Induction of a nematic columnar phase in a discotic hexagonal ordered phase forming system

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Induction of a nematic columnar phase in a discotic hexagonal ordered phase forming system

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The induction of a nematic columnar phase in a discotic hexagonal ordered phase forming system is achieved by mixing hexakispentyloxytriphenylene 1 with a long chain derivative of trinitrofluorenone 3. The difference in chain length has a strong influence on the packing behaviour due to steric effects. The long hydrocarbon chains of the acceptor introduce a strong asymmetry into the electron donor acceptor complex. It could be shown by differential scanning calorimetry, optical microscopy and X-ray measurements that a nematic columnar phase is formed. In this mesophase the triphenylenes form columns but no hexagonal or orthorhombic lattice is built up. Each column behaves like a rod-like nematic mesogen. To prove that the long hexadecane alkyl chains of the acceptor are responsible for this induction, the acceptor 3 was mixed with the non-liquid-crystalline triphenylene derivative 2 containing six hexadecyloxy side groups. The long alkyl chains of the acceptor dissolve perfectly in the side chain region of the discs. No asymmetry is induced and the columns formed can be arranged on a hexagonal lattice resulting in a D_{ho} phase.

1. Introduction

In liquid-crystalline systems interactions between molecules, such as hydrogen bonds, electron donor acceptor, dipole–dipole or steric interactions, play an important role in the formation and stability of the supermolecular structures. These inter-molecular forces can be easily varied by the addition of a second component. This may lead not only to liquid-crystalline systems with lower ordered phases (downgrading of phases) but may also lead to higher ordered phases (upgrading of phases). For calamitic phases both variations have been realized, for example inducing a nematic phase into a smectic liquid crystal [1] or vice versa [2]. In discotic systems the upgrading of order has been shown. Both, phase variation and phase induction, even in non-liquid-crystalline discoid systems has been observed [3]. The driving force for this induction of discotic phases is the electron donor acceptor interaction between electron rich discotic compounds (for example hexakisalkoxytriphenylenes or hexaalkinylbenzenes) and electron poor dopants (for example trinitrofluorenone). Although examples for induced upgrading of discotic systems can be found, no example of downgrading in these systems by the addition of a second component has yet been reported.

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In this paper we describe such a downgrading which leads to an N_c phase starting from a D_{ho} phase. As electron rich compounds hexakispentyloxytriphenylene **1** and hexakishexadecyloxytriphenylene **2** were used. As the mixing compound a trinitrofluorenone derivative **3** with long aliphatic hexadecyl side groups was chosen.

1: $R = C_5H_{11}$
2: $R = C_{16}H_{33}$ 3
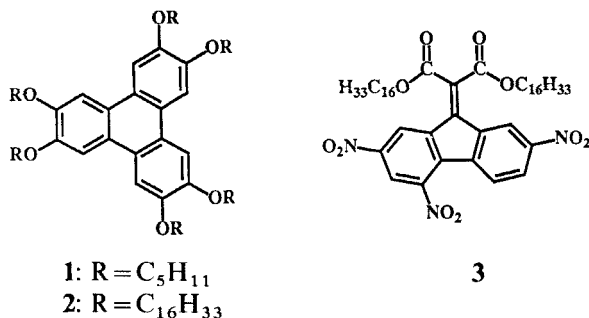
2. Synthesis and characterization

2.1. *Synthesis*

The synthesis of hexakispentyloxytriphenylene **1** is described elsewhere [4]. The hexakishexadecyloxytriphenylene **2** was synthesized in two steps:

(i)   1,2-bishexadecyloxybenzene **4**. One mole of catechole and three moles of hexadecylbromide were dissolved in 640 ml of ethanol and degassed. After the addition of two moles of potassium hydroxide in 40 ml of water the mixture was refluxed for four hours. The mixture was extracted with diethylether and recrystallized from a methanol and toluene mixture.

(ii)   2,3,6,7,10,11-hexakishexadecyloxytriphenylene **2**. 6·2 g (11·1 mmole) of **4** was stirred in a suspension of 60 g of ferric chloride in 70 v/v% sulphuric acid. The mixture was heated to 350 K for one hour. After pouring onto an ice/water mixture the dark residue was filtered and recrystallized from trifluoroacetic acid. Yield 1·2 g (20 per cent); mp 341 K.

^{1}H NMR (CDCl$_3$): 0·95 ppm (t, 18 H), 1·44 ppm (m, 12 H), 1·5–1·7 ppm (m, 144 H), 1·95 ppm (m, 12 H), 4·2 ppm (t, 12 H), 7·8 ppm (s, 6 H).

The (2,4,7-trinitro-9-fluorenylidene)-malonic bishexadecylester **3** was synthesized by a trans esterification of the bis-ethylester [5] with hexadecanole in the melt with tetraisopropyl-orthotitanate as catalyst.

914 mg (2 mmole) of the diethylester and 969 mg (4 mmole) of hexadecanole were melted in a dry nitrogen atmosphere and kept at 420 K. Four drops of a 10 per cent solution of tetra-*iso*-propylorthotitanate in diethyleneglycoledimethylether were added and the melt was stirred for 4 h. To remove the ethanol the pressure was slowly reduced to 1 mbar and kept for four more hours. Recrystallization from chloroform yielded 1·4 g (82 per cent) of the bishexadecylester.

^{1}H NMR (CDCl$_3$): 0·86 ppm (t, 6 H), 1·2–1·4 ppm (m, 52 H), 1·8 ppm (m, 4 H), 4·5 ppm (m, 4 H), 8·07 ppm (d, 1 H), 8·38 ppm (dd, 1 H), 8·77 ppm (dd, 2 H), 9·12 ppm (d, 1 H).

Elemental analysis (calculated for $C_{48}H_{71}N_3O_{10}$): C: calc. 67·90 per cent, found 68·07 per cent; H: calc. 8·31 per cent, found 8·08 per cent; N: calc. 4·94 per cent, found 4·71.

For the preparation of the electron donor acceptor complexes the compounds were dissolved separately in dichloromethane and mixed. After evaporation of the solvent the dark brown residues were dried in vacuum for 3 days at room temperature.

2.2. *Characterization*

By using optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction the physical properties of the samples were examined. Transition temperatures and enthalpies were measured with a Perkin Elmer DSC 4 with a heating rate of $20 \, K \, min^{-1}$. In all cases the data from the second heating scan were taken. For X-ray diffraction measurements a flat plate camera with Ni-filtered Cu–K_{α} radiation, equipped with a Paar hot stage, was used. The samples were prepared in Lindemann glass capillaries. The textures were studied using a Leitz Ortholux II Pol-BK polarizing microscope equipped with a Mettler FP 52 hot stage. Contact samples were prepared as follows. The donor compound was placed between two untreated cover slips and the acceptor was placed at the edge of the upper slip and melted. Capillary forces draw the acceptor into contact with the donor and by heating above the clearing temperature an electron donor acceptor complex is formed.

3. Results and discussion

3.1. *Optical microscopy*

One of the first experiments for the examination of these complexes is the preparation of a contact sample. The contact sample between 1 and 3 at 315 K is shown in figure 1 (*a*). A typical nematic schlieren texture is formed between the crystalline phases of the donor and acceptor, separated from these phases by small isotropic regions. Withdrawing the polarizers the slight brown colour of the electron donor acceptor complex is observed in the contact region indicating that the complex formation is responsible for the phase induction. Starting from this preliminary information several complexes with different molar ratios of donor and acceptor were prepared (see the table and figure 2). Cooling a sample of the 1 : 1 molar complex of 1 and 3 from the isotropic phase reveals nematic droplets which converge at lower temperatures to form a schlieren texture at 323 K (figure 1 (*b*)). In contrast, the contact sample as well as the 1 : 1 mixture of 2 and 3 show only typical textures for a D_{ho} phase (see figure 1 (*c*)).

3.2. *Differential scanning calorimetry*

The phase transition data for the electron donor acceptor complexes of 1 and 3 are given in the table. The corresponding phase diagram is shown in figure 2.

With increasing amount of acceptor the width of the observed D_{ho} phase decreases. The clearing temperatures as well as the melting points decrease and in a 3 : 1 complex of donor to acceptor the D_{ho} phase is monotropic. Increasing the acceptor ratio to a 2 : 1 mixture we observe a complex phase behaviour. Microscopic investigations show that this mixture is biphasic with both crystalline and nematic regions at room temperature. In a 1·5 : 1 and a 1 : 1 mixture a homogeneous monotropic N_c phase is induced. Only after annealing for several days at room temperature does the 1 : 1 complex crystallize and show a melting point at 332 K (see figure 2). Increasing the acceptor ratio to 0·8 : 1 leads to phase separation.

The clearing enthalpies of the transition N_c–isotropic are in the range of 0·8 to $1·3 \, J \, g^{-1}$. As expected because of the lower symmetry of the nematic phase they are
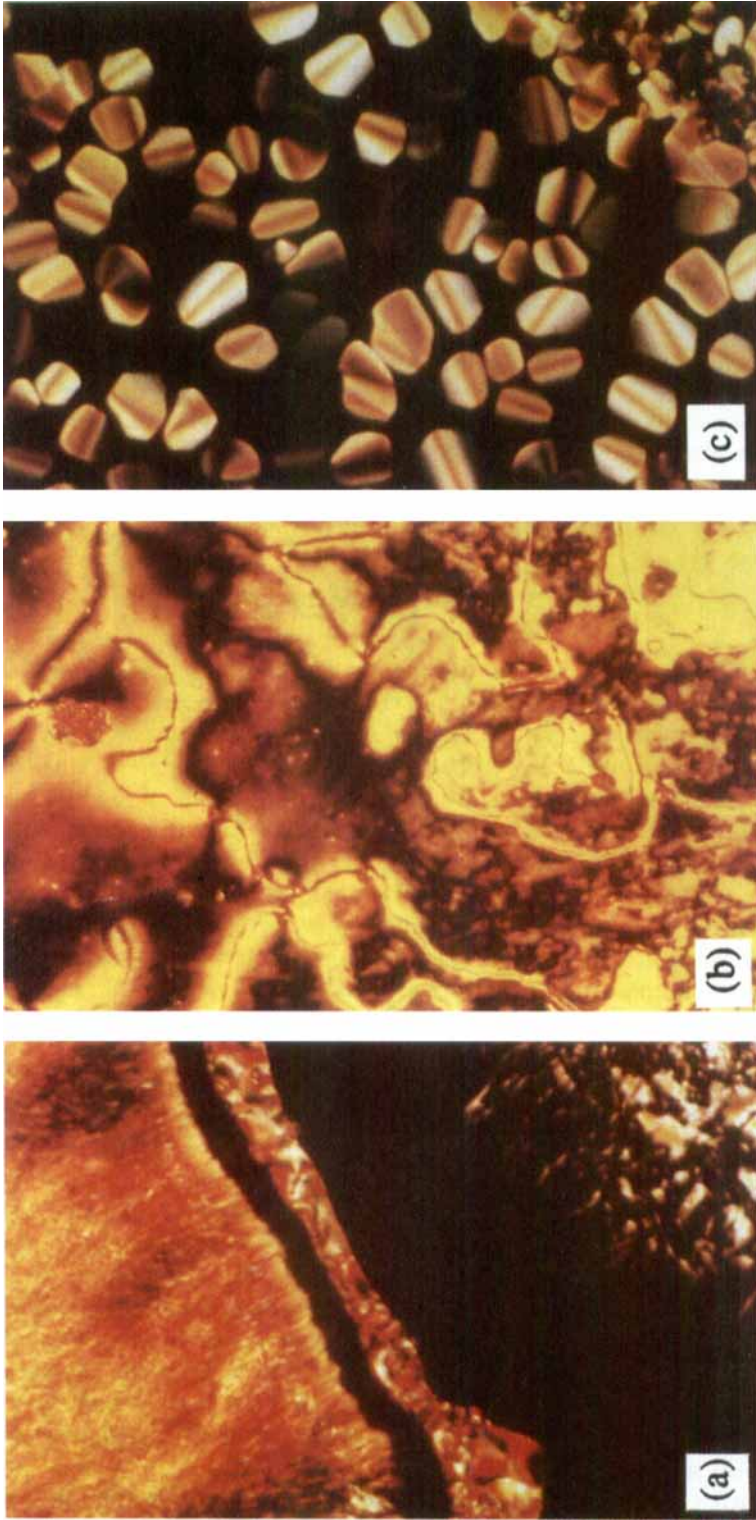
Figure 1. Optical textures of (*a*) contact sample of **1** and **3**, (*b*) 1:1 complex of **1** and **3**, and (*c*) 1:1 complex of **2** and **3**.

Transition data for the electron donor acceptor complexes of **1** and **2** with **3**. For the reader's convenience the data for the pure donors and acceptor are added. †, biphasic sample in the microscope; ( ), monotropic phase transitions.

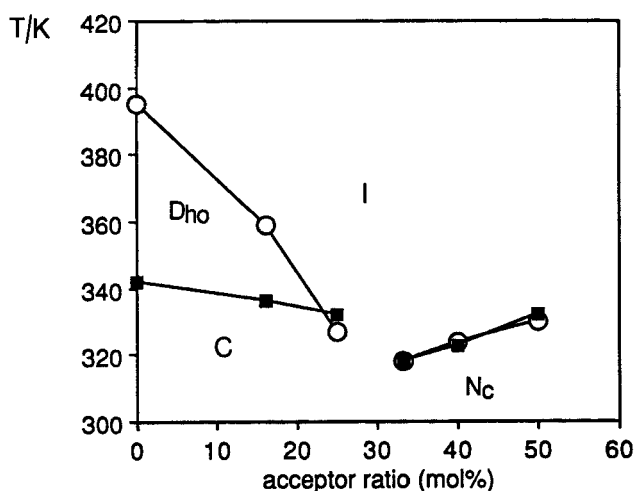| Compound	Acceptor ratio/mol%	Molar ratio of donor to acceptor	Phase behaviour T/K	Clearing enthalpy $\Delta H/\text{J g}^{-1}$
3			C 382 I	
1			C 342 D_{ho} 395 I	11·0
1	16·6	5:1	C 336 D_{ho} 359 I	3.8
1	25	3:1	C 332 (D_{ho} 327) I	1·3
1	33·3	2:1	C 318 I + N_c 318 I†	0·8
1	40	1·5:1	C 323 N_c 324 I	1·3
1	50	1:1	C 332 (N_c 330) I	1·3
2			C 322 I	
2	50	1:1	C 332 D_{ho} 375 I	2·4

Figure 2.   Partial phase diagram of **1** and **3**. C, crystalline; I, isotropic; D_{ho}, discotic hexagonal ordered; N_c, nematic columnar.

smaller than the clearing enthalpies for the transition D_{ho}–isotropic. The latter decreases with increasing acceptor content. This behaviour is in agreement with that of other discotic electron donor acceptor complexes [3].

3.3. *X-ray diffraction*

The X-ray diffraction pattern of the N_c phase of the 1 : 1 complex of **1** and **3** is shown in figure 3 (*a*). The sample orients spontaneously in the capillary tube during preparation. Thus the photograph shows distinct equatorial (A) and meridional (B) reflections. The meridional reflections in the wide angle region indicate the intra-columnar packing of the aromatic cores of donor and acceptor units with a distance of 0·35 nm. The diffuse reflection (C) corresponding to 0·42 nm is related to the alkyl chains of donor and acceptor. The reflections (A) along the equator in the small angle region corresponding to 1·9 nm indicate the intercolumnar packing. In an oriented D_{ho}
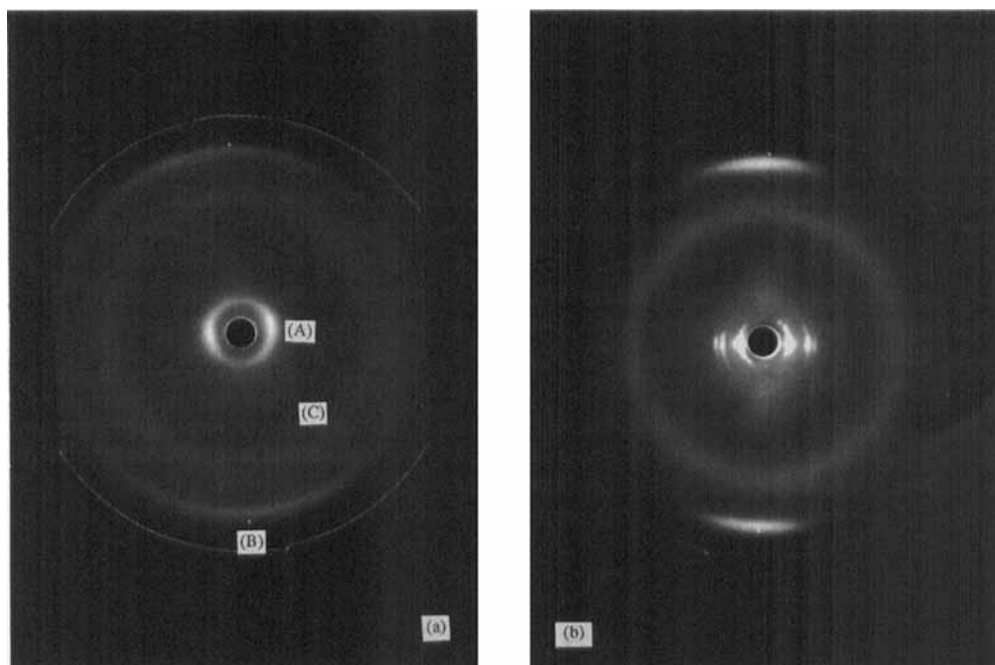
Figure 3.   X-ray diffraction patterns (flat plate camera photographs) of a (*a*) N_c phase of a 1 : 1 complex of **1** and **3** and (*b*) D_{ho} phase of a 1 : 1 complex of **2** and **3**.

phase these reflections are sharp and well oriented at the equator. In the case of the N_c phase the reflections are more diffuse and have a larger radial expansion. This expansion can be correlated to the persistence length in the corresponding lattice. Evaluation of this correlation length from the full width half maximum of the small angle reflection show that in the nematic columnar phase each column has, on average, only one nearest neighbour with the same orientation. In a D_{ho} phase this persistence length is about 20 columns or more. As a conclusion, we can say that columns having a 0·35 nm distance between the aromatic cores with a short range order between the columns indicate clearly a nematic columnar phase.

In addition to these results, the flat plate camera photograph of the 1 : 1 complex between **2** and **3** shows the typical diffraction pattern of a D_{ho} phase (see figure 3 (*b*)). The wide angle reflection indicates the ordered columnar structure of the mesophase and the sharp reflections in the small angle region are due to the hexagonal lattice.

4.   Discussion

The newly synthesized electron acceptor **3** consists of two different parts. An electron withdrawing headgroup and long aliphatic hydrocarbon chains. In the observed complexes of both **1** and **2** with **3** the headgroup of **3** has the same effect as in the case of the unsubstituted trinitrofluorenone [3]. In both cases, the acceptor is inserted into the columnar structure of the discotic donor (**1** or **2**, figure 4). The enhancement of the core–core interaction due to complex formation within the columns stabilizes the columnar structure of both systems. However, clear differences are found as far as the influence of the long aliphatic chains of the acceptor on the
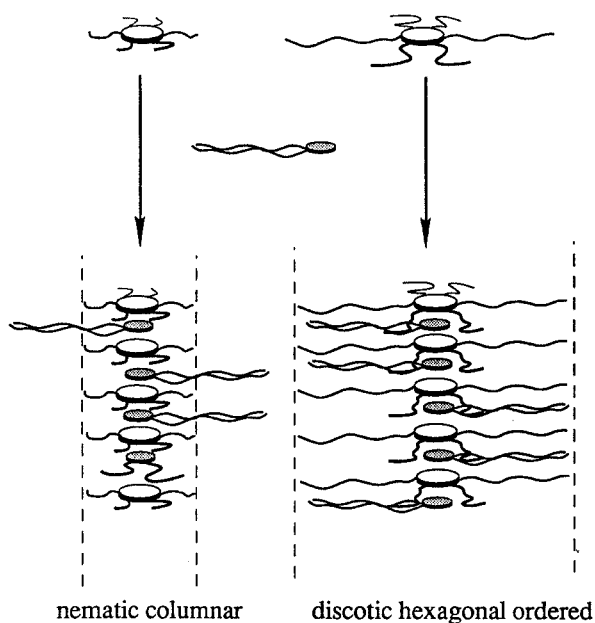
nematic columnar   discotic hexagonal ordered

Figure 4. Schematic representation of the formation of N_c and D_{ho} phases by mixing both 1 and 2 with 3.

packing of the columns is concerned. The hexadecyl side groups of 3 disturb the side group region of the triphenylene 1 having short alkyl chains. As a result a strong asymmetry and an increase of the volume of the alkyl chain region is induced. Thus the columnar interactions are reduced and the packing of the columns on a hexagonal lattice is prevented. The columns are easily separated and are floating in a sea of alkyl chains. As shown by DSC, optical microscopy and X-ray experiments this leads to the induction of a nematic columnar phase in an originally discotic hexagonal ordered liquid crystal. While the packing of triphenylene 1 appears to be disrupted by the side groups of 3, this same type of disruption does not occur in a mixture of 2 and 3. In this case the long alkyl chains of the acceptor fit perfectly into the side group region of the donor and the asymmetry has no effect on the side group region. Thus the columns form a hexagonal lattice and a D_{ho} phase is found.

It could thus be shown that the concept of phase variation and induction of discotic liquid crystals by electron donor acceptor complex formation can be extended from the upgrading type of induction of highly ordered phases [3] to the downgrading of phases resulting not in a phase destruction but in a liquid crystal phase with a smaller degree of order. This downgrading results from a combination of steric and electron donor acceptor interactions which increases the variety of such liquid-crystalline complexes.

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