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CPI (complementary polytopic interaction) stabilised liquid crystal compounds formed by esters of 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene

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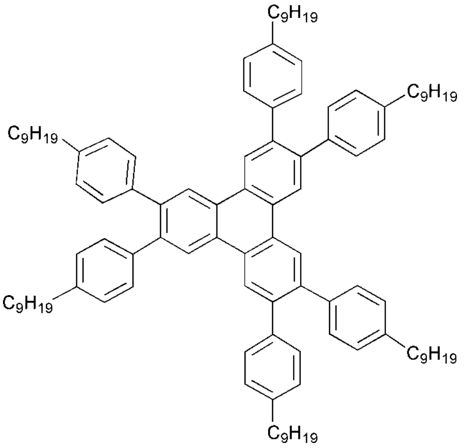
An improved synthesis of 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene **6** is reported which is based on the oxidative coupling of 2-acetoxy-1-hexyloxybenzene **3** to 3,3′,4,4′-tetrakis(hexyloxy)biphenyl **4**. Most of the esters of this phenol **7**–**15**, give an enantiotopic $\mathrm{Col_h}$ columnar liquid crystal phase, which is stable over a wide temperature interval. This can be further enhanced by formation of 1 : 1 CPI compounds with either 2,3,6,7,10,11-hexakis(4-nonylphenyl)triphenylene {PTP9} **1** or hexakis(4-nonylphenyl)dipyrazino[2,3-*f*:2′,3′-*h*]quinoxaline {PDQ9} **2**. As with other triphenylene derivatives, these additives can also be used to induce liquid crystal behaviour in otherwise non-mesogenic esters.

Introduction

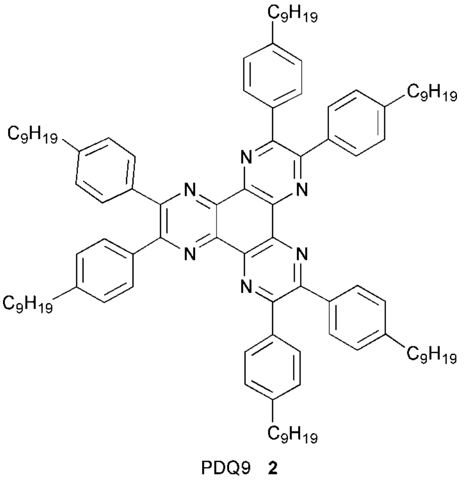
2,3,6,7,10,11-Hexakis(4-nonylphenyl)triphenylene {PTP9} **1**[1] and hexakis(4-nonylphenyl)dipyrazino[2,3-*f*:2′,3′-*h*]quinoxaline {PDQ9} **2** form 1 : 1 compounds with a wide range of triphenylene compounds.[1–6] Within the columnar π-stacked systems produced it is envisaged that the molecular components are stacked in an alternating manner and, in the relevant mesophases, these columns are usually arranged on a hexagonal lattice as shown in Fig. 1.[2] The compounds are formed with an exact 1 : 1 stoichiometry and are virtually immiscible with an excess of either of the individual components, the phase diagram showing a wide miscibility gap.[2] The interaction between the molecules, whilst strong, does not involve charge transfer and, like many other π-stacking interactions, has to be explained as a sum of atom-centred van der Waals and quadrupolar terms.[7–11] We have termed this a complementary polytopic interaction (CPI).[2] Formation of CPI compounds with **1** and **2** can be used to enhance the mesophase range of triphenylene-based discotic liquid crystals (low molar mass,[2,4,5] homopolymer and block copolymer[5]), to induce mesophase behaviour in non-mesogenic triphenylene derivatives,[4,5] to improve their conductivity and alignment properties[3,4,6] and to induce microphase separation in block copolymer systems.[5] Further examples are described in this paper wherein we also report the synthesis and liquid crystal properties of a series triphenylene compounds **7**–**15** that bear five hexyloxy chains and one acyloxy chain.

Results and discussion

The key precursor to the esters **7**–**15** is 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene **6** (Scheme 1). Several ways of making this intermediate have been reported in the literature. It has been reported that it can be prepared by selective removal of one hexyl substituent from 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (HAT6) using a controlled amount of boron tribromide, 9-Br-BBN, or *B*-bromocatecholborane.[12,13] In our hands the best yield obtained in this way was 70%; the residue being unreacted HAT6. Furthermore, separation of the product from unreacted HAT6 is difficult, requiring extensive column chromatography. Selective cleavage of the methyl substituent from monomethoxypentakis(hexyloxy)triphenylene with lithium diphenylphosphide can be higher yielding.[14] However, it proves difficult to obtain reproducibly high yields in this way. To do so the amount of lithium diphenylphosphide and the reaction time have to be controlled very carefully. Often we find that the product obtained is contaminated with unreacted starting material or the products of polydealkylation. Both decrease the yield and make purifying the product difficult. A simple, reproducible alternative is the oxidative



PTP9 **1**



PDQ9 **2**

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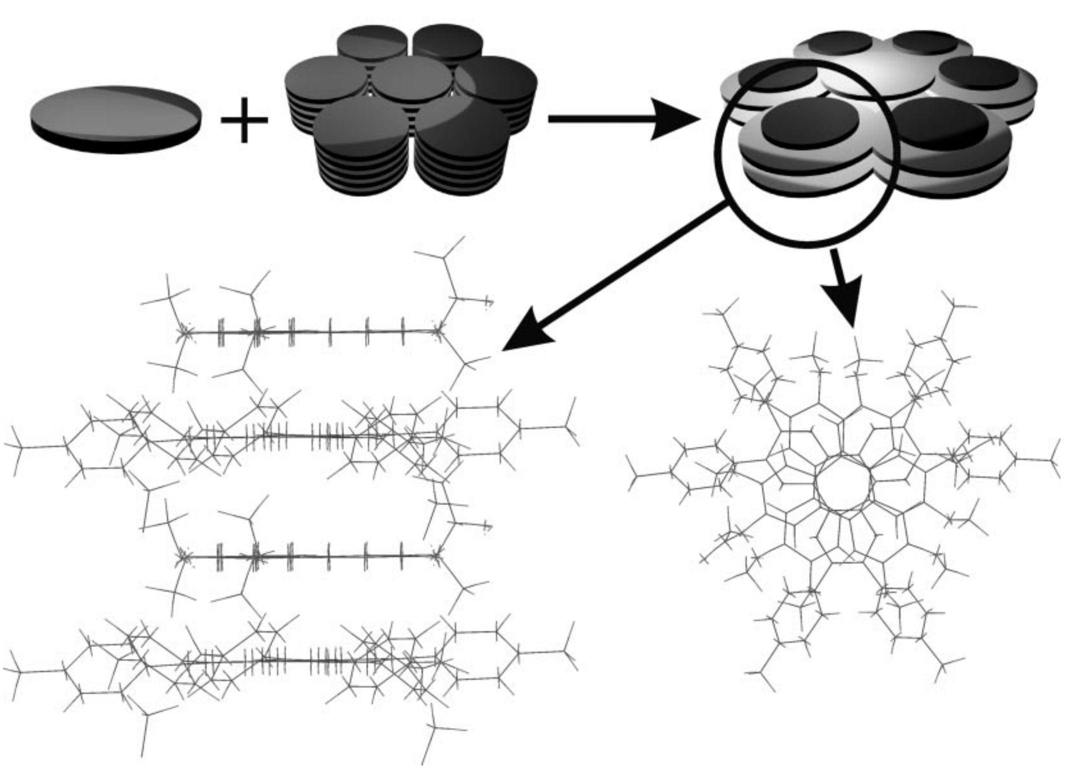


Fig. 1 The packing of molecules **2** and **7** into columnar stacks. Schematic view (top) and (below) molecular structure as predicted by the COSMIC force-field using XEDs (extended electron distribution).[9,10]

coupling of 2-acetoxy-1-hexyloxybenzene **3** to 3,3′,4,4′-tetrakis(hexyloxy)biphenyl **4** using the iron(III) chloride–methanol oxidation–reduction protocol.[15] The crude product of this reaction is a mixture of the acetate **5** and the hydrolysed material **6**. Refluxing this crude mixture with potassium carbonate in 5% aqueous ethanol gives a good yield of the desired phenol **6** as a sole product. The triphenylene esters **7**–**15** were prepared by reacting **6** with the appropriate acid chloride in the presence of pyridine. The products were purified by column chromatography and recrystallised from ethanol or hexane.

The liquid crystal properties of these esters were studied using polarizing microscopy and differential scanning calorimetry (DSC). For esters **7**–**14** enantiotropic liquid crystal behaviour was observed and the optical textures of the mesophase were similar of those seen for many Col$_h$ materials. The DSC results are summarised in Table 1 and these are unexceptional. Where a direct comparison can be made with the corresponding esters with five pentyloxy chains and one acyloxy chain[14] it is found that in the hexyloxy series the melting and clearing transition are, on average about 15 °C lower (compare data for compounds **8**–**11** and **14** to that given in reference 14). Most (except for ester **11**) have a wider mesophase range than the hexakis(hexyloxy) compound HAT6.[15] As in the pentyloxy series, increasing the polarity with benzene ring substituents such as nitro, fluoro, or cyano raises both melting and clearing points but does not significantly affect the mesophase range.[16] Presumably this reflects a stronger intermolecular interaction. On the other hand, increasing the size of the ester group (compound **9**, **14**, **15**) markedly decreases the mesophase range. Presumably this reflects the increasing difficulty of incorporating the bulk of the ester group within the fluid intercolumnar spaces of the Col$_h$ phase. In the pentyloxy series, the derivative with the bulky fluorenyl side-chain is monotropic[14] and, in this hexyloxy series, the ester **15** based around the bulky naphthyl group displays no liquid crystal properties at all.

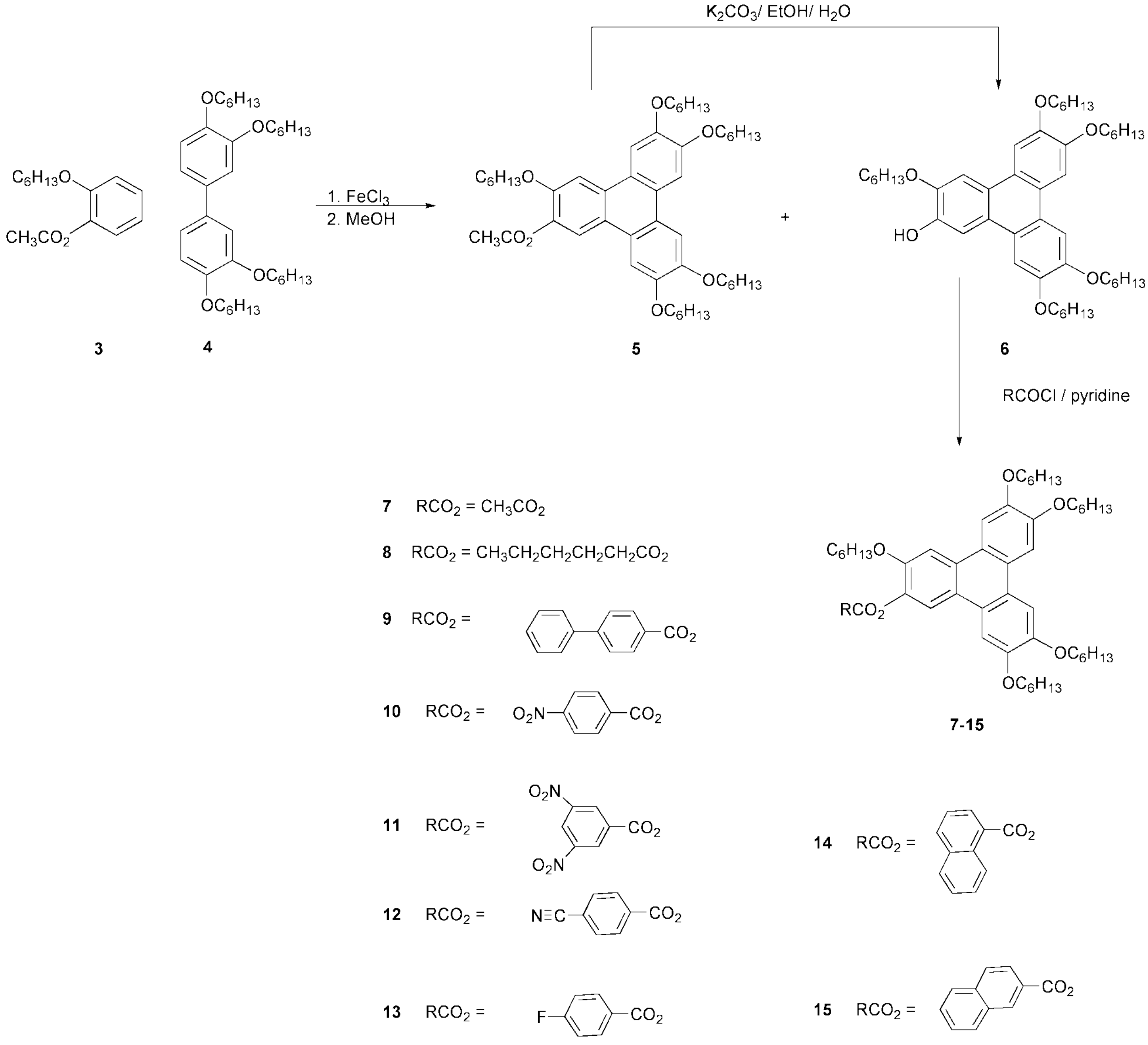
As with other triphenylene-based mesogens the mesophase ranges for compounds **7**–**14** can be enhanced by adding either one mole of PTP9 {2,3,6,7,10,11-hexakis(4-nonylphenyl)triphenylene} **1** or one mole of PDQ9 {hexakis(4-nonylphenyl)-dipyrazino[2,3-*f*:2′,3′-*h*]quinoxaline} **2** (Table 2).[1,2,4,5] In almost every case the optical textures observed for these CPI compounds were typical of the Col$_h$ phase (Fig. 2 shows that for the 1 : 1 mixture of **2** and **15**) and a single enantiotopic mesophase was observed which, when annealed just below the

Table 1 Phase transitions (T/°C) of the triphenylene esters **7**–**15**

Triphenylene	Phase behaviour
7	K 66 (50.2) Col$_h$ 136 (13.9) I
8	K 49 (41.7) Col$_h$ 154 (14.1) I
9	K 55 (27.6) Col$_h$ 147 (11) I
10	K 55 (32.0) Col$_h$ 171 (12.3) I
11	K 110 (22.9) Col$_h$ 192 (6.9) I
12	K 59 (28.5) Col$_h$ 175 (14.0) I
13	K$<$0 Col$_h$ 182 (16.6) I
14	K$<$0 Col$_h$ 121 (3.8) I
15	K 162 (14.1) I
HAT6	K 70 (58.2) Col$_h$ 100 (8.6)

Table 2 Phase transitions (T/°C) of the compounds **1·7**–**1·15** and **2·7**–**2·15**

Compound	Phase behaviour + PTP9 (**1**)	Phase behaviour + PDQ9 (**2**)
7	K$<$0 Col$_h$ 155 (15.4) I	K$<$0 Col$_h$ 214 (29.5) I
8	K$<$0 Col$_h$ 166 (18.7) I	K$<$0 Col$_h$ 218 (31.1) I
9	K$<$0 Col$_h$ 169 (17.0) I	K$<$0 Col$_h$ 228 (29.4) I
10	K$<$0 Col$_h$ 180 (17.9) I	K$<$0 Col$_h$ 237 (29.9) I
11	K$<$0 Col$_{r1}$ 114.5 (0.5) Col$_{r2}$ 169 (13.0) I	K$<$0 Col$_h$ 229 (28.2) I
12	K$<$0 Col$_h$ 175 (17.6) I	K$<$0 Col$_h$ 227 (27.2) I
13	K$<$0 Col$_h$ 174 (19.6) I	K$<$0 Col$_h$ 231 (30.0) I
14	K$<$0 Col$_h$ 151 (10.9) I	K$<$0 Col$_h$ 205 (18.3) I
15	K$<$0 Col$_h$ 176 (19.2) I	K$<$0 Col$_h$ 230 (32.8) I
HAT6	K$<$0 Col$_h$ 155 (19) I	K$<$0 Col$_h$ 240 (33) I



Scheme 1 Synthesis of 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene and its esters **7**–**15**.

Col_h to I transition temperature, gave a homeotropically aligned film. In those cases where it was checked (Table 3), low angle X-ray diffraction studies confirmed the expected $1 : 1/\sqrt{3}$ ratio characteristic of the hexagonal lattice. The exception to this general behaviour was the mixture **11·1**. Here rectangular columnar phases were observed (Tables 2 and 3) along with a very different optical texture. The optical texture for **11·1** (Fig. 3) shows elements separated by a constant angle of about 35° suggesting that the rectangular phase is tilted (on the proviso that the columns are oriented in a planar fashion with their axis parallel to the glass slides). The X-ray data are consistent with an orthorhombic unit cell but can also be fitted to a number of different monoclinic unit cells with various (and wide ranging) length and angle parameters. In the case of **11·1** two different Col_r phases were observed which were very similar in terms of their low angle X-ray behaviour but a clear transition was observed in the DSC at 114 °C. The reasons that this particular ester gives rectangular rather than hexagonal

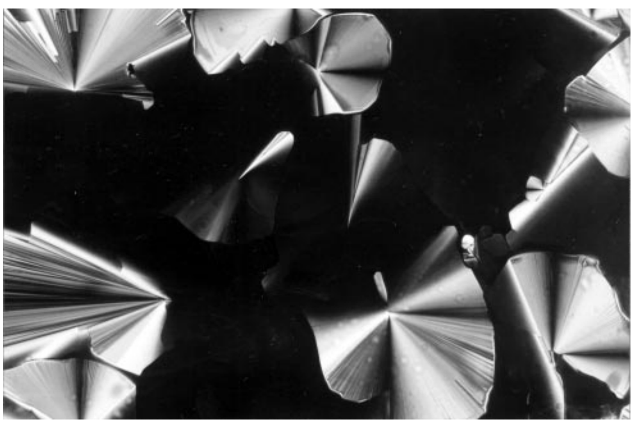


Fig. 2 The optical texture of the induced hexagonal columnar phase formed by the 1 : 1 mixture of **15** and **2** as it appears when viewed under a microscope (× 100) through crossed polarising filters at 220 °C (upon cooling from the isotropic liquid at 10 °C min^{-1}). This texture is typical of that observed for the other hexagonal columnar phases.

Table 3 Low angle X-ray diffraction data for selected compounds

Compound	Temp./°C	Cell type	*a*/Å	*b*/Å	*c*/Å
PDQ9 (**2**)·**7**	150	Hexagonal	28.6	—	3.66
PDQ9 (**2**)·**11**	25	Hexagonal	27.8	—	3.55
PTP9 (**1**)·**7**	100	Hexagonal	27.1	—	3.66
PDQ9 (**2**)·**11**	200	Hexagonal	28.0	—	3.66
PTP9 (**1**)·**11**	25	Orthorhombic	22.03	18.04	3.74
PTP9 (**1**)·**11**	100	Orthorhombic	24.77	19.83	3.66
PTP9 (**1**)·**11**	150	Orthorhombic	24.77	19.83	3.66

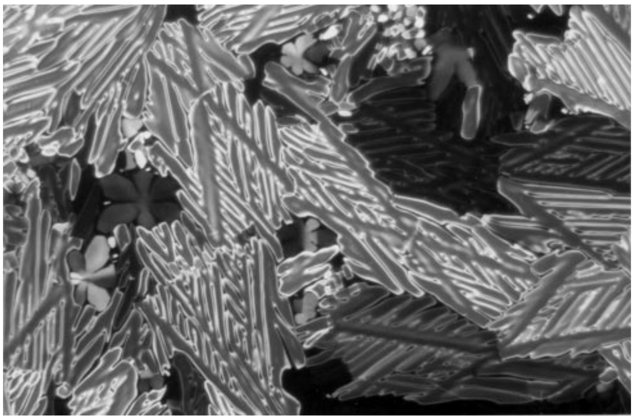


Fig. 3 The optical texture of the rectangular columnar phase formed by the 1 : 1 mixture of **11** and **1** as it appears viewed under a microscope (× 100) through crossed polarising filters at 140 °C (upon cooling from the isotropic liquid at 10 °C min^{-1}).

phases are unclear but this system does possess a particularly bulky, polar side chain substituent. CPI compound formation can also be used to induce liquid crystal behaviour. Hence, neither **1**, **2** or **15** are mesogenic but the 1 : 1 compounds **1·15** and **2·15** give columnar Col$_h$ phases over substantial temperature intervals (Table 2).

Conclusion

As in other triphenylene-based systems[2,4,5] CPI compound formation can be used to enhance the mesophase ranges and to induce liquid crystal behaviour in non-mesogenic systems. These esters also illustrate the way in which the phase behaviour can be modulated by quite subtle engineering of the molecular structure. This becomes particularly important in terms of applications of these materials[17,18] most of which are based on their conductivity and it is also important to note the additional advantages that CPI compound formation also offers in terms of alignment and charge-carrier mobility.[3,6]

Experimental

General procedures and instrumentation

Nuclear magnetic resonance spectra were recorded on a Bruker DPX300 spectrometer. Proton chemical shifts are expressed in parts per million (ppm) downfield of tetramethylsilane ($\delta = 0$ ppm). Mass spectra were recorded on a VG Autospec mass spectrometer. DSC scans were measured on a Perkin-Elmer 7 thermal analysis system at a rate 10 °C min^{-1} and the thermal behaviour of all materials used in the investigation are summarised in Table 1 (single components **7**–**15**) and Table 2 (1 : 1 mixtures of **7**–**15** with **1** and **2**). Microanalyses were carried out at Leeds University Microanalytical Laboratory. All C, H, and N analytical figures are percentage values. Thin layer chromatography was carried out using precoated plastic backed silica plates, which were visualised using ultraviolet light. Flash chromatography signifies column chromatography on Merck silica gel (230–400). Petroleum ether refers to the petroleum fraction boiling between 40 and 60 °C. X-Ray data are summarized in Table 3.

Procedure for making the CPI compounds

1 and **2** were synthesised using previously published methods.[1,19] The compounds of **1** and **2** with triphenylenes **7**–**15** (**1·7**–**15** and **2·7**–**15**) were prepared by the solution method (weighed, dissolved in dichloromethane, evaporated and dried under vacuum for 3 days).

2-Hexyloxyphenol. Catechol (35.0 g, 0.32 mol), potassium carbonate (109.0 g, 0.79 mol) and 1-bromohexane (52.5 g, 0.32 mol) were added to ethanol (300 ml) and heated under reflux for 48 h. After cooling, dichloromethane (300 ml) was added and the solid residues removed by filtration. The solvents were then removed *in vacuo* and the crude product was purified by column chromatography on silica gel to give the title compound (17.9 g, 29%) as a colourless liquid. Found: C, 73.90, H, 9.20, $C_{12}H_{18}O_2$ requires C, 74.19, H, 9.34; δ_H ($CHCl_3$) 6.95–6.83 (m, 4H, Ar*H*), 5.66 (s, 1H, OH), 4.04 (t, *J* 7, 2H, ArOC*H*$_2$), 1.89–1.79 (m, 2H, ArOCH$_2$C*H*$_2$), 1.55–1.35 (m, 6H, C*H*$_2$), 0.95 (t, *J* 7, 3H, CH$_2$C*H*$_3$). MS (FAB), 194 (M$^+$, 100%), 110 (45%), 95 (7%), 83 (12%), 69 (9%), 55 (18%).

2-Acetoxy-1-hexyloxybenzene (3). Acetyl chloride (2.4 g, 30.1 mmol) was added dropwise to a vigorously stirred mixture of 2-hexyloxyphenol (5.0 g, 25.8 mmol) and pyridine (5 ml) in dichloromethane (50 ml). The mixture was stirred for 1 hour and poured onto water. The organic layer was separated, dried ($MgSO_4$), concentrated to give crude product which was purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 3) as eluent to give the title compound as a colourless oil (5.78 g, 95%). Found: C, 71.00, H, 8.35, $C_{14}H_{20}O_3$ requires C, 71.19, H, 8.47; δ_H ($CHCl_3$) 7.21–7.15 (m, 1H, Ar*H*), 7.05–7.01 (m, 1H, Ar*H*), 6.97–6.89 (m, 2H, Ar*H*), 3.97 (t, *J* 6.5, 2H, OC*H*$_2$), 2.30 (s, 3H, COC*H*$_3$), 1.78–1.71 (m, 2H, ArOCH$_2$C*H*$_2$), 1.57–1.30 (m, 6H, C*H*$_2$), 0.90 (t, *J* 6.9, 3H, CH$_2$C*H*$_3$). MS (FAB), 236 (M$^+$, 53%), 194 (100%), 153 (27%), 110 (34%), 85 (7%), 55 (7%).

2-Hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (6). Anhydrous iron chloride (4.7 g, 28.9 mmol) was added to a stirred mixture of 2-acetoxy-1-hexyloxybenzene (3.4 g, 14.4 mmol) and 3,3′,4,4′-tetrakis(hexyloxy)biphenyl (4.0 g, 7.2 mmol) in dichloromethane. The mixture was stirred for 5 h and poured onto methanol (300 ml). The resultant precipitate was filtered off and saponified with potassium carbonate in ethanol (5% water) under reflux overnight. After cooling, water (50 ml) was added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 1) as eluent and then recrystallised from ethanol to yield a white solid (3.59 g 67%, Mp 63.2 °C, lit.[20] 45–46 °C). Found: C, 77.30, H, 9.85, $C_{48}H_{72}O_6$ requires C, 77.38, H, 9.74; δ_H ($CHCl_3$) 7.96 (s, 1H, Ar*H*), 7.83–7.82 (m, 4H, Ar*H*), 7.77 (s, 1H, Ar*H*), 5.92 (1H, s, O*H*), 4.31–4.18 (m, 10H, OC*H*$_2$), 1.99–1.92 (m, 10H, C*H*$_2$), 1.58–1.55 (m, 10H, C*H*$_2$), 1.46–1.38 (m, 20H, C*H*$_2$), 0.97–0.83 (15H, m, C*H*$_3$).

Acetic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (7) . 2-Acetoxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (**7**) can be separated before the saponification step in the preparation of (**6**) as a white solid. Found: C, 76.20, H, 9.60, $C_{50}H_{74}O_7$ requires C, 76.30, H, 9.48; δ_H ($CHCl_3$) 8.08 (s, 1H, Ar*H*), 7.86 (d, 2H, *J* 4.0, Ar*H*), 7.82 (d, 2H, *J* 2.6, Ar*H*), 7.77 (1H, s, Ar*H*), 4.26–4.19 (m, 10H, OC*H*$_2$), 2.41 (s, 3H, OCOC*H*$_3$), 1.98–1.86 (m, 10H, C*H*$_2$), 1.58–1.57 (m, 10H, C*H*$_2$), 1.42–1.32 (m, 20H, C*H*$_2$), 0.96–0.88 (m, 15H, C*H*$_3$). MS (EI), 786 (M$^+$, 89%), 744 (82%), 660 (11%), 491 (5%), 407 (7%), 324 (5%), 295 (10%), 43 (100%).

Hexanoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (8). Hexanoyl chloride (0.10 g, 0.78 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.29 g, 0.39 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 hours at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 1) as eluent and then recrystallised from ethanol as a white solid (0.26 g, 79%). Found: C, 76.75, H, 9.90, $C_{54}H_{82}O_7$ requires C, 76.92, H, 9.80; δ_H ($CHCl_3$) 8.07 (s, 1H, Ar*H*), 7.86 (s, 2H, Ar*H*), 7.81 (2H, d *J* 3.0, Ar*H*), 7.77 (1H, s, Ar*H*), 4.26–4.19 (m, 10H, OC*H*$_2$), 2.67 (2H, t *J* 7.5, OC*H*$_2$), 2.02–1.83 (m, 12H, C*H*$_2$), 1.65–1.35 (m, 34H, C*H*$_2$), 0.99–0.89 (18H, m, C*H*$_3$). MS (EI), 842 (M^+-1, 100%), 744 (62%), 660 (9%), 491 (6%), 407 (6%), 323 (10%), 99 (12%), 71 (10%).

Biphenyl-4-carboxylic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (9). Biphenyl-4-carbonyl chloride (0.17 g, 0.78 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.29 g, 0.39 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 2) as eluent and then recrystallised from ethanol as a grey solid (0.30 g, 83%). Found: C, 79.45, H, 8.75, $C_{61}H_{80}O_7$ requires C, 79.18, H, 8.71; δ_H ($CHCl_3$) 8.37 (d, 2H, *J* 8.4 Ar*H*), 8.23 (s, 1H, Ar*H*), 7.92–7.69 (8H, m, Ar*H*), 7.55–7.36 (4H, m, Ar*H*), 4.28–4.18 (m, 10H, OC*H*$_2$), 1.98–1.87 (m, 8H, C*H*$_2$), 1.83–1.70 (2H, m, C*H*$_2$), 1.62–1.15 (m, 30H, C*H*$_2$), 0.98–0.78 (15H, m, C*H*$_3$). MS (EI), 924 (M^+-1, 100%), 744 (61%), 660 (5%), 295 (6%), 181 (89%), 153 (9%).

4-Nitrobenzoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (10). 4-Nitrobenzoyl chloride (0.15 g, 0.81 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.40 g, 0.54 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 2) as eluent and then recrystallised from ethanol as a yellow solid (0.40 g, 83%). Found: C, 74.0, H, 8.45, N, 1.40, $C_{55}H_{75}NO_9$ requires C, 73.88, H, 8.45, N, 1.57; δ_H ($CHCl_3$) 8.48 (d, 2H, *J* 8.6 Ar*H*), 8.41 (d, 2H, *J* 8.6, Ar*H*), 8.22 (1H, s, Ar*H*), 7.92 (1H, s, ArH), 7.88 (1H, s, ArH), 7.82 (2H, d, *J* 3, ArH), 7.79 (1H, m, Ar*H*), 4.28–4.18 (m, 10H, OC*H*$_2$), 1.98–1.92 (m, 8H, C*H*$_2$), 1.78–1.70 (2H, m, C*H*$_2$), 1.62–1.10 (m, 30H, C*H*$_2$), 0.98–0.78 (15H, m, C*H*$_3$). MS (FAB), 895 (M^++1, 32%), 880 (11%), 811 (12%), 747 (14%), 660 (9%) 311 (94%), 150 (100%).

3,5-Dinitrobenzoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (11). 3,5-Dinitrobenzoyl chloride (0.17 g, 0.75 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.28 g, 0.38 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 2) as eluent and then recrystallised from hexane as a yellow solid (0.30 g, 85%). Found: C, 70.45, H, 8.10, N, 2.70, $C_{55}H_{74}N_2O_{11}$ requires C, 70.34, H, 7.94, N, 2.98; δ_H ($CHCl_3$) 9.36 (s, 2H, Ar*H*), 9.24 (s, 1H, Ar*H*), 8.26 (1H, s, Ar*H*), 7.92 (1H, s, ArH), 7.88 (1H, s, ArH), 7.83 (1H, s, *J* 3, ArH), 7.82 (1H, s, Ar*H*), 7.78 (1H, s, Ar*H*), 4.28–4.18 (m, 10H, OC*H*$_2$), 2.02–1.92 (m, 8H, C*H*$_2$), 1.87–1.75 (2H, m, C*H*$_2$), 1.69–1.18 (m, 30H, C*H*$_2$), 0.99–0.81 (15H, m, C*H*$_3$). MS (EI), 938 (M^+-1, 27%), 878 (41%), 744 (52%), 660 (9%), 415 (10%), 149 (100%).

4-Cyanobenzoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (12). 4-Cyanobenzoyl chloride (0.10 g, 0.59 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.22 g, 0.29 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (2 : 1) as eluent and then recrystallised from ethanol as a pale yellow solid (0.22 g, 87%). Found: C, 77.20, H, 8.70, N, 1.60, $C_{56}H_{75}NO_7$ requires C, 76.94, H, 8.65, N, 1.60; δ_H ($CHCl_3$) 8.41 (d, 1H, *J* 1.9, Ar*H*), 8.39 (d, 1H, *J* 1.9, Ar*H*), 8.20 (s, 1H, Ar*H*), 7.91 (s, 1H, Ar*H*), 7.87 (s, 2H, Ar*H*), 7.86–7.83 (3H, m, Ar*H*), 7.78 (s, 1H, ArH), 4.28–4.18 (m, 10H, OC*H*$_2$), 1.99–1.89 (m, 8H, C*H*$_2$), 1.78–1.73 (2H, m, C*H*$_2$), 1.57–1.52 (m, 10H, C*H*$_2$), 1.44–1.35 (m, 16H, C*H*$_2$), 1.25–1.17 (m, 4H, C*H*$_2$), 0.96–0.85 (m, 12H, C*H*$_3$), 0.81 (3H, t, *J* 7.2, C*H*$_3$). MS (FAB), 874 (M^+, 100%), 789 (12%), 744 (21%), 660 (8%), 322 (7%).

4-Fluorobenzoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (13). 4-Fluorobenzoyl chloride (0.09 g, 0.59 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.22 g, 0.29 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (2 : 1) as eluent and then recrystallised from ethanol as a white solid (0.21 g, 85%). Found: C, 76.05, H, 8.95, $C_{55}H_{75}FO_7$ requires C, 76.18, H, 8.72; δ_H ($CHCl_3$) 8.34–8.30 (m, 2H, Ar*H*), 8.20 (s, 1H, Ar*H*), 8.91–8.79 (m, 5H, Ar*H*), 7.26–7.20 (m, 2H, Ar*H*), 4.27–4.17 (m, 10H, OC*H*$_2$), 1.98–1.90 (m, 8H, C*H*$_2$), 1.79–1.72 (2H, m, C*H*$_2$), 1.59–1.50 (m, 10H, C*H*$_2$), 1.44–1.35 (m, 16H, C*H*$_2$), 1.25–1.17 (m, 4H, C*H*$_2$), 0.96–0.85 (m, 12H, C*H*$_3$), 0.81 (3H, t, *J* 7.2, C*H*$_3$). MS (EI), 866 (M^+-1, 62%), 782 (5%), 744 (14%), 123 (100%), 95 (11%).

1-Naphthoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (14). 1-Naphthoyl chloride (0.09 g, 0.46 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.17 g, 0.23 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 2) as eluent and then recrystallised from ethanol as a grey solid (0.16 g, 80%). Found: C, 78.55, H, 8.95, $C_{59}H_{78}O_7$ requires C, 78.80, H, 8.74; δ_H ($CHCl_3$) 9.11 (d, *J* 8.1, 1H, Ar*H*), 8.59 (d, *J* 7.3, 1H, Ar*H*), 8.26 (1H, s, Ar*H*), 8.13 (1H, d, *J* 8.1 ArH), 7.97–7.82 (5H, m, ArH), 7.66–7.59 (4H, m, ArH), 4.28–4.18 (m, 10H, OC*H*$_2$), 2.17–1.92 (m, 8H, C*H*$_2$), 1.90–1.77 (2H, m, C*H*$_2$), 1.58–1.10 (m, 30H, C*H*$_2$), 0.97–0.81 (12H, m, C*H*$_3$), 0.75 (3H, t, *J* 7.0 C*H*$_3$). MS (EI), 898 (M^+-1, 100%), 744 (27%), 658 (6%), 279 (8%), 155 (90%).

2-Naphthoic acid 3,6,7,10,11-pentakis(hexyloxy)triphenylen-2-yl ester (15). 2-Naphthoyl chloride (0.13 g, 0.67 mmol) was added to 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (0.25 g, 0.34 mmol) in pyridine (1 ml). The reaction mixture was stirred for 3 h at room temperature. Water (5 ml) was then added and the product was extracted with dichloromethane, dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel using dichloromethane and petroleum spirit (1 : 2) as eluent and then recrystallised from ethanol as a pale yellow solid (0.24 g, 81%). Mp 162 °C. Found: C, 78.70, H, 8.75, $C_{59}H_{78}O_7$ requires C, 78.80, H, 8.74; δ_H ($CHCl_3$) 8.91 (s, 1H, Ar*H*), 8.31–8.28 (m, 2H, Ar*H*), 8.06–7.82 (m, 7H, Ar*H*), 7.67–7.60 (m, 3H, Ar*H*), 4.28–4.18 (m, 10H, OC*H*$_2$), 1.98–1.92 (m, 8H, C*H*$_2$), 1.89–1.73 (2H, m, C*H*$_2$), 1.58–1.10 (m, 30H, C*H*$_2$), 0.97–0.81 (12H, m, C*H*$_3$), 0.71 (3H, t, *J* 7.0 C*H*$_3$). MS (EI), 898 (M^+-1, 79%), 744 (36%), 323 (6%), 273 (9%), 155 (100%).

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