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Molecular Design of Liquid-Crystalline Block Molecules: Semifluorinated Pentaerythritol Tetrabenzoates Exhibiting Lamellar, Columnar, and Cubic Mesophases**

Xiao Hong Cheng, Siegmar Diele, and
Carsten Tschierske*

The spontaneous formation of fluid supermolecular assemblies with well-defined morphologies (e.g. layers, interpenetrating networks, columns, and spheroids) is fundamental for structure formation in biological systems as well as for the tailoring of novel materials. Thus, the investigation of the driving forces of this self assembly process and the rational design of molecules which can form specific supermolecular structures on different length scales are contemporary research topics. Molecules, able to self assemble to these well-organized states of soft matter, can be divided into three classes: anisometric molecules (with a rod- or disclike shape), amphiphilic molecules (lipids/surfactants),[1] and block copolymers.[2] Applications for rodlike thermotropic liquid crystals include electrooptical devices, the lyotropic mesophases of surfactant/water systems can be utilized as templates for the preparation of mesoporous materials, and the ordered structures of block copolymers are, for example, applied in the preparation of ordered arrays of nanosized noble metal and semiconductor particles.

In low molecular weight systems, such as thermotropic liquid crystals, the molecular shape is a major design consideration to tailor the mesophase type. For example, calamitic molecules favor layers (smectic phases), disclike molecules organize to columns (columnar phases), and tapered or cone-shaped amphiphilic[3] or dendritic molecules[4] can form cylindrical or spheroidic aggregates which self assemble into columnar or micellar cubic mesophases. This contrasts with block copolymers, for which no specific molecular shape is necessary to produce a wide range of different morphologies. They can be obtained simply by changing the number and size of the incompatible polymer blocks.[2] The same diversity of different phases can also be found in lyotropic amphiphile/solvent systems with dependence on solvent content and temperature.[1]

The question arose if it would be possible to form different supermolecular structures, previously known from block copolymers and lyotropic systems, with low molecular weight molecules, specifically with molecules built up of different building blocks but without a specific anisometric shape or a pronounced amphiphilicity. Indeed, it was recently shown that star-shaped pentaerythritol tetrakis(3,4-dialkoxybenzoates), such as **2H** (Scheme 1)[5, 6] and related linear compounds,[5b,7]

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[*] Prof. C. Tschierske, X. H. Cheng
Institut für Organische Chemie der Universität
06120 Halle (Germany)
Fax: (+49) 345-5527030
E-mail: coqfx@mlucom6.urz.uni-halle.de

Dr. S. Diele
Institut für Physikalische Chemie der Universität
06118 Halle (Germany)

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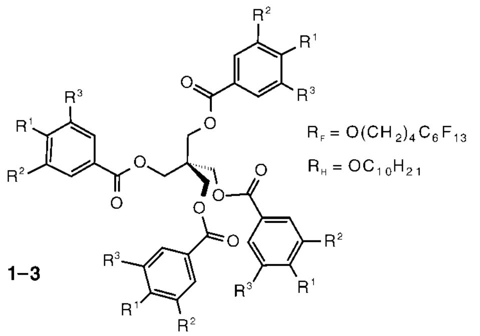

Scheme 1. Basic skeleton of all compounds. The **1** compounds have subsitutents at the R^1 postions only, **2** at R^1 and R^2, and **3** at all R^1–R^3 positions. Substituents are summarized in Table 1.

Table 1. Substituents, thermotropic phase transition temperatures, (T/°C) and corresponding enthalpy values (ΔH/kJ mol^{-1}, in square brackets) of compounds **1F**–**3F** and **1H**–**3H**.[5b]

Compound	R^1	R^2	R^3	Phase transitions[a]
1H	R_H	H	H	Cr 42 Iso
1F	R_F	H	H	Cr 59 [30.5] S_A88° [2.2] Iso
2H	R_H	R_H	H	Cr 54 (Col_{h2} 47°) Iso
2F[9]	R_F	R_F	H	Cr 88 [86.5] Col_{h2} 131° [5.6] Iso
3H	R_H	R_H	R_H	Cr 41(Col_{h2} 8°) Iso
3F	R_F	R_F	R_F	Cr 36 [46.6] Cub_{I2} 101°[b] [1.8] Iso

[a] Abbreviations: Cr = crystalline phase, Col_{h2} = inverted hexagonal columnar mesophase, Cub_{I2} = inverted micellar cubic mesophase, S_A = smectic A phase, Iso = isotropic liquid; values in brackets refer to monotropic (metastable) mesophases. [b] Refers to the heating scan, in the cooling cycle the phase transition occurs at 85 °C.

can form liquid crystalline phases. The occurrence of these phases was explained as a consequence of microsegregation of the more polar central benzoate units from the apolar alkyl chains.[5,7,8] However, while exclusively columnar mesophases have been realized with the pentaerythritol derivatives, attempts to change the mesophase structure by variation of the number of chains have so far failed. Thus, the columnar phase of **2H** was significantly destabilized on grafting additional alkyl chains (**2H**→**3H**) and it was completely lost on reduction of their number (**2H**→**1H**).[5b]

Because perfluorinated chains can stabilize mesophases,[9] we hoped that the analogous compounds **1F** and **3F**, with semifluorinated chains instead of the alkyl chains, could be mesogenic. Indeed, all three molecules **1F**–**3F** exhibit thermodynamically stable, enantiotropic liquid crystalline phases (see Table 1), but most importantly they have completely different mesophases.

By using optical microscopy between crossed polarizers, the formation of a birefringent fanlike texture was observed on cooling compound **1F**, with four semifluorinated chains, to 88 °C. Shearing gave a typical "oily streaks" optical texture with homeotropic regions, which indicates a mesophase with a layer structure (S_A). X-ray scattering has confirmed this phase assignment (one sharp reflex in the small angle region and a diffuse scattering in the wide angle region) with a layer periodicity of d = 3.2 nm. This periodicity is in agreement with these molecules arranged in layers consisting of alternating sublayers of the microsegregated semifluorinated chains and sublayers of the polar benzoate units.

As reported earlier, compound **2F** with eight semifluorinated chains has a hexagonal columnar mesophase (Col_{h2}, a_{hex} = 3.6 nm at T = 80 °C).[10] Here the polar regions form cylinders surrounded by the semifluorinated chains.

No birefringence was found on cooling **3F** which has twelve chains. However, a significant increase in viscosity was observed at 85 °C. Calorimetric measurements indicate a phase transition which occurs at 101 °C in the heating scan and at 85 °C in the cooling scan (scan rate 10 K min^{-1}). Obviously, the transition to this isotropic phase can be significantly supercooled and is typical for three-dimensional ordered mesophases. X-ray investigations of this highly viscous (plastic) isotropic phase indicated two independent sharp reflexes in the small angle region and a diffuse scattering in the wide angle region. This, together with the other observations (optical isotropy, viscosity, supercooling) confirm the existence of a cubic mesophase.

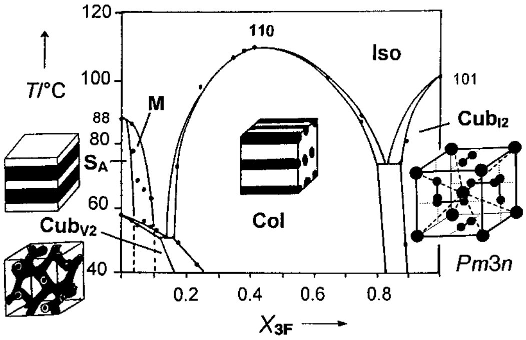

Figure 1. Phase diagram of the binary system **1F/3F** and schematic sketches of the mesophase; crystalline phases are not shown. Abbreviations: M = unknown birefringent mesophase; [14, 15] Cub_{V2} = inverted bicontinuous cubic mesophase; for the other abbreviations see Table 1. In the sketches of the mesophase structures the black regions represent the polar microsegregated regions. By example for a Cub_{V2} phase a Gyroid labyrinth is shown, but the actual structure could be different. The positions of the micelles in the *Pm*3*n* lattice of the Cub_{I2} phase are shown as dots (the size of the dots is not related to the micelle size) whereby two micelles of one type are located at the corners and in the center and six micelles of another type are located pairwise at the face bisectors of the cubes, it is possible that these micelles have a nonspherical shape.[3c, d, 4a, 13]

The cubic mesophase occurs in a phase sequence $S_A \rightarrow Col_{h2} \rightarrow Cub$ on increasing the number of semifluorinated chains and keeping the size of the polar central unit constant. Hence, the polar/apolar interface curvature becomes increasingly negative in the order described above and therefore the cubic 3D lattice of compound **3F** should be built up by discrete spheroidic entities containing the polar parts of the molecules surrounded by a continuum of the nonpolar chains (inverted micellar cubic phases, Cub_{I2}). In order to prove this hypothesis, we investigated binary mixtures of different concentration of compounds **1F** and **3F** by optical microscopy. The results are summarized in the phase diagram shown in Figure 1. The most important observation is that a broad region (X_{3F} = 0.15–0.85) of a columnar mesophase, built up from cylindrical aggregates, is induced between the smectic phase of compound **1F** (planar aggregates) and the cubic phase of **3F**. As the polar/apolar interface curvature is reduced on addition of **1F**, the aggregates forming the cubic phase must be more curved than the cylindrical aggregates in the induced columnar phase. This shows the cubic phase must comprise closed spheroidic aggregates, which additionally confirms the proposed inverted micellar structure of the cubic mesophase of **3F** (Cub_{I2} phase).

For such thermotropic Cub_{I2} phases, *Pm*3*n* lattices have been found almost exclusively.[3, 4, 11] Indeed, the relative positions of the small angle reflexes in the cubic phase of **3F** at $\Theta = 1.57°$ and $1.73°$ correspond to the most intensive reflexes found for other inverted micellar cubic mesophases of the *Pm*3*n* type.[3] Assuming such a *Pm*3*n* lattice, the reflexes can be indexed to 200 and 210, and a cubic lattice parameter $a_{cub} = 5.6$ nm calculated. The number of molecules per unit cell was calculated according to $n = a_{cub}^3 (N_A/M)\rho$ (N_A = Avogadro constant, M = molecular mass), assuming a density of $\rho = 1.4\ \mathrm{g\,cm^{-3}}$[12] to give around 28 molecules per unit cell.

Though the precise shape of the micelles in *Pm*3*n* phases is still under debate, it is now accepted that the unit cells contain eight discrete micellar aggregates of two different types (see Figure 1).[3c, d, 4a, 13] Two aggregates of one type are located at the corners and in the center of the unit cell, forming a body centered sublattice, and six aggregates of the other type are located pairwise at the face bisectors of the cubes. Hence, the 28 molecules should be shared among eight entities forming the unit cell of the *Pm*3*n* lattice, and therefore the cubic lattice should be built up of aggregates consisting of three to four **3F** molecules. The aggregates thus represent micelles built up by the assembly of molecules deformed, on average, to a conelike shape.

A closer inspection of the binary phase diagram (Figure 1) indicates in regions with a high concentration of **1F** ($X_{\mathbf{3F}}$ = 0.10–0.15) another optically isotropic region. Below a temperature of about 50 °C this isotropic phase is highly viscous and plastic, which again points to a cubic mesophase. As this phase occurs between a smectic and an inverted columnar phase it should be an inverted bicontinuous cubic phase consisting of interpenetrating networks of branched columns formed by the polar regions within the apolar continuum of the semifluorinated chains (Cub_{V2}).[14]

In regions of very low concentration of **3F** ($X_{\mathbf{3F}}$ = 0.05–0.10), close to conditions for the smectic phase, an additional birefringent mesophase (M) is induced. Shearing a sample of this mesophase shows bright, homogeneous regions by optical microscopy. We assume that this phase could probably be another intermediate phase with a two- or three-dimensional structure.[15]

These results show that a wide variety of completely different mesophases can be realized by the self assembly of pure samples or binary systems of molecules in which a starlike shape is provided by a tetrahedral central core. Because the flexibility of these molecules allows them to adopt different conformations the actual average conformation changes during the process of self assembly, whereby conformers which fit best with the geometry provided by the interfaces are favored. The interface geometry itself can simply be tailored by changing the space required by the incompatible units. This is a primary difference with classical thermotropic liquid crystals, and with the columnar and cubic mesophases formed by tapered- or cone-shaped amphiphiles and dendrons. For these molecules, the self assembly is facilitated by a complimentary shape provided by a special molecular architecture.[3, 4]

The increased mesophase stability of all fluorinated compounds **1F**–**3F** in comparison to the related alkyl compounds **1H**–**3H** should arise largely from an increased intramolecular polarity contrast on replacing alkyl chains by the semifluoroalkyl chains, which favors microsegregation. The larger cross-section[16] of the fluorinated alkyl chains should be responsible for the transition from a columnar to a micellar cubic phase upon replacing the alkyl chains of **3H** by semifluorinated chains. It should be pointed out that **3F** is the first fluorinated molecule which forms a thermotropic micellar cubic mesophase. Furthermore, the phase sequence $S_A \leftrightarrow (M) \leftrightarrow Cub_{V2} \leftrightarrow Col_{h2} \leftrightarrow Cub_{I2}$ represents the whole sequence of inverted, lyotropic phases of surfactant solvent systems, which is realized here for the first time in a binary systems of only two different low molecular weight block molecules in the absence of any solvent. This observation is of fundamental interest, because it shows that it is indeed possible to design all types of mesophases (smectic, columnar, bicontinuous cubic, and micellar cubic) without the classical concepts of rigidity/anisometry and amphiphilicity.[17] Additionally, these novel compounds represent an interesting borderline case between low molecular weight amphiphiles (surfactants, lipids) and block copolymers.

Experimental Section

For the synthesis of **1F** and **3F** the appropriately substituted benzoic acid (1.2 mmol), *N*-cyclohexyl-*N'*-(2-morpholinoethyl)carbodiimide methyl-*p*-toluene sulfonate (1.4 mmol, 0.61 g), and a catalytic amount of 4-dimethylaminopyridine (10 mg) were added to a suspension of pentaerythritol (0.3 mmol, 41 mg) in a 1:1 mixture of dry CH_2Cl_2 and Freon 113 (40 mL). The reaction mixture was stirred for 72 h at 20 °C and afterwards washed once with water. The aqueous phase was extracted with $CHCl_3$ (20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by preparative centrifugal thin layer chromatography (Chromatotron, Harrison Research) eluted with $CHCl_3$.

1F: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.74-2.25$ (m, 24 H, CH_2), 4.04 (t, ^3J(H,H) = 5.7 Hz, 8 H, OCH_2), 4.62 (s, 8 H, CCH_2), 6.83 (d, ^3J(H,H) = 8.9 Hz, 8 H, H_{ar}), 7.92 (d, ^3J(H,H) = 9.0 Hz, 8 H, H_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 18.14$ (CH_2), 29.46 (CH_2), 31.56 (t, ^2J(C,F) = 22.4 Hz, CH_2CF_2), 43.99 (quart. C), 64.41 (CH_2OCO), 68.39 (OCH_2), 115.24 (HC_{ar}), 123.08 (HC_{ar}), 132.87 (C_{ar}), 164.01 (C_{ar}), 166.94 (C=O); ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C, CF_3Ph): $\delta = -82.42$ (t, ^3J(F,F) = 9.1 Hz, 12 F, CF_3), −116.00 (t, ^3J(F,H) = 14.7 Hz, 8 F, CF_2CH_2), −123.52 (br s, 8 F, CF_2), −124.48 (br s, 8 F, CF_2), −125.14 (br s, 8 F, CF_2), −127.72 (br s, 8 F, CF_2); Elemental analysis for $C_{73}H_{56}F_{52}O_{12}$ (2113): calcd: C 41.49, H 2.67; found: C 41.40, H 2.92.

3F: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.7-2.3$ (m, 72 H, CH_2), 3.92–3.99 (m, 24 H, OCH_2), 4.64 (s, 8 H, CCH_2), 7.17 (s, 8 H, H_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 18.12$ (CH_2), 29.64 (CH_2), 30.57 (CH_2), 31.69 (t, ^2J(C,F) = 22.4 Hz, CH_2CF_2), 43.99 (quart. C), 65.00 (CH_2OOC), 69.44 (OCH_2), 109.11 (C_{ar}), 125.35 (C_{ar}), 143.57 (C_{ar}), 153.78 (CH_{ar}), 166.69 (C=O); ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C, CF_3Ph): $\delta = -82.73$ (br s, 36 F, CF_3), −116.38 (m, 24 F, CH_2CF_2), −123.78 (br s, 24 F, CF_2), −124.47 (br s, 24 F, CF_2), −125.31 (br s, 24 F, CF_2), −128.03 (br s, 24 F, CF_2); Elemental analysis for $C_{153}H_{112}F_{156}O_{20}$ (5234): calcd: C 35.11, H 2.16; found: C 34.91, H 2.23.

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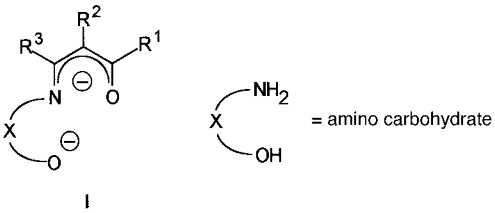
[17] Compounds **1H**–**3H** and **1F**–**3F** are also amphiphilic in a wider sense, because they are built up of two incompatible units, but in contrast to classical amphiphiles, the mesophases of compounds **1F**–**3F** could not be changed by the addition of protic solvents.

New Building Blocks for the Design of Oligonuclear Copper Complexes Based on Amino Carbohydrates[**]

Rainer Wegner, Michael Gottschaldt, Helmer Görls, Ernst-G. Jäger,[*] and Dieter Klemm[*]

Dedicated to Professor Dirk Walther
on the occasion of his 60th birthday

Next to iron, copper is the most important biological element for binding, transport, and activation of molecular oxygen. Copper-containing oxidases for the four-electron reduction of oxygen often display dinuclear (e.g. catechol oxidase)[1] or oligonuclear active centers (e.g. ascorbate oxidase).[2] The great biological importance of such copper complexes has induced intensive studies on oligonuclear model compounds.[3] Our concept for the design of oligonuclear complexes is to use structurally modified amino derivatives of carbohydrates instead of the proteins that are the "backbones" of the natural systems and to bind the metal through tridentate, anionic ligand structures of type **I**.



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[*] Prof. Dr. E.-G. Jäger, Dr. R. Wegner, Dr. H. Görls
Institut für Anorganische und Analytische Chemie der Universität
August-Bebel-Strasse 2, 07743 Jena (Germany)
Fax: (+49) 3641-948102
E-mail: cej@rz.uni-jena.de

Prof. Dr. D. Klemm, M. Gottschaldt
Institut für Organische und Makromolekulare Chemie der Universität
Humboldtstrasse 10, 07743 Jena (Germany)
Fax: (+49) 3641-948202
E-mail: c5koan@rz.uni-jena.de

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