Converting non-Mesogenic to Mesogenic Stacking of Amino-s-Triazine-Based Dendrons with p-CN Phenyl Unit by Eliminating Peripheral Dipole

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Abstract: Three new amino-s-triazine-based dendrons, 1a, 1b, and 1c, containing an aryl-CN moiety in the dendritic skeleton were prepared in 72–81% yields (1a: R1 = –N(n-C8H17)2, R2 = n-OC8H17, 1b: R1 = R2 = –N(n-C8H17)2, 1c: R1 = –N(n-C8H17)2, R2 = –N(n-C4H8)2). Dendrons 1a with N(n-C8H17)2 and n-OC8H17 peripheral substituents, surprisingly, did not show any mesogenic phase during the thermal process. However, non-mesogenic 1a can be converted to mesogenic 1b or 1c by eliminating the peripheral dipole arising from the alkoxy substituent; dendron 1b only comprising the same N(n-C8H17)2 peripheral groups showed a ~25 °C mesogenic range on heating and ~108 °C mesogenic range on cooling. In contrast, dendron 1c possessing different N(n-CmH2m+1)2 (m = 8 versus m = 4) peripheral units, having similar stacking as 1b, exhibited a columnar phase on thermal treatment, but its mesogenic range (~9 and ~66 °C on heating and cooling, respectively) was much narrower than that of 1b, attributed to 1c’s less flexible alkylic chains in the peripheral part of dendron. Dendron 1a with the alkoxy substituent in the peripheral skeleton, creating additional dipole correspondingly, thus, leads to the dendritic molecules having a non-mesogenic stacking. Without the peripheral dipole for intermolecular side-by-side interaction, dendrons 1b and 1c exhibit a columnar phase on thermal treatment because of the vibration from the peripheral alkylic chain.

Keywords: triazine; liquid crystal; dendron

1. Introduction

Dendrimers, probably generated from the combination of peripheral branches and central core, have three-dimensional spatial arrangements and are interesting; their applications in various research areas have been extensively studied [1–9]. Dendrons, containing part of the branched dendritic skeleton, are analogous to dendrimers in peripheral structure; they also have the characteristic of monodispersity and possess peripheral functional groups for specific purposes as dendrimers. Particularly, multiple functionalities can also be installed onto the periphery of dendrons for exhibiting versatile properties [10–17]. Surprisingly, though dendrimers as mesogens in liquid crystals have been extensively investigated because of their uniform packing and non-grained boundaries in the LC states [18–30], dendrons in the related studies are rather limited [31–35]. Possibly, dendrimers are rather symmetrical in chemical structures, which is advantageous for the easy formation of columnar phases [36–49]. The symmetrical structural feature favoring mesophase formation...
of dendrimers was adopted for several dendrons which self-assembled into dendrimers through H-bond interaction [50–56].

We previously demonstrated that the addition of phenyl-CN lateral units in the central linker of dimeric G-3 dendrimers not only effectively broadened the range of columnar phase but also lowered the temperature of solidification on cooling [48], which can be important on the point of view of further practical applications. Discotic columnar (DC) liquid crystals possess good self-assembling ability in a long-range domain; DC materials with broad mesogenic range should be useful as solvating candidates in opto-electronic devices [23,54,57–59]. However, preparation of dimeric dendrimers with some particular functionality in the central linker may not be easy because of the steric effect from both dendronic halves. As we previously reported [48], the yields of the synthesis of dimeric dendrimers consisting of coupling two identical G-3 chloro-dendrons by means of \(N,N'\)-dibenzylpropane-1,3-diamine based central linker are only about 35%. Therefore, in order to simplify the synthesis and improve the yields of DC liquid crystals, we turn our attention to dendron-precursors, by introducing a strong polar CN functionality to the dendritic skeleton and thus hoping to lead the dendrons to exhibit a broader mesogenic range on thermal treatment. Previously, we also demonstrated that breaking the symmetry of the amino-\(s\)-triazine-based dendrimers by linking different peripheral groups in the same molecule successfully converted non-mesogenic to mesogenic dendrimers [44]. Based on the combined strategies, i.e., incorporation of a CN polarity and symmetry-breaking, we efficiently prepared dendrons 1a–1c in 72–81% yields from the reaction of G-3 chloro-dendrons with 4-cyanophenylpiperazine (Scheme 1). Particularly, dendron 1b showed a ~108 °C mesogenic range on cooling, which is better than the mesogenic ranges of most of the previously reported amino-\(s\)-triazine-based dendrimers on thermal treatment [43–49] and should possess potential application in the related opto-electronic devices. If so, compared with dendrimers, their dendron-precursors probably possess lower molecular weights and may be easier in preparation because significant steric effects generally arise from the both dendronic halves in preparing dendrimers. Based on the lower cost in chemicals and the better efficiency in preparation, it is worthwhile to prepare and study dendrons in their solid stackings. We herein wish to report the results.

**Scheme 1.** Preparation of dendrons 1a–c.
2. Experimental Section

2.1. General Methods

Chemicals were used after purchase without further purification. Elemental analyses were performed using an Elementar Unicube analyzer (Elementar, Langenselbold, Germany). NMR spectra were recorded on Bruker AM 300 instrument (Bruker, Billerica, MA, USA) operating at 300 and 75 MHz for $^1$H and $^{13}$C nuclei, respectively. All chemical shifts (δ values) are given in parts per million (ppm); all homocoupling patterns (n, J, H, H values) are given in Hertz. Chemical shifts were measured against TMS as reference signal. The MALDI-TOF mass spectra were obtained from a Voyager-DE PRO (Applied Biosystems) mass spectrometer (Bruker, Billerica, MA, USA). The mesogenic textures and phase transitions were obtained from polarizing optical microscopy and differential scanning calorimetry (Perkin-Elmer DSC Diamond; Perkin Elmer, Waltham, MA, USA). The XRD studies were performed at the temperature of mesogenic ranges. Synchrotron power X-ray diffraction (XRD) measurements were completed at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, with the X-ray wavelength of 1.334431 Å. The powder samples were added into a capillary tube, and the temperature controller is programmable by a PC with a PID feedback system.

2.2. Sample Characterization by POM

4-{4-{4,6-Bis{4-{4,6-bis{4-{4-di(n-octyl)amino,6-(n-octyloxy)-s-triazin-2-yl}-piperazin-1-yl}-s-triazin-2-yl}-piperazin-1-yl}-benzonitrile $^{1a}$ was heated to 210 °C to let $^{1a}$ become isotropic, and then cooled to room temperature at the rate of 20 °C/min in the first thermal cycle. Compound $^{1a}$ was further treated at the rate of 5 °C/min on heating, and then 1 °C/min on cooling in the second cycle. 4-{4-{4,6-Bis{4-{4,6-bis{4-{4-di(n-octyl)amino,6-di(n-octyl)-s-triazin-2-yl}-piperazin-1-yl}-s-triazin-2-yl}-piperazin-1-yl}-benzonitrile $^{1b}$ and 4-{4-{4,6-Bis{4-{4,6-di(n-octyl)amino,6-di(n-butyl)-s-triazin-2-yl}-piperazin-1-yl}-s-triazin-2-yl}-piperazin-1-yl}-benzonitrile $^{1c}$ were treated similarly.

2.3. Sample Characterization by DSC

$^{1a}$ was heated to 210 °C, and then cooled to room temperature at the rate of 10 °C/min in the first cycle. In the second thermal process, $^{1a}$ was then heated and cooled at the rate of 5 °C/min for recording the transition temperature and corresponding enthalpies. $^{1b}$ and $^{1c}$ were accordingly treated.

2.4. Preparation of Chloro-Dendrons $^{G_{3c}}$-Cl and $^{G_{4c}}$-Cl

$^{G_{4c}}$-Cl: Cyanuric chloride (3.68 g, 20.0 mmol) was added to dry DCM (100 mL) at 5 °C, and dioctylamine (4.83 g, 20.0 mmol) in dry DCM (10.0 mL) was then added. The reaction mixture was stirred for 30 min. After the reaction was confirmed to be complete by silica-TLC, KOH (3.37 g, 60.0 mmol) in water (50 mL) was added. After stirring, the organic solvent was separated, dried over MgSO$_4$, and then followed by the addition of dibutylamine (2.58 g, 20.0 mmol) in dry DCM (10.0 mL). After 30 min, trimethylamine (6.07 g, 60.0 mmol) was added, and the reaction mixture was stirred at room temperature for 10 h. After the reaction was confirmed to be complete by silica-TLC, KOH (3.37 g, 60.0 mmol) in water (50 mL) was added. After stirring, the organic solvent was separated, dried over MgSO$_4$, and then concentrated under reduced pressure to dryness to give a colorless liquid, which was purified by chromatography (15 × 2.1 cm of silica; eluates DCM/hexane (1/4 v/v)) to yield $^{G_{4c}}$-Cl as a colorless liquid in 83% yield (7.97 g) with respect to Cyanuric chloride. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): δ$_H$ 0.89 (t, $^3J = 5.4$ Hz, 6H, 2×CH$_3$), 0.93 (t, $J = 5.4$ Hz, 6H, 2×CH$_3$), 1.15 (s, br. 24H, 12×CH$_2$), 1.55 (s, br. 8H, 4×CH$_2$), 3.39–3.51 (m, 8H, 4×CH$_2$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): δ$_C$ 20.2, 20.5, 22.8, 27.0, 27.4, 27.8, 28.2, 29.4, 29.5, 29.7, 29.9, 30.4, 32.0, 46.9, 47.2, 47.3, 47.6, 164.6, 169.1 ppm. MS calculated for C$_{27}$H$_{53}$N$_5$Cl [M + H]$^+$: 483.20; found 483.28. HRMS: calculated for C$_{27}$H$_{53}$N$_5^{35}$Cl [M + H]$^+$: 482.3989; found 482.4003.
G1c-N-NH: G1c-Cl (15.53 g, 32.2 mmol) in THF (10 mL) was added to piperazine (8.32 g, 96.6 mmol) in THF (100 mL), and the resulting solution was stirred at 40 °C for 30 min. Triethylamine (9.78 g, 96.6 mmol) was added, and the solution was stirred for another 15 h. After checking the completion of the reaction by silica-TLC, KOH (5.42 g, 66.6 mmol) in water (50 mL) was added. After stirring the mixture, the organic solvent was separated, dried over MgSO4, and then concentrated under reduced pressure to dryness to give a colorless liquid, which was purified by chromatography (10 × 2.1 cm of silica; eluates DCM/THF (4/1 v/v)) to yield G1c-N-NH as a colorless liquid in 80% yield (13.69 g) with respect to G1c-Cl. 1H NMR (300 MHz, CDCl3, 25 °C): δH 0.89–0.95 (m, 24H, 8 × CH3), 1.25 (s, 2H, 8 × CH2), 1.56 (s, 16H, 8 × CH2), 1.99 (s, 1H, NH), 3.28 (s, 4H, 2 × CH2), 3.45 (s, 16H, 8 × CH2), 3.78 (s, 20H, 10 × CH2) ppm. 13C NMR (75 MHz, CDCl3, 25 °C): δc 14.2, 14.3, 20.5, 22.8, 25.7, 27.4, 28.4, 29.5, 29.6, 30.5, 31.7, 32.0, 43.2, 43.4, 46.8, 47.1, 46.8, 47.2, 47.4, 164.7, 165.2, 165.5, 165.6 ppm. MS calculated for C31H62N7 [M + H]⁺: 532.5087; found 532.5067.

G2c-Cl: G1c-N-NH (10.5 g, 19.8 mmol) in dry DCM (10.0 mL) was added to cyanoic chloride (1.82 g, 9.88 mmol) in dry DCM (50 mL) at 5 °C, and the reaction mixture was then stirred for 30 min. Triethylamine (6.07 g, 60.0 mmol) was added, and the reaction mixture was stirred at room temperature for 18 h. After the reaction was confirmed to be complete by silica-TLC, KOH (3.37 g, 60.0 mmol) in water (50 mL) was added. After stirring, the organic solvent was separated, dried over MgSO4, and then concentrated under reduced pressure to dryness to give a colorless residue, which was purified by chromatography (15 × 2.1 cm of silica; eluates DCM/hexane (1/2 v/v)) to yield G2c-Cl as a colorless solid in 62% yield (7.25 g) with respect to G1c-N-NH. 1H NMR (300 MHz, CDCl3, 25 °C): δH 0.65–0.71 (m, 24H, 8 × CH3), 1.25 (s, 48H, 24 × CH2), 1.56–1.59 (m, 16H, 8 × CH2), 1.99 (s, 1H, NH), 3.28 (s, 4H, 2 × CH2), 3.45 (s, 16H, 8 × CH2), 3.78 (s, 20H, 10 × CH2) ppm. 13C NMR (75 MHz, CDCl3, 25 °C): δc 14.2, 14.3, 20.5, 22.8, 25.7, 27.4, 28.4, 29.5, 29.6, 30.5, 31.7, 32.0, 43.2, 44.5, 46.2, 47.1, 46.8, 47.2, 47.4, 164.7, 165.2, 165.5, 165.6 ppm. MS calculated for C65H129N17Cl [M + H]⁺: 1176.22; found 1175.83. HRMS: calculated for C65H121N17Cl35 [M + H]⁺: 1174.9697; found 1174.9697.

G2c-N-NH (6.63 g, 88%), with respect to G2c-Cl, was obtained from the reaction of G2c-Cl (7.25 g, 6.16 mmol) with piperazine (1.59 g, 18.48 mmol) in a similar manner to prepare G1c-N-NH. 1H NMR (300 MHz, CDCl3, 25 °C): δH 0.85–0.94 (m, 24H, 8 × CH3), 1.25 (s, 48H, 24 × CH2), 1.56 (s, 16H, 8 × CH2), 1.99 (s, 1H, NH), 3.28 (s, 4H, 2 × CH2), 3.45 (s, 16H, 8 × CH2), 3.78 (s, 20H, 10 × CH2) ppm. 13C NMR (75 MHz, CDCl3, 25 °C): δc 14.2, 14.3, 20.5, 22.8, 25.7, 27.4, 28.4, 29.5, 29.6, 30.5, 31.7, 32.0, 43.3, 44.5, 46.2, 47.1, 46.8, 165.1, 165.6, 165.6 ppm. MS calculated for C66H129N17Cl [M + H]⁺: 1224.89; found 1224.37. Elemental analysis calculated for C66H129N17Cl: C 66.67; H 10.62; N 21.73; found C 67.99 H 10.68; N 21.60.

G3c-Cl (0.78 g, 63%), with respect to G2c-N-NH, was obtained from the reaction of G2c-N-NH (1.9 g, 9.97 mmol) with cyanoic chloride (0.09 g, 0.48 mmol) in a similar manner to prepare G2c-Cl. 1H NMR (300 MHz, CDCl3, 25 °C): δH 0.86–0.96 (m, 24H, 8 × CH3), 1.28 (s, 1H, NH), 3.28 (s, 16H, 8 × CH2), 3.46 (s, 32H, 16 × CH2), 3.79+3.83 (2s, 48H, 24 × CH2) ppm. 13C NMR (75 MHz, CDCl3, 25 °C): δc 14.2, 20.5, 22.8, 27.3, 28.3, 29.5, 29.7, 30.5, 32.0, 43.2, 43.3, 43.6, 47.0, 47.3, 164.7, 165.3, 165.5 ppm. MS calculated for C141H254N44Cl [M + H]⁺: 2561.27; found 2561.47. Elemental analysis calculated for C141H254N44Cl: C 66.12; H 10.17; N 22.61; found C 66.38 H 10.15; N 22.21.

G3c-N-NH (2.13 g, 76%), with respect to G2c-N-NH, was obtained from the reaction of G2c-N-NH (2.50 g, 2.0 mmol) with cyanoic chloride (0.18 g, 1.0 mmol) in a similar manner to prepare G2c-Cl. 1H NMR (300 MHz, CDCl3, 25 °C): δH 0.89 (s, 24H, 12 × CH3), 1.29 (s, 1H, NH), 1.60 (s, 1H, NH), 1.72–1.81 (m, 20H, 10 × CH2), 3.46 (s, 16H, 8 × CH2), 3.82 (s, 48H, 24 × CH2) ppm. 13C NMR (75 MHz, CDCl3, 25 °C): δc 14.1, 22.6, 26.0, 27.1, 27.7, 28.1 29.0, 29.2, 29.3, 29.4, 31.8, 43.1, 47.1, 66.6, 165.4, 165.9, 166.2, 177.7 ppm. MS calculated for C141H254N47O4Cl [M – H]⁻:
2564.21; found 2564.00. Elemental analysis calculated for C_{141}H_{252}N_{37}O_{4}Cl: C 66.02; H 9.90; N 20.20; found C 66.22 H 10.02; N 20.26.

2.5. The Typical Procedure for Preparing Dendrons 1a–1c

To a THF (25 mL) solution containing dendron G_{3a}-Cl (0.28 g, 0.10 mmol) and 4-piperazinobenzonitrile (0.03 g, 0.15 mmol), K_{2}CO_{3} (0.04 g, 0.30 mmol) was added, and the resulting suspension was then heated at 110 °C for 18 h in a sealed tube. After the reaction was confirmed to be complete by silica-TLC, the solvent was removed under reduced pressure to dryness, and then a water (50 mL) solution containing K_{2}CO_{3} (0.14 g, 0.10 mmol) was added. The mixture was extracted with DCM (2 × 30 mL). The combined organic extracts were dried over MgSO_{4} and then concentrated under reduced pressure to dryness. The crude solid residue was recrystallized from a DCM/MeOH (20/1 v/v) mixture to give dendron 1a as a colorless solid in 72% yield (0.23 g) with respect to G_{2a}-Cl. \(^{1}H\) NMR (300 MHz, CDCl_{3}, 25 °C): \(\delta = 8.4\) Hz, 2H, 2 × CH; 3.80 + 3.83 (2s, 48H, 24 × CH); 3.49 (s, 32H, 16 × CH); 6.89 (d, \(J = 8.4\) Hz, 2H, 2 × CH) ppm. MS calculated for C_{141}H_{252}N_{37}O_{4}Cl: C 66.08; H 10.60; N 19.57; found C 66.02; H 10.60; N 19.57.

Dendrons 1b and 1c were prepared accordingly from reactions of 4-piperazinobenzonitrile (0.03g, 0.15 mmol) with G_{3b}-Cl (0.30 g, 0.1 mmol) and G_{3c}-Cl (0.27 g, 0.1 mmol), respectively.

Dendron 1b: A colorless solid in 73% (0.20 g). \(^{1}H\) NMR (300 MHz, CDCl_{3}, 25 °C): \(\delta = 8.4\) Hz, 2H, 2 × CH; 3.80 + 3.83 (2s, 48H, 24 × CH); 3.49 (s, 32H, 16 × CH); 6.89 (d, \(J = 8.4\) Hz, 2H, 2 × CH) ppm. MS calculated for C_{183}H_{332}N_{44}O_{4} [M]^{+}: 3160.8; found 3160.9. Elemental analysis calculated for C_{183}H_{332}N_{44}: C 69.80; H 10.60; N 19.57; found C 70.08; H 10.68; N 19.24.

Dendron 1c: A colorless solid in 81% (0.23 g). \(^{1}H\) NMR (300 MHz, CDCl_{3}, 25 °C): \(\delta = 8.4\) Hz, 2H, 2 × CH; 3.80 + 3.83 (2s, 48H, 24 × CH); 3.49 (s, 32H, 16 × CH); 6.89 (d, \(J = 8.4\) Hz, 2H, 2 × CH) ppm. MS calculated for C_{152}H_{268}N_{44}O_{4} [M]^{+}: 2712.1; found 2712.8. Elemental analysis calculated for C_{152}H_{268}N_{44}: C 70.96; H 9.96; N 22.72; found C 70.09 H 9.89; N 22.47.

3. Results and Discussion

We previously reported [43–48] the synthesis of G-2 piperazine-dendrons G_{2a}-N~NH and G_{2b}-N~NH, and G-3 chloro-dendrons G_{3b}-Cl. G_{3c}-N~NH was thus prepared in a similar manner, and, subsequently, reaction of G_{2a}-N~NH and G_{2b}-N~NH with cyanuric chloride produced G_{3a}-Cl and G_{3c}-Cl, respectively (Scheme 2). Reaction of G_{3a}-Cl, G_{3b}-Cl, and G_{3c}-Cl with 4-piperazinobenzonitrile produced dendrons 1a (~72%), 1b (~73%), and 1c (~81%), respectively (Scheme 1). Dendrons 1a,b,c were fully confirmed by \(^{1}H\) and \(^{13}C\) NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectrometry.
Dendron 1a did not exhibit any mesogenic phase either on heating or on cooling. Dendrons 1b and 1c were observed to show a mosaic texture under polarizing optical microscopy (POM) on thermal treatment (Figure 1). The thermal behaviors of dendrons 1a–1c were also examined by differential scanning calorimetry (DSC) (Figures S1–S3) and are summarized in Scheme 3. Surprisingly, dendron 1a directly solidified at ~159 °C from the isotropic state without showing mesogenic phase on cooling, which was confirmed by the studies of POM (Figure S4) and seemed to differ from our previous observation that dendrimers with various peripheral functionalities exhibited better mesogenic ranges than those with identical peripheral functionalities [44]; this will be discussed in detail later. Dendron 1b showed a hexagonal columnar mesophase between ~191 °C and ~83 °C on cooling. Dendron 1c with different peripheral functionalities was, thus, further prepared for comparison; 1c exhibited a hexagonal columnar mesophase between ~187 °C and ~121 °C on cooling. The Iso-to-Col\textsubscript{h} transition temperature of 1b and 1c seems not to differ much from each other, but the mesogenic ranges for 1b (~108 °C) is very different from that of 1c (~66 °C) on cooling because of supercooling of 1b. However, the mesogenic ranges on heating for 1b (between ~169 and ~194 °C) and 1c (between ~181 and ~190 °C) are not so much different.
Figure 1. The POM textures of dendrons 1b (a) and 1c (b), which were taken at 180 °C and 165 °C, respectively, in the second cycle at the cooling rate of 1 °C/min.

Scheme 3. The enthalpies (kJ/mol) of dendrons 1a–1c at various phase transition temperatures. Cr, Cr’, and Cr” all represent the crystalline state but in different packings. Colh and Iso denote the hexagonal columnar and isotropic phases, respectively.

The mesogenic phases of dendrons 1b and 1c were characterized to be hexagonal columnar by powder-XRD (Figure 2). A peak at 33.81 Å, which is sharp and appears in the small-angle region of powder XRD of 1b, arose from the reflection of d10. The two weak signals at 19.45 and 16.86 Å resulted from the reflections of d11 (calculated 19.52 Å) and d20 (calculated 16.91 Å), respectively. The significantly larger linewidth of the broad signal at 12.77 Å than those of d10, d11, and d20 excludes the possibility of assigning the signal to be d21, though the d-spacing is close to the calculated d21 of 12.78 Å. The signal at 12.77 Å can be due to intracolumnar correlations based on its characteristic of the large line-width. The broad signal at 4.35 Å with the characteristic of a weak correlation was attributed to chain correlations. The XRD reflection pattern indicated that the calculated lattice constant a of dendron 1b in the hexagonal columnar phase was 39.04 Å. The XRD reflection pattern of 1c was similar to that of 1b, indicating both dendrons have the same mesophases during the thermal process. The d10, d11, and d20, and the lattice constant a of 1c were 31.75, 18.35, 16.02, and 36.66 Å, respectively. For comparison, the calculated d11 and d20 were 18.33 and 15.88 Å, respectively. It is noteworthy that two broad wide-angle signals at 4.22 and 4.17 Å were observed for 1c, showing the mixed stacking of alkyl halos from the weak correlations of two amino groups, i.e., N(n-C₈H₁₇)₂ and N(n-C₄H₉)₂, as shown in the literature [44].
Dendron 1a, containing another constructing unit IIC with lower dipole moment in skeleton, was also studied by powder-XRD; based on the reflection pattern at 145 °C on cooling (Figure 3), it is reasonable to assume that dendron 1a has a more highly ordered arrangement than 1b and 1c in the related temperature range, which is also supported by the DSC of 1a (Figure S1).

Although, in a previous report [44], we noticed that linking different peripheral functionalities to the same dendritic skeleton can convert the non-mesogenic dendrimer to become mesogenic. This seems not to be applicable to the case of dendrons under current study. Indeed, dendron 1a bearing N(n-C₈H₁₇)₂ and n-OC₈H₁₇ peripheral substituent, did not exhibit any mesogenic behaviors during the thermal process. By contrast, having installed identical N(n-C₈H₁₇)₂ (1b) or different N(n-C₈H₁₇)₂ versus N(n-C₄H₉)₂ (1c) substituents at the periphery, dendrons 1b and 1c were observed to be mesogenic on thermal treatment. To have a deeper understanding of such the observation, the conformations of dendrons 1a–c were studied by CaChe using the MM2 model. The conformation of 1b was obtained by combining the optimized dendron G₃₋Cl [47] with 4-piperazinobenzonitrile and then optimized. The conformations of 1a and 1c were optimized in a similar manner.

The optimized geometries of dendrons 1a–c were quite similar to each other in the gas phase; there were no serious steric congestion in their frameworks, and only part of alkyl group were overlapped in the peripheral moiety (Figure 4; side views: Figure S5). Such minor (almost negligible) variation between the optimized geometries of 1a–c seemed to us unlikely to be responsible for the absence of any mesogenic behavior of 1a with respect to 1b and 1c. We, thus, further calculated the dipole moment of each constructing unit of the dendrons. Dendrons 1a–c consisted of one cyanobenzene II/A unit and two triazine moieties, i.e., IIB and IIC in their dendritic frameworks (Figure 5). For simplicity, the dimethylamino and methoxy moieties were used to replace dialkylamino and alkoxy groups, respectively, for molecular simulation in the gas phase. The frequency and geometry optimizations of
IIA was first performed by the Gaussian 09 at the B3LYP/6-31G** level, and the dipole moment of IIA was calculated to be 7.33 Debye, which is close to that reported in the literature (7.28 Debye) [60–63]. The corresponding optimizations of IIB and IIC were, thus, accomplished in a similar manner. The dipole moment of IIB and IIC were calculated to be 0.03 and 2.22 Debye, respectively. The calculation details and the corresponding conformations of IIA-IIC are provided in supporting information (Table S1 and Figure S6).

Figure 4. The conformations (top views) of dendrons 1a (a), 1b (b), and 1c (c) calculated by CaChe using the MM2 model; Hs are omitted for clarity.

Figure 5. The calculated dipole moments of IIA-IIC. Arrows (red: partially negative; blue: partially positive) indicate the dipole orientations of the fragments.

With the above optimized results, we assumed that dendrons 1b and 1c may form a dimer in the solid stacking because of the intermolecular interaction of dipole unit IIA. On the other hand, electron density maps (EDM) of 1b/1c in LC states were calculated from XRD data [63], and the results clearly reveal that, in these two cases, one disc is significantly larger than the dimensions of one dendron and is close to two dendrons packed with antiparallel alignment of polar -CN ends (Figure 6a). Scaled schematic representations of discs and disc packing, along with corresponding EDMs of 1b,c, are shown in Figure 7. For 1b and 1c, columnar hexagonal packing of discs were obtained from the EDM results and structure simulations. The details for carrying out the EDM analysis and corresponding scaled schematic representations of disc/disc-packing are provided in supporting information (Figure S7). The dimeric dendron-pair in one disc of 1b and 1c, arising from the strong polar interaction of IIA between two dendronic halves, may behave as the reported dendrimers in the condensed phases and thus exhibited mesogenic phases.
on thermal treatment [44–49]. For dendron 1a, it is reasonable to assume that a dimeric unit is also formed first due to the dipole moment IIa. However, another dipole moment from IIC may further increase the side-to-side interaction between dimeric dendron-pair of 1a, thus probably leading to the non-liquid-crystalline behavior. Another possibility of non-mesogenic behaviors of 1a on thermal treatment may arise from the lack of branching in the ether derivatives, which allows for easier crystallization. Both could be supported by the high enthalpy (52.51 kJ/mol) of 1a between isotropic and crystalline state on cooling. Without the dipole interaction and with more branch alkyl chains at the periphery, each paired unit of dendrons 1b and 1c is separated because of the peripheral alkyl vibration, thus resulting in the formation of hexagonal columnar arrangement.

Figure 6. Electron density map (EDM) and scaled disc packing for 1b,c. (a) Schematic representation of one molecule and one disc in the dimer formation model derived from XRD data; (b,c) EDMs (right) and scaled disc packing (left) of 1b and 1c.
For 1b, the broad XRD signals at 12.77 Å can also be attributed to the intracolumnar periodicity as the ratio of the two broad signals of 12.77 and 4.35 Å is 2.94, which is similar to that (12.13 Å/4.17 Å = 2.91) of 1c. Therefore, these ratios suggest that, within columns, each dendron rotates 120° and repeats the same direction every four dendrons. In such packing, the monomer dipoles are also, overall, canceled.

It is worthy to note that the isotropic temperature of dendron 1b (molecular weight: ~3161) on heating was 194.0 °C, which is similar to that of 1c, 189.9 °C (molecular weight: ~2712), and that the Iso-to-Colh transition temperature of 1b on cooling was ~191 °C, which was also close to that of 1c, 187 °C, indicating that the stacking patterns of dendrons 1b and 1c are very similar in the solid state, and the variation of molecular weight for 1b and 1c seem not to have significant influence on the thermal behaviors around their isotropic state. However, the Colh-to-Cr transition temperature of 1b was ~83 °C, which is much lower than that of 1c (~121 °C), and this may be because the peripheral groups of 1b [R1 = R2 = –N(n-C8H17)2] were more flexible than those of 1c [R1 = –N(n-C8H17)2, R2 = –N(n-C4H9)2], resulting in the more difficulty of solidifying of 1b on cooling. Interestingly, the molecular weight of 1a (~2716) was close to that of 1c, but the isotropic temperature of dendron 1a on heating was 180.8 °C, a little less than that of 1c. Additionally, the first transition of 1a on cooling is 159.1 °C, much lower than that of 1c. In principle, the additional peripheral dipole moment of 1a should result in more condensed stacking in the solid state due to the side-by-side interaction, then giving a higher isotropic temperature on heating or the first transition on cooling in comparing with those of 1c. However, the observed thermal behaviors is on the contrary to this assumption, which may be attributed to the isomeric effect of 1a [44,46,47,49]. As shown in Scheme 1, conformational isomers of dendrons 1a were expected to be produced from the reaction of 4-piperazinobenzonitrile with G3a-Cl because G3a-Cl is generated from the combination of two equivalents of G-2 piperazine-dendron and cyanuric chloride. One piperazine-dendron consists of at least four conformational isomers, as demonstrated in Figure 7; therefore, dendrons 1a and 1c should consist of plural isomers in their corresponding preparation, as discussed in the literature [44]. For the rationalization of liquid crystallinity of 1a-c, in addition to the intermolecular dipole-dipole interactions, the bulkiness ratio of the core and alkyl portions can also be an important factor. The 16 C8-chains of 1b as compared to 12 C8-chains result in smaller core/chain bulkiness ratio of 1a to lead to its liquid crystallinity. For 1a and 1c, though the total numbers of chain carbons are the same for the two, the bulkiness of fork-like –N(C4H9)2 of 1c is larger than that of the straight -OC8H17 of 1a to lead to the core/chain bulkiness ratio of 1c to be smaller than that of 1a and, therefore, better liquid crystallinity of 1c.
4. Conclusions

In summary, dendrons 1a–c were efficiently prepared in good yields. Dendron 1a with dialkylamino and alkoxy peripheral substituents does not exhibit any mesogenic phases on thermal treatment because of its strong side-by-side interactions from the peripheral dipole or from the lack of branching in the ether derivatives, which results in easier crystallization. However the non-mesogenic 1a can be converted to be mesogenic 1b or 1c just by changing alkoxy to dialkylamino substituents. Therefore, with the vibration of peripheral alkyl group, dendrons 1b and 1c with only one dipole moiety (aryl-CN) in the dendritic skeleton lead their molecular arrangements to behave similar to those of reported dendritic dimers [44–49] and, thus, exhibit columnar phases on thermal treatment. In addition, the trend of bulkiness ratio of the core and alkyl portions, 1b > 1c > 1a, may also play an important role to the resulting same trend of liquid crystallinity. However, the mesogenic range of dendron 1b is broader than those of dendrimers in reported literatures [44–49], and dendron 1b, possessing fewer synthetic steps and better yield in incorporation of CN unit in the dendritic core, therefore, can be very useful as solvating reagents in the development of opto-electronic devices in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12020185/s1, Figure S1: DSC spectra of 1a, Figure S2: DSC spectra of 1b, Figure S3: DSC spectra of 1c, Figure S4: POM at 136.5 °C of 1a, Figure S5: The conformations of dendrons 1a–c from the side views, Figure S6: The corresponding conformations of IIA–IIC, Figure S7: The details for carrying out the EDM analysis and corresponding scaled schematic representations of disc/disc-packing, Table S1: Computational detail.

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References
1. Newkome, G.R.; Moorefield, C.N.; Vögtle, F. Dendrimers and Dendrons: Concepts, Syntheses, Applications; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2001.
2. Caminade, A.-M.; Turrin, C.-O.; Laurent, R.; Ouali, A.; Delavaux-Nicot, B. Dendrimers: Towards Catalytic, Material and Biomedical Uses; Wiley: New York, NY, USA, 2011.
3. Kato, T.; Uchida, J.; Ichikawa, T.; Sakamoto, T. Functional Liquid Crystals towards the Next Generation of Materials. Angew. Chem. Int. Ed. 2018, 57, 4355–4371. [CrossRef]
4. Sagara, Y.; Yamane, S.; Mitani, M.; Weder, C.; Kato, T. Mechanoresponsive Luminescence: Mechanoresponsive Luminescent Molecular Assemblies: An Emerging Class of Materials (Adv. Mater. 6/2016). Adv. Mater. 2016, 28, 977. [CrossRef]
5. Tang, Y.-H.; Cangiotti, M.; Kao, C.-L.; Ottaviani, M.F. EPR Characterization of Copper(II) Complexes of PAMAM-Py Dendrimers for Biocatalysis in the Presence of Reducing Agents and a Spin Trap. J. Phys. Chem. B 2017, 121, 10498–10507. [CrossRef]
6. Thompson, S.J.; Soukri, M.; Lail, M. Phosphorus Dendrimer Derived Solid Sorbents for CO2 Capture from Post-Combustion Gas Streams. Energy Fuels 2018, 32, 8658–8667. [CrossRef]
7. Lu, Y.-C.; Chien, C.-Y.; Hsu, H.-F.; Lai, L.-L. Adsorbing volatile organic chemicals by soluble triazine-based dendrimers under ambient conditions with the adsorption capacity of pyridine up to 946.2 mg/g. *Molecules* **2021**, *26*, 4862. [CrossRef]

8. Lee, C.-H.; Tsai, M.-R.; Chang, Y.-T.; Lai, L.-L.; Lu, K.-L.; Cheng, K.-L. Preparation of Unconventional Dendrimers that Contain Rigid NH—Triazine Linkages and Peripheral tert-Butyl Moieties for CO2-Selective Adsorption. *Chem. Eur. J.* **2013**, *19*, 10573–10579. [CrossRef] [PubMed]

9. Lee, C.-H.; Soldatov, D.V.; Tzeng, C.-H.; Lai, L.-L.; Lu, K.-L. Design of a Peripheral Building Block for H-Bonded Dendritic Frameworks and Analysis of the Void Space in the Bulk Dendrimers. *Sci. Rep.* **2017**, *7*, 3649. [CrossRef] [PubMed]

10. Connal, L.A.; Vestberg, R.; Hawker, C.J.; Qiao, G.G. Synthesis of Dendron Functionalized Core Cross-linked Star Polymers. *Macromolecules* **2007**, *40*, 7855–7863. [CrossRef]

11. Whitton, G.; Gilles, E.R. Functional aqueous assemblies of linear-dendron hybrids. *J. Polym. Sci. A Polym. Chem.* **2015**, *53*, 148–172. [CrossRef]

12. Kuchkina, N.V.; Yuzik-Klimova, E.Y.; Sorokina, S.A.; Peregudov, A.S.; Antonov, D.Y.; Gage, S.H.; Boris, B.S.; Nikoshvili, L.Z.; Sulman, E.M.; Morgan, D.G.; et al. Polyphenylenepyridyl Dendrons with Functional Periphery and Focal Points: Syntheses and Applications. *Macromolecules* **2013**, *46*, 5890–5898. [CrossRef]

13. Han, Y.; Zhu, B.; Chen, Y.; Br, Z.; Chen, Y. Amphiphilic dendrons with a pyrene functional group at the focal point: Synthesis, self-assembly and generation-dependent DNA condensation. *Polym. Chem.* **2017**, *8*, 4798–4804. [CrossRef]

14. Chen, C.; Chen, Q.; Kang, J.; Shen, J.; Wang, B.; Guo, F.; Chen, Z. Hydrophilic triazine-based dendron for copper and lead adsorption in aqueous systems: Performance and mechanism. *J. Mol. Liq.* **2020**, *298*, 112031. [CrossRef]

15. Zhang, X.; Wang, X.; Qiu, H.; Sun, X.; Han, M.; Guo, Y. Nanoadsorbents preparing from oligoethylene glycol dendron and citric acid: Enhanced adsorption performance for the removal of heavy metal ions. *Colloids Surf. B* **2020**, *189*, 110876. [CrossRef]

16. Liu, Y.; Mu, S.; Liu, X.; Ling, Q.; Hang, C.; Ruiz, J.; Astruc, D.; Gu, H. Ferrocenyl Janus mixed-dendron stars and their stabilization of Au and Ag nanoparticles. *Tetrahedron* **2018**, *74*, 4777–4789. [CrossRef]

17. Calik, F.; Degirmenci, A.; Eceoglu, M.; Sanyal, A.; Sanyal, R. Dendron–Polymer Conjugate Based Cross-Linked Micelles: A Robust and Versatile Nanosystem for Targeted Delivery. *Bioresin. Chem.* **2019**, *30*, 1087–1097. [CrossRef]

18. Soberats, B.; Yoshio, M.; Ichikawa, T.; Zeng, X.; Ohno, H.; Ungar, G.; Kato, T. Ionic Switch Induced by a Rectangular–Hexagonal Phase Transition in Benzenammonium Columnar Liquid Crystals. *J. Am. Chem. Soc.* **2015**, *137*, 13212–13215. [CrossRef]

19. Chico, R.; de Domingo, E.; Dominguez, C.; Donnio, B.; Heinrich, B.; Termine, R.; Golemme, A.; Coco, S.; Espinet, P. High One-Dimensional Charge Mobility in Semiconducting Columnar Mesophases of Isocyano-Triphenylene Metal Complexes. *Chem. Mater.* **2017**, *29*, 7587–7595. [CrossRef]

20. Liu, C.-X.; Wang, H.; Du, J.-Q.; Zhao, K.-Q.; Hu, P.; Wang, B.-Q.; Monobe, H.; Heinrich, B.; Donnio, B. Molecular design of benzotheno[4,3-b]phenothiazine-cored columnar mesogens: Facile synthesis, mesomorphism, and charge carrier mobility. *J. Mater. Chem. C* **2018**, *6*, 4471–4478. [CrossRef]

21. Albrecht, K.; Matsuoka, K.; Fujita, K.; Yamamoto, K. A dendrimer emitter doped in a dendrimer host: Efficient thermally activated delayed fluorescence OLEDs with fully-solution processed organic-layers. *Mater. Chem. Front.* **2018**, *2*, 1097–1103. [CrossRef]

22. Gracia, I.; Feringa, B.; Serrano, J.L.; Termine, R.; Golemme, A.; Omenat, A.; Barberá, J. Functional Carbazole Liquid-Crystal Block Codendrimers with Optical and Electronic Properties. *Chem. Eur. J.* **2015**, *21*, 1359–1369. [CrossRef] [PubMed]

23. Mula, S.; Frein, S.; Russo, V.; Ulrich, G.; Ziesell, R.; Barberá, J.; Deschenaux, R. Red and Blue Liquid-Crystalline Borondipyrromethene Dendrimers. *Chem. Mater.* **2015**, *27*, 2323–2342. [CrossRef]

24. Huitorel, B.; Benito, Q.; Fargues, A.; Barberá, J.; Deschenaux, R. Red and Blue Liquid-Crystalline Borondipyrromethene Dendrimers. *Chem. Mater.* **2015**, *27*, 2323–2342. [CrossRef]

25. Kumar, M.; Kumar, S. Liquid crystals in photovoltaics: A new generation of organic photovoltaics. *Polymers. J.* **2017**, *49*, 85–111. [CrossRef]

26. Pieper, P.; Russo, V; Heinrich, B.; Donnio, B.; Deschenaux, R. Liquid-Crystalline Tris[60]fullerodendrimers. *J. Org. Chem.* **2018**, *83*, 3208–3219. [CrossRef]

27. Eremin, A.; Nádas, H.; Hirankittiwong, P.; Kiang-la, J.; Chatham, N.; Haba, O.; Yonetake, K.; Takezoe, H. Azodendrimers as a photofunctional liquid crystals. *Liq. Cryst.* **2018**, *45*, 2121–2131. [CrossRef]

28. Gruzdev, M.S.; Ramazanova, A.G.; Korolev, V.V.; Chervonova, U.V.; Balmasova, O.V.; Kolker, A.M. Phase Transitions in Mesogenic Third Generation Poly(Piprolinomine) Dendrimer and Its Iron(II) Complex. *Russ. J. Inorg. Chem.* **2020**, *65*, 640–645. [CrossRef]

29. Iguarbe, V.; Barberá, J.; Serrano, J.L. Functional Janus dendrimers containing carbazole with liquid crystalline, optical and electrochemical properties. *Liq. Cryst.* **2020**, *47*, 301–308. [CrossRef]

30. Concóllon, A.; Liang, T.; Schennig, A.P.H.J.; Serrano, J.L.; Romero, P.; Marcos, M. Proton-conductive materials formed by coumarin photoclicked liquid ion liquid crystal dendrimers. *J. Mater. Chem. C* **2018**, *6*, 1000–1007. [CrossRef]

31. Rosen, B.M.; Wilson, C.J.; Wilson, D.A.; Peterca, M.; Imam, M.R.; Percec, V. Dendron-Mediated Self-Assembly, Disassembly, and Self-Organization of Complex Systems. *Chem. Rev.* **2009**, *109*, 6275–6540. [CrossRef]

32. Lyu, X.; Xiao, A.; Shi, D.; Li, Y.; Shen, Z.; Chen, E.-Q.; Zheng, S.; Fan, X.-H.; Zhou, Q.-F. Liquid crystalline polymers: Discovery, development, and the future. *Polymer* **2020**, *202*, 122740. [CrossRef]

33. Park, M.; Kang, D.-G.; Choi, Y.-J.; Yoon, W.-J.; Koo, J.; Park, S.-H.; Ahn, S.; Jeong, K.-U. Kinetically Controlled Polymorphic Superstructures of Pyrene-Based Asymmetric Liquid Crystal Dendron: Relationship Between Hierarchical Superstructures and Photophysical Properties. *Chem. Eur. J.* **2018**, *24*, 9015–9021. [CrossRef]
62. Amanullah; Ali, U.; Ans, M.; Iqbal, J.; Iqbal, M.A.; Shoaib, M. Benchmark study of benzamide derivatives and four novel theoretically designed (L1, L2, L3, and L4) ligands and evaluation of their biological properties by DFT approaches. *J. Mol. Model.* 2019, 25, 223. [CrossRef]

63. Yen, M.-H.; Chaiprapa, J.; Zeng, X.; Liu, Y.; Cseh, L.; Mehl, G.H.; Ungar, G. Added Alkane Allows Thermal Thinning of Supramolecular Columns by Forming Superlattice—An X-ray and Neutron Study. *J. Am. Chem. Soc.* 2016, 138, 5757–5760. [CrossRef] [PubMed]