evaporated (Figure 2a). Atomic force microscopy (AFM) measurements showed that the majority of the sample consisted of a regular island structure of microcrystals, with an average size of about 10 nm, each containing approximately 2.5×10^3 catalyst molecules. From the island density of about 4×10^{10} islands per cm^2, a coverage of 10^{14} molecules per cm^2 was estimated; this was supported by X-ray photoelectron spectroscopy (XPS) results (10^{14} Pd atoms per cm^2). The microcrystal size implies that roughly 35 % of the catalyst molecules were located at the surface of the crystals.

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Induction of Lamellar Mesomorphic Structures in Columnar-Phase-Forming 1,3,5-Triazines through Charge-Transfer Interactions with Electron Acceptors**

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Claudia Schmidt, and Joachim H. Wendorff

The molecular organization in thermotropic liquid-crystalline phases is predominantly associated with a rigid anisometric architecture of the constituent single molecules. Molecular self-organization may, however, also be effected by strong intermolecular forces between nonmesogenic molecules to give noncovalently bonded anisometric aggregates. The two principles can be combined by incorporating an intramolecular functionality into molecules with an anisometric shape.[1] This combination allows the control and manipulation of the structure formed by mesogens through directed intermolecular interactions with a second complementary component. Specific manipulations of columnar mesomorphic structures, for example, may arise from formation of donor – acceptor complexes[2] or from intermolecular hydrogen bonding[3] between two different individual molecules.

"Open-sided" core systems that have the capacity to form columnar phases of single components and also allow the docking of a second component to a molecular recognition site located in the inner core region (side-by-side interactions) are conceivable. Structure formation should then be possible for the same molecule through associations with electron-deficient counterparts through charge-transfer (CT) interactions perpendicular to the molecular periphery (face-to-face interactions) provided that the central part of the molecule coincidentally represents an electron donor (Figure 1). To realize this concept we have synthesized 2,4,6-triarylamino-1,3,5-triazines with long peripheral alkoxy groups and with an electron-rich polar group in the center.[7] The triazines substituted with six lipophilic side chains exhibit columnar mesophases in their pure state.[8] Furthermore, hydrogen bonding with complementary alkoxy-substituted benzoic acids gives rise to the control of the two-dimensional lattice symmetries[1, 9] and even induction of a hexagonal columnar mesophase.[10]

We report here mesomorphic assemblies of the hexagonal columnar (Col_{hd}) phase from sixfold alkoxy-substituted 2,4,6-triarylamino-1,3,5-triazines **1a**, **b**,[8] which act as electron

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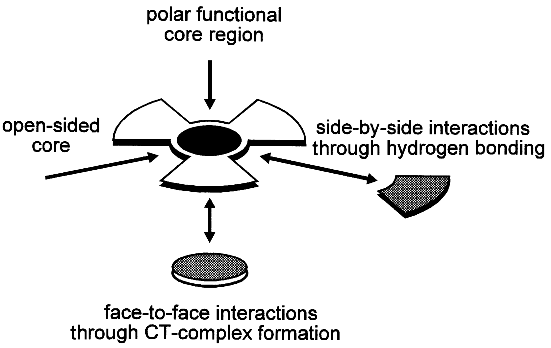
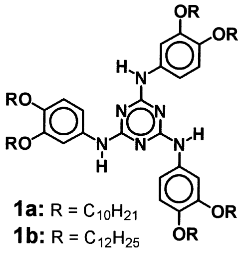
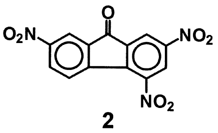


Figure 1. Aspects for controlling the structure formed by functional mesogens that are capable of forming columnar phases through noncovalent associations with complementary molecules by hydrogen bonding or through formation of a donor–acceptor complex.

donors, in mixtures with the nonliquid crystalline acceptors 2,4,7-trinitrofluoren-9-one (**2**) and 2,4,7-trinitrofluoren-9-ylidene malodinitrile (**3**).[11] Polarizing microscopy and differential scanning calorimetry (DSC) studies reveal that the mixtures of the melamines **1** with **2** or **3** exhibit an enantiotropic mesophase at a 1:1 molar ratio of the components (Table 1).



1a: R = $C_{10}H_{21}$
1b: R = $C_{12}H_{25}$



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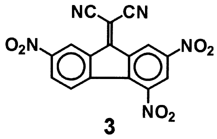

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Table 1. Phase-transition data [°C] for equimolar mixtures of **1** with the acceptors **2** and **3** as determined by DSC; second heating with 10 K min^{-1}, transition enthalpies [kJ mol^{-1}] in parentheses.[a]

1a/2	Cr	68.1 (21.19)	SmA	110.4 (1.91)	I
1b/2	Cr	68.6 (27.05)	SmA	115.0 (2.33)	I
1b/3	Cr	93.7 (17.72)	Col$_r$	147.2 (2.48)	I

[a] Cr: crystalline; SmA: smectic A; Col$_r$: rectangular columnar; I: isotropic.

X-ray investigations were performed to identify the types of mesophase structures displayed by the mixed systems **1/2** and **1/3** in more detail. The X-ray diagrams of the CT complexes derived from **1** and **2** show a set of reflections in the small-angle region and a diffuse scattering in the wide-angle region (Figure 2). These reflections can be indexed as (*h*00) with $h = 1-5$ (Table 2). No mixed reflections (*hkl*) were present. It is thus clear that a structure periodic in just one dimension, that is, a layer structure, exists. The layer spacings amount to 36.2 Å for **1a/2** and 41.5 Å for **1b/2**. The Bragg spacings are given in Table 2. The wide-angle halo indicates that no long-range order is present within the layers. The X-ray investigations, together with the fan-shaped textures observed by polarizing microscopy, point to a smectic A-type mesophase for both **1a/2** and **1b/2**.

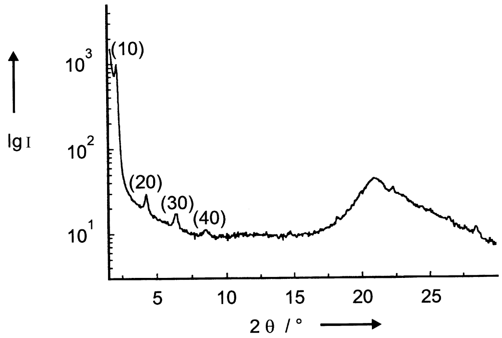

Figure 2. X-ray diffractogram of the 1:1 charge-transfer complex **1b/2**.

Table 2. X-ray data for the mesophases of the binary CT complexes **1/2** and **1/3**.

	Positions of reflections [Å]						Lattice constants [Å]	
Sample	d_{100}	d_{010}	d_{200}	d_{300}	d_{400}	d_{500}	*a*	*b*
1a/2	36.3	–	18.1	12.1	9.0	7.3	36.2	
1b/2	41.5	–	20.7	13.8	10.4	–	41.5	
1b/3	36.3	27.7	18.2	12.9	–	–	36.3	27.6

The X-ray diffraction pattern of the 1:1 mixture of **1b** and **3** differs from the scattering pattern observed for the donor–acceptor complexes **1/2** since not all the reflections can be assigned to a one-dimensional structure. This observation may be considered as an indication of the presence of at least a two-dimensional lattice. Only a diffuse halo, which is characteristic of fluid alkyl chains, is observed at larger scattering angles.

The three aryl substituents of compounds **1** are grafted on to the central 1,3,5-triazine nucleus through secondary amino groups. Since the phenyl rings can rotate around the C–N single bonds it is not only the flexible alkyl side chains but also the core region of the molecules that can adopt certain conformations, which results in a lack of inherent molecular planarity and no specific anisometric shape. Therefore, neither the hexagonal columnar mesophases formed by the triazines in their pure state nor the CT-induced lamellar phases can be explained in a conventional sense as resulting from a rigid disklike or rod-shaped molecular geometry.

The hexagonal lattice constants obtained from X-ray studies are 30.2 Å for compound **1a** and 32.8 Å for **1b**.[8] The values are somewhat smaller than the molecular diameter of radial, two-dimensional conformers of **1a**, **b** in the most extended form, as shown in Figure 3a. We therefore conclude that the columns of the hexagonal mesophases of just the melamines **1** are composed of the polar triphenylaminotriazine cores, which preferably exhibit flat, radial conformations with a two-dimensional random distribution of the flexible side chains. This arrangement gives rise to an optimum space

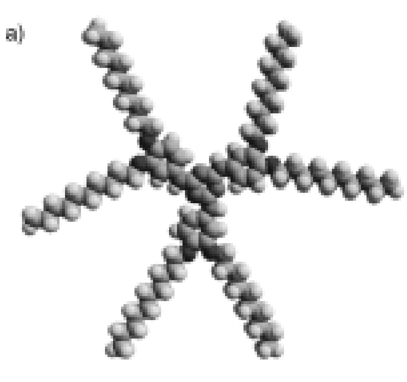

Figure 3. Two-dimensional conformers of the sixfold decyloxy-substituted triarylmelamine **1a** (Cerius 2; force field Dreiding 2). a) Radial conformation with all-*trans* alkoxy chains. b) Linear conformation with elongated chains.

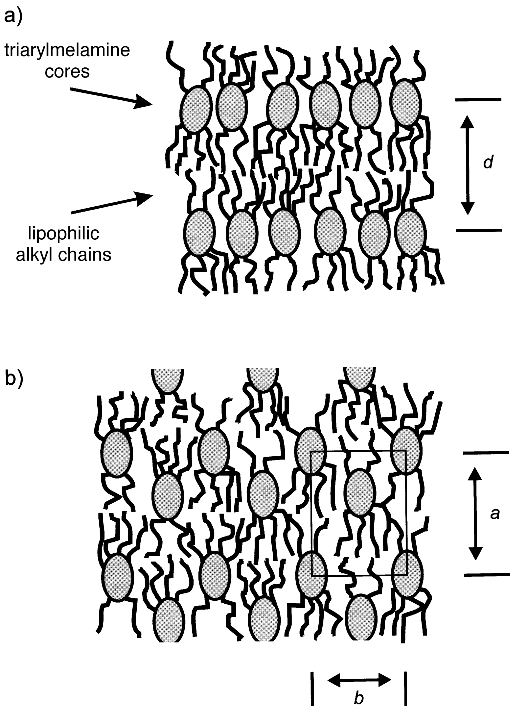

Figure 4. Schematic models for the liquid-crystalline phases of the melamines **1** in binary mixtures with the electron acceptors **2** and **3**. a) Lamellar smectic A-type mesophase for the CT complexes **1/2**. b) Rectangular columnar (Col$_r$) phase for the complex **1b/3**. The shaded ellipses symbolize the linear conformers of the polar triphenylaminotriazine cores (see Figure 3b).

filling in the outer sphere of the molecules. The main driving force for the liquid crystallinity of the triarylmelamines is thus a microsegregation[12] of the polar part from the nonpolar part in such a way that cylindrical aggregates are formed with the polar groups of the molecules located in the center surrounded by a shell of lipophilic chains.

By taking into account that an intercalated structure with close face-to-face contacts between the donor and the acceptor is strongly prefered we are forced to the conclusion that the induction of lamellar phases originates from a two-dimensional linear conformation of the triarylamino-1,3,5-triazines (**1**), which is imposed by the CT interactions with the acceptor molecules **2**. Figure 3b shows such a conformation with extended alkyl chains for the triazine **1a**. The molecular length for linear conformers of the triazines evaluated from molecular mechanics simulations are approximately 41 Å for compound **1a** and 46 Å for **1b**. These values are slightly larger than the layer spacings determined by X-ray studies for the lamellar phases of the binary mixtures with **2** (see Table 2). Thus, the alkyl chains separating the polar cores of neighboring layers seem to interdigitate to some extent. However, the spacings would also be quite reasonable for a noninterdigitated smectic A-type layer structure for the CT complexes **1/2** with a disordered packing of the flexible alkyl groups. A structural model for the lamellar mesophase of the donor–acceptor complexes **1/2** is given in Figure 4a.

The development of a structural model for the 1:1 mixture **1b/3** that displays at least a two-dimensional, regular structure meets with great difficulties since the number of reflections present is very low. By assuming the most simplest case, a rectangular columnar phase, we find that the value of the lattice parameter *a* is similar to the layer thickness in the CT-induced smectic A phases of the binary mixtures **1/2** (see Table 2). The lattice parameter *b* would correspond, in this case, to the lateral side-by-side distance per repeat unit and we would envision a very simple molecular arrangement, namely a columnar structure on a face-centered rectangular array. The problem is, however, that such a face-centered structure would lead to systematic extinctions, which are not observed. We either have to assume that the molecules are systematically shifted, for reasons unknown to us, from the face-centered position[13] as shown in Figure 4b or that a more complex arrangement is displayed. In fact, we cannot rule out the presence of an oblique lattice symmetry.[14]

The steric conformation of the polar core region of the triarylmelamines **1a**, **b** are, on average, the same for CT complexes with both **2** and **3**. Hence the Col$_r$ phase of **1b/3** can be regarded as resulting from a destruction of the CT-induced lamellar phase (Figure 3a), which arises simply by a slight change in the chemical nature of the electron acceptor. Furthermore, one can imagine the rectangular columnar phase of the CT complex **1b/3** to be an intermediate between the hexagonal columnar mesophases formed by the triarylmelamines in their pure state and the lamellar mesomorphic structures induced by donor–acceptor interactions with **2**.

In summary, the triazines **1** are the first examples of electron donors that form columnar phases which give rise to the induction of smectic liquid crystalline structures through donor–acceptor interactions. The formation of the pure triarylmelamine structures as well as of the CT complexes arises from the distinct seggregation of polar from nonpolar molecular regions along with certain specific anisometric conformations that become favored during the process of self-organization. The interplay between different driving forces for self-organization makes these materials attractive for further investigations regarding defined control of supramolecular structures through attractive interactions with complementary molecular species.

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[2] It is, for example, well known that electron-rich, disklike aromatic compounds such as radial multialkynylbenzene derivatives and triphenylene ethers form charge-transfer complexes with flat, nitrofluorenone-based electron acceptors. The CT interactions may cause the stabilization as well as the induction of columnar mesophases. The columnar phases formed by the binary mixtures are usually hexagonal (Col_h) or nematic columnar (N_{col}): H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff, R. Wüstefeld, *Adv. Mater.* **1990**, *2*, 141; M. Ebert, G. Frick, C. Baehr, J. H. Wendorff, R. Wüstefeld, H. Ringsdorf, *Liq. Cryst.* **1992**, *11*, 293; K. Praefcke, J. D. Holbrey, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1996**, *24*, 19.
[3] The association of 2,6-diacylaminopyridines with complementary uracil derivatives, for example, leads to the induction of columnar phases on either a hexagonal[4, 5] or a rectangular[6] two-dimensional array. Here, however, the two components are not mesomorphic by themselves.
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[11] The mixtures were prepared by combining solutions of the triazines **1** with either acceptor **2** or **3** in dichloromethane. Similar to triphenylene ethers, the dark brownish color that appears indicates complex formation through charge-transfer interactions. All thermal investigations were performed after evaporating the solvent, drying the residues in a vacuum, and annealing the samples in the isotropic state.
[12] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485.
[13] With respect to a rectangular columnar phase not with a face-centered but with an asymmetric position of the second molecule, see also G. Lattermann, S. Schmidt, R. Kleppinger, J. H. Wendorff, *Adv. Mater.* **1992**, *4*, 30.
[14] Suggestion by one of the referees.

Combinatorial Surface Chemistry—Is it Possible?[**]

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Combinatorial chemistry and biological-based approaches have emerged as powerful aids for the discovery of novel pharmaceutical agents and biomaterials.[1] Since its introduction in the early 1990s, combinatorial chemistry has revolutionized the medicinal chemistry area. The combinatorial technique, applied to discover novel materials and catalysts, is making significant progress in another research area.[2–4]

However, the basic essence of combinatorial chemistry has yet to be completely employed. Nature is the best combinatorial chemist, showing four deoxyribonucleotides and twenty amino acids underly the whole biological world through the combination of these small molecular species. Indeed, one may think a long polypeptide chain is a combination of different amino acids connected through amide bonds. The long polypeptide chains then fold into a three-dimensional protein structure through noncovalent bonds between the amino acid residues. As a result, the active site of a protein can be envisaged merely as a combination of amino acids in a three-dimensional space.

This fundamental feature of proteins suggests a very interesting clue for the creation of their mimics. Amphiphilic lipid molecules are a class of molecules well studied by surface chemists. At the two-dimensional air–water interface, the hydrophilic polar moiety embeds into the water phase and the hydrophobic alkyl chain orients towards the air phase. When compressed at the interface, the amphiphilic molecules will move and assemble into organized supramolecular structures, known as Langmuir monolayers. If the polar moieties are functionalized with different peptides, such as a peptide library, the self assembly of these functional lipids may form proteinlike supramolecular structures, as illustrated in Figure 1.

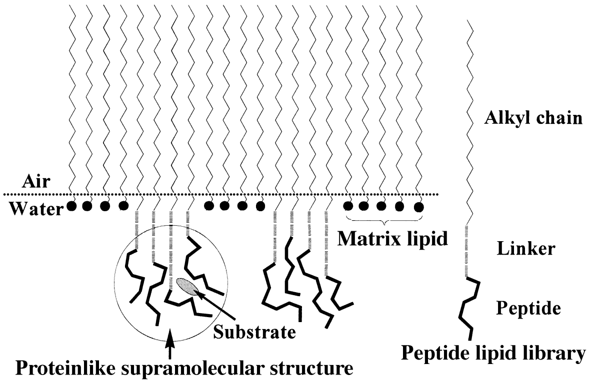

Figure 1. An illustration of the self assembly of peptide–lipid library components at the air–water interface to form proteinlike supramolecular structures.

Yu et al. recently reported that the self assembly of a peptide lipid led to the formation of a collagenlike structure at the air–water interface.[5] Kunitake has shown that two peptide lipids could combine together at the air–water interface to form a unique binding site for a specific peptide guest.[6] Furthermore, it was found that nonpeptide lipids could also combine together at the air–water interface to form receptors for different, small organic guest molecules.[7] These previous works strongly support the feasibility of the proposed two-dimensional combinatorial approach.

We now for the first time report our study of Langmuir monolayers made of peptide lipid libraries. Library **LIB** and three sublibraries **SUB1**, **SUB2**, and **SUB3** (Table 1) were synthesized through the solid-phase peptide synthesis techni-

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