JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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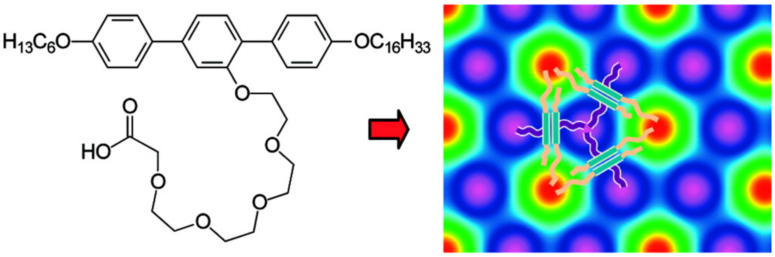
*J. Am. Chem. Soc.*, **2007**, 129 (31), 9578-9579• DOI: 10.1021/ja073079h • Publication Date (Web): 18 July 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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# The Triangular Cylinder Phase: A New Mode of Self-Assembly in Liquid-Crystalline Soft Matter

Feng Liu,[†] Bin Chen,[‡] Ute Baumeister,[§] Xiangbing Zeng,[†] Goran Ungar,*[,†] and Carsten Tschierske*[,‡]

*Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, Great Britain,
Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, Kurt-Mothes Strasse 2,
D-06120 Halle, Germany, and Physical Chemistry, Martin-Luther-University Halle-Wittenberg, Institute of
Chemistry, Mühlpforte 1, D-06108 Halle, Germany*

Received May 2, 2007; E-mail: carsten.tschierske@chemie.uni-halle.de

Liquid-crystalline (LC) materials[1] are of significant interest for numerous applications as optical and electronic organic materials for displays, tuneable lasers, and semiconducting structures.[2] In the future, nanoscale self-patterning of these materials could lead to functional devices based on liquid crystal self-assembly. A broad variety of complex LC phases can be obtained by T-shaped polyphilic molecules with incompatible end chains and side chains.[3,4] This design principle has resulted in a series of honeycomb-like cylinder structures, ranging from squares via pentagons to hexagons and giant cylinder structures where up to ten molecules are arranged end-to-end in the circumference of a cylinder.[3b] The pentagonal cylinder structure is one of the most exciting superstructures, as a periodic tiling of a plane is not possible with regular pentagons.[5] However, the liquid crystalline state, combining order and mobility on a molecular and supramolecular level allows this organization, because it enables the deformation of pentagonal cylinders by slight adjustment of the angles. In this way pentagonal cylinder phases with *p*2*gg* and *p*4*gm* plane group symmetry were observed for these polyphilic LC materials.[3b,4b,c] Moreover, this tiling pattern has demonstrated the concept of topological duality[4b,5] which might be important for the design not only of novel LC structures, but also of new morphologies of polymers[6] and self-organized grids. From a topological point of view the tiling of a plane by pentagons is identical to tiling in a periodic structure consisting of a 1:2 mixture of squares and triangles.[5] This relationship, known as topological duality, is sketched in Figure 1a.[4b] Furthermore, the topological dual of the pentagonal cylinder structure, which is a particular arrangement of triangular and square cylinders, was indeed realized as a unique liquid crystalline superstructure.[4b,c]

Now the question arises as to whether the concept of topological duality could be generalized and applied to designing other new LC superstructures. The hexagonal lattice is an obvious candidate. Also for T-shaped ternary triblock molecules the hexagonal honeycomb structure is one of the most frequently observed modes of self-organization.[3] As shown in Figure 1b, the topological dual of this structure would be the tiling of equilateral triangles. Such a tessellation of triangles was recently reported for 2D grids obtained by structural DNA nanotechology.[7] Herein we show that it is also possible to design molecules which self-organize in a LC phase composed of triangular cylinders.

This structure was obtained with the T-shaped facial amphiphilic three-block molecules **1** in which a terphenyl unit is substituted laterally by a polar and flexible tetraethylene glycol chain, terminated by a hydrogen-bonding carboxylic acid group. In the terminal positions there are two different alkyl chains, a long hexadecyl chain and a significantly shorter hexyl chain.[8]

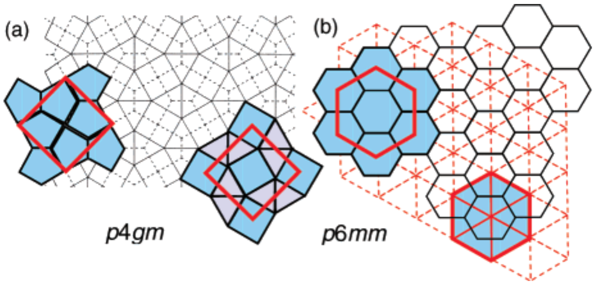
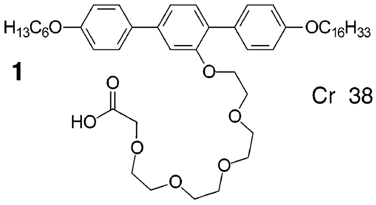


***Figure 1.*** Topological duals: (a) periodic tilings of distorted pentagons and a 1:2 mixture of squares and triangles; (b) tilings of regular hexagons and regular triangles. In each pair of tessellations the nodes and tiles are exchanged; for example, in the hexagonal tiling there are threefold nodes and hexagonal tiles, whereas in the topological dual there are triangular tiles and sixfold nodes.[4b]



**1**

Cr 38 °C Col$_{\text{hex}}\Delta$/*p*6*mm* 67 °C

This compound has a liquid crystalline phase in the temperature range between 38 and 67 °C (see Figure S1, Supporting Information (SI)),[9] with a texture (see Figure 2d) composed of homeotropic regions appearing completely dark between crossed polarizers and birefringent filaments. This texture indicates an optically uniaxial columnar phase which could have either square or hexagonal symmetry.

X-ray scattering was carried out to elucidate the phase structure. The wide-angle scattering is diffuse (see Figure S2) which confirms the liquid crystalline nature of this phase. In the small angle region the powder diffraction pattern (Figure 2a) is characterized by one strong and two weak reflections indexed as (10), (11), and (20) of a hexagonal lattice with the cell parameter $a_{\text{hex}} = 4.8$ nm. This assignment is confirmed by the 2D pattern of an aligned sample shown in Figure 2b. The lattice parameter is only slightly larger than the molecular length of $L = 4.4$ nm end-to-end, with the alkyl chains in the all-trans conformation. Taking this into account, it is reasonable to assume that the rigid rod terphenyl cores self-assemble into a honeycomb-like network with a triangular cross section of the cells. In a hypothetical 3-D unit cell with an assumed one-molecule thickness of 0.45 nm (corresponding to the position of the maximum of the diffuse wide-angle scattering), the number of molecules is calculated as $n = 6.7$ on average (see SI). This means

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[†] University of Sheffield.
[‡] Organic Chemistry, Institute of Chemistry, University Halle.
[§] Physical Chemistry, Institute of Chemistry, University Halle.

10.1021/ja073079h CCC: $37.00 © 2007 American Chemical Society

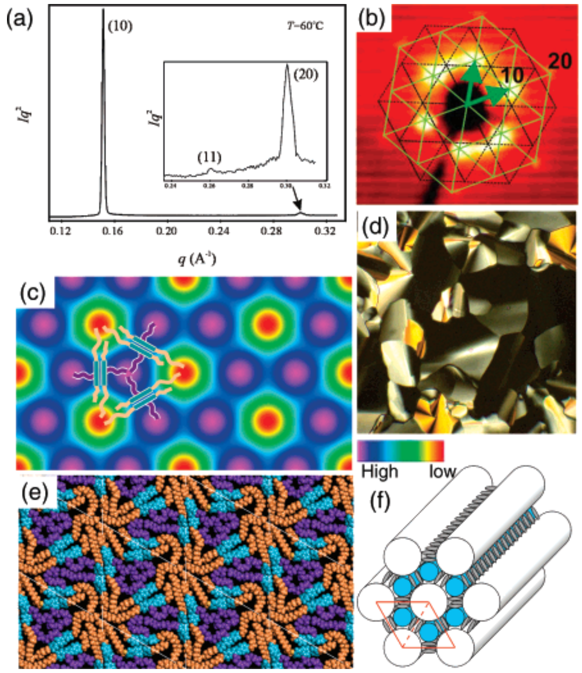

***Figure 2.*** Compound **1**: (a) X-ray diffraction pattern (small angle region) at 60 °C; (b) X-ray diffraction pattern of an aligned sample (for details see SI); (c) reconstructed electron density map; (d) texture as seen between crossed polarizers (60 °C, the dark areas are homeotropically aligned regions); (e) snapshot of a molecular dynamics simulation of the structure viewed down the column axis (for details see SI). For easy comparison with panel c, color coding is as follows: brown = alkyl chains (lowest electron density), blue = terphenyl groups (intermediate/high density), purple = oligo(oxyethylene) groups (highest density). (f) Sketch of the mesophase structure (white, columns containing alkyl chains; gray, terphenyl cores; blue, columns containing polar polyether chains).

an average intercellular wall thickness of approximately two terphenyl units side-by-side. Two is a reasonable value which is typically observed for all previously published cylinder phases.[3,4b,c]

On the basis of the above, a honeycomb structure composed of triangular cylinders is proposed for this LC phase. As shown in Figure 2f, the terphenyl cores form the cylinder walls which are fused together by van der Waals interactions between the terminal alkyl chains forming distinct columns of their own. These alkyl columns constitute the edges of the triangular cylinders. The side walls are built up of terphenyl rods lying perpendicular to the cylinder axis, while the interior is filled with the polar groups. Hydrogen bonding, provided by the COOH groups, gives rise to the cohesive forces required to stabilize the structure. This proposed model is in good agreement with the reconstructed electron density map shown in Figure 2c. The map was obtained from the small angle diffraction intensities measured from the powder pattern (synchrotron radiation, see SI). The map shows six circular high-electron-density regions (blue/purple) grouped around the low-electron-density regions (green/yellow/red) with a hexagonal shape. The high-electron-density regions contain the polyether chains, while the aliphatic chains are located in the low-electron-density regions. The aromatic cores, having an intermediate density (light blue) separate the high-density regions from each other and from the low-density aliphatic areas. Figure 2e shows a snapshot of molecular dynamics simulation of one molecular layer ($c = 0.45$ nm) after annealing with periodic boundaries defined by the experimentally determined unit cell. The simulation confirms efficient space filling and phase separation achieved by this structure. The triangular cylinder structure is in line with the fact that a related compound with the same length of the aromatic core and the same lateral chain, but with the total length of the terminal alkyl chains reduced by four CH$_2$ groups, forms a $\mathrm{Col}_{\mathrm{rec}}/p4mm$ phase composed of square cylinders and, at reduced temperature, a $\mathrm{Col}_{\mathrm{rec}}/p4gm$ phase composed of a 2:1 mixture of triangular and square cylinders.[4b] Hence, increasing the perimeter at constant volume destabilizes the square cylinders and leads to a polygonal honeycomb structure composed only of triangular cylinders.

The above evidence confirms that the $\mathrm{Col}_{\mathrm{hex}}/p6mm$ phase of compound **1**, abbreviated as $\mathrm{Col}_{\mathrm{hex}}\Delta$, represents a novel type of LC phase where space is subdivided into triangular cylinders.[10,11] A related structure has been observed on a larger length scale in morphologies of ABC star triblock copolymers.[6] Hence, it seems that this structure, obtainable on different length scales, is quite a general mode of self-assembly of soft-matter. This mesophase is the predicted topological dual of the hexagonal cylinder phase reported earlier,[3] confirming that topological duality is a helpful concept in predicting and designing new self-assembled nanoscale structures. After the recent report of the structure with the largest polygonal cylinders, so far, ten molecules in circumference,[3b] here the structure is composed of cylinders whose cross section is a polygon with the smallest possible number of sides.

**Acknowledgment.** The work was supported by DFG, EPSRC, and ESF in the framework of the SONS project SCALES, as well as by the Fonds der Chemischen Industrie. F.L. is grateful to the University of Sheffield for a scholarship. We thank Dr. Chris Martin for his help with the synchrotron experiment.

**Supporting Information Available:** Analytical and X-ray data of compounds **1** and details of the methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) For analytical data see Supporting Information, the synthesis will be reported in a proceeding full paper.

(9) $\Delta H$ values: Cr−$\mathrm{Col}_{\mathrm{hex}}$ 41.2 kJ mol$^{-1}$; $\mathrm{Col}_{\mathrm{hex}}$−Iso 3.3 kJ mol$^{-1}$; the $\mathrm{Col}_{\mathrm{hex}}$ phase can be supercooled to ca 5 °C without crystallization (see Figure S1).

(10) This structure is distinct from all previously reported LC $\mathrm{Col}_{\mathrm{hex}}$ phases with $p6mm$ symmetry, where columns are embedded in a fluid continuum and also from the hexagonal honeycomb phases reported more recently, see ref 3a−c and the following: Watanabe, J.; Sekine, N.; Nematsu T.; Sone M.; Kricheldorf, H. R. *Macromolecules* **1996**, *29*, 4816−4818.

(11) If the aromatic walls are regarded as net elements connected by nodes formed by the aliphatic tails, this structure corresponds to a 2D tessellation of type ($3^6$) where each tile is a triangle and six of them meet at each node. However, if a polygonal shape of the projection of the walls and the nodes is presumed, this structure can be described as a three-color tessellation of the type (4.6.12) composed of rectangular (aromatic), hexagonal (EO), and dodecagonal (aliphatic) tiles (see Figure 2c).

JA073079H