Bicontinuous cubic phase with the *Pn3m* space group formed by *N,N,N*-tris(5-alkoxytroponyl)-1,5,9-triazacyclododecanes

Akira Mori[a]; Emi Yamamoto[b]; Kanji Kubo[a]; Seiji Ujiie[c]; Ute Baumeister[d]; Carsten Tschierske[e]

[a] Institute for Materials Chemistry and Engineering, 86, Kyushu University, Kasuga, Fukuoka, Japan [b] Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka, Japan [c] Department of Applied Chemistry, Faculty of Engineering, Oita University, Oita, Japan [d] Institute of Physical Chemistry, Martin Luther University Halle-Wittenberg, Halle, Germany [e] Institute of Organic Chemistry, Martin Luther University Halle-Wittenberg, Halle, Germany

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Bicontinuous cubic phase with the *Pn3m* space group formed by *N,N,N*-tris(5-alkoxytroponyl)-1,5,9-triazacyclododecanes

Akira Mori[a]*, Emi Yamamoto[b], Kanji Kubo[a], Seiji Ujiie[c], Ute Baumeister[d] and Carsten Tschierske[e]

[a]*Institute for Materials Chemistry and Engineering, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan;* [b]*Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan;* [c]*Department of Applied Chemistry, Faculty of Engineering, Oita University, Oita 870-1192, Japan;* [d]*Institute of Physical Chemistry, Martin Luther University Halle-Wittenberg, Mühlpforte, D-06108 Halle, Germany;* [e]*Institute of Organic Chemistry, Martin Luther University Halle-Wittenberg, Kurt-Mothes Strasse 2, D-06120 Halle, Germany*

N,N,N-tris(5-alkoxytroponyl)-1,5,9-triazacyclododecanes and their corresponding benzenoids were synthesised to investigate their mesomorphic properties. The troponoids have a bicontinuous cubic phase with a *Pn3m* space group whereas the benzenoids form a smectic A phase. The thermal stability of the cubic phase of the troponoids is decreased when the length of the alkyl group is increased whereas that of the smectic A phase of the benzenoids behaves reversely. The cubic phase of the troponoid should represent an organisation of the fluid alkyl chains within the interwoven networks whereas the polar azacrown and tropolone units should form the continuum.

Keywords: bicontinuous cubic phase; *Pn3m* space group; troponoid liquid crystals; azamacrocyles

1. Introduction

Cubic phases are optically isotropic and characterised by a three-dimensional periodicity in connection with a local liquid-like disorder of the molecules [1, 2]. They are common in lyotropic systems [3–5] as an intermediate phase at the phase transitions between lamellar and columnar organisations to show bicontinuous cubic phases and between hexagonal columnar phases and micellar solutions to have discontinuous cubic phases. Moreover, many types of compounds with thermotropic cubic phases are also known [6]. Discontinuous thermotropic cubic phases formed by taper shaped amphiphiles [7], dendrimers [8–11], and related compounds [12] are nowadays rather well understood. These molecules have either a nearly spherical molecular shape or capability of spheroidic aggregate formation. In this case, attractive intermolecular interactions such as hydrogen bonding and also micro-segregation effects are required to form these phases [1, 2].

The structural requirements for the formation of bicontinuous cubic thermotropic mesophases, on the other hand, are not so clear, because they can be found in quite different classes of compounds and their occurrence depends strongly on small changes of the molecular structure. Beside flexible amphiphiles [7] and polycatenar molecules [13–15], several other molecules, which are hard to categorise into a common class, show this type of cubic mesophases. Typical examples are 1,2-bis(4-alkoxybenzoyl)hydrazines (BABH-n) [16–18], 4-n-alkoxy-3-nitrobiphenyl-4-carboxylic acids (ANBC-n) [19], binary mixtures of rodlike diols [20], chiral phenylpyrimidine derivatives [21, 22], perfluorinated calamitic compounds [23–25], non-C_3-symmetric oligobenzoesters [26], silver complexes of dialkoxystilbazoles [27], and many others [1–5, 28] (Scheme 1). In addition to the structural diversity, different types of space groups (*Ia3d, Im3m,* and *Pn3m*) are known and in contrast to the lyotropic counterparts, different models for the molecular organisation in these cubic phases are under discussion [29–33]. It seems that the presence of hydrogen bonding groups and/or other polar groups in the rigid core is quite important for rod-like molecules to induce cubic phases. For example, in the case of ANBC-n's a polar nitro group is necessary at the lateral position, in addition to the carboxylic acid group, which forms a dimer through hydrogen bonding. If the lateral polar nitro substituent is absent in ANBC-n's, the cubic phase is lost and replaced by a smectic C (SmC) phase [34–36]. Besides a disturbance of the layer organisation by steric effects, the presence of two strongly competing parts in polarity within these molecules, such as aliphatic *vs.* aromatic, non-polar *vs.* polar, or soft *vs.* hard, is also important for the induction of cubic phases [29].

Recently, we also observed the effect of counter ions in pyridinium liquid crystals where *N*-dodecyl-pyridinium with a chloride counter ion (Py12/Cl) formed a cubic phase (*Pn3m* or *Im3m*) as well as columnar and smectic A (SmA) phases, whereas *N*-dodecylpyridinium with a copolyacrylate counter

ion (Py12/PA-0.7), in which a ratio of ionic carboxylate and carboxylic acid groups is 7:3, showed only a cubic phase (*Pn3m*) with enhancement of the thermal stability [37]. Another example of the thermotropic cubic phase with the *Pn3m* structure was reported in discotic molecules of transition metal complexes based on phthalocyanine [38]. Hence, molecules forming bicontinuous cubic phases should have strong intermolecular interactions at least in one part of the molecule and they should have a relatively strong amphiphilicity, providing rather sharp interfaces between the micro-segregated regions. Other than the structural modifications, it has been recently reported that application of electric field [39, 40] and pressure [41] influenced the transition from a SmC to a cubic phase.

We have synthesised different series of liquid crystals with a tropolone ring as a core structure because this unit provides a large dipole moment, which might lead to attractive intermolecular interactions. Additionally, the rather high polarity difference of these units with respect to aliphatic chains could lead to a stronger micro-segregation than the benzenoid core structure. Indeed it has been shown that such tropolone derivatives exhibit lamellar mesophases even if they comprise only one ring [42–48] and they often have thermally more stable mesophases than the corresponding benzenoids [49–53]. Herein, we report the first troponoid azamacrocycles forming a thermotropic cubic mesophase with the space group *Pn3m*.
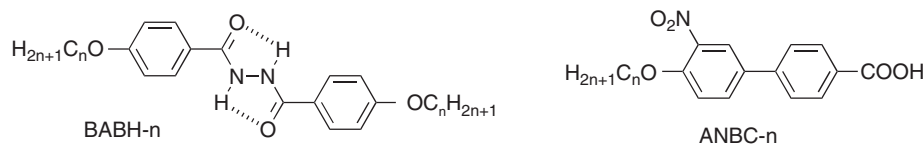
2. Synthesis

Troponoid azamacrocycles (**1**) were synthesised by the condensation of 5-alkoxy-2-methoxytropone (**2**) [54]

and 1,5,9-triazacyclododecane (**3**) under a pressure of 0.5 GPa at 100°C in toluene. Under normal pressure conditions, the reaction was not successful because the electrophilicity of **2** is decreased by the introduction of an electron-donating alkoxyl group at the C-5 position of **2**. The corresponding benzenoids (**4**) were synthesised by condensation of 4-alkoxybenzoyl chlorides with **3** in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP) in refluxing pyridine under normal pressure conditions (Scheme 2).

3. Results and discussion

The thermal behaviours of these compounds were investigated by polarising microscopy, differential scanning calorimetry, and X-ray diffraction (XRD). The transition temperatures are summarised in Table 1. No birefringence could be observed between crossed polarisers if compound **1e** is cooled down (Figure 1(a) and (b)). Pressing on top of the cover glass does not induce a flow of the material, but instead leads to a visco-elastic response and the smooth boundary to the air bubbles becomes irregular (Figure 1(c)). The conoscopic observation at 100°C did not show any conoscope figures, which confirms that the mesophase is optically isotropic.

The XRD pattern of compound **1e** was measured after cooling from the isotropic liquid, at 93°C (6 h exposure time), which showed one intense reflection at $2\theta = 2.45°$, one weak reflection at $2\theta = 4.88°$, two shoulders at 3.04 and 3.66° (Figure 2), and a diffuse wide-angle scattering with a maximum at 4.5Å. A straight line ($r^2 = 0.9998$) was observed for the correlation between $1/d$ (d = peak positions) and $\sqrt{m}$ ($m = h^2 + k^2 + l^2$) [55, 56] to indicate that these

Scheme 1. Typical compounds with cubic mesophases.
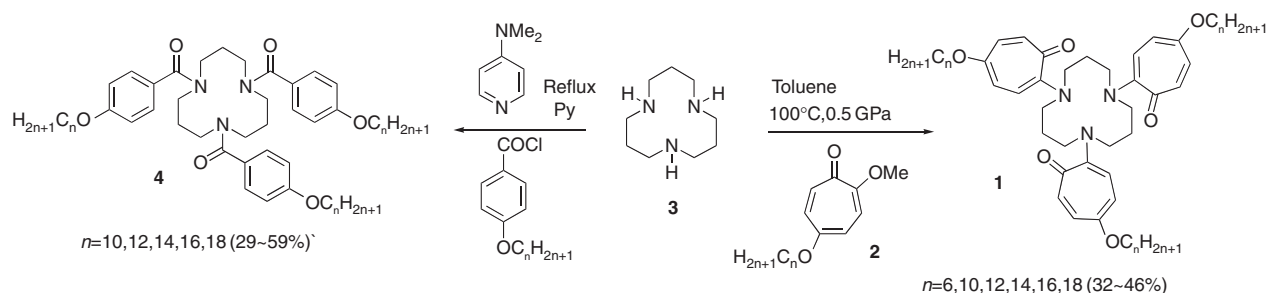
Scheme 2. Synthesis of compounds **1** and **4**.

Table 1. Transition temperatures (°C) of troponoid (**1**) and benzenoid (**4**) azamacrocycles.

	n	Transition temperatures (°C)		n	Transition temperatures (°C)
1a	6	Cr • 131 • Iso			
1b	10	Cr • 121 • Iso	**4a**	10	Cr • 62 • Iso
1c	12	Cr • 98 • Cub • 118 • Iso	**4b**	12	Cr • 63 • Iso
1d	14	Cr • 94 • Cub • 111 • Iso	**4c**	14	Cr • 64 • SmA • 79 • Iso
1e	16	Cr • 92 • Cub • 107 • Iso	**4d**	16	Cr • 70 • SmA • 81 • Iso
1f	18	Cr • 88 • Cub • 98 • Iso	**4e**	18	Cr • 69 • SmA • 87 • Iso

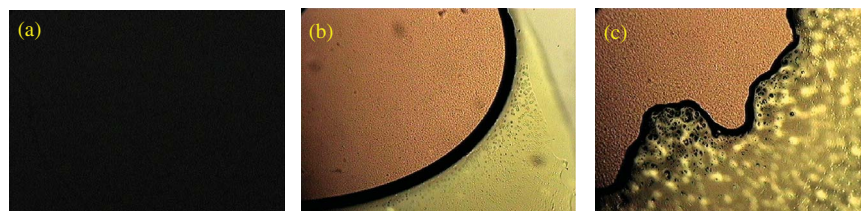Notes: Cr; crystals, Iso; isotropic liquid, Cub; cubic phase, SmA; smectic A phase.

Figure 1. (a) No birefringence under the crossed polarisers at 96°C obtained on the cooling process of **1e**. (b) Photograph of the smooth boundary between the fluid (left) and the air (right) taken by rotating the analyser by 30° under the conditions of (a). (c) Photograph after pressing the cover glass (colour version online).
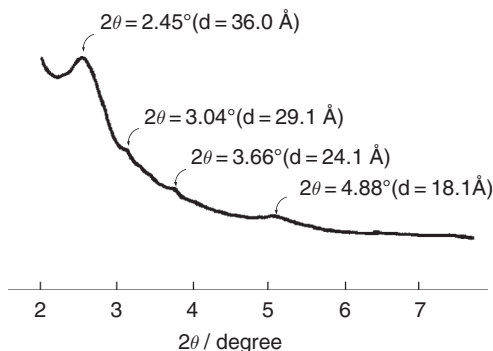

Figure 2. XRD pattern of non-aligned **1e** at 93°C.

Table 2. XRD peaks of the cubic phase of **1e**.

Induces	Observed	Calculated *Pn3m*, a = 720.0 Å
110	-	50.91
111	-	41.57
200	36.0	36.00
211	29.1	29.39
220	-	25.46
221	24.1	24.00
310	-	22.77
311	-	21.71
222	-	20.78
321	-	19.24
400	18.1	18.00

reflections match the relation $1/2 : 1/\sqrt{6} : 1/3 : 1/4$, which leads to the following indices (200), (211), (221), and (400). These reflections can be assigned to the cubic space group *Pn3m* with a lattice parameter $a_{cub} = 72.0$ Å. Table 2 shows the XRD data of **1e**. The unit cell of this cubic structure contains 187 molecules from the calculation[1]. The cubic phase was observed for four homologous compounds **1c–1f**, whereas the corresponding benzenoids **4** had SmA phases, as indicated by textural observations and XRD study. The typical fan texture of compound **4c** is shown in Figure 3(a). This fluid mesophase can be homeotropically aligned and then appears completely black between crossed polarisers. XRD investigations indicate a single layer reflection corresponding to a

layer distance of $d = 38.6$ Å at 67°C. Since the molecular length of the fully extended **4c** is calculated to be 49 Å by the MM2 method, two inter-digitated bilayer structures are proposed for the molecular arrangement in the SmA phase of **4c**, as shown in Figures 3(b) and 3(c). When compared with these two models, the model of Figure 3(c) should be more favoured because three phenyl rings of a jellyfish-like shape are located on the same side to make more effective micro-phase separation and the model has fewer voids between molecules than the model of Figure 3(b).

As discussed above, the troponoids **1** form cubic phases, whereas the corresponding benzenoids **4** with the same chain length show only SmA phases. A
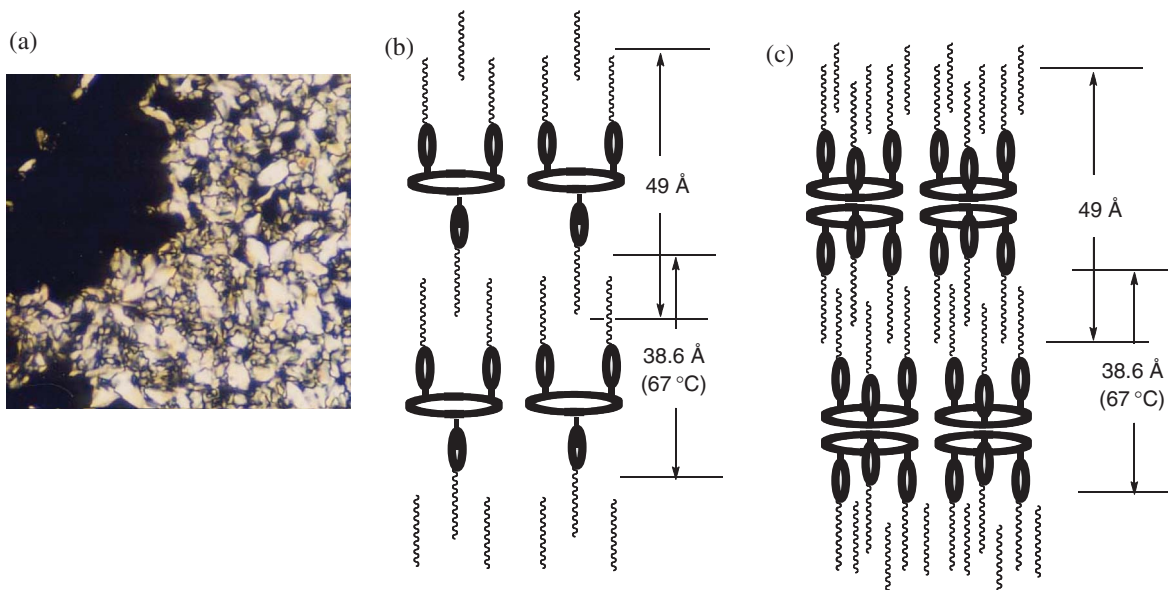
Figure 3. (a) Texture of the smectic A phase of benzenoid **4c** at 75°C obtained on the cooling process from the isotropic liquid. (b), (c) Possible packing models of the smectic A phase of **4c** (colour version online).

discontinuous (micellar) structure is unlikely because these molecules do not have a pronounced taper shape. Furthermore, the *Pn3m* space group has never been observed for a thermotropic cubic phase composed of the pure spheroidic aggregates, although binary mixtures of rod-like amphiphilic diols [20], pyridinium salts [37], and metallomesogens [38] show thermotropic cubic phases with the *Pn3m* space group. Also the fact that the structurally related benzenoids **4** show a lamellar phase is in line with the assumed bicontinuous structure of the cubic phase of the troponoids **1**. Bicontinuous cubic phases are built up by two interpenetrating networks of branched cylinders, which contain one of the incompatible molecular parts. These networks penetrate a continuum formed by the other molecular part [1, 2]. The question arises, which part of the molecules would form the continuum and which is organised within the networks? The comparison of the molecular structures of **1** and

4 might give some hints to elucidate the arrangement of molecules in the mesophase. We proposed the flexible jellyfish-like shape for the SmA phase of benzenoid **4**. If troponoid **1** has the jellyfish-like shape, repulsive dipole interaction between more polar tropolone units should arise to change the structure from the jellyfish-like shape to a more flat disc-like one, as shown in Figure 4(a) and (b). These disc-like molecules overlap to form columns as shown in Figure 4(c), which are branched and undulated to lead to three-dimensional skeletons in the cubic phase (Figure 4(d)). This means that the cubic phase of compounds **1** should represent an organisation of the fluid alkyl chains within the interwoven networks whereas the polar azacrown and tropolone units should form the continuum. Additionally, the increased polarity of the tropolone units in comparison to the benzenoid systems could reinforce the segregation of these molecular parts from the non-polar chains. This sharpens the
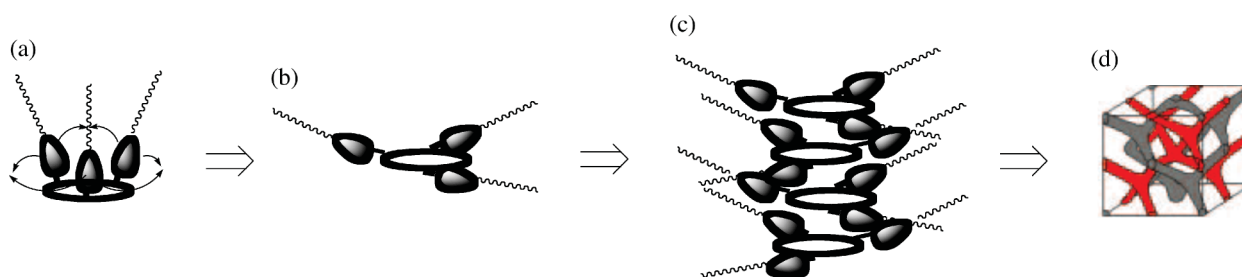

Figure 4. Schematic presentation of structures of troponoid **1**. (a) Jellyfish-like shape. Double-headed arrows mean repulsive interaction between tropolone rings. (b) Disc-like structure. (c) Molecules with disc-like structure form a column. (d) Bicontinuous cubic phase with a *Pn3m* space group (colour version online).

interfaces, which additionally favour the occurrence of a cubic phase.

It is reported that the shape of molecules affected the mechanism of appearance of the cubic phases [38]. Interestingly, the dependence of the thermal stability on the alkyl chain length is reversed in the series **1** and **4** (Table 1). The thermal stability of the mesophase of benzenoids **4** increases with growing chain length whereas that of troponoids **1** decreases. The increase of the thermal stability of the mesophase with rising chain length, as observed for benzenoids **4**, is typical for amphiphilic molecules. A decrease of the thermal stability of the mesophase with increasing chain length often occurs in the vicinity of the transition into another organisation type. Hence, the decrease of the mesophase thermal stability in the case of the troponoids might indicate that the elongation of the chain allows a more efficient space filling in the lipophilic regions, which destabilises the cubic phase and further enlargement of the chain could possibly lead to a lamellar arrangement.

It has been reported that benzenoid azamacrocycles (**5**) with three 3,4-bisdecyloxybenzoyl groups showed a columnar phase [57]. Since compound **4** with a monoalkoxybenzoyl group had a lamellar SmA phase, the additional alkoxy groups disturbed formation of the lamellar arrangement to give rise to the columnar phase (Scheme 3). In the theoretical phase diagram for amphiphilic materials it is known that in lyotropic systems bicontinuous cubic phases with the symmetry of the *Ia3d*, *Im3m*, and *Pn3m* space groups appear between a lamellar phase and a hexagonal phase [7, 58, 59]. In some thermotropic cases, a similar phase sequence (smectic–cubic–columnar) can be found [1, 2, 7]. Therefore it should not be incompatible with the result that compound **1** showed the bicontinuous *Pn3m* cubic phase between the SmA phase of compound **4** with a single alkoxy group and the columnar phase of compound **5** with two alkoxy groups on a benzoyl group.

In conclusion, troponoids **1** represent the first thermotropic azamacrocyclic liquid crystalline molecules with cubic mesophases. This enlarges the diversity of molecular structures capable of forming a thermotropic cubic mesophase. In contrast to most other thermotropic bicontinuous cubic phases with either an *Ia3d* or *Im3m* space group, the space group *Pn3m* is observed for troponoids **1**. The troponoids **1** are the first thermotropic azamacrocyclic liquid crystals with the *Pn3m* space group although a few examples of a thermotropic *Pn3m* cubic phase are known, as in binary mixtures of rod-like amphiphilic diols [20], pyridinium salts [37], and metallomesogens [38]. However, it appears that these examples are composed of structurally modified systems including binary mixtures, ionic structures, and metal ions.

Interestingly, only the troponoids are cubic, whereas the analogous benzene derivatives form exclusively SmA phases. Inter- or intra-molecular repulsive dipole–dipole interactions of the larger and more polar seven-membered tropolone rings than the six-membered benzene rings might give rise to a disturbance of the organisation in layers to transfer the lamellar phase to the cubic phase. These results indicate that the tropolone unit is not only a useful structural unit for the design of smectic and columnar liquid crystalline materials [60] with increased thermal stability of the mesophase, but it also allows the tuning of the mesophase structure, leading to cubic phases. Possibly, other unusual phase structures can also be realised with liquid crystalline molecules containing a troponoid structure [61].

4. Experimental

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University and are summarised in Table 3. NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in CDCl$_3$; the chemical shifts are expressed in δ units. Mass spectra were measured with JEOL 01SG-2 and LMS-700 spectrometers. The stationary phase for column chromatography was Wako gel C-300 and the eluant was a mixture of ethyl acetate and hexane. Transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200; the scanning rate was 5°C min^{-1}) and the mesomorphic
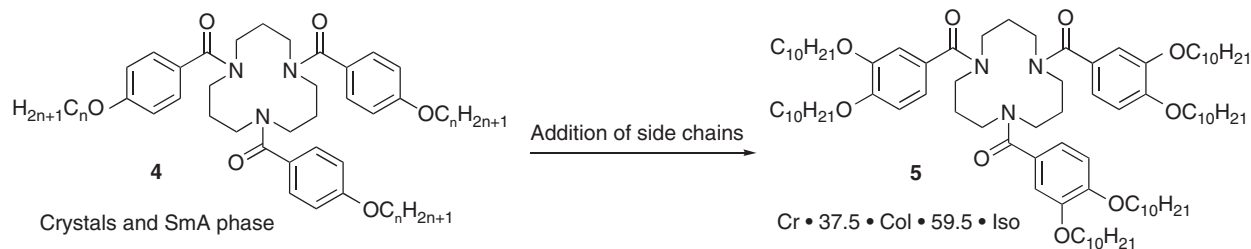
Scheme 3. Effect of the number of the side chain on appearance of mesophases.

Table 3. Elemental analyses for compounds **1** and **4**.

Formula	Percentage required (found)		
	C	H	N
1a $C_{48}H_{69}N_3O_6$	73.53 (73.47)	8.87 (8.83)	5.36 (5.26)
1b $C_{60}H_{93}N_3O_6$	75.67 (75.54)	9.84 (9.79)	4.41 (4.27)
1c $C_{66}H_{105}N_3O_6 \bullet 0.5H_2O$	75.82 (75.93)	10.22 (10.18)	4.02 (4.01)
1d $C_{72}H_{118}N_3O_6 \bullet 0.5H_2O$	76.55 (76.26)	10.53 (10.33)	3.72 (3.57)
1e $C_{78}H_{129}N_3O_6 \bullet 0.5H_2O$	77.18 (77.34)	10.79 (10.66)	3.46 (3.27)
1f $C_{84}H_{141}N_3O_6 \bullet 0.5H_2O$	77.73 (77.90)	11.03 (10.99)	3.24 (3.15)
4a $C_{60}H_{93}N_3O_6 \bullet 0.5H_2O$	74.96 (75.13)	9.86 (9.87)	4.37 (4.37)
4b $C_{66}H_{105}N_3O_6 \bullet 0.5H_2O$	75.82 (75.56)	10.22 (10.49)	4.02 (4.19)
4c $C_{72}H_{117}N_3O_6$	77.16 (77.10)	10.52 (10.47)	3.57 (3.68)
4d $C_{78}H_{129}N_3O_6 \bullet 0.5H_2O$	77.18 (77.10)	10.79 (10.58)	3.46 (3.39)
4e $C_{84}H_{141}N_3O_6 \bullet 0.5H_2O$	77.72 (77.71)	11.03 (10.98)	3.24 (3.22)

phase was observed with a polarising microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). X-ray powder diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-Kα radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

4.1 Synthesis of N,N,N-tris (5-hexyloxy-2-troponyl)-1,5,9-triazacyclododecane

A toluene solution (4 cm³) of 1,5,9-triazacyclododecane (22.3 mg, 0.13 mmol) and 5-hexyloxy-2-methoxytropone (314.3 mg, 1.33 mmol) was heated at 100°C under 0.5 GPa. After 4 d, the solvent was removed under reduced pressure and the residue was chromatographed on a silica-gel column to give *N,N,N*-tris(5-hexyloxy-2-troponyl)-1,5,9-triazacyclododecane (**1a**, 33.1 mg, 32%) yellow crystals. FAB-MS found: m/z, 784 (M + H⁺), calculated for $C_{48}H_{70}N_3O_6$: 784 (M + 1). ¹H-NMR δ 0.91 (9H, t, J = 6.5 Hz), 1.32–1.48 (18H, m), 1.76 (6H, quint, J = 6.5 Hz), 1.91 (6H, quint, J = 6.5 Hz), 3.35 (12H, t, J = 5.8 Hz), 3.87 (6H, t, J = 6.5 Hz), 6.35 (3H, dd, J = 11.1, 2.2 Hz), 6.82 (3H, d, J = 11.1 Hz), 6.92–7.00 (6H, m). ¹³C-NMR δ 14.0 (3C), 22.6 (3C), 24.0 (3C), 25.7 (3C), 29.0 (3C), 31.5 (3C), 47.1 (6C), 68.6 (3C), 110.6 (3C), 123.7 (3C), 130.8 (3C), 136.7 (3C), 153.6 (3C), 158.4 (3C), 182.4 (3C). **1b** (46%), yellow crystals. FAB-MS found: m/z, 952 (M + H⁺), calculated for $C_{60}H_{94}N_3O_6$: 952 (M + 1). **1c** (41%), yellow crystals. FAB-MS found: m/z, 1037 (M + H⁺), calculated for $C_{66}H_{106}N_3O_6$: 1037 (M + 1). **1d** (43%), yellow crystals. FAB-MS found: m/z, 1121 (M + H⁺), calculated for $C_{72}H_{117}N_3O_6$: 1121 (M + 1). **1e** (42%), yellow crystals. FAB-MS found: m/z, 1205 (M + H⁺), calculated φορ $X_{78}H_{130}N_3O_6$: 1205 (M + 1). **1f** (40%), yellow crystals. FAB-MS found: m/z, 1289 (M + H⁺), calculated for $C_{84}H_{142}N_3O_6$: 1289 (M + 1).

4.2 Synthesis of N,N,N-tris(4-decyloxybenzoyl)-1,5,9-triazacyclodecane

A thionyl chloride solution (0.5 cm³) of 4-decyloxybenzoic acid (171.6 mg, 0.62 mmol) was refluxed for 3 h. After excess thionyl chloride was removed, a pyridine solution (3 cm³) of 1,5,9-triazacyclodecane (20.1 mg, 0.12 mmol) and a catalytic amount of DMAP was refluxed for 12 h. The reaction mixture was poured into KHSO₄ solution and extracted with AcOEt. After being dried on MgSO₄, the solvent was removed under reduced pressure. The residue was chromatographed on a silica-gel column to give *N,N,N*-tris(4-decyloxybenzoyl)-1,5,9-triazacyclodecane (**4a**, 33.3 mg, 29%), colourless crystals. FAB-MS found: m/z, 952 (M + H⁺), calculated for $C_{60}H_{94}N_3O_6$: 952 (M + 1). ¹H-NMR δ 0.88 (9H, t, J = 6.8 Hz), 1.28-1.49 (42H, m), 1.77 (6H, quint, J = 6.8 Hz), 2.08 (6H, br s), 3.52 (12H, br s), 3.97 (6H, t, J = 6.8 Hz), 6.88 (6H, d, J = 8.8 Hz), 7.28 (6H, d, J = 8.8 Hz). ¹³C-NMR δ 14.1 (3C), 22.6 (3C), 26.0 (3C), 29.1 (3C), 29.3 (3C), 29.4 (3C), 29.51 (3C), 29.54 (6C), 31.9 (6C), 68.1 (3C), 114.4 (6C), 128.3 (3C), 128.4 (6C), 160.1 (3C), 172.9 (3C). **4b** (58%), colourless crystals. FAB-MS found: m/z, 1037 (M + H⁺), calculated for $C_{66}H_{106}N_3O_6$: 1037 (M + 1). **4c** (55%), colourless crystals. FAB-MS found: m/z, 1121 (M + H⁺), calculated for $C_{72}H_{118}N_3O_6$: 1121 (M + 1). **4d** (59%), colourless crystals. FAB-MS found: m/z, 1205 (M + H⁺), calculated for $C_{78}H_{130}N_3O_6$: 1205 (M + 1). **4e** (38%), colourless crystals. FAB-MS found: m/z, 1289 (M + H⁺), calculated for $C_{84}H_{142}N_3O_6$: 1289 (M + 1).

Acknowledgements

Note

1. Number (*n*) of molecules is calculated by the equation of $n = (\sigma V N)/M$, where σ: density, which is assumed as 1 g/cm³, V: volume (72.0×10^{-8} cm³), N: Avogadro's number, M: molecular weight (1203.99).

References

[1] Diele, S.; Goering, P. In *Handbook of Liquid Crystals*: Demus, D., Goodby, J., Gray, G.W., Spiess, H.-W., Vill, V., Eds.; VCH: Weinheim, 1998; Vol. 2B, pp 887–900.
[2] Diele, S. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 333–342.
[3] Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2647–2671.
[4] Tschierske, C. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 355–370.

[5] Vill, V.; Hashim, R. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 395–409.

[6] Impéror-Clerc, M. *Curr. Opin. Colloid Interface Sci.* **2005**, *9*, 370–376.

[7] Borisch, K.; Diele, S.; Göring, P.; Kresse, H.; Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529–543.

[8] Balagurusamy, V.S.K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539–1555.

[9] Yeardley, D.J.P.; Ungar, G.; Percec, V.; Holerca, M.N.; Johansson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684–1689.

[10] Percec, V.; Cho, W.-D.; Möller, M.; Prokhorova, S.A.; Ungar, G.; Yeardley, D.J.P. *J. Am. Chem. Soc.* **2000**, *122*, 4249–4250.

[11] Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D.J.P. *Chem. Eur. J.* **2002**, *8*, 2011–2025.

[12] Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujiie, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1969–1972.

[13] Nguyen, H.T.; Destrade, C.; Malthête, J. *Liq. Cryst.* **1990**, *8*, 797–811.

[14] Fang, Y.; Levelut, A.-M.; Destrade, C. *Liq. Cryst.* **1990**, *8*, 265–278.

[15] Seo, S.H.; Park, J.H.; Tew, G.N.; Chang, J.Y. *Tetrahedron Lett.* **2007**, *48*, 6839–6844.

[16] Schubert, H.; Hauschild, J.; Demus, D.; Hoffmann, S. *Z. Chem.* **1978**, *18*, 256.

[17] Demikhov, E.I.; Dolganov, V.K.; Korshunov, V.V.; Demus, D. *Liq. Cryst.* **1988**, *3*, 1161–1164.

[18] Kutsuzumi, S.; Mori, H.; Fukatani, M.; Naito, S.; Sakajiri, K.; Saito, K. *Chem. Mater.* **2008**, *20*, 3675–3687.

[19] Gray, G.W.; Jones, B.; Marson, F. *J. Chem. Soc.* **1957**, 393–401.

[20] Lindner, N.; Kölbel, M.; Sauer, C.; Diele, S.; Jokiranta, J.; Tschierske, C. *J. Phys. Chem. B* **1998**, *102*, 5261–5273.

[21] Ema, K.; Yao, H.; Takanishi, Y.; Takezoe, H.; Kusumoto, T.; Hiyama, T.; Yoshizawa, A. *Liq. Cryst.* **2002**, *29*, 221–225.

[22] Takanishi, Y.; Yoshida, S.; Ogasawara, T.; Ishikawa, K.; Takezoe, H.; Ema, K.; Yao, H.; Yoshizawa, A.; Kusumoto, T.; Hiyama, T. *Mol. Cryst. Liq. Cryst.* **2003**, *401*, 133–147.

[23] Guillevic, M.-A.; Bruce, D.W. *Liq. Cryst.* **2000**, *27*, 153–156.

[24] Nishikawa, E.; Yamamoto, J.; Yokoyama, H. *Chem. Lett.* **2001**, *30*, 94–95.

[25] Nishikawa, E.; Yamamoto, J.; Yokoyama, H. *Chem. Lett.* **2001**, *30*, 454–455.

[26] Lehmann, M.; Jahr, M. *Chem. Mater.* **2008**, *20*, 5453–5456.

[27] Donnio, B.; Heinrich, B.; Gulik-Krzywicki, T.; Delacroix, H.; Guillon, D.; Bruce, D.W. *Chem. Mater.* **1997**, *9*, 2951–2965.

[28] Nishikawa, E.; Samulski, E.T. *Liq. Cryst.* **2000**, *27*, 1463–1471.

[29] Levelut, A.-M.; Clerc, M. *Liq. Cryst.* **1998**, *24*, 105–116.

[30] Impéror-Clerc, M.; Veber, M.; Levelut, A.-M. *Chem Phys Chem* **2001**, *2*, 533–535.

[31] Kutsumizu, S.; Morita, K.; Yano, S.; Nojima, S. *Liq. Cryst.* **2002**, *29*, 1459–1468.

[32] Zeng, X.B.; Unger, G.; Impéror-Clerc, M. *Nature Mater.* **2005**, *4*, 562–567.

[33] Zeng, X.B.; Cseh, L.; Mehl, G.H.; Unger, G. *J. Mater. Chem.* **2008**, *18*, 2953–2961.

[34] Gray, G.W.; Hartley, J.B.; Jones, B. *J. Chem. Soc.* **1955**, 1412–1420.

[35] Demus, D.; Kunicke, G.; Neelsen, J.; Sackmann, H. *Z. Phys. Chem.* **1974**, *255*, 71–81.

[36] Tao, Y.-T.; Lee, M.-T. *Thin Solid Films* **1994**, *244*, 810–814.

[37] Ujiie, S.; Mori, A. *Mol. Cryst. Liq. Cryst.* **2005**, *437*, 25–31.

[38] Ichihara, M.; Suzuki, A.; Hatsusaka, K.; Ohta, K. *Liq. Cryst.* **2007**, *34*, 555–567.

[39] Kutsumizu, S.; Yamada, M.; Yamaguchi, T.; Tanaka, K.; Akiyama, R. *J. Am. Chem. Soc.* **2003**, *125*, 2858–2859.

[40] Kutsumizu, S.; Hosoyama, K.; Yamada, M.; Tanaka, K.; Akiyama, R.; Sakurai, S.; Funai, E. *J. Phys. Chem. B* **2009**, *113*, 640–646.

[41] Maeda, Y.; Mori, H.; Kutsuzumi, S. *Liq. Cryst.* **2009**, *36*, 217–223.

[42] Mori, A.; Takeshita, H.; Kida, K.; Uchida, M. *J. Am. Chem. Soc.* **1990**, *112*, 8635–8636.

[43] Mori, A.; Taya, H.; Takeshita, H. *Chem. Lett.* **1991**, *20*, 579–580.

[44] Mori, A.; Hirayama, K.; Kato, N.; Takeshita, H.; Ujiie, S. *Chem. Lett.* **1997**, *26*, 509–510.

[45] Mori, A.; Taya, H.; Takeshita, H.; Ujiie, S. *J. Mater. Chem.* **1998**, *8*, 595–597.

[46] Mori, A.; Takemoto, M.; Vill, V. *Chem. Lett.* **1998**, *27*, 617–618.

[47] Mori, A.; Kato, N.; Takeshita, H.; Nimura, R.; Isobe, M.; Jin, C.; Ujiie, S. *Liq. Cryst.* **2001**, *28*, 1425–1433.

[48] Takemoto, M.; Mori, A.; Ujiie, S.; Vill, V. *Liq. Cryst.* **2002**, *29*, 687–695.

[49] Mori, A.; Uchida, M.; Takeshita, H. *Chem. Lett.* **1989**, *18*, 591–592.

[50] Kida, K.; Mori, A.; Takeshita, H. *Mol. Cryst. Liq. Cryst.* **1991**, *199*, 387–391.

[51] Mori, A.; Kato, N.; Takeshita, H.; Uchida, M.; Taya, H.; Nimura, R. *J. Mater. Chem.* **1991**, *1*, 799–803.

[52] Mori, A.; Mori, R.; Takeshita, H. *Chem. Lett.* **1991**, *20*, 1795–1796.

[53] Mori, A.; Takematsu, S.; Takeshita, H. *Chem. Lett.* **1997**, *26*, 1009–1010.

[54] Mori, A.; Uno, K.; Kubo, K.; Kato, N.; Takeshita, H.; Hirayama, K.; Ujiie, S. *Liq. Cryst.* **2004**, *31*, 285–294.

[55] Shefelbine, T.A.; Vigild, M.E.; Matsen, M.W.; Hajduk, D.A.; Hillmyer, M.A.; Cussler, E.; Bates, F.S. *J. Am. Chem. Soc.* **1999**, *121*, 8457–8465.

[56] Pindzola, B.A.; Jin, J.; Gin, D.L. *J. Am. Chem. Soc.* **2003**, *125*, 2940–2949.

[57] Lattermann, G. *Mol. Cryst. Liq. Cryst.* **1990**, *182B*, 299–311.

[58] Tiddy, G.J.T. *Phys. Rep.* **1980**, *57*, 1–46.

[59] Fazio, D.; Mongin, C.; Donnio, B.; Galerne, Y.; Guillon, D.; Bruce, D.W. *J. Mater. Chem.* **2001**, *11*, 2852–2863.

[60] Hashimoto, M.; Ujiie, S.; Mori, A. *Adv. Mater.* **2003**, *15*, 797–800.

[61] Mori, A.; Yokoo, M.; Hashimoto, M.; Ujiie, S.; Diele, S.; Baumeister, U.; Tschierske, C. *J. Am. Chem. Soc.* **2003**, *125*, 6620–6621.