

Liquid-Crystalline Kagome**

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The kagome (from Japanese; kago = basket, me = hole, eye: meaning a basket with holes) represents a periodic 2D tiling of regular hexagons and triangles in a 1:2 ratio (see Figure 1c). This pattern, also known as trihexagonal tiling,

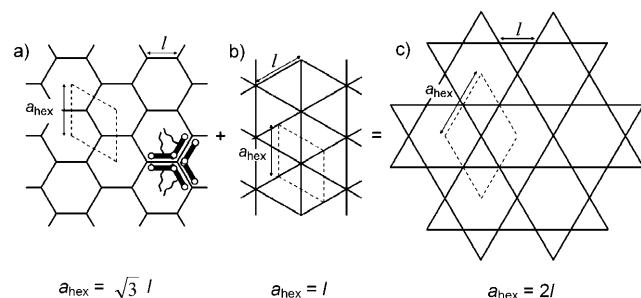
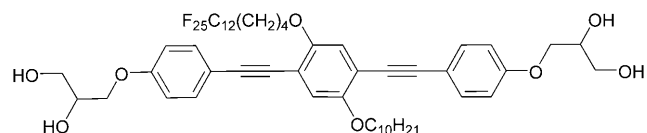


Figure 1. Three polygonal 2D nets with identical vertices and side-lengths showing hexagonal $p6mm$ symmetry formed by a) hexagons, b) triangles, and c) the kagome and the relations between side length l and hexagonal lattice parameter a_{hex} . In the polygonal cylinder phases these nets are extended to infinity in the third dimension. The hexagonal beehive honeycomb organization of some previously reported T-shaped ternary amphiphilic molecules are shown schematically in (a).^[7,8]

is of outstanding interest not only for its aesthetic appeal, but especially as it is of relevance for spin-frustrated magnetic materials.^[1] However, the kagome pattern is rare on a molecular scale, and is mainly restricted to Jarosites^[2] and a few metal–organic frameworks (MOFs), that is, to solid-state materials.^[3] Kagome nets can also be found as atomic planes in a number of metal alloys^[4] and recently 2D kagome nets were obtained by the organization of DNA strands^[5] or organic molecules on solid surfaces.^[6]

Ternary amphiphiles (molecules containing three incompatible types of segments) with a T shape have been shown to spontaneously assemble into liquid-crystalline (LC) phases representing periodic arrays of tessellated infinitely long triangular, square, pentagonal, or hexagonal prisms.^[7–9] In these new types of LC phases, the prism walls are formed by rodlike aromatic segments (Figure 1a). The prismatic cells are filled with fluid chains attached laterally to the rodlike cores. Herein, this concept is extended and used to design a new polyphilic block molecule capable of self-assembly into the LC kagome, a fluid superstructure representing a periodic array combining triangular and hexagonal cells.

Compound **1** (Scheme 1), specifically designed for this purpose, was synthesized by a sequence of preparative steps with a Sonogashira cross-coupling reaction^[10] as the key step



1: Cr 75 °C [6.3] M 86 °C [0.9] Col_{hex}/p6mm 116 °C [4.2] Iso

Scheme 1. Molecular structure and phase-transition temperatures of **1**; values in square brackets indicate the corresponding transition enthalpy values ($\Delta H/k$) mol^{−1}, determined by DSC, first heating scan, 10 K min^{−1}, see Figure S1 in the Supporting Information); Cr = crystalline solid, M = unknown mesophase, Col_{hex}/p6mm = hexagonal columnar LC kagome phase with plane group $p6mm$, Iso = isotropic liquid.

(see Scheme 2). Two chemically different chains, an aliphatic hydrocarbon chain and a semiperfluorinated chain, were attached laterally at opposite sides of a π -conjugated 1,4-bis(phenylethynyl)benzene-based aromatic rod to which glycerol groups, capable of forming cooperative hydrogen bonds, were fixed at each end. Hence, this compound represents a Janus-type,^[11] X-shaped quaternary amphiphile. Two distinct lateral chains were combined to enable the formation of two different compartments by microsegregation; a different volume of the chains^[12] was required to fill

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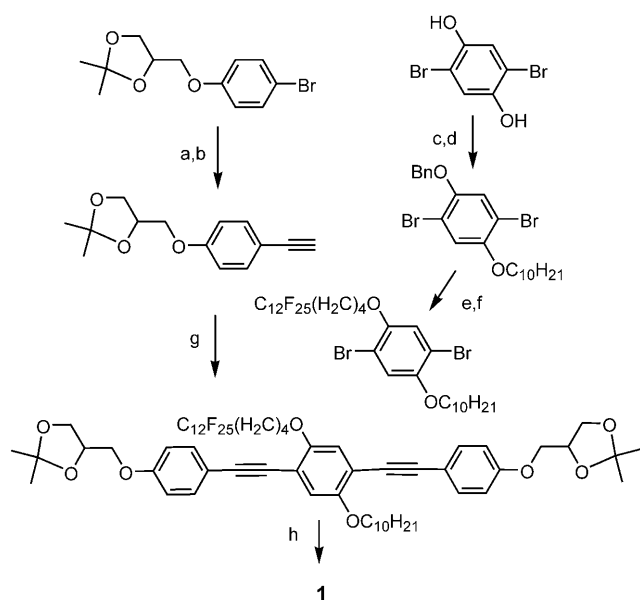
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[**] This work, as part of the European Science Foundation EURO-CORES Programme SONS project SCALES, was supported by the DFG, the EPSRC, the EC Sixth Framework Programme (contract No. ERAS-CT-2003-989409), and by the Government of Sachsen-Anhalt in the framework of the Cluster of Excellence “Nanostructured Materials”. We thank the European Synchrotron Radiation Facility for beamtime on beamline ID02.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.200802957>.



Scheme 2. Synthesis of compound **1**. Reagents and conditions:

a) $\text{H-C}\equiv\text{C-SiMe}_3$, $[\text{Pd}(\text{PPh}_3)_4]$, CuI , Et_3N , reflux, 5 h; b) KOH , MeOH , 20°C , 3 h; c) BnCl , K_2CO_3 , butanone, reflux, 2 h; d) $\text{C}_{10}\text{H}_{21}\text{Br}$, K_2CO_3 , CH_3CN , reflux, 10 h; e) cyclohexene, $\text{Pd}(\text{OH})_2/\text{C}$, EtOAc , reflux, 48 h; f) $\text{C}_{12}\text{F}_{25}(\text{CH}_2)_4\text{Br}$, K_2CO_3 , CH_3CN , reflux, 16 h; g) $[\text{Pd}(\text{PPh}_3)_4]$, CuI , Et_3N , reflux, 6 h; h) pyridinium 4-toluenesulfonate, MeOH/THF , reflux, 6 h. Bn = benzyl.

the very different spaces inside the hexagonal and triangular cylinders in the envisaged kagome structure.

This compound (**1**) forms two LC phases in the temperature range between 75°C and 116°C with a phase transition at 86°C (see also Figures S1 and S2 in the Supporting Information). Our discussion is focused on the high-temperature phase occurring between 86 and 116°C . The texture of this phase, as seen under a microscope between crossed polarizers, is characterized by dark, homeotropically aligned regions and birefringent filaments (Figure 2a), which indicates an optically uniaxial columnar LC phase. It is easy to shear the sample; this destroys the homeotropic texture, converting it into a nonspecific birefringent texture, which indicates the fluidity of the material. The lack of atomic-scale order is additionally confirmed by the diffuseness of the wide-angle X-ray scattering (Figure S3 in the Supporting Information). The small-angle Bragg reflections (Figure 2b) have the ratio of corresponding reciprocal spacing of $1:3^{1/2}:2:7^{1/2}:3\dots$. These can be indexed on a hexagonal 2D lattice ($\text{Col}_{\text{hex}}/p6mm$ phase) with a lattice parameter $a_{\text{hex}} = 5.76\text{ nm}$ (see Table S1 in the Supporting Information). This value corresponds to approximately twice the length of the rigid bolaamphiphilic^[13] moiety of **1** as measured between the ends of the terminal glycerol groups (2.80 nm to 3.05 nm depending on the conformation of the glycerol groups, see Figure S4a,b in the Supporting Information). As shown in Figure 1c, the side length of the polygons (l) is half the hexagonal lattice parameter a_{hex} for the kagome lattice. This result suggests that in the observed hexagonal columnar LC phase the aromatic moieties form a kagome-type net with the hydrogen-bonding glycerol groups at the vertices.

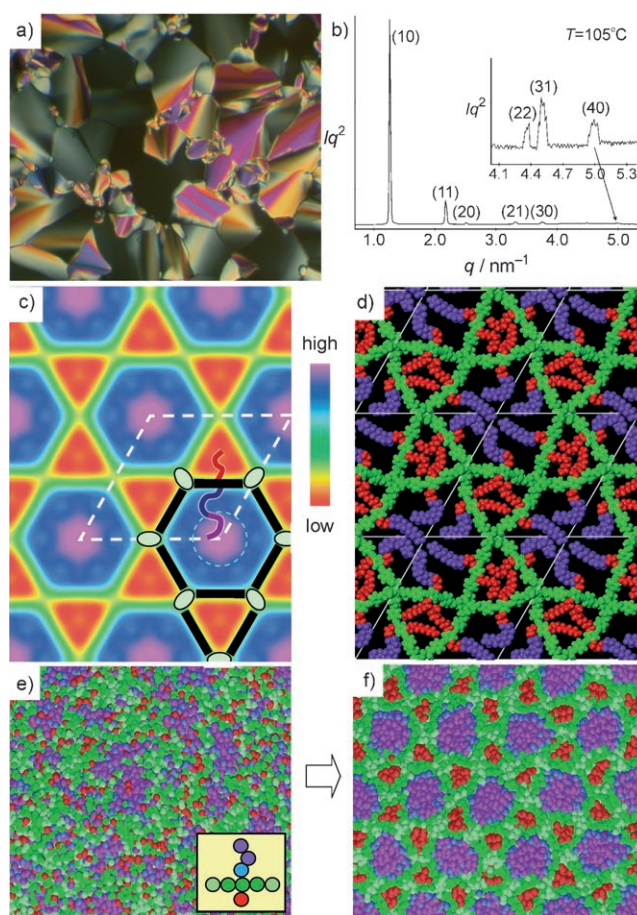


Figure 2. Investigation of compound **1**: a) Texture as seen between crossed polarizers at $T = 100^\circ\text{C}$ (dark areas represent homeotropically aligned regions); b) small-angle region of the X-ray diffraction pattern at $T = 105^\circ\text{C}$; c) electron-density map calculated from this diffraction pattern; the organization of a few molecules is shown on the bottom right; d) snapshot of a molecular dynamics simulation. Dissipative particle dynamics simulation: e) simulation at a temperature corresponding to the isotropic phase, in which some segregation occurs; the inset shows the bead model for the molecule, where similar chemical functional groups are combined into a single bead; f) on cooling, the kagome is formed. For easy comparison, color coding in (c)–(f) is: red: alkyl chains, purple: R_f chains, green: aromatic cores and glycerol units; in (c), (d), and (f) the view is down the columnar axis; further details are described in the Supporting Information.

To confirm the proposed structure, we have used two approaches. We performed high-resolution X-ray diffraction experiments using synchrotron radiation^[14] and from the data thus obtained reconstructed electron density maps.^[9a] Furthermore, we carried out computer simulations of relevant models. The electron density map (Figure 2c; for the reconstruction procedure see the Supporting Information) indicates the 3.6.3.6 trihexagonal tiling of hexagons and triangles, which corresponds to the kagome structure, in which triangles and hexagons have very distinct electron densities. Accordingly, the red triangles with the lowest density should be filled with the nonfluorinated alkyl chains, whereas the semiperfluorinated chains, which provide a much higher electron density, are organized in the blue/purple high-electron-density hexagons. This distribution of the lateral chains is

also in agreement with their different sizes; the shorter alkyl chains fill the small triangles whereas the much larger semiperfluorinated chains fill the hexagons.^[15] Within the hexagons, there is an electron density gradient that changes from highest in the center (purple), where exclusively fluorinated segments are located, to lower electron density near the periphery (blue), where perfluorinated end groups are mixed with the aliphatic spacers (see also the surface plot in Figure S5a in the Supporting Information). The aromatic rodlike moieties are located in the medium-electron-density areas (green), which represent the thin walls separating the hexagonal fluorine from the triangular aliphatic cells.^[16] Calculation of the number of molecules per unit cell, assuming a height of $h = 0.45$ nm (see Table S2 in the Supporting Information), gives a value of approximately eight molecules. This corresponds to an average thickness of the walls separating the distinct compartments of approximately 1.4 aromatic cores. Molecular dynamics simulations (Figure 2d) performed with six molecules per unit cell confirm that phase separation is achieved by the proposed structure and that it is stable under the given boundary conditions, but suggests some overcrowding in the triangular and some deficit in the hexagonal cylinders. It is possible that the stacking of aromatic rods is staggered (see Figure S5b in the Supporting Information), so that the average elevation along the cylinder axis (the “unit cell height”) is reduced, giving the required six molecules per cell. Such staggering could be related to the need for some molecules to contribute both side chains to the hexagonal cylinders to redress their material deficit (see Figure S4 in the Supporting Information).

To examine the formation of the kagome LC phase, dissipative particle dynamics (DPD) simulations were performed following the procedure described by Groot and Warren.^[17] This simulation methodology has been particularly successful for simulations of block copolymers and, given the blocklike nature of compound **1**, should also provide a route to understanding the structure and formation of the kagome. To represent compound **1**, the molecule was simplified into collections of beads, where each bead consists of approximately eight similar atoms (see inset in Figure 2e). The DPD parameters used to describe the terphenyl, hydrophilic, perfluorinated, and alkyl groups were defined based on a training set of molecules for bolaamphiphiles established by Bates and Walker.^[18] The simulations were started using an isotropic phase at high temperature to ensure that any ordered structures observed were not biased by the starting conditions. The temperature was then lowered in small steps and the simulations monitored for any evidence of long-range structure. On cooling from the isotropic liquid (Figure 2e), the kagome structure (Figure 2f) is the first ordered phase observed for this model, thus confirming the X-ray characterization.

This new mesophase represents a highly complex fluid structure, which is composed of five distinct nanometer-sized subphases organized on a $p6mm$ lattice. Four of the molecular segments, glycerol groups (light green), aromatic cores (green and black lines), alkyl chains (red), and perfluorinated ends (purple) are localized in their own domains (see model in

Figure 2c). Only the aliphatic spacers (blue) are mixed with parts of the fluorinated segments in the shells around the fluorinated column cores. This complexity is typical of biological systems, wherein a single cell incorporates many different units to perform distinct biological functions, but, to the best of our knowledge, has never been achieved in any artificial soft-matter structure.^[19] Related polyphilic molecules should lead to numerous other LC phases with even more complex tiling patterns, establishing a new level of complexity in LC design. Likewise, the DPD simulation model developed here should prove to be an efficient tool for the prediction of new morphologies.

Received: June 20, 2008

Published online: October 16, 2008

Keywords: kagome structures · liquid crystals · nanostructures · self-assembly · soft matter

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