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Hydrogen-bonded block mesogens derived from semiperfluorinated benzoic acids and the non-mesogenic 1,2-bis(4-pyridyl)ethylene

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Hydrogen-bonded block mesogens derived from semiperfluorinated benzoic acids and the non-mesogenic 1,2-bis(4-pyridyl)ethylene

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Thermal properties of benzoic acids carrying one or two semiperfluorinated alkoxy tails on the aromatic core have been investigated in binary mixtures with the non-liquid crystalline bidirectional *trans*-1,2-bis(4-pyridyl)ethylene. The hydrogen bonded complexes built from the complementary molecular species show a significantly enhanced mesophase stability compared with the fluorinated acids in their pure states. The mesophase morphologies of the complexes are governed mainly by the number of the partially fluorinated chains grafted to the acid component. Mixed systems comprising the one-chain acids exhibit a smectic C phase followed by a smectic A phase at more elevated temperatures. Incorporation of a second semiperfluorinated chain into the acid leads to the formation of columnar mesophases. These columnar phases of the H-bonded complexes should represent ribbon phases resulting from the collapse of the smectic layers.

1. Introduction

Intermolecular hydrogen bonding is a key interaction for recognition in nature and plays an important role in tailoring the properties of organic materials by self-organization of the molecular building blocks. Well-defined molecular structures with liquid crystalline properties may be obtained via self-assembly of two complementary compounds through hydrogen bonding [1] even if the constituent single molecules alone are non-mesomorphic. For example, Kato and co-workers have exploited the single hydrogen bonding between carboxylic acids and pyridine fragments to induce and/or stabilize mesophases in low molar mass binary mixtures [2], in mixtures with polymeric components [3] and in mesomorphic networks comprising non-liquid crystalline precursers [4].

Double hydrogen-bonded complexes of 2,6-diacylaminopyridines with aromatic acids were described as forming smectic or columnar liquid crystalline phases [5]. We showed that the columnar mesophases of 2,4,6-triarylmelamines bearing six peripheral alkoxy tails [6] can be controlled by double-hydrogen bonding with alkoxy substituted benzoic acids [7]. Triple hydrogen bonds between 2,6-diacylaminopyridines and uracil derivatives were utilized by Lehn and co-workers for the design of mesogenic complexes showing columnar phases [8].

Mesophase morphologies can be further tailored if a perhydrogenated chain is replaced by a perfluorinated segment. The main reasons are the incompatibility of the perfluorinated chains with aliphatic, aromatic and polar molecular segments, their larger cross-sectional area compared with aliphatic chains and their reduced conformational mobility [9]. (Semi)perfluorinated molecular segments have been successfully introduced, for example, into calamitic [10], discotic [11] and polycatenar [12] mesogens and it was be shown that the fluorophobic effect may lead to a significant stabilization and even to modifications of smectic, columnar and cubic mesophases.

However, reports regarding liquid crystals combining hydrogen bonding between two different components and the fluorophobic effect are rather limited. Thus, a few mixed systems of single-chain fluorinated acids and pyridine derivatives were reported to exhibit a smectic A or a cubic mesophase [13]. Recently we presented supramolecular mesogens with double hydrogen bonding between 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 [14].

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We present here efforts towards polyphilic block mesogens composed of a central single hydrogen-bonded polar rod-shaped core and two perfluorinated molecular blocks which are linked to the terminal positions of the central rigid moiety via lipophilic flexible alkyl spacers (figure 1). We report on mesomorphic structure formation by selective pairing of the one-chain and two-chain partially fluorinated benzoic acids **1-[*m*,*n*]** and **2-[*m*,*n*]** with the bidirectional *trans*-1,2-bis(4-pyridyl)ethylene **3** (figure 2).

2. Materials and methods

The partially fluorinated benzoic acids **1** and **2** were prepared by etherification of methyl 4-hydroxybenzoate and ethyl 3,4-dihydroxybenzoate, respectively, with semiperfluorinated 1-bromoalkanes [15], using potassium carbonate as the base, and subsequent basic hydrolysis. Binary mixtures of the acids **1** or **2** with the dipyridyl derivative **3** were obtained by dissolving the desired amounts of the components separately in THF. The solutions were combined and the solvent was evaporated.

Thermal investigations were performed after annealing the residues in the isotropic state. 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. Wide angle X-ray scattering (CuK_α) was carried out with a Nenius PDS 120 (Bruker) equipped with a detector from Inel. Temperature-dependent IR spectroscopy was performed with a Digilab FTS 2000 Series FTIR spectrometer. The samples were placed between two silicon wafers and heated under nitrogen with a heating device from Specac Ltd., England.

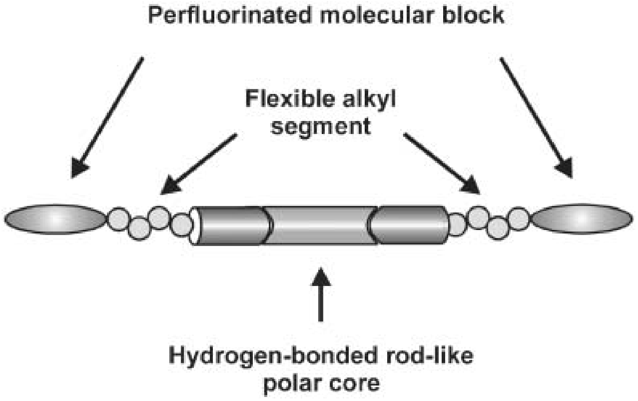


Figure 1. Polyphilic block molecules composed of a rod-shaped hydrogen bonded central core grafted with two terminal fluorinated molecular fragments via lipophilic alkyl spacer segments.

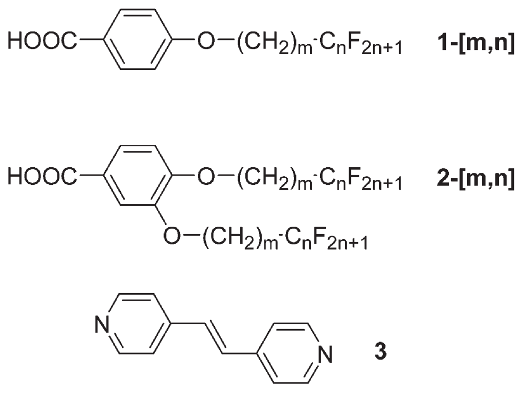


Figure 2. Chemical structure of the semiperfluorinated one-chain and two-chain benzoids acids **1** and **2** and the *trans*-1,2-bis(4-pyridyl)ethylene **3** under investigation.

3. Results and discussion

The thermal behaviour of the pure acids **1** and **2**, and of the respective binary mixtures with the dipyridylethylene **3**, was studied by means of polarizing optical microscopy and differential scanning calorimetry (DSC). Additionally, the mesophases of the 2:1 mixed systems of the partially fluorinated benzoic acids **2-[6,4]** and **2-[4,6]** with the dipyridyl derivative **3** were investigated by X-ray scattering. The phase transition data of the benzoic acids **1** and **2** in their pure state are summarized in table 1. The dipyridyl compound **3** is non-liquid crystalline and melts at 152°C.

The single-chain semiperfluorinated benzoic acids **1** display an enantiotropic smectic C phase due to the dimerization of their carboxylic groups through hydrogen bonding. Dimers of the structurally related hydrocarbon analogues are known to exhibit SmC and nematic mesophases [16], the latter being surpressed in the case of the acids **1** because of the increased segregation tendency by perfluoroalkyl chains.

The incorporation of a second semiperfluorinated chain gives rise to at least monotropic hexagonal columnar mesophases for the two-chain benzoic acids **2**. The columnar phases are related to the formation of discrete benzoic acid dimers via hydrogen bonding [15 *b*] or rather pairs of dimers [17] with a cylindrical shape. The polar core regions segregate from the surrounding semiperfluorinated chains and columns are built up which organize on a two-dimensional hexagonal lattice.

Figure 3 shows as an example the binary phase diagram of the one-chain benzoic acid **1-[4,4]** and the dipyridyl derivative **3**. A smectic A phase is induced for mixtures within the concentration range 10 to 50% of

Table 1. Phase transition temperatures for the semiperfluorinated one-chain and two-chain benzoic acids **1-[*m*,*n*]** and **2-[*m*,*n*]**; by DSC, second heating at 10 K min^{-1}, transition enthalpies (kJ mol^{-1}) in parenthesis. Cr=crystalline; SmC=smectic C; Col$_h$=hexagonal columnar; I=isotropic.

Compound	Cr		SmC	Col$_h$		I	Ref.
1-[4,4]	•	147.3 (11.54)[a]	•	—	170.3 (7.73)	•	
1-[6,4]	•	150.7 (12.92)[a]	•	—	168.5 (8.09)	•	
1-[4,6]	•	164.1 (15.91)	•	—	185.5 (10.37)	•	[15*b*]
1-[6,6]	•	155.7 (12.38)[a]	•	—	176.9 (8.59)	•	[13*c*]
2-[6,4]	•	54.7 (14.21)	—	•	[53.1 (1.79)][b]	•	[15*b*]
2-[4,6]	•	115.7 (37.59)	—	•	[102.0 (1.57)][b]	•	[15*b*]
2-[6,6]	•	88.2 (20.04)	—	•	[75.3 (0.80)][b]	•	

[a] Polymorphism in the solid state was observed. The transition data are for the highest melting modification. [b] Monotropic phase.

the bispyridylethylene **3**. The SmA phases display characteristic focal-conic fan textures, figure 4 (*a*), which can be homeotropically aligned to give pseudoisotropic regions separated by oily streaks. On further cooling, the SmA phases transform into a smectic C phase with typical broken fan-like, marbled and schlieren textures, figure 4 (*b*). The highest clearing temperatures of the binary mixtures are found at a concentration of 67% of the acids, which confirms the existence of 2:1 associates with the dipyridine **3**. The phase transition temperatures of the one-chain fluorinated acids **1** mixed with the bifunctional bipyrydylethylene **3** at a 2:1 molar ratio are collected in table 2.

The phase transition temperatures are remarkably higher than those of respective associates of compound **3** with structurally related non-fluorinated 4-alkoxybenzoic acids reported by Kato *et al.* [2*f*], due to the cooperation of H-bonding and perfluoro groups. Likewise, the melting and isotropization temperatures of the 2:1 complexes **1/3** are much higher than for the

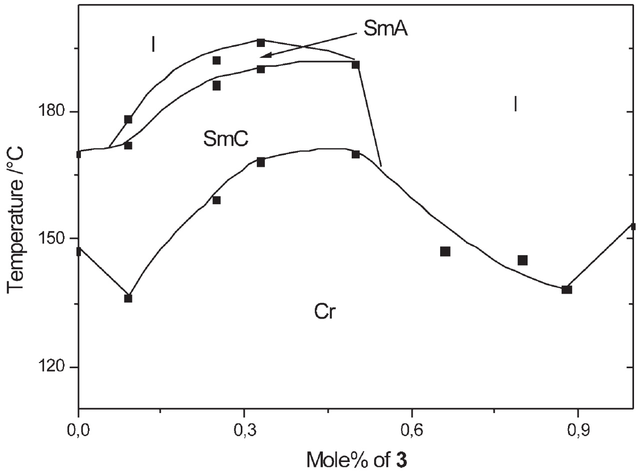
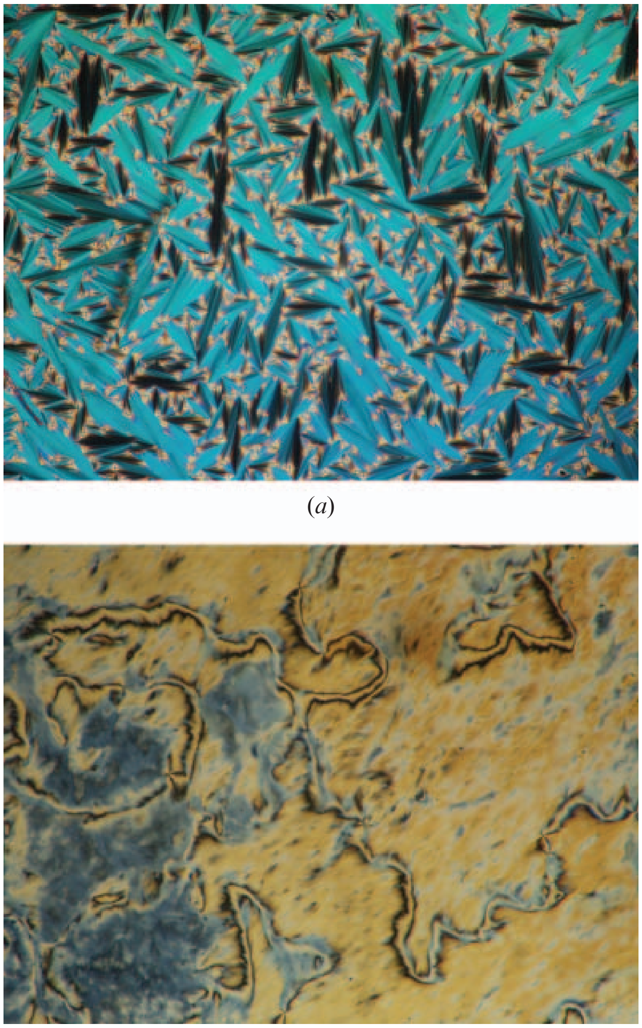


Figure 3. Binary phase diagram for the acid **1-[4,4]** and the bispyridyl compound **3**.


(*a*)

(*b*)

Figure 4. Optical textures for the mesophases of 2:1 hydrogen bonded complexes of the single-chain benzoic acids **1** with the dipyridyl compound **3**; (*a*) smectic A mesophase of **1-[6,6]/3** at 194.9°C; (*b*) smectic C phase of the mixture **1-[6,4]/3** at 173.7°C.

Table 2. Phase transition temperatures for hydrogen-bonded complexes of the partially fluorinated one-chain benzoic acids **1-[*m*,*n*]** with the dipyridyl compound **3** at a 2:1 molar ratio; by DSC, first cooling at 10 K min^{-1}, transition enthalpies (kJ mol^{-1}) in parenthesis. Cr=crystalline; SmC=smectic C; SmA=smectic A; I=isotropic.

Mixture	Cr		SmC		SmA		I
1-[4,4]/3	•	170.7 (38.8)	•	189.5 (1.0)	•	193.9 (16.1)	•
1-[6,4]/3	•	166.2 (46.3)	•	187.5 (1.4)	•	194.7 (18.6)	•
1-[4,6]/3	•	178.1 (48.5)	•	200.7 (2.5)	•	205.9 (15.4)	•
1-[6,6]/3	•	173.7 (46.0)	•	193.7 (2.8)	•	202.7 (14.0)	•

pure benzoic acids **1-[*m*,*n*]**. The 2:1 mixtures of the two-chain fluoroalkoxybenzoic acid **2-[*m*,*n*]** with the dipyridyl compound **3** exhibit a mesophase within the temperature range given in table 3.

The monotropic phases of the acids **2** are replaced by an enantiotropic mesophase and the isotropization temperatures of the 2:1 binary mixtures **2/3** are enhanced compared with the pure acids **2**. The phase transition temperatures of the two-chain benzoic acids **2** mixed with the dipyridine **3** are significantly lower than those of the mixed 2:1 systems **1/3**. On the other hand, the mixtures **2/3** display enlarged mesophase ranges compared with the 2:1 associates of the single-chain acids **1** with the pyridine **3**. As a general trend, elongation of the fluorinated molecular segment leads to an increase of the clearing temperatures for both investigated systems **1/3** and **2/3**, respectively.

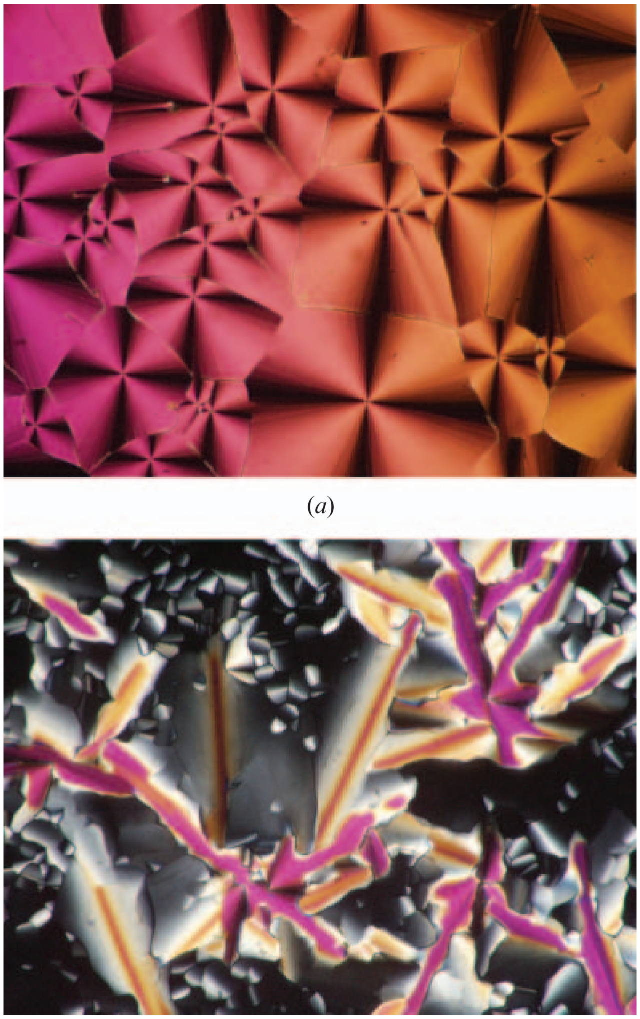
Fern-like textures develop upon cooling the 2:1 compositions **2-[6,4]/3** and **2-[4,6]/3** from the isotropic liquid which coalesce to form spherulitic textures, figure 5 (*a*). The samples do not tend to align homeotropically. The optical textures point to a columnar liquid crystalline phase. The textures of the complex **2-[6,6]/3** are characterized by regions with broken spherulites, mosaic-like domains and pseudoisotropic areas containing birefringent filaments, figure 5 (*b*). These textures are typical for a hexagonal columnar (Col$_h$) mesophase.

The formation of columnar phases of the 2:1 binary mixtures **2-[6,4]/3** and **2-[4,6]/3** were confirmed by X-ray scattering. The small angle reflections can be indexed on the basis of a columnar structure with a two-dimensional oblique lattice (Col$_{ob}$). The lattice parameters are given in table 4.

Table 3. Phase transition temperatures for hydrogen-bonded complexes of the fluorinated two-chain benzoic acids **2-[*m*,*n*]** with the dipyridyl compound **3** at a 2:1 molar ratio; by DSC, first heating at 10 K min^{-1}, transition enthalpies (kJ mol^{-1}) in parenthesis). Cr=crystalline; Col$_{ob}$=columnar, oblique 2D lattice; Col$_h$=hexagonal columnar; I=isotropic.

Mixture	Phase transition temperatures				
2-[6,4]/3	Cr	—	Col$_{ob}$	106.6 (3.21)	I
2-[4,6]/3	Cr	54.8 (50.8)	Col$_{ob}$	133.0 (4.0)	I
2-[6,6]/3	Cr	68.3 (50.4)	Col$_{ob}$	125.3 (3.7)	I

The hydrogen bonding of the fluorinated acids **1** and **2** with the complementary dipyridylethylene **3** is confirmed by temperature dependent IR spectroscopy.



(*a*)

(*b*)

Figure 5. Optical textures for the columnar phases of the two-chain acids **2** in mixtures with the pyridyl derivative **3** at a molar ratio of 2:1: (*a*) **2-[4,6]/3**, second cooling at 1 K min^{-1} at 129.9°C; (*b*) **2-[6,6]/3** first cooling at 1 K min^{-1} at 107.7°C.

Table 4. X-ray diffraction data for the mesophases of the binary 2:1 mixtures of the two-chain benzoic acids **2-[6,4]** and **2-[4,6]** with the dipyridylethylene **3**.

	Reflections/nm			
Mixture	d_{obs}	d_{calc}	Miller indices $(h\,k\,l)$	Lattice constants
2-[6,4]/3	4.46	4.46	100	a=4.54 nm
	3.12	3.12	010	b=3.17 nm
	2.24	2.23	200	γ=79.7°
	1.57	1.56	120	
	1.40	1.40	220	
	1.16	1.19	320	
2-[4,6]/3	3.62	3.62	100	a=3.95 nm
	3.53	3.53	010	b=3.85 nm
	3.26	3.26	110	γ=66.6°
	1.74	1.81	200	
	1.62	1.63	220	
	1.33	1.31	310	
	1.18	1.21	300	

Figure 6 displays, as an example, the FTIR transmission spectra of the 2:1 mixture **1-[6,4]/3** within the mesophase and in the isotropic state along with the spectrum of the pure acid **1-[6,4]** at room temperature.

The absorption band due to the carbonyl group of the acid dimer is located at 1672 cm^{-1}. At the transition to the liquid crystalline phase of the mixed system the band is shifted to 1683 cm^{-1}, indicative of the free carbonyl group of the complex from the benzoic acid and the pyridyl group [2*f*]. In the isotropic state the carbonyl absorption splits into two bands. One band remains almost at the same position as in the mesophase (1688 cm^{-1}). The new band appears at 1728 cm^{-1} and can be attributed to the carbonyl absorption of the free carboxylic acid monomer. This result indicates that the H-bonded complex between the acid and the pyridyl compound breaks in part above the clearing point.

The cross-sectional area of a perfluorinated chain is 0.27–0.31 nm^2 which is large in comparison to alkyl chains (*c.* 0.2 nm^2) and aromatic rod-like moieties (*c.* 0.22 nm^2). In the case of the complexes involving the one-chain acids, the differences between the space-filling of the rigid cores and the terminal fluorinated chains can be compensated for by tilting the parallel aligned H-bonded cores with respect to the layer normal, as shown in figure 7 (*a*). This gives rise to

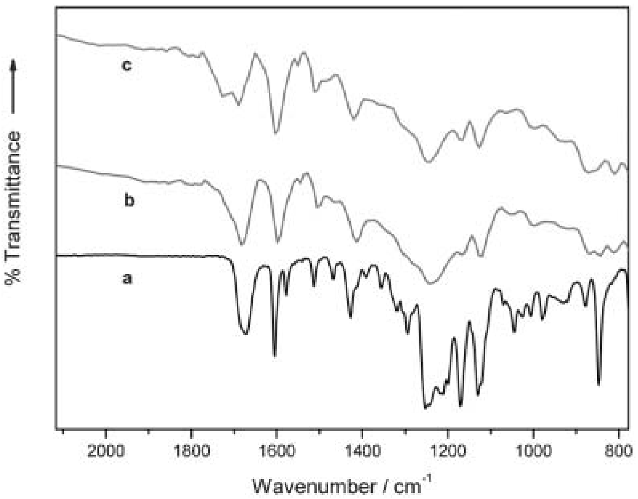
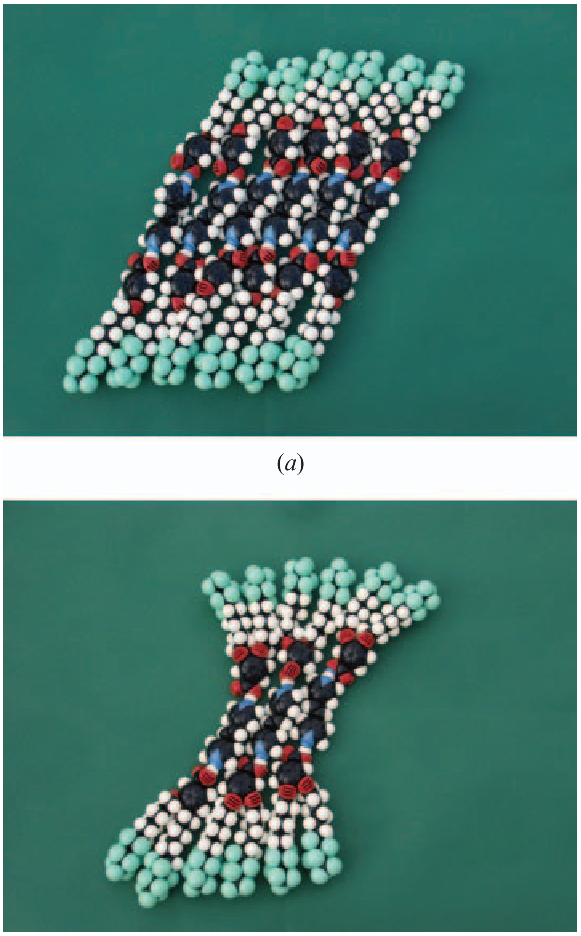


Figure 6. FTIR spectra: (*a*) the pure one-chain semiperfluorinated benzoic acid **1-[6,4]** at room temperature; (*b*) the 2:1 mixture **1-[6,4]/3** at 180°C within the SmC mesophase; (*c*) the same mixture at 220°C in the isotropic state.


(*a*)

(*b*)

Figure 7. CPK models of the 2:1 complexes of the dipyridylethylene **3** with the semiperfluorinated benzois acids **1** and **2** with parallel alignment of the elongated H-bonded central cores. Only more or less all-*trans* conformations of the aliphatic spacers are considered. (a) Tilted SmC phase of the mixed system with the single-chain benzoic acid **1-[6,4]**; (*b*) complex with the two-chain acid **2-[6,4]** with tilted arrangement of the rigid central cores.

non-curved tilted smectic C phases built up by a sequence of distinct H-bonded aromatic, aliphatic and fluoroalkyl sublayers. With increasing temperature the mobility of the flexible alkyl spacers increases. Both, the enhanced spacer mobility at elevated temperatures and the largely elongated rod-shaped central block, may contribute to a compensation for the different space fillings of the aromatic cores and the fluorinated fragments leading to the transition from the SmC phases to non-tilted smectic A mesophases, which is not observed for the pure acids **1**.

Thereby, association of the benzoic acids at the two termini of the dipyridylethylene **3** leads to a significant elongation of the polar rod-shaped central core. In this way, the intramolecular contrast between the rigid H-bonded calamitic cores and the semiperfluorinated alkyl chains is enhanced, resulting in an increase of the thermal stability of the mesophases, as is observed for common liquid crystals with an increasing number of covalently linked rings.

The number of (2:1) supermolecules **2-[6,4]/3** and **2-[4,6]/3**, respectively, within the oblique unit cell was calculated according to $n = V_{\text{cell}}/V_{\text{mol}}$. The volume of the unit cell (V_{cell}) was calculated by assuming a height of 0.45 nm [14, 18]. The molecular volume (V_{mol}) was obtained by using volume increments [19]. The calculations yielded a value of approximately three supermolecules per unit cell.

The linear pre-organization of the extended H-bonded polar cores of the complexes **2/3** should enable sufficiently strong attractive interactions to favour a parallel organization. Figure 7 (*b*) shows a possible arrangement of three supermolecules **2-[6,4]/3** with close and parallel packing of the rod-like cores. As evident from the CPK model, the cross-sectional area of the terminal semiperfluorinated chains significantly exceeds the cross-section of the H-bonded aromatic region. It seems rather unlikely that solely tilting of the molecules can sufficiently compensate for the resulting steric frustration. The smectic layers should break up into ribbon-like segments with curved interfaces due to the different space filling of the fluoroaliphatic and the polar aromatic regions. The ribbon-like aggregates organize to columnar mesophases on a two-dimensional oblique lattice. Further elongation of the semiperfluorinated chains, as realized with the mixed system **2-[6,6]/3**, further increases the difference in space filling of the incompatible micro-segregated closely packed H-bonded polar rods and the fluorinated parts of the molecules, leading to a structural change to a columnar phase with hexagonal 2D lattice symmetry. In a similar fashion, as result of high incompatibility between flexible, bulky and non-polar siloxane moieties and H-bonded polar aromatic mesogenic cores, supramolecular complexes formed by bipyridines and silylated carboxylic acids exhibit phase sequences involving smectic and cubic mesophases [20].

The phase sequence and structure of thermotropic mesophase morphologies found for the 2:1 binary mixtures of the one-chain and two-chain semiperfluorinated benzoic acids **1** and **2** with the dipyridyl **3** are shown schematically in figure 8. The phase sequence SmC–Col_{ob}–Col_{h} is the consequence of the onset and successive increase of the aromatic – fluoroaliphatic interface curvature, by increasing the volume fraction of the semiperfluorinated alkyl chains. The same diversity of different mesophases, i.e. Col_{ob} phases as intermediate between lamellar and hexagonal columnar mesophase morphologies depending on the volume fraction of pendant alkyl fragments, were previously found for polycatenar [21] and double swallow-tailed [22] compounds. The 2:1 associates presented here, can thus be regarded as semiperfluorinated H-bonded polcatenar mesogens that contain sufficiently shorter but more polar rigid cores compared with covalently linked benzoate analogues.

4. Conclusions

The mesophase formation of the binary mixed systems investigated is due to the segregation of the semiperfluorinated segments from the hydrogen bonded central cores. The increased mesophase stability of the complexes compared with the pure acids essentially results from an enlargement of the intramolecular contrast. The single hydrogen bonding motif between the pyridyl fragment and the carboxylic groups leads to a linear pre-organization of the central cores, which provides a parallel alignment of the cores independent of the number of fluorinated end chains. The cross-sectional areas of the incompatible polar H-bonded and fluorinated microsegregated regions largely determine the mesophase type. By adjusting the number of

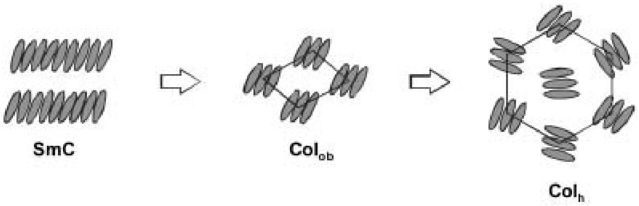


Figure 8. Development of the mesophase morphologies of the H-bonded complexes **1/3** and **2/3** with increasing volume fraction of the semiperfluorinated chains. The chains filling the space between the rigid aromatic aggregates are not shown. The SmA phases of the complexes **1/3** at more elevated temperatures are also not shown.

semiperfluorinated chains lamellar and columnar mesophases are found. The columnar phases should represent ribbon phases resulting from the collapse of the smectic layers. The systems can be regarded as a noncovalent approach towards block mesogens composed of three different and incompatible molecular segments.

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