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Electronic Supplementary Information

Solvent influence on the surface morphology of P3HT thin films revealed by photoemission electron microscopy

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1. Experimental Procedures

The sample preparation and the PEEM measurement procedure was previously reported in [1].

Chlorobenzene, 1,2,4-trichlorobenzene, thiophene and chloroform were purchased from

Sigma Aldrich. 1,2-dichlorobenzene was acquired from VWR International. All solvents are rated at 99% or higher. Rr-P3HT (MW = 37 kg mol/1, regioregularity: 96 %, PDI = 2) was purchased from Rieke Metals. All chemicals were used as received.

Sample preparation was done under a nitrogen atmosphere in a glovebox. The Si substrates (size 1 cm^2) were obtained from Plano GmbH and were cleaned by ultrasonification in distilled water, acetone and isopropyl alcohol for 10 min each and then transferred into the glove box.

Two sample preparation methods were carried out: First, 0.3 wt% solution of rr-P3HT in each solvent was prepared by stirring the solution for 2.5 hours. Then spin coated onto a Si substrate with native SiO_2 layer, accelerating from 10 to 20 rps in 5 s and subsequently rotating at 20 rps for 50 s. Second, heating the solutions 5 °C below the b. p. of the respective solvent for 10 mins. Except for 1,2,4-trichlorobenzene which b.p. (211 °C) exceeds the b.p. of the silicon oil. Therefore, the temperature for TCB was set to 170 °C. We employed the same spinning parameters as mentioned for the at room temperature prepared samples.

Sample transport from the glove box to PEEM was conducted in an air tight cylinder and they were transferred into the PEEM under a stream of nitrogen minimizing contamination of the sample with air. The sample was stored inside the PEEM chamber at a pressure of $<2 \times 10^{-9}$ mbar.

During this project, all PEEM measurements were performed in an IS-PEEM from FOCUS GmbH with an ultimate resolution of ≈ 40 nm. The laser radiation was generated with the Coherent Fidelity-2 laser. The fundamental wavelength (1070 nm) was frequency doubled to a central wavelength of 535 nm by an APE Harmonixx. The sample was illuminated via a normal incidence rhodium mirror in the Focus PEEM.

The polarization direction and the pulse energy were adjusted by a combination of a $\lambda/2$-waveplate and a polarizer. For the presented measurements the laser power was set to 17.5 mW before entering the vacuum chamber through a window, except for chlorobenzene, where the laser power used was 10 mW. A lens focused the light onto the sample, whre the laser spot has a slight elliptical shape with the long axis being around 96 μm and the short axis around 83 μm long. Considering the reflectivity of the rhodium mirror, the laser intensity used during measurements was $\approx$ 55 W/cm^2 for s-polarization and 42 W/cm^2 for p-polarization (laser power 17.5 mW) and $\approx$ 30 W/cm^2 for s-polarization and 22 W/cm^2 for p-polarization (laser power 10 mW). Data analysis had been performed with Python 3.7 as described in [1], however, as the 535 nm photons have less energy compared to the 400 nm photons used before, excitation occurs via a three photon process, which we accounted for.

The thickness of the P3HT films on top of the silicon substrate was determined by carving a line into the film with a pair of metal tweezers. Subsequent AFM profile measurements on this cut delivered the film thickness. The AFM (Bruker Dimension ICON) was operated in tapping mode^{TM} and in an xy-closed loop configuration. To measure the surface topography, the z-sensor signal was utilized.

2. Orientation maps

Figure S1 and Figure S2 display the chain orientation and the local degree of order for representative spots of the samples.

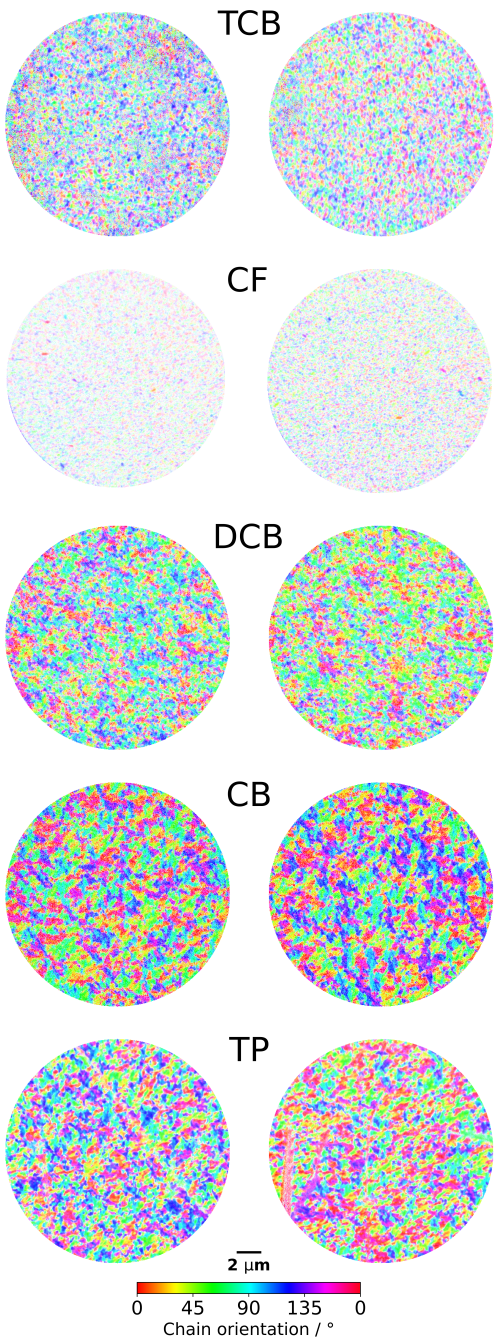

Figure S1: Two representative, evaluated PEEM image series for each solvent showing the combination of chain orientation and local degree of order of P3HT films spun from different solvents: CB, DCB, TCB, TP and CF at room temperature.

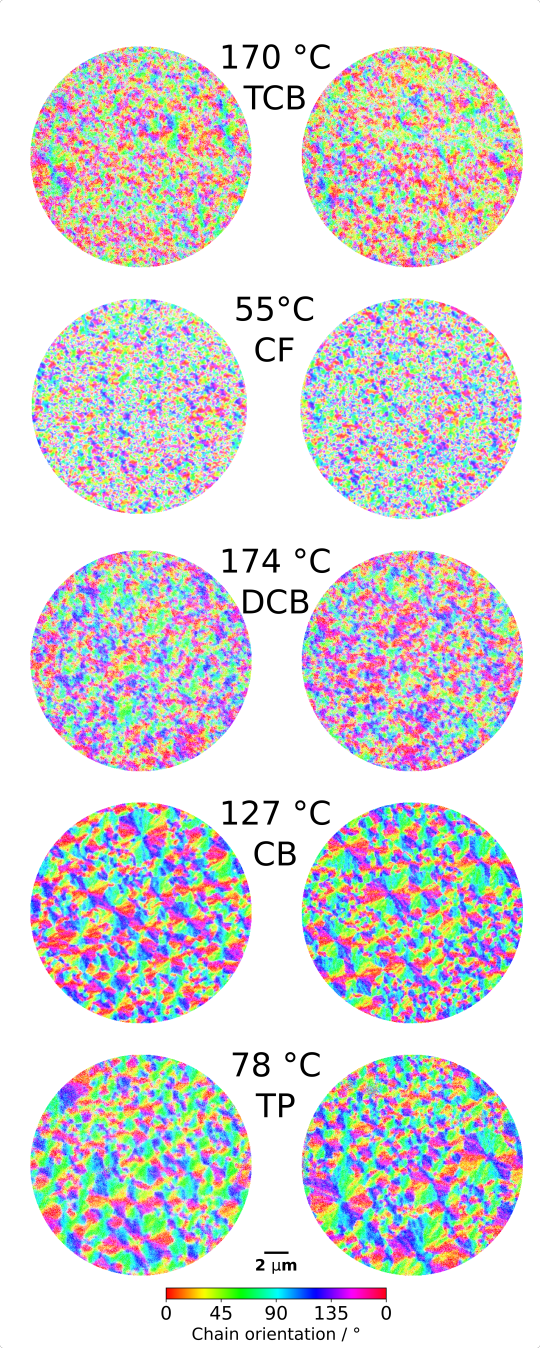

Figure S2: Two representative, evaluated PEEM image series for each solvent showing the combination of chain orientation and local degree of order of P3HT films spun from different solvents: CB, DCB, TCB, TP and CF at elevated temperatures.

3. OPL Plots

Figure S3 displays the received OPLs taken from the samples represented in Figure S1 and Figure S2. For a detailed explanation of the OPL see [1].

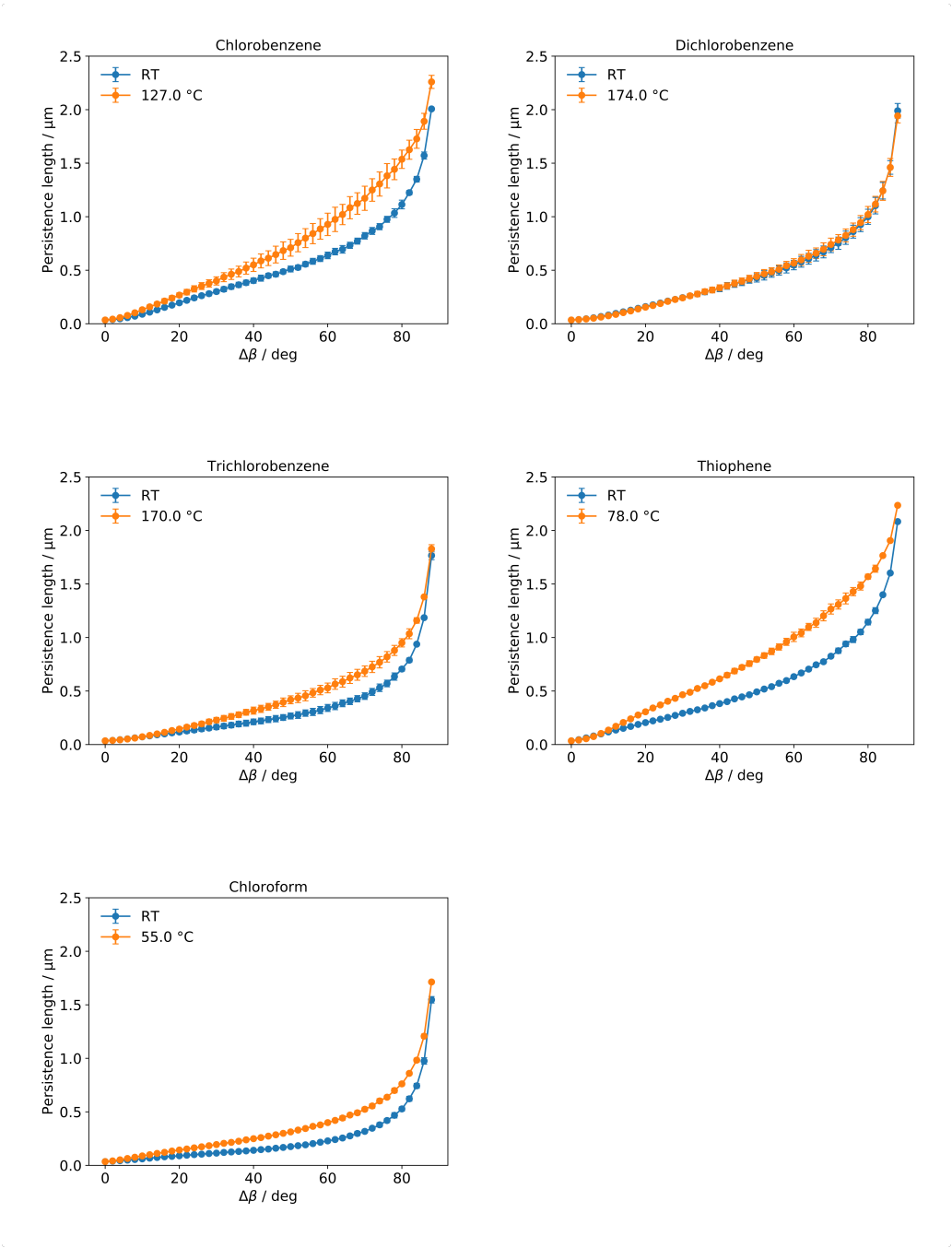

Figure S3: Orientation persistence lengths (OPLs) [1] calculated for the samples spun cast from different solvents at two temperatures.

4. Film thickness

Table 1 displays the film thickness of each sample as determined by AFM. We note, that the surface roughness of the film spun from TCB at RT was to high to safely determine the film thickness. The film spun from thiophene at RT did also exhibit significant surface roughness, therefore we only determined the lower limit of the film thickness.

Table 1: Film thickness, as determined by AFM, for the samples spun at RT and at elevated temperatures, respectively. All values are given in nm.

Solvent	RT	elev. T.
Trichlorobenzene	– *	11.5 ± 1 (170 °C)
Chloroform	55.5 ± 1	95 ± 1 (55 °C)
Dichlorobenzene	8 ± 2	13 ± 1 (174 °C)
Chlorobenzene	19 ± 1	21.5 ± 1 (127 °C)
Thiophene	> 5 #	49 ± 1 (78 °C)

* Not determined due to inhomogeneous film.

This value represents the lower limit of the film thickness.

References

[1] A. Neff, F. Niefind, B. Abel, S. C. B. Mannsfeld, K. R. Siefermann, *Advanced Materials* **2017**, 1701012.