

Electronic Supporting Information

Emergence of polar order and tilt in terephthalate based bent-core liquid crystals

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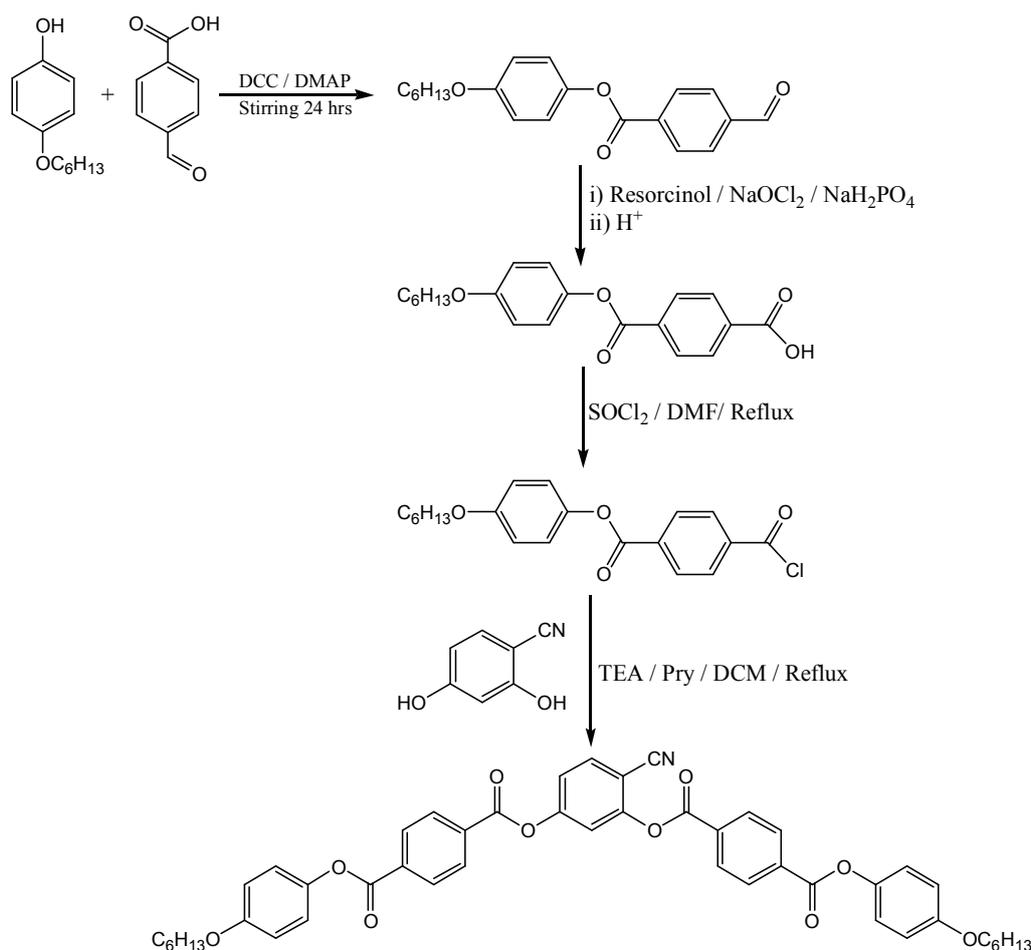
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1. Synthesis and analytical data

The structure characterization of the synthesized bent-core compound is based on ¹H-, ¹³C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in CDCl₃ solutions, with tetramethylsilane as internal standard), MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

Materials: 4-Hexyloxyphenol (Aldrich), resorcinol (Aldrich), tert-butyl alcohol (Aldrich), sodium chlorite (Aldrich), sodium dihydrogenphosphate (Aldrich), potassium carbonate (Fluka), potassium hydroxide (Merck), 4-formylbenzoic acid (Aldrich), thionylchloride (Aldrich), 1,3-dicycloxylcarbodiimide (DCC; Merck), 4-(N,N-dimethylamino) pyridine (DMAP) (Aldrich), 2,4-dihydroxybenzaldehyde (Aldrich) and hydroxylamine hydrochloride (Merck). Chloroform (Merck) and dichloromethane (Merck) were dried separately over calcium chloride (Merck) and distilled before use. Other solvents and chemicals were used without further purification.

The synthetic procedures leading to the target bent core compound **1/6** are outlined in Scheme S1. 2,4-Dihydroxybenzonitrile was synthesized according to the procedure described in Ref. S1. 4-[(4-n-Hexyloxyphenoxy)carbonyl] benzoic acid was prepared using a procedure similar to that one reported in Ref. S2.



Scheme S1. Synthesis of compound **1/6**.

4-[(4-*n*-Hexyloxyphenoxy)carbonyl] benzoic acid. - Formylbenzoic acid (2.0 g, 13.32 mmol) was acylated with 4-*n*-hexyloxyphenol (2.58 g, 13.32 mmol) in the presence of DCC (2.75 g, 13.32 mmol) to give the intermediate 4-hexyloxyphenyl 4-formylbenzoate (2.7 g, yield 62.1%), which was oxidized to the benzoic acid as following: 4-hexyloxyphenyl 4-formylbenzoate (2.89 g, 8.88 mmol) and resorcinol (1.05 g, 9.50 mmol) were dissolved in tert-butyl alcohol (140 mL). Separately, sodium chlorite (3.80 g, 42.01 mmol) and sodium dihydrogenphosphate (3.04 g, 25.35 mmol) were dissolved in water (30 mL). The aqueous solution was added in a dropwise manner into the tert-butyl alcohol solution over a 10-min period. The pale yellow reaction mixture was then stirred at room temperature overnight. Volatile components were removed under vacuum and the residue was dissolved in water (100 mL). The aqueous solution was acidified to pH 3 by adding 1 N aqueous HCl. The liberated white precipitate was isolated, washed successively with water and hexane, dried in the air and recrystallized from ethanol to give the desired acid as white crystals (2.94 g, yield 97%).

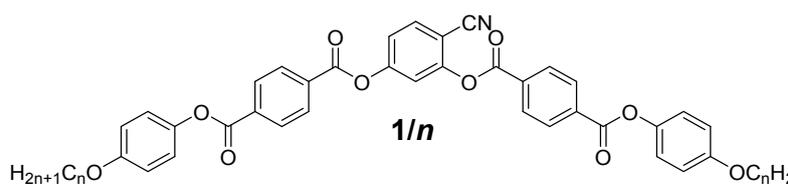
4-Hexyloxyphenyl 4-formylbenzoate. - Yield 62.1%, m.p. 95 °C. ¹H-NMR (400 MHz, CDCl₃): δ 10.14 (s, 1H, Ar-CHO), 8.33 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.99 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.11 (d, 2H, *J* = 9.0 Hz, 2H, Ar-H), 6.92 (d, 2H, *J* = 9.0 Hz, 2H, Ar-H), 3.97 (t, *J* = 8.2 Hz, 2H, Ar-OCH₂CH₂), 1.78–1.74 (m, 2H, Ar-OCH₂CH₂), 1.52–1.28 (m, 12H, CH₂), 0.91 (t, *J* = 7.0 Hz, 3H, CH₃).

4-(4-*n*-Hexyloxyphenoxy)carbonylbenzoic acid. - Yield 97%, phase behaviour: Cr 179 °C SmC 237 °C N 246 °C Isotropic liquid. ¹H-NMR (500 MHz, DMSO-*d*₆) δ 8.21 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.12 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.20 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.99 (d, *J* = 8.7 Hz, 2H, Ar-H), 3.97 (t, *J* = 6.4 Hz, 2H, -OCH₂), 1.77–1.64 (m, 2H, -OCH₂CH₂), 1.48–1.24 (m, 12H, CH₂), 0.88 (t, *J* = 6.7 Hz, 3H, CH₃).

4-Cyano-1,3-phenylene bis[4-(4-*n*-hexyloxyphenoxy)carbonylbenzoate] (1/6).- 4-(4-*n*-Hexyloxy-phenoxy)carbonylbenzoic acid (0.65 g, 1.89 mmol) was refluxed in excess thionylchloride (SOCl₂, 2 mL) under argon atmosphere, after one hour the excess thionylchloride was removed under vacuum, then 4-cyanoresorcinol (0.128 g, 0.94 mmol), triethylamine (0.38 g, 2.27 mmol) and pyridine (cat.) were dissolved in anhydrous 15 mL CH₂Cl₂ and added to the acid chloride and stirring is continued under reflux for 6 hrs. The reaction mixture is then poured into 10 mL of an aqueous solution of 1 N HCl. The organic layer was separated and washed twice with saturated aqueous NaHCO₃ solution. The combined aqueous washes were back-extracted with 30 mL of CH₂Cl₂. The organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The crude products were purified by column chromatography using CHCl₃ as eluent followed by recrystallization from ethanol/chloroform mixture (1:1) then recrystallization from hexane/toluene (9:1) mixture to give the desired bent-core mesogen as white crystals (0.62 g, yield 84 %).

¹H-NMR (400 MHz, CDCl₃): δ 8.43–8.24 (m, 8H, Ar-H), 7.82 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.58 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.36 (dd, *J* = 8.6, 2.1 Hz, 1H, Ar-H), 7.13 (d, *J* = 9.3, 4H, Ar-H), 6.93 (d, *J* = 9.0, 4H, Ar-H), 3.96 (t, *J* = 6.5 Hz, 4H, -OCH₂), 1.87–1.70 (m, 4H, -OCH₂CH₂), 1.57–1.19 (m, 24H, CH₂), 0.90 (t, *J* = 6.9 Hz, 6H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ 164.41, 163.14, 162.81, 157.17, 157.14, 154.56, 153.24, 143.98, 143.94, 134.88, 134.75, 134.12, 132.53, 132.14, 130.63, 130.47, 130.41, 122.20, 122.16, 120.14, 117.26, 115.19, 114.54, 114.58, 104.51, 68.47, 31.56, 29.21, 25.70, 22.59, 14.01. Elemental Analysis: Calc. for C₄₇H₄₅NO₁₀ C, 72.02; H, 5.79; N, 1.79. Found C, 71.86; H, 5.79; N, 1.79 %.

2. Additional data



n = 6: Cr 103 SmC_aP_A 144 SmAP_{AR} ~150 SmAP_R 179 Iso

n = 8: Cr 113 SmAP_A 144 SmA 187 Iso

n = 12: Cr 106 SmAP_A 112 SmA 185 Iso

n = 14: Cr 104 SmC'_sP_A 111 SmC_sP_A 125 SmCP_α (115 M₁ 133) SmCP_α 136 SmCP_R 146 SmA_(P) ~185 SmA 192 Iso

Scheme S2. Phase sequence of compound **1/6** in comparison to the known compounds **1/8**,^{S3} **1/12**^{S3} and **1/14**^{S4} (*T*/°C) as reported in the given references (values on heating, the M₁ phase in brackets is only observed on cooling and replaces the SmCP_α phase in the specified temperature range).

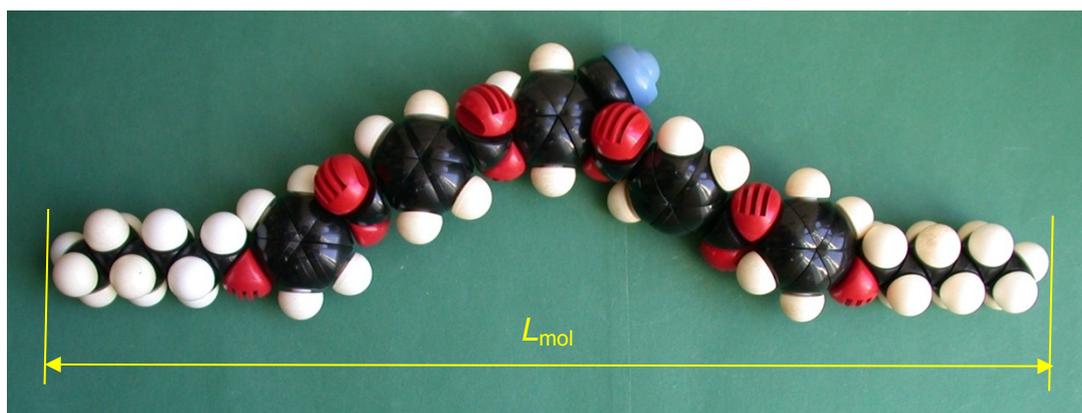


Figure S1. CPK model of compound **1/6** in the conformation used for determination of the molecular length.

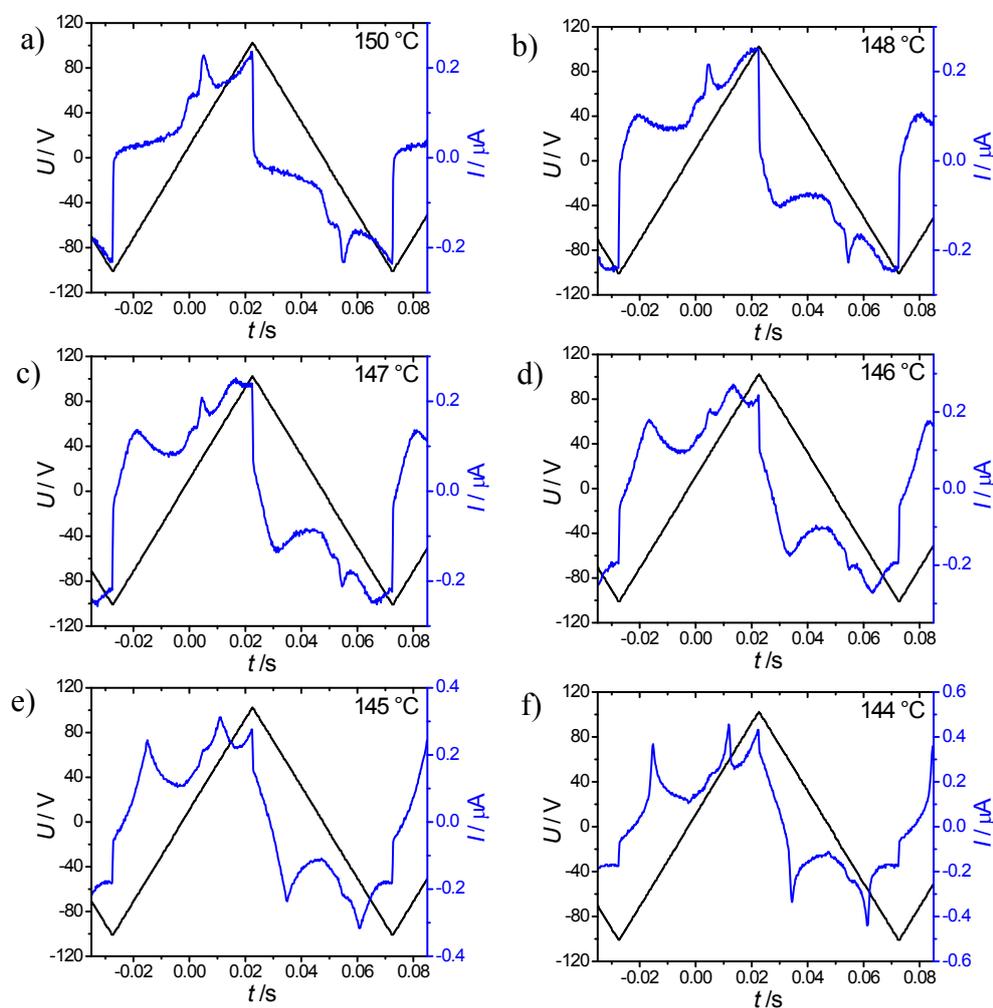


Figure S2. Switching current response curves of compound **1/6** recorded by applying a triangular wave voltage (200 V_{pp} , 10 Hz , $5\text{ k}\Omega$) to a $6\text{ }\mu\text{m}$ coated ITO cell with planar alignment layer at the indicated temperatures around the SmAP_R - SmAP_{AR} - SmC_aP_A phase transitions a) in the SmAP_R region b,c) at the SmAP_R – SmAP_{AR} transition, d) in the SmAP_{AR} region and e, f) upon approaching the SmAP_{AR} - SmC_aP_A transition.

References:

- S1. I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Pancenko and W. Weissflog, *J. Mater. Chem.*, 2001, **11**, 1642.
- S2. M. Alaasar, M. Prehm, M. Poppe, M. Nagaraj, J. K. Vij and C. Tschierske, *Soft Matter*, 2014, **10**, 5003.
- S3 L. Kovalenko , M. W. Schröder , R. A. Reddy , S. Diele , G. Pelzl and W. Weissflog , *Liq. Cryst.*, 2005 , **32**, 857.
- S4 M. Alaasar, M. Prehm, M. Poppe, M. Nagaraj, J. K. Vij and C. Tschierske, *Soft. Matter.*, 2014, **10**, 5003.