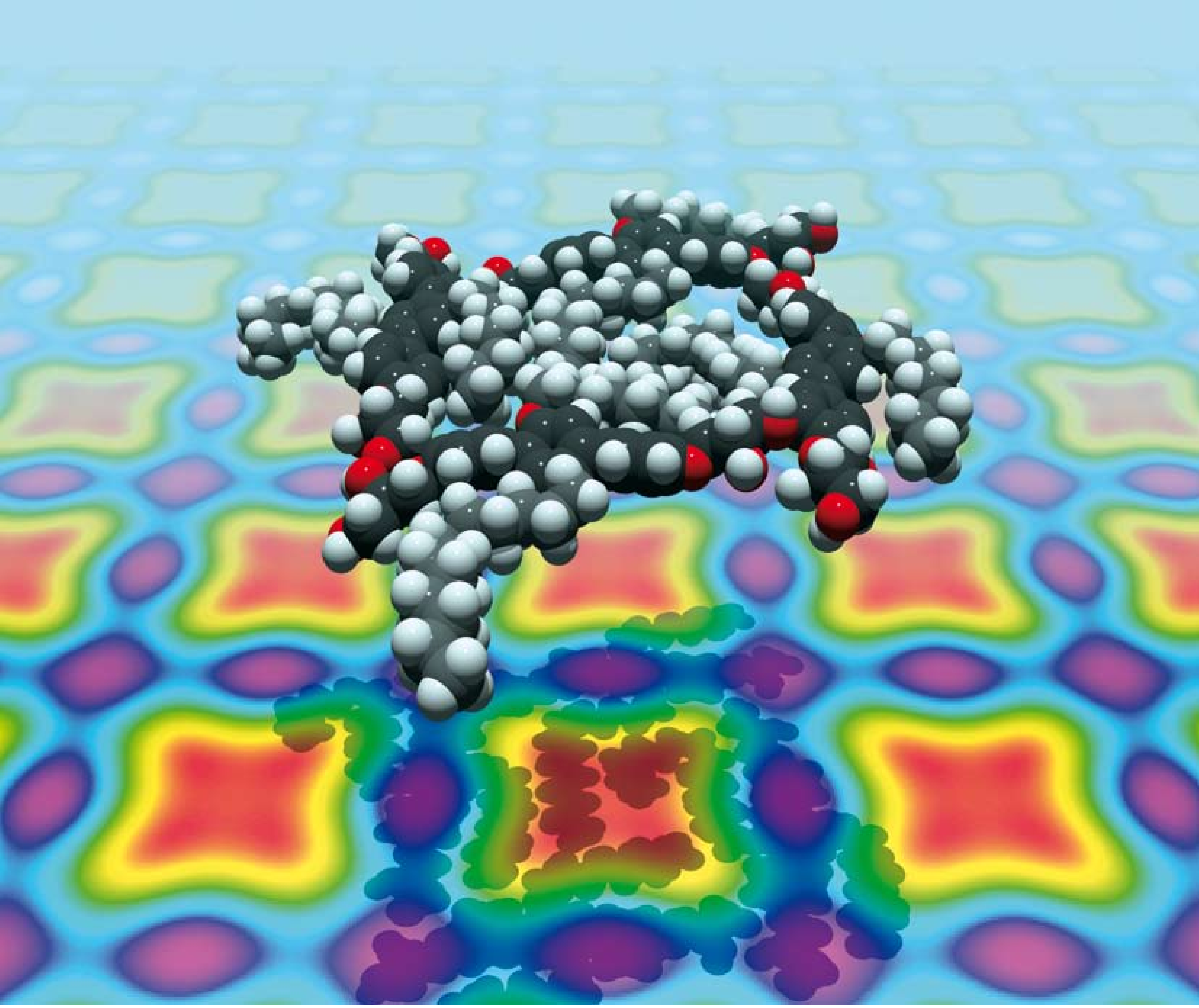
ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 33 | 7 September 2008 | Pages 3809–3940



ISSN 1359-7345

RSC Publishing

COMMUNICATION
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FEATURE ARTICLE
Kei Manabe and Shupei Ishikawa
Oligoarenes as molecular backbones of catalysts: synthesis and applications

1359-7345(2008)33;1-0

X-Shaped polyphilics: liquid crystal honeycombs with single-molecule walls†

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Received (in Cambridge, UK) 25th March 2008, Accepted 16th April 2008
First published as an Advance Article on the web 20th May 2008
DOI: 10.1039/b804945a

X-Shaped ternary five-block molecules, composed of a rigid *tp*-terphenyl core, two terminal glycerol groups and two flexible *n*-alkyl or semiperfluorinated chains fixed laterally to opposite sides of the terphenyl moiety, form liquid crystalline phases built up of honeycomb-like arrays of polygonal cylinders, where the rod-like aromatic cores form cylinder walls with a thickness equal to the width of a single molecule.

T-shaped ternary amphiphiles have turned out to be a valuable source of new superstructures in ordered soft matter systems.[1] Most of their self assembled structures represent honeycomb-like polygonal cylinder arrays which are fundamentally new types of liquid crystalline (LC) materials, distinct from the classical types.[2] T-Shaped bolaamphiphiles, composed of a rod-like core, two polar end groups and a flexible lipophilic lateral chain show the widest variety of cylinder structures.[3] In these cylinder arrays the rod-like aromatic cores form the cylinder walls, the polar terminal groups are located at the edges which bond the individual cylinders together and the lateral chains fill the interior (see Fig. 1(a)).[1,3] Depending on the size of the lateral chains the cross section of the cylinders changes from squares, *via* pentagons, hexagons to giant hexagons and giant pentagons.[1,3] From a molecular structural point of view these block molecules represent π-conjugated systems with flexible lateral chains and functional terminal groups. Such π-conjugated oligomers and polymers have received significant attention as organic electronic materials.[4] Hence, investigation of relatively small model systems, related to the larger oligomers and polymers, provides insight into the fundamental principles of self assembly in these systems. Moreover, from a superstructural point of view these LC honeycombs are related to plane nets obtained with the node-and-spacer concept used in crystal engineering with coordination polymers.[5]

In previous work only one lateral substituent was attached to the rod-like core which gave rise to LC cylinder phases where the walls of the cylinders were formed by two rods arranged side-by-side (Fig. 1(a)).[1,3] Hence the question arose if polygonal honeycombs could be generated with only one molecule thick walls (Fig. 1(b)). For this purpose three series of compounds with two flexible chains, attached at lateral positions on both sides of the rigid core, were synthesized. Molecules **A** with two identical lateral alkyl chains, molecules of type **B** with two different alkyl chains and compounds **C** having two semiperfluorinated lateral chains. The LC phases and phase transition temperatures, determined by DSC and polarizing microscopy are collated in Table 1.

In the series of alkyl substituted compounds **A** the LC phases were only observed as monotropic (metastable) phases for molecules with relatively short chains and the LC phases were lost by increasing the chain length. Melting temperatures were significantly reduced, if the two alkyl chains had different lengths (compounds **B**). However, increasing the chain length difference also reduces the stability of the LC phases (compare compounds **B1**–**B3**).

Hence, only compound **B1** forms a stable (enantiotropic) LC phase. Its optical texture consists of homeotropically aligned regions appearing completely dark between crossed polarizers, birefringent filament-like defects and spherulitic domains (see Fig. 2(b)); this indicates a uniaxial columnar phase. X-Ray investigations show only diffuse scattering at wide angles (d = 0.45 nm, corresponding to the mean distance between the alkyl chains and between the aromatic parts, see Fig. 2(a)), confirming the liquid crystalline nature of this phase. The small angle region is characterized by three Bragg reflections with a reciprocal spacing ratio $1 : 2^{1/2} : 2$ (Fig. 2(a)) indexed as (10), (11) and (20) of a square lattice (Col$_{\mathrm{squ}}$/$p4mm$) with the cell parameter a_{squ} = 2.43 nm. This lattice parameter is consistent with the molecular length of L = 2.4–2.6 nm between the ends of the glycerol groups in a stretched

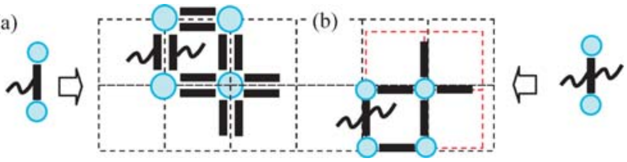

Fig. 1 (a) Double-wall and (b) single-wall square cylinder phases (Col$_{\mathrm{squ}}$/$p4mm$) formed by T- and X-shaped bolaamphiphiles, respectively; view along the cylinder axis.

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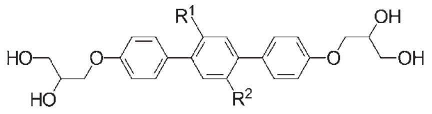
† Electronic supplementary information (ESI) available: Synthesis, analytical data, textures, calorimetric and X-ray data and details of the methods. See DOI: 10.1039/b804945a

Table 1 Data of compounds **A–D**[a]



A: $R^1 = R^2 = OC_nH_{2n+1}$
B: $R^1 = OC_nH_{2n+1}$; $R^2 = OC_mH_{2m+1}$
C: $R^1 = R^2 = O(CH_2)_6\text{-}C_nF_{2n+1}$
D: $R^1 = O(CH_2)_6\text{-}C_nF_{2n+1}$; $R^2 = H$

Compd	*n*	*m*	T/°C	a/nm	n_{wall}
A1	12		Cr 86 ($Col_{squ}/p4mm$ 64) Iso	2.48	1.1
A2	14		Cr 83 (M 65) Iso	—	—
A3	16		Cr 71 Iso	—	—
A4	18		Cr 65 Iso	—	—
B1	14	8	Cr 58 $Col_{squ}/p4mm$ 67 Iso	2.43	1.1
B2	16	6	Cr 90 ($Col_{squ}/p4mm$ 37) Iso	2.42	1.1
B3	18	4	Cr 52 Iso	—	—
C1	4		Cr 64 $Col_{squ}/p4mm$ 92 Iso	2.61	1.2
C2	6		Cr 79 Col_{hex} 98 Iso	3.87	1.3
C3	8		Cr 44 Col_{hex}106 Lam_{Iso}116 Iso	4.01[b]	1.3
C4	10		Cr 71 Lam_{Iso} 158 Iso	3.56[c]	—
D	8		Cr 87 Col_{hex} 229 Iso	4.24	2.1

[a] Transition temperatures (T) were determined from first DSC heating scans (10 K min^{-1}); for synthesis, analytical data, transition enthalpy values, textures and X-ray data (Table S1), see ESI;† abbreviations: Cr = crystalline solid, $Col_{squ}/p4mm$ = square columnar phase with plane group $p4mm$ (square cylinders), Col_{hex}, hexagonal columnar phase (regular hexagonal cylinders), Lam_{iso} = lamellar phase without in-plane order, M = unknown mesophase; Iso = isotropic liquid, a = lattice parameter, n_{wall} = number of molecules in the cross section of the cylinder walls (for calculation, see Table S2, ESI†). [b] Layer spacing for the Lam_{Iso} phase is 3.28 nm. [c] Layer spacing.

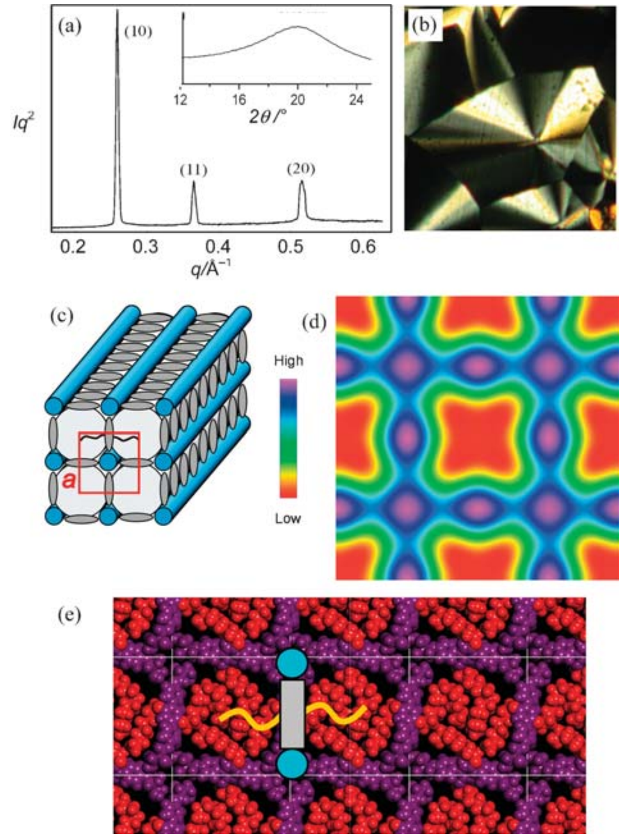


Fig. 2 Compound **B1**: (a) X-ray diffraction pattern at 50 °C on cooling; (b) texture as seen between crossed polarizers (65 °C, the dark areas are homeotropically aligned regions); (c) model showing the organization of the molecules in the $Col_{squ}/p4mm$ phase; (d) electron density map, reconstructed from the diffraction pattern (a); (e) snapshot of a molecular dynamics simulation of the structure viewed down the column axis (for details see ESI†); for easy comparison with (d), color coding is as follows: red = alkyl chains, purple = terphenyls and glycerol units; in addition the position of one molecule is shown.

conformation. Taking this into account it is reasonable to assume that the terphenyl moieties assemble into a honeycomb-like cylinder array with a square cylinder cell cross section. The terphenyls form the cylinder walls and the glycerol units constitute the edges of the square prisms. In a hypothetical 3D unit cell with an assumed one-molecule thickness of 0.45 nm (position of the maximum of the diffuse wide angle scattering), the number of molecules is calculated as n_{cell} = 2.2 on average (see Table S2, ESI†). This means there is an average intercellular wall thickness of approximately only one terphenyl unit (n_{wall} = 1.1).‡ The proposed model (Fig. 2(c)) is in good agreement with the reconstructed electron density map (Fig. 2(d)) which was obtained from the small angle diffraction intensities measured from a powder pattern (synchrotron radiation, see ESI†). The map shows a four-leaf clover shaped low-electron-density region (red/yellow/green) assigned to the alkyl cells filling. The high-electron-density areas (blue/purple), located at the cylinder walls, are assigned to the electron-rich aromatic and glycerol units. The snapshot of the molecular dynamics simulation (Fig. 2(e)) confirms efficient space filling and phase separation achieved by this structure. This type of structure is also proposed for the monotropic Col_{squ} phases of compounds **A1** and **B2** and it is significantly stabilized if the alkyl chains are replaced by semiperfluorinated chains (compound **C1**). The Col_{squ} phases in all four compounds **A1**, **B1**, **B2** and **C1** have nearly the same lattice parameters (a_{squ} = 2.4–2.6 nm) and can be described as single-wall square cylinder phases (see Table 1).

By introducing fluorinated segments an enlargement of the lateral chains is possible without losing the LC properties (compounds **C1–C4**). This enables the formation of other cylinder phases (see Fig. 3). A hexagonal columnar phase (Col_{hex}) was observed for compounds **C2** and **C3** (for textures and X-ray data see Fig. S3 and S4a, ESI†). In both cases the lattice parameter (a_{hex} = 3.9–4.0 nm) is close to $3^{1/2}$ times the molecular length L, which is in line with a honeycomb structure composed of hexagonal cells (Fig. 3(b)).§ The cell wall thickness n_{wall} is about 1.3 molecules on average.‡¶ For compound **C3** a phase transition is seen at 106 °C upon heating (see Fig. S4 and S5, ESI†), and at this temperature the cylinder structure bursts, giving way to a lamellar phase (d = 3.28 nm). Compound **C4** with the longest chains forms this lamellar phase exclusively (d = 3.56 nm). In the lamellar phases the lateral chains and the bolaamphiphilic cores are organized in distinct sublayers.[3b,c,6] A fan like texture, with large black homeotropically aligned regions is observed in this temperature range under a polarizing microscope. Thus the

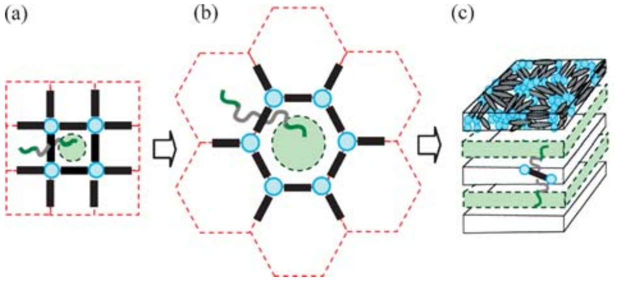


Fig. 3 Transition from (a) the square cylinder phase (Col$_{squ}$/*p*4*mm*) *via* (b) the hexagonal cylinder phase (Col$_{hex}$/*p*6*mm*, views along the cylinder long axis) to (c) the Lam$_{Iso}$ phase as observed for the series of compounds **C1–C4** upon elongation of the perfluorinated segment.

layer phase is optically uniaxial. Studies of birefringence[6d] have indicated that the terphenyl cores are randomly oriented within the layers (Lam$_{Iso}$ phase, see Fig. 3(c)), rather than ordered orientationally or orientationally and positionally as in the Lam$_N$ or Lam$_{Sm}$ phases, respectively, observed for bolaamphiphiles with only one side-chain.[3b,c,6]‖

It is interesting that in spite of losing the ability of parallel alignment in layers, the aromatic cores with two lateral chains retain the capacity to form cylinders. However, addition of the second lateral chain does destabilize the cylinder structures to a certain extent which is apparent if compound **C3** is compared with **D**, having only one lateral chain (Table 1). Compound **D** displays the Col$_{hex}$ cylinder phase in an extremely broad temperature range, with the clearing temperature more than 100 °C higher than that of **C3**. Consistent with all previously reported LC cylinder phases of T-shaped bolaamphiphiles, the cylinder walls in compound **D** are two molecules thick (n_{wall} = 2.1).

In summary, it was shown for the first time that it is indeed possible to design molecules capable of forming LC phases built up by single-molecule-wall polygonal honeycomb lattices. This was achieved by attaching lateral chains at both sides of the rod-like core of bolaamphiphiles. The second chain prevents the molecules from adopting a side-by-side arrangement, removing the double-wall cylinder option. In the single-wall cylinder phases the rotation of the aromatic cores around their long axes is likely to be restricted more than in the double-wall phases of the single chain compounds, which could lead to a closer packing of the cores. In view of this, the present investigation also provides clues for molecular design of π-conjugated oligomers and polymers capable of forming well defined functional superstructures.[3e] Finally, making the two lateral chains different could be an avenue to new types of LC phases where the interior of neighbouring cells is different.

This work, as part of the European Science Foundation EUROCORES programme SONS, project SCALES, was supported by funds from the DFG, EPSRC and the EC Sixth Framework Programme, under contract No. ERAS-CT-2003-989409 and by the Government of Sachsen–Anhalt in the framework of the Cluster of Excellence "Nanostructured Materials". We thank Dr P. Boesecke for help with the experiment on station ID02 and ESRF for the beamtime.

Notes and references

‡ The superstructures reported herein represent ordered fluids, which means that there is a high degree of conformational, rotational and translational mobility as indicated by the diffuse character of the wide angle scattering seen by X-ray diffraction. Hence, these are highly dynamic systems where the number of molecules per unit cell is an average value. Also the number of molecules in the cross section of the cylinder walls (n_{wall}) is an average number which does not necessarily represent an integer number. Hence, the cylinder walls can also be slightly thicker than exactly one molecule.

§ Most likely there is segregation of the perfluorinated segments from the aliphatic spacer units in the square and hexagonal cylinder cells, leading to a core–shell morphology as described for the cylinder phases of T-shaped bolaamphiphiles with semiperfluorinated lateral chains.[3d] Similarly, as shown in Fig. 3(c), in the lamellar phases the nonpolar layers should be subdivided into two alkyl chain layers and an R$_F$-layer in the middle. Hence, compounds **C1–C4** can be regarded as quaternary heptablock molecules. The additional segregation, due to the fluorophobic effect, also contributes to the significant mesophase stabilization upon elongation of the R$_F$ segment from **C1** to **C4** (see Table 1).[3,7] Moreover, these fluorous microenvironments within the polygonal cylinders are of interest for accommodation of fluorous guest molecules (which could change the phase structure) and as microreactors.[8]

¶ The average thickness of the cylinder walls increases slightly with reduction of the valence *v* of the edges (number of cylinder walls interconnected at these edges) from Col$_{squ}$ (v = 4) to Col$_{hex}$ (v = 3). For the Lam$_{Iso}$ phases it can be estimated that between 1.5 and 2.0 molecules are organized in the cross section of the aromatic layers. A similar increase was also observed for T-shaped bolaamphiphiles, where n_{wall} is around two for the cylinder phases and about three molecules are organized side-by-side in the aromatic layers of the Lam phases.[3,6]

‖ In the layers of the lateral chains the R$_F$ chains should be interdigitated, but detailed structure of these Lam phases will be the subject of a separate publication.

1 (*a*) C. Tschierske, *Chem. Soc. Rev.*, 2007, **36**, 1930–1970; (*b*) B. Chen, X. B. Zeng, U. Baumeister, G. Ungar and C. Tschierske, *Science*, 2005, **307**, 96–99.
2 D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, 1998.
3 (*a*) M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.*, 2001, **123**, 6809–6818; (*b*) X. H. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume and C. Tschierske, *J. Am. Chem. Soc.*, 2003, **125**, 10977–10996; (*c*) X.-H. Cheng, M. K. Das, U. Baumeister, S. Diele and C. Tschierske, *J. Am. Chem. Soc.*, 2004, **126**, 12930–12940; (*d*) M. Prehm, F. Liu, U. Baumeister, X. Zeng, G. Ungar and C. Tschierske, *Angew. Chem., Int. Ed.*, 2007, **46**, 7972–7975; (*e*) M. Prehm, G. Götz, P. Bäuerle, F. Liu, G. Ungar and C. Tschierske, *Angew. Chem., Int. Ed.*, 2007, **46**, 7856–7859.
4 A. P. H. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245–3258.
5 (*a*) S. Leiningen, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (*b*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658; (*c*) K. Takaoka, M. Kawano, M. Tominaga and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 2151–2154.
6 (*a*) M. Prehm, X.-H. Cheng, S. Diele, M. K. Das and C. Tschierske, *J. Am. Chem. Soc.*, 2002, **124**, 12072–12073; (*b*) X.-H. Cheng, M. K. Das, S. Diele and C. Tschierske, *Angew. Chem., Int. Ed*, 2002, **41**, 4031–4035; (*c*) N. M. Patel, M. R. Dodge, M.-H. Zhu, R. G. Petschek, C. Rosenblatt, M. Prehm and C. Tschierske, *Phys. Rev. Lett.*, 2004, **92**, 015501; (*d*) N. M. Patel, I. M. Syed, C. Rosenblatt, M. Prehm and C. Tschierske, *Liq. Cryst.*, 2005, **32**, 55–61.
7 G. Johansson, V. Percec, G. Ungar and J. P. Zhou, *Macromolecules*, 1996, **29**, 646–660.
8 S. Sato, J. Iida, K. Suzuki, M. Kawano, T. Ozeki and M. Fujita, *Science*, 2006, **313**, 1273–1276.