

Nanophase segregated mesophase morphology in self-organized novel disc-rod oligomesogens

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Electronic supplementary information

Synthesis of novel disc-rod oligomers

The synthesis of disc-rod oligomesogens is outlined in Scheme 1. Compounds **1-5** and ω -bromo alkoxybiphenyls (RBr) were prepared as reported. Powdered KOH (135 mg, 2.4 mmol) was mixed with DMSO (10 ml) at room temperature and stirred for 10 min. Hexaacetoxy-TCQ (66.8 mg, 0.1 mmol) followed by the appropriate ω -bromo alkoxybiphenyl (2.4 mmol) was added and the reaction mixture was stirred at 55 °C for 24 h and then worked up by addition of ice-water and extracted with dichloromethane. The crude product was purified by column chromatography (silica gel, hexane-ethyl acetate 1:1 followed by dichloromethane) and then crystallized from acetone or precipitated with dichloromethane-ethyl acetate to afford pure yellow material in about 40% yield.

6a: **¹H NMR** (400 MHz; CDCl₃; Me₄Si) δ_{H} 7.71 (s, 3H, Ar-H from TCQ), 7.65 (d, 12H, J = 6.5 Hz, Ar-H from biphenyl), 7.59 (d, 12H, J = 6.5 Hz, Ar-H from biphenyl), 7.49 (d, 12H, J = 8.8 Hz, Ar-H from biphenyl), 6.96 (d, 12H, J = 8.9 Hz, Ar-H from biphenyl), 6.90 (s, 3H, Ar-H from TCQ), 4.2-4.1 (m, 12H, Ar-OCH₂), 3.98-4.05 (m, 12H, Ar-OCH₂), 2.0-1.91 (m, 12H, CH₂), 1.89-1.82 (m, 12H, CH₂), 1.65-1.60 (m, 24H, CH₂). All other compounds give similar spectra except for more number of aliphatic methylene protons.

¹³C NMR (100 MHz, CDCl₃, Me₄Si) δ_C 159.7, 145.1, 132.6, 131.3, 128.3, 127.0, 119.1, 115.0, 110.1, 69.0, 67.9, 29.22, 28.9, 25.8. All other compounds give similar spectra.

FT-IR ν_{max}(KBr)/cm⁻¹ 2922, 2854, 2224, 1620, 1601, 1541, 1506, 1491, 1456, 1377, 1338, 1295, 1251, 1221, 1178, 1105, 822, 721, 667. All other compounds give similar spectra.

Elemental analysis

6a, Found: C, 77.64; H, 6.00; N, 7.01. C₁₃₅H₁₂₆N₁₀O₁₂ requires C, 77.94; H, 6.10; N, 6.73%. **6b**, Found: C, 78.20; H, 6.33; N, 5.81. C₁₄₇H₁₅₀N₁₀O₁₂ requires C, 78.51; H, 6.72; N, 6.23%. **6c**, Found, C, 79.30; H, 7.21; N, 5.50. C₁₅₉H₁₇₄N₁₀O₁₂ requires C, 79.01; H, 7.26; N, 5.79%. **6d**, Found: C, 78.90; H, 7.51; N, 5.80. C₁₇₁H₁₉₈N₁₀O₁₂ requires C, 79.44; H, 7.72; N, 5.42 %.

Monotropic optically isotropic phase of compound 6a: The observation of an optically isotropic texture in a liquid crystalline compound between two birefringent phases, under the crossed polarized microscope, gives rise to possibilities like spontaneous homeotropic alignment of the compound or occurrence of a re-entrant isotropic phase. In our compound **6a** we observe that the optically isotropic phase appears monotropically from the preceding Smectic phase of the compound with sharp and cornered phase boundaries of its domains (Fig.1). The transition to an amorphous solid state is unlikely because of the abrupt extinction of birefringence and first order phase transitions observed in the DSC thermogram and the existence of re-entrant isotropic can be ruled out by the observed high viscosity of the phase. The transition to a homeotropic alignment in this compound can be ruled out by taking into account the values of transition enthalpy and nature of phase transition. Moreover, our attempts to align the higher homologous homeotropically did not yield the desired alignment which precludes the spontaneous alignment of the lower homologue **6a**. The monotropic (thermodynamically unstable) nature of the

optically isotropic phase excludes its characterization by X-ray diffraction studies which would have otherwise provided unequivocal assignment of the phase structure, its symmetry and detailed molecular organization in the phase. On the basis of POM and DSC we can assign the optically isotropic phase to a cubic phase although the symmetry and detailed molecular organization like bicontinuous cubic or micellar cubic could not be established by XRD. Furthermore, the existence of well characterized cubic phases with sharp and cornered phase boundaries of their domains while growing from other phases, as has been observed in this compound **6a**, has been documented between crystalline phase and smectic phases.¹⁻³

References

1. S. Diele, *Curr. Opin. Colloid Interface Sci.* 2002, **7**, 333-342.
2. I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003.
3. C. Tschierske, *J. Mater. Chem.* 1998, **8**, 1486.

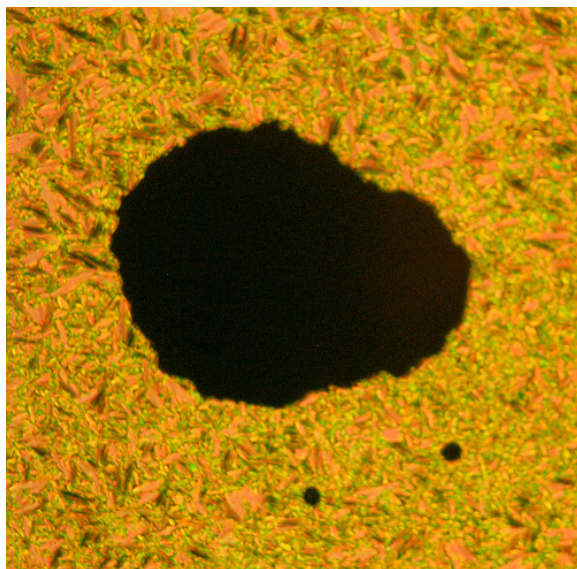


Fig.1. Transition to cubic phase from smectic A phase of compound **6a**.

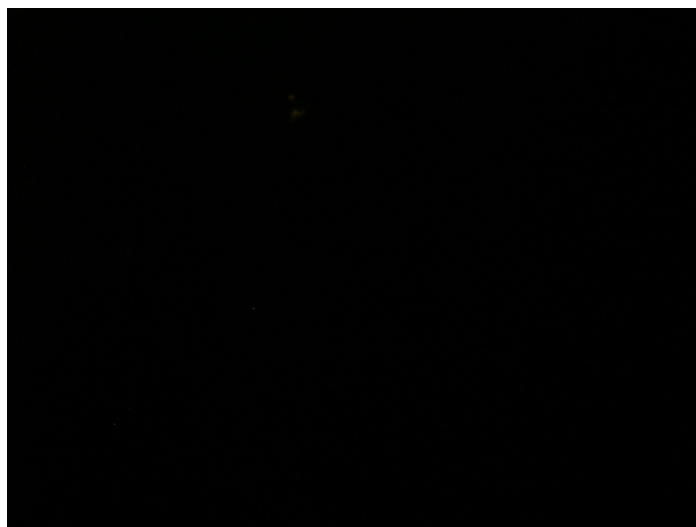


Fig. 2 Polarising optical micrograph of Cubic phase of compound **6a**.

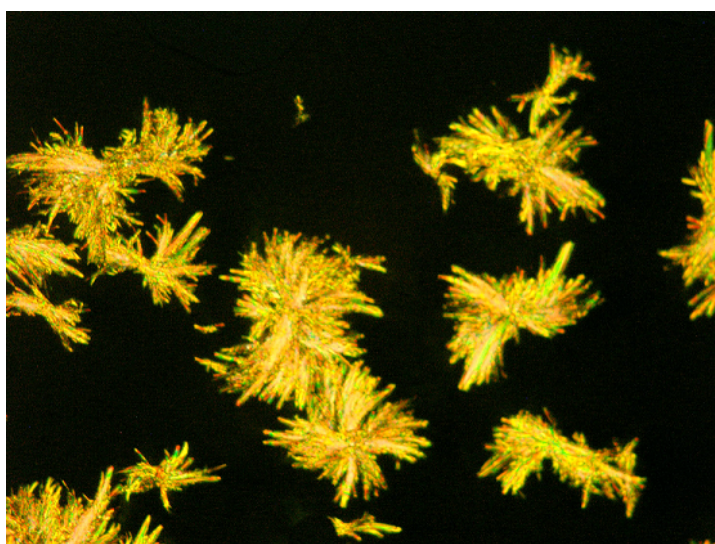


Fig.3 Crystal growth from cubic phase of compound **6a**.

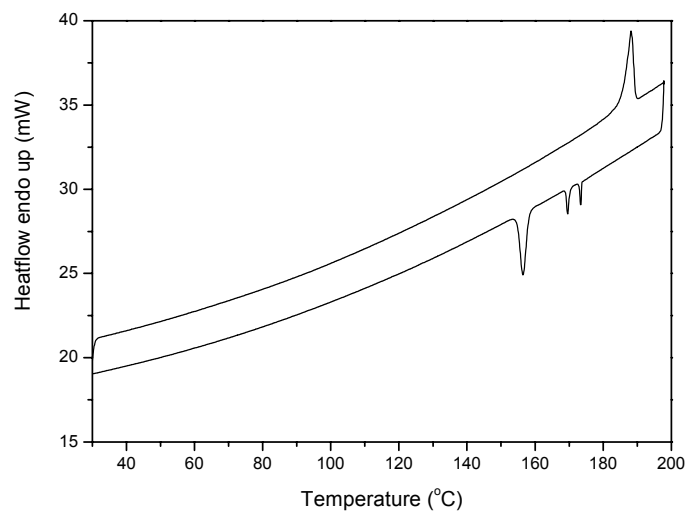


Fig. 4 DSC trace of compound **6a** on heating and cooling (scan rate 5 °C/min).

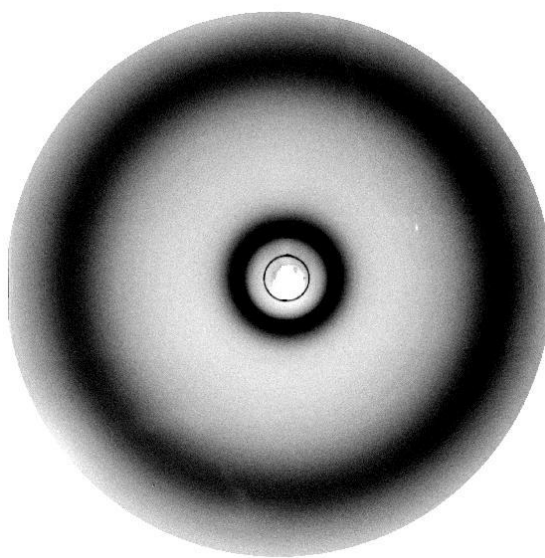


Fig. 5 X-ray diffraction pattern of compound **6d** in the mesophase.

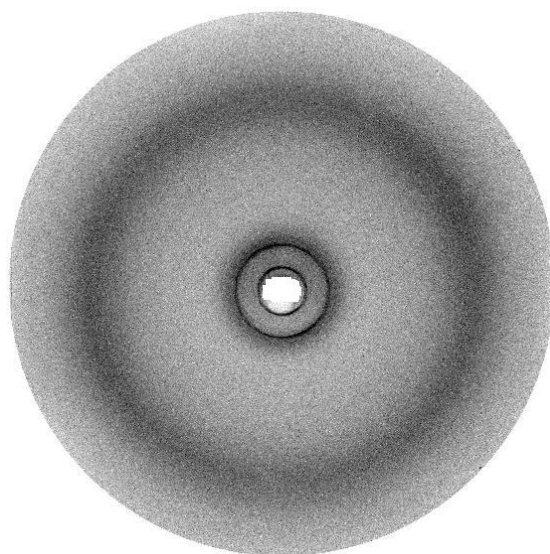


Fig. 6 XRD of compound **6b** in the mesophase.

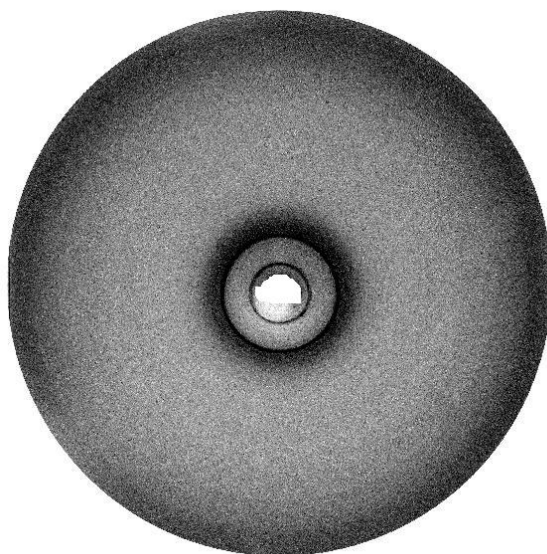


Fig. 7 XRD of compound **6c** in the mesophase.