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Modulating the Phase Behaviour of Lyotropic Discotic Liquid Crystals by Incorporation of an Electron Acceptor

Neville Boden [a] , Richard J. Bushby [a] & John F. Hubbard [a]

[a] SOMS Centre, University of Leeds, Leeds, England, LS2 9JT, UK

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MODULATING THE PHASE BEHAVIOUR OF LYOTROPIC DISCOTIC LIQUID CRYSTALS BY INCORPORATION OF AN ELECTRON ACCEPTOR

NEVILLE BODEN, RICHARD J. BUSHBY AND JOHN F. HUBBARD
SOMS Centre, University of Leeds, Leeds, England, LS2 9JT, UK

ABSTRACT The discotic amphiphile TP6EO2M, in aqueous solution, assembles into columnar aggregates which in turn undergo self-organisation on longer length scales to produce a rich variety of mesophases.[1-3] Adding an electron deficient dopant such as TNF or TAPA leads to the stabilisation of these mesophases and has the potential to introduce new properties such as chirality.

INTRODUCTION

The discogen 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)-triphenylene (TP6EO2M), Figure 1, forms columnar aggregates in aqueous solution. A number of liquid crystal phases are formed by increasing the concentration in solution including a columnar nematic phase, N_c, a discotic hexagonal phase, D_h, a discotic square phase, D_s, and a discotic oblique phase, D_o.[1-4]

We wish to report how the phase behaviour of TP6EO2M in aqueous solution can be modified with the introduction of electron deficient dopants that intercalate between the disc-like molecules in the stacks.

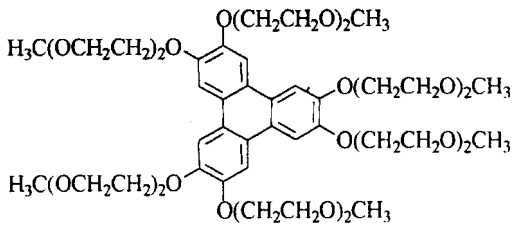
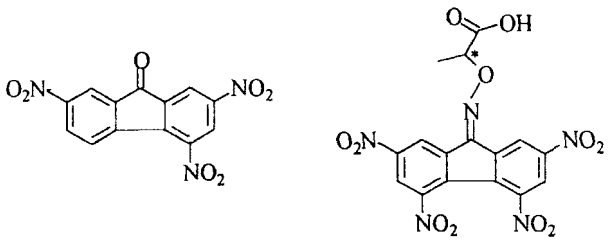


Figure 1 Molecular structure of TP6EO2M.

EXPERIMENTAL

TP6EO2M was synthesised according to established procedures.[5] 2,4,7-Trinitro-9-fluorenone, TNF, and 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid, TAPA, Figure 2, both commercially available were used as supplied (Aldrich) without further purification.



TNF TAPA

Figure 2 Molecular structures of dopants TNF and TAPA.

TP6EO2M doped samples were prepared by dissolving the appropriate amounts of TP6EO2M and dopant in dichloromethane, evaporating the solvent and evacuating at ~10mm Hg for 18 hours. Aqueous samples were prepared by adding deuterium oxide, D_2O, (Aldrich) to the doped TP6EO2M and then sealing the resulting solution, after sonication, in 0.2mm microslides (Camlab).

RESULTS AND DISCUSSION

TP6EO2M / TNF in D_2O

The phase behaviour of the TP6EO2M / TNF mixtures in aqueous solution were investigated by polarising optical microscopy and low angle X-ray diffraction (pinhole camera, Nickel filtered CuK_α at 1.54Å). N_c-I transition temperatures were seen to

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increase by 11°C as the TNF mole fraction was increased from 0-30mol%, the limiting factor being the solubility of the mixture (TNF is insoluble in water). The increased N_c - I transition temperatures of the mixtures, compared with the undoped system, is indicative of the increased rigidity and/or persistence length of the aggregates.[6] As more dopant was added, the mixtures became less soluble. This leads to a more restricted nematic range (25mol% TNF ~ 20-25wt%, undoped ~ 20-50wt%). Low angle X-ray diffraction was used to probe the structure of the aggregates and obtain the side by side separation of the columns which were in the range ~27-38Å for the mixtures studied. For samples with 15mol% or more of TNF a diffraction ring corresponding to the intermolecular separation 3.5Å within the columns was observed. In undoped samples no such diffraction ring is observed. These observations are also consistent with the proposition that addition of TNF induces order (and hence increases the rigidity) in the columnar aggregates.

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TP6EO2M / TAPA in D_2O

Polarising optical microscopy studies of water penetration into TP6EO2M doped with (-)-TAPA (between 5 and 30 mol% dopant) revealed a number of mesophases. In Figure 3 there is an increasing concentration of amphiphile from left to right. Crystal, K, D^*_h (chiral analogue of D_h), N^*_c (cholesteric), and I phases are present as well as what appears to be an intermediate phase between the N^*_c and I phases. The N^*_c - I transitions temperatures were not significantly raised compared with the N_c - I transitions of the undoped system. A diffuse reflection, from X-ray diffraction, corresponding to 3.5Å (for more than 10mol% dopant) was observed indicating an increased order within the aggregates compared with the undoped system.

The pitch of the N^*_c phase as determined by laser diffraction (Helium / Neon laser operating at 632nm) was found to be in the range 4 - 13 μm depending on the mole fraction of (-)-TAPA and concentration of the mixture in D_2O. The pitch decreased with

increasing (-)-TAPA mole fraction and increased with increasing water content. Figure 4 shows the optical texture of a magnetically aligned sample of TP6EO2M doped with 10mol% (-)-TAPA in D_2O. The distance between successive lines, in Figure 4, corresponds to half the cholesteric pitch. A novel optical texture was seen for thin samples, i.e. for thicknesses of the order of or less than the pitch, in the the N^*_c phase, shown in Figure 5 for a 10mol% doped sample. This blue 'platelet' texture appears instead of the usual fingerprint texture for cholesterics. Thicker samples, i.e. with a thickness greater than the pitch, exhibited the fingerprint texture. Both thin and thick samples showed the same N^*_c - I transition temperatures indicating that the different optical textures observed are the same phase. What appears to be a distinct phase

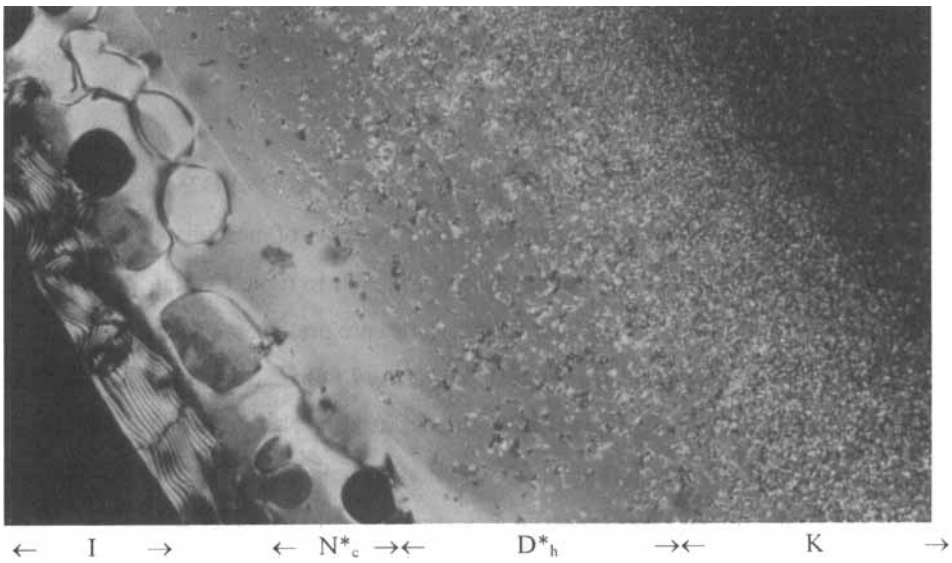

Figure 3 Contact preparation of 10mol% (-)-TAPA doped TP6EO2M in D_2O, 25°C, crossed polars, x150. (See Color Plate III).

between N^*_c and I in Figure 3 is therefore where the thickness of the sample preparation is less than or equal to the pitch.

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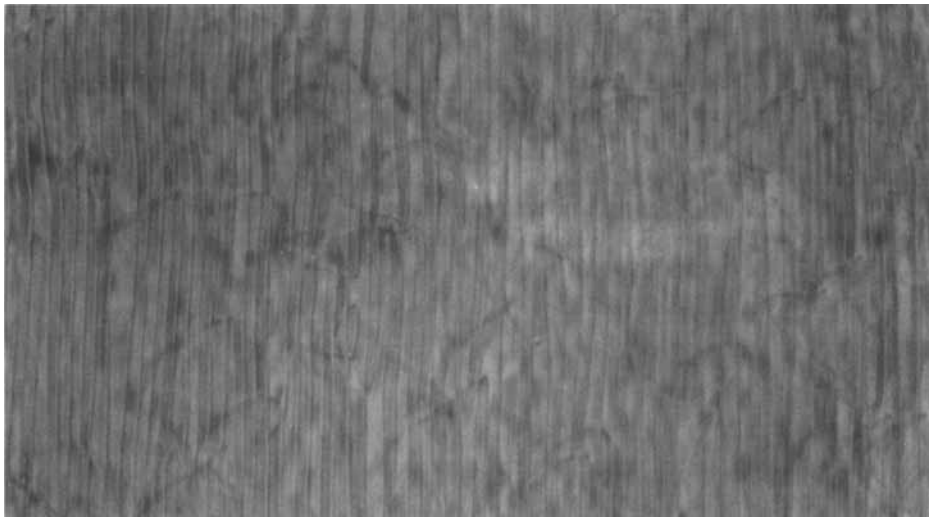

Figure 4 200μm sample, 10mol% (-)-TAPA / TP6EO2M in D_2O, 62wt% D_2O 5°C, 7T magnetic field direction is perpendicular to pitch lines, x150. (See Color Plate IV).

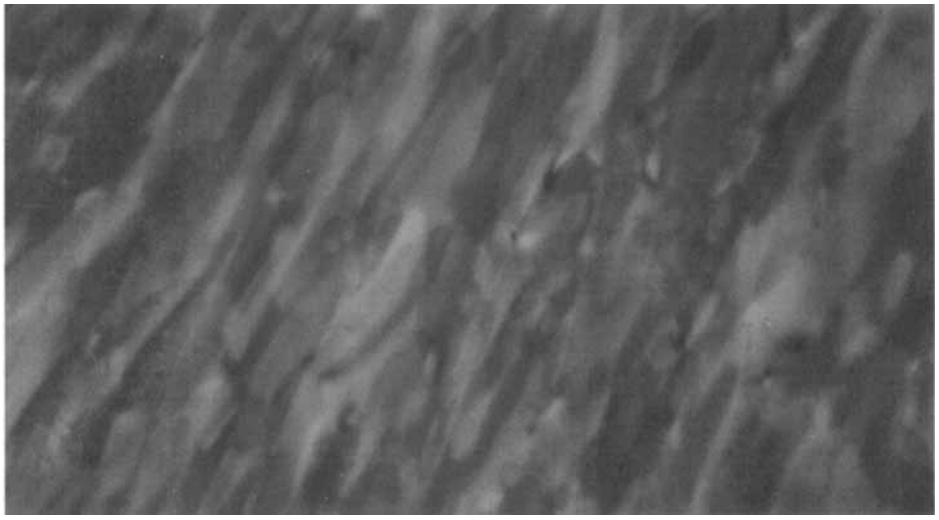

Figure 5 ~10μm sample, 10mol% (-)-TAPA / TP6EO2M in D_2O, 73wt% D_2O 15°C, crossed polars, x150. (See Color Plate V).

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REFERENCES

1. N. Boden, R J. Bushby, C. Hardy, J Phys. Lett., Paris, 46, No.7, L-325 (1985).
2. N .Boden, R J. Bushby, L .Ferris, C. Hardy, F. Sixl, Liquid Crystals, 1, No.2, 109 (1987),
3. N. Boden, R J. Bushby, C. Hardy, F. Sixl, Chem. Phys. Lett., 123, No. 5, 359 (1986).
4. P.J.B. Edwards, PhD Thesis, University of Leeds, (1993).
5. N. Boden, R C.Borner, R J. Bushby, A N. Cammidge, and M V. Jesudason, Liquid Crystals, 15, No. 6, 851 (1993).
6. R. Hentschke, Liquid Crystals, 10, No.5, 691 (1991).

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