Liquid Crystals

Multiple Levels of Order in Linked Disc–Rod Liquid Crystals**

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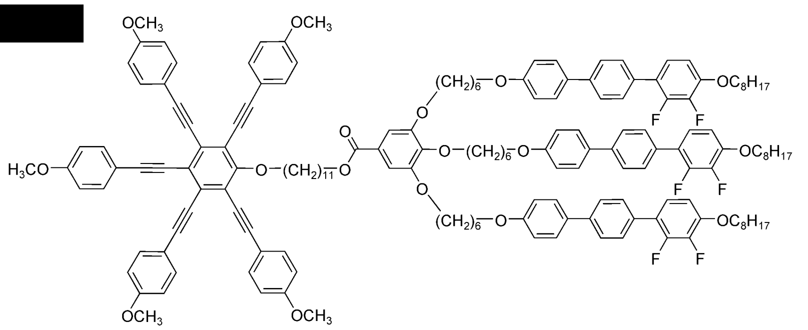
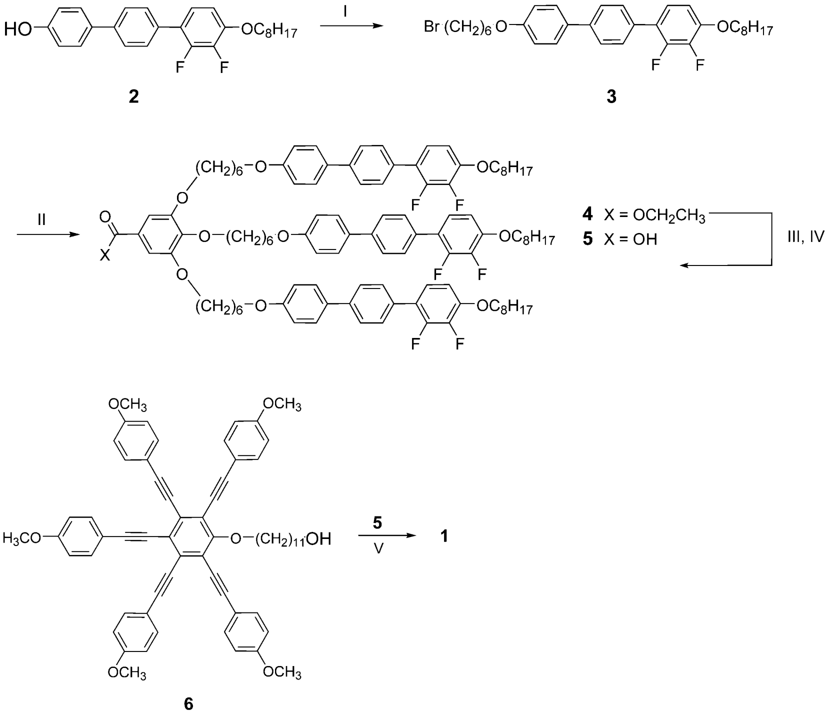
For thermotropic liquid-crystalline systems, molecular shape and mesophase structure is, in most cases, closely linked. Rod-shaped mesogens form layered (smectic) liquid-crystal phases showing 1D positional order; disc-shaped mesogens order into columnar structures with 2D order. Notable exceptions are various classes of rod-shaped mesogens that self-organize into columnar phases, such as polycatenars,[1a] neat soaps,[1b] mesogens with strongly interacting lateral substituents,[2] and oligomeric/dendritic structures,[3] in which steric factors prevent a layered organization. So far, all reported layered phases of discotic molecules are actually highly ordered columnar lamellar ($\mathrm{Col_L}$) phases.[4] Disc-shaped molecules self-organizing into 1D layered phases (smectic A or C) have not been explored systematically.[5] Current developments in nanoscience have caused a resurgence of research on disc-shaped self-assembly systems, particularly in view of applications such as easy-processable and self-healing, organic, photo- and electron-conducting systems. A combination of these properties with the advantages of smectic systems (fast, bistable switching) is of technological relevance as well as fundamental interest, as it extends the basic understanding of structure–property relationships in soft self-organizing systems.

Herein, we present an example of a class of materials that contain a disc-shaped moiety and rod-shaped groups (see Scheme 1), which exhibits a nematic and various smectic mesophases. This work is crucially different from earlier research[6] in that in this system, the (volume-)fractions of the discs and rods are better matching and, importantly, the cross-sections of the disc matches the cross-section of the three rods,[7] thus favoring a layered organization.



Scheme 1. Structure of the investigated disc-rod mesogen.



Scheme 2. Synthesis of the disc–rod mesogen. Key: I) $\mathrm{Br(CH_2)_6Br}$ (5 equiv), $\mathrm{K_2CO_3}$, KI, butanone, reflux 16 hrs; II) Ethyl gallate, $\mathrm{K_2CO_3}$, KI, butanone, reflux 16 hrs; III) aqueous KOH, EtOH/THF (1:1), heat to reflux 2 hrs; IV) aqueous HCl; V) DCC, DMAP, *p*TSA, $\mathrm{CH_2Cl_2}$, room temperature 5 days.

The synthesis of target compound **1** is outlined in Scheme 2. Preparation of the discotic mesogen **6** and the rod-shaped terphenyl **2** have been described elsewhere.[8] A spacer was attached to **2** by means of a Williamson alkylation under standard conditions. Alkylation of **3** to ethyl gallate yielded **4**, which was saponified to the free carboxylic acid under basic conditions. A DCC-mediated esterification with the discotic mesogen **6** yielded the target material. Detailed reaction procedures and structure analysis are provided in the Supporting Information. The mesophase behavior of the target material and its precursors was investigated by optical polarizing microscopy (OPM) and differential scanning calorimetry (DSC). The results are summarized in Table 1.

Terphenyl moieties are known to display smectic mesophases.[5a] Also in **4**, in which three mesogens have been linked, smectic phases are observed. Attachment of the discotic nematogen in **1** introduces an additional nematic phase at high temperatures. The nematic phase (Figure 1a),

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Table 1: Mesopmorphic properties of **1** and its precursors.

Mesogen	Phase behavior[a,b]										
6	Cr	132 (37)							N	246 (0.2)	I
3	Cr	107 (50)			SmC	137 (<0.1)	SmA	172 (5.5)			I
4	Crx_1	83 (5.5)	Crx_2	123 (35)	SmC	165 (0.3)	SmA	205 (18)			I
1	Crx_1	83 (10.5)	Crx_2	115 (31)	SmC	134 (17)	SmA	135 (<0.2)	N	159 (1.5)	I

[a] Transition temperatures (measured for heating runs) in [°C] and latent heat values (between the brackets) in [$kJ\,mol^{-1}$]. [b] Phase assignments: Cr = crystalline; Crx = soft crystal; x_1, x_2 = undetermined phase structure, SmC = smectic C; SmA = smectic A; N = nematic; I = isotropic.

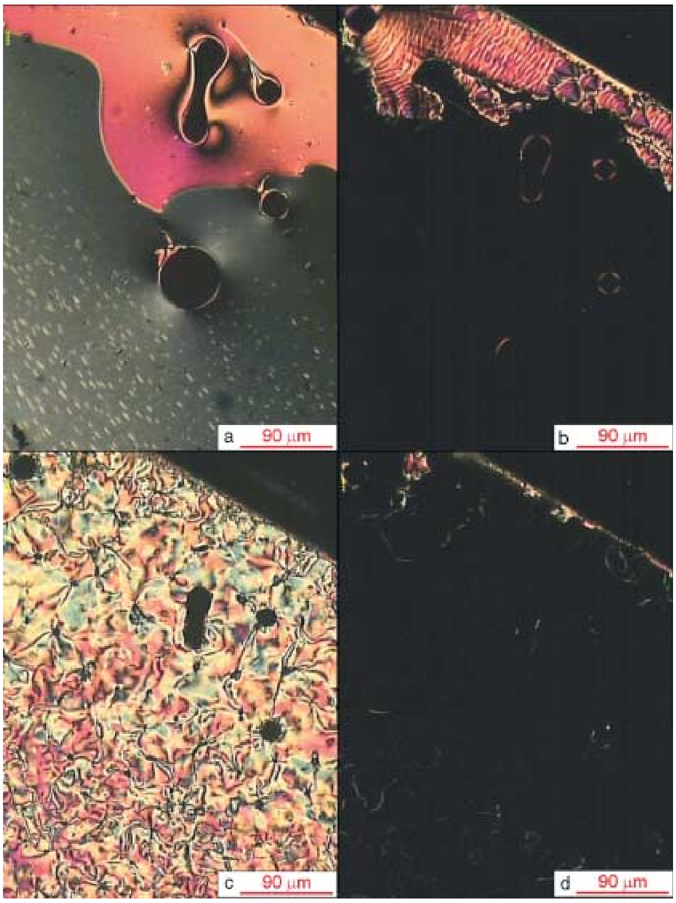

Figure 1. Optical microscopy pictures of **1** at a) $T = 150$ °C (nematic); b) $T = 132$ °C (SmA); c) $T = 130$ °C (SmC); and d) $T = 90$ °C (Crx_2). All pictures are taken with crossed polarizers. The scale bar represents 90 μm.

which displays a characteristic Schlieren texture with twofold and fourfold brushes, has a low viscosity and aligns easily between two unprepared glass slides. When the nematic phase is cooled, typical textures of a SmA (fan texture with homeotropic areas, from 135°) and a SmC phase (Schlieren texture, from 132 °C) are observed (Figures 1b and c). At the transition to the soft-crystalline Crx_2 phase, a very low birefringent texture appears (Figure 1d). In this phase the viscosity has increased drastically and no further changes in the optical texture are observed on cooling into the crystalline phase. The DSC traces of **1** are shown in the Supporting Information.

The phase structure of **1** in the various mesophases was further investigated by using detailed X-ray diffraction (XRD), see Figure 2. In the nematic phase two diffuse reflections are observed, which indicates a complete absence of positional order. The broad small angle reflection with a d-spacing of 29 Å corresponds to the average length of the rods ($\approx$32 Å) and diameter of the discs ($\approx$20 Å), which indicates a molecularly mixed nematic phase and confirms chemical compatibility of the different entities (Figure 3a).[9] Close to the transition to the SmA phase, some pretransitional ordering (small angle reflections with $d = \approx 50$ Å and ≈ 25 Å) is observed, thus pointing towards phase segregation between the discs and rods and indicating that at lower temperatures in the nematic phase, the entire mesogen is the building block rather than the submolecular units.

In the SmA and the SmC phase, sharp small angle reflections become apparent, attributed to layer formation. The layer spacing of ≈ 102 Å ($d_{002} = \approx 51$ Å) corresponds to a bilayer lamellar system with the discs and the rods segregated (thus SmA_2 and SmC_2 phases),[10] schematically shown in Figure 3b. The sharp reflections and the presence of a number of higher-order reflections show that the layered organization is well-defined. The lack of sharp reflections in the wide-angle area indicates the absence of positional order both in the rod layer and in the disc layer. Thus, the discs are essentially organized as calamitic mesogens within a SmA or SmC phase. However, because of free-volume requirements, rotation around the long axis parallel to the layer normal is suppressed and hence, some orientational order of the short axis of the disc perpendicular to the layer normal must be assumed. However, the homeotropic optical texture does not suggest any correlation between adjacent disc layers.

In the SmC phase, characterized by a Schlieren texture and indicative of some correlation of the tilt across the layers, the spacing decreases with decreasing temperature, which is a signature for tilting of the mesogenic units. As the partly fluorinated terphenyls show strong SmC behavior, it was expected that these moieties are responsible for the tilting. Hence, a tilt angle θ_t was calculated considering that only the rods are tilting [Eq (1)].

$$\theta_t = \cos^{-1}\left(\frac{d_{\text{rod,SmC}}}{d'_{\text{rod,SmA}}}\right) = \alpha(T_{CA} - T)^{\gamma} \qquad (1)$$

Here $\frac{d_{\text{rod,SmC}}}{d'_{\text{rod,SmA}}}$ is the ratio between the thickness of the rod layer in the SmC and the extrapolated SmA phase[11a] at temperature T, α is a material constant, T_{CA} is the SmC–SmA transition temperature and γ is a empirically determined constant: $\gamma = 0.35$.[11b] To check this assumption, the temperature dependence of the tilt was compared to that of precursor **4**. The values obtained after fitting the experimental data with Equation (1) are in close proximity for **1** and **4** ($\alpha(\mathbf{1}) = 5.4 \pm 0.1°\,K^{-0.35}$ and $\alpha(\mathbf{4}) = 5.1 \pm 0.1°\,K^{-0.35}$), and hence there is a strong argument that indeed the rods are tilting and the discs remain essentially oriented perpendicular to the layer normal. However at present, based on these results, we can not exclude fully any tilting of the discs.

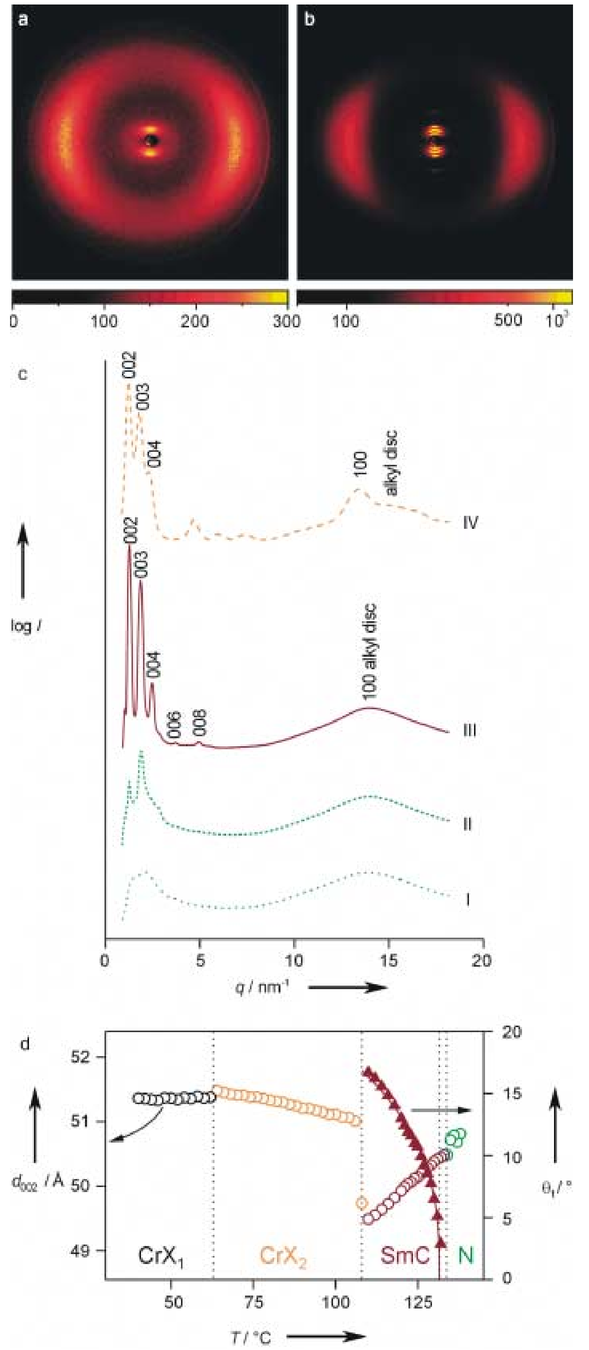

Figure 2. a) Aligned X-ray diffractogram of **1** at 150 °C (nematic, linear *z* scale). b) Aligned X-ray diffractogram of 1 at 132 °C (SmC, logarithmic *z*-scale). c) Integrated X-ray diffraction patterns of **1** at (I) 150 °C (nematic); (II) 136 °C (nematic); (III) 132 °C (SmC); (IV) 90 °C (Crx_2). d) Temperature dependence of the layer spacing, *d* (open circles) and the tilt angle, θ_t (in the SmC phase, triangles), taken from the (002) reflection. Note that θ_t is calculated based on the assumption that only the rods are tilting. The solid line represents a fit by using Equation (1), in which α is the (only) fitting parameter.[11]

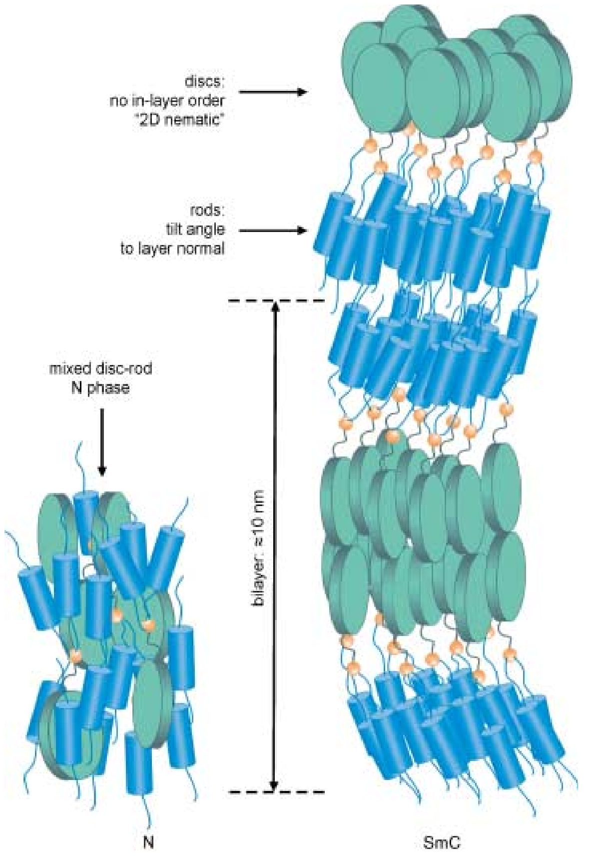

Figure 3. Representation of the order in the N (left) and SmC_2 (right) phase of **1**.

The diffraction pattern in the Crx_2 and the Crx_1 phase is characterized by a slight widening of the small angle reflections and the presence of a sharp wide angle reflection at 4.7 Å, thus indicating positional order of the mesogens within the layers. The absence of the characteristic reflection at 3.5 Å, assigned to the close (columnar-like) packing of the disc-shaped moieties, indicates that both the SmC–Crx_2 and the Crx_2–Crx_1 transition can be assigned to a further ordering of the rods.[12] These localized phase transitions of the rod-shaped moieties again show the independence of the phase behavior of different layers.

In summary, we have prepared a novel liquid-crystalline material, in which discotic and calamitic mesogens are combined. The material shows a rich phase behavior with a nematic and several smectic phases. To our knowledge this is the first molecular system with discotic mesogens that shows a 1D SmA/C phase. Two levels of order are present in the smectic phases. The first is the well-defined layering, induced by the incompatibility of the discs and rods. Independent of the lamellar order and, indeed, independent of each other, there is another level of organization in the different layers. Phase transitions can occur, which can be solely assigned to a change in organization in one of the two sublayers (e.g. the tilting of the rods at the SmA to SmC phase transition). It is anticipated that also phase transitions may occur in the layer of discs, giving rise to phases in which a layer of columns is formed between layers of rods. The concept of shape-induced phase segregation is a versatile approach to such systems and a wide range of new nanosized phase architectures is anticipated.

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Keywords: liquid crystals · mesophases · nanostructures · self-assembly

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[4] a) It is noted that the lamellar columnar phases (Col_L or D_L phases) in which mesogens are ordered in layers and in columns that are 2D positionally ordered phases, and are therefore not comparable to SmA or SmC phases, which show 1D order. The first example of Col_L phase is published in: b) K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst.* **1986**, *140*, 131.

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[7] The cross section is considered the cross-sectional area of the mesogens perpendicular to the phase normal. For the discs, the cross section is the $\varnothing_D \times d_D$ (diameter × witdh) = $20 \times 4 = \approx 80$ Å^2. Rods have characteristic cross sections of ≈ 25 Å^2, and thus three rods in the molecule will have a cross section of ≈ 75 Å^2. Exact values depend on side groups and the exact organization of the mesogens in the layers.

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[9] Also mesogens with incompatible submolecular units (e.g. with siloxane or fluoroalkyl groups) often show microphase segregation. In these systems the phase segregation is already observed in the isotropic phase.

[10] To confirm the presence of the (001) reflection, which is missing in our X-ray diffraction data, additional SAXS measurements were conducted. In these experiments reflections (001) to (004) were observed at $q_{00l} = 0.617$, 1.222, 1.847 and 2.420 nm^{-1}, corresponding to layer spacings of $d_{00l} = 101.9$, 51.4, 34.0 and 26.0 Å.

[11] a) Note that the thickness of both the disc and rod layers are estimated after calculating the (sub)molecular dimensions by molecular modeling software. b) P. G. de Gennes, J. Prost in *The Physics of Liquid Crystals*, 2nd ed., Oxford University Press, New York, **1993**, p. 528.

[12] The rod-shaped precursor **4** shows a similar phase transition SmC–Smx_1–Smx_2 phase transitions and, hence, the transitions are assigned to phase transitions predominantly localized in the rod-layer.