

Supporting information

Lowest unoccupied molecular orbital managing function of CN-substituted dibenzofuran in high triplet energy hosts for blue thermally-activated delayed fluorescent organic light-emitting diodes

Sung Yong Byeon,⁺ Kyung Hyung Lee,⁺ 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

⁺ Sung Yong Byeon and Kyung Hyung Lee contributed equally

Experimental

General information

3-Bromo-2-fluorobenzonitrile, palladium(II) acetate, 9*H*-carbazole-3,6-dicarbonitrile, tetrakis(triphenylphosphine)palladium(0) (P&H tech), cesium carbonate, potassium carbonate, sodium carbonate, magnesium sulfate (MgSO₄), *N,N*-dimethylformamide (DMF) (Duksan Sci. Co.), acetic anhydride, acetic acid, sulfuric acid, *N,N*-dimethylacetamide (DMAc) (Daejung Chemical & Metal Co.), iodobenzene diacetate, iodine, potassium hexacyanoferrate(II) trihydrate, (Thermo Fisher Scientific, Inc) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-phos), dimethylsulfoxide-d₆ (Sigma-Aldrich Co. LLC.) 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 ¹H and ¹³C 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 HOMO and LUMO energy levels were estimated using a cyclic voltammetry (Ivium Tech., Iviumstat). The mass spectra were recorded using a Advion, Expression^L CMS spectrometer in APCI mode.

Synthesis

3-(Dibenzo[*b,d*]furan-4-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 a round-bottomed flask (RB) and dissolved in THF (50 ml). A 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 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 MgSO₄. A white solid was obtained after further purification using column chromatography with an eluent of methylene chloride (MC):n-hexane (HEX).

Yield 80%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.15 (t, 1H, J=6.9Hz), 8.01 (t, 1H, J=7.7Hz), 7.86 (d, 1H, J=8.4Hz), 7.76 (d, 1H, J=8.1Hz), 7.69-7.62 (m, 2H), 7.53 (t, 1H, J=7.8Hz), 7.40 (d, 1H, J=7.2Hz), 7.28 (t, 1H, J=7.7Hz), 7.17 (d, 1H, J=7.8Hz), MS (APCI) m/z 287.3 [(M+H)⁺].

2-Fluoro-3-(8-iododibenzo[*b,d*]furan-4-yl)benzonitrile

3-(Dibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile (10.0 g, 34.81 mmol) and iodobenzene diacetate (5.6 g, 17.40 mmol) were poured into RB and dissolved in mixed solvent of acetic anhydride / acetic acid (50:50, 50 ml) with stirring. Iodine (4.4 g, 17.40 mmol) was poured into reaction mixture and it was stirred for 30 min, and then sulfuric acid (0.3 ml) was slowly

added into the reaction mixture overnight. The reaction mixture was poured into the ice water for neutralization, and filtered to obtain a pale yellow solid. A white solid was obtained after washing with n-hexane. The obtained solid was a mixture of non-substituted, mono-substituted and di-substituted compounds with a mixing ratio of 8:80:12. The mixture was not isolated in this synthetic step.

Yield 85%. MS (APCI) m/z 413.5 [(M+H)⁺].

3-(2,8-Diododibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile

The same synthetic procedure to prepare 2-fluoro-3-(8-iododibenzo[*b,d*]furan-4-yl)benzonitrile was used except for the amount of iodobenzene diacetate (11.2 g, 34.81 mmol) and iodine (8.8 g, 34.81 mmol). The obtained solid were a mixture of non-substituted, mono-substituted and di-substituted compound with mixing ratio of 8:23:69. The mixture was not isolated in this synthetic step.

Yield 70%. MS (APCI) m/z 540.2 [(M+H)⁺].

6-(3-Cyano-2-fluorophenyl)dibenzo[*b,d*]furan-2-carbonitrile

2-Fluoro-3-(8-iododibenzo[*b,d*]furan-4-yl)benzonitrile (3.0 g, 7.26 mmol), potassium hexacyanoferrate(II) trihydrate (0.9 g, 2.18 mmol), palladium(II) acetate (0.08 g, 0.36 mmol), X-phos (0.5 g, 1.09 mmol) and sodium carbonate (2.3 g, 21.78 mmol) were poured into the RB, dissolved in DMAc (25 ml), and heated to 130 °C with stirring for 10 h. The reaction mixture was cooled to room temperature and extracted with MC and distilled water (DW). The obtained organic phase was dehydrated using MgSO₄ and a white solid was obtained after further purification using column chromatography with an eleuent of MC:HEX.

Yield 60%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.64 (s, 1H), 8.30 (d, 1H, J=7.8Hz), 8.06 (t, 2H, J=7.7Hz), 7.81 (d, 1H, J=8.7Hz), 7.64 (t, 1H, J=7.5Hz), 7.59-7.52 (m, 3H), MS (APCI) m/z 313.1 [(M+H)⁺].

4-(3-Cyano-2-fluorophenyl)dibenzo[*b,d*]furan-2,8-dicarbonitrile

The same synthetic procedure to prepare 6-(3-cyano-2-fluorophenyl)dibenzo[*b,d*]furan-2-carbonitrile was used except the amount of the potassium hexacyanoferrate(II) trihydrate (1.8 g, 4.36 mmol) and sodium carbonate (4.6 g, 43.56 mmol).

Yield 50%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.93 (s, 1H), 8.87 (s, 1H), 8.28 (s, 1H), 8.17-8.11 (m, 3H), 8.05 (t, 1H, J=8.3Hz), 7.64 (t, 1H, J=7.8Hz), MS (APCI) m/z 338.2 [(M+H)⁺].

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

3-(Dibenzo[*b,d*]furan-4-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 (15 ml). Cesium carbonate (1.5 g, 4.70 mmol) was poured into the pressure tube and the reaction mixture was heated to 130 °C 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 MgSO₄. A white solid was obtained after further purification using column chromatography using an eleuent of MC:HEX. The white solid was recrystallized in toluene and vacuum sublimated to obtain a highly pure product.

Yield 75%. ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.86 (s, 1H), 8.68 (s, 1H), 8.47 (d, 1H, J=7.5Hz), 8.29 (d, 1H, J=7.5Hz), 8.12 (t, 1H, J=8.0Hz), 8.05 (d, 1H, J=8.5Hz), 7.80 (d, 1H, J=8.5Hz), 7.70 (d, 1H, J=8.5Hz), 7.56 (t, 1H, J=8.5Hz), 7.47 (d, 1H, J=7.5Hz), 7.42 (d, 1H, J=8.0Hz), 7.35 (t, 1H, J=7.8 Hz), 7.21 (d, 1H, J=8.5Hz), 7.00-6.96 (m, 2H), 6.59 (d, 1H,

$J=7.5\text{Hz}$) ^{13}C NMR (125MHz, DMSO- d_6): 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. MS (APCI) m/z 484.8 [(M+H) $^+$].

9-(2-Cyano-6-(8-cyanodibenzo[*b,d*]furan-4-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (4DBFCN-2CNCZ)

The same synthetic procedure to prepare 4DBF-2CNCZ compound was used except for the starting material change from 3-(dibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile to 6-(3-cyano-2-fluorophenyl)dibenzo[*b,d*]furan-2-carbonitrile (1.0 g, 3.20 mmol).

Yield 85 %. ^1H NMR (500 MHz, CDCl_3) δ 8.20 – 8.16 (m, 2H), 8.13 (ddd, $J = 7.8, 5.6, 1.5$ Hz, 2H), 8.10 – 8.08 (m, 1H), 7.96 (t, $J = 7.9$ Hz, 1H), 7.72 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.64 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.61 (dd, $J = 8.5, 1.5$ Hz, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.09 (m, 2H), 6.98 (dd, $J = 8.6, 0.4$ Hz, 1H), ^{13}C NMR (125MHz, CDCl_3): δ 157.2, 153.2, 142.7, 137.7, 137.5, 136.3, 134.8, 131.7, 131.0, 130.6, 128.4, 126.0, 125.9, 124.4, 124.3, 123.1, 122.5, 122.3, 120.7, 119.3, 118.8, 115.3, 114.6, 112.2, 111.6, 107.6, 105.4. MS (HR-FAB) m/z : Found 510.1355 [(M+H) $^+$]. Calculated for $\text{C}_{34}\text{H}_{15}\text{N}_5\text{O}$ 510.1350.

9-(2-Cyano-6-(2,8-dicyanodibenzo[*b,d*]furan-4-yl)phenyl)-9*H*-carbazole-3,6-dicarbonitrile (4DBF2CN-2CNCZ)

The same synthetic procedure to prepare the 4DBF-2CNCZ compound was used except for the change of starting material from 3-(dibenzo[*b,d*]furan-4-yl)-2-fluorobenzonitrile to 6-(3-cyano-2-fluorophenyl)dibenzo[*b,d*]furan-2,8-dicarbonitrile (1.2 g, 3.84 mmol).

Yield 80%. ^1H NMR (500 MHz, CDCl_3) δ 8.22 – 8.21 (m, 2H), 8.20 (dd, $J = 7.8, 1.6$ Hz, 1H), 8.13 – 8.09 (m, 2H), 8.06 (d, $J = 1.6$ Hz, 1H), 8.01 (t, $J = 7.8$ Hz, 1H), 7.72 (dd, $J = 8.6,$

1.7 Hz, 1H), 7.68 (dd, $J = 8.5, 1.5$ Hz, 2H), 7.53 (d, $J = 1.6$ Hz, 1H), 7.23 (d, $J = 8.5$ Hz, 2H), 6.95 – 6.92 (m, 1H). ^{13}C NMR (125MHz, CDCl_3): δ 157.4, 154.6, 142.3, 142.2, 137.0, 136.4, 135.6, 135.3, 133.0, 131.7, 131.4, 131.2, 131.1, 130.8, 130.7, 130.6, 128.3, 128.1, 127.0, 126.3, 126.2, 126.0, 125.9, 124.0, 122.6, 122.4, 122.3, 118.8, 117.8, 117.2, 114.9, 114.7, 112.4, 111.2, 111.0, 108.8, 108.7, 105.8, 105.7. MS (HR-FAB) m/z : Found 535.1307 $[[\text{M}+\text{H}]^+]$. Calculated for $\text{C}_{35}\text{H}_{14}\text{N}_6\text{O}$ 535.1302

Comment [K]: 업 exact mass가 맞습니다.

Device fabrication and measurements

Blue TADF devices were fabricated based on the device structure of ITO (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 ITO is indium tin oxide, 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 hosts with the host compositions of 50:50. 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), TSPO1 is diphenylphosphine oxide-4-(triphenylsilyl)phenyl and TPBi is 1,3,5-tris(*N*-phenylbenzimidazol-2-yl) benzene. 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.

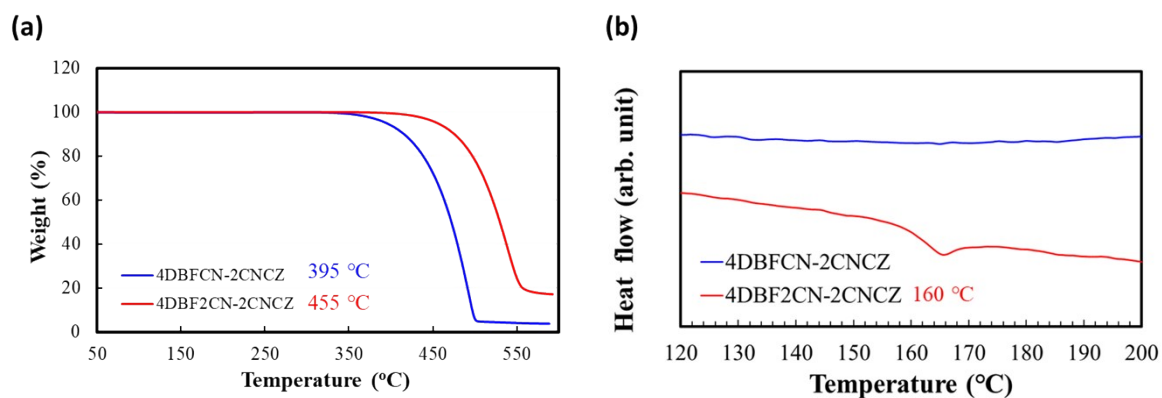


Figure S1. (a) TGA and (b) DSC of 4DBFCN-2CNCZ and 4DBF2CN-2CNCZ hosts at a heating ratio of 10°C/min and thermal decomposition temperature at 5% weight loss.

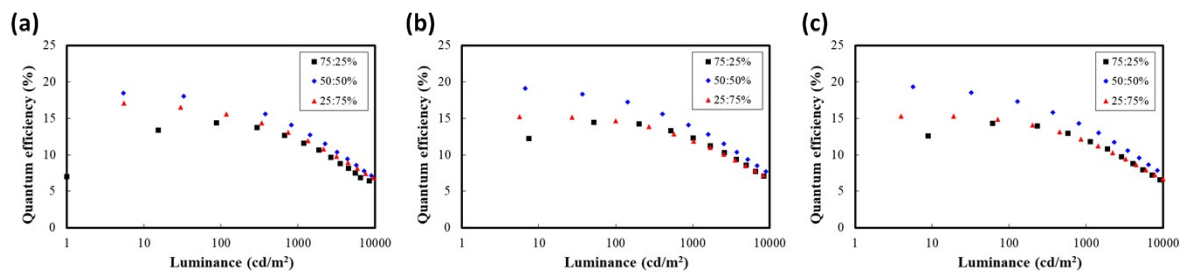


Figure S2. (a) 4DBF-2CNCZ, (b) 4DBFCN-2CNCZ and (c) 4DBF2CN-2CNCZ hosts of different ratio of the mCBP and n type hosts (75:25, 50:50 and 25:75%) of the EQE-L curves.

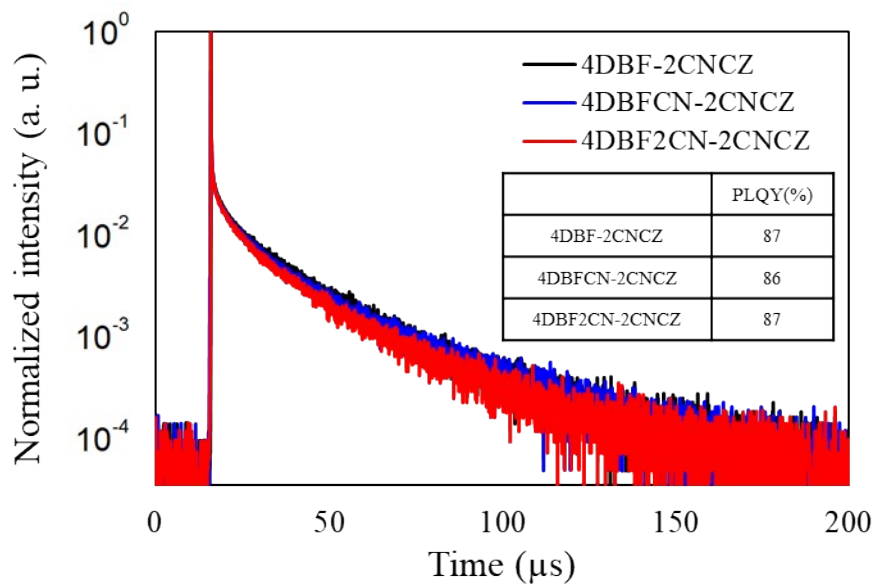


Figure S3. PLQY and transient PL of mCBP:n-type hosts:5CzCN (40:40:20%) films.

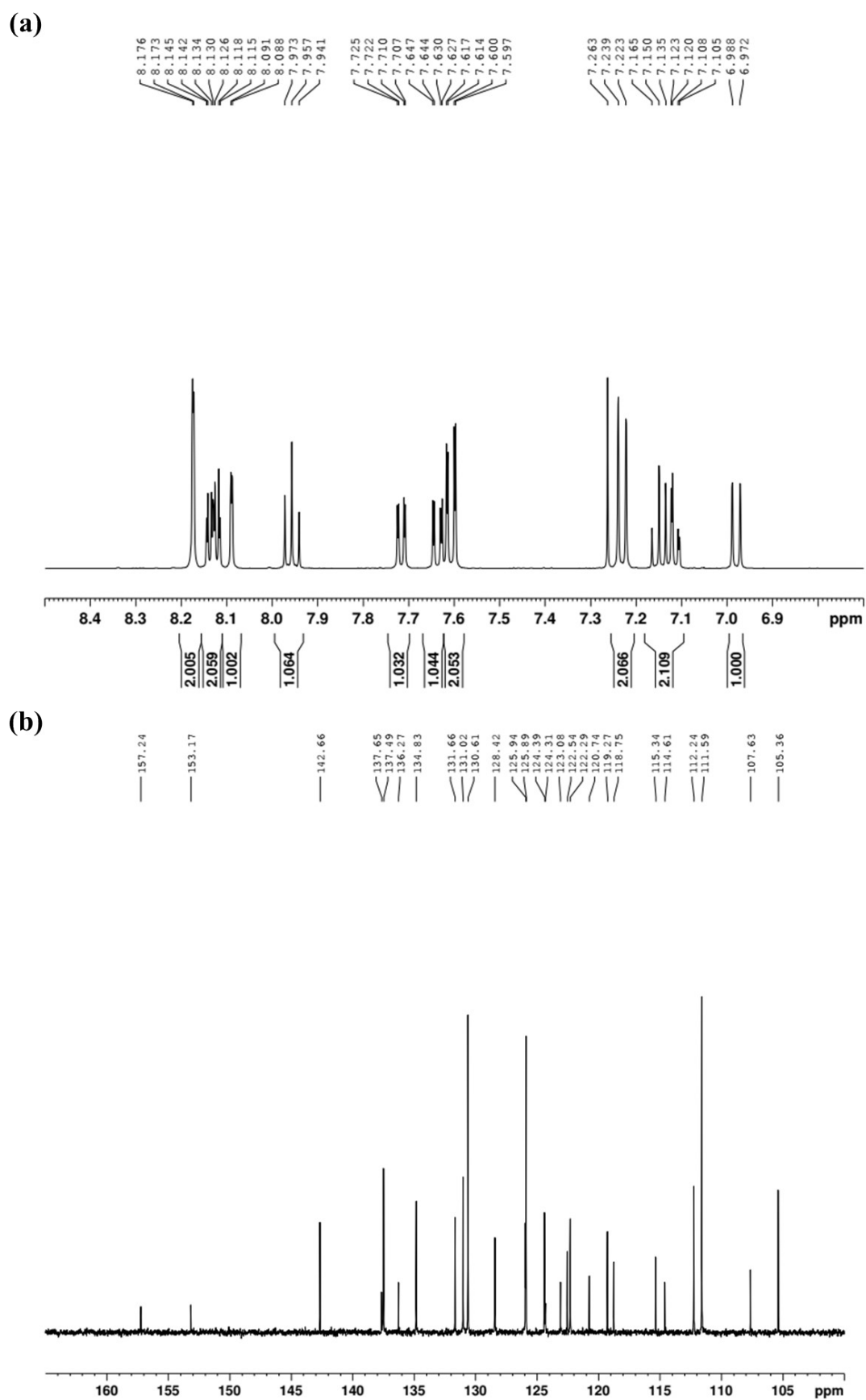


Figure S4. (a) ^1H and (b) ^{13}C NMR data of 4DBFCN-2CNCZ.

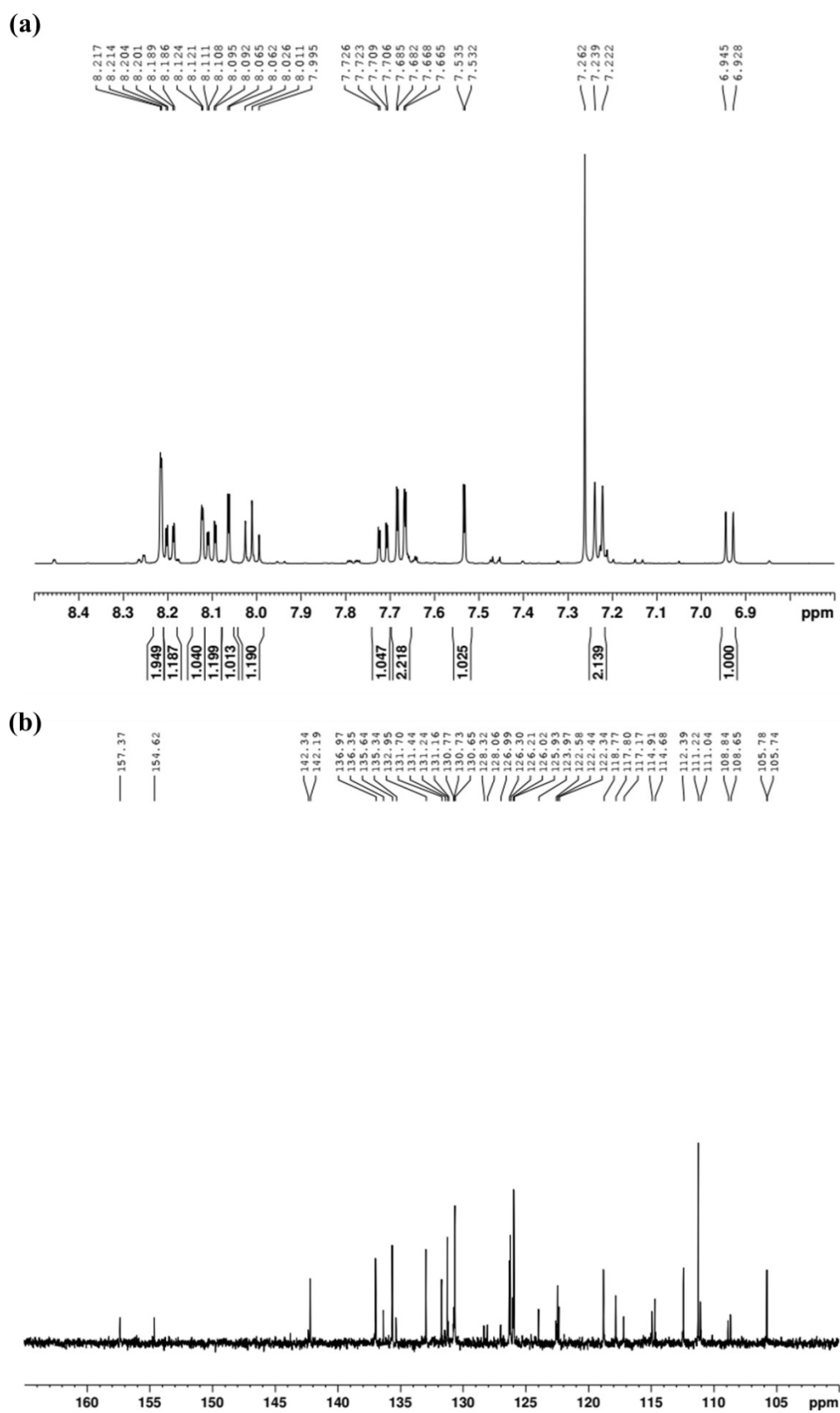


Figure S5. (a) ^1H and (b) ^{13}C NMR data of 4DBF2CN-2CNCZ.