

Ladder-type Conjugated Oligomers Prepared by Scholl Oxidative Cyclodehydrogenation Reaction: Synthesis, Characterization and Application in Field Effect Transistor

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S1. Materials

Unless otherwise stated, all of reagents and chemicals used were purchased from Aldrich or Sinopham Chemical Reagent Company. Toluene and tetrahydrofuran (THF) were distilled with sodium wires and benzophenone added under nitrogen (N_2) immediately prior to use, and N,N-dimethylformamide (DMF) used without purification was of high pressure liquid chromatography grade.

S2. Measurements and Characterization

1H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE III HD 400 MHz. FT-NMR spectrometer in deuterated dichloromethane (CD_2Cl_2) and chloroform ($CDCl_3$). Chemical shifts are in ppm units using tetramethylsilane (TMS; $\delta=0$) as an internal standard. Gel permeation chromatography (GPC) measurements were recorded on an Agilent/Wyatt 1260 gel permeation chromatograph. The calibration was managed by employing commercially available Polystyrene. Differential scanning calorimetry (DSC) measurements were carried out on a TA Q2000 differential scanning calorimeter with one heat-cool cycle from 0 °C to 300 °C at a rate of 10 °C/min under a constant N_2 flow. Thermal gravimetric analysis (TGA) measurements were done on a Perkin Elmer Pyris 1 thermo gravimetric analyzer heating from 50 to 650 °C with a warming rate of 10 °C/min, under dry N_2 flow. Cyclic voltammetry was operated on a T30/FRA2 electrochemical workstation. Using ferrocene (4.8 eV under vacuum) as the internal standard, the measurements of the products films coated on a glassy carbon electrode (~ 0.08 cm 2) were performed in an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile at a scan rate of 100mV/s at room temperature under the protection of N_2 . The reference electrode was an Ag/AgNO $_3$ electrode and a platinum wire was applied as the counter electrode. A Perkin-Elmer Lambda 750 UV-visible spectrophotometer was employed for UV spectra in THF solution. The infrared spectra were measured with KBr pellets on a Thermofisher Nicolet 6700 Fourier transformation infrared (FT-IR) spectrometer, where the percentage of transmittance or absorbance vs the wave number (in cm $^{-1}$) was plotted. Photoluminescence spectra (PL) were performed in THF solvent on a Photo Technology International, Inc. QM40 fluorescence lifetime spectrometers at room temperature. The PL quantum yields (Φ_F) were estimated using fluorescein ($\Phi_F = 92$ % in 0.1 M NaOH) or quinine sulfate ($\Phi_F = 54$ % in 0.1 M H $_2$ SO $_4$) or as standards. And the PL lifetimes were recorded on the same QM40 spectrometers by means of a time - corrected single photon counting system at room temperature. The samples were analyzed by AB SCIEX 5800 matrix assisted laser desorption ionization-time of flight mass spectrometer (MALDI-TOF). Elemental analysis was performed on VARIO EL3 instrument (ELEMENTAR, Germany). X-ray crystallographic data were collected on a P4 Bruker diffractometer equipped with a Bruker SMART μ K CCD area detector (employing the program SMART) and a rotating anode utilizing graphite-monochromatic $M_o K_{\alpha}$ radiation ($\lambda = 0.71073$ Å). Data processing was carried out by use of the

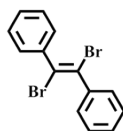
program SAINT, while the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. The structures were resolved by using the direct-methods procedure in the Bruker SHELXL program library and refined by full-matrix least-squares methods on F2. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

S3. FET device fabrication

Some commercially available highly p-doped SiO₂ (300 nm)/Si wafers were washed by acetone and methanol, H₂O₂/H₂SO₄ and deionized water in turn. The conjugated oligomers in THF solution (1 mg/mL) were spin-coated on these clean SiO₂/Si wafers at the rotating speed of 6000 r/min. The thin films as the semiconductor were thermal annealing at 150 °C in a vacuum environment. The 50 nm thick gold source and drain electrodes (the typical channel length and width are both 1000 μm) were vapor-deposited on the oligomer thin film. A kind of ion gel, the mixture of a triblock co-oligomer, poly(styrene-block-methyl methacrylate-block styrene) (PS-PMMA-PS; M_{PS} = 4.3 kg/mol, M_{PMMA} = 12.5 kg/mol, M_W = 21.1 kg/mol), and an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in an ethyl propionate solution, were used as the top gate dielectrics. The weight ratio of the solvent, ionic liquid and the oligomer was maintained at 20:9.3:0.7. The prepared ionic solution was drop-casted to cover the surfaces of oligomer film and the drain and source electrodes. Then the transistor channels were covered with a thin Al foil (thickness of 0.03 mm) to form the top-gate electrode. Finally, a thin gold wire was inserted into the gel films, between the channel and top gate metal, as the reference electrode.

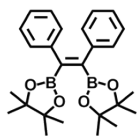
S4. Synthesis Procedures

Synthesis of the monomers: (*E*)-1,2-dibromo-1,2-diphenylethene (**1**)



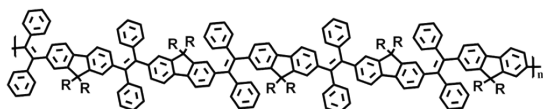
A solution of diphenyl acetylene (9 g, 0.050 mol) in 400 mL carbon tetrachloride (CCl₄) was in a flask, and the liquid bromine in CCl₄ (40 mL) was dropped in the flask slowly at -12 °C kept by ice brine bath. The saturated aqueous solution of Na₂SO₃ was added in the solution to wash the resulting mixture after 1h reaction. A recrystallization in dichloromethane (CH₂Cl₂) after removing the water. Finally, a white crystal obtained was monomer **1**. (9.84 g, 58%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.49 (m, 4H), 7.46 – 7.40 (m, 4H), 7.39 – 7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.77, 128.39, 118.07; elemental analysis calcd (%) for C₁₄H₁₀Br₂ (338.04): C 49.74; H 2.98; Found: C 49.54, H 3.01.

(Z)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenylethene (2)



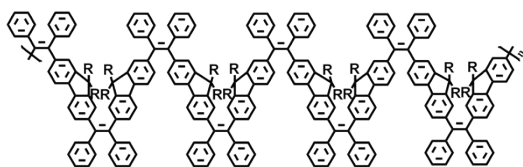
A 100-mL flask, equipped with a magnetic stirring bar, septum inlet, and a reflux condenser, was charged with tetrakis(triphenylphosphine)platinum (Pt(PPh₃)₄) (1 mol%) and bis(pinacolato)diboron (12.03 g, 47.24 mmol) and then flushed with N₂. DMF (75 mL) and diphenylacetylene (7.64 g, 43.72 mmol) were successively added. After being stirred for 24 h at 90 °C, the reaction mixture was extracted with CH₂Cl₂, repeatedly washed with cold water to remove DMF (7 times), and finally dried over anhydrous magnesium sulfate. Kugelrohr distillation (0.15 mm Hg) gave the monomer **2** (12.76 g, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 – 7.04 (m, 4H), 7.03 – 7.00 (s, 2H), 6.94 (m, 4H), 1.32 (s, 24H); ¹³C NMR (100 MHz, CDCl₃) δ 129.30, 127.40, 125.76, 84.05, 24.88, 24.59; MS (MALDI-TOF): m/z (%): 455.2165 (100) [M+Na]⁺; elemental analysis calcd (%) for C₂₆H₃₄B₂O₄ (432.17): C 72.26, H 7.93; Found: C 72.37, H 7.84.

Synthesis of the linear type oligomer: (E)-poly(2,7-(1,2-diphenylethene)-9,9-dioctylfluorene) (L-PDPF)



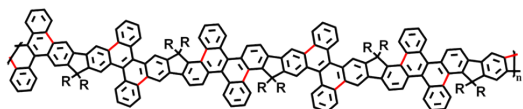
A round-bottomed flask equipped with a magnetic stir bar was charged with 200 mL dry toluene, 2M K₂CO₃ (70 mL), 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (5.10 g, 9.13 mmol), **1** (2.73 g, 8.07 mmol) and a catalytic amount of tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (1.0 mol %) under argon atmosphere. The reaction was at 95 °C for 5 days avoiding light. The product was extracted with toluene and concentrated on a rotavap, a yellow solid was obtained. And the residue was dissolved in a minimal amount of THF and then precipitated into methanol. Then the unreacted monomers, impurities and catalyst were removed by Soxhlet extraction with acetone. The obtained product was yellow green solid (3.50 g, 44.7%). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.95 – 7.60 (m, 6H), 7.60 – 7.31 (m, 6H), 7.30 – 7.01 (m, 4H), 2.22 – 1.86 (m, 4H), 1.41 – 0.87 (m, 24H), 0.83 – 0.78 (m, 6H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 152.27, 126.51, 121.93, 120.37, 32.20, 30.41, 29.63, 24.38, 23.01, 14.24. FT-IR (KBr, cm⁻¹): 3060, 3029, 3008 (Ar-H); 2950, 2926, 2853 (-C-H); 1608 (C=C); 1458, 1412 (CH₂); 1329 (CH₃); 757, 719, 696 (Ar-H); elemental analysis calcd (%) for C₄₃H₅₀ (566.93): C 91.18, H 8.82; Found: C 91.42, H 8.58.

Synthesis of the zigzag type oligomer: (Z)-poly(2,7-(1,2-diphenylethene)-9,9-dioctylfluorene) (Z-PDPF)



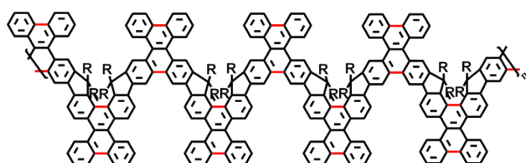
A flask equipped with a magnetic stir bar was charged with 100 mL dry toluene, 2M K_2CO_3 (30 mL), 2,7-dibromo-9,9-dioctylfluorene (5.85 g, 10.67 mmol), **2** (4.61 g, 10.67 mmol) and a catalytic amount of $Pd(PPh_3)_4$ (1.0 mol %) under argon atmosphere. The reaction was at 95 °C for 5 days avoiding light. The product was extracted with toluene and concentrated on a rotavap, a yellow solid was obtained. And the residue was dissolved in a minimum amount of THF and then precipitated into methanol. Then the unreacted monomers, impurities and catalyst were removed by Soxhlet extraction with acetone. The final product was yellow solid (5.41 g, 52%). 1H NMR (400 MHz, CD_2Cl_2) δ 7.45 – 7.34 (m, 2H), 7.33 – 7.20 (m, 2H), 7.13 – 7.01 (m, 12H), 1.88 – 1.59 (m, 4H), 1.30 – 0.98 (m, 24H), 0.88 – 0.84 (m, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 144.54, 140.89, 139.30, 131.56, 127.43, 40.13, 29.29, 24.44, 22.71, 14.01, 13.94, 13.91. FT-IR (KBr, cm^{-1}): 3079, 3056, 3023 (Ar-H); 2925, 2853 (-C-H); 1596(C=C); 1465, 1443 (CH_2); 1377, 1350 (CH_3); 772, 726, 698 (Ar-H); elemental analysis calcd (%) for $C_{43}H_{50}$ (566.93): C 91.18, H 8.82; Found: C 91.36, H 8.64..

Oxidation of *L*-PDPF (*L*-PDPF-O)



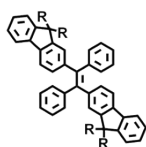
A 25 mL nitromethane solution of $FeCl_3$ (6 g) was added dropwise to a solution of **L-PDPF** (2.05 g) in 50 mL CH_2Cl_2 . The mixture was stirred at room temperature overnight under argon protection. Then the reaction was quenched with methanol and the resulting mixture was washed for several times with methanol. The organic layer was picked up and rotary evaporated to get an orange solid **L-PDPF-O** (1.25 g, 61%). 1H NMR (400 MHz, CD_2Cl_2) δ 1.88 – 1.73 (m, 4H), 1.40 – 0.89 (m, 24H), 0.87 – 0.82 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 144.82, 137.24, 128.54, 125.34, 108.39, 30.11, 29.50, 28.14, 24.33, 24.16, 22.57, 21.70, 21.13, 21.10; FT-IR (KBr, cm^{-1}): 2955, 2924, 2852 (-C-H); 1653 (C=C); 1458 (CH_2); 1377 (CH_3); elemental analysis calcd (%) for $C_{43}H_{46}$ (562.96): C 91.83, H 8.17; Found: C 91.58, H 8.42.

Oxidation of *Z*-PDPF (*Z*-PDPF-O)



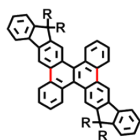
The same concentration nitromethane solution of FeCl_3 as above was added dropwise to a solution of **Z-PDPF** (2.52 g) in 50 mL CH_2Cl_2 . The mixture was stirred at room temperature overnight under argon protection. Then the reaction was quenched with methanol and the resulting mixture was washed for several times with methanol. The organic layer was collected and rotary evaporated to obtain a red solid **Z-PDPF-O** (1.41 g, 55%). ^1H NMR (400 MHz, CD_2Cl_2) δ 2.36 – 1.97 (m, 4H), 1.32 – 1.03 (m, 24H), 0.90 – 0.82 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 129.81, 125.38, 30.05, 29.30, 29.22, 29.17, 29.13, 27.15, 25.50, 24.61, 22.68, 20.80, 13.87. FT-IR (KBr, cm^{-1}): 2956, 2923, 2851 (-C-H); 1641 (C=C); 1462 (CH_2); 1377 (CH_3). elemental analysis calcd (%) for $\text{C}_{43}\text{H}_{46}$ (562.96): C 91.83, H 8.17; Found: C 91.91, H 8.09

Synthesis of the model molecule for L-PDPF: (*E*)-1,2-diphenylethene-1,2-bis(9,9-dioctyl-9H-fluoren-2-yl) (**L-DPBF**)



A round-bottom flask was charged with 8.00 g 2-boric acid-9,9-dioctylfluorene the obtained from Aldrich, **1** (3.00 g) and an appropriate amount of $\text{Pd}(\text{PPh}_3)_4$ (1.0 mol %). Then 60 mL dry THF and 20 mL 3M KOH solution were added in the flask under argon atmosphere. The reaction mixture was stirred at 80 °C avoiding light for 3 days. The product was extracted with toluene and most of the solvent was concentrated on a rotavap. Column chromatography of the product over silica gel with petroleum ether as eluent to obtain **L-DPBF** (5.20 g, 47%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.63 – 7.54 (m, 2H), 7.44 (m, 2H), 7.30 – 7.22 (m, 6H), 7.17 – 7.09 (m, 6H), 7.08 – 6.98 (m, 8H), 1.85 – 1.69 (m, 8H), 1.35 – 0.91 (m, 48H), 0.88 – 0.82 (m, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 150.98, 150.05, 143.13, 131.52, 131.39, 127.48, 31.85, 29.98, 29.96, 29.33, 29.29, 29.27, 23.80, 23.61, 22.65, 22.63, 13.87; MS (MALDI-TOF): m/z (%): 956.5812 (100) $[\text{M}^+]$; elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{92}$ (957.50): C 90.32, H 9.68; Found: C 90.37, H 9.63.

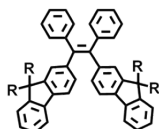
Oxidation of L-DPBF (**L-DPBF-O**)



A 25 mL nitromethane solution of FeCl_3 (6 g) was added dropwise to a solution of **L-DPBF** (2.56 g) in 50 mL CH_2Cl_2 at room temperature by stirred overnight, then the reaction was quenched by the addition of methanol. The reaction mixture was washed with methanol for many times and concentrated on a rotavap to obtain **L-DPBF-O** (1.02 g, 40%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.20 – 8.08 (d, 2H), 7.97 – 8.08 (m, 16H), 7.07 – 6.95 (s, 2H), 1.71 – 1.18

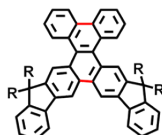
(m, 68H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 131.61, 130.04, 127.93, 108.39, 32.18, 30.24, 30.11, 29.53, 29.51, 24.33, 24.25, 22.99, 14.23; MS (MALDI-TOF): m/z (%): 952.5186 (100) $[\text{M}^+]$; elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{88}$ (953.47): C 90.70, H 9.30; Found: C 90.85, H 9.15.

Synthesis of the model molecule for Z-PDPF: (*Z*)-1,2-diphenylethene-1,2-bis(9,9-dioctyl-9H-fluoren-2-yl) (*Z*-DPBF)



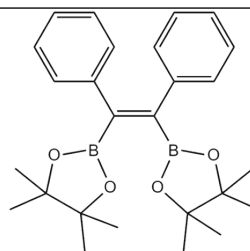
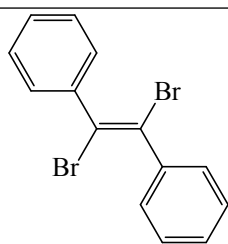
A round-bottomed 50 mL flask was charged with the compound **2** (3.64 g 8.43 mmol), 2-bromo-9,9-dioctylfluorene (11.86 g, 25.29mmol) and the catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (1.0 mol %). Then 10 mL dry toluene and 2.5 mL 2M K_2CO_3 solution was added in the flask under argon atmosphere. The reaction mixture was stirred at 80 °C avoiding light for 3 days. The product was extracted with toluene and the solvent was concentrated on a rotavap. Column chromatography of the product over silica gel with petroleum ether as eluent to obtain **Z-DPBF** (4.7 g, 30%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.63 – 7.54 (m, 2H), 7.50 – 7.41 (m, 2H), 7.29 – 7.21 (m, 6H), 7.13 – 7.08 (m, 6H), 7.08 – 6.98 (m, 8H), 1.82 – 1.63 (m, 8H), 1.31 – 0.89 (m, 48H), 0.87 – 0.82 (m, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 150.98, 150.05, 144.49, 143.13, 140.95, 140.86, 139.45, 127.49, 126.64, 126.28, 118.75, 109.99, 40.19, 31.86, 22.64, 13.89, 13.88, 13.87; MS (MALDI-TOF): m/z (%): 956.7587 (100) $[\text{M}^+]$; elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{92}$ (957.50): C 90.32, H 9.68; Found: C 90.43, H 9.57.

Oxidation of Z-DPBF (Z-DPBF-O)



A 25 mL nitromethane solution of FeCl_3 (6 g) was added dropwise to a solution of **Z-DPBF** (2.35 g) in 50 mL CH_2Cl_2 at room temperature by stirred overnight, then the reaction was quenched by the addition of methanol. The reaction mixture was washed with methanol for many times and concentrated on a rotavap to obtain the oxide **Z-DPBF-O** (1.46 g, 62%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.16 – 8.09 (m, 2H), 7.82 – 7.07 (m, 12H), 7.06 – 6.96 (m, 4H), 6.66 – 6.54 (m, 2H), 1.34 – 1.28 (m, 68H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 129.82, 129.61, 125.38, 30.05, 29.67, 29.50, 29.35, 29.30, 29.22, 27.15, 24.61, 22.68, 20.80, 13.87; MS (MALDI-TOF): m/z (%): 952.7182 (100) $[\text{M}^+]$; elemental analysis calcd (%) for $\text{C}_{72}\text{H}_{88}$ (953.47): C 90.70, H 9.30; Found: C 90.54, H 9.46.

Table S1. Summary of crystal data and reflection collection parameters for compounds **1** and **2**.



Empirical formula	$C_{14}H_{10}Br_2$	$C_{26}H_{34}B_2O_4$
Formula weight	338.04	432.15
Crystal size, mm	0.19 x 0.17 x 0.15	0.23 x 0.15 x 0.12
Crystal system	Monoclinic	Monoclinic, P2(1)/c
space group	P2(1)/c	P2(1)/c
a, Å	5.6911(19)	15.526(5)
b, Å	17.259(6)	6.539(5)
c, Å	7.0675(16)	25.120(5)
a, deg	90	90
β , deg	117.647(19)	90.019(10)
γ , deg	90	90
V , Å ³	614.9(3)	2550(2)
Z	2	4
Calculated density, Mg/m ³	1.826	1.126
F(000)	328	928
Temperature, K	293(2)	296(2)
Wavelength, Å	0.71073	0.71073
μ (Mo Ka), mm ⁻¹	6.559	0.073
$2\theta_{max}$, deg (Completeness)	49.96(99.5 %)	25.00(97.1 %)
no. of collected reflections	3039	11668
no. of unique ref. (R_{int})	1071 (0.0382)	4347 (0.0567)
Data/restraints/parameters	1071 / 7 / 73	4347 / 0 / 290
R_1 , w R_2 [obs $I > 2\sigma(I)$]	0.0409, 0.0949	0.1206, 0.2428
R_1 , w R_2 (all data)	0.0447, 0.0966	0.1632, 0.2586
residual peak/hole, e. Å ⁻³	1.790 / -0.831	0.405 / -0.308
transmission ratio	0.4395 / 0.3688	0.9913 / 0.9835
Goodness-of-fit on F^2	1.048	1.037

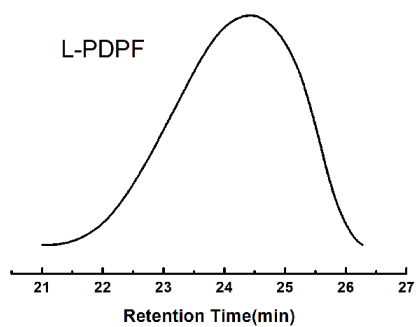


Fig. S1 The GPC data of L-PDPF

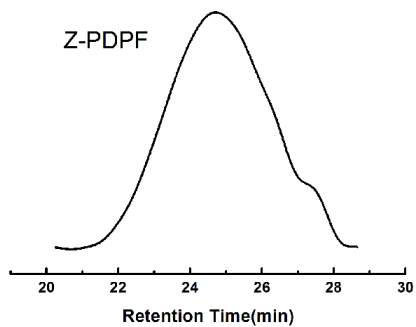


Fig. S2 The GPC data of Z-PDPF.

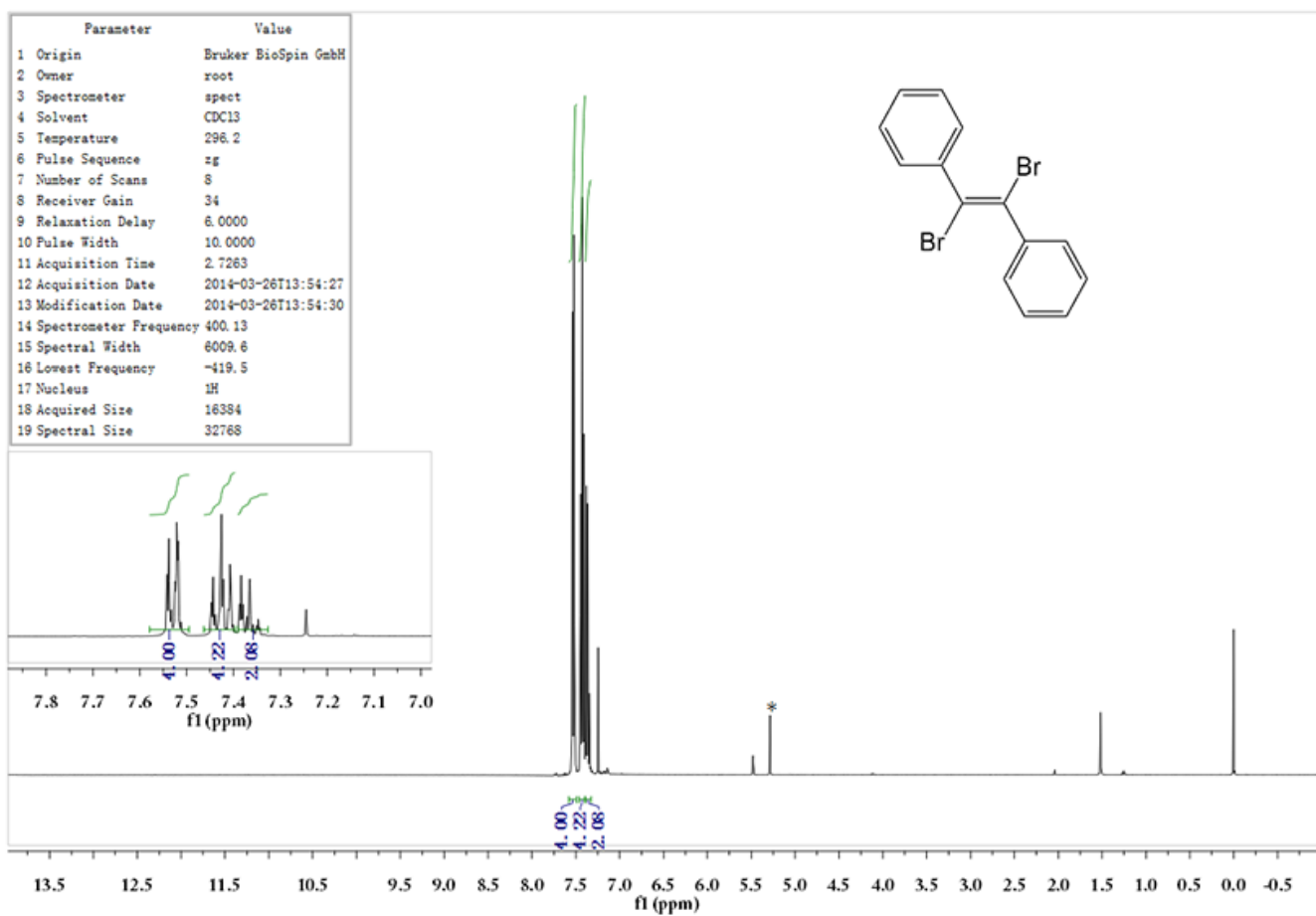


Fig. S3 ¹H NMR spectrum of monomer 1.

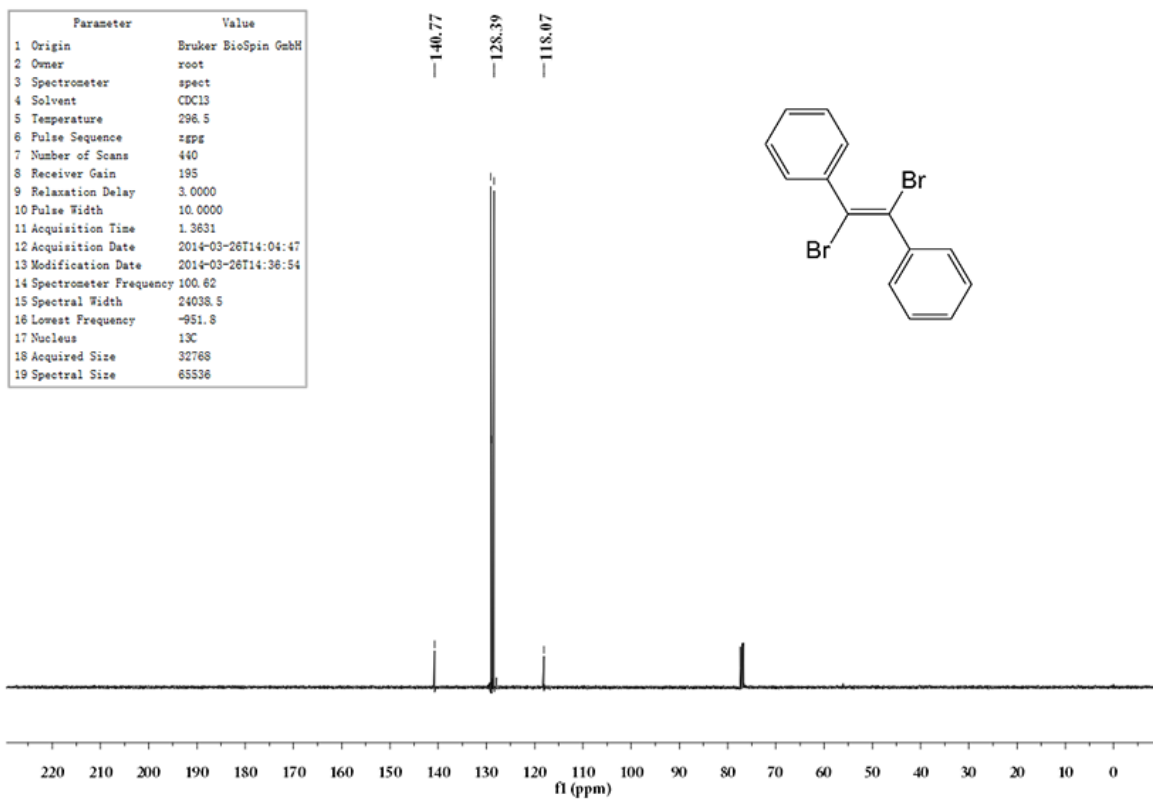


Fig. S4 ^{13}C NMR spectrum of monomer 1.

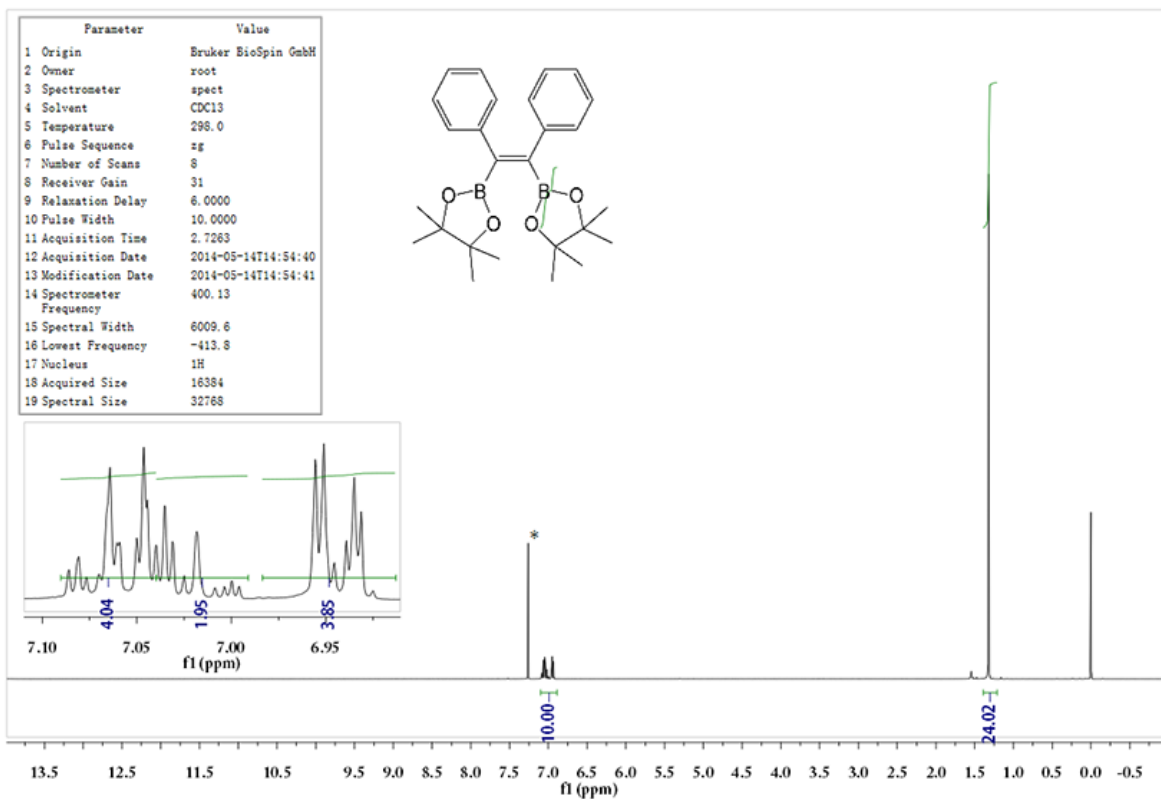


Fig. S5 ^1H NMR spectrum of monomer 2.

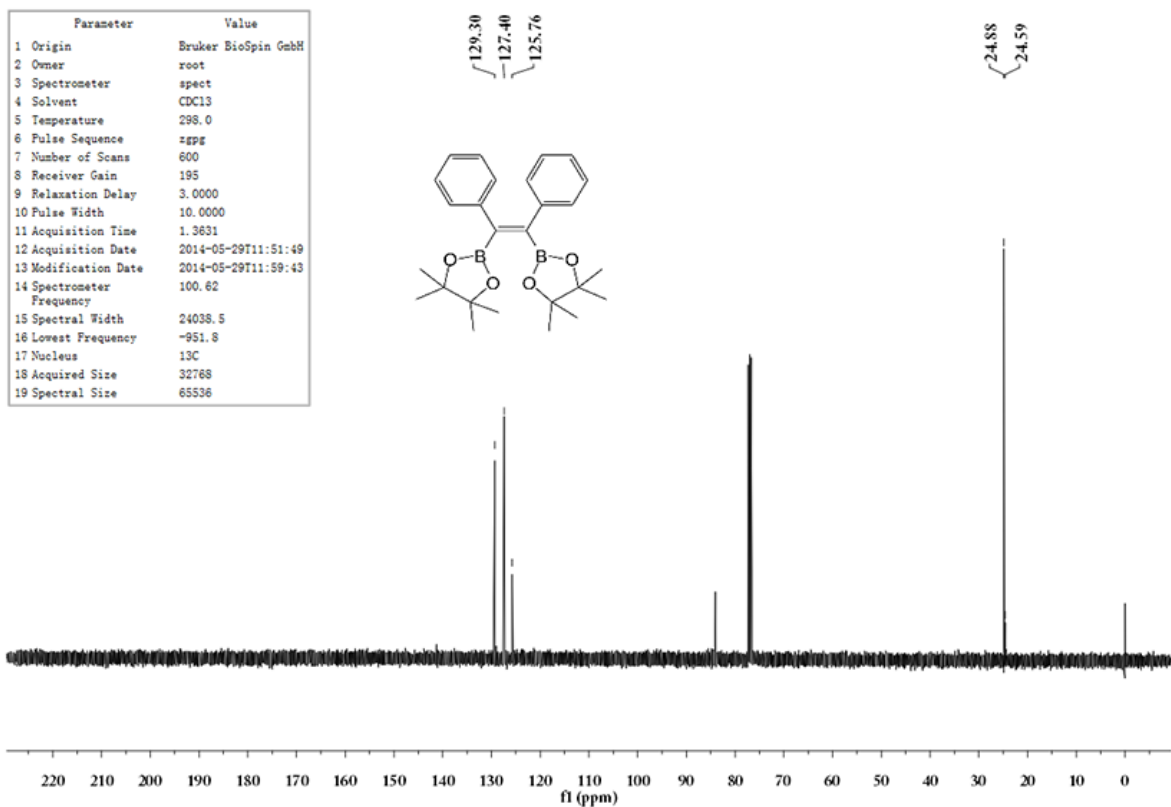


Fig. S6 ^{13}C NMR spectrum of monomer 2.

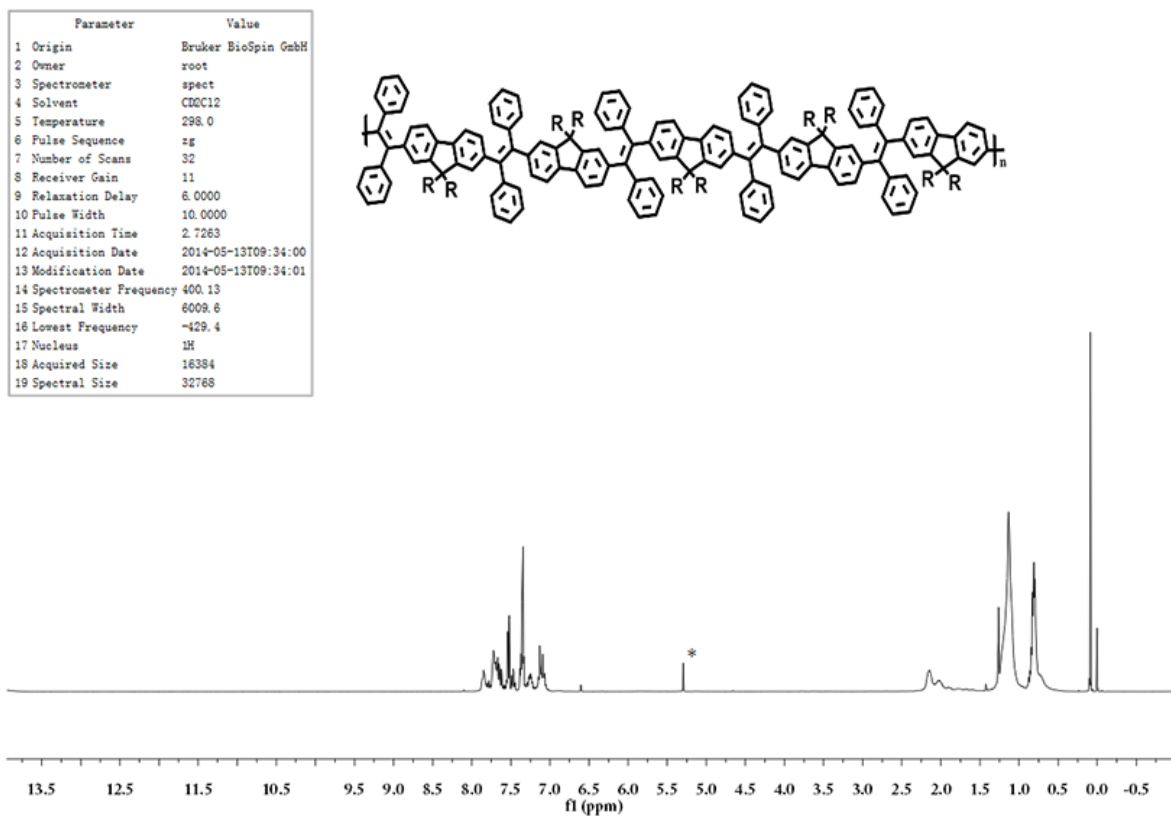


Fig. S7 ^1H NMR spectrum of L-PDPF. R: C_8H_{17}

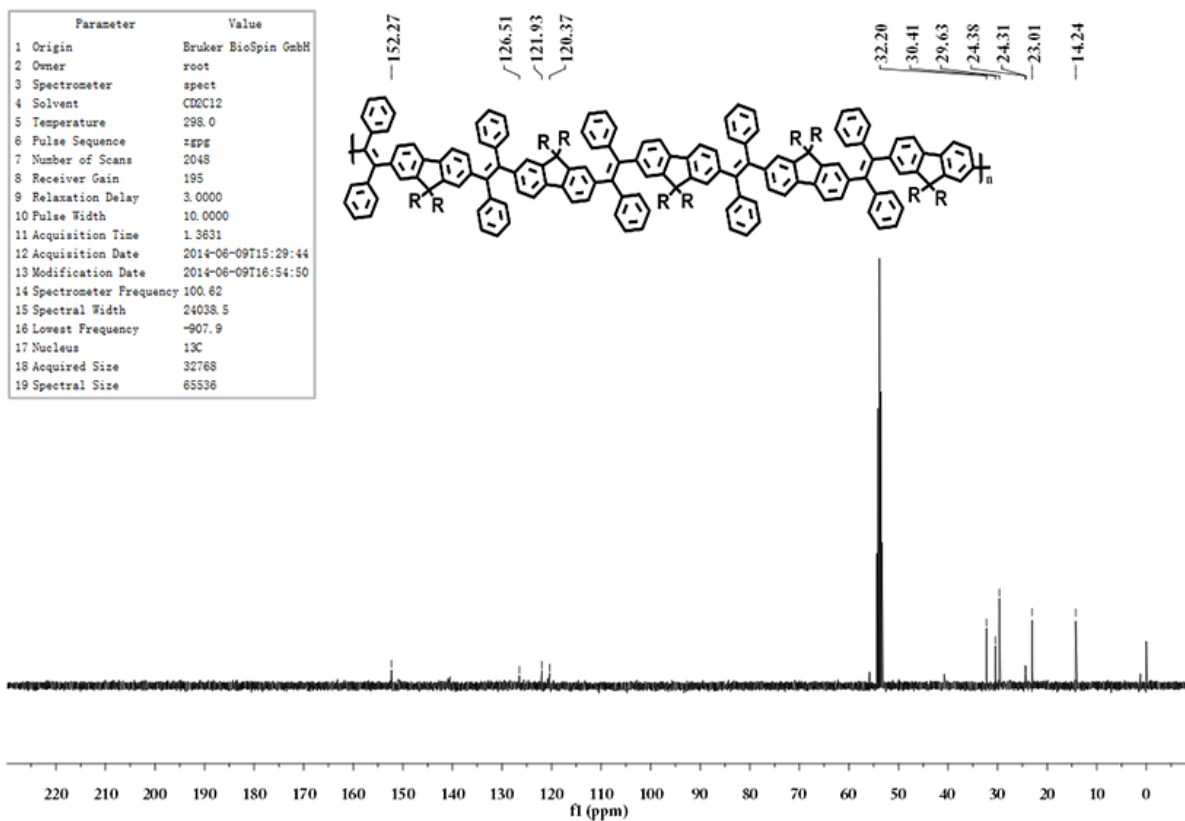


Fig. S8 ¹³C NMR spectrum of L-PDPF. R: C₈H₁₇

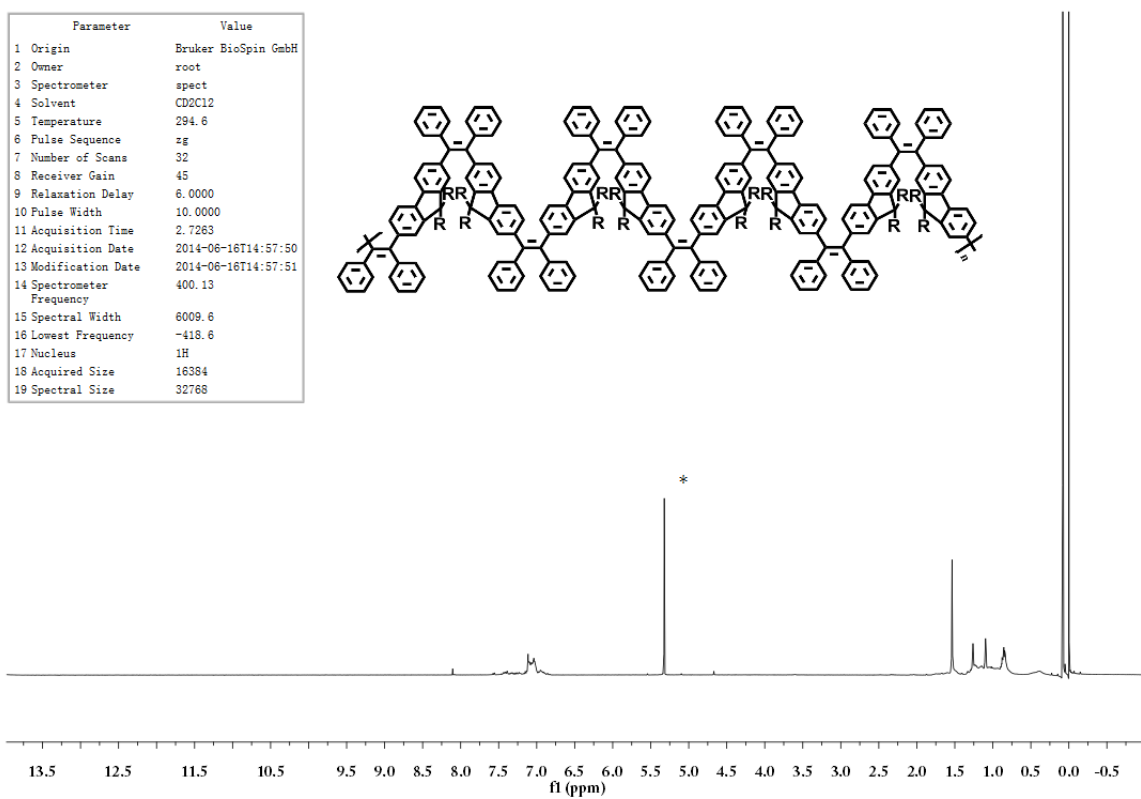


Fig. S9 ¹H NMR spectrum of Z-PDPF. R: C₈H₁₇

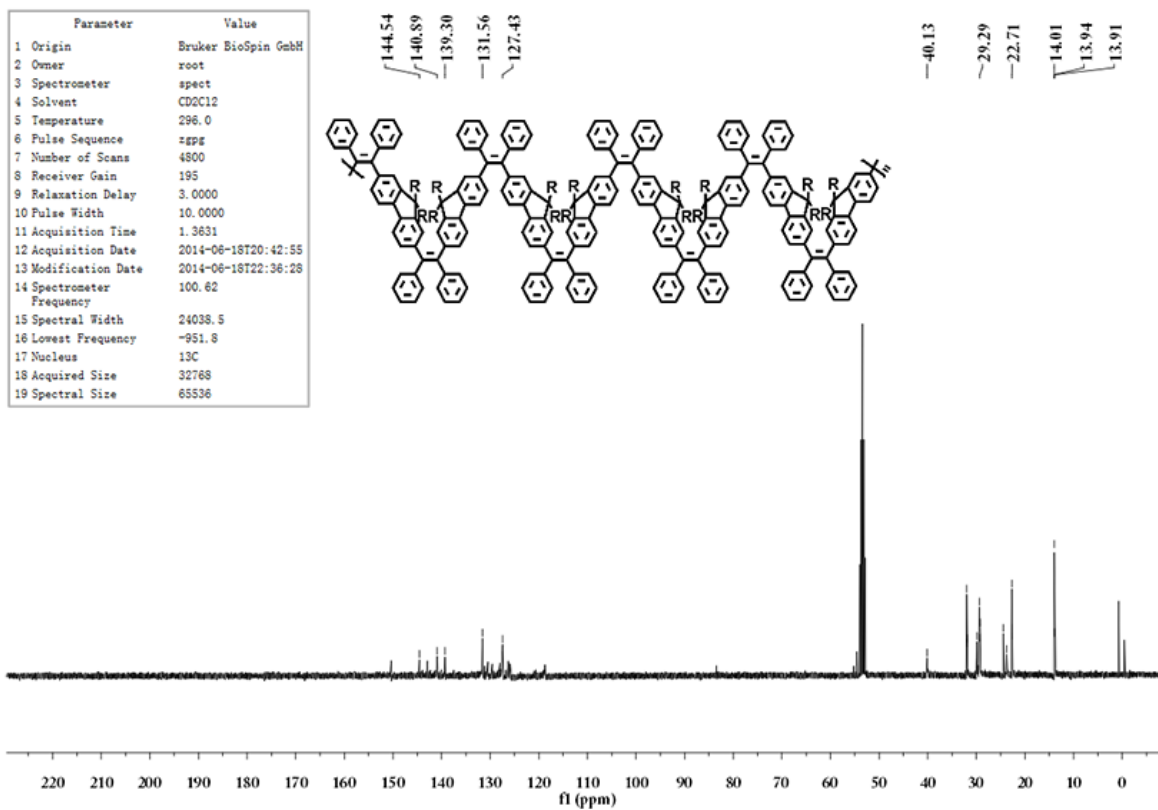


Fig. S10 ¹³C NMR spectrum of *Z*-PDPF. R: C₈H₁₇

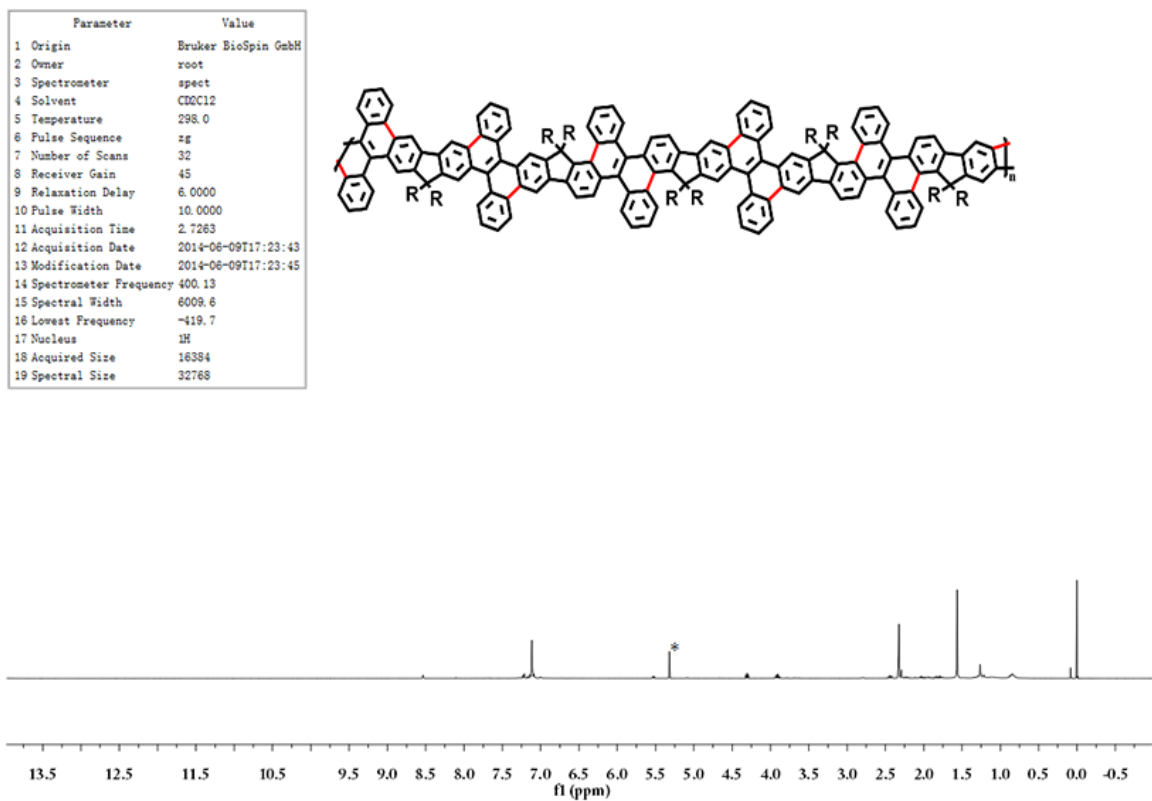


Fig. S11 ¹H NMR spectrum of *L*-PDPF-O. R: C₈H₁₇

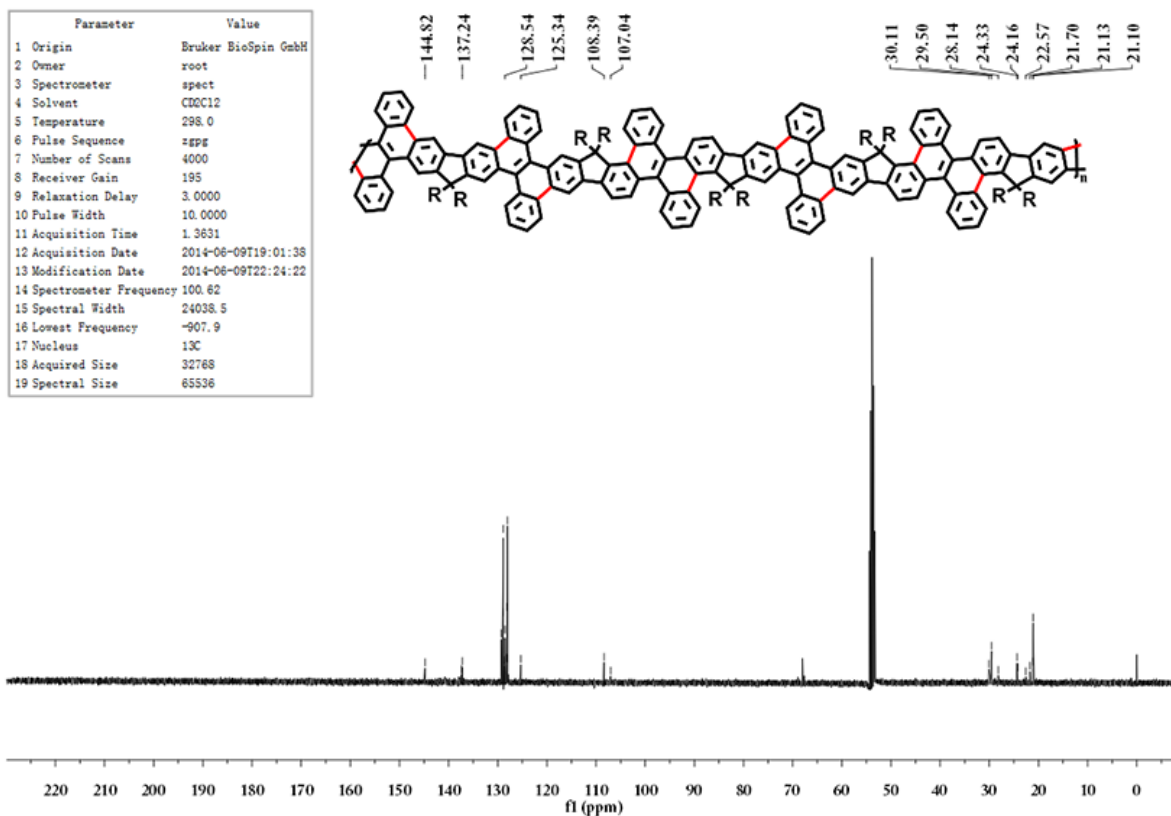


Fig. S12 ¹³C NMR spectrum of L-PDPF-O. R: C₈H₁₇

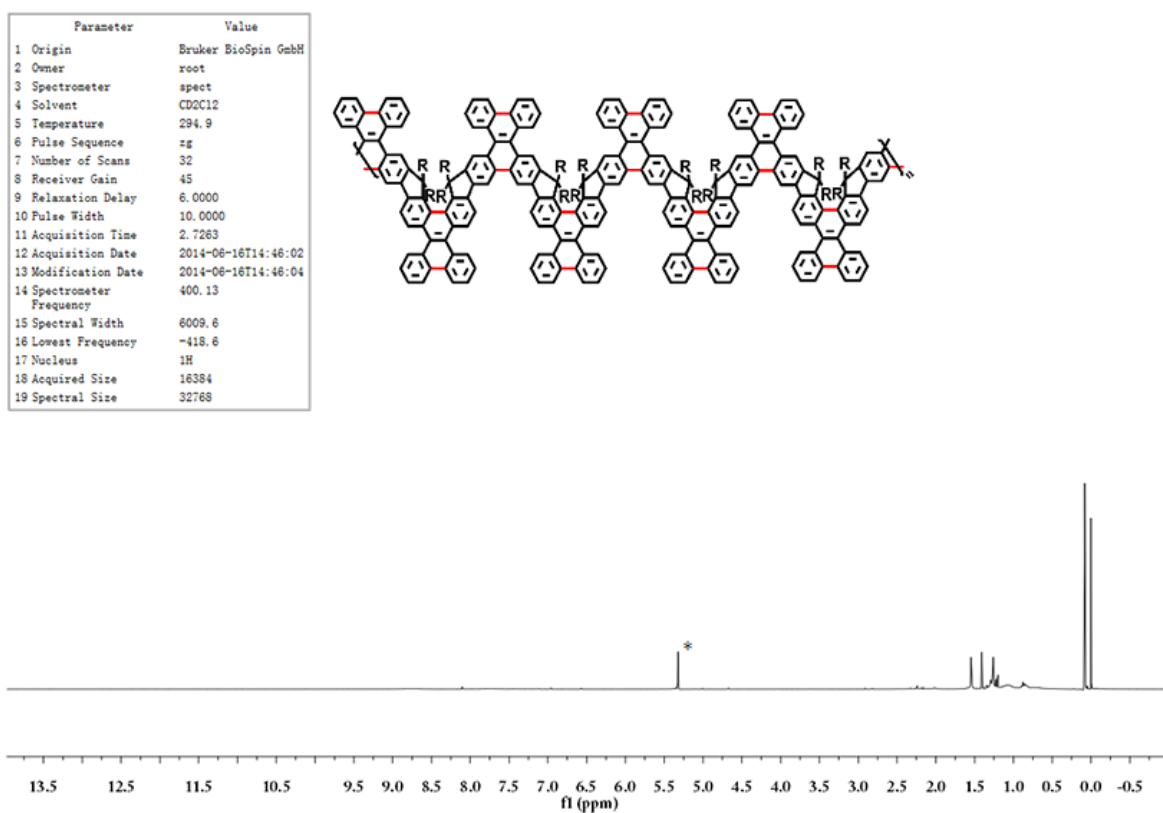


Fig. S13 ¹H NMR spectrum of Z-PDPF-O. R: C₈H₁₇

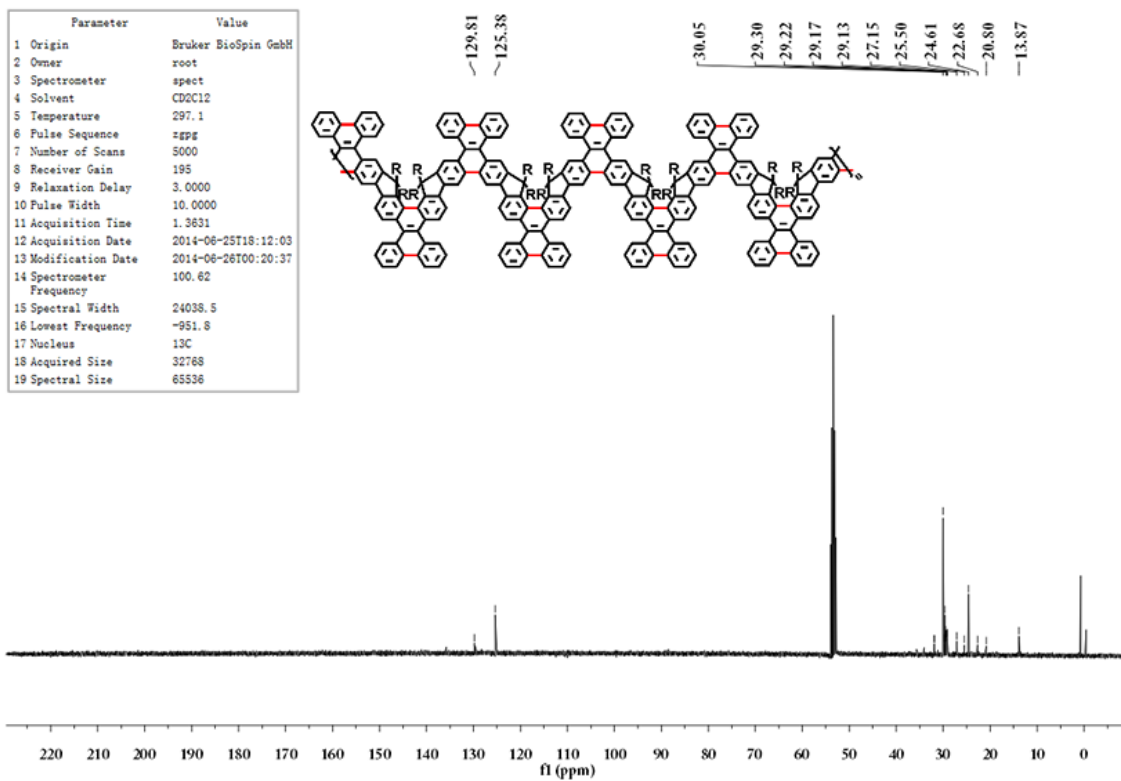


Fig. S14 ¹³C NMR spectrum of Z-PDPF-O. R: C₈H₁₇

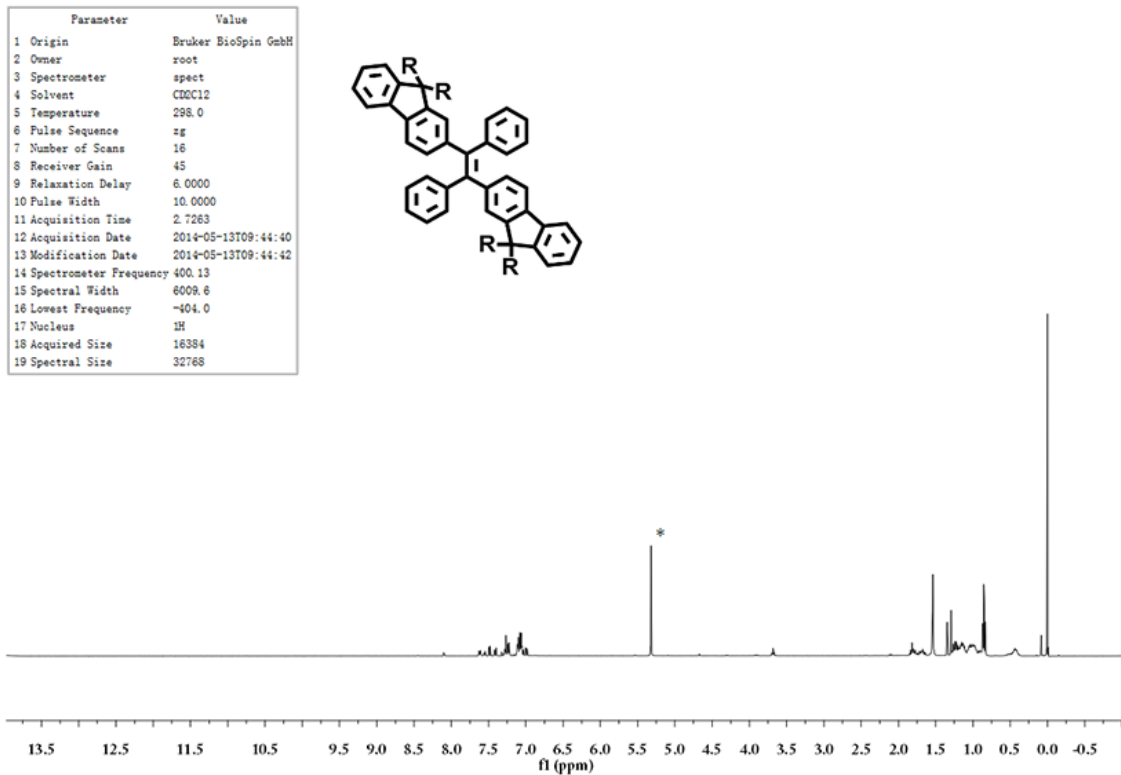


Fig. S15 ¹H NMR spectrum of L-DPBF. R: C₈H₁₇

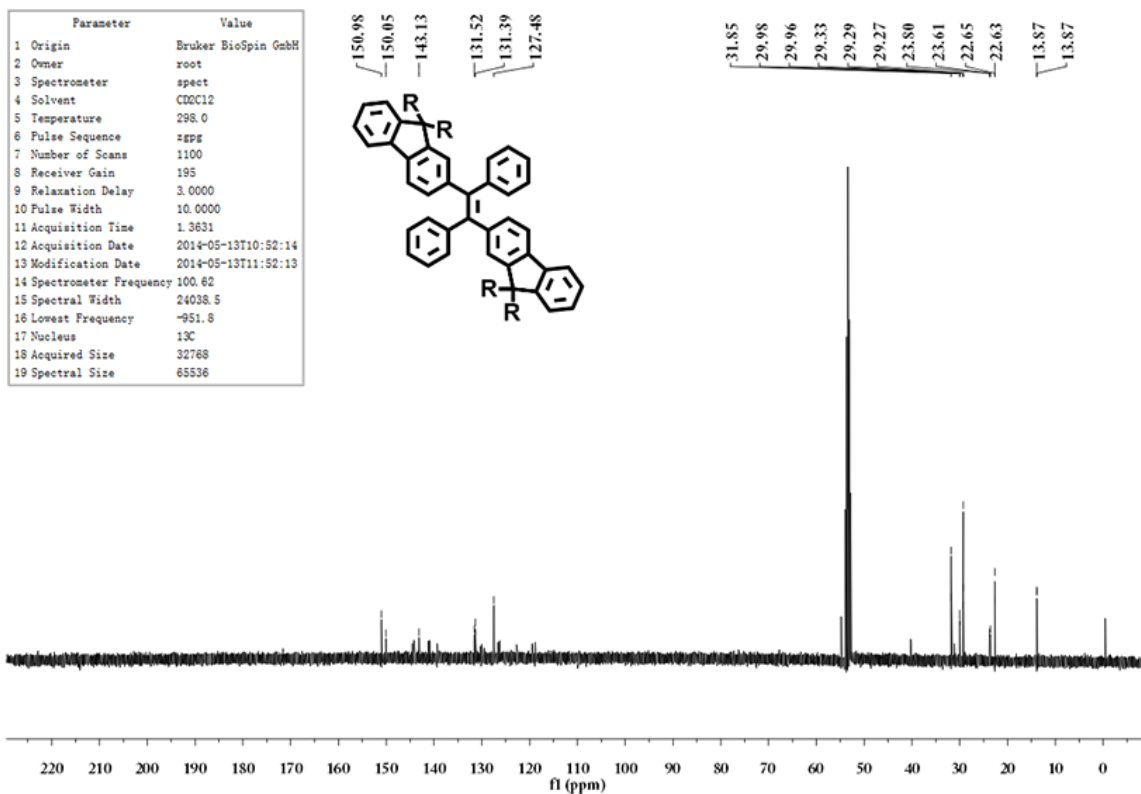


Fig. S16 ^{13}C NMR spectrum of L-DPBF. R: C_8H_{17}

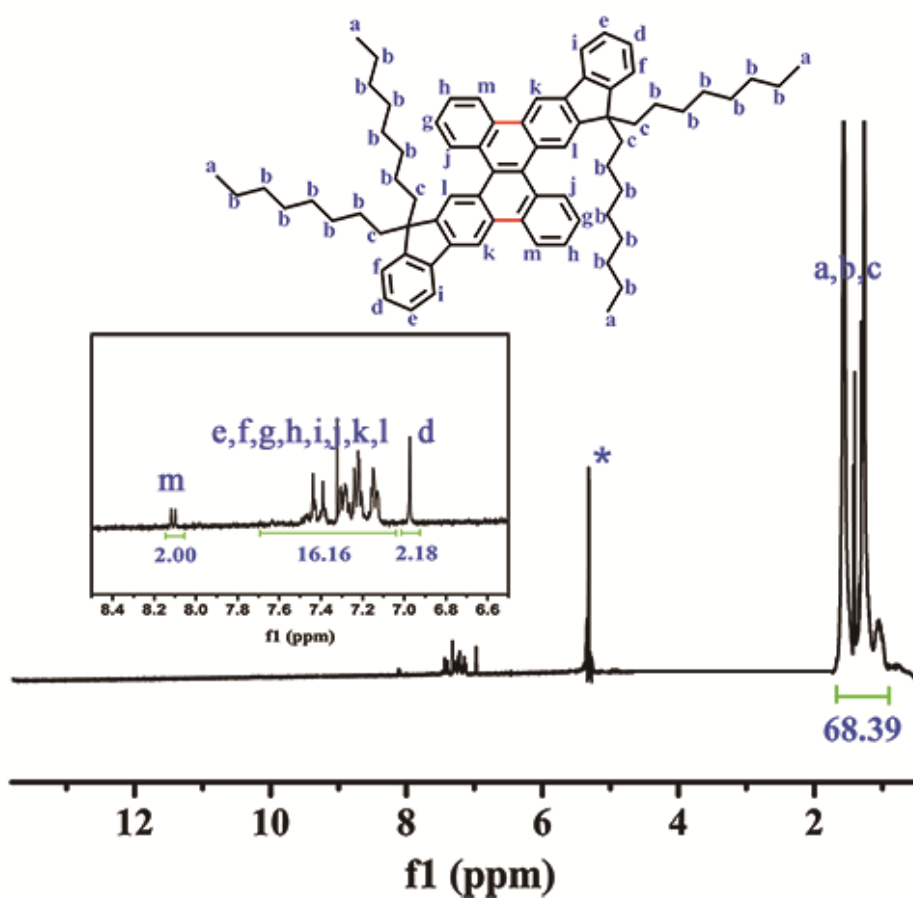


Fig. S17 ^1H NMR spectrum of L-DPBF-O. The inserted is the amplifications of the aromatic domain. R: C_8H_{17}

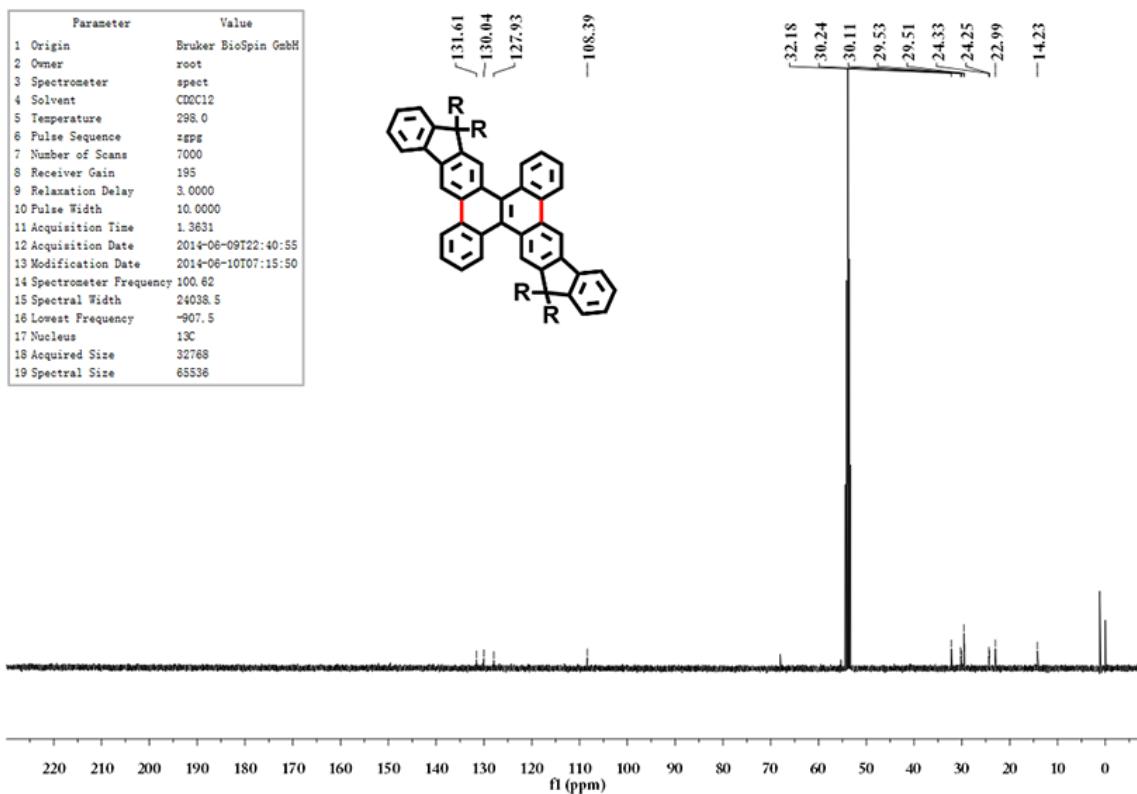


Fig. S18 ¹³C NMR spectrum of L-DPBF-O. R: C₈H₁₇

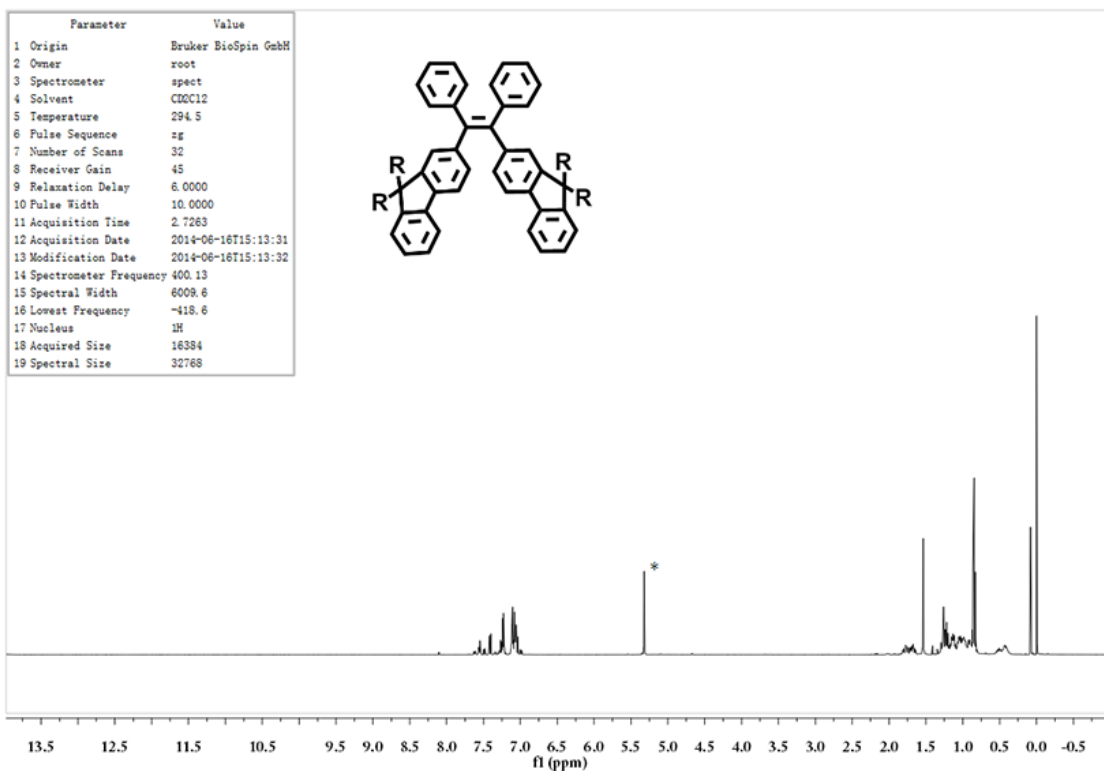


Fig. S19 ¹H NMR spectrum of Z-DPBF. R: C₈H₁₇

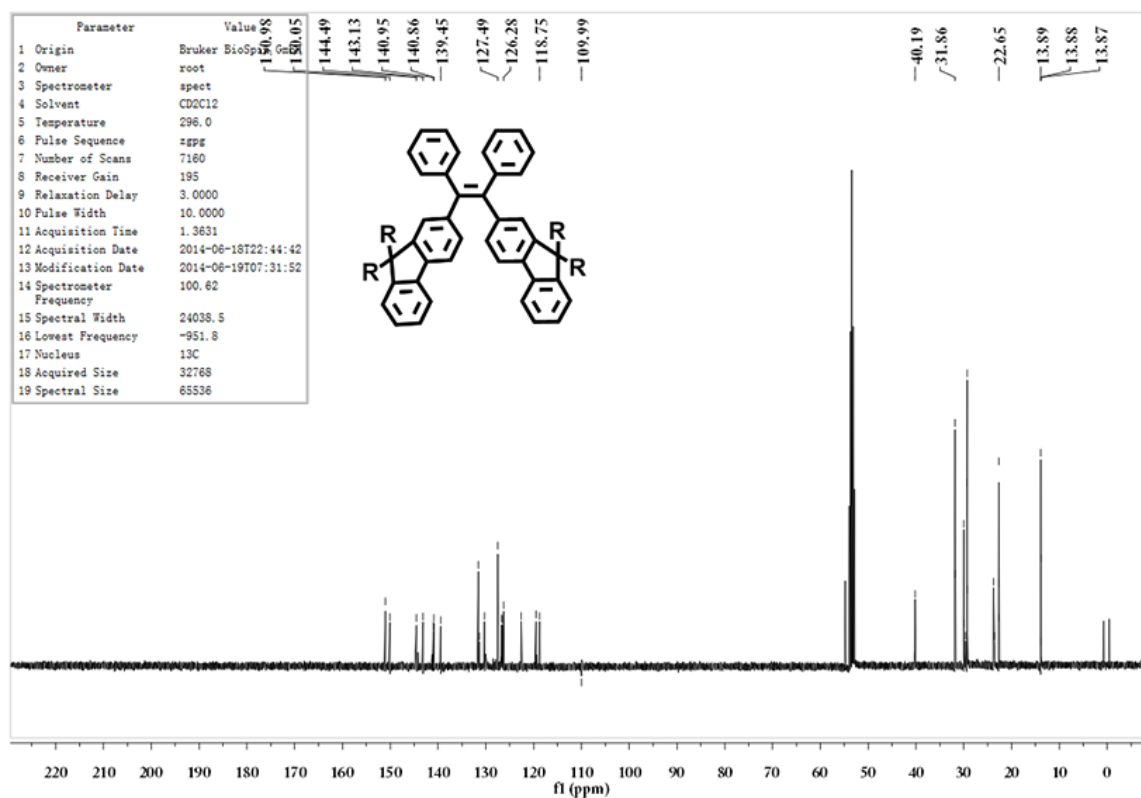


Fig. S20 ¹³C NMR spectrum of *Z*-DPBF. R: C₈H₁₇

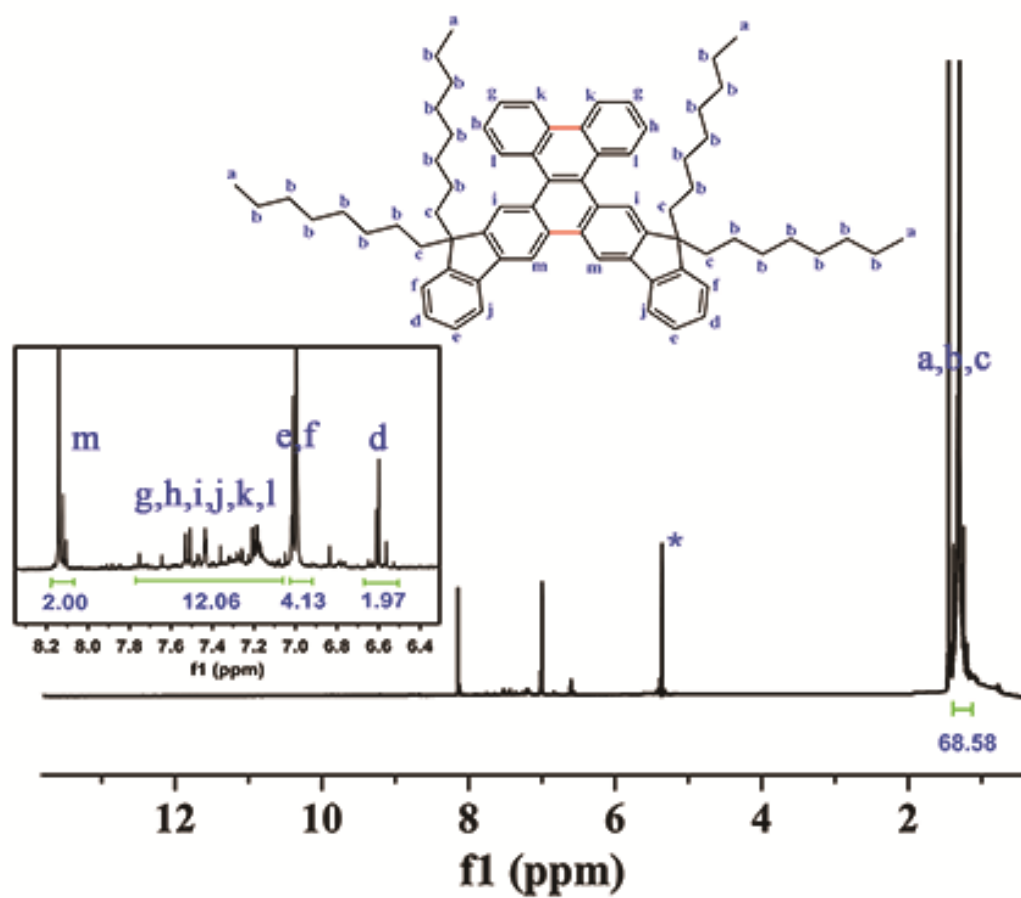


Fig. S21 ¹H NMR spectrum of *Z*-DPBF-O. The inserted is the amplifications of the aromatic domain. R: C₈H₁₇

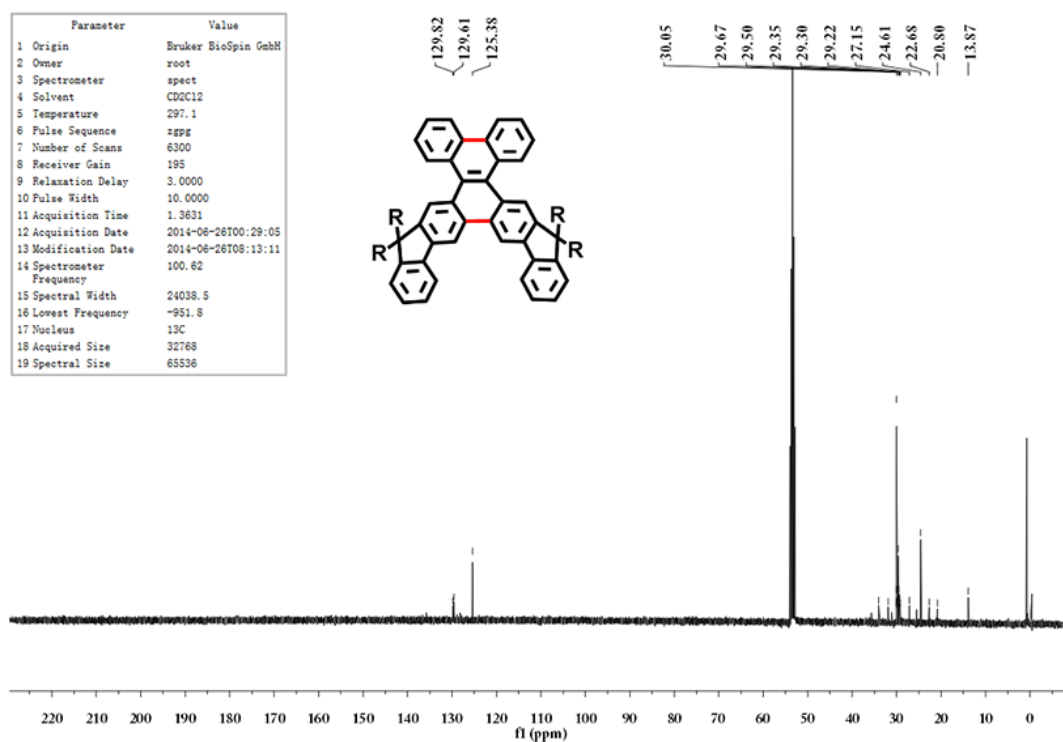


Fig. S22 ¹³C NMR spectrum of **Z-DPBF-O**. R: C₈H₁₇

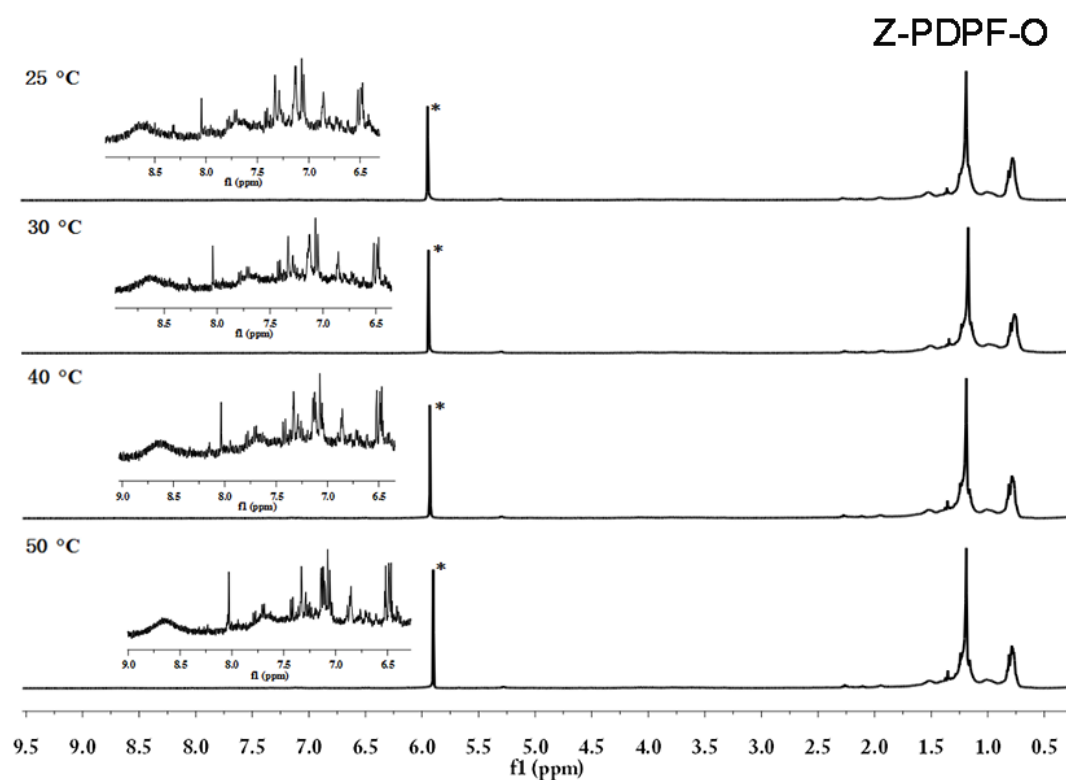


Fig. S23 ¹H NMR spectra of **Z-PDPF-O** at the variable temperatures (25 °C to 50 °C) in 1,1,2,2-tetrachloroethane-d₂. The inserted are the amplifications of the aromatic domain.

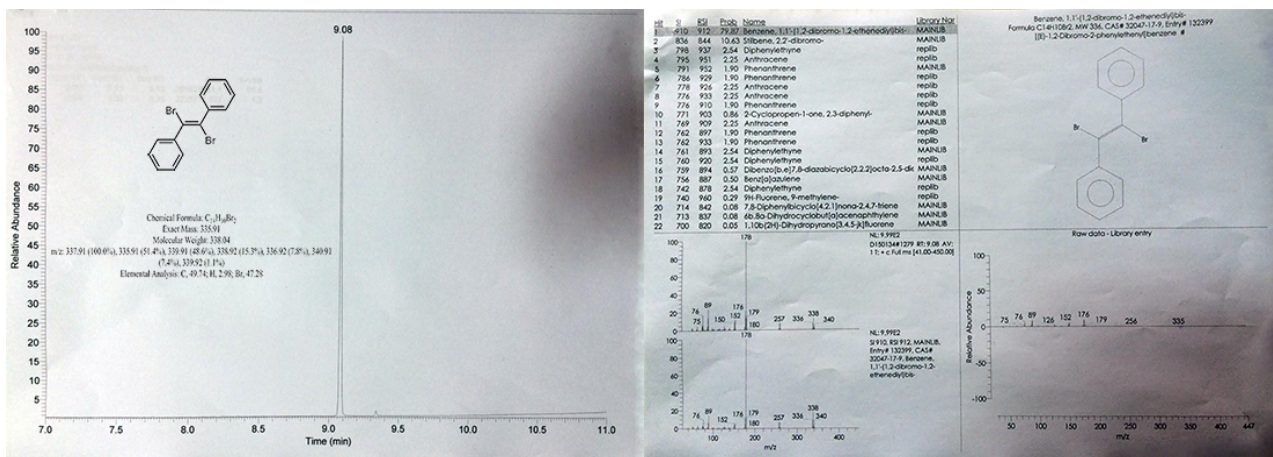


Fig. S24 The GC-MS of monomer 1.

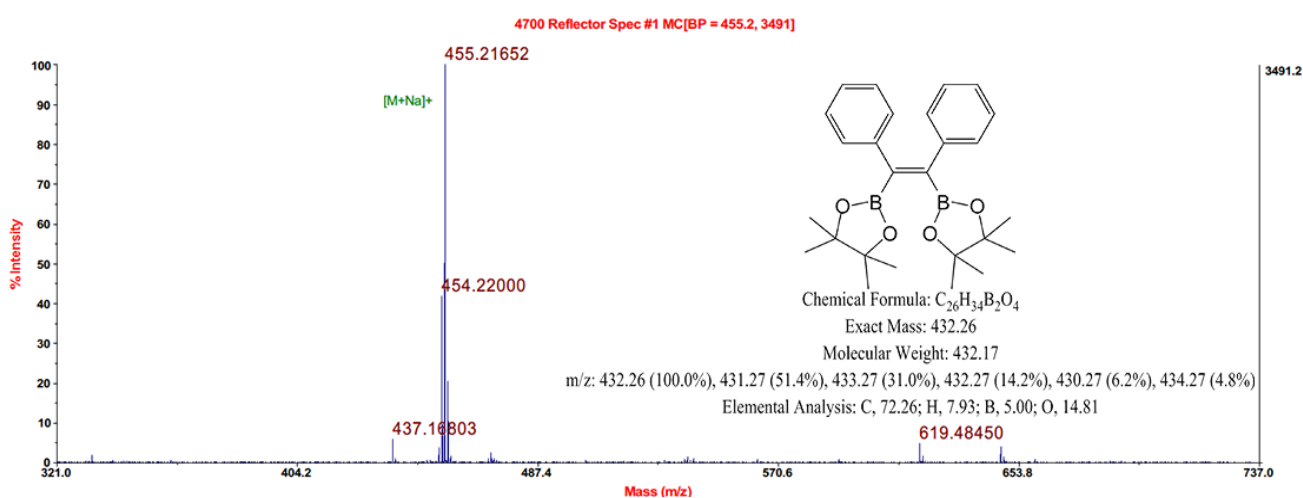


Fig. S25 The MALDI-TOF of monomer 2.

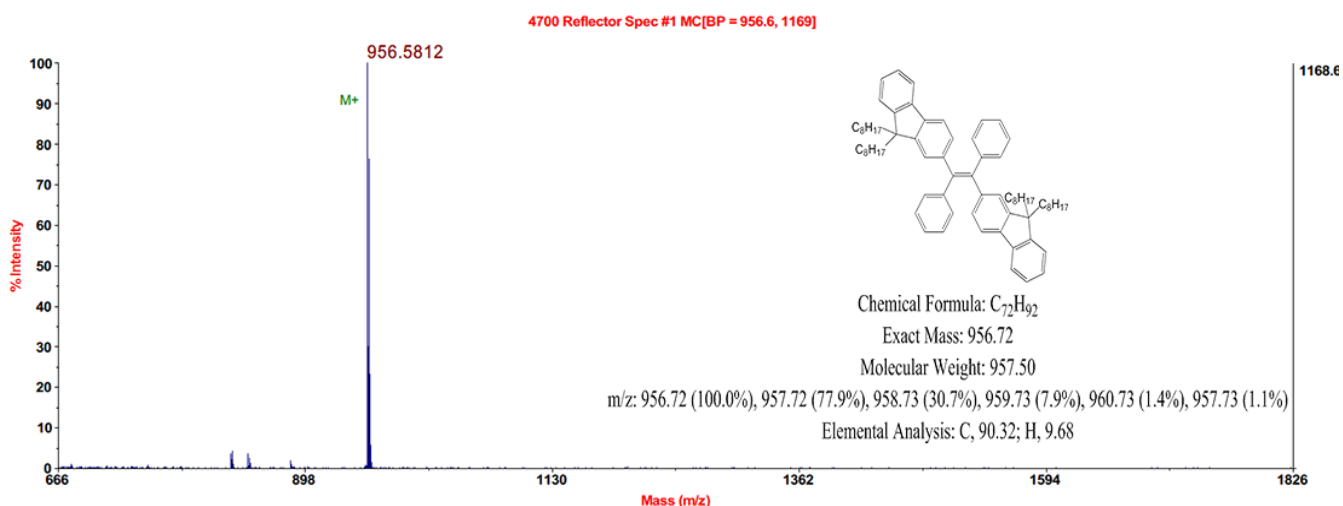


Fig. S26 The MALDI-TOF of L-DPBF.

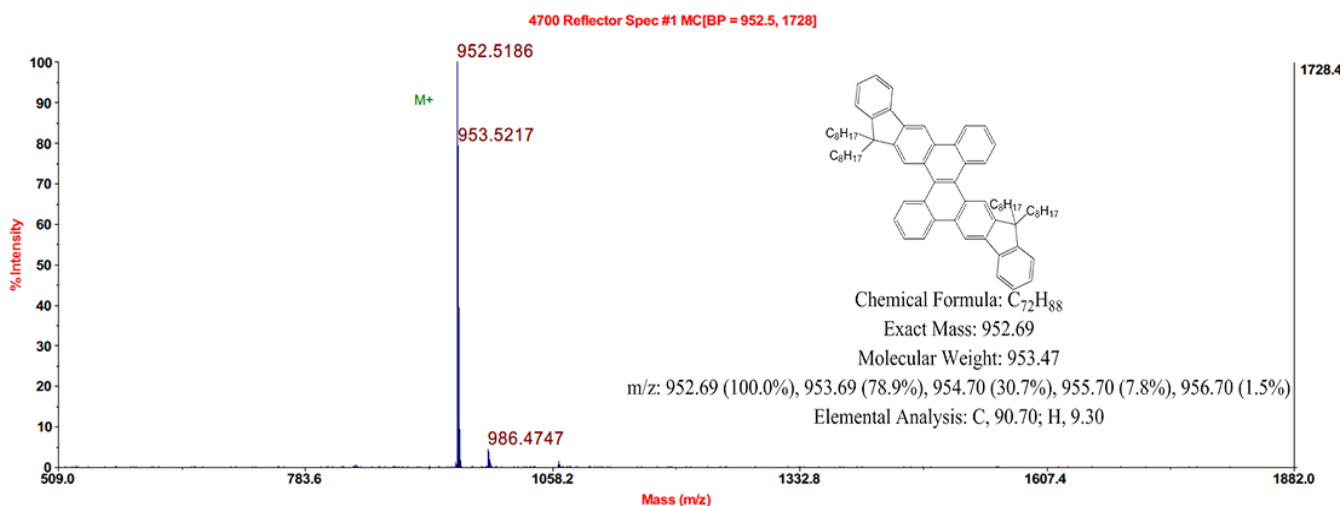


Fig. S27 The MALDI-TOF of L-DPBF-O.

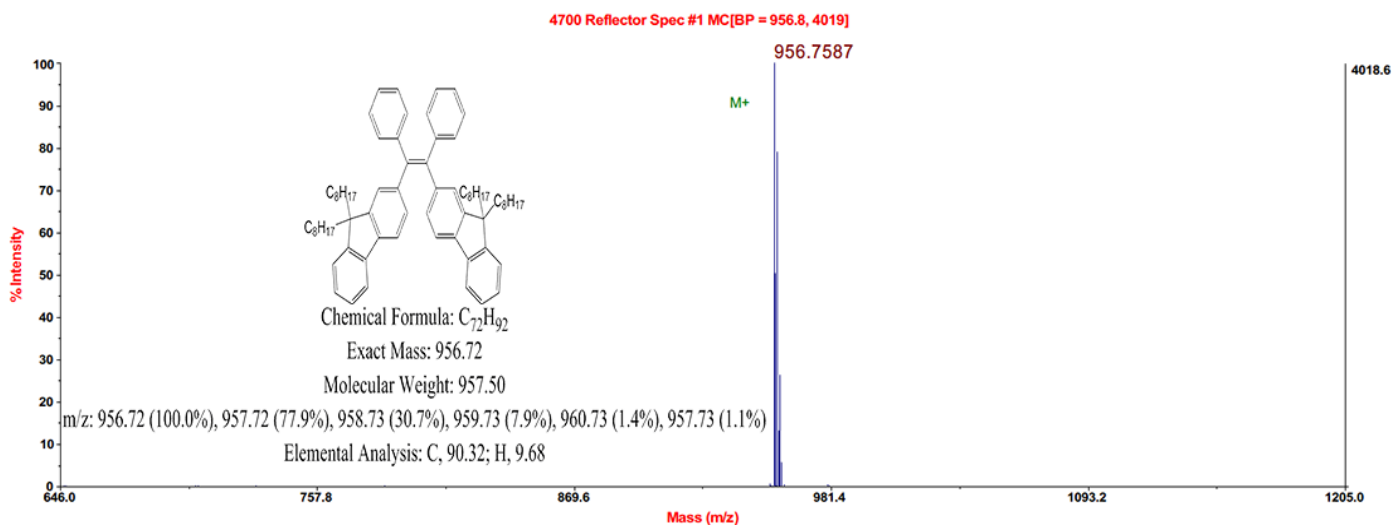


Fig. S28 The MALDI-TOF of Z-DPBF.

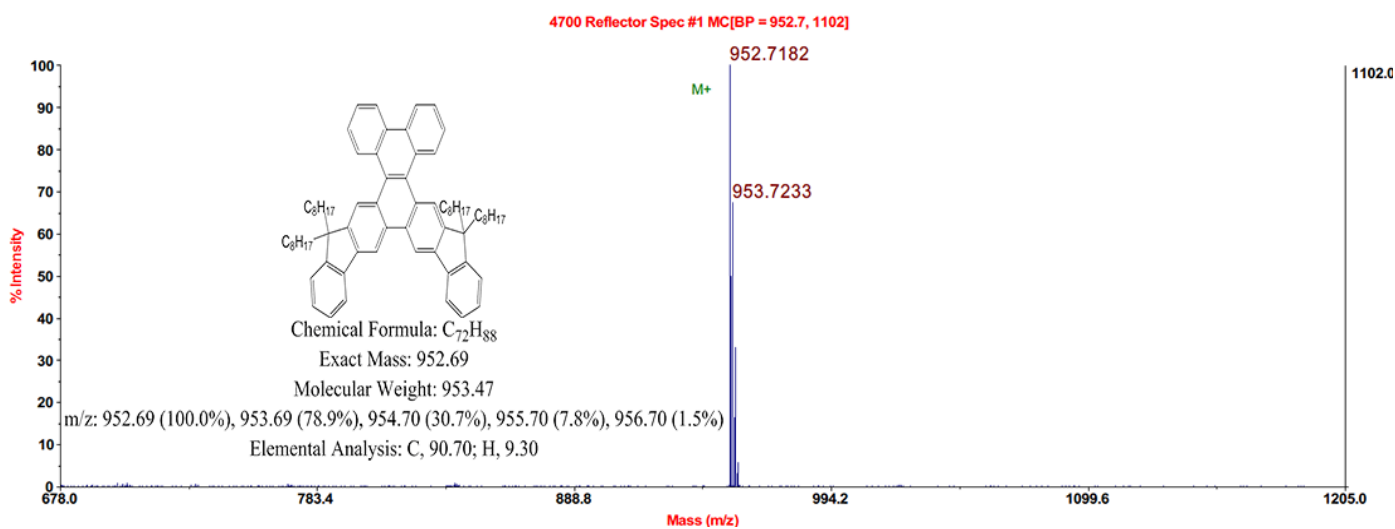


Fig. S29 The MALDI-TOF of Z-DPBF-O.

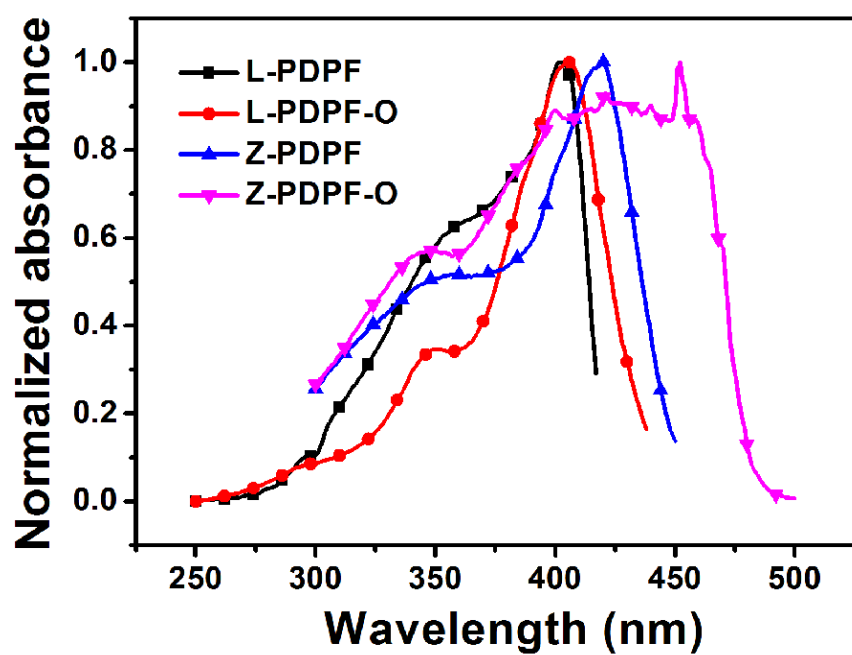


Fig. S30 The absorption spectra of L-PDPF, L-PDPF-O, Z-PDPF and Z-PDPF-O in THF solution.

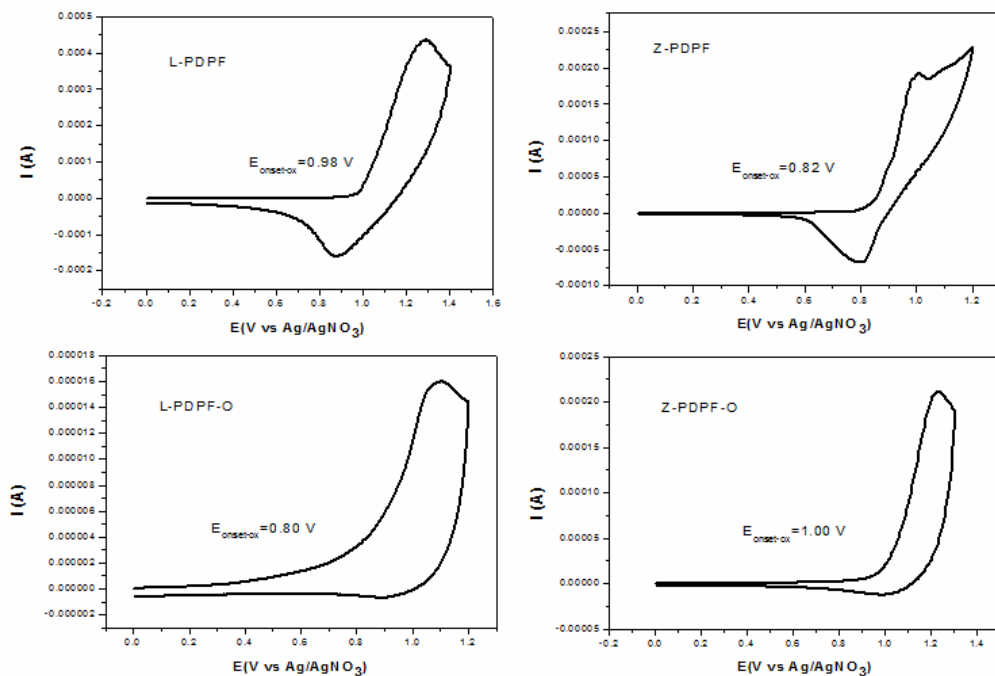


Fig. S31 The cyclic voltammograms of L-PDPF, L-PDPF-O, Z-PDPF and Z-PDPF-O.

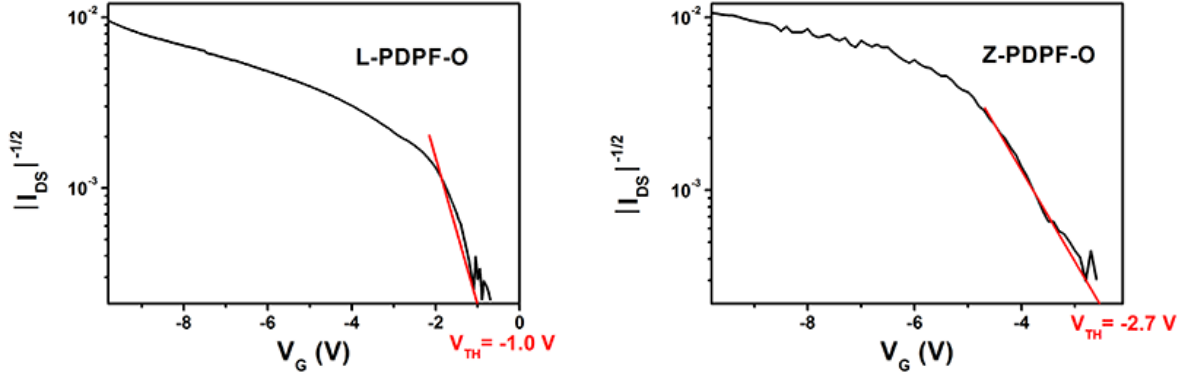


Fig. S32 The square root of absolute value of drain current as a function of gate voltage for **L-PDPF-O** and **Z-PDPF-O**.

According to the above V_{TH} values and the metal-oxide semiconductor FET formula for the saturation regime, $I_{DS} = \frac{\mu WC_i}{2L} (V_G - V_{TH})^2$, the calculations of the charge carrier mobility (μ) are below:

L-PDPF-O

$$I_{DS} = 6.39 \times 10^{-5}, \quad V_G = -9 \text{ V}, \quad C_i = 20 \mu\text{F}/\text{cm}^2, \quad W = L = 1000 \mu\text{m}, \quad V_{TH} = -1 \text{ V}$$

$$\begin{aligned} \mu &= 2LI_{DS} / [WC_i(V_G - V_{TH})^2] = 2I_{DS} / [C_i(V_G - V_{TH})^2] \\ &= 2 \times 6.39 \times 10^{-5} / [20 \times 10^{-6} \times (-9 + 1)^2] \\ &= 0.10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \end{aligned}$$

Z-PDPF-O

$$I_{DS} = 1.30 \times 10^{-4}, \quad V_G = -9 \text{ V}, \quad C_i = 20 \mu\text{F}/\text{cm}^2, \quad W = L = 1000 \mu\text{m}, \quad V_{TH} = -2.7 \text{ V}$$

$$\begin{aligned} \mu &= 2LI_{DS} / [WC_i(V_G - V_{TH})^2] = 2I_{DS} / [C_i(V_G - V_{TH})^2] \\ &= 2 \times 1.30 \times 10^{-4} / [20 \times 10^{-6} \times (-9 + 2.7)^2] \\ &= 0.33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \end{aligned}$$

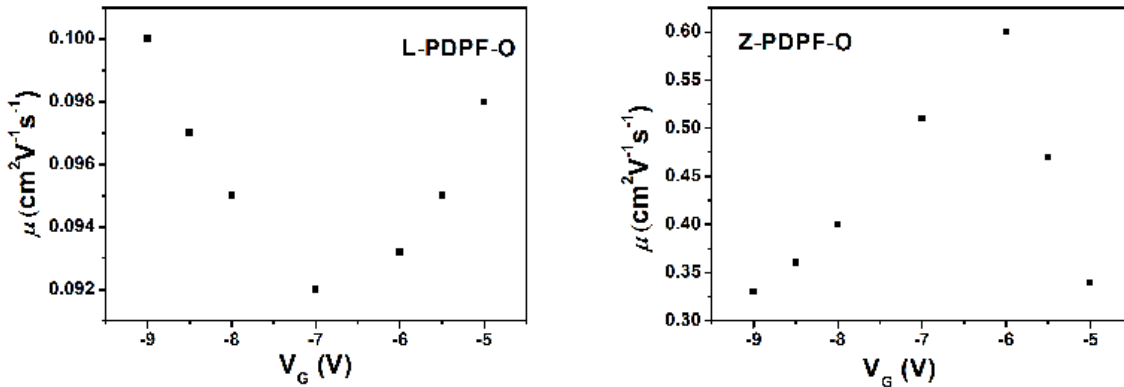


Fig. S33 The mobility plots versus gate voltages for **L-PDPF-O** and **Z-PDPF-O**.