Electronic Supplementary Information

An Effective Strategy to Enhance the Dielectric Constant of Organic Semiconductors – CPDTTPD-Based Low Bandgap Polymers Bearing Oligo(Ethylene Glycol) Side Chains

Jeroen Brebels,[a] Evgenia Douvogianni,[b] Dries Devisscher,[a] Raghavendran Thiruvallur Eachambadi,[c] Jean Manca,[c] Laurence Lutsen,[d] Dirk Vanderzande,[a,d] Jan C. Hummelen,[b] and Wouter Maes*[a,d]*

(a) UHasselt – Hasselt University, Institute for Materials Research (IMO-IMOMEC), Design & Synthesis of Organic Semiconductors (DSOS), Agoralaan, 3590 Diepenbeek, Belgium

(b) Stratingh Institute for Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

(c) UHasselt – Hasselt University, X-LAB, Agoralaan, 3590 Diepenbeek, Belgium

(d) IMEC, Associated lab IMOMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium

Corresponding authors: E-mail: j.c.hummelen@rug.nl; wouter.maes@uhasselt.be

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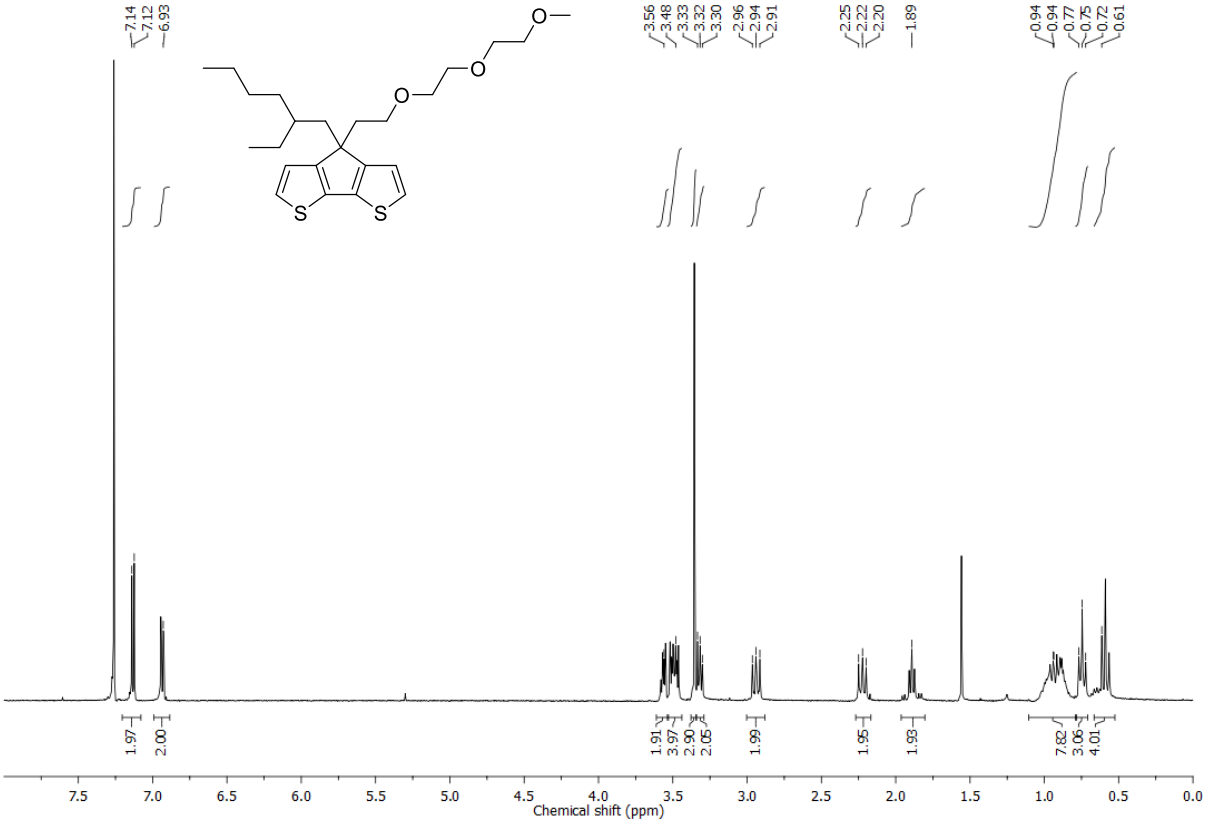
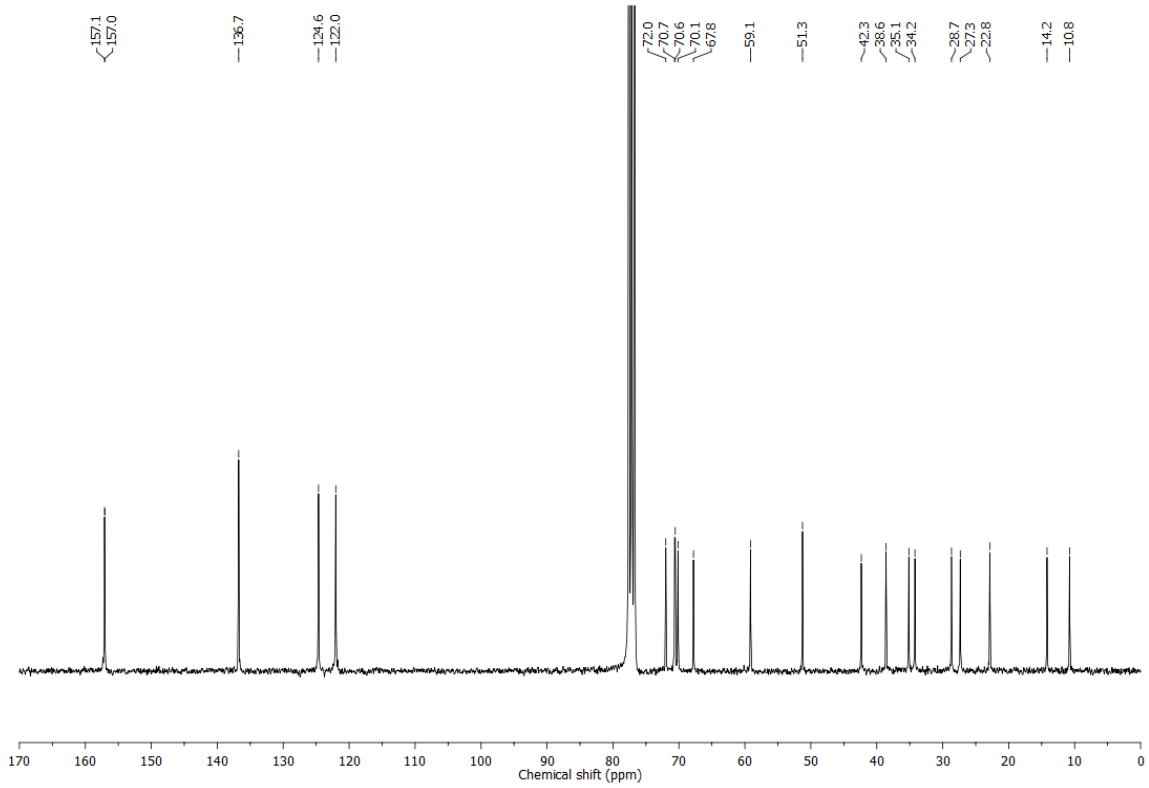
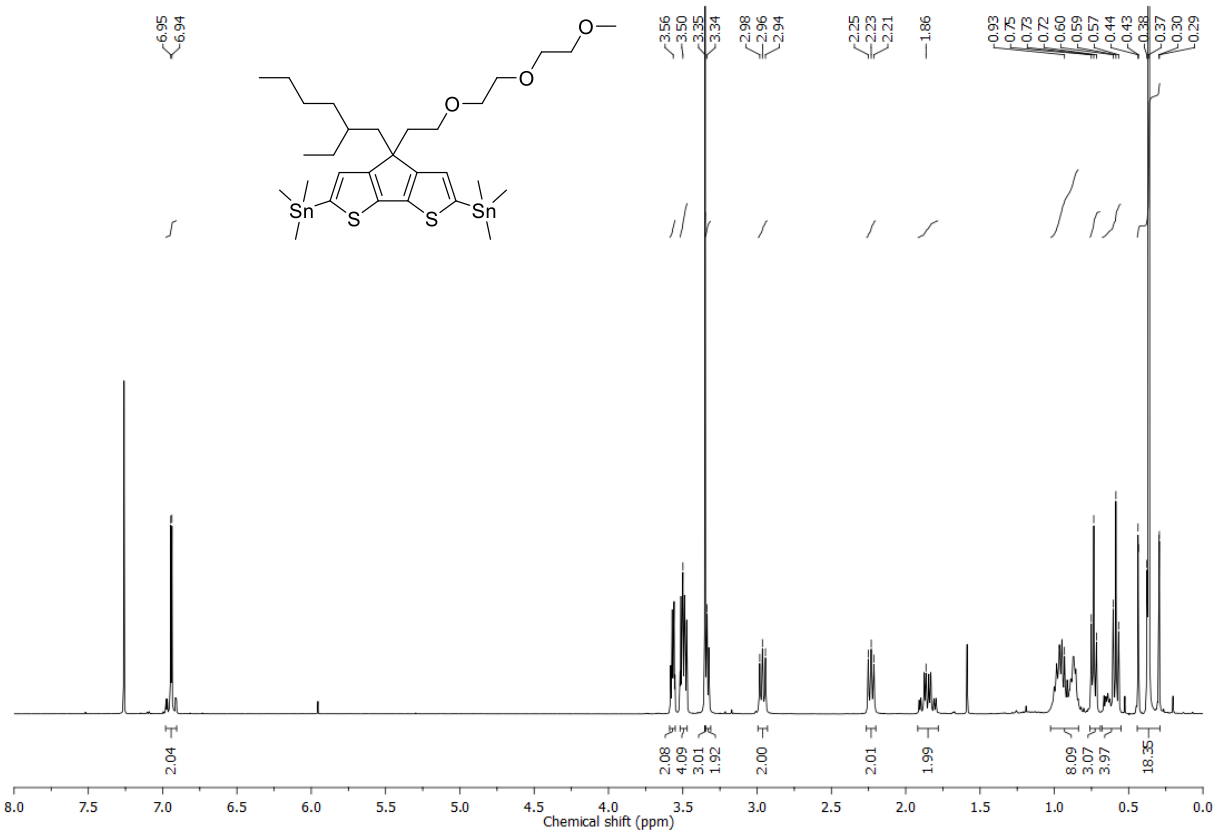
1. ^{1}H and ^{13}C NMR spectra

4-(2-ethylhexyl)-4-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene (5)





(4-(2-ethylhexyl)-4-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (6)



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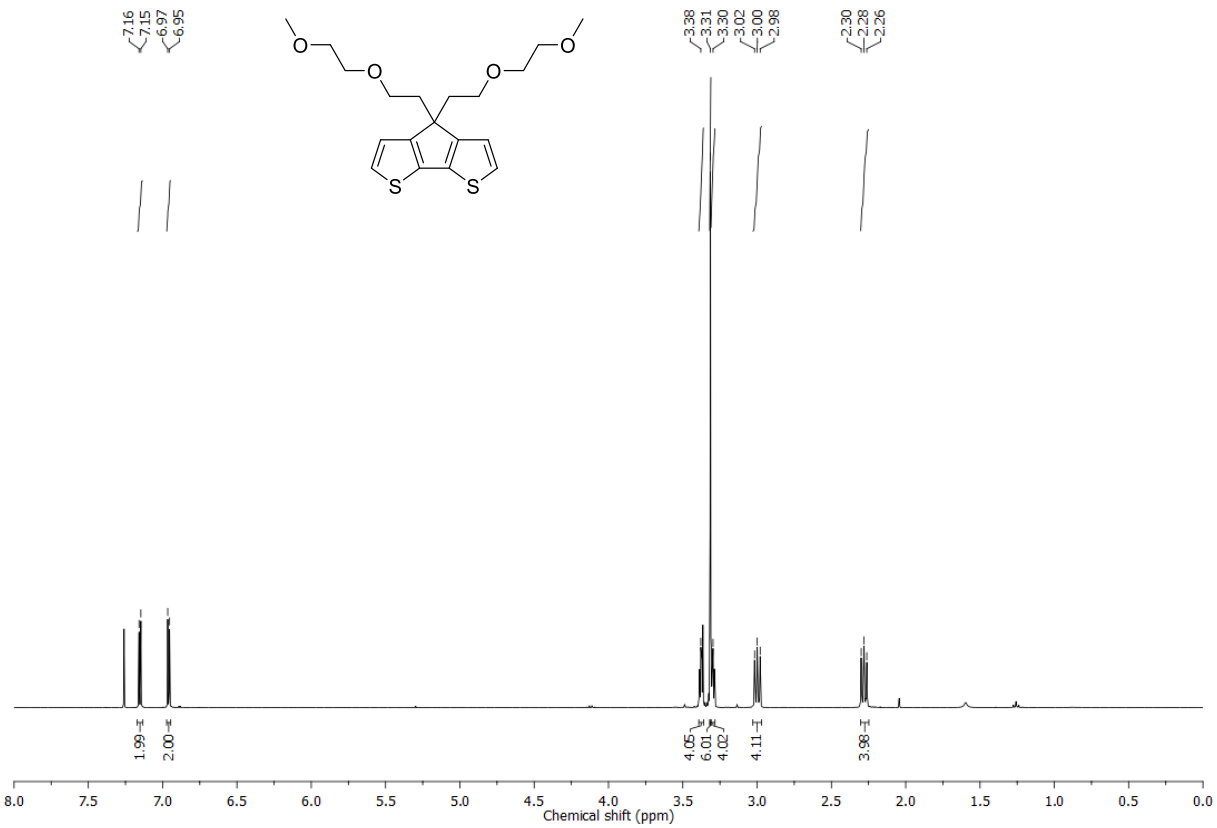
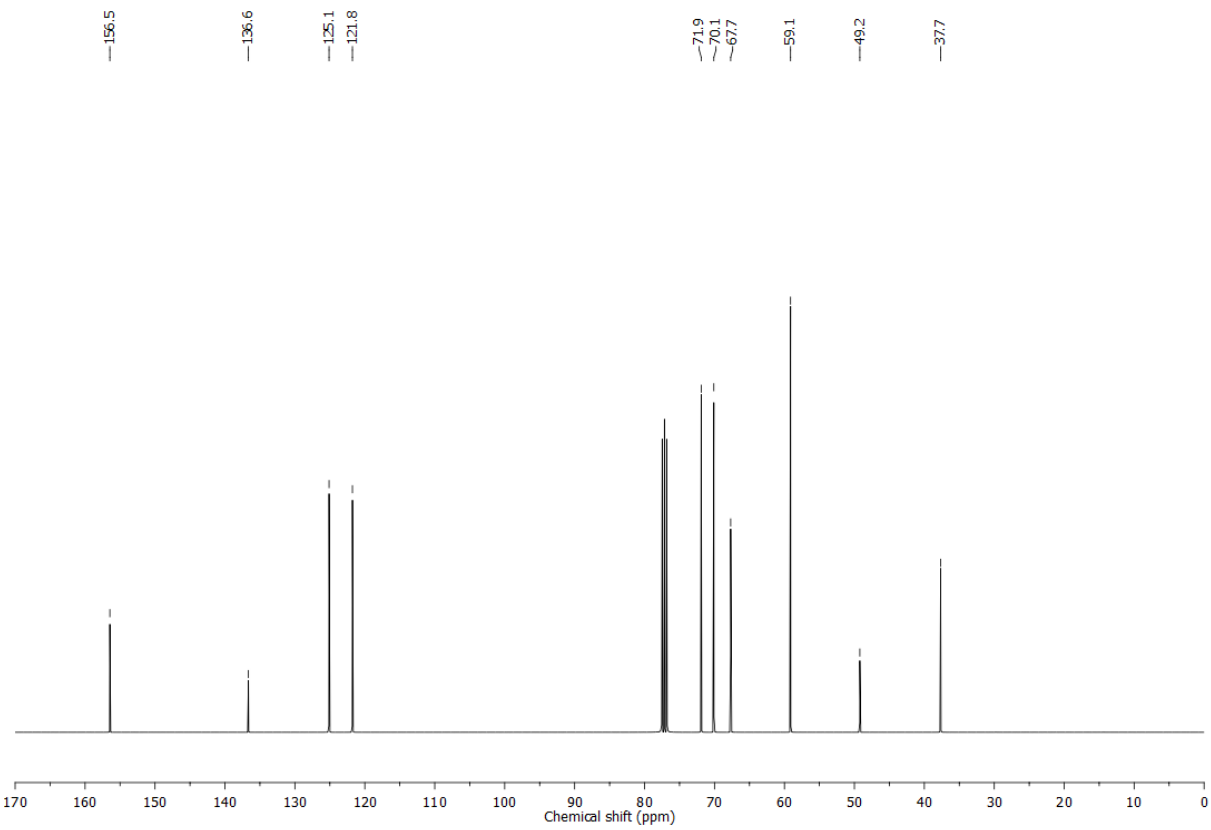
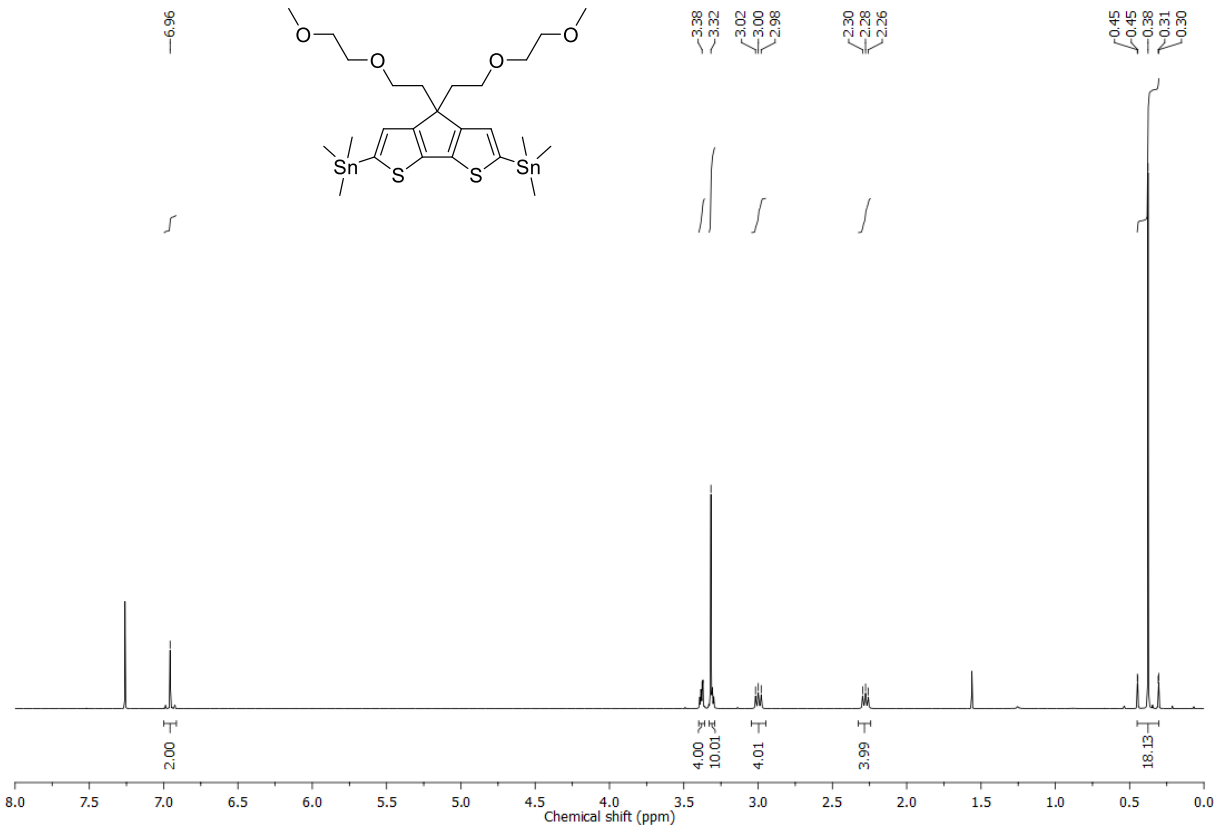
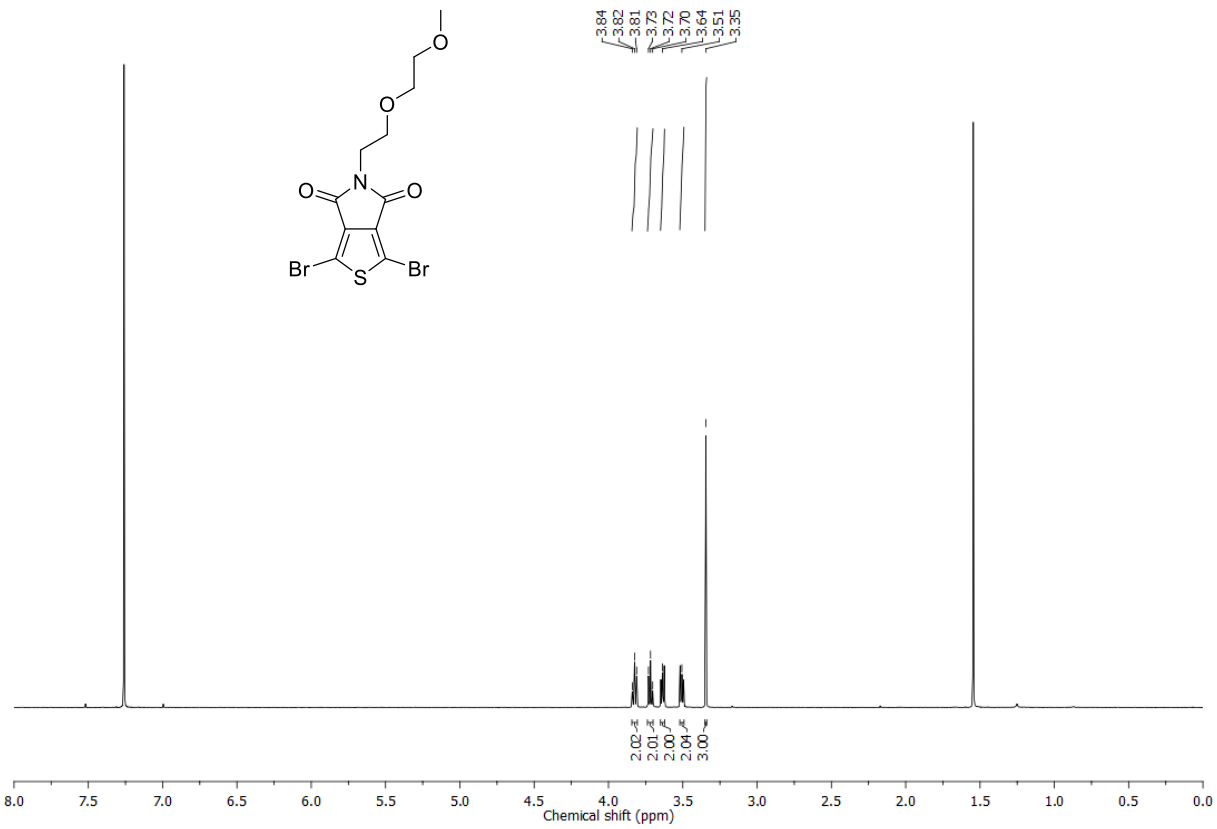


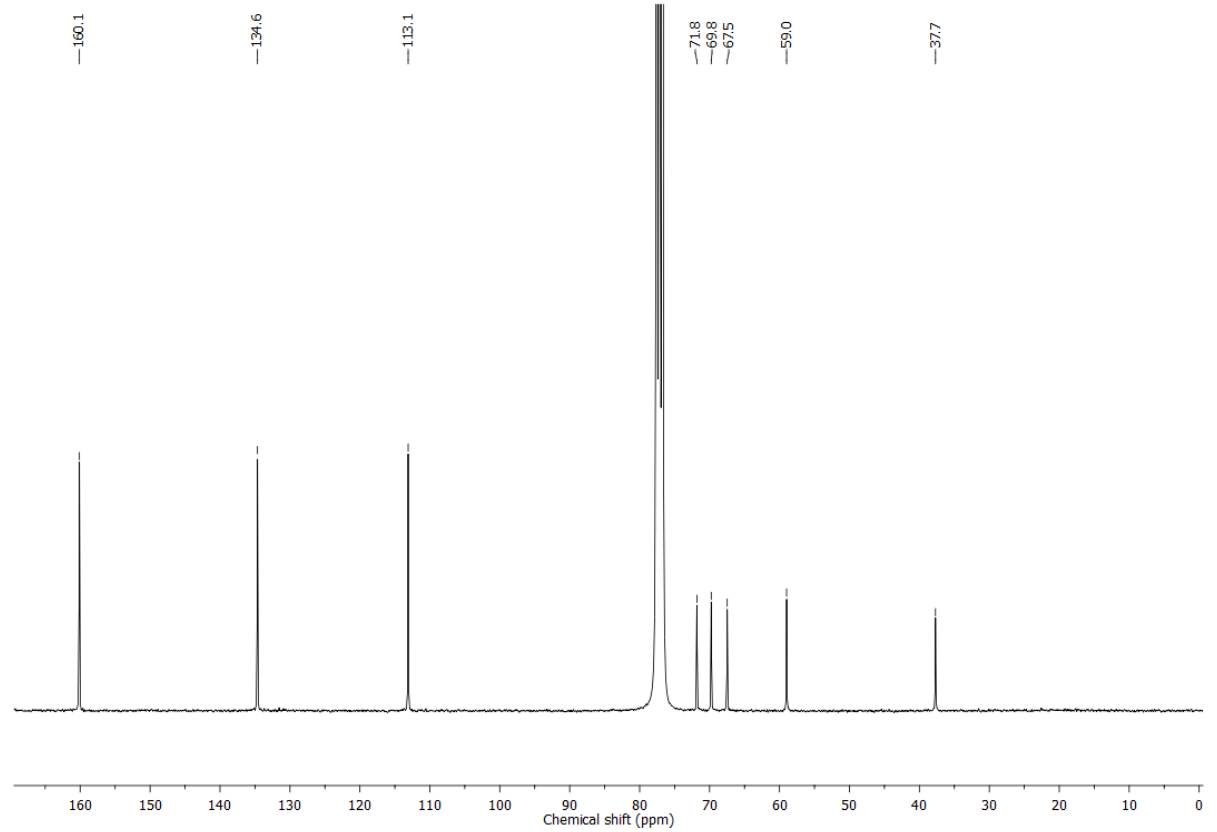


(4,4-bis(2-(2-methoxyethoxy)ethyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (9)



1,3-dibromo-5-(2-(2-methoxyethoxy)ethyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (15)





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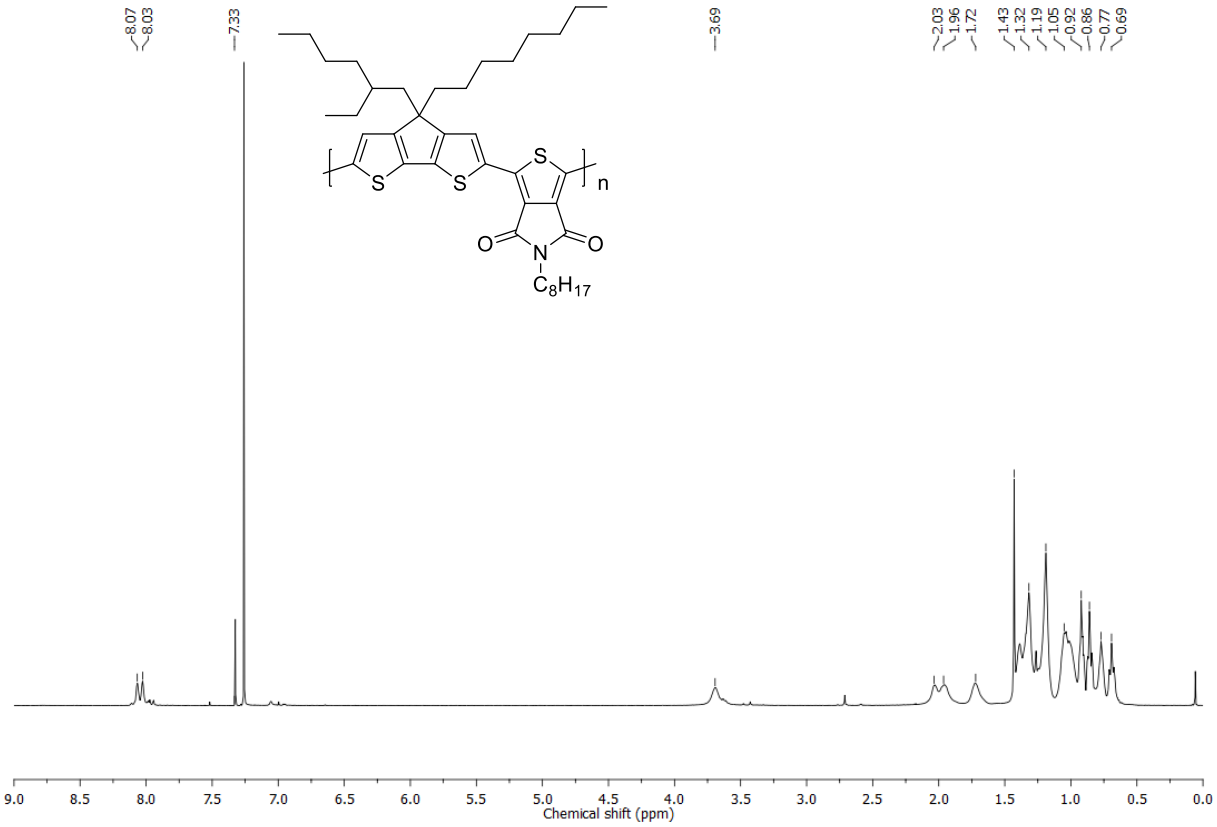
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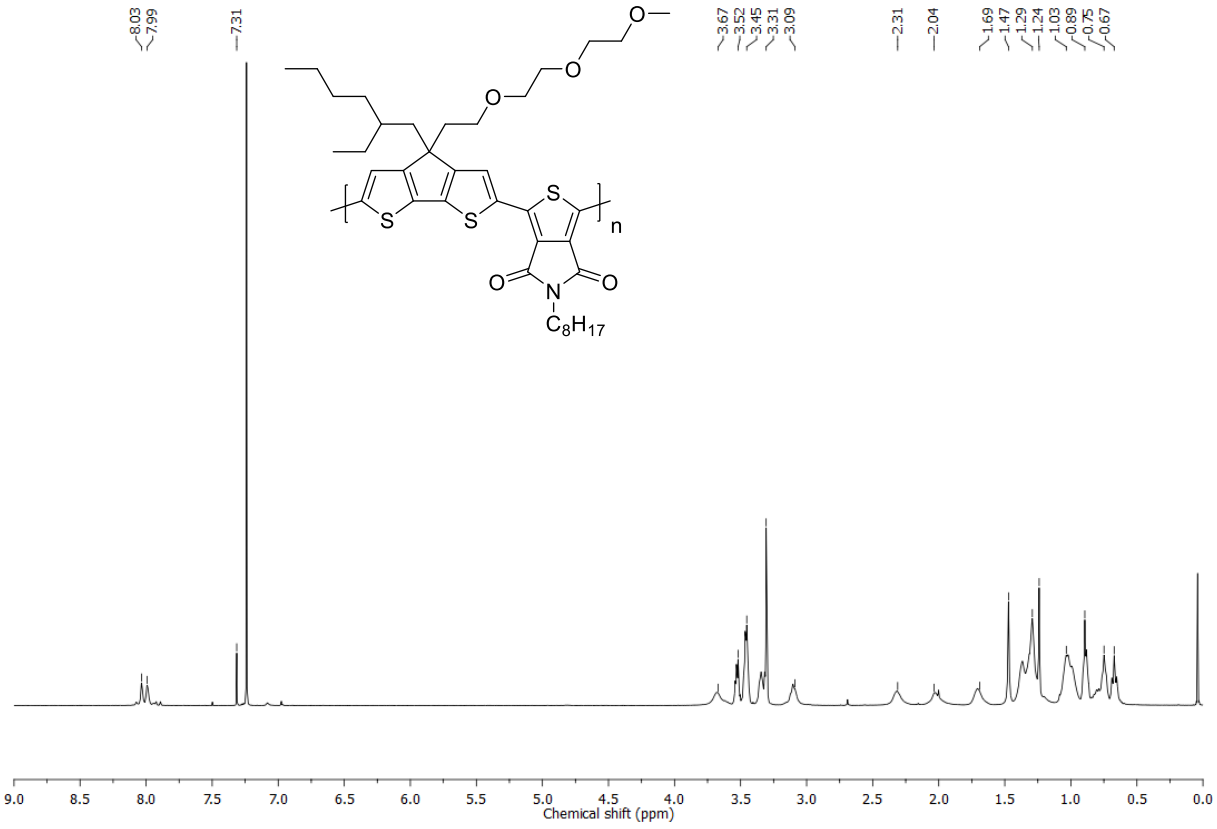
0.86
0.77
0.69
S
S
S
n
O
O
N
C8H17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

P2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3.31
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2.31
2.04
1.69
1.47
1.29
1.24
1.03
0.89
0.75
0.67
O
O
O
S
S
S
n
O
O
N
C8H17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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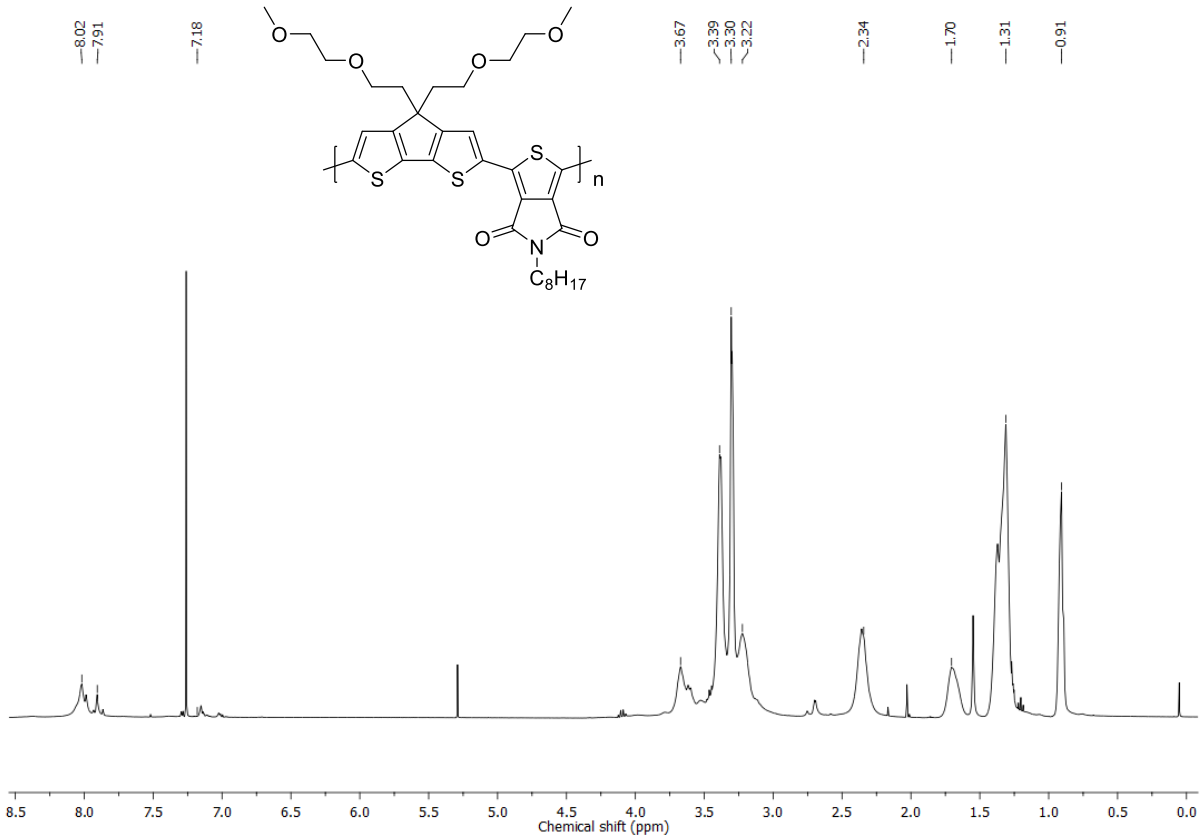
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)

P3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1.31
0.91
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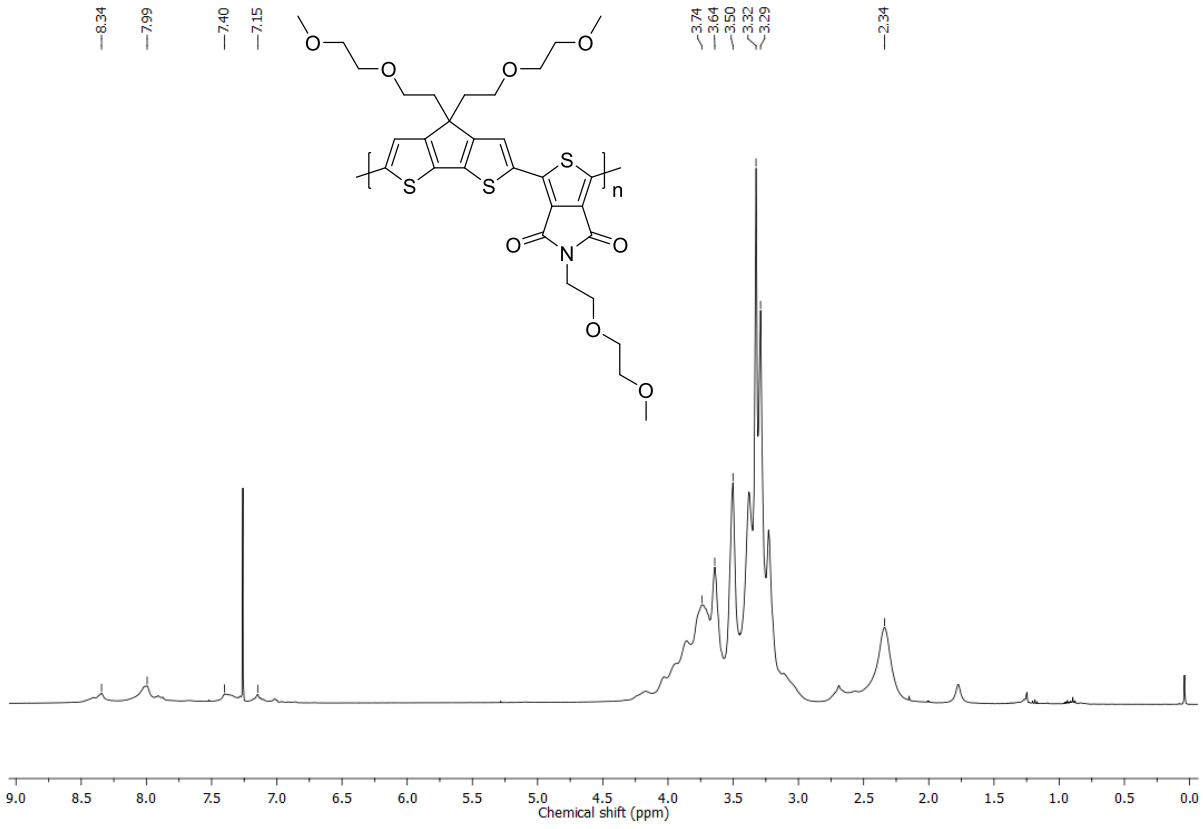
S
n
N
C_8H_{17}
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

P4


8.34
7.99
7.40
7.15
3.74
3.64
3.50
3.32
3.29
2.34
O
S
n
N
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

2. MALDI-TOF analysis

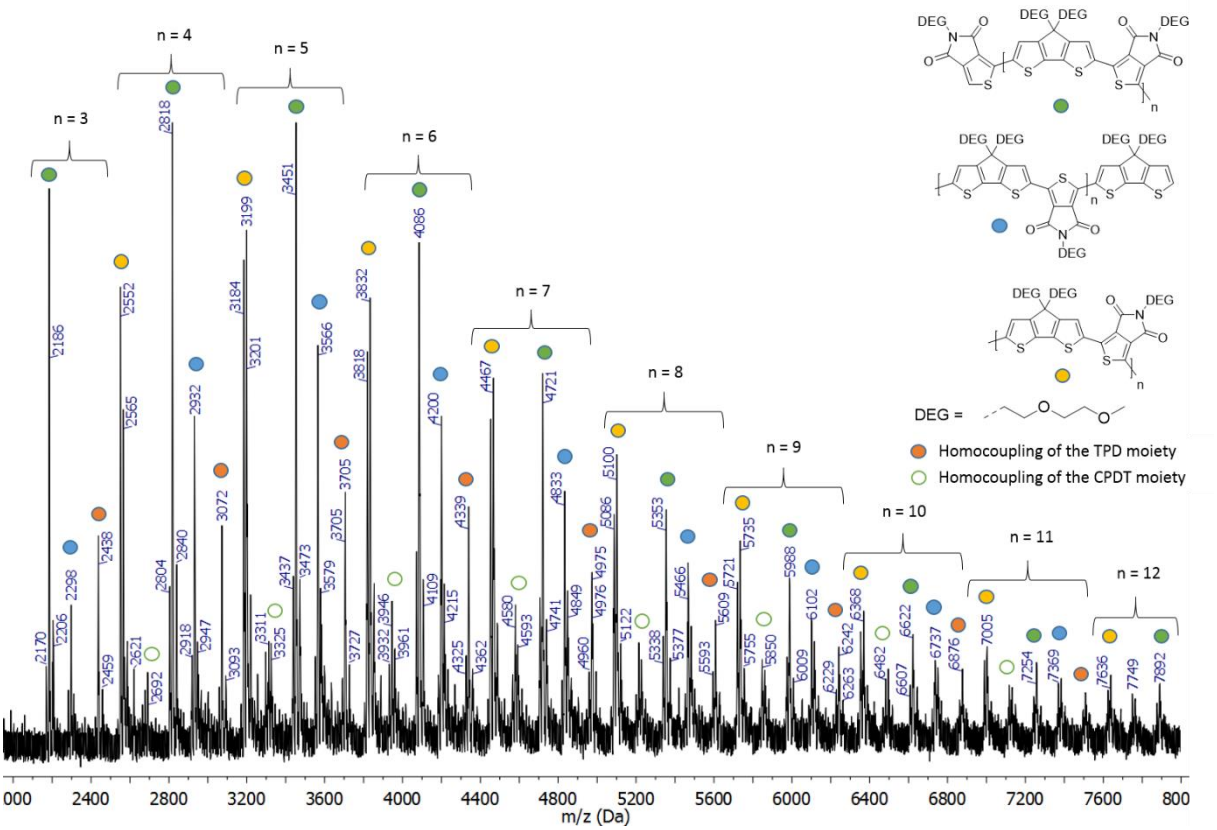


Figure S1. MALDI-TOF mass spectrum of polymer **P4**.

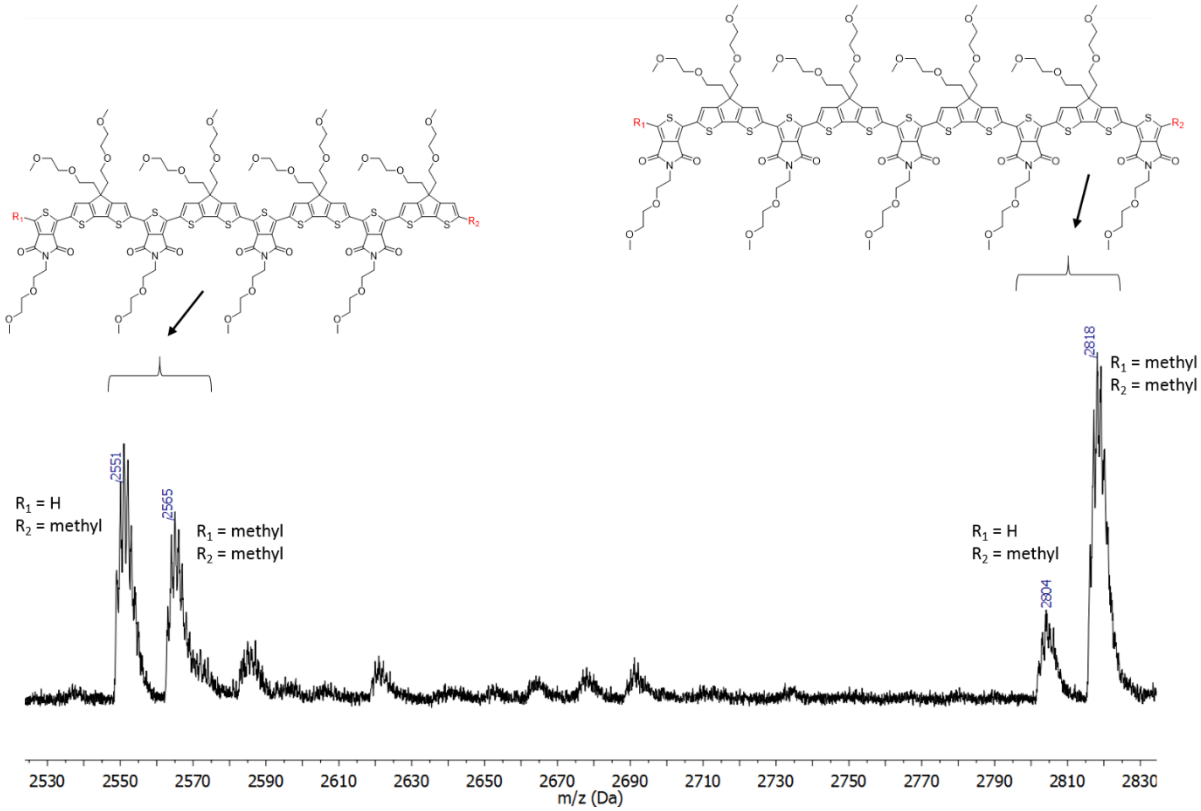


Figure S2. MALDI-TOF mass spectrum of **P4** (zoom from *m/z* 2525 to 2835 g mol^{-1}) with peak assignment and end group identification.

3. Thermal analysis

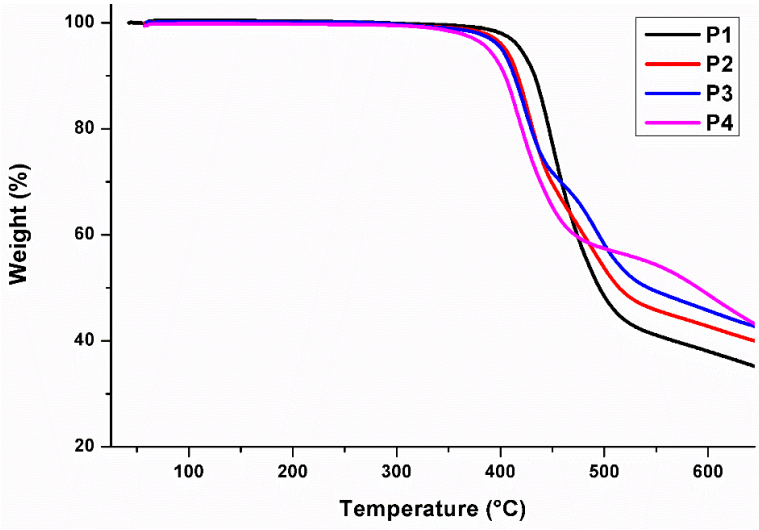


Figure S3. TGA analysis of polymers **P1**–**P4**.

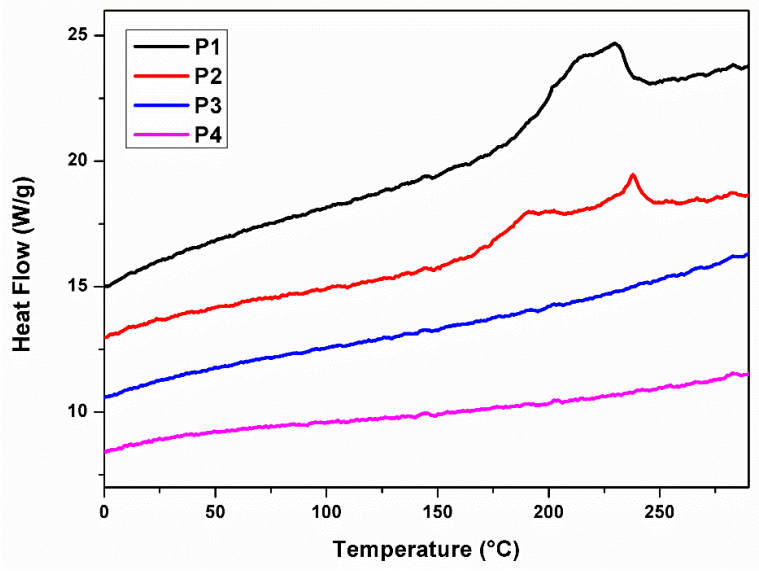


Figure S4. RHC second heating profiles for polymers **P1**–**P4** (heating at 500 K min^{-1} after cooling at 20 K min^{-1}; curves shifted vertically for clarity, endo up).

4. Cyclic voltammetry

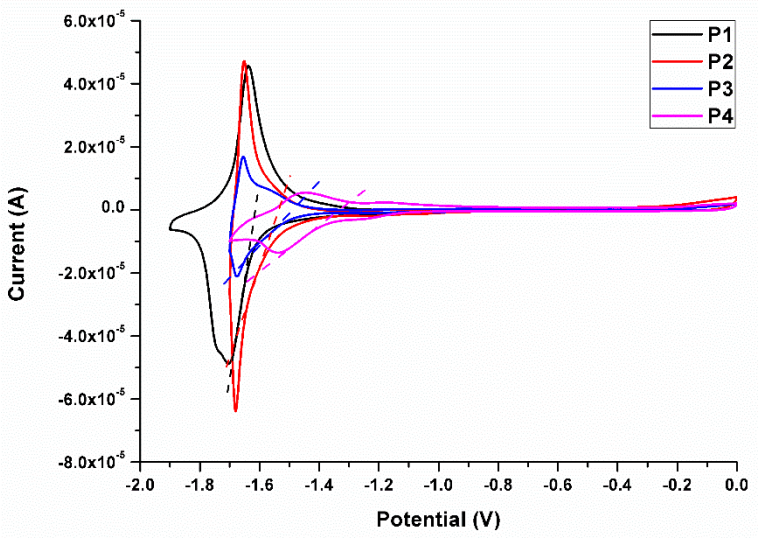


Figure S5. Cyclic voltammograms (reduction) of polymers **P1**–**P4**.

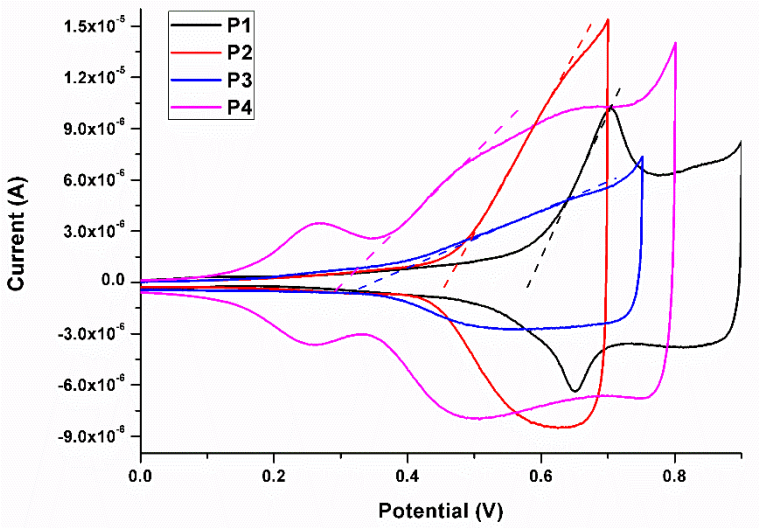


Figure S6. Cyclic voltammograms (oxidation) of polymers **P1**–**P4**.

5. Impedance spectroscopy

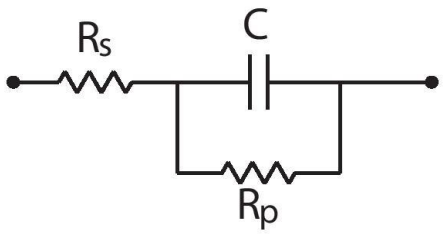
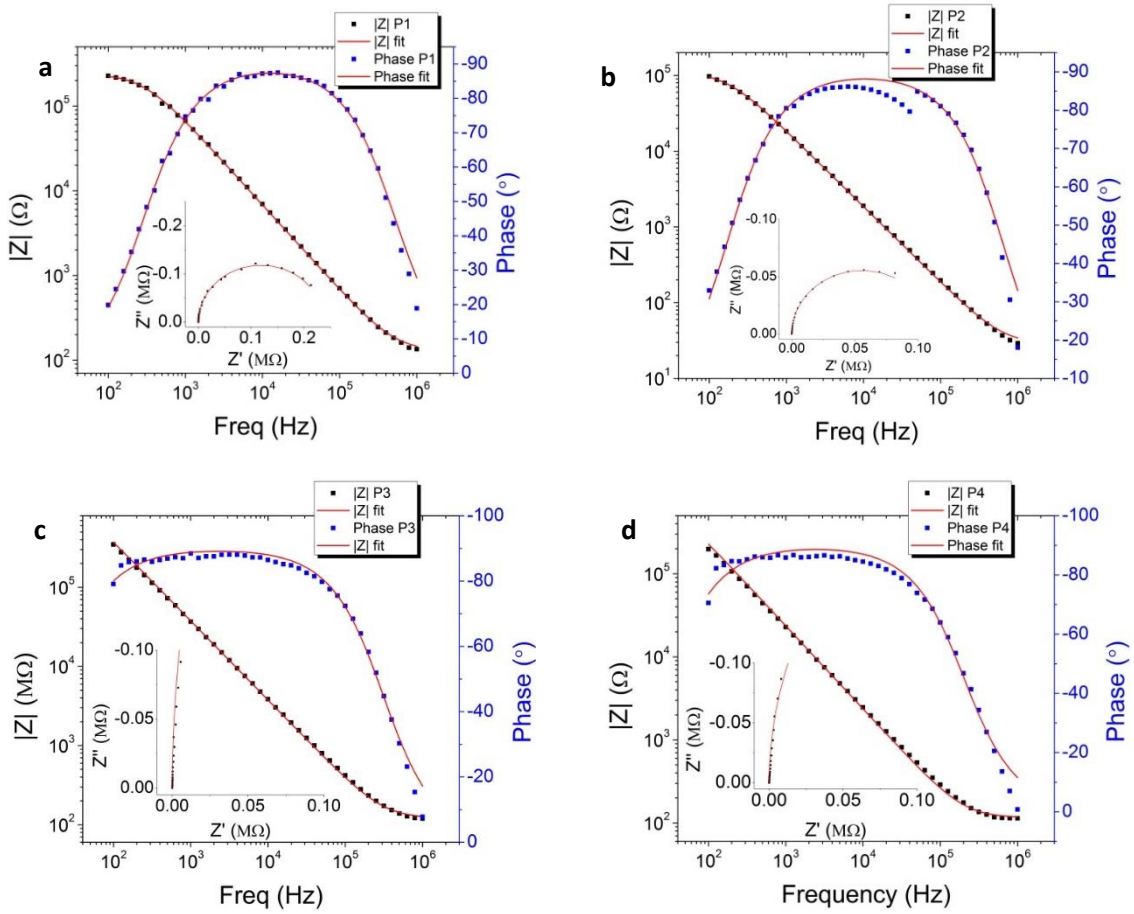


Figure S7. Equivalent circuit used for fitting the impedance data. R_s represents the series resistance (in the range of Ω) due to plate resistance and probe effects. The parallel resistance (R_p, in the range of MΩ) originates from the fact that dielectric materials used within the capacitor are not perfect insulators and allow some amount of current to pass through when the voltage is applied. C represents the ideal capacitor.



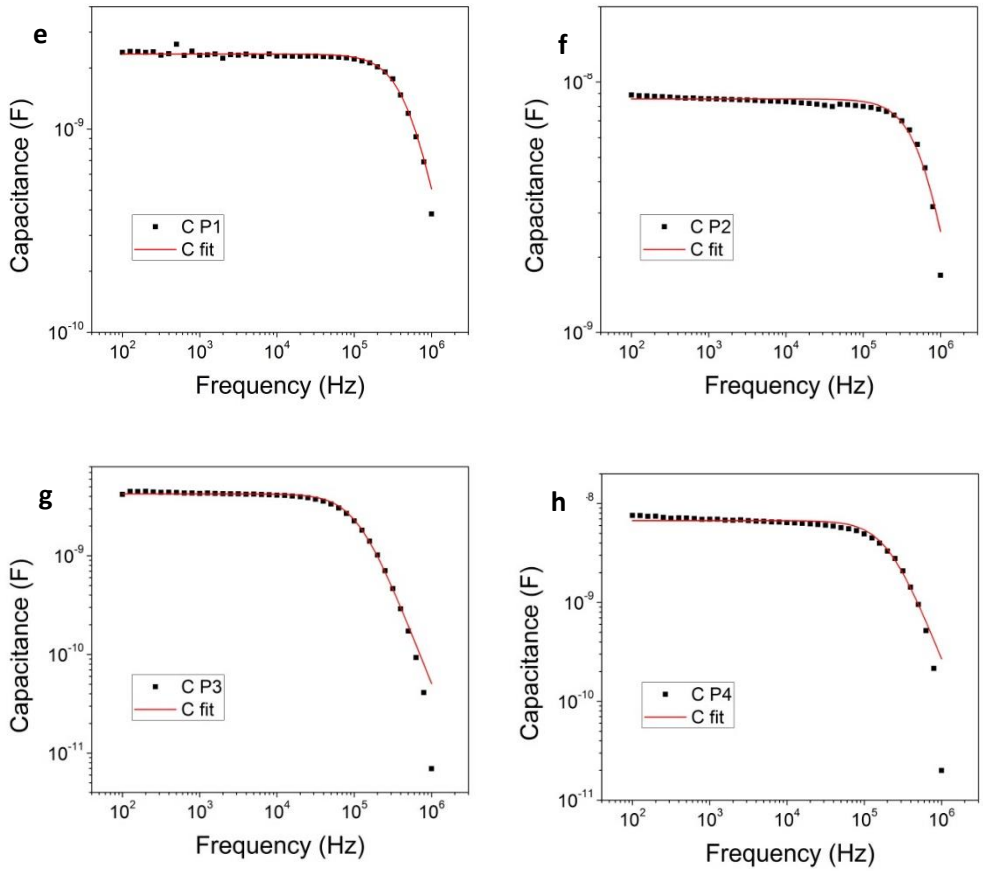
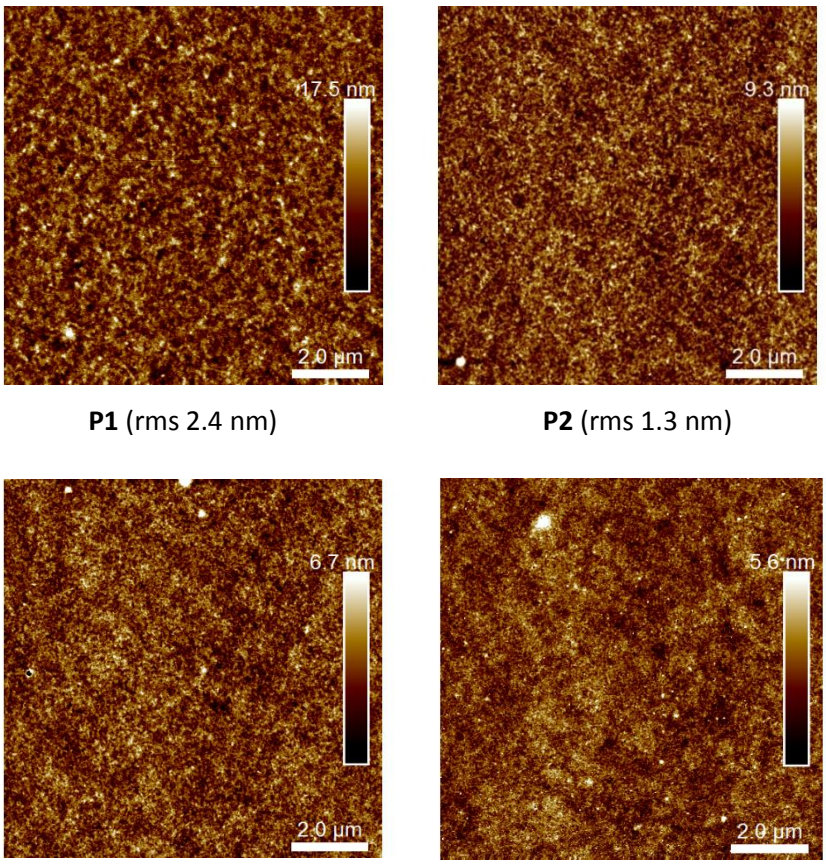


Figure S8. Impedance measurements for polymers **P1**–**P4**. (**a**, **b**, **c**, **d**) The measured data of the magnitude (|Z|, black square) and the phase (blue square) are plotted against the frequency, while the red lines represent the fit over the measured data. In the insets, the Nyquist diagrams of the devices are plotted, showing the behavior of a real capacitor. (**e**, **f**, **g**, **h**) Capacitance plotted over frequency (black squares) and the applied fitting (red line).



P1 (rms 2.4 nm) **P2** (rms 1.3 nm)

P3 (rms 1 nm) **P4** (rms 0.8 nm)

Figure S9. AFM height images of the films applied for the impedance measurements.

6. Solar cell optimization data

Table S1. Most important optimization data of the solar cell devices based on **P1–P4** and [70]PCBM.

Polymer	Solvent[a]	Ratio	Additive[b]	V_{oc} / V	J_{sc} / mA cm^{-2}	FF	Best PCE[c] / %
P1	ODCB	1:2	/	0.82	6.25	0.42	2.13 (1.8)
P1	ODCB	1:2	2% CN	0.84	7.16	0.41	2.44 (2.34)
P1	CB	1:2	2% DIO	0.78	5.93	0.54	2.52 (2.07)
P2	ODCB	1:2	2% CN	0.46	6.73	0.33	1.01 (0.90)
P2	ODCB	1:2	2% DIO	0.72	4.36	0.59	1.85 (1.74)
P2	ODCB	1:2	3% DIO	0.68	4.47	0.59	1.79 (1.60)
P3	CB	1:1.5	/	0.64	4.25	0.44	1.20 (1.12)
P3	CB	1:1.5	2% CN	0.68	10.05	0.54	3.69 (3.62)
P3	CB	1:1.5	2% DIO	0.64	11.02	0.60	4.22 (4.22)
P3	ODCB	1:1.5	4% DIO	0.64	10.99	0.55	3.90 (3.77)
P3	Anisole	1:1.5	/	0.66	4.81	0.48	1.54 (1.48)
P3	Anisole	1:1.5	2% AA	0.66	3.97	0.52	1.36 (1.21)
P4	ODCB	1:2	/	0.64	9.47	0.56	3.40 (3.37)
P4	ODCB	1:2	2% DIO	0.60	11.26	0.51	3.46 (3.43)
P4	ODCB	1:2	2% CN	0.62	11.17	0.50	3.49 (3.32)
P4	Anisole	1:2	/	0.62	4.35	0.49	1.32 (1.30)

[a] CB = chlorobenzene, ODCB = *ortho*-dichlorobenzene. [b] CN = 1-chloronaphthalene, DIO = 1,8-diiodooctane, AA = *p*-anisaldehyde. [c] Average efficiencies over at least 3 devices in brackets.