A facile synthesis of a room-temperature chiral discotic nematic liquid crystal based on pentaalkynylbenzene core

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This is an Accepted Manuscript of an article published by Taylor & Francis in Liquid Crystals on 25 March 2021, available online: https://doi.org/10.1080/02678292.2021.1900433

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The preparation of discotic liquid crystal with a wide thermal nematic phase range remains a challenge. Here, a method to synthesize a class of discotic liquid crystal with exclusive and stable chiral nematic phase over a wide temperature range, based on pentaalkynylbenzene core, is presented and the mesogenic properties are well studied.

Keywords: Discotic liquid crystal; chiral nematic, room-temperature, pentaalkynylbenzene core

1. Introduction

Owing to the spontaneously one dimensional stacks in disk-shaped molecules caused by the driving forces of nanophase segregation and the minimization of free volume, columnar mesomorphism have dominated the field of discotic liquid crystals (DLCs) and received particular interest in charge transport [1-4]. Very few examples of DLCs exhibit a less ordered nematic phase (N_D), which have been found commercial use as active switching components and optical compensation films to widen the viewing angle in display technologies [5, 6]. As well, most currently reported discotic nematogens show the N_D phase at high temperature and over a narrow thermal range [7]. Chiral DLCs raised significant interest since the tilted phase of chiral discotic dibenzopyrene derivatives was reported ferroelectric for the first time [8, 9]. Taing and co-workers developed a strategy to incorporate chiral branched chain into discotic nematogen [10]. However, the incorporation of chirality unexpectedly enhances the nucleation and crystal growth well above the temperature ranges of their hypothetical nematic phases. Up to now, efforts to induce the excellent chiral nematic phase (N_D*) behaviour of DLCs have proven limited [11]. Rare cases realized the implementation of thermally stable N_D* phase at room temperature [12]. This makes the development of the chiral discotic nematogens highly attractive and desirable.

Pentaalkynylbenzene (PA) derivatives have been one of the most widely investigated systems for various discotic nematogens [13, 14]. In this case, the reduced stacking interactions contributed by the conformational flexible and sterically hindered cores; the phenyl rings are generally not in plane because of the rotational freedom provided by ethynyl linkers which prevents columnar stacking, together with the attachment of the alkyl side-chains which generate insufficient packing volume, favour the nematic mesomorphism in DLCs [15-17]. Besides, the orientational freedom of the PA group increases *via* increasing the terminal alkyl chain length. Thus, the chiral functionalisation of the PA core are highly expected to tailor the discotic nematogens with desirable mesomorphic and other physical properties for the use of chiral DLCs in devices.

Liquid crystalline (LC) dendrimer systems bearing optically-active mesogens provides a strategy towards realizing the N_D* phase behaviour in discogens [18]. A conceptually related PA-chiral tail system was expected to induce the excellent N_D* properties (Scheme 1). Here, we report the facile synthesis and full characterisation of analogous PA material modified with a chiral dithiolane function. The precursor PA derivative **5** with a hydroxyl end shows the N_D phase above 100 °C and the incorporation of the chirality *via* an esterification reaction with (R)-(+)-1,2-dithiolane-3-pentanoic acid surprisingly contributes to forming a room-temperature N_D* phase which persists over a wide thermal range.

2. Experimental

2.1 Materials and methods

All chemicals were purchased from Sigma-Aldrich and used as received. All solvents were of AR quality and used without further purification. Column chromatographic

separations were performed on silica gel (60-120, 100-200 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (TLC Silicagel 60 F_{254}, Merck KGaA, Germany).

The chemical structures of the synthesised compounds were determined by a combination of spectroscopic techniques. ^{1}H-NMR characterizations of intermediates and discogens were recorded at 400 MHz on a JEOL Eclipse 400 FT NMR spectrometer at ambient temperatures. Deuterated chloroform ($CDCl_3$) was used as a solvent and tetramethylsilane was used as an internal standard. UV/Vis spectra were recorded on Lambda 25 (Perkin-Elmer). The LC properties of the synthesised compounds were investigated using polarized light optical microscopy (POM) and differential scanning calorimetry (DSC) studies. DSC data was collected on a Mettler-Toledo DSC822e in nitrogen against an indium standard. Phase assignments of the samples were carried out using an Olympus BX51 polarizing microscope. The microscope was equipped with a Mettler-Toledo FP900 heating stage. High-resolution small-angle powder diffraction experiments were recorded on Beamlines BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 °C was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. *q* calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of *n*-alkanes. A Pilatus detector was used for SAXS. Synchrotron radiation circular dichroism (SRCD) spectroscopy experiments were performed at beamline B23 of the Diamond Light Source. An intense synchrotron-generated light beam of 0.8 x 1.5 mm^2 in diameter was used in the spectrometer, with the ability of samples to be scanned in *xy* plane and rotated. The beam was deflected vertically

through the sample held horizontally between two quartz glass windows in a Linkam hot stage.

2.2 Synthesis

All reactions were conducted under nitrogen. The precursor PA derivative **5** with a hydroxyl end was synthesized by a referenced method (see the details in Supporting Information). For the preparation of the target chiral discogen **6**, precursor discogen **5** (100.0 mg, 0.09 mmol), (R)-(+)-1, 2-Dithiolane-3-pentanoic acid (65.0 mg, 0.32 mmol) and DMAP (37.0 mg, 0.30 mmol) were dissolved in dry DCM (15 ml). The mixture was deoxygenated with bubbling nitrogen for 1 hour. Then DIC (0.16 ml, 1.00 mmol) was added in one portion and it was stirred at RT under nitrogen atmosphere for 3 days. The solvent was evaporated and the product was purified by column chromatography (hexane/ethyl acetate 4:1) to obtain the first spot on the TLC plate. After re-crystallization in hexane, yellow crystals **6** was obtained (0.11 g, 93.1%). The target chiral discogen **6** was stored in *vacuum* desiccators in the dark.

2.3 Preparation of homeotropic cell

The helical pitch of chiral discogen here was measured by a homeotropic cell. The test cell was purchased from Japan (KSHH-25/A107P1NSS, E.H.C., Tokyo, Japan) and the known cell gap = 25 μm is used to calculate the helical pitch. On a heating stage with temperature higher than isotropic transition temperature of chiral discogen (105 °C), the cell gap was filled with material by capillary force and the cell was left for another 2 hours before Polarized light optical microscopy (POM) observation. Besides, the homeotropic cell method was also used to calculate the helical twist power (HTP) of chiral discogen in hydroxyl-end achiral discogen. Mixture of 50 mol% chiral discogen in host matrix was dissolved in dichloromethane by stirring. Thereafter, the solvent was

completely evaporated in an oven at 70 °C overnight. On a heating stage with temperature higher than the isotropic transition temperature of host LC (180 °C), the cell gap was filled with mixture by capillary force and the cell was left for another 2 hours before POM observation.

3. Results and discussion

3.1 Synthetic route of chiral discogen 6

Control of the mesogenic properties is an important factor in the structural design. Essentially, the attachment of laterally linked flexible alkyl side-chains **3** (Scheme S1) was used to promote the desired N_D phase behaviour. Indeed, the discogen **5** exhibits exclusively the nematic phase. The inclusion of hydroxyl moiety within the flexible spacer would provide convenient access to target compound **6**. The target compound **6** was synthesized by the route depicted in Scheme 1. The synthesis of intermediates **1**-**5** have been reported before [19, 20]. Compound **6** was prepared conveniently by one step and the simple esterification reaction between precursor discogen **5** and (R)-(+)-1, 2-dithiolane-3-pentanoic acid led to a high yield of compound **6** up to 93.1%. All compounds were characterized by ^{1}H-NMR and Mass Spectrometry (MS) (Figure S1-8). Note the dithiolanes here or lipoic acid, have been regularly used for the attachment to gold and other metal surfaces as dithiolates [21]. The group is also known to polymerize somewhat easily. Thus the target chiral discogen **6** was stored in a *vacuum* desiccator in the dark.

3.2 Mesophase behavior of chiral discogen 6

Thermal transitions and phase assignments were characterized by differential scanning calorimetry (DSC) together with polarized light optical microscopy (POM). Compound **5** was light-yellow crystals at room temperature and it displayed a melting transition at

104 °C to mesophase (Figure S9). Upon further heating, the mesophase was cleared at 152 °C with a transition heat (ΔH) of 0.61 kJ/mol. On cooling, the appearance of a well-defined *schlieren* texture (Figure S10) happened at 151 °C and it remained stable down to 83 °C. POM and DSC investigations on compound **6** confirmed a thermodynamically stable (enantiotropic) chiral nematic phase. In Figure 1, the observed POM texture at 75 °C was characteristic oily streaks, similar to the appearance of chiral nematic phase (N*) formed by rod-shaped mesogens [22]. By changing the polarizer angles from 0° to 110°, the reflective colour in texture went through orange, blue, grayish green and yellow, successively because of the helically twisted LC structure. The DSC traces obtained from heating and cooling runs for chiral discogen was shown in Figure 2. On heating, a N_D* phase was observed at 49 °C, preceded by a crystal-crystal transition at lower temperature, and it turned into an isotropic liquid at 95 °C (ΔH = 0.20 kJ/mol). Formation of the N_D* phase from isotropic state on cooling started from 94 °C with a transition enthalpy of 0.12 kJ/mol, followed by a slow crystallisation occurring at a low temperature of 5 °C. These low transition enthalpies for discogen **5** and chiral discogen **6** are consistent with the formation of the less common nematic discotic rather than columnar discotic mesophases [6]. Diffractograms of mesophases of chiral discogen **6** (Figure S11b and c) displaying a weak small angle peak with broad low intensity reflections for the lateral packing and stacking of the molecules further support the assignments as nematic DLC phase. The calculated *d*-spacing of around 19.97 Å for the signal in the small angle region corresponds to the separation between the PA units and thus approximates the diameter

of a single PA disk (~19 Å). Generally, the chiral phase behaviour of discogen **6** was exclusive and stable over a wide temperature range up to 46 °C.

3.3 Helical pitch of chiral discogen 6

On cooling from 93 ℃ to 44 ℃ in Figure S12, the helical pitch in the N_D* phase of discogen **6** increased and the reflective colour in texture tended to change from grayish green to red. As the colour in texture varied by lowing temperature during POM observation, the question that whether the helical pitch in N_D* phase of dicogen **6** reflect the visible light selectively remained. To explore this question, we recorded synchrotron radiation circular dichroism (SRCD) spectra of discogen **6** as a function of temperature (Figure S13). Above the isotropic temperature, the CD signals around 235 nm, 270 nm, 380nm and 425 nm correspond to the characteristic UV-Vis absorption (Figure S15b). The Cotton effect is positive because the optical rotation first increases as the wavelength decreases in the vicinity of absorption band for chiral discogen. The largest jump (the largest increase in ellipticity) at 467 nm is seen between 95 and 100 °C, i.e. at the isotropic-mesophase transition temperature, coinciding with the transition temperature observed by DSC in Figure 2. The CD band outside the chromophoric absorption region is resulted from the scattering effects [23]. It should be noted that the CD band close to 467 nm did not increase by lowering temperature. Thus, the helical structure did not reflect visible light selectively and the wavelength of reflection band is not related to helical pitch by the relation $\lambda = np$, where n is the average refractive index of chiral discogen. When the chiral discogen was prepared in a homeotropic cell (Figure S14), bundles of well-defined lines were observed. This can be used to evaluate the helical pitch in the chiral discogen. In such a homeotropic anchoring cell, the long molecular axis is generally inclined relative to the glass plates and the chiral helical axis is parallel to the bounding substrate. These lines are interpreted by assigning the chiral LC phase a virtual

layer and often the layer thickness is equal to the half of helical pitch. The pitch in the helical LC structure, estimated from twice the distance between adjacent lines [24], is 5.7 μm, indicating a long helical pitch in discogen **6** outside the visible spectrum. Consequently, the changed colours on cooling during the POM observation of chiral discogen cannot be related to the selective reflection phenomena.

3.4 UV-Vis studies of discogens

Both compounds **5** and **6** showed the blue fluorescence under the long wavelength of UV lamp (365 nm) in dichloromethane (Figure S15-17) because the π-conjugated structure in discotic molecules has a strong ultraviolet absorption. In Figure S15a, the characteristic absorption of discogen **5** exhibits the maxima centered at 238, 261 and 351 nm with two shoulder peaks at 378 and 421 nm, a consequence of the multialkynyl benzene core. For target discogen **6**, a minor blue shift of representative absorption bands appears at 233, 259 and 348 nm with two shoulder peaks around 378 and 420 nm. The decrease of the UV-Vis peaks for discogen **6** can be attributed to the promoted molecular motion from the flexible pentanoic tail, evidenced by the promoted mesophase behaviour of compound **6** as expected in Table S1.

3.5 Contact measurements of discogen 6 and other LCs

A contact experiment between precursor discogen **5** and target chiral discogen **6** was conducted to study the influence of branching and chirality in detail. The materials were placed between two glass substrates that allowed them to mix in isotropic state freely. Figure 3a shows a POM image of the contact zone between the N_D phase of compound **5** and the isotropic liquid of **6**. The flow of discogen **6** (as an isotropic liquid) into the nematic material **5** forms a fingerprint-like texture in Figure 3b. Further cooling lead to the co-existence of fingerprint-like texture and the N_D* phase area of the pure mesogen

6. Crystallization of **5** occurs at lower temperatures. During the whole cooling process, no discernable phase boundary was observed.

The mixing behaviour of chiral discogen **6** with a well-studied rod-shaped mesogen **R1** in previous work was further explored here [25]. As a reference experiment, a contact sample between disk-shaped **6** and **R1** was made as above (Figure S18). Under POM observation, the contact sample on cooling exhibits the formation of individual characteristic mesophase of pure materials, leaving an isotropic mixing region in the middle of the sample. Further cooling result in the shift of the two mesophase interfaces towards each other, indicating the solubility of one material in the other to a certain extent. The mixture did not show linear mixing behaviour at room temperature in Figure S18c, but rather showed a minimum in the clearing temperature at intermediate concentrations [26]. At 24 °C, a dark gap (an isotropic area) is seen in the middle of the photograph and the interfaces meet and slowly mix characterized by some colourful ordered lines, which can be attributed to the induced chiral mesophase in the **R1**. Based on the assumption of a linear concentration gradient, a phase diagram of the mixture can be sketched, as shown in Figure S19. It should be noted here that the phase diagram is interpreted qualitatively only. The gap in the intermediate concentrations (x-axis) means the two compounds are immiscible.

3.6 Helical twisting power of chiral discogen 6 in host LCs

The helical twisting power HTP (β_M, a measure for the ability of a chiral dopant to twist a nematic LC) of discogen **6** was determined in a homeotropic cell by mixing **6** with two different nematic LC hosts, rod-shaped 5CB and disk-shaped **5** [27]**.** Discogen **5** and **6** are completely miscible. In Figure 4, a typical fingerprint texture of the chiral nematic phase was obtained and the pitch of the helical structure can be estimated from twice the distance between two adjacent lines, due to the identity period of $L = P/2$ [24]. The helical

pitch for 50 mol% of **6** in **5** at 110 °C is 33.04 μm. The calculated HTP value of **6** is 0.06 μm^{-1}. Patterns in Figure S20 show a diverging cholesteric pitch under homeotropic anchoring condition. In the strongly distorted director configuration, the dark areas represent a pseudo-isotropic homeotropically aligned nematic phase. The helical pitch for 5CB doped with 1 mol% of **6** is 57.18 μm. The HTP value of **6** in 5CB is 1.75 μm^{-1}. Phase separation occurred when the dopant concentrations is higher than 1 mol% of **6** in 5CB. The different HTP values of chiral discogen **6** in two host systems indicate that there is a much stronger interaction between **6** and calamitic host 5CB than discotic host **5**, because of the more complicated chemical structure of discogen host (the molecular diameter is much larger than its thickness and overall). The rod-like 5CB host with lower molecular weight allows the chirality to transfer more easily and efficiently in spite of the poor miscibility with chiral discogen **6**.

4. Conclusions

In summary, a class of chiral discogen based on pentaalkynylbenzene core is prepared and the LC properties are well studied. The presented synthesis of pentaalkynylbenzene ester is a fast and versatile method to yield target product effectively. The integration of chiral dithiolane tail with precursor discogen results in the excellent N_D* phase behaviour of chiral discogen, which is depicted as exclusive and stable over a wide temperature range. This simple and potentially universal design on DLCs will provide a new way towards the development of new anisotropic soft materials for their usability in devices.

Acknowledgements

H.Y. thanks the China Scholarship Council (CSC) for a doctoral scholarship. We also thank Dr G. Siligardi, Dr R. Hussain and Dr T. Jávorfi for the beamline test at B23 Diamond Light Source.

Disclosure statement

No potential conflict of interest was reported by the authors.

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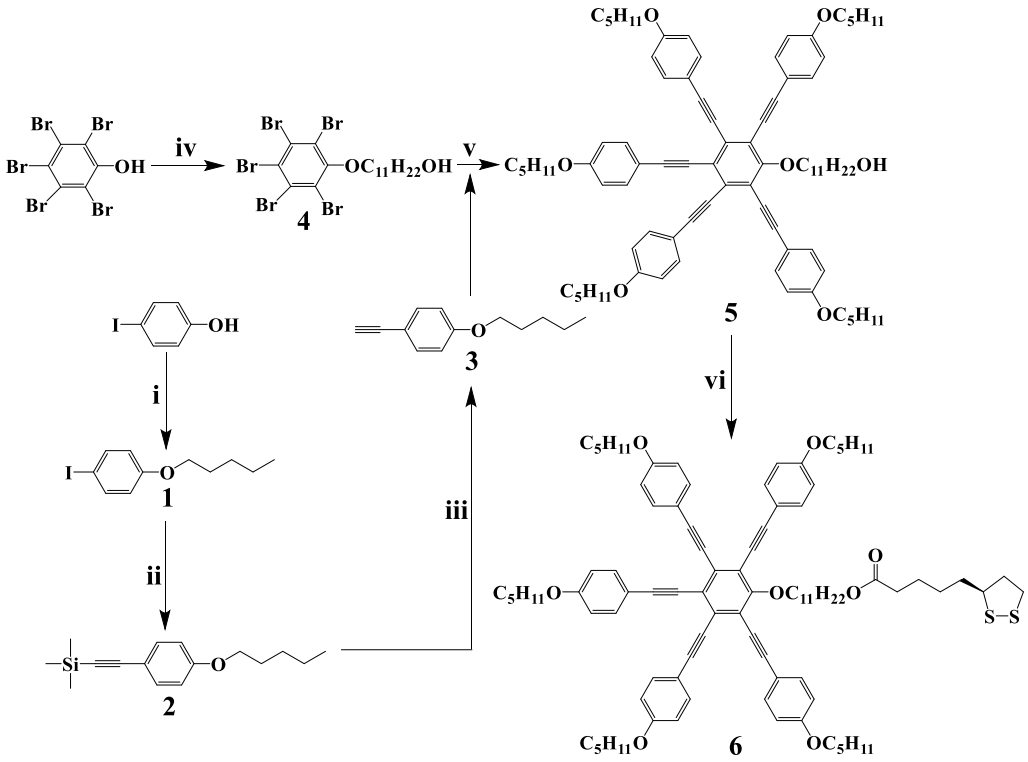

Scheme 1. Synthetic route of chiral discogen **6** (N_D*). (i) 1-Bromopentane/K_2CO_3/Butanone/95 °C, (ii) TMSA/CuI/NEt_3/$Pd(PPh_3)_2Cl_2$/RT, (iii) KF/DMF/H_2O/RT, (iv) 11-Bromo-1-undecanol/K_2CO_3/Butanone/N_2/95 °C, (v) PPh_3/NEt_3/$Pd(PPh_3)_2Cl_2$/LiBr/CuI/THF/N_2/102 °C, (vi) (R)-(+)-1, 2-Dithiolane-3-pentanoic acid/DMAP/DIC/DCM/N_2/RT.

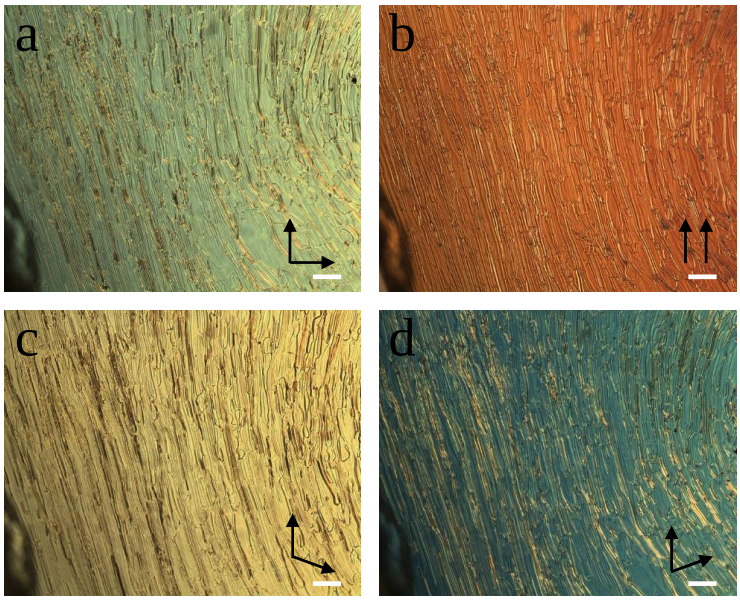

Figure 1. Polarized light optical microscopy (POM) micrographs(x 50 µm) of chiral discogen **6** (N_D*) (a) 75 °C (90° crossed polarizer), (b) 75 °C (0° crossed polarizer), (c) 75 °C (110° crossed polarizer), (d) 75 °C (70° crossed polarizer).

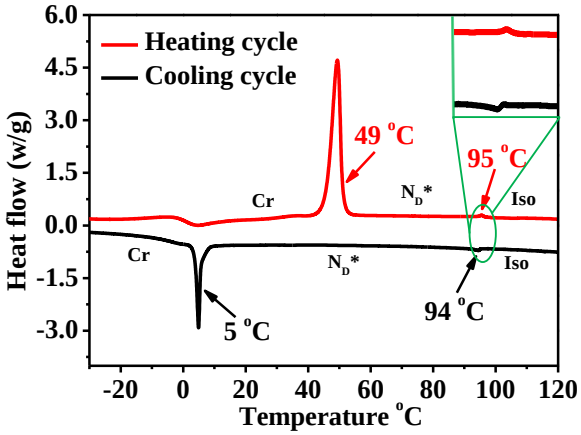

Figure 2. Differential scanning calorimeter (DSC) results of compound **6** at heating and cooling rate of 10 °C /min.

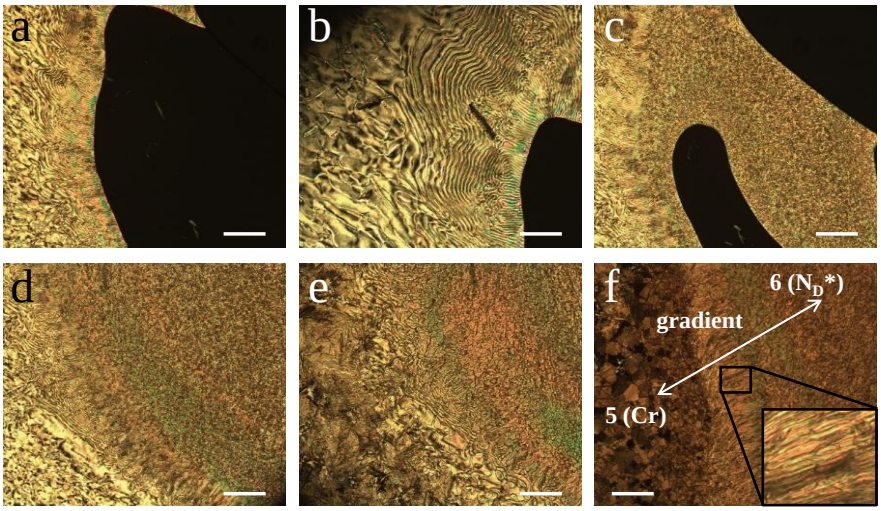

Figure 3. POM micrographs (90° crossed polarizer) of a contact experiment for **5** (left) and **6** (right) between untreated glass slides (a) 128 °C (x 200 µm), (b) 128 °C (x 100 µm), (c) 113 °C (x 200 µm), (d) 94 °C (x 200 µm), (e) 85 °C (x 200 µm), (f) 47 °C (x 200 µm).

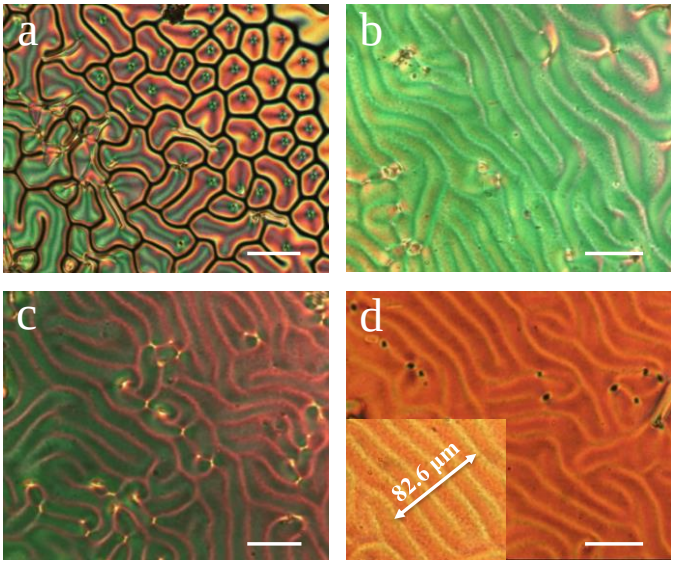

Figure 4 POM micrographs (90° crossed polarizer) (x 50 µm) of induced N_D*phase of **5** doped with 50 mol% of **6** in a homeotropic cell (a) 75 °C, (b) 95 °C, (c) 105 °C, (d) 110 °C.