Mesophase Morphologies of Hydrogen-Bonded Complexes of Biphenyl-Substituted Diamino-1,3,5-triazines with Semiperfluorinated Benzoic Acids

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Two 2,4-diamino-6-biphenyl-4-yl-1,3,5-triazines carrying either one semiperfluorinated or two lipophilic alkoxy chains at the terminal position of the biphenyl moiety have been investigated in binary mixtures with two-chain and three-chain partially fluorinated benzoic acids by means of polarizing microscopy, differential scanning calorimetry, and X-ray diffraction. Equimolar compositions of the triazines with the complementary two-chain benzoic acid form descrete hydrogen-bonded heterodimers. The dimeric supermolecules organize to rectangular columnar phases in the *c*2*mm* plane group. The $\mathrm{Col_r}$ phases are composed of infinite ribbons of parallel aligned H-bonded rigid polar cores which are separated by aliphatic/fluorinated regions. H-bonded associates of the fluorinated triazine with three equivalents of the two-chain acid form a rectangular columnar phase (*p*2*m* symmetry). Replacing the one fluorinated chain of the triazine by two alkoxy groups leads to a columnar phase on a two-dimensional square lattice (*p*4*mm*) in a 1:3 mixture with the two-chain benzoic acid. The 1:3 mixed systems of the triazines with the three-chain aromatic acid display micellar cubic phases.

1. Introduction

Liquid crystals represent a fascinating state of matter which combines order and mobility at a molecular and supermolecular level. According to the classical approach, thermotropic mesogens are designed such that flexible alkyl tails are grafted to an anisometric rodlike or disc-shaped moiety. The alkyl chains provide the mobility whereas the order arises from the packing arrangement of the rigid groups.

Beside the molecular shape and space filling effects, the nanoscale segregation of chemically incompatible molecular fragments, not only rigid/flexible but also, i.e., polar/nonpolar, play an important role in thermotropic mesomorphic self-assembly and in tailoring mesophase morphologies.[1−4] Thereby, nonlamellar phases such as columnar or cubic phases may result by increasing the size of one segment of incompatible subunits. This was demonstrated, for example, with taper-shaped polyhydroxy amphiphiles,[5,6] cone-shaped dendrimers,[7] polycatenar,[8] and swallow-tailed[9] mesogens.

One approach toward increasing the intramolecular contrast is to replace hydrocarbon chains at least in part by perfluorinated molecular segments. (Semi)perfluorinated alkyl chains have been incorporated into calamitic,[10−14] discotic,[15,16] and in polycatenar mesogens[17] as well as non-anisometric liquid crystals such as taper-shaped[18,19] and tetrahedral[20] compounds. The fluorophobic effect may lead to a stabilization as well as to modifications of smectic, columnar, and cubic mesophases.

In this respect, we presented 2,4-diamino-6-phenyl-1,3,5-triazines carrying either one or two partially fluorinated chains at the phenyl substituent.[21] The single-chain compounds exhibit a lamellar (SmA) mesophase with intercalation of the polar rodlike aromatic cores. The two-chain

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semiperfluorinated triazine forms a reverse discontinuous (micellar) cubic phase. Binary mixtures of a one-chain triazine with the two-chain fluorinated triazine exhibit an inverted bicontinuous cubic and a hexagonal columnar phase as an intermediate between the lamellar and micellar cubic mesophases of the pure compounds.

A second approach to reinforce the intramolecular polarity gradient consists in introducing highly polar hydrogen bonds.[22] Thus, it could be shown that the columnar mesophases of 2,4,6-triarylamino-1,3,5-triazines bearing six alkoxy chains can be controlled by hydrogen bonding with alkoxy-substituted benzoic acids.[23,24] The cross-sectional shape of cylindrical aggregates of the melamine−benzoic acid complexes and, therefore, the two-dimensional lattice symmetry, hexagonal or rectangular, are defined by the number and positions of alkoxy tails of the acid component.

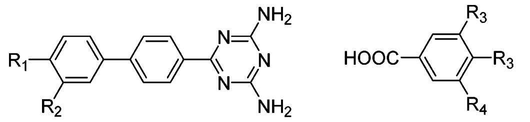
Reports related to supramolecular mesogens combining the fluorophobic effect and hydrogen bonding are rather scare. Examples are semiperfluorinated amphiphilic polyhydroxy derivatives[25,26] and dimers of semiperfluorinated benzoic acids.[18,19,26,27] Here, mesomorphic structure formation is due to the self-assembly of just a single molecular component.

Mixed systems of single-chain fluorinated acids with pyridine derivatives were reported to exhibit smectic or cubic mesophases.[28−32] Incorporation of a second semiperfluorinated chain into the acid component leads to the formation of columnar phases.[32]

H-bonded heterodimers of a sixfold alkoxy modified triarylmelamine with semiperfluorinated benzoic acids exhibit hexagonal columnar mesophases.[33] The segregation of fluorinated parts from lipophilic side chain regions leads to a superstructure within the hexagonal lattice. The molecular recognition induced $\mathrm{Col_h}$ phases of 1:1 compositions of a triarylmelamine incorporating just three aliphatic chains with fluorinated benzoic acids are formed by pairs of hydrogen-bonded dimeric supermolecules.

Recently, we presented supramolecular mesogens with double hydrogen bonding between nonmesomorphic alkoxy-substituted 2,4-diamino-6-phenyl-1,3,5-triazines and two-chain semiperfluorinated benzoic acids. The H-bonded complexes organize to columnar phases with rectangular, oblique, or hexagonal lattice symmetry depending on the number of alkoxy chains of the triazine and on the molar content of the complementary components.[34]

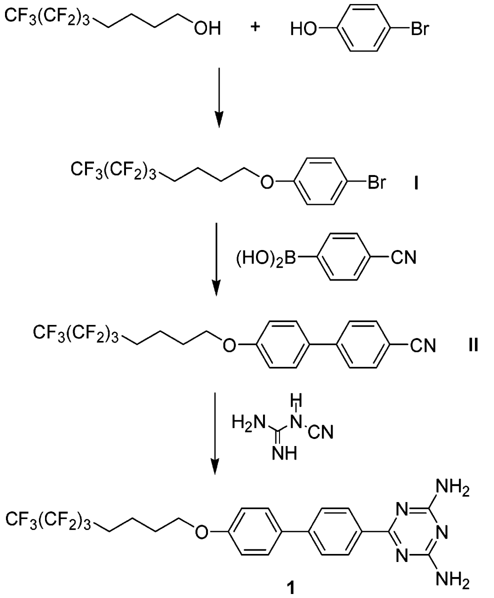
Chart 1. Chemical Structures of the Biphenyl-Substituted Diamino-1,3,5-triazines 1 and 2 and of the Complementary Semiperfluorinated Benzoic Acids 3 and 4



1: $R_1 = -O(CH_2)_4C_4F_9$; $R_2 = H$
2: $R_1 = R_2 = -OC_{10}H_{21}$

3: $R_3 = -O(CH_2)_4C_6F_{13}$; $R_4 = H$
4: $R_3 = R_4 = -O(CH_2)_4C_6F_{13}$

Scheme 1. Synthesis of the Semiperfluorinated Diamino-1,3,5-triazine 1



We extend here our approach toward combining molecular recognition between two complementary species and fluorinated molecular blocks. The concept is to increase the intramolecular contrast of incompatible counterparts by elongation of the rod-shaped aromatic core of the amino-substituted aryltriazine component. We report mesomorphic structure formation of the twofold amino-substituted 1,3,5-triazines **1** and **2** grafted with either one semiperfluorinated alkoxy segment or with two lipophilic alkoxy tails to the heterocyclic core via a biphenyl moiety in mixtures with the two-chain and three-chain partially fluorinated benzoic acids **3** and **4** (Chart 1).

2. Results and Discussion

2.1. Synthesis. The synthesis of the single-chain diamino-1,3,5-triazine **1** is outlined in Scheme 1. Mitsunobu etherification of 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctane-1-ol[18,21,25,34] with 4-bromophenol yielded the semiperfluorinated phenylether **I**. The bromo-substituted compound **I** was converted into the cyanobiphenyl **II** by Suzuki cross-coupling reaction with 4-cyanophenylboronic acid. The semiperfluorinated twofold amino-substituted aryl-1,3,5-triazine **1**, finally, was prepared by reaction of the nitrile **II** with dicyandiamide in the presence of potassium hydroxide and ethylene glycolmonomethylether as the solvent.

The twofold decyloxy modified triazine **2**[35] was prepared in a similar manner. 3,4-Bis-decyloxy-phenyl bromide was subjected to metal halogen exchange that afforded the

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Table 1. Phase Transition Temperatures (deg C) of the Pure Compounds 1−4[a]

compound	phase transitions
1	Cr 230.4 (8.95) SmA 281.2 (2.83) I
2	Cr 105.3 (5.13) Col_h 155.1 (1.77) I
3	Cr 115.7 (37.59) [Col_h 102.0 (1.57)][b] I
4	Cr 51.0 (7.1) Col_h 81.1 (2.7) I

[a] Differential scanning calorimetry (DSC); second heating at 10 K/min; the transition enthalpies (kJ/mol) are in parentheses; (Cr) crystalline; (SmA) smectic A; (Col_h) hexagonal columnar; (I) isotropic. [b] Monotropic phase transition.

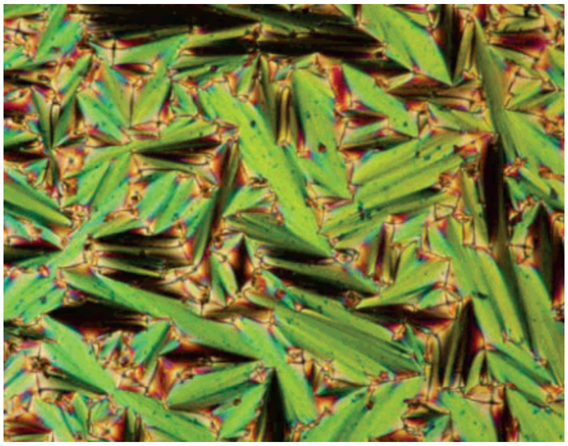

Figure 1. Optical texture obtained for the SmA mesophase of the partially fluorinated triazine **1**.

corresponding lithiated species which afterward was treated with trimethyl borate to yield the 3,4-bis-decyloxy-phenylboronic acid. Pd(0)-catalyzed C,C-coupling reaction of the boronic acid with 4-bromobenzonitrile effected the appropriate twofold decyloxy-substituted cyanobiphenyl. Finally, the formation of the diamino-1,3,5-triazine **2** was achieved by treatment of the 3′,4′-bis-decyloxy-biphenyl-4-carbonitrile with dicyandiamide.

The semiperfluorinated benzoic acids **3** and **4** were obtained by etherification of the respective ethyl hydroxy benzoates with 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecane in the presence of potassium carbonate followed by basic hydrolysis.[21,25]

2.2. Mesomorphic Properties of the Pure Amino-Modified Biphenyltriazines 1 and 2 and of the Semiperfluorinated Benzoic Acids 3 and 4. The phase transition temperatures and associated enthalpy values of the amino-modified biphenyltriazines **1** and **2** and of the semiperfluorinated benzoic acids **3** and **4** are given in Table 1.

The 1,3,5-triazine **1** grafted with one fluoroalkoxy segment at the terminus of the biphenyl moiety displays an enantiotropic smectic A (SmA) mesophase as it is clearly evident from the typical focal-conic fan textures observed between crossed polarizers (Figure 1). Interestingly, the phenyl-substituted analogue with the same semiperfluoroalkoxy chain forms only a monotropic SmA phase.[21]

A bilayer structure with intercalation of the polar aromatic cores and with the fluorinated chains building up a separate sublayer seems to be most likely, similar to the lamellar SmA_d phases described for structurally related semiperfluorinated aminotriazines involving just a single phenyl ring.[21]

Table 2. Phase Transition Temperatures (deg C) of 1:1 Mixed Systems of the Diaminotriazines 1 and 2 with the Twofold Semiperfluorinated Benzoic Acid 3[a]

mixture	Cr		Col_r		I
1/3[b]		180.4 (2.37)		219.6 (2.53)	
2/3		105.1 (24.40)		146.1 (1.92)	

[a] Differential scanning calorimetry (DSC); second heating at 10 K/min; the transition enthalpies (kJ/mol) are in parentheses; (Cr) crystalline; (Col_r) rectangular columnar; (I) isotropic. [b]Polymorphism in the solid state is observed. Only the highest melting modification is given.

The two-chain decyloxy modified triazine **2** very recently was reported to exhibit a hexagonal columnar (Col_h) mesophase.[35] This behavior was discussed in terms of the formation of hydrogen-bonded hexameric rosettes with disclike shape which assemble to parallel aligned columns on a hexagonal two-dimensional (2D) lattice.

It is consistent that the incorporation of a second phenyl fragment at the heterocyclic triazine nucleus influences the balance of intramolecular contrast such that a mesophase stabilization (compound **1**) and even mesophase induction (compound **2**) results for the triazines **1** and **2** compared with chemically familiar diaminotriazines with shorter only phenyl-substituted rigid aromatic cores.[21,34]

The semiperfluorinated carboxylic acids **3** and **4** exhibit a hexagonal columnar phase. The columnar phases are related to the formation of descrete benzoic acid dimers via hydrogen bonding.[25] Thereby, the monotropic phase of the two-chain acid **3** is replaced by an enantiotropic one by incorporation of a third partially fluorinated chain into the acid **4**.

2.3. Equimolar Mixtures of the Diamino-1,3,5-triazines 1 and 2 with the Semiperfluorinated Benzoic Acid 3. The investigated 1:1 mixtures of the triazines **1** and **2** with the partially fluorinated benzoic acid **3** display a thermotropic mesophase. The isotropization temperatures of the mixed systems are higher than that for the pure benzoic acid. The monotropic phase of the two-chain acid **3** is replaced by enantiotropic mesophases. On the other hand, the clearing temperatures of the 1:1 compositions **1**,**2/3** are lower than those of the respective diaminotriazines **1** and **2** in their pure state. The 1:1 compositions display spherulitic optical textures which point to a columnar liquid crystalline phase. The phase transition temperatures are given in Table 2.

The mesophase of the 1:1 mixture of the semiperfluorinated triazine **1** with the two-chain benzoic acid **3** was investigated by X-ray scattering. The small angle reflections can be indexed on the basis of a two-dimensional rectangular unit cell with a centered *c*2*mm* lattice symmetry (Table 4). The lattice parameters are $a = 53.8$ Å and $b = 35.5$ Å. This result confirms the phase assignment made by polarizing microscopy.

IR-spectroscopic investigations previously have shown that association of phenyl-substituted diamino-1,3,5-triazines with complementary benzoic acids is related to double-hydrogen bonding between the nitrogen heterocycle substituted with two exocyclic primary amino groups and the carboxylic group of the acid.[34] Thereby, in equimolar compositions, preferentially, heterodimers are formed with a rodlike shape of the polar H-bonded core.[34] Hence, it is reasonable to

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suggest that molecular recognition of the biphenyltriazines **1** and **2** with the fluorinated acid **3** at an equimolar ratio of the complementary molecular species leads to descrete heterodimers with a pronounced rod-shaped polar central core as well. This assumption is also in line with the fact that hydrogen bonding of diamino-1,3,5-triazines with acids at a stiochiometric ratio occurs only at the sites that flank the smallest substituent of the triazine.[36]

The linear pre-organization of the extended hydrogen-bonded cores should enable sufficiently strong attractive interactions to favor a parallel organization. The volume fraction of the two bulky semiperfluorinated chains of the benzoic acid **3** is significantly larger than that of the single fluorinated chain at the opposite position of the H-bonded central core in the case of the heterodimers **1/3** and even exceeds the cross-sectional area of the two alkyl chains in 1:1 complexes involving the triazine **2**. Therefore, a favorable dense packing within the mesophase can be achieved by an antiparallel alignment of the dimeric supermolecules.

The number of 1:1 supermolecules **1/3** was calculated according to $n = V_{\mathrm{cell}}/V_{\mathrm{mol}}$. The volume cell ($V_{\mathrm{cell}}$) was evaluated by assuming a height of 4.5 Å.[26,34] The molecular volume was calculated using volume increments.[37] The calculations yielded a value of approximately six heterodimers per unit cell.

Figure 2a shows a possible arrangement of three supermolecules **1/3** with close and antiparallel packing of the polar rodlike cores. As evident from the CPK model, the cross-sectional area of the terminal semiperfluorinated chains exceeds the cross section of the closely aligned central H-bonded aromatic region. Obviously, tilting of the molecules only cannot sufficiently compensate for the resulting steric frustration. The smectic layers should break up into infinite ribbonlike segments with curved interfaces due to the different space filling of the fluoroaliphatic and aromatic regions. The ribbonlike aggregates organize to columnar mesophases on a two-dimensional rectangular lattice (Figure 2b).

The maximum molecular dimension of an H-bonded rodlike dimer **1/3** amounts to approximately 45 Å. This value is slightly larger than the lattice parameter *b* determined by X-ray. Hence, the lattice parameter *b* should correspond to the height of the ribbons taking into account the fluid nature of the flexible alkyl segments. The lattice parameter *a* matches nearly twice the lateral dimension of the ribbons by assuming on average three dimers arranged parallel within one ribbon. These experimental findings further support our assumption that predominantly hydrogen-bonded dimers with a rodlike shape are formed in equimolar mixed systems of the triazines **1**,**2** with the benzoic acid **3**.

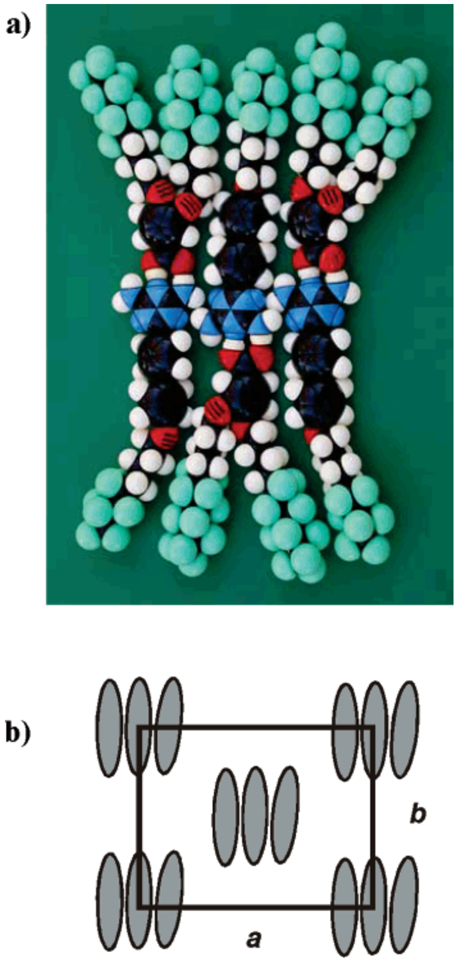

Figure 2. (a) CPK model showing an antiparallel arrangement of three dimers **1**/**3**. The hydrogen-bonded rodlike cores are closely packed side-by-side and form a smectic sublayer. (b) Schematic presentation of the ribbon phase of equimolar hydrogen-bonded complexes of the diamino-1,3,5-triazines **1** and **2** with the semiperfluorinated two-chain acid **3** with rectangular columnar ($\mathrm{Col_r}$) organization (two-dimensional *C*2*mm* space group). The chains filling the space between the rigid aromatic aggregates are not shown.

Table 3. Phase Transition Data (deg C) of Mixtures of the Triazines 1 and 2 with 3 equiv (mol %) of the Partially Fluorinated Benzoic Acids 3 and 4[a]

mixture	phase transitions
(1:3) **1**/**3**	$\mathrm{Cr_1}$ 104.3 (45.32) $\mathrm{Cr_2}$ 119.4 (13.67) $\mathrm{Col_r}$ (*P*2*m*) 151.4 (0.45) I
(1:3) **2**/**3**	Cr 84.9 (63.27) $\mathrm{Col_{sq}}$ (*P*4*mm*) 98.1 (1.31) I
(1:3) **1**/**4**	$\mathrm{Cr_1}$ 72.1 (36.26) $\mathrm{Cr_2}$ 84.3 (1.76) Cub 107.5 (1.36) I
(1:3) **2**/**4**	Cr 60.2 (44.30) Cub 92.4 (1.49) I

[a] Differential scanning calorimetry (DSC); second heating at 10 K/min; the transition enthalpies (kJ/mol) are in parentheses; (Cr) crystalline; ($\mathrm{Col_r}$) rectangular columnar; ($\mathrm{Col_{sq}}$) columnar, square 2D lattice; (Cub) cubic; (I) isotropic.

2.4. Mixed Systems of the Triazines 1 and 2 with Three equiv of the Benzoic Acids 3 and 4. The twofold amino-substituted 1,3,5-triazine core of compounds **1** and **2** allows for docking of up to three acid equiv. Table 3 summarizes the phase transition data of 1:3 mixtures of **1** and **2** with the semiperfluorinated benzoic acids **3** and **4**. As a general trend, the melting and clearing temperatures are lower in comparison to the appropriate 1:1 mixed systems but higher than those of the pure benzoic acids.

The optical textures of the (1:3) complex of the triazines **1** and **2** with the two-chain partially fluorinated carboxylic acid **3** are characterized by regions of broken spherulites, mosaiclike regions, and pseudoisotropic areas containing birefringent filaments (Figure 3). These textures are characteristic for a columnar mesophase.

The X-ray diffraction pattern of the (1:3) binary mixture of the fluorinated diaminotriazine **1** with the two-chain acid

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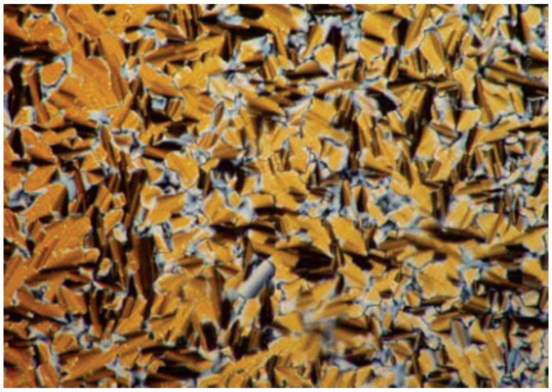

Figure 3. Photomicrograph (crossed polarizers) observed on cooling for the columnar phase of the 1:3 mixed system **1**/**3**.

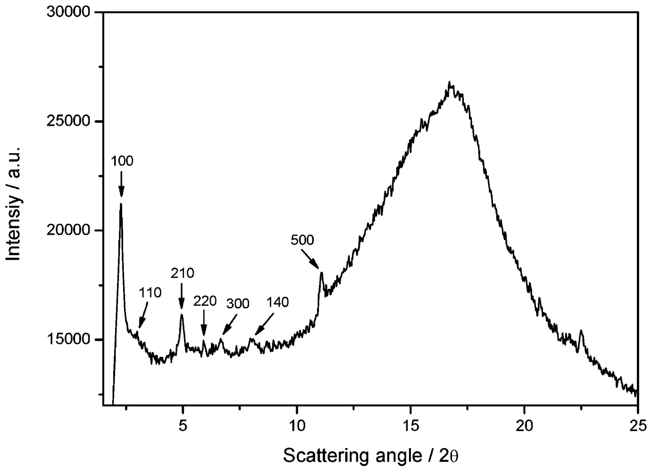

Figure 4. Wide angle X-ray diffractogram obtained for the columnar phase of the 1:3 mixture **1**/**3**.

3 gives evidence for a columnar mesophase on a two-dimensional rectangular lattice (Figure 4). The small angle reflections can be indexed on the basis of a simple noncentered rectangular unit cell with *P*2*m* symmetry. The lattice parameters are given in Table 4. The diffuse scattering that appears in the wide angle region indicates that no periodical ordering of the molecules is present within the columns.

This $\mathrm{Col_r}$ phase type so far was reported, for example, for a cyanobiphenyl-substituted carbosilane dendrimer,[38] for facial amphiphiles based on *p*-terphenyl derivatives,[39,40] for a phthalocyanine compound bearing peripheral steric hindrance groups,[41] and for H-bonded heterodimers of triarylmelamines with twofold alkoxy-modified benzoic acids.[24]

Most likely, the elongated biphenyl core of the triazine **1**, substituted with a single semiperfluorinated chain leads to a noncircular shape of the hydrogen-bonded central core of the 1:3 associates **1**/**3**. The partially fluorinated peripheral tails become unequally distributed arround the core region. The result is an ellipsoidal shape of the supermolecules (Figure 5a). The majority of the chains segregate in layers whereas in the perpendicular direction the density of the fluorinated chains is reduced. Ellipsoidal aggregates are formed which are composed of three distinct molecular regions, the polar hydrogen-bonded central core, surrounded by the lipophilic alkyl segments, and, finally, a shell of the fluorinated molecular fragments. The parallel alignment of these aggregates leads a rectangular columnar ($\mathrm{Col_r}$) phase (Figure 5b).

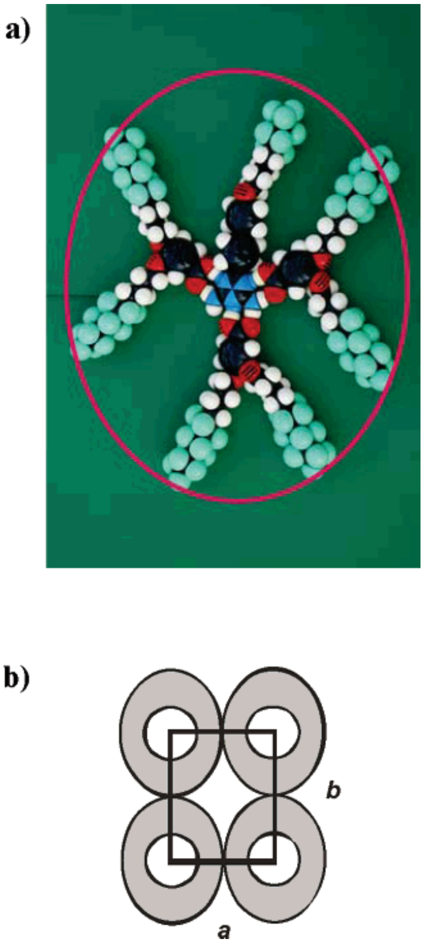

Figure 5. (a) CPK model of the semiperfluorinated biphenyltriazine **1** associated with 3 equiv of the two-chain partially fluorinated benzoic acid **3** via hydrogen bonding. (b) Possible arrangement of the hydrogen-bonded 1:3 complexes **1**/**3** in their columnar mesophases with two-dimensional *P*2*m* lattice symmetry.

As evident from the CPK model, the maximum length of the long axis of the ellipse amounts to approximately 47 Å. This value is in excellent aggreement with the lattice parameter *b* (45.5 Å) determined by X-ray. The lattice parameter *a* (39.0 Å) corresponds to the lateral side-by-side distance of adjacent H-bonded 1:3 associates **1/3** with ellipsoidal shape.

The wide angle X-ray spectroscopy (WAXS) diffractogram obtained for the mesophase of the (1:3) complex **2**/**3** displays (100) and (110) reflections in the small angle region with a reciprocal spacing ratio of $1{:}\sqrt{2}$. This leads us to conclude that the (1:3) mixture **2**/**3** exhibits a columnar phase with a square lattice (*p*4*mm*). All further small angle reflections of higher order can be indexed accordingly with high accuracy (Table 4). The lattice parameter can be calculated to $a_{\mathrm{sq}} = 43.7$ Å.

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Table 4. X-ray Diffraction Data for the Mesophases of the Binary 1:1 and 1:3 Mixtures of the Diamino-1,3,5-triazines 1 and 2 with the Two-Chain Semiperfluorinated Benzoic Acid 3

	reflections (Å)		Miller indices	lattice constants
mixture	d_{obs}	d_{calc}	(*hkl*)	(Å)
1/**3** (1:1)	29.61	29.61	110	$a = 53.80$
Col$_r$ (*C*2*mm*)	26.90	26.90	200	$b = 35.46$
	17.65	17.73	020	
	15.93	16.00	310	
	11.02	10.71	420	
	7.91	7.96	530	
1/**3** (1:3)	39.04	39.04	100	$a = 39.04$
Col$_r$ (*P*2*m*)	29.61	29.61	110	$b = 45.44$
	17.87	17.94	210	
	14.96	14.81	220	
	13.26	13.01	300	
	11.04	10.91	140	
	7.96	7.81	500	
2/**3** (1:3)	43.68	43.68	100	$a_{sq} = 43.68$
Col$_{sq}$ (*P*4*mm*)	31.51	31.03	110	
	14.81	14.56	300	
	11.28	10.92	400	
	10.67	10.59	410	
	9.85	9.77	420	
	8.94	8.74	500	
	7.99	8.11	520	
	7.83	7.72	440	
	7.28	7.18	610	

Obviously, replacing the single partially fluorinated segment at the biphenyl fragment of the triazine component by two lipophilic alkyl tails partly compensates for the asymmetric shape of the central H-bonded core region of the 1:3 aggregates with the two-chain acid **3**.

In fact, the H-bonded 1:3 complex between the triazine **2** and the two-chain partially fluorinated benzoic acid **3** should have a cross-sectional shape which is in between a circle with minimized interfacial areas and an "ideal" square with maximal space filling. Thus, it should be a square with rounded corners.[26] Considering almost stretched conformations of the alkyl segments as shown in Figure 6a, the length of each side of the square is ca. 45 Å, This value is very close to the measured lattice parameter of 43.7 Å.

The columns in the Col$_{sq}$ phase have a more pronounced squarelike shape instead of an elliptical cross-sectional shape. This enhances the symmetry and gives rise to the change in the lattice type (Figure 6b). Hence, the Col$_{sq}$ phase of the (1:3) mixed system **2**/**3** can be regarded as an intermediate stage in the transition from a rectangular to a hexagonal two-dimensional lattice.

Columnar mesophases with two-dimensional square lattice symmetry have been previously reported for calamitic bolaamphiphiles with semiperfluorinated lateral chains,[26] for transition metal complexes,[41−43] and for an inositol liquid crystal.[44]

Hydrogen bonding of the diaminotriazines **1** and **2** with three molecules of the two-chain benzoic acid **3** reinforces the polarity of the core region. At the same time, the nonpolar and fluorophilic nature of the molecular periphery is enhanced by increasing the number of semiperfluorinated chains. Obviously, the polar/nonpolar balance as the main driving force toward mesophase formation is not disturbed, which along with the particular two-dimensional shape of 1:3 associates **1**/**3** and **2**/**3** leads to Col$_r$ or Col$_{sq}$ phases.

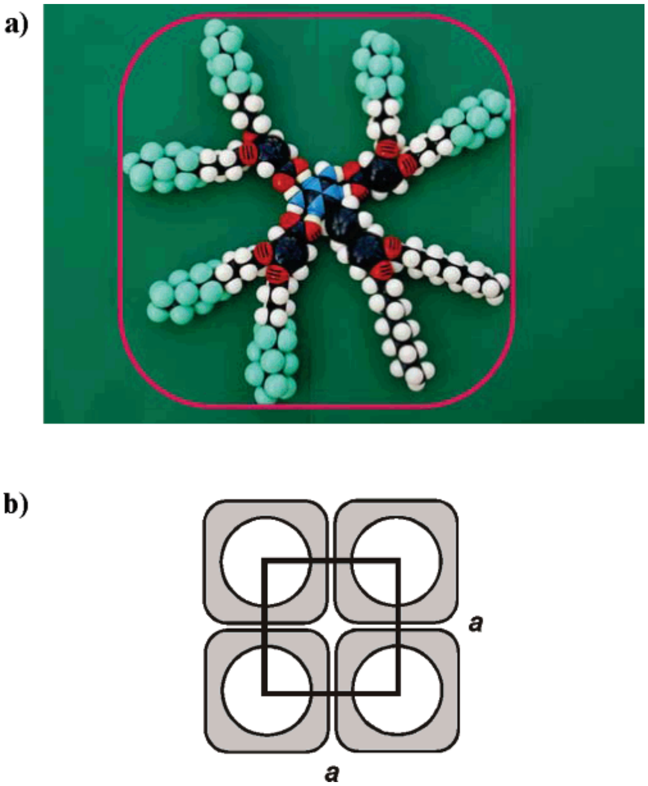

Figure 6. (a) CPK model of the hydrogen-bonded 1:3 complex of the triazine **2** with the benzoic acid **3**. Only almost stretched conformations of the flexible alkyl spacer segments are considered. (b) Model of the organization of the 1:3 mixed system **2**/**3** in the Col$_{sq}$ phase.

The binary 1:3 mixtures of the amino-substituted triazines **1** and **2** with the three-chain semiperfluorinated benzoic acid **4** form 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 beside the melting transition an additional phase transition occurs at elevated temperatures which is accomponied by a remarkable decrease in viscosity. The mixed systems show a pronounced tendency toward supercooling. These observations are a strong hint toward the existence of a cubic mesophase.

Attaching a third semiperfluorinated chain to the acid component increases the space requirement of the fluorinated molecular block of the (1:3) H-bonded aggregates. Therefore, the aggregates forming the cubic phases of the 1:3 mixed systems **1**,**2**/**4** must be more strongly curved than the cylindrical aggregates in the columnar phases of the 1:3 compositions with the two-chain acid **3**. Thus, the cubic phases of the 1:3 compositions **1**,**2**/**4** should be a reverse discontinuous micellar cubic (Cub$_{I2}$) phase built up by closed spheroidic micelles of the polar cores surrounded by the nonpolar fluorinated chains.

Unfortunately, we were not able to determine the three-dimensional lattice type of the cubic phases by X-ray. However, the space group *Pm*3*n* is most frequently found for thermotropic Cub$_{I2}$ phases.[5,7]

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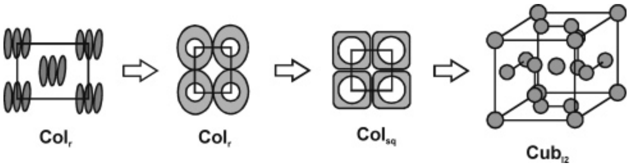

Figure 7. Mesophase morphologies of the H-bonded complexes of the triazines **1** and **2** with the partially fluorinated benzoic acids **3** and **4** depending on the volume fractions of the (semiperfluorinated) alkoxy tails.

The phase sequence and structure of thermotropic mesophase morphologies found for binary mixed systems of the diaminotriazines with the semiperfluorinated benzoic acids at 1:1 and 1:3 molar ratios are shown schematically in Figure 7.

The phase sequence is the consequence of the onset and successive increase of the aromatic-(fluoro)aliphatic interface curvature by increasing the volume fraction of the (semiperfluorinated) alkyl chains.

3. Conclusions

The diamino-functionalized nitrogen heterocycle of the biphenyl-modified 1,3,5-triazines allows for molecular recognition with semiperfluorinated benzoic acids. Thereby, a "first-order" effect toward controlling mesomorphic structure formation arises from the molar content of the acid component which defines the molecular geometry of the H-bonded polar central core. A "second-order" effect is due to controlling the interface curvature of assembled aggregates by the volume fractions of peripheral (semiperfluorinated) tails. As a third molecular component the elongated rigid biphenyl building block of the triazines accounts for tailoring mesophase morphologies of the binary complementary mixed systems. The result of cooperative interplay of these features is the phase sequence Col_r (*c*2*mm*)−Col_r (*p*2*m*)−Col_{sq} (*p*4*mm*)−Cub_i. The concept to combine the fluorophobic effect and nanoscale segregation of incompatible molecular blocks by noncovalent attractive intermolecular interactions between complementary molecular species provides a much more convenient and variable approach toward tailoring thermotropic mesophase morphologies than covalent alternatives.

Experimental Section

Instrumental. IR spectra were obtained with a Digilab FTS 2000 Series FT-IR spectrometer equipped with a MIRacle single reflection Horizontal ATR accessory (PIKE Technologies). NMR spectra were recorded with a Bruker AMX 300 spectrometer. For mass spectra, a Finnigan SSQ MAT 710 spectrometer was used. Texture observations were made using 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 Kα) have been 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 mixed systems of the triazines **1** and **2** with the benzoic acids **3** and **4** 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.

Synthesis of the Semiperfluorinated 2,4-Diamino-1,3,5-triazine 1. *1-Bromo-4-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorooctyl-1-oxy)-benzene* ***I.*** To a solution of 20 mL dry THF containing 2 g (6.8 mmol) 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctane-1-ol, 1.18 g (6.8 mmol) 4-bromophenol, and 2.7 g (10 mmol) triphenylphosphine, 1.8 g (10 mmol) diisopropylazodicarboxylate (DIPA) was added dropwise with stirring at room temperature. The orange-red color of DIPA disappeared immediately with slight liberation of heat. The mixture was stirred at room temperature for 24 h. The reaction mixture was acidified with 1 N HCl. The solution was extracted with ethyl acetate (3 × 50 mL). The organic layer was dried with Na_2SO_4. After filtration, the solvent was evaporated in vacuum. The residue was purified by distillation at 92−96 °C to yield 2.7 g (90%) of clear oil. ^{1}H NMR ($CDCl_3$): $\delta = 7.40$ (d, 2H, phenyl, $J = 9.0$ Hz), 6.79 (d, 2H, phenyl, $J = 9.0$ Hz), 3.96 (t, 2H, CH_2−O−phenyl, $J = 5.7$ Hz), 2.08−2.26 (m, 2H, CH_2CF_2), 1.86 (m, 4H, CH_2) ppm.

4′-(1H,1H,2H,2H,3H,3H,4H,4H-Perfluorooctyl-1-oxy)-biphenyl-4-carbonitrile ***II.*** A mixture of 0.5 g (3.4 mmol) 4-cyano-phenylboronic acid, 1.53 g (3.4 mmol) 1-bromo-4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctyl-1-oxy)-benzene **I**, 7.5 mL 1 M aqueous $NaHCO_3$ solution, 0.08 g (2% mol) tetrakis(triphenylphosphin)-palladium(0) $Pd(PPh_3)_4$, and 25 mL 1,2-dimethoxy-ethane was stirred at reflux under an argon atmosphere. The reaction progress was monitored by thin-layer chromatography (TLC). After the reaction was complete, the mixture was extracted with ethyl acetate (3 × 50 mL). The organic phases were dried with Na_2SO_4 and evaporated after filtration. Purification of the crude product was performed by flash cromatography using light petroleumether/ethyl acetate (3:1) as eluant. Yield: 1.05 g (65%), $C_{21}H_{16}F_9NO$ (469.38). Cr 100.6 (21.57) SmA 114.9 (4.47) I. IR: $\nu = 2360$, 2224, 1605, 1495, 1231, 1213, 1129, 1075, 1038, 827 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.71$ (dd, 4H, phenyl, $J = 8.7$ Hz), 7.52 (d, 2H, phenyl, $J = 8.7$ Hz), 7.01 (d, 2H, phenyl, $J = 8.7$ Hz), 4.06 (t, 2H, CH_2−O−phenyl, $J = 5.4$ Hz), 2.12−2.27 (m, 2H, CH_2CF_2), 1.79−1.97 (m, 4H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 159.41$ (1C, C−Ph−O), 145.17 (1C, C−Ph), 132.50 (2C, CH−Ph), 131.02 (1C, C−Ph), 128.39 (2C, CH−Ph), 127.11 (2C, CH−Ph), 119.07 (1C, CN), 115.02 (2C, CH−Ph), 110.16 (1C, *C*−Ph−CN), 67.33 (1C, CH_2−O), 30.56 (1C, *C*H_2−CF_2), 28.64 (1C, CH_2), 17.27 (1C, CH_2) ppm. MS *m*/*z* (%): 469 (M^+).

2,4-Diamino-6-(4′-(1H,1H,2H,2H,3H,3H,4H,4H-perfluorooctyl-1-oxy)-biphenyl-4-yl)-1,3,5-triazine ***1.*** 0.7 g (1.5 mmol) 4′-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctyl-1-oxy)-biphenyl-4-carbonitrile **II**, 0.126 g (1.5 mmol) dicyandiamide, and 0.084 g (1.5 mmol) potassium hydroxide were added to 20 mL diethyleneglycolmonomethylether. The mixture was heated at reflux (130 °C) with stirring for 5 h. After cooling to room temperature, the mixture was poured into ice/water. The precipitate was collected by filtration. Purification of the crude product was effected by recrystallization from ethanol. Yield: 0.49 g (63%), $C_{23}H_{20}F_9N_5O$ (553.38). IR: $\nu = 3487$, 3401, 3125, 2930, 2877, 2360, 1672, 1251, 1180, 1131, 1072, 811 cm^{-1}. ^{1}H NMR (DMSO-d_6): $\delta = 8.30$ (d, 2H, phenyl, $J = 8.7$ Hz),7.69 (dd, 4H, phenyl, $J = 8.7$ Hz), 7.02 (d, 2H, phenyl, $J = 8.7$ Hz), 6.71 (s, 4H, NH_2), 4.05 (t, 2H, CH_2−O−phenyl, $J = 6.0$ Hz), 2.28 (m, 2H, CH_2CF_2), 1.84 (m, 2H, CH_2), 1.72 (m, 2H, CH_2) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 170.82$ (1C, triazine), 168.16 (2C, triazine), 159.38 (1C, C−Ph−O), 144.72 (1C, C−Ph), 135.94 (1C, C−Ph−triazine), 132.32 (1C, C−Ph) 129.20 (2C, CH−Ph), 128.77 (4C, CH−Ph), 115.79 (2C, CH−Ph), 68.82 (1C, CH_2−O), 32.44 (1C, *C*H_2−CF_2), 28.56 (1C, CH_2), 17.62 (1C, CH_2) ppm. MS *m*/*z* (%): 553 (M^+).

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