

Electronic Supporting Information

Effects of Molecular Chirality on Self-assembly and Switching in Liquid Crystals at the Cross-over Between Rod-like and Bent Shapes

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1. Synthesis and analytical data of compounds

3,7-Dimethyl-1-octanol (Aldrich, 99.0%), (*S*)-(-)- β -citronellol (Aldrich, $\geq 99.0\%$, $[\alpha]_D^{20} -5.3^\circ$, neat), 4-benzyloxyphenol (Alfa Aesar), potassium carbonate anhydrous (AlfaAesar, 99%), palladium 10 % on carbon (Alfa Aesar), 4-formylbenzoic acid (Aldrich, 97%), resorcinol (Merck), tert-butyl alcohol (Merck), sodium chlorite (Sigma-Aldrich), Sodium dihydrogen phosphate monohydrate (Merck), 2,4-dihydroxybenzaldehyde (Merck), hydroxylamine hydrochloride (Merck, %99), *N,N'*-dicyclohexylcarbodiimide (Merck) and 4-(dimethylamino)pyridine (Merck) were purchased commercially. Solvents were purchased or distilled. 2-Butanone (Merck) and THF (Merck %99) were purchased commercially as dry solvents and were used without further purification. Anhydrous solvent CH_2Cl_2 was dried over di-phosphorus pentoxide (Merck) and distilled under a N_2 atmosphere. Hexane, ethyl acetate, chloroform, dichloromethane and ethanol were distilled for use in crystallization and column chromatography. Analytical thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel 60 F254 (Merck). Column chromatography was performed using silica gel 60 (Merck, pore size 60 Å, 230-400 mesh particle size).

1.1 2,4-Dihydroxybenzotrile A

2,4-Dihydroxybenzotrile was prepared from commercially available 2,4-dihydroxybenzaldehyde by the formation of the oxime, followed by dehydration as described ref.^{S1,S2}.

Yield: 71%, colorless crystals, m.p. 175 °C. ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 10.51 (s, OH), 7.31 (d, *J* ≈ 8.5 Hz; 1 Ar-H), 6.37 (d, *J* ≈ 2.2 Hz; 1 Ar-H), 6.28 (dd, *J* ≈ 8.5 Hz, *J* ≈ 2.2 Hz; 1 Ar-H). ¹³C-NMR (125 MHz, DMSO-d₆): δ (ppm) = 162.59, 161.61, 89.45 (Ar-C), 134.12, 108.00, 102.31 (Ar-CH), 117.58 (s, CN).

1.2 4-[4-(3,7-Dimethyloctyloxy)phenoxy]benzoic acids (S)-B and rac-B

4-[4-(*S*)-3,7-Dimethyloctyloxyphenoxy]benzoic acid (**(S)-B**) and 4-[4-(3,7-Dimethyloctyloxy)phenoxy]benzoic acid **rac-B** were synthesized according to procedures reported in the literature^{S2}. Firstly, 4-benzyloxyphenol was alkylated with 3,7-dimethyloctyltosylate^{S3} (prepared from the commercially available 3,7-dimethyl-1-octanol by tosylation) and (*S*)-3,7-dimethyloctyl-1-bromide (prepared from (*S*)-3,7-dimethyl-1-octanol by reaction with conc. aqu. HBr/conc. H₂SO₄^{S4}), respectively, followed by hydrogenolytic debenylation (H₂, 10 % Pd/C in THF). Esterification of the obtained 4-alkyloxyphenols^{S5,S6} with 4-formylbenzoic acid using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP)^{S7}, followed by NaClO₂ oxidation^{S8} leads to final compounds (**(S)-B**) and **rac-B**. (*S*)-3,7-dimethyl-1-octanol was obtained from (*S*)-(-)-β-citronellol by catalytic hydrogenation (H₂, Pd/C in MeOH) as described previously^{S4}. Spectroscopic data and preparation procedures of (*S*)-4-(3,7-dimethyloctyloxy)phenyl benzyl ether, 4-(3,7-dimethyloctyloxy)phenyl benzyl ether, (*S*)-4-(3,7-dimethyloctyloxy)phenol and 4-(3,7-dimethyloctyloxy)phenol were given in ref.^{S9}.

4-(*S*)-3,7-Dimethyloctyloxyphenyl 4-formylbenzoate

To a mixture of (*S*)-4-(3,7-dimethyloctyloxy)phenol (2.50 g, 10 mmol) and 4-formylbenzoic acid (1.50 g, 10 mmol) in dry CH₂Cl₂ (60 ml) *N,N'*-dicyclohexylcarbodiimide (DCC) (2.37 g, 11.6 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.27 g, 2.2 mmol) were added and this mixture was stirred for 24h at room temperature under argon atmosphere. The end of reaction was monitored by TLC (chloroform). The reaction mixture was filtered on silica gel with CH₂Cl₂. After removing the solvent in vacuo, the crude product was purified by column chromatography on silica gel, eluting with CH₂Cl₂.

Yield: 65 %; colorless crystals, m.p. 47 °C, R_f 0.7 (CHCl₃). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 10.17 (s, 1H; Ar-CHO), 8.38 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 8.04 (d, *J* ≈ 8.3 Hz; 2 Ar-H), 7.15 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 9.0 Hz; 2 Ar-H), 4.06-3.99 (m, 2H, OCH₂), 1.83-1.77 (m, 1H, CH), 1.69-1.52, 1.38-1.10 (2m; 9H, 1 CH, 4 CH₂), 0.97 (d, *J* ≈ 6.5 Hz, 3 H, CH₃), 0.89 (d, *J* ≈ 6.6 Hz; 6H, 2 CH₃). ¹³C-NMR (125 MHz, CDCl₃): δ (ppm) = 191.58 (CHO), 164.55 (CO), 157.11, 143.94, 139.49, 134.65 (Ar-C), 130.73, 129.63, 122.20, 115.16 (Ar-CH), 66.75 (OCH₂), 39.26, 37.29, 36.20, 24.68 (CH₂), 29.84, 27.96 (CH), 22.74, 22.63, 19.67 (CH₃).

4-(3,7-Dimethyloctyloxy)phenyl 4-formyl benzoate

This compound was prepared similarly to 4-(*S*)-3,7-Dimethyloctyloxyphenyl 4-formylbenzoate from 4-(3,7-dimethyloctyloxy)phenol and 4-formylbenzoic acid by esterification.

Yield: 59 %; colorless crystals, m.p. 47 °C, R_f 0.7 (CHCl₃). **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 10.15 (s, 1H; Ar-CHO), 8.37 (d, $J \approx 8.3$ Hz; 2 Ar-H), 8.03 (d, $J \approx 8.3$ Hz; 2 Ar-H), 7.16 (d, $J \approx 9.0$ Hz; 2 Ar-H), 6.98 (d, $J \approx 9.0$ Hz; 2 Ar-H), 4.07-3.96 (m, 2H, OCH₂), 1.80-1.77 (m, 1H, CH), 1.67-1.51, 1.37-1.13 (2m; 9H, 1 CH, 4 CH₂), 0.96 (d, $J \approx 6.5$ Hz, 3 H, CH₃), 0.89 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃).

4-[4-(*S*)-3,7-Dimethyloctyloxyphenoxy-carbonyl]benzoic acid (*S*)-B

4-(*S*)-3,7-Dimethyloctyloxyphenyl 4-formylbenzoate (1.91 g, 5 mmol) and resorcinol (0.71 g, 6.4 mmol) were dissolved in tert-butyl alcohol (80 ml). Then, the aqueous solution of NaClO₂ (2.6 g, 29 mmol) and NaH₂PO₄·H₂O (2.1 g, 15 mmol) was added dropwise with stirring to this mixture. The mixture was stirred overnight at room temperature. The end of reaction was monitored by TLC (hexane:ethyl acetate / 2:1). After removing the solvent in vacuo, the residue was poured into 80 ml water and then the aqueous solution was acidified to pH 2 by adding 1 N HCl. The obtained precipitate was filtered and washed with water and hexane.

Yield: 90 %; colorless crystals, m.p. 159 °C, R_f 0.04 (CHCl₃). **¹H-NMR** (400 MHz, CDCl₃): δ (ppm) = 8.21 (d, $J \approx 8.5$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.5$ Hz; 2 Ar-H), 7.06 (d, $J \approx 9.0$ Hz; 2 Ar-H), 6.88 (d, $J \approx 9.0$ Hz; 2 Ar-H), 3.97-3.89 (m, 2H, OCH₂), 1.89-1.77 (m, 1H, CH), 1.69-1.52, 1.38-1.18 (2m; 9H, 1 CH, 4 CH₂), 0.88 (d, $J \approx 6.6$ Hz, 3 H, CH₃), 0.81 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). **¹³C-NMR** (125 MHz, DMSO-d₆): δ (ppm) = 167.14 (COOH), 164.59 (CO), 156.42, 143.80, 136.10, 135.46 (Ar-C), 130.91, 129.44, 122.63, 114.98 (Ar-CH), 66.14 (OCH₂), 38.66, 36.58, 35.60, 24.05 (CH₂), 29.24, 27.36 (CH), 22.56, 22.45, 19.42 (CH₃).

4-[4-(3,7-Dimethyloctyloxy)phenoxy-carbonyl]benzoic acid *rac*-B

This compound was prepared similarly to 4-[4-(*S*)-3,7-Dimethyloctyloxyphenoxy-carbonyl]benzoic acid from 4-(3,7-Dimethyloctyloxy)phenyl 4-formyl benzoate by NaClO₂ oxidation.

Yield: 86 %; colorless crystals, m.p. 159 °C, R_f 0.04 (CHCl₃). **¹H-NMR** (400 MHz, DMSO-d₆): δ (ppm) = 8.22 (d, $J \approx 8.4$ Hz; 2 Ar-H), 8.13 (d, $J \approx 8.3$ Hz; 2 Ar-H), 7.22 (d, $J \approx 9.0$ Hz; 2 Ar-H), 7.00 (d, $J \approx 9.0$ Hz; 2 Ar-H), 4.05-3.97 (m, 2H, OCH₂), 1.79-1.73 (m, 1H, CH), 1.57-1.49, 1.36-1.10 (2m; 9H, 1 CH, 4 CH₂), 0.92 (d, $J \approx 6.5$ Hz, 3 H, CH₃), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH₃). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) = 170.58 (COOH), 164.70 (CO), 157.10, 144.00, 134.20, 133.61 (Ar-C), 130.31, 130.20, 122.25, 115.18 (Ar-CH), 66.77 (OCH₂), 39.26, 37.29, 24.68 (CH₂), 29.85, 27.99 (CH), 22.74, 22.63, 19.67 (CH₃).

1.3 (*S*)-2 and *rac*-2

A mixture of (*S*)-**B** or *rac*-**B** (1.19 g, 3.0 mmol) with the 4-cyano-resorcinol (0.20 g, 1.5 mmol), DCC (0.61 g, 3 mmol) and DMAP (0.073 g, 0.6 mmol) in dry dichloromethane (50

ml) was stirred at room temperature under an argon atmosphere for 24 h. The end of the reaction was monitored by TLC (chloroform). The reaction mixture was filtered on silica gel with CH₂Cl₂ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent and crystallized from ethanol/dichloromethane.

4-Cyano-1,3-phenylene bis[4-(4-(S)-3,7-Dimethyloctyloxyphenoxycarbonyl)benzoate]

(S)-2: Yield: 38%, colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.40-8.31 (m, 8 Ar-H), 7.84 (d, *J* ≈ 8.5 Hz; 1 Ar-H), 7.60 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.38 (dd, *J* ≈ 8.5 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 7.15 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 6.95 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 4.06-3.97 (m, 4H, 2 OCH₂), 1.88-1.80 (m, 2H, 2 CH), 1.69-1.49, 1.39-1.16 (2m, 18H, 2 CH, 8CH₂), 0.95 (d, *J* ≈ 6.5 Hz; 6H, 2 CH₃), 0.88 (d, *J* ≈ 6.6 Hz; 12H, 4 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.40, 163.13, 162.80 (CO), 157.14, 157.11, 154.55, 153.23, 143.96, 143.92, 134.74, 132.52, 104.50 (Ar-C), 134.86, 134.11, 132.12, 130.62, 130.46, 130.40, 122.18, 122.15, 117.25, 115.18 (Ar-CH), 114.70 (CN), 66.78 (OCH₂), 39.23, 37.27, 36.19, 24.64 (CH₂), 29.84, 27.96 (CH), 22.69, 22.59, 19.64 (CH₃). C₅₅H₆₁NO₁₀ (896.08); Anal. Calc.: C, 73.72; H, 6.86; N, 1.56. Found: C, 73.46; H, 6.64; N, 1.53%.

4-Cyano-1,3-phenylene bis[4-(4-(3,7-Dimethyloctyloxyphenoxy)carbonyl)benzoate]

rac-2: Yield: 35%, colorless crystals. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.40-8.31 (m, 8 Ar-H), 7.84 (d, *J* ≈ 8.5 Hz; 1 Ar-H), 7.60 (d, *J* ≈ 2.1 Hz; 1 Ar-H), 7.38 (dd, *J* ≈ 8.5 Hz and *J* ≈ 2.1 Hz; 1 Ar-H), 7.15 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 6.95 (d, *J* ≈ 8.9 Hz; 4 Ar-H), 4.06-3.97 (m, 4H, 2 OCH₂), 1.88-1.80 (m, 2H, 2 CH), 1.69-1.49, 1.39-1.16 (2m, 18H, 2 CH, 8CH₂), 0.95 (d, *J* ≈ 6.6 Hz; 6H, 2 CH₃), 0.88 (d, *J* ≈ 6.6 Hz; 12H, 4 CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) = 164.40, 163.13, 162.80 (CO), 157.14, 157.11, 154.56, 153.23, 143.96, 143.92, 134.74, 132.52, 104.50 (Ar-C), 134.86, 134.11, 132.12, 130.62, 130.46, 130.40, 122.18, 122.15, 117.25, 115.18 (Ar-CH), 114.53 (CN), 66.78 (OCH₂), 39.23, 37.27, 36.19, 24.64 (CH₂), 29.85, 27.96 (CH), 22.69, 22.59, 19.64 (CH₃). C₅₅H₆₁NO₁₀ (896.08); Anal. Calc.: C, 73.72; H, 6.86; N, 1.56. Found: C, 73.41; H, 6.58; N, 1.37%.

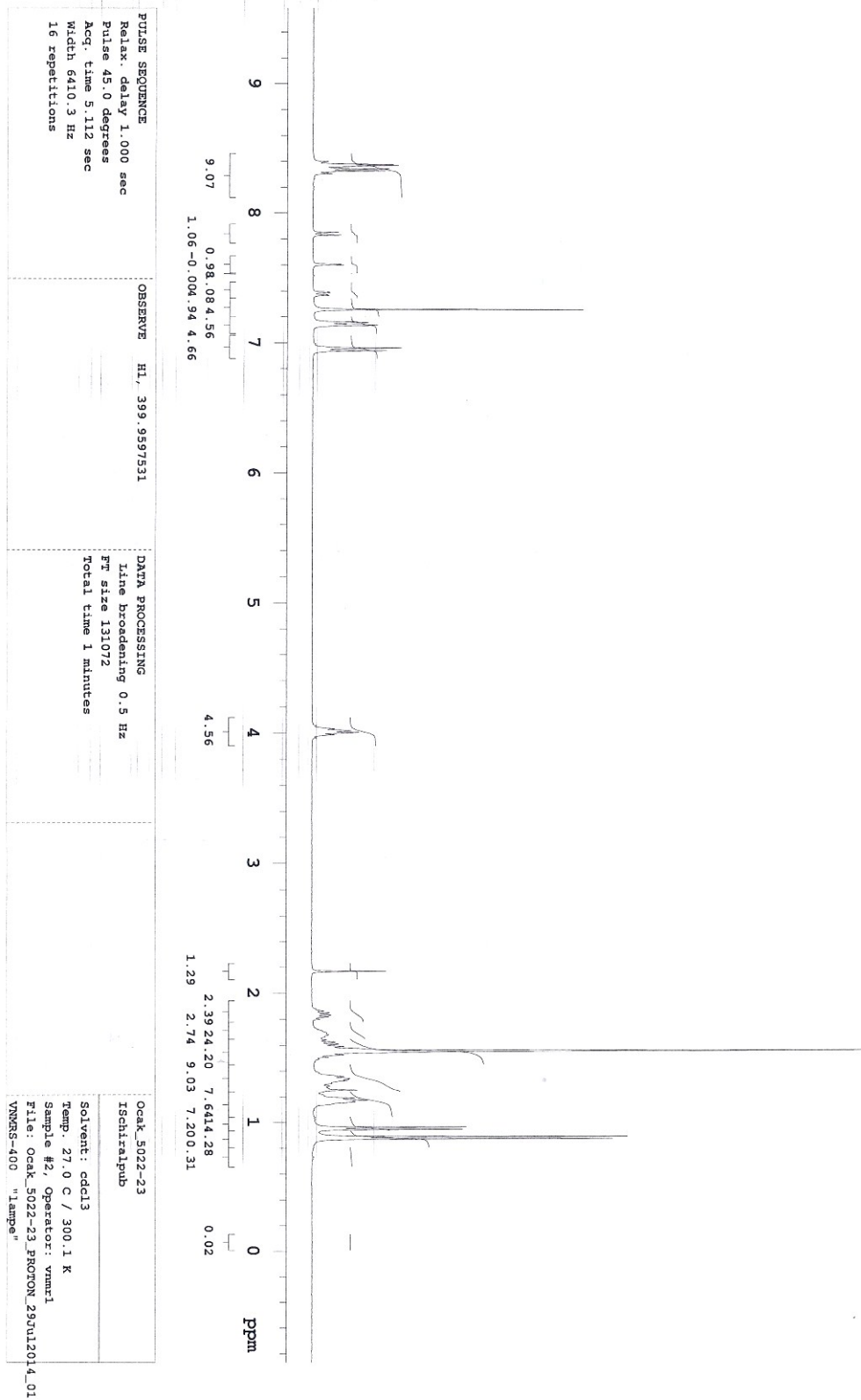


Figure S1. ^1H -NMR spectrum of compound (*S*)-2 (CDCl_3 , 400 MHz).

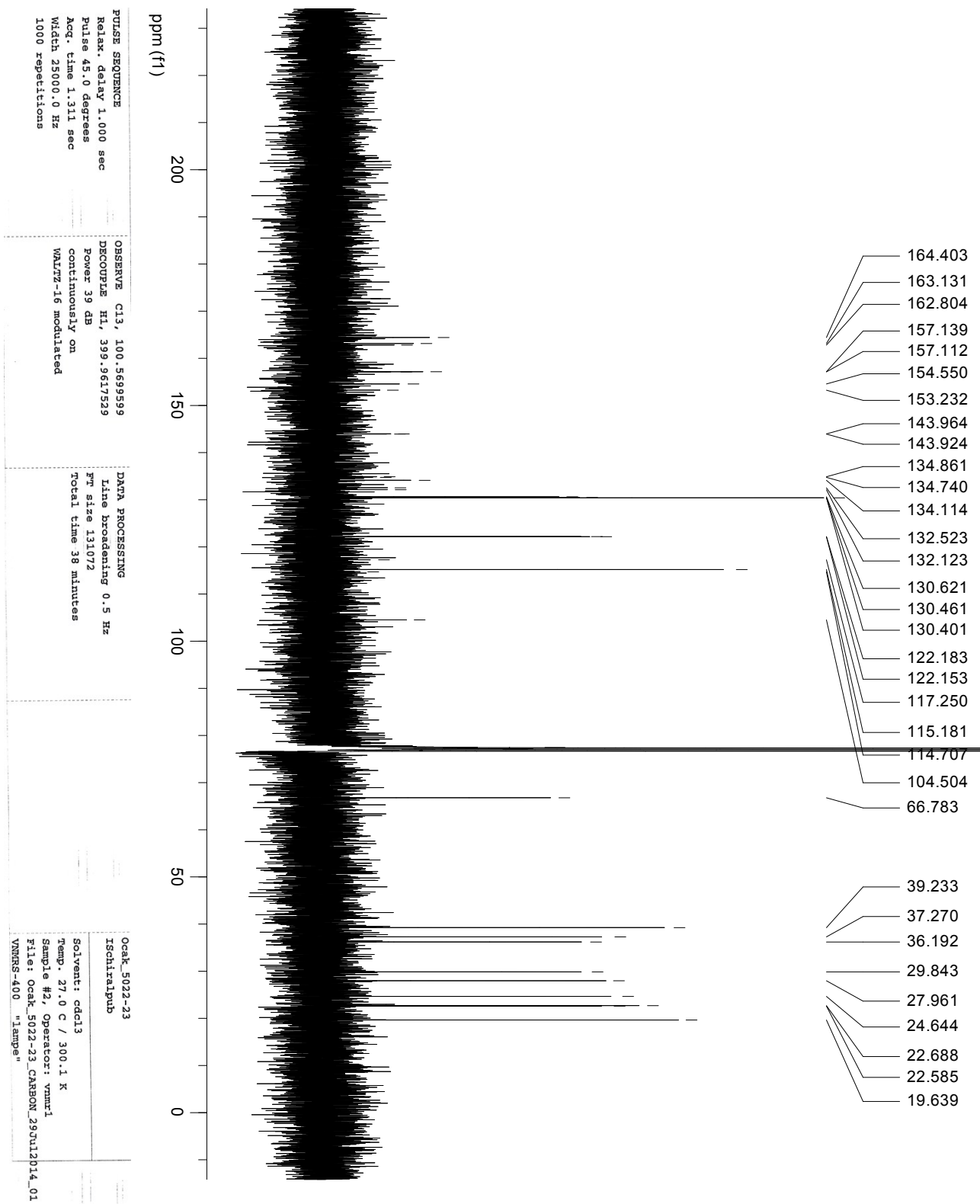


Figure S2. ^{13}C -NMR spectrum of compound (*S*)-2 (CDCl_3 , 100 MHz).

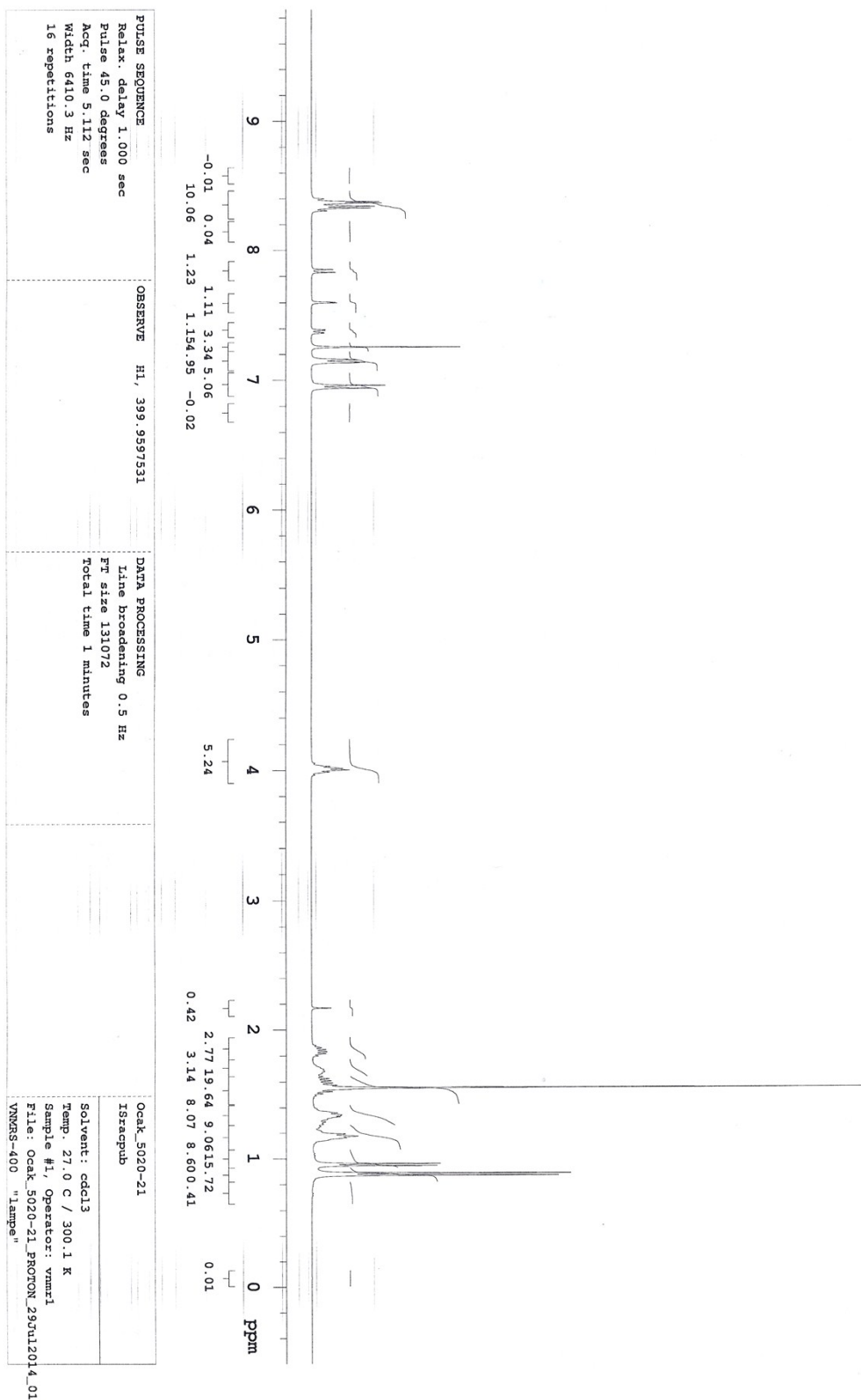


Figure S3. $^1\text{H-NMR}$ spectrum of compound *rac-2* (CDCl_3 , 400 MHz).

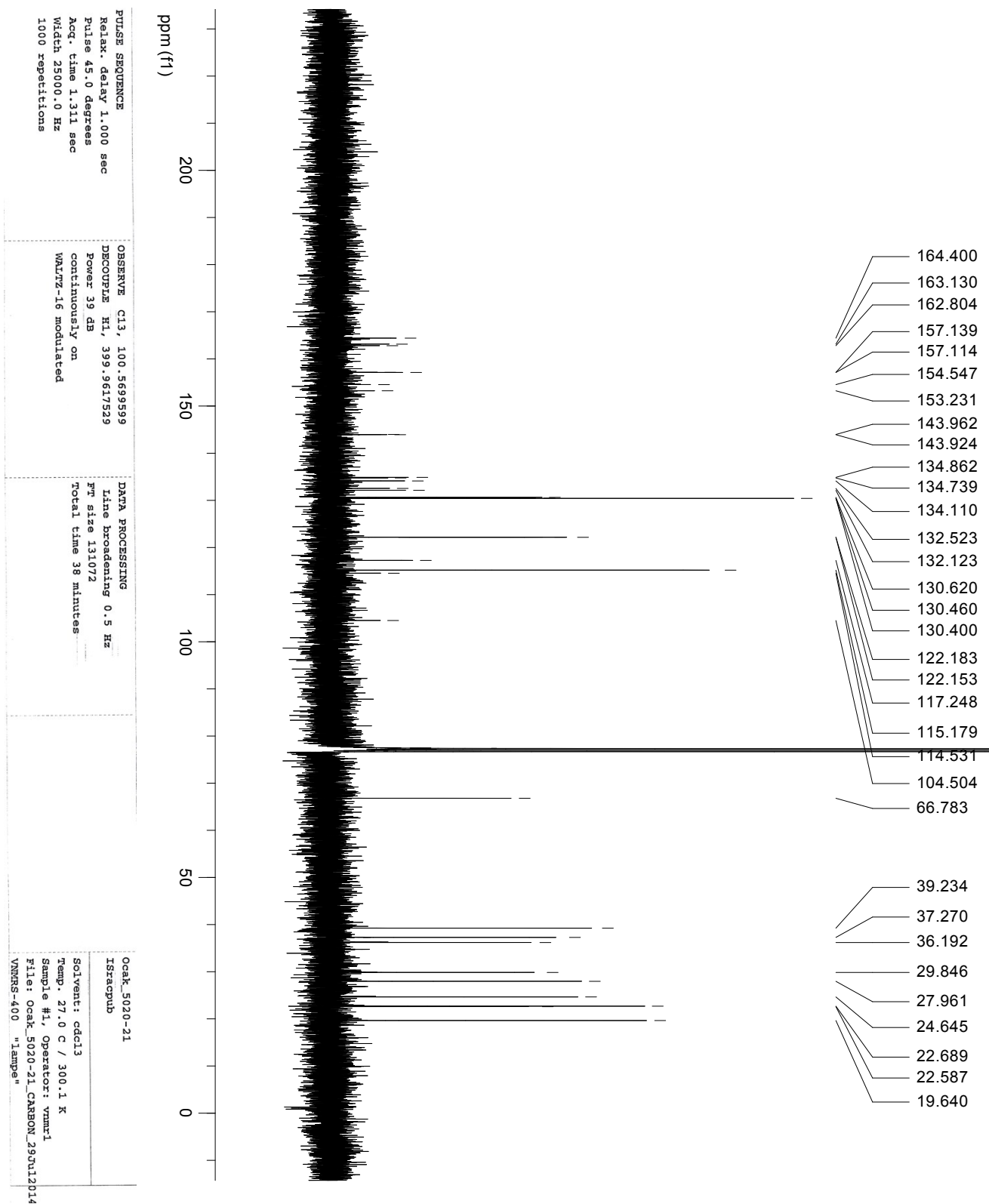


Figure S4. ¹³C-NMR spectrum of compound *rac-2* (CDCl₃, 100 MHz).

2. Additional Data

2.1 Textures

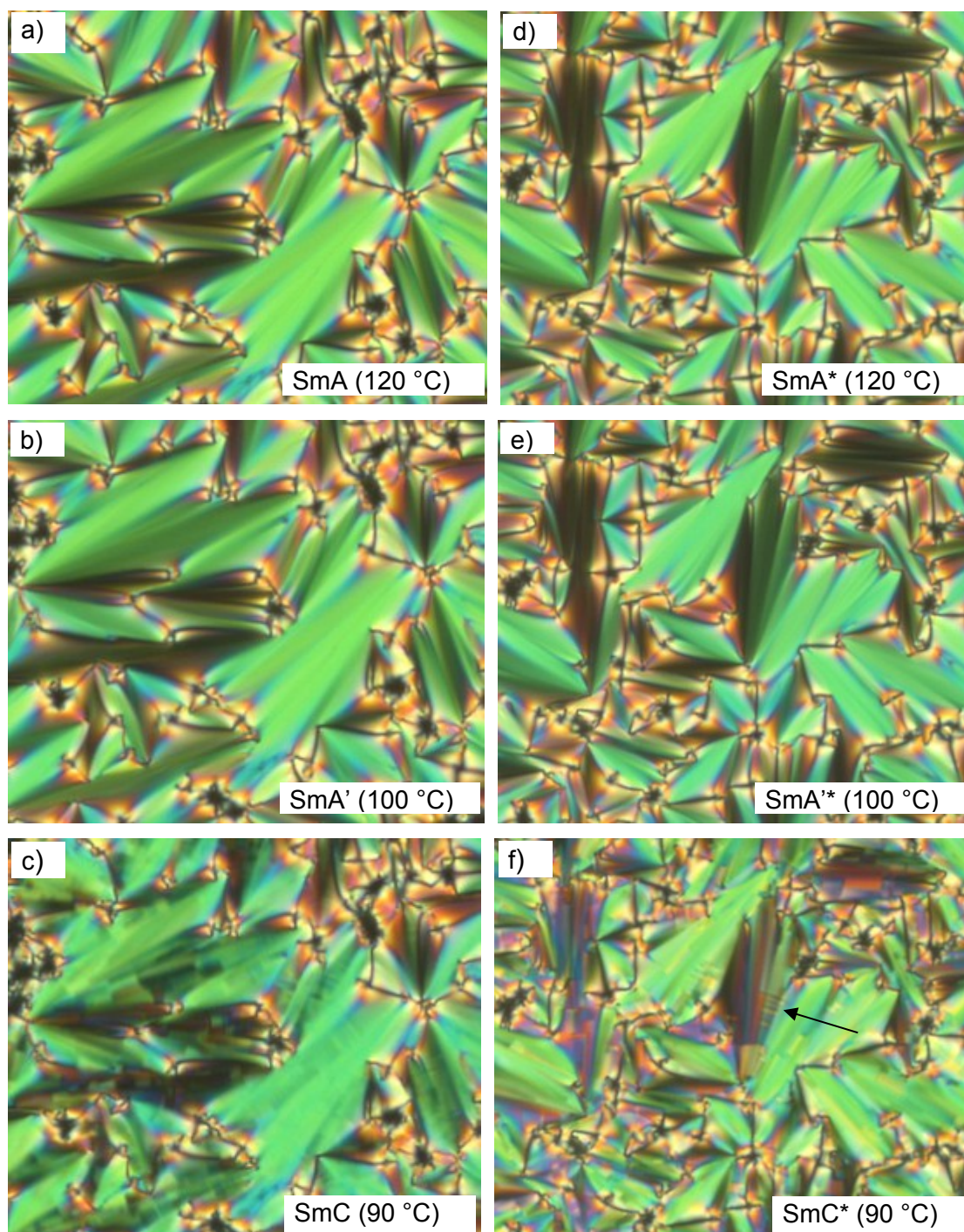


Figure S5. Textures of a-c) *rac*-2 and d-f) (*S*)-2 in the SmA, SmA' and SmC phases, as observed between crossed polarizers in a planar cell (6 μm ITO cell); the arrow in f) indicates the stripe pattern due to helix formation in the SmC* phase.

2.2 Switching current curves and electro-optical data

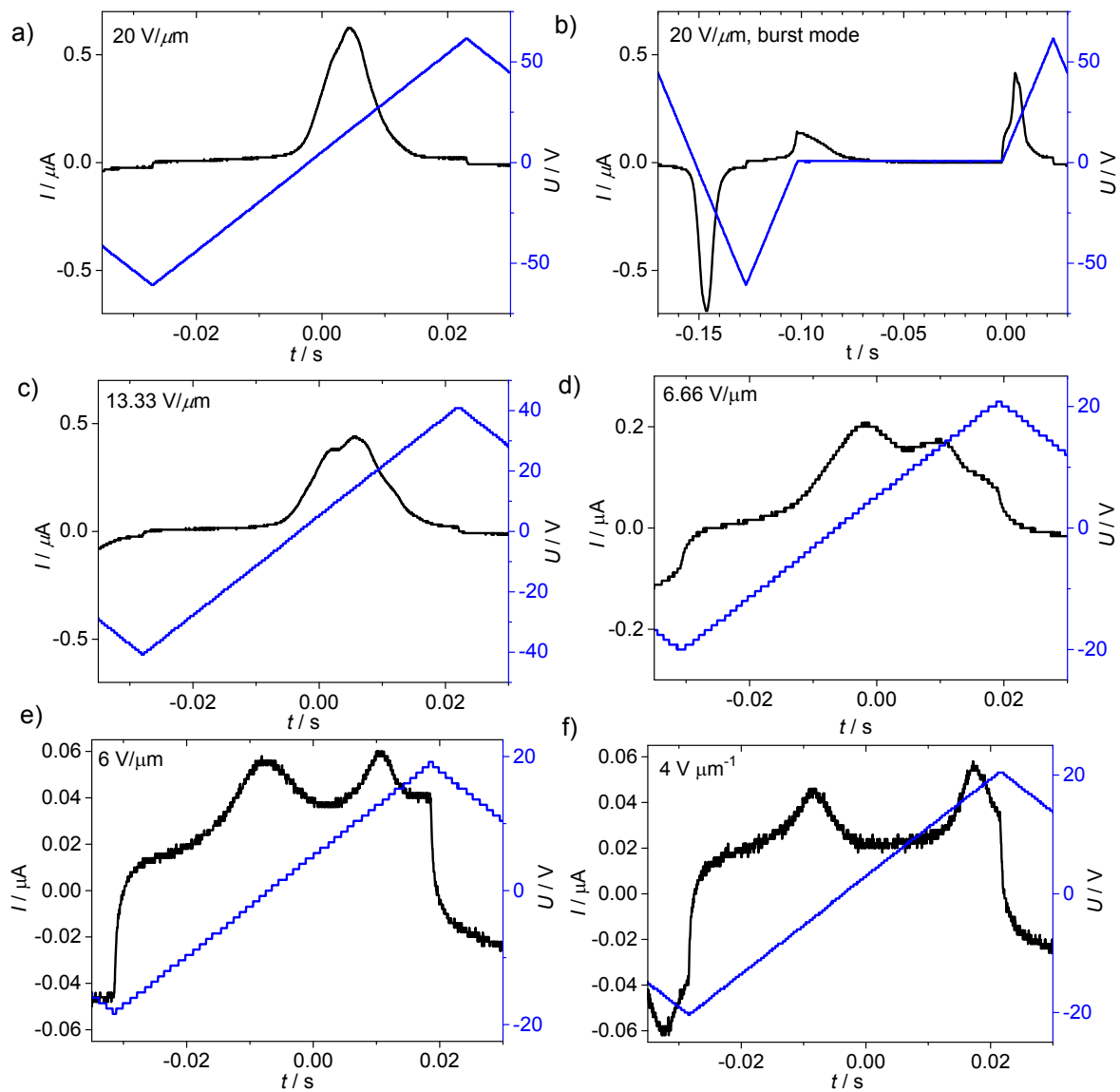


Figure S6. Polarization current responses obtained for *rac-2* under a triangular wave field (10 Hz, 5 k Ω) in a 6 μm ITO cell in the SmC_s ' P_A phase at $T = 74$ $^\circ\text{C}$; a,c-f) at different E -field strengths and b) under a triangular wave field with additional relaxation time at 0V; different scales were used for the Y-axes.

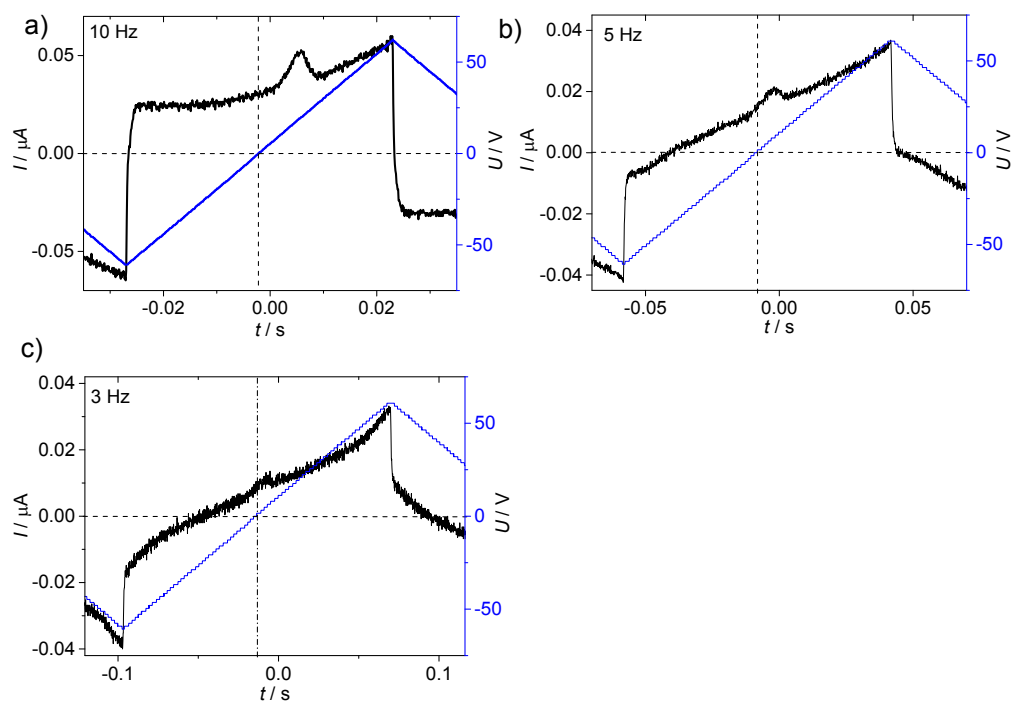


Figure S7. Polarization current peak obtained in (S)-2 under a triangular wave field ($20 \text{ V}_{\text{pp}} \mu\text{m}^{-1}$, 10 Hz, $5 \text{ k}\Omega$) in a $6 \mu\text{m}$ ITO cell in the SmC^* phase at $T = 90 \text{ }^\circ\text{C}$ as observed using different frequencies.

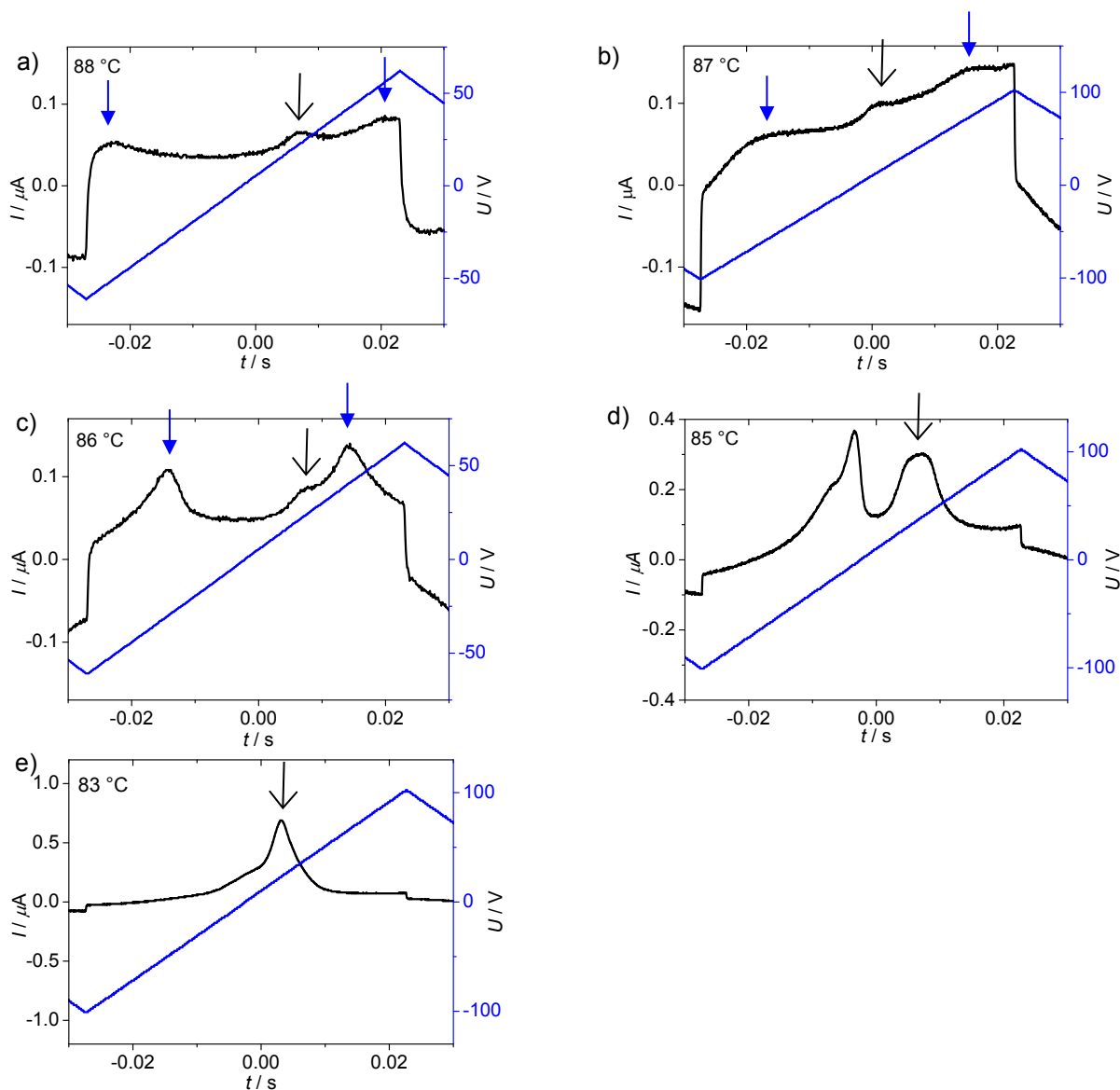


Figure S8. Polarization current responses obtained for (*S*)-**2** under a triangular wave field ($20 \text{ V}_{\text{pp}} \mu\text{m}^{-1}$, 10 Hz, 5 k Ω) in a 6 μm ITO cell at the transition from a) SmC* to b-e) SmCP_R* with decreasing temperature.

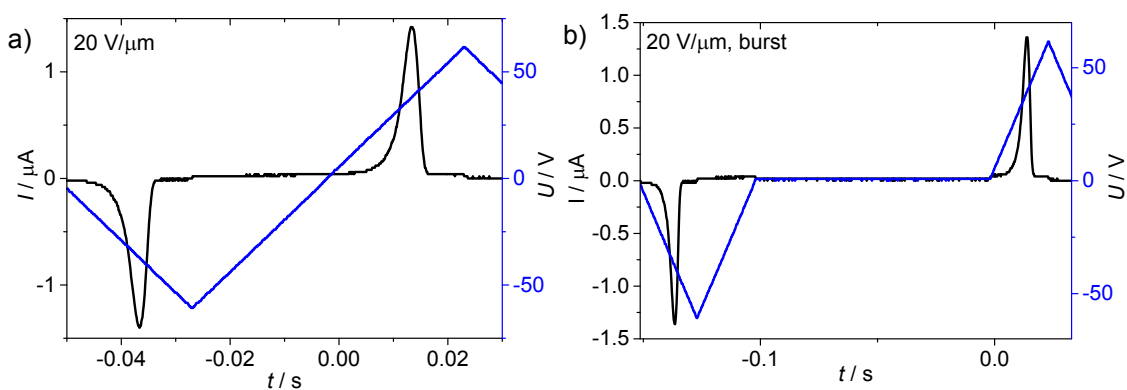


Figure S9. Polarization current responses obtained for (*S*)-**2** under a triangular wave field ($20 \text{ V}_{\text{pp}} \mu\text{m}^{-1}$, 10 Hz, 5 k Ω) in a 6 μm ITO cell in the SmC_s'P_F* phase at $T = 74 \text{ }^\circ\text{C}$ a) under a simple triangular wave field and b) with additional relaxation time at 0V.

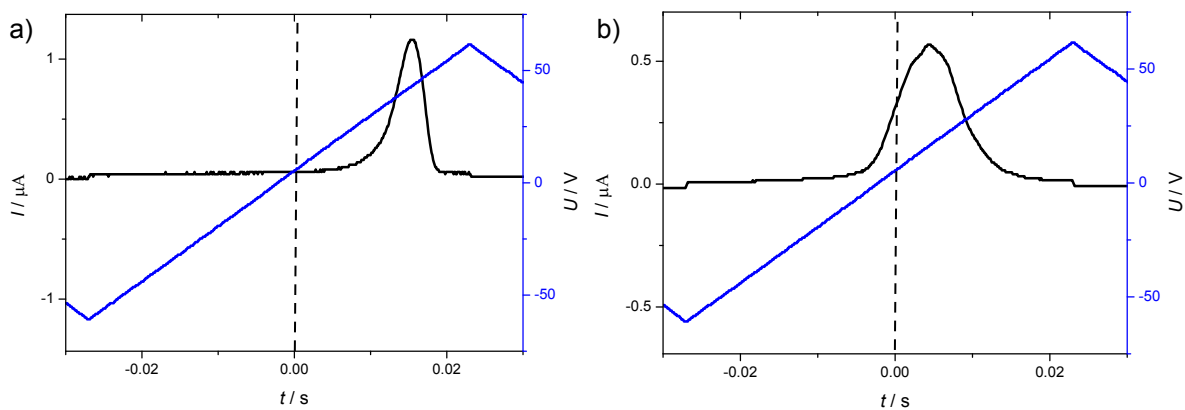


Figure S10. Polarization current responses obtained for a) *(S)*-**2** and b) *rac*-**2** under a triangular wave field ($20 \text{ V}_{\text{pp}} \mu\text{m}^{-1}$, 10 Hz, 5 k Ω) in a 6 μm ITO cell in the $\text{SmC}_a' \text{P}_A^{(*)}$ phase at $T = 70 \text{ }^\circ\text{C}$.

Table S1. Temperature dependence of the spontaneous polarization of *rac*-**2** and *(S)*-**2**.

$T / ^\circ\text{C}$	P_s / nCcm^{-2}	
	<i>rac</i> - 2	<i>(S)</i> - 2
92		1.3
90		3.3
88		6.6
87		30
86	106	
85	109	121
83	146	203
80	263	250
74	298	275
64	305	302

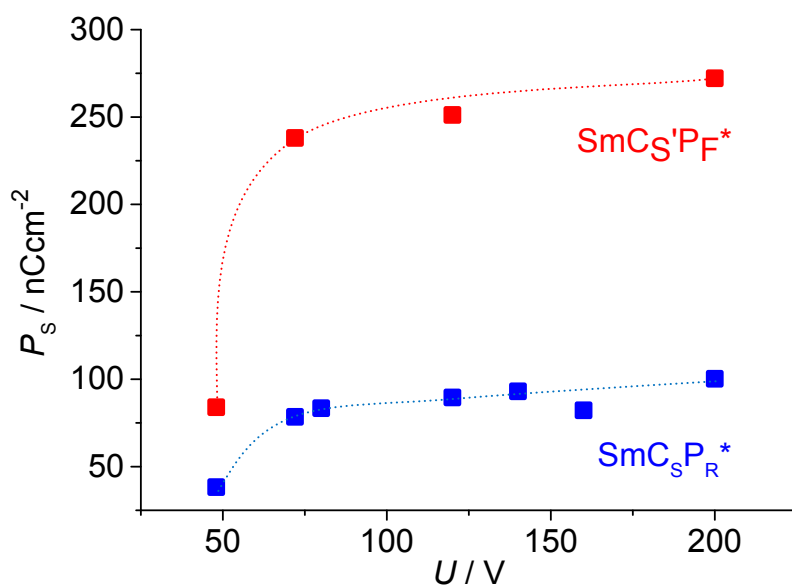


Figure S11. Field strength dependence of the polarization current responses of (S)-2 in the SmC_sP_R* phase at $T = 83$ °C and in the SmC_s'P_F* phase at $T = 74$ °C as observed under a triangular wave field (10 Hz, 5 kΩ) in a 6 μm ITO cell.

References

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