

## A New Type of Square Columnar Liquid Crystalline Phases Formed by Facial Amphiphilic Triblock Molecules

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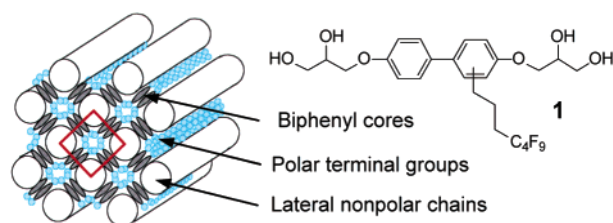
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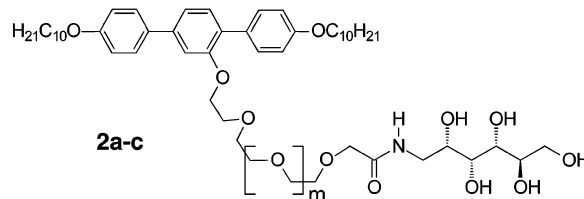
Supramolecular chemistry aims to develop highly complex chemical systems from simple components interacting via non-covalent intermolecular forces.<sup>1</sup> A prime objective is to understand the fundamental mechanism involved in this process, namely the transfer of information, imprinted in the molecular structure, to a well-defined supramolecular assembly.<sup>2,3</sup> Liquid crystalline phases are self-organized structures, formed spontaneously under thermodynamic control and therefore can be used as model systems for these investigations. Layerlike structures (smectic phases) and regular arrangements of columns (columnar phases) are two important basic organizational modes of such materials. Columnar liquid crystalline phases<sup>4</sup> are formed, for example, by surfactant-solvent systems, amphiphilic or dendritic molecules, block copolymers, and disklike molecules. Until recently, molecules mainly composed of only two different incompatible subunits have been investigated. In such systems the columns are formed by one of the incompatible molecular moieties, and these columns adopt a regular 2D packing within the continuum of the second component. In these rather simple systems the hexagonal 2D lattice is the most favored organization, but rectangular and oblique lattices have also been found, which can be regarded as slightly deformed variants of the hexagonal 2D organization. Square lattices (Col<sub>squ</sub>), on the other hand, are rare in these systems.<sup>5</sup>

Recently, a rather complex mesophase with a square lattice was reported for compounds **1**,<sup>6b</sup> composed of a rodlike rigid biphenyl core, two polar hydrogen bonding groups at the termini, and a semiperfluoroalkyl chain as a lateral substituent.<sup>6</sup> As shown in Figure 1, in this square columnar liquid crystalline phase, space is subdivided into three sets of distinct subspaces. The nonpolar lateral chains organize into infinite columns, and the bolaamphiphilic units form networks of square-shaped shells around these columns. The polar groups at the ends of the biphenyl cores segregate into separate columns, which lie parallel to the nonpolar columns. The hydrogen-bonding networks within these polar columns provide the necessary cohesive forces which interconnect the biphenyl cores end-to-end.<sup>6b</sup>

Herein we report a new complex liquid crystalline phase with a square lattice in which the positions of the polar and nonpolar columns are reversed, i.e. in which the polar column is located inside the square and the lipophilic columns containing alkyl chains are at the corners interconnecting the aromatic rods end-to-end. This structure was realized with compounds **2a–c** in which a rodlike *p*-terphenyl unit is connected with two lipophilic decyloxy end chains and a large polar group is attached to a lateral position at the *p*-terphenyl core. This polar group consists of a rather flexible



**Figure 1.** Square columnar mesophase formed by the triblock molecules **1** (the nonafluoroheptyl chain can be positioned in ortho or meta position).<sup>6b</sup>



oligo(oxyethylene) unit with a terminal carbohydrate unit, providing strong attractive intermolecular interactions via hydrogen bonding. The self-organization of these novel compounds was studied by polarized light microscopy, differential scanning calorimetry, and X-ray diffraction. The transition temperatures and lattice parameter of the mesophases are collated in Table 1.

All three compounds **2a–c** have a broad region of a liquid crystalline phase. On cooling from the isotropic liquid state these mesophases grow with spherulitic textures or as filament textures with black optically isotropic areas (see Figure 2a). The optically isotropic areas indicate that these mesophases are optically uniaxial. The diffraction pattern obtained from a well aligned sample of the mesophase of compound **2b** is shown in Figure 2b. It is characterized by a nearly circular diffuse wide-angle scattering with a maximum at  $D = 0.48$  nm which confirms the liquid crystalline nature of this phase. In the small-angle region there are several reflections which were indexed on a square lattice, plane group  $p4mm$ . The lattice parameter is  $a_{\text{squ}} = 4.0$  nm. The number of molecules in the unit cell, assuming a thickness of 0.48 nm (corresponding to  $D$ ), was calculated as  $n = 5.8$  on average.

These findings can be explained by the model shown in Figure 3. Accordingly, the calamitic cores form walls bounding square-shaped channels occupied by the microsegregated polar lateral chains. The thickness of the partitioning walls ( $n_{\text{wall}}$ ) amounts to approximately three terphenyl cores. This proposed model is in complete agreement with the reconstructed electron density map shown in Figure 4, which was obtained from the small-angle diffraction intensities, measured from the high-resolution powder pattern (synchrotron source). The intensities and a description of the electron density reconstruction procedure are given in the SI.

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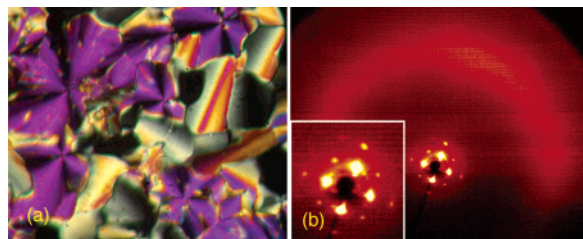
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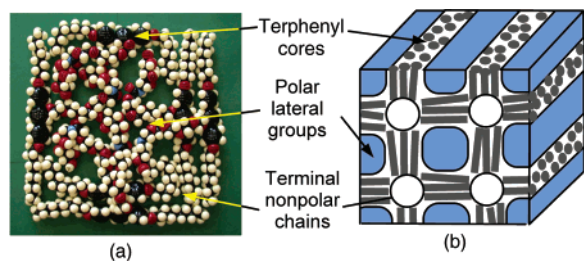
**Table 1.** Properties of Compounds **2a–c**<sup>a,b</sup>

cmpd	<i>m</i>	<i>T</i> /°C ( $\Delta H$ /kJ mol <sup>-1</sup> )	<i>a</i> <sub>squ</sub> /nm	<i>n</i> <sub>cell</sub>	<i>n</i> <sub>wall</sub>
<b>2a</b>	1	Cr • 88 • Col <sub>squ</sub> • 146 • Iso (1.0) <sup>c</sup> (3.8)	3.9 (130 °C)	5.7	2.9
<b>2b</b>	2	Cr • -6 • Col <sub>squ</sub> • 141 • Iso (2.1) <sup>c</sup> (4.5)	4.0 (125 °C)	5.8	2.9
<b>2c</b>	4	Cr • -7 • Col <sub>squ</sub> • 117 • Iso (2.3) <sup>c</sup> (4.0)	4.2 (70 °C)	5.9	2.9

<sup>a</sup> Phase transition temperatures (*T*) and corresponding enthalpy values ( $\Delta H$ ) were determined by DSC (second heating scan, 10 °C min<sup>-1</sup>); abbreviations: Cr = crystalline solid, Col<sub>squ</sub> = square columnar mesophase Iso = isotropic liquid; lattice parameters (*a*<sub>squ</sub>) were obtained from the Guinier pattern; *n*<sub>cell</sub> = number of molecules per unit cell as calculated from the unit cell volume (assuming *h* = 0.48 nm) and the molecular volume (estimated from the crystal volume increments<sup>7</sup>); *n*<sub>wall</sub> = number of terphenyl cores arranged in the cross section of the cylinder wall separating adjacent polar columns. <sup>b</sup> The synthesis and the analytical data are described in the Supporting Information. <sup>c</sup> Only partial crystallization was observed.



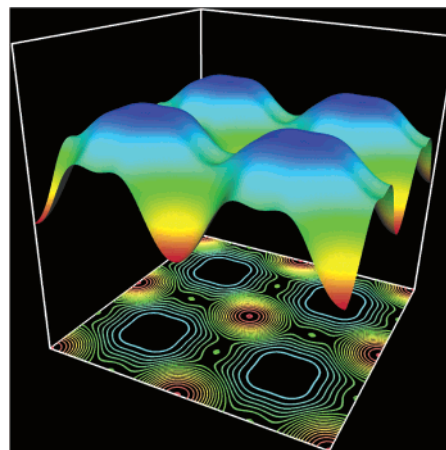
**Figure 2.** (a) Texture (crossed polarizers) of the mesophase of **2b** at 138 °C, the dark areas are homeotropically aligned regions; (b) X-ray diffraction pattern of an aligned sample (surface alignment on a glass substrate, X-ray beam along the column long axis) of **2b** at 137 °C.



**Figure 3.** Organization of compound **2b** in the square columnar mesophase Col<sub>squ</sub> (*p4mm*). (a) CPK models of six molecules **2b** organized in a square, (b) sketch of the mesophase.

The map clearly shows the square cross section of the central oxyethylene column and circular section of the aliphatic columns along the cell edges. According to the Guinier X-ray diffraction patterns compounds **2a** and **2c** have the same type of Col<sub>squ</sub> phases (ratio of the spacings corresponds to 1:2<sup>1/2</sup>:2).

It is remarkable that the bolaamphiphiles **1** as well as facial amphiphiles **2** form square columnar mesophases. This shows that the T-shaped molecular structure coupled with the presence of three sufficiently incompatible subunits provides a powerful design principle for creating new superstructures from low-molecular mass molecules.<sup>8</sup> The important difference between compounds **1** and **2** is that the positions of the polar and nonpolar chains attached to the rodlike core are exchanged. Within the mesophases formed,



**Figure 4.** Electron density map (surface and contour plot) of the Col<sub>squ</sub> phase of **2b**. Four unit cells are shown. Density regions: high (blue) = polar, medium (green) = terphenyl, low (yellow-brown) = aliphatic.

this leads to a reversal of positions of the polar and lipophilic columns with respect to the terphenyl ribbons. Hence, the strongest cohesive forces (H-bonds) are now located in the interior of the square channels delimited by the terphenyl cores, rather than at the corners, as in the mesophases of compounds **1**.

In summary, the Col<sub>squ</sub> phase of compound **2** represents a novel type of columnar LC phase, which results from the segregation of three incompatible molecular moieties into their own subspaces. The results show that it is indeed possible to tailor the precise mesophase morphology of low-molecular mass multiblock molecules by directed molecular design.<sup>2</sup>

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**Supporting Information Available:** Analytical and X-ray data of compounds **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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