

# Structural factors controlling the transition between columnar-hexagonal and helical mesophase in triphenylene liquid crystals†

Andrew N Cammidge\* and Hemant Gopee

School of Chemical Sciences, University of East Anglia, Norwich, UK NR4 7TJ.  
E-mail: a.cammidge@uea.ac.uk

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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  $Col_h$  mesophases. Triphenylenes having four hexylthio and two hexyloxy substituents also give  $Col_h$  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.

## Introduction

Discotic liquid crystals<sup>1</sup> have received widespread attention since their discovery in 1977,<sup>2</sup> not least because columnar arrangement of (aromatic) cores gives rise to a low-dimensional conduction pathway.<sup>3,4</sup> Discotic liquid crystals based on the triphenylene nucleus are particularly attractive because simple derivatives are relatively easy to synthesise.<sup>1</sup> Furthermore, it is known that (homeotropic) alignment during slow cooling from the isotropic phase is easily achieved when the material is sandwiched in-between suitable substrates. Photoconductivity studies have revealed a charge carrier mobility of about  $10^{-7} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$  along the columns of hexaalkoxytriphenylenes<sup>5</sup> in their  $Col_h$  mesophases (the anisotropy factor is about  $10^3$ ).

Hexakis(hexylthio)triphenylene<sup>6</sup> has unique properties. In addition to the  $Col_h$  mesophase a more ordered helical (H) phase<sup>7,8</sup> is formed at lower temperatures. Charge carrier mobility in this phase is substantially higher ( $10^{-5} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$ )<sup>9-11</sup> and the dramatic increase is attributed to the long-range molecular order in the helical phase. It is interesting to note that the helical phase is not observed if the chain length is changed,<sup>7</sup> or indeed if the heteroatom is substituted for selenium.<sup>12</sup>

A number of attempts have been made to generate more ordered columnar mesophases from unsymmetrically substituted triphenylene derivatives. Selective hydrolytic removal of 1–3 alkyl chains from hexaalkoxytriphenylenes (or selective alkylations) can be readily achieved.<sup>13-17</sup> Removal of three chains (one from each “benzene”) gives two isomeric trihydroxytriphenylenes<sup>13,14</sup> which can be separated and further functionalised. In this way mixed chain derivatives have been prepared in order to promote interdigitation of alkyl chains (and increase order).<sup>18</sup> Two short reports outline deoxygenation of the intermediates to give tris(pentyloxy)triphenylenes.<sup>19,20</sup> These can be further functionalised by bromination<sup>19,20</sup> and the bromides displaced to yield tris(pentyloxy)tris(pentylthio)triphenylenes<sup>20</sup> (which, as would be expected, do not exhibit the helical mesophase).

This paper describes rational, atom-efficient syntheses of isomerically pure triphenylenes which are directly comparable to helical phase-forming hexakis(hexylthio)triphenylene

because the only change to structure is replacement of 2 or 4 sulfides by alkoxides.

## 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.<sup>21-23</sup> Alternatively terphenyls can be constructed and cyclised to the triphenylene is a separate step.<sup>24-26</sup> 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<sup>27</sup> of 4-bromoveratrole **9** with phenylboronic acid **10** yielded 3,4-dimethoxybiphenyl **11**. Oxidative coupling with veratrole using ferric chloride<sup>21,28</sup> yielded 2,3,6,7-tetramethoxytriphenylene **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(hexyloxy)triphenylene **13**. Bromination with molecular bromine introduced bromide at both free  $\beta$ -positions to give 2,3-dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene **14**.<sup>29</sup> 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<sup>26</sup> to give 2,3,7,10-tetrakis(hexyloxy)triphenylene **20**. Bromination again gave exclusive substitution at the free  $\beta$ -positions yielding 2,7-dibromo-3,6,10,

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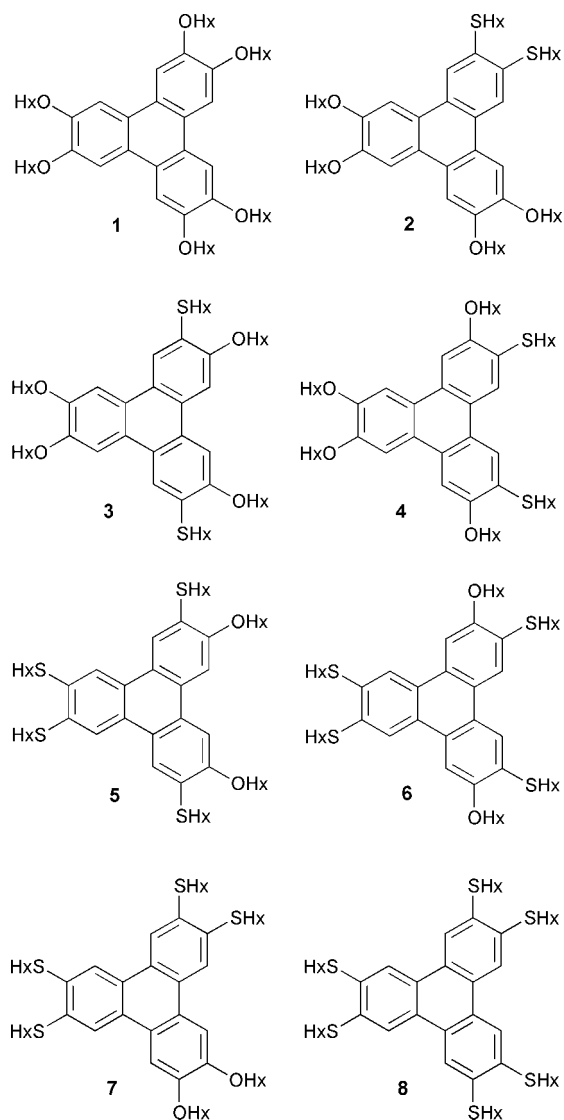


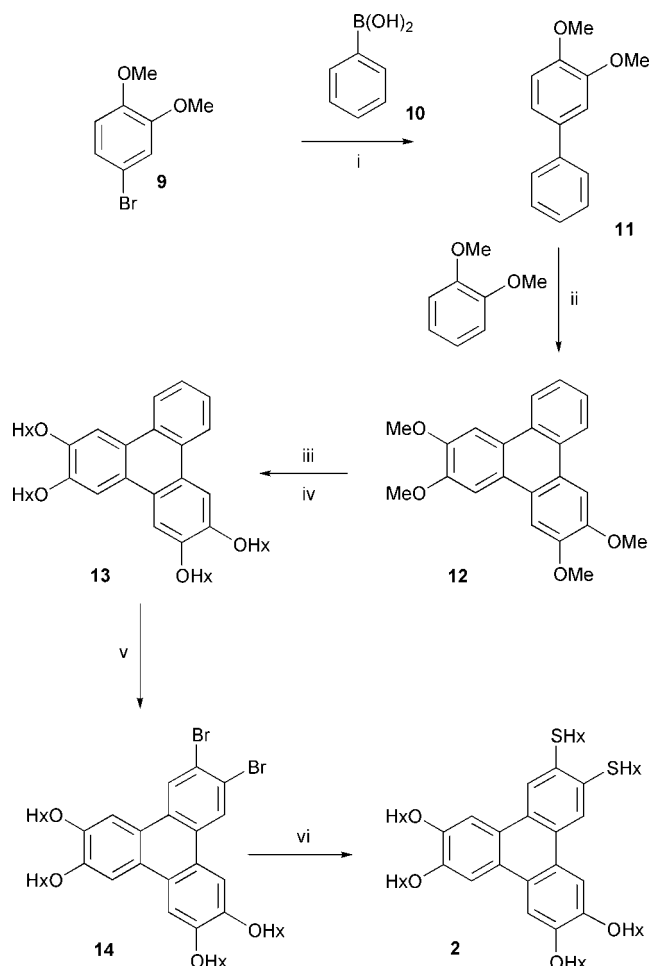
Fig. 1 Target molecules 1–8.

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 triphenyl **29**. As expected, cyclisation to the corresponding triphenylene **30** could not be achieved using ferric chloride and required photochemical oxidation ( $h\nu-I_2$ ). The four free  $\beta$ -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**.

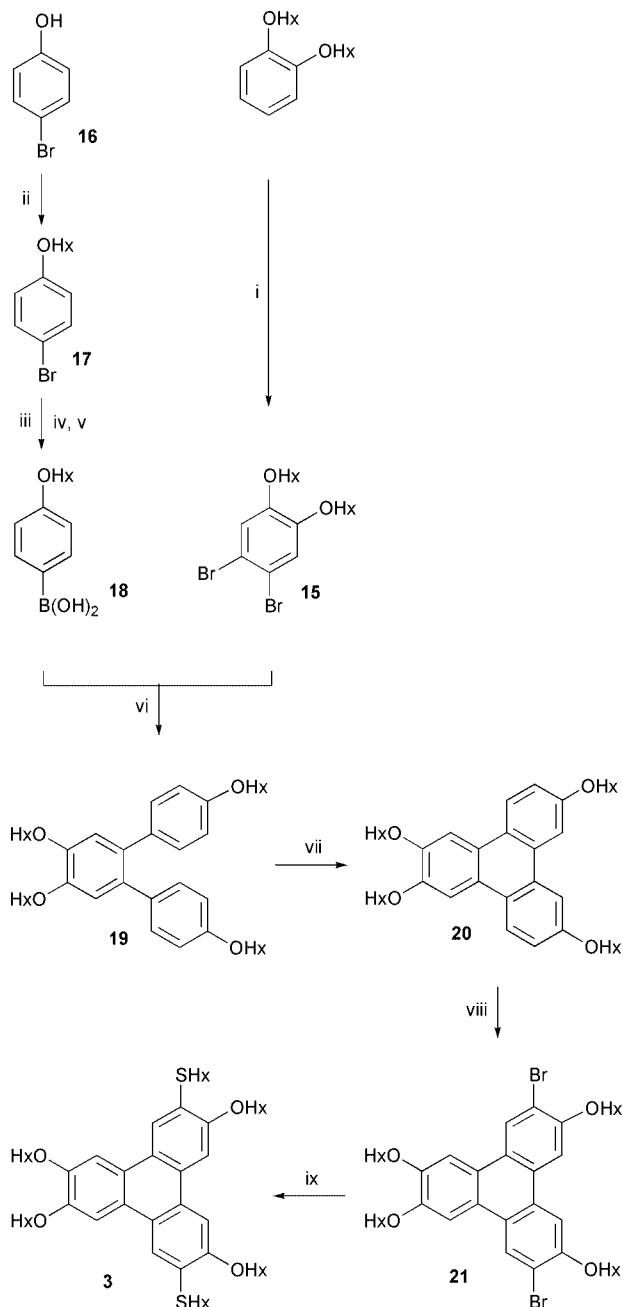


Scheme 1 Hx = *n*-hexyl. Reagents and conditions: (i) PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 4 h, (ii) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (iii) HBr, HOAc, reflux, 24 h, (iv) HxBr, EtOH, K<sub>2</sub>CO<sub>3</sub>, reflux, 24 h, (v) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, –5 °C, 2 h, (vi) HxSH, KO<sup>t</sup>Bu, NMP, 70 °C, 24 h.

Treatment with ferric chloride did not yield the expected triphenylene **37** but rather **36**, in which cyclisation with concomitant chlorination had occurred. Chlorination presumably occurs *via* an oxidation–chlorination–oxidation (aromatization) pathway<sup>30</sup> (Scheme 7) which leads to our assumption that chloride is introduced at the 7,10-positions. Photochemical cyclisation was therefore successfully employed affording **37** in reasonable yield.

Bromination of **37** was attempted using the conditions which proved successful for the synthesis of **31** and **34** (Scheme 8). In the case of **37**, however, prolonged treatment with bromine in dichloromethane yielded a mixture of products which were presumed to be polybromides. Examination of the <sup>1</sup>H NMR spectrum of the crude product confirmed that none of the desired tetrabromide was present. Progressively more forcing bromination conditions were used (raised temperature, Lewis acid catalyst) but the desired product was never observed.

Alternative, longer routes were therefore investigated for the synthesis of **7**. Bromination of dichloride **36** was attempted (Scheme 9) because it was envisaged that the dibromodichlorotriphenylene **38** could be easily converted to **7** by displacement of both halides. Treatment of **36** with bromine at room temperature gave smooth dibromination. However, it was clear from the <sup>1</sup>H NMR spectrum of the product that 1,4-dibromide **39** had been formed. Attempts to prepare **38** (the expected thermodynamic product) using alternative conditions (Lewis acid and elevated temperature, iodine monochloride) were all unsuccessful. It was hoped that synthesis of **7** could be achieved in a stepwise manner (Scheme 10). Consequently dichloride **36** was treated with hexanethiol to give 2,3-bis(hexyloxy)-7,

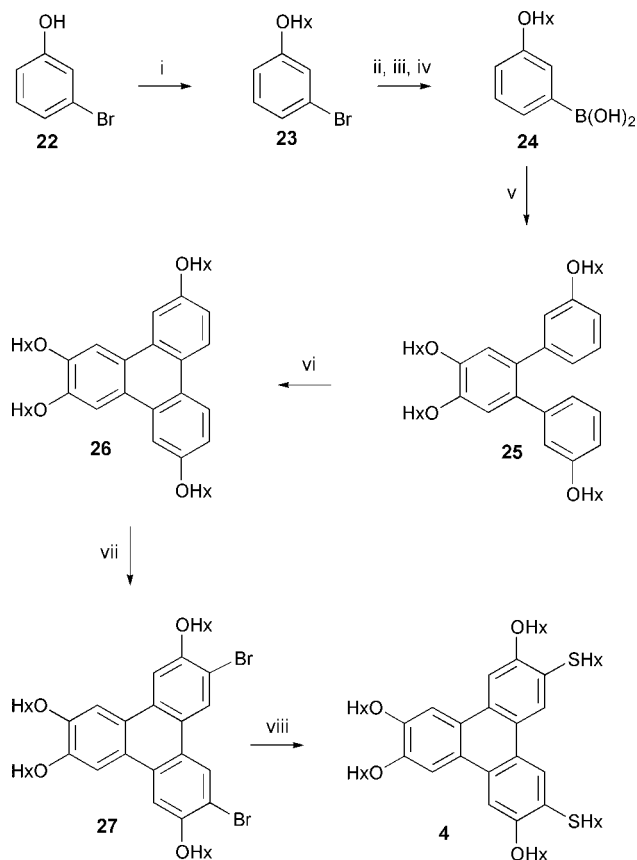


**Scheme 2** Hx = *n*-hexyl. Reagents and conditions: (i) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 2 h, (ii) HxBr, EtOH, K<sub>2</sub>CO<sub>3</sub>, reflux, (iii) Mg, Et<sub>2</sub>O, (iv) B(OMe)<sub>3</sub>, (v) H<sub>3</sub>O<sup>+</sup>, (vi) PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 4 h, (vii) hv, I<sub>2</sub>, benzene, 72 h, (viii) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 30 min, (ix) HxSH, KO<sup>t</sup>Bu, NMP, 70 °C, 24 h.

10-bis(hexylthio)triphenylene **40**. It was hoped that bromination would yield dibromide **41** which could be converted to **7** by another nucleophilic displacement. Surprisingly, treatment of **40** with bromine resulted in no reaction, even at elevated temperatures.

### Mesophase behaviour

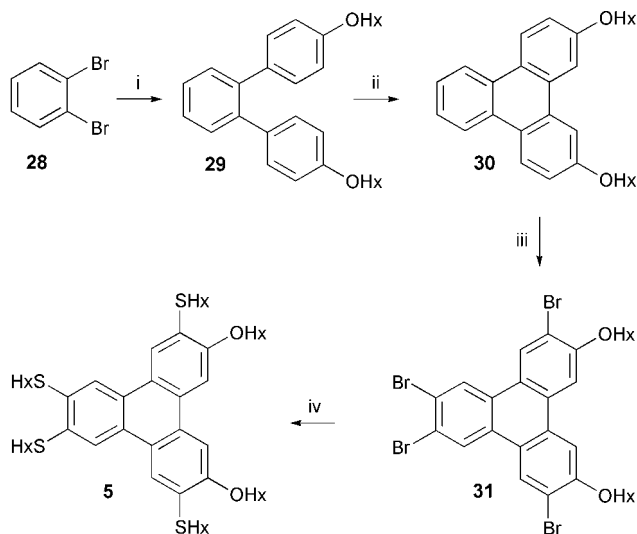
The mesophase behaviour of the novel triphenylene derivatives was investigated by polarising optical microscopy and differential scanning calorimetry (DSC). As expected, intermediate terphenyls, both di- and tetra-substituted triphenylenes and dialkoxytetrahalogenotriphenylenes proved to be non-mesogenic. Dibromotetrakis(hexyloxy)triphenylenes **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



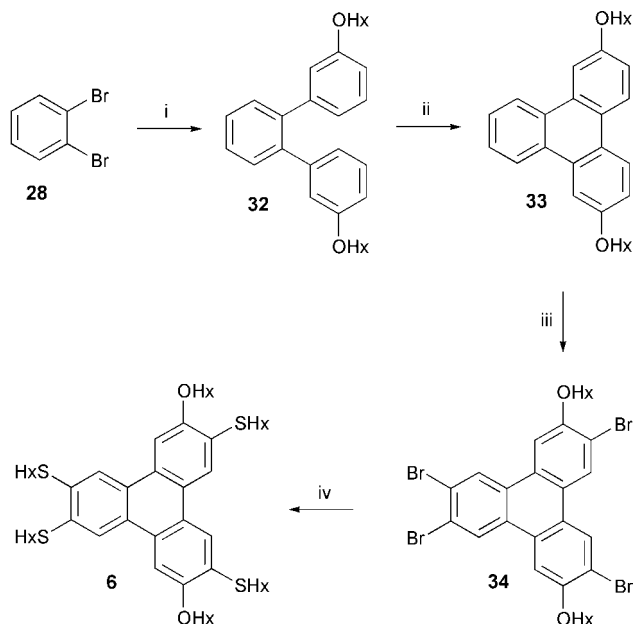
**Scheme 3** Hx = *n*-hexyl. Reagents and conditions: (i) HxBr, EtOH, K<sub>2</sub>CO<sub>3</sub>, reflux, (ii) Mg, Et<sub>2</sub>O, (iii) B(OMe)<sub>3</sub>, (iv) H<sub>3</sub>O<sup>+</sup>, (v) PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 4 h, (vi) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (vii) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 30 min, (viii) HxSH, KO<sup>t</sup>Bu, NMP, 70 °C, 24 h.

been pre-cooled to –80 °C reveals melting points (K–Col<sub>h</sub>) of 63 °C and 40 °C respectively. Both have clearing points around 179 °C. Their columnar phases (assigned as Col<sub>h</sub> 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



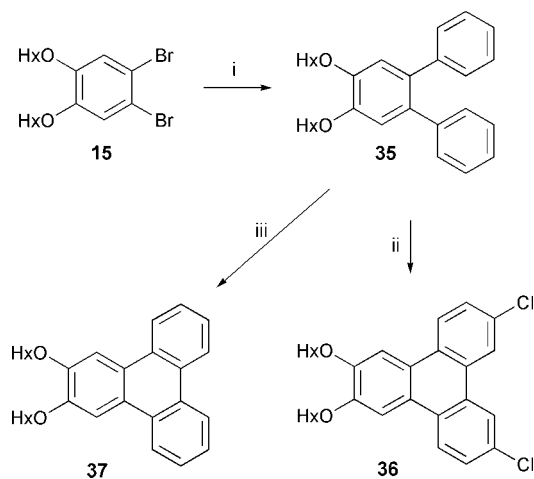
**Scheme 4** Hx = *n*-hexyl. Reagents and conditions: (i) **15**, PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 4 h, (ii) hv, I<sub>2</sub>, benzene, 72 h, (iii) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (iv) HxSH, KO<sup>t</sup>Bu, NMP, 70 °C, 24 h.



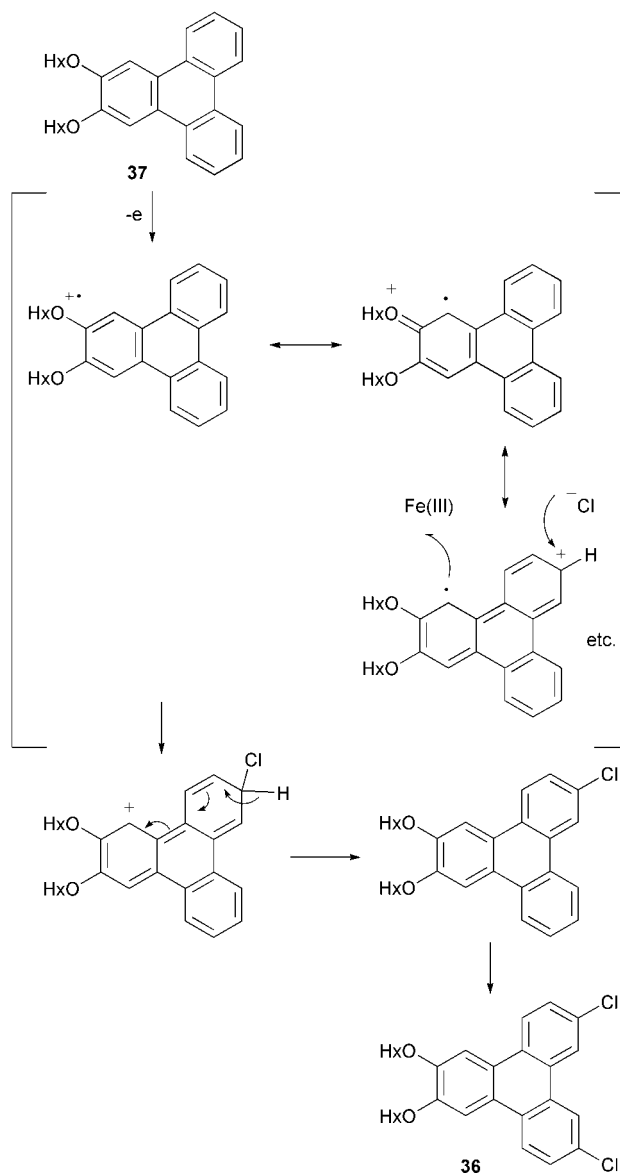
**Scheme 5** Hx=*n*-hexyl. Reagents and conditions: (i) **24**, PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 4 h, (ii) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (iii) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (iv) HxSH, KO<sup>t</sup>Bu, NMP, 70 °C, 24 h.

cooled, a monotropic Col<sub>h</sub> 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–Col<sub>h</sub>) of 24 °C and clears at 102 °C. The material cools into a Col<sub>h</sub> 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 Col<sub>h</sub> 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 Col<sub>h</sub> mesophase (as evidenced by microscopy) at 97 °C which is stable down to below ambient



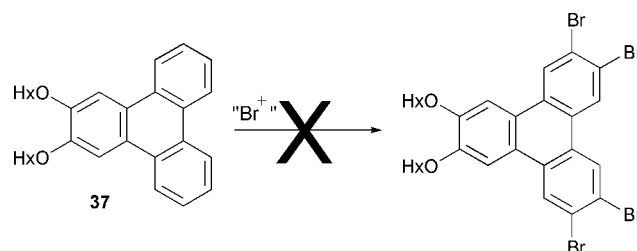
**Scheme 6** Hx=*n*-hexyl. Reagents and conditions: (i) **10**, PdCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, PPh<sub>3</sub>, toluene–EtOH–H<sub>2</sub>O, reflux, 48 h, (ii) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, (iii) *hν*, I<sub>2</sub>, benzene, 72 h.



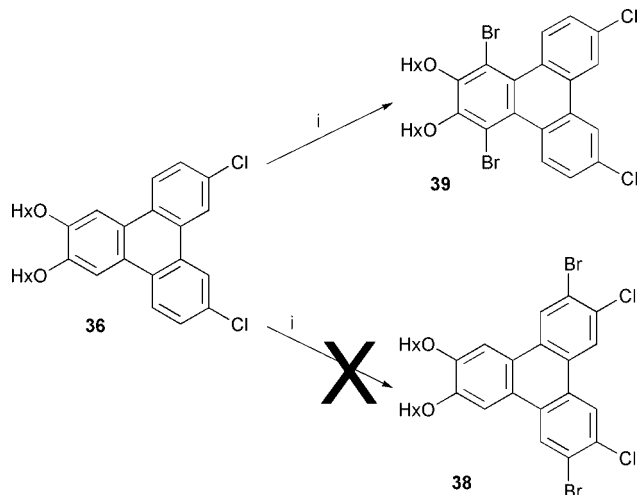
**Scheme 7** Mechanism for the formation of **36**.

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 Col<sub>h</sub> 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 transition<sup>6</sup> (1.1 J g<sup>-1</sup> compared to 0.8 J g<sup>-1</sup> for Col<sub>h</sub>-I and 4.7 J g<sup>-1</sup> for K–Col<sub>h</sub>) leads to the preliminary assignment that this is indeed a Col<sub>h</sub>-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



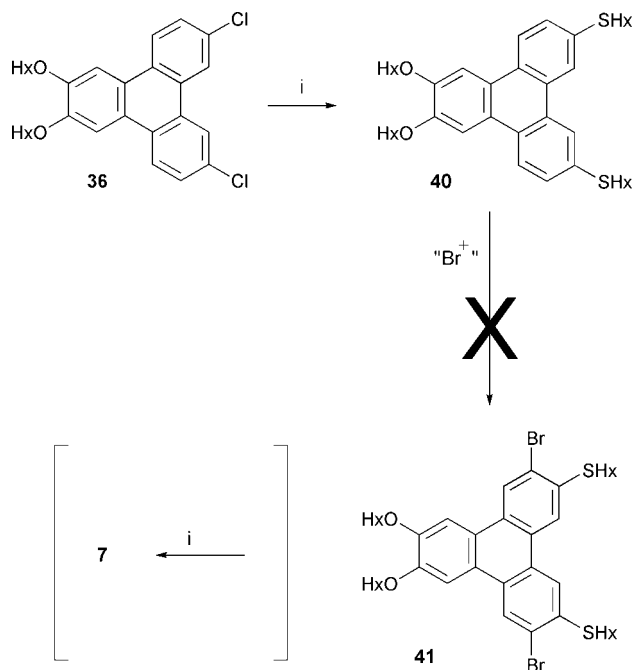
**Scheme 8** Attempted bromination of 2,3-bis(hexyloxy)triphenylene **37**.



**Scheme 9** Reagents and conditions: (i) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h.

crystallisation is observed when the sample is cooled down to  $-40\text{ }^{\circ}\text{C}$  (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 **8**—derivatives with different chain lengths exhibit Col<sub>h</sub> 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-tetrakis(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  $40\text{ }^{\circ}\text{C}$ <sup>9</sup>). 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

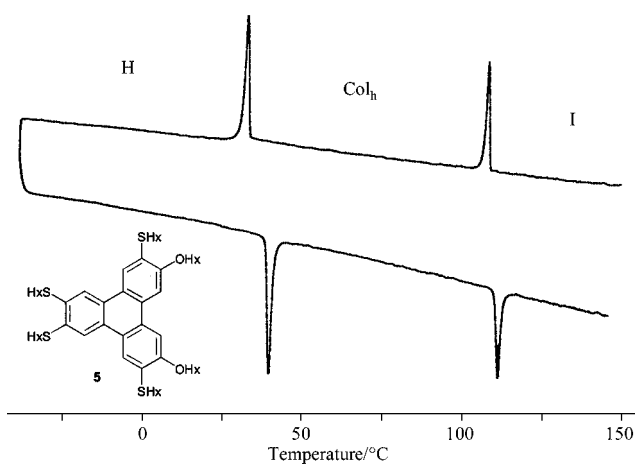


**Scheme 10** Reagents and conditions: (i) HxSH, KO<sup>t</sup>Bu, NMP,  $70\text{ }^{\circ}\text{C}$ , 24 h.

**Table 1** Transition temperatures ( $^{\circ}\text{C}$ ) of dibromotetrakis(hexyloxy)-triphenylenes

Compound Structure	Heating		Cooling	
	K-Col <sub>h</sub>	Col <sub>h</sub> -I	I-Col <sub>h</sub>	Col <sub>h</sub> -K
<b>14</b> <sup>29</sup>	130	141	140	97
<b>21</b>	40 <sup>a</sup>	179	176	<RT
<b>27</b>	63 <sup>a</sup>	179	175	<RT

<sup>a</sup>Observed if sample is pre-cooled to  $-80\text{ }^{\circ}\text{C}$ .



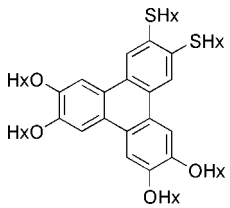
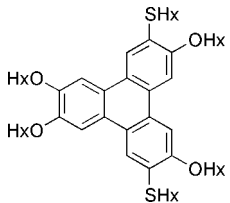
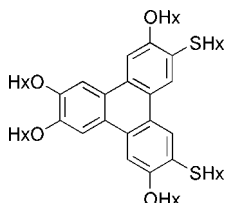
**Fig. 2** DSC of **5** (heating/cooling rate  $5\text{ }^{\circ}\text{C min}^{-1}$ ).

triphenylenes and other discotic liquid crystals<sup>31</sup>) and this property is also likely to be important for device fabrication.

## Conclusions

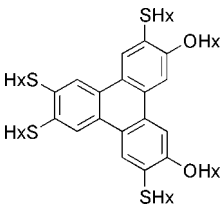
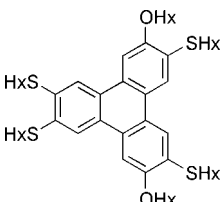
A series of mixed hexyloxy-/hexylthio-triphenylenes has been synthesised to determine the structural features governing the formation of helical mesophases. It has been shown that four sulfide substituents (plus two alkoxides) are required to induce the additional, more ordered phase. Furthermore, the 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 Col<sub>h</sub> 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 Col<sub>h</sub>

**Table 2** Transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{J g}^{-1}$ ) of tetrakis(hexyloxy)bis(hexylthio)triphenylenes

Compound	Structure	Heating		Cooling	
		K–Col <sub>h</sub> ( $\Delta H$ )	Col <sub>h</sub> –I ( $\Delta H$ )	I–Col <sub>h</sub> ( $\Delta H$ )	Col <sub>h</sub> –K ( $\Delta H$ )
2		(K–I 86)		81 (0.5)	52 (5.6)
3		24 <sup>a</sup> (3.3)	102 (0.7)	99 (0.8)	<0
4		45 <sup>a</sup> (4.5)	123 (0.8)	118 (0.8)	<0

<sup>a</sup>Observed if sample is pre-cooled to  $-80^{\circ}\text{C}$ .

**Table 3** Transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{J g}^{-1}$ ) of bis(hexyloxy)tetrakis(hexylthio)triphenylenes

Compound	Structure	Heating			Cooling		
		K–Col <sub>h</sub> ( $\Delta H$ ) <sup>a</sup>	H–Col <sub>h</sub> ( $\Delta H$ )	Col <sub>h</sub> –I ( $\Delta H$ )	I–Col <sub>h</sub> ( $\Delta H$ )	Col <sub>h</sub> –H ( $\Delta H$ )	D–K
5		72 (4.7)	38 (1.3)	111 (0.8)	108 (0.8)	32 (1.1)	< -40
6		54 (4.0)	—	100.5 (0.6)	97 (0.8)	—	<RT

<sup>a</sup>Observed if sample is pre-cooled to  $-80^{\circ}\text{C}$ .

phase. 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  $^{\circ}\text{C min}^{-1}$ . Column chromatography was performed at atmospheric

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-Dimethoxybiphenyl 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 (0.51 g,  $4.83 \times 10^{-3}$  mol) and triphenylphosphine (2.53 g,  $9.66 \times 10^{-3}$  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 product was purified by column chromatography (eluting with 1:1 dichloromethane–petroleum ether) to give the title compound as colourless crystals (21.32 g, 62%).

Anal. Found: C 78.33; H 6.57 (C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> requires C 78.50; H 6.54%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 300 MHz) 7.56 (2H, m), 7.42 (2H, t,  $J=7.2$ ), 7.33 (1H, m), 7.16–7.14 (2H, m), 6.95 (1H, d,  $J=8.1$ ), 3.95 (3H, s), 3.92 (3H, s);  $\delta_{\text{C}}$  (75.45 MHz; CDCl<sub>3</sub>) 149.5, 148.9, 141.3, 134.5, 128.9, 127.1, 119.6, 111.7, 110.7, 56.1, 56.0;  $m/z$  (EI) 214 (M<sup>+</sup>, 100%).

### 2,3,6,7-Tetramethoxytriphenylene 12

Veratrole (20 g, 0.148 mol) and 3,4-dimethoxybiphenyl **11** (8.0 g, 0.037 mol) were dissolved in dichloromethane (150 mL). Iron(III) chloride (45 g, 0.29 mol) was added and the mixture stirred for 2 hours at room temperature. Methanol was then carefully added followed by water. The mixture was extracted with dichloromethane (3 × 150 mL) and the solvents evaporated. The crude product was purified by column chromatography (eluting with 4:1 petroleum ether–ethyl acetate) to give **12** as colourless crystals (9.37 g, 72%).

Anal. Found: C, 75.74; H 5.72 (C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> requires C, 75.86; H 5.75%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 300 MHz) 8.51 (2H, m), 8.00 (2H, s), 7.80 (2H, s), 7.61 (2H, m), 4.14 (6H, s), 4.13 (6H, s);  $\delta_{\text{C}}$  (75.45 MHz, CDCl<sub>3</sub>) 149.5, 148.9, 128.9, 126.2, 123.6, 122.9, 121.0, 104.6, 104.2, 56.1, 55.9;  $m/z$  (EI) 348 (M<sup>+</sup>, 100%).

### 2,3,6,7-Tetrahydroxytriphenylene

2,3,6,7-Tetramethoxytriphenylene **12** (12.0 g, 0.034 mol) was added to a refluxing mixture of hydrobromic acid–acetic acid (1:1, 500 mL). The solution was refluxed for 24 hours. The solvents were evaporated and dilute sodium hydrogen carbonate was added. The mixture was extracted with ethyl acetate and purified by column chromatography (using dichloromethane as eluent) to give the title compound (9.66 g, 96%) which was used without further purification.

$\delta_{\text{H}}$  (d<sub>6</sub>-Acetone), TMS, 300 MHz) 8.46 (2H, m), 8.11 (2H, s), 7.91 (2H, s), 7.53 (2H, m), 2.05 (4H, br s);  $m/z$  (EI) 292 (M<sup>+</sup>, 100%).

### 2,3,6,7-Tetrakis(hexyloxy)triphenylene 13

2,3,6,7-Tetrahydroxytriphenylene (10.0 g, 0.03 mol), 1-bromohexane (29.7 g, 0.80 mol) and anhydrous potassium carbonate (25.0 g, 0.80 mol) were stirred in refluxing ethanol (200 mL) under nitrogen for 24 hours. The solids were then filtered off and washed with ethanol. The solvents were evaporated and dilute sulfuric acid was added. The mixture was extracted with dichloromethane (3 × 150 mL) and the solvents evaporated. The crude residue was dissolved in dichloromethane and precipitated with methanol. The solid was recrystallised from ethanol to give the title compound as a colourless solid (20.6 g, 95%).

Anal. Found: C, 80.13; H, 9.55 (C<sub>42</sub>H<sub>60</sub>O<sub>4</sub> requires C, 80.25; H 9.55%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 300 MHz) 8.49 (2H, m), 8.02 (2H, s), 7.85 (2H, s), 7.58 (2H, m), 4.28 (8H, s), 1.94 (8H, m), 1.58 (8H, m), 1.40 (16H, m), 0.94 (12H, t,  $J=7$ );  $\delta_{\text{C}}$  (75.45 MHz; CDCl<sub>3</sub>)

149.8, 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<sup>+</sup>, 30%).

### 2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene 14

2,3,6,7-Tetrakis(hexyloxy)triphenylene **13** (2.0 g,  $3.2 \times 10^{-3}$  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 solution (20%) was added. The mixture was extracted using 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 (C<sub>42</sub>H<sub>60</sub>O<sub>4</sub> requires C, 64.12; H 7.38%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, 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);  $\delta_{\text{C}}$  (75.45 MHz; CDCl<sub>3</sub>) 150.2, 149.3, 129.3, 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<sup>+</sup>, 100%).

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

Potassium *tert*-butoxide (0.855 g,  $7.63 \times 10^{-3}$  mol) was added to a stirred solution of hexanethiol (0.90 g,  $7.63 \times 10^{-3}$  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,  $1.90 \times 10^{-3}$  mol) was added and the solution was stirred for 24 hours. 1-Bromohexane (0.63 g,  $3.75 \times 10^{-3}$  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 (Na<sub>2</sub>SO<sub>4</sub>) 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 (C<sub>54</sub>H<sub>84</sub>O<sub>4</sub>S<sub>2</sub> requires C, 75.35; H 9.77; S 7.44%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 300 MHz) 8.34 (2H, s), 7.92 (2H, s), 7.81 (2H, s), 4.26–4.20 (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);  $\delta_{\text{C}}$  (75.45 MHz; CDCl<sub>3</sub>) 150.0, 149.5, 135.6, 127.8, 124.6, 124.2, 123.2, 107.4, 107.3, 69.9, 69.7, 34.3, 31.7, 31.6, 29.4, 29.0, 28.9, 25.8, 22.7, 22.6, 14.1;  $m/z$  (FABMS) 860 (M<sup>+</sup>, 100%).

### 1,2-Dibromo-4,5-bis(hexyloxy)benzene 15

1,2-Bis(hexyloxy)benzene (5.00 g, 0.017 mol) was stirred in dichloromethane at 0 °C. Bromine (6.00 g, 0.0375 mol) was added drop-wise and the solution stirred for a further 2 hours. A solution of sodium metabisulfite was added and the organic layer separated. The aqueous layer was further extracted with dichloromethane (3 × 150 mL). The combined organic extracts were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvents evaporated to give the title compound as a colourless oil (5.50 g, 70%) which was used without further purification.

$\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 300 MHz) 7.06 (2H, s), 3.94 (4H, t,  $J=6.6$ ), 1.84–1.75 (4H, m), 1.50–1.30 (12H, m), 0.93–0.87 (6H, t,  $J=6.9$ ).

### 4,4',5',4''-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl 19

4-Hexyloxyphenylboronic acid **18** (15.0 g, 0.056 mol), 1,2-dibromo-4,5-bis(hexyloxy)benzene **15** (10.00 g, 0.023 mol), sodium carbonate (8.00 g, 0.075 mol), palladium chloride (0.12 g,  $3.44 \times 10^{-4}$  mol) and triphenylphosphine (0.12 g,

$6.88 \times 10^{-4}$  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 was added. The mixture was extracted with dichloromethane ( $4 \times 150$  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 (9.86 g, 68%).

Anal. Found: C 79.9; H 9.87 ( $C_{42}H_{62}O_4$  requires C 80.00; H 9.84%);  $\delta_H$  ( $CDCl_3$ , TMS, 300 MHz) 7.03 (2H, d,  $J=8.8$ ), 6.89 (2H, s), 6.74 (6H, d,  $J=8.8$ ), 4.04 (4H, t,  $J=6.6$ ), 3.91 (4H, t,  $J=6.6$ ), 1.88–1.71 (8H, m), 1.59–1.03 (32H, m), 0.93–0.83 (12H, m);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 157.6, 148.2, 133.9, 132.7, 130.8, 116.3, 113.9, 69.4, 67.8, 31.4, 29.2, 29.1, 25.6, 22.4(3), 22.4(0), 13.8;  $m/z$  (EI) 630 ( $M^+$ , 50%).

### 2,3,7,10-Tetrakis(hexyloxy)triphenylene 20

4,4',5',4''-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl **19** (2.071 g,  $4.3 \times 10^{-3}$  mol) and iodine (1.09 g,  $4.3 \times 10^{-3}$  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 further extracted with dichloromethane ( $3 \times 100$  mL) and the combined organic extracts were dried ( $MgSO_4$ ). The solvent was removed *in vacuo* and the crude product purified by column chromatography (eluting with 1 : 1 petroleum ether–dichloromethane) to give the title compound (1.43 g, 53%) as a colourless solid.

Mp 85 °C. Anal. Found: C 80.18; H 9.50 ( $C_{42}H_{60}O_4$  requires C 80.25; H 9.55%);  $\delta_H$  ( $CDCl_3$ , 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);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 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, 29.4, 25.9, 25.8, 22.7, 14.1;  $m/z$  (EI) 628 ( $M^+$ , 40%).

### 2,7-Dibromo-3,6,10,11-tetrakis(hexyloxy)triphenylene 21

2,3,7,10-Tetrakis(hexyloxy)triphenylene **20** (2.40 g,  $3.82 \times 10^{-3}$  mol) was stirred in dichloromethane (10 mL) at 0 °C. Bromine (1.24 g,  $7.64 \times 10^{-3}$  mol) was added drop-wise and the solution stirred for 30 minutes. A solution of sodium metabisulfite was then added and the mixture extracted with dichloromethane ( $3 \times 100$  mL). The combined organic layers were dried ( $MgSO_4$ ) and the crude product purified by column chromatography (eluting with 1 : 4 dichloromethane–petroleum ether). The product was recrystallised from propan-2-ol to give the title compound (2.50 g, 83%).

Anal. Found: C 64.08; H 7.45; Br 20.31 ( $C_{42}H_{58}O_4Br_2$  requires C 64.12; H 7.38; Br 20.36%);  $\delta_H$  ( $CDCl_3$ , TMS, 300 MHz) 8.33 (2H, s), 7.39 (2H, s), 7.36 (2H, s), 4.15–4.06 (8H, m), 1.99–1.88 (8H, m), 1.62–1.38 (24H, m), 0.98–0.94 (12H, m);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 153.5, 149.5, 128.5, 127.6, 124.9, 122.2, 113.5, 105.8, 105.4, 69.4, 31.8, 31.7, 29.5, 29.3, 25.9, 22.8, 22.7, 14.1;  $m/z$  (FABMS) 786 ( $M^+$ , 100%).

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

Potassium *tert*-butoxide (3.57, 0.030 mol) was added to a stirred solution of hexanethiol (3.54 g, 0.030 mol) in NMP (25 mL). The solution was heated to 100 °C for 5 minutes and then cooled to 70 °C. 2,7-Dibromo-3,6,10,11-tetrakis(hexyloxy)triphenylene **21** (2.50 g,  $3.18 \times 10^{-3}$  mol) was added and the solution was stirred for 24 hours. 1-Bromohexane (1.25 g,  $7.57 \times 10^{-3}$  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 extracted with diethyl ether ( $3 \times 50$  mL). The organic extracts were combined, washed with brine, dried

( $Na_2SO_4$ ) 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 (0.55 g, 20%).

$\delta_H$  ( $CDCl_3$ , TMS, 300 MHz) 8.29 (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), 0.96–0.89 (18H, m);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 155.9, 149.4, 128.2, 126.6, 124.2, 124.1, 123.3, 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, 22.6, 14.1;  $m/z$  (FABMS) 861 ( $M^+ + H$ , 100%); Acc. Mass (ES) 861.5879 ( $C_{54}H_{85}O_4S_2$  ( $M + H$ ) = 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** (10.00 g, 0.023 mol), sodium carbonate (8.00 g, 0.075 mol), palladium chloride (0.12 g,  $3.44 \times 10^{-4}$  mol) and triphenylphosphine (0.12 g,  $6.88 \times 10^{-4}$  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 extracted with dichloromethane ( $4 \times 150$  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 (10.40 g, 72%).

Anal. Found: C 79.89; H 9.88 ( $C_{42}H_{62}O_4$  requires C 80.00; H 9.84%);  $\delta_H$  ( $CDCl_3$ , 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 (4H, m), 1.56–1.26 (24H, m), 0.93–0.83 (12H, m);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 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 ( $M^+$ , 65%).

### 2,3,6,11-Tetrakis(hexyloxy)triphenylene 26

3,4',5',3''-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl **25** (1.0 g,  $1.59 \times 10^{-3}$  mol) was stirred in dichloromethane (20 mL) at room temperature. Iron(III) chloride (0.51 g,  $3.17 \times 10^{-3}$  mol) was added and the mixture stirred for a further two hours. Methanol and water were then added and the mixture extracted with dichloromethane ( $3 \times 100$  mL). The combined organic phases were dried ( $MgSO_4$ ) and the solvents were evaporated. Purification of the crude product by column chromatography (eluting with 1 : 4 dichloromethane–petroleum ether) followed by recrystallisation with methanol gave the title compound (0.57 g, 56%) as a cream powder.

Mp 101 °C; Anal. Found: C 80.44; H 9.56 ( $C_{42}H_{60}O_4$  requires C 80.25; H 9.55%);  $\delta_H$  ( $CDCl_3$ , TMS, 300 MHz) 8.44 (2H, d,  $J=9.0$ ), 7.91 (2H, s), 7.85 (2H, d,  $J=2.4$ ), 7.20 (2H, dd,  $J=2.4$  and 9.0), 4.26–4.15 (8H, m), 1.97–1.84 (8H, m), 1.60–1.25 (24H, m), 0.96–0.85 (12H, m);  $\delta_C$  (75.45 MHz;  $CDCl_3$ ) 157.6, 149.6, 129.9, 124.4, 124.2, 123.3, 114.5, 107.2, 106.9, 69.4, 68.2, 31.5, 29.3, 25.6, 22.4, 13.8;  $m/z$  (EI) 628 ( $M^+$ , 10%).

### 2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene 27

2,3,6,11-Tetrakis(hexyloxy)triphenylene **26** (0.50 g,  $7.96 \times 10^{-4}$  mol) was stirred in dichloromethane (10 mL) at 0 °C. Bromine (0.25 g,  $1.59 \times 10^{-3}$  mol) was added drop-wise and the solution stirred for 30 minutes. A solution of sodium metabisulfite was then added and the mixture was extracted with dichloromethane ( $3 \times 100$  mL). The combined organic layers were dried ( $MgSO_4$ ), the solvents evaporated and the crude product purified by column chromatography (eluting with 1 : 1 dichloromethane–petroleum ether) and recrystallised from propan-2-ol to give the title compound (0.40 g, 64%) as a colourless solid.

Anal. Found: C 64.42; H 7.43; Br 20.00 ( $C_{42}H_{58}O_4Br_2$  requires C 64.12; H 7.38; Br 20.36%);  $\delta_H$  ( $CDCl_3$ , TMS,



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);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 153.9, 149.9, 129.1, 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<sup>+</sup>, 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<sup>-3</sup> 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 (Na<sub>2</sub>SO<sub>4</sub>) 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.

$\delta_H$  (CDCl<sub>3</sub>, 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,  $J=7.2$ ), 1.99–1.90 (8H, m), 1.78–1.71 (4H, m), 1.61–1.32 (36H), 0.96–0.85 (18H, m);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 155.7, 149.6, 127.9, 125.9, 124.2, 123.4, 122.9, 107.4, 103.9, 69.6, 68.9, 32.2, 31.5, 31.4, 31.3, 29.2, 29.1, 28.8, 28.6, 25.7, 25.6, 22.5, 22.4, 13.9;  $m/z$  (FABMS) 861 (M+H, 100%); Acc. Mass (FAB) 861.5888 (C<sub>54</sub>H<sub>85</sub>O<sub>4</sub>S<sub>2</sub> (M+H) = 861.5889).

#### 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<sup>-4</sup> mol) and triphenylphosphine (0.38 g, 1.44 × 10<sup>-3</sup> mol) were stirred under reflux in a mixture of toluene, ethanol and water, (3 : 3 : 1, 200 mL) for 24 hours. The solvents were evaporated, water was added and the mixture was extracted 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 (3.80 g, 70%).

Anal. Found: C 83.61; H 8.92 (C<sub>30</sub>H<sub>38</sub>O<sub>2</sub> requires C 83.72; H 8.84%);  $\delta_H$  (CDCl<sub>3</sub>, TMS, 300 MHz) 7.36 (4H, m), 7.05 (4H, d,  $J=8.8$ ), 6.75 (4H, d,  $J=8.8$ ), 3.91 (4H, t,  $J=6.6$ ), 1.88–1.73 (4H, m), 1.55–1.30 (12H, m), 0.92–0.88 (6H, m, -C<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 157.9, 140.2, 133.9, 130.8, 130.5, 127.0, 113.9, 67.8, 31.4, 29.1, 25.6, 22.4, 13.9;  $m/z$  (EI) 430 (M<sup>+</sup>, 38%).

#### 3,6-Bis(hexyloxy)triphenylene 30

1,2-Bis(4-hexyloxyphenyl)benzene **29** (1.83 g, 4.25 × 10<sup>-3</sup> mol) and iodine (1.08 g, 4.25 × 10<sup>-3</sup> 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 further extracted with dichloromethane (3 × 100 mL) and the combined organic phases were dried (MgSO<sub>4</sub>). The solvents were removed *in vacuo* and the crude product purified by column chromatography (eluting with 4 : 1 petroleum ether–dichloromethane) to give the title compound (1.09 g, 60%).

Mp 137 °C. Anal. Found: C 84.07; H 8.46 (C<sub>30</sub>H<sub>36</sub>O<sub>2</sub> requires C 84.11; H 8.41%);  $\delta_H$  (CDCl<sub>3</sub>, TMS, 300 MHz) 8.54 (4H, m,  $J=9.2$ ), 7.95 (2H, s), 7.58–7.55 (2H, m), 7.25–7.29 (2H, m), 4.19 (4H, t,  $J=6.6$ ), 1.92–1.88 (4H, m), 1.59–1.36 (12H, m), 0.97–0.92 (6H, m);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 158.4, 130.9, 128.9,

126.2, 124.8, 124.0, 122.7, 115.9, 106.9, 68.1, 31.5, 29.2, 25.7, 22.4, 13.9;  $m/z$  (EI) 428 (M<sup>+</sup>, 50%).

#### 2,3,6,11-Tetrabromo-7,10-bis(hexyloxy)triphenylene 31

3,6-Bis(hexyloxy)triphenylene **30** (0.50 g, 1.16 × 10<sup>-3</sup> mol) was stirred in dichloromethane (10 mL) at room temperature. Bromine (1.86 g, 0.012 mol) was added drop-wise and the solution stirred for 24 hours. A solution of sodium metabisulfite was then added and the mixture extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried (MgSO<sub>4</sub>), the solvents evaporated and the crude product purified by column chromatography (eluting with 1 : 4 dichloromethane–petroleum ether). The product was recrystallised from pentanol to give the title compound (0.49 g, 56%).

Mp 140 °C. Anal. Found: C 48.22; H 4.28; Br 43.07 (C<sub>30</sub>H<sub>32</sub>O<sub>2</sub>Br<sub>4</sub> requires C 48.39; H 4.30; Br 43.01%);  $\delta_H$  (CDCl<sub>3</sub>, TMS, 300 MHz) 7.98 (2H, s), 7.89 (2H, s), 7.26 (2H, s), 4.16 (4H, t,  $J=6.5$ ), 2.03–1.94 (4H, m), 1.66–1.40 (12H, m), 0.99–0.95 (6H, m);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 155.1, 129.4, 127.9, 127.7, 126.9, 122.8, 122.5, 114.1, 104.7, 69.4, 31.7, 29.2, 25.9, 22.7, 14.1;  $m/z$  (FABMS) 744 (M<sup>+</sup>, 50%).

#### 3,6-Bis(hexyloxy)-2,7,10,11-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(hexyloxy)-triphenylene **31** (2.50 g, 3.36 × 10<sup>-3</sup> 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 (Na<sub>2</sub>SO<sub>4</sub>) 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 (C<sub>54</sub>H<sub>84</sub>O<sub>2</sub>S<sub>4</sub> requires C 72.65; H 9.42; S 14.35%);  $\delta_H$  (CDCl<sub>3</sub>, TMS, 300 MHz) 8.22 (2H, s), 8.20 (2H, s), 7.65 (2H, s), 4.27 (4H, t,  $J=6.5$ ), 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);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 156.3, 135.8, 128.5, 127.4, 127.0, 123.2, 123.0, 122.9, 103.9, 66.1, 33.9, 32.1, 31.8, 31.6, 29.3, 29.0, 28.9, 26.0, 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<sup>-4</sup> mol) and triphenylphosphine (0.53 g, 1.97 × 10<sup>-3</sup> mol) were stirred under reflux in a mixture of toluene, ethanol and water (3 : 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 g, 82%).

$\delta_H$  (CDCl<sub>3</sub>, TMS, 300 MHz) 7.45–7.37 (4H, m), 7.11 (2H, t,  $J=7.8$ ), 6.76–6.67 (6H, m), 3.73 (4H, t,  $J=6.6$ ), 1.68–1.60 (4H, m), 1.42–1.26 (12H, m), 0.92–0.87 (6H, m);  $\delta_C$  (75.45 MHz; CDCl<sub>3</sub>) 158.7, 142.9, 140.5, 130.4, 128.8, 127.5, 122.1, 115.7, 113.4, 67.8, 31.4, 28.9, 25.5, 22.5, 13.9; Acc. Mass (FAB) 431.2950 (C<sub>30</sub>H<sub>39</sub>O<sub>2</sub> (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(III) 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<sub>4</sub>) 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 84.03; H 8.46 (C<sub>30</sub>H<sub>36</sub>O<sub>2</sub> requires C 84.11; H 8.41%); δ<sub>H</sub> (CDCl<sub>3</sub>, TMS, 300 MHz) 8.56 (2H, m), 8.43 (2H, d, *J* = 9.0), 8.01 (2H, d, *J* = 2.3), 7.43 (2H, m), 7.23 (2H, dd, *J* = 9.0 and 2.3), 4.16 (4H, t, *J* = 6.6), 1.90–1.83 (4H, m), 1.57–1.375 (12H, m), 0.96–0.91 (6H, t, *J* = 7.0); δ<sub>C</sub> (75.45 MHz; CDCl<sub>3</sub>) 158.0, 130.3, 130.2, 127.2, 124.5, 124.1, 123.6, 116.5, 106.8, 68.4, 31.7, 29.5, 25.9, 22.7, 14.1; *m/z* (EI) 428 (M<sup>+</sup>, 80%).

### 2,3,7,10-Tetrabromo-6,11-bis(hexyloxy)triphenylene 34

2,7-Bis(hexyloxy)triphenylene **33** (1.76 g, 4.11 × 10<sup>-3</sup> 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<sub>4</sub>) 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%).

Mp 180 °C. Anal. Found: C 48.51; H 4.30; Br 42.89 (C<sub>30</sub>H<sub>32</sub>O<sub>2</sub>Br<sub>4</sub> requires C 48.39; H 4.30; Br 43.01%); δ<sub>H</sub> (CDCl<sub>3</sub>, TMS, 300 MHz) 8.06 (2H, s), 7.89 (2H, s), 7.10 (2H, s), 4.06 (4H, t, *J* = 6.4), 1.99–1.92 (4H, m), 1.64–1.42 (12H, m), 0.99–0.95 (6H, m); δ<sub>C</sub> (75.45 MHz; CDCl<sub>3</sub>) 154.1, 128.9, 127.4, 127.1, 126.8, 123.3, 122.9, 114.3, 104.2, 69.2, 31.5, 29.0, 25.6, 22.5, 13.9; *m/z* (FABMS) 744 (M<sup>+</sup>, 100%).

### 2,7-Bis(hexyloxy)-3,6,10,11-tetrakis(hexylthio)triphenylene 6

Potassium *tert*-butoxide (6.77, 0.060 mol) was added to a stirred solution of hexanethiol (4.13 g, 0.060 mol) in NMP (30 mL). The solution was heated to 100 °C for 5 minutes and then cooled to 70 °C. 2,3,7,10-Tetrabromo-6,11-bis(hexyloxy)triphenylene **34** (3.00 g, 4.03 × 10<sup>-3</sup> mol) was added and the solution stirred for 48 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 further extracted with diethyl ether (3 × 100 mL). The organic extracts were combined, washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated. The crude product was purified by column chromatography over silica gel (eluting with 9:1 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (1.13 g, 38%).

Anal. Found: C 72.72; H 9.38; S 14.00 (C<sub>54</sub>H<sub>84</sub>O<sub>2</sub>S<sub>4</sub> requires C 72.65; H 9.42; S 14.35%); δ<sub>H</sub> (CDCl<sub>3</sub>, TMS, 300 MHz) 8.33 (2H, s), 8.26 (2H, s), 7.78 (2H, s), 4.27 (4H, t, *J* = 6.4), 3.11–3.06 (8H, m), 1.99–1.94 (4H, m), 1.82–1.73 (8H, m), 1.63–1.25 (36H, m), 0.97–0.83 (18H, m); δ<sub>C</sub> (75.45 MHz; CDCl<sub>3</sub>) 155.8, 136.5, 128.0, 127.6, 127.2, 123.9, 123.7, 122.7, 103.9, 69.0, 34.1, 32.1, 31.7, 31.6, 31.5, 29.8, 29.3, 29.0, 28.9, 25.9, 22.7, 22.6, 22.5, 14.1; *m/z* (FABMS) 892 (M, 65%).

### 1,2-Bis(hexyloxy)-3,4-diphenylbenzene 35

Phenylboronic acid **10** (4.20 g, 0.034 mol), 1,2-dibromo-4,5-bis(hexyloxy)benzene **15** (5.00 g, 0.012 mol), sodium carbonate

(6.00 g, 0.056 mol), palladium chloride (0.06 g, 3.28 × 10<sup>-4</sup> mol) and triphenylphosphine (0.18 g, 6.88 × 10<sup>-4</sup> mol) were stirred under reflux in a mixture of toluene, ethanol and water (3:3:1, 100 mL) for 48 hours. 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<sub>30</sub>H<sub>38</sub>O<sub>2</sub> requires C 83.72; H 8.84%); δ<sub>H</sub> (CDCl<sub>3</sub>, 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); δ<sub>C</sub> (75.45 MHz; CDCl<sub>3</sub>) 148.5, 141.6, 133.2, 129.9, 127.8, 126.2, 116.2, 69.4, 31.4, 29.2, 25.6, 22.5, 13.8; *m/z* (EI) 430 (M<sup>+</sup>, 50%).

### 2,3-Bis(hexyloxy)triphenylene 37

1,2-Bis(hexyloxy)-3,4-diphenylbenzene **35** (1.50 g, 6.90 × 10<sup>-3</sup> mol) and iodine (1.08 g, 4.25 × 10<sup>-3</sup> 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<sub>4</sub>). The solvent was evaporated and the crude product purified by column chromatography (eluting with 4:1 petroleum ether–dichloromethane) to give the title compound (0.85 g, 57%).

Mp 123 °C. Anal. Found: C 84.09; H 8.48 (C<sub>30</sub>H<sub>36</sub>O<sub>2</sub> requires C 84.11; H 8.41%); δ<sub>H</sub> (CDCl<sub>3</sub>, TMS, 300 MHz) 8.66 (2H, m), 8.50 (2H, m), 8.03 (2H, s), 7.65–7.26 (4H, m), 4.25 (4H, t, *J* = 6.6), 1.98–1.93 (4H, m), 1.60–1.38 (12H, m), 0.96–0.85 (6H, t, *J* = 7.0); δ<sub>C</sub> (75.45 MHz; CDCl<sub>3</sub>) 150.1, 132.4, 129.4, 128.4, 127.8, 124.5, 123.6, 123.1, 106.5, 69.4, 31.7, 29.4, 25.9, 22.7, 14.1; *m/z* (EI) 428 (M<sup>+</sup>, 100%).

### 2,3-Bis(hexyloxy)-7,10-dichlorotriphenylene 36

1,2-Bis(hexyloxy)-3,4-diphenylbenzene **35** (3.80 g, 8.85 × 10<sup>-3</sup> mol) was stirred in dichloromethane (300 mL) at room temperature. Iron(III) 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 give a brown solid which was purified by column chromatography (eluting with 4:1 petroleum ether–dichloromethane) to give the title compound (2.24 g, 51%).

Mp 127 °C. Anal. Found: C 72.19; H 6.87; Cl 14.25 (C<sub>30</sub>H<sub>34</sub>O<sub>2</sub>Cl<sub>2</sub> requires C 72.43; H 6.89; Cl 14.25%); δ<sub>H</sub> (CDCl<sub>3</sub>, TMS, 270 MHz) 8.36 (2H, d, *J* = 2.0), 8.28 (2H, d, *J* = 8.9), 7.81 (2H, s), 7.53 (2H, dd, *J* = 8.9, 2.0), 4.21 (4H, t, *J* = 6.6), 1.98–1.89 (4H, m), 1.61–1.55 (4H, m), 1.44–1.38 (8H, m), 0.93 (6H, t, *J* = 7.0); δ<sub>C</sub> (67.94 MHz; CDCl<sub>3</sub>) 149.6, 131.9, 128.9, 127.9, 127.3, 124.0, 123.0, 122.6, 105.9, 77.3, 76.9, 76.4, 69.1, 31.5, 29.1, 25.7, 22.5, 13.9; *m/z* (FABMS) 495 (M+H, 100%).

### 2,3-Bis(hexyloxy)-1,4-dibromo-7,10-dichlorotriphenylene 39

2,3-Bis(hexyloxy)-7,10-dichlorotriphenylene **36** (1.00 g, 2.01 × 10<sup>-3</sup> 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<sub>4</sub>). The solvent was removed *in vacuo* and the crude

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 23.83 (C<sub>30</sub>H<sub>32</sub>O<sub>2</sub>Cl<sub>2</sub>Br<sub>2</sub> requires C 54.99; H 4.92; Cl 10.82; Br 24.39%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 270 MHz) 9.05 (2H, d,  $J=8.9$ ), 8.25 (2H, d,  $J=2.0$ ), 7.46 (2H, dd,  $J=8.9$  and 2.0), 4.11 (4H, t,  $J=6.6$ ), 1.98–1.82 (4H, m), 1.60–1.48 (4H, m), 1.40–1.24 (8H, m), 0.94–0.89 (6H, m);  $\delta_{\text{C}}$  (67.94 MHz; CDCl<sub>3</sub>) 150.3, 133.7, 130.7, 129.1, 128.9, 127.6, 126.4, 122.8, 113.3, 74.1, 31.5, 30.1, 25.6, 22.5, 13.9;  $m/z$  (EI) 652.9 (M<sup>+</sup>, 100%).

### 2,3-Bis(hexyloxy)-7,10-bis(hexylthio)triphenylene 40

Potassium *tert*-butoxide (1.35 g, 0.012 mol) was added to a stirred solution of hexanethiol (1.42 g, 0.012 mol) in NMP (20 mL). 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<sup>-3</sup> 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 (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated. The crude product was purified by column chromatography (eluting with 4 : 1 petroleum ether–dichloromethane) and recrystallised from ethanol to give the title compound (0.69 g, 52%).

Mp 77 °C. Anal. Found: C 76.34; H 9.18; S 9.61 (C<sub>42</sub>H<sub>60</sub>O<sub>2</sub>S<sub>2</sub> requires C 76.31; H 9.15; S 9.70%);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS, 270 MHz) 8.47 (2H, d,  $J=1.7$ ), 8.31 (2H, d,  $J=8.9$ ), 7.88 (2H, s), 7.56 (2H, dd,  $J=8.9$ , 1.7), 4.20 (4H, t,  $J=6.6$ ), 3.07 (4H, t,  $J=7.3$ ), 1.96–1.90 (4H, m), 1.75–1.69 (4H, m), 1.59–1.27 (24H, m), 0.96–0.86 (12H, m);  $\delta_{\text{C}}$  (67.94 MHz; CDCl<sub>3</sub>) 149.3, 134.5, 128.7, 128.1, 127.7, 123.6, 123.2, 106.3, 69.1, 34.0, 31.4, 31.3, 29.1, 28.4, 25.6, 22.5, 22.4, 13.9;  $m/z$  (FABMS) 660 (M, 100%).

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