Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 800-803

New benzodithiophene-pyrrolopyrroledione-thienopyrazine random terpolymers for organic photovoltaics

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Experimental details

Instruments.

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) or an Agilent 600 MHz DD2 nuclear magnetic resonance (NMR) spectrometer. The number-average (M_n) and weight-average (M_w) polymers' molecular weights were measured through gel permeation chromatography (GPC) using a Waters 717-2410 instrument with polystyrene as the reference standard and chloroform as the eluent. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Thermogravimetric analysis (TGA) measurements were done by a "Derivatograph-C" (MOM, Hungary) at a heating rate 20°C/min in argon. HOMO/LUMO of the polymer films were determined by cyclic voltammetry (CV) experiments on a computer controlled potentiostat "Autolab type III" at a scan rate of 100 mVs^{-1}. A platinum plate with pristine polymer film, Ag/AgNO$_3$ (0.1 M in anhydrous acetonitrile), and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively, in a nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) solution (0.1 M in anhydrous acetonitrile). Assuming the absolute energy level of Fc/Fc$^+$ to be -4.44 eV versus vacuum level, thus the HOMO and LUMO energy levels were obtained from the equation of $E_{HOMO}/E_{LUMO} = -(E_{ox}/E_{red} + 4.44)$ (eV), where oxidation/reduction onset potential (E_{ox}/E_{red}) were determined from the position at which the current raised initially from the baseline.

Device fabrication and characterization

We have fabricated the PSCs using the conventional device configuration i.e., ITO/PEDOT:PSS/active layer/ PFN/Al. The commercially purchased indium tin oxide coated glass substrates with sheet resistance about 10 Ohm/cm^2, were cleaned thoroughly in detergent and then sequentially ultra-sonicated in deionized water, acetone, and isopropyl alcohol sequentially for 15 min and then dried in vacuum oven at 40°C for 12 hrs. The solution of poly(3,4-ethylelenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was spin onto the ITO substrates at 3500 rpm for 40 s and heated at 110°C for 20 min, to achieve the thickness about 40 nm. The photoactive layer solution was prepared by mixing copolymer (donor) and PC$_{71}$BM (acceptor) with different ratios (from 1:1, to 1:3) in chloroform or chloroform/DIO with total concentration of 12 mg/mL in each blend. The active layer blend solution was spin cast on the top of the PEDOT:PSS at 2500 rpm for 20 s to achieve the thickness of 95±5 nm and then dried at room temperature. After that a thin layer of poly[(9,9-bis(3-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was spin from the solution (0.1 mg/mL in methanol) onto the top of active layer and dried for some time at room temperature. After that finally 100 nm thick aluminum (Al) was deposited through thermal evaporation at the based pressure below 1x10-4 mbar, on the top of PFN layer to complete the devices.

Photovoltaic performance investigation of the fabricated PSCs was done using a Keithley 2400 source meter and solar simulator under the simulated AM1.5G irradiation of 100 mW/cm^2. The incident photon to current conversion efficiency (IPCE) of the PSCs were measured using Bentham PVE300 IPCE system.

Synthesis and characterization of the compounds

Monomers **M1-M3** were obtained as reported (see Refs. 29-31 of the main text).

Polymers synthesis

Synthesis of polymer P1. Polymerization was performed via the Stille cross-coupling reaction. Monomers **M1** (0.4433 g, 0.5 mmol) and **M2** (0.3413 g, 0.5 mmol) were dissolved in toluene (14 ml), and the solution was flushed with argon for 20 min; $Pd(Ph_3P)_4$ (27 mg, 0.023 mmol) was added under argon, and the mixture was flushed with argon for more 20 min. Then the mixture was heated to reflux for 48 h. After cooling to room temperature, the mixture was slowly poured into methanol (400 ml). The polymer was collected by filtration and then purified via Soxhlet extraction by washing sequentially with methanol, hexane, and chloroform for 20 h. The polymer was obtained from the chloroform fraction by rotary evaporation to yield the final polymer **P1** as a dark solid with a 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 9.40–6.50 (br, Ar), 5.00–3.20 (br, CH_2), 2.25–0.25 (br, Alk). Anal. calcd (%): for $C_{64}H_{90}N_2O_4S_4$: C, 71.20; H, 8.40; N, 2.59; S, 11.88; found: C 70.20, H 8.26, N 2.63, S 10.91.

Synthesis of terpolymer P2. A mixture of **M1** (0.4433 g, 0.5 mmol), **M2** (0.2560 g, 0.375 mmol), and **M3** (0.1732 g, 0.125 mmol) in toluene was used to synthesize **P2** according to the procedure described above for **P1**. The polymer was obtained as a black solid with an 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.20–5.80 (br, Ar), 5.00–3.25 (br, CH_2), 2.50–0.25 (br, Alk). Anal. calcd (%) for: $C_{304}H_{430}F_2N_{10}O_{14}S_{17}$: C, 72.56; H, 8.61; N, 2.78; S, 10.83; F, 0.76; found: C, 71.80; H, 8.36; N, 2.83; S, 9.76; F, 0.72.

Synthesis of terpolymer P3. A mixture of **M1** (0.4423 g, 0.5 mmol), **M2** (0.1707 g, 0.25 mmol), and **M3** (0.3464 g, 0.25 mmol) in toluene was used to synthesize **P3** according to the procedure described above for **P1**. The polymer was obtained as a black solid with an 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.50–6.00 (br, Ar), 5.00–3.50 (br, CH_2), 2.70–0.25 (br, Alk). Anal. calcd (%) for $C_{176}H_{250}F_2N_6O_6S_9$: C, 73.59; H, 8.77; N, 2.93; S, 10.04; F, 1.32; found: C, 73.21; H, 8.32; N, 2.96; S, 9.64; F, 1.56.

Synthesis of terpolymer P4. A mixture of **M1** (0.4423 g, 0.5 mmol), **M2** (0.0853 g, 0.125 mmol), and M3 (0.5196 g, 0.375 mmol) in toluene was used to synthesize **P4** according to the procedure described above for **P1**. The polymer was obtained as a black solid with an 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 9.00–6.00 (br, Ar), 5.25–3.50 (br, CH_2), 2.50–0.25 (br, Alk). Anal. calcd (%) for $C_{400}H_{570}F_6N_{14}O_{10}S_{19}$: C, 74.39; H, 8.90; N, 3.04; S, 9.43; F, 1.77; found: C, 74.35; H, 8.46; N, 3.08; S, 7.92; F, 1.76.

Synthesis of polymer P5. A mixture of **M1** (0.4423 g, 0.5 mmol) and **M3** (0.6928 g, 0.5 mmol) in toluene was used to synthesize **P5** according to the procedure described above for **P1**. The polymer was obtained as a black solid with an 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 9.50–6.25 (br, Ar), 4.75–3.50 (br, CH_2), 2.50–0.25 (br, Alk). Anal. calcd (%) for $C_{112}H_{150}F_2N_4O_2S_5$: C, 75.46; H, 8.48; N, 3.14; S, 8.99; F, 2.13; found: C, 74.72; H, 8.23; N, 3.15; S, 8.43; F, 2.03.

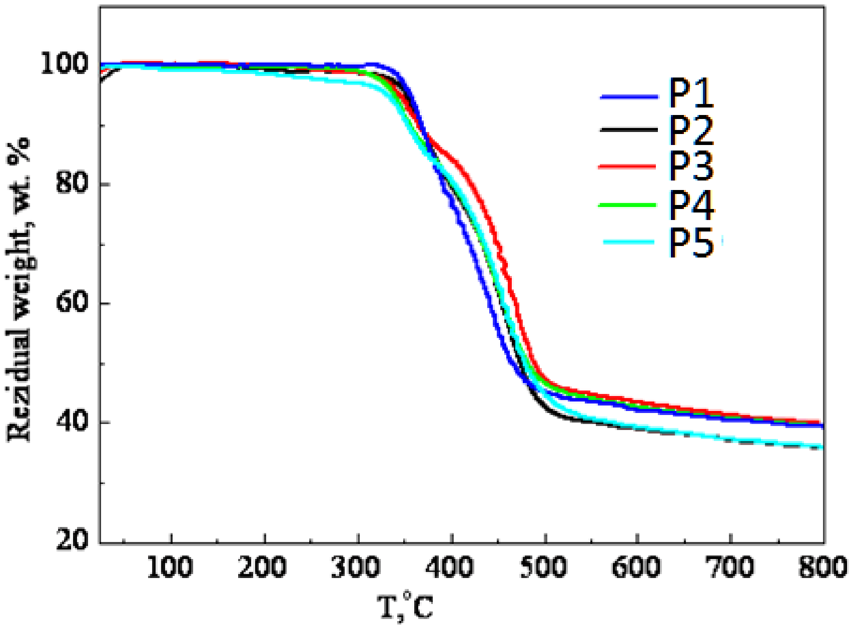

Figure S1. TGA plots for terpolymers **P1**–**P5** at heating rate of 20 °C/min

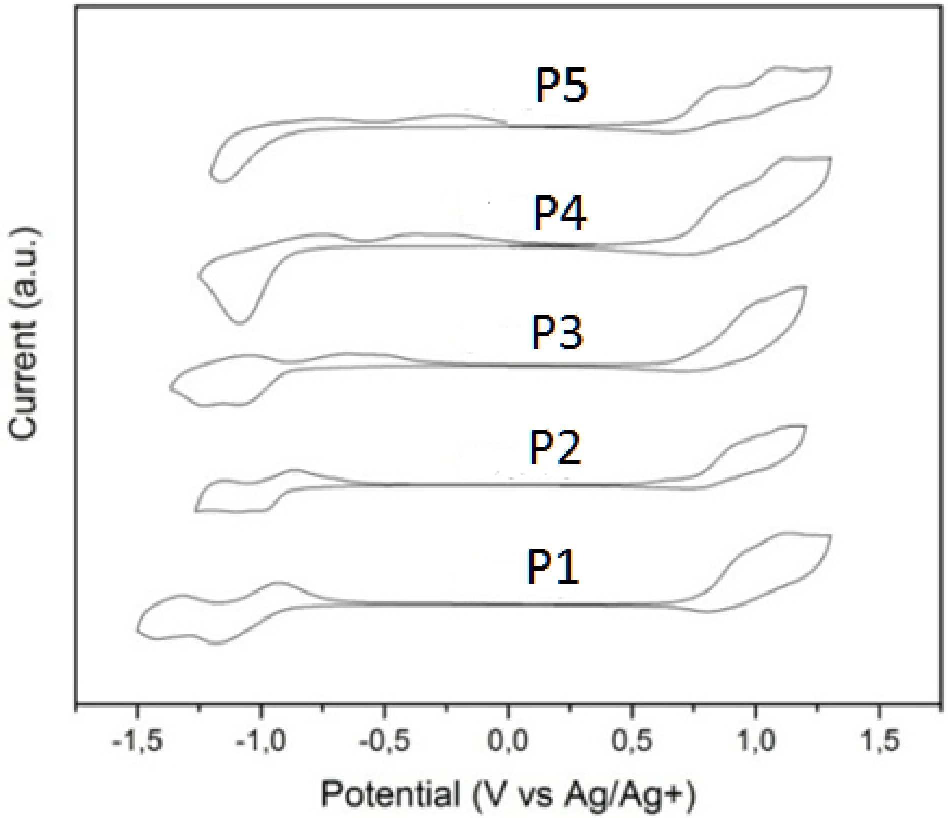

Figure S2. Cyclic voltammograms of the copolymers films in 0.1 M $(Bu_4N)PF_6$ in acetonitrile, at scan rate of 80 mV/s

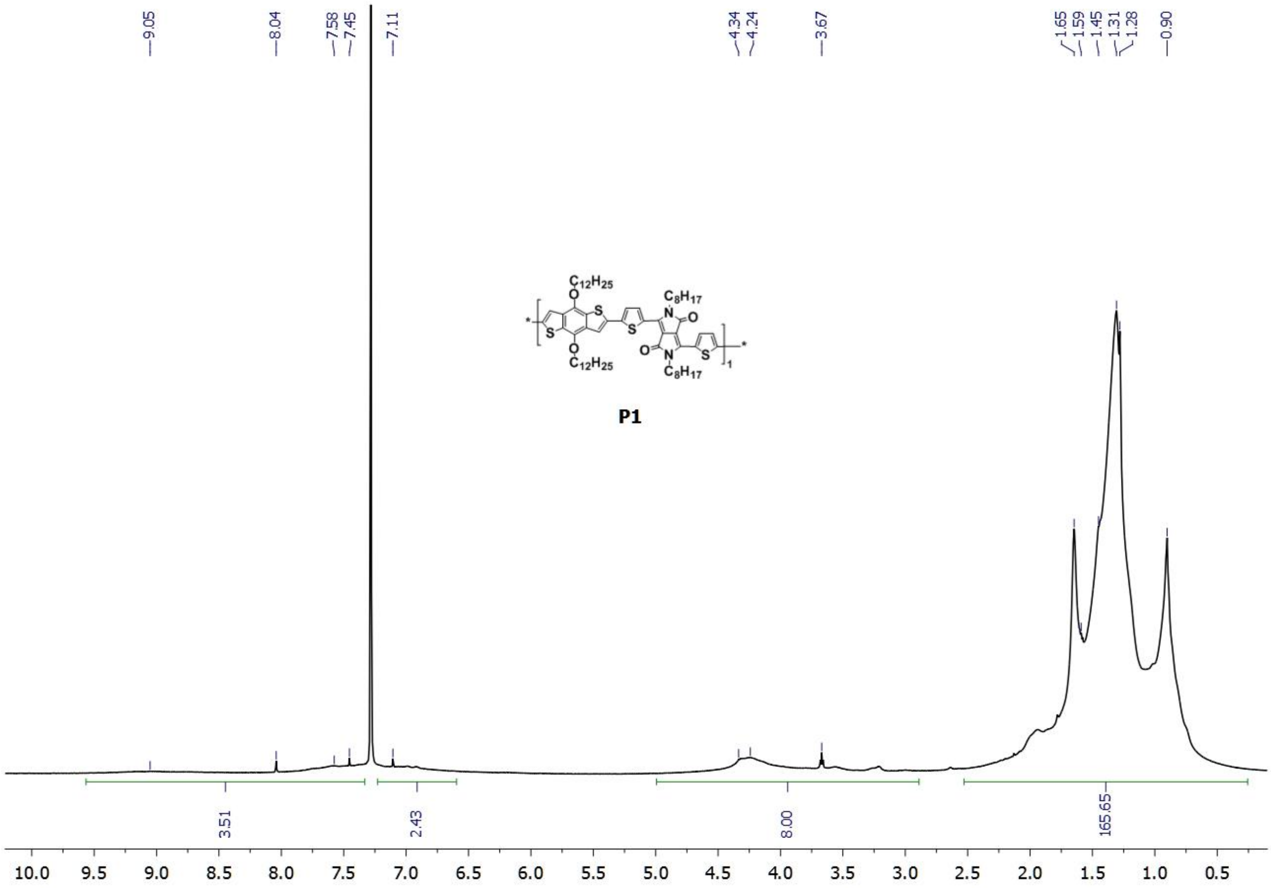

Figure S3 ^{1}H NMR spectrum of copolymer **P1** in $CDCl_3$.

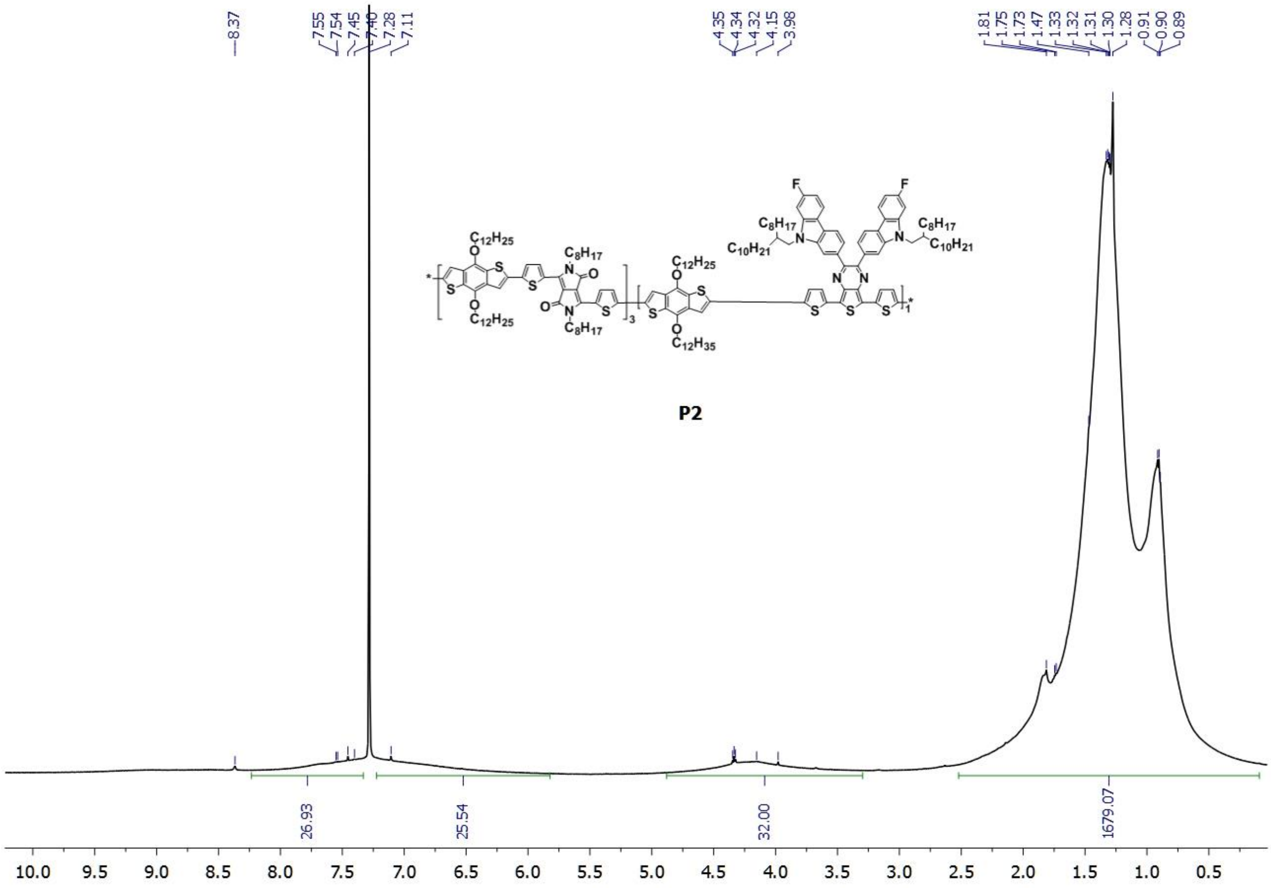

Figure S4 ^{1}H NMR spectrum of copolymer **P2** in $CDCl_3$.

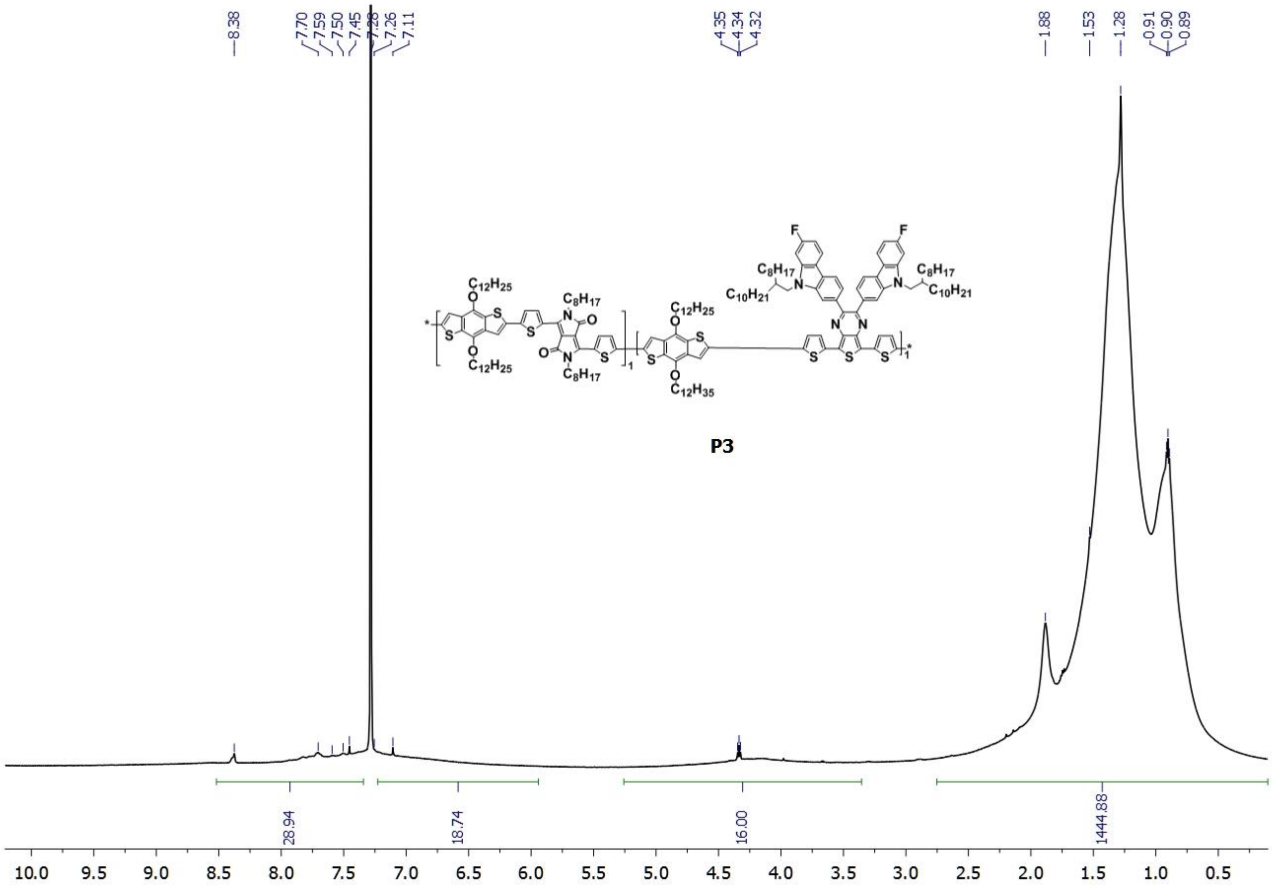

Figure S5 ^{1}H NMR spectrum of copolymer **P3** in $CDCl_3$.

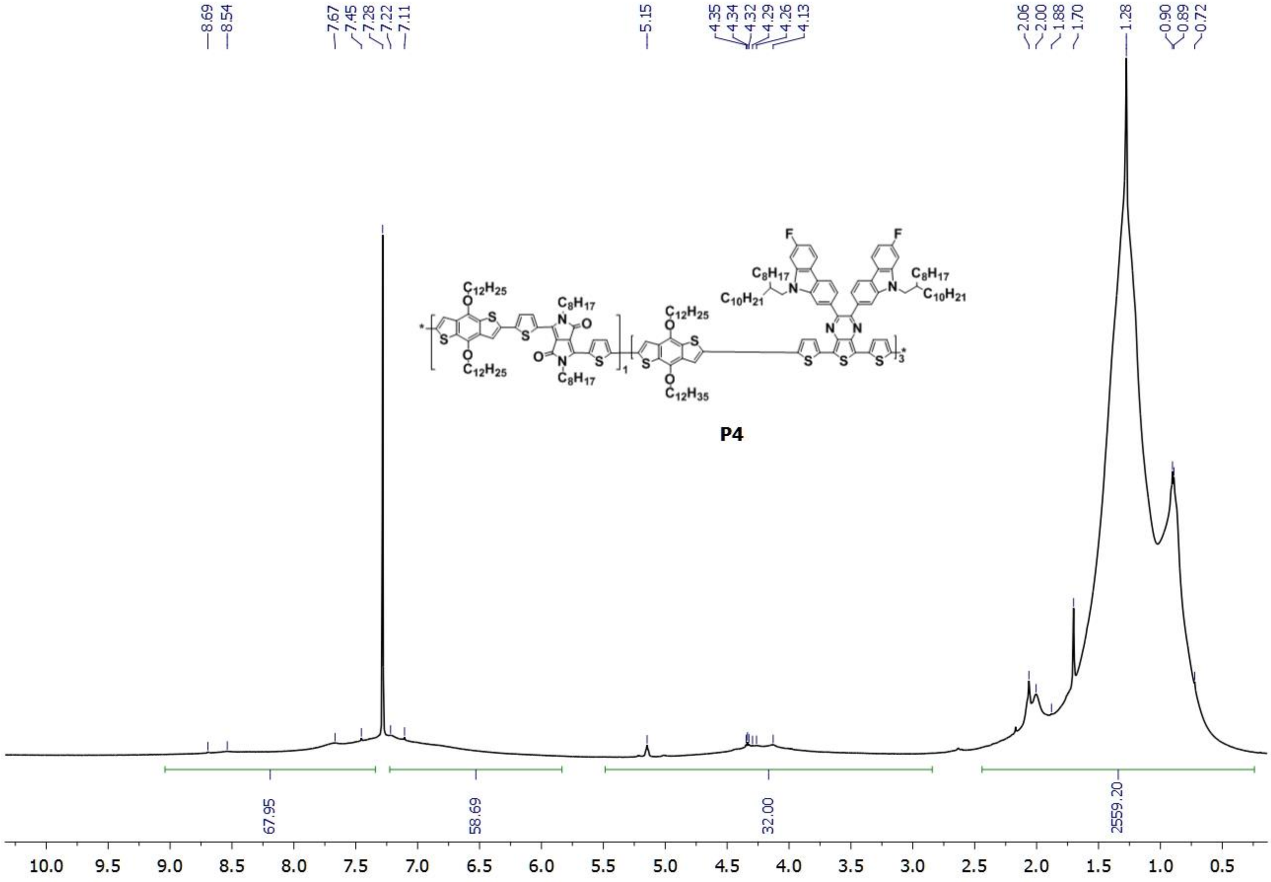

Figure S6 ^{1}H NMR spectrum of copolymer **P4** in $CDCl_3$.

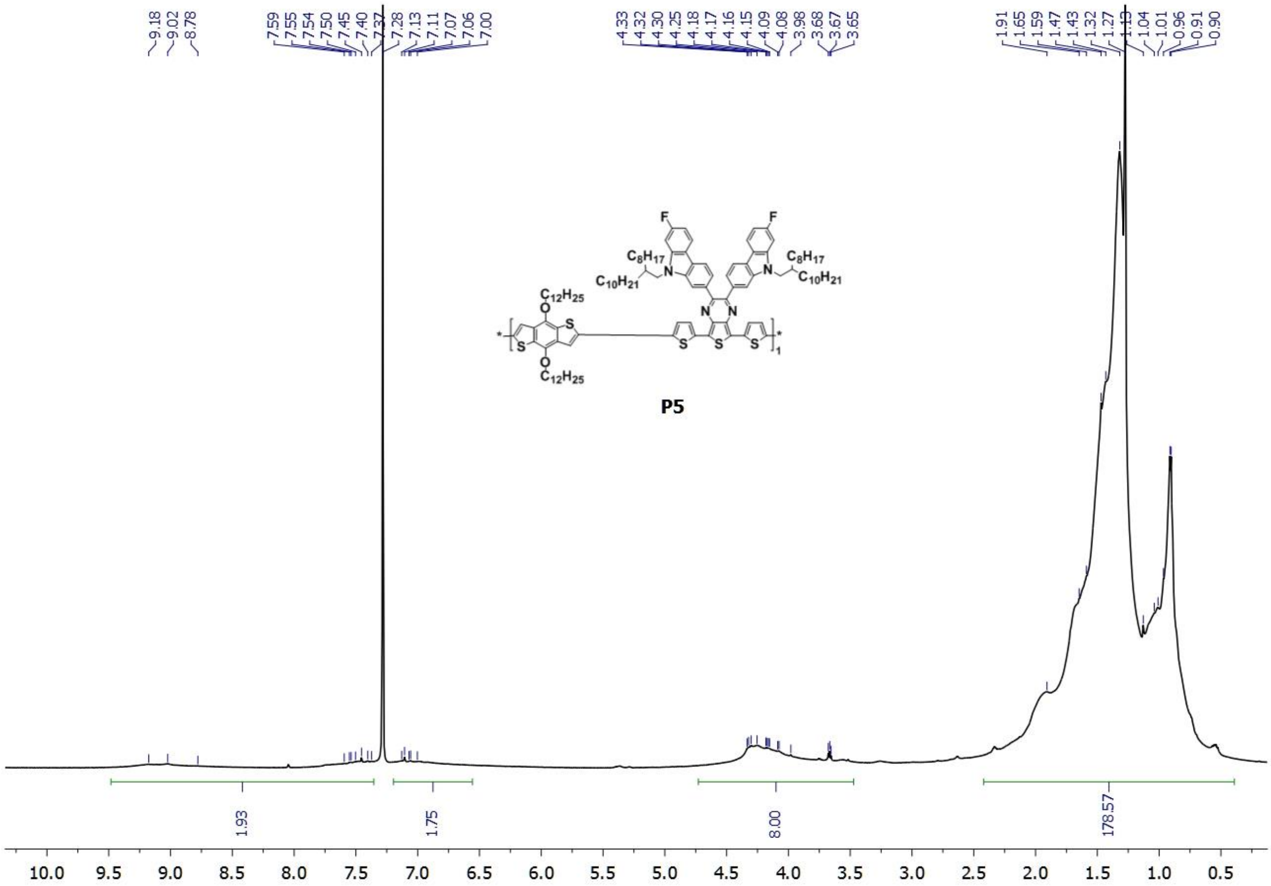

Figure S7 ^{1}H NMR spectrum of copolymer **P5** in $CDCl_3$.