Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 682–685

Microwave-assisted synthesis of thiazolothiazole-containing conjugated polymers as promising charge-transport materials for perovskite solar cells

**Alina V. Lolaeva, Aleksandra N. Zhivchikova, Marina M. Tepliakova,
Mikhail V. Gapanovich, Evgenia O. Perepelitsina, Azaliia F. Akhkiamova,
Dimitri A. Ivanov, Nikita A. Slesarenko, Albert G. Nasibulin,
Alexander V. Akkuratov and Ilya E. Kuznetsov**

S1. Materials and instrumentation

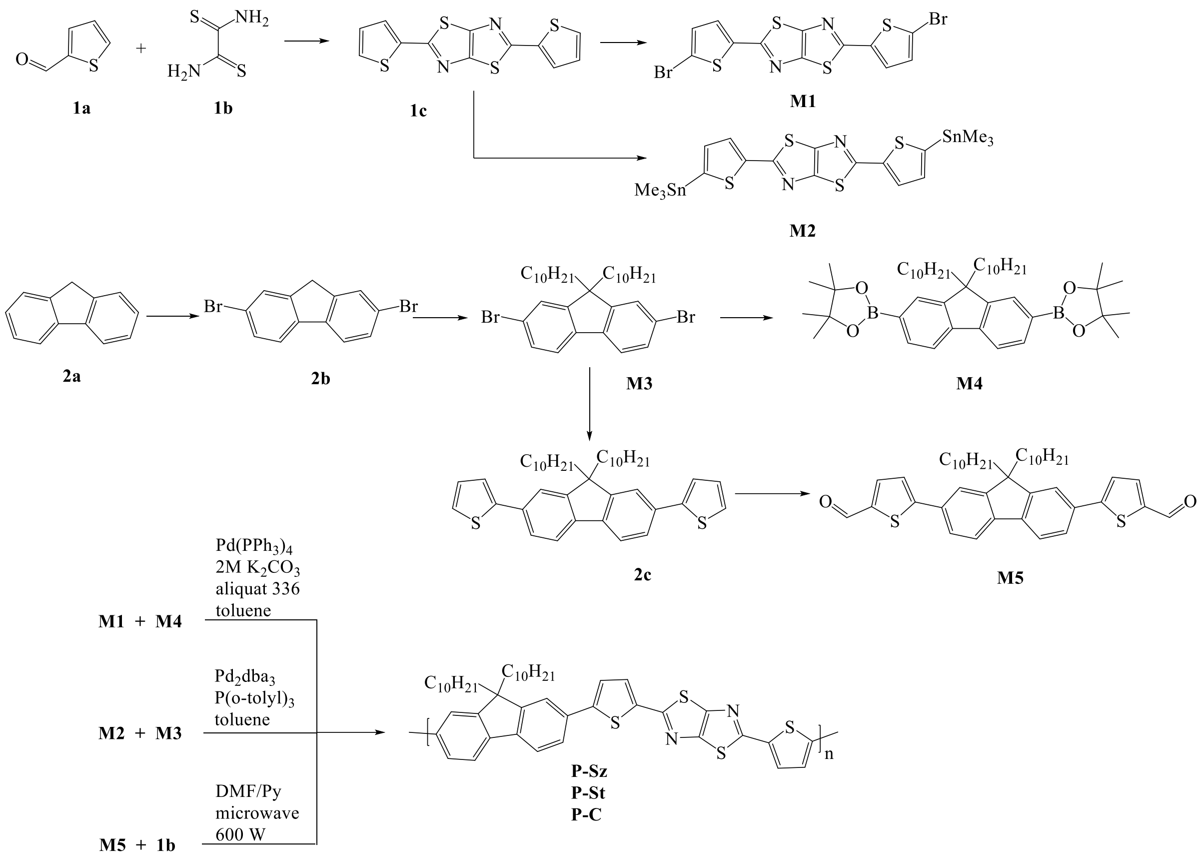
All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures.

Absorption spectra were measured on scanning spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained using Bruker AVANCE 500 instrument. AFM images were obtained using NTEGRA PRIMA instrument (NT-MDT, Russia). Cyclic voltammetry measurements were performed for thin films (150–250 nm) of polymers **P-Sz, P-St, P-C** deposited on a glassy carbon disc electrode following the previously reported procedure [S1]. The thermal properties of the polymers were investigated by thermal gravimetry analysis (TGA) using Q50 TA instruments under nitro-gen with a heating rate of 10 ºC min^{-1}. Differential scanning calorimetry (DSC) was performed using Netzsch DSC 214 Polyma instrument at the same conditions.

Molecular weight characteristics of conjugated polymers were obtained using Waters liquid chromatograph equipped with a Waters 2414 differential refractive index detector and a PDA 996 diode array spectrophotometric detector. Two PLgel 5µm MIXED-C columns connected in series were used. Tetrahydrofuran (THF) was used as the eluent, the elution rate was 1 ml min^{-1}, T_{col}=35˚C, T_{ref}=45˚C. To construct a calibration dependence, standard samples of polystyrene with a narrow polydispersity coefficient (MW from 580 to 3.7×10^6 Da) were used. The obtained chromatograms were processed using the Empower software.

The *J-V* curves were recorded in the glovebox under the illumination (100 mW cm^{-2}) provided by Newport Verasol AAA solar simulator using Advantest 6240A source-measurement units.

S2. Synthesis of monomers and polymers



S1. Synthesis of monomers and polymers.

Synthesis of compound 1c

Compound **1c** was prepared using thiophene-2-carbaldehyde **1a** and dithiooxamide **1b** following the procedure reported previously [S2]. A yellow powder of 2,5-di(thiophen-2-yl)thiazolo[5,4-*d*]-thiazole was obtained with the yield 45%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.56 (d, 2H); 7.44 (d, 2H); 7.10 (t, 2H).

Synthesis of monomer M1

2,5-Di(thiophen-2-yl)thiazolo[5,4-*d*]thiazole **1c** was brominated with *N*-bromosuccinimide in *N,N*-dimethylformamide to give a monomer **M1** with the yield 81% [S2]. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.29 (d, 2H); 7.06 (d, 2H).

Synthesis of monomer M2

Monomer **M2** was prepared following the procedure reported previously [S3]. Solution of **M1** (1 g, 3.26 mmol, 1.0 eq.) in THF (30 ml) was placed into a 100 ml three-neck round-bottom flask, which was previously evacuated/backfilled with argon three times. The flask was then cooled to -78 °C in an acetone bath, and LDA (13 mmol, 4.0 eq., in THF) was added dropwise. The reaction mixture was stirred at -50 °C for 4 h. Then the solution of chloro(trimethyl)stannane (2.66 g, 13.4 mmol, 4.1 eq.) in THF (5 ml) was added in one portion. The mixture was stirred at RT for 2 h. The solvent was removed at the rotary evaporator producing a viscous oily residue, recrystallized from propan-2-ol, which afforded the target compound 2,5-bis(5-

(trimethylstannyl)thiophen-2-yl)thiazolo[5,4-*d*]thiazole with the yield of 55%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.63 (d, 2H); 7.15 (d, 2H); 0.40 (s, 18H).

Synthesis of compound 2b

Compound **2b** was prepared following the procedure reported previously [S4]. Fluorene **2a** was brominated with iodine and bromine in dichloromethane to give white crystals of 2,7-dibromo-9*H*-fluorene **2b** with the yield 90%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.62 (s, 2H); 7.58 (d, 2H); 7.48 (d, 2H); 3.83 (d, 2H).

Synthesis of monomer M3

Compound **M3** was prepared using compound **2b** (10 g, 31 mmol), 1-bromodecane (13.6 g, 62 mmol), potassium iodide (0.5 g, 3.1 mmol), potassium hydroxide (8.64 g, 155 mmol), and dimethyl sulfoxide (50 ml) following the procedure reported previously [S5]. White crystals of monomer **M3** were obtained with the yield 93%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.50 (dd, 2H); 7.44 (dd, 2H); 7.42 (s, 2H); 1.87-1.91 (m, 4H); 1.26-1.03 (m, 32H); 0.84 (t, 6H).

Synthesis of monomer M4

Compound **M4** was prepared using compound **M3** (5.31 g, 8.8 mmol), *n*-butyllithium in hexane (2.5 M in hexane, 10.6 ml, 26 mmol), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (5.73 g, 31 mmol) and THF (50 ml) following the procedure reported previously [S6]. White crystals of monomer **M4** were obtained with the yield 78%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.83 (dd, 2H); 7.77 (s, 2H); 7.75 (dd, 2H); 2.01-2.04 (m, 4H); 1.42 (s, 24H); 1.30-1.00 (m, 32H); 0.88 (t, 6H).

Synthesis of compound 2c

Compound **M3** (9.79 g, 16.19 mmol) and 2,5-bis(trimethylstannyl)thiophene (12.08 g, 32.38 mmol) were placed under argon in a two-necked round-bottom flask equipped with a reflux condenser. Then toluene (10 ml) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added. The mixture was heated at reflux within 24 h, and then the solvent was removed by reduced pressure evaporation. The crude product was purified by column chromatography (toluene/hexane, 1:2) to give compound **2c** with the yield 40%. The resulting compound has similar chemical shifts to the previously prepared compound in another work [S7]. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.66 (d, 2H); 7.59 (dd, 2H); 7.54 (d, 2H); 7.37 (dd, 2H); 7.27 (dd, 2H); 7.09 (dd, 2H); 1.98-2.01 (m, 4H); 1.24-1.03 (m, 32H); 0.81 (t, 6H). Chemical analysis (%) for $C_{41}H_{54}S_2$: C, 80.60; H, 8.91; S, 10.49; found C, 80.44; H, 8.84; S, 10.59

Synthesis of monomer M5

Phosphorus oxychloride (12.5 g, 82 mmol) was slowly added to anhydrous DMF (19 ml, 17.9 g, 245 mmol) while cooling for 30 min. Then compound **2c** (5 g, 8.2 mmol) in anhydrous DMF (10 ml) was added to the reaction mixture while cooling for 30 minutes. The mixture was stirred at RT for 5 h. The mixture was poured into a flask with ethyl acetate (50 ml) and washed with water (3×20 ml). The organic phase was dried over anhydrous $MgSO_4$ and then the solvent was removed by reduced pressure evaporation. The crude product was purified by recrystallization from hexane. A yellow powder of monomer **M5** was obtained with the yield 46%. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 9.93 (s, 2H); 7.79 (dd, 2H); 7.77 (s, 2H); 7.71 (dd, 2H); 7.65 (d, 2H); 7.51 (d, 2H); 2.05 (m, 4H); 1.32-1.06 (m, 32H); 0.83 (t, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 182.68, 154.78, 152.27, 142.26, 141.65, 137.40, 132.43, 125.73, 124.04, 120.70, 120.70, 120.70, 55.57, 40.21, 31.84, 29.87, 29.49, 29.26, 29.16, 23.77, 22.63, 14.09. The NMR spectra match well to those reported previously [S7]. Chemical analysis (%) for $C_{43}H_{54}O_2S_2$: C, 77.43; H, 8.16; O, 4.80; S, 9.61; found C, 78.08; H, 8.47; S, 11.70.

Synthesis of polymer P-Sz

The polymer **P-Sz** was synthesized and purified following the general procedure reported previously [S8]. **P-Sz** was synthesized from **M1** (0.066 g, 0.143 mmol) and **M4** (0.1 g, 0.143 mmol). Yield = 62%. M_W = 7 kDa, M_W/M_n=1.5. Chemical analysis (%) for $C_{45}H_{54}N_2S_4$: C, 71.95; H, 7.25; N, 3.73; S, 17.07; found C, 71.64; H, 8.22; N, 4.02; S, 17.33.

Synthesis of polymer P-St

The polymers **P-St** was synthesized and purified following the general procedure reported previously [S9]. **P-St** was synthesized from **M2** (0.3 g, 0.496 mmol) and **M3** (0.314 g, 0.496 mmol). Yield = 50%. M_W= 4.8 kDa, M_W/M_n=1.6. Chemical analysis (%) for $C_{153}H_{178}N_8S_{16}Sn_2$: C, 63.82; H, 6.23; N, 3.89; S, 17.81; Sn, 8.25; found C, 63.26; H, 6.11; N, 4.19; S, 18.26.

Synthesis of polymer P-C

P-C was synthesized from **M2** (0.291 g, 0.436 mmol) and dithioxamide **1b** (0.052 g, 0.436 mmol). Monomer **M2** and compound **1b** were dissolved in a mixture of solvents DMF/Pyridine (1.5 ml/1.5 ml) in a 10 ml teflon reactor and placed in a microwave reactor 600 W. This was heated with stirring for 30 minutes. Then more compound **1b** (0.012 g, 0.099 mmol) was added to the reaction mixture, and heating was continued 10 min. Then furfural (1 ml, 12 mmol) was added, and heating was continued in a microwave reactor for 10 min. Then the mixture was cooled down to room temperature, and polymer was precipitated with acetone (30 ml). The precipitate was then subjected to Soxhlet extraction with acetone and dichloromethane. The yield of the purified polymer **P-C** was 32%. M_W = 11.2 kDa, M_W/M_n = 2.0. Chemical analysis (%) for $C_{45}H_{54}N_2S_4$: C, 71.95; H, 7.25; N, 3.73; S, 17.07; found C, 72.21; H, 7.13; N, 3.79; S, 16.48.

Fabrication of perovskite solar cells

Glass/ITO substrates (Kintec, 15 Ω/sq.) were cleaned by sonication in acetone, water, and propan-2-ol for 15 minutes. Before deposition of ETL substrates were exposed to air plasma at 50% power for 5 minutes. The SnO_2 (15% nanoparticles in H_2O, Alfa Aesar) was spin-coated at 4000 rpm under ambient conditions. Further films were annealed at 175°C for 30 min, introduced into glovebox and additionally annealed at 100°C for 5 min. The passivating layer [6,6]-phenyl-C_{61}-butyric acid (PCBA) (0.2 mg ml^{-1} in chlorobenzene) was spin-coated at 3000 rpm and annealed at 100°C for 10 min. The powders of CH_3NH_3I and PbI_2 were dissolved in the mixture of DMF and NMP (4:1) to give the 1.4 M solution of the $CH_3NH_3PbI_3$ ink. The perovskite ink was spin-coated at 4000 rpm, quenched with antisolvent at 20 sec, and left to dry at 4000 rpm for 40 sec, and afterwards without rotation at room temperature for 20 min. Next, the devices were slowly heated to 80°C and annealed at this temperature for 5 minutes. Solutions of polymers **P-C**, **P-St**, **P-Sz** in chlorobenzene (7 mg ml^{-1}) were spin-coated atop the perovskite film at 2k,3k,4k,5k rpm to reveal the optimal deposition conditions. Thin layer of MoOx (10 nm) and silver electrode (100 nm) were deposited through the shadow mask using thermal evaporation under reduced pressure (10^{-5} mbar) resulting in the active area of photovoltaic cells 0.16 cm^2.

Table S1. Selection of solvents for polymer synthesis from monomer **M5** and dithioxamide.

Solvent	Reaction time, min	Yield, %	M_W, Da	PDI
1,2-Dichlorobenzene	60	10	2020	1.9
Dioxane	75	13	3900	1.4
DMF	16	45	18670	4.2
o-Xylene	60	11	2610	2.2
THF	360	4	1850	1.5
N,*N*-Dimethylacetamide	150	52	3140	2.4
Pyridine	660	40	5000	2.4
DMF/Pyridine (50:50)	50	32	11200	2.0

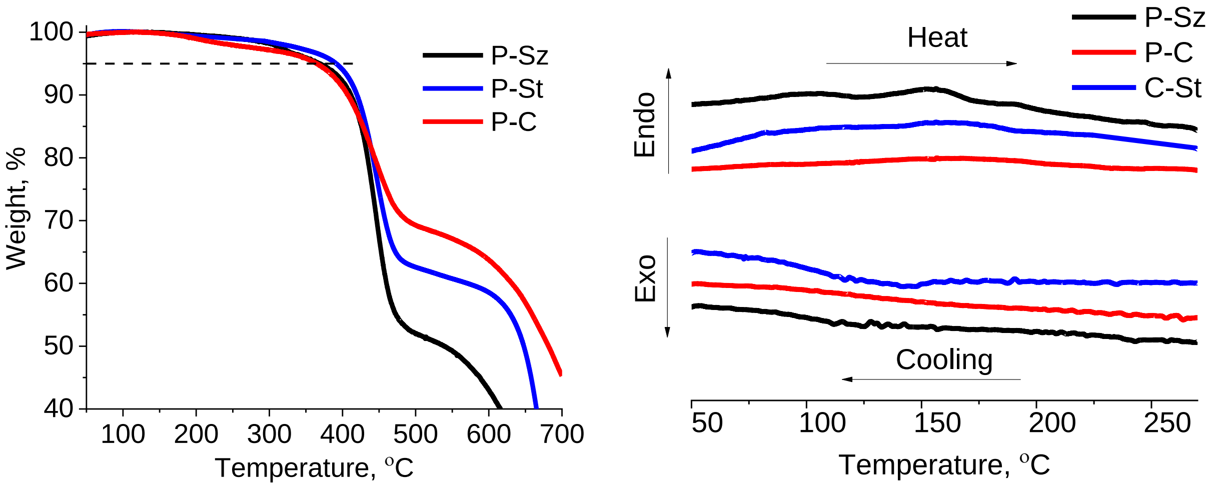


Figure S1. TGA and DSC curves of polymers **P-Sz, P-St, P-C**

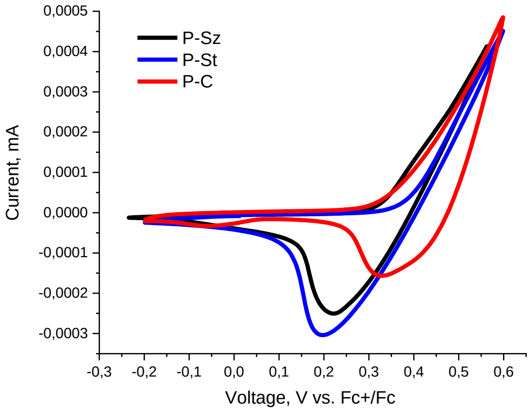


Figure S2. Cyclic voltammograms for films of **P-Sz, P-St, P-C**

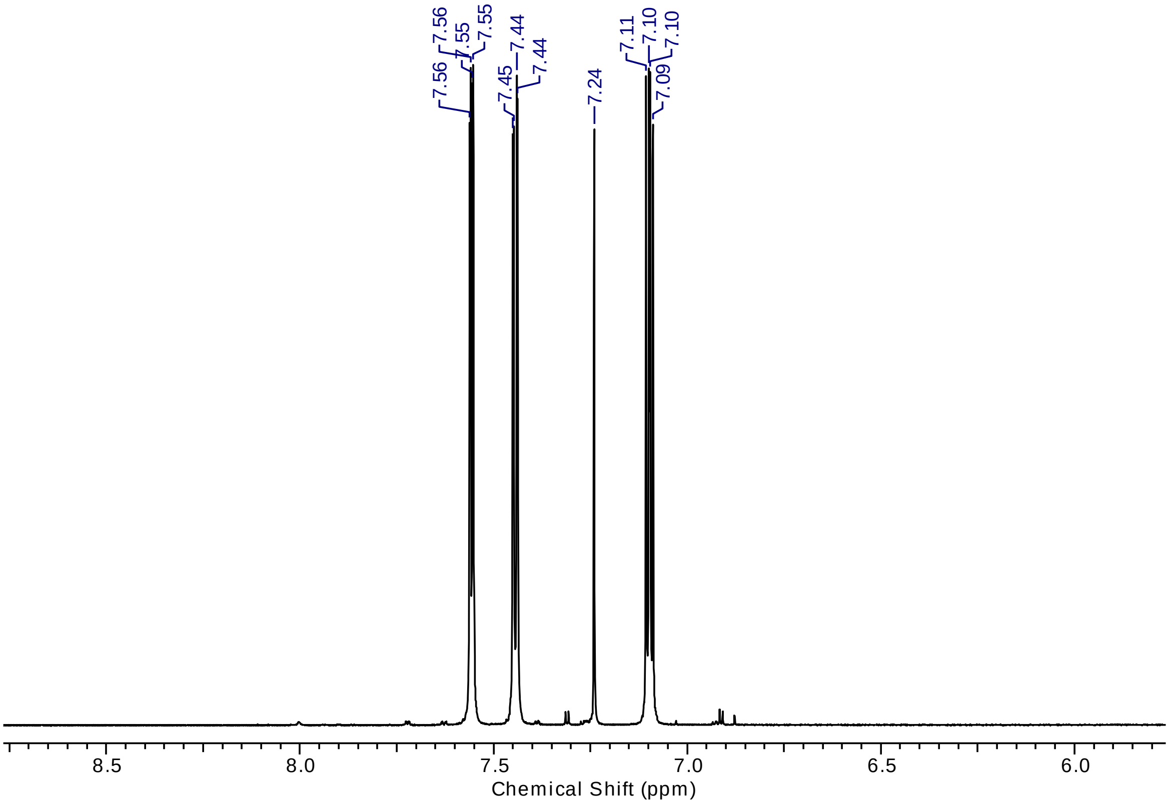


Figure S3. ^{1}H NMR spectrum of compound **1c**.

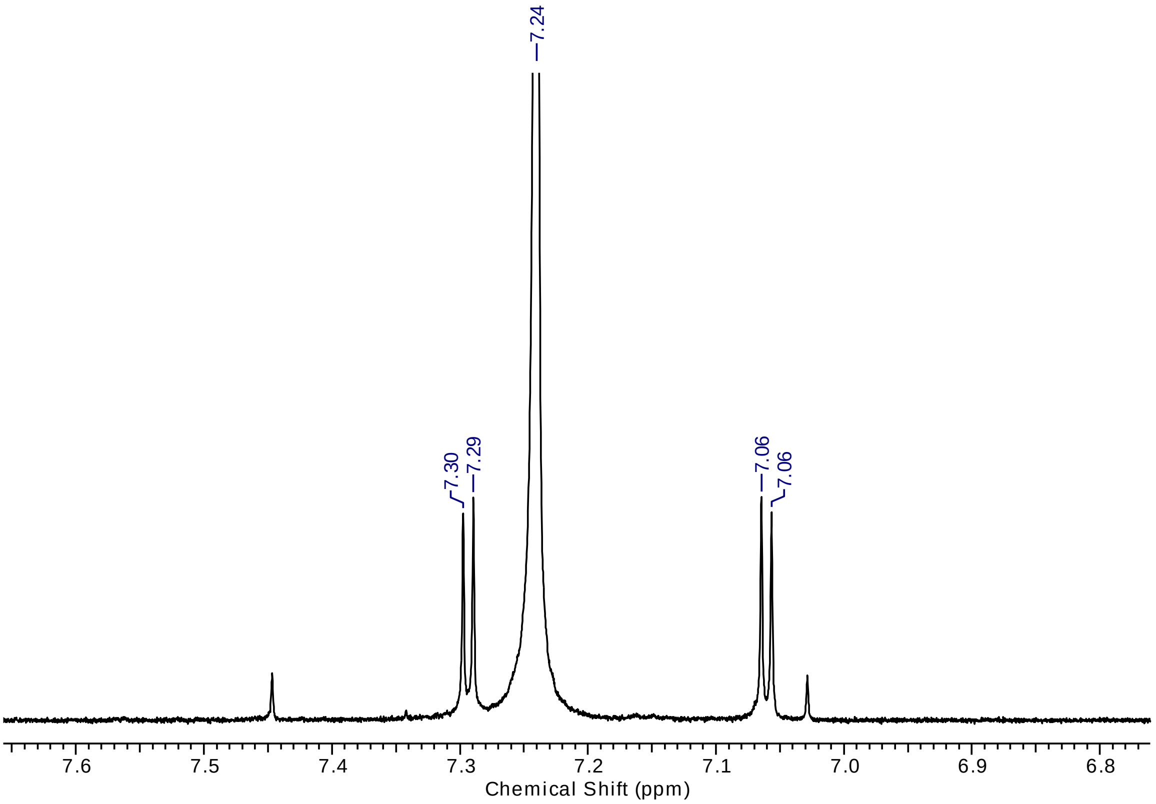


Figure S4. ^{1}H NMR spectrum of monomer **M1**.

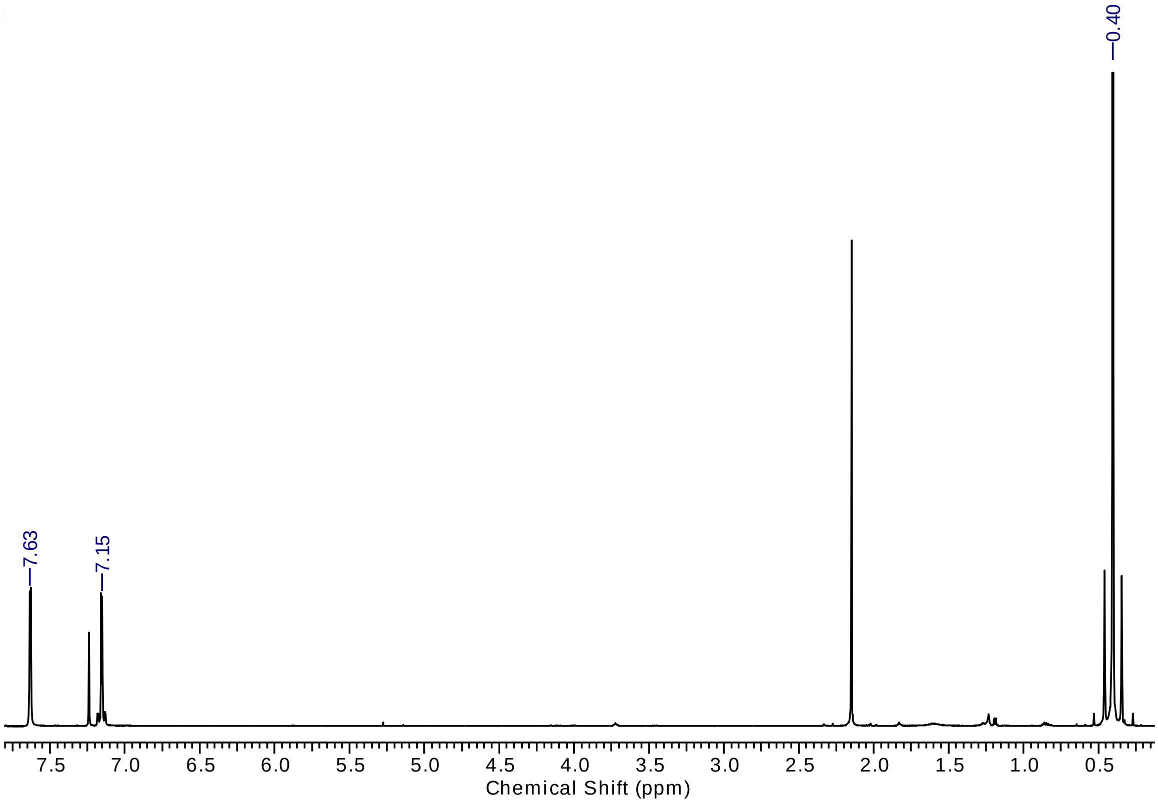


Figure S5. ^{1}H NMR spectrum of monomer **M2**.

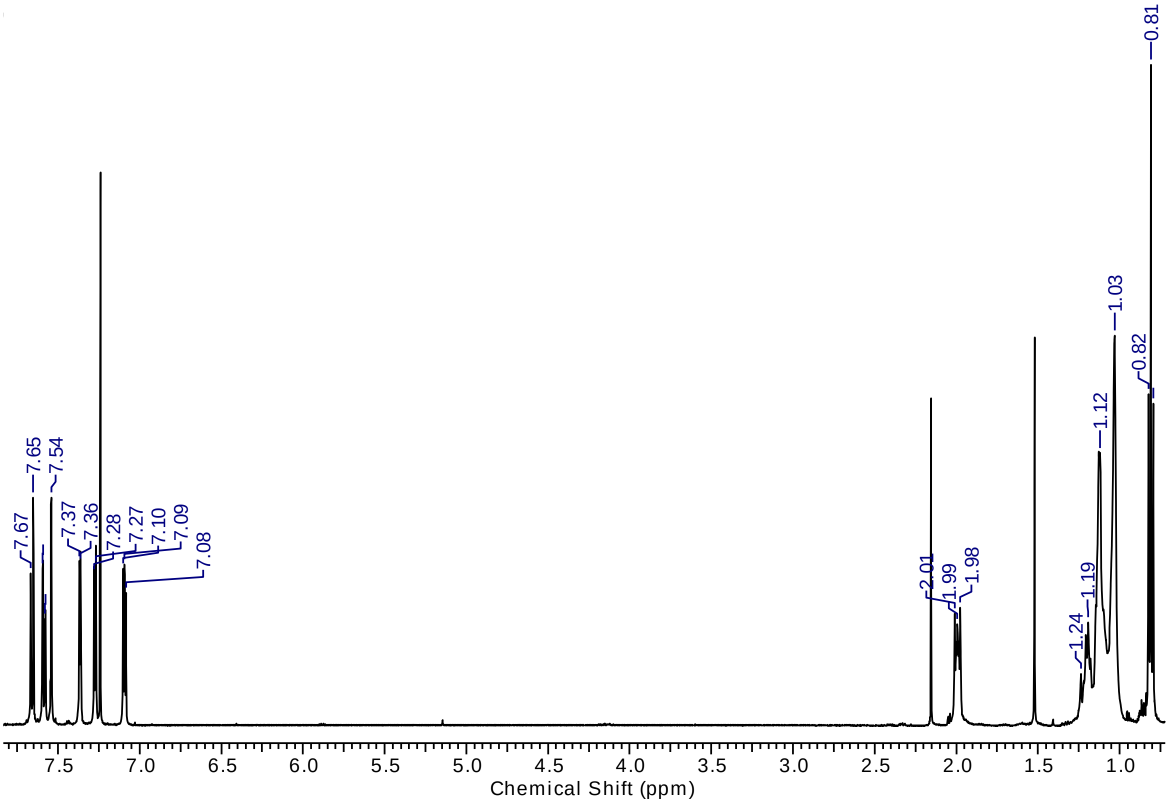


Figure S6. ^{1}H NMR spectrum of compound **2c**.

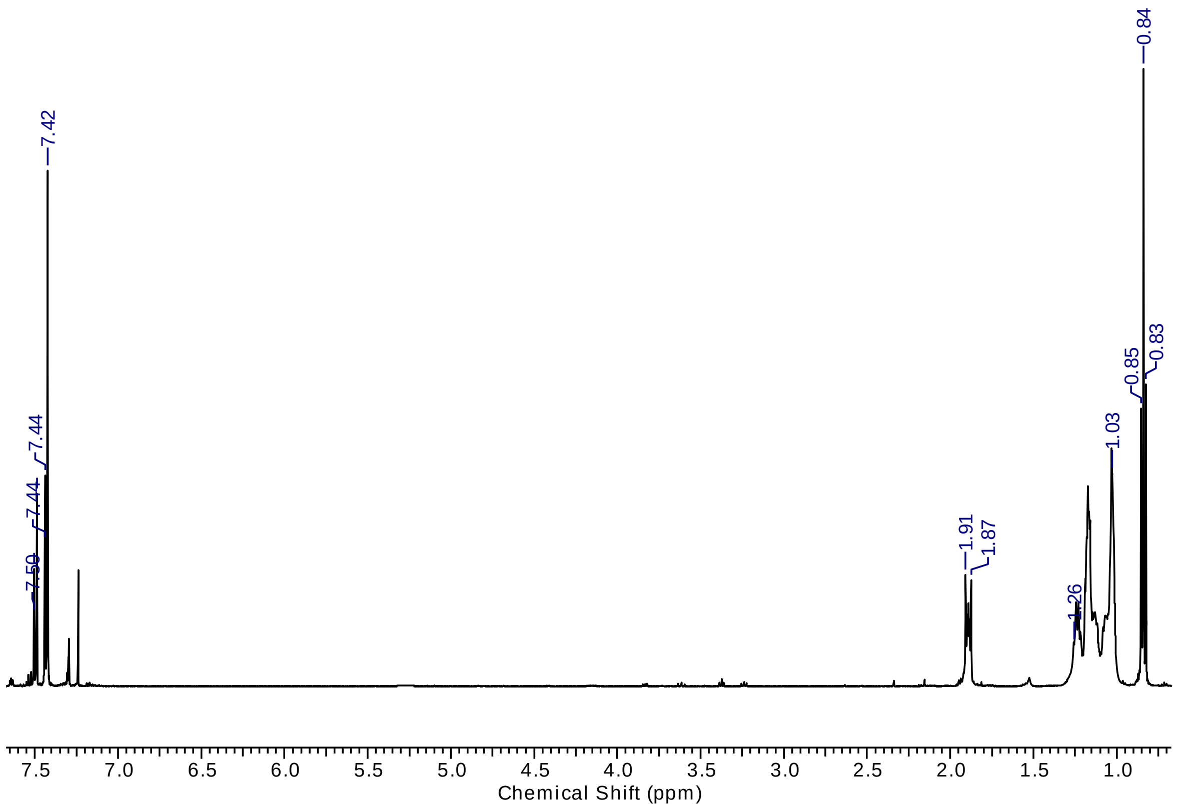


Figure S7. ^{1}H NMR spectrum of monomer **M3.**

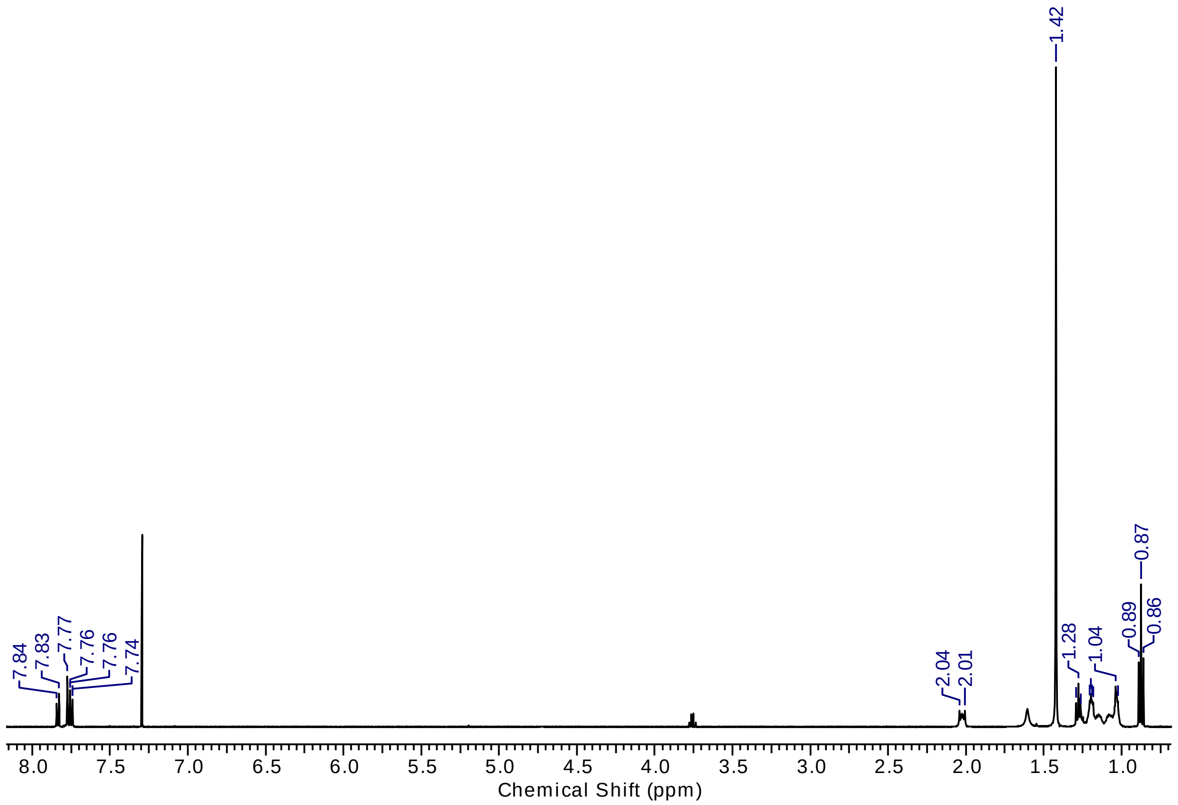


Figure S8. ^{1}H NMR spectrum of monomer **M4.**

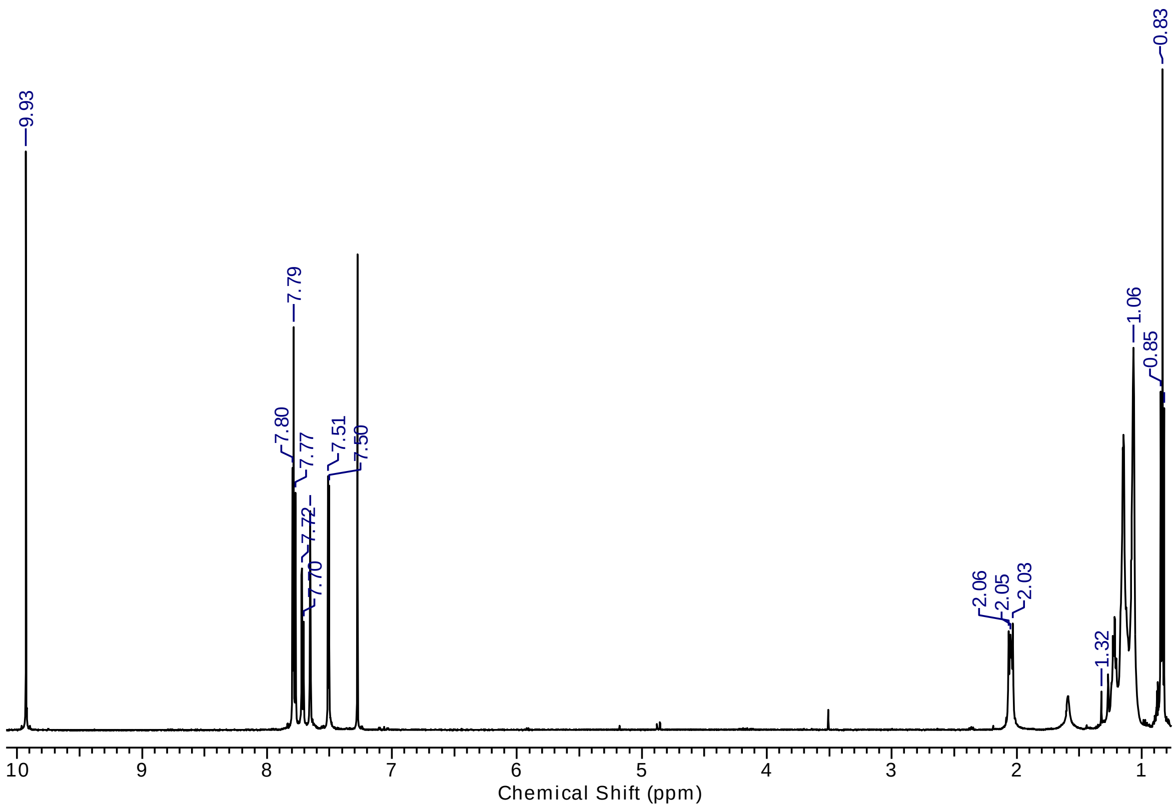


Figure S9. ^{1}H NMR spectrum of monomer **M5.**

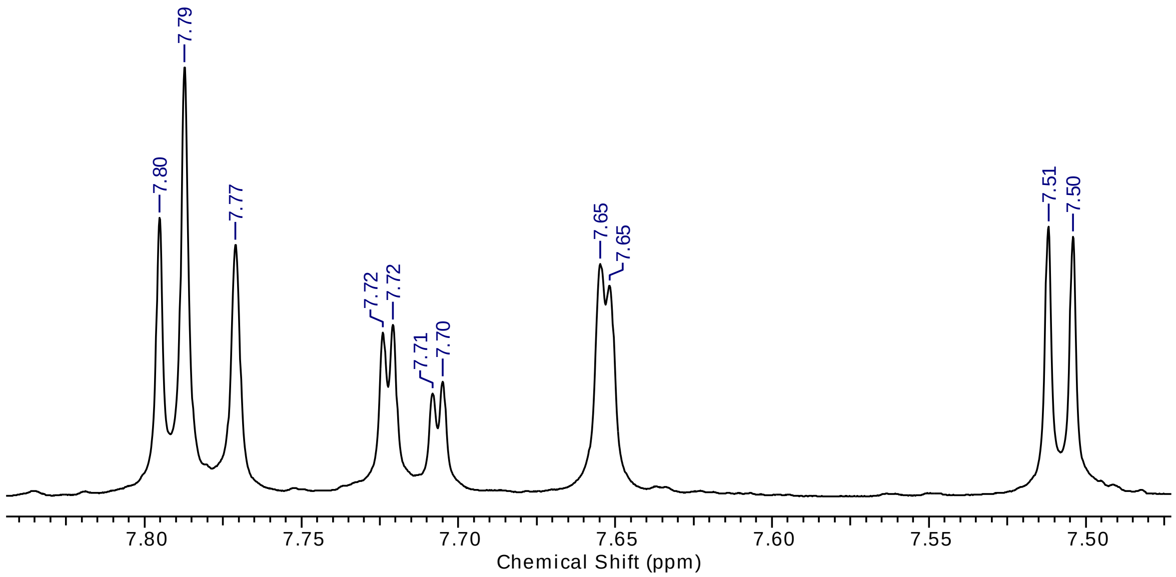


Figure S10. ^{1}H NMR spectrum of monomer **M5.**

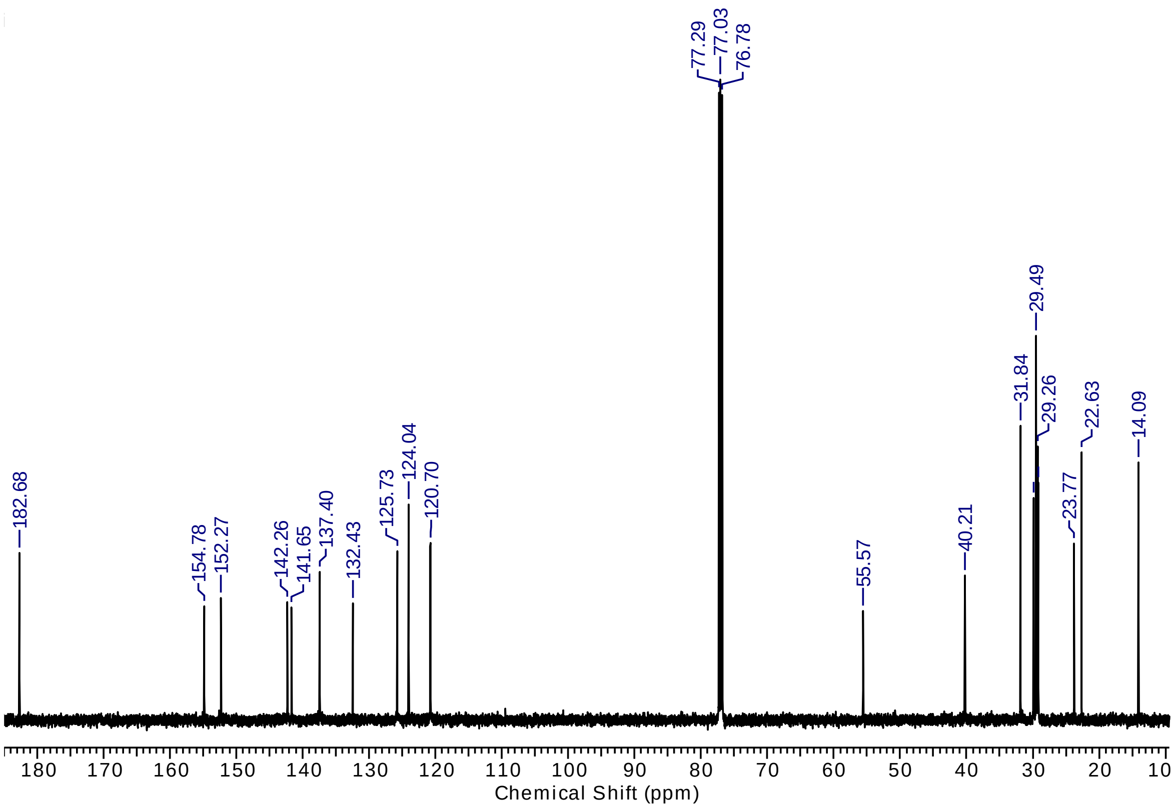
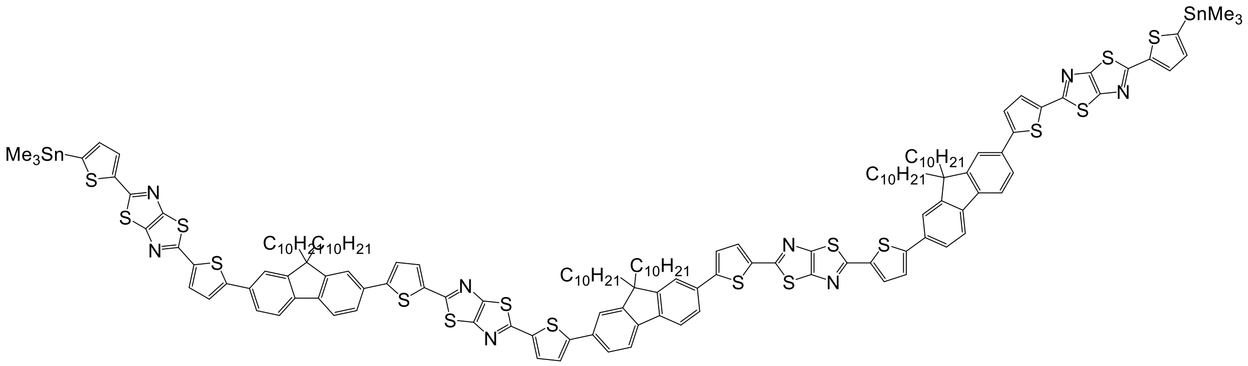


Figure S11. ^{13}C NMR spectrum of monomer **M5.**



Elemental Analysis: C, 63.82; H, 6.23; N, 3.89; S, 17.81; Sn, 8.25

Figure S12. Proposed structure **P-C.**

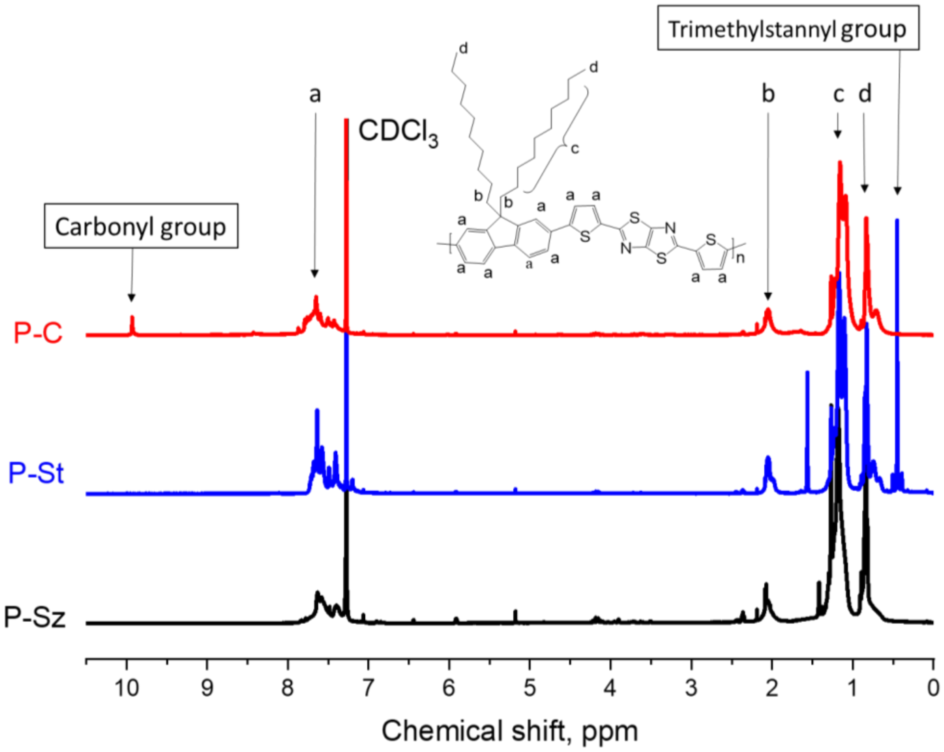


Figure S13 ^{1}H NMR spectra of polymers **P-Sz**, **P-St**, **P-C**

The polymers were investigated by ^{1}H NMR spectroscopy (Figure S13). It can be seen that the proton spectra are very similar. In particular, the signals in the range of 7.2-7.6 ppm correspond to the protons of the thiophene and fluorene moieties (part *a*). The signals at 2.1 ppm are related to CH_2 groups of decyl chains on fluorene block (part *b*). The broad multiplet in the range of 1.0-1.4 ppm is related to sixteen methylene groups. The signal at 0.8 ppm belongs to terminal CH_3 groups. Despite of the fact that on the final stage of Stille polymerization the end-capping of polymer backbone was performed by adding of excess of trimethyl(2-thienyl)-stannane and bromobenzene, the signals of residual trimethylstannyl groups in the NMR spectrum of **P-St** were observed. The presence of trimethylstannyl groups was also confirmed by elemental analysis (see Figure S12). In view of the low molecular weight of **P-St**, the presence of $SnMe_3$ fragments will noticeably affect the elemental composition. Additionally, in the NMR spectrum of **P-C**, the singlet of carbonyl groups at 10 ppm can be seen. Generally, the analysis of spectra showed that the polymer backbone structure is similar for all compounds.

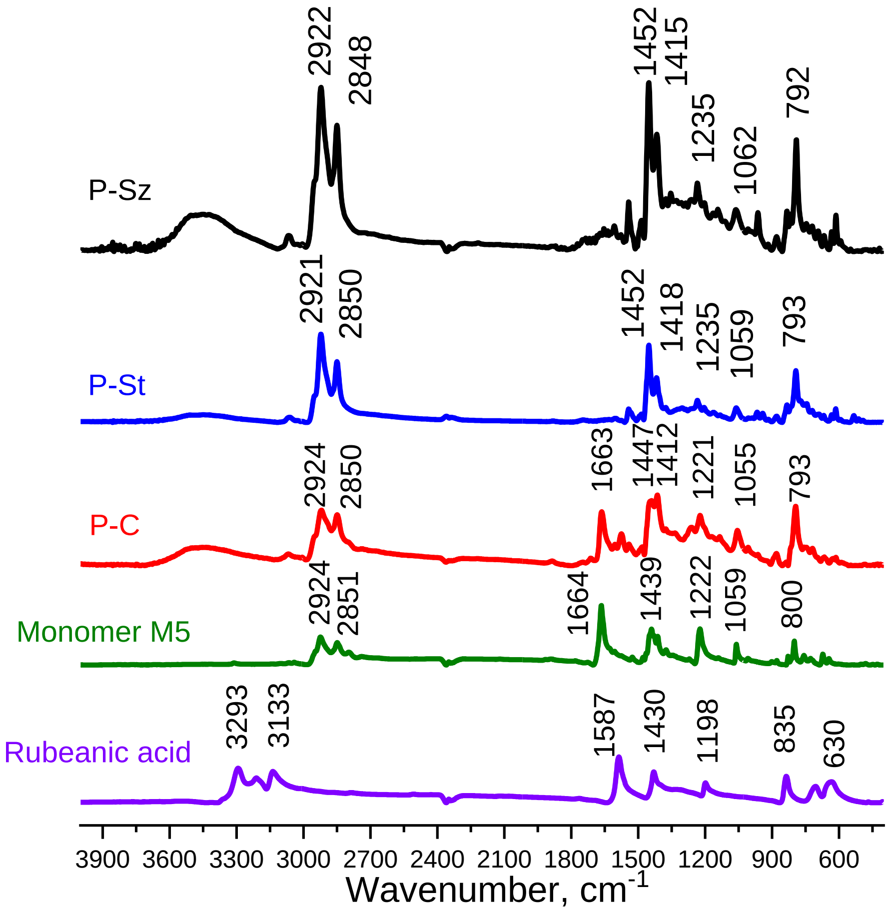


Figure S14 FT-IR spectra of polymers **P-Sz, P-St, P-C**, monomer **M5,** and thioxamide (rubeanic acid).

The FTIR spectra (Figure S14) confirmed the similar structure of all polymers. The spectrum of polymer **P-C** differs from those of **P-Sz** and **P-St** by peak at 1663 cm^{-1}, which can be assigned to carbonyl groups. This is also supported by the spectra of the starting compound **5** containing carbonyl groups with signal at 1664 cm^{-1}. The signals at 2950-2850 cm^{-1} attributed to the C-H stretching of alkyl substituents of the fluorene moiety. The C=C vibrations in aromatic rings can be seen at 1450-1440 cm^{-1}. The typical C-S stretching peaks in thiophene and thiazolo[5,4-*d*]thiazole rings are registered at ~1220 cm^{-1} and ~1050 cm^{-1}. The peak appeared at 793 cm^{-1} can be attributed to C-H out-of-plane bending vibration of the thiophene ring. IR data indicate that the polymer **P-C** obtained by the alternative method possesses a very similar structure to **P-Sz** and **P-St**.

References

S1. A. V. Akkuratov, F. A. Prudnov, L. N. Inasaridze and P. A. Troshin, *Tetrahedron Lett.*, 2017, **58**, 97.

S2. I. H. Jung, J. Yu, E. Jeong, J. Kim, S. Kwon, H. Kong, K. Lee, H. Y. Woo and H.-K. Shim, *Chem. - Eur. J.* 2010, **16**, 3743.

S3. P. M. Kuznetsov, S. L. Nikitenko, I. E. Kuznetsov, P. I. Proshin, D. V. Revina, P. A. Troshin and A. V. Akkuratov, *Tetrahedron Lett.*, 2020, **61**, 152037.

S4. H.-H. Lu, Y.-S. Ma, N.-J. Yang, G.-H. Lin, Y.-C. Wu and S.-A. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 9634.

S5. B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.*, 1998, **10**, 1863.

S6. B. Balan, C. Vijayakumar, S. Ogi and M. Takeuchi, *J. Mater. Chem.*, 2012, **22**, 11224.

S7. S. Zhang, J. Gao, W. Wang, C. Zhan, S. Xiao, Z. Shi and W. You, *ACS Appl. Energy Mater.*, 2018, **1**, 1276.

S8. M. Manuela, M. Raposo, C. Herbivo, V. Hugues, G. Clermont, M. C. R. Castro, A. Comel and M. Blanchard-Desce, *Eur. J. Org. Chem.*, 2016, 5263.

S9. B. Luszczynska, A. V. Akkuratov, M. Z. Szymanski, D. K. Susarova, B. G. R. Dupont, S. D. Babenko, L. N. Inasaridze, P. Bujak, P. A. Troshin and J. Ulanski, *Synth. Met.*, 2018, **24**, 67.