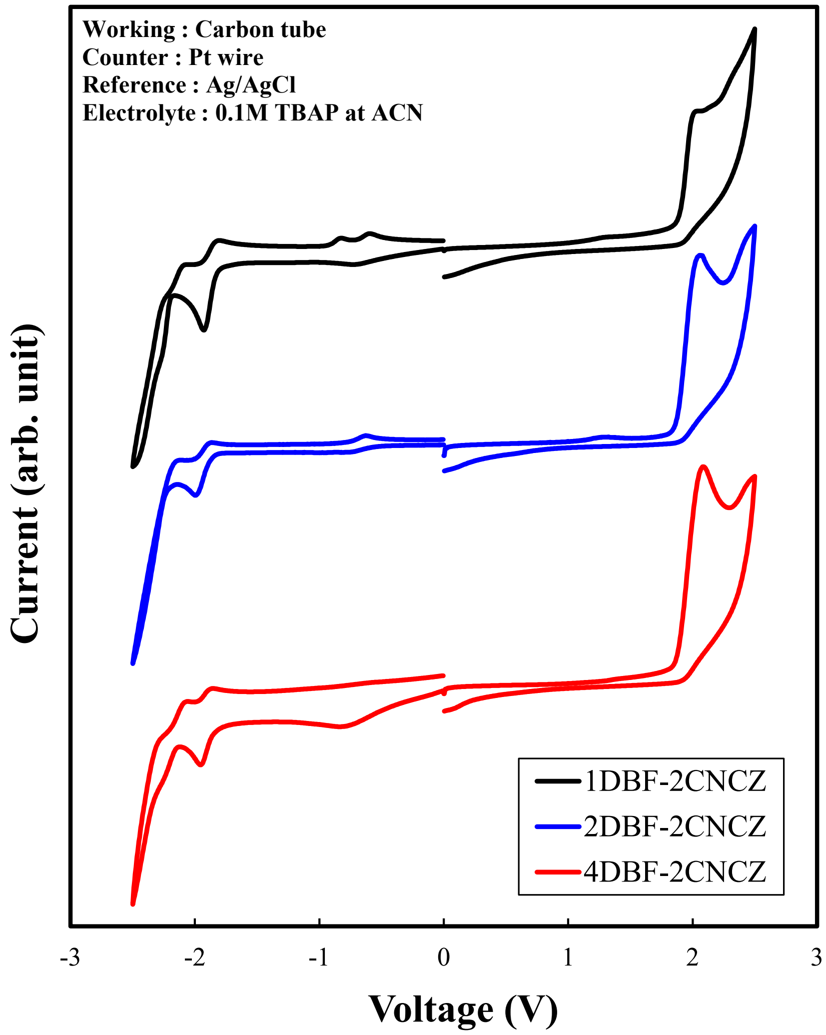


Figure S1. Oxidation and reduction scan data of ET host materials carried out by cyclic voltammetry

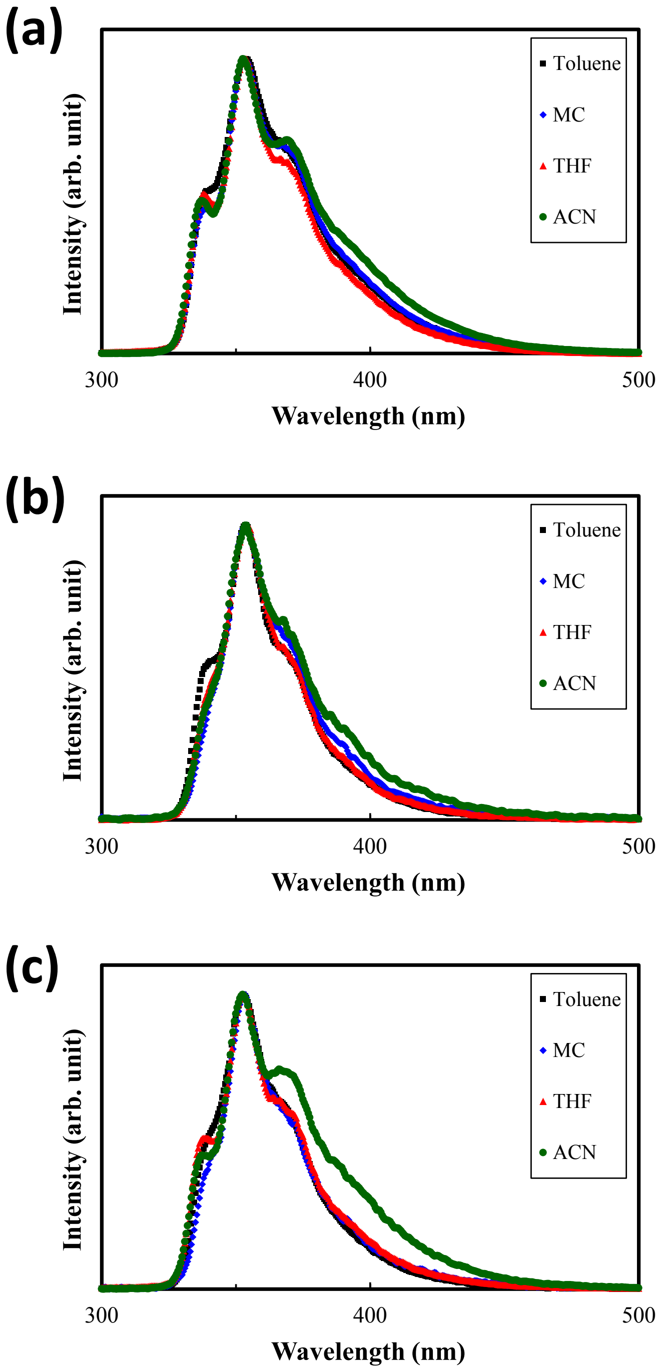


Figure S2 The emission spectra of 1DBF-2CNCZ (a), 2DBF-2CNCZ (b) and 4DBF-2CNCZ (c) under different solvent polarity.

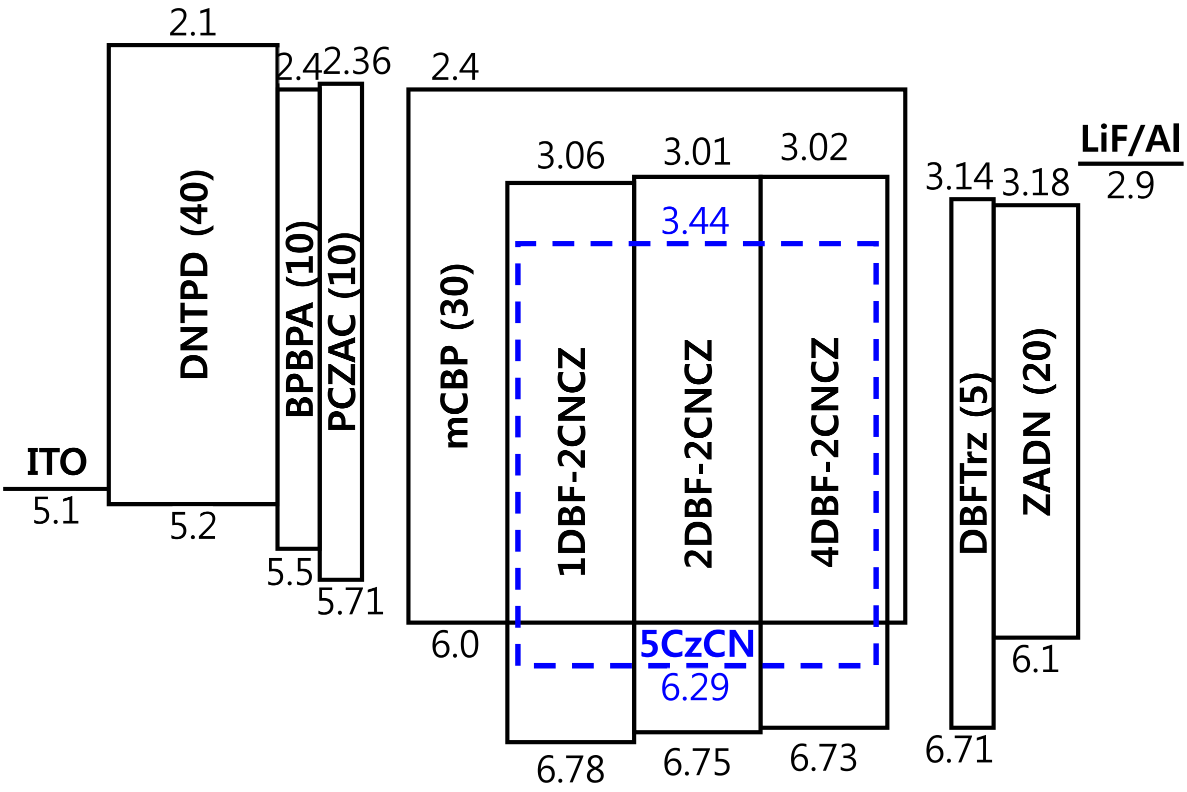


Figure S3 Device structure and energy level diagram of the TADF devices.

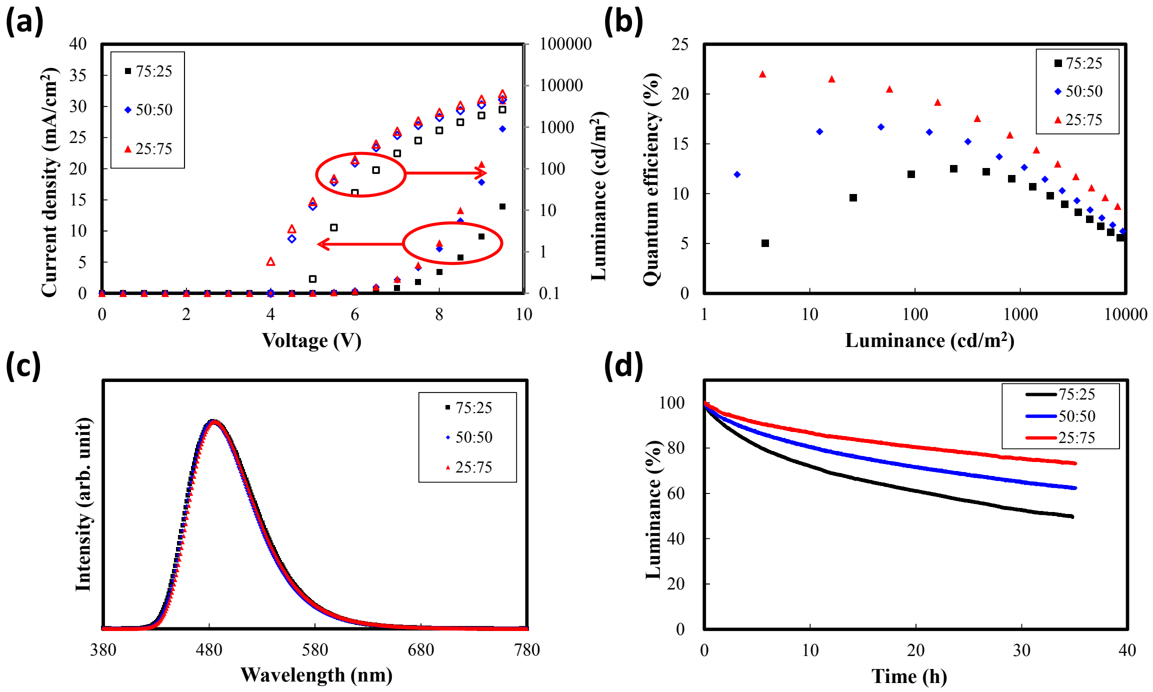


Figure S4 Current density and luminance plots against voltage sweep (a), external quantum efficiency (b), electroluminescence spectra (c) and device lifetime at different concentration of 2DBF-2CNCZ host material.

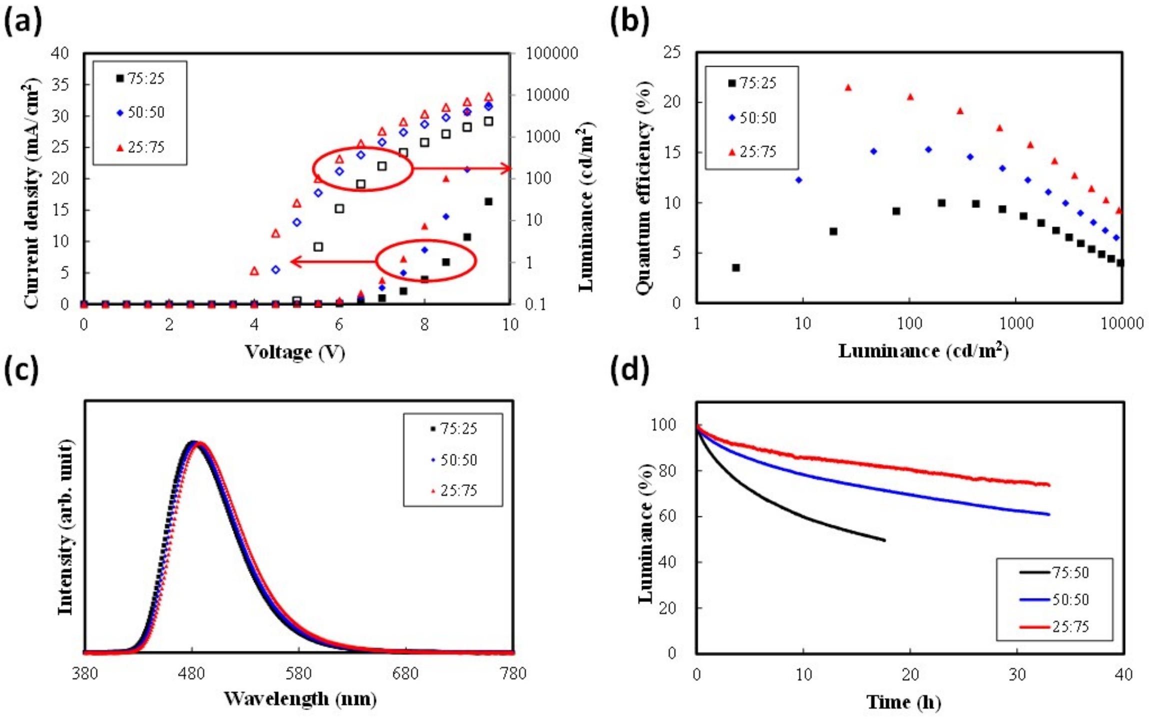
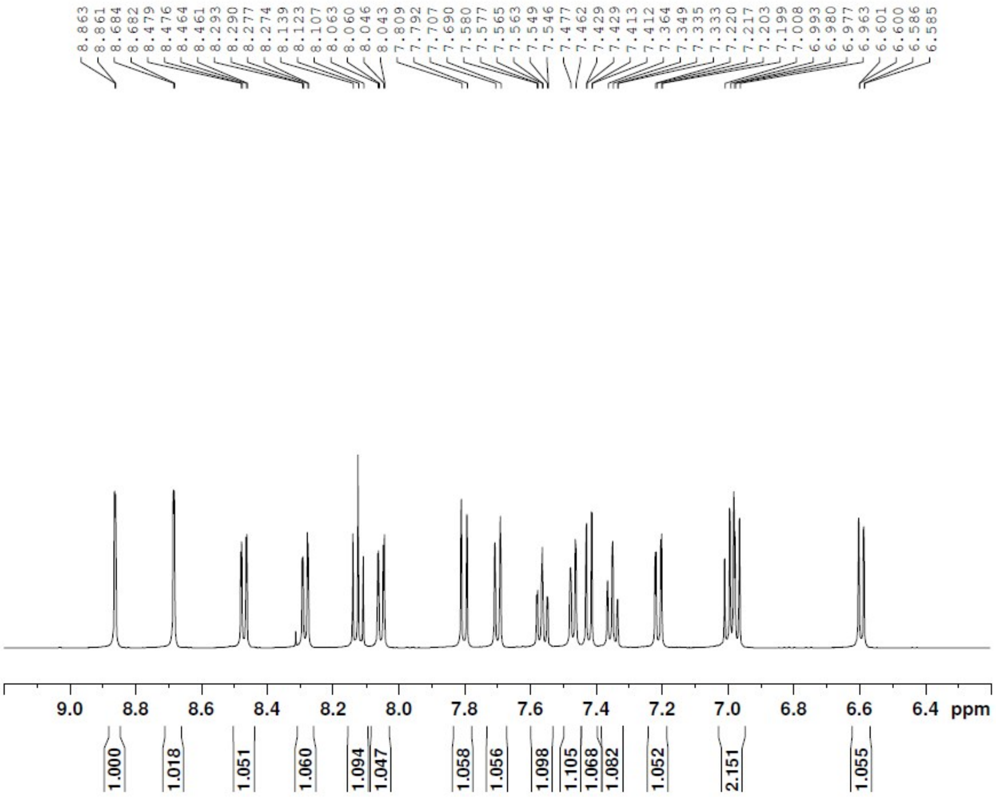
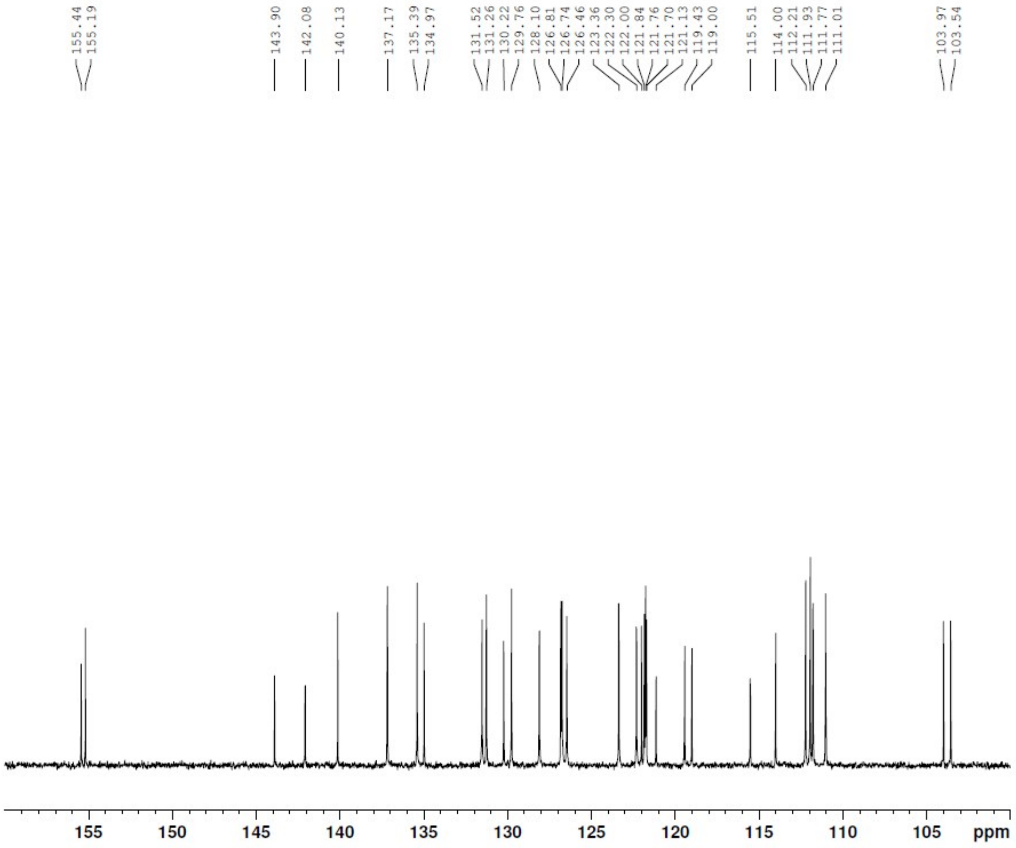


Figure S5 Current density and luminance plots against voltage sweep (a), external quantum efficiency (b), electroluminescence spectra (c) and device lifetime at different concentration of 4DBF-2CNCZ host material.

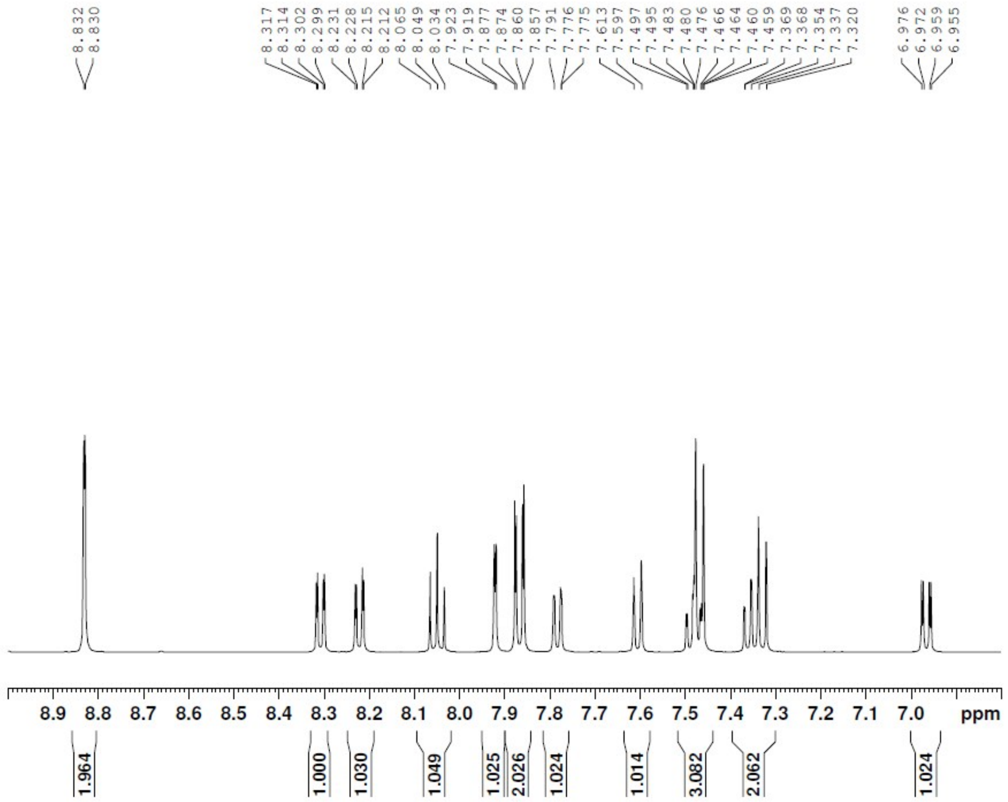
(a) 1DBF-2CNCZ – 1H



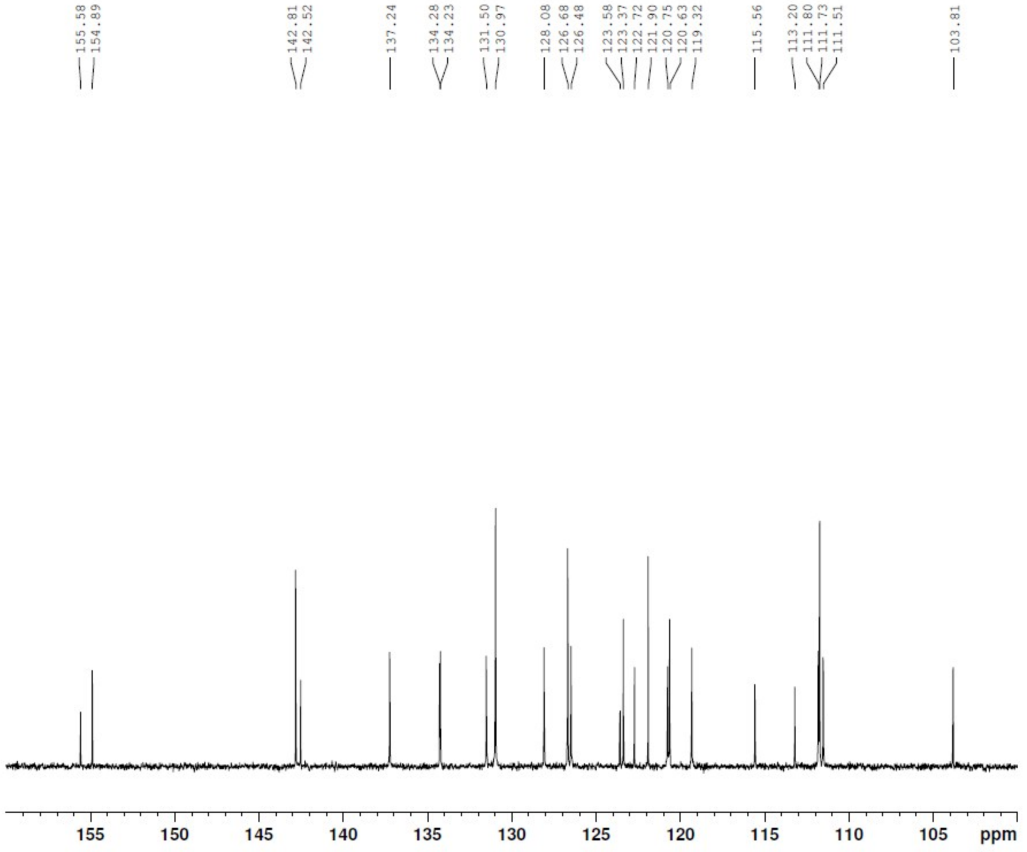
1DBF-2CNCZ – 13C



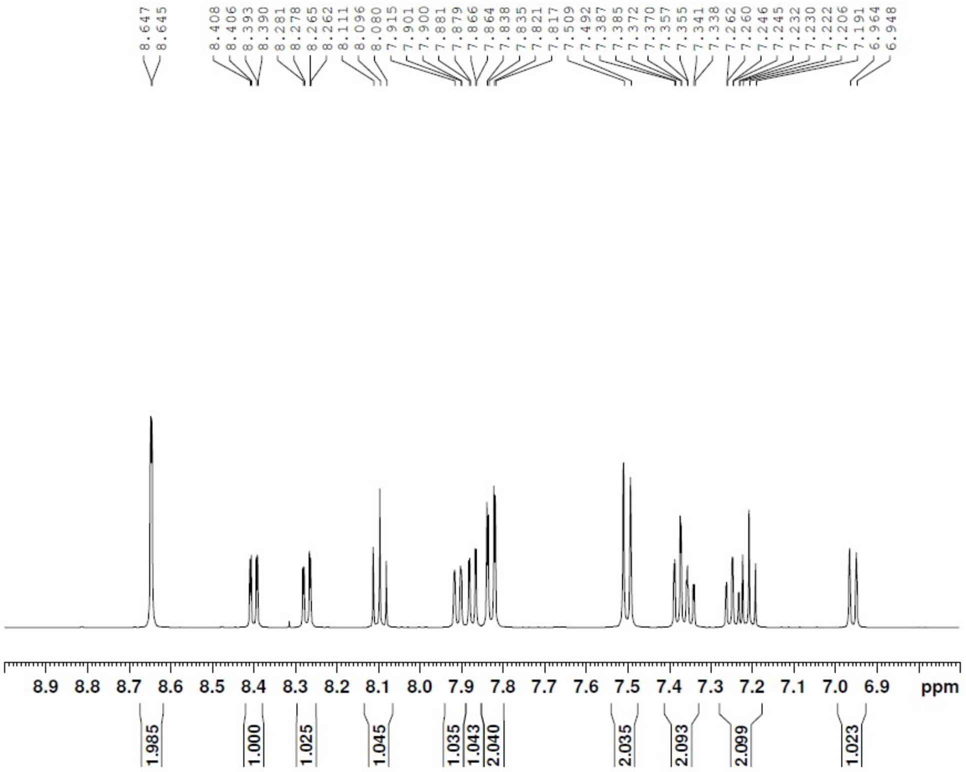
(b) 2DBF-2CNCZ – 1H



2DBF-2CNCZ – 13C



(c) 4DBF-2CNCZ – 1H



4DBF-2CNCZ – 13C

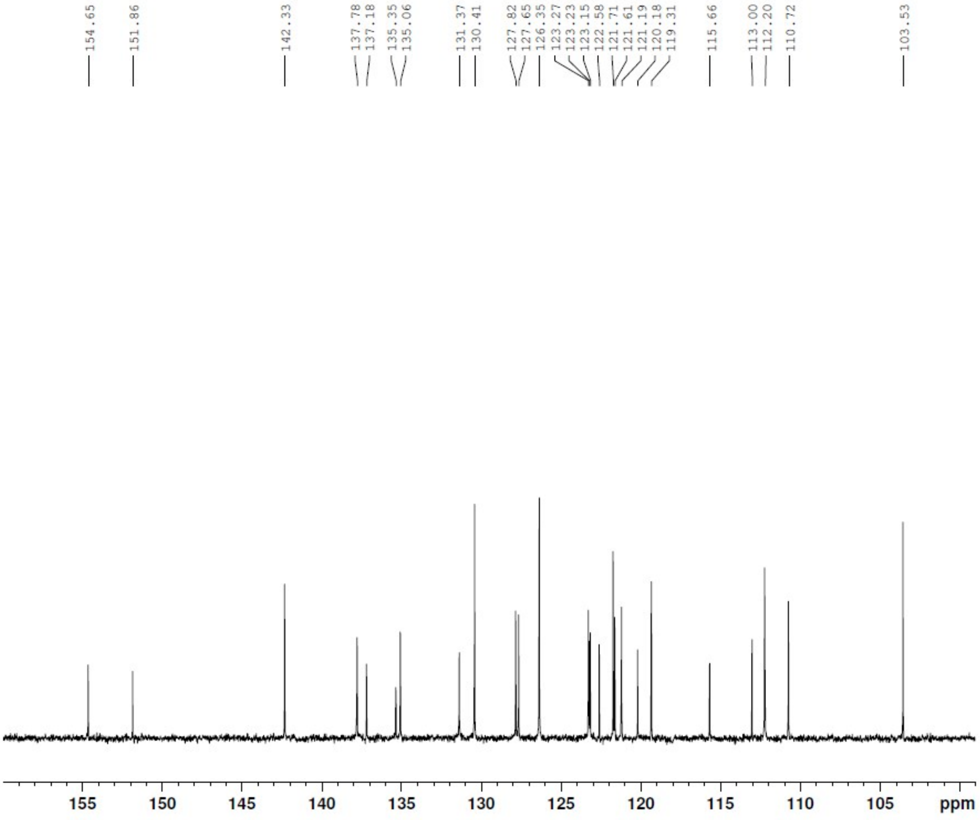


Figure S6 ^{1}H and ^{13}C NMR spectra of the final compounds

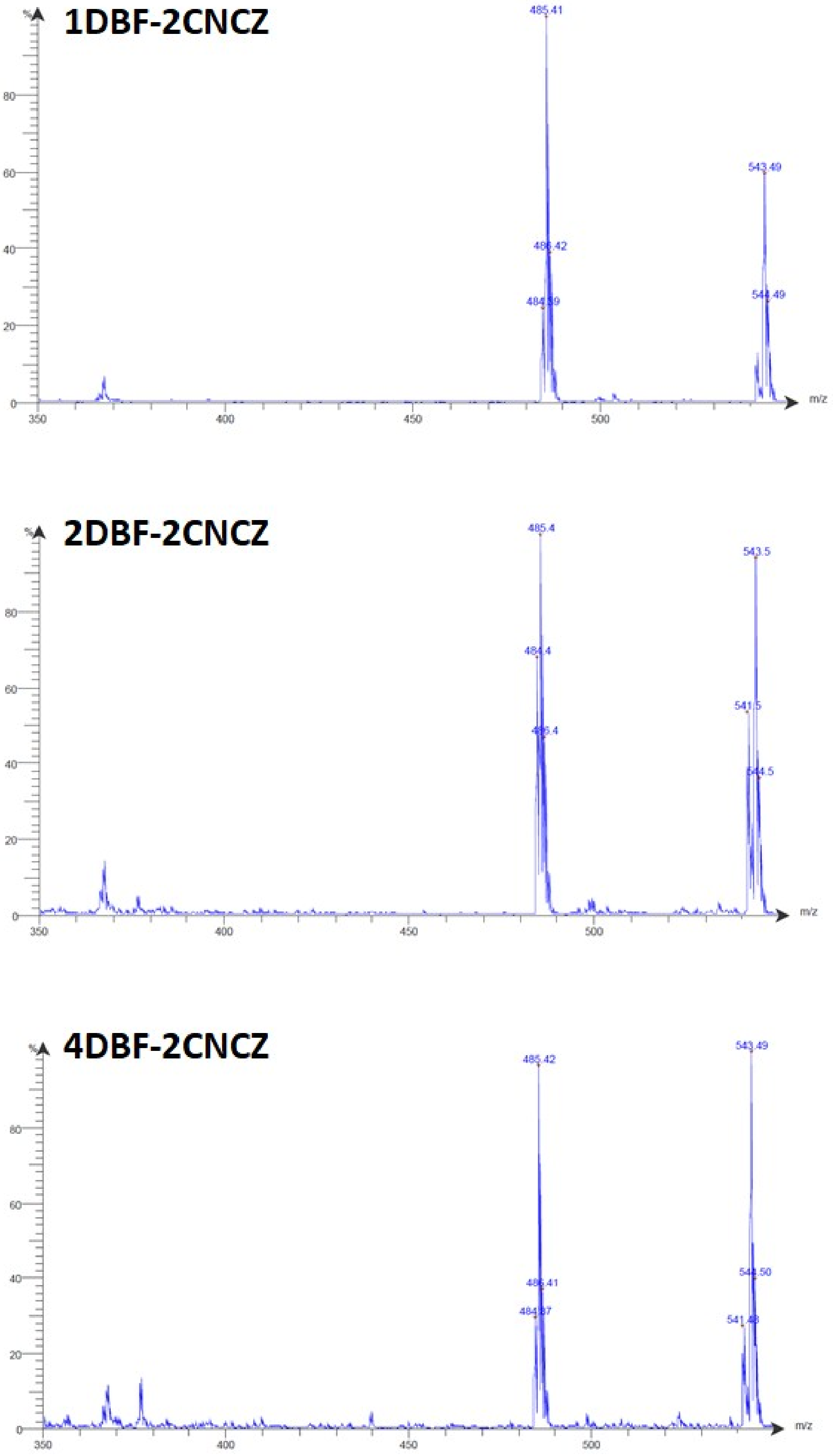


Figure S7. Mass spectra of the final compounds of 1DBF-2CNCZ, 2DBF-2CNCZ and 4DBF-2CNCZ.

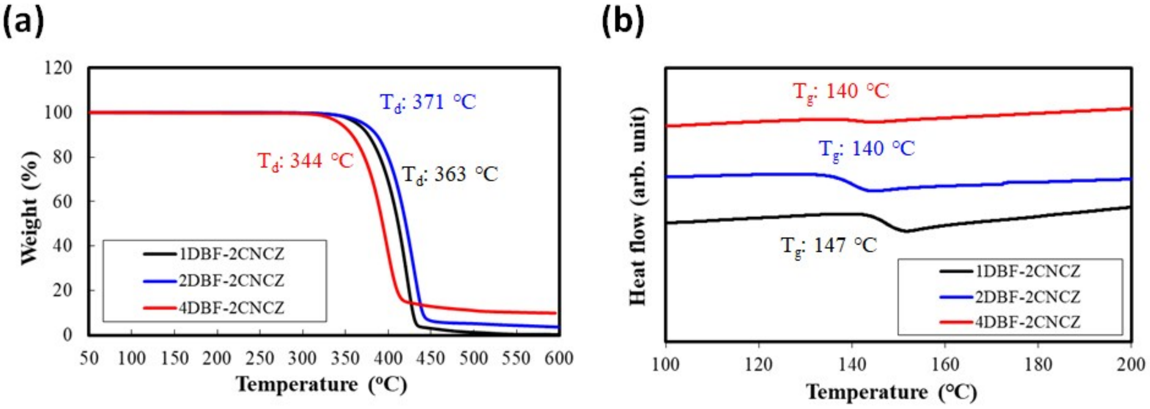


Figure S8. (a) Thermogravimetric analysis (TGA) and (b) Differential scanning calorimetry (DSC) results of 1DBF-2CNCZ, 2DBF-2CNCZ and 4DBF-2CNCZ.

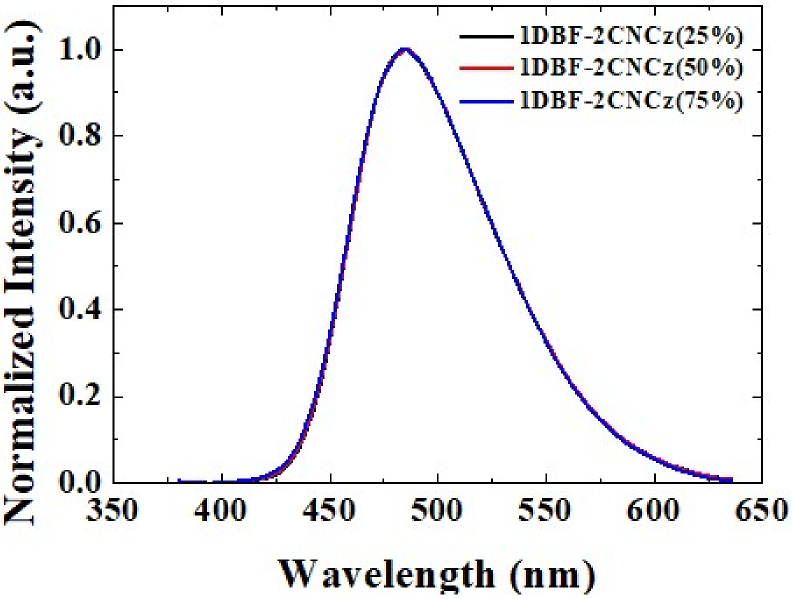


Figure S9. The PL emission spectra of the 5CzCN doped (20 wt%) mixed host system consisting of the mCBP and the 1DBF-2CNCZ host at compositions of 75:25, 50:50 and 25:75.