Selective ether cleavages: simple routes yielding di- and tri-functional hexaalkoxytriphenylenes

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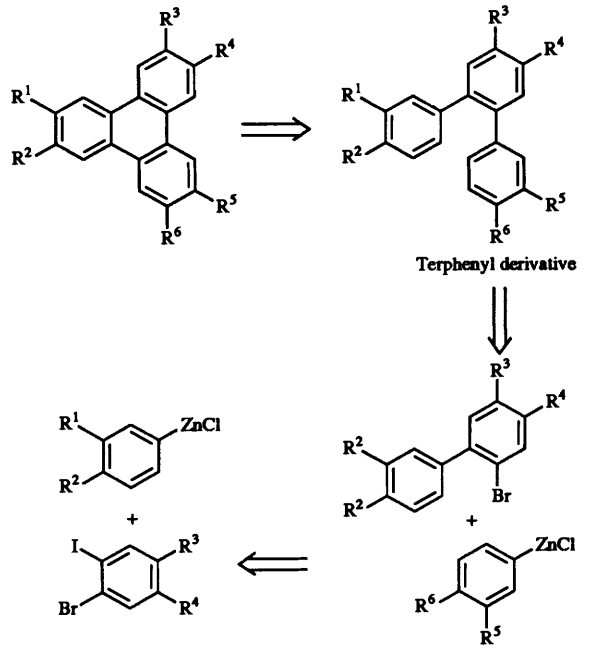
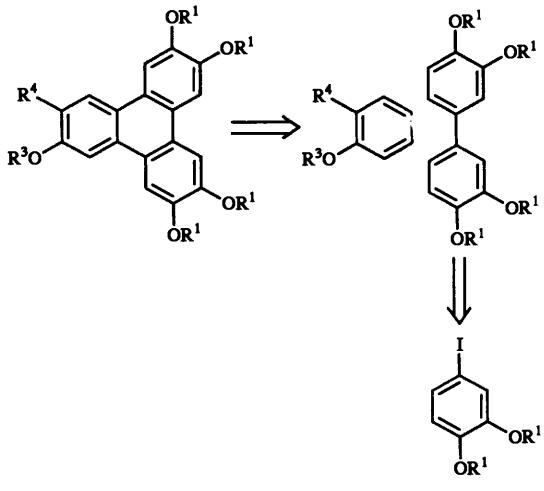
Discotic hexasubstituted triphenylene derivatives represent a promising class of materials, *e.g.* with respect to their photoconductive properties. To tailor the processibility and mesophase behaviour of such materials specifically functionalized cores as precursor molecules for discotic oligomers, polymers and networks or amphiphiles are required. The paper presents various synthetic strategies, all based on selective ether cleavage methods, leading to new highly functionalized triphenylenes.

2,3,6,7,10,11-Hexaalkoxytriphenylenes represent one of the most studied class of discotic liquid crystals. Derivatization of these highly symmetric molecules is necessary for varying the molecular architecture as well as for tailoring mesophase properties and processibility. The molecular engineering towards more advanced discotic triphenylenes started with the preparation of discotic main chain and side group polymers[1] thus leading to enhanced mesophase stabilities and mechanical properties. The synthesis of mono- and di-functional triphenylene monomers was achieved by statistical methods. Meanwhile discotic liquid crystals—in particular triphenylenes—have received increased attention due to the rapid charge migration along the columnar stacks[2] and the fabrication of nano-size materials by mono- and multi-layer techniques.[3,4] For the further elaboration of this novel class of materials new synthetic strategies are required for matching the demands of the more sophisticated investigations involving the tailoring of processible materials with defined mesophase and mechanical properties. In a first approach we reported[5] on the improved synthesis of monofunctional discotic triphenylenes as precursor molecules for oligomeric and polymeric discotics. The next step for the exploration of the potential usefulness of discotic columnar triphenylenes involves the preparation of highly functionalized triphenylene cores *e.g.* for the preparation of discotic columnar networks or polymerizable amphiphiles. Indeed different research groups are presently working on new synthetic routes[5–7] allowing the preparation of compounds that were until recently available only in poor yields or were even unavailable. Until now 2,3,6,7,10,11-hexaalkoxytriphenylenes have been synthesized by trimerization of an *o*-dialkoxybenzene derivative.[8] *Via* this route a statistical mixture of triphenylenes carrying at least two different alkoxy groups is available.[1,9] A limitation results from the reaction conditions that are incompatible with some interesting functionalities, *e.g.* hydroxyaryl groups, olefins, some crown ethers and other cationic complexants. A new strategy described by Borner and Jackson[6] passing through a terphenyl intermediate allows the preparation of highly functionalized triphenylene cores (Scheme 1). This sophisticated method is particularly useful for the preparation of triphenylene cores with less than six alkoxy groups. Similarly unsymmetrically substituted triphenylenes have been obtained using arylboronic acids.[10]

A simpler approach for functionalized triphenylenes (Scheme 2) has been recently described by Boden *et al.*[7] and Henderson *et al.*[5] This so called 'biphenyl route' allows the possibility of large scale preparation. However this reaction proceeds under the same conditions as the classical trimerization and thus



Scheme 1 Synthesis of triphenylene derivatives *via* the 'terphenyl route'



Scheme 2 Synthesis of triphenylene derivatives *via* the 'biphenyl route'

suffers from similar functional limitations. It is consequently necessary to introduce the desired groups at the last step. In the present paper we describe different methods of selective ether cleavage allowing the synthesis of triphenylenes carrying two or three different alkoxy groups with a definite regiochemistry. The triphenylene cores used as starting material are always simple compounds easily available either by the classical trimerization or by the 'biphenyl route'. In order to simplify the following discussion the pentyloxy groups will not be taken in account as 'functional groups'. Thus, for example, compounds **1** and **5** will be considered as difunctional triphenylenes and compounds **13a** and **17** as trifunctional cores.

Preparation of difunctional triphenylenes

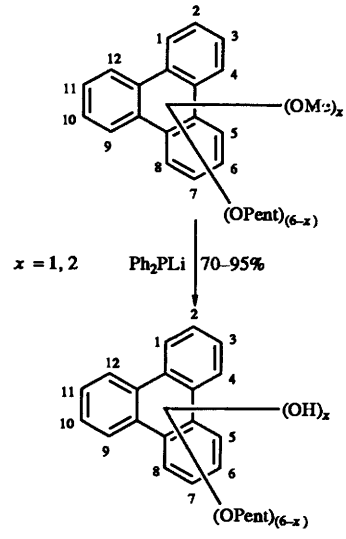
The ability of lithium diphenylphosphide (Ph_2PLi) to selectively cleave methyl, allyl and benzyl aryl ethers is well known from the literature.[11] It has been previously shown that the selectivity can be exploited to afford the 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (95%)[5] and the 2,7-dihydroxy-3,6,10,11-tetrahexyloxytriphenylene (yield not reported)[7] (Scheme 3).

By extending this procedure 2,6-dihydroxy-3,7,10,11-tetrapentyloxy-, 2,7-dihydroxy-3,6,10,11-tetrapentyloxy- and 2,11-dihydroxy-3,6,7,10-tetrapentyloxy-triphenylene have been prepared while 2,3-dihydroxy-6,7,10,11-tetrapentyloxytriphenylene has been isolated only in poor yield (~ 20%) probably due to the greater instability of the intermediate *ortho*-dianion and the lower reactivity of the second methoxy group. Indeed, the cleavage of the second methyl requires the use of a large excess of Ph_2PLi and is much slower than for the other isomers. As previously shown it is possible to take advantage of this behaviour to prepare a triphenylene carrying two different functional groups.[5]

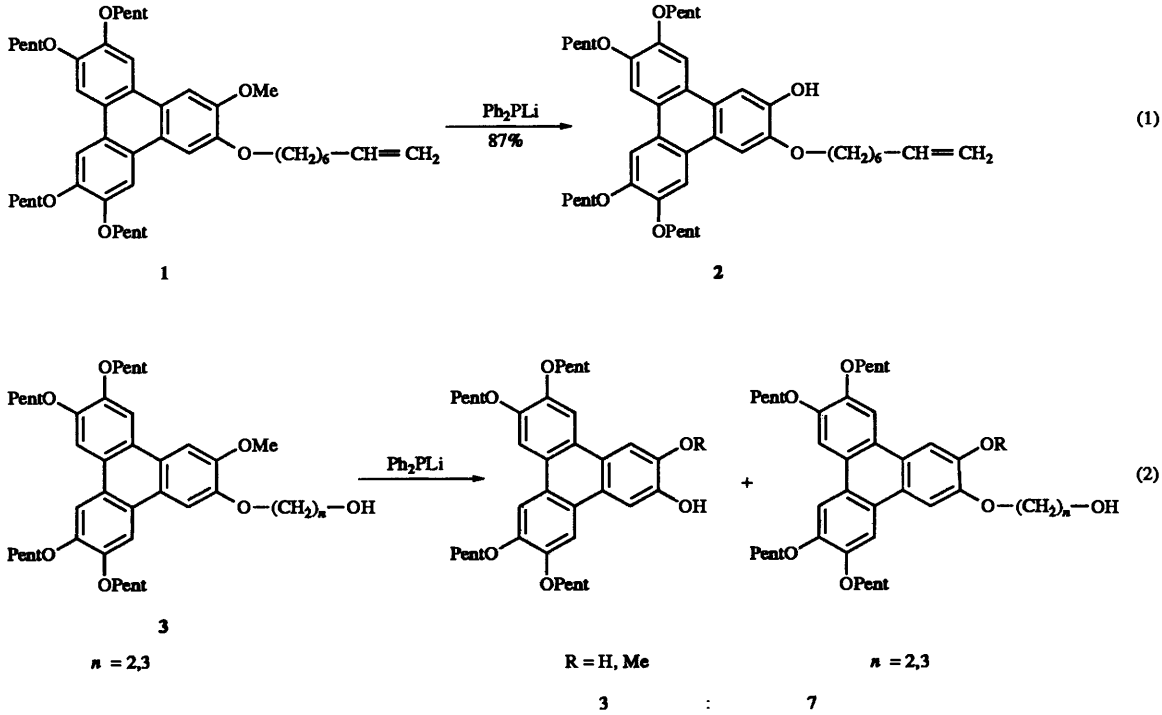
It is worthwhile reporting that the cleavage step is compatible with an olefinic group[5] [Scheme 4, eqn. (1)] while hydroxyalkyl chains are partially cleaved [Scheme 4, eqn. (2)].

Dihydroxytetrapentyloxytriphenylenes are key intermediates for the synthesis of polymerizable derivatives and amphiphiles which can also be polymerized to main chain polymers (*e.g.* polymalonates[4b]) (Scheme 5).

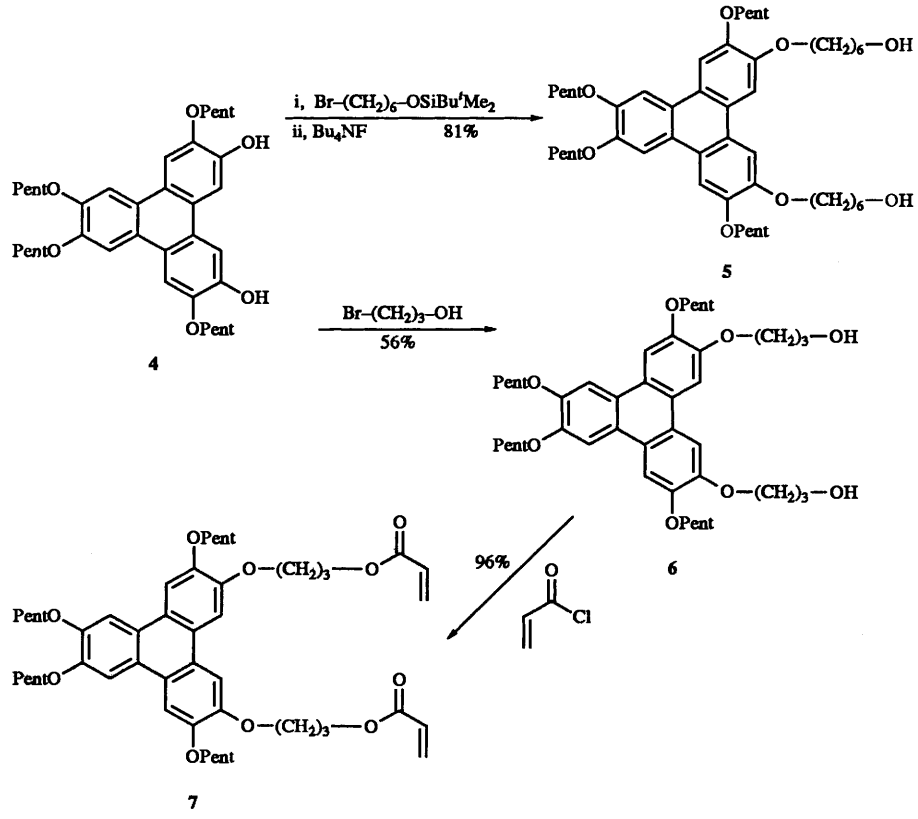
Since 2,3-dihydroxy-6,7,10,11-tetrapentyloxytriphenylene which is the target precursor molecule for the preparation of difunctionalized compounds carrying the same functionality in the 2,3 position, is not available by the described selective ether cleavage we followed a different approach. The biphenyl coupling with *o*-dihydroxybenzene does not yield the corresponding 2,3-dihydroxytriphenylene but one free phenolic group is tolerated by the reaction conditions providing the simplest approach for monofunctionalized derivatives. 2,3-Difunctionalized cores can be obtained starting from the 2-hydroxy-3-methoxy-6,7,10,11-tetrapentyloxytriphenylene **8** which is synthesized from tetrapentyloxybiphenyl and *o*-methoxyphenol (71% yield) according to the coupling conditions previously described.[5] It is possible to cleave the



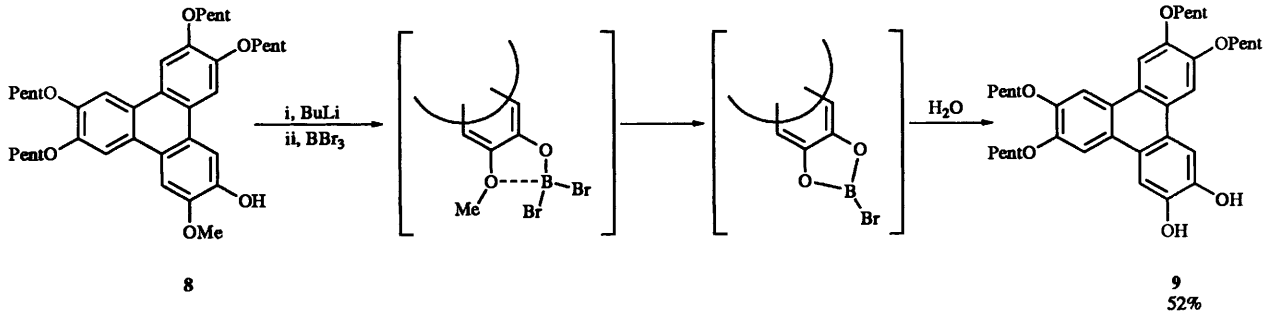
Scheme 3 Preparation of mono- and di-hydroxytriphenylene cores by selective methyl aryl ether cleavage



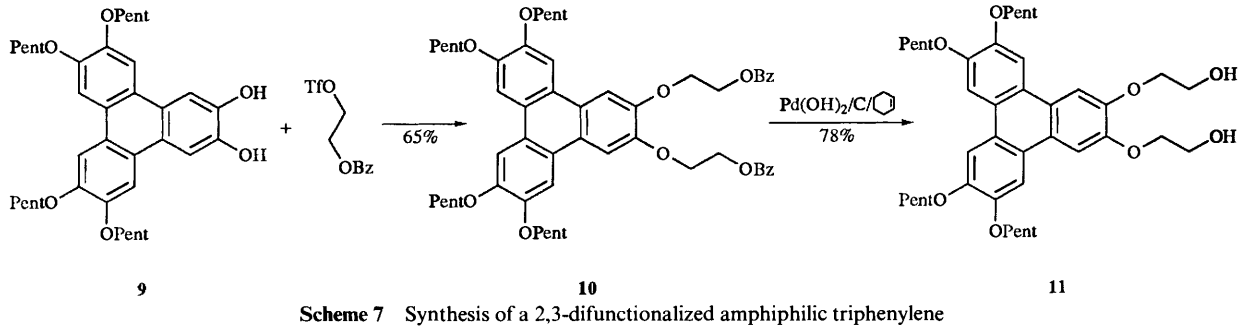
Scheme 4 Functional compatibility with the ether cleavage



Scheme 5 Synthesis of discoid polymerizable, **7**, or amphiphilic, **5**, **6**, triphenylenes



Scheme 6 Preparation of the 2,3-dihydroxy-6,7,10,11-tetrapentyloxytriphenylene by ether cleavage with intramolecular assistance



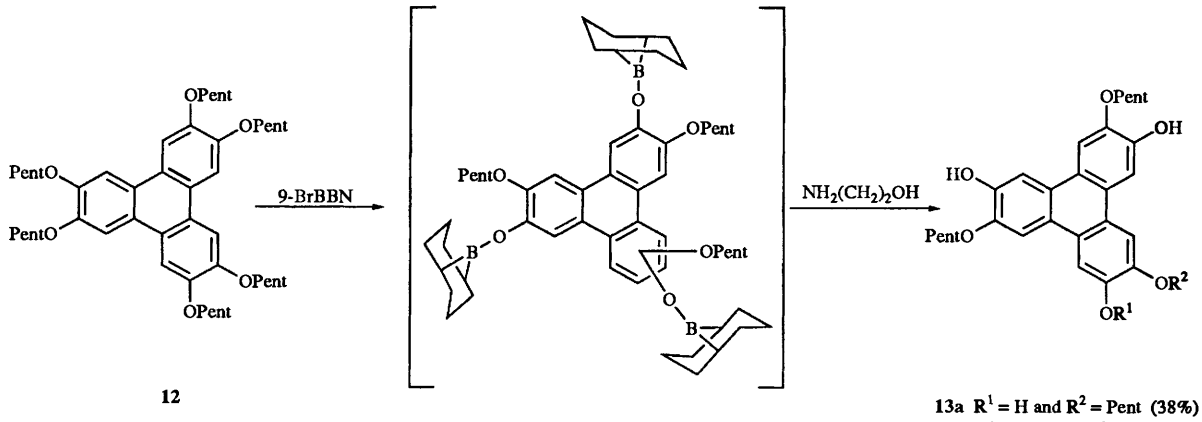
Scheme 7 Synthesis of a 2,3-difunctionalized amphiphilic triphenylene

methoxy group with BBr_3 by means of intramolecular assistance (Scheme 6).

Employing the same procedure starting from the 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene, the yield is sometimes reduced (39–51%). The 2,3-dihydroxy derivative **9** is unstable even at low temperature and has to be functionalized rapidly after isolation. We were interested in the preparation of the amphiphile **11**. However alkylation by 1,2-bromoethanol is too slow (75 °C, 24 h) and the dihydroxytriphenylene **9** undergoes degradation. The functionalization can be carried out by using a reactive trifluoromethanesulfonate (triflate) (Scheme 7).

Preparation of trifunctional triphenylenes

Triphenylenes carrying three polymerizable groups are of particular interest as cross-linkers for the synthesis of discotic elastomers and networks. They are more easily handled than the corresponding hexafunctional derivatives and the mesophase

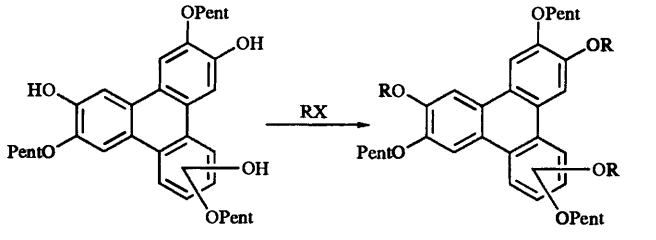


Scheme 8 Simple synthesis of trihydroxytripentyloxytriphenylenes

stability is less affected by the functionalization. For this reason we have developed a one step synthesis leading to trihydroxytripentyloxytriphenylenes starting from the easily available 2,3,6,7,10,11-hexapentyloxytriphenylene **12** (HPT).† Using a very bulky Lewis acid such as 9-bromo-9-borabicyclo[3.3.1]-nonane (9-BrBBN)[12] allows the cleavage of only one pentyl group per benzene ring (Scheme 8). The resulting symmetric (**13a**) and non-symmetric (**13b**) trihydroxytripentyloxytriphenylenes can be very easily separated by a simple single chromatography on silica gel. It has to be noted that the corresponding mixture of symmetric and non-symmetric trimethoxytripentyloxytriphenylenes immediately available by trimerization of *o*-pentyloxyanisole is extremely difficult to separate by chromatography.

9-BrBBN can also be used to provide mono- and di-functional derivatives by a statistical approach giving better yields than those previously described.[1] This procedure allows the reaction to be scaled up to kilogram amounts.

The two derivatives **13a** and **13b** can be converted by classical alkylations (Scheme 9) into different trifunctional derivatives



RX = MeI R = Me (86%) **14**
= Br-$(CH_2)_6$-HC=CH_2 R = $(CH_2)_6$HC=CH_2 (78%) **15**

Scheme 9 Synthesis of trifunctional triphenylenes

(cross-linkers for liquid crystalline networks, derivatives for phase behaviour studies, side-on amphiphiles).

The triolefin **15** can be used as cross-linker for the preparation of networks having a polysiloxane backbone.[13]

The following two examples illustrate how highly functionalized triphenylenes can be obtained by using either of the two ether cleavages. The C_3-symmetric trimethoxytripentoxytriphenylene **14a** is a useful precursor for the regiocontrolled synthesis of a highly functionalized cross-linker of interest for the preparation of discotic elastomers with permanent director orientation.[13] The addition of 2.5 equiv. of Ph_2PLi to **14a** yields a mixture of mono-, di- and tri-hydroxytriphenylenes in which the dihydroxy derivative is the major compound. When using a larger excess of Ph_2PLi, degradations are observed and the 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene is never isolated in good yield. The mixture of mono-, di- and trihydroxytriphenylenes is alkylated with the 8-bromooct-1-ene[14] and the resulting compounds are separated on silica gel (Scheme 10).

The last methoxy group of **17** is then cleaved by the same reagent (Ph_2PLi) to give the corresponding phenol **18**. The latter can be easily converted in two steps into the methacrylate **19** (Scheme 11). *Via* hydrosilylation to polysiloxane backbone it has been shown that the olefinic double bond reacts 70 times faster than the methacrylate thus giving a preformed elastomer which can be oriented by a mechanical field.[13] The slow reaction of the methacrylate fixes the network anisotropy providing monodomain samples.

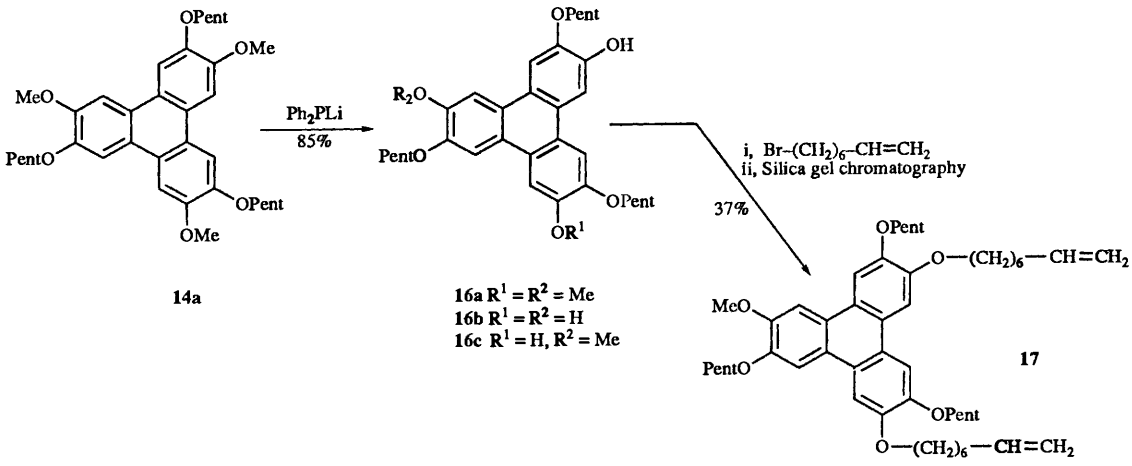
The regiocontrol provided by the above described synthesis is not always necessary and a shorter procedure yielding regioisomeric mixtures could be of interest. To achieve this goal, we have protected the hydroxy group of the 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene **20** by a bulky silyl group. This reaction furnishes a triphenylene core **21** on which the 9-BrBBN is able to cleave only two pentyl chains (no side-product resulting from triple cleavage has been observed) thus showing the principle of protection of a benzene ring by steric hindrance (Scheme 12).

The resulting dihydroxy derivatives **22a–d** could give a mixture of compounds **13a** and **13b** by simple desilylation but could also be used to prepare **18**. For the latter case a mixture of four regioisomers should be isolated however the three functional groups will always be distributed on the three different benzene rings. The advantage of the suggested synthesis is that the overall yield starting from the *o*-dipentyloxybenzene should be much higher than for the procedures presented in Schemes 8–11 even if the two regioisomers **13a** and **13b** (precursors of **14**) are used together. In addition compound **22a** can be easily separated from the other regioisomers during the column chromatography. This derivative could be used as precursor for the synthesis of a polymerizable amphiphile (Scheme 13).

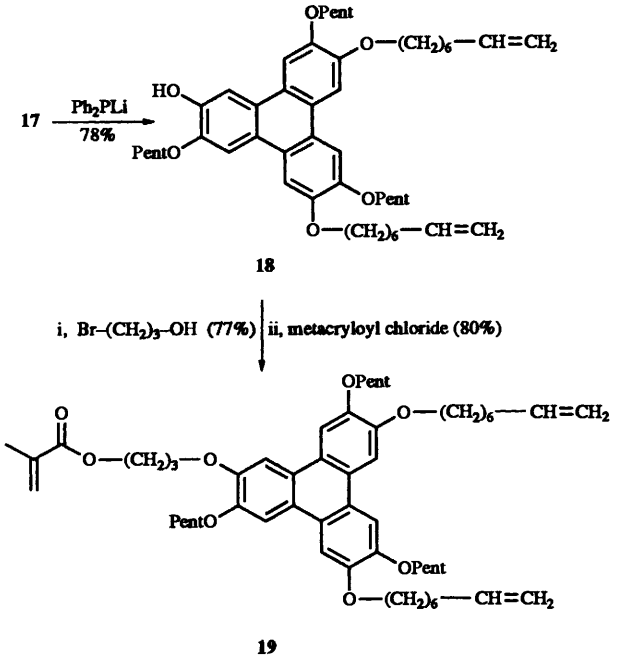
Conclusions

The present paper demonstrates the usefulness of different methods of selective ether cleavage to prepare a large series of highly functionalized triphenylenes starting from simple hexaalkoxy substituted cores. The compounds presented are all of potential interest for basic studies or for the preparation of

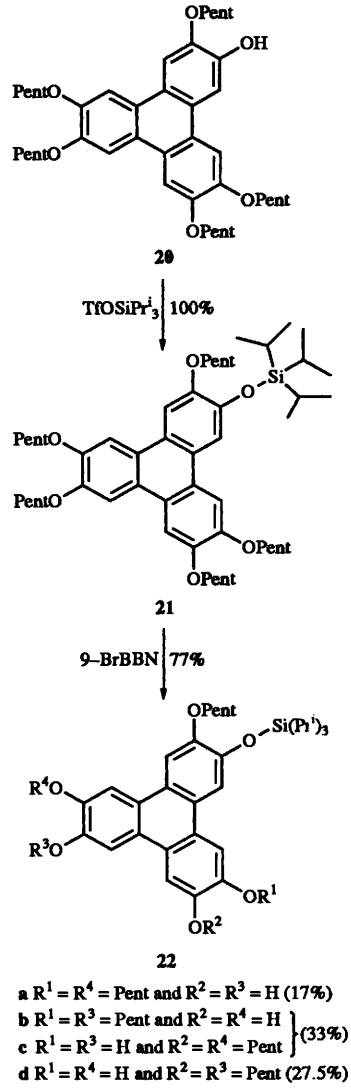
† HPT is synthesized by the same method and in the same yield as the hexahexyloxytriphenylene in ref. 7.



Scheme 10 Double functionalization of the symmetric derivative **14a** with Ph_2PLi as selective ether cleavage agent



Scheme 11 Preparation of a highly functionalized triphenylene core useful as a cross-linker for elastomer synthesis



Scheme 12 Double ether cleavages by steric protection of a single benzene ring

liquid crystalline polymers and networks. In addition we think that the developed strategies could be extended to other poly-aromatic systems, *e.g.* dibenzopyrenes or truxenes.

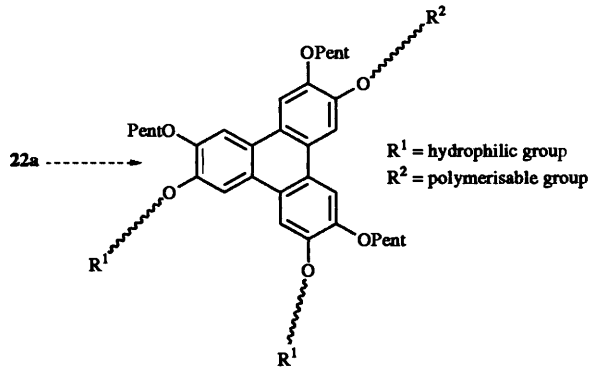
Experimental

Phase types and transitions were determined using polarizing microscopy and a DSC 7 (Perkin-Elmer) with heating and cooling rates of 10 K min^{-1}. ^1H NMR were recorded on a 200 MHz FT-NMR spectrometer AC-200 Bruker; *J* values are given in Hz. IR spectra were measured on an FT-IR 5 DXC Nicolet spectrometer. The mass spectrometer used was a Finnigan MAT 95.

Synthesis of 2,11-dihydroxy-3,6,7,10-tetrapentyloxytriphenylene 4

The dimethoxydipentyloxybiphenyl (mixture of 3 isomers) was prepared from *o*-pentyloxyanisole *via* iodination and Ullmann-coupling following the same procedure as for the synthesis of 3,3',4,4'-tetrapentyloxybiphenyl,[5] to give a mixture of isomers (77% on a 150 g scale), R_f 0.25 (CH_2Cl_2–light petroleum, 2:1) mp 74–82 °C (Found: C, 74.25; H, 8.9. $C_{24}H_{34}O_4$ requires C, 74.57; H, 8.87); δ_H(200 MHz; $CDCl_3$) 7.08–6.88 (6 H, m, ArH), 4.06 and 4.02 (4 H, 2 × t, *J* 6.6 and 6.8, OCH_2), 3.91 and 3.88 (6 H, 2 × s, OCH_3), 1.92–1.78 (4 H, m, OCH_2CH_2), 1.50–1.37 [8 H, m, $OCH_2CH_2(CH_2)_2$] and 0.92 [6 H, t, *J* 6.8, $O(CH_2)_4CH_3$]; *m/z* (EI) 387 (M^+, 100%).

2,11-Dimethoxy-3,6,7,10-triphenylene was prepared *via* the



Scheme 13 Possible preparation of a polymerizable amphiphile derived from triphenylene

'biphenyl route'[5] by coupling the dimethoxydipentyloxybiphenyl prepared above with dipentyloxybenzene. The 2,11-isomer was separated from the 2,6- and the 2,7-isomers by column chromatography (CH_2Cl_2–light petroleum, 2:1) R_f(2,11) 0.5, R_f(2,6 and 2,7) 0.7, at the 10 g scale: 9% of 2,11-isomer and 30% of 2,6- and 2,7-isomers. Data for the 2,11-isomer mp 106 °C; δ_H(400 MHz; $CDCl_3$) 7.82, 7.81 and 7.80 (6 H, 3 × s, ArH), 4.24 and 4.22 (8 H, 2 × t, *J* 6.8 and 6.5, OCH_2), 4.08 (6 H, s, OCH_3), 2.03–1.88 (8 H, m, OCH_2CH_2), 1.61–1.39 [16 H, m, $OCH_2CH_2(CH_2)_2$] and 0.96 [12 H, t, *J* 7.0, $O(CH_2)_4CH_3$]; *m/z* (EI) 632 (M^+, 100%).

The cleavage of the two methyl groups was achieved following the previously described method.[5,11] A mixture of 2,11-dimethoxy-3,6,7,10-triphenylene (1.60 g, 2.5 mmol) and BuLi (7.5 mmol, 3 equiv.) and diphenylphosphine (7.5 mmol, 3 equiv.) was refluxed until cleavage was completed (~ 1 h). The reaction was monitored by TLC [CH_2Cl_2–hexane, 3:2, R_f(reagent) 0.4, R_f(product) 0.2]. The reaction mixture was purified by silica gel chromatography to give the diphenol **4** (1.15 g, 75%), mp 142.5 °C; ν_{max}(KBr)/cm^{-1} 3540 and 3400 (free and bonded OH) and 2870 and 2950 (CH arom.); δ_H(400 MHz; $CDCl_3$) 7.92, 7.79 and 7.73 (6 H, 3 × s, ArH), 5.85 (2 H, s, OH), 4.26 and 4.21 (8 H, 2 × t, *J* 6.4 and 6.5, OCH_2), 2.05–1.85 (8 H, m, OCH_2CH_2), 1.61–1.39 [16 H, m, $OCH_2CH_2(CH_2)_2$] and 0.95 [12 H, t, *J* 7.0, $O(CH_2)_4CH_3$]; the structure was confirmed by NOE spectroscopy: ArH^{irrad} (7.92) ⟶ OH^{enh}, OH^{irrad} ⟶ ArH^{enh} (7.92) and OCH_2^{enh} (4.26), ArH^{irrad} (7.79) ⟶ ArH^{enh} (7.73) and OCH_2^{enh} (4.21), ArH^{irrad} (7.73) ⟶ ArH^{enh} (7.79) and OCH_2^{enh} (4.26); *m/z* (EI) 604 (M^+, 17%) and 57 (100, $Butyl^+$).

Synthesis of the 2,6- and 2,7-dihydroxytetrapentyloxytriphenylenes

A mixture of 2,6- and 2,7-dimethoxytetrapentyloxytriphenylenes was submitted to the same ether cleavage conditions as for the 2,11-isomer. The two products (83% global yield) were separated by silica gel chromatography (CH_2Cl_2–hexane, 3:2) to give the 2,6-isomer (0.73 g, 14%), R_f (CH_2Cl_2–hexane, 4:1) 0.65; mp 82.5 °C and the 2,7-isomer (3.51 g, 66%), R_f (CH_2Cl_2–hexane, 4:1) 0.56, mp 180 °C; δ_H(200 and 400 MHz) and *m/z* (EI) in agreement with the suggested structures.

Synthesis of amphiphiles 2,11-bis(6-hydroxyhexyloxy)-3,6,7,10-tetrapentyloxytriphenylene 5 and 2,11-bis(3-hydroxypropoxy)-3,6,7,10-tetrapentyloxytriphenylene 6

Alkylation was performed following the previously described procedure.[14] Both non protected and silicon protected ω-bromo alcohols can be used for the alkylation step but the protected one allows a longer reflux time, sometimes necessary to complete the reaction, without increasing the risk of polyether formation. The reactions were monitored by TLC. The mixtures were then extracted with CH_2Cl_2 and dried over $MgSO_4$. The crude disilylated intermediate was dissolved in THF (to give a solution of 0.05 mol dm^{-3}) and Bu_4NF (2 equiv. per silyl group) was added. The reaction was heated for 2 h at 50 °C. CH_2Cl_2 was then added and the mixture was washed with water. The organic phase was dried over $MgSO_4$. The crude amphiphiles **5** and **6** were purified by silica gel chromatography.

For **5**, eluent: CH_2Cl_2–AcOEt, 3:2, R_f 0.3 gives pure compound **5** (105 mg, 81% from 95 mg of **4**); phase behaviour: *c* 65 °C (D_h 55 °C) *i* (Found: C, 74.4; H, 9.5. $C_{50}H_{76}O_8$ requires C, 74.59; H, 9.5%); δ_H(200 MHz; $CDCl_3$) 7.81 (6 H, s, ArH), 4.21 (12 H, t, *J* 6.6, $ArOCH_2$), 3.67 (4 H, t, *J* 5.8, CH_2OH), 2.05–1.85 (12 H, m, OCH_2CH_2), 1.70–1.30 [28 H, m, $OCH_2CH_2(CH_2)_{[2\ or\ 3]}$] and 0.95 (12 H, t, *J* 7.0, CH_3); *m/z* (FD) 806 ($[M + 1]^+$, 100%).

For **6**, eluent: CH_2Cl_2–AcOEt, 1:1, R_f 0.35 gives pure compound **6** (0.84 g, 56% from 1.26 g of **4**); phase behaviour: *c* 87 °C D_1 99 °C D_2 118 °C *i*; δ_H(200 MHz; $CDCl_3$) 7.83, 7.81 and 7.78 (6 H, 3 × s, ArH), 4.42 [4 H, t, *J* 5.7, $OCH_2(CH_2)_2OH$], 4.22 and 4.21 (8 H, 2 × t, *J* 6.5 and 6.7, OCH_2Bu), 3.96 (4 H, t, *J* 5.2, CH_2OH), 2.24–2.15 (4 H, m, $OCH_2CH_2CH_2OH$), 1.98–1.85 (8 H, m, OCH_2CH_2Pr), 1.63–1.37 [16 H, m, $OCH_2CH_2(CH_2)_2$] and 0.96 (12 H, t, *J* 6.9, CH_3); *m/z* (FD) 721 ($[M + 1]^+$, 100%).

Synthesis of 2,11-bis[3-(acryloyloxy)propoxy]-3,6,7,10-tetrapentyloxytriphenylene 7

Compound **6** (0.75 g, 1.04 mmol), diisopropylethylamine (0.544 cm^3, 3.12 mmol), acryloyl chloride (0.28 g, 3.12 mmol) and 2,6-di-*tert*-butyl-*p*-cresol (70 mg, 0.32 mmol) were added at 0 °C under argon to CH_2Cl_2 (20 cm^3). The reaction was stirred for 2 h at room temperature and then washed with K_2CO_3. The organic phase was dried over $MgSO_4$. The crude diacrylate was purified by silica gel chromatography (CH_2Cl_2–AcOEt, 150:1) to give pure diacrylate **7** (0.83 g, 96%), R_f(CH_2Cl_2–AcOEt, 100:1) 0.5; mp 86 °C (Found: C, 72.5; H, 8.3. $C_{50}H_{68}O_{10}$ requires C, 72.43; H, 8.26%); δ_H(200 MHz; $CDCl_3$) 7.85 and 7.82 (6 H, 2 × s, ArH), 6.43 (2 H, dd, J_{trans} 17.1, J_{gem} 1.5, $COCH{=}CH_2$), 6.13 (2 H, dd, J_{cis} 10.2, J_{trans} 17.2, $COCH{=}CH_2$), 5.82 (2 H, dd, J_{cis} 10.3, J_{gem} 1.6, $COCH{=}CH_2$), 4.48 [4 H, t, *J* 6.4, $OCH_2(CH_2)_2OCO$], 4.33 [4 H, t, *J* 6.2, $O(CH_2)_2CH_2OCO$], 4.22 and 4.21 (8 H, 2 × t, *J* 6.5 and 6.6, OCH_2Bu), 2.33–2.27 (4 H, m, $OCH_2CH_2CH_2OCO$), 2.01–1.87 (8 H, m, OCH_2CH_2Pr), 1.59–1.39 [16 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (12 H, t, *J* 7.0, CH_3); *m/z* (FD) 830 ($[M + 1]^+$, 100%).

Synthesis of 2,3-dihydroxy-6,7,10,11-tetrapentyloxytriphenylene 9

Butyllithium (1.5 mol dm^{-3} in hexane; 0.26 cm^3, 0.39 mmol) was added at −78 °C and under argon to a solution of compound **8** (0.24 g, 0.39 mmol) CH_2Cl_2 (10 cm^3). BBr_3 (0.43 cm^3, 0.39 mmol) was then added to the mixture at −78 °C. The mixture was stirred for 90 min at room temperature and then the reaction was quenched with water and again stirred for 30 min. The mixture was extracted with CH_2Cl_2 and the organic solution was dried over $MgSO_4$ to afford the crude diphenol **9** which was purified by silica gel chromatography (CH_2Cl_2–AcOEt, 1:0 then 19:1) to give the pure compound (122 mg, 52%) as a white solid which cannot be stored, R_f(CH_2Cl_2) 0.1; mp 130 °C; δ_H(200 MHz; $CDCl_3$) 7.87, 7.78 and 7.75 (6 H, 3 × s, ArH), 5.66 (2 H, s, OH), 4.20 and 4.15 (8 H, 2 × t, *J* 6.6 and 6.6, OCH_2), 2.05–1.85 (8 H, m, OCH_2CH_2), 1.65–1.35 [16 H, m, $O(CH_2)_2(CH_2)_2$] and 0.93 and 0.94 (12 H, 2 × t, *J* 7.0 and 7.0, CH_3); *m/z* (EI) 604 (M^+, 100%).

Synthesis of 2,3-bis(2-benzyloxyethoxy)-6,7,10,11-tetrapentyloxytriphenylene 10

Compound **9** (0.100 g, 0.17 mmol) and pentan-2-one (4 cm^3) were introduced into a two necked flask equipped with a reflux condenser under argon. After complete dissolution, K_2CO_3 (0.9 g, 6.6 mmol) and benzyloxyethyl trifluoromethanesulfonate (0.141 g. 0.5 mmol) were added and the reaction was heated at 75 °C for 1 h. The reaction was monitored by TLC. The reaction mixture was extracted with CH_2Cl_2 and the organic solution was dried over $MgSO_4$ to afford the crude dibenzyl derivative **10** which was purified by silica gel chromatography (CH_2Cl_2–hexane, 3:2 then 4:1) to give the pure product (93 mg, 65%), R_f(CH_2Cl_2) 0.44; phase behaviour: *c* 71.5 °C (D_h 62 °C) *i* (Found: C, 77.2; H, 8.4. $C_{56}H_{72}O_8$ requires C, 77.03; H, 8.31%); δ_H(200 MHz; $CDCl_3$) 7.92, 7.81 and 7.79 (6 H, 3 × s, triph ArH), 7.50–7.20 (10 H, m, benz ArH), 4.66 (4 H, s, OCH_2Ph), 4.42 (4 H, t, *J* 4.7, $OCH_2CH_2OCH_2Ph$), 4.21 and 4.16 (8 H, 2 × t, *J* 6.6 and 6.6, OCH_2Bu), 3.93 (4 H, t, *J* 5.0, $OCH_2CH_2OCH_2Ph$), 2.00–1.85 (8 H, m, OCH_2CH_2Pr), 1.65–1.35 [16 H, m, $O(CH_2)_2(CH_2)_2$] and 0.95 (12 H, t, *J* 7.1, CH_3); *m/z* (FD) 873 (M^+, 100%).

Synthesis of 2,3-bis(2-hydroxyethoxy)-6,7,10,11-tetrapentyloxytriphenylene 11[15]

Compound **10** (80 mg, 0.092 mmol) and cyclohexene (1 cm^3) were introduced into a two necked flask equipped with a reflux condenser and flushed with argon. After complete dissolution, ethanol (2 cm^3) and $Pd(OH)_2/C$ (20%; 10 mg) were added and the reaction was heated at 75 °C for ~4 h. The reaction was monitored by TLC. The reaction was then diluted with CH_2Cl_2 and filtered through Celite. Purification by silica gel chromatography (CH_2Cl_2–AcOEt, 1:1 then 0:1) gave amphiphile **11** (49 mg, 78%), R_f(AcOEt) 0.65; phase behaviour: *c* 128 °C D_h 139 °C *i* (Found: C, 72.4; H, 8.8. $C_{42}H_{60}O_8$ requires C, 72.80; H, 8.73%); δ_H(200 MHz; $CDCl_3$) 7.82, 7.76 and 7.70 (6 H, 3 × s, ArH), 4.30 (4 H, t, *J* 4.1, OCH_2CH_2OH), 4.21 and 4.16 (8 H, 2 × t, *J* 6.6 and 6.6, OCH_2Bu), 4.04 (4 H, br s, OCH_2CH_2OH), 3.68 (2 H, br s, OH), 2.00–1.85 (8 H, m, OCH_2CH_2Pr), 1.65–1.35 [16 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (12 H, t, *J* 7.0, CH_3); *m/z* (EI) 693 (M^+, 100%).

Synthesis of 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene 13a and 2,6,11-trihydroxy-3,7,10-tripentyloxytriphenylene 13b

2,3,6,7,10,11-Hexapentyloxytriphenylene **12** (0.300 g, 0.4 mmol), CH_2Cl_2 (3 cm^3) and 9-bromo-9-borabicyclo[3.3.1]nonane (9-BrBBN) (1 mol dm^{-3} in CH_2Cl_2; 1.81 cm^3, 1.8 mmol, 4.5 equiv.) were introduced into a flask under argon. The reaction mixture was stirred for 30 h at room temperature and then slowly quenched by the addition of 2-aminoethanol (0.11 cm^3, 1.8 mmol). Water was added to the mixture which was then extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and purified by silica gel chromatography (CH_2Cl_2–hexane, 3:2 then 1:0) to give pure compounds **13a** (81 mg, 38%) and **13b** (101 mg, 47%).

Compound **13a**, R_f(CH_2Cl_2–hexane 3:2) 0.51; mp 140 °C; ν_{max}(KBr)/cm^{-1} 3540 and 3450 (free and bonded OH) and 2870, 2950 and 2970 (CH arom.); δ_H(200 MHz; $CDCl_3$) 7.90 and 7.77 (6 H, 2 × s, ArH), 5.88 (3 H, s, OH), 4.24 (6 H, t, *J* 6.6, OCH_2), 2.05–1.85 (6 H, m, OCH_2CH_2), 1.65–1.35 [12 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (9 H, t, *J* 6.9, CH_3); *m/z* (EI) 534 (M^+, 100%).

Compound **13b**, R_f(CH_2Cl_2–hexane 3:2) 0.16; mp 146 °C; δ_H(200 MHz; $CDCl_3$) 7.91, 7.90, 7.76, 7.70 and 7.69 (6 H, 5 × s, ArH), 5.87, 5.85 and 5.84 (3 H, 3 × s, OH), 4.26 and 4.23 (6 H, t, *J* 6.3 and 5.3, OCH_2), 2.05–1.80 (6 H, m, OCH_2CH_2), 1.65–1.35 [12 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (9 H, t, *J* 7.0, CH_3); *m/z* (EI) 534 (M^+, 100%).

Statistic preparation of mono- and di-functional triphenylenes by means of 9-BrBBN

Compound **12** (1.1 kg, 1.48 mol), CH_2Cl_2 (3 dm^3) and 9-BrBBN (1 mol dm^{-3} in CH_2Cl_2; 1.67 dm^3, 1.67 mol, 1.13 equiv.) were introduced into a flask under argon. The reaction was stirred for 30 h at room temperature. The solvent was then distilled off and acetic anhydride (2.5 dm^3) and concentrated H_2SO_4 (10 cm^3) were added to the residue. The mixture was heated for 15 min at 120 °C and then ice (5 dm^3) was introduced into the flask. The mixture was stirred for 30 min and then filtered and the residue was washed with water and methanol and purified by preparative HPLC (Zorbax PRO 10-Silica gel, spherical, 10 m, 300 × 440 mm, hexane–AcOEt, 97:3, 70 dm^3 h^{-1}, 20–25 bar, 280 nm) to give unchanged compound **12** (283 g, 26%), monoacetoxypentapentyloxytriphenylene (434 g, 39%) and diacetyloxytetrapentyloxytriphenylene (110 g, 10%). When working with 2.5 equiv. of 9-BrBBN monoacetoxypentapentyloxytriphenylene (20%), diacetoxytetrapentyloxytriphenylene (30%) and triacetoxytripentyloxytriphenylene (5%) were isolated. For analytical data see ref. 1.

Preparation of the trimethoxytripentyloxytriphenylenes 14a and 14b

Compound **13a** was alkylated following the previously reported method.[14] The residue was purified by silica gel chromatography (CH_2Cl_2–hexane, 3:2) to give pure compound **14a** (88 mg, 86%). Compound **13b** has been alkylated by the same procedure.

Compound **14a**, R_f(CH_2Cl_2) 0.50; mp 146 °C (Found: C, 75.0; H, 8.3. $C_{36}H_{48}O_6$ requires C, 74.97; H, 8.39%); δ_H(200 MHz; $CDCl_3$) 7.82 and 7.79 (6 H, 2 × s, ArH), 4.24 (6 H, t, *J* 6.8, OCH_2), 4.09 (9 H, s, OCH_3), 2.05–1.88 (6 H, m, OCH_2CH_2), 1.65–1.35 [12 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (9 H, t, *J* 7.0, CH_3).

Compound **14b** (non symmetric isomer), R_f(CH_2Cl_2) 0.4; mp 118 °C; ν_{max}(KBr)/cm^{-1} 2870, 2950 and 2970 (CH arom.); δ_H(200 MHz; $CDCl_3$) 7.83–7.78 (6 H, m, ArH), 4.24 (6 H, t, *J* 6.8, OCH_2), 4.09 (9 H, s, OCH_3), 2.05–1.88 (6 H, m, OCH_2CH_2), 1.65–1.35 [12 H, m, $O(CH_2)_2(CH_2)_2$] and 0.96 (9 H, t, *J* 7.0, CH_3); *m/z* (EI) 576 (M^+, 100%).

Preparation of non symmetric 2,6,11-tris[(oct-7-en-1-yl)-oxy]tripentyloxytriphenylene 15

Compound **13b** was alkylated by the previously reported method.[14] The residue was purified by silica gel chromatography (CH_2Cl_2–hexane, 1:2 then 1:1) to give pure non symmetric compound **15** (70 mg, 78%), R_f(CH_2Cl_2–hexane, 1:1) 0.5; phase behaviour: *c* 29 °C D_h 47 °C (Found: C, 79.0; H, 9.4. $C_{57}H_{84}O_6$ requires C, 79.12; H, 9.78%; δ_H(200 MHz; $CDCl_3$) 7.81 (6 H, s, ArH), 5.81 (3 H, tdd, J_{trans} 17.0, J_{cis} 10.2 and *J* 6.6, CH_2CH=CH_2), 4.99 (3 H, d, J_{trans} 17.0, CH_2CH=CH_2), 4.93 (3 H, d, J_{cis} 9.6, CH_2CH=CH_2), 4.21 (12 H, t, *J* 6.5, OCH_2), 2.05–1.82 (18 H, m, CH_2CH=CH_2 and OCH_2CH_2), 1.65–1.35 [30 H, m, $O(CH_2)_2(CH_2)_{[2\ or\ 3]}$] and 0.95 (9 H, t, *J* 7.0, CH_3); *m/z* (EI) 866 (M^+, 100%).

Preparation of a mixture of triphenylenes 16a, 16b and 16c

The cleavage of the methyl groups was achieved following the previously described method.[5,11] Starting with compound **14a** (0.88 g, 3.83 mmol), BuLi (2.5 equiv.) and diphenylphosphine (2.5 equiv.), the cleavage was achieved by refluxing the mixture for 30 min. The reaction was monitored by TLC. The crude reaction mixture was purified by silica gel chromatography. Only the fractions containing compound **16c** were collected

(CH_2Cl_2–hexane, 3:2) to give a **16c** enriched mixture (714 mg, ~85%), $R_f(CH_2Cl_2)$ **16a** 0.57, **16b** 0.69 and **16c** 0.63; δ_H(**16c**, 200 MHz; $CDCl_3$) 7.92, 7.81, 7.78, 7.75 and 7.74 (6 H, 5 × s, ArH), 5.90 (1.4 H, br s, OH), 4.27 and 4.24 (6 H, 2 × t, *J* 7.1 and 5.4, OCH_2), 4.08 (3 H, s, OCH_3), 2.05–1.85 (6 H, m, OCH_2CH_2), 1.65–1.35 [12 H, m, $OCH_2CH_2(CH_2)_2$] and 0.97 and 0.96 [9 H, 2 × t, *J* 6.9 and 6.9, $O(CH_2)_4CH_3$], *m/z* (**16c**, EI) 548 (M^+, 100%).

Synthesis of 2-methoxy-6,10-bis[(oct-7-en-1-yl)oxy]-3,7,11-tripentyloxytriphenylene 17

A mixture of compounds **16a**, **16b** and **16c** was alkylated following the previously reported method.[14] The residue was purified by silica gel chromatography (CH_2Cl_2–hexane, 1:1) to give pure compound **17** (370 mg, 37%), R_f(**17**) 0.72, R_f(mono-olefin) 0.62, R_f(triolefin) 0.80; mp 50 °C (Found: C, 78.0; H, 9.4. $C_{50}H_{72}O_6$ requires C, 78.08; H, 9.44%); ν_{max}(KBr)/cm^{-1} 2850 and 2950 (CH arom., olefin); δ_H(200 MHz; $CDCl_3$) 7.85–7.75 (6 H, m, ArH), 5.81 (2 H, tdd, J_{trans} 17.0, J_{cis} 10.2 and *J* 6.5, $CH_2CH{=}CH_2$), 4.98 (2 H, d, J_{trans} 17.0, $CH_2CH{=}CH_2$), 4.92 (2 H, d, J_{cis} 10.2, $CH_2CH{=}CH_2$), 4.24 and 4.21 (10 H, 2 × t, *J* 6.4, OCH_2), 4.08 (3 H, s, OCH_3), 2.15–1.85 (14 H, m, $CH_2CH{=}CH_2$ and OCH_2CH_2), 1.65–1.35 [24 H, m, $O(CH_2)_2(CH_2)_{[2\text{ or }3]}$] and 0.95 (9 H, t, *J* 7.0, CH_3); *m/z* (EI) 768 (M^+, 100%).

Synthesis of 2-hydroxy-6,10-bis[(oct-7-en-1-yl)oxy]-3,7,11-tripentyloxytriphenylene 18

The cleavage of the methyl group was achieved following the previously described method.[11] Starting with compound **17** (0.388 g, 0.5 mmol), BuLi (1.4 equiv.) and diphenylphosphine (1.4 equiv.), the cleavage was completed by refluxing the mixture 1 h. The reaction was monitored by TLC [Aluminiumoxid 60 F_{254} type E, CH_2Cl_2–hexane, 3:2, R_f(**17**) 0.3, R_f(**18**) 0.0]. The residue was purified by silica gel chromatography (CH_2Cl_2–hexane, 3:2, R_f 0.4) to give the title compound (297 mg, 78%), mp 58 °C; ν_{max}(KBr)/cm^{-1} 3550 (free OH), 3450 (bonded OH) and 2850 and 2950 (CH arom., olefin); δ_H(200 MHz; $CDCl_3$) 7.94, 7.81, 7.80 and 7.75 (6 H, 4 × s, ArH), 5.89 (1 H, s, OH), 5.81 (2 H, tdd, J_{trans} 17.0, J_{cis} 10.2 and *J* 6.6, $CH_2CH{=}CH_2$), 4.99 (2 H, d, J_{trans} 17.0, $CH_2CH{=}CH_2$), 4.93 (2 H, d, J_{cis} 10.0, $CH_2CH{=}CH_2$), 4.32–4.14 (10 H, m, OCH_2), 2.15–1.82 (14 H, m, $CH_2CH{=}CH_2$ and OCH_2CH_2) and 1.68–1.35 [24 H, m, $O(CH_2)_2(CH_2)_{[2\text{ or }3]}$], 0.96 (9 H, t, *J* 7.0, CH_3); *m/z* (EI) 754 (M^+, 100%).

Synthesis of 2-[3-(methacryloyloxy)propoxy]-6,10-bis-[(oct-7-en-1-yl)oxy]-3,7,11-tripentyloxytriphenylene 19

First, compound **18** was alkylated following the previously reported method.[14] The residue was purified by silica gel chromatography (CH_2Cl_2–AcOEt, 1:0 then 19:1) to give the pure intermediate (239 mg, 77%), R_f(CH_2Cl_2–AcOEt, 19:1) 0.65; mp 76.5 °C; ν_{max}(KBr)/cm^{-1} 3400 (OH) and 2850 and 2940 (CH arom., olefin); δ_H(200 MHz; $CDCl_3$) 7.81 and 7.78 (6 H, 2 × s, ArH), 5.81 (2 H, tdd, J_{trans} 17.0, J_{cis} 10.2 and *J* 6.6, $CH_2CH{=}CH_2$), 4.99 (2 H, d, J_{trans} 17.3, $CH_2CH{=}CH_2$), 4.93 (2 H, d, J_{cis} 10.3, $CH_2CH{=}CH_2$), 4.42 [2 H, t, *J* 5.7, $OCH_2(CH_2)_2OH$], 4.21 [10 H, t, *J* 6.3, $OCH_2(CH_2)_{[3\text{ or }5]}$], 3.96 (2 H, dt, *J* 5.7 and 5.7, CH_2OH), 2.90 (1 H, s, OH), 2.25–1.87 [16 H, m, $OCH_2CH_2CH_2OH$, $CH_2CH{=}CH_2$ and $OCH_2CH_2(CH_2)_{[2\text{ or }4]}$], 1.68–1.35 [24 H, m, $O(CH_2)_2(CH_2)_{[2\text{ or }3]}$] and 0.96 (9 H, t, *J* 6.9, CH_3); *m/z* (EI) 812 (M^+, 100%). This intermediate was acylated to provide **19** (see second step).

Secondly, the intermediate triphenylene derivative (194 mg, 0.24 mmol), diisopropylethylamine (0.22 cm^3, 1.25 mmol), acryloyl chloride (0.12 cm^3, 1.25 mmol) and 2,6-di-*tert*-butyl-*p*-cresol (50 mg, 0.23 mmol) were added at 0 °C and under argon to CH_2Cl_2 (2.5 cm^3). The reaction was stirred 4 h at room temperature and then washed with aqueous K_2CO_3. The organic phase was dried over $MgSO_4$. The crude diacrylate was purified by silica gel chromatography (CH_2Cl_2–hexane 3:2 then 1:0) to give pure compound **19** (169 mg, 80%), $R_f(CH_2Cl_2)$ 0.65; phase behaviour: *c* 51 °C (D_h 43 °C) *i* (Found: C, 76.2; H, 9.1. $C_{56}H_{80}O_8$ requires C, 76.33; H, 9.15%); ν_{max}(KBr)/cm^{-1} 2860 and 2950 (CH arom., olefin) and 1725 (CO); δ_H(200 MHz; $CDCl_3$) 7.84 and 7.81 (6 H, 2 × s, ArH), 6.11 [1 H, s, $OCOC(CH_3){=}CH_2$], 5.81 (2 H, tdd, J_{trans} 17.0, J_{cis} 10.2 and *J* 6.6, $CH_2CH{=}CH_2$), 5.54 [1 H, s, $OCOC(CH_3){=}CH_2$], 4.99 (2 H, d, J_{trans} 15.5, $CH_2CH{=}CH_2$), 4.93 (2 H, d, J_{cis} 9.5, $CH_2CH{=}CH_2$), 4.45 [2 H, t, *J* 6.3, $OCH_2(CH_2)_2OCO$], 4.32 (2 H, t, *J* 6.2, CH_2OCO), 4.21 [10 H, t, *J* 6.5, $OCH_2(CH_2)_{[3\text{ or }5]}$], 2.38–2.22 (2 H, m, $OCH_2CH_2CH_2O$), 2.15–1.85 [17 H, m, $OCOC(CH_3){=}CH_2$, $CH_2CH{=}CH_2$ and $OCH_2CH_2(CH_2)_{[2\text{ or }4]}$], 1.68–1.35 [24 H, m, $O(CH_2)_2(CH_2)_{[2\text{ or }3]}$] and 0.95 (9 H, t, *J* 7.0, CH_2CH_3); *m/z* (EI) 881 (M^+, 100%).

Synthesis of 2-(triisopropylsilyloxy)-3,6,7,10,11-pentapentyloxytriphenylene 21

Compound **20** (0.5 g, 0.74 mmol), diisopropylethylamine (0.16 cm^3, 0.89 mmol) and triisopropylsilyl trifluoromethanesulfonate (0.26 cm^3, 0.96 mmol) were added under argon to CH_2Cl_2 (5 cm^3). The reaction mixture was stirred for 1 h at room temperature and then washed with water. The organic phase was dried over $MgSO_4$. The crude product was purified by silica gel chromatography (CH_2Cl_2–hexane, 1:2 then 1:1) to give pure compound **21** (0.615 g, 100%), R_f(CH_2Cl_2–hexane, 1:2) 0.27; mp 40 °C; ν_{max}(KBr)/cm^{-1} 2860 and 2950 (CH arom.); δ_H(200 MHz; $CDCl_3$) 7.87, 7.80 and 7.74 (6 H, 3 × s, ArH), 4.28–4.12 (10 H, m, OCH_2), 2.03–1.83 (10 H, m, OCH_2CH_2), 1.65–1.25 {23 H, m, $O(CH_2)_2(CH_2)_2$ and $Si[CH(CH_3)_2]_3$}, 1.16 {18 H, d, *J* 6.8, $Si[CH(CH_3)_2]_3$} and 1.35–0.70 [33 H (including the doublet at 1.16), m, CH_2CH_3]; *m/z* (EI) 831 ($[M + 1]^+$, 100%).

Synthesis of dihydroxy-triisopropylsilyloxytripentyloxytriphenylenes 22a, 22b, 22c and 22d

Compound **21** (0.5 g, 0.6 mmol), CH_2Cl_2 (5 cm^3) and 9-BrBBN (1 mol dm^{-3} in CH_2Cl_2; 1.5 cm^3, 1.5 mmol, 2.5 equiv.), were introduced into a flask under argon. The reaction mixture was stirred for 30 h at room temperature and then was slowly quenched by the addition of 2-aminoethanol (0.1 cm^3, 1.6 mmol). Water was added to the mixture and then it was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and purified by silica gel chromatography (CH_2Cl_2–hexane, 1:1 then 3:2 then 1:0). The column affords pure compound **22a** (69 mg, 17%), pure compound **22d** (137 mg, 33%) and a mixture of compounds **22b** and **22c** (114 mg, 27.5%).

Compound **22a**, R_f(CH_2Cl_2–hexane, 3:2) 0.14; mp 141 °C; δ_H(200 MHz; $CDCl_3$) 7.91, 7.90, 7.84, 7.73, 7.71 and 7.69 (6 H, 6 × s, ArH), 5.86 and 5.84 (2 H, 2 × s, OH), 4.32–4.12 (6 H, m, OCH_2), 2.05–1.88 (6 H, m, OCH_2CH_2), 1.65–1.25 {15 H, m, $O(CH_2)_2(CH_2)_2$ and $Si[CH(CH_3)_2]_3$}, 1.17 {18 H, d, *J* 6.7, $Si[CH(CH_3)_2]_3$} and 0.96 and 0.95 (9 H, 2 × t, *J* 6.8 and 6.8, CH_2CH_3); *m/z* (FD) 691 ($[M + 1]^+$, 100%).

Compounds **22b** and **22c**, R_f(CH_2Cl_2–hexane, 3:2) 0.61; δ_H(200 MHz; $CDCl_3$) 7.95–7.70 (6 H, m, ArH), 5.90–5.86 (2 H, m, OH), 4.32–4.10 (6 H, m, OCH_2), 2.05–1.88 (6 H, m, OCH_2CH_2), 1.65–1.25 {15 H, m, $O(CH_2)_2(CH_2)_2$ and $Si[CH(CH_3)_2]_3$}, 1.16 and 1.15 {18 H, 2 × d, *J* 6.7 and 6.7, $Si[CH(CH_3)_2]_3$} and 0.96 and 0.95 (9 H, 2 × t, *J* 7.0 and 7.0, CH_2CH_3); *m/z* (FD) 691 ($[M + 1]^+$, 100%).

Compound **22d**, R_f(CH_2Cl_2–hexane, 3:2) 0.54; mp 110 °C; δ_H(200 MHz; $CDCl_3$) 7.95–7.68 (6 H, m, ArH), 5.89 and 5.86 (2 H, 2 × s, OH), 4.32–4.10 (6 H, m, OCH_2), 2.05–1.85 (6 H, m, OCH_2CH_2), 1.65–1.25 {15 H, m, $O(CH_2)_2(CH_2)_2$ and $Si[CH(CH_3)_2]_3$}, 1.17 {18 H, d, *J* 6.6, $Si[CH(CH_3)_2]_3$} and 1.00 and 0.88 (9 H, m, CH_2CH_3); *m/z* (FD) 691 ($[M + 1]^+$, 100%).

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