Columnar mesophase from a new hybrid siloxane-triphenylene

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The design, the synthesis and the mesomorphic properties of a new disc-like mesogen based on a hexasubstituted triphenylene core terminated with pentamethyldisiloxane pendant groups are reported. The siloxane fragments were grafted to the six terminal olefinic branches of a triphenylene precursor by a Pt-catalysed hydrosilylation reaction. Both the hexaolefinic and the hexasiloxane derivatives are mesomorphic, showing a rectangular columnar (Col$_R$—p2gg) mesophase between 55 and 88 °C for the former, and a broad hexagonal (Col$_H$—p6mm) mesophase between ambient temperature and 125 °C for the latter. The liquid crystalline behaviour was investigated by means of differential scanning calorimetry, polarised-light optical microscopy, and X-ray diffractometry. The mesophase temperature range and stability were considerably extended for the hybrid compound with respect to the siloxane-free compound. This behaviour is explained on the basis of enhanced microsegregation between the chemically distinct constituent components of the molecule.

Introduction

Discotic molecules, already used in phase compensation films, also offer a unique possibility as potential one-dimensional charge carrier systems[1] when self assembled in hexagonal columnar mesophases (Col$_H$). Indeed, electronic interactions as well as electron and exciton migrations are strongly favoured within the columns since the stacking periodicity along the column is short compared to the intercolumnar distance. As such, discotic liquid crystals are seen as promising organic semiconductors for applications in the domain of molecular electronics, optoelectronics, photoconductivity, photovoltaic, and electro-luminescent devices.[2] However, the limited efficiency of the charge-carrier mobility (10^{-3}–0.5 cm^2 V^{-1} s^{-1} compared to that found in graphite of 3 cm^2 V^{-1} s^{-1}), a parameter which is essential to estimate for an optimal design, is in part due to the lack of short-range order of the intra-columnar stacking in the liquid-crystalline mesophase. The improvement of these properties requires perfectly stable monodomains of the materials and, ideally, it would also be more favourable if they could operate at ambient temperature. Liquid crystals offer many alternative advantages to organic monocrystals in that they can be easily macroscopically aligned (monodomains) and processed; moreover, structural defects can be self-healed because of the molecular fluctuations. Various methods for increasing the extent of ordering, facilitating the processing and improving the performances of the charge mobility have been employed. Among these, the freezing-in of the columnar order into stable, room temperature glasses appears to be an attractive strategy since the anisotropic properties and macroscopically aligned monodomains can be easily vitrified into various shapes. Triphenylene-containing liquid crystals have been the most studied for such prospects, and examples of triphenylene-containing liquid crystalline polymers,[3] elastomers,[4] networks,[5] oligomers,[6] as well

as a wide range of symmetrically and non-symmetrically monomeric systems[7] have been reported to address these points.

However, hybrid molecular systems that combine a siloxane part with an organic disc-like group have been scarcely considered. Only one hybrid siloxane–triphenylene (Fig. 1) has been reported, showing a stable Col$_H$ mesophase from room temperature up to 141 °C.[8] In general, the attachment of a flexible siloxane part to a calamitic mesogenic structure, *via* an alkyl spacer, maintains the liquid crystalline properties but considerably reduces the transition temperatures with respect to the aliphatic analogues. Moreover, the bulkiness of these groups disfavours crystallisation, and these hybrids show a strong tendency to freeze-in the mesophase on cooling due to a strong supercooling effect. Consequently, the mesophase temperature range becomes more accessible than their free-siloxane analogues. The tri-block molecular architecture of such low-molar mass hybrids consists of three chemically incompatible molecular species covalently linked together, namely a polarisable rod-like mesogenic core, an aliphatic part and the siloxane moieties. The most studied structure consists of a calamitic mesogenic moiety with a chain (or a polar group) at one end, and a linear siloxane group at the other extremity connected *via* an aliphatic spacer.[9] The way the siloxane groups are combined with the mesogenic units has also been analysed. Such groups can be attached laterally to a mesogenic unit,[10,15g] fixed at both extremities of a calamitic unit (this topology was found to lower the mesophase stability),[11] or used as bridges between two mesogenic groups.[12] Liquid crystalline systems were also obtained with more complex molecular topologies by attaching mesogenic side groups to cyclic[13] and tetrahedral siloxanes,[14] polyhedral silsesquioxanes[15] and end-functionalised polycarbosilane dendrimers.[16] Recently, reticulation of alternate co-oligomers of disiloxane calamitic mesogen with cyclosiloxane yielded new liquid crystalline elastomers.[17] In all cases, the mesomorphism results, on the one hand, from a conflict between the preferential anisotropic order of the mesogenic units and the flexibility and bulkiness of the siloxane moieties (by reducing the packing efficiency of the molecules within the
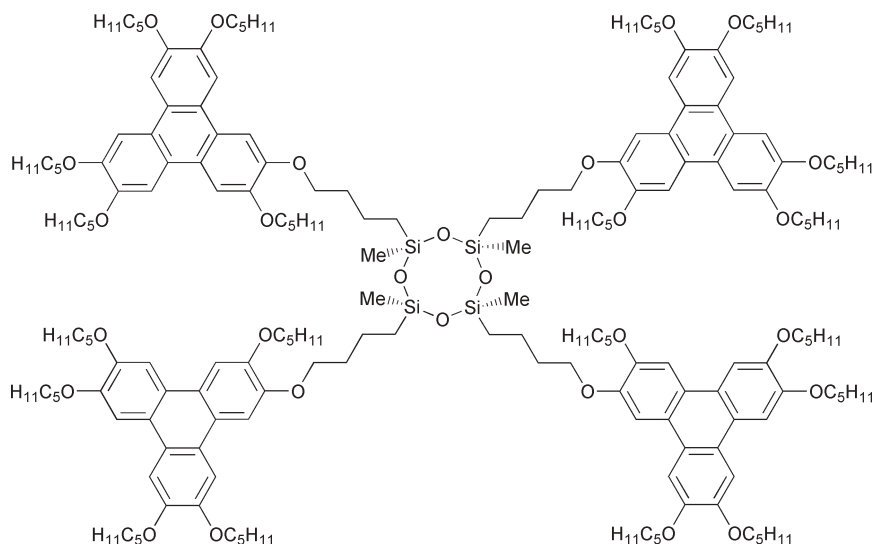
Fig. 1 Chemical structure of the hybrid triphenylene siloxane tetramer.

mesophases) and, on the other hand, from the chemical incompatibility between the siloxane tails and the hydrocarbon mesogenic cores which will show a propensity to microsegregate in space, and thus stabilise the mesophases.

Low molar mass hybrid-containing liquid crystals thus form an interesting class of mesogenic materials since they combine the properties of mesomorphic materials with those of their poly(dimethyl)siloxane polymer analogues,[18] namely the low melt viscosity of the former with the glass-forming tendency and the mechanical stability of the latter. In this context we were interested in designing and synthesising a new hybrid discotic material, and in investigating its thermal behaviour.

Indeed, these materials offer a better possibility of supramolecular ordering with a good segregation between molecular moieties of different natures, and moreover the ordering is not constrained by the presence of a long polymeric backbone.

Results

Materials

The outline of the synthetic route of the hexasubstituted triphenylenes is indicated in the reaction scheme (Scheme 1). The triphenylene central core was synthesised according to
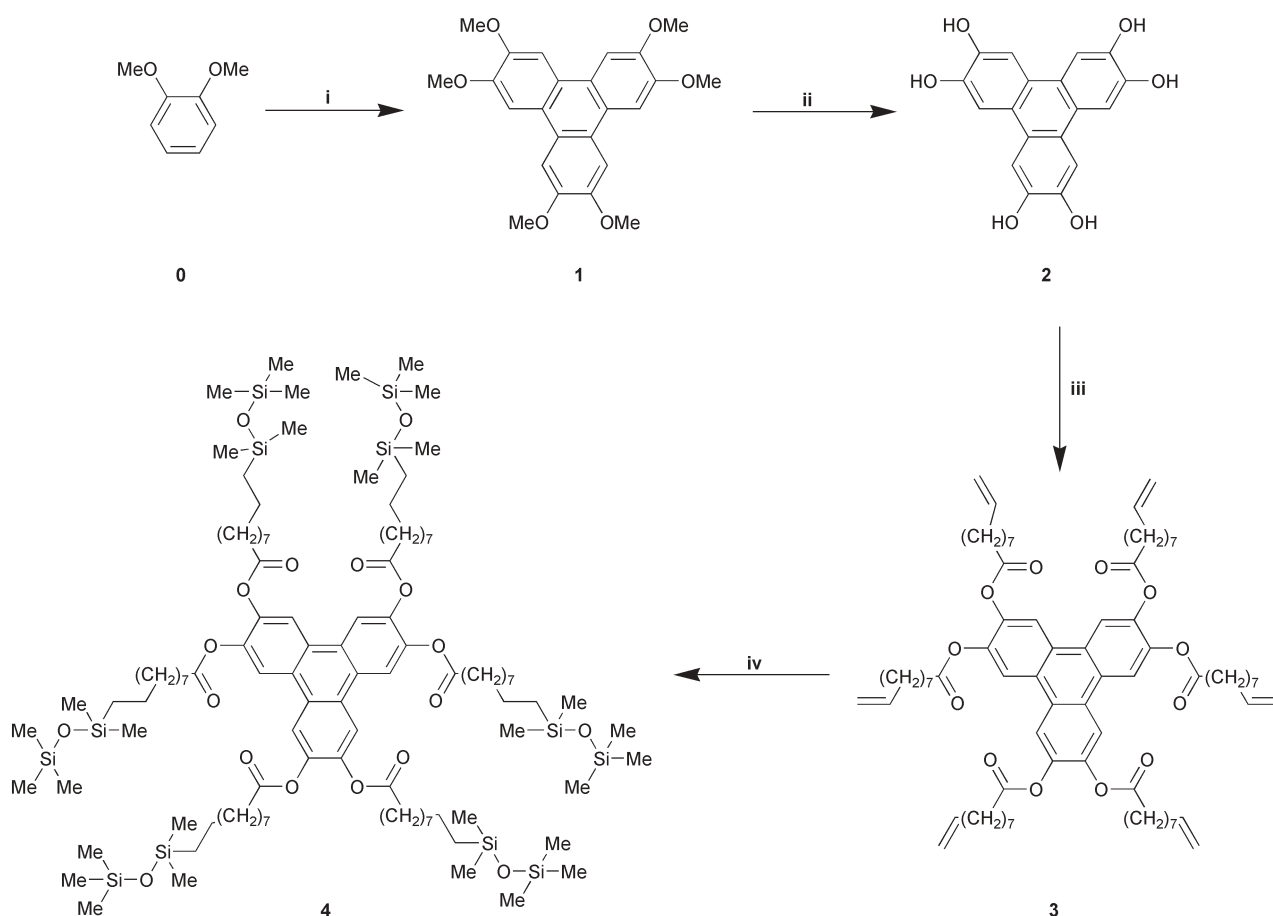
Scheme 1

Table 1 Transition temperatures and corresponding enthalpies of compounds **3** and **4**

Compound	DSC Cycle[a]	Transition	Temperature/°C T_{POM}	Temperature/°C T_{ONSET} (T_{Peak})	Enthalpy ΔH/kJ mol^{-1}
3	h1	Crys–Col$_R$	55	53 (56)	50.1
		Col$_R$–IL	88	82 (87)	1.8
	c1	IL–Col$_R$	82	81 (80)	−1.8
	h2	Crys′–Crys		47 (51)	34.5
		Crys–Col$_R$		53 (58)	6.7
		Col$_R$–IL		85 (89)	1.7
	c2	IL–Col$_R$		84 (83)	−1.65
4	h1	Col$_H$–IL	125	118 (121)	5.1
	c1	IL–Col$_H$	118	116 (113)	−2.45
	h2	Col$_H$–IL		115 (122)	3.0
	c2	IL–Col$_H$		115 (112)	−2.45

[a]h1: first heating, c1: first cooling, h2: second heating, c2: second cooling.

the literature, using the trimerisation[19] reaction of veratrol (**0**) in the presence of iron(III) chloride to give 2,3,6,7,10,11-hexamethoxytriphenylene (**1**) in 83% yield. The latter was then subjected to a complete demethylation reaction using boron tribromide followed by the esterification of the resulting crude 2,3,6,7,10,11-hexahydroxytriphenylene (**2**) with dec-9-enoic acid to give 2,3,6,7,10,11-hexakis(non-8-enylcarbonyl-oxy)triphenylene (**3**). The targeted compound was obtained by hexa-hydrosilylation reaction of the hexaester (**4**) with penta-methyldisiloxane in the presence of a platinum catalyst.

Liquid crystalline properties

The mesomorphic behaviour of the two discotic materials **3** and **4** was examined by DSC and phase assignments were based on the combination of powder X-ray diffraction (XRD) and polarised optical microscopy (POM). The transition temperatures, phase sequence and some thermodynamic data are listed in Table 1.

Optical microscopy. Compound **3** was found to be mesomorphic from 55 °C up to 88 °C. On slow cooling from the isotropic liquid, the microscopic preparation revealed a texture which is typical of that of a columnar mesophase with large dendritic monodomains (Fig. 2). On cooling, the crystallisation was confirmed by the rapid change of the LC texture into very narrow domains with sharp boundaries; note that this transformation occurred at a much lower temperature than the crystal-to-mesophase transformation determined on heating. Compound **4** was found to be mesomorphic at ambient temperature, and its optical texture revealed characteristic features shown by columnar mesophases including cylindrical and developable domains, with large homeotropic areas (Fig. 3). It cleared at 125 °C. No sign of crystallisation of the sample could be detected on cooling, and the texture remained unchanged, the mesophase appearing less fluid. It is interesting to note
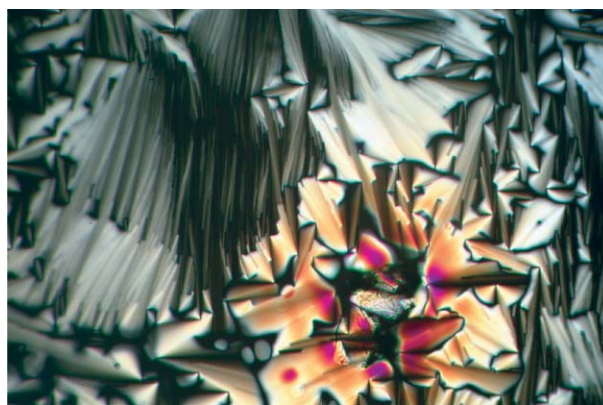

Fig. 3 Optical texture of **4** in the hexagonal mesophase.

that the clearing temperature is much higher in the siloxane derivative **4** (125 °C compared to 88 °C for the derivative deprived of a siloxane part (**3**)), and that the temperature range of the columnar mesophase is also much larger, despite the fact that the presence of bulky siloxane groups may be thought to prevent good stacking of the triphenylene cores.

DSC. Two endothermic peaks were observed for compound **3** during the first heating (h1) from room temperature up to 100 °C (Fig. 4). The broad peak at 53 °C corresponds to the melting of the crystalline phase into the mesophase, followed by a small one at 82 °C, associated to the clearing temperature. However, during the second heating (h2), a crystal-to-crystal phase transformation took place, which was hardly visible in
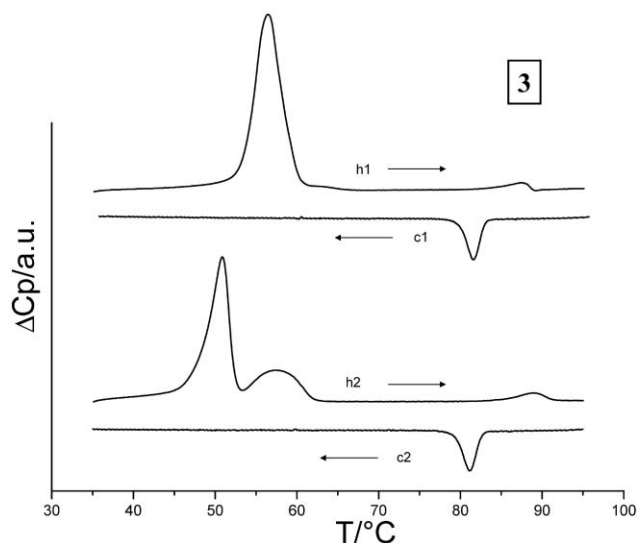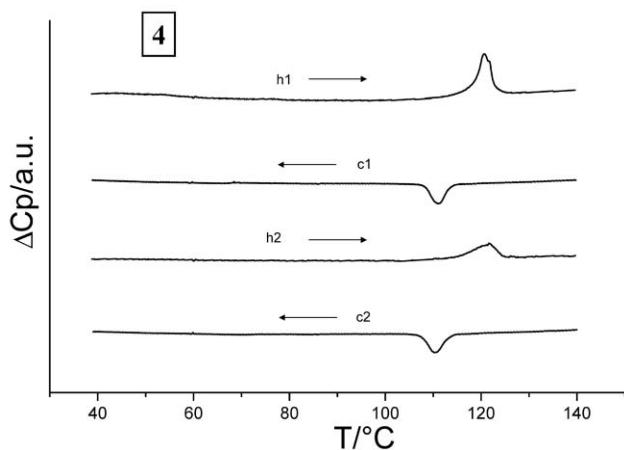

Fig. 2 Optical texture of **3** in the rectangular mesophase.

Fig. 4 DSC traces of **3**.

Fig. 5 DSC traces of **4**.

Fig. 7 X-Ray diffraction pattern of **4** recorded at 60 °C in the hexagonal mesophase.

h1. This indicates that the compound has crystallised (or partially crystallised) in a different crystalline form from the melt. Nevertheless a very good reproducibility of the cooling cycles was observed (c1 and c2), and no sign of crystallisation was detected in neither of them. The DSC traces of **4** (Fig. 5) were much simpler. They consist of a single endothermic peak at *ca.* 111–120 °C, corresponding to the mesophase-to-isotropic liquid transformation. This behaviour was perfectly reproduced during the following heating and cooling cycles. As deduced from POM, no other transition (such as crystallisation or glass transition) were seen down to room temperature.

X-Ray characterisation. The mesomorphism of the two triphenylene derivatives **3** and **4** was confirmed and the nature of the mesophase determined by means of small-angle X-ray diffraction (XRD). The temperature–XRD measurements were carried out over the whole mesomorphic temperature range (starting from room temperature up to the isotropic liquid). A good agreement was found between the transition temperatures determined by both POM and DSC techniques with those determined by XRD.

The X-ray patterns obtained for the olefinic compound **3** (Fig. 6) consisted of three sharp small-angle reflections (20.45, 15.4 and 11.8 Å), with decreasing intensity, and of a diffuse halo in the wide angle part, at *ca.* 4.5 Å. The diffuse scattering in the wide angle region corresponds to the liquid-like conformation of the molten aliphatic chains and to the disordered stacking of the flat aromatic parts in the columns. The three sharp reflections were indexed as 11 ($d_{11} = d_{1\bar{1}} = d_{20}$) for the first reflection, 21 and 31 ($d_{31} = d_{02}$) for the second and third order reflections respectively. This corresponds to a 2D arrangement of columns with a rectangular *p2gg* 2D space group ($h + k \neq 2n$), and thus to a rectangular mesophase, commonly
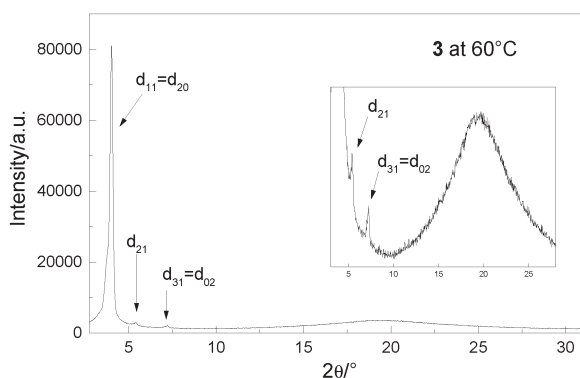

Fig. 6 X-Ray diffraction pattern of **3** recorded at 60 °C in the rectangular mesophase (pseudo-hexagonal).
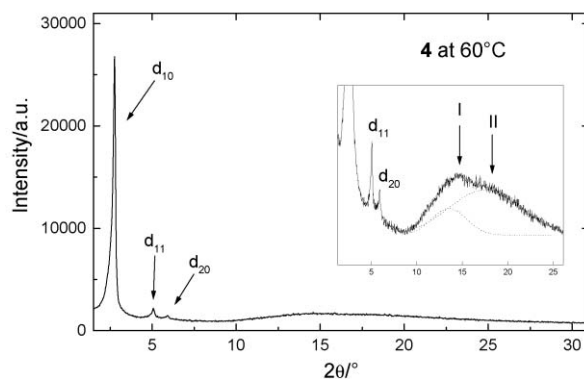
refereed to as a pseudo-hexagonal phase. The lattice parameters are $a = 40.9$, $b = 23.6$ Å, with $a/b = \sqrt{3}$, and the area of one column, S, is 483 Å². The pattern recorded at 60 °C (Fig. 5) was chosen as a representative example. The position of the reflections remains unchanged in the mesomorphic temperature range.

Between room temperature and up to 125 °C, the X-ray diffraction patterns also confirmed the existence of a liquid crystalline mesophase for the organosiloxane triphenylene (**4**). The diffraction patterns obtained at 60 °C (Fig. 7), chosen as a representative example, consisted of three, sharp small-angle reflections (28.35, 16.35 and 14.1 Å) and of two diffuse and broad scattering halos in the wide angle region. The reciprocal spacings of the three sharp reflections were in the ratio 1, $\sqrt{3}$, $\sqrt{4}$ corresponding to the indexation $(hk) = (10)$, (11) and (20) which are characteristic of a 2D hexagonal lattice, and thus to a hexagonal columnar mesophase (Col$_H$ phase). One of the two halos is associated with the liquid-like order of the molten aliphatic chains and of the rigid flat aromatic parts (**II**), at *ca.* 4.5 Å, while the other one, slightly more intense and diffuse (**I**) at *ca.* 6.4 Å, corresponds to the interactions between the terminal siloxane moieties. Identical X-ray patterns were obtained at any other temperature of the mesomorphic range, with no variation of position of the reflections. The inter-columnar distance, a, is 32.7 Å and the lattice area, S, is 928 Å².

Discussion

In 1979, Destrade *et al.*[20] reported the mesomorphic behaviour of the 2,3,6,7,10,11-hexakis(alkanoyloxy)triphenylenes, some of the earliest discotic liquid crystalline materials. These materials were found to exhibit a rather rich polymorphism showing a Col$_R$ mesophase from the heptanoyloxy up to long chain-length homologues, and from the undecanoyloxy homologue onwards, two additional mesophases sandwiching the Col$_R$ one, namely a high temperature Col$_H$ mesophase (with a temperature range of *ca.* 10–20 °C), and an ordered unidentified low-temperature one. The Col$_R$ existed over a wide temperature range of *ca.* 60 °C on average. It is thus interesting to observe the dramatic effect of the chemical modification of the pendant groups on the mesomorphic properties. The hexakis(alkanoyloxy)triphenylene homologue of **3** (*i.e.* with saturated chains) displays a Col$_R$ mesophase ($n = 10$: Crys 75 Col$_R$ 125.5 I). The presence of the unsaturation at the chain extremity leads to a decrease of both the melting and clearing points, and in addition to a reduction of the mesomorphic temperature range, as already observed in several cases of calamitic compounds.[21] It is important also to note the absence of any periodicity of 3.5–3.6 Å related to a stacking of the aromatic cores as in many other mesogenic triphenylene derivatives.[20] This clearly indicates a tilt of the aromatic cores with respect to the columnar axis as reported in the crystalline

phase of triphenylene substituted with six ethyleneoxy chains,[22] very presumably induced by the dipolar interactions between the carboxylate groups along the columns. Thus, the symmetry of the mesophase remains rectangular.

In the same way, the introduction of siloxane moieties at the end of the aliphatic chains leads also to a dramatic change of the temperature of transition, compound **4** being columnar mesomorphic even at room temperature. This is a general trend already observed in organosiloxane calamitic liquid crystals. As for **3**, the aromatic cores are tilted with respect to the columnar axis as revealed by the absence of any signal in the diffraction pattern at 3.5–3.6 Å. However, in the case of **4**, the only columnar mesophase observed is hexagonal in nature. As a matter of fact, the addition of terminal siloxane moieties clearly leads to a more homogeneous crown around the central triphenylene cores, thus reducing the cross-sectional anisotropy and the hexagonal packing can then be achieved with a complete rotational disorder along the columnar axis. It is interesting to note that a similar molecular engineering including microsegregation effects[23] has been applied to other triphenylene derivatives by attaching terminal fluoroalkylated chains[24] or terminal peripheral sugar moieties,[25] leading to similar effects with in particular a broadening of the mesomorphic range.

As a conclusion, the molecular engineering of compounds **3** and **4** proved to be useful to considerably decrease the temperature of transitions of triphenylene derivatives, to enlarge the mesomorphic range and to tune the type of columnar mesophase (rectangular or hexagonal). In the present case however, the tilted arrangement of the triphenylene cores within the columns is not the best configuration for an optimised photoconduction process along the columnar axis. On the other hand, such molecular engineering can be useful when tilted arrangements are needed for ferroelectric columnar mesophases for example. The charge transport properties of derivatives **3** and **4** are currently being investigated, and molecular engineering of similar derivatives with non-tilted arrangement of the aromatic cores within the columns is now in progress.

Experimental

Synthetic methods

2,3,6,7,10,11-Hexamethoxytriphenylene (1). A solution of veratrol (**0**) (13.82 g, 100 mmol) in dichloromethane (140 ml) was added dropwise to a suspension of $FeCl_3 \cdot H_2O$ (53 g) in dichloromethane (300 ml) and concentrated sulfuric acid (0.7 ml). After complete addition (15 min), the reaction mixture was further stirred for 3 h at room temperature, then 400 ml of methanol were slowly added under vigorous stirring. The obtained mixture was further stirred for 30 additional minutes and the precipitate was filtered off, washed with methanol (5 × 100 ml) and dried under reduced pressure to give **1** as a slightly beige powder (11.5 g, 83%). Elemental analysis: found (calculated for $C_{24}H_{24}O_6$; MW = 408.46 g mol^{-1}): %C = 70.81 (70.57); %H = 6.01 (5.92); %O = 23.22 (23.50). ^{1}H NMR: 300 MHz; CDCl$_3$; δ_H (ppm): 4.05 (s, 18 H, OMe), 7.80 (s, 6 H, ArH).

2,3,6,7,10,11-Hexahydroxytriphenylene (2). Hexamethoxytriphenylene (**1**) (1.02 g, 2.5 mmol) was dissolved in dichloromethane (20 ml) and the obtained solution was cooled to −70 °C and maintained under a nitrogen atmosphere. A solution of BBr$_3$ (1 M, CH$_2$Cl$_2$, 30 ml) was then added dropwise to the reaction mixture over a period of 30 min. After complete addition, the reaction temperature was gradually allowed to reach room temperature and stirring was continued for 8 h. The reaction mixture was then slowly poured into crushed ice (100 g) and the obtained mixture was stirred

vigorously until the ice melted. It was then extracted with diethyl ether (6 × 150 ml) and the combined organic extracts were washed with half saturated NaCl solution (200 ml), dried over magnesium sulfate and evaporated to dryness. This afforded 2,3,6,7,10,11-hexahydroxytriphenylene (**2**) as a grey solid; the yield was quantitative. This compound was used without further purification.

2,3,6,7,10,11-Hexakis(non-8-enylcarbonyloxy)triphenylene (3). To a suspension of 2,3,6,7,10,11-hexahydroxytriphenylene (**2**) (0.64 g, 2 mmol), dec-9-enoic acid (3.40 g, 20 mmol) and DMAP (124 mg) in dichloromethane (40 ml) cooled to 0 °C, a solution of DCC (4.12 g, 20 mmol) in dichloromethane (40 ml) was slowly added. After complete addition, the reaction mixture was stirred for 15 min at 0 °C and for 6 h at room temperature. The urea was then filtered off and the obtained yellowish solution was evaporated to dryness. The beige-yellow residue thus obtained was purified by filtration over a short silica gel column using dichloromethane as eluent. The beige solid was then dissolved in 10 ml of dichloromethane followed by a slow addition of 100 ml of ethanol. The obtained precipitate was filtered off, washed with ethanol (50 ml) and dried to give 2,3,6,7,10,11-hexakis-(dec-9-enylcarbonyloxy)-triphenylene (**3**) as a white powder. Yield 1.4 g , 65%. Elemental analysis: found (calculated for $C_{78}H_{108}O_{12}$; MW = 1237.72 g mol^{-1}): %C = 75.92 (75.69); %H = 8.95 (8.80); %O = 15.24 (15.51). ^{1}H NMR; 300 MHz; CDCl$_3$; δ_H (ppm): 1.40 (s, 48 H), 1.74–1.85 (m, 12 H), 2.03–2.09 (m, 12 H), 2.59–2.67 (m, 12 H), 4.94–5.06 (m, 12 H), 5.73–5.93 (m, 6 H), 8.22 (s, 6 H, ArH).

2,3,6,7,10,11-Hexakis{[10-(pentamethyldisiloxanyl)decanoyl]oxy}triphenylene (4). To a suspension of **3** (1.24 g, 1 mmol) and 1,1,1,3,3-pentamethyldisiloxane (5 ml), divinyl(tetramethyl)disiloxane platinum complex (Pt:DVTMS) (5 µl) was added under an argon atmosphere. The obtained mixture was refluxed for 3 h, then a solution of Pt:DVTMS (5 µl) in toluene (thiophene free, 15 ml) was added to the reaction mixture which was further stirred for 3 h at 85 °C. It was then cooled, diluted with 10 ml of cyclohexane and filtered over a short silica gel column using cyclohexane–toluene (1 : 1 v/v) as eluent. After evaporation of solvent pure 2,3,6,7,10,11-hexakis{[10-(pentamethyldisiloxanyl)decanoyl]oxy}triphenylene (**4**) was obtained as a slightly grey pasty material. Yield : 1.76 g, 83%. Microanalysis: found (calculated for $C_{108}H_{204}O_{18}Si_{12}$; MW = 2127.85 g mol^{-1}): %C = 61.12 (60.96); %H = 9.82 (9.66); %O = 13.25 (13.53). ^{1}H NMR; 300 MHz; CDCl$_3$; δ_H (ppm): 1.33–1.57 (m, 150 H), 1.77–1.81 (m, 24 H), 2.59–2.67 (m, 24 H), 8.25 (s, 6 H, ArH). ^{13}C NMR; 50 MHz; CDCl$_3$; δ_C (ppm): 171.07, 142.11, 127.57, 118.12, 34.20, 33.43, 29.46, 29.39, 29.27, 24.93, 23.28, 18.38, 1.96, 0.33.

Materials

1,1,1,3,3-Pentamethyldisiloxane, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), dichloromethane, toluene and boron tribromide (Fluka); divinyltetramethyldisiloxane platinum complex (Pt:DVTMS in xylene 2.1–2.4%, ABCR); veratrol (Aldrich); dec-9-enoic acid (AGIPAL); iron(III)chloride monohydrate (FeCl$_3 \cdot$H$_2$O) (Merck).

Characterisations

^{1}H NMR spectra were recorded on a Bruker AC 300 MHz spectrometer using CDCl$_3$ as solvent.

DSC

The transition and enthalpies were determined by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operating at a scanning rate of ± 5 and 10 min^{-1}.

POM

The optical textures were studied using a polarising microscope Orthoplan (Leica) working in the transmission mode and associated with a Mettler hot stage.

XRD

The XRD patterns were obtained with two different experimental set-ups; in the experiments, the crude powder was filled in Lindemann capillaries of 1 and 0.5 mm diameter for **3** for **4** respectively. A linear monochromatic Cu-Kα_1 beam was obtained using a Guinier camera or a Debye–Scherrer camera equipped with a bent quartz monochromator and an electric oven. A first set of diffraction patterns was registered with a gas curved counter "Inel CPS 120" associated with a data acquisition computer system; periodicities up to 60 Å can be measured, and the sample temperature is controlled within ± 0.05 °C. The second set of diffraction patterns was registered on both photographic films and image plate; the cell parameters were calculated from the positions of the reflections at the smallest Bragg angle, which was in all cases the most intense. Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ± 0.3 °C. In each case, exposure times were varied from 1 to 24 h.

Acknowledgement

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