

Induction of the Columnar Phase of Unconventional Dendrimers by Breaking the C_2 Symmetry of Molecules

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Abstract: Two triazine-based unconventional dendrimers were prepared and characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Differential scanning calorimetry, polarizing microscopy, and powder XRD studies showed that these dendrimers display columnar liquid-crystalline phases during thermal treatment. This is ascribable to breaking of their C_2 symmetry. The molecu-

lar conformations of prepared dendrimers were obtained by computer simulation with the MM3 model of the CaChe program in the gas phase. The simulation showed that the conformations of the prepared dendrimers are

rather flat and disfavor formation of the LC phase. However, due to C_2 -symmetry breaking, the prepared dendrimers have structural isomers in the solid state and thus show the desired columnar phases. This new strategy should be applicable to other types of unconventional dendrimers with rigid frameworks.

Keywords: dendrimers • liquid crystals • nitrogen heterocycles • symmetry breaking

Introduction

Dendrimers are monodisperse three-dimensional molecules with a definite molecular weight, shape, and size. These molecules, consisting of cores, linkages, and peripheral groups, can be prepared by convergent, divergent, and combinatorial methods.^[1] Recently, dendrimers have been the subject of much study due to their potential to function as catalysts,^[2] molecular micelles,^[3] light-harvesting molecules,^[4] drug-transporting agents,^[5] nanoparticle stabilizers,^[6] sensors,^[7] and porous materials.^[8] Dendrimers have also been observed to exhibit columnar liquid-crystalline (LC) phases and have found potential applications in light-emitting diodes, photovoltaics, and field-effect transistors,^[9] because columnar liquid crystals (LCs) often have good charge-carrier mobility, no grain boundaries, and uniform alignment.^[9b,10]

Triazine-based dendrimers have been extensively studied.^[11] Several series of dendrimers were first prepared by Simanek and Lim^[11c] and Takagi et al.,^[11b] by using the triazine moiety as a linkage. Interestingly, the triazine unit in the dendritic framework has been observed to show strong π - π interaction with tetrafluorobenzoquinone in solution,^[12] that is, the dendritic triazine moiety prefers face-to-face π - π interaction in solid stacking, which in turn will favor formation of the columnar LC phase during the thermal process.

Most of the traditional disk-shaped molecules that exhibit columnar LC phases have C_3 or higher symmetry, and disks efficiently self-assemble into columnar stacks through intramolecular π - π and/or H-bonding interactions.^[13] Several traditional disk-shaped molecules with C_2 symmetry showing columnar LC phases have also been disclosed.^[14] The introduction of a chiral moiety into C_2 -symmetrical molecules or tilting bent molecules to lead to the formation of columnar LC phases is also possible but has rarely been reported.^[15]

Owing to the versatile combination of cores, linkages, and peripheral groups, the molecular conformations of dendrimers are not as easy to control as those of traditional disk-shaped compounds, which characteristically contain a rigid disk-like core and a large number of surrounding flexible chains. Hence, it remains challenging to develop a general method for inducing columnar LC phases of dendrimers.^[16] Most dendrimers with columnar phases consist of rigid cores, flexible linkages, and peripheral mesogens or functional alkyl chains.^[17] Induction of H-bonding interaction between dendrons, leading to the generation of columnar LC phases, is another viable approach.^[17,18] Dendritic columnar mesogens containing rigid cores, rigid linkages, and flexible peripheral chains are unconventional and very interesting because their morphologies can be controlled by restricted

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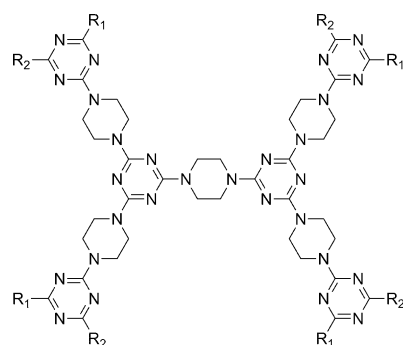
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conformational freedom, and cavities may thus be created within the dendritic framework for incorporation of guest molecules.^[17a,b,19]

Many traditional disk-shaped compounds with C_3 or C_2 symmetry have been observed to display columnar LC phases, but very few unconventional dendrimers with C_3 or C_2 symmetry that exhibit a columnar LC phase have been described in the literature.^[20] In our research on unconventional dendrimers based on the triazine moiety, we previously prepared C_3 -symmetrical G_2 and G_3 dendrimers which displayed a columnar LC phase during the thermal process.^[20b] In view of applications, lower generations of LC dendrimers have advantages of correspondingly lower viscosity and low cost of production. Previously, we showed that C_2 -symmetrical $[2N(C_8)_2G_2N]_2$ (Figure 1) does not display any



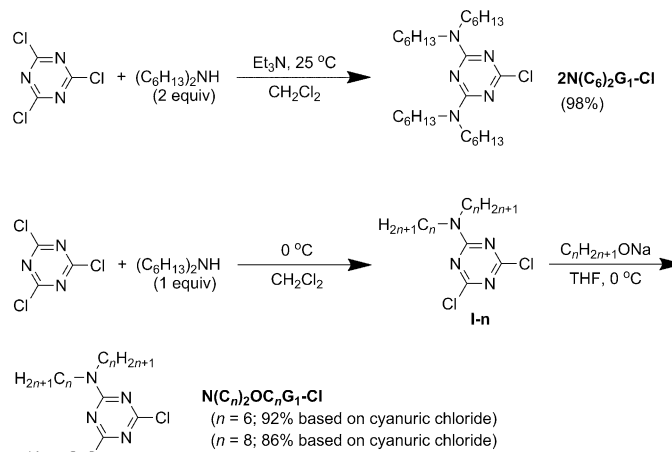
$[2N(C_8)_2G_2N]_2$: $R_1 = R_2 = N(C_6H_{15})_2$
 $[2N(C_6)_2G_2N]_2$: $R_1 = R_2 = N(C_6H_{13})_2$
 $[N(C_8)_2OC_8G_2N]_2$: $R_1 = N(C_6H_{15})_2$, $R_2 = OC_6H_{15}$
 $[N(C_6)_2OC_6G_2N]_2$: $R_1 = N(C_6H_{13})_2$, $R_2 = OC_6H_{13}$

Figure 1. Structures of $[2N(C_n)_2G_2N]_2$ and $[N(C_n)_2OC_nG_2N]_2$ ($n = 6, 8$).

LC phase.^[20b] To improve the related properties, we first varied the length of dendritic peripheral alkyl chains, a general approach adopted for traditional rod-like LC materials, and prepared $[2N(C_6)_2G_2N]_2$ (Figure 1), which also does not exhibit any LC phase. Applying the concept of tilting bent molecules to the dendritic system, we broke the C_2 symmetry of the triazine-based dendrimers and prepared $[N(C_n)_2OC_nG_2N]_2$ ($n = 6, 8$; Figure 1), which display a columnar LC phase during thermal treatment. Interruption of molecular symmetry has been adopted to prepare columnar LC dendrimers with flexible linkages, in which the peripheral mesogens may play an important role in inducing the LC phases.^[21] To the best of our knowledge, this is the first time that, in the field of unconventional dendrimers, nonmesogenic dendrimers were successfully converted to mesogenic dendrimers simply by breaking their symmetry. This method may be important in designing LC dendrimers with some specific properties. For example, a rigid disk-shaped molecule with good light-emitting or electron transporting property can be used as the dendritic core and then modified to display the desired mesogenic phase for better alignment, and this is a possible advantage over conventional mesogenic dendrimers.

Results and Discussion

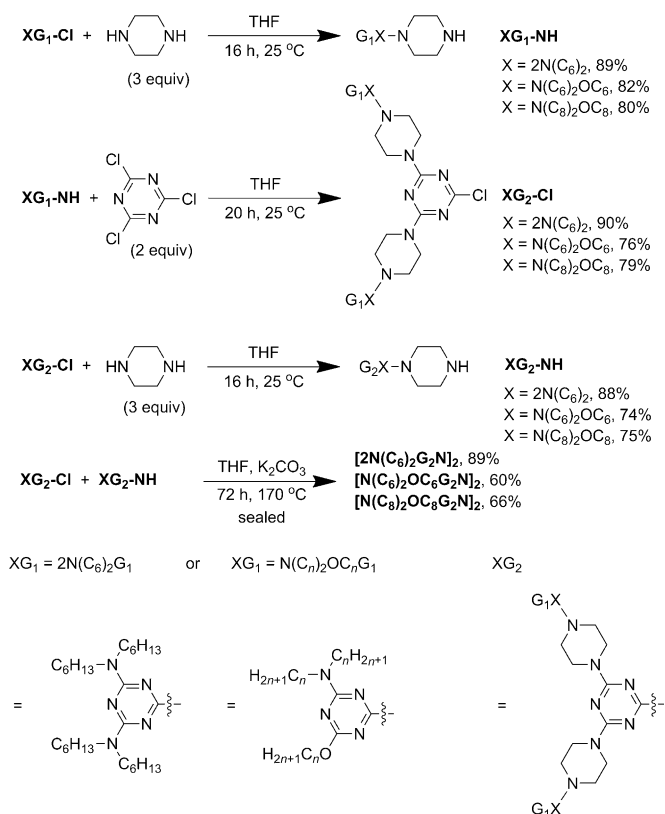
The preparation of dendrimer $[2N(C_8)_2G_2N]_2$ and its precursors has been reported previously.^[11a,d] Dendrons $2N(C_6)_2G_1-Cl$ and $N(C_n)_2OC_nG_1-Cl$ ($n = 6, 8$) were prepared according to Scheme 1. Reaction of cyanuric chloride with two equiva-



Scheme 1. Preparation of dendrons $2N(C_6)_2G_1-Cl$ and $N(C_n)_2OC_nG_1-Cl$ ($n = 6, 8$).

lents of dihexylamine in dry CH_2Cl_2 in the presence of triethylamine gave $2N(C_6)_2G_1-Cl$ in 98% yield. Reaction of cyanuric chloride with one equivalent of dihexylamine in dry CH_2Cl_2 yielded compound **I-6**, which was further treated with sodium hexyloxide in THF to give dendron $N(C_6)_2OC_6G_1-Cl$ in 92% yield (based on cyanuric chloride). Dendrion $N(C_8)_2OC_8G_1-Cl$ was prepared in 86% yield in a similar manner. Dendrons $X-G_1NH$, $X-G_2Cl$, and $X-G_2NH$ ($X = 2N(C_6)_2$ or $N(C_n)_2OC_n$, $n = 6, 8$) were prepared in 75–90% yield as shown in Scheme 2. Reaction of $X-G_2NH$ with $X-G_2Cl$ in THF in the presence of K_2CO_3 at $170^\circ C$ in a sealed tube for 72 h gave dendrimers $[2N(C_6)_2G_2N]_2$, $[N(C_6)_2OC_6G_2N]_2$, and $[N(C_8)_2OC_8G_2N]_2$ in 60–90% yield, which were characterized by 1H and ^{13}C NMR spectroscopy and mass spectrometry. For example, the mass spectrum of $[N(C_8)_2OC_8G_2N]_2$ (Figure 2) clearly shows the corresponding $[M]^+$ peak at m/z 2367.5. All three dendrimers in the current study, $[2N(C_6)_2G_2N]_2$, $[N(C_6)_2OC_6G_2N]_2$, and $[N(C_8)_2OC_8G_2N]_2$, were further characterized by microanalysis, and the errors for calculated and experimental percentages of C, H, and N were within 0.3%.

As shown in Scheme 3, dendrimer $[2N(C_8)_2G_2N]_2$, which melts at about $132^\circ C$ on heating and solidifies at about $117^\circ C$ on cooling, does not exhibit any LC behavior. Similarly, dendrimer $[2N(C_6)_2G_2N]_2$ is not liquid-crystalline and exhibits a melting point of about $229^\circ C$ on heating and a solidification point of about $221^\circ C$ on cooling. The molecular structure of dendrimer $[2N(C_6)_2G_2N]_2$ is similar to that of $[2N(C_8)_2G_2N]_2$, but the two have different peripheral chain lengths. However, the melting point of $[2N(C_6)_2G_2N]_2$ is much higher than that of $[2N(C_8)_2G_2N]_2$, and the solidifi-



Scheme 2. Preparation of dendrimers $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ and $[\text{N}(\text{C}_n)_2\text{OC}_n\text{G}_2\text{N}]_2$ ($n = 6, 8$).

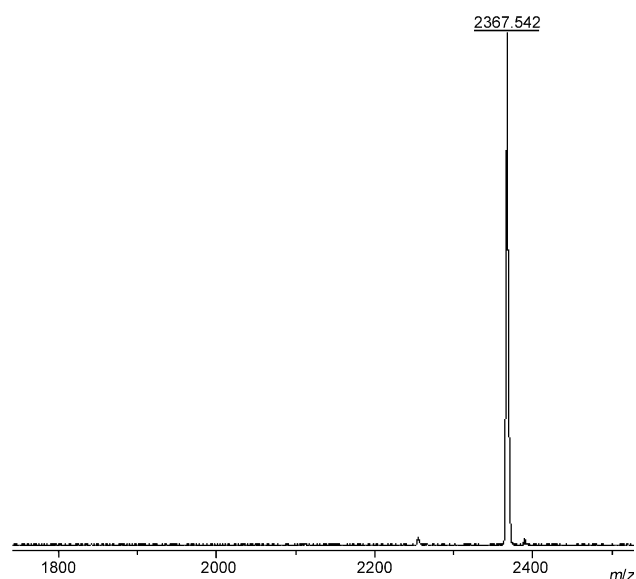
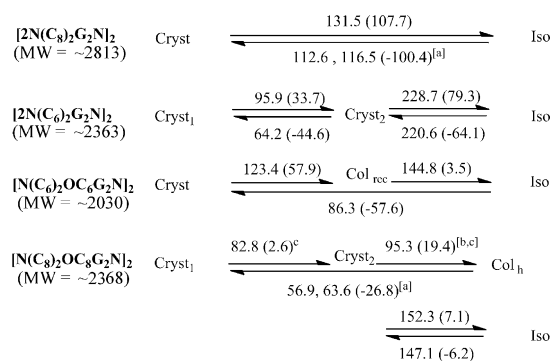


Figure 2. MALDI-TOF mass spectrum of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$.

cation points of $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ and $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ also behave similarly. This may be due to the different crystallinities of the two dendrimers. As demonstrated in Figure 1, the peripheral chains of $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ are shorter than those of $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ so the thermal vibration from the



Scheme 3. Phase-transition temperatures and corresponding enthalpies $[\text{kJ mol}^{-1}]$ (in parentheses) of the dendrimers $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$, $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$, $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$, and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$. Cryst, Col_{rec}, Col_h, and Iso denote the crystalline, rectangular columnar, hexagonal columnar, and isotropic phases, respectively. The transition temperatures and corresponding enthalpies were recorded for the second cycles between the isotropic and room temperatures. [a] Two transitions significantly overlapped; the enthalpies are integrated together. [b] Two transitions partially overlapped and the enthalpy is integrated individually (the values integrated together are shown in Figure S2 in the Supporting Information).

flexible alkyl chains of $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ is smaller, leading to better crystallinity in the solid stacking. Such behavior disfavors the formation of an LC phase in our case. The generation of LC phases for most rodlike materials involves increasing the flexible-chain length to reduce their crystallinity. This strategy failed for dendrimers in this study; dendrimer $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ does not display any LC phase during thermal treatment, and its melting point and solidification point are much lower than those of the shorter-chain analogue $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$, although the peripheral alkyl chain lengths only differ by two C atoms. To effectively modulate the molecular crystallinity and induce columnar LC phases, the C_2 symmetry breaking strategy was adopted, and dendrimers $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ were prepared. Each of the dendrons $\text{N}(\text{C}_n)_2\text{OC}_n\text{G}_2\text{-Cl}$ and $\text{N}(\text{C}_n)_2\text{OC}_n\text{G}_2\text{-NH}$ ($n = 6, 8$) consists of two structural isomers (Figure 3), which lead to isomer mixtures of dendrimers $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ from the reaction of $\text{N}(\text{C}_n)_2\text{OC}_n\text{-Cl}$ with $\text{N}(\text{C}_n)_2\text{OC}_n\text{-NH}$ ($n = 6, 8$; Figure S1 in Supporting Information); the structure in Figure 1

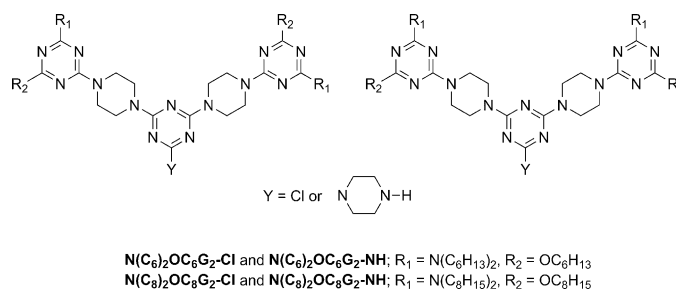


Figure 3. Structural isomers of $\text{N}(\text{C}_n)_2\text{OC}_n\text{G}_2\text{-Cl}$ and $\text{N}(\text{C}_n)_2\text{OC}_n\text{G}_2\text{-NH}$ ($n = 6, 8$).

shows only one of them. Most of them do not exhibit C_2 symmetry.

As expected, $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ exhibits a rectangular columnar phase on heating (Scheme 3), and shows a small domain texture under a polarizing optical microscope (Figure 4a). The mesophase range is only about 21 °C in the

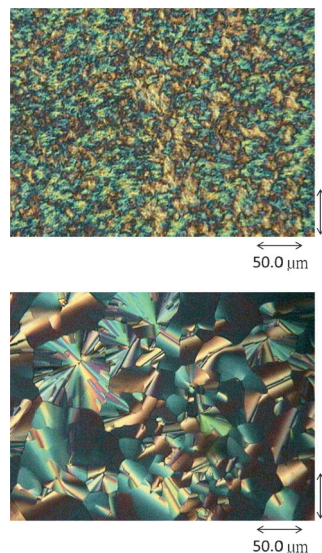


Figure 4. POM textures of a) $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ at 140 °C on heating (top) and b) $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ at 140 °C on cooling (bottom).

heating process. Dendrimer $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ shows considerable supercooling behavior and does not show any liquid-crystalline phase in the cooling process, which was confirmed by successive differential scanning calorimetry, powder XRD, and polarized optical microscopy (POM) investigations. The identity of the rectangular columnar phase of $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ was further studied by powder XRD. As shown in Figure 5, two sharp peaks at 26.0 and 18.8 Å, indexed as d_{20} and d_{11} , respectively, occur in the small-angle region. The weak mid-angle signal at 12.2 Å is indexed as d_{40} . The lattice constants are calculated to be $a=51.9$ and $b=20.2$ Å. Due to the lack of characteristic reflections, the symmetry of $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ cannot be determined.

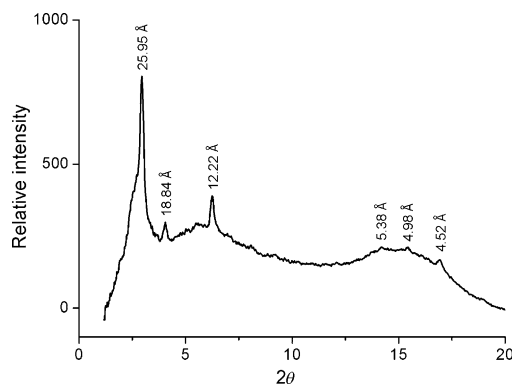


Figure 5. XRD pattern of $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ at 140 °C on heating.

The wide-angle halos at 5.4, 5.0, and 4.5 Å are all attributable to the liquid-like correlation of the molten chains, showing mixed stacking of *N*-alkyl and *O*-alkyl groups.

Dendrimer $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ has a higher melting point but does not display any LC behavior during the thermal process. Similarly, dendrimer $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ with a lower melting point also does not display any liquid-crystalline phase. However, $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ not only shows a lower melting point compared to $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$, but also exhibits a columnar phase on heating. These observations are interesting and suggest that dendrimer $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ is potentially columnar mesogenic. Indeed, $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ exhibits a columnar phase, evidenced by its fan-shaped texture under a polarizing optical microscope (Figure 4b). The mesophase ranges are found to be about 56 °C on heating and 83 °C on cooling, which are significantly wider than those of $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$. The identity of the columnar phase of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ was further investigated by powder XRD (Figure 6). A sharp peak at 31.2 Å was detected in the

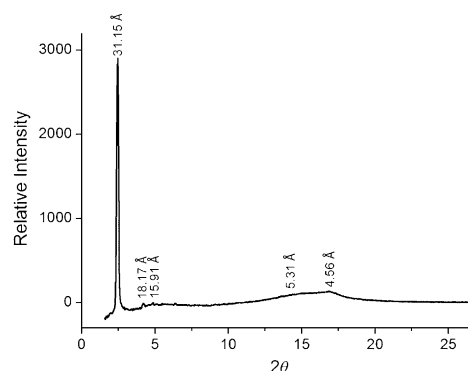


Figure 6. XRD pattern of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ at 140 °C on cooling.

small-angle region and is indexed as d_{10} . Two additional weak signals at 18.2 and 15.9 Å are indexed as d_{11} and d_{20} , respectively. The XRD pattern is indicative of a hexagonal columnar phase and the lattice constant is calculated to be $a=36.0$ Å. The two broad wide-angle halos at 5.31 and 4.56 Å are both attributable to the liquid-like correlations of the molten chains of the mixed stacking of *N*-alkyl and *O*-alkyl groups.

As shown in our previous work,^[20b] C_3 -symmetrical G_2 dendrimer $(\text{G}_2\text{N}-\text{N})_3\text{T}$ has a three-leaf fan conformation and thus efficiently assembles into a columnar stack. Although the three-leaf fan conformation of C_3 -symmetrical G_3 dendrimer $(\text{G}_3\text{N}-\text{N})_3\text{T}$ is not evident, the congestion from the dendritic framework significantly deforms the molecular planarity. Both effects significantly reduce the face-to-face π - π interaction between molecules in the solid stacking, and thus the columnar LC phase is displayed during thermal treatment.

As a model compound representing the new dendrimers in Figure 1, $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ was computed by using the MM3 model to reveal its equilibrium molecular conforma-

tion. The simulation was carried out in the gas phase and, for simplicity, only one structure, as shown in Figure 1, was calculated. The starting conformation of $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_1\text{-Cl}$ was first established by combining one planar triazine with one dioctylamine and octanol, in which all-*trans* conformation was adopted for the alkyl chains, and then optimized. The equilibrium conformation of $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_1\text{-NH}$ was then obtained by combining optimized $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_1\text{-Cl}$ with piperazine in chair form and then optimized. The conformation of $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{-Cl}$ was obtained by combining one planar triazine with two optimized $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_1\text{-NH}$ units and then optimized. The conformation of $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{-NH}$ was obtained in a similar manner to that of $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_1\text{-NH}$. The conformation of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ was obtained by combining optimized $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{-Cl}$ with optimized $\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{-NH}$ and then optimized.

In the optimized conformation of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$, shown as space-filling model in Figure 7, one G_2 moiety par-

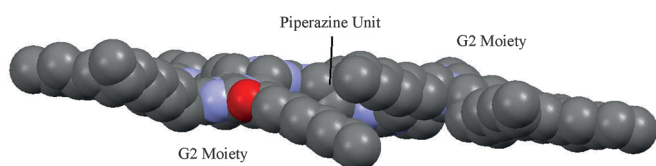


Figure 7. Conformation of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$. O red, N blue, C gray, H omitted.

tially lies above the other G_2 moiety due to the chair form of the central piperazine unit. For $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$, the molecular congestion from the peripheral alkyl chains and dendritic frameworks seems not to significantly deform the molecular planarity, and thus leads to a rather flat overall structure, similar to that of $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$.^[22] However, $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ does not exhibit any LC phase on thermal treatment, but $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ shows a columnar phase. Similarly, $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ does not display any LC behavior, but $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ does give a columnar mesophase during the thermal process. The reason for the difference between $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ [or $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$] and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ [or $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$] should be the C_2 -symmetry breaking. It is well known that compounds containing structural isomers tend to give reduced overall intermolecular interactions in the solid state. For example, both (*R*)-(-)-2-amino-1-propanol and (*S*)-(+)-2-amino-1-propanol have a melting point of 24–26 °C, but the melting point of (±)-2-amino-1-propanol is 8 °C.^[23] The dendrimer $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$, consisting of several possible structural isomers with the same molecular weight (see Supporting Information Figure S1), therefore should lead to less face-to-face π - π interactions with adjacent molecules in the solid stacking when compared with $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$. A similar effect can be applied to dendrimers with C_3 symmetry, resulting in the formation of the columnar phase during the thermal process. The columnar liquid crystallinity of

$[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ and the noncolumnar LC behavior of $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ during the thermal process can be rationalized by using this concept.

In addition, the textures of both $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ were obtained between untreated glasses under a polarizing optical microscope. The texture of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ is composed of larger domains than that of $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$, which implies chain-length dependence of dendritic alignment. More detailed studies of dendritic mesogens with mixed peripheral alkyl chains should be worthwhile for their potential efficient alignment.

Conclusion

A strategy of breaking C_2 symmetry for inducing columnar phases of unconventional triazine-based dendrimers has been demonstrated. By using this method, two second-generation unconventional dendrimers were observed to display columnar phases during the thermal process. Although the molecular conformation and molecular weight of $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$ and $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ are similar to those of $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ and $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ (Scheme 3), only the former display columnar phases on thermal treatment due to C_2 -symmetry breaking. We believe that this approach should be applicable to other unconventional dendritic systems. In particular, some disk-shaped molecular cores displaying good light-emitting or electron-transporting properties can be modified by this approach to subsequently show LC phases and better alignment. In addition, this approach also leads to lower-generation dendrimers exhibiting columnar phases, which not only efficiently reduces the synthetic cost but also significantly reduces the viscosity of the dendritic mesogens.

Experimental Section

Preparation of dendrimers: Preparation of the dendrimer $[\text{2N}(\text{C}_8)_2\text{G}_2\text{N}]_2$ was the subject of earlier work.^[11a,d] The dendrimers, $[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$, $[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$, and $[\text{N}(\text{C}_8)_2\text{OC}_8\text{G}_2\text{N}]_2$, were prepared as follows: **X-G₂-Cl** (1 mmol) and **X-G₂-NH** (1 mmol) were added to a sealed tube, containing THF (15 mL) and K_2CO_3 (0.5 g, 5 mmol). The resulting mixture was heated at 170 °C for 72 h. Water (20 mL) was added to the mixture and the solution was extracted with CH_2Cl_2 (20 mL \times 2). The combined extracts were washed with water (20 mL), dried over MgSO_4 , and concentrated at reduced pressure. The residue was purified by chromatography (SiO_2 , 2.1 \times 15 cm; eluent: THF) to yield the crude product, which was further recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (1/20) to give the pure desired dendrimer.

$[\text{2N}(\text{C}_6)_2\text{G}_2\text{N}]_2$ (89.3%): $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 0.89 (brs, 48H, $16 \times \text{CH}_3$), 1.30 (brs, 92H, $48 \times \text{CH}_2$), 1.58 (brs, 32H, $16 \times \text{CH}_2$), 3.46 (brs, 32H, $16 \times \text{CH}_2$), 3.80 + 3.82 (2s, 40H, $20 \times \text{CH}_2$); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.06, 22.70, 26.99, 28.18, 31.84, 43.16, 46.96, 47.14, 165.10, 165.42, 165.49; MS calcd for $\text{C}_{134}\text{H}_{248}\text{N}_{36}$ [M]⁺: 2363; found 2363; elemental analysis calcd (%) for $\text{C}_{134}\text{H}_{248}\text{N}_{36}$: C 68.09, H 10.58, N 21.33; found C 68.09, H 10.61, N 21.31.

$[\text{N}(\text{C}_6)_2\text{OC}_6\text{G}_2\text{N}]_2$ (59.7%): $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 0.86–0.91 (m, 36H, $12 \times \text{CH}_3$), 1.30–1.43 (m, 72H, $36 \times \text{CH}_2$), 1.60 (brs, 16H, $8 \times \text{CH}_2$), 1.71–1.81 (m, 8H, $4 \times \text{CH}_2$), 3.47–3.52 (m, 16H, $8 \times \text{CH}_2$),

3.82 (brs, 40H, 20×CH₂), 4.27 (t, *J*=6.9 Hz, 8H, 4×CH₂); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.03, 22.63, 25.72, 26.74, 27.66, 28.03, 28.97, 31.65, 31.71, 43.19, 47.04, 47.18, 66.57, 165.45, 165.91, 166.16, 170.74; MS calcd for C₁₁₀H₁₉₆N₃₂O₄ [M]⁺: 2030; found 2030; elemental analysis calcd (%) for C₁₁₀H₁₉₆N₃₂O₄: C 65.05, H 9.73, N 22.07; found C 65.12, H 9.81, N 22.13.

[N(C₈)₂OC₈G₂N]₂ (65.7%) ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 0.86–0.90 (m, 36H, 12×CH₃), 1.30–1.44 (m, 120H, 60×CH₂), 1.58 (brs, 16H, 8×CH₂), 1.72–1.81 (m, 8H, 4×CH₂), 3.47–3.52 (m, 16H, 8×CH₂), 3.82 (brs, 40H, 20×CH₂), 4.28 (t, *J*=6.9 Hz, 8H, 4×CH₂); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.10, 22.65, 26.05, 27.07, 27.69, 28.07, 29.01, 29.25, 29.32, 29.42, 31.85, 43.19, 47.14, 66.58, 165.44, 165.92, 166.16, 170.73; MS calcd for C₁₃₄H₂₄₄N₃₂O₄ [M]⁺: 2367; found 2367; elemental analysis calcd (%) for C₁₃₄H₂₄₄N₃₂O₄: C 67.98, H 10.39, N 18.93; found C 67.96; H 10.44, N 18.87.

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