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Liquid Crystals

Two- and Three-Dimensional Liquid-Crystal Phases from Axial Bundles of Rodlike Polyphiles: Segmented Cylinders, Crossed Columns, and Ribbons between Sheets**

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The design of programmed molecules for assembly into complex nanostructures has received considerable attention in recent years.[1–3] One successful approach to complex soft matter has been achieved with polyphilic star-shaped molecules, both polymeric[4] and molecular.[3,5,6] T-shaped bolaamphiphiles in particular provide a series of novel honeycomb liquid-crystal (LC) morphologies (Figure 1 a,b). In these honeycombs rodlike units form polygonal cylinder frames, with the terminal hydrogen-bonding groups fusing the cylinder walls and the flexible lateral chains filling the cell interior (Figure 1 a, b).[3] By adding a second side chain[7] incompatible with the first, we recently obtained new structures based on periodic multicolor tiling patterns. Some are of unprecedented complexity, with tiles of several different shapes and "colors".[8,9] However, increasing the side-chain volume leads to lamellar phases (Figure 1 c)[10] and, by introducing branches, to inversion of the honeycombs, with the column core now inhabited by bundles of aromatic rods coaxial with the columns (Figure 1 d).[11,12]

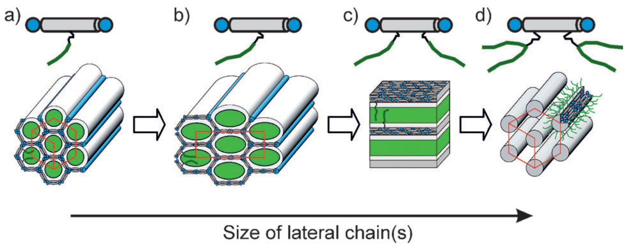
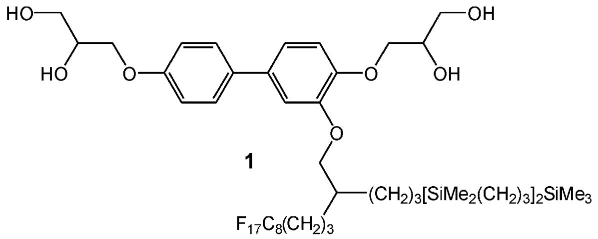


Figure 1. Sequence of LC phases formed by rodlike bolaamphiphiles with incompatible lateral and terminal groups, upon increasing the size of the lateral chain(s): a, b) polygonal cylinder phases (rods normal to column);[3] c) lamellar phases (rods in plane of layer);[10] and d) axial-bundle phases (bundles of rods parallel to columns).[11,12] Molecules displaying these phases are sketched above: gray aromatic core, blue glycerol, green side chain.

Herein we report a new type of bolaamphiphile (**1**, Scheme 1) having a lateral chain with two incompatible branches, a semiperfluorinated (R_F) and a carbosilane one (R_{Si}). For this compound, three new LC phases were discovered with decreasing temperature, each with an intriguing structure: a hexagonal 3D phase with correlated modulated columns, a 3D phase with crossed columns, and a phase with columns between layers.

Compound **1** (see the Supporting Information for the synthesis)[13] shows these three stable LC phases (Scheme 1) separated by reversible transitions. On cooling from the isotropic liquid, a spherulitic texture develops, typical of columnar LC (Figure 2 a). All mesophases have positive birefringence as confirmed by polarizing microscopy with a λ-retarder. The colors of the fans (Figure 2 c, middle) reveal the orientation of the slow axis as tangential rather than



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Cr 65 $\mathrm{Lam}_{\mathrm{Sm}}/p2mm$ 68 $Cmmm$ 71 $P6/mmm$ 135 Iso
27.6 *1.2* *0.8* *2.6*

Scheme 1. Structure, transition temperatures T [°C], and enthalpies ΔH [kJ mol^{-1}] (bottom, italics) of compound **1** (for differential scanning calorimetry, see Figure S1 in the Supporting Information). Cr = crystalline phase, $\mathrm{Lam}_{\mathrm{Sm}}/p2mm$ = lamellar phase with in-plane periodicity correlated between layers on a $p2mm$ lattice, $Cmmm$ = orthorhombic crossed-column phase, $P6/mmm$ = 3D hexagonal axial bundle phase (see Figure 3), Iso = isotropic liquid.

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radial, that is, coincident with the columnar director. Since the slow axis is known to be parallel to the biphenyl axis, it follows that the biphenyls are coaxial with the columns.

That all three phases under discussion are LC is confirmed by the lack of any sharp X-ray diffraction at wide angles (see Figure 2d,e). The high-temperature phase has hexagonal symmetry (Figure 2d,f, $a_{hex} = 3.73$ nm). In both diffraction patterns the sixfold axis is randomly oriented within the plane of the film (horizontal in Figure 2d–f). Notably, in addition to the *hk*0, there is also a weak but distinct Bragg reflection on the equator at 1.8 nm; it is indexed as (001) (Figure 2f). This reflection appears at the isotropization temperature and persists almost unchanged down to the crystal phase (Figure 2g). The periodicity $c = 1.8$ nm along the columns corresponds to the length of the bolaamphiphile ($l = 1.8$–2.1 nm). The correlation length along [001] is 150 nm, indicating long-range order. We note that, although *hkl* cross-reflections are not observed, this phase has true 3D long-range order. Otherwise, the vertical width of the (001) GISAXS reflection (Figure 2f) would have exceeded that of the *hk*0 reflections. The suggested space group of the 3D hexagonal phase is *P*6/*mmm*. As shown above (Figure 2c), in this phase the biphenyls are parallel to the column axis, surrounded by the molten swallow-tailed side chains. From the volume of the unit cell we calculate the number of molecules per cell to be 14 (for calculation, see Table S2 in the Supporting Information). The 14 molecules sit side by side in a bundle, and each bundle is centered at a vertex of a simple 3D hexagonal unit cell (see Figure 3a). The segmentation of the columns is due to segregation of the aromatic and the terminal glycerol groups.

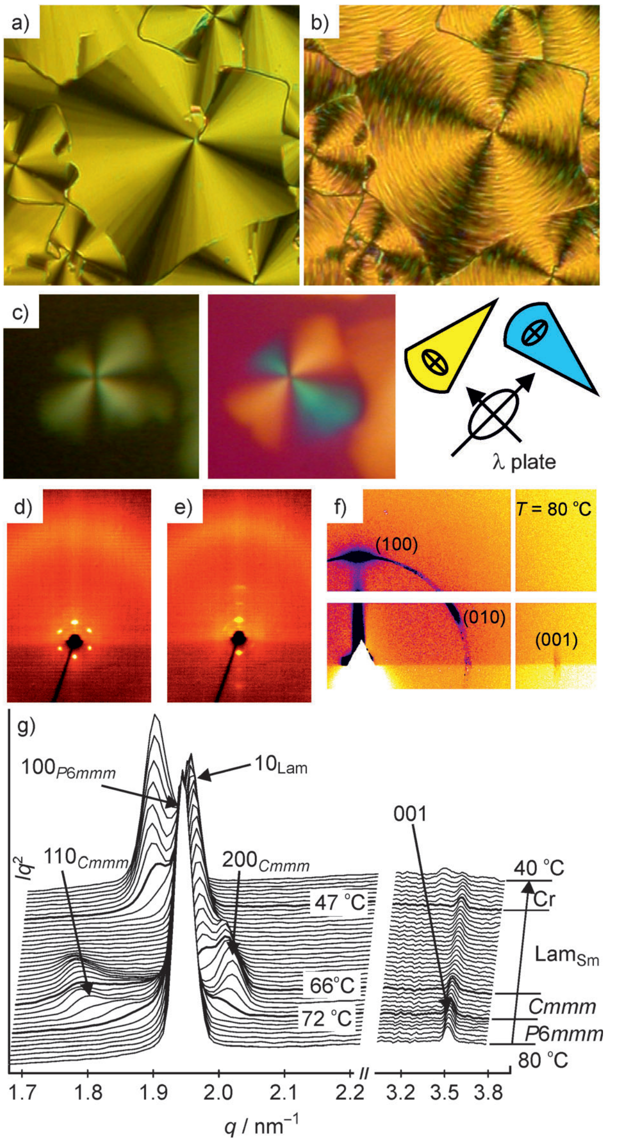

Figure 2. Mesophases of **1**. a) Polarized optical texture at $T = 90$ °C (*P*6/*mmm* phase) and b) at $T = 65$ °C (Lam_{Sm}/*p*2*mm* phase); c) single spherulite of the *P*6/*mmm* phase between crossed polarizers (left), with λ-retarder plate (middle), and indicatrix orientation of the retarder (right); d) XRD pattern (surface-aligned sample) at $T = 125$ °C (*P*6/*mmm*) and e) at $T = 59$ °C (Lam_{Sm}/*p*2*mm* phase); f) grazing-incidence small-angle X-ray scattering (GISAXS) pattern at $T = 80$ °C (*P*6/*mmm*); g) powder SAXS on continuous cooling at 5 K min^{-1}, covering the three LC phases and the crystal; two regions of interest are shown; the "001" peak changes from $001_{P6/mmm}$ via 001_{Cmmm} to $01_{\text{Lam}_{\text{Sm}}}$.

A 3D phase with $R\bar{3}m$ symmetry, in which the bundles are longitudinally shifted by ± *c*/3 between adjacent columns, was reported for related terphenyl-based bolaamphiphiles with two swallow tail side chains.[12] A possible reason for there being no longitudinal shift in **1** is that it has only one swallow tail attached to one end of the biphenyl, hence molecules on

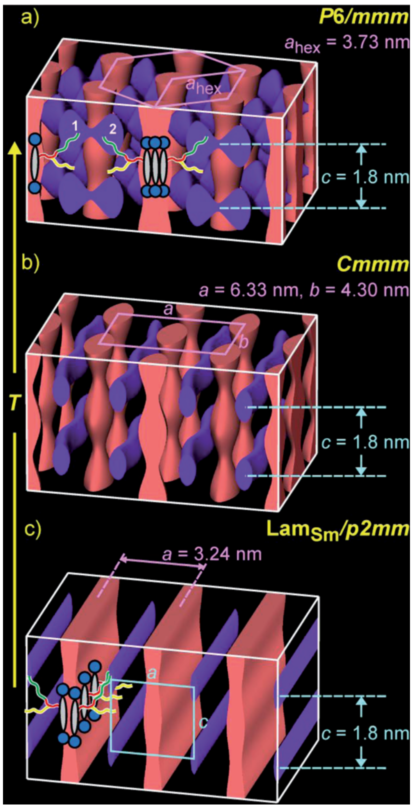

Figure 3. Electron-density maps obtained from synchrotron powder patterns of compound **1** at a) $T = 80$ °C; b) $T = 60$ °C, and c) $T = 52$ °C. Red = low density (bolaamphiphilic moieties); blue = high density (richest in R_F chains); molecules are sketched in (a) and (c).

neighboring columns could fit well together if mutually rotated by 180° in an antiparallel configuration. In contrast, the two side groups at each end of the related terphenyl compounds (Figure 1 d) would clash, hence the longitudinal shift in the $R\bar{3}m$ phase.

On decreasing the temperature, a transition to a lamellar phase (see Figure 2 b,e) takes place via an intermediate phase (for powder SAXS of the complete series on cooling, see Figure 2 g). The transition exotherms are relatively broad, and in the XRD patterns the intermediate phase can only be found coexisting with one of the two adjacent phases (see also the GISAXS pattern in Figure S2 and the temperature dependence of *d* spacings in Figure S3 in the Supporting Information). All but one of the diffraction peaks of the intermediate phase index on a rectangular 2D lattice of *c2mm* symmetry with lattice parameters $a = 6.33$ nm and $b =$ 4.30 nm (see Table S1 in the Supporting Information). However, the (001) reflection of the *P6*/*mmm* phase persists in the intermediate phase unaltered. Hence, the intermediate phase is 3D orthorhombic, $c = 1.80$ nm, space group *Cmmm*. As can be seen from the maps in Figure 3 a,b, at the *P6*/*mmm*–*Cmmm* transition the averaged column cross section turns from circular to elliptical. Figure 3 b also shows the presence of undulating R$_{\mathrm{F}}$-rich columns lying perpendicular to the main biphenyl columns. Thus, this crossed column mesophase consists of two orthogonal interpenetrating sets of columns, the modulated columns of the rod bundles and the undulating R$_{\mathrm{F}}$-rich columns.[14]

Interestingly, the *P6*/*mmm*–*Cmmm* transition occurs by continuous deformation of the hexagonal lattice (see the splitting of the $(100_{P6/mmm})$ reflection into (110_{Cmmm}) and (200_{Cmmm}) in Figure 2 g and Figure S3 in the Supporting Information). This finding is indicative of a second-order transition. Accordingly, it is expected that local domains of orthorhombic order also exist in the hexagonal phase, with three equally probable orientations in the *xy* plane; that is, the ribbons undergo correlated rotation. The idea is illustrated in Figure 4, where three orthorhombic cells (Figure 4 a) are superimposed (Figure 4 b). Note the maxima in electron density (purple) where three undulated ribbons overlap. These density maxima (e.g. the two labeled 1 and 2) are clearly seen in Figure 3 a (the dotted line in Figure 4 is the front plane in Figure 3 a). Moreover, in Figure S4 in the Supporting Information we added together three electron-density maps of Figure 3 b with three in-plane orientations: −60°, 0° and +60°. The combined map is almost indistinguishable from that of the hexagonal phase in Figure 3 a. Thus, we can conclude that the bundle columns are actually noncircular ribbons even in the *P6*/*mmm* phase, and XRD gives the time–space average. The reason for the noncircular shape is thought to be the need for the side chains on all biphenyls to access the surface and the peripheral corona, a situation unachievable with 14 biphenyls densely packed in a circular cylinder. Incidentally, there is a continuous slow increase in the number of molecules in a bundle as temperature decreases (see *d* spacing vs. temperature plot in Figure S3 and Table S2 in the Supporting Information). This widening of the ribbons helps stop their rotation and locks them in a mutually parallel orientation, with the consequent *P6*/*mmm*→*Cmmm* symmetry breaking.

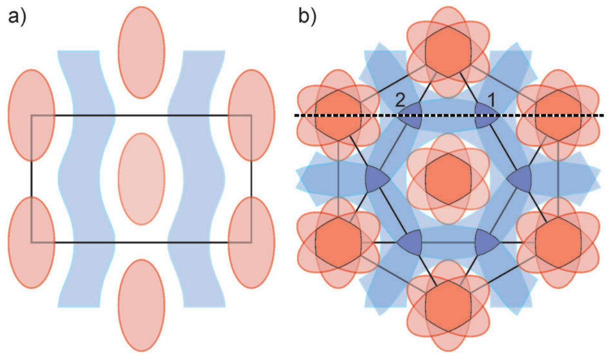

Figure 4. a) Schematic top view of the crossed columns of the *Cmmm* phase; b) superposition of three figures (a) after in-plane rotation by −60°, 0°, and +60°.

On further cooling, at the transition to the Lam$_{\mathrm{Sm}}$/*p2mm* phase, the ribbons fuse to form infinite sheets. Indeed, the layer spacing $a = 3.24$ nm is only slightly larger than $a/2 =$ 3.16 nm of the *Cmmm* phase (Figure 3 c). As typically observed for T-shaped amphiphiles with large lateral substituents, in lamellar (Lam) phases the rodlike units are parallel to the layer plane.[3,10] As shown by the persistence of the (001) reflection through the *P6*/*mmm*–*Cmmm*–Lam sequence (Figure 2 g), this periodicity is retained, confirming that the Lam phase has 2D long-range order (correlated layer phase, Lam$_{\mathrm{Sm}}$/*p2mm*).[15] At the *Cmmm*–Lam$_{\mathrm{Sm}}$ transition the R$_{\mathrm{F}}$-rich columns are retained but change from undulated to straight. Thus, the Lam$_{\mathrm{Sm}}$ phase features fluorinated columns between aromatic sheets.[16] This arrangement can be compared to a similar morphology recently reported in a rod–coil miktoarm star terpolymer.[17]

General comments on the phase sequence in laterally substituted bolaamphiphiles can be made with reference to Figure 1. The mesophases on the right (axial-bundle phases of compounds with large branched side chains) and on the left (polygonal honeycombs in compounds with smaller side chains), are the inverse of each other. Loosely speaking, if the aromatic and glycerol moiety is replaced by polar groups and water, the situation is analogous to direct (left) and inverse (right) lyotropic phases in polar and apolar amphiphiles. Even the elliptical deformation of the column cross section, which leads to rectangular phases when the Col–Lam transition is approached, is similar to the behavior observed in other self-organized amphiphilic systems. Current results suggest that at least in some of those amphiphiles the hexagonal phase may also consist of rotationally averaged ribbons.

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