Tailoring Thermotropic Mesophase Morphologies by Molecular Recognition and Fluorophobic Effect

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Received August 25, 2008. Revised Manuscript Received November 5, 2008

An alkoxyphenyl-substituted melamine derivative has been investigated in binary mixtures with two-chain and three-chain semiperfluorinated benzoic acids. Equimolar mixtures of the melamine with the complementary benzoic acids form discrete hydrogen-bonded heterodimers with elongated central core. The dimeric supermolecules involving two-chain partially fluorinated acids organize to infinite bilayer ribbons composed of distinct lipophilic, H-bonded polar aromatic and fluorinated regions, respectively. The two-dimensional lattice symmetry of the ribbon phases, rectangular or oblique, are defined by the positions of the fluorinated chains at the phenyl ring of the acid component. Heterodimers of the melamine with a three-chain partially fluorinated benzoic acid display a hexagonal columnar phase consisting of extended columnar aggregates with circular shape with a distinct lipophilic region in the center surrounded by side-by-side arranged H-bonded polar rodlike segments and, finally, by a shell of fluorinated fragments. Additionally, a cubic phase is observed at more elevated temperatures above the Col_h phase. Docking of 2 or 3 equiv. of the two-chain benzoic acids to the melamine core leads to the formation of cylindrical aggregates with a polar hydrogen-bonded aromatic center surrounded by lipophilic alkyl segments and an outer sphere of fluorinated molecular blocks. The aggregates organize to hexagonal columnar mesophases.

1. Introduction

Mesogenic self-assembly is mainly affected by segregation of incompatible molecular subunits in space into distinct microdomains.[1−4] The mesophase morphologies are largely determined by the mean lateral area of the competing molecular blocks. Linear mesogens mostly display nematic or smectic mesophases. Increasing the wedgelike character of a mesogen, i.e., building taper-shaped or cone-shaped structures, leads in principle first to bicontinuous cubic (Cub_v), then to columnar, and finally to spheroidic cubic phases (Cub_I).[4,5] Therefore, for nonlamellar thermomesophases of taper shaped amphiphiles, usually two different types are observed. In reversed phases (type 2; negative curvature of the polar/apolar interface) the stronger cohesive forces such as hydrogen bonding are located inside the aggregates. In normal phases (type 1), they are located in the outer sphere surrounding the aggregates.[6]

Three-chain polycatenar compounds usually exhibit nematic and smectic C phases. Increasing the number of flexible chains attached to the termini of the elongated rodlike core leads to a break up of the layers into ribbonlike aggregates which can organize to bicontinuous cubic and columnar mesophases. Thus, smectic C, cubic, and columnar phases were observed for tetracatenar molecules, whereas exclusively columnar mesophases were found for penta- and hexacatenar compounds.[7]

A powerful tool toward designing highly organized soft matter arises from strong cohesive forces such as hydrogen bonding between identical or complementary molecules.[8] The individual molecular species need not necessarily to be mesogenic in their own right.

For example, Kato et.al. investigated the mesomorphic properties of various pyridine derivatives in mixtures with carboxylic acids.[9−13] The columnar mesophases of alkoxy-substituted triarylmelamines[14] can be controlled by hydrogen-bonding with alkoxybenzoic acids.[15,16] Double hydrogen-bonded aggregates of 2,6-diacylaminopyridines with benzoic acids exhibit smectic or columnar liquid crystalline phases.[17,18]

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10.1021/cm802298v CCC: $40.75

Triple H-bonded complexes of diacylaminopyridines with uracil derivatives display columnar phases.[19,20]

Because of the incompatibility of perfluorinated segments with hydrogenated, aromatic, and polar molecular parts, molecules combining both structural features show distinct amphiphilic behavior. Aside from calamitic[21−23] and discotic[24,25] liquid crystals, semiperfluorinated molecular blocks have been introduced into nonanisometric mesogens such as amphiphilic polyhydroxy derivatives,[26,27] tetrahedral,[28,29] and taper-shaped[30−32] compounds. The fluorophobic effect may lead to the stabilization, modification and even induction of thermotropic mesophases. For example, amino substituted phenyl-1,3,5-triazines grafted with partially fluorinated alkyl chains display lamellar or inverted discontinuous (micellar) cubic phases[33] depending on the number of chains, whereas related hydrocarbon analogues are nonmesomorphic in their pure states.[34]

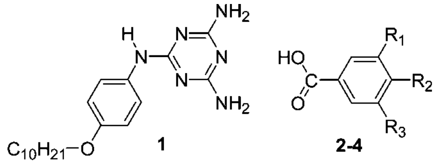
So far, only few examples of supramolecular mesogens are known that arise from the combination of molecular recognition between complementary molecular components and the fluorophobic effect.

Thus, hydrogen-bonded complexes derived from pyridine derivatives and one-chain fluorinated acids exhibit smectic and cubic mesophases.[35−39] Mixed systems comprising two-chain partially fluorinated benzoic acids show columnar phases.[39]

Equimolar compositions of alkoxy modified triarylmelamines with semiperfluorinated benzoic acids form hexagonal columnar mesophases.[40] Segregation of fluorinated blocks from lipophilic side chain regions leads to a superstructure within the hexagonal lattice.

Hydrogen-bonded associates of nonmesomorphic 2,4-diamino-6-phenyl-1,3,5-triazines with two-chain semiperfluorinated aromatic acids organize to columnar phases with rectangular, oblique or hexagonal lattice symmetry.[34] The two-dimensional unit cell can be regulated by the number of alkoxy tails of the triazine component and by the molar content of the two complementary species.

Chart 1. Chemical Structures of the Decyloxyphenyl Substituted Melamine 1 and of the Complementary Semiperfluorinated Benzoic Acids 2−4



	R_1	R_2	R_3
2-[6,4]	$O(CH_2)_6C_4F_9$	H	$O(CH_2)_6C_4F_9$
3-[6,4]	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	H
3-[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
4-[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$

Equimolar mixed systems of biphenyl modified diamino-1,3,5-triazines with a two-chain partially fluorinated benzoic acid form descrete H-bonded heterodimers. The dimeric supermolecules exhibit rectangular columnar phases with *C*2*mm* plane group. Hydrogen-bonded aggregates with three acid equivalents form either a rectangular columnar phase with *p*2*m* lattice symmetry or a columnar liquid crystalline phase on a two-dimensional square lattice. Here, the chemical nature of terminal alkyl moieties at the biphenyl core, fluoroaliphatic or lipophilic, along with the elongated biphenyl-triazine core mainly accounts for the 2D lattice symmetry.[41]

The elongation of the rod-shaped aromatic core of amino substituted triazines by replacing a phenyl ring by a biphenyl unit means one approach toward increasing the intramolecular contrast. The concept we follow here is to reinforce the intramolecular polarity gradient by inserting a secondary amino group between the phenyl ring and the nitrogen heterocycle of the triazine component. We report mesomorphic properties of the alkoxyphenyl substituted melamine derivative **1** in mixtures with the two-chain and three-chain semiperfluorinated benzoic acids **2−4** (Chart 1). The expectation is that the mixed systems assemble to polyphilic three-block supermolecules composed of a flexible lipophilic fragment, a fluorophilic segment and a central polar molecular block (Figure 1).

2. Results and Discussion

2.1. Equimolar Compositions of the Complementary Components. *2.1.1. General Trends.* The phase transition temperatures of the aryl-modified melamine derivative **1** and of the semiperfluorinated benzoic acids **2−4** are collected in Table 1.

The alkoxyphenyl substituted melamine 1 shows a direct transition from the crystalline state to the isotropic liquid.

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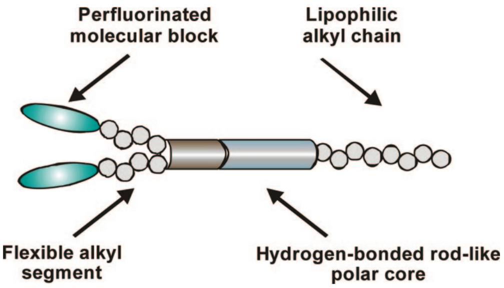

Figure 1. Polyphilic three-block molecules composed of a fluorinated molecular fragment, a hydrogen-bonded central core, and a lipophilic flexible alkyl moiety.

Table 1. Phase Transition Temperatures (°C) for the Pure Melamine 1 and the Semiperfluorinated Benzoic Acids 2−4, DSC, Second Heating with 10 K/min, Monotropic Phase Transitions[a] in Square Brackets

compd	phase transitions[b]
1	Cr 206.0 I
2-[6,4]	Cr 58.8 I
3-[6,4]	Cr 54.7 [Col$_h$ 53.1] I
3-[4,6]	Cr 115.7 [Col$_h$ 102.0] I
4-[4,6]	Cr 51.0 Col$_h$ 81.1 I

[a] Obtained from the second DSC cooling scan. [b] Cr = crystalline; Col$_h$ = hexagonal columnar; *I* = isotropic.

Table 2. Transition Temperatures (°C) and Associated Enthalpy Values (kJ/mol) of Equimolar Compositions of the Melamine 1 with the Semiperfluorinated Benzoic Acids 2−4, DSC, Second Cooling with 10 K/min, Phase Transition Enthalpies (kJ/mol) in Brackets

mixture	phase transitions[a]
1/2-[6,4]	Col$_r$ 108.3 (2.2) I
1/3-[6,4]	Col$_{ob}$ 138.2 (2.6) I
1/3-[4,6]	Col$_{ob}$ 168.9 (2.8) I
1/4-[4,6]	Col$_h$ 118.6 (1.2) Cub$_I$ 145.9 (0.12) I

[a] Col$_r$ = rectangular columnar; Col$_{ob}$ = columnar, oblique lattice; Col$_h$ = hexagonal columnar; Cub$_I$ = micellar cubic; *I* = isotropic.

The semiperfluorinated acid **2**-[6,4] is nonliquid crystalline as well. Changing the positions of the fluorinated tails at the phenyl ring of the acid from 3,5 to 3,4 gives rise to monotropic hexagonal columnar (Col$_h$) phases for the two-chain acids **3**. The benzoic acid **4**-[4,6] fitted with three partially fluorinated alkoxy chains displays an enantiotropic Col$_h$ phase. The columnar phases are related to the formation of descrete disklike benzoic acid dimers via hydrogen bonding.[42]

Equimolar mixed systems of the melamine **1** with the semiperfluorinated benzoic acids **2−4** exhibit thermotropic mesophases within the temperature ranges given in Table 2. The monotropic phases of the two-chain acids **3** are replaced by enantiotropic liquid crystalline phases. It is particular noteworthy that association between the two nonmesomorphic complementary compounds **1** and **2** leads to the induction an enantiotropic phase.

The isotropization temperatures of the 1:1 mixtures are remarkably higher than those of the corresponding pure fluorinated acids. No crystallization is observed for the 1:1 compositions. The equimolar binary mixture **1/3**-[4,6] displays an increased clearing temperature compared to the mixed system of the melamine **1** with the homologous benzoic acid **3**-[6,4]. Thus, elongation of the fluorinated molecular segment along with reducing the number of flexible chain segments leads to an enhanced thermodynamic mesophase stability of the triazine/benzoic acid systems **1/3**.

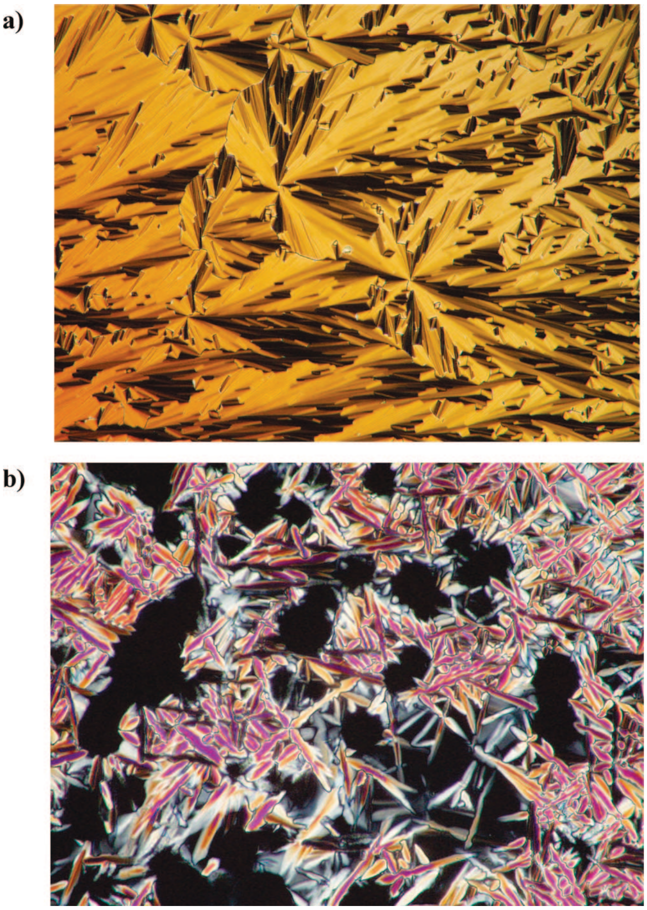

Figure 2. Optical textures observed for the mesophases of the alkoxyphenylmelamine **1** in mixtures with the semiperfluorinated benzoic acids **2−4** at a molar ratio of 1:1: (a) **1/3**-[6,4], first cooling at 1 K min^{-1} at 129.8 °C; (b) **1/4**-[4,6] second cooling at 1 K min^{-1} at 105.8 °C.

Fernlike optical textures develop on cooling the equimolar composition of the triazine **1** with the two-chain acids **2** and **3** from the isotropic liquid which collate to form spherulitic textures (Figure 2a). The textures of the 1:1 mixture **1/4**-[4,6] are characterized by mosaic-like regions, domains with broken spherulites and pseudoisotropic areas containing birefringent lancets (Figure 2b). Though both texture types are indicative for a columnar mesophase, the mentioned differences may point to different two-dimensional lattice structures depending on the positions and number of fluoroalkyl chains of the benzoic acid component.

Upon being heated, the birefringent mesophase of the binary mixture of the melamine **1** with the three-chain semiperfluorinated benzoic acid **4**-[4,6] transforms into a highly viscous optically isotropic phase. Even shearing does not induce any birefringence within the temperature range of this phase. DSC traces reveal an additional phase transition at more elevated temperatures, which is accompanied by a remarkable decrease in viscosity. These observations are a strong hint toward the existence of a cubic mesophase.

Figure 3 shows the FTIR transmission spectrum of the 1:1 mixture **1/3**-[4,6] recorded at 130 °C within the me-

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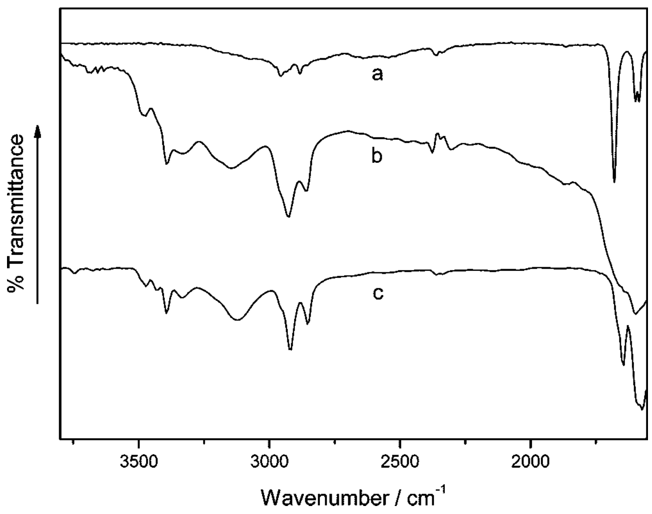

Figure 3. FTIR spectra of (a) the pure partially fluorinated benzoic acid **3**-[4,6], (b) the 1:1 mixture **1/3**-[4,6] recorded at 130 °C within the liquid crystalline phase, and (c) the amino-substituted 1,3,5-triazine **1** in its pure state.

sophase and the spectra of the pure acid **3**-[4,6] and the melamine **1**. The absorption band at 3120 cm^{-1} of the amino substituted triazine **1** is shifted to 3150 cm^{-1} in the spectrum of the 1/3-[4,6] mixture. A new absorption appears for the complex at 1867 cm^{-1} that is assigned to a hydrogen bridge between the hydroxyl group of the acid and the endocyclic nitrogen of the heterocycle.[43,44] The carbonyl absorption at 1680 cm^{-1} for the pure benzoic acid maintains its position in the mixture with the melamine **1**. This behavior seems to be reasonable if one takes into account that the hydrogen bonding of the acid dimers is replaced by a hydrogen bridge between the carboxylic group and an exocyclic amino group of the melamine component. In the isotropic state an absorption maximum appears at 3195 cm^{-1} with an additional shoulder at almost the same position as in the mesophase (3160 cm^{-1}) (see the Supporting Information, Figure S4). This result suggests that the H-bonded complex breaks at least in part above the clearing point.

From the IR investigations, it can be deduced that the association between the melamine **1** and the complementary benzoic acids **2**−**4** is due to double hydrogen bonding between the nitrogen heterocycle substituted with exocyclic amino groups and the carboxylic groups. Similar hydrogen bonding motifs have been reported, i.e., for complexes of structurally related 2-fold amino substituted alkoxyphenyl-1,3,5-triazines with semiperfluorinated benzoic acids[34] and for mixtures of 2,6-diacylaminopyridines with 4-alkoxybenzoic acids.[17]

*2.2.2. Equimolar Mixtures of the Melamine **1** with the 3,5-Disubstituted Benzoic Acid **2**.* Figure 4 displays the wide-angle X-ray diffractogram obtained for the mesophase of the equimolar **1/2**-[6,4] mixture. In the X-ray pattern, only reflections with $h + k = 2n$ have been observed in the small-angle region. These reflections can be assigned to a centered rectangular lattice (*C*2*mm*) with the lattice parameters a = 6.5 nm and b = 7.1 nm.

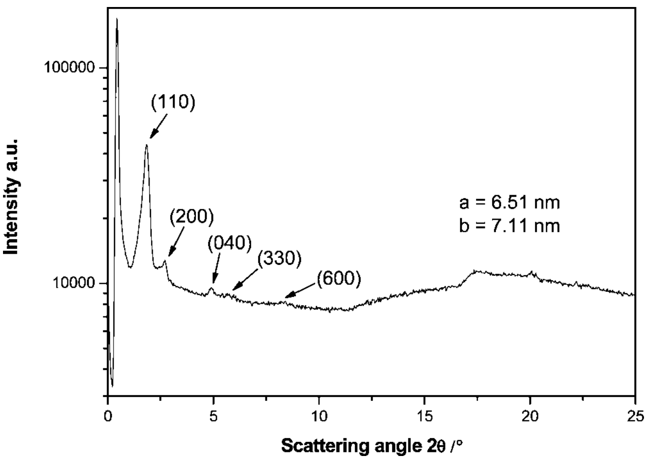

Figure 4. Wide-angle X-ray diffractogramm (at 90 °C) for the rectangular columnar phase of the equimolar complex of the triazine **1** with the benzoic acid **2**-[6,4] grafted with two semiperfluorinated chains in the 3,5-position of the phenyl ring.

It is reasonable to suggest that docking of just 1 equiv. of the benzoic acid **2** to the melamine heterocycle **1** preferably occurs opposite from the bulky phenyl group for steric reasons leading to heterodimeric supermolecules **1/2**-[6,4] with a pronounced rodlike core geometry. Heterodimers with a rodlike shape of the polar H-bonded core recently also have been reported for equimolar compositions of aryl substituted diamino-1,3,5-triazines with complementary benzoic acids.[34,41]

An efficient space filling within the mesophase should be accomplished by a close side-by-side organization of the elongated aromatic units. As it is evident from CPK models, the length of H-bonded dimers **1/2** amounts to approximately 4.5 nm considering almost stretched conformations of the flexible alkyl segments. The lattice parameter b matches nearly twice the molecular length. Therefore, it is most likely that hydrogen-bonded bilayer aggregates are present in the rectangular lattice.

Figure 5a shows a possible bilayer organization of eight closely packed supermolecules **1/2**. The cross-section of the lipophilic region is significantly smaller than that of the fluorinated region. The resulting different space filling within the segregated domains gives rise to a frustration within the layers which causes their collapse with formation of bilayer ribbons arranged in a rectangular *C*2*mm* lattice (Figure 5b). The ribbons can be regarded as small bandlike segments of the layers.

The proposed ribbon model seems reasonable because it enables the segregation of fluorophilic and lipophilic moieties into separate regions whereby the parallel organization of the polar H-bonded cores is maintained.

The number of heterodimers **1/2** was calculated according to $n = V_{\mathrm{cell}}/V_{\mathrm{mol}}$. The cell volume ($V_{\mathrm{cell}}$) was evaluated by assuming a height of 4.5 Å.[34,41] The molecular volume was calculated using volume increments.[45] The calculations yielded a value of approximately 16 molecules per unit cell.

The lattice parameter b corresponds to the height of the bilayer ribbons considering the fluid nature of the flexible alkyl chains, whereas the lattice constant a is in accordance

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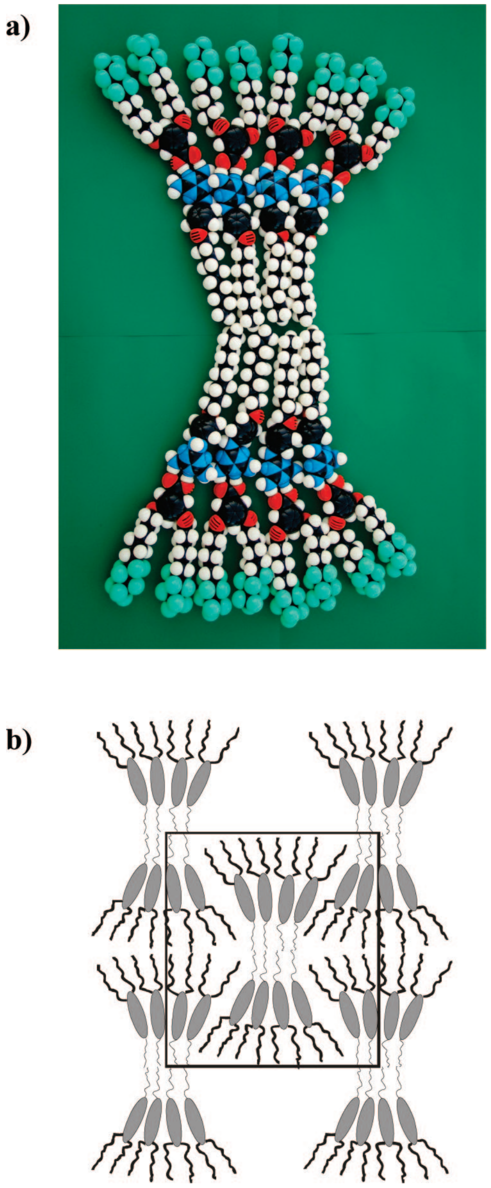

Figure 5. (a) CPK model showing a possible bilayer arrangement of eight hydrogen-bonded **1**/**2**-[6,4] dimers. Only more or less stretched conformations of the flexible alkyl chains are considered. (b) Schematic presentation of the bilayer ribbon phase of equimolar complexes of the alkoxyphenyl substituted melamine **1** with the two-chain semiperfluorinated benzoic acid **2**-[6,4] with rectangular columnar organization (two-dimensional *C*2*mm* space group).

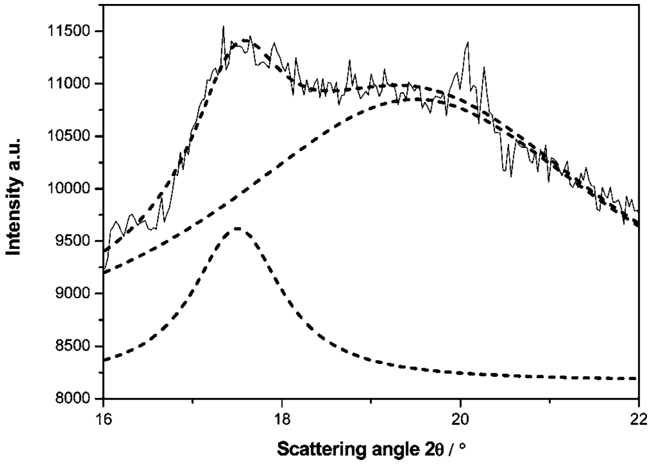

Figure 6. Profile of the wide-angle scattering in the rectangular columnar phase of the mixed system **1**/**2**-[6,4] with splitting into two maxima.

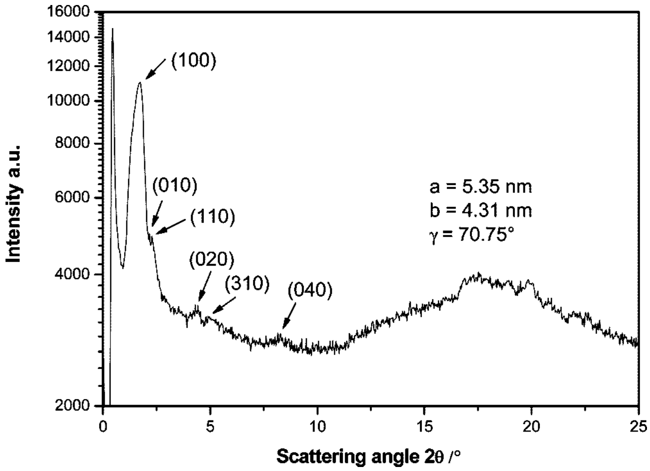

Figure 7. Wide-angle X-ray diffractogram of the columnar mesophase of the equimolar mixed system **1**/**3**-[6,4] at 120 °C.

with the lateral dimension of the ribbons by assuming on average four neighboring dimers within one ribbon.

The diffuse scattering in the wide-angle region of the WAXS diffractogram of the 1:1 mixed system **1**/**2** exhibits an asymmetric profile that has been analyzed as consisting of two maxima at $2\theta = 17.5$ and 19.5° (Figure 6). The first value can be attributed to the perfluorinated segments, whereas the second is commonly observed for fluid aliphatic regions.[46] This result further supports the assumption that the chemically incompatible aliphatic and fluorinated parts segregate in space with formation of a bilayer ribbon phase.

*2.1.3. Equimolar Complexes of the Triazine **1** with the Two-Chain Benzoic Acids **3**.* The WAXS diffractogram of the 1:1 complex **1**/**3**-[6,4] is shown in Figure 7. The small-angle scatterings fit best by assuming a two-dimensional oblique lattice (Col$_{ob}$). The lattice parameters of the Col$_{ob}$ phase of the equimolar **1**/**3**-[6,4] mixture amount to $a = 5.3$ nm, $b = 4.3$ nm, and $\gamma = 70.7°$. The number of H-bonded dimers **1**/**3**-[6,4] within the cross-section of the oblique lattice was calculated to be about eight.

One can imagine that the molecular organization of elongated H-bonded heterodimers **1**/**3** within the oblique unit cell resembles a bilayer arrangement, which is also in line with the appearance of two maxima in the wide-angle regime of the WAXS diffractogram at 1.75 and 2.0 nm. However, fixing the two semiperfluorinated tails at the 3,4-positions of the benzoic acid changes the symmetry of the acid component. As the consequence, the H-bonded heterodimers **1**/**2** and **1**/**3** differ with respect to their molecular topology.

It follows from CPK models that shifting of the rigid rodlike cores of the **1**/**3** dimers against each other leads to a more efficient space filling compared to the heterodimers **1**/**2** (Figure 8a). However, the cross-section of the segregated semiperfluorinated chains still exceeds the cross-sectional area of the alkyl chain regions. It follows that solely tilting the molecules cannot sufficiently compensate for the resulting steric frustration. The smectic layers break up into ribbonlike

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segments with curved interfaces due to the different space filling of the fluorinated and lipophilic regions. The ribbonlike aggregates organize to columnar mesophases on a two-dimensional oblique lattice (Figure 8b).

*2.1.4. 1:1 Mixture of Compound **1** with the Three-Chain Acid **4**.* The X-ray diffractogram obtained for the mesophase of the alkoxyphenylmelamine **1** with the three-chain partially fluorinated benzoic acid **4**-[4,6] at an equimolar ratio of the components is characterized by (100) and (110) reflections in the small-angle region with a reciprocal spacing ratio of 1:$\sqrt{3}$. This is unambiguously typical for a hexagonal columnar mesophase. The hexagonal lattice constant amounts to a_{hex} = 6.75 nm. The length of the hydrogen-bonded supermolecules **1/4** in its most extended conformation is L = 4.4 nm. The ratio a_{hex}/L amounts to 1.53. This value is on the same order of magnitude as those found for the Col_h phases of taper-shaped mesogens.[6,47,48]

The incorporation of a third semiperfluorinated chain into the acid component increases the wedge-shaped character of the H-bonded melamine/acid heterodimers. We assume that the hexagonal columnar phase of the equimolar associates **1/4** should consist of extended columnar aggregates built up by a distinct lipophilic region of strongly coiled fluid alkyl chains in the center surrounded by the polar aromatic segments arranged side-by-side and, finally, by a shell of the fluorinated moieties (Figure 9).

The number of dimers **1/4** arranged in a single slice of the columns was estimated to be approximately 10. Because of the elongated rigid hydrogen-bonded aromatic units, this value is larger than that found for other wedge-shaped compounds.[6,48−50]

Thus, the hexagonal columnar phase of the H-bonded heterodimers **1/4** should be characterized by an average cylindrical diameter of the columns, whereas the Col_r and Col_{ob} phases of equimolar compositions **1/2** and **1/3** involving the respective two-chain semiperfluorinated benzoic acids represent ribbon phases that are built by ribbonlike segments of a collapsed smectic layer structure.

Nontheless, it should be noticed that we cannot completely rule out a structural model for the Col_h phase of the 1:1 mixture **1/4** involving a bilayer ribbonlike aggregate that is rotationally disordered. This type of model has been used to explain the columnar phases of polycatenar compounds.[7] However, a disordered ribbon arrangement would not explain the phase sequence Col_h → Cub of the 1:1 mixture **1/4** because polycatenar mesogens display only (bicontinuous) cubic phases as intermediate between lamellar and columnar mesomorphic organization. The formation of a micellar cubic phase has never been proven for polycatenar compounds.

With respect to the temperature regime, the cubic phase of the 1:1 mixture **1/4** occurs above the respective hexagonal columnar phase. Taking into account the increased molecular mobility at more elevated temperatures, the aggregates forming the cubic phase should be more strongly curved than cylindrical aggregates in the Col_h phase of the 1:1 mixture **1/4**. Therefore, the cubic mesophase should be a discontinuous cubic (Cub_I) phase built up by closed micelles with an inner lipophilic core and an outer spheroidic region of the fluorinated tails. A transition from a hexagonal columnar phase composed of aggregates with an average circular cross sectional shape to a micellar cubic phase upon heating so far has been reported, i.e., for amphiphilic taper-shaped polyhydroxy derivatives.[48]Hence, this columnar−cubic dimorphism further supports our structural model for the Col_h phase of the 1:1 mixture **1/4** given schematically in Figure 9.

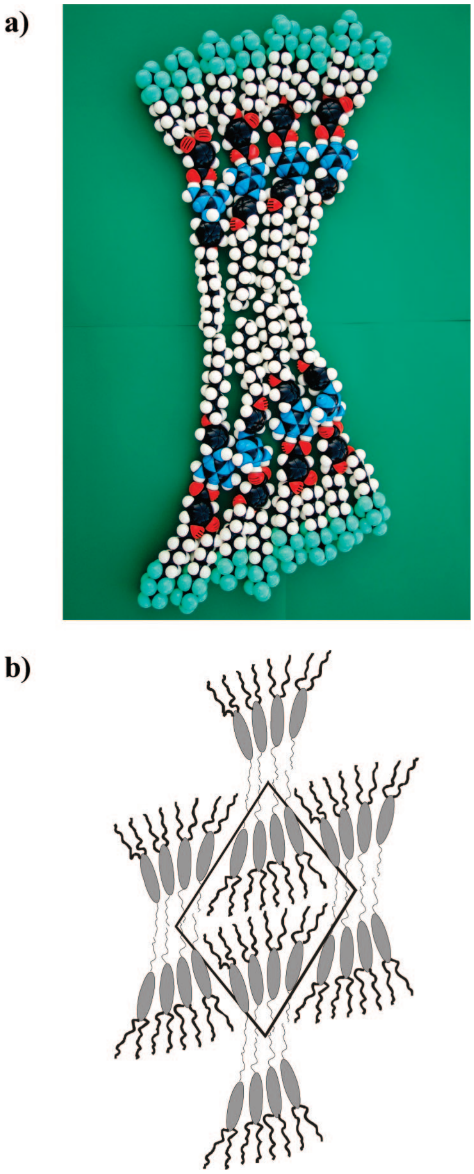

Figure 8. (a) CPK model showing a bilayer segment with eight heterodimers of the melamine **1** with the fluorinated benzoic acid **3**-[6,4] with tilted arrangement of parallel aligned elongated cores. (b) Model for the molecular arrangement of the H-bonded supermolecules **1/3** in their columnar mesophases with two-dimensional oblique lattice symmetry (Col_{ob}).

The structures of the columnar and of the micellar phases of the equimolar melamine/benzoic acid compositions **1/2−4** are special as aliphatic and semiperfluorinated segments are separated by the H-bonded aromatic cores. In this respect,

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(47) Sauer, C.; Diele, S.; Lindner, N.; Tschierske, C. *Liq. Cryst.* **1998**, *25*, 109.

(48) Borisch, K.; Diele, S.; Göring, P.; Kresse, H.; Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529.

(49) Percec, V.; Heck, J.; Tomazos, D.; Falkenberg, F.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans.* **1993**, 2799.

(50) Praefcke, K.; Marquardt, P.; Stephan, W.; Levelut, A.-M.; Wachtel, E. *Mol. Cryst. Liq. Cryst.* **1991**, *203*, 149.

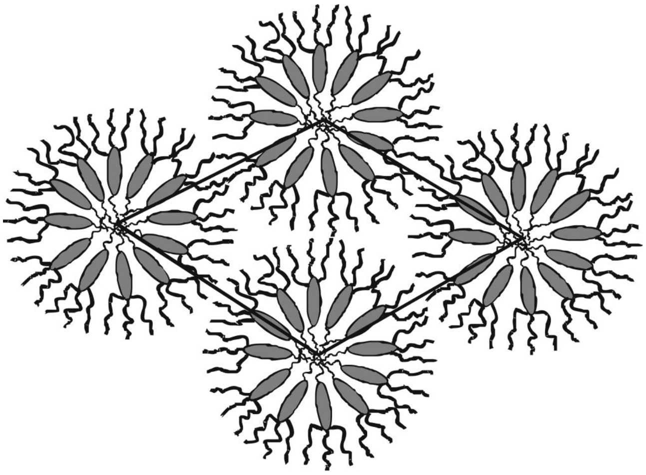

Figure 9. Model for the organization of hydrogen-bonded heterodimers of the melamine **1** with the three-chain semiperfluorinated benzoic acid **4** in the hexagonal columnar (Col$_h$) phase.

Table 3. Phase Transition Data (°C) of Selected Binary Mixed Systems of the Melamine 1 **with 2 and 3 Equiv. of the Benzoic Acids** 2 **and** 3 **(DSC, second cooling with 10 K/min, transition enthalpies (kJ/mol) in parenthesis)**

mixture	Cr		Col$_h$		I	a_{hex} (nm)
(1:2) 1/2-[6,4]	•	–37.0 (1.7)	•	83.1 (2.8)	•	3.85
(1:3) 1/2-[6,4]	–		•	73.3 (4.3)	•	4.03
(1:2) 1/3-[6,4]	•	–42.2 (2.2)	•	106.5 (4.4)	•	3.61
(1:3) 1/3-[4,6]	•	72.8 (8.8)	•	148.6 (6.6)	•	4.18

the novel hydrogen-bonded heterodimers **1/2−4** cannot be regarded as to belong to either a normal or a reversed phase type forming mesogen. The Col$_h$ phase of the 1:1 mixture **1/4** is a special type of core−shell arrangement. This model corresponds to the complex hexagonal phase initially proposed by A.-M. Levelut for polycatenar mesogens[51] but which was later withdrawn.

Furthermore, it should be noted that the mesophase morphologies of the equimolar mixed systems **1/2−4** are quite different from the phase behavior reported for structurally similar tricatenar mesogens bearing two bulky fluorocarbon chains at one end and one slim alkyl chain at the other end of the rod-shaped core. In that case, the strong steric dipole arising from the pronounced taper shape inhibits the segregation of the incompatible end groups. The steric dipole is compensated for by an antiparallel packing of the molecules in a smectic phase, built up by a sequence of aromatic and mixed fluoroaliphatic sublayers.[46] Probably, additional hydrogen bonding between aminotriazine moieties not involved in association with the acid components contributes to the parallel arrangement of neighboring melamine/acid heterodimers **1/2−4**.

2.2. Mixtures of the Melamine 1 **with 2 and 3 Equiv. of the Fluorinated Acids** 2 **and** 3. Mesomorphic structure formation is not limited to equimolar compositions of the complementary melamine/benzoic acid components. Table 3 summerizes the phase transition temperatures of selected (1:2) and (1:3) mixed systems of the triazine **1** with the two-chain fluorinated acids **2** and **3**.

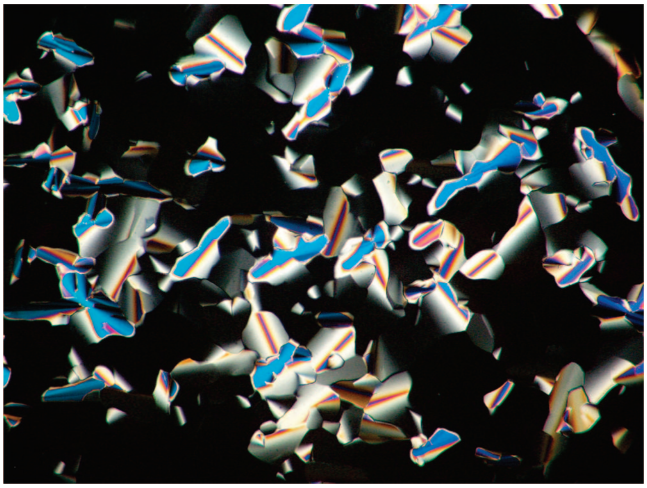

Figure 10. Photomicrograph (crossed polarizers) observed on cooling for the hexagonal columnar (Col$_h$) phase of the (1:2) mixed system **1/2**-[6,4] at 64 °C.

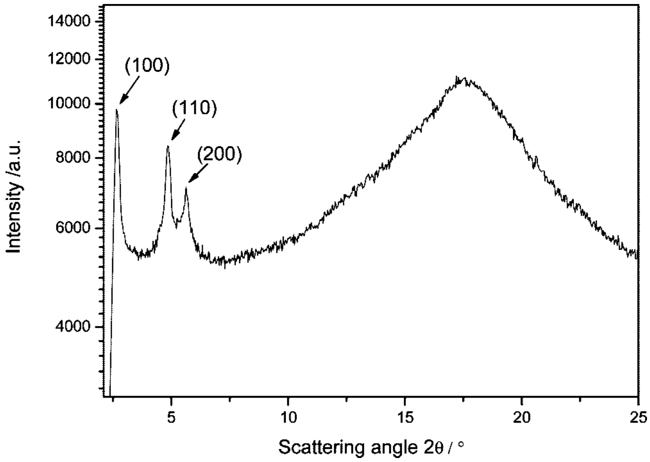

Figure 11. Wide-angle X-ray diffractogram obtained for the Col$_h$ phase of the (1:2) mixture **1/2**-[6,4] at 70 °C.

The isotropization temperatures of the (1:2) binary mixed systems are lower than those of the respective equimolar complexes. A further decrease in the clearing temperatures is observed for the (1:3) mixture **1/2**-[6,4] compared with the mixture containing 2 equiv. of the acid **2**-[6,4]. The mixed systems **1/3** involving 3,4-disubstituted benzoic acids show higher clearing temperatures than those with the acid **2**-[6,4] grafted with the two semiperfluorinated chains at the 3,5-positions of the phenyl ring.

The mesophase textures of the investigated (1:2) and (1:3) compositions are identical and can be characterized by the observation of large homeotropic aligned regions containing birefringent filaments (Figure 10), which is typical for hexagonal columnar phases.

The WAXS diffractogram for the (1:2) **1/2**-[6,4] complex is given in Figure 11. The X-ray diffraction pattern of the mesophase of the mixed system **1/2**-[6,4] at a 1:2 molar ratio exhibits three sharp reflections in the small angle region and a diffuse halo in the wide angle region. The ratio of positions of the reflections is $1:3^{1/2}:2$, proving the existence of a hexagonal columnar (Col$_h$) mesophase. The hexagonal lattice constants a_{hex} for the mixtures of the melamine **1** with two and three acid equivalents are given in Table 3.

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(51) Levelut, A.-M.; Malthete, J.; Destrade, C.; Nguyen, H.-T. *Liq. Cryst.* **1987**, *2*, 877.

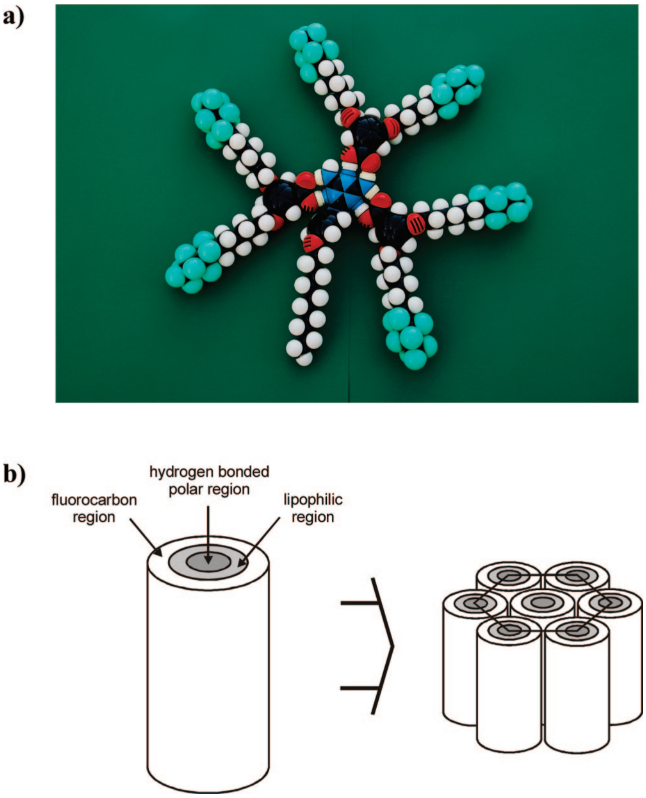

Figure 12. (a) CPK model of the hydrogen-bonded (1:3) complex of the melamine **1** with the two-chain semiperfluorinated benzoic acid **2**-[6,4]. (b) Hexagonal columnar mesophase of the melamine **1** in mixtures with 2 or 3 equiv. of the two-chain fluorinated benzoic acids **2** and **3**.

Interestingly, the hexagonal lattice constants of the 1:2 and 1:3 compositions **1/2**,**3** are considerably smaller compared with the intercolumnar distance determined for the Col_h phase of the equimolar mixture **1/4**. Therefore, the molecular organization of 1:2 and 1:3 aggregates within their Col_h phase should be different from that of the melamine **1** associated with one equivalent of the fluorinated acid **4**-[4,6].

CPK models reveal that docking of two or three molecules of the semiperfluorinated benzoic acids **2** and **3** at the melamine core leads to H-bonded associates with a pronounced circular geometry (Figure 12a). Cylindrical aggregates are formed that consist of three distinct molecular regions, the polar hydrogen-bonded aromatic region located in the center surrounded by the lipophilic alkyl segments and, finally, the fluorinated blocks distributed arround the cylindrical core region. The parallel alignment of these aggregates leads to the two-dimensional hexagonal lattice symmetry (Figure 12b).

The diameter of the (1:3) mixture of the melamine **1** and the acid **2**-[6,4], for example, evaluated from the CPK model amounts to approximately 4.4 nm. This value is in excellent agreement with the hexagonal lattice constant (4.0 nm) determined by X-ray diffraction.

3. Conclusions

The hydrogen-bonded complexes of the alkoxyphenylmelamine with the complementary semiperfluorinated benzoic acids can be considered as noncovalent analogues of block mesogens composed of three different and incompatible molecular segments. Docking of 1 equiv. of the acids preferentially leads to heterodimers with elongated aromatic cores. Microsegregation along with the linear preorganization of the extended H-bonded polar segments favors a parallel bilayer-like arrangement. However, the stabilization of layered mesophases is in competition with the disturbance provided by the different space requirements of the fluorinated and lipophilic molecular blocks. Numerous different columnar phases are formed. The two-dimensional lattice symmetries are tailored by adjusting the positions and the number of semiperfluorinated tails of the acid component.

Because of the particular arrangement of the heterodimers with nanospheres of lipophilic and fluorophilic segments separated by the polar H-bonded cores, the mesophases cannot be classified as common nonlamellar phases of the normal or the reversed type.

The special core−shell arrangement of the hexagonal columnar phase and the micellar cubic phase of the 1:1 mixture with the three-chain fluorinated acid provide a major difference to the mesophase structures of covalently constructed polycatenar compounds.

A further approach toward controlling the molecular topology arises from the molar content of the acid. Hydrogen-bonding with two or three acid molecules defines a cylindrical molecular geometry of the melamine/benzoic acid associates, which consequently organize to hexagonal columnar mesophases.

Hence, the cooperative interplay of hydrogen bonding, nanoscale segregation of incompatible molecular blocks, and controlling the interface curvature of assembled aggregates by the volume fractions of molecular fragments segregated in different subspaces accounts for tailoring the mesophase morphologies of the complementary molecular species.

Acknowledgment. This work was supported by the Land Brandenburg, Germany, and the Fonds der Chemischen Industrie. We are very grateful to B. Smarsly for the kind support in performing X-ray measurements at the Max Planck Institute of Colloids and Interfaces, Potsdam-Golm, Germany.

Supporting Information Available: Experimental procedures, analytical data, DSC traces, and temperature-dependent IR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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