

Supporting Information

Electron-beam lithography of cinnamate polythiophene films: Conductive nanorods for electronic applications

N. Maximilian Bojanowski,^a Christian Huck,^{b,c} Lisa Veith,^b Karl-Philipp Strunk,^d Rainer Bäuerle,^{a,d} Christian Melzer,^d Jan Freudenberg,^a Irene Wacker,^b Rasmus R. Schröder,^b Petra Tegeder,^{b,c} Uwe H. F. Bunz^{a,b}*

a. Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg,

b. Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225, 69120 Heidelberg.

c. Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg

d. InnovationLab GmbH, Speyerer Straße 4, 69115 Heidelberg, Germany,
E-mail: uwe.bunz@oci.uni-heidelberg.de

Table of Content

1. General information.....	2
2. Synthetic and experimental procedures	4
3. Additional spectra.....	8
4. Film retention	10
5. Additional scanning electron micrographs	11
6. Conductivity measurements and transistor characteristics	14
7. XPS and UPS spectra	17
8. References	18
9. NMR spectra.....	19

1. General information

For experiments conducted under an atmosphere of nitrogen, standard Schlenk and glovebox (Unilab-2000, MBRAUN) techniques were used. The addition of solvents or reagents was carried out using nitrogen flushed stainless steel cannulas and plastic syringes. THF was dried over sodium and freshly distilled before use. P3HT (LOT = M107, $M_w = 2.4 \times 10^4$ g/mol) was purchased from Ossila Ltd. For spectroscopic and analytic characterizations, the following devices were used:

^1H NMR spectra were recorded at room temperature on the following spectrometers: Bruker AC-300 (300.51 MHz), Bruker Avance 500 (500.13 MHz) or Bruker Avance 600 (600.25 MHz). Chemical shifts (δ) were measured relatively to the shift of residual protons in deuterated solvents or relatively to an internal standard and values are given in parts per million (ppm). Coupling constants (J) are stated in Hertz (Hz). Signal patterns are noted according to usual conventions (s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, sext=sextet, dd=doublet of doublet, dt=doublet of triplet, ddd=doublet of doublet of doublet, etc., br. s=broad signal, m=multiplet).

^{13}C NMR spectra were recorded at room temperature on the following spectrometers: Bruker Avance 300 (75.48 MHz), Bruker Avance 500 (125.76 MHz) or Bruker Avance III (150.93 MHz). Chemical shifts (δ) were measured relatively to the solvent signals or relatively to an internal standard and values are given in parts per million (ppm). ^{13}C NMR spectra were collected using proton decoupling algorithms.

High resolution mass spectra (HR-MS) were either recorded on a Bruker ApexQe hybrid 9.4 T FT-ICR-MS (ESI+, DART+), a Finnigan LCQ (ESI+) or a JEOL JMS-700 (EI+) mass spectrometer at the Institute of Organic Chemistry of Heidelberg University.

Elemental analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario Micro Cube.

Analytical gel permeation chromatography (GPC) was performed using a JASCO PU 2080 HPLC pump equipped with three different commercially available Polymer Standards Service (PSS) cross-linked poly(styrene) columns (5 μm particle size, $L \times \text{I.D.}$ 30 cm \times 8 mm) in line. The consecutive exclusion sizes were 100 \AA , 1000 \AA , and 100000 \AA respectively. For detection a JASCO UV-2075 Plus detector and a JASCO RI-2031 detector were used. The column was operated with chloroform as eluent and a flow rate of 1.0 mL/s.

UV/VIS spectra were recorded on a Jasco UV-VIS V-660 or Jasco UV-VIS V-670 and processed with the software JASCO Spectra ManagerTM II.

Scanning electron microscopy (SEM) images: The surface of the sample (silicon wafer with gold contacts) was electrically connected to the SEM carrier using sticky copper tape and silver paint. Samples were imaged without further coating to allow direct imaging of the materials and correlation of secondary electron yield (contrast variations) with materials properties such as work function. Images were recorded in a Crossbeam 540 (Carl Zeiss Microscopy, Oberkochen, Germany) at 1.5 keV landing energy using low probe current.

Atomic force microscopy (AFM) was carried out on a Bruker Nanoscope MultiMode VIII in the ScanAsyst PeakForce mode. The resulting images were treated with the software Gwyddion for row alignment and scar correction.

Conductivity measurements were carried out as 2-point measurements.

2. Synthetic and experimental procedures

Synthesis and characterization: 2-(2,5-Dibromothiophen-3-yl)ethan-1-ol (1.12 g, 3.92 mmol, 1 eq.) and triethylamine (TEA, 475 mg, 4.7 mmol, 1.2 eq.) were dissolved in dry DCM (10 mL) under nitrogen atmosphere and added to a flask containing cinnamon acid chloride (1.30 g, 7.83 mmol, 2 eq.). The mixture was stirred for 24 h, extracted with diethyl ether (2x 20 mL) and washed with water (50 mL). The solvent was removed in vacuo and the residue subjected to flash chromatography (SiO₂, petroleum ether/ethyl acetate 10:1). The solvent was removed in vacuo to give the title compound as a pale-yellow solid. The crude product was recrystallized in DCM to afford white crystals of **3** (1.35 g, 84%). Mp (dec.) > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.72 (d, *J*=16.1 Hz, 1 H), 7.51 - 7.60 (m, 2 H), 7.33 - 7.47 (m, 3 H), 6.91 (s, 1 H), 6.45 (d, *J*=16.1 Hz, 1 H), 4.38 (t, *J*=6.7 Hz, 2 H), 2.98 (t, *J*=6.7 Hz, 2 H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 166.7, 145.2, 138.4, 134.3, 131.1, 130.4, 128.9, 128.1, 117.8, 110.9, 63.0, 29.1 ppm. HR-MS (ESI+) *m/z*: [M+Na]⁺ calcd. for C₁₅H₁₂Br₂O₂SNa 438.8802; found 438.8797. Elem. anal. calcd. for C₁₅H₁₂Br₂O₂S: C 43.30 H 2.91; found C 43.19, H 3.14.

2-(2,5-Dibromothiophen-3-yl)ethyl cinnamate **3** (156 mg, 375 μmol, 1 eq.) was dissolved in dry THF (8 mL) and cooled to 0 °C under argon atmosphere. *i*PrMgCl (2 M in THF, 190 μL, 375 μmol, 1 eq.) was added dropwise and stirring was maintained for 1 h at 0 °C. The solution was warmed to room temperature and Ni(dppp)Cl₂ (1.00 mg, 1.87 μmol, 1 mol%) was added. The reaction was stirred under argon at 60 °C for 3 h. Saturated aqueous solutions of NH₄Cl and CHCl₃ were added, the aqueous layer was separated and extracted with CHCl₃ (3x 20 mL). The combined organic layers were dried over MgSO₄, filtered, and the filtrate concentrated *in vacuo*. The crude product purified by twofold precipitation via dissolution in a small amount of CHCl₃ and subsequent addition to methanol to afford the title compound as an orange solid.

After Soxhlet extraction (methanol, hexane, DCM and chloroform), the chloroform fraction was precipitated into methanol to afford **P3ZT** as a deep purple-golden solid (75.0 mg, 75%). M.p. 178 °C, dec. > 300 °C. The M_w was estimated to be 1.7×10^4 g/mol with a PDI of 1.74. ^1H NMR (500 MHz, CDCl_3): $\delta =$ ^1H NMR (300 MHz, CDCl_3) $\delta = 7.60 - 7.74$ (m, 1 H), 7.48 (br s, 2 H), 7.35 (br s, 3 H), 7.14 (br s, 1 H), 6.32 - 6.49 (m, 1 H), 4.30 - 4.60 (m, 2 H), 3.13 - 3.27 (m, 1 H), 2.90 - 3.12 (m, 1 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): $\delta = 166.8, 145.1, 135.3, 134.3, 133.7, 132.4, 130.3, 129.3, 128.9, 128.1, 117.9, 63.9, 28.8$ ppm.



Figure S1. Picture of **P3ZT** under daylight.

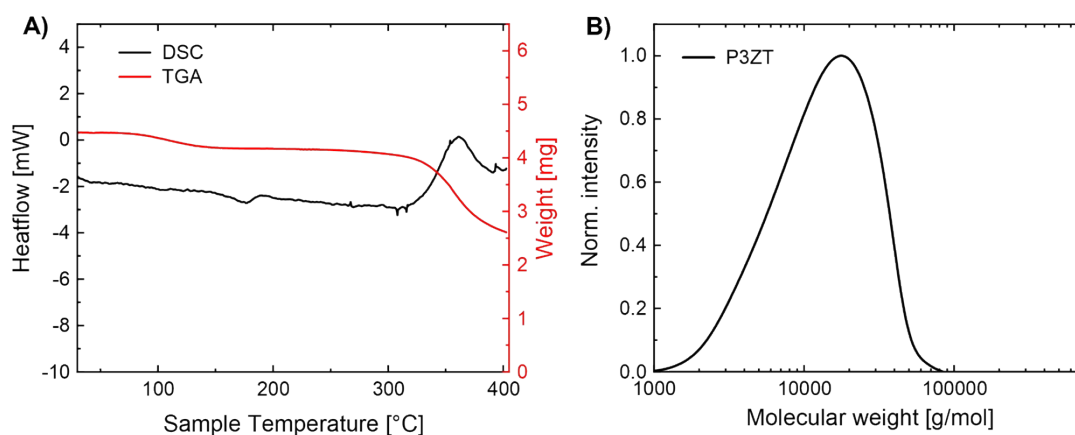


Figure S2. **A)** TGA and DSC and **B)** molecular weight distribution of **P3ZT**. Initial decrease in weight at 100 °C is attributed to solvent evaporation. DSC indicates a melting point at 178 °C.

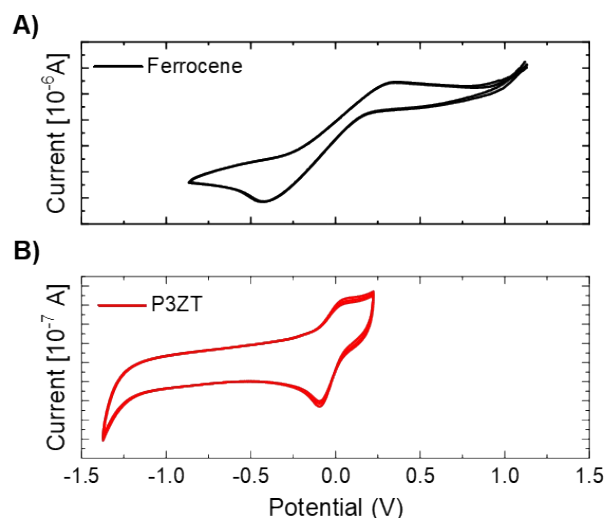


Figure S3. Cyclic voltammetry of **P3ZT** against an external standard (ferrocene) in THF.

Sample fabrication:

All wafers were successively cleaned via ultra-sonication in acetone, isopropanol, washed with water and dried in a stream of nitrogen:

- a) undoped silicone wafers for IR transmission measurements
- b) end-of-line substrates with 90 nm thermally grown SiO₂ and prefabricated Au contact pads
- c) highly-doped silicon wafer with 100 nm thick thermally grown oxide for transistor applications

The undoped silicone wafer and the end-of-line substrate were cleaned via oxygen plasma prior to use. The highly doped silicon wafer was placed in Caro's acid and was heated to 100 °C for 20 min. After cleaning with water and drying, a 150 mM solution of Al(NO₃)₃ · 9 H₂O in ethanol was spin-coated (5000 rpm; 40 s) onto the substrate. The wafer was directly heated to 300 °C for 30 min. For the formation of the self-assembled monolayer, the substrate was placed in a 15.0 mM solution of 12-cyclohexyldodecylphosphonic acid (CDPA) in isopropanol at room temperature for 16 h. Then the substrate was cleaned via ultra-sonication in isopropanol for 10 min, rinsed with water and dried in a stream of nitrogen. The capacitance of the dielectric layer amounted to 26 nF cm⁻².

P3ZT was spin coated on cleaned wafers from filtered solutions (10 mg/mL in chloroform) at 1000 rpm inside a nitrogen filled glovebox. Film thicknesses were measured using a Bruker DekTak XT profilometer.

UV crosslinking was done inside a nitrogen filled glovebox using a $\lambda = 254$ nm 15 W tube lamp from Herolab.

EBL: Spin-coated layers were nanopatterned using a Raith eLINE Plus nanofabrication system. Electrons with an energy of 15 keV and a beam current of 340 pA were used to structure the sample. Undoped silicon was used to enable the IR measurement. Squares (50x50 μm , used for IR transmission microscopy) as well as the USAF 1951 target (groups 10-15) were written on the sample with exposure doses ranging from 400 to 5000 $\mu\text{C}/\text{cm}^2$. Contact pads of the transistor structure were written with an exposure dose of 1500 $\mu\text{C}/\text{cm}^2$ and finger structures were additionally stitched to contact pads with an exposure dose of 2500 $\mu\text{C}/\text{cm}^2$. After exposure, unexposed material was removed by development in chloroform under ambient conditions.

IR transmission microscopy of films required a transparent (undoped) silicon wafer as a substrate. Large-area samples irradiated with UV light (254 nm) were measured using a FTIR spectrometer (Bruker IFS 66v/s). Samples were illuminated by unpolarized light emitted from a thermal light source. Transmitted light was collected with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The whole beam path was evacuated to avoid atmospheric water and carbon dioxide absorption. Spectra were recorded with a resolution of 4 cm^{-1} and 200 scans. The transmittance of the layer was normalized to that of the bare substrate to get the relative transmittance spectra. Small-area samples produced by EBL were characterized using a Bruker Tensor 27 spectrometer coupled to a Hyperion 1000 IR microscope. Light was focused onto the sample and collected using two 36x reverse Cassegrain objectives. The whole beam path was purged with dried air to avoid atmospheric water and carbon dioxide absorption. Exposed layers were located using white light microscopy and centered in the IR beam whose

extent was specified by a circular aperture with a diameter of 50 μm . Spectra were recorded with a resolution of 2 cm^{-1} and at least 2000 scans.

Doping process and transistor fabrication:

The resulting nanorods were sequentially doped via spin-coating of a FeCl_3 solution in DMF (1 mg/mL) according to literature.¹ The doped structures were washed with acetonitrile after doping. **TIPS-Pen** was spin-coated from 10 mg/mL in toluene at 1000 rpm.

Devices were measured inside a nitrogen-filled glovebox using a commercially probe card station with a Keithly 4200-SCS parameter analyzer.

3. Additional spectra

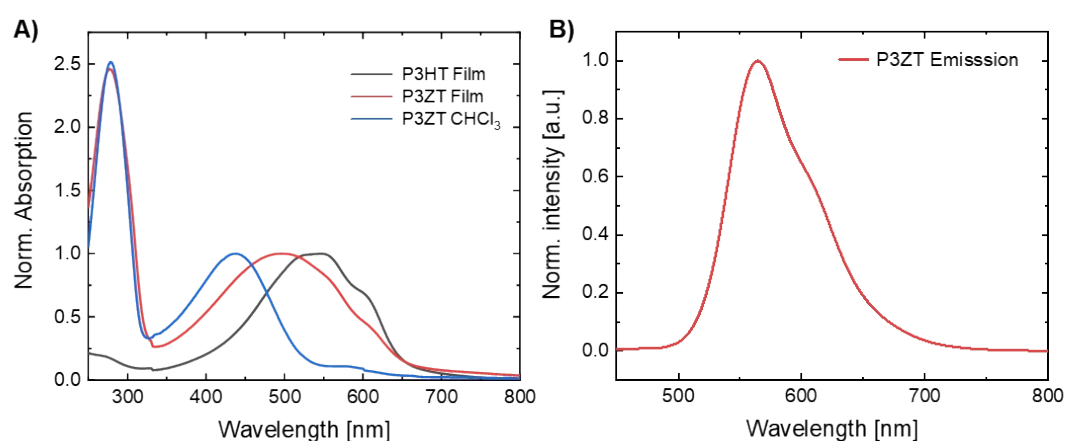


Figure S4. A) Normalized absorption spectra of **P3ZT** film and solution and **P3HT** film and B) emission spectra of **P3ZT** in solution (CHCl_3).

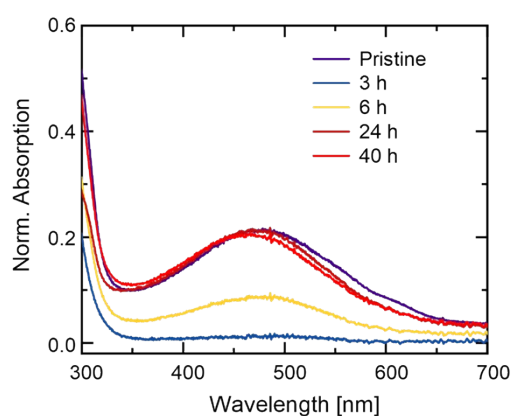


Figure S5. Absorption spectra after UV irradiation for prolonged times at 254 nm.

Complete set of IR spectra:

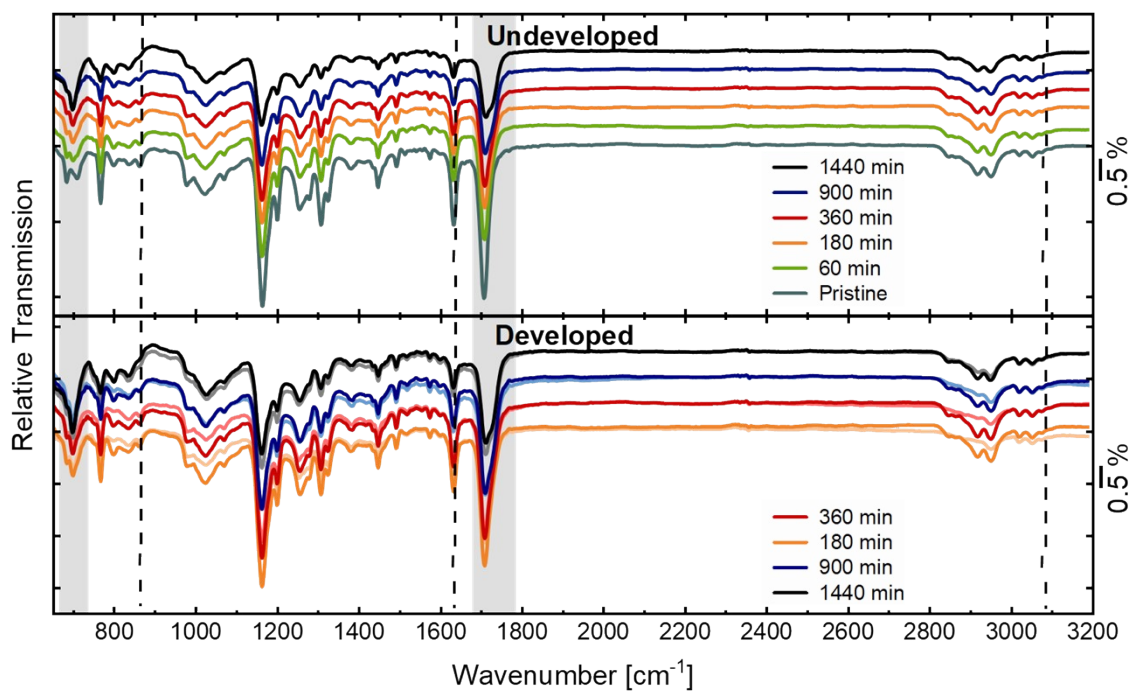


Figure S6. Complete set of IR spectra for cross-linking of **P3ZT** through UV light radiation. Comparing the transmission spectra before and after development as indicated by the dotted lines, reveals minimal loss of material further proving a complete desolubilization.

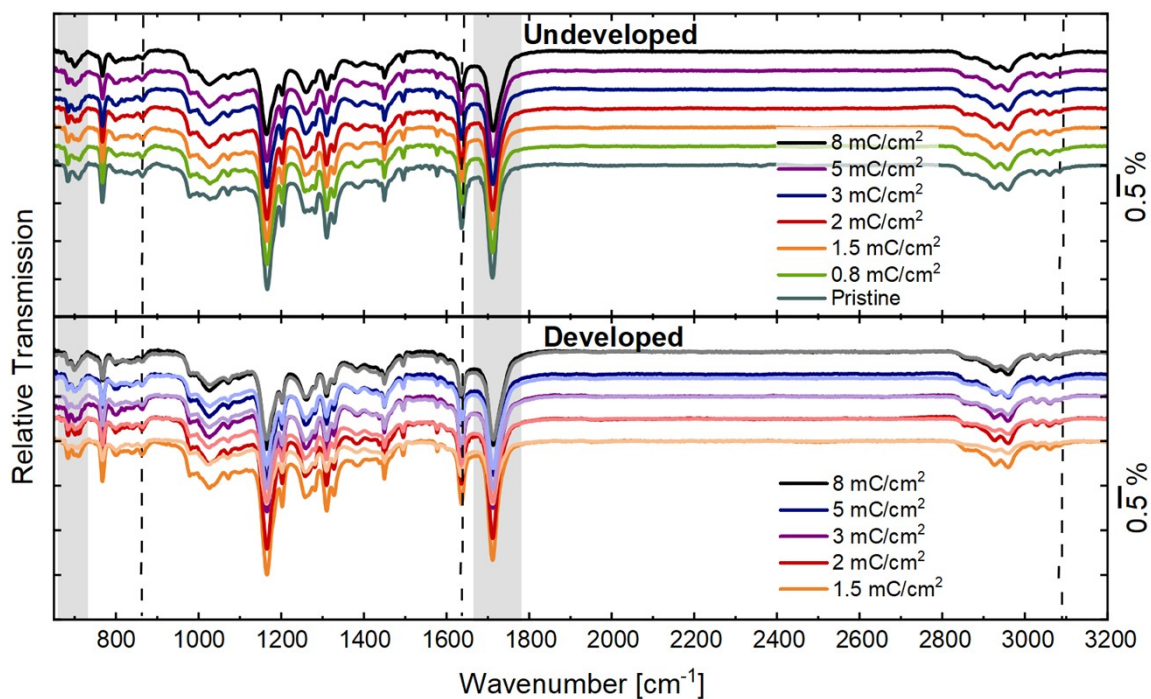


Figure S7. Complete set of IR spectra for cross-linking of **P3ZT** through electron beam radiation.

4. Film retention

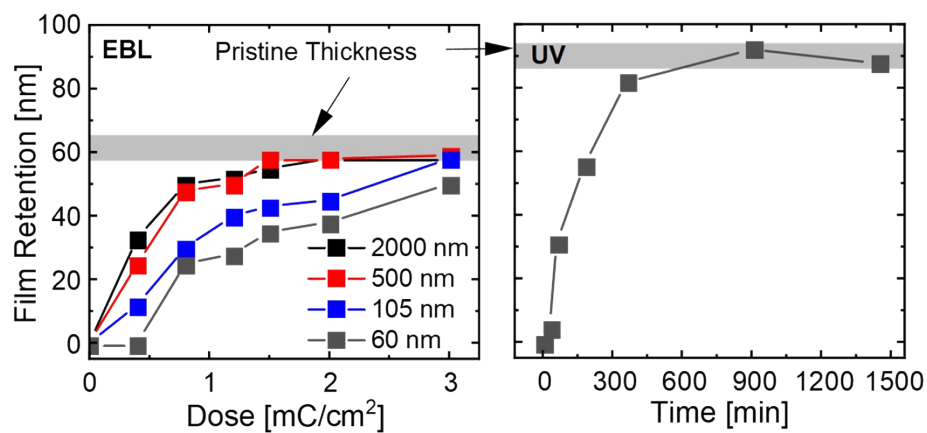


Figure S8. Film retention curve (film thickness after development) for cross-linking of **P3ZT** through EBL irradiation (left) and UV radiation (right). EBL was done at 10 keV where the thickness was measured at structures of different horizontal extent (smallest dimension given).

5. Additional scanning electron micrographs

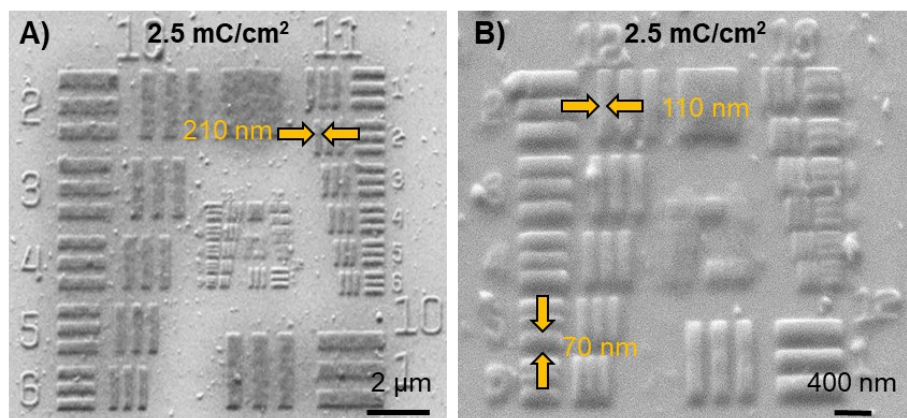


Figure S9. A) SEM images of a structure written at 2.5 mC/cm². B) The 12-5 group in the bottom left of the SEM still exhibits trenches between the bars of nominal width of 68 nm. Starting with group 13-1 (top right, nominal width 61 nm) the trenches start to disappear.

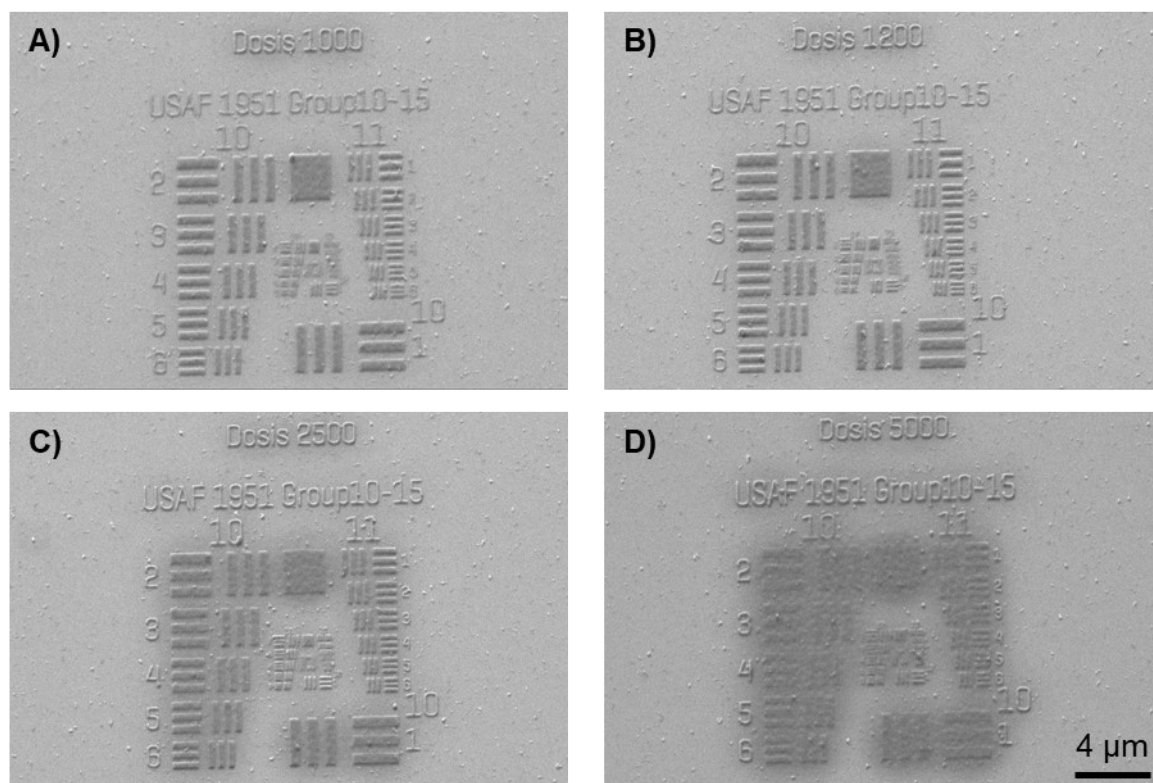


Figure S10. SEM images (SESI Detector) of structures of P3ZT written at A) 1.0 mC/cm², B) 1.2 mC/cm², C) 2.5 mC/cm², and D) 5.0 mC/cm². An over exposure is apparent at highest dose.

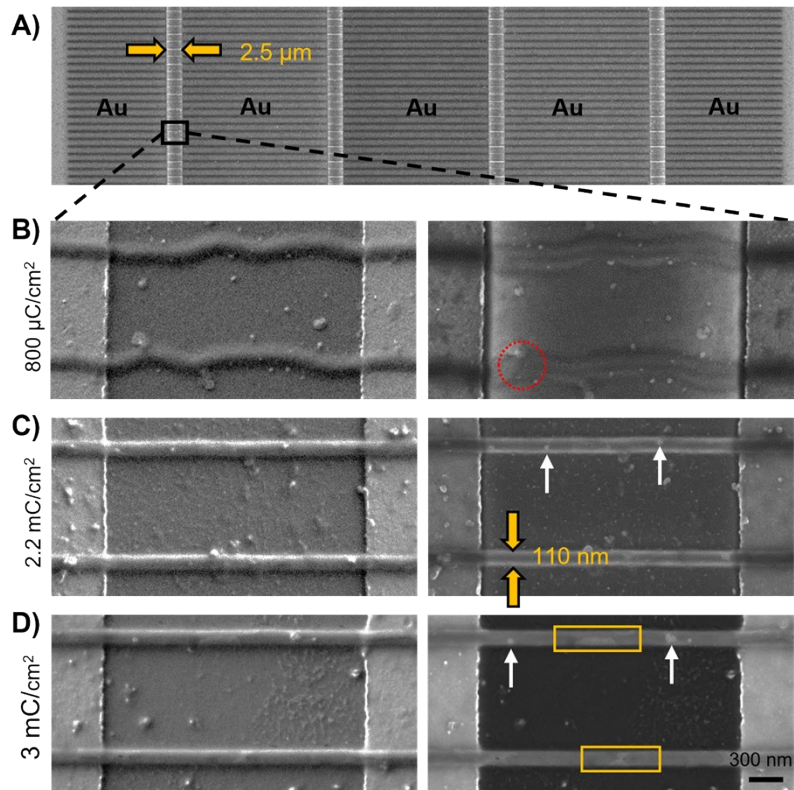


Figure S11. EBL nanostructured **P3ZT** on pre-patterned end-of-line substrates as seen in secondary electron SEM images. **A)** Overview image of parallel lines across multiple gold contacts. **B-D)** Magnified section of individual lines written by different EBL electron dose (0.8 to 3 mC/cm²). Left side: SESI detector, right side: In-lens detector. While the SESI detector is largely sensitive to topology (note the 3D effect in the images) the In-lens detector contrast reflects the yield of secondary electrons, which can be attributed to the work function. In **B)** interruptions of the lines are visible (red circle). In **D)** variations of contrast along the lines are visible (orange rectangles), which are different from the variations due to contamination (white arrows)

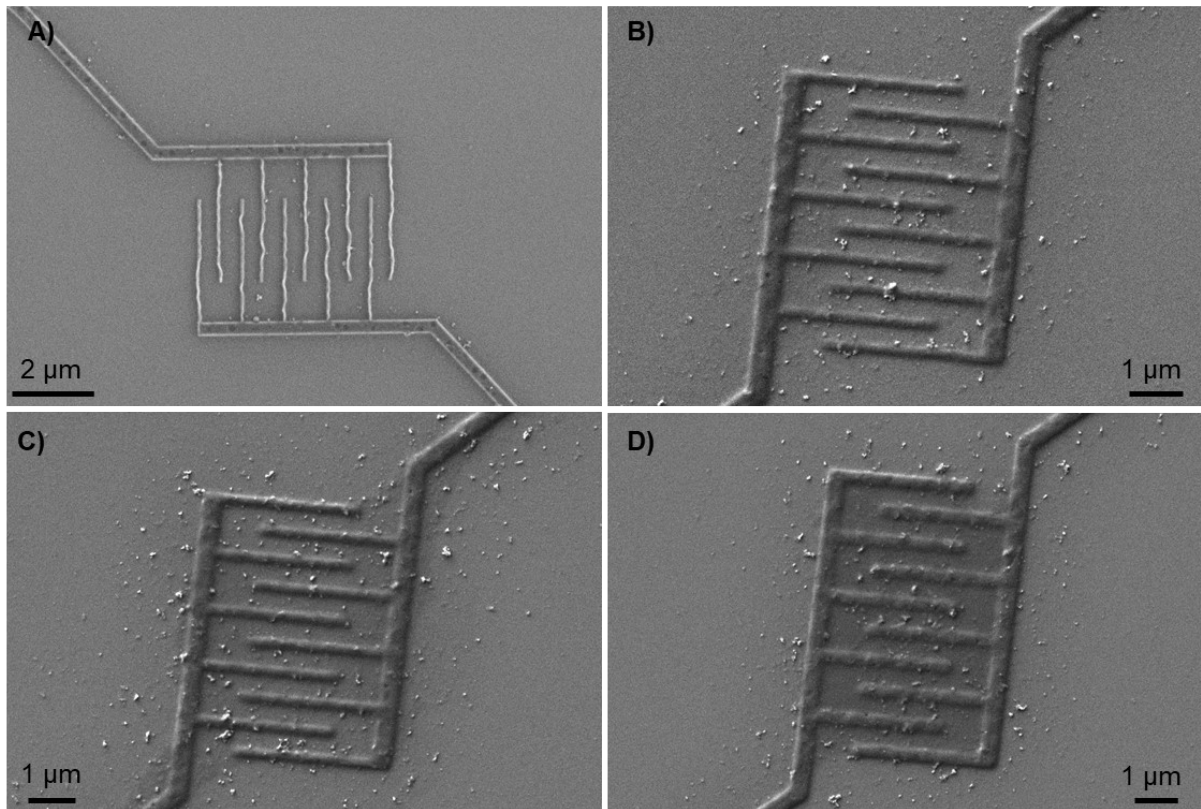


Figure S12. EBL nanostructured **P3ZT** towards a nanotransistor for different sizes of finger structure: A = 20 nm, B = 50 nm, C = 100 nm and D = 200 nm. The channel length L (500 nm) and width W (2.5 μm) are designed to be constant (see Table S1).

Table S1. Theoretical dimensions of the nanotransistor ($L_{\text{theor.}} = 500$ nm) and those determined by SEM imaging.

Contact size (theo.) [nm]	Contact size (meas.) [nm]	Channel length (meas.) [nm]
20*	70 ± 5	400 ± 10
50	210 ± 10	350 ± 10
100	180 ± 20	410 ± 5
200 [§]	220 ± 10	450

* Lines are inhomogeneous. [§] Overexposed structures.

6. Conductivity measurements and transistor characteristics

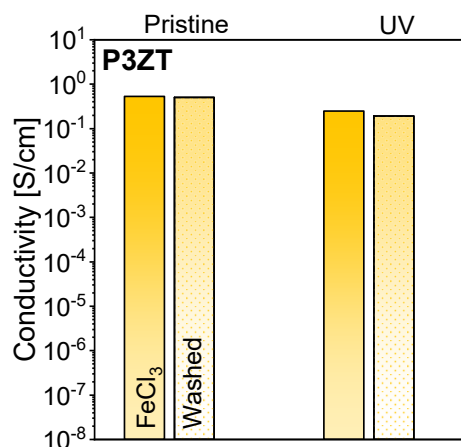


Figure S13. Conductivity of pristine and UV-crosslinked films of P3ZT. After doping with FeCl₃ the sample was washed.

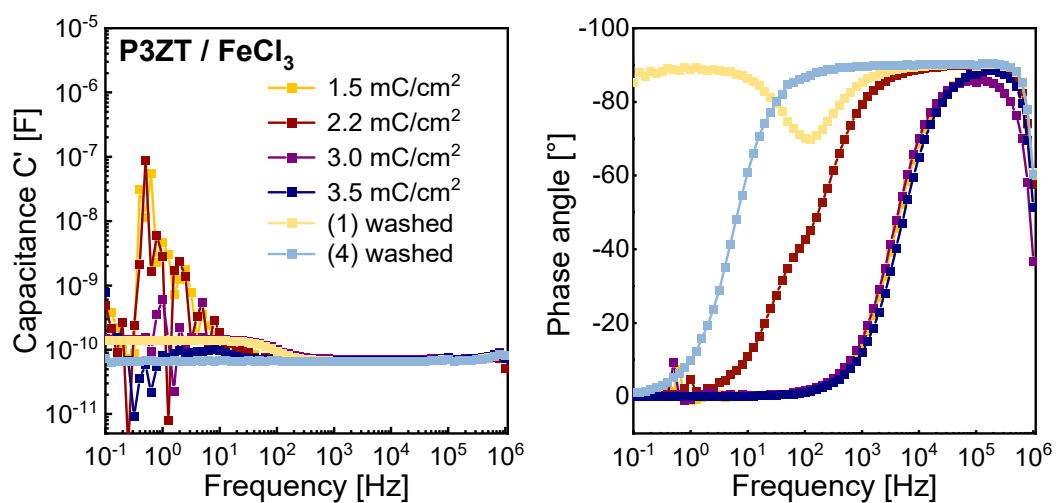


Figure S14. Impedance measurements of the conductive nanowires after doping with FeCl₃. Shown is the complex value of the capacitance and the phase shift as a function of frequency. In lighter colors the corresponding washed samples are shown.

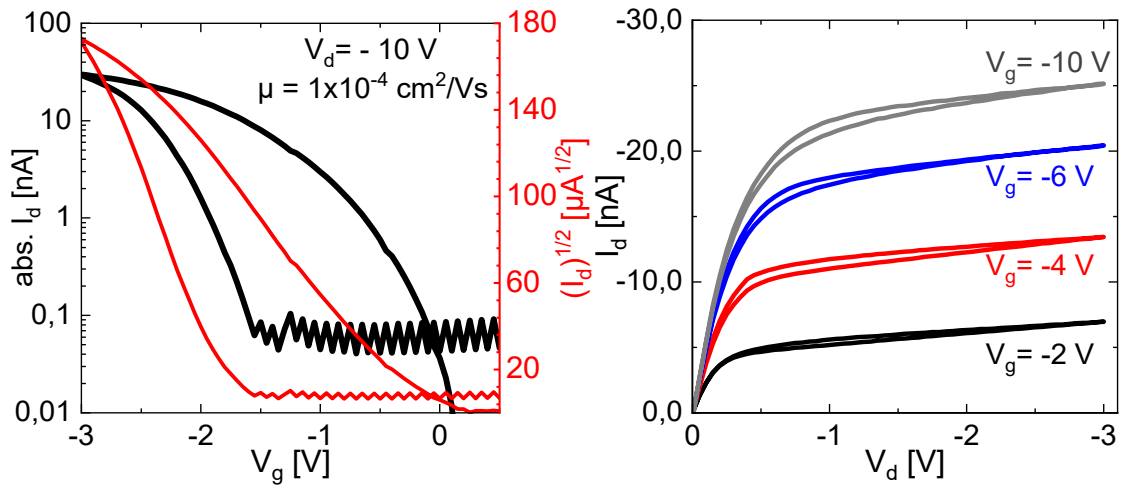


Figure S15. Input and output characteristics of TIPS-Pen.

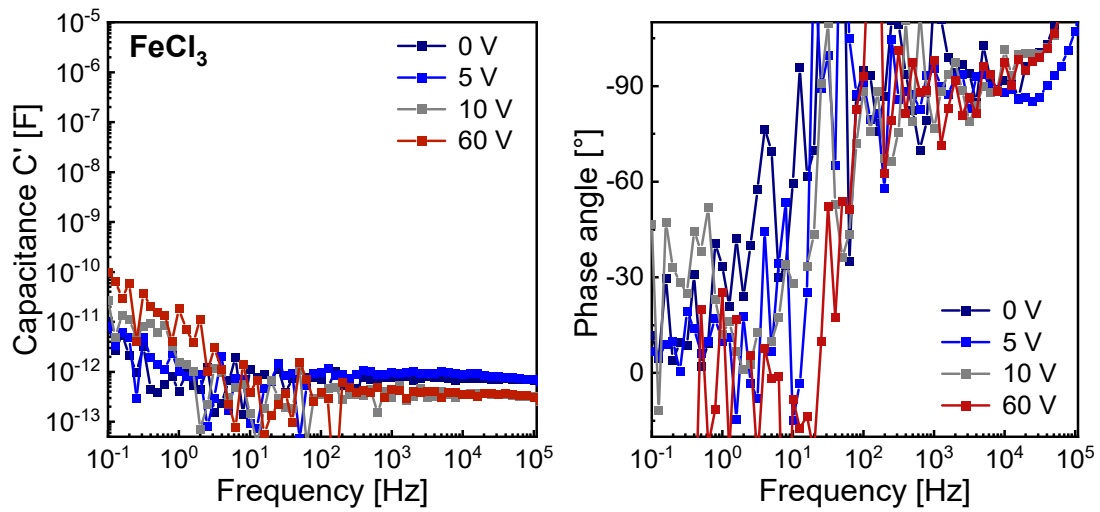


Figure S16. Impedance measurements of the nanotransistor after doping with FeCl_3 for different applied DC voltages V_D .

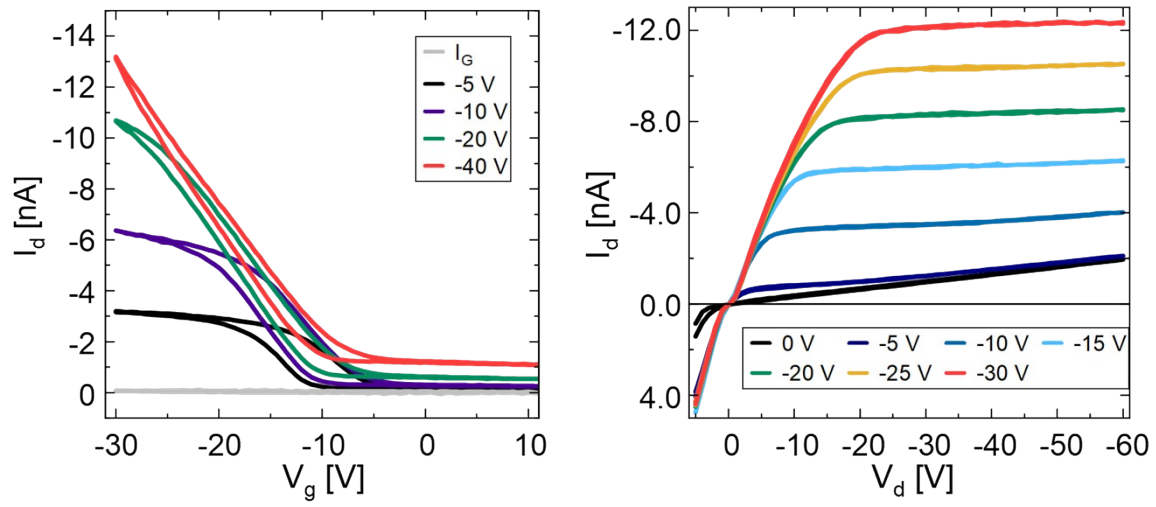


Figure S17. Input characteristic of TIPS-Pen of the nanotransistor for different drain voltages and output characteristic of the same nanotransistor for different gate voltages.

7. XPS and UPS spectra

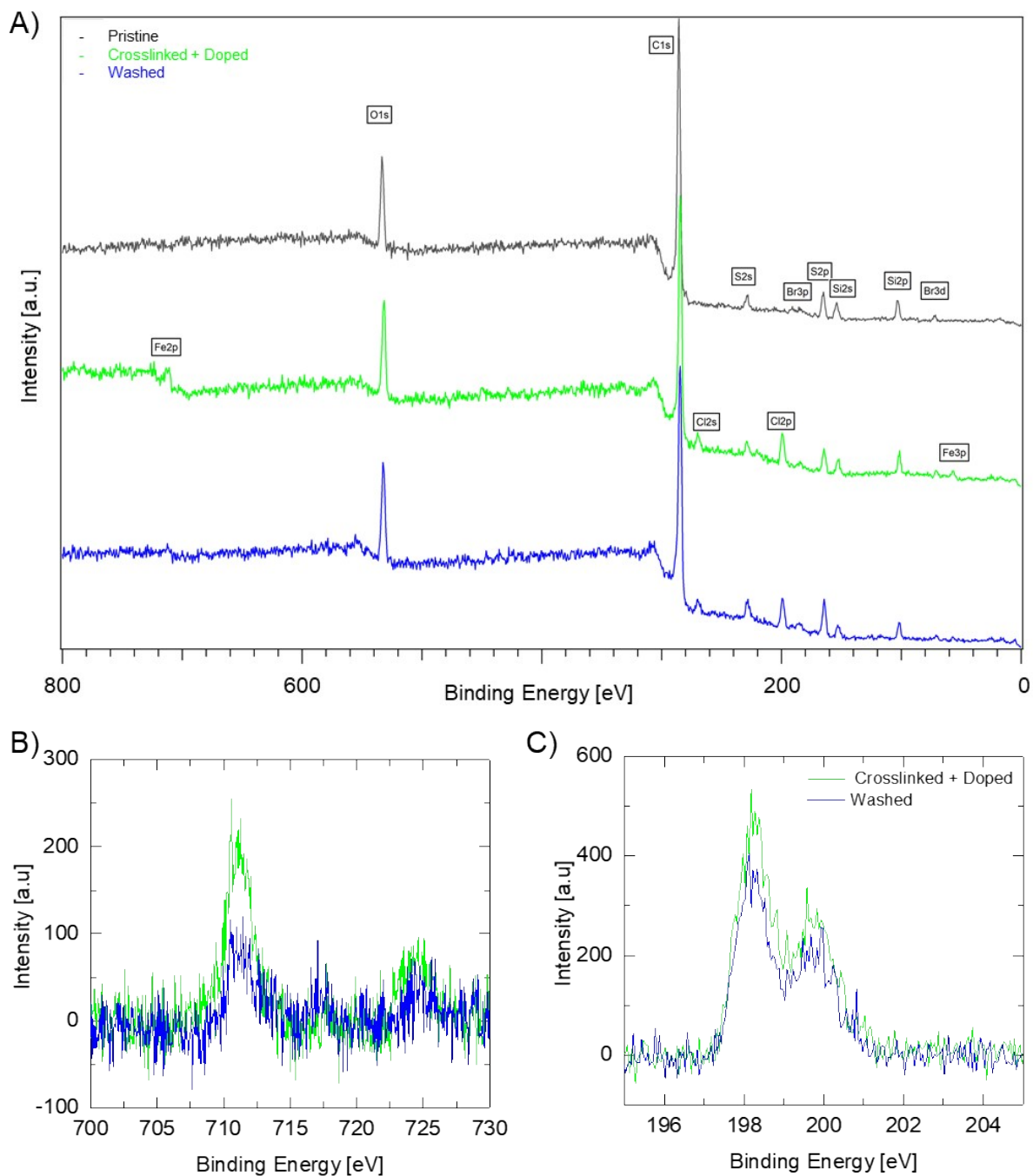


Figure S18. XPS spectra of P3ZT on Si/SiO₂ substrate. **A)** Survey of the whole spectra for a pristine sample (black), for a UV crosslinked (3h) and FeCl₃-doped sample (green) and washed as described with MeCN (blue). **B)** The Fe2p and **C)** Cl2p signals detailed for crosslinked/doped and for washed samples.

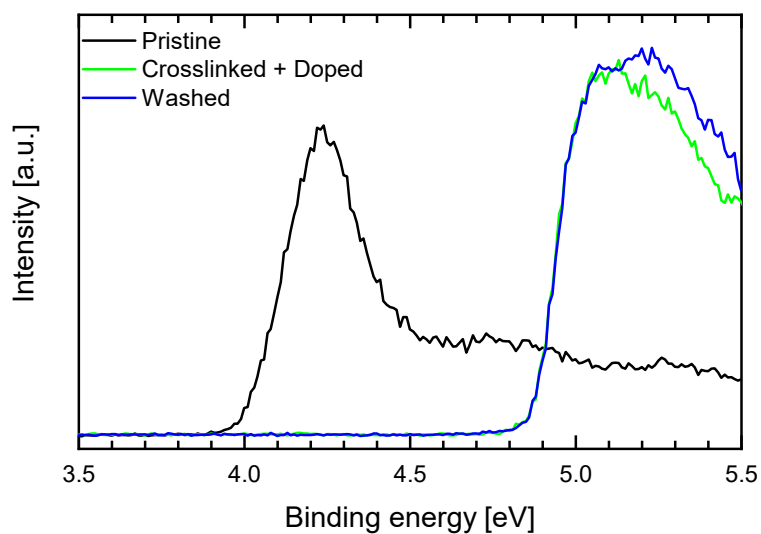


Figure S19. Secondary electron cut-off (SEC) from XPS to determine the work function (WF) of pristine **P3ZT**, of a UV crosslinked (3h) and FeCl₃-doped sample (green) and washed with MeCN (blue). The intersection of the tangent with the x-axis is determined.

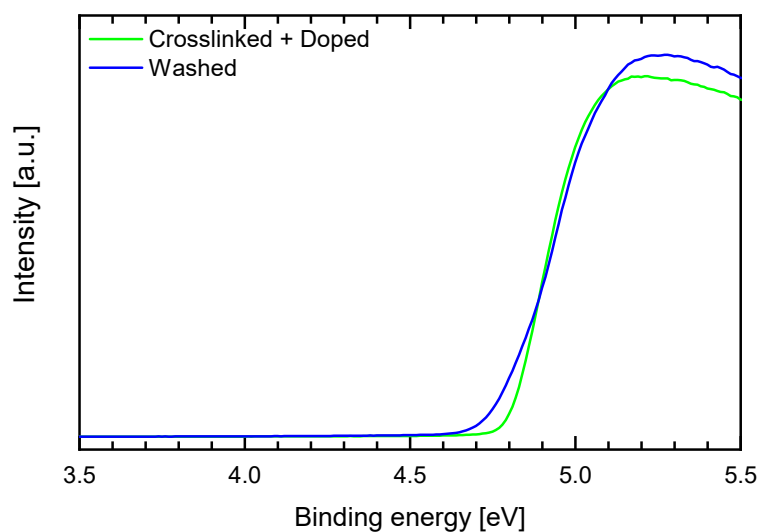


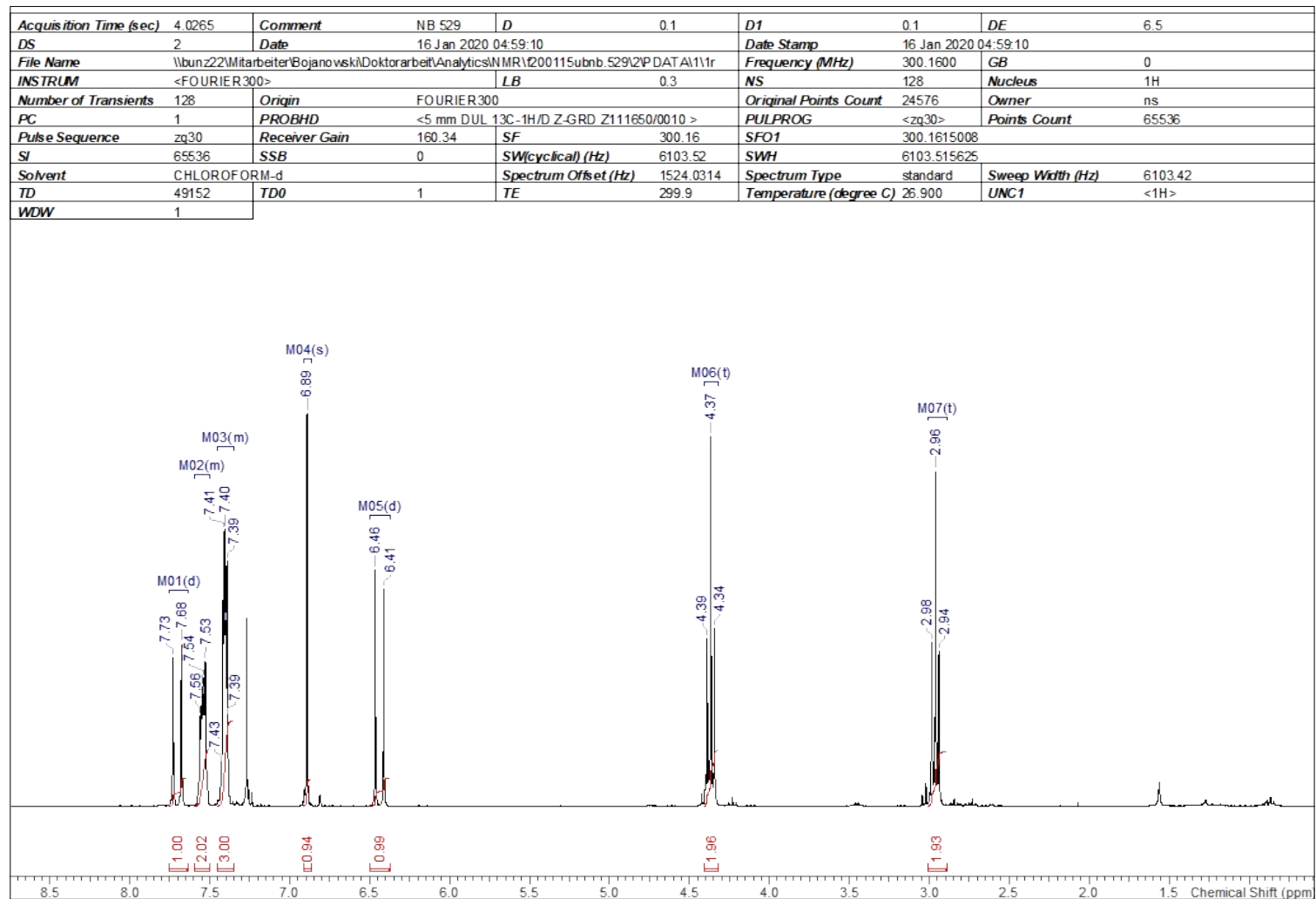
Figure S20. Secondary electron cut-off (SEC) from UPS to determine the WF of a UV crosslinked (3h) and FeCl₃-doped sample (green) and washed with MeCN (blue). The intersection of the tangent with the x-axis is determined.

8. References

- 1 I. E. Jacobs, E. W. Aasen, J. L. Oliveira, T. N. Fonseca, J. D. Roehling, J. Li, G. Zhang, M. P. Augustine, M. Mascal and A. J. Moulé, *J. Mater. Chem. C*, 2016, **4**, 3454–3466.

9. NMR spectra

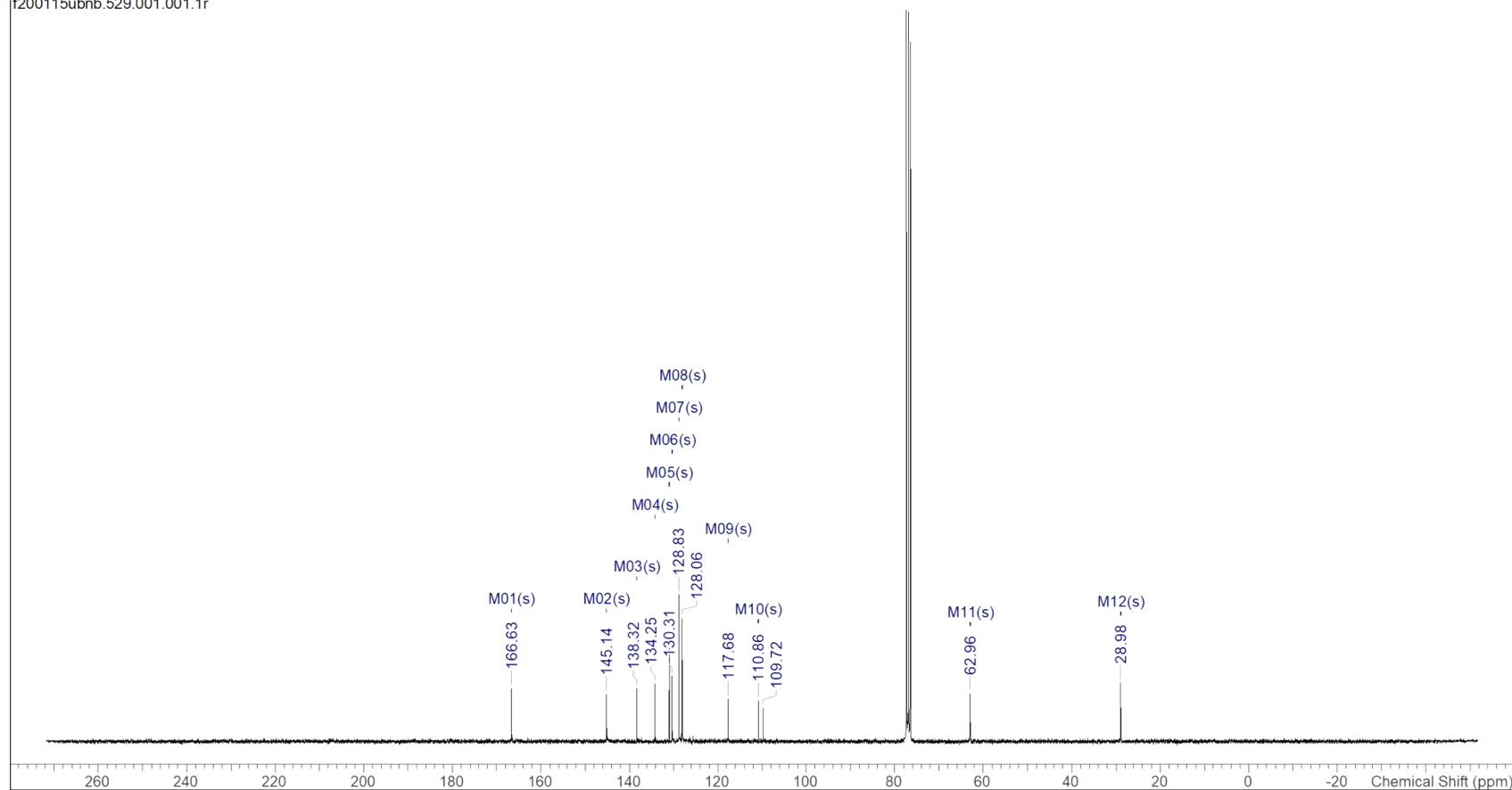
¹H NMR spectra of 3



¹³C NMR spectra of 3

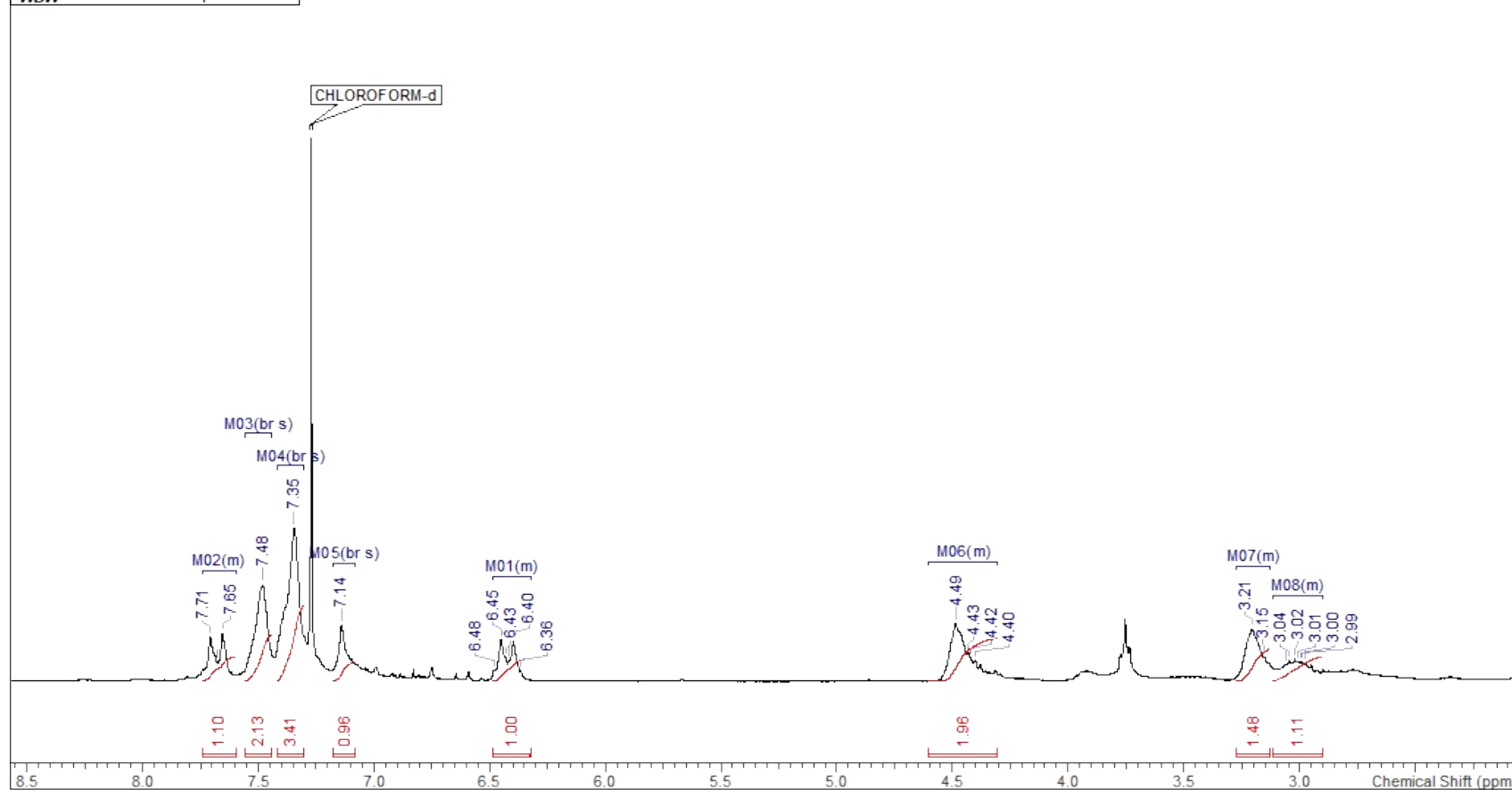
Acquisition Time (sec)	1.3422	Comment	NB 529	D	0.03	D1	2	DE	6.5
DS	2	Date	15 Jan 2020 19:21:12	Date Stamp	15 Jan 2020 19:21:12	Frequency (MHz)	75.4753	GB	0
File Name	\\bunz22\Mitarbeiter\Bojanowski\Doktorarbeit\Analytics\NMR\200115ubnb.529\1\1\1r			Frequency (MHz)	75.4753	GB	0	Nucleus	13C
INSTRUM	<FOURIER300>			LB	1	NS	10240	Original Points Count	32768
Number of Transients	10240	Origin	FOURIER300	Original Points Count	32768	Owner	ns	Points Count	32768
PC	1.4	PROBHD	<5 mm DUL 13C-1H/D Z-GRD Z111650/0010 >	PULPROG	<zpgpg30>	SFO1	75.4835943141236	Solvent	CHLOROFORM-d
Pulse Sequence	zpgpg30	Receiver Gain	501.19	SF	75.475292032	Spectrum Offset (Hz)	8302.2842	Spectrum Type	standard
SI	32768	SSB	0	SW(cyclical) (Hz)	24414.06	SWH	24414.0625	Sweep Width (Hz)	24413.32
TE	300.1	Temperature (degree C)	27.100	UNC1	<13C>	TD	65536	WDW	1

f200115ubnb.529.001.001.1r



¹H NMR spectra of P3ZT

Acquisition Time (sec)	3.6351	Comment	Z104275_0201 (PABBO 300S1 BBF-H-D-05 Z)	D	0.1	D1	0.1
DE	6.5	DS	2	Date	23 Jan 2020 16:12:01	Date Stamp	23 Jan 2020 16:12:01
File Name	\\bunz22\mitarbeiter\Bojanowski\Doktorarbeit\Analytics\NMR\va200123ubnb234\1\PD\DATA\1\1r			Frequency (MHz)	300.5100	GB	0
INSTRUM	<spect>	LB	0.3	NS	16	Nucleus	1H
Origin	spect	Original Points Count	32768	Owner	ns	PC	1
PROBHD	<Z104275_0201 (PABBO 300S1 BBF-H-D-05 Z)>			PULPROG	<zq30>	Points Count	65536
Receiver Gain	406.00	SF	300.510030343375	SFO1	300.51150255	Pulse Sequence	zq30
SI	65536	SSB	0	SW(cyclical) (Hz)	9014.42	SWH	9014.42307692308
Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	1498.4125	Spectrum Type	standard	Sweep Width (Hz)	9014.29
TD	65536	TD0	2	TE	300.0021	Temperature (degree C)	27.002
WDW	1	UNC1	<1H>				



¹³C NMR spectra of **P3ZT**

Acquisition Time (sec)	1.5897	Comment	NB 227b	D	1.5	D1	1.5	DE	18
DS	2	Date	10 Feb 2020 21:34:13			Date Stamp	10 Feb 2020 21:34:13		
File Name	E:\Bojanowski\Doktorarbeit\Analytics\NMR\c200210ubnb.227b\1\PDATA\1\1r					Frequency (MHz)	100.6631	GB	0
INSTRUM	<spect>	LB	1	NS	3200	Nucleus	13C	Number of Transients	3200
Origin	spect	Original Points Count	49066	Owner	ns	PC	1.4	Points Count	65536
PROBHD	<Z130030_0004 (CPP BBO 400S1 BB-H&F-D-05 LT)>					PULPROG	<zpgg30>	Points Count	65536
Pulse Sequence	zpgg30	Receiver Gain	2050.00	SF	100.663059	SFO1	100.67413193649		
SI	65536	SSB	0	SW(cyclical) (Hz)	30864.20	SWH	30864.1975308642		
Solvent	CHLOROFORM-d			Spectrum Offset (Hz)	11071.9609	Spectrum Type	standard	Sweep Width (Hz)	30863.73
TD	98132	TD0	400	TE	294.9992	Temperature (degree C)	21.999	UNC1	<13C>
WDW	1								

c200210ubnb.227b.001.001.1r.esp

