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Converting Nonliquid Crystals into Liquid Crystals by *N*-Methylation in the Central Linker of Triazine-Based Dendrimers

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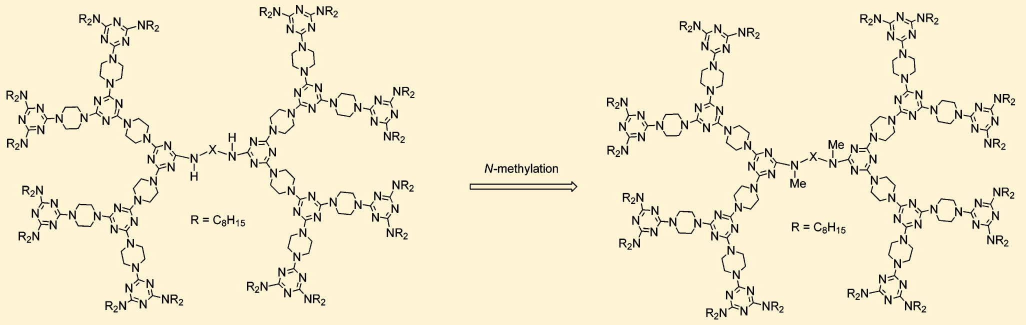
Supporting Information



Non-Liquid Crystalline 1a ($X = C_2H_4$) and **1b**($X = C_4H_8$)

Liquid Crystalline 2a ($X = C_2H_4$) and **2b**($X = C_4H_8$)

ABSTRACT: Two triazine-based dendrimers were successfully prepared in 60−75% yields. These newly prepared dendrimers **2a** and **2b** containing the $-NMe(CH_2)_2NMe-$ and the $-NMe(CH_2)_4NMe-$ linkers between two G_3 dendrons, respectively, exhibit columnar phases during the thermal process. However, the corresponding dendrimers **1a** and **1b** containing the $-NH(CH_2)_2NH-$ and the $-NH(CH_2)_4NH-$ linkers between two G_3 dendrons, respectively, do not show any LC phases on thermal treatment. Computational investigations on molecular conformations reveal that *N*-methylation of the dendritic central linker leads dendrimers to possess more isomeric conformations and thus successfully converts non-LC dendrimers (**1a** and **1b**) into LC dendrimers (**2a** and **2b**).

■ INTRODUCTION

Dendrimers are highly branched macromolecules and often structurally consist of central cores, linkage units, and peripheral functional groups in a treelike molecular architecture. These molecules are constructed by step-by-step processes in an iterative manner and show unusual chemical and physical properties due to their three-dimensional topologies and multifunctionalities. Usually, they can be efficiently prepared by convergent, divergent, and combinatorial methods[1] and have attracted great attention recently in academic and industrial research because of their well-defined chemical architecture and multiple functions in one single molecule, thus emerging as potential materials in the fields of catalysts,[2] drug carriers,[3] nanoparticle stabilizers,[4] photoelectric materials,[5] sensors,[6] and porous materials.[7]

Dendrimers have been observed to exhibit columnar liquid crystalline (LC) phases and found useful in photovoltaics and field transistors[8] due to their nongrained boundary and uniform alignment.[8b,9] However, various combinations of cores, linkage units, and peripheral functionalities of dendrimers lead their molecular conformations to be versatile, and therefore, it is not as easy to control their molecular shapes as those of traditional rodlike or disk-shaped LC molecules. The LC phases of traditional dendrimers that contain flexible spacers and mesogenic units are generally induced by their peripheral mesogenic moieties.[10] Incorporated with various mesogenic moieties, the LC dendrimers are observed to exhibit nematic, lamellar smectic, or columnar mesophases.[11−13] The induction of the H-bond interaction between the dendrons or in the dendritic frameworks, resulting in the formation of LC phases, represents another viable approach,[14] which however, has not been extensively investigated as that of the traditional rodlike or disk-shaped molecules.[15]

On the other hand, synthesis and study of molecules containing the 1,3,5-triazine unit, first prepared by Takagi, have been employed in recent decades because of their potential applications in the CO_2 adsorption and the drug transfer.[16,17]

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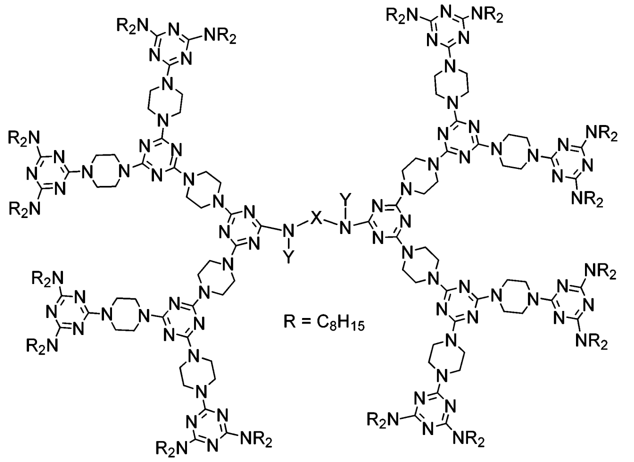
The triazine unit in the dendritic framework has also been observed to show the face-to-face $\pi-\pi$ interaction with tetrafluorobenzoquinone in solution,[18] indicating the dendritic triazine moiety prefers such the interaction in solid stacking, which in turn will favor the formation of columnar LC phase during the thermal process.

Instead of traditional LC dendrimers,[11−13] we are more interested in the synthesis and study of unconventional triazine-based LC dendrimers,[19] which contain rigid cores, rigid linkages, and flexible peripheral chains, because their morphology is controlled by restricted conformational freedom and cavities may thus be created in the dendritic frameworks to incorporate guest molecules as demonstrated in other dendritic systems.[20] Previously, we prepared unconventional triazine-based dendrimers **1a** and **1b**, which contain the $-NH(CH_2)_2NH-$ and the $-NH(CH_2)_4NH-$ linkers between two G_3 dendrons, respectively. It was discovered that they do not show any LC phase. However, dendrimer **1c**, containing the $-NH(CH_2)_3NH-$ linkers between two G_3 dendrons, exhibits a columnar LC phase on thermal treatment (Figure 1).[19d] In continuing to study the influence on mesogenic behaviors from the variation of central linkers in unconventional triazine-based dendrimers, we further synthesize compounds **2a** and **2b**, containing the $-NMe(CH_2)_2NMe-$ and the $-NMe(CH_2)_4NMe-$ linkers between two G_3 dendrons, respectively, and discover that dendrimers **2a** and **2b** exhibit columnar phases on thermal treatment. In other words, methylation of nitrogens in the flexible central linker of triazine-based dendrimers successfully converts nonliquid crystals into liquid crystals. We herein wish to report these results.



1a: Y = H, X = C_2H_4, **1b**: Y = H, X = C_4H_8, **1c**: Y = H, X = C_3H_6

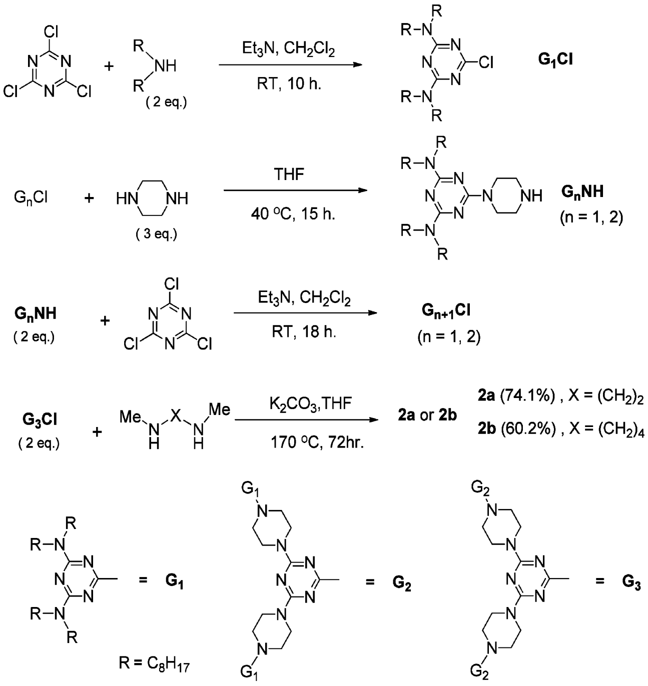
2a: Y = Me, X = C_2H_4, **2b**: Y = Me, X = C_4H_8

Figure 1. Chemical structures of dendrimers **1a−c** and **2a,b**.

RESULTS AND DISCUSSION

The synthesis of dendrons **2a** and **2b** is shown in Scheme 1. Dendron **G₃Cl** was prepared according to literature.[19] (*N,N*-Dimethylamino)ethane was allowed to react with 1 equiv of **G₃Cl** in THF at 70 °C for 24 h. Then another 1 equiv of **G₃Cl**, followed by 3 equiv of K_2CO_3, was added, and the resulting mixture was heated at 170 °C for 72 h in a sealed tube. Dendrimer **2a** was obtained in ~74% yield after purification. Dendrimer **2b** was obtained in ~60% yield in a similar manner.

Scheme 1. Preparation of Dendrimers 2a and 2b



Both dendrimers were characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. As an example, the mass spectrum of **2b** is shown in Figure 2, which clearly shows a peak of m/z at 6062.96 from $[M + H]^+$ ion. Dendrimers **2a** and **2b** in the current study were further characterized by microanalysis, and the errors for calculated and experimental percentages for C, H and N are within 0.3%.

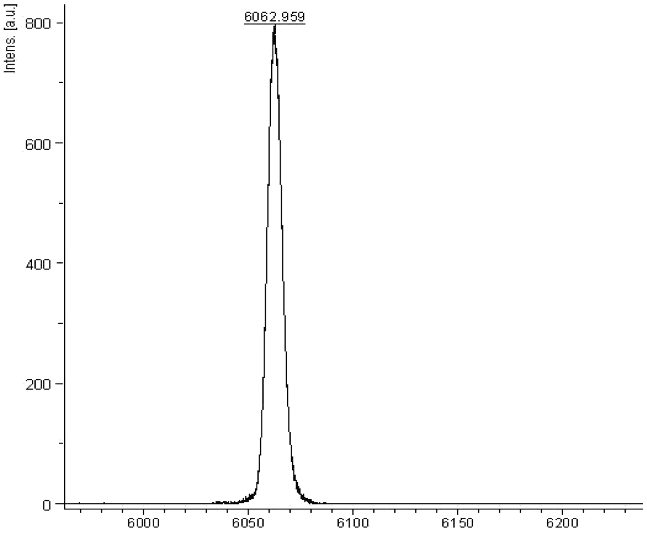


Figure 2. MALDI-TOF mass spectrum of **2b**.

As indicated in our previous study, dendrimers **1a** and **1b** containing the $-NH(CH_2)_2NH-$ and the $-NH(CH_2)_4NH-$ linkers between two G_3 moieties, respectively, do not show any LC phases.[19d] Dendrimer **1a** melts at ~147 °C on heating and solidifies at ~90 °C on cooling. Dendrimer **1b** melts at ~132 °C and solidifies at ~100 °C in the heating and cooling processes, respectively. However, dendrimers **2a** and **2b** containing the $-NMe(CH_2)_2NMe-$ and the $-NMe-$

$(CH_2)_4NMe$– linkers between two G_3 moieties, respectively, were observed to exhibit columnar phases during the thermal process, which are evidenced by their big domain textures under a polarizing optical microscope (POM) (Figure 3a (top) and b (bottom)). Dendrimer **2a** is monotropic, and its mesogenic ranges on cooling is ca. 22°. The mesogenic ranges of dendrimer **2b** are ca. 12° in the heating and ca. 21° in the cooling. It seems that two Me groups at the N positions of the central linker significantly affect the condense-phase molecular stacking of the dendrimers.

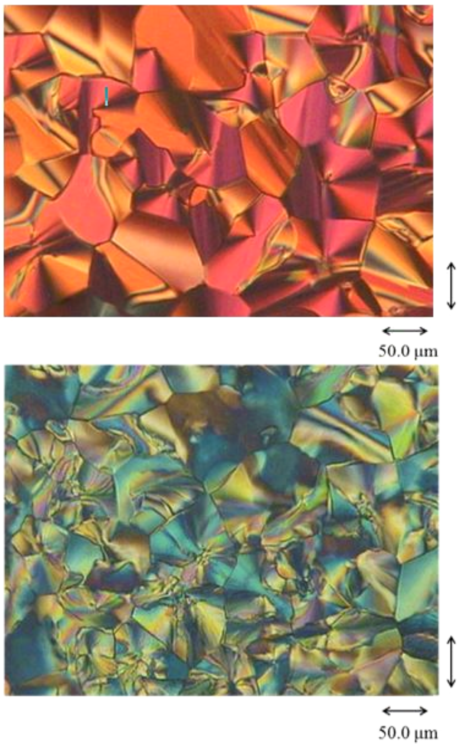


Figure 3. (a) POM texture of **2a** at 90 °C on cooling (top); (b) POM texture of **2b** at 104 °C on cooling (bottom).

The identity of the columnar phases of **2a** and **2b** was further investigated by powder X-ray diffraction (XRD), and the results are shown in Figures 4 and 5. Their diffraction patterns are similar, which indicates the formation of the same LC phase. For example, dendrimer **2a** shows a sharp peak at 35.34 Å in the small-angle region, which is indexed as *d*10, and two additional weak signals at 20.37 and 17.70 Å, indexed as *d*11 and *d*20, respectively. The signal at 13.29 Å, appearing as a broad hump, may arise from the intracolumnar disk correlation, and the broad wide-angle halo at 4.52 Å can be attributed to liquid-like correlations of the molten alkyl chains. The XRD pattern is indicative of a hexagonal columnar phase and the lattice constant *a* is calculated to be 40.81 Å. In a similar manner, the lattice constant of the hexagonal columnar mesophase of **2b** was found to be 38.62 Å.

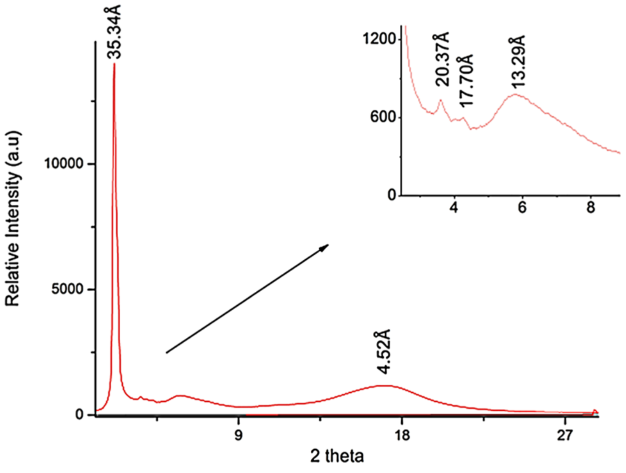


Figure 4. XRD pattern of dendrimer **2a** at 90 °C on cooling.

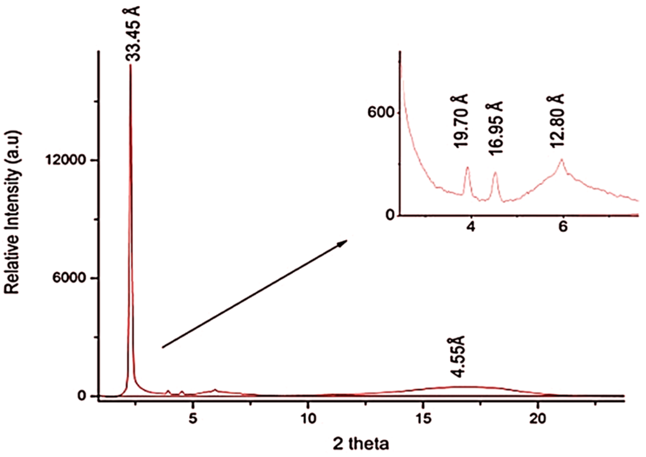


Figure 5. XRD pattern of dendrimer **2b** at 104 °C on cooling.

To understand the influence arising from the *N*-methyl groups of the central linker in the solid state, 1,4-bis(*N*-*tert*-butylamino)butane **3** and 1,4-bis(*N,N*-*tert*-butylmethylamino)-butane **4** were used as model compounds for simulation. Compound **3** possibly exists as **3-I**, **3-II** (= **3-III**), or **3-IV**, in which the central alkyl chain is arranged in a zigzag conformation (Figure 6). It is reasonable to assume that structure **3-I** is the most stable structure of compound **3** because both *tert*-butyl moieties are away from the central alkyl chain and the repulsive force between them is less; structure **3-II** is less stable because one of the *tert*-butyl moieties are close to the central alkyl chain and the corresponding repulsive force is more significant. As expected, the heat of formation for structure **3-I** was calculated to be 13.77 kcal/mol using MM2 model in CaChe program, and the heat of formation for structure **3-II** was calculated to be 16.27 kcal/mol in a similar manner. The difference of heat of formation between **3-I** and **3-II** is ~2.50 kcal/mol. However, the heat of formation of **4-I** was calculated to be 30.35 kcal/mol, which is close to that of **4-II** (30.80 kcal/mol); their difference is only ~0.45 kcal/mol, which is reasonable because the size difference between the methyl group and the *tert*-butyl moiety is much less than that between H and the *tert*-butyl moiety (see the equilibrium molecular conformations of **3-I**, **3-II**, **4-I**, and **4-II** in the SI). On the basis of this result, it is reasonable to assume that dendrimer **1b** exists as structure **1b-I** in the solid state, but dendrimer **2b** may also exist as **2b-II** together with **2b-I**. In other words, dendrimer **2b** contains at least two kinds of conformational structures, that is, **2b-II** and **2b-I**. For structure **2b-I**, there is only one dendritic skeleton, i.e., **A**, but for structure **2b-II** there may be two dendritic skeletons, i.e., **B** and **C**; in skeleton **B**, the left G_3 moiety is on the top of the right G_3 moiety, and in skeleton **C**, the right G_3 moiety is on the top of

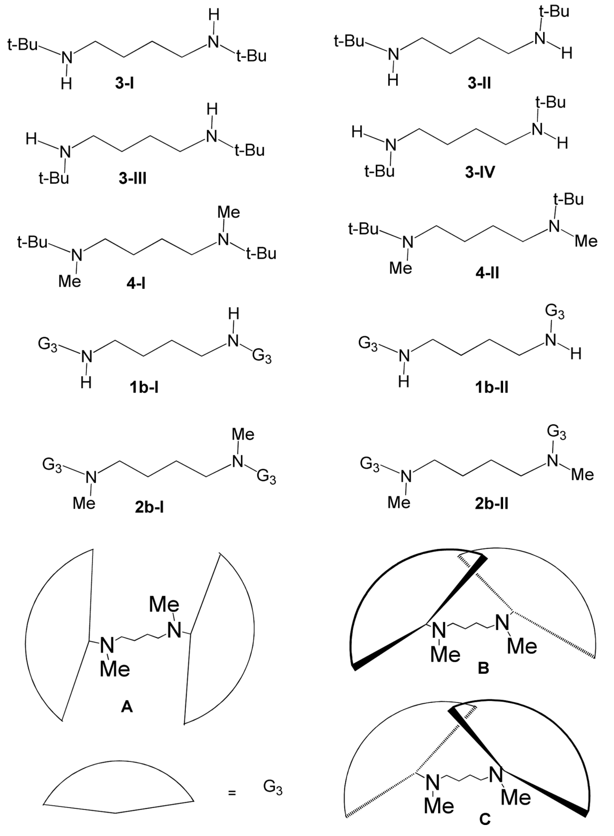
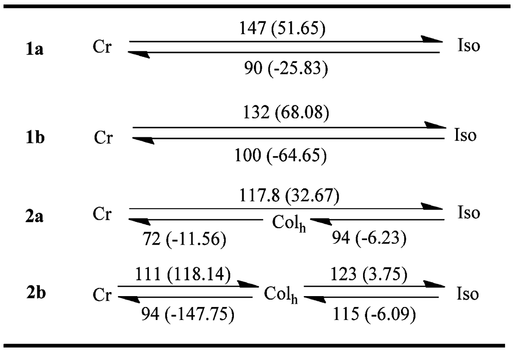


Figure 6. Possible conformations of model compounds **3** and **4** and the possible conformations of dendrimers **1b** and **2b**.

Scheme 2. Phase-Transition Temperature and Corresponding Enthalpies (kJ/mol), in Parentheses, of Dendrimers 1a,b and 2a,b[a]



[a] Cr, Col$_h$, and Iso denote the crystalline, hexagonal columnar, and isotropic phases, respectively.

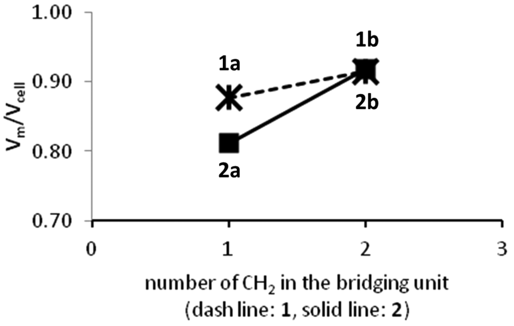


Figure 7. V_m/V_{cell} ratios of **1a,b** and **2a,b**.

Table 1. Crystallographic Data of Compounds 2a and 2b[a]

compd	phase	M_r	T (°C)	V_m (Å^3)	S_{col} (Å^2)	V_{cell} (Å^3)	V_m/ V_{cell}
2a	Col$_h$	6034	90	10533	1442	12979	0.81
2b	Col$_h$	6062	104	10688	1292	11628	0.92

[a] M_r is the molecular weight. V_m and V_{cell} are the molecular and cell volumes, respectively. S_{col} is the area of one columnar stratum. The equations and calculations corresponding to these values are detailed in the Supporting Information.

left G_3 moiety (Figure 6). Generally, compounds containing isomeric structures have lower melting points than those in pure form, which indicates structural isomers possibly tend to give reduced overall intermolecular interactions in the solid state. For example, both (*R*)-(−)-1-amino-2-propanol and (*S*)-(+)-1-amino-2-propanol have melting points at 24−26 °C, but the meting point of (±)-2-amino-1-propanol is at −2 °C.[21] Therefore, the face-to-face $\pi-\pi$ interaction with adjacent molecules in the solid state of **2b** is thus reduced due to the isomeric effect, which successfully converts nonliquid crystals of **1a** and **1b** to be liquid crystals of **2a** and **2b** during the thermal processes (Scheme 2). The clearing temperature of dendrimer **1a** is higher than that of **2a**, and similar behaviors were observed in dendrimers **1b** and **2b**, which further confirms that face-to-face interaction between adjacent molecules in dendrimers **2a** and **2b** is slightly reduced due to the isomeric effect when compared with those of **1a** and **1b**.

In our previous study, it was discovered that the analogous dendrimers with isomeric conformations have larger V_m/V_{cell} ratios.[19b] Therefore, the V_m/V_{cell} ratios of dendrimers **2a** and **2b** were calculated for comparison with those of **1a** and **1b** (Figure 7). Based on the powder-XRD, the molecular volume, cell volume, cell area, and number of molecules per cell of **2a** and **2b** were estimated as shown in Table 1, assuming a density of ca. 1 g/mL in the mesophase according to literature method.[22] The data can then be used for the realization of dendrimer packing in the columnar phase. If the thickness of a columnar stratum is ∼4.5 Å, then the number of molecules per cell would be ca. 0.5. However, more reasonably, if the thickness of a columnar stratum is 9 Å, then the number of molecules per cell would be ca. 1. For both compounds, similar numbers of molecules per cell are obtained. Therefore, for both compounds **2a** and **2b**, a columnar slice is consisted of one molecule. For the nonmesogenic compounds **1a** and **1b**, analogous data were also calculated using the crystalline XRD assuming both formed the columnar hexagonal crystalline phase. Since the calculated volumes are corrected with temperatures and the XRD data for the four compounds are collected at different temperatures, the volumes of the four compounds cannot be fairly compared. The temperature factor can be removed if the ratios of V_m/V_{cell} are compared. As shown in Figure 7, the V_m/V_{cell} ratio of dendrimer **2b** is similar to that of **1b**, but the V_m/V_{cell} ratio of dendrimer **2a** is smaller than that of **1a**. Generally, the isomeric effect reduces the face-to-face interaction between adjacent molecules, then decreasing the isotropic temperature and increasing the V_m/V_{cell} ratio in dendrimers, as shown in our previous study,[19b] but the present result, decreasing the isotropic temperature without increasing the V_m/V_{cell} ratio, seems not to be consistent with the previous result.

Undoubtedly, the presence two methyl groups connected to the nitrogens of the central linker in dendrimer **2b** leads the

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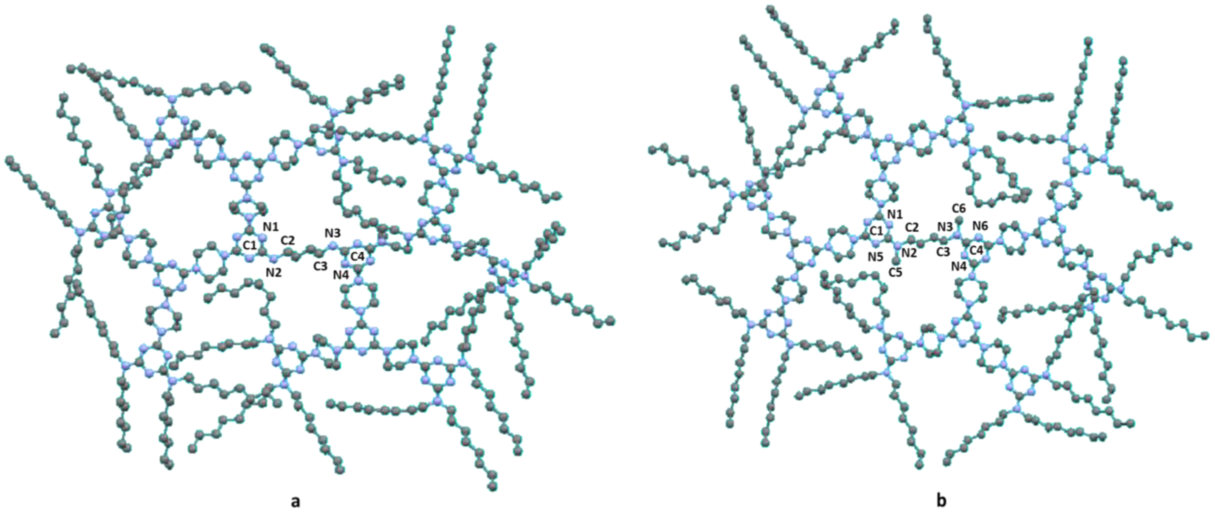

Figure 8. Equilibrium molecular conformations of (a) **1b-I** and (b) **2b-I** in a ball-and-stick model (N, purple; C, gray; H, omitted).

Table 2. Distances (*D*) of Intramolecular H-Bonds in 1b-I and 2b-I and Their Corresponding Angles (*A*)

structure	*D* of N1−H (at C2) (Å)/*A* of N1−H−C2 (deg)	*D* of N4−H (at C3) (Å)/*A* of N4−H−C3 (deg)	*D* of N5−H (at C5) (Å)/*A* of N5−H−C5 (deg)	*D* of N6−H (at C6) (Å)/*A* of N6−H−C6 (deg)
1b-I	2.37/96.6	2.45/91.9		
2b-I	2.25 /100.6	2.30/99.3	2.30/99.2	2.29/98.2

dendritic conformation of **2b** to be different from that of **1b**. To compare their differences, structures **1b-I** and **2b-I** as examples were further simulated using the MM2 model in the CaChe program in the gas phase because most dendrimers **1b** and **2b** exist as **1b-I** and **2b-I** in the solid state, respectively. The starting conformation of **G$_1$-Cl** was first established by combining one planar triazine with two dioctylamine moieties, whereby the linear alkyl chain is formulated in zigzag form and then optimized. The optimized conformation of G$_1$-NH was obtained by combining optimized **G$_1$-Cl** with piperazine in the chair form. The optimized conformation of **G$_2$-Cl** was obtained by combining a planar triazine moiety with the two optimized **G$_1$-NH** units analogously. In a similar manner, the optimized conformations of **G$_2$-NH** and **G$_3$-Cl** were thus obtained. Structure **1b-I** was first formulated by combining two optimized **G$_3$-Cl** with a 1,4-diaminobutane moiety, in which the central alkyl chain is formulated in zigzag form and then optimized. The optimized conformation of dendrimer **2b-I** was obtained similarly (Figure 8).

On the basis of the optimized molecular conformations, two intramolecular H-bonds were discovered in structure **1b-I** and four intramolecular H-bonds were discovered in structure **2b-I** (Table 2). Apparently, the H-bond interactions in **2b-I** are much stronger than those in **1b-I**. This indicates that the central linker in **2b-I** is more rigid and is less distorted than that in **1b-I** (see the SI). For example, the distances of N1−N3 and N2−N4 are 6.96 and 6.81 Å in structure **1b-I**, respectively, which are shorter than those in structure **2b-I** (N1−N3:7.31 Å; N2−N4:7.83 Å). Because of the more distorted conformation of **1b-I**, the solid stacking in dendrimer **1b** may possess more void space inside the dendritic framework than that in dendrimer **2b**. However, the face-to-face interaction between adjacent molecules of **2b** is due to the lower isomeric effect, leading the dendritic framework of **2b** to be more fluffy than that of **1b**. As a result, the two conflicting factors balance, and dendrimers **1b** and **2b** show almost the same V_m/V_{cell} ratio, as shown in Figure 7. When the central linker is shorter, the congestion from two G$_3$ dendrons becomes more vigorous and the distorted effect to allow dendrimer **1a** to be more porous dominates. Therefore, the V_m/V_{cell} ratio of **1a** is bigger than that of **2a**. This may explain that dendrimers **2a** and **2b** exhibit columnar phases on thermal treatment due to the isomeric effect but do not exhibit bigger V_m/V_{cell} ratios when compared with those of noncolumnar dendrimers **1a** and **1b**. It is found that the solubility of dendrimers accordingly decreases in the first-four generations and then suddenly increases when the dendritic generation is greater than 4. At higher generations ($n > 4$), the dendritic skeletons become more and more distorted and more void spaces are created, leading the solubility of dendrimers to increase.[17b,23] This phenomenon is consistent with our observations.

■ CONCLUSIONS

In summary, two new dendrimers **2a** and **2b**, containing the $-NMe(CH_2)_2NMe-$ and the $-NMe(CH_2)_4NMe-$ linkers between two G$_3$ moieties, respectively, were successfully prepared and observed to exhibit columnar phases on thermal treatment. However, dendrimers **1a** and **1b** containing the $-NH(CH_2)_2NH-$ and the $-NH(CH_2)_4NH-$ linkers between two G$_3$ moieties, respectively, do not show any LC phases during the thermal process. Using dendrimer **2b** as an example for molecular simulation in the gas phase, we note that **2b** possesses three kinds of isomeric structures that are more fluffy due to the lower molecular face-to-face interaction. However, one of the isomer structures (**2b-I**), majorly existing in dendrimer **2b**, is less distorted in the central linker due to the stronger H-bond interaction. This, on the other hand, leads **2b** to possess less void space in the dendritic stacking. As a result, the V_m/V_{cell} ratio of **2b** is similar to that of **1b**. When the central linker of dendrimers is shorter, the effect to be more porous due to the distorted conformation dominates, and thus, the V_m/V_{cell} ratio of **2a** is smaller than that of **1a**. Previously, we

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found that dendrimers containing isomeric conformations generally reduce the adjacent face-to-face interaction and then increase bigger V_m/V_{cell} ratio, and now we further demonstrate that dendrimers containing isomeric conformations may reduce the adjacent face-to-face interaction without increasing V_m/V_{cell} ratio in the solid state. In addition, methylation at the nitrogens of the central dendritic linker, leading the non-LC dendrimers into LC dendrimers, is worthy of further study and should be applicable to other types of unconventional dendrimers with rigid frameworks.

EXPERIMENTAL SECTION

Sample Characterization by POM. Compound **2a** or **2b** was heated to isotropic temperature and then cooled to room temperature at a rate of 20 °C/min in the first thermal process and then heated at a rate of 5 °C/min and cooled at the rate of 0.5 °C/min in the second thermal process.

Sample Characterization by DSC. Compound **2a** was heated to isotropic temperature and then cooled to room temperature at a rate of 10 °C/min in the first thermal process and then heated and cooled at a rate of 5 °C/min in the second thermal process. The transition temperature and corresponding enthalpies were recorded for the second cycles. Compound **2b** was treated similarly.

General Procedure for Preparing Dendrimers 2a and 2b. **G$_3$-Cl** (0.3 g, 0.1 mmol), prepared according to our previous procedure,[19] and the corresponding (*N*,*N*-dimethylamino)alkane (0.1 mmol) were dissolved in dry THF (15 mL) in a sealed tube and then heated at 70 °C for 24 h. Potassium carbonate (0.04 g, 0.3 mmol) and **G$_3$-Cl** (0.3 g, 0.1 mmol) were then added, and the tube was sealed. 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 × 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 × 15 cm; eluent: CH_2Cl_2 containing 5% THF) to yield the crude product, which was further recrystallized from CH_2Cl_2−CH_3OH (1:20) to give the pure desired dendrimer.

Dendrimer **2a** (0.45 g, 74.1%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 0.87 (t, J = 6.6 Hz, 96H),1.28 (s br, 320H), 1.54 (s br, 64H), 3.10 (s br, 6H), 3.45 (s br, 68H), 3.80 (s br, 96H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 14.2, 22.7, 27.1, 27.4, 28.1, 28.3, 29.3, 29.5, 29.7, 31.9, 43.1, 46.9, 47.2, 165.1, 165.4. MS calcd for $C_{350}H_{651}N_{84}$ $(M + H)^+$ 6035.4, found 6035.5. Anal. Calcd for $C_{350}H_{650}N_{84}$: C, 69.65; H, 10.86; N, 19.49. Found: C, 69.45; H, 10.93; N, 19.47.

Dendrimer **2b** (0.36 g, 60.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 0.88 (t, J = 6.6 Hz, 96H), 1.28 (s br, 320H), 1.58 (s br, 64H), 3.05 (s br, 6H), 3.45 (s br, 68H), 3.79 (s br, 100H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ 14.3, 22.8, 27.3, 27.5, 28.3, 28.4, 29.4, 29.6, 29.8, 32.1, 43.3, 47.0, 47.3, 165.2, 165.5. MS calcd for $C_{352}H_{655}N_{84}$ $(M + H)^+$: 6063.4, found 6063.0. Anal. Calcd for $C_{352}H_{654}N_{84}$: C, 69.72; H, 10.89; N, 19.40. Found: C, 69.75; H, 10.87; N, 19.24.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00555.

^{1}H and ^{13}C NMR spectra, DSC, and XRD for all new products (PDF)

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Notes

The authors declare no competing financial interest.

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