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## Liquid Crystals

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### Star-like discotic liquid crystals

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# Star-like discotic liquid crystals

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The game of molecular engineering of liquid crystalline systems via a combination of molecular architecture and functionalization of mesogens has opened interesting perspectives in the field of liquid crystals. Here we report on the synthesis and characterization of star-like heptameric triphenylenes. The discotic subunits in these molecules have been arranged in a hexagonal fashion around a central discotic core, thus leading to a new type of molecular arrangement for discotic liquid crystals. These oligomers do not crystallize and combine a well-defined structure with a discotic polymer-like processing.

## 1. Introduction

In the past few years, besides the synthesis of new mesogens, molecular engineering of liquid crystals (LC) with respect to molecular architecture and functionalization has become increasingly important [1-4]. Especially the incorporation of mesogenic units in main chain and side group polymers has to be emphasized. The first discotic polymers **A**, **B**—see figure 1—could be obtained by mono- and di-functionalization of triphenylene derivatives [5-13]. Apart from discotic main chain and side group polymers, stiff discotic polymers **C** [14-16] are known. Concerning their properties, they resemble calamitic rigid-rod polymers, but they differ in structural aspects through the spinal fixation of the main chain. Dimeric discotic liquid crystals **D** [11, 17] have been synthesized as model compounds to compare their

dynamic and structural characteristics with those of discotic main chain polymers. In the case of the so called 'Diabolo mesogens' **E** [18], the discogenic units are linked via the centres of the discs. Further structural variations of low molar mass materials, as well as those of the polymeric type have been obtained by combination of calamitic and discotic mesogenic units **F**, **G**, **H** [19, 20].

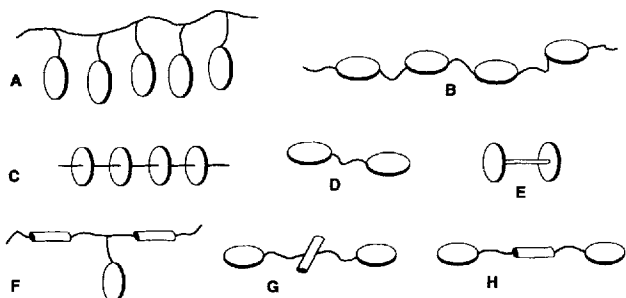


Figure 1. Different molecular architectures for discotic liquid crystals and related structures.

\* Author for correspondence.

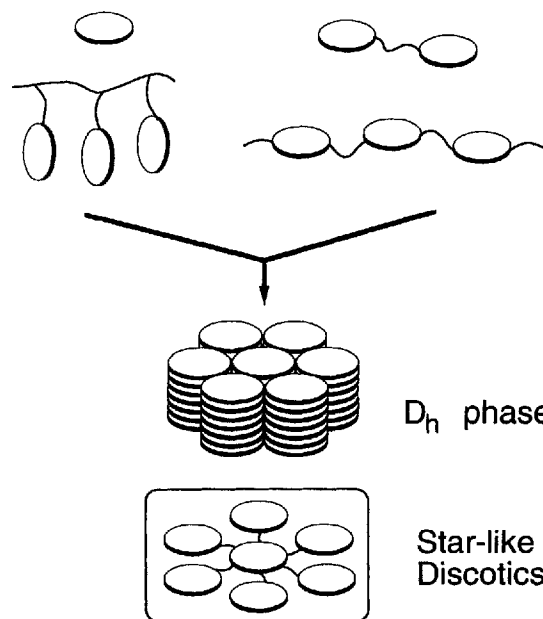
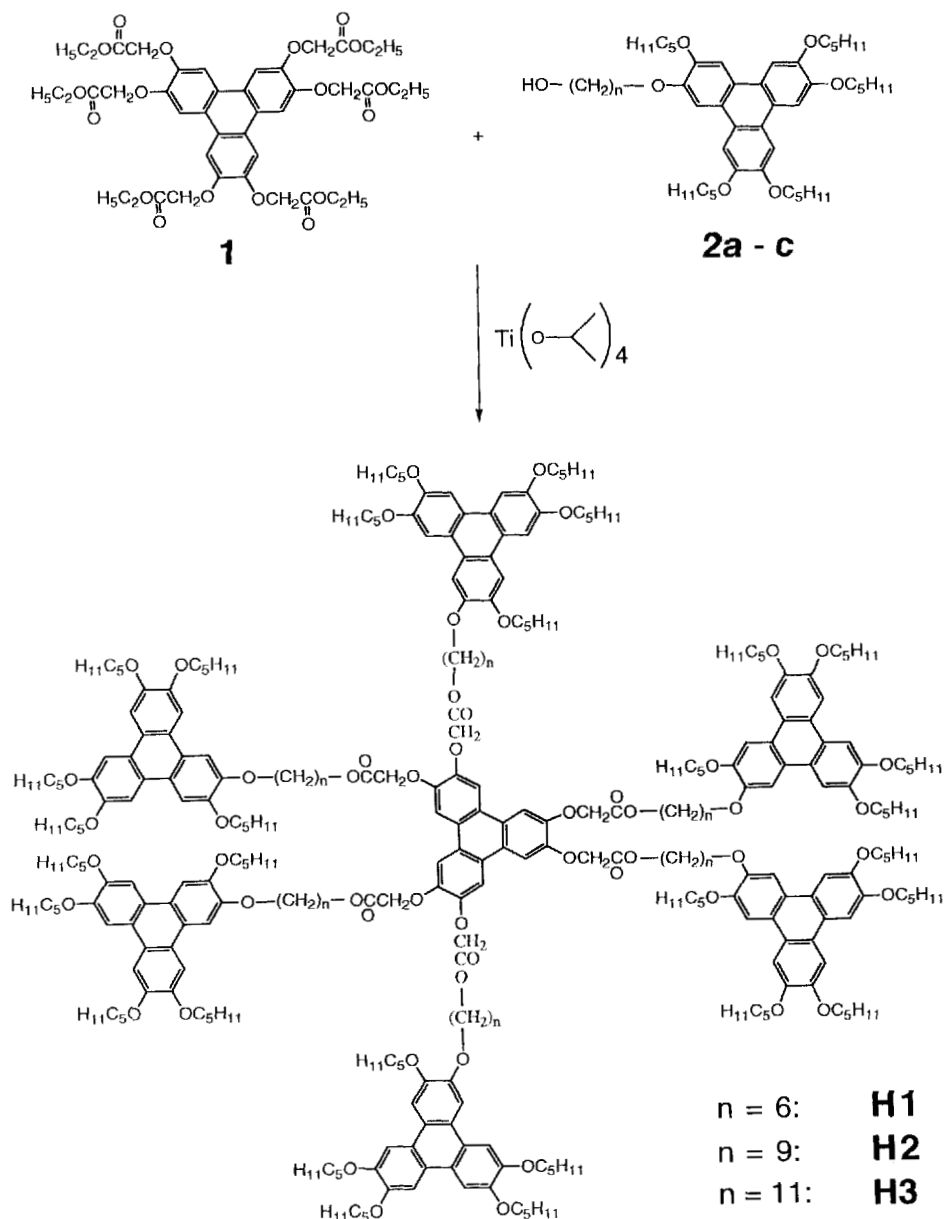


Figure 2. Analogy between the arrangement of discs in a hexagonal columnar mesophase and a star-like heptamer.



Scheme 1. Synthesis of star-like heptamers.

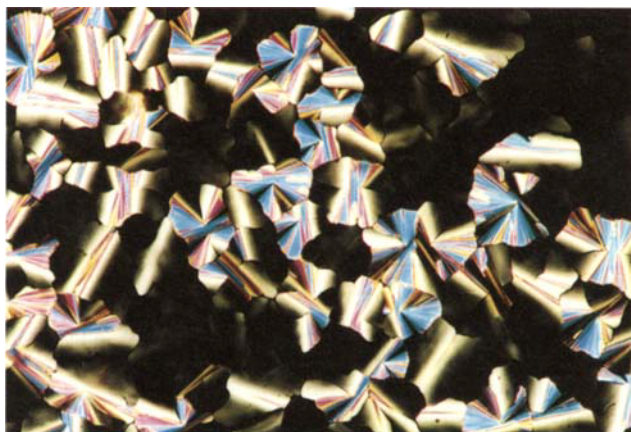
Many of the structural variations known for discotic liquid crystalline compounds are based on mono- and di-functionalized derivatives of hexa-alkoxytriphenylene. Investigations of low molar mass as well as polymeric compounds have shown that the mesophases formed have predominantly a hexagonal columnar structure ( $D_h$ )—see figure 2.

The supramolecular structure of the  $D_h$  mesophase comprising a hexagonal arrangement of triphenylene units can be preformed by star-like heptameric discotic molecules in which six peripheral units are each covalently linked to a central triphenylene via a flexible spacer.

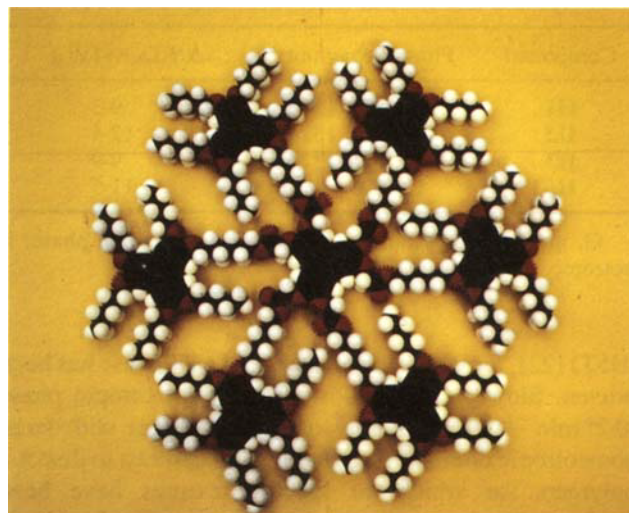
This concept has been realized by the synthesis of three star-like heptameric triphenylenes **H1**, **H2** and **H3** where the spacer unit has been varied in its length (see Scheme 1) [3].

## 2. Synthesis

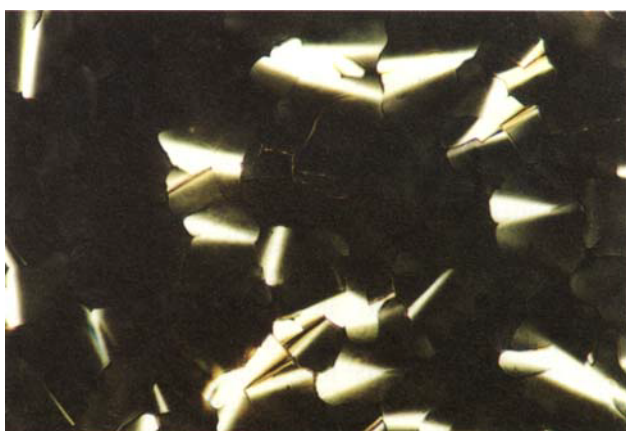
The synthesis of the three heptamers is shown in Scheme 1. The triphenylene-hexaester **1**, as well as the alcohols **2a–c** were obtained following standard procedures [5]. Transesterification of the hexaester with a triphenylene-alcohol **2a–c**, in the melt using titanium orthoisopropylate as catalyst [21], provided the heptamers



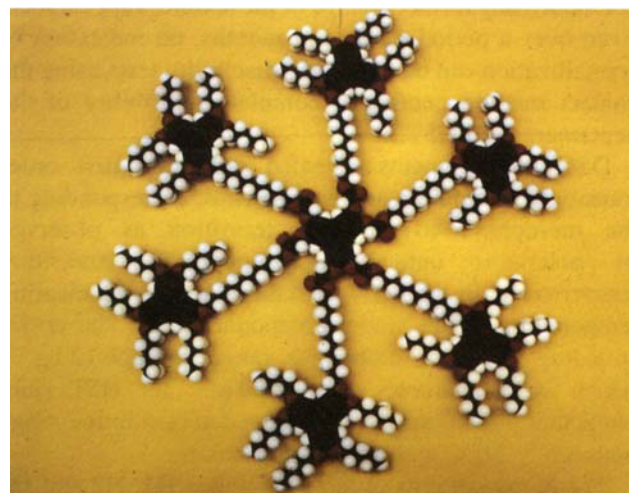
(a)



(a)



(b)



(b)

Figure 3. (a) Mosaic texture of **H3** at room temperature; (b) homeotropic orientation of **H2** at room temperature.

Figure 5. CPK models of (a) **H1** and (b) **H3**.

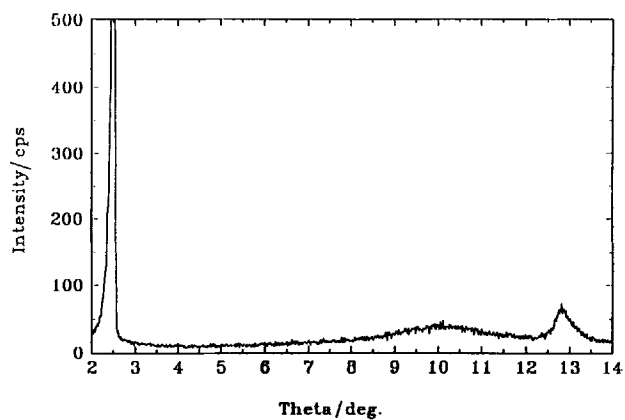


Figure 4. Goniometer scan of **H3** at room temperature.

**H1**, **H2** and **H3**. Excess of the alcohol was separated by preparative GPC (Sephadex LH 20). NMR, analytical GPC and elemental analysis data are consistent with the heptameric structure.

### 3. Characterization of mesophase behaviour

The compounds exhibit enantiotropic liquid crystal-line phases over broad temperature ranges. Between crossed polarizers, the growth of domains with hexagonal symmetry (digitated stars) is observed for all three heptamers on slowly cooling from the isotropic phase. Upon further cooling, these domains eventually lead to the formation of a mosaic texture with homeotropic domains (see figure 3), as described for hexapentyloxytriphenylene

Table 1. Transition temperatures and enthalpies of heptamers **H1**, **H2** and **H3** and the model compound **H5T**.

Compound	Phase behaviour/°C	$\Delta H(D_h \rightarrow I)/J g^{-1}$
<b>H1</b>	g ... D <sub>h</sub> 137 I	9.3
<b>H2</b>	g ... D <sub>h</sub> 152 I	12.4
<b>H3</b>	g ... D <sub>h</sub> 132 I	9.9
<b>H5T</b>	C 69 D <sub>h</sub> 122 I	11.5

G, glassy; C, crystalline; D<sub>h</sub>, discotic hexagonal phase; I, isotropic.

(H5T) [22], for which the existence of a D<sub>h</sub> phase has been proven. Slowly cooling down from the isotropic phase (0.2° min<sup>-1</sup>) yields highly oriented samples with large homeotropic domains (see figure 3), in contrast to discotic polymers for which no specific textures have been obtained. The textures are mobile down to 10–15 K below the clearing point. Annealing below that temperature range, as well as cooling down to room temperature, does not induce any further change of the texture's appearance. Even over a period of several months, no indication of crystallization can be detected. Miscibility tests using the contact method confirmed complete miscibility of the heptamers with H5T.

DSC measurements revealed only one first order transition, for cooling and heating runs, corresponding to the mesophase to isotropic transition as observed by polarizing optical microscopy. The transition temperatures are higher—see table 1—than the clearing temperature of the model compound **H5T**. The corresponding transition enthalpies range from 9–12 J g<sup>-1</sup>, which is comparable with 11.5 J g<sup>-1</sup> for **H5T** [23]. No actual glass transition could be detected in the range between -30°C and the clearing points.

The X-ray patterns of the compounds **H1**, **H2** and **H3** exhibit only one single peak in the small angle range and two diffuse scattering maxima in the wide angle range using the Guinier Goniometer (for example, figure 4). With the Guinier film method, additional weak reflections could be detected in the case of **H3**. The positions of the reflections in the small angle area exhibit the relation 1:3<sup>1/2</sup>:2:7<sup>1/2</sup>, indicating the existence of a hexagonal columnar mesophase. Table 2 summarizes the values found for the heptamer **H3**. The diffuse halo with a maximum at about 0.44 nm (see table 3) arises from the liquid-like order of the alkyl chains. The additional diffuse scattering at higher angles is due to the intra-columnar stacking of the triphenylene units within the columns. The number of about 45 correlated molecules within the columns is estimated from the full width at half maximum and corresponds well to **H5T**. No indication of crystallization could be derived from the X-ray patterns of any of three heptamers at room temperature. This is consistent

Table 2. Observed ( $d_{\text{meas}}$ ) and calculated ( $d_{\text{calc}}$ ) reflections for the D<sub>h</sub> phase of **H3**.

$d_{\text{meas}}/\text{nm}$	Indices	$d_{\text{calc}}/\text{nm}$
1.76	(100)	—
1.02	(110)	1.02
0.88	(200)	0.88
0.67	(210)	0.67
0.44	$d_{\text{Halo}}$	—
0.35	$d_{\text{intra}}$	—

Table 3. X-ray data for the mesophases of the heptamers compared with **H5T** ( $a_{\text{hex}}$ -hexagonal lattice constant;  $L_{\text{intra}}$ -intracolumnar correlation lengths according to the Scherrer equation [24]).

Compound	$d_{(100)}/\text{nm}$	$d_{\text{Halo}}/\text{nm}$	$d_{\text{intra}}/\text{nm}$	$a_{\text{hex}}/\text{nm}$	$L_{\text{intra}}/\text{nm}$
<b>H1</b>	1.68	0.44	0.35	1.95	13.7
<b>H2</b>	1.75	0.44	0.35	2.02	18.6
<b>H3</b>	1.77	0.44	0.35	2.04	15.7
<b>H5T</b>	1.76	0.45	0.36	2.03	12.3

with the experimental findings from polarizing microscopy and differential scanning calorimetry.

#### 4. Discussion

As anticipated, the star-like heptamers exhibit a hexagonal columnar mesophase (D<sub>h</sub>). The hexagonal pre-organization of the triphenylene units as illustrated in figure 5 [25], leads to an increase in the clearing temperature of up to 30° compared with H5T. The clearing temperatures are of similar magnitude to those of dimeric triphenylene derivatives [11]. The different mesophase stabilities of the three heptamers can be discussed with reference to the spacer element  $-(\text{CH}_2)_n-$ . The lattice parameters are basically independent of the spacer length and thus are dominated by the six peripheral triphenylene units. The spacer elements have to be adapted according to this distance. In the series of heptamers investigated, the spacer element in **H2**  $-(\text{CH}_2)_9-$  seems to be most appropriate, as reflected by the clearing point.

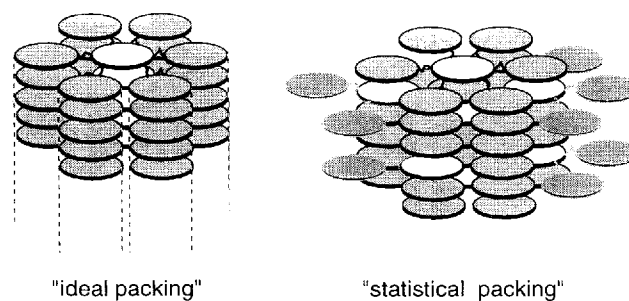
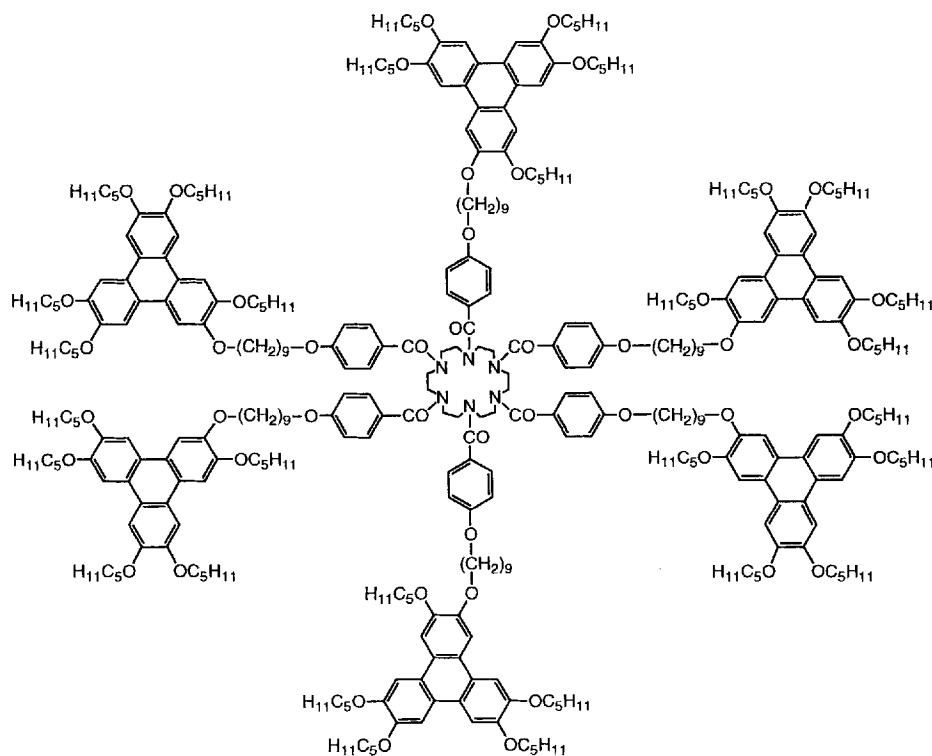


Figure 6. Possible arrangement of star-like heptamers **H1**, **H2** and **H3** in a hexagonal mesophase.



Scheme 2. Heptamer with a hydrophilic aza-crown as the central core.

**H2** and **H3**  $(-\text{CH}_2)_{11}-$ ) exhibit about the same value for the hexagonal lattice constant, indicating that for **H3** the spacer has to adopt a more disordered conformation/arrangement, resulting in a lower clearing temperature. A comparable dependency of mesophase stability has been found for triphenylene main chain polymers with different spacer lengths [8].

In principle there are two possibilities for the packing of the heptamers in a hexagonal mesophase. On the one hand, the heptamers as molecular units could stack on top of each other (see figure 6: 'ideal packing'); on the other hand the single triphenylene subunits of the heptamer could arrange themselves statistically forming the hexagon (see figure 6: 'statistical packing'). The 'ideal packing' is expected to be entropically unfavourable; thus the arrangement of the three heptamers in the hexagonal mesophases can be described using the statistical model. The entropic drawback of the 'ideal packing' could be balanced by additional specific interactions furnishing materials which then form superlattices. Possibly a hydrophilic spacer segment as in ethyleneoxides would diminish the probability of forming a statistical packing, since this would result in an unfavourable arrangement of the spacer with the hydrophobic alkyl side chains. Such an internal microphase separation of central and peripheral molecular units has been achieved in the meantime by the choice of a hydrophilic central core like the discoid

aza-crown in Scheme 2, as well as by the use of a smaller central core like benzene. A detailed study of these superlattice forming materials will be the subject of a forthcoming publication.

## 5. Experimental

The X-ray studies ( $\text{CuK}_\alpha$  radiation = 0.154 nm) of the mesophase have been performed using a Guinier goniometer (Huber G644, FRG) and a Guinier film camera. The triphenylene samples were melted in glass capillaries with diameters of 1 mm. The sample temperature were controlled by a Huber temperature device HTC 9634. A Perkin-Elmer DSC 7 was used for DSC measurements (heating and cooling rates  $10^\circ \text{min}^{-1}$ ). NMR spectra have been recorded on a Bruker 400 MHz FT-NMR spectrometer Aspect 300.

### 5.1. Synthesis of star-like heptameric triphenylenes **H1**, **H2** and **H3**

#### 5.1.1. 2,3,6,7,10,11-Hexakis-[3,6,7,10,11-pentakis(pentyloxy)triphenylene-2-oxihexyloxy]carbonylme-thyleneoxy]-triphenylene **H1**

30 mg (0.0354 mmol) of triphenylene-hexaester **1** and 247 mg (0.3185 mmol) of triphenylene-hexanol **2a** were dissolved in 1 ml of anhydrous dichloromethane in a Schlenk-tube. The solvent was carefully evaporated using dry nitrogen. The tube was heated for 5 min at  $110^\circ\text{C}$

before two drops of the catalyst solution (10 per cent tetra(isopropyl)-orthotitanate (Merck) in anhydrous diethylene glycol dimethyl ether) were added to the melt. Condensation was performed for 1 h at normal pressure, 1.5 h at 125°C at reduced pressure (15 mbar) and 6 h under oil pump vacuum (0.007 mbar), while the temperature was raised gradually to 140°C to avoid solidifying of the melt. The mixture was dissolved in THF and the heptamer separated by preparative GPC from excess of monomer (Sephadex LH 20; eluent: anhydrous THF). Precipitation in methanol yielded 156 mg (84 per cent) of the desired product. Elemental analysis:  $C_{324}H_{456}O_{54}$  ( $M_w = 5215.15$ ) required C: 74.61, H: 8.82; found C: 74.73, H: 8.78 per cent.  $^1H$  NMR ( $CDCl_3$ , 400 MHz),  $\delta$  [ppm] = 7.74–7.69 (m; arom.; 42 H), 4.86 (s;  $-O-CH_2-CO-$ ; 12 H), 4.26 (t;  $-CO-O-CH_2-CH_2-$ ; 12 H), 4.18 (m;  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.90 (m;  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.74 (m;  $-CO-O-CH_2-CH_2-$ ; 12 H), 1.59–1.38 (m;  $-(CH_2)_x$ ; 144 H) 0.94 (m;  $-CH_3$ ; 90 H).

#### 5.1.2. 2,3,6,7,10,11-Hexakis-[3,6,7,10,11-pentakis (pentyloxy)triphenylene-2-oxynonyloxycarbonylmethyleneoxy]-triphenylene **H2**

The reaction was carried out in an analogous way to the above procedure for **H1**; Yield: 428.8 mg (92.8 per cent). Elemental analysis:  $C_{342}H_{492}O_{54}$  ( $M_w = 5467.64$ ) required C: 75.12, H: 9.08; found C: 75.04, H: 9.11.  $^1H$  NMR: ( $CDCl_3$ , 400 MHz),  $\delta$  [ppm] = 7.81/7.79 (s/s; arom.; 42 H), 4.89 (s;  $-O-CH_2-CO-$ ; 12 H), 4.20 (m;  $-CO-O-CH_2-CH_2-$ ; 12 H and  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.93 (m;  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.65 (m;  $-CO-O-CH_2-CH_2-$ ; 12 H), 1.58–1.28 (m;  $-(CH_2)_x$ ; 180 H), 0.95 (m;  $-CH_3$ ; 90 H).

#### 5.1.3. 2,3,6,7,10,11-Hexakis-[3,6,7,10,11-pentakis (pentyloxy)triphenylene-2-oxundecyloxycarbonylmethyleneoxy]-triphenylene **H3**

The reaction was carried out in an analogous way to the above procedure for **H1**; Yield: 120.1 mg (90.3 per cent). Elemental analysis:  $C_{354}H_{516}O_{54}$  ( $M_w = 5635.96$ ) required C: 75.43, H: 9.23; found C: 75.52, H: 9.30,  $^1H$  NMR: ( $CDCl_3$ , 400 MHz),  $\delta$  [ppm] = 7.81/7.79 (s/s; arom.; 42 H), 4.89 (s;  $-O-CH_2-CO-$ ; 12 H), 4.20 (m;  $-CO-O-CH_2-CH_2-$ ; 12 H, and  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.93 (m;  $C_{ar}-O-CH_2-CH_2-$ ; 72 H), 1.64 (m;  $-CO-O-CH_2-CH_2-$ ; 12 H), 1.57–1.22 (m;  $-(CH_2)_x$ ; 204 H), 0.95 (m;  $-CH_3$ ; 90 H).

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