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Structure formation of functional sheet-shaped mesogens

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The combination of anisometric sub-units with an additional intramolecular functionality has frequently resulted in the creation of supramolecular systems not only able to form thermotropic mesophases due to their anisotropic molecular shape but also capable of structure formation resulting from their amphiphilic properties and/or from non-covalent intermolecular interactions with complementary components. This article summarizes different examples of this interplay of structure formation tendencies based on functionalized sheet-like liquid crystals.

The formation of thermotropic liquid crystalline phases is predominantly caused by an anisometric molecular shape[1] whereas amphiphilic molecules characterized by combined hydrophilic and lipophilic groups may exhibit lyotropic mesophases in the presence of a solvent[2] or two-dimensional supramolecular assemblies at an air–water interface.[3] Yet the shape of a single molecule is not the only structure controlling factor. Form-anisotropic aggregates giving rise to mesomorphic structure formation can also be formed by specific intermolecular interactions between identical or different individual molecules. Such attractive interactions may, for example, arise from ionic structures,[4] dipole–dipole interactions,[5] hydrogen bonding[6] or charge transfer effects.[7]

The combination of anisometric sub-units with an additional intramolecular functionality, furthermore, offers a powerful tool to design molecular architectures which are characterized by the fact that their self-organization results from a complex interplay and/or competition of different factors and driving forces of structure formation. In this way, by creating multifunctional chemical primary structures, a much greater scope is offered for control and manipulation of supramolecular assemblies than can be achieved with monofunctional mesogens.

In the case of rod-like mesogens an additional functional sub-unit can be incorporated either along or perpendicular to the main molecular axis.[8] The flat molecular geometry of disc-like or, more generally, sheet-like[9] compounds allows two possibilities to be combined with an additional intramolecular function (Fig. 1). The functional sub-unit can be fixed at one or more positions at the periphery of the molecule *via* flexible spacers (A) or it can be an integrated part of the rigid central molecular core (B).

This paper is concerned with examples of functionalized sheet-like systems of both general structure types A and B, given schematically in Fig. 1, which are not only able to form thermotropic mesophases due to the anisotropic molecular shape but also capable of structure formation resulting from amphiphilic properties and/or from non-covalent intermolecular interactions with complementary components, the latter giving rise to a manipulation or an induction of columnar liquid crystalline phases. However, it is far beyond the scope of the present paper to give a comprehensive overview of this topic.

Mesophase structures usually formed by flat sheet-shaped molecules and phase manipulation by doping with electron acceptors

It was discovered in 1977 that hexa-*n*-alkanoyloxybenzene derivatives exhibit mesophases with a columnar structure,[10] and since then a wide variety of liquid crystalline compounds of quite different chemical structures have been prepared possessing a flat or nearly flat rigid core surrounded by a specific number of peripheral long chain alkyl substituents (three to twelve).

Several types of mesophases formed by those sheet-like molecules have been identified which differ with respect to the state of order[11] (Fig. 2). The mesophase exhibiting the lowest state of order is the nematic discotic (N_D) phase, well established, *e.g.* for radial multialkynylbenzene derivatives,[12] in which the planes of the flat molecules are oriented more or less parallel to each other giving rise to a preferred orientational order of the short molecular axis.

In contrast to the common N_D phase, the nematic columnar (N_{col}) phase is characterized by a columnar stacking of the molecules. However, these columns do not form two-dimen-

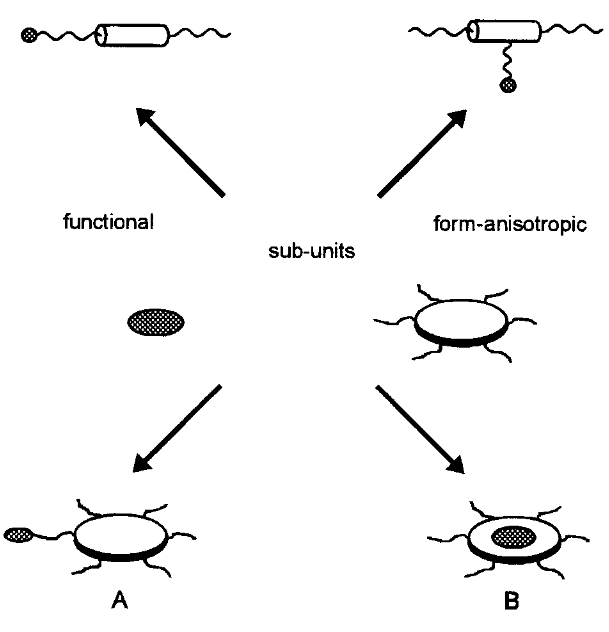

Fig. 1 Multifunctional supramolecular systems by intramolecular combination of anisometric and functional molecular sub-units

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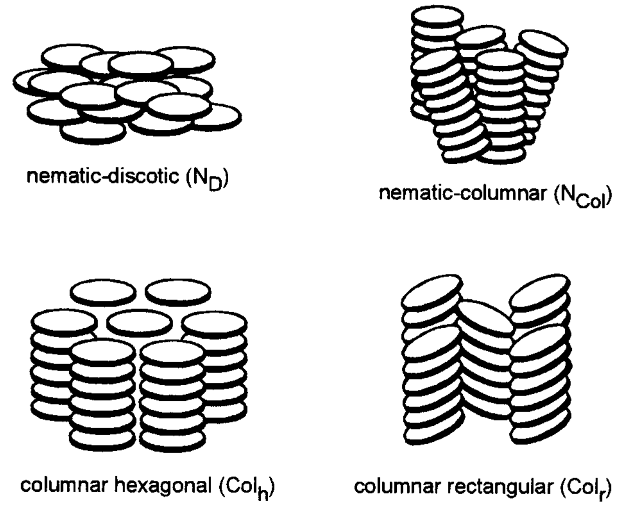


Fig. 2 Typical examples of thermotropic mesophases formed by low molar mass or polymeric sheet-like molecules

sional lattice structures. They display a positional short range order and an orientational long range order.[13]

A parallel alignment of the columns results in columnar phases with a two-dimensional lattice symmetry such as columnar hexagonal ($\mathrm{Col_h}$), oblique ($\mathrm{Col_{ob}}$; not shown in Fig. 2) and rectangular ($\mathrm{Col_r}$), the latter usually arising from a tilt of the average molecular plane against the column axis.

Furthermore, the molecules may be arranged in a regular ordered manner or, in the case of a liquid-like ordering, aperiodically (disordered) within each column. For example, disc-like mesogens based on the triphenylene core surrounded by six alkoxy substituents usually exhibit a hexagonal columnar ordered ($\mathrm{Col_{ho}}$) phase.[11,14]

Organic compounds containing electron donor units can be doped with acceptor molecules and it is well-established that disc-like electron-rich systems such as triphenylenes and multialkynes form charge-transfer complexes with rather flat but non-liquid crystalline electron acceptors like 2,4,7-trinitrofluoren-9-one (TNF).[15] Donor–acceptor interaction may lead to manipulations as well as the induction of columnar mesophases. The columns are then formed by mixed stacks of the flat donor molecules and the electron acceptor.

Charge-transfer (CT) interaction of hexagonal columnar phase-forming hexaalkoxytriphenylenes with TNF results in a stabilization of the already existing mesophase.[15b,c] Even using non-mesogenic triphenylene derivatives, doping with TNF gives rise to the induction of hexagonal columnar phases.[15b]

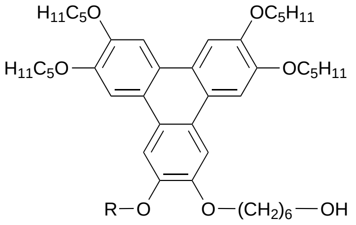
Nematic discotic hexaalkynylbenzene compounds were found to exhibit CT-induced $\mathrm{Col_{ho}}$ liquid crystalline structures[15b] whereas binary mixtures of non-liquid crystalline pentakis(phenylethynyl)benzene ethers and an electron acceptor were found to form nematic-columnar ($\mathrm{N_{col}}$) as well as ordered hexagonal columnar ($\mathrm{Col_{ho}}$) structures due to the donor–acceptor interactions.[13,16]

Considering the donor function as part of the rigid central molecular cores that, apart from the thermal properties of the pure compounds, give rise to control of structure formation through intermolecular CT interactions it follows that radial multiynes and triphenylenes are representatives of functional sheet-like mesogens of the general structure type B (Fig. 1).

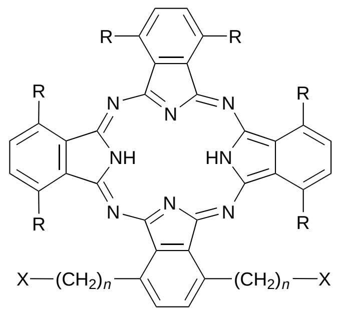
Low molar mass sheet-like molecules bearing peripheral polar substituents

Studies on the spreading behaviour of disc-like liquid crystals have shown that aromatic core systems fitted with a specific number of equal long aliphatic chains, such as benzene-hexa-*n*-alkanoates or hexaalkoxy(acyloxy)triphenylene derivatives, form monolayers at the air–water interface with only a low compressibility.[17] It is therefore obvious that those compounds lack distinct amphiphilic properties. A powerful tool towards sheet-like molecules with more pronounced hydrophilic and hydrophobic regions consists of the asymmetrical incorporation of one or two terminal polar substituents at the periphery of an extended core *via* flexible spacers. In this way it might be possible to combine liquid crystalline behaviour and amphiphilic self-organization within one molecule.[18]

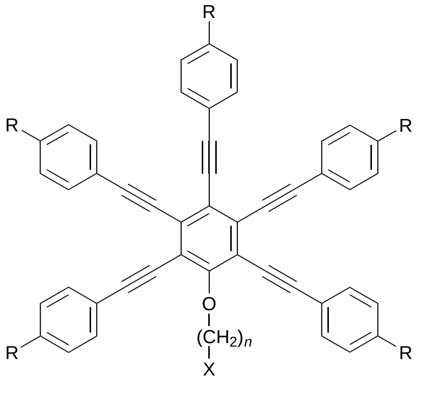
Members of three families of flat molecules **1a**,**b**, **2a–e** and **3a–d** are consistent with the general structure type of amphiphilic sheet-shaped compounds given schematically in Fig. 3.



1a $R = C_5H_{11}$
b $R = (CH_2)_6OH$



2a $R = C_8H_{17}$ $X = CO_2H$ $n = 3$
b $R = C_{10}H_{21}$ $X = CO_2H$ $n = 3$
c $R = C_8H_{17}$ $X = OH$ $n = 6$
d $R = C_6H_{13}$ $X = OH$ $n = 4$
e $R = C_{10}H_{21}$ $X = OH$ $n = 4$



3a $R = C_5H_{11}$ $X = CO_2H$ $n = 10$
b $R = C_5H_{11}$ $X = OH$ $n = 11$
c $R = H$ $X = CO_2H$ $n = 10$
d $R = H$ $X = OH$ $n = 11$

Whereas the triphenylene **1a** exhibits a hexagonal columnar ordered ($\mathrm{Col_{ho}}$) phase the two-fold hydroxy terminated compound **1b** forms a monotropic lamellar LC phase with a well defined double-layer packing of associated pairs of discs (arising from partial overlapping of the OH-containing tails) and a local columnar intralayer ordering.[19] Doping of **1b** with

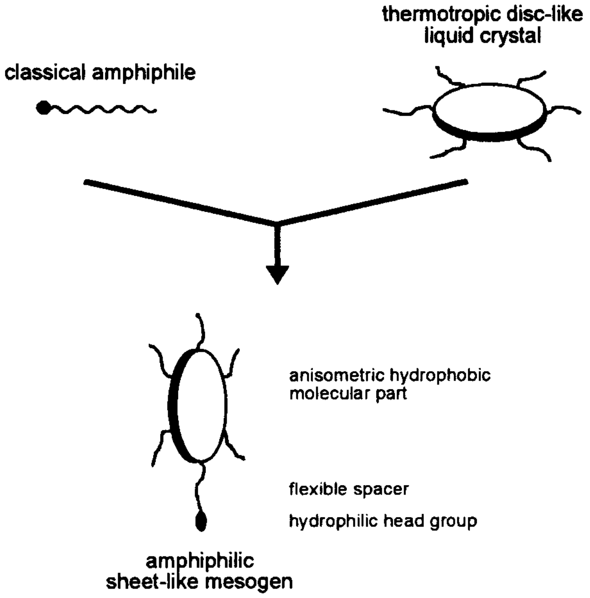


Fig. 3 Peripheral attachment of a hydrophilic functional sub-unit to a rigid sheet-like molecular part

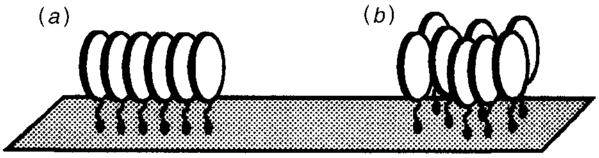


Fig. 4 Schematical presentation of the molecular edge-on orientation of sheet-shaped amphiphiles bearing terminal polar head groups with (*a*) columnar ordering parallel to the surface and (*b*) two-dimensional nematic-discotic (N_D) like arrangement. Lateral flexible side groups are not shown, only one hydrophilic function per molecule is presented.

TNF leads to an enantiotropic charge-transfer-induced hexagonal columnar ordered (Col_{ho}) phase.[20]

Unlike the phthalocyanine dicarboxylic acids **2a,b,** especially designed as materials for Langmuir–Blodgett (LB) film fabrication,[21] the two-fold hydroxy substituted compound **2c** exhibits an enantiotropic columnar phase with a two-dimensional hexagonal lattice symmetry as bulk material[22] whereas the phthalocyanines **2d,e** form monotropic columnar phases.[23]

The pentaalkynylbenzene derivatives **3a,b** bearing five lateral pentyl substituents form a nematic-discotic (N_D) mesophase on both heating and cooling; the appropriate laterally unsubstituted compounds **3c,d** are only crystalline materials.[24] Charge-transfer interaction of the five-fold pentyl-modified pentaynes **1a,b** with TNF results in the induction of hexagonal columnar ordered (Col_{ho}) mesophases whereas the lateral unsubstituted penaalkynes **3c,d** form a CT-induced nematic columnar (N_{Col}) phase in mixtures with TNF.[24] This behaviour agrees well with the thermal properties of radial hexaalkynylbenzene derivatives and pentakis(arylethynyl)phenyl ethers without a terminal polar functionality.[12,13,16] It indicates that it is not the incorporated polar function but the lateral substitution pattern that determines the liquid crystalline structure formation of the pentaynes **3a–d**.

All sheet-like systems **1–3** functionalized by one or two polar terminal groups form monolayers on a pure water subphase.[21–23,25,26] It is a common feature that, independent of the different chemical structures of the flat, sheet-like cores, the average areas per molecule in the compressed monolayers of the compounds **1–3** are less than the area requirement for the central molecular parts lying flat on the water surface. However, the collapse areas agree quite well with an edge-on arrangement[27] of the compounds **1–3** with a molecular orientation of the plane of the rings more or less perpendicular to the water (Fig. 4).

The peripheral attachment of just one or two hydroxy groups to the triphenylene core (compounds **1a,b**) leads to monolayers with higher collapse pressures compared to those of symmetrically substituted members such as hexapentyloxytriphenylene.[25]

The behaviour of the hydroxy substituted phthalocyanines **2c–e** at the air–water interface is very similar to the structurally related two-fold carboxy terminated compounds **2a,b**. During compression a sharp increase in the surface pressure–area isotherms is observed indicating a transition from the two-dimensional gas phase into the compressed state.[21–23] In contrast to oligomers derived from **2c**[22] the surface pressure–area isotherms of **2a–e** show only a small hysteresis during expansion of the monolayers.

In the case of sheet-like multialkynylbenzene compounds only the incorporation of terminal hydrophilic substituents (compounds **3**) gives rise to amphiphilic properties. Only three-dimensional crystallization was described for the radial symmetrical hexakis[(4-hexyl-phenyl)ethynyl]benzene at the air–water interface.[27] The π–A isotherms of the hydroxy or carboxy terminated pentaynes **3a–d** show no phase transition during compression but a direct transition to a solid condensed form.[26] Attributed to the presence of only one hydrophilic terminal substituent, the collapse pressure of the pentaynes **3**, however, is relatively low on a pure water subphase.[26] The monolayer stability can be enhanced significantly either by incorporation of a second polar head group as demonstrated for tetraalkynylbenzene derivatives with two neighbouring hydrophilic functions attached to the *ortho* positions of the central benzene ring *via* flexible spacers[28] or by supplementary interactions of the hydrophilic head groups with counterions dissolved in the subphase.[29]

The two-dimensional monolayer assemblies of the edge-on oriented sheet-shaped amphiphiles **1–3** can vary from a columnar stacking parallel to the surface[25,27] to a nematic–discotic (N_D) like arrangement;[28] the latter was proved for compounds **3**. The monolayer arrangements presented schematically in Fig. 4, which are quite different from those of classical amphiphiles, may not only arise from decreasing the available area per molecule during the compression process but also arise from a spontaneous aggregation of the edge-on oriented molecules immediately after spreading resulting in condensed monolayer islands which are pushed together during compression.[28,30]

Successful attempts to prepare LB multilayers have been reported for members of all three series of non-classical amphiphiles **1–3** (triphenylenes **1**,[19,20,31] phthalocyanines **2**,[21–23,33] pentaynes **3**[26,29,32]).

It is common for all amphiphiles **1–3** that dipping of a hydrophobic substrate through the compressed monolayer results in transfer of a monolayer each time the substrate passes the surface boundary. During first immersion the first monolayer is transferred so that the hydrophobic rigid cores face the substrate surface. A second monomolecular layer with the disc-shaped cores in the opposite direction is formed on top of the first monolayer during withdrawal of the substrate [Fig. 5(*a*)]. The edge-on orientation of the amphiphiles at the air–water interface is preserved during the formation of the LB films. This Y-type deposition gives rise to a bilayer packing of the molecules perpendicular to the substrate (head-to-head and tail-to-tail arrangement of molecular monolayers).

Further structural characteristics of LB films made from compounds of the series **1–3** other than those mentioned above are not uniform. For example, the mesomorphic double-layer structure of the two-fold hydroxy terminated triphenylene **1b** is preserved during the formation of the LB multilayers with a columnar ordering parallel to the solid support and the

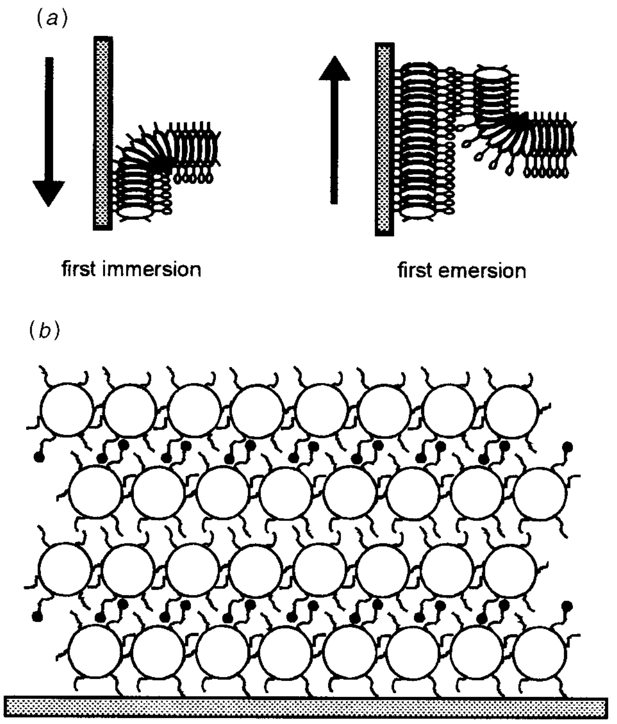


Fig. 5 Langmuir–Blodgett (LB) multilayers of sheet-shaped molecules asymmetrically incorporating hydrophilic substituents. (*a*) Fabrication of the LB films; (*b*) schematic presentation of the two-dimensional structure for the single component LB film derived from the amphiphilic pentayne **3b** (refs. 26,29).

periodicity of the rectangular lattice relative to the normal determined by the distance between next nearest pairs of edge-on oriented molecules.[19] The bilayer spacings observed for the LB films of the phthalocyanines **2a,b** are less than the calculated molecular dimensions that might be explained by a tilt of the planes of the molecules from the normal or by an interdigitation of chains in adjacent layers.[21] The pentaynes **1a,b** form Y-type bilayers with edge-on orientation of the discs. The main molecular axis of the molecules is tilted against the normal of the surface. The flexible molecular segments of neighbouring molecules are interdigitated[26,29] (Fig. 5). A hexagonal layer packing perpendicular to the surface proved to be possible in the LB films of the laterally unsubstituted pentaalkynyl carboxylic acid **3c** without lateral substituents.[26,30]

Fig. 6 illustrates the richness of supramolecular assemblies of functionalized disc-like mesogens such as **1–3** arising from the combination of a hydrophilic sub-unit with a flat hydrophobic anisometric core, the latter offering the opportunity to be combined with an additional donor function.

Functional polymers bearing disc-shaped side groups

Compared with calamitic polymers, the variety of polymers incorporating disc-shaped units, predominantly based on the triphenylene core, is rather limited. Triphenylene main chain polymers are usually either non-mesomorphic or exhibit hexagonal columnar ($\mathrm{Col_{ho}}$) phases.[34] Attaching triphenylene groups to polysiloxane, polyacrylate, polymethacrylate or polyester backbones, respectively, gives rise to triphenylene side chain polymers which, depending on the chemical nature of the main chain and/or the spacer length, were found to be amorphous or to form columnar mesophases with either hexagonal or rectangular lattices.[35] Doping of non-mesogenic triphenylene polymers induces either nematic-columnar ($\mathrm{N_{col}}$; side chain polymers) or hexagonal columnar ordered ($\mathrm{Col_{ho}}$; main chain polymers) mesophases.[36] Apart from investigations on thermal properties a few examples of polymeric triphenylene derivatives have been described capable of forming highly ordered LB multilayers.[19,20,31]

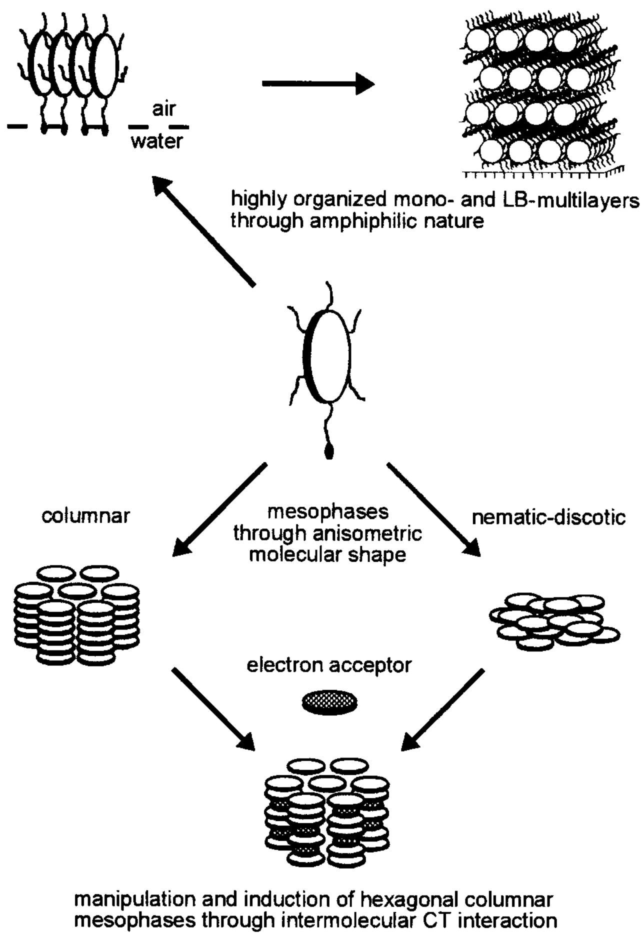


Fig. 6 Modes of structure formation of functional sheet-shaped mesogens as an outcome of amphiphilic properties, anisometric molecular shape and intermolecular donor–acceptor interactions

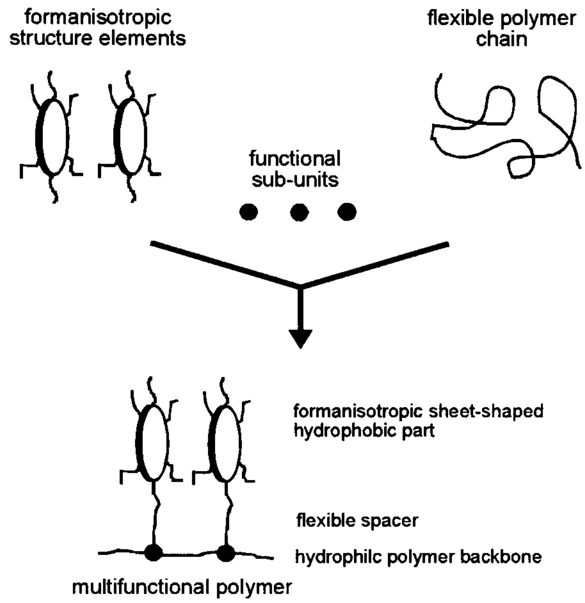
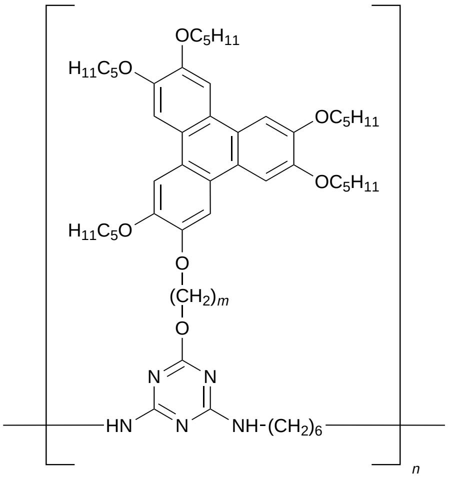


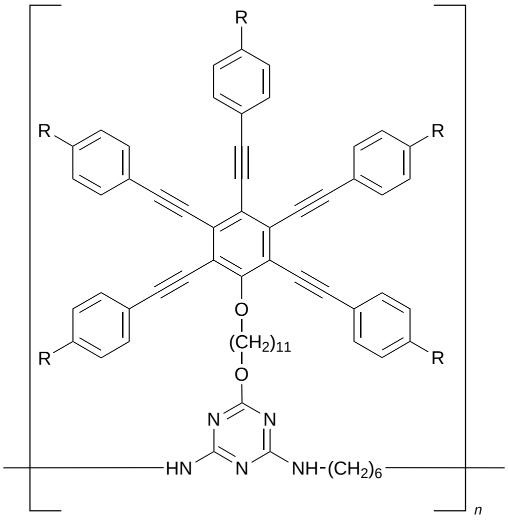
Fig. 7 Molecular architecture of functional polymers attached with sheet-shaped side groups

An effective approach towards controlling supramolecular structures at interfaces as well as in the mesomorphic bulk state involves the attachment of sheet-like sub-units to a functional hydrophilic backbone having the tendency to form associated structures *via* complementary hydrogen bonding. This requires the combination of anisometric structural elements with a flexible polymer chain and with an additional functional sub-unit.

This concept outlined schematically in Fig. 7 was realized recently by the synthesis of oligomers characterized by the attachment of either triphenylene (**4a,b**) or pentaalkyne (**5a,b**) side groups to amino substituted 1,3,5-triazine moieties in the backbone.[37]



4a $m = 11$
b $m = 6$



5a R = C_5H_{11}
b R = H

All oligomers **4** and **5** form stable monolayers when spread on the water surface.[37] The collapse areas of the triphenylene oligomers **4** and of the oligomeric pentaynes **5** are close to those of the respective hydroxy- or carboxy-terminated monomers **1** and **3**. This indicates an edge-on orientation of the hydrophobic triphenylene or pentaalkyne side groups for each triazine oligomer **4** and **5** while the amino substituted triazine rings serve as anchor groups at the water surface.

The amphiphilic triphenylene **4a**, furthermore, has been reported to form LB films with a bilayer packing of edge-on oriented triphenylene groups (Y-type deposition) and with interdigitation of the flat cores.[38] The structural model given in Fig. 8 displays columnar in-plane packing where alternate triphenylene group belongs to a different backbone and the orientations of adjacent disc-shaped groups are alternating. This type of columnar structure is caused by spacial restrictions imposed by exceeding the distance between chemical attachments of the neighbouring sheet-like cores along the backbone.

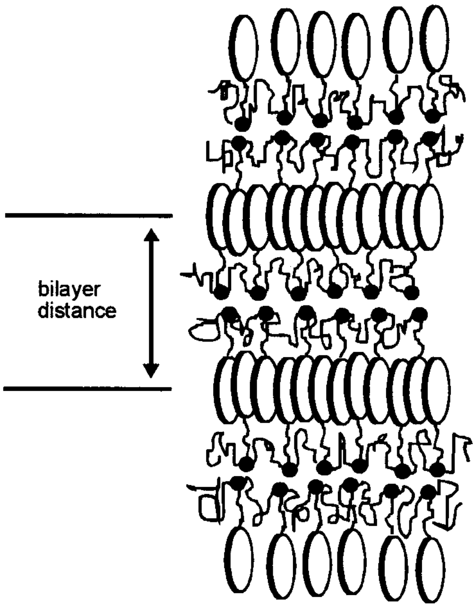


Fig. 8 Model for molecular bilayer arrangement of the triphenylene oligomers **4** in LB multilayers and in the mesomorphic bulk state; flexible lateral alkyl chains are not shown

These restrictions disturb closest face-to-face intracolumnar packing and favour the interdigitation of triphenylene groups belonging to different backbones.[38b]

With the exception of the laterally unsubstituted pentayne **5b** the triazine oligomers exhibit an enantiotropic mesophase in the bulk. The structure displayed by the oligomers with disc-like side groups corresponds to a smectic A like arrangement, which is highly surprising.[37] The magnitude of the layer dimensions indicates that no single-layer arrangement takes place but rather a double-layer one (Fig. 8). The double-layer structure is stabilized by the formation of hydrogen bonds between the aminotriazine segments of the polymer backbone. It is thus apparent that the interactions between the backbone segments frustrate the structure preferred by the disc-like units.

The molecular dimensions of the LB films and the double-layer spacing within the mesomorphic bulk state of the triphenylene oligomer **4a** are very close. This implies that the layer structure in the bulk LC state is preserved during the formation of the LB films on the solid substrate although the two mechanisms of structure formation are quite different.[38a]

Doping of the triphenylene oligomer **4b** with the acceptor TNF results in the induction of a rectangular columnar (Col_{rd}) mesophase. No such strong effect was found for the doped compound **4a** characterized by the longer spacer. The mesogenic organization of mixtures from **4a** and TNF remains a lamellar layer structure. Thus, the mesophase arrangements of the donor–acceptor complexes are a function of the spacer connecting the triphenylene side groups with the main chain.[37] However, the rectangular lattice spacings (**4b**/TNF) as well as the double-layer dimensions (**4a**/TNF) indicate that the structure formation of the binary mixtures result from both, intermolecular charge-transfer interactions and intermolecular hydrogen bonding.

It follows that the structures displayed by the functional triazine based oligomers **4** and **5** are the result of a delicate balance of interactions which may compete with each other (Fig. 9).

Covalently linked donor–acceptor twin mesogens based on flat electron-rich donor sub-units

Charge-transfer interactions of two individual molecules each incorporating either a donor or an acceptor function, in the

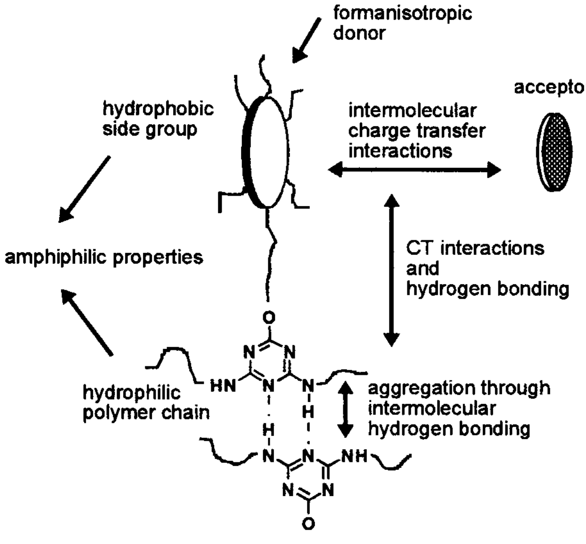
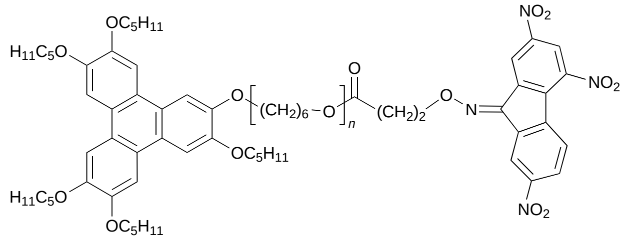


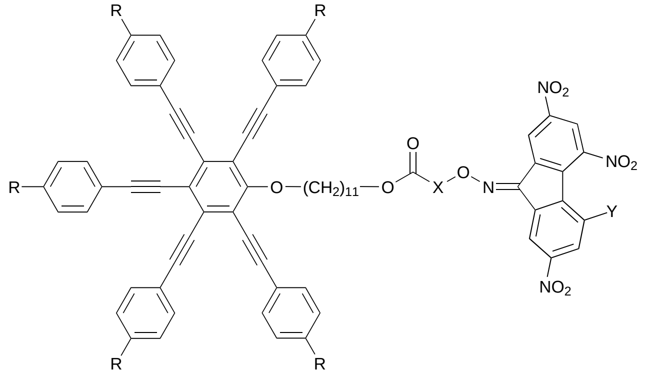
Fig. 9 Interplay of different driving forces to control the structure formation of the 1,3,5-triazine based triphenylene and pentaalkyne oligomers **4** and **5**

case of sheet-shaped triphenylene ethers or radial multialkynylbenzene derivatives as the donor molecules, give rise to a manipulation or an induction of columnar mesophases. The columnar phases, then, are usually of the hexagonal or nematic-columnar type.

However, the components need not necessarily be derived from separated molecules but from mesogens which incorporate both donor and acceptor functions into a single molecule. Such an approach consists of a chemical linkage of a flat anisometric phase forming moiety with an acceptor functional sub-unit *via* a flexible spacer. This concept has been realized by coupling of electron-rich triphenylene (**6**) or pentayne (**7**,**8**) units and electron-poor trinitrofluorenones (Fig. 10).



6a $n=0$
b $n=1$



7a–c X = $(CH_2)_2$ Y = H R = H (**7a**), R = CH_3 (**7b**) R = C_5H_{11} (**7c**)
8a–c X = C^*HCH_3 Y = NO_2 R = H (**8a**), R = CH_3 (**8b**) R = C_5H_{11} (**8c**)

The triphenylene based CT-twin molecules **6** are characterized by connecting the donor and acceptor moieties *via* spacers of different length.[39] Keeping the spacer length constant, structural modifications were performed at the lateral sphere of the pentayne units of compounds **7** in order to influence the magnitude of the molecules and thus the efficiency of expected intermolecular charge transfer interactions.[40] The twin molecules **8** incorporate an asymmetric carbon as an additional intramolecular functionality.[41]

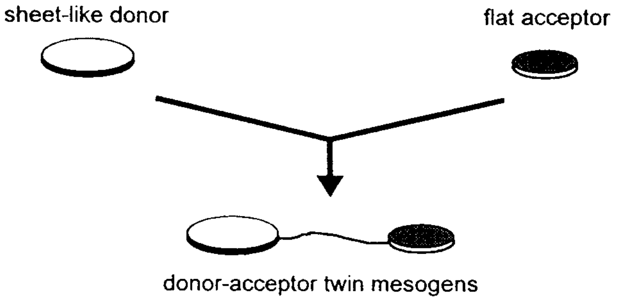


Fig. 10 Covalently linked charge transfer twin mesogens based on flat donor and acceptor sub-units

The mesophase structure of the triphenylene based CT-twin compounds **6** is characterized by an arrangement of the molecules in columns in such a way that mixed stacks occur. Each column is connected in one direction with two neighbouring columns chemically *via* the flexible spacers. The intercolumnar packing has been described as possessing an orthorhombic symmetry with $a \neq b$ (for compound **6a**) or in case of compound **6b** as displaying either an orthorhombic lattice with tilted planes of the discs or as a hexagonal two-dimensional structure.[39]

The donor–acceptor molecules **7** based on sheet-like pentaalkynes exhibit a rectangular columnar phase with $a=b$ and with a high intracolumnar periodicity resulting from closely face-to-face arranged alternating donor and acceptor moieties of the molecules.[41] Whereas the molecules in the columns are connected through charge-transfer interactions, the chemical linkage of the donor and acceptor sub-units facilitates the intercolumnar packing. These special features give rise to a three-dimensional order, at least in the case of compound **7a**[41] (Fig. 11).

Thus, it is not the chemical nature of the donor molecular moieties but the linkage with an intramolecular acceptor functionality that dominates the structure formation of the charge-transfer twin mesogens **6** and **7**, *e.g.* the formation of rectangular symmetries of intercolumnar packing instead of common hexagonal or nematic-columnar.

A further approach towards control of mesomorphic structures of sheet-shaped CT-twin mesogens arises from chirality as an additional intramolecular function. Preliminary structure investigations give rise to the conclusion that the twin compounds **8** incorporating an asymmetric carbon exhibit a nematic-columnar mesophase with a helical twisting of the columns.[41,42]

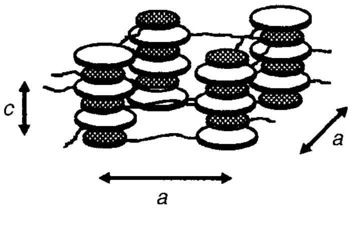
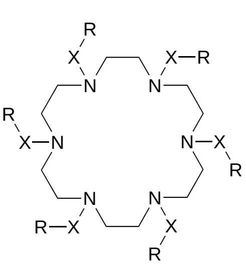


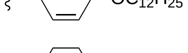
Fig. 11 Structure model of the rectangular columnar mesophase of the pentayne based donor–acceptor twin mesogens **7**

Functional heterocyclic azacoronands and 1,3,5-triazines

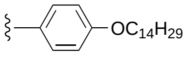
Suitably substituted *N*-acylated macrocyclic oligoamides, *e.g.* **9**–**12**, differing in the heterocyclic ring size as well as in the number of nitrogen atoms incorporated into the saturated central cores have been found to exhibit thermotropic hexagonal columnar mesophases.[43] The central cavity in the columns led to these phases being described as tubular.[43a]



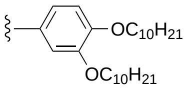
9 X = CO; R =

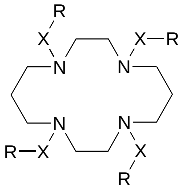


10 X = CO; R =

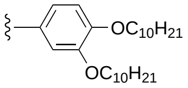


11 X = CO; R =





12 X = CO; R =



In contrast to macrocyclic amides such as compounds **9**–**12** alkyl-substituted azacrowns show no mesophase behaviour due to an increased conformational flexibility of the ring system. However, complexation of transition metal salts by highly flexible benzyl substituted cyclic amines bearing a certain number of peripheral long alkoxy chains (for example, **10** and **12**; X = CH_2 instead X = CO) gives rise to the induction of columnar liquid crystalline phases.[44] Coordination to the metal ions (*e.g.* Cu^{2+}, Ni^{2+} or Co^{3+}) imposes the desired conformational rigidity of the functional central macrocyclic rings. In this way, the sheet-like molecular geometry of azacrowns and the complex formation properties of macrocyclic ligands, leading to specific host–guest systems, can be combined.[44a]

The polar central core of cyclic azacoronands fitted with long lipophilic hydrocarbon chains gives rise to azamacrocycles with distinct amphiphilic properties. Beside the benzoyl substituted compounds **9** and **10** certain acylated[43b,45] and alkylated[46] hexacyclene and cyclam derivatives have been shown to form stable monolayers at the air–water interface. The arrangement of either amine or amide derivatized azacrowns, in general, is the same at the interface.[46] Within the monolayer the molecules adopt an orientation in which the hydrophilic macrocycle lies flat on the water surface (side-on arrangement). In the condensed state the hydrophobic alkyl chains are oriented more or less perpendicular to the interface in a close-packed all-*trans* conformation (Fig. 12).

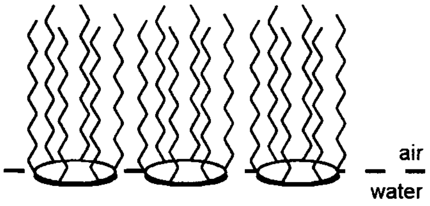


Fig. 12 Schematic presentation of the side-on arrangement of sheet-like amphiphiles with a polar central core surrounded by a certain number of hydrophobic alkyl chains

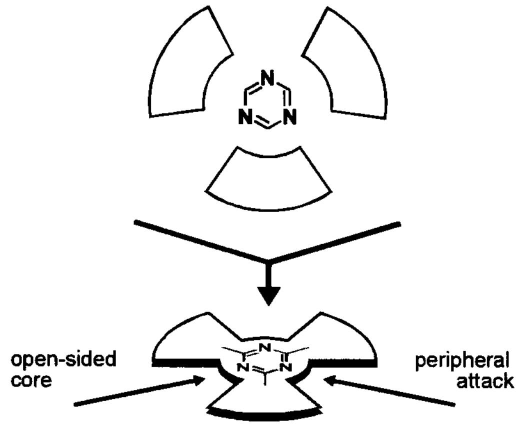
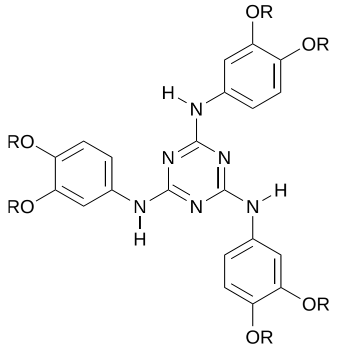


Fig. 13 1,3,5-Triazines as central parts of functional sheet-shaped molecules with open-sided cores

Combining a flat anisometric molecular shape with an intramolecular functionality located in the central core region in the case of 'closed' aromatic core systems (triphenylene ethers, radial multiynes) as well as in the case of 'hollow' core systems (azacrowns) gives rise to manipulations of as well as the induction of columnar mesophases due to specific intermolecular interactions (charge-transfer complex formation, metal complex formation). However, these functionalities do not allow side-by-side interactions with a complementary component.

Such an approach may consist of 'open-sided' core systems having the capacity to form columnar mesophases as single components but also enabling control of structure formation by a peripheral attack of a second component to the inner (functional) core region (Fig. 13).



13a R = $C_{10}H_{21}$
b R = $C_{12}H_{25}$
c R = $C_{16}H_{33}$

Following this concept, recently the 2,4,6-triarylamino-1,3,5-triazines **13** have been prepared bearing six long peripheral alkoxy chains.

The melamines **13** form enantiotropic columnar mesophases although they are characterized by a lack of inherent molecular planarity.[47] In the case of the heterocyclic mesogens **13a,b** the columns are arranged in a hexagonal array with an aperiodic intracolumnar stacking of the molecules (Col_{hd}). Further elongation of the lateral alkyl chain length results in a major structural change. Compound **13c** exhibits the rarely observed ordered rectangular columnar (Col_{ro}) phase.

The mesomorphic triarylmelamines are characterized by a heterocyclic 1,3,5-triazine core with a three-fold substitution with secondary amino groups promoting attractive interactions with complementary functional molecules *via* intermolecular hydrogen bonding (side-by-side attack).

Binary mixtures of the melamine **13a** with non-mesogenic 3,5-dialkoxy substituted benzoic acids exhibit a hexagonal columnar disordered (Col_{hd}) phase at least at an equimolar ratio of the components. The intercolumnar distances are a function of the length of the alkoxy groups of the acid component.[48] A 3,4-dialkoxy substitution pattern of the benzoic acid gives rise to a change of the columnar mesophase structure of the melamine **13a** from a hexagonal to a rectangular lattice (Col_{rd}) in binary mixtures with the aromatic acids.[48] Equimolar mixtures of the melamines **13** and 4-alkoxybenzoic acids exhibit a hexagonal columnar disordered (Col_{hd}) structure.[49] In the case of the melamine **13a** the hexagonal lattice constants increase with increasing number of methylene groups of the *para*-alkoxy substituted benzoic acid component.[49] The appearance of a calamitic phase characteristic of 4-alkoxybenzoic acids in their pure state, due to a dimerization of the acids, is not observed. Hence, associations with the aminotriazines **13** completely frustrate the tendency of the aromatic acids to form dimers.

Furthermore, the triarylmelamines **13** are characterized by a polar central heterocyclic core and long non-polar alkoxy side chains. Amphiphilic properties arise from this combination of different structure elements and the triazines **13** form monolayers on the water surface. Similarly, as found for amphiphilic azamacrocycles a molecular side-on arrangement is observed with the amino modified triazine ring as the most hydrophilic molecular part lying flat[47] (Fig. 12).

Thus, azamacrocycles and 1,3,5-triazines bearing long aliphatic side chains are two classes of sheet-like molecules possessing both mesomorphic and amphiphilic behaviour. Furthermore functional units embedded in the central cores, in certain cases, give rise to an induction of mesomorphic properties by metal complexation of azacoronands whereas molecular recognition due to intermolecular hydrogen bonding allows control of the hexagonal lattice constants as well as variation of the two-dimensional lattice type of the columnar-phase-forming triarylmelamines (Fig. 14).

Outlook

The few examples discussed here may show that it is possible to combine molecular sub-units of a flat sheet-like anisometric shape with an additional intramolecular functionality in various ways. Functional disc-like systems can result that combine structure forming tendencies due to amphiphilic properties and those arising from an anisometric molecular geometry within one molecule. The intramolecular function, furthermore, may allow control of and/or induction of supramolecular (columnar) structures by non-covalent interactions with complementary components. However, those intramolecular functionalities presented here usually do not facilitate reversible control of a supramolecular assembly once obtained either in single component or mixed multicomponent systems. They might therefore be considered as functions of the first generation.

Reversible control of columnar structures, such as generation, manipulation and destruction, might be possible by combining a disc-shaped molecular part, probably already incorporating a function of the first generation, with an additional reversibly switchable sub-unit (function of the second generation).

Compounds **14** are the first representatives of CT-triple molecules consisting of a sheet-like pentayne donor and a TNF based acceptor which are covalently linked *via* a rod-like sub-unit incorporating an azobenzene moiety (Fig. 15). The compounds exhibit a nematic mesophase at elevated temperatures and form a glassy state at room temperature.[41] It seems possible to combine here the structure formation of disc-like donor–acceptor twin mesogens with the ability of the azo group present in the spacer to be switched by light.

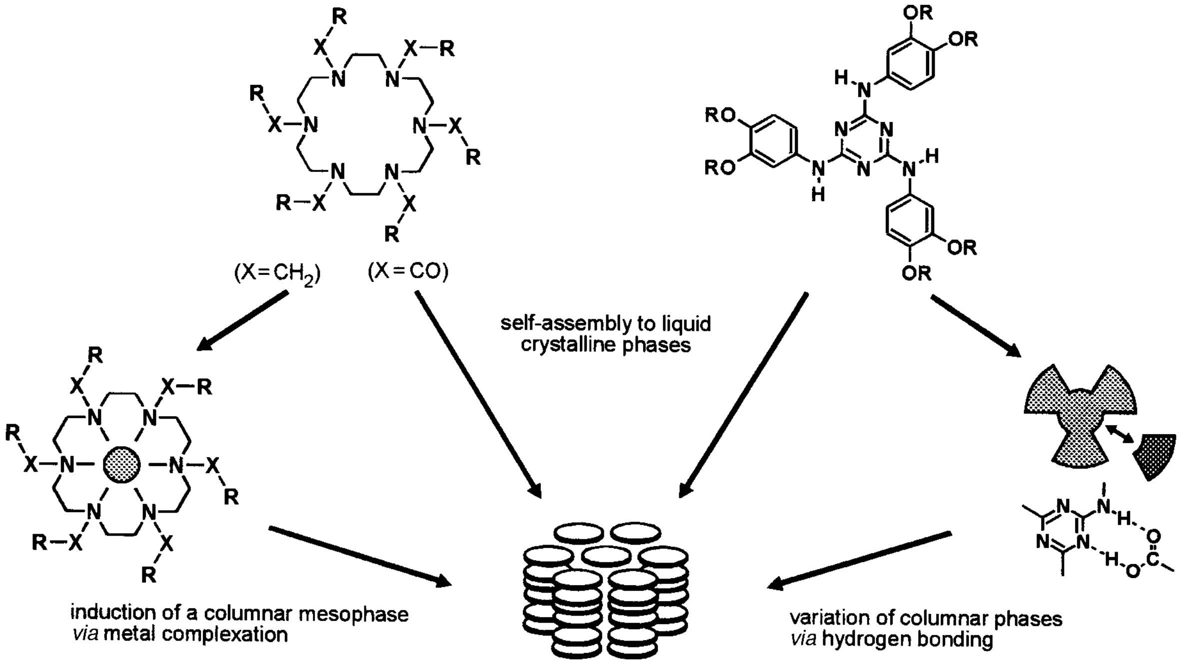
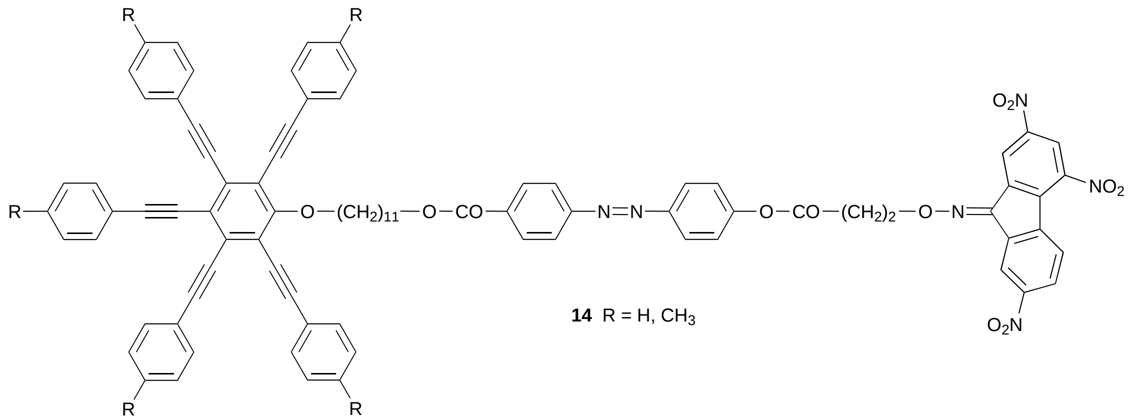


Fig. 14 Aspects of mesomorphic structure formation of functional azacrowns and triarylmelamines


14 R = H, CH$_3$

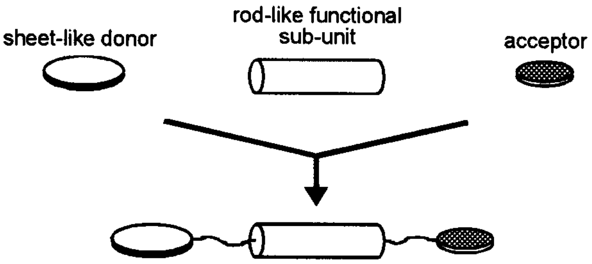


Fig. 15 Donor–acceptor triple mesogens incorporating an additional calamitic functional sub-unit

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