Structure Formation Control of Disc-Shaped Molecules

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STRUCTURE FORMATION CONTROL OF DISC-SHAPED MOLECULES

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Supramolecular assemblies of radial multialkynylbenzene derivatives are presented which arise either from specific interactions with interfaces or from the covalent linkage of different molecular fragments. Surface-assisted molecular orientation control was investigated at the air/water interface, on photo-oriented azobenzene films and on rubbed polyimide orientation layers, respectively. Surface alignment generates edge-on or tilted orientations of the aromatic discs. Two- and three-dimensional architectures are formed which differ remarkably from the nematic-discotic bulk phases of the compounds. On the other hand, linking chemically a pentaalkynylbenzene donor moiety with an intramolecular acceptor function leads to charge-transfer mesogens, displaying novel types of mesophases which cannot be achieved with binary mixtures of flat donor and acceptor components.

1. INTRODUCTION

Since the discovery in 1977 that hexa-n-alkanoyloxybenzene derivatives exhibit mesophases with a columnar structure [1], a wide variety of non-calamitic liquid crystalline compounds have been reported possessing a flat or nearly flat rigid core surrounded by a certain number of long flexible alkyl substitutents.

Similar as for rod-shaped mesogens, several types of liquid crystalline bulk phases can be formed by disc-like molecules [2]. In the nematic discotic (N_D) phase the planes of the flat molecules are oriented more or less

parallel to each other resulting in a preferred orientational order of the short molecular axis. The nematic columnar (N_{Col}) phase is characterized by a columnar stacking of the molecules and a nematic arrangement of the columns. A parallel alignment of the columns results in columnar mesophases with a two-dimensional lattice symmetry such as columnar hexagonal (Col_h) or rectangular (Col_r). Within each column, the molecules may be arranged in a periodically ordered manner or disordered in case of a liquid-like arrangement.

Self-organization with formation of liquid crystalline structures also can be achieved by specific intermolecular interactions giving rise to non-covalently bonded anisometric aggregates. For example, hydrogen bonding may lead to discrete supermolecules with a pronounced flat disc-like shape which favours the formation of columnar aggregates [3–6]. Charge transfer complex formation of flat donor molecules such as triphenylene ethers and multialkynylbenzene derivatives with electron acceptors may cause manipulations as well as inductions of columnar mesophases [7–9].

Even though the mesomorphic behaviour can be tailored by the chemical composition and can be manipulated by directed supramolecular interactions, the liquid crystalline diversity of disc-shaped compounds is limited [10].

Exemplified for multiynes of benzene, first introduced in the late 1980's [11,12] this contribution covers aspects which offer a greater scope for control and manipulation of supramolecular assemblies than can be reached solely as result of a flat anisometric shape of single molecules or aggregates.

2. SURFACE ASSISTED MOLECULAR ORIENTATION CONTROL

Water insoluble amphiphilic molecules composed of a hydrophilic head group and a lipophilic flexible tail are known to form ordered monomolecular layers at the air/water interface [13]. The self-organization arises from the affinity of the polar groups towards the water whereas the hydrophobic chains tend to turn away from the interface.

A powerful tool to create disc-like molecules with pronounced hydrophilic and hydrophobic regions consists of the asymmetric incorporation of terminal polar substituents to the periphery of an extended flat core via flexible spacers. In this way it is possible to combine liquid crystalline behaviour and amphiphilic self-organization [14]. This concept has been realized, i.e., with benzene centred multiynes which carry hydroxy or hydrocarboxy groups linked to the inner phenyl ring by methylene spacers (Fig. 1).

1: m = 11; X = OH
2: m = 10; X = COOH

| R	H	C_5H_{11}	C_3H_7	CH_3
	1a	1b	1c	1d
	2a	2b		
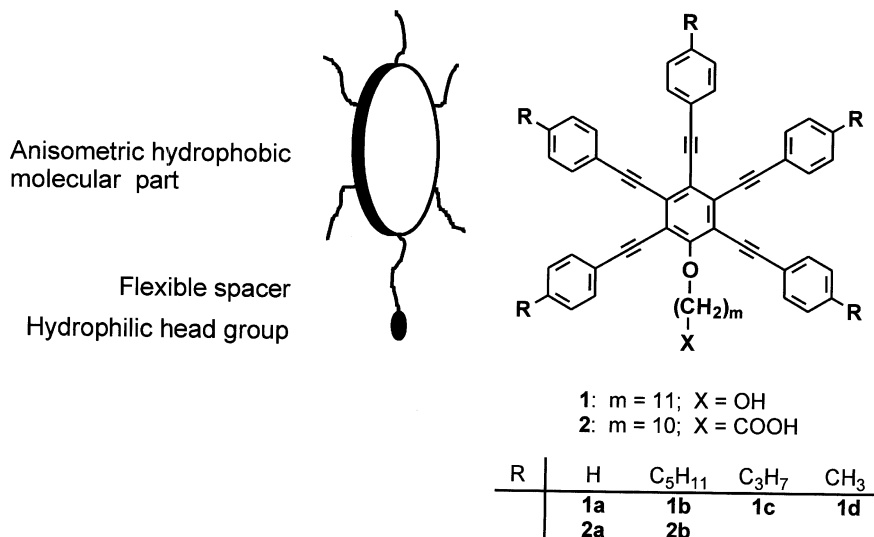
FIGURE 1 Amphiphilic benzene centred pentaalkynes **1** and **2** carrying a terminal hydroxy or hydrocarboxy group.

The peripherally unsubstituted pentaynes **1a,2a** show no liquid crystalline properties in their pure state [15,16]. The five-fold alkyl substituted homologues **1b-d** and **2b** exhibit an enantiotropic nematic-discotic (N_D) mesophase [15,17,18].

The phase behaviour of the pentakis(arylethynyl)benzene derivatives **1** and **2** in mixtures with 2,4,7-trinitro-9-fluorenone (TNF) as electron acceptor strongly depends on the substituents attached to the periphery of the penta-alkyne donor. Equimolar mixtures of the laterally unsubstituted members **1a,2a** and TNF exhibit a CT-induced nematic columnar (N_{Col}) phase [15,16]. In case of the pentyl [15] and propyl substituted homologues **1b,c** and **2b** donor-acceptor interaction with TNF leads to the induction of a hexagonal columnar ordered (Col_{ho}) mesophase. The pentayne **1d** incorporating five methyl groups does not show mesophase induction in mixtures with TNF. The equimolar mixture with TNF exhibits an N_D phase but with a broader mesophase range than the pure compound **1b** [17]. The N_D phase displayed by the pure compounds **1** and **2** and the CT-induced columnar mesophases are shown schematically in Figure 2.

Detailed investigations regarding amphiphilic properties were performed with the pentakis(arylethynyl)benzenes **1a,b** carrying a terminal hydroxy substituent and with the carboxylic acids **2a,b**.

Independent of the lateral substitution pattern (R = H, pentyl) the unsymmetrical pentaalkynes **1** and **2** form monolayers when spread at the

N_D N_{col} Col_h
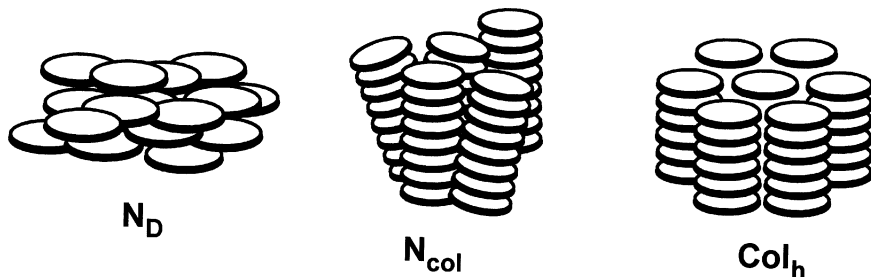
FIGURE 2 Thermotropic liquid crystalline phases formed by the pentayne donors **1** and **2** in their pure state and of binary mixtures with electron deficient TNF: N_D = nematic discotic phase; N_{Col} = nematic columnar phase; Col = columnar mesophases.

air/water interface. The surface pressure – area isotherms show no phase transitions during compression but a direct transition to a solid condensed phase [16]. The collapse areas indicate an up-right standing of the extended aromatic cores on the water surface. The collapse pressure of the pentaynes **1a,b** and **2a,b**, however, is relatively low on a pure water subphase [16] which is attributed to the presence of only one hydrophilic substituent. The monolayer stability can be enhanced significantly by interactions of the hydrophilic head groups with counterions present in the subphase [19,20].

Within the monolayers the rigid edge-on oriented cores of the pentayne amphiphiles **1,2** are face-to-face shifted each against the other resulting in a two-dimensional nematic-discotic (N_D)-like arrangement [21](Fig. 3a). The two-dimensional monolayer assemblies of the pentaalkynes not only arise from decreasing the available area per molecule during the compression process. As evident from Brewster angle microscopy and surface potential – area isotherms, spontanious aggregation of the perpendicularly oriented molecules immediately after spreading results in condensed monolayer islands which are pushed together during compression [21,22].

The compressed monolayers can be transferred onto solid substrates by the Langmuir-Blodgett (LB) technique [16,19,20,23]. Y-deposition gives rise to bilayer edge-on packing of the molecules perpendicular to the substrate with head-to-head and tail-to-tail arrangement of molecular monolayers (Fig. 3b). The flexible molecular segments of neighbouring molecules are interdigitated. Furthermore, alternating LB films were constructed by deposition of pentayne monolayers with arachidate spacer layers [20]. The multilayer structure obtained in this way consists of monolayers with distinct layer spacings determined by the molecular dimensions of the fatty acid and the multiyne. The hydrocarbon wings of the discs do not penetrate into the close packed chains of the neighbouring
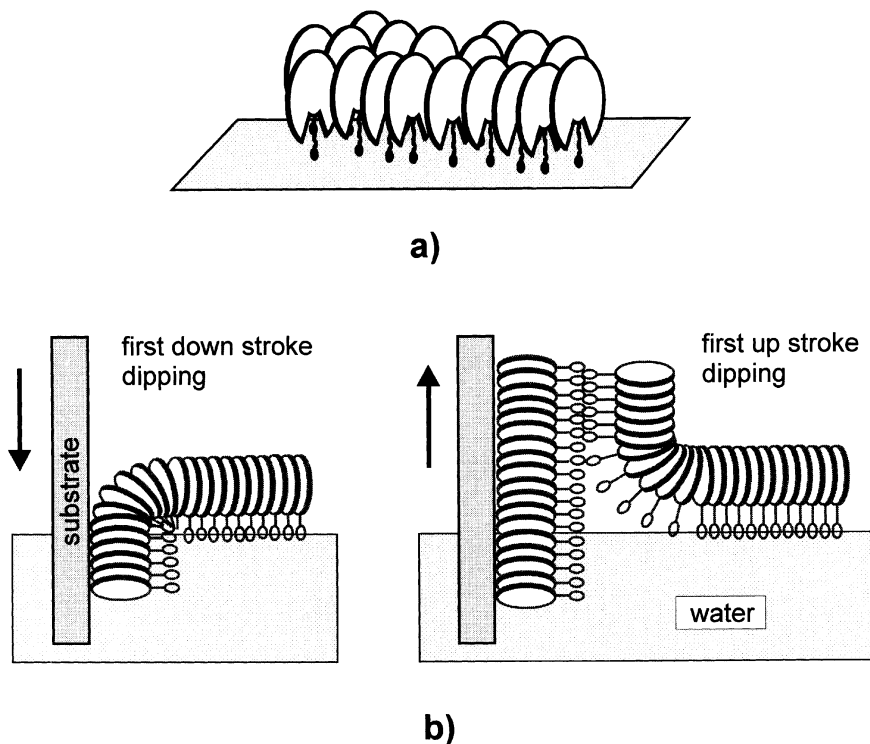
FIGURE 3 Self-organization of the pentaynes **1** and **2** arising from amphiphilicity: a) monolayers at the air/water interface with the aromatic cores oriented perpendicular to the surface; b) Multilayer deposition of edge-on oriented pentayne amphiphiles. Y-type bilayers are formed with opposite orientation of the flat hydrophobic cores.

fatty acid layers and the pentayne has only a slight tilt with respect to the surface normal.

It follows, that spreading and subsequent LB film deposition results in a higher degree of ordering compared with the original nematic-discotic phases of the pure pentaalkynylbenzene amphiphiles.

Certain device applications involving liquid crystals require a strict molecular orientation control on suitable substrates. Consequently, there have been extensive reports on the alignment control of calamitic mesogens [24,25]. However, surface-assisted orientational control is not restricted to rod-like mesogens. This was demonstrated, for example, with discotic nematogens based on a triphenylene core by rubbed polymer films [26] and by the photoalignment technique [27].

The five-fold pentyl substituted member (**1b**) of the pentayne amphiphiles and the methyl modified homologue **1d** were chosen to elucidate orientation photocontrol of nematic-discotic multiyne chromophores by photoreactive polymer thin films [28,29].

A thin film of a semicrystalline azobenzene side chain polymer (poly[4-(4-cyanophenylazo)phenoxy methacrylate [30]) was obliquely exposed to non-polarized light followed by annealing above T_g of the polymer [27–29]. This procedure generates a uniform spacial orientation of the azobenzenes with a pretilt angle of their longitudinal axis of approximately 20° [28].

A thin film of either compound **1b** or **1d** was spin-coated on top of the photoirradiated azobenzene layer. The pentayne films do not show optical anisotropy at room temperature due to polycrystalline structures. Birefringence is induced upon heating into the N_D phase and disappears thoroughly above the clearing temperatures of compounds **1b** and **d**, respectively. The optical anisotropy revives on cooling at the transition from the isotropic to nematic-discotic phase and can be maintained at room temperature by supercooling. The measurement of retardation as a function of rotation angle of the films reveals a tilted alignment of the pentayne molecules. The average pretilt angles of the orientational director of both compounds were estimated to be approximately 70° from the substrate surface [28]. It follows that the photoinduced molecular orientation of the azobenzene units is transferred to the pentayne nematogens to give a tilted alignment. Furthermore, the luminescence properties of the benzene centred multiynes **1** [31] along with alignment on a photopatterned azobenzene orientation layer give rise to micropatterned polarized blue photoluminescence [28]. Maximum photoluminescence intensity was observed when the excitation was carried out from the direction parallel with the orientational director of the pentayne molecules.

A problem regarding long-term stability of the oriented films, however, may result from the tendency of the monomers to crystallize upon slow cooling and storing at room temperature. To avoid crystallization we followed the concept to combine mesogenic properties with glass forming tendencies by linking chemically a defined number of anisometric molecular sub-units.

The star-like oligomers **3** (Fig. 4) consist of three flat multiyne moieties grafted to a central linking unit *via* flexible spacers [18].

The pentayne oligomers exhibit a nematic-discotic (N_D) mesophase and are, thus, isomorphic with the corresponding hydroxy terminated monomers **1** which serve as starting materials for the synthesis of compounds **3a-c**. The N_D phases of the star-shaped trimers **3b** and **3c** can be quenched into a glassy state.

Spin-coating films of the star-shaped pentayne oligomer **3b** were prepared on glass substrates provided with a rubbed polyimide orientation

3	a	b	c
R	CH_3	C_3H_7	C_5H_{11}
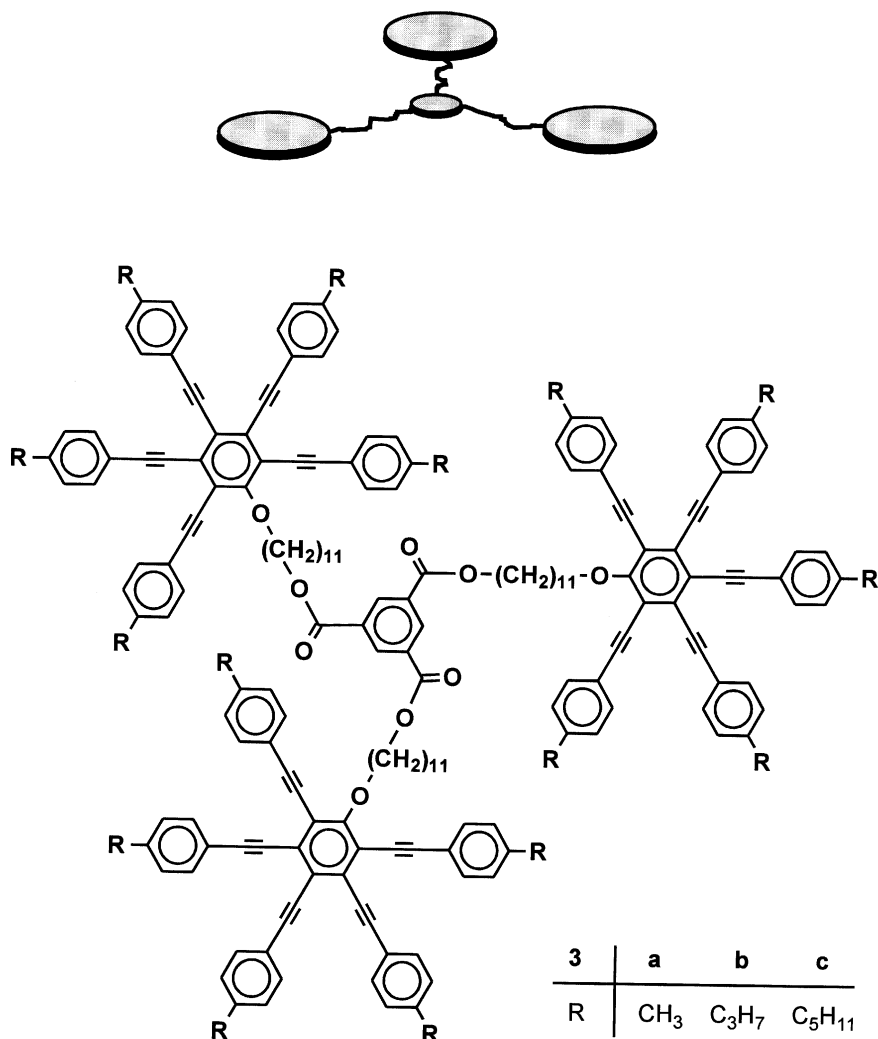
FIGURE 4 Star-shaped nematic discotic pentayne oligomesogens **3**.

layer [18]. The films were heated above the clearing temperature followed by slow cooling to the N_D phase. After annealing within the mesophase, the films were cooled down to room temperature. In accordance with the thermal bulk properties no crystallization occurs during the cooling. The thermal treatment along with the polyimide alignment layer gives rise to a three-dimensional orientation. Birefringence measurements of the glassy films as a function of incident angle of probing light from the surface normal

D. Janietz
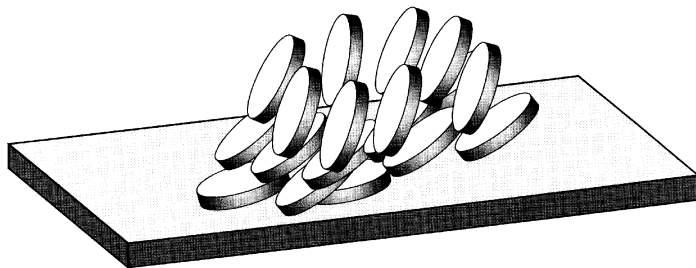
FIGURE 5 Schematic presentation of the tilted hybrid orientation of the pentaynes **1** on photoaligned azobenzene layers and of the star-oligomers **3** on rubbed polymer orientation layers.

indicate a tilted alignment of the disc-shaped groups. The average pre-tilt angle of the planes of the flat aromatic pentaalkynylbenzene cores was estimated to be approximately 14° relative to the substrate surface. Similar as in case of the oriented films of the monomeric discotic nematogens **1** on photoirradiated azobenzene layers [28], the tilt angles continuously alter in order to minimize the free energy at the outermost film/air interface.

The tilted hybrid orientations of the molecular discs of both pentaynes (**1** and **3**) (Fig. 5) induced either by photoalignment or by rubbed polyimide orientation layers, on the one hand, are quite similar. On the other hand, this type of molecular organization differs remarkably from the one that can be reached with the amphiphiles **1** at the air/water interface and in LB-multilayers.

3. PENTAYNE BASED DONOR ACCEPTOR TWIN MESOGENS

The CT-induced mesophases of the pentaynes **1** and **2** and of structurally related radial multialkynylbenzene derivatives [9] mixed with TNF are of the nematic columnar and/or the hexagonal columnar type. It was expected that the attachment of an intramolecular acceptor function to the periphery of the anisometric pentayne core would offer a broader scope for the control and richness of columnar structures. This concept has been realized with the donor-acceptor twin molecules **4** and **5** with an electron deficient nitrofluorenone coupled with a pentaalkyne group by a flexible spacer segment [17,32] (Fig. 6).

Structural modifications were performed at the lateral sphere of the pentayne units of compounds **4** and **5** in order to modify the dimension of the donor molecular part whereas the spacer length was kept constant. The twin molecules **5** additionally comprise a centre of chirality within the spacer sequence.
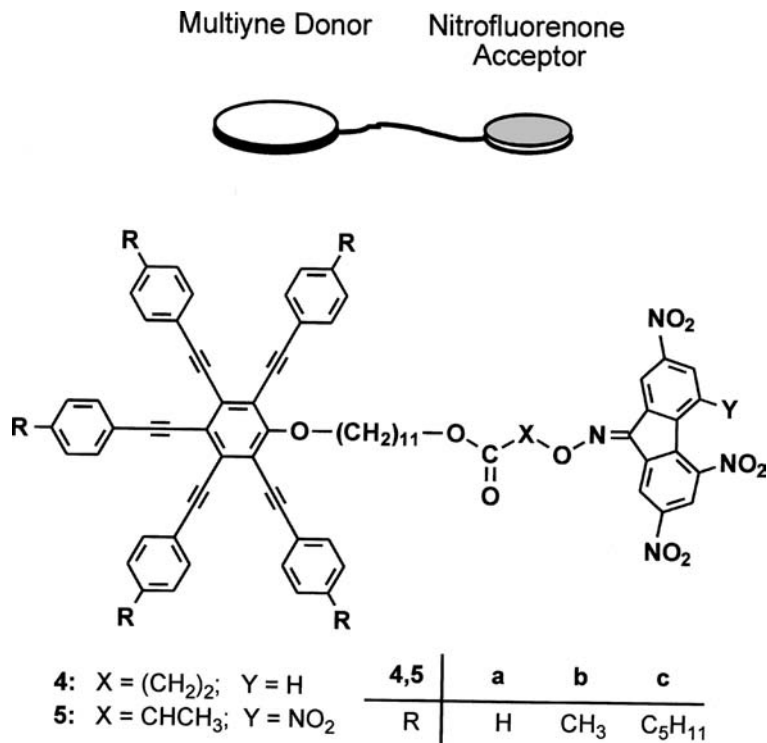
FIGURE 6 Charge-transfer twin mesogens **4** and **5** with covalently linked pentaalkyne and nitrofluorenone sub-units.

The pentayne twin molecules **4** display a columnar phase with a rectangular lattice symmetry (Col$_r$ with a = b) and a periodical intracolumnar ordering [17]. The donor and acceptor groups of the CT twins are placed in an alternating fashion in neighbouring columns. The intracolumnar periodicity is due to charge-transfer interactions perpendicular to the column axis. The two-dimensional rectangular lattice is attributed to the chemical linkage of the donor and acceptor moieties. A structural model for the Col$_r$ phase of the CT-twin mesogens **4** is presented schematically in Figure 7a.

In case of the laterally unsubstituted member **4a** these special features give rise to a correlation between the two-dimensional rectangular array and the one-dimensional lattice along the column axis. Compound **4a** is the first example of a mesogen which exhibits a rectangular columnar plastic (Col$_{rp}$) phase [17] bridging the gap between the crystalline state and ordered columnar mesophases. Attaching lateral alkyl substituents to the periphery of the pentayne donor group of compounds **4** leads to a partial

a) **b)**
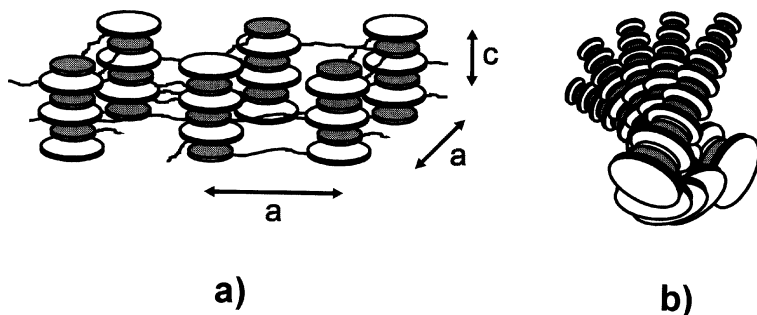
FIGURE 7 Structural models for the mesophases formed by pentayne based donor-acceptor twin molecules; a) rectangular columnar phases of compounds **4;** b) helically twisted nematic columnar phases of the chiral CT-twins **5**.

(**4b**) or complete (**4c**) disappearance of the three-dimensional positional order. This behaviour may be due to increasing distortions resulting from interdigitation of the side chains into neighbouring columns to an increasing extent with elongation of the chain length.

Thus, the covalent linkage of a pentaalkyne donor molecular moiety with an acceptor function by a simple alkyl spacer facilitates the formation of rectangular symmetries of intercolumnar packing instead of common hexagonal columnar or nematic-columnar arrangements. A similar behaviour was also reported for CT-complexes of discotic oligomers additionally forming hydrogen bonded strands between the polymer backbones [33].

Compounds **5** incorporating an asymmetric carbon within the alkyl spacer exhibit a chiral nematic-columnar (N_{col}^*) mesophase with a helical twisting of the columns [17] (Fig. 7b). The more bulky chiral alkyl spacer of the mesogens **5a-c**, thus, is suggested to act as a disturbing unit which prevents a parallel alignment of the columns to form a two-dimensional lattice. On the other hand, the chiral spacer can be regarded as an additional intramolecular function which induces chirality within the mesophase.

It follows that the chemical linkage of the flat pentayne donor with the nitrofluorenone based acceptor moieties gives rise to mesomorphic structures of the CT-twin compounds **4** and **5** which differ significantly from the ones that can be obtained by simply mixing the two penta-alkyne donor and acceptor components.

Noteworthy, that similar as reported for structurally related triphenylene based CT-twins [34] the mesomorphic order of compounds **4** and **5** can be quenched into a glassy state which is a behaviour rather typical for liquid crystalline polymers.

4. PENTAYNE BASED DISC-ROD TRIPLE MESOGENS WITH CHARGE TRANSFER INTERACTIONS

A disadvantage for certain applications is that disc-like and rod-like mesogens are not miscible and that phase separation occurs at a macroscopic scale. Even the chemical linkage of molecular sub-units with different anisometric shapes *via* flexible spacers [35–37] does not necessarily lead to mesomorphic properties of thus obtained rod-disc molecules.

The covalent linkage of three different structural elements, in particular, the combination of a disc-like donor, a rod-shaped molecular moiety and an intramolecular acceptor function, promoting structure formation tendencies by CT-interactions, may avoid destruction of mesomorphic order. This could be demonstrated with the non-symmetric triple molecules **6** (Fig. 8) composed of an enlarged pentaalkynylbenzene donor group linked to a nitrofluorenone acceptor by a rod-shaped azobenzene moiety [38,39].

The pentayne trimers **6** exhibit an enantiotropic mesophase which can be frozen in a glassy state at room temperature. The liquid crystalline structure of the disc-rod mesogens **6a,b** corresponds to a nematic-columnar (N_{Col}) like molecular arrangement [39]. The individual columns are formed through an intercalated stacking of the flat donor and acceptor moieties of different molecules. The flexible spacer segments connecting the three rigid molecular sub-units adopt more or less stretched
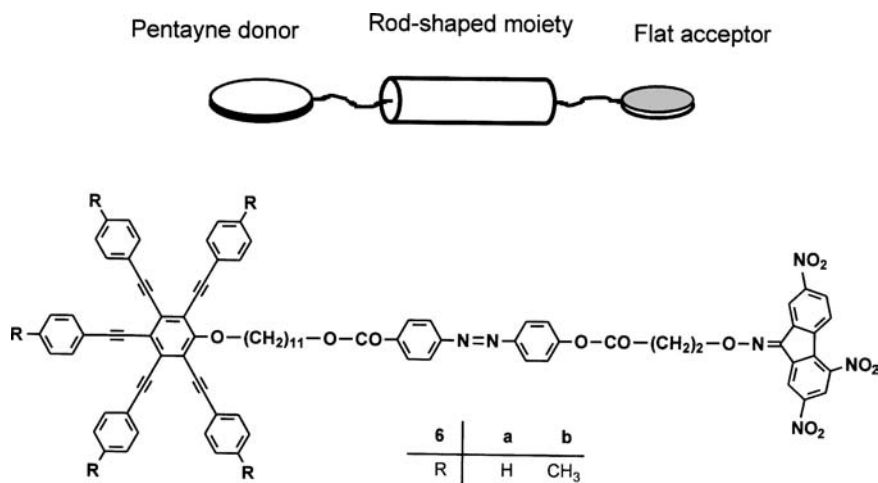
FIGURE 8 Triple compounds **6** formed through chemical linkage of a radial pentayne donor moiety, a rod-shaped azobenzene group and a flat nitrofluorenone acceptor.
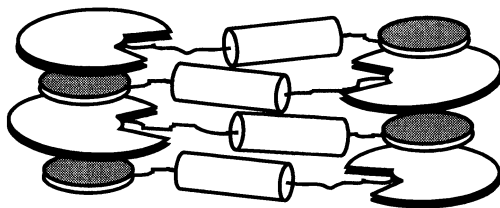
FIGURE 9 Structural model for the nematic columnar like liquid crystalline phase of the disc-rod triple mesogens **6**.

conformations. This gives an arrangement of the rod-shaped moieties with their long axis predominantly oriented perpendicular rather than parallel to the column axis (Fig. 9). The columns separated by the calamitic molecular fragments do not assemble on a two-dimensional lattice. Instead they orient in a common direction. The mesophases which are formed by the disc-rod CT-trimers **6**, thus, combine features of both calamitic and columnar liquid crystalline phases. Similar mesomorphic structures, but with a more pronounced intracolumnar ordering, have been reported for charge transfer triple compounds incorporating a triphenylene donor molecular fragment instead a pentayne sub-unit [38,40].

The fact that the liquid crystalline phases of compounds **6a,b** have to be attributed to CT-interactions has been further confirmed by omitting the acceptor sub-unit. Structurally related pentayne based disc-rod dimers with a rigid rod-shaped azobenzene group substituted with a single alkyl chain instead of an acceptor function do not display any mesomorphic behaviour [41].

Furthermore, the ability of the rod-shaped azo group placed between the donor and the acceptor moieties to be switched by light along with liquid crystalline structure formation make the triple mesogens **6** promising materials for optical data storage as it is in fact evident from optical grating experiments [42].

CONCLUSIONS

Attractive interactions of amphiphilic pentaalkynylbenzene derivatives with an air/water interface lead to a replacement of the three-dimensional mesomorphic bulk structure by two-dimensional supramolecular assemblies at the interface. The molecular orientation of pentayne nematogens can be further regulated by alignment layers such as photoirradiated azobenzene and rubbed polymers. In this way the original nematic-discotic domain structure is replaced by a (tilted) three-dimensional orientation of the aromatic discs.

Providing a flat electron-rich pentayne moiety with an intramolecular acceptor sub-unit gives rise to novel types of liquid crystalline phases that cannot be reached with binary mixtures consisting of disc-like donor and acceptor molecules. The structure formation of the donor-acceptor mesogens results from a delicate balance between non-covalent intermolecular charge-transfer interactions, the chemical linkage of the pentayne donor with the acceptor and steric effects. The relative orientation of the mixed donor-acceptor stacks to each other is mainly effected by the chemical nature of the spacer, aliphatic, chiral aliphatic or additionally comprising a rod-shaped molecular fragment.

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