A series of novel triphenylenes has been synthesised by a combination of palladium catalysed coupling, oxidative cyclisation, bromination and nucleophilic aromatic substitution. The new derivatives are designed to have structures which are intermediate between the known symmetrical materials hexakis(hexyloxy)triphenylene and hexakis(hexylthio)triphenylene. The compounds having four hexyloxy and two hexylthio substituents form only Col₈ mesophases. Triphenylenes having four hexylthio and two hexyloxy substituents also give Col₈ mesophases but 3,6-bis(hexyloxy)-2,7,10,11-tetrakis(hexylthio)triphenylene 5 is unique in that it cools into a stable, more ordered phase. The low temperature phase, which appears to be indefinitely stable at ambient temperature, is assumed to be helical based on transition enthalpy data.

### Results and discussion

#### Synthesis

The target molecules of this study are shown in Fig. 1, along with the reference compounds hexakis(hexylthio)triphenylene 8 and hexakis(hexyloxy)triphenylene 1.

The synthesis of unsymmetrically substituted triphenylenes can be achieved by coupling certain biphenyls and benzene derivatives. Alternatively terphenyls can be constructed and cyclised to the triphenylene in a separate step. The first strategy was employed for synthesis of 2,3,6,7-tetrakis(hexyloxy)-10,11-bis(hexylthio)triphenylene 2 as shown in Scheme 1. Suzuki coupling of 4-bromoveratrole 9 with phenylboronic acid 10 yielded 3,4-dimethoxybiphenyl 11. Oxidative coupling with veratrole using ferric chloride 22 yielded 2,3,6,7-tetrahydroxytriphenylene 12 directly. This oxidative coupling is successful because of the complementary functionality on the two partners (the biphenyl is most susceptible to oxidation and the dialkoxybenzene is susceptible to electrophilic attack). Removal of the methyl groups (HBr in acetic acid) followed by realkylation with 1-bromohexane afforded 2,3,6,7-tetrakis(hexylthio)triphenylene 13. Bromination with molecular bromine introduced bromide at both free β-positions to give 2,3-dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene 14. Displacement of the bromides using hexanethiol yielded 2.

Syntheses of the isomers 3 and 4 were achieved following related strategies (Schemes 2 and 3). The synthesis of 3 started with 4-bromophenol 16 which was alkylated and converted to the corresponding boronic acid via formation of the Grignard reagent and quench with trimethyl borate. Double Suzuki coupling with 1,2-dibromo-3,4-bis(hexyloxy)benzene 15 (prepared by bromination of 1,2-bis(hexyloxy)benzene) gives terphenyl 19. Treatment of 19 with ferric chloride results in no formation of triphenylene product because the electronic (directing) effects of the 4′-alkoxy substituents do not favour either location of positive charge on the 3′-position or electrophilic attack on the 3″-position. Consequently cyclisation was achieved photochemically 23 to give 2,3,7,10-tetrakis(hexyloxy)triphenylene 20. Bromination again gave exclusive substitution at the free β-positions yielding 2,7-dibromo-3,6,10,
11-tetrakis(hexyloxy)triphenylene 21. Substitution of the bromides with hexanethiol gave 3.

Synthesis of 4 was achieved following an almost identical strategy starting from 3-bromophenol. In this case, however, intermediate terphenyl 25 can be easily cyclised to triphenylene 26 by treatment with ferric chloride. Bromination and substitution with hexanethiol yielded 4.

The synthesis of bis(hexyloxy)tetrakis(hexylthio)triphenylenes 5 and 6 was achieved following related coupling–cyclisation protocols as shown in Schemes 4 and 5. Suzuki coupling between 1,2-dibromobenzene and 4-hexyloxyphenylboronic acid 18 gave terphenyl 29. As expected, cyclisation to the corresponding triphenylene 30 could not be achieved using ferric chloride and required photochemical oxidation (hv–I2).

The four free β-positions of triphenylene 30 were smoothly brominated with molecular bromine to give tetrabromide 31 and nucleophilic displacement of the bromides with hexanethiol afforded target 3,6-bis(hexyloxy)-2,7,10,11-tetrakis(hexylthio)triphenylene 5. Synthesis of 6 followed an almost identical route. However, in this case it was again possible to cyclise intermediate terphenyl 32 to triphenylene 33 simply using ferric chloride.

It was envisaged that synthesis of the isomeric triphenylene 7 could be achieved following a similar strategy via 2,3-bis(hexyloxy)triphenylene 37 (Scheme 6). 1,2-Dibromo-3,4-bis(hexyloxy)benzene 15 and phenylboronic acid were coupled together under Suzuki conditions to give the terphenyl 35.
It was hoped that bromination would yield dibromide which could be converted into another nucleophilic displacement. Surprisingly, treatment of with bromine resulted in no reaction, even at elevated temperatures.

Mesophase behaviour

The mesophase behaviour of the novel triphenylene derivatives was investigated by polarising optical microscopy and differential scanning calorimetry (DSC). As expected, intermediate terphenyls, both di- and tetra-substituted triphenylenes and dialkoxytetrahalogenotriphenylenes proved to be non-mesogenic. Dibromotetraakis(hexyloxy)triphenylene 14, 21 and 27 do, however, exhibit enantiotropic liquid crystal phases (Table 1). The 2,7- and 3,6-dibromides 21 and 27 are particularly interesting. First heating of samples which have been pre-cooled to −80 °C reveals melting points (K–Colh) of 63 °C and 40 °C respectively. Both have clearing points around 179 °C. Their columnar phases (assigned as Colh on the basis of their characteristic textures) are stable down to below ambient temperature.

Mixed hexyloxy-hexylthio-triphenylenes show mesophase behaviour which is dependent on the position and relative number of substituents. 2,3,6,7-Tetrakis(hexyloxy)-10,11-bis(hexylthio)triphenylene 2 melts directly from the crystalline solid to isotropic liquid at 86 °C. When the isotropic liquid is 10-bis(hexylthio)triphenylene 40. It was hoped that bromination would yield dibromide which could be converted into 7 by another nucleophilic displacement. Surprisingly, treatment of 40 with bromine resulted in no reaction, even at elevated temperatures.

**Scheme 2** Hx = n-hexyl. Reagents and conditions: (i) Br₂, CH₂Cl₂, 0 °C, 2 h, (ii) HxBr, EtOH, K₂CO₃, reflux, (iii) Mg, Et₂O, (iv) B(OH)₃, (v) H₂O⁺, (vi) PhCl, Na₂CO₃, PPh₃, toluene–EtOH–H₂O, reflux, 4 h, (vii) hv, I₂, benzene, 72 h, (viii) Br₂, CH₂Cl₂, 0 °C, 30 min, (ix) HxSH, KO′Bu, NMP, 70 °C, 24 h.

**Scheme 3** Hx = n-hexyl. Reagents and conditions: (i) HxBr, EtOH, K₂CO₃, reflux, (ii) Mg, Et₂O, (iii) B(OH)₃, (iv) H₂O⁺, (v) PhCl, Na₂CO₃, PPh₃, toluene–EtOH–H₂O, reflux, 4 h, (vii) hv, I₂, benzene, 72 h, (viii) Br₂, CH₂Cl₂, 0 °C, 30 min, (ix) HxSH, KO′Bu, NMP, 70 °C, 24 h.

**Scheme 4** Hx = n-hexyl. Reagents and conditions: (i) 15, PdCl₂, Na₂CO₃, PPh₃, toluene–EtOH–H₂O, reflux, 4 h, (ii) hv, I₂, benzene, 72 h, (iii) Br₂, CH₂Cl₂, rt, 2 h, (iv) HxSH, KO′Bu, NMP, 70 °C, 24 h.
cooled, a monotropic Colh mesophase forms at 81 °C which remains until the sample recrystallises at 52 °C. Substitution of hexylthio groups at the 2,7- or 3,6-positions (3 and 4) leads to materials with enhanced mesophase stability and also suppresses crystallisation. Triphenylene 3 (pre-cooled to −80 °C) has a melting point (K–Colh) of 24 °C and clears at 102 °C. The material cools into a Colh phase at 99 °C and does not recrystallise down to below 0 °C. Similarly triphenylene 4 (which on first heating gives a melting point of 45 °C) gives a Colh phase from 118 °C down to below ambient temperature (Table 2). No additional transitions are observed for either sample by microscopy or DSC.

Triphenylenes 5 and 6, which have four hexylthio- and two hexyloxy-substituents, are closely related to hexakis(hexylthio)triphenylene 8 and were considered most likely to exhibit the helical phase. 2,7-Bis(hexyloxy)-3,6,10,11-tetrakis(hexylthio)triphenylene 6, as prepared, is liquid crystalline at room temperature. DSC (after cooling to −80 °C) reveals a melting point of 54 °C and a clearing point of 100.5 °C. Cooling the sample gives rise to a Colh mesophase (as evidenced by microscopy) at 97 °C which is stable down to below ambient temperature. No further transitions were evident by microscopy or DSC.

Isomeric 3,6-bis(hexyloxy)-2,7,10,11-tetrakis(hexylthio)triphenylene 5 is unique in this series. First heating reveals a melting point of 72 °C and clearing point of 111 °C. When the sample is cooled a Colh mesophase is produced below 108 °C. Further cooling gives another, reversible transition at 32 °C (38 °C on heating) (Fig. 2). The enthalpy of this transition6 (1.1 J g⁻¹ compared to 0.8 J g⁻¹ for Colh–I and 4.7 J g⁻¹ for K–Colh) leads to the preliminary assignment that this is indeed a Colh–H transition. The transition can also be observed by microscopy as a discernible brightening of the homeotropic regions of the sample. The phase appears to be indefinitely stable at ambient temperature and no

Scheme 5 Hx = n-hexyl. Reagents and conditions: (i) 24, PdCl₂, Na₂CO₃, PPh₃, toluene–EtOH–H₂O, reflux, 4 h, (ii) FeCl₃, CH₂Cl₂, rt, 2 h, (iii) Br₂, CH₂Cl₂, rt, 2 h, (iv) HxSH, K₂Bu, NMP, 70 °C, 24 h.

Scheme 6 Hx = n-hexyl. Reagents and conditions: (i) 10, PdCl₂, Na₂CO₃, PPh₃, toluene–EtOH–H₂O, reflux, 48 h, (ii) FeCl₃, CH₂Cl₂, rt, 2 h, (iii) Br₂, benzene, 72 h.

Scheme 7 Mechanism for the formation of 36.

Scheme 8 Attempted bromination of 2,3-bis(hexyloxy)triphenylene 37.
crystallisation is observed when the sample is cooled down to 
$-40^\circ C$ (DSC) (Table 3).

These observations provide further evidence that formation of helical mesophases in triphenylene discogens requires specific molecular structure. Previously the phase has only been observed for symmetrical hexakis(hexylthio)triphenylene derivatives with different chain lengths exhibit Colh phases only. We have now shown that an additional phase (assumed to be helical) is formed when 3,6-bis(hexyloxy)-2,7,10,11-tetakis(hexylthio)triphenylene 5 is cooled. Its isomer 2,7-bis(hexyloxy)-3,6,10,11-tetrakis(hexylthio)triphenylene 6, however, does not show this behaviour. This observation further emphasises the structural subtlety required for generation of the additional, more ordered mesophase. Most important, perhaps, is the observation that the more ordered phase of 5 can be cooled to ambient temperature and below (the helical phase of 8 can only be supercooled to about $40^\circ C$). This observation opens up the possibility of using the materials in room temperature devices. It is likely that the phase can be stabilised further through careful synthetic modification and through formation of mixtures. All the materials tend to form homeotropically aligned films when cooled from the isotropic liquid (typical for triphenylenes and other discotic liquid crystals) and this property is also likely to be important for device fabrication.

### Conclusions

A series of mixed hexyloxy-hexylthio-triphenylenes has been synthesised to determine the structural features governing the formation of helical mesophases. It has been shown that four sulfide substituents (plus two alkoxides) are required to induce the additional, more ordered phase. Furthermore, the position of substitution is crucial for its formation. 3,6-Bis(hexyloxy)-2,7,10,11-tetrakis(hexylthio)triphenylene 5 gives the phase when cooled from the Colh mesophase and it is stable below ambient temperature. However, its isomer 2,7-bis(hexyloxy)-3,6,10,11-tetrakis(hexylthio)triphenylene 6 only gives the Colh...
Further studies are underway to extend the series and confirm the structure of the low temperature phase of 5.

**Experimental**

NMR spectra were recorded on either a JEOL EX270 FT or Varian 300 MHz spectrometer (coupling constants are quoted in Hz). Elemental analyses were performed on a Carlo Erba 1106 elemental analyser at UEA. Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea. Transition temperatures were observed using an Olympus BH-2 polarising microscope with a TMS 92 thermal analyser and Linkham THM 600 cell. Differential scanning calorimetry was performed on a TA DSC 10 instrument with a heating/cooling rate of 5 or 10 °C min⁻¹. Column chromatography was performed at atmospheric pressure.

**Table 2** Transition temperatures (°C) and enthalpies (J g⁻¹) of tetrakis(hexyloxy)bis(hexylthio)triphenylenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K–Colh (ΔH)</td>
<td>Colh–I (ΔH)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>(K–I 86)</td>
<td>81 (0.5)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>24° (3.3)</td>
<td>102 (0.7)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>45° (4.5)</td>
<td>123 (0.8)</td>
</tr>
</tbody>
</table>

*Observed if sample is pre-cooled to −80 °C.

**Table 3** Transition temperatures (°C) and enthalpies (J g⁻¹) of bis(hexyloxy)tetrakis(hexylthio)triphenylenes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K–Colh (ΔH)</td>
<td>H–Colh (ΔH)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>72 (4.7)</td>
<td>38 (1.3)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>54 (4.0)</td>
<td>—</td>
</tr>
</tbody>
</table>

*Observed if sample is pre-cooled to −80 °C.
pressure using Lancaster silica gel 60, 0.060–0.2 mm (7–230 mesh). Commercially available starting materials were used without further purification.

3.4-Dimethoxyphenyl 11
Phenylboronic acid 10 (39.3 g, 0.322 mol), 4-bromoveratrole 9 (35 g, 0.161 mol), sodium carbonate (50 g, 0.483 mol), palladium chloride (0.5 g, 4.83×10⁻³ mol) and triphenylophosphine (2.53 g, 9.66×10⁻³ mol) were stirred under reflux in a mixture of toluene, ethanol and water (3 : 3 : 1, 200 mL) for 48 hours. The solvents were evaporated, water added and the mixture extracted with dichloromethane (4 × 150 mL). The crude residue was dissolved in dichloromethane and washed with ethanol. The solvents were evaporated and the title compound as colourless crystals (21.32 g, 62%).

Anal. Found: C, 80.13; H, 9.55 (C₂H₂O₂ requires C, 80.25; H 9.55%); δ₁H (CDCl₃, TMS, 300 MHz) 7.91 (2H, s), 4.62 (4H, s), 2.81 (6H, t, J = 7.7); δ₁C (75.45 MHz; CDCl₃) 150.0, 149.9, 149.4, 129.2, 126.2, 124.4, 123.9, 123.1, 107.4, 107.3, 69.8, 69.5, 31.7(6), 31.7(4), 29.4(8), 29.4(2), 25.9, 22.7, 14.1; m/z (EI) 628 (M⁺, 30%).

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene 14
2,3,6,7-Tetrahalohexyloxytriphenylene 13 (2.0 g, 3.2×10⁻³ mol) was dissolved in dichloromethane (100 mL). The mixture was cooled using an ice–salt bath and bromine (3.0 g, 0.019 mol) was added drop-wise until the red colour persisted. The mixture was stirred for 2 hours following which sodium metabisulfite (20%) was added. The mixture was extracted with dichloromethane (3 × 150 mL) and the crude product was precipitated by addition of excess methanol. Purification by column chromatography (using petroleum ether–dichloromethane (4 : 1) as eluent) gave the title compound (2.12 g, 85%).

Anal. Found: C, 64.36; H 7.43 (C₂H₂O₂ requires C, 64.12; H 7.38%); δ₁H (CDCl₃, TMS, 300 MHz) 8.62 (2H, s), 7.79 (2H, s), 7.76 (2H, s), 4.23 (8H, m), 1.95 (8H, m), 1.49 (24H, m), 0.88 (12H, m); δ₁C (75.45 MHz; CDCl₃) 150.2, 149.3, 123.9, 127.6, 124.5, 121.7, 120.2, 106.7, 106.4, 69.6, 69.4, 31.7, 29.4, 25.9, 22.7, 14.1; m/z (EI) 786 (M⁺, 100%).

2,3,6,7-Tetrakis(hexyloxy)-10,11-bis(hexylthio)triphenylene 2
Potassium tert-butoxide (0.855 g, 7.63×10⁻³ mol) was added to a stirred solution of hexanethiol (0.90 g, 7.63×10⁻³ mol) in 1-methyl-2-pyrrolidone (NMP) (10 mL). The solution was heated to 100°C for 5 minutes and then cooled to 70°C. 2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene 14 (1.50 g, 1.90×10⁻³ mol) was added and the solution was stirred for 24 hours. 1-Bromohexane (0.63 g, 3.75×10⁻³ mol) was added and the mixture stirred for 24 hours at room temperature. The solution was worked up by addition of water and the organic layer separated. The aqueous layer was further extracted with diethyl ether (3 × 20 mL). The organic extracts were combined, washed with brine, dried (Na₂SO₄) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 9 : 1 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (0.57 g, 35%).

Anal. Found: C, 75.15; H 9.70; S 7.48 (C₄H₆O₂S₂ requires C, 75.35; H 7.67; S 7.48%); δ₁H (CDCl₃, TMS, 300 MHz) 8.34 (2H, s), 7.92 (2H, s), 7.81 (2H, m), 4.26–4.40 (8H, m), 3.09 (4H, t, J = 7.4) 1.99–1.90 (8H, m), 1.79–1.72 (4H, m), 1.63–1.38 (36H, m), 0.95–0.85 (18H, m); δ₁C (75.45 MHz; CDCl₃) 150.0, 149.5, 135.6, 127.8, 124.6, 123.6, 122.9, 121.0, 104.6, 104.2, 56.1, 55.9; m/z (EI) 348 (M⁺, 100%).

1,2-Dibromo-4,5-bis(hexyloxy) benzene 15
1,2-Bis(hexyloxy)benzene (5.00 g, 0.017 mol) was stirred in 1,2-bis(hexyloxy)benzene (5.00 g, 0.017 mol) and triphenylphosphate (0.855 g, 7.63×10⁻³ mol) and stirred for 2 hours following which sodium metabisulfite (20%) was added. The mixture was extracted with dichloromethane (3 × 150 mL). The combined organic extracts were washed with brine, dried (Na₂SO₄) and the solvents evaporated. The crude product was purified by column chromatography (using dichloromethane (4 : 1) as eluent) and recrystallised from ethanol to give the title compound (15.0 g, 70%) which was used without further purification.

Anal. Found: C, 75.35; H 7.67; S 7.48 (C₄H₆O₂S₂ requires C, 75.35; H 7.67; S 7.48%); δ₁H (CDCl₃, TMS, 300 MHz) 8.34 (2H, s), 7.92 (2H, s), 7.81 (2H, m), 4.26–4.40 (8H, m), 3.09 (4H, t, J = 7.4) 1.99–1.90 (8H, m), 1.79–1.72 (4H, m), 1.63–1.38 (36H, m), 0.95–0.85 (18H, m); δ₁C (75.45 MHz; CDCl₃) 150.0, 149.5, 135.6, 127.8, 124.6, 123.6, 122.9, 121.0, 104.6, 104.2, 56.1, 55.9; m/z (EI) 348 (M⁺, 100%).

6.88 x 10^{-4} \text{ mol}) were stirred under reflux in a mixture of toluene, ethanol and water (3 : 3 : 1, 100 mL) for 24 hours. The solvents were evaporated and water added, and the mixture was further treated with dichloromethane (4 x 150 mL) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 1:4 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (0.55 g, 20%).

δ_{1} (CDCl₃, TMS, 300 MHz) 7.29 (2H, s), 7.86 (2H, s), 7.75 (2H, s), 4.28–4.20 (8H, m), 3.08 (4H, t, J = 7.4), 1.99–1.92 (8H, m), 1.80–1.70 (4H, m), 1.58–1.25 (36H, m), 0.89–0.83 (18H, m); δ_{c} (75.45 MHz; CDCl₃) 155.9, 149.4, 128.2, 126.6, 124.2, 121.3, 106.9, 104.4, 69.7, 69.1, 32.5, 31.7, 31.5, 29.5, 29.4, 29.1, 28.9, 25.9, 25.8, 22.7, 14.1; m/z (FABMS) 861 (M+ + H, 100%); Acc. Mass (ES) 861.5887 (C₄₈H₅₆O₄S₂ (M + H) = 861.5889).

3.4',5',3'-Tetrakis(hexyloxy)-1,1'-2',1'-terphenyl 25

3-Hexyloxyphenylboronic acid 24 (15.0 g, 0.056 mol), 1,2-dibromo-4,5-bis(hexyloxy)benzene 15 (10.0 g, 0.023 mol), sodium carbonate (8.00 g, 0.075 mol), palladium chloride (0.12 g, 3.44 x 10^{-4} \text{ mol}) and triphenylphosphate (0.12 g, 6.88 x 10^{-4} \text{ mol}) were stirred under reflux in a mixture of toluene, ethanol and water (3 : 3 : 1, 100 mL) for 24 hours. The solvents were evaporated, water added and the mixture was further treated with dichloromethane (4 x 150 mL). The solvents were evaporated and the crude product was purified by column chromatography (eluting with 1:4 petroleum ether–dichloromethane) to give the title compound as a colourless oil (10.5 g, 72%).

δ_{1} (CDCl₃, TMS, 300 MHz) 7.10 (2H, t, J = 7.9), 6.95 (2H, s), 6.75–6.66 (6H, m), 4.06 (4H, t, J = 6.6), 3.73 (4H, t, J = 6.6), 1.89–1.79 (4H, m), 1.70–1.61 (24H, m), 0.93–0.83 (12H, m); δ_{c} (75.45 MHz; CDCl₃) 158.9, 148.7, 143.2, 133.3, 128.9, 122.4, 116.3, 116.2, 113.2, 69.6, 68.0, 31.7, 31.6, 29.4, 29.2, 25.8, 25.7, 22.7, 14.1; m/z (EI) 630 (M+, 40%).

2.3,6,11-Tetrakis(hexyloxy)triphenylene 20

2,3,6,11-Tetrakis(hexyloxy)triphenylene 20 (2.40 g, 3.82 x 10^{-3} \text{ mol}) was stirred in dichloromethane (10 mL) at 0°C. Bromine (1.24 g, 7.64 x 10^{-3} \text{ mol}) was added drop-wise and the solution stirred for 30 minutes. A solution of sodium metabisulphite was then added and the mixture extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried (MgSO₄) and the crude product purified by column chromatography (eluting with 1:4 dichloromethane–petroleum ether) to give the title compound (2.50 g, 83%) as a colourless solid.

δ_{1} (CDCl₃, TMS, 300 MHz) 157.6, 149.6, 129.9, 124.4, 124.2, 123.3, 106.9, 104.4, 69.7, 69.1, 32.5, 31.7, 31.5, 29.5, 29.4, 29.1, 25.6, 22.4(3), 22.4(0), 13.8; m/z (EI) 630 (M+, 50%).

2.3,7,10-Tetrakis(hexyloxy)-1,1'-2',1'-terphenyl 19

1-Bromohexane (1.25 g, 6.74 x 10^{-3} \text{ mol}) and iodine (1.09 g, 4.3 x 10^{-3} \text{ mol}) were dissolved in benzene (250 mL). The mixture was stirred and irradiated with ultra-violet light at room temperature for 72 hours. Sodium metabisulfite solution was added to the irradiated solution and the mixture extracted with dichloromethane (3 x 150 mL). The combined organic extracts were dried (MgSO₄). The solvent was further extracted with dichloromethane (3 x 150 mL) and the product was recrystallised from propan-2-ol to give the title compound (2.50 g, 83%) as a colourless solid.

δ_{1} (CDCl₃, TMS, 300 MHz) 8.38 (2H, d, J = 9.1), 7.95 (2H, d, J = 2.6), 7.90 (2H, s), 7.25 (2H, dd, J = 9.1 and 2.6), 4.24–4.16 (8H, m), 1.96–1.85 (8H, m), 1.59–1.34 (24H, m), 0.96–0.90 (12H, m); δ_{c} (75.45 MHz; CDCl₃) 157.8, 143.9, 130.5, 124.6, 124.3, 123.7, 116.2, 107.2, 107.0, 69.6, 68.5, 31.7, 29.5, 24.9, 25.9, 25.8, 22.7, 14.1; m/z (EI) 628 (M+, 40%).
300 MHz) 8.33 (2H, s), 7.75 (2H, s), 7.60 (2H, s), 4.27–4.18 (8H, m), 2.67–1.91 (8H, m), 1.62–1.25 (24H, m), 0.97–0.92 (12H, m); δC (75.45 MHz; CDCl3) 153.9, 149.9, 121.9, 127.4, 123.9, 122.9, 112.4, 107.1, 105.1, 69.6, 69.4, 31.8, 31.7, 29.5, 29.3, 25.9, 25.8, 22.7, 22.6, 14.1; m/z (FABMS) 786 (M⁺, 10%).

2,3,6,11-Tetrakis(hexyloxy)-7,10-bis(hexylthio)triphenylene 4

Potassium tert-butoxide (5.00 g, 0.045 mol) was added to a stirred solution of hexanethiol (5.25 g, 0.045 mol) in NMP (30 mL). The solution was heated to 100 °C for 5 minutes and then cooled to 70 °C. 2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene 27 (3.50 g, 4.45 × 10⁻² mol) was added and the solution was stirred for 24 hours. 1-Bromohexane (3.00 g, 0.019 mol) was added and the mixture stirred at room temperature for 24 hours. The reaction was worked up by addition of water and the organic layer separated. The aqueous layer was further extracted with diethyl ether (3 × 50 mL). The organic extracts were combined, washed with brine, dried (Na₂SO₄) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 9:1 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (1.22 g, 32%) as a colourless solid.

δH (CDCl₃, TMS, 300 MHz) 8.33 (2H, s), 7.86 (2H, s), 7.84 (2H, s), 4.28–4.22 (8H, m), 3.07 (4H, t, J ~ 6.5 Hz), 2.03–1.94 (4H, m), 1.90–1.86 (8H, m), 1.59–1.36 (12H, m), 0.97–0.92 (12H, m); δC (75.45 MHz; CDCl3) 155.7, 149.6, 127.9, 125.9, 124.2, 123.4, 122.1, 115.7, 104.0, 69.4, 31.7, 29.5, 25.9, 22.7, 22.6, 14.1; m/z (FABMS) 861 (M⁺, 10%).

1.2-Bis(4-hexyloxyphenyl)benzene 29

4-Hexyloxyphenylboronic acid 18 (8.47 g, 0.038 mol), 1,2-dibromobenzene 28 (3.00 g, 0.013 mol), sodium carbonate (6.36 g, 0.06 mol), palladium chloride (0.13 g, 7.11 × 10⁻² mol) and triphenylphosphine (0.38 g, 1.44 × 10⁻² mol) were stirred under reflux in a mixture of toluene, ethanol and water, (3 : 1 : 200 mL) for 24 hours. The solvents were evaporated, water was added and the mixture was stirred with dichloromethane (4 × 150 mL). The solvents were evaporated and the crude product was purified by column chromatography (eluting with 1:4 petroleum ether–dichloromethane), to give the title compound as a colourless oil (3.8 g, 70%).

Anal. Found: C 48.22; H 4.28; Br 43.01%; δH (CDCl3, TMS, 300 MHz) 7.98 (2H, s), 7.89 (2H, s), 7.26 (2H, s), 4.16 (4H, t, J = 6.5 Hz), 2.03–1.94 (4H, m), 1.66–1.40 (12H, m), 0.99–0.95 (6H, m); δC (75.45 MHz; CDCl3) 155.1, 129.4, 127.9, 127.7, 126.9, 122.8, 114.1, 104.7, 69.4, 31.7, 29.5, 22.7, 14.1; m/z (FABMS) 786 (M⁺, 50%).

3.6-Bis(hexyloxy)-7,10-tetrakis(hexylthio)triphenylene 5

Potassium tert-butoxide (5.60, 0.050 mol) was added to a stirred solution of hexanethiol (5.95 g, 0.050 mol) in NMP (30 mL). The solution was heated to 100 °C for 5 minutes and then cooled to 70 °C. 2,3,6,11-Tetrabromo-7,10-bis(hexylthio)triphenylene 31 (2.50 g, 3.36 × 10⁻² mol) was added and the mixture stirred for 24 hours. 1-Bromohexane (2.50 g, 0.015 mol) was added and the reaction stirred for a further 24 hours at room temperature. The solution was worked up by addition of water and the organic layer separated. The aqueous layer was further extracted with diethyl ether (3 × 50 mL). The organic extracts were combined, washed with brine, dried (Na₂SO₄) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 9:1 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (0.98 g, 33%).

Anal. Found: C 72.62; H 9.52; S 14.38 (C₅₄H₈₄O₂S₄ requires C 72.65; H 9.42; S 14.35%); δH (CDCl3, TMS, 300 MHz) 8.22 (2H, s), 8.20 (2H, s), 7.65 (2H, s), 4.27 (4H, t, J = 6.5 Hz), 3.08 (8H, m), 2.03–1.94 (4H, m), 1.83–1.73 (8H, m), 1.63–1.34 (36H, m), 0.98–0.90 (18H, m); δC (75.45 MHz; CDCl3) 156.3, 135.8, 128.5, 127.4, 127.0, 123.2, 123.0, 122.9, 103.9, 66.1, 33.9, 32.1, 22.7, 31.8, 31.6, 29.3, 28.0, 28.9, 260, 22.7, 22.6, 14.1; m/z (FABMS) 893 (M⁺ + H⁺, 100%).

1.2-Bis(3-hexyloxyphenyl)benzene 32

3-Hexyloxyphenylboronic acid 24 (11.30 g, 0.043 mol), 1,2-dibromobenzene 28 (5.00 g, 0.018 mol), sodium carbonate (8.80 g, 0.083 mol), palladium chloride (0.18 g, 9.84 × 10⁻³ mol) and triphenylphosphine (0.53 g, 1.97 × 10⁻² mol) were stirred under reflux in a mixture of toluene, ethanol and water (3 : 1 : 200 mL) for 24 hours. The solvents were evaporated and water was added. The mixture was extracted with dichloromethane (4 × 150 mL) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 1:4 petroleum ether–dichloromethane) to give the title compound as a colourless oil (7.50%, 82%).

δH (CDCl3, TMS, 300 MHz) 7.45–7.37 (4H, m), 7.11 (2H, t, J = 7.8 Hz), 7.66–7.67 (6H, m), 3.73 (4H, t, J = 6.6 Hz), 1.68–1.60 (4H, m), 1.42–1.26 (12H, m), 0.92–0.87 (6H, m); δC (75.45 MHz; CDCl3) 158.7, 142.9, 140.5, 130.4, 128.8, 127.5, 127.4, 115.7, 113.4, 67.8, 31.4, 28.9, 25.5, 22.5, 13.9; Acc. Mass (FAB) 431.2950 (C₅₄H₈₄O₂ (M⁺ + H⁺) requires 431.2950).
2.7-Bis(hexyloxy)triphenylene 33

1.2-Bis(3-hexyloxyphenyl)benzene 32 (5.0 g, 0.012 mol) was stirred in dichloromethane (200 mL) at room temperature. Iron(n) chloride (3.80 g, 0.023 mol) was added and the mixture stirred for a further two hours. Methanol and water were then added and the mixture extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried (MgSO\(_4\)) and the solvents were evaporated. Purification of the crude product by column chromatography (eluting with 1:4 dichloromethane–petroleum ether) gave the title compound (3.38 g, 68%) as a cream powder.

Mp 102.5 °C. Anal. Found: C 48.39; H 4.30; Br 43.01%); C\(_{30}\)H\(_{32}\)O\(_2\)Br\(_4\) requires C 48.39; H 4.30; Br 43.01%)

Bromine (6.57 g, 0.04 mol) was added and the solution stirred in dichloromethane (10 mL) at room temperature. Potassium metabisulfite solution was added to the mixture and the mixture was then cooled (ice–salt bath) and methanol (100 mL) was added carefully with stirring. The solvents were evaporated and the product was recrystallised from pentanol to give the title compound (2.08 g, 68%).

The product was recrystallised from pentanol to give the title compound (2.13 g, 68%).

Mp 180 °C. Anal. Found: C 48.51; H 4.30; Br 43.01%); \(\delta_1\) (CDCl\(_3\), TMS, 300 MHz) 8.06 (2H, s), 7.89 (2H, s), 7.10 (2H, s), 7.06 (8H, s), 2.56 (12H, s), 2.20 (4H, s), 1.99–1.93 (4H, m), 1.64–1.42 (12H, m) 0.99–0.95 (6H, m); \(\delta_C\) (75.45 MHz; CDCl\(_3\)) 154.1, 128.9, 127.4, 127.6, 121.9, 123.1, 122.0, 114.3, 104.2, 69.2, 31.5, 29.0, 25.6, 22.5, 13.9; \(\text{m/z}\) (FABMS) 744 (M\(^+\), 100%).

2.7-Bis(hexyloxy)triphenylene 33 (1.76 g, 4.11 × 10\(^{-3}\) mol) was stirred in dichloromethane (10 mL) at room temperature. Bromine (6.57 g, 0.04 mol) was added and the solution stirred for 24 hours. A solution of sodium metabisulfite was added and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried (MgSO\(_4\)) and the crude product was purified by column chromatography (eluting with 1:4 dichloromethane–petroleum ether). The product was recrystallised from pentanol to give the title compound (2.08 g, 68%).

2.7-Bis(hexyloxy)triphenylene 33 (1.76 g, 4.11 × 10\(^{-3}\) mol) was stirred in dichloromethane (10 mL) at room temperature. Bromine (6.57 g, 0.04 mol) was added and the solution stirred for 24 hours. A solution of sodium metabisulfite was added and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried (MgSO\(_4\)) and the solvents were evaporated and water was added. The mixture was extracted with dichloromethane (4 × 100 mL). The crude product was purified by column chromatography (eluting with 1:4 petroleum ether–dichloromethane) to give the title compound as a colourless oil (3.40 g, 86%) which crystallised on standing.

Anal. Found: C 83.67; H 8.76 (C\(_{30}\)H\(_{34}\)O\(_2\) requires C 83.72; H 8.84%); \(\delta_1\) (CDCl\(_3\), TMS, 300 MHz) 7.22–7.10 (10H, m), 6.95 (2H, s), 4.06 (4H, t, \(J = 6.8\)), 1.89–1.80 (4H, m), 1.57–1.26 (12H, m), 0.93–0.88 (6H, t, \(J = 6.9\)), \(\delta_C\) (75.45 MHz; CDCl\(_3\)) 148.5, 141.6, 133.2, 129.9, 127.8, 126.2, 116.2, 69.4, 31.9, 29.2, 25.6, 22.5, 13.8; \(\text{m/z}\) (EI) 430 (M\(^+\), 50%).

2.3-Bis(hexyloxy)triphenylene 37

1.2-Bis(hexyloxy)-3,4-diphenylbenzene 35 (1.50 g, 6.90 × 10\(^{-3}\) mol) and iodine (1.08 g, 4.25 × 10\(^{-3}\) mol) were dissolved in benzene (250 mL). The mixture was stirred and irradiated with ultra-violet light at room temperature for 72 hours.

Sodium metabisulfite solution was added to the mixture and the organic phase separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic phases dried (MgSO\(_4\)). The solvent was evaporated and the crude product purified by column chromatography (eluting with 1:1 petroleum ether–dichloromethane) to give the title compound (0.85 g, 57%).

2,3-Bis(hexyloxy)-7,10-dichlorotriphenylene 39

This compound was obtained from a mixture of 2,3,7,10-tetrabromo-6,11-bis(hexyloxy)triphenylene 34 (3.38 g, 68%) as a cream powder.

2,7-Bis(hexyloxy)triphenylene 33 (3.80 g, 8.85 × 10\(^{-3}\) mol) was stirred in dichloromethane (300 mL) at room temperature. Iron(n) chloride (45.0 g, 0.27 mol) was slowly added and the solution stirred for two hours. The reaction mixture was then cooled (ice–salt bath) and methanol (100 mL) carefully added with stirring. The solvents were evaporated and dichloromethane was added to the residue. The organic phase was washed with water and the aqueous layer extracted with dichloromethane (3 × 150 mL). The solvent was evaporated to a brown solid which was purified by column chromatography (eluting with 1:1 petroleum ether–dichloromethane) to give the title compound (2.24 g, 51%).

2.3-Bis(hexyloxy)-1,4-dibromo-7,10-dichlorotriphenylene 39

2,3-Bis(hexyloxy)-7,10-dichlorotriphenylene 39 (1.00 g, 2.01 × 10\(^{-3}\) mol) was stirred in dichloromethane (100 mL) and bromine (1.60 g, 0.01 mol) was added. The mixture was stirred at room temperature for 2 hours. Sodium metabisulfite solution was added and the organic phase separated. The aqueous layer was further extracted with dichloromethane (3 × 100 mL) and the combined organic phases were dried (MgSO\(_4\)). The solvent was removed \(\text{in vacuo}\) and the crude product purified by column chromatography (eluting with 4:1 petroleum ether–dichloromethane) to give the title compound (2.94 g, 100%).

2.3-Bis(hexyloxy)-1,4-dibromo-7,10-dichlorotriphenylene 39

2.3-Bis(hexyloxy)-7,10-dichlorotriphenylene 39 (1.00 g, 2.01 × 10\(^{-3}\) mol) was stirred in dichloromethane (100 mL) and bromine (1.60 g, 0.01 mol) was added. The mixture was stirred at room temperature for 2 hours. Sodium metabisulfite solution was added and the organic phase separated. The aqueous layer was further extracted with dichloromethane (3 × 100 mL) and the combined organic phases were dried (MgSO\(_4\)). The solvent was removed \(\text{in vacuo}\) and the crude product purified by column chromatography (eluting with 4:1 petroleum ether–dichloromethane) to give the title compound (2.94 g, 100%).
product purified by column chromatography (eluting with 1:1 petroleum ether–dichloromethane) to give the title compound (0.93 g, 70%).

Mp 169 °C. Anal. Found: C 54.66; H 4.79; Cl 10.77; Br 23.61; S 9.61 (C42H60O2S2 requires C 54.51; H 4.99; Cl 10.88; Br 23.47; S 9.62%).

100%.

The solution was heated to 100 °C for 5 minutes and then cooled to 70 °C. 2,3-Bis(hexyloxy)-7,10-dichlorotriphenylene 36 (1.00 g, 2.01 × 10^-3 mol) was added and the solution was stirred for 2 hours. 1-Bromohexane (2.80 g, 0.016 mol) was added and the reaction stirred for 24 hours at room temperature. The solution was worked up by addition of water and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The organic extracts were combined, washed with brine, dried (Na2SO4) and the product purified by column chromatography (eluting with 2:1 petroleum ether–dichloromethane) to give the title compound (0.69 g, 52%).

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References


