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Liquid Crystals

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Asymmetry in liquid crystalline hexaalkoxytriphenylene discotics

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Asymmetry in liquid crystalline hexaalkoxytriphenylene discotics

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The synthesis and phase behaviour of a new series of unsymmetrically substituted hexaalkoxytriphenylene-based liquid crystals are reported. One of the hexyloxy chains in hexahexyloxytriphenylene (HAT6) is replaced by either a shorter or a longer chain, HAT-$(OC_6H_{13})_5(OC_nH_{2n+1})$. Compounds with chain lengths n of 2–14, 16 and 18 were prepared and investigated. Compounds with $n \geqslant 13$ were not liquid crystalline. For all compounds with $n \leqslant 12$ Col_h textures were observed by polarizing microscopy. X-ray investigations showed that the intercolumnar distance gradually increased with n from $n=2$ to $n=12$, while the interdisk distance (3.6 Å) remained constant. A small odd–even effect on the increase of the intercolumn distance with n was observed. This effect was also found in the change of ΔH of isotropization with n.

1. Introduction

Columnar discotic mesophases have attracted considerable interest over the last decade, which has led to a detailed characterization and classification of these phases [1]. Such materials could be interesting as one-dimensional (hole) conductors and find application in, for example, nanowires. The possibility for strong π–π interactions between the polyaromatic cores of hexaalkoxytriphenylenes (HATs) in the hexagonal columnar (Col_h) phase can lead to highly organized columns and a relatively high charge carrier mobility [2–4]. Additional stabilization of the columnar mesophase is expected to lead to improved charge mobility, thus making these materials potential candidates for application in photovoltaic devices [5].

In the Col_h phase the motions of the core and the alkyl chains are strongly correlated [6]. Due to this coupling, an important factor that determines the stability of the columns is the length of the alkyl chains, which surround the disk-like aromatic cores. The interplay between these two motions originates from tail–tail van der Waals interactions and core–core π–π interactions, and results in the potential of HATs to act as molecular wires.

In this study we report the synthesis of a series of novel triphenylene molecules (figure 1), which contain an element of asymmetry due to the presence of five hexyloxy chains and one alkyl chain that is either shorter or longer. We study the liquid crystalline phase behaviour by polarizing optical microscopy (POM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC).

2. Results and discussion

2.1. *Synthesis*

The compounds (series **4-*n***) were synthesized via the biphenyl route, starting from tetrakishexyloxybiphenyl and the appropriate 1-hexyloxy-2-alkoxybenzene (see scheme 1) [7]. 2-Hexyloxyphenol was obtained by reacting 1-bromohexane with a tenfold excess of catechol. Subsequent reaction with another 1-bromoalkane gave the appropriate 1-hexyloxy-2-alkoxybenzenes (**2-*n***) in

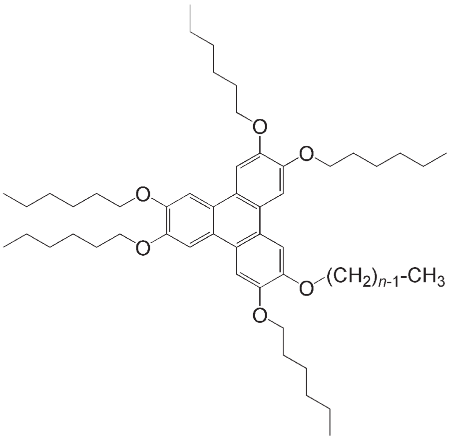

Figure 1. Structure of the triphenylenes studied (n=2–14, 16, 18).

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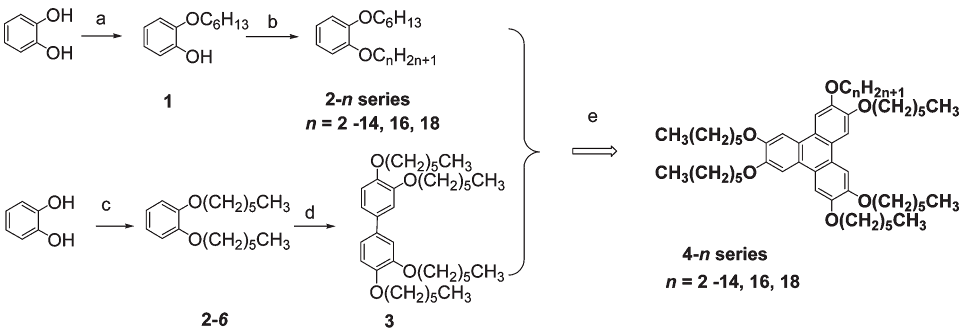

Scheme 1. General procedure for the synthesis of HAT-$(OC_6H_{13})_5(OC_nH_{2n+1})$ derivatives **4-*n***. (a) $C_6H_{13}Br$, ethanol, K_2CO_3; (b) $C_nH_{2n+1}Br$, 2-butanone (CH_3CN), K_2CO_3 (Cs_2CO_3); (c) $C_6H_{13}Br$, CH_3CN, Cs_2CO_3; (d) ICl, $CHCl_3$; Cu powder, heat; (e) $FeCl_3$, CH_2Cl_2, CH_3OH.

good yield. The biphenyl derivative **3** was obtained in two steps from 1,2-bishexyloxybenzene in overall 19% yield. First, 1,2-bis-hexyloxy-4-iodobenzene was obtained in almost quantitative yield by reaction with iodine monochloride. Reaction with copper powder at 275°C gave the biphenyl derivative. The coupling towards the triphenylene derivatives (series **4-*n***) was carried out with $FeCl_3$ as a catalyst under anhydrous conditions. In order to avoid dealkylation, anhydrous conditions and a short reaction time (0.5–1 h) was used.

2.2. *Characterization*

POM shows that all members of the **4-*n*** series of compounds with $n \leqslant 12$ exhibit enantiotropic liquid crystalline phases. The fan-like optical texture is typical for a hexagonal columnar discotic mesophase (Col_h), commonly observed for triphenylene derivatives (figure 2) [8].

As a typical example, the DSC thermogram of compound **4–12** is shown in figure 3. The Cr–Col_h and Col_h–I transitions upon heating, and the I–Col_h and Col_h–Cr transitions upon cooling, respectively, are seen. Compound **4–12** could be cooled significantly below the melting point, with a crystallization point at about 26°C (table 1). The transition temperatures and corresponding enthalpies of all compounds in the **4-*n*** series are given in table 1. The melting points and isotropization temperatures of this series are plotted in figure 4.

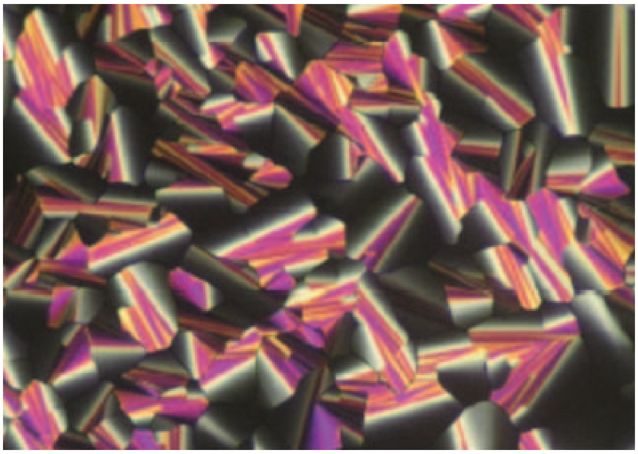

Figure 2. Optical texture of **4–2** at 78°C, indicative of a Col_h phase observed upon cooling from the isotropic state.

All the compounds, with $n \leqslant 12$, exhibit a liquid crystalline Col_h phase. As can be seen from table 1 and figure 4, compounds **4–13** to **4–18** are not liquid crystalline, although they can be supercooled considerably before crystallization occurs. The highest melting point is found for **4–6**. This is not unreasonable, since the 6-fold symmetry probably allows an optimal packing in regard of both π–π interactions and intercolumn interference. With increasing length of one of the alkyloxy chains, the melting points gradually decrease to below 40°C.

The isotropization temperatures have a maximum for **4–5** and decrease both for shorter and longer chains. For longer chains than hexyloxy the asymmetry increases and the isotropization temperatures decrease rapidly. This leads to a gradual decrease of the temperature range for the LC phase, with the result that for $n \geqslant 13$ no liquid crystalline phases are observed anymore. The isotropization temperatures do not have their maximum for the fully symmetrical **4–6** but for **4–5**. For the class of 6-fold symmetrical HATs it was found that the isotropization temperatures decrease strongly with longer alkyl chains [9]. For compound **4–5** the balance between a higher isotropization temperature due to a shorter chain, and a lower isotropization temperature due to asymmetry, is apparently just in favour of the first effect. For **4–4**, **4–3**, and **4–2** the increasing asymmetry leads to a lowering of the isotropization temperature.

Figure 5 shows the isotropization enthalpy as a function of *n*. Less energy is required for molecules

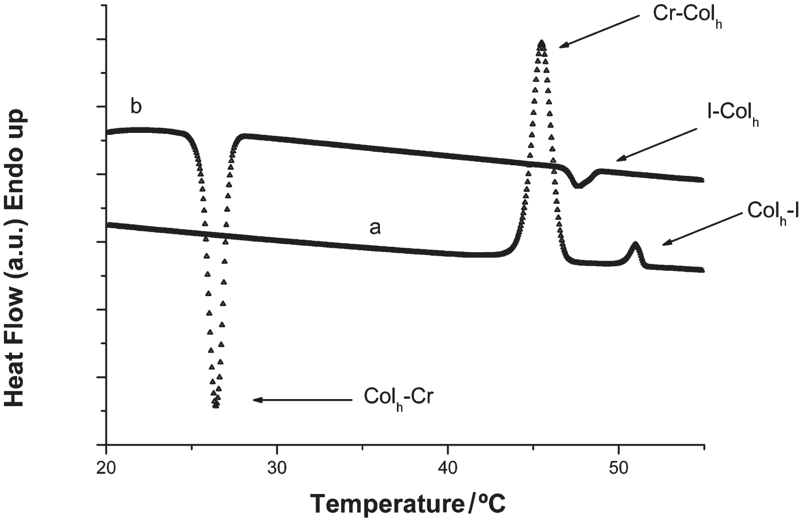

Figure 3. DSC trace of compound **4–12** for (*a*) the second heating and (*b*) cooling runs (5°C min^{-1}).

with a longer alkyl chain to go into highly disordered isotropic state, indicating a lower thermal stability of the liquid crystalline phase. The increase of *n* increases the asymmetry of the system resulting in a less stable mesophase, and a narrower mesophase region.

For the systems with smaller *n*, such as **4–4**, where the isotropization enthalpy is comparable to that of **4–5**, close packing of the molecules plays an important role. Going to smaller values of *n*, the intercalation of the other five hexyloxy chains around the triphenylene molecule will progressively disturb the system, resulting in a strong decrease of transition temperatures and isotropization enthalpies, as shown in figures 4 and 5.

XRD of the liquid crystalline phases was used to determine the intercolumn and interdisk distances. The *d*-spacings obtained by X-ray diffraction are given in table 2. Intercolumn distances were calculated from the small angle peaks, assuming that a Col$_h$ phase is present. The intracolumn distance follows directly from the wide angle (0 0 1) peak in the diffractograms. For all liquid crystalline compounds the interdisk distance was the same (3.6 Å), a typical value for the π–π stacking of triphenylene discotics [10]. For a few of the compounds analysed the interdisk spacing could not be deduced from the X-ray measurements, due to the high tendency of these compounds to align with the columns parallel to the surface during sample preparation. The

Table 1. Transition temperatures (°C) and transition enthalpies (kJ mol^{-1}; in parentheses) of the **4-*n*** series of compounds, obtained with DSC at a rate of 5°C min^{-1}.

	Heating					Cooling				
Compound	Cr		Col$_h$		I	I		Col$_h$		Cr
4–2	•	58.7 [37.9]	•	81.3 [4.0]	•	•	79.2 [3.8]	•	33.4 [36.0]	•
4–3	•	62.3 [42.5]	•	87.9 [4.6]	•	•	84.7 [4.5]	•	36.6 [38.2]	•
4–4	•	61.0 [44.1]	•	98.4 [5.8]	•	•	96.1 [5.8]	•	35.7 [38.1]	•
4–5	•	59.0 [35.5]	•	100.8 [5.7]	•	•	98.8 [5.8]	•	39.9 [36.7]	•
4–6	•	66.6 [39.6]	•	98.1 [4.9]	•	•	96.1 [4.8]	•	48.1 [42.1]	•
4–7	•	59.6 [38.2]	•	97.2 [4.9]	•	•	95.3 [4.7]	•	44.0 [38.7]	•
4–8	•	54.8 [40.1]	•	91.3 [4.5]	•	•	86.2 [4.5]	•	33.9 [39.1]	•
4–9	•	49.7 [40.2]	•	82.4 [4.4]	•	•	79.9 [4.2]	•	29.1 [38.2]	•
4–10	•	45.0 [37.8]	•	71.8 [3.2]	•	•	68.3 [3.2]	•	23.3 [36.1]	•
4–11	•	46.8 [41.2]	•	62.9 [3.1]	•	•	59.6 [3.2]	•	25.8 [39.2]	•
4–12	•	45.5 [43.9]	•	50.9 [2.6]	•	•	47.6 [2.6]	•	26.4 [41.2]	•
4–13	•	41.0 [32.3]			•	•			27.1 [26.9]	•
4–14	•	39.7 [29.2]			•	•			25.3 [27.7]	•
4–16	•	38.4 [23.7]			•	•			24.9 [22.9]	•
4–18	•	36.1 [35.5]			•	•			19.7 [31.0]	•

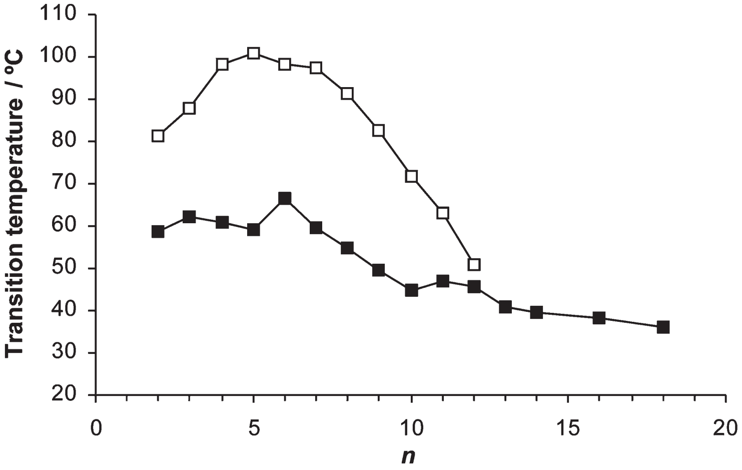

Figure 4. Dependence of the melting points (■) and isotropization temperatures (□) of series **4-*n*** on the number of carbon atoms *n* in the alkyl chains.

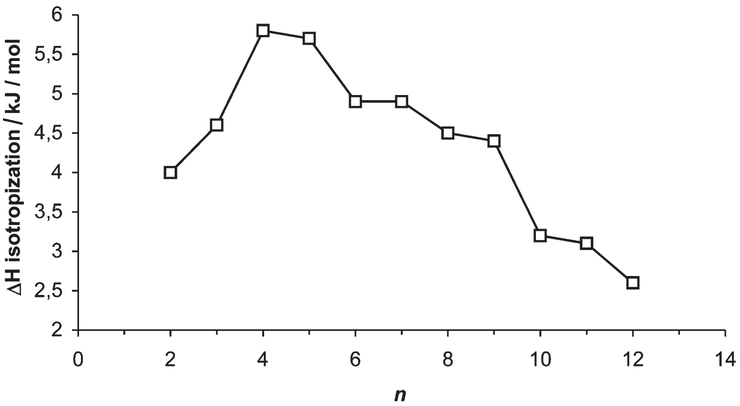

Figure 5. Dependence of the isotropization enthalpy ΔH on *n* for compounds **4-*n***.

intercolumn distances increase with *n*, as can be seen in figure 6. In addition, upon increasing *n* the concomitant increase of the intercolumn distance levels off. This suggests that upon further increase of the chain length ($n \geqslant 7$), the chain that is sticking out is largely bent upwards or downwards, but will still have a component parallel to the plane of the aromatic core. As a result, the disks themselves become asymmetric, which will

Table 2. Layer spacing and columnar distances for the mesophase of series **4-*n***, deduced from X-ray measurements.

Compound	*d*-spacing/Å	Intercolumn distance/Å[b]	Interdisk distance/Å
4–2	17.49	20.19	—[a]
4–3	17.72	20.46	—[a]
4–4	17.92	20.69	3.62
4–5	18.13	20.93	3.60
4–6	18.34	21.17	3.61
4–7	18.43	21.28	—[a]
4–8	18.64	21.52	3.66
4–9	18.76	21.66	—[a]
4–10	18.98	21.91	3.65
4–11	19.00	21.93	3.63
4–12	19.08	22.03	3.60

[a] Could not be determined.
[b] Intercolumnar distance is $2/\sqrt{3} \times d$.

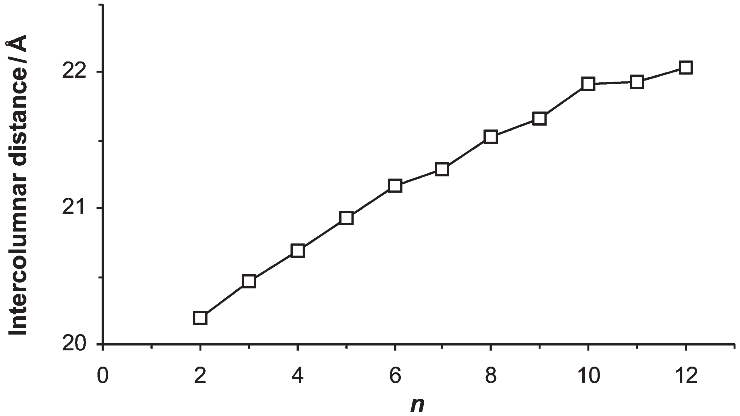

Figure 6. The intercolumnar distances for the **4-*n*** series as a function of *n*.

lead to a decrease of the core–core overlap between the disks in the columns. Therefore, the π–π interactions will be diminished, and this will lead to a strong destabilization of the columnar phase.

Furthermore, a small but distinct odd–even effect becomes apparent in the increase in the intercolumn distance above n=6. This increase is larger on going from odd n to the next even n, than from an even spacer length to the next odd one. This is probably related to the observation that, seen from a fixed point, the increase of the distance of the atom in the alkyl chain that is furthest removed from that point of reference is different in going from an odd to an even spacer length, than from an even to an odd spacer length. This is schematically depicted in figure 7. Preece *et al.* have observed similar odd–even effects for a series of HAT5-derived compounds [8, 11]. In fact, related odd–even effects can also be discerned in figure 4 (isotropization temperatures) and more clearly in figure 5 (isotropization enthalpies). Upon going from n=6 to n=12 the change in ΔH values on going from odd n to even n are much larger than on going from even n to odd n. For n<5 the reverse effect seems to take place.

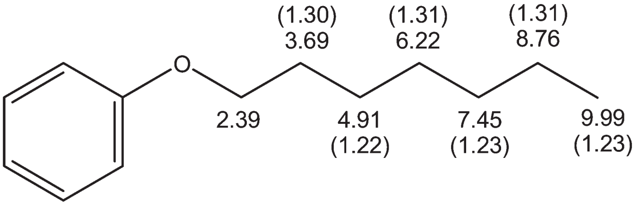

Figure 7. Geometrical basis of odd–even effects: distance between *ipso* C atom in aromatic core and the designated C atom in the spacer, and (in parentheses) the increase in distance (all in Å).

These trends for both n<5 and n>6 indicate that the stability of the mesophase is strongly related to the actual distance between the aromatic core and the terminal atoms in the spacer, rather than to the number of carbon atoms in the tail. Increase of the chain length from an odd number of carbon atoms to the next even number of carbon atoms leads to a larger increase in the intercolumn distance than an increase of this length from an even to the next odd number of carbon atoms (figure 7). This can be clarified by the distance of a carbon atom in the alkyl chain to the aromatic core. These distances are depicted in figure 7 for a model compound with a heptyloxy chain. As can be seen, the increase from an odd n to the next even value of n (1→2, 3→4, 5→6) is ~1.31 Å, and therefore distinctly larger than that from an even n to the next odd value of n (2→3, 4→5, 6→7), which is ~1.23 Å. A further investigation of the effects of this molecular asymmetry on a variety of physical properties of triphenylene systems is currently in progress in our laboratories.

3. Conclusions

A new series of columnar discotic LC materials are reported, based on a triphenylene core with five hexyloxy chains and one alkoxy chain with n carbon atoms. For $n \leqslant 12$ this class of materials exhibits a $\mathrm{Col_h}$ mesophase. For compounds with $n \geqslant 13$ no mesophase is present. The observed maxima in isotropization temperatures and isotropization enthalpies display an intricate balance between the π–π stacking of the triphenylene cores and the organization of the alkyl chain (interpenetration, orientation with respect to the aromatic core, intercolumn distance). Finally, distinct odd–even effects on the intercolumn distances are observed, which are related to the actual distance between the aromatic core and the terminal atom in the alkyl chain.

4. Experimental

4.1. *Measurements*

^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained with a Bruker spectrometer, using $CDCl_3$ as a solvent. Melting points, thermal phase transition temperatures and optical investigation of the liquid crystalline phases were determined on samples between ordinary glass slides using an Olympus BH-2 polarizing microscope equipped with a Mettler FP82HT hot stage, which was controlled by a Mettler FP80HT central processor. DSC thermograms were obtained on a Perkin-Elmer DSC-7 system using 2–5 mg samples in 30 µl sample pans and a scan rate of 5°C min^{-1}. ΔH is calculated in kJ mol^{-1}. Temperature-dependent X-ray curves were measured on a Philips X'pert Pro MRD machine equipped with an Anton Paar camera for temperature control. For the measurements in the small angle region, the sample was spread in the isotropic or the liquid crystalline phase on a thin glass slide (about 15 µm thick), which was placed on a temperature-regulated flat copper sample stage. This sample preparation sometimes caused very high intensities of X-ray reflections because of partial or complete surface alignment of the molecules in the liquid crystalline state. The accurate masses were obtained using a Finnigan MAT 95 mass spectrometer operating in the 70 eV EI mode at a resolution 5500.

4.2. *Synthesis*

All solvents were PA quality. All reactions were carried out under nitrogen atmosphere. Dry CH_2Cl_2 was freshly distilled from CaH_2. All compounds gave NMR spectra in agreement with the proposed structure and show correct elemental analyses or accurate masses. Specimen synthesis details are given below.

4.2.1. 2-Hexyloxyphenol, 1 [12]. A mixture of catechol (10.1 g, 92 mmol), 1-bromohexane (3.1 g, 19 mmol) and anhydrous potassium carbonate (15 g) in ethanol (100 ml) was stirred under reflux for 26 h. The solvent was partially evaporated and 250 ml of water added to the system. After extraction with 3 × 100 ml CH_2Cl_2 and washing with brine (200 ml), the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica with petroleum ether (40/60)/CH_2Cl_2 (2/1) as eluant, to give 2-hexyloxyphenol as a pale yellow oil (2.02 g, 10.4 mmol, 55%). ^1H NMR: δ 6.87–7.04 (4H, m, ArH), 5.86 (1H, s, OH), 4.02–4.08 (2H, t, J=6.49 Hz, OCH_2), 1.77–1.91 (2H, m, CH_2CH_2O), 1.35–1.54 (6H, m, CH_2), 0.95–1.01 (3H, t, J=6.38 Hz, CH_3). ^{13}C NMR: δ 146.04 (1-ArCOH), 145.85 (2-ArCO–R), 121.31 (6-ArC), 120.11 (3-ArC), 114.51 (5-ArC), 111.65 (4-ArC), 68.90 (OCH_2), 31.62–22.66 (4 × CH_2), 14.08 (2 × CH_3).

4.2.2. 1-Ethyloxy-2-hexyloxybenzene, 2–2. A solution of 5.9 g (30 mmol) of **1**, 11.3 g (0.10 mol) of bromoethane, 10 g K_2CO_3 and a catalytic amount of KI in 30 ml of 2-butanone was refluxed for 2 days under anhydrous conditions. After refluxing, the reaction mixture was worked up using the same procedure as for compound **1**. Compound **2–2** was obtained as a pale yellow oil, (6.07 g, 27 mmol, 89%). ^1H NMR: δ 6.91 (4H, bs, ArH), 3.65–4.45 (4H, m (t+q overlap), OCH_2), 1.71–2.34 (2H, m, CH_2CH_2O), 1.10–1.59 (9H, m, 1 × CH_3 and 3 × CH_2), 0.92–0.99 (3H, t, J=6.25 Hz, CH_3). ^{13}C NMR: δ 150.14 (1-ArC–O), 149.92 (2-ArC–O), 122.04 (6-ArCH), 121.94 (3-ArCH), 114.93 (5-ArCH), 111.83 (4-ArCH), 70.15 (OCH_2CH_2), 65.55 (OCH_2CH_3), 32.64, 30.27, 26.73, 23.65 (4 × CH_2), 15.92 (1 × CH_3, OCH_2CH_3), 15.04 (1 × CH_3, hexyloxy tail).

4.2.3. 1-Hexyloxy-2-octadecyloxybenzene, 2–18. From 7.0 g (36 mmol) of **1**, 15.6 g (46.8 mmol) of 1-bromooctadecane, 7 g K_2CO_3 and a catalytic amount of KI in 100 ml 2-butanone, 10.9 g (24.4 mmol, 68%) of **2–18** was obtained as a white solid, m.p. 43°C. ^1H NMR: δ 6.87 (4H, s, ArH), 3.95–4.01 (4H, t, J=6.84 Hz, OCH_2), 1.73–1.87 (4H, m, OCH_2CH_2), 1.24–1.45 (36H, m, CH_2), 0.83–0.92 (6H, dt, CH_3). ^{13}C NMR: δ 149.20 (2 × ArC–O), 120.98 (3,6-ArCH), 114.03 (4,5-ArCH), 69.25 (2 × OCH_2), 22.65–31.94 (20 × CH_2), 14.06 and 14.15 (2 × CH_3).

4.2.4. 3,3′,4,4′-Tetrakishexyloxybiphenyl, 3 [12]. A mixture of **2–6** (10 g, 36 mmol) and iodine monochloride (8.8 g, 54 mmol) in $CHCl_3$ was stirred at room temperature for 2.5 h. The mixture was washed twice with 150 ml of 1M sodium metabisulphite solution followed by washing with 100 ml of water. The organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product (1,2-bis-hexyloxy-4-iodobenzene) was obtained (13 g, 89%) as an intermediate for the synthesis of **3**. The crude compound was used in the next reaction without further purification.

For the coupling reaction a mixture of 9.0 g (22 mmol) of 1,2-bis-hexyloxy-4-iodobenzene and 6.3 g (0.1 mol) copper powder were heated at 275°C for 1 h, while the reaction mixture was vigorously stirred. After cooling the mixture to room temperature, 250 ml of CH_2Cl_2 was added and the reaction mixture filtered through Hyflo. The crude compound was recrystallized from a mixture of methanol and ethanol (1/1), yielding

2.35 g (4.24 mmol, 38%) of **3**, m.p. 79°C. ^{1}H NMR: δ 7.06–7.10 (4H, dd, ArH), 6.91–6.95 (2H, dd, ArH), 4.00–4.11 (8H, dt, OCH_2), 1.78–1.92 (8H, m, OCH_2CH_2), 1.28–1.51 (24H, m, CH_2), 0.90–0.97 (12H, t, J=6.82 Hz, CH_3). ^{13}C NMR: δ 149.24 (3, 3′-ArC–O), 148.44 (4, 4′-ArC–O), 134.31 (6,6′-ArC–CAr), 119.28 (5,5′-ArCH), 114.07 (2,2′-ArCH), 113.06 (1,1′-ArCH), 69.35 ($4\times OCH_2$), 22.65, 25.75, 29.34, 31.63 ($16\times CH_2$), 14.04 ($4\times CH_3$).

4.2.5. 2-Ethoxy-3,6,7,10,11-pentakishexyloxytriphenylene, 4–2. To a solution of **2–2** (5.7 g, 25.7 mmol) and **3** (9.24 g, 16.7 mmol) in 50 ml of dry CH_2Cl_2 was carefully added 14 g of $FeCl_3$ under anhydrous conditions. The mixture was stirred under N_2 for 0.5–1 h at 35°C. On addition of 300 ml of methanol to the reaction mixture the triphenylene compound crystallized from solution. The mixture was cooled to −35°C and then filtered. The crystals were washed several times with cold methanol. The crude product was subjected to column chromatography using CH_2Cl_2/PE (40/60) (1/1) as eluant. After recrystallization from a mixture of ethanol, methanol and 2-butanone, 3.7 g (29%) of **4–2** was obtained. ^{1}H NMR: δ 7.83 (6H, s, ArH), 4.19–4.35 (12H, m, OCH_2), 1.86–2.00 (12H, m, OCH_2CH_2), 1.36–1.59 (33H, m, CH_2 and CH_3), 0.89–0.96 (15H, t, J=6.71 Hz, CH_3). ^{13}C NMR: δ 148.66–148.98 (2,3,6,7,10,11-ArC–O), 123.56–123.63 ($6\times$ArC–centre), 107.16–107.31 ($6\times$ArC–H), 69.71 ($5\times OCH_2$), 65.20 ($1\times OCH_2CH_3$), 22.68, 25.87, 29.35, 31.71 ($15\times CH_2$), 15.04 ($1\times OCH_2CH_3$), 14.01($5\times CH_3$). M^+: calcd 772.5642; found 772.5660.

4.2.6. 11-Octadecyloxy-2,3,6,7,10-pentakishexyloxytriphenylene, 4–18. From 0.53 g (1.2 mmol) of **2–18**, 0.22 g (0.41 mmol) of **3** and 1.0 g $FeCl_3$, 0.11 g (0.11 mmol, 28%) of **4–18** was obtained by the same procedure as described for **4–2**. ^{1}H NMR: δ 7.83 (6H, s, ArH), 4.19–4.26 (12H, t, J=6.5 Hz, OCH_2), 1.90–1.97 (12H, m, OCH_2CH_2), 1.25–1.57 (60H, m, CH_2), 0.87–0.96 (18H, m, CH_3). ^{13}C NMR: δ 148.95 (2,3,6,7,10,11-ArC–O), 123.60 ($6\times$centre–ArC), 107.29 ($6\times$ArC–H), 69.70 ($6\times OCH_2$), 22.70–31.95 ($36\times CH_2$), 14.10, 14.16 ($6\times CH_3$). M^+: calcd 996.8146; found 996.8145.

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