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Mesomorphic Hydrogen-Bonded Complexes of Complementary Semiperfluorinated Components

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Abstract: 2,4-Diamino-6-phenyl-1,3,5-triazines carrying one or two semiperfluorinated chains at the phenyl substituent have been investigated in binary mixtures with partially fluorinated benzoic acids by polarizing microscopy, differential scanning calorimetry, and X-ray diffraction. The number and positions of the fluorinated tails of the acid component were systematically modified. Equimolar mixtures of the triazines with the aromatic acids form discrete hydrogen-bonded heterodimers with an elongated central core. Mesomorphic properties are observed only if at least three terminal fluoroalkyl chains are grafted to the hydrogen-bonded rigid core. The dimeric supermolecules exhibit columnar mesophases with rectangular or oblique two-dimensional lattice symmetry or bicontinuous cubic phases. The mesophases of the dimers are ribbon phases resulting from the collapse of smectic layers. Thereby, the phase type is defined by the number and positions of the fluorinated tails of the two components. Docking of two or three equivalents of two-chain benzoic acids to the diaminotriazine core leads to the formation of cylindrical aggregates, which organize into hexagonal columnar phases, whereas 1:2 and 1:3 mixtures of the two-chain triazine with a three-chain fluorinated aromatic acid display micellar cubic phases.

Keywords: fluorophobic effect • hydrogen bonds • liquid crystals • mesophases • supramolecular chemistry

Introduction

Segregation of incompatible molecular segments into distinct regions is one of the fundamental driving forces for mesogenic self-organization of amphiphilic block molecules.[1,2] Thereby, amphiphilicity describes any chemical or structural intramolecular contrast emerging from covalent combination of hydrophilic/lipophilic or rigid/flexible building blocks.[2]

The mesophase morphologies are essentially determined by the volume fractions of the competing molecular fragments. Molecules with nearly equal space requirements of the incompatible parts preferably organize into layer structures (smectic phases). Increasing the size of one molecular component leads to aggregates with a finite mean interface curvature. Hence, the phase sequence bicontinuous cubic (Cub_V), columnar (Col) and, finally, micellar cubic (spheroidic, Cub_I) occurs on successively increasing the wedge-like character of a mesogen, that is, by building taper- or cone-shaped molecular geometries.[3]

Nonlamellar phases may also occur for calamitic mesogens if two or three alkyl chains are grafted to the termini of the rod-like unit. Thus, smectic C, bicontinuous cubic, and columnar mesophases were observed for polycatenar compounds with increasing number of flexible end chains.[4] In these columnar phases, smectic layers are disrupted into stripes which adopt a periodic 2D organization.

Replacement of an alkyl chain by a (semi)perfluorinated tail significantly reinforces the intramolecular contrast and thus enhances the tendency for nano-segregation. The main reasons are incompatibility of fluorinated chains with aliphatic and aromatic fragments, as well as the increased stiffness and the larger size of perfluorinated entities compared with alkyl chains.[5] (Semi)perfluorinated alkyl chains have been successfully incorporated into liquid crystals with a rigid core,[6] and into mesogens without a pronounced anisometric shape.[7] The thermal stability of liquid crystalline phases usually increases and the mode of soft-matter organization may be significantly influenced by the fluorophobic effect.

Hydrogen-bonded mesomorphic complexes[8] originating from complementary molecular entities fitted with lipophilic

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chain segments can be regarded as noncovalent analogues of amphiphilic diblock molecules. Thereby, the introduction of hydrogen bonding reinforces the intramolecular polarity gradient.

Certain hydrogen-bonding motifs were exploited to induce and/or stabilize thermotropic smectic and columnar mesophases, such as single hydrogen bonding between carboxylic acids and pyridine fragments,[9] double hydrogen bonding of 2,6-diacylaminopyridines with aromatic carboxylic acids[10] and triple hydrogen bonding between 2,6-diacylaminopyridines and uracil derivatives.[11]

With our initial work in this field we ascertained the threefold arylamino-substituted 1,3,5-triazine core as a molecular component suitable for controlling the lattice parameters of columnar mesophases via H-bond-initiated heterodimerization with complementary alkoxybenzoic acids.[12]

Strong cohesive forces emerging from hydrogen bonding between complementary molecules and simultaneous introduction of (partially) fluorinated structural units may lead to noncovalently associated three-block molecules with distinct regions of a polar hydrogen-bonded (rigid) core, lipophilic alkyl chain segments and fluorinated building blocks. Thereby, the cooperative interplay of enhanced polar/nonpolar microsegregation and tailoring the space requirement of lipophilic and fluorinated segments should provide a suitable approach to tailoring thermotropic mesophase morphologies.[13]

In this respect, mesogenic complexes have been derived from fluorinated acids and pyridine derivatives which exhibit smectic or columnar phases depending on the number of fluoroalkyl chains of the acid component.[14]

Hydrogen-bonded associates of non-mesogenic 2,4-diamino-6-phenyl-1,3,5-triazines with two-chain semiperfluorinated benzoic acids organize into columnar phases.[15] The two-dimensional unit cell can be controlled by the number of alkoxy tails of the triazine component and by the molar content of the two complementary counterparts.

In one approach to increasing the intramolecular contrast, the rod-shaped core of the amino triazine component was elongated by replacing the phenyl ring by a biphenyl unit. Here, the terminal substitution pattern at the biphenyl moiety and the elongated biphenyl triazine core mainly account for the 2D lattice symmetries of columnar mesophases.[16]

Alternatively, a secondary amino group was inserted between the phenyl ring and the nitrogen heterocycle of the triazine component to reinforce the intramolecular polarity gradient.[17] Whereas the two-dimensional lattice symmetries of the resulting columnar mesophases are tailored by adjusting the number and positions of fluorinated fragments of the acid component, the additional secondary amino function of the triazine accounts for the (frustrated) bilayer structure.

A major advantage of our noncovalent approach to polyphilic block molecules is that it enables in a simple fashion a diversity of systematic structural modifications, that is, by incorporation of lipophilic and/or fluorophilic chain segments selectively in one or both of the components. The polyphilic three-block triazine/acid complexes reported so far were designed such that, except for one example,[16] the triazine component contains flexible lipophilic alkyl chains, whereas the complementary acid provides the fluorinated molecular block. To further tailor the intramolecular contrast and the molecular topology, we appended semiperfluorinated segments to both of the complementary species (Figure 1). We present here mesomorphic structure formation of the semiperfluorinated diamino-substituted 1,3,5-triazines **1** and **2** in mixtures with the partially fluorinated benzoic acids **3**–**6** (Scheme 1). The number and the positions of the fluorinated tails of the two components were systematically modified.

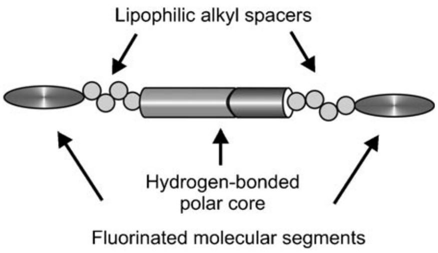
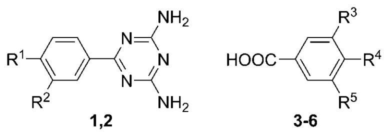


Figure 1. Construction of hydrogen-bonded three-block molecules with fluorinated molecular fragments at terminal positions of the two complementary counterparts.



1,2 **3-6**

compound	R^1	R^2	R^3	R^4	R^5
1-[*n*,*m*]	$O(CH_2)_nC_mF_{2m+1}$	H			
2-[*n*,*m*]	$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$			
3-[*n*,*m*]			H	$O(CH_2)_nC_mF_{2m+1}$	H
4-[*n*,*m*]			$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$	H
5-[*n*,*m*]			$O(CH_2)_nC_mF_{2m+1}$	H	$O(CH_2)_nC_mF_{2m+1}$
6-[*n*,*m*]			$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$

Scheme 1. Semiperfluorinated diamino-1,3,5-triazines **1** and **2** and complementary partially fluorinated benzoic acids **3**–**6**.

Results and Discussion

Thermal properties of pure triazines 1 and 2 and semiperfluorinated carboxylic acids 3–6: One-chain diamino-1,3,5-triazines **1-[*n*,*m*]** exhibit a lamellar (SmA_d) phase.[18] The molecules are aligned antiparallel and shifted against each other so that the polar aromatic parts are interdigitated. The semiperfluorinated chains build up a separate sublayer. Pure two-chain triazine **2-[4,4]** forms a reverse discontinuous cubic (Cub_{I2}) phase consisting of closed spheroidic inverted micelles of the polar parts surrounded by the nonpolar fluorinated chains.[18]

Single-chain partially fluorinated benzoic acids **3-[*n*,*m*]** display an enantiotropic smectic C phase due to dimerization of their carboxylic groups through hydrogen bonding.[7a,14c,e] Incorporation of a second semiperfluorinated tail gives rise to at least monotropic hexagonal columnar mesophases for two-chain acids **4-[*n*,*m*]**.[7a,14e,15–17] Changing the positions of the fluorinated chains at the phenyl ring of the acid from 3,4 to 3,5 suppresses mesomorphic behaviour in benzoic acids **5-[*n*,*m*]**.[17] Benzoic acids **6-[*n*,*m*]** fitted with three fluorinated alkoxyl chains again display a Col$_{h}$ phase.[7a,16,17] The columnar phases of carboxylic acids **4** and **6** are related to the formation of discrete benzoic acid dimers and segregation of the polar central region from the surrounding semiperfluorinated chains.[7a]

The phase transition data of compounds **1**–**6** are summarized in Table 1.

Table 1. Phase transition temperatures of **1**–**6** in their pure states (DSC, second heating with 10 K min^{-1}, transition enthalpies [kJ mol^{-1}] in parentheses, monotropic phase transitions in brackets).[a]

Compound	Transition temperatures [°C]	Reference
1-[6,4]	Cr 175.6 (55.4) [SmA 170.8 (−0.4)] I	[18]
1-[4,6]	Cr 182.1 (17.1) SmA 200.9 (0.5) I	[18]
2-[4,4]	Cr 82.7 (1.4) Cub$_{I2}$ 140.4 (0.4) I	[18]
3-[4,4]	Cr[b] 147.3 (11.5) SmC 170.3 (7.7) I	[14e]
3-[6,4]	Cr[b] 150.7 (12.9) SmC 168.5 (8.1) I	[14e]
3-[4,6]	Cr 164.1 (15.9) SmC 185.5 (10.4) I	[7a,14e]
3-[6,6]	Cr[b] 155.7 (12.4) SmC 176.9 (8.6) I	[14c,e]
4-[6,4]	Cr 54.7 (14.2) [Col$_{h}$ 53.1 (−1.8)] I	[7a,14e,15,17]
4-[4,6]	Cr 115.7 (37.6) [Col$_{h}$ 102.0 (−1.6)] I	[7a,14e,15–17]
4-[6,6]	Cr 88.2 (20.0) [Col$_{h}$ 75.3 (−0.8)] I	[14e,15]
5-[4,4]	Cr 90.3 (33.8) I	
5-[6,4]	Cr 58.8 (38.5) I	[17]
5-[4,6]	Cr 84.7 (27.4) I	
5-[6,6]	Cr 82.7 (28.0) I	
6-[4,4]	Cr 12.6 (8.3) Col$_{h}$ 40.8 (1.6) I	[7a]
6-[4,6]	Cr 51.0 (7.1) Col$_{h}$ 81.1 (2.7) I	[7a,f,16,17]
6-[6,6]	Cr 37.1 (14.1) Col$_{h}$ 70.0 (2.4) I	[7g]

[a] Cr: crystalline; SmA: smectic A; Cub$_{I2}$: inverted micellar cubic; SmC: smectic C; Col$_{h}$: hexagonal columnar; I: isotropic. [b] Polymorphism in the solid state was observed.

Equimolar mixtures of diamino-1,3,5-triazines 1 and 2 with one-and two-chain partially fluorinated benzoic acids 3 and 4: First we investigated 1:1 mixtures of triazines **1** with carboxylic acids **3**, whereby both components have just one semiperfluorinated alkoxy tail. Surprisingly, we found no evidence for mesomorphic properties of equimolar **1/3** mixtures. The investigated complexes **1/3** show a direct transition to the isotropic liquid at temperatures quite different from the phase transition temperatures of the single components (Table 2).

While the SmA phases of triazines **1** and SmC phases of pure benzoic acids **3** disappear, the single melting transitions of **1/3** mixtures with stoichiometric molar ratio can be regarded as a hint that aminotriazines **1** and benzoic acids **3** do not act as individual molecular species and association of the two components occurs. However, the two fluorinated fragments of (hydrogen-bonded) heterodimers **1/3** are clearly not sufficient for balanced intramolecular contrast to force mesomorphic structure formation.

Table 2. Phase transition temperatures T [°C] of selected equimolar mixtures of one-chain triazines **1** with single-chain semiperfluorinated benzoic acids **3** (DSC, 2nd heating with 10 K min^{-1}; transition enthalpies E [kJ mol^{-1}] in parentheses).[a]

Mixture	Cr	T (E)	Iso
1-[6,4]/3-[4,4]	●	200.7 (59.4)	●
1-[6,4]/3-[6,4]	●	188.5 (39.3)	●
1-[6,4]/3-[4,6]	●	205.3 (57.0)	●
1-[4,6]/3-[4,4]	●	206.0 (49.2)	●
1-[4,6]/3-[6,4]	●	194.5 (55.9)	●
1-[4,6]/3-[4,6]	●	209.3 (61.2)	●
1-[4,6]/3-[6,6]	●	194.3 (56.6)	●

[a] Cr: crystalline; I: isotropic.

Incorporation of at least a second partially fluorinated fragment into one of the complementary molecular species produces liquid crystallinity. The phase transition temperatures of selected appropriate 1/1 **1/4** and **2/3** mixtures are given in Table 3.

The isotropization temperatures of the 1/1 mixtures **1/4** are in excess of the melting temperatures of the appropriate pure carboxylic acids **4-[*n*,*m*]**. The monotropic phases of two-chain acids **4** are replaced by enantiotropic mesophases. On the other hand, the clearing temperatures of the mixed systems are lower than those of the respective diaminotriazines **1-[*n*,*m*]** in their pure states. Association of the single-chain acids **3-[*n*,*m*]** with two-chain triazine **2-[4,4]** leads to a decrease of the clearing temperatures compared with pure carboxylic acids **3**, whereas the mesophase ranges are remarkably enlarged.

Table 3. Phase transition temperatures T [°C] (DSC, second heating with 10 K min^{-1}, transition enthalpies E [kJ mol^{-1}] in parentheses) and lattice parameters a and b [Å] of equimolar mixtures of three-chain systems **1/4** and **2/3**.[a]

Mixture	Cr		Col$_{r}$	T (E)	Iso	a	b
1-[6,4]/4-[6,4]	●	133.4 (6.6)	●	150.4 (2.3)	●	59.0	42.5
1-[4,6]/4-[4,6]	●	79.5 (5.9)	●	161.5 (2.8)	●	66.6	44.6
1-[4,6]/4-[6,6]	●	101.1 (11.2)	●	170.9 (1.9)	●	59.2	48.6
2-[4,4]/3-[4,4]	●	78.5 (5.8)	●	142.5 (2.6)	●	58.1	42.8
2-[4,4]/3-[4,6]	●	86.4 (10.4)	●	164.1 (2.8)	●	56.9	44.1

[a] Cr: crystalline; Col$_{r}$: rectangular columnar; Iso: isotropic.

The equimolar binary mixtures involving triazine and/or acid components with fluorohexyl chain segments display increased isotropization temperatures compared to the mixtures with exclusively short C$_4$ fluorinated end chains.

If one keeps the number of fluorinated methylene groups constant an increase of the phase transition temperatures is found on elongation of the nonfluorinated alkyl spacers.

This behaviour seems surprising keeping in mind the increased molecular mobility with increasing the number of flexible chain fragments. Apparently, regardless of the flexibility, elongation of the lipophilic molecular block amplifies the intramolecular contrast such that both elongation of the fluorophilic block and increasing the number of lipophilic methylene groups cooperatively contribute to enhanced phase transition temperatures of triazine/benzoic acid systems **1/4** and **2/3**.

On cooling of the 1/1 mixtures **1/4** and **2/3** from the isotropic liquid state, spherulitic textures can be observed between crossed polarizers. These features are indicative of columnar mesophases. Figure 2 shows, as a typical example, the texture of the **1-[6,4]/4-[6,4]** mixed system.

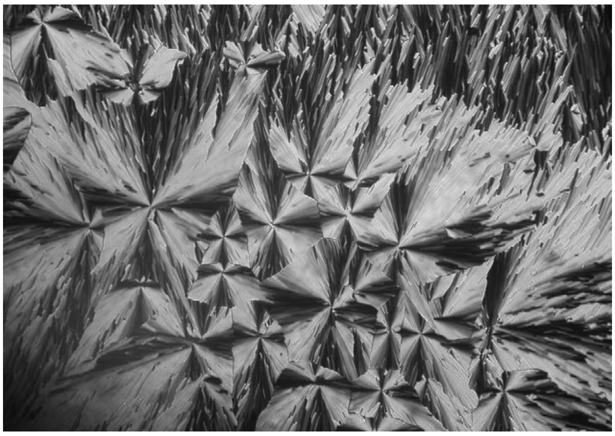


Figure 2. Optical texture of the equimolar mixture **1-[6,4]/4-[6,4]**.

The X-ray diffraction pattern obtained for the mesophases of the equimolar compositions **1/4** and **2/3** show only reflections with $h+k=2n$ in the small-angle region (Figure 3). These reflections can be assigned to a centred rectangular cell with *c2mm* plane group. The lattice parameters are given in Table 3. These findings confirm the phase assignment made by polarizing microscopy.

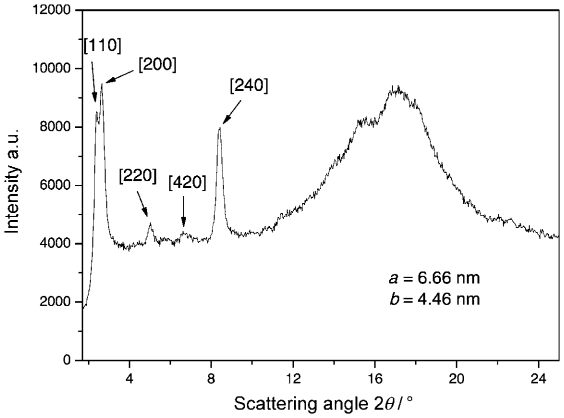


Figure 3. WAXS diffractogram for the mesophase of the 1/1 mixture **1-[4,6]/4-[4,6]**.

Association of amino-1,3,5-triazines with complementary benzoic acids is related to double-hydrogen bonding between the nitrogen heterocycle substituted with exocyclic amino groups and the carboxyl group of the acid.[12a,15,17] Thereby, it is most reasonable to suggest that docking of just one equivalent of the semiperfluorinated benzoic acids **3** or **4** to the respective triazines **1** or **2** preferentially occurs opposite to the bulky phenyl group for steric reasons.[15–17] This leads to heterodimeric supermolecules with a pronounced rod-shaped core geometry. The average molecular topology of the three-chain hydrogen-bonded supermolecules is the same, independent of whether the two fluorinated tails are grafted to the 3,4-positions of the phenyl ring of the triazine or the benzoic acid component.

Close side-by-side packing of the rigid hydrogen-bonded cores should be strongly favoured whereby, the most efficient space filling is achieved by an antiparallel assembly. The antagonistic parts of the molecules segregate into different sublayers. Figure 4a shows a possible arrangement of four supermolecules **1-[6,4]/4-[6,4]** with close and antiparallel packing of the polar rod-like cores. The cross section of the central polar region is smaller than that of the terminal semiperfluorinated chains. The different space filling within the segregated regions provides significant steric frustration of the smectic layer structure, which results in a collapse

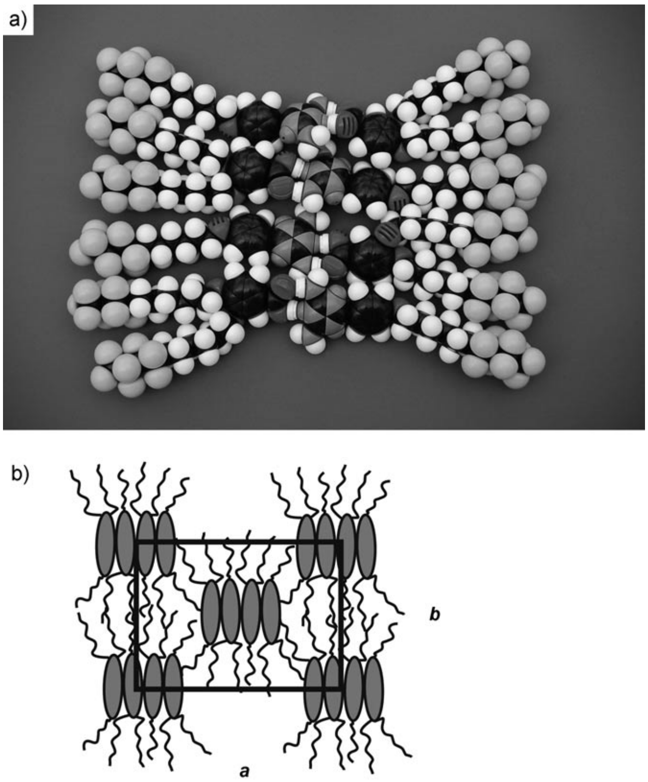


Figure 4. a) CPK model of four hydrogen-bonded dimers **1-[6,4]/4-[6,4]** with antiparallel alignment of the rod-shaped central polar cores. b) Schematic of the ribbon phase of equimolar hydrogen-bonded complexes **1/4** and **2/3** with rectangular columnar (Col$_r$) organization (two-dimensional *c2mm* space group).

and the formation of ribbon-like segments. These ribbons arrange in a two-dimensional lattice with *c2mm* symmetry (Figure 4b).

Interestingly, heterodimers of a structurally related, exclusively alkoxy substituted diamino-1,3,5-triazine with the two-chain semiperfluorinated acids **4-[*n*,*m*]** display a ribbon phase with a 2D noncentered *p2gg* lattice.[15] In this case, the shape of the individual ribbons can be regarded as consisting of pairs of irregular pentagons which are held together by hydrogen bonding. The pentagonal cylinders have a cross section in which not all side lengths and angles are exactly the same. The deformed pentagonal cylinder pairs organize in a herringbone pattern.

Replacement of an alkoxy chain of the heterodimers by a partially fluorinated fragment equalizes the outer sphere of the ribbons. In this way, increasing the symmetry of the ribbon shape changes the two-dimensional space group from *p2gg* to *c2mm*.

The lattice parameters *b* match quite well with the maximum molecular dimensions of rod-shaped hydrogen-bonded dimers **1/4** and **2/3**. Therefore, the lattice parameter *b* can be attributed to the thickness of the ribbons, whereas the parameter *a* indicates a periodicity perpendicular to it. From the lattice parameter *a* it can be calculated that on average four dimers should be arranged side-by-side in the lateral diameter of the ribbons.

Equimolar complexes of one-chain diamino-1,3,5-triazine 1 with two- and three-chain semiperfluorinated benzoic acids 5 and 6: Equimolar mixtures of single-chain triazines **1** with benzoic acids **5** and **6** exhibit an enantiotropic liquid-crystalline phase within the temperature range given in Table 4.

Table 4. Phase transition data T [°C] of 1:1 compositions of single-chain triazines **1-[*n*,*m*]** with semiperfluorinated benzoic acids **5** and **6** (DSC, 2nd heating at 10 K min^{-1}; phase transition enthalpies E [kJ mol^{-1}] in parentheses; lattice constants a, b [Å], γ [°]).[a]

Mixture	Cr	T (E)	Col$_{ob}$	T (E)	Iso	a	b	γ
1-[6,4]/5-[4,4]	●	71.3 (17.9)	●	118.6 (1.2)	●			
1-[6,4]/5-[4,6]	●	72.2 (2.2)	●	143.6 (3.2)	●	48.3	40.4	68.4
1-[4,6]/5-[4,4]	●	73.4 (10.2)	●	105.3 (2.7)	●			
1-[4,6]/5-[4,6]	●	78.2 (5.4)	●	124.2 (1.6)	●			
1-[6,4]/6-[4,4]	●	78.3 (11.0)	●	111.0 (0.7)	●			
1-[4,6]/6-[4,6]	●	43.1 (1.7)	●	129.8 (2.3)	●	47.8	36.4	67.6

[a] Cr: crystalline; Col$_{ob}$: columnar, oblique lattice; Iso: isotropic.

Noteworthily, association of the complementary components leads to mesophase induction for the nonliquid-crystalline two-chain benzoic acids **5**. The isotropization temperatures of the 1/1 mixtures **1/5,6** are higher than those of the corresponding fluorinated acids **5** and **6**. On the other hand, the clearing temperatures of the **1/5,6** mixtures are lower than those of the equimolar mixtures of triazine **1** with the 3,4-difluoroalkoxy-substituted benzoic acids **4**. It is thought that attaching two fluorinated tails at the 3,5-positions of the benzoic acids and incorporation of a third semiperfluorinated chain into the acid component leads to unfavourable steric interactions to a certain extent. The enhanced steric demands are in competition with stabilizing effects arising from microsegregation, which leads to a decrease in thermodynamic mesophase stability.

Optical textures with spherulitic regions and pseudofocal conic fan-like regions are characteristic of equimolar mixtures of diaminotriazines **1** with two- and three-chain partially fluorinated acids **5** and **6** (Figure 5). Though these textural features are indicative of a columnar mesophase, they are different from the textures observed for the 1/1 mixtures **1/4** and **2/3**. This suggests that changing the substitution pattern of the acid component causes a change in 2D lattice symmetry.

Figure 5. Optical texture of the equimolar binary mixture **1-[6,4]/5-[4,4]**.

The mesophases of mixtures **1-[6,4]/5-[4,6]** and **1-[4,6]/6-[4,6]** were investigated by X-ray diffraction. The small-angle reflections can be indexed to a columnar phase with a two-dimensional oblique lattice (Col$_{ob}$). The lattice parameters are given in Table 4.

The 3,5-substitution pattern of the fluorinated benzoic acids **5** and grafting a third semiperfluorinated fragment to the phenyl nucleus of acids **6** reinforces the wedge-shaped character of the hydrogen-bonded triazine/benzoic acid heterodimers. The space requirement of the fluorinated region at one terminus of the dimeric supermolecules increases. The enlarged cross-sectional area of the terminal fluorinated blocks of antiparallel-oriented dimers resulting from the change in substitution pattern of the acid partly can be compensated by shifting of the rigid rod-like cores of the **1/5,6** dimers against each other (Figure 6a). The remaining differences in volume fraction of the incompatible fluorinated and hydrogen-bonded aromatic microdomains is finally bal-

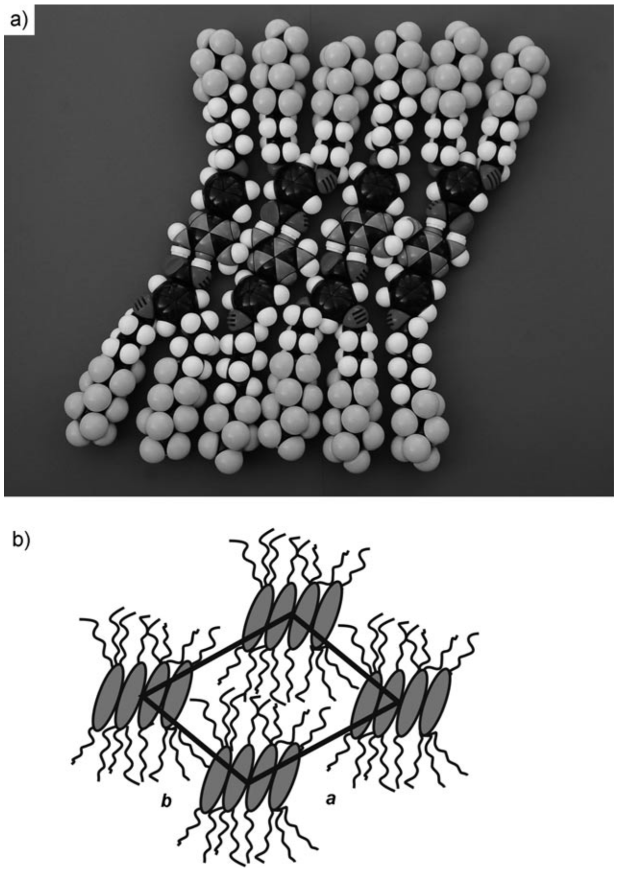


Figure 6. a) CPK model showing four hydrogen-bonded heterodimers **1-[6,4]/5-[4,6]** with tilted arrangement of antiparallel aligned rod-like central cores. b) Model for the molecular arrangement of hydrogen-bonded heterodimers of one-chain partially fluorinated triazines **1** with semiperfluorinated benzoic acids **5** and **6** in the columnar mesophases with two-dimensional oblique lattice symmetry ($\mathrm{Col_{ob}}$).

anced by disruption of the tilted smectic layers with formation of ribbons which organize into columnar mesophases on a two-dimensional oblique lattice (Figure 6b).

The number of heterodimers per unit cell was calculated by dividing the unit cell volume by the molecular volume, determined by using volume increments.[19] The unit cell is defined by the lattice parameters and by assuming a height of $h = 4.5$ Å.[7b,15–17] The number of heterodimers obtained in this way is approximately six for the 1/1 mixture **1-[6,4]/5-[4,6]** and four for the **1-[4,6]/6-[4,6]** equimolar mixture.

Table 5. Phase transition data T [°C] of equimolar mixed systems of two-chain triazine **2** with selected semiperfluorinated benzoic acids **4–6** (DSC, second heating with 10 K min^{-1}, transition enthalpies E [kJ mol^{-1}] in parentheses).[a]

Mixture	Cub	T (E)	Iso
2-[4,4]/4-[6,4]	●	80.3 (1.4)	●
2-[4,4]/4-[4,6]	●	123.7 (0.5)	●
2-[4,4]/5-[6,4]	●	81.1 (1.9)	●
2-[4,4]/6-[4,6]	●	104.8 (0.6)	●

[a] Cub: cubic; Iso: isotropic.

Equimolar mixtures of partially fluorinated two-chain diamino-1,3,5-triazine 2 with two-and three-chain benzoic acids 4–6: As a next step towards modifying the molecular shape of the triazine/acid dyads, we attached a second partially fluorinated chain to the triazine component. Table 5 summarizes the phase transition temperatures of 1/1 mixtures of two-chain triazine **2** with the two-and three-chain semiperfluorinated benzoic acids **4–6**. Each investigated binary 1/1 mixture of triazine **2** with the benzoic acids **4–6** forms a highly viscous, optically isotropic phase. Even shearing the samples does not induce any birefringence, as one should expect for homeotropically aligned smectic or columnar mesophases. Calorimetric investigations reveal that a phase transition occurs at elevated temperatures which is accompanied by a remarkable decrease in viscosity. The mixtures show a strong tendency towards supercooling. No recrystallization can be detected by differential scanning calorimetry (DSC) on second and further heating and cooling cycles. These observations are a strong hint to the existence of a cubic mesophase and point to the presence of a three-dimensional lattice within this mesophase.

The cubic phases should be the consequence of increased interface curvature of heterodimers of two-chain semiperfluorinated triazine **2** with the two- and three-chain acids **4–6**. Cubic phases are usually found as intermediates between lamellar and columnar phases or between columnar mesophases and micellar solutions. Considering that the rectangular columnar phases of 1/1 complexes **1/4** and **2/3** and the $\mathrm{Col_{ob}}$ phases of **1/5**,**6** are ribbon phases consisting of fragments of layers, the cubic phases of 1/1 mixtures of the triazine **2** with carboxylic acids **4–6** should be bicontinuous cubic phases ($\mathrm{Cub_V}$). They should consist of two interwoven but unconnected networks of branched cylinders, probably built up by ribbons. Thermotropic bicontinuous cubic phases composed of ribbons so far have been discussed for amphiphilic rod-like biphenyl derivatives.[20]

The 1/1 associates presented here can be regarded as hydrogen-bonded semiperfluorinated polycatenar mesogens that contain shorter but more polar rigid cores compared with covalently linked benzoate analogues. Interestingly, rectangular columnar phases with *C2mm* plane group have never been reported for covalent polycatenar liquid crystals.

Mixtures of triazines 1 and 2 with two and three equivalents of two- and three-chain fluorinated acids 4–6: The diamino-1,3,5-triazine core provides three molecular-recognition sites for hydrogen bonding. Hence, mesomorphic structure formation is not restricted to 1/1 mixtures of the complementary triazine/benzoic acid components. The phase transition data of selected 1/2 and 1/3 mixtures of triazines **1** and **2** with two-chain fluorinated acids **4** and **5** and with three-chain benzoic acid **6-[6,6]** are collected in Table 6.

In Figure 7, binary mixed systems of the triazines **1-[4,6]** and **2-[4,4]** with the one-chain and two-chain benzoic acids **3,4,5-[4,6]** are compared. In this way, by keeping constant the partially fluorinated chain segments of the two molecular species, direct comparison of mesomorphic properties in

Table 6. Phase transition temperatures T [°C] for the mesophases of 1/2 and 1/3 hydrogen-bonded complexes of 1,3,5-triazines **1** and **2** with semiperfluorinated two-chain and three-chain benzoic acids **4**–**6** (DSC, second heating with 10 K min^{-1}, transition enthalpies E [kJ mol^{-1}] in parentheses); hexagonal lattice constants a_{hex} [Å].[a]

Mixture	Cr	T (E)	Phase	T (E)	Iso	a_{hex}
1/2 1-[4,6]/5-[4,6]	●	48.9 (2.5)	Col$_h$	114.1 (2.4)	●	38.0
1/3 2-[4,4]/4-[4,6]	●	71.1 (62.8)	Col$_h$	113.4 (3.5)	●	35.6
1/3 2-[4,4]/5-[6,6]			Col$_h$	78.6 (2.8)	●	38.9
1/2 2-[4,4]/6-[6,6]	●	12.4 (2.6)	Cub	94.5 (1.2)	●	
1/3 2-[4,4]/6-[6,6]	●	22.6 (7.0)	Cub	91.4 (1.4)	●	

[a] Cr: crystalline; Col$_h$: hexagonal columnar; Cub: cubic; Iso: isotropic.

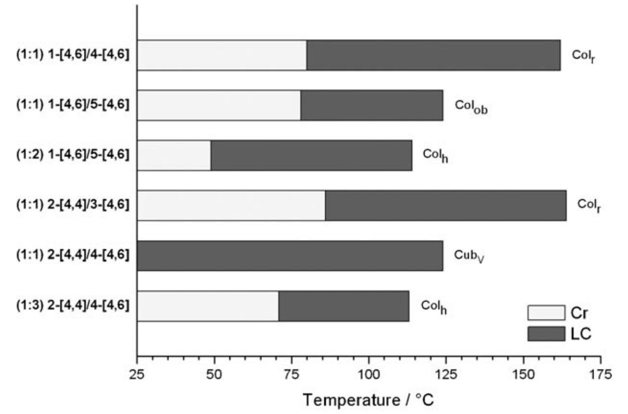


Figure 7. Influence of the number and positions of fluorinated chains and of the molar content of the benzoic acids **3**–**5** on the thermodynamic mesophase stability of binary mixtures with diamino-1,3,5-triazines **1** and **2**.

Figure 8. Optical texture of hydrogen-bonded 1/3 mixture **2-[4,4]/5-[6,6]**.

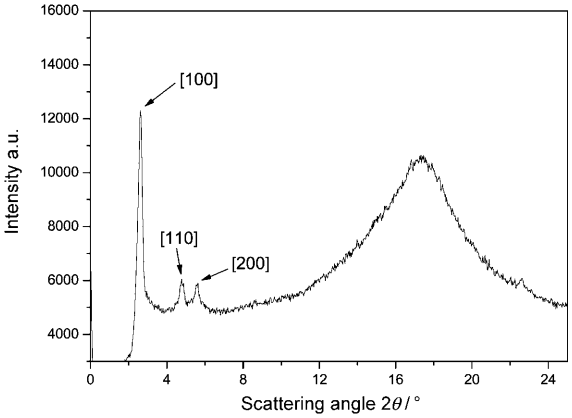


Figure 9. Wide-angle X-ray diffractogram of the mesophase of 1/3 binary mixture **2-[4,4]/5-[6,6]**.

dependence on the number and positions of fluorinated tails and on the molar content of the acid component is possible.

For 1/1 mixtures involving single-chain triazine **1-[4,6]** the phase stability is governed by the positions of the semiperfluorinated chains of the acids. The mixture of triazine **1-[4,6]** with benzoic acid **4-[4,6]** with the two partially fluorinated chains in the 3,4-positions has a significantly higher clearing temperature in comparison with the isomeric 3,5-disubstituted acid **5-[4,6]**. In the case of equimolar mixtures of two-chain triazine **2-[4,4]** the isotropization temperature considerably decreases on attaching a second fluorinated tail to the acid component.

The mesophase stability decreases with increasing content of the acids. Additional (dynamic) hydrogen bonding between H-donor groups and H-acceptor groups of the triazine that are not involved in complex formation with the acids, should take place within the ribbons and/or along the column axis and, aside from micro-segregation, should account for the mesophase stability. Therefore, as the number of free NH groups gradually decreases with increasing number of associated acid molecules, one would expect lowering of the isotropization temperature, consistent with the experimental findings.

The optical textures of the investigated 1/2 and 1/3 mixtures of triazines **1** and **2** with the two-chain partially fluorinated benzoic acids are characterized by regions with broken spherulites, mosaic-like domains and pseudo-isotropic areas containing birefringent lancets (Figure 8). These features are typical for hexagonal columnar (Col$_h$) mesophases.

The wide-angle X-ray scattering (WAXS) pattern of the **2-[4,4]/5-[6,6]** (1/3) complex (Figure 9) exhibits three sharp reflections in the small-angle region and a diffuse halo in the wide-angle regime. The ratio of the positions of the reflections of $1/3^{1/2}/2$ proves the existence of a hexagonal columnar mesophase. The hexagonal lattice constants for the investigated mixtures of triazines **1** and **2** with two and three equivalents of two-chain acids **4** and **5** are given in Table 6.

CPK models (Figure 10) reveal a more or less pronounced circular core geometry for 1/2 and 1/3 associates of diaminotriazines **1** and **2** with two-chain carboxylic acids **4** and **5**.

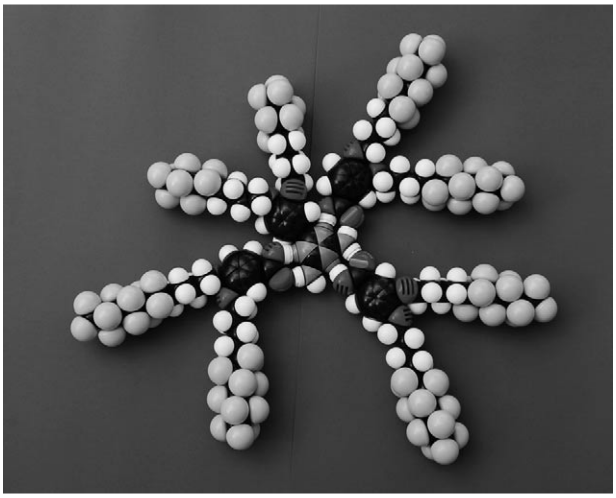


Figure 10. CPK model showing a 1/3 associate of two-chain triazine **2-[4,4]** with two-chain benzoic acid **4-[4,6]**.

The hydrogen-bonded polar aromatic cores are located in the center, surrounded by the lipophilic alkyl segments and, finally, by a shell of the fluorinated blocks. If one considers a random distribution of the peripheral groups, it follows that radial symmetrical cylinders are formed which organize to columnar phases with two-dimensional hexagonal symmetry.

The diameter of the 1/3 aggregates of triazine **2-[4,4]** with acid **4-[4,6]**, for example, is approximately 44 Å, in fair agreement with the hexagonal lattice constant ($a_{\mathrm{hex}}=35.6$ Å) determined by X-ray diffraction if one bears in mind the fluid nature of the peripheral alkyl spacers and interdigitation of semiperfluorinated chains of neighbouring columns to a certain extent.

The binary 1/2 and 1/3 mixtures of two-chain triazine **2-[4,4]** with three-chain fluorinated aromatic acid **6-[6,6]** display a highly viscous, optically isotropic cubic phase. Attaching a third semiperfluorinated tail to the acid component increases the volume fraction of the fluorinated molecular block. Therefore, the aggregates forming the cubic phases of the 1/2 and 1/3 mixed systems **2-[4,4]/6-[6,6]** must be more strongly curved than the cylindrical aggregates in the columnar phases of the apparent 1/3 compositions with two-chain acids **4** and **5**. Accordingly, the cubic phases of the 1/2 and 1/3 mixtures **2/6** should be a reverse discontinuous micellar cubic ($\mathrm{Cub_{I2}}$) phase built up by closed spheroidic micelles of the polar cores surrounded by a continuum of the nonpolar fluorinated chains.

Bicontinuous cubic phases can be found in all types of mesophase-forming materials, whereas the occurrence of micellar cubic phases is more restricted. They are well known for lyotropic systems[21] and in the phase sequence of block copolymers if one of the blocks has an especially large volume fraction.[22] In low molecular weight compounds micellar cubic phases only can be found provided that one of the incompatible molecular fragments is large enough to afford efficient overcrowding of the molecular periphery. Examples are conic dendrimers,[3e] coil–rod–coil block compounds,[23] amphiphilic polyhydroxy derivatives[3a,b] and hydrazides[24] and star-shaped molecules with semiperfluorinated chains.[25] In all these cases the chemically distinct molecular blocks are linked covalently to each other. The hydrogen-bonded triazine/acid associates reported here provide a new noncovalent approach to thermotropic micellar phases.

The phase sequence and structure of mesophase morphologies found for binary mixtures of the semiperfluorinated diaminotriazines with the fluoroalkoxybenzoic acids are shown schematically in Figure 11. The type of thermotropic mesophase depends on the hydrophilic/fluorophilic interface curvature, which is governed by carefully adjusting the volume fraction of the peripheral semiperfluorinated alkyl chain. Noteworthily, this phase sequence could not been realized with structurally related diaminotriazine/benzoic acid mixtures reported previously. The diversity of mesophase morphologies presented here could be achieved by attaching semiperfluorinated tails to both complementary molecular species.

Conclusion

Complex mesophase morphologies were achieved with noncovalently associated three-block molecules comprising distinct polar, lipophilic and fluorophilic fragments. These were realized with hydrogen-bonded complexes of diamino-functionalized 1,3,5-triazines and complementary benzoic acids. The molar content of the two components defines the molecular geometry of the hydrogen-bonded central polar core. The interface curvature of the assembled aggregates is controlled by the volume fraction of peripheral semiperfluorinated tails. The resulting phase sequence covers the range from columnar with two-dimensional rectangular and obli-

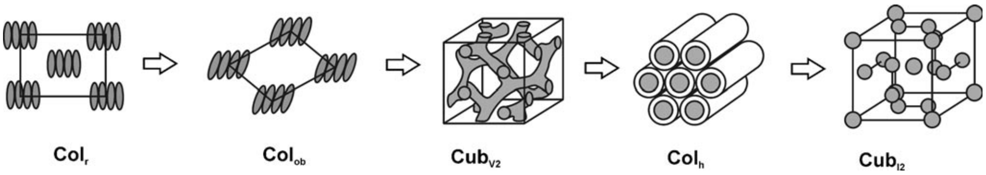


Figure 11. Mesophase morphologies of the hydrogen-bonded complexes of diaminotriazines **1** and **2** with benzoic acids **3**–**6** depending on the volume fractions of the semiperfluorinated alkoxy tails of the complementary molecular species.

que lattice symmetry, consisting of band-like segments of frustrated smectic layer, to micellar cubic. The transition from the ribbon phases to hexagonal columnar occurs via an intermediary three-dimensional bicontinuous cubic phase. Hence, the cooperative interplay of molecular recognition, nanoscale segregation of incompatible molecular blocks and adjusting the molecular topology by the space requirement of lipophilic and fluorinated segments provides a powerful tool for tailoring thermotropic mesophase morphologies.

Experimental Section

Textures were observed with an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photomicrographs were obtained with an Olympus E20 digital mirror reflex camera. Calorimetric investigations were performed with a Netzsch DSC 200. The X-ray studies ($Cu_{K\alpha}$) were carried out with a Nenius PDS 120 (Bruker) equipped with a detector from Inel. Photographs of CPK models were obtained with a Nikon D50 digital mirror reflex camera. The binary mixtures of triazines **1** and **2** with the benzoic acids **3**–**6** were prepared by dissolving the components separately in THF, combining the solutions and evaporating the solvent. Further investigations were performed after annealing the samples in the isotropic state.

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