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# Control over Nanostructures and Associated Mesomorphic Properties of Doped Self-Assembled Triarylamine Liquid Crystals

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Abstract: We have synthesized a series of triarylamine-cored molecules equipped with an adjacent amide moiety and dendritic peripheral tails in a variety of modes. We show by <sup>1</sup>H NMR and UV/Vis spectroscopy that their supramolecular self-assembly can be promoted in solution upon light stimulation and radical initiation. In addition, we have probed their molecular arrangements and mesomorphic properties in the bulk by integrated studies on their film state by using differential scanning calorimetry (DSC), variable-temperature polarizing optical microscopy (VT-POM), variable-tempera-

## Introduction

The precise control over molecular organization by using supramolecular self-assemblies has risen to prominence in order to access organic materials and devices displaying improved (or even emergent) functional properties.<sup>[1,2]</sup> For instance, focusing on organic electronics and p-type (semi)conductors, self-assemblies of oligothiophenes,<sup>[3]</sup> phthalocyanines,<sup>[4]</sup> and of various polycyclic aromatic hydrocarbons,<sup>[5]</sup> when substituted by appropriate solubilizing groups, can produce 1D and 2D nanostructures with improved structure–property relationships both in the bulk and in solution. Still in the field of organic electronics, triarylamine molecules are among the most promising hole transporting units.<sup>[6]</sup> From their monomer or covalent polymer derivatives, various types of triaryl-

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ture X-ray diffraction (VT-XRD), and atomic force microscopy (AFM). Differences in the number and the disposition of the peripheral tails significantly affect their mesomorphic properties associated with their lamellar- or columnar-packed nanostructures, which are based on segregated stacks of the triphenylamine cores and the lipophilic/lipophobic periphery. Such structural tuning is of interest for implementation of these soft self-assemblies as electroactive materials from solution to mesophases.

amine-based materials have been reported and implemented in electronic devices including organic light-emitting diodes (OLEDs),<sup>[6c]</sup> organic field-effect transistors (OFETs),<sup>[6e]</sup> and organic photovoltaic cells (OPVs),<sup>[6b,d]</sup> but also as non-linear optical (NLO) materials  $^{\scriptscriptstyle [7a,b]}$  and as photoconductors for the Xerox process in laser printers and photocopiers.<sup>[6a]</sup> Most of the triarylamines were used in the solid state, although a few examples of triarylamines in the liquid<sup>[8]</sup> and liquid crystalline<sup>[9]</sup> state have also been studied in the context of pursuing higher device processability and device performance. However, only very few examples of triarylamine self-assembled structures and their associated properties have been described, including those for which the self-assembled properties are brought by their conjugation with other structuring  $\pi$ -functional groups.<sup>[10]</sup> Recently, we have discovered a new type of light-triggered self-assembly by using triarylamine cores substituted with amide lateral groups.<sup>[11]</sup> The detailed mechanism of this unique supramolecular polymerization is very complex,<sup>[11h]</sup> but it can be summarized for compound A as follows (Figure 1): i) the oxidation of a catalytic quantity of triarylamines to their radical cations A<sup>++</sup>, with concomitant reduction of the chlorinated solvent producing chloride counterions, ii) the formation (above a critical concentration of 10 nm) of a nucleus of at least six triarylammonium radicals in a double columnar arrangement involving hydrogen bonds, iii) the stacking of neutral triarylamines onto the nucleus and subsequent growth of the primary fibril, and iv) the lateral secondary aggregations of fibrils by van der Waals forces to reach larger bundles of fibers.

In addition to this unique supramolecular polymerization process, we measured outstanding conductivities<sup>[11c]</sup> higher than  $5 \times 10^3$  Sm<sup>-1</sup> for these nanostructured fibers, whereas Akande et al. have determined theoretical mobilities as high as

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Figure 1. Schematic and simplified representation of the hierarchical self-assembly process for compound A under light irradiation in chlorinated solvents. The supramolecular polymerization starts by the oxidation of neutral molecule A to its radical cation  $A^{\cdot+}$  (i), a critical number of radicals then aggregate in a nucleation structure (ii) from which double columnar fibrils grow by supramolecular association of neutral molecule A (iii), finally, fibrils are bundled in larger and stiffer fibers by lateral associations (iv).

 $12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .<sup>[11d]</sup> These self-assembly process and related optoelectronic properties were also exploited recently by the group of Kumar et al. to improve the efficiency of OPVs.<sup>[11f]</sup> We have also probed the physical reasons for such a conductivity in these wires by studying their electronic, optical, and magnetic signatures, which were fully explained by the formation of highly efficient charge-transfer complexes (characterized as supramolecular polarons) between triarylammonium radicals and neutral triarylamines in the stacked structures.<sup>[11g]</sup> By investigating the scope and limitations for a successful light-triggered supramolecular polymerization, we have found that the existence of long alkyl chains at the peripheral moieties of the triarylamine core is one of the favored choices together with an amide hydrogen-bonding site for stabilizing the assembled form in the harmony of multiple non-covalent interactions.<sup>[11a,g]</sup> Interestingly, one can expect that such a molecular shape is also in common with general requirements for designing functional soft materials including organic gelators<sup>[12]</sup> and plasticor liquid-crystalline organics<sup>[13]</sup> composed of a  $\pi$ -conjugated core surrounded by soft peripheral moieties. A systematic study on the rarely known controlled self-assembly of triarylamines is thus supposed to provide us with a beneficial insight for their implementation as functional materials. Here, we report on the synthesis of triarylamine-cored dendritic molecules containing an amide group and on some of their supramolecular polymerization and functional properties in solution and in the bulk. In particular, we focus on the control of their nanostructures in the liquid-crystal phase by modifying their peripheral groups, which are further related to their characteristic mesomorphic properties.

#### **Results and Discussion**

#### Synthesis of triarylamine-cored dendritic molecules G1-G3 and G3DT

To investigate potential liquid crystal properties of triarylamine-based molecules equipped with an amide moiety and soft peripheral tails, we have introduced a variable number of

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dendritic moieties to surround the triphenylamine core. 3,4,5-Tri(dodecyloxy)-benzene<sup>[17]</sup> and tris(tetraethyleneglycol monomethylether)-benzene<sup>[18]</sup> groups were chosen due to their successful use in previous reports on supramolecular liquid crystal materials. Triarylamines with different numbers, n, of the 3,4,5tri(dodecyloxy)-benzene moiety (G1-G3 with n=1, 2, 3, respectively) were prepared starting from the previously reported compounds 1, 2, and 4,<sup>[11a]</sup> respectively (Scheme 1). The nitro group of triarylamine 1 was initially reduced with tin chloride and the resulting amine was then treated with 3,4,5tris(dodecyloxy)benzoyl chloride to give compound G1 equipped with one dendritic tail positioned on the amide. Starting from compound 2 and after deprotection of the benzyl groups and concomitant reduction of the nitro group by using palladium on charcoal, a first introduction of the dendritic tail was achieved following a similar procedure as reported for compound G1 and leading to compound 3. Two more tails were then attached after reaction with (3,4,5-tris(dodecyloxy)phenyl)methanol under Mitsunobu conditions<sup>[16]</sup> to afford G3. The synthesis of G3DT was carried out in a similar



Scheme 1. Synthesis of triarylamine-cored molecules G1–G3 and G3DT. a)  $R = C_8H_{17}$ : 1) SnCl<sub>2</sub>, EtOH/CH<sub>3</sub>CN, 2) Ar-COCl, Et<sub>3</sub>N, THF (G1: 84%, two steps); R=Bn: 1) H<sub>2</sub>, Pd/C, MeOH/AcOEt, 2) Ar-COCI, Et<sub>3</sub>N, THF (3: 45%, two steps), b) Ar-CH2OH or Ar'-CH2OH, diisopropyl azodicarboxylate (DIAD), PPh3, THF (G3: 41 %; G3DT: 46 %), c) Ar-CH<sub>2</sub>OH, DIAD, PPh<sub>3</sub>, THF (G2: 43 %). Ar = arvl, Bn = benzvl.

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way from compound **3** with the introduction of two tris(tetraethyleneglycol monomethylether)-benzene tails. Triarylamine **G2** with two tails on the phenolic moieties was also readily synthesized under the similar Mitsunobu conditions from compound **4**. With a series of the dendritic molecules **G1–G3** and **G3DT** in hand, we investigated their light-triggered self-assembly properties in solutions, their supramolecular organization in the bulk and their related mesomorphic properties.

#### Light-triggered supramolecular polymerization of G1–G3 and G3DT from solution and photophysical properties of their self-assemblies

Because of the presence of an amide bond in their immediate periphery, we have first studied the possibility to light-trigger the self-assemblies of triarylamines **G1–G3** and **G3DT** in chloroform. Indeed, it was found earlier that the support by the amide hydrogen-bonding network is critical for the success of the self-assembly in solution, which is also in harmony with van der Waals interactions due to peripheral alkyl chains or phenyl rings.<sup>[11]</sup>

To generate triarylammonium radicals, 2 mM chloroform solutions of **G1–G3** and **G3DT** were exposed to a 20 W halogen lamp ( $10 \text{ W cm}^{-2}$ ) at room temperature. The subsequent signatures of the self-assembly process initiated by a catalytic quantity of radical cations were monitored by <sup>1</sup>H NMR, UV/Vis/NIR, and photoluminescence spectroscopy. In all cases, after 10– 20 min of light irradiation, disappearance of the specific <sup>1</sup>H NMR signals assigned to the triphenylamine core was observed, which amounts for their strong anisotropic stacking and radical migration through the supramolecular columns and as demonstrated in previous studies (Figures 2a and S1-S4 in the Supporting Information).<sup>[11]</sup> After keeping these irradiated solutions in the dark for three days, the proton resonances of the triphenylamine core partly reappear as broad signals for G1, G3, and G3DT indicating partial disassembly. The reversible character of the present light-triggered self-assembly process is shown by the additional 10 min irradiation, which leads again to the disappearance of the signals (Figures S1-S4 in the Supporting Information). In the particular case of G2, at room temperature and after three days in the dark, the absence of resonance signals for the triphenylamine core indicates stronger supramolecular interactions, which are explained by the less hindered character of the amide substituent compared to other derivatives (Figures 2a and S2 in the Supporting Information).

The response of the system followed by UV/Vis/NIR spectroscopy also indicates a self-assembly process, which is in agreement with our previous studies.<sup>[11h]</sup> Two typical absorption bands appear upon irradiation: one in near-infrared (NIR) ( $\lambda =$ 800–830 nm), which is characteristic of the stabilized radical cation in the self-assembly (and importantly confirming the doped nature of the assembly), and one in the blue region ( $\lambda =$  400–450 nm), which accounts for the stacking of the triar-



**Figure 2.** a) <sup>1</sup>H NMR spectra of a 2 mM solution of **G2** in CDCl<sub>3</sub> before light irradiation and after 10 min irradiation by using a 20 W power white light lamp. b) UV/Vis/NIR spectra for a 0.1 mM solution of **G2** in CHCl<sub>3</sub> upon light irradiation for 15 min, absorption spectra were detected by using a 10 mm quartz cuvette. c) Photoluminescence spectra ( $\lambda_{ex}$ =400 nm) for a 0.1 mM solution of **G2** upon light irradiation in chloroform. d) Plots of maximum emission wavelength ( $\lambda_{em}$ ) for **G1**, **G2**, **G3**, and **G3DT** as a function of light irradiation time in chloroform.

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ylamine core (Figures 2 b and S5 in the Supporting Information). The accumulation of the radical cationic species saturates at roughly the same time scale than the one monitored by <sup>1</sup>H NMR spectroscopy (10– 20 min for **G1** and **G2**,  $\approx$  60 min for **G3** and **G3DT**).

Finally, light irradiation of G1-G3 and G3DT in chloroform also led to a strong enhancement of the emission intensities observed in the green region ( $\lambda =$ 480-537 nm) as revealed by photoluminescence spectroscopy (Figures 2c and S6 in the Supporting Information). This characteristic behavior of such triarylamines can be explained as a sort of aggregation-induced emission (AIE),<sup>[11g, 19]</sup> which is likely contributing by the restriction of intramolecular rotations in aggregates to lessen the nonradiative decay of the photo-ex-



Figure 3. DSC thermograms for the triarylamines a) G1, b) G2, c) G3, and d) G3DT with a heating/cooling rate of  $5^{\circ}$ Cmin<sup>-1</sup>. Data are taken from the second heat and cool. Dashed lines correspond to data recorded during the first heat.

cited states. The enhanced emission peaks are expected to appear in the higher wavelength region compared to the weak emission from the molecularly dissolved triarylamines ( $\approx$  450 nm with structural bands corresponding to  $\pi$ - $\pi$ \* transitions<sup>[4b, 20]</sup>).

This is the case for **G3**, **G3DT**, and **G2** showing a significant redshift by 50, 33, and 10 nm, respectively (Figure 2 d). It is observed, however, that the emission of **G1** is blueshifted by 14 nm upon continuous light irradiation. Although the reason for this tendency is unclear, differences in the stacking configuration of the triarylamine cores may affect the excited state of aggregates influencing the AIE properties as it is the case for other systems in the literature.<sup>[21]</sup> To better understand such fine effects, we turned to a precise structural analysis of these self-assemblies in the bulk after evaporation of the previously irradiated solutions.

# Differential scanning calorimetry and polarized optical microscopy experiments

The thermal behavior of the dendritic molecules **G1–G3** and **G3DT** in the bulk were first studied by differential scanning calorimetry (DSC) measurements at a scan rate of  $5 \,^{\circ}$ C min<sup>-1</sup>. Variable-temperature polarized optical microscopy (VT-POM) experiments were then carried out on films made from these molecules. The films were sandwiched between two glass plates and fabricated either 1) by drop-cast of chloroform solutions followed by slow evaporation of the solvent or 2) by thermal annealing of neat materials. The DSC curve of **G1** shows reversible phase transition at 6.5 and  $-7.3 \,^{\circ}$ C in the second heating and cooling cycle, respectively (Figure 3a).

However, POM observations on a film made of **G1** at room temperature show a high degree of birefringence with spherulite textures typical for a highly ordered structure of discotic assemblies<sup>[22]</sup> (Figures 4a and S10 in the Supporting Information), suggesting that the crystalline phase is kept over this transition. Additionally, VT-POM revealed a second phase transition at 53 °C, accompanied by complete disappearance of birefringence (Figure S11 in the Supporting Information).<sup>[23,24]</sup>

The DSC curve of G2 shows two phase transition peaks in the second heating cycle (Figure 3 b), which correspond to the transition from the initial crystalline phase into the highly ordered mesophase at -16°C, characterized by focalconic-like POM textures (Figure S12 in the Supporting Information),<sup>[25a]</sup> and further transition to another mesophase at 44 °C. The waxy nature of the film indicates that the first mesophase can be classified as plastic,<sup>[22b,26]</sup> whereas a liquid crystalline (LC) property was found for the second mesophase due to a fluid character of the film as shown by shearing between two glass plates (Figure S13 c in the Supporting Information). VT-POM experiments show that the second mesophase finally transits to an isotropic phase at 77 °C (Figures 4b and S13a-c in the Supporting Information), as also supported by observation of a peak by µDSC analysis at a slower heating rate of  $0.2 \,^{\circ}$ C min<sup>-1</sup> (Figure S9 in the Supporting Information).

The combined data from the DSC and VT-POM measurements show that the outline of the thermal behavior of **G3** is similar to that of **G2** (Figures 3c, 4c–d, S14, and S15 in the Supporting Information). Two independent non-fluid phases were defined (with a transition at -4.1 °C), followed by the LC phase over a range comprised between 64 and 72 °C. Typical pseudo focalconic textures<sup>[25b]</sup> were observed for the second

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Figure 4. Cross-polarized optical micrographs for thin films made from lightirradiated solutions of a) triarylamine G1 at room temperature after annealing, b) triarylamine G2 at 65 °C, c) triarylamine G3 at room temperature without annealing, d) triarylamine G3 at room temperature after annealing, e) triarylamine G3DT at room temperature after annealing, and f) triarylamine G3DT at room temperature after annealing and further shearing.

crystalline (or plastic) phase, with their birefringent colors and shapes changing measurably at the LC phase (Figures S14 and S15 in the Supporting Information). The transition from the plastic to the LC phase was also revealed by shearing experiments between two glass plates (Figure S16 in the Supporting Information). For **G3DT**, in which the alkyl chains of the peripheral tails are partially replaced by tetraethylene glycol chains, a different thermal behavior is observed compared with the original **G3** (Figure 3 d). A DSC experiment indicates that the LC phase of **G3DT** appeared at a much lower temperature and over a larger range (7–23 °C), whereas VT-POM shows a platelike texture instead of a fan-shaped one (Figures 4e–f and S17 in the Supporting Information). In the literature, similar textures can be seen for LC phases with lamellar packing,<sup>[26d,e]</sup> indicating the possible existence of a layered molecular order in the film made of **G3DT**.

We subsequently carried out variable-temperature (VT) X-ray diffraction XRD experiments to shed light on the detailed supramolecular organizations for compounds **G1–G3** and **G3DT** in the film state. The combined results of the DSC, VT-POM, and VT-XRD experiments are presented in Table 1.

#### X-ray diffraction (XRD) studies

XRD were measured for films of **G1–G3** and **G3DT** fabricated in between two mica substrates in a similar manner to the POM experiments described above.

XRD of **G1** at 23 °C shows a diffraction pattern containing three sets of periodical (1, 1/2, 1/3,...) peaks (37.31, 18.82, 12.35, 9.27; 33.77, 16.89, 11.34, 8.23; 29.44, 14.64 in [Å]), indicating a lamellar-like molecular arrangement (Figures 5a and S18 and Table S2 in the Supporting Information) in the film state.<sup>[27]</sup>

For the as-prepared film of G2 at room temperature, a 2D hexagonal lattice is observed with  $a_{hex} = 58.8$  Å, characterized by typical diffraction peaks in the ratio of  $1:1/\sqrt{3}:1/2:1/\sqrt{7}$  for d spacing (Figures 5 b and S19 and Table S3 in the Supporting Information). The estimated number of molecules per columnar disk (Z = 4.83) suggests a pentameric arrangement of G2 forming a disk in the columnar assembly. The observed  $d_{11}$ value of 29.0 Å, corresponding to the radius of the disk in the columnar hexagonal (Col<sub>h</sub>) arrangement, is slightly smaller than the estimated radius of fan-shaped G2 (33 Å, Figure S31 in the Supporting Information). We therefore assume a "pizzalike" assembly as illustrated in Figure S19b in the Supporting Information, as it fits well with partial intercalation of the peripheral chains between one another. In contrast, it was found that thermal annealing over the melting point of G2 changes the molecular order in the film. After annealing, variable-tem-

Table 1. Phase properties of the triarylamines G1–G3 and G3DT.				
	Thermal behavior <sup>(a)</sup>	Lattice parameters		
G1	Cr <sub>1</sub> 6.6 (18.8) Cr <sub>2</sub> 53 (- <sup>[b]</sup> ) Iso	Cr <sub>2</sub> (Lam) (23 °C): $d$ = 37.3, 33.8, and 29.4 Å <sup>[d]</sup>		
G2	Cr $-15$ (8.4) ${\rm Col}_{\rm hp}$ 45 (1.4) ${\rm Col}^{\rm (f)}$ 77 $(-^{\rm (b)})$ lso	Col <sub>hp</sub> (23 °C): $a$ = 58.8 Å, $Z$ = 4.83 <sup>[g]</sup> (annealed) Lam (65 °C) $d$ = 53.5 Å (65 °C)		
G3	Cr $-4.1$ (33.6) $Col_{hrp}$ 64 (1.2) Col 73 (–^{(b)}) Iso	Col <sub>hrp</sub> (23 °C): $a$ = 39.4 Å (hexagonal), $a$ = 68.2 Å, $b$ = 39.4 Å (rectangular), $Z$ = 1.53 <sup>[g]</sup> Col (68 °C) $d$ = 32.1 Å		
G3DT	Cr 7 (23.4) $\text{Col}_{\text{ret}};$ Lam $(\text{Col}_{h})^{[e]}$ 23 (25.1 $^{[c]})$ Iso	Col <sub>tet</sub> (12 °C): $a = 73.6$ Å, $Z = 5.78^{[g]}$ Lam: (23 °C) $d = 63.1$ Å Col <sub>h</sub> (23 °C) <sup>[e]</sup> : $a = 65.2$ Å, $Z = 3.95^{[g]}$		

[a] The phase transition temperatures (in [°C]) and the enthalpies (in parentheses, in [kJ mol<sup>-1</sup>]) were determined during the 2nd heating cycle of DSC experiments at 5 °C min<sup>-1</sup>. [b] Not detectable during the 2nd heating cycles by DSC. The phase transition was observed with VT-POM. [c] Total value integrating multiple transition peaks observed on the 2nd heating cycle. [d] Taken from the largest *d* spacings of three periodical peak sets (Table S2 in the Supporting Information). Cr = crystalline, Lam = lamellar order possessing phase,  $Col_h = hexagonal$  columnar phase,  $Col_{hrp} = pseudo-hexagonal$  columnar phase,  $Col_{tet} = tetragonal$  columnar phase, p = plastic phase, r = rectangular packing. [e] After continuous XRD detections for a few days. [f] Suggested by VT-POM (Figure S13 in the Supporting Information). [g] Number of molecules per columnar disk, see the Supporting Information for details.

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Figure 5. SAXS/WAXS patterns for films prepared by drop-casting light-irradiated solutions of a) G1, b) G2, c) G3 at room temperature, and d) G3DT at various temperatures.

perature XRD at 65 °C shows a relatively strong diffraction peak at d=53.5 Å with the following *d*-spacing ratio of 1:2, 1:3, 1:4, and 1:6, indicating the existence of an ordered lamellar (Lam) packing (Figure S19c in the Supporting Information).

Even at 23 °C, the diffraction pattern shows only slight differences, suggesting that the thermal transition from Col<sub>h</sub> to Lam is an irreversible process. An interlayer distance of 55.2 Å (i.e., *d* at 23 °C) is almost comparable to the inter-columnar distance (i.e.,  $a_{\text{hex}}$ ) of the Col<sub>h</sub> packing observed for the as-prepared film; thus we can assume that the oligomeric structure described above for self-assembled **G2** in each disk is retained also in the Lam phase.

For G3 at 23 °C, a 2D hexagonal lattice is observed with a =39.4 Å (Figures 5 c and S20 and Table S4 in the Supporting Information), which is significantly smaller than that for G2 forming a pentameric assembly in the columnar disk as described above. In this case, a single molecular columnar assembly is the most likely explanation for G3 from the lattice parameter (Z=1.53).<sup>[28]</sup> Interestingly, in this diffraction pattern, a 2D rectangular lattice was concurrently observed with a = 68.2 Å, b =39.4 Å (i.e., a (hexagonal)). Thus the phase is denoted as the pseudo-hexagonal columnar phase (Col<sub>hrp</sub>)<sup>[29]</sup> with a 2D hexagonal packing arrangement for the whole molecules and a 2D rectangular symmetry for the cores. As illustrated in Figure S21 in the Supporting Information, such a molecular arrangement is reasonable for G3, having two different linkers (an amide and two ether groups) adjacent to the triarylamine core, whereas the whole molecular shape presents a high symmetry due to the three-directional deposition of the same peripheral tails. VT-XRD at the LC phase (68 °C) shows only a diffraction at d=32.1 Å and disappearance of following peaks in the wider angle region (Figure S20 in the Supporting Information), whereas only a slight thermal change in the birefringent textures on VT-POM was observed up to this temperature as mentioned above. These results suggest that the LC phase of G3 maintains less ordered columnar packing (Col) possessing only orientational order with an average inter-columnar distance (d).

Triethylamine G3DT, in which the peripheral dodecyl-oxy chains of G3 were partially altered by tetraethylene glycol chains, exhibits more complicated phase changes (Figures 5d and S22 and Table S5 in the Supporting Information). At 12°C, a tetragonal columnar (Col<sub>tet</sub>) phase was determined with a relatively large column size (a = 73.6 Å). The middle angle diffraction then changes to a periodical pattern (1, 1:2, 1:3, 1:4,...), which can be attributed to a phase possessing a lamellar order and with an inter-layer distance of 63.1 Å. Although the phase transition between  $\text{Col}_{\text{tet}}$  and the lamellar phase (Lam) is a reversible process, the additional transition from Lam towards  $Col_h$  (a = 65.2 Å) is also observed when XRD detection was continued at 23 °C for a few days (Figures S22 and S23 in the Supporting Information). Existence of these different phases can be rationally supported by the observation of multiple phase transition peaks at around 23  $^\circ\text{C}$  on the DSC analysis for <code>G3DT</code> (Figure 3 d). Interestingly, even in the isotropic phase, two broadened diffractions are observed at the small angle region (Figure S22 f in the Supporting Information). This indicates that the columnar aggregates of G3DT remain in the isotropic phase and confirms the existence of the amide hydrogenbonding network through the columnar stacks even with very bulky substituents. This self-assembled structure is also likely

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reinforced by the phase-separation of co-existing hydrophobic dodecyl-oxy chains and hydrophilic tetraethylene glycol chains at the periphery of **G3DT**.<sup>[30]</sup> The decreasing average inter-columnar distance from 63.1 (at 23 °C) to 57.0 (by heating at 40 °C) and 55.2 Å (by heating at 68 °C), might be attributed to the partial interdigitation of these peripheral chains between the columns due to their higher disorder at higher temperatures.

In the wide angle region, overlaps of several diffractions were observed at 4.2–5.4 Å for **G1** and **G2**. These peaks can be identified as two orders in the lattice: 1) distances between the nitrogen centers of adjacent triphenylamine cores  $(4.8 \text{ Å})^{[11g,h]}$  in the columnar stacks and 2) typical distances between peripheral alkyl chains  $(4.2–4.9 \text{ Å}).^{[25,26,31]}$  The broadness of this halo with the order of **G1** < **G2** < **G3**, and **G3DT** at room temperature indicates enhanced "fluidity" of the peripheral moieties according to an increased number of the side chains. Observation of additional peaks at twice distance (8.2–9.6 Å) for **G1–G3** is consistent with a period in the stack involving two triphenylamine disks with alternated orientations and handedness,<sup>[26d,f]</sup> and named as the "snow-flake" molecular arrangement according to our previous experimental and theoretical studies.<sup>[11h]</sup>

#### Atomic force microscopy (AFM) measurements

To further understand the supramolecular organizations of the present assembled systems, AFM was performed on films prepared by drop-casting irradiated chloroform solutions of **G1**–**G3** on mica substrates, followed by evaporation of the solvent.

As shown in Figure 6a, stacked layers of multiple nanosheets are observed for **G1** when imaged at room temperature. Formation of such a structure is in good agreement with a lamellar



Figure 6. AFM height images obtained for a) G1, b) G2, and c) G3. d) AFM surface elastic modulus image obtained for G3.

character of the molecular arrangement estimated by XRD, as described above. Several observations can then be combined: 1) the thickness of each sheet is 3.5 nm (Figure S24c in the Supporting Information), a value comparable to the molecular size of **G1** in the lamellar packing as previously estimated by XRD, 2) according to strongly birefringent spherulites observed by POM, the molecular surface of **G1** should not be in parallel but rather perpendicular to the substrate in the as-prepared film, 3) the layer stacks form larger scale of superstructures in a radial fashion similar to the observation by POM without a cross-polarizer (Figures S24b and S10c in the Supporting Information). By combining these three observations, one can estimate that the sheets consist in assembled monolayers of **G1** as illustrated in Figure S24d in the Supporting Information.

In contrast, AFM images of films made of **G2** show fibrillar objects with an average diameter of 30 nm, which further aggregate into densely packed bundles (Figures 6b and S25 in the Supporting Information). The flexible aspect of these micrometric fibers accounts satisfyingly for the soft character of columnar plastic phase observed for **G2** by XRD and POM at this temperature.

Similarly to the case of G1, nanosheets forming terrace structures are observed for G3 (Figures 6c and S26 in the Supporting Information), whereas the surface elastic modulus image (Figure 6d) shows more distinct microstructures,<sup>[32]</sup> indicating that the thin layers further consist of fibrous components. The morphological differences observed for the nanostructures of G2 and G3, exhibiting both Col<sub>h</sub> phases, can possibly be attributed to the respective compositions of the columnar structures. On the one hand, the columns of G2 have a high 2D symmetry due to the pentameric assembly of the G2 molecules in each composing disks (Figures S19b and c in the Supporting Information), consequently bundling into thick fibers omnidirectionally. On the other hand, G3 forms single molecular columns bearing less 2D symmetry (because of its two different linkers) and leading to a pseudo-hexagonal packing (Figure S21 in the Supporting Information). Such a molecular arrangement is thought to result in spread sheet structures rather than individually completed fibers and bundles.

#### Summary of the self-assembled structures and of their related mesomorphic properties

Compounds **G1–G3** and **G3DT** readily self-assemble by light irradiation in solution and variation of the peripheral tails attached to the triarylamine core dramatically affect the modes and properties of the supramolecular materials in the bulk, as summarized in Figure 7.

Lamellar-like arrangement is preferred in the case of **G1** equipped with a single dendritic moiety containing three dodecyl chains, resulting in a layer-by-layer stack of the monolayer nanosheets. Introduction of two identical dendritic tails at the peripheral positions, in contrast, induces the pentameric assembly of **G2** in a hexagonally packed columnar stack, which finally leads to thick bundles of nanofibers with micrometerscale lengths. However, thermal annealing of the as-prepared film produces an irreversible transition to the lamellar molecu-

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**Figure 7.** Summary of the proposed supramolecular self-assemblies of **G1**–**G3** and **G3DT**. [a] After thermal annealing of the as-prepared film. [b] Under heated conditions. [c] Observed for as-prepared films at RT.

lar order. Furthermore, when all the three corners of the triarylamine core are occupied by the dendritic tails, triethylamine G3 forms unimolecular columns further bundled into a nanosheet structure. This is likely due to an anisotropic alignment of the triarylamine cores mono-substituted by an amide moiety in a pseudo-hexagonal molecular packing. The columnar alignment of G3 is also maintained in the LC phase, whereas the lateral positional order of the columns is lost at these temperatures as indicated by VT-XRD measurements. Triarylamine G3DT shows a complex phase behavior with columnar phases transiting between tetragonal, lamellar, and hexagonal packing at ambient temperature. This property can reflect the soft nature of the assemblies due to partial wrapping of the core by flexible tetraethylene glycol chains. The Gemini-type amphiphilic structure<sup>[33]</sup> of **G3DT** also affects the composition of the columnar structures as estimated by XRD analysis; triarylamine G3DT tends to form an oligomeric assembly ( $Z \approx 4$  to 6) in the disks, whereas G3 prefers a single-molecular columnar stacking. Indeed, two poorly compatible peripheral chains (i.e., hydrocarbons and ethylene glycols) substituting a discotic molecule are often segregated in distinct layers, inducing superstructures with multi-columnar orders.[33d]

With respect to the mesomorphic properties, **G1–G3** and **G3DT** show unique characteristics, influenced by their structural differences: 1) **G1** displays two independent crystalline phase, 2) both **G2** and **G3** display two independent mesophases with a columnar plastic phase at ambient temperature and LC phases upon heating, 3) **G3DT** displays a LC phase at room temperature. Noteworthy, the transition temperature into the LC phase was by 20 °C lower for **G2** (having only two peripheral tails in a molecule) than for **G3** (in which the tails cover all three corners of the core); this is explained by the difference in the molecular arrangement of the respective columnar packing and the resulting number of aggregation of flexible alkyl chains. Additionally, the drastic lowering of the LC transition below room temperature for **G3DT** can be attributed to the relatively disordered character of the peripheral stacks composed of tetraethylene glycol chains having higher flexibility and electrically repulsive character.  $^{\left[ 34\right] }$ 

We can also correlate the morphology in the bulk and films with our spectroscopic analyzes in solution. Interestingly, the nanosheet structure for G1 can be correlated with its 14 nm blue-shifted emission upon continuous light irradiation in solution. In contrast, G2, G3, and G3DT form columnar structures that align the triarylamine core,<sup>[11h]</sup> and show significant redshifts in solution. In addition, for all these derivatives, the characteristic NIR absorption bands (Figure S7 in the Supporting Information) and fluorescent emissions (Figure S8 in the Supporting Information) were also observed in the film state at similar maximum wavelengths to those in light-irradiated solution (Table S1 in the Supporting Information). This tendency indirectly indicates that the light-triggered self-assembly in solution can take place in a similar manner with organizations explained in the film state for the present triarylamines.<sup>[35]</sup> This is also of particular interest to produce doped self-assemblies in the liquid crystal state.

#### Conclusion

To summarize, we have designed and synthesized a series of amide-containing triphenylamine-cored dendritic molecules by tuning their peripheral moieties. Self-assembly can be triggered from solution and their doped character, as well as their characteristic stacked structures, remain in the bulk after solvent evaporation as investigated by DSC, VT-POM, VT-XRD, and AFM. By combining these multidimensional analyses, we obtained some insights into the controlled self-assembly of triarylamines: 1) triphenylamine cores can be aligned into ordered supramolecular organizations in the bulk by introducing appropriate peripheral moieties leading to multiple non-covalent interactions, 2) modification of the peripheral moieties (number, positional relationships with the amide moiety, and their variation) largely defines the molecular packing of lamellar and columnar assemblies of triarylamines, further affecting the formation of various supramolecular nanostructures, 3) such structural differences also change their mesomorphic properties exhibiting characteristic phase transition behaviors across crystalline states and plastic/liquid crystalline mesophases. The structure-property relationships revealed here provide us with useful orientations for the design of soft materials for optoelectronics based on the framework of doped supramolecular conducting nanostructures.

# **Experimental Section**

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All reagents and solvents were purchased at the highest commercial quality and used without further purification unless otherwise noted. Dry solvents were obtained by using a double column SolvTech purification system. Microscope glass slides (soda-lime, 76×26 mm, 1 mm thickness) and cover slips ( $20 \times 20$  mm) for the fabrication of thin films (for POM, UV/Vis/NIR, and photoluminescence experiments) were purchased from the Carl Roth GmbH. Wet column chromatography was performed by using silica gel (high-purity grade, pore size 60 Å, 230–400 mesh, 40–63  $\mu$ m parti-

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cle size, Fluka). UV/Vis-NIR spectra were recorded on Cary 5000 UV/ Vis/NIR spectrometer (Agilent Technology). Fluorescence spectra were recorded on FluoroMax-4 spectrofluorometer (HORIBA-JOBIN YVON). FTIR spectra were recorded on a VERTEX70 FT-IR spectrometer (Bruker) and are reported as wave number  $\tilde{\nu}$  in [cm<sup>-1</sup>] with band intensities as "s" (strong), "m" (medium), or "w" (weak). Polarizing optical microscopy (POM) experiments were done by using a Leica DMR polarization microscope (Leica) equipped with a digital camera (COOLPIX995, Nikon). Temperature-variable POM experiments were done by using a temperature-controlled stage (Linkam Scientific Instruments). Differential scanning calorimetry was performed on a DSC 8500 (PerkinElmer). X-ray diffraction (XRD) experiments have been performed with two setups: an Elexience spectrometer with a distance sample to detector of 1.5 m with a wavelength of  $\lambda = 1.54$  Å and a Nanostar spectrometer (Bruker-Anton Paar) that operates with a pinhole collimator and a wire proportional gas detector. Atomic force microscopy (AFM) images were obtained by scanning the samples by using a Nanoscope 8 (Bruker) operated in peak-force tapping mode. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and <sup>13</sup>C NMR spectra at 100 MHz at room temperature. The spectra were internally referenced to the residual proton solvent signal. For <sup>1</sup>H NMR assignments, the chemical shifts are given in [ppm]. Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), and quartet (q) with coupling constants (J) listed in [Hz], or multiplet (m). Hydrogen multiplicities of <sup>13</sup>C signals were assigned with the help of DEPT 135 and HSQC measurements, and are reported as s (C), d (CH), t (CH<sub>2</sub>), and q (CH<sub>3</sub>).

Compounds 1, 2, and 4 were prepared following procedures reported in the literature.  $^{\left[ 11a\right] }$ 

Compound G1: A mixture of triarylamine 1 (0.12 g, 0.22 mmol) and tin(II) chloride dihydrate (0.61 g, 2.7 mmol) in ethanol (4 mL) and acetonitrile (5 mL) was stirred while heating to reflux overnight. The reaction mixture was then treated with EtOAc and aqueous NaHCO<sub>3</sub> solution. After filtration, the separated organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was then evaporated to give the amine as a solid, which was used without further purification. To a solution of 3,4,5-tris(dodecyloxy)benzoyl chloride<sup>[14]</sup> (0.31 g, 0.44 mmol) in THF (4 mL) was added a solution of amine (0.12 g, 0.22 mmol) and triethylamine (93 µL, 0.67 mmol) in THF (4 mL) dropwise at 0  $^{\circ}$ C. After stirring for 2 h at 0  $^{\circ}$ C, the mixture was warmed to room temperature and further stirred for 3 h. The reaction mixture was concentrated in vacuum and the residue was purified by column chromatography (cyclohexane to cyclohexane/ EtOAc 96:4;  $R_f = 0.48$  with cyclohexane/AcOEt 95:5) to give compound G1 (0.22 g, 84%) as a pale brown solid. M.p. 53 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.86$  (s, 1 H), 7.36 (d,  ${}^{3}J = 9.6$  Hz, 2 H), 7.08 (s, 2H), 6.94 (d,  ${}^{3}J=8.8$  Hz, 4H), 6.89 (d,  ${}^{3}J=8.4$  Hz, 2H), 6.73 (d,  ${}^{3}J=$ 8.8 Hz, 4 H), 3.98-3.91 (m, 6 H), 3.85 (t, <sup>3</sup>J=6.6 Hz, 4 H), 1.78-1.65 (m, 12 H), 1.43-1.34 (m, 12 H), 1.27-1.24 (m, 60 H), 0.83-0.79 ppm (m, 15H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 163.9 (s), 155.2 (s), 152.2 (s), 149.8 (s), 145.0 (s), 141.0 (s), 129.9 (s), 126.0 (d), 121.8 (d), 121.3 (d), 117.1 (s), 115.3 (d), 109.8 (d), 74.3 (t), 74.0 (t), 69.1 (t), 66.3 (t), 32.0 (t), 30.3 (t), 30.2 (t), 29.8 (t), 29.7 (3×t), 29.6 (t), 29.5 (t), 29.4 (4×t), 29.2 (t), 26.1 (2×t), 26.0 (t), 22.7 (t), 14.1 ppm (q) (Signals for the two non-equivalent dodecyloxy groups and the two octoxy groups are partially overlapped.); IR (neat):  $\tilde{v} = 3229$  (br), 3043 (w), 2918 (s), 2850 (s), 1796 (w), 1650 (m), 1583 (w), 1507 (s), 1466 (m), 1417 (m), 1343 (m), 1235 (s), 1109 (s), 823 cm<sup>-1</sup> (m).

**Compound 3**: A mixture of triarylamine **2** (4.1 g, 8.1 mmol) and palladium on carbon (0.40 g, 10 wt%) in methanol (50 mL) and EtOAc (100 mL) was stirred under a hydrogen gas atmosphere at room temperature for 21 h. The reaction mixture was filtered on

celite and rinsed with methanol. The solvent was evaporated to give the reduced intermediate amino-triarylamine (2.3 g), which was used without further purification. To a solution of 3,4,5-tris(dodecyloxy)benzoyl chloride<sup>[14]</sup> (0.85 g, 1.2 mmol) in THF (3 mL) was added a solution of amino-triarylamine (0.29 g, 0.98 mmol) and triethylamine (0.17 mL, 1.2 mmol) in THF (7 mL) dropwise at 0°C. The mixture was stirred for 20 h while warmed slowly to room temperature. The reaction mixture was diluted with EtOAc and washed with saturated aqueous NH<sub>4</sub>Cl solution and brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was then removed in vacuum. The residue was purified by column chromatography (dichloromethane to dichloromethane/EtOAc/methanol 70:3:3;  $R_f = 0.50$  with dichloromethane/EtOAc/methanol 70:3:2) to give compound 3 (0.42 g, 45%) as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.75$  (brs, 1 H), 7.40 (dd,  ${}^{3}J = 8.8$ ,  ${}^{4}J = 2.0$  Hz, 2H), 7.05 (s, 2H), 6.98-6.93 (m, 6H), 6.76-6.74 (m, 4H), 4.06-4.01 (m, 6H), 1.85-1.74 (m, 8H), 1.51-1.47 (m, 6H), 1.38-1.28 (m, 46H), 0.91–0.88 ppm (m, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>/MeOD 97:3):  $\delta =$ 166.2 (s), 153.1 (s), 152.4 (s), 146.2 (s), 141.4 (s), 140.4 (s), 130.0 (s), 129.6 (s), 126.5 (d), 122.3 (d), 120.8 (d), 116.2 (d), 106.0 (d), 73.6 (t), 69.4 (t), 31.9 (t), 30.3 (t), 29.7 (4×t), 29.6 (t), 29.4 (3×t), 26.1 (2×t), 22.7 (t), 14.1 ppm (q) (Signals for the two non-equivalent dodecyloxy groups are partially overlapped.); IR (neat):  $\tilde{\nu} = 3535$  (br), 3367 (br), 2919 (s), 2850 (s), 1682 (w), 1617 (w), 1592 (m), 1585 (s), 1539 (w), 1493 (s), 1338 (m), 1228 (s), 1121 (s), 829 cm<sup>-1</sup> (s).

Compound G3DT: To a mixture of triarylamine 3 (0.14 g, 0.15 mmol), Ar'-CH\_2OH  $^{\scriptscriptstyle [15]}$  (0.35 g, 0.49 mmol), and triphenylphosphine (0.13 g, 0.49 mmol) in THF (5 mL) was added a solution of DIAD (90 µL, 0.45 mmol) in THF (1 mL) dropwise at 0 °C. The mixture was warmed to room temperature and then stirred at 60 °C for 24 h. The solvent was then removed in vacuum, and the residue was purified by column chromatography (dichloromethane to dichloromethane/methanol 20:1,  $R_{\rm f}$  = 0.39 with dichloromethane/ methanol 10:1) to give compound G3DT (0.16 g, 46%) as a yellow solid. M.p. 23 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.66 (s, 1 H), 7.43 (d,  ${}^{3}J$ =9.2 Hz, 2 H), 7.03–6.96 (m, 8 H), 6.86 (d,  ${}^{3}J$ =8.8 Hz, 4 H), 6.66 (s, 4H), 4.89 (s, 4H), 4.17-4.12 (m, 12H), 4.04-3.98 (m, 6H), 3.84 (t,  ${}^{3}J = 5.2$  Hz, 8 H), 3.78 (t,  ${}^{3}J = 5.2$  Hz, 4 H), 3.72–3.69 (m, 12 H), 3.66– 3.61 (m, 48H), 3.54-3.51 (m, 12H), 3.36-3.35 (m, 18H), 1.84-1.70 (m, 6H), 1.50–1.43 (m, 6H), 1.34–1.25 (m, 48H), 0.87 ppm (t,  ${}^{3}J =$ 6.8 Hz, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.5 (s), 154.7 (s), 153.2 (s), 152.8 (s), 145.3 (s), 141.5 (2×s), 138.2 (s), 132.5 (s), 131.6 (s), 130.1 (s), 125.8 (d), 122.4 (d), 121.5 (d), 115.7 (d), 107.3 (d), 105.9 (d), 73.6 (t), 72.3 (t), 71.9 (t), 70.8 (t), 70.6 (2×t), 70.5 (t), 69.7 (t), 69.5 (t), 68.9 (t), 59.0 (q), 31.9 (2×t), 30.3 (t), 29.7 (4×t), 29.64 (3× t), 29.40 (3×t), 26.1 (t), 22.7 (t), 14.1 ppm (q) (Aliphatic signals assigned to the dodecyloxy and tetraethylene glycol monomethylether chains are not completed due to overlaps of the signals for non-equivalent chains.); IR (neat):  $\tilde{\nu} = 3515$  (br), 3350 (br), 2922 (s), 2854 (s), 1690 (w), 1662 (w), 1640 (w), 1585 (m), 1528 (w), 1502 (s), 1466 (m), 1436 (m), 1332 (m), 1230 (m), 1103 (s), 827 cm<sup>-1</sup> (m).

**Compound G3**: To a mixture of triarylamine **3** (0.26 g, 0.28 mmol), (3,4,5-tris-(dodecyloxy)phenyl)methanol<sup>[16]</sup> (0.45 g, 0.68 mmol), and triphenylphosphine (0.19 g, 0.71 mmol) in THF (8 mL) was added a solution of DIAD (0.14 mL, 0.71 mmol) in THF (1 mL) dropwise at 0 °C. The mixture was warmed to room temperature and then stirred at 60 °C for 22 h. The solvent was then removed in vacuum and the residue was purified by column chromatography (cyclohexane to cyclohexane/EtOAc 20:1;  $R_f$ =0.22 with cyclohexane/EtOAc 7:1) and preparative thin-layer chromatography (cyclohexane/EtOAc 20:1) to give compound **G3** (0.25 g, 41%) as a pale orange solid. M.p. 72 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.56 (s, 1 H), 7.42 (d, <sup>3</sup>J=8.8 Hz, 2 H), 7.03-7.01 (m, 5 H), 6.97 (d, <sup>3</sup>J=9.6 Hz, 2 H),

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6.88 (d,  ${}^{3}J$ =9.2 Hz, 4 H), 6.61 (s, 4 H), 4.89 (s, 4 H), 4.02–3.94 (m, 18 H), 1.79–1.77 (m, 18 H), 1.53–1.44 (m, 18 H), 1.34–1.23 (m, 144 H), 0.88–0.85 ppm (m, 27 H);  ${}^{13}$ C NMR (100 MHz, CDCI<sub>3</sub>):  $\delta$ =165.4 (s), 154.9 (s), 153.3 (2×s), 145.4 (s), 141.6 (s), 141.5 (s), 138.1 (s), 131.9 (s), 131.5 (s), 130.0 (s), 125.9 (d), 122.3 (d), 121.4 (d), 115.7 (d), 106.3 (d), 105.9 (d), 73.6 (t), 73.5 (t), 70.8 (t), 69.2 (t), 32.0 (t), 31.9 (t), 30.4 (t), 29.8 (t), 29.7 (t×2), 29.4 (t×3), 26.2 (t), 26.1 (2×t), 22.7 (t), 14.1 ppm (q) (Aliphatic signals assigned to four non-equivalent dodecyloxy groups are not completed due to overlaps of the signals for four non-equivalent dodecyl chains.); IR (neat):  $\tilde{\nu}$ =3285 (br), 3038 (w), 2920 (s), 2851 (s), 1639 (w), 1585 (m), 1508 (s), 1474 (m), 1434 (m), 1378 (w), 1335 (m), 1231 (s), 1117 (s), 1003 (m), 824 cm<sup>-1</sup> (m).

Compound G2: To a mixture of triarylamine 4 (80 mg, 0.24 mmol), (3,4,5-tris-(dodecyloxy)phenyl)methanol<sup>[16]</sup> (0.33 g, 0.50 mmol), and triphenylphosphine (0.14 g, 0.53 mmol) in THF (7 mL) was added DIAD (0.10 mL, 0.53 mmol) dropwise at 0°C. The mixture was stirred for 26 h while warmed slowly to room temperature, and the solvent was removed in vacuum. The residue was purified by column chromatography (cyclohexane to cyclohexane/EtOAc 75:25;  $R_{\rm f}$  = 0.46 with cyclohexane/EtOAc 70:30) to give compound **G2** (0.17 g, 43%) as a pale brown solid. M.p.  $77 \degree C$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.29-7.27$  (m, 2H), 7.01–6.98 (m, 4H), 6.93– 6.91 (m, 2H), 6.88-6.86 (m, 4H), 6.61 (s, 4H), 4.89 (s, 4H), 3.98-3.92 (m, 12H), 1.82-1.70 (m, 12H), 1.47-1.44 (m, 12H), 1.33-1.25 (m, 96 H), 0.89–0.85 ppm (m, 18 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta =$ 168.1 (s), 154.8 (s), 153.3 (s), 145.3 (s), 141.5 (s), 138.1 (s), 132.0 (s), 131.4 (s), 125.8 (d), 122.3 (d), 121.3 (d), 115.6 (d), 106.3 (d), 73.5 (t), 70.8 (t), 69.2 (t), 32.0 (t), 30.4 (q), 29.8 (t), 29.7 (2×t), 29.5 (t), 29.4  $(t \times 2)$ , 26.2 (t), 22.7 (t), 14.1 ppm (q) (Aliphatic signals assigned to two non-equivalent dodecyloxy groups are not completed due to overlaps of the signals for two non-equivalent dodecyl chains.); IR (neat):  $\tilde{v} =$  3290 (br), 3038 (w), 2917 (s), 2851 (s), 1654 (w), 1641 (w), 1591 (m), 1498 (s), 1466 (m), 1437 (m), 1373 (m), 1333 (m), 1313 (m), 1231 (s), 1211 (s), 1112 (s), 996 (m), 853 (w), 834 (m), 823 (m), 811 cm<sup>-1</sup> (w).

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# **FULL PAPER**

# Liquid Crystals

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Soutrol over Nanostructures and Associated Mesomorphic Properties of Doped Self-Assembled Triarylamine Liquid Crystals



**Changing by packing**: Chemically tailored triarylamine derivatives readily self-assemble upon visible light irradiation (see figure) to produce doped liquid crystals with complex mesophase behaviors.



#### Self-assembled stacks of...

...triarylamines are generated by simple light irradiation. These p-doped columnar arrangements can produce a variety of liquid crystalline mesophases, which strongly depend on the lateral substitutions. For more information, see the Full Paper by Giuseppone and co-workers on page  $\blacksquare$  ff.