

Correlated Layer Structures: A Novel Type of Liquid Crystalline Phase with 2D-Lattice

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Supramolecular chemistry aims at developing highly complex chemical systems from simple components interacting by noncovalent intermolecular forces. A prime topic in this field concerns the investigation of the fundamental mechanism involved in the translation of the information, imprinted in the molecular structure into well-defined complex supramolecular assemblies.¹ Soft matter, which combines order and mobility on a microscopic and macroscopic level, is especially of great interest in this respect, because such fluid self-organized systems are of fundamental importance for technical applications as well as for the understanding of the basic requirements for the formation of living matter. Supramolecular structures organized in a two-dimensional (2D) lattice, are common in all types of organized soft matter.² They can be found as columnar mesophases (Col) built up by cylindrical polymolecular aggregates formed by surfactant–solvent systems, amphiphilic and dendritic molecules,³ block copolymers, and disklike liquid crystals.⁴ However, they have also been observed in the phase sequences of polar⁵ or polycatenar rodlike molecules⁶ and so-called banana-shaped molecules,⁷ which according to their specific shape preferably organize in liquid crystalline phases with layer structures (smectic LC; Sm). For these molecules a 2D-lattice may result from a frustration of the organization in layers due to polar interactions^{5,7} or for steric reasons.⁶ As shown in Figure 1 this frustration can lead to modulated layer structures, rectangular or oblique ribbon phases, and hexagonal columnar phases (Col_h).

Recently, compounds such as **1**⁸ and related molecules,⁹ composed of a rodlike rigid aromatic core, two polar hydrogen-bonding groups at the terminal ends and a semiperfluorinated chain in a lateral position¹⁰ were found to form novel types of smectic liquid crystalline phases. In these mesophases the rodlike mesogenic segments are organized parallel to the layer planes (see Figure 3), which contrasts the structures of all conventional smectic liquid crystalline phases where these units are orthogonal or tilted with an angle unequal to 90° with respect to the layer normal.¹¹

Herein we report how a slight change of the chemical structure of such compounds can modify the molecular self-organization, leading to a new mesophase with a 2D-lattice. For this purpose we have synthesized compound **2** in which the linear semiperfluorinated chain of compound **1** is replaced by a branched chain, composed of an aliphatic and a semiperfluorinated wing (see Figure 2). This molecule represents a quaternary five-block molecule which is composed of four incompatible molecular parts, a rigid aromatic core, two polar 2,3-dihydroxypropoxy groups (“diol groups”) interacting via cooperative H-bonding, a perfluorinated (R_F), and a hydrocarbon chain (R_H). The self-organization of this novel compound was studied by polarized light optical microscopy, differential scanning calorimetry, and X-ray diffraction.

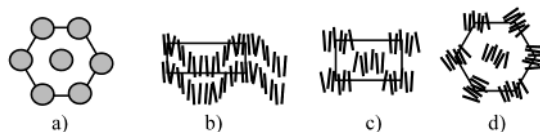


Figure 1. Columnar mesophases: (a) Col_h phase formed by disklike molecules and columnar aggregates; (b) modulated smectic phase (SmA~), (c) centered rectangular columnar ribbon phase (Col_r) and (d) Col_h phase formed by rodlike molecules. Only nontilted arrangements are shown.

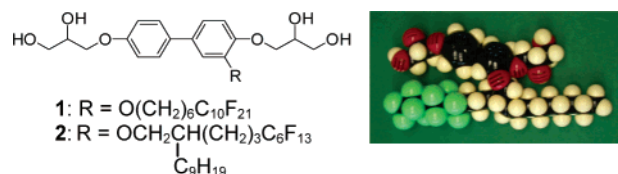


Figure 2. Molecular structures of compounds **1** and **2** and CPK model of a possible H-shaped conformation of compound **2**.

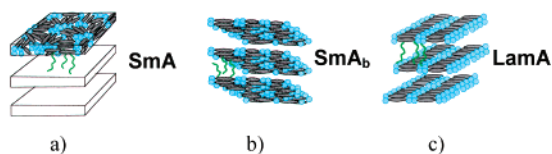


Figure 3. The mesophases of compound **1**: (a) SmA phase; (b) biaxial SmA_b phase with orientational correlation between adjacent 2D layers with nematic order; (c) LamA phase: the H-bonding networks are segregated within the layers giving rise to a periodicity within the aromatic sublayers, but adjacent layers are not positional correlated.^{8,9}

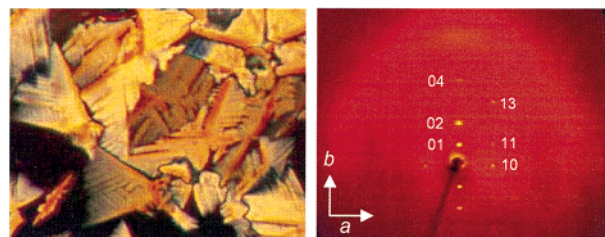


Figure 4. (a) Texture (crossed polarizers) of the mesophase of **2** as it grows from the isotropic liquid state at 131 °C; (b) X-ray diffraction pattern of an aligned sample (surface alignment on a glass substrate) of **2** at 98 °C.

Compound **2** has a broad region of a liquid crystalline phase between the melting point at 66 °C ($\Delta H = 21.6 \text{ kJ mol}^{-1}$) and the transition to the isotropic liquid state at 131 °C ($\Delta H = 7.3 \text{ kJ mol}^{-1}$). On cooling from the isotropic liquid state the mesophase grows with a fern-like texture (see Figure 4a) which coalesces to a mosaiclike texture, but also regions with a spherulitic texture can be found. These textural features provide a first hint on a columnar structure of this mesophase. Also the diffraction pattern obtained by investigation of well aligned samples, shown in Figure 4b, is typical for a columnar mesophase. It is characterized by a diffuse

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Figure 5. Proposed model of the organization of compound **2** in the columnar mesophase Col_r ($p2mm$). Due to the positional correlation between the layers and the additional electron density modulation within the lipophilic sublayers, an in-plane periodicity in a -direction can be found in the diffraction pattern of **2** which cannot be detected for the LamA phase of **1**.⁸

wide angle scattering with a maximum at $D = 0.46$ nm which confirms the liquid crystalline state of this mesophase. Remarkably, this scattering is located on the meridian of the 2D X-ray diffraction pattern, which means that the molecules have a preferred direction perpendicular to the b -axis. In the small-angle region there are several reflections which were, according to the extinction rules, indexed to a *noncentered* rectangular lattice of the 2D space group $p2mm$. The lattice parameter can be calculated to $a = 1.7$ nm and $b = 2.7$ nm. The number of molecules in a unit cell with a thickness of 0.46 nm (corresponding to D) was calculated to be in average $n = 2$. All these findings can be explained by the model shown in Figure 5. Accordingly, the calamitic cores form sublayers which are organized parallel to a and which are separated by sublayers of the nonpolar lateral chains. These chains should be organized in average parallel to the layer planes. This model explains, why the maximum of the wide angle scattering is found on the meridian. The parameter a should be due to an additional periodicity along a which corresponds to the molecular length measured between both terminal diol groups ($L = 1.7$ – 2.1 nm). Therefore, this periodicity can be explained by the segregation of the polar diol groups from the biphenyl cores and corresponds to the distance between the microsegregated columns of the hydrogen-bonding networks of the terminal diol groups. The parameter b corresponds to the layer distance, if a bilayer structure is assumed, that is the thickness of the aromatic sublayers amounts two biphenyl cores. In this case the thickness of the aromatic sublayers (0.9 nm) amounts to one-third of the total layer distance (2.7 nm). This additional periodicity in b -direction can explain that the 03 reflection (on the meridian) is very weak, whereas the 01, 02, and 04 reflections are strong.

It can be assumed that the two-dimensional lattice results from the positional correlation between adjacent layers. However, it is quite unusual that a noncentered lattice is found, because for space filling reasons a centered lattice, with an alternation of the H-bonding networks in adjacent aromatic sublayers, is much more likely. Hence, there must be a special organizing force which stabilizes this noncentered lattice with respect to a centered one. This organizing force should be provided by the incompatibility of the hydrocarbon and perfluorinated parts of the lateral chains within the nonpolar sublayers.

Both compounds **1** and **2** form mesophases with layer structures. The remarkable differences between the self-organization of compound **1** which forms positionally noncorrelated smectic phases and compound **2** which forms a correlated structure should be the result of the different topology of the connection between the lateral chain and the bolaamphiphilic core. In the case of compound **1** the lateral chain is fixed at one of the terminal ends, leading to a more

or less T-like shape of the molecules. Here, the R_F segments have a preferred direction perpendicular to the layer planes and the segregation of the R_H and R_F segments gives rise to R_F -rich and R_F -poor sublayers parallel to the aromatic sublayers.⁸ In the case of compound **2**, however, the lateral chain is branched which leads to an H-like average shape of the molecules as shown in Figure 2. For this reason the lateral chains become organized predominately parallel to the aromatic cores, and hence parallel to the layer planes. In this case the segregation of the fluorinated segments cannot lead to formation of distinct R_F -sublayers, but instead to columns with an enhanced concentration of R_F -segments. As shown in Figure 5, these columns are separated by regions with an enhanced concentration of R_H -segments. This segregation within the lipophilic sublayers reinforces the segregation also within the aromatic sublayers. Additionally, it leads to a coupling of the layers, giving rise to the positional correlation between adjacent layers. Hence, the model of the mesophase of compound **2**, shown in Figure 5, is in complete agreement with the determined lattice parameter and all other experimental findings.

In summary, the mesophase of compound **2** represents a novel type of columnar LC phase, which result from a positional correlation between smectic layers formed by rodlike molecules. Because of the special arrangement of the rod like parts of the molecules parallel to the layer planes, this columnar phase is distinct from all other columnar mesophases shown in Figure 1b–d. In contrast to columnar mesophases of disklike molecules or columnar aggregates of simple amphiphilic molecules, in which cylinders of one component are surrounded by a fluid continuum (see Figure 1a), in this new mesophase the space is subdivided into four distinct sets of compartments: columns of the H-bonding networks, ribbons of aromatic rods, columns containing the R_F chains and regions with an enhanced concentration of R_H chains. The results also show that quite simple low molecular weight molecules, if appropriately designed, can lead to rather complex self-organized systems.

Acknowledgment. The work was supported by the DFG and the European Commission (RTN LCDD).

Supporting Information Available: Analytical data of **2** (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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JA0289999