Different Modes of Deformation of Soft Triangular Honeycombs at the Sub-5 nm Scale

Marco Poppe, Changlong Chen, Silvio Poppe, Christoph Kerzig, Feng Liu,* and Carsten Tschierske*

Patterning on the sub-5 nm length scale is a contemporary challenge for further miniaturization of microelectronic circuits. Here, the first soft self-assembled triangular patterns are reported showing transitions between regular and two different kinds of isosceles (acute and obtuse angled) triangles on this length scale, formed by liquid crystalline honeycombs of polyphilic block molecules involving a fluorinated oligo(para-phenylene ethynylene) core. The type of formed triangular pattern depends on the degree and position of fluorination and on temperature. They are the first soft honeycombs combining tilted and nontilted organizations in a uniform nanostructure, where the tilted molecules in only one or two sides of the triangular prismatic cells dominate the shape and the size of the morphology.

Nanoscale patterning has advanced in recent years with different kinds of nanostructures. Triangular tiling patterns, for example, were achieved in nets on surfaces, with metal–organic and covalent organic frameworks, by means of structural DNA/RNA nanotechnology and with triangular molecules. In soft matter systems honeycombs composed of triangular prismatic cells are known to be formed either by block copolymers on more than 100 nm scale or on a smaller length scale by T-shaped and X-shaped polyphilic block molecules involving a rod-like core-unit. In these honeycombs the shape of the prismatic is mainly determined by the ratio between the length of the rigid cores forming the honeycomb walls, and the volume of the lateral chains filling the space inside the resulting prismatic cells. In this case triangular honeycombs were obtained by combination of long rods with comparatively short lateral chains, but all previously reported nanostructures based on a monohedral triangular tiling involved exclusively regular triangles, leading to a hexagonal symmetry of the resulting net or honeycomb. To obtain irregular triangles the input of additional information is required.

Here, we report the first long range periodic soft matter structures composed of isosceles triangles and formed by self-assembly of a single type of molecular rods. The compounds represent X-shaped molecules involving a fluorinated rod-like oligo(para-phenylene ethynylene) (OPE) core with sticky hydrogen bonding glycerol units at both ends and two soft dodecylxy side chains at opposite sides of the OPE cores, inhibiting their clustering into layers. For the parent nonfluorinated compound H (see Figure 1) with two dodecylxy chains and all X = H, the formation of a hexagonal columnar liquid crystalline (LC) phase based on a regular triangular honeycomb was observed (C6h4a phase). Fluorination of the peripheral benzene rings removes the triangular honeycomb and replaces it by a bicontinuous cubic phase (Cubh, see Figure S10, Supporting Information). The effect of fluorination of the two inner benzene ring adjacent to the donor-substituted central ring, leading to an alternating donor–acceptor system is reported herein. It was found that for these compounds the triangular honeycomb structure is retained and stabilized. Even more interestingly, at lower temperature the triangular prismatic cells become distorted by tilting of the OPEs in some of the honeycomb walls, thus leading to new rectangular columnar LC phases composed of isosceles triangular prismatic cells.

The synthesis of the X-shaped compounds Fp was carried out in a sequence of Sonogashira cross coupling reactions as outlined in the Supporting Information. An overview over the phase sequences of the fluorinated compounds Fp compared to the nonfluorinated compound H is shown in Figure 1a (for numerical data, see Table S1 in the Supporting Information). In general, fluorination of the two inner benzene rings widens the LC phase range by reduction of the melting point and stabilizes the LC phases. The most dramatic stabilizing effect by +64 K compared to compound H is found for F2356 involving two tetrafluorinated rings. The effect of the electrostatic π–π interactions between aromatic units is obviously stronger than the steric distortion due to the bulkier fluorines and thus stabilizes LC self-assembly.

All compounds Fp show a hexagonal columnar mesophase with ππmm symmetry on cooling from the isotropic liquid, as indicated by the typical textures (Figures S2a,c and S3a, Supporting Information) and, the sharp Bragg reflections in small-angle X-ray scattering (SAXS) showing the reciprocal d-spacings in the ratio...
Figure 1. a) Structure (subscript n indicates the position(s) of the F-atom(s)) and LC phases of compounds Fₙ (recorded by DSC on cooling, 10 K min⁻¹) in comparison with compound H (all X = H).[12] For numerical data, transitions on heating, DSC traces and transition enthalpies, see Table S1 and Figure S1 (Supporting Information); abbreviations: Cr = crystalline solid, Colhex(a) = hexagonal columnar LC phase with triangular honeycomb structure and p6mm plane group; Cub/la3d = Cubₜ phase with la3d space group (double gyroid, see Figure S10, Supporting Information), M = unknown mesophase, Colrec/c2mm = rectangular columnar LC phases with isosceles triangular honeycomb structure and c2mm plane groups (see Figure 2); b–e) SAXS diffractograms of the Colhex(a)/p6mm phases of compounds H and Fₙ; f–i) reconstructed ED maps (for details, see Supporting Information). The red lines in (f) indicate a unit cell and black lines indicate the triangular tiling pattern of the OPE cores.
Δ angle for faces contribute with their projection and therefore the critical have the major influence on the birefringence, but the two other organization of the molecules. In this case the tilted molecules transition to the biaxial Col rec(b). For phase transition temperatures and enthalpies, see Table S1 and Figure S1c,d in the Supporting Information.

Compound F2356 having four instead of only two fluorines at each inner ring shows a similar phase sequence on cooling as compound F23 (Figure 1a). However, the ratio of $a_{\text{rec}}/b_{\text{rec}}$ is very distinct from that found for the $c2mm$ phase of F23. Taking the diffraction pattern at 208 °C as an example (Figure 2e), the lattice parameter $b_{\text{rec}} = 4.21$ nm is almost equal to $a_{\text{rec}}$, in contrast, $a_{\text{rec}} = 6.58$ nm is much smaller than the calculated distance $d = \sqrt{3/2} a_{\text{rec}} = 7.40$ nm in the hexagonal lattice. This means that in this case the rods forming the honeycomb walls in direction $b$ are nontilted or only weakly tilted, whereas those in the remaining walls are significantly tilted (see Figure 2f,g), thus being just the other way around than observed for F23. The tilt is estimated according to $\cos \beta = (a_{\text{rec}}/2)^2 + (b_{\text{rec}}/2)^2/L_{\text{mol}} = 3.91/4.5$ as $\beta = 29.8^\circ$, and developed a maximum of 35.7° upon continuous cooling. That the fundamental structure once again represents an isosceles triangular tiling is evident from the reconstructed ED map, shown in Figure 2f. Though in this structure the ratio between tilted and nontilted walls is 2:1, the planar textures other way around than for F23 (Figure 1a).

In the dark homeotropic areas of the uniaxial Col hex(3) phase (Figure 3a) the columns are arranged perpendicular to the surfaces and therefore it always appears optically isotropic if viewed along the columns. Depending on the surfaces and the alignment conditions either of these alignments, planar or homeotropic, can be obtained selectively. In an (almost) uniformly homeotropic alignment of the Col hex(3) phase with a surface tiling by regular triangles (Figure S3h, Supporting Information) a birefringent mosaic texture develops at the transition to the biaxial Col rec(3) phase (Figure 3a→b) with uniform orientation of the 2D lattice, i.e., uniform direction of the acute angled triangles over areas covering several 100 μm² (Figure S3h→i, Supporting Information). This transition is reversible and an isotropic texture is recovered at the transition back to the uniaxial hexagonal lattice with undeformed triangles on heating (Figure S3i→j, Supporting Information).

Overall, the number of tilted honeycomb walls per unit cell increases with growing fluorination from F3 with only one tilted to F2356 involving two tilted walls around each triangular prismatic cell. If the electrostatic surface potentials maps of the OPE cores of compounds F3, F23, and F2356 are compared (Figure 3e–g), the electron density of the π-faces of the inner
benzene rings decreases with increasing fluorination (color changes from yellow to green) whereas the surface potential of the outer rings and especially the acetylene units remains relatively high. Thus, a main contribution to mesophase stabilization and development of tilt is assumed to result from an increasing contribution of electrostatic interactions between the electron deficit fluorinated benzenes with the electron rich acetylene units of the adjacent molecules.\[15\] This requires a longitudinal shift of the aromatics which leads to a tilt in the range of \(\approx 40^\circ\) (Figure 3h), being close to the experimentally observed tilt \(\beta\). The increasing contribution of \(\pi-\pi\) stacking is also in line with the WAXS patterns (Figure 2h). Whereas the shoulder at \(d \approx 0.36\) nm develops gradually stronger from \(F_3\), \(F_{23}\) to \(F_{2356}\), this scattering is still diffuse in all cases, which indicates a short correlation length of \(\pi-\pi\) stacking, and that the system is still in the fluid state. In addition to the molecular mobility the rotational barrier around the C–C bonds along the OPE core is less than 10 kJ mol\(^{-1}\),\[19\] leading to a fast equilibrium of different rotamers.\[20\]

To explain the origin of the formation of prismatic cells enclosed by shells composed of sides involving tilted and others involving nontilted rods, it must be considered that the space required by the alkyl chains decreases with lowering temperature and the space inside the triangular cells can be adjusted by tilting. Because efficient \(\pi-\pi\) stacking requires a certain fixed tilt angle close to \(40^\circ\), tilting is not possible for all three walls as this would reduce the available space too much to accommodate the lateral chains. In the case of \(F_{23}\) with weak \(\pi-\pi\) stacking, the ratio of tilted and nontilted molecules is 1:2.\[21\] While in the case of \(F_{2356}\) the strongest driving force for tilted organization requires that most molecules become tilted, two thirds of them tilt significantly while only one third does not tilt or tilts only slightly. Thus, there is a delicate balance of competitive \(\pi-\pi\) stacking and temperature dependent space filling effects, which determines the mode of deformation of the triangular cells (Figure 3i–k).

In summary, aromatic fluorination of X-shaped bolaphilic OPEs at the inner benzene rings stabilizes triangular honeycombs (Figures 1a and 3j). The packing of the cores along the cylinder walls becomes denser due to polar interactions between the electron deficit fluorinated rings and the electron rich acetylenes, the developing \(\pi\)-stacking requires a longitudinal shift which then leads to a significant tilt of the molecules in the cylinder walls, thus providing two new types of triangular honeycombs composed of isosceles triangular prismatic cells, being either acute or obtuse angled (Figure 3i,k). These tunable soft triangular patterns have potential for use in nanoscale patterning and for soft nanolithography with regular and non-regular triangular patterns on the sub-5 nm length scale. Furthermore, the combination of different modes of \(\pi\)-stacking in these uniform LC soft matter structures could lead to promising materials for photophysical and charge carrier applications.\[22\]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 3. a–d) Transition from Col\(_{\text{hex}}\)/p6\(\text{mm}\) to Col\(_{\text{hex}}\)/c2\(\text{mm}\) of compound \(F_3\) as observed by polarizing microscopy in the indicated phases at the given temperatures; the insets in (b,d) show the textures with additional \(\lambda\)-retarder plate, indicating negative birefringence in (b) and positive birefringence in (d); the direction of the polarizers is shown by arrows and the indicatrix slow axis by a dashed line in (c); for more details, see Figures S3 and S4 in the Supporting Information. e–g) Comparison of the electrostatic surface potential maps of model compounds for \(F_3\), \(F_{23}\), and \(F_{2356}\) (with \(n = 1\)) as determined by DFT calculation (B3LYP functional and 6–31G basis set, for \(F_{23}\), see Figure S12 in the Supporting Information); red indicates high and blue low negative surface potential; h) shows the staggered arrangement of \(F_{2356}\) in the tilted cylinder walls of the Col\(_{\text{rec}}(\alpha)/c2\text{mm}\) phase with \(\pi\)-stacking between the tetrafluorobenzene acceptor units and the adjacent triple bonds as donors, leading to a tilt of \(\approx 40^\circ\); i–k) models showing the organization of the rods in the distinct triangular honeycombs, red lines represent the deformation directions of the triangles; for 3d models and possible modes of tilt correlation, see Figure S11 in the Supporting Information.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bolaamphiphiles, columnar phases, honeycombs, liquid crystals, oligo(phenylene ethynylene), soft patterning, triangular tiling

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[21] Note that as the lattice parameter b shrinks, a rec expands a little to keep the volume decreasing not too much with lowering temperature (Figures 2c and S6).
[22] Already in solution compounds H and F2356 have promising photochemical properties such as pronounced visible-light absorption, blue-light emission and an attractive HOMO–LUMO gap, see Figures S13 and S15.