Electronic supplementary information for *Soft Matter*

Bistable linear electro-optical switching in the B_7' phase of novel bent-core molecules

Synthetic procedure for the intermediates of compound **Ia** and the spectral and analytical data obtained for these compounds as well as for compounds **Ib** and **Ic.**

4-*n*-Dodecyl 4-nitrobenzoate, 2

4-Nitrobenzoic acid (2g, 1.19×10^{-2} mol), *n*-dodecyl alcohol (2.2g, 1.19×10^{-2} mol) and a catalytic amount of DMAP in dichloromethane (50ml) were stirred for 15 minutes at room temperature. To this stirred mixture DCC (2.67g, 1.31×10^{-2} mol) was added and stirring was continued for further 2 hr. The precipitated urea was filtered off and washed thoroughly with chloroform. The filtrate was concentrated to obtain the crude material, which was passed through a column of silica gel (60-120mesh) using chloroform as an eluant. The product obtained from the column was further purified by crystallization using *n*-hexane (b.p.65-70˚C). Yield 3.5g (87%); m. p. 41-42˚C; IR (nujol) ν_{max}: 2920, 2850, 1716, 1714, 1606, 1527, 1458, 1465, 1469, 1377, 1352, 1290 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, 2H, ^3J 8.9 Hz, Ar-H), 8.20 (d, 2H, ^3J 8.92 Hz, Ar-H), 4.36 (t, 2H, ^3J 6.6 Hz, 2H, Ar-COO-CH_2), 1.82-1.75 (quin, 2H, Ar-COO-CH_2-$\underline{CH_2}$-), 1.46-1.26 (m, 18H, (-CH_2-)$_9$), 0.87 (t, 3H, ^3J 6.6 Hz -CH_3); $C_{19}H_{29}NO_4$ requires C 68.03, H 8.70, N 4.17; found C 67.67 H 8.82, N 3.84%.

4-*n*-Dodecyl 4-aminobenzoate, 3

Compound **2** (3.0g) in 1,4-dioxane (30ml) and 5%Pd-C (0.6g) were stirred in an atmosphere of hydrogen at 60 ˚C until the reaction was complete which was monitored by thin layer chromatography using Merck 60 silica gel plates. The reaction mixture was filtered hot and the solvent was evaporated to obtain the product which was crystallized using *n*-hexane (b.p.65-70˚C). Yield 2.4g (88%); m. p. 76-77 ˚C; IR (nujol) ν_{max}: 3415, 3332, 3220, 2920, 2850, 2725, 2669, 1687, 1685, 1637, 1596, 1514, 1458, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, 2H, ^3J 8.72 Hz, Ar-H), 6.64 (d, 2H, ^3J 8.70 Hz, Ar-H), 4.25 (t, 2H, ^3J 6.64 Hz, 2H, Ar-COO-CH_2), 4.03 (s, 2H, Ar-NH_2) 1.76-1.69 (quin, 2H, Ar-COO-CH_2-$\underline{CH_2}$-), 1.42-1.26 (m, 18H, (-CH_2-)$_9$), 0.88 (t, 3H, ^3J 6.6 Hz, -CH_3); $C_{19}H_{31}NO_2$ requires C 74.72, H 10.22, N 4.58; found C 74.0, H 10.24, N 4.2 %.

4-(4-*n*-Dodecyloxycarbonylphenyliminomethyl) benzoic acid, 4

A mixture of compound **3** (2g, 0.65× 10^{-2} mol), 4-formylbenzoic acid (0.98g, 0.65× 10^{-2} mol) and a few drops of acetic acid in toluene (25ml) was refluxed for 5 hr using a Dean-Stark apparatus. The reaction mixture was cooled to room temperature and the crystallized product was filtered and dried. Yield 2.3g (80%); m. p. 118-119°C; IR (KBr) ν_{max}: 3058, 2954, 2918, 2848, 2667, 2542, 1940, 1712, 1681, 1697, 1595, 1569, 1471, 1278 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.52 (s, 1H, -CH=N-), 8.23 (d, 2H, ^3J 8.2 Hz, Ar-H), 8.09 (d, 2H, ^3J 8.2 Hz, Ar-H), 8.02 (d, 2H, ^3J 8.2 Hz, Ar-H), 7.24 (*d*, 2H, ^3J 8.52 Hz, Ar-H), 4.33 (t, 2H, ^3J 6.64 Hz, Ar-COO-CH$_2$-), 1.80-1.75 (quin, 2H, Ar-COO-CH$_2$-$\underline{\mathrm{CH_2}}$-), 1.45-1.27 (m, 18H, (-CH$_2$-)$_9$), 0.88 (t, 3H, ^3J 6.5 Hz, -CH$_3$); $C_{27}H_{35}NO_4$ requires C 74.11, H 8.06, N 3.20; found C 74.35 H 7.81, N 2.91%.

1,3-Phenylene bis [4-(4-*n*-tridecyloxycarbonylphenyliminomethyl) benzoate], Ib

Yield 80%; m. p. 133.0; IR (KBr) ν_{max}: 2952, 2920, 2848, 1745, 1739, 1737, 1712, 1596, 1467, 1278 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.54 (s, 2H, 2×-CH=N-), 8.32 (d, 4H, ^3J 8.32 Hz, Ar-H), 8.11 (d, 4H, ^3J 8.52 Hz, Ar-H), 8.07 (d, 4H, ^3J 8.36 Hz, Ar-H), 7.53 (t, 1H, ^3J 8.18 Hz, Ar-H), 7.26 (*d*, 4H, ^3J 8.48 Hz, Ar-H), 7.24-7.21 (m, 3H, Ar-H), 4.33 (t, 4H, ^3J 6.64 Hz, 2× Ar-COO-CH$_2$-), 1.82-1.75 (quin, 4H, ^3J 6.76 Hz, 2 × Ar-COO-CH$_2$-$\underline{\mathrm{CH_2}}$-), 1.55-1.26 (m, 40H, 2 × (-CH$_2$-)$_{10}$), 0.88 (t, 6H, ^3J 6.7 Hz, 2 × -CH$_3$); $C_{62}H_{76}N_2O_8$ requires C 76.20, H 7.83, N 2.87; found C 75.9, H 7.66, N 2.74%.

1,3-Phenylene bis [4-(4-*n*-tetradecyloxycarbonylphenyliminomethyl) benzoate], Ic

Yield 75%; m. p. 133.0; IR (KBr) ν_{max}: 2922, 2852, 1737, 1732, 1726, 1718, 1463, 1280 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.54 (s, 2H, 2×-CH=N-), 8.32 (d, 4H, ^3J 8.32Hz, Ar-H), 8.11 (d, 4H, ^3J 8.48 Hz, Ar-H), 8.07 (d, 4H, ^3J 8.32 Hz, Ar-H), 7.53(t, 1H, ^3J 8.12 Hz, Ar-H), 7.26 (*d*, 4H, ^3J 8.48 Hz, Ar-H), 7.24-7.21 (m, 3H, Ar-H), 4.33 (t, 4H, ^3J 6.64 Hz, 2× Ar-COO-CH$_2$-), 1.82-1.75 (quin, 4H, ^3J 7.0 Hz, 2× Ar-COO-CH$_2$-CH$_2$-), 1.53-1.27 (m, 44H, 2× (-CH$_2$-)$_{11}$), 0.87 (t, 6H, ^3J 6.8 Hz, 2 × -CH$_3$); $C_{64}H_{80}N_2O_8$ requires C 76.46, H 8.02, N 2.79; found C 75.98, H 7.91, N 2.45%.

Colour figures 2, 3, 5, 7, 8, 9 and 11

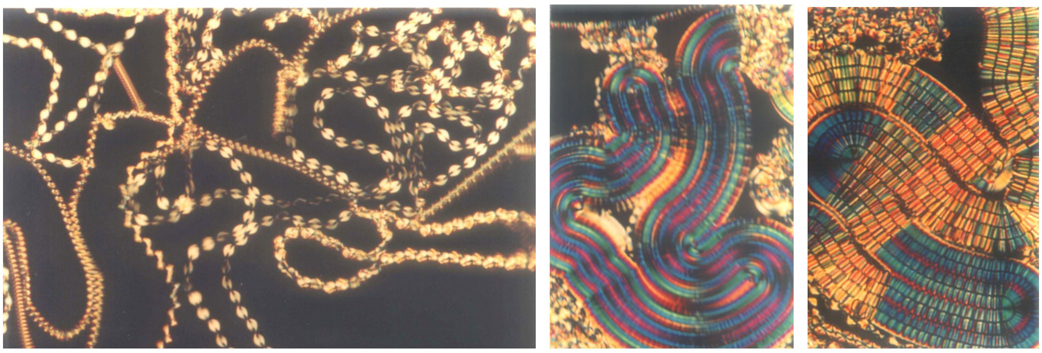

Fig. 2: (a) A texture of the helical filamentary growth pattern obtained on cooling the isotropic liquid of compound **Ia,** 139.8°C; (b) and (c) other beautiful textures obtained on slow cooling the isotropic liquid of compound **Ia**, 139˚C.

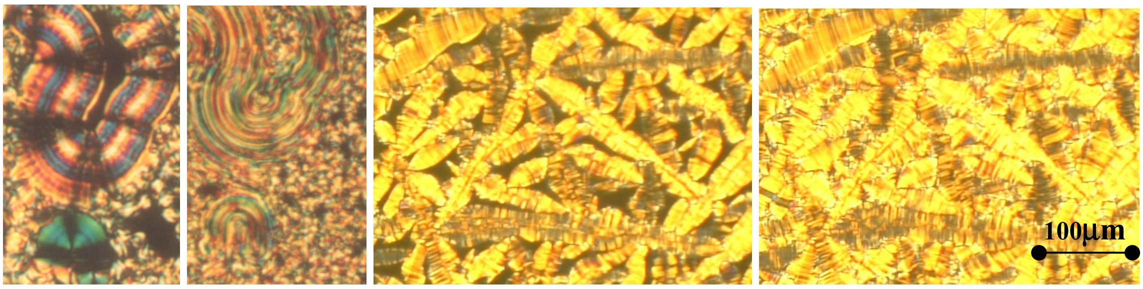

Fig. 3: Textures observed in 8µm and 5µm thick films on cooling the isotropic liquid of compound **Ia** without the application of any field; (a) 8µm film at 135°C; (b) 8µm film at128°C; (c) 5µm film at 135°C; (d) 5µm film at 128°C.

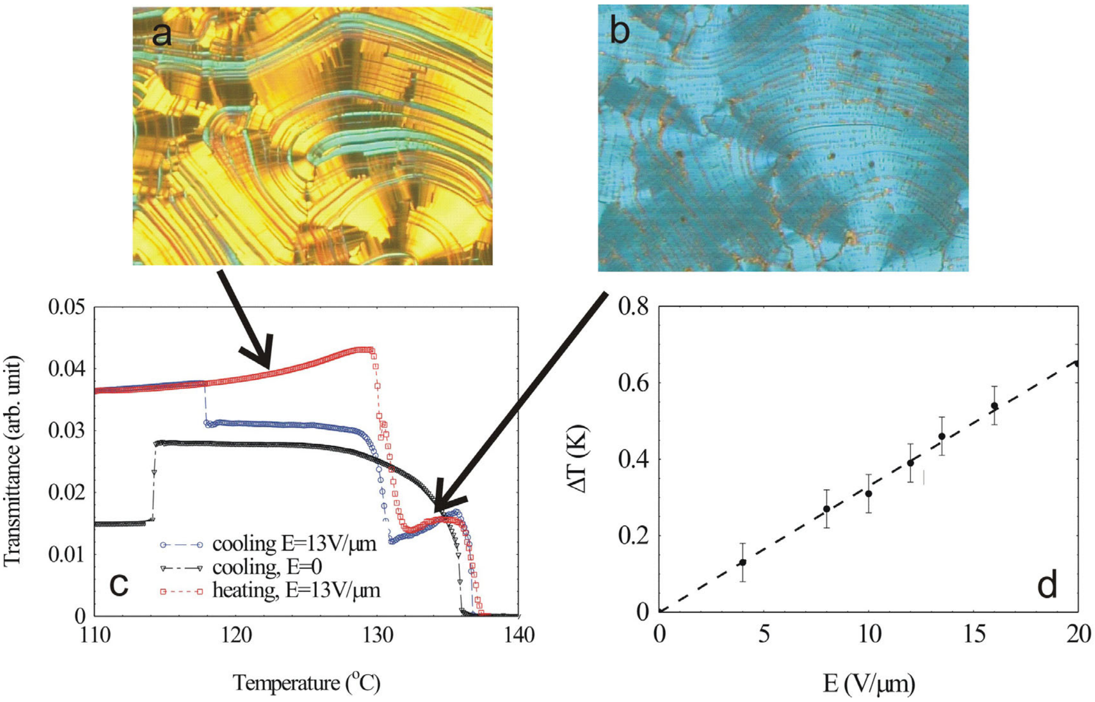

Fig. 5: (a) Texture of compound **Ia** obtained by applying a rectangular electric field of 13Vμm^{-1} (34Hz) at 128°C; (b) at 133°C; (c) transmittance as a function of temperature on heating and cooling, at zero field and under 13Vμm^{-1} field (34Hz); (d) shift of the phase transition temperature as a function of the amplitude of the applied field.

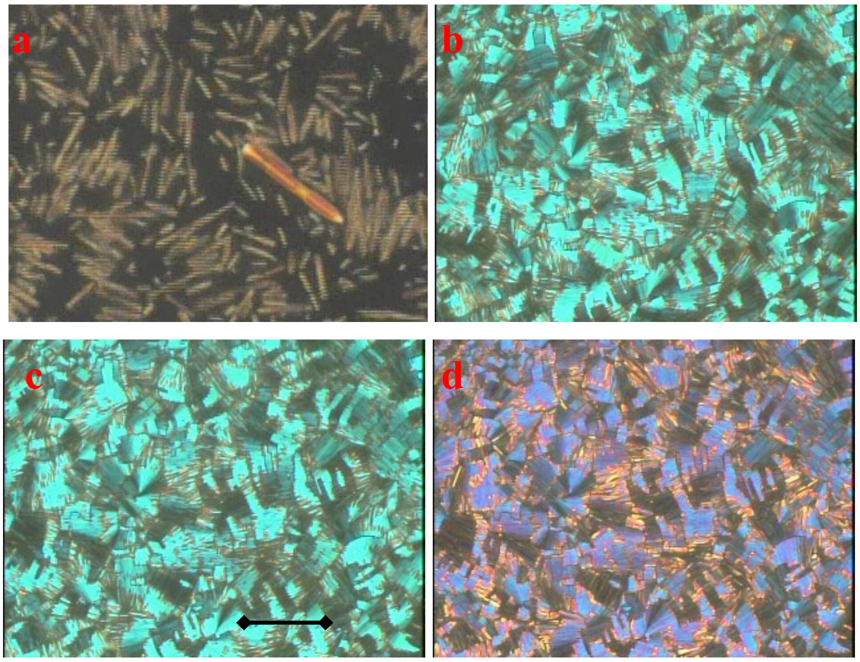

Fig. 7: Electro-optical observations in the B_7' phase. (a) $E=12V\mu m^{-1}$, f=13Hz, $T=136^{o}C$; (b) and (c) $E=+18V\mu m^{-1}$ and $E=-18V\mu m^{-1}$, $T=132^{o}C$; (d) E=0 after turning off from $E=-18V\mu m^{-1}$. (bar indicates 0.1mm length)

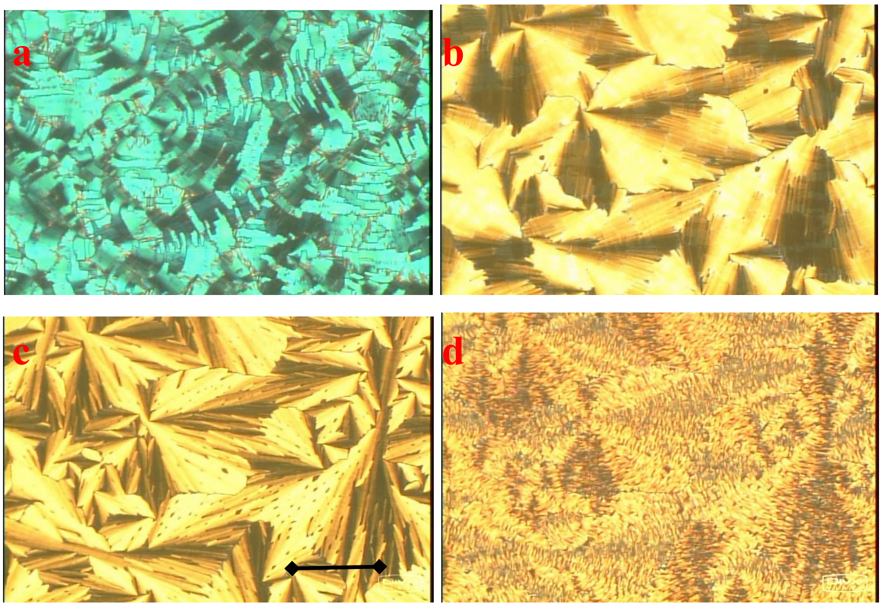

Fig. 8: Electro-optical switching in the B_2 phase. (a) On cooling from the B_7' phase under application of a field of $12V\mu m^{-1}$, $T=125^{o}C$; (b) the texture after turning off the field (same area as in a); (c) a field of $12V\mu m^{-1}$ is on for a long time; (d) E=0 after prolonged field application. (bar indicates 0.1mm length).

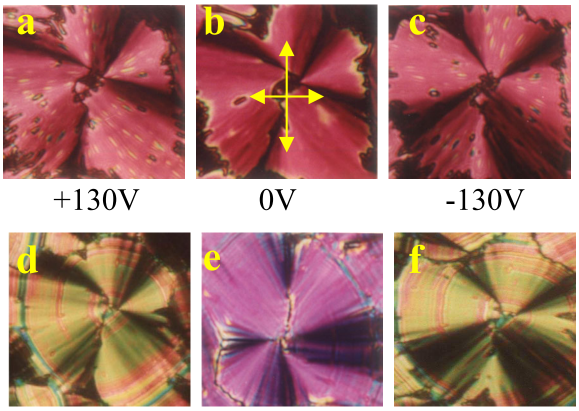

Fig. 9: (a), (b) and (c) Bistable switching domains obtained in B_7' phase, T=137°C; (d), (e) and (f) tristable switching domains obtained in the B_2 (SmC_aP_A) phase, T=125°C by applying dc voltage; cell gap:8 μm.

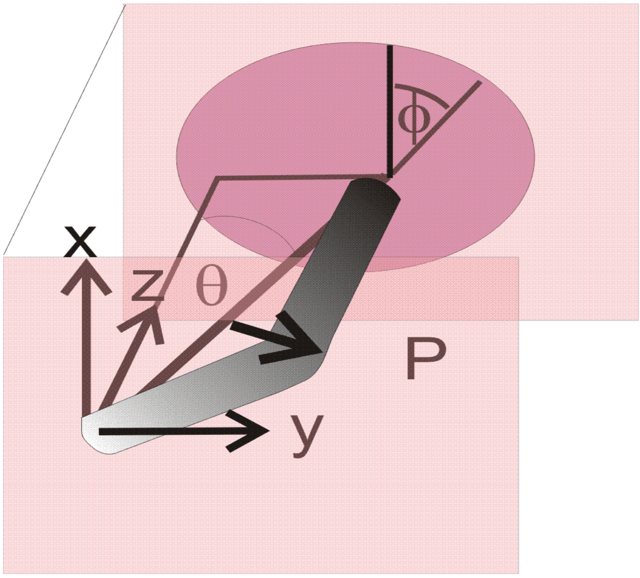

Fig. 11: Director and layer structure of the double tilted SmC_G phase of bent-core molecules.