Liquid Crystals

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Complex Liquid-Crystalline Superstructure of a π-Conjugated Oligothiophene**

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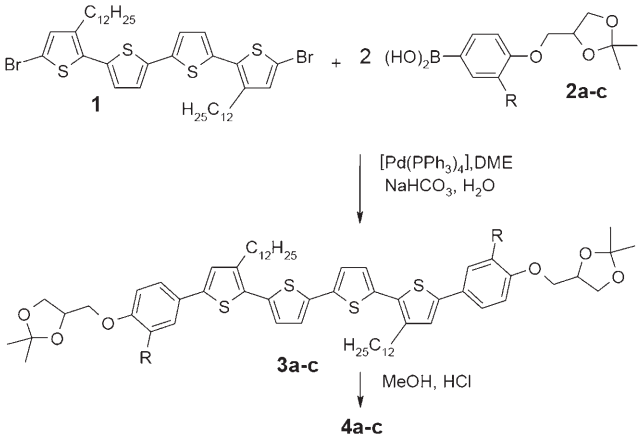
Amphiphiles consisting of a short rod-like aromatic core and terminally and laterally attached chains incompatible with the core and with each other have been shown to form a wide range of novel liquid-crystal (LC) phases.[1,2] Most prominent among them are honeycomb phases, an inverted version of columnar phases in which the hard aromatic rods separate the soft channels.[1,2] Bolaamphiphiles are one type of such LC-forming compounds, having a biphenyl core, a polar group at each end, and a nonpolar chain attached laterally.[1] The purpose of the present work is twofold: 1) to investigate the possibility of introducing significantly longer rod-like moieties (in the oligomer range), thus scaling up the honeycomb nanostructures and widening the scope of potential applications, and 2) to incorporate a building block with proven electronic conductivity[3,4] to demonstrate that self-assembled π-conjugated nanostructures of high complexity can be produced with potentially superior electrical properties and ease of alignment.

Herein, we present the first example of a honeycomb-like structure involving π-conjugated oligothiophenes. Several examples of thermotropic nematic, smectic,[5] and recently also columnar organization of oligothiophene-based π-conjugated systems[6] have been reported. However, the self-organized structures obtained in this way were still relatively simple, restricted to layers and columns.[5–7] The structure described herein is composed of cylinders with a large square cross section, separated by π-conjugated walls. The compound forming this arrangement was designed by combining a rod-like oligothiophene core, two polar hydrogen-bonding groups at the ends to provide a bolaamphiphilic structure, and a number of lipophilic alkyl chains laterally attached to the rod-like core.[8,9] The length of the π-conjugated rod is about three times that of the previous biphenyl-based bolaamphiphiles, resulting in a substantial structural scale-up.

These new materials were synthesized by palladium-catalyzed cross-coupling reactions[10] of α,α′-dibrominated quaterthiophene **1** and glycerol-functionalized benzene boronic acid **2**,[1a] with subsequent deprotection of the diol groups (Scheme 1). The final glycerol-functionalized oligothiophenes **4a–4c** were purified by centrifugal TLC and subsequent



Scheme 1. Synthesis of compounds **4a–c** (**a** R = H, **b** R = CH_3, **c** R = C_6H_{13}).

repeated crystallization (see the Supporting Information for synthetic procedures and analytical data). Compounds **4a–c** were investigated by polarizing microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. As summarized in Table 1, compound **4a** with two dodecyl chains shows an enantiotropic liquid-crystalline phase, whereas compound **4b** with two additional methyl groups in the periphery shows only a monotropic (metastable) mesophase on cooling from the isotropic melt. Compound **4c**, in which the methyl groups are replaced by longer hexyl groups, is not liquid-crystalline. This finding indicates that these peripheral chains inhibit LC phase formation, probably by disturbing hydrogen bonding between the polar groups.

The following discussion is focused on the liquid-crystalline compound **4a**. Upon cooling this compound from the isotropic liquid state, a transition to a birefringent fluid phase can be observed. The melting point is 130 °C and the

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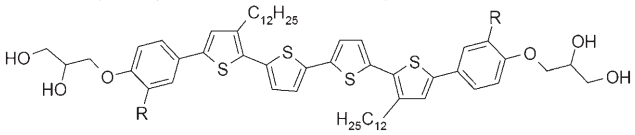
Table 1: Liquid-Crystalline Behavior of Compounds **4a–c**.



Compd	R	Phase transitions[a]
4a	H	Cr 130 (31.5) $Col_{squ}/p4mm$ 151 (3.4) Iso
4b	CH_3	Cr 122 (46.8) (M 109 (0.5))[b] Iso
4c	C_6H_{13}	Cr 126 (35.4) Iso

[a] Transition temperatures (T [°C]) and transition enthalpy values (ΔH [kJ mol^{-1}], in parentheses) as determined by DSC (peak temperatures in the second heating scan) at a scanning rate of 10 K min^{-1}; abbreviations: Cr = crystalline solid, $Col_{squ}/p4mm$ = square columnar liquid-crystalline phase with plane group $p4mm$, M = unknown mesophase, Iso = isotropic liquid; [b] monotropic mesophase, observed only on cooling.

transition to the isotropic liquid takes place at 151 °C (for DSC traces, see Figure S1 c in the Supporting Information). In the temperature range of the liquid-crystalline phase, a spherulitic texture typical for columnar phases can be observed between crossed polarizers (Figure 1 a). In addition to the birefringent texture, large optically isotropic regions can also be observed (Figure 1 b). These findings indicate an optically uniaxial LC phase, which could be either a hexagonal or a square columnar phase.

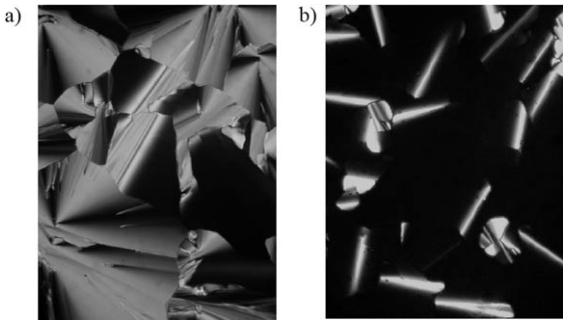


Figure 1. Polarized optical photomicrographs of the Col_{squ} phase of compound **4a** at 140 °C as seen between crossed polarizers (a color version is shown in Figures S1 a and b in the Supporting Information); dark areas, especially visible in (b), represent homeotropically aligned regions in which the orientation of the long cylinder axes is uniform and perpendicular to the substrate surfaces.

The X-ray powder diffraction pattern is shown in Figure 2 (see also Figure S2 in the Supporting Information). The wide-angle scattering is diffuse and has its maximum at $d = 0.48$ nm, which confirms the liquid-crystalline nature of this phase. In the small-angle region, two intense peaks corresponding to distances $d = 3.52$ and 2.49 nm and an additional weak peak corresponding to $d = 1.77$ nm were observed. These peaks can be indexed to the (10), (11), and (20) reflections of a square lattice with $p4mm$ plane group symmetry and a lattice parameter $a_{squ} = 3.5$ nm. This lattice parameter corresponds to the length L of the molecule **4a** measured between the two diol groups, which is between $L = 3.3$ and 3.7 nm, depending

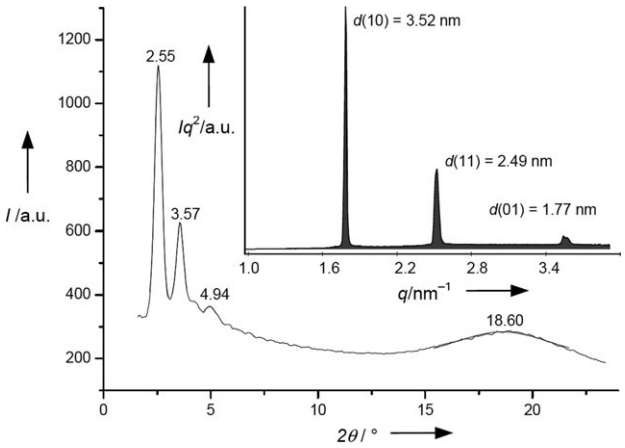


Figure 2. X-ray powder diffraction pattern of compound **4a** at 135 °C. The inset shows the high-resolution powder pattern obtained with a synchrotron source.

on the conformation. Taking this value into account, it is reasonable to assume that the rigid rod-like oligothiophene moieties self-assemble into a honeycomb-like network with a square cross section of the cells. As shown in Figure 3 a, the oligothiophene cores form the cylinder walls, which are fused together by the hydrogen-bonding networks at the termini, thus forming distinct columns running parallel to the edges. The hydrogen-bonding networks within these columns give rise to the formation of the square net structure, but they also provide the attractive forces with a component parallel to the columns, thus leading to the cylinder structure. The interior of the square cells is filled with the lateral dodecyl chains. The number of molecules in the unit cell, assuming a thickness of 0.48 nm (corresponding to the maximum of the diffuse wide-angle scattering) was calculated as $n = 4$ on average. Accordingly, the thickness of the partitioning walls amounts to approximately two aromatic cores.

This model is in complete agreement with the reconstructed electron density map shown in Figure 3 b, which was obtained from the intensities of the three small-angle reflections measured from the high-resolution powder pattern obtained with a synchrotron source (see inset in Figure 2). The intensities and a description of the electron-density reconstruction procedure are given in the Supporting Information. The map clearly shows the square cross section of the regions with lowest electron density (red), representing the central alkyl columns, and a higher electron density for the square frames around these columns, formed by the aromatic cores and the diol groups. Consistent with the model, the electron density is the highest (purple) in the middle of the cylinder walls where the electron-rich sulfur atoms of the thiophene rings are located. The hydrogen-bonding networks of the diol groups provide an intermediate electron density (blue) at the edges.

The above results confirm that it is possible to construct complex self-organized superstructures by appropriate molecular design of extended π-conjugated rods. Though liquid-crystalline cylinder phases were recently reported for bolaamphiphilic biphenyl derivatives[1] and facial amphiphilic

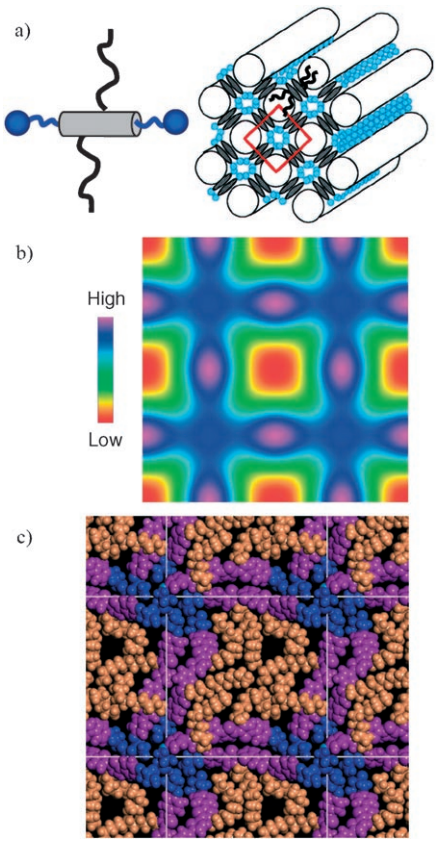


Figure 3. a) Organization of compound **4a** in the $Col_{squ}/p4mm$ phase; white = cylinders of the alkyl chains; blue = hydrogen-bonding networks; gray = aromatic cores. b) Reconstructed electron density map; four unit cells are shown. Density regions: high (pink) = thiophenes; medium (blue) = polar regions; low (green-yellow-red) = aliphatic regions. c) A snapshot of the molecular dynamics simulation of the structure viewed down the column axis for easy comparison with (b). Color coding (brown = alkyl chains, blue = 2,3-dihydroxypropyloxy groups, purple = aromatic cores) is similar to the ascending order of expected electron densities using the color scale in (b); for details of the simulation see the Supporting Information.

terphenyl derivatives with only one lateral chain,[2] the work reported herein has shown that this concept can be successfully extended to much larger rod-like cores and to molecules with more than one lateral chain. These results open new possibilities for the directed self-assembly of π-conjugated organic materials into complex superstructures, which are potentially useful for the design of functional devices by liquid-crystal self-assembly. In this respect, it is interesting to note that the direction of these cylinders with respect to the surfaces can be tailored by modification of the surface properties of the substrate, as is common in LC display technology. The observation of completely dark areas with relatively large size by polarized microscopy (Figure 1b) indicates that in these regions the cylinder networks adopt a uniform alignment with the cylinder long axes aligned perpendicular to the surfaces, potentially providing a conducting path between the surfaces. In the bright texture, seen in Figure 1a, there is a preferred alignment of the cylinders parallel to the surfaces; such a configuration is required for applications in field-effect transistors.[7b] Future work will focus on exploring the electronic properties of the LC phases of these π-conjugated LC materials and the crystalline phases developing below the LC transitions, which is of interest for their potential use in self-organized organic electronic devices.

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