

Supporting Information

Mirror Symmetry Breaking in Fluorinated Bent-Core Mesogens

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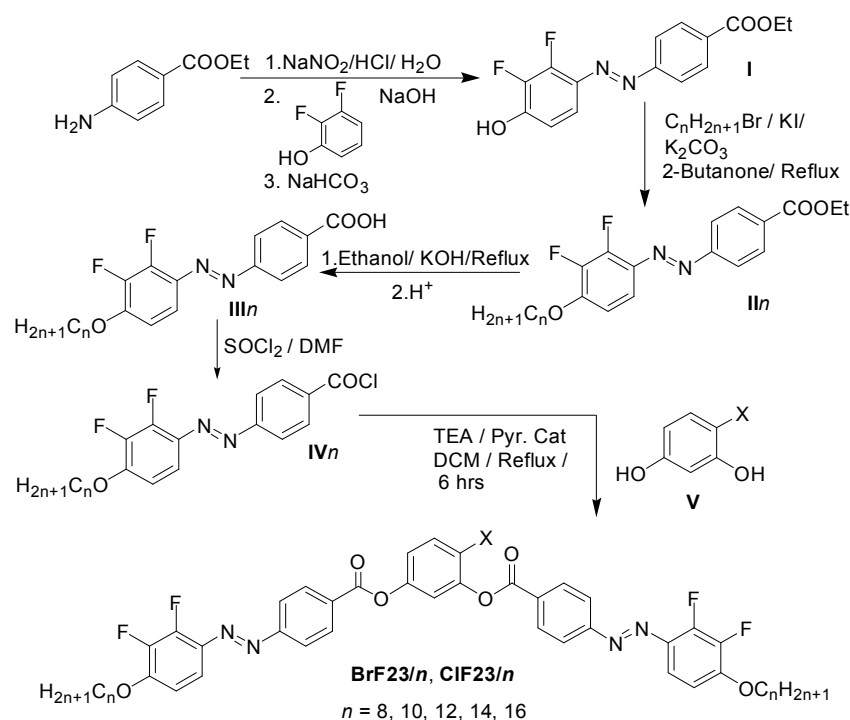
1. Synthesis and Analytical Data

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 $^1\text{H-NMR}$ (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 the new bent-core compounds BrF_2n and ClF_2n

The synthesis of the bent-core compounds under investigation is shown in Scheme S1. The intermediates compounds **I**, **II n** as well as their corresponding acids **III n** were synthesized using the same methods reported by us in Ref. [S1]. The synthesis details as well as the analytical data of the final materials (**BrF $_2n$** and **ClF $_2n$**) are described below.

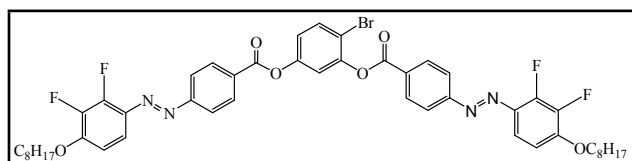


Scheme S1. Synthesis of the new bent-core molecules.

The final bent-core compounds were prepared as following: excess thionyl chloride (3 mL) and a catalytic amount of *N,N*-dimethylformamide (DMF) were added to 2.4 mmol of the acid **III n** and the reaction mixture was heated under reflux with for one hour. The excess of thionyl chloride was removed under reduced pressure followed by dissolving the obtained acid chloride (**IV n**) in dry dichloromethane (DCM, 20 mL). To this solution 4-substituted resorcinol (1.2 mmol) previously dissolved in DCM (10 mL), triethylamine (TEA, 2.8 mmol) and few drops

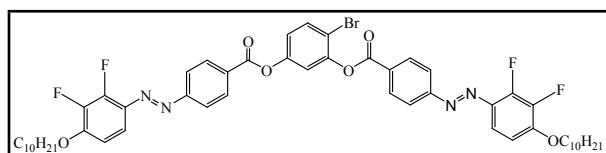
of pyridine as a catalyst were added and the reaction mixture was then refluxed for 6 hours under an argon atmosphere. At the end of the reaction as indicated by TLC, the solution was cooled to the room temperature, washed with 10% HCl (2×50 mL) and several times with cold water then extracted with DCM (3×50 mL) and dried over anhydrous sodium sulphate. The obtained crude materials was chromatographed on silica gel using dichloromethane as eluent followed by recrystallization from chloroform/ethanol mixture to give the final bent core compounds as orange crystals. The analytical data obtained are as follow:

1.2.1. 4-Bromo-1,3-phenylene bis-[4-(2,3-difluoro-4-octyloxyphenylazo)benzoate], BrF₂8:



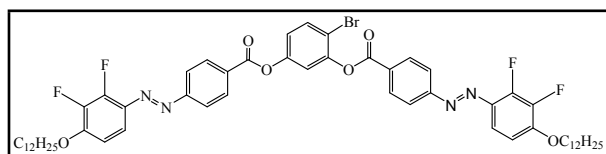
¹H-NMR (500 MHz, CDCl₃) δ 8.39 (d, $J = 8.7$ Hz, 2H, Ar-H), 8.33 (d, $J = 8.7$ Hz, 2H, Ar-H), 8.07 – 7.95 (m, 4H, Ar-H), 7.73 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.65 – 7.55 (m, 2H, Ar-H), 7.36 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.16 (dd, $J = 8.7, 2.7$ Hz, 1H, Ar-H), 6.87 – 6.77 (m, $J = 8.5$ Hz, 2H, Ar-H), 4.15 (t, $J = 6.6$ Hz, 4H, -OCH₂CH₂), 1.93 – 1.79 (m, 4H, -OCH₂CH₂), 1.59 – 1.14 (m, 20H, CH₂), 0.90 (t, $J = 6.9$ Hz, 6H, CH₃). Elemental Analysis: Calc. for C₄₈H₄₉BrF₄N₄O₆ C, 61.74; H, 5.29; N, 6.00. Found C, 61.80; H, 5.27; N, 5.56 %.

1.2.2. 4-Bromo-1,3-phenylene bis-[4-(4-decyloxy-2,3-difluorophenylazo)benzoate], BrF₂10:



¹H-NMR (500 MHz, CDCl₃) δ 8.39 (d, $J = 8.7$ Hz, 2H, Ar-H), 8.33 (d, $J = 8.7$ Hz, 2H, Ar-H), 8.09 – 7.97 (m, 4H, Ar-H), 7.73 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.66 – 7.55 (m, 2H, Ar-H), 7.36 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.16 (dd, $J = 8.7, 2.6$ Hz, 1H, Ar-H), 6.87 – 6.77 (m, 2H, Ar-H), 4.15 (t, $J = 6.5$ Hz, 4H, -OCH₂CH₂), 1.95 – 1.78 (m, 4H, -OCH₂CH₂), 1.60 – 1.18 (m, 28H, CH₂), 0.89 (t, $J = 6.9$ Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₂H₅₇BrF₄N₄O₆ C, 63.09; H, 5.80; N, 5.66. Found C, 63.00; H, 5.93; N, 5.60 %.

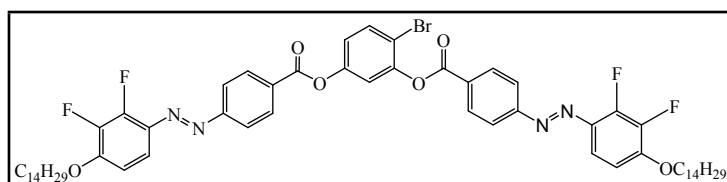
1.2.3.4-Bromo-1,3-phenylene bis-[4-(4-dodecyloxy-2,3-difluorophenylazo)benzoate], BrF₂12:



¹H-NMR (500 MHz, CDCl₃) δ 8.39 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.33 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.07 – 7.96 (m, 4H, Ar-H), 7.73 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.66 – 7.55 (m, 2H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 6.86 – 6.77 (m, 2H, Ar-H), 4.14 (t, *J* = 6.5 Hz, 4H, -OCH₂CH₂), 1.93 – 1.80 (m, 4H, -OCH₂CH₂), 1.60 – 1.15 (m, 36H, CH₂), 0.88 (t, *J* = 6.9 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₆H₆₅BrF₄N₄O₆ C, 64.30; H, 6.26; N, 5.36. Found C, 64.30; H, 6.30; N, 5.28 %.

1.2.4. 4-Bromo-1,3-phenylene tetradecyloxyphenylazo)benzoate], BrF₂14:

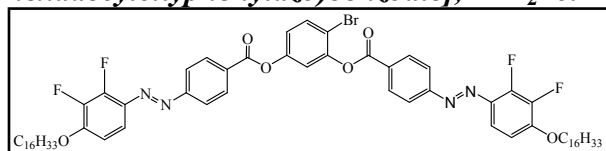
bis-[4-(2,3-difluoro-4-



¹H-NMR (500 MHz, CDCl₃) δ 8.39 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.09 – 7.96 (m, 4H, Ar-H), 7.74 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.67 – 7.55 (m, 2H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 6.90 – 6.73 (m, 2H, Ar-H), 4.14 (t, *J* = 6.5 Hz, 4H, -OCH₂CH₂), 1.98 – 1.76 (m, 4H, -OCH₂CH₂), 1.59 – 1.16 (m, 44H, CH₂), 0.88 (t, *J* = 6.9 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₀H₇₃BrF₄N₄O₆ C, 65.39; H, 6.68; N, 5.08. Found C, 65.44; H, 6.61; N, 5.10 %.

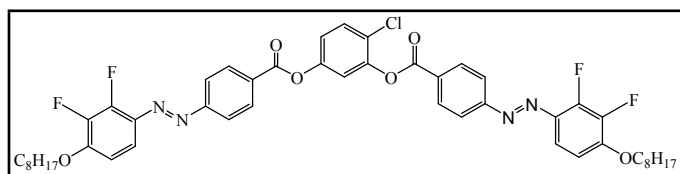
1.2.5. 4-Bromo-1,3-phenylene hexadecyloxyphenylazo)benzoate], BrF₂16:

bis-[4-(2,3-difluoro-4-



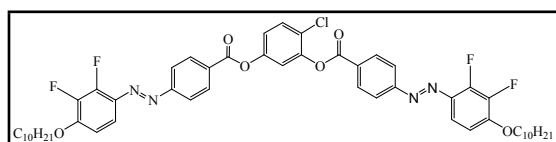
¹H-NMR (500 MHz, CDCl₃) δ 8.39 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.07 – 7.96 (m, 4H, Ar-H), 7.73 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.65 – 7.56 (m, 2H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 6.86 – 6.78 (m, 2H, Ar-H), 4.14 (t, *J* = 6.5 Hz, 4H, -OCH₂CH₂), 1.93 – 1.80 (m, 4H, -OCH₂CH₂), 1.59 – 1.15 (m, 52H, CH₂), 0.88 (t, *J* = 6.9 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₄H₈₁BrF₄N₄O₆ C, 66.37; H, 7.05; N, 4.84. Found C, 66.36; H, 6.94; N, 4.83 %.

1.2.6. 4-Chloro-1,3-phenylene bis-[4-(2,3-difluoro-4-octyloxyphenylazo)benzoate], ClF₂8:



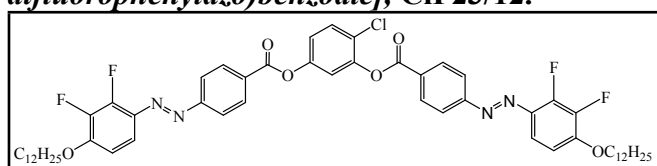
¹H-NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.33 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.07 – 7.98 (m, 4H, Ar-H), 7.64 – 7.56 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.8, 2.7 Hz, 1H, Ar-H), 6.86 – 6.77 (m, 2H, Ar-H), 4.15 (t, *J* = 6.6 Hz, 4H, -OCH₂CH₂), 1.92 – 1.82 (m, 4H, -OCH₂CH₂), 1.58 – 1.23 (m, 20H, CH₂), 0.90 (t, *J* = 6.9 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₄₈H₄₉ClF₄N₄O₆ C, 64.82; H, 5.55; N, 6.30. Found C, 64.79; H, 5.48; N, 6.25 %.

1.2.7. 4-Chloro-1,3-phenylene bis-[4-(4-decyloxy-2,3-difluorophenylazo)benzoate], ClF₂10:



¹H-NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 8.8, 2H, Ar-H), 8.33 (d, *J* = 8.8, 2H, Ar-H), 8.06 – 7.99 (m, 4H, Ar-H), 7.65 – 7.55 (m, 3H, Ar-H), 7.36 (d, *J* = 2.7 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.8, 2.7 Hz, 1H, Ar-H), 6.85 – 6.79 (m, 2H, Ar-H), 4.15 (t, *J* = 6.6 Hz, 4H, -OCH₂CH₂), 1.92 – 1.82 (m, 4H, -OCH₂CH₂), 1.58 – 1.20 (m, 28H, CH₂), 0.89 (t, *J* = 6.9 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₂H₅₇ClF₄N₄O₆ C, 66.06; H, 6.08; N, 5.93. Found C, 66.10; H, 6.00; N, 5.88 %.

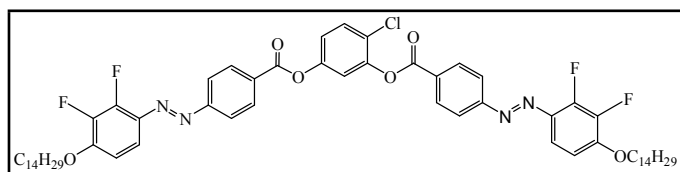
1.2.8. 4-Chloro-1,3-phenylene bis-[4-(4-dodecyloxy-2,3-difluorophenylazo)benzoate], ClF₂12:



¹H-NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.09 – 7.97 (m, 4H, Ar-H), 7.66 – 7.53 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 6.88 – 6.76 (m, 2H, Ar-H), 4.15 (t, *J* = 6.5 Hz, 4H, -OCH₂CH₂), 1.95 – 1.79 (m, 4H, -OCH₂CH₂), 1.64 – 1.16 (m, 36H, CH₂), 0.88 (t, *J* = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₆H₆₅ClF₄N₄O₆ C, 67.15; H, 6.54; N, 5.59. Found C, 67.16; H, 6.46; N, 5.56 %.

**1.2.9. 4-Chloro-1,3-phenylene
tetradecyloxyphenylazo)benzoate], ClF₂14:**

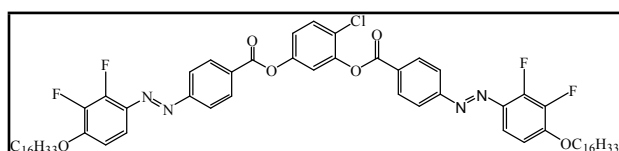
bis-[4-(2,3-difluoro-4-



¹H-NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.8, 2H, Ar-H), 8.09 – 7.97 (m, 4H, Ar-H), 7.66 – 7.54 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.8, 2.7 Hz, 1H, Ar-H), 6.88 – 6.74 (m, 2H, Ar-H), 4.15 (t, *J* = 6.5 Hz, 4H, -OCH₂CH₂), 1.95 – 1.79 (m, 4H, -OCH₂CH₂), 1.64 – 1.17 (m, 44H, CH₂), 0.88 (t, *J* = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₀H₇₃ClF₄N₄O₆ C, 68.13; H, 6.96; N, 5.30. Found C, 68.09; H, 6.92; N, 5.32 %.

**1.2.10. 4-Chloro-1,3-phenylene
hexadecyloxyphenylazo)benzoate], ClF₂16:**

bis-[4-(2,3-difluoro-4-



¹H-NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.32 (d, *J* = 8.6, 2H, Ar-H), 8.07 – 7.95 (m, 4H, Ar-H), 7.66 – 7.53 (m, 3H, Ar-H), 7.36 (d, *J* = 2.6 Hz, 1H, Ar-H), 7.21 (dd, *J* = 8.8, 2.7 Hz, 1H, Ar-H), 6.90 – 6.75 (m, 2H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -OCH₂CH₂), 1.92 – 1.79 (m, 4H, -OCH₂CH₂), 1.58 – 1.18 (m, 52H, CH₂), 0.88 (t, *J* = 6.7 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₄H₈₁ClF₄N₄O₆ C, 69.01; H, 7.33; N, 5.03. Found C, 69.05; H, 7.35; N, 5.01 %.

2. $^1\text{H-NMR}$ Spectra

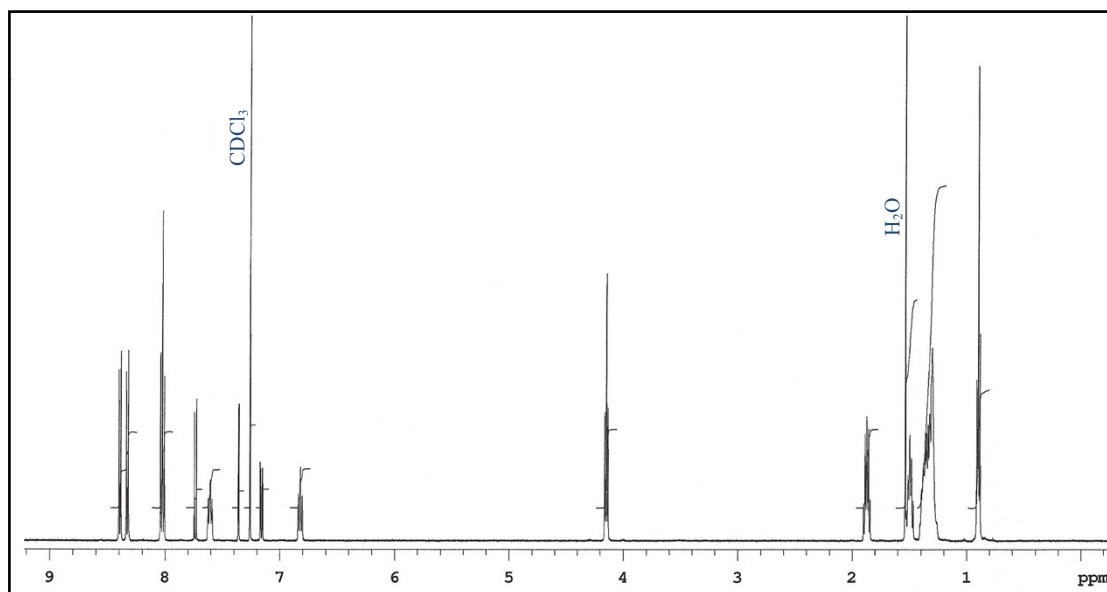


Figure S1. $^1\text{H-NMR}$ Spectrum of compound **BrF₂8** (500 MHz, CDCl_3).

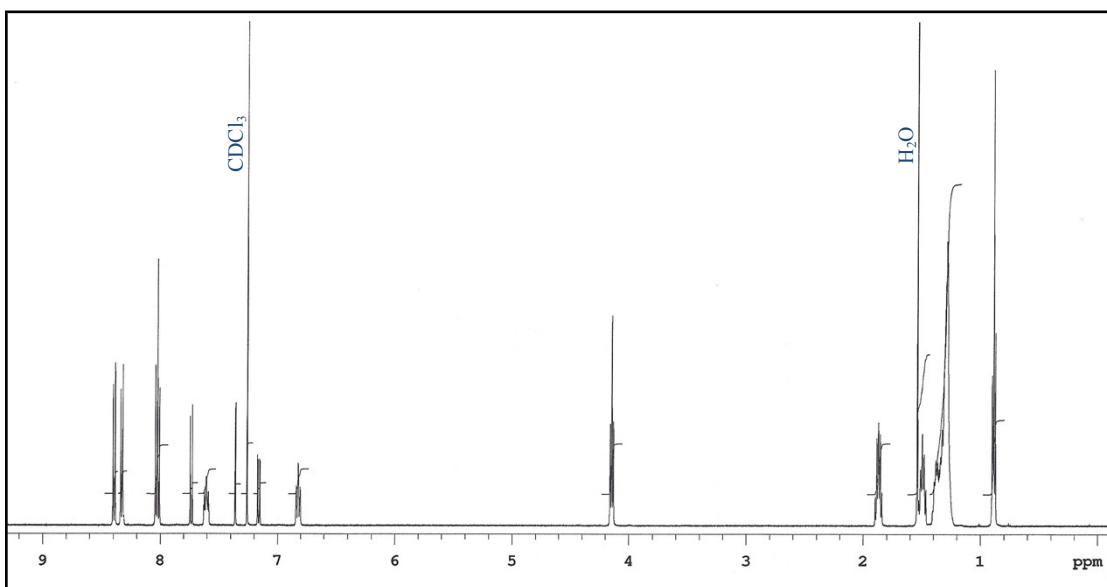


Figure S2. $^1\text{H-NMR}$ Spectrum of compound **BrF₂10** (500 MHz, CDCl_3).

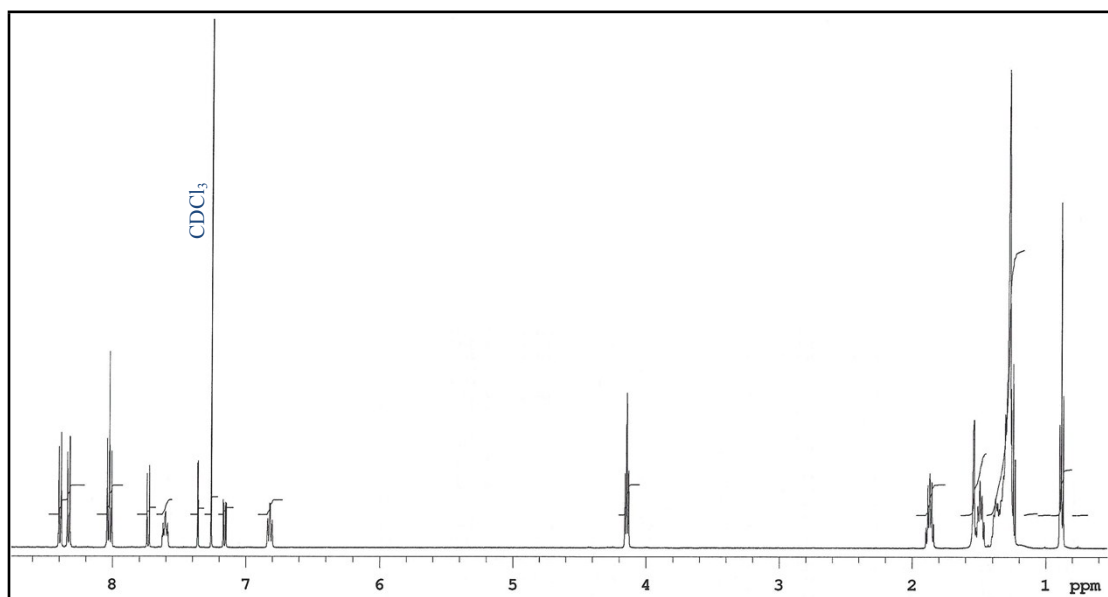


Figure S3. $^1\text{H-NMR}$ Spectrum of compound **BrF₂12** (500 MHz, CDCl_3).

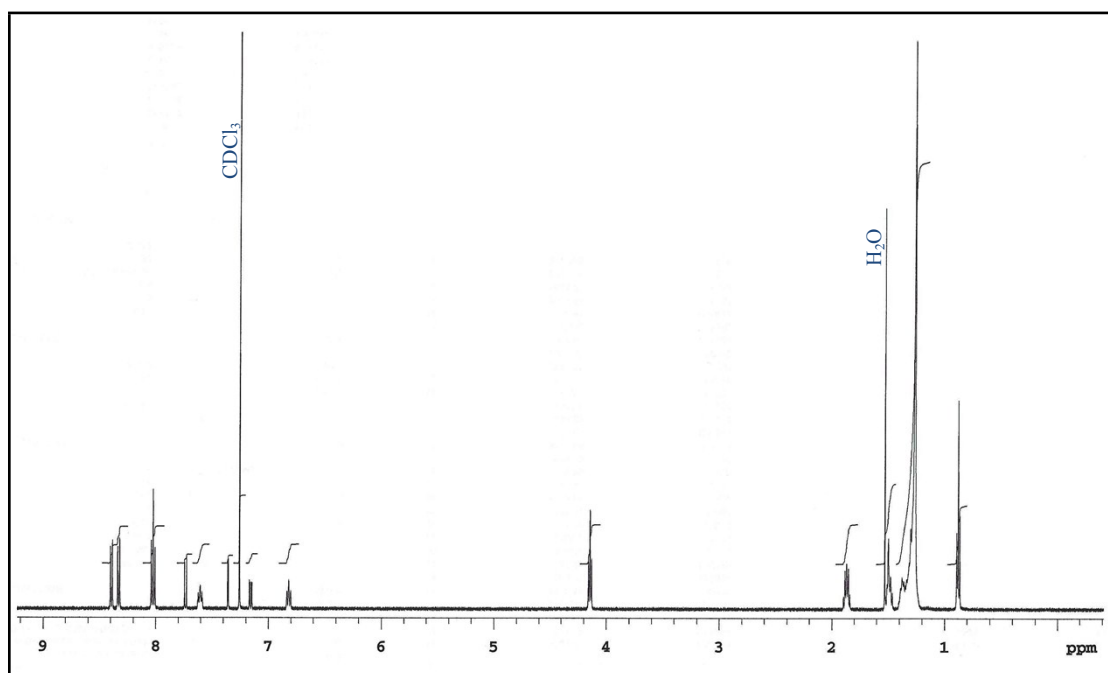


Figure S4. $^1\text{H-NMR}$ Spectrum of compound **BrF₂14** (500 MHz, CDCl_3).

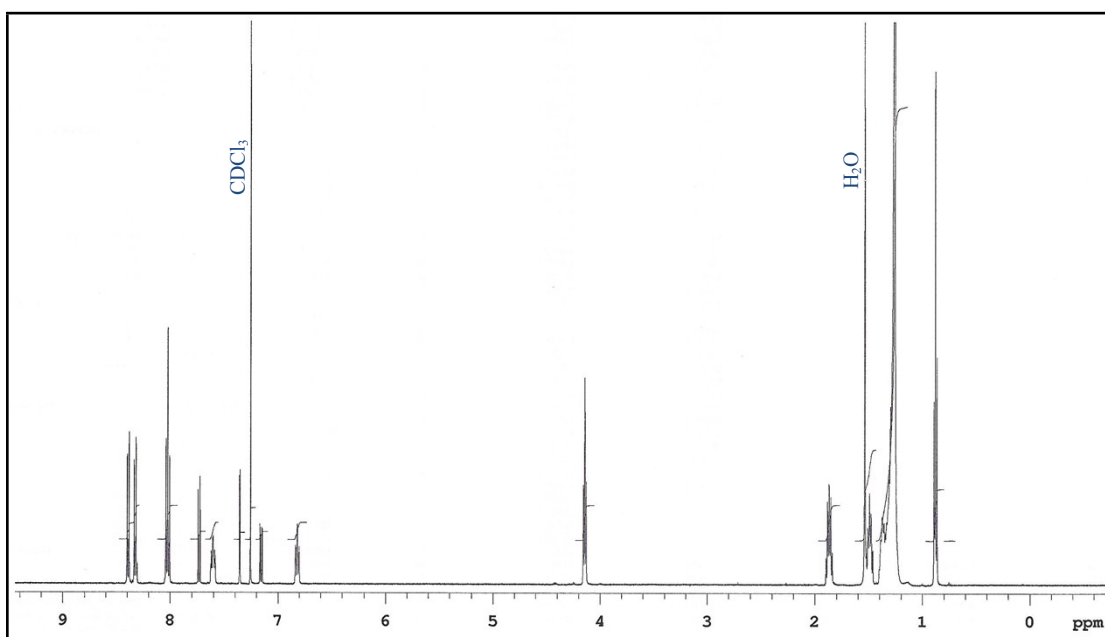


Figure S5. $^1\text{H-NMR}$ Spectrum of compound **BrF₂16** (500 MHz, CDCl_3).

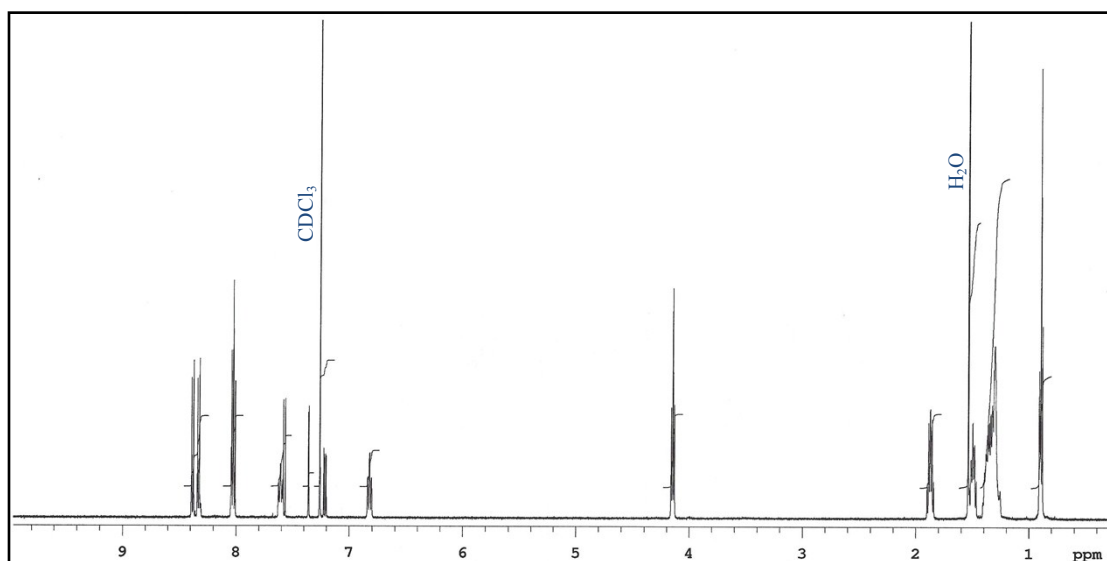


Figure S6. $^1\text{H-NMR}$ Spectrum of compound **ClF₂8** (500 MHz, CDCl_3).

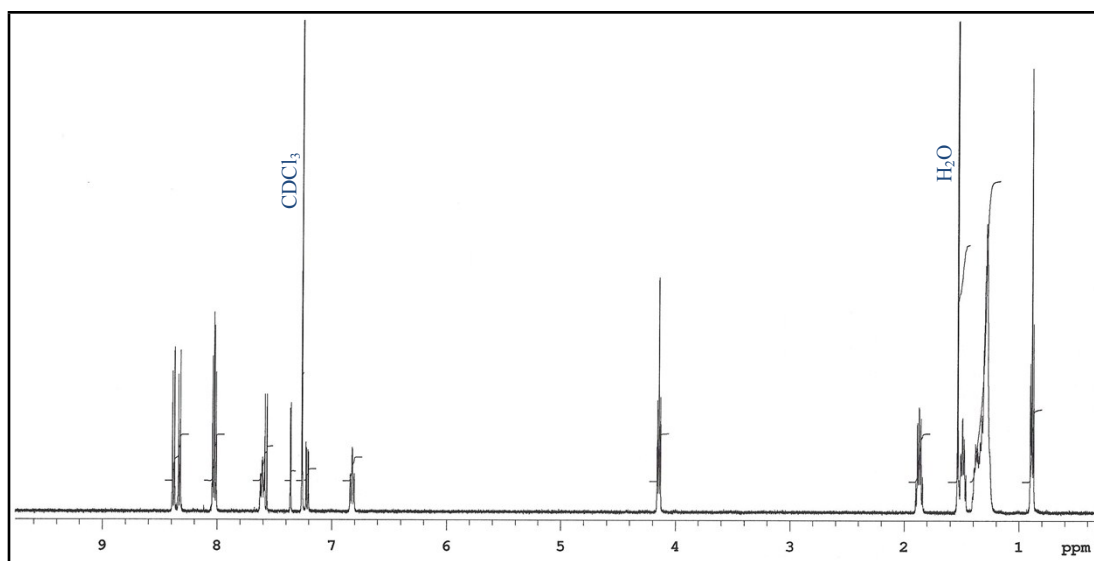


Figure S7. $^1\text{H-NMR}$ Spectrum of compound **ClF₂10** (500 MHz, CDCl_3).

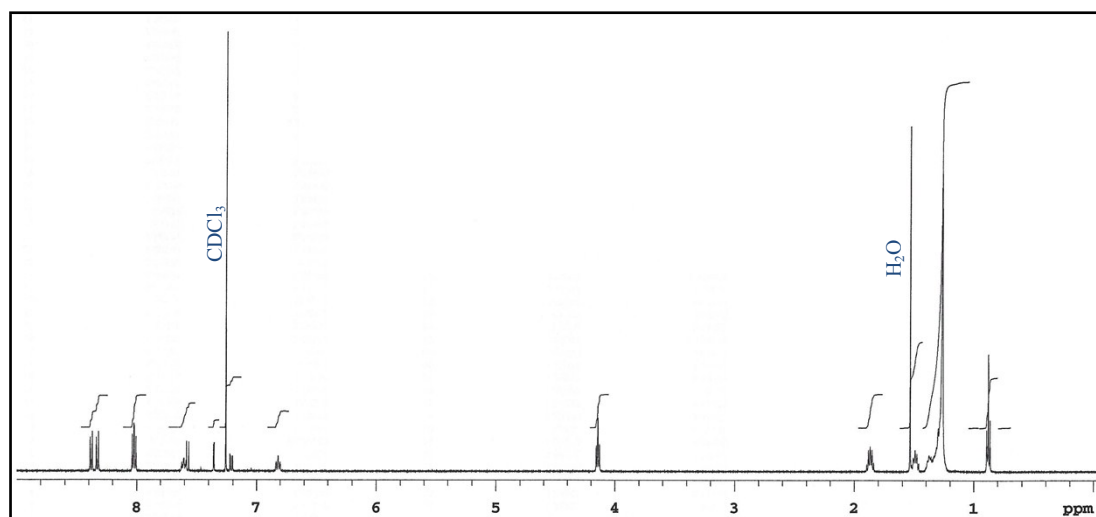


Figure S8. $^1\text{H-NMR}$ Spectrum of compound **ClF₂12** (500 MHz, CDCl_3).

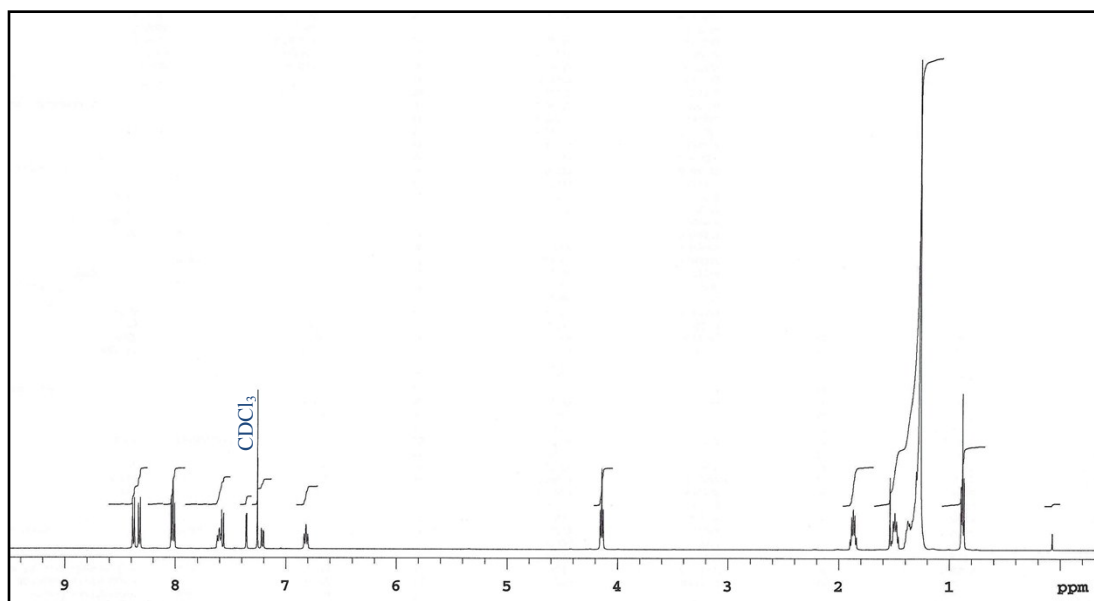


Figure S9. $^1\text{H-NMR}$ Spectrum of compound **ClF₂14** (500 MHz, CDCl_3).

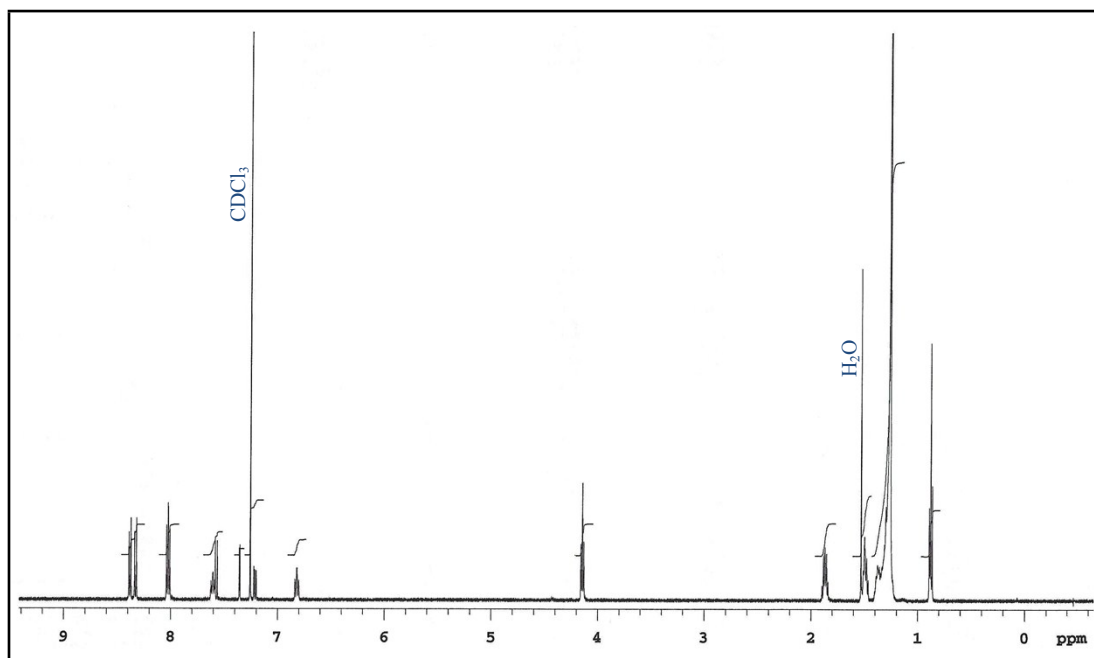


Figure S10. $^1\text{H-NMR}$ Spectrum of compound **ClF₂16** (500 MHz, CDCl_3).

3. Additional data

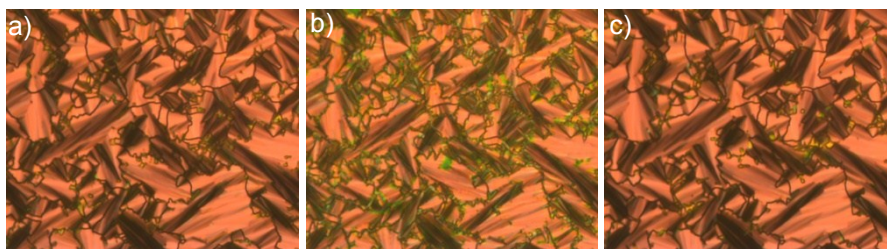


Figure S11. SmC_sP_{AR} phase of **BrF₂₁₆** at 93 °C: a) texture as observed after application of $E = +10 \text{ V}\mu\text{m}^{-1}$, b) at $E = 0$, after switching off the applied field and c) texture after application of $E = -10 \text{ V}\mu\text{m}^{-1}$.

4. References

S1. M. Alaasar, M. Prehm, Y. Cao, F. Liu and C. Tschierske, *Angew. Chem. Int. Ed.*, 2016, **55**, 312-316.