Swallow-Tailed Polycatenars: Controlling Complex Liquid Crystal Self-Assembly and Mirror Symmetry Breaking at the Lamellae-Network Cross-Over

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1. Introduction

Using sunlight as a sustainable energy source is of vital interest for the survival of the continuously growing mankind. As known from nature, efficient light-harvesting requires the aggregation and defined organization of arrays of \( \pi \)-conjugated molecules in soft systems is of importance for the design of new materials with application relevant optimized properties. Here, soft self-assembly of functional multi-chained \( \pi \)-conjugated 5,5′-diphenyl-2,2′-bithiophenes is investigated. Focus is on molecules with a 3,5-disubstitution pattern at one end and no or only a single chain at the other end. By elongation of the single terminal chain, a transition from lamellar phases to helical networks is observed. With lowering the temperature, the lamellar phase types change from smectic via hexatic to crystalline. In some cases, different kinds of orders are combined in a single uniform lamellar structure. Moreover, a transition from uniform (synclinic) to alternating (anticlinic) tilt in adjacent layers is observed with decreasing chain length or rising temperature, due to a change of the molecular conformation from tuning fork like to Y-shaped. For compounds terminated with a long chain, helical self-assembly of the \( \pi \)-conjugated rods in networks takes place, leading either to a racemic \((Ia3d, gyroid)\) or a spontaneous mirror symmetry broken \((I23)\) bicontinuous cubic phase and a chiral isotropic liquid phase \((Iso)\) as well. This work establishes rules for controlling the self-assembly of functional \( \pi \)-conjugated rods in soft matter and fluids.

Controlling the spatial organization of \( \pi \)-conjugated molecules in soft systems is of importance for the design of new materials with application relevant optimized properties. Here, soft self-assembly of functional multi-chained \( \pi \)-conjugated 5,5′-diphenyl-2,2′-bithiophenes is investigated. Focus is on molecules with a 3,5-disubstitution pattern at one end and no or only a single chain at the other end. By elongation of the single terminal chain, a transition from lamellar phases to helical networks is observed. With lowering the temperature, the lamellar phase types change from smectic via hexatic to crystalline. In some cases, different kinds of orders are combined in a single uniform lamellar structure. Moreover, a transition from uniform (synclinic) to alternating (anticlinic) tilt in adjacent layers is observed with decreasing chain length or rising temperature, due to a change of the molecular conformation from tuning fork like to Y-shaped. For compounds terminated with a long chain, helical self-assembly of the \( \pi \)-conjugated rods in networks takes place, leading either to a racemic \((Ia3d, gyroid)\) or a spontaneous mirror symmetry broken \((I23)\) bicontinuous cubic phase and a chiral isotropic liquid phase \((Iso)\) as well. This work establishes rules for controlling the self-assembly of functional \( \pi \)-conjugated rods in soft matter and fluids.

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amplification effects, observed in some of the Cub_{h}i phases,[27–32] in the adjacent non-cubic tetragonal[33] and the isotropic liquid phases (Iso_i)[6] of these achiral polycatenar compounds[24–26] has renewed the interest in this class of compounds.[37–39] Such spontaneously chiral soft matter systems are of potential technological interest and might also be of importance for the understanding of the mechanism of emergence of uniform chirality.[40–42]

In this work we explore structural modification of 5,5'-diphenyl-2,2'-bithiophene-based polycatenar compounds[27a,28,29,33,34a] and we establish the fundamental understanding of these effect on the mesogenic self-assembly at the crossover from lamellar phases to helical networks. The study focuses on new series of compounds with an 3,5-disubstitution pattern at one end and being either non-terminated (Bm/H) or terminated with only a single alkyl chain at the other end (Bm/n and B'n). Although the 3,5-disubstitution pattern was used in few cases for the design of columnar LCs,[43–48] Cub_{h}i phases,[9,24,36,49–52] and functional liquids,[53] it is much less common compared to the huge number of examples of materials with 3,4-disubstitution and the 3,4,5-trisubstitution patterns.[9]

H_{2m+1}C_{m}O

H_{2m+1}C_{m}O

R

B_{x}= 1, R = H, OC_{n}H_{2n+1}
B'_{x}= 0, R = OC_{n}H_{2n+1}

B10/H (R = H): Dicatenar
Bm/n. B'6/n (n > 0): Tricatenar

It is shown that these new swallow-tailed[54,55] compounds provide access to unique materials combining a rich diversity of different modes of self-assembly. Firstly, they offer a new access to the anticlinic-tilted smectic phases (SmC_a). Secondly, several higher ordered hexatic (Hex) and crystalline lamellar mesophases, including those combining smectic and hexatic self-assembly in a single uniform structure, are observed. Thirdly, chiral and achiral Cub_{h}i phases, birefringent 3D mesophases and a mirror symmetry broken isotropic liquid (Iso_i) involving helically organized bithiophene units are obtained by only tiny changes of the molecular structure. An understanding of this exceptionally wide diversity of self-assembled soft matter structures is based on transitions between tuning fork like and Y-like conformations leading to distinct degrees of intercalation, and thus, to the transition between lamellar organizations and helical self-assembly in networks.

2. Methods

The synthesis of the compounds was performed as described in Scheme 1, for details see the Supporting Information.[56] The compounds were investigated by optical microscopy between crossed or slightly uncrossed polarizers (polarizing microscopy = POM) in films between glass plates and in freely suspended thin films, by differential scanning calorimetry (DSC) and by X-ray scattering, small-angle scattering (SAXS) and wide-angle scattering (WAXS), of powder-like samples and aligned samples. The used instrumentation and other details are described in the Supporting Information.

Scheme 1. Synthesis of compounds under investigation. Reagents and conditions: i) DCC, DMAP, DCM, RT; ii) [Pd(PPh_{3})_{4}], THF/sat. NaHCO_{3}-solution, reflux; iii) NBS, THF, RT, absence of light; iv) C_{n}H_{2n+1}Br, K_{2}CO_{3}, Bu_{4}NI, MEK, reflux; v): 1) benzoic acid + SOCl_{2}, 2) 6a-c/OH, pyridine, DMAP, DCM, RT.

3. Results and Discussion

3.1. Effects of Alkyl Chain Number and Chain Distribution

For compounds with decyl chains, as example, the effect of the number and position of the chains was investigated (Figure 1 and Table S6, Supporting Information). As shown in Figure 1, there is a transition from a synclinic tilted lamellar phase (SmC_a) via Cub_{h}i to Col_{hex} upon increasing the number of alkyl chains from three via four to five. Compounds with two chains (e.g., B10/H) form only lamellar phases, those with five and more chains exclusively columnar phases (Col_{hex}, G10/10) and those with three and four chains can form lamellar, Cub_{h}i, as well as columnar phases, depending on structural details. For example, a non-symmetric chain distribution (A10/10,[27a] A10/H,[27a] and B10/10) is favorable for Cub_{h}i phase formation, whereas the more symmetric analogs C10/10 and D10/10 form only a smectic phase (SmC_a).
of these achiral molecules. Generally, the 3,5-disubstitution pattern lowers all transition temperatures compared to the related 3,4- and the 3,4,5-substituted compounds, which shifts the LC ranges toward ambient temperature (Figure 1). Only for compound F10/10 having the 3,5-disubstitution at both ends soft self-assembly is completely lost due to this effect.

3.2. Self-Assembly of Compound B10/H with Two Chains at the Same End

Compound B10/H has only two chains which are both attached at the same 3,5-substituted end of a rod-like core. It shows three reproducible phase transitions in the DSC traces (Figure 2d and Table 1). On cooling the first transition from the isotropic liquid to a synclinic SmC\(_c\) phase takes place at 169 °C (3.0–2.8 kJ mol\(^{-1}\)). As shown in Figure 2a, the optical extinction brushes in POM are inclined with the direction of the analyzer by an angle of ≈40°. This corroborates with a uniform tilt direction of the molecules in adjacent layers (synclinic tilt = SmC\(_C\)).

The diffuse WAXS with a maximum at \(d = 0.45\) nm confirms the liquid-like order in the layers (Figure 2e) and the sharp small angle scattering at \(d = 4.21\) to 4.26 nm (Figure 2f, Figure S22c, Supporting Information) corresponds to the molecular length \(l_{\text{mol}} = 4.2\) nm (Figure 3a). In the 2D scattering patterns of aligned samples the wide angle scattering maximum is inclined to the layer reflection with a tilt angle of \(\beta = 37°\) (Figure 2e and Figure S22a,b, Supporting Information). In a smectic phase with this \(d\)-value and a tilt of 37° the required molecular length would be \(L = d/\cos\beta = 5.3\) nm. This is significantly longer than \(l_{\text{mol}}\) and therefore excludes the fully intercalated and non-segregated packing shown in Figure 3a. In contrast, the full segregation of the aromatic and aliphatic units in the antiparallel packing with intercalation of only the aromatic cores leads to a layer thickness of 5.5 nm (Figure 3b) which is close to 5.3 nm. This mode of packing is not only supported by the segregation of the flexible aliphatic chains from the rigid polyaromatic units, but also allows a side-by-side packing of an equal number of chains and aromatic cores (2/2) in the respective layers, which minimizes the interfacial curvature, and thus supports the lamellar organization.

Upon cooling, at the phase transition at 111 °C, the homeotropic texture becomes smoother and no change is visible in the planar regions, and there is no visible change at the next phase transition at 80 °C, either (Figure 2b,c). The birefringence as well as the inclination of the extinctions in planar alignment is retained in all three phases, meaning that the tilt correlation and the tilt angle do not change markedly (Figure 2a–c). Also the SANS pattern remains almost the same in all three mesophases, that is, all of them represent synclinic tilted lamellar phases (Figure S22c,e,f, Supporting Information). Clear changes can be observed for the wide-angle scattering, which has a diffuse character in the SmC\(_C\) range and becomes narrower and asymmetric at 111 °C (Figure 2e). The angular scattering profile can be deconvoluted into a sharper peak at \(d = 0.46\) nm and a diffuse one with a maximum at \(d = 0.42\) nm (Figure 2e, Figure S22g, Supporting Information). This scattering pattern is similar to that reported by Heppke et al. for the so-called SmM\(_S\)/SmM phases of chiral rod-like compounds and their racemates. Based on the powder X-ray scattering data in

Moreover, the 3,4-disubstitution pattern of the three chain compound C10/10 favors smectic phases whereas the isomeric compound B10/10 with 3,5-disubstitution pattern forms a Cub\(_{bi}\) phase, indicating the importance of the molecular shape, being tuning fork like for the smectogenic 3,4-disubstituted compound C10/10 and Y-like for the cubogenic 3,5-disubstituted compound B10/10. Interestingly, the Cub\(_{bi}\) phase is achiral with \(l_{3d}\) space group for the taper shaped tricatenar compounds A10/H and B10/10 which have the alkyl chains at only one end and becomes chiral with \(l_{3d}\) space group for the tetracatenars compound A10/10 with an additional chain at the opposite end. This indicates the importance of chain number (and chain volume) for the selection of the Cub\(_{bi}\) phase type and emergence of mirror symmetry breaking in the soft matter phases.
Figure 2e,f, we propose a model where aliphatic and aromatic segments are fully segregated (Figure 3b). The synclinic SmC$_s$ layers of the aromatic cores, providing the diffuse scattering with a maximum at $d = 0.42$ nm, alternate with higher ordered and also synclinic tilted Hex$_l$-like (Figure 2h) alkyl chain layers,[59–61] giving rise to the sharper scattering at $d = 0.46$ nm. Similar segregated structures with different order in the distinct sublayers have been found for swallow-tailed molecules with
Table 1. Phase transitions and lattice parameters of the di- and tricatenars B10/n depending on the 4′-alkyl chain length (n).

| Comp. | n | Phase transitions T [°C] | ΔH[kJ mol⁻¹] | d/nm (T [°C]) | d_cub/ nm (T [°C]) |
|-------|---|--------------------------|--------------|--------------|-------------------|
| B10/H | H | H: Cr 91 [10.9] Hexd, 113 [5.9] SmC₁ 171 [3.0] Iso | – | 4.26 [140] |
|       |   | C: Iso 169 [−2.8] SmC₁, 111 [−5.9] Hexd, 80 [−5.3] CG < 20 Cr | – | 4.33 [100] |
| B10/6 | OC₁₂H₂₅ | H: Cr 98 [24.3] SmC₁ 151 [0.4] Cubb₁/ia 3d 191 [1.8]Iso | 4.5 [120] | 10.9 [170] |
|       |   | C: Iso 187 [−0.1] Iso, 155 [−0.7] Cubb₁/ia 3d + SmQ + SmC₁, 76 [−21.7] Cr | – | – |
| B10/8 | OC₁₄H₂₇ | H: Cr 102 [30.5] Cubb₁/ia 3d 126 [−3] M1 138 [−189] [2.1] Iso | – | 11.0 [180] |
|       |   | C: Iso 183 [−0.1] Iso, 168 [−0.6] Cubb₁/ia 3d 58 [−19.3] Cr | – | – |
| B10/10| OC₁₆H₃₃ | H: Cr 116 [53.4] Cubb₁/ia 3d 185 [2.3] Iso | – | 11.3 [150] |
|       |   | C: Iso 177 [−1.3] Cubb₁/ia 3d 89 [−33.5] Cr | – | – |
| B10/16| OC₁₄H₃₃ | H: Cr 114 [74.3] Cubb₁/ia 3d [−3] 160 Cubb₁/ia 3d [23] 173 [2.0] Iso | – | 11.5 [130] |
|       |   | C: Iso 166 [−0.1] Iso, 164 [−0.7] Cubb₁/ia 3d 75 [−17.1] Cr | – | 17.7 [165] |
| B10/22| OC₂₂H₄₅ | H: Cr 104 [34.8] Cubb₁/ia 3d [23] 171 [2.8] Iso | – | 18.1 [140] |
|       |   | C: Iso 166 [−1.7] Cubb₁/ia 3d 159 [−0.7] Cubb₁/ia 3d [23] 73 [−43.4] Cr | – | – |

4° Peak temperatures as obtained by DSC at a scanning rate of 10 K min⁻¹ on heating (H) or cooling (C); Iso, isotropic liquid; SmQ, low birefringent mesophases with mosaic-like texture, presumably representing a tetragonal 3D phase composed of helical networks with 90° four-way junctions (see Figure 7c).[33] M1, low birefringent mesophase with non-specific texture (see Figure S10a, Supporting Information), only observed on heating; Cubb₁/ia 3d, oblique columnar phase (Figures S11 and S21c, Supporting Information); for the other abbreviations, see Figure 1; for DSC traces, see Figure 2a and Figure S2, Supporting Information; for X-ray data, see Tables S1 and S2, Supporting Information. All three phases can coexist in different ratios depending on the precise conditions; due to slow transitions no DSC peaks can be observed.

3.3. Synclinic Tilted Lamellar Phases of Compounds B10/n

The synclinic SmCₖ phase, observed for the two-chain compound B10/H is retained for the 4′-hexyloxy substituted tricatenar compound B10/6 where it is stable up to 151 °C; above this temperature it is replaced by an optically isotropic Cubb₁ phase (Table 1). This is in line with the growing interfacial curvature caused by the space required by the additional alkyl chain at the apex, which becomes even more important at higher temperature due to thermal expansion. The layer spacing in the SmCₖ phase is d = 4.5 nm which, despite of the expanded molecular length of L_{mol} = 5.1 nm, is only slightly larger than for B10/H without the additional apex chain. This means that the organization should be dominated by an antiparallel packing of thermolecules with fully segregated aromatic and alkyl chain layers, as shown in Figure 3d. This retains the layer spacing of the smectic phase despite of the elongation of the molecule, and is likely to provide an increased tendency to assume interfacial curvature (2 rods vs 3 chains side-by-side), leading to a transition from lamellar to Cubb₁ phases. The longer homologues show exclusively cubic phases and therefore will be discussed further below.

3.4. Anticlinic Smectic Phases of the Swallow-Tailed Compounds B6/n with Short 3,5-Chains

In the series of compounds B6/n with two shorter hexyloxy chains at the 3,5-substituted end the transition temperatures are much higher and smectic phases can be found up to a longer apex chain length of n = 10, for which a Cubb₁ phase coexists with a smectic phase and for the next homologue B6/12 exclusively the Cubb₁ phase is observed (Table 2). However, as shown below, the smectic phases of all compounds B6/n have anticlinic tilt (SmCₖ) and there are no additional hexatic or crystalline low temperature phases, irrespectively if the 4′-chain is odd- or even-numbered (B6/6 vs B6/5, see Table 2), or if it is an alkyl (B6/6a) or alkoxy chain.[65]

The optical textures of planar samples of the smectic phase show dark extinction brushes parallel to the polarizer and analyzer (Figure 4b,c), thus indicating that the optical axis is parallel to the layer normal. Homeotropic samples show birefringent schlieren textures with dominating two brush disclinations, but also few 4-brush disclinations can be found (Figure 4a). This texture is in line with an anticlinic tilted SmCₖ phase.[66–70] In the synclinic tilted SmCₖ phases there would be only 4-brush disclinations, whereas in a non-tilted SmA₁ phase,[71,72] exclusively two brush disclinations would be expected.[73] Thus, the textures in planar as...
well as in homeotropic alignment indicate the formation of an anticlinic SmC\(a\) phase for the compounds B6/\(n\) (see also Figure S13, Supporting Information). The anticlinic tilt is corroborated by investigation of freely suspended (FS) films of compound B6/5 (Figure S16a,b, Supporting Information), where the Schlieren texture, involving half-integer and rare integer defects, remains the same at oblique incidence, independent on the tilt direction of the film with respect to the beam direction.

For compounds B6/4–B6/10 the layer spacing is around \(d = 4.2\ \text{nm}\) and almost independent on the alkyl chain length (Table 2 and Figure S19a–c, Supporting Information). Only for B6/10 a slight increase of the layer spacing to \(d = 4.4\ \text{nm}\) is observed. The completely intercalated and fully segregated organization of B6/4, shown in Figure 3e, would lead only to a value of \(L = 4.3\ \text{nm}\) for the molecular pairs which would not allow the development of a reasonable tilt and therefore appears less likely. Only mixing of the 4′-alkyl chains with the aromatic rods in the partly intercalated structure in Figure 3f leads to pairs with a length of 5.0 nm allowing a significant tilt. Moreover, in this arrangement the molecules can easily assume a Y-shape, where the 3,5-chains tend to be aligned almost parallel to the layer planes (Figure 3f,h). This reduces the out-of-plane inter-layer fluctuations and favors the anticlinic character of tilt.\(^{[66,74]}\) Simultaneously, in this Y-conformation the chains are less ordered and therefore no hexatic phase can be observed in the series of compound B6/\(n\).
Y-conformation becomes difficult for longer 3,5-chains (compounds B10/n) which favor a parallel alignment of the alkyl chains (Figure 3c) to maximize the dispersion interactions and to minimize the excluded volume.\[^{[74]}\] The resulting tuning fork like conformation (Figure 3g) supports the synclinic tilt correlation by allowing more interlayer fluctuations.\[^{[74]}\]

For compounds 6/n with a longer 4'-alkyl chain (n > 10) the intercalation of the incompatible aromatics and alkyl chains becomes unfavorable and these chains are forced to be located in common layers with the 3,5-chains (as shown for B6/6 and B6/4 in Figure 3d,e). This enlarges the effective cross-sectional area of the alkyl chains, thus increasing the interface curvature (Table 2). This makes the transition into the tilted smectic phase unfavorable and these chains are forced to be located in common layers with the 3,5-chains (as shown for B6/6 and B6/4 in Figure 3d,e). This enlarges the effective cross-sectional area of the alkyl chains, thus increasing the interface curvature (Table 2).

3.5. Lamellar Phases in the Series B6/n with Short Cores: Transitions from Anticlinic Smectic to Synclinic Tilted and Non-Tilted Hexatic Phases

The series of compounds B6/n with a shorter five-ring core forms lamellar phases only for the compounds with n = 6 and 8 (Table 3). The X-ray scattering pattern confirms a smectic phase (Figures S23a,b and S24a, Supporting Information) with a diffuse wide angle scattering (Figure 5h) in the high-temperature smectic phase of B6/6. The typical fan-like textures with dark extinction lines parallel to the polarizers in planar alignment and a low birefringent schlieren texture with two- and four brush disclinations in homeotropic alignment indicate a SmC\(_{\parallel}\) phase (Figure 5a,b), which is additionally confirmed by investigation of FS films, as described above for B6/5 (see Figure S16c, Supporting Information).

The layer spacing of B6/6 is with \(d = 4.3\) nm almost the same as for the longer molecule B6/6 (\(d = 4.2\) nm) and quite a bit longer than the single molecular length of B6/6 (\(l_{\text{mol}} = 3.9\) nm). This excludes the fully intercalated and completely segregated packing (similar to Figure 3e) and indicates an only partly intercalated packing with the alkyl chain at the apex mixed between the aromatic cores, the same as described for compounds B6/n and shown in Figure 3f and Figure S26c, Supporting Information. These pairs have a length \(L = 4.8\) nm allowing a bit smaller tilt of about 20–25°. On cooling B6/6 there are additional phase transitions. These transitions are mostly clearly seen in homeotropic samples, where the schlieren

Table 2. Phase transitions and lattice parameters of the swallow-tailed tricatenars B6/n with different groups at the apex.

| Comp.\(^{[n]}\) | R            | Phase transitions T [°C] \(\Delta H\) [kJ mol\(^{-1}\)] | \(d/\text{nm} (T [°C])\) | \(a_{\text{sub}}/\text{nm} (T [°C])\) |
|----------------|--------------|----------------------------------------------------------|----------------------------|------------------------------------------|
| B6/4           | OC\(_{3}\)H\(_{3}\) | H: Cr 138 [29.0] SmC\(_{\parallel}\) 215 [1.4] N 220 [0.4] Iso C: Iso 177 [1.7] N 191 [1.9] | 4.2 (180) | – |
| B6/5           | OC\(_{5}\)H\(_{11}\) | H: Cr 139 [32.2] SmC\(_{\parallel}\) 209 [2.2] Iso C: Iso 130 [2.5] N 180 [2.5] | 4.1 (180) | – |
| B6/6           | OC\(_{6}\)H\(_{13}\) | H: Cr 123 [25.9] SmC\(_{\parallel}\) 203 [1.7] Iso\(^{[1]}\) 208 [0.1] Iso C: Iso 205 [1.0] N 199 [1.5] | 4.1 (160) | – |
| B6/8           | OC\(_{4}\)H\(_{12}\) | H: Cr 117 [21.7] SmC\(_{\parallel}\) 184 [0.9] Iso\(^{[1]}\) 200 [0.1] Iso C: Iso 196 [0.9] N 177 [0.8] SmC\(_{\parallel}\) 196 [2.7] | 4.2 (150) | – |
| B6/10          | OC\(_{10}\)H\(_{21}\) | H: Cr 115 [65.3] SmC\(_{\parallel}\) 145 [−1] M1 150 [−1] M2 151−156 [−1] Cub\(_{\parallel}\)//i\(_{\text{a}}3d\) 198 [2.7] Iso C: Iso 191 [−0.3] Iso\(^{[1]}\) 178 [−1] Cub\(_{\parallel}///i_{\text{a}}3d\) 105 [−1] SmC\(_{\parallel}\) 83 [−61.3] | 4.4 (120) | 10.0 (170) |
| B6/12          | OC\(_{12}\)H\(_{25}\) | H: Cr 111 [55.8] Cub\(_{\parallel}///i_{\text{a}}3d\) 197 [2.9] Iso C: Iso 189 [−2.1] Cub\(_{\parallel}///i_{\text{a}}3d\) 91 [−55.9] | – | 10.2 (160) |
| B6/16          | OC\(_{6}\)H\(_{13}\) | H: Cr 103 [27.2] Cub\(_{\parallel}///i_{\text{a}}3d\) 191 [3.1] Iso C: Iso 182 [−2.1] Cub\(_{\parallel}///i_{\text{a}}3d\) 91 [−29.4] | – | 10.6 (150) |
| B6/22          | OC\(_{12}\)H\(_{41}\) | H: Cr 94 [45.7] Cub\(_{\parallel}///i_{\text{a}}3d\) 180 [2.4] Iso C: Iso 173 [−2.1] Cub\(_{\parallel}///i_{\text{a}}3d\) 78 [−44.6] | – | 11.3 (140) |
| B6/6a          | C\(_{5}\)H\(_{13}\) | H: Cr 124 [28.9] SmC\(_{\parallel}\) 206 [0.9] Iso\(^{[1]}\) 209 [0.2] Iso C: Iso 206 [−0.3] Iso\(^{[1]}\) 203 [−1.9] SmC\(_{\parallel}\) 88 [−23.3] | 4.2 (150) | – |
| B6/7Me         | OCH(CH\(_{3}\))C\(_{2}\)H\(_{13}\) | H: Cr 116 [32.0] Cub\(_{\parallel}///i_{\text{a}}3d\) 130 [1.8] Iso C: Iso 121 [−1.5] Cub\(_{\parallel}///i_{\text{a}}3d\) 8 < 20 | – | 8.9 (125) |

\(^{[n]}\)Phase temperatures as obtained by DSC at a scanning rate of 10 K min\(^{-1}\) on heating (H) or cooling (C); SmC\(_{\parallel}\), anticlinic tilted SmC phase; M2, 3D mesophases with medium birefringence (see Figure 7); for the other abbreviations, see Figure 1 and Table 1; for DSC traces, see Figure S3a–h, Supporting Information; for X-ray data, see Tables S1 and S5, Supporting Information; \(^{[1]}\)Enthalpy for both transitions Iso⇔N⇔SmC\(_{\parallel}\); \(^{[2]}\)Enthalpy value cannot be determined because the transition is slow; these transition temperatures were obtained by optical investigations.

\(^{[n]}\)Phase transitions and lattice parameters of the swallow-tailed tricatenars B6/n with different groups at the apex.
Table 3. Phase transitions and lattice parameters of the swallow-tailed tricatenars B’6/n depending on the length of the 4’-alkyl chain (n).

| Comp. | n | Phase transitions T [°C] [ΔH [kJ mol⁻¹]] | α_sub/nm (T [°C]) |
|-------|---|-----------------------------------------|------------------|
| B’6/6 | 6 | H: M 109 [4.3] HexF 144 [7.3] HexF 147 [0.1] SmC 159 [4.4] Iso | – |
|       |   | C: Iso 156 [−4.3] SmC 145 [0−0.1] HexF 141 [−6.5] HexF 104 [−3.3] M | |
| B’6/8 | 8 | H: Cr 114 [10.9] HexB 125 HexF 128 [2.9] SmC 135 [1.0] Iso 142 [0.2] Iso | – |
|       |   | C: Iso 140 [−0.3] Iso 130 [−1.0] SmC 127 HexF 123 [−2.7] HexB 107 [−11.2] Cr | |
| B’6/10| 10| H: Cr 113 [44.8] SmQ + Cubb/loTd 128 [0.2] Iso 117 [2.2] Iso | 9.2 (115) |
|       |   | C: Iso 131 [−0.2] Iso 118 [−0.4] SmQ + Cubb/loTd 103 [−26.1] Cr | |
| B’6/12| 12| H: Cr 114 [52.3] Cubb/loTd 133 [2.8] Iso | 9.4 (125) |
|       |   | C: Iso 123 [−1.1] Cubb/loTd 98 [−51.1] Cr | |
| B’6/16| 16| H: Cr 102 [62.3] Cubb/loTd 128 [3.6] Iso | 9.6 (120) |
|       |   | C: Iso 125 [−3.0] Cubb/loTd 92 [−52.6] Cr | |
| B’6/20| 20| H: Cr 106 [90.9] Cubb/loTd 124 [3.9] Iso | 10.0 (115) |
|       |   | C: Iso 119 [−3.2] Cubb/loTd 88 [−85.2] Cr | |

*Peak temperatures as obtained by DSC at a scanning rate of 10 K min⁻¹ on heating (H) or cooling (C); HexB, hexatic B phase (molecules are orthogonal to the layer planes); M, unknown low temperature lamellar phase (see Figures S15 and S24b, Supporting Information); for other abbreviations, see Figure 1 and Table 1; for DSC traces, see Figure S4, Supporting Information; for X-ray data, see Tables S1 and S5, Supporting Information; b) Transition enthalpy for both transitions CrB-HexF s-SmCa; c) Both forms of the smectic B phase (s), CrB-HexFs, and SmCa-HexFs (s), are present, but SmCa is the high temperature phase; d) Both forms of the smectic B phase (s), CrB-HexFs, and SmCa-HexFs (s), are present, but SmCa is the high temperature phase.*

A sequence of different lamellar phases is also observed for the next homologue B’6/8 (Figure 6), however the phases are distinct from those of B’6/6. The high temperature phase is again a SmC a phase (Figure 6a). On cooling the birefringence of the schlieren texture decreases, the fans become broken (Figure 6b) and the wide-angle scattering sharpens slightly, in line with a SmC a-HexFs transition (Figure 6c). Again the layer spacing increases due to the chain stretching (Figure 6f), but this effect is even larger than for B’6/6. In powder patterns the wide angle scattering remains symmetric and in aligned samples it has a maximum around the equator, as typical for the transition to hexF phase (Figure 6e and Figure S25, Supporting Information). The stripe patterns across the fans, occurring at the transition to HexF (Figure 6b) and the wide-angle scattering sharpens slightly, in line with a SmC a-HexFs transition (Figure 6e). Again the layer spacing increases due to the chain stretching (Figure 6f), but this effect is even larger than for B’6/6. In powder patterns the wide angle scattering remains symmetric and in aligned samples it has a maximum around the equator, as typical for the transition to hexF phase (Figure 6e and Figure S25, Supporting Information). The stripe patterns across the fans, occurring at the transition to HexF (Figure 6b) and the wide-angle scattering sharpens slightly, in line with a SmC a-HexFs transition (Figure 6e). Again the layer spacing increases due to the chain stretching (Figure 6f), but this effect is even larger than for B’6/6. In powder patterns the wide angle scattering remains symmetric and in aligned samples it has a maximum around the equator, as typical for the transition to hexF phase (Figure 6e and Figure S25, Supporting Information).
a continuous reduction and removal of the tilt at the transition to HexB (Figure S16c–f, Supporting Information). For the following homologues of the series B′6/n the smectic and hexatic phases are removed and replaced by the Cubbi phase.

**3.6. Cubbi Phases**

The formation of the optically isotropic Cubbi phases from the birefringent SmC phases (SmCn/SmCn′) is indicated by the
appearance of optically isotropic areas (Figure 7g), whereas the transition from theotropic liquids (Iso, Iso,\textsuperscript{[8]} to Cub\textsubscript{bi} is only detected by a significant increase of viscosity. While the liquids flow under gravity, the isotropic Cub\textsubscript{bi} phases represent viscoelastic solids which occasionally can grow as single crystals.\textsuperscript{[80]} In most cases this transition is associated with a small DSC peak, often accompanied by a significant hysteresis of the phase transition on cooling. Moreover, transitions involving

Figure 6. Investigation of the lamellar phases of compound B’6/8. a–c) Optical textures as observed between crossed polarizers in samples combining regions with planar alignment (fan-textures) with those having homeotropic alignment (gray), on cooling at the given temperatures in the indicated phases; the insets show the corresponding textures of freely suspended films (for details, see Figure S16c–f, Supporting Information); d) DSC heating and cooling traces at 10 K min\textsuperscript{-1}; e) change of the shape of the WAXS (see also Figure S25, Supporting Information), and f) plots of the d-values of layer spacing and WAXS maximum depending on temperature; in e) the inset on the left shows the 2D scattering pattern of an aligned sample at the indicated temperature and that on the right shows the development of the orientational order parameter (S) depending on temperature (see Figure S25, Supporting Information).
Cub$_{6n}$ phases are often slow and then become invisible in the DSC traces. In the X-ray scattering patterns the cubic phases are identified by the presence of several sharp small angle Bragg peaks together with a completely diffuse wide angle scattering, the latter confirming the LC state (Figures S20b and S21b, Supporting Information). The cubic lattice type can be deduced from the relative positions of the most intense small angle scatterings either corresponding to the (211) and (220) indices of the la$\bar{3}d$ lattice (Figure 7a and Figure S20a, Supporting Information) or the (321), (400) and (420) indices of the I$\bar{2}$3 lattice (Figure 7b and Figure S21a, Supporting Information). The assignment to the distinct lattices is for polycatenar compounds easily confirmed by optical investigations between not fully crossed polarizers, where the I$\bar{2}$3 phase shows a conglomerate of dark and bright domains which invert their brightness by rotating the analyzer into the opposite direction (Figure 7e). This indicates the presence of chiral domains as typical for the triple network I$\bar{2}$3 structure (Figure 7b). In contrast, for the Cub$_{6n}$ phases with double network structure and space group la$\bar{3}d$ (Figure 7a) no such domains can be found (Figure 7f). In the Cub$_{6n}$ phases the rod-like cores are organized in the networks which are separated by the continuum of the alkyl chains (Figure 7a,b). The orientation of the rods is on average perpendicular or slightly tilted to the networks and in this configuration the crowded periphery of the polycatenars inhibits a parallel arrangement of the tightly packed polyaromatic rods. This mismatch leads to a helical twist $\Phi$ along the networks (Figure 7d) and the network junctions allow a transmission of uniform helix sense over macroscopic distances. The double gyroid with la$\bar{3}d$ space group (Figure 7a) involves two interwoven enantiomorphic networks with opposite helicity and connected by three way junctions, leading to an achiral overall structure. This helically twisted organization in the achiral la$\bar{3}d$ phases of rod-like molecules was recently supported by soft resonant X-ray scattering. In this structure the twist between two three-fold junctions is 70.5°, which must fit with the total of the twists $\Phi$ between adjacent molecules located on the way between two junctions. If a mismatch arises other alternative structures are formed. The most common is the triple network structure with I$\bar{2}$3 symmetry (Figure 7b), previously known as “$\bar{I}m\bar{3}m$” phase,

Figure 7. a–c) The major helical network structures presently known for polycatenar mesogens. d) development of the helical twist by clashing of the end groups attached to rod-like cores; the helices propagate along the red, blue, and yellow networks. e,f) Textures of Cub$_{6n}$ phases observed under slightly uncrossed polarizers (in e the contrast is enhanced). g–j) Representative optical textures of birefringent intermediate phases as observed between crossed polarizers; g) coexisting SmC$_s$, Cub$_{6n}$/la$\bar{3}d$, and SmQ phases on cooling B10/6 from Iso$_{6n}$ between non-treated microscopic glass plates (for textures in an ITO cell, see Figure S9, Supporting Information); h) SmQ phase of B6/10 as growing from Iso$_{6n}$ on slow cooling (for the SmQ-Cub$_{6n}$/la$\bar{3}d$ transition, see Figure S10b, Supporting Information) and i,j) development of the M1 and M2 phases on heating compound B6/10; i) low birefringent mosaic texture (white arrow) of the M1 phase (see also Figure S10a, Supporting Information) with bright crystalites of the M2 phase with higher birefringence (yellow arrow) which in j) become dominating and transform into the Cub$_{6n}$/la$\bar{3}d$ phase on further heating. b) Reproduced with permission, Copyright 2020, The Royal Chemical Society. c) Reproduced with permission, Copyright 2020, Wiley-VCH.
transition temperatures, including the Iso\textsubscript{1}\textsuperscript{*}. Iso transition, that is, the upper critical temperature of mirror symmetry breaking. Therefore, the transition temperatures of B6/7Me are much lower and the Iso\textsubscript{0}\textsuperscript{*} phase of B6/8 is suppressed (see also Section 3.8).

The cubic phases in the series B6/n and B6'/n have exclusively the la\textsubscript{3}d space group, whereas in the series of compounds B10/n with longer 3,5-chains an additional cubic phase with I\textsubscript{23} space group is observed for \( n \geq 16 \). For B10/16 the formation of either the chiral Cub\textsubscript{6}\textsuperscript{a} / I\textsubscript{23} or the achiral Cub\textsubscript{6}/ I\textsubscript{a}3\textsubscript{d} phase depends on the conditions; on heating there is a la\textsubscript{3}d – I\textsubscript{23} transition whereas on cooling only the I\textsubscript{a}3\textsubscript{d} phase is found (Table 1). For B10/22 with the longest alkyl chain exclusively the I\textsubscript{23} phase is observed on heating and cooling. This shows that a certain minimum chain length (or chain volume) is required for the formation of the mirror symmetry broken Cub\textsubscript{6}\textsuperscript{a}/I\textsubscript{23} phase.\[^\text{15b,27–32}\] Only in one case, for the compound with the longest total chain length (B10/22), a columnar phase (Col\textsubscript{ab}) accompanies the Cub\textsubscript{6}\textsuperscript{a}/I\textsubscript{23} phase as a high temperature phase, resulting from the further increased interface curvature provided by this long chain (see Table 1 and Figure S11, Supporting Information). However, the Col\textsubscript{ab} phase is metastable and can only be observed on cooling, whereas on heating a direct Cub\textsubscript{6}/I\textsubscript{a}3\textsubscript{d}–I\textsubscript{23}–Iso transition takes place.

### 3.7. Birefringent Mesophases with 3D Lattice

For compounds with a total chain length of \( m + n = 16 \) to 18, being located at the transition from lamellar to Cub\textsubscript{6}/la\textsubscript{3}d organization (compounds B10/6, B10/8, B6/10, and B6'/10, see Tables 1–3) Cub\textsubscript{6} phase formation is accompanied by the formation of other birefringent mesophases with 3D lattice, either representing distorted versions of the Cub\textsubscript{6}/ia\textsubscript{3}d phase,\[^\text{200}\] or arising from alternative helix packings (e.g., SmQ, see Figure 7c\[^\text{134}\]). The formation of these intermediate phases at the lamellae-to-network transition is strongly dependent on the conditions, including thermal history of the sample, heating and cooling rates, boundary conditions, and modes of alignment. Often their formation is slow and therefore these transitions do not show up in the DSC traces (see Figures S2–S4, Supporting Information). Usually they are metastable and are rapidly replaced by the developing Cub\textsubscript{6}/la\textsubscript{3}d phase, being the more stable phase. Therefore, their investigation, especially by X-ray scattering, is difficult and we can only describe qualitatively some typical observations. One of the intermediate phases is likely to be the SmQ phase which is characterized by a low birefringent mosaic-like texture, typically appearing gray, even in thick samples.\[^\text{144}\] It is often observed on cooling from the mirror symmetry broken Iso\textsubscript{0}\textsuperscript{*} phase (see next section) and once formed it rapidly transforms into the Cub\textsubscript{6}/la\textsubscript{3}d phase on further cooling or isothermal with time. This helical network phase with tetragonal I4\textsubscript{22}2 symmetry and 90° four-way network junctions was recently solved (Figure 7c).\[^\text{135}\] It is proposed to represent an intermediate state at the transition from the mirror symmetry broken Iso\textsubscript{0}\textsuperscript{*} phase with uniform helix sense to the racemic la\textsubscript{3}d phase, requiring the inversion of the helix sense for half of the networks. We assume that the low birefringent phases occurring at the Iso\textsubscript{0}\textsuperscript{*}–Cub\textsubscript{6} transition of B10/6 (Figure 7g) and B6'/10 (Figure 7h) are likely to represent a SmQ phase, too. Also the low birefringent phase designated as M1 (compounds B10/8, B6/10, Tables 1 and 2) could possibly be the SmQ phase, though a specific texture cannot be observed in these cases (Figure 7i and Figure S10a, Supporting Information) and confirmation by X-ray scattering is not possible due to metastability and coexistence with other phases. Only the M2 phase of B6/10, having higher birefringence (Figure 7j), is likely to be different and related to similar birefringent 3D phases with tetragonal\[^\text{31,24,84–87}\] orthorhombic\[^\text{88}\] or rhombohedral symmetry.\[^\text{89}\]

In summary, formation of birefringent 3D phases is a general phenomenon, associated with the lamellar-Cub\textsubscript{6}/la\textsubscript{3}d cross-over. In each of the investigated series it is observed for only one or two homologues with a certain chain length of \( m + n = 16 \) to 18. Upon further chain elongation the non-cubic phases are removed and exclusively the Cub\textsubscript{6} phases remain with the sequence la\textsubscript{3}d \( \rightarrow \) I\textsubscript{23}. Notably, in the investigated series of compounds there are obviously no birefringent 3D phases occurring as intermediate phases at the transition between the la\textsubscript{3}d and I\textsubscript{23} phases.

### 3.8. Mirror Symmetry Broken Isotropic Liquid Phase Iso\textsubscript{1}\textsuperscript{*}

The formation of an isotropic liquid mesophase showing a conglomerate of chiral domains with opposite optical rotation (Iso\textsubscript{1}\textsuperscript{*}, see Figure 8a,b) is associated with the lamellar-to-Cub\textsubscript{6} transition upon alkyl chain elongation, too. This chiral liquid formed by achiral molecules is considered as a percolated liquid with a dynamic helical network structure, which provides a long range transmission of uniform chirality in the enantio-meric domains of the conglomerate, but without assuming a long range cubic lattice.\[^\text{29,30–32,134}\] The helical self-assembly is supported by transiently chiral helical molecular conformational, as provided by the twisted 5,5'-diphenyl-2,2'-bithiophene core of the reported compounds.\[^\text{32,134}\]

Interestingly, FS films can be drawn in the Iso\textsubscript{0}\textsuperscript{*} range; Figure 8d shows the FS film of the Iso\textsubscript{0}\textsuperscript{*} phase of B6/8. Those films have non-uniform thickness (Figure S28e, Supporting Information) and appear without any visible texture between crossed polarizers, though the films are metastable and limited in size. Like liquid fibers subjected to the Rayleigh-plateau instability, liquid films exhibit thinning instability and collapse too.\[^\text{99}\] In smectics, it is the 1D periodic structure which is responsible for stabilization of freely suspended films.\[^\text{91}\] The unexpected film formation of the Iso\textsubscript{0}\textsuperscript{*} phase can be attributed to the dynamic network structure, which, like in the case of polymers (and some oligomesogens\[^\text{22}\]), stabilizes the films and leads to a non-Newtonian behavior. Additionally, correlation of the nano clusters can be induced by the free surfaces, similar to some nematic phases forming dynamic metastable films.\[^\text{90}\] The films are even stable across the Iso\textsubscript{1}\textsuperscript{*}–Iso transition. Also heating of the FS SmC\textsubscript{a} film to the SmC\textsubscript{a}–Iso\textsubscript{1}\textsuperscript{*} transition temperature leads to Iso\textsubscript{1}\textsuperscript{*} films (Figure 8e,f and Figure S27, Supporting Information). Only in sufficiently thick films (>100 µm) mirror symmetry breaking takes place and domains of opposite chirality can be observed, thinner films appear to be achiral. Interestingly, these chiral domains have
an unequal distribution with one sign of chirality dominating. Once this imbalance has developed the film becomes rapidly homochiral, due to the huge chirality amplification capability of the Iso\(\text{I}^*\) phase. The capability of chirality amplification was previously reported for samples between glass substrates as shown in Figure S4, Supporting Information of ref. [34a]. Due to the ubiquitous presence of tiny chirality sources in the environment, in most cases the FS Iso\(\text{I}^*\) films of sufficient thickness appear homogeneously chiral almost from the beginning.

In the series of compounds Bm\(m/n\) and B'6/\(n\) the formation of the Iso\(\text{I}^*\) phase is associated with the SmC-to-Cub\(b_{\text{in}}\)/la\(3d\) transition, irrespectively if the SmC phase is synclinic or anticlinic. It is observed for a medium chain length around \(n = 6–10\) (B10/\(n\); \(n = 6, 8\), B6/\(n\); \(n = 6–10\) and B'6/\(n\); \(n = 8, 10\), see Tables 1–3). For most compounds it is only observed on cooling as a monotropic phase replacing the la\(3d\) phase, but for compounds B'6/8, B6/8 and B6/6a it is an enantiotropic phase occurring directly above SmC\(C\) (without accompanying Cub\(b_{\text{in}}\) phase) and having the broadest enantiotropic Iso\(\text{I}^*\) range for B6/8. As shown in Figure 8c, the Iso-Iso\(\text{I}^*\) transition is associated with a small enthalpy in the DSC traces which is attributed to the chirality synchronization.[30,31] Previous temperature dependent SAXS experiments have indicated a continuously decreasing line width, and hence, growing correlation length of the helical aggregates around the continuous Iso-Iso\(\text{I}^*\) transition, and a jump to resolution limited Bragg peaks at the discontinuous Iso\(\text{I}^*\) to Cub\(b_{\text{in}}\) transition.[31,34a]

The Iso-Iso\(\text{I}^*\) transition was also investigated by optical rotation and circular dichroism.[27a] Based on all these investigations the model of a dynamic network structure of the Iso\(\text{I}^*\) phase was suggested.[30–32,34a,42] Recent results of NMR relaxation and NMR diffusion measurements at the Cub\(b_{\text{in}}\)-Iso-Iso transitions of other achiral polycatenar molecules support this model of a local Cub\(b_{\text{in}}\)-like structure of the Iso\(\text{I}^*\) type phases.[94a] and theoretical work supports the importance of network formation for mirror symmetry breaking.[56] In the case reported here, the spontaneous chirality evolves by the chirality synchronization in the dynamic helical superstructure of the Iso\(\text{I}^*\) phase.[12] In fact, there is some similarity with the Iso\(\text{I}^*\) phase occurring besides chirality frustrated LC phases of permanently chiral molecules (*),[11a,b,96,97] the most prominent example being the BPIII phase.[98] It should be noted, that Iso-Iso\(\text{I}^*\) transitions have previously been reported to occur besides cubic LC phases,[13b,97a] but the helical network structure and the capability of these Iso\(\text{I}^*\) phases of mirror symmetry breaking, first reported in ref. [27a], were not recognized at that time. Moreover, liquid state polymorphism is a general feature of complex liquids, which is not yet fully recognized,[42,99,100] but of great importance for biosystems, too.[32,101]

The Iso\(\text{I}^*\) phase and related isotropic mesophases often appear in proximity to the SmQ phase, a birefringent 3D phase with tetragonal lattice (Figure 7c)[13,30] and therefore, it is likely that the local structure in the dynamic networks of the Iso\(\text{I}^*\) phases of the investigated compounds is similar to the helical network structure with 90° four-way junctions as recently proposed for this SmQ phase (Iso\(\text{I}^*\)[SmQ]).[33] For compounds B6/6, B6/8, B'6/8 and B6/6a the Iso\(\text{I}^*\) phase appears between the achiral isotropic liquid (Iso) and the anticlinic SmC\(C\) phase, in these cases without any competing SmQ or la\(3d\) phase and it is formed on heating as well as on cooling, without the strong hysteresis being typical for the Iso\(\text{I}^*\)→la\(3d\) transition (Figure 8c). In these cases the SmQ-like local network structure in the Iso\(\text{I}^*\) phase transforms directly into an achiral lamellar phase, without requiring a helix inversion. Interestingly, as soon as the la\(3d\) phase emerges in the phase sequence, also other 3D phases (SmQ, M1, M2) appear, which can be explained by the required helix inversion at the Iso\(\text{I}^*\)→la\(3d\) transition. The transition from the conglomerate of the chiral Iso\(\text{I}^*\) phases to the racemic la\(3d\) phase requires a helix inversion for half of the networks which is a collective process in the networks and therefore requires a significant activation energy which...
makes this inversion slow. Therefore, a homogeneous chiral intermediate phase, not requiring helix inversion (e.g., SmQ) is formed first. However, it is metastable and in a second step slowly transforms into the racemic la3d phase by partial helix inversion. As the achiral la3d phase becomes dominating with growing chain length, the chiral Iso1 phase disappear together with the SmQ phase and the other non-cubic 3D phases. It is likely that with chain elongation the local structure of the Iso/ Iso phase becomes la3d like, which is achiral. Whereas for the compounds Bn/n and B'6/n exclusively the chiral Iso1 phase and achiral isotropic liquid phases could be observed, in the related series of the tetracatenars compounds An/n with one more chain and significantly larger chain volume (3,4,5-trisubstitution, see compound A10/10 in Figure 1) the Iso1 phase appears again and occurs in proximity to the mirror symmetry broken Cubbi phase. Therefore, it appears likely that there are two different types of Iso1 phases having different local network structures, being either SmQ-like with 90° four-way junctions (Figure 7c) for those located close to the lamellar–Cubbi cross-over (Iso1, compounds B and B') and I23-like with almost 120° three-way junctions for those occurring besides the Cubbi phase (Iso1, compounds A, see Figure 7b). An achiral Iso phase, presumably with local la3d structure was detected for related 3,5-substituted tricatenars with azobenzene cores and 3,4,5-substituted benzil based tetracatenars, which completes the overall sequence Iso1–Iso1–Iso1–Iso1 (3,5 substitution pattern at one compounds is the formation of a series of hexatic low temperature phases. At the transition to the hexatic phases the tilt correlation becomes synclinic (HexF, HexI) or the tilt is removed (HexB, see Figure 2g–i). In addition, new variants of hexatic phases combining hexatic order of the alkyl chains with more disordered aromatic cores (HexI) were observed. Finally, it is shown that the SmC-Cubbi transitions are accompanied by the formation of additional modes of self-assembly, among them birefringent 3D mesophases, as the tetragonal SmQ phase (Figure 7c) and a mirror symmetry broken isotropic liquid phase (Iso1, Figure 8). It is shown that for the latter freely suspended films can be drawn, which can become local mirror symmetry broken and even homogeneously chiral, due to the chirality synchronization in the dynamic helical network with proposed SmQ-like local structure. A sequence of chiral (Iso1) and achiral (Iso1) percolated liquids with local network structures, resembling those of the adjacent cubic and non-cubic LC network phases is proposed to occur depending on the alkyl chain length and thus changing intermolecular twist (Figure 9).

4. Summary

This work provides a systematic investigation of the structure-property relations of a new kind of swallow-tailed polycatenar compounds at the transition from lamellar to helical network phases. The compounds involve the functional 5,5′-diphenyl-2,2′-bithiophene core, which is of interest as fluorescent (AIE active) and charge carrying unit for the development of new multifunctional organic electronic materials. As well known, the local organization of these π-conjugated rods determines the application relevant properties and, therefore, the understanding of the fundamental rules of their soft self-assembly is of general interest.

The effect of the alkyl chain number and alkyl chain distribution is shown in Figure 1. The main focus is on swallow-tailed compounds having the rarely used 3,5-disubstitution pattern at one end combined with a non-substituted or 4′-alkyloxysubstituted apex (Scheme 1). Their conformation can change depending on alkyl chain length and temperature between a Y-like and a tuning fork like shape (Figure 3g,h); the main self-assembled structures formed by these compounds and their development depending on the molecular structure are summarized in Figure 9. By chain elongation a transition from lamellar phases to bicontinuous cubic phases, first with achiral la3d space group and upon further chain elongation with the chiral and spontaneous mirror symmetry broken Cubbi phase (Figure 7a,b), followed by a columnar phase (Col), is observed. The lamellar phases represent tilted smectic phases which are synclinic tilted if the 3,5-chains are sufficiently long, and become antclinic tilted for shorter chains. Thus, this molecular structure provides a new class of antclinic SmC materials, being of interest for antiferroelectric and orthoconic LCs for display applications. Another specific feature of these compounds is the formation of a series of hexatic low temperature phases. At the transition to the hexatic phases the tilt correlation becomes synclinic (HexF, HexI) or the tilt is removed (HexB, see Figure 2g–i). In addition, new variants of hexatic phases combining hexatic order of the alkyl chains with more disordered aromatic cores (HexI) were observed.
Overall, this work contributes to the general understanding of the soft matter self-assembly at the lamellae-network transition and the mechanism of spontaneous mirror symmetry breaking in fluids, being of technological interest for the development of novel functional materials and devices.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anticlinic smectic phases, bicontinuous cubic phases, bithiophenes, helical networks, hexatic phases, liquid crystals, mirror symmetry breaking, polycatenars

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Optical core. of (almost) equal length in the terminal chains, examples are molecules having a branched terminal chain with two branches.
Besides the major optical and X-ray scattering investigation methods used here, cubic phases have in some cases also been characterized by means of soft resonance X-ray scattering and imaging methods, like AFM and TEM, especially for the larger compounds used for the azobenzenes, no SmCs and SmBs with reduced core order. Because only short hexyl chains were used for the azobenzenes, no SmCs and SmBs with reduced core order. Hence, it appears that there is a competition between the development of long range orientational order and helical self-assembly as the parallel packing of the molecules becomes distorted and the preferred average molecular conformation changes from rod-like to helical by chain elongation.

Compared to the related azobenzene based compounds with 3,5-disubstitution pattern at one end, the smectic phases of compounds Bm/n and B’s/n have larger tilt angles. Due to the larger tilt, the tilt correlation is stronger and no indications of uniaxial smectic phases with or without helical superstructure can be found. Though HexB phases were observed in both series, the SmI, phases of the azobenzenes are replaced by SmI

\[ \text{Bm/n} \], and \[ \text{B's/n} \] phases with reduced core order. Because only short hexyl chains were used for the azobenzenes, no SmC, and I2 phases and transitions associated with these phases could be observed.