

A modified route to unsymmetrically substituted triphenylenes, new functionalised derivatives and twins, and the smallest reported triphenylene mesogen.

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## Abstract

We report the unexpected observation of columnar mesophase formation in a simple 2,7-dibromotetramethoxytriphenylene – by far the most lightly substituted discotic mesogen in this class. This derivative was prepared alongside the 3,6-dibromotriphenylene isomer to demonstrate an alternative, modified synthetic strategy that permits late-stage interchange of alkyl chain substituents. The new method is employed alongside the original route to deliver several new materials, including a conjugated ferrocene-triphenylene-ferrocene triad, a BODIPY-triphenylene-BODIPY triad and a new nematic twin linked through imine bridges.

## 1. Introduction

The triphenylene nucleus remains the most widely studied and versatile core [1-5] in discotic systems. [6] New synthetic chemistry gives access to complex, often unsymmetrical derivatives, for both applications and to probe liquid crystal behaviour. Our group has made a number of contributions to this area, most recently concentrating on unsymmetrical, differentially substituted [7-11] and twinned systems. [12-15] Recent goals have been to explore structural parameters linked to discotic nematic mesophase formation [16] and to exploit the strong tendency of triphenylene-based systems to form mesophases to incorporate additional organic functionality into discotic phases. [17] Selected highlights include the intriguing nematic dehydroannulene twins **1**, [12] pyrazine linked twin **2** [18] and mesogenic triphenylene-perylene-triphenylene triads **3**. [19]

Figure 1

## 2. Discussion

### **Lath-shaped dehydroannulene twins based on dialkoxytriphenylene precursors.**

Construction of strained, flat, twinned systems from tetraalkoxytriphenylenes linked through their respective 3,6-positions revealed a switch in behaviour from columnar to nematic behaviour. [17] We have argued that the void region in the annulene will disfavour columnar organisation on space-filling grounds, promoting nematic organisation. The molecules themselves present a shape that deviates from the disk in symmetrical hexasubstituted triphenylene monomers. We reasoned that lath-shaped derivatives would be produced if 2,3-dialkoxytriphenylenes were employed as precursors to related twinned structures. Indeed, we recently reported straightforward access to such precursors. [15]

The synthesis of lath-shaped twin **12** is shown in Scheme 1. Suzuki-Miyaura coupling [20] between 1,2-dibromo-4,5-bis(hexyloxy)benzene **5** [8] and benzene boronic acid **4** gave terphenyl **6**. Careful oxidative closure with FeCl<sub>3</sub> [21, 22] gave 2,3-bis(hexyloxy)triphenylene **7** and treatment with bromine smoothly led to substitution at the 3,6-positions. Dibromide **8** underwent Sonagashira coupling with protected acetylene **9**, and deprotection with sodium hydride gave the triphenylene diacetylene precursor **11**. As expected for a tetrasubstituted triphenylenes, precursor **11** is non-mesogenic and melts directly to an isotropic liquid at 92°C. The synthesis of strained dehydroannulene twins has been optimised for **1**, [12] and employs carefully controlled, high-dilution conditions. Similar conditions were employed here, adding diacetylene **11** to CuCl/Cu(OAc)<sub>2</sub> over 21h (high dilution). MALDI-MS indicated formation of the desired twin, but analysis of aliquots from the reaction during the addition showed that the product had unexpectedly low solubility. Soxhlet extraction using THF was required to isolate the product, which crystallised on cooling. Solubility is so low that it proved impossible to obtain NMR spectra at room temperature. Twin **12** was eventually characterised by performing the NMR spectroscopy in deuterated tetrachloroethane at 80°C. Qualitatively, twin **12** shows strong fluorescence (480nm and 520nm) and a large Stokes shift. It remains a crystalline solid to at least 300 °C.

Scheme 1.

### **A modified route to tetralkoxytriphenylenes and unexpected observation of columnar mesophase formation in a short-chain system.**

We and others have developed convenient routes to differentially substituted triphenylenes. For most of our work we have employed tetraalkoxytriphenylene precursors, adding additional functionality through electrophilic reaction (usually bromination) at the vacant  $\beta$ -sites. [8, 9] The reactions are efficient, but if a different alkoxy substituent is required (to modify transition temperatures for example) the synthesis must be repeated from the beginning. We reasoned that an alternative could lead to common intermediates (tetrahydroxytriphenylenes) that could be substituted at will in the final steps of the syntheses. An ideal route would be scalable so a further possible advantage of a new route would be easy isolation of intermediates (by crystallisation rather than chromatography). 3,6-Dibromotriphenylenes are the most frequently used precursors in our work. The original route to the tetrahexyloxy-derivative (R = n-hexyl) [8] is shown alongside the modified strategy in Scheme 2.

Scheme 2

The new route takes initial advantage of the ready availability of 3-bromoanisole **13** and veratrole **14** (both are inexpensive). The former is readily converted to the corresponding boronic acid **17**, and the latter is easily brominated to give dibromoveratrole **19**. Both syntheses can be performed on large scale, and the products are isolated in high yield and purity by simple crystallisation. Suzuki-Miyaura coupling between the two components yields the corresponding terphenyl **21** which is converted to tetramethoxy triphenylene **23** by treatment with ferric chloride. Again this intermediate is easily isolated without chromatography. Bromination using bromine in cold dichloromethane gave the dibromide **25** which precipitated directly from the reaction solution. In fact, dibromide **25** (a high melting-point crystalline solid) proved to be very poorly soluble in organic solvents. A number of cross-coupling reactions employing **25** were attempted without success due to this insolubility. Nevertheless **25** proved to be a versatile and useful intermediate. Demethylation (hydrolysis) was achieved using boron tribromide and the resulting tetrahydroxytriphenylene **26** was used directly in the subsequent alkylation reaction using 1-bromohexane and potassium carbonate in refluxing ethanol to give the dibromotriphenylene **27** for subsequent functionalisation (see below).

In parallel to this synthesis we performed the analogous route to the 2,7-dibromo-tetramethoxytriphenylene isomer **31** (scheme 3). The synthesis was straightforward but, somewhat surprisingly, triphenylene **31** shows a wide-range columnar hexagonal mesophase (Cr 188 Col<sub>h</sub> 267 I). Triphenylene **31** is therefore by far the most lightly substituted triphenylene reported (and perhaps the most lightly substituted discotic mesogen). Triphenylene discotics typically bear much longer substituent chains and this observation is difficult to rationalise when known triphenylene discogens, and isomer **27**, are considered. It is most likely that the observation of columnar

behaviour stems from unique packing constraints in this isomer due to the large, polarisable bromine substituents.

### Scheme 3

#### New functionalised and twinned triphenylenes

Alkoxytriphenylenes are strong promoters of mesogenic behaviour but the core itself is also an electron-rich, extended aromatic structure leading to potential application as a component in molecular and supramolecular electron-transfer systems, absorbers and emitters. [6] The 3,6-dibromotriphenylene **27** was employed as intermediate to demonstrate efficient introduction of complementary functionality in fully-conjugated (directly linked) triphenylene-centred triads. Ferrocene [23] and BODIPY [24] units were selected as complementary partners due their rich redox and optical absorption/emission characteristics.

Bis-(ferrocenyl)triphenylene **33** was prepared in a single step by Suzuki-Miyaura coupling between 3,6-dibromotriphenylene **27** and excess ferrocene boronic acid **32**. The isolated triad is an orange, crystalline solid that unsurprisingly melts directly to an isotropic liquid at 202 °C. The bis-BODIPY triphenylene **36** required the corresponding dialdehyde precursor **34** and this was prepared by treating dibromotriphenylene **27** with butyl lithium at -78 °C followed by quenching the lithiated intermediate with DMF. Workup and recrystallization yielded the dialdehyde **34** as a yellow (non-mesogenic) solid. Dialdehyde **34** was stirred in neat, degassed pyrrole and catalytic TFA was added to induce condensation and formation of the bis(dipyrrromethane) **35** which was isolated by removal of excess pyrrole (distillation) and recrystallization. Treatment of the intermediate **35** with chloranil and DIPEA base, followed by addition of boron trifluoride afforded the bis-BODIPY triad **36** as a dark non-mesogenic solid. Bis-BODIPY **36** shows characteristic fluorescence behaviour but the emission is very weak, suggesting interaction between the triphenylene core and BODIPY fragments. The redox and photophysical properties of these two new classes of triad are currently under investigation and will be reported in due course.

### Scheme 4

Dialdehyde **34** was finally employed to construct a new twinned triphenylene **37** through imine linkages. Analogous non-mesogenic derivatives were recently reported by Peng and co-workers who described their interesting self-assembly in solution. [25] Consequently dialdehyde **34** was condensed with 1,3-phenylenediamine in refluxing toluene, removing the water from the reaction as it formed using a Dean-Stark trap. Twin **37** precipitated from the reaction on cooling and was isolated as a yellow solid. The thermal behaviour of this twin reinforced our earlier speculation that such structures favour nematic mesophase formation – the compound exclusively forms a nematic mesophase above 276 °C.

### 3. Experimental

#### 4',5'-Bis(hexyloxy)-1,1':2'',1''-terphenyl **6**

1,2-Dibromo-4,5-bis(hexyloxy)benzene **5** (10 g, 0.0229 mol), benzene boronic acid **4** (8.39 g, 0.0687 mol), palladium chloride (0.3252 g, 1.83 mmol), triphenylphosphine (1.9226 g, 7.34 mmol) and sodium carbonate (7.29 g, 0.0684 mol) were stirred in a mixture of toluene, ethanol and water (1:1:1, 240 mL). The reaction was heated at reflux for 16 hours. After 16 hours, benzene boronic acid (8.39 g, 0.0687 mol), palladium chloride (0.3252 g, 1.83 mmol), triphenylphosphine (1.9226 g, 7.34 mmol) and sodium carbonate (7.29 g, 0.0684 mol) were added to the reaction mixture, to ensure the reaction proceeded to completion. After 40 hours, the reaction was quenched with hydrochloric acid (200 mL, 2M). The organics were extracted with dichloromethane and dried over magnesium sulphate. The solvents were removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63 $\mu$ ). The column was eluted using a 1:9 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **6** was obtained as a colourless oil (6.71 g, 68%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.22-7.11 (m, 10H), 6.95 (s, 2H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.88-1.82 (m, 4H), 1.56-1.46 (m, 4H), 1.37-1.33 (m, 8H), 0.93-0.90 (m, 6H) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  148.4, 141.6, 133.1, 130.0, 127.8, 126.1, 116.2, 69.5, 31.6, 29.3, 25.7, 22.6, 14.0 ppm.

#### 2,3-Bis(hexyloxy)triphenylene **7**

A solution of 4',5'-bis(hexyloxy)-1,1':2'',1''-terphenyl **6** (5.68 g, 0.0136 mol) in dichloromethane (250 mL) was stirred at room temperature. Iron (III) chloride (10.697 g, 0.0660 mol) was added and the reaction mixture was stirred for a further 2h. The reaction mixture was cooled to -10°C and methanol (50 mL) was added. The solvents were removed *in vacuo*, and the resulting crude residue dissolved in dichloromethane. This was then washed with water (4 x 100 mL) and the organics were collected then dried over MgSO<sub>4</sub>. The solvents were removed *in vacuo* and the crude product was loaded onto a silica gel column (pore size 40-63 $\mu$ ). The column was eluted using a 1:9 mixture of dichloromethane/petroleum ether. After removal of solvents, the pure product **7** was obtained as a colourless solid (3.62 g, 62%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (dd, *J* = 1.1, 8.0 Hz, 2H),  $\delta$  8.51 (dd, *J* = 1.1, 8.0 Hz, 2H), 8.03 (s, 2H), 7.67-7.59 (m, 4H), 4.26 (t, *J* = 6.6 Hz, 4H), 2.01-1.96 (m, 4H), 1.63-1.59 (m, 4H), 1.48-1.42 (m, 8H), 1.02-0.99 (m, 6H); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  149.7, 129.7, 129.2, 127.0, 126.2, 124.3, 123.4, 122.9, 106.8, 69.4, 31.8, 29.4, 25.9, 22.8, 22.8, 14.2 ppm.

#### 7,10-Dibromo-2,3-bis(hexyloxy)triphenylene **8**

2,3-Bis(hexyloxy)triphenylene **7** (3.4 g, 7.93 mmol) was stirred in dichloromethane (150 mL) at 0°C. Bromine (0.89 mL, 2.79 g, 0.017 mol) was added dropwise *via* pipette and the mixture stirred for a further 2 h at 0°C and then allowed to warm to room temperature. The reaction mixture was washed with sodium metabisulphite solution (20%, 100 mL) and the crude product extracted with dichloromethane. The combined organic layers were dried over MgSO<sub>4</sub>, and the solvent removed *in vacuo*. The crude product was recrystallized from pentanol, giving the pure product **8** as a colourless

powder (3.26 g, 70%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.64 (d, *J* = 2.0 Hz, 2H), 8.32 (d, *J* = 9.0 Hz, 2H), 7.91 (s, 2H), 7.73 (dd, *J* = 2.0, 9.0 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 1.98-1.92 (m, 4H), 1.60-1.53 (m, 4H), 1.44-1.37 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 150.1, 130.6, 129.6, 128.7, 126.2, 124.7, 123.6, 120.6, 106.5, 69.4, 31.7, 29.3, 25.8, 22.7, 14.1 ppm.

#### 4,4'-(6,7-Bis(hexyloxy)triphenylene-2,11-diyl)bis(2-methylbut-3-yn-2-ol) **10**

A mixture of 7,10-dibromo-2,3-bis(hexyloxy)triphenylene **8** (1.37 g, 2.33 mmol), copper (I) iodide (0.027 g, 0.14 mol) and bis(triphenylphosphine)palladium(II) dichloride (0.098 g, 0.14 mol) were stirred in degassed triethylamine (50 mL) under nitrogen. The reaction mixture was heated at reflux for 30 minutes. 2-Methyl-but-3-yn-2-ol (1.13 ml, 0.98 g, 0.012 mol) was added *via* syringe and the reaction heated under reflux for 16 hours. On completion, the crude mixture was washed with water and the organics were extracted with dichloromethane. The organic extracts were combined and dried over MgSO<sub>4</sub>. The solvent was removed *in vacuo* and the crude product loaded onto a silica gel column (pore size 40-63μ). The column was eluted using a 3:1:1 mixture of dichloromethane, ethyl acetate and petroleum ether respectively. After removal of solvents, the pure product **10** was obtained as a pale yellow solid (1.10 g, 80%). Mp. 148-150 °C; IR (thin film) ν 3351, 2931, 2859, 1614 cm<sup>-1</sup>; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.66 (s, 2H), 8.37 (d, *J* = 8.6 Hz, 2H), 7.92 (s, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 2.14 (br s, 2H), 1.97-1.92 (m, 4H), 1.72 (s, 12H), 1.59-1.55 (m, 4H), 1.42-1.38 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 150.1, 130.1, 129.6, 128.3, 127.2, 124.2, 123.0, 120.5, 106.8, 94.5, 82.7, 69.5, 66.0, 31.8, 31.8, 31.2, 29.4, 25.9, 22.8, 14.2 ppm; HRMS (ASAP (Solid)) *m/z* calculated for C<sub>40</sub>H<sub>48</sub>O<sub>4</sub> [M]<sup>+</sup>: 592.3547; found: 592.3533.

#### 7,10-Diethynyl-2,3-bis(hexyloxy)triphenylene **11**

4,4'-(6,7-Bis(hexyloxy)triphenylene-2,11-diyl)bis(2-methylbut-3-yn-2-ol) **10** (1.0 g, 1.69 mmol) was stirred in anhydrous toluene (50 mL) under nitrogen, and the mixture heated to reflux. Sodium hydride (0.18 g, 7.59 mmol) was added portion-wise, and after the addition was complete, the reaction was heated at reflux for a further 3 h. Upon completion the reaction mixture was poured onto cold water, and extracted with dichloromethane. The organic extracts were combined and dried over MgSO<sub>4</sub>, and the solvent removed *in vacuo*. The crude product was loaded onto a silica gel column (pore size 40-63μ) and the column was eluted with a 1:9 mixture of ethyl acetate/petroleum ether. After removal of solvents, the pure product **11** was obtained as a yellow solid (0.48 g, 60%). Mp. 92-94 °C; IR (thin film) ν 3287, 2926, 2857, 2105, 1614 cm<sup>-1</sup>; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 2H), 8.40 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 1.98-1.92 (m, 4H), 1.61-1.56 (m, 4H), 1.42-1.39 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 6H) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 150.3, 130.5, 130.1, 128.3, 127.8, 124.2, 123.1, 120.0, 106.8, 84.2, 77.9, 69.5, 31.8, 29.4, 25.9, 22.8, 14.2 ppm; HRMS (ASAP (Solid)) *m/z* calculated for C<sub>34</sub>H<sub>36</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 477.2788; found: 477.2788.

#### Triphenylene twin **12**

Copper (I) chloride (187 mg, 1.89 mmol) and copper (II) acetate (377 mg, 1.89 mmol) were stirred in anhydrous pyridine (50 mL) at 60 °C under nitrogen. 7,10-Diethynyl-2,3-bis(hexyloxy)triphenylene **11** (400 mg, 0.839 mmol) dissolved in anhydrous pyridine (15 mL), was added *via* syringe pump to the reaction at a rate of 0.012 mL/min. After addition was complete, the reaction was stirred at 60°C for a further 24 h. Upon completion, the solvent was removed *in vacuo* and the crude product underwent soxhlet extraction with THF. The THF solution was left to stand overnight, and the pure

product **12** was obtained by filtration as a yellow solid (30 mg, 5%). Mp. > 300 °C; <sup>1</sup>H-NMR (500 MHz, (Cl<sub>2</sub>CD)<sub>2</sub>, 80°C) δ 9.51 (s, 4H), 8.37 (d, *J* = 8.4 Hz, 4H), 7.98 (s, 4H), 7.57 (d, *J* = 8.4 Hz, 4H), 4.29 (s, 8H), 1.97 (s, 8H), 1.63 (s, 8H), 1.48 (s, 16H), 1.01 (s, 12H) ppm; MS (MALDI): *m/z* 948.5 (M<sup>+</sup>, 100%).

#### 3,3'',4',5'-Tetramethoxy-1,1':2',1''-terphenyl **21**

1,2-Dibromo-4,5-dimethoxybenzene **19** (0.500 g, 1.69 mmol), 3-methoxyphenylboronic acid **17** (1.28 g, 8.45 mmol), triphenylphosphine (0.160 g, 0.608 mmol) and potassium carbonate (1.17 g, 8.45 mmol) were stirred in toluene then bis(triphenylphosphine)palladium(II) chloride (0.0827 g, 0.101 mmol) was added to the mixture and refluxed under nitrogen for 24h. Water was added and the mixture extracted with DCM (3x100 ml). The organic layer was dried with MgSO<sub>4</sub> and evaporated. The solid was recrystallized from DCM and ethanol (6:4), giving the product **21** as an off-white solid (0.55 g, 92%). Mp 133 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500MHz): δ 7.14 (t, *J* = 8.0 Hz, 2H), 6.95 (s, 2H), 6.77 (dd, *J* = 8.0, 2.5 Hz, 2H), 6.74 (dd, *J* = 8.0, 2.5 Hz, 2H), 9.4 (s, 6H), 3.63 (s, 6H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 159.5, 148.6, 143.2, 133.3, 129.3, 122.7, 115.8, 113.9, 112.7, 56.5, 55.5 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 350.15 found 350.20.

#### 2,3,6,11-Tetramethoxytriphenylene **23**

Terphenyl **21** (4.00 g, 11.4 mmol) was stirred in DCM (70 ml) and nitromethane (2 ml) at room temperature. Iron(III) chloride (7.55 g, 45.7 mmol) was added slowly over 2 h and further stirred for 2 h. The solid was filtered off and washed several times with methanol and dried in vacuo to give the triphenylene product **23** as a colourless solid (3.87 g, 98%). Mp 206 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500MHz) δ 8.48 (d, *J* = 9.0 Hz, 2H), 7.88(s, 2H), 7.87 (d, *J* = 2.5 Hz, 2H), 7.23 (dd, *J* = 9.0, 2.5 Hz, 2H), 4.12 (s, 6H), 4.02 (s, 6H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 158.5, 149.8, 130.3, 129.0, 124.9, 121.2 114.6, 106.5, 105.1, 56.4, 56.1 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 348.14 found 348.20.

#### 3,6-Dibromo-2,7,10,11-tetramethoxytriphenylene **25**

2,3,6,11-Tetramethoxytriphenylene **23** (0.504 g, 1.44 mmol) was stirred in dichloromethane (30 ml) and cooled to 0 °C. Bromine (0.505 g, 3.17 mmol) was added drop wise and stirred 2 h. The mixture was washed with sodium metabisulfite (20%). The product that precipitated on standing was filtered off and washed several times with ethanol and dried. Triphenylene **25** was isolated as an off white solid (0.69 g, 93%). Mp >300 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.61 (s, 2H), 7.85 (s, 2H), 7.75 (s, 2H), 4.15 (s, 6H), 4.13(s, 6H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 154.0, 150.0, 129.2, 127.6, 124.0, 123.1, 112.6, 107.3, 105.4, 56.1, 55.1 ppm: MS (MALDI): *m/z* calculated For C<sub>22</sub>H<sub>19</sub>Br<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup>: HRMS 506.9615 found: 506.9626.

#### 4,4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl **29**

1,2-Dibromo-4,5-dimethoxybenzene **19** (2.47 g, 8.330 mmol), 4-methoxyphenylboronic acid **28** (18.7 g, 90.9 mmol), palladium (II)chloride (0.10 g, 0.533 mmol), triphenylphosphine (0.28 g, 1.052 mmol) and sodium carbonate (3.60 g, 0.031 mmol) were stirred in a mixture of toluene, ethanol and water (3:3:1). The resulting mixture was then refluxed under nitrogen and monitored with TLC until completion for 192 h. 2M HCl and water (200 ml) were added then the mixture extracted with DCM (3x150 ml). The organic solution was evaporated and the residue was slowly crystallized from dichloromethane and ethanol (1:1). The product was further purified by column chromatography on silica eluting with DCM and petroleum ether (7:3) giving the product **29** as colourless solid (2.2 g,

75%). Mp 146 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.05 (d, *J* = 8.5 Hz, 4H), 6.89 (s, 2H), 6.77 (d, *J* = 8.5 Hz, 4H), 3.92 (s, 6H), 3.77 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz): δ 158.2, 148.1, 134.2, 132.7, 131.1, 113.8, 113.5, 56.2, 55.3 ppm. MS (MALDI): *m/z* 350.4 (M<sup>+</sup>, 100%). HRMS, (ESI) [C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>] [M+H]<sup>+</sup>: Calculated: 349.1434; Found: 349.1431.

#### 2,3,7,10-Tetramethoxytriphenylene **30**

4,4',4'',5'-tetramethoxy-1,1':2',1''-terphenyl **29** (1.92 g, 0.006 mol) was stirred in DCM (70 ml) and nitromethane (4 ml) at room temperature. Iron(III) chloride (2.72 g, 0.016 mol) was added in portions over 2 h and the mixture was further stirred for 2 h. Cold methanol was then added slowly and the mixture was washed several times with water. The aqueous layer was further extracted with DCM (3x150 ml). The combined organic phases were dried with MgSO<sub>4</sub> and the solvents evaporated. The residue obtained was slowly recrystallized from dichloromethane and methanol (2:1), giving 2,3,7,10-Tetramethoxytriphenylene **30** as a colourless solid (0.99 g, 52%). Mp 170 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.42 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 2.5 Hz, 2H), 7.89 (s, 2H), 7.30 (dd, *J*=9.0 Hz, 2.5, 2H), 4.11 (s, 6H), 4.03 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 158.2, 148.9, 130.3, 125.9, 124.6, 124.2, 123.3, 106.2, 104.3, 56.1, 55.7 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 348.14 found 348.10.

#### 2,7-Dibromo-3,6,10,11-tetramethoxytriphenylene **31**

2,3,7,10-Tetramethoxytriphenylene **30** (0.50 g, 1.44 mmol) was stirred in DCM (20 ml) and cooled at 0°C. Bromine (0.507 g, 3.17 mmol) was added dropwise and the mixture was stirred. The reaction was monitored by TLC to completion. The mixture was washed with sodium metabisulfite (20%) and extracted with DCM (3x150 ml). The organic layer was dried with MgSO<sub>4</sub> and the solvent was evaporated. The crude product was purified by column chromatography eluting with DCM and petroleum ether (7:3) and the solid obtained was recrystallized from DCM and isopropanol (1:1) to give pure Triphenylene **31** as a colourless solid (0.44 g, 61%). Cr 188 Col<sub>h</sub> 267 I. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.61 (s, 2H), 7.85 (s, 2H), 7.75 (s, 2H), 4.15 (s, 6H), 4.13 (s, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 154.1, 149.3, 128.7, 128.0, 122.1, 113.2, 104.5, 103.8, 56.5, 56.2 ppm. MS (MALDI): *m/z* calculated for C<sub>22</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>4</sub> (M<sup>+</sup>, 100%): 505.96 found 505.96.

#### Demethylation of 3,6-dibromo-2,7,10,11-tetramethoxytriphenylene **25**

3,6-Dibromo-2,7,10,11-tetramethoxytriphenylene **25** (4.00 g, 7.94 mmol) was stirred in DCM (30 ml) at -80°C and boron tribromide (11.9 g, 0.05 mmol) was added slowly to the mixture. The reaction was allowed to stir overnight at room temperature. The reaction was cooled in ice, ethanol was added dropwise and then the solvents evaporated to dryness in vacuo. The intermediate **26** (colourless solid, 3.42 g, 96%), was used without further purification. <sup>1</sup>H-NMR (500 MHz, d<sub>6</sub>-acetone) δ 8.70 (s, 2H), 8.16 (s, 2H), 8.02 (s, 2H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) 153.5, 147.5, 130.7, 128.2, 124.0, 123.4, 110.8, 109.5, 109.4 ppm. MS (MALDI): *m/z* calculated for C<sub>18</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>4</sub> (M<sup>+</sup>, 100%) 449.90 found 449.90.

#### 3,6-Dibromo-2,7,10,11-tetrahexyloxytriphenylene **27**

3,6-Dibromo-2,7,10,11-tetrahydroxytriphenylene **26** (2.23 g, 5.00 mmol) in degassed ethanol (30 ml) was stirred with bromohexane (4.95 g, 0.03 mol) and K<sub>2</sub>CO<sub>3</sub> (4.15 g, 0.03 mol) at reflux under nitrogen for 24 h. The mixture was filtered and solvent evaporated. Dilute H<sub>2</sub>SO<sub>4</sub> was added and the

mixture was extracted with DCM (3x100 ml). The organic layer was dried with MgSO<sub>4</sub> and evaporated. The solid obtained was recrystallized from DCM: ethanol (2:1) to give the title compound **27** as a colourless solid (3.70 g, 94%).

### Ferrocenyl triphenylene **33**

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene **27** (0.500 g, 0.64 mmol), ferrocene boronic acid **32** (1.17 g, 5.10 mmol), triphenylphosphine (0.120 g, 0.46 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.71 g, 5.10 mmol) were stirred in degassed toluene for 20 mins. Bis(triphenylphosphine)palladium(II) chloride (0.054 g, 0.076 mmol) was added and the reaction was allowed to reflux under nitrogen for 1 h. Dilute sodium hydroxide solution was added and the mixture extracted with dichloromethane (3x100ml). The organic layer was dried with MgSO<sub>4</sub> and then evaporated. The resulting solid was recrystallized from DCM: ethanol (2: 3) to give Ferrocenyl triphenylene **33** as an orange solid (0.40 g, 56%). Mp 202 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.75 (s, 2H), 7.92 (s, 2H), 7.79 (s, 2H), 5.00-5.04 (m, 4H), 4.38-4.42 (m, 4H), 4.28 (t, *J*=7.0 Hz, 4H), 4.30 (t, *J*=7.0 Hz, 4H), 2.05 (q, *J*=7.0 Hz, 4H), 1.97 (q, *J*=7.0 Hz, 4H), 1.67 (q, *J*=7.0 Hz, 4H), 1.61 (q, *J*=7.0 Hz, 4H), 1.35-1.52 (m, 16H), 0.98 (t, *J*=7.0 Hz, 6H), 0.95 (t, *J*=7.0 Hz, 6H) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz) δ 155.7, 149.9, 128.4, 127.8, 123.8, 123.2, 108.1, 104.6, 83.6, 77.2, 70.2, 70.0, 69.4, 69.0, 68.9, 32.1, 29.9, 26.26.3, 23.1, 14.5 ppm. HRMS: *m/z* calculated For C<sub>62</sub>H<sub>77</sub>Fe<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup>: 997.4519 found: 997.4516.

### 3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde **34**

2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene **27** (3 g, 3.81 mmol) was stirred in anhydrous THF (50 mL) under nitrogen at -78°C. *n*-BuLi (2.5 M in hexanes, 9.23 mL, 23.1 mmol) was added *via* syringe and the mixture stirred for 3 h, monitored by TLC. Anhydrous DMF (1.78 mL, 1.69 g, 23.1 mmol) was added *via* syringe and the reaction left to warm to room temperature overnight. Upon completion the reaction was quenched with water and extracted with DCM. The organics were combined and dried over MgSO<sub>4</sub>, before being concentrated *in vacuo*. The crude product was recrystallized from DCM and ethanol giving the desired product **34** as a yellow solid (1.89 g, 73%). Mp. 208-210 °C; IR (thin film) ν 2932, 2859, 1683 cm<sup>-1</sup>; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 10.61 (s, 2H), 8.93 (s, 2H), 7.71 (s, 2H), 7.63 (s, 2H), 4.26-4.21 (m, 8H), 1.99-1.93 (m, 8H), 1.63-1.57 (d, 8H), 1.45-1.38 (m, 16H), 0.97-0.94 (m, 12H) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 189.6, 159.3, 150.9, 134.8, 124.9, 124.5, 124.3, 122.8, 107.8, 104.6, 69.7, 68.8, 31.8, 31.8, 29.5, 29.3, 26.1, 26.0, 22.8, 22.8, 14.2 ppm; HRMS (ESI<sup>+</sup>) *m/z* calculated for C<sub>44</sub>H<sub>60</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 685.4463; found: 685.4463.

### 2,2',2'',2'''-((3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-diyl)bis(methanetriyl))tetrakis(1*H*-pyrrole) **35**

3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde **34** (419 mg, 0.611 mmol) and freshly distilled pyrrole (20 mL) were degassed with argon for 10 minutes. TFA (5 μL, 6.96 mg, 0.061 mmol) was added *via* syringe and the mixture stirred at room temperature until TLC analysis showed full consumption of the aldehyde (45 min). Upon completion, the crude mixture was diluted with DCM and washed with aqueous NaOH solution. The organics were combined and dried over MgSO<sub>4</sub>, before being concentrated *in vacuo*. The crude product was distilled under vacuum to remove the excess pyrrole, and the remaining residue recrystallized from dichloromethane and ethanol, yielding the desired product **35** as a light brown powder (262.5 mg, 47%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.27 (br s, 4H), 8.08 (s, 2H), 7.81 (s, 2H), 7.73 (s, 2H), 6.69 (td, *J* = 1.6, 2.6 Hz, 4H), 6.16 (dd, *J* = 2.6, 5.9 Hz,

4H), 5.99-5.97 (m, 4H), 5.92 (s, 2H), 4.21 (t,  $J = 6.4$  Hz, 4H), 4.13 (t,  $J = 6.4$  Hz, 4H), 1.96-1.90 (m, 4H), 1.79-1.73 (m, 4H), 1.61-1.55 (m, 8H), 1.44-1.32 (m, 16H), 0.96-0.91 (m, 12H) ppm;  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 149.6, 132.5, 131.1, 128.9, 124.4, 124.3, 123.2, 116.9, 108.4, 107.5, 107.0, 104.9, 69.7, 67.0, 39.3, 31.8, 31.8, 29.5, 26.0, 25.9, 22.8, 22.7, 14.2, 14.2 ppm.

#### Bis-BODIPYtriphenylene **35**

*p*-Chloranil (245.67 mg, 0.992 mmol) was stirred in anhydrous DCM (35 mL) at  $-40^\circ\text{C}$  under nitrogen. 2,2',2'',2'''-((3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-diyl)bis(methanetriyl))tetrakis(1*H*-pyrrole) **35** (416.6 mg, 0.454 mmol) was added in anhydrous DCM (50 mL) dropwise *via* an addition funnel over 10 min. The mixture was stirred at  $-40^\circ\text{C}$  for 3 h then DIPEA (0.95 mL, 704.35 mg, 5.45 mmol) was added, and the mixture stirred for a further 30 min.  $\text{BF}_3\cdot\text{OEt}_2$  (1.01 mL, 1.160 mg, 8.18 mmol) was added slowly and the reaction allowed to warm to room temperature overnight. Upon completion, the crude product was filtered through Celite, washed with aqueous  $\text{NaHCO}_3$  solution and extracted with DCM. The organics were combined and dried over  $\text{MgSO}_4$ , before being concentrated *in vacuo*. The crude product was recrystallised from dichloromethane and ethanol, giving the bisBODIPY triphenylene **36** as a dark red solid (205 mg, 45%). Mp.  $150\text{-}160^\circ\text{C}$  (decomp.);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 2H), 7.97 (s, 2H), 7.94 (s, 2H), 7.90 (s, 4H), 6.85 (d,  $J = 4.1$  Hz, 4H), 6.48 (dd,  $J = 1.9, 4.1$  Hz, 4H), 4.31 (t,  $J = 6.4$  Hz, 4H), 4.18 (t,  $J = 6.4$  Hz, 4H), 2.02-1.97 (m, 8H), 1.71-1.67 (m, 8H), 1.45-1.39 (m, 16H), 0.97-0.94 (m, 12H) ppm;  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 150.7, 144.1, 135.9, 131.7, 131.3, 129.9, 127.0, 124.5, 123.3, 122.1, 118.4, 107.5, 105.2, 69.8, 69.2, 31.8, 31.5, 29.5, 29.1, 26.0, 25.8, 22.8, 22.6, 14.2, 14.1 ppm; HRMS (ESI $^+$ )  $m/z$  calculated for  $\text{C}_{60}\text{H}_{70}\text{B}_2\text{F}_4\text{N}_4\text{O}_4$   $[\text{M}+\text{NH}_4]^+$ : 1026.5876; found: 1026.5853.

#### Diiminetriphenylene Twin **37**

3,6,7,10-Tetrakis(hexyloxy)triphenylene-2,11-dicarbaldehyde **34** (100 mg, 0.146 mmol) and 1,3-diaminobenzene (15.79 mg, 0.146 mmol) were heated in degassed toluene (20 mL) at reflux under Dean-Stark conditions under nitrogen. After 4 days, the reaction mixture was allowed to cool to room temperature, and the resulting precipitate collected by filtration. The precipitate was washed with methanol then hexane, giving the twin **37** as a yellow solid (42 mg, 19%). Mp. Cr  $276^\circ\text{C}$   $\text{N}_\text{D} > 300^\circ\text{C}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.72 (s, 4H), 9.34 (s, 4H), 7.91 (t,  $J = 2.1$  Hz, 2H), 7.89 (s, 4H), 7.79 (s, 4H), 7.50 (t,  $J = 7.9$  Hz, 2H), 7.31 (dd,  $J = 2.1, 7.9$  Hz, 4H), 4.32 (t,  $J = 6.4$  Hz, 8H), 4.28 (t,  $J = 6.4$  Hz, 8H), 2.03-1.96 (m, 16H), 1.69-1.59 (m, 16H), 1.47-1.40 (m, 32H), 0.98-0.94 (m, 24H) ppm.

## 4. Conclusions

The versatile modified synthetic route to differentially substituted triphenylenes had been developed. The route provides a useful intermediate for rapid, late-stage exchange of side-chain substituents. Remarkably one intermediate, 2,7-dibromo-3,6,10,11-tetramethoxytriphenylene **31** displays a wide-range columnar mesophase. The new synthetic procedure has been employed alongside established routes to prepare new twinned structures. The dehydroannulene twin **12** based on 2,3-bis(hexyloxy)triphenylene presents a lath shape and is a high melting crystalline solid. Imine linked twin **37** presents a structure related to previously examined nematic twins, and

similarly displays only a nematic mesophase on heating. Syntheses of conjugated triad structures incorporating ferrocene and BODIPY components linked to an electron-rich triphenylene core have been achieved.

## 5. Acknowledgements

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#### List of Legends

Figure 1. Recently reported functionalised triphenylenes and twins.

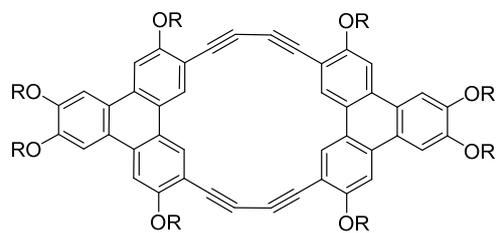
Scheme 1. The synthesis of lath-shaped triphenylene twin **12**.

Scheme 2. The original and modified route to useful dibromotriphenylene intermediates.

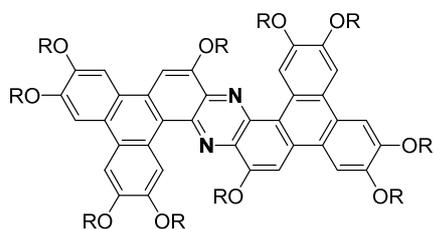
Scheme 3. The synthesis of mesogenic 2,7-dibromotetramethoxytriphenylene **31**.

Scheme 4. Synthesis of ferrocenyl triphenylene **33**, bisBODIPY triphenylene **36** and nematic twin **37**.

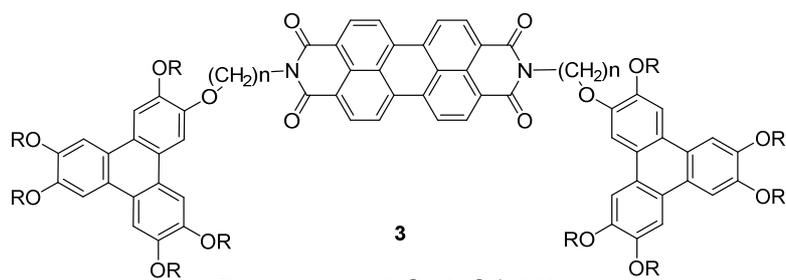
Figure 1



R = n-hexyl, Cr 209 N<sub>D</sub> >280 I

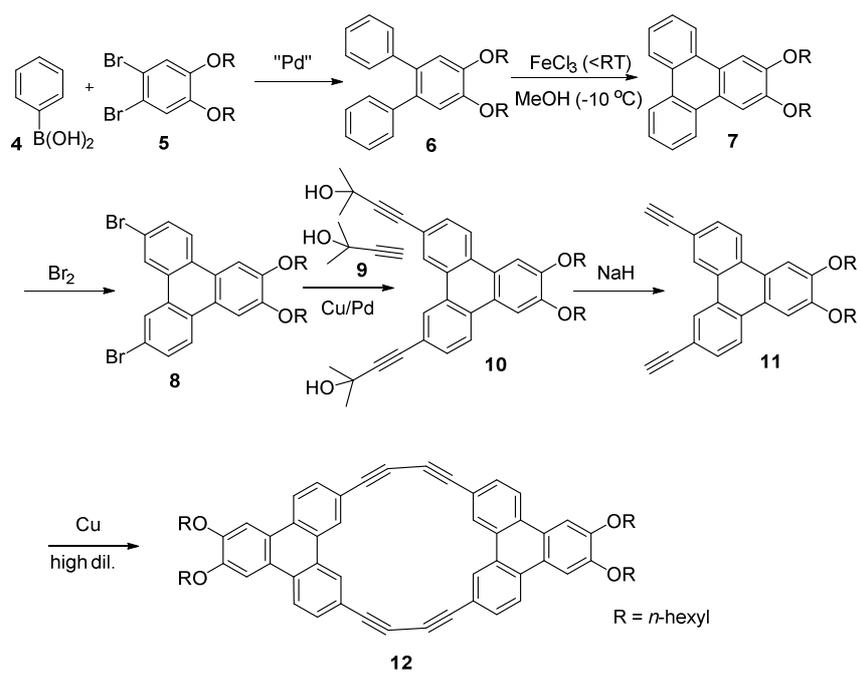


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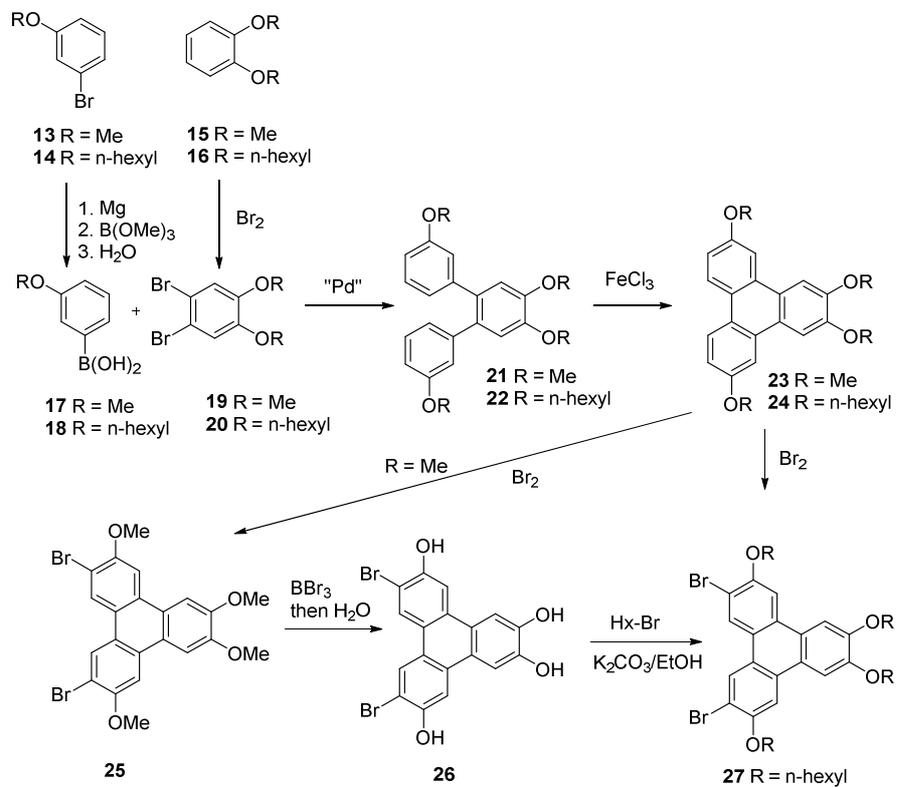


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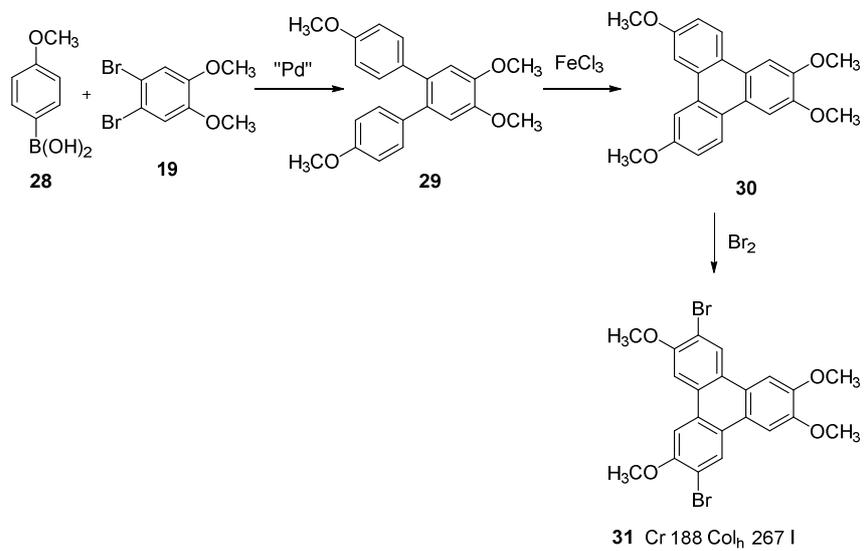
Scheme 1



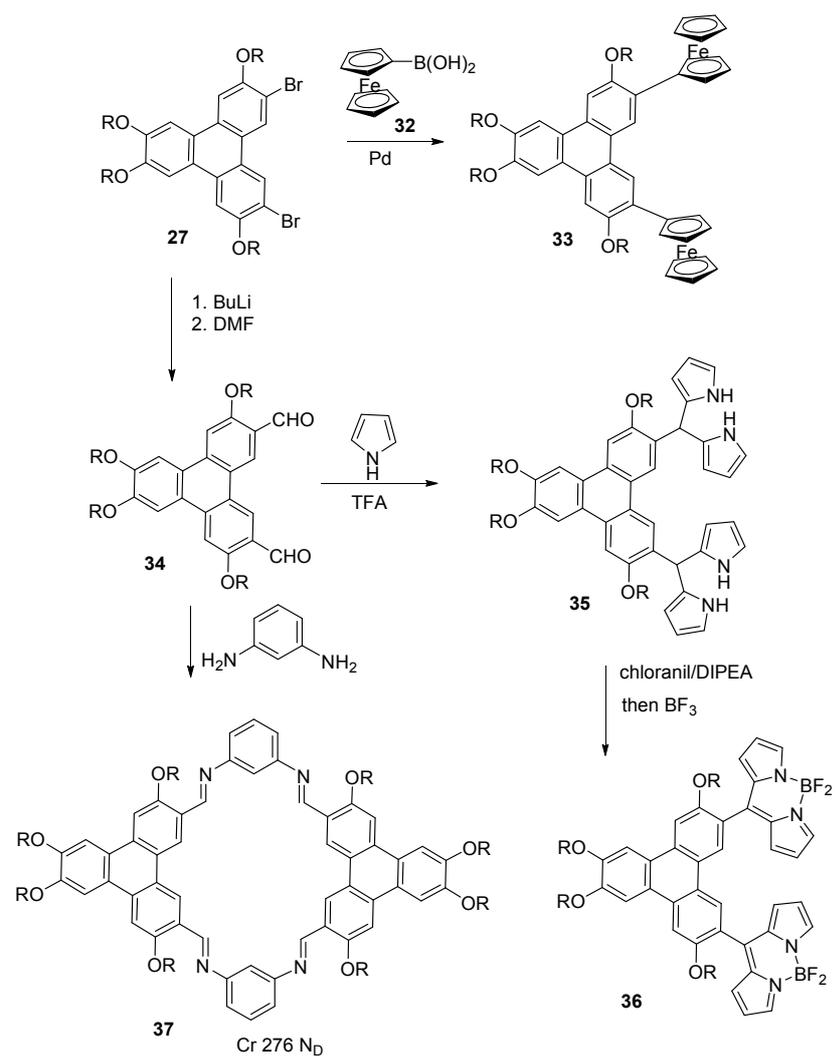
Scheme 2



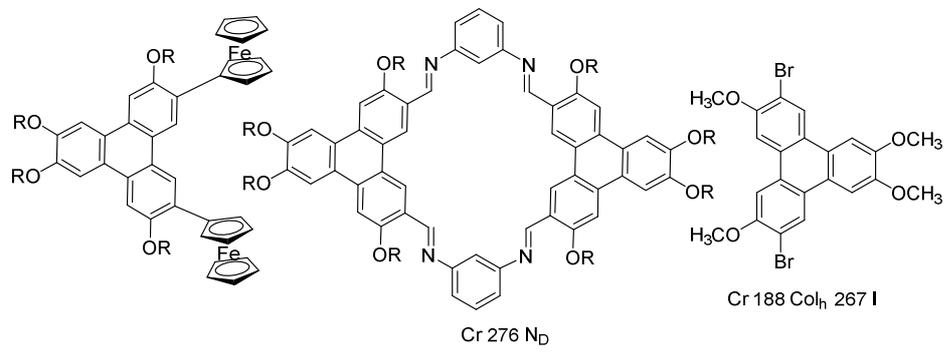
Scheme 3



Scheme 4.



Graphical abstract



Functionalised triphenylenes...and the "smallest" triphenylene discotic liquid crystal