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Extended triphenylenes: synthesis, mesomorphic properties and molecularly resolved scanning tunneling microscopy images of hexakis(dialkoxyphenyl)triphenylenes and dodeca(alkoxy)tris(triphenylenylene)s†

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Palladium-catalyzed cross-coupling between 3,4-dialkoxyphenylboronic acids (**1a–d**) and 2,3,6,7,10,11-hexabromotriphenylene (**2**) provided 2,3,6,7,10,11-hexakis[3,4-bis(alkoxy)phenyl]triphenylenes, $C_{18}H_6[C_6H_3(OC_nH_{2n+1})_2]_6$ where $n = 6$, 8, 10, and 12 (**3a–d**). Cyclodehydrogenation of the aryl-substituted triphenylenes **3a–d** using ferric chloride oxidation followed by methanol reduction produced 6,6′,6″,7,7′,7″,10,10′,10″,11,11′,11″-dodecaalkoxy-2,3′:3,2″:2′,3″-tris(triphenylenylene)s, $C_{54}H_{18}(OC_nH_{2n+1})_{12}$ where $n = 6$, 8, 10, and 12 (**4a–d**). The mesomorphic properties of the compounds **3a–d** and **4a–d** were investigated by differential scanning calorimetry (DSC) measurements, polarizing microscopy, and wide angle X-ray diffraction (WAXD). The triphenylenes **3a–d** exhibited a columnar mesophase in the range of 111–126, 85–104, 74–103, and 47–101 °C, respectively. Upon oxidation of the moiety, the columnar mesophases shift to higher temperatures and exist in a much broader range of temperatures: for the tris(triphenylenylene)s **4a–d**, they have been observed in the range of 180–430, 150–370, 120–322, and 104–306 °C, respectively. Finally, the self-assembly at the interface between a solution of **4c** and a graphite substrate has been studied by scanning tunneling microscopy. Molecularly resolved imaging revealed a highly ordered monolayer exhibiting a two-dimensional hexagonal lattice.

Introduction

Columnar discotic liquid crystals have been the subject of considerable interest in recent years.[1–6] The liquid-crystal forming molecules generally consist of an aromatic core, a disc-like mesogen, surrounded by aliphatic side chains. These discotic molecules form the fluid nematic phase (N_D) and/or the more viscous columnar phase (Col). In the columnar mesophase, the aromatic cores are stacked on top of each other in columns separated by the fluid peripheral aliphatic chains. The columnar phases are classified according to the two-dimensional lattice symmetry of the columnar packing (hexagonal: Col_h, rectangular: Col_r, oblique: Col_{ob}) and order (*e.g.* Col_{ho}) or disorder (*e.g.* Col_{hd}) within the columns.[4–6] The columnar arrangement of the discotic molecules allows energy migration, due to the overlap of the π-electron orbitals between the neighboring aromatic cores.[6] Thus, the columns act like 'molecular wires' with the charge carriers hopping along the axis of the columns from mesogen to mesogen. Liquid crystalline materials could give uniform films with a high degree of molecular orientation, which promotes large overlap between the aromatic π-orbitals of the charge carrier transporting chromophore.

Triphenylene derivatives are the most well-known representatives of discotic liquid crystals forming columnar mesophases.[4–16] Their self-assembly behavior on surfaces has been investigated for physisorbed monolayers on highly oriented pyrolytic graphite (HOPG)[17–19] and for chemisorbed monolayers on gold surfaces.[20,21] It has also been reported recently that hexaalkoxytriphenylenes and hexaalkylthiotriphenylenes, $C_{18}H_6(XR)_6$ where X = O and S; R = alkyl, exhibit large hole mobilities of 10^{-3} to 10^{-1} cm^2 V^{-1} s^{-1},[9–12] which are intermediate between those observed for some organic single crystals and those of amorphous polymers.

Recently, we have synthesized hexaalkyl-substituted derivatives of hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene, $C_{42}H_{12}R_6$ (HBC-C_{12}).[22–24] These hexabenzocoronene derivatives form a hexagonal columnar ordered mesophase (Col_{ho}) with a remarkably large phase width (*ca.* 300 K)[23] and exhibit extremely high charge carrier mobilities.[24] Very recently, we have successfully synthesized hexaaryl-substituted derivatives of hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene, $C_{42}H_{12}(C_6H_4R)_6$ where $R = C_{12}H_{25}$ (HBC-PhC_{12}).[25] The aryl-substituted derivatives exhibited three distinct improvements over the alkyl-substituted HBCs: they possessed longer-range order in the Col_{ho} mesophase, they had much higher solubility than the alkyl-substituted HBCs, and they remained in the mesophase at room temperature. As a consequence of this improved ordering, they have been shown to possess the highest charge carrier mobility, 0.46 cm^2 V^{-1} s^{-1}, reported so far for any mesophase.[26] Noteworthy, this value is even larger than that found for the helical columnar mesophase (H) of hexakis(hexylthio)triphenylene, $C_{18}H_6(SC_6H_{13})_6$.[10–12] The consistently higher charge carrier mobility over a large temperature range, if compared with the alkyl-substituted derivatives, and the significantly better processing properties represent a crucial improvement for the use of these discotic mesophases for the development of molecular electronic devices.

The *n*-alkyl and *n*-alkylphenyl derivatives of hexabenzocoronene have been found to form monomolecular adsorbate layers on the basal plane of HOPG, which can be visualized using scanning tunneling microscopy (STM).[22] These molecules arrange into close-packed arrays on the graphite surface

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†The IUPAC name for dodeca(alkoxy)tris(triphenylenylene) is 2,3,6,7,12,13,16,17,22,23,26,27-dodeca(alkoxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]-trinaphthylene.

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with the alkyl side chains aligned along the crystallographic axes of the (001) surface of HOPG.

To further our studies on polycyclic aromatic hydrocarbons (PAHs)[27–31] and to examine the role of heteroatom incorporation in the periphery—which cannot be done with the HBC derivatives due to ether cleavage during the final oxidative cyclodehydrogenation, and as a natural progression analogous to that of HBC-C_{12} to HBC-PhC_{12}—we have synthesized hexaaryl-substituted derivatives of triphenylene, $C_{18}H_6[C_6H_3(OR)_2]_6$ and investigated their self-assembly behavior at the solid–liquid interface on HOPG by means of STM. The *ortho*-diarylated PAHs, such as the hexaaryl-substituted triphenylenes, could be cyclodehydrogenated to afford the larger planar PAHs. Herein, we report the synthesis and the mesomorphic properties of 2,3,6,7,10,11-hexakis[3,4-bis(alkoxy)phenyl]triphenylenes, $C_{18}H_6[C_6H_3(OC_nH_{2n+1})_2]_6$ where $n=6$, 8, 10, and 12 (**3a–d**), and the corresponding ring-closed aromatic hydrocarbons, dodecaalkoxy-substituted supertriphenylenes (Fig. 1), 6,6′,6″,7,7′,7″,10,10′,10″,11,11′,11″-dodecaalkoxy-2,3′:3,2″:2′,3″-tris(triphenylenylene)s, $C_{54}H_{18}(OC_nH_{2n+1})_{12}$ where $n=6$, 8, 10, and 12 (**4a–d**). The authors wish to note that an alternative nomenclature for the core has been suggested, that of dodecabenzotrinaphthylene.[32] In addition, the STM investigation at the solid–liquid interface allowed us to gain insight into the structure of these derivatives upon physisorption on an atomically flat conductive solid substrate.

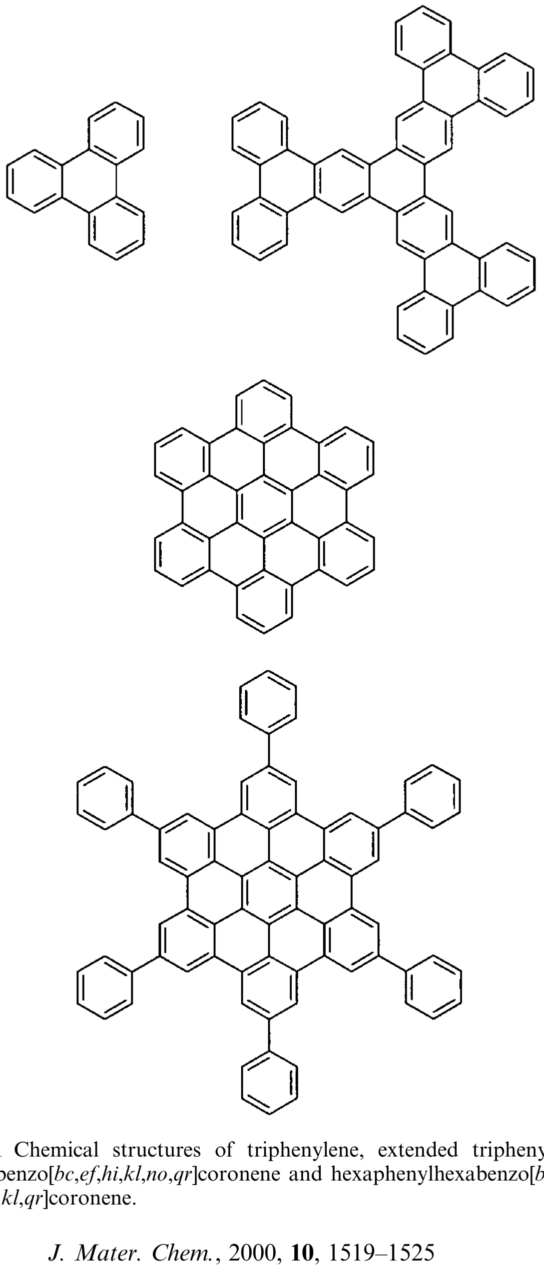


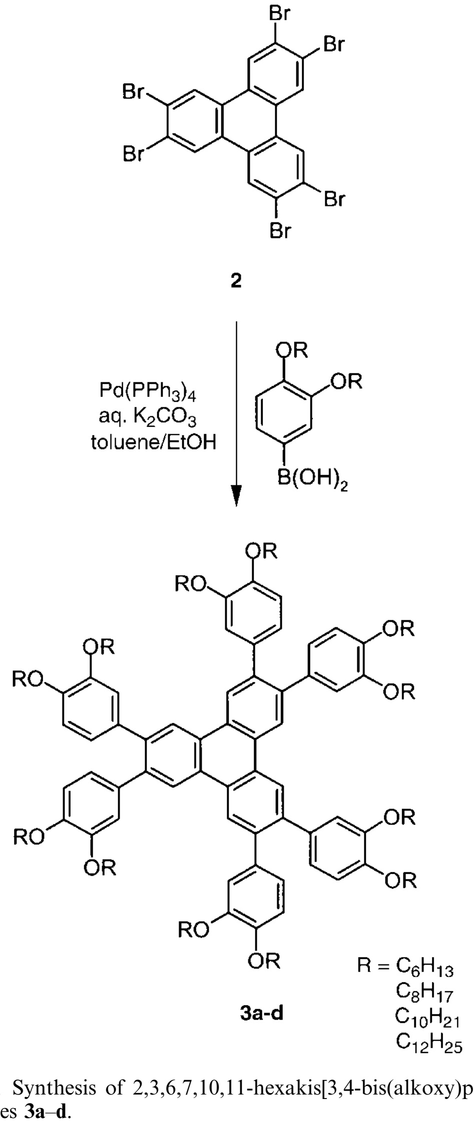
Fig. 1 Chemical structures of triphenylene, extended triphenylene, hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene and hexaphenylhexabenzo[*bc*,*ef*,*hi*,*no*,*kl*,*qr*]coronene.

Results and discussion

Synthesis

3,4-Dialkoxyphenylboronic acids, $C_6H_3(OC_nH_{2n+1})_2B(OH)_2$ where $n=6$, 8, 10, and 12 (**1a–d**), were prepared in a three-step reaction according to the literature procedures.[33–35] Thus, 1-bromo-3,4-dimethoxybenzene was demethylated to give 1-bromo-3,4-dihydrobenzene, which was then *o*-alkylated to afford 1-bromo-3,4-dialkoxybenzenes. The bromobenzene derivatives were then converted into the corresponding arylboronic acids **1a–d**. 2,3,6,7,10,11-Hexabromotriphenylene, $C_{18}H_6Br_6$, (**2**) was prepared by bromination of triphenylene according to the literature procedure.[36]

The synthesis of the hexaaryl-substituted triphenylenes **3a–d** is shown in Scheme 1. Palladium-catalyzed cross-coupling (Miyaura–Suzuki cross-coupling)[37–41] between the arylboronic acids **1a–d** and the hexabromotriphenylene **2**, in which a ninefold molar excess of the boronic acids **1a–d** over the hexabromide **2** was used, gave the aryl-substituted triphenylenes **3a–d** in 90–96% yields, respectively. Despite the fact that the solubility of the hexabromotriphenylene **2** was minimal in the refluxing solvent (*ca.* a 3 : 1 mixture of toluene and ethanol), the sixfold aryl–aryl cross-coupling took place to produce the triphenylenes **3a–d** in extremely high yields. The triphenylenes



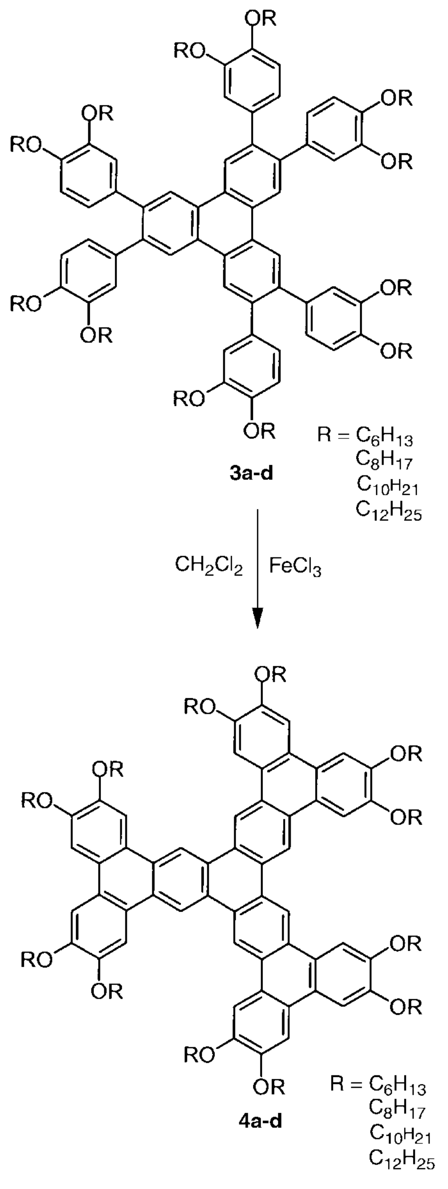
Scheme 1 Synthesis of 2,3,6,7,10,11-hexakis[3,4-bis(alkoxy)phenyl]triphenylenes **3a–d**.

3a–d are white solids and soluble in common organic solvents such as hexane, toluene, and dichloromethane at room temperature.

As shown in Scheme 2, cyclodehydrogenation of the triphenylenes **3a–d** with ferric chloride oxidation followed by reductive work-up with methanol (Boden–Bushby cyclization)[42–47] produced the larger planar PAH, supertriphenylenes **4a–d**, as a pale yellow solid in 70–80% yields, respectively. The solubility of the compounds **4a–d**, like hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene derivatives, is low because of the aggregation of large planar aromatic cores. The hexyloxy derivative **4a** is soluble in dichloromethane, hot hexane, and hot toluene, whereas the longer alkoxy derivatives **4b–d** are soluble in hot organic solvents such as dichloromethane and toluene.

Mesomorphic properties

The thermal properties of the triphenylenes **3a–d** and the supertriphenylenes **4a–d** were examined by differential scanning calorimetry (DSC) measurements and polarizing optical microscopy. For the non-planarized aryltriphenylene derivatives **3a–d**, there is a drastic reduction in the mesophase onset temperature, T_{meso}, from 111 °C to 74 °C, whereas the isotropization temperature, T_{iso} of such molecules remains fairly constant. These figures are similar to those reported for other triphenylene derivatives in the literature. The ring-closed triphenylenes **4a–d** exhibit increased T_{meso} and T_{iso} transition temperatures. These transition temperatures are listed in Table 1. Decomposition, measured by thermogravimetric analysis (TGA), occurs between 240 °C and 280 °C for all compounds.



Scheme 2 Synthesis of dodecaalkoxy-substituted extended triphenylenes **4a–d**.

Room temperature and mesophase packing behavior for the triphenylenes **3a–d** and the supertriphenylenes **4a–d** in the mesophase were investigated by X-ray diffraction and optical polarizing microscopy. No definite room temperature or mesophase unit cell could be determined for any of the compounds *via* X-ray diffraction, owing to the presence of only the (100) reflection and the relatively disordered alkyl region (Fig. 2). Optical microscopy shows textures that can be assigned to a columnar mesophase.

The addition of phenyl spacers, which turned out to be crucial to the improved properties of the hexabenzocoronene derivatives, did not improve the mesophase behavior of the arylalkoxytriphenylenes **3a–d**. According to WAXD data, these systems are relatively disordered, showing no higher reflections other than inter-columnar packing distance. Also the presence of the (001) reflection is very weak, indicating a very low degree of intra-columnar order. The mesophase widths were not dramatically increased, and there is no indication of a mesophase at room temperature, as seen in the HBC-PhC_{12}. It is fair to note that the reason for the different behavior observed upon addition of the phenyl spacers in the case of HBC-PhC_{12} and for alkoxytriphenylenes is not yet clear. We originally believed that the steric hindrance of the tilted phenyl spacers would limit the mobility within the column. Indeed, in the case of HBC-PhC_{12}, the librational motion of the aromatic cores was suppressed, as shown in Heteronuclear Multiple Quantum NMR experiments.[25] Similar experiments to determine the librational motion of the aryl triphenylene derivatives are ongoing and will hopefully elucidate some of the dynamics of the molecules in columnar structures.

The extension of the aromatic π-system from the triphenylene derivatives to the supertriphenylene derivatives gave rise to dramatic increases of both the transition temperatures and of the phase widths of the columnar mesophases. This hints at the relative importance of efficient π–π interactions for the formation and stability of columnar structures. Besides, the relative insolubility of these molecules is one consequence of this improved π–π interaction. However, efficient π–π interactions are not sufficient to generate a highly ordered mesophase. This is not surprising, as HBC-C_{12} exhibits relatively lower order, when compared to HBC-PhC_{12}. However, the lack of any long-range order in these mesophases is intriguing. Compared to the HBCs, which have 13 fused benzene rings,

Table 1 Observed transitions for compounds **3a–d** and **4a–d**

Compound	Observed transitions
3a	$\mathrm{Cr} \underset{(111)}{\longrightarrow} \mathrm{Col} \underset{(126)}{\longrightarrow} \mathrm{I}$
3b	$\mathrm{Cr} \underset{(85)}{\longrightarrow} \mathrm{Col} \underset{(104)}{\longrightarrow} \mathrm{I}$
3c	$\mathrm{Cr} \underset{(74)}{\longrightarrow} \mathrm{Col} \underset{(103)}{\longrightarrow} \mathrm{I}$
3d	$\mathrm{Cr} \underset{(47)}{\longrightarrow} \mathrm{Col} \underset{(101)}{\longrightarrow} \mathrm{I}$
4a	$\mathrm{Cr} \underset{(180)}{\longrightarrow} \mathrm{Col} \underset{(430)}{\longrightarrow} \mathrm{I}$
4b	$\mathrm{Cr} \underset{(150)}{\longrightarrow} \mathrm{Col} \underset{(370)}{\longrightarrow} \mathrm{I}$
4c	$\mathrm{Cr} \underset{(122)}{\longrightarrow} \mathrm{Col} \underset{(322)}{\longrightarrow} \mathrm{I}$
4d	$\mathrm{Cr} \underset{(104)}{\longrightarrow} \mathrm{Col} \underset{(306)}{\longrightarrow} \mathrm{I}$

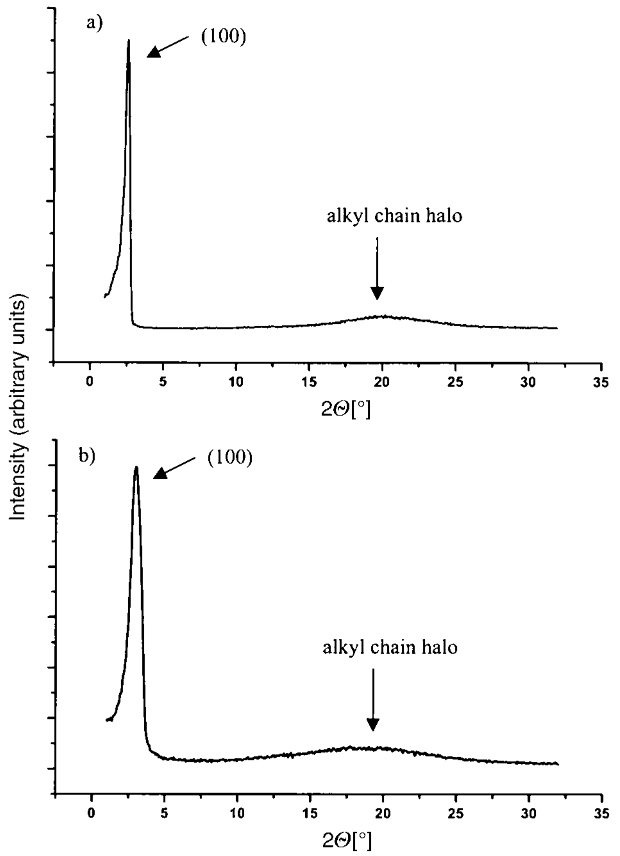


Fig. 2 Typical wide-angle diffraction data taken in the mesophase, a) shows the unclosed triphenylene derivative **3d** at 90 °C, b) shows the final extended triphenylene derivative **4d** at 200 °C. Though it is difficult to assign any mesophase structure based on these data, textures seen in cross-polarized microscopy indicate some kind of columnar mesophase.

the supertriphenylenes possess 14 fused benzene rings, and thus comparable "amounts" of π–π interactions. However, the spatial arrangement of these aromatic π systems is different for each class of molecule. HBC derivatives possess D_{6h} symmetry, while the supertriphenylenes possess only D_{3h} symmetry. Thus, it is likely that the decreased π-interactions due to a columnar packing characterised by a uniaxial rotation, owing to the periodicity of favorable π-overlap of the molecules, can account for the relative disorder of these mesophases.

STM Imaging

STM imaging of **4c** at the interface between an almost saturated solution in 1,2,4-trichlorobenzene and the basal plane of HOPG revealed highly ordered monolayers (Fig. 3). Here the π-conjugated cores of the molecules appear bright due to a high coupling with the conducting electrons of the HOPG substrate, while the darker parts in the image can be ascribed to the aliphatic chains.[48] The molecular arrangement is characterized by an almost hexagonal lattice (unit cell: $a=(3.3\pm0.1)$ nm; $b=(3.1\pm0.1)$ nm; $\alpha=(60.1\pm0.7)°$). The resolution achieved here did not allow us to resolve the structure of the alkyl side chains, probably due to their molecular dynamics. Based on the lattice spacings two different types of molecular packing may be suggested: one with two-fold symmetry, like the one observed in previous studies on alkylated triphenylenes with long alkyl side chains,[17] or alternatively one where the three-fold symmetry of the molecule is reflected also in the monolayer structure. Presently one cannot decide between the two models unambiguously.

Interestingly, similar investigations on the non-planarized analogue **3c** molecule, did not enable us to achieve molecularly resolved images. We attribute this to a weaker interaction of the smaller aromatic core with the substrate induced by the tilt of the lateral benzene rings with respect to the plane of the triphenylene core.

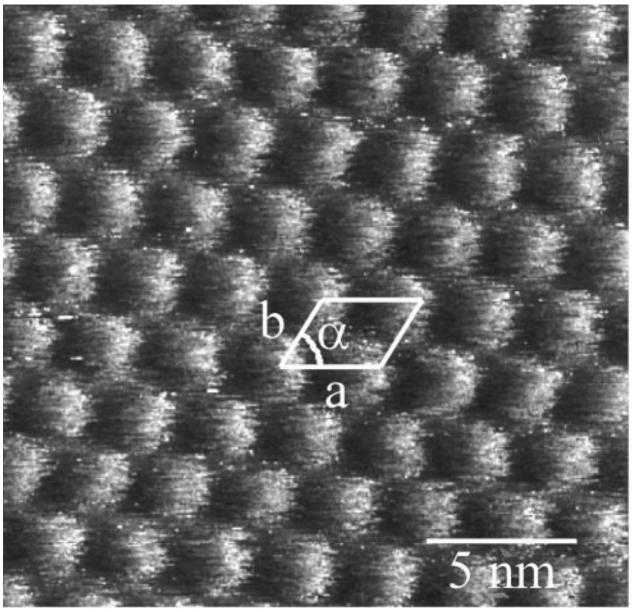


Fig. 3 STM image in constant height mode of **4c** recorded with a tip bias $(U_t)=1.0$ V and an average tunneling current $(I_t)=35$ pA.

Conclusion

Two new classes of molecules, based on a triphenylene core, were synthesized with very high yields using a standard Suzuki cross-coupling reaction between the alkoxy arylboronic acid and hexabromotriphenylene to yield the aryl-substituted triphenylenes **3a–d**, and with subsequent oxidative cyclodehydrogenation to yield the final extended cores **4a–d**. The planarized **4c** molecules self-assembled on graphite were visualized with STM revealing a two-dimensional lattice. On the other hand, both classes of triphenylene-based molecules form columnar thermotropic mesophases, though it was not possible to determine the unit cell for any of the derivatives due to the presence of only one peak in the WAXD. Unfortunately, the increase in order observed in the case of the HBC-PhC$_{12}$ was not observed for the triphenylene analogue possessing phenyl spacers between the aromatic triphenylene core and the side-group alkoxy chains. We believe that more detailed investigations of the dynamics of these molecules, in comparison to HBC-PhC$_{12}$, will shed new light onto the unexpectedly disordered behavior of these discotic mesogens.

Experimental

General

1-Bromo-3,4-dimethoxybenzene, boron tribromide, 1-bromoalkane, *n*-butyllithium, trimethyl borate, triphenylene, bromine, and ferric chloride were used as received.

The chemical structures of intermediates and final products were characterized by ^{1}H and ^{13}C NMR spectra, recorded on a Bruker AX-300 NMR spectrometer. The purity of the compounds was checked by thin-layer chromatography and Field-Desorption (FD) Mass Spectrometry. Phase transition temperatures of the compounds were determined on a Mettler DSC with a heating and cooling rate of 10 K min^{-1}. A Zeiss Axiophot optical microscope equipped with polarizers and a nitrogen-purged hot stage was used for all optical microscopy. WAXD studies were performed by means of a Θ–Θ X-ray diffractometer, equipped with a 1-D Siemens photomultiplier detector and a rotating copper anode source ($K\alpha$: $\lambda = 1.5418$ Å) operating at a bias of 30 KV. UV-VIS measurements were performed on a Perkin-Elmer Lambda 15 spectrometer.

The STM investigation at the solid–liquid interface was employed using a home-made beetle type Scanning Tunneling Microscope.[49] First, the lattice of a freshly cleaved HOPG (001) surface (Advanced Ceramics Corp, grade ZYH) was visualized for at least one hour until a thermal equilibrium (absence of mechanical drift of the system) was reached. A drop of an almost saturated solution in 1,2,4-trichlorobenzene was applied to the basal plane of the substrate. Then the Pt/Ir tip was immersed in the organic solution. By varying the tunneling parameters it was possible to visualise either the first organic layer that was physisorbed on the basal plane of the conductive substrate or the HOPG lattice underneath. This allowed the calibration of the piezo to be accomplished *in situ*. The STM images were recorded in constant height mode under ambient conditions. Unit cells were averaged over several images after their correction for the piezo drift making use of SPIP software (SPIP Scanning Probe Image Processor, Version 1.700, Image Metrology ApS, Lyngby, Denmark).

Synthesis of 2,3,6,7,10,11-Hexakis[3,4-dialkoxyphenyl]-triphenylenes (3a–d)

1-Bromo-3,4-dihydroxybenzene, 1-bromo-3,4-dialkoxybenzenes, and 3,4-dialkoxyphenylboronic acids **1a**–**d** were prepared according to the procedures in refs. 26, 27 and 28. The spectroscopic data of the compounds prepared agreed with those in refs. 27 and 28 and were used without further purification for the next step for the synthesis. 2,3,6,7,10,11-Hexabromotriphenylene (**2**) was prepared according to the procedure in ref. 29 and used without further purification for the next reaction.

1-Bromo-3,4-dihydrobenzene. To a solution of 1-bromo-3,4-dimethoxybenzene (29.3 g, 135 mmol) in dichloromethane (100 mL) at −78 °C was added dropwise a 1.0 M solution of boron tribromide in dichloromethane (300 mL, 300 mmol). The mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature overnight with stirring. Water (200 ml) was added carefully to the mixture. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on silica gel with a 3 : 1 mixture of acetone and petroleum ether (bp 30–40 °C) as eluent to yield 24.9 g (98%) of a brownish solid.

1-Bromo-3,4-bis(hexyloxy)benzene. A mixture of 1-bromohexane (11.9 g, 72.0 mmol), 1-bromo-3,4-dihydroxybenzene (5.68 g, 30.0 mmol), and anhydrous potassium carbonate (22.1 g, 160 mmol) in acetone (100 mL) was heated under reflux at 80 °C for 16 h. The reaction mixture was allowed to cool to room temperature and the inorganic material was filtered off. The filtrate was concentrated under reduced pressure and the crude oil was chromatographed on silica gel using a 1 : 3 mixture of toluene and petroleum ether (bp 30–40 °C) as eluent to yield 9.3 g (87%) of a colorless oil.

1-Bromo-3,4-bis(octyloxy)benzene. Synthesized as described for the preparation of 1-bromo-3,4-bis(hexyloxy)benzene. Quantities: 1-bromooctane (13.9 g, 72.0 mmol), 1-bromo-3,4-dihydroxybenzene (5.68 g, 30.0 mmol), anhydrous potassium carbonate (22.1 g, 160 mmol), acetone (100 mL). Yield: 9.2 g (74%) of a colorless oil.

1-Bromo-3,4-bis(decyloxy)benzene. Synthesized as described for the preparation of 1-bromo-3,4-bis(hexyloxy)benzene. Quantities: 1-bromodecane (15.9 g, 72.0 mmol), 1-bromo-3,4-dihydroxybenzene (5.68 g, 30.0 mmol), anhydrous potassium carbonate (22.1 g, 160 mmol), acetone (100 mL). Yield: 10.7 g (76%) of a white solid.

1-Bromo-3,4-bis(dodecyloxy)benzene. Synthesized as described for the preparation of 1-bromo-3,4-bis(hexyloxy)benzene. Quantities: 1-bromododecane (31.1 g, 125 mmol), 1-bromo-3,4-dihydroxybenzene (10.0 g, 52.9 mmol), anhydrous potassium carbonate (35.9 g, 260 mmol), acetone (200 mL). Yield: 20.6 g (74%) of a white solid.

3,4-Bis(hexyloxy)phenylboronic acid (1a). To a solution of 1-bromo-3,4-bis(hexyloxy)benzene (8.94 g, 25.0 mmol) in tetrahydrofuran (100 mL) at −70 °C was added dropwise a 1.6 M solution of *n*-butyllithium in hexane (23 mL, 37 mmol). The mixture was maintained at this temperature for 1 h before trimethylborate (8.5 mL, 75 mmol) was added slowly to the mixture. The reaction mixture was stirred for 1 h at −60 °C and allowed to warm to room temperature overnight. After addition of aqueous 3 M hydrochloric acid (40 mL) the mixture was stirred for 30 min. The organic layer was concentrated under reduced pressure. The residue was recrystallized from hexane (400 mL) to give 4.22 g (52%) of a white solid.

3,4-Bis(octyloxy)phenylboronic acid (1b). Synthesized as described for the preparation of the arylboronic acid (**1a**). Quantities: 1-bromo-3,4-bis(octyloxy)benzene (8.82 g, 21.4 mmol), tetrahydrofuran (100 mL), *n*-butyllithium (20 mL of a 1.6 M solution in hexane, 32 mmol), trimethylborate (7.3 mL, 64 mmol), aqueous 3 M hydrochloric acid (40 mL). Yield: 3.22 g (40%) of a white solid.

3,4-Bis(decyloxy)phenylboronic acid (1c). Synthesized as described for the preparation of the arylboronic acid (**1a**). Quantities: 1-bromo-3,4-bis(decyloxy)benzene (10.4 g, 22.2 mmol), tetrahydrofuran (150 mL), *n*-butyllithium (21 mL of a 1.6 M solution in hexane, 34 mmol), aqueous 3 M hydrochloric acid (40 mL). Yield: 3.34 g (35%) of a pale pink solid.

3,4-Bis(dodecyloxy)phenylboronic acid (1d). To a solution of 1-bromo-3,4-bis(dodecyloxy)benzene (9.52 g, 18.1 mmol) in tetrahydrofuran (150 mL) at −20 °C was added slowly a 1.6 M solution of *n*-butyllithium in hexane (17 mL, 27 mmol). The mixture was allowed to cool to −35 °C and stirred for 30 min. Trimethylborate (6.2 mL, 55 mmol) was added slowly to the mixture. The reaction mixture was stirred for 30 min at −30 °C and allowed to warm to room temperature overnight. Aqueous 3 M hydrochloric acid (40 mL) was added slowly and the mixture was stirred for 30 min at room temperature. The organic layer was concentrated under reduced pressure and hexane (300 mL) was added to the residue. The insoluble solid in hot hexane was removed by filtration. The hot filtrate was concentrated to one-half of its original volume, cooled to room temperature, and allowed to stand overnight. The precipitate was filtered and washed with hexane to yield 3.04 g (34%) of a pale pink solid.

2,3,6,7,10,11-Hexabromotriphenylene (2). To a solution of triphenylene (2.26 g, 9.91 mmol) in nitrobenzene (80 mL) with iron powder (0.18 g, 3.6 mmol) was added bromine (4.4 mL, 85 mmol) dropwise over 5 min. The solution was allowed to stand for 16 h and heated under reflux at 205 °C for 2 h. The mixture was cooled to room temperature, mixed with diethyl ether (300 mL), and filtered. The crude solid was recrystallized from 1,2-dichlorobenzene to yield 6.41 g (92%) of white needles.

2,3,6,7,10,11-Hexakis[3,4-bis(hexyloxy)phenyl]triphenylene (3a). To a mixture of 2,3,6,7,10,11-hexabromotriphenylene (**2**) (0.704 g, 1.00 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.501 g, 0.433 mmol) in toluene (50 mL) was added a suspension of 3,4-dihexyloxyphenylboronic acid (**1a**) (2.92 g, 9.07 mmol) in ethanol (14 mL) and an aqueous solution of potassium carbonate (1.68 g, 12.2 mmol, 7 mL of water). The mixture was heated under reflux at 120 °C for 16 h. The reaction mixture was cooled to room temperature and poured into toluene (100 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Petroleum ether (bp 30–40 °C, 200 mL) was added to the residue. The resultant precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel with toluene to give the crude yellow solid. Chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1 : 2–2 : 3–1 : 1–3 : 2) to yield 1.80 g (96%) of 2,3,6,7,10,11-hexakis[3,4-bis(hexyloxy)phenyl]triphenylene (**3a**) as a white solid.

Compound **3a**: ^{1}H NMR (CDCl$_3$) δ 8.67 (s, 6 H), 6.93 (d, J=8 Hz, 6 H), 6.83 (d, J=8 Hz, 6 H), 6.73 (s, 6 H), 3.97 (t, J=7 Hz, 12 H), 3.69 (t, J=7 Hz, 12 H), 1.92–1.71 (m, 12 H), 1.71–1.54 (m, 12 H), 1.54–1.16 (m, 72 H), 0.97–0.76 (m, 36 H); ^{13}C NMR (CDCl$_3$) δ 14.67, 23.52, 26.59, 26.64, 30.10, 32.45, 32.54, 53.54, 53.90, 54.12, 54.27, 54.62, 54.98, 70.19, 114.43, 117.41, 123.15, 125.99, 129.52, 135.34, 140.80, 149.28, 149.50; UV-VIS (CHCl$_3$) λ_{max} (ε): 263 (4780), 313 (12 200); *m*/*z* (FD): 1887.4 (calc. 1886.8); mp 126 °C.

2,3,6,7,10,11-Hexakis[3,4-bis(octyloxy)phenyl]triphenylene (3b). Synthesized as described for the preparation of the triphenylene **3a**. Quantities: 2,3,6,7,10,11-hexabromotriphenylene (**2**) (0.632 g, 0.900 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.501 g, 0.433 mmol), toluene (45 mL), 3,4-bis(octyloxy)phenylboronic acid (**1b**) (3.08 g, 8.15 mmol), ethanol (13 mL), anhydrous potassium carbonate (1.50 g, 10.9 mmol), and water (7 mL). Yield: 1.80 g (90%) of 2,3,6,7,10,11-hexakis[3,4-bis(octyloxy)phenyl]triphenylene (**3b**) as a white solid.

Compound **3b**: ^{1}H NMR (CDCl$_3$) δ 8.67 (s, 6 H), 6.95 (d, J=8 Hz, 6 H), 6.84 (d, J=8 Hz, 6 H), 6.71 (s, 6 H), 3.96 (t, J=7 Hz, 12 H), 3.68 (t, J=7 Hz, 12 H), 1.88–1.71 (m, 12 H), 1.71–1.54 (m, 12 H), 1.54–1.12 (m, 120 H), 0.94–0.74 (m, 36 H); ^{13}C NMR (CDCl$_3$) δ 14.61, 23.45, 26.83, 26.87, 30.03, 30.07, 30.12, 30.16, 30.22, 32.63, 53.42, 53.78, 54.13, 54.35, 54.50, 54.86, 70.09, 114.32, 117.33, 123.03, 125.86, 129.40, 135.22, 140.67, 149.17, 149.36; UV-VIS (CHCl$_3$) λ_{max} (ε): 264 (6390), 313 (16 900); *m*/*z* (FD): 2223.5 (calc. 2223.5); mp 104 °C.

2,3,6,7,10,11-Hexakis[3,4-bis(decyloxy)phenyl]triphenylene (3c). Synthesized as described for the preparation of the triphenylene **3a**. Quantities: 2,3,6,7,10,11-hexabromotriphenylene (**2**) (0.562 g, 0.800 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.501 g, 0.433 mmol), toluene (40 mL), 3,4-bis(decyloxy)phenylboronic acid (**1c**) (3.13 g, 7.21 mmol), ethanol (12 mL), anhydrous potassium carbonate (1.33 g, 9.64 mmol), and water (6 mL). Yield: 1.88 g (92%) of 2,3,6,7,10,11-hexakis[3,4-bis(decyloxy)phenyl]triphenylene (**3c**) as a white solid.

Compound **3c**: ^{1}H NMR (CDCl$_3$) δ 8.67 (s, 6 H), 6.95 (d, J=8 Hz, 6 H), 6.84 (d, J=8 Hz, 6 H), 6.71 (s, 6 H), 3.98 (t, J=7 Hz, 12 H), 3.70 (t, J=7 Hz, 12 H), 1.89–1.73 (m, 12 H), 1.73–1.56 (m, 12 H), 1.56–1.11 (m, 168 H), 0.95–0.76 (m, 36 H); ^{13}C NMR (CDCl$_3$) δ 14.62, 23.46, 26.85, 26.89, 30.03, 30.14, 30.18, 30.23, 30.28, 30.39, 30.41, 30.44, 30.50, 32.71, 53.42, 53.77, 53.97, 54.13, 54.34, 54.50, 54.69, 54.85, 70.10, 114.34, 117.36, 123.03, 125.86, 129.41, 135.22, 140.66, 149.17, 149.36; UV-VIS (CHCl$_3$) λ_{max} (ε): 263 (8290), 313 (21 900); *m*/*z* (FD): 2560.0 (calc. 2560.1); mp 103 °C.

2,3,6,7,10,11-Hexakis[3,4-bis(dodecyloxy)phenyl]triphenylene (3d). Synthesized as described for the preparation of the triphenylene **3a**. Quantities: 2,3,6,7,10,11-hexabromotriphenylene (**2**) (0.478 g, 0.681 mmol), tetrakis(triphenylphosphine)-palladium(0) (0.393 g, 0.340 mmol), toluene (35 mL), 3,4-bis(hexyloxy)phenylboronic acid (**1d**) (3.03 g, 6.18 mmol), ethanol (10 mL), anhydrous potassium carbonate (1.13 g, 8.19 mmol), and water (5 mL). Yield: 1.84 g (93%) of 2,3,6,7,10,11-hexakis[3,4-bis(dodecyloxy)phenyl]triphenylene (**3d**) as a white solid.

3d: ^{1}H NMR (CDCl$_3$) δ 8.65 (s, 6 H), 6.95 (d, J=8 Hz, 6 H), 6.83 (d, J=8 Hz, 6 H), 6.70 (s, 6 H), 3.97 (t, J=7 Hz, 12 H), 3.67 (t, J=7 Hz, 12 H), 1.85–1.71 (m, 12 H), 1.71–1.53 (m, 12 H), 1.49–1.11 (m, 216 H), 0.90–0.76 (m, 36 H); ^{13}C NMR (CDCl$_3$) δ 14.62, 23.45, 26.85, 26.89, 30.03, 30.14, 30.24, 30.29, 30.45, 30.47, 30.54, 32.71, 53.42, 53.77, 54.13, 54.50, 54.70, 54.85, 70.09, 114.34, 117.36, 123.02, 125.85, 129.41, 135.22, 140.66, 129.17, 149.35; UV-VIS (CHCl$_3$) λ_{max} (ε): 263 (5910), 313 (15 600); *m*/*z* (FD): 2897.4 (calc. 2896.8); mp 101 °C.

Synthesis of 2,3,6,7,12,13,16,17,22,23,26,27-dodecaalkoxyhexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylenes (4a–d)

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(hexyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (4a). To a solution of 2,3,6,7,10,11-hexakis[3,4-bis(hexyloxy)phenyl]triphenylene (**3a**) (1.50 g, 0.796 mmol) in dichloromethane (80 mL) was added a suspension of ferric chloride (1.17 g, 7.22 mmol) in dichloromethane (80 ml). The mixture was vigorously stirred for 1 h at room temperature. Methanol (400 mL) was added to the reaction mixture. The resultant precipitate was filtered and washed with a 4 : 1 mixture of methanol and dichloromethane. The precipitate was chromatographed on silica gel using a 3 : 1 mixture of dichloromethane and petroleum ether (bp 3040 °C) to yield the crude solid. Recrystallization from toluene gave 1.19 g (80%) of a pale yellow solid. Recrystallization from toluene gave 1.19 g (80%) of 2,3,6,7,12,13,16,17,22,23,26,27-dodecakis(hexyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (**4a**) as a pale yellow solid.

4a: ^{1}H NMR (CS$_2$/CDCl$_3$) δ 9.45 (s, 6 H), 8.25 (s, 6 H), 7.75 (s, 6 H), 4.38 (t, J=7 Hz, 12 H), 4.24 (t, J=7 Hz, 12 H), 2.15–1.88 (m, 24 H), 1.83–1.61 (m, 24 H), 1.61–1.35 (m, 48 H), 1.15–0.90 (m, 36 H); ^{13}C NMR (CS$_2$–CDCl$_3$) δ 14.56, 14.58, 23.45, 26.66, 26.83, 30.28, 30.53, 32.47, 32.59, 53.08, 53.44, 53.80, 54.16, 54.52, 69.68, 70.02, 107.34, 108.49, 117.32, 124.04, 125.13, 128.47, 128.53, 149.50, 150.54; UV-VIS (CHCl$_3$) λ_{max} (ε): 265 (7070), 289 (7350), 312 (9580), 325 (11 000), 356 (12 900), 377 (8900); *m*/*z* (FD): 1881.1 (calc. 1880.8).

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(octyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (4b). Synthesized as described for the preparation of the compound **4a**. Quantities: 2,3,6,7,10,11-hexakis[3,4-bis(octyloxy)phenyl]triphenylene (**3b**) (1.48 g, 0.667 mmol), dichloromethane (75 mL), ferric chloride (1.01 g, 6.23 mmol), and dichloromethane (75 mL). Chromatography: dichloromethane and subsequent hot toluene. Yield: 1.04 g (70%) of 2,3,6,7,12,13,16,17,22,23,26,-27-dodecakis(octyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (**4b**) as a pale yellow solid.

4b: ^{1}H NMR (CS$_2$–CDCl$_3$) δ 9.53 (s, 6 H), 8.18 (s, 6 H), 7.71 (s, 6 H), 4.31 (t, J=7 Hz, 12 H), 4.18 (t, J=7 Hz, 12 H), 2.10–1.82 (m, 24 H), 1.76–1.53 (m, 24 H), 1.53–1.16 (m, 96 H), 1.01–0.76 (m, 36 H); ^{13}C NMR (CS$_2$–CDCl$_3$) δ 14.74, 14.80, 23.56, 23.61, 27.11, 27.27, 30.24, 30.26, 30.41, 30.45, 30.52, 30.65, 32.72, 53.08, 53.45, 53.80, 54.16, 54.52, 69.68, 69.99, 107.42, 108.54, 117.42, 124.12, 125.17, 128.53, 128.60, 149.52, 150.53; UV-VIS (CHCl$_3$) λ_{max} (ε): 265 (10 700), 289 (11 000), 313 (14 300), 325 (16 300), 356 (19 500), 377 (13 500); *m*/*z* (FD): 2217.6 (calc. 2217.4).

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(decyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (4c). Synthesized as described for the preparation of the compound **4b**. Quantities: 2,3,6,7,10,11-hexakis[3,4-bis(decyloxy)phenyl]triphenylene (**3c**) (1.63 g, 0.638 mmol), dichloromethane (60 mL), ferric chloride (0.95 g, 5.86 mmol), and dichloromethane (60 mL). Yield 1.15 g (71%) of 2,3,6,7,12,13,16,17,22,23,26,27-dodecakis(decyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (**4c**) as a pale yellow solid.

Compound **4c**: ^{1}H NMR (CS_2–$CDCl_3$) δ 9.64 (s, 6 H), 8.28 (s, 6 H), 7.79 (s, 6 H), 4.40 (t, $J = 7$ Hz, 12 H), 4.27 (t, $J = 7$ Hz, 12 H), 2.12–1.82 (m, 24 H), 1.76–1.55 (m, 24 H), 1.55–1.10 (m, 144 H), 1.01–0.76 (m, 36 H); ^{13}C NMR (CS_2–$CDCl_3$) δ 14.65, 14.68, 23.47, 23.51, 27.06, 27.23, 30.16, 30.40, 30.47, 30.53, 30.58, 32.66, 32.68, 53.08, 53.44, 53.80, 54.16, 54.52, 69.74, 70.04, 107.48, 108.55, 117.50, 124.10, 125.20, 128.60, 128.66, 149.57, 150.59; UV-VIS ($CHCl_3$) λ_{max} (ε): 265 (9130), 289 (9390), 313 (12 200), 325 (13 900), 356 (16 600), 377 (11 600); *m*/*z* (FD): 2554.6 (calc. 2554.1).

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(dodecyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (4d). Synthesized as described for the preparation of the compound **4b**. Quantities: 2,3,6,7,10,11-hexakis[3,4-bis(dodecyloxy)phenyl]triphenylene (**3d**) (1.76 g, 0.608 mmol), dichloromethane (50 mL), ferric chloride (0.98 g, 6.05 mmol), and dichloromethane (50 mL). Yield 1.36 g (78%) of 2,3,6,7,12,13,16,17,22,23,26,27-dodecakis(dodecyloxy)hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (**4d**) as a pale yellow solid.

Compound **4d**: ^{1}H NMR (CS_2–$CDCl_3$) δ 9.64 (s, 6 H), 8.24 (s, 6 H), 7.76 (s, 6 H), 4.35 (t, $J = 7$ Hz, 12 H), 4.22 (t, $J = 7$ Hz, 12 H), 2.07–1.86 (m, 24 H), 1.76–1.53 (m, 24 H), 1.53–1.09 (m, 192 H), 0.98–0.76 (m, 36 H); ^{13}C NMR (CS_2–$CDCl_3$) δ 14.69, 14.71, 23.50, 23.53, 27.09, 27.25, 30.17, 30.45, 30.49, 30.56, 30.62, 32.70, 53.08, 53.45, 53.80, 54.16, 54.52, 69.74, 70.04, 107.50, 108.58, 117.49, 124.12, 125.21, 128.59, 128.66, 149.57, 150.59; UV-VIS ($CHCl_3$) λ_{max} (ε): 265 (13 800), 289 (14 200), 313 (18 500), 325 (21 100), 356 (25 200), 377 (17 500); *m*/*z* (FD): 2890.9 (calc. 2890.7).

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References

1 C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthete and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 1981, **71**, 111.

2 C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.

3 S. Chandrasekar, *Liq. Cryst.*, 1993, **14**, 3.

4 A. J. Leadbetter, in *Thermotropic Liquid Crystals (Critical reports on applied chemistry; v. 22); Structural classification of liquid crystals*, ed. G. W. Grey, John Wiley & Sons, Chichester, 1987, pp. 23–25.

5 S. Takenaka, *Chemistry of Liquid Crystals (Kikan Kagaku Sosetsu, No 22); Design and synthesis of discotic molecules*, The Chemical Society of Japan, Gakkai-Shuppan, Tokyo, 1994, pp. 60–72.

6 A. N. Cammidge, R. J. Bushby, S. Chandrasekar, N. Boden and B. Movaghar, in *Handbook of Liquid Crystals, Vol. 2 B: Low Molecular Weight Liquid Crystals II; Discotic Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Grey, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, pp. 693–798.

7 F. Closs, K. Siemensmeyer, T. Frey and D. Funhoff, *Liq. Cryst.*, 1993, **14**, 629.

8 H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf and K. Siemensmeyer, *Liq. Cryst.*, 1993, **15**, 565.

9 D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher and K. Siemensmeyer, *Phys. Rev. Lett.*, 1993, **70**, 457.

10 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, *Nature (London)*, 1994, **371**, 141.

11 J. Simmerer, B. Glüsen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K.-H. Etzbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf and D. Haarer, *Adv. Mater.*, 1996, **8**, 815.

12 A. M. van de Craats, J. M. Warman, M. P. de Haas, D. Adam, J. Simmerer, D. Haarer and P. Schuhmacher, *Adv. Mater.*, 1996, **8**, 823.

13 E. O. Arikainen, N. Borden, R. J. Bushby, J. Clements, B. Movaghar and A. Wood, *J. Mater. Chem.*, 1995, **5**, 2161.

14 N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan and T. Kreouzis, *Phys. Rev. B*, 1995, **52**, 13274.

15 E. O. Arikainen, N. Borden, R. J. Bushby, J. Clements, B. Movaghar and A. Wood, *J. Mater. Chem.*, 1995, **5**, 2161.

16 S. Tanaka, C. Adachi, T. Koyama and Y. Taniguchi, *Chem. Lett.*, 1998, 975.

17 L. Askadskaya, C. Boeffel and J. P. Rabe, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, **97**, 517.

18 J.-C. Gabriel, N. B. Larsen, M. Larsen, N. Harrit, J. S. Pedersen, K. Schaumburg and K. Bechgaard, *Langmuir*, 1996, **12**, 1690.

19 F. Charra and J. Cousty, *Phys. Rev. Lett.*, 1998, **80**, 1682.

20 H. Schönherr, F. J. B. Kremer, S. Kumar, J. A. Rego, H. Wolf, H. Ringsdorf, M. Jaschke, H.-J. Butt and E. Bamberg, *J. Am. Chem. Soc.*, 1996, **118**, 13051.

21 N. Boden, R. J. Bushby, P. S. Martin, S. D. Evans, R. W. Owens and D. A. Smith, *Langmuir*, 1999, **15**, 3790.

22 A. Stabel, P. Herwig, K. Müllen and J. P. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1609.

23 P. Herwig, C. W. Kayser, K. Müllen and H.-W. Spiess, *Adv. Mater.*, 1996, **8**, 510.

24 A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts and J. D. Brand, *Adv. Mater.*, 1998, **10**, 36.

25 A. Fechtenkötter, K. Saalwächter, M. A. Harbison, K. Müllen and H.-W. Spiess, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 3039.

26 A. M. van de Craats, J. M. Warman, A. Fechtenkötter, J. D. Brand, M. A. Harbison and K. Müllen, *Adv. Mater.*, 1999, **11**, 1469.

27 F. Morgenroth, E. Reuther and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 631.

28 V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1604.

29 M. Müller, V. S. Iyer, C. Kübel, V. Enkelmann and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1607.

30 V. S. Iyer, K. Yoshimura, V. Enkelmann, R. Epsch, J. P. Rabe and K. Müllen, *Angew. Chem., Int. Ed.*, 1998, **37**, 2696.

31 M. Müller, C. Kübel and K. Müllen, *Chem. Eur. J.*, 1998, **4**, 2099.

32 N. Boden, R. J. Bushby, G. Headdock, O. R. Lozman and A. Wood, unpublished work.

33 J. W. Goodby, M. Hird, K. J. Toyne and T. Watson, *J. Chem. Soc., Chem. Commun.*, 1994, 1701.

34 S. J. Cross, J. W. Goodby, A. W. Hall, M. Hird, S. M. Kelly, K. J. Toyne and C. Wu, *Liq. Cryst.*, 1998, **25**, 1.

35 C. Sauer, S. Diele, N. Lindner and C. Tschierske, *Liq. Cryst.*, 1998, **25**, 109.

36 R. Breslow, B. Jaus, R. Q. Kluttz and C.-Z. Xia, *Tetrahedron*, 1982, **38**, 863.

37 N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513.

38 R. B. Miller and S. Dugar, *Organometallics*, 1984, **3**, 1261.

39 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

40 K. Kishikawa, M. C. Harris and T. M. Swager, *Chem. Mater.*, 1999, **11**, 861.

41 J. Tellenböker and D. Kuck, *Angew. Chem., Int. Ed.*, 1999, **38**, 919.

42 N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge and M. V. Jesudason, *Liq. Cryst.*, 1993, **15**, 851.

43 N. Boden, R. J. Bushby and A. N. Cammidge, *J. Chem. Soc., Chem. Commun.*, 1994, 465.

44 R. C. Borner and R. F. W. Jackson, *J. Chem. Soc., Chem. Commun.*, 1994, 845.

45 N. Boden, R. J. Bushby and A. N. Cammidge, *Synthesis*, 1995, 31.

46 E. Brenna, C. Fuganti and S. Serra, *J. Chem. Soc., Perkin Trans. 1*, 1998, 901.

47 N. Boden, R. J. Bushby and Z. B. Lu, *Liq. Cryst.*, 1998, **25**, 47.

48 R. Lazzaroni, A. Calderone, J. L. Brèdas and J. P. Rabe, *J. Chem. Phys.*, 1997, **107**, 99.

49 P. Samorí, V. Francke, K. Müllen and J. P. Rabe, *Chem. Eur. J.*, 1999, **5**, 2312.