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Novel conjugated copolymers with dithienyl and cyclopentadithienyl substituted dicyanoethene acceptor blocks

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Contents

Experimental details

Materials. Hexane solutions (1.6 *M* and 2.5 *M*) *n*-butyl lithium (BuLi), *N*,*N*-dimethyl-carbamoyl chloride, 2-bromothiophene, trimethyltin cloride (1 *M* THF solution), *N*-bromo-succinimide, malononitrile, ammonium acetate, and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma–Aldrich and Acros Organics with purity not less than 95% and were used as received. Chlorotrimethylsilane was purchased from ABCR GMbH and was distilled prior to use. Toluene, THF, and diethyl ether were dried by refluxing over calcium hydride, DMF and pyridine were refluxed over calcium oxide for 3–5 h. After that, dry solvents were distilled and stored over 3 Å molecular sieves. Other solvents were purified under standard conditions and freshly distilled prior to use.

General. Gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation, a Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 500 Å was used. ^{1}H, ^{13}C, ^{29}Si NMR spectra and their nucleus correlations were recorded using a Bruker Avance II 300 spectrometer at 300, 75 and 60 MHz, respectively. Elemental analysis of C and H elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using $BaCl_2$ was applied to analyze sulfur. Experimental error for elemental analysis is 0.30-0.50%. Knoevenagel condensation was carried out in the microwave “Discovery” (CEM corporation, USA), using a

standard method with the open vessel option. Thermogravimetric analysis (TGA) was performed using a TG50 Mettler Toledo device. All measurements were done in dynamic mode at 10 °C min^{-1} heating rate, in the range of 50–70 °C with nitrogen/air flow rate 200 ml min^{-1}. UV-visible spectra were recorded on a Shimadzu UV-2501PC spectrophotometer over a range of 250−1000 nm both in solutions and in thin films. Cyclic voltammetry was carried out using solid compact layers of the oligomers, which in turn were made by electrostatically rubbing the materials onto a glassy carbon electrode using IPC-Pro M potentiostat. Measurements were made in acetonitrile solution using 0.1 *M* Bu_4NPF_6 as a supporting electrolyte. The scan rate was 200 mV s^{-1}. The glassy carbon electrode was used as a working electrode. Potentials were measured relative to a saturated calomel electrode (SCE). Solution CV measurements were done in *o*-dichloro-benzene/acetonitrile (4:1) mixture of solvents for 10^{-3} *M* solutions in a standard three-electrode cell equipped with a glassy carbon working electrode (s = 2 mm^2), platinum plate as the counter electrode, and SCE as the reference electrode. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from CV experiments in films according to following equation: LUMO = e(φ_{red}+4.40)(eV) and HOMO = -e(φ_{ox}+4.40)(eV).

Di(thiophen-2-yl)methanone (1) was synthesized according to Ref. [S1]. Butyllithium (2.5 *M* solution, 37.5 ml, 0.094 mol) was added dropwise to a solution of 2-bromothiophene (15.27 g, 0.094 mol) in dry diethyl ether (45 ml) at -78°C, and the mixture was stirred at -40 °C for 1 h. After cooling to -60 °C, *N*,*N*-dimethylcarbamyl chloride (5.06 g, 0.047 mol) was added, and the mixture was stirred at -40 °C for 1 h. After heating to room temperature, the solution was poured into 1 *N* HCl solution and kept overnight. The resulting mixture was extracted with diethyl ether (2 x 100 ml). The combined organic phases were washed twice with water, dried over anhydrous Na_2SO_4, and the solvent was removed by evaporation. The crude product was purified by recrystallization twice from toluene and twice from ethanol to yield the product as a yellowish powder with m.p.= 91 °C; yield: 8.15 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.90 (dd, J_1 = 0.9 Hz, J_2 = 1.2 Hz), 7.70 (dd, J_1 = 0.9 Hz, J_2 = 1.2 Hz), 7.20 (dd, J_1 = 0.9 Hz, J_2 = 3.9 Hz). Anal. calcd. for $C_9H_6OS_2$(%): C, 55.64; H, 3.11; O, 8.24; S, 33.01. Found: C, 55.54; H, 2.98; S, 32.86.

Bis(5-bromothiophen-2-yl)methanone (2) was synthesized according to Ref. [S1]. Bromine (19 ml, 0.36 mol) was added to a vigorously stirred solution of compound **1** (17.6 g, 0.09 mol) in $CHCl_3$ (20 ml). The mixture was stirred at room temperature for 36 h, and then another portion of bromine (19 ml, 0.36 mol) was added at room temperature. After stirring for 2 h, the resultant mixture was poured into cold 10% NaOH aqueous solution. The product was extracted with $CHCl_3$ (2 x 50 ml). The combined organic phases were washed consequently with

Na_2SO_3, brine and twice with water, dried over anhydrous Na_2SO_4, and the solvent was removed by evaporation. The crude product was dissolved in boiling hexane, and the insoluble residue was filtered off. The solvent was evaporated from the transparent filtrate to afford a yellow powder with m.p. = 117 °C; yield: 29.7 g (93%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.60 (d, 2H, J = 3.9 Hz), 7.15(d, 2H, J = 3.9 Hz). Anal. calcd. for $C_9H_4Br_2OS_2$(%): C, 30.70; H, 1.15; S, 18.22. Found C, 30.75; H, 1.19; S, 18.16.

2-[Bis(5-bromothiophen-2-yl)methylidene]malononitrile (3). A mixture of compound **2** (5.0 g, 0.014 mol) and malononitrile (9.38 g, 0.142 mol) in pyridine (125 ml) was stirred at room temperature for 72 h. The solvent was evaporated from the dark violet solution. The excess of malononitrile was removed by a multiple treatment with hot water. The pure product was obtained by column chromatography on silica gel using hexane – dichloromethane (1:1) mixture as the eluent to yield an orange powder; yield: 5.39 g (95%). M.p.= 186 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.52 (d, 2H, *J* = 4.2 Hz), 7.22 (d, 2H, *J* = 4.2 Hz). Anal. calcd. for $C_{12}H_4Br_2N_2S_2$ (%): C, 36.02; H, 1.01; Br, 39.94; N, 7.00; S, 16.03. Found: C, 35,85; H, 0,79; N, 6,87; S,15,98.

2,2´-Bithiophene was synthesized according to the reported procedure [S2] from 2-bromo-thiophene (195 g, 1.19 mol) and magnesium metal (14.7 g, 0.61 mol) using Pd(dppf)Cl_2 (0.853 g, 1.2 mmol, 2 mol%) as the catalyst; yield; 93.0 g (96%), transparent crystals, m. p. = 31 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.19 (m, 4H, 2,2',4,4'-ThH), 7.01 (dd, 2H, J_1=3.7 Hz, J_2=1.2 Hz, 3.3'-ThH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 123.7 (4-C, 4'-C), 124.3 (3-C, 3'-C), 127.7 (5-C, 5'-C), 137.3 (2-C, 2'-C).

3,3´,5,5´-Tetrabromo-2,2´-bithiophene was synthesized according to the reported procedure [S**Error! Bookmark not defined.**] from 2,2'-bithiophene (32.7 g, 0.197 mol) and bromine (44 ml, 0.865 mol). Purification was performed by recrystallization from toluene and ethanol; yield: 79 g (82%), white crystals, m.p. = 138 °C (lit. m.p. 140 °C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 112.1 (3-CBr, 3'-CBr), 114.8 (5-CBr, 5'-CBr), 129.5 (2-C, 2'-C), 133 (4-C, 4'-C).

3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (4) was synthesized according to the reported procedure [S2] using 3,3',5,5'-tetrabromo-2,2'-bithiophene (21.21 g; 0.044 mol), BuLi (2.5 *M* solution, 36.8 ml, 0.092 mol) and chlorotrimethylsilane (11.7 ml; 0.092 mol). The product was purified by recrystallization from ethanol; yield: 13.4 g (65%), white crystals, m.p. = 85 °C (lit. m.p. 86 °C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.15 (s, 2H), 0.33 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 142.9 (2-C, 2'-C), 137 (4-C, 4'-C), 133.9 (5-C, 5'-C), 112.9 (3-CBr, 3'-CBr), -0.39 ($SiMe_3$).

2,6-Bis(trimethylsilyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (5) was synthesized according to the reported procedure [S3] from 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (3.0 g, 6.4 mmol), 5.6 ml (1.11 mmol), BuLi (2.5 *M* solution, 2.0 ml, 1.32 mmol), TMEDA and *N,N*-dimethyl carbamoyl chloride (0.69 g, 6.4 mmol); yield: 1.81 g (84%), m.p.= 82°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.07 (s, 2H), 0.31 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 183.12 (C=O), 154.33 (4-C), 144.88 (5-C), 144.14 (2-C), 127.10 (3-C), -0.24 ($SiMe_3$).

2,6-Dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (6) was synthesized according to the reported procedure [S4] from compound **5** (3.0 g, 8.9 mmol) and NBS (3.5 g, 19.6 mmol). The pure product appeared as a dark-violet powder; yield: 2.90 g (93%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.98 (s, 2H). Anal. calcd. for $C_9H_2Br_2OS_2$ (%): C, 30.88; H, 0.58; Br, 45.65; O, 4.57; S, 18.32. Found: C, 31.03; H, 0.57; Br, 45.34; S, 18.24.

2-(2,6-Dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-ylidene)malononitrile (7). A mixture of ketone **6** (3.12 g; 8.91 mmol) and malononitrile (3.53 g, 53.5 mmol) in dry pyridine (65 ml) was stirred at room temperature for 3 h. The solvent was evaporated from the dark grey suspension. The excess of malononitirle was removed by washing with hot water. The pure product was obtained by recrystallization from hot chloroform to yield a grey powder (2.77 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.45 (s, 2H). Anal. calcd. for $C_{12}H_2Br_2N_2S_2$(%): C, 36.21; H, 0.51; Br, 40.14; N, 7.04; S, 16.11. Found: C, 36.01; H, 0.53; Br, 40.42; N, 6.87; S, 15.99.

4,4-Didecyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (8) was synthesized according to the reported procedure [S5] from 2,6-dibromo-4,4-didecyl-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (1.41 g, 2.23 mmol), BuLi (1.6 *M*, 3.1 ml, 4.90 mmol) and trimethyltin chloride (1.0 *M* solution, 4.90 ml, 4.90 mmol) to give a yellowish viscous liquid. The yield of the crude product was 1.71 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.09 (s, 2H), 1.24 (m, 36H), 0.89 (s, 6H), 0.39 (s, 18H).

General procedure of copolymer synthesis. A mixture of the monomers (1:1, mol/mol) was dissolved in toluene (to provide ca. 10% solution), and this was de-aerated by bubbling argon for 10 min. The reaction was carried out in a microwave oven with a slow temperature raising 90→120 °C during 18-20 h. After the reaction was completed, the product was extracted with $CHCl_3$ (2 x 25 ml). The combined organic phases were washed with water, dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was dissolved in excess boiling $CHCl_3$ and passed through a pad of silica (ca. 20 ml). The solution was concentrated by evaporation to a minimum volume and the polymeric product was precipitated by dropwise addition of ethanol. The precipitate obtained was dried in a vacuum and placed into a Soxhlet

extractor. The oligomeric fraction was removed by consequent partial dissolution with acetone and ethyl acetate under reflux conditions. After that, the polymer was reprecipitated with ethanol from a chloroform solution, and the procedure was repeated. The polymeric powder was dried in a vacuum.

Copolymer P1, a dark-violet powder, was obtained from compound **8** (0.83 g, 1.04 mmol) and dibromide **3** (0.41 g, 1.04 mmol); yield: 0.47 g (65%). Anal. calcd. For $C_{42}H_{54}N_2S_4Si$ (%): C, 67.87; H, 7.32; N, 3.77; S, 17.25. Found: C, 67.49; H, 7.15; N, 3.65; S, 16.92. GPC: M_n=25500, M_w=42500, PDI=1.67.

Copolymer P2, a dark-red powder, was obtained from compound **8** (0.95 g, 1.19 mmol) and dibromide **7** (0.47 g, 1.19 mmol); yield: 0.66 g (75%). Anal. calcd. For $C_{42}H_{52}N_2S_4Si$ (%): C, 68.06; H, 7.07; N, 3.78; S, 17.30; Si, 3.79. Found: C, 67.67; H, 6.76; N, 3.53; S, 16.93. GPC: M_n=17000, M_w=23300, PDI=1.37.

References

[S1] K. Shi, W. Zhang, C. Wei, Z. Lin, X. Liu, G. Yu, *J. Polym. Sci. A.*, 2018, **56**, 1012.

[S2] S. Qu and H. Tian, *Chem. Commun*., 2012, **48**, 3039.

[S3] F. V. Drozdov, N. M. Surin, S. M. Peregudova, V. A. Trukhanov, P. V. Dmitryakov, S. N. Chvalun, D. Yu. Parashchuk and S. A. Ponomarenko, *Polym. Sci. B*, 2019, **61**, 56.

[S4] Y. A. Getmanenko, M. Fonari, C. Risko, B. Sandhu, E. Galán, L. Zhu, P. Tongwa, D. K. Hwang, S. Singh, H. Wang, S. P. Tiwari, Y.-L. Loo, J.-L. Brédas, B. Kippelen, T. Timofeeva and S. R. Marder, *J. Mater. Chem. C*, 2013, **1**, 1467.

[S5] L. Huo, H.-Y. Chen, J. Hou, T. L. Chen and Y. Yang, *Chem. Commun*., 2009, 5570.

^{1}H NMR spectra of monomers

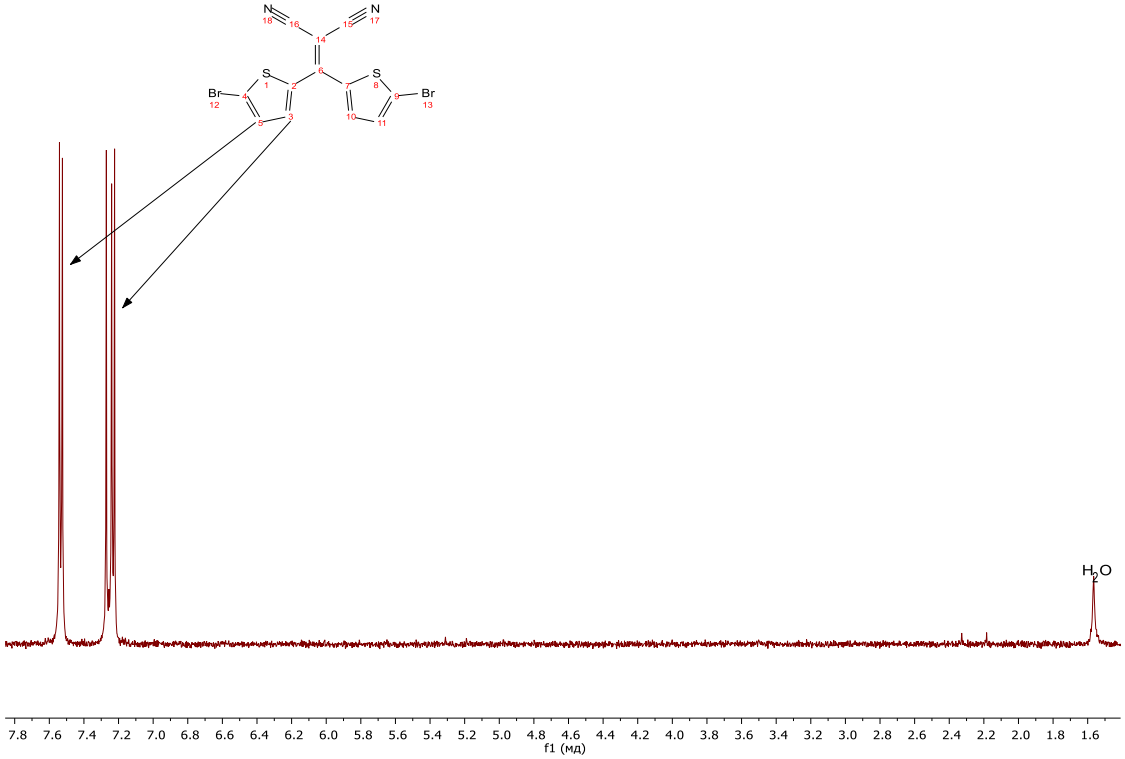

Figure S1. ^{1}H NMR spectrum of compound **3**

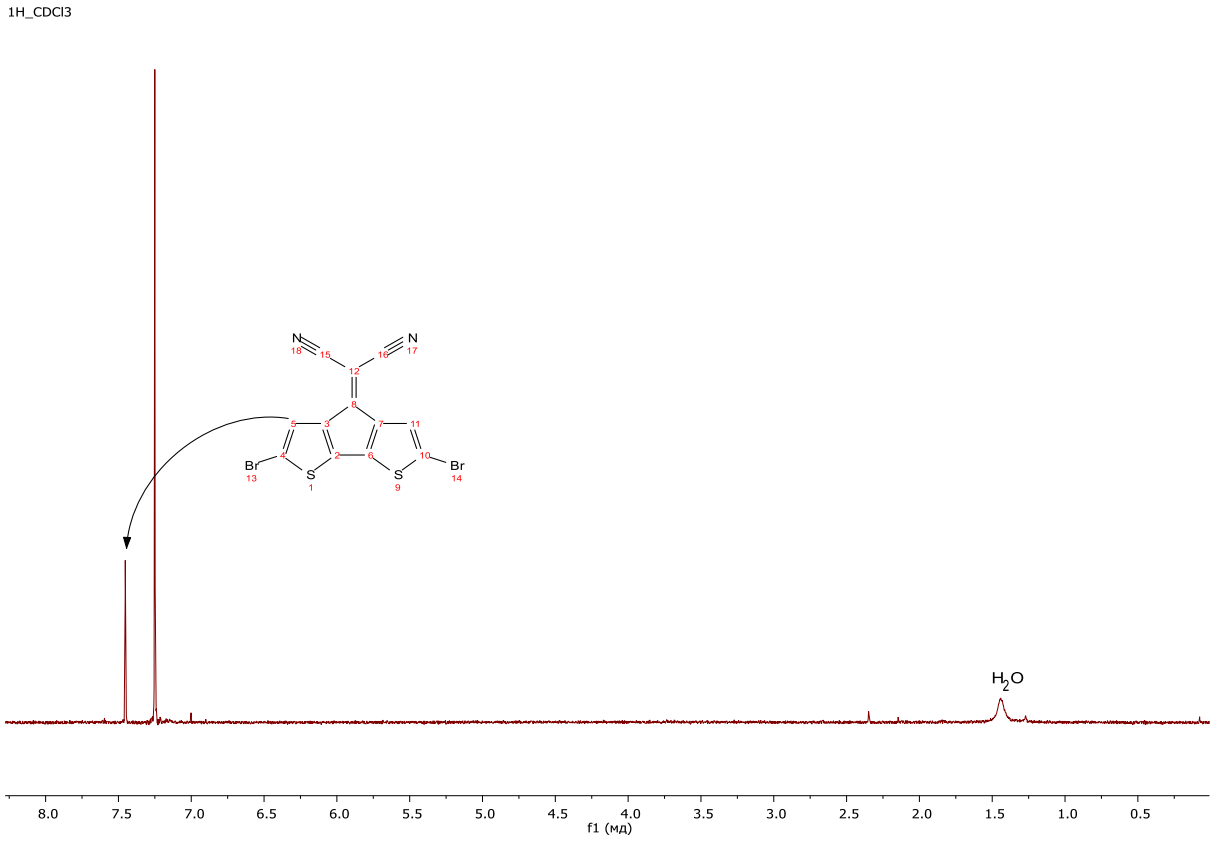

Figure S2. ^{1}H NMR spectrum of compound **7**

^{13}C NMR spectra of monomers

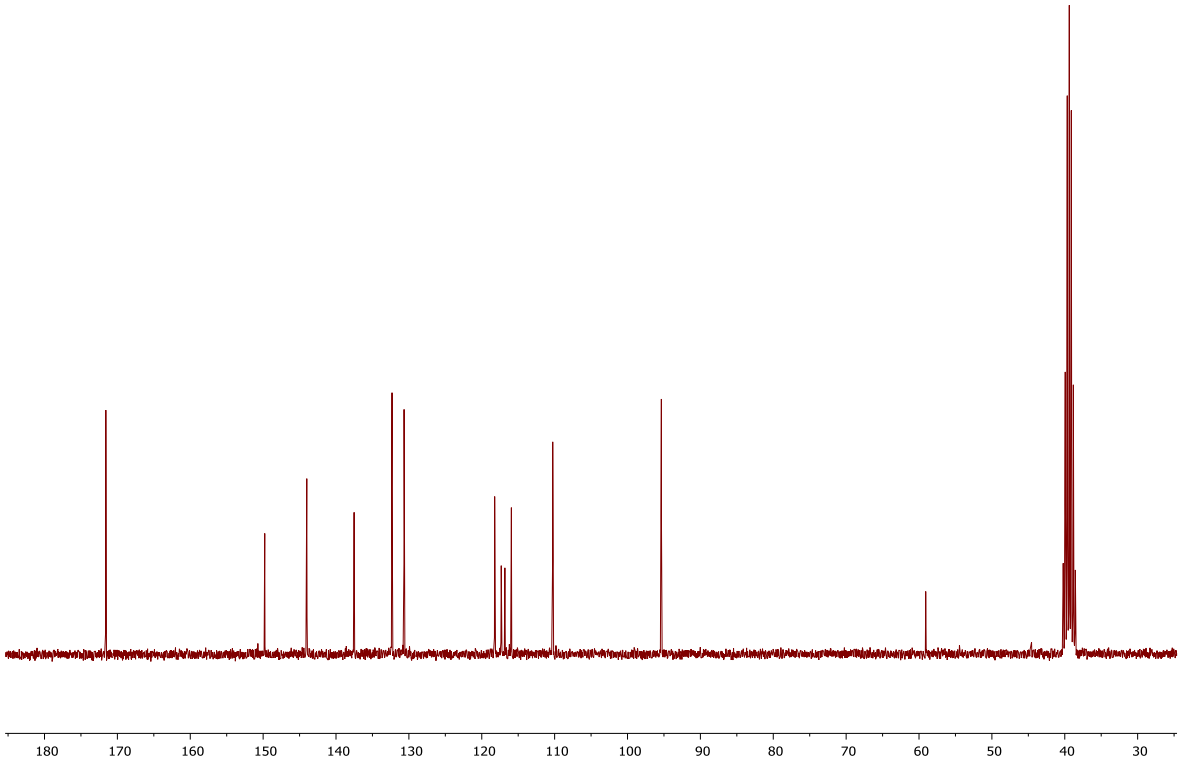

Figure S3. ^{13}C NMR spectrum of compound **3**

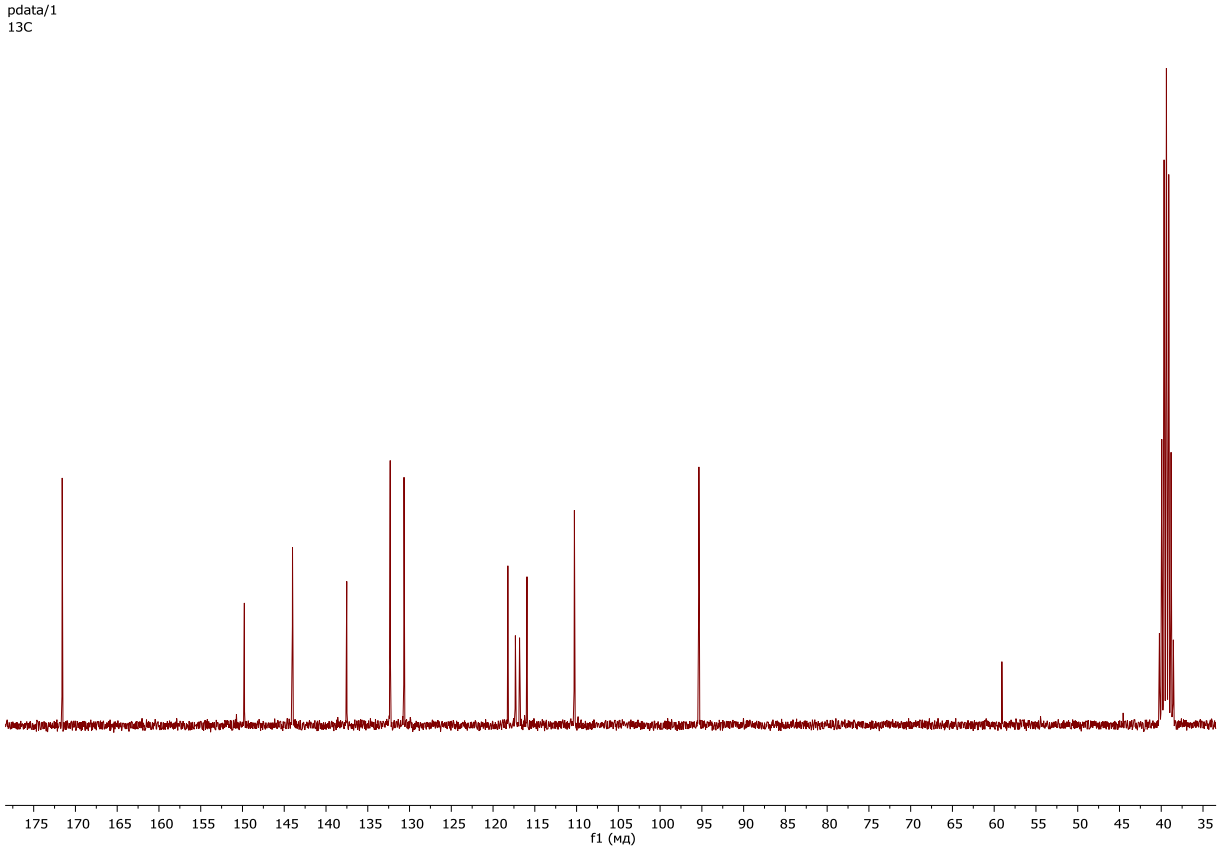

Figure S4. ^{13}C NMR spectrum of compound **7**

^{1}H, ^{13}C, ^{29}Si NMR spectra of copolymers

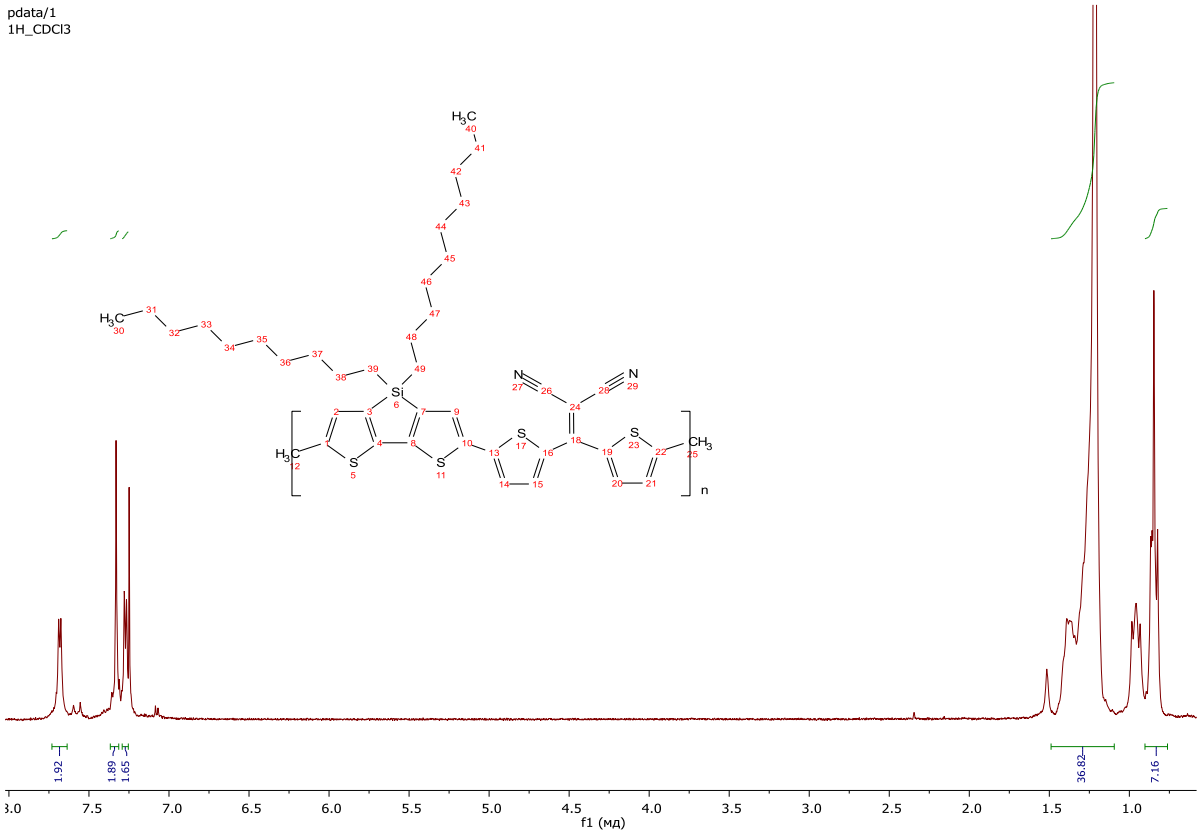

Figure S5. ^{1}H NMR spectrum of copolymer **P1**

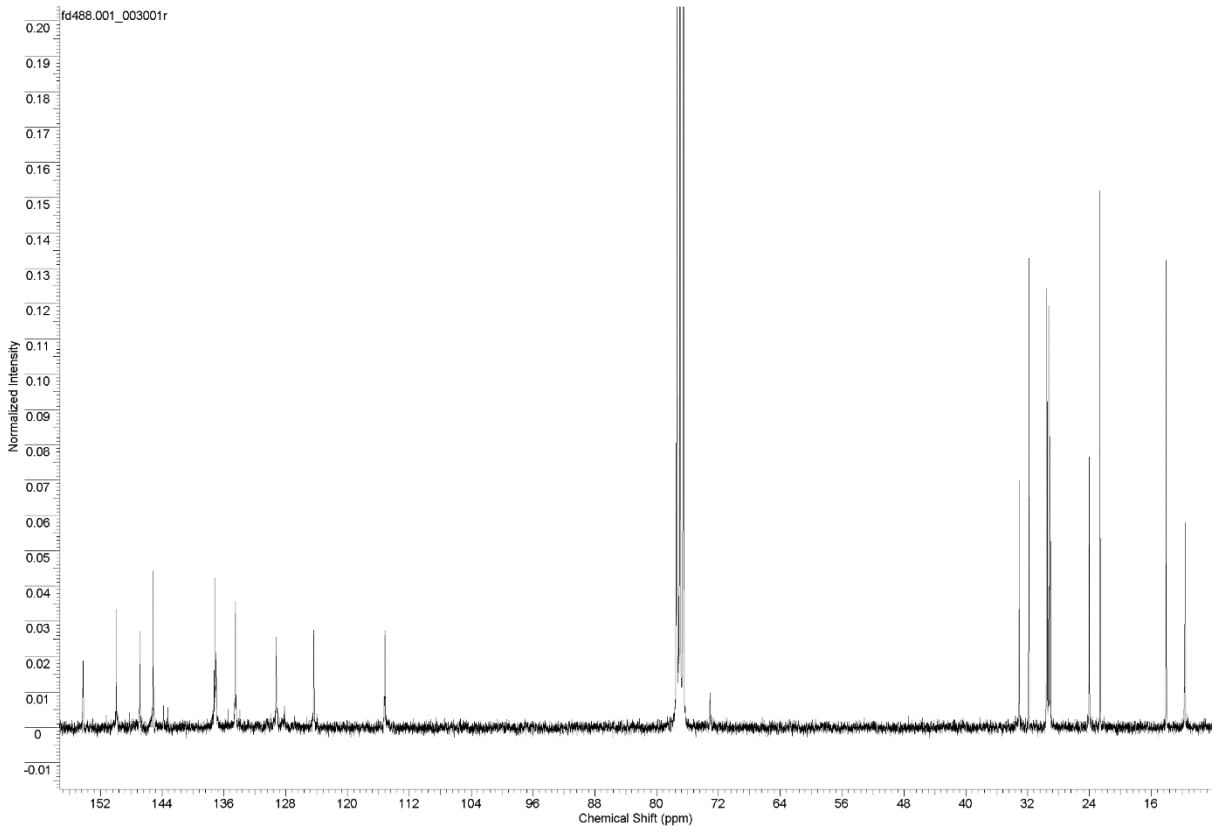

Figure S6. ^{13}C NMR spectrum of copolymer **P1**

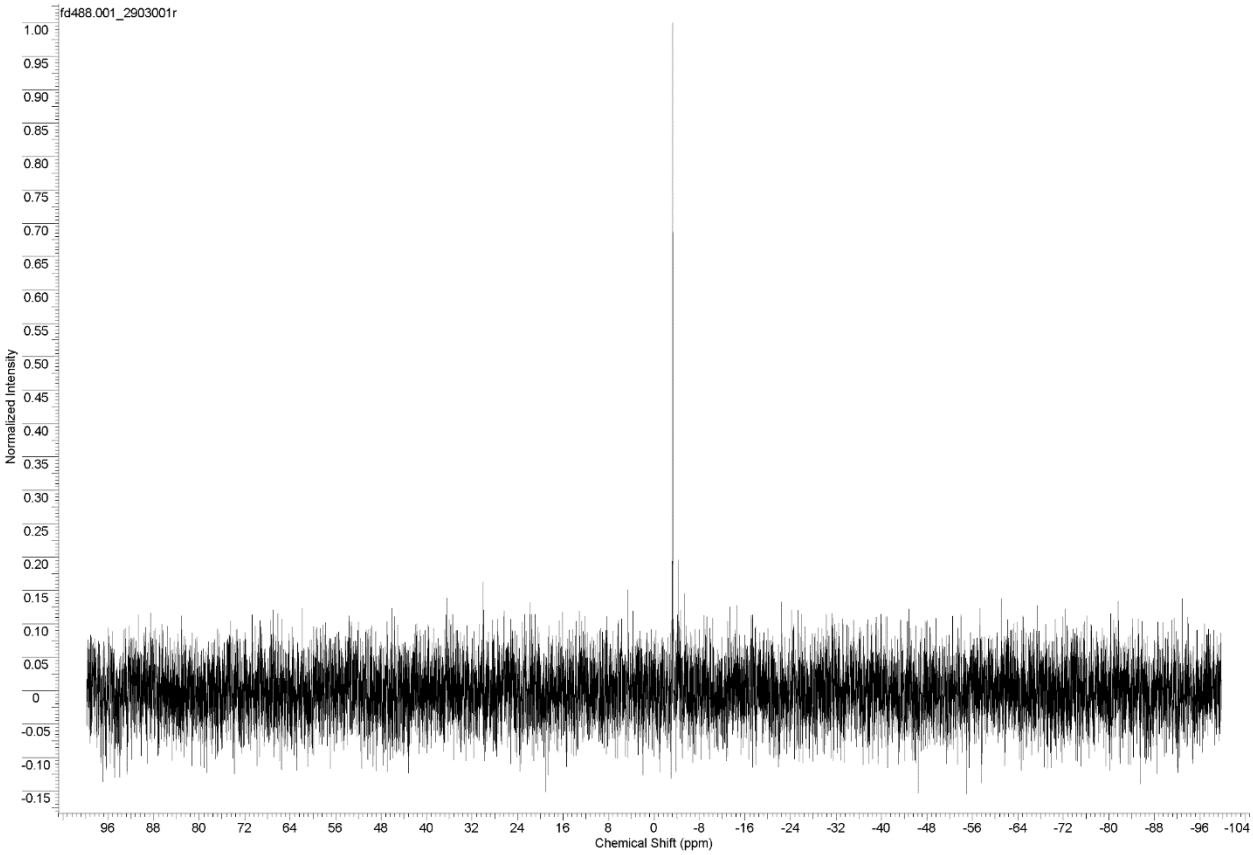

Figure S7. ^{29}Si NMR spectrum of copolymer **P1**

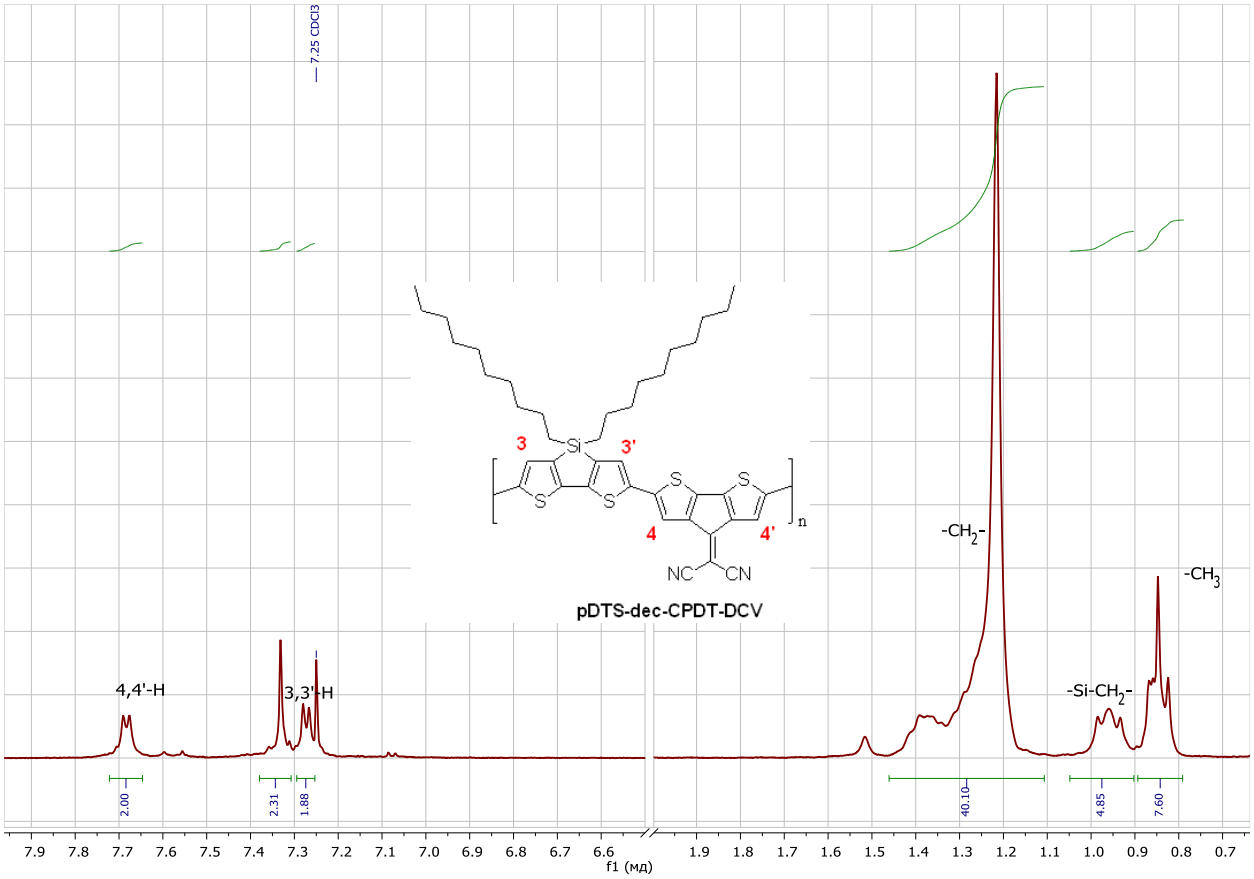

Figure S8. ^{1}H NMR spectrum of copolymer **P2**

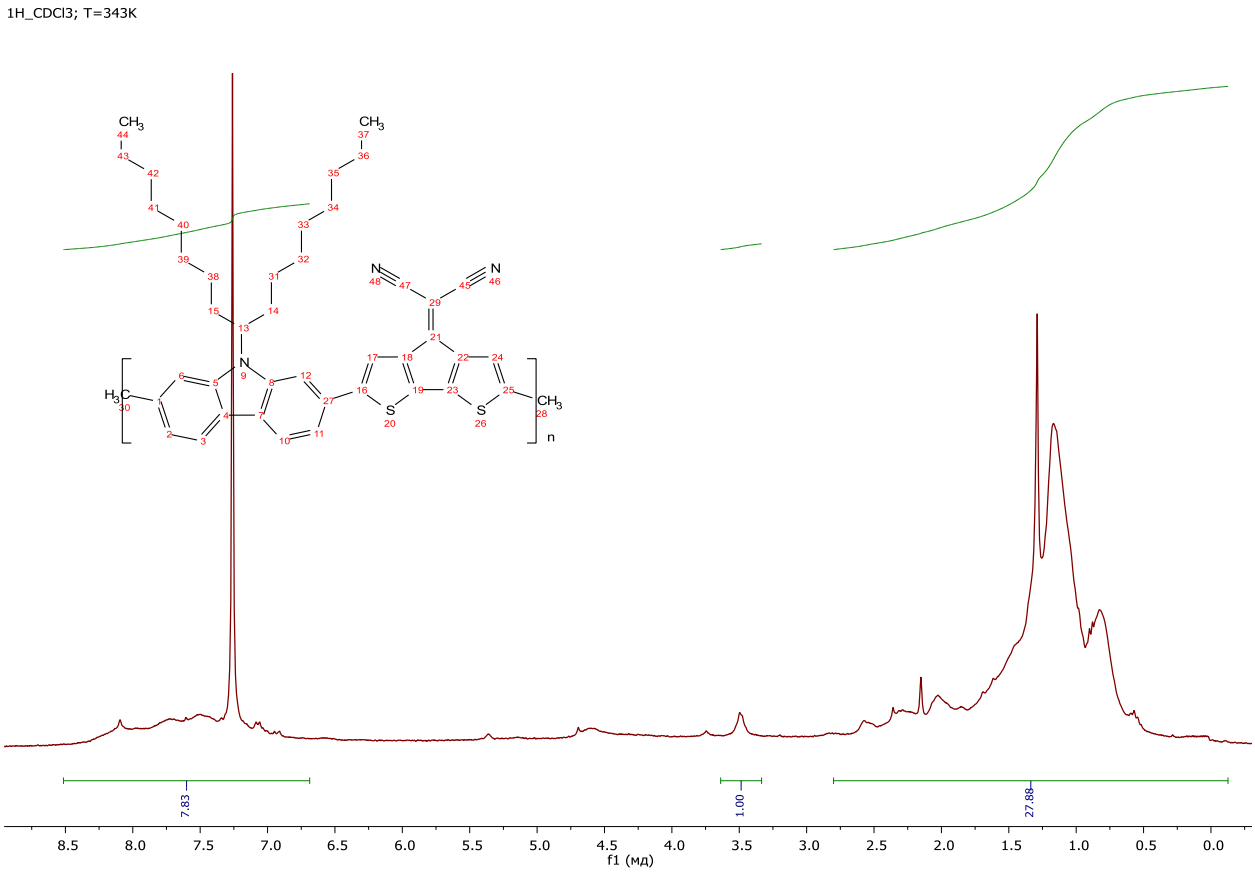

Figure S9. ^{13}C NMR spectrum of copolymer **P2**