Supporting Information

Dibenzo[*b*,*d*]furan/thiophene-fused double boron-based multiresonance emitters with narrowband ultrapure green electroluminescence

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I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. Absorption spectra were obtained on a HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. To reduce the fluctuation in the excitation intensity, the xenon lamp was kept on for 1 hour prior to the experiments. The excited state lifetimes were obtained using an HORIBA TEMPRO-01 instrument. Thermogravimetric analysis (TGA) was carried out using DTG-60(H) at a rate of 10 ºC/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) thermograms were recorded on DSC 200PC equipment under nitrogen atmosphere at a rate of 10 ºC/min. Cyclic voltammogram were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in DCM as electrolyte and ferrocene/ferrocenium (Fc/Fc$^+$) as standard. Three-electrode system (Ag/Ag$^+$, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurement.

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. 1,2-Dichlorobenzene [98%, extra dry, with molecular sieves, water $\leqslant$ 50 ppm (by K.F.), Energy Seal] was purchased from Shanghai Energy Chemical CO., Ltd.

II. OLED Fabrication and Characterization

ITO (indium tin oxide) glass substrates with a sheet resistance of 15 Ω per square were

cleaned with alkaline detergent, boiled deionized water, and deionized water thoroughly in ultrasonic bath and then treated with O_2 plasma for 10 min. All the organic layers were deposited onto the ITO-coated substrates by thermal evaporation in a high vacuum chamber below 5×10^{-4} mbar in an inert gas glovebox. The quartz crystal oscillators controlled the thicknesses of deposited films. The as-fabricated OLEDs were measured in the inert gas glovebox without any encapsulation. Current density of OLEDs was measured by KEYSIGHT B1500A. The luminance and EL spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

III. Theoretical Calculation

All theoretical calculations were performed using Gaussian 09 serials software. The ground-state structures and FMOs were obtained by B3LYP density functional method with basis set 6-31G*.[1,2] The S_1 and T_1 energies were calculated by time-dependent DFT (TD-DFT) method with the same parameters for ground-state calculations. The HOMO and LUMO distributions were visualized using Gauss view 5.0 software. Natural Transition Orbital (NTO) analysis were carried out on S_1 and T_1 geometry under CAM-B3LYP/6-31G(d) method.[3] In addition, the polarizable continuum model (PCM) was applied to take account of the polarization effect of the solid-state environment with taking the toluene as reference solvent. Electron densities were calculated by using Multiwfn 3.7 program with crystal geometry.[4]

The rate constants of radiative decay (k_R), the rate constants of intersystem crossing (k_{ISC}) and reverse intersystem crossing (k_{RISC}) could be estimated using the following equations.[5]

$$\Phi_P = C_1 \Phi_{PL}$$

$$\Phi_d = C_2 \Phi_{PL}$$
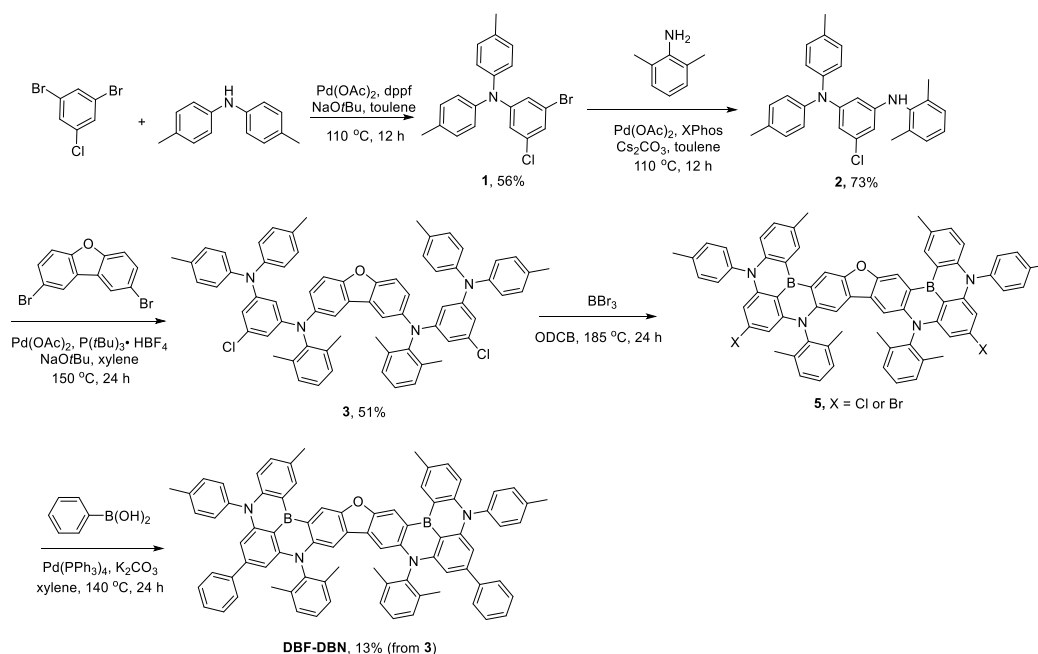
$$k_R = \Phi_P/\tau_p = \Phi_{PL}C_1/\tau_p$$

$$k_{ISC} = (1-\Phi_P)/\tau_p = (1-\Phi_{PL}C_1)/\tau_p$$

$$k_{RISC} = \Phi_d/(k_{ISC}\tau_p\tau_d\Phi_p) = C_2/[C_1\tau_d(1-\Phi_{PL}C_1)]$$

Where Φ_p and Φ_d represent prompt and delayed fluorescence components and can

be distinguished from the total Φ_{PL} by comparing the integrated intensities of prompt (C_1) and delayed components (C_2) in the transient PL spectra.

IV. Synthesis and Characterization

Scheme S1. Synthetic route to **DBF-DBN**.

3-Bromo-5-chloro-*N,N*-di-*p*-tolylaniline (1): A dried round bottle flask with a magnetic stir bar was charged with corresponding 1,3-dibromo-5-chlorobenzene (10 g, 36 mmol), di-*p*-tolylamine (7 g, 36 mmol), Pd(OAc)$_2$ (234 mg, 1.4 mmol), dppf (1.2 g, 2 mmol), NaOtBu (4.6 g, 48 mmol) and toluene 100 mL under a N$_2$ atmosphere. The mixture was stirred for 12 h at 110 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/DCM = 100/1) to provide the compound **1** as a white solid in 56% yield (7.78 g, 20.2 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.33 (s, 6H), 6.83 (t, *J* = 1.6 Hz, 1H), 6.95 (t, *J* = 1.6 Hz, 1H), 6.97 (t, *J* = 1.6 Hz, 1H), 6.99(d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.0, 119.1, 121.5, 122.9, 123.0, 125.7, 130.4, 134.3, 135.4, 144.0, 150.6 ppm. HRMS (ESI$^+$): calcd for C$_{20}$H$_{17}$^{79}Br^{35}ClN [M+H]$^+$, 386.0306, found 386.0307, calcd for C$_{20}$H$_{17}$^{81}Br^{35}ClN [M+H]$^+$, 388.0285; found 388.0272; calcd for C$_{20}$H$_{17}$^{81}Br^{37}ClN [M+H]$^+$, 390.0256
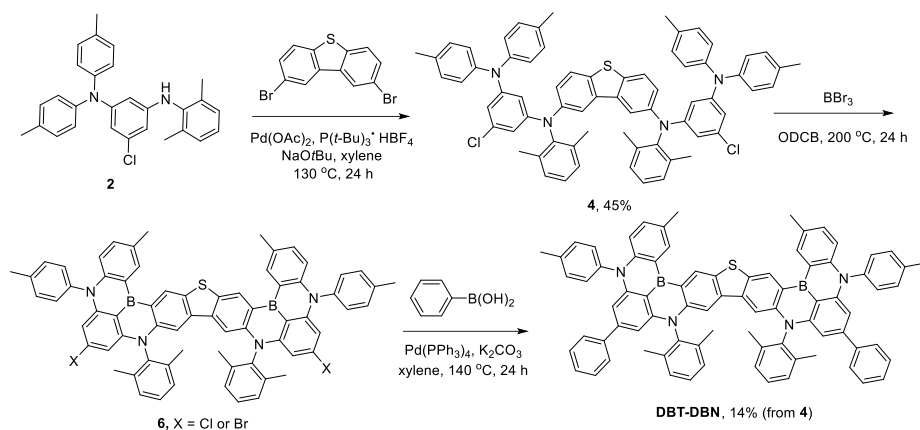
found 390.0246.

5-Chloro-N^1-(2,6-dimethylphenyl)-N^3,N^3-di-p-tolylbenzene-1,3-diamine (2): A dried round bottle flask with a magnetic stir bar was charged with compound **1** (7 g, 18 mmol), 2,6-dimethylaniline (2.2 mL, 18 mmol), Pd(OAc)$_2$ (117 mg, 0.7 mmol), XPhos (667 mg, 1.4 mmol), Cs$_2$CO$_3$ (11.7 g, 36 mmol) and toluene 50 mL under a N$_2$ atmosphere. The mixture was stirred for 12 h at 110 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by recrystallization (EtOH) to provide the compound **2** as a white solid in 73% yield (5.59 g, 13.1 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.18 (s, 6H), 2.31 (s, 6H), 5.05 (br, 1H), 5.90 (t, J = 1.6 Hz, 1H), 6.09 (t, J = 2.0 Hz, 1H), 6.34 (t, J = 1.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 4H), 7.04-7.07 (m, 7H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 18.5, 21.0, 105.6, 106.2, 112.2, 125.3, 126.3, 128.7, 130.0, 133.1, 135.5, 136.2, 137.5, 144.9, 148.1, 150.3 ppm. HRMS (ESI$^+$): calcd for C$_{28}$H$_{27}$^{35}ClN$_2$ [M+H]$^+$, 427.1936; found 427.1935, C$_{28}$H$_{27}$^{37}ClN$_2$ [M+H]$^+$, 429.1906; found 429.1915.

N^1,$N^{1'}$-(Dibenzo[b,d]furan-2,8-diyl)bis(5-chloro-N^1-(2,6-dimethylphenyl)-N^3,N^3-di-p-tolylbenzene-1,3-diamine) (3): A dried round bottle flask with a magnetic stir bar was charged with compound **2** (5.0 g, 11.7 mmol), 2,8-dibromodibenzo[b,d]furan (1.9 g, 5.9 mmol), Pd(OAc)$_2$ (76.4 mg, 0.46 mmol), P(tBu)$_3$•HBF$_4$ (267 mg, 0.92 mmol), NaOtBu (1.4 g, 14.7 mmol) and xylene 50 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 150 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/DCM = 8/1) to provide the compound **3** as a white solid in 51% yield (3.06 g, 3.01 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.07 (s, 12H), 2.21 (s, 12H), 6.24 (s, 2H), 6.42 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.4 Hz, 8H), 6.96 (d, J = 8.8 Hz, 8H), 7.04-7.14 (m, 8H), 7.27 (d, J = 9.6 Hz, 2H), 7.31 (d, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.1, 20.9, 109.9, 111.2, 112.0, 113.5, 122.1, 124.9, 125.1, 125.2, 127.4, 129.6, 130.0, 133.2, 135.4, 137.7, 141.0, 142.6, 144.6, 148.8, 150.0, 152.5 ppm. HRMS (ESI$^+$): calcd for C$_{68}$H$_{58}$^{35}Cl^{35}ClN$_4$O

[M+H]$^+$, 1017.4060; found 1017.4060, calcd for $C_{68}H_{58}{}^{35}Cl^{37}ClN_4O$ [M+H]$^+$, 1019.4031; found 1019.4030.

Synthesis of DBF-DBN: A Schlenk tube with a magnetic stir bar was charged with compound **3** (2.0 g, 1.97 mmol), BBr$_3$ (3.0 mL, 31.50 mmol) and ODCB 10 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 185 ºC. the mixture was cooled to 0 ºC. Then the reaction mixture was carefully quenched by addition of *N,N*-diisopropylethylamine (DIPEA, 10.5 mL, 63.01 mmol). The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After filtration and evaporation, the crude product was purified by column chromatography on Al$_2$O$_3$ (hexane/DCM = 4/1) to provide compound **5** as a yellow solid 696 mg, then a Schlenk tube with a magnetic stir bar was charged with compound **5**, phenylboronic acid (301.7 mg, 2.48 mmol), Pd(PPh$_3$)$_4$ (28.6 mg, 0.0248 mmol), K$_2$CO$_3$ (342.2 mg, 2.48 mmol), xylene 5 mL and H$_2$O 0.5 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 140 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on Al$_2$O$_3$ (hexane/DCM = 4/1) to provide the compound **DBF-DBN** as a yellow solid in 13% yield (289.1 mg, 0.26 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.96 (s, 12H), 2.55 (s, 6H), 2.60 (s, 6H), 6.32 (s, 2H), 6.42 (s, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.92 (s, 2H), 7.28-7.43 (m, 22H), 7.50 (d, J = 8.0 Hz, 4H), 8.87 (s, 2H), 9.19 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 17.8, 21.2, 21.6, 102.1, 104.3, 106.5, 116.1, 116.2, 117.4, 124.4, 125.9, 127.5, 127.9, 128.1, 128.6, 128.7, 129.3, 129.8, 130.3, 131.9, 132.4, 134.4, 137.8, 138.5, 139.7, 139.8, 142.4, 142.6, 145.6, 145.7, 146.3, 147.7, 152.7 ppm. HRMS (ESI$^+$): calcd for $C_{80}H_{62}B_2N_4O$ [M+H]$^+$, 1117.5183; found 1117.5180.
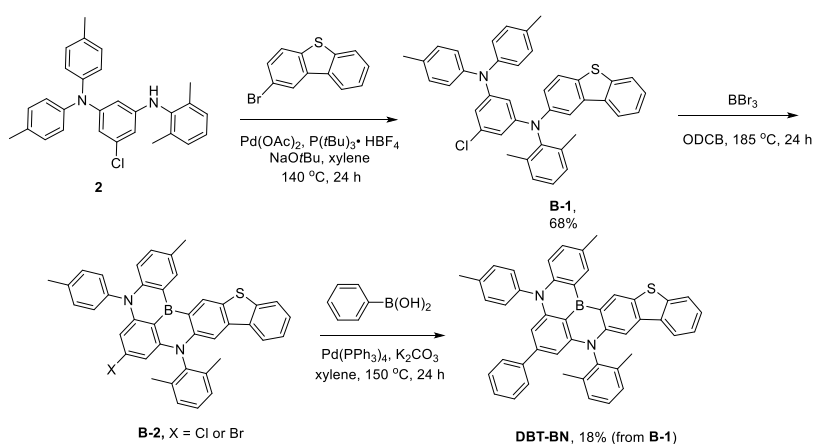
Scheme S2. Synthetic route to **DBT-DBN**.

***N¹,N¹′*-(Dibenzo[*b,d*]thiophene-2,8-diyl)bis(5-chloro-*N¹*-(2,6-dimethylphenyl)-*N³,N³*-di-*p*-tolylbenzene-1,3-diamine) (4):** A dried round bottle flask with a magnetic stir bar was charged with compound **2** (5 g, 11.7 mmol), 2,8-dibromodibenzo[*b,d*]thi-ophene (2.0 g, 5.9 mmol), Pd(OAc)$_2$ (76.4 mg, 0.46 mmol), P(*t*Bu)$_3$•HBF$_4$ (267 mg, 0.92 mmol), NaO*t*Bu (1.4 g, 14.7 mmol) and xylene 50 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 130 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/DCM = 8/1) to provide the compound **4** as a white solid in 45% yield (2.72 g, 2.63 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.07 (s, 12H), 2.21 (s, 12H), 6.31 (s, 2H), 6.44 (d, J = 4.4 Hz, 4H), 6.90-6.96 (m, 16H), 7.02 (d, J = 8.8 Hz, 2H), 7.07-7.14 (m, 6H), 7.49 (s, 2H), 7.54 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.0, 20.9, 109.9, 111.4, 113.5, 113.9, 121.6, 123.3, 124.6, 125.2, 127.5, 129.5, 129.8, 130.0, 133.3, 133.5, 135.4, 136.3, 137.8, 142.3, 142.7, 144.5, 148.3, 150.0 ppm. HRMS (ESI$^+$): calcd for C$_{68}$H$_{58}$^{35}Cl^{35}ClN$_4$S [M+Na]$^+$, 1055.3651, found 1055.3652, calcd for C$_{68}$H$_{58}$^{35}Cl ^{37}ClN$_4$S [M+Na]$^+$, 1057.3622; found 1057.3641.

Synthesis of DBT-DBN: A Schlenk tube with a magnetic stir bar was charged with compound **4** (2 g, 1.94 mmol), BBr$_3$ (2.98 mL, 31 mmol) and ODCB 10 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 200 ºC. the mixture was cooled to 0 ºC. Then the reaction mixture was carefully quenched by addition of

N,N-diisopropylethylamine (DIPEA, 10.3 mL, 62 mmol). The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography on Al_2O_3 (hexane/DCM = 4/1) to provide a yellow solid 624 mg, then a Schlenk tube with a magnetic stir bar was charged with compound **6**, phenylboronic acid (214.6 mg, 1.76 mmol), $Pd(PPh_3)_4$ (20.3 mg, 0.0176 mmol), K_2CO_3 (243 mg, 1.76 mmol), xylene 5 mL and H_2O 0.5 mL under a N_2 atmosphere. The mixture was stirred for 24 h at 140 °C. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on Al_2O_3 (hexane/DCM = 4/1) to provide the compound **DBT-DBN** as a yellow solid in 14% yield (308.8 mg, 0.27 mmol). ^1H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.94 (s, 12H), 2.55 (s, 6H), 2.63 (s, 6H), 6.39 (s, 2H), 6.44 (s, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 2H), 7.30-7.36 (m, 20H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 4H), 8.86 (s, 2H), 9.43 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 17.8, 21.3, 21.6, 102.2, 104.5, 107.7, 116.4, 117.5, 124.4, 126.1, 127.5, 127.9, 128.6, 129.1, 129.2, 129.3, 129.6, 130.3, 131.9, 132.5, 133.0, 134.5, 137.7, 138.6, 138.8, 139.2, 139.8, 142.6, 143.6, 145.6, 145.7, 146.3, 147.8 ppm. HRMS (ESI $^+$): calcd for $C_{80}H_{62}B_2N_4S$ [M+H]$^+$, 1133.4954; found 1133.4956.

Scheme S3. Synthetic route to **DBT-BN.**

5-Chloro-*N¹*-(dibenzo[b,d]thiophen-2-yl)-*N¹*-(2,6-dimethylphenyl)-*N³,N³*-di-*p*-tolyl benzene-1,3-diamine (B-1): A dried round bottle flask with a magnetic stir bar was charged with compound **2** (5 g, 11.7 mmol), 2-bromodibenzo[*b,d*]thiophene (4.0 g,

11.8 mmol), Pd(OAc)$_2$ (76.4 mg, 0.46 mmol), P(t-Bu)$_3$•HBF$_4$ (267 mg, 0.92 mmol), NaOtBu (1.4 g, 14.7 mmol) and xylene 50 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 140 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/DCM = 8/1) to provide the compound **B-1** as a white solid in 68% yield (4.84 g, 7.96 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.08 (s, 6H), 2.22 (s, 6H), 6.33 (t, J = 1.6 Hz, 1H), 6.48 (t, J = 1.6 Hz, 1H), 6.60 (t, J = 2.0 Hz, 1H), 6.90-6.99 (m, 8H), 7.04 (dd, J = 8.8 Hz, J = 2.0 Hz 1H), 7.10-7.18 (m, 3H), 7.38-7.45 (m, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.79-7.82 (m, 1H), 7.93-7.95 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.0, 20.9, 110.9, 112.1, 113.2, 114.4, 121.0, 121.9, 123.0, 123.3, 124.2, 124.9, 126.8, 127.6, 129.5, 130.0, 132.4, 133.1, 135.3, 135.5, 136.6, 137.8, 140.4, 142.3, 142.9, 144.6, 148.1, 150.0 ppm. HRMS (ESI$^+$): calcd for C$_{40}$H$_{33}$^{35}ClN$_2$S [M+Na]$^+$, 609.2126; found 609.2114, calcd for C$_{40}$H$_{33}$^{37}ClN$_2$S [M+Na]$^+$, 611.2096; found 611.2071.

Synthesis of DBT-BN: A Schlenk tube with a magnetic stir bar was charged with compound **B-1** (1.2 g, 1.94 mmol), BBr$_3$ (1.49 mL, 15.5 mmol) and ODCB 10 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 185 ºC. the mixture was cooled to 0 ºC. Then the reaction mixture was carefully quenched by addition of *N,N*-diisopropylethylamine (DIPEA, 5.15 mL, 31 mmol). The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na$_2$SO$_4$. After filtration and evaporation, the crude product was purified by column chromatography on Al$_2$O$_3$ (hexane/DCM = 4/1) to provide a yellow solid 276 mg, then a Schlenk tube with a magnetic stir bar was charged with compound **B-2**, phenylboronic acid (214.6 mg, 1.76 mmol), Pd(PPh$_3$)$_4$ (20.3 mg, 0.0176 mmol), K$_2$CO$_3$ (243 mg, 1.76 mmol), xylene 5 mL and H$_2$O 0.5 mL under a N$_2$ atmosphere. The mixture was stirred for 24 h at 150 ºC. Then the solution was filtered through a celite pad and washed with dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on Al$_2$O$_3$

(hexane/DCM = 4/1) to provide the compound **DBT-BN** as a yellow solid in 18% yield (230 mg, 0.35 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 1.95 (s, 6H), 2.51 (s, 3H), 2.57 (s, 3H), 6.29 (s, 1H), 6.41 (s, 1H), 6.74 (d, J = 8.4 Hz, 1H), 7.22-7.45 (m, 16H), 7.79-7.85 (m, 2H), 8.78 (s, 1H), 9.40 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 17.8, 21.3, 21.6, 102.2, 104.6, 107.1, 117.5, 122.0, 122.2, 123.2, 124.1, 124.3, 127.5, 127.6, 127.9, 128.7, 129.0, 129.2, 130.0, 130.3, 131.4, 131.9, 132.5, 134.5, 135.6, 135.9, 137.9, 138.6, 138.9, 139.5, 139.8, 141.4, 142.6, 143.8, 145.6, 145.7, 146.3, 147.8 150.6 ppm. HRMS (ESI[+]): calcd for C$_{46}$H$_{35}$BN$_2$S [M+H][+], 659.2687; found 659.2681.

V. Crystal Data

Table S1. Crystal data for **DBT-DBN** (CCDC 2235320)
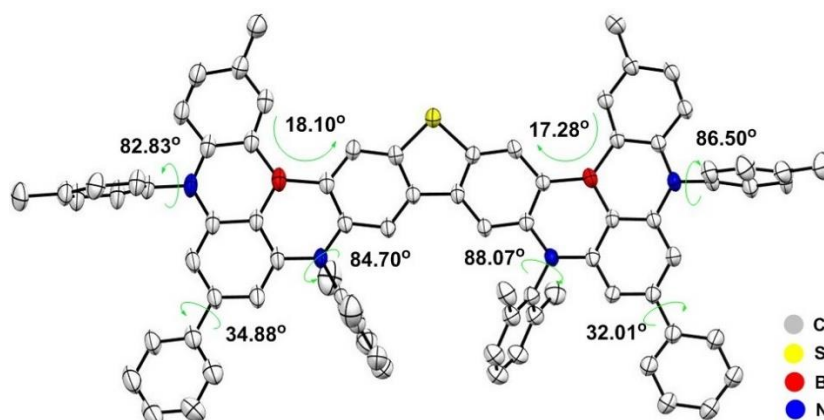
Identification code	mo_hw_339_200k_0m_a
Empirical formula	C$_{80}$H$_{62}$B$_2$N$_4$S
Formula weight	1133.01
Temperature/K	300.00
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	8.1533(19)
b/Å	16.228(4)
c/Å	24.673(5)
α/°	90.389(7)
β/°	96.302(7)
γ/°	94.832(8)
Volume/Å^3	3232.7(13)
Z	2
ρ$_{calc}$g/cm^3	1.164
μ/mm^{-1}	0.098

F(000)	1192.0
Crystal size/mm^3	0.42 × 0.13 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.136 to 49
Index ranges	-9≤h≤9, -18≤k≤18, -28≤l≤28
Reflections collected	33985
Independent reflections	10639 [R_{int} = 0.1341, R_{sigma} = 0.1301]
Data/restraints/parameters	10639/721/863
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0775, wR_2 = 0.1688
Final R indexes [all data]	R_1 = 0.2007, wR_2 = 0.2406
Largest diff. peak/hole / e Å^{-3}	0.36/-0.20

VI. Additional Spectra and Data

i. Density functional theory (DFT) calculations
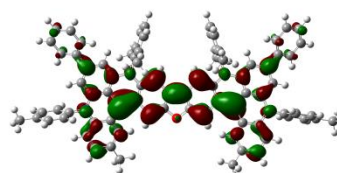
HOMO-1 (-4.688 eV)   **LUMO (-1.583 eV)**
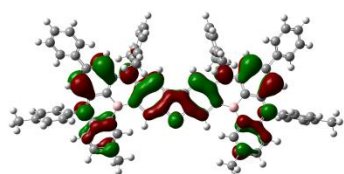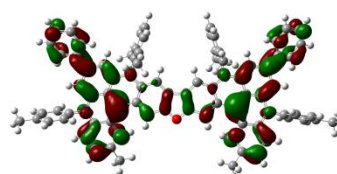
HOMO (-4.606 eV)   **LUMO+1 (-1.039 eV)**

Fig. S1. Theoretical calculation results of **DBF-DBN**, S_1 = 2.63 eV, T_1 = 2.21 eV, ΔE_{ST} = 0.42 eV, S_1 = 472 nm (@S_0), f = 0.1035 ($S_0{\rightarrow}S_1$).
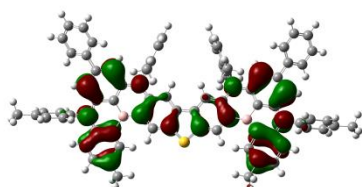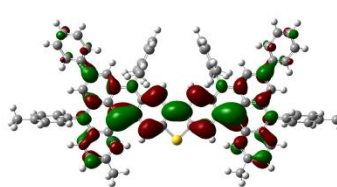
HOMO-1 (-4.730 eV)   **LUMO (-1.582 eV)**
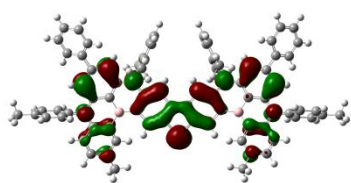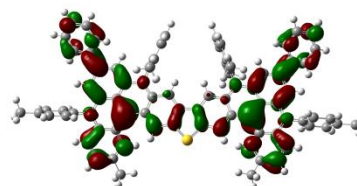
HOMO (-4.584 eV)   **LUMO+1 (-1.081 eV)**

Fig. S2. Theoretical calculation results of **DBT-DBN**, $S_1 = 2.59$ eV, $T_1 = 2.19$ eV, $\Delta E_{ST} = 0.40$ eV, $S_1 = 478$ nm (@S_0), $f = 0.0739$ ($S_0 \rightarrow S_1$).
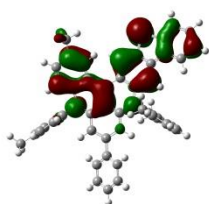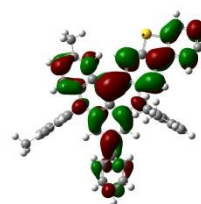
HOMO-1 (-5.361 eV)   **LUMO (-1.453 eV)**
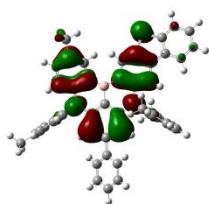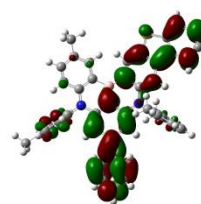
HOMO (-4.729 eV)   **LUMO+1 (-0.6577 eV)**

Fig. S3. Theoretical calculation results of **DBT-BN**, $S_1 = 2.80$ eV, $T_1 = 2.36$ eV, $\Delta E_{ST} = 0.44$ eV, $S_1 = 442$ nm (@S_0), $f = 0.2352$ ($S_0 \rightarrow S_1$).

ii. Photophysical properties
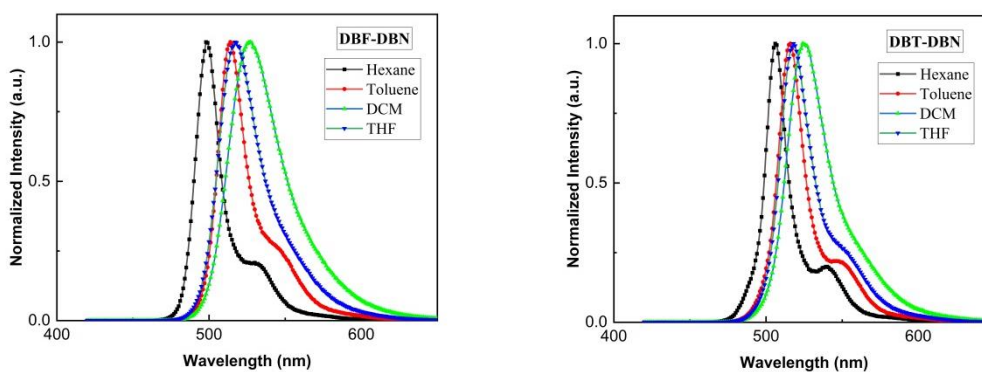
Fig. S4. The photoluminescence spectra measured in different polar solvents (1×10^{-5} M, 298 K) of **DBF-DBN** and **DBT-DBN.**

Table S2. Summary of photoluminescence spectra data in different polar solvents.

Compound	DBF-DBN		DBT-DBN	
	λ_{em}[nm]	FWHM[nm]	λ_{em}[nm]	FWHM[nm]
n-hexane	498	19	508	18
toluene	514	22	516	19
THF	518	33	518	25
DCM	527	41	524	32

Table S3. Summary of photoluminescence performances for **DBT-DBN** and **DBF-DBN** in CBP film (2 wt%) at 298 K.

Compound	λ_{em} [nm]	$\Phi_{PL}{}^a$ [%]	$\tau_p{}^b$ [ns]	$\tau_d{}^c$ [μs]	$C_1{}^d$ [%]	$C_2{}^d$ [%]	$k_{RISC}{}^e$ [$\times 10^6$ s^{-1}]	$k_R{}^f$ [$\times 10^6$ s^{-1}]
DBF-DBN	529	90.0	21.00	39.34	21.52	78.48	0.11	9.22
DBT-DBN	525	89.9	71.08	32.68	3.97	96.03	0.74	0.50

[a]Absolute photoluminescence quantum yield. [b]Prompt lifetime. [c]Delayed lifetime. [d]Proportion of prompt (C_1) and delayed (C_2) components which are calculated from transient spectra. [e]Calculated from $k_{RISC}= C_2/[C_1\tau_d(1-\Phi_{PL}C_1)]$. [f]Calculated from $k_R = C_1\Phi_{PL}/\tau_p$.
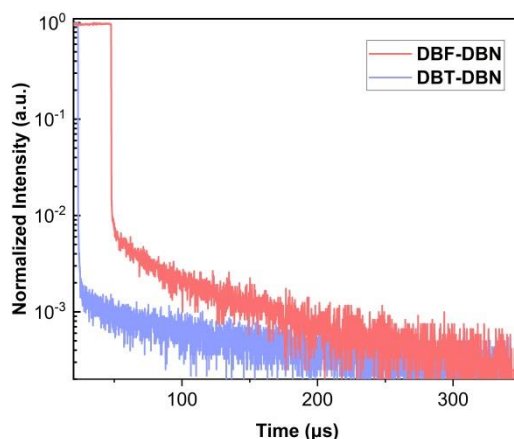
Fig. S5. Transient photoluminescence spectra in the film (2 wt% in CBP) at room temperature and normal atmospheric pressure.
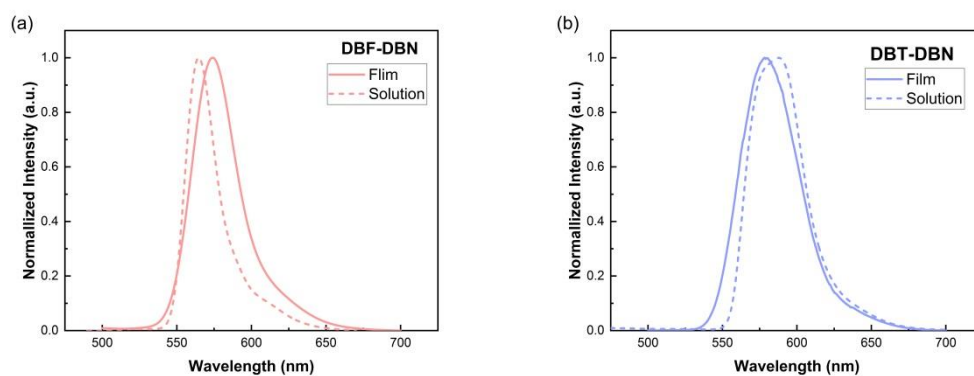
Fig. S6. Phosphorescence spectra of (a) **DBF-DBN** and (b) **DBT-DBN** in the film (2 wt% in CBP) and toluene (1×10^{-5} mol L^{-1}) at 77 K.
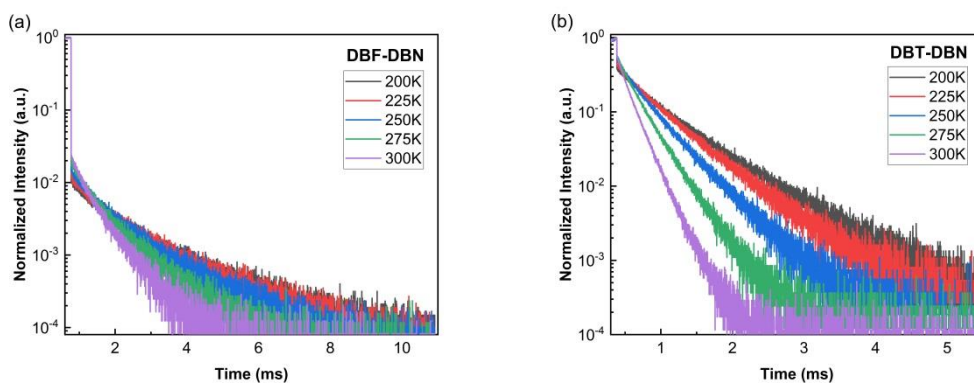
Fig. S7. Temperature-dependent transient photoluminescence spectra in CBP film (2 wt%) under high vacuum (1 mm Hg).

iii. Electrochemistry
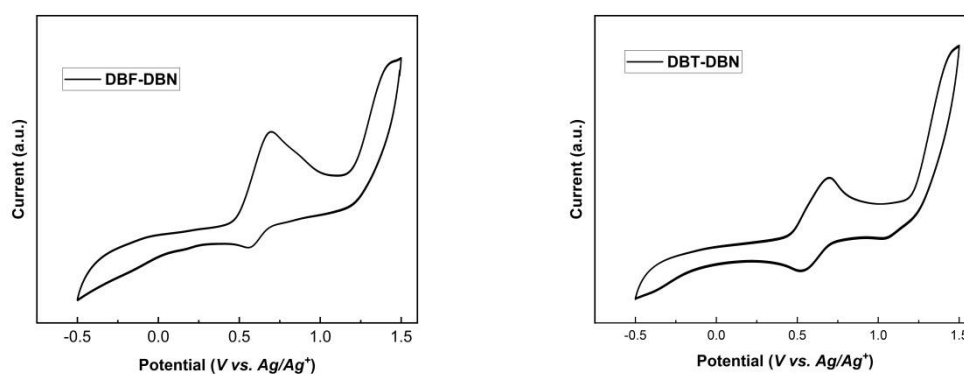
Fig. S8. Cyclic voltammograms of **DBF-DBN** and **DBT-DBN** measured in dry

dichloromethane containing 0.1 M of tetrabutylammonium hexafluorophosphate.

Table S4. Summary of electrochemistry properties of **DBF-DBN** and **DBT-DBN**.

Compound	HOMO[a] [eV]	LUMO[b] [eV]	$E_g{}^c$ [eV]
DBF-DBN	-5.21	-2.81	2.40
DBT-DBN	-5.19	-2.80	2.39

[a]Measured in dry dichloromethane solution, where $E_{HOMO} = -4.8 - (E_{ox} - E_{Fc})$. [b]Estimated according to the absorption spectra and the HOMO energy levels. [c]Calculated from the absorption spectra.

iv. Thermodynamics
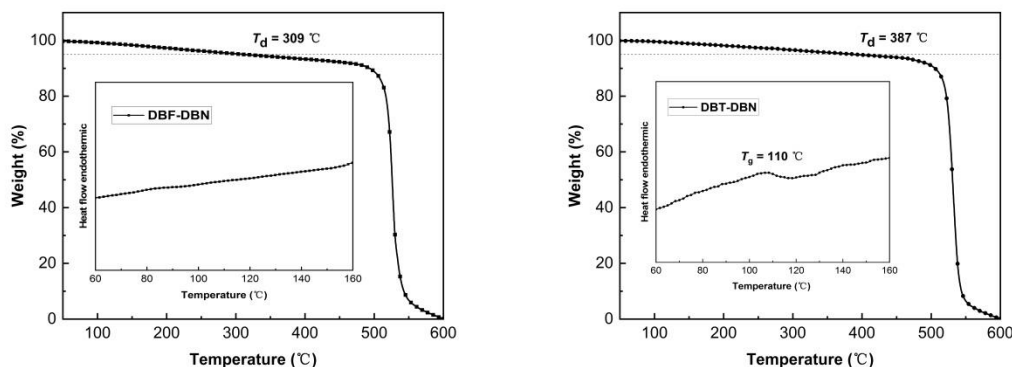
Fig. S9. TGA thermograms and DSC curves of **DBF-DBN** and **DBT-DBN**.

v. Device performance
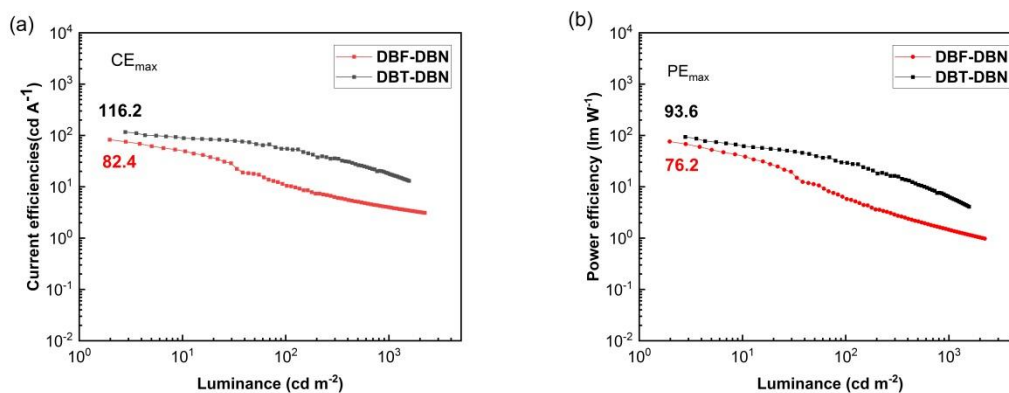
Fig. S10. Current efficiencies and power efficiency−luminance characteristics of **DBF-DBN**- and **DBT-DBN**-based OLEDs.
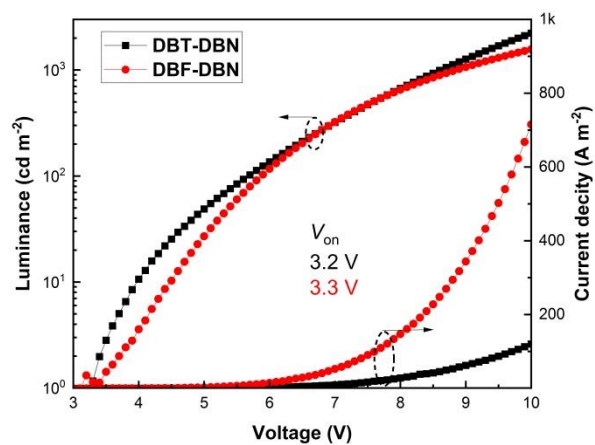
Fig. S11. Current density-voltage-luminance of OLEDs using **DBF-DBN** and **DBT-DBN** as emitters.

VII. References

(1) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(2) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785-789.

(3) P. K. Samanta, D. Kim, V. Coropceanu and J.-L. Brédas, *J. Am. Chem. Soc.* **2017**, *139*, 4042-4051.

(4) T. Lu and F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.

(5) K. Masui, H. Nakanotani and C. Adachi, *Org. Electron*. **2013**, *14*, 2721-2726.

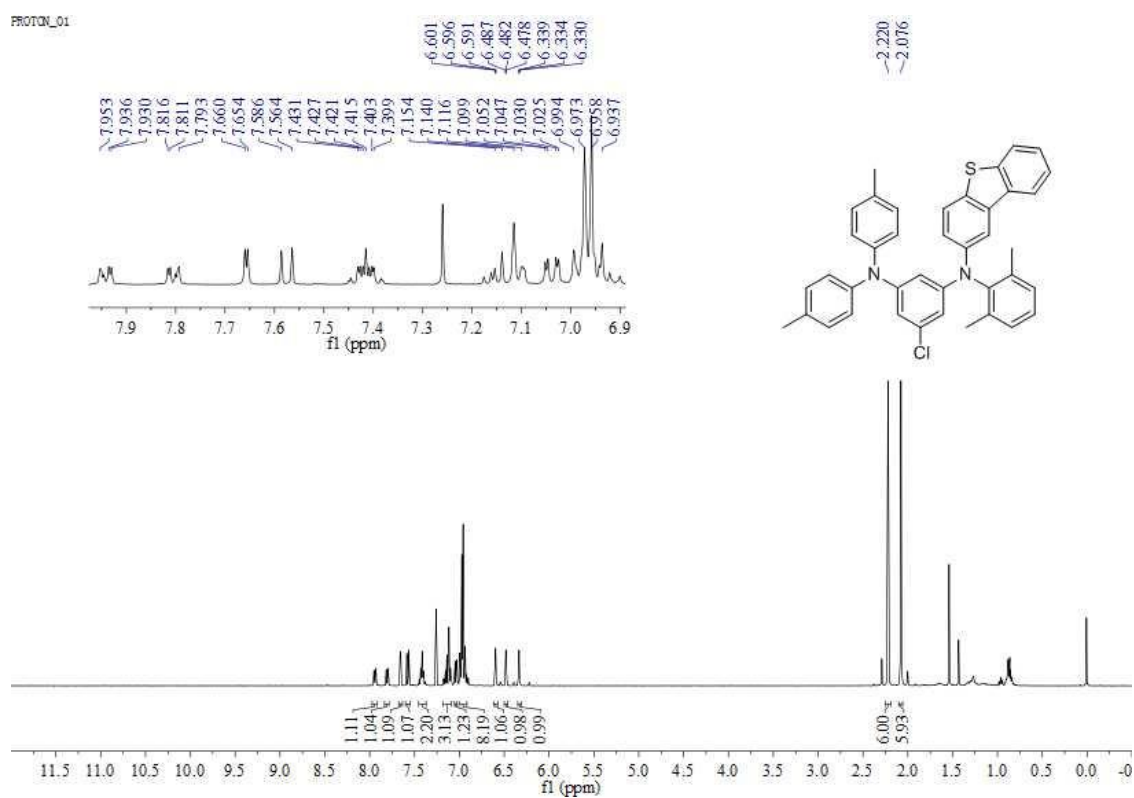# IX. Copies of ¹H and ¹³C NMR spectra

¹H NMR spectrum of **1** in CDCl₃
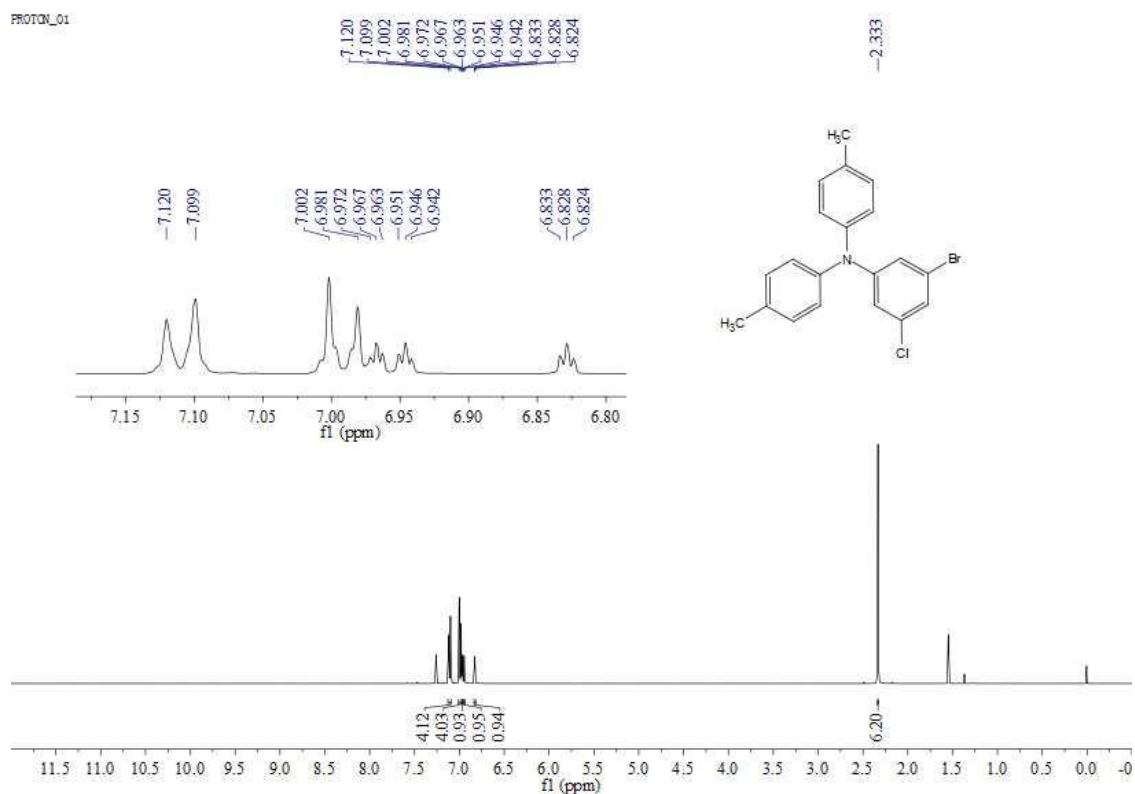
¹³C NMR spectrum of **1** in CDCl₃
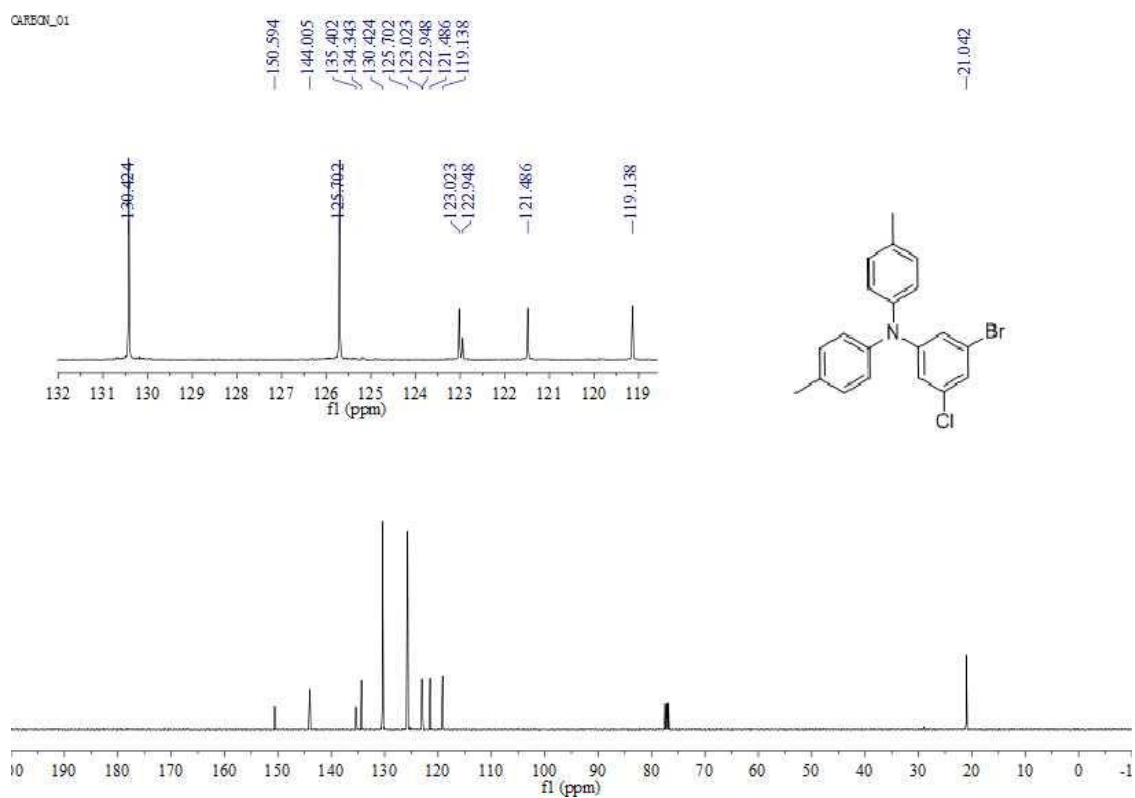
^{1}H NMR spectrum of **2** in CDCl$_3$

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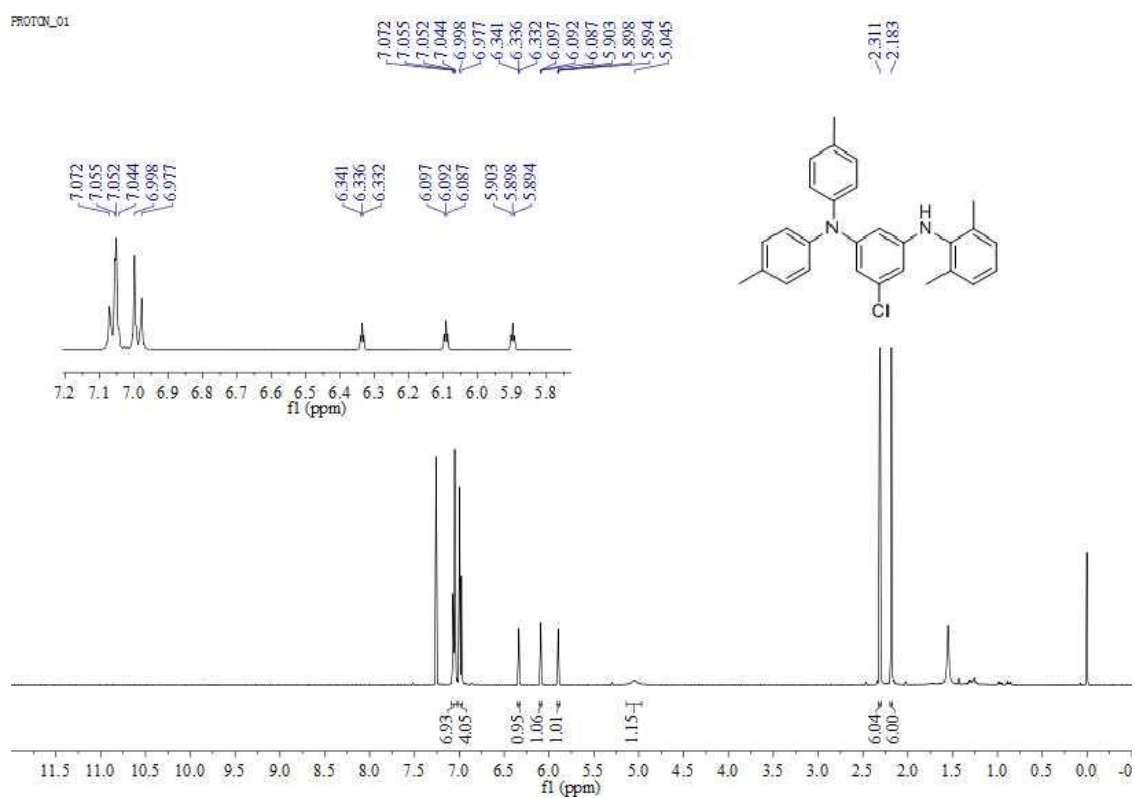
^{13}C NMR spectrum of **2** in CDCl$_3$

CARBON_01
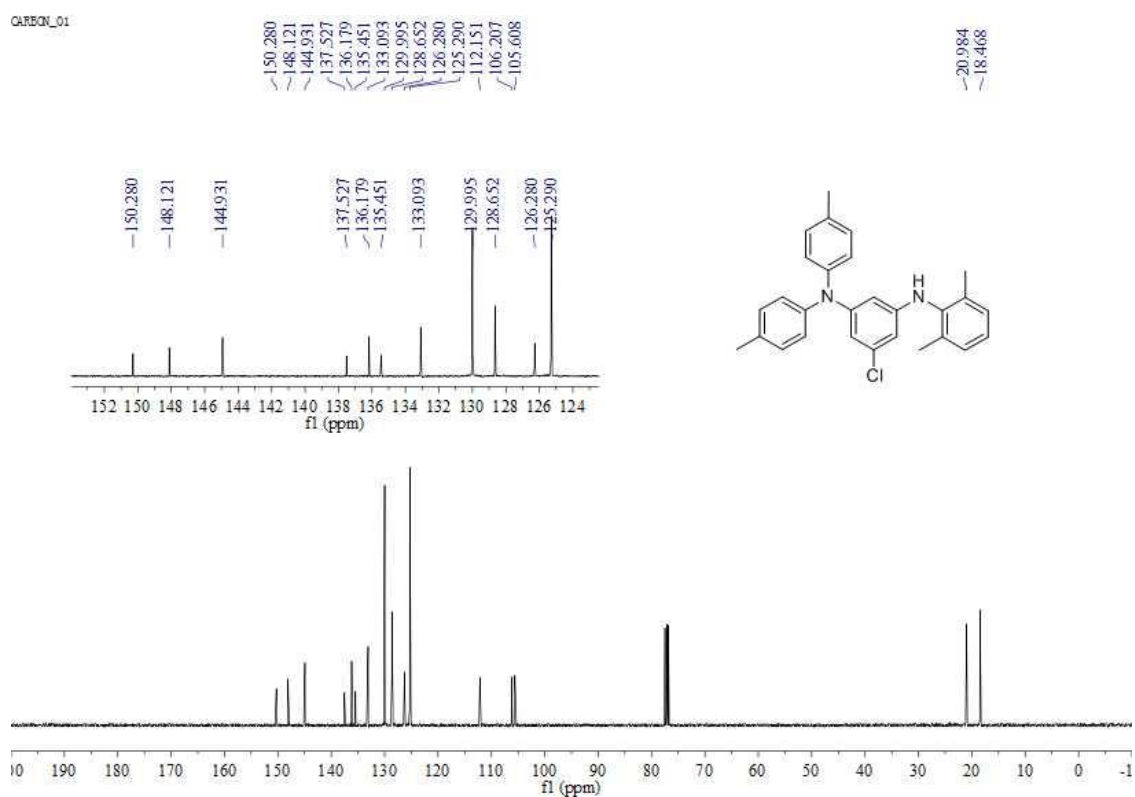
¹H NMR spectrum of **3** in CDCl₃
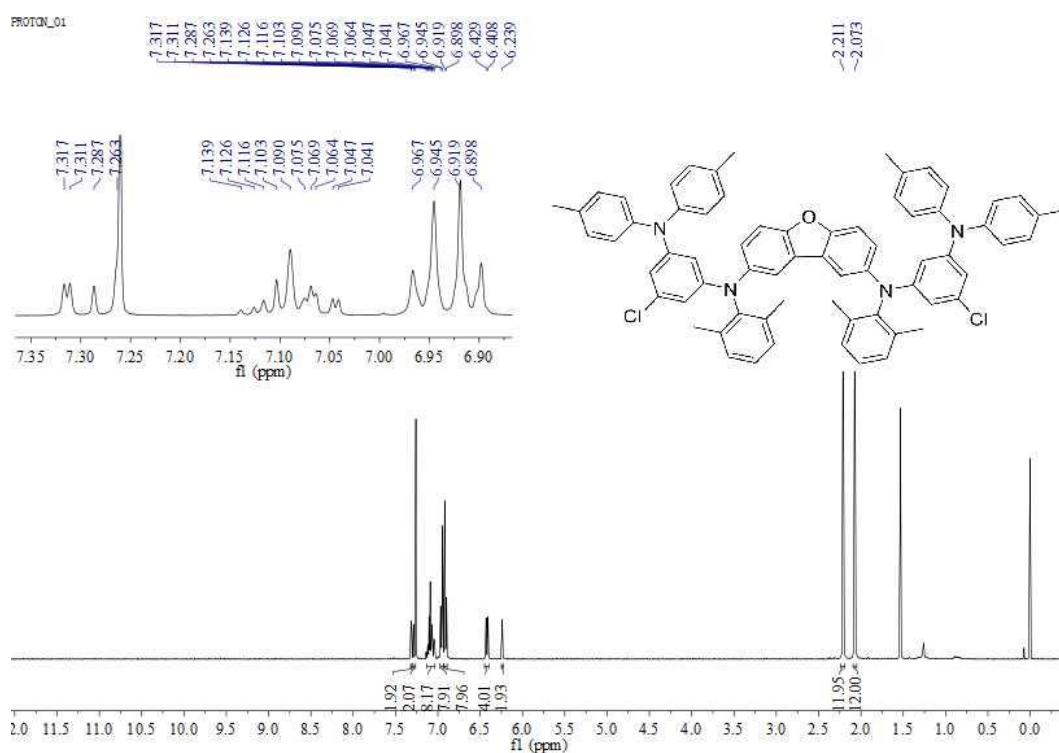
¹³C NMR spectrum of **3** in CDCl₃

^{1}H NMR spectrum of **DBF-DBN** in CDCl$_3$

PROTON_01

^{13}C NMR spectrum of **DBF-DBN** in CDCl$_3$

CARBON_01
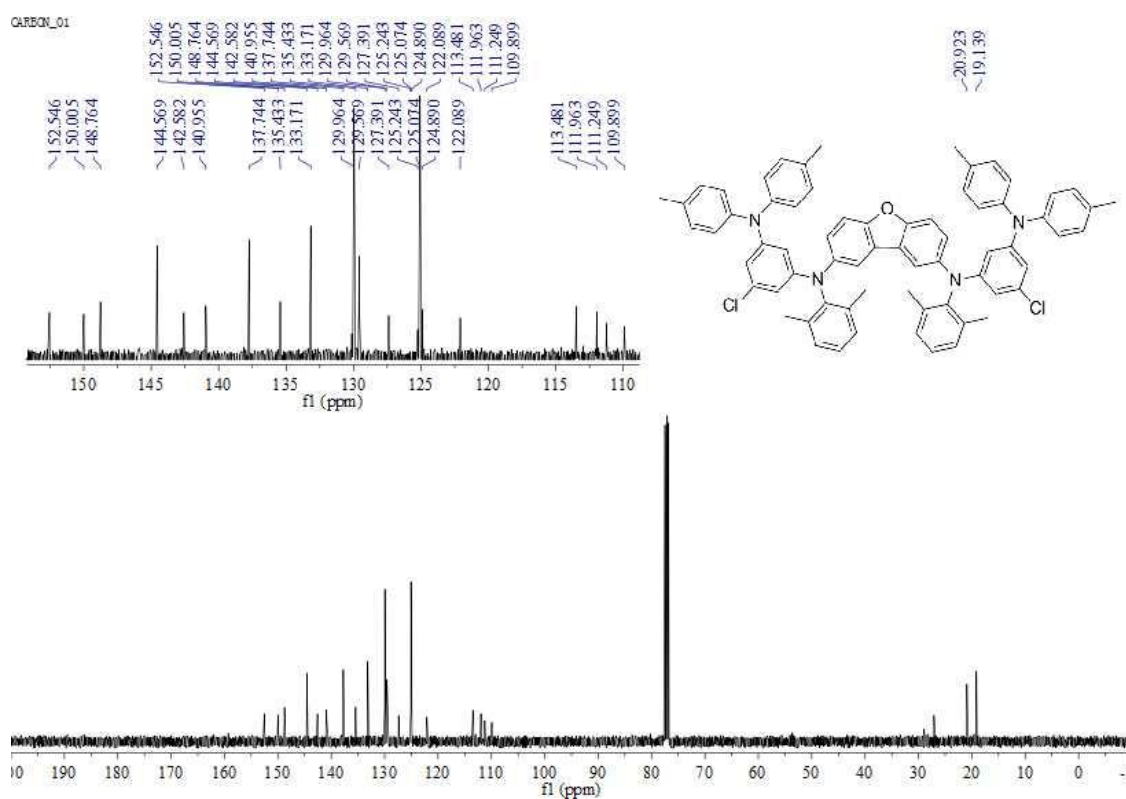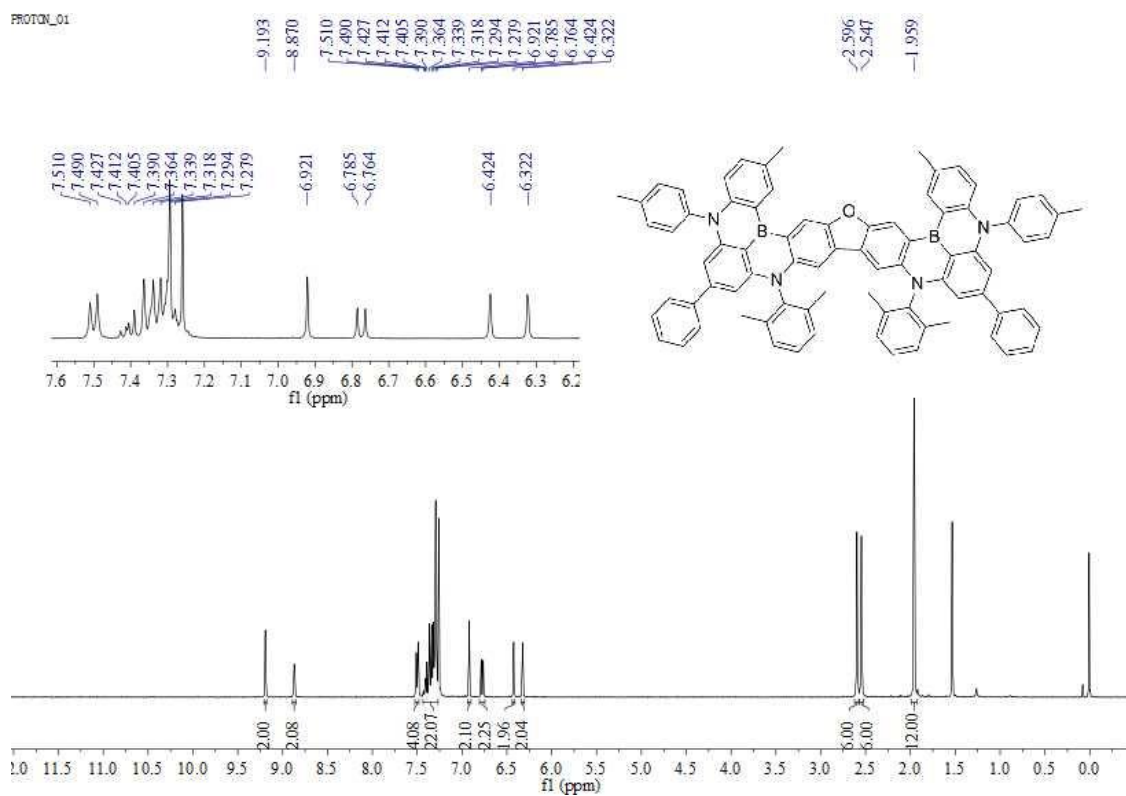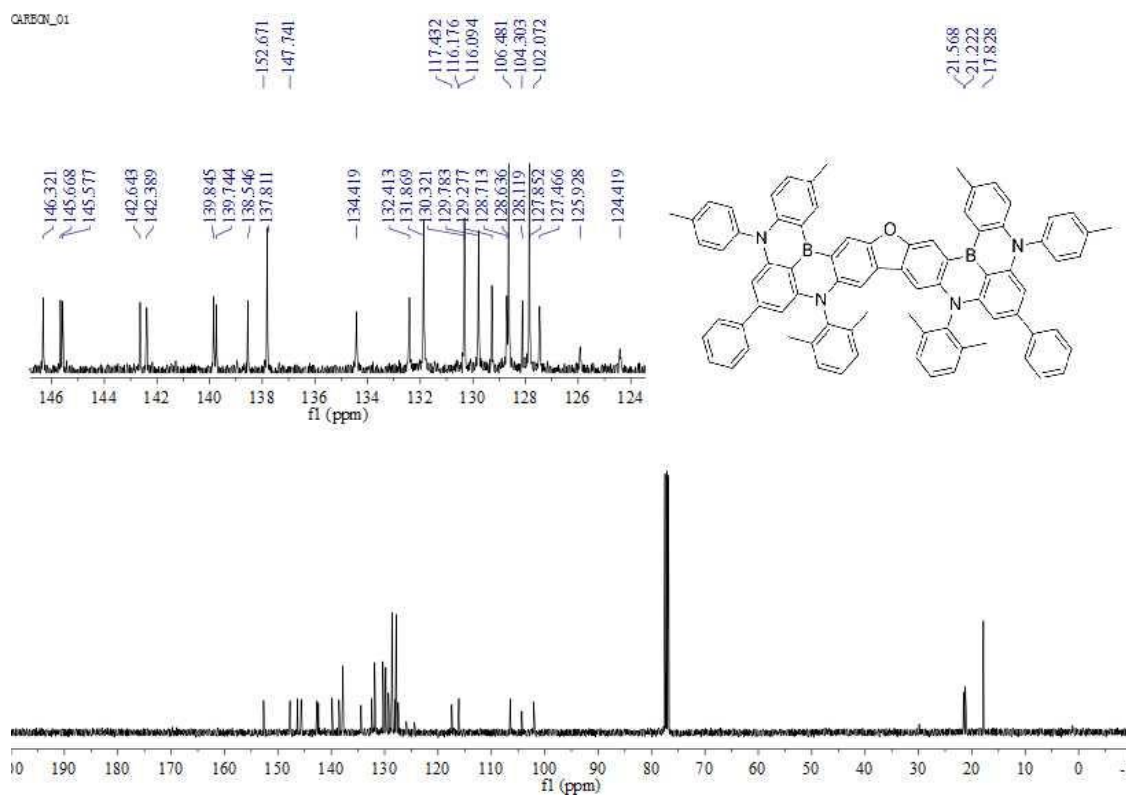
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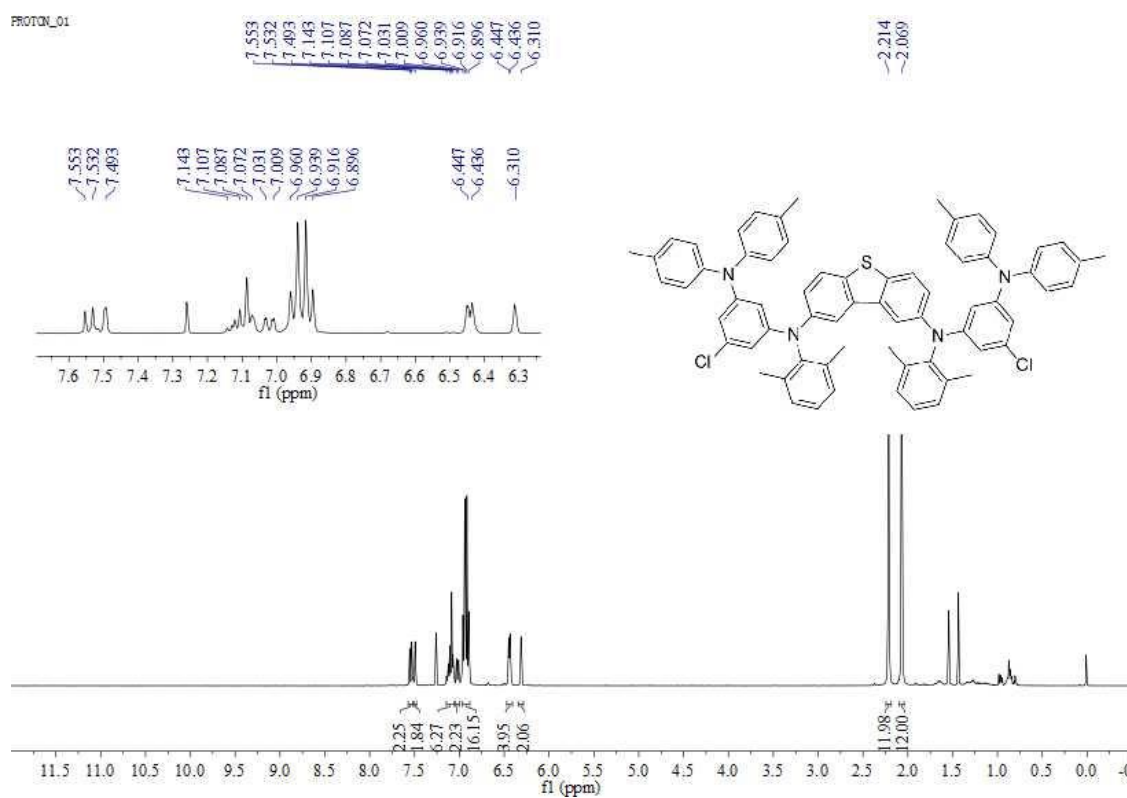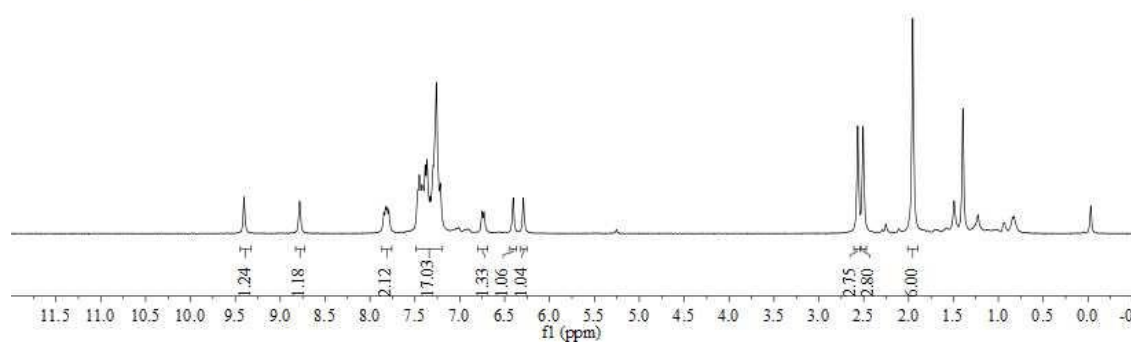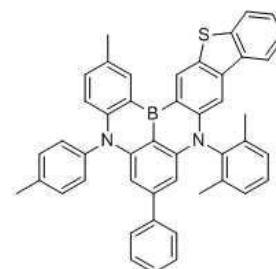

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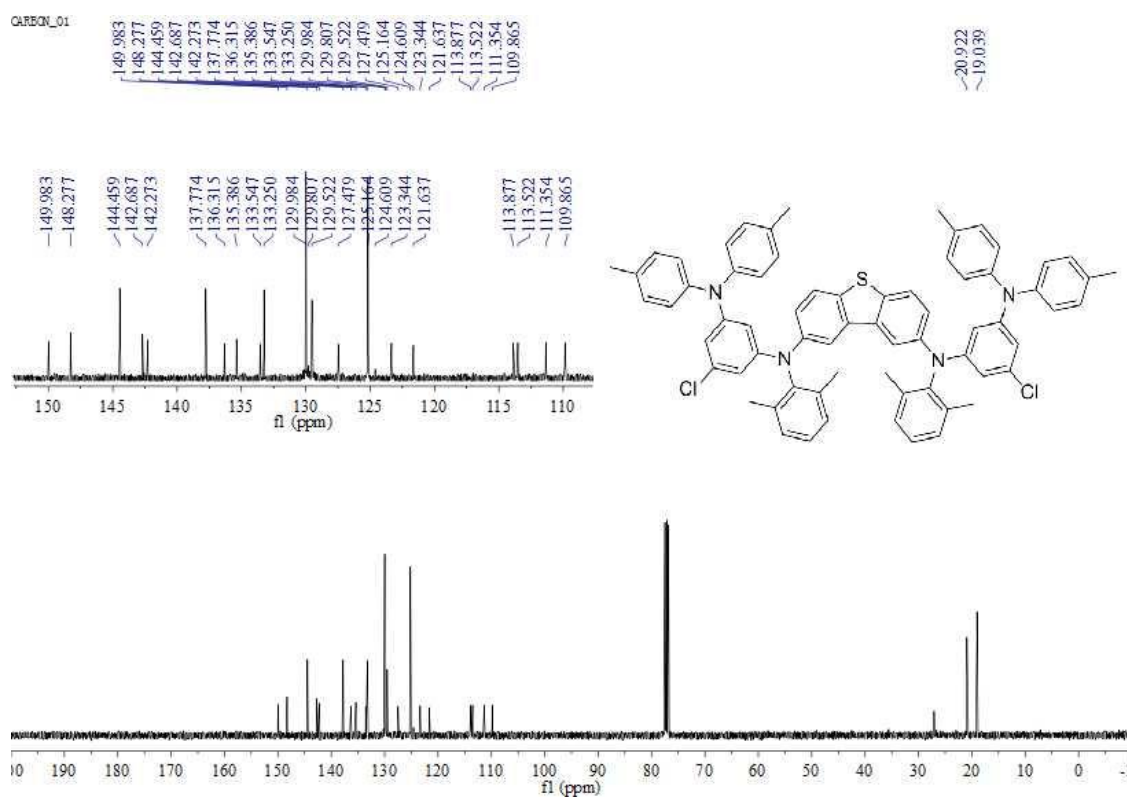
¹H NMR spectrum of **DBT-DBN** in CDCl₃
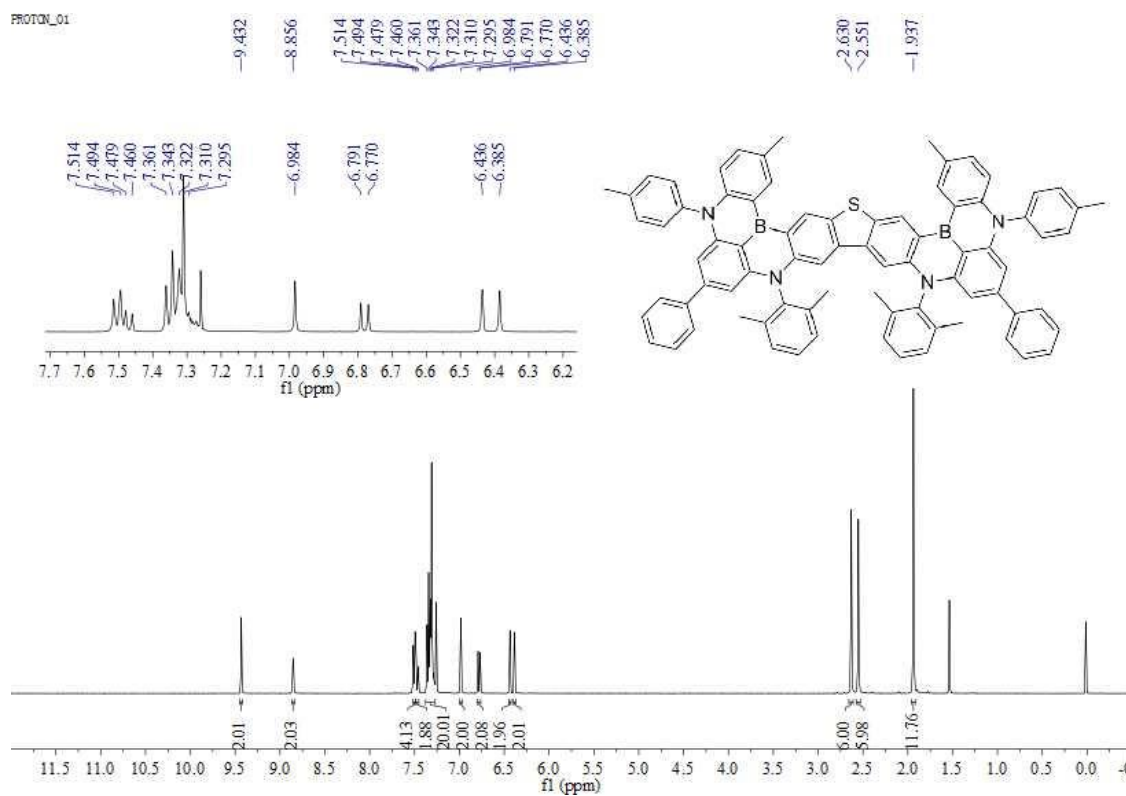
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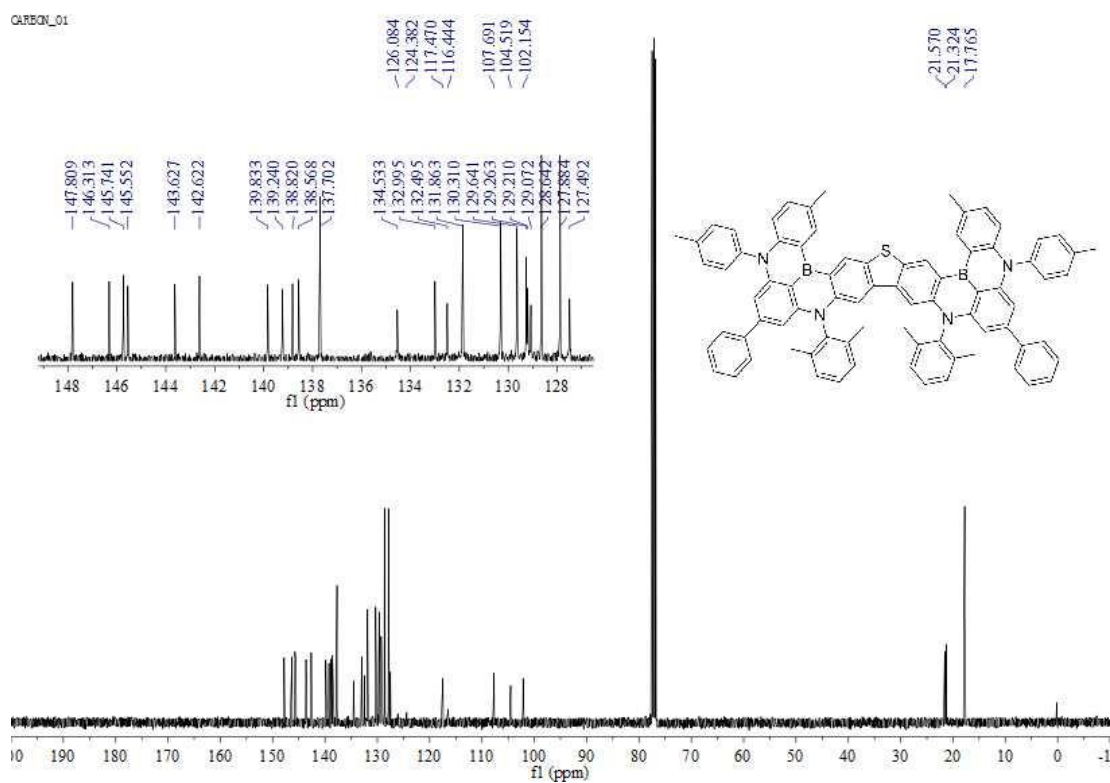
CARBON_01

^{1}H NMR spectrum of **B-1** in CDCl$_3$

^{13}C NMR spectrum of **BN-1** in CDCl$_3$

¹H NMR spectrum of **DBT-BN** in CDCl₃

¹³C NMR spectrum of **DBT-BN** in CDCl₃