Liquid Crystals

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Liquid-Crystalline Triangle Honeycomb Formed by a Dithiophene-Based X-Shaped Bolaamphiphile**

Xiaohong Cheng, Xing Dong, Guanghui Wei, Marko Prehm, and Carsten Tschierske**

The formation of well-defined two-dimensional (2D) arrays is of current interest because of potential nanotechnological applications. Solid-state 2D arrays have been obtained with metallorganic frameworks and as grids on solid surfaces.[1] Series of liquid-crystalline (LC) arrays of polygonal honeycomb-like cylinder networks have been reported recently as self-assembled equilibrium structures formed by T-shaped polyphilic molecules composed of a rigid aromatic core, two hydrogen-bonding polar end groups, and a hydrophobic lateral chain.[2] Though these LC phases represent highly dynamic fluid structures, they can form well-defined 2D lattices over quite large areas owing to their self-healing ability. In these LC arrays the honeycomb frames are formed by walls of parallel arranged rodlike aromatics units aligned perpendicular to the resulting channels. The hydrogen-bonding networks between the end groups fuse these walls to form polygonal honeycombs, and the resulting prismatic cells inside these honeycombs (the channels) are filled with the lateral chains.[2] The cross sections of the known honeycombs range from rhombuses and squares to pentagons and hexagons (see Figure 1 b–d) to a series of giant cylinders with a circumference of up to ten molecules.[2–4]

Herein we report a new LC phase which represents the smallest possible LC honeycomb, composed of triangular cells (Figure 1 a).[5,6] In this array the hydrogen-bonding groups are organized to form vertices with a valence of six. This is the first example of a self-assembled honeycomb array (including grids and solid-state structures) where hydrogen bonding forms vertices with such a high valence. It is also shown that this new LC phase structure requires a change of the molecular topology from T-shaped to X-shaped.

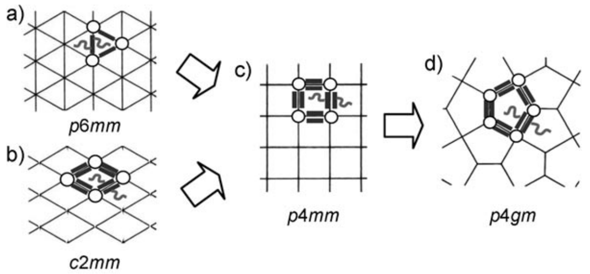

Figure 1. Tiling patterns and their 2D lattices; the views result from cuts through the self-assembled LC polygonal honeycomb phases perpendicular to the cylinder long axis (white dots: columns incorporating the H-bonding networks, bold lines: aromatic cores). a) A triangle honeycomb formed by the X-shaped bolaamphiphile **2/6** and b–d) tilings with rhombuses, squares, and pentagons, as reported previously for T-shaped bolaamphiphiles.[2,3]

Two series of new bolaamphiphiles incorporating a rigid rodlike 5,5′-diphenyl-2,2′-dithiophene core[7] and with glycerol groups at both ends were synthesized (see the Supporting Information). The T-shaped compounds **1** have an alkyl chain at only one of the thiophene rings, whereas in compounds **2** both thiophenes are alkylated. In the preferred molecular conformation, in which the thiophene rings are oriented in an alternating fashion,[8] the two lateral chains are located at opposite sides of the aromatic core, and hence molecules of type **2** adopt an X-shaped conformation (see Figure S5a in the Supporting Information).[9,10] Compounds **1** and **2** form LC phases; the phase types and transition temperatures are collated in Table 1. The LC phases of compounds **1**(12,0), **1**(18,0), and **2** represent enantiotropic phases (thermodynamic equilibrium structures), whereas compound **1**(10,0) has only a monotropic (metastable) LC phase which rapidly crystallizes. Crystallization also takes place upon cooling compounds **1**(12,0) and **1**(18,0) below the melting point, whereas no crystallization was observed for the double-chain compounds **2** even after prolonged storage (>3 months) at room temperature. Between crossed polarizers, all compounds show optical textures typical for LC phases with 2D periodicity (columnar phases; see Figure 3 a and Figure S1 in the Supporting Information). In all cases some areas of the textures appear dark between crossed polarizers, which indicates that all columnar phases are optically uniaxial. This restricts the possible phase symmetries to square and hexagonal. All columnar phases are optically negative; that is, the high refractive index axis, which is known to be parallel to the long axis of the π-conjugated cores, is perpendicular to the column axis as indicated by the textures recorded with a λ retarder plate where the direction of the blue fans is parallel to the high index axis (see Figure 3 b).

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[*] Prof. Dr. X. Cheng, X. Dong, G. Wei
Key Laboratory of Medicinal Chemistry for Natural Resources,
Yunnan University
Kunming, Yunnan 650091 (P.R. China)
Fax: (+86) 871-503-2905
E-mail: xhcheng@ynu.edu.cn
Dr. M. Prehm, Prof. Dr. C. Tschierske
Institut für Chemie
Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Strasse 2, 06120 Halle/Saale (Germany)
Fax: (+49) 345-552-5664
E-mail: carsten.tschierske@chemie.uni-halle.de

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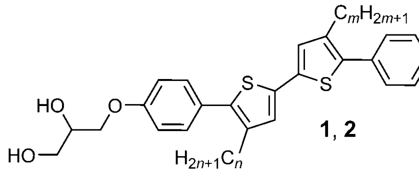
Table 1: Data on bolaamphiphiles **1** and **2**.[a]



1, 2

Cmpd. (*m*,*n*)	Phase transitions *T*/°C [Δ*H*/kJ mol^{-1}]	*a* [nm]	n_{cell} (n_{wall})
1(10,0)	Cr 154 Col$_{squ}$/*p4mm* 150 Iso [31.7] [4.6]	3.0	4.3 (2.1)
1(12,0)	Cr 155 Col$_{squ}$/*p4mm* 166 Iso [19.2] [3.9]	3.0	4.2 (2.1)
1(18,0)	Cr 95 Col$_{squ}$/*p4gm* 170 Iso [23.8] [4.6]	7.5	21.4 (2.1)
2(6,6)	Cr <20[b] Col$_{hex}$/*p6mm* 85 Iso [1.0]	2.8	3.1 (1.0)
2(12,12)	Cr <20[b] Col$_{squ}$/*p4mm* 62 Iso [1.0]	2.8	2.6 (1.3)

[a] Determined by differential scanning calorimetry (10 K min^{-1}) and confirmed by polarizing spectroscopy, peak temperatures from the first heating scan are given; abbreviations: Cr = crystalline solid, Iso = isotropic liquid, Col$_{hex}$/*p6mm* hexagonal columnar phase with plane group *p6mm* (triangular cylinders), Col$_{squ}$/*p4mm* = square columnar phase with plane group *p4mm* (square cylinders), Col$_{squ}$/*p4gm* = square columnar phase with plane group *p4gm* (pentagonal cylinders); n_{cell} = number of molecules per unit cell with an assumed height of 0.45 nm, n_{wall} = number of molecules in the cross-section of the cylinder walls (see Table S2 in the Supporting Information); the structures of the LC phases are shown in Figure 1; for **1**(10,0) values in parenthesis refer to monotropic phase transitions (in this case the values for clearing transition were taken from the second heating scan). [b] No crystallization was observed even after storage for three months.

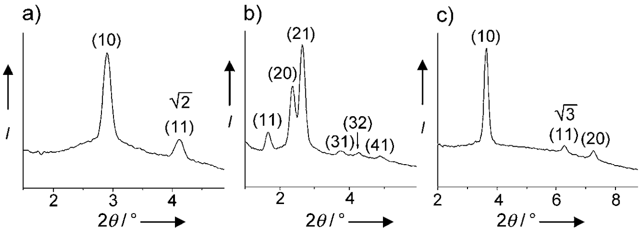


Figure 2. SAXS powder pattern of a) **1**(12,0) at 143 °C (Col$_{squ}$/*p4mm*); b) **1**(18,0) at 150 °C (Col$_{squ}$/*p4gm*); c) **2**(6,6) at 70 °C (Col$_{hex}$/*p6mm*) with indexation.

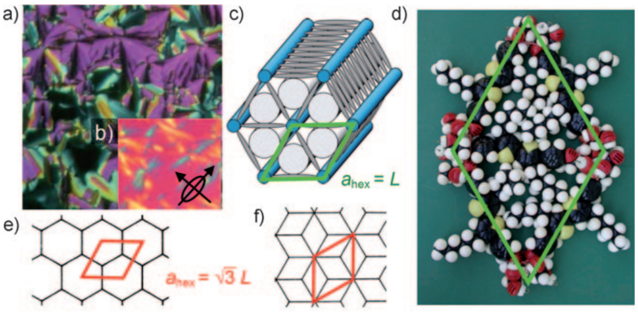


Figure 3. Triangular cylinder phase (Col$_{hex}$/*p6mm*) of compound **2**(6,6). a) Texture between crossed polarizers at *T* = 70 °C; the dark areas represent homeotropically aligned regions. b) Texture with λ retarder plate and indicatrix; in the fans the high-index axis is radial; since the columns are tangential in the fans the high-index axis is perpendicular to the columns.[13] c,d) Model showing the organization of the molecules; the hexagonal lattice (green) coincides with the cylinder walls formed by the π-conjugated rodlike cores. e,f) Alternative hexagonal lattices (red) formed by hexagonal or rhombic cylinders which would give much larger lattice parameters (*L* = molecular length).

This confirms that in the LC phases of **1** and **2** the arenes are perpendicular to the columns, as required for polygonal honeycombs.

The X-ray diffraction patterns show diffuse wide-angle scatterings with maxima around $d = 0.45$–0.46 nm, confirming the LC nature of all mesophases (see Figure S2 in the Supporting Information). Indexing of the small-angle X-ray scattering (SAXS) patterns (Figure 2) leads to the phase assignments with plane groups shown in Table 1 (see also Tables S1 and S2 in the Supporting Information).

Square columnar phases were identified for compounds **1** and compound **2**(12,12). In all cases, with exception of **1**(18,0), these square phases can be assigned to a simple lattice with plane group *p4mm* (ratio of reciprocal spacing is $1{:}\sqrt{2}({:}\,2)$, see Figure 2a and Table S1 and Figures S2a and S3 in the Supporting Information). The lattice parameter is close to the length of the molecule ($L = 2.9$ nm between the ends of the glycerol groups in the most stretched conformation, see Figure S5a in the Supporting Information). This is in line with a square honeycomb structure of these mesophases.

Compound **1**(18,0) has a square phase with a completely different diffraction pattern where the 10 reflex is missing (Figure 2b). Based on the observed diffraction pattern (*hk* no conditions, $h0$: $h = 2n$ and $0k$: $k = 2n$), it can be indexed to a *p4gm* plane group with $a_{squ} = 7.5$ nm. The intensity distribution of the reflections in the *p4gm* phase of compound **1**(18,0) is identical to that observed previously for related compounds with *p4gm* lattice forming pentagonal honeycomb structures (see Figure S4 in the Supporting Information).[2b,7a,11] Also the lattice parameter is in agreement with a pentagonal honeycomb, where pairs of pentagonal cylinders are arranged in a herringbone-like fashion (Figure 1 d). Moreover, this phase assignment is completely in line with the development of the phase types in the series **1**(10,0) to **1**(18,0), where increasing the chain length changes the shape of the cylinders from square to pentagonal.[12]

Compound **2**(6,6) behaves distinctly from all other compounds, as it forms a hexagonal columnar phase (ratio of reciprocal spacing is $1{:}\sqrt{3}:2$, see Table S1 in the Supporting Information and Figures 2c and 3a–d) from below room temperature up to 85 °C. The lattice parameter $a_{hex} = 2.8$ nm is in the range of the molecular length; this is expected for triangular cylinder phases, as in this case the position and direction of the rodlike cores coincides with this lattice (Figure 3c,d).[5] In any alternative honeycomb structure with hexagonal symmetry, formed by either hexagons or rhombuses, a_{hex} would be much larger and in this case would correspond to $1.73\,L$ (see Figure 3e,f).[2b] For the proposed triangular cylinder structure the number of molecules in a hypothetical 3D unit cell is calculated to be $n_{cell} = 3.1$ on average (see Table S2 in the Supporting Information). Since there are three walls per unit cell, the average thickness of the walls ($n_{\mathrm{wall}} = n_{\mathrm{cell}}/3$) is only one rodlike core ($n_{\mathrm{wall}} = 1.0$). This should result from the steric disturbance of a side-by-side packing caused by the two lateral groups at opposite sides of the aromatic core in the preferred X-shaped conformation. Figure 3 d shows that complete space filling and correct lattice parameters are achieved in this arrangement.[14,15]

In contrast to compounds **2** with two lateral chains[16] all compounds **1** with only one chain form cylinder walls where the average thickness of the walls (n_{wall}, see Table 1) is about two aromatic units placed side-by-side (Figure 4 d,e). This dependence of the cylinder wall thickness on the number of chains at the aromatic unit leads to the surprising observation that compound **2**(6,6), with two hexyl chains, forms triangular cylinders, whereas compound **1**(12,0), with its single lateral chain occupying approximately the same volume, and even compound **1**(10,0), with a smaller chain volume, form the larger square cylinders. A major reason should be that in the double-wall honeycombs of the T-shaped molecules the aromatic cores and the polar glycerol groups are located inside the unit cells, and these groups fill a significant part of the space inside the cells (see Figure 4 e). In contrast, in the case of single-wall cylinders formed by X-shaped molecules the bolaamphiphilic units are positioned on the lattice and hence, they contribute to the space filling in two adjacent cells, effectively leaving more space available for the lateral chains (Figure 4 a).[17] Moreover, the relatively short hexyl chains (length 0.9 nm) would not be able to reach the centers of square cylinders built up by the relatively long diphenyldithiophene cores (side length ca. 3 nm), thus disfavoring any honeycomb with square or larger cells.

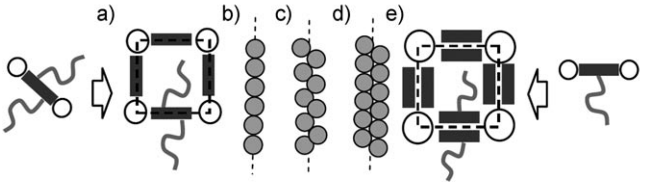


Figure 4. Dependence of wall thickness on the number of lateral chains, shown for square honeycomb phases; a,e) cuts through one cylinder; b–d) cuts through a cylinder wall along the cylinder axis. a,b) Single-wall structure of X-shaped bolaamphiphiles; c) staggered organization of the aromatic cores as in **2**(12,12), and d,e) double-wall cylinders of the T-shaped molecule **1**(12,0).

In summary, the triangular cylinder phase is a new LC phase of ternary bolaamphiphiles, and it is shown that the change from a T-shaped to an X-shaped structure provides an additional tool for the directed design of polygonal honeycombs. In addition, the dynamic hydrogen-bonding networks provided by the flexible glycerol groups[2] allow access to networks having vertices with high valences which cannot be achieved with the more restricted classical hydrogen-bonding building blocks, such as carboxylic acids, amides, and carboxylic acid/pyridine complexes. This opens new possibilities for the directed assembly of π-conjugated and other functional organic materials[7b,8,18] into well-defined nanoscale superstructures. This fundamental concept should not be restricted to liquid-crystalline soft-matter structures, but should also be applicable to the design of grids on surfaces and solid-state materials.

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[16] A slightly larger value of $n_{\mathrm{wall}} = 1.3$ is found for the square honeycomb phase of compound **2**(12,12), which can be explained by a staggered organization of the arenes along the cylinder walls (see Figure 4c).

[17] This effect is only partly compensated by the expansion of the unit cells (for square phases from $a_{\mathrm{squ}} = 2.8$ for **2**(12,12) to $a_{\mathrm{squ}} = 3.0$ nm for **1**(12,0), due to the fact that the diameter of the polar columns is increased in honeycombs with double-wall cylinders (the number of glycerol groups organized side-by-side in the polar columns is doubled).

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