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Liquid Crystalline Octopus: An Alternative Class of Mesomorphic Dendrimers

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ABSTRACT: The synthesis and the mesomorphic properties of a new series of liquid crystalline dendrimers, referred thereafter as to *octopus dendrimers* owing to their eight sidearms, are reported. In these dendritic systems, the arborescence is constituted of mesogenic segments and aliphatic spacers, and as such they differ quite substantially from the classical end-functionalized dendrimers whose dentritic core is more flexible. Such a molecular design was adopted in order for the internal mesogenic segments—constituting the skeleton of the dendrimer—to participate at every level of the molecular organization within the mesophases. The dendritic branches, prepared by a mixed convergent/divergent method, were attached to a tetrapodant central core to yield second generation dendrimers via amido linkage. X-ray diffraction studies showed that the acidic dendron precursors and the final dendrimers exhibit a hexagonal columnar mesophase, whose mesophase stability was found to depend on the number and position of the terminal alkoxy chains. The high density of aliphatic chains imposes curved interfaces at all hierarchical levels of the dendrimers, i.e., between the pro-mesogenic units, the aliphatic spacers, and the terminal chains, forcing the molecules to adopt a wedgelike conformation, promoting the self-assembling toward a supramolecular columnar organization. Because of their original molecular structure, the internal columnar "hard" core of the columns is compatible with an onion-type structure, i.e., made up of successive, concentric crowns occupied by aromatic and aliphatic constituents, as deduced from the analysis of the X-ray diffraction data.

Introduction

The development of new supramolecular architectures with specific properties is a fundamental aspect of the research in the field of molecular-based materials. Of particular interest is the combination of precise functionalities incorporated within large and well-defined structures. Dendritic molecules or dendrimers are one type of such new and interesting macromolecules or oligomers that have been found suitable to overcome the drawbacks of linear polymers.[1] One of their main originalities with respect to other high-molecular-weight compounds is that they possess a perfectly controlled, branched structure, a consequence of their layer-wise construction. Dendrimers are either built outward or inward a highly functional core species by an iterative synthesis consisting of successive and specific elementary steps. Such sequential convergent and divergent modes of construction lead to an almost total control of the ultimate molecular architecture. Indeed, these synthetic methodologies provide a high degree of control of the molecular size and shape as well as the definite number of functional moieties in precise locations. In principle, these dendrimers are obtained with narrow molecular weight distributions and without chain entanglements.[1]

The combination of mesomorphic properties and dendritic structures is a new approach in the field of liquid crystals. The interest in the construction of such multifunctional, practically monodisperse, macromolecular objects arises from their ability to self-assemble into mesophases and from their potential utilization as photonic, electronic, and ionic transport based-applications, depending on the functionality sought.[1] Moreover, owing to their branched nature, liquid crystal dendrimers possess properties halfway between those of polymers and of single monomeric species. The viscosity is generally found to be lower than in polymers, and they still possess important features characteristic of polymers such as mesophase stabilization and good processing. The first examples of reported mesomorphic dendrimers were the so-called hyperbranched dendritic polymers, obtained solely by random polymerization of AB_m-type anisotropic monomers having two different functional groups ($m \geq 2$, $A \neq B$).[2] Because of their statistical mode of construction, these interesting polymers are characterized by a high degree of branching (without any cross-link) and are usually polydisperse; i.e., the number of branches and thus the total number of mesogenic moieties are not controlled.[3] Only a few representatives of such hyperbranched liquid crystals have been so far synthesized, with the mesogenic units as branching points[2,4] and/or as end groups.[5] Nowadays, the field of monodisperse liquid crystal dendrimers has properly expanded as evidenced by the development of many new structures found compatible with the formation of various mesophases including shape-persistent,[6] supramolecular,[7] and end-group dendrimers.[8−13]

Synthetic chemists of liquid crystalline dendrimers have mainly concentrated their effort on the study of the side-group systems,[8−13] as schematically represented in Figure 1a—they can be described as side-chain dendrimers by analogy to side-chain polymers. Such side-chain dendrimers possess a nonmesogenic, flexible core with a globular nature, to the terminal branches of which the various mesogens or pro-mesogenic units are connected. The most commonly used

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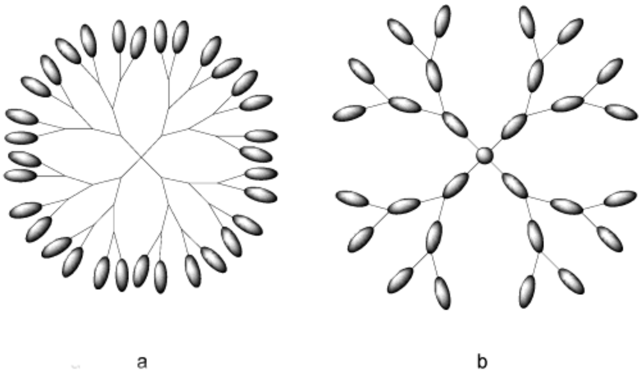


Figure 1. Schematic 2D representation of (a) side-chain and (b) main-chain liquid crystalline dendrimer.

dendritic cores are polypropyleneimines (DAB),[8] polyamidoamines (PAMAM),[9] polysiloxanes,[10] and polycarbosilanes.[11] Induction of liquid crystalline properties was achieved either by grafting classical calamitic mesogens such as alkylcyanobiphenyl, cholesteryl, or phenyl benzoate derivatives or by connecting nonmesogenic groups such as perfluoroalkyl chains[12] or polyalkylated benzoate moieties.[13] In general, the choice of the chemical structure of the terminal units grafted at the periphery of the macromolecules appeared crucial to determine the nature of the mesomorphism of the entire compound, the treelike scaffolding being constrained into a limited number of conformations. In the former examples, smectic phases were observed as for the monomeric parents, while columnar phases were induced for the polyalkoxy benzoate systems. These latter examples also prove the importance of microphase separation in stabilizing or inducing mesomorphism since perfluoroalkyl and polyalkoxy benzoates are not mesomorphic themselves. The chemical incompatibility between the flexible dendritic core and the functionalized terminal groups leads to AB-block structures[14] and enhances microphase separation at a molecular level and helps to stabilize further smectic and/or columnar supramolecular arrangements.[15] The mesophase stability therefore depends on the degree of amphiphilicity and on the core conformation (enthalpy/entropy balance) as well as on the judicious choice of the mesogenic units.

Regarding the dendrimers studied here, the branching points are no longer single atoms (C, N, Si) but consist of rigid and anisotropic molecular moieties instead, these units being linked together through long and flexible alkyl spacers (Figure 1b). Large anisotropic groups are now present at every level of the dendritic hierarchy, and the dendrimers will be forced to adopt constrained and regular structures. As such, the anisometric branches will not radiate isotropically as in side-chain dendrimers, but on the contrary will preferentially favor an anisotropic order by a gain in the enthalpy of the system in order to produce the most stable structure. Consequently, complementary or/and cooperative effects such as the amplification of the properties are expected to occur. Such main-chain dendrimers may represent an interesting alternative for the development of original molecular materials having a new architecture (Figure 1b) and maybe new ways to self-organize into mesophases. As far as we are aware, the most closely related compounds being previously reported are the so-called *willow* dendrimers synthesized by Percec et al. some years ago; these systems exhibited nematic and smectic phases.[16] Shibaev also foresaw the elaboration of such compounds but has not yet reported on their synthesis and physical properties.[17]

In this paper, the design and synthetic methodology of novel dendrimers are reported together with their complete analytical characterization. Such second generation dendrimers have been named *octopus* dendrimers owing to their eight sidearms. Their thermal behavior and the unequivocal assignment of the mesophases are described, and a model accounting for the molecular organization of these octopus dendrimers into the columnar phases is discussed.

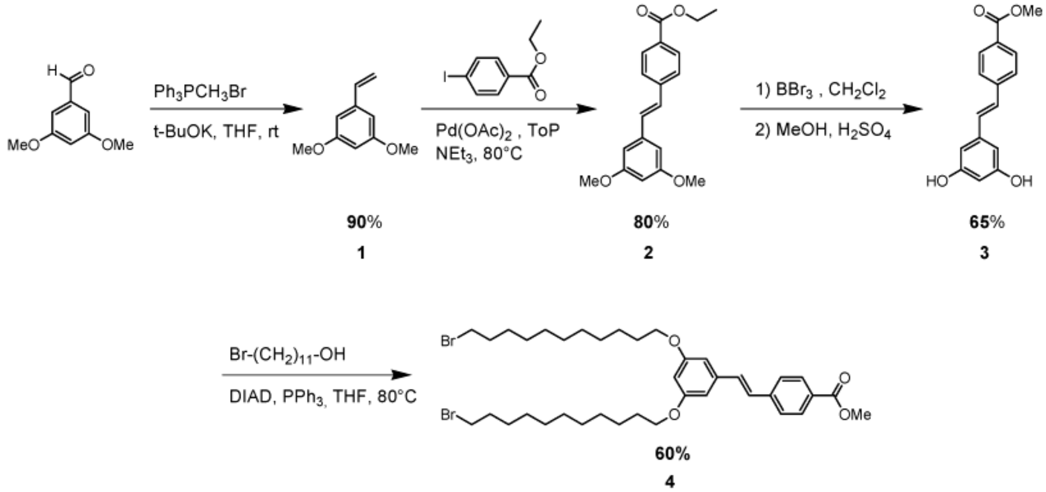
Synthetic Methodology

Conventional end-group dendrimers, where the core matrix is either a PAMAM, DAB, or carbosilane, are usually built up using a divergent approach, that is, constructed outward a central core, and the mesogenic moieties are attached to the periphery at the final stage of the synthesis. For the presently described dendrimers, this approach appeared unsatisfactory as a number of additional steps were required prior to synthesizing the mesogenic moiety at each generation, before moving up to the next generation, with the consequent diminishing overall reaction yields hampered by reactivity and purification problems. Therefore, to improve the reactivity of the connecting sites and to facilitate the purification of the dendritic materials, a mixed convergent/divergent synthesis was elaborated for the preparation of these dendrimers (Schemes 1−3). The constitutive parts of the stilbenic branches, **4** and **7**, were prepared separately (Schemes 1 and 2) and assembled selectively together in the next stage of the procedure (Scheme 3). These acidic building blocks were then coupled to a small tetra-podand core unit, functionalized by four amino groups, to yield the final dendrimers (Scheme 3). The anisotropic unit selected was a stilbene-based moiety, due to both its thermal stability and the versatility of its chemistry. Such a poorly mesogenic segment,[18] despite its anisotropy and rigidity, was also chosen in order to test whether mesomorphism could be induced solely by the dendrimerization process. Recall that another family of rather different stilbene-containing dendrimers, the so-called stilbenoid shape-persistent dendrimers, has been reported by Meier and Lehmann[6c−e] to show mesomorphism.

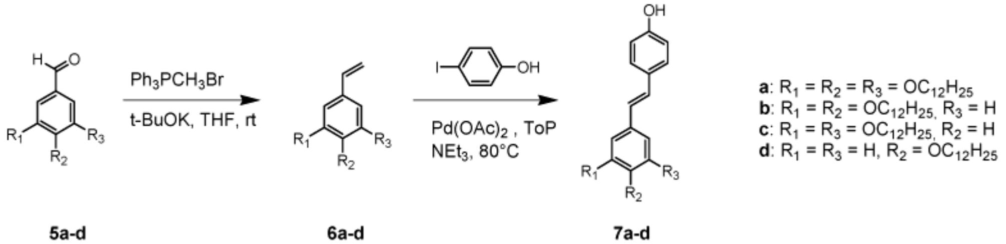
Both the internal and terminal constitutive parts of the dendritic branches were prepared using standard chemical reactions, starting from the commercially available 3,5-dimethoxybenzaldehyde for the internal branch and 4-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 3,5-dihydroxybenzyl alcohol, and 3,4,5-trihydroxymethyl benzoate for the construction of the peripheral mesogenic units.

The internal branching unit, **4**, was prepared in several steps as shown in Scheme 1. The starting material, 3,5-dimethoxy benzaldehyde, was quantitatively converted into the corresponding styrene compound (**1**) by a Wittig reaction. The coupling of this styrene derivative with the appropriate ethyl 4-iodobenzoate via a palladium-catalyzed Heck reaction then produced the dimethoxystilbene ester derivative, **2**, in good yields. The dihydroxy compound **3** was obtained in two successive steps including first the demethylation with BBr_3, immediately followed by the in-situ reesterification of the acid function since the ester group

Scheme 1. Preparation of the Internal Branching Unit 4



Scheme 2. Preparation of the Terminal Groups 7a−d



did not survive the demethylation. Finally, bromoundecanol was grafted to the free hydroxy groups of **3** by a Mitsunobu etherification to yield the prefunctionalized internal core moiety, **4**.

The various mono-, di-, and trialkoxystilbenoid-like moieties, **7a−d**, were all prepared by identical synthetic sequences, including the prior quantitative conversion of the appropriate alkoxy-substituted benzaldehydes (**5a−d**) into the corresponding styrenes (**6a−d**), followed in a second step by the coupling with iodophenol by a palladium-catalyzed Heck reaction (Scheme 2). The overall reaction yields were dependent on the substitution pattern.

The esters, precursors of the acidic stilbenic moieties **8**, were obtained by a straightforward double alkylation between the internal unit **4** and the appropriate stilbenoide derivative (**7a−d**); their subsequent hydrolysis yielded the acid monodendrons **8a−d** (Scheme 3). The targeted second generation dendrimers (**10a−c**) were obtained by the amidation reaction of the acid monodendrons with the tetraamino core *N*,*N*,*N′*,*N′*-tetrakis-(3-aminopropyl)-1,4-butanediamine (DAB; Generation 1.0). For the reaction to proceed more efficiently, it was necessary to preliminarily activate the acid function of the monodendrons by diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate, **9**.[19] Unfortunately, the dendrimer **10d** could not be prepared due to the complete insolubility of **8d** in organic solvents.

All the final compounds were isolated as either air-stable waxy solids (**8a**, **10a**), crystalline materials (**8b**, **8d**, **10b**), or viscous oils (**8c**, **10c**) and were soluble in most organic solvents, except **8d**. The acidic stilbenic arms were purified by repeated crystallizations in petroleum ether and the dendrimers by flash chromatography. Compounds **8** and **10** were characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and the final dendrimers by additional MALDI−TOF spectroscopy. In all cases, the results were in good agreement with the proposed structures.

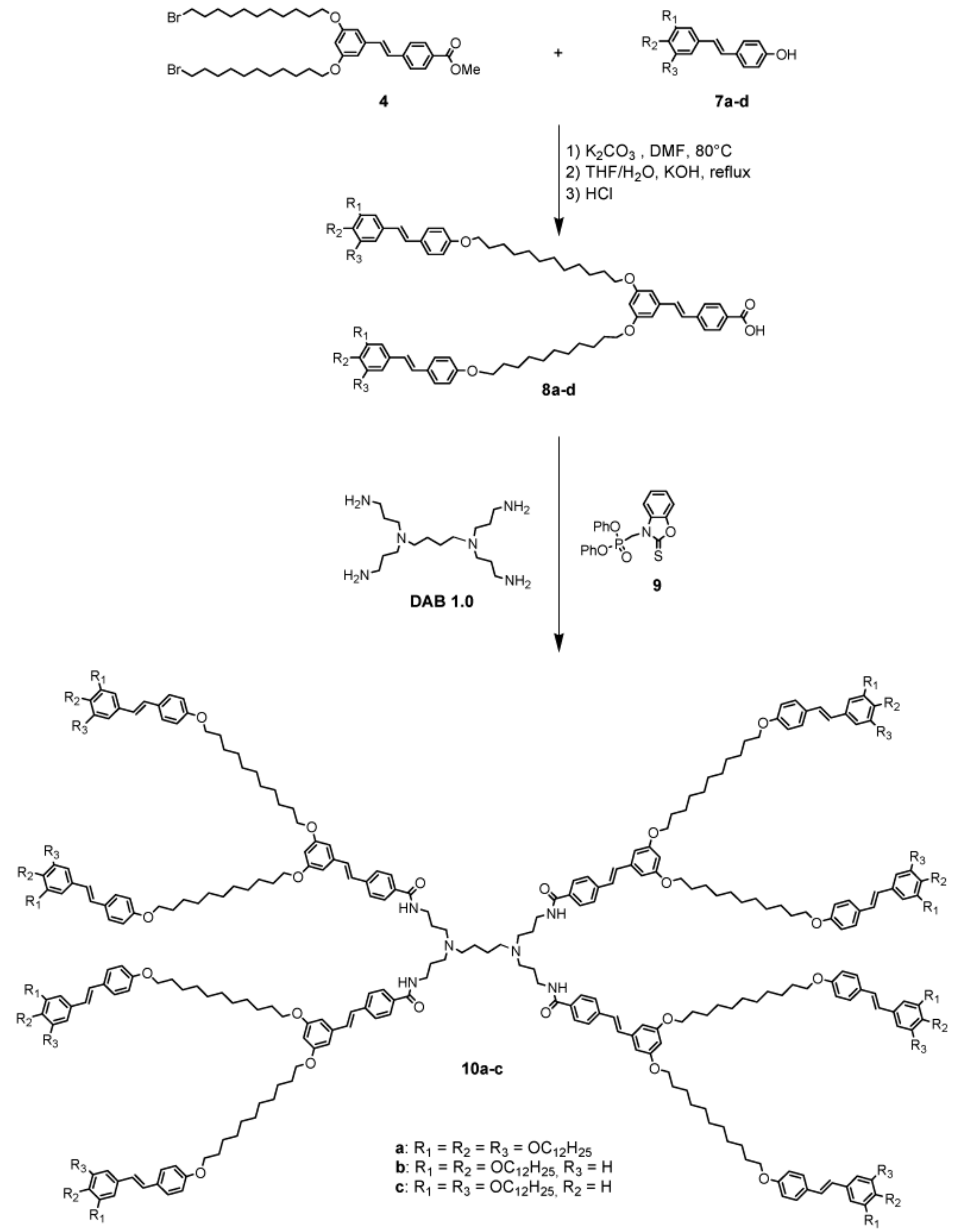
Results

The compounds discussed in this study are schematically represented in Scheme 3. In the present work, stabilization and/or induction of the mesomorphic properties, when compared to the thermal behavior of the low-molar-weight monomeric precursors, was observed upon the incorporation of the nonmesogenic stilbene moieties within the arborescent scaffolding according to **10a−c**, yielding a new family of high-molar-weight liquid crystalline dendrimers.

The thermal behavior of the acidic moieties and of the dendrimers was examined by three complementary techniques: polarized-light optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

POM Experiments. The liquid crystalline behavior of the acids **8a**,**c** and of the three dendrimers **10a−c** was first evidenced by the observation of large and homogeneous fluid domains, which coalesced on increasing the temperature further; in contrast, **8b** and **8d** were found to melt directly into the isotropic liquid at 146 and 193 °C, respectively, without showing any mesophase. No obvious and recognizable optical texture could be observed under the polarized microscope, except for dendrimer **10b** for which a texture displaying rather large cylindrical domains was observed (Figure 2); such defects are usually characteristic of a columnar phase. The two acids, **8a** and **8c**, appeared liquid crystalline at room temperature, with the mesophase stability decreasing in accordance with the reduction of the number of terminal aliphatic chains. The corresponding dendrimers, **10a** and **10c**, were also found to be mesomorphic near the ambient and with again an

Scheme 3. Preparation of the Stilbenic Branches (Acids 8a−d) and Octopus Dendrimers 10a−c



important decrease of the mesophase-to-isotropic liquid transition temperature on going from **10a** to **10c**. Notwithstanding, whereas the acid **8b** was devoid of mesomorphism, a mesophase was induced for the dendrimer **10b**, which existed at much higher temperatures than that of **10a** or **10c**, but over a narrower temperature range. Note that the ester compounds, precursors of **8a−d**, were not liquid crystalline either.

Optical microscopy was thus not a conclusive technique in giving an unequivocal mesophase assignment but was nevertheless sufficient to prove induction of mesomorphism by dendrimerization.

DSC Measurements. Confirming the results of the microscopic observations, several transitions likely associated with a liquid crystalline behavior were detected by DSC. The acidic branches (**8a**, **8c**) and the dendrimers (**10a−c**) exhibited complicated DSC traces during the first heating scan. However, on subsequent heating−cooling cycles, more simple and reproducible thermograms were obtained, an indication of the good thermal stability of the compounds. The traces consisted of either a glass- or crystal-to-mesophase transition and a mesophase-to-isotropic liquid transition (Figure 3). The transition temperatures of the acids and dendrimers are gathered in Table 1.

X-ray Diffraction Studies. Temperature-dependent X-ray diffraction experiments were systematically carried out in order to identify unequivocally the nature of the mesophases. Qualitatively similar X-ray patterns were obtained for all the acidic branches and dendrimers, whatever the number and the position of the peripheral aliphatic chains, and confirmed the existence of liquid crystalline mesophases. The X-ray patterns consisted of a diffuse scattering halo in the wide-angle region, centered around 4.5 Å, corresponding to the liquidlike order of the molten aliphatic chains. In the

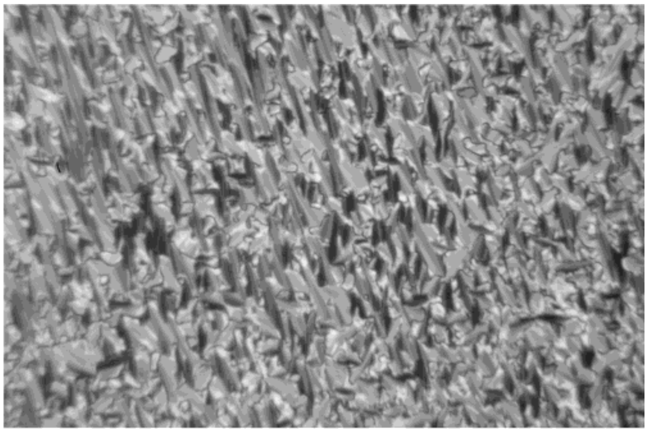


Figure 2. Optical texture of **10b** at 100 °C.

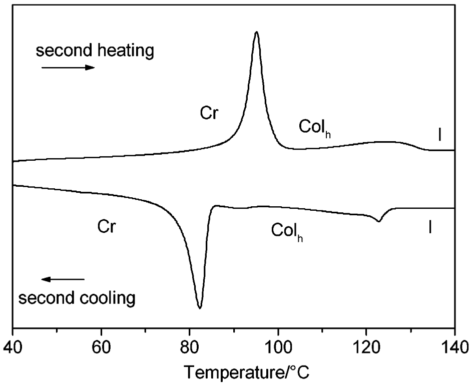


Figure 3. DSC thermogram of **10b**.

small-angle region, two and up to five sharp reflections (**10b**, Figure 4) were observed, with the reciprocal spacings in the ratios 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{12}$, which were indexed as $(hk) = (10), (11), (20), (21)$, and (22); these reflections are in agreement with a 2D hexagonal lattice. The results of these investigations are summarized in Table 1. The X-ray pattern of one representative is shown in Figure 4.

Discussion

All the new compounds synthesized, with the exception of the two acidic branches (**8b**, **8d**), are mesomorphic, self-assembling into a hexagonal columnar mesophase. The nature of the mesophase was by all means expected due to the mismatch between the aromatic surface areas and that of the aliphatic ones, resulting in the curvature of the interfaces and hence to columnar mesophases. These results are indeed in agreement with other findings[7,13] and with some of our previous work on side-chain dendrimers for which the increasing number of peripheral chains grafted per terminal groups was associated with a change of morphology from lamellar to columnar structures.[9b,c] As far as the dendrimers **10a**−**c** are concerned, the parameters of the hexagonal lattices, a, are in overall good agreement with the molecular dimensions estimated by molecular dynamics simulation; the diameters of the dendrimers in their most extended flat conformation were found to vary between 110 and 120 Å. For such a simulation, the aliphatic chains (terminal and internal) were considered in their liquidlike conformation, i.e., with some amount of gauche conformations. This similarity suggests that the octopus dendrimers preferably adopt an oblate shape that is a flat extended or a wedgelike conformation with the anisotropic blocks lying more or less in planes perpendicular to the columnar axis, rather than a prolate conformation (cylindrical) within the columns.[9b] However, the small discrepancy between the estimated molecular diameters (110−120 Å) and the measured lattice parameters (85−95 Å) of the Col$_h$ mesophases, corresponding to a molecular contraction of about 10−20%, can only be partly attributed to the liquidlike state of the molten aliphatic chains which cannot account for more than a few percent only. This thus indicates that the small rigid segments have to be tilted with respect to the columnar axis, i.e., the stilbene groups are not contained in the hexagonal plane, and/or the orientation within the plane perpendicular to the columnar axis of their long molecular axis is nonradial, i.e. there is no preferential direction of the molecular axes of the stilbene units in this plane.

To propose a possible molecular arrangement of these compounds within the columns, the number of *octopus* able to fill a columnar slice 4.5 Å thick was first calculated. This distance corresponds to the average liquidlike correlations between the mesogens in a liquid crystalline phase and has recently been justified by a simple geometrical model for some other liquid crystalline dendrimers.[9b] Let us remark that in nondiscoid systems a columnar slice does not have a particular significant meaning, and it does not necessarily imply that in the present case the columns result from the stacking of flat dendrimeric or supramolecular dendritic disks on top of each other (vide infra), as in purely discotic materials. However, this approach permits the calculation of a linear density along the columnar axis and a comparison with other low-molecular-weight liquid crystalline materials forming columnar structures. Thus, the molecular volumes, V_M, were estimated considering a density of 1 g cm^{-3} for the molecules in the mesophase and corrected by a temperature factor.[20] Such a value for the density of dendrimers in the mesomorphic state is totally acceptable, and similar densities have been measured in side-chain dendrimers without changing from the first generation to the fifth.[9c] The volume of one columnar slice 4.5 Å thick thus equals Sh, where S is the columnar cross section (Table 1) and h the thickness of the slice. The number of molecules per slice can thus be directly obtained by $N = hS/V_M$. It showed that while two dendrimers **10a** are necessary to fill such a slice, three dendrimers **10b** are needed. On average, this corresponds to about 48 aliphatic chains that radiate out of the interface of such defined cylindrical slice. Interestingly, for **10c**, one isomeric compound of **10b**, which can be regarded as a structural intermediate of **10a** and **10b**, the number of molecules satisfying these conditions is reduced, and $N = 2.5$, i.e., with only 40 radiating aliphatic chains. This may explain the smaller phase stability of the latter with respect to the more densely packed dendrimers. Such a substitution pattern (in the 3,5-position of the terminal aromatic ring) has often been found incompatible with mesophase formation and/or broad mesomorphic temperature ranges. This result has been verified many times, particularly in polycatenar liquid crystals,[21] showing the importance of an aliphatic chain in the para position in promoting and stabilizing mesomorphism. Thus, since more than one molecule is necessary to circumvent the dimension of the columns, the formation of the mesophase likely results from a self-assembling process of octopus molecules having a wedgelike con-

Table 1. Thermal Behavior and X-ray Characterization of the Dendritic Branches and Octopus Dendrimers[a]

		indexation					
compd	transition temperature/°C	d_{meas}/Å	I	hk	d_{calc}/Å	mesophase parameters	N
8a	Col$_h$ 52 (15.5^b) I	64.5	VS	10	64.7	$T = 30$ °C	6.3
		37.5	S	11	37.35	$a = 74.7$ Å	
		24.4	S	21	24.45	$S = 4830$ Å^2	
		4.5	br	h		$V_{cell} = 21\,750$ Å^3	
8b	Cr 146 I						
8c	g −35 (0.1^c) Col$_h$ 28 (16.7^b) I	55.2	VS	10	54.8	$T = 25$ °C	5.6
		31.7	S	11	31.6	$a = 63.3$ Å	
		27.05	M	20	27.4	$S = 3470$ Å^2	
		20.8	S	21	20.7	$V_{cell} = 15\,600$ Å^3	
		4.5	br	h			
8d	Cr 193 I						
10a	Cr −3 (95.6^b) Col$_h$ 84 (17.8^b) I	77.0	VS	10	77.0	$T = 60$ °C	2.1
		44.5	S	11	44.45	$a = 88.9$ Å	
		4.5	br	h		$S = 6850$ Å^2	
						$V_{cell} = 30\,810$ Å^3	
10b	Cr 95 (227^b) Col$_h$ 132 (17.8^b) I	82.45	VS	10	82.45	$T = 100$ °C	2.9
		47.55	S	11	47.6	$a = 95.2$ Å	
		41.4	M	20	41.2	$S = 7850$ Å^2	
		31.1	S	21	31.15	$V_{cell} = 35\,320$ Å^3	
		23.8	M	22	23.8		
		4.5	br	h			
10c	g −25 (0.1^c) Col$_h$ 42 (17.5^b) I	75.5	VS	10	75.1	$T = 30$ °C	2.5
		43.0	S	11	43.3	$a = 86.7$ Å	
		28.5	S	21	28.4	$S = 6510$ Å^2	
		4.5	br	h		$V_{cell} = 29\,300$ Å^3	

[a] Detailed indexation at a given temperature (T) [d_{meas} and d_{calc} are the measured and calculated diffraction spacings ($\langle d_{10}\rangle = (1/N_{hk})[\sum_{hk} d_{hk}(h^2 + k^2 + hk)^{1/2}]$, where N_{hk} is the number of hk reflections); I is the intensity of the diffraction signal (VS = very strong, S = strong, M = medium, br = broad); hk is the indexation of the two-dimensional lattice; a is the lattice parameter ($a = (2/\sqrt{3})\langle d_{10}\rangle$), S is the lattice area ($S = a\langle d_{10}\rangle$), V_{cell} is the volume of the hexagonal cell (hS)]. N = number of molecules per slice of columns hS. [b] ΔH (kJ mol^{-1}). [c] ΔC_p (kJ mol^{-1} K^{-1}).

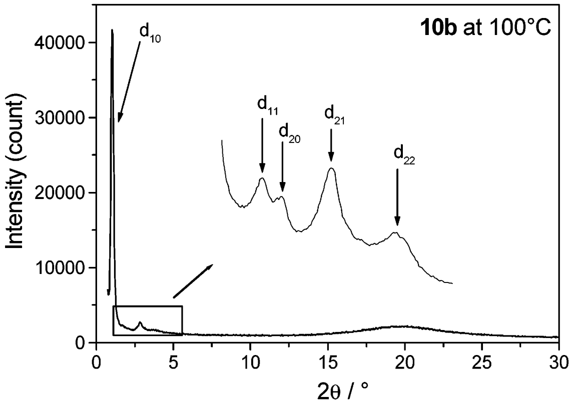


Figure 4. X-ray pattern of **10b** at 100 °C.

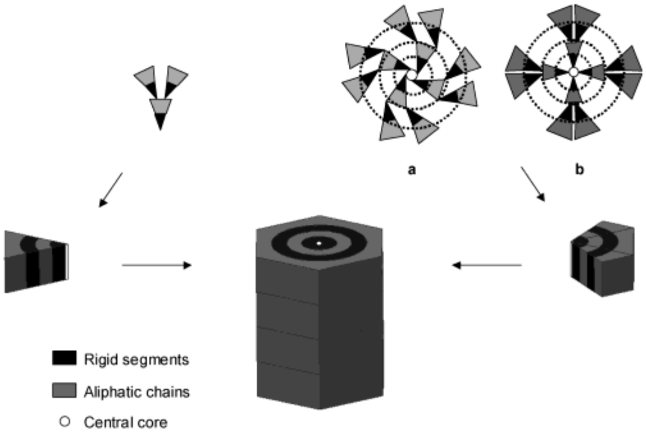


Figure 5. Schematic representation of the self-assembling and self-organization processes of the octopus in the Col$_h$ phase with (a) bent and (b) tilted conformations.

formation into supramolecular columns, the latter further self-organizing into a 2D hexagonal lattice.

On the basis of these results, a simple model accounting for the organization of these dendrimers in the mesophase can be proposed. Considering both the diblock chemical nature of these *octopus* and the similarity between the molecular dimensions and intercco-lumnar distances, an onion structure for the columns is most likely probable. As seen above, to satisfy the parameters determined by X-ray diffraction, the molecules must adopt a nearly flat conformation. However, the liquidlike order of the chains does not by itself explain the slight contraction of the cell with respect to the molecular diameters. Clearly, the overall molecular conformation of the dendrimer in the mesophase is driven by the steric congestion of the terminal aliphatic chains and depends on the segregation between the different constitutive blocks. Indeed, to compensate molecular areas at the various interfaces at every level of the arborescence, the internal and external rigid segments have to be tilted. This arrangement may be additionally further stabilized by inter-mesogen interactions. To do so, the constitutive anisotropic segments may deviate from the radial direction within a plane perpendicular to the columnar axis (Figure 5a). However, such a unique arrangement would be energetically unfavorable because of the strong elastic energy involved and to the small stabilizing enthalpy due to the nonoptimized inter-mesogen contacts in the plane perpendicular to the columnar axis. One can also consider that these segments are tilted with respect to the columnar axis, each mesogenic subunit belonging to the same level of the dendrimer hierarchy not necessarily lying in the same plane (Figure 5b). As such, the dendrimeric supramolecular association would be more stabilized due to the enhancement of the inter-mesogen interactions and to the consequent gain in enthalpy.

However, the packing would not be optimized along the stacking direction, since the segment could point up and down the axis. Clearly, these systems are not static and molecular diffusion does take place; all the conformational possibilities lying between these two extreme structures may occur, with the aim to tend preferentially toward the model with the most stable molecular conformation. As observed by Percec et al.,[7] columnar structures are obtained from the self-assembling of the most stable molecular conformation having either a wedgelike or conical-like shape. In the case of the *octopus* dendrimers, and on the basis of our X-ray results, the most probable molecular shape is that of a wedge (Figure 5), which self-assemble together into columns (Figure 5).

Regarding the precursor acid monodendrons, the fact that the same mesophase was observed, with dimensions of the same order of magnitude, strongly supports that the dendrimers and the monodendrons are similarly organized and that the former likely adopt wedgelike shapes. It was found that on average six dendritic branches like **8a** and **8c**[22] were necessary to satisfy the space-filling requirements of a slice 4.5 Å thick. The smaller number of monodendrons, at first expected, able to fill such slices is due to the substantial reduction of the lattice parameters compared to those of the *octopus*, clearly in connection to the absence of the central DAB core moiety. As the supramolecular dendrimers described by Percec et al.,[7] the acids adopt also a wedge shape and likely self-assemble into supramolecular associations that are stabilized further by H-bonding interactions due to the focal free acid function. Moreover, since they benefit from more degrees of freedom, they are not as densely packed and not as constrained to occupy the available volume than the corresponding dendrimers. These supermolecules can also adopt other conformations as well as exchange their positions in the transverse direction to the columnar axis and along this axis. For these dendritic acids, the wedge shape is stabilized by the incompatibility of the different molecular blocks, the large number of terminal chains, and the ability to form intermolecular hydrogen bonds when assembled into columns.

Conclusions

Several novel liquid crystalline dendrimers have been synthesized, containing stilbene groups as the basic elementary constitutive rigid-rod-like subunits. They were obtained by a mixed divergent−convergent method, consisting of the preparation of the acid branches and their subsequent grafting onto a multibranched central core through an amido linkage. They showed a $\mathrm{Col_h}$ mesophase, with various temperature ranges, the transition temperatures and mesophase stability being influenced by the substitution pattern of the terminal branches. Preliminary calculations suggest that these dendrimers self-arranged into onion-type columns, though this model should be confirmed further by extending this study to provide a more comprehensive structural characterization. Moreover, the preparations of higher generation dendrimers are currently being carried out in order to study the influence of the generation number on the mesomorphic properties.

These optimistic results offer many opportunities in the design of a wide range of new systems of this type. In fact, this concept can be extended to other homolithic systems (i.e., one type of elementary anisometric brick) and to the construction of heterolithic systems (i.e., several different anisotropic bricks). Since the disposition of the mesogenic species forming the dendritic matrix is perfectly controlled, it is possible to consider a range of novel morphologies to be formed. For instance, it is possible to envisage *segmented* "block-type" dendrimers, where the two halves of the dendrimer contain different mesogenic units. Alternatively, *alternated* dendrimers can be built in which the branching mesogenic unit is different at each generation. Such dendrimers and co-dendrimers are currently under investigation and will be reported in due course.

Experimental and Method of Characterization

Techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer in $CDCl_3$ or d_6-THF solutions. MALDI−TOF spectra were recorded on a Bruker biflex III spectrometer in a dithranol matrix (1,8,9-anthracenetriol). The optical textures of the mesophases were studied with a Nikon polarizing microscope equipped with a Mettler FP8 hot stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C $\mathrm{min^{-1}}$ on heating. The apparatus was calibrated with indium (156.6 °C, 28.4 J $\mathrm{g^{-1}}$) and gallium (29.8 °C) as the standards. The XRD patterns were obtained with three different experimental setups. In all cases, a linear monochromatic Cu Kα_1 beam ($\lambda = 1.5405$ Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye−Scherrer-like and a flat film geometry were used in the second and third experimental setups, respectively. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature was controlled to within ±0.3 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature was controlled to within ±0.05 °C. Finally, the last set of diffraction patterns was recorded on image plate, and periodicities up to 350 Å can be measured, and the sample temperature was controlled to within ±0.01 °C. In each case, exposure times were varied from 1 to 24 h depending on the specific reflections being sought (weaker reflections obviously taking longer exposure times).

General Procedures. *Preparation of Internal Branch* (**4**). (**1**) A solution of 3,5-dimethoxybenzaldehyde (11.77 g, 0.07 mol), methyltriphenylphosphonium bromide (27.8 g, 0.078 mol), and *t*-BuOK (8.74 g, 0.078 mol) in dry THF (100 mL) was stirred for 2 h at room temperature under argon. Then, the reaction was quenched by adding 10 mL of a saturated aqueous solution of NH_4Cl. The solvents were removed under vacuum. The crude product was extracted with CH_2Cl_2, and the organic layer was washed with water and dried over $MgSO_4$, and the solvent was evaporated. Pure **1** was isolated by column chromatography on silica gel (eluent petroleum ether−CH_2Cl_2: 7−3) as a colorless oil (10.2 g, 90%). ^{1}H NMR ($CDCl_3$): δ 6.66 (dd, 1H, $J = 10.8$ and 17.1 Hz), 6.58 (d, 2H, $J = 2.35$ Hz), 6.4 (t, 1H, $J = 2.35$ Hz), 5.74 (d, 1H, $J = 17.1$ Hz), 5.26 (d, 1H, $J = 10.8$ Hz), 3.82 (s, 6H).

(**2**) A solution of **1** (10 g, 0.06 mol), $Pd(OAc)_2$ (0.54 g, 2.4 mmol), tri(*o*-tolyl)phosphine (ToP, 1.1 g, 3.6 mmol), and 4-iodoethylbenzyl ester (15.3 g, 0.055 mol) in dry NEt_3 (100 mL) was stirred for 2 h at 60 °C under argon. Then the mixture was stirred for 1 day at 80 °C. After the reaction was complete, the solvent was evaporated. The crude product was dissolved in CH_2Cl_2 and washed with water and dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent petroleum ether−CH_2Cl_2: 3−7) to obtain a yellow solid which was crystallized from hexane to yield pure **2** (14 g, 80%) as a white solid. ^{1}H NMR ($CDCl_3$): δ 8.04 (d, 2H, $J = 8.3$ Hz), 7.56 (d, 2H, $J = 8.3$ Hz), 7.14 (s, 2H), 6.70 (d, 2H, $J = 2.\ 2$ Hz), 6.44 (t, 1H, $J = 2.2$ Hz), 4.39 (q, 2H, $J = 7.1$ Hz), 3.85 (s, 6H), 1.41 (t, 3H, $J = 7.1$ Hz).

(**3**) **2** (6 g, 0.019 mol) was dissolved in CH_2Cl_2 (100 mL). The solution was cooled at −40 °C, and BBr_3 (96 mL, 0.096 mmol) was added dropwise. Then, the mixture was warmed to room temperature for 1 day. The mixture was poured onto an ice bath, and the solvents were removed under reduce pressure. The crude product was dissolved in MeOH (100 mL) and H_2SO_4 (5 mL). The mixture was refluxed overnight, and then the solvent was removed in vacuo. The crude product was dissolved in ethyl acetate, washed with a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and then concentrated in a vacuum. Pure **3** (3.3 g, 65%) was obtain by precipitation in petroleum ether as a yellow solid. ^{1}H NMR (CD_3OD): δ 8.04 (d, 2H, $J = 8.3$ Hz), 7.66 (d, 2H, $J = 8.3$ Hz), 7.18 (d, 2H, $J = 3.4$ Hz) 6.60 (s, 2H), 6.3 (s, 1H), 3.03 (s, 3H).

(**4**) **3** (1.6 g, 5.58 mmol), 1-bromoundecanol (3.1 g, 0.012 mol), and triphenylphosphine (2.66 g, 0.012 mol) were dissolved in dry THF (50 mL) under argon. The solution was then cooled to 0 °C, and diisopropyl azodicarboxylate (DIAD, 2.3 mL, 0.012 mol) was added dropwise. After complete addition, the mixture was refluxed overnight. The solvent was removed, and the crude product was purified by column chromatography on silica gel (eluent petroleum ether−CH_2Cl_2: 3−7) to give **4** (2.5 g, 60%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.03 (d, 2H, $J = 8.3$ Hz), 7.55 (d, 2H, $J = 8.3$ Hz), 7.12 (s, 2H), 6.67 (s, 2H), 6.42 (s, 1H), 3.98 (t, 4H, $J = 6.6$ Hz), 3.93 (s, 3H), 3.42 (t, 4H, $J = 6.8$ Hz), 1.83 (m, 8H), 1.4 (m, 36H).

Preparation of the Terminal Branches (**7a**−**d**).

(**6a**−**d**) A solution of the appropriate aldehyde **5a**−**d** (1 equiv), methyltriphenylphosphonium bromide (1.1 equiv), and *t*-BuOK (1.1 equiv) in dry THF ($c = 0.5$ mol/L) was stirred for 2 h at room temperature under argon. Then, the reaction was quenched by adding a small amount of a saturated aqueous solution of NH_4Cl. The solvents were removed under vacuum. The crude product was extracted with CH_2Cl_2, and the organic layer was washed with water and dried over $MgSO_4$ and the solvent evaporated. Pure vinyl compound (**6a**−**d**) was isolated by column chromatography on silica gel (eluent petroleum ether−CH_2Cl_2: 7−3). **6a**: 93%, white solid. ^{1}H NMR ($CDCl_3$): δ 6.61 (m, 3H), 5.62 (d, 1H, $J = 17.6$ Hz), 5.17 (d, 1H, $J = 10.9$ Hz), 3.97 (m, 6H), 1.78 (m, 6H), 1.27 (m, 54H), 0.89 (t, 9H, $J = 6.7$ Hz). **6b**: 85%, white solid. ^{1}H NMR ($CDCl_3$): δ 6.90 (m, 3H), 6.64 (dd, 1H, $J = 10.9$ Hz and $J = 17.6$ Hz), 5.60 (d, 1H, $J = 17.6$ Hz), 5.13 (d, 1H, $J = 10.9$ Hz), 4.01 (m, 4 H), 1.82 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H, $J = 6.7$ Hz). **6c**: 95%, white solid. ^{1}H NMR ($CDCl_3$): δ 6.64 (dd, 1H, $J = 10.9$ Hz and $J = 17.6$ Hz), 6.55 (d, 2H, $J = 2.4$ Hz), 5.71 (d, 1H, $J = 17.6$ Hz), 5.23 (d, 1H, $J = 10.9$ Hz), 3.95 (t, 4H, $J = 6.5$ Hz), 1.74 (m, 4H), 1.28 (m, 36H), 0.89 (t, 6H, $J = 6.7$ Hz). **6d**: 90%, white solid. ^{1}H NMR ($CDCl_3$): δ 7.34 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.7$ Hz), 6.67 (dd, 1H, $J = 17.6$ Hz and $J = 10.9$ Hz), 5.61 (d, 1H, $J = 17.6$ Hz), 5.13 (d, 1H, $J = 10.9$ Hz), 3.97 (t, 2H, $J = 6.5$ Hz), 1.78 (m, 2H), 1.28 (m, 18H), 0.89 (t, 3H, $J = 6.7$ Hz).

(**7a**−**d**) A solution of the appropriate vinyl compound (**6a**−**d**) (1.2 equiv), $Pd(OAc)_2$ (0.04 equiv), ToP (0.06 equiv), and 4-iodophenol (1 equiv) in dry NEt_3 ($c = 0.3$ mol/L) was stirred for 2 h at 60 °C under argon. Then the mixture was stirred for 1 day at 80 °C. After the reaction was complete, the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with water and dried over $MgSO_4$, and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent petroleum ether−CH_2Cl_2: 3−7) followed by an additional recrystallization in petroleum ether. **7a**: 75%, white solid. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, 2H, $J = 8.7$ Hz), 6.86 (m, 4H), 6.69 (s, 2H), 4.81 (s, 1H), 3.99 (m, 6H), 1.79 (m, 6H), 1.27 (m, 54H), 0.89 (t, 9H, $J = 6.7$ Hz). **7b**: 60%, white solid. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, 2H, $J = 8.6$ Hz), 6.90 (m, 7H), 4.94 (s, 1H), 4.01 (m, 4H), 1.82 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H, $J = 6.7$ Hz). **7c**: 65%, white solid. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, 2H, $J = 8.7$ Hz), 6.87 (m, 4H), 6.31 (d, 2H, $J = 2.0$ Hz), 6.38 (s, 1H), 3.96 (m, 4H), 1.77 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H, $J = 6.7$ Hz). **7d**: 40%, white solid. ^{1}H NMR ($CDCl_3$): δ 7.40 (m, 4H), 6.87 (m, 10H), 3.97 (t, 2H, $J = 6.3$ Hz), 1.79 (m, 2H), 1.27 (m, 18H), 0.89 (t, 3H, $J = 6.7$ Hz).

Preparation of the Acidic Branches (**8a**−**d**). A solution of the appropriate phenol derivative **7** (2.4 equiv), compound **4** (1 equiv), and K_2CO_3 (10 equiv) in DMF ($c = 0.05$ mol/L) was stirred for 2 days at 80 °C. Then, the solvent was evaporated under reduce pressure. The crude product was extracted with CH_2Cl_2, and the organic layer was washed with a saturated aqueous solution of NH_4Cl, dried over $MgSO_4$, concentrated in vacuo, and purified by column chromatography on silica gel (eluent CH_2Cl_2−petroleum ether: 7−3) to give a yellow viscous oil. Then, this oil was solubilized in THF ($c = 0.02$ mol/L) and added to an aqueous solution of KOH (40 equiv). The mixture was refluxed to complete reaction and precipitated in a aqueous solution of HCl (10%). The acid **8** was then filtrated, washed with water and dried under reduce pressure, and purified by crystallization in petroleum ether. **8a**: 60%, colorless waxy solid. ^{1}H NMR (CD_2Cl_2): δ 8.09 (d, 2H, $J = 8.5$ Hz), 7.58 (d, 2H, $J = 8.5$ Hz), 7.42 (d, 4H, $J = 8.8$ Hz), 7.14 (s, 2H), 6.88 (m, 8H), 6.69 (s, 6H), 6.44 (s, 1H), 4.01 (m, 20H), 1.79 (m, 20H), 1.37 (m, 136), 0.89 (t, 18H, $J = 6.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 160.6, 158.8, 153.3, 142.6, 138.5, 138.0, 132.9, 131.8, 130.7, 130.0, 127.7, 127.5, 127.3, 126.7, 126.4, 114.7, 105.4, 105.0, 73.5, 69.2, 68.1, 31.9, 30.4, 29.7, 29.6, 29.4, 29.3, 26.1, 22.7, 14.1. Anal. Calcd for $C_{137}H_{219}O_{12}$: C, 79.91%; H, 10.77%; O, 9.32%. Found: C, 79.97%; H, 10.87%; O, 9.13%. MALDI−TOF MS: molecular weight calcd for $C_{137}H_{219}O_{12}$: *m/z*: 2057.2. Found: *m/z*: 2057.7. **8b**: 70%, white solid. ^{1}H NMR (CD_2Cl_2): δ 8.05 (d, 2H, $J = 8.2$ Hz), 7.55 (d, 2H, $J = 8.2$ Hz), 7.40 (d, 4H, $J = 8.8$ Hz), 6.97 (m, 16H), 6.67 (s, 2H), 6.43 (s, 1H), 3.99 (m, 16H), 1.81 (m,16H), 1.27 (m, 100H), 0.89 (t, 12H, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 160.5, 158.6, 149.2, 148.8, 130.9, 130.6, 130.2, 127.4, 126.4, 126.3, 119.6, 114.6, 113.8, 111.4, 105.4, 69.3, 68.0, 31.9, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1. Anal. Calcd for $C_{113}H_{172}O_{10}$: C, 80.28%; H, 10.25%; Found: C, 80.17%; H, 10.28%. MALDI−TOF MS: molecular weight calcd for $C_{113}H_{172}O_{10}$: *m/z*: 1689.6. Found: *m/z*: 1690.3. **8c**: 80%, colorless viscous oil. ^{1}H NMR (CD_2Cl_2): δ 8.09 (d, 2H, $J = 8.2$ Hz), 7.58 (d, 2H, $J = 8.2$ Hz), 7.42 (d, 4H, $J = 8.8$ Hz), 6.84 (m, 19H), 3.96 (m, 16H), 1.79 (m, 16H), 1.27 (m, 100H), 0.89 (t, 12H, $J = 6.7$ Hz). ^{13}C NMR ($CDCl_3$): δ 160.6, 160.5, 158.9, 142.5, 139.6, 138.5, 130.7, 129.8, 128.6, 127.7, 126.6, 126.4, 114.7, 114.0, 107.1, 105.4, 104.8, 100.5, 68.1, 31.9, 29.6, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. Anal. Calcd for $C_{113}H_{172}O_{10}$: C, 80.28%; H, 10.25%; O, 9.46%. Found: C, 79.26%; H, 10.20%; O, 9.39%. MALDI−TOF MS: molecular weight calcd for $C_{113}H_{172}O_{10}$: *m/z*: 1689.6. Found: *m/z*: 1689.5. **8d**: 70%, white solid. ^{1}H NMR ($CDCl_3$): δ 8.07 (m, 2H), 7.60 (m, 2H), 7.42 (m,4H), 7.13 (m, 2H), 6.88 (m, 16H), 6.68 (m, 2H), 6.44 (s, 1H), 4.01 (m, 12H), 1.79 (m, 12H), 1.37 (m, 64H), 0.89 (t, 6H).

Procedure for the Octopus Dendrimers (**10a**−**c**). To a solution containing the monodendron acid **8a**−**c** (4.8 equiv), condensing agent **9** (5.28 equiv), and NEt_3 (4.8 equiv) in 1-methyl-2-pyrrolydinone (NMP, $c = 0.1$ mol/L) was added a solution of DAB-G1 (1 equiv) in NMP ($c = 0.02$ mol/L). The solution was stirred at room temperature (**8a**, **8c**) or at 60 °C (**8b**) for 2 days and then poured into 5% aqueous $NaHCO_3$. The precipitate was filtered out and purified by column chromatography on alumina gel (eluent CH_2Cl_2−MeOH: 99−1) to give the desired pure dendrimer **10a**−**c**. **10a**: 40%, colorless waxy solid. ^{1}H NMR (CD_2Cl_2): δ 7.76 (d, 8H, $J = 7.9$ Hz), 7.48 (d, 8H, $J = 8.2$ Hz), 7.40 (d, 16H, $J = 8.8$ Hz), 6.95 (m, 68H), 6.37 (s, 4H), 3.95 (m, 80H), 3.46 (m, 8H), 2.47 (m, 12H), 1.77 (m, 80H) 1.45 (m, 556H), 0.88 (t, 72H, $J = 6.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 167.1, 161.0, 159.3, 153.7, 140.4, 139.1, 138.1, 134.0, 133.2, 130.9, 130.3, 128.1, 127.8, 127.5, 126.8, 115.0, 105.5, 104.8, 101.6, 73.8, 69.3, 68.5, 32.3, 30.7, 30.1, 30.0, 29.8, 29.7, 26.5, 26.4, 23.1, 14.3. Anal. Calcd for $C_{564}H_{908}N_6O_{44}$: C, 79.87%; H, 10.84%; N, 0.99%; O, 9.3%, Found: C, 79.61%; H, 10.95%; N, 1.00%; O, 7.82%. MALDI−TOF MS: molecular weight calcd for $C_{564}H_{908}N_6O_{44}$: *m/z*: 8477.3. Found: *m/z*: 8481.0. **10b**: 25%, white solid. ^{1}H NMR (CD_2Cl_2): δ 7.80 (m, 8H), 7.42 (m, 24H), 6.98 (m, 68H), 6.62 (m, 8H), 6.40 (s, 4H), 4.01 (m, 64H), 3.47 (m, 8H), 2.49 (m, 12H), 1.79 (m, 64H), 1.27 (m, 412H), 0.89 (t, 48H, $J = 6{,}8$ Hz). ^{13}C NMR ($CDCl_3$): 160.5, 158.6, 149.3, 148.8, 138.6, 130.9, 130.2, 127.4, 126.4, 126.3, 119.6, 114.6, 113.9, 111.4, 105.3, 69.3, 68.0, 31.9, 29.7, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. Anal. Calcd for $C_{468}H_{720}N_6O_{36}$: C, 80.22%; H, 10.36%; N, 1.2%. Found: C, 79.46%; H, 10.38%; N, 1.01%. MALDI−TOF MS: molecular weight calcd for $C_{468}H_{720}N_6O_{36}$: *m*/*z*: 7005.9. Found: *m*/*z*: 7006.68. **10c**: 45%, colorless viscous oil. ^{1}H NMR (CD_2Cl_2): δ 7.75 (d, 8H, $J = 8.8$ Hz), 7.43 (m, 24H), 6.98 (m, 40H), 6.61 (s, 24H), 6.41 (m, 16H), 3.92 (m, 64H), 3.48 (m, 8H), 2.49 (m, 12H), 1.76 (m, 64H), 1.27 (m, 412H), 0.89 (t, 48H, $J = 6.6$ Hz). ^{13}C NMR ($CDCl_3$): δ 166.9, 160.3, 159.8, 158.8, 149.5, 143.7, 140.0, 139.4, 138.5, 133.3, 130.5, 129.6, 129.1, 128.3, 127.6, 127.3, 126.3, 114.5, 113.8, 106.9, 105.1, 104.6, 101.2, 100.4, 100.3, 67.9, 54.1, 53.6, 53.0, 52.5, 51.9, 29.4, 22.5, 13.9. Anal. Calcd for $C_{468}H_{720}N_6O_{36}$: C, 80.22%; H, 10.36%; N, 1.2%. Found: C, 80.11%; H, 10.39%; N, 0.77%. MALDI−TOF MS: molecular weight calcd for $C_{468}H_{720}N_6O_{36}$: *m*/*z*: 7005.9. Found: *m*/*z*: 7005.3.

Supporting Information Available: Mass spectra for **10a**, **10b**, and **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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