Supplementary Information (SI)

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1. Materials

(a) The BCN materials S2141 and S110 were synthesized following the route shown in Figure

S1 and were purified by column chromatography and repeated crystallization.



Figure S1: Scheme: The synthetic pathway used for preparation of bent core nematic LCs S2141 (n=14) and S110 (n=10)

The physical data obtained for the two compounds are given below.

2,7-Naphthalene bis [4-(E-4-*n*-tetradecyloxy-α-methylcinnamoyloxy)-3-chlorobenzoate] (S2141)

m.p. 94°C. IR (KBr) v_{max} : 2922, 2852, 1739, 1732, 1595, 1504, 1454 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ_{H} : 8.37 (d, 2H, J=2.02 Hz, Ar-H), 8.20 (d, 2H, J=6.41 Hz, Ar-H), 7.95 (m, 2H, Ar-H), 7.94 (s, 2H, 2 × Ar-C<u>H</u>=C(CH₃)-), 7.70 (d, 2H, J=2.08 Hz, Ar-H), 7.48 (d, 4H, J=8.77 Hz, Ar-H), 7.43 (d, 2H, J=8.46 Hz, Ar-H), 7.38 (d, 2H, J=6.63 Hz, Ar-H), 6.96 (d, 4H, J=8.78Hz, Ar-H), 4.0 (t, 4H, J=6.52Hz, 2 × Ar-OCH₂-), 2.30 (d, 6H, J=1.16 Hz, 2 × -CH=C(C<u>H₃)</u>COO-), 1.84-1.77 (quin, 4H, J=6.65 Hz, 2 × Ar-OCH₂-C<u>H₂-CH₂-), 1.52-1.23(m, 44H, 20 × -CH₂-C<u>H₂-CH₂-), 0.88 (t, 6H, J=6.6 Hz, 2 × -CH₂- C<u>H₃)</u>. Elemental analysis: C₇₂H₈₆Cl₂O₁₀ requires C 73.14, H 7.34; found C 73.59, H 7.61 %.</u></u>

2,7-Naphthalene bis [4-(E-4-*n*-decyloxy-α-methylcinnamoyloxy)-3-chlorobenzoate] (S110)

m.p. 96.5 °C. IR (KBr) v_{max} : 2923, 2852, 1743, 1724, 1625, 1604, 1510, 1456 cm⁻¹. ¹H NMR (400MHz, CDCl₃) δ_{H} : 8.38 (d, 2H, J=1.87 Hz, Ar-H), 8.21 (d, 2H, J=6.52 Hz, Ar-H), 7.99-7.97 (m, 2H, Ar-H), 7.95 (s, 2H, 2 × Ar-C<u>H</u>=C(CH₃)-), 7.70 (d, 2H, J=1.62 Hz, Ar-H), 7.49 (d, 4H, J=8.69 Hz, Ar-H), 7.43 (d, 2H, J=8.45 Hz, Ar-H), 7.37 (d, 2H, J=6.41 Hz, Ar-H), 6.96 (d, 4H, J=8.69 Hz, Ar-H), 4.01 (t, 4H, J=6.52Hz, 2 × Ar-OCH₂-), 2.31(d, 6H, J=1 Hz, $2 \times -CH=C(C\underline{H}_3)COO-$), 1.81 (quin, 4H, J=7.61 Hz, $2 \times Ar-OCH_2-C\underline{H}_2-CH_2-$), 1.56-1.45 (m, 30H, $15 \times -CH_2-C\underline{H}_2-CH_2-$), 0.88 (t, 6H, J=6.93 Hz, $2 \times -CH_2-C\underline{H}_3$). Elemental analysis: $C_{64}H_{70}Cl_2O_{10}$ requires C 72.45, H 6.44; found C 72.67, H 6.81 %.

- (b) The bent core liquid crystal material ClPbis10BB was synthesized at Kent State University generally following the recipe described by K. Fodor-Csorba.^[1] ClPbis10BB was purified by column chromatography and repeated by recristallization.
- (c) The chiral dopant BDH 1281 was purchased from Merck, Chemicals, and used without any further purification

2. Differential Scanning Calorimetry (DSC)

DSC was done using a PerkinElmer Pyris Diamond DSC (Tokyo, Japan).

Figure S2 shows the DSC results at different increasing chiral dopant concentrations for the BCIPbis10BB-BDH1281 mixtures. One sees that both the transition enthalpies and the isotropic to BPIII phase transition temperatures are decreasing with increasing dopant concentrations, and by 7.2wt% of chiral dopant, DSC could no longer detect the phase transition. This result is consistent with the standard BPIII-isotropic transition, which, unlike the BPI- or BPII-isotropic transitions, ends in a critical point on a chirality/temperature phase diagram.^{[2],[3]}



Figure S2: DSC spectra of ClPbis10BB–BDH1281 mixtures at different dopant concentrations. Mixtures 1, 2, 3 respectively contain 3.2, 4.9, 7.2 wt% of BDH1281. The cooling rate was 10 °C/min. The arrows mark the Iso-BPIII transitions. The baselines have been offset to make the curves easy to compare.

3. Optical microscopic studies of the rod-shape LC material, 6008.

In order to appreciate the special role of bent-core molecules in formation of BPIII phases, we added chiral dopants to one of the simplest calamitic LC materials 6008, which exhibits nematic and tilted smectic (SmC) mesophases. The 6008 is completely

miscible with CIPBis10BB, and the two compounds were previously paired to study mixtures of bent-core and rod-shaped LCs.^[4] Typical textures at different temperatures, concentrations and alignment layers are shown in Figure S3. We found that no BPIII appeared until >5wt% concentrations of BDH1281 in 6OO8. At still higher concentrations BPI/BPII formed with platelet textures (see Fig. S3(c)), but with a much narrower (less than 1°C) temperature range than obtained for the BPIII phase in the bent-cores.



Figure S3: Polarizing Optical Microscopic textures in transmission of 6008 doped with BDH1281 at different concentrations and temperatures. (a) 1.4wt% of BDH1281 at 75°C, no alignment layer, (b) 1.4wt% of BDH1281 at 74.2 °C, planar alignment layer, (c) 7.2wt% of BDH1281 at 77.8 °C, no alignment layer, (d) 7.2wt% of BDH1281 at 72.4 °C, no alignment layer; (e)7.2wt% of BDH1281 at 71.3 °C, planar alignment. Pictures illustrate 0.1mm x 0.18mm areas.

4. References

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