Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Stackhouse, Philip J. and Hird, Michael(2008) 'Influence of branched chains on the mesomorphic properties of symmetrical and unsymmetrical triphenylene discotic liquid crystals', Liquid Crystals, 35: 5, 597 — 607
To link to this Article: DOI: 10.1080/02678290802040026
URL: http://dx.doi.org/10.1080/02678290802040026

Liquid Crystals,
Vol. 35, No. 5, May 2008, 597–607

Influence of branched chains on the mesomorphic properties of symmetrical and unsymmetrical triphenylene discotic liquid crystals

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(Received 30 November 2007; final form 7 March 2008)

A series of novel symmetrical and unsymmetrical triphenylene-based discotic liquid crystalline materials with one or six branched peripheral alkoxy chains have been prepared. These materials have been compared with analogous known symmetrical and unsymmetrical compounds to reveal a balance between steric and space-filling effects of the peripheral branched chains, which significantly affects intermolecular forces of attraction and packing, and hence affects melting and isotropisation temperatures of the liquid crystalline materials. The desired result of reduction of melting points and enhancement of isotropisation temperatures has been accomplished by use of branched alkoxy chains in both symmetrical and unsymmetrical materials.

Keywords: discotic liquid crystals; triphenylenes; branched chains; unsymmetrical triphenylenes; mesophase enhancement

1. Introduction

Discotic liquid crystal research is now more than 30 years old, but it is still early days compared to the relatively well-established area of calamitic liquid crystals (*1–3*). Of all disc-shaped structures that can give rise to liquid crystalline properties, triphenylenes are, to date, the most widely investigated materials since the triphenylene core is readily accessible through established synthetic routes, and is excellent at conferring liquid crystalline properties (*4*). Hexa-esters and hexa-ethers of triphenylene are the most widely investigated discotic materials since they have a strong tendency to form columnar mesophases, which are of interest for one-dimensional energy and electron transport, and they have also found a use in optical compensation films in opto-electronic devices (*4–7*).

The significant technological importance of triphenylene-based discotic liquid crystalline materials makes it essential that structure–property relationships are fully explored. One such area of structure–property relationships that can be explored is in the nature of the peripheral alkoxy chains in hexaalkoxytriphenylene derivatives. The branching of peripheral chains in discotic liquid crystals has been examined before and has shown promising results; the first room temperature nematic discotic materials, for example, based upon benzene, contained branched alkyl chains in their periphery, and reported stabilisation of the mesophase (*8*). Other investigations into the effects of branched chains on coronenes established other beneficial effects of branched peripheral chains including the enhanced solubility of highly branched materials (*9, 10*). The effects of branched chains on coronenes also reduced the melting and clearing points of the investigated material, which is an effect that is also observed in tricycloquinazoline derivatives and is generally attributed to enhanced or reduced core–core interactions in the respective materials, which can consequently affect charge mobility (*9–13*). This reduction in clearing temperatures is not entirely consistent with the results from the aforementioned benzene-based systems, which exhibited enhanced mesophases. Indeed other investigations into benzene, cyclohexane and triphenylene-based materials have shown that the picture is somewhat more complex and it is possible to widen the mesophase temperature range by appropriate tuning of the branched nature of the peripheral chain (*14*).

In our investigations, we have examined symmetrical and unsymmetrical examples of branched alkoxy chain substituents for their effect on the melting points and liquid crystalline transition temperatures of hexa-substituted triphenylene-based discotic liquid crystalline materials. These investigations have been undertaken with a view to reducing melting points and increasing the clearing points of hexaalkoxy-substituted triphenylenes in order to permit the design of molecular architectures that will exhibit ordered columnar mesophases with a wide range in temperature, with low melting points and high clearing points, which will be of significant technological benefit in the future.

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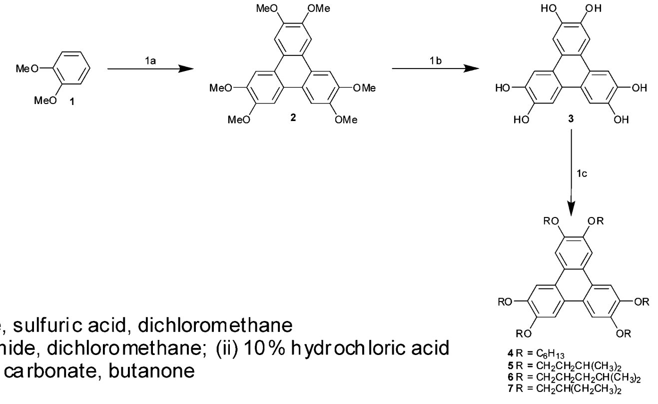
ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290802040026
http://www.informaworld.com

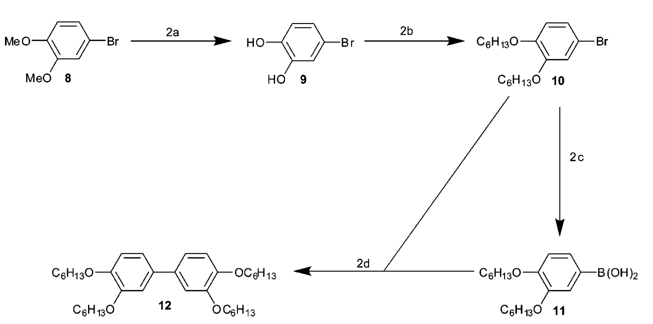
2. Results and discussion

This research was aimed at evaluating structure–property relationships in triphenylene-based discotic liquid crystalline materials, with a view to enhancing columnar liquid crystal phase stability and reduction of melting points. In order to accomplish this goal, several symmetrical and unsymmetrical branched-chain triphenylenes were prepared (see Schemes 1–3). The materials prepared were compared to the wholly symmetrical 2,3,6,7,10,11-hexabutoxytriphenylene (HAT4, **28**), 2,3,6,7,10,11-hexapentyloxytriphenylene (HAT5, **29**) and 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6, **4**), in terms of their melting points, mesophase stability and morphology. Unsymmetrical compounds that have been prepared all possess five hexyloxy chains and one unique chain to facilitate comparisons with HAT6, which was selected for comparison since its mesomorphic properties have been well-established previously (*15–19*). Several straight-chain analogues of the unsymmetrical triphenylenes have also been synthesised for comparison of the effect of changing the chain length and branching on the melting points and liquid crystalline transition temperatures. Since it is known that liquid crystal phase morphology is relatively consistent for hexaalkoxytriphenylenes, which mostly exhibit columnar mesophases, it is unsurprising that the novel compounds prepared exhibit exclusively the hexagonal columnar mesophase (*1, 15, 20*). The branching of the alkoxy chain in the novel compounds, although not affecting the mesophase morphology, has a significant effect upon melting and isotropisation temperatures. The branched chain should exert a highly significant influence on both the melting point and clearing point of the examined material, since the branch will have two significant, and competing, effects on the packing of the molecules and hence the intermolecular forces of attraction between the molecules. The branched chain is expected to exert significant steric influence on the packing of the triphenylene cores, which is likely to reduce melting and clearing points. The second effect that the branch is expected to exert is that of space-filling, by increasing the degree of



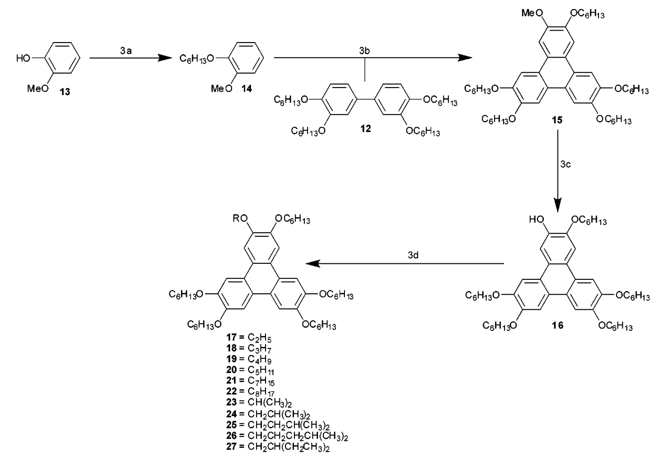
1a... Iron(III) chloride, sulfuric acid, dichloromethane
1b... (i) Boron tribromide, dichloromethane; (ii) 10% hydrochloric acid
1c... RBr, potassium carbonate, butanone

Scheme 1. Synthesis of symmetrical triphenylenes.



2a... (i) Boron tribromide, dichloromethane; (ii) 10% hydrochloric acid
2b... 1-Bromohexane, potassium carbonate, butanone
2c... (i) Magnesium, tetrahydrofuran; (ii) trimethyl borate; (iii) 10% hydrochloric acid
2d... Tetrakis(triphenylphosphine)palladium(0), sodium carbonate, water, 1,2-dimethoxyethane

Scheme 2. Synthesis of 3,3′,4,4′-tetrahexyloxybiphenyl.



3a... 1-Bromohexane, potassium carbonate, butanone
3b... Iron(III) chloride, dichloromethane
3c... (i) *n*-Butyllithium, diphenylphosphine, tetrahydrofuran; (ii) 10% hydrochloric acid
3d... RBr, potassium carbonate, butanone

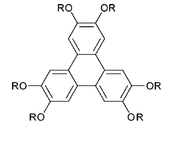
Scheme 3. Synthesis of unsymmetrical triphenylenes.

space-filling in the periphery of the disc-shaped molecules, it is expected that melting points and columnar liquid crystal phase stability should both increase. Whilst these two effects of the branching of the alkoxy chains surrounding the triphenylene core are conflicting, the overall outcome may lead to the desirable properties of lower melting points and enhanced columnar liquid crystal phase stability, although it was obviously unclear at the outset which effect (steric or space-filling) would ultimately be the decisive factor.

Table 1 shows three known symmetrical triphenylene based liquid crystalline materials HAT4 (**28**), HAT5 (**29**) and HAT6 (**4**), these materials show a trend of decreasing melting and clearing points as the chain length increases. This decrease in melting and clearing temperature is due to the decreasing rigidity of the chain as the length increases; hence those compounds with short alkoxy chains (C_2 or below), which are extremely rigid and do not exhibit mesomorphic behaviour since the melting points are so high (*20*).

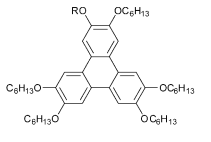
Table 2 shows how the level of symmetry within the molecule is important to melting points and liquid crystal phase stability. Whilst in Table 1 the driving force for melting and clearing temperatures was the rigidity of the system, in Table 2 the overall rigidity is relatively constant, and the minor alterations in the rigidity offered by altering one chain has little overall effect on the system, which is mainly driven by symmetry. This effect is evidenced by the increasing clearing points (Table 2) as the chain length increases from C_2 (**17**) to C_5 (**20**) and system approaches symmetry (**4**), then clearing temperatures fall off at a similar rate as the chain length exceeds the optimum

Table 1. Transition temperatures of symmetrical straight-chain triphenylenes.



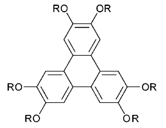
		Transition temperatures /°C				
Compound	R	Cr		Col$_h$		I
28 (*23*)	$-C_4H_9$	•	88	•	144	•
29 (*24*)	$-C_5H_{11}$	•	69	•	122	•
4	$-C_6H_{13}$	•	67.6	•	100.1	•

Table 2. Transition temperatures of unsymmetrical straight-chain triphenylenes.



		Transition temperatures /°C				
Compound	R	Cr		Col$_h$		I
17	$-C_2H_5$	•	57.3	•	79.1	•
18	$-C_3H_7$	•	60.6	•	84.8	•
19	$-C_4H_9$	•	59.7	•	95.1	•
20	$-C_5H_{11}$	•	57.7	•	94.5	•
4	$-C_6H_{13}$	•	67.6	•	100.1	•
21	$-C_7H_{15}$	•	58.4	•	94.7	•
22	$-C_8H_{17}$	•	52.0	•	86.0	•

Table 3. Transition temperatures of symmetrical branched-chain triphenylenes.



Compound	R	Transition temperatures /°C				
		Cr		Col_h		I
5	$-CH_2CH_2CH(CH_3)_2$	•	130.3	-	-	•
6	$-CH_2CH_2CH_2CH(CH_3)_2$	•	91.8	•	122.1	•
7	$-CH_2CH(CH_2CH_3)_2$	•	29.5	•	120.0	•

six-carbon length, hence distorting the symmetry (*15*). The major exception to this trend is compound **20**, where the clearing temperature is slightly lower than **19**; this anomaly is caused by a slight odd–even effect of the chain length on the molecular packing (*15*).

As is shown in Table 3, compound **5** does not exhibit mesomorphic behaviour, which is unsurprising given the high melting point and high re-crystallisation temperature (127.8°C). The high melting point of compound **5** indicates that the space-filling effect of the branched chain has increased the melting point in comparison to compound **28**, as predicted. However, given the high melting point and recrystallisation temperature, it is not possible to determine if there has been an increase in liquid crystal phase stability but it would seem likely given the unexpected effect upon the clearing points of **6** and **7**. It would be expected that the transition temperatures would drop significantly due to the steric effect of the chain, as occurs in calamitic systems, where typically the temperatures can drop by an average value of approximately 30°C (*21*). However, this is not the case in discotic systems as the isotropisation temperatures of compounds **6** and **7** remain relatively high.

Compound **5** can be further compared with 2,3,6,7,10,11-hexabutoxytriphenylene (HAT4, **28**), since the material shares the same carbon chain length, and with 2,3,6,7,10,11-hexapentyloxytriphenylene (HAT5, **29**), which possesses the same mass units. The melting point of compound **5**, when compared with the transition temperatures of HAT4 (**28**) and HAT5 (**29**) shows that the compound **5** has the highest melting point and its melting point is higher than the clearing point of HAT5 (**29**). This increase in stability shows how the space-filling effect has significantly increased the level of intermolecular attractions.

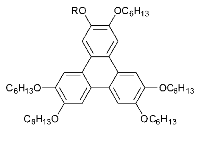
Moving the branched unit away from the triphenylene core by one CH_2, as in compound **6** relative to compound **5**, considerably reduces the melting point, which is not surprising given the additional conformational flexibility of the chain. Hence, the lower melting point permits the observation of the columnar mesophase. In addition to the effect of lowering the melting point, comparisons of the clearing point of compound **6** with the clearing point of HAT6 (**4**) show that the space-filling effect of the branch has drastically enhanced columnar mesophase stability, with an increase in temperature of more than 20°C, bringing the clearing point back to a similar value as would be exhibited by the straight chain analogue of HAT5 (**29**). This is highly significant since it would be expected that although the chain lengths of the two compounds are the same, the steric effect of the branch would decrease the clearing point of the material which should lead to **6** exhibiting a significantly lower clearing point than HAT5 (**29**). The space-filling effect of the branched chain can also be observed in the effect on the melting point of the two compounds, whereby compound **6** has a higher melting point than **29**. It would be expected that due to the steric effect of the branched chain that the melting point of compound **6** should be lower than compound **29**, which is not the case.

Modification of the branched nature of the material, switching from a methyl branch to an ethyl branch, as in compound **7** has drastically reduced the melting point of the material (29.5°C) yet retains the high clearing point (120.0°C). Reducing the chain length from **6** to **7** should have increased the melting point and columnar phase stability due to increased rigidity; however the steric effect of the branch has significantly reduced the melting point and has slightly reduced columnar phase stability. Comparing **7** with the analogous HAT4 (**28**) and HAT6 (**4**), reveals that the columnar phase stability is reduced compared with HAT4, but enhanced relative to HAT6. The reduction in liquid crystal phase stability (*cf.* **28**) is attributable to the significant steric effect of the branch. The increase in liquid crystal phase stability when compared with **4**, is due to a combination of the increased rigidity offered by shorter chain lengths and the space-filling effect of the branch. The melting point of compound **7** when compared with HAT4 and HAT6, however, reveals that **7** has a significantly reduced melting point compared with the analogous **28** (by ~60°C) and **4** (by ~40°C), which is due to the significant steric effect of the branch.

The encouraging results obtained from the wholly symmetrical branched-chain hexa-substituted triphenylenes (Table 3) led to the preparation of several unsymmetrical examples of branched alkoxy chain triphenylenes. These compounds were prepared in order to further investigate the effect of the steric and space filling effect of the branch in the peripheral alkoxy chain, and to allow for the further tuning of the structure–property relationships that have already been highlighted. The modification of a single chain allows for the direct comparison of the effect upon the system with the parent compound, which in this case was 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6, **4**), which was selected for its well-established physical properties (*15–19*).

As shown in Table 4, compound **23** has a depressed melting point relative to the parent compound (HAT6, **4**). There are two complementary factors for this effect, firstly the molecule has lost C3 symmetry, which will significantly reduce the level of molecular ordering, and hence reduce the melting point of the material, as was observed previously (Table 2). Secondly, the steric effect caused by the introduction to the molecule of the isopropoxy chain will disrupt molecular packing of the triphenylene cores and thus reduce the melting point. The steric influence of the isopropoxy chain on the packing of the molecules and subsequent reduction in π–π interactions, also accounts for the loss of the liquid crystal phase from compound **23**. It is reasonable, therefore, to assume that by moving the steric bulk away from the triphenylene core, there will be a subsequent reduction of the steric influence on the packing of the molecules, and hence there will be a corresponding increase in both melting point and liquid crystal phase stability. This proves to be the case since in compound **24**, moving the steric bulk away from the triphenylene core by one CH_2 unit increases the melting point of the material, although the melting point is still lower than that of the parent compound **4**. Alleviation of the steric effect on the triphenylene core by moving the steric bulk away from the core allows for closer contact of the core units to one another, which enhances π–π interactions and hence liquid crystalline phase behaviour, which was absent in compound **23**, is seen in compound **24**. Comparing the melting point and clearing point of **24** with **18**, which has the same chain length, and **19**, which possess the same mass, reveals little difference in melting point. The clearing point of **24**, however, remains similar to the $T_{\text{Col-I}}$ value of **18**, despite the increase in mass; this is due to the steric influence of the branched chain.

Table 4. Transition temperatures of unsymmetrical branched-chain triphenylenes.



		Transition temperatures /°C				
Compound	R	Cr		Col_h		I
23	$–CH(CH_3)_2$	•	54.6	-	-	•
24	$–CH_2CH(CH_3)_2$	•	59.4	•	85.4	•
25	$–CH_2CH_2CH(CH_3)_2$	•	54.5	•	105.0	•
26	$–CH_2CH_2CH_2CH(CH_3)_2$	•	61.5	•	105.3	•
27	$–CH_2CH(CH_2CH_3)_2$	•	44.4	•	78.1	•

Further increasing the distance of the branched unit away from the core by an additional CH_2 unit has a significant effect on the transition temperatures of the material. Compound **25** benefits from lower melting points compared with the parent compound (HAT6, **4**), and the analogous compounds **19** and **20**, indicating that the steric effect of the branch is exerting a significant influence on intermolecular forces. By contrast with the effect on the melting point, the clearing point of **25** is 5°C higher than the parent compound and 10°C higher than the analogous straight-chain compounds **19** and **20**. This effect is highly unusual, since the reduction in symmetry and the steric effect of the branch should have significantly reduced columnar liquid crystal phase stability. The increased intermolecular forces generated by the space-filling effect of the branch in this case are sufficient to overcome these effects, and hence, columnar liquid crystal phase stability is increased. Unlike the decreased melting point observed in **25**, compound **26** possesses a higher melting point than the analogous compound **20** and a significantly enhanced melting point over **25**. This unusual reversal of effect on melting point is due to the space-filling effect of the branch and the marginally improved symmetry dominating over the marginally reduced steric effect.

It is somewhat unexpected that the columnar mesophase stabilities of compounds **25** and **26** are virtually identical. The greater steric influence of the branched chain in compound **25** should mean that the $T_{\text{Col-I}}$ value should be significantly lower than for compound **26**. This observation further reinforces the fact that there are two competing effects of the branch, *i.e.* that the steric effects of the branch reduce liquid crystal phase stability, and that the space-filling effects of the branch increases intermolecular attraction, and thus enhances columnar mesophase stability. In the case of compound **25**, the space filling effect of the branch is sufficient to counter the greater steric effect and thus the $T_{\text{Col-I}}$ values of compounds **25** and **26** are almost identical.

Modification of the branched nature of the peripheral chain, switching from a methyl branch to an ethyl branch, as in compound **27**, has had a drastic effect upon the melting and clearing points, just as the symmetrically branched **7** did. Compound **27** has a melting point that is significantly reduced compared with the parent compound (HAT6, **4**) and the straight-chain analogue of **19**. This dramatic reduction in melting point is due to the steric effect of the branch, which also affects the clearing point of the material, which is also reduced relative to compounds **4** and **19**. These observations highlight the "balancing act" between the steric and space-filling effects of the branch as the branched nature changes from **26** to **27**, the balance of the steric / space-fill moves away from the space-filling effect, and towards the dominance of the steric effect. This effect is in contrast to the effect of the branching in compound **7**, where the steric effect enhanced the clearing point relative to HAT6 (**4**), but reduced the clearing point relative to HAT4 (**28**). This observation suggests that the space-filling effect is cumulative, whereby the six branched groups have a larger overall effect on the $T_{\text{Col-I}}$ value than when there is only one branched chain, and the cumulative effect of the steric factor is less significant.

3. Experimental

Characterisation

NMR spectra were recorded using a JEOL JNM Eclipse 400 spectrometer, and all spectra are recorded relative to tetramethylsilane, which was used as an internal standard. Melting points and transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope, and liquid crystal transition temperatures were confirmed by differential scanning calorimetry (Mettler DSC822e). The purity of final products was analysed by HPLC using a Gilson 233XL autosampler, 321 binary solvent pump, Hewlett Packard 1100 series Diode Array Detector and a Phenomenex Luna 5 µm C18(2) column. Preparatory HPLC was performed using a Gilson 233XL autosampler, 321 binary solvent pump, 151 UV/VIS detector and a Phenomenex Luna 5 µm C18(2) column.

Synthesis

2,3,6,7,10,11-Hexamethoxytriphenylene (2).

Ferric chloride (40.00 g, 0.242 mol) and sulfuric acid (50 ml, 98%) were added to a solution of veratrole (compound **1**, 30.00 g, 0.217 mol) in dichloromethane (500 ml). The mixture was stirred for 18 h before methanol (200 ml) and water (200 ml) were added. The purple precipitate was filtered off and washed with methanol and water to yield a purple solid. Yield: 7.85 g (26%). ^{1}H NMR (CDCl$_3$): δ 4.08 (18H, s), 7.74 (6H, s). ^{13}C NMR (CDCl$_3$): δ 56.01, 104.2, 123.14, 148.71. MS *m*/*z*: 408 (M$^+$). M.p.: >300°C.

2,3,6,7,10,11-Hexahydroxytriphenylene (3).

Boron tribromide (60.00 g, 0.239 mol), was added dropwise to a stirred, cooled (−78°C) solution of compound **2** (12.19 g, 0.0299 mol) in dichloromethane (900 ml) under an atmosphere of dry nitrogen. The mixture was stirred at −78°C for 2 h, and then warmed to room temperature overnight. Ice was added slowly to the mixture, which was acidified with 10% hydrochloric acid to give a dark precipitate. The dark precipitate was filtered off and washed with water to yield a dark grey solid. Yield: 8.94 g (95%). ^{1}H NMR (DMSO-D6): δ 7.60 (6H, s), 9.32 (6H, s). MS *m*/*z*: 324 (M$^+$). M.p.: >300°C.

2,3,6,7,10,11-Hexahexyloxytriphenylene (4).

A stirred mixture of compound **3** (2.30 g, 0.007 mol), butanone (500 ml), 1-bromohexane (20.80 g, 0.126 mol), and potassium carbonate (52.20 g, 0.378 mol) was heated under reflux for 4 days (TLC analysis revealed a complete reaction). The mixture was filtered to remove the potassium carbonate and the solvent was removed *in vacuo*. The product was purified by column chromatography (silica gel, dichloromethane, followed by 3:1 hexane/dichloromethane) to yield a yellow solid. The product was dissolved in dichloromethane and boiled in the presence of activated charcoal (2 min) and the solvent was removed *in vacuo*. The yellow waxy solid was recrystallised from ethanol–ethyl acetate (3:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 2.6 g (46%). ^{1}H NMR (CDCl$_3$): δ 0.94 (18H, t), 1.34–1.45 (24H, m), 1.58 (12H, quint), 1.94 (12H, quint), 4.23 (12H, t), 7.83 (6H, s). ^{13}C NMR (CDCl$_3$): δ 14.04, 22.65, 25.84, 29.41, 31.68, 69.69, 107.31, 123.58, 148.95. MS *m*/*z*: 829 (M$^+$+1). Transition temperatures (°C): Cr 67.6 Col$_h$ 100.1 I. Elemental analysis: calculated for $C_{54}H_{84}O_6$, C 78.26, H 10.14; found, C 78.50, H 10.36%.

2,3,6,7,10,11-Hexa-3-methylbutoxytriphenylene (5).

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **3** (1.00 g, 3.09 mmol), butanone (120 ml), 1-bromo-3-methylbutane (3.73 g, 0.0247 mol), and potassium carbonate (4.25 g, 0.0308 mol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 1.13 g (49%). ^{1}H

NMR ($CDCl_3$): δ 1.01 (36H, d, J=6.60 Hz), 1.82 (12H, q, J=6.60 Hz, J=6.96 Hz), 1.94 (6H, nonete, J=6.60 Hz, J=6.96 Hz), 4.25 (12H, t, J=6.60 Hz), 7.82 (6H, s). ^{13}C NMR ($CDCl_3$): δ 22.72, 25.20, 38.04, 67.99, 107.07, 123.50, 148.88. MS *m/z*: 744 (M^+). Transition temperatures (°C): Cr 132.0 I. Elemental analysis: calculated for $C_{48}H_{72}O_6$, C 77.38, H 9.74; found, C 77.34, H 9.90%.

*2,3,6,7,10,11-Hexa-4-methylpentyloxytriphenylene (**6**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **3** (1.00 g, 3.09 mmol), butanone (120 ml), 1-bromo-4-methylpentane (4.60 g, 0.0279 mol) and potassium carbonate (4.25 g, 0.0308 mol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.60 g (23%). ^{1}H NMR ($CDCl_3$): δ 0.96 (36H, d, J=6.60 Hz), 1.43–1.49 (12H, m), 1.68 (6H, nonete, J=6.60 Hz), 1.91–1.98 (12H, m), 4.21 (12H, t, J=6.60 Hz), 7.83 (6H, s). ^{13}C NMR ($CDCl_3$): δ 22.63, 27.32, 27.91, 35.31, 69.93, 107.20, 123.56, 148.89. MS *m/z*: 828 (M^+). Transition temperatures (°C): Cr 91.8 Col_h 122.1 I. Elemental analysis: calculated for $C_{54}H_{84}O_6$, C 78.21, H 10.21; found, C 77.97, H 10.28%.

*2,3,6,7,10,11-Hexa-2-ethylbutoxytriphenylene (**7**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **3** (0.50 g, 1.54 mmol), butanone (120 ml), 1-bromo-2-ethylbutane (2.29 g, 0.0139 mol) and potassium carbonate (2.00 g, 0.0145 mol). The product was purified by column chromatography (silica gel, 1:1 hexane/dichloromethane, followed by 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.06 g (5%). ^{1}H NMR ($CDCl_3$): δ 1.01 (36H, t, J=7.51 Hz), 1.55 (24H, q), 1.84 (6H, septet), 4.12 (12H, d, J=5.87 Hz), 7.82 (6H, s). ^{13}C NMR ($CDCl_3$): δ 11.34, 23.61, 41.10, 71.63, 106.90, 123.43, 149.18. MS *m/z*: 829 (M^++1). Transition temperatures (°C): Cr 29.8 Col_h 120.0 I. Elemental analysis: calculated for $C_{54}H_{84}O_6$, C 78.21, H 10.21; found, C 78.49, H 10.46%.

*4-Bromocatechol (**9**).*

The same procedure was carried out as detailed in the synthesis of compound **3**, using the following quantities: boron tribromide (350.00 g, 1.39 mol) 4-bromoveratrole (**8**, 100.5 g, 0.463 mol), dichloromethane (1000 ml). In this case no precipitate formed, so the mixture was extracted into diethyl ether and washed with water (twice). The ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow powder. The powder was stirred in hexane/dichloromethane solution (10:1) for 2 h, and filtered to yield a colourless powder. Yield: 60.72 g (69%). ^{1}H NMR ($CDCl_3$): δ 5.22 (1H, s), 5.37 (1H, s), 6.74 (1H, d), 6.92 (1H, dd), 7.01 (1H, d). MS *m/z*: 188 (M^+), 190 (M^+). M.p.: 85–89°C, lit. M.p.: 85–86°C (*22*).

*4-Bromo-1,2-dihexyloxybenzene (**10**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **9** (75.20 g, 0.398 mol), butanone (900 ml), 1-bromohexane (198.0 g, 1.2 mol) and potassium carbonate (165.5 g, 1.20 mol). The product was purified by column chromatography (silica gel, 1:1 hexane/dichloromethane) to yield an orange oil. Yield: 124.27 g (87%). ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, 2 × t), 1.33 (6H, m), 1.46 (6H, m), 1.78 (4H, 2 × sext), 3.94 (4H, 2 × t), 6.71 (1H, d), 6.96 (1H, d), 6.97 (1H, dd). MS *m/z*: 358 (M^++1), 356 (M^++1).

*3,4-Dihexyloxyphenylboronic acid (**11**).*

A solution of compound **10** (93.00 g, 0.261 mol) in dry tetrahydrofuran (250 ml), was added dropwise to a stirred, refluxing mixture of magnesium (8.14 g, 0.339 mol), and dry tetrahydrofuran (1250 ml) under an atmosphere of dry nitrogen. The stirred mixture was heated under reflux for 2 h, and cooled to −78°C. Trimethyl borate (54.30 g, 0.522 mol) was added dropwise and stirred at −78°C for 2 h, then warmed to room temperature overnight. The mixture was acidified with 10% hydrochloric acid, stirred for 2 h and extracted into diethyl ether (twice) and washed with water (twice). The ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The cream-coloured solid was dissolved in ethyl acetate, and hexane was added to precipitate out the colourless powder. Yield: 44.7 g (53%). ^{1}H NMR (DMSO-d_6): δ 0.83 (6H, 2 × t), 1.22–1.29 (8H, m), 1.34–1.42 (4H, m), 1.64 (4H, quint), 3.88 (4H, 2 × t), 6.84 (1H, d), 7.29 (1H, dd), 7.30 (1H, d), 7.79 (2H, s). M.p.: 129.0–129.5°C. MS *m/z*: 912 (M^+ of trimeric anhydride).

*3,3′,4,4′-Tetrahexyloxybiphenyl (**12**).*

A stirred mixture of sodium carbonate (6.24 g, 0.0588 mol), water (30 ml), compound **10** (10.50 g, 0.0294 mol), tetrakis(triphenylphosphine)palladium(0)

(1.70 g, 0.00147 mol) and compound **11** (11.36 g, 0.0353 mol) in 1,2-dimethoxyethane (500 ml) was heated under reflux for 24 h (TLC revealed a complete reaction). The product was extracted into ether (twice) and washed with water and brine. The ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, 1:1 dichloromethane/hexane), and recrystallised from ethanol/ethyl acetate (2:1) to yield colourless crystals. Yield: 14.84 g (98%). ^1H NMR ($CDCl_3$): δ 0.90 (12H, 2 × t), 1.32–1.36 (16H, m), 1.45–1.50 (8H, m), 1.83 (8H, 2 × quint), 4.03 (8H, 2 × t), 6.92 (2H, d), 7.04–7.07 (4H, m). MS *m/z*: 554 (M^+). M.p.: 76.4–78.1°C, lit. m.p. 75–76°C (*22*).

*1-Hexyloxy-2-methoxybenzene (**14**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **13** (14.90 g, 0.120 mol), butanone (500 ml), 1-bromohexane (39.65 g, 0.240 mol) and potassium carbonate (33.00 g, 0.239 mol). The product was purified by column chromatography (silica gel, 1:1 hexane/dichloromethane) to yield an orange oil. Yield: 10.26 g (41%). ^1H NMR ($CDCl_3$): δ 0.89 (3H, t), 1.33 (2H, sextet), 1.33 (2H, quint), 1.44 (2H, quint), 1.83 (2H, quint), 3.83 (3H, s), 3.99 (2H, t), 6.84–6.90 (4H, m). MS *m/z*: 208 (M^+).

*2,3,6,7,10-Pentahexyloxy-11-methoxytriphenylene (**15**).*

A mixture of compound **12** (28.64 g, 0.0517 mol), compound **14** (10.75 g, 0.0517 mol), iron(III) chloride (17.11 g, 0.103 mol) and dichloromethane (250ml) was stirred together under an atmosphere of dry nitrogen overnight. Methanol (60 ml) and water (120 ml) was added to the mixture and the crude product was extracted into dichloromethane (twice), washed with water and brine, and the combined organic extracts were dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a waxy solid, which was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane) to yield a light purple solid. Yield: 23.75 g (61%). ^1H NMR ($CDCl_3$): δ 0.94 (12H, t), 1.36–1.41 (24H, m), 1.56–1.61 (10H, m), 1.95 (10H, 2 × quint), 4.10 (3H, s), 4.24 (10H, t), 7.82 (1H, s), 7.84 (1H, s), 7.85 (1H, s), 7.85 (2H, s), 7.86 (1H, s). MS m/z: 758 (M^+). Transition temperatures (°C): Cr 47.1 I.

*2,3,6,7,10-Pentahexyloxy-11-hydroxytriphenylene (**16**).*

n-Butyllithium (21.96 ml, 2.5M, 0.0549 mol), was added dropwise to a stirred, cooled (–5°C) solution of diphenylphosphine (10 ml, 9.29 g, 0.0499 mol) in tetrahydrofuran (200 ml), under an atmosphere of dry nitrogen. The mixture was stirred for 30 min, then a solution of compound **15** (13.45 g, 0.0177 mol) in tetrahydrofuran (300 ml) was added dropwise. After 30 min the mixture was warmed to room temperature and then heated under reflux (overnight). The mixture was acidified with 10% hydrochloric acid, and stirred for 2 h. The product was extracted into diethyl ether (twice) and washed with water (twice). The ethereal extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane, with increasing volume fractions of dichloromethane), to yield a dark purple waxy solid. Yield: 10.01 g (76%). ^1H NMR ($CDCl_3$): δ 0.93–0.96 (15H, m), 1.34–1.45 (20H, m), 1.54–1.63 (10H, m), 1.92–1.96 (10H, m), 4.23 (8H, 2 × t), 4.29 (2H, t), 7.78 (1H, s), 7.82–7.83 (4H, m), 7.97 (1H, s). M.p.: 47.7–50.1°C, lit. m.p. 45–46°C (**22**).

*2-Ethoxy-3,6,7,10,11-pentahexyloxytriphenylene (**17**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.2 g, 0.269 mmol), butanone (110 ml), 1-bromoethane (0.04 g, 0.367 mmol), and potassium carbonate (0.11 g, 0.797 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.12 g (58%). ^1H NMR ($CDCl_3$): δ 0.93 (15H, t), 1.35–1.42 (20H, m), 1.53–1.61 (13H, m), 1.94 (10H, quint), 4.22 (2H, t), 4.23 (6H, t), 4.25 (2H, t), 4.31 (2H, quartet), 7.83 (5H, s), 7.84 (1H, s). ^{13}C NMR ($CDCl_3$): δ 14.05, 15.01, 22.65, 25.80, 25.83, 29.33, 29.41, 31.67, 107.12, 107.19, 107.33, 107.41, 123.54, 123.63, 123.66, 123.70, 148.65, 148.85, 148.89, 148.95, 148.98. MS *m/z*: 773 (M^+). Transition temperatures (°C): Cr 57.3 Col_h 79.1 I. Elemental analysis: calculated for $C_{50}H_{76}O_6$, C 7.68, H 9.91; found, C 77.49, H 9.72%.

*2,3,6,7,10-Pentahexyloxy-11-propoxytriphenylene (**18**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.2 g, 0.269 mmol), butanone (120 ml), 1-bromopropane (0.04 g, 3.25 mmol) and potassium carbonate (0.11 g, 0.797 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.13 g (61%). ^1H NMR ($CDCl_3$): δ 0.93 (15H, t), 1.14 (3H, t), 1.35–1.45 (10H, m), 1.8 (10H, quint), 1.93 (10H, quint), 1.97 (2H, quint), 4.19 (2H, t), 4.22 (10H, t), 7.83 (6H, s). ^{13}C NMR (CDCl$_3$): δ 10.66, 14.06, 22.67, 22.82, 25.87, 29.44, 31.70, 69.74, 107.38, 123.63, 148.99. MS *m*/*z*: 787 (M$^+$). Transition temperatures (°C): Cr 60.6 Col$_h$ 84.8 I. Elemental analysis: calculated for $C_{51}H_{78}O_6$, C 77.82, H 9.99; found, C 77.76, H 10.18%.

*2-Butoxy-3,6,7,10,11-pentahexyloxytriphenylene (**19**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.50 g, 0.672 mmol), butanone (120 ml), 1-bromobutane (0.20 g, 1.46 mmol) and potassium carbonate (0.28 g, 2.03 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.34vg (63%). ^{1}H NMR (CDCl$_3$): δ 0.94 (15H, t), 1.04 (3H, t), 1.34–1.44 (18H, m), 1.54–1.65 (14H, m), 1.94 (12H, quint), 4.23 (10H, t), 4.24 (2H, t), 7.84 (6H, s). ^{13}C NMR (CDCl$_3$): δ 13.98, 14.05, 19.38, 22.66, 25.84, 29.41, 31.48, 31.68, 68.34, 69.68, 107.28, 123.58, 148.93. MS *m*/*z*: 801 (M$^+$). Transition temperatures (°C): Cr 59.7 Col$_h$ 95.1 I. Elemental analysis: calculated for $C_{52}H_{80}O_6$, C 77.5, H 10.06; found, C 77.82, H 10.35%.

*2,3,6,7,10-Pentahexyloxy-11-pentyloxytriphenylene (**20**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.2 g, 0.269vmmol), butanone (120 ml), 1-iodopentane (0.10 g, 0.505 mmol) and potassium carbonate (0.11 g, 0.797 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol / toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.04vg (18%). ^{1}H NMR (CDCl$_3$): δ 0.92 (15H, t), 0.97 (3H, t), 1.35–1.50 (22H, m), 1.58 (12H, quint), 1.94 (12H, quint), 4.23 (12H, t), 7.84 (6H, s). ^{13}C NMR (CDCl$_3$): δ 14.06, 22.66, 25.84, 29.40, 31.68, 69.68, 107.28, 123.57, 148.93. MS *m*/*z*: 815 (M$^+$). Transition temperatures (°C): Cr 57.7 Col$_h$ 94.5 I. Elemental analysis: calculated for $C_{53}H_{82}O_6$, C 78.09, H 10.14; found, C 77.83, H 10.31%.

*2-Heptyloxy-3,6,7,10,11-pentahexyloxytriphenylene (**21**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.20 g, 0.269 mmol), butanone (120 ml), 1-bromoheptane (0.06 g, 0.335 mmol) and potassium carbonate (0.11 g, 0.797 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol / toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.09 g (40%). ^{1}H NMR (CDCl$_3$): δ 0.91 (3H, t), 0.92 (15H, t), 1.33–1.44 (24H, m), 1.58 (12H, quint), 1.84 (2H, quint), 1.93 (12H, quint), 4.22 (12H, t), 7.83 (6H, s). ^{13}C NMR (CDCl$_3$): δ 14.07, 22.64, 22.67, 25.87, 29.19, 29.43, 31.70, 31.87, 107.34, 123.61, 148.97. MS *m*/*z*: 843 (M$^+$). Transition temperatures (°C): Cr 58.0 Col$_h$ 86.3 I. Elemental analysis: calculated for $C_{55}H_{86}O_6$, C 78.34, H 10.28; found, C 78.64, H 10.56%.

*2,3,6,7,10-Pentahexyloxy-11-octyloxytriphenylene (**22**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.2 g, 0.269 mmol), butanone (120 ml), 1-bromooctane (0.06 g, 0.310 mmol) and potassium carbonate (0.11 g, 0.797 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.20 g (56%). ^{1}H NMR (CDCl$_3$): δ 0.89 (3H, t), 0.93 (15H, t), 1.29–1.43 (28H, m), 1.58 (12H, quint), 1.95 (12H, quint), 4.23 (12H, t), 7.83 (6H, s). ^{13}C NMR (CDCl$_3$): δ 14.07, 22.67, 25.87, 26.21, 29.34, 29.43, 31.70, 31.86, 107.34, 123.61, 148.97. MS *m*/*z*: 857 (M$^+$+1). Transition temperatures (°C): Cr 52.0 Col$_h$ 96.0 I. Elemental analysis: calculated for $C_{56}H_{88}O_6$, C 78.46, H 10.35; found, C 78.57, H 10.40%.

*2,3,6,7,10-Pentahexyloxy-11-(1-methylethoxy)triphenylene (**23**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.50 g, 0.672 mmol), butanone (110 ml), 2-bromopropane (0.25 g, 2.03 mmol) and potassium carbonate (0.28 g, 2.03 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.44 g (91%). ^{1}H NMR (CDCl$_3$): δ 0.93 (15H, t, J=6.96 Hz), 1.32–1.44 (18H, m), 1.40 (2H, quint), 1.45 (6H, d, J=6.05 Hz), 1.58 (10H, quint), 1.93 (10H, quint), 4.22 (10H, t, J=6.60 Hz), 4.71 (1H, septet, J=6.05 Hz), 7.81-1.84 (5H, m), 7.93 (1H, s). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.32, 22.65, 25.3, 25.84, 25.86, 29.36, 29.38, 29.40, 31.64, 31.68, 69.36, 69.52, 69.62, 69.79, 73.11, 107.01, 107.20, 107.41, 107.48, 112.69, 123.40, 123.45, 123.50, 123.59, 123.62, 124.59, 148.87, 149.04, 149.09, 150.35. MS *m/z*: 786 (M$^+$). Transition temperatures (°C): Cr 54.6 I. Elemental analysis: calculated for $C_{51}H_{78}O_6$, C 7.82, H 9.99; found, C 78.00, H 10.14%.

*2,3,6,7,10-Pentahexyloxy-11-(2-methylpropoxy)triphenylene (**24**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.96 g, 1.29 mmol), butanone (120 ml), 1-bromo-2-methylpropane (0.50 g, 3.65 mmol) and potassium carbonate (0.50 g, 3.62 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.77 g (75%). ^{1}H NMR ($CDCl_3$): δ 0.93 (15H, t, J=7.15 Hz), 1.13 (6H, d, J=6.60 Hz), 1.41 (20H, quint), 1.58 (10H, quint), 1.94 (10H, quint), 2.26 (1H, nonette), 4.00 (2H, d, J=6.42 Hz), 4.21–4.25 (10H, m), 7.82–7.84 (6H, m). ^{13}C NMR ($CDCl_3$): δ 14.05, 19.41, 22.65, 25.84, 28.57, 29.41, 29.47, 31.68, 69.6, 69.69, 69.71, 69.84, 76.02, 107.25, 107.25, 107.32, 107.34, 107.50, 107.57, 123.55, 123.59, 123.63, 123.65, 148.92, 148.94, 148.97, 148.98, 149.00, 149.19. MS *m/z*: 801 (M$^+$+1). Transition temperatures (°C): Cr 59.4 Col$_{\mathrm{h}}$ 85.4 I. Elemental analysis: calculated for $C_{52}H_{80}O_6$, C 77.95, H 10.06; found, C 77.74, H 10.14%.

*2,3,6,7,10-Pentahexyloxy-11-(3-methylbutoxy)triphenylene (**25**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.50 g, 0.672 mmol), butanone (70 ml), 1-bromo-3-methylbutane (0.20 g, 1.32 mmol) and potassium carbonate (0.28 g, 2.02 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane) and preparatory HPLC, recrystallised from ethanol and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.12 g (22%). ^{1}H NMR ($CDCl_3$): δ 0.94 (15H, t, J=7.33 Hz), 1.04 (6H, d, J=6.60 Hz), 1.36-1.43 (21H, m), 1.54–1.61 (10H, quint), 1.83 (2H, q) 1.94 (10H, quint), 4.22 (10H, t, J=6.78 Hz), 4.27 (2H, t, J=6.60 Hz), 7.84 (6H, s). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.66, 22.74, 25.84, 29.41, 31.68, 69.65, 69.70, 107.12, 107.33, 123.59, 148.91, 148.93, 148.97. MS *m/z*: 815 (M$^+$+1). Transition temperatures (°C): Cr 54.5 Col$_{\mathrm{h}}$ 105.0 I. Elemental analysis: calculated for $C_{53}H_{82}O_6$, C 78.09, H 10.14; found, C 77.98, H 10.24%.

*2,3,6,7,10-Pentahexyloxy-11-(4-methylpentyloxy)triphenylene (**26**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.50 g, 0.672 mmol), butanone (120 ml), 1-bromo-4-methylpentane (0.22 g, 1.33 mmol) and potassium carbonate (0.28 g, 2.02 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.34 g (61%). ^{1}H NMR ($CDCl_3$): δ 0.93 (15H, t, J=7.15 Hz), 0.96 (6H, d, J=6.60 Hz), 1.38–1.40 (22H, m), 1.54–1.62 (10H, m), 1.68 (1H, sept), 1.93 (12H, quint), 4.21 (2H, t, J=5.13 Hz), 4.22 (10H, t, J=6.60 Hz), 7.83 (6H, s). ^{13}C NMR ($CDCl_3$): δ 14.05, 22.62, 22.65, 25.84, 27.33, 27.90, 29.41, 31.68, 35.30, 69.69, 69.99, 107.28, 107.32, 123.58, 148.92, 148.95. MS *m/z*: 828 (M$^+$). Transition temperatures (°C): Cr 61.5 Col$_{\mathrm{h}}$ 105.3 I. Elemental analysis: calculated for $C_{54}H_{84}O_6$, C 78.21, H 10.21; found, C 77.71, H 11.1%.

*2-(2-Ethylbutoxy)-3,6,7,10,11-pentahexyloxytriphenylene (**27**).*

The same procedure was carried out as detailed in the synthesis of compound **4**, using the following quantities: compound **16** (0.5 g, 0.672 mmol), butanone (110 ml), 1-bromo-2-ethylbutane (1.50 g, 9.09 mmol) and potassium carbonate (0.28 g, 2.03 mmol). The product was purified by column chromatography (silica gel, 4:1 hexane/dichloromethane), recrystallised from ethanol/toluene (10:1) and dried (phosphorus pentoxide) to yield a colourless waxy solid. Yield: 0.34 g (61%). ^{1}H NMR ($CDCl_3$): δ 0.93 (15H, t, J=7.15 Hz), 1.01 (6H, t, J=7.33 Hz), 1.38–1.42 (24H, m), 1.51–1.64 (10H, m), 1.85 (1H, sept), 1.93 (10H, quint), 4.12 (2H, d, J=5.87 Hz), 4.22 (10H, t, J=5.68 Hz), 7.82–7.84 (6H, m). ^{13}C NMR ($CDCl_3$): δ 11.36, 14.06, 22.67, 23.63, 25.87, 29.44, 29.51, 31.70, 41.11, 69.70, 69.73, 69.82, 71.76, 106.99, 107.34, 107.37, 107.51, 107.53, 123.48, 123.57, 123.63, 123.66, 148.95, 148.99, 149.23. MS *m/z*: 829 (M$^+$+1). Transition temperatures (°C): Cr 44.4 Col$_{\mathrm{h}}$ 78.1 I. Elemental analysis: calculated for $C_{54}H_{84}O_6$, C 78.21, H 10.21; found, C 78.09, H 10.47%.

4. Conclusions

Two series of novel branched alkoxy chain triphenylene based discotic liquid crystalline materials have been prepared. The novel materials have been compared with known discotic liquid crystalline materials for their mesophase stabilities and morphologies. This comparison has revealed that the delicate balance between steric and space-filling effects of the peripheral branched chains often favours the space-filling effect with respect to the clearing point of the material and the steric effect often wins out with respect to the melting point. This has led to the generation of materials with enhanced isotropisation temperatures and reduced melting points compared with their straight chain analogues.

The low melting point of **7**, illustrates how the steric effect can reduce the melting point, whilst the space filling effect maintains the high clearing point. This effect is emphasised by **27**, where the same branch reduces the melting point, but the clearing point is also reduced, indicating that the space-filling effect of multiple peripheral chains is important. The clearing points of compounds **25** and **26** highlight the importance of the space filling effect, given that both compounds exhibit enhanced isotropisation temperatures relative to the parent compound **4**, when the steric effect of the branch and reduction in symmetry would have otherwise significantly reduced the clearing point.

Acknowledgements

The authors wish to thank the EPSRC for funding; Julie Haley, Carol Kennedy and Hull University's mass spectrometry staff for their assistance with the analytical data.

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