

Supramolecular Helical Mesomorphic Polymers. Chiral Induction through H-Bonding.

*Joaquín Barberá, Laura Puig, Pilar Romero, José Luis Serrano, Teresa Sierra**

Instituto de Ciencia de Materiales de Aragón. C.S.I.C.-Universidad de Zaragoza

Química Orgánica, Facultad de Ciencias

50009-Zaragoza, Spain.

e-mail: tsierra@unizar.es

Supporting Information

Shynthesis

General procedure for the preparation of alkoxy substituted anilines.

An argon-flushed flask containing a suspension of the corresponding alkoxy substituted nitrocompound (14 mmol), ethanol (75 ml), cyclohexene (25 ml) and $\text{Pd}(\text{OH})_2/\text{C}$ -10% (1.4 mmol) was heated under reflux with continuous stirring for 4h (monitoring by thin layer chromatography determined the end of the reaction). The mixture was allowed to cool and then filtered through a pad of celite. The solvent was removed and the product recrystallized from ethanol. Yield 90-100%

Analytical data.

p-decyloxyaniline. R_f 0.5 (2:1, hexane:ethylacetate). ^1H NMR (300 MHz, CDCl_3): δ 0.86 (t, $J=6.3$ Hz, 3H), 1.25-1.75 (m, 16H), 3.88 (t, $J=6.6$ Hz, 2H), 6.83 (d, $J=9$ Hz, 2H), 7.03 (d, $J=9$ Hz, 2H). IR (nujol, NaCl): 3409, 3328, 3125, 3062-2500, 1618, 1257, 820 cm^{-1}

3,4-didecyloxyaniline. R_f 0.3 (80:20, hexane:ethylacetate). ^1H NMR (300 MHz, CDCl_3): δ 0.86 (t, $J=6.3$ Hz, 6H), 1.25-1.80 (m, 32H), 3.3 (s, broad, 2H), 3.85-3.93 (m, 4H), 6.18 (dd, $J=2.7; 8.4$ Hz, 1H), 6.28 (d, $J=2.7$ Hz, 1H), 6.71 (d, $J=8.4$ Hz, 1H). IR (nujol, NaCl): 3389, 3299, 3202, 3000-2850, 1614, 1230, 791 cm^{-1}

3,4-didodecyloxyaniline. R_f 0.4 (80:20, hexane:ethylacetate). ^1H NMR (400 MHz, CDCl_3): δ 0.88 (t, $J=6.4$ Hz, 6H), 1.2-1.81 (m, 40H), 3.42 (s, broad, 2H), 3.87-3.95 (m, 4H), 6.19 (dd, $J=2.4; 8.4$ Hz, 1H), 6.30 (d, $J=2.4$ Hz, 1H), 6.73 (d, $J=8.4$ Hz, 1H). IR (nujol, NaCl): 3203, 3000-2850, 1610, 1230, 790 cm^{-1}

3,4,5-tridecyloxyaniline. R_f 0.4 (80:20, hexane:ethylacetate). ^1H NMR (300 MHz, CDCl_3): δ 0.86 (t, $J=6.3$ Hz, 9H), 1.10-1.77 (m, 48H), 3.44 (s, broad, 2H), 3.80-3.90 (m, 6H), 5.89 (s, 2H). IR (nujol, NaCl): 3411, 3331, 3206, 3000-2855, 1599, 1237, 815 cm^{-1}

General procedure for the preparation of alkoxy substituted triaryl-amino-1,3,5-triazines.

A mixture of the corresponding aniline (12 mmol), cyanuric chloride (4 mmol) and anhydrous potassium carbonate (12 mmol) in 2-butanone (75 ml) was refluxed under argon atmosphere overnight. The reaction mixture was then cooled and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (100 ml) and poured into water (100 ml). The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with successive HCl 1N (100 ml), brine and dried over anhydrous magnesium sulfate.

After filtration, the solvent was removed. The product was purified by flash chromatography on silicagel, eluting with hexane/ethylacetate mixtures. The products were recrystallized from absolute ethanol. Yield 50-60%

2,4,6-Tris [4-decyloxyphenyl-1-amino]-1,3,5-triazine. T-OC₁₀

R_f 0.6 (85:15, hexane:ethylacetate). ¹H NMR (300 MHz, CDCl₃): δ 0.86 (t, J=6.3 Hz, 9H, CH₃), 1.10-1.77 (m, 48H, CH₂), 3.91 (t, J=6.6 Hz, 6H, CH₂-O-phenyl), 6.82 (d, J=8.4 Hz, 6H, phenyl), 6.86 (s, broad, 3H, NH), 7.38 (d, J=8.7 Hz, 6H, phenyl). ¹³C NMR (300 MHz, CDCl₃): δ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 31.9, 68.3, 114.6, 122.7, 131.4, 155.5, 164.6. IR (nujol, NaCl): 3405, 3381, 2951-2852, 1629, 1230, 828 cm⁻¹. MS (FAB+) m/z: 822 (M⁺), 824 (100%, M⁺+2H⁺). Elemental analysis: calculated for C₅₁H₇₈N₆O₃ (%): C 74.45 H 9.49 N 10.22. Found: C 74.60 H 10.10 N 10.43

2,4,6-Tris [3,4-didecyloxyphenyl-1-amino]-1,3,5-triazine. T-2OC₁₀

R_f 0.3 (10:1, hexane:ethylacetate). ¹H NMR (300 MHz, CDCl₃): δ 0.86 (t, J=6.3 Hz, 18H, CH₃), 1.1-1.41 (m, 84H, CH₂), 1.72-1.79 (m, 12H, CH₂), 3.87 (s, broad, 6H, CH₂-O-phenyl), 3.92 (t, J=6.3 Hz, 6H, CH₂-O-phenyl), 6.77 (d, J=8.7 Hz, 3H, phenyl), 6.95 (d, J=8.4 Hz, 3H, phenyl), 7.01 (s, broad, 3H, NH), 7.06 (s, 3H, phenyl). ¹³C NMR (300 MHz, CDCl₃): δ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.9, 31.90, 69.1, 69.9, 108.2, 113.4, 114.6, 132.1, 145.5, 149.4, 164.6. IR (nujol, NaCl): 3405, 3381, 2952-2503, 1625, 1224, 835 cm⁻¹. MS (FAB+) m/z: 1290 (M⁺), 1292 (100%, M⁺+2H⁺). Elemental analysis: calculated for C₈₁H₁₃₈N₆O₆ (%): C 75.34 H 10.69 N 6.51. Found: C 75.39 H 10.60 N 6.36

2,4,6-Tris [3,4-didodecyloxyphenyl-1-amino]-1,3,5-triazine. T-2OC₁₂

R_f 0.3 (90:10, hexane:ethylacetate). ¹H NMR (300 MHz, CDCl₃): δ 0.89 (t, J=6.4 Hz, 18H, CH₃), 1.1-1.46 (m, 108H, CH₂), 1.76-1.81 (m, 12H, CH₂), 3.85 (s, broad, 6H, CH₂-O-phenyl), 3.97 (t, J=6.3 Hz, 6H, CH₂-O-phenyl), 6.78 (d, J=7.5 Hz, 3H, phenyl), 6.82 (s, 3H, NH), 6.98 (d, J=6 Hz, 3H, phenyl), 7.11 (s, 3H, phenyl). ¹³C NMR (300 MHz, CDCl₃): δ 14.1, 22.7, 26.1, 29.4, 29.5, 29.7, 31.9, 69.2, 70.0, 108.4, 113.4, 114.7, 132.2, 145.6, 149.5, 164.6. IR (nujol, NaCl): 3400-3200, 2955-2800, 1601, 1578, 1223, 847 cm⁻¹. MS (FAB+) m/z: 518 (100%), 1460 (M⁺+2H⁺). Elemental analysis: calculated for C₉₃H₁₆₂N₆O₆ (%): C 76.54 H 11.11 N 5.76. Found: C 76.72 H 11.75 N 5.85.

2,4,6-Tris [3,4,5-tridecyloxyphenyl-1-amino]-1,3,5-triazine. T-3OC₁₀
 R_f 0.5 (85:15, hexane:ethylacetate). ¹H NMR (300 MHz, CDCl₃): δ 0.86 (t, J=6.3 Hz, 27H, CH₃), 1.10-1.71 (m, 144H, CH₂), 3.85 (s, broad, 6H, CH₂-O-phenyl), 3.89 (t, J=6.3 Hz, 12H, CH₂-O-phenyl), 6.70 (s, 6H, phenyl), 6.94 (s, broad, 3H, NH). ¹³C-RMN (300 MHz, CDCl₃): δ 14.1, 22.7, 26.2, 29.4, 29.5, 29.7, 29.7, 29.8, 30.4, 31.9, 69.1, 73.5, 100.3, 133.7, 134.6, 153.1, 164.3. IR (nujol, NaCl): 3393-3120, 2919-2853, 1582, 1227, 808 cm⁻¹. MS (FAB+) m/z: 709 (100%), 1758 (M⁺), 1761 (M⁺+3H⁺). Elemental analysis: calculated for C₁₁₁H₁₉₈N₆O₉ (%): C 75.77 H 11.26 N 4.78. Found: C 76.04 H 11.78 N 4.77

Evaluation of the density of the materials from x-ray data.

Dimerisation of triazine Tri-2C₁₀ in the pure state as well as in its complexes is supported by a qualitative evaluation of the density of the mesophases. The relationship between the density (ρ) and the number of molecules in the unit cell (Z) is given by the following equation: $\rho = (M/N)/(V/Z)$, where M is the molar mass (expressed in g), N the Avogadro's number, and V the unit cell volume (expressed in cm³). For a hexagonal lattice, $V = (\sqrt{3}/2)a^2c \cdot 10^{-24}$, where a and c are the lattice parameters.

Assuming that the density of the organic compounds is near 1 g cm⁻³, it is deduced that in the pure triazine Tri-2C₁₀ there are two molecules per unit cell ($Z = 2$) and thus each disc within the column is a dimer with a mean stacking distance between discs (c parameter) of about 4.4-4.5 Å. This interdisc distance is typical of many discotic mesogens and corresponds well to the large-angle diffuse halo detected in the X-ray patterns of this compound.

For the three complexes the c parameter is directly deduced from the X-ray patterns, and this allows the calculation of the density using the above-mentioned equations. From these calculations it is clear that there are two triazine molecules per disc and the estimated mesophase density is 1.0 g cm⁻³ for Tri-2C₁₀/Adip[1:1] and Tri-2C₁₀/Adip[2:1], and 1.1 g cm⁻³ for Tri-2C₁₀/Adip[4:1].

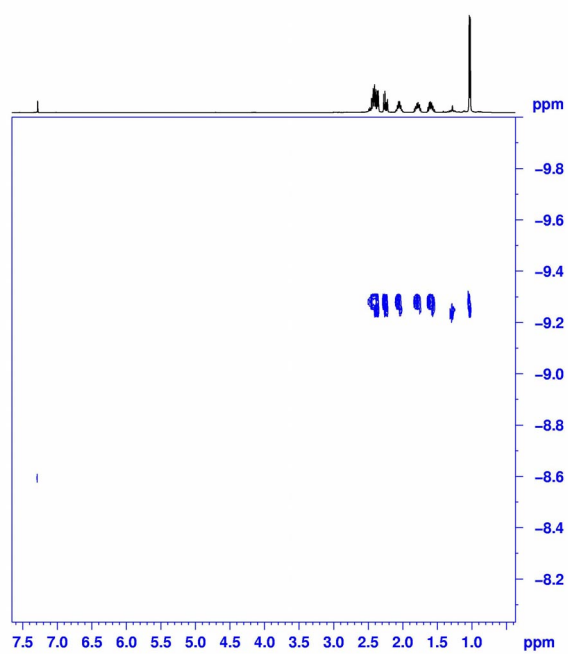


FIGURE SI1. DOSY spectrum of R-(3)-methyladipic acid (MeAdip)

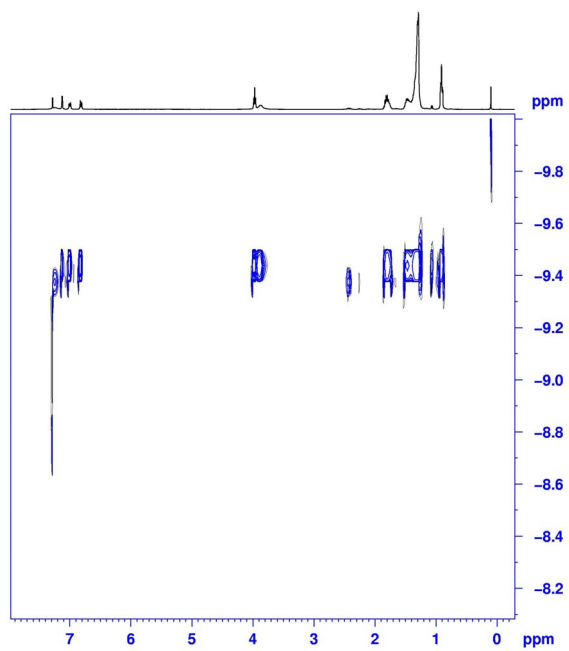
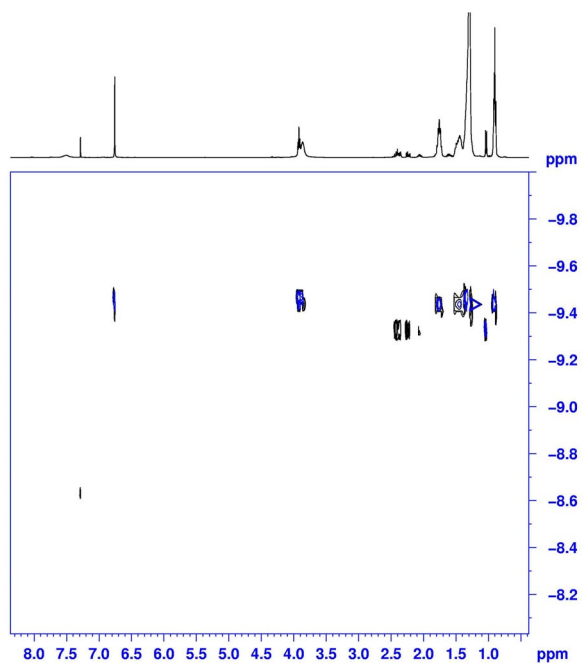


FIGURE SI2. DOSY spectrum of T-2OC₁₀/MeAdip[4:1]

a)



b)

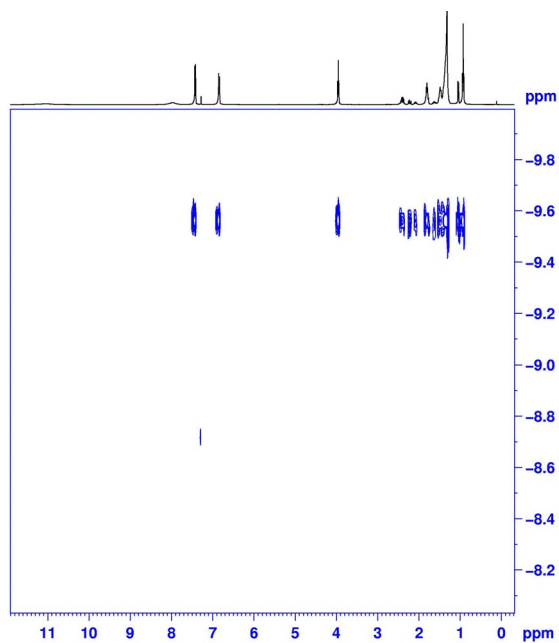


FIGURE S13. DOSY spectra of a) T-3OC₁₀/MeAdip[1:1][#] and b) T-OC₁₀/MeAdip[2:1][#]. [#] The different proportions between triazine and acid have been selected depending on whether monomers (triazine T-3OC₁₀) or dimers (T-OC₁₀) are the constituent units of the disks within the columns. Thus, according to the chosen proportions the final structure should be the same, i.e. figure 5d.

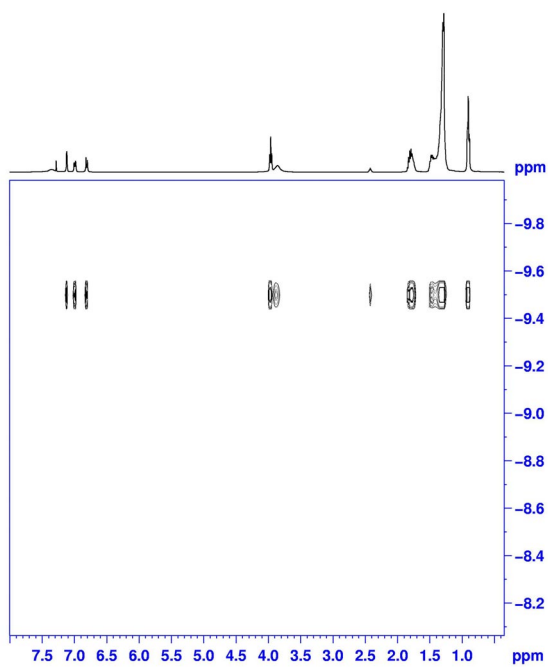


FIGURE SI4. DOSY spectrum of the hetero-complex formed by the triazine T-2OC₁₀ and adipic acid -T-2OC₁₀/Adip[2:1]-

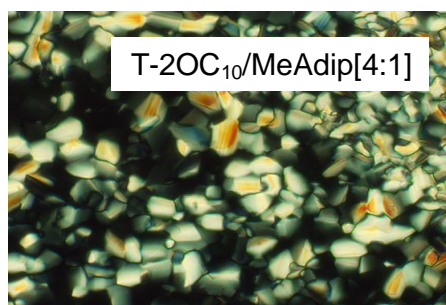
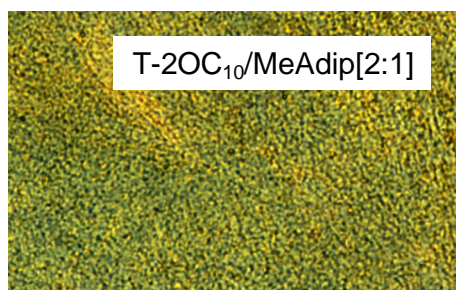
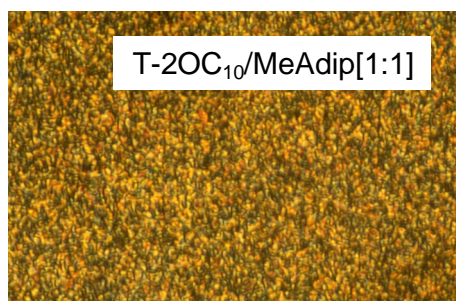
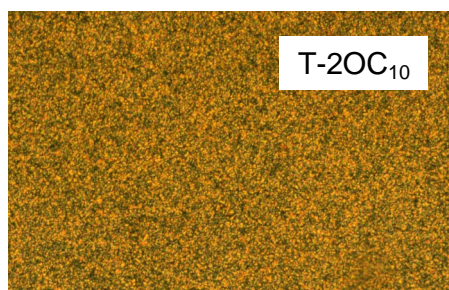


FIGURE SI5. Photomicrographs of the textures of the hexagonal columnar mesophases showed by the triazine component as well as by the three mixtures taken at room temperature.

Thermal data of T-2OC₁₀ and caproic acid complexes:

T-2OC₁₀/caproic acid [1:1] **Col_h** 64.1 °C (3.4 kJ/mol) I

T-2OC₁₀/caproic acid [1:2] **Col_h** 55.7 °C (2.6 kJ/mol) I

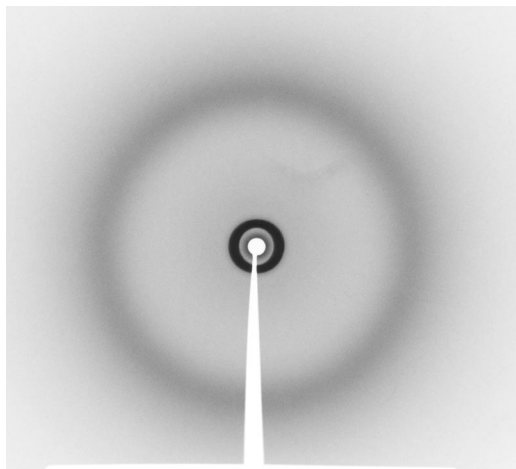


FIGURE SI6. x-ray diffraction pattern of the complex T-2OC₁₀/caproic acid [1:1], taken at room temperature. No halo at high angles corresponding to an ordered stacking is observed.

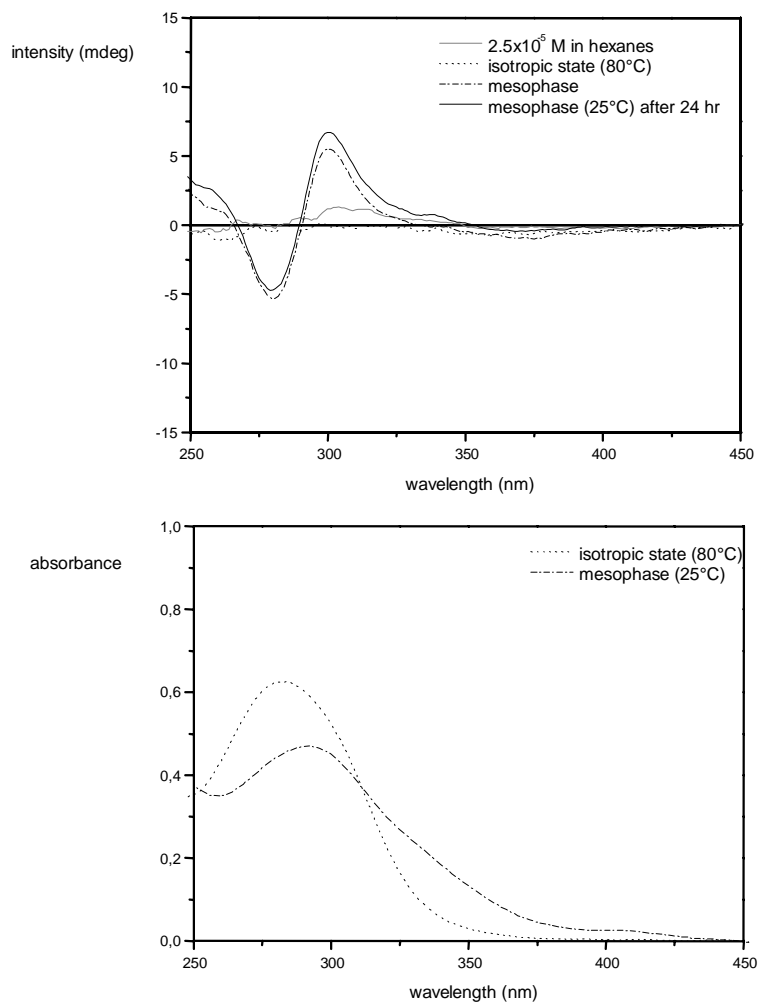


FIGURE SI7. CD spectrum of T-2OC12-MeAdip[1:1] in solution (in the isotropic liquid (80 °C), in solution (10 mm cell, 2.5×10^{-5} M in hexanes) and in the mesophase, both in the freshly formed mesophase and after 24 h. The UV spectrum in the region under study is shown below.

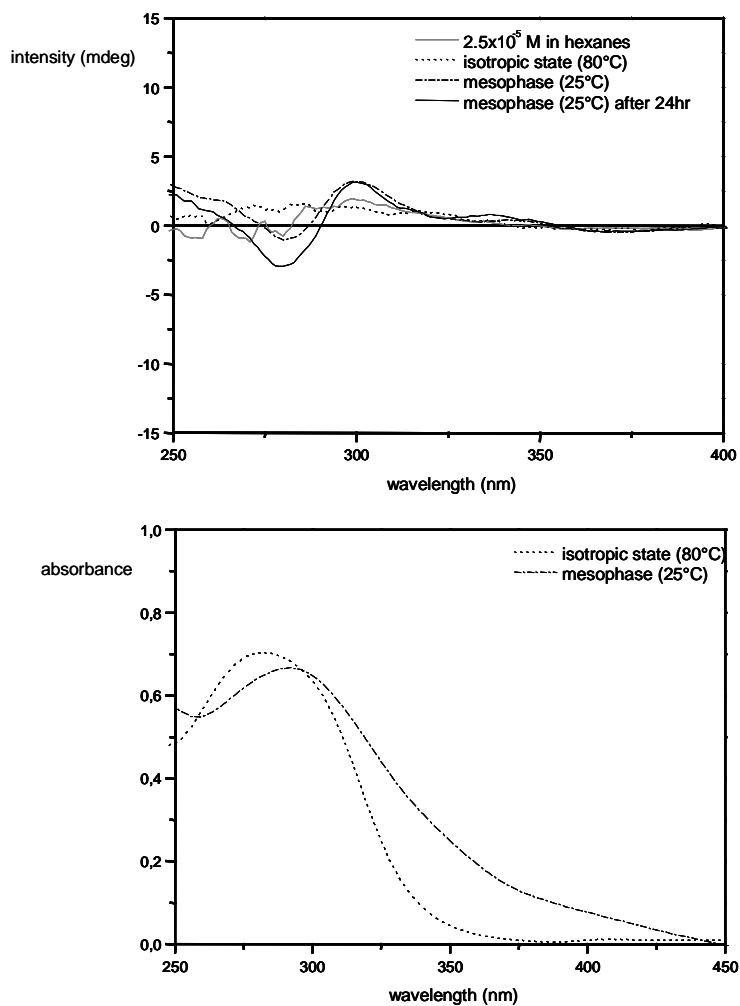


FIGURE S18. CD spectrum of T-2OC12-MeAdip[2:1] in solution (in the isotropic liquid (80 °C), in solution (10 mm cell, 2.5×10^{-5} M in hexanes) and in the mesophase, both in the freshly formed mesophase and after 24 h. The Uv spectrum in the region under study is shown below.

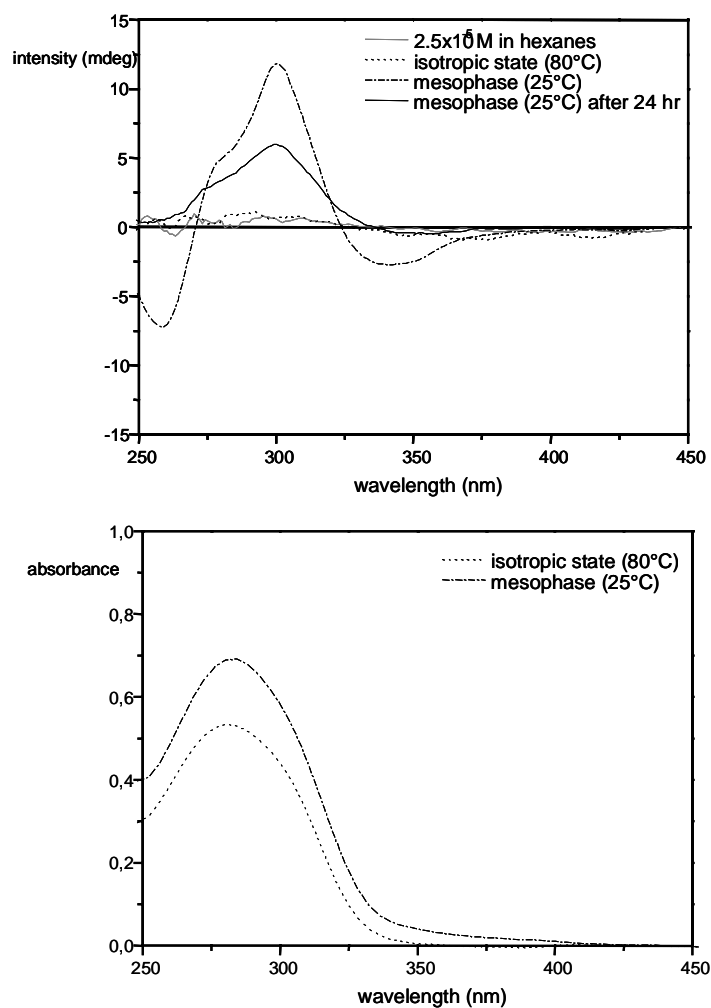


FIGURE SI9. CD spectrum of T-2OC12-MeAdip[4:1] in solution (in the isotropic liquid (80 °C), in solution (10 mm cell, 2.5×10^{-5} M in hexanes) and in the mesophase, both in the freshly formed mesophase and after 24 h. The Uv spectrum in the region under study is shown below.