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Supporting Information

Wide thermal range frustrated liquid crystal phase in chiral dimers

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Experimental

1. General information

The requisite precursors were purchased either from Aldrich or local Companies and used as received. Solvents purchased from local companies were purified and dried as per the literature methods prior to the use. The target dimers were purified by recrystallization technique choosing appropriate mixture of solvents (see synthetic procedure for details). The intermediates were purified by column chromatographic and/or recrystallization techniques. Chromatography was performed using either silica gel (60-120, 100-200 and 230-400 mesh) or neutral aluminium oxide as stationary phases. Thin layer chromatography was performed using aluminium sheets pre-coated with silica gel (Merck, Kieselgel60, F_{254}). ^{1}H NMR spectra were recorded using Bruker AMX-400 (400 MHz) spectrometer. For ^{1}H NMR spectra, the chemical shifts are reported in ppm relative to $SiMe_4$ (TMS) as an internal standard and coupling constants are presented in Hz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave numbers (cm^{-1}). Microanalytical data was obtained from a Eurovector model EA3000 CHNS elemental analyzer. Mass spectra were recorded on a JOEL JMS-600H spectrometer in FAB^+ mode using 3-nitrobenzyl alcohol as a liquid matrix. The energy-minimized space-filling molecular structures of dimers were obtained using MM2 computations of the CS *ChemDraw3D* (version 5) program. The phase behaviour of the compounds was determined using a polarizing optical microscope (POM) (Leica DCF 320) equipped with a programmable hot stage (Melter FP90). For this purpose, untreated clean glass slides were used initially; for confirmation of assignments, two

differently surface-coated slides, one treated for homogeneous alignment, the other for homeotropic alignment were used. The phase transition temperatures and associated enthalpies were determined from thermograms recorded at a scanning rate of 5 ^{o}C/min on a differential scanning calorimeter (DSC) (Perkin Elmer DSC-7 with the PC system operating on Pyris software) apriorically calibrated using pure indium as a standard. The optical properties of the mesophases were probed with the help of Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer. X-Ray measurements were performed on unaligned (powder) samples with CuK_{∞} (λ = 0.15418 nm) radiation using the PANalytical X'Pert PRO MP X-ray diffractometer consisting of a focusing elliptical mirror and a fast resolution detector (PIXCEL).

2. Synthesis and molecular structural characterization of dimers

To a dry 100 ml round bottom flask equipped with a magnetic stir bar, reflux condenser and nitrogen inlet were added 0.87 mmol of cholesteryl ω-(3-hydroxy-4-formylphenoxy)alkanoate (**2-3** / **2-5**), 0.87 mmol of 4-aminophenyl 4-(*n*-alkoxy)benzoate (**3-8** / **3-10**), 50 ml of absolute ethanol and two drops of glacial acetic acid. The resultant reaction mixture was heated to reflux for 2 h to obtain a thick yellow precipitate, which was isolated by filtering the hot reaction mixture, washed with very hot absolute ethanol, and dried in *vacuo* to afford the requisite dimer in almost pure form. The compound was further purified by repeated recrystallizations from a mixture of CH_2Cl_2-hexanes (1:10).

1-8,3 : *4-(4-(4-Cholesteryl-oxy-4-oxobutoxy)-2-hydroxybenzylideneamino)phenyl 4-(octyloxy)benzoate*.

Yield: 81 %; a bright yellow solid [Found: C, 77.74; H, 8.44; N, 1.56. $C_{59}H_{81}NO_7$ requires C, 77.34; H, 8.91; N, 1.53]; IR (KBr Pellet): ν_{max} in cm^{-1} 3054, 2987, 1726, 1607 and 896; ^{1}H NMR (400MHz, $CDCl_3$): δ 13.65 (s, 1H, 1×OH), 8.53 (s, 1H, 1×CH=N), 8.15 (d, J = 8.9 Hz, 2H, Ar), 7.28 (m, 5H, Ar), 6.99 (d, J = 8.9Hz, 2H, Ar), 6.48 (m, 2H, Ar), 5.38 (br d, J = 4.8 Hz, 1H, 1 × olefinic), 4.65 (m, 1H, 1×CHOCO), 4.05 (m, 4H, 2×OCH_2), 2.51 (t, J = 7.3, 2H, 1×CH_2), 2.33-0.89 (m, 45H, 6× CH, 18 × CH_2, 1 × CH_3), 1.02 (s, 3H, 1×CH_3), 0.91 (d, J = 6.52, 3H, 1 ×CH_3), 0.87 (d, J = 1.8, 3H, 1×CH_3), 0.85 (d, J = 1.8, 3H, 1×CH_3) and 0.67 (s, 3H, 1×CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 172.41, 165, 163.71, 163.64, 163.30, 161.62, 149.49, 146.13, 139.65,

133.58, 132.30, 122.68, 121.88, 121.43, 114.35, 113.18, 107.48, 101.72, 74.15, 68.37, 67.04, 56.72, 56.18, 50.07, 42.34, 39.76, 39.53, 38.16, 37.01, 36.62, 35.79, 31.89, 31.80, 31.10, 29.32, 29.21, 29.11, 28.22, 28.01, 27.83, 26, 24.58, 24.29, 23.84, 22.80, 22.63, 22.55, 21.05, 19.31,18.73, 14.07 and 11.86; MS (FAB+): m/z for $C_{59}H_{81}NO_7$, Calculated: 915.6, Found: 915.6.

1-10,3 : *4-(4-(4-Cholesteryloxy-4-oxobutoxy)-2-hydroxybenzylideneamino)phenyl 4-(decyloxy)-benzoate*.

Yield: 82 %; a bright yellow solid [Found: C, 77.64; H, 8.97; N, 1.52. $C_{61}H_{85}NO_7$ requires C, 77.58; H, 9.07; N, 1.48]; IR (KBr Pellet): ν_{max} in cm^{-1} 3054, 2986, 1728, and 1606; ^{1}H NMR (400MHz, $CDCl_3$): δ 13.61 (s, 1H, 1×OH), 8.53 (s, 1H, 1 × CH=N), 8.15 (d, J = 8.92 Hz, 2H, Ar), 7.27 (m, 5H, Ar), 6.97 (d, J = 8.96 Hz, 2H, Ar), 6.48 (m, 2H, Ar), 5.38 (br d, J = 4.28 Hz, 1H, 1×olefinic), 4.64 (m, 1H, 1×CHOCO), 4.05 (m, 4H, 2×OCH_2), 2.50 (t, J = 7.4, 2H, 1 ×CH_2), 2.33-0.88 (m, 49H, 6×CH, 20×CH_2, 1 × CH_3), 1.02 (s, 3H, 1×CH_3), 0.91 (d, J = 6.52, 3H, 1×CH_3), 0.87 (d, J = 1.72, 3H, 1×CH_3), 0.86 (d, J = 1.72, 3H, 1×CH_3) and 0.68 (s, 3H, 1×CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 172.41, 165, 163.71, 163.64, 163.29, 161.62, 149.49, 146.13, 139.65, 133.58, 132.29, 122.68, 121.87, 121.43, 114.35, 113.18, 107.48, 101.72, 74.15, 68.37, 67.04, 56.72, 56.18, 50.06, 42.34, 39.76, 39.53, 38.16, 37.01, 36.61, 36.20, 35.79, 31.89, 31.10, 29.54, 29.35, 29.30, 29.10, 28.22, 28.01, 27.83, 25.98, 24.57, 24.29, 23.84, 22.80, 22.67, 22.55, 21.05, 19.31,18.72, 14.09 and 11.86; MS (FAB+): m/z for $C_{61}H_{85}NO_7$, Calculated: 943.63, Found: 943.8.

1-8,5 : *4-(4-(6-Cholesteryloxy-6-oxohexyloxy)-2-hydroxybenzylideneamino)phenyl 4-(octyloxy)-benzoate* :

Yield: 87 %; a bright yellow solid [Found: C, 77.16; H, 9.16; N, 1.53. $C_{61}H_{85}NO_7$ requires C, 77.58; H, 9.07; N, 1.48]; IR (KBr Pellet): ν_{max} in cm^{-1} 3054, 2986, 1728, and 1606; ^{1}H NMR (400MHz, $CDCl_3$): δ 13.65 (s, 1H, 1×OH), 8.54 (s, 1H, 1 × CH=N), 8.15 (d, J = 8.92 Hz, 2H, Ar), 7.28 (m, 5H, Ar), 6.98 (d, J = 8.96 Hz, 2H, Ar), 6.48 (m, 2H, Ar), 5.38 (br d, J = 4.28 Hz, 1H, 1×olefinic), 4.63 (m, 1H, 1×CHOCO), 4.03 (m, 4H, 2×OCH_2), 2.35-0.88 (m, 51H, 6×CH, 21×CH_2, 1×CH_3), 1.02 (s, 3H, 1×CH_3), 0.91 (d, J = 6.50, 3H, 1×CH_3), 0.87 (d, J = 1.76, 3H, 1×CH_3), 0.86 (d, J = 1.76, 3H, 1×CH_3) and 0.67 (s, 3H, 1×CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ

172.95, 164.94, 163.74, 163.63, 163.52, 161.61, 149.45, 146.14, 139.69, 133.54, 132.29, 122.66, 121.86, 121.43, 114.34, 113.03, 107.56, 101.62, 73.83, 68.36, 67.88, 56.71, 56.17, 50.06, 42.33, 39.75, 39.52, 38.17, 37.01, 36.61, 36.20, 35.79, 34.56, 31.89, 31.79, 29.31, 29.20, 29.10, 28.77, 28.22, 28, 27.84, 25.98, 25.57, 24.76, 24.28, 23.84, 22.79, 22.63, 22.55, 21.04, 19.31, 18.72, 14.06 and 11.85; MS (FAB+): m/z for $C_{61}H_{85}NO_7$, Calculated: 943.63, Found: 943.8.

1-10,5: *4-(4-(6-Cholesteryloxy-6-oxohexyloxy)-2-hydroxybenzylideneamino)phenyl 4-(decyloxy)-benzoate*

Yield: 87 %; a bright yellow solid [Found: C, 77.49; H, 8.98; N, 1.91. $C_{63}H_{89}NO_7$ requires C, 77.82; H, 9.23; N, 1.44]; IR (KBr Pellet): ν_{max} in cm^{-1} 3056, 2948, 1725, and 1606; ^1H NMR (400MHz, $CDCl_3$): δ 13.61 (s, 1H, 1×OH), 8.53 (s, 1H, 1×CH=N), 8.14 (d, J = 8.96 Hz, 2H, Ar), 7.27 (m, 5H, Ar), 6.97 (d, J = 8.96 Hz, 2H, Ar), 6.47 (m, 2H, Ar), 5.37 (br d, J = 3.72 Hz, 1H, 1×olefinic), 4.62 (m, 1H, 1×CHOCO), 4.04 (t, J = 6.56 Hz, 2H, 1×OCH_2), 4.01 (t, J = 6.44 Hz, 2H, 1×OCH_2), 2.32-0.88 (m, 55H, 6×CH, 23×CH_2, 1×CH_3), 1.02 (s, 3H, 1×CH_3), 0.91 (d, J = 6.60, 3H, 1×CH_3), 0.87 (d, J = 1.72, 3H, 1×CH_3), 0.86 (d, J = 1.72, 3H, 1×CH_3) and 0.68 (s, 3H, 1×CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ 172.96, 164.95, 163.74, 163.63, 163.52, 161.61, 149.47, 146.14, 139.69, 133.54, 132.29, 122.67, 121.87, 121.42, 114.34, 113.02, 107.57, 101.60, 73.83, 68.36, 67.88, 56.70, 56.16, 50.05, 42.33, 39.75, 39.53, 38.17, 37.01, 36.61, 36.20, 35.79, 34.57, 31.87, 29.54, 29.36, 29.30, 29.10, 28.77, 28.22, 28. 01, 27.83, 25.98, 25.57, 24.77, 24.29, 23.84, 22.80, 22.67, 22.56, 21.04, 19.32, 18.72, 14.10 and 11.86; MS (FAB+): m/z for $C_{63}H_{89}NO_7$, Calculated: 971.66, Found: 972.4.