ADVANCED
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Supporting Information

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Supporting Information For *Advanced Functional Material*

Molecular glass constructed by 9,9′-spirobifluorene and peripheral carbazole: A spin-coated small molecular materials for deep blue OLED

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Experimental

Materials.

Fluorene, 1,6-dibromo-hexane, $FeCl_3$, carbazole, *N*-bromosuccinimide (NBS) and $Pd(PPh_3)_4$ were purchased from Aldrich and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried and purified by fractional distillation over sodium/benzophenone. Column chromatography was performed using silica gel (200-300 mesh).

Instrumentation.

The ^{1}H NMR and spectra were recorded on AVANCZ 500 spectrometers at 298K by utilizing deuterated chloroform ($CDCl_3$) or Dimethyl Sulphoxide (DMSO) as solvent and tetramethylsilane (TMS) as standard. The compounds were characterized by Flash EA 1112, CHNS-O elemental analysis instrument. The LC/TOF/MS mass spectra were recorded using an APPLIED BIOSYSTEMS QSTAR instrument. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The differential scanning calorimeter (DSC) analysis was determined using a NETZSCH (DSC-204) instrument at 10 °C /min under nitrogen flushing. The powder x-ray diffraction was detected with a Rigaku x-ray diffractometer (D/max r A, using Cu Kα radiation of wavelength 1.542 Å). Cyclic voltammetry (CV) were performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk (Φ=3mm) as working electrode, platinum wire as auxiliary electrode, with porous ceramic wick, Ag/Ag^+ as reference electrode, standardized for the redox couple ferricinium / ferrocene. Cyclic voltammetric studies were carried out containing 0.1M [*n*-NBu_4][BF_4] dried in an oil pump vacuum at 80 °C as supporting electrolyte. All solutions were purged with nitrogen stream for 10 min before measurement. The procedure was performed at room temperature and nitrogen atmosphere was maintained over the solution during measurements.

LEDs Fabrication and Measurement.

The typical device configuration fabricated by spin-coating was the ITO/PEDOT;PSS/TCPC-6, TCPC-4 and Mod II/Ba/Al. The indium–tin-oxide (ITO)-coated glass with a sheet resistance of <50 $\Omega\ \square^{-1}$ was used as substrate. Pre-treatment of ITO included a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The PEDOT:PSS (polyethylene dioxythiophene/polystyrene sulfonate) layer was deposited onto ITO-coated substrate as the buffer layer. The TCPC-6, TCPC-4 and Mod II film was formed on PEDOT:PSS layer by spin-coating its chloroform solutions with concentration of 7 mg/ml,5 mg/ml and 5 mg/ml respectively. The cathode Ba was deposited by thermo-evaporation and followed by a thick Al capping layer. The electroluminescent (EL) spectra and Commission Internationale De L´Eclairage (CIE) coordination of these devices were measured by a PR650 spectroscan spectrometer. The luminance-current density-voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.

2-bromofluorene ***(1)***. A mixture of fluorene (5g, 30mmol) and $FeCl_3$ (0.26g, 4.4mmol) was dissolved in anhydrous N,N-dimethylformide (50ml). An *N*-bromosuccinimide (9g, 50mmol) in N, N-dimethylformide (50ml) was added dropwise to the reaction flask at room temperature in darkness. The reaction mixture was stirred at room temperature for 24 hours, the resulting solution was treated with HCl (0.1 M, 10ml) and neutralized with $NaHCO_3$, and then it was extracted with chloroform for several times. After filtration and solvent evaporation, the residual solid was recrystallized in hexane to give a white crystal solid (yield 80%). ^1H NMR (500 MHz, $CDCl_3$): δ7.766-7.751 (d, 1H, Ar-H), δ7.682 (s, 1H, Ar-H), δ7.650-7.634 (d, 1H, Ar-H), δ7.546-7.531 (d, 1H, Ar-H), δ7.510-7.491 (d, 2H, Ar-H), δ7.398-7.368 (t, 1H, Ar-H), δ7.342-7.310 (t, 1H, Ar-H), δ3.890 (s, 2H, Ar-CH_2-Ar). MS (m/z) 244.2. Anal. Calcd for $C_{13}H_9Br$: C, 63.70; H, 3.70 Found: C, 63.59; H, 3.76.

N-(6-bromohexane)-carbazole ***(2-C6)***. The carbazole (10g, 59.8mmol) and 1,6-dibromo-hexane (9.48ml, 61.4mmol) in THF (100ml) was added to NaH, which has been disposed by dry petroleum ether. Then the mixture was stirred at room temperature for 24h and then the residual solid of NaH was filtrated. After the solvent was removed by rotary evaporation, the solid was purified by column chromatography (silica gel, hexane/CH_2Cl_2). Recrystallization from ethanol afforded a white solid (yield 45%). ^1H NMR (500 MHz, $CDCl_3$): δ8.11-8.09 (d, 2H, Ar-H), δ7.47-7.45 (t, 2H, Ar-H), δ7.40-7.39 (d, 2H, Ar-H), δ7.23-7.21 (t, 2H, Ar-H), δ4.31-4.30 (t, 2H, N-CH_2), δ3.36-3.35 (t, 2H, Br-H), δ1.92-1.86 (m, 2H, CH_2), δ1.84-1.78 (m, 2H, CH_2), δ1.49-1.44 (m, 2H, CH_2), δ1.42-1.38 (m, 2H, CH_2). Anal. Calcd for $C_{18}H_{20}NBr$: C, 65.46; H, 6.10; N, 4.24 Found: C, 65.44; H, 6.10; N, 4.12.

N-(4-bromobutane)-carbazole ***(2-C4)***. The procedure was followed to prepare 2-C6 from carbazole (5g, 30mmol) and 1,4-dibromo-butane (3.58ml, 30.3mmol), and purified with column chromatography using petroleum ether/CH_2Cl_2 as the eluent to afford a white solid (yield 35%). ^1H NMR (500 MHz, $CDCl_3$): δ8.14-8.13 (d, 2H, Ar-H), δ7.62-7.60 (d, 2H, Ar-H), δ7.45-7.42 (t, 2H, Ar-H), δ7.19-7.17 (t, 2H, Ar-H), δ4.42-4.40 (t, 2H, N-CH_2), δ3.56-3.55 (t, 2H, Br-H), δ1.88-1.78 (m, 4H, CH_2). Anal. Calcd for $C_{16}H_{16}NBr$: C, 63.59; H, 5.34; N, 4.63 Found: C, 63.55; H, 5.33; N, 4.55.

9,9´-bis(N-carbazolyl-hexyl)-2-bromofluorene ***(3-C6)***. After 1 (0.7g, 2.8mmol) in THF (20ml) was added to NaH and refluxed for 15min, the solution of 2-6C (2.03g, 6.15mmol) in THF (60ml) was added slowly to the mixture and refluxed for 48h. After the mixture was cooled to room temperature, it was filtrated the residual solid of NaH. The solvent was removed by rotary evaporation and the solid was purified by column chromatography (silica gel, hexane/CH_2Cl_2). Recrystallization from hexane afforded white solid (yield 95%). ^{1}H NMR (500 MHz, DMSO): δ8.12-8.10 (d, 4H, Ar-H-car), δ7.76-7.75 (d, 1H, Ar-H-flu), δ7.72-7.71 (d, 1H, Ar-H-flu), δ7.57 (s, 1H, Ar-H-flu), δ7.48-7.47 (d, 4H, Ar-H-car), δ7.42-7.39 (t, 4H, Ar-H-car), δ7.28-7.25 (m, 4H, Ar-H-flu), δ7.18-7.15 (t, 4H, Ar-H-car), δ4.26-4.23 (m, 4H, N-CH_2), δ1.83-1.82 (m, 4H, CH_2), δ1.53-1.52 (m, 4H, CH_2), δ1.01 (m, 8H, CH_2), δ0.40-0.38 (m, 4H, CH_2). Anal. Calcd for $C_{49}H_{47}N_2Br$: C, 79.12; H, 6.37; N, 3.77 Found: C, 79.13; H, 6.32; N, 3.18.

9,9′-bis(N-carbazolyl-butyl)-2-bromofluorene ***(3-C4)***. The procedure was followed to prepare 3-C6 from 1 (0.7g, 2.8mmol) and 2-4C (1.73g, 5.73mmol), and purified with column chromatography using petroleum ether/CH_2Cl_2 as the eluent to afford a white solid (yield 69%). ^{1}H NMR (500 MHz, DMSO): δ8.11-8.09 (d, 4H, Ar-H-car), δ7.76-7.75 (d, 1H, Ar-H-flu), δ7.72-7.70 (d, 1H, Ar-H-flu), δ7.59 (s, 1H, Ar-H-flu), δ7.49-7.47 (d, 4H, Ar-H-flu), δ7.41-7.38 (t, 8H, Ar-H-car), δ7.29-7.27 (m, 2H, Ar-H-flu), δ7.25-7.24 (d, 1H, Ar-H-flu), δ7.17-7.15 (t, 4H, Ar-H-car), δ4.13-4.12 (m, 4H, N-CH_2), δ1.99-1.98 (m, 4H, CH_2), δ1.48-1.47 (m, 4H, CH_2), δ0.63-0.62 (m, 4H, CH_2). Anal. Calcd for $C_{45}H_{39}N_2Br$: C, 78.59; H, 5.72; N, 4.07 Found: C, 78.61; H, 5.69; N, 3.98.

The Characterization of TCPC-4.

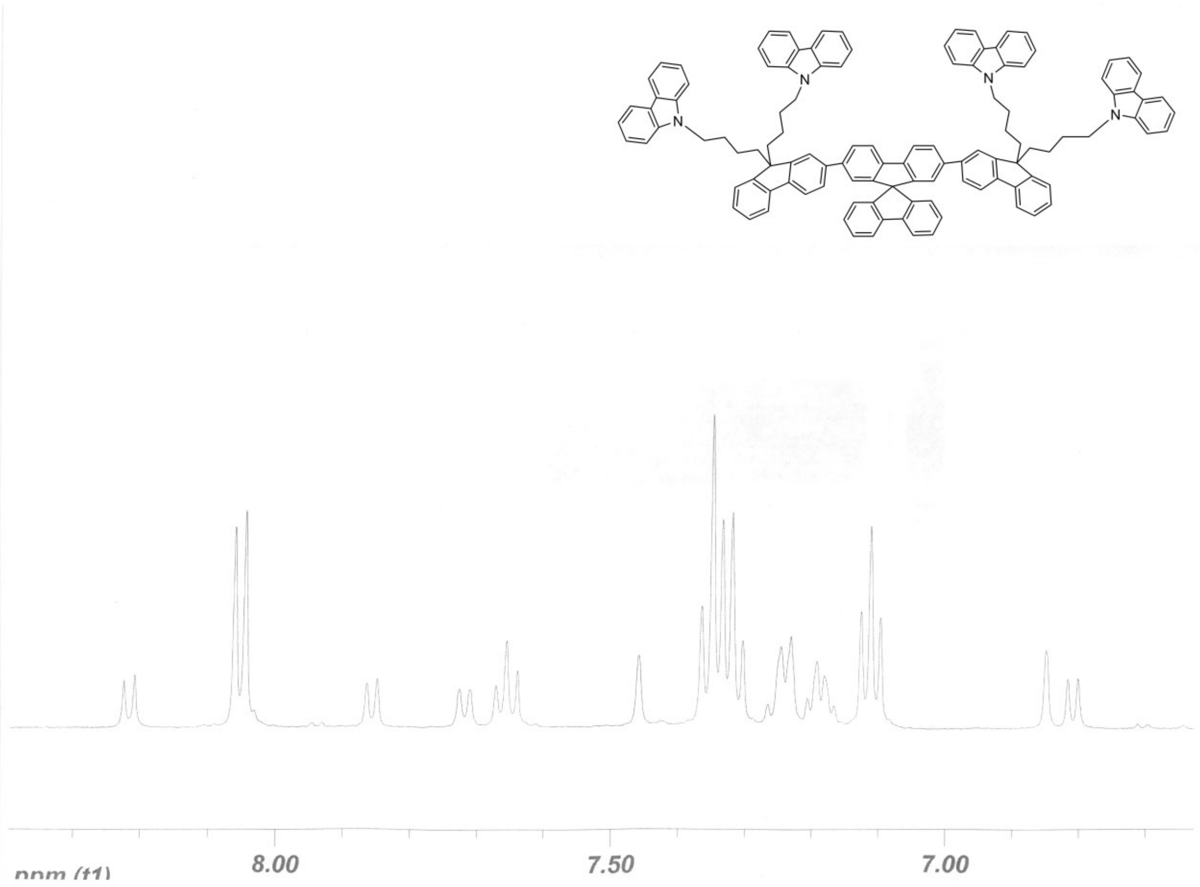


Figure S1 The ^{1}H NMR spectra in aromatic range of **TCPC-4**.

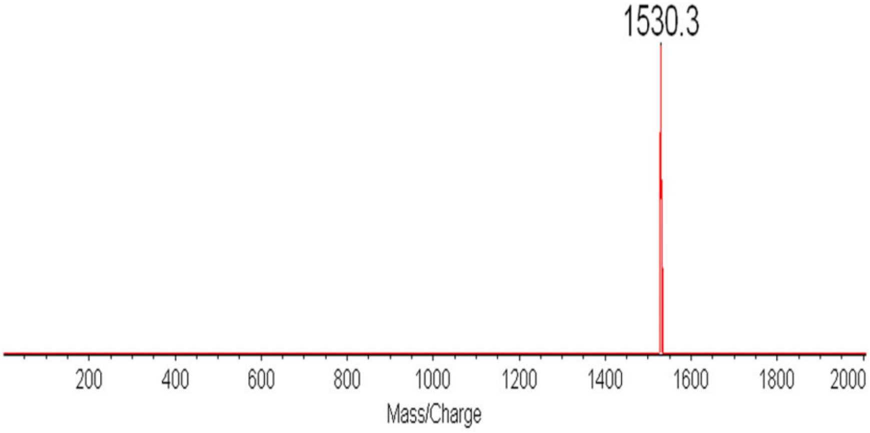
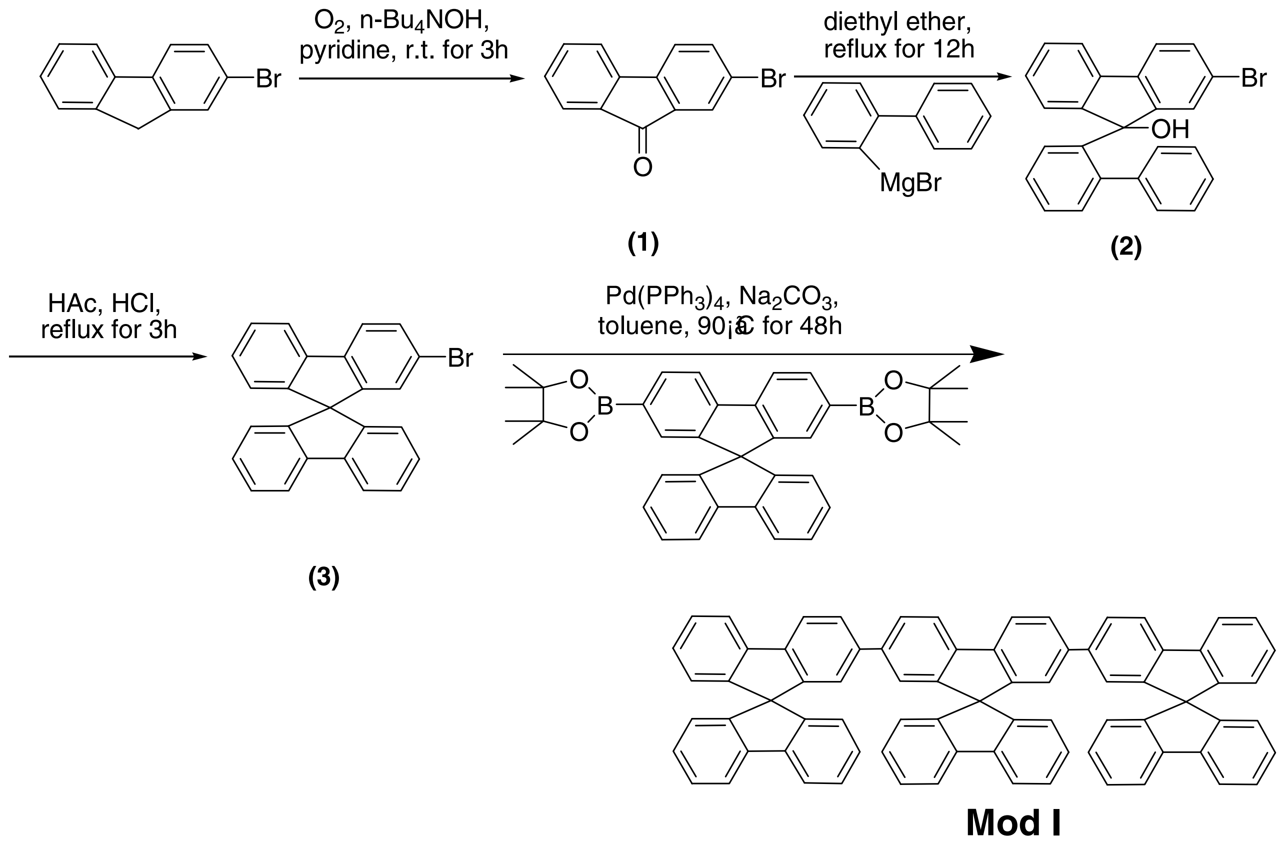


Figure S2 The time-of-fly mass spectrum of **TCPC-4**.

The Synthesis of Mod I and Mod II.

Scheme S1. The route of synthesis of **Mod I**.



2-bromofluorenone ***(1).*** A solution of 2-bromofluorene (1.2g, 4.9mmol) and tetrabutylamonium hydroxide in methanol (0.2ml) in pyridine (15ml) was vigorously stirred at room temperature while a stream of oxygen was passed the stirred liquid until a great deal of solid appeared. The mixture was poured into water and then filtrated, to give yellow solid (yield 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.77 (s, 1H, Ar-H), δ7.67-7.66 (d, 1H, Ar-H), δ7.63-7.60 (d, 1H, Ar-H), δ7.52-7.51 (m, 2H, Ar-H), δ7.41-7.40 (d, 1H, Ar-H), δ7.35-7.31 (m, 1H, Ar-H). MS (m/z) 258.0. Anal. Calcd for $C_{13}H_7BrO$: C, 60.26; H, 2.72 Found: C, 59.88; H, 2.80.

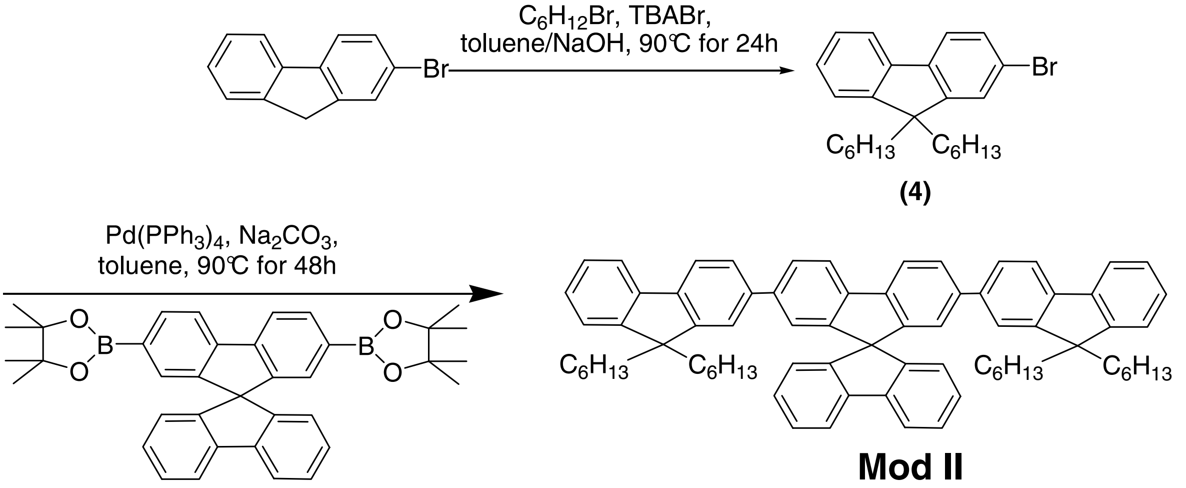
2-bromo-9-(2′-biphenyl)-9′-fluorenol ***(2).*** A solution of 2-bromobiphenyl (0.82ml, 5mmol) in 20 ml dry diethyl ether was added to the magnesium (108mg, 4.5ml) and a little of iodine to initiate the Grignard reaction. After the reaction initiated, the solution was added dropwise in such a way that the solution gently refluxed, and the reaction mixture was refluxed for 2h until magnesium complete disappeared. Afterward, solid of **(1)** (1.03g, 4mmol) was added to the Grignard solution by several times and mixture was refluxed overnight. After the mixture was cooled to room temperature, solution was removed. The solid was stirred into saturated ammonium chloride solution for 2h. Then was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the yellow solid was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2) to white solid (yield 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.54 (t, 1H, Ar-H), δ7.47-7.46 (t, 1H, Ar-H), 7.34-7.32 (m, 2H, Ar-H), δ7.31-7.29 (t, 1H, Ar-H), δ7.21-7.20 (m, 3H, Ar-H), δ7.14-7.13 (m, 1H, Ar-H), δ7.00 (m, 2H, Ar-H), δ6.99-6.91 (d, 1H, Ar-H), δ6.84-6.82 (t, 1H, Ar-H), δ6.70-6.86 (m, 1H, Ar-H), δ6.60-6.57 (m, 1H, Ar-H), δ6.13-6.08 (d, 1H, Ar-H), δ5.95-5.94 (d, 1H, Ar-H). MS (m/z) 412.3. Anal. Calcd for $C_{25}H_{17}BrO$: C, 72.65; H, 4.15 Found: C, 71.90; H, 4.13.

2-bromo-9,9′-spirofluorene (3). **(2)** (0.7g, 1.7mmol) was dissolved in boiling acetic acid (12ml), and several drops of concentrated hydrochloric acid were added. The mixture was refluxed at 130 °C for 3h. After the mixture was cooled to room temperature, some water added to the resulting solution and white solid appeared at once. The precipitate was collected and dried in a vacuum to afford white solid (yield 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ7.85-7.84 (d, 2H, Ar-H), δ7.81-7.80 (d, 1H, Ar-H), δ7.71-7.69 (d, 1H, Ar-H), δ7.50-7.47 (d, 1H, Ar-H), δ7.40-7.35 (m, 3H, Ar-H), δ7.14-7.11 (t, 3H, Ar-H), 6.84 (s, 1H, Ar-H), δ6.73-6.71 (m, 3H, Ar-H). MS (m/z) 394.3. Anal. Calcd for $C_{25}H_{15}Br$: C, 75.96; H, 3.82 Found: C, 75.09; H, 3.78.

Mod I. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene (170.4mg, 0.3mmol) and **(3)** (237.2mg, 0.6mmol) were added to the Na_2CO_3 (2.0 M/L) and toluene (toluene/water was at a 3:2 ratio), and $Pd(PPh_3)_4$ acted as catalyst. After the reaction mixture was stirred at 90 °C for 2 day under a nitrogen atmosphere, some water was added to the resulting solution and then the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified by column chromatography on silica gel (silica gel, petroleum ether/CH_2Cl_2) to afford white solid (yield 55%). ^{1}H NMR (500 MHz,

$CDCl_3$): δ7.83-7.81 (d, 6H, Ar-H), δ7.78-7.76 (d, 2H, Ar-H), δ7.72-7.70 (d, 2H, Ar-H), δ7.68-7.66 (d, 2H, Ar-H), δ7.35-7.30 (m, 12H, Ar-H), δ7.08-7.03 (m, 8H, Ar-H), δ6.82 (s, 2H, Ar-H), δ6.77 (s, 2H, Ar-H), δ6.70-6.69 (m, 6H, Ar-H), δ6.65-6.63 (d, 2H, Ar-H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 149.6, 149.3, 149.1, 148.7, 148.6, 141.8, 141.2, 141.0, 140.9, 140.8, 140.5, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.1, 124.2, 124.1, 123.9, 122.6, 122.5, 120.0, 119.9, 66.1. TOF-MS $(M+H)^+$ 944.9 (100%).

Scheme S2. The route of synthesis of **Mod II**.



2-bromo-9,9'-dihexanelyfluorene ***(4).*** 2-bromofluorene (1 g, 4.08 mmol), 1-bromo-hexane (1.7 ml, 12 mmol), TBABr (0.129 g, 0.4 mmol) and NaOH (0.48 mL, 50% W/W) were mixed in a 100 mL round-bottomed flask under a nitrogen atmosphere. The mixture was heated at 90 °C for 24 hours. After the mixture was cooled to room temperature, some water was added to the resulting solution and then it was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the yellow liquid was purified by column chromatography (silica gel, cyclohexane) to afford colorless oil (yield 41 %). ^1H NMR (500 MHz, $CDCl_3$): δ7.670-7.651 (m, 1H, ArH), δ7.560-7.542 (d, 1H, ArH), δ7.469 (s, 1H, ArH), δ7.336-7.275 (m, 4H, ArH), δ1.95-1.92 (m, 4H, CH_2), δ1.12-1.09 (m, 4H, CH_2), δ1.04-1.03 (m, 8H, CH_2), δ0.78-0.75 (m, 6H, CH_3), δ0.59-0.57 (m, 4H, CH_2). MS (m/z) 414.2.

Mod II. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene (94mg, 0.165mmol) and **(4)** (150mg, 0.364mmol) were added to the Na_2CO_3 (2.0 M/L) and toluene (toluene/water was at a 3:2 ratio), and $Pd(PPh_3)_4$ acted as catalyst. After the reaction mixture was stirred at 90 °C for 2 day under a nitrogen atmosphere, some water was added to the resulting solution and then the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified by column chromatography on silica gel (silica gel, petroleum ether/CH_2Cl_2) to afford white solid (yield 50%). ^1H NMR (500 MHz, $CDCl_3$): δ7.97-7.95 (d, 2H, Ar-H), δ7.91-7.90 (d, 2H, Ar-H), δ7.70-7.69 (d, 2H, Ar-H), δ7.65-7.64 (d, 2H, Ar-H), δ7.60-7.59 (d, 2H, Ar-H), δ7.43-7.41 (m, 4H, Ar-H), δ7.35-7.33 (d, 2H, Ar-H), δ7.31-7.28 (t, 6H, Ar-H), δ7.19-7.16 (t, 2H, Ar-H), δ7.00 (s, 2H, Ar-H), δ6.90-6.89 (d, 2H, Ar-H), δ1.95-1.92 (m, 8H, CH_2), δ1.09-0.99 (m, 24H, CH_2), δ0.74-0.72 (m, 12H, CH_3), δ0.61-0.58 (m, 8H, CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): δ151.3, 150.0, 149.9, 148.8, 141.9, 141.5, 140.7, 140.6, 140.3, 139.8, 127.9, 127.8, 127.2, 126.9, 126.7, 126.0, 124.3, 122.8, 122.5, 121.2, 120.2, 120.1, 119.6, 55.1, 40.3, 31.3, 29.6, 22.7, 22.5, 14.0. TOF-MS $(M+H)^+$ 981.1 (100%).

The Characterization of Mod I and Mod II.

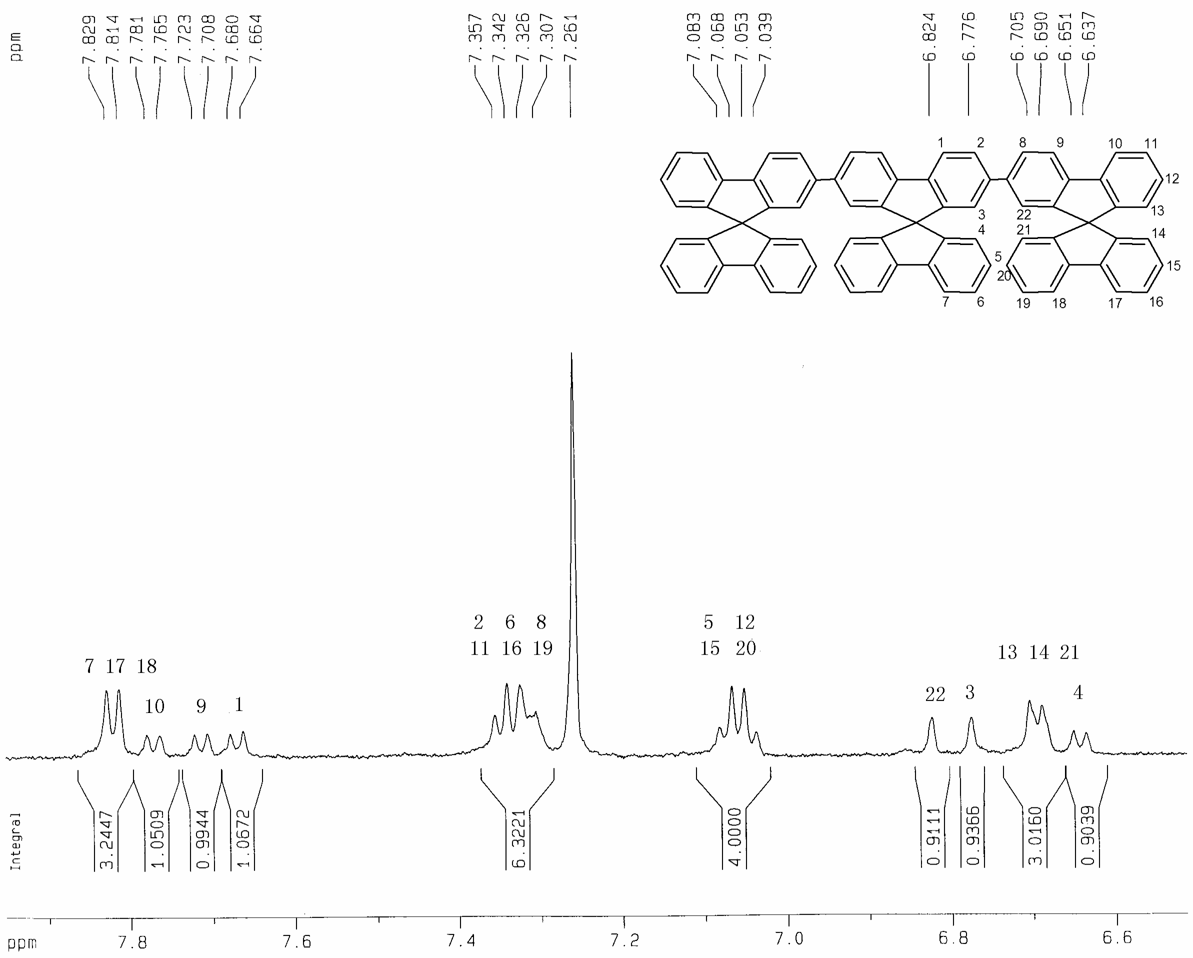


Figure S3 The ^{1}H NMR spectra in aromatic range of **Mod I**.

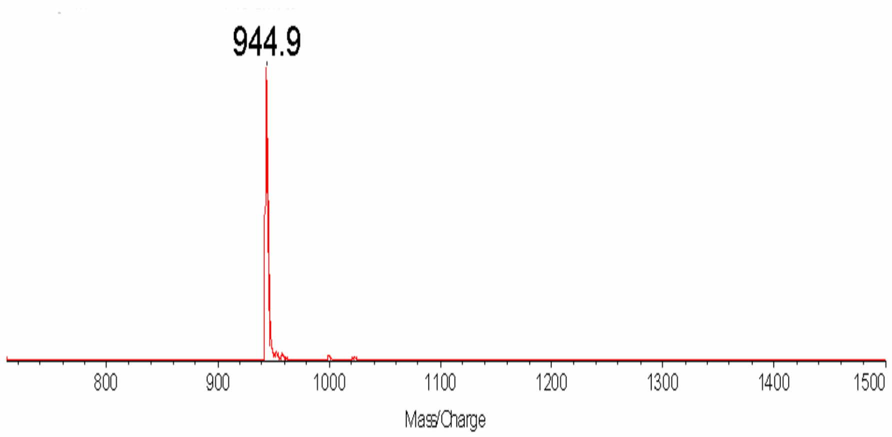


Figure S4 The time-of-fly mass spectrum of **Mod I**.

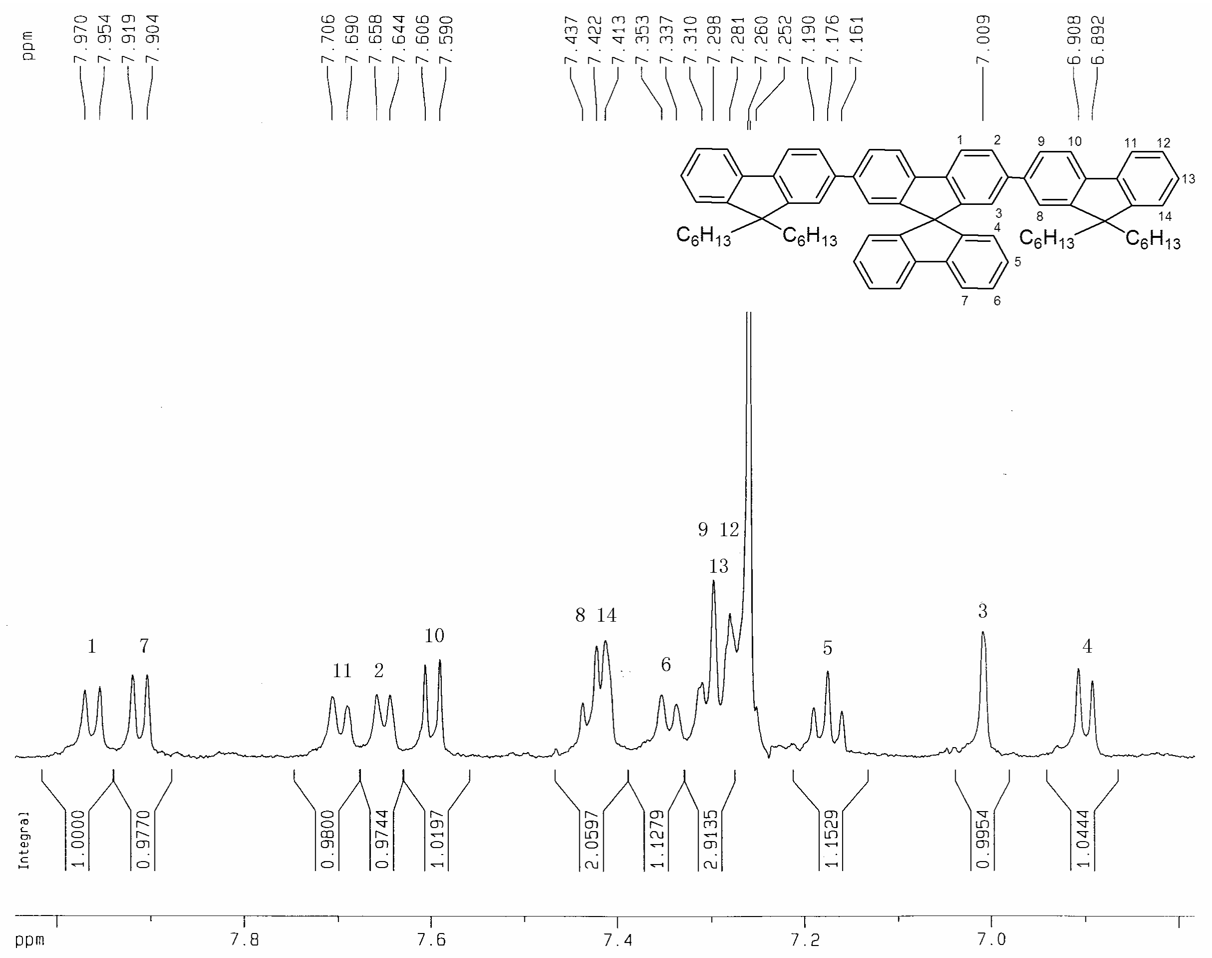


Figure S5 The ^{1}H NMR spectra in aromatic range of **Mod II**.

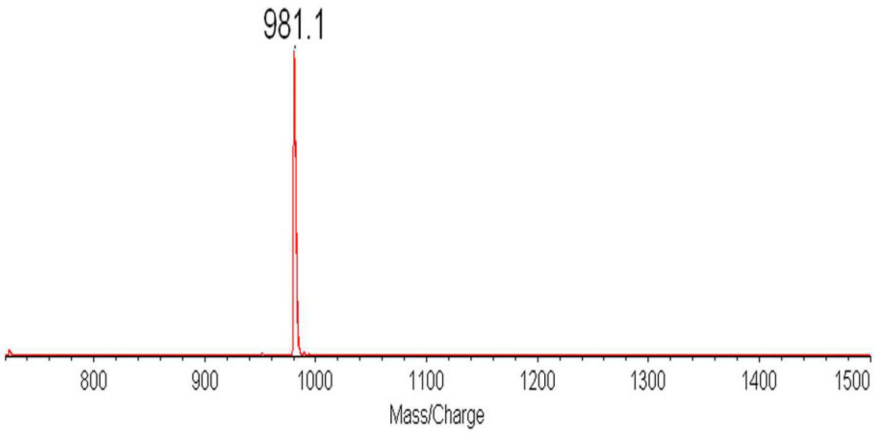


Figure S6 The time-of-fly mass spectrum of **Mod II**.