Plastic- and liquid-crystalline architectures from dendritic receptor molecules

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Host molecules with U-shaped receptor cavities have been derivatized at their convex side with two n-hydrocarbon tails (1), two first-generation (2), and two second-generation (3) monodendritic hydrocarbon tails. Although hosts 1 and 2 display plastic-crystalline behavior, evidence suggests that host 3 forms a cubic liquid-crystalline phase. In this phase, molecules of 3 are arranged in spherical supramacromolecular assemblies, in which the receptor cavities are situated in the core and the hydrocarbon tails at the periphery. The 1:1 host-guest complex of 3 with methyl 3,5-dihydroxybenzoate forms a similar liquid-crystalline phase, with the guest included in the core of the assemblies.

The development of dendrimers (1–5) has provided present-day chemistry with a wealth of new possibilities in the construction of macromolecular architectures with well-defined and predictable sizes and shapes. Initially, dendrimers were prepared by using covalent bonding between the different generations. Many convergent and divergent synthetic routes have been developed, in which the convergent approach especially is successful in achieving a high purity and monodispersity of the macromolecules (6, 7). Recent alternative approaches involve the coupling of the generations of the dendrimer by metal coordination, to give "metallodendrimers" (8, 9). The spherical shape of dendrimers is thought to exist in solution, but little is known about their shape in the solid state, although this physical parameter is undoubtedly of great influence on their unique physical properties. In the melt and the solid state, a variety of techniques has suggested that the molecules can adopt either spherical (10–12) or rod-like (13) shapes. These techniques, however, cannot easily discriminate between discrete molecules and their aggregates. A completely different and relatively new approach in dendrimer construction involves the formation of the macromolecules in a "supramacromolecular" way, i.e., by means of self-assembly of relatively small, but well-defined, building blocks, so-called "monodendrons." During the past decade, the Percec group has extensively studied this new research area (14–17). A monodendron structure is used that is based on the gallic acid (3,4,5-trihydroxybenzoic acid) building block. It has been demonstrated that derivatives of this molecule can self-assemble into predictable macroscopic structures in the crystalline and liquid-crystalline state. The molecular order in these assemblies has been analyzed by x-ray diffraction techniques, which can provide direct information about the size and the three-dimensional shape of the constituting monodendritic building blocks (14, 15). The shape of the monodendrons was predicted with the help of molecular modeling calculations and confirmed by ^{1}H NMR measurements (16). The first-generation monodendron, a gallic acid substituted with three dodecyl groups (Fig. 1), forms a flat, tapered disk. Its tapered shape (comparable to a slice of pizza) is expressed in the supramolecular architectures formed by this compound upon self-assembly: upon heating to the isotropic melt, the molecules organize themselves into columnar structures, which further arrange into a hexagonal lattice (17). The coupling of three of these tapered building blocks to another gallic acid derivative yields the second-generation monodendron (Fig. 1). In this molecule, for steric reasons only a restricted and cooperative rotation of the benzyl ether groups is allowed, which requires the two external benzyl ether moieties to be positioned orthogonal to the internal one, resulting in an overall conical shape. Upon cooling from the isotropic melt, these conical monodendrons self-assemble into spherical structures, which have become known as supramolecular dendrimers. These can organize further into a cubic liquid-crystalline lattice (16). In contrast to the wide abundance of lyotropic systems that exhibit such a cubic symmetry (18, 19), there are relatively few examples known of thermotropic systems exhibiting cubic phases (20–24).

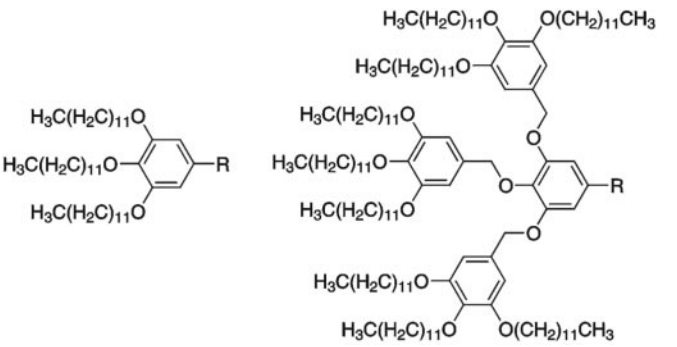

Fig. 1. Structures of first- and second-generation monodendrons based on the gallic acid building block [R = COOH or C(O)OCH$_3$].

The utility of focal point substituted dendrimers has been demonstrated in a variety of research topics, e.g., solvatochromism (25), self-assembly (26), and the development of light-harvesting systems (27). In this article, we describe our initial efforts to functionalize first- and second-generation monodendrons based on gallic acid at their origin with recognition units, i.e., the well-documented molecular clip receptors (28). These host molecules are well known for their ability to bind 1,3-dihydroxybenzene guests in solution (29). More recently, however, they have also been used as building blocks for the construction of well-defined nanosized aggregates in water (30–32) and the solid state (33, 34). The physical properties of the dendrimer-functionalized host molecules will be compared with the properties exhibited by the unfunctionalized monodendrons.

Experimental Procedures

Experimental procedures are published as supporting information on the PNAS web site, www.pnas.org.

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Abbreviations: TOPM, thermal optical polarization microscopy; DSC, differential scanning calorimetry; MDB, methyl 3,5-dihydroxybenzoate.

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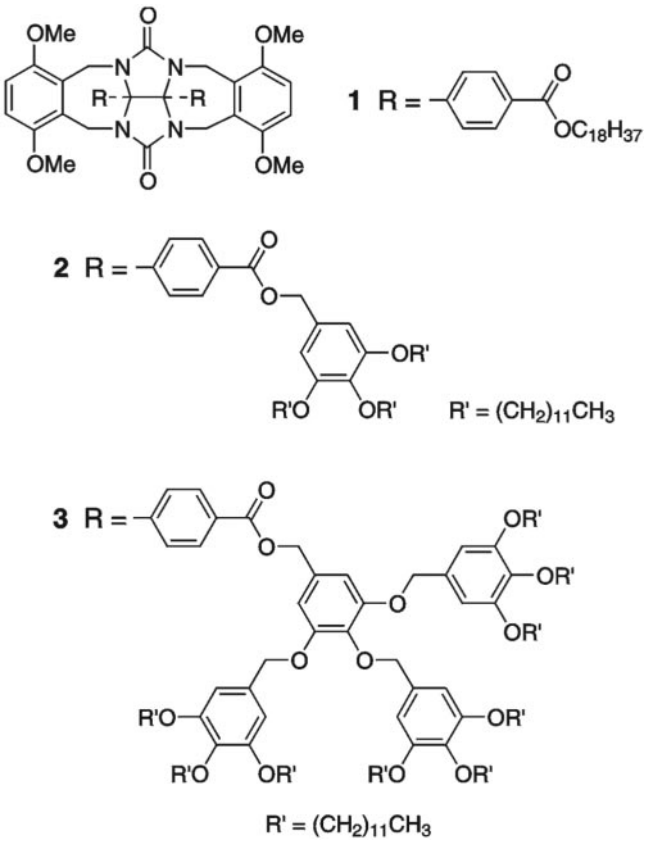

Scheme 1.

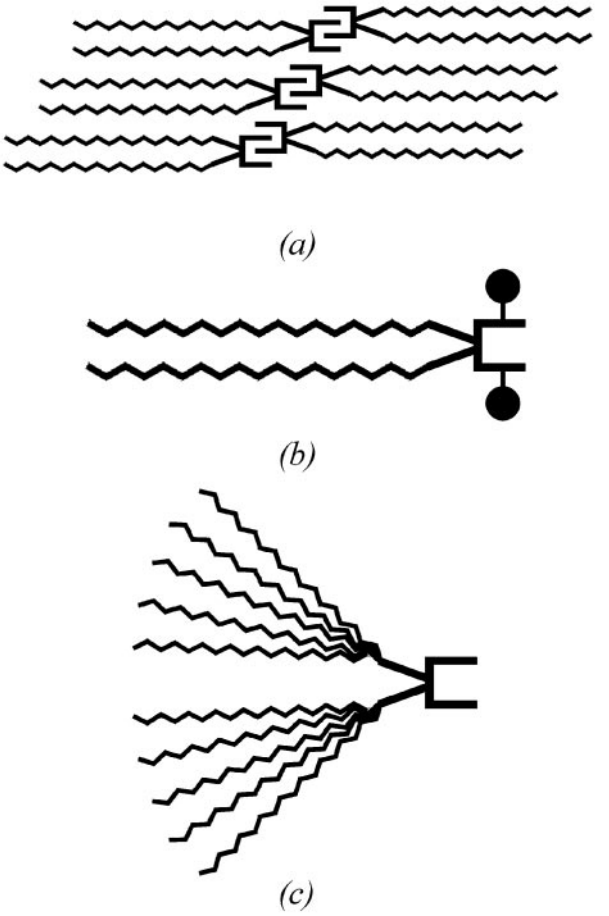

Fig. 2. (*a*) Schematic drawing of the lamellar structure formed by molecules of **1**; note the $\pi-\pi$ interactions between the host head-groups. (*b*) Schematic drawing showing how the strong $\pi-\pi$ interactions between the dimers can be broken by the attachment of bulky substituents to the side-walls of the hosts, or (*c*) by increasing the steric bulk of the aliphatic tails.

Results and Discussion

Design. It has been recently demonstrated that host molecule **1** (Scheme 1), which is functionalized at its convex side with two octadecyl tails, can dimerize by means of a mutual cavity-filling process (Fig. 2*a*). The dimers form extended two-dimensional sheets as a result of strong π–π interactions between the dimeric host molecules (33, 34). The material has an extended lamellar structure and behaves as a plastic-crystalline but malleable solid. One of our objectives was to make host molecule **1** truly liquid-crystalline. To achieve this goal we reasoned that it would be necessary to break the lamellar architectures formed by the dimers. This can be accomplished, at least in principle, by attaching bulky substituents (e.g., tert-butoxy groups) to the side walls of the host (Fig. 2*b*). The bulkiness near the cavity would, however, also inhibit host–host dimerization as well as the possibility to complex guest molecules. An alternative and more feasible approach would be to increase the bulkiness at the convex side of the host (Fig. 2*c*). Following the latter approach, host molecules were designed and synthesized that are functionalized at their convex side with tapered (molecule **2**) or conical monodendrons (molecule **3**) (Scheme 1). Detailed synthetic procedures are described in the supporting information on the PNAS web site (see Scheme 2, which is published as supporting information). The self-association properties of the host molecules in solution were investigated by ^{1}H NMR dilution titrations in $CDCl_3$. Hosts **2** and **3** appeared to dimerize through mutual cavity filling. The dimerization constants, $K_{dimer} = 16 \pm 5\ M^{-1}$ measured for **2**, and $K_{dimer} = 18 \pm 5\ M^{-1}$ for **3**, were similar to the dimerization constant of **1** in $CDCl_3$ ($K_{dimer} = 18 \pm 5\ M^{-1}$). Molecular modeling calculations on **2** and **3** clearly showed that the increase in steric bulk imposed by the tails eventually should inhibit a close packing of the dimers (Fig. 3).

Physical Properties of the Host with Tapered Monodendrons. Upon cooling a sample of **2** from the isotropic melt at a rate of 10°C min^{-1}, thermal optical polarization microscopy (TOPM) showed no evolution of a texture. Instead, the viscosity of the material gradually increased until solidification into a glassy material occurred at approximately 75°C. However, if the sample was extensively annealed (>24 h) at 125°C, a birefringent, spherulitic texture, which at the edges was surrounded by viscous glassy domains very slowly evolved (see Fig. 10, which is published as supporting information on the PNAS web site). The material was not malleable, and upon shearing the thin film cracked, indicating a crystalline nature of the material. Upon further cooling (at 10°C min^{-1}) after annealing, the viscous glassy domains surrounding the texture solidified at 75°C. In the consecutive heating run, the material became slightly malleable at 74°C, whereafter at 78°C polymorphous regions evolved at the edges of the glassy domains and solidification of the sample occurred. At 97°C the material became fully malleable, and at slightly higher temperature the glassy domains turned into a smectic-like texture. Isotropization occurred at 133°C. The differential scanning calorimetry (DSC) thermogram of **2** recorded at a rate of 10°C min^{-1} (Fig. 4, dashed traces) showed only one transition in the first cooling run, namely at −47°C. Upon heating, the TOPM-observed solidification at 78°C was visible as a negative peak (cold crystallization) at 76°C in the DSC spectrum. The second cold crystallization exotherm visible at 100°C is related

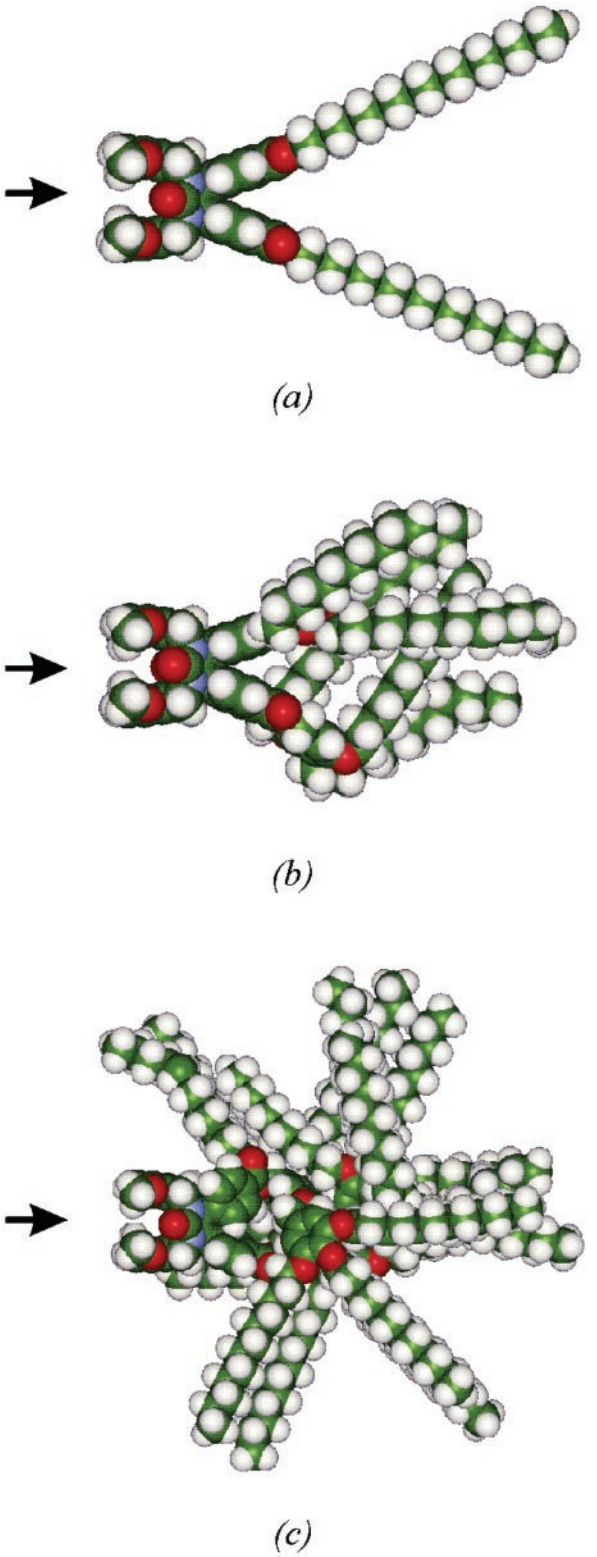

Fig. 3. Computer-modeled representations of (*a*) host **1**, (*b*) host **2**, and (*c*) host **3**. The increase in steric bulk imposed by the increase in monodendron generation number is clearly visible. The arrows indicate the location of the receptor part of the molecules.

to the malleable structure observed by TOPM at 97°C and was followed by isotropization at 134°C. The two cold crystallization exotherms indicate that the material was cooled at a too fast rate

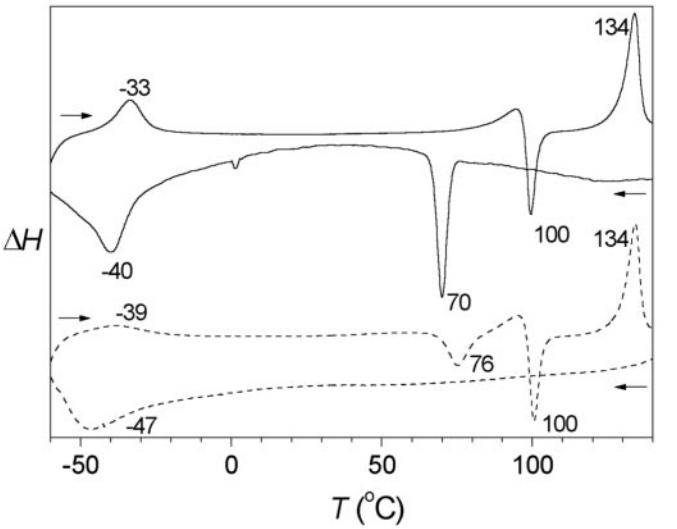

Fig. 4. DSC thermograms of the first cooling run and second heating run of host **2** taken at rates of 2°C min^{-1} (solid line) and at 10°C min^{-1} (dashed line).

to allow a complete ordering of the molecules. When the DSC thermogram was recorded at a rate of 2°C min^{-1}, a different thermal behavior was observed (Fig. 4, solid traces). In the cooling run, a clear exotherm related to the TOPM-observed solidification was observed at 70°C (Table 1). In the subsequent heating run, only one of the two exotherms caused by cold crystallization remained (at 100°C), and isotropization occurred at 134°C. The remaining cold crystallization exotherm could be further reduced by carrying out the cooling and heating run at an even lower rate, (i.e., 0.5°C min^{-1}).

The large endotherm involved with isotropization suggests that **2** is crystalline throughout its whole temperature range. This notion was confirmed by variable temperature x-ray powder diffraction measurements of the compound, which showed sharp, complex x-ray patterns characteristic of crystalline materials (see Fig. 10). When the sample was quickly cooled from the isotropic melt (at a rate of 10°C min^{-1}), a more simple x-ray pattern resulted with a relatively low number of reflections. Upon heating the sample to 100°C a complex diffraction pattern was obtained again, indicative of a rearrangement of the molecules into a more organized state. This apparent ordering corresponds to the second cold crystallization exotherm ob-

Table 1. Phase transition temperatures and enthalpies of hosts 2 and 3 and of the 1:1 host-guest complex of 3 and MDB

Host or complex	Transition*	T (°C)†	ΔH (kJ mol^{-1})†
2	$K \rightarrow K^1$	−33.1 (−39.7)	14.92 (−57.69)
	$K^1 \rightarrow I$	134.0 (71.5)	34.04 (−14.58)
3	$K \rightarrow K^1$	−15.8 (−24.8)	78.94 (−330.5)
	T_g	73 (—)‡	
	$K^1 \rightarrow$ Cub	94.74 (93)§	−0.97 (—)‡
	Cub → I	102.4 (100)§	2.86 (—)‡
3:MDB	$K \rightarrow K^1$	−19.6 (−31.6)	62.5 (−71.0)
	T_g	65 (49)	
	$K^1 \rightarrow$ Cub	66 (66)§	—‡
	Cub → I	85 (87)§	—‡

*K, K^1: crystalline phases; I: isotropic phase.
†Determined by DSC at a rate of 2°C min^{-1}, values obtained from the second heating run; in parenthesis: values obtained from the first cooling run.
‡No transition was observed.
§Transition was observed only with TOPM.

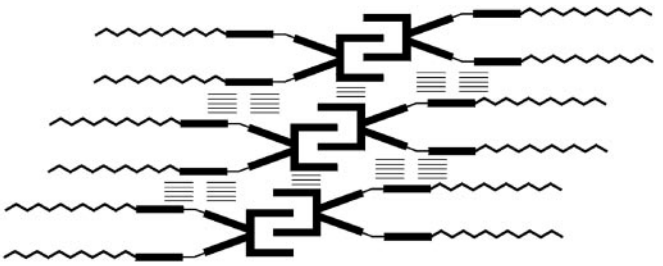

Fig. 5. Proposed intermolecular ordering of the molecules of **2**, highlighting the π–π interactions between the aromatic rings of the dimers. Only one of the alkyl tails of the monodendrons is shown for clarity reasons.

served in the DSC thermogram. When the sample was slowly cooled (1°C min^{-1}) from the isotropic melt, a complex diffraction pattern with many reflections was obtained. Although several low-angle reflections were found, neither a set of equally spaced reflections, indicative of a long-range lamellar ordering similar to that observed for **1**, nor low-angle reflections in a spacing ratio of 1:1/$\sqrt{}$3:1/2, attributable to an ordering in a hexagonal lattice, were observed. From the observed spherulitic texture and malleability of the material it may tentatively be concluded that the molecules of **2**, like those of **1**, form a plastic crystal and are arranged in arrays of stacked dimers. This ordering can be explained by assuming that the tapered monodendrons attached to **2** have an aligned arrangement. In this arrangement, the steric bulk from the tapered tails is expressed only in the direction perpendicular to the strongly π-stacked dimers, and it is very likely that the interactions between the aromatic rings of the tails make the packing even stronger (Fig. 5). A remarkable aspect of the thermal behavior of **2** is that the compound has difficulties to order itself. At a cooling rate of 10°C min^{-1}, **2** does not return to a crystalline state, but rather cools to an amorphous solid, without evidence of an exotherm in the DSC thermogram that corresponds to a crystallization event. At a low cooling rate, the crystallization exotherm is present, but the large degree of supercooling (>60°C) of the transition is evidence of the difficult ordering (35). Similar difficulties in crystallization have been observed for related tapered monodendritic compounds (35, 36). It has been rationalized that the presence of the alkyl chains, and in particular the *meta*-substituted ones, in combination with the high molecular weight of the compounds makes it difficult for the molecules to return to the crystalline state without extensive annealing.

In summary, it can be concluded that functionalization of a diphenylglycoluril host with two first-generation monodendrons does not induce liquid crystallinity into the material. Bulkier alkyl tails apparently are required, as are present in host **3**, which is functionalized with two second-generation monodendrons.

Physical Properties of the Host with Conical Monodendrons. Upon cooling a sample of **3** from the isotropic melt at a rate of 10°C min^{-1}, the appearance of a highly viscous optically isotropic oil was observed by TOPM at circa 100°C (see Fig. 11, which is published as supporting information on the PNAS web site). Further cooling led to a further increase in viscosity, until the material solidified into a glassy material at 93°C. Cooling of the sample at lower rates or extensive annealing at various temperatures did not result in the formation of an anisotropic texture. When the sample was heated, a sudden change from a glassy material into a viscous optically isotropic liquid was observed at 94°C, followed by isotropization at 104°C. The DSC thermogram (Fig. 6, Table 1) did not show any transitions related to the phenomena observed with TOPM in the cooling run at a rate of 10°C min^{-1}. A large exotherm at −25°C was, however, clearly

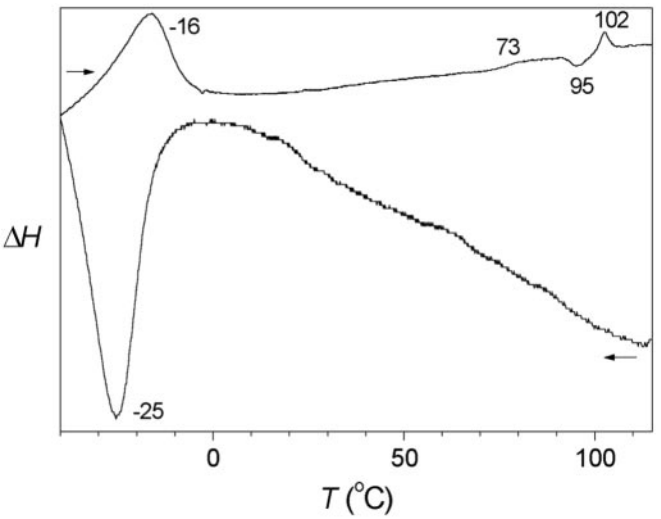

Fig. 6. DSC thermogram of the first cooling run and second heating run of host **3** taken at a rate of 10°C min^{-1}.

evident. Upon heating the sample from −65°C, a large endotherm at −16°C was observed, followed by a glass transition temperature (T_g) at 73°C. Then a small exothermic transition at 95°C was visible, followed by an isotropization endotherm at 102°C. These transitions correlate reasonably well with the temperature range in which the viscous isotropic liquid phase was observed by TOPM. A lower heating or cooling rate (e.g., 2°C min^{-1}) did not influence the DSC thermogram. Repeated cooling and heating runs were identical, which confirms that the observed phase transitions are reversible.

For **3**, the observation of a viscous isotropic liquid is reminiscent of the behavior of several other second-generation monodendrons functionalized with methyl esters or carboxylic acids (16). Its thermal properties also strongly resemble those of polymers prepared from styrene and methacrylate functionalized monodendrons (37). This finding suggests that host **3**, just like the aforementioned monodendrons, can form a cubic liquid-crystalline phase. The large transitions below 0°C are attributed to the melting and the crystallization of the alkyl tails, whereas the small exothermic peak at 95°C is associated with the formation of an enantiotropic cubic liquid-crystalline phase. Cubic phases are characterized by their optically isotropic textures and the consequence of the occurrence of this phase is that the molecules of **3**, in analogy to the other conical monodendritic compounds, most probably are arranged in (pseudo)spherical assemblies over the whole measured temperature range. Because of the particular conical shape of **3**, it is proposed that the host head-groups are situated in the core of the spherical assembly and the monodendrons tails at the periphery forming a supramacromolecular dendrimer (Fig. 7). The spherical assemblies can in turn organize themselves into a cubic lattice. A limited number of host molecules will be packed in such a supramacromolecular dendrimer, the formation of which is governed by van der Waals interactions between the alkyl tails and π-stacking interactions between the aromatic rings of the monodendrons and the host cavities (16). Additional evidence for the organization of **3** as a supramacromolecular dendrimer comes from the observation of a T_g value that is higher than the observed melting temperature of the compound. Although the T_g in a single phase system is always lower than this temperature, they can be reversed in a microphase-separated system as the cooperative motion of each phase is independent (37). In the case of **3**, melting and crystallization are associated with the alkyl tails, whereas the T_g is associated with the cooperative motion of the

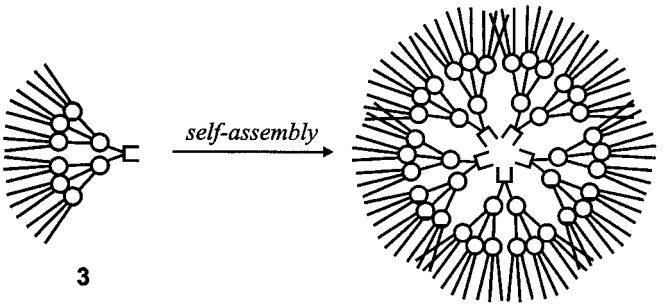

Fig. 7. Schematic two-dimensional representation of the proposed self-assembly of host molecule **3** into a spherical aggregate (supramacromolecular dendrimer), in which all of the host cavities are located in the core and the aliphatic tails at the periphery of **3**.

benzyl groups in the tails and with the interactions between the host head-groups. No information about the precise organization of the host head-groups within the core can be obtained from the thermal experiments, i.e., it remains unknown whether the cavities form dimers just like in the case of host **1**. X-ray powder diffraction measurements have been carried out but the analysis turns out to be very complex. These investigations should provide conclusive evidence about the exact architecture of the self-assembly. These measurements should also give information about the size of the spherical assemblies, which will in turn will enable the number of molecules of **3** in the assembly to be calculated.

Host-Guest Complex of 3 and Methyl 3,5-Dihydroxybenzoate (MDB). If a limited number of host molecules **3** are organized in a supramacromolecular dendrimer, it is of interest to investigate whether a strongly binding guest such as MDB can be complexed in the receptor cavities, while retaining the supramacromolecular dendritic structure (Fig. 8). The 1:1 ratio of **3** and MDB was prepared by slow evaporation of both components in a 4:1 (vol/vol) $CHCl_3$/MeOH mixture, followed by cooling of the complex from the isotropic melt. The complex was studied by TOPM, which showed the appearance of an optically isotropic phase at 87°C upon cooling from the melt. The viscosity of this phase gradually increased until solidification into a glassy material occurred at 66°C. Upon heating the sample from room temperature, the glassy material turned viscous again at 66°C. This viscosity gradually decreased until isotropization occurred at 85°C. In the cooling run of the DSC thermogram (Fig. 9, Table 1), no transitions related to the TOPM observed viscous phase were observed. However, a T_g at 49°C and a large exotherm at

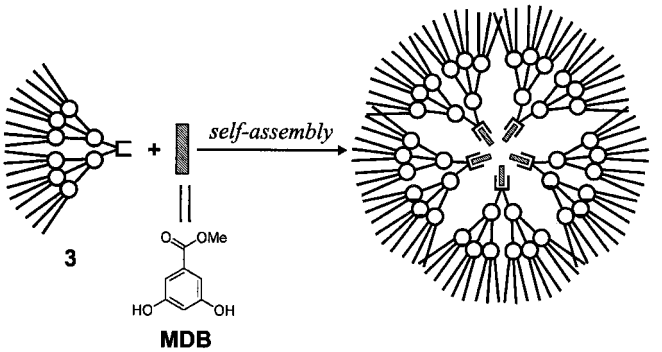

Fig. 8. Schematic representation of the proposed self-assembly of the host–guest complex of **3** and MDB into a supramacromolecular dendrimer, in which the guests are located in the core of the dendrimer.

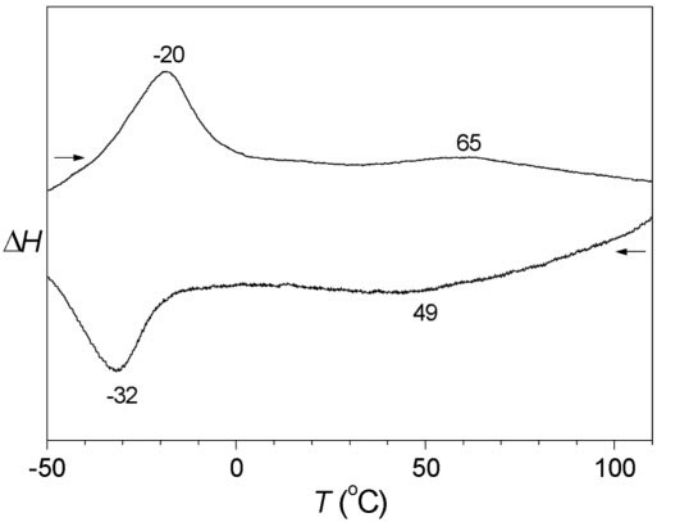

Fig. 9. DSC thermogram of the first cooling run and second heating run of the 1:1 host–guest complex between **3** and MDB taken at a rate of 10°C min^{-1}.

−32°C, related to crystallization of the glass, were evident. Upon heating, an endotherm at −20°C was visible, which is correlated to the crystal-to-glass transition. Although a T_g was observed at 65°C, no isotropization transition was visible by DSC. Repeated heating and cooling runs were identical, and the absence of phase separation suggests that the observed thermal behavior can be attributed to the 1:1 host-guest complex.

The observation of an optically isotropic phase, in conjunction with the transitions observed in the DSC thermogram, together resembling the thermogram of uncomplexed **3**, suggests that the 1:1 host-guest ratio of **3** and MDB also forms a supramacromolecular dendritic structure. Further evidence for the complexation of MDB within the cavities of **3** was obtained from reflectance Fourier transform IR measurements. The IR spectrum of a thin film of uncomplexed **3** showed two absorptions caused by the ester and urea carbonyl groups, at 1,739 and 1,721 cm^{-1}, respectively. In the sample of a thin film of the freshly prepared host-guest complex, neither of these vibrations was shifted. After heating the film to the isotropic melt, followed by slow cooling to 20°C, the ester carbonyl stretching vibration of **3** remained unaffected whereas the stretching vibration of the urea carbonyl function had shifted to 1,718 cm^{-1}. In addition, the absorption caused by the OH stretching vibration of MDB narrowed considerably and shifted from 3,381 to 3,338 cm^{-1}. These shifts are indicative of a well-defined hydrogen-bonding interaction between the two components, and the observed IR values of the complex are almost identical to those observed for the related solid-state host-guest complex between host **1** and MDB (34).

Although complexation of guests in **3** does not appear to severely influence the self-assembly behavior of the hosts in the supramacromolecular dendrimer, it can be foreseen that the size and probably also the shape of the dendritic spheres will be altered. The change in the transition temperatures of the complex compared with those of the free host supports this assumption. The arrangement of the assemblies of the host-guest complex into a cubic lattice is expected to be more difficult for the host-guest complex than for the free host.

The ability of **3** to complex guests and still form supramacromolecular dendrimers can be of great practical interest, because the bound guest molecules in such an assembly are in very close proximity. This spatial organization opens up the possibility to use the assemblies of **3** as nanoreactors, e.g., for the polymerization of bound guest molecules (the use of the spher-

ical assemblies formed by **3** as nanoreactors can be seen as a solid-state analogue of reverse micellar catalysis) (38). In analogy to the polymerization of conical monodendrons, guest molecules that are derivatized with e.g., vinyl or methacrylate functions can possibly be polymerized when they are complexed within a self-assembled supramacromolecular dendrimer of **3**. It will be particularly interesting to see whether the degree of polymerization can be controlled by the number of hosts present in the superstructure. This would be an interesting method to prepare polymers or oligomers with a controlled size. After the polymerization reaction, it will be relatively easy to separate the components, e.g., by simple extraction of the hosts, which then can be reused in further reactions.

Conclusions

To induce liquid crystallinity in host molecules derived from diphenylglycoluril, the volume of the alkyl tails at the back of these molecules was gradually increased. When the hosts were functionalized with two first-generation monodendrons, which adopt a tapered shape, no liquid crystallinity was observed, probably because the tails are not bulky enough to counterbalance the strong $\pi-\pi$ interactions between the head-groups of the hosts. The desired effect was achieved, however, by functionalizing the hosts with two second-generation monodendrons. Because of the bulky conical shape of these units, strong $\pi-\pi$ interactions between the head-groups of the hosts are no longer possible. Comparison of the physical properties of compound **3** with those of related compounds described in the literature revealed that the molecules probably arrange themselves in the form of supramacromolecular dendrimers. The latter dendrimers further organize themselves into rarely observed thermotropic cubic phases.

The cavities of the hosts in the core of the self-assembled dendrimers appear to be able to complex small guests, which opens the possibility of using the supramacromolecular dendrimers as nanoreactors, e.g., for the controlled polymerization of polymerizable guests.

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