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Mesomorphic Block Molecules: Semiperfluorinated 1,3,5-Triazine Derivatives Exhibiting Lamellar, Columnar, and Cubic Mesophases

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New 2,4-diamino-6-phenyl-1,3,5-triazines carrying one or two semiperfluorinated chains at the phenyl substituent have been synthesized. The thermotropic liquid crystalline properties of the compounds were investigated by polarizing microscopy, differential scanning calorimetry, and X-ray diffraction. The single-chain compounds exhibit a lamellar (SmA) mesophase with intercalation of the polar rodlike aromatic subunits. The two-chain partially fluorinated triazine forms a reverse discontinuous (micellar) cubic phase (Cub_{I2}). Additionally, binary mixtures of a single-chain triazine with the two-chain semiperfluorinated triazine were investigated. Inverted bicontinuous cubic (Cub_{V2}) and hexagonal columnar (Col_{h2}) phases are induced as intermediate between the lamellar and the micellar cubic mesophases of the pure compounds. On addition of protic solvents such as formamide, the Cub_{I2} phase of the two-chain triazine is replaced by a lyotropic columnar mesophase.

Introduction

The molecular shape is a major design principle of low molar mass thermotropic liquid crystals. Thereby, the mesophase morphologies are mainly governed by the volume fractions of chemically incompatible molecular fragments such as rigid/flexible or polar/nonpolar building blocks combined within one molecule which separate in different subspaces. For example, linear rod-shaped molecules favor a layer arrangement (smectic mesophases). Increasing the wegdelike shape of a mesogen may lead to mesophases with curved interfaces. Thus, the phase sequence bicontinuous cubic (Cub_V), columnar (Col), and, finally, micellar cubic (Cub_I) can be found by increasing the size of one segment of incompatible subunits such as it has been successfully demonstrated, that is, with taper-shaped polyhydroxy amphiphiles[1,2] and with cone-shaped dendrimers.[3−5]

Mesophase morphologies can be further tailored if a perhydrogenated chain is replaced by a perfluorinated segment. The most simple examples are smectic liquid crystalline phase forming diblock molecules combining hydrocarbon and fluorocarbon chains.[6,7] Grafting fluorinated chains to calamitic mesogens leads to an enhanced stability of their smectic phases compared to the hydrocarbon analogues[8−10] whereas nematic phases are generally suppressed. It also could be demonstrated that the fluorophobic effect may lead to the induction, stabilization, and modifications of lamellar, columnar, and cubic phases of nonanisometric mesogens such as taper-shaped[11−13] and tetrahedral[14,15] compounds and semiperfluorinated amphiphilic polyhydroxy derivatives.[16,17]

We could show that the columnar mesophases of 2,4,6-triarylmelamines bearing six peripheral alkoxy tails[18] can be controlled by hydrogen bonding with alkoxy substituted ben-

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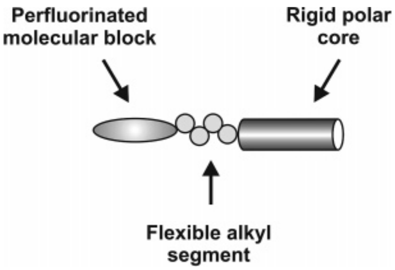
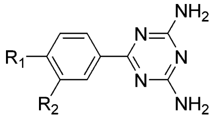


Figure 1. Polyphilic block molecules composed of a rigid aromatic polar core linked to a fluorinated molecular segment via a flexible alkyl spacer.

Chart 1. Chemical Structure of Non-Mesomorphic Alkoxyphenyl Substituted Diamino-1,3,5-triazines



R_1 = $-OC_{12}H_{25}$; R_2 = H
R_1 = R_2 = $-OC_{10}H_{21}$

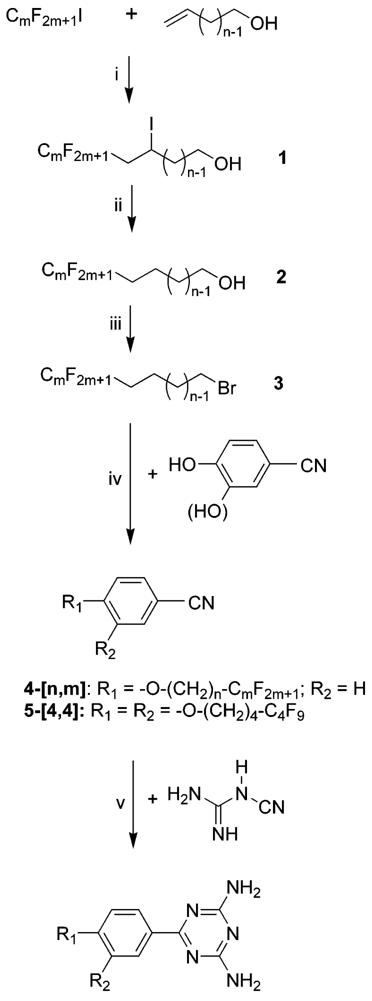
zoic acids.[19,20] The number and positions of the alkoxy chains of the acid component defines the cross-sectional shape of cylindrical aggregates of the melamine−benzoic acid complexes and, therefore, the two-dimensional lattice symmetry, rectangular or hexagonal.

Charge-transfer interactions of the melamines with electron acceptors such as 2,4,7-trinitrofluorenone (TNF) impose a conformational change of the melamine core to a more wedgelike shape. This molecular conformation along with separation of the incompatible lipophilic chains and the polar cores into distinct sublayers leads to the induction of lamellar smectic A liquid crystalline phases.[21,22] Thereby, an optimum space filling arises from an antiparallel alignment of the melamines.

This means that a noncovalent approach toward the transition of mesophase morphologies from Col_h via Col_r to lamellar could be realized by strong attractive interactions of the alkoxy substituted triarylmelamines with complementary components.

Recently we presented 2,4-diamino-6-phenyl-1,3,5-triazines carrying one or two alkoxy chains at the phenyl substituent (Chart 1). H-bonded dimers with two-chain semiperfluorinated benzoic acids organize to infinite ribbons with parallel aligned central cores. The cross-sectional shape of the ribbons and the two-dimensional lattice of the ribbon phases, rectangular or oblique, are determined by the number of alkoxy chains of the triazine component. Docking of 2 or 3 equiv of the semiperfluorinated acids to the aminotriazine core leads to cylinders with a circular cross section which organize to Col_h mesophases.[23]

Scheme 1. Synthesis of the Diamino Substituted Semiperfluorinated One-Chain and Two-Chain 1,3,5-Triazines 6 and 7[a]



4-[n,m]: R_1 = $-O-(CH_2)_n-C_mF_{2m+1}$; R_2 = H
5-[4,4]: R_1 = R_2 = $-O-(CH_2)_4-C_4F_9$

6-[n,m]: R_1 = $-O-(CH_2)_n-C_mF_{2m+1}$; R_2 = H
7-[4,4]: R_1 = R_2 = $-O-(CH_2)_4-C_4F_9$

[a] Reagents and conditions: (i) $(Ph_3P)_4Pd(0)$, hexane, 0−20 °C, 36 h; (ii) Bu_4Sn, 80 °C, 30 min; (iii) Bu_4NHSO_4, HBr, H_2SO_4, 100 °C, 12 h; (iv) **4-[*n*,*m*]**: K_2CO_3, DMF, Ar, 65 °C, 2h; **5-[4,4]**: K_2CO_3, KI (cat.), acetone, Ar, reflux, 16 h; (v) ethylene glycolmonomethyl ether, KOH, reflux, 5 h.

However, the alkoxy modified diaminotriazines are nonmesomorphic by themselves. Because (semi)perfluorinated chains can stabilize mesophases as a result of their incompatibility with aliphatic, aromatic, and polar molecular regions, their larger cross-sectional area compared with aliphatic chains, and their reduced mobility,[24,25] we expected that replacing the alkoxy groups of the diaminotriazines by semiperfluorinated chains may lead to mesomorphic behavior.

We present here the one-chain and two-chain semiperfluorinated diamino-1,3,5-triazines **6** and **7** which can be regarded as polyphilic three-block molecules composed of a polar amino substituted (hetero)aromatic rodlike core, a flexible lipophilic molecular segment, and a fluorinated block (Figure 1).

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Table 1. Phase Transition Temperatures of the Semiperfluorinated 1,3,5-triazines 6 and 7[a]

compound		transition temperature	
6-[4,4]	Cr	187.7 (29.7)	I
	Cr	[167.0 (−10.8) SmA 172.4 (−0.3)]	I
6-[6,4]	Cr	175.6 (55.4)	I
	Cr	[151.5 (−12.0) SmA 170.8 (−0.4)]	I
6-[4,6]	Cr	182.1 (17.1) SmA 200.9 (0.5)	I
6-[6,6]	Cr	180.1 (50.0) SmA 192.8 (0.4)	I
7-[4,4]	Cr	82.7 (1.4) Cub_{I2} 140.4 (0.4)	I

[a] DSC, second heating at 10 K/min; phase transition enthalpies (kJ/mol) in parenthesis; values in square brackets refer to monotropic phase transitions; Cr = crystalline, SmA = smectic A phase, Cub_{I2} = inverted micellar cubic mesophase, I = isotropic liquid.

Results and Discussion

Synthesis. The synthesis of the semiperfluorinated compounds **6** and **7** is presented in Scheme 1. The initial step is the palladium(0)-catalyzed radical addition of 1-iodoperfluoroalkanes to ω-alken-1-ols resulting in the iodides **1**. Reduction of compounds **1** with tributyltinhydride yielded the semiperfluorinated alcohols **2**.[11,16] The alcohols **2** were converted to the corresponding bromides **3**[11,16] by reaction with aqueous HBr in the presence of catalytic amounds of sulfuric acid and tetrabutylammonium hydrogensulfate. The semiperfluorinated benzonitriles **4** and **5** were obtained by etherification of the appropriate hydroxybenzonitriles with the bromides **3** in the presence of potassium carbonate as the base. The semiperfluorinated twofold amino substituted aryl-1,3,5-triazines **6** and **7**, finally, were prepared by reaction of the benzonitriles **4** and **5** with dicyandiamide in the presence of potassium hydroxide and ethylene glycolmonomethyl ether as the solvent. Purity and structure of the final products were confirmed by thin-layer chromatography, ^{1}H NMR spectroscopy, and ^{19}F NMR sectrocopy. Full details are given in Experimental Section.

Mesomorphic Properties of the Pure Compounds 6 and 7. The thermal properties of the synthesized 1,3,5-triazines **6** and **7** were studied by optical polarizing microscopy and differential scanning calorimetry (DSC). The mesophase of the one-chain partially fluorinated compound **6-[4,6]** additionally was investigated by X-ray scattering. The phase transition temperatures are given in Table 1.

The compounds **6-[4,4]** and **6-[6,4]** incorporating the shorter fluorinated segment exhibit a monotropic liquid crystalline phase. Elongation of the perfluoroalkyl chain length enhances the thermodynamic mesophase stability, and the diaminotriazines **6-[4,6]** and **6-[6,6]** form an enantiotropic phase. The hexyl modified members of the triazines **6** show lower phase transition temperatures compared with those of the appropriate homologues incorporating four methylene units. This behavior can be attributed to an increased flexibility of the terminal chain by elongation of the alkyl spacer length.

The liquid crystalline phases of all one-chain fluorinated triazines **6**, as evident from polarized optical microscopy, show pseudo-isotropic regions which are separated by oily streaks (Figure 2). These optical textures are consistent with a smectic A phase.

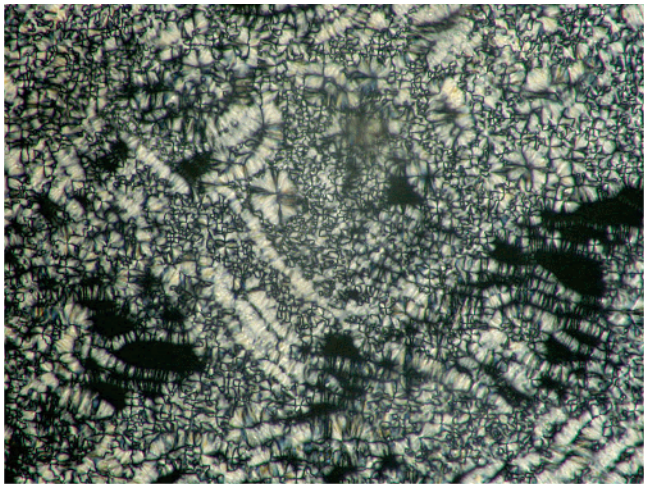

Figure 2. Optical photomicrograph (crossed polarizers) observed on cooling for the monotropic SmA phase of the pure one-chain 1,3,5-triazine **6-[6,4]** at 176.0 °C.

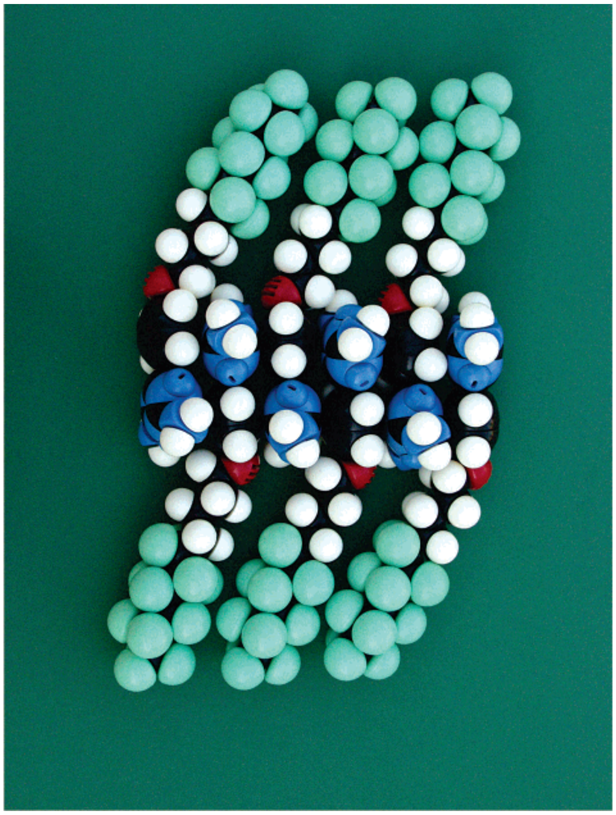

Figure 3. CPK model of the smectic A mesophase of the single-chain semiperfluorinated triazine **6-[4,6]**.

The X-ray diffraction pattern of compound **6-[4,6]** exhibits one distinct reflection in the small angle region corresponding to $d = 3.7$ nm and a diffuse scattering in the wide angle region. This diffraction pattern indicates a layer structure with only short-range order in the layers which is in accordance with the optical investigations (SmA). The layer spacing is larger than the molecular length ($L = 2.4$ nm as evaluated from CPK models) but less than twice the length. Therefore, an intercalated bilayer structure can be assumed. As evident from CPK models (Figure 3) the d spacing matches well with an antiparallel alignment of the molecules which are shifted against each other so that the polar aromatic parts are interdigitated. The perfluorinated chains build up a separate sublayer. Lamellar structures with distinct fluoro sublayers were also reported, that is, for the smectic A_d phases of fluorinated biphenyls,[10,25,26] for partially fluorinated benzoates,[27] and for semiperfluorinated liquid crystals containing just a single benzene unit.[28,29]

The two-chain semiperfluorinated triazine compound **7-[4,4]** forms a highly viscous optically isotropic mesophase above the melting point. Even shearing the samples does not induce any birefringence as one should expect for homeotropically aligned smectic or columnar mesophases. Calorimetric investigations reveal that above the melting transition an additional phase transition occurs which is accomponied by a remarkable decrease in viscosity. The crystallization and the transition from the liquid state to the mesophase can be supercooled by approximately 10 K. These observations are a strong hint toward the existence of a cubic mesophase and point to the presence of a three-dimensional lattice within this mesophase.

The volume fraction of the semiperfluorinated molecular fragment of compound **7-[4,4]** is enlarged compared with the single-chain analogues **6** whereas the size of the polar diaminotriazine part remains the same. Therefore, the cubic phase of compound **7-[4,4]** should be of the reversed type (type-2 phase) with aggregates comprising the polar moieties surrounded by a continuum of the nonpolar chains.

Binary Mixtures of the Two-Chain Compound 7 with the One-Chain 1,3,5-Triazine 6-[4,6]. It has been shown that mixing of structurally related compounds, which form different mesophase morphologies as pure compounds, may provide a powerful tool to distinguish between different types of cubic mesophases.[1,2,15,16] We applied this method to binary mixtures consisting of the two-chain triazine **7-[4,4]** and the partially fluorinated one-chain compound **6-[4,6]**.

Optical polarizing microscopy, performed on contact preparations and on mixtures with defined compositions, reveal that a new birefringent mesophase is induced within a broad concentration range between the SmA phase and the cubic phase of the pure compounds **6-[4,6]** and **7-[4,4]**, respectively. The appearance of spherulitic and mosaic-like optical textures (Figure 4a) is typical for a hexagonal columnar (Col_h) liquid crystalline phase built up of cylindrical aggregates.

An additional optically isotropic phase appears in regions with a high concentration of compound **6-[4,6]** (Figure 4b). The high viscosity again points to a cubic mesophase.

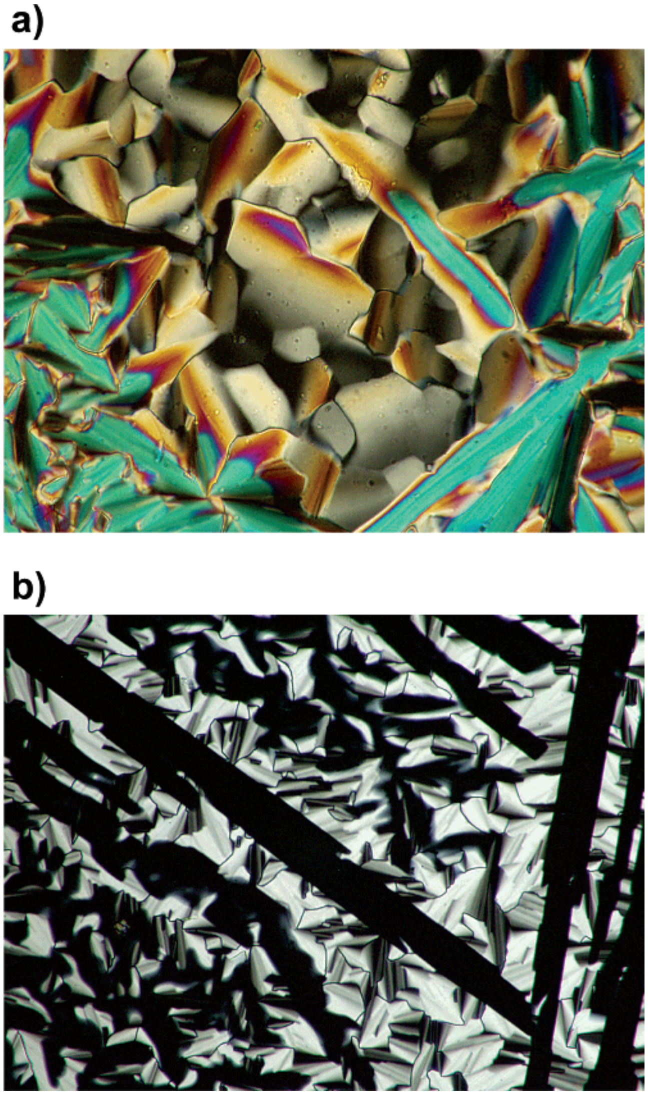

Figure 4. Photomicrographs of the mesophase textures observed on cooling binary mixtures of the fluorinated diaminotriazines **6-[4,6]/7-[4,4]**: (a) Col_h mesophase at 176.7 °C ($X_{\mathbf{7-[4,4]}} = 0.25$); (b) transition from the Col_h phase to the Cub_{V2} phase ($X_{\mathbf{7-[4,4]}} = 0.10$) at 176 °C.

The polar/apolar interface curvature becomes increasingly negative on increasing the content of the two-chain semiperfluorinated triazine **7-[4,4]**. Because the induced cubic phase occurs as intermediate between the SmA phase and the induced inverted hexagonal columnar (Col_{h2}) mesophase, it can be concluded that, in analogy to lyotropic systems,[30] this cubic phase should be a reversed bicontinuous cubic phase (Cub_{V2}). It should consist of two interwoven but nonconnected networks of branched cylinders formed by the polar regions within the apolar continuum of the semiperfluorinated chains.

The aggregates forming the cubic phase of **7-[4,4]** must be more strongly curved than the cylindrical aggregates in the induced columnar phase. The cubic mesophase of the pure compound **7-[4,4]**, therefore, should be a reverse discontinuous micellar cubic phase (Cub_{I2}) built up by closed spheroidic inverted micelles of the polar parts surrounded by the nonpolar fluorinated chains. Unfortunately, as a result of the low number and low intensity of reflections in the X-ray diffraction patterns we were not able to determine the three-dimensional lattice type of the cubic phase. However, the space group $Pm3n$ is most frequently found for thermotropic Cub_{I2} phases.[1-3]

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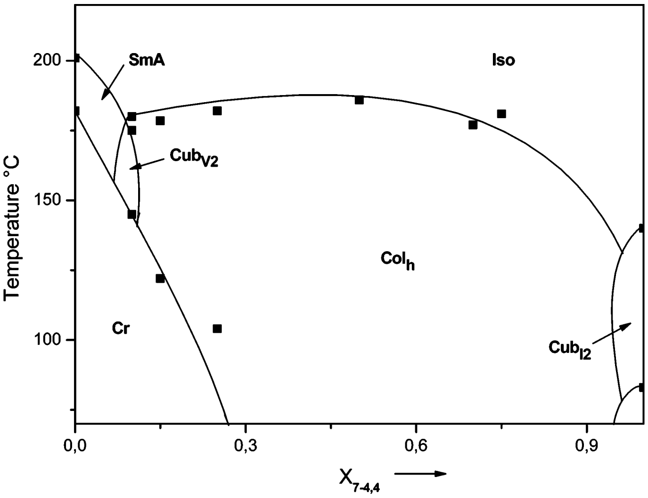

Figure 5. Binary phase diagram of the system **6-[4,6]**/**7-[4,4]**.

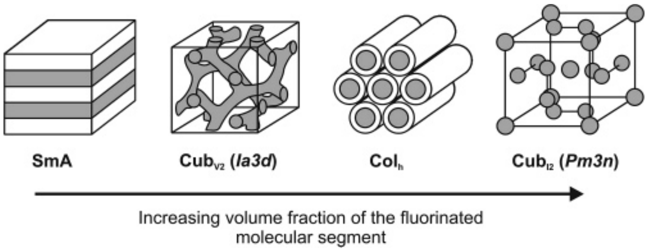

Figure 6. Schematic presentation of the sequence of mesophase morphologies of binary mixed systems **6**/**7** depending on the volume fractions of the semiperfluorinated molecular segments.

The phase diagram of the system **6-[4,6]**/**7-[4,4]** obtained by investigation of binary mixtures is shown in Figure 5.

The phase sequence and structure of the thermotropic mesophase morphologies found for the binary mixtures **6-[4,6]**/**7-[4,4]** are shown schematically in Figure 6. The phase sequence covers the whole range of inverted lyotropic mesophases found for amphiphile/solvent systems depending on the solvent content and temperature. It is realized here without any solvent by mixing of two structurally related low molar mass molecules which exhibit different mesophase morphologies as pure compounds, hence, by gradually changing the average volume fractions of incompatible molecular fragments. The same thermotropic polymorphism was reported for binary mixtures of partially fluorinated amphiphilic diols without an extended rodlike molecular segment.[16]

Lyotropic Properties. The triazines **6-[4,6]** and **7-[4,4]** were additionally investigated with respect to their lyotropic properties with protic solvents. In the contact region of the cubic mesophase of the two-chain compound **7-[4,4]** with formamide, for example, a hexagonal columnar phase is induced (maximum stability 136 °C). Most likely, the solvent molecules are built between the polar diaminotriazine headgroups. Therefore, the size of the hydrophilic groups increases, and accordingly the interface curvature is reduced. This gives rise to a transition from strongly curved closed micelles in the discontinuous cubic phase of compound **7-[4,4]** to less curved cylindrical aggregates leading to the lyotropic hexagonal columnar phase. Hence, this behavior further confirms the inverted micellar structure (Cub$_{I2}$) of the cubic mesophase of compound **7-[4,4]**.

On the contrary, the mesophase morphology (SmA) of the single-chain partially fluorinated triazine **6-[4,6]** could not be modified on addition of formamide.

Conclusions

A new family of fluorinated diamino-1,3,5-triazines has been synthesized. Contrary to the hydrocarbon analogues the compounds show thermotropic liquid crystalline behavior. The mesophase formation is essentially due to an increased intramolecular polarity contrast upon replacing alkyl chains by semiperfluorinated chains, which favors a microsegregation. Depending on the number of semiperfluorinated terminal chains the triazines form either lamellar (SmA) or micellar cubic (Cub$_{I2}$) mesophases as pure compounds. In strong analogy to inverted lyotropic phases of surfactant/solvent systems, the phase sequence SmA−Cub$_{V2}$−Col$_{h2}$−Cub$_{I2}$ was realized in a solvent-free binary system of a semiperfluorinated one-chain triazine with a two-chain fluorinated triazine. Hence, the combination of polar−nonpolar microsegregation along with tailoring the interface curvature by the space requirement of the incompatible molecular blocks predominantly determines the different mesophase morphologies of the fluorinated triazine derivatives.

Experimental Section

Instruments. IR spectra were recorded using a Digilab FTS 2000 series FT-IR spectrometer equipped with a MIRacle single reflection Horizontal ATR accessory (PIKE Technologies).^{1}H NMR and ^{19}F NMR spectra were obtained with a Bruker AMX 300 spectrometer. Texture observations were made using an Olympus BHS polarizing microscope fitted 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 have been carried out using the Guinier method where the sample was held in Lindemann capillaries and the scattered Cu Kα was detected by a film.

Materials. Unless otherwise noted, all starting materials were purchased from commercial sources and were used as obtained. The semiperfluorinated alkyl derivatives **1**−**3** were prepared as described previously.[11,16,23] The purity of intermediates and final products was checked by thin-layer chromatography.

Synthesis of the Semiperfluorinated Alkoxybenzonitriles 4. A mixture of 4-hydroxybenzonitrile, the appropriate semiperfluorinated 1-bromoalkane, and K_2CO_3 in dry dimethylformamide (DMF) was heated to 65 °C and stirred under an argon atmosphere for 2 h. After cooling to room temperature the mixture was poured into ice/water and acidified with 10% HCl to pH = 4−5. The solution was extracted with Et_2O, the combined organic layers were dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by recrystallization from petroleum ether.

4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-Perfluorooctyl-1-oxy)benzonitrile, 4-[4,4]. 4-[4,4] was prepared from 0.63 g (5.3 mmol) of 4-hydroxybenzonitrile, 2.06 g (5.8 mmol) of 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctane, and 2.2 g (15.9 mmol) of K_2CO_3 in 40 mL of DMF. Yield: 73% (1.52 g). $C_{15}H_{12}F_9NO$ (393.25). Pale oil. Mp: 20 °C. ^1H NMR ($CDCl_3$): $\delta = 7.6$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 4.05 (t, 2H, OCH_2, $J = 5.7$ Hz), 2.1−2.3 (m, 2H, CH_2CF_2), 1.7−2.1 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, $CH_2C\mathit{F}_2$), −125 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,6*H*,6*H*-Perfluorodecyl-1-oxy)benzonitrile, 4-[6,4]. 4-[6,4] was prepared from 0.43 g (3.6 mmol) of 4-hydroxybenzonitrile, 1.53 g (4.0 mmol) of 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,6*H*,6*H*-perfluorodecane, and 1.48 g (10.8 mmol) of K_2CO_3 in 20 mL of DMF. Yield: 90% (1.34 g). $C_{17}H_{16}F_9NO$ (412.30). White crystals. Mp: 42 °C. ^1H NMR ($CDCl_3$): $\delta = 7.6$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 4.05 (t, 2H, OCH_2, $J = 6.3$ Hz), 2.0−2.2 (m, 2H, CH_2CF_2), 1.4−1.9 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, $CH_2C\mathit{F}_2$), −125 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-Perfluorodecyl-1-oxy)benzonitrile, 4-[4,6]. 4-[4,6] was prepared from 0.34 g (2.9 mmol) of 4-hydroxybenzonitrile, 1.46 g (3.2 mmol) of 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecane, and 1.2 g (8.7 mmol) of K_2CO_3 in 20 mL of DMF. Yield: 89% (1.27 g). $C_{17}H_{12}F_{13}NO$ (493.23). White crystals. Mp: 66 °C. ^1H NMR ($CDCl_3$): $\delta = 7.6$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 4.05 (t, 2H, OCH_2, $J = 5.9$ Hz), 2.1−2.3 (m, 2H, CH_2CF_2), 1.8−2.0 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81$ (3F, CF_3), −114 (2F, CH_2CF_2), −122 (2F, $CF_3(CF_2)_3C\mathit{F}_2$), −123 (2F, $CF_3(CF_2)_2C\mathit{F}_2$), −123.5 (2F, $CF_3CF_2C\mathit{F}_2$), −126 (2F, $CF_3C\mathit{F}_2$)

4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,6*H*,6*H*-Perfluorododecyl-1-oxy)benzonitrile, 4-[6,6]. 4-[6,6] was prepared from 0.51 g (4.3 mmol) of 4-hydroxybenzonitrile, 2.26 g (4.7 mmol) of 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,-6*H*,6*H*-perfluorododecane, and 1.78 g (12.9 mmol) of K_2CO_3 in 20 mL of DMF. Yield: 72% (1.61 g). $C_{19}H_{16}F_{13}NO$ (521.32). White crystals. Mp: 68 °C. ^1H NMR ($CDCl_3$): $\delta = 7.6$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 4.05 (t, 2H, OCH_2, $J = 6.3$ Hz,), 2.0−2.2 (m, 2H, CH_2CF_2), 1.4−1.9 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81$ (3F, CF_3), −115 (2F, CH_2CF_2), −122.5 (2F, $CF_3(CF_2)_3C\mathit{F}_2$), −123.5 (2F, $CF_3(CF_2)_2C\mathit{F}_2$), −124 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

3,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-Perfluorooctyl-1-oxy)benzonitrile, 5-[4,4]. A total of 0.69 g (5.1 mmol) of 3,4-dihydroxybenzonitrile, 4 g (5.6 mmol) of 1-bromo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctane, 4.2 g (30.6 mmol) of K_2CO_3, and 0.2 g of KI were added to 30 mL of dry acetone under an argon athmosphere, and the mixture was heated to reflux for 16 h (TLC). The mixture was cooled to room temperature and poured into ice/water. The aqueous layer was extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. Purification was performed by recrystallization from light petroleum ether. Yield: 86% (3.00 g). $C_{23}H_{19}F_{18}NO_2$ (683.37). White crystals. Mp: 51 °C. ^1H NMR ($CDCl_3$): $\delta = 7.25$ (dd, 1H, phenyl, $J_1 = 1.9$ Hz, $J_2 = 8.3$ Hz), 7.1 (s, 1H, phenyl), 6.85 (d, 1H, phenyl, $J = 1.9$ Hz), 4.08 (t, 2H, OCH_2, $J = 5.8$ Hz), 4.04 (t, 2H, OCH_2, $J = 5.9$ Hz), 2.1−2.3 (m, 4H, CH_2CF_2), 1.8−2.0 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, $CH_2C\mathit{F}_2$), −125 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

Synthesis of the Semiperfluorinated Alkoxyphenyltriazines 6 and 7. The appropriate semifluorinated alkoxybenzonitril, dicyandiamide, and KOH were added to 20 mL of ethyleneglycolmonomethyl ether. The mixture was stirred and heated at reflux for 5 h. After cooling to room temperature the mixture was poured into ice/water. The resulting precipitate was collected by filtration. Purification of the crude products was effected by recrystallization from ethanol.

2,4-Diamino-6-(4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctyl-1-oxy)-phenyl)-1,3,5-triazine, 6-[4,4]. 6-[4,4] was prepared from 0.8 g (2.0 mmol) of **4-[4,4]**, 0.17 g (2.0 mmol) of dicyandiamide, and 0.11 g (2.0 mmol) of KOH. Yield: 59% (0.56 g). $C_{17}H_{16}F_9N_5O$ (477.33). White crystals. IR: $\nu = 3540$, 3412, 3293, 3164, 2947, 2872, 1652, 1192, 1130, 1068, 1251, 816 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.3$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 5.1 (s, 4H, NH_2), 4.05 (t, 2H, OCH_2, $J = 5.9$ Hz), 2.1−2.3 (m, 2H, CH_2CF_2), 1.8−2.0 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, $CH_2C\mathit{F}_2$), −125 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

2,4-Diamino-6-(4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,-6*H*,6*H*-perfluorodecyl-1-oxy)-phenyl)-1,3,5-triazine, 6-[6,4]. 6-[6,4] was prepared from 0.8 g (1.9 mmol) of **4-[6,4]**, 0.16 g (1.9 mmol) of dicyandiamide, and 0.11 g (2.0 mmol) of KOH. Yield: 75% (0.72 g). $C_{19}H_{20}F_9N_5O$ (505.38). White crystals. IR: $\nu = 3532$, 3408, 3273, 3144, 2947, 2872, 1659, 1198, 1128, 1047, 1251, 816 cm^{-1}. ^1H NMR (DMSO-*d*): $\delta = 8.2$ (d, 2H, phenyl, $J = 8.9$ Hz), 7.0 (d, 2H, phenyl, $J = 8.9$ Hz), 6.65 (4H, s, NH_2), 4.05 (t, 2H, OCH_2, $J = 5.9$ Hz), 2.15−2.35 (m, 2H, CH_2CF_2), 1.4−1.8 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, $CH_2C\mathit{F}_2$), −125 (2F, $CF_3CF_2C\mathit{F}_2$), −126.5 (2F, $CF_3C\mathit{F}_2$).

2,4-Diamino-6-(4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecyl-1-oxy)-phenyl)-1,3,5-triazine, 6-[4,6]. 6-[4,6] was prepared from 0.7 g (1.43 mmol) of **4-[4,6]**, 0.12 g (1.43 mmol) of dicyandiamide, and 0.08 g (1.43 mmol) of KOH. Yield: 79% (0.65 g). $C_{19}H_{16}F_{13}N_5O$ (577.11). White crystals. IR: $\nu = 3532$, 3408, 3273, 3144, 2957, 2872, 1653, 1195, 1135, 1039, 1251, 816 cm^{-1}. ^1H NMR (DMSO-*d*): $\delta = 8.3$ (d, 2H, phenyl, $J = 8.9$ Hz), 7.0 (d, 2H, phenyl, $J = 8.9$ Hz), 6.15 (4H, s, NH_2), 4.05 (t, 2H, OCH_2, $J = 5.9$ Hz,), 2.2−2.4 (m, 2H, CH_2CF_2), 1.7−1.9 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81$ (3F, CF_3), −114 (2F, CH_2CF_2), −122 (2F, $CF_3(CF_2)_3C\mathit{F}_2$), −123 (2F, $CF_3(CF_2)_2C\mathit{F}_2$), −123.5 (2F, $CF_3CF_2C\mathit{F}_2$), −126 (2F, $CF_3C\mathit{F}_2$),

2,4-Diamino-6-(4-(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*,5*H*,5*H*,-6*H*,6*H*-perfluorododecyl-1-oxy)-phenyl)-1,3,5-triazine, 6-[6,6]. 6-[6,6] was prepared from 0.8 g (1.5 mmol) of **4-[6,6]**, 0.13 g of dicyandiamide, and 0.09 g of KOH. Yield: 49% (0.44 g). $C_{21}H_{20}F_{13}N_5O$ (605.40). White crystals. IR: $\nu = 3532$, 3400, 3293, 3164, 2947, 2882, 1653, 1197, 1142, 1049, 1251, 816 cm^{-1}. ^1H NMR (DMSO-*d*): $\delta = 8.15$ (d, 2H, phenyl, $J = 8.9$ Hz), 6.95 (d, 2H, phenyl, $J = 8.9$ Hz), 6.6 (4H, s, NH_2), 4.0 (t, 2H, OCH_2, $J = 6.4$ Hz), 2.1−2.3 (m, 2H, CH_2CF_2), 1.4−1.8 (m, 8H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.$ (3F, CF_3), −114 (2F, CH_2CF_2), −122 (2F, $CF_3(CF_2)_3C\mathit{F}_2$), −123 (2F, $CF_3(CF_2)_2C\mathit{F}_2$), −123.5 (2F, $CF_3CF_2C\mathit{F}_2$), −126 (2F, $CF_3C\mathit{F}_2$).

2,4-Diamino-6-(3,4-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctyl-1-oxy)-phenyl)-1,3,5-triazine, 7-[4,4]. 7-[4,4] was prepared from 3 g (4.4 mmol) of **5-[4,4]**, 0.37 g (4.4 mmol) of dicyandiamide, and 0.25 g (4.4 mmol) of KOH. Yield: 76% (2.57 g). $C_{25}H_{23}F_{18}N_5O_2$ (767.45). Pale yellow crystals. IR: $\nu = 3464$, 3318, 3194, 2939, 2708, 1628, 1198, 1134, 1072, 1265, 810 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.0$ (dd, 1H, phenyl, $J_1 = 2.0$ Hz, $J_2 = 8.4$ Hz), 7.9 (d, 1H, phenyl, $J_1 = 2.0$ Hz,), 6.9 (d, 1H, phenyl, $J_2 = 8.5$ Hz), 5.1

(4H, s, NH_2), 4.15 (t, 2H, OCH_2, $J = 5.7$ Hz), 4.1 (t, 2H, OCH_2, $J = 5.8$ Hz), 2.2−2.3 (m, 4H, CH_2CF_2), 1.8−2.0 (m, 4H, CH_2). ^{19}F NMR ($CDCl_3$): $\delta = -81.5$ (3F, CF_3), −115 (2F, CH_2CF_2), −125 (2F, $CF_3CF_2CF_2$), −126.5 (2F, CF_3CF_2).

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