Electronic Supplementary Materials (ESI) for ChemComm.

Through-Space Charge Transfer Polybenzonorbornenes with Thermally Activated Delayed Fluorescence and Full-Color Piezochromism Property

Qiang Li[#a,d], Fangfang Huang[#b], Xiaofan Xu[c], Xingdong Wang[a], Zhihua Ma[b], Zewei Quan*[c], Jize Liu[b], Hui Tong[a, d] Shiyang Shao*[a,b] and Lixiang Wang*[a,d]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: lixiang@ciac.ac.cn*

[b] *School of Materials Science and Engineering, Hainan University, Haikou, 570228, China E-mail: ssyang@hainanu.edu.cn*

[c] *Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China. E-mail: quanzw@sustech.edu.cn.*

[d] *School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China.*

Measurements and Instruments

General information. The chemicals and reagents were carried out as sourced commercially without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were measured by Bruker Avance NMR spectrometers (400/500 MHz) in $CDCl_3$ or DMSO. Matrix-assisted laser desorption/ ionization time of flight (MALDI-TOF) mass spectra were applied in monomers with AXIMA CFR MS apparatus (COMPACT). Elemental analysis was performed on Bio-Rad elemental analysis system. Cyclic voltammetry (CV) was recorded on an CHI610E electrochemical workstation using Bu_4NClO_4 (0.1 M) the supporting electrolyte and ferrocene as an external reference at a scan rate of 50 mV s^{-1}. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the compounds were calculated according to equations of $E_{HOMO}/E_{LUMO} = -(4.80 + E_{onset}{}^{ox}/E_{onset}{}^{red})$, in which $E_{onset}{}^{ox}$ and $E_{onset}{}^{red}$ are the onset of oxidation and reduction potentials respectively. Thermal gravimetric analysis (TGA) was performed under an N_2 flow on a Perkin-Elmer-TGA 7 system and the temperature of degradation (T_d) corresponded to 5% weight loss.

Single-crystal analysis. The crystallographic data were collected by a Bruker D8 VENTURE diffractometer equipped with graphite monochromated Cu Kα radiation (λ =1.54184 Å) at 293 K, using the phi and omega scans technique. The structure was solved by direct methods, and all the non−hydrogen atoms were refined anisotropically on F2 by full−matrix least−squares using SHELXL package.

Atmospheric-Pressure 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 350 nm.

In-Situ High-Pressure PL Spectra Measurement. The high-pressure environment was generated *via* using a diamond anvil cell (DAC), equipped by a 400 μm diameter culet diamond. The T301 steel gaskets with a 150 μm diameter and ~45 μm thickness hole in the center were placed in DAC. The polymers were loaded in the gasket hole together with a small ruby ball to measure the pressure through the standard ruby fluorescence technique, respectively. Silicone oil was utilized as the pressure-transmitting medium. All the high-pressure experiments were conducted at room temperature. In-situ high-pressure PL spectra were recorded by the NOVA spectrometer with the 325 nm laser excitation. The PL micrographs of the crystals were captured using the CCD camera equipped on the microscope, and recorded under the same exposure time of high-pressure experiment.

Quantum chemical calculations. The calculations were conducted by Gaussian 09 program using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) method with M06-2X hybrid functional. All structures were optimized using DFT (S_0 and T_1 states) or TDDFT (S_1 state) method with a def2-SVP basis set in the gas phase. The calculation of electron density difference between ground state and excited state, and contribution of atoms to frontier molecular orbitals (FMOs) are performed by Multiwfn software (version 3.7)[1]. Reduced density gradient (RDG)[2] and interfragment charge transfer (IFCT) analysis was performed by Multiwfn (version 3.7)[1] and plotted by VMD software (version 1.9.3).

Analysis of Rate Constants. The rate constants of radiative decay ($k_{r,S}$) and reverse intersystem crossing (k_{RISC}) were determined from the following equations.[3]

$$k_p = 1/\tau_p$$

$$k_d = 1/\tau_d$$

$$k_F = \Phi_F/\tau_p$$

$$\Phi_{PL} = k_F/(k_F + k_{IC})$$

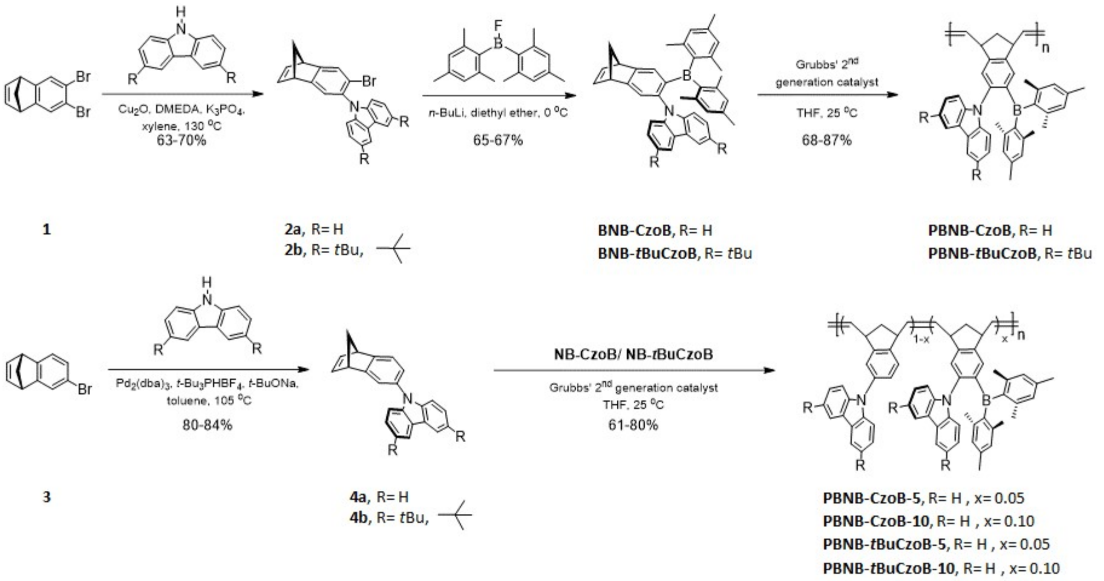
$$\Phi_F = k_F/(k_F + k_{IC} + k_{ISC})$$

$k_{RISC} = k_p k_d/(k_p - k_{ISC})$

Where k_p and k_d represent the decay rate constants for prompt and delayed fluorescence, respectively, which are in reciprocal relationship with the decay time constants (τ_p and τ_d) experimentally determined from transient PL characteristics. Φ_F indicate prompt fluorescence components and can be estimated from the total Φ_{PL} by comparing the integrated intensities of their PL spectra in O_2 and N_2.

Device fabrication and characterization. The solution-processed OLEDs were fabricated with configuration of ITO/PEDOT:PSS (40 nm)/PVK (15 nm)/mCP : x wt% polymer (40 nm)/ mSiTRZ (12 nm)/TmPPPyTz (55 nm)/LiF (1 nm)/Al(100 nm). The pre-cleaned ITO substrates were treated by UV-ozone for 1 h. Then, PEDOT: PSS layer was deposited by spin-coating onto the ITO surface with speed of 7000 rpm. After baking at 120 °C for 1 h in oven, the substrates were taken into glovebox filled with N_2. Subsequently, PVK layer was spin-coated from 1,2-dichlorobenzene solution onto PEDOT: PSS layer and annealed at 100 °C for 10 min. Subsequently, emissive layer was deposited on PVK layer by spin-coating the polymer solutions with speed of 1500 rpm and then annealed at 100 °C for 10 min. Finally, mSiTRZ, TmPPPyTz, LiF and Al were thermally deposited on emissive layer in sequence under a chamber pressure less than 6×10^{-7} Torr. The current density-voltage-luminance characteristics of the devices were tested using Keithley 2000 and Keithley 2400 (equipped with calibrated silicon photodiode), and the EL spectra were recorded by a CS2000 spectrometer. The EQE was calculated using the current density, luminance and EL spectra assuming a Lambertian distribution.

Synthesis



Scheme S1. Synthesis of benzonorbornene monomers and polymers.

Synthesis of 6,7-dibromo-1,4-dihydro-1,4-methanonaphthalene (1). Under argon atmosphere, 1,2,4,5-tetrabromobenzene (20.0 g, 50.8 mmol), cyclopentadiene (5.9 g, 50.8 mmol), and toluene (800 mL) were added to a dried two-necked flask (2000 mL), and the mixture was cooled to 0 °C. Under mechanical stirring, *n*-BuLi solution (2.5 M, 55.9 mmol) was added dropwise to the reaction mixture through a constant-pressure dropping funnel. The mixture was then stirred at 0 °C for 2 hours and at room temperature for additional 4 hours. To quench the residual lithium compounds, 10 mL of methanol was added to the reaction mixture. Subsequently, 1000 mL of saturated brine was used to wash the mixture three times. The organic phase was dried, and the solvent was evaporated under reduced pressure. Further purification was performed with silica gel column chromatography (eluent: petroleum ether) to yield compound **1** (8.7 g, Yield: 57%) as a colorless oily liquid, which became white solid upon storage. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 2H), 6.75 (s, 2H), 3.84 (s, 2H), 2.30 (d, *J* = 7.4 Hz, 1H), 2.23 (d, *J* = 7.4 Hz, 1H). **Note**: Commercially purchased cyclopentadiene reagent requires purification through distillation before use and should be stored at -17 °C.

Synthesis of 9-(7-bromo-1,4-dihydro-1,4-methanonaphthalen-6-yl)-9H-carbazole (2a). Compound **1** (15.0 g, 50.0 mmol), carbazole (4.2 g, 25.0 mmol), copper(I) oxide (0.73 g, 5.0 mmol), potassium phosphate (15.9 g, 75.0 mmol), *N*,*N*'-dimethylethylenediamine (1.1 mL, 10.0 mmol), and anhydrous *m*-xylene (80 mL) was added to a 250 mL two-necked flask. The flask was purged with argon and sealed under argon flow. The mixture was stirred and heated to 130 °C for 48 hours. After the reaction was cooled to room temperature, 200 mL saturated ammonium chloride aqueous solution was added. The mixture was extracted with chloroform (200 mL), and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether) to obtain compound **2a** (6.1 g, yield: 63%) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (m, 2H), 7.64 (s, 1H), 7.37 (m, 2H), 7.24-7.29 (m, 3H), 7.07 (m, 2H), 6.85 (s, 2H), 3.99 (s, 1H), 3.90 (s, 1H), 2.39 (m, 2H).

Synthesis of 9-(7-bromo-1,4-dihydro-1,4-methanonaphthalen-6-yl)-3,6-di-tert-butyl-9H-carbazole (2b). Compound **1** (13.5 g, 45.0 mmol), 3,6-*di-tert*-butylcarbazole (6.3 g, 22.5 mmol), copper(I) oxide (0.64 g, 4.5 mmol), potassium phosphate (14.3 g, 67.5 mmol), *N*, *N*'-dimethylethylenediamine (1.0 mL, 9.0 mmol), and anhydrous *m*-xylene (60 mL) were added to a 250 mL two-necked flask under argon stmosphere. The mixture was stirred and heated to 130 °C for 48 hours. After the reaction was cooled down to room temperature, 200 mL saturated ammonium chloride aqueous solution was added. The mixture was extracted with chloroform (200 mL), and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane = 25/1, *v*/*v*) to give the compound **2b** (7.9 g, Yield: 70%) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (m, 2H), 7.63 (s, 1H), 7.42 (m, 2H), 7.18 (s, 1H), 6.99 (m, 2H), 6.84 (m, 2H), 3.98 (s, 1H), 3.86 (s, 1H), 2.38 (m, 2H), 1.45 (m, 18H).

Synthesis of 6-bromo-1,4-dihydro-1,4-methanonaphthalene (3). 2,5-Dibromoiodobenzene (30.0 g, 82.9 mmol), cyclopentadiene (9.6 g, 145.1 mmol), and toluene (1000 mL) were added to a dried two-necked flask (2000 mL) under argon atmosphere, and the mixture was cooled to 0 °C. Under mechanical stirring, *n*-BuLi solution (2.5 M, 91.2 mmol) was added dropwise to the reaction flask through a constant-pressure dropping funnel. The reaction mixture was reacted at 0 °C for 2 hours and then at room temperature for additional 4 hours. To quench the residual lithium compounds, 10 mL of methanol was added to the reaction mixture. Subsequently, 1000 mL of saturated brine was used to wash the mixture three times. The organic phase was dried, and the solvent was evaporated under reduced pressure. Further purification was performed with silica gel column chromatography (eluent: petroleum ether) to yield compound **3** (14.7 g, Yield: 80%) as a colorless oily liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.08-7.01 (m, 2H), 6.79-6.71 (m, 2H), 3.83 (s, 2H), 2.28 (d, J = 7.2 Hz, 1H), 2.21 (d, J = 7.2 Hz, 1H).

Synthesis of 9-(7-(dimesitylboraneyl)-1,4-dihydro-1,4-methanonaphthalen-6-yl)-9H-carbazole (BNB-CzoB). Compound **2a** (3.5 g, 9.1 mmol) and anhydrous tetrahydrofuran (70 mL) were added to a dried 250 mL two-necked flask. The solution was purged with argon and cooled to -78 °C. The *n*-BuLi (2.5 M, 10.0 mmol) was added dropwise and kept stirring for 1.5 hours. Bis(trimethylphenyl)boron fluoride (4.9 g, 18.2 mmol) was dissolved in anhydrous THF (20 mL) and added to the reaction mixture under argon atmosphere at 0 °C. The solution was warmed to room temperature and reacted for 8 hours. The residual lithium compounds were quenched by addition of methanol (5 mL), followed by washing with 100 mL of saturated brine solution three times. The mixture was extracted with 100 mL of diethyl ether, and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane = 20/1, *v*/*v*) to give **BNB-CzoB** (3.4 g, Yield: 67%) as pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.50 (s, 1H), 7.30 (s, 1H), 7.24-7.14 (m, 3H), 7.08 (m, 3H), 6.85 (s, 2H), 5.87 (s, br, 4H), 3.96 (dd, J = 8.7, 1.4 Hz, 2H), 2.41 (m, 2H), 2.13-0.84 (br, 18H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.38, 151.74, 143.47, 142.59, 141.94, 141.35, 139.90, 129.96, 124.45, 123.69, 119.29, 118.68, 110.61, 70.25, 50.66, 50.11, 20.96. MALDI TOF-MS: calcd for $C_{41}H_{38}BN$: 555.3, found: 555.3 $[M]^+$.

Synthesis of 3,6-di-tert-butyl-9-(7-(dimesitylboraneyl)-1,4-dihydro-1,4-methanonaphthalen-6-yl)-9H-carbazole (BNB-tBuCzoB). Compound **2b** (5.0 g, 9.9 mmol) and anhydrous tetrahydrofuran (80 mL) were added to a dried 250 mL two-necked flask. The solution was purged with argon and cooled to -78 °C. The *n*-BuLi (2.5 M, 10.4 mmol) was added dropwise and kept stirring for 1.5 hours. Bis(trimethylphenyl)boron fluoride (5.3 g, 19.8 mmol) was dissolved in anhydrous THF (25 mL) and added to the reaction mixture under argon atmosphere at 0 °C. The solution was warmed to room temperature and reacted for 8 hours. The residual lithium compounds were quenched by methanol (5 mL), followed by washing with 100 mL of saturated brine solution three times. The mixture was extracted with 100 mL of diethyl ether, and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product purified by silica gel column chromatography (eluent: petroleum ether/dichloromethane = 30/1, *v*/*v*) to give **BNB-*t*BuCzoB** (4.3 g, Yield: 65%) as pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.49 (s, 1H), 7.34-7.20 (m, 3H), 7.08 (m, 2H), 6.84 (m, 2H), 6.74 (s, br, 2H), 5.77 (s, br, 2H), 3.94 (s, 2H), 2.41 (s, 2H), 2.26-0.88 (br, 18H), 1.43 (m, 18H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.26, 151.27, 143.46, 142.51, 141.50, 141.20, 140.58, 130.11, 123.53, 122.90, 122.05, 114.91, 109.89, 70.08, 53.35, 50.66, 50.08, 34.56, 32.14, 21.09. MALDI TOF-MS: calcd for $C_{49}H_{54}BN$: 667.4, found: 667.4 $[M]^+$.

Synthesis of 9-(1,4-dihydro-1,4-methanonaphthalen-6-yl)-9H-carbazole (4a). Compound **3** (4.4 g, 20.0 mmol), carbazole (3.3 g, 20.0 mmol), $Pd_2(dba)_3$ (0.92 g, 1.0 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (1.2 g, 4.0 mmol), sodium *tert*-butoxide (3.8 g, 40.0 mmol), and anhydrous toluene (50 mL) were added to a dried 250 mL two-necked flask under argon atmosphere. The mixture was stirred and heated at 105 °C for 6 hours. After the reaction was cooled to room temperature, 200 mL saturated ammonium chloride aqueous solution was added. The mixture was extracted with diethyl ether (100 mL), and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether) to give the product **4a** (5.2 g, Yield: 84%) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (m, 2H), 7.38 (m, 6H), 7.26 (m, 2H), 7.10 (m, 2H), 6.88 (m, 2H), 3.98 (d, J = 20.1 Hz, 2H), 2.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92, 151.30, 143.07, 142.98, 141.24, 133.70, 125.75, 123.16, 122.93, 122.21, 120.73, 120.20, 119.59, 110.03, 70.27, 50.58, 50.22.

Synthesis of 3,6-di-tert-butyl-9-(1,4-dihydro-1,4-methanonaphthalen-6-yl)-9H-carbazole (4b). Compound **3** (4.8 g, 22.0 mmol), 3,6-di-*tert*-butylcarbazole (6.1 g, 22.0 mmol), $Pd_2(dba)_3$ (1.0 g, 1.1 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (1.4 g, 4.4 mmol), sodium *tert*-butoxide (4.2 g, 44.0 mmol), and anhydrous toluene (80 mL) were added to a dried 250 mL two-necked flask under argon atmosphere. The mixture was stirred and heated at 105 °C for 6 hours. After the reaction was cooled to room temperature, 200 mL saturated ammonium chloride aqueous solution was added. The mixture was extracted with diethyl ether (100 mL), and the combined organic layers was dried, filtered and evaporated the solvent under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether) to give the product **4b** (7.4 g, Yield: 80%) as flocculent solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 1.2 Hz, 2H), 7.45 (dd, J = 8.6, 1.8 Hz, 2H), 7.36 (m, 4H), 7.10 (dd, J = 7.4, 1.9 Hz, 1H), 6.88 (m, 2H), 3.98 (d, J = 23.7 Hz, 2H), 2.41 (m, 2H), 1.48 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.73, 150.69, 143.06, 142.95, 142.41, 139.64, 134.23, 123.41, 123.11, 122.60, 122.11, 120.50, 116.10, 109.43, 70.22, 50.57, 50.19, 34.73, 32.08.

General synthetic procedure for polybenzonorbornenes. The polybenzonorbornenes were synthesized by ring-opening metathesis polymerization of benzonorbornene monomers with Grubbs' 2nd-generation catalyst (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (tricyclohexylphosphine) ruthenium). Under argon atmosphere, the monomers (with a total molar amount of 1.0 mmol) were dissolved in anhydrous tetrahydrofuran (THF) with concentration of 20 mg/mL. Then, the Grubbs catalyst (0.004 mmol) dissolved in anhydrous THF (2 mL) was injected to the mixture to initiate polymerization. After stirring at 25 °C for 1 h, the polymerization was terminated by adding vinyl ethyl ether (0.3 mL). The reaction mixture was precipitated in acetone (200 mL), filtered and dissolved in dichloromethane (100 mL). To this solution was added H_2O_2 (10 wt% in water, 75 mL) and stirred at room temperature for 1 hour. The organic layer was separated, dried over Na_2SO_4, and then applied to silica gel column chromatography using CH_2Cl_2 as eluent. The eluate was concentrated and reprecipitated in methanol to give the polymers as fibers in yields of 61~87%.

PBNB-CzoB. White fiber (225.8 mg, yield: 68%). **BNB-CzoB** (333.9 mg, 0.6 mmol) were used in the polymerization. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H), 7.54-6.70 (m, 7H), 6.25-5.29 (m, 5H), 3.94 (m, 2H), 2.88-0.85 (m, 20H). Anal. Calcd. for $C_{41}H_{38}BN$: C, 88.64; H, 6.89; N, 2.52. found: C, 89.27; H, 6.12; N, 2.08. M_n=213 kDa, PDI=1.64.

PBNB-CzoB-5. White fiber (230.0 mg, yield: 61%). **BNB-CzoB** (27.8 mg, 0.05 mmol) and compound **6a** (292.0 mg, 0.9 mmol) were used in the polymerization. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31-7.73 (m, 2H), 7.23 (m, 8H), 5.66 (m, 2H), 4.00 (m, 2H), 2.19 (m, 2H), 1.58-0.64 (m, 4H).Anal. Calcd. for $C_{23.9}H_{18.05}B_{0.05}N$: C, 89.81; H, 5.64; N, 4.46. found: C, 89.97; H, 5.40; N, 4.62. M_n=148 kDa, PDI=1.70.

PBNB-CzoB-10. White fiber (230.0 mg, yield: 61%). **BNB-CzoB** (55.6 mg, 0.1 mmol) and compound **6a** (292.0 mg, 0.9 mmol) were used in the polymerization.^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.88-6.37 (m, 9H), 5.46 (m, 2H), 4.05 (m, 2H), 2.42 (m, 2H), 1.35 (m, 5H). Anal. Calcd. for $C_{24.8}H_{19.1}B_{0.1}N$: C, 89.75; H, 5.70; N, 4.36. found: C, 90.31; H, 5.29; N, 4.21. M_n=130 kDa, PDI=1.77.

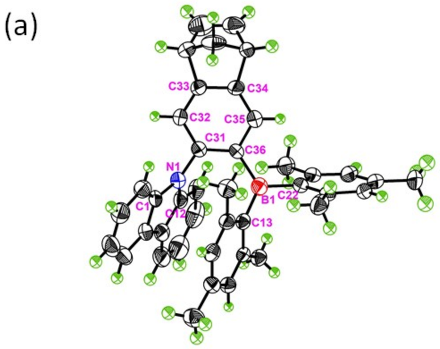
PBNB-*t*BuCzoB. White fiber (290.0 mg, yield: 87%). **BNB-*t*BuCzoB** (333.9 mg, 0.5 mmol) were used in the polymerization. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.54-6.75 (m, 6H), 6.48-5.69 (m, 6H), 3.97 (m, 2H), 2.83-0.83 (m, 38H). Anal. Calcd. for $C_{49}H_{54}BN$: C, 88.13; H, 8.15; N, 2.1. found: C, 88.66; H, 8.00; N, 1.75. M_n=129 kDa, PDI=1.73.

PBNB-*t*BuCzoB-5. White fiber (330.0 mg, yield: 76%). **BNB-*t*BuCzoB** (33.4 mg, 0.05 mmol) and compound **6b** (398.6 mg, 0.95 mmol) were used in the polymerization. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.71 – 6.89 (m, 7H), 5.70 (s, 2H), 4.05 (m, 2H), 2.70 (m, 1H), 1.81 (m, 1H), 1.67 – 0.92 (m, 20H). Anal. Calcd. for

$C_{31.9}H_{34.05}B_{0.05}N$: C, 88.70; H, 7.94; N, 3.28. found: C, 88.81; H, 7.53; N, 2.92. M_n=159 kDa, PDI=1.81.

PBNB-*t*BuCzoB-10. White fiber (350.0 mg, yield: 80%). **BNB-*t*BuCzoB** (66.8 mg, 0.1 mmol) and compound **6b** (377.6 mg, 0.9 mmol) were used in the polymerization. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 2H), 7.96-6.71 (m, 7H), 5.72 (m, 2H), 4.09 (m, 2H), 2.69-2.18 (m, 2H), 1.95-0.98 (m, 21H). Anal. Calcd. for $C_{32.8}H_{35.1}B_{0.1}N$: C, 88.67; H, 7.95; N, 3.22. found: C, 88.44; H, 8.02; N, 2.90. M_n=221 kDa, PDI=1.66.

Supplementary Figures and Tables



Angles [°]		Bond length [Å]	
C(31)-N(1)-C(1)	125.09	C(1)-N(1)	1.396
C(31)-N(1)-C(12)	125.83	C(12)-N(1)	1.387
C(1)-N(1)-C(12)	108.45	C(31)-N(1)	1.437
C(36)-B(1)-C(22)	119.10	C(31)-C(36)	1.409
C(36)-B(1)-C(13)	120.41	C(36)-B(1)	1.570
C(13)-B(1)-C(22)	120.04	C(22)-B(1)	1.589
		C(13)-B(1)	1.576

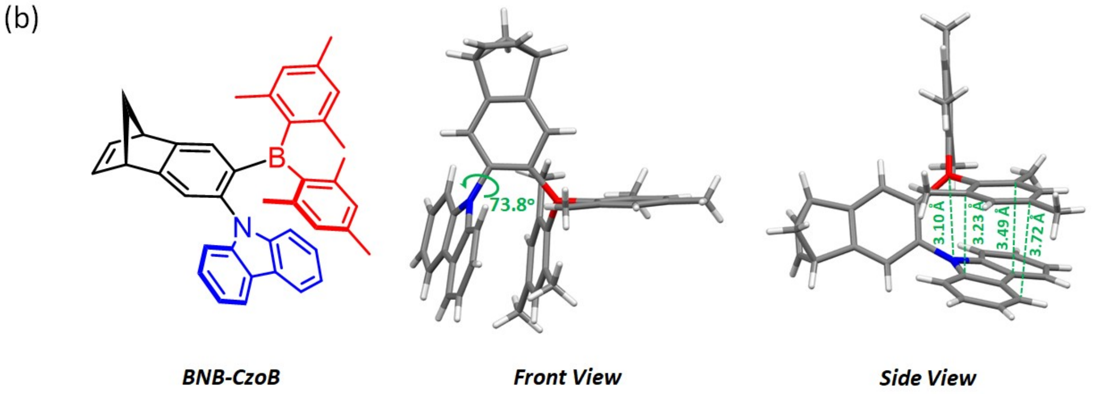


Figure S1. (a) X-ray crystal structure and structure refinement for **BNB-CzoB**; (b) Single-crystal structure of **BNB-CzoB** and the aligning pattern of donor and acceptor (CCDC number:2410822)[4].

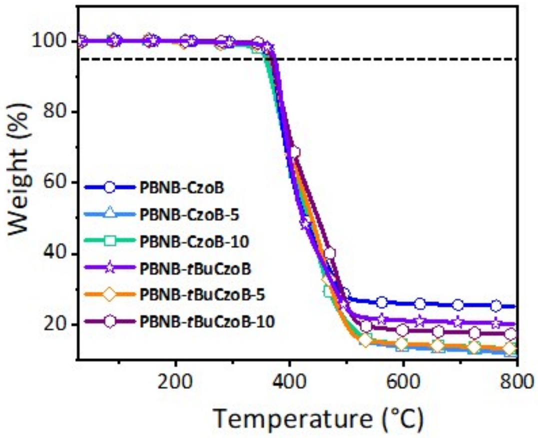


Figure S2. Thermogravimetric analysis (TGA) curves for polynorbornenes.

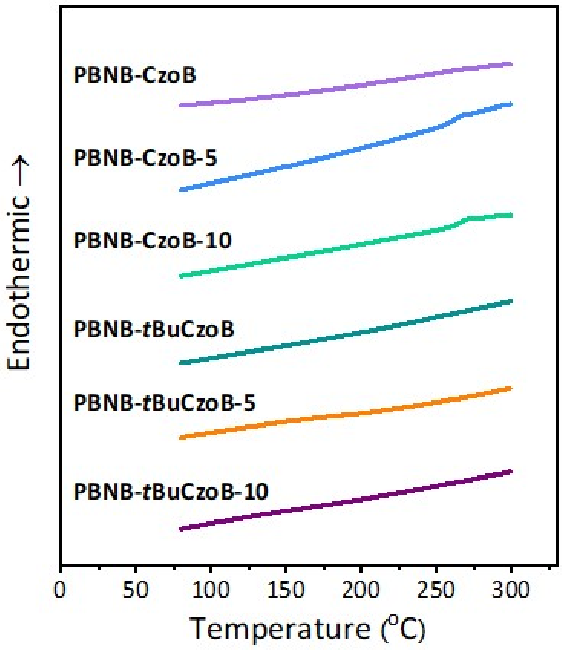


Figure S3. Differential scanning calorimetry (DSC) curves for polybenzonorbornenes.

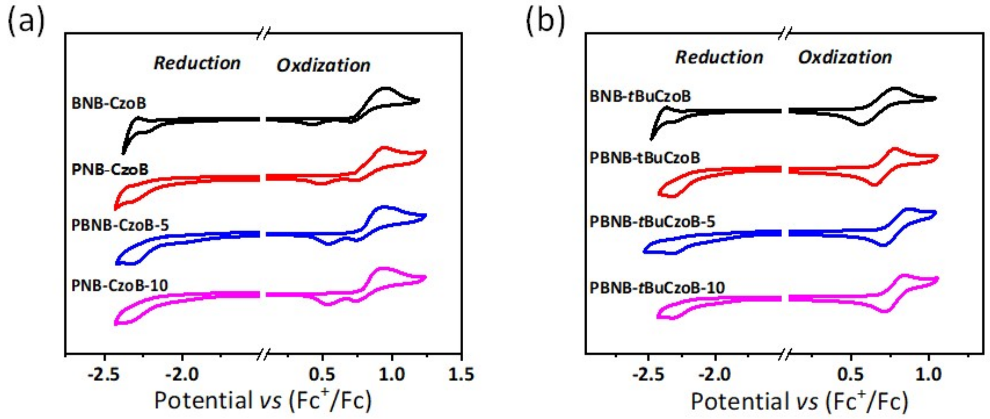


Figure S4. Cyclic voltammetry (CV) characteristics for monomers and polynorbornenes in dichloromethane (for oxidation) and tetrahydrofuran (for reduction) solution (electrolyte: Bu_4NClO_4; scan rate: 50 mV s^{-1}).

Table S1. Molecular weights and thermal properties of polynorbornenes.

Polymer	M_n (Da) [a]	M_w (Da) [b]	PDI [c]	T_d (°C) [d]	T_g (°C) [e]
PBNB-CzoB	213, 000	349, 000	1.64	369	---[f]
PBNB-CzoB-5	148, 000	251, 000	1.70	361	259
PBNB-CzoB-10	130, 000	230, 000	1.77	358	263
PBNB-*t*BuCzoB	129, 000	223, 000	1.73	369	---[f]
PBNB-*t*BuCzoB-5	159, 000	288, 000	1.81	369	---[f]
PBNB-*t*BuCzoB-10	221, 000	367, 000	1.66	374	---[f]

[a] Number-average molecular weight; [b] Weight-average molecular weight; [c] Polymer dispersity index; [d] Thermal decomposition temperature; [e] Glass transition temperature; [f] No obvious T_gs were observed at test temperature range.

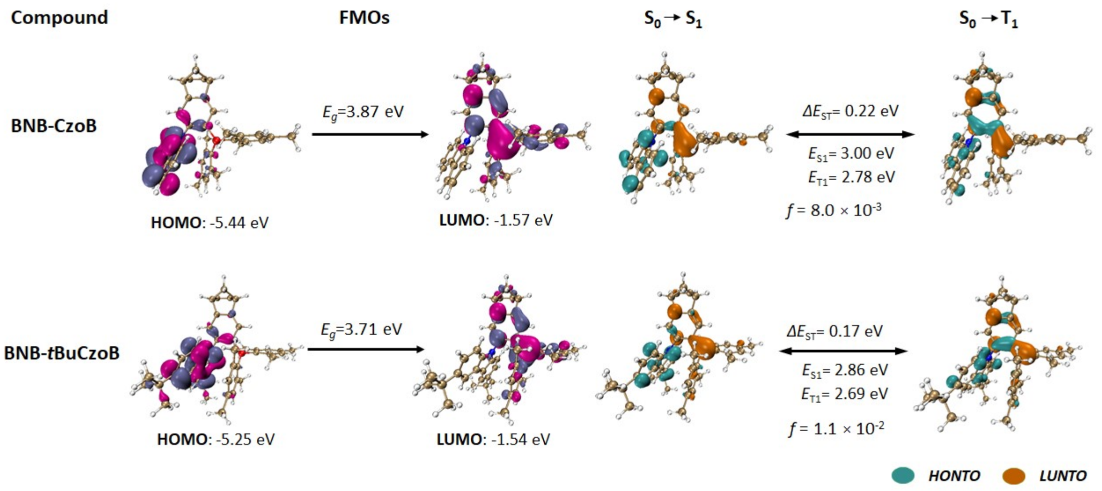


Figure S5. Frontier molecular orbitals (FMOs) distributions, natural transition orbitals (NTOs) for S_0-S_1 and T_0-T_1 transitions, and energy levels of S_1/T_1 states for benzonorbornene compounds by DFT andTD-DFT calculations (PBE0/6-31G(d)).

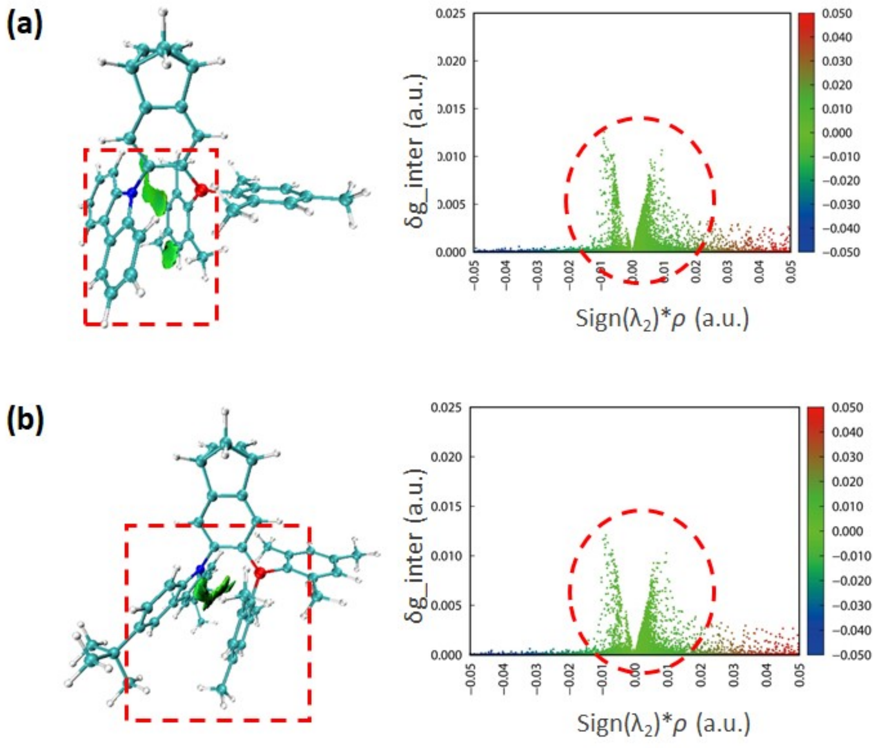


Figure S6. Reduced density gradient (RDG) isosurface map and corresponding scatter diagram (plots of RDG to sign(λ_2)*ρ) for benzonorbornene compounds.

Table S2. Summary of TD-DFT calculation results for **BNB-CzoB** and **BNB-*t*BuCzoB**.

Compound	Optimized structure	Transition	Wavelength (nm)	Energy (eV)	Oscillator strength	electron configurations
BNB-CzoB	S_0	S_0-S_1	413.40	2.9991	0.0080	H → L 97.9%
		S_0-T_1	446.74	2.7753	0.0000	H → L 60.3%, H-6 → L 11.9%, H-4 → L 6.9%
		S_0-T_2	409.62	3.0268	0.0000	H-2 → L 29.3%, H-4 → L 23.9%, H-6 → L 6.3%
		S_0-T_3	401.83	3.0855	0.0000	H-1 → L+1 59.7%, H → L+5 8.0%, H-7 → L+1 5.1%
BNB-*t*BuCzoB	S_0	S_0-S_1	432.80	2.8647	0.0106	H → L 98.3%
		S_0-T_1	460.51	2.6923	0.0000	H → L 74.0%, H-6 → L 6.6%
		S_0-T_2	409.55	3.0273	0.0000	H-4 → L 35.8%, H-6 → L 9.9%, H-2 → L 8.1%, H → L 6.7%, H-6 → L+2 6.2%
		S_0-T_3	405.68	3.0562	0.0000	H-1 → L+1 52.6%, H → L+5 10.3%, H-7 → L+1 7.2%

Table S3 Cartesian coordinates for optimized ground state geometry of **BNB-CzoB**.

Atom	**Coordinates (Å)**		
	X	**Y**	**Z**
C	-3.40451202	4.329723	1.597197
C	-2.42368035	5.161419	1.236907
C	-2.07530716	4.856969	-0.22242
C	-1.46982376	3.457164	-0.22248
C	-2.49925967	2.580609	0.152082
C	-3.73148054	3.450808	0.387517
C	-3.49271855	4.492861	-0.73523
C	-0.21263316	2.972846	-0.51623
C	-2.27163477	1.224634	0.232827
C	0.02793301	1.593314	-0.40107
C	1.73466582	0.518083	-1.8841
C	3.12865527	0.281494	-1.84213
C	3.60573818	0.853853	-0.60713
C	2.4795481	1.411832	0.041041
N	1.34648391	1.160403	-0.71886
C	0.97039173	0.184582	-3.00122
C	1.61430032	-0.44305	-4.0611
C	2.98697556	-0.72588	-4.01748
C	3.7490655	-0.35795	-2.91695
C	4.86513054	0.96497	-0.01476
C	4.9862231	1.637827	1.193079

C	3.86166688	2.205634	1.809588
C	2.59660583	2.102318	1.246215
C	2.44080563	-2.96053	0.688855
C	1.23038045	-2.48217	0.190276
C	0.55194003	-1.4309	0.857344
C	1.12079603	-0.93292	2.054341
C	2.32655265	-1.45127	2.528008
C	3.01505819	-2.45297	1.852415
C	4.34571376	-2.94649	2.343849
C	0.71247477	-3.08027	-1.09124
C	0.42935689	0.080895	2.930523
B	-0.80240622	-0.86046	0.28249
C	-3.70916937	-3.34626	1.044395
C	-2.57106098	-2.55221	1.195228
C	-2.07512834	-1.7973	0.10278
C	-2.77536873	-1.89209	-1.12735
C	-3.89412472	-2.7164	-1.24318
C	-4.38273131	-3.45467	-0.16825
C	-5.57576488	-4.3543	-0.32085
C	-1.94127619	-2.50223	2.563241
C	-2.32166554	-1.16009	-2.36226
C	-0.98247277	0.684703	-0.01739
H	-3.84516844	4.210623	2.580147
H	-1.88834277	5.867551	1.860758
H	-1.51638424	5.622924	-0.76179
H	-4.68975478	2.930066	0.406168
H	-3.48954738	4.053243	-1.73825
H	-4.18801973	5.335986	-0.68713
H	0.59504659	3.622072	-0.84318
H	-3.07428408	0.542838	0.503269
H	-0.0854713	0.424744	-3.0458
H	1.0412277	-0.71152	-4.94411
H	3.45898971	-1.22092	-4.86065
H	4.81766351	-0.55346	-2.89635
H	5.73916762	0.537794	-0.49879
H	5.96079187	1.736547	1.661595
H	3.98114625	2.741165	2.747265
H	1.72843403	2.544589	1.723409
H	2.95361508	-3.75211	0.145433
H	2.74074002	-1.05123	3.451926
H	4.39236122	-2.95536	3.437009
H	4.55731556	-3.95754	1.984242
H	5.15286849	-2.29405	1.989475
H	1.25151304	-4.00018	-1.33399

H	-0.35244615	-3.31979	-1.02685
H	0.85185179	-2.39165	-1.93249
H	-0.29653364	0.69134	2.389978
H	-0.10648307	-0.42087	3.745765
H	1.15792392	0.752187	3.393908
H	-4.07703314	-3.90076	1.905799
H	-4.40035524	-2.78074	-2.2048
H	-6.29013019	-3.95279	-1.04575
H	-5.275496	-5.34711	-0.67712
H	-6.09658208	-4.49382	0.630673
H	-2.48125314	-3.15041	3.25862
H	-0.89587484	-2.82059	2.540656
H	-1.96168674	-1.48925	2.979058
H	-2.28413353	-0.07898	-2.19998
H	-1.32024084	-1.47829	-2.66978
H	-2.99978396	-1.35239	-3.19809

Table S4 Cartesian coordinates for optimized ground state geometry of **BNB-*t*BuCzoB**.

Atom	**Coordinates (Å)**		
	X	**Y**	**Z**
C	4.65599979	3.12770559	-3.248883
C	3.59385806	3.54630107	-3.942003
C	2.60742394	4.1606539	-2.945712
C	2.12069516	3.00737985	-2.073872
C	3.23455103	2.56527017	-1.34451
C	4.40125712	3.45183273	-1.775005
C	3.62520957	4.78127028	-1.953731
C	0.90030403	2.380589	-1.93487
C	3.12419672	1.50905737	-0.46737
C	5.04694129	-2.40514069	0.6461624
C	3.86454213	-1.74807883	0.3070979
C	3.16696569	-0.97620787	1.2717905
C	3.72741869	-0.89652216	2.5718778
C	4.92644557	-1.54913849	2.8633533
C	5.60128191	-2.31840068	1.9205193
C	6.8651261	-3.05066997	2.2706154
C	3.34286555	-1.94061794	-1.092348
C	3.0980089	-0.08744257	3.6767197
B	1.82803379	-0.1928743	0.9231575
C	-1.20680789	-1.78830038	2.7518335
C	-0.06244574	-1.64418763	1.9710576
C	0.53581429	-0.36745684	1.8130632
C	-0.04506742	0.72250728	2.5028064

C	-1.18528523	0.53249843	3.2861594
C	-1.79274853	-0.7108648	3.4145734
C	-3.05160346	-0.88588599	4.2148588
C	0.4735983	-2.86763617	1.2751531
C	0.56810738	2.10038173	2.5292289
C	1.87733595	0.86331155	-0.25552
C	0.78277026	1.3166511	-1.024657
C	-0.84119282	-0.53964555	-1.44436
C	-2.21028666	-0.78508359	-1.195364
C	-2.72707869	0.39707729	-0.545204
C	-1.64610337	1.30008288	-0.434427
N	-0.49751364	0.70471185	-0.937253
C	-0.07520611	-1.44760809	-2.166117
C	-0.68050958	-2.62995521	-2.581853
C	-2.78434297	-1.98130197	-1.618742
C	-3.98679386	0.76889153	-0.082387
C	-3.10111446	2.91218888	0.5490193
C	-1.82932102	2.56875345	0.1033869
C	-2.02722858	-2.9308723	-2.309492
C	-2.6826567	-4.24232547	-2.756032
C	-1.70596413	-5.15833403	-3.498552
C	-3.20085454	-4.99868177	-1.521997
C	-3.85891839	-3.93745532	-3.697333
C	-4.19603504	2.03203241	0.4759792
C	-5.59404912	2.41558983	0.973533
C	-5.63986057	3.83385241	1.5484507
C	-6.59362673	2.34105652	-0.192054
C	-6.02981568	1.43967748	2.0785369
H	5.51201622	2.57437979	-3.617062
H	3.392855	3.40841492	-4.997929
H	1.83466802	4.80965283	-3.360146
H	5.27159988	3.45224847	-1.117419
H	3.16283918	5.13850119	-1.02743
H	4.23094104	5.56959859	-2.410025
H	0.02826894	2.68027318	-2.509807
H	3.98732432	1.16633941	0.0982387
H	5.55086889	-3.00153318	-0.112416
H	5.34317248	-1.45365208	3.8643956
H	7.40748113	-2.550205	3.0778368
H	6.64685387	-4.0710626	2.6081945
H	7.53325624	-3.13078569	1.4080518
H	2.3768081	-2.45642452	-1.089706
H	3.20093738	-0.98654478	-1.60789
H	4.03645209	-2.54378017	-1.684466

H	2.98399197	0.96437493	3.3959164
H	2.10338007	-0.4605841	3.9350491
H	3.7188187	-0.11971145	4.5761252
H	-1.65748133	-2.77512592	2.8424112
H	-1.6088441	1.38849425	3.8089447
H	-3.12512149	-0.14447178	5.0159678
H	-3.93617732	-0.76707016	3.5773198
H	-3.1057793	-1.88148332	4.6655198
H	0.00952718	-3.77373921	1.6746957
H	0.25677538	-2.83695516	0.2011597
H	1.55644376	-2.96135155	1.3953659
H	1.27660979	2.27053108	1.7167067
H	-0.20800542	2.86880497	2.468053
H	1.10349892	2.26169017	3.4731817
H	0.95845524	-1.23565918	-2.41372
H	-0.07804428	-3.33479701	-3.144496
H	-3.83644584	-2.16437138	-1.414934
H	-4.81150893	0.06544222	-0.167236
H	-3.23938476	3.90401991	0.9655892
H	-1.00725361	3.27368682	0.1700899
H	-2.21738094	-6.0816605	-3.789572
H	-1.32430814	-4.69044437	-4.412152
H	-0.85250912	-5.43655115	-2.871289
H	-3.67745225	-5.93955884	-1.820602
H	-3.93923457	-4.4114477	-0.967697
H	-2.38042612	-5.23371299	-0.836084
H	-3.51471801	-3.40618798	-4.590516
H	-4.34451015	-4.86642716	-4.017756
H	-4.61697815	-3.3157738	-3.211663
H	-6.65483339	4.0591828	1.8920335
H	-4.96817449	3.94666802	2.4060099
H	-5.3704748	4.58562035	0.7990876
H	-7.60137808	2.60400914	0.1496477
H	-6.63932955	1.3365285	-0.623321
H	-6.31203824	3.03382947	-0.991603
H	-5.33678891	1.47684709	2.9254269
H	-7.03118679	1.69506843	2.4442015
H	-6.06045028	0.40746406	1.7164012

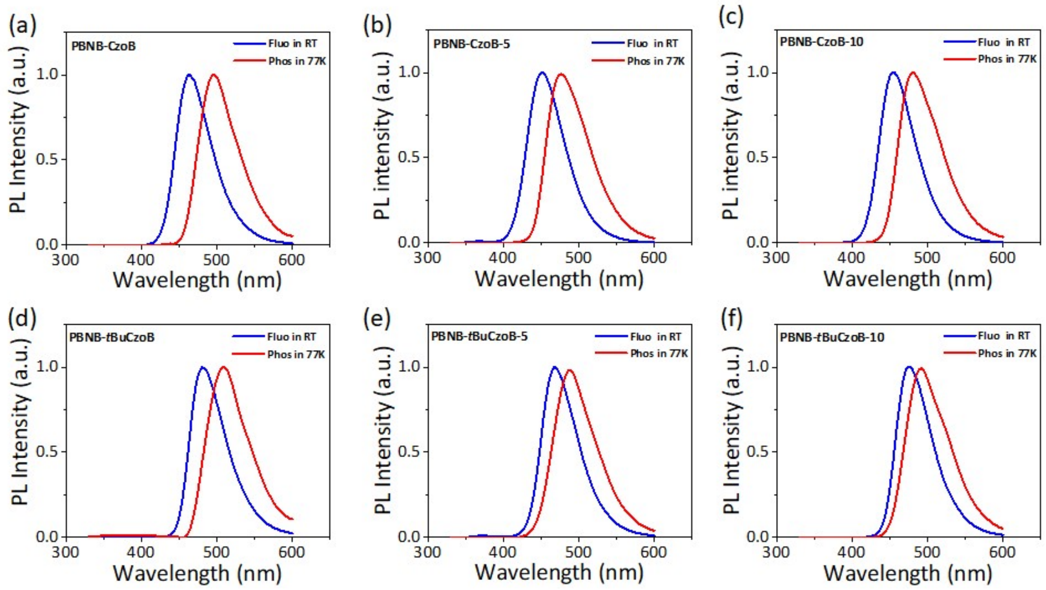


Figure S7. PL spectra and phosphorescent spectra (77K) (extinction wavelength: 460 nm; delay time: 1ms) for polybenzonorbornen-es in film.

Table S5. Photophysical properties for polybenzonorbornenes.

Polymer	λ_{em} [a] (nm)	τ_p/τ_d [b] (ns/μs)	PLQY [c] (%)	S_1 [d] (eV)	T_1 [e] (eV)	ΔE_{ST} [f] (eV)	k_{RISC} [g] ($\times 10^4$ s^{-1})	HOMO [h] (eV)	LUMO [i] (eV)
PBNB-CzoB	463	24.3/42.8	71	2.94	2.76	0.18	2.9	-5.58	-2.67
PBNB-CzoB-5	462	24.1/56.4	73	2.99	2.81	0.18	2.4	-5.59	-2.70
PBNB-CzoB-10	463	21.2/75.7	79	2.95	2.78	0.17	3.0	-5.59	-2.71
PBNB-*t*BuCzoB	478	26.5/47.4	90	2.82	2.69	0.13	3.1	-5.46	-2.68
PBNB-*t*BuCzoB-5	476	22.5/95.1	91	2.86	2.74	0.12	3.2	-5.50	-2.72
PBNB-*t*BuCzoB-10	477	24.5/76.9	94	2.84	2.73	0.11	3.3	-5.50	-2.72

[a] Measured in deoxygenated toluene ($1*10^{-5}$ mol L^{-1}). [b] Prompt and delayed fluorescence lifetimes. [c] Measured for neat films in N_2. [d] Singlet state energy level calculated from fluorescence spectra. [e] Triplet energy level calculated from phosphorescent spectra at 77 K. [f] $\Delta E_{ST} = S_1 - T_1$. [g] RISC rate constants from S_1 to T_1 state. [h, i] Calculated from onset of oxidation/reduction potentials via cyclic voltammetry in dichloromethane solution ($1*10^{-5}$ mol L^{-1}).

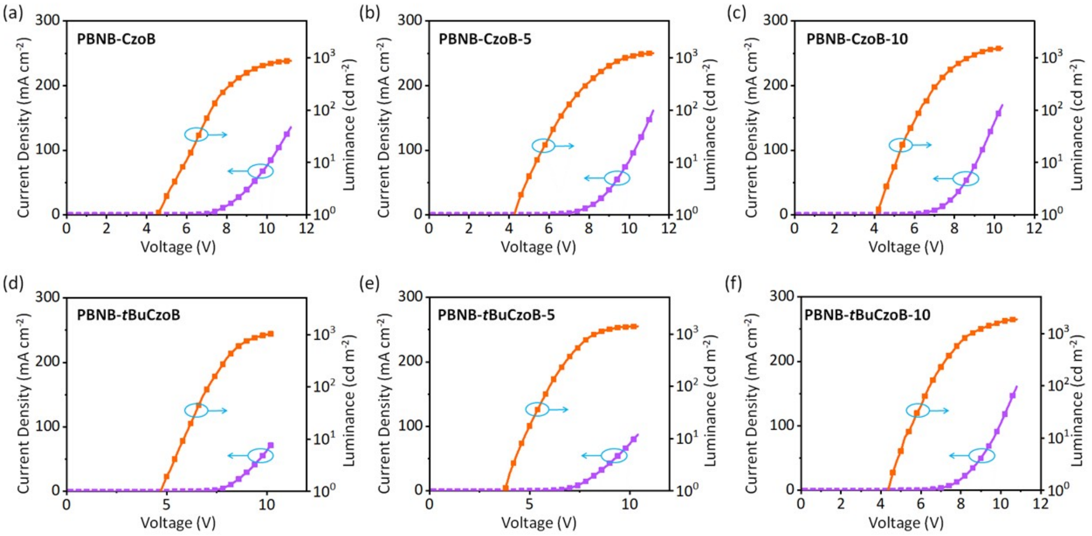


Figure S8 Plots of current density and luminance versus voltage for the OLED devices.

Table S6. Summary of device performance for solution-processed OLEDs based on polybenzonorbornenes.

Polymer	**V_{on} [a] (V)**	**LE[b] (cd A^{-1})**	**EQE [c] (%)**	**FWHM [d] (nm)**	**CIE [e] (x, y)**
		Maximum value/@100 cd m^{-2}			
PBNB-CzoB	4.8	4.0/2.8	2.3/1.6	66	0.18, 0.25
PBNB-CzoB-5	4.4	5.7/4.4	4.3/3.3	55	0.16, 0.17
PBNB-CzoB-10	4.2	7.4/5.1	5.5/3.7	53	0.16, 0.17
PBNB-*t*BuCzoB	4.6	9.2/8.6	4.2/3.9	66	0.20, 0.36
PBNB-*t*BuCzoB-5	4.4	9.6/7.4	6.1/4.6	54	0.16, 0.23
PBNB-*t*BuCzoB-10	4.0	15.0/13.2	9.5/8.3	52	0.15, 0.23

[a]Turn-on voltage at luminance of 1 cd m^{-2}; [b] Luminous efficiency; [c] External quantum efficiency; [d] Full-width at half-maximum for EL emission; [c] CIE coordinates at luminance of 100 cd m^{-2}.

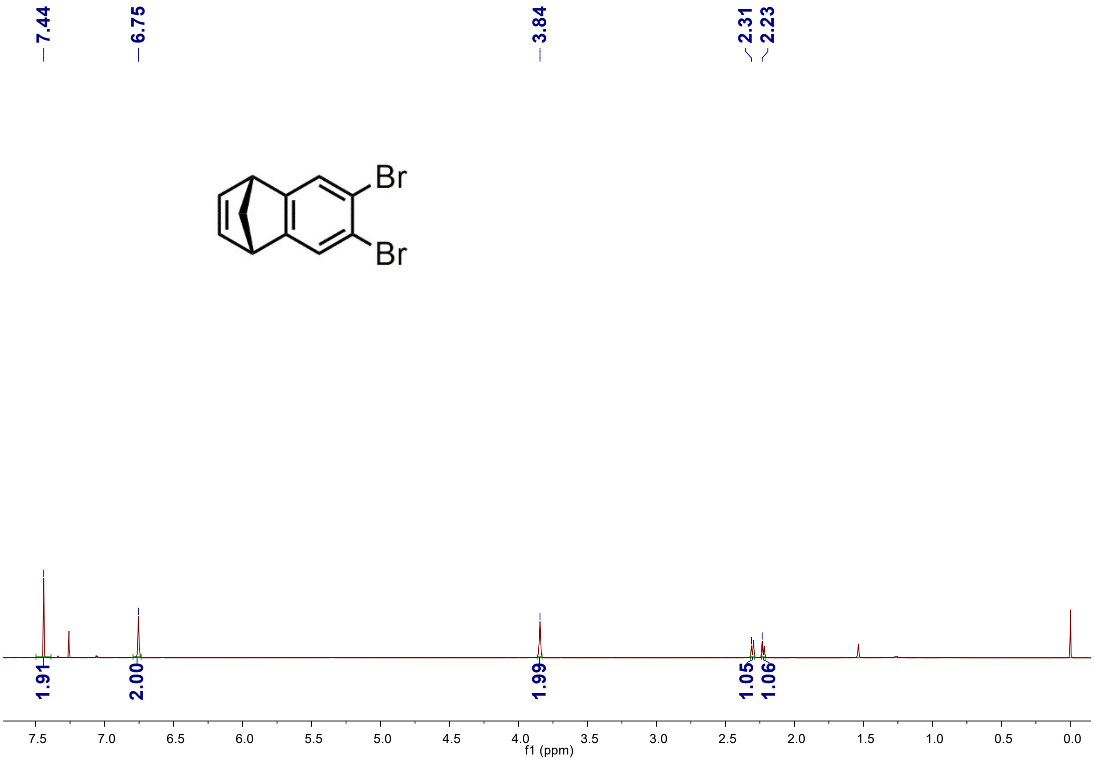


Figure S9. ^{1}H NMR spectrum of **1** in $CDCl_3$.

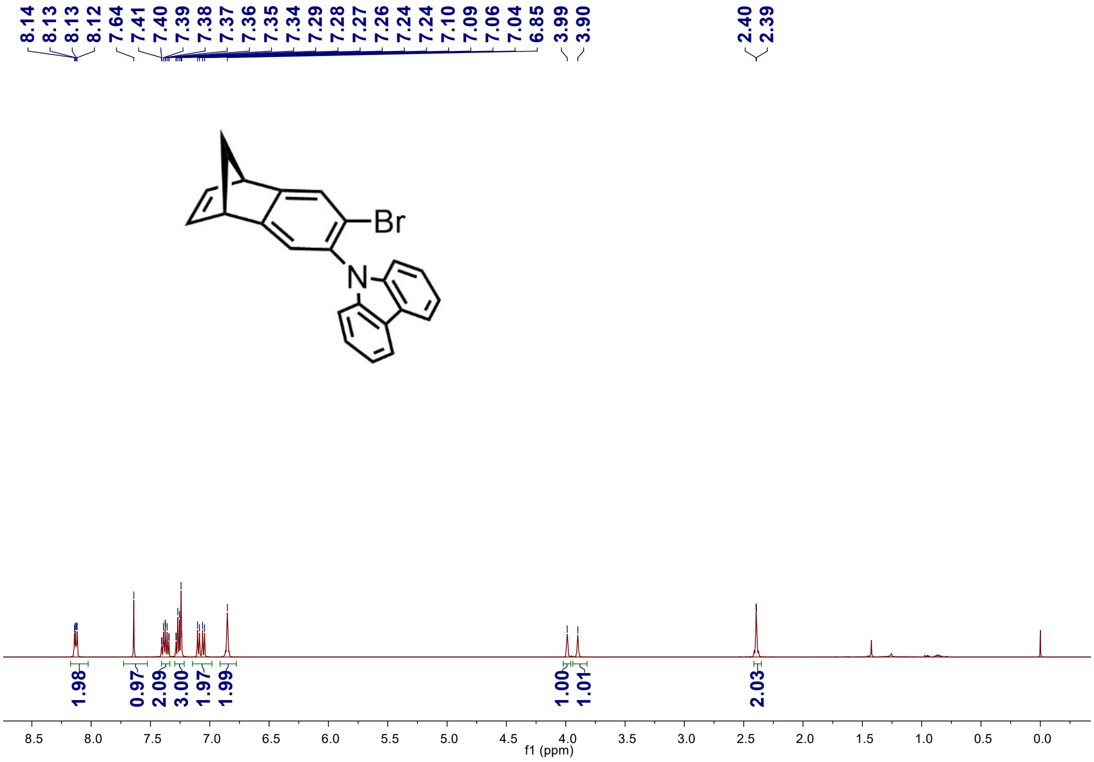


Figure S10. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

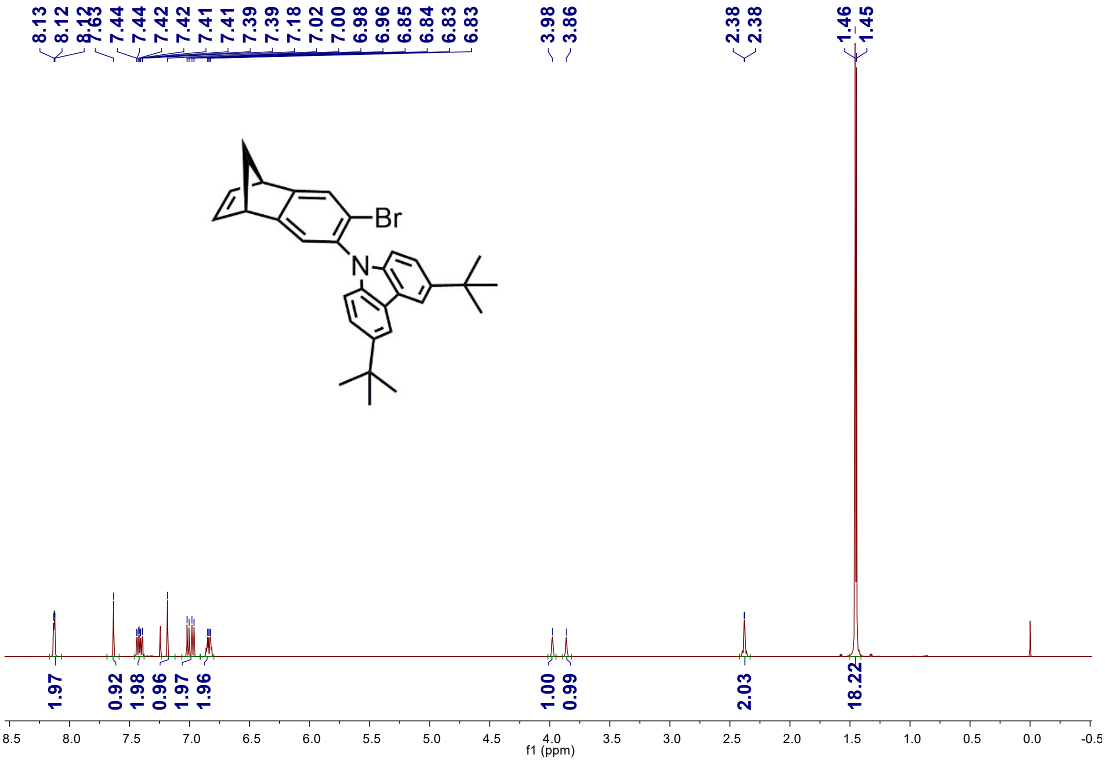


Figure S11. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

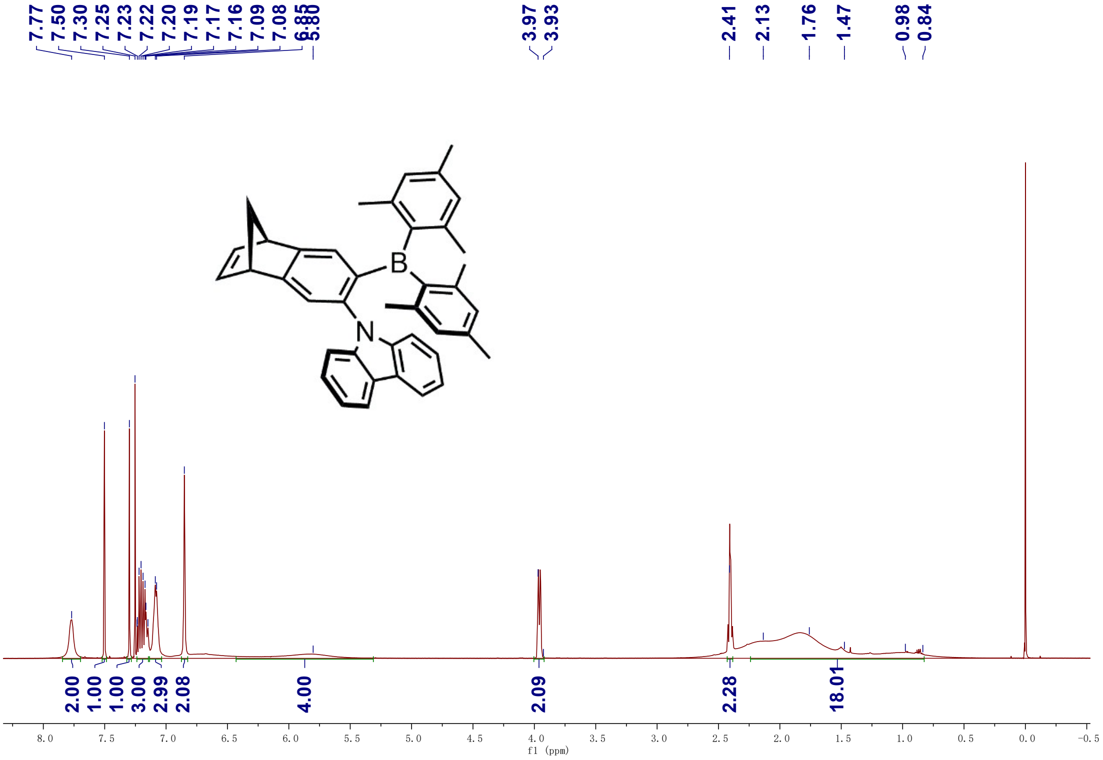


Figure S12. ^{1}H NMR spectrum of **BNB-CzoB** in $CDCl_3$.

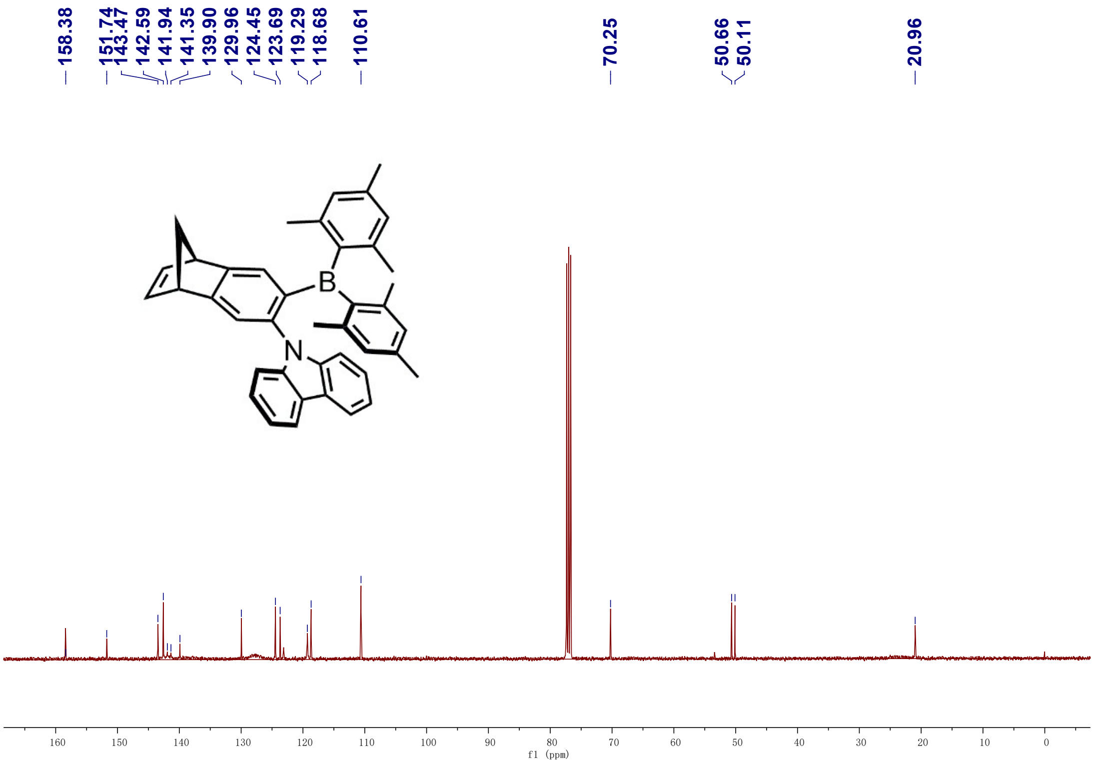


Figure S13. ^{13}C NMR spectrum of **BNB-CzoB** in $CDCl_3$.

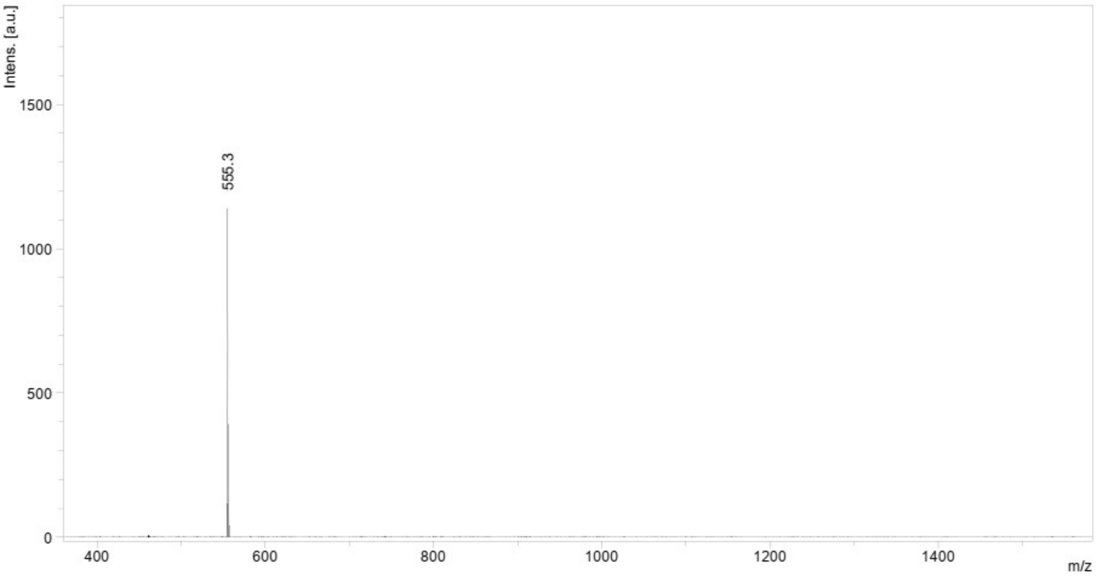


Figure S14. Mass spectrometric spectrum of **BNB-CzoB**.

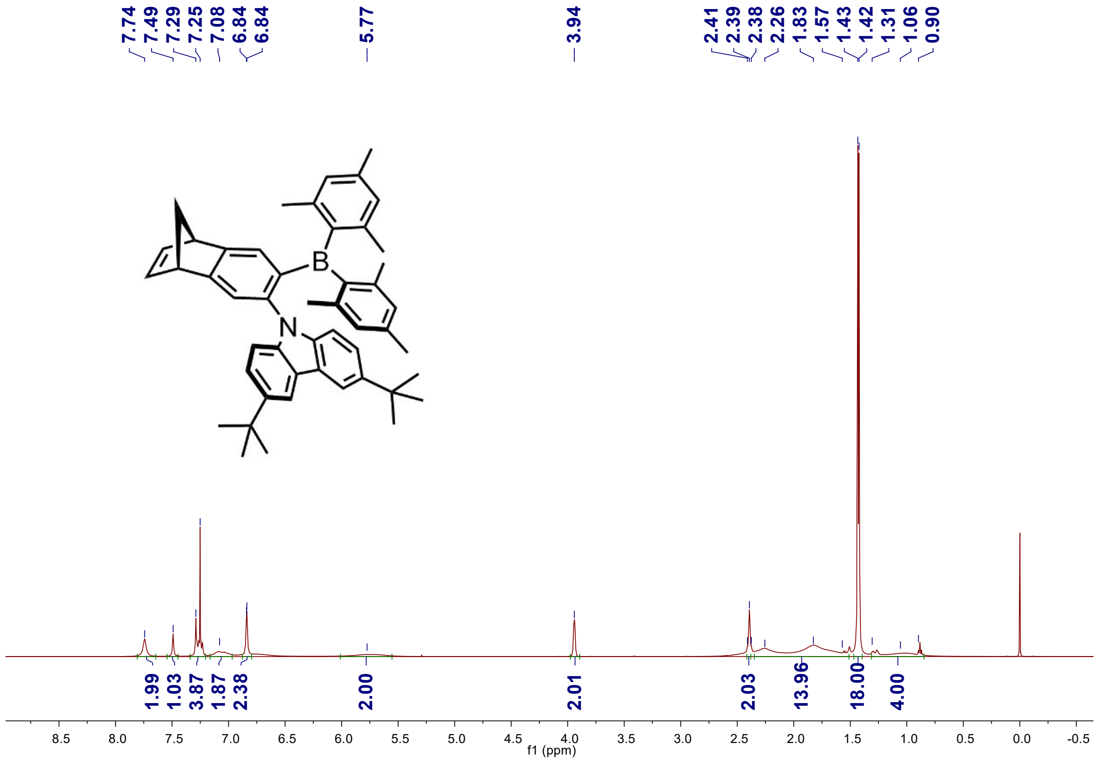


Figure S15. ^{1}H NMR spectrum of **BNB-*t*BuCzoB** in $CDCl_3$.

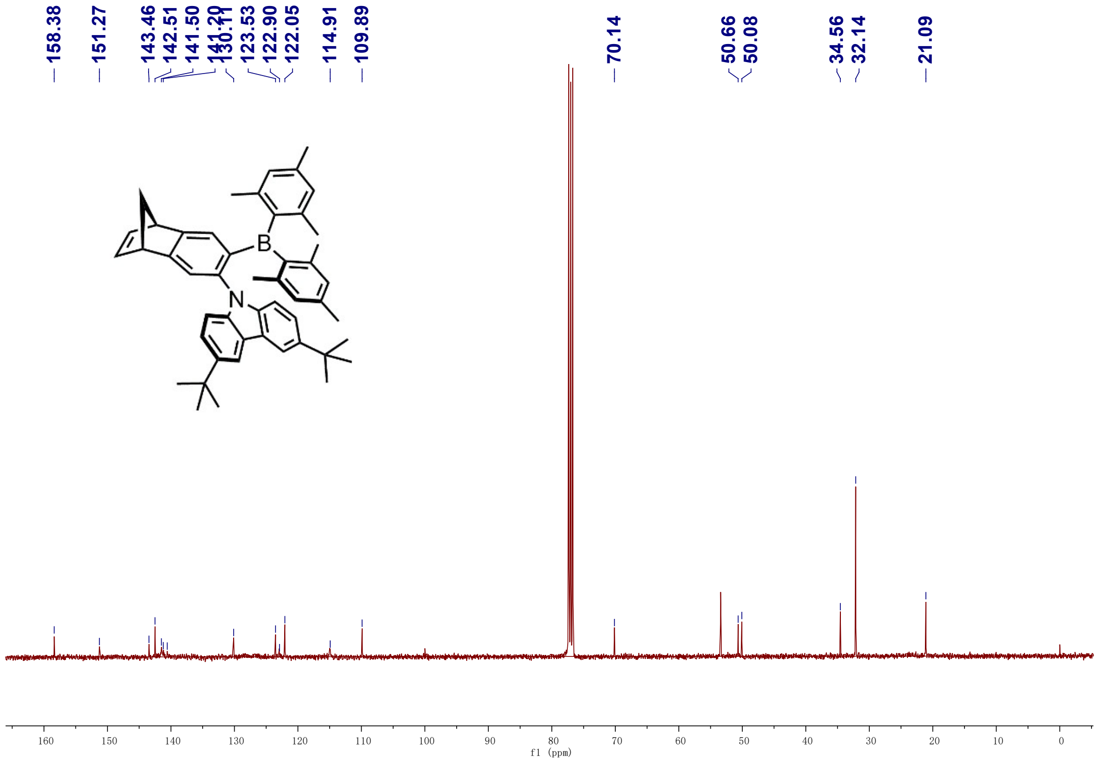


Figure S16. ^{13}C NMR spectrum of **BNB-*t*BuCzoB** in $CDCl_3$.

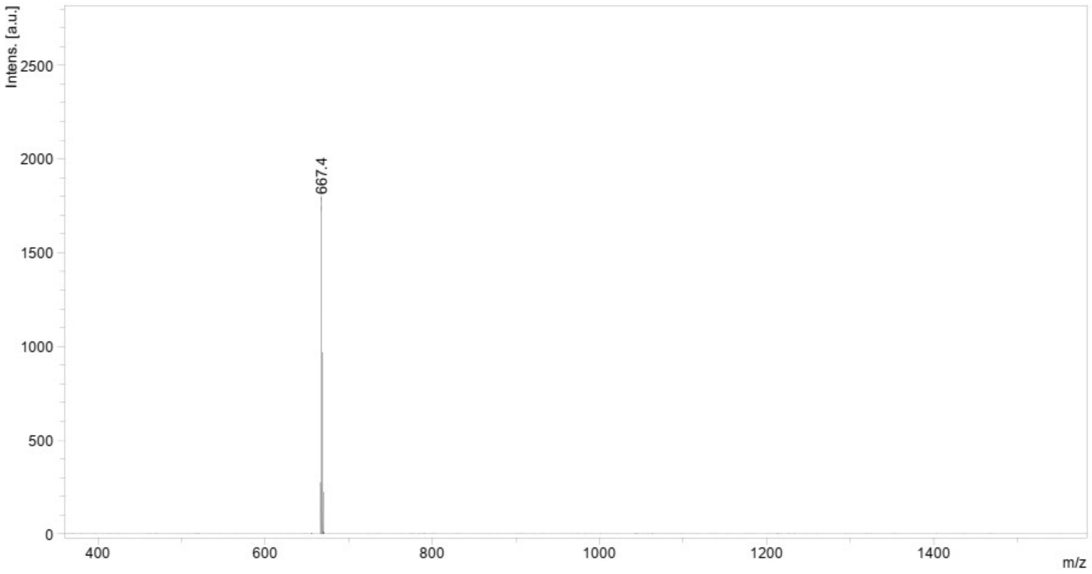


Figure S17. Mass spectrometric spectrum of **BNB-*t*BuCzoB**.

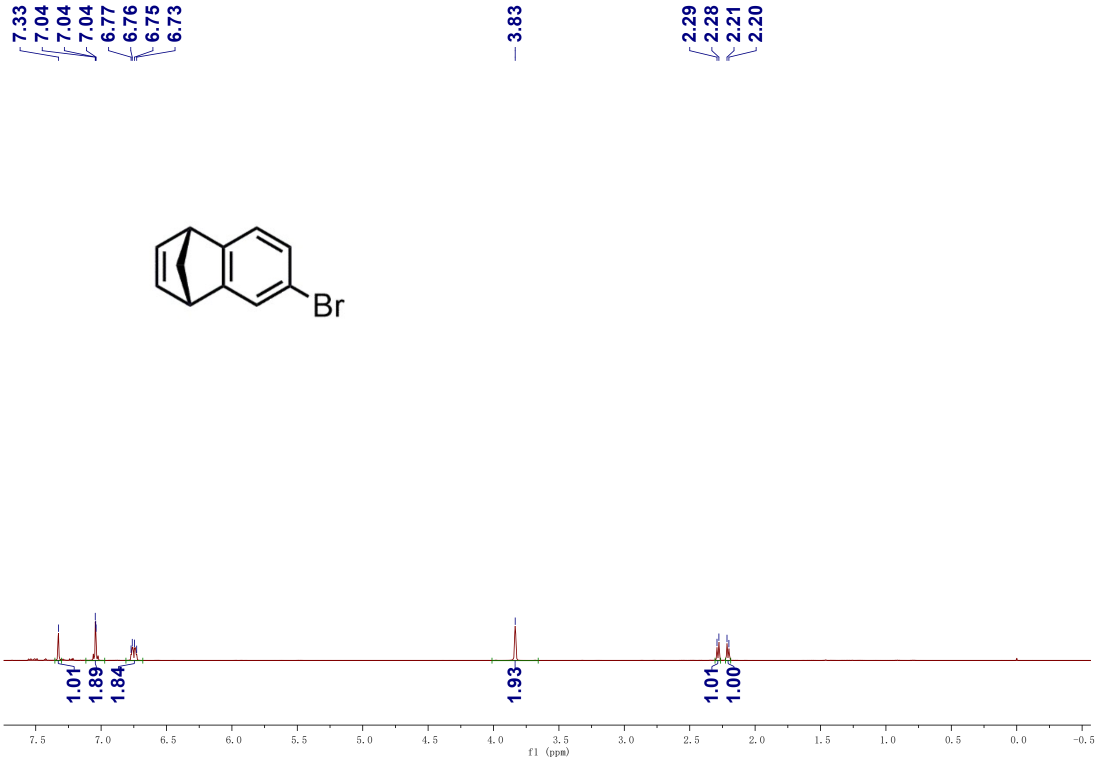


Figure S18. ^{1}H NMR spectrum of **3** in $CDCl_3$.

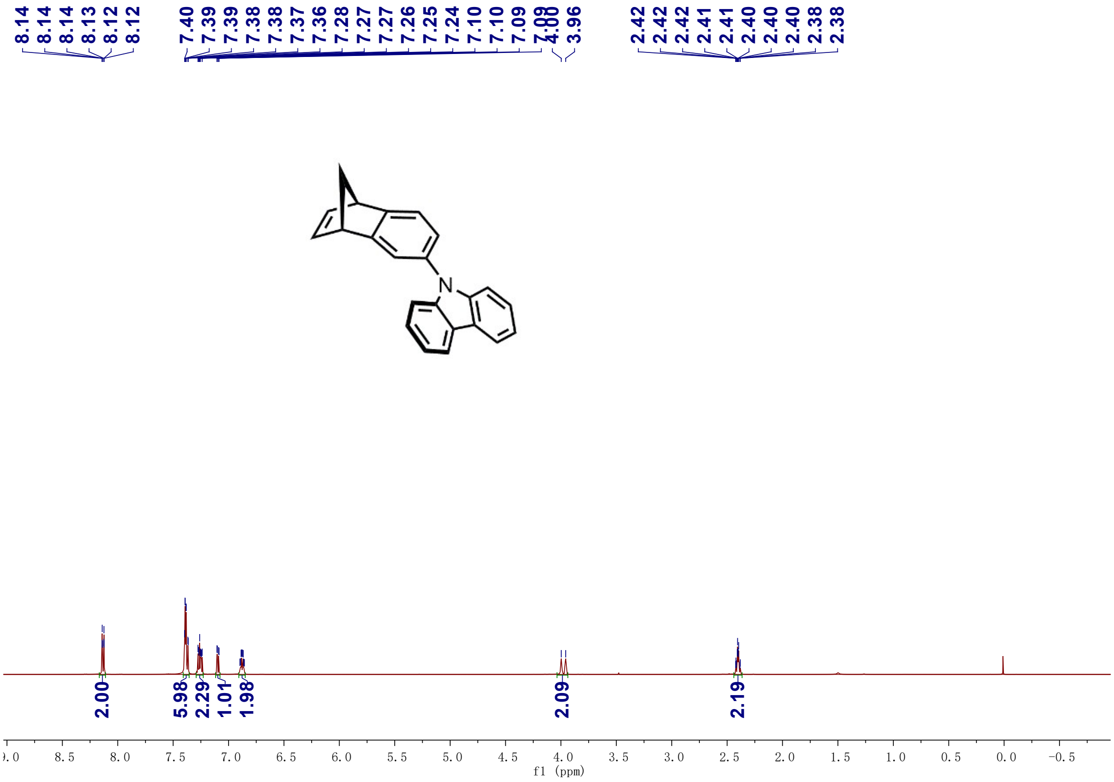


Figure S19. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

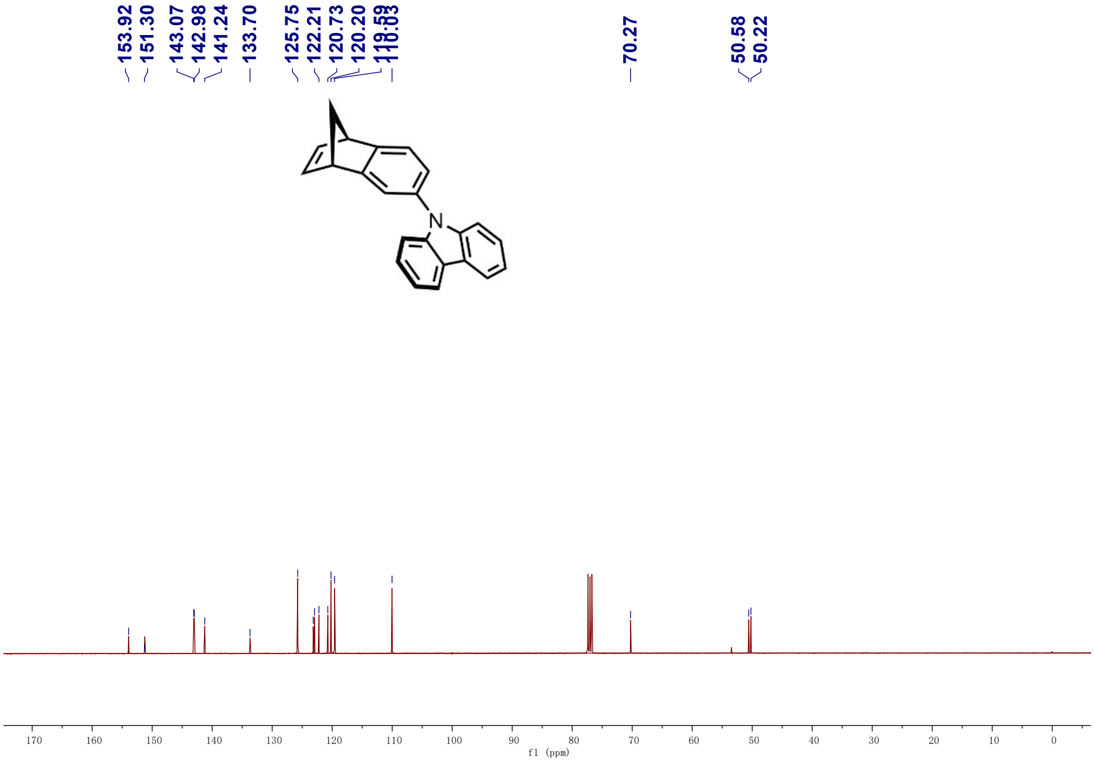


Figure S20. ^{13}C NMR spectrum of **4a** in $CDCl_3$.

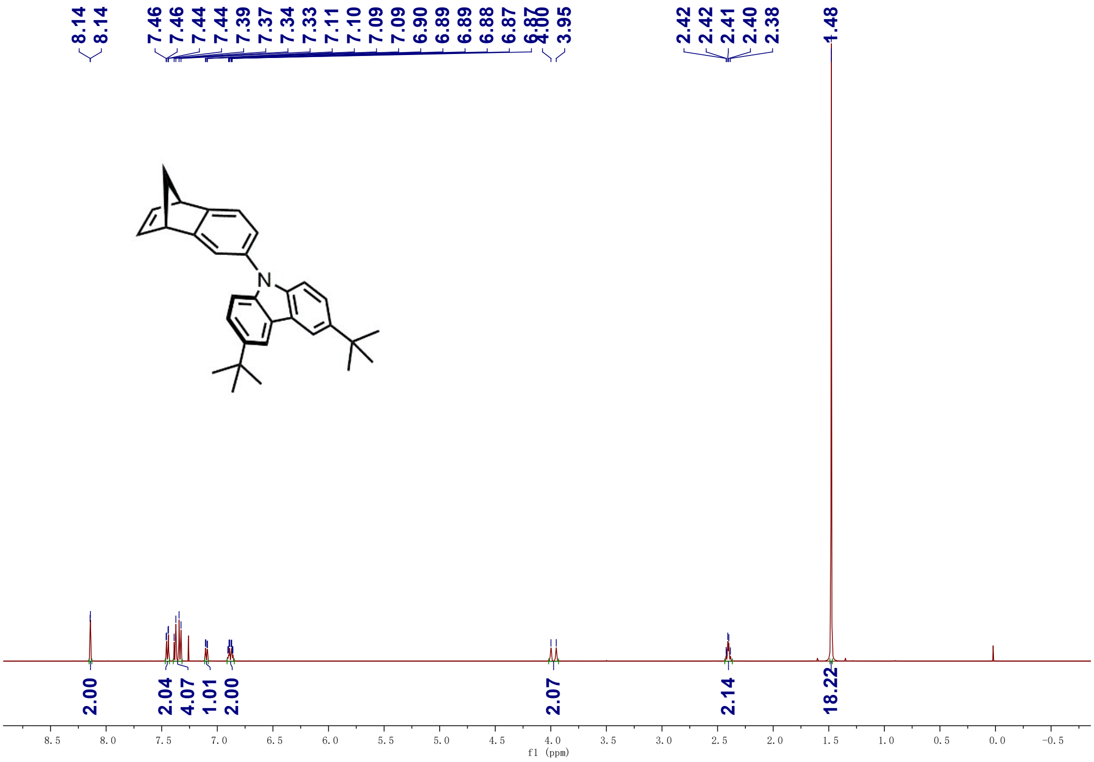


Figure S21. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

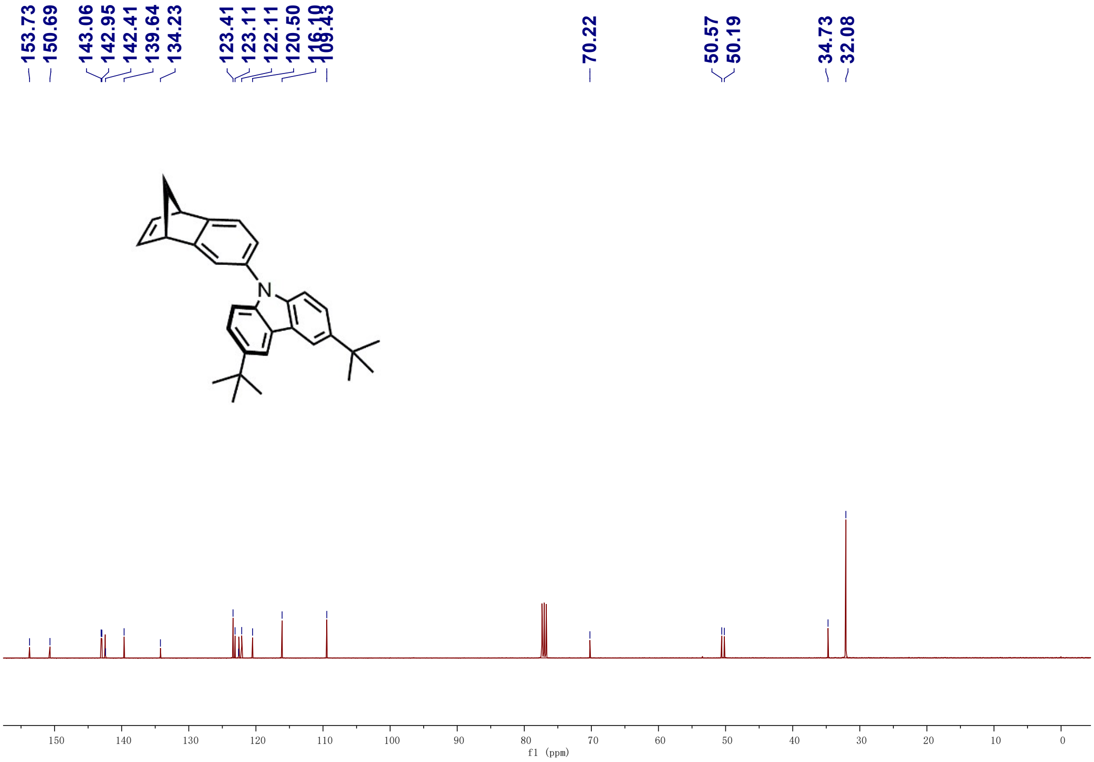


Figure S22. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

References.

1 T. Lu, F. Chen, *J. Comput. Chem.* 2012, **33**, 580-592.

2 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* 2010, **132**, 6498-6506.

3 N. Ikeda, S. Oda, R. Matsumoto, M. Yoshioka, D. Fukushima, K. Yoshiura, N. Yasuda, T. Hatakeyama, *Adv. Mater.* 2020, **32**, 2004072.

4 S. Shao, *CSD Commun.* 2024, DOI: 10.5517/ccdc.csd.cc2lxngn.