Coassembly of a Hexagonal Columnar Liquid Crystalline Superlattice from Polymer(s) Coated with a Three-Cylindrical Bundle Supramolecular Dendrimer

Virgil Percec,*[a] Cheol-H. Ahn,[a] Tushar K. Bera,[a] Goran Ungar,[b] and Duncan J. P. Yeardley[b]

Abstract: The synthesis and structural analysis of a polymer containing twin-dendritic benzamide side-groups (i.e. poly{*N*-[3,4-bis(*n*-dodecan-1-yloxy)-5-(1-methacryloyl-*n*-undecan-1-yloxy)-phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)-benzamide}) (**19**) are described. The disc-like side groups of this polymer self-assemble into supramolecular cylindrical dendrimers through hydrogen bonding acting along the column long axis, creating a novel architecture consisting of a polymer chain(s) coated with a three-cylindrical bundle supramolecular dendrimer. This polymer self-organizes in a thermotropic nematic liquid crystalline (LC) phase. The low molar mass twin dendritic benzamide, **7-12/12**, which has a similar structure to that of the polymer side groups, self-assembles into supramolecular cylindrical dendrimers, which self-organize on a two-dimensional hexagonal columnar (Φ_h) LC lattice. Coassembly of the polymer **19** with **7-12/12** produces a novel two-dimensional Φ_h LC superlattice. The mechanism responsible for this coassembly provides access to libraries of functional two-dimensionl Φ_h superlattices.

Keywords: dendrimers · liquid crystals · superlattices · three-cylindrical bundle

Introduction

Previous publications from our laboratories reported the design, synthesis, and structural analysis of flat tapered[1,2] and conical[2,3] monodendrons that self-assemble into cylindrical and spherical supramolecular dendrimers, respectively. Cylindrical dendrimers form two-dimensional (2-D) hexagonal columnar (Φ_h) lattices, while the spherical dendrimers form three-dimensional (3-D) cubic liquid-crystalline (LC) lattices. The attachment of a polymerizable group to the core of the flat tapered monodendrons followed by polymerization produces, regardless of the degree of polymerization (DP), cylindrical polymers with the polymer backbone penetrating through their center.[4] Functionalization of the core of the conical monodendrons with a polymerizable group, followed by polymerization up to a specific degree of polymerization, yields spherical polymers. Above this degree of polymerization, cylindrical supramolecules are produced.[5] Both the cylindrical and spherical macromolecular dendrimers self-organize in lattices similar to those of the corresponding supramolecular objects created from their low molar mass building blocks. Related cylindrical polymers which do not, however, self-organize into lattices have been reported by other laboratories.[6,7]

Herein we will demonstrate the synthetic capabilities of mini-monodendrons as models or maquettes for the elaboration of novel architectural motifs from larger generations of dendritic building blocks.[8,9,10] The role of these mini-monodendrons is analogous to that of simple peptides used in the understanding of the molecular engineering involved in the assembly of more complex proteins, or of maquettes used by sculptors and architects to appreciate various aspects of full-size objects.[11] The capability of mini-monodendrons is illustrated by elaborating a new architectural motif. The synthesis and characterization of the simplest examples of twin-tapered dendritic benzamides and bisdendritic benzamides obtained from dissimilar monodendrons that self-assemble into supramolecular cylindrical dendrimers that, in turn, self-organize in a 2-D Φ_h LC lattice, will be described first. The attachment of a polymerizable group to the periphery of a twin-monodendritic benzamide selected from

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the first series of experiments followed by polymerization produces a novel architecture consisting of polymer(s) coated with a three-cylindrical bundle supramolecular dendrimer. Coassembly of this new architecture with the low molar mass twin-dendritic benzamide with the same structure as the polymer's side groups generates a novel Φ_h LC superlattice.

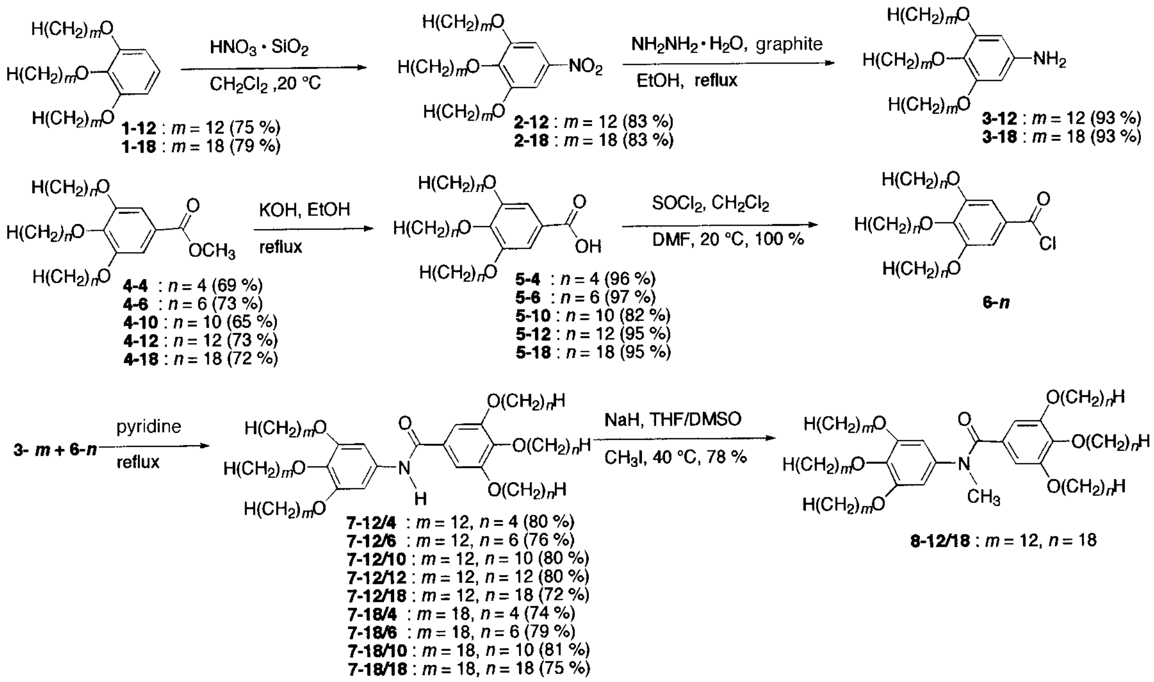
The new architecture described here provides a synthetic concept that could become as powerful as that of the 3- and 4-helix bundle protein motifs used by Nature to create binding and catalytic cavities,[12,13] even if the detailed self-assembly mechanisms of these two systems are quite different.

Results and Discussion

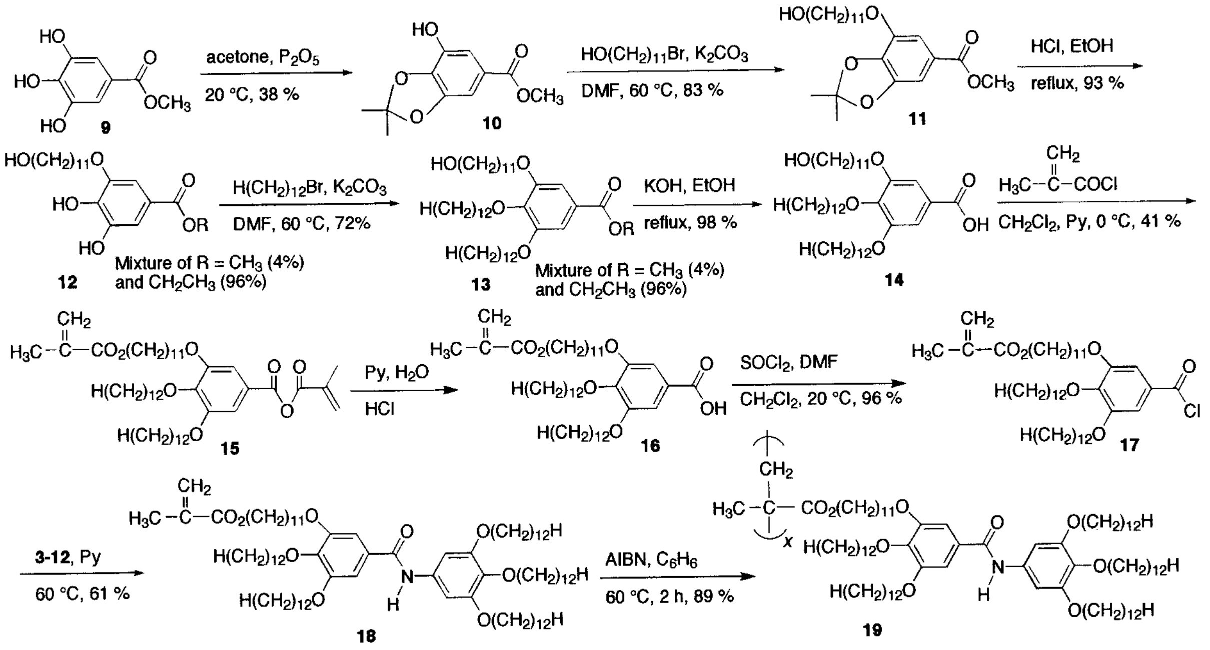
Synthesis of benzamides 7-*m*/*n* and of monomer 18: Scheme 1 outlines the synthesis of *N*-[3,4,5-tris(*n*-alkan-1-yloxy)phenyl]-3,4,5-tris(*n*-alkan-1-yloxy)benzamides (**7-*m*/*n***) and of the *N*-methylated derivative of **7-12/18**, that is, **8-12/18**. In the first step, 1,2,3-trihydroxybenzene was alkylated with 1-bromododecane and 1-bromooctadecane, respectively, in DMF at 60 °C using K_2CO_3 as a base to produce 3,4,5-tris(*n*-alkan-1-yloxy)benzene (**1-*m***, $m = 12, 18$) in 75 and 79% yields after recrystallization from acetone. Nitration of **1-*m*** was carried out with HNO_3 supported on SiO_2 at 20 °C for 15 min to produce 3,4,5-tris(*n*-alkan-1-yloxy)-1-nitrobenzene (**2-*m***) in 83% yield after recrystallization from acetone. HNO_3/SiO_2[14,15] suppressed oxidative demethylation of **1-*m*** and nitrated selectively only at the 1 position of **1-*m***. Reduction of **2-*m*** with $NH_2NH_2 \cdot H_2O$ over graphite powder in ethanol produced 3,4,5-tris(*n*-alkan-1-yloxy)-1-aminobenzene (**3-*m***) in 93% yield.[16,17]

3,4,5-Tris(*n*-alkan-1-yloxy)benzoic acids (**5-*n***) were synthesized by the alkylation[18] of methyl-3,4,5-trihydroxybenzoate (methyl gallate) with 1-bromoalkane (65–72% yield after recrystallization from acetone), followed by the hydrolysis[19] of the resulting **4-*n*** with KOH in refluxing EtOH (82–97% yield). Chlorination of **5-*n*** with $SOCl_2$ in the presence of a catalytic amount of DMF was complete at 20 °C within 1 h and produced the benzoyl chlorides **6-*n*** in 100% yield. In the subsequent step the benzoyl chlorides **6-*n*** were used without further purification. Amidation[20] of **3-*m*** with **6-*n*** in refluxing pyridine yielded **7-*m*/n** (72–81% yield after recrystallization from isopropanol). Compound **7-12/18** was methylated with CH_3I in anhydrous THF by using a suspension of NaH as base and a catalytic amount of DMSO to yield **8-12/18** in 78% yield after recrystallization from isopropyl alcohol.

The synthesis of monomethacrylate functionalized benzamide monomer **18** is shown in Scheme 2. 3,4-Isopropyliden-5-hydroxy methylbenzoate (**10**) was synthesized[21] in 38% yield from 3,4,5-trihydroxy methylbenzoate (**9**) with P_2O_5 in acetone at 20 °C for 1 h. The hydroxy group of 3,4-isopropyliden-5-hydroxy methylbenzoate was etherified with 1-bromoundecanol in DMF at 60 °C using K_2CO_3 as base to yield the yellow oily compound **11** in 83% yield. The isopropylidene protective group was cleaved with HCl in refluxing EtOH for 2 h to produce **12** in 93% yield after recrystallization from CH_2Cl_2/hexane (1/1). During this step a partial transesterification of the methyl ester **12** with ethanol took place. The resulting mixture of **12** was etherified with 1-bromododecane in DMF at 60 °C using K_2CO_3 as base to yield **13** in 72% yield after precipitation from THF solution into MeOH. The ester group of **13** was hydrolyzed with KOH in refluxing EtOH to yield the hydroxy acid **14** in 98% yield. Esterification of **14** with methacryloyl chloride at 0 °C for 3 h in dry CH_2Cl_2 in the presence of dry pyridine led to the mixed ester anhydride **15**. Compound **15** was heated for 10 min in a mixture of pyridine (50 mL) and H_2O (15 mL) to cleave the mixed ester anhydride and maintain the methacryloyl ester group. The reaction mixture was acidified with dilute HCl, extracted with Et_2O, washed with a solution of $NaHCO_3$ and



Scheme 1. Synthesis of bis-dendritic benzamides **7-*m*/*n*** and methyl benzamide **8-12/18**.



Scheme 2. Synthesis and polymerization of bis-dendritic benzamide methacrylate, **19**.

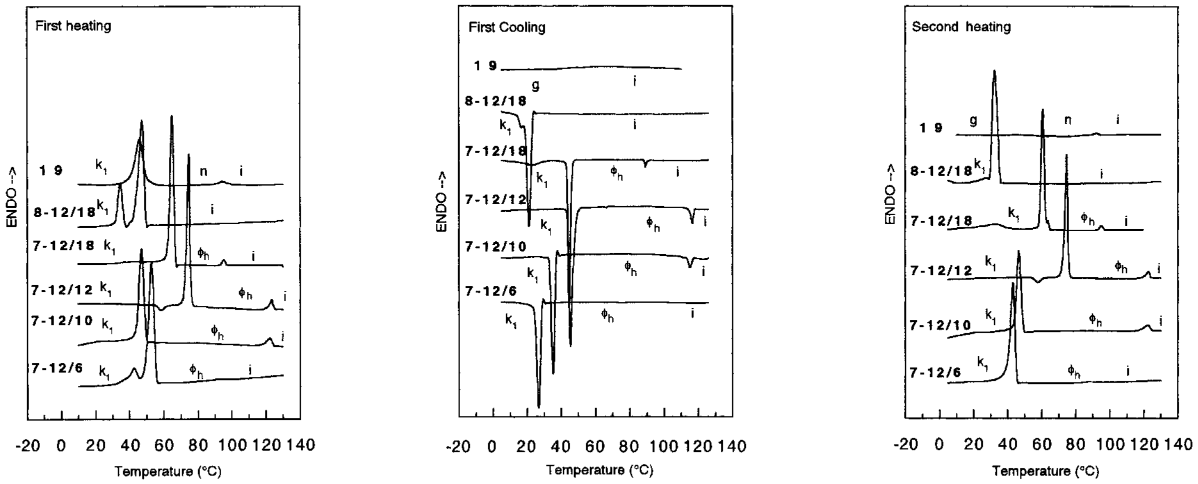


Figure 1. First heating (left), first cooling (center), and second heating (right) DSC traces of **7-12/18**, **7-12/12**, **7-12/10**, **7-12/6**, **8-12/8**, and **19**.

dried over anhydrous $MgSO_4$. Et_2O was distilled and the remaining solid was recrystallized from $MeOH/CHCl_3$ (1/2) to yield **16** in 41.0% yield. Chlorination of **16** with $SOCl_2$ in the presence of a catalytic amount of DMF was complete at 20 °C in 1 h and produced the benzoyl chloride **17** in 96% yield. Amidation of **17** with **3-12** was carried out in pyridine at 60 °C for 4 h to produce the monomethacrylate functionalized benzamide **18** in 61% yield after purification by column chromatography (SiO_2, hexane/EtOAc; 10/1).

Polymerization of 18: Radical polymerization of **18** initiated with AIBN was carried out in benzene at 60 °C. This polymerization was very fast (89% conversion in 2 h, at 6.08×10^{-2} mol L^{-1} monomer concentration), most probably due to self-organization of the polymerizable groups in a microreactor surrounded by three supramolecular columns. A gel formed in the early stage of this polymerization. Although kinetic analysis were needed to evaluate this process, it resembled another related process that we recently reported.[5b] The resulting polymer was purified by column chromatography (SiO_2, hexane) to separate the unreacted monomer; $M_n = 58800$, $M_w/M_n = 2.16$ (GPC with polystyrene standards). When this polymerization was carried out in a less concentrated solution (4.36×10^{-2} mol L^{-1}), the reaction mixture was homogeneous throughout the polymerization process. After purification as above the resulting polymer had $M_n = 55095$ and $M_w/M_n = 1.64$ (GPC with polystyrene standards).

Thermal analysis of benzamides 7-*m*/*n* and of polymer 19: All compounds were analyzed by a combination of techniques consisting of differential scanning calorimetry (DSC), thermal optical polarized microscopy (TOPM), and X-ray diffraction (XRD) experiments. Transition temperatures were determined by DSC with 10 °C min^{-1} (see Experimental Section) and the assignment of various phases was done by a combination of XRD and TOPM.

Figure 1 presents the first heating, the second heating, and first cooling DSC traces of benzamides **7-12/6**, **7-12/10**, **7-12/**

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12, and **7-12/18** and of the polymer **19** with $M_n = 55095$ and $M_n/M_w = 1.64$. These benzamides exhibited an enantiotropic columnar hexagonal (Φ_h) liquid crystalline (LC) phase. In all cases, the Φ_h phase was confirmed by TOPM and XRD. A fan-shaped focal conic texture representative of the Φ_h phase is shown in Figure 2. Transition temperatures and the corresponding enthalpy changes are summarized in Table 1. The degree of supercooling of the isotropization temperature is 6 °C for **7-12/12** and **7-12/18**, 7 °C for **7-12/10**, and 17 °C for **7-12/6**. A degree of supercooling of 6 and 7 °C is in the expected range[1,4b] even if the diamides **7-12/10** and **7-12/6** are generated from two monodendrons with highly dissimilar alkyl groups. The enthalpy changes associated with the isotropization of **7-12/10** (0.87 kcal mol^{-1}) and **7-12/18** (0.76 kcal mol^{-1}) are close to that of **7-12/12** (1.22 kcal mol^{-1}). This demonstrates that even diamides with dissimilar but long alkyl tails can easily self-assemble in a cylinder which self-organizes in a hexagonal columnar LC lattice. The larger degree of supercooling of **7-12/6** (17 °C) is again in the range of expected values[22b] and can be explained by its lower enthalpy change (0.21 kcal mol^{-1}), which demonstrates a higher difficulty for the self-assembly of this diamide to a cylinder of sufficient perfection required for self-organization in a hexagonal columnar LC lattice. This can easily be understood if we consider that **7-12/4** does not form a hexagonal columnar LC lattice at all (Table 1). Again, this result is in line with reported data, that is, related diamides with short alkyl tails form only crystalline phases.[22b] The benzamides containing combinations of dissimilar long and short alkyl chains, that is, **7-12/4**, **7-18/4**, **7-18/6**, and **7-18/10**, or similar long alkyl chains, that is, **7-18/18**, form only a crystalline phase. The *N*-methylated benzamide **8-12/18** also displays only crystalline melting at 32 °C. The crystals of its precursor benzamide **7-12/18** melt into a Φ_h phase at 61 °C, followed by isotropization at 95 °C. The behavior of the latter demonstrates that hydrogen bonding is responsible for the formation of the LC phase of **7-*m*/*n***.

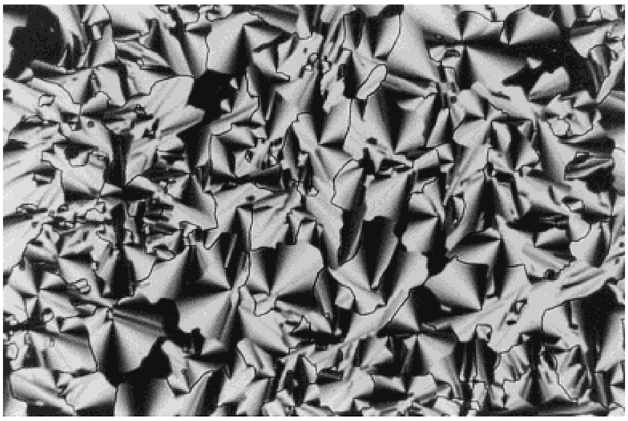


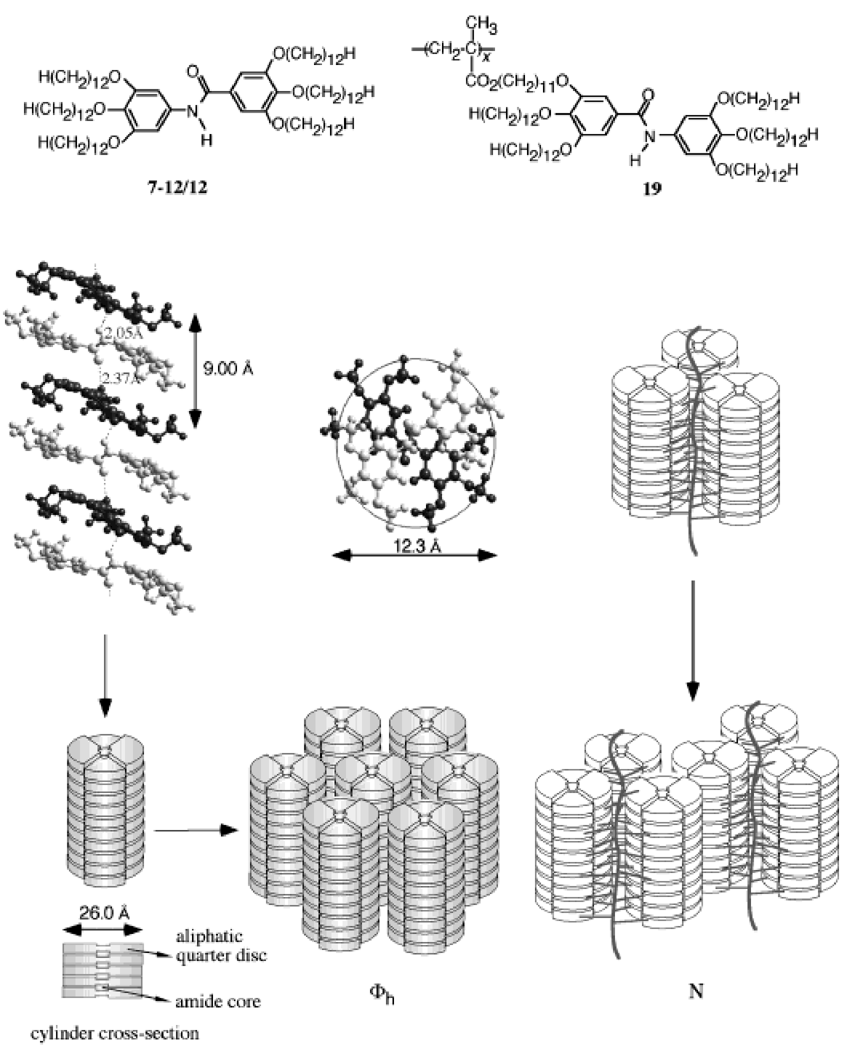
Figure 2. Optical polarized micrograph of the Φ_h mesophase of **7-12/12** observed at 113 °C on cooling with 0.5 °C min^{-1} from isotropic melt.

On heating, the polymer **19** with $M_n = 55095$ and $M_n/M_w = 1.64$ exhibits a mesophase which undergoes isotropization at 95 °C. This transition is not seen on cooling but it appears at 92 °C on subsequent heating scans (Figure 1). A nematic texture is observed for this mesophase. The polymer with a broader molecular weight distribution does not show an isotropization peak on heating or cooling by DSC unless the sample is annealed at 55 °C for 12 h. In this case, it showed an isotropization peak only on heating at 69 °C ($\Delta H = 0.17$ kcal mol^{-1}). However, both on heating and on cooling an isotropization transition can be seen on TOPM. In this case, mesophase formation is slow owing to the broad polydispersity of the sample. In view of its birefringence and

Table 1. Thermal characterization of **7-*m*/*n***, **8–12/18**, and **19** by DSC.

	Phase transition [°C] and corresponding enthalpy changes [kcal mol^{-1}]	
Compound	Heating[a]	Cooling
7–12/4	k_1 47 (6.32) k_2 76 (10.26) i	i 28 (−7.30) k_1
	k_1 76 (10.55) i	
7–12/6	k_1 43 (9.93) k_2 53 (1.20) Φ_h 92 (0.21) i	i 75 (−0.17) Φ_h 27 (−9.98) k_1
	k_1 43 (9.60) Φ_h 91 (0.20) i	
7–12/10	k_1 47 (9.90) Φ_h 122 (0.97) i	i 115 (−0.89) Φ_h 35 (−10.31) k_1
	k_1 47 (10.46) Φ_h 122 (0.99) i	
7–12/12	k_1 74.5 (16.11) Φ_h 123 (1.22) i	i 117 (−1.16) Φ_h 45.5 (−15.55) k_1
	k_1 74 (16.10) Φ_h 122 (1.27) i	
7–12/18	k_1 65 (23.90) Φ_h 95 (0.76) i	i 89 (−0.67) Φ_h 45 (−19.98) k_1
	k_1 61 (20.06) Φ_h 95 (0.75) i	
8–12/18	k_1 35 (9.79) k_2 47 (28.81) i	i 21 (−21.47) k_1
	k_1 32 (22.55) i	
7–18/4	k_1 63 (3.08) −k 65 (1.76) k_2 74 (22.98) i	i 52 (−20.73) k_1
	k_1 65 (8.62) k_2 70 (12.26) k_3 74 (2.28) i	
7–18/6	k_1 49 (11.89) k_2 72 (18.06) i	i 54 (−20.36) k_2 39 (−0.41) k_1
	k_1 44 (0.84) k_2 67 (19.88) i	
7–18/10	k_1 59 (0.74) k_2 70 (21.64) i	i 50 (−20.92) k_1
	k_1 64 (5.31) k_2 70 (15.66) i	
7–18/18	k_1 67 (32.38) −k 70 (34.98) k_2 95 (46.24) i	i 55 (−37.23) k_1
	k_1 67 (31.90) −k 73 (45.24) k_2 94 (53.47) i	
19	k_1 46 (5.22) n 95 (0.23) i	i 34 g
	k_1 47 (0.45) n 92 (0.22) i	

[a] Data from the first heating and cooling scans are on the first line, and data from the second heating are on the second line; k = crystalline, g = glassy, n = nematic, i = isotropic, Φ_h = hexagonal columnar.



Scheme 3. Self-assembly of **7-12/12** into supramolecular cylindrical dendrimers that self-organize in a Φ_h lattice and of **19** in a three-cylindrical bundle supramolecular dendrimer.

lack of any Bragg-like X-ray diffraction (see Table 4), the mesophase of **19** is nematic. Detailed characterization of polymer **19** will be discussed later.

Structural analysis of benzamides 7-*m*/*n*: Bragg diffraction peaks corresponding to lattice spacing in a ratio of 1:1/$\sqrt{3}$:1:/$\sqrt{4}$ which are characteristic of a 2-D Φ_h lattice are exhibited at small angles by the benzamides **7-12/6, 7-12/10, 7-12/12**, and **7-12/18** in their LC phase. The diameter of the supramolecular cylinders self-assembled from these benzamides (a, Å in Table 2) increases with increasing length of the alkyl tails in the following order: 22.5 Å (**7-12/6**), 24.5 Å (**7-12/10**), 26.0 Å (**7-12/12**), and 28.3 Å (**7-12/18**). The difference between the column diameter obtained from fully extended all-*trans* conformations of alkyl tails and the experimental one obtained by XRD is the result of alkyl tail shrinkage. This shrinkage is calculated as given in expression 1, where R_{ext} = average measured radius for the model based on fully extended conformation (19.6 Å), R_{exp} = radius determined by XRD (13.0 Å), and R_{core} = radius of rigid aromatic core including methoxy groups (6.15 Å, Scheme 3). A shrinkage of 48% of alkyl tails in their melted state would be required.

$$\%\,\text{shrinkage} = \frac{R_{\text{ext}} - R_{\text{exp}}}{R_{\text{ext}} - R_{\text{core}}} \times 100 \qquad (1)$$

Table 2. Characterization of **7–12/*n*** by XRD.

Compound	T [°C]	d_{100} [Å]	d_{110} [Å]	d_{200} [Å]	$<d_{100}>$[a] [Å]	a[b] [Å]	R[b] [Å]	S[b] [Å]	ρ[c] [gcm^{-3}]	μ[d]
7–12/6	80	19.5	11.2	9.7	19.5	22.5	11.3	13.0	0.97	1.0
7–12/10	80	21.1	12.3	10.6	21.2	24.5	12.3	14.1	0.96	1.0
7–12/12	80	22.5	12.9	11.1	22.5	26.0	13.0	15.0	0.98	1.0
7–12/18	80	24.5	14.1	12.3	24.5	28.3	14.2	16.4	0.95	1.0

[a] $<d_{100}> = (d_{100} + \sqrt{3}d_{110} + \sqrt{4}d_{200})/3$. [b] $a = 2d_{100}\sqrt{3}$, $R = d_{100}/\sqrt{3}$, $S = 2R/\sqrt{3}$. [c] Experimental density at 20 °C. [d] μ = Number of molecular units per 4.6 Å stratum of the column.

In a previous publication[22b] from our laboratories, we reported that 1,2-bis[3,4,5-tris-(dodecan-1-yloxy)benzamide] ethanes (**12-AG-DA**) self-assemble into supramolecular cylinders with a diameter of 34.3 Å. These cylinders self-organize in a Φ_h LC phase. XRD results combined with density measurements demonstrated a model in which two side-by-side **12-AG-DA** molecules form a layer 4.60 Å in thickness. An ABAB stacking of two adjacent pairs of side-by-side **12-AG-DA** molecules rotated by 90° around the column axis produces a 9.2 Å quasi-repeat unit. Hydrogen bonding along the column axis was demonstrated to be responsible for this self-assembly process[22b] (see Figures 1 and 6 in ref. [22b]).

Compounds **7-12/6, 7-12/10, 7-12/12**, and **7-12/18** produce a Φ_h LC phase from supramolecular cylinders comprising only one **7-*m*/*n*** molecule per 4.6 Å column layer (Table 2). If we compare the a parameter of the hexagonal lattice of **7-12/12** (26.0 Å), which has the same alkyl chain length as **12-AG-DA**, with the a parameter of the equivalent **12-AG-DA** (a = 34.3 Å) reported previously,[22b] we obtain a ratio of 1.35 which is fairly close to $\sqrt{2}$ (Scheme 4). This ratio should be $\sqrt{2}$ if the intracolumnar repeat and the columnar structures are the same in both cases, except that in **12-AG-DA** there were two adjacent molecules per column cross-section[22b] and only one in the present benzamide **7-12/12**. The cross-section areas of these two columns should be in the ratio 2:1. Scheme 3 (middle-left and center) shows the side view (left) and top view (center) of the hydrogen-bonded supramolecular column obtained from **7-12/12** containing only methoxy groups

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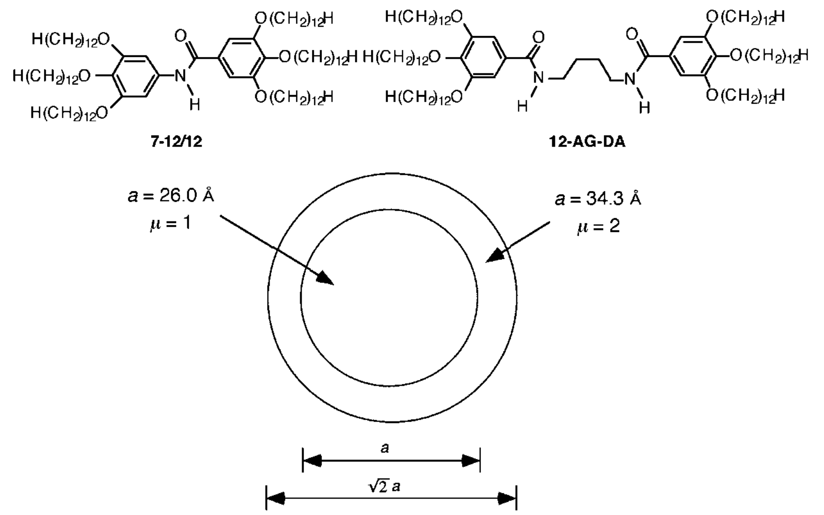

Scheme 4. Comparison of the supramolecular columns generated by the self-assembly of **7-12/12** and of the 1,2-bis[3,4,5-tris(dodecan-1-yloxy)benzamido]ethane **12-AG-DA** (see ref. [22b] for details).

instead of dodecyloxy groups (for simplicity). The geometry of the single molecule was first optimized by MOPAC quantum mechanics program using the MNDO method. Intermolecular stacking was then optimized by using the CERIUS-2 Open Force Field and the periodic boundary condition in the column direction. Molecules were initially positioned with the projections of their long axes at right angles to each other. The two types of molecules with alternating orientations are shown lighter and darker for clarity. Strong hydrogen bonds are shown by the model to develop between amide hydrogen and oxygen in the column direction, their length being 2.05 Å and 2.37 Å respectively. The distance between similarly oriented molecules along the column axis is 9 Å according to the model or an average distance of 4.5 Å between molecules. This compares favourably with the experimental value of 4.6 Å obtained by X-ray structure analysis (Table 2). A circle of 12.3 Å diameter is drawn in the top view of the model (Scheme 3) as a rough indication of the extent of the rigid core of the column, which includes methoxy groups. This criss-cross arrangement of cores with the aromatic rings rotated out of the plane of the amide groups accounts for filling the core space and is schematically illustrated on the bottom-left part of Scheme 3. This out-of-plane arrangement of the benzene and amide groups is in agreement with the near 60° dihedral angle of the two benzene rings, that is well-established for benzanilide and related compounds.[23]

Structural analysis of binary mixtures of benzamide 7-12/12 with polymer 19: Binary mixtures of **7-12/12** with polymer **19** ($M_n = 55\,095$, $M_w/M_n = 1.64$) were prepared from CH_2Cl_2 solutions. Figure 3 presents the DSC traces of the first and second heating and cooling scans of **7-12/12**, **19** and of their binary mixtures. The DSC heating scan after annealing at 55 °C for 12 h was almost identical to the first DSC heating scan and its results are summarized in Table 2. A hexagonal columnar (Φ_h) liquid crystalline phase was produced for mixtures containing more than 80 mol% of **7-12/12**. The mixtures containing between 60 and 20 mol% of **7-12/12,** exhibit a new phase. The mixture containing 60 to 80 mol% of **7-12/12** has a biphasic region. The results of the thermal characterization are summarized in Table 3. The range of the new phase is marked with dotted lines. Figure 4 presents the dependence of transition temperatures on composition for all mixtures. The range of the new phase is marked with dotted lines. Table 4 presents the results of XRD. The most intriguing feature of the X-ray diffractogram of the new phase is the presence of a 45 Å reflection, that is, corresponding to twice the spacing of the strongest peak which, in the case of ordinary Φ_h phase in pure **7-12/12**, indexed as 10. Further, there is the fact that pure polymer does not develop

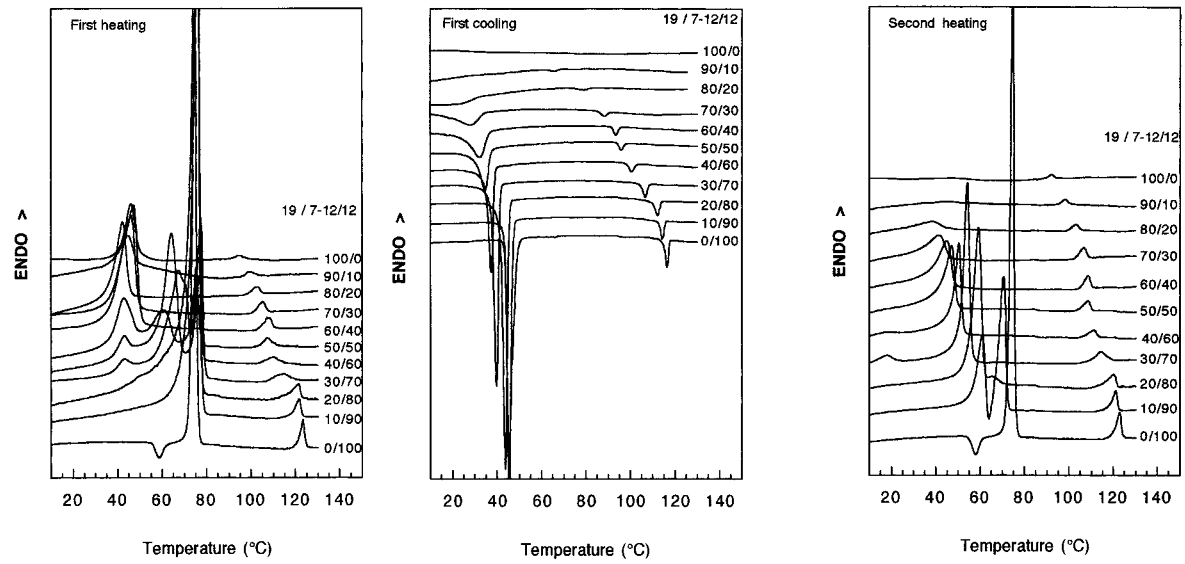

Figure 3. DSC traces of the mixtures of **19** ($M_n = 55\,095$, $M_w/M_n = 1.64$) with **7-12/12** (mol/mol): first heating (left); first cooling (center); second heating (right)

Table 3. Thermal characterization of **19/7** + **12/12** mixtures by DSC.

19/7 + **12/12** (mol/mol)	Phase transitions [°C] and corresponding enthalpy changes [kcal mol^{-1}] Heating[a]	Heating after annealing[b]	Cooling
100/0	k_1 46 (5.22) n 95 (0.23) i k_1 47 (0.45) n 92 (0.22) i	k_1 47 n 92 (0.20) i	i 34 g
90/10	k_1 45 (3.94) n 99 (0.31) i g 6 g 30 n 98 (0.31) i	g 25 k_1 42 (2.5) Φ_h 100(0.30) i	i 66 (−0.11) n 46 g 14 g
80/20	k_1 42 (5.07) Φ_h 103 (0.32) i k_1 38 (2.07) Φ_h 103 (0.42) i	k_1 39 (4.19) Φ_h 81 (0.18) i	i 79 (−0.16) Φ_h 33 g
70/30	k_1 46 (7.59) Φ_h 106 (0.43) i k_1 42 (3.23) Φ_h 107 (0.55) i	k_1 49 (8.04) Φ_h 107 (0.55) i	i 88 (−0.31) Φ_h 28 (−3.19) k_1
60/40	k_1 47 (9.6) Φ_h108 (0.45) i k_1 45 (5.02) Φ_h 109 (0.59) i	k_1 51 (9.86) Φ_h 108 (0.6) i	i 93 (−0.41) Φ_h 32 (−4.2) k_1
50/50	k_1 33 k_2 61 (10.43), k_3 75 (3.25) Φ_h107(0.64) i k_1 47 (6.58) Φ_h 108 (0.6) i	k_1 50 (10.24) Φ_h 108 (0.6) i	i 96 (−0.46) Φ_h 35 (−5.92) k_1
40/60	k_1 43 k_2 64 (13.69) k_3 77 (3.2) Φ_h 110 (0.51) i k_1 50 (7.11) Φ_h 111 (0.57) i	k_1 51 (6.24) Φ_h 111(0.58) i	i 111 (−0.48) Φ_h 37 (−6.89) k_1
30/70	k_1 43 k_2 67 k_3 77 (46.3) Φ_h 115 (1.3) i k_1 54.03 (10.39) Φ_h 114.4 (0.86) i	k_1 55 (11.58) Φ_h 114 (0.83) i	i 107 (−0.67) Φ_h 40 (−10.58) k_1
20/80	k_1 76 (39.15) Φ_h121 (0.75) i k_1 59 (13.04) Φ_h 120 (0.98) i	k_1 67 (9.91), 74 (1.42), 79 (0.42) Φ_h 120 (1.14) i	i 112 (−0.74) Φ_h 44 (−12.55) k_1
10/90	k_1 76 (35.29) Φ_h 121 (0.75) i k_1 61 (6.07) 70 (8.39) Φ_h 121(0.89) i	k_1 74 (19.69) Φ_h 122(0.95) i	i 114 (−0.84) Φ_h 46 (−13.84) k_1
0/100	k_1 75 (16.11) Φ_h 123 (1.22) i k_1 74 (16.1) Φ_h 122 (1.27) i		i 116 (−1.16) Φ_h 46 (−15.55) k_1

[a] Data from the first and the second heating scans are on the first and the second line respectively. The cooling scan data are from the first cooling. [b] Annealed at 55 °C for 12 h ; k = crystalline, g = glassy, n = nematic, i = isotropic, Φ_h = hexagonal columnar.

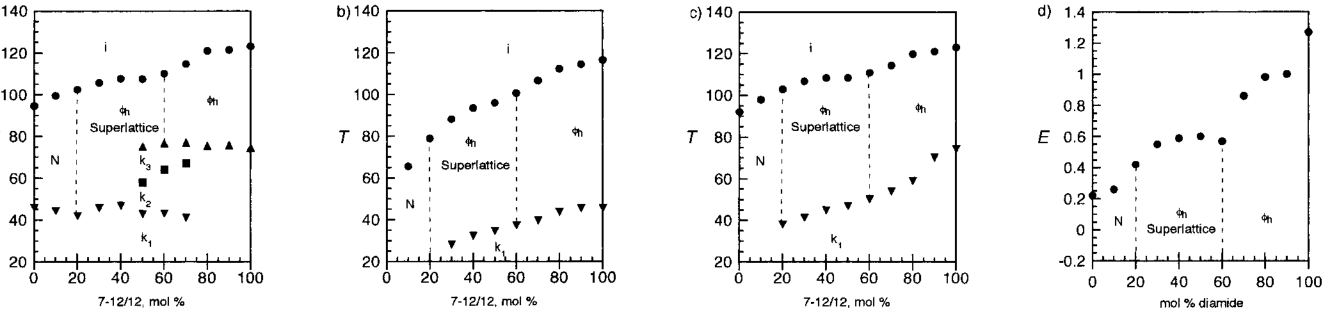

Figure 4. Dependence of transition temperature on composition for the mixtures of **19** (M_n = 55095, M_w/M_n = 1.64) with **7-12/12**: a) first heating; b) first cooling; c) second heating. ▼: $T_{k1-\Phi h}$; T_{k1-n} or T_{k1-k2} and their reverse transitions; ■: T_{k2-k3}; ▲: $T_{k3-\Phi h}$ and their reverse transitions; ●: $T_{\Phi h-i}$ or T_{n-i} and their reverse transitions; d) enthalpy changes associated with the $T_{\Phi h-i}$ transition. T = termperature in °C. E = isotropisation enthalpy in kcal mru^{-1}.

Table 4. X-ray characterization of **19/7 – 12/12** mixtures.

19/7 – 12/12 (mol/mol)	T [°C]	Superlattice reflection [Å]	d_{100} [Å]	d_{110} [Å]	d_{200} [Å]	$<d_{100}>$ [a] [Å]	a[b] [Å]
100/0[c]	60	43.0 d	23.0 d				
80/20[d]	65	44.8	22.3	12.8		22.3	25.7
60/40[e]	60	45.0 w	22. 2			22.2	25.6
50/50[f]	66	46.0 wb	22.2			22.2	25.6
30/70[f]	85	vvw	22.9			22.9	26.4
20/80[f]	85	–	22.9			22.9	26.1
10/90[f]	85	–	22.9	12.9 vw	11.3	22.9	26.1
0/100[f]	90	–	22.5	13.0		22.5	26.0

[a] $<d_{100}> = (d_{100} + \sqrt{3}\,d_{110} + \sqrt{4}\,d_{200})/3$. [b] $a = 2<d_{100}>/\sqrt{3}$. [c] Annealed overnight at 60 °C. [d] Annealed 5 h at 65 °C. [e] Cooled from isotropic state at 6 °C min^{-1}. [f] As received. (vw = very weak, vvw = very very weak, wb = wide broad, w = wide, d = diffuse).

sharp diffraction peaks even after prolonged annealing. Instead it shows two diffuse peaks (centered around 23 and 42 Å) indicating short-range order of the type found as long-range order in the mixtures. Characteristically, the 43 Å diffraction peak decreases in intensity as the proportion of polymer decreases and it disappears around the ratio of **19** /**7-12/12** = 2/8. When polymer **19** with M_n = 58800 and M_w/M_n = 2.16 was used to prepare binary mixtures with **7-12/12**, a similar trend was observed except that a biphasic region was observed for the isotropization transitions.

These results can be explained by postulating a new type of columnar liquid crystal phase with a 2-D hexagonal superlattice which is only formed in the case of mixtures. The structure of this superlattice viewed along the columns is shown in Scheme 5. The circles represent individual columns and the three-pointed stars represent the PMA strands which contain one or several backbones. The polymer backbones are situated on the nodes of a regular hexagonal lattice (superlattice) whose unit cell size is twice the size of the unit cell (subcell) of the sublattice

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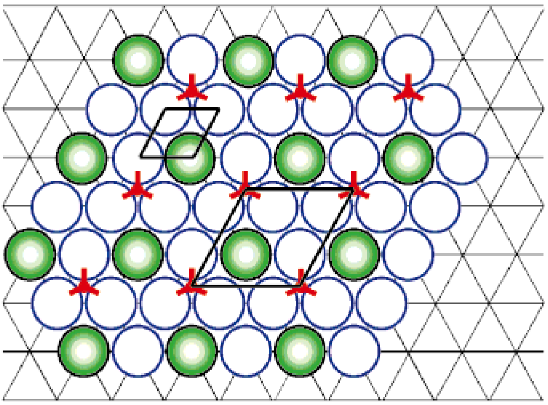
0947-6539/99/0503-1076 $ 17.50+.50/0

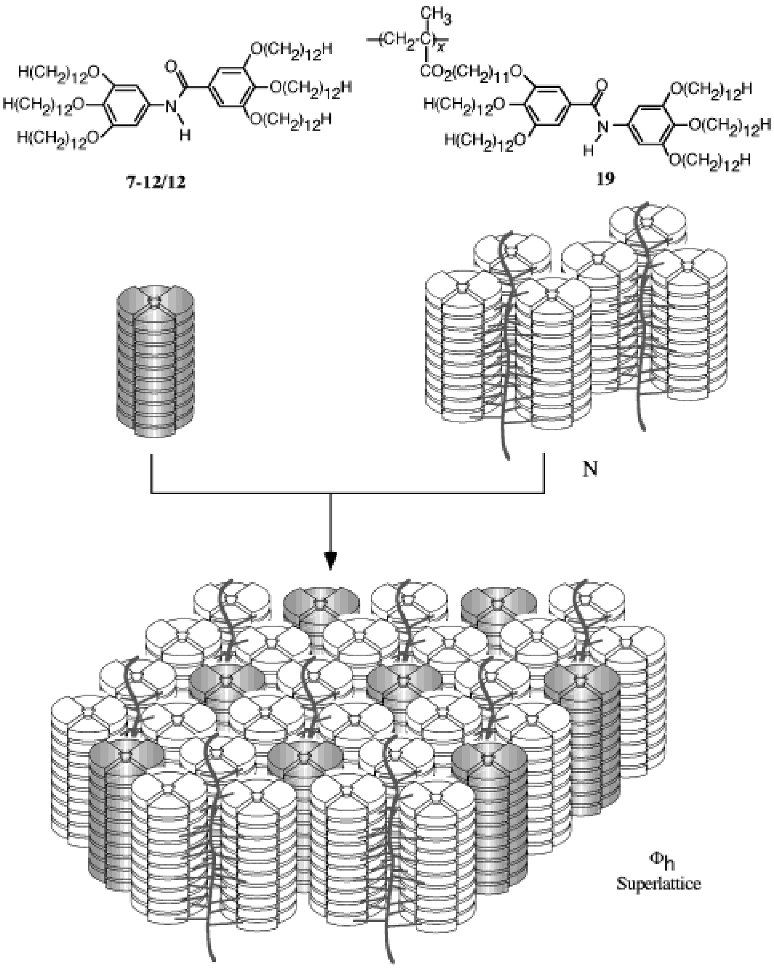


Scheme 5. Schematic representation of the supramolecular columnar hexagonal liquid crystalline superlattice.

formed by individual columns. The true unit cell drawn with thick solid lines has four times the area of the subcell drawn with dashed lines and contains four supramolecular columns of benzamides. In this way microphase separation between the PMA backbone(s) and aliphatic chains is achieved, while maintaining close proximity with three nearest neighbour columns as required by molecular connectivity.

The reason that the pure polymer does not form an ordered hexagonal columnar structure is explained by the fact that one out of four columns in the above unit cell (columns cross-hatched in the Schemes 3 and 5) is not in direct contact with the segregated polymer backbones hence a hexagonal columnar structure does not satisfy the conflicting requirements for molecular connectivity, space filling and microphase separation. A three-cylindrical bundle like the one generated from **19** can theoretically form a oblique columnar lattice instead. Nevertheless, no Bragg-like diffraction was obtained and therefore, as discussed in the thermal characterization section, polymer **19** forms only a nematic phase. However, the addition of free low molar mass benzamide **7-12/12** allows the formation of the columnar superlattice as the added compound is free to self-assemble and fill the hatched columns. **7-12/12** also can coassemble with the polymer side groups and enhance the perfection of the three-cylinder bundle supramolecular dendrimer. A polymer **19** to monomer **7-12/12** molar ratio of 3/1 or less is most appropriate for the above structure but a 4/1 mixture already displays a well ordered superlattice, presumably with some distortion. The mechanism of coassembly of this columnar superlattice is shown schematically in Scheme 6.

Mechanism of self-assembly of the polymer(s) coated with a three-cylindrical bundle supramolecular dendrimer: The self-assembly of the bis- and twin-dendritic benzamides described here relies on the ability of two successive molecules rotated by 90° to form a disc-like shape and on the intermolecular hydrogen bonding between building blocks along the long axis of the supramolecular cylinder (Scheme 3). This molecular wire type hydrogen bonding process has been demonstrated and exploited in the construction of only a few other Φ_h LC assemblies.[16b,22] More frequently, the stabilization of a Φ_h LC assembly is accomplished through intermolecular hydrogen bonding that occurs perpendicular to the column axis. Two mechanisms are encountered in this case. In the first, hydrogen bonding between complementary building blocks generates discotic molecules that self-assemble in a column.[24] In the second case, an intramolecular hydrogen bonding mechanism occurs that extends the rigidity of a discotic molecule which generates the supramolecular column.[25] The main difference between the axial versus transverse hydrogen bonding mechanisms in the construction of these supramolecular columns is that the axial one generates a supra-



Scheme 6. Coassembly of the hexagonal columnar liquid crystalline superlattice from **7-12/12** and **19**.

molecular polymer-backbone-like effect. This effect plays an important role both during the self-assembly and during the polymerization of the twin-dendritic benzamide monomer.

Since the shape of two molecules of **7-12/12** successively rotated by 90° is disc-like, at the first sight the architecture of polymer **19** should be almost identical to that of a polymer with conventional disc-like mesogenic side groups except that it contains two spacers from each disc-like side group. Side chain liquid crystalline polymers with disc-like mesogenic side groups have been always reported to exhibit a thermotropic columnar mesophase.[26] However, in all these cases[26] the single spacer connecting the disc-like mesogen to the polymer backbone was at least twice as long as that of the alkyl substituents attached to the disc-like side groups. This very long spacer length was considered the main structural requirement for the formation of a columnar lattice decoupled from the polymer backbone. Nevertheless, even in these cases, when X-ray analysis of the side chain polymer with discotic side groups was available, it indicated a rectangular columnar rather than a hexagonal columnar lattice.[26c,d] In our three-cylinder bundle supramolecular dendrimer the spacer attaching the twin dendritic bisamide to the backbone is even shorter than the alkyl groups of the diamide (i.e. eleven versus twelve methylene groups). It is this shorter spacer length and the two spacers to a disc-like side group that determine the self-assembly of this new architectural supramolecular dendrimer motif. A simple geometrical calculation shows that most probably only one backbone in an almost all-*trans* extended conformation penetrates between the three-column bundle, although if the conformation is different, more than one backbone is not excluded. In addition, the hydrogen bonding along the cylinder axis is required to stabilize the columnar and the very compact three-cylinder bundle supramolecular dendrimer assembly which coats the extended backbone. This mechanism should be applicable to the elaboration of functional libraries of hexagonal columnar superlattices.

Experimental Section

Materials: 1-Bromobutane (97 %), 1-bromohexane (97 %), 1-bromodecane (98 %), 1-bromododecane (98 %), 1-bromooctadecane (97 %), methyl 3,4,5-trihydroxybenzoate (98 %), $SOCl_2$ (97 %), hydrazine monohydrate (98 %) (all from Aldrich), 1,2,3-trihydroxybenzene (99 %), DMF (99.9 %), pyridine (99.9 %), graphite powder (Grade No.38), P_2O_5 (99.1 %), CH_3I (99 %), NaH (80 % dispersion in oil) (all from Fisher), 1-bromoundecanol (99 %), and methacryloyl chloride (97 %) (both from Fluka) were used as received. The nitrating agent (25 % HNO_3 on silica gel by titration with 1N NaOH using phenolphthalein as an indicator) was prepared according to a literature procedure[14] and was used after drying in air for seven days. Benzene (thiophene-free, Fisher Scientific) used for the free radical polymerizations was washed three times with concentrated H_2SO_4 and dried over $MgSO_4$. CH_2Cl_2 (ACS reagent grade, Fisher Scientific) used for the preparation of blends was refluxed over CaH_2 and freshly distilled before use. Pyridine was dried over KOH, distilled and stored over KOH. All other chemicals were commercially available and were used as received.

Techniques: ^{1}H NMR (200 MHz) spectra were recorded on a Varian Gemini 200 MHz spectrometer. The purity of the products was determined by a combination of thin-layer chromatography (TLC) on silica gel plates (Kodak) with fluorescent indicator and high pressure liquid chromatography (HPLC) using a Perkin-Elmer Series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven, Nelson Analytical 900 Series integrator data station, and two Perkin-Elmer PL gel columns of 5×10^2 and 1×10^4 Å. THF was used as solvent. Detection was by UV absorbance at 254 nm at 40 °C. Relative molecular weights were determined by reference to polystyrene standards. Thermal transitions were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). In all cases, the heating and cooling rates were 10 °C min^{-1}. The transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks. Indium was used as calibration standard. An Olympus BX-40 optical polarized microscope (100 × magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions and characterize anisotropic textures.

X-ray diffraction (XRD) patterns were recorded by using either a helium-filled flat plate wide angle (WAXS) camera or a pinhole-collimated small angle (SAXS) camera, and also by using an Image Plate area detector (MAR Research) with a graphite-monochromatized pinhole-collimated beam and a helium tent. The samples, in glass capillaries, were held in a temperature-controlled cell (±0.1 °C). Ni-filtered $Cu_{K\alpha}$ radiation was used. Densities (ρ) were determined by flotation in gradient columns. Elementary analysis was performed at MHW laboratories in Phoenix. Molecular modeling was performed by using either CSC Chem3D from Cambridge Scientific Computing Inc., MacroModel (Columbia University) on a Silicon Graphics machine, or MOPAC programme using CERIUS 2 force field on a Silicon Graphics machine.

Synthesis

3,4,5-tris(*n*-dodecan-1-yloxy)benzene (**1-12**): To a round-bottom flask equipped with a N_2 inlet–outlet containing a stirring mixture of 1,2,3-trihydroxybenzene (31.5 g, 0.25 mol) and K_2CO_3 (249.0 g, 1.20 mol) in DMF (400 mL) at 60 °C, 1-bromododecane (176.5 g, 0.60 mol) was added in small portions over 10 min. After 4 h at 60 °C, the reaction mixture was poured into vigorously stirring ice/H_2O (2 L). The creamy, granular solid was filtered and washed with H_2O. After recrystallization from acetone, 94.8 g (75.1 %) of white crystals were obtained. Purity (HPLC), 99+ %; m.p. 39–40 °C (ref. [16]: 39.5–40.5 °C); TLC (20/1 hexane/EtOAc): $R_f = 0.68$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9 H, CH_3, $J = 6.6$ Hz), 1.26 (overlapped peaks, 48 H, $\mathrm{CH_3(C}H_2\mathrm{)_8}$), 1.47 (m, 6 H, $\mathrm{C}H_2\mathrm{(CH_2)_2O}$), 1.78 (m, 6 H, $\mathrm{C}H_2\mathrm{CH_2O}$), 3.90 (overlapped t, 6 H, CH_2O, $J = 6.3$ Hz), 6.55 (d, 2 H, 4,6 position, $J = 8.1$ Hz), 6.90 (d, 1 H, 5 position, $J = 8.4$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 ($\mathrm{CH_3}C\mathrm{H_2}$), 26.1 ($C\mathrm{H_2CH_2CH_2O}$), 29.4 ($\mathrm{CH_3CH_2CH_2}C\mathrm{H_2}$), 29.5 ($\mathrm{CH_3CH_2CH_2CH_2(}C\mathrm{H_2)_5}$), 29.9 ($C\mathrm{H_2CH_2O}$, 1,3 position), 30.3 ($C\mathrm{H_2CH_2O}$, 2 position), 31.9 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 69.0 ($CH_2O$, 1,3 position), 73.3 ($C\mathrm{H_2O}$, 2 position), 106.7 (4,6 position), 123.1 (5 position), 138.4 (2 position), 153.4 (1,3 position); elemental analysis calcd (%): C 79.93, H 12.46; found: C 79.73, H 12.63.

3,4,5-Tris(*n*-octadecan-1-yloxy)benzene (**1-18**): Compound **1-18** was synthesized by the same general procedure described for the synthesis of **1-12**. From 1,2,3-trihydroxybenzene (5.0 g, 0.04 mol), K_2CO_3 (33.2 g, 0.24 mol), and 1-bromooctadecane (46.7 g, 0.14 mol) in DMF (140 mL) at 60 °C, 27.9 g (79.3 %) of white crystals were obtained after recrystallization from acetone. Purity (HPLC), 99+ %; m.p. 64–65 °C; TLC (20/1 hexane/EtOAc): $R_f = 0.70$. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.89$ (t, 9 H, CH_3, $J = 6.1$ Hz), 1.25 (overlapped peaks, 90 H, $\mathrm{CH_3(C}H_2\mathrm{)_{15}}$), 1.79 (m, 6 H, $\mathrm{C}H_2\mathrm{CH_2O}$), 4.08 (overlapped t, 6 H, CH_2O, $J = 6.2$ Hz), 6.64 (d, 2 H, 4,6 position, $J = 8.0$ Hz), 7.00 (d, 1 H, 5 position, $J = 8.3$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 13.9$ (CH_3), 22.5 ($\mathrm{CH_3}C\mathrm{H_2}$), 26.8 ($C\mathrm{H_2CH_2CH_2O}$), 29.1 ($\mathrm{CH_3CH_2CH_2}C\mathrm{H_2}$), 29.7 ($\mathrm{CH_3CH_2CH_2CH_2(}C\mathrm{H_2)_{11}}$), 30.1 ($C\mathrm{H_2CH_2O}$), 31.9 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 69.2 ($C\mathrm{H_2O}$, 1,3 position), 73.5 ($CH_2O$, 2 position), 106.7 (4,6 position), 123.4 (5 position), 138.7 (2 position), 153.7 (1,3 position).

3,4,5-Tris(*n*-dodecan-1-yloxy)-1-*n*itrobenzene (**2-12**): Compound **2-12** was synthesized by the nitration of **1-12** with $SiO_2 \cdot HNO_3$ according to a literature procedure.[14–16] To a stirred suspension of HNO_3 (63.0 g, 0.25 mol, 25 % on SiO_2) in CH_2Cl_2 (400 mL) was rapidly added **1-12** (31.6 g, 0.05 mol) in CH_2Cl_2 (100 mL). The resulting red solution was stirred at room temperature for 15 min, after which time the SiO_2 was filtered and washed several times with CH_2Cl_2. The solvent was evaporated on a rotary evaporator and the resultant orange oil was dissolved in hexanes (50 mL). Upon addition of MeOH (600 mL) with vigorous shaking, the product separated as a yellow solid. The solid was filtered, washed with cold MeOH, and dried in air. Recrystallization from acetone yielded 28.0 g (82.8 %) of white crystals. Purity (HPLC), 99+ %; m.p. 54.5–55.5 °C (ref. [27]: 58–59 °C); TLC (20/1 hexane/EtOAc): $R_f = 0.49$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 5.9$ Hz), 1.26 (overlapped peaks, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, CH_2CH_2O), 4.04 (overlapped t, 6H, CH_2O, $J = 6.3$ Hz), 7.47 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_3CH_2), 26.1 ($CH_2CH_2CH_2O$), 29.4 ($CH_3CH_2CH_2CH_2$), 29.5 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.9 (CH_2CH_2O, 3,5 position), 30.3 (CH_2CH_2O, 4 position), 31.9 ($CH_3CH_2CH_2$), 69.3 (CH_2O, 3,5 position), 73.7 (CH_2O, 4 position), 101.9 (*ortho* to NO_2), 143.0 (*ipso* to NO_2), 144.0 (*para* to NO_2), 152.6 (*meta* to NO_2); elemental analysis calcd (%): C 74.61, H 11.48, N 2.07; found: C 74.24, H 11.88, N 2.02.

3,4,5-Tris(*n*-octadecan-1-yloxy)-1-nitrobenzene (**2-18**): Compound **2-18** was synthesized by the same general procedure described for the synthesis of **2-12**. Over a stirred suspension of HNO_3 (39.2 g, 0.11 mol, 25 % on SiO_2) in CH_2Cl_2 (300 mL) was rapidly added **1-18** (20.0 g, 0.023 mol) in CH_2Cl_2 (70 mL). Recrystallization from acetone yielded 17.5 g (83.1 %) of white crystals. Purity (HPLC), 99+ %; m.p. 76.5–77.5 °C; TLC (20/1 hexane/EtOAc): $R_f = 0.50$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.89$ (t, 9H, CH_3, $J = 6.2$ Hz), 1.30 (overlapped peaks, 90H, $CH_3(CH_2)_{15}$), 1.81 (m, 6H, CH_2CH_2O), 4.03 (overlapped t, 6H, CH_2O, $J = 6.3$ Hz), 7.47 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 22.8 (CH_3CH_2), 26.0 ($CH_2CH_2CH_2O$), 29.2 ($CH_3CH_2CH_2CH_2$), 29.7 ($CH_3CH_2CH_2CH_2(CH_2)_{11}$), 30.0 ($CH_2CH_2O$, 3,5 position), 30.3 ($CH_2CH_2O$, 4 position), 31.9 ($CH_3CH_2CH_2$), 69.3 ($CH_2O$, 3,5 position), 73.7 ($CH_2O$, 4 position), 101.8 (*ortho* to NO_2), 143.1 (*ipso* to NO_2), 144.2 (*para* to NO_2), 152.6 (*meta* to NO_2).

3,4,5-Tris(*n*-dodecan-1-yloxy)-1-aminobenzene (**3-12**): Compound **3-12** was synthesized by the reduction of **2-12** with $NH_2NH_2 \cdot H_2O$ over graphite powder.[16,17] Compound **2-12** (40.6 g, 0.60 mol), $NH_2NH_2 \cdot H_2O$ (15.0 g, 0.20 mol), and graphite (30.0 g) were heated in reluxing EtOH (400 mL) for 24 h under an Ar atmosphere. The cooled mixture was diluted with CH_2Cl_2 (400 mL). Graphite was filtered and washed several times with CH_2Cl_2. The colorless solution was concentrated in a rotary evaporator and the resultant white solid was dissolved in CH_2Cl_2 (300 mL). After precipitation in MeOH (2 L), the obtained white solid was collected by filtration and washed with cold MeOH. After drying under vacuum over P_2O_5, 36.0 g (92.8 %) of a white powder was obtained. Purity (HPLC), 99+ %; m.p. 71.5–72.5 °C (ref. [16]: 75 °C); TLC (10/1 hexane/EtOAc): $R_f = 0.25$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 6.3$ Hz), 1.26 (overlapped m, 54H, $CH_3(CH_2)_9$), 1.46 (m, 6H, $CH_2(CH_2)_2O$), 1.76 (m, 6H, CH_2CH_2O), 3.46 (bs, 2H, NH_2), 3.84 (t, 2H, CH_2O on 4 position, $J = 6.4$ Hz), 3.91 (t, 4H, CH_2O on 3,5 position, $J = 6.3$ Hz), 5.91 (s, 2H, *ortho* to NH_2); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_3CH_2), 26.1 ($CH_2CH_2CH_2O$), 29.4 ($CH_3CH_2CH_2CH_2$), 29.5 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.9 (CH_2CH_2O, 3,5 position), 30.3 (CH_2CH_2O, 4 position), 31.9 ($CH_3CH_2CH_2$), 68.8 (CH_2O, 3,5 position), 73.5 (CH_2O, 4 position), 94.3 (*ortho* to NH_2), 130.2 (*para* to NH_2), 142.3 (*ipso* to NH_2), 153.6 (*meta* to NH_2); elemental analysis calcd (%): C 78.07, H 12.33, N 2.17; found: C 78.28, H 12.67, N 2.12.

3,4,5-Tris(*n*-dodecan-1-yloxy)-1-aminobenzene (**3-18**): Compound **3-18** was synthesized by the same general procedure described for the synthesis of **3-12**. Compound **2-18** (12.0 g, 0.013 mol), $NH_2NH_2 \cdot H_2O$ (3.92 g, 0.078 mol), and graphite (11.1 g) were heated in reluxing EtOH (170 mL) for 24 h under an Ar atmosphere. After recrystalization from a $CHCl_3$/MeOH (1/1), 10.8 g (93.2 %) of a white powder was obtained. Purity (HPLC), 99+ %; m.p. 74–75 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.27$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 6.3$ Hz), 1.26 (overlapped m, 90H), 1.76 (m, 6H, CH_2CH_2O), 3.43 (bs, 2H, NH_2), 3.86 (t, 2H, CH_2O on 4 position, $J = 6.3$ Hz), 3.91 (t, 4H, CH_2O on 3,5 position, $J = 6.3$ Hz), 5.91 (s, 2H, *ortho* to NH_2); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_3CH_2), 26.1 ($CH_2CH_2CH_2O$), 29.4 ($CH_3CH_2CH_2CH_2$), 29.5 ($CH_3CH_2CH_2CH_2(CH_2)_{11}$), 29.9 ($CH_2CH_2O$, 3,5 position), 30.3 ($CH_2CH_2O$, 4 position), 31.9 ($CH_3CH_2CH_2$), 68.8 ($CH_2O$, 3,5 position), 73.5 ($CH_2O$, 4 position), 94.3 (*ortho* to NH_2), 130.2 (*para* to NH_2), 142.3 (*ipso* to NH_2), 153.6 (*meta* to NH_2).

Methyl 3,4,5-tris(*n*-butan-1-yloxy)benzoate (**4-4**): The synthesis of **4-4** was performed using a modification of a literature procedure.[18] A 500 mL three-neck flask containing a Teflon-coated magnetic stirrer was charged with methyl 3,4,5-trihydroxybenzoate (11.1 g, 0.06 mol), K_2CO_3 (51.0 g, 0.36 mol), and DMF (300 mL). The mixture was purged with N_2, then 1-bromobutane (32.9 g, 0.24 mol) was added dropwise. The reaction mixture was heated at 60 °C for 8 h with stirring under N_2, then it was cooled to room temperature. The reaction mixture was dissolved in Et_2O (400 mL) and transferred to a separatory funnel. The mixture was washed four times with H_2O (700 mL), once with dilute HCl (500 mL), and once with H_2O (500 mL). The organic phase was separated and dried over $MgSO_4$. The solvent was evaporated and the crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent to yield 15.2 g (69.0 %) of a liquid. Purity (HPLC), 99+ %; TLC (10/1 hexane/EtOAc): $R_f = 0.54$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.89$ (t, 9H, CH_3, $J = 6.3$ Hz), 1.29 (m, 6H, $CH_2(CH_2)_2OPh$), 1.75 (m, 6H, CH_2CH_2OPh), 3.90 (s, 3H, CO_2CH_3), 4.00 (m, 6H, CH_2OPh, $J = 6.3$ Hz), 7.24 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 20.7 (CH_2CH_3), 32.9 (CH_2CH_2OPh), 73.4 (CH_2OPh), 107.7 (*ortho* to CO_2CH_3), 124.6 (*ipso* to CO_2CH_3), 142.3 (*para* to CO_2CH_3), 152.8 (*meta* to CO_2CH_3), 166.9 ($PhCO_2CH_3$).

Methyl 3,4,5-tris(*n*-hexan-1-yloxy)benzoate (**4-6**): Compound **4-6** was synthesized by the same general procedure described for the synthesis of **4-4**. From methyl 3,4,5-trihydroxybenzoate (11.1 g, 0.06 mol), K_2CO_3 (51.0 g, 0.36 mol) and 1-bromohexane (39.6 g, 0.24 mol) in DMF (300 mL) at 60 °C, 19.7 g (72.6 %) of a liquid was obtained. Purity (HPLC), 99+ %; TLC (10/1 hexane/EtOAc): $R_f = 0.54$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.89$ (t, 9H, CH_3, $J = 6.2$ Hz), 1.27 (overlapped m, 18H, $CH_3(CH_2)_3$), 1.75 (m, 6H, CH_2CH_2OPh), 3.91 (s, 3H, CO_2CH_3), 4.02 (m, 6H, CH_2OPh, $J = 6.3$ Hz), 7.24 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 22.7 (CH_2CH_3), 26.2–30.1 ($(CH_2)_2$), 31.9 ($CH_2CH_2CH_3$), 52.0 (CO_2CH_3), 69.1 (CH_2OPh, *meta* to CO_2CH_3), 73.4 (CH_2OPh, *para* to CO_2CH_3), 107.7 (*ortho* to CO_2CH_3), 124.6 (*ipso* to CO_2CH_3), 142.3 (*para* to CO_2CH_3), 152.8 (*meta* to CO_2CH_3), 166.9 ($PhCO_2CH_3$).

Methyl 3,4,5-tris(*n*-decan-1-yloxy)benzoate (**4-10**): A 500 mL 3-*n*eck flask containing a Teflon-coated magnetic stirrer was charged with methyl 3,4,5-trihydroxybenzoate (5.5 g, 0.03 mol), K_2CO_3 (25.5 g, 0.18 mol) and DMF (170 mL). The mixture was sparged with N_2, then 1-bromodecane (26.5 g, 0.12 mol) was added dropwise. The reaction mixture was heated at 60 °C for 8 h with stirring under N_2 atmosphere, then it was cooled to RT and poured into ice/H_2O (1 L). The precipitate was filtered and the crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as an eluent. The product was recrystallized from acetone to yield 11.8 g (65.0 %) of white crystals. Purity (HPLC), 99+ %; m.p. 29–30 °C (ref. [28]: 29 °C); TLC (10/1 hexane/EtOAc): $R_f = 0.56$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 6.7$ Hz), 1.27 (overlapped m, 42H, $(CH_2)_7$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (t, 6H, CH_2OPh, $J = 6.2$ Hz), 7.25 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 22.6 (CH_2CH_3), 26.0–30.3 [$(CH_2)_6$], 31.9 ($CH_2CH_2CH_3$), 52.1 (CO_2CH_3), 69.1 (CH_2OPh, *meta* to CO_2CH_3), 73.4 (CH_2OPh, *para* to CO_2CH_3), 107.9 (*ortho* to CO_2CH_3), 124.6 (*ipso* to CO_2CH_3), 142.3 (*para* to CO_2CH_3), 152.7 (*meta* to CO_2CH_3), 166.8 ($PhCO_2CH_3$).

Methyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate (**4-12**): Compound **4-12** was synthesized by the same general procedure described for the synthesis of **4-10**. From methyl 3,4,5-trihydroxybenzoate (11.1 g, 0.06 mol), K_2CO_3 (51.0 g, 0.36 mol), and 1-bromododecane (60.3 g, 0.24 mol) in DMF (300 mL) at 60 °C, 30.3 g (73.3 %) of white crystals were obtained. Purity (HPLC), 99+ %; m.p. 43 °C (ref. [19]: 39–42.5 °C) ; TLC (10/1 hexane/EtOAc): $R_f = 0.56$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 6.3$), 1.27 (overlapped m, 54H, $(CH_2)_9$), 1.78 (m, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (m, 6H, CH_2OPh, $J = 6.3$), 7.25 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_2CH_3), 26.1–30.2 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 52.1 (CO_2CH_3), 69.1 (CH_2CH_2OPh), 73.4 (CH_2OPh), 107.7 (*ortho* to CO_2CH_3), 124.6 (*ipso* to CO_2CH_3), 142.3 (*para* to CO_2CH_3), 152.8 (*meta* to CO_2CH_3), 166.9 ($PhCO_2CH_3$).

Methyl 3,4,5-tris(*n*-octadecan-1-yloxy)benzoate (**4-18**): Compound **4-18** was synthesized by the same procedure described for the preparation of **4-10**. From methyl 3,4,5-trihydroxybenzoate (7.4 g, 0.04 mol), K_2CO_3 (33.2 g, 0.24 mol), and 1-bromooctadecane (46.6 g, 0.14 mol) in DMF (250 mL) at 60 °C, 27.1 g (72.1 %) of white crystals were obtained. Purity (HPLC), 99+ %; m.p. 61–62 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.56$; ^{1}H NMR

(200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 5.8$ Hz), 1.26 (overlapped m, 90H, $(CH_2)_{15}$), 1.80 (q, 6H, CH_2CH_2OPh), 3.89 (s, 3H, CO_2CH_3), 4.01 (t, 6H, CH_2OPh $J = 6.2$ Hz), 7.25 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 22.6 (CH_2CH_3), 26.1–30.5 ($(CH_2)_{13}$), 31.9 ($CH_2CH_2CH_3$), 52.2 (CO_2CH_3), 69.0 (CH_2CH_2OPh), 73.1 (CH_2OPh), 107.7 (*ortho* to CO_2CH_3), 124.6 (*ipso* to CO_2CH_3), 142.3 (*para* to CO_2CH_3), 152.8 (*meta* to CO_2CH_3), 167.0 ($PhCO_2CH_3$).

3,4,5-Tris(*n*-butan-1-yloxy)benzoic acid (5-4): The synthesis of **5-4** was performed by using a modification of a literature procedure.[18] In a 125 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar was placed **4-4** (14.0 g, 0.038 mol), 95 % EtOH (140 mL), and KOH (14.9 g, 0.27 mol). The mixture was refluxed for 2 h with stirring. The extent of reaction was followed by TLC. The reaction mixture was cooled to RT and the solution was acidified with dilute HCl to pH 1. The solution was poured into H_2O (1 L) to precipitate 12.9 g (96.2 %) of a white solid. Purity (HPLC), 99+ %; m.p. 62–63 °C (ref. [22b]: 65–67 °C); TLC (10/1 hexane/EtOAc): $R_f = 0$. ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.93$ (t, 9H, CH_3, $J = 6.7$ Hz), 1.52 (m, 6H, CH_3CH_2), 1.79 (m, 6H, CH_2CH_2OPh), 4.04 (m, 6H, CH_2OPh), 7.34 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 20.9 (CH_2CH_3), 32.9 (CH_2CH_2OPh), 73.2 (CH_2OPh), 107.9 (*ortho* to CO_2H), 124.7 (*ipso* to CO_2H), 142.5 (*para* to CO_2H), 152.8 (*meta* to CO_2H), 167.0 ($PhCO_2H$).

3,4,5-Tris(*n*-hexan-1-yloxy)benzoic acid (5-6): Compound **5-6** was synthesized by the same procedure described for the preparation of **5-4**. From **4-6** (17.2 g, 0.038 mol) and KOH (14.9 g, 0.27 mol) in 95 % EtOH (160 mL), 16.2 g (97.3 %) of a white solid was obtained. Purity (HPLC), 99+ %; m.p. 38–39 °C (ref. [22b]: 38–40 °C); TLC (10/1 hexane/EtOAc): $R_f = 0$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.86$ (t, 9H, CH_3, $J = 6.8$ Hz), 1.26 (m, 18H, $CH_3(CH_2)_3$), 1.75 (m, 6H, CH_2CH_2OPh), 3.99 (m, 6H, CH_2OPh), 7.33 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta =$ 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1–30.3 ($(CH_2)_2$), 31.6 ($CH_2CH_2CH_3$), 69.5 (CH_2CH_2OPh, *meta* to CO_2H), 73.5 (CH_2OPh, *para* to CO_2H), 107.9 (*ortho* to CO_2H), 124.7 (*ipso* to CO_2H), 142.5 (*para* to CO_2H), 152.8 (*meta* to CO_2H), 167.0 ($PhCO_2H$).

3,4,5-Tris(*n*-decan-1-yloxy)benzoic acid (5-10): Compound **5-10** was synthesized by the same procedure described for the preparation of **5-4**. From **4-10** (11.8 g, 19.5 mmol) and KOH (7.7 g, 0.14 mol) in 95 % EtOH (110 mL), 9.49 g (82.3 %) of a white solid was obtained. Purity (HPLC), 99+ %; m.p.51–52 °C (ref. [22b]: 53–54 °C); TLC (10/1 hexane/EtOAc): $R_f = 0$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J =$ 6.9 Hz) 1.27 (overlapped m, 36H, $(CH_2)_6$), 1.47 (m, 6H, $CH_2CH_2CH_2OPh$), 1.79 (m, 6H, CH_2CH_2OPh), 4.02 (m, 6H, CH_2OPh), 7.32 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_2CH_3), 26.1–30.3 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 69.1 (CH_2CH_2OPh, *meta* to CO_2H), 73.5 (CH_2OPh, *para* to CO_2H), 108.6 (*ortho* to CO_2H), 123.7 (*ipso* to CO_2H), 143.1 (*para* to CO_2H), 152.8 (*meta* to CO_2H), 172.2 ($PhCO_2H$).

3,4,5-Tris(*n*-dodecan-1-yloxy)benzoic acid (5-12): Compound **5-12** was synthesized by the same procedure described for the preparation of **5-4**. From **4-12** (5.1 g, 7.3 mmol) and KOH (2.9 g, 51.1 mmol) in 95 % EtOH (40 mL), 4.7 g (95.3 %) of a white solid was obtained. Purity (HPLC), 99+ %; m.p. 60–61 °C (ref. [16]: 60 °C); TLC (10/1 hexane/EtOAc): $R_f = 0$. ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 9H, CH_3, $J = 6.7$ Hz), 1.26 (overlapped m, 54H, $(CH_2)_9$), 1.79 (m, 6H, CH_2CH_2OPh), 4.02 (m, 6H, CH_2OPh), 7.32 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta =$ 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1–30.2 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 69.2 (CH_2CH_2OPh), 73.6 (CH_2OPh), 108.5 (*ortho* to CO_2H), 123.7 (*ipso* to CO_2H), 143.1 (*para* to CO_2H), 152.9 (*meta* to CO_2H), 172.2 ($PhCO_2H$).

3,4,5-Tris (*n*-octadecan-1-yloxy)benzoic acid (5-18): Compound **5-18** was synthesized by the same procedure described for the preparation of **5-4**. From **4-18** (25.1 g, 0.026 mol) and KOH (11.7 g, 0.21 mol) in 95 % EtOH (250 mL), 24.2 g (95.3 %) of a white solid was obtained. Purity (HPLC), 99+ %; m.p. 83–84 °C; TLC (10/1 hexane/EtOAc): $R_f = 0$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t,9H, CH_3, $J = 5.6$ Hz), 1.26 (m, 90H, $CH_3(CH_2)_{15}$), 1.79 (q, 6H, $ArOCH_2CH_2$), 4.02 (t, 6H, $ArOCH_2$, $J =$ 6.2 Hz), 7.31 (s, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta =$ 14.0 (CH_3), 22.6 (CH_2CH_3), 26.1–30.5 ($(CH_2)_{13}$), 31.9 ($CH_2CH_2CH_3$), 69.0 (CH_2CH_2OPh), 73.1 (CH_2OPh), 107.7 (*ortho* to CO_2H), 124.6 (*ipso* to CO_2H), 142.3 (*para* to CO_2H), 152.8 (*meta* to CO_2H), 172.0 ($PhCO_2H$).

3,4,5-Tris(*n*-alkan-1-yloxy)benzoyl chloride (6-*n*): A two-neck round-bottom flask with a Teflon-coated magnetic stirrer was charged with **5-*n*** (1.0 equiv), CH_2Cl_2, and a catalytic amount of DMF. The reaction flask was flushed with N_2, sealed with a rubber septum, and cooled in an ice bath. $SOCl_2$ (1.1 equiv) was added dropwise to the cooled reaction mixture. The ice bath was removed and the reaction mixture was stirred for 1 h. The solvent was evaporated and the resulting compound was dried under vacuum. The product was used for the next step without further purification.

***N*-[3,4,5-tris(*n*-butan-1-yloxy) phenyl]-3,4,5-tris (*n*-dodecan-1-yloxy)benzamide (7-12/4)**: A solution of **3-12** (2.6 g, 4.0 mmol) and **6-4** (1.6 g, 4.0 mmol) in pyridine (80 mL) were refluxed for 2 h. The pale brown mixture was poured onto ice/H_2O, extracted with Et_2O, and washed several times with 5 % and concentrated HCl. The crude product was recrystallized twice from isopropanol to yield 3.2 g (80.3 %) of light brown crystals. Purity (HPLC), 99+ %; m.p. 76 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.17$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH_3, $J = 6.1$ Hz), 1.26 (overlapped m, 60H, $CH_3(CH_2)_9$ and CH_3CH_2), 1.79 (m, 12H, $PhOCH_2CH_2$), 3.91 (m, 12H, $PhOCH_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.72 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.0$ (CH_3), 20.9, 22.7 (CH_2CH_3), 26.1 ($CH_2CH_2CH_2OPh$), 29.4–32.9 (CH_2CH_2OPh and $(CH_2)_7CH_2CH_3$), 69.0, 69.3 (CH_2OPh), 99.2 (*ortho* to NHCO), 105.9 (*ortho* to CONH), 124.7 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 141.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.1 (CONH).

***N*-[3,4,5-tris(*n*-hexan-1-yloxy)phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)benzamide (7-12/6)**: Compound **7-12/6** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-12** (2.6 g, 4.0 mmol) and **6-6** (2.2 g, 4.0 mmol) in pyridine (80 mL), 3.2 g (76.3 %) of light brown crystals were obtained. Purity (HPLC), 99+ %; thermal transitions and corresponding enthalpy changes are summarized in Table 1; TLC (10/1 hexane/EtOAc): $R_f = 0.17$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH_3, $J = 5.9$ Hz), 1.26 (overlapped m, 72H, $CH_3(CH_2)_9$ and $CH_3(CH_2)_3$), 1.80 (m, 12H, $PhOCH_2CH_2$), 3.90 (m, 12H, $PhOCH_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.72 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_2CH_3), 26.1 ($CH_2CH_2CH_2OPh$), 28.9–32.6 ($CH_2CH_2CH_3$ and $(CH_2)_7CH_2CH_3$), 69.2, 69.6 (CH_2OPh), 99.8 (*ortho* to NHCO), 106.4 (*ortho* to CONH), 125.1 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.8 (CONH); elemental analysis calcd (%): C 76.62, H 11.55, N 1.32; found: C 76.54, H 11.49, N 1.22.

***N*-[3,4,5-tris(*n*-decan-1-yloxy)phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)benzamide (7-12/10)**: Compound **7-12/10** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-12** (2.6 g, 4.0 mmol) and **6-10** (2.5 g, 4.0 mmol) in pyridine (80 mL), 3.9 g (79.8 %) of light brown crystals were obtained. Purity (HPLC), 99+ %; thermal transitions and corresponding enthalpy changes are summarized in Table 1; TLC (10/1 hexane/EtOAc): $R_f = 0.19$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta =$ 0.88 (t, 18H, CH_3, $J = 6.0$ Hz), 1.27 (overlapped m, 96H, $CH_3(CH_2)_9$ and $CH_3(CH_2)_7$), 1.82 (m, 12H, $PhOCH_2CH_2$), 3.91 (m, 12H, $PhOCH_2$), 6.91 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.74 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.7 (CH_2CH_3), 26.0 ($CH_2CH_2CH_2OPh$), 28.9–32.6 ($(CH_2)_5CH_2CH_3$ and $(CH_2)_7CH_2CH_3$), 69.2, 69.6 (CH_2OPh), 99.8 (*ortho* to NHCO), 106.4 (*ortho* to CONH), 125.1 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.8 (CONH); elemental analysis calcd (%): C 77.91, H 11.93, N 1.17; found: C 78.03, H 11.71, N 1.06.

***N*-[3,4,5-tris(*n*-dodecan-1-yloxy)phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)benzamide (7-12/12)**: Compound **7-12/12** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-12** (2.6 g, 4.0 mmol) and **6-12** (2.8 g, 4.0 mmol) in pyridine (80 mL), 4.2 g (80.1 %) of light brown crystals were obtained. Purity (HPLC), 99+ %; thermal transitions and corresponding enthalpy changes are summarized in Table 1; TLC (10/1 hexane/EtOAc): $R_f = 0.19$; ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH_3, $J = 5.6$ Hz), 1.26 (m, 108H, $CH_3(CH_2)_9$), 1.79 (m, 12H, $PhOCH_2CH_2$), 3.91 (m, 12H, $PhOCH_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.72 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 22.8 (CH_2CH_3), 26.2 ($CH_2CH_2CH_2OPh$), 28.4–32.6 ($(CH_2)_7CH_2CH_3$), 69.3, 69.6 (CH_2OPh), 99.8 (*ortho* to NHCO), 106.5 (*ortho* to CONH), 125.1 (*ipso* to CONH), 133.5, 134.9 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.0,

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153.3 (*meta* to CONH and NHCO), 167.0 (*C*ONH); elemental analysis calcd (%): C 78.43, H 12.13, N 1.10; found: C 78.28, H 12.07, N 1.12.

***N*-[3,4,5-tris(*n*-octadecan-1-yloxy)phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)-benzamide (7-12/18)**: Compound **7-12/18** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-12** (2.6 g, 4.0 mmol) and **6-18** (3.8 g, 4.0 mmol) in pyridine (80 mL), 4.5 g (72.1%) of light brown crystals were obtained. Purity (HPLC), 99+%; thermal transitions and corresponding enthalpy changes are summarized in Table 1; TLC (10/1 hexane/EtOAc): $R_f = 0.20$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH$_3$, $J = 5.6$ Hz), 1.26 (m, 144H, CH$_3$(C*H*$_2$)$_9$ and CH$_3$(C*H*$_2$)$_{15}$), 1.79 (m, 12H, ArOCH$_2$C*H*$_2$), 3.99 (m, 12H, ArOC*H*$_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.58 (s, 1H, N*H*); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_3$), 22.8 (*C*H$_2$CH$_3$), 26.2 (*C*H$_2$CH$_2$CH$_2$OPh), 28.4–32.6 ((*C*H$_2$)$_7$CH$_2$CH$_3$ and (*C*H$_2$)$_{13}$CH$_2$CH$_3$), 69.6 (*C*H$_2$OPh), 99.8 (*ortho* to NHCO), 106.5 (*ortho* to CONH), 125.1 (*ipso* to CONH), 134.5 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.2 (*meta* to CONH and NHCO), 167.0 (CONH); elemental analysis calcd (%): C 79.51, H 12.43, N 0.93; found: C 79.28, H 12.67, N 1.12.

***N*-[3,4,5-tris(*n*-butan-1-yloxy)phenyl]-3,4,5-tris(*n*-octadecan-1-yloxy)benzamide (7-18/4)**: Compound **7-18/4** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-18** (3.6 g, 4.0 mmol) and **6-4** (1.6 g, 4.0 mmol) in pyridine (80 mL), 3.7 g (74.1%) of light brown crystals were obtained. Purity (HPLC), 99+%; m.p. 74 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.17$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH$_3$, $J = 6.1$ Hz), 1.26 (overlapped m, 96H, CH$_3$(C*H*$_2$)$_{15}$ and CH$_3$C*H*$_2$), 1.79 (m, 12H, PhOCH$_2$C*H*$_2$), 3.91 (m, 12H, PhOC*H*$_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.72 (s, 1H, NH); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.0$ (*C*H$_3$), 20.9, 22.7 (*C*H$_2$CH$_3$), 26.1 (*C*H$_2$CH$_2$CH$_2$OPh), 29.4–32.9 (*C*H$_2$CH$_2$OPh and (*C*H$_2$)$_{13}$CH$_2$CH$_3$), 69.0, 69.3 (*C*H$_2$OPh), 99.2 (*ortho* to NHCO), 105.9 (*ortho* to CONH), 124.7 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 141.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.1 (CONH).

***N*-[3,4,5-tris(*n*-hexan-1-yloxy)phenyl]-3,4,5-tris(*n*-octadecan-1-yloxy)benzamide (7-18/6)**: Compound **7-18/6** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-18** (3.6 g, 4.0 mmol) and **6-6** (2.2 g, 4.0 mmol) in pyridine (80 mL), 4.7 g (79.3%) of light brown crystals were obtained. Purity (HPLC), 99+%; m.p. 67 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.18$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, C*H*$_3$, $J = 5.9$ Hz), 1.26 (overlapped m, 108H, CH$_3$(C*H*$_2$)$_{15}$ and CH$_3$(C*H*$_2$)$_3$), 1.80 (m, 12H, PhOCH$_2$C*H*$_2$), 3.90 (m, 12H, PhOC*H*$_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.72 (s, 1H, N*H*); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_3$), 22.7 (*C*H$_2$CH$_3$), 26.1 (*C*H$_2$CH$_2$CH$_2$OPh), 28.9–32.6 (*C*H$_2$CH$_2$CH$_3$and (*C*H$_2$)$_{13}$CH$_2$CH$_3$), 69.2, 69.6 (*C*H$_2$OPh), 99.8 (*ortho* to NHCO), 106.4 (*ortho* to CONH), 125.1 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.8 (CONH).

***N*-[3,4,5-tris(*n*-decan-1-yloxy)phenyl]-3,4,5-tris(*n*-octadecan-1-yloxy)benzamide (7-18/10)**: Compound **7-18/10** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-18** (3.6 g, 4.0 mmol) and **6-10** (2.5 g, 4.0 mmol) in pyridine (80 mL), 4.8 g (81.1%) of light brown crystals were obtained. Purity (HPLC), 99+%; m.p. 70 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.19$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, C*H*$_3$, $J = 6.0$ Hz), 1.27 (overlapped m, 132H, CH$_3$(C*H*$_2$)$_{15}$ and CH$_3$(C*H*$_2$)$_7$), 1.82 (m, 12H, PhOCH$_2$C*H*$_2$), 3.91 (m, 12H, PhOC*H*$_2$), 6.91 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.74 (s, 1H, N*H*); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_3$), 22.7 (*C*H$_2$CH$_3$), 26.0 (*C*H$_2$CH$_2$CH$_2$OPh), 28.9–32.6 ((*C*H$_2$)$_5$CH$_2$CH$_3$ and (*C*H$_2$)$_{13}$CH$_2$CH$_3$), 69.2, 69.6 (*C*H$_2$OPh), 99.8 (*ortho* to NHCO), 106.4 (*ortho* to CONH), 125.1 (*ipso* to CONH), 133.8, 134.9 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.1, 153.3 (*meta* to CONH and NHCO), 166.8 (CONH).

***N*-[3,4,5-tris(*n*-octadecan-1-yloxy)phenyl]-3,4,5-tris(*n*-octadecan-1-yloxy)-benzamide (7-18/18)**: Compound **7-18/18** was synthesized by the same procedure described for the preparation of **7-12/4**. From **3-18** (3.6 g, 4.0 mmol) and **6-18** (3.8 g, 4.0 mmol) in pyridine (80 mL), 5.5 g (75.1%) of light brown crystals were obtained. Purity (HPLC), 99+%; m.p. 94 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.19$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH$_3$, $J = 5.6$ Hz), 1.26 (m, 180H, CH$_3$(C*H*$_2$)$_{15}$), 1.79 (m, 12H, ArOCH$_2$C*H*$_2$), 3.99 (m, 12H, ArOCH$_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.58 (s, 1H, N*H*); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_3$), 22.8 (*C*H$_2$CH$_3$), 26.2 (*C*H$_2$CH$_2$CH$_2$OPh), 28.4–32.6 ((*C*H$_2$)$_{13}$CH$_2$CH$_3$), 69.6 (*C*H$_2$OPh), 99.8 (*ortho* to NHCO), 106.5 (*ortho* to CONH), 125.1 (*ipso* to CONH), 134.5 (*para* to CONH and NHCO), 142.4 (*ipso* to NHCO), 153.2 (*meta* to CONH and NHCO), 167.0 (CONH).

Methyl *N*-[3,4,5-tris(*n*-octadecan-1-yloxy)phenyl]-3,4,5-tris(*n*-dodecan-1-yloxy)benzamide (8-12/18): A flame-dried apparatus consisting of a round bottom flask equipped with an additional funnel, N$_2$ inlet–outlet and magnetic stirrer was cooled under a flow of N$_2$. The apparatus was charged with anhydrous THF (15 mL) suspension of NaH, 80% in mineral oil (15.6 mg, 0.65 mmol) and a catalytic amount of DMSO. **7-12/18** (1.0 g, 0.65 mmol) in anhydrous THF (15 mL) was added dropwise. After 3 h, CH$_3$I (0.11 g, 0.78 mmol) was added dropwise. During the reaction, aliquots were removed for ^{1}H NMR analysis (δ 7.58 (CONH) disappears, δ 3.43 (CONH$_3$) appears). After 3 h, the reaction was complete. The reaction mixture was added dropwise into H$_2$O (50 mL) and stirred for 30 min. The precipitate was filtered, washed 3 times with dilute HCl and recrystallized from isopropanol to yield 0.78 g (77.7%) of light brown crystals. Purity (HPLC), 99+%; m.p. 32 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.25$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 0.88$ (t, 18H, CH$_3$, $J = 5.6$ Hz), 1.26 (m, 144H, CH$_3$(C*H*$_2$)$_9$ and CH$_3$(C*H*$_2$)$_{15}$), 1.79 (m, 12H, ArOCH$_2$C*H*$_2$), 3.43 (s, 3H, CONCH$_3$), 3.99 (m, 12H, ArOC*H*$_2$), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 14.1$ (CH$_3$), 22.8 (*C*H$_2$CH$_3$), 26.2 (*C*H$_2$CH$_2$CH$_2$OPh), 28.4–32.6 ((*C*H$_2$)$_7$CH$_2$CH$_3$ and (*C*H$_2$)$_{13}$CH$_2$CH$_3$), 34.7 (CON*C*H$_3$), 69.6 (*C*H$_2$OPh), 99.8 (*ortho* to N(CH$_3$)CO), 106.5 (*ortho* to CONCH$_3$), 125.1 (*ipso* to CONCH$_3$), 134.5 (*para* to CONCH$_3$ and N(CH$_3$)CO), 142.4 (*ipso* to N(CH$_3$)CO), 153.2 (*meta* to CONCH$_3$ and N(CH$_3$)CO), 164.0 (CONCH$_3$).

3,4-Isopropyliden-5-hydroxymethylbenzoate (10): Compound, **10** was synthesized according to a literature procedure.[21] From 3,4,5-trihydroxy methylbenzoate (36.8 g, 0.2 mol) and P$_2$O$_5$ (42.6 g, 0.3 mol) in acetone was obtained 17.1 g (38.2%) of a white powder. Purity (HPLC), 99+%; m.p. 114–115 °C (ref. [21]: 114–116 °C) ; TLC (20/1 hexane/EtOAc): $R_f = 0.26$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 1.71$ (s, 6H, C(C*H*$_3$)$_2$), 3.87 (s, 3H, CO$_2$CH$_3$), 5.37 (s, 1H, OH), 7.01 (d, 1H, 2-position, $J = 1.5$ Hz), 7.31 (d, 1H, 6-position, $J = 1.6$ Hz).

3,4-Isopropyliden-5-(1-hydroxyundecan)methylbenzoate (11): Compound **11** was synthesized by the etherification of **10** with 1-bromoundecanol. To a round-bottom flask equipped with a N$_2$ inlet–outlet containing a mixture of **10** (5.0 g, 22 mmol) and anhydrous K$_2$CO$_3$ (6.9 g, 50 mmol) in DMF (90 mL) at 60 °C, 1-bromoundecanol (6.2 g, 26 mmol) was added in small portions. After 4 h, the reaction mixture was poured into ice/H$_2$O (1 L), followed by acidification with concentrated HCl to pH 2. The yellow, oily compound was filtered and vacuum-dried for 6 h to give 7.0 g (83.4%) of a yellow waxy compound. Purity (HPLC), 98.5%; TLC (10/1 hexane/EtOAc): $R_f = 0.47$; ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 1.29$ (m, 14H, PhOCH$_2$CH$_2$(C*H*$_2$)$_7$), 1.56 (q, 2H, HOCH$_2$C*H*$_2$, $J = 6.5$ Hz), 1.71 (s, 6H, C(CH$_3$)$_2$), 1.80 (q, 2H, PhOCH$_2$C*H*$_2$), 3.63 (t, 2H, HOC*H*$_2$, $J = 6.6$ Hz), 3.86 (s, 3H, CO$_2$CH$_3$), 4.07 (t, 2H, PhOC*H*$_2$, $J = 6.8$ Hz), 7.10 (d, 1H, 2-position, $J = 1.4$ Hz), 7.27 (d, 1H, 6-position, $J = 1.5$ Hz).

3,4-Dihydroxy-5-(1-hydroxyundecan)alkylbenzoate (12): Over a mixture of **11** (6.0 g, 15 mmol) and pure EtOH (90 mL), 12 N HCl (15 mL) was added. The mixture was refluxed for 2 h and poured onto ice/H$_2$O (800 mL). The resulting white solid was filtered and recrystallized from CH$_2$Cl$_2$ and hexane to yield 5.0 g (93.2%) of a mixture containing 4% methylbenzoate and 96% ethylbenzoate. Purity (HPLC), 99+%; m.p. 91–92 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta = 1.22$ (m, 14H, PhOCH$_2$CH$_2$(C*H*$_2$)$_7$), 1.48 (q, 2H, HOCH$_2$C*H*$_2$, $J = 6.6$ Hz), 1.74 (q, 2H, PhOCH$_2$C*H*$_2$, $J = 7.2$ Hz), 3.54 (t, 2H, HOC*H*$_2$, $J = 6.6$ Hz), 3.79 (s, 3H, CO$_2$CH$_3$), 3.99 (t, 2H, PhOC*H*$_2$, $J = 6.7$ Hz), 4.23 (q, 2H, CO$_2$C*H*$_2$CH$_3$, $J = 7.1$ Hz), 7.09 (d, 1H, 2-position, $J = 1.8$ Hz), 7.23 (d, 1H, 6-position, $J = 1.9$ Hz).

3,4-Didodecyloxy-5-(1-hydroxyundecan)alkylbenzoate (13): To a round-bottom flask equipped with a N$_2$ inlet–outlet containing a mixture of **12** (4.5 g, 13 mmol) and K$_2$CO$_3$ (7.6 g, 55 mmol) in DMF (70 mL) at 60 °C, 1-bromododecane (6.8 g, 27 mmol) was added. After 4 h, the reaction mixture was poured onto ice/H$_2$O (1 L). The resulting light brown solid was filtered and purified by precipitation from THF solution into MeOH to yield 6.3 g (72.8%) of a white waxy compound. Purity (HPLC), 99+%; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.87$ (m, 6H, CH_3), 1.26 (m, 50H, $PhOCH_2CH_2(CH_2)_7$), 1.46 (m, 2H, $HOCH_2CH_2$), 1.77 (m, 6H, $PhOCH_2CH_2$), 3.63 (t, 2H, $HOCH_2$, $J = 6.6$ Hz), 3.97 (s, 3H, $COOCH_3$), 4.01 (t, 6H, $PhOCH_2$, $J = 6.5$ Hz), 4.33 (q, 2H, $COOCH_2CH_3$, $J = 7.1$ Hz), 7.25 (s, 2H, *ortho* to CO_2).

3,4-Didodecyloxy-5-(1-hydroxyundecan)benzoic acid (14): A solution of KOH (3.4 g, 60 mmol) in H_2O (6 mL) was added to a mixture of **13** (6.0 g, 8.7 mmol) in EtOH (54 mL). The mixture was refluxed for 3 h, then acidified with concentrated HCl. After refluxing for 15 min, the reaction mixture was poured onto ice/H_2O (1 L). The product was filtered and recrystallized from hexane/CH_2Cl_2 (10/1) to yield 5.8 g (98.2%) of white crystals. Purity (HPLC), 99+%; m.p. 52–53 °C; TLC (10/1 hexane/EtOAc): $R_f = 0$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (m, 6H, CH_3), 1.29 (m, 50H, $PhOCH_2CH_2(CH_2)_7$), 1.47 (m, 2H, $HOCH_2CH_2$), 1.77 (m, 6H, $PhOCH_2CH_2$), 3.61 (t, 2H, $HOCH_2$, $J = 6.4$ Hz), 4.01 (m, 6H, $PhOCH_2$), 7.33 (s, 2H, *ortho* to CO_2).

3,4-Didodecyloxy-5-(1-*m*ethacryloyloxyundecanyloxy)benzoic acid (16): To a 100 mL flask, **14** (5.0 g, 7.4 mmol), dry CH_2Cl_2 (30 mL), and dry pyridine (0.9 mL, 73.8 mmol) were added. Methacryloyl chloride (1.3 g, 12.6 mmol) was added dropwise at 0 °C and the reaction was stirred at room temperature for 3 h. To the reaction mixture, H_2O was added, and the product was extracted with CH_2Cl_2. The solution was dried over $MgSO_4$ and the solvent was distilled in a rotary evaporator. The resulting product was heated for 10 min in pyridine (50 mL) and H_2O (15 mL) to cleave the mixed ester anhydride **15**. After acidification with dilute HCl, the mixture was extracted by Et_2O. The organic layer was washed with a solution of $NaHCO_3$ and dried over anhydrous $MgSO_4$. The solvent was distilled in a rotary evaporator and the product was recrystallized from MeOH/$CHCl_3$ (1/2) to give 2.3 g (41.0%) of white crystals. Purity (HPLC), 99+%; m.p. 49–50 °C; TLC (10/1 hexane/EtOAc): $R_f = 0$. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (m, 6H, CH_3), 1.26 (m, 50H, $PhOCH_2CH_2(CH_2)_7$), 1.53 (m, 2H, $CO_2CH_2CH_2$), 1.70 (m, 6H, $PhOCH_2CH_2$), 1.94 (m, 3H, $CH_3C{=}CH_2$), 3.96 (m, 6H, $PhOCH_2$), 4.13 (t, 2H, CO_2CH_2, $J = 6.7$ Hz), 5.54 (s, 1H, $C{=}CH_2$,*trans*), 6.10 (s, 1H, $C{=}CH_2$, *cis*), 7.29 (s, 2H, *ortho* to CO_2); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 18.3 ($CH_2{=}C(CH_3)$), 22.7 (CH_2CH_3), 26.1–30.2 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 66.1 (CO_2CH_2), 69.3 (CH_2CH_2OPh), 73.7 (CH_2OPh), 110.0 (*ortho* to CO_2H), 122.7 ($CH_2{=}C(CH_3)$), 127.3 (*ipso* to CO_2H), 138.1 ($CH_2{=}C(CH_3)$), 144.7 (*para* to CO_2H), 152.9 (*meta* to CO_2H), 172.2 (CO_2H).

3,4-Didodecyloxy-5-(1-*m*ethacryloxyundecan)benzoyl chloride (17): Into a round-bottom flask equipped with magnetic stirrer, compound **16** (2.0 g, 2.7 mmol) was dissolved in dry CH_2Cl_2 (11 mL). Dry DMF (two drops) was added and the solution was stirred for 5 min. $SOCl_2$ (1.0 mL, 5.4 mmol) was slowly added to the reaction mixture over several min. An aliquot was analyzed by ^{13}C NMR spectroscopy ($\delta = 172.2$ ($PhCO_2H$) disappears, $\delta = 167.7$ (PhCOCl) appears), indicating complete conversion at the end of the addition. The solvent was removed on a rotary evaporator at room temperature and the residual $SOCl_2$ was removed under vacuum for 4 h at room temperature to yield 2.0 g (96.3%) of a light yellow solid. Compound **17** was used immediately in the next step without further purification. Purity (HPLC), 99+%; m.p. 40–42 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (m, 6H, CH_3), 1.26 (m, 50H, $PhOCH_2CH_2(CH_2)_7$), 1.47 (m, 2H, $CO_2CH_2CH_2$), 1.70 (m, 6H, $PhOCH_2CH_2$), 1.94 (m, 3H, $CH_3C{=}CH_2$), 3.99 (m, 6H, $PhOCH_2$), 4.14 (t, 2H, CO_2CH_2, $J = 6.7$ Hz), 5.54 (s, 1H, $C{=}CH_2$,*trans*), 6.10 (s, 1H, $C{=}CH_2$, *cis*), 7.33 (s, 2H, *ortho* to CO_2); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 18.3 ($CH_2{=}C(CH_3)$), 22.7 (CH_2CH_3), 26.1–30.2 ($(CH_2)_7$), 31.9 ($CH_2CH_2CH_3$), 66.1 (CO_2CH_2), 69.3 (CH_2CH_2OPh), 73.7 (CH_2OPh), 110.0 (*ortho* to COCl), 122.7 ($CH_2{=}C(CH_3)$), 127.3 (*ipso* to COCl), 138.1 ($CH_2 = C(CH_3)$), 144.7 (*para* to COCl), 152.9 (*meta* to COCl), 167.7 (COCl).

***N*-[3,4-Didodecyloxy-5-(1-*m*ethacryloxyundecan)phenyl]3,4,5-tris(*n*-dodecan-1-yloxy)benzamide (18)**: Compound **18** was synthesized according to the general procedure described for **7–2/12** at 60 °C for 4 h, starting from **3-12** (1.3 g, 2.0 mmol), **17** (1.5 g, 2.0 mmol), and pyridine (30 mL). The resulting brown solid was purified by column chromatography (SiO_2, hexane/EtOAc 10/1) to yield 1.7 g (60.9%) of a white solid. Purity (HPLC), 99+%; m.p. 73–74 °C; TLC (10/1 hexane/EtOAc): $R_f = 0.33$; ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 0.88$ (m, 15H, CH_3), 1.26 (m, 104H, $PhOCH_2CH_2(CH_2)_7$), 1.58 (m, 2H, $CO_2CH_2CH_2$), 1.78 (m, 12H, $PhOCH_2CH_2$), 1.94 (m, 3H, $CH_3C{=}CH_2$), 3.98 (m, 12H, $PhOCH_2$), 4.13 (t, 2H, $COOCH_2$, $J = 6.6$ Hz), 5.54 (s, 1H, $C{=}CH_2$,*trans*), 6.09 (s, 1H, $C{=}CH_2$, *cis*), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to COHN), 7.61 (s, 1H, NHCO); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 14.1$ (CH_3), 18.2 ($CH_2{=}C(CH_3)CO$), 22.8 (CH_2CH_3), 26.2 ($CH_2CH_2CH_2OPh$), 28.4–32.6 ($(CH_2)_7CH_2CH_3$), 65.9 (CO_2CH_2), 69.3, 69.6 (CH_2OPh), 99.8 (*ortho* to NHCO), 106.5 (*ortho* to CONH), 122.2 ($CH_2{=}C(CH_3)CO$), 125.1 (*para* to CONH), 129.9 (*ipso* to CONH), 133.5 (*para* to NHCO), 138.0 ($CH_2 = C(CH_3)CO$), 140.5 (*ipso* to NHCO), 153.2, 153.4 (*meta* to CONH and NHCO), 165.0 ($CH_2{=}C(CH_3)CO$), 165.5 (CONH); elemental analysis calcd (%): C 77.03, H 11.51, N 1.03; found: C 76.95, H 11.38, N 1.12.

Free radical polymerization of 18

Method A: Compound **18** (1.8 g, 1.31 mmol), AIBN (18 mg, 1 wt%), and dry benzene (3.0 mL) were introduced in a Schlenk tube. The solution was degassed by four freeze-pump-thaw cycles and the polymerization mixture was heated at 60 °C under N_2. After 18 h, the resulting polymer was diluted with hexanes and purified from unconverted monomer by column chromatography (SiO_2, hexanes). Finally, the purified polymer **19** was dissolved in CH_2Cl_2 and was precipitated in cold MeOH to yield 1.56 g (87%) of a light yellow solid; $M_n = 55095$ and $M_w/M_n = 1.64$ (GPC with polystyrene standards).

Method B: Compound **18** (1.0 g, 0.73 mmol), AIBN (10 mg, 1 wt%), and dry benzene (1.2 mL) were introduced in a Schlenk tube. The solution was degassed by four freeze-pump-thaw cycles and the polymerization mixture was heated at 60 °C under N_2. After 2 h, the increase in the viscosity of the reaction mixture made stirring impossible. The resulting polymer was dissolved in $CHCl_3$ and was precipitated into methanol. The polymer **19** was purified from unconverted monomer by column chromatography (SiO_2, hexanes) to yield 0.9 g (89.3%) of a light yellow solid; $M_n = 58800$ and $M_w/M_n = 2.16$ (GPC with polystyrene standards).

Preparation of the binary mixtures of 7-12/12 with 19: Mixtures of **7-12/12** and **19** were prepared by weighing the individual components in glass vials, then adding dry CH_2Cl_2 to give an equal final volume of a homogeneous solution. Then solvent was removed under a gentle stream of dry N_2 and the vials were placed under vacuum for 12 h at 20 °C before thermal analysis. Annealed samples were prepared under vacuum at 55 °C for 12 h before thermal analysis.

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