Supporting Information

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

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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:

$^1$H 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 ($\delta$) 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=quinet, 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 ($\delta$) 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 ApexQehybrid 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 × I.D. 30 cm × 8 mm) in line. The consecutive exclusion sizes were 100 Å, 1000 Å, and 100000 Å 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 Manager™ 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 (SiO$_2$, 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. $^1$H NMR (300 MHz, CDCl$_3$): 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. $^{13}$C{${^1}$H} NMR (75 MHz, CDCl$_3$): 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 C$_{15}$H$_{12}$Br$_2$O$_2$SNa 438.8802; found 438.8797. Elem. anal. calcd. for C$_{15}$H$_{12}$Br$_2$O$_2$S: 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)Cl$_2$ (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 NH$_4$Cl and CHCl$_3$ were added, the aqueous layer was separated and extracted with CHCl$_3$ (3x 20 mL). The combined organic layers were dried over MgSO$_4$, filtered, and the filtrate concentrated in vacuo. The crude product purified by twofold precipitation via dissolution in a small amount of CHCl$_3$ 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 ºC, dec. > 300 ºC. The $M_w$ was estimated to be $1.7 \times 10^4$ g/mol with a PDI of 1.74. 

$^1$H NMR (500 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. $^{13}$C{$^1$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 ºC is attributed to solvent evaporation. DSC indicates a melting point at 178 ºC.
Figure S3. Cyclovoltammetry 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 SiO$_2$ 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(NO$_3$)$_3$ * 9 H$_2$O 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-cyclohexyldecylphosphonic 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 µC/cm$^2$. Contact pads of the transistor structure were written with an exposure dose of 1500 µC/cm$^2$ and finger structures were additionally stitched to contact pads with an exposure dose of 2500 µC/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 FeCl₃ 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 **P3HT** film and solution and **P3HT** film and B) emission spectra of **P3ZT** in solution (CHCl₃).

**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 \( \mu \)m) 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\(^\text{§}\)          | 220 ± 10                  | 450                         |

* Lines are inhomogeneous. \(^\text{§}\) 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 FeCl$_3$-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 FeCl$_3$-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

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$^1$H NMR spectra of P3ZT
13C NMR spectra of P3ZT

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