

## Supporting Information (SI)

# Asymmetric multiple resonance thermally activated delayed fluorescence emitters for sky-blue and pure blue electroluminescence

Hua-Xiu Ni,<sup>#</sup> Xu-Feng Luo,<sup>#</sup> Li Yuan, Jia-Jun Hu Wen-Wei Zhang,<sup>\*</sup> and You-Xuan Zheng<sup>\*</sup>

State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China. E-mail: yxzheng@nju.edu.cn, wwzhang@nju.edu.cn.

<sup>#</sup>Ni and Luo contributed equally to this paper.

### 1. Instrumentation and materials.

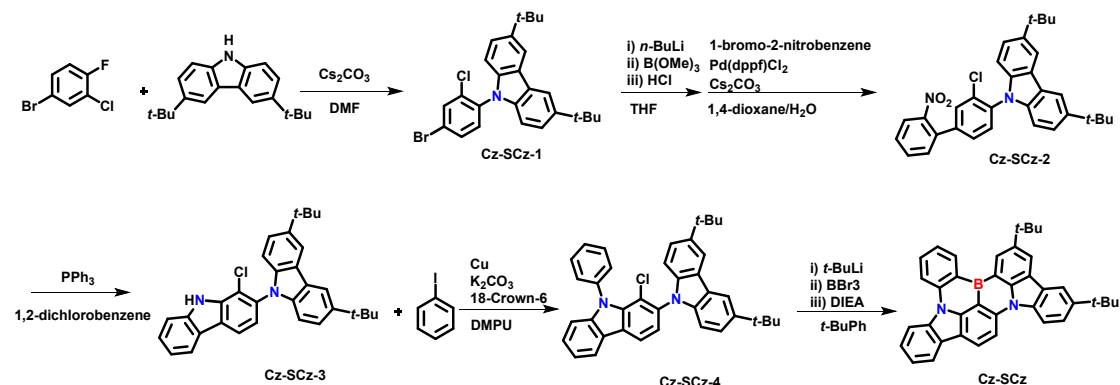
All solvents and reagents were commercially available without further purifications.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer, Bruker ARX 500 NMR spectrometer and reported as parts per million (ppm) from the internal standard TMS. High-resolution mass spectra were recorded on a MICROTOF-Q III instrument. Absorption and photoluminescence spectra were measured on a UV-3100 a Hitachi F-4600 photoluminescence spectrophotometer, respectively. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system at room temperature with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO<sub>3</sub> (0.1 M) in CH<sub>3</sub>CN as the reference electrode, *tetra*-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc<sup>+</sup>/Fc as the internal standard, the scan rate was 0.1 V/s. The absolute photoluminescence quantum yields and the decay lifetimes of the compounds were measured with HORIBA FL-3 fluorescence spectrometer. Thermogravimetric

analysis (TGA) was performed on a Pyris 1 DSC under nitrogen at a heating rate of 10 °C min<sup>-1</sup>.

## 2. Experimental section

### 2.1 Synthesis of Cz-SCz



**Synthesis of 9-(4-bromo-2-chlorophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (Cz-SCz-1):** 3,6-Di-*tert*-butyl-9*H*-carbazole (3.11 g, 11.0 mmol) and cesium carbonate (9.82 g, 30.0 mmol) were dissolved in dry DMF (150 mL) at room temperature under a nitrogen atmosphere. After stirring for 30 min at room temperature, 4-bromo-2-chloro-1-fluorobenzene (2.13 g, 10 mmol) was added into solution. The mixture was stirred at 150 °C for 12 h, and cooled to room temperature, and then water was added, and the aqueous layer was extracted with ethyl acetate. The combined organic was washed with water, evaporated under reduced pressure to obtain the crude product. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue was then purified by flash chromatography (eluent: petroleum ether/dichloromethane = 6:1, v/v) to obtain Cz-SCz-1 as a white powder (4.30 g, yield = 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 1.7 Hz, 2H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 1.47 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.17, 139.12, 133.71, 123.72, 123.45, 116.42, 109.32, 77.35, 77.03, 76.72, 34.77, 32.03.

**Synthesis of 3,6-di-*tert*-butyl-9-(3-chloro-2'-nitro-[1,1'-biphenyl]-4-yl)-9*H*-carbazole (Cz-SCz-2):** *n*-BuLi (4.1 mL, 5.2 mmol, 1.60 M solution in hexanes) was added dropwise to a solution of Cz-SCz-1 (4.30 g, 9.2 mmol) in anhydrous THF (60 mL) at -78 °C to get a pale-yellow solution. After stirring for 1.5 h, trimethyl borate (1.56 g, 15 mmol) was added to the solution. The resulting solution was stirred at -78 °C for 40 min and allowed to warm to room temperature overnight. Then water was

added to the solution, and diluted HCl was used to tune the pH to 7. The aqueous was extracted with dichloromethane and concentrated under reduced pressure to get the (5-chloro-2,4-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)boronic acid as white solid, which was used for afterward reactions without further purification. Thus obtained crude (3-chloro-4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)boronic acid (4.0 g) was added to the mixture of 1-bromo-2-nitrobenzene (2.0 g, 10.0 mmol), Pd(dppf)Cl<sub>2</sub> (0.7 g, 0.9 mmol), Cs<sub>2</sub>CO<sub>3</sub> (8.8 g, 27.0 mmol) in a mixed solvent of 1,4-dioxane (64 mL) and water (16 mL), then the mixture was stirred at 110 °C for 12 h. The resulted solution was extracted with ethyl acetate and water, the organic was separated and concentrated under reduced pressure. The crude product was purified by flash chromatography (petroleum ether/dichloromethane = 3:1) to obtain Cz-SCz-2 as a yellow powder (1.82 g, yield = 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 1.5 Hz, 2H), 8.00 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.70 (ddd, *J* = 17.6, 11.9, 1.6 Hz, 2H), 7.62-7.53 (m, 3H), 7.49 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.38 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 1.49 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.94, 143.08, 139.27, 138.89, 135.57, 134.53, 133.63, 133.40, 132.79, 131.92, 130.68, 130.44, 129.37, 129.14, 127.69, 124.58, 123.70, 123.46, 116.36, 109.60, 77.37, 77.05, 76.73, 34.79, 32.06.

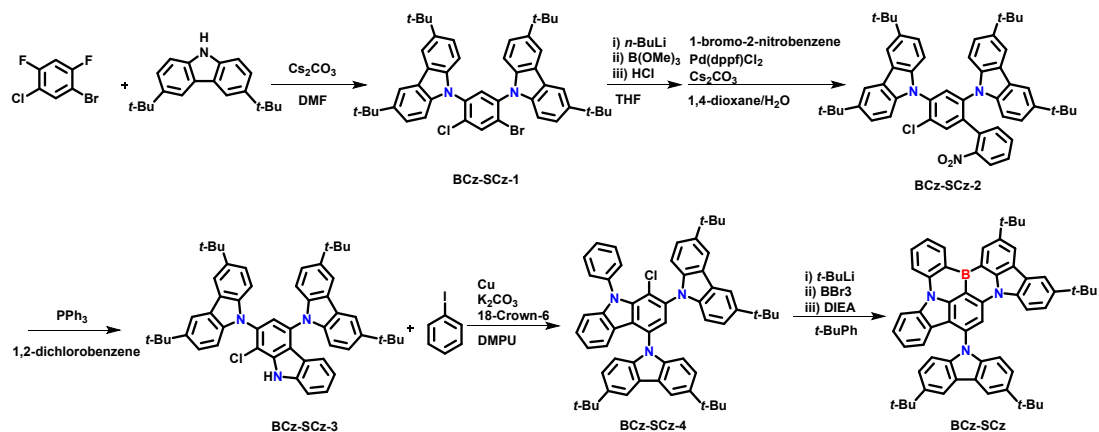
**Synthesis of 3',6'-di-*tert*-butyl-1-chloro-9*H*-2,9'-bicarbazole (Cz-SCz-3):** To the mixture of Cz-SCz-2 (1.82 g, 4.0 mmol) and triphenylphosphine (4.23 g, 16.4 mmol), *o*-dichlorobenzene was added under a nitrogen atmosphere. The reaction mixture was refluxed at 200 °C for overnight. The progress of the reaction was monitored by TLC analysis. Furthermore, the reaction mixture was washed with water and dichloromethane, and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to get the dark black colored residue. The crude mixture purified on column chromatography (petroleum ether/dichloromethane = 3:1, v/v) as an eluent offered Cz-SCz-3 as a yellow solid (0.5 g, yield = 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.46 (s, 1H), 8.21-8.10 (m, 4H), 7.54 (ddd, *J* = 11.0, 9.3, 4.5 Hz, 2H), 7.45 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.38-7.31 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 1.48 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.75, 139.92, 139.80, 137.90, 132.35, 126.93, 124.21, 123.58, 123.39, 123.28, 121.28, 120.91, 120.60, 119.28, 116.30, 111.26, 109.59, 77.34, 77.03, 76.71, 34.77, 32.07.

**Synthesis of 3',6'-di-*tert*-butyl-1-chloro-9-phenyl-9*H*-2,9'-bicarbazole (Cz-SCz-4):** A mixture of Cz-SCz-3 (0.71 g, 1.4 mmol), iodobenzene (0.44 g, 2.0 mmol) in 0.4 mL 1,3-dimethyl-tetrahydropyrimidin-2(1*H*)-one (DMPU) in a sealed tube were heated to 200 °C overnight with Cu powder (8.30 mg, 1.3 mmol) as catalyst, 18-crown-6 (94.0 mg, 1.4 mmol) as phase transfer catalyst, and K<sub>2</sub>CO<sub>3</sub> (0.33 g, 2.2 mmol) as base. The resulting mixture was washed with 20 mL three times and extracted with 20 mL dichloromethane before dried with Na<sub>2</sub>SO<sub>4</sub>. The final product Cz-SCz-4 was obtained through column chromatography with eluent of petroleum ether as white solid (0.50 g, yield = 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (dd, *J* = 7.9, 5.3 Hz, 2H), 8.15 (s, 2H), 7.51 (d, *J* = 4.4 Hz, 4H), 7.49-7.41 (m, 4H), 7.37 (dd, *J* = 7.7, 6.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 1.47 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.83, 142.56, 139.85, 138.08, 137.57, 133.62, 129.57, 129.01, 128.60, 126.97, 125.66, 123.51, 123.15, 122.18, 121.73, 120.88, 120.28, 119.10, 116.67, 116.22, 110.79, 109.53, 77.35, 77.03, 76.72, 34.74, 32.07.

**Synthesis of 9-(4-bromo-2-chlorophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (Cz-SCz):** To a solution of Cz-SCz-4 (0.50 g, 0.9 mmol) in *tert*-butylbenzene was slowly added *t*-BuLi (2.5 M in hexane, 1.5 mL, 2.5 mmol) at 0 °C. After reacting for 1 h at 70 °C, BBr<sub>3</sub> (0.4 mL, 3.9 mmol) was slowly added at -30 °C, and then the mixture was stirred at room temperature for 0.5 h. After addition of NEt(i-Pr)<sub>2</sub> (0.85 mL) at 0 °C, the reaction mixture was further stirred at 130 °C for 12h. After cooling to room temperature, the reaction mixture was carefully quenched by addition of saturated brine. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 50:1, v/v) and recrystallization from chloroform/methanol to afford Cz-SCz as a yellow solid (0.10 g, yield = 16%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.17 (dd, *J* = 7.6, 1.5 Hz, 1H), 9.06 (d, *J* = 1.8 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.49 (dd, *J* = 10.4, 5.2 Hz, 3H), 8.38 (dd, *J* = 8.7, 3.9 Hz, 2H), 8.27 (d, *J* = 1.9 Hz, 1H), 8.21 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.87 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.67 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.61-7.52 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 1.69 (s, 9H), 1.57 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.46, 143.65, 142.80, 141.00, 140.56, 140.02, 138.06, 137.21, 136.04, 135.59, 130.78, 128.13, 126.13, 125.45, 124.15, 124.06, 123.50, 123.42, 121.25, 121.08, 119.43, 119.23, 116.11, 115.37, 113.81, 113.54, 113.01,

106.00, 76.30, 75.99, 75.67, 34.24, 33.82, 31.29, 30.85. HRMS (MALDI-TOF,  $m/z$ ):  $[M]^+$  calcd for  $C_{38}H_{33}BN_2$ , 529.2815; found, 529.2815.

## 2.2 Synthesis of BCz-SCz



**Synthesis of 9,9'-(4-bromo-6-chloro-1,3-phenylene)bis(3,6-di-*tert*-butyl-9*H*-carbazole) (BCz-SCz-1):** A solution of cesium carbonate (4.81 g, 15 mmol) and 3,6-*di-tert*-butylcarbazole (3.00 g, 11.0 mmol) in dry DMF (100 mL) was stirred for 30 min at room temperature, then 1-bromo-5-chloro-2,4-difluorobenzene (1.14 g, 5.0 mmol) was added into solution. The mixture was stirred at 150 °C for 12 h, and cooled to room temperature, and then water (250 mL) was added, and the aqueous layer was extracted with ethyl acetate. The combined organic was washed with water (100 mL), and evaporated under reduced pressure to obtain the crude product. The residue was then purified by flash chromatography (petroleum ether/dichloromethane = 6:1) to obtain BCz-SCz-1 as a white powder 3.52 g, (yield = 94%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.20 (s, 1H), 8.13 (s, 4H), 7.61 (s, 1H), 7.49 (d,  $J = 8.6$  Hz, 4H), 7.11 (dd,  $J = 8.5, 6.0$  Hz, 4H), 1.46 (s, 36H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.43, 143.36, 138.96, 138.86, 137.38, 136.23, 135.77, 133.88, 132.18, 123.83, 123.61, 123.52, 123.30, 116.48, 109.34, 109.31, 34.76, 31.98.

**Synthesis of 9,9'-(5-chloro-2'-nitro-[1,1'-biphenyl]-2,4-diyl)bis(3,6-di-*tert*-butyl-9*H*-carbazole) (BCz-SCz-2):** *n*-BuLi (3.2 mL, 5.2 mmol, 1.60 M solution in hexanes) was added dropwise to a solution of BCz-SCz-1 (3.52 g, 4.7 mmol) in anhydrous THF (60 mL) at -78 °C to get a pale-yellow solution. After stirring for 1.5 h, trimethyl borate (0.73 g, 7.1 mmol) was added to the solution. The resulting solution was stirred at -78 °C for 40 min and allowed to warm to room temperature overnight. Then water was added to the solution and diluted HCl was used to tune the

pH to 7. The organic was extracted with dichloromethane and concentrated under reduced pressure to obtain the (5-chloro-2,4-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)boronic acid as white solid, which was used for afterward reactions without further purification. Thus obtained crude (5-chloro-2,4-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)boronic acid (1.83 g) was added to the mixture of 1-bromo-2-nitrobenzene (0.54 g, 2.7 mmol), Pd(dppf)Cl<sub>2</sub> (0.30 g, 0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.44 g, 7.5 mmol) in a mixed solvent of 1,4-dioxane (20 mL) and water (5 mL), then the mixture was stirred at 110 °C for 12 h. The resulted solution was extracted with ethyl acetate and water, the organic was separated and concentrated under reduced pressure. The crude product was purified by flash chromatography (petroleum ether/dichloromethane = 3:1) to obtain BCz-SCz-2 as a yellow powder (1.41 g, yield = 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (s, 2H), 7.97 (s, 2H), 7.87 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H), 7.51 (d, *J* = 9.3 Hz, 2H), 7.40 (d, *J* = 6.3 Hz, 2H), 7.32 (s, 2H), 7.29-7.23 (m, 3H), 7.17 (s, 1H), 6.95 (s, 1H), 1.47 (s, 18H), 1.39 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.81, 143.32, 139.38, 139.01, 138.13, 136.81, 135.75, 132.95, 132.80, 131.79, 131.67, 131.38, 129.18, 124.83, 123.63, 116.43, 109.38, 77.34, 77.02, 76.71, 34.77, 34.67, 32.01, 31.91.

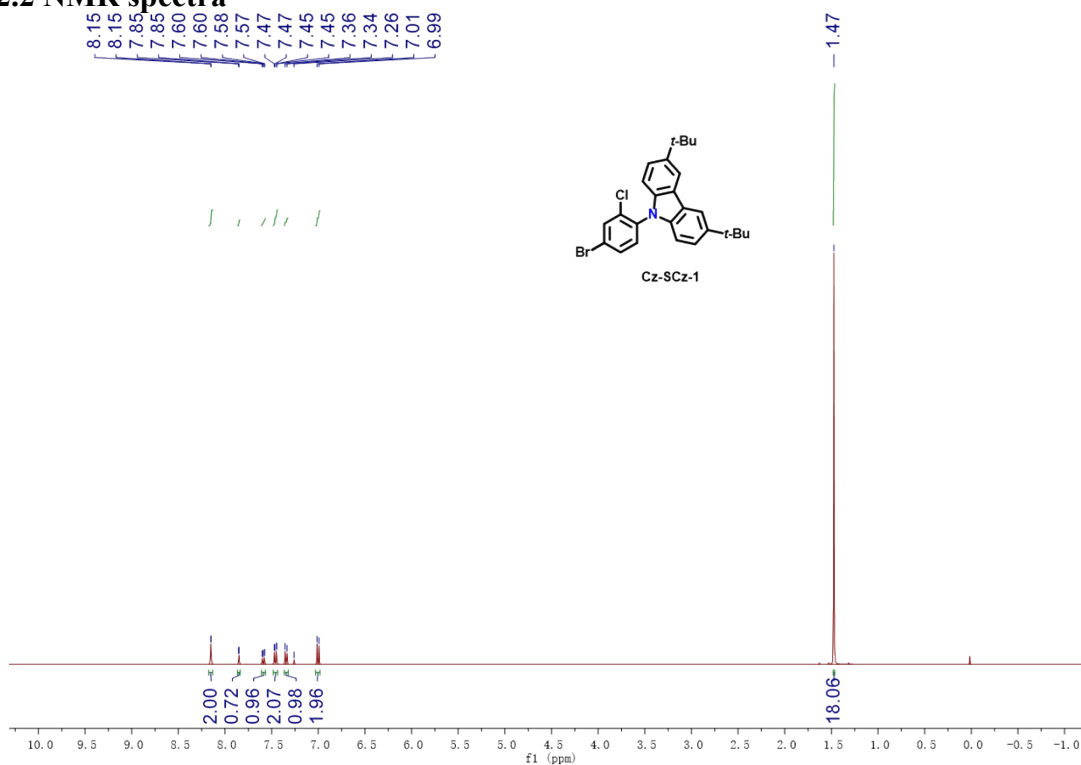
**Synthesis of 3,3'',6,6''-tetra-*tert*-butyl-1'-chloro-9'*H*-9,2':4',9''-tercarbazole (BCz-SCz-3):** To the mixture of BCz-SCz-2 (1.41 g, 1.8 mmol) and triphenylphosphine (1.93 g, 7.4 mmol), *o*-dichlorobenzene was added under a nitrogen atmosphere. The reaction mixture was refluxed at 200 °C for overnight. The progress of the reaction was monitored by TLC analysis. Further, the reaction mixture was washed with water and dichloromethane, and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to get the dark black colored residue. The crude mixture purified on column chromatography (petroleum ether/dichloromethane = 3:1, v/v) as an eluent offered BCz-SCz-3 as a yellow solid (1.01 g, yield = 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 8.21 (d, *J* = 1.7 Hz, 2H), 8.16 (d, *J* = 1.7 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 2H), 7.45-7.41 (m, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.93-6.88 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 1.47 (d, *J* = 3.8 Hz, 36H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.10, 143.00, 139.95, 139.56, 139.20, 139.16, 132.84, 131.19, 127.14, 123.85, 123.70, 123.54, 123.44, 121.56, 121.44, 120.76, 116.37, 116.34, 114.24, 110.75, 109.90, 109.59, 77.33, 77.01, 76.69, 34.76, 32.03, 32.01.

**Synthesis of 3,3'',6,6''-tetra-*tert*-butyl-1'-chloro-9'-phenyl-9'*H*-9,2':4',9''-tercarbazole (BCz-SCz-4):** A mixture of BCz-SCz-3 (1.01 g, 1.3 mmol), iodobenzene (0.44 g, 2.0 mmol) in 0.5 mL 1,3-dimethyl-tetrahydropyrimidin-2(1*H*)-one in a sealed tube were heated to 200 °C overnight with Cu powder (8.3 mg, 1.3 mmol) as catalyst, 18-crown-6 (78.9 mg, 0.3 mmol) as phase transfer catalyst, and K<sub>2</sub>CO<sub>3</sub> (0.22 g, 2.0 mmol) as base. The resulting mixture was washed with 20 mL three times and extracted with 20 mL dichloromethane before dried with Na<sub>2</sub>SO<sub>4</sub>. The final product BCz-SCz-4 was obtained through column chromatography with eluent of petroleum ether as white solid (0.61 g, yield = 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (dd, *J* = 10.6, 1.7 Hz, 2H), 8.12 (t, *J* = 2.7 Hz, 2H), 7.72-7.58 (m, 3H), 7.58-7.38 (m, 8H), 7.38-7.30 (m, 1H), 7.20-7.08 (m, 4H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 9.7 Hz, 1H), 1.47 (dd, *J* = 11.8, 4.6 Hz, 36H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.96, 143.06, 142.94, 142.78, 139.59, 139.42, 139.31, 138.66, 137.86, 134.03, 131.12, 130.22, 129.68, 129.13, 128.88, 127.35, 127.13, 123.89, 123.61, 123.54, 123.38, 123.30, 122.99, 121.52, 121.06, 120.08, 116.35, 116.26, 115.90, 77.32, 77.01, 76.69, 34.77, 34.71, 32.01.

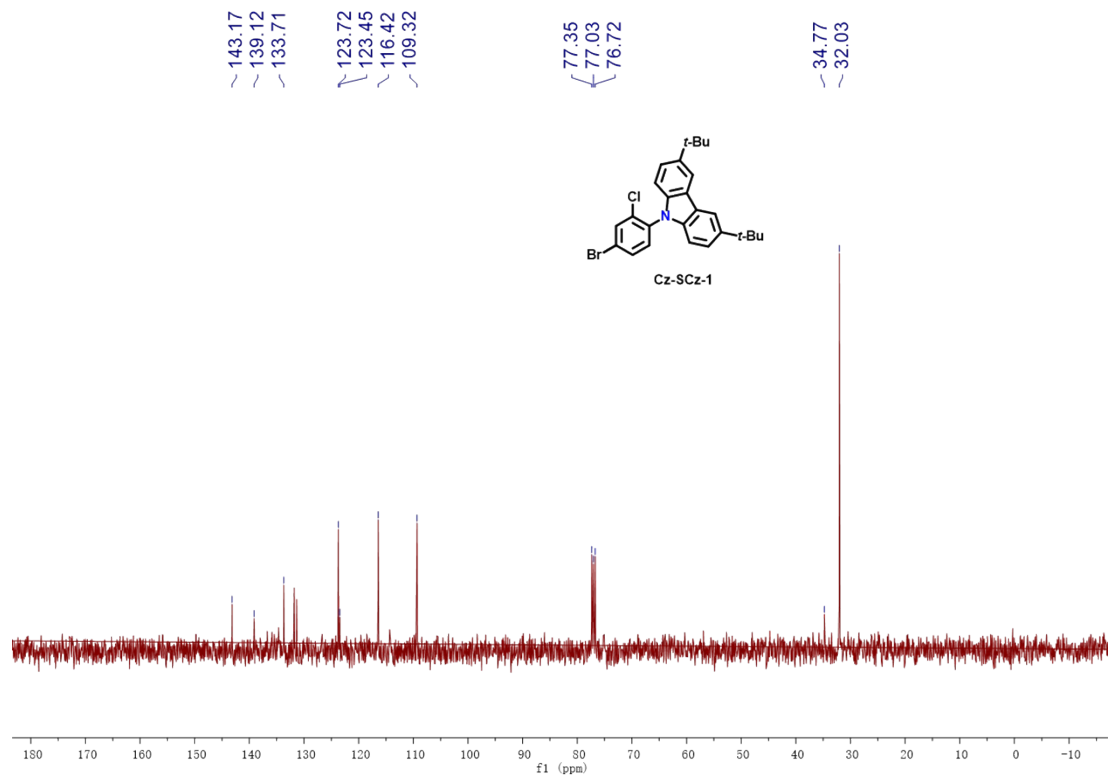
**Synthesis of 9-(4-bromo-2-chlorophenyl)-3,6-di-*tert*-butyl-9*H*-carbazole (BCz-SCz):** To a solution of BCz-SCz-4 (0.61 g, 0.7 mmol) in *tert*-butylbenzene was slowly added *t*-BuLi (2.5 M in hexane, 1.0 mL, 2.5 mmol) at 0 °C. After reacting for 1 h at 70 °C, BBr<sub>3</sub> (0.2 mL, 2.5 mmol) was slowly added at -30 °C, and then the mixture was stirred at room temperature for 0.5 h. After addition of NEt(*i*-Pr)<sub>2</sub> (0.5 mL) at 0 °C, the reaction mixture was further stirred at 130 °C for 24 h. After cooling to room temperature, the reaction mixture was carefully quenched by addition of saturated brine. The product was extracted with dichloromethane, and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 50:1, v/v) and recrystallization from chloroform/methanol to afford BCz-SCz as a yellow solid (0.15 g, yield = 26%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.34 (dd, *J* = 7.7, 1.4 Hz, 1H), 9.20 (d, *J* = 1.8 Hz, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 8.69-8.53 (m, 3H), 8.31 (dd, *J* = 19.1, 1.7 Hz, 3H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.05-7.93 (m, 1H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.52 (td, *J* = 8.7, 1.7 Hz, 2H), 7.42 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = 7.9, 0.8 Hz, 1H), 1.72 (s, 9H), 1.50 (d, *J* = 10.2 Hz, 27H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.90, 144.19, 142.94, 142.25, 141.96, 140.84, 140.64, 138.43,

138.27, 137.08, 136.23, 135.62, 131.09, 128.30, 126.15, 124.46, 123.81, 123.59, 123.48, 123.04, 122.64, 122.38, 121.83, 121.40, 119.81, 116.22, 115.79, 115.36, 113.06, 112.93, 111.52, 109.16, 106.00, 76.30, 75.99, 75.67, 31.27, 31.04, 30.74, 28.68. HRMS (MALDI-TOF, m/z): [M]<sup>+</sup> calcd for C<sub>58</sub>H<sub>57</sub>BN<sub>3</sub>, 806.4646; found, 806.4645.

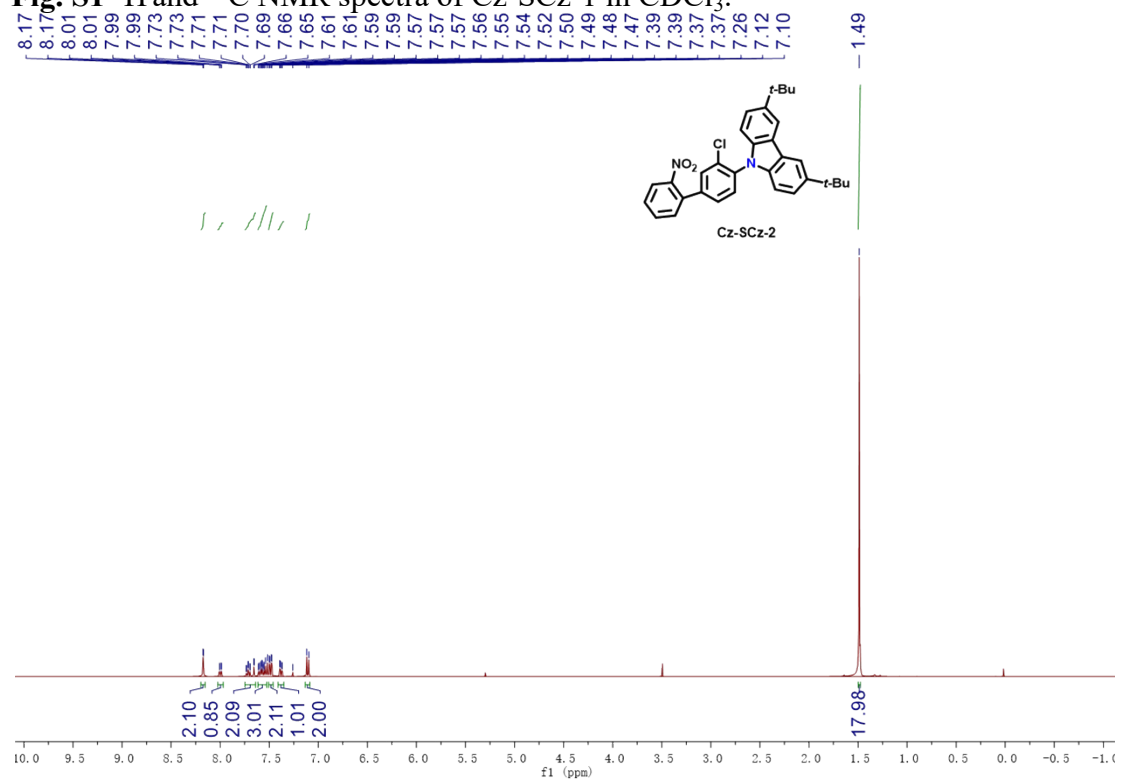
## 2.2 NMR spectra

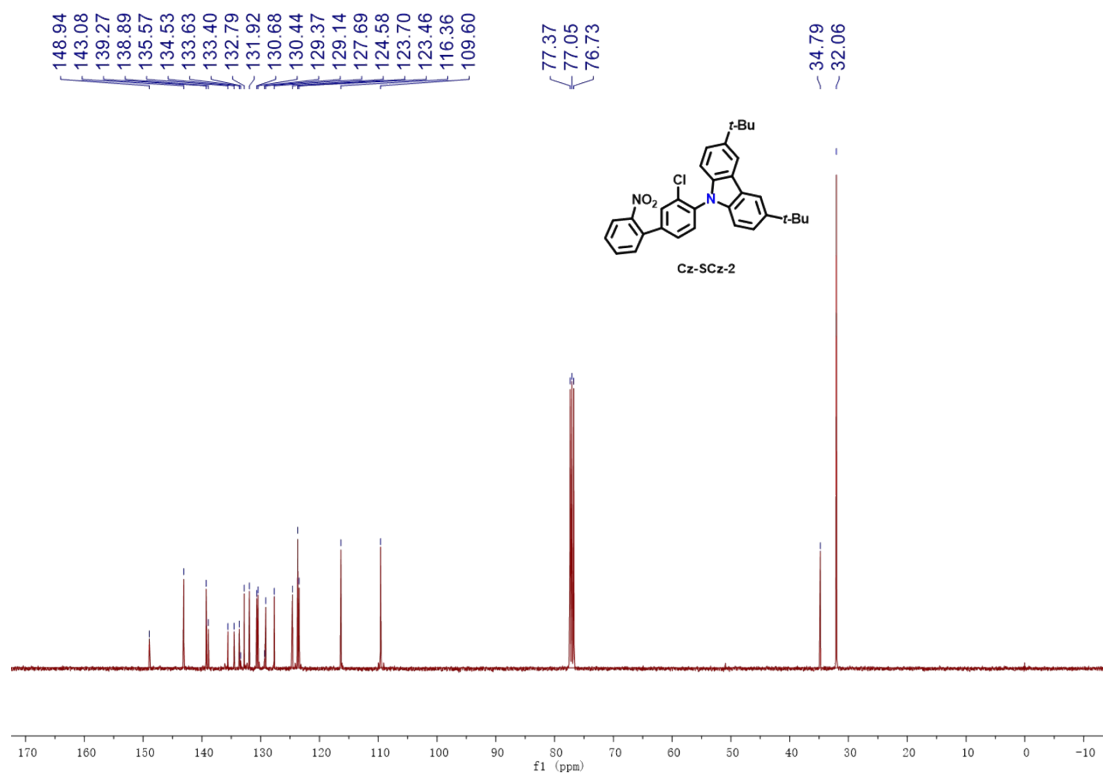




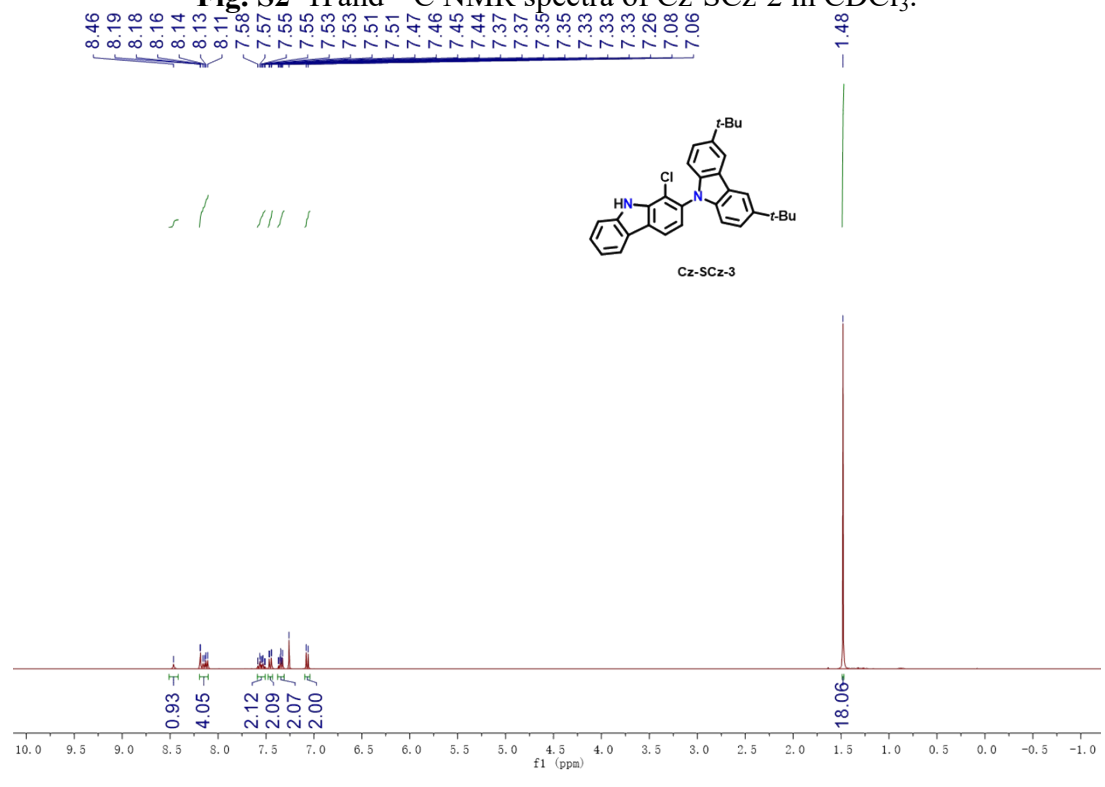


**Fig. S1**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Cz-SCz-1 in  $\text{CDCl}_3$ .





**Fig. S2** <sup>1</sup>H and <sup>13</sup>C NMR spectra of Cz-SCz-2 in CDCl<sub>3</sub>.



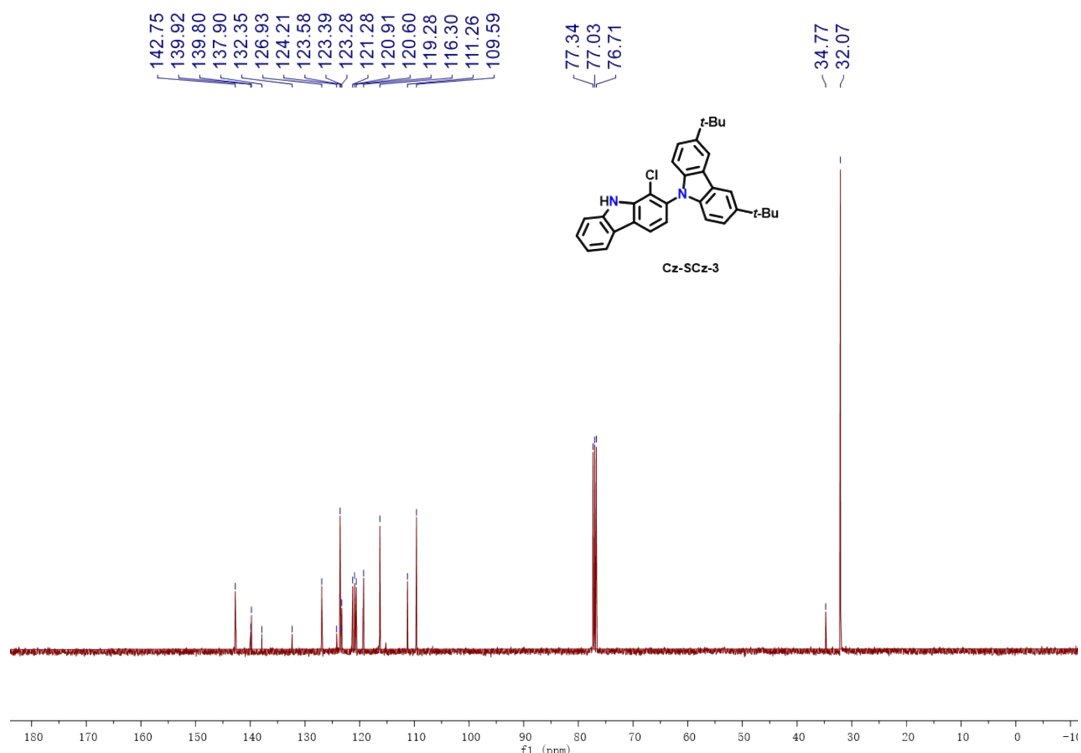
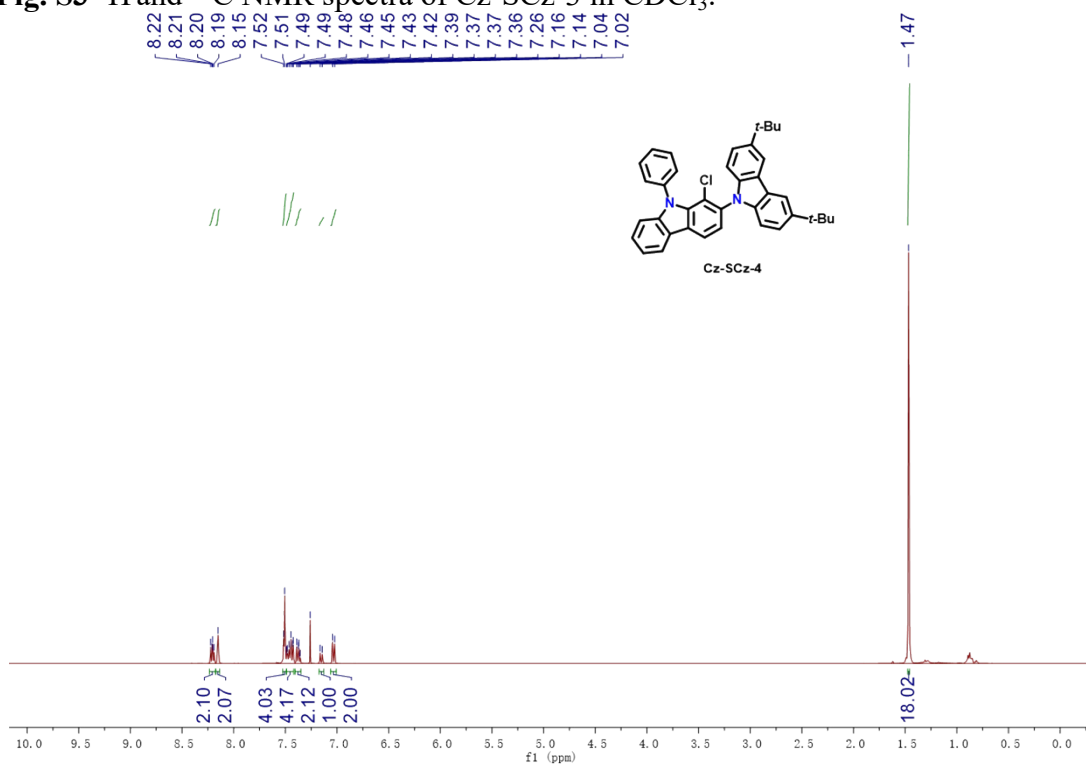
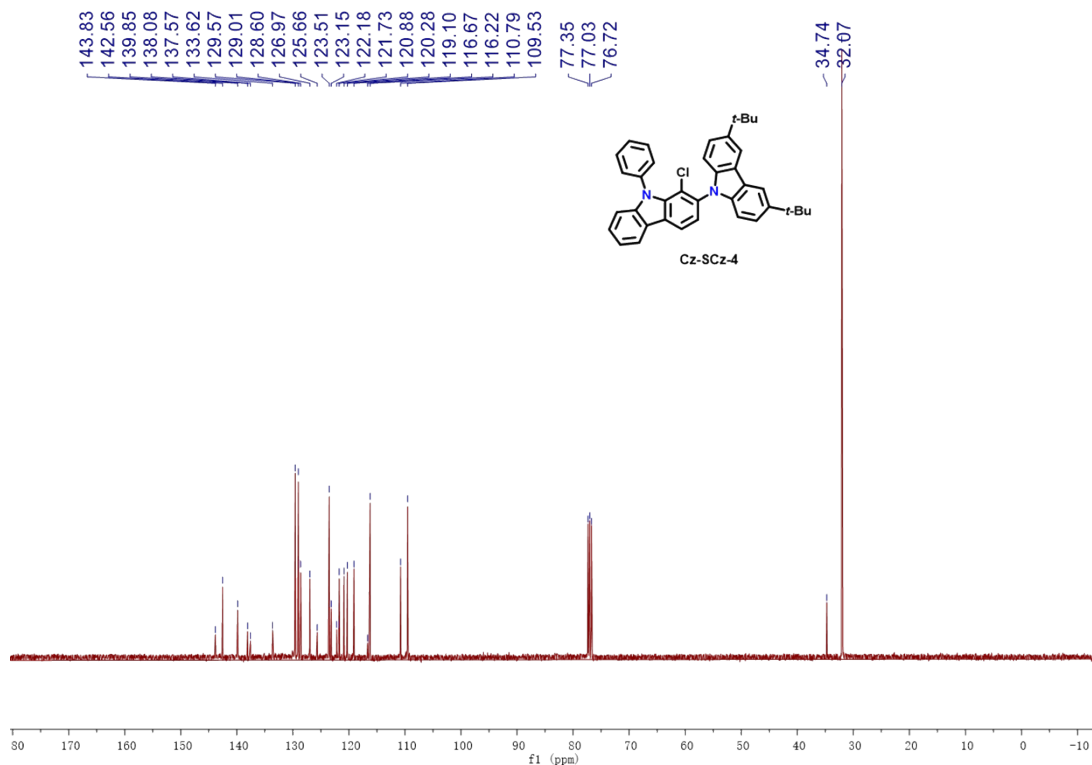
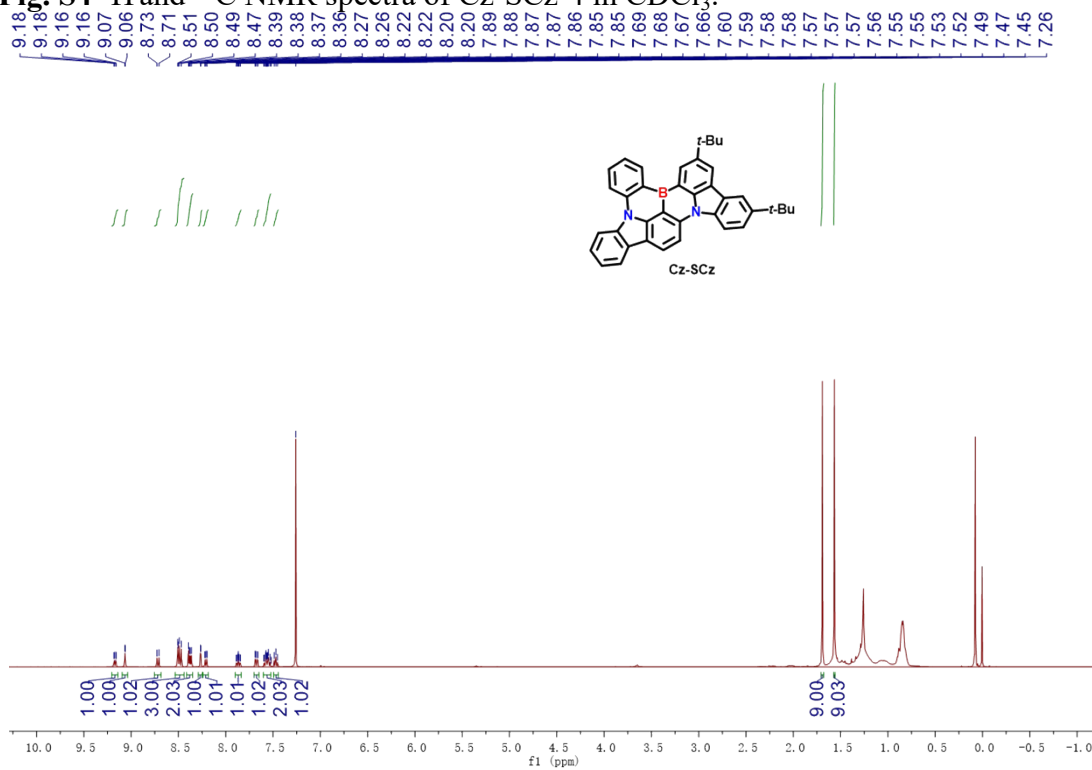


Fig. S3  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Cz-SCz-3 in  $\text{CDCl}_3$ .





**Fig. S4**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Cz-SCz-4 in  $\text{CDCl}_3$ .



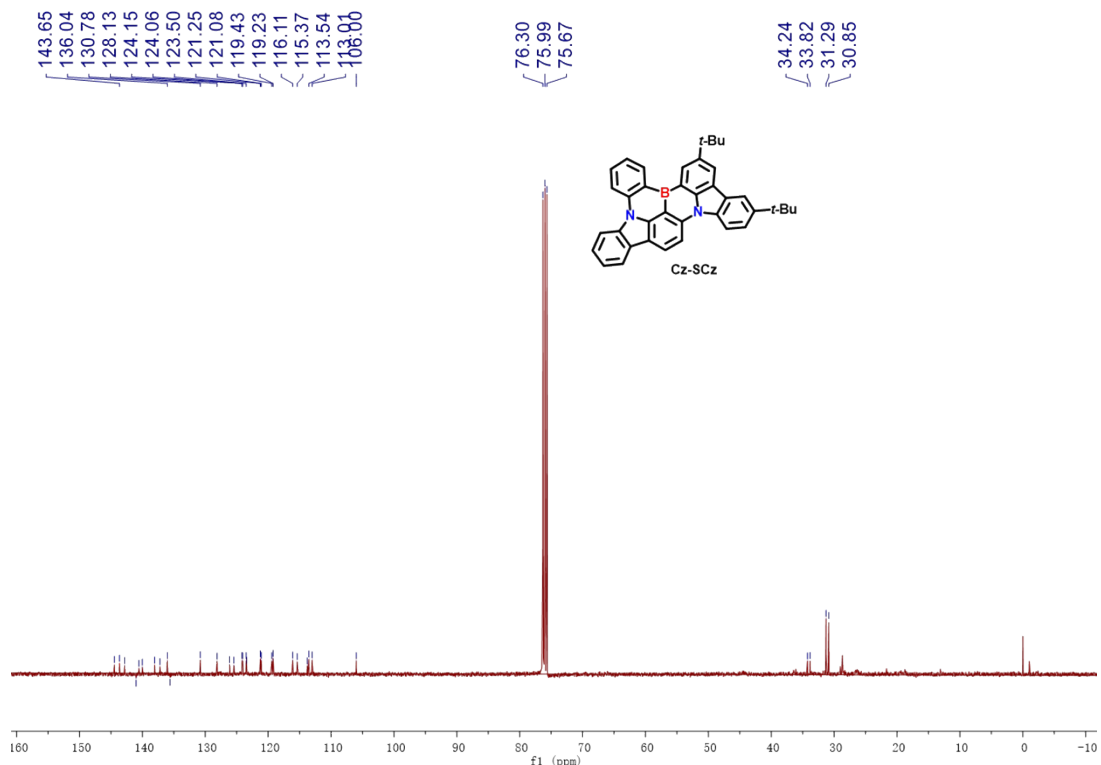
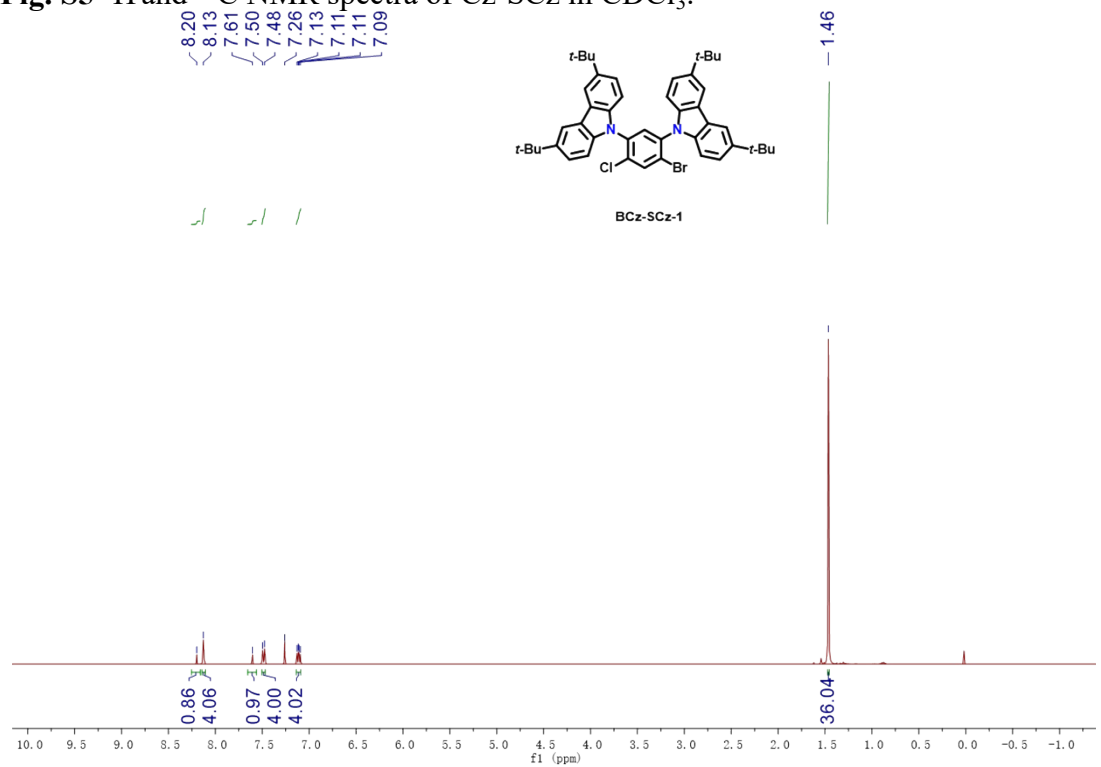
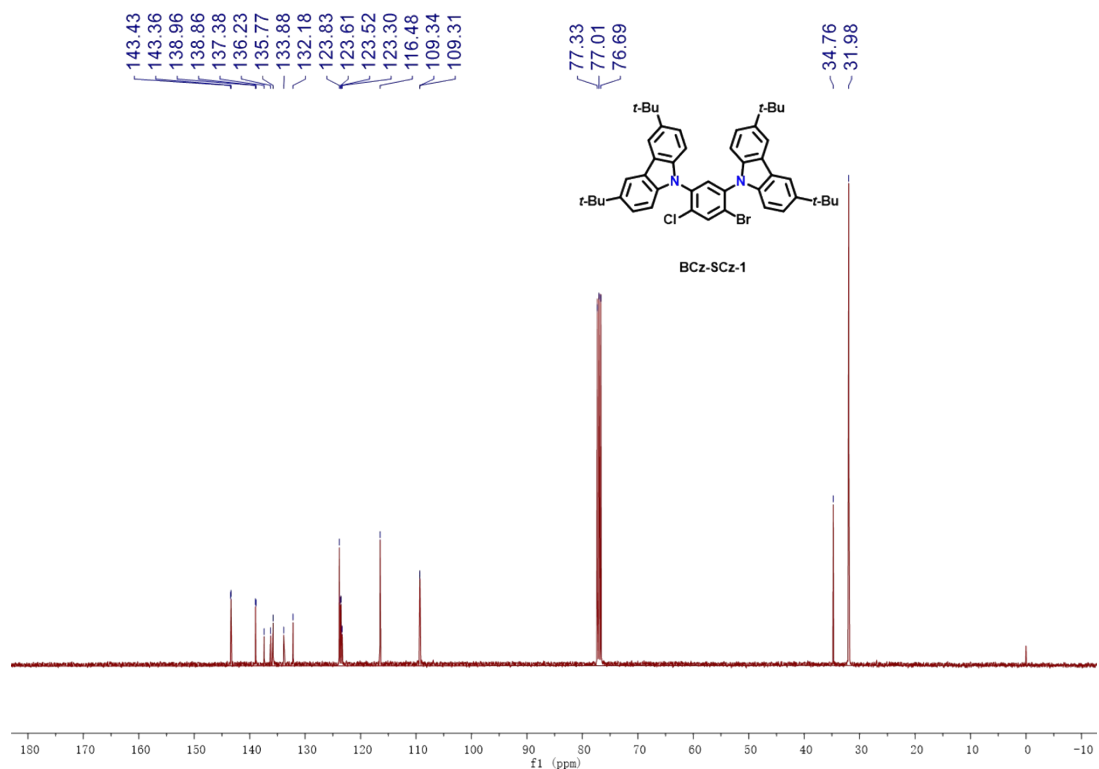
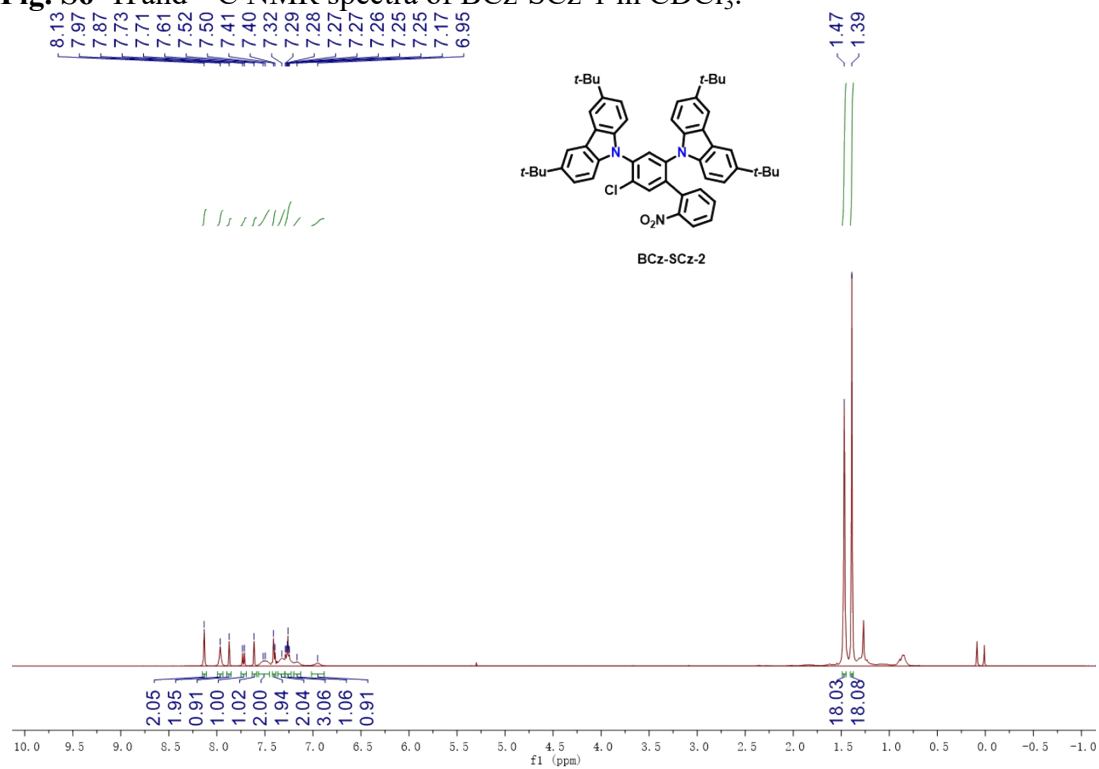


Fig. S5  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Cz-SCz in  $\text{CDCl}_3$ .





**Fig. S6**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of BCz-SCz-1 in  $\text{CDCl}_3$ .



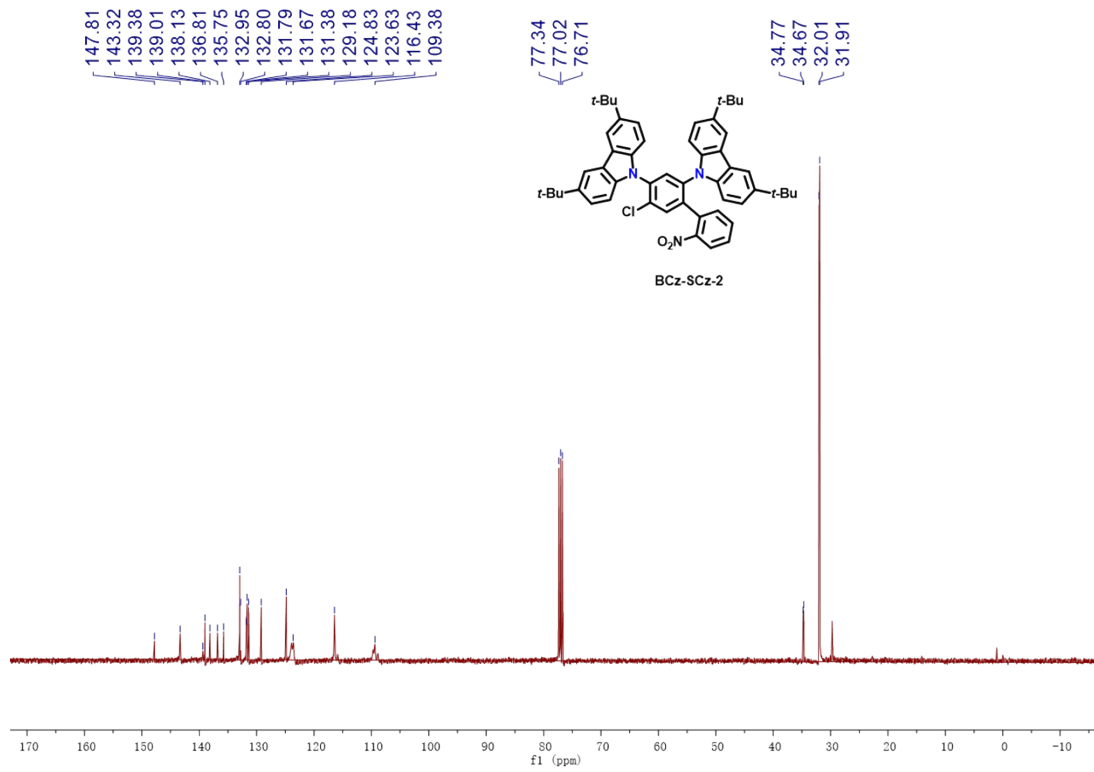
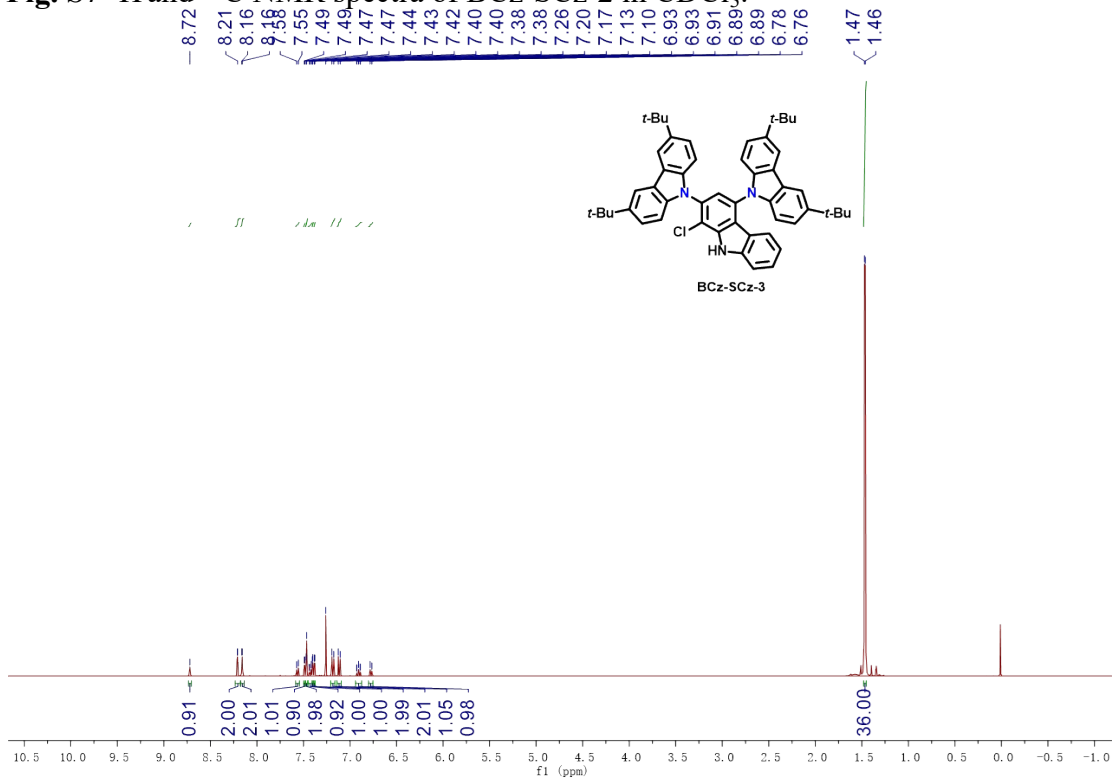


Fig. S7  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of BCz-SCz-2 in  $\text{CDCl}_3$ .



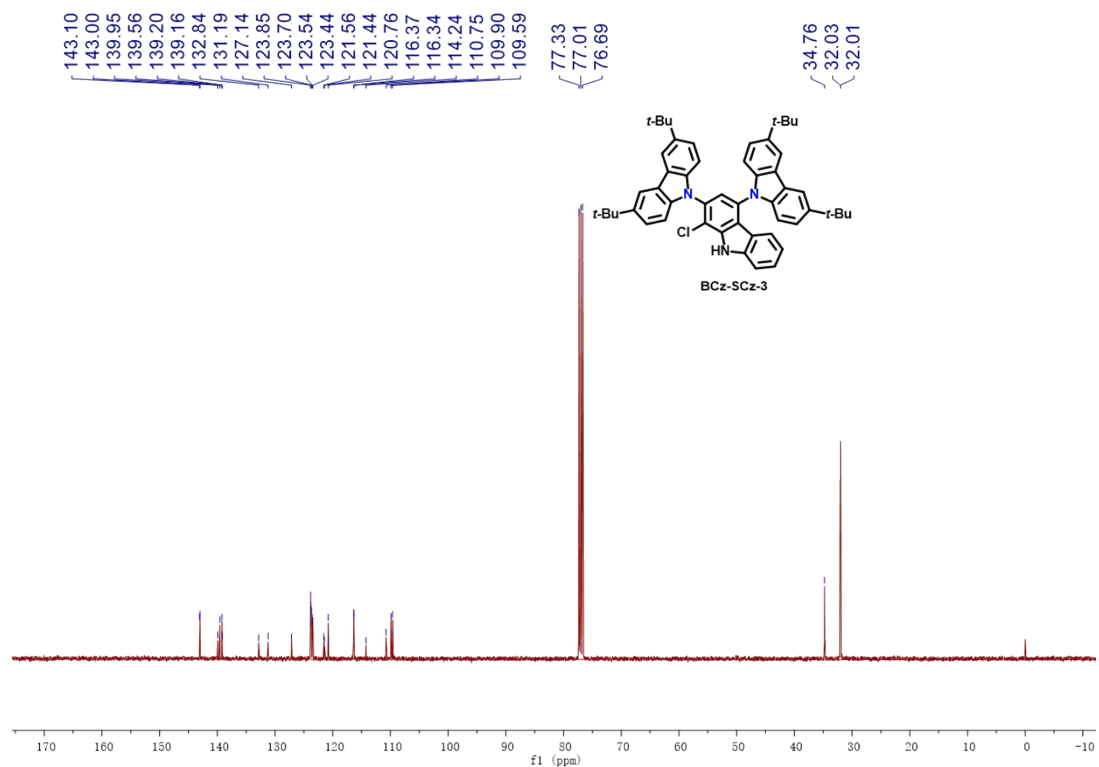
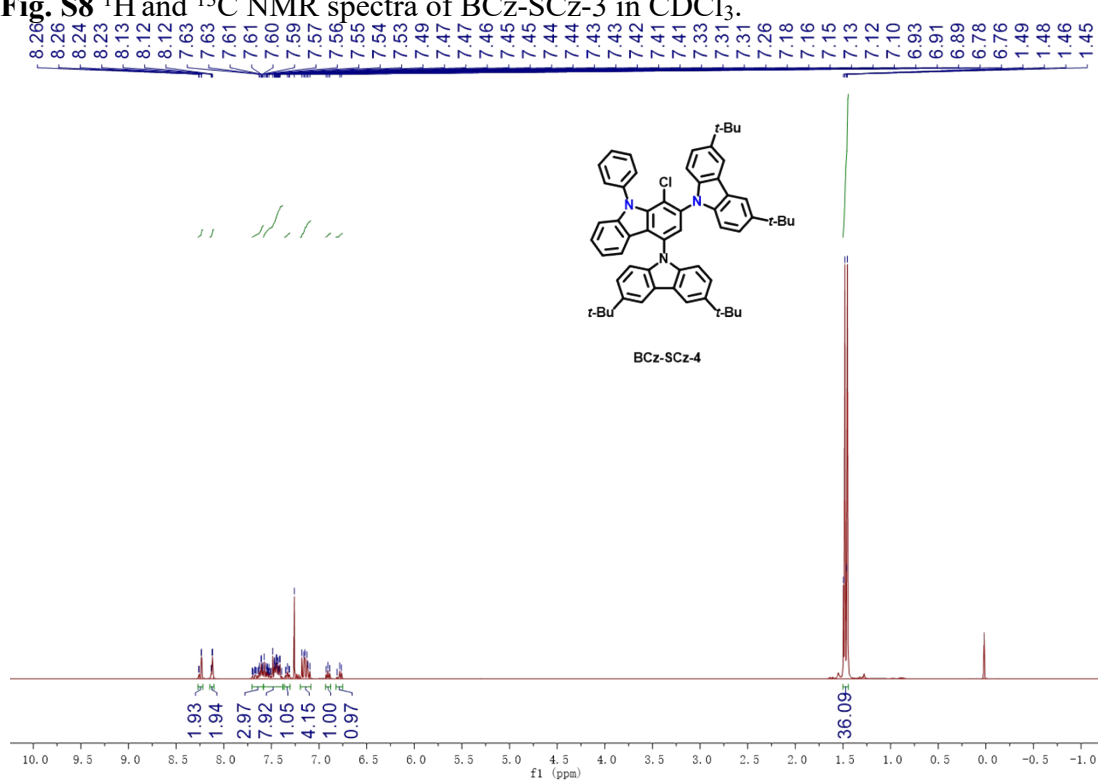
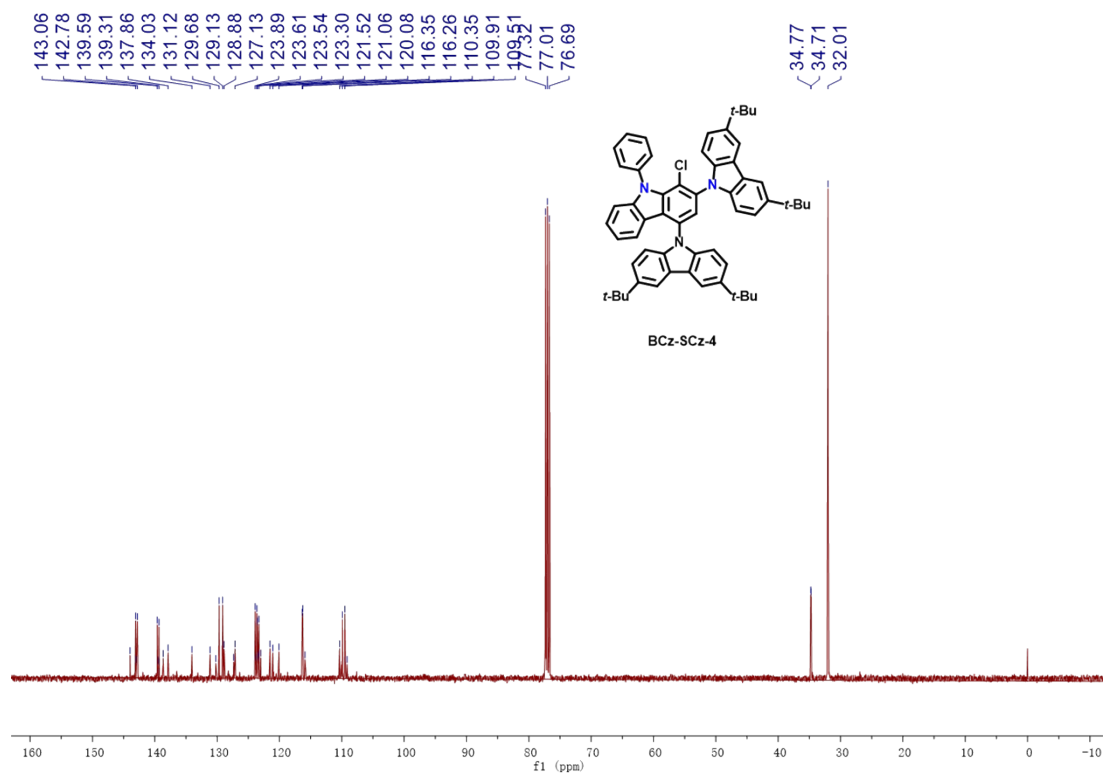


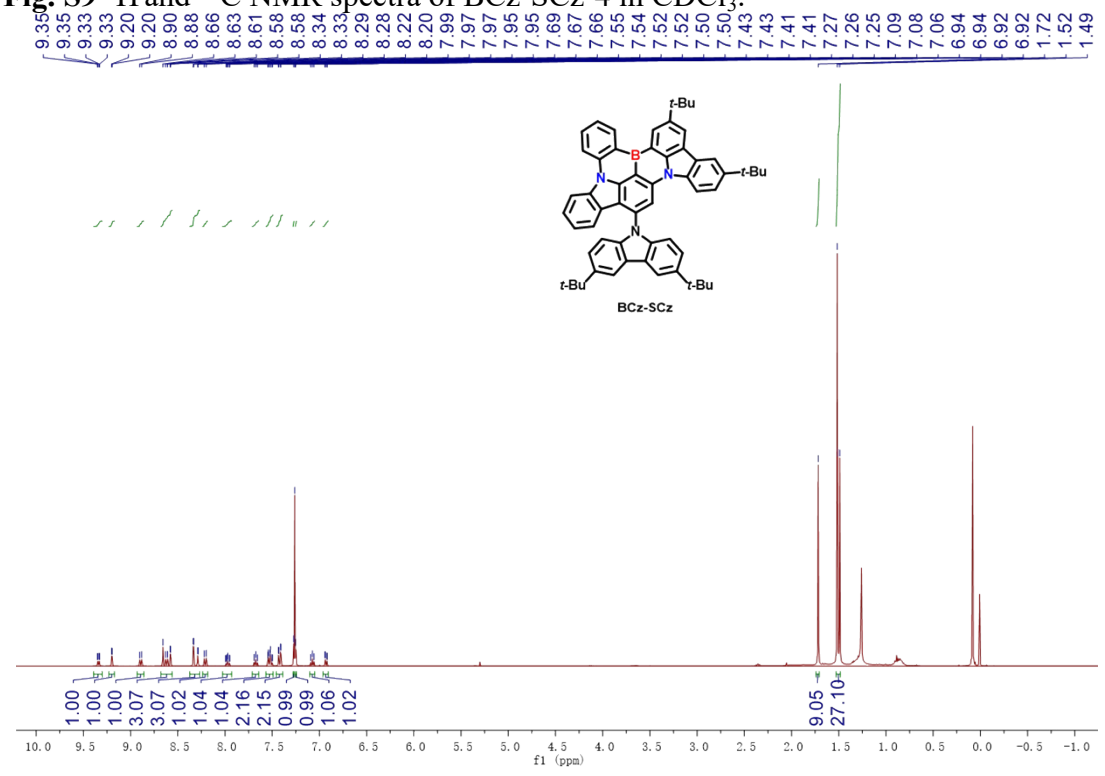
Fig. S8  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of BCz-SCz-3 in  $\text{CDCl}_3$ .

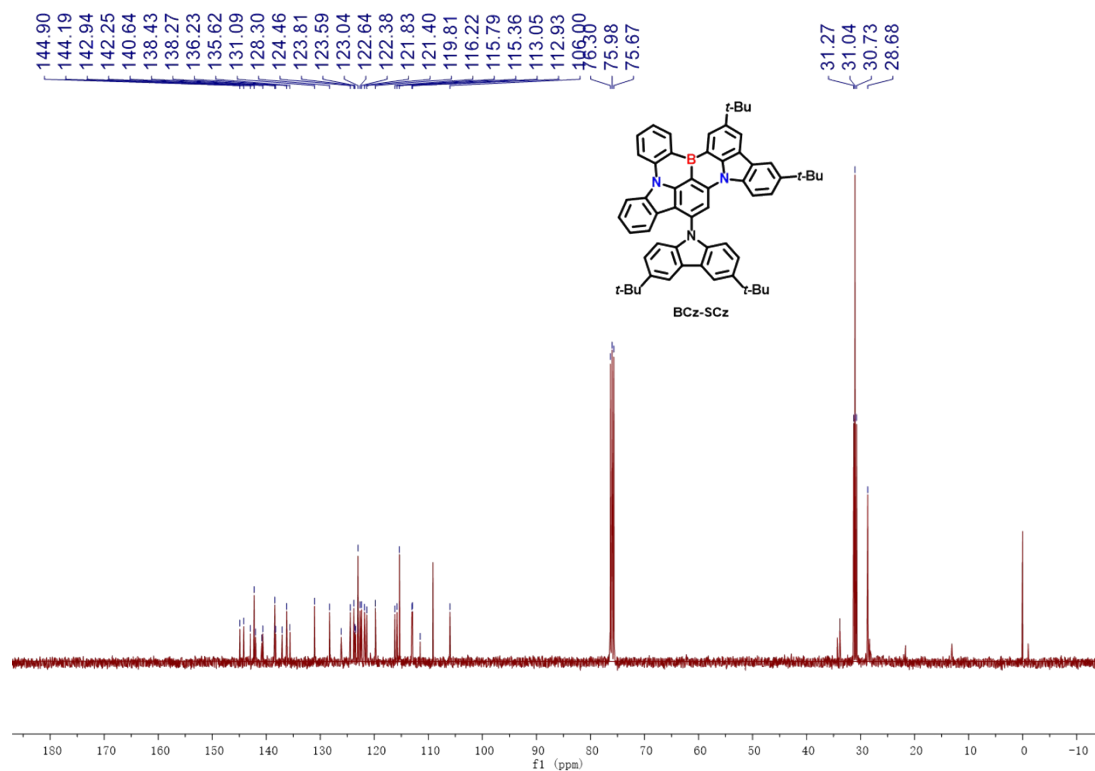






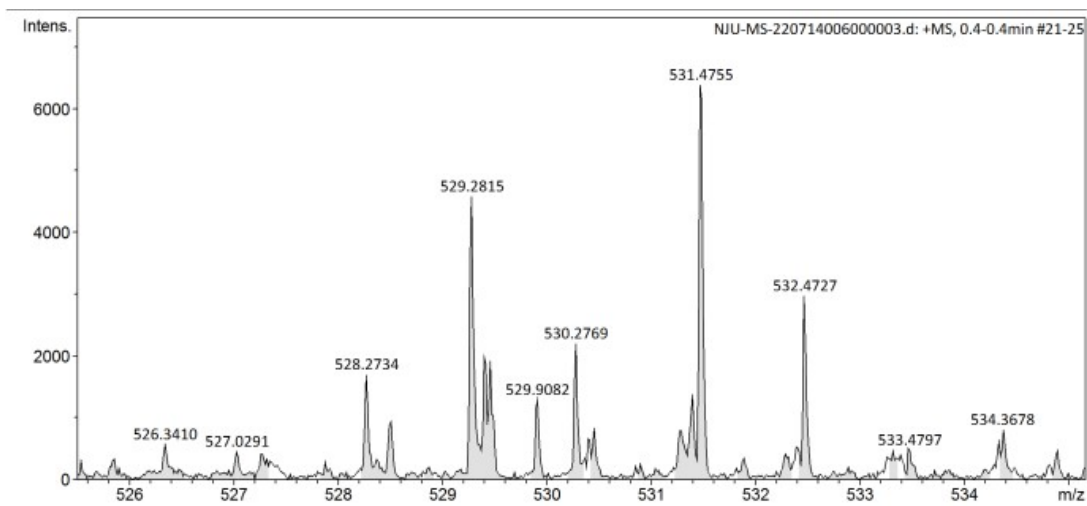
**Fig. S9**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of BCz-SCz-4 in  $\text{CDCl}_3$ .

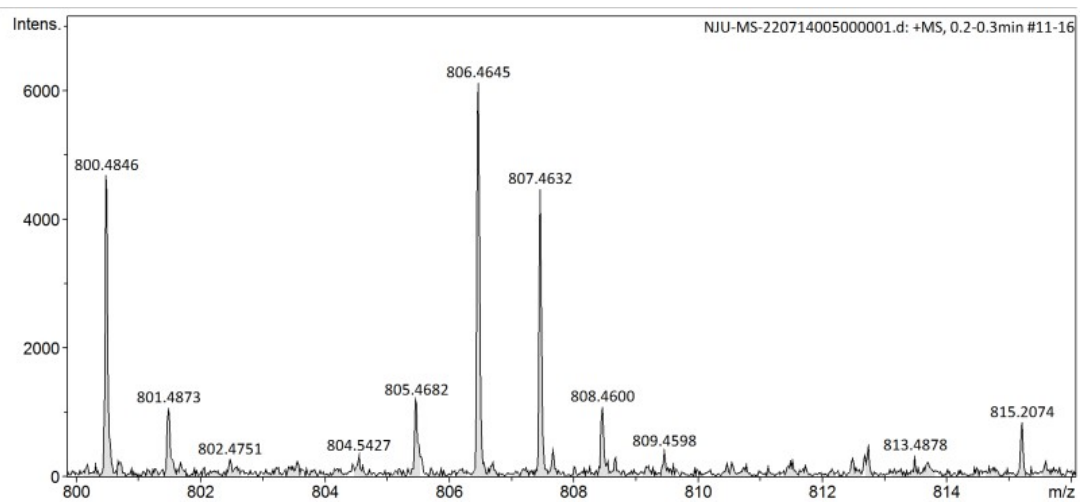




**Fig. S10**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of BCz-SCz in  $\text{CDCl}_3$ .

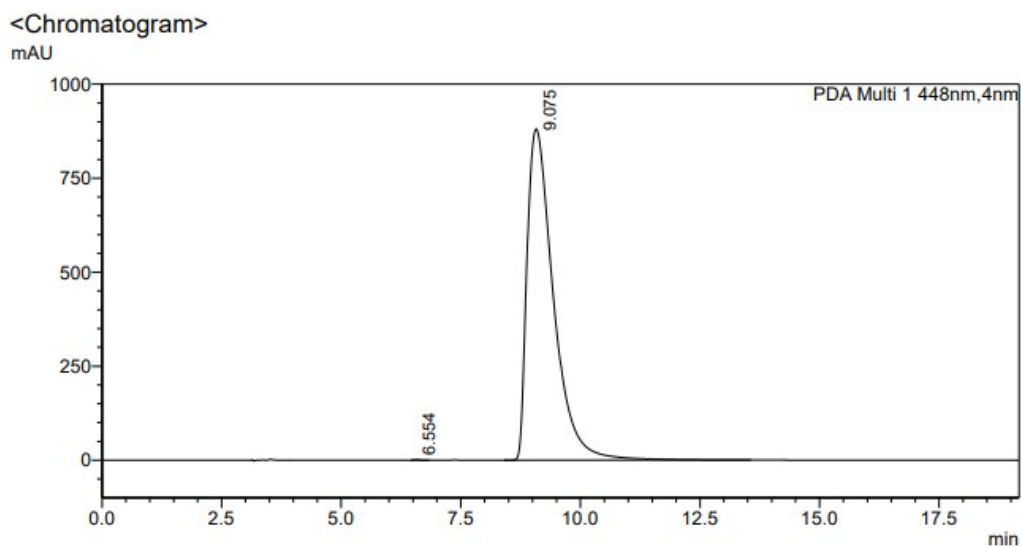
### 2.3 Mass spectra





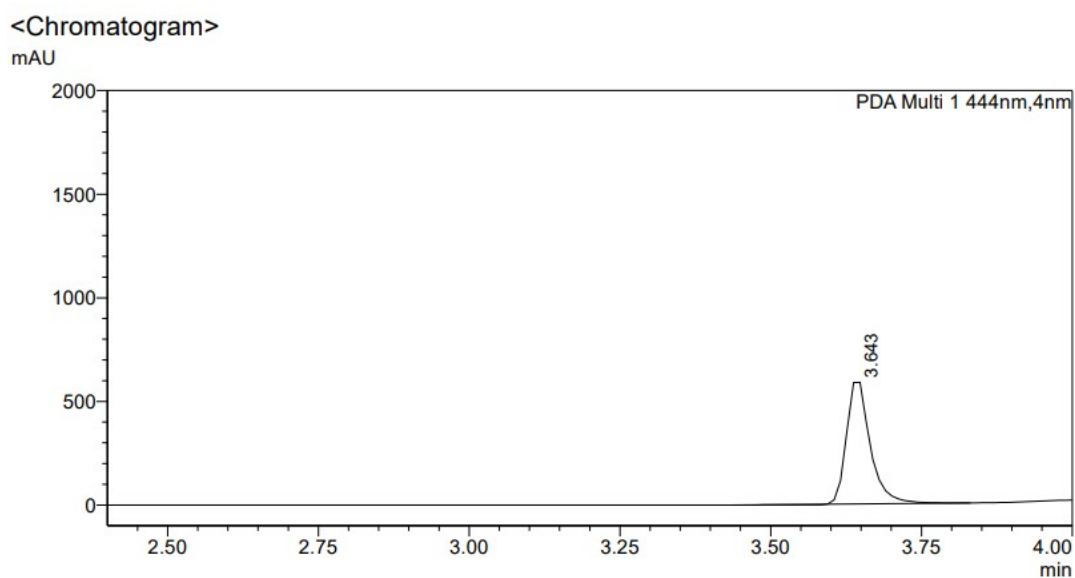
**Fig. S11** High resolution mass spectra of Cz-SCz and BCz-SCz.

## 2.4 High performance liquid chromatography spectra



<Peak Table>

PDA Ch1 448nm			
Peak#	Ret. Time	Area	Area%
1	6.554	13432	0.040
2	9.075	33785139	99.960
总计		33798572	100.000



<Peak Table>

PDA Ch1 444nm			
Peak#	Ret. Time	Area	Area%
1	3.643	1611867	100.000
总计		1611867	100.000

**Fig. S12.** High performance liquid chromatography spectra of Cz-SCz (up) and BCz-SCz (down).

### 3. Supplementary data

#### 3.1 Thermal gravimetric analyzer

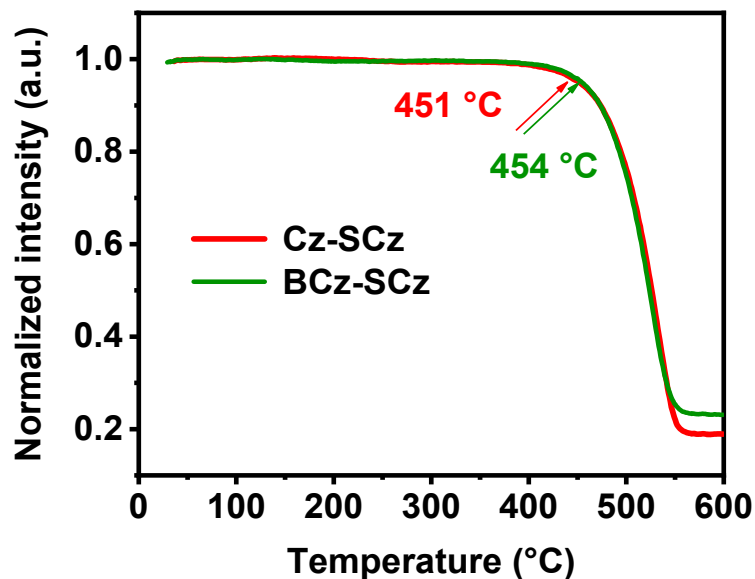


Fig. S13 TGA curves of Cz-SCz and BCz-SCz.

#### 3.2 Crystal data

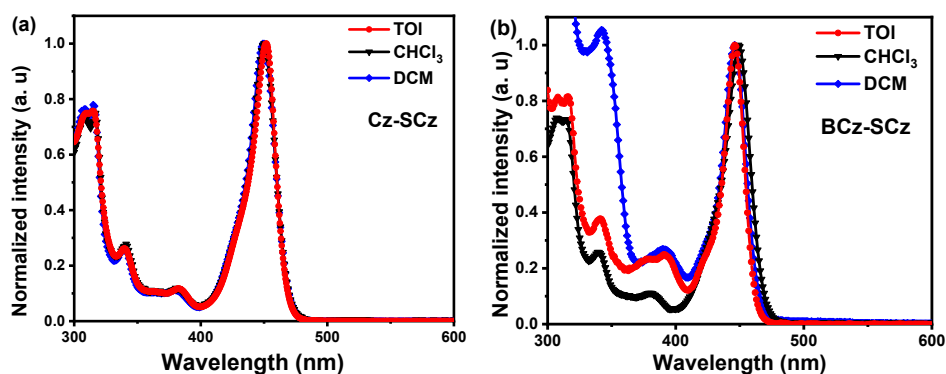
**Table S1.** Crystal data and structure refinement for BCz-SCz.

CCDC number	2304704
Empirical formula	C <sub>58</sub> H <sub>56</sub> BN <sub>3</sub>
Formula weight	805.86
Temperature/K	193.00
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> /Å	13.2726(3)
<i>b</i> /Å	13.3635(3)
<i>c</i> /Å	15.1957(4)
$\alpha$ /°	67.3960(10)
$\beta$ /°	75.2330(10)
$\gamma$ /°	78.5720(10)
Volume/Å <sup>3</sup>	2390.82(10)
<i>Z</i>	2
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.119
$\mu$ /mm <sup>-1</sup>	0.064

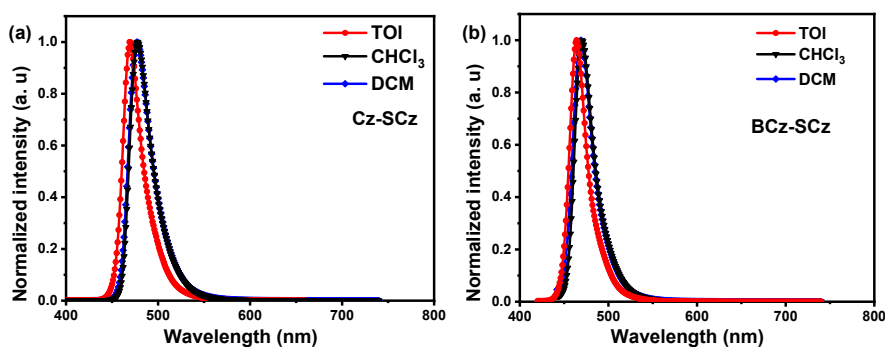
$F(000)$	860.0
Crystal size/mm <sup>3</sup>	0.15 × 0.12 × 0.11
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	3.904 to 55.026
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -16 ≤ l ≤ 19
Reflections collected	22433
Independent reflections	15024 [Rint = 0.0390, Rsigma = 0.07195]
Data/restraints/parameters	15024/1346/1222
Goodness-of-fit on $F^2$	1.011
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0390$ , $wR_2 = 0.0719$
Final R indexes [all data]	$R_1 = 0.1169$ , $wR_2 = 0.2531$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.51/-0.41
Flack parameter	1.1(10)

$$R_I^a = \frac{\sum ||F_o| - |F_c||}{\sum F_o}, wR_2^b = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

### 3.2 Absorption and photoluminescence spectra of both emitters in various solvents

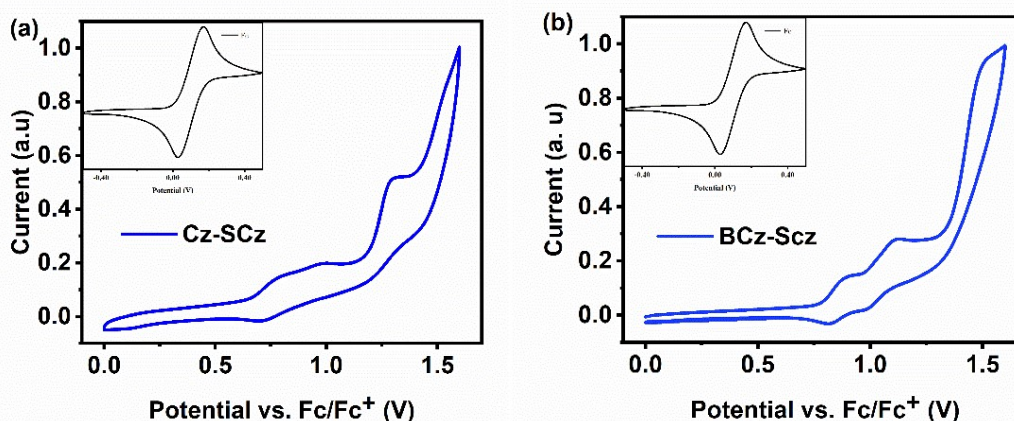


**Fig. S14** UV-vis absorption spectra of Cz-SCz (a), BCz-SCz (b) in various solvents (concentration:  $1 \times 10^{-5}$  M).



**Fig. S15** Photoluminescence spectra of Cz-SCz (a), BCz-SCz (b) in various solvents (concentration:  $1 \times 10^{-5}$  M).

### 3.3 Cyclic voltammogram curves and theoretical calculation



**Fig. S16** Cyclic voltammogram curves of Cz-SCz (a), BCz-SCz (b) measured in CH<sub>3</sub>CN containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate.

**Table S2.** Electrochemical properties of Cz-SCz and BCz-SCz.

	$E_{\text{ox,onset}}^{\text{a}}$ V	$E_{\text{g,opt}}^{\text{b}}$ eV	$E_{\text{HOMO}}^{\text{c}}$ eV	$E_{\text{LUMO}}^{\text{d}}$ eV
Cz-SCz	0.75	2.64	-5.38	-2.74
BCz-SCz	0.89	2.67	-5.52	-2.85

<sup>a</sup>The onset of oxidation curve; <sup>b</sup>Optical gap ( $1240/\lambda_{\text{onset}}$ ); <sup>c</sup> $E_{\text{HOMO}} = -[E_{\text{ox}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8]$  eV;

<sup>d</sup> $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{\text{g,opt}})$ .

**Table S3.** Summary of TD-DFT calculation for BCz-SCz and Cz-SCz at the S<sub>0</sub> structure at the B3LYP/6-31G(d) level and related photophysical data.

Compound	Transition	Wavelength (nm)	Energy (eV)	Oscillator strength ( <i>f</i> )
Cz-SCz	S <sub>0</sub> -S <sub>1</sub>	427.87	2.8977	0.4978
	S <sub>0</sub> -S <sub>2</sub>	375.55	3.3014	0.0618
	S <sub>0</sub> -S <sub>3</sub>	3.5431	349.93	0.0612
BCz-SCz	S <sub>0</sub> -S <sub>1</sub>	433.09	2.8628	0.4235
	S <sub>0</sub> -S <sub>2</sub>	423.34	2.9287	0.2105
	S <sub>0</sub> -S <sub>3</sub>	379.22	3.2694	0.0425

### 3.4. Device Fabrication and Characterization

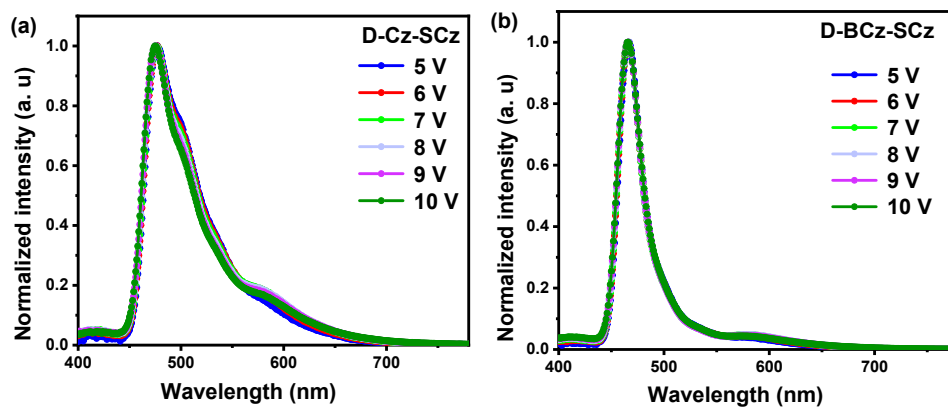


Fig. S17 EL spectra of Cz-SCz and BCz-SCz taken at various voltages from 5 to 10 V.

Table S4. Cartesian coordinates of aforementioned compounds

Cz-SCz			
Atom	X	Y	Z
C	0.451842	-1.43484	-0.00422
C	0.676678	-2.81271	0.205077
C	1.973608	-3.31887	0.30089
C	3.075472	-2.46668	0.185998
C	2.821132	-1.10052	-0.02206
C	1.547087	-0.53306	-0.09926
B	1.442606	0.986341	-0.14823
N	-0.82327	-0.86122	-0.07251
C	-1.00108	0.524585	0.030202
C	-2.37929	0.817994	0.117613
C	-3.0856	-0.44537	0.00785
C	-2.10727	-1.45863	-0.13211
C	0.000104	1.512718	0.044306
C	-0.47314	2.834504	0.22745
C	-1.82815	3.173386	0.346883
C	-2.78303	2.137609	0.27485
C	-4.44743	-0.75753	-0.01747
C	-4.87041	-2.07731	-0.2026
C	-3.87431	-3.05933	-0.38539
C	-2.5094	-2.77731	-0.36076
C	-2.30942	4.624151	0.548551
C	-6.35576	-2.48219	-0.23234
C	-7.29301	-1.27892	-0.01481
C	-6.6947	-3.11318	-1.60396
C	-6.63075	-3.5139	0.887628



C	-1.14517	5.631497	0.598261
C	-3.24039	5.026676	-0.62034
C	-3.08804	4.72838	1.881903
C	4.511299	-2.60251	0.300545
C	5.068048	-1.29757	0.166186
N	4.011201	-0.38336	-0.08144
C	5.339729	-3.69928	0.555
C	6.709734	-3.49795	0.700709
C	7.244442	-2.20497	0.619891
C	6.438263	-1.09472	0.361066
C	4.02316	0.985612	-0.42114
C	5.215642	1.611861	-0.82539
C	5.226304	2.960399	-1.15912
C	4.047551	3.710612	-1.12182
C	2.861565	3.080021	-0.77056
C	2.791547	1.716426	-0.41059
H	-0.14941	-3.4896	0.362803
H	2.111666	-4.38071	0.486938
H	0.262254	3.625675	0.294467
H	-3.84262	2.365614	0.351809
H	-5.16849	0.044111	0.098307
H	-4.16907	-4.08919	-0.5637
H	-1.80606	-3.57471	-0.55689
H	-8.33546	-1.61619	-0.03314
H	-7.11888	-0.7961	0.953637
H	-7.1775	-0.52353	-0.80058
H	-7.75079	-3.40773	-1.6368
H	-6.09396	-4.00707	-1.80289
H	-6.51476	-2.40126	-2.41764
H	-6.41098	-3.08888	1.873745
H	-7.68446	-3.81832	0.875332
H	-6.0219	-4.4165	0.769222
H	-1.54103	6.643024	0.742783
H	-0.46044	5.423412	1.428083
H	-0.56674	5.63395	-0.33273
H	-3.59824	6.054812	-0.48588
H	-4.11859	4.375885	-0.68725
H	-2.71099	4.973287	-1.57863
H	-2.44745	4.461664	2.73035
H	-3.44632	5.753748	2.035263
H	-3.95993	4.065681	1.900207
H	4.913637	-4.69431	0.651568
H	7.364259	-4.34198	0.898342
H	8.309395	-2.05289	0.771292
H	6.88331	-0.10958	0.359275
H	6.125531	1.040842	-0.9357
H	6.159793	3.419834	-1.47322

H	4.054448	4.762471	-1.39284
H	1.940018	3.650305	-0.80834

BCz-SCz			
Atom	X	Y	Z
C	-1.56826	-0.27307	-0.15307
C	-0.22965	0.166687	-0.11343
C	0.828317	-0.73159	0.104062
C	0.56497	-2.09997	0.29084
C	-0.78606	-2.50536	0.224787
C	-1.8773	-1.65243	0.036085
C	1.335562	-3.27838	0.651375
C	0.410354	-4.36212	0.781225
N	-0.89302	-3.87829	0.460543
C	2.693175	-3.48007	0.934362
C	3.120351	-4.73929	1.360186
C	2.199092	-5.78492	1.527269
C	0.838899	-5.60968	1.248903
C	-2.12712	-4.55531	0.314854
C	-2.16473	-5.95932	0.203385
C	-3.37852	-6.62429	0.052846
C	-4.57884	-5.9052	-0.01691
C	-4.53903	-4.51555	0.043899
C	-3.33624	-3.78724	0.211574
N	-2.65994	0.589103	-0.33314
N	2.157165	-0.21694	0.14659
C	-3.97944	0.149066	-0.09989
C	-4.86559	1.249657	-0.19288
C	-4.06465	2.410401	-0.55423
C	-2.71198	1.978067	-0.65785
C	3.182455	-0.49963	-0.7796
C	4.324335	0.282721	-0.45523
C	3.97579	1.080678	0.710719
C	2.633814	0.756818	1.049034
C	-4.40765	3.735568	-0.8198
C	-3.4269	4.664403	-1.21263
C	-2.10321	4.200747	-1.3478
C	-1.73136	2.875112	-1.08368
C	-4.39806	-1.16586	0.185191
C	-5.7862	-1.30487	0.448577
C	-6.69378	-0.23652	0.391968
C	-6.22003	1.049798	0.050567
C	3.187133	-1.35598	-1.88031
C	4.354615	-1.43399	-2.6471
C	5.514058	-0.68073	-2.34944
C	5.477365	0.181647	-1.23979

C	4.676635	2.015847	1.478347
C	4.066989	2.635317	2.583292
C	2.732885	2.282308	2.892948
C	2.006383	1.350206	2.144303
C	6.803308	-0.77725	-3.19664
C	6.65888	-1.76414	-4.37827
C	7.15143	0.620876	-3.77808
C	7.976407	-1.26502	-2.3021
C	4.861999	3.670771	3.410851
C	4.053426	4.208347	4.614351
C	6.160315	3.017662	3.960008
C	5.239832	4.875981	2.505725
C	-3.8278	6.129933	-1.49012
C	-2.62249	6.997547	-1.91985
C	-4.88511	6.175144	-2.62764
C	-4.43542	6.749985	-0.20134
C	-8.17852	-0.40359	0.697821
C	-8.69167	-1.8462	0.814008
B	-3.28086	-2.23497	0.161027
H	0.021467	1.209781	-0.21034
H	3.400094	-2.6663	0.835078
H	4.16929	-4.90474	1.582029
H	2.539364	-6.74881	1.891646
H	0.152235	-6.42013	1.442488
H	-1.25018	-6.53094	0.176101
H	-3.38288	-7.70617	-0.03629
H	-5.52299	-6.42371	-0.14701
H	-5.46259	-3.96383	-0.07917
H	-5.44524	4.04148	-0.73013
H	-1.32622	4.879549	-1.67535
H	-0.70572	2.582638	-1.2521
H	-6.16079	-2.282	0.723094
H	-6.92003	1.879341	-0.00995
H	2.317367	-1.94905	-2.13743
H	4.353736	-2.10277	-3.49843
H	6.346093	0.781371	-0.98601
H	5.701209	2.25848	1.213509
H	2.240599	2.739786	3.741809
H	0.987195	1.099394	2.41478
H	7.59659	-1.79711	-4.94485
H	6.442888	-2.78157	-4.03248
H	5.863756	-1.45724	-5.06749
H	8.068279	0.565644	-4.37829
H	7.311925	1.359293	-2.98527
H	6.341714	0.986478	-4.41995
H	7.762197	-2.25743	-1.88896
H	8.901938	-1.32848	-2.88801

H	8.153557	-0.58247	-1.46414
H	4.662728	4.928242	5.172819
H	3.140972	4.723675	4.293248
H	3.77185	3.40393	5.30363
H	6.732986	3.746642	4.546825
H	6.805243	2.656743	3.1518
H	5.922892	2.165752	4.607411
H	4.339341	5.36541	2.117024
H	5.814943	5.616229	3.076128
H	5.847464	4.56102	1.650619
H	-2.95693	8.025768	-2.09804
H	-1.84874	7.028438	-1.14423
H	-2.16869	6.630128	-2.84742
H	-5.17993	7.212332	-2.82969
H	-5.7882	5.614784	-2.36329
H	-4.48064	5.746832	-3.55181
H	-3.70408	6.742721	0.614908
H	-4.73625	7.78883	-0.38498
H	-5.31954	6.196948	0.133216
H	-8.4084	0.128772	1.633876
H	-8.75317	0.115676	-0.08281
H	-9.77314	-1.8502	0.988117
H	-8.49724	-2.41522	-0.10281
H	-8.22235	-2.37864	1.649296

**Table S5.** The relevant parameters of devices.

Device	$\lambda_{EL}^{[a]}$ [nm]	FWHM <sup>[b]</sup> [nm]	EQE <sup>[c]</sup> [%]	CE <sup>[c]</sup> [cd A <sup>-1</sup> ]	PE <sup>[c]</sup> [lm W <sup>-1</sup> ]	$V_{on}^{[f]}$ [V]	CD <sup>[f]</sup> [mA cm <sup>-2</sup> ]
D-Cz-SCz	476	56	16.1/6.6/3.5	25.3/14.2/7.4	18.5/9.0/3.6	4.3/5.0/6.5	0.01/1.3/14.7
D-BCz-SCz	468	28	20.5/7.5/4.0	21.2/7.5/4.2	16.6/5.4/2.1	4.0/4.8/6.4	0.005/1.6/24.5

[a] Electroluminescence peak. [b] Full width at half maximum of electroluminescence spectrum. [c] Values at maximum, 100 and 1000 cd m<sup>-2</sup>. [f] Values at turn on, 100 and 1000 cd m<sup>-2</sup>.