

Supporting Information

Spirofluorene-Locked Carbazole Based Multiple Resonance Thermally Activated Delayed Fluorescence Emitters for Efficient Solution-Processed Narrowband Green OLEDs

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Experimental Details

General information. The chemicals and reagents were obtained from commercial sources (TCI (Shanghai), SigmaAldrich (China) and Energy Chemical (Beijing)) and were used directly. *N, N*-dimethylformamide (DMF) was dried by CaH₂, while tetrahydrofuran (THF) and 1,4-dioxane were distilled from sodium/benzophenone before use. ¹H and ¹³C NMR spectra were recorded by Bruker Avance NMR spectrometers in CDCl₃ or (CD₃)₂SO with tetramethylsilane (TMS) as the internal standard. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra was measured on AXIMA CFR MS apparatus (COMPACT). Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer-TGA 7 at heating rate of 10 °C/min with continuous nitrogen flow. Cyclic voltammetry (CV) was carried out in electrochemical workstation (CHI610E) with a typical three-electrode cell (glassy-carbon work electrode, calomel reference electrode and platinum counter electrode) using *n*-Bu₄NClO₄ (0.1 M) as supporting electrolyte and ferrocene as reference at a scan rate of 50 mV·s⁻¹. The oxidation and reduction curves were recorded in dichloromethane and THF (2 mg/mL), respectively. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the emitters were calculated according to equations of $E_{\text{HOMO}}/E_{\text{LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$, in which $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$ are the onset of oxidation and reduction potentials respectively.

Photophysical measurements. UV-visible absorption was measured by PerkinElmer Lambda 35 UV-vis spectrometer, and photoluminescence (PL) spectra was measured by PerkinElmer LS 50B spectrofluorometer, respectively. PL decay curves were detected on Edinburgh fluorescence spectrometer (FLSP-980). The absolute PLQY values were measured by integrating sphere on Hamamatsu Photonics C9920-2 with excitation wavelength of 345 nm.

Computational method. The calculations were performed with Gaussian 09 package^[1] using density functional theory (DFT) for frontier molecular orbital (FMO) distributions, and time-dependent density functional theory (TD-DFT) for electron excitation transition analysis at the B3LYP/6-31G(d,p) level. Natural transition orbitals (NTO) were performed by Multiwfn (version 3.5)^[2] and drawn by VMD software (version 1.9.3). The calculation of RMSD was also completed by VMD software.

Calculation for the Photophysical Parameters. The calculation formulas for the rate constant of radiative decay from S₁ (k_r^S), non-radiative decay rate constant from T₁ (k_{nr}^T), intersystem crossing (k_{ISC}) and reverse intersystem crossing (k_{RISC}) are expressed as following list^[3]:

$$k_r^S = \Phi_p/\tau_p$$

$$k_{nr}^T = 1/\tau_d - \Phi_p k_{RISC}$$

$$k_{ISC} = (1 - \Phi_p)/\tau_p$$

$$k_{RISC} = \Phi_d / (k_{ISC} \tau_p \tau_d \Phi_p)$$

where τ_p and τ_d are the lifetimes of the prompt and delayed components, and Φ_p and Φ_d are the prompt and delayed components of the PL quantum efficiency, respectively.

Synthetic Procedures

9-(tert-butyldimethylsilyl)-3-iodo-9H-carbazole (2)

NaH (60%, dispersed in Paraffin Liquid) (4.8 g, 120.0 mmol) was added into a solution of 3-iodo-9H-carbazole (**1**, 29.3 g, 100.0 mmol) in dry DMF (100 mL). After the mixture was stirred for 5 hours at room temperature, solution of tert-butyldimethylsilyl chloride (22.6 g, 150.0 mmol) in DMF (100 mL) was added dropwisely. After stirring for 5 hours, the mixture was poured into water (600 mL) and extracted with dichloromethane (100 mL×3), then the combined organic layers were dried with sodium sulphate, filtered, and concentrated by rotary evaporation. The residue was subjected to silica gel column chromatography using hexane as eluent to give **2** as a white solid (35.8 g, 88%). ¹H NMR (500 MHz, DMSO) δ 8.53 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 0.96 (s, 9H), 0.74 (s, 6H).

1'-bromo-3',6'-di-tert-butyl-9-(tert-butyldimethylsilyl)-9H-3,9'-bicarbazole (3)

A mixture of **2** (16.3 g, 40.0 mmol), 1-bromo-3,6-di-tert-butyl-9H-carbazole (14.3 g, 40.0 mmol), CuI (1.14 g, 6.0 mmol), diaminocyclohexane (2.28 g, 20.0 mmol) and K₃PO₄ (17.0 g, 80.0 mmol) in dry 1,4-dioxane (200 mL) was heated at 100 °C and stirred for 48 hours under argon atmosphere. After cooling to room temperature, the mixture was poured into water (600 mL) and filtered to afford the filter cake as crude product, which was further purified by silica gel column chromatography (dichloromethane/hexane = 1/6, v/v) to give **3** as a white solid (16.5 g, 65%). ¹H NMR (400 MHz, DMSO) δ 8.40 (s, 1H), 8.34 (s, 1H), 8.22 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.44-7.39 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 1.42 (s, 9H), 1.39 (s, 9H), 1.04 (s, 9H), 0.82 (s, 6H).

2,15-di-tert-butyl-8H-spiro[diindolo[3,2-a:1',2',3'-fg]acridine-13,9'-fluorene] (4)

A solution of n-butyllithium (12.0 mL, 2.5 M, 30.0 mmol) in n-hexane was added dropwise into a solution of **3** (8.7 g, 20.0 mmol) in anhydrous tetrahydrofuran (THF) (120 mL) at -78 °C. After stirring at -78 °C for 2 hours, a solution of 9-fluorenone (6.3 g, 35.0 mmol) in anhydrous THF (20 mL) was slowly added at -78 °C. Then the reaction mixture was warmed to room temperature, which was added HCl aqueous solution (1 M, 30 mL), 300 mL distilled water and 150 mL ethyl acetate. The aqueous layer was separated and extracted with ethyl acetate (100 mL×3). The combined organic layers were dried with sodium sulphate. After removal of solvent under reduced pressure, the crude product was dissolved in anhydrous THF (100 mL), and then boron trifluoride-diethyl etherate (10 mL) was added slowly at room temperature. The reaction mixture was stirred for 3 hours, and slowly quenched by 100 mL

NaHCO₃ aqueous solution. Then the aqueous layer was separated and extracted with ethyl acetate (50 mL×3). The combined organic layers were dried with sodium sulphate, filtered and concentrated under reduced pressure. The crude product was dissolved in THF, and then tetrabutylammonium fluoride trihydrate (8.4 g, 30 mmol) was added. The mixture was stirred at room temperature for 4 hours, followed by pouring into water and extracting aqueous layer with ethyl acetate. The organic layers were collected and applied on silica gel column chromatography (dichloromethane/hexane = 1/3, v/v) to give the product **4** as a white solid (4.8 g, 40%). ¹H NMR (400 MHz, DMSO) δ 11.47 (s, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 8.33 (s, 1H), 8.22 (d, *J* = 7.6 Hz, 2H), 7.97 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 3H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.35 (t, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 1.47 (s, 9H), 1.04 (s, 9H).

8-(2-bromo-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-2,15-di-tert-butyl-8H-spiro[diindolo[3,2-a:1',2',3'-fg]acridine-13,9'-fluorene] (5)

Anhydrous DMF (40 mL), **4** (910.0 mg, 1.5 mmol), 9-(2-bromo-3-fluorophenyl)-3,6-di-tert-butyl-9H-carbazole (722.0 mg, 1.6 mmol) and cesium carbonate (977.4 mg, 3.0 mmol) were added into a 100 mL Schlenk flask under argon atmosphere. The mixture was heated to 140 °C and stirred for 24 hours and then cooled to room temperature, which was slowly poured into water (200 mL) and stirred for 30 minutes. The precipitate was filtered and dried under vacuum, and purified by column chromatography using dichloromethane/hexane (1/5) as eluent, giving **5** as a white solid (1.4 g, 90 %). ¹H NMR (500 MHz, DMSO) δ 8.65 (d, *J* = 9.0 Hz, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.34 (s, 1H), 8.30 (d, *J* = 7.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 1H), 7.99 (s, 1H), 7.93-7.87 (m, 3H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.46-7.41 (m, 2H), 7.18-7.13 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.06-7.02 (m, 3H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.51 (t, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 1.47 (s, 9H), 1.44 (s, 9H), 1.41 (s, 9H), 1.05 (s, 9H).

8,8''-(2-bromo-1,3-phenylene)bis(2,15-di-tert-butyl-8H-spiro[diindolo[3,2-a:1',2',3'-fg]acridine-13,9'-fluorene]) (6)

Anhydrous DMF (40 mL), **4** (1.88 g, 3.1 mmol), 2-bromo-1,3-difluorobenzene (288.0 mg, 1.5 mmol) and cesium carbonate (1.95 g, 6.0 mmol) were added into a 100 mL Schlenk flask under argon atmosphere. The mixture was heated to 140 °C and stirred for 24 hours and then cooled to room temperature, which was slowly poured into water (200 mL) and stirred for 30 minutes. The precipitate was filtered and dried under vacuum, and purified by column

chromatography using dichloromethane/hexane (1/5, v/v) as eluent, giving **6** as a white solid (1.2 g, 60 %). ¹H NMR (400 MHz, DMSO) δ 8.62 (d, *J* = 9.2 Hz, 2H), 8.36 (d, *J* = 9.2 Hz, 4H), 8.28 (d, *J* = 7.6 Hz, 2H), 8.24 (d, *J* = 7.6 Hz, 2H), 7.98 (s, 2H), 7.94 (s, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.52-7.40 (m, 6H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.06-7.03 (m, 8H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.53 (t, *J* = 7.2 Hz, 2H), 6.28 (s, 2H), 1.46 (s, 18H), 1.04 (s, 18H).

SpDCz

A solution of *n*-butyllithium in *n*-hexane (0.36 mL, 2.5 M, 0.9 mmol) was added dropwise into a solution of **5** (830.0 mg, 0.8 mmol) in anhydrous *m*-xylene (40 mL) at -30 °C under argon atmosphere. When the addition was finished, the reaction mixture was slowly warmed to 40 °C and stirred for 1 hour. After boron tribromide (0.24 mL, 2.5 mmol) was added at -30 °C, the reaction mixture was slowly warmed to 50 °C and stirred for 3 hours. N, N-diisopropylethylamine (0.42 mL, 2.5 mmol) was then added at 0 °C and the mixture was stirred at 125 °C for 20 hours. After cooling to room temperature and quenching with 2 mL water, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate. The combined organic layers were dried with sodium sulphate, filtered, and concentrated under rotary evaporation. The residue was then subjected to column chromatography using dichloromethane/hexane (1/5, v/v) as eluent to afford **SpDCz** as a yellow solid (503.0 mg, 65 %). ¹H NMR (500 MHz, CDCl₃) δ 8.86 (s, 1H), 8.74 (d, *J* = 9.5 Hz, 1H), 8.65 (d, *J* = 7.0 Hz, 1H), 8.62 (d, *J* = 9.5 Hz, 1H), 8.41 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.33-8.30 (m, 3H), 8.23 (s, 1H), 8.18 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 2H), 7.98 (t, *J* = 8.0 Hz, 1H), 7.81 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.08-7.04 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.43 (s, 1H), 1.58 (s, 9H), 1.54 (s, 9H), 1.52 (s, 9H), 1.13 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 153.77, 145.49, 145.32, 144.71, 144.05, 143.99, 143.16, 142.50, 141.45, 140.20, 138.22, 137.25, 137.04, 134.72, 134.56, 132.87, 132.62, 129.79, 129.67, 128.44, 127.99, 127.03, 126.85, 126.61, 125.39, 125.21, 124.35, 123.81, 123.57, 123.23, 122.44, 121.84, 121.04, 120.56, 120.45, 120.30, 117.55, 117.25, 114.00, 113.72, 113.68, 113.22, 108.68, 108.35, 58.16, 35.12, 34.81, 34.79, 32.18, 31.95, 31.82, 31.73. MALDI-TOF MS: calcd for C₇₁H₆₂BN₃: 967.5, found: 967.5 [M]⁺.

DSpDCz

A solution of *n*-butyllithium in *n*-hexane (0.36 mL, 2.5 M, 0.9 mmol) was added dropwise into a solution of **6** (1.1 g, 0.8 mmol) in anhydrous *m*-xylene (40 mL) at -30 °C under argon atmosphere. When the addition was finished, the reaction mixture was slowly warmed to 40 °C and stirred for 1 hour. After boron tribromide (0.24 mL, 2.5 mmol) was added at -30 °C,

the reaction mixture was slowly warmed to 50 °C and stirred for 3 hours. N, N-diisopropylethylamine (0.42 mL, 2.5 mmol) was then added at 0 °C and the mixture was stirred at 125 °C for 20 hours. After cooling to room temperature and quenching with 2 mL water, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate. The combined organic layers were dried with sodium sulphate, filtered, and concentrated under rotary evaporation. The residue was then subjected to column chromatography using dichloromethane/hexane (1/5, v/v) as eluent to afford **DSpDCz** as a yellow solid (600.7 mg, 58 %). ¹H NMR (500 MHz, CDCl₃) δ 8.60 (m, 4H), 8.33-8.29 (m, 4H), 8.19 (m, 4H), 8.10 (d, *J* = 8.0 Hz, 4H), 7.85 (s, 1H), 7.81 (s, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 4H), 7.20 (d, *J* = 7.2 Hz, 4H), 7.06 (t, *J* = 7.2 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 2H), 6.42 (s, 2H), 1.55 (s, 18H), 1.13 (s, 18H). ¹³C NMR (126 MHz, C₂D₂Cl₄) δ 153.16, 145.10, 143.69, 141.95, 141.54, 139.61, 137.45, 136.46, 134.10, 133.78, 131.62, 128.93, 128.61, 127.88, 127.78, 127.61, 126.07, 125.72, 124.98, 124.88, 124.46, 123.53, 122.36, 121.72, 120.94, 120.54, 120.28, 120.00, 116.96, 113.46, 113.25, 113.03, 112.95, 108.46, 57.46, 34.21, 31.44, 31.20. MALDI-TOF MS: calcd for C₇₁H₆₂BN₃: 1294.6, found: 1294.6 [M]⁺.

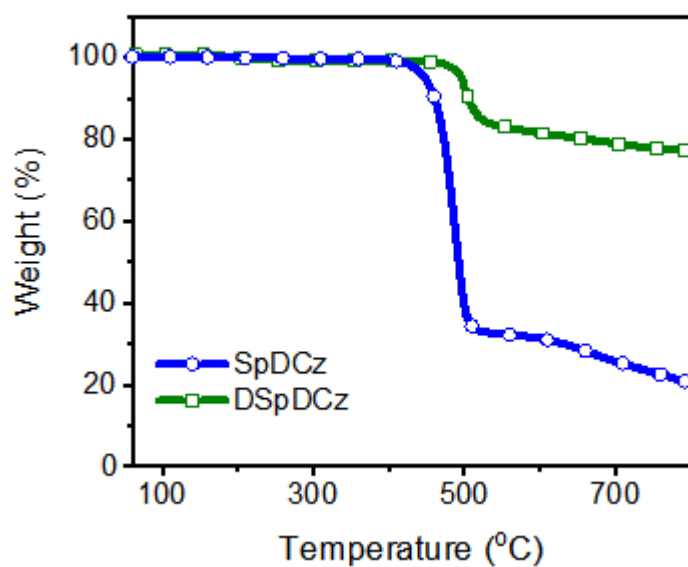


Figure S1. Thermogravimetric analysis (TGA) curves for SpDCz and DSpDCz.

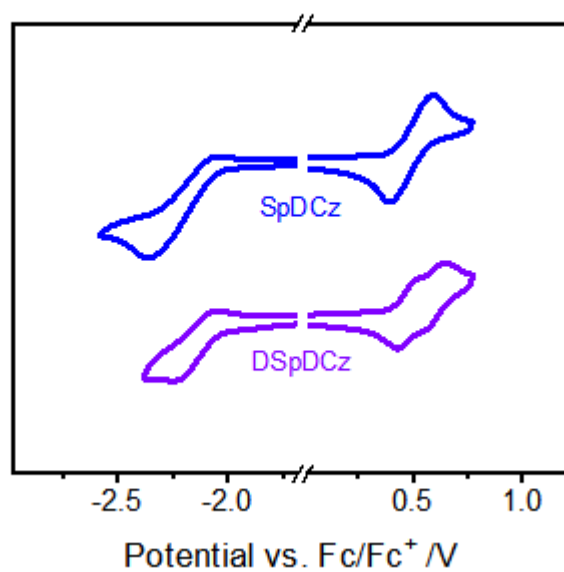


Figure S2. Cyclic voltammetry characteristics for SpDCz and DSpDCz.

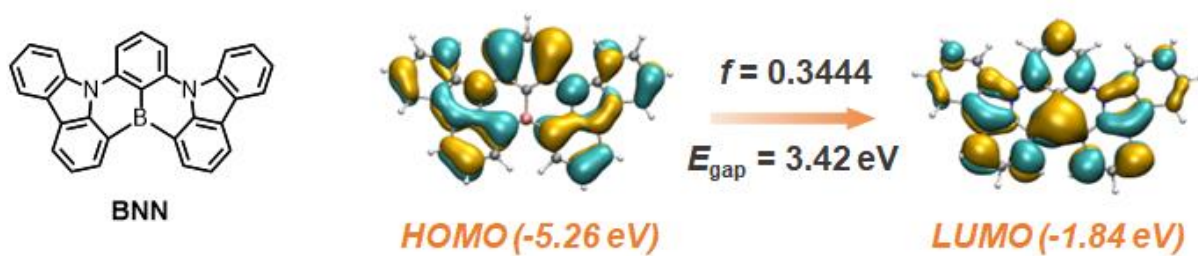


Figure S3. HOMO/LUMO distributions, energy gaps and oscillator strength (f) for BNN.

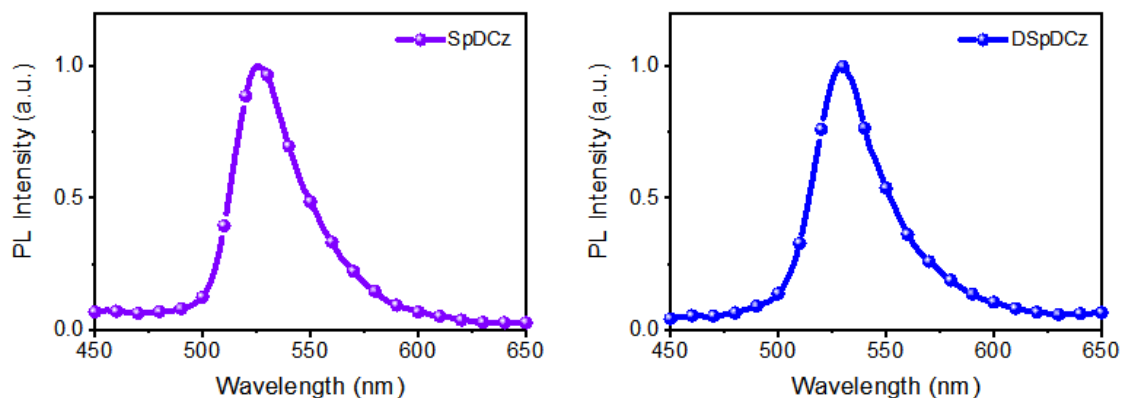


Figure S4. Phosphorescence spectra in toluene at 50 K for SpDCz and DSpDCz (delay time: 1 ms; excitation wavelength: 350 nm).

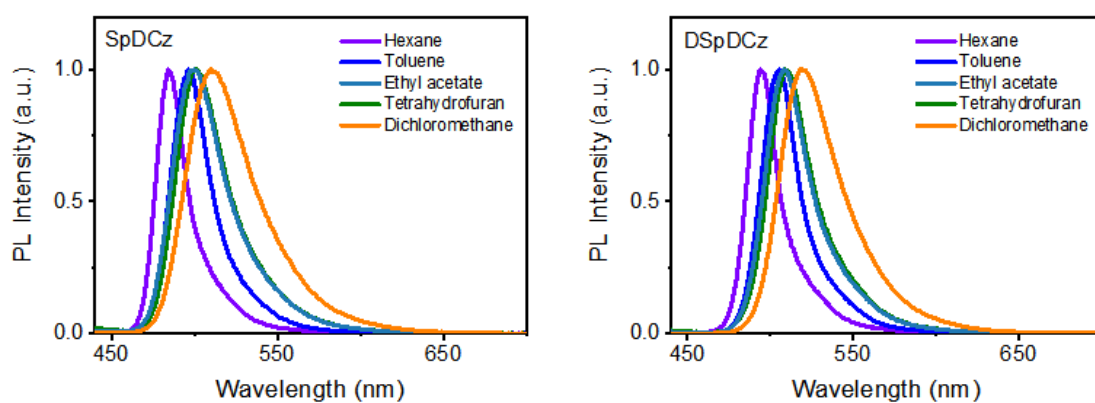


Figure S5. PL spectra for SpDCz and DSpDCz in solvents with different polarity (10^{-5} mol L^{-1}).

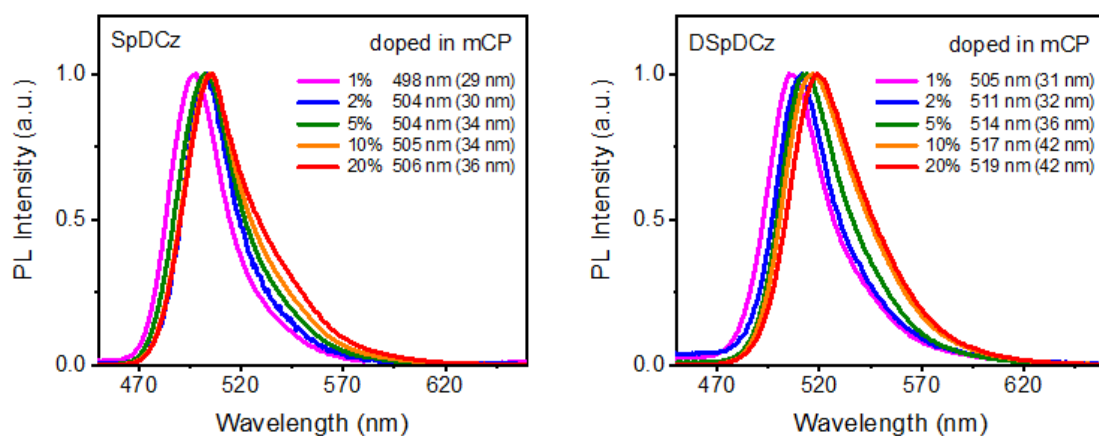


Figure S6. Dependence of PL spectra on doping concentration for SpDCz and DSpDCz.

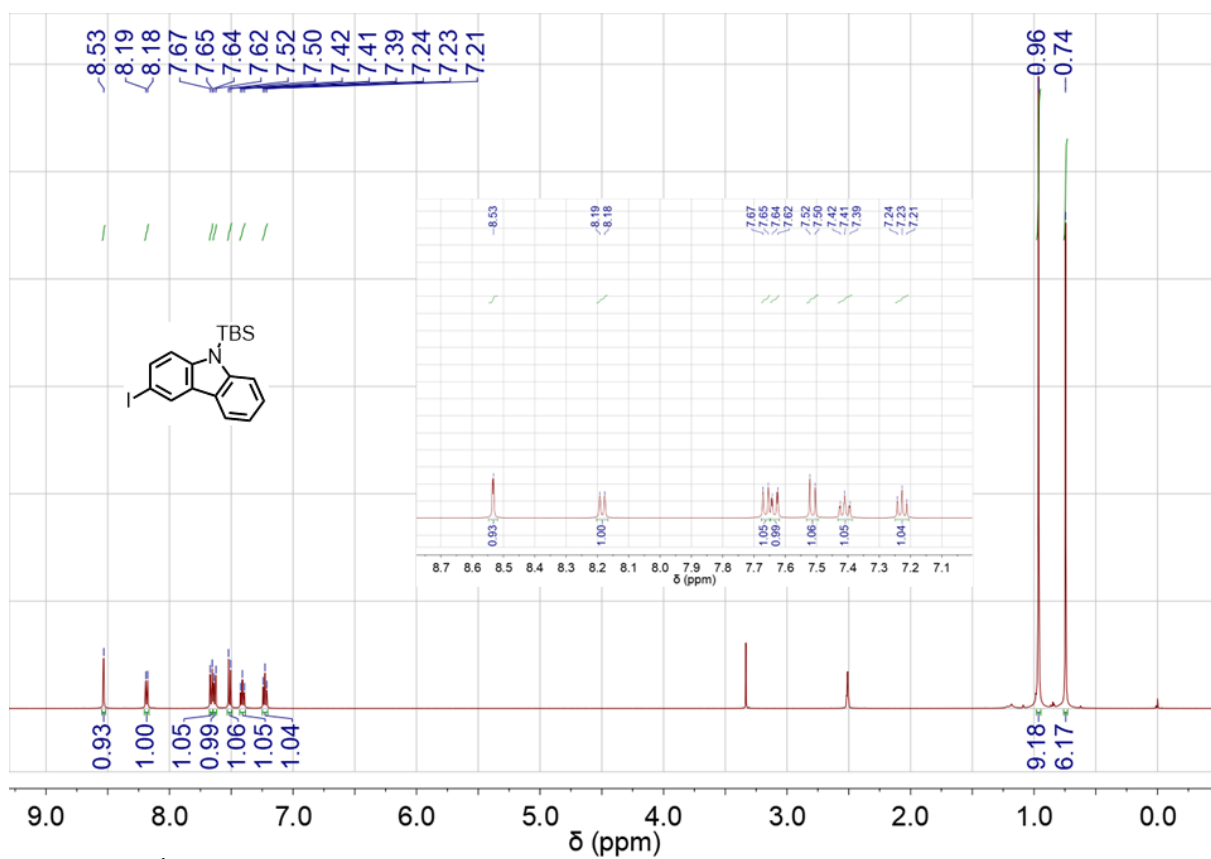


Figure S7. ^1H NMR spectra of **2**.

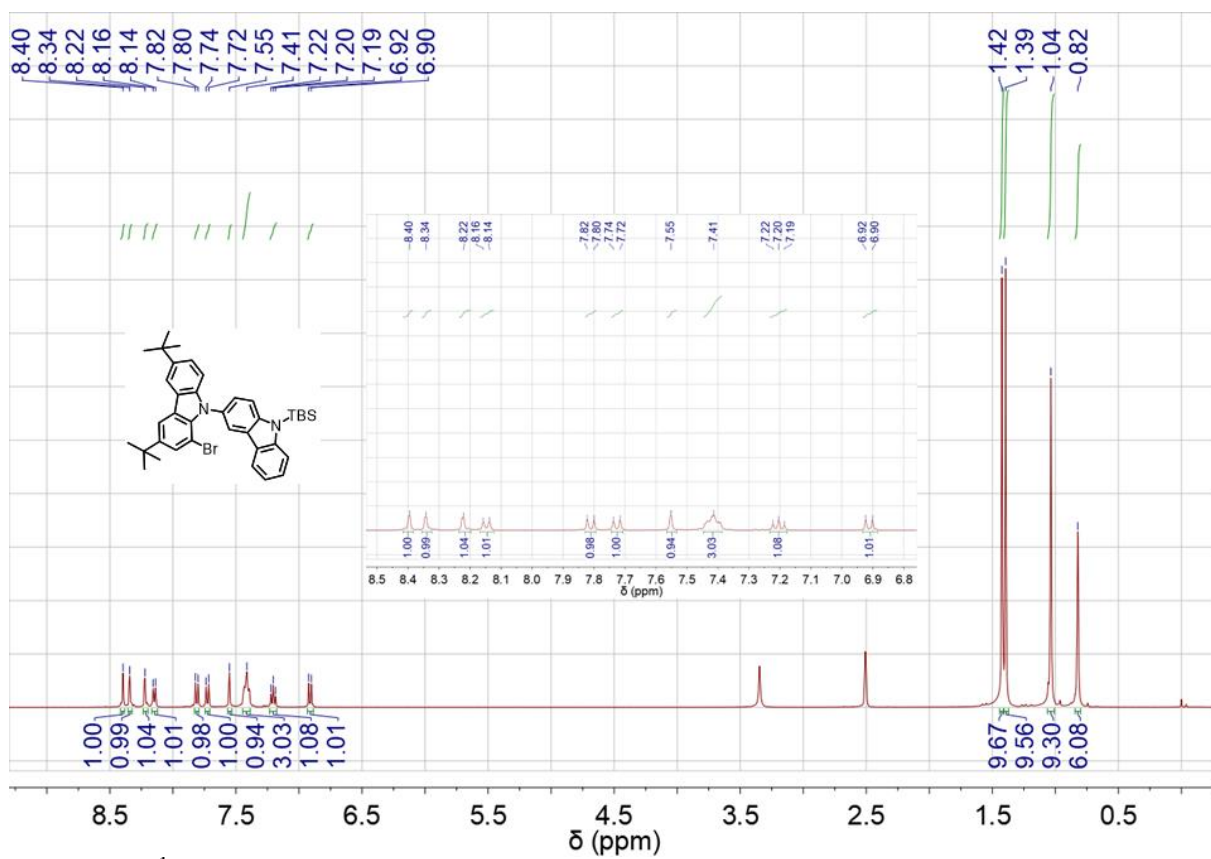


Figure S8. ^1H NMR spectra of **3**.

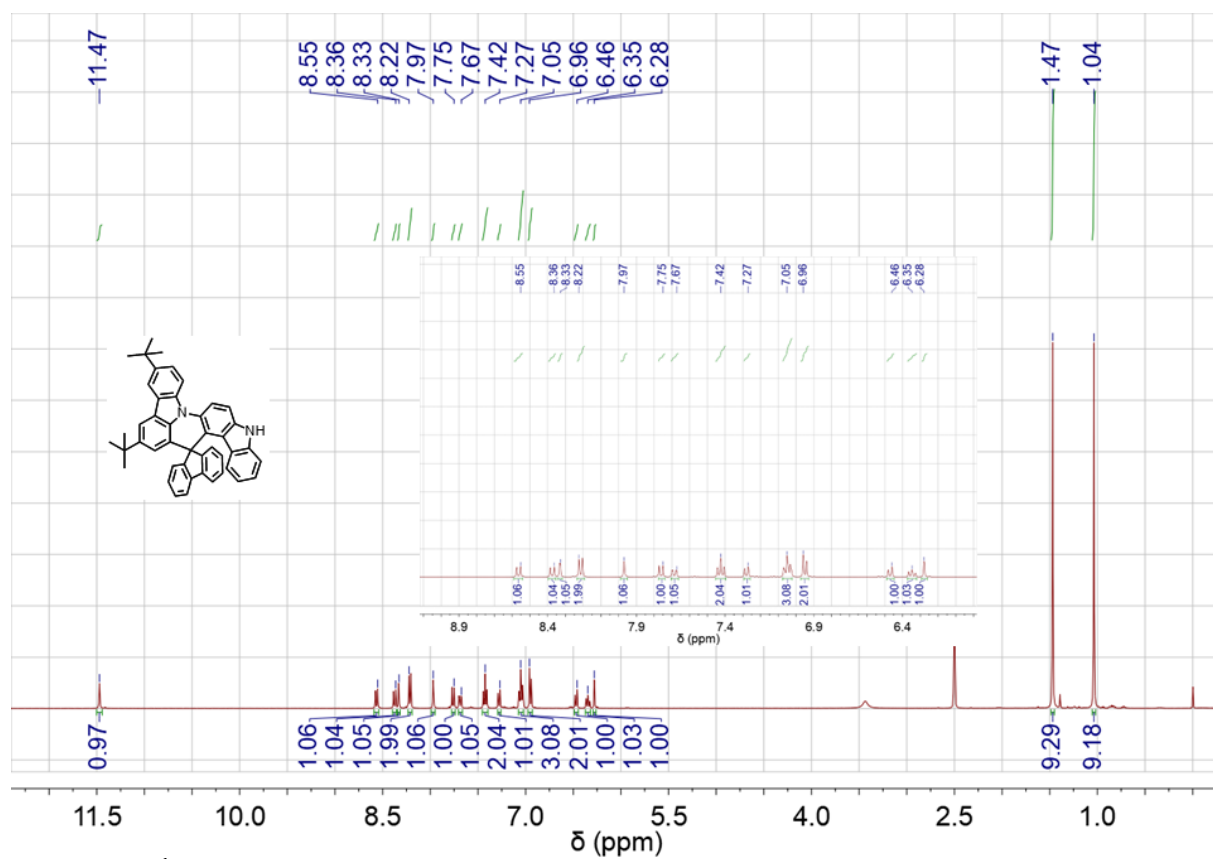


Figure S9. ^1H NMR spectra of **4**.

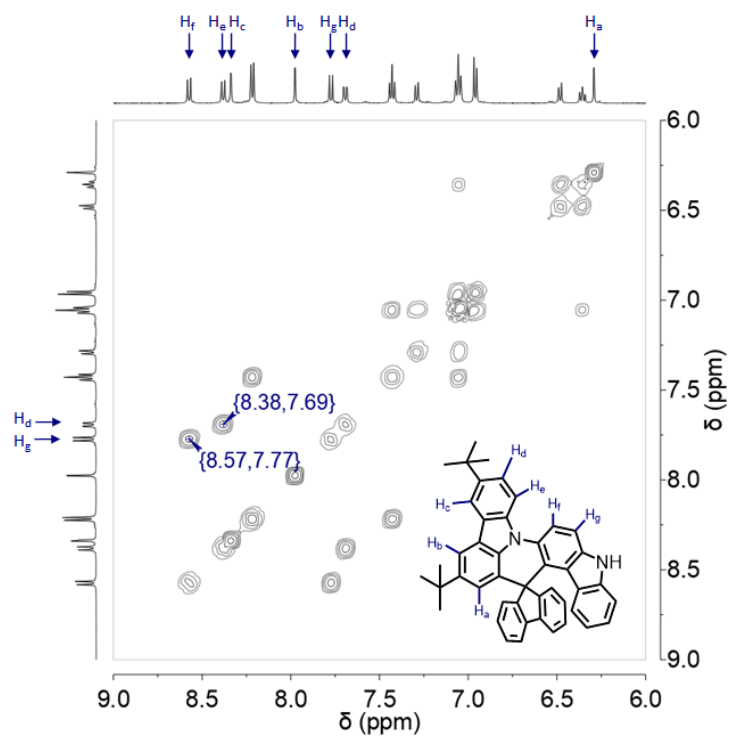


Figure S10. ^1H - ^1H COSY spectra of **4**.

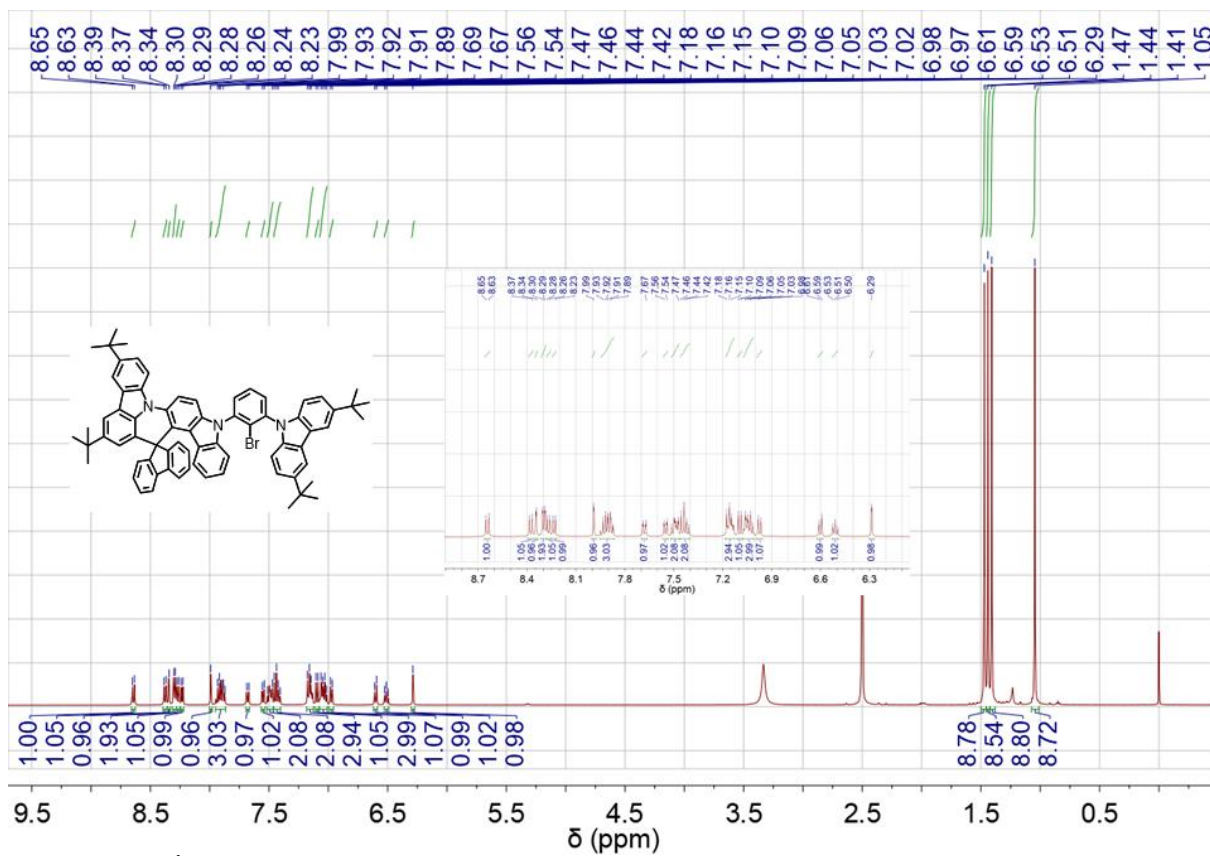


Figure S11. ¹H NMR spectra of 5.

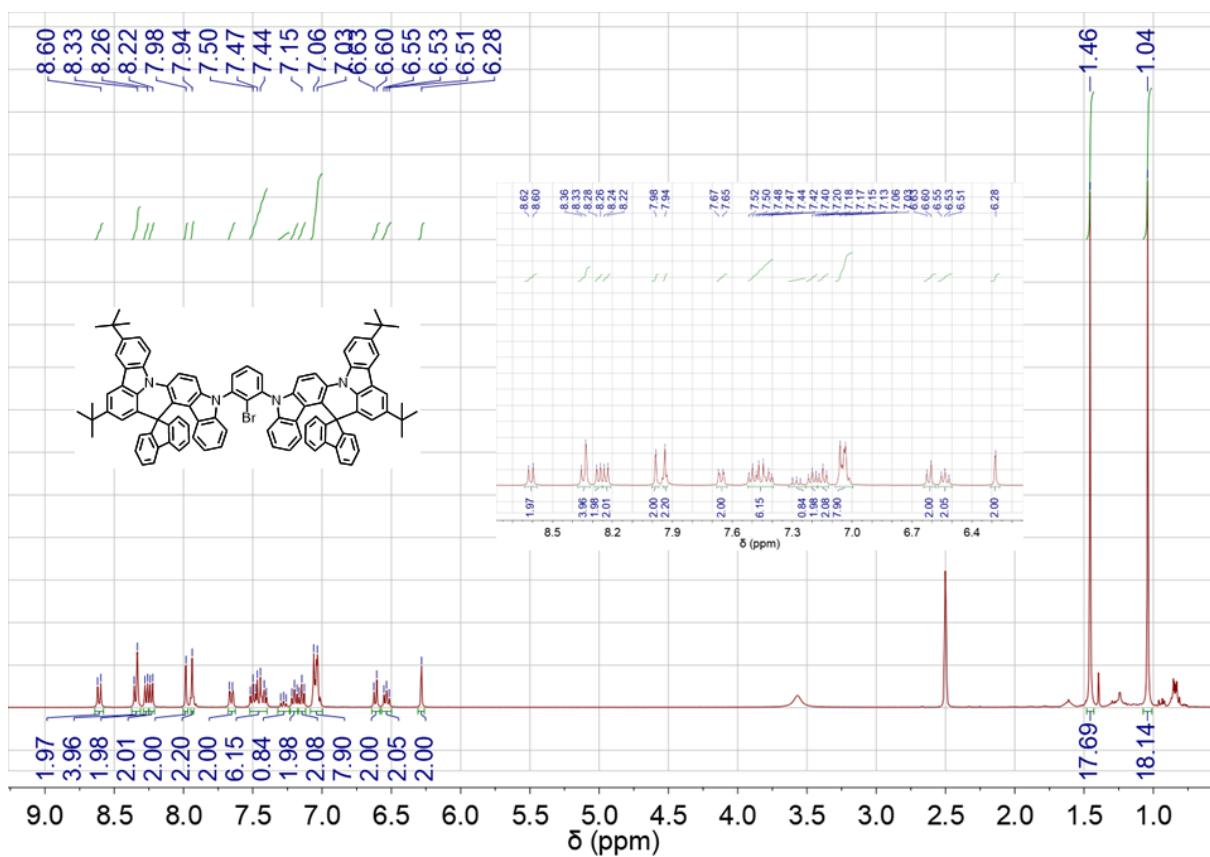


Figure S12. ¹H NMR spectra of 6.

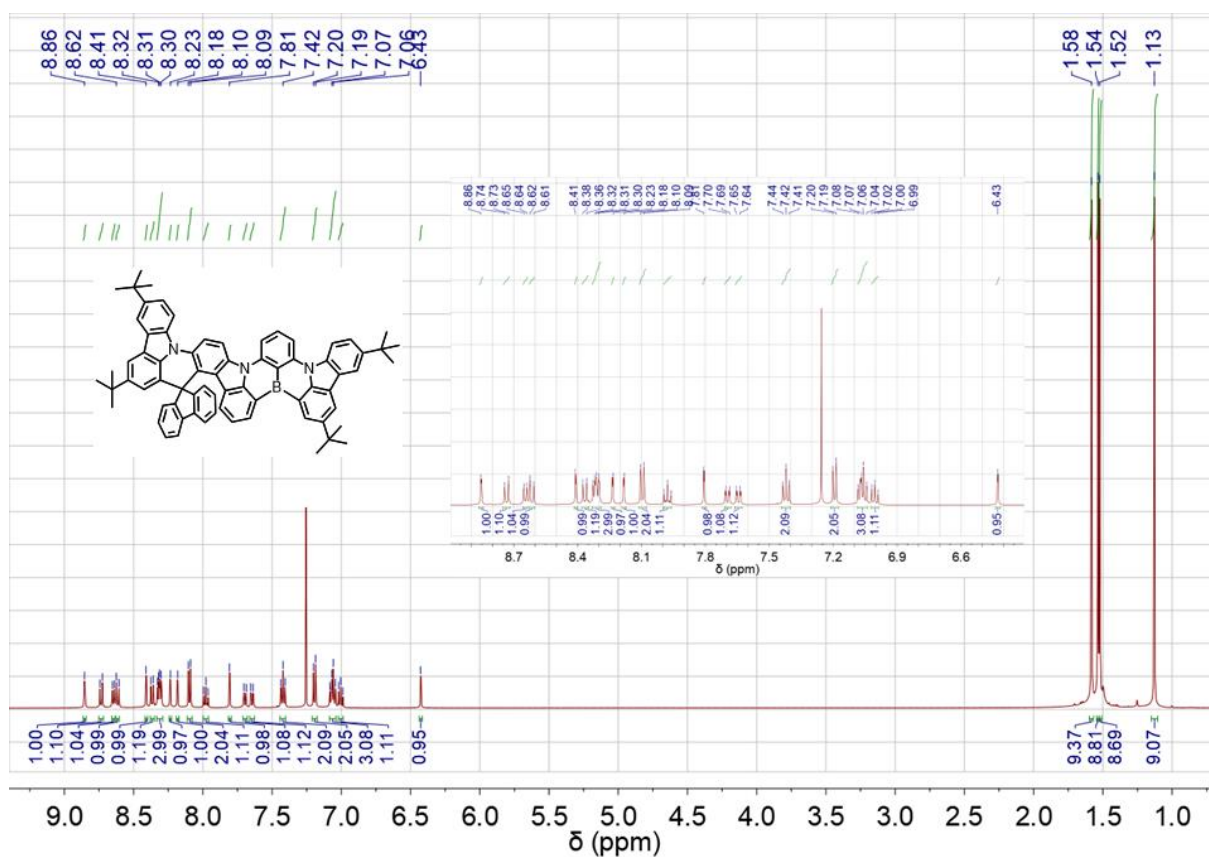


Figure S13. ^1H NMR spectra of SpDCz.

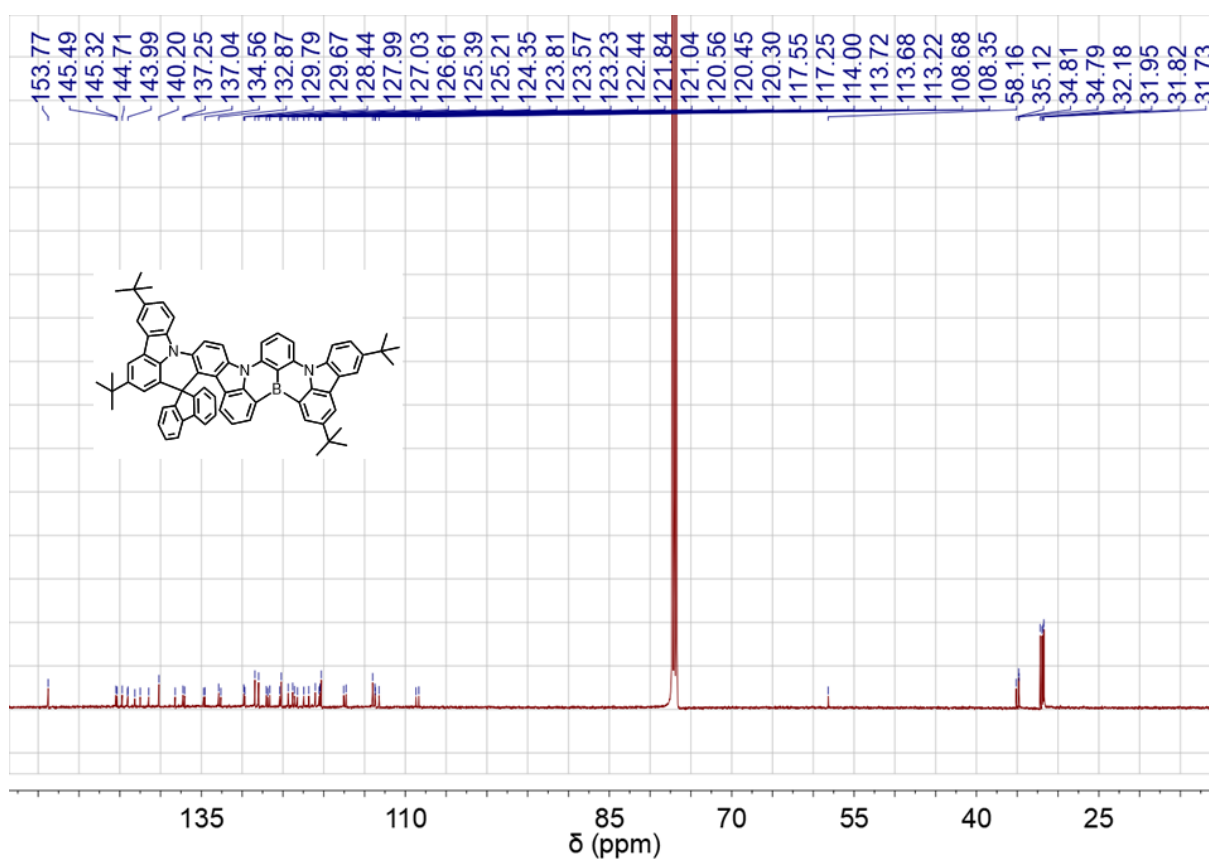


Figure S14. ^{13}C NMR spectra of SpDCz.

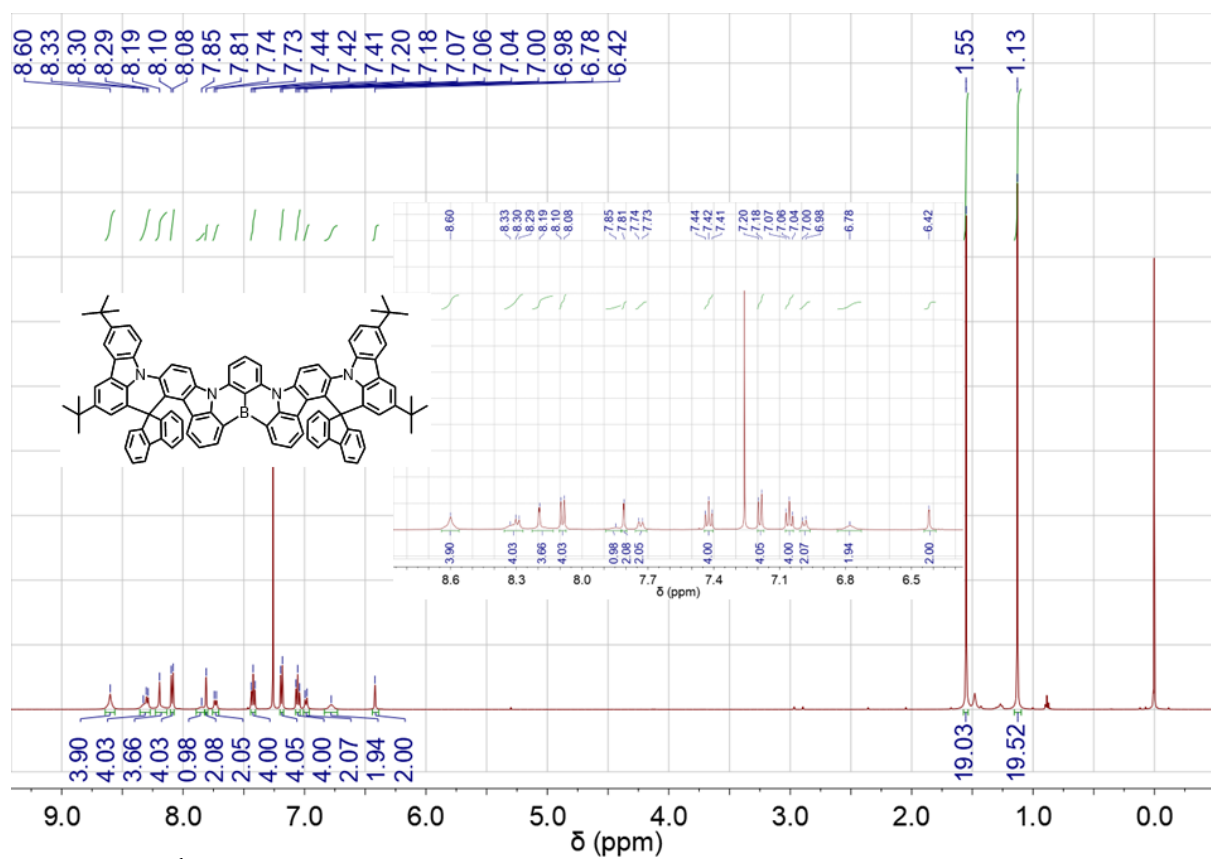


Figure S15. ¹H NMR spectra of DSpDCz.

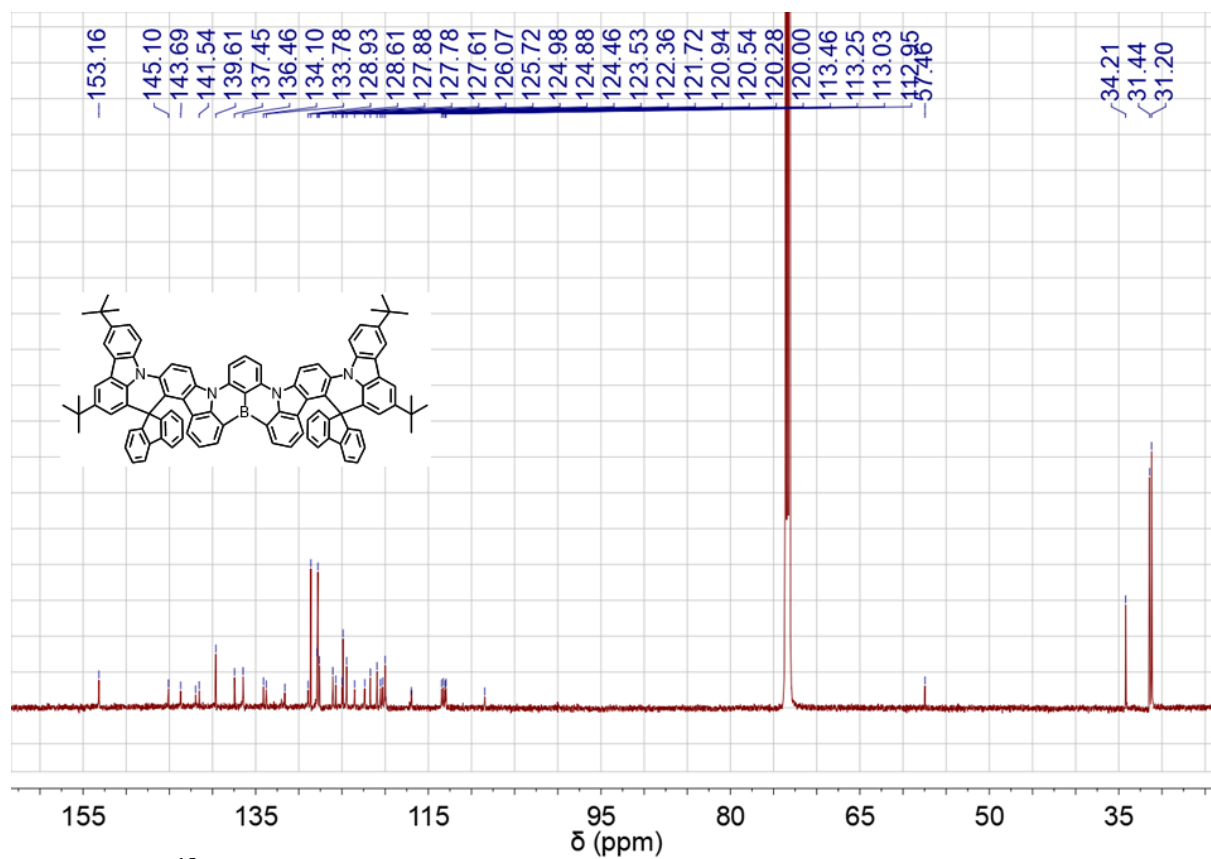


Figure S16. ¹³C NMR spectra of DSpDCz.

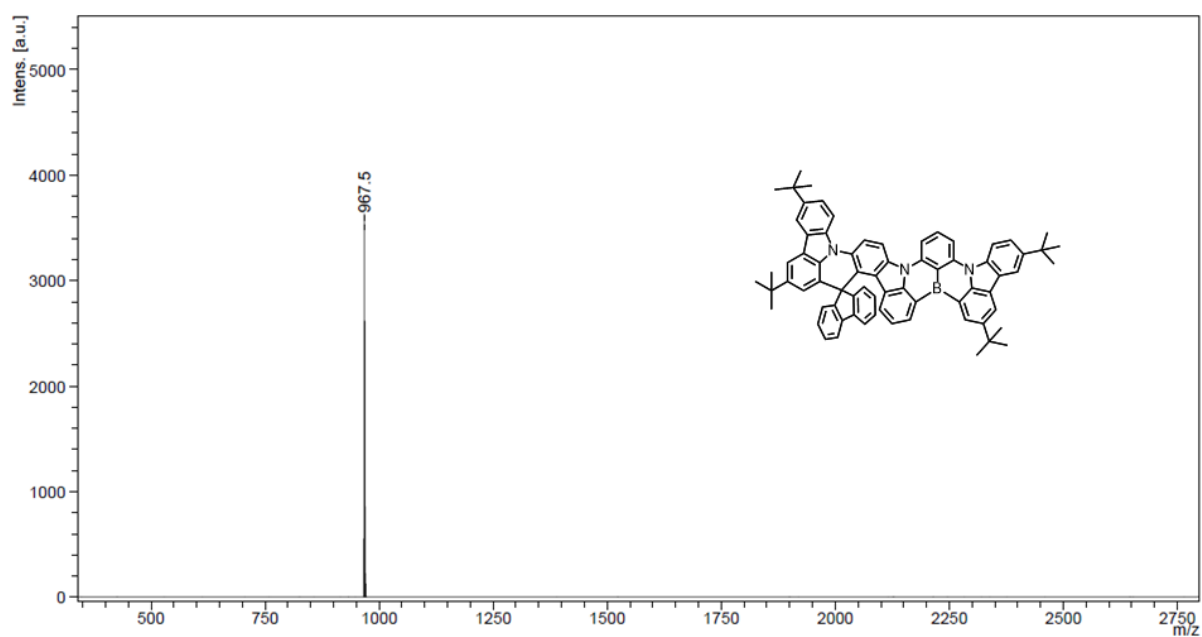


Figure S17. MALDI-TOF of SpDCz.

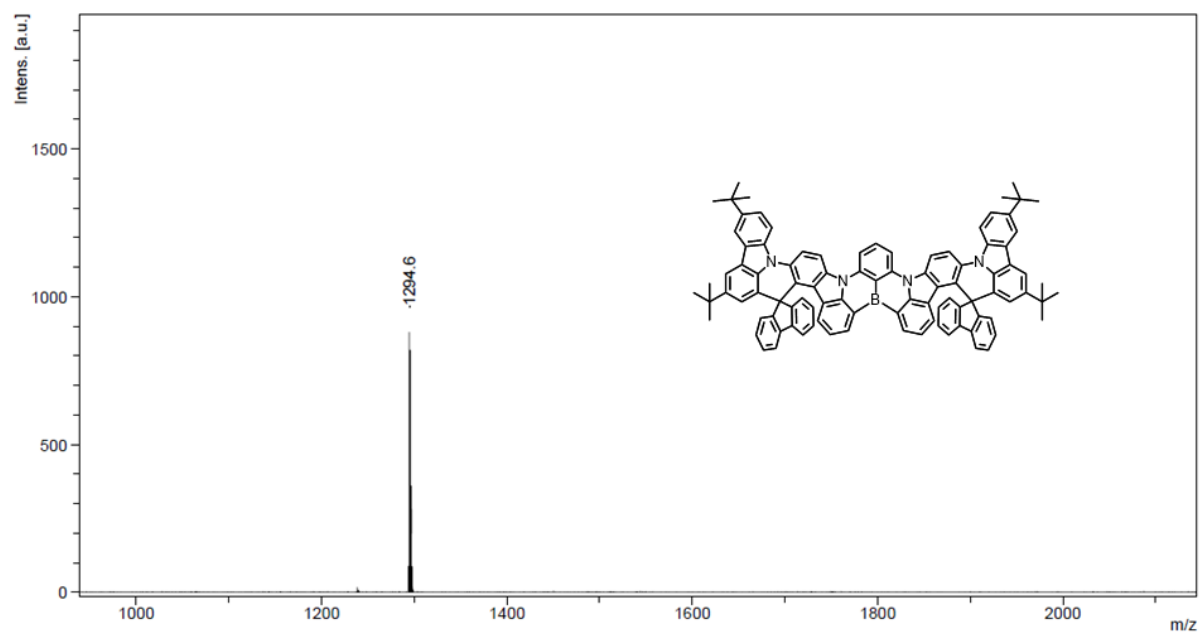


Figure S18. MALDI-TOF of DSpDCz.

References

- [1] Frisch, M. J. et al. Gaussian 09, Revision C.01. (Gaussian, 2010).
- [2] T. Lu and F. Chen, *J Comput Chem*, **2012**, *33*, 580-592.
- [3] T. Furukawa, H. Nakanotani, M. Inoue, C. Adachi, *Sci. Rep.* **2015**, *5*, 8429.