

Electronic supplementary information for the paper

“Statistical carbazole-fluorene-TTBTBTT terpolymers as promising electron donor materials for organic solar cells”

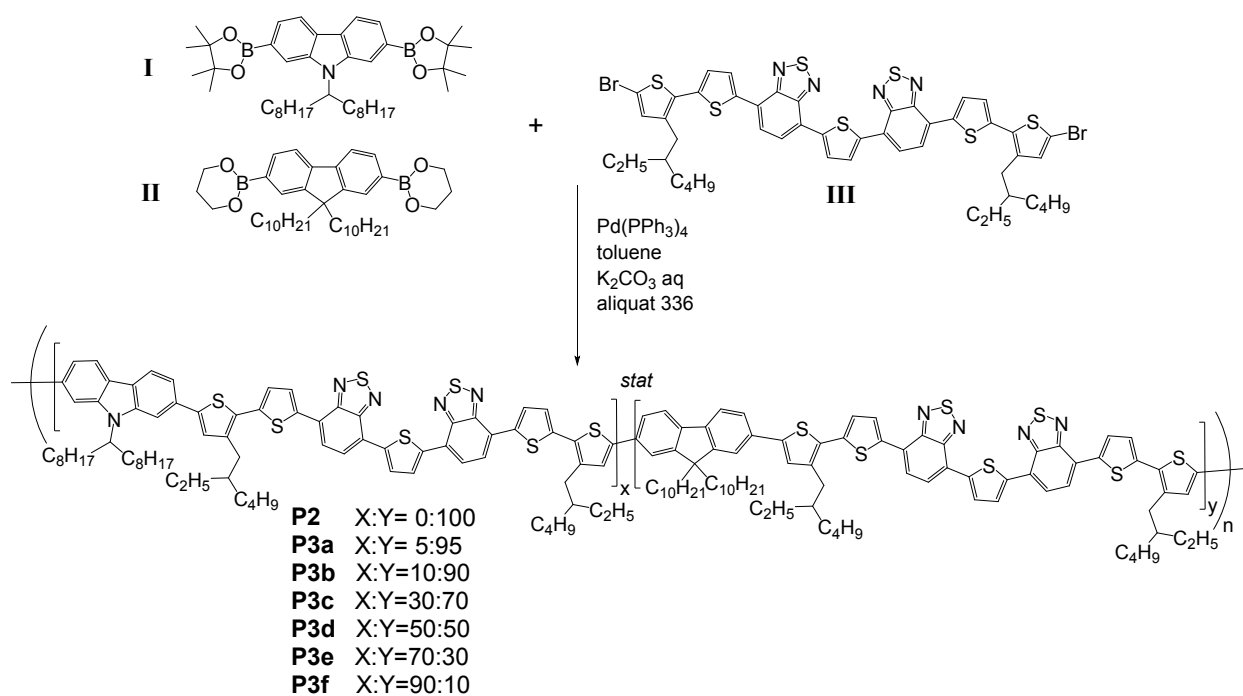
Iliya E. Kuznetsov,^{a,b} Alexander V. Akkuratov,^a Diana K. Susarova,^a Denis V. Anokhin,^c
Yuriy L. Moskvina,^d Mikhail V. Klyuev,^b Alexander S. Peregodov,^e and Pavel A. Troshin^{a*}

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General procedure for synthesis of P2 and P3a-f

Monomers **I** (x mmol), **II** ($1-x$ mmol) and **III** (1443.8 mg, 1 mmol) taken in precise stoichiometric amounts were introduced into a 150 mL round-bottom three necked flask equipped with a thermometer and reflux condenser. Toluene (75 mL), 2M aqueous solution of K_2CO_3 (6 mL), aliquat 336 (1 drop, ca. 80 mg) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added in the listed here sequence. The reaction mixture was degassed, immersed into an oil bath and heated at reflux for 3-6 hours. The molecular weight characteristics of the formed product were monitored every 30 min using gel permeation chromatography (GPC). The reaction was stopped when the weight average molecular weight M_w reached ca. 150000 g/mol or product started to form a precipitate on the walls of the flask. To terminate the reaction, we introduced 0.1 mmol of phenylboronic acid, heated the mixture at reflux for additional 1 h and then introduced 2 mmol of bromobenzene and continued the heating for additional 2 h. Afterwards, the reaction mixture was cooled down to room temperature, the polymer was extracted with 500 mL of toluene, the resulting solution was washed 3 times with deionized water (250 mL), dried and concentrated in vacuum (rotary evaporator) to 40 mL. Addition of 150 mL of methanol precipitated the crude polymer. Subsequent purification was achieved using several additional dissolving/precipitation cycles. Finally, the precipitated polymer flakes were filtered into a cellulose thimble and processed using Soxhlet extraction with hexanes (12 h), acetone (12 h), dichloromethane (12 h), chloroform (8 h) and chlorobenzene (12 h). The chlorobenzene extract was concentrated in vacuum and precipitated in methanol. The obtained solid was collected by filtration and dried in vacuum. The resulting crude polymer was further purified from the residual Pd catalyst as described in K. T. Nielsen, K. Bechgaard, F. C. Krebs, *Macromolecules* **2005**, 38, 658-659 and K.T. Nielsen, K. Bechgaard, F.C. Krebs, *Synthesis* **2006**, 10, 1639-1644. The total yield of the purified polymers varied between 80 and 90% depending on the initial molecular weight and number of the applied dissolving/precipitation cycles. All prepared polymer samples were transferred immediately inside argon glove box where they were stored in the absence of direct light.



Scheme 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. AFM images were obtained using NTEGRA PRIMA instrument (NT-MDT, Russia). Absorption spectra (for solutions of polymers in DCB and thin films) and PL spectra were obtained using Avantes AvaSpec-2048 optical fiber spectrometer.

GIWAXS measurements of thin films deposited on PEDOT:PSS were performed using XeuSS SAXS/WAXS (Xenocs, France) machine coupled to GeniX3D generator ($\lambda = 1.54 \text{ \AA}$). The 2D data were collected with the incidence angle of 0.2° using Pilatus 300k and Rayonix LX170-HS detectors with sample to detector distances of 130 and 9 cm, respectively. The modulus of the scattering vector s ($s = 2\sin\theta/\lambda$, where θ is the Bragg angle) was calibrated using seven diffraction orders of silver behenate powder.

Molecular weight characteristics of conjugated polymers were obtained using Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column ($0.78 \times 30 \text{ cm}$, 5-500 kDa). The measurements were performed using freshly distilled THF or toluene as eluents (flow rate 0.5 ml/min). The column was calibrated using a series of commercial polystyrene standards obtained from Fluka (THF as eluent) or using custom-made F8BT standards with $\text{PDI} < 1.5$ (toluene used as eluent). Molecular weights of the F8BT standards were cross-checked additionally using "Waters Alliance GPCV 2000" instrument equipped with multi-angle scattering detector HELEOS II (Wyatt). Each polymer sample was analyzed in several (3-5) concentrations to discriminate effects of aggregation on the molecular weight characteristics of the material. All polymers showed very weak (or no) aggregation when they were analyzed in toluene at low concentrations.

Cyclic voltammetry measurements

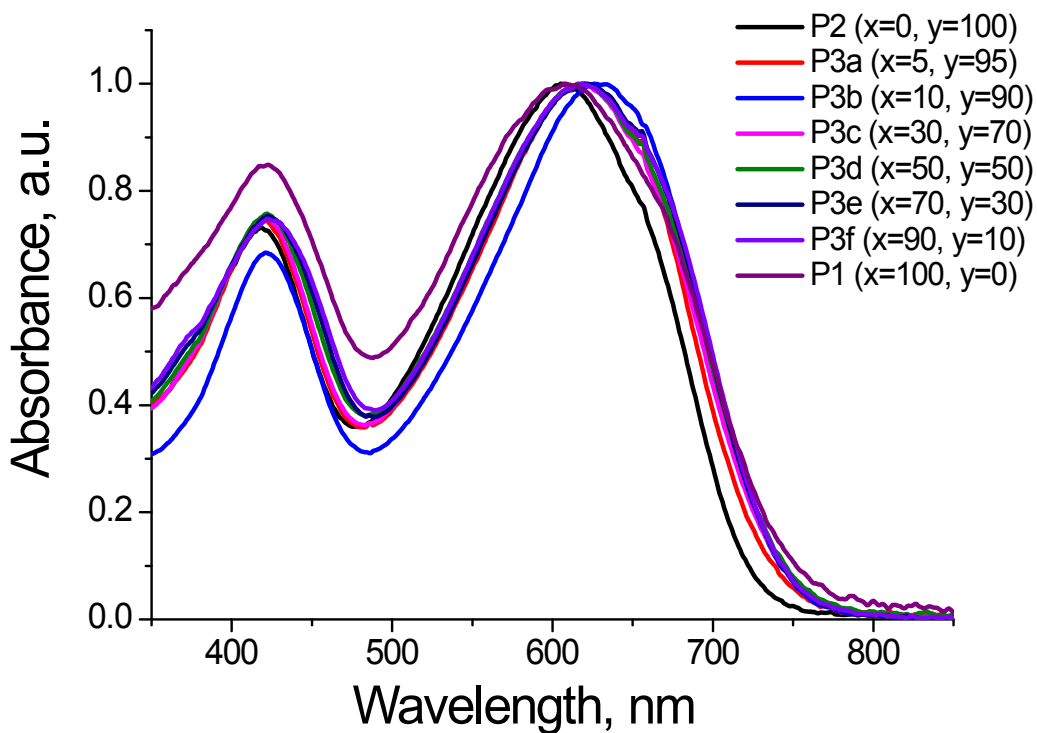
The cyclic voltammetry measurements were performed for thin films (150-250 nm thick) of polymers P1, P2 and P3a-f deposited on glassy carbon disc electrode (working electrode, $d=5 \text{ mm}$, BAS Inc.) by drop casting from a mixture of 1,2-dichlorobenzene, chlorobenzene, and chloroform (1:1:3 v/v). The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu₄NPF₆ in acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in a 0.01 M solution of AgNO₃ in 0.1 M TBAP (CH₃CN) as a reference Ag/Ag⁺ electrode (BAS Inc.). Ferrocene was used as an internal reference. The electrolyte solution was purged with argon before the measurements were performed. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV/s.

Fabrication and characterization of organic solar cells

The conjugated polymer **P1**, **P2** or **P3a-f** (7 mg) and fullerene derivative ([60]PCBM or [70]PCBM, 7-28 mg) were dissolved together in 1 mL of 1,2-dichlorobenzene while stirring at room temperature for 48 hrs. 1,8-diiodooctane (DIO) was added to the blend solution to achieve 0.12 to 6.0% volume concentration. The prepared solution was filtered through a PTFE 0.45 μm syringe filter and subjected to spin-coating at 700-2100 rpm for 150 sec. on the top of the annealed PEDOT:PSS (Clevios HTL) films deposited on the patterned ITO electrodes. The obtained films were transferred immediately into a glove box and thermally annealed under an argon atmosphere at 95 °C for 10 min. The top electrode comprising Ca (20 nm) and Ag (100 nm) was deposited by thermal evaporation at a pressure below 4×10^{-6} mbar in a vacuum chamber integrated inside an MBraum glovebox. The size of the active area in photovoltaic cells was $\sim 0.5 \text{ cm}^2$ as defined by a shadow mask.

The current-voltage (I-V) characteristics of the devices were obtained in the dark and under simulated 100 mW/cm^2 AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator integrated into an MBraun glove box. The intensity of the illumination was checked every time before each measurement using a calibrated silicon diode with a known spectral response. The I-V curves were recorded under an inert atmosphere using Kethley 2400 source-measurement unit. The active areas of all of the devices were measured with good accuracy just after the J-V measurements to estimate the short circuit current densities. The obtained J_{SC} values were reconfirmed by integrating the EQE spectra against a standard AM1.5 spectrum. The EQE spectra were measured under normal atmospheric conditions without applying any special encapsulation or protection to the photovoltaic devices using a specially designed setup, from LOMO instruments, Russia.

a



b

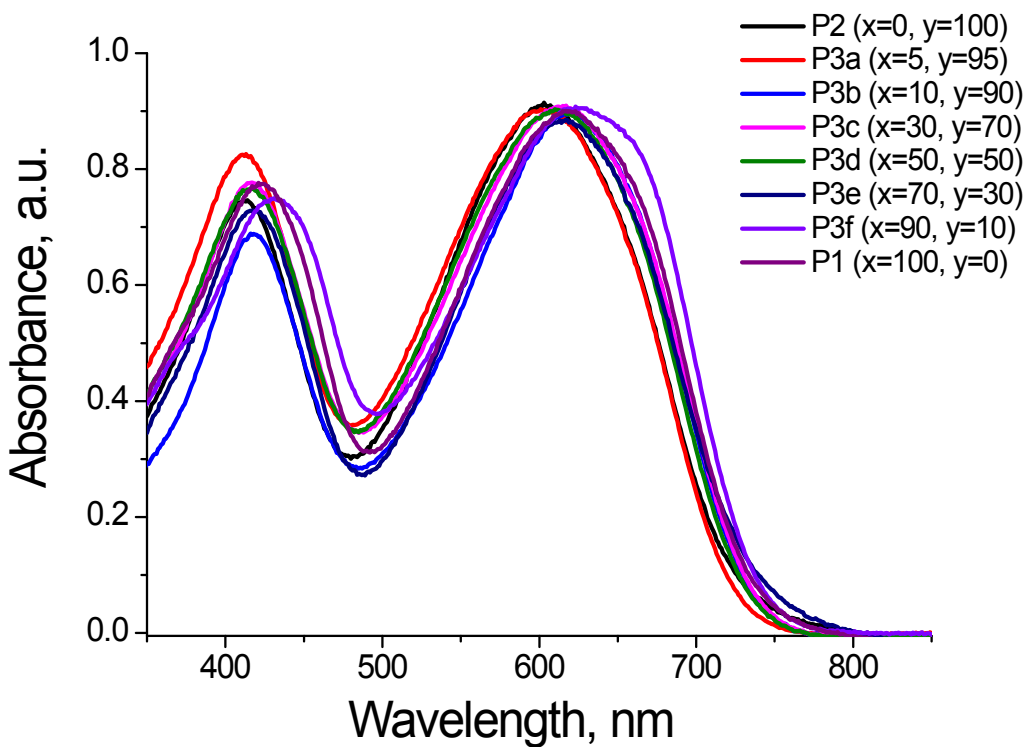


Figure S1. Absorption spectra of solutions of **P1**, **P2** and **P3a-f** in 1,2-dichlorobenzene (a) and their thin films spin-coated from 1,2-dichlorobenzene at 600-800 rpm (b)

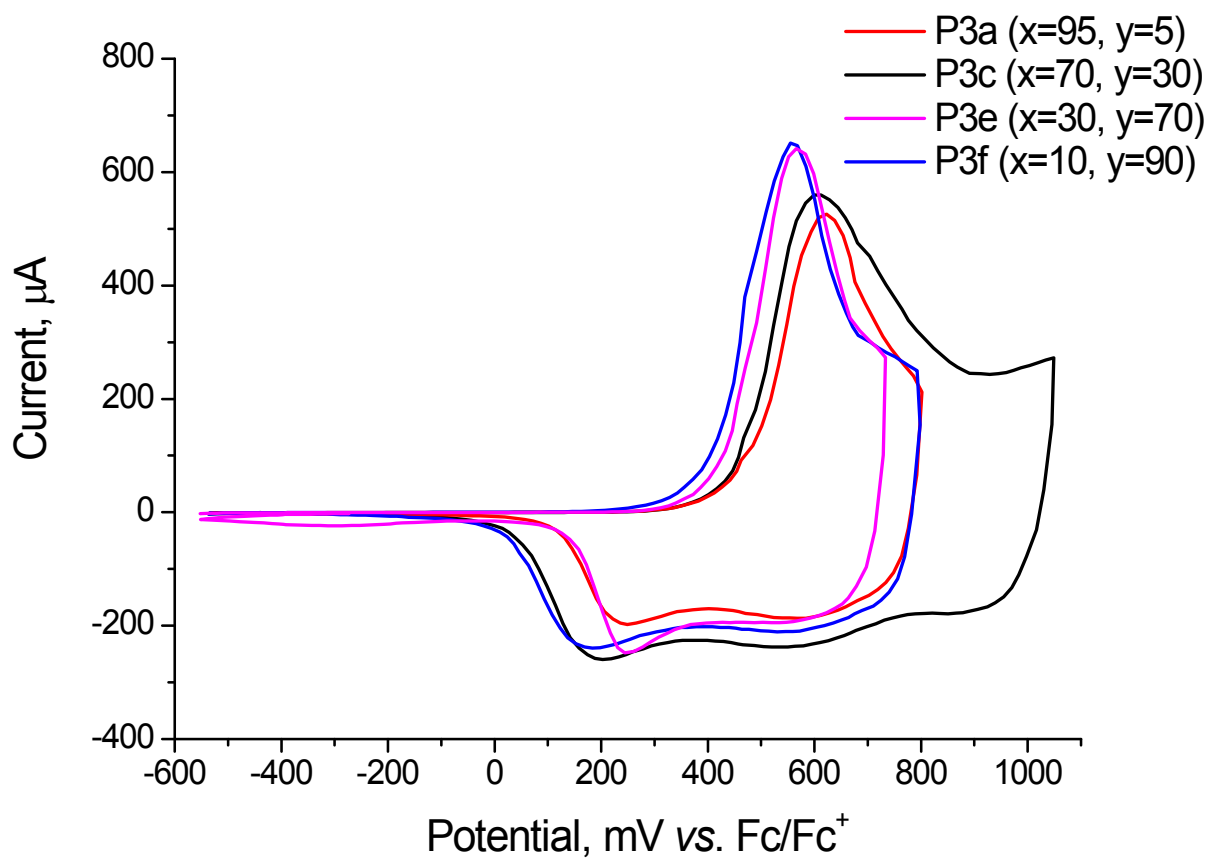
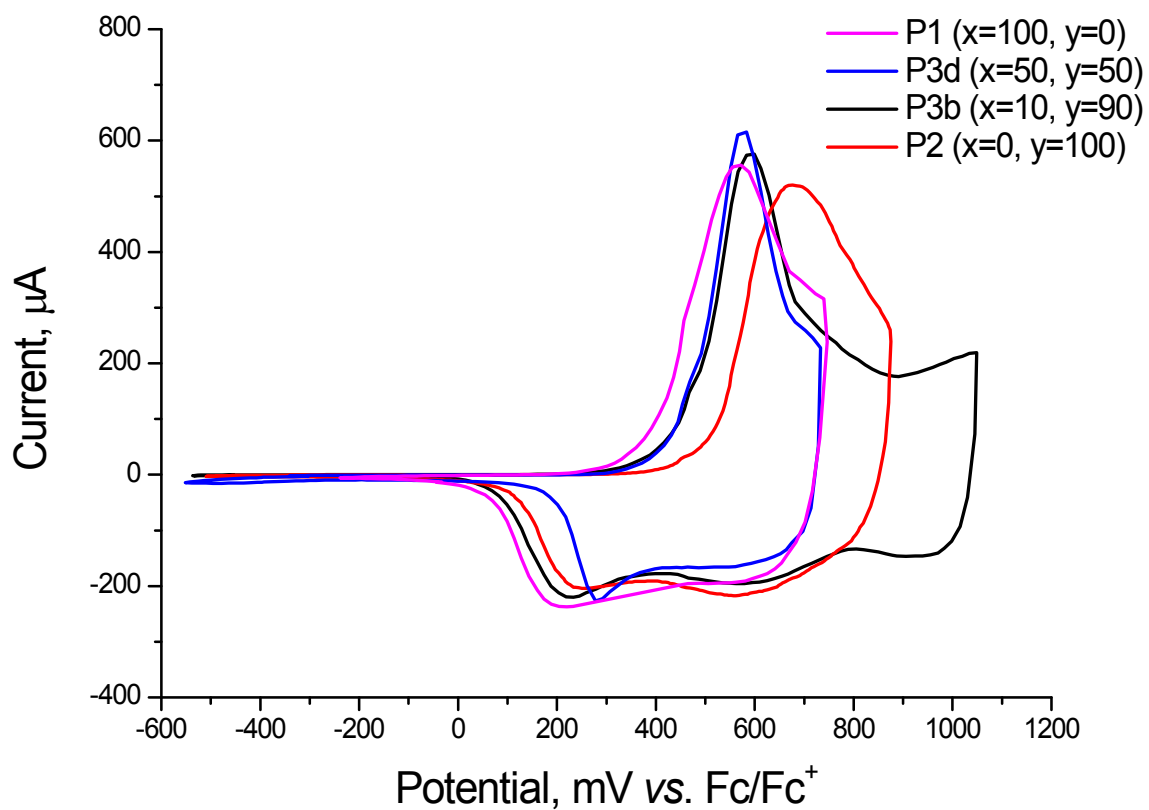


Figure S2. Cyclic voltammograms of **P1**, **P2** and **P3a-f**

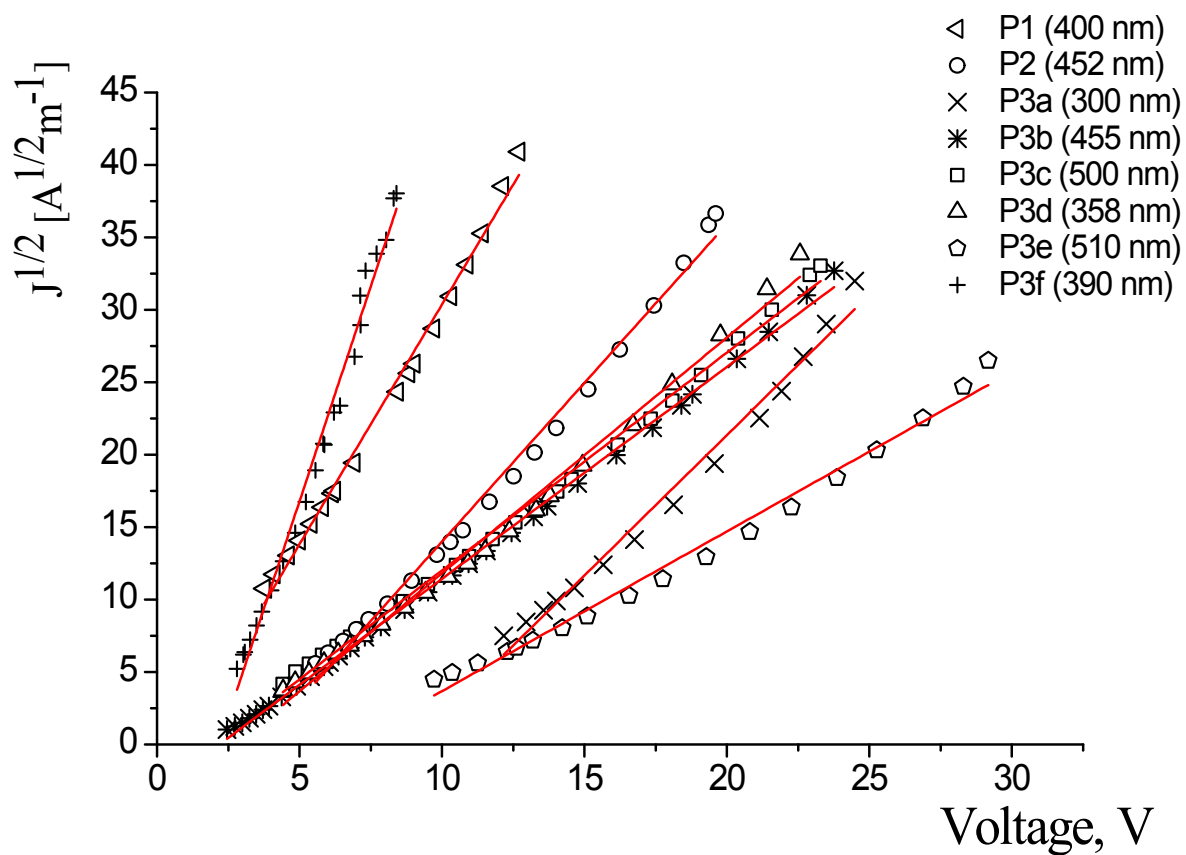


Figure S3. $J^{1/2}$ -V plots for hole-only devices ITO/PEDOT:PSS/polymer/MoO₃ (20 nm)/Ag

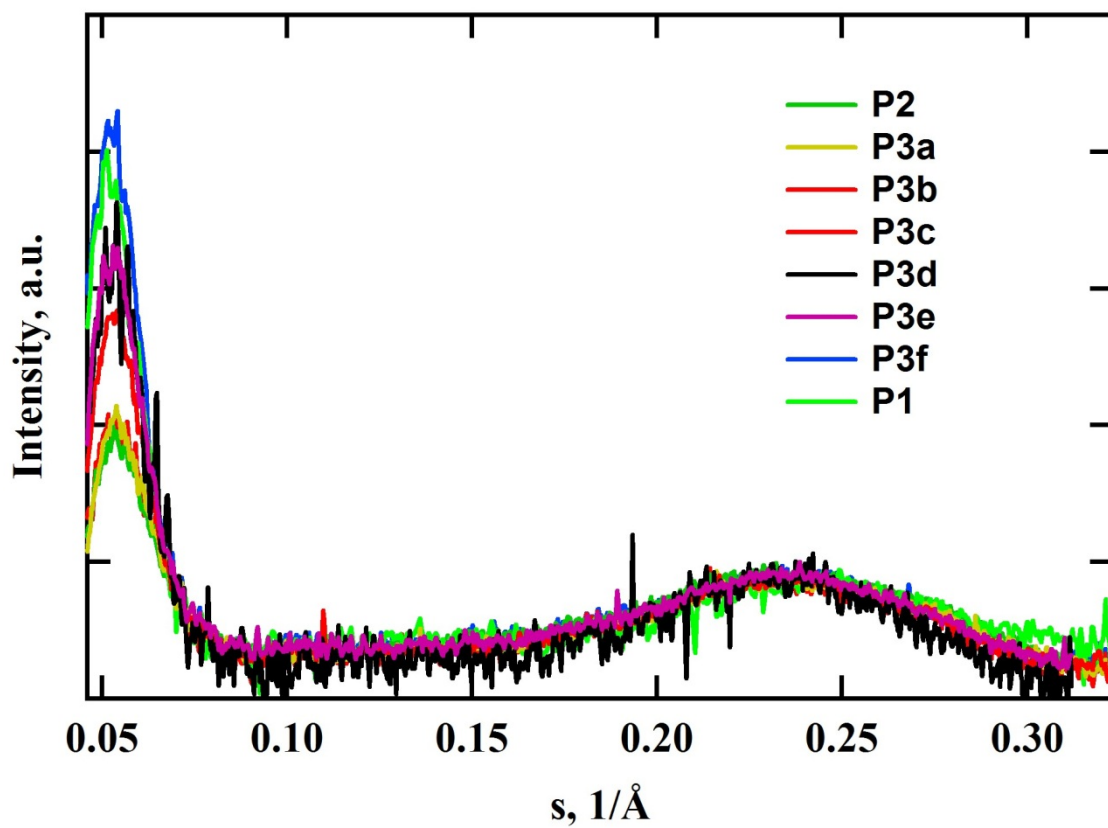


Figure S4. GIWAXS diffraction profiles for thin films of conjugated polymers **P1**, **P2** and **P3a-f**

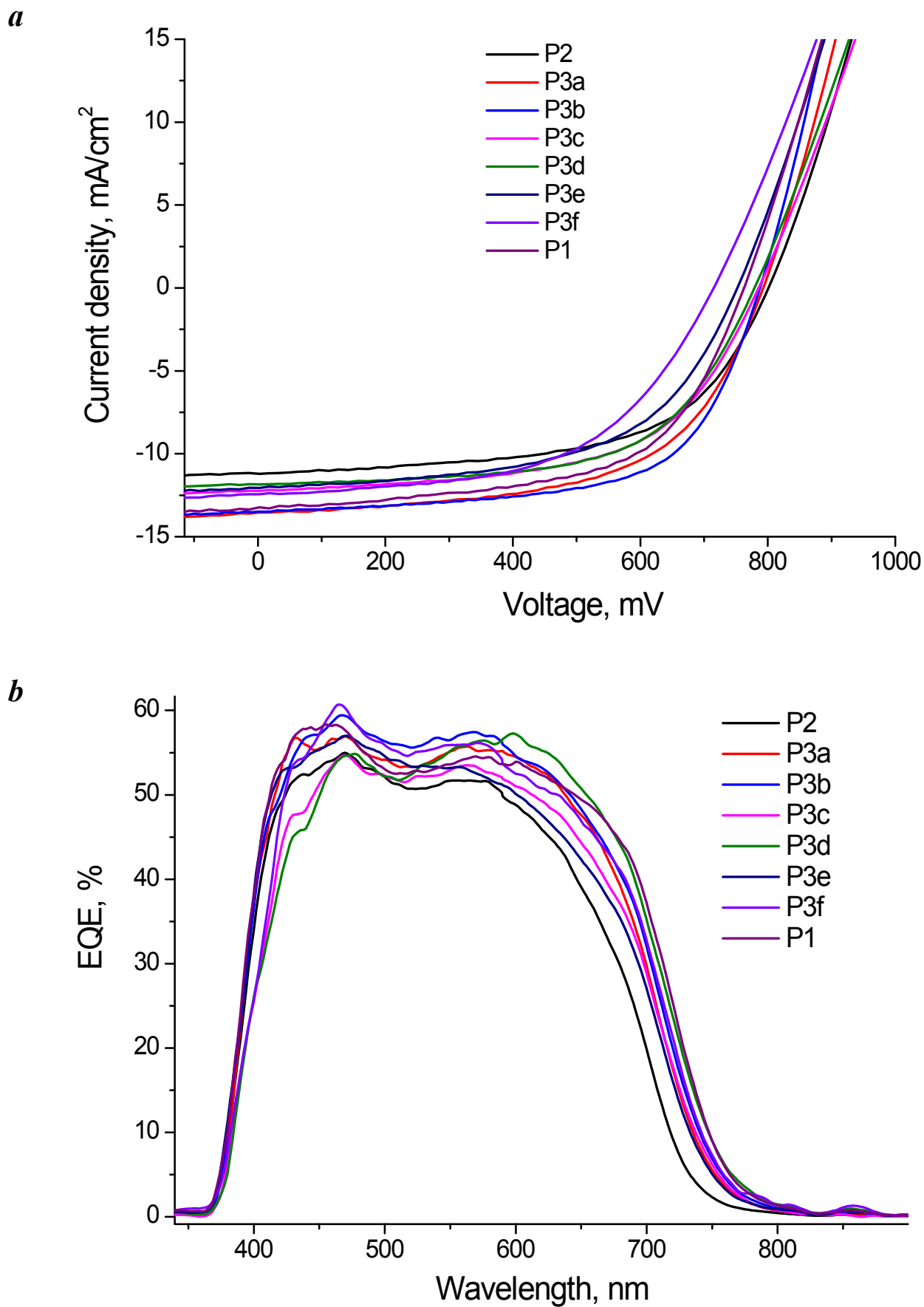


Figure S5. J-V plots (a) and EQE spectra (b) for organic solar cells based on the blends of polymers **P1**, **P2** and **P3a-f** with [70]PCBM

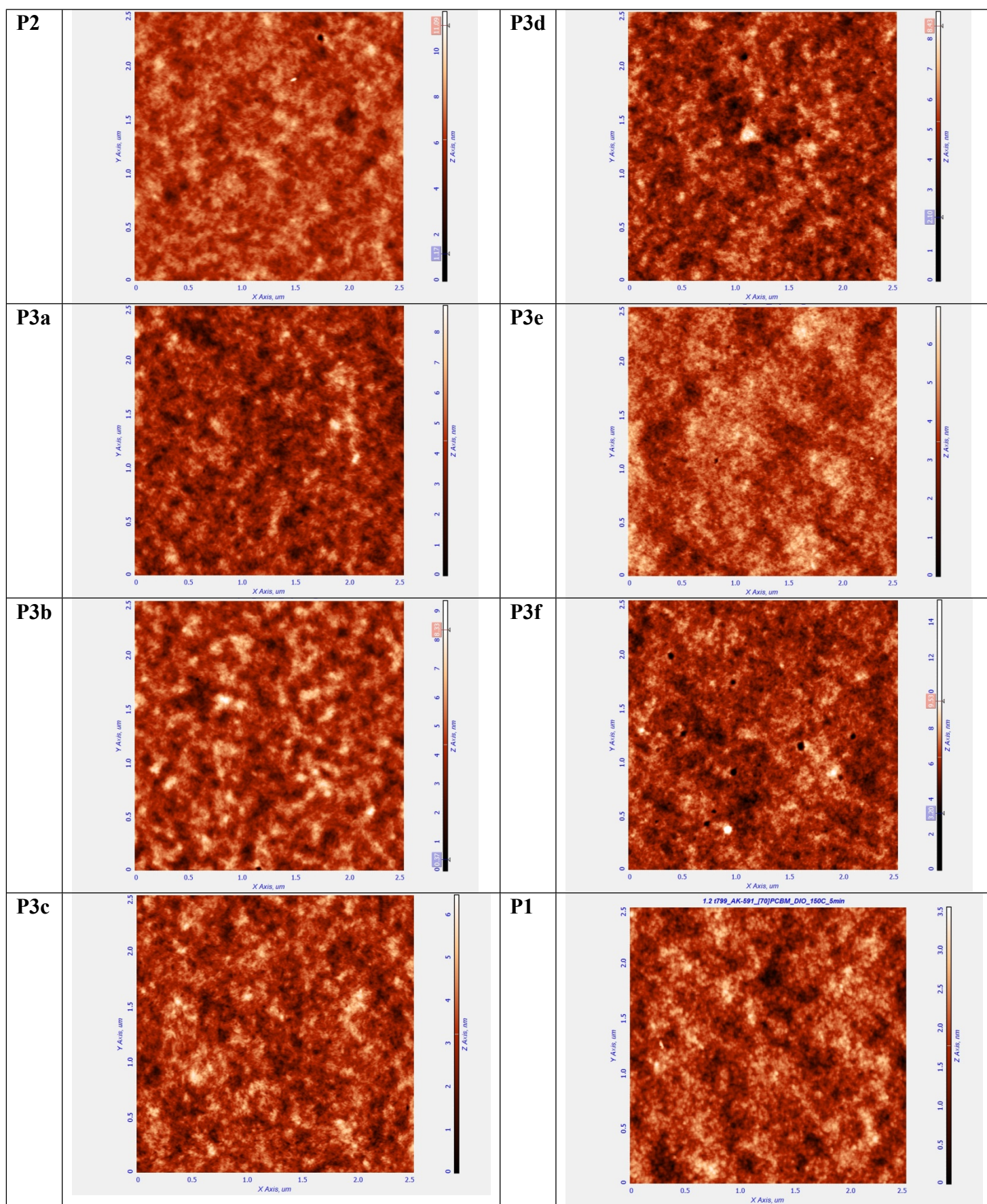


Figure S6. AFM images for the blends P1/[70]PCBM (1:2), P2/[70]PCBM (1:3.5), P3a/[70]PCBM (1:2), P3b/[70]PCBM (1:2.5), P3c/[70]PCBM (1:2.5), P3d/[70]PCBM (1:2.5), P3e/[70]PCBM (1:2) and P3f/[70]PCBM (1:1.5) processed using optimal amounts of 1,6-diiodooctane (DIO) as indicated in Table 2 of the main text

Table S1. Parameters of the solar cells based on the blends of **P1**, **P2**, **P3a-f** and [70]PCBM processed without additives

Polymer	Weights of polymer and [70]PCBM (mg per 1 mL of DCB), optimal spin coating frequency	V _{OC} , mV	J _{SC} , mA/cm ²	FF, %	η, %
P1	9 mg/ 9 mg; 800 rpm	770	13.5	54	5.7
P2	8 mg/ 36 mg; 1600 rpm	788	11.3	55	4.9
P3a	7 mg/ 14 mg; 1100 rpm	810	11.7	52	4.9
P3b	6 mg/ 15 mg; 1100rpm	796	13.1	57	5.9
P3c	7 mg/ 17.5 mg; 1000 rpm	790	10.8	53	4.6
P3d	6 mg/ 9 mg; 1100 rpm	786	11.0	54	4.7
P3e	6 mg/ 9 mg; 1000 rpm	777	10.1	56	4.4
P3f	7 mg/ 17.5 mg; 1000 rpm	729	11.8	52	4.5

Table S2. Parameters of the solar cells based on the blends of **P1**, **P2**, **P3a-f** and [60]PCBM

Polymer	Weights of polymer and [60]PCBM (mg per 1 mL of DCB), optimal spin coating frequency and DIO concentration	V _{OC} , mV	J _{SC} , mA/cm ²	FF, %	η, %
P1	9 mg/ 11.25 mg; 800 rpm; 0.6% DIO	776	10.4	62	5.0
P2	8 mg/ 20 mg; 1000 rpm; without DIO	822	9.9	56	4.6
	8 mg/ 20 mg; 1000 rpm; 0.6% DIO	811	8.6	63	4.4
P3a	8 mg/ 12 mg; 1200 rpm; without DIO	799	10.6	52	4.4
P3b	6 mg/ 15 mg; 1000 rpm; 0.6% DIO	813	10.3	61	5.1
P3c	7 mg/ 10.5 mg; 800 rpm; 0.6% DIO	814	10.0	57	4.6
P3d	6 mg/ 9 mg; 1000 rpm; 0.6% DIO	751	9.8	57	4.2
P3e	6 mg/9 mg; 800 rpm; 0.6% DIO	777	10.4	52	4.2
P3f	7 mg/ 14 mg; 1000 rpm; 0.6% DIO	725	11.5	51	4.3

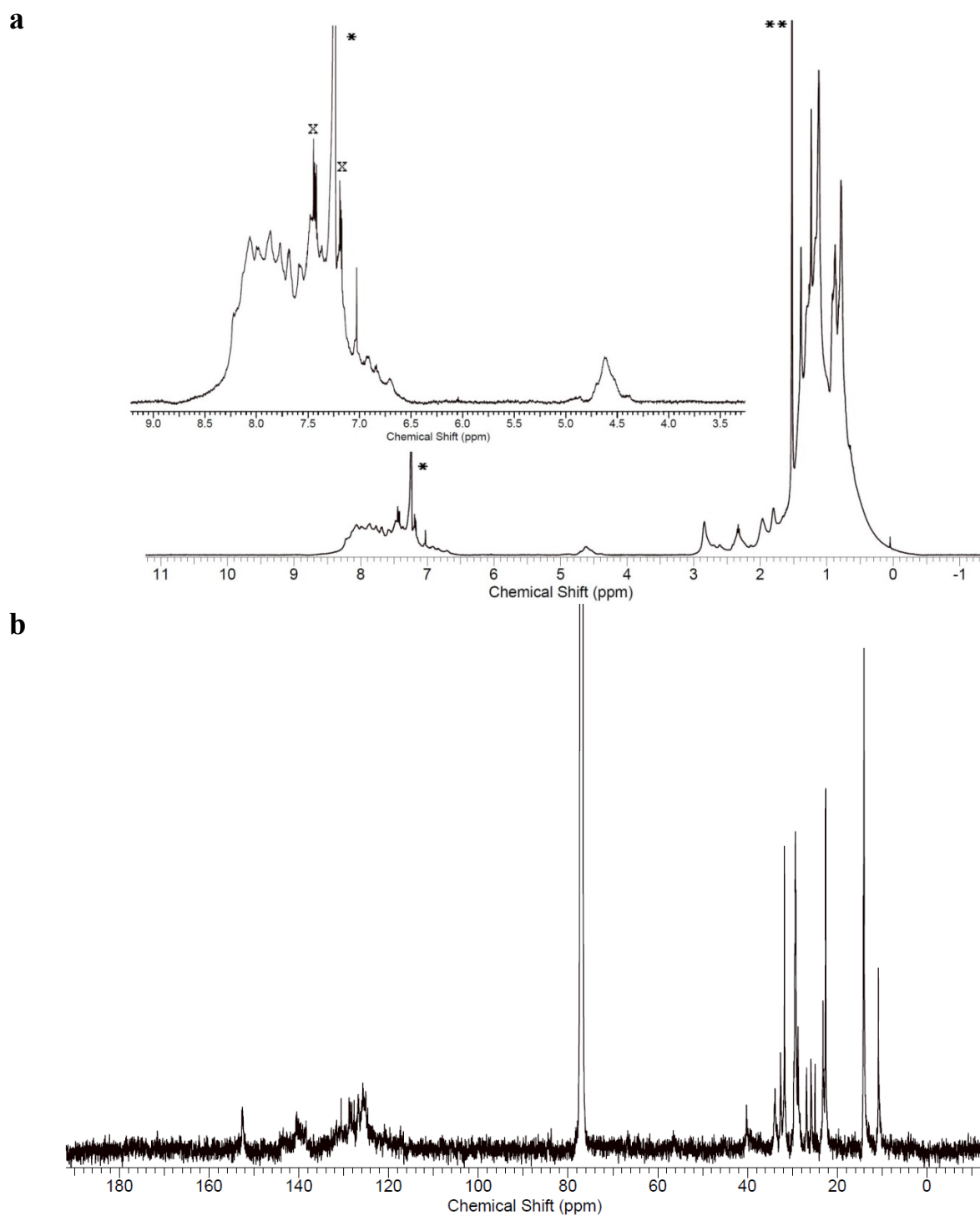


Figure S7. (a) ^1H NMR spectrum of polymer P1 (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “**” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer P1 (125 MHz, CDCl_3).

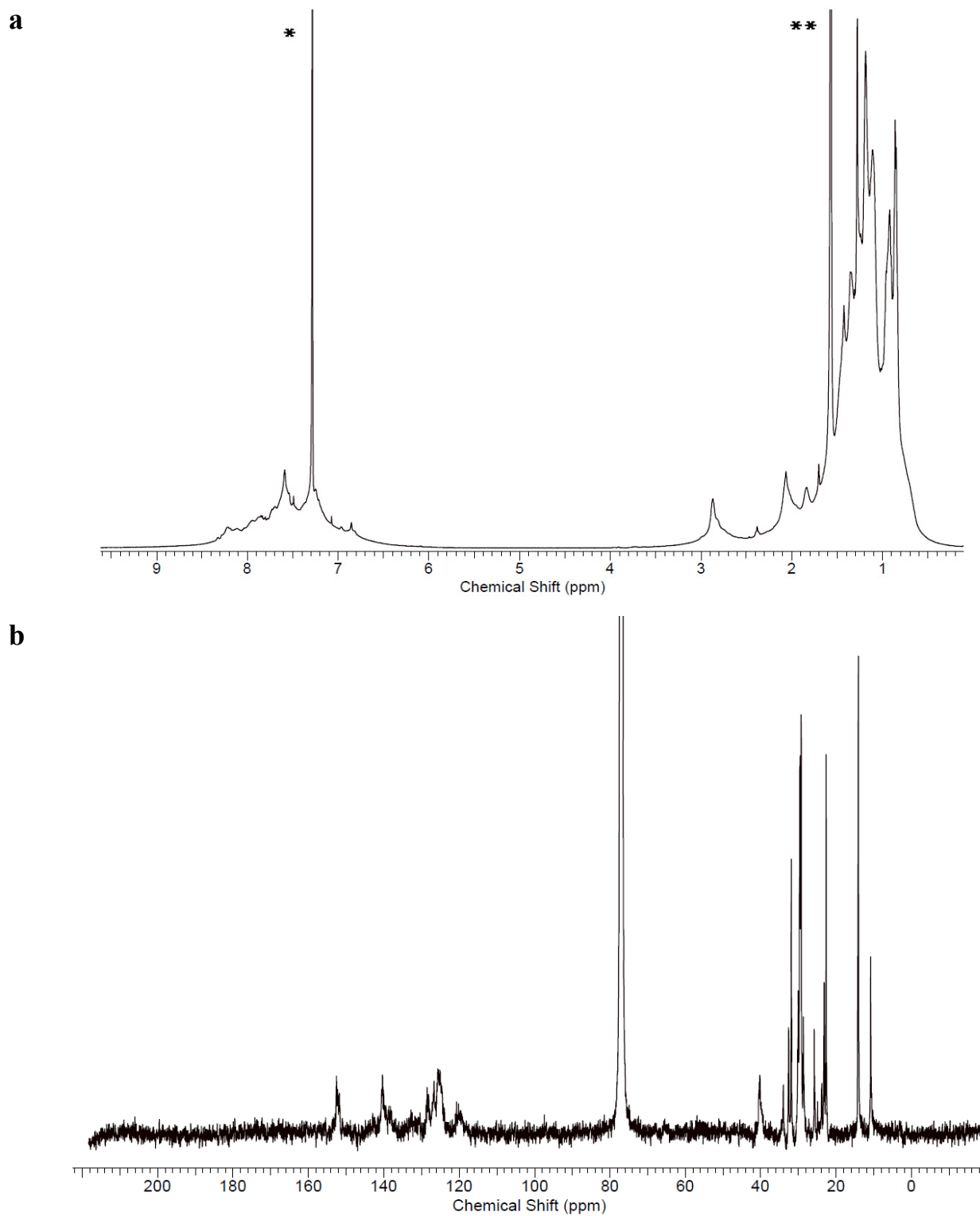


Figure S8. (a) ^1H NMR spectrum of polymer P2 (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “***” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer P2 (125 MHz, CDCl_3).

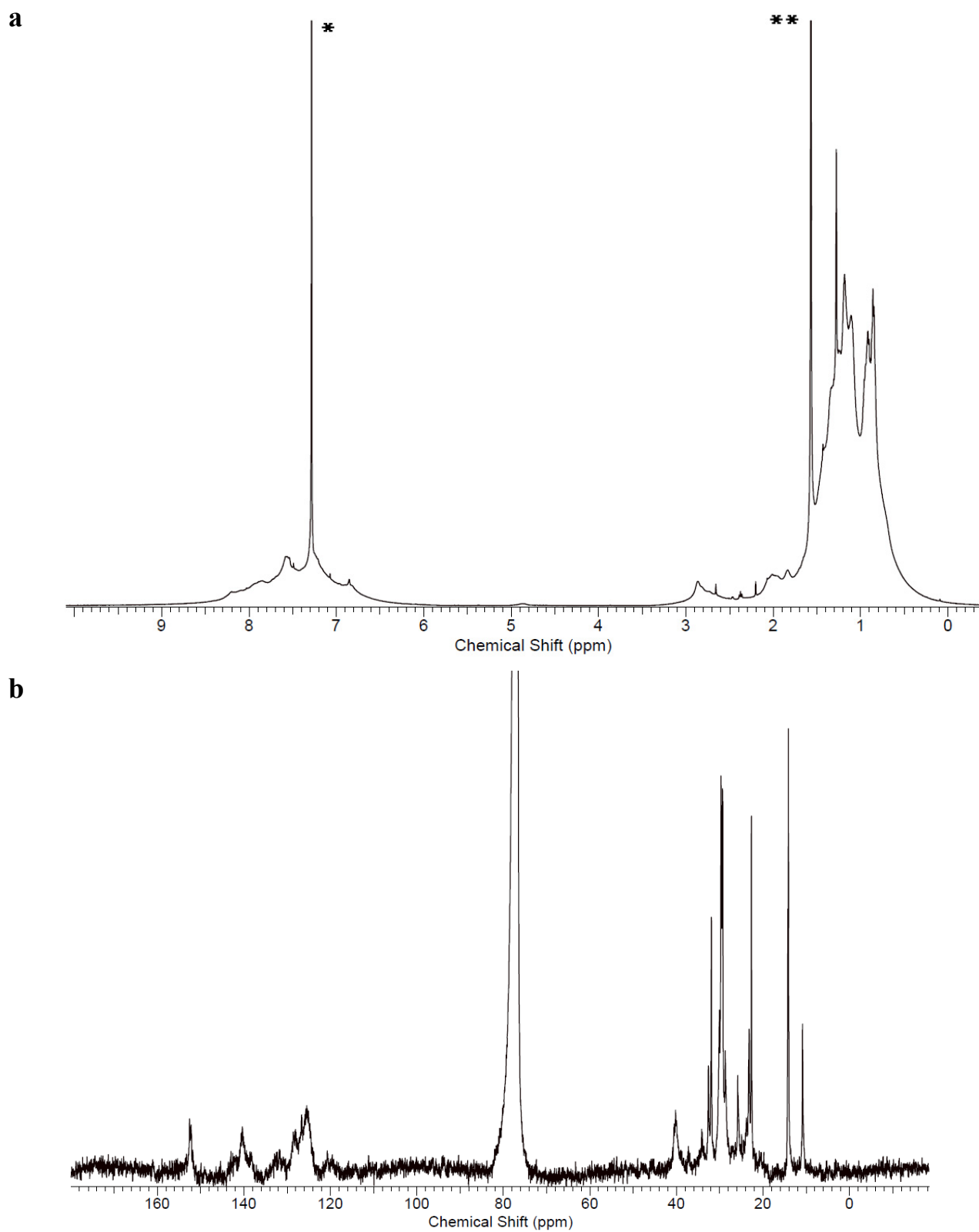


Figure S9. (a) ^1H NMR spectrum of polymer **P3a** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “**” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3a** (125 MHz, CDCl_3).

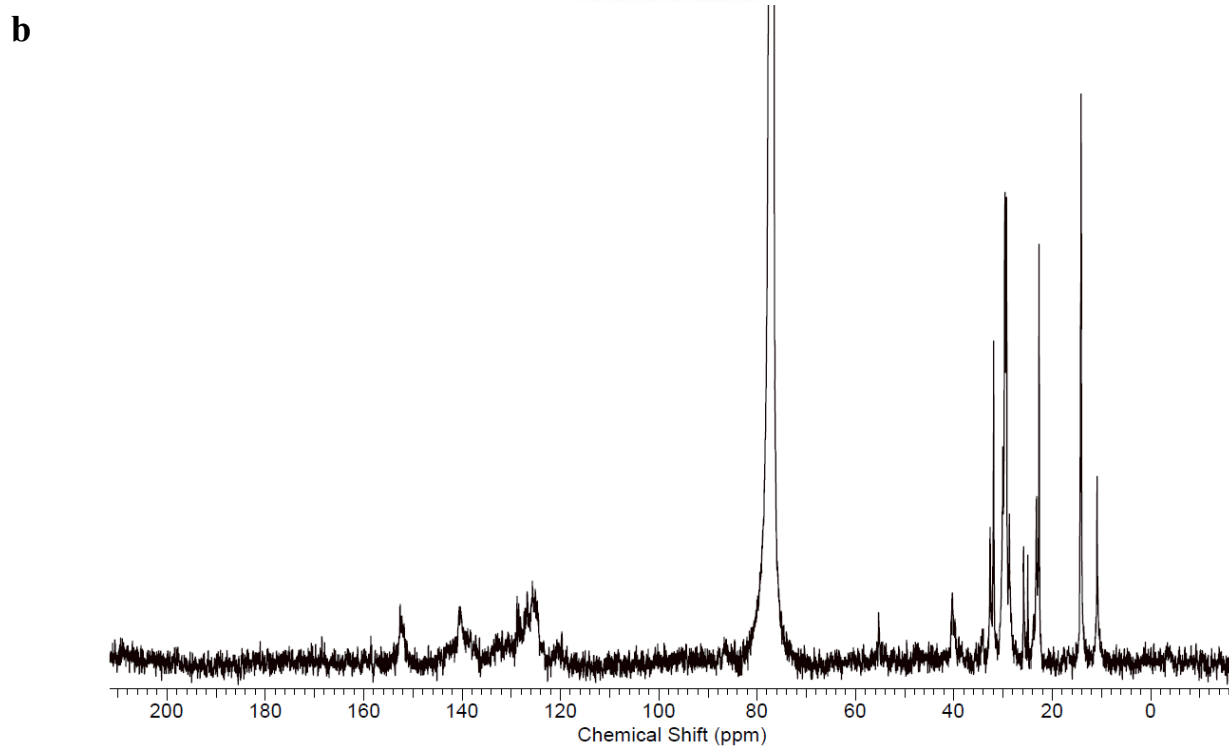
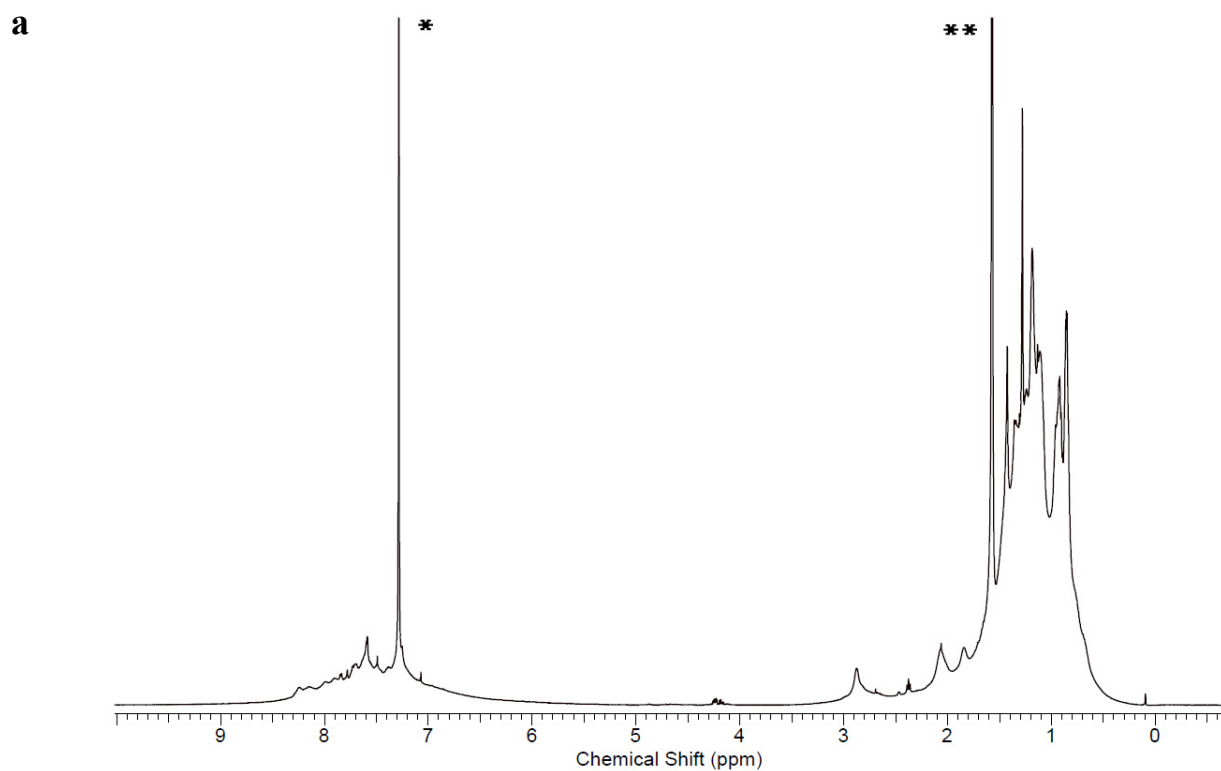


Figure S10. (a) ^1H NMR spectrum of polymer **P3b** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “**” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3b** (125 MHz, CDCl_3).

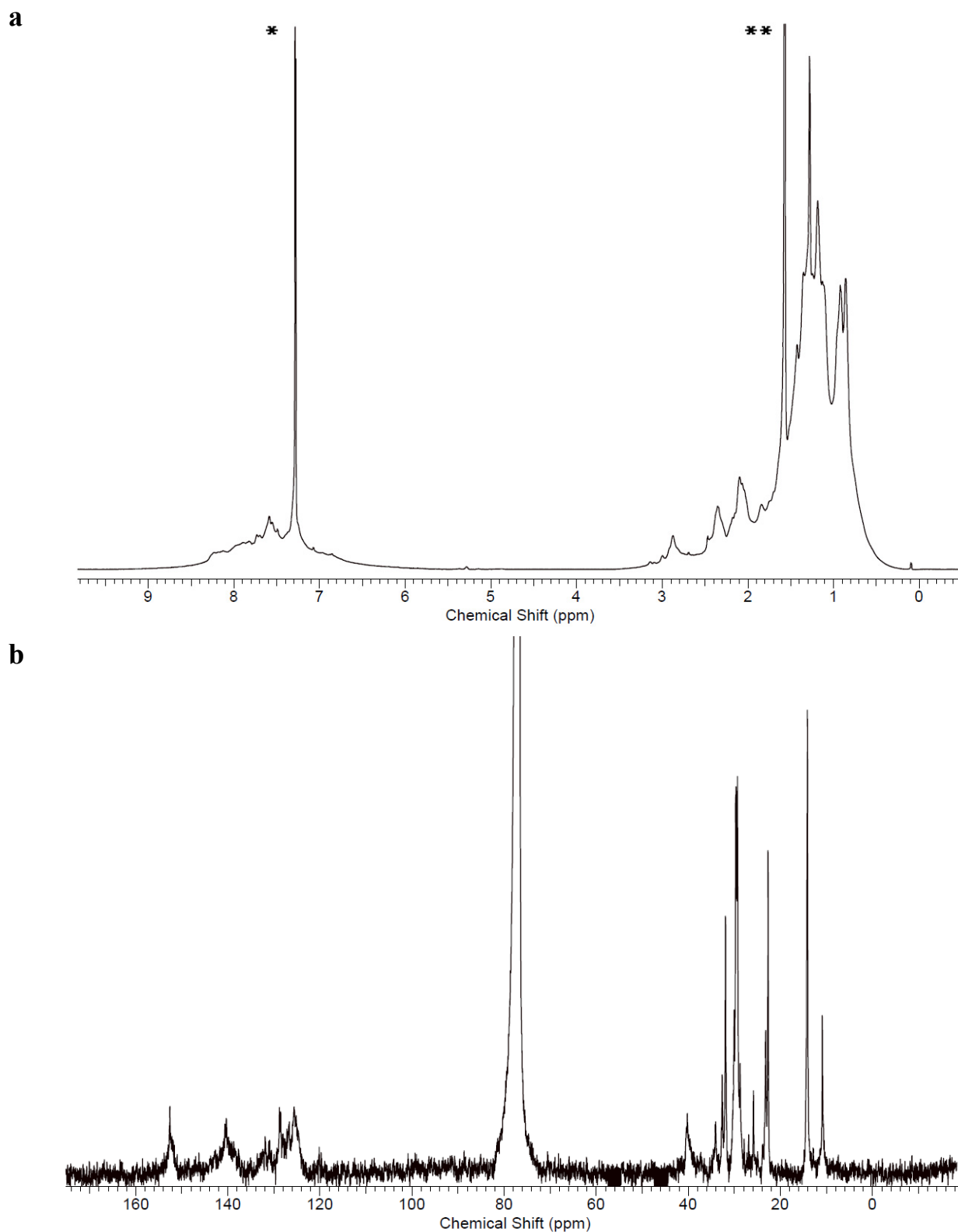


Figure S11. (a) ^1H NMR spectrum of polymer **P3c** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “***” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3c** (125 MHz, CDCl_3).

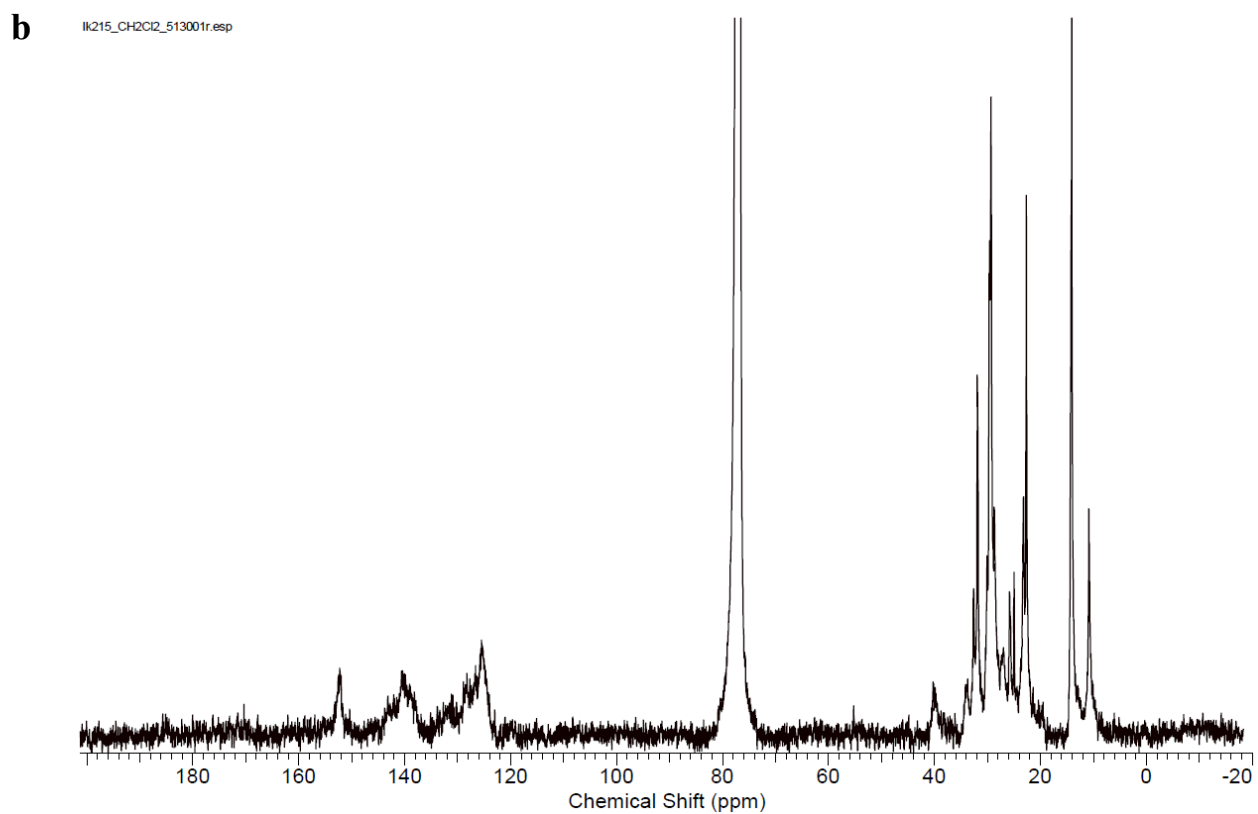
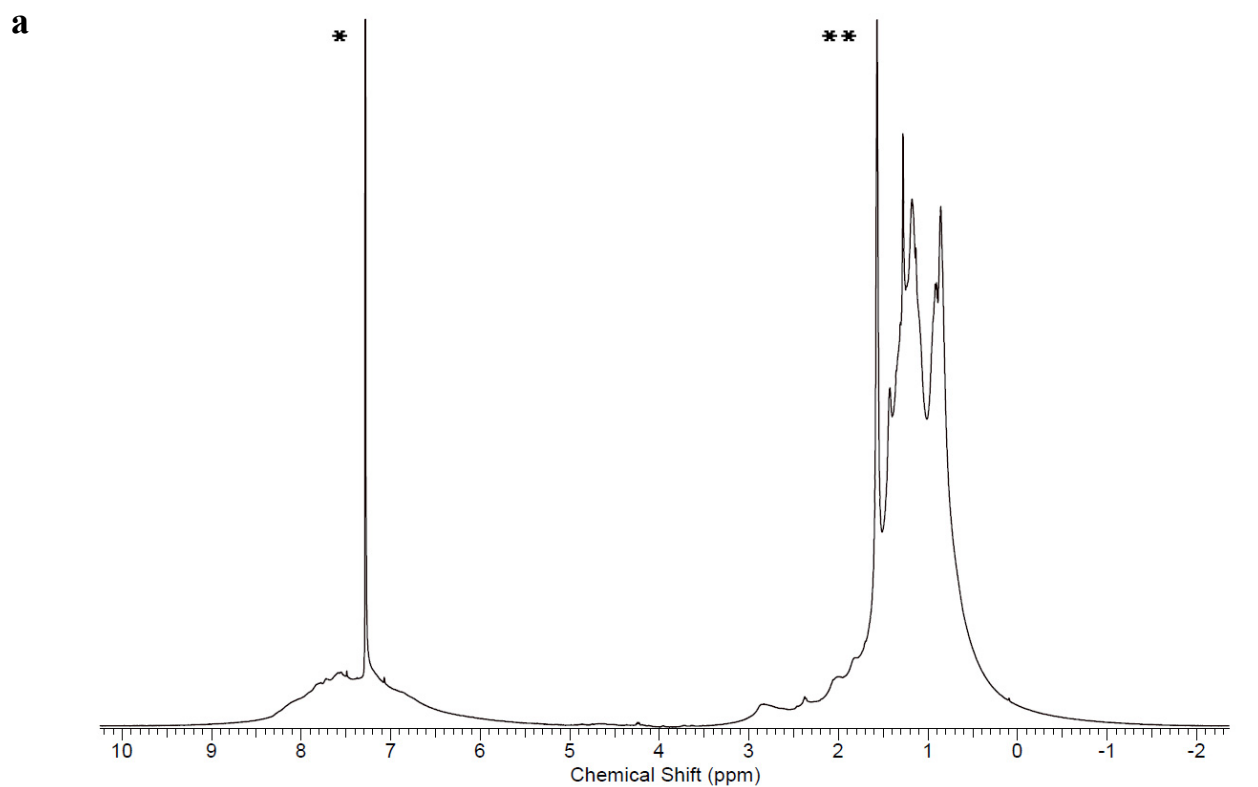


Figure S12. (a) ^1H NMR spectrum of polymer **P3d** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “***” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3d** (125 MHz, CDCl_3).

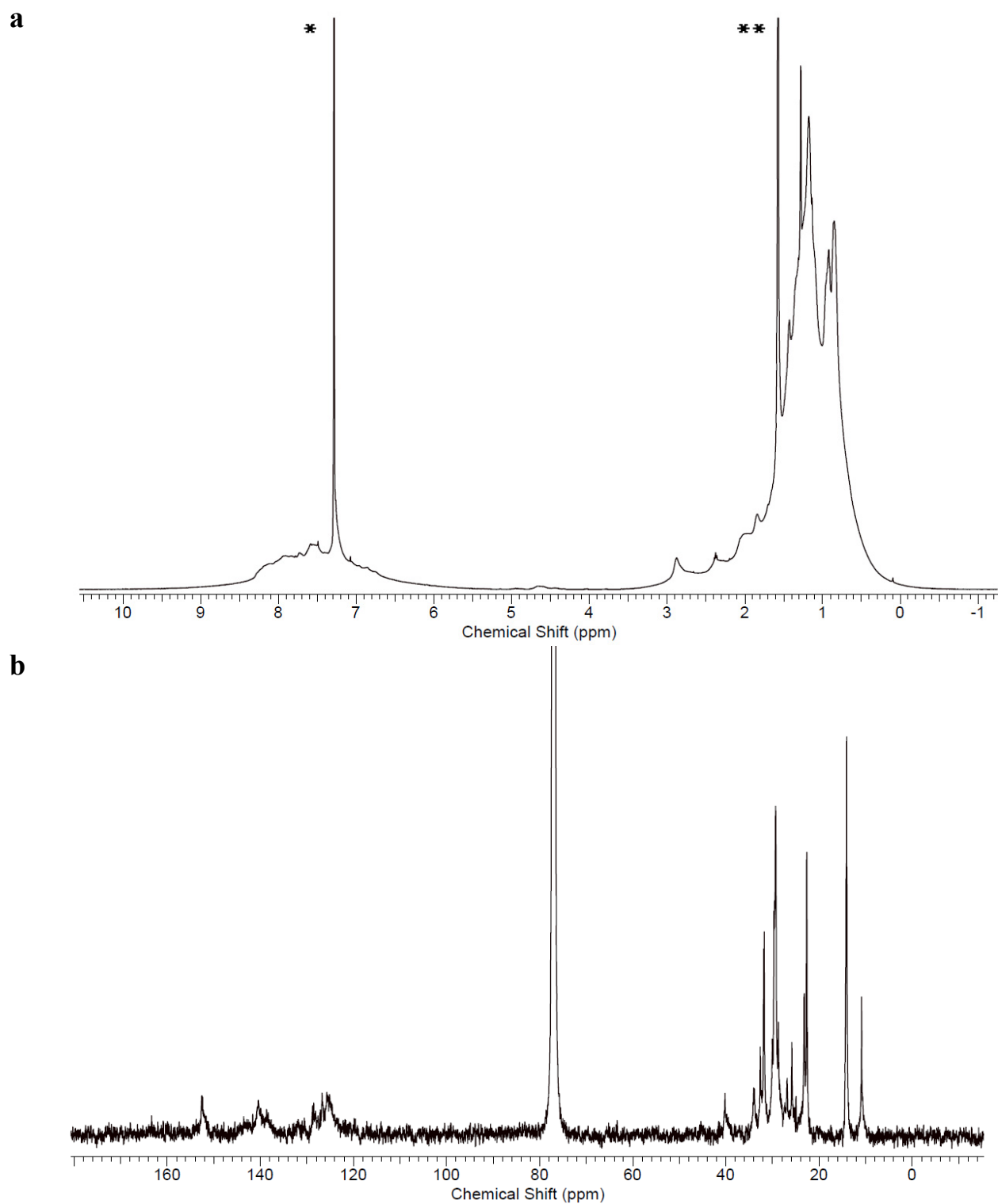


Figure S13. (a) ^1H NMR spectrum of polymer **P3e** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “**” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3e** (125 MHz, CDCl_3).

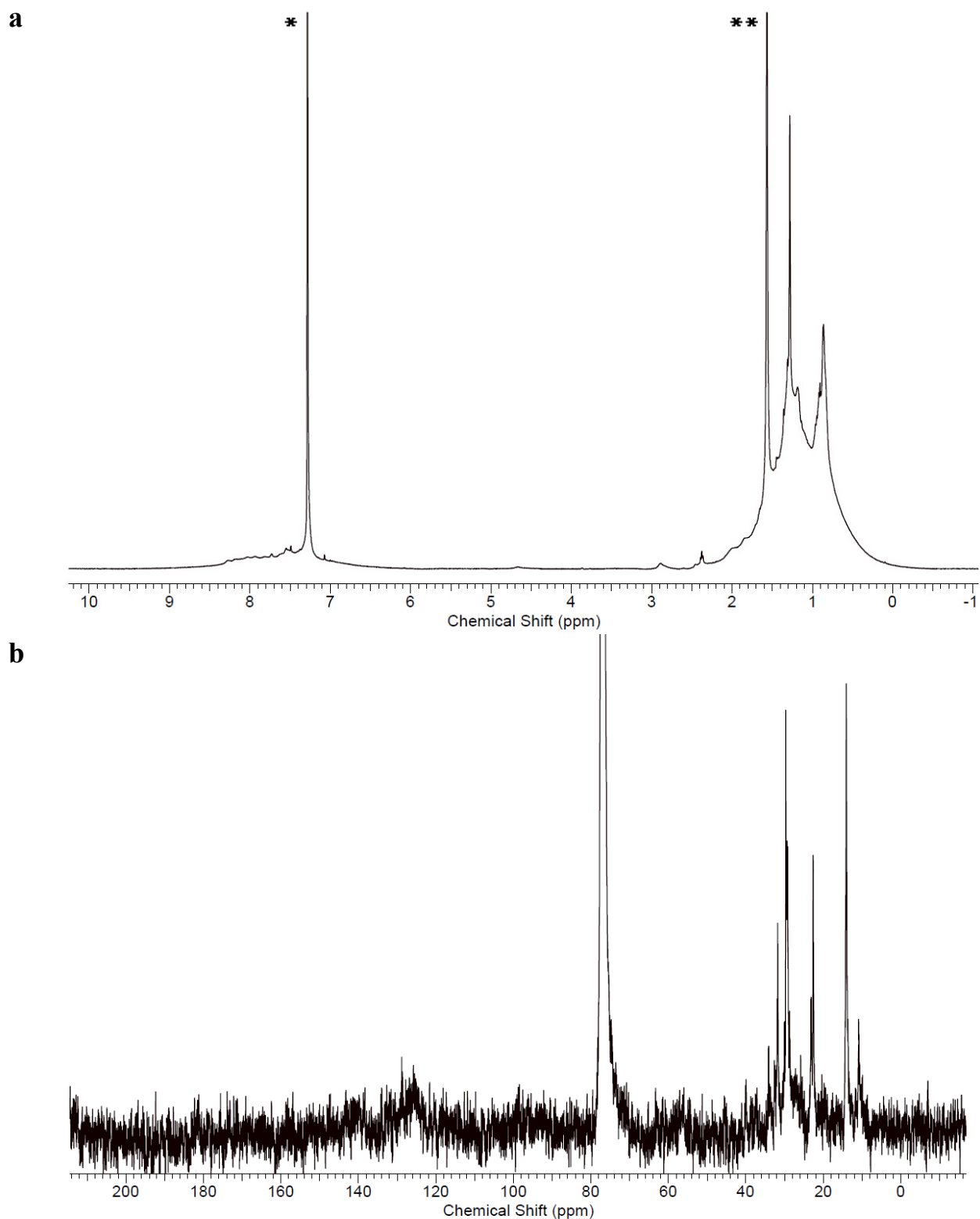


Figure S14. (a) ^1H NMR spectrum of polymer **P3f** (500 MHz, CDCl_3). Symbol “*” denotes residual CHCl_3 signal, “**” states for H_2O in CDCl_3 , signals of the trace solvent impurity (1,2-dichlorobenzene) is marked with “x”. (b) ^{13}C NMR spectrum of polymer **P3f** (125 MHz, CDCl_3).