

Supporting Information for

Synthesis and aggregation behavior of a glycolated naphthalene diimide bithiophene copolymer for application in low-level n-doped organic thermoelectrics

*Young-hun Shin[§], Hartmut Komber[‡], Davide Caiola[#], Marco Cassinelli[#], Hengda Sun[¶],
Dominik Stegerer[§], Marcel Schreiter[§], Kilian Horatz[‡], Franziska Lissel^{‡Δ}, Xuechen Jiao,[¶]
Christopher R. McNeill,[¶] Simone Cimò^{#%}, Chiara Bertarelli^{#%}, Simone Fabiano[¶], Mario
Caironi[#], Michael Sommer^{§*}*

[§] Technische Universität Chemnitz, Institut für Chemie, Straße der Nationen 62, 09111
Chemnitz, Germany

[‡] Leibniz Institut für Polymerforschung Dresden e. V., Hohe Straße 6, 01069 Dresden,
Germany

[#] Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via
Pascoli 70/3, Milano 20133, Italy

[¶] Laboratory of Organic Electronics, Department of Science and Technology, Linköping
University, SE-60174 Norrköping, Sweden

^Δ Technische Universität Dresden, Mommsenstraße, 01062 Dresden, Germany

[¶] Department of Materials Science and Engineering, Monash University, Wellington Road,
Clayton, Victoria, 3800, Australia

[%] Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di
Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Instrumentation

NMR spectroscopy. NMR spectra were recorded on a Bruker Avance NEO 600 spectrometer (^1H : 600 MHz; TU Chemnitz) and on a Bruker AVANCE III 500 spectrometer (^1H : 500 MHz, ^{13}C : 125.8 MHz; IPF Dresden). The VT experiments were carried out on the Bruker AVANCE III 500 spectrometer using Bruker VT accessory BVT-3000. The spectra were referenced to the residual solvent peak (CDCl_3 : $\delta(^1\text{H}) = 7.26$ ppm, $\delta(^{13}\text{C}) = 77.0$ ppm; $\text{C}_2\text{D}_2\text{Cl}_4$: $\delta(^1\text{H}) = 5.98$ ppm, $\delta(^{13}\text{C}) = 73.7$ ppm; o-DCB- d_4 : $\delta(^1\text{H}) = 6.94$ ppm; dioxane- d_8 : $\delta(^1\text{H}) = 3.53$ ppm; DMF- d_7 : $\delta(^1\text{H}) = 8.05$ ppm; THF- d_8 : $\delta(^1\text{H}) = 1.73$ ppm). Chemical shifts (δ) are reported in ppm.

Size exclusion chromatography. SEC measurements of all samples were carried out on four SDplus $10^4 \text{ \AA}$ 5 μm columns with pore sizes ranging from 10^3 to $10^6 \text{ \AA}$ (Polymer Standards), connected in series with a RID20A RI detector and a SPD20AV UV detector (Shimadzu) calibrated with polystyrene standards. THF was used as eluent at 40 °C with a flow rate of 1.0 mL/min.

MALDI-ToF mass spectrometry. MALDI-ToF MS were recorded with a Bruker autoflex speed in reflectron mode. The laser of this instrument is a smartbeam-II with a wavelength of 355 nm using the software flexControl 3.4. All measurements were carried out using a standard set of parameters (see Table S2). The sample plate was cleaned using a reported procedure.¹ At the beginning of each set of measurements in positive reflectron mode, the instrument was calibrated with a 1:1 mixture of 2,5-dihydroxybenzoic acid (2,5-DHB) and polyethylene glycol (PEG) ($M_w = 6650$ Da) with 1 vol.-% NaTFA in acetone as described in the literature.²

UV-vis spectroscopy. UV-vis spectra were recorded at 25 °C on a Cary 60 UV-Vis (Agilent Technologies) in chloroform solutions ($c = 0.02$ mg/mL). Films were fabricated by spin coating

with 1000 rpm speed for 60 second on glass substrate under air at 25°C. Absorption was measured using a Flame-S UV-Vis spectrometer from Ocean Optics controlled by the OceanView 1.5.2 software. All measurements were carried out under air.

Cyclic voltammetry. CV measurements were done at room temperature with a PalmSens4 potentiostat with NBu₄PF₆ (0.1 M) as electrolyte under argon with a scan rate of 50 mV/s. Film samples for measurements were prepared by drop casting onto the glassy carbon working electrode and measured in dry acetonitrile.

Differential scanning calorimetry. DSC measurements were carried out on a DSC 2500 (TA Instruments) under nitrogen atmosphere. Heating and cooling rates were 10 K/min. The mass of the samples for each measurement was approximately 2-5 mg.

Thermogravimetric analysis. TGA measurements were done on a TGA/DSC3+ (Mettler-Toledo) within the temperature range 30 °C to 650 °C at a heating rate of 10 K/min under argon. Isotherm measurement was done by measuring at 305 °C for 15 min.

AFM measurements. The surface morphology of the samples was investigated by using an Agilent 5600 LS Atomic Force Microscope operating in tapping mode.

GIWAXS measurements. Grazing-incidence wide-angle X-ray scattering measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron.³ The beam energy was fixed at 12 keV, with the total exposure time for each scattering pattern set to 3 s, with a new spot used for each exposure to minimise X-ray induced damage. The scattering pattern was recorded using a Pilatus 2M detector placed at ~ 67 cm away from the sample, calibrated using the standard sample of silver behenate (AgBeh). The entire beam path from the X-ray source to the detector were placed under vacuum to minimise diffuse scattering from air and enhance signal-to-noise ratio of the scattering pattern. GIWAXS patterns were taken as a function of

angle of incidence with the data shown taken near the critical angle, identified as the angle that gave the highest scattering intensity. Data reduction was performed in Igor Pro using an altered version of the NIKA analysis package.⁴

Electrical conductivity measurements. In order to evaluate the electrical conductivity of the materials, thin films with homogenous thickness of some tens of nanometers were deposited on glass substrates (low-alkali 1737F Corning glass) with lateral dimensions of 2 cm x 1.3 cm. After being cut with a diamond tip, substrates were first rinsed in distilled water and acetone, and then sonicated in 2-propanol for 10 minutes. Afterwards, an oxygen plasma treatment (in a Zepto Plasma System from Diener Plasma Surface Technology) was carried out for 10 minutes at 100 W. The deposition of thin films was performed via spin coating inside a nitrogen-filled glovebox. The deposition process was carried out at 1500 rpm/s for 60 s followed by thermal annealing at 120°C for 60 min. Electrical contacts, made of silver paste, were deposited manually at a distance of about 0.9 cm. The electrical resistance of thin films was measured in a nitrogen atmosphere by two-point measurements technique using an Agilent B1500A Semiconductor Device Parameter Analyzer. The film thickness was then measured with a Lyncée Tec optical profilometer equipped with a 5X objective, after having produced a scratch with a scalpel. Films were ~20 nm thin.

Thermoelectric device fabrication and characterization. For N-DiPrBI doped P(EO-NDIT2), N-DiPrBI and P(EO-NDIT2) were separately dissolved in chlorobenzene at 5 mg/mL. The two solutions were then mixed together in different volume ratios, spin coated at 1500 rpm/s for 60 s and thermally annealed at 120°C for 60 min, resulting in ~20 nm thin films. TDAE-doped samples were prepared by exposing the pristine P(EO-NDIT2) film to TDAE vapor. For the Seebeck coefficient measurements, the solutions were spun on glass substrates pre-patterned with two parallel gold electrodes having dimension: length $L = 12$ mm, width $W = 0.5$ mm,

height $H = 30$ nm (the distance between the electrodes was 0.5 mm). The samples were then annealed at 100 °C for 15 min on a hotplate. A temperature gradient (ΔT) across the sample was fixed by two Peltier modules, and the thermovoltage (ΔV) was probed between the two separate electrodes. The Seebeck coefficient was obtained from the slope of ΔV measured at different ΔT values.⁵ Electrical conductivity was measured using a Keithley 4200-SCS semiconductor parameter analyzer and determined from the I–V slope. All solution mixing, device fabrication and thermoelectric characterizations were done inside N₂ filled glovebox.

Doping protocols

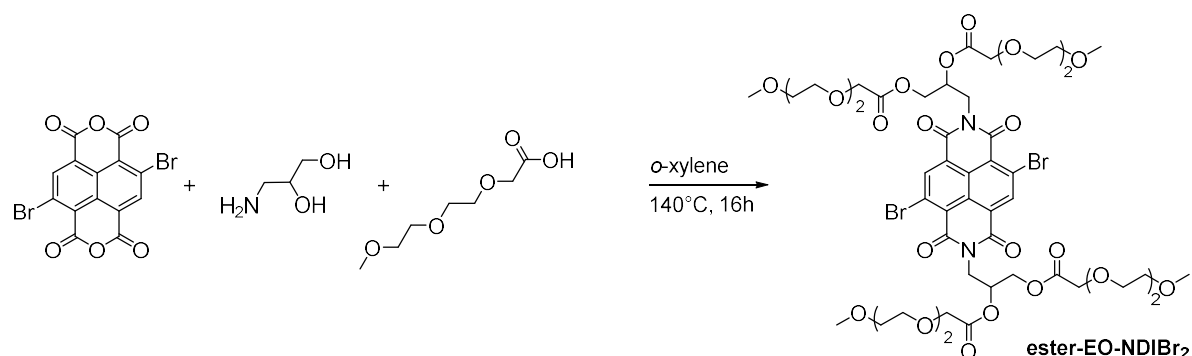
Doping protocol CB RT. Both polymer and dopants were dissolved separately in chlorobenzene in air with a concentration of 5 g/L. The polymeric solution was stirred at room temperature for 12 hours. The dopant solution was added gradually to the polymeric one inside a nitrogen-filled glovebox before the deposition of thin films.

Doping protocol CB 80 °C. Both polymer and dopant were dissolved in chlorobenzene in air with a concentration of 5 g/L. The polymeric solution was stirred at room temperature for 12 hours. Then the solution was heated at 80°C for 20 min, removed from the hotplate and the gradual addition of the dopant solution was done within 10 min from the removal.

Doping protocol o-DCB. Both polymer and dopants were dissolved in 1,2-dichlorobenzene in air with a concentration of 5 g/L. The polymeric solution was stirred at 90°C for 12 hours and then the dopant was added gradually inside a nitrogen-filled glovebox before the deposition of the thin films.

Materials and Synthesis

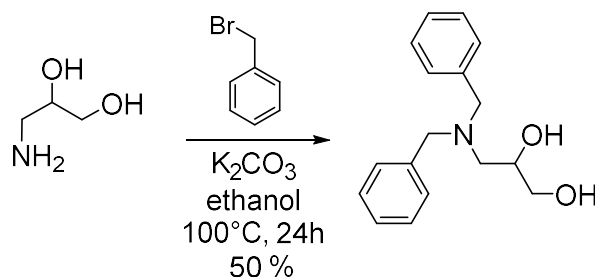
Synthesis of ester-EO-NDIBr₂



To a solution of 2,6-dibromonaphthalene-1,4,6,8-tetracarboxylic dianhydride (NDABr₂) (5 g, 11.74 mmol, 1 eq) in o-xylene (117.4 mL, 0.1 M), 3-amino-1,2-propanediol (2.246 g, 1.911 mL, 24.65 mmol, 2.1 eq) and [2-(2-methoxyethoxy)ethoxy]acetic acid (158.11 g, 136.65 mL, 73 eq) were added at room temperature. The reaction mixture was stirred at 140 °C for 16 h. The solvent was removed under high vacuum and the organic phase was washed with saturated NaHCO₃ solution and water three times. The organic phase was dried over MgSO₄. After evaporation of the solvent, further purification was done by column chromatography using methanol and ethyl acetate (4:1).

Synthesis of 2,3-bis(methoxy(triethyleneoxide))propan-1-amine (EO-amine)

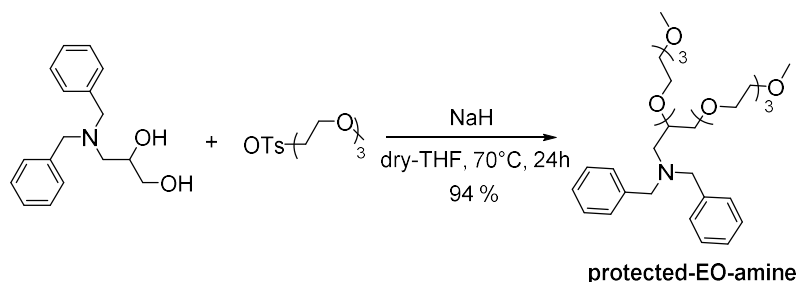
1st step: Synthesis of 3-(N,N-dibenzylamino)-propane-1,2-diol



To a round bottom flask, 3-amino-1,2-propanediol (5 g, 54.88 mmol, 1 eq) and ethanol (200 mL, 0.275 M) were added. To the mixture, K₂CO₃ (23.89 mg, 163.64 mmol, 3 eq) was added and the whole was stirred vigorously at 100°C. Benzyl bromide (19.55 mL, 163.64 mmol, 3 eq) was added dropwise to the suspension within 30 min. The reaction mixture was stirred and refluxed for 24 h and finally cooled down to RT. The white suspension in a yellowish solution was filtered off and the solvent was evaporated. The remaining organic phase was washed with saturated NaHCO₃ solution and water twice each. A slightly yellow oil was obtained after column chromatography with a mixture of ethyl acetate and petrol ether (1:2) as eluent. After evaporating the solvents under high vacuum, white crystals in 88% yield were obtained.

¹H NMR (600 MHz, CDCl₃, 25°C): δ 7.36 – 7.25 (10H; H_{ar}), 3.82 (3H; CH and 1H of Ar-CH₂), 3.64 (dd, 11.4 Hz, 3.7 Hz, 1H; 1H of CH₂OH), 3.53 (d, 13.5 Hz, 2H; 1H of Ar-CH₂), 3.39 (dd, 11.4 Hz, 4.6 Hz, 1H; 1H of CH₂OH), 2.72 (dd, 12.9 Hz, 9.1 Hz, 1H; 1H of NCH₂CH), 2.50 (dd, 12.9 Hz, 4.0 Hz, 1H; 1H of NCH₂CH).

2nd step: Etherification of 3-(dibenzylamino)propane-1,2-diol (protected-EO-amine)

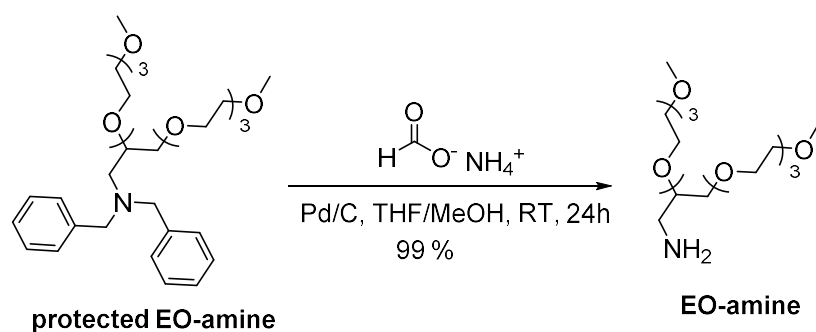


To a suspension of NaH (2.0 g, 80.6 mmol, 2.21 eq) in 125 mL dry THF, a solution of 3-(dibenzylamino)propane-1,2-diol (9.9 g, 36.5 mmol, 1 eq) in 65 mL dry THF was added dropwise. The reaction mixture was stirred for 1 hour at RT and the temperature was raised to 70°C. A solution of *p*-tosyltris(oxyethylene)monomethyl ether in 60 mL dry THF was added dropwise within 30 min. Reaction mixture was stirred at 70°C for 24h. After cooling down to RT, methanol was added to quench residual NaH, and the solvent was removed under reduced pressure. Further purification was done by column chromatography with ethyl acetate as eluent. After evaporating the solvent, a colorless oil in 94% yield was obtained.

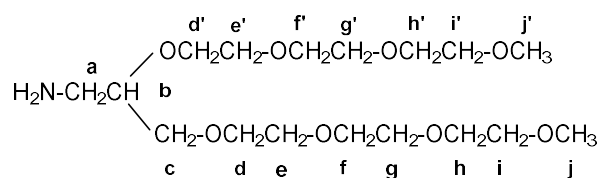
¹H NMR (600 MHz, CDCl₃, 25°C): δ 7.33 (d, 7.8 Hz, 4H; o-H_{ar}), 7.29 (t, 7.8 Hz, 4H; m-H_{ar}), 7.22 (t, 7.6 Hz, 2H; p-H_{ar}), 3.75-3.38 (31H; CH, all CH₂O, Ar-CH₂), 3.37 and 3.36 (2 x s, 6H, OCH₃), 2.59 (dd, 13.5 Hz, 6.0 Hz, 1H; 1H of NCH₂CH), 2.54 (dd, 13.5 Hz, 5.5 Hz, 1H; 1H of NCH₂CH).

Elemental analysis (%) for C₃₁H₄₉NO₈ : C 65.32, H 9.56, N 2.61. (calculated : C 66.05 H 8.76 N 2.48 O 22.70)

3rd step: Synthesis of the EO-amine (deprotection)

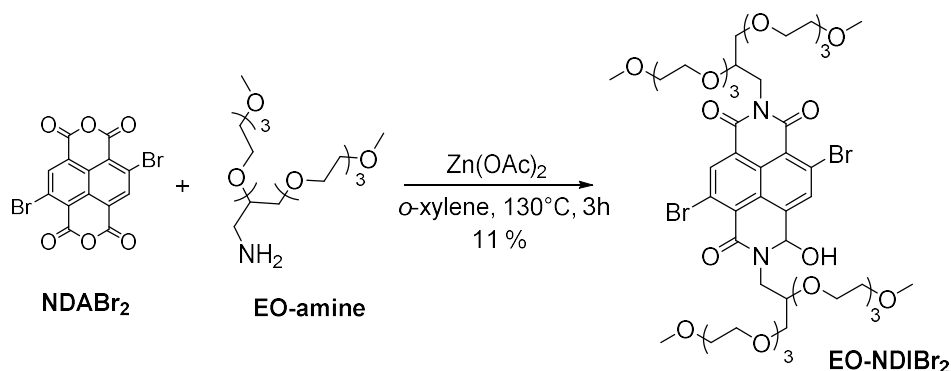


To a suspension of Pd/C (1.36 g, 100 mg/mmol of protected EO-amine) in THF (70 mL, 0.2 M), protected EO-amine (7.68 g, 13.6 mmol, 1 eq) was added. To this mixture, ammonium formate (4.3 g, 68.1 mmol, 5 eq) in methanol (20 mL, 0.8 M) was added under argon. The reaction mixture was stirred under argon at RT for 24 h. The reaction mixture was filtered over celite, and the filter cake was washed with copious amounts of methanol. After evaporation of the solvent, a slightly yellow oil in 99% yield was obtained.

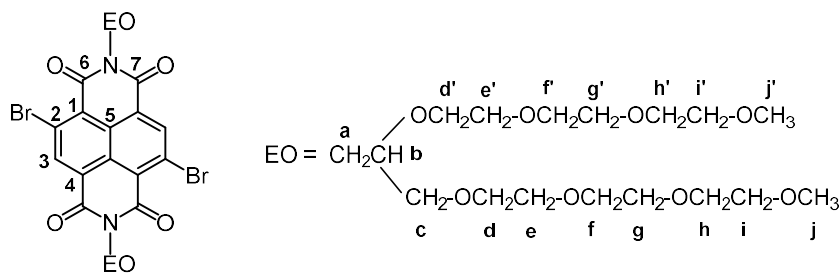


¹H NMR (600 MHz, CDCl₃, 25°C): δ 3.85-3.45 (27H; b-i, d'-i'), 3.38 (s, 6H; j, j'), 2.90 (dd, 13.1 Hz, 3.5 Hz, 1H; 1H of a), 2.78 (dd, 13.1 Hz, 6.5 Hz, 1H; 1H of a), 2.4 (br, 2H; NH₂).

Synthesis of EO-NDIBr₂



To a suspension of NDABr₂ (2 g, 4.7 mmol, 1 eq) in o-xylene (162 mL, 0.029 M), Zn(OAc)₂ (861.5 mg, 9.4 mmol, 2 eq) was added and the mixture was stirred vigorously for 10 min. The temperature was elevated to 130°C and EO-amine was added dropwise within 30 min. The reaction mixture was stirred at 130°C for 3 h. The crude mixture was cooled down to RT and the solvent evaporated under high vacuum. The organic phase was washed with water three times and dried over MgSO₄. A yellowish oil was obtained after column chromatography with methanol/ ethyl acetate (1:1.5) as eluent in 11% yield.



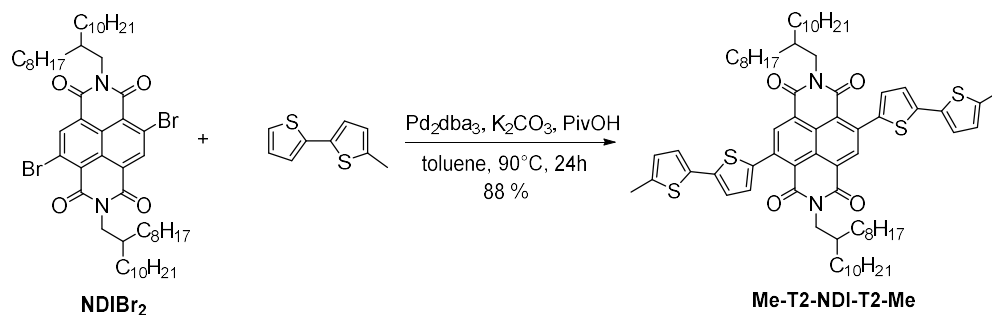
¹H NMR (500 MHz, C₂D₂Cl₄, 30°C): δ 8.96 (s, 2H; 3), 4.47 and 4.25 (2 x m, 4H; a), 3.98 (quin, 5.6 Hz, 2H; b), 3.76 and 3.66 (2 x m, 4H; d'), 3.64 (8H; c,d), 3.6-3.35 (40H; e-i,e'-i'), 3.33 and 3.29 (2 x s, 12H; j,j').

¹H NMR (500 MHz, C₂D₂Cl₄, 120°C): δ 9.00 (s, 2H; 3), 4.52 and 4.33 (2 x m, 4H; a), 4.05 (quin, 5.9 Hz, 2H; b), 3.85 -3.4 (52H; c-i,d'-i'), 3.38 and 3.33 (2 x s, 12H; j,j').

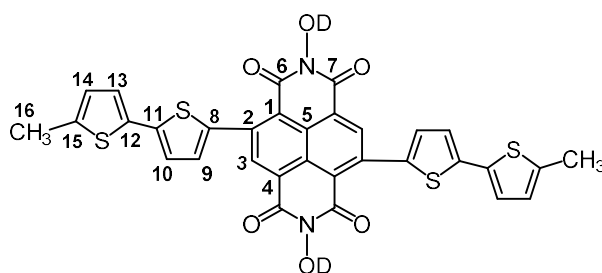
^{13}C NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 30°C): δ 160.74 (7), 160.52 (6), 138.71 (3), 128.04 (2), 127.46 (5), 124.98 (4), 123.79 (1), 75.88 (b), 71.92 (c), 71.53 and 71.46 (i,i'), 70.58 (d), 70.5-69.5 (e-h,e'-h'), 69.34 (d'), 58.62 and 58.59 (j,j'), 41.88 (a).

Elemental analysis (%) for $\text{C}_{48}\text{H}_{74}\text{Br}_2\text{N}_2\text{O}_{20}$: C 49.65, H 6.79, N 2.52. (calculated : C 50.59 H 6.62 Br 13.46 N 2.36 O 29.96)

Synthesis of model compound Me-T2-NDI-T2-Me



NDIBr₂ (178.7 mg, 0.181 mmol, 1 eq), 5-methyl-2,2'-bithiophene (135.5 mg, 0.752 mmol, 4.14 eq), K₂CO₃ (75.26 mg, 0.543 mmol, 3 eq) and PivOH (18.53 mg, 0.181 mmol, 1 eq) were weighted into a pre-dried vial with a metal cap. The solids were flushed with argon for 10 min and degassed. Then, dry-toluene (3.63 mL) was added. Pd₂dba₃ (1.66 mg, 1 mol%) was added under argon and the whole stirred at 90°C for 22 h. The reaction was monitored by TLC (dichloromethane:petrol ether 1:1). The crude mixture was cooled down to RT and solvent was evaporated under reduced pressure. A blue powder was obtained after column chromatography with dichloromethane: petrol ether (1:1) in 88% yield.

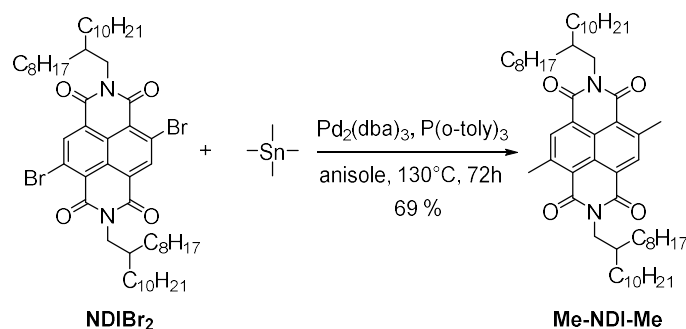


¹H NMR (500 MHz, CDCl₃): δ 8.78 (s, 2H; 3), 7.28 (d, 3.8 Hz, 2H; 9), 7.16 (d, 3.8 Hz, 2H; 6), 7.05 (d, 3.5 Hz, 2H; 13), 6.70 (m, 2H; 14), 4.10 (d, 7.1 Hz, 4H; NCH₂), 2.52 (s, 6H; 16), 2.06 (m, 2H; CH), 1.45-1.15 (64H, CH₂ of octadecyl (OD) moiety), 0.9-0.8 (12H; CH₃).

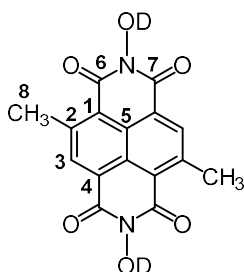
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120°C): δ 8.82 (s, 2H; 3), 7.34 (d, 3.8 Hz, 2H; 9), 7.20 (d, 3.8 Hz, 2H; 6), 7.11 (d, 3.6 Hz, 2H; 13), 6.76 (m, 2H; 14), 4.14 (d, 7.4 Hz, 4H; NCH_2), 2.56 (s, 6H; 16), 2.06 (m, 2H; CH), 1.55-1.2 (64H, CH_2 of octadecyl (OD) moiety), 0.9-0.8 (12H; CH_3).

^{13}C NMR (500 MHz, CDCl_3): δ 162.60 (6 and 7), 141.34 (11), 140.18 (15), 139.46 (2), 138.74 (8), 136.51 (3), 134.50 (12), 129.94 (9), 127.52 (5), 126.15 (14), 125.37 (4), 124.38 (13), 123.30 (10), 122.50 (1), 44.97 (NCH_2), 36.55 (CH), 31.89, 31.66, 30.07, 29.6, 29.57, 29.33, 29.30, 26.44, 22.65 (all CH_2 of OD moiety), 15.41 (16), 14.08 (CH_3).

Synthesis of model compound Me-NDI-Me



To a pre-dried glass vial with a metal cap, NDIBr₂ (142.1 mg, 0.144 mmol, 1 eq) and tetramethyltin (51.6 mg, 0.288 mmol, 2 eq) were added, flushed with argon for 5 min, and degassed anisole (2.89 mL, 0.05 M) was added. P(o-tolyl)₃ (1.76 mg, 4 mol%) and Pd₂dba₃ (1.32 mg, 1 mol%) were added under argon. The vial was sealed with a metal cap and the whole stirred for 72h at 130°C. Yellowish crystals were obtained after column chromatography with dichloromethane: petrol ether 1:1 in 69% yield.

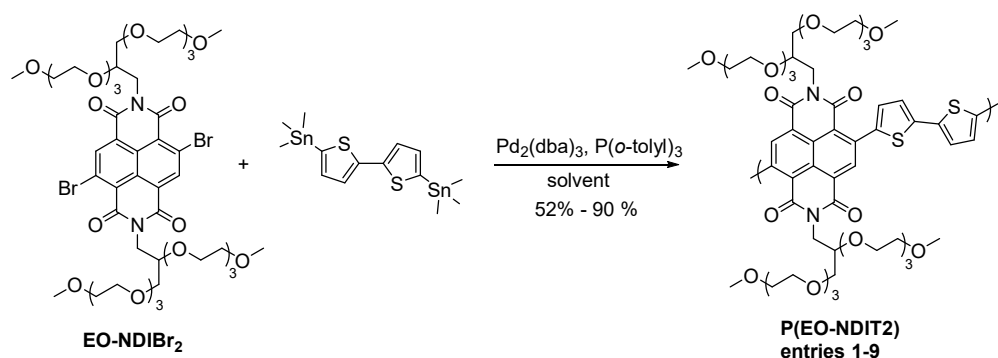


¹H NMR (500 MHz, CDCl₃): δ 8.59 (s, 2H; 3), 4.13 (d, 7. Hz, 4H; NCH₂), 3.09 (s, 6H; 8), 1.98 (m, 2H; CH), 1.45-1.1 (64H, CH₂ of octadecyl (OD) moiety), 0.9-0.8 (12H; CH₃).

¹H NMR (500 MHz, C₂D₂Cl₄, 120°C): δ 8.62 (s, 2H; 3), 4.20 (d, 7. Hz, 4H; NCH₂), 3.15 (s, 6H; 8), 2.08 (m, 2H; CH), 1.55-1.2 (64H, CH₂ of octadecyl (OD) moiety), 0.95-0.85 (12H; CH₃).

^{13}C NMR (500 MHz, CDCl_3): δ 164.03 (6), 163.15 (7), 145.37 (2), 136.10 (3), 126.66 (5), 124.97 (4), 123.24 (1), 44.71 (NCH_2), 36.52 (CH), 31.85, 31.66, 30.02, 29.6, 29.5, 29.3, 26.44 (all CH_2 of OD moiety), 23.86 (8), 22.65 (CH_2 of OD moiety), 14.08 (CH_3).

Polymerization



Synthesis of P(EO-NDIT2), entries 1-3 (synthesis data from entry 1).

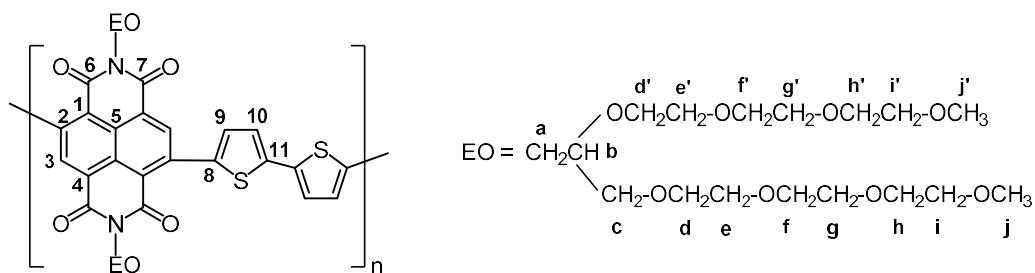
To a pre-dried glass vial, EO-NDIBr₂ (56.8 mg, 1.1 eq) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (21.95 mg, 1 eq) were added and the vial was flushed with argon. Degassed anisole (0.9 mL) was added followed by P(o-tolyl)₃ (0.5434 mg, 4 mol%) and Pd₂dba₃ (0.409 mg, 1 mol%) under argon. The vial was sealed and the mixture stirred for 48 h at 130°C. The reaction mixture was cooled down to RT and diluted with chloroform and precipitated into ethyl acetate. The crude mixture was collected and purified by Soxhlet extraction with ethyl acetate, acetone and chloroform. The chloroform fraction gave a blue colored solid in 90% yield. $M_{n,\text{NMR}} = 11$ kg/mol.

Synthesis of P(EO-NDIT2), entries 4, 5, 7 and 9 (synthesis data from entry 9).

To a pre-dried glass vial with two metal caps, EO-NDIBr₂ (130.2 mg, 1.1 eq) was added. After that 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was added (50.32 mg, 1 eq) and the mixture flushed with argon for 5 min. Degassed, dry DMF (5.12 mL, 0.02 M) was added followed by P(o-tolyl)₃ (1.246 mg, 4 mol%) and Pd₂dba₃ (0.937 mg, 1 mol%) while flushing with argon. The vial was sealed and the mixture stirred for 48 h at 85°C. Subsequently, the reaction mixture was cooled down to RT and diluted with chloroform and precipitated with ethyl acetate. The crude mixture was collected and purified by Soxhlet extraction with ethyl acetate, acetone and chloroform. The chloroform fraction gave a blue colored solid in 77% yield. SEC (25°C, chloroform): $M_{n,SEC} = 4.32 \times 10^5$ kg/mol, $M_{w,SEC} = 3.2 \times 10^7$ kg/mol, $M_{n,NMR} = 116$ kg/mol.

Synthesis of P(EO-NDIT2), entries 6 and 8 (synthesis data from entry 6).

To a pre-dried glass vial, EO-NDIBr₂ (66.5 mg, 1.1 eq) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (25.73 mg, 1.1 eq) were added, and the vial was flushed with argon. Degassed chlorobenzene (1 mL) was added followed by P(o-tolyl)₃ (0.637, 4 mol%) and Pd₂dba₃ (0.493 mg, 1 mol%) under argon. The vial was sealed and the reaction mixture stirred at 130°C for 48 h. Subsequently, the reaction mixture was cooled down to RT and diluted with chloroform and precipitated into ethyl acetate. The crude mixture was collected and purified by Soxhlet extraction with ethyl acetate, acetone and chloroform. The chloroform fraction gave a blue colored solid in 76 % yield. SEC (25°C, chloroform): $M_{n,SEC} = 1.2 \times 10^3$ kg/mol, $M_{w,SEC} = 6.0 \times 10^5$ kg/mol, $M_{n,NMR} = 42$ kg/mol.



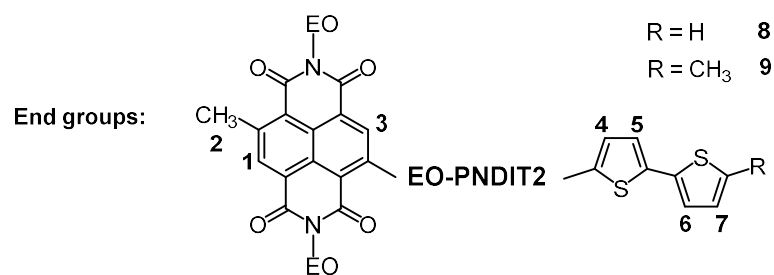
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 30°C): δ 8.83 (s, 2H; 3), 7.40 (br, 4H; 9 and 10), 4.46 and 4.22 (2 x br; a), 4.01 (br; b), 3.80 (m; 1H of d'), 3.75-3.35 (1H of d', c-i, e'-i'), 3.35 and 3.30 (2 x s; j, j').

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120°C): δ 8.90 (s, 2H; 3), 7.45 (br, 4H; 9 and 10), 4.52 and 4.32 (2 x m; a), 4.08 (m; b), 3.83 (m; 1H of d'), 3.8-3.4 (1H of d', c-i, e'-i'), 3.38 and 3.33 (2 x s; j, j').

^1H NMR (500 MHz, CDCl_3 , 30°C): δ 8.84 (s, 2H; 3), 7.38 (br, 4H; 9 and 10), 4.48 and 4.26 (2 x br; a), 4.02 (br; b), 3.82 and 3.72 (d'), 3.7-3.4 (c-i, e'-i'), 3.36 and 3.33 (2 x s; j, j').

^{13}C NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 30°C): δ 162.1 and 162.0 (6, 7), 139.8, 139.5 and 139.0 (2, 8, 11), 136.3 (3), 130.4 (9), 127.5 (5), 125.2 (4), 124.7 (10), 122.6 (1), 76.1 (b), 72.1 (c), 71.6 and 71.5 (i, i'), 70.7 (d), 70.5-69.7 (e-h, e'-h'), 69.5 (d'), 58.6 (j, j'), 41.8 (a).

Selected end group and T2-T2 homocoupling (hc) signals



¹H NMR (500 MHz, CDCl₃, 30°C): δ 8.78 (s; 3), 8.66 (s; 1), 7.23 (d; T2-T2 hc), 7.19 (d; T2-T2 hc), 7.18 (d; 5_{Me}), 7.08 (d; 6_{Me}), 7.07 (dd; 7_H), 6.72 (m; 7_{Me}), 3.14 (s; 2), 2.53 (s; 9).

¹H NMR (500 MHz, C₂D₂Cl₄, 120°C): δ 8.84 (s; 3), 8.69 (s; 1), 7.31 (d; 5_H), 7.29 (d; T2-T2 hc), 7.25 (d; T2-T2 hc), 7.22 (d; 5_{Me}), 7.14 (d; 6_{Me}), 7.12 (dd; 7_H), 6.77 (m; 7_{Me}), 3.20 (s; 2), 2.57 (s; 9).

Characterization

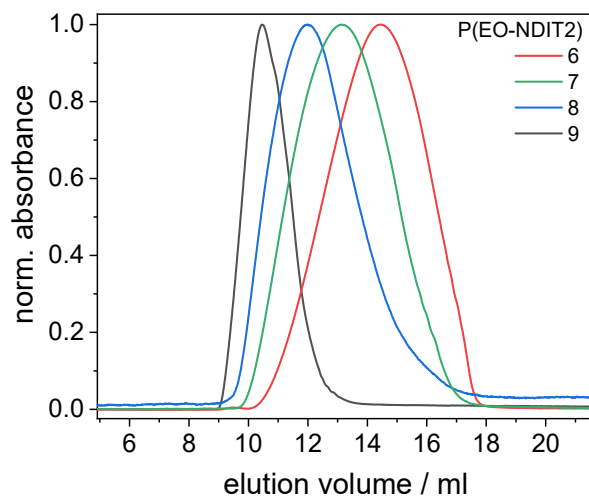


Figure S1. SEC plots of entries 6, 7, 8 and 9 in chloroform at RT. (molecular weights against PS calibration: entry 6: $M_{n,SEC} = 1.2 \times 10^3$ / $M_{w,SEC} = 6.0 \times 10^5$ kg/mol; entry 7: $M_{n,SEC} = 3.8 \times 10^3$ / $M_{w,SEC} = 2.77 \times 10^5$; entry 8: $M_{n,SEC} = 1.21 \times 10^4$ / $M_{w,SEC} = 9.14 \times 10^5$ kg/mol; entry 9: $M_{n,SEC} = 4.32 \times 10^5$ / $M_{w,SEC} = 3.2 \times 10^6$ kg/mol)

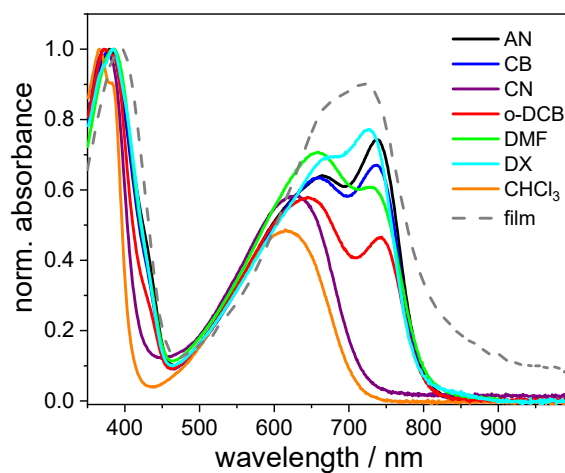


Figure S2. UV-vis spectra of P(EO-NDIT2) (entry 9) in solution. AN: anisole, CB: chlorobenzene, CN: 1-chloronaphthalene, o-DCB: 1,2-dichlorobenzene, DMF: dimethylformamide, DX: 1,4-dioxane, CHCl₃: chloroform. Film: as spun film from chloroform solution.

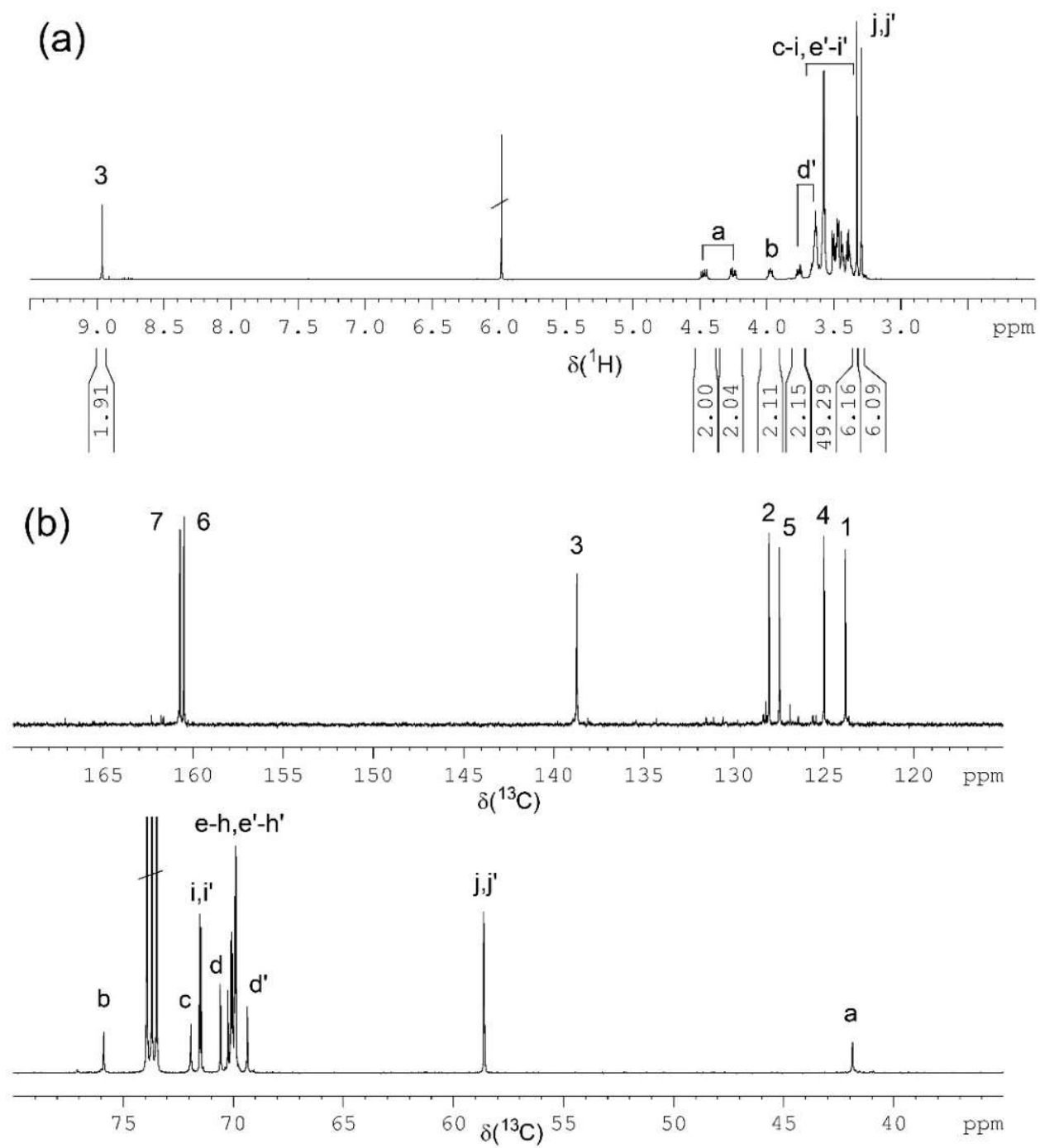


Figure S3. ^1H (a) and ^{13}C NMR spectrum (b) of EO-NDIBr₂ (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$).

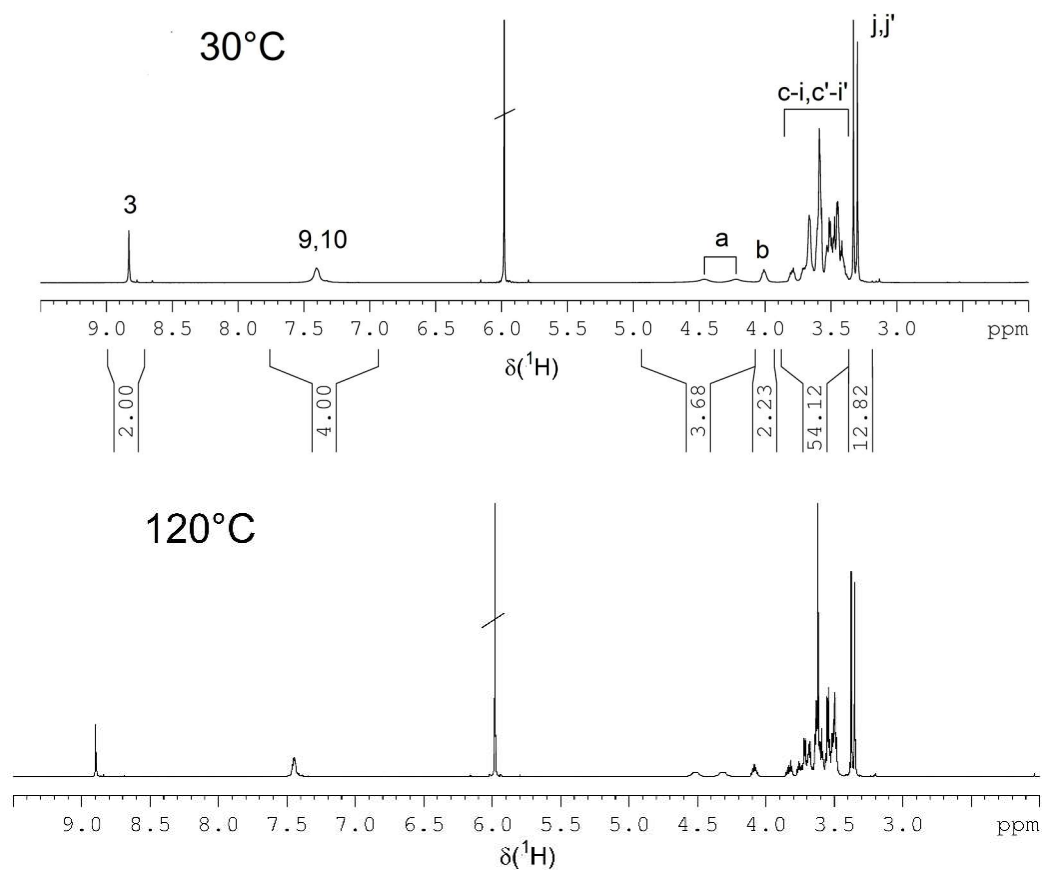


Figure S4. ^1H NMR spectra (500 MHz) of P(EO-NDIT2) at 30°C and 120°C in $\text{C}_2\text{D}_2\text{Cl}_4$.

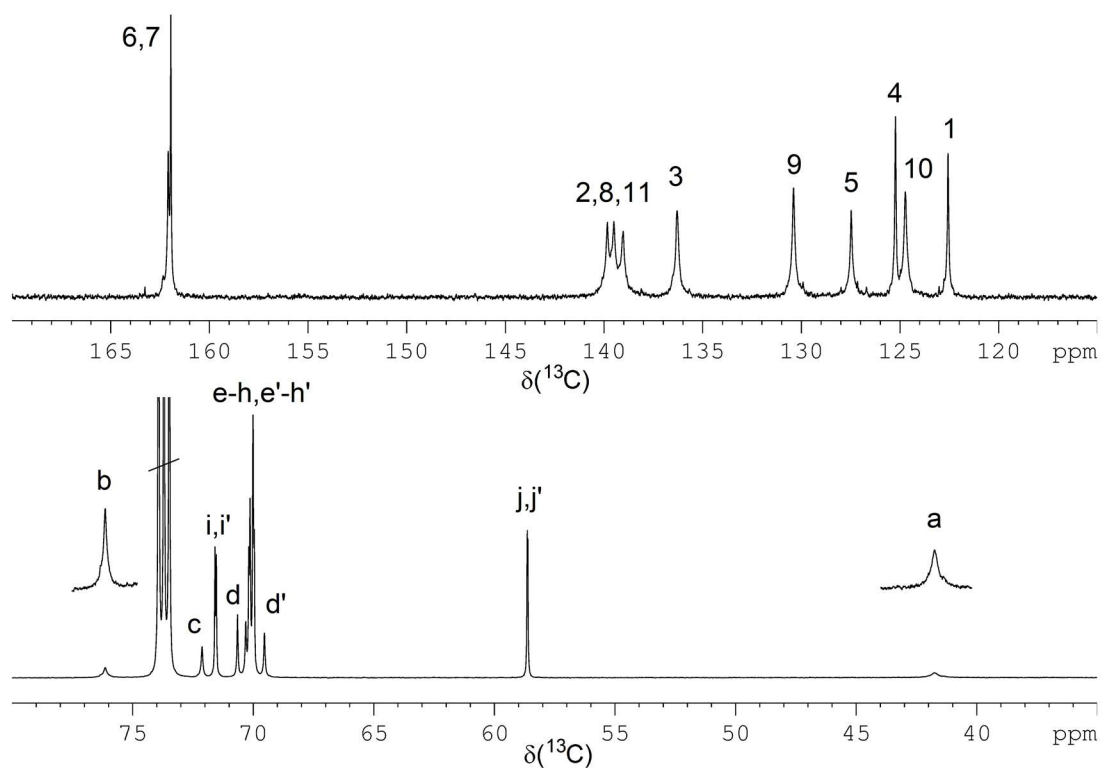


Figure S5. ^{13}C NMR spectra (500 MHz) of P(EO-NDIT2) at 30°C in $\text{C}_2\text{D}_2\text{Cl}_4$.

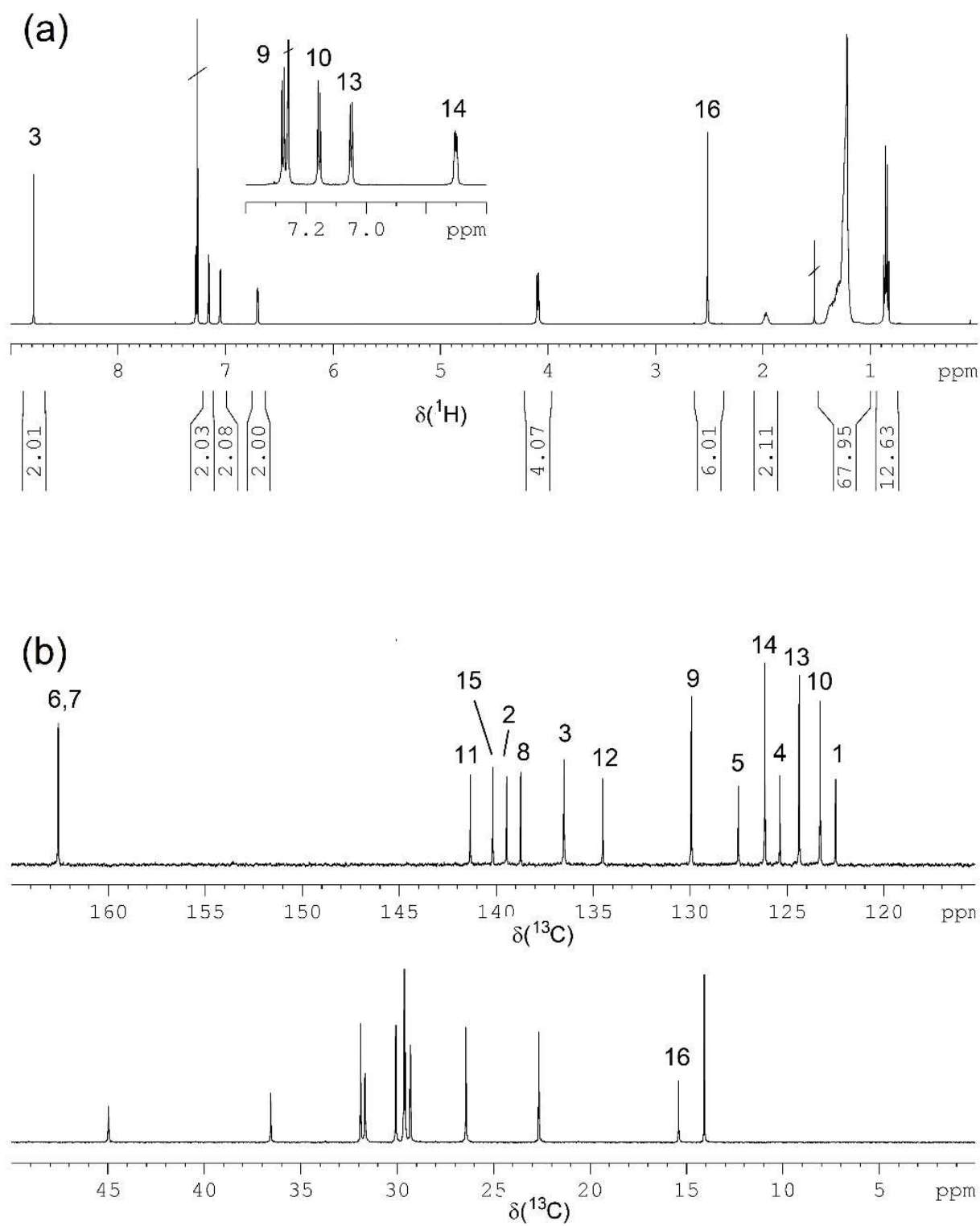


Figure S6. ^1H (a) and ^{13}C NMR spectrum (500 MHz) (b) of Me-T2-NDI-T2-Me (CDCl_3).

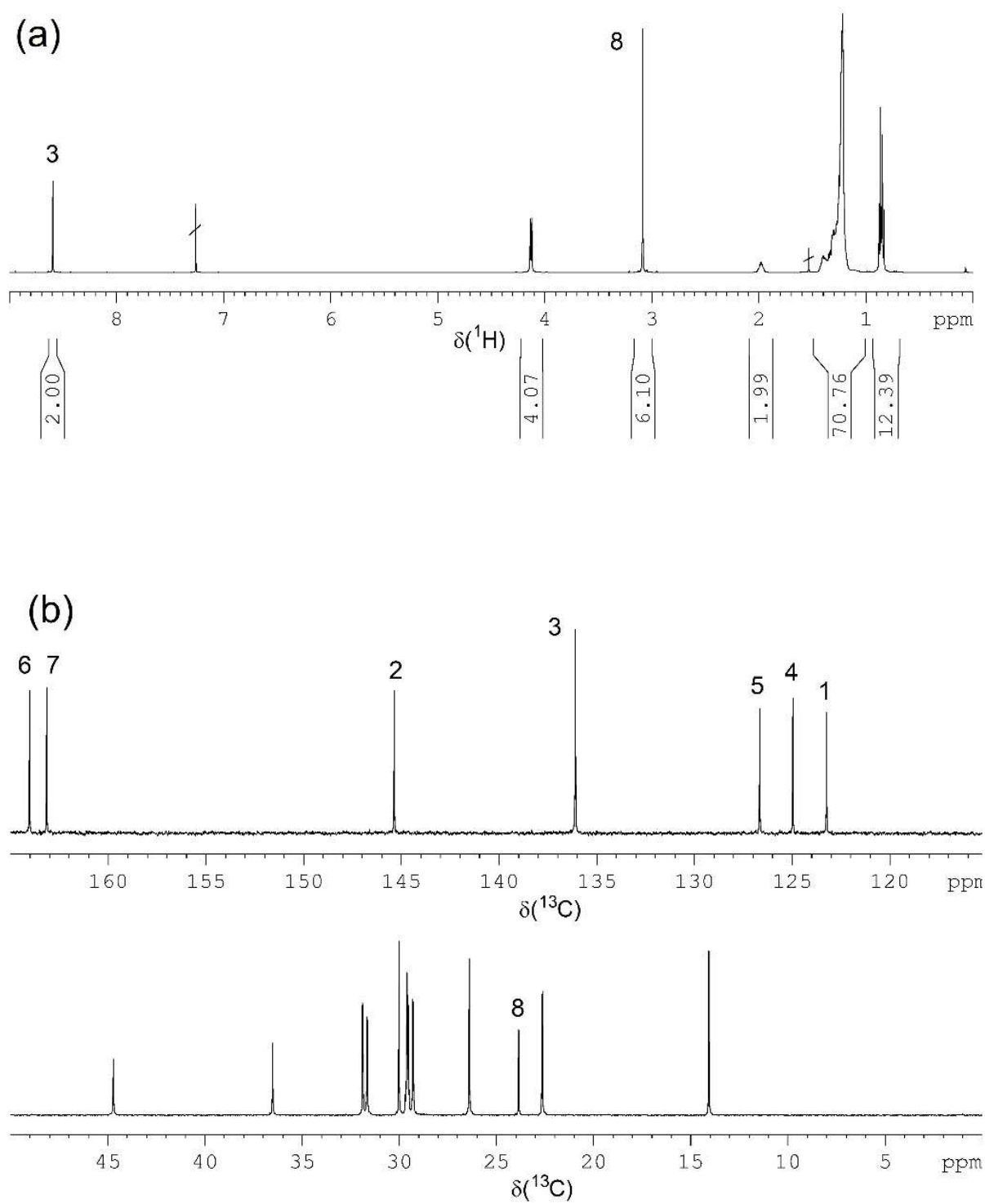


Figure S7. ^1H (a) and ^{13}C NMR spectrum (500 MHz) (b) of Me-NDI-Me (CDCl_3).

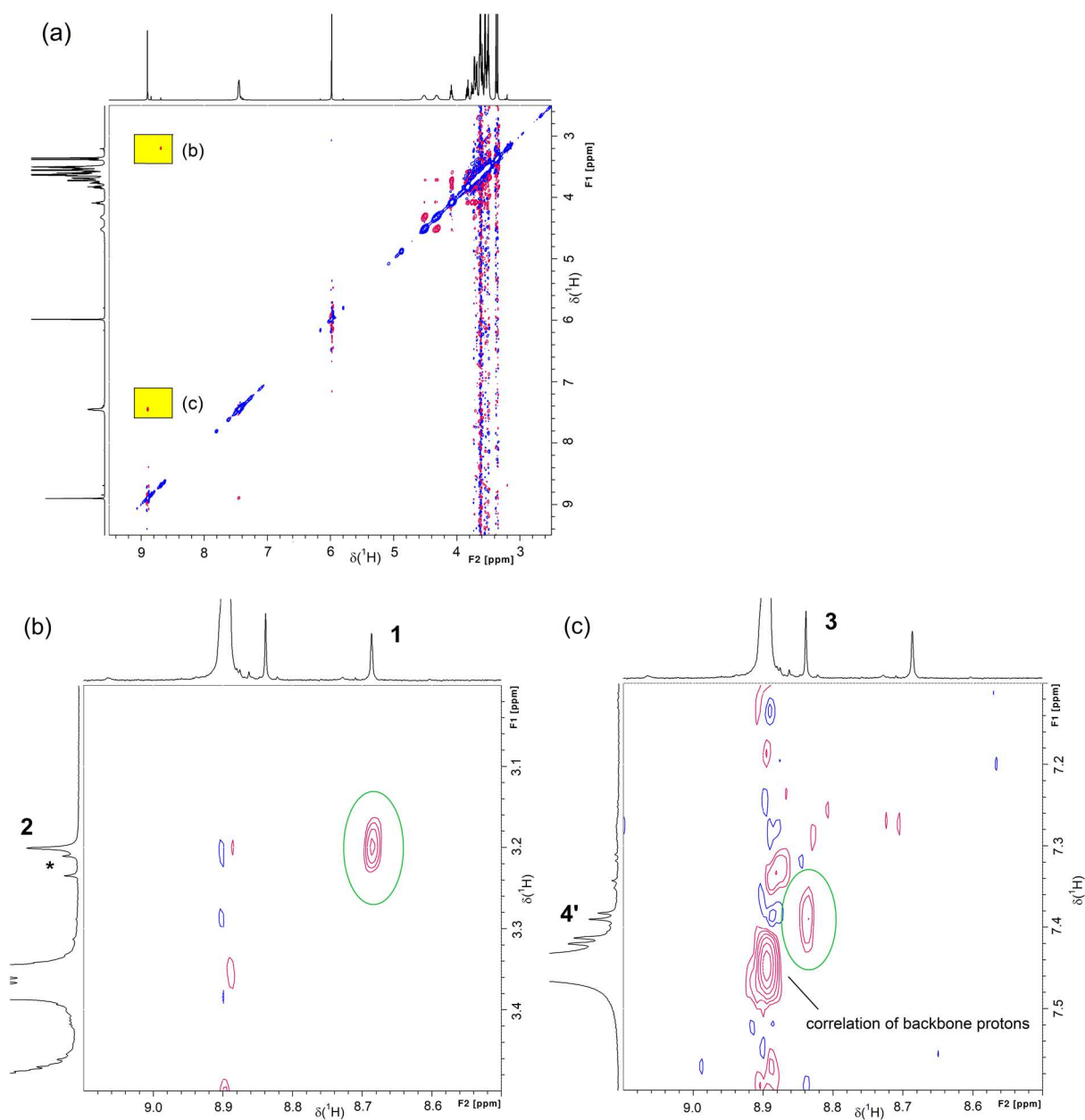


Figure S8. ROESY spectrum of P(EO-NDIT2) (entry 1) (a) and enlarged regions showing the through space correlations between NDI proton 1 and methyl proton 2 (b) and between NDI proton 3 and thiophene proton 4' (500 MHz, C₂D₂Cl₄ @ 120°C).

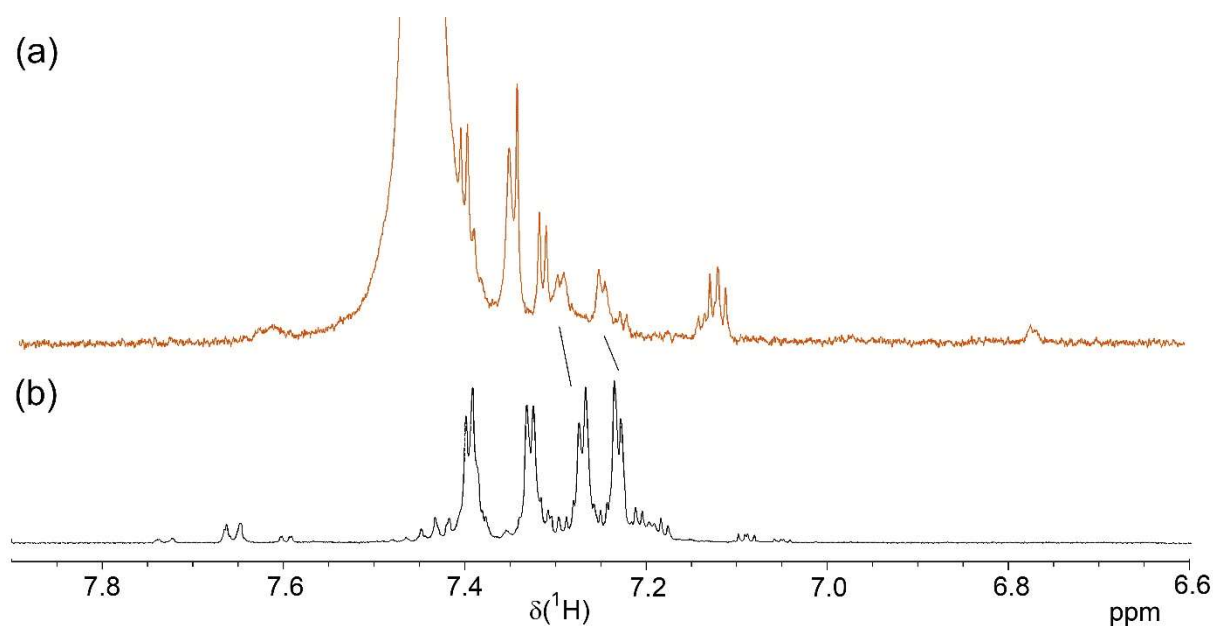


Figure S9. ^1H NMR spectrum (region) of (a) P(EO-NDIT2) (*entry 2*) and (b) OD-PNDIT4 at 120°C in $\text{C}_2\text{D}_2\text{Cl}_4$ (500 MHz).

MALDI-ToF MS

Sample preparation: The matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and the polymer were both dissolved in chloroform ($c = 10 \text{ mg/mL}$). The additives Na-/Ag-/NH₄-trifluoroacetic acid (TFA) were dissolved in tetrahydrofuran. The matrix and the polymer were mixed in a 20:1 ratio. Afterwards, 1 vol.-% (regarding the amount of matrix solution) of additive solution was added. The samples were prepared on a standard steel sample plate (Bruker “MTP 384 target plate ground steel BC” Part-No.: 8280784) using the dried droplet method: the individual matrix/analyte solutions were dripped on the plate ($V = 1 \text{ } \mu\text{l}$) and dried in air for several seconds until the solvent had completely evaporated.^{6–8}

Table S1. Parameters for positive reflectron mode MALDI ToF MS.

Parameter	Value
m/z range	1k - 55k
Sample rate	1.0
Shots per measurement	500
Matrix suppression	till 1k m/z
Measurements per spectra	10
Random walk	Off
Electronic gain	Enhanced
Detector gain	100x
Realtime smooth	Off
Laser-frequency	1000 Hz
Laser-size	Large (60 - 70 μm)

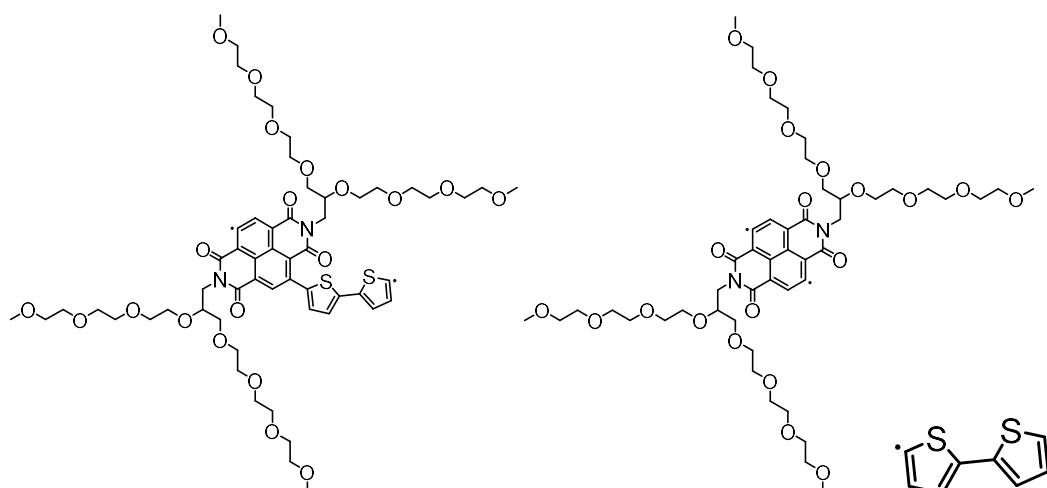
P(EO-NDIT2) (*entry 9*) was measured in reflectron mode using DCTB (Figure S10). Next to the pure matrix-analyte mixture, three different salts were tested as additives (Na-/Ag-/NH₄-TFA) (Figure S11). The MALDI spectra of the P(EO-NDIT2) (*entry 9*) using different salt additives show that the addition of the salts has an influence on signal intensity but not on the number of signals. Especially NaTFA increases signal intensity compared to the measurement without any additive, but nevertheless, all spectra exhibit four signal series in total. The additive NaTFA gave the qualitatively best spectrum, i.e. the highest signal intensities, and was used for further evaluations.

The MALDI spectrum (Figure S12) contains four signal series, two major and two minor ones. The first series (red) is a major series and contains 11 defined signals, starting with a signal at 3375 m/z. The second one (green) starts at 3522 m/z, contains defined 10 signals and is also a major series. The third one (orange) starts at 3672 m/z and with defined 7 signals it is one of the minor series. The fourth one (pink) starts at 4386 m/z and with 6 signals is the least defined series.

Although the polymer is detectable until about 30 kg/mol (Figure S10), defined signals are only observed until $\sim 15\text{kg/mol}$. Consequently, while values for M_n , M_w and $\bar{D}$ could be

calculated, they are not reliable and do not represent the actual molecular weight distribution.^{9,10} Nevertheless, the four signal series can be used to calculate the molar mass of the repeating unit (RU) and the end groups of the polymer.

Calculations of the mean values of the differences between the individual signals give a molar mass of the repeating unit (RU) of $1162.9 \text{ Da} \pm 1$ (1. signal series (red)), $1162.9 \text{ Da} \pm 0.9$ (2. signal series (green)), $1161.3 \text{ Da} \pm 0.6$ (3. signal series (orange)) and $1161.4 \text{ Da} \pm 0.5$ (4. signal series (pink)). The mean value of these four values is $1162.1 \text{ Da} \pm 0.4$, which will be used for further calculations and discussions. The theoretical molar mass of the repeating unit is $M_{\text{theo.}} = 1161.3 \text{ Da}$ (Scheme S1). The repeating unit is made of the naphthalene diimide (NDI) block ($M_{\text{theo.}} = 997.1 \text{ Da}$) and the bithiophene (TT) block ($M_{\text{theo.}} = 164.2 \text{ Da}$).



Scheme S1. Molecular structure of the repeating unit (RU) ($M_{\text{theo.}} = 1161.3 \text{ Da}$) (left), the NDI-block (NDI) ($M_{\text{theo.}} = 997.1 \text{ Da}$) (middle) and bithiophene (T2) ($M_{\text{theo.}} = 164.2 \text{ Da}$) (right).

The theoretical molar mass of the repeating unit is 1161.3 Da , the average molar mass calculated from the MALDI spectrum is $1162.1 \text{ Da} \pm 0.4$. The difference between these values might be caused by small inaccuracies during the calibration process and rounding errors during calculations. Nonetheless, the molecular structure of the repeating unit is confirmed by

MALDI-ToF MS. The molar mass of the end groups (EG) of a polymer can be calculated with the following formula⁵:

$$M_{EG} = M_{Signal} - n \cdot M_{RU} - M_{cation} \quad (1)$$

M_{EG} is the total mass of all end groups. Hence, different end group combinations are possible. Due to the addition of the NaTFA salt there is an excess of sodium cations, with $M_{cation} = M_{Na} = 23$ Da. Each of the four signal series represents a different end group combination. We find three dominant combinations of end groups (Table S2): (1) methyl groups at both ends (1. signal series (red)); (2) a methyl and a hydrogen end group (2. signal series (green)); (3) hydrogen at each end (3. signal series (orange)). The first (red) and second (green) signal series are the major series containing the highest number of signals and the highest signal intensities, implying that these end group combinations are the dominant ones. For the fourth signal series (pink) a possible combination was not found: The calculated total molar mass of the end groups of 880 Da (formula (1) $4386 - (3 \times RU = 1161) - (Na = 23)$) is too large for an end group-combination containing TT-blocks and too small for a combination containing NDI-blocks. A possible explanation might be a side chain cleaving found dominantly at an NDI located at the end group, yet this could not be confirmed.

Table S2. Possible end group combinations for the polymer P(EO-NDIT2) (entry 9).

Signal series	Possible combinations [Da]	1. measured signal [m/z]	Error [Da]
1. (red)	$Na^+ + CH_3 + NDI + 2 \times [RU] + CH_3$ $\Rightarrow 23 + 15 + 997 + 2 \times 1161 + 15 = \mathbf{3372}$	3375	3
2. (green)	$Na^+ + CH_3 + 3 \times [RU] + H$ $\Rightarrow 23 + 15 + 3 \times 1161 + 1 = \mathbf{3522}$	3522	0
3. (orange)	$Na^+ + H + T2 + 3 \times [RU] + H$ $\Rightarrow 23 + 1 + 164 + 3 \times 1161 + 1 = \mathbf{3672}$	3672	0
4. (pink)	unknown	4386	n/a

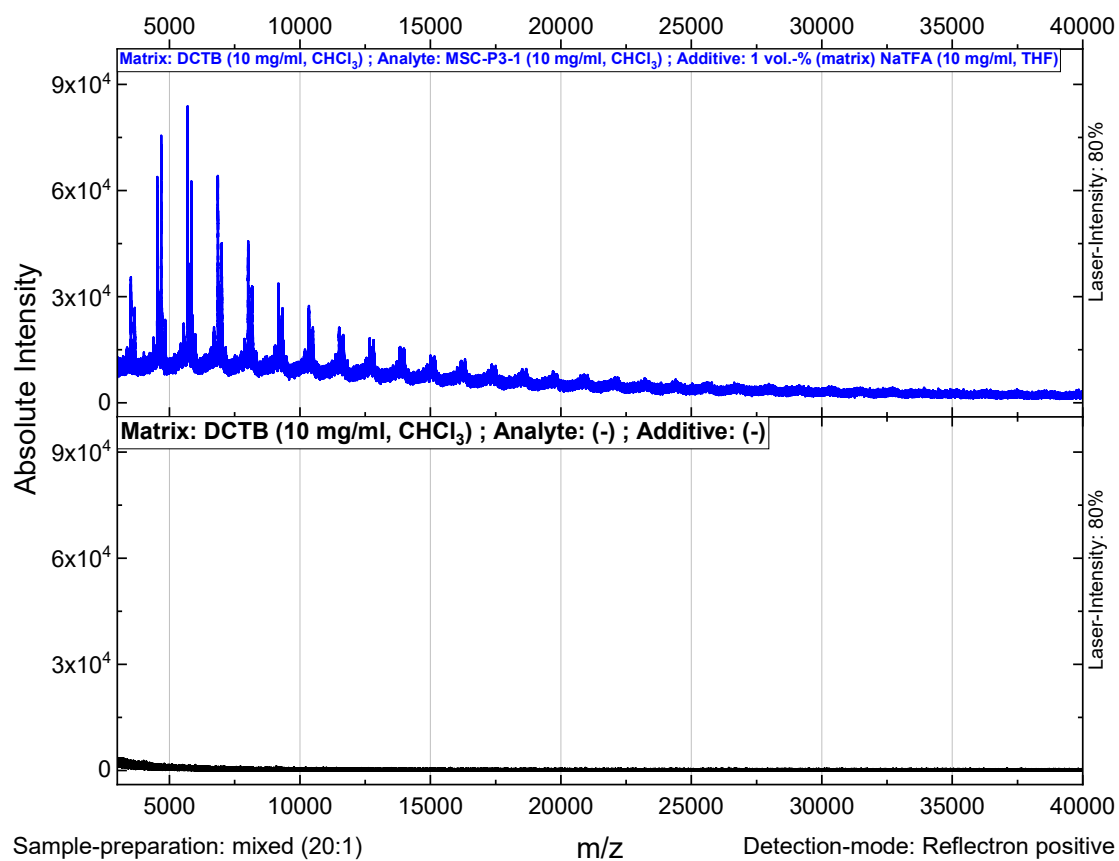


Figure S10. Reflectron positive mode MALDI-ToF MS spectra (raw) of P(EO-NDIT2) (*entry* 9) a) mixed with matrix DCTB (20:1) (blue) and b) pure matrix DCTB (black).

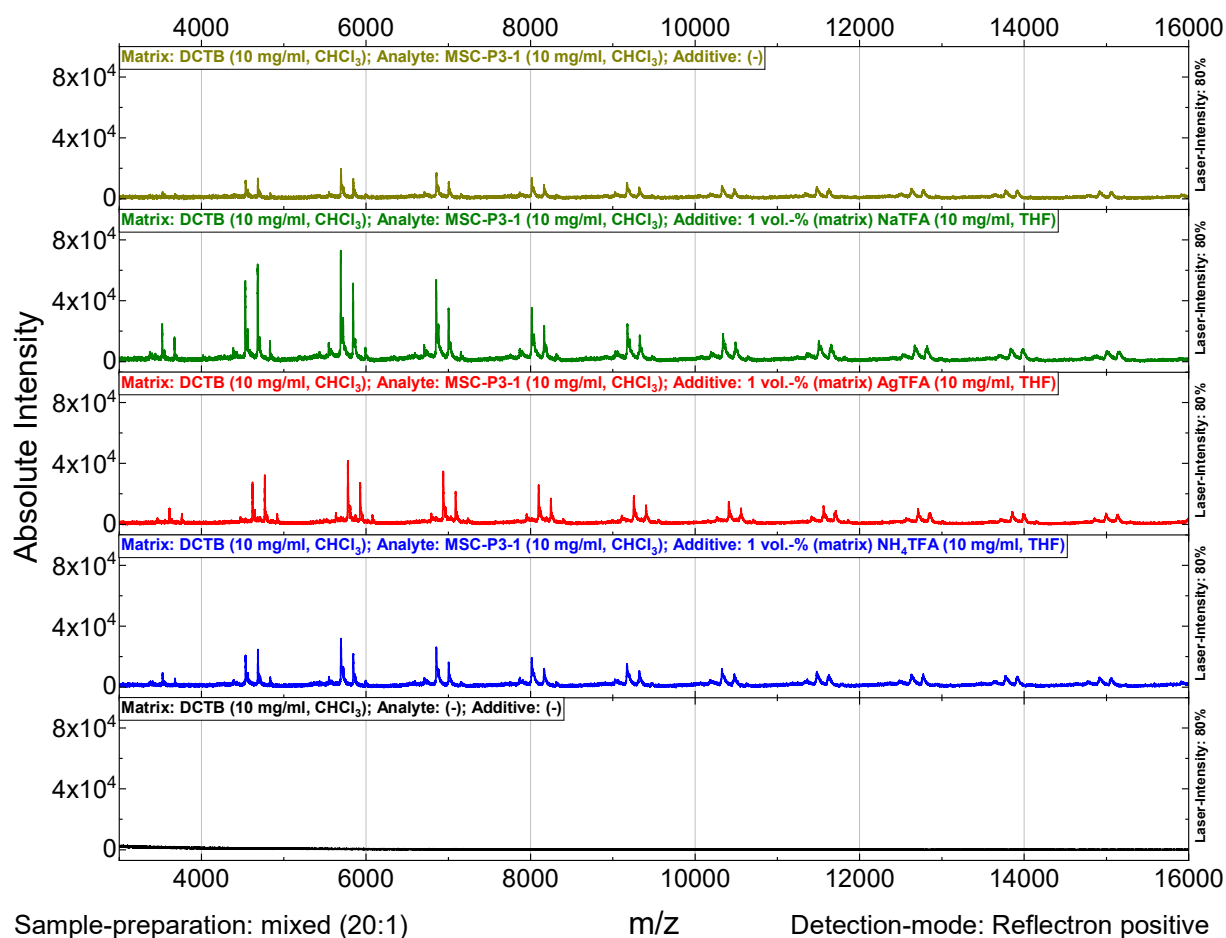


Figure S11. Reflectron positive mode MALDI-ToF MS spectra of P(EO-NDIT2) (*entry* 9) mixed with matrix DCTB (20:1) and a) no additive (yellow), b) 1 vol.-% (matrix) NaTFA (10 mg/mL, THF) (green), c) 1 vol.-% (matrix) AgTFA (10 mg/mL, THF) (red) and d) 1 vol.-% (matrix) NH₄TFA (10 mg/mL, THF) (blue). The lowest spectrum is the pure matrix DCTB (black). Spectra a)-d) were smoothed and manually baseline corrected.

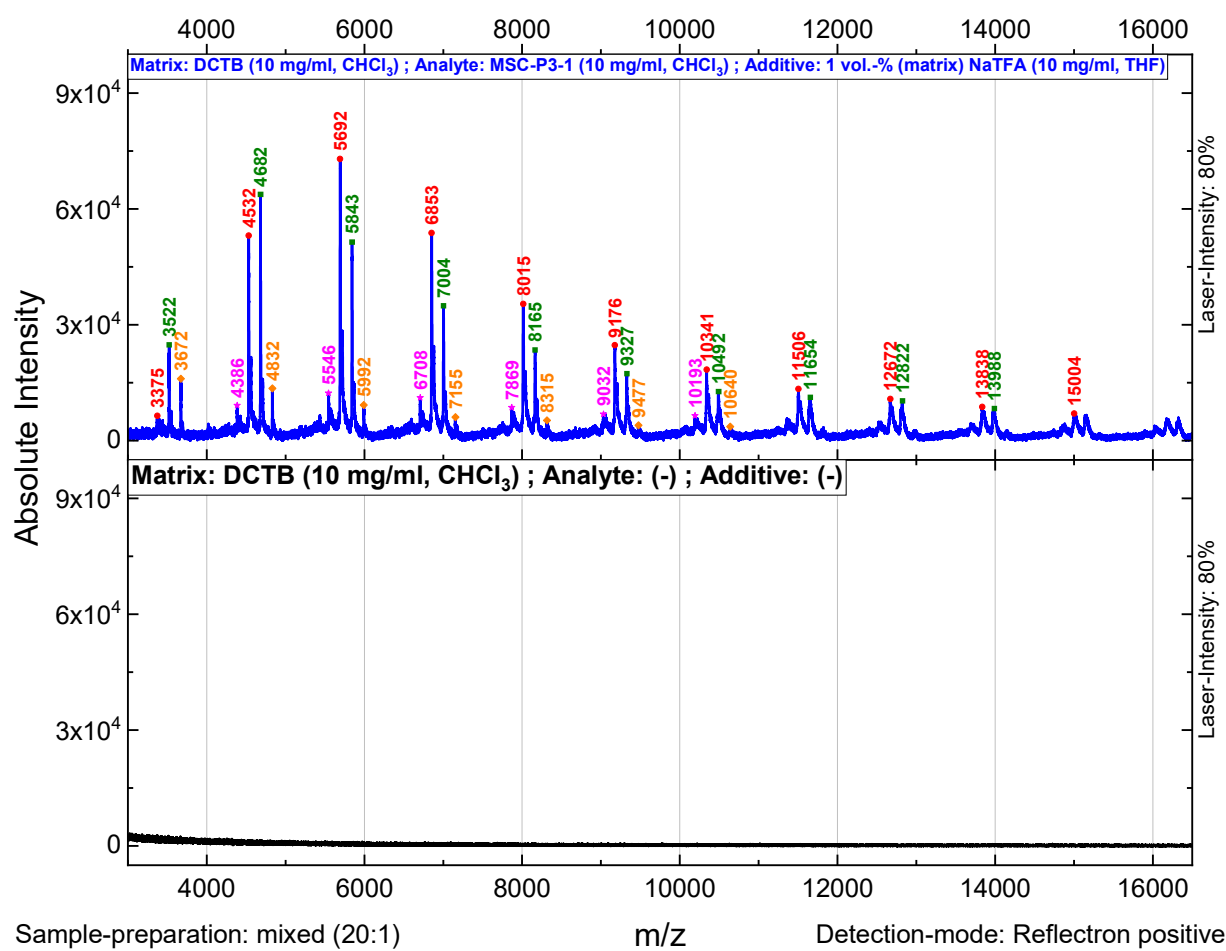


Figure S12. Reflectron positive mode MALDI-ToF MS spectra of a) P(EO-NDIT2) (*entry 9*) mixed with matrix DCTB (20:1) (blue) and b) pure matrix DCTB (black). Spectrum a) was smoothed, manually baseline corrected and peak picked.

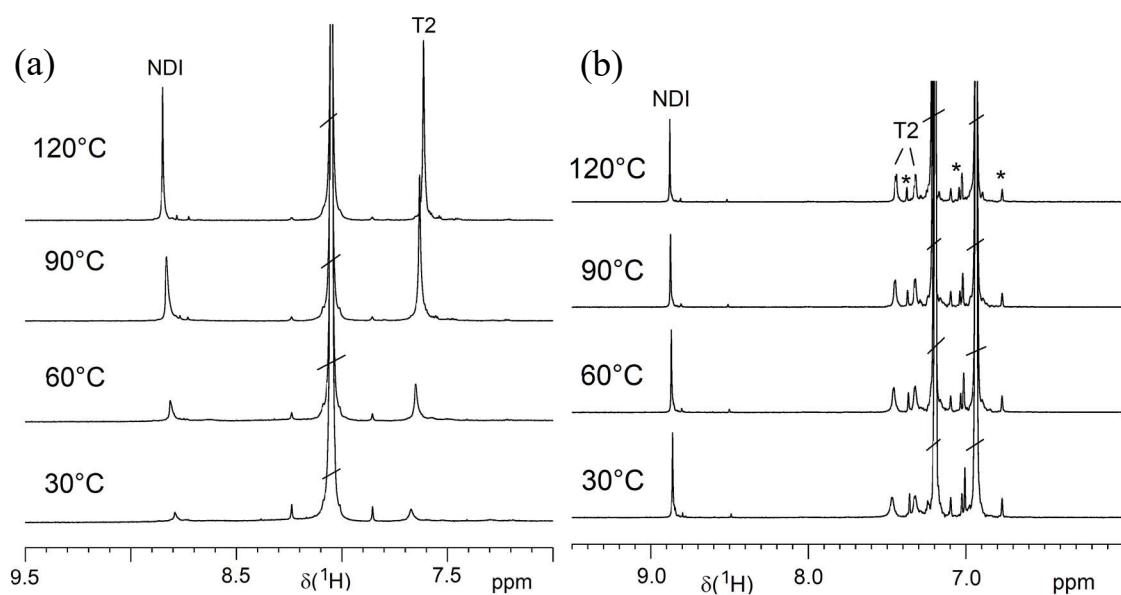


Figure S13. Temperature-dependent aggregation of P(EO-PNDIT2) (*entry 3*) in (a) DMF- d_7 and (b) *o*-DCB- d_4 probed by ^1H NMR spectroscopy. The region of aromatic protons is shown (for EO side chain signals compare Figure 5 and 6). * marks ^{13}C satellites of the solvent signal.

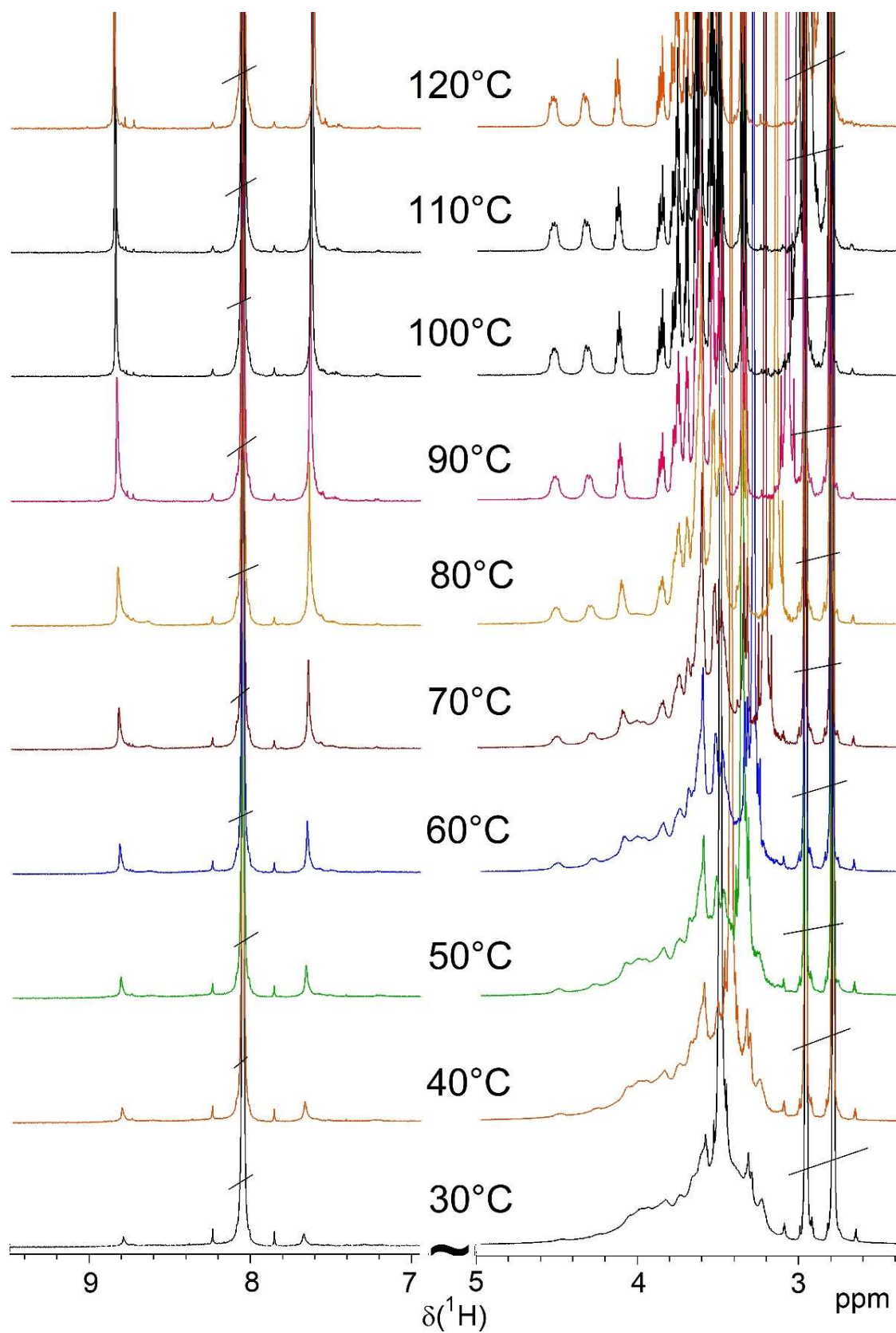


Figure S14. ^1H NMR spectra (500 MHz) (regions) of EO-PNDIT2 (*entry 3*) at different temperatures in DMF-d_7 .

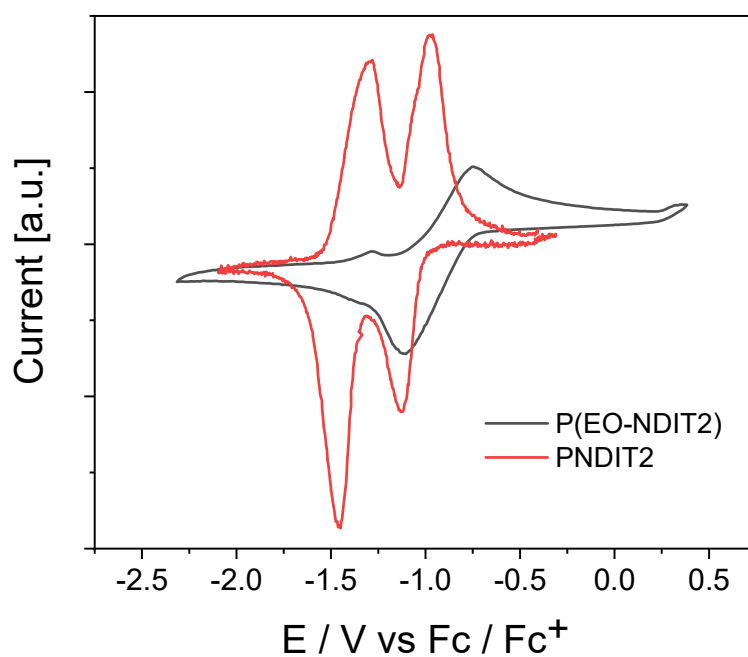


Figure S15. Cyclic voltammetry of PNDIT2 and P(EO-NDIT2) (*entry 9*). Measurements were done on films and using ferrocene (-4.8 eV) as internal standard. LUMO levels: PNDIT2 -3.75 eV, P(EO-NDIT2) -3.88 eV.

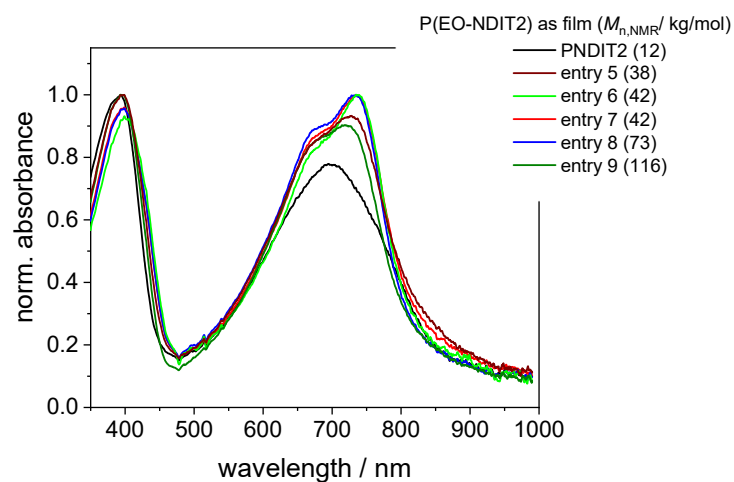


Figure S16. UV-vis absorption of P(EO-NDIT2) thin film with different molecular weight at room temperature. The film was made by spin coating (1000 rpm, 60s) CB solutions (20 mg/mL).

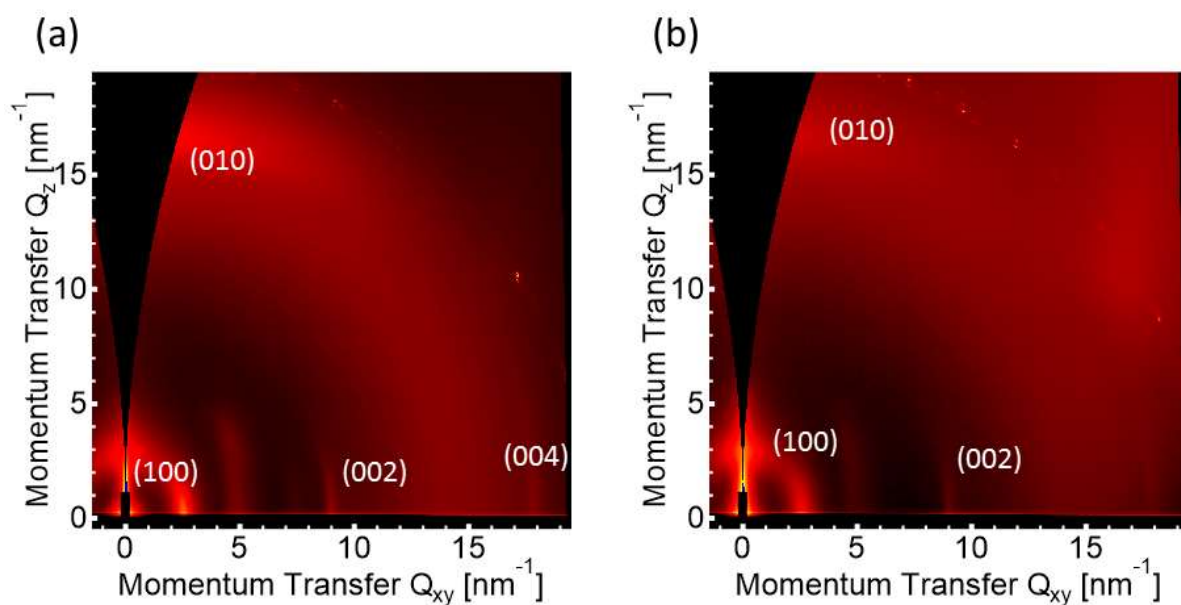


Figure S17. Two-dimensional GIWAXS patterns of P(EO-NDIT2) processed by (a) CB and (b) *o*-DCB.

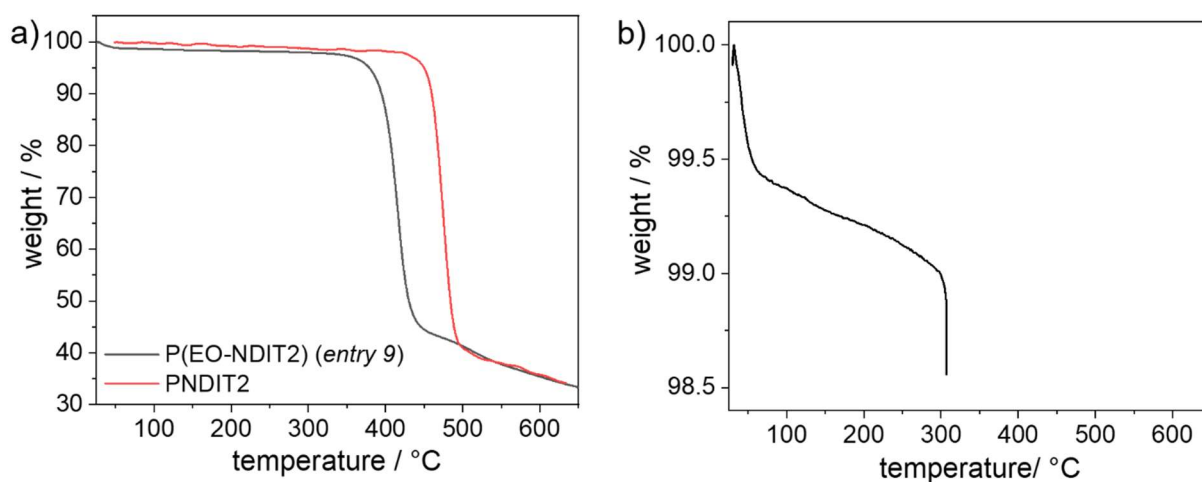


Figure S18. TGA plot of a) P(EO-NDIT2) (*entry 9*) and PNDIT2 with 10 K/min heating rate and b) P(EO-NDIT2) (*entry 9*) from 30 °C to 305 °C at 10 K/min followed by an isothermal step at 305°C for 15 min.

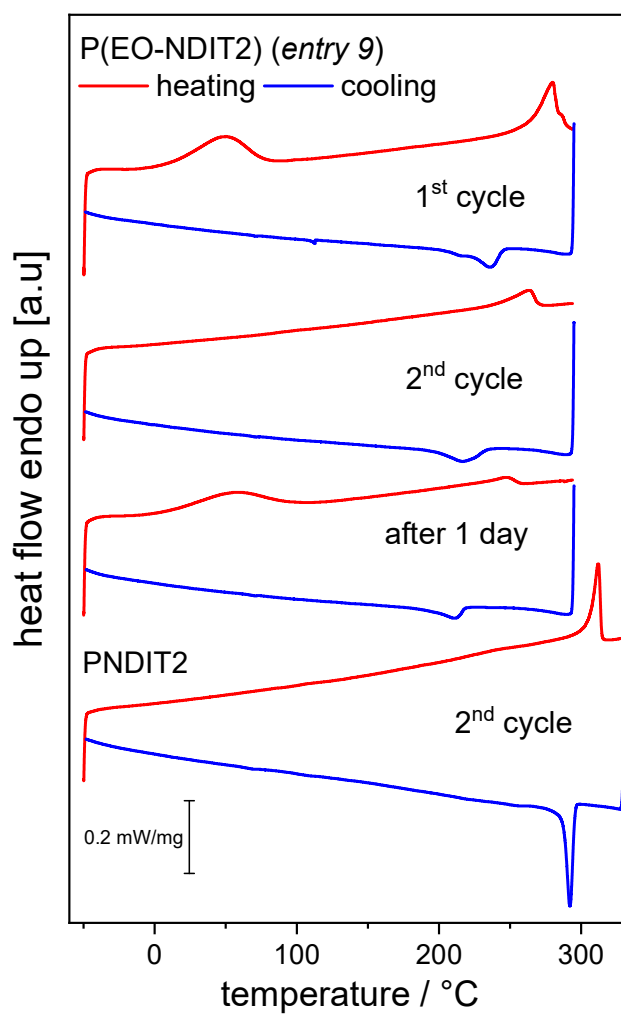


Figure S19. DSC measurements of P(EO-NDIT2) (*entry 9*) with heating/cooling rates of 10 K/min from -50 °C to 295 °C under argon. After the second cycle, one more cycle was measured with same condition 24 hours later. The 2nd cycle of PNDIT2 was measured as reference under the same conditions.

Table S3. Summary of T_m , T_c , ΔH_m and ΔH_c of P(EO-NDIT2) (*entry 9*) and PNDIT2

entry	cycle	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
9	1	280 / 49 ^b	245	12.9 / 18.7 ^b	5.8
	2	263	217	4.7	4.9
	1 ^a	247 / 55 ^b	211	2.0 / 13 ^b	2.9
PNDIT2	2	312	292	10.7	10.4

^aheating/cooling 24h after 2nd cycle. ^bside chain transition.

The thermal properties were investigated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). Compared to PNDIT2 with 2-octyldodecyl side chains, the thermal stability of P(EO-NDIT2) was significantly lower due to the EO side chains. Onset degradation temperatures of PNDIT2 and P(EO-NDIT2) were 419 °C and 306 °C, respectively (Figure S17a). Thus, DSC measurements had to be conducted under a reduced temperature range and with high temperature limits where chain degradation likely occurred (Figure S18). In the first heating cycle, P(EO-NDIT2) shows two endothermal transitions at 49 °C and 280 °C, which are ascribed to side chain and main chain melting, respectively. The corresponding melting enthalpies were 18.7 and 12.9 J/g, respectively. This side chain melting, apparently enabled by the flexible EO side chains, is commonly not seen for PNDIT2 with 2-octyldodecyl side chains. The melting enthalpy for main chain melting occurs at lower temperature than for PNDIT2 (T_m = 312 °C for the sample used here with a comparably high molecular weight). Upon cooling of P(EO-NDIT2), backbone crystallization was seen but the corresponding crystallization enthalpy was roughly halved (5.8 J/g). Side chain crystallization was not observed. Further cycles confirmed this trend of decreasing enthalpies to proceed, all enthalpy values of the backbone transitions continuously decreased. We ascribe this behavior to side chain cross-linking during the DSC experiment, as the maximum temperature was close to the onset of degradation. An isothermal TGA experiment at the maximum temperature used in DSC

(305 °C) also indicated degradation (Figure S17b). This picture was further confirmed by the fact that DSC samples were completely insoluble in common solvents after thermal cycling. All transition temperatures and enthalpies are collected in table S3.

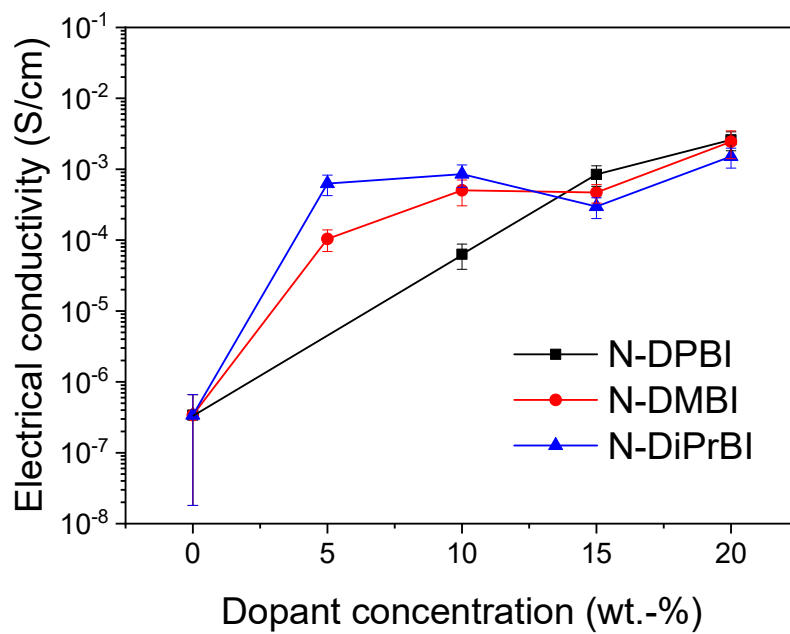


Figure S20. P(EO-NDIT2) (*entry 4*) solution doped with several N-benzimidazole based n-dopants.

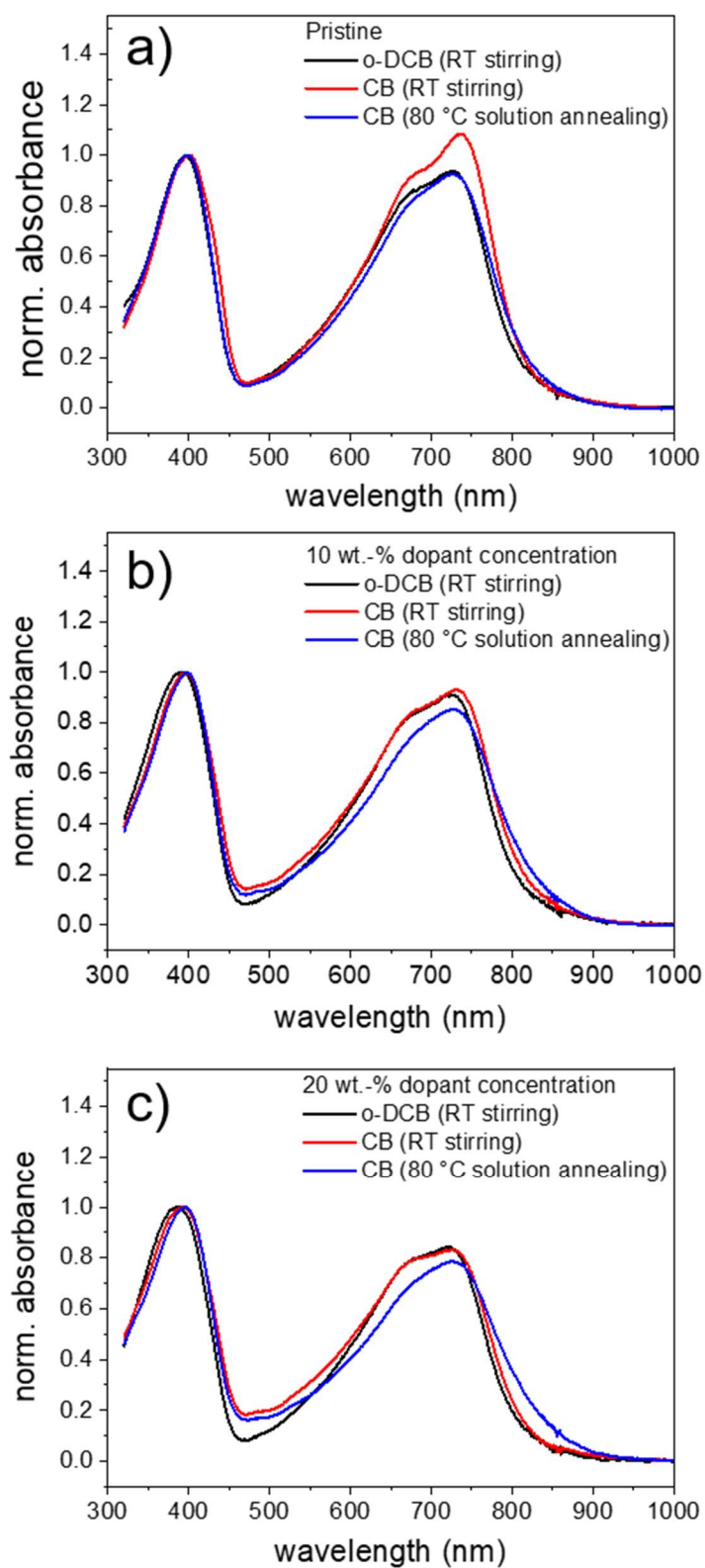


Figure S21. UV-vis spectroscopy of pristine and doped films of P(EO-NDIT2) (*entry 4*): a) pristine, b) 10 wt.-% N-DiPrBI, c) 20 wt.-% N-DiPrBI.

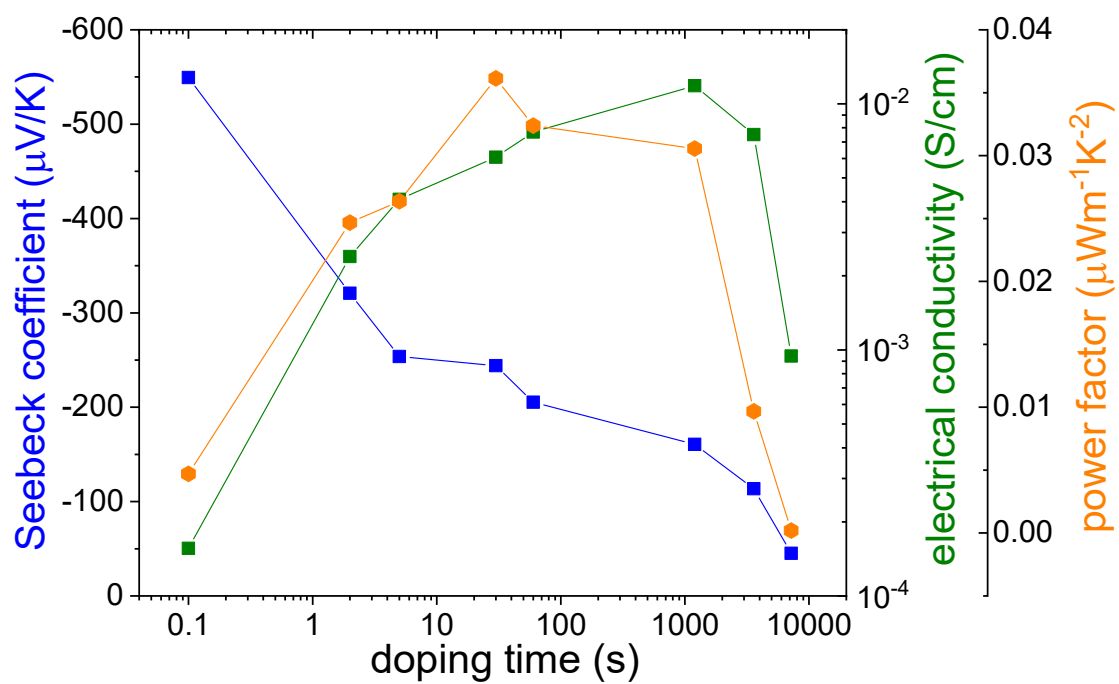


Figure S22. Vapor doping of P(EO-NDIT2) with tetrakis(dimethylamino)ethylene (TDAE).

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