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Liquid crystals

Liquid-Crystal Engineering with Anchor-Shaped Molecules: Honeycombs with Hexagonal and Trigonal Symmetries Formed by Polyphilic Bent-Core Molecules**

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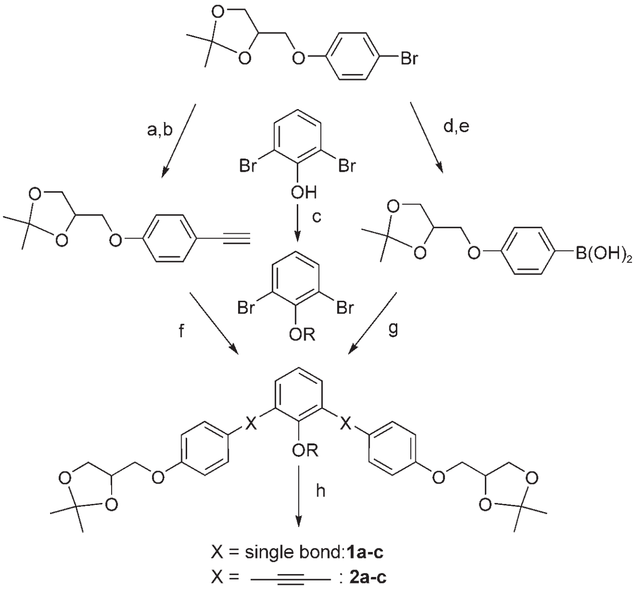
The design of programmed molecules capable of organizing in a predictable way to form complex superstructures is an attractive target of contemporary research.[1] Supramolecular chemistry and crystal engineering have advanced largely by using the node and spacer approach for the construction of polygonal frames and infinite 2D or 3D nets by means of coordination chemistry.[2] Chevron-shaped bidentate ligands have been used for the design of discrete supramolecular hexagons[3] and polyhedra either in solution or in the crystalline state.[4] In contrast to solid-state structures, which, once formed, cannot be modified, liquid crystals (LCs) can easily respond to external stimuli by changing their organization.[5,6] In recent years chevron-shaped (bent-core) LC molecules have attracted significant interest, owing to their ability to exhibit ferroelectric and antiferroelectric properties.[7] Herein we use polyphilic molecules with a bent aromatic core to design two new types of honeycomb-like LC phases with hexagonal, and for the first time, also with trigonal symmetry.

For this purpose, π-conjugated bent aromatic cores were functionalized at the ends with glycerol units, capable of forming cooperative hydrogen bonds, and with a long, flexible nonpolar chain (either alkyl or semiperfluoroalkyl) attached to the bay region, that is, to the 2-position of the central benzene ring of the bent core. This approach resulted in a new type of LC molecule with anchor-like shape. Two types of molecules were synthesized as shown in Scheme 1, according to the methods described in the Supporting Information;[8–11] one based on a relatively short *m*-terphenyl core (compounds **1a**–**c**), the other based on a larger tolane-derived bent moiety (compounds **2a**–**c**) with additional triple bonds inserted between the benzene rings of the *m*-terphenyl core of compounds **1a**–**c**.



Scheme 1. Synthesis of compounds **1** and **2**: Reagents and conditions: a) $\text{H-C}\equiv\text{C-SiMe}_3$, $[\text{Pd(PPh}_3)_4]$, CuI, Et_3N, reflux;[9] b) KOH, MeOH, 20 °C;[9] c) RBr ($\text{R}=\text{C}_{12}\text{H}_{25}$, $\text{-(CH}_2)_n\text{C}_m\text{F}_{2m+1}$[10]), K_2CO_3, CH_3CN, reflux, 20 h, d) *n*BuLi, THF, B(OMe)_3, −85 °C; e) $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4/\text{H}_2\text{O}$;[17b] f) $[\text{Pd(PPh}_3)_4]$, CuI, Et_3N, reflux, 5 h;[9] g) $[\text{Pd(PPh}_3)_4]$, NaHCO_3, glyme, H_2O, reflux, 6 h;[11] h) compounds **1a**–**c**: 10% HCl, MeOH, reflux, 6 h; compounds **2a**–**c**: pyridinium 4-toluenesulfonate, MeOH, reflux, 6 h.

All compounds with a sufficiently long chain in the bay position (**1b**,**c** and **2a**–**c**) form hexagonal columnar (Col_{hex}) LC phases (Table 1). The phases were identified by their textures (Figure 1a, and Supporting Information, Figure S1), indicating optically uniaxial columnar LC phases, and from the $1{:}3^{1/2}{:}2{:}7^{1/2}$ ratio of reciprocal small-angle X-ray spacings,

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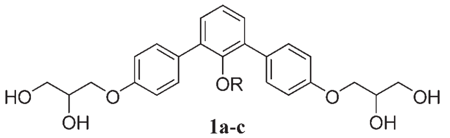
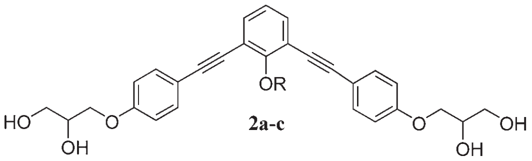
Table 1: LC Phase transitions and other parameters of compounds **1** and **2**.[a]





Comp.	R	T [°C] [ΔH/kJ mol^{-1}]	a_{hex} [nm]	n_{cell}	n_{wall}
1a	$(CH_2)_6C_4F_9$	Cr 130 [18.1] Iso			
1b	$(CH_2)_4C_6F_{13}$	Cr 135 [24.3] (Col$_{hex}$ 132 [n.d.[b]]) Iso			
1c	$(CH_2)_{11}C_8F_{17}$	Cr 121 [9.9] Col$_{hex}$/*p6mm* 137 [12.3] Iso	4.37	6.0	2.0
2a	$C_{12}H_{25}$	Cr 94 [24.5] (Col$_{hex}$/*p*3*m*1 85 [6.3]) Iso	2.82	3.1	2.1
2b	$(CH_2)_4C_6F_{13}$	Cr 63 [4.6] Col$_{hex}$/*p*3*m*1 190 [18.4] Iso	2.88	3.1	2.1
2c	$(CH_2)_{11}C_8F_{17}$	Cr 77 [10.5] Col$_{hex}$/*p6mm* 140 [8.5] Iso	5.12	7.8	2.6

[a] Transition temperatures and enthalpies (values in square brackets) were recorded by DSC (10 K min^{-1}) and confirmed by polarizing microscopy, values in round brackets refer to monotropic (metastable) mesophases; abbreviations: Cr = crystalline solid, Col$_{hex}$/*p6mm* and Col$_{hex}$/*p*3*m*1 = hexagonal columnar LC phases with *p6mm* and *p*3*m*1 lattices, respectively, Iso = isotropic liquid, a_{hex} = hexagonal lattice parameter, n_{cell} = number of molecules in a 3-d unit cell defined assuming a height of 0.45 nm, and n_{wall} = number of molecules found in the cross section of the cylinder walls (calculation of these values is described in the SI) [12]; [b] not determined due to rapid crystallization.

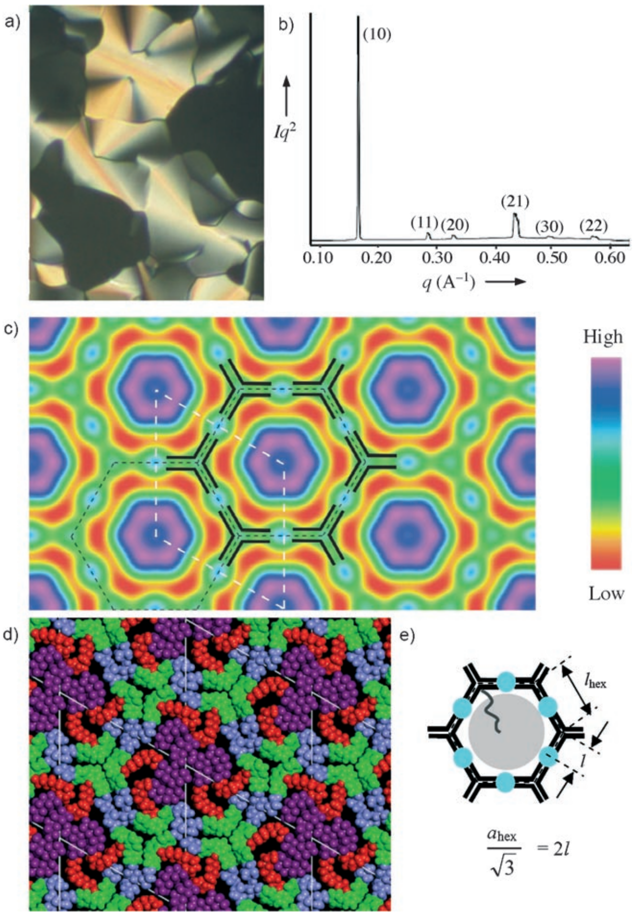


Figure 1. Col$_{hex}$/*p6mm* phase of compound **1c**: a) texture between crossed polarizers at T = 135 °C; b) X-ray diffraction pattern (small angle region) at 127 °C; c) reconstructed electron density map. See text for details and color coding; d) snapshot of a molecular dynamics simulation (for easy comparison the color coding is the same as in (c); e) model of molecular organization; blue circles represent hydrogen bonding networks of glycerol groups, black wavy lines represent semiperfluorinated chains; c–e) viewed along the cylinder axis.

typical of a two-dimensional hexagonal lattice (Figure 1b, and Supporting Information, Figure S2). In all Col$_{hex}$ phases the wide-angle diffraction is diffuse (Supporting Information, Figure S2b), confirming that these are true LC phases. Remarkably, there are two distinct types of Col$_{hex}$ phases. The Col$_{hex}$ phases of **2a** and **2b** with the larger tolane-based bent core have relatively small hexagonal lattice parameters (a_{hex}) around 2.8–2.9 nm. On the other hand compound **2c** with the longest alkyl chain (R), as well as the *m*-terphenyl-based compound **1c** with the shorter bent core have significantly larger a_{hex} values of approximately 5.1 and 4.4 nm, respectively. This striking difference suggests that the Col$_{hex}$ phases of these compounds have distinctly different structures.

We focus first on compounds **1c** and **2c**, which have large lattice parameters. A 0.45 nm-high unit cell contains six molecules of the *m*-terphenyl derivative **1c** (Table 1).[12] Therefore, we propose a model where six bent aromatic units of **1c** form the circumference of a hexagonal cylinder (6-hexagon, see Figure 1e). The individual molecules are interconnected by rows of hydrogen bonding running lengthwise along the middle of each cylinder wall. These H-bonding networks also help glue the cylinders together into a double-walled hexagonal honeycomb. The cells of this honeycomb lattice are filled by the long semiperfluorinated chains. The side length of the hexagons (l_{hex}) is related to the hexagonal lattice parameter (a_{hex}) through $l_{hex} = a_{hex}/3^{1/2}$. A side of the hexagon is made up of two arms (of length $l = l_{hex}/2$), one from each of the two adjacent chevron molecules. From the a_{hex}-value of compound **1c**, it can be calculated that the distance l between the end of the diol group and the apex of the molecule is 1.3 nm, in agreement with the molecular model. The proposed phase structure was confirmed by the electron-density map $\rho(x,y)$, reconstructed from small-angle diffraction intensities (synchrotron radiation). In the map (Figure 1c), fluorinated segments comprise the areas of highest electron density ρ (purple), followed by the small regions of glycerol groups (deep blue dots) and the aromatic cores (large green regions). The position of some molecules is indicated in Figure 1c by black chevrons. The alkyl segments of the semiperfluorinated chains account for the lowest density (yellow/red) moats surrounding the fluorinated regions. Figure 1d shows a snapshot of a molecular dynamics simulation of one molecular layer ($c = 0.45$ nm) after annealing, with periodic boundaries defined by the experimentally determined unit cell. The simulation confirms efficient space-filling and microphase separation.

The structure of the Col$_{hex}$ phase formed by compound **2c** with a tolane-based bent core is fundamentally the same as that described for **1c**, but, owing to the larger aromatic core ($l = 1.5$ nm for each arm, compared to $l = 1.3$ nm for **1c**), the hexagonal lattice parameter is enlarged to $a_{hex} = 5.12$ nm.

For compounds **2a** and **2b,** with the same tolane-based core as **2c**, but with shorter chains, the lattice parameter ($a_{hex} \approx 2.8$–2.9 nm) is nearly half that for **2c** ($a_{hex} = 5.12$ nm) and the number of molecules per unit cell is only three, suggesting that for these compounds only three molecules form a cylinder frame (Table 1).[12] As shown in Figure 2c and g, this result is achieved if every other corner of the hexagonal frame contains glycerol groups, the other corners being the apexes of the aromatic chevrons.[13] In this structure, the symmetry is reduced to trigonal (plane group $p3m1$). Constructing an electron-density map for this non-centrosymmetric structure is rather ambiguous since the phase angle of most reflections can take up any value, rather than being limited to 0 and π as in the centrosymmetric group $p6mm$. For this reason we resorted to building mesoscale $\rho(x,y)$ models of likely structures using relative ρ values and volume fractions of the different molecular regions, calculated from molecular models (see Supporting Information, Table S6). The geometric models of the electron-density maps for compounds **2a** and **2b**, respectively, are shown in Figures 2a and e, and consist of polygons of fixed ρ values (the same colour code is used as in Figure 1). The structure factor amplitudes F_{hk} and phase angles ϕ_{hk} are calculated analytically from the models. A reasonably good match between observed and calculated (F^2_{hk}) intensities is obtained (see Supporting Information, Tables S7a,b). Using the ϕ_{hk} values thus obtained, together with amplitudes $I^{1/2}_{hk}$ from measured intensities I_{hk}, "experimental" electron-density maps are calculated (see Figures 2c,g). The match between the models and the real structures can best be judged by comparing the experimental maps (Figures 2c,g) with those Fourier-reconstructed from the models (Figures 2b,f, respectively). For the comparison to be meaningful, in the reconstructions in Figures 2b,f we used the same range of h and k, that is, the same number of Fourier terms, as in the reconstructions in Figures 2c,g.[14]

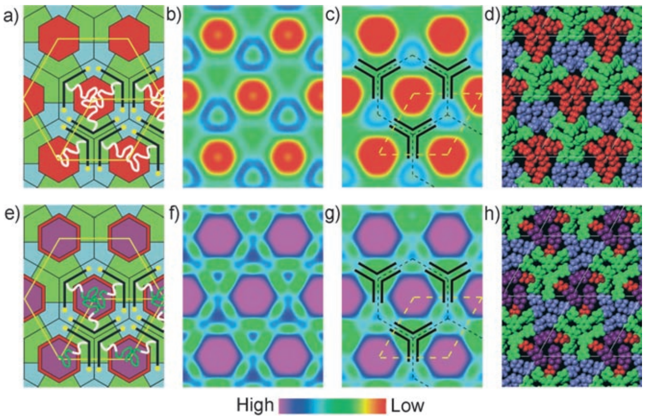


Figure 2. Col$_{hex}$/$p3m1$ phases viewed along the cylinder long axis: a–d) compound **2a**; e–h) compound **2b**; a,e) model electron density maps; b,f) Fourier-approximated model maps; c,g) maps calculated from the diffraction data; d,h) snapshots of molecular dynamics simulations; the color code is the same as used in Figure 1 (see text for details).

The above procedure thus confirms the proposed 3-hexagon structure of the trigonal Col$_{hex}$/$p3m1$ honeycomb phase. At the same time, the results illustrate the usefulness of the procedure itself. To our knowledge, this is the first electron-density structure determination of a non-centrosymmetric liquid crystal, and also the first report of a LC phase with trigonal symmetry.[15] Note that the Laue symmetry (the symmetry of the diffraction pattern) of a trigonal structure is still hexagonal $p6mm$, hence common X-ray techniques would fail to detect a trigonal liquid crystal. Again, dynamics simulations (Figures 2d,h) do not contradict the proposed structures. The non-centrosymmetric mode of self assembly in this LC system is of potential interest for nonlinear optics applications.[16]

Overall, the structures of the LC phases of the bent-core bolaamphiphiles are governed by the 120° bend of the aromatic core, which favors the formation of hexagonal honeycombs. There are two distinct types of hexagons, 3-hexagons and 6-hexagons, leading to $p3m1$ and $p6mm$ lattices, respectively. Either enlarging the perimeter of the hexagons by extending the chevron-shaped core, or reducing the volume of the chains, can lead to the change from 6-hexagons to 3-hexagons. The defining parameter is the ratio between the length of the backbone and the volume of the attached chains, that is, the circumference/area ratio of the polygon. A similar relation was found for the cylinder phases formed by linear tectons (T-shaped bolaamphiphiles).[17,18] However, in the cylindrical arrays of linear compounds, the hydrogen bonding networks were located at the nodes of the honeycomb (Figure 3a).[17] In the $p3m1$ phases of compounds **2a,b** (Figure 3c) only every other node contains H-bonds, whereas in the $p6mm$ phase of compounds **1c** and **2c** (Figure 3b) none of the nodes do. Instead, H-bonds are located within the walls,

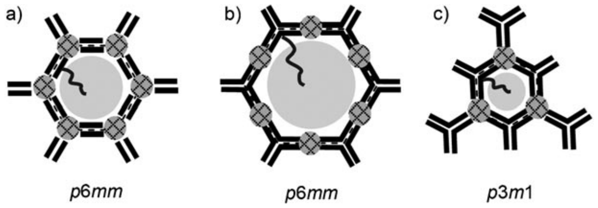


Figure 3. Comparison of hexagonal honeycombs formed by a) linear and b,c) bent-core bolaamphiphiles; columns containing the hydrogen bonding networks are represented by cross-hatched circles.

and the bends in the cores are found at the nodes. In this respect, the present hexagonal structure is the inverse of all previously reported hexagonal LC cylinder phases formed by T-shaped molecules.[17–19]

In summary, it has been shown that the fundamental design principles, developed for the construction of individual polygonal supermolecules and polygonal grids in solid-state chemistry[2,20] can successfully be applied to the design of new ordered soft-matter structures by means of liquid-crystal engineering.

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[1] J. W. Steed, J. L. Atwood, *Encyclopedia of Supramolecular Chemistry*, Marcel Dekker, New York, **2004**; J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.

[2] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327; S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417–425.

[3] Hexagonal grids by metal coordination: T. Yamamoto, A. M. Arif, P. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309–12317; H.-B. Yang, A. M. Hawkridge, S. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman, P. J. Stang, *J. Am. Chem. Soc.* **2007**, *129*, 2120–2129; by hydrogen bonding: C. V. K. Sharma, M. J. Zaworotko, *Chem. Commun.* **1996**, 2655–2656; by covalent bonding: A. P. Cote, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915.

[4] M. Tominaga, K. Suzuki, T. Murase, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 11950–11951; S. Sato, J. Iida, K. Suzuki, M. Kawano, T. Ozeki, M. Fujita, *Science* **2006**, *313*, 1273–1276.

[5] C. Tschierske, *Annu. Rep. Prog. Chem. Sect. C* **2001**, *97*, 191–268; B. Donnio, D. Guillon, *Adv. Polym. Sci.* **2006**, *201*, 45–155; T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44–74; *Angew. Chem. Int. Ed.* **2006**, *45*, 38–68; M. Lee, B.-K. Cho, W.-C. Zin, *Chem. Rev.* **2001**, *101*, 3869–3892; I. M. Saez, J. W. Goodby, *J. Mater. Chem.* **2005**, *15*, 26–40; G. Ungar, X. Zeng, *Soft Matter* **2005**, *1*, 95–106.

[6] *Handbook of Liquid Crystals, Vol. 1–3* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**.

[7] R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907–961; H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys.* **2006**, *45*, 597–625.

[8] Owing to the presence of two stereogenic centers in racemic form, all compounds represent mixtures of four distinct stereoisomers.

[9] W. B. Austin, N. Bilow, W. J. Kelleghan, K. S. Y. lau, *J. Org. Chem.* **1981**, *46*, 2280–2286.

[10] G. Johansson, V. Percec, G. Ungar, J. P. Zhou, *Macromolecules* **1996**, *29*, 646–660.

[11] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–519; M. Hird, G. W. Gray, K. J. Toyne, *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 187–204.

[12] 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, there are no well-defined crystal-like structures. Instead, these are highly dynamic systems with distinct regions with enhanced concentration of aromatic cores, regions containing polar hydrogen-bonding groups and regions containing nonpolar segments. Therefore, the number of molecules per unit cell is an average value. Also the number of molecules in the cross section of the cylinder walls is an average number which does not necessarily represent an integer number. Hence, the cylinder walls can also be slightly thicker or thinner than exactly two molecules.

[13] In this structure a_{hex} is related to the length of one arm of the bent-core unit ($l = 1.5$–1.6 nm, depending on the conformation of the glycerol group) by the relation $l = a_{\text{hex}}/3^{1/2}$.

[14] Note for example, how the Fourier series truncation smears out the narrow dip owing to the aliphatic shell around the fluorinated central hexagon (compare Figure 2e and 2f). The dip is however clearly visible in the map of compound **1c** (Figure 1c), having 11 rather than four carbon atoms in the aliphatic spacer. It should be remembered that the main cause of smearing in the $\rho(x,y)$ maps is the intrinsic dynamic disorder of the liquid crystal.

[15] Note that, despite the trigonal symmetry, the shape of the honeycomb is still hexagonal. A honeycomb formed by triangular cylinders was achieved recently, but in this case the symmetry is hexagonal *p6mm*, as long as all cylinders are identical.[18c]

[16] G. Hennrich, A. Omenat, I. Asselberghs, S. Foerier, K. Clays, T. Verbiest, J. L. Serrano, *Angew. Chem.* **2006**, *118*, 4310–4313; *Angew. Chem. Int. Ed.* **2006**, *45*, 4203–4206.

[17] a) C. Tschierske, *Chem. Soc. Rev.* **2007**, *36*, 1930–1970; b) M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain, S. Diele, *J. Am. Chem. Soc.* **2001**, *123*, 6809–6818; c) X. H. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske, *J. Am. Chem. Soc.* **2003**, *125*, 10977–10996; d) X. H. Cheng, M. K. Das, U. Baumeister, S. Diele, C. Tschierske, *J. Am. Chem. Soc.* **2004**, *126*, 12930–12940; e) M. Prehm, F. Liu, U. Baumeister, X. Zeng, G. Ungar, C. Tschierske, *Angew. Chem.* **2007**, *119*, 8118–8121; *Angew. Chem. Int. Ed.* **2007**, *46*, 7972–7975; f) M. Prehm, G. Götz, P. Bäuerle, F. Liu, X. Zeng, G. Ungar, C. Tschierske, *Angew. Chem.* **2007**, *119*, 8002–8005; *Angew. Chem. Int. Ed.* **2007**, *46*, 7856–7859.

[18] a) B. Chen, U. Baumeister, G. Pelzl, M. Kumar Das, X.-B. Zeng, S. Diele, G. Ungar, C. Tschierske, *J. Am. Chem. Soc.* **2005**, *127*, 16578–16591; b) B. Chen, X.-B. Zeng, U. Baumeister, G. Ungar, C Tschierske, *Science* **2005**, *307*, 96–99; c) F. Liu, B. Chen, U. Baumeister, X. Zeng, G. Ungar, C. Tschierske, *J. Am. Chem. Soc.* **2007**, *129*, 9578–9579.

[19] These honeycomb structures can also be regarded as new LC phases of bent-core molecules. All previously reported columnar phases of such molecules were modulated smectic phases composed of infinite ribbons of parallel molecules.[7] The latter structures cannot form in our current compounds, because the chain in the middle disfavors any arrangement into layers or ribbons; hexagonal columnar phases were also reported for bent-core molecules with more than two terminal alkyl chains (polycatenar bent-core molecules); a model was proposed where the bent cores are organized into C_3 symmetric triplets which stack into columns. It was suggested that these columns are rotationally disordered within a fluid continuum formed by the terminal alkyl chains. No indication of trigonal long-range order was noted: J. Matraszek, J. Mieczkowski, D. Pociecha, E. Gorecka, B. Donnio, D. Guillon, *Chem. Eur. J.* **2007**, *13*, 3377–3385.

[20] S. Stepanow, N. Lin, D. Payer, U. Schlickum, F. Klappenberger, G. Zoppellaro, M. Ruben, H. Brune, J. V. Barth, K. Kern, *Angew. Chem.* **2007**, *119*, 724–727; *Angew. Chem. Int. Ed.* **2007**, *46*, 710–713.