

## Electronic Supplementary Information for

# Shear alignment and 2D charge transport of tilted smectic liquid crystalline phases - XRD and FET studies

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## Experimental Part

### Synthesis

All chemical reactions (Fig. 1) were conducted under inert atmosphere (Ar). All chemicals were purchased from *Sigma-Aldrich* unless otherwise stated. THF and toluene were dried in a *MBraun MB-SPS-800 solvent purification* (drying) system. Cyclohexane for column chromatography was distilled before usage. <sup>1</sup>H and <sup>13</sup>C NMR solution spectra were recorded on a *Bruker Avance 250 DPX* at 250 and 62.5 MHz, respectively. All spectra were recorded at room temperature in CDCl<sub>3</sub> as solvent. HRMS was recorded under ESI conditions on a *Bruker Daltonics micrOTOF-Q* spectrometer.

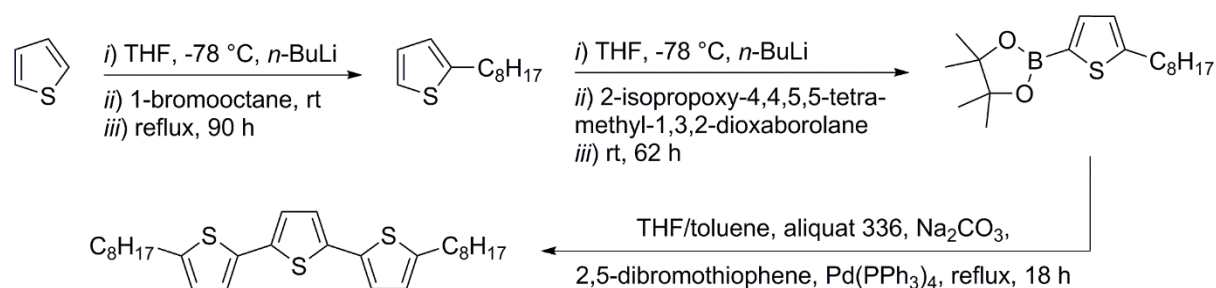


Fig. 1: Schematic drawing of the synthesis route of 5,5''-dioctyl-2,2':5',2''-terthiophene (8-TTP-8) using thiophene as starting material.

### Step 1: Synthesis of 2-octylthiophene<sup>1</sup>

*n*-BuLi (1.6 M in hexanes, 34.30 mL, 54.86 mmol) was slowly added to a solution of thiophene (6.00 g, 5.70 mL, 71.32 mmol) in THF (dry, 60 mL) at -78 °C. The cooling bath was removed and the solution was stirred for one hour. 1-Bromooctane (10.59 g, 9.50 mL, 54.86 mmol) was added at room temperature. The mixture was refluxed for 90 hours. The solution was washed with brine (60 mL). The aqueous phase was extracted with Et<sub>2</sub>O (2x 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The product was isolated over fractional vacuum distillation (*p* = 0.14 mbar) in form of a colorless liquid (8.15 g, 41.5 mmol, 76%). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.12 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1 Hz, 3.4 Hz, 1H), 6.80 (ddd, *J* = 5.1 Hz, 3.4 Hz, 1.2 Hz, 1H), 2.84 (t, *J* = 7.7 Hz, 2H), 1.78-1.64 (m, 2H), 1.43-1.26

(m, 10H), 0.91 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$ -NMR (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 146.0, 126.7, 124.0, 122.8, 32.01, 31.97, 30.1, 29.5, 29.4, 29.3, 22.8, 14.3.

### Step 2: Synthesis of 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane<sup>2</sup>

*n*-BuLi (2.5 M in hexanes, 8.6 mL, 21.39 mmol) was slowly added to a solution of 2-octylthiophene (4.00 g, 20.37 mmol) in THF (dry, 40 mL) at  $-78$  °C. The mixture was stirred for 25 minutes at  $-78$  °C and subsequently warmed up to room temperature over 100 minutes. After cooling again to  $-78$  °C 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.17 g, 4.6 mL, 22.41 mmol) was added slowly at this temperature. The cooling bath was removed and the solution was stirred for 62 hours at room temperature. The reaction mixture was rinsed with  $\text{Et}_2\text{O}$  (100 mL) and washed with saturated  $\text{Na}_2\text{CO}_3$  solution (2x 50 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure. The product was isolated in form of a brown liquid (6.51 g, 20.20 mmol, 99%). The product was used without further purification.  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.46 (d,  $J = 3.4$  Hz, 1H), 6.85 (d,  $J = 3.4$  Hz, 1H), 2.85 (t,  $J = 7.5$  Hz, 2H), 1.74-1.61 (m, 2H), 1.36-1.24 (m, 10H), 1.33 (s, 12H), 0.87 (t,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$ -NMR (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 153.8, 137.4, 125.8, 83.9, 31.9, 31.7, 30.2, 29.3, 29.2, 29.1, 24.8, 22.7, 14.1.

### Step 3: Synthesis of 5,5''-dioctyl-2,2':5',2''-terthiophene<sup>3</sup>

A mixture of 2,5-dibromothiophene (1.00 g, 0.48 mL, 4.13 mmol), aliquat 336 (4.00 mL),  $\text{Na}_2\text{CO}_3$  (1 M, 12.40 mL, 12.40 mmol) and 4,4,5,5-tetramethyl-2-(5-octylthiophene-2-yl)-1,3,2-dioxaborolane (3.04 g, 9.43 mmol) in THF/toluene (50:50, 120 mL) was degassed for one hour. A solution of tetrakis(triphenylphosphin)palladium (215 mg, 186  $\mu\text{mol}$ ) in THF (degassed, 20 mL) was added. The reaction mixture was refluxed for 18 hours. The solution was washed with brine (100 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure. Purification via column chromatography on silica gel (solvent cyclohexane) yielded the product in form of a yellow solid (840.0 mg, 1.78 mmol, 43%).  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ) (Fig. 2a):  $\delta$  (ppm) = 6.97 (s, 2H), 6.96 (d,  $J = 3.6$  Hz, 2H), 6.67 (d,  $J = 3.6$  Hz, 2H), 2.78 (t,  $J = 7.6$  Hz, 4H), 1.74-1.60 (m, 4H), 1.42-1.21 (m, 20H), 0.93-0.84 (m, 6H).  $^{13}\text{C}$ -NMR (62.5 MHz,  $\text{CDCl}_3$ ) (Fig. 2b):  $\delta$  (ppm) = 145.5, 136.3, 134.8, 124.9, 123.6, 123.3, 32.0, 31.8, 30.3, 29.5, 29.4, 29.2, 22.8, 14.3. MS (ESI-TOF): Calculated for  $\text{C}_{28}\text{H}_{40}\text{S}_3$   $[\text{M}+\text{H}]^+$ : 472.2292, found: 472.2292.

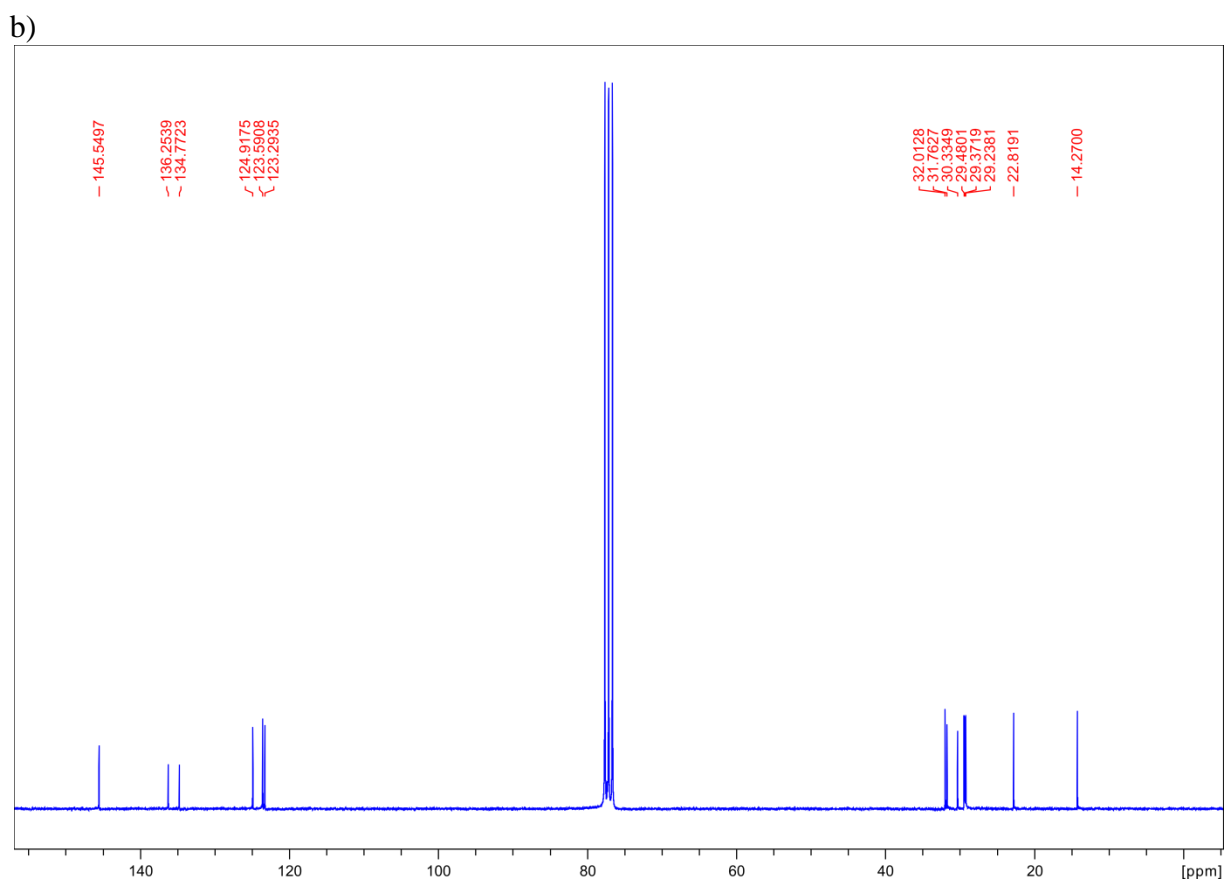
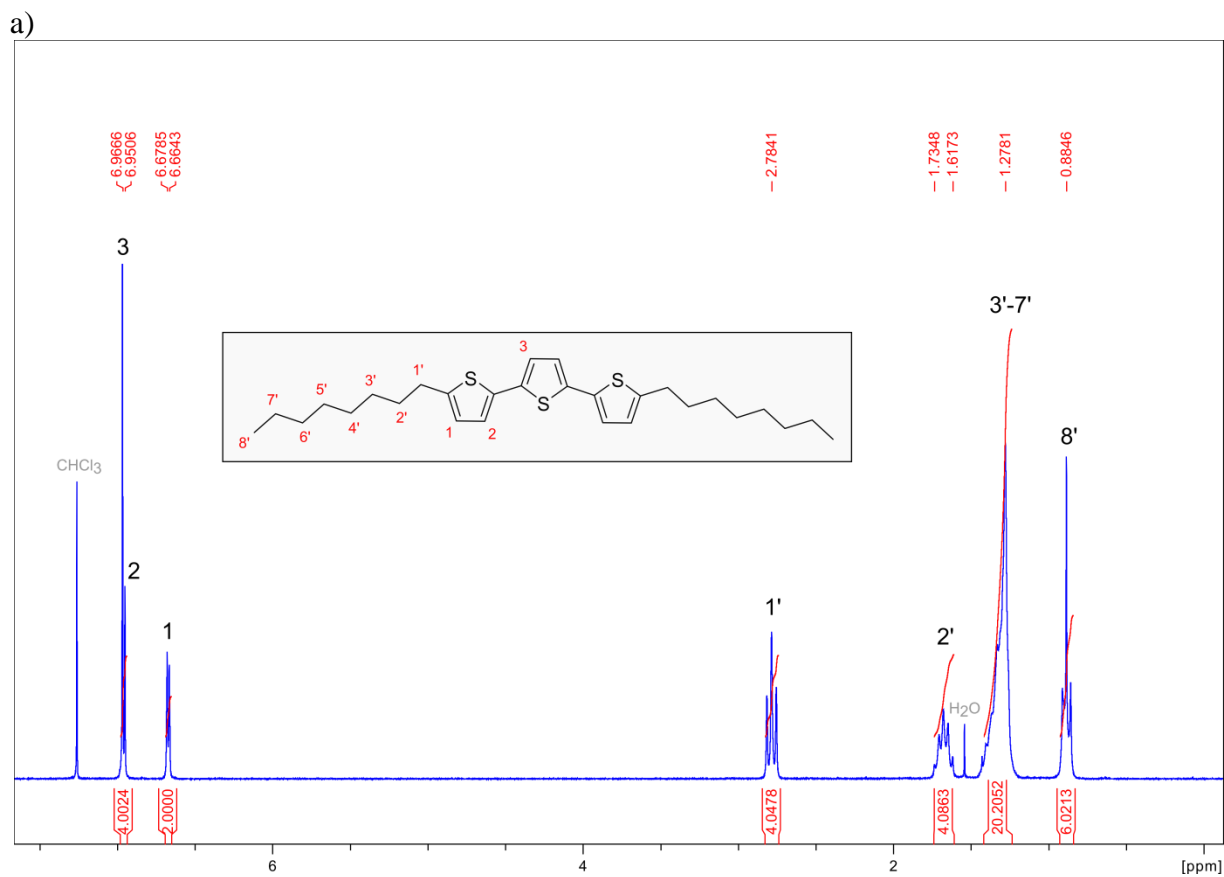


Fig. 2: NMR solution spectra of the synthesized and purified 8-TTP-8: a)  $^1\text{H}$  data (250 MHz,  $\text{CDCl}_3$ ) and b)  $^{13}\text{C}$  data (62.5 MHz,  $\text{CDCl}_3$ ).

## Characterization

### Polarizing microscopy (POM)

Phase transition temperatures and characteristic textures (Fig. 3a-d) were obtained with an Olympus BH-2 polarizing microscope with a Linkam LTS350 heating stage.

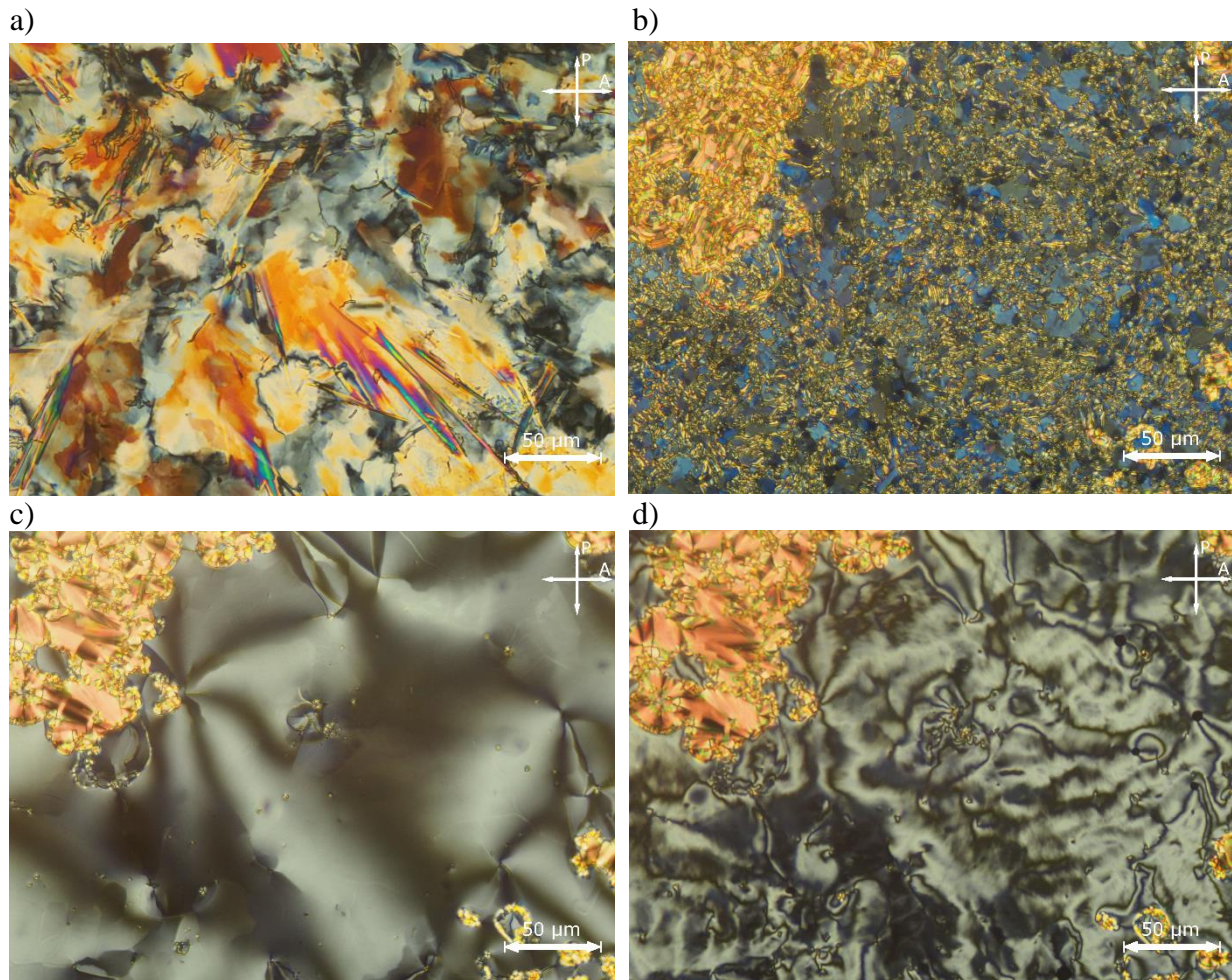


Fig. 3: POM images of 8-TTP-8 in a) the crystalline phase at 50°C, b) the crystal G phase at 70°C, c) the SmF phase at 77°C and d) the SmC phase at 90°C.

Investigations on film textures on the transistor substrate were also carried out with polarizing microscopy. Films of 8-TTP-8 were prepared by mechanically shearing the SmC phase over the interdigitating electrodes of the FET substrate using a microscopy glass slip. Shearing of SmC phases does not only align the orientation of the smectic layers but also the tilt direction of the SmC director into the direction of shear. The SmC-sheared films were afterwards cooled down to the corresponding temperatures of the other phases (Fig. 4a-h).

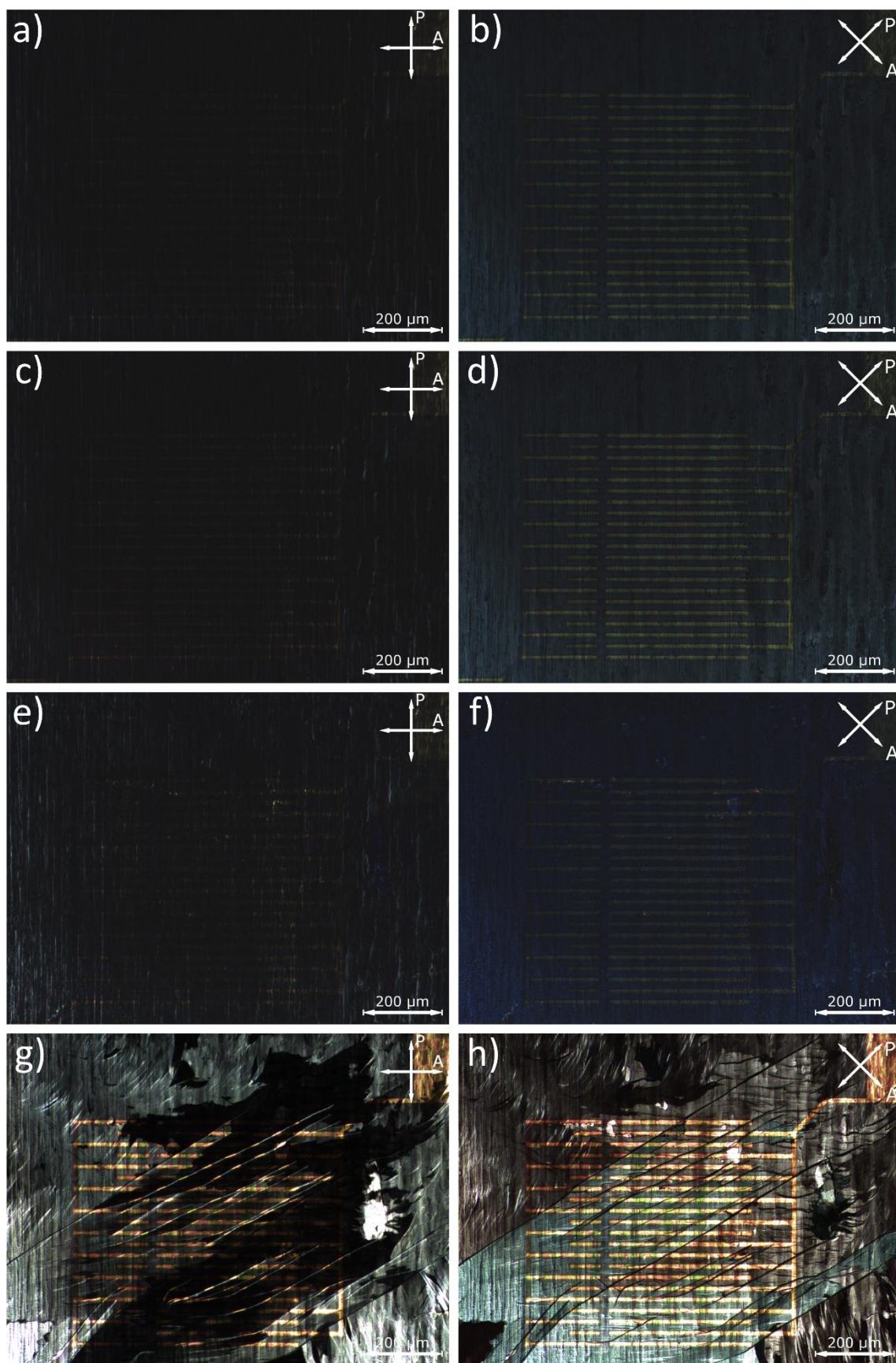


Fig. 4: Shear aligned films of 8-TTP-8: a) SmC phase at 90°C, c) SmF phase at 75°C, e) crystal G phase at 70°C and g) the crystalline phase at 50°C. b, d, f, h) Corresponding images via rotating the film with the direction of shear 45° to the crossed polarizers to get maximum birefringence.

Non-sheared films in all phases of 8-TTP-8 are shown in Fig. 5a-d. The films show non-uniform tilt directions in all tilted smectic phases.

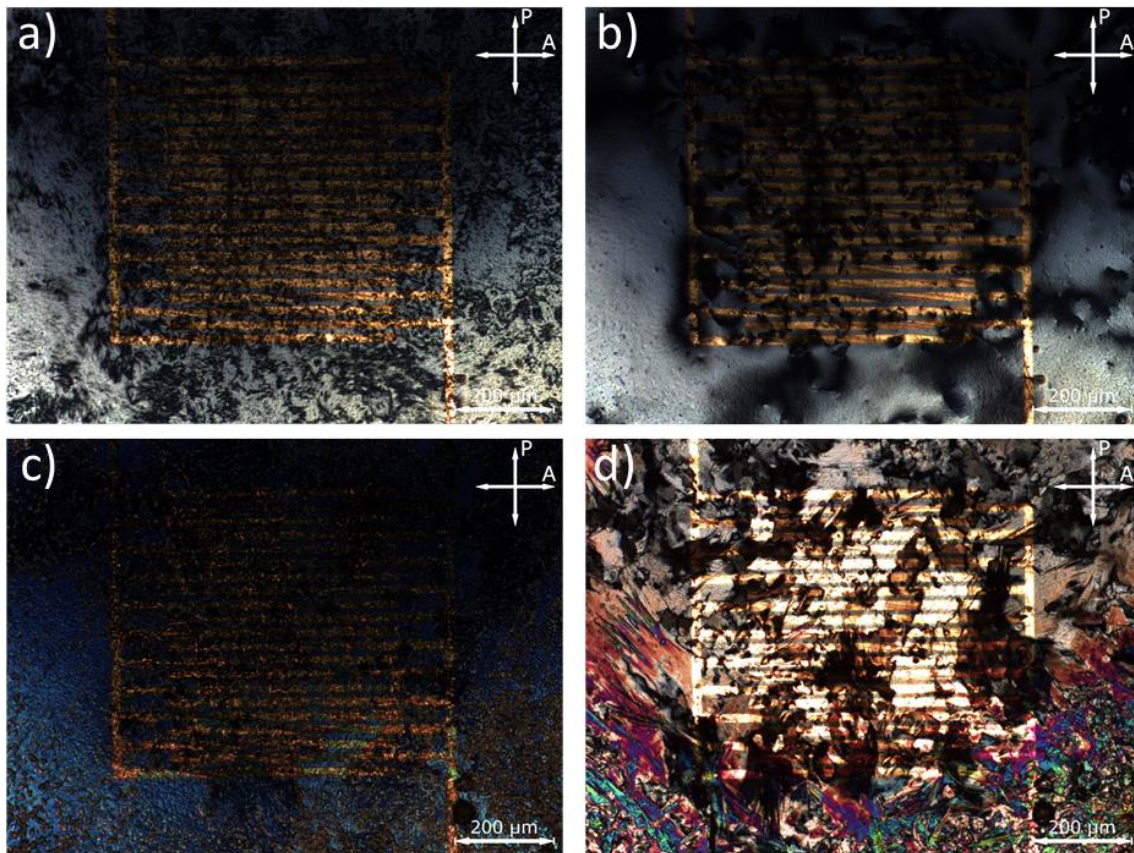


Fig. 5: Non-sheared films in all phases with non-uniform directions of director tilt. a) SmC phase at 90°C (Schlieren texture), b) SmF phase at 75°C (Schlieren-mosaic texture), c) crystal G phase at 70°C (mosaic texture) and g) the crystalline phase at 50°C (polydomain).

### Atomic force microscopy (AFM)

The thickness of the films on the FET substrates (Fig. 6) prepared by mechanical shearing was investigated with AFM in tapping mode with a scan size of 5 - 10  $\mu\text{m}$  and a rate of 0.3 Hz with 256 lines per image. The height difference between the surface of the film and the FET substrate leads to the film thickness, which was around 1  $\mu\text{m}$  for the prepared films.

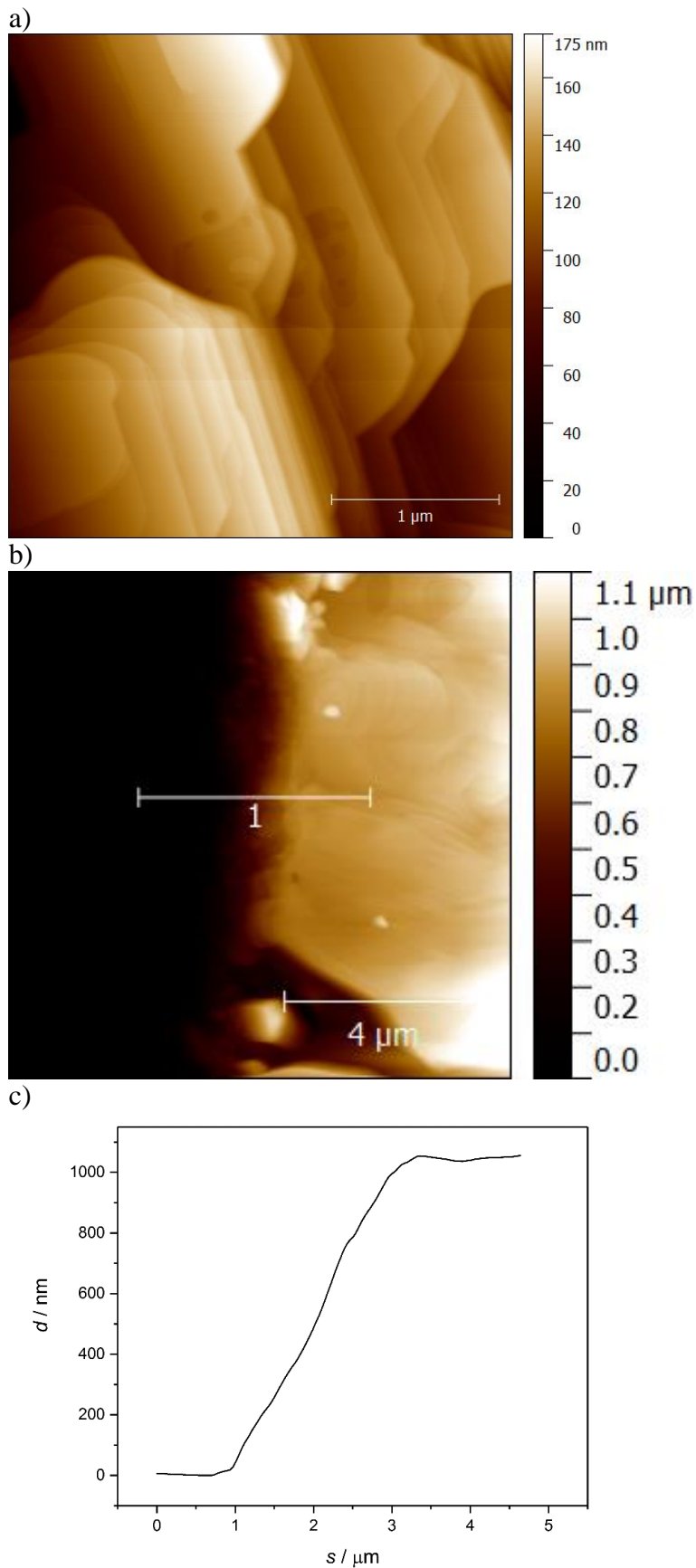


Fig. 6: a) AFM image of the film surface of 8-TTP-8 prepared by shear alignment in the liquid crystalline SmC phase at 90°C and cooled down to the crystalline phase at 25°C on the FET substrate. b) AFM image of the edge of the same film. c) Corresponding height profile, which shows a film thickness of about 1  $\mu\text{m}$ .

## Cyclic voltammetry

The cyclic voltammetry measurements were carried out in dichloromethane with tetrabutylammonium hexafluorophosphate as conducting salt. As working and counter electrode platinum was used, whereas a silver wire covered with silver chloride functioned as pseudo reference. The redox couple  $\text{Fc}/\text{Fc}^+$  was used as standard for calibration of the pseudo reference electrode. The three electrodes were controlled with a Metrohm Autolab PGSTAT 101 potentiostat. The differential pulse voltammetry (DPV) was carried out with a modulation amplitude ( $\Delta E$ ) of 0.025 V and a scan rate of  $10 \text{ mV s}^{-1}$ . The half-wave potential  $E_{1/2}$  can be calculated via equation (1) using the position of the peak in the DPV and half of the modulation amplitude.<sup>4</sup>

$$E_{1/2} = E_{\text{Peak}} + \frac{\Delta E}{2} \quad (1)$$

In the cyclic voltammogram (Fig. 7a) an electrochemically irreversible oxidation process is observed. To enable a reliable determination of the oxidation potential an additional differential pulse voltammogram was performed (Fig. 7b). The position of the highest occupied molecular orbital (HOMO) was determined from the DPV and accounts to  $-5.5 \text{ eV}$ .

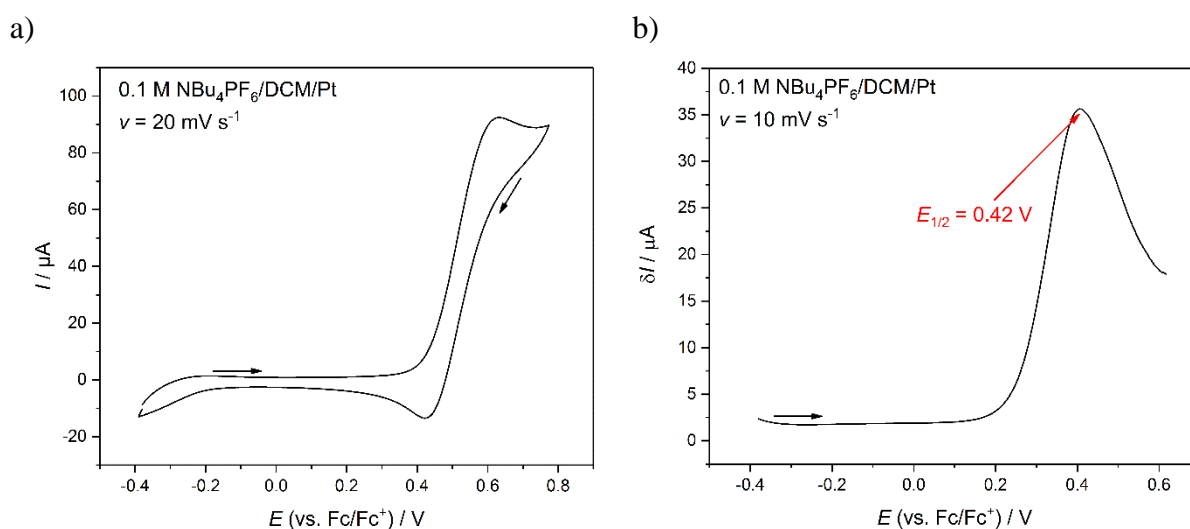


Fig. 7: a) Cyclic voltammogram and b) differential pulse voltammogram of the oxidation of 8-TTP-8 determined in dichloromethane with a concentration of  $0.1 \text{ mg mL}^{-1}$ .

## FET measurements

The characterizations were carried out under nitrogen atmosphere using a Keithley 2636 dual channel source meter. The charge carrier mobilities ( $\mu_{\text{FET}}$ ) were determined from the transfer characteristics curves (Fig. 8a-c) using the conventional transistor equation for the saturated region.



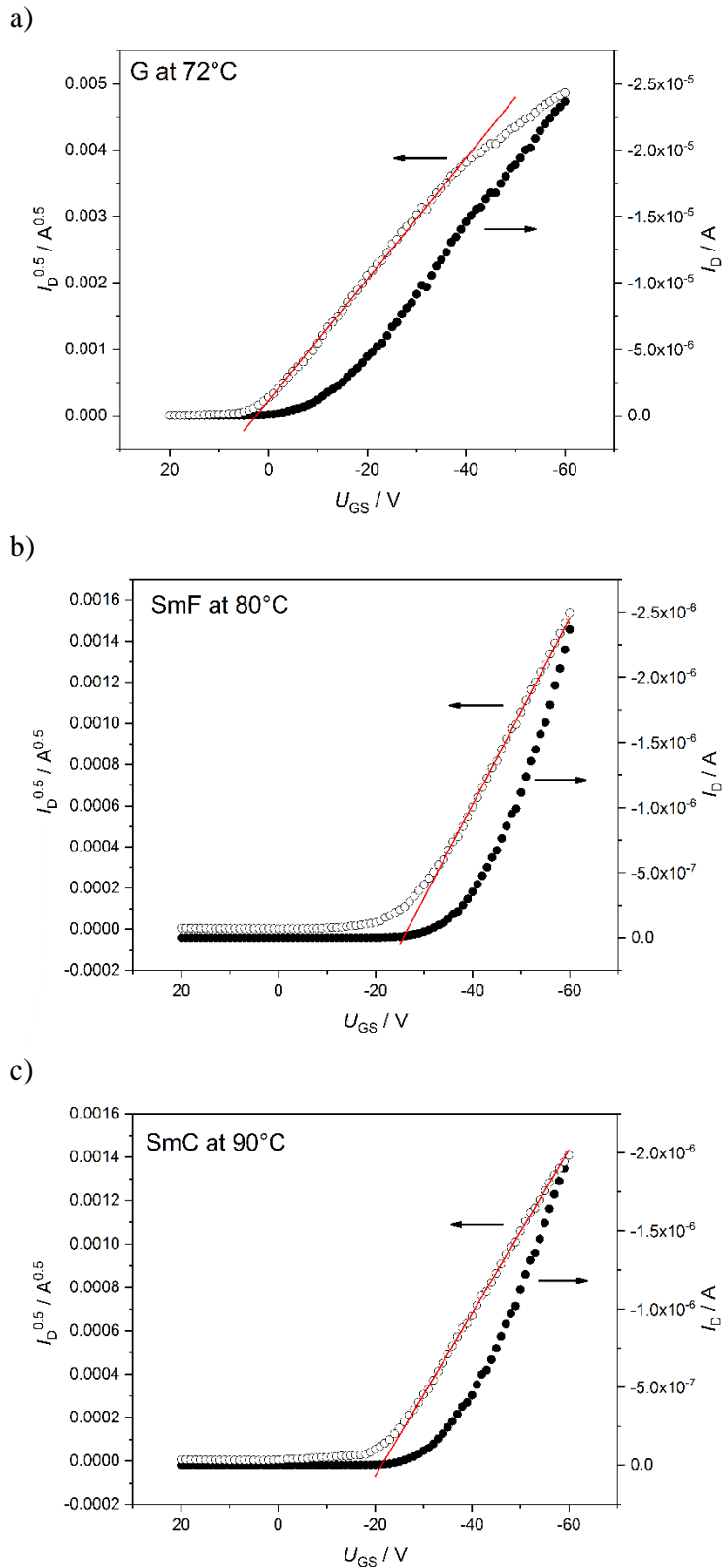


Fig. 8: Transfer characteristics curves at a constant  $U_{SD}$  of -60 V for the liquid crystalline phases of 8-TTP-8, where the hole mobility  $\mu_{FET}$  is directly proportional to the slope of the  $I_D^{0.5}$  plot (red lines). a) G phase at 72°C with  $\mu_{FET} = 1.2 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , b) SmF phase at 80°C with  $\mu_{FET} = 3 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , c) SmC phase at 90°C with  $\mu_{FET} = 2 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

## References

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