

Rational design of a difluorobenzo[*c*]cinnoline-based low-bandgap copolymer for high-performance polymer solar cells

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S1. Experimental section

1.1. Materials

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-2,5-pyrrolo[3,4-*c*]pyrrole-1,4-dione (M2) was purchased from Shenzhen Derthon Optoelectronic Materials Science & Technology Co., LTD. All the other raw materials were purchased from J&K Scientific, Chem Greatwall (Wuhan, China), Energy chemical or Alfa Aesar in analytical grade. Tetrahydrofuran (THF), ether and toluene were dried and distilled from sodium/benzophenone prior to use. N,N-dimethylformamide (DMF) was dried and distilled under reduced pressure. All chromatographic separations were carried out on silica gel (200-300 mesh). All other solvents and chemicals used in this work were analytical grade and used without further purification. Compound **1**¹ and compound **2**^{2,3} were synthesized according to the procedure reported in the literatures.

1.2. Synthesis of bis(4-(2-hexyldecyl)thiophene)-5,5'-difluoro-2,2'-dinitro-[1,1'-biphenyl] (**3**)

To a mixture of compound **1** (2.01 g, 4.57 mmol) and compound **2** (6.00 g, 10.04 mmol) in degassed toluene (50 mL), Pd(PPh₃)₄ (0.21 g, 0.18 mmol) was added and then refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into 100 mL water and extracted with dichloromethane (30 mL×3). The combined organic layer was washed with water and dried over anhydrous MgSO₄. It was distilled to remove off solvent. The residue was purified by silica gel column chromatography using petroleum ether/CH₂Cl₂ (3:1, v:v) as eluent to obtain compound **3** as a light yellow crystals (3.27 g, 80.15%).¹H NMR (400 MHz, CDCl₃, δ/ppm): 8.57–8.55 (d, *J* = 6.96Hz, 2H), 7.44 (s, 2H), 7.12 (s, 2H), 7.09-7.08 (d, *J* = 4.82Hz, 2H), 2.61–2.59 (d, *J* = 6.81 Hz, 4H), 1.64–1.59 (m, 2H), 1.37–1.26 (m, 48H), 0.93–0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 161.73, 159.13, 143.39, 143.23, 133.28, 133.24, 132.90, 130.80, 130.12, 130.05, 125.53, 124.23, 124.09, 123.79, 123.75, 119.02, 118.76, 38.99, 33.36, 31.92, 31.90, 30.01, 29.69, 29.63, 29.34, 26.64, 26.62, 22.68, 14.10. FT-ICR MS (C₅₂H₇₄F₂N₂O₄S₂) [M-NO₂]⁺ m/z: calcd for 846.5124; found 846.5124.

1.3. Synthesis of 2,9-difluoro-3,8-bis(4-(2-hexyldecyl)-2-thienyl)benzo[*c*]cinnoline (**4**)

LiAlH₄ (0.68 g, 18.00 mmol) and anhydrous ether (70 mL) were added to a 500-mL three-necked round-bottomed flask equipped with a condenser under nitrogen atmosphere. Compound **3** (1.79 g, 2.00 mmol) in anhydrous ether (25 mL) and benzene (25 mL) was added into the

reaction mixture. After stirring for 2 h at room temperature, the reaction mixture was heated at 45°C for 15 min. Water (10 mL) was then slowly added to the reaction mixture to decompose excess LiAlH₄. The reaction mixture was filtered and solvents were evaporated. The yellow solid was collected and purified by column chromatography on silica gel using dichloromethane as the eluent to afford 1.31 g (79% yield) as yellow needle-like crystals. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.01–8.99 (d, *J* = 7.50 Hz, 2H), 8.09–8.06 (d, *J* = 11.50 Hz, 2H), 7.56 (s, 2H), 7.08 (s, 2H), 2.63–2.62 (d, *J* = 6.75 Hz, 4H), 1.68 (m, 2H), 1.31–1.27 (m, 48H), 0.88–0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 161.73, 159.13, 143.37, 142.49, 134.96, 131.21, 130.11, 126.71, 126.67, 123.43, 107.46, 107.21, 38.99, 35.08, 31.93, 30.03, 29.70, 29.65, 29.35, 26.66, 22.69, 14.11. FT-ICR MS (C₅₂H₇₄F₂N₂S₂) [M]⁺ *m/z*: calcd for 829.5334; found 829.5337.

1.4. Synthesis of 2,9-difluoro-3,8-bis(5-bromo-4-(2-hexyldecyl)-2-thienyl) benzo[*c*]cinnoline (**M1**)

To a solution of compound **4** (0.83 g, 1.00 mmol) in CHCl₃ (50 mL), *N*-bromosuccinimide (NBS, 0.37 g, 2.10 mmol) was added under an ice bath. The mixture was then stirred for 5 h at room temperature under dark condition. After the solvent was distilled off, the crude solid was recrystallized from ethanol/ petroleum ether (4:1) to afford monomer **M1** as a light yellow crystal (0.79 g, 80 %). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 8.93–8.91 (d, *J* = 7.29 Hz, 2H), 8.08–8.06 (d, *J* = 11.22 Hz, 2H), 7.42 (s, 2H), 2.58–2.57 (d, *J* = 6.78 Hz, 4H), 1.74 (m, 2H), 1.32–1.27 (m, 48H), 0.88–0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 161.58, 159.00, 142.66, 142.34, 134.54, 130.62, 129.50, 125.78, 125.63, 120.46, 119.53, 112.83, 107.59, 107.34, 38.63, 34.35, 33.44, 31.92, 30.02, 29.69, 29.63, 29.35, 26.59, 22.69, 14.12. Anal. calcd for C₅₂H₇₂Br₂F₂N₂S₄: C 63.27, H 7.35, and N 2.84. Found: C 63.31, H 7.34, and N 2.83. FT-ICR MS (C₅₂H₇₂Br₂F₂N₂S₂) [M]⁺ *m/z*: calcd for 985.3544; found 985.3551.

1.5. Synthesis of the polymer **PDFBC-DPP**

In an atmosphere of nitrogen, **M1** (197.42 mg, 0.20 mmol) and **M2** (155.34 mg, 0.20 mmol) were added into a two-neck flask. Next, 5 mL of toluene and 2 mL of aqueous K₃PO₄ (1.6 M) were added into the mixture. The reaction mixture was subjected to three freeze-pump-thaw cycles degassing process in order to remove O₂. Finally, Pd₂(dba)₃ (3.66 mg, 0.004 mmol) and P(*o*-tol)₃ (4.89 mg, 0.016 mmol) were added to the reaction mixture and heated at 100°C for 72 h. The reaction mixture was cooled to room temperature and slowly added to methanol (200 mL). Then, precipitate was purified through continuous Soxhlet extractions with methanol, acetone, hexane,

dichloromethane and chloroform. At last, the polymer was precipitated into acetone and collected via filtration and dried under high vacuum for 24 h. Finally, the blue-black solid was obtained (0.17 g, yield: 62.96%). ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.07-8.92 (br, 4H), 8.76-8.64 (br, 4H), 8.14-7.05 (br, 6H), 3.98 (d, 4H), 2.84 (d, 4H), 1.88 (m, 4H), 1.58–1.25 (m, 54H), 0.87–0.85 (m, 24H).

1.6. Characterization

The NMR spectra were measured using Bruker AVANCE 400 MHz spectrometer. Mass spectra were measured using a Solarix FF-ICR-MS Analyzer in the MALDI mode. Solution and thin film (on a quartz substrate) UV-vis absorption spectra were recorded using a Perkin-Elmer Lambda 25 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammoniumhexafluorophosphate (0.1 M) in CH₃CN using an electrochemical workstation with a scan rate of 100 mV s⁻¹ using the polymer thin film on ITO (indium tin oxide) glass as the working electrode, Pt wire as the counter electrode, and Ag/AgNO₃ electrode as the reference electrode. The potentials were referenced to ferrocene/ferrocenium couple by using ferrocene as an internal standard. Thermogravimetric analyses (TGA) were performed by using a Netzsch TG209 analyzer under nitrogen atmosphere at a heating rate of 20 °C min⁻¹. The average molecular weight and poly dispersity index (PDI) of the polymers were determined by Waters 1515 gel permeation chromatography (GPC) analysis with polystyrene as the standard. The morphology of blended film was observed using a Digital Instruments Enviro Scope atomic force microscope (AFM) in the tapping mode. **Differential scanning calorimetric measurement (DSC) was performed on a TA DSC Q10 instrument at a heating rate of 10 °C min⁻¹. Wide angle X-ray diffraction (WAXRD) of the polymer films was performed by Bruker D8 ADVANCE with Cu-K_α radiation.**

1.7. Fabrication and characterization of the polymer solar cells

The photovoltaic cells were constructed in the traditional sandwich structure through several steps. The BHJ solar cells were prepared on pre-patterned commercial indium tin oxide (ITO) glass substrates. The active area of each solar cell device is 0.06 cm². The ITO coated glass substrates were cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol, then treated with a nitrogen-oxygen plasma oven for 5 min. The photovoltaic cells were constructed in the

conventional device configuration with traditional sandwich structure through the following several steps. First, a poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, from Bayer AG) thin film was spin-coated from an aqueous solution on a cleaned ITO glass substrate giving a thickness of about 30 nm (measured by Ambios Technology XP-2 surface profilometer), and then it was baked at 150 °C for 15 min. Secondly, an active layer (about 110 nm) was spin-coated on top of the PEDOT-PSS from the a solution of chlorobenzene (20 mg mL⁻¹ in CB) of the polymer: PCBM blends (1:1 - 1:3 weight ratio), and then annealed at 100°C for 15 min in a nitrogen-filled glove box. Finally, 0.5 nm of LiF and 100 nm of aluminum (Al) cathodes were deposited on the top of the active layer in a vacuum of 2×10^{-4} Pa to complete the photovoltaic device fabrication. Current density-voltage (*J-V*) characteristics were measured by a Keithley 2400 Source Meter under AM 1.5G 100 mW cm⁻² irradiation, and the incident light intensity was calibrated using a standard Si solar cell. The IPCE data were obtained using a solar cell spectral response measurement system (QER3011,Enli Technology Co. Ltd).

S2. Thermal properties

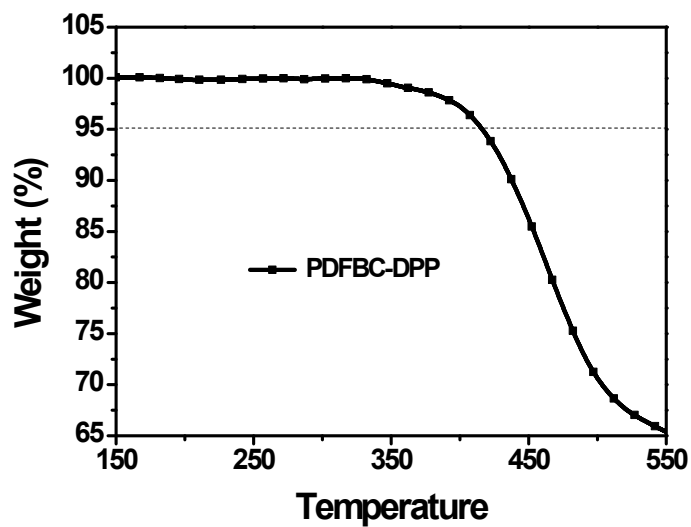


Fig. S1 TGA curves for the PDFBC-DPP

S3. Theoretical calculation

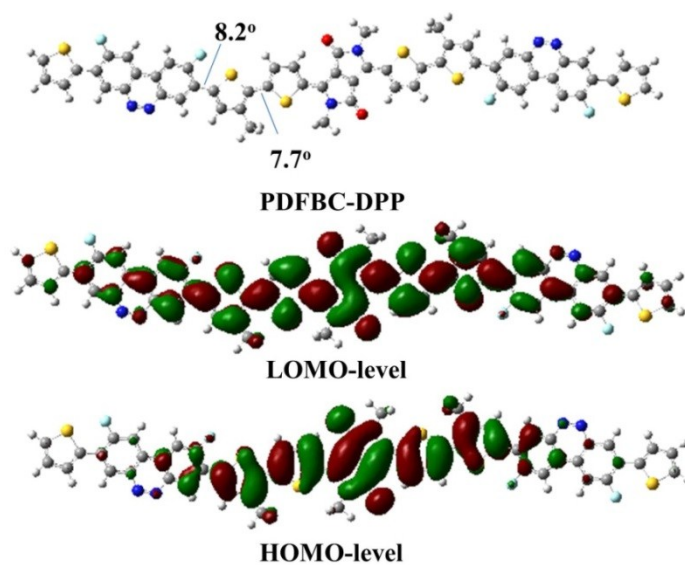


Fig. S2 Optimized frontier molecular orbitals using DFT evaluated at the B3LYP/6-31G(d) level of theory.

S4. Optical and electrochemical properties

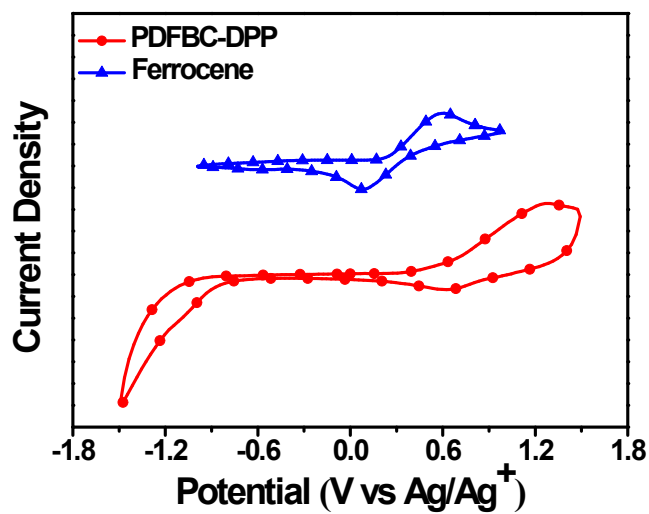


Fig. S3 Cyclic voltammogram of PDFBC-DPP in CH₃CN/0.1 M Bu₄NPF₆

Table S1: Optical and Electrochemical Properties of PDFBC-DPP

Polymer	Solution	Solution	Film ^a	λ_{onset} (nm)	E_g^{opt} (eV)	HOMO (eV) ^b	LUMO (eV) ^b	E_g^{EC} (eV)
	λ (CF) (nm)	λ (<i>o</i> -DCB) (nm)	λ (nm)					
PDFBC-DPP	664/713	664/713	671/725	793	1.56 ^c	-5.35	-3.82	1.53

a. Cast from chloroform solution.

b. HOMO= -e ($E_{\text{ox}} + 4.77$) (eV); LUMO= -e ($E_{\text{red}} + 4.77$) (eV)

S5. Photovoltaic properties

Table S2 Photovoltaic properties and hole mobilities of the polymer **PDFBC-DPP**.

Active layer	DIO: CB (volume)	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF (%)	PCE_{max} (PCE_{ave})(%)	μ_h (cm ² V ⁻¹ s ⁻¹)
PDFBC-DPP:PC ₆₁ BM=1:1	3: 97	0.80	13.15	0.68	7.33(7.01)	
PDFBC-DPP:PC ₆₁ BM=1:2	3: 97	0.79	12.12	0.69	6.95(6.64)	
PDFBC-DPP:PC ₆₁ BM=1:3	3: 97	0.79	10.28	0.70	6.05(5.72)	
PDFBC-DPP:PC ₆₁ BM=1:1	0	0.79	8.30	0.53	3.57(3.45)	
PDFBC-DPP:PC ₇₁ BM=1:1	0	0.79	11.87	0.65	6.11(5.97)	1.03×10 ⁻⁴
PDFBC-DPP:PC ₇₁ BM=1:1	1: 99	0.78	13.42	0.68	7.14(7.06)	
PDFBC-DPP:PC ₇₁ BM=1:1	2: 98	0.78	14.58	0.70	7.92(7.63)	1.85×10 ⁻⁴
PDFBC-DPP:PC ₇₁ BM=1:1	3: 97	0.78	13.86	0.71	7.71(7.52)	

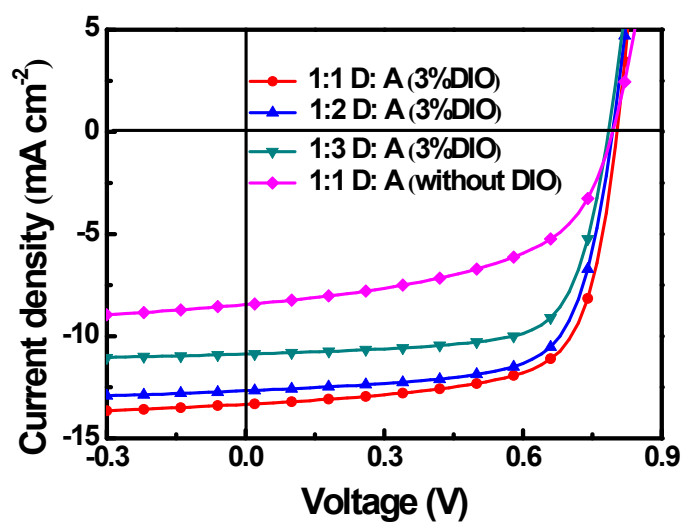


Fig. S4 J - V curves of the PSC devices with different weight ratio (PDFBC-DPP: PC₆₁BM) under the illumination of AM 1.5 G, 100 mW cm⁻²

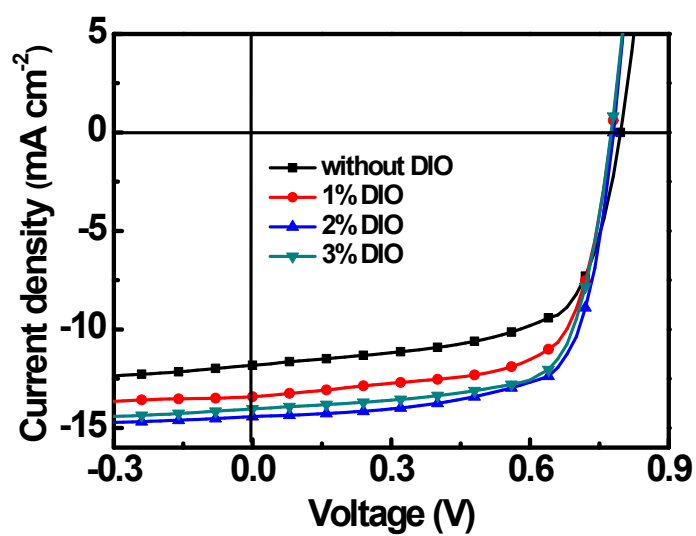


Fig. S5 J - V curves of the PSC devices (PDFBC-DPP: PC₇₁BM=1: 1) under the illumination of AM 1.5 G, 100 mW cm⁻²

S6. ^1H NMR, ^{13}C NMR and MS data

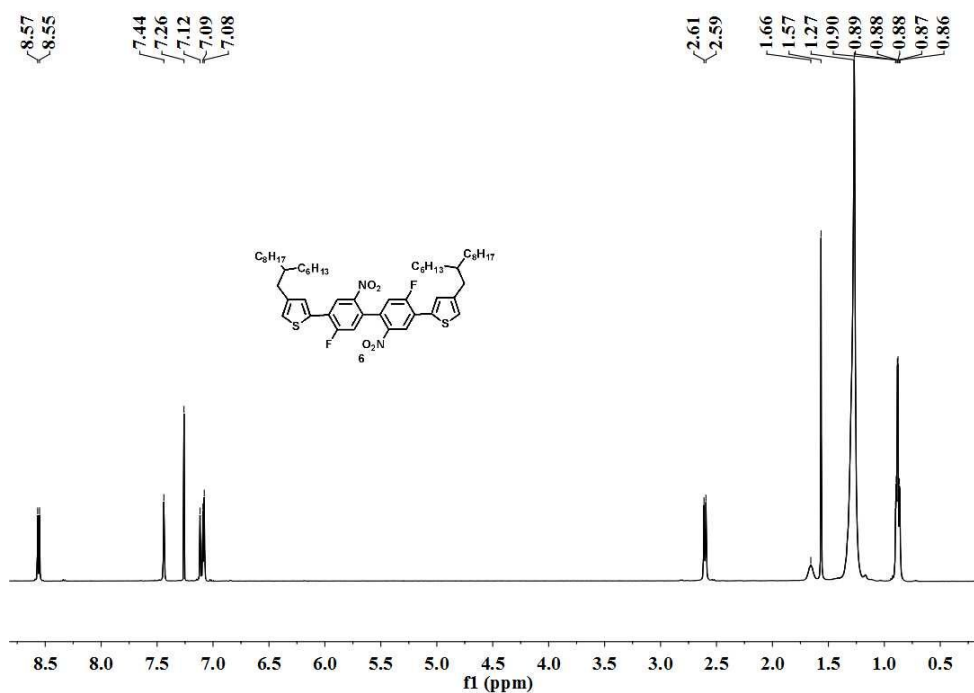


Fig. S6 ^1H NMR spectrum of 4,4'- bis(4-(2-hexyldecyl)thiophene)- 5,5'-difluoro-2,2'-dinitro- [1,1'-biphenyl]

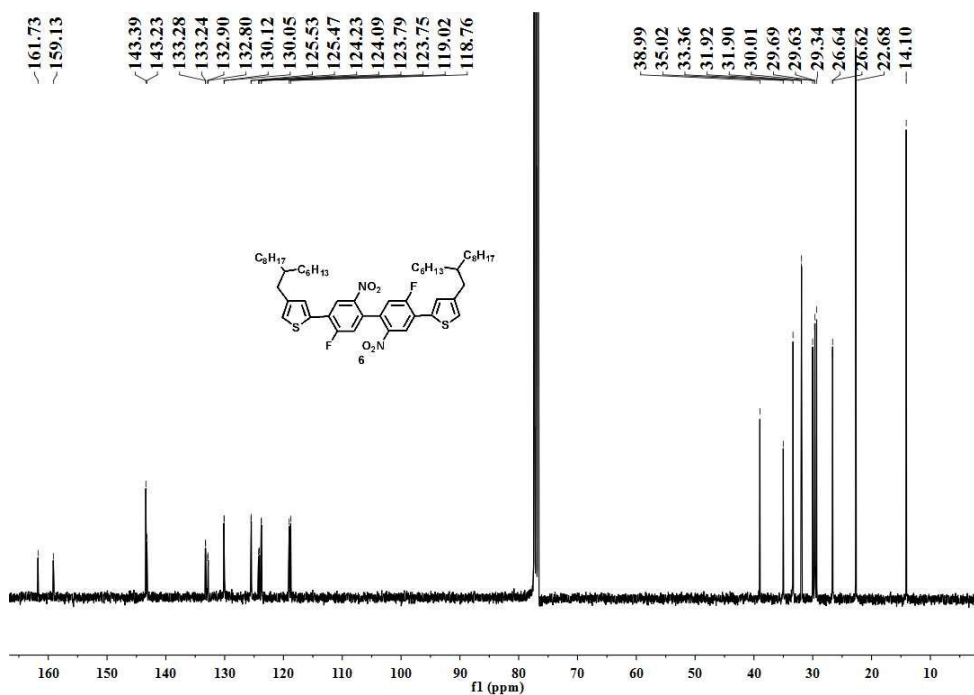


Fig. S7 ^{13}C NMR spectrum of 4,4'- bis(4-(2-hexyldecyl)thiophene)- 5,5'-difluoro-2,2'-dinitro- [1,1'-biphenyl]

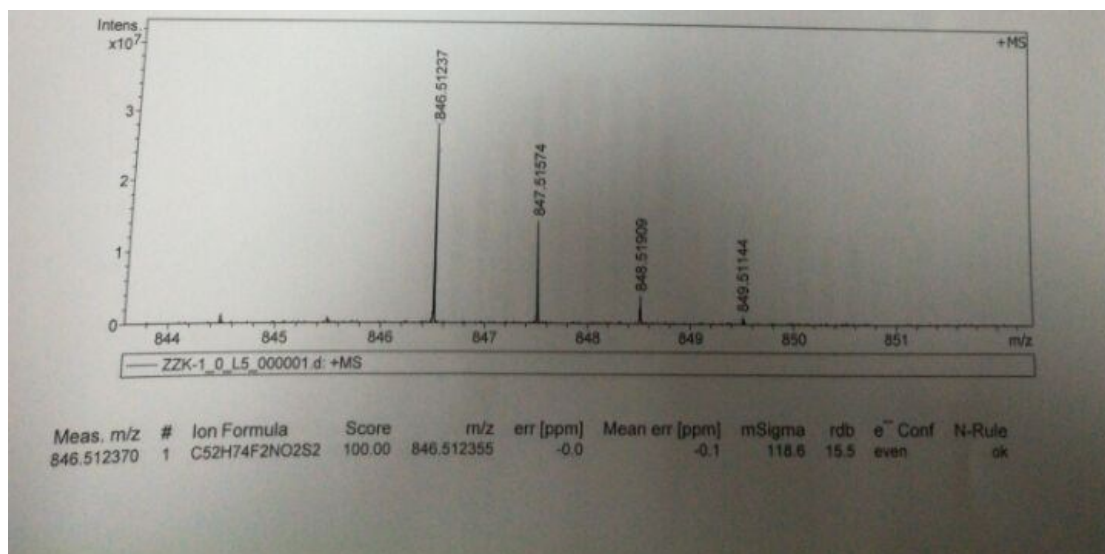


Fig. S8 MS spectrum of 4,4'- bis(4-(2-hexyldecyl)thiophene)-5,5'-difluoro-2,2'-dinitro- [1,1'-biphenyl]

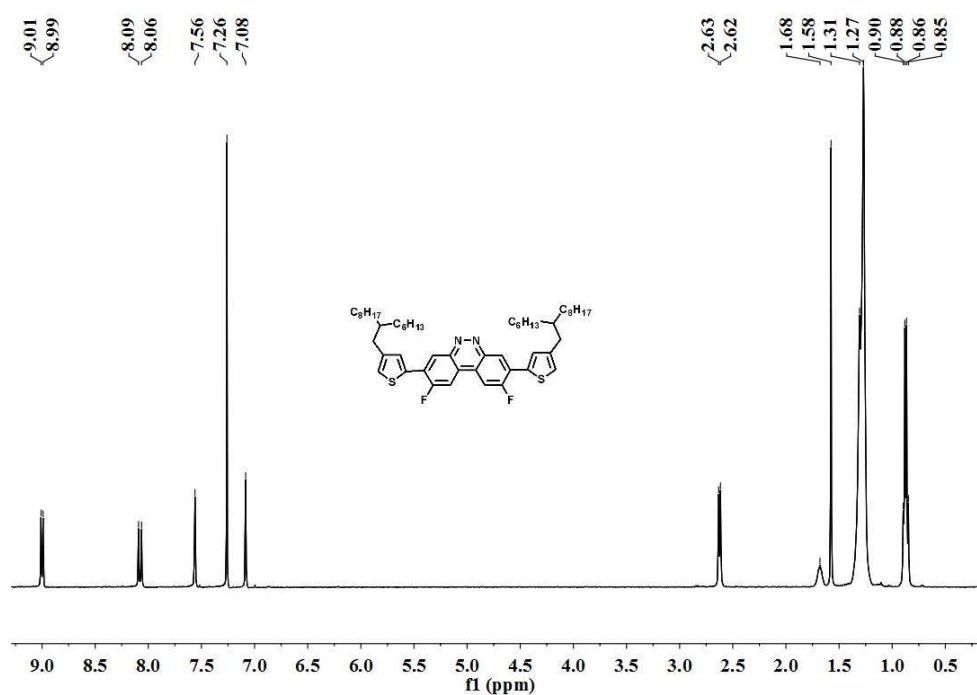


Fig. S9 ^1H NMR spectrum of 2,9-difluoro-3,8-bis(4-(2-hexyldecyl)-2-thienyl)benzo[c]cinnoline

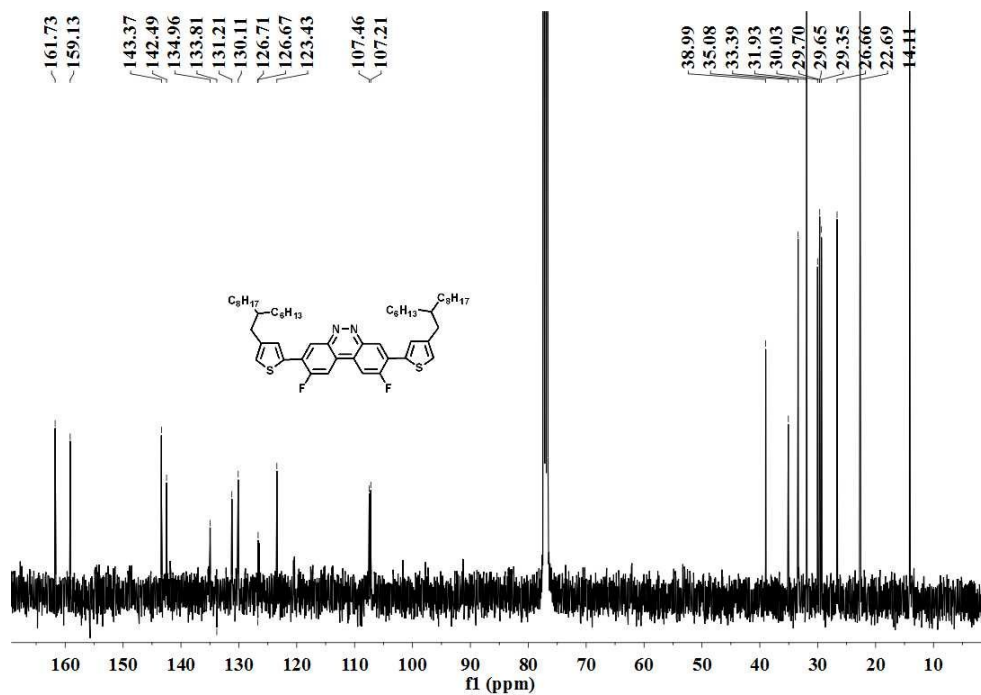


Fig. S10 ¹³CNMR spectrum of 2,9-difluoro-3,8-bis(4-(2-hexyldecyl)-2-thienyl)benzo[c]cinnoline

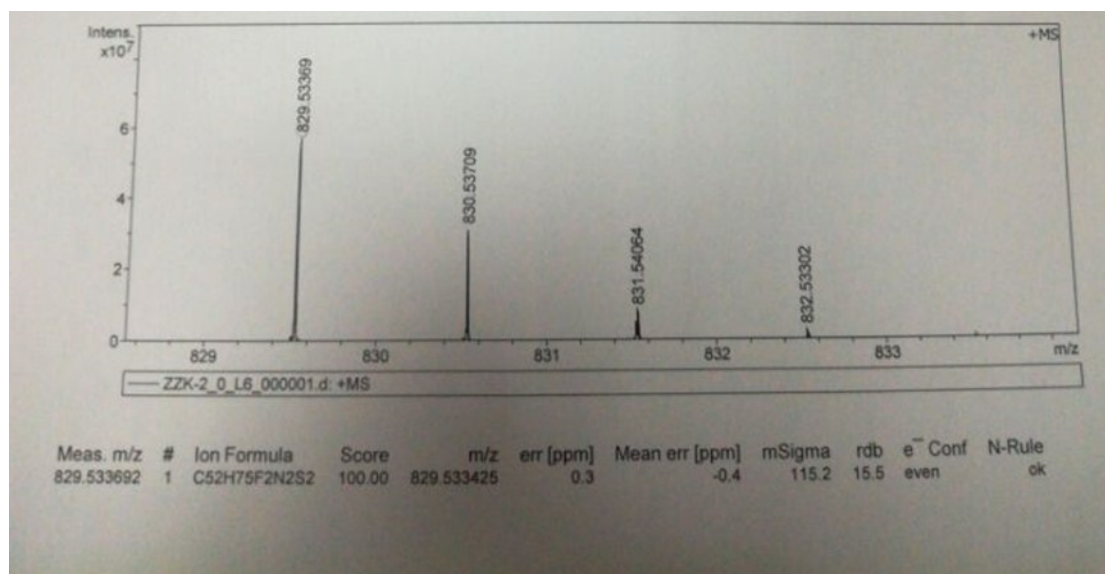


Fig. S11 MS spectrum of 2,9-difluoro-3,8-bis(4-(2-hexyldecyl)-2-thienyl)benzo[c]cinnoline

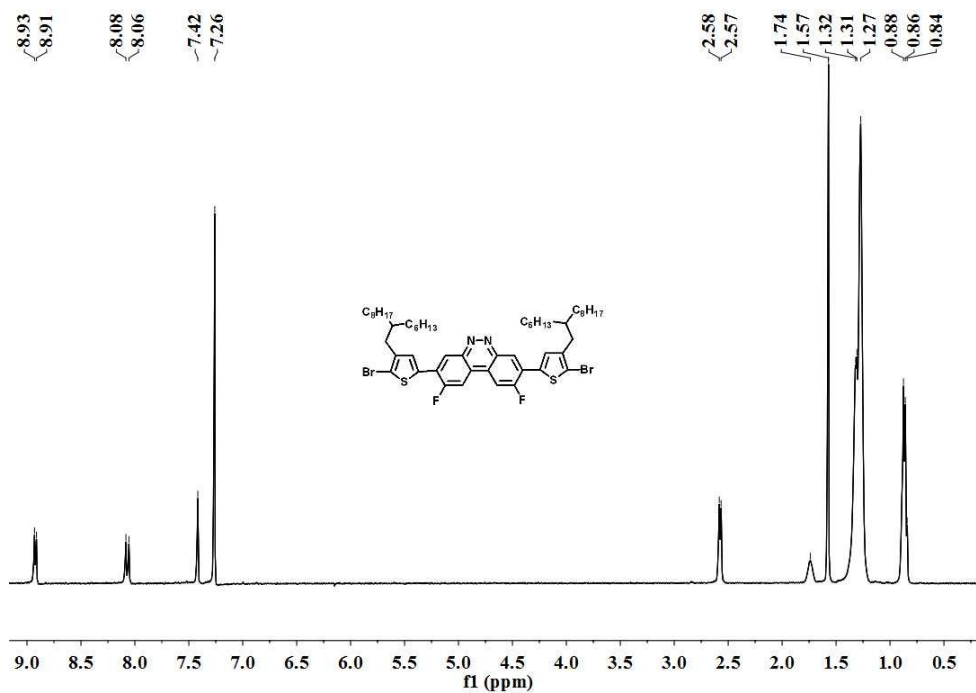


Fig. S12 ^1H NMR spectrum of 2,9-difluoro-3,8-bis(5-bromo-4-(2-hexyldecyl)-2-thienyl)-benzo[c]cinnoline

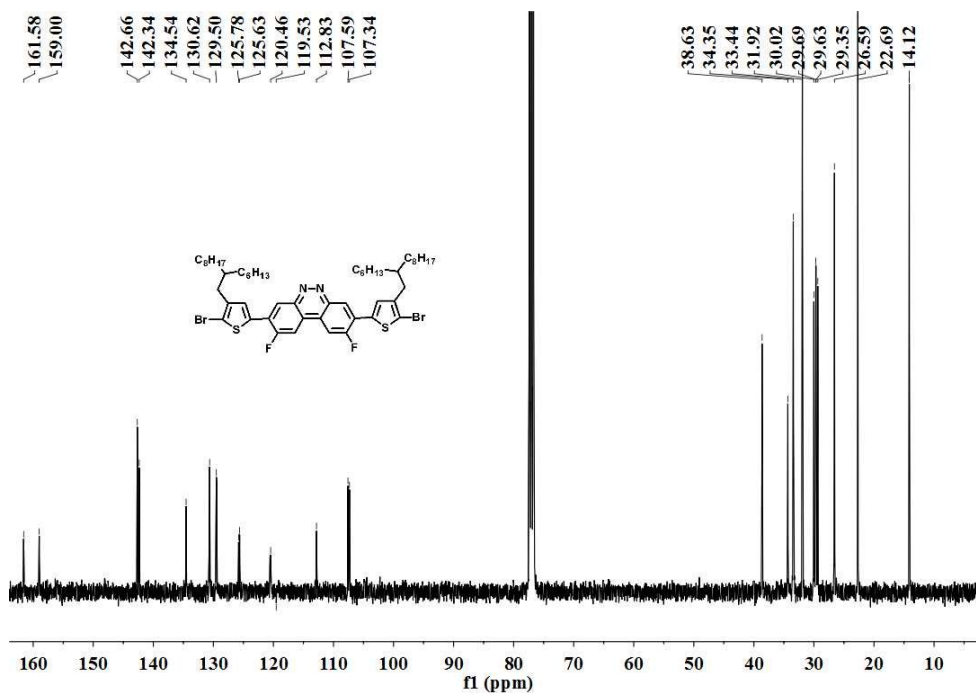


Fig. S13 ^{13}C NMR spectrum of 2,9-difluoro-3,8-bis(5-bromo-4-(2-hexyldecyl)-2-thienyl)-benzo[c]cinnoline

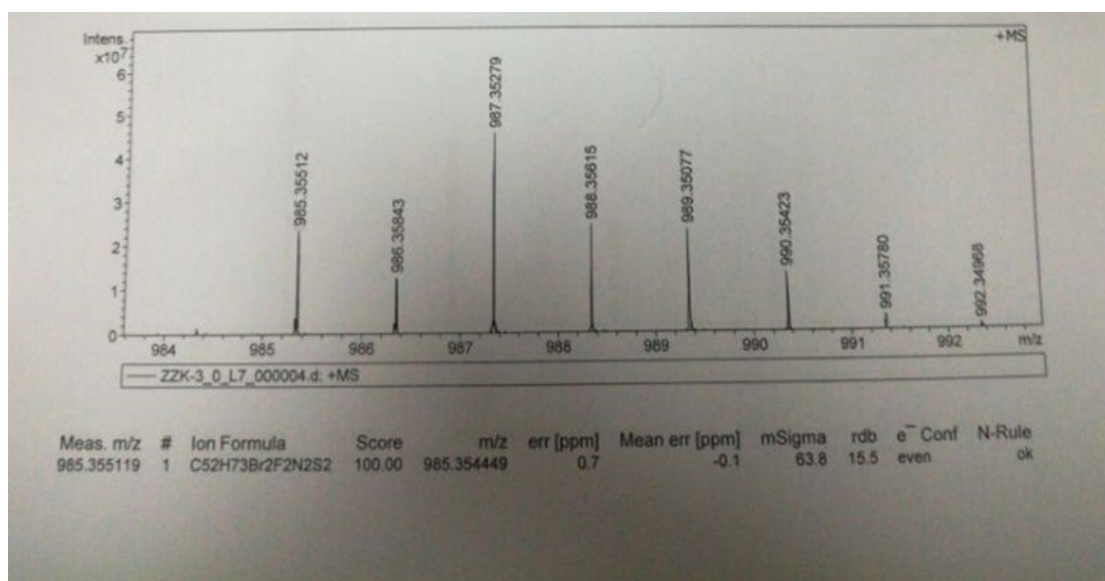


Fig. S14 MS spectrum of 2,9-difluoro-3,8-bis(5-bromo-4-(2-hexyldecyl)-2-thienyl)benzo[c]cinnoline (M_1)

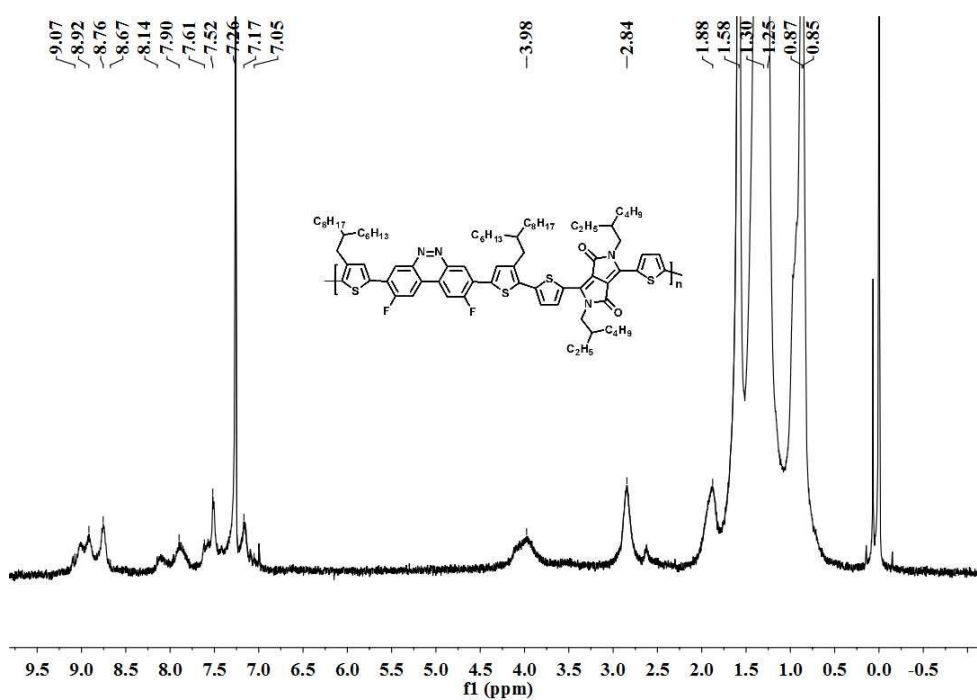


Fig. S15 ^1H NMR spectrum of PDFBC-DPP

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