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Liquid Crystals

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New mesogen with thermotropic cubic phase: 3,4,5-tris-(11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluorohexadecyloxy)benzoic acid

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A new mesogen, 3,4,5-tris(11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-hexadecyloxy) benzoic acid, with a thermotropic cubic phase was synthesized. The phase behaviour of the fluorinated compound and its corresponding non-fluorinated analogue was investigated by differential scanning calorimetry, polarizing optical microscopy, and synchrotron small-angle X-ray diffraction. The fluorinated compound, which contains three partially perfluorinated alkoxy moieties and one carboxylic acid group capable of forming hydrogen bonding, exhibits a very interesting sequence of isotropic, cubic and hexagonal columnar phases, whereas its non-fluorinated compound does not have a liquid crystalline phase. The cubic phase exists over a wide temperature range (from $\sim 200^{\circ}\text{C}$ to $\sim 30^{\circ}\text{C}$ on cooling) and is hence amenable to various physical measurements and potential applications. The ability to self-assemble molecules into ordered superstructure via both partially perfluorinated chains and hydrogen bonding provides new insight for the development of novel liquid crystalline materials.

1. Introduction

Liquid crystals (LCs) are typically “soft” and respond easily to external stimuli. The responsive nature and diversity of LCs provide tremendous opportunities as well as challenges for insights in fundamental science that opens the door to various applications. Conventional LC materials, which have become the quintessential molecular electronic materials of modern technology, are mostly formed by rod-like or disc-like molecules that have flexible chains attached to rigid cores [1]. However, recently there has been resurgence in the synthesis of new and exciting LCs in which the molecular shape has been distorted away from the conventional rod-like or disk-like forms. A feature of the majority of these so-called non-conventional LCs is amphiphilicity, i.e. the molecules have at least two chemically different building blocks that are incompatible [2]. In these molecules, segregation of the incompatible groups is driven by the enthalpy of demixing, which leads to the formation of a distinct subspace with a minimal energy. Among the non-conventional LCs, thermotropic cubic phases, which represent ordered supermolecular arrangements and are optically isotropic, are attracting much interest due to their tremendous biological significance and potential

application in drug delivery systems, etc, although the history of cubic phases dates from the first synthesis of nitrobiphenyl carboxylic acids by Gray in the 1950s [3–11]. Compared with the lyotropic cubic system, relatively few thermotropic compounds with isotropic cubic phases have been reported, although they have currently been recognized in a wider range of materials such as polyhydroxy molecules, dendritic molecules and metallomesogens; a cubic phase is often observed at relatively high temperature [12]. In this paper we reported a new mesogen, 3,4,5-tris(11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluorohexadecyloxy)benzoic acid, that exhibits a very interesting sequence of cubic and hexagonal columnar phases, whereas its methyl ester and its non-fluorinated analogue do not show a liquid crystalline phase. To the best of our knowledge, this is the first compound with the general structure of 3,4,5-tris(partially perfluorinated alkoxy)benzoic acid that exhibits a cubic phase.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded in $\text{C}_4\text{D}_8\text{O}$ or CDCl_3 . Chemical shifts are in δ units (ppm) with

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residual solvent peak as the internal standard. Column chromatography was carried out on silica gel (60–200 mesh). Analytical TLC was performed on commercially coated 60 mesh F₂₅₄ glass plates. Spots were rendered visible by exposing the plate to UV light. Textures and transition temperatures for target compounds were observed by optical microscopy using a Leitz polarizing microscope in conjunction with a Linkam TMS temperature controller. Calorimetric measurements were performed in a Perkin Elmer DSC using indium as a standard calibration. Elemental analysis was performed by Robertson Microlet Inc. The Mass spectrum was performed by Mass Spectrometry and Proteomics Facility of Ohio State University. Small-angle X-ray diffraction (SAXD) experiments were carried out at the European Synchrotron Facility, Grenoble. Samples were contained in thin X-ray capillaries which were flame sealed in nitrogen atmosphere. The temperature of the capillary was varied in steps using a Linkam heating stage. The normalized two dimensional diffraction patterns were azimuthally averaged to obtain the intensity, $I(q)$, as function of scattering vector (q).

2.2. Synthesis

The partially perfluorinated compound **6** was synthesized generally along the lines of Percec and co-workers, starting from perfluorohexyl iodide by radical addition, reduction, bromination, Williamson ether formation and hydrolysis in six steps (scheme 1) [13]. A key reaction is the radical addition of perfluorohexyl iodide to 9-decen-1-ol (**1**) to form a partially perfluorinated chain. Such a reaction may be completed by using the expensive $(\text{Ph}_3\text{P})_4\text{Pd}(0)$ as a catalyst or traditional radical initiator such as azo or peroxides at high reaction temperatures in a low yield [14]. We synthesized the iodide **2** by using inexpensive copper as a catalyst in a high yield, followed by reduction under the condition of LiAlH_4 to give partially perfluorinated alkyl alcohol **3**. The alcohol **3** was brominated with aqueous 48% HBr in the presence of cetyltrimethylammonium bromide as phase transfer agent to give bromide **4**, which was reacted with methyl 3,4,5-trihydroxybenzoate in the presence of K_2CO_3 to obtain the methyl ester **5** followed by hydrolysis to obtain the fluorinated compound **6**. Its corresponding non-fluorinated analogue (3,4,5-tris-hexadecyloxy-benzoic acid, **10**) was easily synthesized starting from 1-bromohexadecane **8**, which was reacted with methyl 3,4,5-trihydroxybenzoate in the presence of K_2CO_3 to obtain the methyl benzoate **9** followed by hydrolysis (scheme 2). Their structures were identified by ^1H NMR, ^{13}C NMR, MS and elemental analysis.

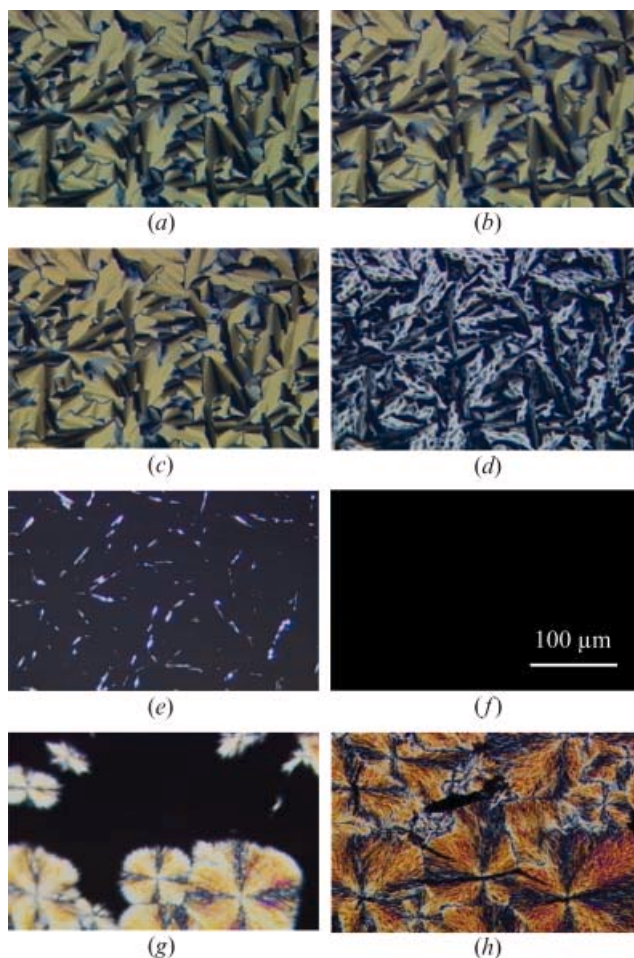


Figure 1. Cross-polarized optical texture micrographs of the target fluorinated compound **6** on heating at (a) 24°C, (b) 52°C, (c) 73°C, (d) 78°C (transition from hexagonal columnar phase to isotropic cubic), (e) 79°C and (f) 81°C, and its non-fluorinated analogue **10** on cooling at (g) 71°C (crystal growing from conventional isotropic phase) and (h) at 42°C (crystal).

For **6**, ^1H NMR ($\text{C}_4\text{D}_8\text{O}$): δ 1.40 (m, 30H), 1.55 (m, 6H), 1.64 (m, 6H), 1.82 (m, 6H), 2.20 (m, 6H), 4.10 (m, 6H), 7.34 (s, 2H). IR (KBr) ν_{max} (cm^{-1}): 2926, 2854, 1688, 1588, 1506, 1471, 1431, 1368, 1320, 1238, 1210, 1145, 1124. MALDI-TOF MS (M+H): calculated for $\text{C}_{55}\text{H}_{64}\text{F}_{39}\text{O}_5$, 1545.413; found, 1545.495. MS (M-OH): calculated for $\text{C}_{55}\text{H}_{62}\text{F}_{39}\text{O}_4$, 1527.398; found, 1527.553. Elemental analysis: calculated for $\text{C}_{55}\text{H}_{63}\text{F}_{39}\text{O}_5$, C 42.76, H, 4.11; found, C 43.02, H 3.97.

For **10**, ^1H NMR (CDCl_3): δ 0.88 (m, 9H), 1.26 (m, 72H), 1.46 (m, 6H), 1.82 (m, 6H), 4.03 (m, 6H), 7.33 (s, 2H). ^{13}C NMR: δ 14.13, 22.72, 26.07, 26.10, 29.30, 29.40, 29.59, 29.67, 29.70, 29.74, 30.35, 31.96, 69.19, 73.57, 108.55, 123.64, 143.15, 152.86, 171.84. IR (KBr) ν_{max} (cm^{-1}): 2918, 2850, 1684, 1588, 1469, 1431, 1334, 1123. MALDI-TOF MS (M+H): calculated for

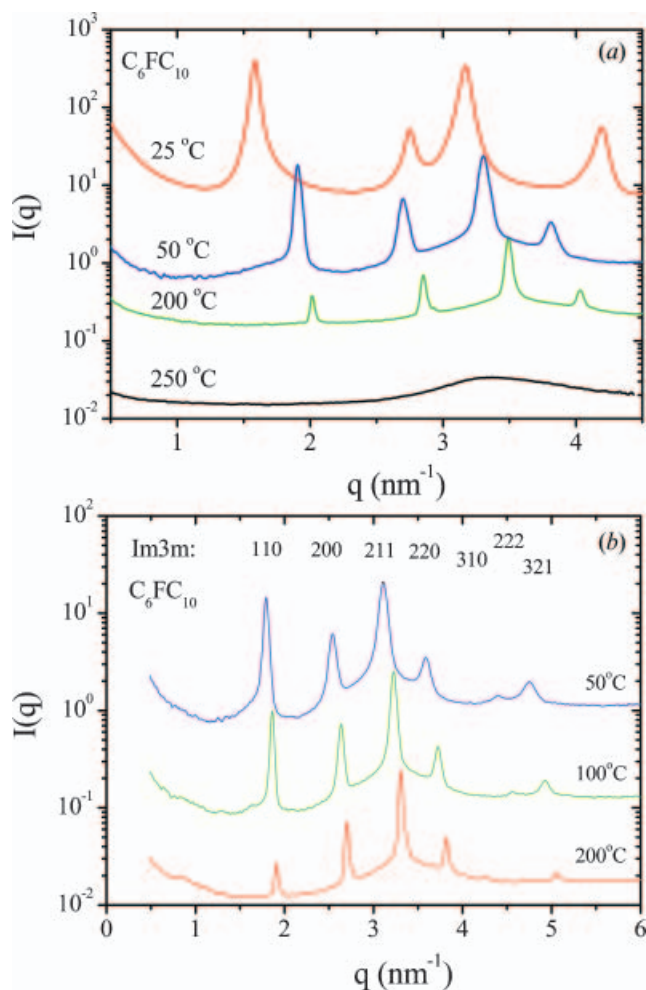


Figure 2. Powder averaged small-angle X-ray diffraction pattern for **6**. For clarity, successive patterns are displaced by a factor of 10. (a) On cooling the cubic phase appears at 200 °C, with increased lattice spacing at 50 °C before transforming to hexagonal columnar phase below 30 °C. (b) Evolution of the cubic phase while cooling the sample. The peak positions and multiplicities can be indexed to space group symmetry $Im\bar{3}m$ with lattice parameters of 4.4 nm and 4.7 nm at 200 °C and 50 °C, respectively.

$C_{55}H_{103}O_5$, 843.781; found, 843.856. MS (M-OH): calculated for $C_{55}H_{101}O_4$, 825.765; found, 825.875. Elemental analysis: calculated for $C_{55}H_{102}O_5$, C 78.32, H 12.19; found, C 78.04, H 12.42.

3. Results and discussion

The phase behaviour of the fluorinated compound **6**, its methyl ester **5** and its non-fluorinated analogue **10** was investigated by differential scanning calorimetry and polarizing optical microscopy (POM) equipped with a temperature controller. Preliminary results showed that the fluorinated compound **6** had a sequence of very interesting liquid crystalline phases, whereas both its

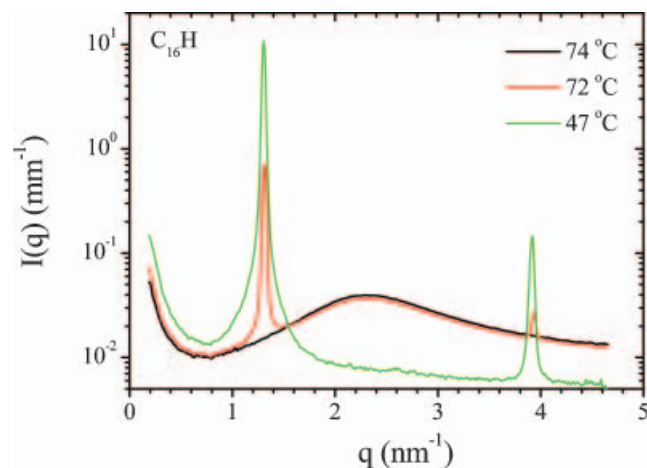


Figure 3. Small-angle X-ray diffraction pattern for **10** at 74 °C (isotropic phase), 72 °C (coexistence of isotropic and crystal phase) and 42 °C (crystal phase).

methyl ester **5** and non-fluorinated analogue **10** do not show any liquid crystalline phase. When the material **6** was heated up starting from 24 °C, the fan texture under crossed polarizing microscope was maintained until it started to gradually disappear and turn completely black at 81 °C (figures 1 a–f). As expected, no change on the optically isotropic phase was observed under the crossed polarized microscope with further heating up to 300 °C.

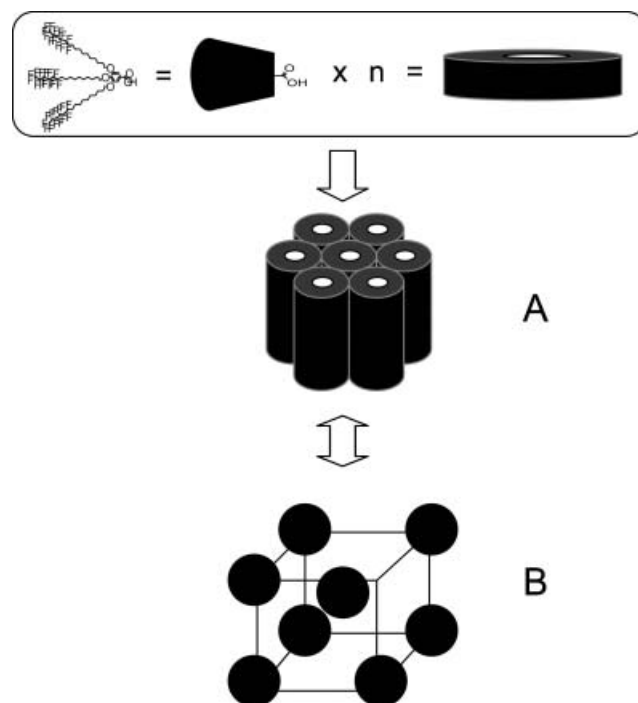
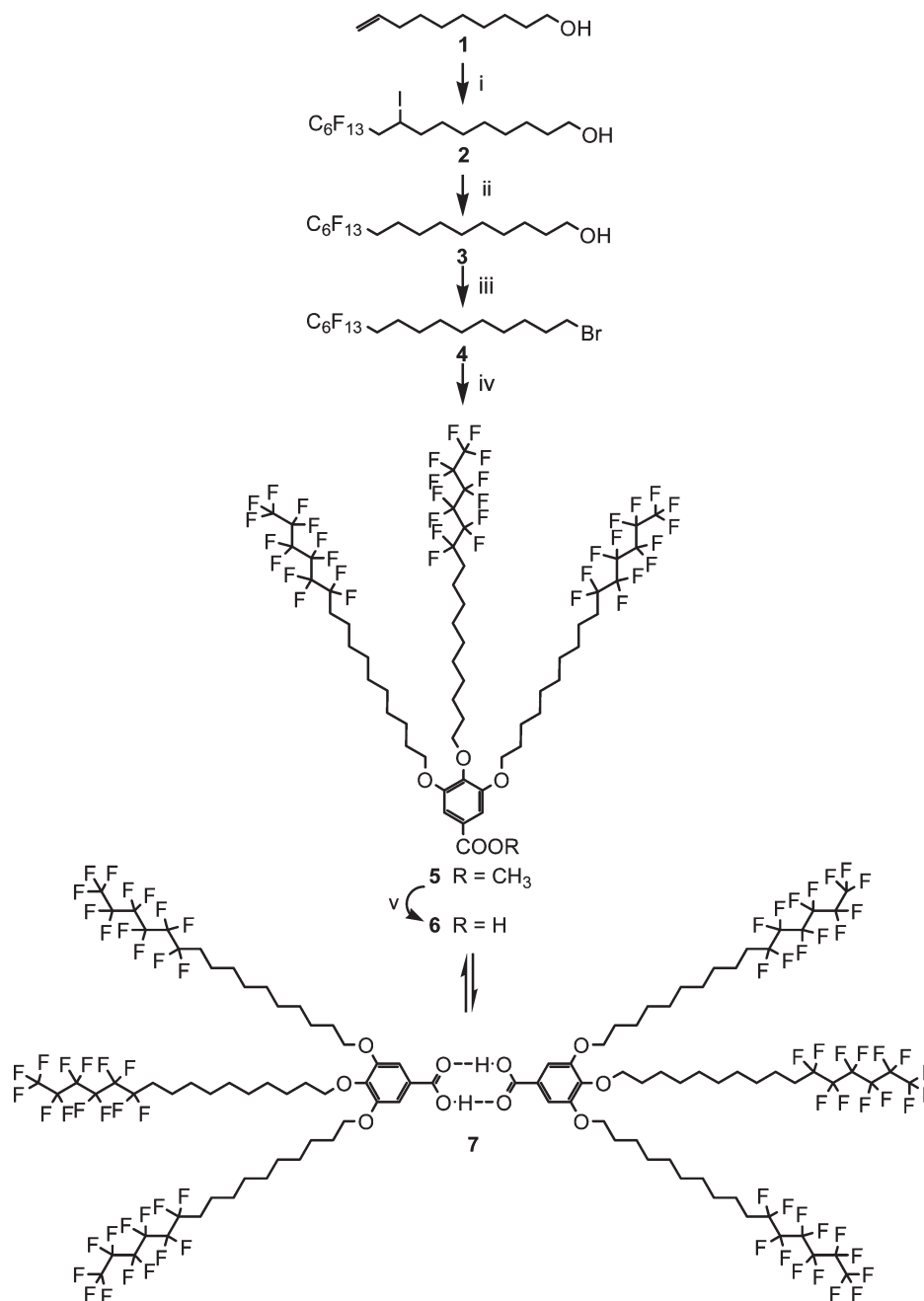


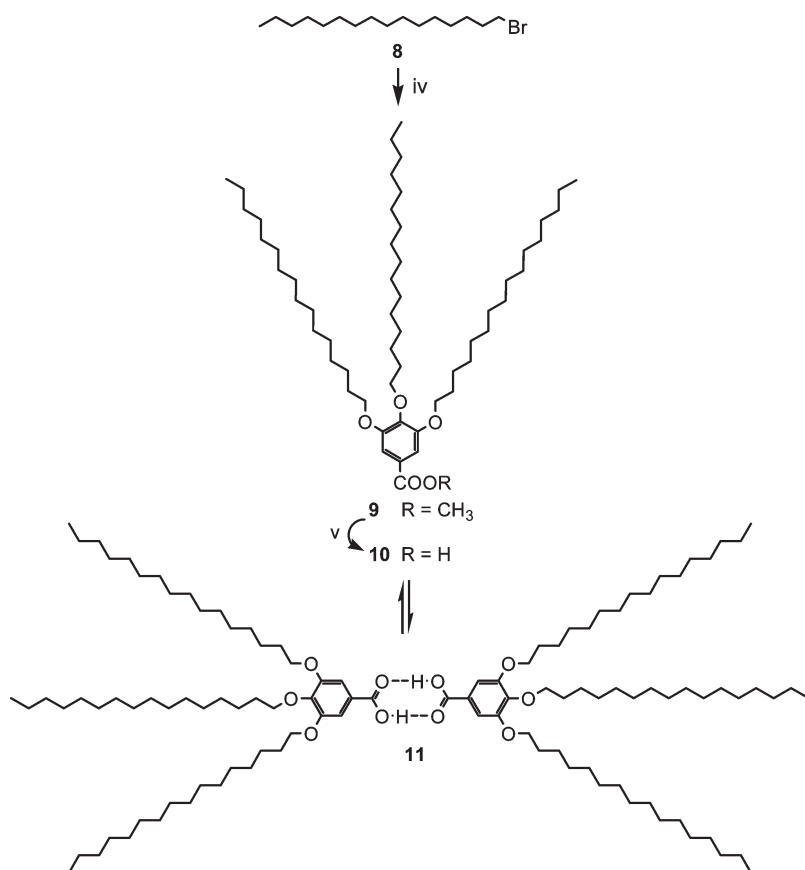
Figure 4. Schematic representation of the transition from (A) hexagonal columnar phase to (B) body centered cubic phase ($Im\bar{3}m$) of compound **6**.



Scheme 1. Synthesis of 3,4,5-tris(11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-hexadecyloxy)benzoic acid **6** and its potential hydrogen-bonded complex **7**. Reagents and conditions: (i) $\text{C}_6\text{F}_{13}\text{I}$, Cu; (ii) LiAlH_4 , Et_2O ; (iii) 48% HBr, cetyltrimethylammonium bromide; (iv) methyl 3,4,5-trihydroxybenzoate, K_2CO_3 , DMF; (v) KOH, EtOH, H_2O .

A similar sequence of phase changes was observed by SAXD when the sample was heated at 1°C min^{-1} . In order to characterize these phases better, SAXD patterns were recorded when the sample was cooled in steps from the isotropic phase at 250°C . Figure 2a shows that the isotropic to cubic phase transition occurs just above 200°C . This cubic phase remains stable down

to 30°C with increasing lattice spacing (in figure 2a the cubic peaks are shifted to smaller q values as the temperature is lowered). Upon further cooling, a hexagonal-like structure appears below 30°C . In figure 2a, the pattern at 25°C was recorded prior to heating the sample. Figure 2b depicts evolution of the cubic phase as the temperature is decreased. When it is



Scheme 2. Synthesis of 3,4,5-tris(non-fluorinated alkoxy)benzoic acid and its potential hydrogen-bonded complex. Reagents and conditions: (iv) methyl 3,4,5-trihydroxybenzoate, K_2CO_3 , DMF; (v) KOH, EtOH, H_2O .

fully developed, the ratio of peak positions is $1:\sqrt{2}:\sqrt{3}:2:\sqrt{5}:\sqrt{6}:\sqrt{7}:\sqrt{8}$ and the multiplicities of peaks are consistent with a body centered cubic structure (space group $Im\bar{3}m$). The cubic lattice parameter increases from 4.4 nm at 200°C to 4.7 nm at 50°C. This corresponds to a change in nearest neighbour distance of 3.82 nm to 4.07 nm and is consistent with the dimer size of molecule **6**.

Below 30°C, a hexagonal-like columnar phase with characteristic $1:\sqrt{3}:2:\sqrt{7}:3$ peak positions appears, which is similar to the cubic to hexagonal transition observed in certain lyotropic systems [15]. While heating the sample, the hexagonal phase can remain stable up to 70°C and sometimes even with two different lattice spacings. The phase sequence of **6**, isotropic phase → cubic phase → hexagonal phase, observed when cooling the sample from isotropic phase is more reproducible. The equilibrium hexagonal diffraction pattern in figure 2 a corresponds to a lattice parameter of 4.6 nm. This means that the nearest neighbour distances are similar in both the cubic and hexagonal phases. The POM textures shown in figure 1 indicate this gradual transition from hexagonal to cubic phase

when the sample is heated from room temperature. Based on the lattice parameters, the transition from hexagonal to cubic phase could involve a change in the columnar-like packing of compound **6** dimer molecules to dendrimer-like spherical packing. It is worth noting here that the phase transition temperature of the fluorinated compound depends on its thermal history. Upon different heating and cooling cycles, the transition temperature is different. In contrast, the non-fluorinated analogue does not have any liquid crystalline phase. Figure 3 depicts the corresponding SAXD pattern of compound **10** recorded when cooling the sample from the isotropic phase.

Interestingly, a tiny change of the hexagonal columnar phase texture from figure 1 a to 1 c was observed with temperature, which might originate from the effect of temperature on the hydrogen bond. Moreover, it is not surprising that the methyl ester **5** does not have a liquid crystalline phase since the ester **5** ($-\text{COOCH}_3$) lacks the capability of forming a hydrogen bond. Its non-fluorinated analogue **10** has the capability of forming hydrogen bond but still does not exhibit a

liquid crystalline phase. The reason stems from the unique properties of the perfluorinated chains, which are more rigid, less miscible and possess larger steric bulk than the corresponding perhydrogenated alkanes, which enhance the stability of mesophases such as columnar phase and cubic phase [16]. So the combination of partially perfluorinated chains and hydrogen bonding leads to the liquid crystalline phase behaviour of target compound **6** in contrast to its methyl ester **5** and its non-fluorinated analogue **10** both of which do not exhibit a liquid crystalline phase. The self-assembly of **6** in hexagonal phase and cubic phase is schematically shown in figure 4. The transition from hexagonal to cubic phase upon heating the sample implies a rod to sphere type change in the packing. Detailed investigations of phase transitions in these interesting liquid crystalline phases are in progress.

4. Conclusions

We demonstrated the synthesis and characterization of the new mesogen, 3,4,5-tris-(11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluorohexadecyloxy)benzoic acid with a very interesting phase sequence. This is the first compound with the general structure of 3,4,5-tris (partially perfluorinated alkoxy)benzoic acid that exhibits a cubic phase. The cubic phase is stable over a wide temperature range from about 200°C to 30°C on cooling, which makes it suitable for detailed investigations of phase transitions and potential applications. This research would provide new insight for self-assembling molecules into ordered superstructure via both perfluorinated chains and hydrogen bonds.

Acknowledgement

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