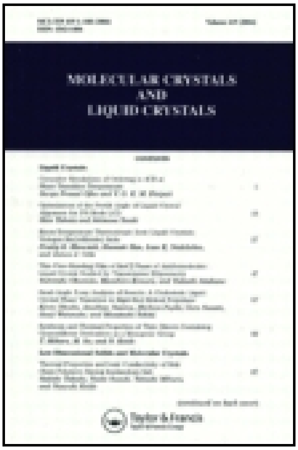

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Mixed Alkyl-Alkoxy Triphenylenes

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MIXED ALKYL-ALKOXY TRIPHENYLENES

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Liquid crystal formation in triphenylenes is influenced by subtle changes to the substituents attached to the core. We describe a series of triphenylenes in which 2, 4 or 6 of the alkoxy chains of parent hexa(hexyloxy)triphenylene are replaced by n-heptyl chains (giving mixed alkyl-alkoxy triphenylenes). This series permits direct comparison to derivatives which exhibit the rare helical mesophase. The syntheses have been achieved employing palladium catalysed coupling reactions in key steps. It appears, however, that incorporation of alkyl substituents suppresses mesophase formation in these materials demonstrating further the unique role played by sulfur in the helical-phase forming materials.

Keywords: triphenylene; discotic; columnar; helical mesophases; alkyl triphenylenes

INTRODUCTION

Discotic liquid crystals [1] have received widespread attention since their discovery in 1977 [2]. They are particularly attractive for application in molecular electronics because the columnar arrangement of (aromatic) cores gives rise to a low-dimensional conduction pathway [3,4]. Furthermore, discotic liquid crystals based on the triphenylene nucleus are relatively easy to synthesise [1]. It is also known that (homeotropic) alignment during slow cooling from the isotropic phase is easily achieved when the material is sandwiched in-between suitable substrates making device fabrication straightforward. Photoconductivity studies have revealed a charge carrier mobility of about $10^{-7}\,m^2v^{-1}s^{-1}$ along the columns of hexaalkoxytriphenylenes [5] in their Col_h mesophases. This charge mobility is anisotropic (the anisotropy factor is about 10^3).

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Until recently, hexakis(hexylthio)triphenylene [6] was unique amongst columnar liquid crystals. In addition to the Col_h mesophase, this material forms a more ordered helical (H) phase [7,8] at lower temperatures. Charge carrier mobility in this phase is substantially higher ($10^{-5}\ m^2v^{-1}s^{-1}$) [9–11] and the dramatic increase is attributed to the long-range molecular order in the helical phase. We have been interested in investigating the structural factors which control the formation of this more ordered mesophase and recently reported the effect of sequential replacement of oxygen for sulfur in hexyloxytriphenylenes [12]. One derivative does indeed display a stable helical mesophase at room temperature. It is interesting to note that the helical phase is not observed if the chain length is changed [7], or indeed if the heteroatom is substituted for selenium [13].

In this paper we describe the synthesis and characterization of further members of the series in which the "heteroatom" is replaced by a methylene group. Like sulfur, the methylene group carries increased steric bulk compared to oxygen and it was hoped that this would induce packing effects which would lead to the formation of a stable helical phase.

RESULTS AND DISCUSSION

Synthesis

The target molecules of this study are shown in Figure 1, along with the reference alkoxy/alkylthio derivatives.

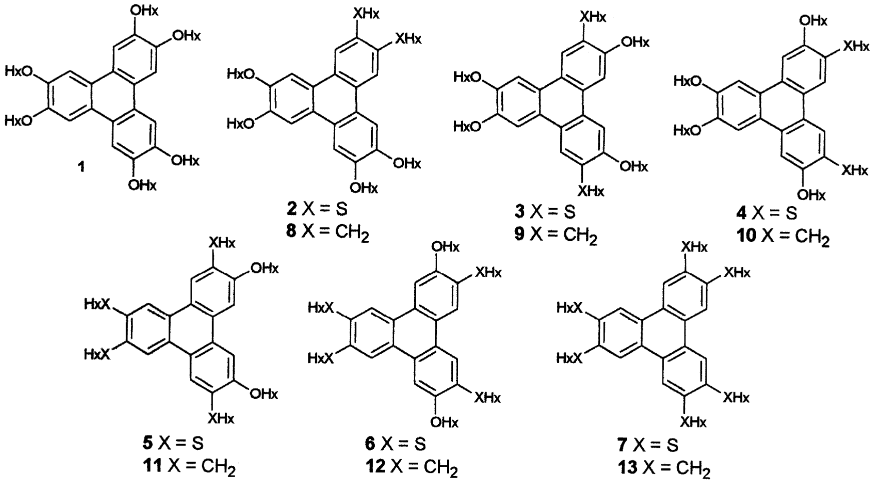


FIGURE 1 Target and reference compounds (Hx = n-hexyl).

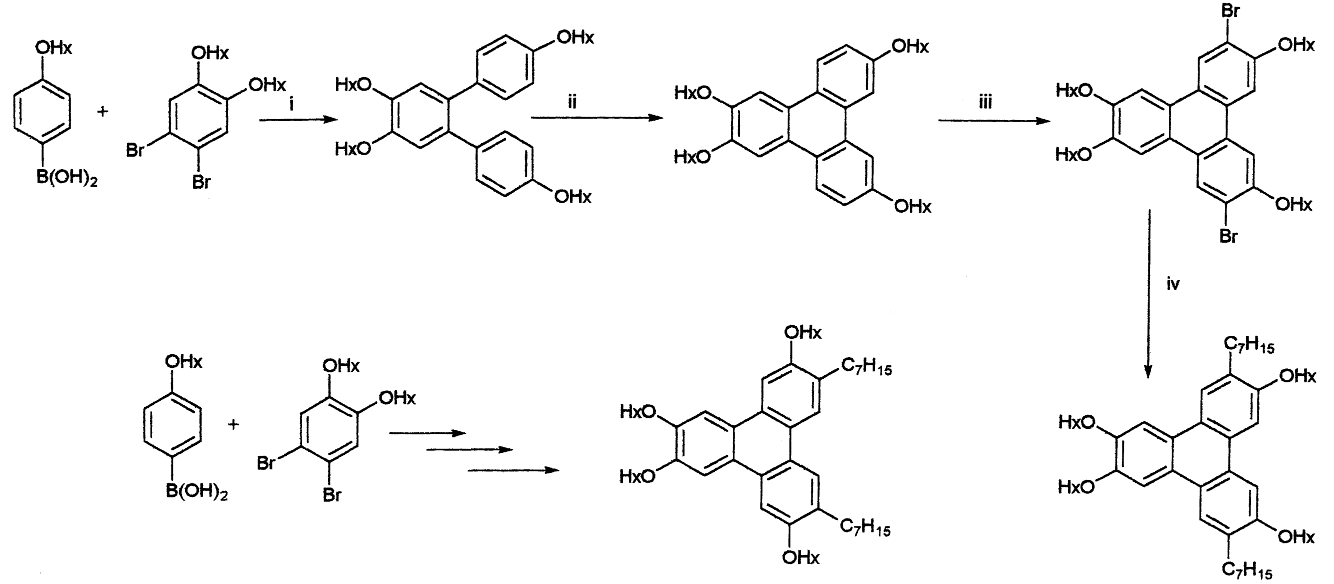
The syntheses follow our previous work whereby unsymmetrical triphenylenes are constructed by oxidative ring-closure of the corresponding *ortho*-terphenyls (themselves typically prepared by palladium catalysed cross-coupling of aryl bromides with aryl boronic acids [12]. Bromination of the di- or trialkoxy triphenylenes introduces bromide at each of the free β-positions. Alkyl chains were most conveniently introduced via another palladium catalysed cross-coupling between the triphenylene bromides and heptylzinc iodide. Representative syntheses are shown in Schemes 1 and 2. Symmetrical hexaheptyltriphenylene **13** was most conveniently prepared from triphenylene hexatriflate (Scheme 3).

THERMAL BEHAVIOUR

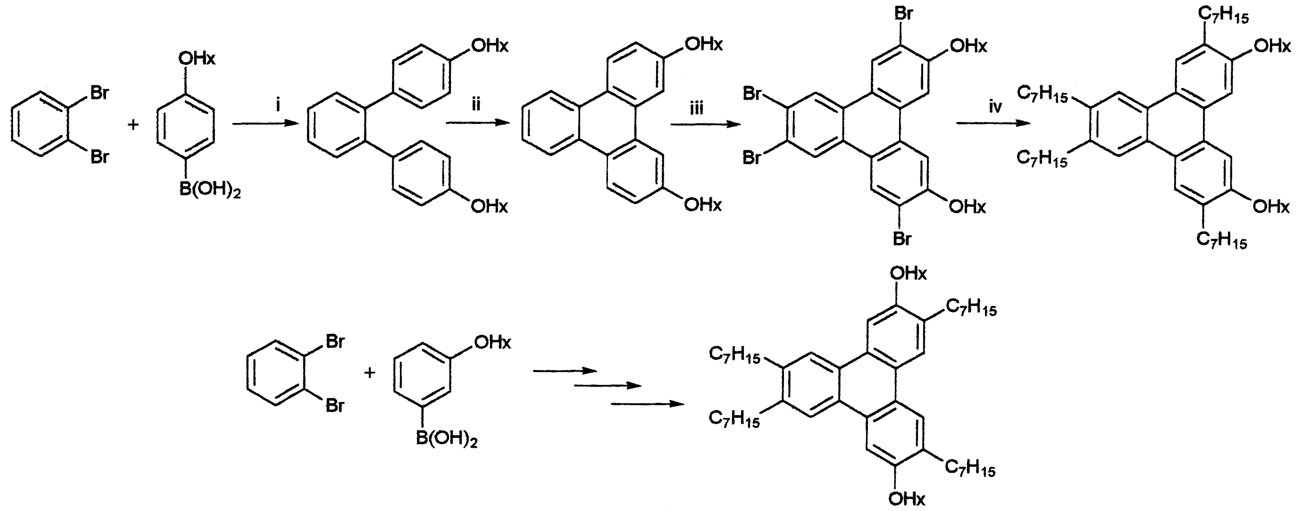
The thermal behaviour of the novel triphenylene derivatives was investigated by polarising optical microscopy and differential scanning calorimetry (DSC) and the results summarized in the table along with those for the mixed alkoxy/alkylthio triphenylenes and the dibromide precursors. Disappointingly, none of the novel alkyltriphenylenes proved to be mesogenic. All are relatively low-melting, crystalline solids, demonstrating the sensitivity of such discotic liquid crystals to even slight structural perturbations. It is interesting to speculate the reasons for the destabilization of the mesophase when alkyl groups are introduced. Comparison with the mesogenic dibromides is perhaps most useful. Somewhat surprisingly, the dibromides give a mesophase over a broad temperature range. Introduction of a heteroatom onto the triphenylene core therefore seems to provide the driving force for formation of a columnar mesophase. It should be noted that the tetrahexyloxytriphenylenes are not mesogenic [12]. It is interestingly also that no mesophase is observed for the hexaalkynyl triphenylenes [14] and it can be speculated therefore that the extension of the core through introduction of a polarisable substituent (O, S, Br) is responsible for the induction of mesogenic behaviour in these systems. Similarly, further substitution of hexasubstituted triphenylenes leads to enhanced mesophase stability [15].

ABSORPTION AND FLUORESCENCE SPECTRA

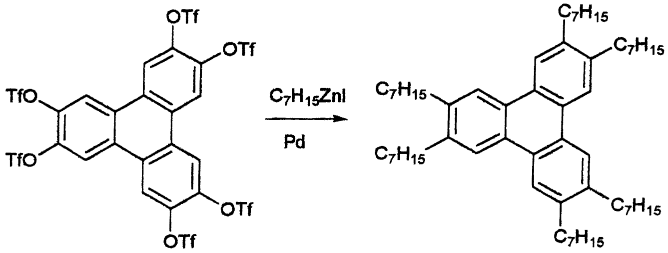
The alkyl and mixed alkyl/alkoxy triphenylenes prepared in this study are highly fluorescent and could find applications as dopants (liquid crystal mixtures) for use in light emitting devices (such as OLEDs). A preliminary study of the fluorescence spectra of the novel derivatives was therefore undertaken and typical spectra (for **12**) are shown in Figure 2.



SCHEME 1 Hx = n-hexyl. *Reagents and conditions*: (i) $PdCl_2$, Na_2CO_3, PPh_3, toluene/EtOH/H_2O, reflux, 4h, (ii) hν, I_2, benzene, 72h, (iii) Br_2, CH_2Cl_2, 0°C, 30 min, (iv) $C_7H_{15}ZnI$. Pd(dppf), THF, reflux, 2h.



SCHEME 2 Hx = n-hexyl. *Reagents and conditions*: (i) $PdCl_2$, Na_2CO_3, PPh_3, toluene/EtOH/H_2O, reflux, 4h, (ii) hν, I_2, benzene, 72h, (iii) Br_2, CH_2Cl_2, rt, 2h, (iv) $C_7H_{15}ZnI$. Pd(dppf), THF, reflux, 2h.



SCHEME 3 (no legend).

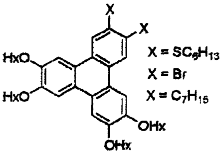
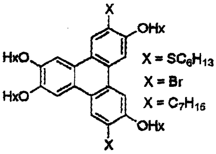
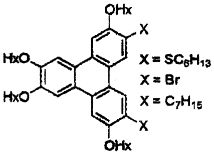
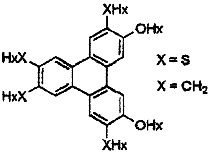
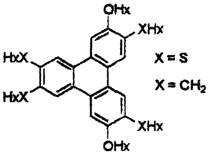
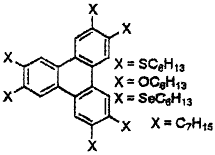
CONCLUSIONS

The synthesis and characterization of a series of triphenylenes is described in which 2, 4 or 6 of the alkoxy chains of parent hexa(hexyloxy)triphenylene are replaced by heptyl chains (giving mixed alkyl-alkoxy triphenylenes). This series provides a direct comparison to the derivatives which give rise to the rare helical mesophase. The syntheses have been achieved employing palladium catalysed coupling reactions as key steps. It appears, however, that incorporation of alkyl substituents suppresses mesophase formation in these materials, which further demonstrates the unique role played by sulfur in the helical-phase forming materials. More generally, it appears that attachment of polarisable substituents directly to the core is responsible for producing stable columnar mesophases. Some of the novel alkyl triphenylenes are highly fluorescent making them attractive for applications (in mixtures) in light emitting devices.

EXPERIMENTAL

NMR spectra were recorded on either a Varian 300 MHz or 400 MHz spectrometer (coupling constants are quoted in Hz). Elemental analyses were performed on a Carlo Erda 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. 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.

TABLE Transition Temperatures (°C) of the Novel Alkyl Triphenylenes and Related Dicogens.

Structure	Heating		Cooling	
	K-Col$_h$	Col$_h$-I	I-Col$_h$	Col$_h$-K
	(K-1 86) 130	 141	81 140 (K-164)	52 97
	24 40	102 179	99 176 (K-170)	< 0 < RT
	45 63	123 179	118 175 (K-175)	< 0 < RT
	72 [H-Col 38]	111	108 [Col-H 32] (K-155)	< 40
	54	100.5	97 (K-157)	< RT
	(K-H 62)[H-Col 70] 68 40	93 97 72	 (K-175)	

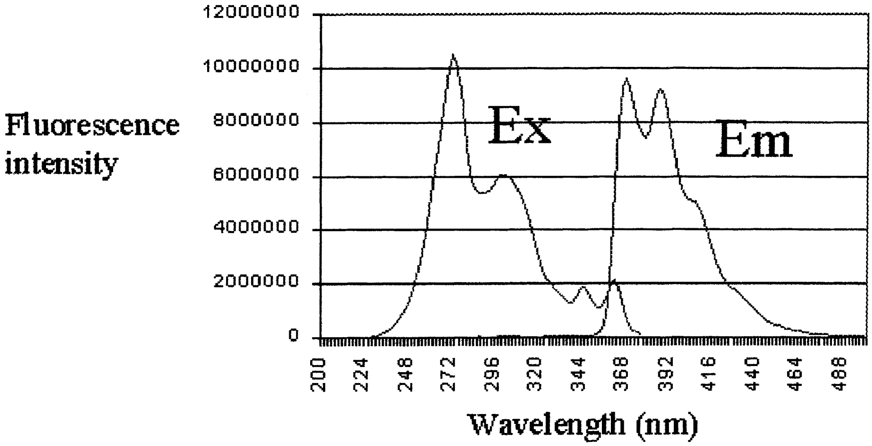


FIGURE 2 Fluorescence excitation (Ex) and emission (Em) spectra for **12** in dichloromethane (1×10^{-5} M).

2,3-DIHEPTYL-6,7,10,11-TETRAKIS(HEXYLOXY) TRIPHENYLENE 8

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene [12] (0.500 g, 6.36×10^{-4} mol), tris(dibenzylideneacetone)dipalladium (0) (0.10 g, 2.54×10^{-5} mol), 1,1'-bis(diphenylphosphino)ferrocene (0.056 g, 1.02×10^{-3} mol) were stirred in refluxing THF (2 mL) for 15 minutes. n-Heptylzinciodide (8.10 mL, 0.83 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (10 mL) was then added and the organic layer extracted with dichloromethane (50 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether / dichloromethane) to give the pure *title compound* (0.40 g, 78%).

Mp 84°C; Anal (Found: C 81.04; H 10.72. $C_{56}H_{88}O_4$ Requires C 81.50; H 10.75%); δ_H ($CDCl_3$, TMS, 300 MHz) 8.17 (2H, s), 7.98 (2H, s), 7.82 (2H, s), 4.26–4.20 (8H, m), 2.84 (4H, t, J = 7.1) 1.98–1.89 (8H, m), 1.72–1.67 (4H, m), 1.58–1.25 (40H, broad m), 0.95–0.88 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 149.5, 149.2, 139.4, 127.3, 124.2, 124.0, 123.3, 1.7.6, 69.9, 33.3, 31.9, 31.8, 31.7, 29.9, 29.8, 29.4, 29.3, 25.9, 22.8, 22.7, 14.1, 14.0; *m/z* (EI) 824.7 (M^+, 100%); HRMS: Found 824.6678. $C_{56}H_{88}O_4$ (M^+) Requires 824.6683.

2,7-DIHEPTYL-3,6,10,11-TETRAKIS(HEXYLOXY) TRIPHENYLENE 9

2,7-Dibromo-3,6,10,11-tetrakis-(hexyloxy)triphenylene [12] (0.100 g, 1.27×10^{-4} mol), tris(dibenzylideneacetone)dipalladium (0) (0.020 g, 2.18×10^{-5} mol), 1,1′-bis(diphenylphosphino)ferrocene (0.011 g, 2.0×10^{-5} mol) were stirred in refluxing THF (2 mL) for 15 minutes. n-Heptylzinciodide (2.0 mL, 0.83 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (10 mL) was then added and the organic layer extracted with dichloromethane (50 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether/dichloromethane) to give the pure *title compound* (0.09 g, 87%).

Mp 70°C; Anal (Found: C 81.48; H 11.02. $C_{56}H_{88}O_4$ Requires C 81.50; H 10.75%); δ_H ($CDCl_3$, TMS, 400 MHz) 8.16 (2H, s), 7.91 (2H, s), 7.75 (2H, s), 4.26–4.19 (8H, m,), 2.84 (4H, t, J = 7.7) 1.98–1.89 (8H, m), 1.74–1.70 (4H, m), 1.69–1.25 (40H, broad m), 0.95–0.85 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 156.1, 148.8, 132.1, 128.4, 124.1, 123.5, 123.2, 107.0, 103.6, 69.5, 67.9, 31.8, 31.6, 31.5, 31.0, 30.3, 29.6, 29.3, 29.1, 25.9, 25.7, 22.6, 22.5, 13.9, 13.8; *m/z* (FAB) 824.4 (M^+, 100%).

2,11-DIHEPTYL-3,6,7,10-TETRAKIS(HEXYLOXY) TRIPHENYLENE 10

2,11-Dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene [12] (0.750 g, 9.54×10^{-4} mol), tris(dibenzylideneacetone)dipalladium (0) (0.150 g, 1.64×10^{-4} mol), 1,1′-bis(diphenylphosphino)ferrocene (0.084 g, 1.43×10^{-3} mol) were stirred in refluxing THF (3 mL) for 15 minutes. n-Heptylzinciodide (15.0 mL, 0.83 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (20 mL) was then added and the organic layer extracted with dichloromethane (50 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether/dichloromethane) to give the pure *title compound* (0.64 g, 82%).

Mp 75°C; Anal (Found: C 81.25; H 10.81. $C_{56}H_{88}O_4$ Requires C 81.50; H 10.75%); δ_H ($CDCl_3$, TMS, 400 MHz) 8.26 (2H, s), 7.89 (2H, s), 7.71 (2H, s), 4.25–4.18 (8H, m), 2.84 (4H, t, J = 7.5) 1.97–1.88 (8H, m), 1.74–1.70 (4H, m), 1.59–1.25 (40H, broad m), 0.96–0.87 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 155.2, 148.4, 130.8, 126.9, 123.6, 123.2, 122.1, 106.8, 102.4, 68.8, 67.0, 30.9, 30.8, 30.7, 30.1, 29.4, 28.8, 28.5, 28.4, 28.3, 25.0, 24.9, 21.7, 21.6, 21.5, 13.1, 13.0; ***m/z*** (FAB) 824.4 (M^+, 100%).

2,3,7,10-TETRAHEPTYL-6,11-BISHEXYLOXYTRIPHENYLENE 12

2,3,7,10-Tetrabromo-6,11-bishexyloxytriphenylene [12] (1.00 g, 1.34×10^{-3} mol), tris(dibenzylideneacetone)dipalladium (0) (0.200 g, 2.18×10^{-4} mol), 1,1′-bis(diphenylphosphino)ferrocene (0.112 g, 2.02×10^{-4} mol) were stirred in refluxing THF (5 mL) for 15 minutes. n-Heptylzinciodide (20.0 mL, 0.83 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (20 mL) was then added and the organic layer extracted with dichloromethane (100 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether / dichloromethane) to give the pure *title compound* (0.71 g, 65%).

Mp 57°C; δ_H ($CDCl_3$, TMS, 300 MHz) 8.25 (2H, s), 8.22 (2H, s), 7.87 (2H, s), 4.21 (4H, t, J = 6.2), 2.86–2.82 (8H, m) 1.96–1.87 (4H, m), 1.72–1.70 (8H, m), 1.64–1.25 (44H, broad m), 1.15–0.73 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 156.2, 139.6, 132.1, 128.2, 128.0, 124.2, 123.5, 103.7, 68.1, 33.3, 32.0, 31.8, 31.7, 31.2, 30.4, 29.9, 29.8, 29.6, 29.3, 26.1, 22.7, 22.6, 14.1; ***m/z*** (EI) 820.7 (M^+, 100%); HRMS: Found 820.7093. $C_{58}H_{92}O_2$ (M^+, 100%) Requires 820.7097.

2,3,6,11-TETRAHEPTYL-7,10-BISHEXYLOXYTRIPHENYLENE 11

2,3,6,11-Tetrabromo-7,10-bishexyloxytriphenylene [12] (0.50 g, 6.72×10^{-4} mol), tris(dibenzylideneacetone)dipalladium (0) (0.200 g, 2.18×10^{-4} mol), 1,1′-bis(diphenylphosphino)ferrocene (0.112 g, 2.02×10^{-4} mol) were stirred in refluxing THF (5 mL) for 15 minutes. n-Heptylzinciodide (8.0 mL, 0.86 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (20 mL) was then added and the organic layer extracted with dichloromethane (100 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether/dichloromethane) to give the pure *title compound* (0.40 g, 72%).

Mp 57°C; δ_H ($CDCl_3$, TMS, 300 MHz) 8.31 (2H, s), 8.26 (2H, s), 7.76 (2H, s), 4.21 (4H, t, J = 6.), 2.86–2.81 (8H, m) 1.94–1.58 (4H, m), 1.77–1.69 (8H, m), 1.62–1.25 (44H, broad m), 0.96–0.88 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 156.6, 139.1, 132.1, 128.9, 127.2, 124.6, 123.5, 123.1, 103.7, 68.0, 33.3, 32.0, 31.8, 31.7, 31.1, 30.4, 30.3, 29.9, 29.7, 29.5, 29.4, 26.1, 22.8, 22.7, 14.2; *m/z* (EI) 820.7 (M^+, 100%); HRMS: Found 820.7093. $C_{58}H_{92}O_2$ (M^+, 100%) Requires 820.7097.

TRIPHENYLENE-2,3,6,7,10,11-HEXATRIFLATE

2,3,6,7,10,11-Hexahydroxytriphenylene (2.0 g, 6.17×10^{-3} mol) was added to dry dichloromethane (50 mL) and pyridine (11.70 g, 13 mL, 0.15 mol) at −20°C. Trifluoromethanesulphonic anhydride (12.53 g, 0.045 mol) was slowly added to the solution. The flask was allowed to warm to room temperature and the solution stirred overnight. Dilute hydrochloric acid was added to the reaction mixture and the organic layer was extracted with dichloromethane (3×150 mL). The solvents were evaporated and the residue recrystallised from isopropanol to give the pure *title compound* (5.16 g, 75%).

Mp 169°C; δ_H ($CDCl_3$, TMS, 300 MHz) 8.59 (6H, s, Ar-H), δ_C (75.45 MHz; $CDCl_3$) 141.0, 129.0, 119.6; *m/z* (FABMS) 1115.5 (M^+, 50%).

2,3,6,7,10,11-HEXAHEPTYLTRIPHENYLENE

Triphenylene-2,3,6,7,10,11-hexatriflate (0.900 g, 1.11×10^{-3} mol), tris(dibenzylide-neacetone)dipalladium (0) (0.120 g, 1.34×10^{-4} mol), 1,1′-bis(diphenylphosphino)ferrocene (0.30 g, 5.3×10^{-4} mol) were stirred in refluxing THF (5 mL) for 15 minutes. n-Heptylzinciodide (15.0 mL, 0.86 M) was added dropwise and the solution was refluxed for a further 2 hours. Dilute hydrochloric acid (20 mL) was then added and the organic layer extracted with dichloromethane (100 mL × 3). The organic layer was concentrated *in vacuo* and methanol added to precipitate the crude product. This was further purified by column chromatography (eluting with petroleum ether/dichloromethane) to give the pure *title compound* (0.52 g, 78%).

Mp 75°C; δ_H ($CDCl_3$, TMS, 300 MHz) 8.30 (6H, s), 2.84 (12H, t, J = 7.8), 1.76–1.69 (12H, m), 1.54–1.30 (48H, broad m), 0.92–0.88 (18H, m); δ_C (75.45 MHz; $CDCl_3$) 139.5, 127.7, 123.3, 33.2, 31.8, 31.6, 29.7, 29.2, 22.6, 14.0; *m/z* (FABMS) 816.5 (M^+, 100%); HRMS: Found 816.7512. $C_{60}H_{96}$ (M^+, 100%) Requires 816.7510.

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