Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Conjugated Terpolymers by Incorporating Anthracene Units into the Backbones of the Diketopyrrolopyrrole-Based Polymers as Electron Donors for Photovoltaic Cells

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1. Materials and Characterization.

The reagents and starting materials were commercially available and used without any further purification, if not specified elsewhere. Compound 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (monomer **2**) and 2,5-bis(trimethylstannyl)thiophene (monomer **1**) were synthesized according to the previous report. (*J. Am. Chem. Soc.*, 1995, **117**, 12426-12435)

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz and 500MHz spectrometer. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. Gel permeation chromatography (GPC) analysis was performed on an PL-GPC 220 High Temperature Chromatograph at 150 ^{o}C equipped with a IR5 detector; polystyrene was used as the calibration standard and 1,2,4-trichlorobenzene as eluent; the flow rate was 1.0 mL/min. Thermogravimetric analysis (TGA) was carried out from room temperature to 550 ^{o}C with a heating rate of 10 ^{o}C/min. under a dry nitrogen flow. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a glassy carbon working electrode, a Pt counter electrode and a Ag/AgCl (saturated KCl)reference electrode on a computer-controlled CHI660C instruments at room temperature; the scan rate was 100 mV·s^{-1}, and n-Bu$_4$NPF$_6$ (0.1 M) was used as the supporting electrolyte. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc+) was measured under the same conditions. The onset oxidation and reduction potentials were presented by reference to the redox potential of ferrocene/ferrocenium (Fc/Fc+). UV-vis absorption spectra were measured with JASCO V-570 UV-Vis spectrophotometer. The GIXRD data were obtained at beamline of 1W1A of the Beijing Synchrotron Radiation Facility. AFM- images were obtained on a Nanoscope V AFM (Digital Instruments) in tapping mode.

Synthesis of PADPP1. 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrr-ole-1,4-dione (monomer **2**) (228.6 mg, 0.225 mmol), 2,5-bis(trimethylstannyl)thiophene (monomer **1**) (102.8 mg, 0.25 mmol) and 2,6-dibromoanthracene (8.3 mg, 0.025 mmol) (monomer **3**) were taken in a Schlenk tube under nitrogen atmosphere with 10 mL of anhydrous toluene. Tris(dibenzylideneacetone)dipalladium (0) (Pd$_2$(dba)$_3$) (4.4 mg, 0.01 mmol) and tri(o-tolyl)phosphine (P(o-tol)$_3$) (3.5 mg, 0.08 mmol) were added in one portion. The tube was charged with nitrogen through a freeze–pump–thaw cycle for three times. The mixture was stirred for 72 h at 100 °C under nitrogen. After cooling to room temperature, the highly viscous black gel-like solution was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone, hexane and chloroform sequentially. The residue was collected and dried under vacuum to afford **PADPP1** (155.2 mg, 71.2%). ^{1}H NMR (500 MHz; 1,1,2,2-tetrachloroethane-d$_2$; 100 ^{o}C): δ = 8.79 (m, br), 6.98 (m, br), 3.94 (m, br), 1.90 (m, br), 1.33-1.17 (m, br), 0.91-0.79 (m, br). ^{13}C NMR (100 MHz, solid): δ = 160.8, 140.8, 137.1, 129.0, 124.5, 108.7, 45.8, 39.0, 30.5, 23.5, 14.8. M_w/M_n (GPC): 184/63 kDa, PDI = 2.8. Anal. calcd for $[(C_{18}H_{10}S)_1(C_{58}H_{88}N_2O_2S_3)_9]_n$: C, 74.28; H, 9.26; N, 2.89; S, 10.28. Found: C, 73. 58; H, 8.75; N, 2.81;S, 10.20.

Synthesis of PADPP2. Monomer **2** (203.2 mg, 0.2 mmol), monomer **1** (102.8 mg, 0.25 mmol) and monomer **3** (16.7 mg, 0.05 mmol) were taken in a Schlenk tube under nitrogen atmosphere with 10 mL of anhydrous toluene. Tris(dibenzylideneacetone)dipalladium (0) (Pd$_2$(dba)$_3$) (4.4 mg, 0.01 mmol) and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$) (3.5 mg, 0.08 mmol) were added in one portion. The tube was charged with nitrogen through a freeze−pump−thaw cycle for three times. The mixture was stirred for 72 h at 100 °C under nitrogen. After cooling to room temperature, the highly viscous black gel-like solution was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone, hexane and chloroform sequentially. The residue was collected and dried under vacuum to afford **PADPP2** (152.6 mg, 75.9%). ^{1}H NMR (500 MHz; 1,1,2,2-tetrachloroethane-d$_2$; 100 ^{o}C): δ = 8.67 (m, br), 7.96 (m, br), 7.74 (m, br), 7.48-7.13 (m, br), 6.89 (m, br), 3.94-3.88 (m, br), 2.09-1.90 (m, br), 1.33-1.18 (m, br), 0.79 (m, br). ^{13}C NMR (100 MHz, solid): δ = 160.8, 153.2, 141.1, 137.1, 129.0, 124.2, 108.5, 45.9, 38.9, 30.5, 23.5, 14.8. M_w/M_n (GPC): 167/59 kDa, PDI = 2.7. Anal. calcd for $[(C_{18}H_{10}S)_2(C_{58}H_{88}N_2O_2S_3)_8]_n$: C, 74.61; H, 9.07; N, 2.78; S, 10.36. Found: C, 73.20; H, 8.86; N, 2.74; S, 11.01.

Synthesis of PADPP3. Monomer **2** (177.8 mg, 0.175 mmol), monomer **1** (102.8mg, 0.25 mmol) and monomer **3** (23.1mg, 0.075 mmol) were taken in a Schlenk tube under nitrogen atmosphere with 10 mL of anhydrous toluene. Tris(dibenzylideneacetone)dipalladium (0) (Pd$_2$(dba)$_3$) (4.4 mg, 0.01 mmol) and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$) (3.5 mg, 0.08 mmol) were added in one portion. The tube was charged with nitrogen through a freeze−pump−thaw cycle for three times. The mixture was stirred for 72 h at 100 °C under nitrogen. After cooling to room temperature, the highly viscous black gel-like solution was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone, hexane and chloroform sequentially. The residue was collected and dried under vacuum to afford **PADPP3** (144.4 mg, 78.5%). ^{1}H NMR (500 MHz; 1,1,2,2-tetrachloroethane-d$_2$; 100 ^{o}C): δ = 8.78 (m, br), 8.00 (m, br), 7.75 (m, br), 7.48-7.35 (m, br), 6.98 (m, br), 3.92 (m, br), 1.94-1.90 (m, br), 1.33-1.19 (m, br), 0.79 (m, br). ^{13}C NMR (100 MHz, solid): δ = 160.8, 140.8, 137.1, 129.0, 124.2, 108.7, 45.9, 38.7, 30.6, 23.5, 14.8. M_w/M_n (GPC): 175/69 kDa, PDI = 2.6. Anal. calcd for $[(C_{18}H_{10}S)_3(C_{58}H_{88}N_2O_2S_3)_7]_n$: C, 75.01; H, 8.84; N, 2.66; S, 10.45. Found: C, 74.60; H, 8.45; N, 2.46; S, 10.20.

Synthesis of PDPP3T. Monomer **2** (254.0 mg, 0.25 mmol) and monomer **1** (102.8mg, 0.25 mmol were taken in a Schlenk tube under nitrogen atmosphere with 10 mL of anhydrous toluene. Tris(dibenzylideneacetone)dipalladium (0) ($Pd_2(dba)_3$) (4.4 mg, 0.01 mmol) and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$) (3.5 mg, 0.08 mmol) were added in one portion. The tube was charged with nitrogen through a freeze−pump−thaw cycle for three times. The mixture was stirred for 72 h at 100 °C under nitrogen. After cooling to room temperature, the highly viscous black gel-like solution was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone, hexane and chloroform sequentially. The residue was collected and dried under vacuum to afford **PDPP3T** (169.9 mg, 72.3%). ^{1}H NMR (500 MHz; 1,1,2,2-tetrachloroethane-d$_2$; 100 ^{o}C): δ = 8.78 (m, br), 6.98 (m, br), 3.95 (m, br), 1.90 (m, br), 1.33-1.17 (m, br), 0.78-0.77 (m, br). ^{13}C NMR (100 MHz, solid): δ = 160.9, 141.0, 137.4, 129.1, 124.8, 108.7, 45.9, 38.6, 30.4, 23.4, 14.7.M_w/M_n (GPC): 155/72 kDa, PDI = 2.3. Anal. calcd for $(C_{58}H_{88}N_2O_2S_3)_n$: C, 73. 99; H, 9.42; N, 2.98; S, 10.22. Found: C, 73. 27; H, 9.19; N, 2.91; S, 9.69.

2. DSC analysis of PADPP1, PADPP2, PADPP3 and PDPP3T

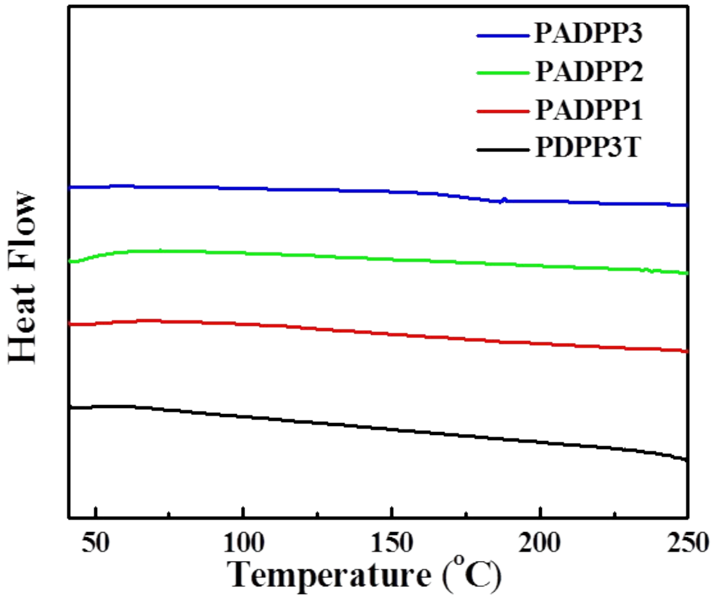


Fig. S1 DSC curves (endo up) of **PADPP1**, **PADPP2**, **PADPP3** and **PDPP3T**: heating rate: 10 ^{o}C/min, from 40 ^{o}C to 250 ^{o}C under nitrogen atmosphere.

3. Cyclic voltammograms of PADPP1, PADPP2, PADPP3 and PDPP3T

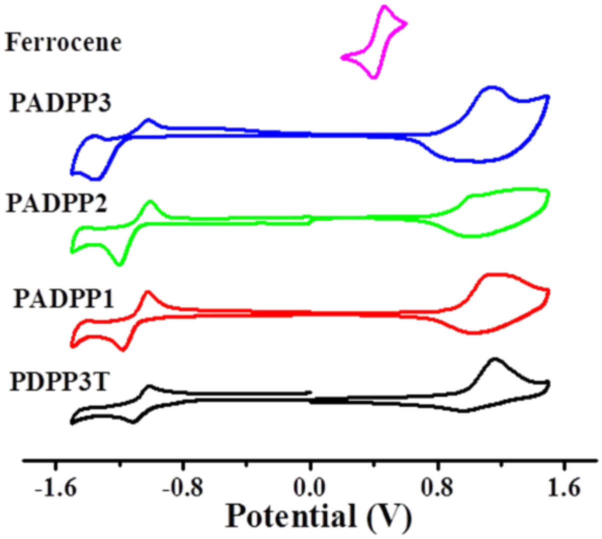


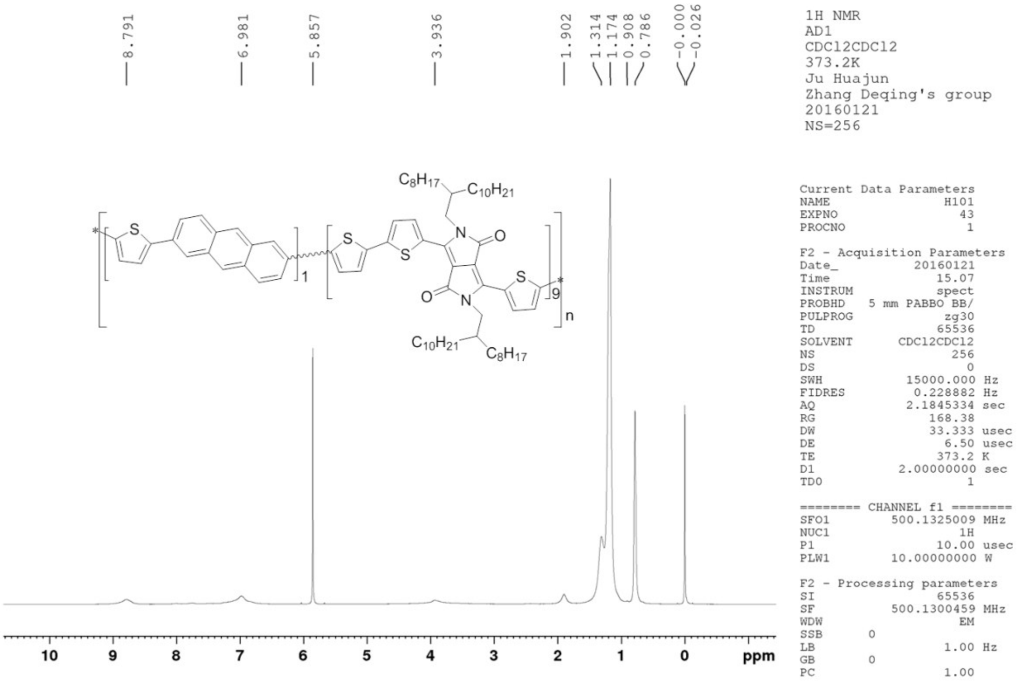
Fig. S2 Cyclic voltammograms of thin films of **PADPP1**, **PADPP2**, **PADPP3** and **PDPP3T** at a scan rate of 100 mVs^{-1}, with Pt as the working and counter electrodes and an Ag/AgCl electrode (saturated KCl) as the reference electrode, and n-Bu$_4$NPF$_6$ (0.1M) as supporting electrolyte.

4. Fabrication of photovoltaic cells

OPVs were fabricated with ITO as the positive electrode and Al as the negative electrode. The patterned tin oxide (ITO) glass (sheet resistance = 15 Ω^{-1}) was pre-cleaned in an ultrasonic bath of acetone and isopropyl alcohol and treated in an ultraviolet-ozone chamber (Jelight Company, USA) for 30 min. A thin layer (30 nm) of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass and baked at 150 ^{o}C for 15 min. A *o*-dichlorobenzene solution (10mg/mL of polymer) of the respective polymers with PC$_{71}$BM was subsequently spin-coated on the PEDOT: PSS layer to form the active layer. The thickness (ca. 100-120 nm) of the active layer was measured using an Ambios Technology XP-2 profilometer. A Ca (ca. 20 nm) and aluminium layer (ca. 70 nm) were then evaporated onto the surface of the active layer under vacuum (ca. 10^{-5} Pa) to form the negative electrode. The active area of the device was 4.0 mm^2. The *J–V* curves were measured with a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp coupled with AM1.5 solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2}. The incident photon to converted current efficiency (IPCE) spectra was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and a 500 W xenon lamp.

5. ^{1}H NMR and solid State ^{13}C NMR spectra

^{1}H NMR of **PADPP1**



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Ju Huajun
Zhang Deqing's group
20160121
NS=256

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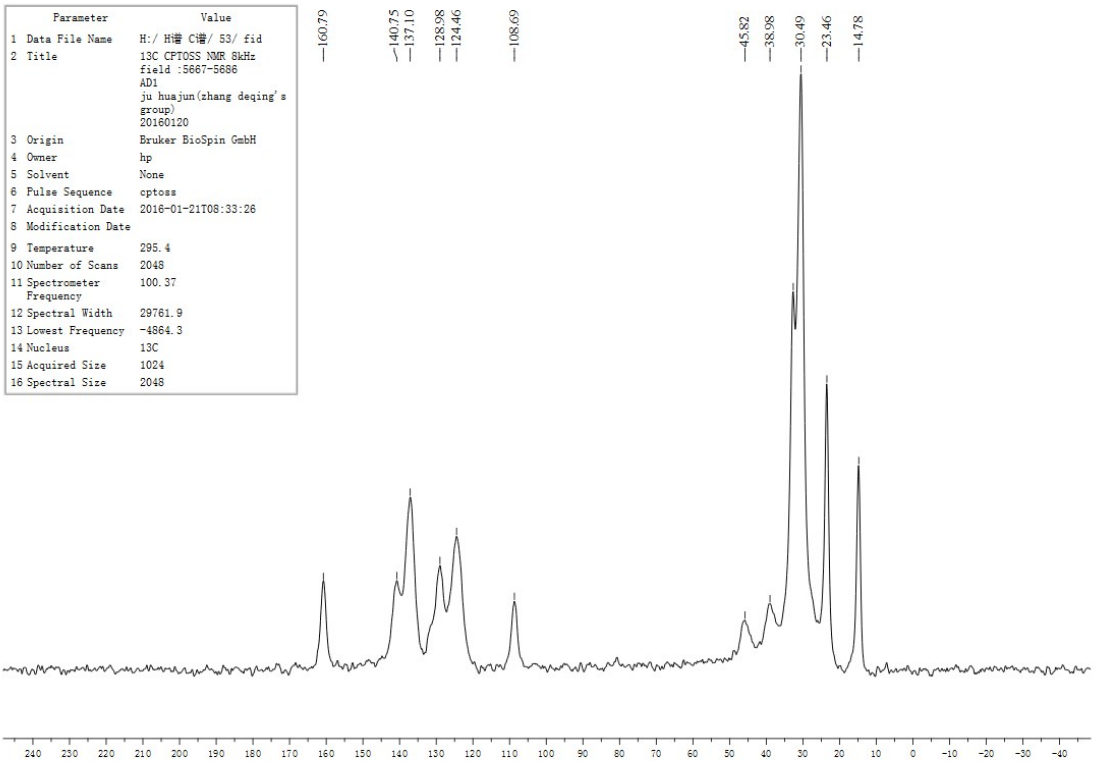

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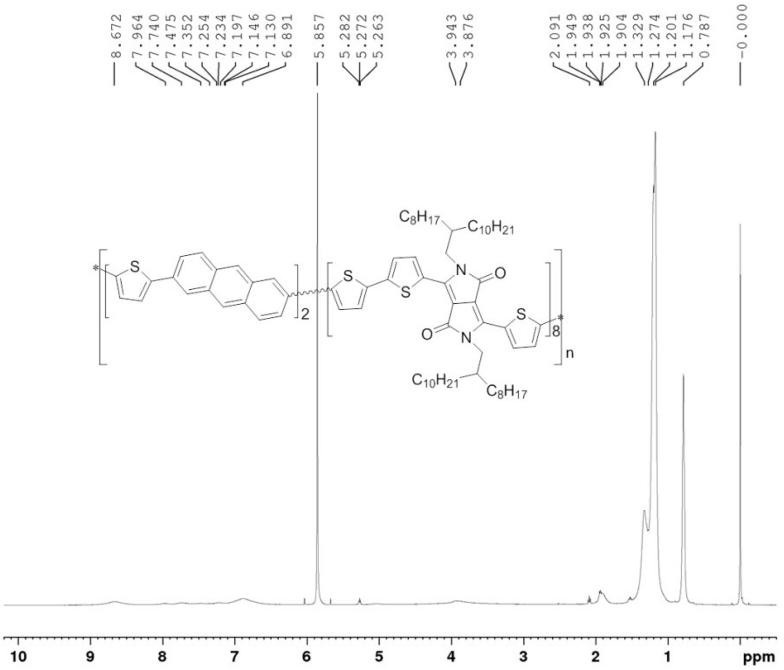

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Ju Huajun
Zhang Deqing's group
20160121
NS=896

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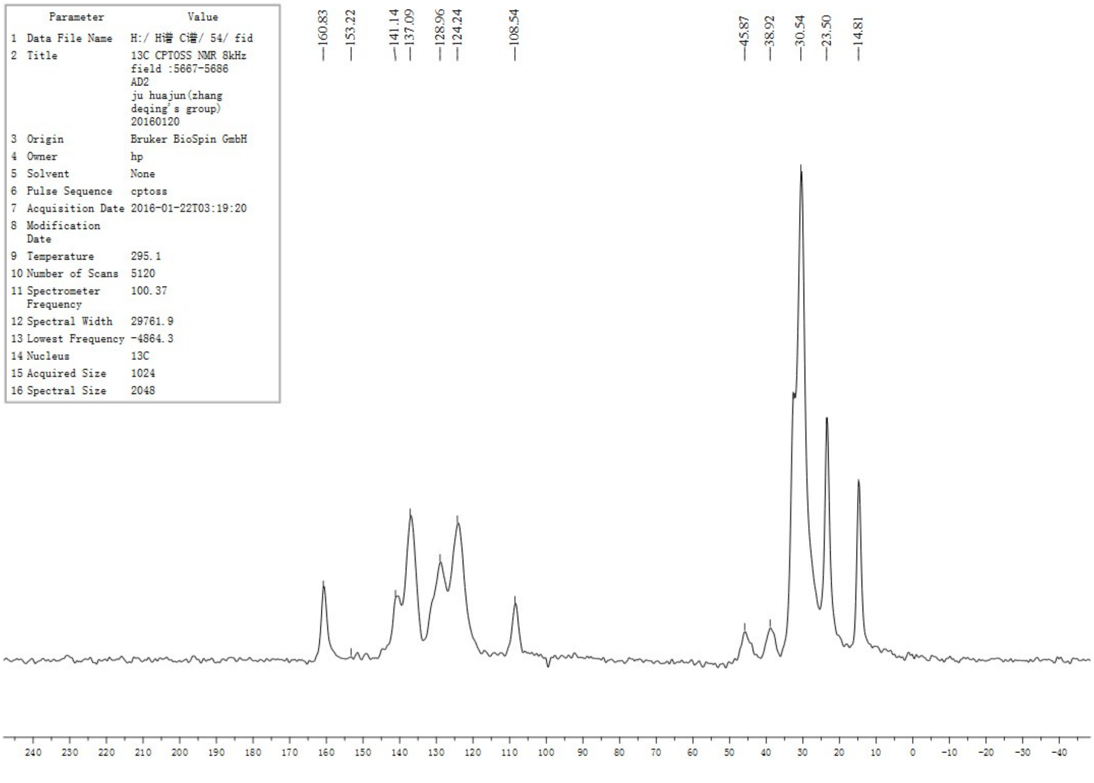

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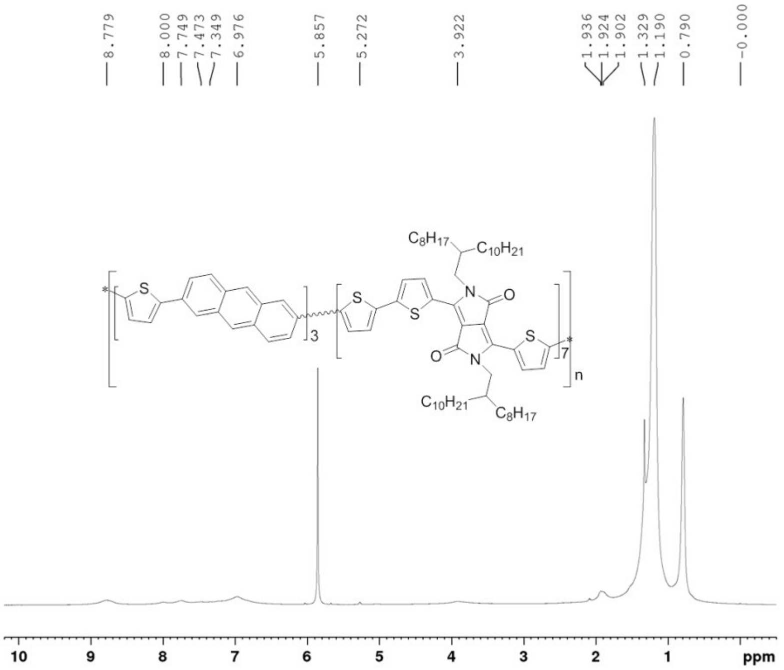

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Ju Huajun
Zhang Deqing's group
20160121
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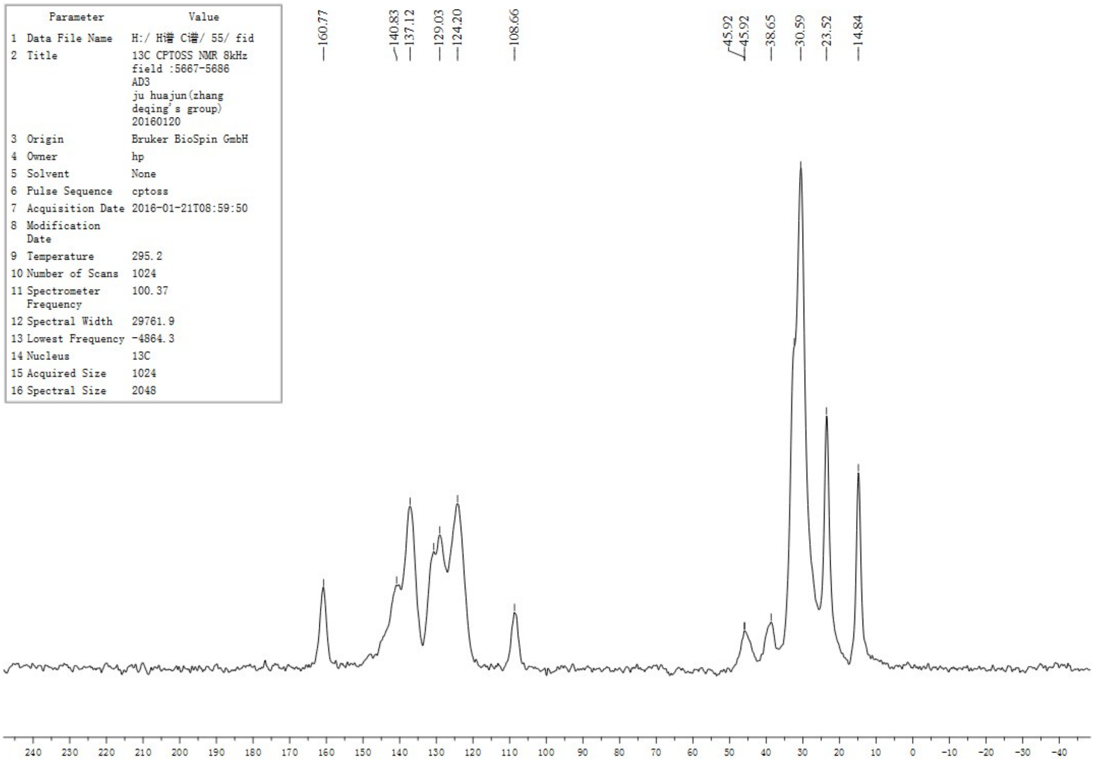

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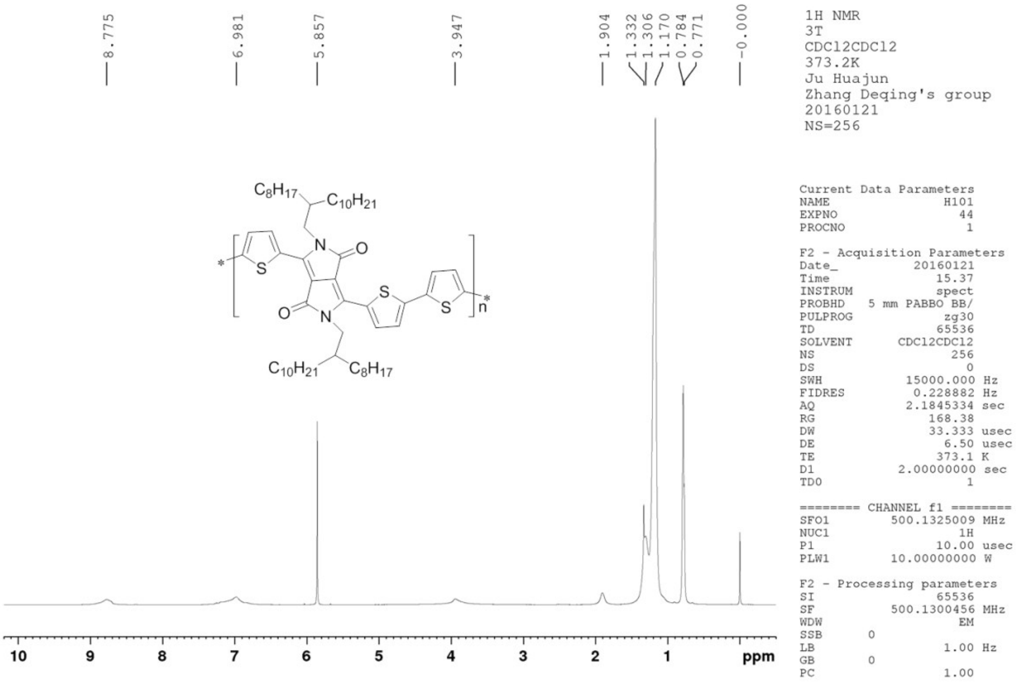

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Ju Huajun
Zhang Deqing's group
20160121
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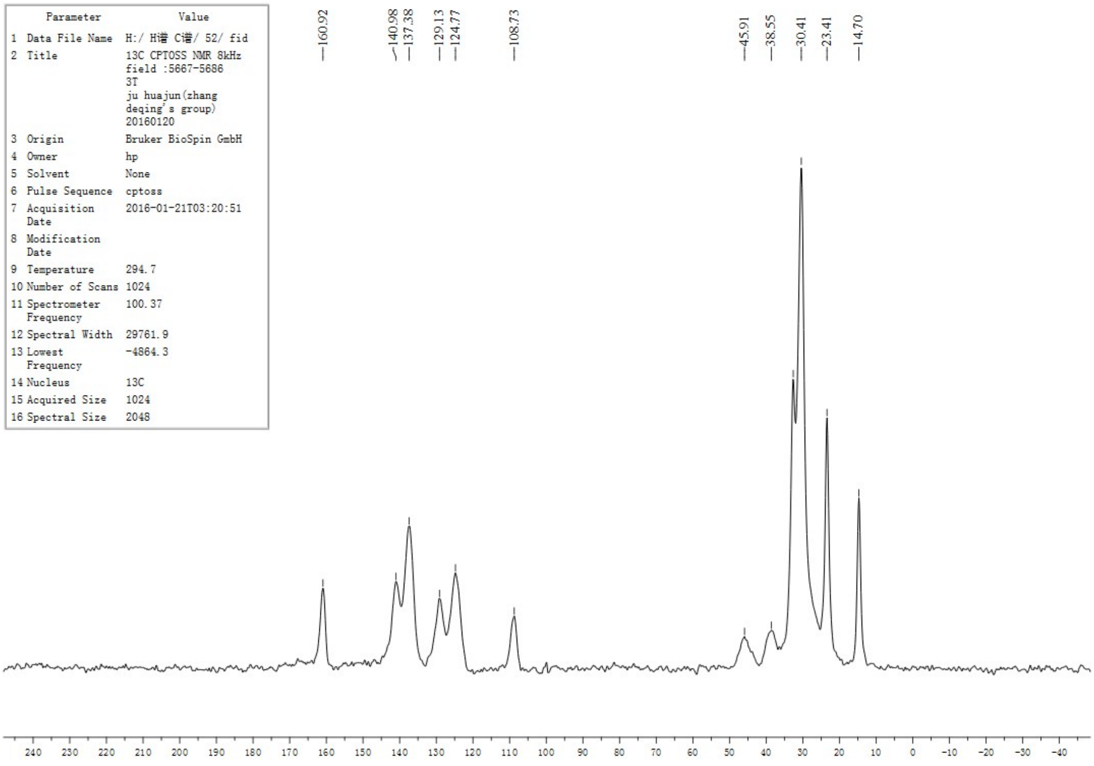
Solid State ^{13}C NMR of **PDPP3T**



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