End functionalised liquid crystalline bent-core molecules and first DAB derived dendrimers with banana shaped mesogenic units † ‡

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New series of non-symmetric bent-core compounds with a terminal carboxylic function as well as its benzyl esters and pentafluorophenyl esters have been synthesised. For most pentafluorophenylesters and for a benzylester with fluorine atoms in the ortho positions to the alkoxy chain different types of columnar ribbon phases (Col_rP_A and $Col_{ob}P_A$) and a polar smeetic SmCPA phase have been observed. Both the columnar and the smectic phases show antiferroelectric switching behaviour. Based on these functionalised banana-shaped molecules the first example of an amphiphilic bent-core molecule with a terminal 1-acylaminopropane-2,3-diol unit and DAB derived dendrimers of the first as well as the second generation have been synthesised and their physical properties have been investigated. Neither the diol-terminated bent-core molecule nor the dendrimers show any electrooptical response. Dendrimers with long aliphatic chains as well as the amphiphile form non-polar bilayer smectic phases, whereas dendrimers with shorter chains organise into a mesophase with a 2D lattice (Col). It seems that hydrogen bonding at the periphery of the bent-core units is unfavourable for the formation of polar smectic phases.

Introduction

Until recently, most liquid crystals have been designed to be either low molecular weight for display applications or high molecular weight for prototypical polymers.¹ Dendritic liquid crystals,^{2,3} on the other hand, combine the unique features of low molecular weight materials with those of polymers. Moreover, dendrimers exhibit a variety of physical properties that make them attractive for applications in different fields of science.⁴ They offer a very elegant and effective way of adding funtionalisation together with an unprecedented level of control of the precise nature and location of specific functionalities and overall molecular architectures.⁵

So far, a variety of mesogens have been connected to a dendrimeric matrix.² In most cases the mesogenic cores were fixed to the periphery of a dendrimer,^{6,7} but also some reports have appeared where mesogenic units are incorporated into the dendrimer core⁸ or into a hyperbranched polymer architecture.⁹ There are very few reports concerning liquid crystalline (LC) dendrimeric materials in which mesogenic groups are laterally attached to a dendrimeric core,⁷ and a relatively large group of materials in which a dendrimeric core is connected with mesogens via one of their terminal positions.⁶ Also a first

report about dendrimers with disc-like mesogenic units has recently been presented.¹⁰ Though there are few reports about bent-core units incorporated in polymer structures,¹¹ according to the best of our knowledge, there is only one work concerning attachment of banana-shaped molecules to a dendritic core, more precisely to a first generation carbosilane core.12

Bent-core molecules are of prime interest in contemporary liquid crystal research, due to their special properties provided by the distinct molecular shape.^{13,14} The fascinating features of these materials are the occurrence of a polar order within the layers and the appearance of different types of structural chirality in these systems composed of configurationally nonchiral molecules.^{15,16} The polar order, which is a consequence of the restricted rotation of these molecules due to their bent shape, gives rise to interesting application properties of such materials, e.g. as ferroelectric^{16,17} or antiferroelectric¹⁵ switching materials which can be used for display devices,¹⁸ highly efficient switchable NLO materials¹⁹ and as components for optical wave guides. The occurrence of chirality in these systems is of fundamental scientific interest, especially as it has recently been found that this chirality can be switched in external electric fields.²⁰ Another interesting feature concerns the modulation of the mesophase structure by the formation of ribbon-like aggregates or undulated layers, which organise into different columnar and modulated smectic phases (SmC̃ phases, B1 phases and B7 subtypes).^{21,20c} This modulation of the smectic layers can be due to an escape from a macroscopic polarisation, due to splay modulation²² or due to steric reasons as a result of the different space filling of distinct molecular parts.^{20c} Hence, it was decided to investigate novel supermolecular systems containing banana-shaped units joined to a

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[#] Electronic supplementary information (ESI) available: Procedures and analytical data, tables with X-ray data, 2D diffraction pattern of I-Pfp16, and DSC traces of 1-Pfp14. See http://www.rsc.org/suppdata/ jm/b4/b415910a/

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Fig. 1 Cartoon of a dendrimer with terminally attached bent-core units and possible organisation of this dendrimer within a smectic phase.

DAB core *via* a terminal carboxylic function. Fig. 1 shows a cartoon of the general structure of the target systems; the structures of the unsymmetrical bent-core molecules used for the synthesis of the dendrimers are shown in Fig. 2.

This paper is divided into two parts. The first part is devoted to the synthesis and the physical properties of new series of unsymmetrical banana-shaped molecules, which will be attached in the further step to the dendritic system. As is shown in Fig. 2, these new banana-shaped compounds consist of five aromatic rings. The bent 3,4'-biphenyldiol core^{23,11d} is connected with two different aromatic branches. One of them carries an alkoxy chain with either 12, 14 or 16 carbon atoms. Most important from the further functionalisation point of view, these monomeric molecules contain a free carboxylic end-group ($R^4 = H$). This kind of compound is relatively easy to convert in further steps, for example, into ester or amide derivatives to design new supermolecular architectures incorporating bent-core mesogenic units. The bent-core unit was additionally modified by introduction of lateral fluorine substituents positioned at the peripheral benzene rings (R_1, R_2) and $R_3 = H$ or F), because such substituents are known to influence the mesomorphic properties of bent-core molecules significantly.^{17c,24} The length of the spacer unit which connects the bent aromatic core with the terminal carboxyl group was altered as well, whereby C_4 (m = 3) or C_{10} (m = 9) alkyleneoxy spacers have been chosen.

Having the monomers prepared, these building blocks could be used to finally obtain the dendrimer compounds. The second part of this report concerns the synthesis and physical properties of DAB dendrimers of the first and the second generation and also of an amphiphilic, diol-terminated, bent-core molecule.



Fig. 2 The general structure of unsymmetrical banana-shaped compounds, where: m = 9 (series I), m = 3 (series II); n = 12, 14 or 16; \mathbb{R}^1 , \mathbb{R}^2 , $\mathbb{R}^3 = \mathbb{H}$ or F (series IF); $\mathbb{R}^4 = \mathbb{B}z$ (benzyl), H (free carboxylic acid) or Pfp (pentafluorophenyl).

The designation of the compounds is as follows: The endfunctionalized bent-core molecules are grouped into two classes (I and II) depending on the spacer length. Additional F substituents at the rigid core are indicated by an additional letter F (*e.g.* IF). The functional end group is indicated by a letter code ($\mathbf{H} = \text{COOH}$, $\mathbf{Bz} = \text{benzylester}$, $\mathbf{Pfp} = \text{penta$ $fluorophenyl ester}$) and this is followed by a number indicating the length of the terminal chain (12, 14, 16). The dendrimers are described by the generation number as a roman number, followed by the length of the terminal chains (*e.g.* 1-12).

Synthesis

The general synthetic procedure to get the COOH terminated bent-core compounds and their pentafluorophenyl esters is outlined in Scheme 1. 4'-Benzyloxy-3-biphenylol (**A**) and the 4-benzoyloxybenzoic acids (**B**) were obtained according to methods described elsewhere.^{16,23b} Esterification of **A** with **B** using DCC/DMAP, followed by hydrogenolytic debenzylation gave the intermediates C^{16a} which were used for the etherification with the functionalised benzoic acids **D** (for the synthesis, see the electronic supplementary information (ESI)[‡]) to yield the benzyl esters **I-Bz***n*, **IF-Bz***n* and **II-Bz***n*. Hydrogenolysis of these benzyl esters lead to the carboxylic acids **I-H***n*, **IF-H***n* and **II-H***n*, which were used for the preparation of the corresponding pentafluorophenyl esters **I-Pfp***n*, **IF-Pfp***n* and **II-Pfp***n* using DCC in the presence of the acylation catalyst DMAP as condensation agent.

The way to get the dendrimeric compounds of the first and the second generation is outlined in Scheme 2. The final compound **1-16** was obtained *via* condensation reaction of the DAB dendrimer of the first generation with the pentafluorophenyl ester derivative **I-Pfp16**.^{6c} The second generation



I-Pfpn, IF-Pfpn, II-Pfpn

Scheme 1 Synthesis of the unsymmetrical banana-shaped compounds $(R^1-R^3 = H, F; m = 3, 9; n = 12, 14, 16).$



Scheme 2 Synthesis of the first and second generation DAB dendrimers 1-16 and 2-16 with peripheral bent-core mesogenic units. The synthesis of the dendrimers 1-12 and 2-12 with shorter end chains (n = 12) and spacers (m = 3) was done in the same way as described for 1-16.

dendrimer was achieved by coupling of the carboxylic acid **I-H16** to the DAB-(8) dendrimer in the presence of diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)-phosphate as a condensing agent.²⁵ A 1.1 molar excess amount of either **I-Pfp16** or **I-H16** for every primary amino end group present in the dendrimer was used. The synthesis of the dendrimers **1-12** and **2-12** with shorter alkyl chains and shorter spacer units was done using the same method as for the synthesis of **1-16**

(pentafluorophenylester method^{6c}). The syntheses of the end functionalised bent-core molecules **I-Bz16**, **I-H16** and **I-Pfp16** as well as the dendrimers **1-16** and **2-16** are described in the experimental section. The other experimental procedures and analytical data are collated in the ESI.[‡]

Results and discussion

The bent shaped precursors are reported first, followed by the dendrimers. Some of the bent shaped building blocks show liquid crystalline properties, which are in most cases mono-tropic (metastable). Therefore, in Tables 1–4 the transition temperatures are given for the cooling process and the melting points obtained in the first heating (mp) are also provided in Tables 1–3.

Banana-shaped compounds with terminal carboxylic groups

Series I. In the compounds of series I, a decamethyleneoxy spacer separates the bent aromatic core and the carboxylic group (11-substituted derivatives of the undecanoic acid). Three groups of compounds have been obtained in this series: either with 14 or 16 carbon atoms in the terminal alkoxy group and without fluoro substituent (\mathbf{R}^1 , $\mathbf{R}^3 = \mathbf{H}$). The third group consists of compounds with 14 carbon atoms in the alkoxy chain and with one fluorine atom in the ortho position to this terminal alkoxy chain (see Table 1). To check the influence of shortening the spacer length for the compounds of series II the length of the oxyalkylene spacer was reduced to four carbon atoms (5-substituted derivatives of pentanoic acid, see Table 2). For the obtained compounds polarised light optical microscopic (POM) investigation, as well as differential scanning calorimetric (DSC) measurements have been performed. The transition temperatures and associated enthalpy values are shown in Tables 1 and 2.

The benzyl ester (**Bz**) compounds in all three series do not reveal liquid crystalline phases. The carboxylic acids **I-H14** and **I-H16** have much higher melting temperatures than their benzyl ester analogues. The samples can be slightly supercooled and

| | | R⁴O () | | 5 ⁻ ~ | OC _n H _{2n+1} | | |
|---------------------------|----------------|-------------------|-------------------------------|-------------------|--|--|--|
| Comp. | \mathbb{R}^1 | R^4 | п | mp | Phase transitions | | |
| I-Bz14 | Н | Bz | 14 | 98 | Iso 67 [70.9] Cr | | |
| I-H14 | Н | Н | 14 | 127 | Iso 120 [46.6] M ₁ 91 [41.3] Cr ₂ | | |
| I-Pfp14 | Н | C_6F_5 | 14 | 88 | Iso 76 [13.1] Col _r P _A 59 [0.9] Col _{ob} P _A 50 [17.9] Cr | | |
| I-Bz16 | Н | Bz | 16 | 100 | Iso 74 [83.4] Cr | | |
| I-H16 | Н | Н | 16 | 126 | Iso 122 [44.0] M ₁ 94 [41.5] Cr | | |
| I-Pfp16 | Н | C_6F_5 | 16 | 80 | Iso 83 [13.9] Col _{ob} P _A 59 [30.5] Cr | | |
| IF-Bz14 | F | Bz | 14 | 91 | Iso 71 [17.2] Cr ₁ 60 [51.8] Cr ₂ | | |
| IF-H14 | F | Н | 14 | 126 | Iso 120 [43.9] M ₂ 65 [11.5] Cr | | |
| IF-Pfp14 | F | C_6F_5 | 14 | 92 | Iso 82 [14.4] ColrP _A 61 [12.6] M 41 [10.9] Cr | | |
| ^a Abbreviation | s. Iso = isotr | pric liquid: Col. | $\mathbf{P}_{i} = antiferred$ | selectric switchi | ng polar oblique columnar mesonhase: Col P. = antiferroelectric | | |

Table 1 Melting points ($T/^{\circ}C$, first heating), phase transition temperatures ($T/^{\circ}C$), and, in parentheses, their enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$) given for the second scan of cooling (DSC, 10 K min⁻¹) for compounds of series I ($R^3 = H$)^{*a*}

^{*a*} Abbreviations: Iso = isotropic liquid; $Col_{ob}P_A$ = antiferroelectric switching polar oblique columnar mesophase; Col_rP_A = antiferroelectric switching polar rectangular columnar mesophase; M, M₁, M₂ = not identified mesophase; Cr = crystalline solid.

Table 2 Melting points $(T/^{\circ}C)$, first heating), phase transition temperatures $(T/^{\circ}C)$, and, in parentheses, their enthalpy values $(\Delta H/kJ \text{ mol}^{-1})$ given for the second scan of cooling (DSC, 10 K min⁻¹) for compounds of series \mathbf{II}^{a}



Table 3 Melting points ($TI^{\circ}C$, first heating), phase transition temperatures ($TI^{\circ}C$), and, in parentheses, their enthalpy values ($\Delta H/kJ \text{ mol}^{-1}$) given for the second scan of cooling (DSC, 10 K min⁻¹) for fluorine substituted compounds of series I



Table 4 Phase transition temperatures $(T/^{\circ}C)$, and, in parenthesis, their enthalpy values $(\Delta H/kJ \text{ mol}^{-1})$ given for the second scan of cooling (DSC, 10 K min⁻¹) for the synthesised dendrimers.

| Comp. | G | n | т | Phase transitions |
|-------|--------|----|---|---|
| 1-12 | First | 12 | 3 | Iso 151 [25.5] Col _r 104 [5.0] Cr |
| 1-16 | First | 16 | 9 | Iso 144 [32.5] Sm 113 [41.0] Cr |
| 2-12 | Second | 12 | 3 | Iso 162 [12.2] Col _r 120 [29.3] Cr |
| 2-16 | Second | 16 | 9 | Iso 149 [24.0] Sm 122 [105.0] Cr |

upon cooling a crystallisation can be seen, but the apparently crystalline material is still soft and it is possible to shear these samples. This (soft crystalline) mesophase is assigned as M_1 . The carboxylic acid **IF-H14**, which has one lateral fluoro substituent at the rigid core, exhibits a monotropic liquid crystalline phase (M_2). However, due to rapid crystallisation it was not possible to investigate any of these carboxylic acids in more detail.

The most interesting liquid crystalline properties reveal the pentafluorophenylester (**Pfp**) derivatives **I-Pfp14**, **I-Pfp16**, and **IF-Pfp14**. For compound **I-Pfp14** two monotropic mesophases were detected (DSC traces are shown in Fig. S2 of the ESI[‡]). The phase transition is clearly visible during POM studies as the texture drastically changes. The mesophase formed at the

transition from the isotropic liquid is of rather low viscosity and appears with the typical texture as shown in Fig. 3a. The lower temperature phase exhibits well-developed spherulites (Fig. 3b,c). In the circular domains the extinction brushes are inclined by $+\theta$ and $-\theta$ from the direction of the polarisers, indicating a tilted arrangement with a tilt angle of about $\theta \sim 18^{\circ}$. The textures of both mesophases are characteristic for some variants of columnar ribbon phases of bent-core molecules. The material shows antiferroelectric switching under an applied electric field, as demonstrated in Fig. 4. At the transition from the isotropic liquid into the high temperature mesophase, two well-separated peaks per half period of the applied triangular wave voltage arise and the texture shown in Fig. 3d develops. Decreasing the temperature leads to the development of two new peaks between the peaks of the high temperature phase. Upon further decreasing the temperature the two peaks of the high temperature phase disappear and only the two new peaks remain. The value of the spontaneous polarisation increases from 45 nC cm⁻² in the high temperature phase to $P_{\rm S} = 450 \text{ nC cm}^{-2}$ in the low temperature phase. The textural features and the switching behaviour of this material are very similar to phases of some bent-core molecules investigated by Szydlowska et al.^{21b} These two phases were denoted as B1rev phase (non-tilted, high temperature phase) and B1rev, tilted phase (low temperature phase; tilted analogue of B_{1rev}), and are made up by broken layers (ribbons), in which the 2D density modulations are in the plane perpendicular to the spontaneous polarisation vectors. Thus, it was considered that in the case of I-Pfp14 the same phases occur, *i.e.*, the upper phase is an orthogonal B_{1rev} mesophase and the lower one is a $B_{1rev, tilted}$ version with a tilted organisation of the molecules. It should be pointed out that the structure of columnar phases with a polarisation direction along the columns cannot be adequately described by the 17 plane groups, because, due to the polar direction, the



Fig. 3 Optical textures (crossed polarisers) of compound **I-Pfp14**: (a) Col_rP_A phase at 76 °C, (b) phase transition between Col_rP_A and Col_{ob}P_A at 58 °C, (c) Col_{ob}P_A phase at 57 °C), (d) Col_rP_A phase at 76 °C. Pictures (a–c) were taken upon cooling from the isotropic liquid without applying an electric field, and (d) after applying an electric field (60 $V_{pp} \mu m^{-1}$). The arrows indicate the positions of polariser and analyser.



Fig. 4 Spontaneous polarisation measurements for compound **I-Pfp14** in the Col_{ob}P_A phase at 58 °C (B) and in Col_rP_A phase at 75 °C (A). The current response in one half period of the triangular wave voltage is shown. Changing of value of P_S as well as the position of the peaks confirms the existence of two different phases. The occurrence of two current peaks within one half period of the applied triangular wave voltage indicates an antiferroelectric switching process in both phases.

upper and the lower ends of the columns become different. Therefore, it was suggested^{21c} to use the 80 layer groups instead.²⁶ However, as shown in the ESI‡ (Fig. S3), there are different ways to organise the polar columns in an antiferroelectric manner within a rectangular or an oblique lattice and these correspond to different settings in the layer groups number 46 (pmmn, orthorhombic/rectangular) and number 7 (p112/a, monoclinic/oblique). Because the precise organisation within the columns is not completely clear, and hence an unique assignment to a specific set of lattice parameters is not possible, the more general descriptions Col_rP_A and Col_{ob}P_A are used here for the assignment of polar columnar phases with a polarisation direction perpendicular to the 2D lattice. Hence, the B_{1rev} phase is assigned as Col_rP_A, whereas the B_{1rev,tilted} phase is assigned as ColobPA. Models showing the arrangement of the molecules in these columnar mesophases are shown in Fig. 5b,c.

For compound I-Pfp16, which has a terminal hexadecyloxy chain, only one liquid crystalline phase was detected. During cooling from the isotropic phase the characteristic texture of a columnar phase grows (similar to the texture shown in Fig. 3c). All these features are very similar to those of the low temperature phase of I-Pfp14 (which is a ColobPA phase). The X-ray diffraction pattern of an aligned sample of this mesophase (see Fig. S1 of the ESI[‡]) can be indexed on the basis of an oblique lattice (see Fig. 5c) and the lattice parameters for the plane group p2, neglecting the polarisation directions are a = 4.2 nm, b = 2.35 nm and $\gamma = 95^{\circ}$ ($T = 80^{\circ}$ C, see also Table S1 in ESI[‡]). The angle between the preferred direction of the outer scattering (caused by the lateral molecular arrangement within the ribbons) and the 10-reflection indicates a 46° tilt of the molecules with respect to the normal to the *b*-axis, *i.e.* to the normal to the broken layers. The parameter *a* is in rather good agreement with the total molecular length of **I-Pfp16** $(d_{10}/L = 4.2 \text{ nm}/6.1 \text{ nm} = 0.69 = \cos 46^\circ$, L = 6.1 nm in a 120° bent V-shaped conformation with all trans alkyl chains). The unit cell volume was calculated



Fig. 5 Models of some columnar banana phases. (a) Model for nonswitchable Colr phases (B1 phase) as suggested for short chain bentcore molecules, here the 2D lattice is in the plane of the polarisation vectors (corresponding to the bend direction), the molecules are nontilted. (b) Col_rP_A phase (compound I-Pfp14, high temperature phase), here the 2D-lattice is perpendicular to the plane of the polarisation vectors, the molecules are non-tilted; the 2D lattice is rectangular. (c) The Col_{ob}P_A phase (compound I-Pfp14, low temperature phase, compound I-Pfp16) is related to the Col_rP_A phase, but the molecules are additionally tilted, resulting in an oblique type lattice. Only one of the three possible models, differing in the polarisation direction in adjacent ribbons is shown, all three structures are compared in Fig. S3 in the ESI[‡]. Only the aromatic bent-core units are shown. The space between the ribbons is filled by the conformationally disordered terminal chains. The polarisation directions are indicated by dots (out of the plane) and crosses (into the plane).

according to $V_{\text{cell}} = ab(\sin \gamma)h_{\text{eff}} = 5.1 \text{ nm}^3$ with a height $h_{\text{eff}} = 0.52 \text{ nm}.^{27}$ Using the volume increments of Immirzi and Perini²⁸ the volume of a molecule was calculated to $V_{\text{mol}} = 1.47 \text{ nm}^3$, and from these values, according to $n = V_{\text{cell}}/V_{\text{mol}}$, a number of about 3–4 molecules (n = 3.5) in the cross section of each ribbon is calculated. This columnar phase, similarly to those described above, responds to the electric field. Two current peaks indicate an antiferroelectric switching with a spontaneous polarisation value of about 500 nC cm⁻², hence this phase is designated as Col_{ob}P_A.

The third material in this group of compounds, **IF-Pfp14**, has a tetradecyloxy terminal chain as **I-Pfp14**, but it possesses a fluorine atom in the *ortho* position to this alkoxy chain. In the POM studies lancet-like textures (see Fig. 6a) with some circular domains were observed, where the extinction brushes are parallel to the direction of polariser and analyser (see Fig. 6b). This texture is very similar to that of the high temperature phase of **I-Pfp14**, suggesting that this mesophase is also a columnar phase. The position of the extinction crosses parallel to polariser and analyser points to a non-tilted molecular alignment in the ribbons. Applying a triangular



Fig. 6 The textures (crossed polarisers) of the columnar phase of compound **IF-Pfp14** taken at 80 °C (a) cooled from the isotropic phase, (b) circular domain with extinction brushes parallel to the polarisers, (c) after applying an electric field, (d) under d.c. electric field (30 V μ m⁻¹); note the pronounced change of birefringence. The arrows indicate the positions of polariser and analyser.

voltage to the sample does not cause any brush movement, however, two current peaks per half period of the applied a.c. voltage are visible. The switching process is accompanied by pronounced changes of the birefringence (Fig. 6c,d). This points to a switching process by rotation around the molecular long axis, as seen in the SmAP_A phases^{29,24b} and in some columnar type banana phases.^{21b,d,20b,c} The antiferroelectricity of the phase is additionally confirmed by the low value of the static dielectric constant. Only a weak ($\Delta \epsilon \sim 5$) high-frequency mode (above 10 kHz), most probably related to the collective rotation around the long molecular axis, is observed, as seen in Fig. 7. From all these investigations it can be concluded that the mesophase of **IF-Pfp14** is the same as the high temperature phase of **I-Pfp14** (Col_rP_A), *i.e.* the introduction of the fluoro substituent suppresses the tilted Col_{ob}P_A phase.

Series II: influence of shortening of the spacer unit

In the series II the alkyl chain carrying the carboxylic function was shortened to five carbon atoms. The transition temperatures as well as the enthalpy values for these materials are shown in Table 2. Similar to the analogous compound I-Bz14, the benzyl ester derivatives II-Bz14 and II-Bz12 do not exhibit mesogenic properties. The difference for the corresponding free acids and the pentafluorophenylester derivatives is not so significant, considering both the melting and clearing temperatures. However, a slight decrease of the melting temperature and a small increase of the clearing temperature for compounds II-H14 and II-Pfp14 in comparison with compounds I-H14 and I-Pfp14, respectively, was observed. The most important difference in the mesomorphic behaviour reveals the pair of pentafluorophenyl ester derivatives I-Pfp14 and II-Pfp14. Whereas the homologue I-Pfp14 with long spacer shows two columnar phases (see above), its counterpart with the short spacer exhibits a SmCPA phase, as indicated by the very typical texture. This means that on reducing the



Fig. 7 3-D frequency-temperature dependence of the real (top) and imaginary (bottom) parts of the dielectric constant for compound **IF-Pfp14**.

spacer length a transition from polar columnar phases $(Col_r P_A, Col_{ob} P_A)$ to a polar smectic phase (non-modulated layers, SmCP_A) takes place. In the microscopic studies, upon cooling from the isotropic state under an applied d.c. field of 10 V μm^{-1} the characteristic circular domains can be grown. The extinction brushes are directed along the polariser directions, indicating an anticlinic molecular organisation. Moreover, the birefringence of the textures obtained in a thin glass cell, estimated from the tabulated interference colours of a quartz wedge, was $\Delta n = 0.06$. This can suggest that the molecules are aligned with their banana planes on the glass surface. Application of a low frequency a.c. electric field influences the texture. For some small domains a brush rotation appears (see Fig. 8). Removing the field pushes the brushes immediately back to their initial orientation, which is an indication of an antiferroelectric switching process taking place by a collective rotation of the molecules around a tilt cone. This behaviour could reflect the molecular switching from an anticlinic-antiferroelectric (SmC_AP_A) to



Fig. 8 Changes of the extinction brush direction of the domains of the SmCP_A phase of **II-Pfp14** in a 5 μ m ITO cell under an electric field (± 200 V) at 79 °C.

synclinic-ferroelectric (SmC_SP_F) arrangement, *i.e.* the homogeneous chiral state seems to be the preferred organisation of **II-Pfp14** under the given experimental conditions.

In contrast to **II-Pfp14** the homologous compound **II-Pfp12** with shorter terminal alkyl chain shows no liquid crystalline phase.

Influence of the number and position of lateral fluorine atoms

To evaluate the role of fluorine atoms on the properties of the investigated system, additionally to **IF-Bz14**, three compounds with lateral fluoro substituents have been synthesised (see Table 3). To compare the properties of the fluorinated compounds the benzyl ester derivatives with tetradecyloxy terminal chains were chosen. The fluorine atoms are either attached in *ortho* position to the alkoxy terminal chain (one or two fluorine atoms) and/or one fluorine atom is connected in *ortho* position to the spacer chain. Only one of these derivatives, compound **IFa-Bz14**, exhibits a liquid crystalline phase. In the microscopic study, upon cooling from the isotropic liquid the growing of a texture characteristic for columnar mesophases is observed, as shown in Fig. 9. However, due to its monotropic character more detailed measurements were impossible (therefore it is assigned as Col_x).

Banana-shaped amphiphile III: the influence of hydrogen bonding

Because of the end functionalisation, the monomeric bananashaped materials described here are attractive on their own. Particularly, the pentafluorophenylester derivatives exhibit interesting liquid crystalline behaviour, possibly due to the bulky pentafluorophenyl end groups, located at the interlayer interfaces (and inter-ribbon interfaces). The engineering of the interlayer interfaces seems to be an important tool to modify the mesophase structures of bent-core molecules.³⁰ Branched end chains,^{17a,b,f} as well as bulky oligosiloxane¹⁶ or



Fig. 9 The textures (crossed polarisers) of compound IFa-Bz14 at 73 $^{\circ}$ C (a, b) during the growing process and (c) as a fully developed texture (different region).

carbosilane³¹ end groups, for example, lead to a transition from the antiferroelectric switching behaviour, which is usually observed for the tilted smectic phases of banana molecules (SmCP_A-phases) to a ferroelectric switching.¹⁶ For such compounds a strong decoupling of the smectic layers driven by microsegregation of the branched units is discussed to be mainly responsible for the stabilisation of the macroscopic polar ferroelectric states.¹⁶

The free COOH groups, capable of hydrogen bonding, seem to be not advantageous for the formation of mesophases in the case of bent-core molecules. All synthesised compounds with terminal COOH groups show rather high melting points and only highly ordered (soft crystalline) mesophases (M₁, M₂) were observed. Compound III (Fig. 10), which was obtained from the pentafluorophenylester I-Pfp16 and 1-amino-2,3propandiol has a hydrogen bonding 1-acylaminopropane-2,3diol group at its end. Textural investigations of the mesophase of III indicate small focal conic defects, surrounded by dark areas. Shearing leads to a birefringent texture, similar to that shown in Fig. 11b. When the material III was used as dopant for a SmC* matrix, it did not induce an antiferroelectric SmC_A* phase, as proven with other bent-core materials.³² Furthermore, the phase is not switchable under an applied electric field. The X-ray diffraction pattern (Guinier method, powder pattern) showed layer reflections from second up to the sixth order (first order reflection is hidden by the beam stop; for details, see Table S2 in ESI[‡]), indicating a layer structure with quite sharp interlayer interfaces. This is possibly due to the mesophase stabilising effect of the diol unit by intermolecular hydrogen bonding and due to the fact that these polar end groups can segregate into distinct sublayers.³³ The layer distance is d = 9.2 nm. This amounts to about 1.5 times the molecular length (L = 6.1 nm in a 120° bent V-shaped conformation with all *trans* alkyl chains), indicating a bilayer structure in which the molecules III adopt an antiparallel end to end packing. The formation of a bilayer structure is in accordance with the suggested segregation of the



Fig. 10 Compound III, the phase transition temperatures $(T^{\circ}C)$ and their enthalpy values $(\Delta H/kJ \text{ mol}^{-1})$ on cooling are: Iso 155 [47.4 kJ mol⁻¹] Sm 96 [42.0 kJ mol⁻¹] Cr. The melting point in the first heating is at 156 °C.



Fig. 11 Textures (crossed polarisers) of the first generation dendrimer 1-16 at: (a) 118 $^{\circ}$ C, (b) 108 $^{\circ}$ C, after shearing.

polar 1-acylaminopropane-2,3-diol groups from the aliphatic and aromatic molecular segments. However, because no aligned samples could be obtained, it is not completely clear if the molecules are tilted within the smectic layers or not (hence this mesophase is designated as Sm). In addition, this compound is not stable, because the diol groups give rise to a transesterification reaction with the ester groups within the mesogenic core at higher temperatures and especially upon applying an electric field. Therefore additional compounds of this type were not synthesised.

Dendrimeric compounds

Though the mesomorphic properties of some of the fluorinated derivatives were quite promising, non-substituted derivatives have been chosen for further functionalisation to get dendrimeric materials, because these unsubstituted bent-core derivatives are available in larger quantities due to the much shorter synthetic routes. The dendrimeric compounds 1-16 and 2-16 were obtained as shown in Scheme 2. The dendrimers 1-12 and 2-12 were synthesised using the same method as for 1-16. The structures of the final dendrimeric compounds were characterised by ¹H, ¹³C NMR by elemental analysis, as well as by MALDI-TOF mass spectrometry. For 1-12 and 2-12 ESI-MS was used in addition. The MALDI-TOF mass spectrum of compound 1-16 (see Fig. 12), for example, shows one signal that is clearly due to the formation of the desired dendrimer with four banana-shaped units. The m/z value (4086.9 - 22.9 = 4064.0) corresponds to the calculated value of 4086.9 (molecular mass + Na⁺). The results for the other dendrimers are listed in the experimental part and the ESI[‡]. However, attempts to prepare the third and fourth generation dendrimers 3-12 and 4-12 using one of the methods mentioned above leads to an incomplete functionalisation of the dendrimeric core and hence no sufficiently pure products could be obtained.

The transition temperatures of the dendrimers are recorded in Table 4. Generally, the clearing temperatures of the dendrimers are significantly higher than those of the corresponding bent-core precursors (acids, benzyl esters and pentafluorophenyl esters). Furthermore, there is only partial and very slow crystallisation upon cooling. Therefore, defined melting temperatures cannot be given, but all mesophases are enantiotropic. For dendrimer **1-16** a non-specific, grainy texture was observed upon cooling from the isotropic liquid, which might represent a not well developed fan texture of a smectic phase (see Fig. 11a). Though it was possible to shear the sample between glass plates (see Fig. 11b), the viscosity of



Fig. 12 MALDI-TOF spectrum of 1-16 CH₂Cl₂ solvent, HABA matrix.

the material was too high to fill the cells for electrooptical measurements. In the small angle region, the X-ray diffraction pattern of a non-oriented sample of 1-16 (Guinier pattern) showed three reflections corresponding to the second, third and fourth order reflections of a layer periodicity, corresponding to a distance d = 9.1 nm (first order reflection is hidden by the beam stop, for details, see Table S2 in ESI[‡]). Remarkably, this distance is nearly the same as found for the mesophase of the amphiphilic compound III. In the wide angle region a diffuse scattering was found, confirming the liquid crystalline character of this mesophase. If a layer structure is assumed, the measured layer thickness d is smaller than the molecular dimension of the complete dendrimer ($L_{den} = 12.2$ nm, defined by the molecular diagonal of the whole dendrimer, as estimated by molecular modelling, ChemDraw 3D), but about 1.5 times as large as the bent mesogenic units $(L_{\rm mes} = 6.1 \text{ nm in a } 120^{\circ} \text{ bent V-shaped conformation with all}$ trans alkyl chains). This can be explained by a layer structure where the dendritic parts and the terminal alkyl chains are segregated into distinct sublayers, similar as suggested for the amphiphilic compound III. Folding of the alkyl chains and the dendrimeric part should be responsible for the reduction of the layer distance ($d/L_{\rm den} \approx 0.75$), but as in the case of III, a tilted organisation of the molecules cannot be completely excluded. The textures of the second generation dendrimer 2-16 are similar to those seen for compound 1-16. The viscosity of the liquid crystalline phase is slightly lower in comparison with the first generation dendrimer, and in this case it was possible to fill the measurement cells by means of capillary forces. However, the electrooptical measurements for these dendrimers show no response to the applied electric field up to an applied voltage of 400 V in a 5 µm cell.

The dendrimers 1-12 and 2-12 with shorter alkyl chains and spacer units show textures (see Fig. 13) which are different from those of the dendrimers 1-16 and 2-16. These textures are more similar to those observed for non-switchable Col_r phases (see models shown in Fig. 5a,b). The powder X-ray diffraction pattern of 2-12 (see Table S3 in the ESI[‡]) is characterised by six sharp Bragg reflections in the small angle region and a diffuse scattering in the wide angle region. The



Fig. 13 Texture (crossed polarisers) of the first generation dendrimer **1-12** as it grows upon cooling from the isotropic liquid (dark areas) at 151 °C.

small angle reflections exclude a simple layer structure and can be indexed on the basis of a rectangular lattice with the parameter 7.4 nm and 5.6 nm (Col_r). Attempts to get aligned samples with **1-12** or **2-12** were not successful and therefore a more precise assignment of the phase structure was not possible. Both dendrimers show no response to an applied electric field up to an applied voltage of 400 V in a 5 μ m cell.

Conclusions

To conclude, three new series of monomeric banana-shaped compounds have been synthesised and their physical properties have been investigated. Most of the benzyl protected acid derivatives exhibit exclusively crystalline phases, whereas most pentafluorophenylester derivatives exhibit monotropic banana phases. For the compounds with long spacer units (I-Pfp14, I-Pfp16 and IF-Pfp14) two different antiferroelectric switchable columnar phases (Col_rP_A and Col_{ob}P_A) have been identified, whereas for the counterpart with shorter spacers an antiferroelectric SmCPA phase (SmCAPA) has been observed. Reduction of the alkyl chain length to C_{12} leads to a complete loss of the liquid crystalline properties. These end functionalised bent-core molecules represent valuable starting materials for the further functionalisation, leading to supermolecular LC materials. Preliminary attempts in this direction have been made. One bent-core molecule with a polar diol group at one terminus was synthesised, which shows a non-switchable smectic phase with bilayer structure. Four dendrimeric compounds with DAB cores of the first and the second generations and bent-core molecules at the periphery have also been synthesised. All dendrimers exhibit rather high viscosities, which is unfavourable for detailed investigation of these materials. Maybe the viscosity is due to a reduced flexibility of the central dendrimeric cores because of the presence of the amide groups (linking groups between the dendrimer cores and the bent mesogenic units), which introduce hydrogen bonding interactions. For none of the synthesised dendrimers a switching process could be found. From these investigations it can be concluded that the amphiphilic molecule III as well as the two dendrimers 1-16 and 2-16 behave quite similarly, showing non-polar smectic phases with bilayer structures. The dendrimers **1-12** and **2-12** with shorter aliphatic segments form modulated smectic phases (rectangular columnar ribbon phases Col_r). Also these mesophases are non-switchable. It seems that hydrogen bonding at the periphery of bent-core molecules is unfavourable for the formation of polar smectic phases with bent-core molecules.³⁴

Experimental

General

The mesophase identification was based on microscopic examination of the textures formed by samples between two glass plates. A Nikon Optiphot-2-Pol polarising microscope equipped with a Mettler FP82HT hot stage was used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements performed with a Perkin-Elmer DSC-7 apparatus at the cooling rate of 10 K min⁻¹. The changes of textures under electric field, spontaneous polarisation and dielectric dispersion were studied in glass cells with ITO electrodes, 5 µm thick, supplied by Linkam. The dielectric dispersion studies were performed with a Solartron SI 1260 Impedance Analyser in the frequency range 10 Hz-10 MHz. Spontaneous electric polarisation was measured using the switching current method under triangular wave voltage. Tilt angle was estimated as an angle between the directions that give extinctions of light that propagates through the planar cell placed between crossed polarises. Molecular dimensions were estimated by molecular modelling (ChemDraw 3D) or by CPK models. The X-ray investigations on non-oriented samples were carried out in capillary tubes (diameter: 1 mm) using a Guinier film camera (HUBER Diffraktionstechnik, Germany). X-Ray patterns of the partially oriented sample (drop on a glass plate, surface aligned at the sample-air interface) of I-Pfp16 were taken by a 2D-detector HI-Star (Siemens, Germany).

Solvents were purified and rigorously dried over appropriate drying agents and distilled prior to use. All atmospheresensitive reactions were carried out under dry argon using standard Schlenk techniques. DAB dendrimers (ALDRICH) were used as received.

In order to confirm the molecular structure of the synthesised compounds the following analytical methods were applied. ¹H NMR spectra were recorded on a spectrometer operating at 400 (Varian Gemini 2000) or 500 (Varian Inova) MHz, whereas ¹³C spectra were recorded at 100 and 125 MHz. As the internal standard the signals of the residual protonated species of the deuterated solvent were used. Chemical shifts are given in ppm. Analytical TLC was performed on silica gel, F-254 precoated silica gel glass or aluminium plates (Merck). Visualisation was accomplished with UV light and/or using iodine vapour. Column chromatography was carried out either at atmospheric pressure or under flash conditions using silica gel (230-400 mesh, Merck). Silica gel 60 PF254 (with gypsum, Merck) was used for centrifugal force mediated preparative thin layer chromatography in conjunction with a Chromatotron from Harrison Research Europe (Muttenz). Composition of the synthesised compounds, determined by elemental analysis performed on CHNS elemental analyser (Leco & Co), confirmed expected molecular structures.

General procedures for the synthesis of the benzylesters, carboxylic acids and the pentafluorophenylesters are given together with the analytical data for the hexadecylsubstituted derivatives. The synthesis of the dendrimers **1-16** and **2-16** and their analytical data are also given here, whereas the analytical data of all other molecules are collected in the ESI \ddagger . Abbreviations: DCC: *N*,*N'*-dicyclohexylcarbodiimide; DMAP: 4-(dimethylamino)pyridine; NMP: *N*-methylpyrrolidone; TEA: triethylamin.

Synthetic procedures and analytical data

Benzylesters. The appropriate carboxylic acid (5.0 mmol), phenol (5.0 mmol) and DMAP (0.1 mmol) were dissolved in dry CH₂Cl₂ (50 ml). The reaction mixture was cooled down to 0 °C and DCC (5.5 mmol) dissolved in dry CH₂Cl₂ (10 ml) was slowly added. After adding the last portion of DCC the cooling bath was removed and the mixture was stirred at room temperature for 2-5 days. The precipitated solid was removed by filtration, and the solvent was evaporated. The crude product was purified by sequential column chromatography or centrifugal thin layer chromatography on a Chromatotron with CH₂Cl₂ and CH₂Cl₂-MeOH mixtures (up to 10%) MeOH), followed by repeated crystallisation from methanol and hexane. Yield was between 80 and 95%. I-Bz16: ¹H NMR $(\delta \text{ ppm, CDCl}_3): 0.87 \text{ (t, 3H, CH}_3, J = 7.0 \text{ Hz}): 1.25-1.34 \text{ (m,}$ 34H, CH₂); 1.45–1.47 (m, 4H, CH₂); 1.57–1.69 (m, 2H, CH₂); 1.79-1.83 (m, 4H, CH₂); 2.34 (t, 2H, OOCCH₂, J = 7.6 Hz); 4.03 (t, 2H, OCH₂, J = 6.5 Hz); 4.04 (t, 2H, OCH₂, J = 6.8 Hz); 5.10 (s, 2H, OCH₂Bzl); 6.96 (dd, 2H, Ar-H, $J_1 = 9.0$ Hz, $J_2 = 4.8$ Hz); 6.97 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 5.2$ Hz); 7.18–7.23 (m, 1H, Ar–H); 7.28 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 5.2$ Hz); 7.32–7.35 (m, 5H, Ar–H); 7.37 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz); 7.44 (bs, 1H, Ar–H); 7.49 (d, 2H, Ar-H, J = 5.2 Hz); 7.64 (dd, 2H, Ar-H, J₁ = 8.8 Hz, $J_2 = 4.8$ Hz); 8.14 (dd, 4H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz); 8.29 (dd, 2H, Ar–H, J_1 = 8.4 Hz, J_2 = 4.4 Hz); ¹³C NMR (δ ppm, CDCl₃): 14.12, 22.71, 24.97, 26.00, 29.12, 29.22, 29.33, 29.36, 29.37, 29.46, 29.57, 29.60, 29.67, 29.71, 31.94, 34.35, 66.05, 68.33, 68.42, 114.31, 114.42, 120.38, 120.50, 120.98, 121.49, 122.06, 122.13, 124.63, 126.86, 128.10, 128.18, 128.48, 129.78, 131.78, 132.26, 132.37, 136.14, 137.71, 142.12, 150.84, 151.30, 155.40, 163.54, 163.79, 164.23, 164.40, 164.83, 173.55; Elemental analysis: Calcd. for C₆₇H₇₈O₁₀: C 77.42, H 7.18%; Found: C 77.38, H 7.15%.

Carboxylic acids. The appropriate benzyl ester (5.0 mmol) was dissolved in THF (50 ml). The solution was flashed with nitrogen and 200 mg of Pd/C (10% Merck) was added. After flushing with hydrogen the hydrogenation was carried out at 2 atm. with shaking (Parr hydrogenation apparatus) for 4 h. Then the solution was filtered, THF evaporated under reduced pressure and the crude product was purified by column chromatography (eluent CH₂Cl₂/10% MeOH). The repeated crystallisation from methanol gave the desired products with yields of 80 to 90%. **I-H16**: ¹H NMR (δ ppm, CDCl₃): 0.87 (t, 3H, CH₃, J = 7.0 Hz); 1.26–1.36 (m, 34H, CH₂); 1.44–1.48 (m,

4H, CH₂); 1.63 (quintet, 2H, CH₂, J = 7.5 Hz); 1.78–1.84 (m, 4H, CH₂); 2.34 (t, 2H, OOCCH₂, J = 7.5 Hz); 4.03 (t, 2H, OCH₂, J = 6.5 Hz); 4.04 (t, 2H, OCH₂, J = 6.5 Hz); 6.96 (dd, 2H, Ar-H, $J_1 = 9.0$ Hz, $J_2 = 5.0$ Hz); 6.97 (dd, 2H, Ar-H, $J_1 = 9.0$ Hz, $J_2 = 5.0$ Hz); 7.20–7.22 (m, 1H, Ar–H); 7.28 (dd, 2H, Ar–H, $J_1 = 8.5$ Hz, $J_2 = 4.5$ Hz); 7.37 (dd, 2H, Ar–H, $J_1 = 8.5$ Hz, $J_2 = 4.5$ Hz); 7.44 (bs, 1H, Ar–H); 7.49 (d, 2H, Ar–H, J = 5.0 Hz); 7.63 (dd, 2H, Ar–H, $J_1 = 8.5$ Hz, $J_2 = 4.5$ Hz); 8.14 (dd, 4H, Ar–H, $J_1 = 9.0$ Hz, $J_2 = 5.0$ Hz); 8.29 (dd, 2H, Ar–H, $J_1 = 9.0$ Hz, $J_2 = 4.5$ Hz); ¹³C NMR (δ ppm, CDCl₃): 14.05, 22.67, 24.71, 25.97, 25.99, 29.04, 29.12, 29.18, 29.30, 29.31, 29.34, 29.44, 29.55, 29.58, 29.65, 29.67, 29.68, 31.92, 33.65, 68.38, 68.47, 114.40, 114.51, 120.43, 120.54, 121.12, 121.64, 122.10, 122.17, 124.66, 126.97, 128.23, 129.82, 131.83, 132.32, 132.43, 137.81, 142.23, 150.98, 151.49, 155.53, 163.65, 163.91, 164.30, 164.46, 164.89, 177.71; Elemental analysis: Calcd. for C₆₀H₇₄O₁₀: C 75.44, H 7.81%; Found: C 75.38, H 7.48%.

Pentafluorophenylesters. The appropriate carboxylic acid (5.0 mmol), pentafluorophenol (5.0 mmol) and DMAP (0.1 mmol) were dissolved in dry CH₂Cl₂ (50 ml). The reaction mixture was cooled down to 0 °C and DCC (5.5 mmol) dissolved in dry CH₂Cl₂ (10 ml) was slowly added. After adding the last portion of DCC the cooling bath was removed and the mixture was stirred at room temperature for 2-5 days. The precipitated solid was removed by filtration, and the solvent was evaporated. The crude product was purified by centrifugal thin layer chromatography on a Chromatotron (eluent CH₂Cl₂), followed by repeated crystallisation from isopropanol and hexane. Yield was between 80 and 95%. **I-Pfp16** ¹H NMR (δ ppm, CDCl₃): 0.87 (t, 3H, CH₃, J = 6.8 Hz); 1.20-1.52 (m, 38H, CH₂); 1.73-1.85 (m, 6H, CH₂); 2.65 (t, 2H, OOCC H_2 , J = 7.6 Hz); 4.04 (t, 2H, OCH₂, J = 6.4 Hz); 4.04 (t, 2H, OCH₂, J = 6.6 Hz); 6.96 (d, 2H, Ar–H, J = 8.8 Hz); 6.97 (d, 2H, Ar–H, J = 9.2 Hz); 7.21 (td, 1H, Ar–H, $J_1 = 4.6$ Hz, $J_2=2$ Hz); 7.27 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz); 7.37 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz); 7.44 (bs, 1H, Ar–H); 7.49 (d, 2H, Ar–H, J =5.2 Hz); 7.64 (dd, 2H, Ar–H, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz); 8.14 $(dd, 4H, Ar-H, J_1 = 8.8 Hz, J_2 = 4.8 Hz); 8.29 (dd, 2H, Ar-H, J_1 = 8.8 Hz); 8.29 (dd, 2H, Ar-H, J_2 = 4.8 Hz); 8.29$ $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz); ¹³C NMR (δ ppm, CDCl₃): 14.15, 22.74, 24.81, 26.03, 28.87, 29.14, 29.34, 29.40, 29.46, 29.60, 29.63, 29.70, 29.74, 31.97, 33.39, 68.33, 68.43, 114.31, 114.42, 120.39, 120.50, 120.99, 121.52, 122.07, 122.12, 124.64, 126.85, 128.19, 129.78, 131.78, 132.26, 132.37, 137.72, 142.12, 150.83, 151.30, 155.39, 163.51, 164.23, 164.39, 164.81; Elemental analysis: Calcd. for C₆₆H₇₃F₅O₁₀: C 70.70, H 6.56%; Found: С 70.67, Н 6.93%.

Dendrimer of the first generation 1-16. To a solution of BAB-(4) dendrimer (54 mg, 0.17 mmol), TEA (5 ml) in dichloromethane (10 ml) the pentafluorophenylester **I-Pfp16** (841 mg, 0.75 mmol) in CH₂Cl₂ (5 ml) was added. The solution was stirred at room temperature for 7 days. After that the reaction mixture was washed with water (\times 2), aqueous sodium hydroxide, water (\times 2), and finally with brine. Crystallisation from MeOH–EtOH–CHCl₃ (10 : 9 : 1), isopropanol and sequential chromatographic separations (CH₂Cl₂) followed by crystallisation from methanol gave a colourless solid with yield 40%. ¹H NMR (δ ppm, CDCl₃): 0.87 (t, 12H, CH₃, J = 6.8 Hz); 1.20-1.47 (m, 154H, CH2); 1.59-1.62 (m, 16H, CH2); 1.76-1.84 (m, 18H, CH₂); 2.15 (t, 8H, NHOCCH₂, J = 7.6 Hz); 2.34 (bs, 4H, NCH₂); 2.39 (t, 8H, NCH₂, $J_1 = 6.4$ Hz); 3.27 (td, 8H, NHC H_2 , $J_1 = 6.4$ Hz, $J_2 = 6.4$ Hz); 4.01 (t, 8H, OCH₂, J = 6.8 Hz); 4.03 (t, 8H, OCH₂, J = 6.8 Hz); 6.46 (t, 4H, NH, J = 5.6 Hz); 6.96 (d, 16H, Ar–H, J = 8.8 Hz); 7.18–7.21 (m, 4H, Ar-H); 7.26 (d, 8H, Ar-H, J = 8.8 Hz); 7.36 (d, 8H, Ar-H, J = 8.8 Hz); 7.43 (bs, 4H, Ar-H); 7.48 (d, 8H, Ar-H, J = 4.8 Hz); 7.62 (d, 8H, Ar–H, J = 8.8 Hz); 8.12 (d, 8H, Ar-H, J = 8.8 Hz); 8.14 (d, 8H, Ar-H, J = 8.8 Hz); 8.28 (d, 8H, Ar–H, J = 8.4 Hz); ¹³C NMR (δ ppm, CDCl₃): 14.14, 22.73, 25.91, 26.02, 27.15, 29.14, 29.39, 29.47, 29.51, 29.59, 29.62, 29.68, 29.72, 31.95, 36.84, 38.20, 51.97, 53.88, 68.33, 68.41, 106.32, 114.29, 114.39, 120.34, 120.48, 120.96, 121.46, 122.04, 122.10, 124.60, 126.83, 128.15, 129.76, 131.74, 132.23, 132.34, 137.68, 142.06, 150.79, 151.27, 155.36, 163.48, 163.75, 164.19, 164.35, 164.77, 173.18; MALDI-TOF MS: molecular weight calc. for $C_{256}H_{328}N_6O_{36}$: m/z: 4086.9 [M + Na]⁺; found: m/z: 4086.9 [M + Na]⁺; Elemental Analysis: Calcd. for C₂₅₆H₃₂₈N₆O₃₆: C 75.63, H 8.13, N 2.07%; Found: C 74.32, H 7.83, N 2.10%.

Dendrimer of the second generation 2-16. To a solution of the acid I-H16 (653 mg, 683 mmol), condensing agent 5 (300 mg, 776 mmol), TEA (69 mg, 683 mmol) in NMP (10 ml) was added a solution of BAB-(8) (60 mg, 78 mmol) in NMP (2 ml). The solution was stirred in room temperature for 7 days, and then poured into 5% aqueous sodium hydrogen carbonate. The precipitate was filtered out, washed with water and dried. Crystallisation from methanol, column chromatography (silica gel, CH_2Cl_2) followed by crystallisation from methanol gave a slightly yellow solid with yield 40%. ¹H NMR (δ ppm, CDCl₃): 0.81 (t, 24H, CH₃, J = 6.8 Hz); 1.20–1.43 (m, 886H, CH₂); 1.20-1.43 (m, 24H, CH₂); 1.54-1.64 (bs, 16, CH₂); 1.70-1.78 (m, 52H, CH₂); 2.10 (bs, 16H, OOCCH₂); 2.33–2.36 (bs, 40H, NCH₂); 3.36 (bs, 16H, NHCH₂); 4.01 (t, 16H, OCH₂, J =6.8MHz); 4.03 (t, 16H, OCH₂, J = 6.8MHz); 6.96 (d, 16H, Ar–H, J = 8.8 Hz); 6.98 (d, 16H, Ar–H, J = 8.8 Hz); 7.18–7.21 (m, 16H, NH, Ar–H); 7.25 (d, 16H, Ar–H, J = 8.8 Hz); 7.37 (d, 16H, Ar-H, J = 8.8 Hz); 7.41 (bs, 8H, Ar-H); 7.47 (d, 16H, J)Ar-H, J = 4.8 Hz); 7.60 (d, 16H, Ar-H, J = 8.8 Hz); 8.11 (d, 16H, Ar-H, J = 8.8 Hz); 8.12 (d, 16H, Ar-H, J = 8.8 Hz); 8.27 (d, 16H, Ar–H, J = 8.4 Hz); ¹³C NMR (δ ppm, CDCl₃): 14.35, 22.93, 26.22, 29.34, 29.60, 29.73, 29.83, 29.90, 29.92, 29.93, 32.16, 38.12, 51.58, 52.24, 54.32, 68.56, 68.64, 114.57, 114.67, 120.63, 120.80, 121.21, 121.72, 122.36, 122.42, 124.91, 127.10, 128.46, 130.09, 132.55, 132.66, 137.98, 142.35, 151.09, 151.58, 155.68, 163.82, 164.09, 164.55, 164.72, 165.14; MALDI-TOF MS: molecular weight calc. for C₅₂₀H₆₇₂N₁₄O₇₂: *m/z*: 8294.1 $[M + Na]^+$; found: m/z: 8294.1 $[M + Na]^+$; Elemental Analysis: Calcd. for C₅₂₀H₆₇₂N₁₄O₇₂: C 75.51, H 8.19, N 2.37%; Found: C 75.16, H 8.15, N 2.60%.

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