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A convenient synthesis of a 2,7-difunctional tetra(alkoxy)triphenylene involving 4,4′-diacetoxy-3,3′-dialkoxybiphenyl as a key precursor and its conversion to extended hybrid mesogenic compounds

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A convenient synthesis of a 2,7-difunctional tetra(alkoxy)triphenylene involving 4,4′-diacetoxy-3,3′-dialkoxybiphenyl as a key precursor and its conversion to extended hybrid mesogenic compounds

Andrés Zelcer[a], Florencia Cecchi[a], Pablo Alborés[a], Daniel Guillon[b], Benoît Heinrich[b], Bertrand Donnio[b]* and Fabio D. Cukiernik[a]*

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A new rational pathway to 2,7-difunctionalised-β-hexa-substituted triphenylenes is presented, requiring less protection/deprotection and purification steps than more conventional synthetic procedures in the framework of the 'biphenyl route'. Main improvements are deprotection via alkaline hydrolysis of an ester in ethanol/water medium instead of using toxic and pyrophoric reagents like lithium diphenylphosphide, and the use of easily prepared brominated precursors instead of iodinated reagents for biphenyl synthesis. 4,4′-Diacetoxy-3,3′-bis(hexyloxy)biphenyl has been synthesised under this scheme, and characterised by proton nuclear magnetic resonance (^{1}H NMR) spectrometry, elemental analysis and single-crystal crystallography. It crystallises in the *P*-1 space group, and exhibits a layered structure built-up through dipolar, C–H . . . π and C–H . . . O=C non-covalent interactions. This compound has been oxidatively coupled with 1,2-bis(hexyloxy)benzene to yield 2,7-dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene, a non-mesogen key precursor for the synthesis of the corresponding liquid-crystalline 2,7-difunctional triphenylenes. Indeed, a reactive 2,7-difunctional mesogen was prepared and used to produce new triphenylene-siloxane hybrid monomeric, trimeric and polymeric mesogens. All of them exhibited columnar hexagonal (Col_h) mesophases.

Keywords: liquid crystals; triphenylenes; biphenyl route; siloxane; polymer

1. Introduction

Since the discovery of discotic columnar liquid crystals (LC) [1], there has been an increasing interest in the design and synthesis of new discoid mesogenic materials [2]. In particular, triphenylene-based discotic mesogens, introduced shortly after [3,4], have been widely studied because of their one-dimensional (1D) charge migration [5,6], which combined with the ordering and dynamics of their mesomorphic behaviour offers many potential applications (electronic transport, photovoltaics, etc.) [7–12]. For example, β-hexa-substituted triphenylenes show a variety of mesophases as different functional groups are incorporated in terminal positions, going from mono- to hexa-functionalised triphenylenes [13,14]. Functionalised triphenylenes can then be incorporated in more complex systems, like dimers [15–17], oligomers [18–21], polymers [22–25], elastomers [26,27] and supramolecular systems [28–31], showing new mesomorphic behaviours and different physical properties. Although triphenylenes have been incorporated as side-groups in a wide variety of liquid crystal polymers (LCPs) [23,24], studies on main-chain triphenylene-based LCP have been developed to a lesser extent, certainly because of the synthetic difficulty to obtain difunctional triphenylenes. Among difunctional triphenylenes (2,7-; 3,6-; 2,3- and 2,6-isomers), isomer 2,7- is particularly interesting because, in this case, the whole width of the aromatic core separates both functional groups, effectively coupling the dynamics of the discotic core and the lateral functions. Additionally, the study and analysis of 2,7-isomers has been scarce, and only recently a few reports appeared [22,32–35].

Synthesis of unsymmetrically functionalised triphenylenes [36–39] is usually achieved either statistically or following a rational synthetic pathway. The first method involves the synthesis of an hexakis(alkoxy)triphenylene (HAT) followed by the partial dealkylation with BBr_3 [40,41] or *B*-bromocatecholborane [42]. As a result, mixed hydroxy(alkoxy)triphenylenes are obtained, which are the key precursors for the synthesis of functional

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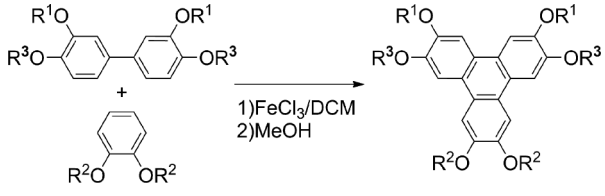
triphenylenes after Williamson's etherification. Nevertheless, the ether cleavage step yields a mixture of different isomers, requiring extensive and troublesome chromatographic separation of products, leading to low yields for a specific isomer.

Rational pathway consists in the synthesis, step by step, of every triphenylene precursor, producing mostly the aimed isomer. Different synthetic strategies can be employed for the synthesis of the triphenylene moiety. The main difference among them is the starting aromatic core that suffers cyclisation [43]: naphtyl, phenantryl, therphenyl [44] and biphenyl compounds can be used. Cyclisation can take place photochemically, by Diels–Alder cycloaddition, by Suzuki reaction or by oxidative coupling, the latter one being the most widely used procedure in the field of LC.

The 'biphenyl route', developed by Bushby and co-workers [45], involves an oxidative coupling between 3,3′,4,4′-tetra(alkoxy)biphenyls and 1,2-di(alkoxy)benzene or *o*-alkoxyphenol esters. This synthetic route, exemplified in Scheme 1 for a 2,7-difunctional-hexa-substituted-triphenylene, is usually used to obtain unsymmetrical substituted triphenylenes. The overall yield of the reaction is good, as long as the appropriate biphenyl is accessible. The synthesis of the biphenyl precursors is generally afforded by Suzuki reaction or Ullman coupling starting from 4-iodo-1,2-di(alkoxy)benzene. The substitution pattern of the resulting triphenylene core depends on the choice of the biphenyl and phenyl moieties, and this route has been extensively used to prepare monohydroxy penta(alkoxy)triphenylene from tetra(alkoxy) biphenyls and *o*-alkoxyphenol acetate [20,45].

Unfortunately, only few functional groups can resist acidic and oxidant synthetic conditions of oxidative coupling ($FeCl_3$, CH_2Cl_2). Therefore, the usual synthetic scheme involves the use of protecting groups in the β-positions designed to bear the functional alkoxy chains; deprotection leads to the already mentioned key hydroxy-triphenylenes precursors, obtained in this case in a simpler way than in the statistical synthesis. Methoxy group is widely used as a protecting group as it is selectively cleaved by lithium diphenylphosphide [46,47], either added or generated *in situ* from butyllithium. However, this is an expensive, toxic and pyrophoric deprotecting reagent. Studies have been performed to avoid the use of this kind of reactants; for example, Kumar et al. [48] analysed the use of ionic liquids as cleaving agents in the statistical synthesis, a well-known issue in the field of 'green chemistry' [49]. Protecting groups that are removed during the oxidative coupling were also proposed [50].

Here, we propose to retain the advantages of the rational synthesis by the biphenyl route, but use a much friendlier protecting group, namely acetyl. Indeed, it is easily removed by KOH in an ethanol/water mixture, involving a simpler chemistry, in the context of rational synthesis. Even if this protecting group has been widely used in the phenyl precursor of the biphenyl route, no reports of its use in the biphenyl moiety are found in the literature. Specifically, for 2,7-difunctional triphenylenes, a 4,4′-diprotected biphenyl is needed. In this work, the synthesis, structural and chemical characterisation of 4,4′-diacetoxy-3,3′-bis(hexyloxy)biphenyl is presented. Although this is an obvious precursor for the synthesis of 2,7-difunctional triphenylenes, the most recent report of a similar compound dates back to 1967 [51], before discotic liquid crystals were first described. We show that, with this compound, 2,7-difunctional triphenylenes can be obtained in a simple and friendly way with satisfactory yields and high purity. Indeed, the synthesis of the mesogenic compound 3,6,10,11-tetrakis(hexyloxy)-2,7-di(hidroxy)triphenylene (**6**) from the biphenyl is reported here. This functional triphenylene is the starting point for 2,7-difunctional triphenylenes, as is exemplified with the synthesis of a series of new mesogens with different degree of molecular extension. Starting from a terminal 2,7-difunctional hexa(alkoxy)triphenylene (**7**) with reactive terminal double bonds, a 2,7-terminally disiloxane 'decorated' monomeric triphenylene (**8**), a siloxane-bridged linear triphenylene trimer (**9**) and a hybrid siloxane-triphenylene main-chain discotic LC polymer (**10**) were prepared.

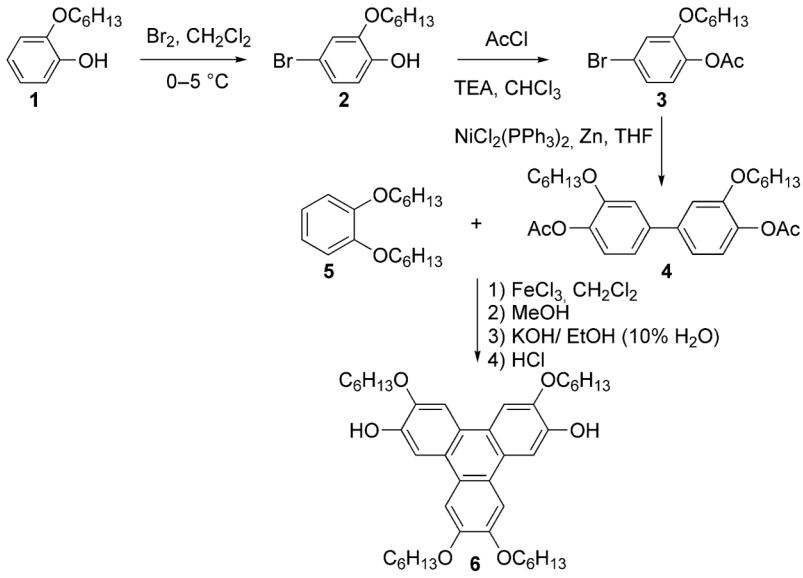


Scheme 1. Synthesis of 2,7-difunctional triphenylenes by the 'biphenyl route', with R^3 being the functional group at terminal position.

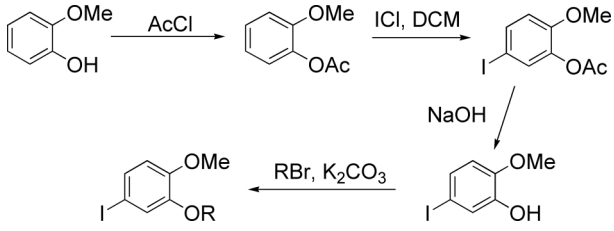
2. Results and discussion

2.1 General synthetic strategy

The synthetic scheme followed in this article for the synthesis of diphenol **6** is depicted in Scheme 2. The new precursor 4,4′-diacetoxy-3,3′-bis(hexyloxy) biphenyl (**4**) allows the synthesis of triphenylene **6**, the key precursor for difunctional triphenylenes, in a simpler way. Most of the reported previous syntheses of similar precursors employ methoxy groups



Scheme 2. Synthesis of 2,7-dihydroxy-tetrakis(hexyloxy)triphenylene by the 'biphenyl route' suggested in this work, employing acetyl as protecting group.



Scheme 3. Traditional route to biphenyl precursors.

for protection of the hydroxyl groups that will bear the functionality. Methoxy groups show two disadvantages that renders those synthetic routes troublesome. On the first place, due to the activating nature of the remaining hydroxyls, an extra protection/deprotection step is required in order to selectively introduce a reactive iodide on the *para* position of the methoxy substituent (Scheme 3) [32–35]. Moreover, selectively cleaving a methoxy chain, when other alkyl ethers are present, requires the use of lithium diphenylphosphide which is a pyrophoric bulky nucleophile.

Previous work using isopropoxide as a protective group gave low yields since iodination of rings bearing more than one kind of alkoxyde yields a mixture of isomers which is difficult to separate [50]. The synthetic strategy employed here makes use of bromide instead of iodine as a reactive group. Selective bromination of the position *para* to the phenol in presence of the alkoxy chain is obtained using moderately low temperatures, without introducing new protecting groups. Reductive homocoupling of this aryl halide using a nickel catalyst and Zn as a reducing agent was employed [52].

Using this new precursor, the triphenylene core was successfully obtained by oxidative coupling with di(alkoxy)benzene following the well-known biphenyl route, as shown in Scheme 2. Triphenylene **6** was thus obtained, which is the starting point for 2,7-difunctional triphenylenes. It is interesting to note the different reaction behaviour of alkoxyesters during oxidative coupling. Trimerisation of *o*-alkoxyphenylesters or *o*-alkoxyphenylsulphonates [53] results in tars that are supposed to consist of iron complexes or phenol oxidation products, giving very low yields of trihydroxy-tri(alkoxy)triphenylenes. On the other hand, coupling of tetra(alkoxy)biphenyls with *o*-alkoxyphenylesters is a standard method to obtain penta(alkoxy)monohydroxy-triphenylenes [20,45]. In the new route we propose herein, an alkoxyesterbiphenyl is used in an oxidative coupling for the first time.

The phenol **6** was subsequently converted in this work into different triphenylene compounds exhibiting different degrees of molecular complexity and extension. In the first step, **6** has been transformed via Williamson's etherification into a 2,7-terminally difunctional triphenlyene, **7**. The presence of the terminal functional groups allowed, in a second step, the synthesis of either a terminally di-decorated monomer, a linear trimer or a main-chain polymer. For all of these transformations, we choose terminal double bonds as functional groups, and hydrosylilation as the reaction allowing both the addition of a third molecular block and the incorporation of these triphenylenes into more extended materials. The choice of siloxane moieties as a third molecular block

obeys to the lowering effect as it is expected to exhibit on melting temperatures [19,54].

2.2 Synthesis and characterisation of 4,4′-diacetoxy-3,3′-bis(hexyloxy)biphenyl (4)

Compound **2** has been obtained from the partial substitution of catechol, followed by a *para* bromination of 2-hexyloxyphenol **1** (Scheme 2). Reaction temperature has been carefully controlled, in order to avoid polybromination. Besides being more economical, bromination of alkoxyphenols is more convenient than iodination, since iodinating reagents tend to oxidise alkoxy chains, giving tars difficult to purify. Phenol group was then masked by acetylation, yielding compound **3** in high yields. The new biphenyl intermediate **4** was synthesised by reductive homocoupling of compound **3**. Under typical Ullman conditions (copper and high temperatures) no reaction was detected; therefore, copper was replaced by $NiCl_2[P(Ph)_3]_2$ and Zn [52], and reaction was carried out in a THF solution. Under these conditions, satisfactory yields (ca. 35%) have been obtained with high reproducibility.

Compound **4** has been satisfactorily characterised by nuclear magnetic resonance (NMR) and elemental analysis (see Section 3 and Supporting Information, online only); its molecular and crystalline structures have been elucidated by single-crystal X-ray crystallography.

It crystallises without any solvent molecule in a triclinic *P*-1 space group with one molecule per unit cell. The inversion centre is located just in between both phenyl rings, which are strictly co-planar. The plane containing the acetoxy O–C–O moiety makes an angle of 74.59(13)° with the phenyl rings, whereas each of the acetoxy groups faces opposite sides of the biphenyl core. The alkyl chains run essentially along the biphenyl-containing plane with a mean dihedral angle of 5.13(13)° and are also located facing opposite biphenyl sides. (Figure S1).

When view along the *c* direction, the crystal packing evidences a layer arrangement of whole molecules with different inter- and intra-layer short-contact interactions and an inter-layer distance close to 3.6 Å (Figure S2a). On the other hand, view along the *a* direction offers a 1D tilted columnar-like arrangement of the planar molecules with a piling distance of 7.8 Å and a column–column distance of ca. 9 Å (core centre–core centre) (Figure S2b).

A closer inspection of the inter-molecular short-contact interactions (Figure S3), allows discriminating which one rules the inter-layer structuring and which ones the intra-layer one. Table S1 lists the relevant short-contact distances. With respect to inter-layer interaction, the combination of the aromatic biphenyl core–alkyl chain short contact (C2 . . . C8_d) and the acetoxy–alkyl chain (O3 . . . C7_d) one dominates. In the case of the intra-layer interaction, the head-to-tail O . . . H_3C acetoxy–acetoxy short contact (O3 . . . C14_c, essentially dipolar in nature) and the acetoxy methyl–alkyl chain contact (C14 . . . C9_i) govern the in-plane layer propagation. Remarkably, the acetoxy groups, by means of its O_3 oxygen atom, gets involved in both, inter- and intra-layer interaction, becoming a key factor in the whole packing architecture.

2.3 Synthesis and characterisation of 2,7-dihydroxy-tetrakis(hexyloxy)triphenylene (6)

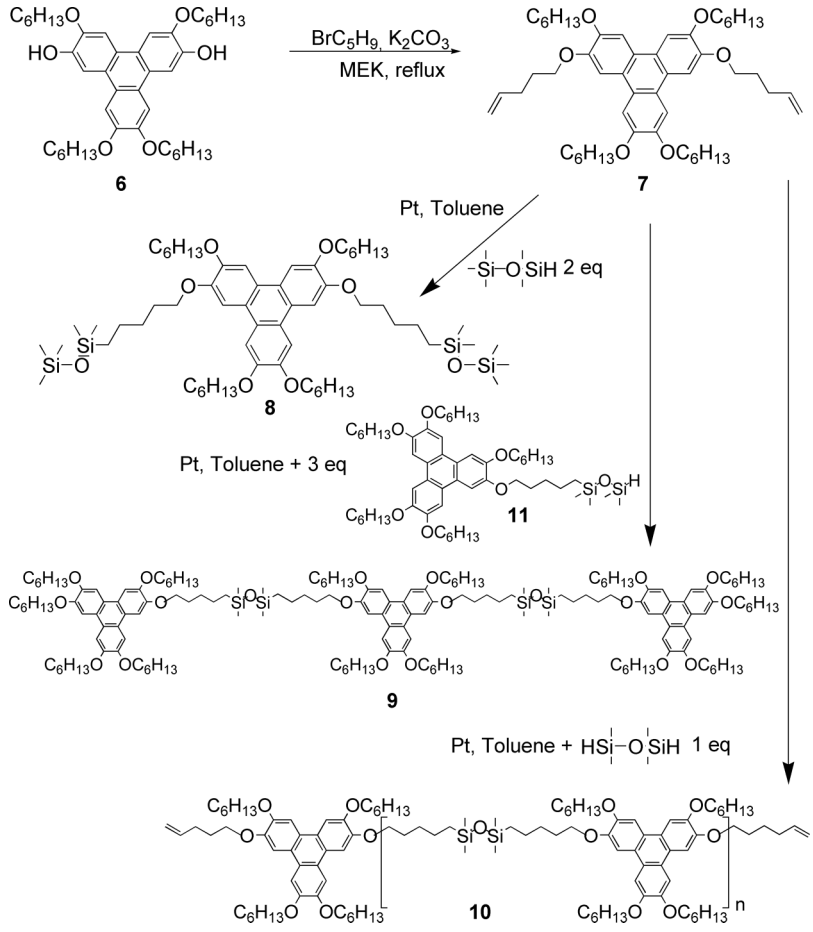
Diphenol **6** was prepared, by oxidative coupling of biphenyl **4** and 1,2-bis(hexyloxy)benzene **5** with $FeCl_3$, followed by a reductive methanol work up procedure (Scheme 2). Partial hydrolysis of acetyl groups takes place during reaction, which is then completed by saponification with KOH in ethanol (10% of H_2O). Cyclisation should take place with the *s-cis*-conformer of **4**, whereas the *s-trans*-conformer has been detected in its crystalline phase. However, free rotation around the central C–C bond in **4** is expected in a solution at room temperature, yielding a *s-cis*-conformer concentration high enough to warrant reaction.

Compound **6** has been satisfactorily characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and matrix-assisted laser desorption ionisation-time-of-flight-mass spectrometry (MALDI-TOF-MS) (see Section 3 and Supporting Information). Its thermal behaviour was studied by differential scanning calorimetry (DSC) and phase textures were observed and recorded by polarised optical microscopy (POM). DSC analysis (Figure S4) showed two narrow endothermic peaks at 56°C (ΔH_1 = 14 kJ/mol) and 190°C (ΔH_2 = 47 kJ/mol) during the first heating cycle, and their respective associated exothermic peaks in the cooling cycle. The second endothermic peak agrees with the previously reported 'melting point' for this compound [32]. Although optical textures on cooling (Figure S5) could be reminiscent of LC phases, relative values of ΔH_1 and ΔH_2 do not allow a straightforward association of these two peaks as corresponding to a melting transition (Cr → LC) and a clearing transition (LC → Iso), respectively, as is usually seen in alkoxy-substituted triphenylenes [13,55,56]. Moreover, a variable-temperature X-ray diffraction (XRD) structural analysis (Figure S6) confirmed that the first transition to be a Cr1→ Cr2 transition, whereas the second one corresponds to a direct melting to the isotropic phase. Columnar plastic phases have been reported for related compounds [57–59]; however, we have no evidence of such phases being present for this compound.

2.4 A terminally 2,7-difunctional triphenylene obtained from 6: synthesis, characterisation and mesomorphic properties of 3,6,10,11-tetrakis (hexyloxy)-2,7-bis(pent-4-enyloxy-) triphenylene (7)

Dialkene **7** was prepared by Williamson's etherification of **6** with 5-bromo-pent-1-ene (Scheme 4) and satisfactorily characterised by elemental analysis, ^{1}H NMR, ^{13}C NMR and MS-MALDI-TOF; its mesomorphic properties have been investigated by means of DSC (Figure S7), POM (Figure 1a) and XRD studies (Figure 2a).

This compound exhibits a columnar hexagonal (Col_h) mesophase from 59°C to 97°C. Structural and thermal details are reported in Table 1; additional experimental results are given as Supporting Information. Its mesomorphic range is slightly wider than that of hexakis(hexyloxy)triphenylene (**HAT-6**: Cr 68°C Col_h 98°C I) [58], as clearing temperature was not affected but melting point (m.p.) was lowered by terminal functionalisation, as was previously seen for other terminally functionalised alkene analogues [19,56,59,60]. Table 2 collects thermal data for a family of alkene-terminated hexa-subsituted triphenylenes [19]. The general trend is that clearing point remains almost constant for the whole series, in accordance with the accepted model in which clearing temperature is governed by core–core interactions and the terminal chains play a secondary role. Referred to the saturated analogue, **HAT-6**, progressive introduction of terminal unsaturations gives rise to a fall in m.p. – as expected for double C=C bonds disturbing aliphatic chains packing in the solid state. Once the number and position of these unsaturations allows the onset of either additional intermolecular interactions or a geometrically more favourable situation for efficient packing, the crystalline phase becomes again stabilised, as reflected in the increasing m.p. for symmetrically trisubstituted and hexa-substituted derivatives [19]. The unit cell volume of dialkene **7** (1316 Å^3) lies in between those of monoalkene **12** and both trialkene analogues **13** and **14** (1350 and 1300 Å^3, respectively).



Scheme 4. Synthesis of dialkene **7**, 'di-decorated' monomer **8** and siloxane-bridged trimer **9** and polymer **10** obtained from diphenol **6**.

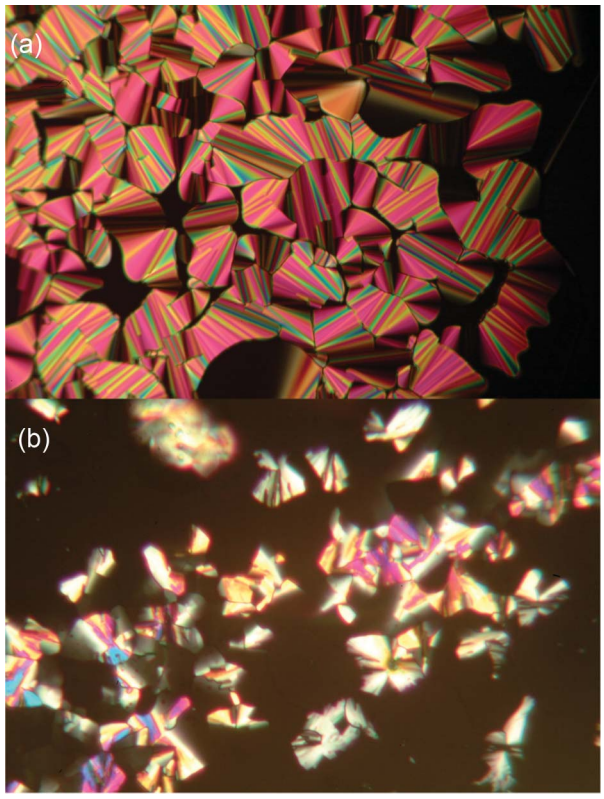


Figure 1. Selected POM pictures of (a) dialkene **7** at 95°C and (b) trimer **9** at 86°C on cooling from the isotropic phase in both cases.

2.5 Three-block hybrid compounds obtained from 7: synthesis, characterisation and mesomorphic properties of hybrid siloxane 2,7-substituted triphenylenes

Hybrid siloxane-triphenylenes were prepared by the reaction of **7** with appropriate silanes, using Karstedt's catalyst in toluene. Hydrosilylation of dialkene **7** (Scheme 4) with pentamethyldisiloxane (PMDS), yielded compound **8** in high yield. The linear trimer **9** was obtained using a hybrid triphenylene-silane **11** [19] as hydrosilylating agent. Reaction of the alkene with a 1:1 stoichiometric ratio of tetramethyldisiloxane (TMDS), yielded the main-chain hybrid polymer **10**.

MS confirms the structure of synthesised compounds and provides useful information about the polymer structure. For low molecular weight compounds **8** and **9**, molecular mass and isotopic distributions on $M^{+\cdot}$ agree with the expected ones. For the as-prepared polymer, previous to fractional precipitation, MALDI experiments show the presence of two distinct sets of signals with the typical weight distribution of a step-growth polymerisation [61]. On each of these sets, the peaks are separated by 931.5 uma, corresponding to monomer **7** + TMDS. The first of these set of peaks corresponds to a general formula

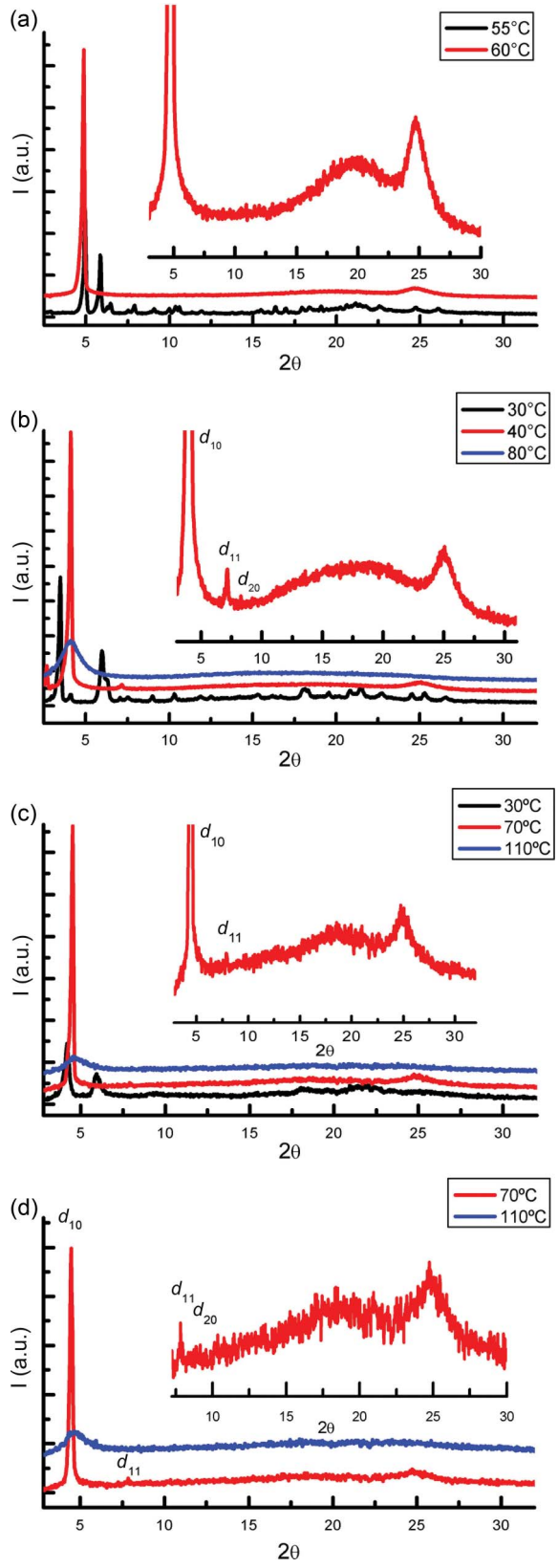


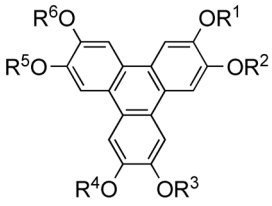
Figure 2. XRD patterns of (a) dialkene **7**; (b) compound **8**; (c) trimer **9** and (d) polymer **10**.

Table 1. Mesomorphism of 2,7-terminally difunctional compounds **7** and **8**, trimer **9** and polymer **10**.

	Phase sequence[a]	X-ray diffraction T (°C)	d_{exp} (Å)[b]	hk	d_{calc} (Å)	Mesophase parameters
7	Cr_1 52.8 (28.4) Cr_2 59.2 (9.1) Col_h 96.7 (4.9) I	60	17.84 VS 4.47 Br (CH_2) 3.58 Sh (π–π)	10		$a = 20.6$ Å $S = 367$ Å^2 $V = 1316$ Å^3
8	Cr 28.9 (35.7) Col_h 78.3 (4,4) I	50	21.44 VS 12.40 M 6.3 Br ($OSiMe_2$) 4.5 Br (CH_2) 3.5 Sh (π–π)	10 11	21.46 12.39	$a = 24.8$ Å $S = 532$ Å^2 $V = 1888$ Å^3
9	Cr 44.2 (75.2) Col_h 99.2 (13.8) I	70	19.15 VS 11.15 W 4.7 Br (CH_2) 3.6 Sh (π–π)	10 11	19.23 11.10	$a = 22.1$ Å $S = 426$ Å^2 $V = 1523$ Å^3
10	G -40 Col_h 106 I	70	19.48 VS 11.25 M 9.69 W 4.6 Br (CH_2) 3.6 Sh (π–π)	10 11 20	19.45 11.23 9.72	$a = 22.5$ Å $S = 438$ Å^2 $V = 1577$ Å^3

Notes: [a]Phase – transition temperature (°C) (transition enthalpies (kJ/mol)). Phases Cr: crystal, Col_h: columnar hexagonal, I: isotropic liquid.
[b]VS: very strong; M: medium; Br: Broad; Sh: Sharp.

Table 2. Thermal behaviour of alkene-terminated hexasubsituted triphenylenes compared to those of their saturated analogues.



12: R^1: $-(CH_2)_3CH=CH_2$; R^2,R^3,R^4,R^5,R^6: $-C_6H_{13}$
13: R^2,R^4,R^6: $-(CH_2)_3CH=CH_2$; R^1,R^3,R^5: $-C_6H_{13}$
14: R^2,R^4,R^5: $-(CH_2)_3CH=CH_2$; R^1,R^3,R^6: $-C_6H_{13}$
15: R^1,R^2,R^3,R^4,R^5,R^6: $-(CH_2)_3CH=CH_2$

Compound[a]	Thermal behaviour[b]
HAT-6	Cr 68 Col_h 98 I
HAT-5	Cr 69 Col_h 122 I
12	Cr 57 Col_h 95 I
7	Cr_1 53 Cr_2 59 Col_h 97 I
13	Cr 65 Col_h 96 I
14	Cr 48 Col_h 96 I
15	Cr 78 Col_h 97 I

Notes: [a]HAT-5 and 6 [58], compounds 12–15 [19].
[b]Phase, transition temperature. For phase abbreviations see Table 1.

$(\mathbf{7})_n(TMDS)_{n-1}$, compatible with polymers terminated by alkene groups at both ends. The second set of signals corresponds to compounds of general formula $(\mathbf{7})_n(TMDS)_n$, and is attributable to linear polymeric chains terminated with one silane group and one alkene, but also to cyclic species. These experiments also show that the signal corresponding to the dimer in the $(\mathbf{7})_n(TMDS)_n$ series escapes to the general distribution, its intensity being one order of magnitude higher than the rest. This behaviour can be explained by formation of cyclic dimers, as has already been observed in triphenylene-based polyethers [32]. Interestingly, no signal corresponding to compounds of general formula $(\mathbf{7})_{n-1}(TMDS)_n$ is found. This fact is attributable to the volatility of TMDS, producing a defect of this reactant during the polymerisation. This stoichiometric mismatch between monomers determines the extent of reaction and thus the weight-average molecular weight (Mw) of the resulting polymer.

Terminal group analysis by NMR indicates an average degree of polymerisation of 14.3 units. Gel permeation chromatography showed a symmetric distribution with number-average molecular weight (Mn) of 14,000 and Mw of 28,000. The resulting polydispersity index of 2 is typical of step-growth polymerisation [61]. The Mn and Mw values are comparable to others found in literature and are higher than many main-chain triphenylene-based polymers obtained by classical polymerisation pathways [23]. An Mn value higher than 10,000 is enough to assume that transition temperatures and other mesomorphic properties have reached their limiting values [61,62].

POM, DSC and XRD studies showed all three hybrid compounds **8**–**10** exhibit Col_h mesophases.

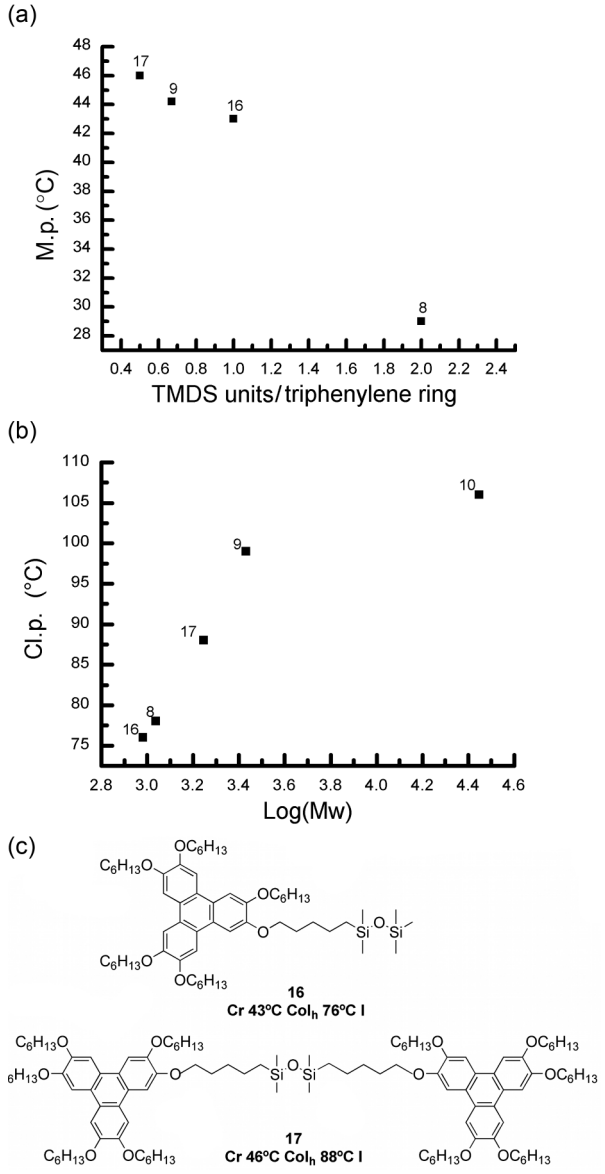


Figure 3. Thermal analysis of hybrid triphenylene-siloxane monomers **8** and **16**, dimer **17**, trimer **9** and polymer **10** series; (a) melting point behaviour vs. disiloxane moieties per triphenylene group ratio for low molar mass compounds; (b) clearing point trend as molecular mass increases along the series; (c) molecular representation and thermal properties of previously reported monomer **16** and dimer **17** employed in both analysis [19]. For compound numbering, see Scheme 4.

Representative POM textures and XRD patterns are included in Figures 1 and 2, respectively; DSC traces for each compound are presented in Figure S7. Thermal and structural data are reported on Table 1.

Thermal behaviour of this series of compounds is analysed in Figure 3, which also includes data for some previously reported siloxane-containing triphenylenes [19]. Figure 3a shows that melting temperatures of low molarmass compounds progressively decrease as the number of siloxane moieties per triphenylene ring increases. From this point of view, the introduction of this third molecular block was successful; indeed, m.p. for compound **8** is close to room temperature. Figure 3b, on the other hand, shows that clearing temperatures monotonically increase with molecular mass, as previously reported for other linear oligomers and polymers [20]. Saturation behaviour can be inferred from this figure, which shows that polymer **10** exhibits the saturation value and therefore its mesomorphic properties have been fully developed. Moreover, due its polymeric nature and the inclusion of siloxane bridges, **10** is LC from well below room temperature to 106°C.

Most reported triphenylene-based main-chain polymers are polyesters or polyethers. Most polyethers were prepared from mixtures of difunctional isomers. Those polyesters exhibiting high clearing points do also exhibit glass transition temperatures (Tg) above room temperature. Only one polyester exhibiting Tg below room temperature has been reported [63], with also a very low clearing point (31°C). Moreover, it exhibits a nematic phase. In the case of polyethers, some pure 2,7-isomers have been prepared. Those containing OH groups as polymeric chain termination (obtained directly from polymerisation) exhibited narrow mesomorphic ranges starting at ca. 100°C [32]. Materials for which a columnar mesophase has been found from below room temperature to ca. 100°C have been prepared by capping these OH-terminated polymers in a post-functionalisation step [22,64]. The introduction of flexible siloxane spacers and the absence of –OH groups on the final material leads in the case of polymer **10** to a similar mesomorphic behaviour without the need of a post-functionalisation step. The combination *o*-discotic mesogens and siloxane linkers in a main-chain hybrid LC polymer is new; although the preparation similar systems based on hexa-*peri*-benzocoronene has been mentioned [65], no results have been published.

Information about the organisation of compounds **8**–**10** in the Col$_h$ mesophase at a molecular level can be inferred from XRD patterns (Figure 2). Indeed, in addition to signals in the wide-angle region corresponding to the 10, 11 and 20 planes of a hexagonal array, a sharp signal at ca. 3.6 Å typical of π stacking, as well as a broad signal around 4.5 Å corresponding to molten aliphatic chains, are present for all three compounds. The typical signal of liquid-like dimethylsiloxane moieties around 6.3 Å was only observed for compound **8**. The lack of this signal for both trimer **9** and polymer **10** is indicative that no microsegregation of siloxane moieties occurs in their mesophases. The relative dilution of the bulky siloxane moieties among the alkyl chains leads to fewer siloxane–siloxane contacts in **9** and **10** than in **8**.

3. Experimental

3.1 General

Catechol, acetyl chloride, triethylamine, bromohexane, Zn dust (<10 μm) and anhydrous $FeCl_3$ were used as purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA). 1,1,1,3,3-PMDS (ABCR, Aldrich), 1,1,3,3-TMDS (ABCR, Aldrich), 5-bromo-pent-1-ene (Aldrich) and Karstedt's catalyst 2% on xylenes (ABCR) were used as purchased. $NiCl_2[P(Ph)_3]_2$, 2-hexyloxyphenol **1** and 1,2-bis(hexyloxy)benzene **5** were prepared following published procedures [32,66,67]. Solvents were dried and purified following the standard procedures [68]. Sulphur-free toluene was prepared shaking with cold H_2SO_4, followed by washing with water. It was dried first with $CaCl_2$ and then distilled from Na/benzophenone. CH_2Cl_2 was first treated with concentrated H_2SO_4, then washed with water, $NaHCO_3$ and finally with water again. It was then dried with $CaCl_2$ and then distilled from P_2O_5. MeOH was distilled from $Mg(MeO)_2$. THF was distilled from Na/benzophenone. All the described syntheses have been carried out under Ar atmosphere, using Schlenk techniques.

3.2 Physicochemical measurements

Elemental analysis was carried out at *Servicio a Terceros* of INQUIMAE, Buenos, Argentina, on a Carlo Erba CHNS-O EA1108 analyser. ^{1}H NMR and ^{13}C NMR were measured either on a Bruker AM500 or a Bruker Avance 300 spectrometer, using $CDCl_3$ as solvent and its residual peaks as internal references (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). MALDI-TOF mass spectra were obtained in a Bruker Daltonics OmniFlex.

Mesomorphic properties have been studied by means of variable temperature POM, DSC and variable temperature XRD techniques. POM has been carried out between crossed polarisers using a Leitz DMRX microscope equipped with a Leitz 1350 hot-stage. DSC experiments have been performed either on a Shimadzu DSC-50 calorimeter or a TA DSCQ1000, with heating and cooling rates of 5°C/min. For the XRD experiments, the powdered samples were contained in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-Kα_1 beam (λ = 1.5418 Å) was obtained using a Debye–Scherrer camera, equipped with a bent quartz monochromator and an electric oven. Diffraction patterns (exposure time ca. 45 min) were registered every 10°C, from ca. 30°C up to ca. 200°C, with a gas curved counter 'Inel CPS 120'; with this system, periodicities up to 60 Å can be measured, and the sample temperature is controlled within ±0.05°C.

3.3 X-Ray crystallographic data collection and refinement of the structure

A single crystal of compound **4** was coated with perfluoropolyether, picked up with nylon loop and mounted in an Oxford Xcalibur, Eos, Gemini CCD area-detector diffractometer using graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å) at 298 K. Final cell constants were obtained from least-squares fits of several thousand strong reflections. Data were corrected for absorption with CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.66, applying an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [69]. The structure was solved by direct methods with SHELXS-97 [70] and refined by full-matrix least-squares on F^2 with SHELXL-97 [70]. All non-hydrogen atoms were anisotropically refined and hydrogen atoms bound to carbon were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Final crystallographic data and values of R_1 and wR are listed in Table S2 while the angles and distances are listed in Table S3. CCDC 908440 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk/data_request/cif).

3.4 Synthesis

3.4.1 4-Bromo-2-(hexyloxy)phenol (2)

In a two-necked 250-mL flask equipped with a pressure-compensed funnel were placed 2-(hexyloxy) phenol (**1**) (26.4 g; 136 mmol) and dichloromethane (85 mL). The flask was placed in an ice bath, and while the mixtures cooled to 278 K a vessel bubbler, with a Na_2CO_3 solution, was placed in the remaining neck in order to neutralise the HBr vapours generated. A solution of Br_2 (8 mL; 156 mmol) in CH_2Cl_2 (25 mL) was loaded into the addition funnel and added drop-wise in continuous stirring over a period of 90 min, giving a red solution. The ice bath was removed and the solution stirred until it remained colourless. Water (50 mL) was added to the mixture, then, the contents of the flask were poured carefully into a separation funnel. The organic phase was washed with $NaHCO_3$(ss) and water again, dried over $NaSO_4$ and evaporated. Distillation of crude product under reduced pressure afforded compound **2** as a colourless oil (24.5 g; 66%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ = 6.97 (dd, J = 8.3, 2.1 Hz 1H,); 6.95 (d, J = 2.1 Hz 1H); 6.79 (d, J = 8.3 Hz, 1H); 5.57 (s, 1H); 4.01 (t, J = 6.6 Hz, 2H); 1.81 (q, J = 7.1, 2H); 1.46 (m, 2H); 1.36–1.33 (m, 4H); 0.91 (t, J = 7.1 Hz, 3H).

3.4.2 4-Bromo-2-(hexyloxy)phenyl acetate (3)

4-Bromo-2-(hexyloxy)phenol (**2**) (24.5 g; 90 mmol) was added to a solution of triethylamine (12 mL; 49 mmol) in $CHCl_3$ (30 mL). The mixture was cooled down to 278 K in an ice bath. Acetyl chloride (12.5 mL; 168 mmol) was added drop-wise and the solution stirred until reactant was not detected by thin layer chromatography (TLC). Water (30 mL) and $CHCl_3$ (10 mL) were carefully added, and the organic phase was washed with $NaHCO_3$(ss) until the aqueous layer was basic. The organic solution was dried (Na_2SO_4) and solvent removed *in vacuo*. Distillation of crude under reduced pressure product afforded compound **3** as a lightly yellow oil (22.6 g; 80%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 7.07$ (d, $J = 2.1$ Hz, 1H); 7.05 (dd, $J = 8.3$, 2.1 Hz, 1H); 6.89 (d, $J = 8.3$ Hz, 1H); 3.95 (t, $J = 6.6$ Hz, 2H); 2.28 (s, 3H); 1.75 (q, $J = 6.7$ Hz, 2H); 1.43 (m, 2H); 1.35–1.32 (m, 4H); 0.91 (t, 3H).

3.4.3 4,4′-Diacetoxy-3,3′-bis(hexyloxy)biphenyl (4)

$NiCl_2[P(Ph)_3]_2$(2.538 g; 4 mmol) and $N(CH_2CH_3)_4I$ (1.089 g; 4 mmol) were dried and degassed applying three cycles of vacuum/argon. Zn dust (5.014 g; 78 mmol) and dried and deoxygenated THF (95 mL) were added under argon atmosphere. The mixture was stirred for 30 min. A deoxygenated solution of compound **3** (11.436 g; 36 mmol) in THF (10 mL) was added and the reaction mixture stirred at 56°C for 20 h in an argon atmosphere. Then, the suspension was filtered through compacted silica, washed with ethyl ether, then the filtrate concentrated *in vacuo*. The resulting solid was purified by column chromatography (silica, cyclohexane/ethyl acetate up to 20:1) and crystallised in methanol/ethanol (1:1), to yield a white solid (3.019 g; 35%). Analysis: Found (calcd) for $C_{28}H_{38}O_6$ (470.60): C: 71.5 (71.46), H: 8.1 (8.14). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 7.06$–7.08 (m, 6H); 4.03 (t, $J = 6.5$ Hz 4H); 2.33 (s, 6H); 1.79 (q, $J = 7.0$ Hz 4H); 1.46 (m, 4H); 1.36–1.33 (m, 8H); 0.91 (t, $J = 7.1$ Hz 6H) (see Supporting Information).

Single crystals of compound **4** suitable for X-ray structure determination were obtained by slow evaporation of a $CDCl_3$ solution.

3.4.4 2,7-Dihydroxy-3,6,10,11-tetrakis (hexyloxy)triphenylene (6)

Biphenyl **4**(1.205 g; 3 mmol) and 1,2-bis(hexyloxy) benzene **5** (3.596 g; 13 mmol) and a stirring bar were placed on a Schlenk round flask connected to a vacuum–argon line. The flask was closed with a septum and the reactants were dried and degassed applying three cycles of vacuum/argon. Dry CH_2Cl_2 (30 mL) was added under argon atmosphere and the solution was degassed with three *freeze-pump-thaw* cycles. The stirred solution was cooled down in an ice bath, and anhydrous $FeCl_3$ (7.12 g; 44 mmol) was loaded in a Schlenk tube from a glovebox (O_2, H_2O < 2 ppm). The iron chloride was slowly added to the stirred flask under opposite continuous flow of argon both from the flask and from the tube containing $FeCl_3$. A vessel bubbler, with a $NaHCO_3$ solution, was placed in the neck to neutralise the HCl vapours generated and a small, continuous flow of argon was maintained. The ice bath was removed, and HCl started to evolve when the mixture reached at room temperature. The reaction mixture took a deep green colour, and was stirred for 90–120 min, until no more HCl evolution was evident from the formation of CO_2 in the bubbler. The reaction was cooled down on an ice bath and carefully quenched by adding drop-wise dry, degassed methanol (35 mL). The solution momentarily takes a reddish tint and gases evolve. The resulting mixture was filtered cold, washing with cold methanol (5°C) to give an almost white solid (lightly green taint) dried and kept *in vacuo*. KOH (1.64 g; 29 mmol) was solved in a mixture of ethanol (35 mL)/water (4 mL), and solution degassed by bubbling argon during 30 min. The solid previously obtained was then added, and the reaction mixture stirred under reflux for 3 h in an argon atmosphere. The still warm solution was poured in a mixture of ice (50 g) with HCl(c) (5 mL) contained in a separation funnel. A white (slightly violet) solid was formed. CH_2Cl_2 (25 mL) was added, and the aqueous phase was discarded. The organic layer was washed with water, dried (Na_2SO_4), and the solvent removed *in vacuo*. Purification by column chromatography (silica, cyclohexene/acetone 100:1–100:5) and recrystallisation from isopropanol afforded diphenol **6** (1.017 g, 60%). Analysis: Found (calcd) for $C_{42}H_{60}O_6$ (660.92): 76.4 (76.33), H: 9.2 (9.15). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 7.96$ (s, 2H); 7.82 (s, 2H); 7.74 (s, 2H); 5.89 (s, 2H); 4.29 (t, $J = 6.5$ Hz, 4H); 4.21 (t, $J = 6.7$ Hz, 4H); 1.97–1.90 (m, 8H); 1.59–1.53 (m, 8H); 1.43–1.36 (m, 16H); 0.96–0.93 (m, 12H).^{13}C NMR (500 MHz, $CDCl_3$, 25°C): $\delta =$ 148.89; 145.71; 145.16; 123.90; 123.17; 122.93; 107.30; 106.41; 104.14; 69.23; 69.07; 31.64; 29.28; 25.82; 25.78; 22.64; 22.60; 14.03 (see Supporting Information). MS (MALDI-TOF): 660.70 ($[M]^{+\bullet}$); 661.69 ($[M+1]^{+\bullet}$); 662.68 ($[M+2]^{+\bullet}$); 663.71 ($[M+3]^{+\bullet}$).

3.4.5 3,6,10,11-Tetrakis(hexyloxy)-2,7-bis (pent-4-enyloxy-)triphenylene (7)

2,7-Dihydroxy-3,6,10,11-tetrakis(hexyloxy) triphenylene (**6**) (1.14 g; 1.7 mmol) and 2.1 g (15 mmol) of K_2CO_3 were added to 45 mL of dried

dimethylformamide, and the solution degassed applying three cycles vacuum/argon. 5-Bromo-pent-1-ene (0.7 mL; 5.9 mmol) was added and the mixture was heated at 90°C for 20 h. The solution was poured over 300 mL of CH_2Cl_2, K_2CO_3 was filtered off and the filtrate evacuate under vacuum. The product was solved in 50 mL of CH_2Cl_2, washed with HCl (d) and dried with $MgSO_4$. After removal of the solvent, the product was purified by flash chromatography on silica gel (cyclohexane/CH_2Cl_2 from 200:40 to 170:90) and crystallised from a mixture ethanol/cyclohexane 40:1, yielding 1.23 g (89.6%) of a white solid. Analysis: Found (calcd) for $C_{52}H_{76}O_6$ (797.16): C, 78.12 (78.39); H, 9.59 (9.61). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ = 7.84 (s, 4H); 7.83 (s, 2H); 5.94 (ddt, J = 17.0, 10.2, 6.7 Hz, 2H); 5.12 (dc, J = 17.1, 1.7 Hz 2H); 5.03 (ddt, J = 10.2, 2.0, 1.2, 2H); 4.25 (t, J = 6.5 Hz, 4H); 4.233 (t, J = 6.6 Hz, 4H); 4.227 (t, J = 6.6 Hz, 4H); 2.34–2.38 (m, 4H); 2.04 (q, J = 7.0 Hz, 4H); 1.97–1.91 (m, 8H); 1.61–1.55 (m, 8H); 1.43–1.36 (m, 16H); 0.94 (t, J = 7.0 Hz, 12H). MS (MALDI-TOF): 796.6 ($[M]^{+\bullet}$); 797.6 ($[M+1]^{+\bullet}$); 798.6 ($[M+2]^{+\bullet}$); 799.6 ($[M+3]^{+\bullet}$).

3.4.6 3,6,10,11-Tetrakis(hexyloxy)-2,7-bis [5-(1,1,3,3,3-pentamethyldisiloxanyl)-pentyloxy]-triphenylene (8)

Compound **7** (0.408 g; 0.5 mmol) and 1,1,1,3,3-pentamethyldisiloxane (PMDS: 0.5 mL; 0.25 mmol) were dissolved in 3 mL of dry toluene, and 8 μL of catalyst was added. The solution was left under agitation, in the dark, at room temperature for 20 h. The solvent was removed, the mixture dried, and purified by flash chromatography on silica gel using light petroleum/CH_2Cl_2 (2:1), yielding 428 mg (76.45%) of little yellow waxy solid. Analysis: Found (calcd) for $C_{62}H_{108}O_8Si_4$ (1093.86): C, 67.70 (68.08); H, 10.07 (9.95). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ = 7.84 (s, 6H); 4.23 (t, J = 6.5 Hz, 12H); 1.94 (m, 12H); 1.58 (m, 12H); 1.44–1.37 (m, 20H); 0.94 (t, J = 6.9 Hz, 12H); 0.59 (t, J = 7.9 Hz, 4H); 0.07 and 0.06 (s, 30H). ^{13}C NMR (500 MHz, $CDCl_3$, 25°C): δ = 148.98; 123.62; 107.38; 69.72; 69.68; 31.69; 29.86; 29.43; 29.27; 25.85; 23.23; 22.67; 18.39; 14.06; 1.98; 0.35. MS (MALDI-TOF): 1092.7 ($[M]^{+\bullet}$); 1093.7 ($[M+1]^{+\bullet}$); 1094.7 ($[M+2]^{+\bullet}$)

*3.4.7 Trimer (**9**)*

Seventy-four milligrams (93 μmol) of alkene **7** and an excess of silane **11** (266 mg; 0.28 mmol) were dissolved in 5 mL of dry toluene. Two microlitres of catalyst was added and the mixture was stirred for 24 h. Then, additional of 2 μL of catalyst was added and the mixture was stirred for 72 h. The solvent was evaporated and the crude sample was chromatographed on silica (cyclohexane/CH_2Cl_2; 1.2:1 up to 1:4). A pink solid was obtained, which was dissolved in THF (1.5 mL), precipitated by dropping on cold methanol, and filtered, yielding 186 mg (74.3%) of a slightly pink product. Analysis: Found (calcd) for $C_{166}H_{264}O_{20}Si_4$ (Mw = 2692.20): C, 73.40 (74.06); H, 9.50 (9.88). ^{1}H NMR ($CDCl_3$) δ = 7.82 and 7.80 (18H); 4.21 (m, 36H); 1.93 (m, 36H); 1.57 (m, 36H); 1.39 (m, 64H); 0.93 (m, 42H); 0.59 (t, 8H); 0.06 (s, 24H). ^{13}C NMR ($CDCl_3$) δ = 148.95; 123.59; 107.32; 69.68; 31.68; 29.91; 29.42; 29.31; 25.85; 23.27; 22.65; 18.43; 14.05; 0.39. MS (MALDI-TOF): 2689.9 ($[M]^{+\bullet}$); 2690.8 ($[M+1]^{+\bullet}$); 2691.7 ($[M+2]^{+\bullet}$); 2692.6 ($[M+2]^{+\bullet}$).

*3.4.8 Polymer (**10**)*

Compound **7** (0.4450 g; 0.56 mmol) and 77.3 mg (0.56 mmol) of 1,1,3,3-TMDS were dissolved in 0.4 mL of dry toluene, and 4 μL of catalyst were added. The solution was heated at 60°C for 5 days. Then, 4 mL of THF were added, the mixture filtered through a 0.45-μm teflon membrane and the filtrate evaporated, yielding 0.498 g of a white solid. One hundred milligram of product were dissolved in 1 mL $CHCl_3$ and precipitated by drop-wise addition of 2 mL methanol, yielding 49.5 mg of a lightly yellow solid.

4. Conclusions

A new rational pathway to 2,7-di(hydroxy) triphenylenes, requiring less protection/deprotection and purification steps than in usual procedures, was developed. Moreover, the conditions used for this synthesis are more convenient than those previously reported, avoiding using dangerous and expensive reagents like diphenylphosphide. The key intermediate in this new synthetic pathway, biphenyl **4**, was fully characterised, including crystallographic characterisation. We showed how this reaction scheme can effectively be used to synthesise the difunctional phenol 2,7-di(hydroxy)-3,6,10–11-tetrakis(hexyloxy) triphenylene. This key precursor to difunctional triphenylenes was in turn used to synthesise a mesogenic triphenylene containing two functional (alkene) groups in the terminal positions of the 2 and 7 chains. This dialkene compound showed to be useful for preparing siloxane-containing three-block mesogenic materials with different molecular extent. The influence of both molecular mass and siloxane moieties on their mesomorphic properties has been analysed.

The introduction of siloxane bridges in a main-chain discotic polymer led to an extended mesophase range, from well below room temperature to above 100°C. We envisage that the development of new functional organic materials will be unlocked due to the availability of these precursors.

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