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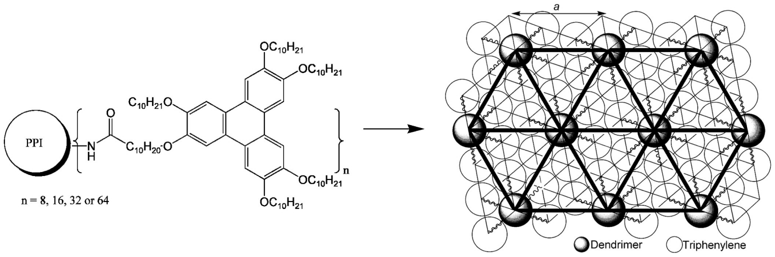

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# Discotic Liquid Crystalline Poly(propylene imine) Dendrimers Based on Triphenylene

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***Abstract:*** The design, synthesis, and mesomorphic properties of a new series of homodendrimers consisting of the commercially available poly(propylene imine) (PPI) dendrimers ($G = 1-5$), PPI$-(NH_2)_n$ ($n = 4$, 8, 16, 32, 64), functionalized with a discotic triphenylene moiety are reported. The liquid crystalline behavior was investigated by means of differential scanning calorimetry (DSC), polarizing-light optical microscopy (POM), and X-ray diffractometry (XRD). All of the homodendrimers showed mesomorphic properties, with the second to fifth generations giving a hexagonal columnar mesophase (Col$_h$) and the first generation a rectangular columnar mesophase (Col$_r$). The X-ray study reveals that these mesophases show a highly ordered structure with segregation of triphenylenes and dendrimers into separate columns and a regular stacking distance inside the triphenylene columns. GPC analysis showed that the dendrimers had good monodispersity and MALDI-TOF studies of the first three generations gave good evidence that all of the terminal amino groups of the dendrimers were functionalized with a discotic unit.

## Introduction

In the past decade or so, dendrimers[1−3] have been attracted a great deal of attention because of their suitability for use as building blocks in supramolecular chemistry and molecular scaffolding in nanotechnology.

This high level of interest has been generated because of the structural properties of these materials. The molecules have a monodisperse globular shape and bear a large number of end groups that play an important role in determining the properties of the system. Various examples are available of dendrimers that behave as unimolecular micelles, whether it be with a hydrophobic core and hydrophilic periphery or vice versa, and the use of these systems in selective extraction has been described.[4−6] Diverse applications include templates for the formation of mesoporous silicas,[7,8] the harvesting of light,[9] catalytic nanoreactors,[10,11] drug delivery systems,[12,13] and liquid crystalline dendrimers.[14−16]

The incorporation of mesogenic units at the periphery of dendrimers gives rise to an interesting phenomenon, namely, the struggle between the preferred arrangements of the dendrimer core and the peripheral mesogenic units. To minimize their free energy, dendrimers tend to adopt a 3D spherical structure, but the attachment of anisotropic mesogenic units causes this globular shape to be distorted because of the strong interactions between such units. Indeed, liquid crystalline phases can arise in this type of system. Percec et al. showed that the attachment of rodlike units gives both nematic and smectic phases[17−19] which occur because of the parallel alignment of the mesogenic units with respect to one another. Such an arrangement causes the dendrimer core to be distorted from its ideal conformation. Our group has recently shown that it is possible to evolve from a SmA phase to a Col$_h$ phase, via SmC and Col$_r$ phases, by changing from a homodendrimer functionalized with a terminally attached mesogenic unit bearing a single alkyl chain to a homodendrimer with a terminally attached unit bearing two alkyl chains, passing through co-dendrimers consisting of both units.[20] Columnar hexagonal liquid crystalline phases were also observed by Lattermann et al.[21,22] in poly-

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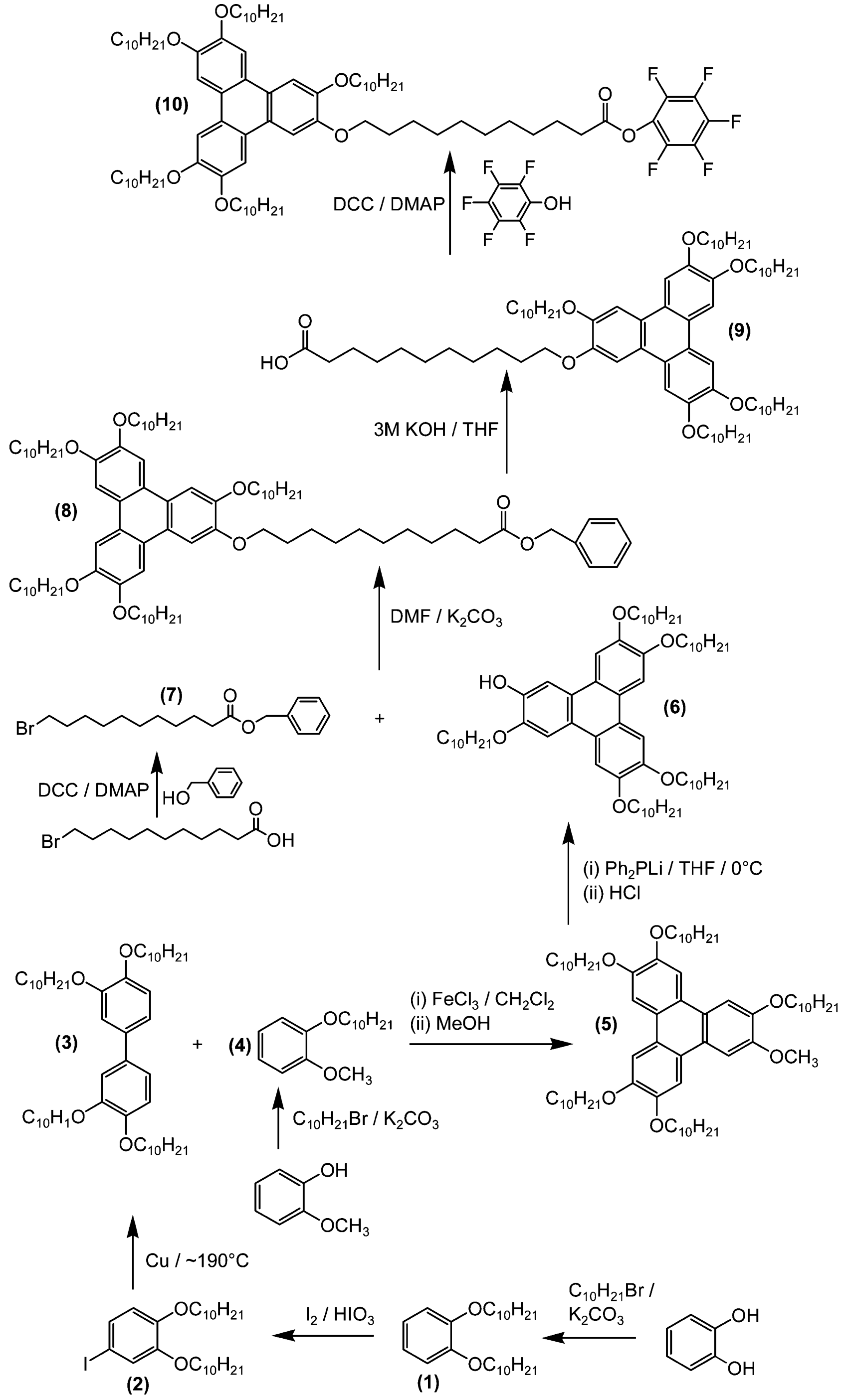
***Scheme 1.*** Synthetic Route to Mesogenic Unit



(propylene imine) (PPI) dendrimers acylated with simple carboxylic acids. A great deal of work has been carried out on LC dendrimers containing calamitic units but, to the best of our knowledge, very little work has been carried out on discotic units.

Discotic liquid crystals were discovered just over 25 years ago by Chandrasekhar, with his work on the hexaesters of benzene.[23] Hexasubstituted derivatives of triphenylene were among the first examples to be discovered[24−26] and these systems give columnar phases. A lot of attention has recently been focused on these compounds because of their photoconductive properties.[27,28] The discs tend to assemble into columns through face−face packing of the aromatic units, thereby allowing a pathway for energy or charge transfer (because of

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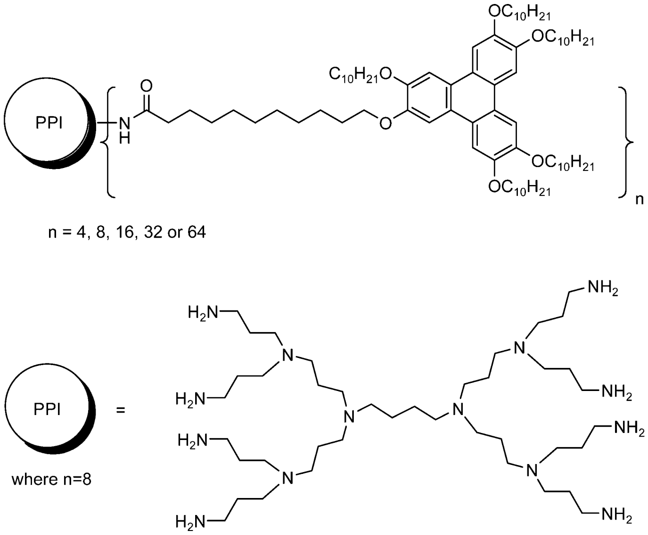

***Figure 1.*** PPI−(NHCO-Disc$C_{10}$)$_n$ functionalized dendrimers with discotic mesogen.

***Table 1.*** GPC and MALDI-TOF Data for Dendrimers

| dendrimer | Ip (GPC) | theoretical Mw | MALDI-TOF | $Mw_{exp}/Mw_{theor}$ |
|---|---|---|---|---|
| PPI-(NHCO-Disc$C_{10}$)$_4$ | 1.12 | 5084.3 | 5084.0 | 1.00 |
| PPI-(NHCO-Disc$C_{10}$)$_8$ | 1.11 | 10293.1 | 10308.3 | 1.00 |
| PPI-(NHCO-Disc$C_{10}$)$_{16}$ | 1.10 | 20746.3 | 20756.8 | 1.00 |
| PPI-(NHCO-Disc$C_{10}$)$_{32}$ | 1.16 | 41653.8 | [a] | |
| PPI-(NHCO-Disc$C_{10}$)$_{64}$ | 1.23 | 83447.8 | [a] | |

[a] The high Mw of these compounds precludes the measurement of this value.

the large $\pi-\pi$ overlap of the discotic units), with the alkyl chains acting as insulators.[29] The low stability and poor processibility of the low molar mass discotic molecules has led to the search for ways to improve these properties. One way that has been suggested is polymerization and, as a result, much work has been carried out on creating polymer LCs that incorporate triphenylenes.[30−32] These materials can be processed more easily to give ordered macrodomains. To date, however, studies concerning the use of dendrimers as the support have not been carried out.

In this paper, we report the synthesis of a series of homodendrimers of the first five generations of PPI that incorporate discotic triphenylene mesogenic units. The characterization of both the chemical and mesogenic properties of these materials is described.

## Results and Discussion

**Synthesis and Characterization.** A series of PPI dendrimers modified with a reactive triphenylene unit was synthesized. These dendrimers were synthesized by reaction of the activated pentafluorophenol ester of the acid group of the mesogenic unit (see Scheme 1) with the terminal primary amine groups of the corresponding PPI dendrimer (generations 1−5).[33−35] These reactions gave PPI−(NHCO-Disc$C_{10}$)$_n$, where $n = 4, 8, 16, 32$, or 64 (see Figure 1). All of the compounds were isolated as yellowish air-stable solids that were soluble in dichloromethane and chloroform.

The structures of the target compounds were established using $^1$H and $^{13}$C NMR spectroscopy, gel permeation chromatography (GPC), mass spectrometry (MALDI-TOF), and elemental analysis. The polydispersity index was obtained from the GPC measurements (mobile phase: $CH_2Cl_2$, calibration standard: polystyrene) and this information, combined with the results of the MALDI-TOF analysis (see Table 1), demonstrated that the dendrimers did not contain significant amounts of free primary amines. Indeed, in the dendrimers obtained for generations 1−3, there was no evidence for the presence of any free amine and all of the dendrimer terminal groups were bound to a mesogenic unit.

**Differential Scanning Calorimetry (DSC).** The phase transitions of the functionalized dendrimers PPI−(NHCO-Disc$C_{10}$)$_4$ to PPI−(NHCO-Disc$C_{10}$)$_{64}$ were measured using DSC at a heating rate of 10 °C min$^{-1}$. All samples were dried in a vacuum desiccator prior to analysis.

All of the functionalized dendrimers exhibited liquid crystalline behavior. DCS traces (second scan) for all the functionalized dendrimers are shown in Figure 2 and the phase-transition temperatures and enthalpic data for the compounds are given in Table 2.

It can be seen from the results in Table 2 that there is only a small variation in the transition temperatures for dendrimer generations 2−5 in terms of transitions from crystal to mesophase and mesophase to isotropic liquid. The transitions for the generation 1 dendrimer (bottom trace) occur at a higher temperature, both on heating and cooling, and the mesophase range is smaller. The similarities in temperature and enthalpy (in terms of J.g$^{-1}$ and for $\Delta H$ per mesogenic unit) of the crystal-to-mesophase transition show that mesophase formation is independent of the dendrimer generation, a situation also found by various other groups.[33,36,37] The corresponding low molecular weight compound, hexadecyloxytriphenylene, passes to the liquid crystalline state at a similar temperature to the first generation dendrimer and at a higher temperature than the higher generation dendrimers. Furthermore, the parent compound is mesogenic over a shorter temperature range than the dendrimeric systems (C 58 °C Col$_{ho}$ 69 °C I). [26,38]

**Polarizing Optical Microscopy (POM).** Samples of the five dendrimers were introduced between glass slides for study by POM. On heating, the changes observed for all samples were consistent with the DSC traces obtained. Generation 2 passed to an isotropic state at approximately 106 °C on heating and on subsequent cooling (2 °C min$^{-1}$) the mesophase began to form at approximately 105 °C (see Figure 3a). Further cooling led to the growth of a pseudo-focal-conic fan texture (see Figure 3b). This texture is indicative of a hexagonal columnar (Col$_h$) mesophase,[39] which is not unexpected given the fact that

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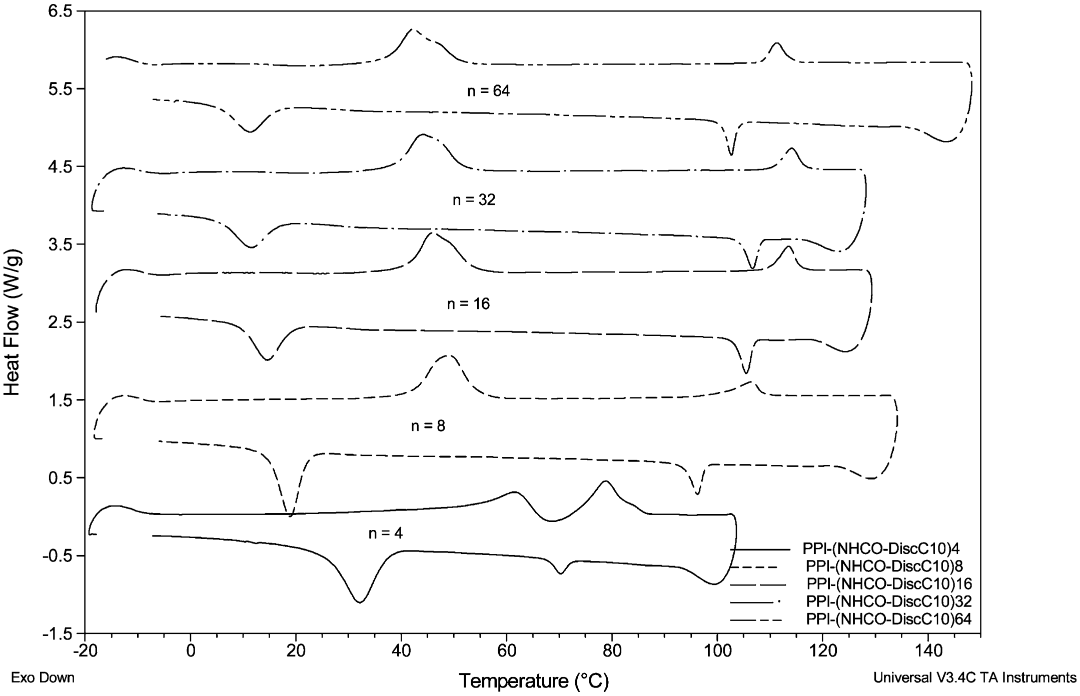

***Figure 2.*** DCS traces for PPI−(NHCO-Disc$C_{10}$)$_n$; second heating and cooling cycles, rate of 10 °C min$^{-1}$

***Table 2.*** Thermal Data Determined by DSC for PPI−(NHCO-Disc$C_{10}$)$_n$ (Second Scan)

| n[a] | transitions[c] °C, (Δ*H*) Jg$^{-1}$ | mesophase range °C | $\Delta H_{\mathrm{Col-I}}$/m.u.[d] kJ |
|---|---|---|---|
| 4h[b] | C 61 (37.1) $\mathrm{Col_r}$ 79 (20.7) I | 18 | |
| 4c[b] | I 70 (3.1) $\mathrm{Col_r}$ 32 (33.7) C | 38 | 3.9 |
| 8h | C 49 (28.7) $\mathrm{Col_h}$ 107 (6.3) I | 58 | |
| 8c | I 96 (6.2) $\mathrm{Col_h}$ 19 (28.0) C | 77 | 8.0 |
| 16h | C 46 (26.7) $\mathrm{Col_h}$ 114 (7.0) I | 68 | |
| 16c | I 106 (6.5) $\mathrm{Col_h}$ 15 (21.2) C | 91 | 8.4 |
| 32h | C 44 (27.4) $\mathrm{Col_h}$ 114 (6.3) I | 70 | |
| 32c | I 107 (6.0) $\mathrm{Col_h}$ 12 (19.8) C | 95 | 7.8 |
| 64h | C 42 (24.9) $\mathrm{Col_h}$ 111 (5.1) I | 69 | |
| 64c | I 103 (5.3) $\mathrm{Col_h}$ 11 (17.5) C | 92 | 6.9 |

[a] *n*: number of discotic units in the dendrimer. [b] h: heating process, c: cooling process. [c] C = crystal, $\mathrm{Col_r}$ = rectangular columnar mesophase, $\mathrm{Col_h}$ = hexagonal columnar mesophase, I = isotropic liquid. [d] Enthalpy of the columnar-to-isotropic liquid transition per mesogenic unit.

hexaalkoxytriphenylenes form both ordered and disordered $\mathrm{Col_h}$ phases.[38,40] The other generations (3−5) showed similar behavior, although the mesophase forms at slightly higher temperatures on cooling. The texture of the mesophase of the generation 1 dendrimer is somewhat different (see Figure 3c) and it was not possible to assign a mesophase from the texture alone.

**X-ray Diffraction (XRD).** The five compounds in this series were investigated by X-ray diffraction in their liquid-crystal phases. For the sake of comparison, the low-molecular mass analogue hexakis(decyloxy)triphenylene (Disc$C_{10}$), which shows a hexagonal columnar mesophase, was also studied. The measurements performed on the second, third, fourth, and fifth generations (*n* = 8, 16, 32, and 64, respectively) confirm that the mesophase, as expected from their optical textures (Figure 3b), is hexagonal columnar. However, the mesophase of the first generation compound does not have hexagonal symmetry and the diffraction maxima observed in the X-ray patterns are consistent with a rectangular columnar structure. On the other hand, the diffractograms recorded at room temperature for all compounds are typical of crystalline phases.

The data obtained for the five compounds are shown in Table 3. The patterns for generations 2−5 contain a large number of reflections with a reciprocal spacing ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$..., which is typical of a two-dimensional hexagonal lattice. In addition, two diffuse haloes are observed. The first halo corresponds to a distance of about 4.5 Å and is characteristic of the molten hydrocarbon chains. This type of halo is typically observed in all kinds of rodlike and disklike liquid crystals. The second halo, which corresponds to a distance of about 3.53−3.55 Å, is not as broad as the first and arises from stacking of the triphenylene rings. The mesophases of these compounds (including the first generation) can therefore be described as ordered columnar.

The X-ray patterns are practically identical for the four generations between 2 and 5. The measured spaces (Table 3) are very similar and, consequently, the lattice parameters *a* and *c* deduced from these spaces are practically the same.

The relative intensities of the different reflections are qualitatively compared in Table 3 and from these data it can be seen that the strongest reflection in all the patterns is (2 1 0). This means that there is a strong modulation of the electronic density wave with a period $\sqrt{7}$ times shorter than the (1 0 0) spacing. This is consistent with the existence in the hexagonal columnar mesophase of a hexagonal sublattice generated by segregated columns containing either the stacked triphenylenes or the dendrimer. This model is schematically represented in Figure 4 and is supported by the occurrence of scattering at 3.53−3.55 Å in the X-ray patterns. Such scattering reflects the tendency of the triphenylene cores to stack on top of each other. In the proposed structure, each dendrimer column is surrounded by six columns of triphenylene molecules. The resulting supercolumns consist of seven individual columns that form a

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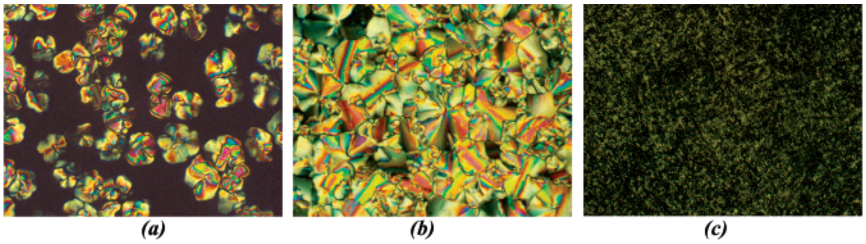
(a) (b) (c)

***Figure 3.*** Optical texture of (a) PPI−(NHCO-Disc$C_{10}$)$_8$ I−$Col_h$ transition at 95 °C. (b) PPI−(NHCO-Disc$C_{10}$)$_8$ $Col_h$ mesophase at 89 °C (c) PPI−(NHCO-Disc$C_{10}$)$_4$ $Col_r$ mesophase at 73 °C.

***Table 3.*** X-ray Results for the Mesophases of the Dendrimers and the Model Compound[a]

| compound | h k l | dobs (Å) | dcalc (Å) | intensity[b] | mesophase type and lattice constants (Å) |
|---|---|---|---|---|---|
| PPI−(NHCO-Disc$C_{10}$)$_4$ | 2 0 0 | 51.8 | 52.0 | s | $Col_r$ |
| | 4 0 0 | 26.1 | 26.0 | m | $a = 104$ |
| | 4 1 0 | 24.2 | 24.35 | vw | $b = 69.5$ |
| | 1 3 0 | 22.5 | 22.6 | s | $c = 3.8$ |
| | 4 2 0 | 21.9 | 21.8 | s | |
| | 3 3 0 | 19.5 | 19.3 | w | |
| | | 4.5 | | d | |
| | 0 0 1 | 3.54 | | d | |
| PPI−(NHCO-Disc$C_{10}$)$_8$ | 1 0 0 | 57.8 | 57.7 | s | $Col_h$ |
| | 1 1 0 | 33.7 | 33.3 | vw | $a = 66.6$ |
| | 2 0 0 | 28.6 | 28.8 | m | $c = 3.53$ |
| | 2 1 0 | 21.8 | 21.8 | vs | |
| | 3 0 0 | 19.0 | 19.2 | w | |
| | 3 1 0 | 15.9 | 16.0 | m | |
| | 4 0 0 | 3.53 | 14.4 | w | |
| | 3 2 0 | 13.2 | 13.2 | w | |
| | 4 1 0 | 12.5 | 12.6 | w | |
| | | 4.5 | | d | |
| | 0 0 1 | 14.4 | | d | |
| PPI−(NHCO-Disc$C_{10}$)$_{16}$ | 1 0 0 | 58.1 | 57.8 | s | $Col_h$ |
| | 1 1 0 | 33.4 | 33.35 | vw | $a = 66.7$ |
| | 2 0 0 | 28.9 | 28.9 | m | $c = 3.55$ |
| | 2 1 0 | 21.7 | 21.8 | vs | |
| | 3 0 0 | 19.1 | 19.25 | w | |
| | 3 1 0 | 16.0 | 16.0 | m | |
| | 4 0 0 | 14.4 | 14.4 | w | |
| | 3 2 0 | 13.2 | 13.2 | w | |
| | 4 1 0 | 12.7 | 12.6 | w | |
| | | 4.5 | | d | |
| | 0 0 1 | 3.55 | | d | |
| DAB−(NHCO-Disc$C_{10}$)$_{32}$ | 1 0 0 | 58.4 | 57.85 | s | $Col_h$ |
| | 2 0 0 | 28.7 | 28.9 | m | $a = 66.8$ |
| | 2 1 0 | 22.0 | 21.9 | vs | $c = 3.54$ |
| | 3 0 0 | 18.7 | 19.3 | w | |
| | 3 1 0 | 16.1 | 16.0 | m | |
| | 4 1 0 | 12.7 | 12.6 | w | |
| | | 4.5 | | d | |
| | 0 0 1 | 3.54 | | d | |
| DAB(NHCODisc$C_{10}$)$_{64}$ | 1 0 0 | 58.0 | 58.0 | s | $Col_h$ |
| | 1 1 0 | 33.2 | 33.5 | vw | $a = 67.0$ |
| | 2 0 0 | 29.2 | 29.0 | m | $c = 3.55$ |
| | 2 1 0 | 22.0 | 21.9 | vs | |
| | 3 0 0 | 19.2 | 19.3 | w | |
| | 3 1 0 | 16.0 | 16.1 | m | |
| | 4 0 0 | 14.5 | 14.5 | w | |
| | 3 2 0 | 13.3 | 13.3 | vw | |
| | 4 1 0 | 12.8 | 12.7 | w | |
| | | 4.5 | | d | |
| | 0 0 1 | 3.55 | | d | |
| Disc$C_{10}$ | 1 0 0 | 21.95 | 22.0 | vs | $Col_h$ |
| | 1 1 0 | 12.8 | 12.7 | d | $a = 25.3$ |
| | | 4.5 | | d | $c = 3.56$ |
| | 0 0 1 | 3.56 | | w | |

[a] The temperature of the experiments was 70 °C for all the dendrimers and 65 °C for hexakis(decyloxy)triphenylene (Disc$C_{10}$). [b] vs: very strong; s: strong; m: medium; w: weak; vw: very weak; d: diffuse.

hexagonal lattice with an *a* parameter of about 67 Å. This value is $\sqrt{7}$ times larger than the parameter of the sublattice, which consists of the individual columns (ca. 25.3 Å). The sublattice parameter corresponds roughly to the diameter of the hexasubstituted triphenylene (containing conformationally disordered substituents) and is in good agreement with the hexagonal lattice

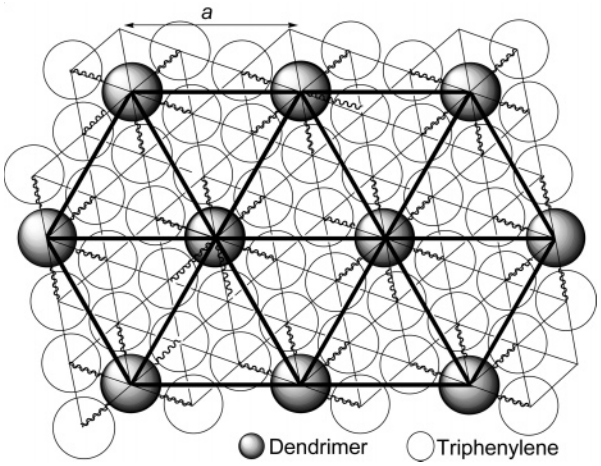

***Figure 4.*** Structural model for generations 2−5.

constant of the columnar mesophase of the analogous low molecular mass compound hexakis(decyloxy)triphenylene (DiscC$_{10}$). The diffraction maxima and the lattice constants deduced for this compound are included in Table 3. The stacking distance (*c* constant) for this compound is practically identical to those observed in the dendrimers.

The proposed structural model is valid for generations 2−5. The difference between the generations concerns the length of column required to accommodate a complete molecule. In each columnar "slice", which is ca. 3.54 Å thick, there are six triphenylenes surrounding a portion of dendrimer. Given this situation, it is clear that the molecules of generation 2 (containing 8 triphenylene units) fill one and one-third of a slice. Similarly, molecules of generation 3 (containing 16 triphenylenes) fill two and two-thirds of a slice, molecules of generation 4 (containing 32 triphenylenes) fill five and one-third of a slice, and molecules of generation 5 (containing 64 triphenylenes) fill 10 and two-thirds of a slice. Using this model, the calculated density for the mesophase of each of the four compounds is ca. 0.94 g/cm$^3$. In this model, the flexible dendrimeric part adopts a cylindrical arrangement with the four generations having a similar diameter but their height increasing from ca. 4.7 Å for the generation bearing 8 triphenylenes up to 38 Å for the generation bearing 64. This behavior is usual for terminal functionalized liquid crystalline dendrimers, in which the interactions between the promesogenic units determine the supramolecular structure and the dendrimeric central core adopts the geometry necessary to allow this molecular arrangment.[16,20,31]

As mentioned above, the X-ray patterns of the mesophase of the first generation dendrimer are indexed in terms of a two-dimensional rectangular packing of columns. In this case, there is also evidence of segregation of triphenylenes and dendrimer into separate columns. This evidence is based on the following points:

There is scattering that corresponds to a distance of 3.55 Å, which is characteristic of the stacking of triphenylene rings.

The second reflection (2 0 0) is weak, whereas the two subsequent reflections [(1 3 0) and (4 2 0)] are much stronger. This again reveals the existence of a strong modulation of the electronic density wave at distances that correspond to the separations between the segregated columns. In this case, there is no single intercolumnar distance as the symmetry of the packing is no longer hexagonal. Although it is difficult to determine the exact organization of the individual columns in the resulting sublattice, the fact that reflections (1 3 0) and (4 2 0) are strong suggests that the triphenylene columns lie on these planes and the probable structure is represented in Figure 5. In a similar way to the structure proposed for generations 2−5, there are six triphenylene columns around each dendrimer column. This arrangement, in contrast to that represented in Figure 4 for the other generations, has a distorted hexagonal structure. The distortion is probably related to the tilt of the triphenylene discs, which in turn accounts for the smaller cross section of the columns. It is clear that only four out of the six triphenylene rings that surround the dendrimer can belong to the same molecule. One and a half molecules are therefore necessary to fill each columnar slice. In this situation, and owing to the tilt of molecule, the separation between two adjacent triphenylenes along the column axis must be slightly higher than the experimentally measured face-to-face separation of 3.54 Å. It seems reasonable that the tilt can be estimated bearing in mind that the packing density must be preserved while the cross-sectional area has decreased compared to that in the hexagonal packing arrangement. Thus, the tilt angle can be estimated as $\cos^{-1}(104 \times 69.5)/(67^2\sqrt{3})$. This gives a tilt angle of ca. 21.5° and the deduced *c* constant for generation 1 is 3.8 Å, which gives a packing density for this dendrimer of 0.92 g/cm$^3$.

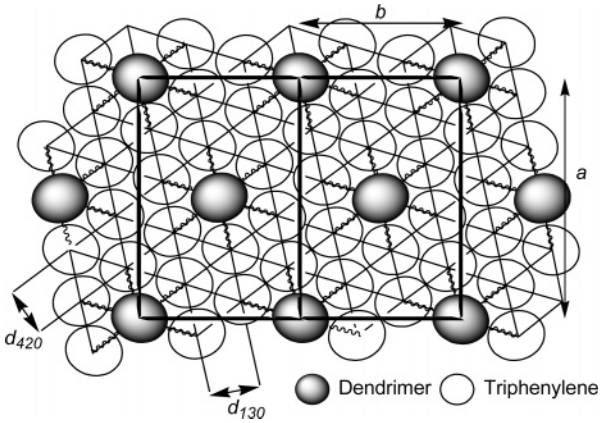

***Figure 5.*** Structural model for generation 1.

## Conclusions

We have shown that the attachment of discotic triphenylene moieties to the commercially available PPI−(NH$_2$)$_n$ dendrimers produces highly ordered columnar mesophases, which are hexagonal in the second to fifth generations and rectangular for the first generation. These materials show certain improvements over the analogous low molecular weight unit, hexakis(decyloxy)triphenylene. For example, the mesophase temperature range of the dendrimers is larger and the materials also become liquid crystalline at lower temperatures. Compared to the columnar dendrimers previously described in the literature,[22,36] these compounds show a highly ordered structure in two respects: (1) A regular stacking distance is measured by X-ray diffraction in the mesophase (i.e., the mesophases are ordered columnar) and (2) there is segregation of triphenylenes and dendrimers into separate columns. These segregated columns pack into a two-dimensional lattice, the symmetry of which depends on the generation number: the mesophase is Col$_r$ for the first generation and Col$_h$ for the other dendrimers. The work described here opens up possibilities for the synthesis of discotic dendrimers as interesting new materials for applications such as, for example, molecular electronics.[41]

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**Supporting Information Available:** Experimental section, techniques, synthesis of discotic mesogen, synthesis of discotic LC dendrimers, and general procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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