Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Dark conglomerate phases of azobenzene derived bent-core mesogens – Relations between molecular structure and mirror symmetry breaking in soft matter

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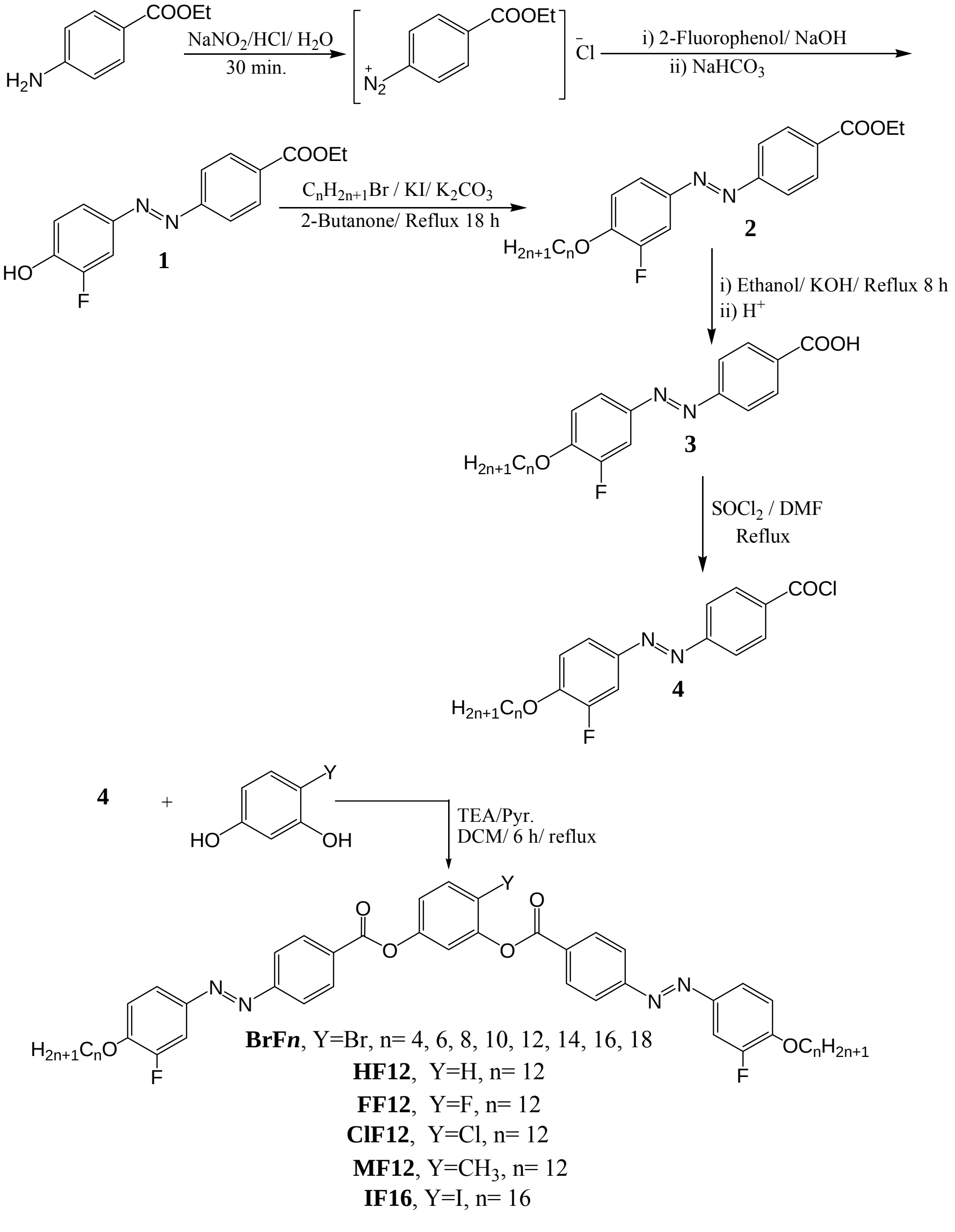
Content

1. Synthesis and Analytical Data

1.1 Characterization methods

Thin layer chromatography (TLC) was performed on aluminium sheet precoated with silica gel. Analytical quality chemicals were obtained from commercial sources and used as obtained. The solvents were dried using the standard methods when required. The purity and the chemical structures of all compounds synthesized were confirmed by the spectral data. The structure characterization of the synthesized bent-core compounds is based on ^{1}H-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

1. 2. Synthesis of compounds BrF*n* and its related analogues



Scheme S1. Synthesis of the new bent-core molecules.

The synthesis of the bent-core compounds under investigation is shown in Scheme 1. The intermediates compounds 4-(4-*n*-alkyloxy-3-fluorophenylazo)benzoates **2** and 4-(4-*n*-alkyloxy-3-fluorophenylazo)benzoic acids **3** were synthesized according to the methods described before [S1]. The final bent-core compounds were prepared as follows. 2.4 mmol of the appropriate acid **3** was heated under reflux with thionyl chloride (3 mL) and a catalytic amount of *N,N*-dimethylformamide (DMF) for one hour. The excess of thionyl chloride was removed by distillation under reduced pressure. The acid chloride (**4**) was then dissolved in dry dichloromethane (DCM, 20 mL). To this solution, the 4-substituted resorcinol (1.2 mmol) previously dissolved in DCM (10 mL) was added, followed by addition of triethylamine (TEA, 2.8 mmol) and a catalytic amount of pyridine. The solution was then refluxed for 6 hours under an argon atmosphere. After cooling the reaction mixture to the room temperature, it was washed with 10% HCl (2 × 50 mL) and several times with cold water then extracted with DCM (3 × 50 mL) and finally dried over anhydrous sodium sulphate. The crude residue obtained after removal of solvent was chromatographed on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded an orange material which was recrystallized twice from chloroform/ethanol mixture to give the final bent core compounds.

1.2.1. ***4-Bromo-1,3-phenylene bis-[4-(4-butyloxy-3-fluorophenylazo)benzoate],*** **BrF4*:***
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.33 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.03-7.99 (m, 4H, Ar-H), 7.82-7.78 (m, 2H, Ar-H), 7.78 – 7.70 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.15 (t, *J* = 6.5 Hz, 4H, -$O\underline{CH_2}CH_2$), 1.93 – 1.82 (m, 4H, -$OCH_2\underline{CH_2}$), 1.62 – 1.48 (m, 4H, CH_2), 1.01 (t, *J* = 7.4 Hz, 6H, CH_3). Elemental Analysis: Calc. for $\mathbf{C_{40}H_{35}BrF_2N_4O_6}$ C, 61.15; H, 4.49; N, 7.13. Found C, 61.16; H, 4.47; N, 7.12 %.

1.2.2. ***4-Bromo-1,3-phenylene bis-[4-(3-fluoro-4-hexyloxyphenylazo)benzoate]],*** **BrF6*:***
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.31 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.02-7.97 (m, 4H, Ar-H), 7.83 – 7.78 (m, 2H, Ar-H), 7.75 – 7.69 (m, 3H, Ar-H), 7.34 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.14 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 7.08 (t, *J* = 8.2 Hz, 2H, Ar-H), 4.12 (t, *J* = 6.5 Hz, 4H, -$O\underline{CH_2}CH_2$), 1.91 – 1.82 (m, 4H, -$OCH_2\underline{CH_2}$), 1.55 – 1.30 (m, 12 H, CH_2), 0.90 (t, *J* = 6.9 Hz, 6H, CH_3). Elemental Analysis: Calc. for $\mathbf{C_{44}H_{43}BrF_2N_4O_6}$ C, 62.78; H, 5.15; N, 6.66. Found C, 62.76; H, 5.15; N, 6.66 %.

1.2.3. ***4-Bromo-1,3-phenylene bis-[4-(3-fluoro-4-octyloxyphenylazo)benzoate],*** **BrF8*:***
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.03-7.96 (m, 4H, Ar-H), 7.86-7.81 (m, 2H, Ar-H), 7.78 – 7.67 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.15 (dd, *J* = 7.7, 3.9 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.5 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -$O\underline{CH_2}CH_2$), 1.97 – 1.81 (m, 4H, - $OCH_2\underline{CH_2}$), 1.62 – 1.11 (m, 20H, CH_2), 0.90 (t, *J* = 6.6 Hz, 6H, CH_3). Elemental Analysis: Calc. for $\mathbf{C_{48}H_{51}BrF_2N_4O_6}$ C, 64.21; H, 5.73; N, 6.24. Found C, 64.20; H, 5.73; N, 6.24 %.

1.2.4. ***4-Bromo-1,3-phenylene bis-[4-(4-decyloxy-3-fluorophenylazo)benzoate],*** **BrF10*:***
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.03-7.96 (m, 4H, Ar-H), 7.86-7.81 (m, 2H, Ar-H), 7.78–7.70 (m, 3H, Ar-H), 7.35 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -$O\underline{CH_2}CH_2$), 1.93 – 1.81 (m, 4H, - $OCH_2\underline{CH_2}$), 1.57 – 1.19 (m, 28H, CH_2), 0.88 (t, *J* = 6.8 Hz, 6H, CH_3). Elemental Analysis: Calc. for $\mathbf{C_{52}H_{59}BrF_2N_4O_6}$ C, 65.47; H, 6.23; N, 5.87. Found C, 65.47; H, 6.21; N, 5.87 %.

1.2.5. ***4-Bromo-1,3-phenylene bis-[4-(4-dodecyloxy-3-fluorophenylazo)benzoate],*** **BrF12*:***

^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.39 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.03-7.96 (m, 4H, Ar-H), 7.86-7.81 (m, 2H, Ar-H), 7.78–7.70 (m, 3H, Ar-H), 7.35 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.94 – 1.81 (m, 4H, - OCH$_2\underline{CH_2}$), 1.58 – 1.20 (m, 36H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{56}H_{67}BrF_2N_4O_6$** C, 66.59; H, 6.69; N, 5.55. Found C, 66.57; H, 6.69; N, 5.57 %.

1.2.6. ***4-Bromo-1,3-phenylene bis-[4-(3-fluoro-4-tetradecyloxyphenylazo)benzoate],*** **BrF14*:***

^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.39 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.03-7.96 (m, 4H, Ar-H), 7.86-7.81 (m, 2H, Ar-H), 7.78–7.70 (m, 3H, Ar-H), 7.35 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.5 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.93 – 1.81 (m, 4H, - OCH$_2\underline{CH_2}$), 1.58 – 1.19 (m, 44H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{60}H_{75}BrF_2N_4O_6$** C, 67.59; H, 7.09; N, 5.26. Found C, 67.58; H, 7.11; N, 5.29 %.

1.2.7. ***4-Bromo-1,3-phenylene bis-[4-(3-fluoro-4-hexadecyloxyphenylazo)benzoate],*** **BrF16*:***

^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.38 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.32 (d , *J* = 8.6 Hz, 2H, Ar-H), 8.02–7.95 (m, 4H, Ar-H), 7.85–7.79 (m, 2H, Ar-H), 7.77–7.70 (m, 3H, Ar-H), 7.35 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.2 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.91–1.83 (m, 4H, -OCH$_2\underline{CH_2}$), 1.56–1.20 (m, 52H, CH$_2$), 0.88 (t, *J* = 6.9 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{64}H_{83}BrF_2N_4O_6$** C, 68.49; H, 7.45; N, 4.99. Found C, 68.50; H, 7.44; N, 4.50 %.

1.2.8. ***4-Bromo-1,3-phenylene bis-[4-(3-fluoro-4-octadecyloxyphenylazo)benzoate],*** **BrF18*:***

^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.39 (d, J = 8.8 Hz, 2H, Ar-H), 8.33 (d, J = 8.8 Hz, 2H, Ar-H), 8.03-7.98 (m, 4H, Ar-H), 7.85-7.79 (m, 2H, Ar-H), 7.78–7.70 (m, 3H, Ar-H), 7.35 (d, J = 2.6 Hz, 1H, Ar-H), 7.16 (dd, J = 8.8, 2.6 Hz, 1H, Ar-H), 7.10 (t, J = 8.4 Hz, 2H, Ar-H), 4.14 (t, J = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.98–1.82 (m, 4H, -OCH$_2\underline{CH_2}$), 1.62–1.14 (m, 60H, CH$_2$), 0.88 (t, J = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{68}H_{91}BrF_2N_4O_6$** C, 69.31; H, 7.78; N, 4.75. Found C, 69.32; H, 7.78; N, 4.74 %.

1.2.9. ***1,3-Phenylene bis-[4-(4-dodecyloxy-3-fluorophenylazo)benzoate],*** **HF12*:***

^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.37 – 8.32 (m, 4H, Ar-H), 8.00 – 7.95 (m, 4H, Ar-H), 7.85 – 7.79 (m, 2H, Ar-H), 7.74 (dd, *J* = 11.9, 2.3 Hz, 2H, Ar-H), 7.52 (t, *J* = 8.2 Hz, 1H, Ar-H), 7.28 – 7.25 (m, *J* = 3.8 Hz, 1H, Ar-H), 7.22 (dd, *J* = 8.2, 2.2 Hz, 2H, Ar-H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.95 – 1.82 (m, 4H, -OCH$_2\underline{CH_2}$), 1.57 – 1.18 (m, 36H, CH$_2$), 0.88 (t, *J* = 6.9 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{56}H_{68}F_2N_4O_6$** C, 72.23; H, 7.36; N, 6.02. Found C, 72.30; H, 7.35; N, 6.12 %.

1.2.10. ***4-Chloro-1,3-phenylene bis-[4-(4-dodecyloxy-3-fluorophenylazo)benzoate],*** **ClF12*:***

^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.35 (dd, *J* = 20.6, 8.5 Hz, 4H, Ar-H), 8.05–7.91 (m, *J* = 8.3, 5.5 Hz, 4H, Ar-H), 7.82 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.74 (d, *J* = 11.9 Hz, 2H, Ar-H), 7.57 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.35 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 7.10 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 1.95 – 1.80 (m, 4H, -OCH$_2\underline{CH_2}$), 1.63 – 1.17 (m, 36H, CH$_2$), 0.88 (t, *J* = 6.7 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{56}H_{67}ClF_2N_4O_6$** C, 69.66; H, 6.99; N, 5.80. Found C, 69.78; H, 6.93; N, 5.87 %.

1.2.11. ***4-Methyl-1,3-phenylene bis-[4-(4-dodecyloxy-3-fluorophenylazo)benzoate],*** **MF12*:***

^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.42 – 8.27 (m, *J* = 10.6, 8.6 Hz, 4H, Ar-H), 8.04 – 7.93 (m, *J* = 8.3, 6.5 Hz, 4H, Ar-H), 7.82 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.74 (dd, *J* = 11.9, 2.4 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.19 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.17 – 7.03 (m, 3H, Ar-H), 4.14 (t, J = 6.5 Hz, 4H, 4H, -O<u>CH2</u>CH$_2$), 2.30 (s, 3H, 4H, CH$_3$), 1.95 – 1.80 (m, 4H, 4H, -OCH$_2$<u>CH2</u>), 1.63 – 1.17 (m, 36H, 4H, CH$_2$), 0.88 (t, J = 6.7 Hz, 6H, 4H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{57}H_{70}F_2N_4O_6}$ C, 72.43; H, 7.46; N, 5.93. Found C, 72.51; H, 7.51; N, 5.93 %.

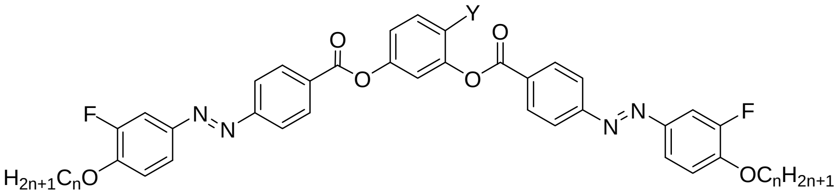
1.2.12. ***4-Fluoro-1,3-phenylene bis-[4-(4-dodecyloxy-3-fluorophenylazo)benzoate],*** **FF12*:***
^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.40 – 8.24 (m, 4H, Ar-H), 8.04 – 7.93 (m, 4H, Ar-H), 7.83 (d, J = 8.4 Hz, 2H, Ar-H), 7.74 (d, J = 12.1 Hz, 2H, Ar-H), 7.35 – 7.27 (m, 2H, Ar-H), 7.22 – 7.15 (m, 1H, Ar-H), 7.10 (t, J = 8.6 Hz, 2H, Ar-H), 4.14 (t, J = 6.5 Hz, 4H, -O<u>CH2</u>CH$_2$), 1.95 – 1.78 (m, 4H, -OCH$_2$<u>CH2</u>), 1.62 – 1.19 (m, 36H, CH$_2$), 0.88 (t, J = 6.7 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{56}H_{67}F_3N_4O_6}$ C, 70.86; H, 7.11; N, 5.90. Found C, 70.78; H, 6.98; N, 6.01 %.

1.2.13. ***4-Iodo-1,3-phenylene bis-[4-(3-fluoro-4-hexadecyloxyphenylazo)benzoate],*** **IF16*:***
^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.40 (d, J = 8.5 Hz, 2H, Ar-H), 8.33 (d, J = 8.5 Hz, 2H, Ar-H), 8.09–7.89 (m, 5H, Ar-H), 7.80 (d, J = 8.7 Hz, 2H, Ar-H), 7.78–7.67 (m, 2H, Ar-H), 7.33 (d, J = 2.6 Hz, 1H, Ar-H), 7.10 (t, J = 8.0 Hz, 2H, Ar-H), 7.04 (dd, J = 8.7, 2.6 Hz, 1H, Ar-H), 4.14 (t, J = 6.5 Hz, 4H, O<u>CH2</u>CH$_2$), 1.98–1.77 (m, 4H, OCH$_2$<u>CH2</u>), 1.65–1.03 (m, 52H, CH$_2$), 0.88 (t, J = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{64}H_{83}F_2IN_4O_6}$ C, 65.74; H, 7.15; N, 4.79. Found C, 65.70; H, 7.21; N, 4.81 %.

2. Additional Data of compounds BrF*n*

2.1 Phase transitions and DSC Data

Table S1. Phase transition temperatures (T/°C), mesophase types, and transition enthalpies [ΔH/kJ.mol^{-1}] of compounds **BrF*n***, **IF*n***, **HF12**, **FF12**, **ClF12** and **MF12** as observed in the second heating scan (10 K min^{-1}, peak temperatures).



Compd.	Y	*n*	Phase transitions
BrF4	Br	4	Cr 156 [57.3] Iso
BrF6	Br	6	DC 106 [27.4] Cr 126 [8.9][a] Iso
BrF8	Br	8	DC 104 [23.5] Iso
BrF10	Br	10	DC 106 [24.3] Iso
BrF12	Br	12	DC 106 [24.8] Iso
BrF14	Br	14	DC 106 [24.7] Iso
BrF16	Br	16	Cr 100 [28.5] Iso
BrF18	Br	18	Cr 102 [33.7] Iso
IF16	I	16	Cr 111 [30.2] Iso
HF12	H	12	Cr$_1$ 81 [21.2] Cr$_2$ 138 [40.5] Iso
FF12	F	12	Cr 120 [62.4] Iso
ClF12	Cl	12	Cr 115 [49.6] Iso
MF12	CH$_3$	12	Cr 90 [41.4] Iso

[a] Partially crystallized sample.

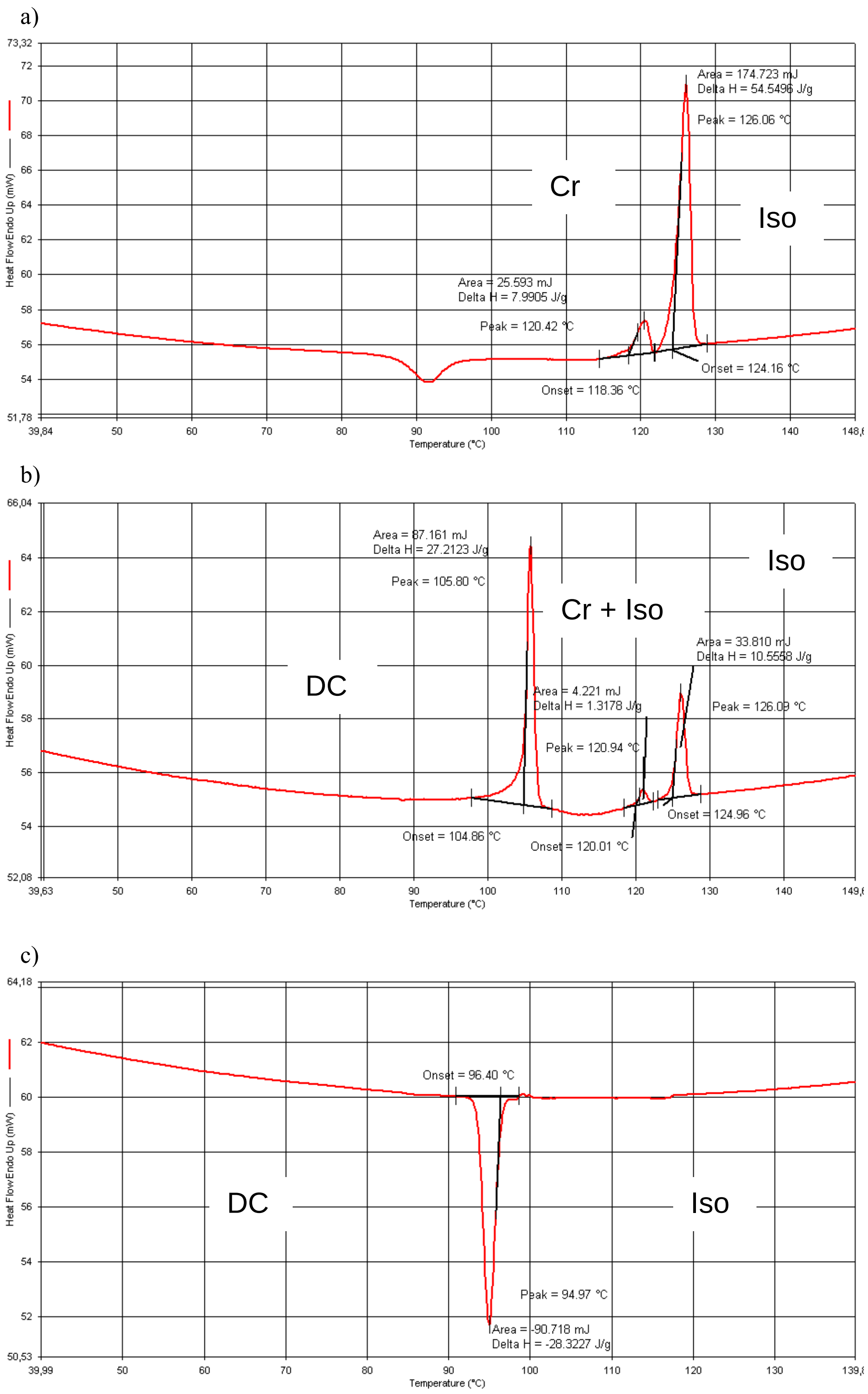
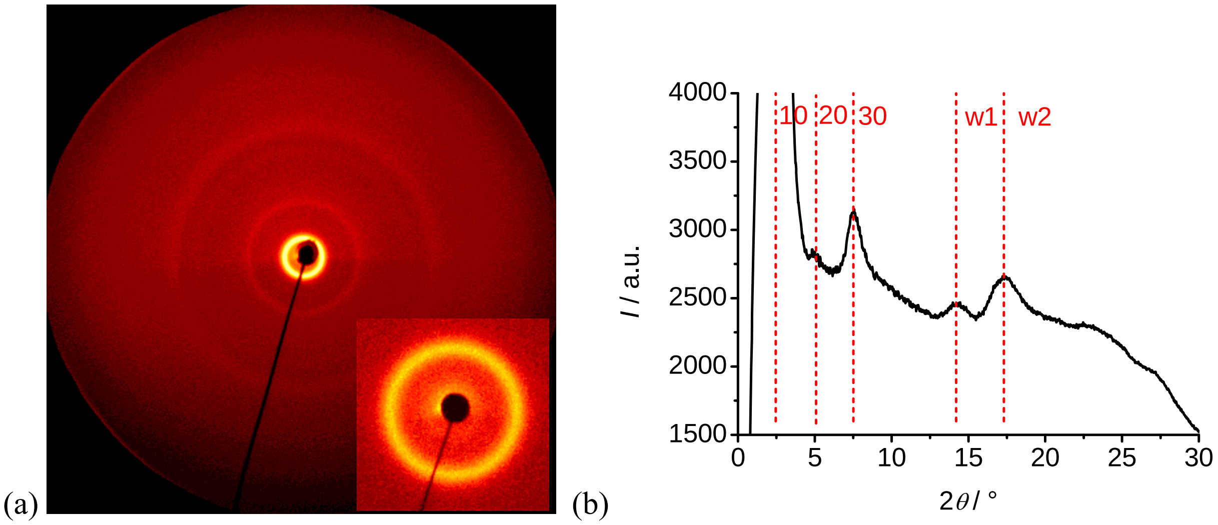


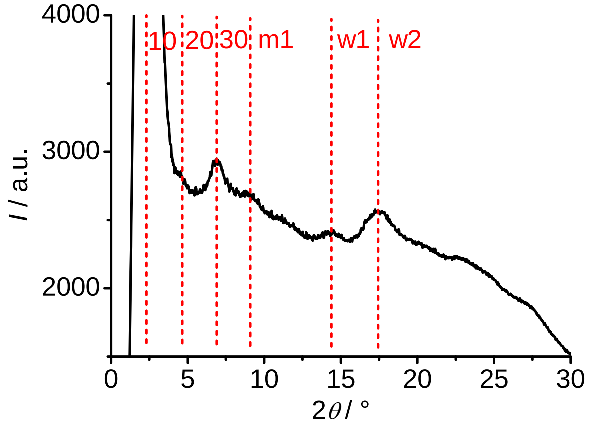
Figure S1. DSC heating and cooling traces of compound **BrF6:** a) and c) first and second heating runs with 10 K min^{-1} and b) first cooling run with 10 K min^{-1}.

2.2 XRD data



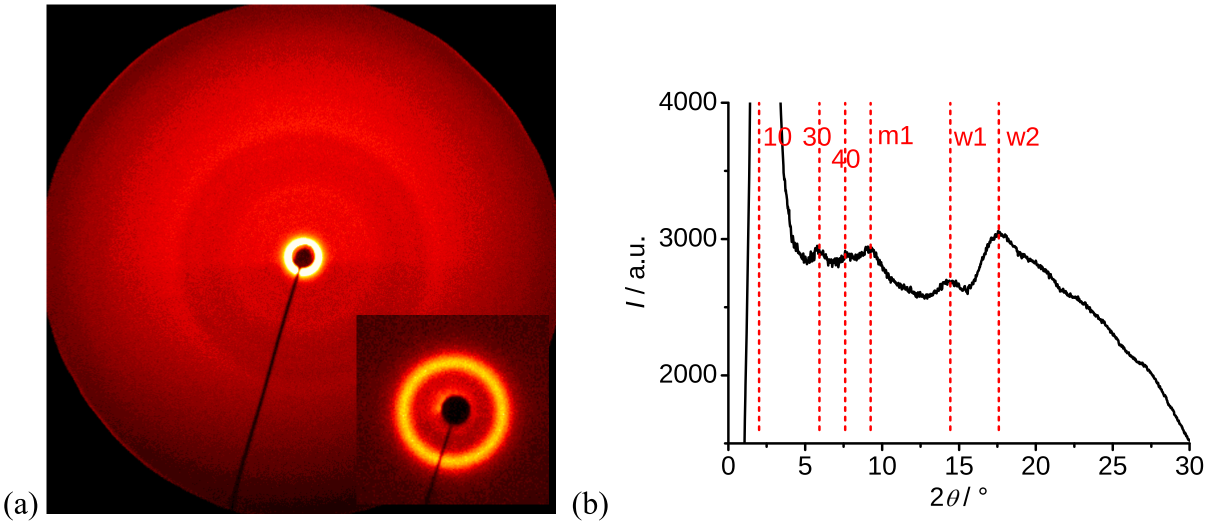
Reflex	$2\theta/°$	d/nm	d_{calc}/nm	d_{obs}-d_{calc}/nm
10	2.55	3.46		
20	5.09	1.74	1.73	0.01
30	7.50	1.18	1.15	0.03
w1	14.20	0.62		
w2	17.30	0.51		

Figure S2. a) 2D XRD pattern of the DC phase of **BrF6** at $T = 90$ °C, the inset shows the small angle region; b) diffraction intensity profile as a function of 2θ with the visible reflections.



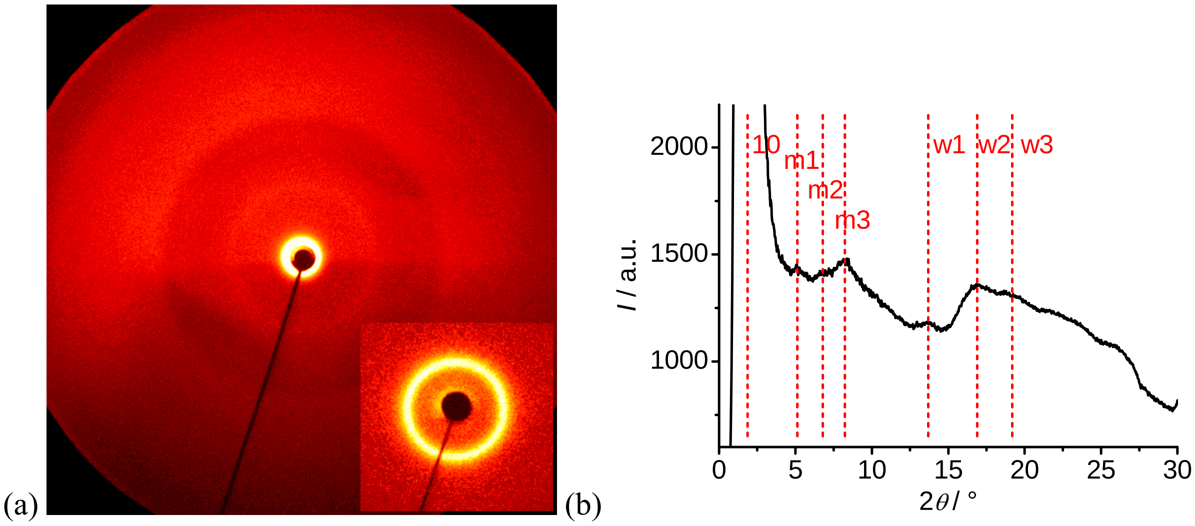
Reflex	$2\theta/°$	d/nm	d_{calc}/nm	d_{obs}-d_{calc}/nm
10	2.34	3.78		
20	4.57	1.93	1.89	0.04
30	6.80	1.30	1.26	0.04
m1	8.80	1.01		
w1	14.30	0.62		
w2	17.40	0.51		

Figure S3. Diffraction intensity profile as a function of 2θ with the visible reflections of the DC phase of **BrF8** at $T = 90$ °C, (c) diffraction intensity profile as a function of 2θ with the visible reflections.



Reflex	$2\theta/°$	d/nm	d_{calc}/nm	d_{obs}-d_{calc}/nm
10	2.00	4.41		
30	5.90	1.50	1.47	0.03
40	7.83	1.13	1.10	0.03
m1	9.20	0.96		
w1	14.30	0.62		
w2	17.50	0.51		

Figure S4. a) 2D XRD pattern of the DC phase of **BrF12** at $T = 90$ °C, the inset shows the small angle region; b) diffraction intensity profile as a function of 2θ with the visible reflections.



Reflex	$2\theta/°$	d/nm
10	1.89	4.76
m1	5.15	1.72
m2	6.79	1.30
m3	8.93	0.99
w1	13.50	0.66
w2	16.96	0.52
w3	18.40	0.48

Figure S5. a) 2D XRD pattern of the DC phase of **BrF14** at $T = 90$ °C, the inset shows the small angle region; b) diffraction intensity profile as a function of 2θ with the visible reflections.

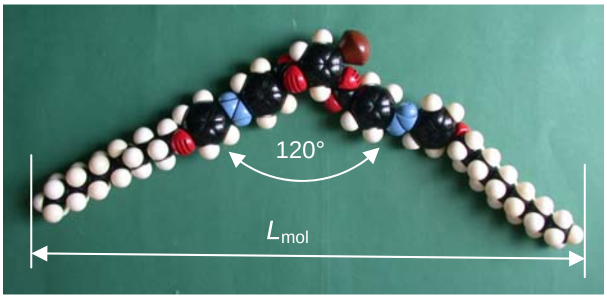


Fig. S6. Molecular conformation used to determine the molecular length.

2.3 Mixtures with 5-CB

The investigated mixtures between the **BrF*n*** compounds and 5-CB were prepared by mixing the appropriate **BrF*n*** compounds in molar ratio 1:1 with 5-CB in DSC pans and melting them together in the isotropic liquid state with vigorous stirring followed by cooling with stirring to room temperature.

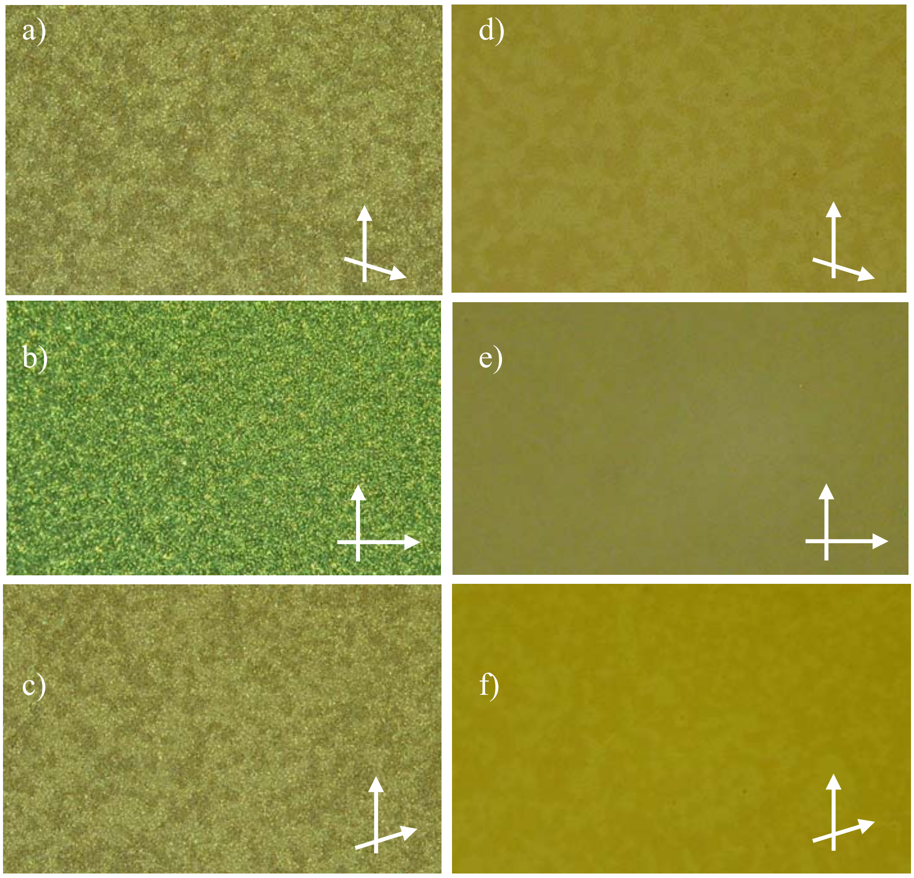


Figure S7. Textures of the 1:1 mixture of compound **BrF12** and **5-CB:** a-c) Chiral crystalline phase at 25 °C d-e) DC phase at 50 °C; b), e) between crossed polarizers; a) and d) after rotating one polarizer by 9° from the crossed position in clock-wise direction; c) and f) after rotating one polarizer by 9° from the crossed position in anticlock-wise direction.

3. Additional data of compounds IF*n*

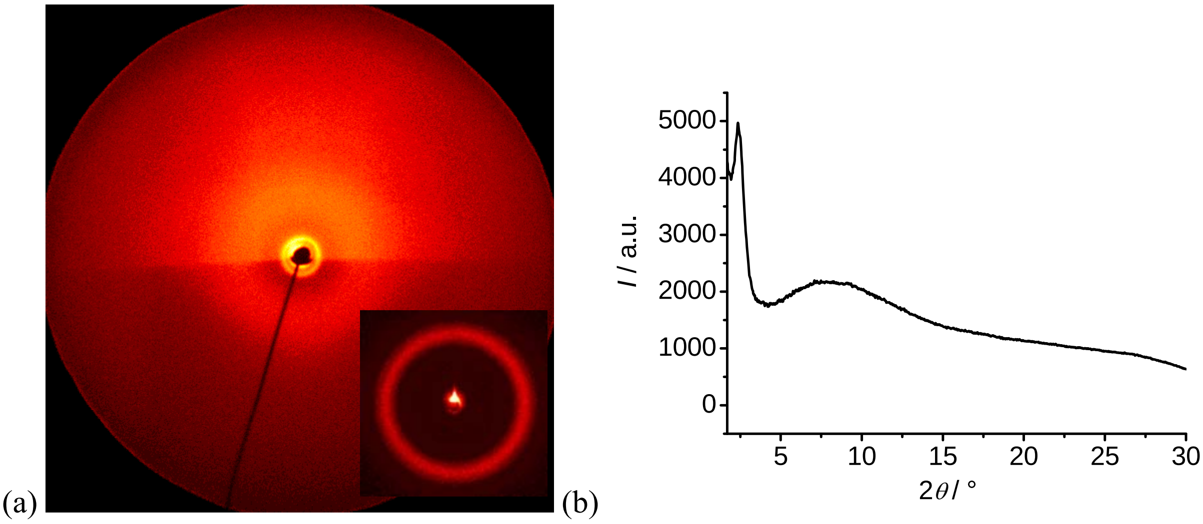


Figure S8. a) 2D XRD pattern of the DC phase of **IF8** at $T = 90$ °C, the inset shows the small angle region; b) 2θ-scan over this XRD pattern.

4. Additional data of compounds FF12, ClF12 and MF12

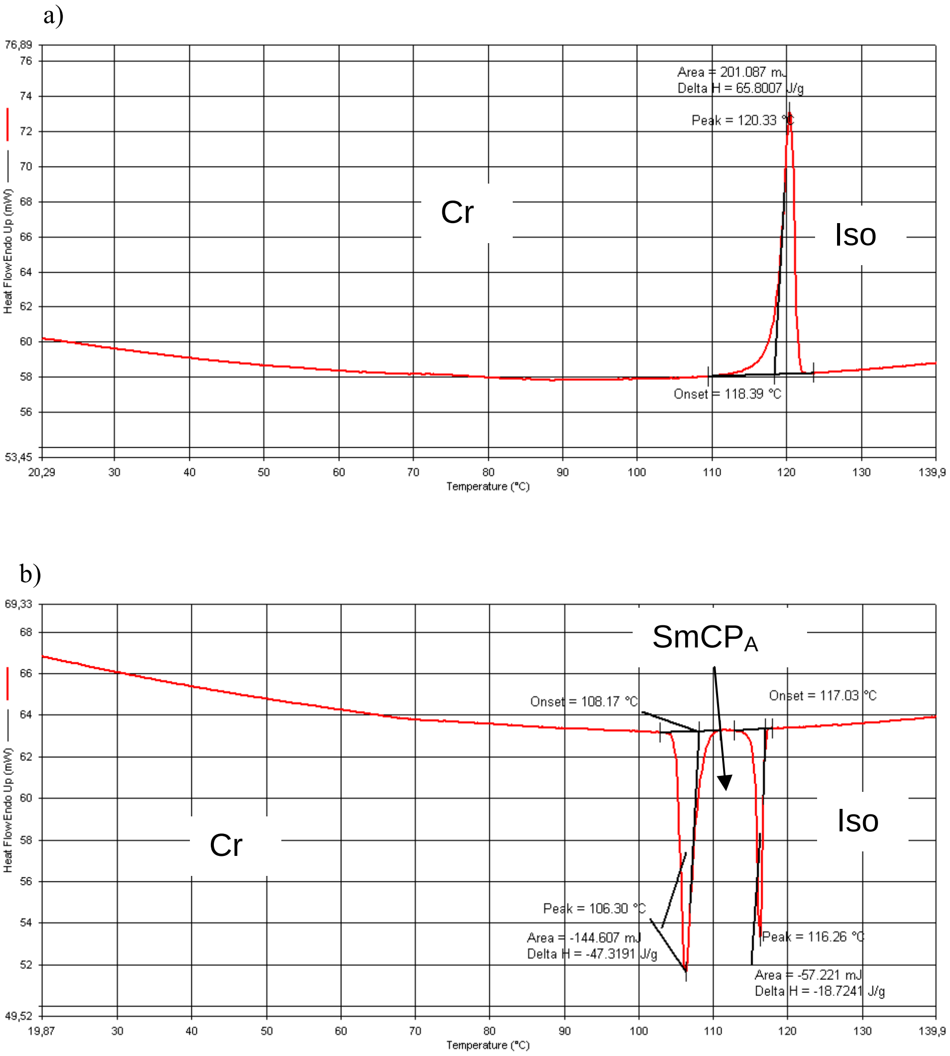


Figure S9. DSC heating and cooling traces of compound **FF12:** a) second heating run with 10 K min^{-1} and b) second cooling run with 10 K min^{-1}.

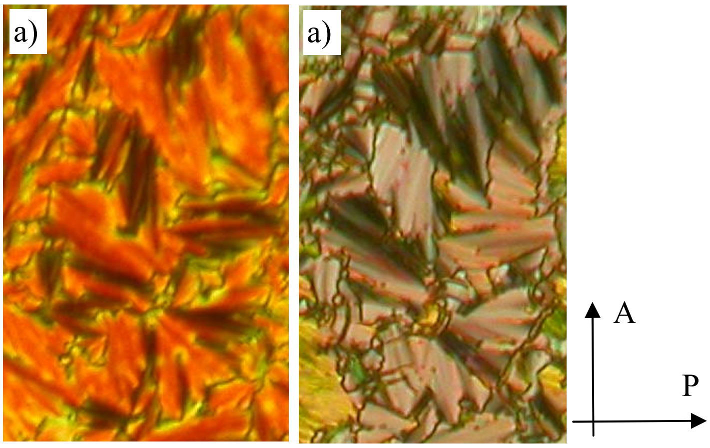


Figure S10. Optical textures of the SmCPA phase of compound **ClF12** between crossed polarizers at *T* = 94 °C in a 6 μm ITO cell a) at 0V and b) under a DC field of +10V.

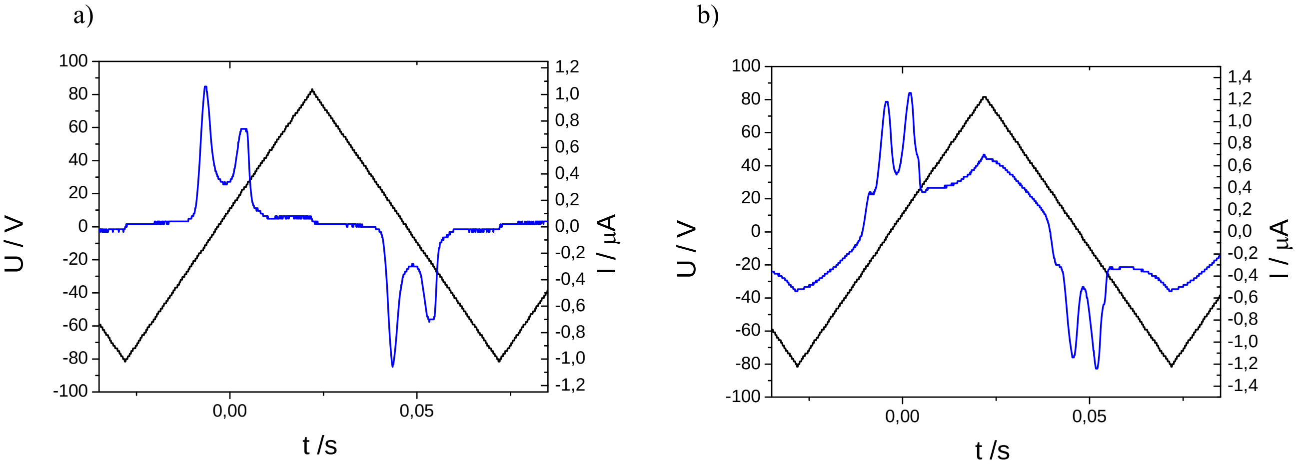


Figure S11. Switching current response curves recorded by applying a triangular wave voltage (160 V_{pp}, 10 Hz, 5 kΩ) to a 6 μm coated ITO cell with homogeneous PI alignment layer in the SmC_aP_A phase**:** a) **ClF12** at *T* = 94 °C and c) **FF12** at *T* = 114 °C.

5. References

S1. M. Alaasar, M. Prehm, C. Tschierske, *Liq.Cryst.*, 2014, **41**, 126.