α-Halogenation of triphenylene-based discotic liquid crystals: towards a chiral nucleus

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In an attempt to prepare chiral discotic liquid crystals based on a helically twisted triphenylene nucleus a route has been developed for the introduction of α-fluoro, -chloro and -bromo substituents and it is shown that multiple α-halogenation is also possible. The monosubstituted derivatives all show enhanced mesophase stability whilst formation of the mesophase is suppressed for the polyhalogenated derivatives. Rather surprisingly, reaction of 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6) with iodine monochloride results in chlorination rather than iodination.

Ferroelectric discotic liquid crystals[1–3] are potentially attractive for device applications.[1] Most effort in the search for these has concentrated on the creation of chiral discogens[1,3] and has relied on the relatively weak chirality imparted by the introduction of a chiral centre into the highly disordered side-chain region[3] or by adding chiral 'dopants'.[4] Much stronger chirality would presumably be imparted if a helical twist could be imparted to the central aromatic core. Given the known chirality of 4,5-disubstituted phenanthrenes[5–7] it seems reasonable to assume that suitable α-substitution of a triphenylene nucleus would convert it from a planar to a propeller-like geometry.† Indeed this has already been demonstrated in the case of 1,12-diiodotriphenylene, where the X-ray crystal structure shows that the nucleus possesses a strong helical twist.[6] Electrophilic substitution of triphenylenes in the α position is difficult because of steric hindrance. However, we recently reported that, in those electron-rich derivatives in which all of the β-positions are blocked by alkoxy groups, the α-positions can be nitrated.[8,9] Here we show that these α positions can also be halogenated[9,10] and explore the effect of α-substituents on the geometry of triphenylene-based discotic mesogens. Because of the size of the halogeno substituents and the fact that polyhalogenated derivatives can be made this seemed the best path to discogens with chiral nuclei.

Calculations

Whereas simple model-building suggests that the α-nitro group in 1-nitro-2,3,6,7,10,11-hexahexyloxytriphenylene could be accommodated without upsetting the planarity of the aromatic core, provided it was orthogonal to the π-system,[8] MNDO and PM3 calculations on 1-nitro-2,3,6,7,10,11-hexamethoxytriphenylene suggest that there is a lower energy minimum in which the nitro group remains conjugated with the π-system of the aromatic nucleus but in which the nucleus develops a helical twist (Plate 1)[11] with the nitro group lying below the opposing *peri*-hydrogen. Similar calculations in which the geometries of the α-fluoro, α-chloro and α-bromo derivatives of hexamethoxy triphenylene were optimised all show a similar chiral twist (Plate 2) increasing in magnitude along the series α-F > α-Cl > α-Br > α-NO_2. The calculated dihedral angles C(12)—C(12α)—C(12β)—C(1) for the chloro, bromo and nitro derivatives proved fairly independent of the MO method employed but for the flouro derivative the calculated twist was significantly method-dependent. The calculated dihedral angles C(12)—C(12α)—C(12β)—C(1) by the MNDO method were 23.9 (α-F), 25.4 (α-Cl), 25.9 (α-Br) and 28.5° (α-NO_2); by the AM1 method they were 12.8 (α-F), 19.6 (α-Cl) and 25.8° (α-Br); and by the PM3 method they were 2.5 (α-F), 20.7 (α-Cl), 24.5 (α-Br) and 25.5° (α-NO_2). A feature of all of these (and related) calculations is the way in which the introduction of the α-substituent and twisting of the nucleus induces an up-down-up-down orientation of the alkoxy groups at positions 2,3,6 and 7. The effect on position 2 is purely steric and that on the remaining positions presumably minimises local dipolar interactions.

Synthesis

Potentially the greatest twist in the triphenylene nucleus would be imparted by introducing the largest possible halogen, an α-iodo substituent.[6] Hence our initial experiment was to treat 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6) **1** with iodine monochloride.[10] To our surprise we obtained not the monoiodo derivative but a mixture of 1-chloro-2,3,6,7,10,11-hexahexyloxytriphenylene **2**, 1,8-dichloro-2,3,6,7,10,11-hexahexyloxytriphenylene **3** and 1,5-dichloro-2,3,6,7,10,11-hexahexyloxytriphenylene **4** (Scheme 1). Exhaustive treatment with iodine monochloride gave a tetrachloro derivative with two equally intense aryl hydrogen singlets in the ^1H NMR spectrum, which must therefore be 1,4,5,9-tetrachloro-2,3,6,7,10,11-hexahexyloxytriphenylene **5** (Scheme 2). Although iodine monochloride normally acts as an iodinating agent[12] it is known that in some circumstances it can act as a chlorinating agent,[13,14] particularly if the substrate is one that is readily oxidised. These reactions probably involve an initial one-electron oxidation step and proceed through the aryl radical cation.[13] In support of this notion, we noted that an intense green coloration, typical of the $(\mathrm{HAT6})^{\bullet+}$ radical cation,[15] developed in the course of our reaction. We suggest that the most reasonable mechanism is one in which the iodine monochloride oxidises the HAT6 to the radical cation $(\mathrm{HAT6})^{\bullet+}$, which then undergoes nucleophilic attack by chloride.[10] Further support for this mechanism is provided by an alternative synthesis of

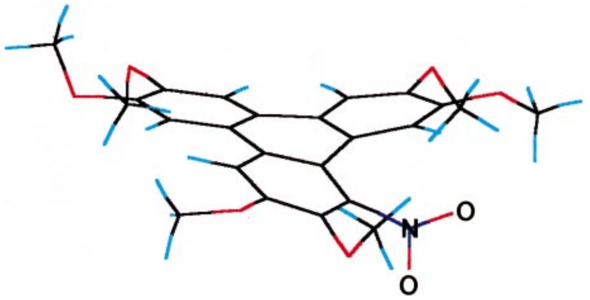

Plate 1 Energy minimised structure of 1-nitro-2,3,6,7,10,11-hexamethoxytriphenylene

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† Professor K. Praefcke has independently concluded that α-halogenation provides a potential route to chiral triphenylene-based discotics and we thank him for helpful discussions and communication of unpublished results.

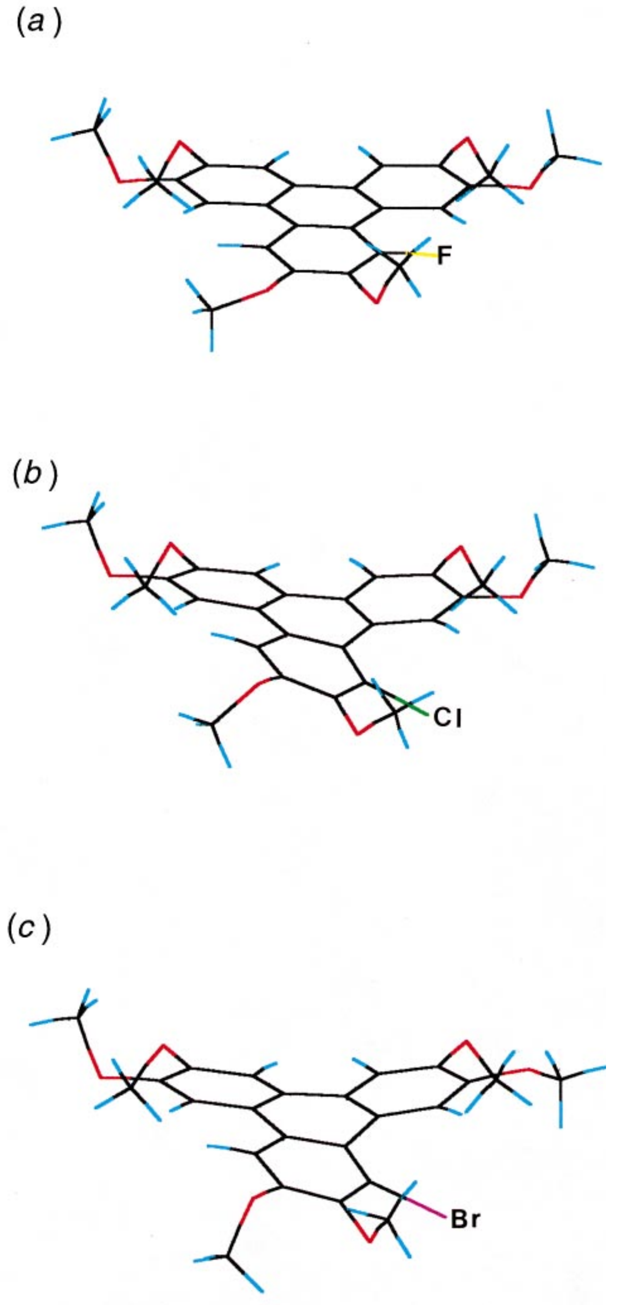
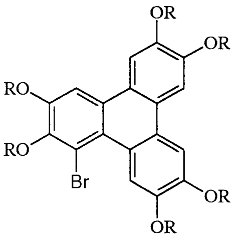


Plate 2 Energy minimised structure of **(a)** 1-nitro-2,3,6,7,10,11-hexamethoxytriphenylene, **(b)** 1-chloro-2,3,6,7,10,11-hexamethoxytriphenylene and **(c)** 1-bromo-2,3,6,7,10,11-hexamethoxytriphenylene

the monochloride **2** in which the reaction is deliberately carried out in a two-step manner. HAT6 **1** is oxidised to $(\mathrm{HAT6})^{\bullet +}$ with [bis(trifluoroacetoxy)iodo]benzene and then the reaction worked up with tetrabutylammonium chloride.[16] Praefcke *et al.* have now reported a more conventional synthesis of the monochloride **2** using aluminium trichloride and sulfuryl chloride in 1,2-dichlorobenzene and of the corresponding monobromide (1-bromo-2,3,6,7,10,11-hexahexyloxytriphenylene **6**) using bromine in carbon tetrachloride at low temperature.[11] If HAT6 **1** is treated with excess bromine in dichloromethane at room temperature a tribromide is obtained showing three equal aromatic hydrogen singlets in the ^{1}H NMR spectrum and which is assigned the structure **7** (Scheme 3). The alternative structures, the 1,4,5- and 1,8,9-tribromides, which would also formally account for the NMR spectrum, seem highly improbable on steric grounds. The fact that this tribromo compound **7** and not the symmetrical 1,5,9-tribromo derivative was formed seems surprising. It may well be that the



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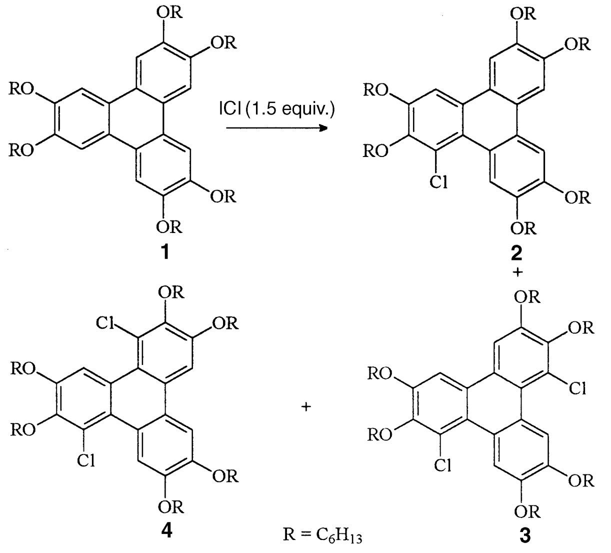
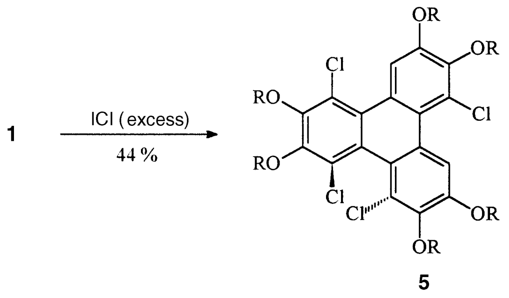
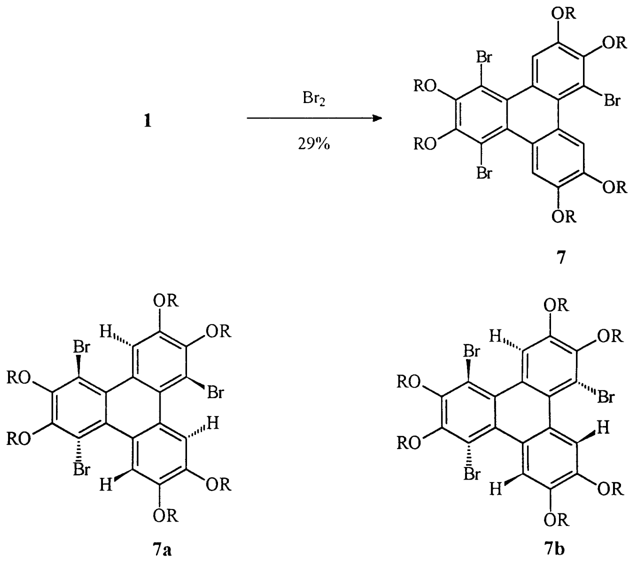


Scheme 1



Scheme 2



Scheme 3

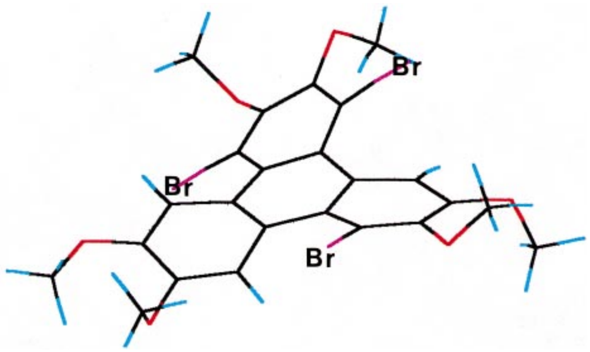
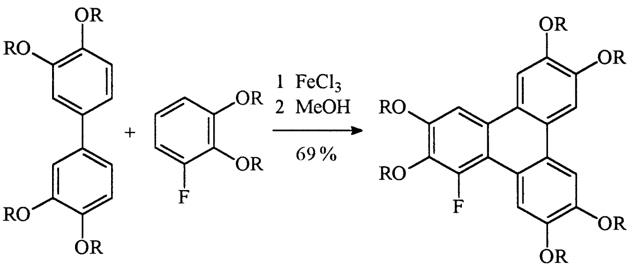


Plate 3 Energy minimised structure of 1,4,8-tribromo-2,3,6,7,10,11-hexamethoxytriphenylene



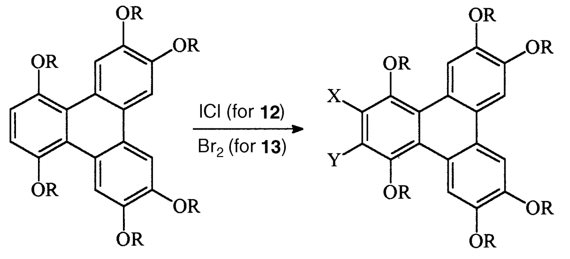
8 **9** **10**

Scheme 4

regiochemistry of some of these reactions is determined by steric rather than electronic factors. MNDO calculations on 1,4,8-tribromo-2,3,6,7,10,11-hexamethoxytriphenylene produced two energy minima. The absolute minimum corresponds to the normal propeller-shaped conformation, and is shown in Plate 3. The second local minimum is one in which the 'stacking' of the bromine at C(8) and the hydrogen at C(9) are reversed. On the assumption that the reversal of this arrangement has a reasonably high energy barrier it is possible that formulae **7a** and **7b** represent isolable isomers. This is potentially an unusual form of isomerism.

We have not attempted to prepare 1-fluoro-2,3,6,7,10,11-hexahexyloxytriphenylene **10** by direct substitution, but it is easy to prepare using the iron(III)-mediated coupling of 3,3′,4,4′-tetrahexyloxybiphenyl **8** and 1-fluoro-2,3-dihexyloxybenzene **9** (Scheme 4).[17] The ^{1}H NMR spectrum of this product showed one low field aromatic hydrogen at δ 8.51 with a splitting of 8 Hz. This splitting could plausibly be interpreted as the result of an *ortho* coupling and raises the possibility that the product did not have the desired structure, but instead was the alternative coupling product 3-fluoro-1,2,6,7,10,11-hexahexyloxytriphenylene. However, this seems unlikely in view of the absence of the peak at *ca.* δ 9 which is characteristic of triphenylenes containing an α-alkoxy substituent.[17] The correctness of the assigned structure was confirmed by NOE experiments.‡ The signal at δ 8.51 proved to be that for the hydrogen at the 12-position and the splitting to be due to a through-space coupling between the fluorine and hydrogen.[18]

We have also investigated the substitution reactions of derivatives without the symmetrical 2,3,6,7,10,11-substitution pattern.[17] In the case of 1,4,6,7,10,11-hexahexyloxytriphenylene **11** treatment with iodine monochloride gives the monochloro compound **12** and treatment with bromine gives the dibromo compound **13** (Scheme 5). The preference for attack in the β-position is not surprising and presumably reflects 'steric control'.



11

12 X = Cl, Y = H, 19%
13 X = Br, Y = Br, 28%

Scheme 5

Discussion

The phase behaviour of the new compounds reported in this paper and of related systems is summarised in Table 1. The polyhalogeno derivatives **5** and **7** proved to be oils at room temperature and the derivatives **12** and **13** showed no liquid crystal behaviour. The monofluoro compound **10**, monochloro compound **2** and monobromo compound **6** are crystalline solids which show enantiotropic behaviour, exhibiting a columnar liquid crystal phase with a polarising microscopy texture typical of that of a D_h phase. Miscibility studies on the monochloro and monobromo derivatives **2** and **6** confirm this assignment.[11]

It is interesting to note that, despite the presumed non-planarity of the nucleus, most of these α-substituted compounds still show an enhanced mesophase range as compared to the parent compound HAT6 **1**. Within the series of halogenated compounds, the K–D transition is essentially constant, whereas the D–I transition temperature steadily decreases. The effect of substituents on the stability of the D_h phase is complex and not fully understood but, in general, electron-withdrawing groups tend to exert a stabilising effect.[11] Local dipolar interactions may also be important in stabilising a columnar arrangement.[8] Hence, relative to HAT6 **1**, the mononitro compound **10** shows a higher clearing point and this may be attributed to the stabilisation of the columnar stacks through strong local (opposed) dipolar interactions or alternatively to the fact that this is the substituent with the strongest electron-withdrawing effect. In the cases of the monofluoro compound **10**, the monochloro compound **2** and the monobromo compound **6**, the stability of the columnar arrangement decreases as the steric bulk of the substituent increases, the strength of the local dipolar interactions decreases and the electron-withdrawing effect of the substituent decreases. An α-methyl substituent destroys the liquid crystal behaviour altogether.[17] This weak donor substituent is large enough to destroy the planarity of the nucleus but not polar enough to give a significant dipole.

Direct proof of the chirality of these systems has yet to be achieved although it is clear from our calculations that they cannot be planar. This is further supported by the X-ray crystal structure of 1,12-diiodotriphenylene.[6] In terms of a practicable, resolved chiral system it is important to note that the 4,5-disubstituted phenanthrenes all racemise at relatively low temperatures.[5,7] The calculated barrier[11] to racemisation for 1,12-dichloro-2,3,6,7,10,11-hexamethoxytriphenylene is 179 kJ mol^{-1}, suggesting that it may be possible to resolve compounds such as the tetrachloro derivative **5** at room temperature. For a practical chiral discotic liquid crystal based on these principles it seems important to introduce large substituents and preferably multiple large substituents that do not destroy the

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‡ These assignments have been independently verified by more extensive NMR studies of our product by Dr J. Jakupovic and Professor K. Praefcke, Technische Universität, Berlin.

Table 1 Transition temperatures of compounds as determined by optical microscopy (K = crystal phase, D_h = discotic hexagonal liquid crystal phase and I = isotropic liquid phase)

compound	K–D_h	D_h–I	K–I
2,3,6,7,10,11-hexahexyloxytriphenylene **1**	67	100	—
1-nitro-2,3,6,7,10,11-hexahexyloxytriphenylene[a]	<25[b]	136	
1-fluoro-2,3,6,7,10,11-hexahexyloxytriphenylene **10**	39	116	—
1-chloro-2,3,6,7,10,11-hexahexyloxytriphenylene **2**	37[c]	98	—
1-bromo-2,3,6,7,10,11-hexahexyloxytriphenylene **6**[d]	37	83	—
1-methyl-2,3,6,7,10,11-hexahexyloxytriphenylene[e]	—	—	60
1,4,5,9-Tetrachloro-2,3,6,7,10,11-hexahexyloxytriphenylene **5**	—	—	<25
1,4,8-Tribromo-2,3,6,7,10,11-hexahexyloxytriphenylene **7**	—	—	<25
2-chloro-1,4,6,7,10,11-hexahexyloxytriphenylene **12**	—	—	52
2,3-dibromo-1,4,6,7,10,11-hexahexyloxytriphenylene **13**	—	—	70

[a]Ref. 8. [b]Ref. 11 gives 43 °C. [c]Ref. 11 gives 31 °C. [d]Ref. 11. [e]Ref. 17.

liquid crystal behaviour. Unfortunately, the tetrachloro and tribromo derivatives **5** and **6** have proved to be oils. The discovery of other polybrominated and polychlorinated derivatives that are liquid crystalline seems to offer the most promising way forward.

Experimental

Phase behaviour was determined on an Olympus BH-2 microscope with a Mettler FP82HT hotstage. Samples for combustion analyses were routinely dried at 25 °C and 0.3 mmHg.

NMR Spectra were recorded on a General Electric QE300 or a Bruker AM400 instrument. Chemical shifts (δ) are given relative to tetramethylsilane, coupling constants (J) are given in Hz and the solvent used was $CDCl_3$ (0.03% $SiMe_4$).

Mass spectra were obtained on a VG Autospec instrument and were recorded by the mass spectrometry staff of the School of Chemistry, University of Leeds. All peaks >20% are reported.

Column chromatography on silica refers to the use of Merck Kieselgel Type 60.

Except for the dichloro derivatives **3** and **4**, ^{1}H NMR and thin layer chromatography (TLC) showed that all of the halogenation products were obtained as single isomers.

Light petroleum refers to the 40–60 °C boiling fraction.

Molecular orbital calculations

The geometries shown in Plates 1–3 were optimised at the PM3 level.

1-Chloro-2,3,6,7,10,11-hexahexyloxytriphenylene 2

2,3,6,7,10,11-Hexahexyloxytriphenylene **1** (1.0 g, 1.2 mmol) was dissolved in dichloromethane (60 cm^3) after which iodine monochloride (0.30 g, 1.8 mmol) was added in one portion. The mixture was stirred for 20 min before saturated aqueous sodium metabisulfite (60 cm^3) was added and stirred for a further 20 min. The organic phase was separated and the aqueous layer extracted with dichloromethane (3 × 20 cm^3), the combined organic phase and extracts then being dried with magnesium sulfate. After removal of solvents *in vacuo* the residual oily solid was purified by column chromatography on silica eluting with 7% v/v diethyl ether–light petroleum and recrystallised from ethanol to give the title compound **2** (0.26 g, 25%) as a white solid, K–D 37 °C, D–I 98 °C (Found: C, 75.05; H, 9.6. $C_{54}H_{83}ClO_6$ requires C, 75.1; H, 9.7%); δ_H 0.95 (18H, t, J 7, CH_3), 1.4–1.6 (36H, m, CH_2), 1.95 (12H, m, CH_2), 4.15 (2H, t, J 6.5, OCH_2), 4.25 (10H, m, OCH_2), 7.8 (4H, s, Ar-H), 9.05 (1H, s, Ar-H); m/z 862 (M^+, 100%).

An inseparable mixture of 1,8-*dichloro*-2,3,6,7,10,11-*hexahexyloxytriphenylene* **3** and 1,5-*dichloro*-2,3,6,7,10,11-*hexahexyloxytriphenylene* **4** (0.13 g, 12%) was also isolated as the first fraction off the column (Found: C, 72.35; H, 9.15; Cl, 8.15. $C_{54}H_{82}Cl_2O_6$ requires C, 72.21; H, 9.2; Cl, 7.9%); δ_H 0.95 (18H, t, J 7, CH_3), 1.4–1.6 (36H, m, CH_2), 1.95 (12H, m, CH_2), 4.1–4.3 (12H, m, OCH_2), 7.70 (2H, s, ArH), 7.71 (2H, s, ArH), 8.65 (2H, s, Ar-H 9 and 12 of **3**), 8.80 (1H, s, Ar-H), 8.83 (1H, s, Ar-H).

Synthesis of 2 using [bis(trifluoroacetoxy)iodo]benzene

2,3,6,7,10,11-Hexahexyloxytriphenylene **1** (1.0 g, 1.2 mmol) was added to dichloromethane (45 cm^3) and cooled to 0 °C before [bis(trifluoroacetoxy)iodo]benzene (0.6 g, 1.4 mmol) was added and stirred for 15 min. Whilst maintaining the temperature below 3 °C, tetrabutylammonium chloride (0.67 g, 2.4 mmol) was added and stirred for 15 min before being allowed to warm to room temperature and stirred for a further 20 min. The reaction mixture was poured onto methanol (100 cm^3) and the solvents removed *in vacuo*. The residual solid was purified by column chromatography on silica eluting with 7% v/v diethyl ether–light petroleum and recrystallised from ethanol to give 1-*chloro*-2,3,6,7,10,11-*hexahexyloxytriphenylene* **2** (0.42 g, 40%) as a white solid, which exhibited spectroscopic data identical to those of a previously prepared sample of **2**.

1,4,5,9-Tetrachloro-2,3,6,7,10,11-hexahexyloxytriphenylene 5

2,3,6,7,10,11-Hexahexyloxytriphenylene **1** (1.0 g, 1.2 mmol) was dissolved in dichloromethane (40 cm^3) and stirred whilst iodine monochloride (excess) was added. The reaction was followed by TLC eluting with 40% v/v dichloromethane–light petroleum. Once the reaction had been driven to one product (as shown by TLC), saturated aqueous sodium metabisulfite (40 cm^3) was added and stirred for 20 min. After separation of the organic phase and extraction of the aqueous phase with dichloromethane (3 × 25 cm^3), the combined dichloromethane fractions were dried ($MgSO_4$) and the solvent evaporated to give a dark oil. This oil was purified by column chromatography on silica eluting with 25% v/v dichloromethane–light petroleum to give the title compound **5** (0.51 g, 44%) as a colourless oil; δ_H 0.95 (18H, t, J 7, CH_3), 1.3–1.6 (36H, m, CH_2), 1.90 (12H, m, CH_2), 3.9–4.3 (12H, m, OCH_2), 8.53 (1H, s, Ar-H), 9.01 (1H, s, Ar-H); m/z 966 (M^+, 100%).

1,4,8-Tribromo-2,3,6,7,10,11-hexahexyloxytriphenylene 7

2,3,6,7,10,11-Hexahexyloxytriphenylene **1** (0.4 g, 0.48 mmol) was stirred in dichloromethane (20 cm^3) whilst bromine (6 drops) was added carefully, and then stirred for a further 1.5 h. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica eluting with 50% v/v dichloromethane–light petroleum to give the title compound **7** (0.15 g, 29%) as a pale yellow oil (Found: C, 60.75; H, 7.95. $C_{54}H_{81}Br_3O_6$ requires: C, 60.85; H, 7.66%); δ_H 0.95 (18H, t, J 7, CH_3), 1.3–1.6 (36H, m, CH_2), 1.9 (12H, m, CH_2), 4.05–4.25 (12H, m, OCH_2), 8.4 (1H, s, Ar-H), 8.48 (1H, s, Ar-H), 8.64 (1H, s, Ar-H); m/z 1066 (M^+, 100%).

1-Fluoro-2,3-dihexyloxybenzene 9

3-Fluorocatechol (5 g, 0.039 mol), 1-bromohexane (14.2 g, 0.086 mol) and potassium carbonate (11.8 g, 0.086 mol) were added to ethanol (100 cm^3) and heated under reflux for 3 days. After cooling, dichloromethane (100 cm^3) was added and the solid residues removed by filtration through Celite. Once the solvents had been removed *in vacuo*, the oily residue was purified by column chromatography on silica eluting with 30% v/v dichloromethane–light petroleum to give the title compound (10.5 g, 91%) as a colourless oil (HRMS: found M$^+$, 296.2149. $C_{18}H_{29}FO_2$ requires *M*, 296.2152); δ_H 0.9 (6H, t, *J* 7, CH_3), 1.3–1.5 (12H, m, CH_2), 1.8 (4H, m, CH_2), 4.0 (4H, m, OCH_2), 6.6–6.7 (2H, m, Ar-H), 6.91 (1H, m, Ar-H); *m*/*z* 296 (M$^+$, 100%).

1-Fluoro-2,3,6,7,10,11-hexahexyloxytriphenylene 10

3,3′,4,4′-Tetrahexyloxybiphenyl **8** (1.0 g, 1.8 mmol) and 1-fluoro-2,3-dihexyloxybenzene **9** (2.14 g, 7.2 mmol) were added to a stirred suspension of ferric chloride (2.35 g, 14.4 mmol) in dichloromethane (60 cm^3). After stirring for 2 h the crude reaction product was precipitated by adding the reaction mixture to methanol (200 cm^3). This precipitate was filtered and washed with methanol before being allowed to dry and purified by column chromatography on silica eluting with 8% v/v diethyl ether–light petroleum. Subsequent recrystallisation from ethanol afforded the title compound **10** (1.05 g, 69%) as a white solid, K–D 39 °C, D–I 116 °C (Found: C, 76.8; H, 9.95; F, 2.3. $C_{54}H_{83}FO_6$ requires: C, 76.55; H, 9.87; F, 2.24%); δ_H 0.95 (18H, t, *J* 7, CH_3), 1.3–1.64 (36H, m, CH_2), 1.95 (12H, m, CH_2), 4.15–4.3 (12H, m, OCH_2), 7.67 (1H, s, Ar-H), 7.8 (2H, s, Ar-H), 7.85 (1H, s, Ar-H), 8.51 (1H, d, *J* 8, Ar-H); *m*/*z* 846 (M$^+$, 100%).

2-Chloro-1,4,6,7,10,11-hexahexyloxytriphenylene 12

1,4,6,7,10,11-Hexahexyloxytriphenylene **11** (0.5 g, 0.6 mmol) was dissolved in dichloromethane (30 cm^3) and cooled to 0 °C (ice–salt slurry). Iodine monochloride (0.12 g, 7.4 mmol) was added dropwise in dichloromethane solution (*ca.* 2 cm^3) and stirred for 20 min at 0 °C before being allowed to warm to room temperature. Saturated aqueous sodium metabisulfite (35 cm^3) was added and the organic phase separated and washed with water before the solvents were removed *in vacuo*. The resulting crude product was purified by column chromatography on silica eluting with 20% v/v dichloromethane–light petroleum and recrystallised from ethanol to give the title compound **12** (0.10 g, 19%) as a white solid, mp 52 °C (Found: C, 74.9; H, 9.7; Cl, 4.05. $C_{54}H_{83}ClO_6$ requires: C, 75.1; H, 9.7, Cl, 4.10%); δ_H 0.91 (18H, t, *J* 7, CH_3), 1.4–1.6 (36H, m, CH_2), 1.80 (12H, m, CH_2), 4.1–4.3 (12H, m, OCH_2), 7.1 (1H, s, Ar-H), 7.7 (1H, s, Ar-H), 7.8 (1H, s, Ar-H), 9.1 (1H, s, Ar-H), 9.17 (1H, s, Ar-H); *m*/*z* 862 (M$^+$, 100%).

2,3-Dibromo-1,4-6,7,10,11-hexahexyloxytriphenylene 13

1,4,6,7,10,11-Hexahexyloxytriphenylene **11** (0.57 g, 0.7 mmol) was added to dichloromethane (30 cm^3) and cooled to 0 °C. Bromine (*ca.* 0.5 cm^3) was added dropwise and the reaction stirred for 3 h before being poured onto methanol (150 cm^3). The solvents were removed *in vacuo* and the resulting crude product purified by column chromatography on silica eluting with 30% v/v dichloromethane–light petroleum. Recrystallisation from ethanol gave the title compound **12** (0.19 g, 28%) as a white solid, mp 70 °C (Found: C, 65.5; H, 8.55; Br, 15.9. $C_{54}H_{82}Br_2O_6$ requires: C, 65.7; H, 8.37, Br, 16.2%); δ_H 0.9 (18H, t, *J* 7, CH_3), 1.3–1.7 (36H, m, CH_2), 1.85 (12H, m, CH_2), 3.73 (4H, t, *J* 6.5, OCH_2), 4.2 (8H, m, OCH_2), 7.7 (2H, s, Ar-H 8 and 9), 8.98 (2H, s, Ar-H 5 and 12); *m*/*z* 986 (M$^+$, 100%).

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