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δ-Methyl Branching in the Side Chain Makes the Difference: Access to Room-Temperature Discotics

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Dedicated to Prof. Henning Hopf on the occasion of his 75th birthday

Although discotic liquid crystals are attractive functional materials, their use in electronic devices is often restricted by high melting and clearing points. Among the promising candidates for applications are [15]crown-5 ether-based liquid crystals with peripheral *n*-alkoxy side chains, which, however, still have melting points above room temperature. To overcome this problem, a series of *o*-terphenyl and triphenylene [15]crown-5 ether derivatives was prepared in which δ-methyl-branched alkoxy side chains of varying lengths substitute the peripheral linear alkoxy chains. The mesomorphic properties of the novel crown ethers were studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction.

δ-Methyl branching indeed lowers melting points resulting in room-temperature hexagonal columnar mesophases. The mesophase widths, which ranged from 87 to 30 K for *o*-terphenyls, significantly increased to 106–147 K for the triphenylenes depending on the chain lengths, revealing the beneficial effect of a flat mesogen, due to improved π–π interactions.

1. Introduction

Thermotropic discotic liquid crystals, which self-assemble into columnar mesophases upon a change in temperature have received increasing interest since their discovery by Chandrasekhar in 1977.[1,2] Their high charge-carrier mobility, ability to self-heal defects, efficient synthetic access and good solubility, as well as easy processing through spin-coating or drop-casting procedures, make them highly attractive as functional materials for various device applications, such as sensors,[3] organic solar cells,[4] organic light-emitting diodes (OLEDs),[5] and organic field-effect transistors (OFETs).[6] However, in contrast to dendritic, amphiphilic, H-bonded, or star-shaped mesogens,[7] most discotic liquid crystals, carrying a central rigid aromatic or heteroaromatic core functionalized with flexible peripheral alkyl side chains, enter their mesophases at elevated temperatures.[8] Thus, melting points that are often far above room temperature and clearing points close to the decomposition temperature, limit further application in devices, for example, ferroelectric switches.[9] Several strategies have therefore been developed to circumvent this problem and to make room-temperature mesophases possible, for example, the replacement of *n*-alkoxy groups by thioethers lowered the melting transition temperature.[10] Another strategy based on seminal work by Collard and Lillya[11] used the introduction of branched peripheral side chains rather than linear alkyl (or alkoxy) tails.[12] In particular, core units bearing dove-tailed,[13] swallow-tailed,[14] dihydrocitronellyl, phytyl,[15] or other bitailed systems[16,17] in the periphery were studied.

To address transition-temperature lowering in crown-ether-based mesogens, previously we systematically varied the crown size, symmetry, and salt complexation of *o*-terphenyl- and triphenylene-substituted derivatives, such as **1** and **3**, respectively, with linear alkoxy side chains in the periphery (Scheme 1).[18] The investigation of mesomorphic properties showed that the complexation of salts with soft anions not only increasing the flatness of the core from *o*-terphenyl to triphenylene, but also improved the mesophase stability, however, melting transitions remained far above room temperature.[18c,19] The reduction of size, molecular symmetry and flexibility of the central crown resulted in broader mesophase widths and lower melting points, however, ambient temperature mesophases could not be accessed.[18b,c] Thus, an alternative method for melting-point depression was necessary without compromising the mesophase stability. Taking the reports on branched side chains[11,12] into account, we anticipated that the attachment of δ-methyl-branched tails to the most promising candidates among the previous series, **1** and **3**, might lead to room-temperature columnar mesophases. Moreover, we might be able to check whether the improved π–π interaction in the flat triphenylene[20] would improve the mesophase stability, as compared to *o*-terphenyl, while maintaining low melting transition temperatures, due to hydrophobic interactions of the δ-methyl-branched side chains.

Thus, our design concept featured *o*-terphenyls **2b**–**f** and triphenylenes **4b**–**f** carrying δ-methyl-branched side chains as key target compounds (Scheme 1). These were compared with

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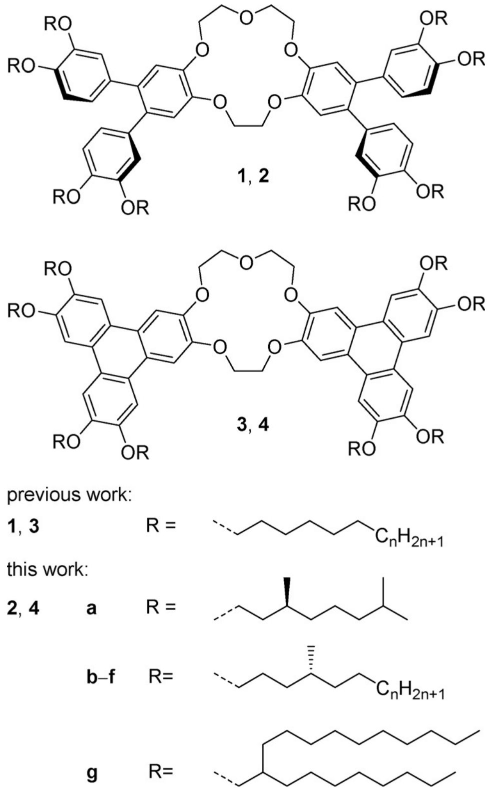
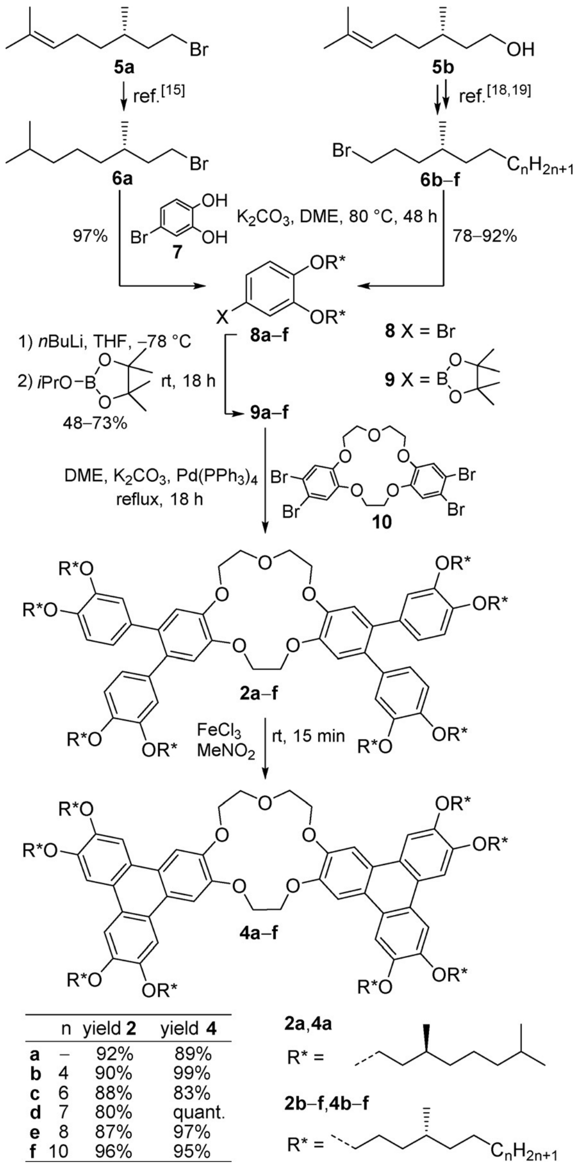


Scheme 1. Known liquid-crystalline crown ethers **1** and **3**[18b] as well as the novel derivatives **2** and **4**.



	n	yield 2	yield 4
a	–	92%	89%
b	4	90%	99%
c	6	88%	83%
d	7	80%	quant.
e	8	87%	97%
f	10	96%	95%

Scheme 2. Synthesis of [15]crown-5 derivatives **2** and **4**. For details see the Supporting Information.

o-terphenyls **1** and triphenylenes **3** bearing linear alkyl chains. To check whether other types of branching would serve a similar purpose, dihydrocitronellyl-substituted *o*-terphenyl **2a** and triphenylene **4a** and the corresponding swallow-tailed derivatives **2g** and **4g** were studied as well. Both dihydrocitronellyl (**a**) and swallow-tailed 2-octyldodecyl (**g**) were selected as benchmark side chains with a known propensity to support room-temperature mesomorphism.[14] The comparison of pairs of compounds (*o*-terphenyl and triphenylene) for each branching type or chain length should allow the separation of the contribution of the flatness of the π systems on the mesomorphic properties from the effect of branching. The results towards these goals are reported below.

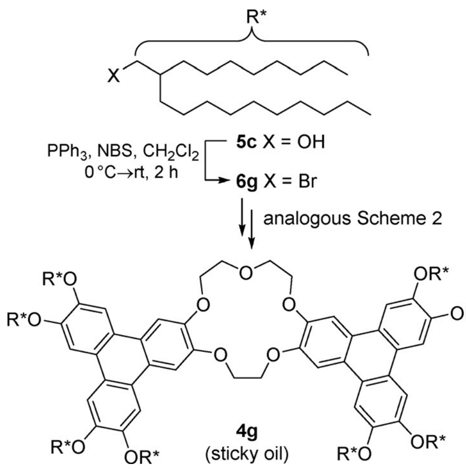
2. Results and Discussion

The synthesis of the target [15]crown-5 derivatives **2** and **4** started from commercially available (*S*)-citronellyl bromide (**5a**) and (*S*)-citronellol (**5b**), respectively (Scheme 2).

First, *o*-terphenyl and triphenylene crown ethers **2a** and **4a** with dihydrocitronellyl chains were prepared. Williamson etherification of bromide **6a**[21] with 4-bromobenzene-1,2-diol (**7**) afforded 4-bromo-1,2-bis{[(3*S*)-3,7-dimethyloctyl]oxy}benzene (**8a**), which was converted into borolane **9a** following the recently reported method by Ong et al.[22] A fourfold Suzuki coupling with **10**[18b,23a] and subsequent Scholl reaction of the resulting bis(*o*-terphenyl)[15]crown-5 derivative **2a** with $FeCl_3$[19] provided the corresponding triphenylene **4a**. Bromides **6b–f**[24a,d] with δ-methyl-branched side chains were obtained from citronellol (**5b**) by chain elongation of the OH terminus with oxidative cleavage of the double bond and nucleophilic substitution with various alkyl cuprates as key steps (Scheme S1 in the Supporting Information).[24,25] Bromides **6b–f** were converted into the respective terphenyls **2b–f** and triphenylenes **4b–f** as described for **2a** and **4a** (Scheme 2).

Crown-ether derivative **4g** with peripheral swallow-tailed alkyl side chains was prepared from commercially available 2-octyl-1-dodecanol (**5c**) following a similar route as described for **2a** and **4a** (Scheme 3; see the Supporting Information for details).[26]

The mesomorphic properties of crown ethers **2** and **4** were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (WAXS, SAXS). The details of the DSC measurements are summarized in



Scheme 3. Crown ethers with swallow-tailed alkyl side chains.

Table 1. Phase transitions of mesogenic [15]crown-5 ether derivatives **2** and **4** determined by DSC upon first cooling (heating/cooling rate 10 $\mathrm{K\,min^{-1}}$).[a,b]

Compd	Cr	T_m [°C] (ΔH [$\mathrm{kJ\,mol^{-1}}$])	$\mathrm{Col_h}$	T_c [°C] (ΔH [$\mathrm{kJ\,mol^{-1}}$])	I
2a	+	26 (2.6)[c]	–	–	+
2b	+	−51.7 (0.9)	+	35.7 (4.7)	+
2c	+	−48.2 (4.9)	+	29.8 (3.8)	+
2d	+	−30.0 (16.5)	+	27.7 (4.2)	+
2e	+	−27.9 (15.9)	+	27.2 (5.9)	+
2f	+	−5.0 (48.9)	+	25.0 (6.2)	+
4a	+	56 (0.6)	+	131 (2.9)	+
4b	+	−11.8 (1.6)	+	135.4 (3.1)	+
4c	+	−11.3 (0.9)	+	126.2 (4.5)	+
4d	+	−27.5 (6.8)	+	97.7 (2.2)	+
4e	+	−11.8 (21.6)	+	109.3 (3.5)	+
4f	+	10.7 (48.3)	+	94.9 (4.4)	+

[a] Observed phases: Cr = crystalline, $\mathrm{Col_h}$ = columnar hexagonal, I = isotropic liquid. [b] For **2g**, **4g** no transitions were observed in the DSC. [c] DSC upon second heating.

Table 1. According to the DSC studies, dihydrocitronellyl-substituted *o*-terphenyl **2a** was nonmesomorphic, whereas the corresponding triphenylene **4a** displayed monotropic mesomorphism (Figure S2 in the Supporting Information). Melting and clearing transitions at 56 and 131 °C, respectively, were observed upon first cooling (Table 1).

In contrast, *o*-terphenyl crown ethers **2b**–**f** and the corresponding triphenylene derivatives **4b**–**f** with δ-methyl-branched alkyl chains showed enantiotropic mesophases at ambient temperatures, irrespective of the chain lengths (Table 1). Typical DSC curves are shown in Figure 1 for derivatives **2f** and **4f**. The DSC curve of **2f** (Figure 1a) revealed an isotropic-to-mesophase transition at 25 °C and a crystallization at −5 °C upon the first and second cooling. Upon second heating, however, a crystal-to-mesophase transition at −22 °C and a mesophase-to-isotropic transition at 33 °C were detected. Strong supercooling caused a decrease of the mesophase ranges to 30 K, as compared with those in the heating cycles (55 K). In contrast, the DSC curve of **4f** (Figure 1b) exemplifies the much broader mesophase for triphenylene crown ethers. The clearing point was detected at 95 °C and the melting point was visible at 11 °C, upon first and second cooling. The crystal-to-mesophase transition was detected at 24 °C and the isotropic melting at 94 °C, upon second heating. As can be seen from Table 1, melting points increased from **2b** to **2f** with increasing chain length, whereas clearing points decreased in the same order, resulting in mesophase widths ranging from 87 (for **2b**) to 30 K (for **2f**).

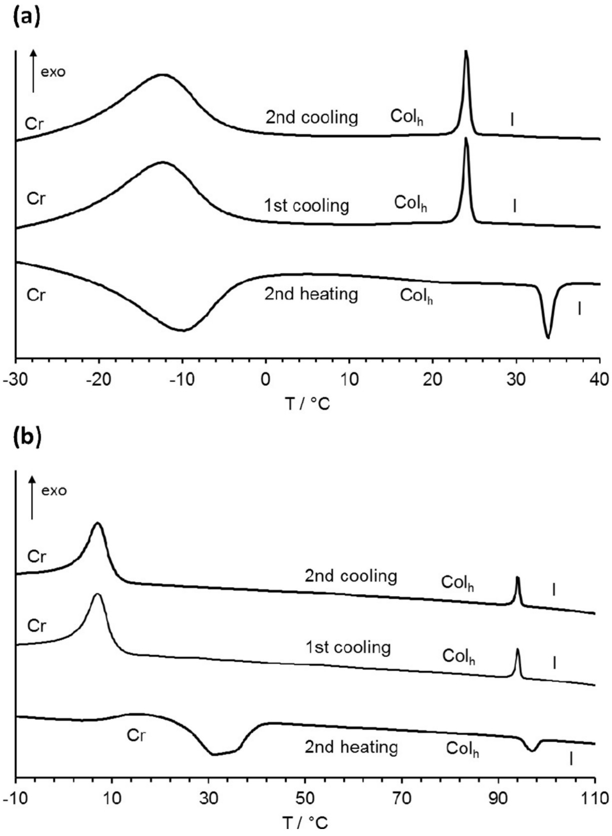


Figure 1.

The presence of flat triphenylene units in crown ethers **4b**–**f** significantly improved the mesophase stability, that is, clearing points were shifted up to 135 °C for **4b** with 4-methyldecyloxy chains and 95 °C for **4f** bearing the longest δ-methyl-branched alkyl chain, whereas melting points (T_m) remained at subambient temperatures. Thus, mesophase widths between 147 (for **4b**) and 84 K for (**4f**) were observed.

To check whether swallow-tailed alkyl side chains were capable of melting point depression and phase stabilization, crown-ether derivatives **2g** and **4g** were studied as benchmark substrates.[14a] However, both compounds were sticky oils and neither *o*-terphenyl **2g** nor triphenylene **4g** showed any liquid-crystalline properties (Figures S1 and S2 in the Supporting Information). Thus, depression of the melting points could be indeed achieved when employing swallow-tailed chains, but this result was accompanied with complete loss of mesomorphism even for the flatter triphenylene **4g**. It should be noted that Barberá, Torres, and co-workers[17] previously reported the complete suppression of columnar mesomorphism of triazolehemiporphyrazine- and phthalocyanine-derived metallomesogens by increasing the number of peripheral side chains or the use of branched chains. The authors rationalized steric hindrance between the chains leading to increased molecular thickness which makes columnar stacking difficult.

For the *o*-terphenyl crown-ethers **2**, polarizing optical microscopy (POM) studies revealed unspecific textures, as exemplarily shown for **2 b,c** (Figure 2 a, Figure 2 b). In contrast, POM studies revealed broken fan-shaped textures characteristic of hexagonal columnar mesophases for triphenylenes **4 b,c** (Figures 2 c and 2 d). The remaining textures are shown in Figure S3 (see the Supporting Information).

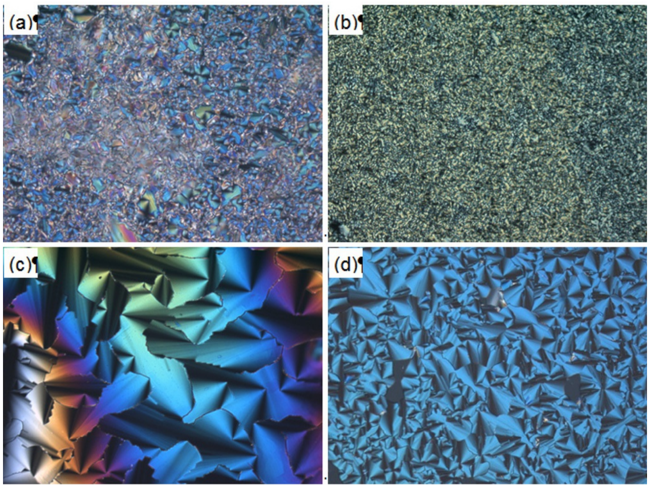


Figure 2. Unspecific textures of **2 b** at 35 °C (a) and **2 c** at 30 °C (b). Broken fan-shaped textures of **4 b** at 120 °C (c) and **4 c** at 110 °C (d) as seen between crossed polarizers upon cooling from the isotropic liquid (magnification ×200; cooling rate 2 K min^{-1}).

More insight into the mesophase geometries of both series (**2** and **4**) was obtained by X-ray diffraction (WAXS, SAXS) measurements. With the exception of **2 b** (being measured quite close to its clearing point), all measurements were conducted in the middle of the respective mesophases, that is, at room temperature for **2 c–f** and between 57 and 80 °C for **4 a–f**. The experimentally observed *d* values, lattice spacings, and proposed indexing are summarized in Table 2.

The diffractograms of all compounds revealed characteristic reflections of columnar hexagonal mesophase geometries upon cooling from the isotropic melt. For the series of *o*-terphenyl crown ethers (**2**), two indicative diffractogram patterns were obtained. In the small-angle (SAXS) region of **2 b** three assignable reflections were observed with the inner ring in the diffractogram being much stronger than the other ones (Figure 3 a). Despite their weak intensity, the relative *d* values of the outer reflections are $1{:}1/\sqrt{3}{:}1/2$ and could, thus, be indexed accordingly as (10), (11), and (20). Hence, the phase was assigned as Col$_h$ (plane group *p6mm*). In the wide-angle X-ray scattering (WAXS) profile of *o*-terphenyl crown ether **2 b** a diffuse wide-angle halo was detected at 4.6 Å, which corresponds to the liquid-like disorder of the molten alkyl chains (Figure 3 b).[1]

Table 2. XRD results for [15]crown-5 based mesogens **2** and **4**.

Compd	Mesophase	Lattice spacing [Å]	*d* spacing observed [Å]	Miller Indices
2 b	Col$_h$ at 35 °C	$a=34.7$	30.1	(10)
	p6mm		17.4	(11)
			15.3	(20)
			4.6	(halo)
2 c	Col$_h$ at 24 °C	$a=38.3$	33.1	(10)
	p6mm		4.6	(halo)
2 d	Col$_h$ at 24 °C	$a=39.1$	33.9	(10)
	p6mm		4.5	(halo)
2 e	Col$_h$ at 24 °C	$a=39.8$	34.5	(10)
	p6mm		4.6	(halo)
2 f	Col$_h$ at 24 °C	$a=41.8$	36.2	(10)
	p6mm		4.6	(halo)
4 a	Col$_h$ at 57 °C	$a=31.8$	27.5	(10)
	p6mm		4.9	(halo)
4 b	Col$_h$ at 80 °C	$a=33.2$	28.8	(10)
	p6mm		4.7	(halo)
4 c	Col$_h$ at 57 °C	$a=35.5$	30.8	(10)
	p6mm		4.7	(halo)
4 d	Col$_h$ at 57 °C	$a=36.5$	31.6	(10)
	p6mm		4.7	(halo)
4 e	Col$_h$ at 57 °C	$a=37.4$	32.4	(10)
	p6mm		4.7	(halo)
4 f	Col$_h$ at 57 °C	$a=39.1$	33.9	(10)
	p6mm		4.7	(halo)

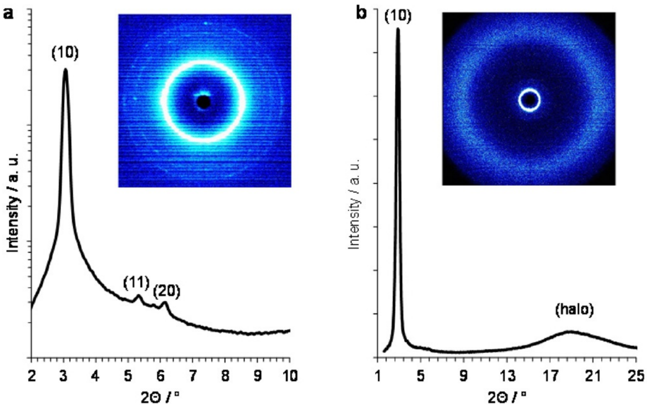


Figure 3. a) Small-angle and b) wide-angle X-ray scattering profile of the LC phase of *o*-terphenyl crown ether **2 b** at 35 °C. Inset: the corresponding diffraction images.

In contrast, for **2 c–f** only a single intense reflection was visible in the SAXS profile, which was indexed as (10). Despite missing further *d* values, a Col$_h$ phase could be confirmed, due to the oriented regular hexagon pattern within the (10) ring. The hexagon is clearly visible by integrating the data over 2 theta, whereupon all inter-reflection angles were determined to be 60° (Figure 4 a). In this case, the X-ray beam points are parallel to the optical axis of the molecules, and therefore, hits the hexagonal lattice directly on its face. All *o*-terphenyl crown

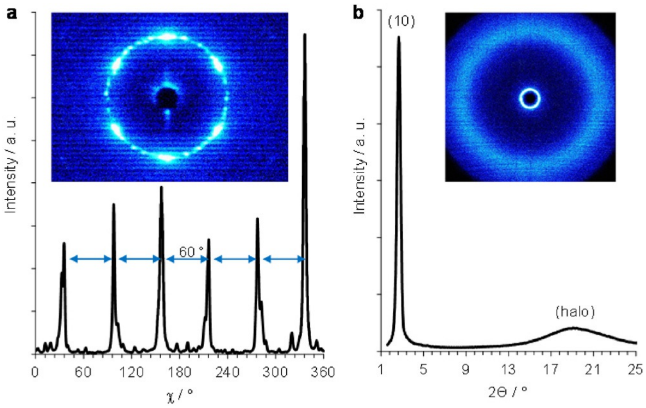


Figure 4. Azimuthal intensity profile of the hexagon in a) the SAXS pattern and b) the WAXS profile of the LC phase of *o*-terphenyl crown ether **2c** at 24 °C. Inset: the corresponding diffraction images.

ethers **2b–f** showed a diffuse wide-angle halo, which was detected between 4.5 and 4.6 Å, as shown for **2c** as a typical example (Figure 4b).

The lattice parameter *a* was calculated using the equation $a = d_{10}/\cos 30^\circ$ and the respective SAXS data for the (10) peak. The values of *a* increased linearly with increasing chain length, from 34.7 (**2b**) to 41.8 Å (**2f**) as shown in Figure 5.

The triphenylene series **4** provided only the intense (10) reflection in SAXS experiments. A representative diffraction pattern is shown in Figure 6a for the derivative **4b**. Besides this intense peak, which is also visible in the WAXS, a broad halo in the wide angle region was observed between 4.7 and 4.9 Å. Even though the higher ordered reflections were missing, which may be caused by the molecular form factor, the Col_h mesophase was assigned due to the characteristic textures seen under the polarized microscope.[23]

The lattice parameters *a* of the triphenylenes **4** were calculated as described above, giving values between 33.2 (**4b**) and 39.1 Å (**4f**). Figure 5 clearly reveals a linear increase of *a* with increasing chain length, but for a certain side-chain length the value of the triphenylene **4** is always smaller than that of the corresponding *o*-terphenyl **2**.

According to the XRD data of triphenylenes **4**, the following packing model for the Col_h phase is proposed. As shown in Figure 7, the hexagonal lattice is defined by "columns" of crown ethers with a lattice parameter *a*.

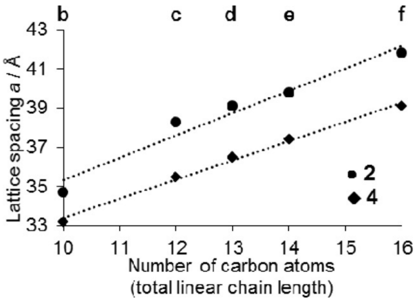


Figure 5. Lattice spacing *a* of derivatives **2b–f** and **4b–f**.

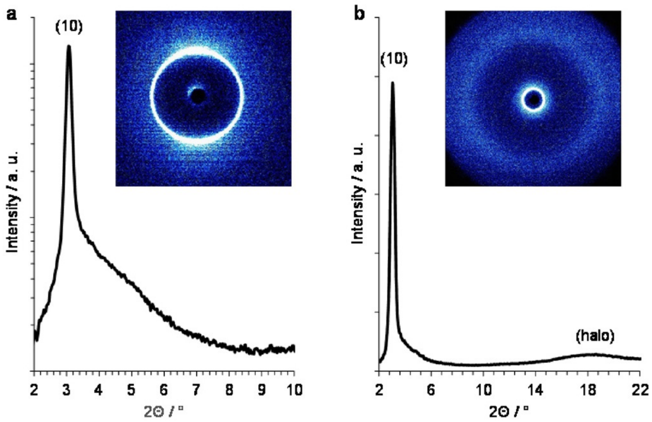


Figure 6. a) SAXS and b) WAXS profile of the LC phase of triphenylene crown ether **4b** at 80 °C. Inset: the corresponding diffraction images.

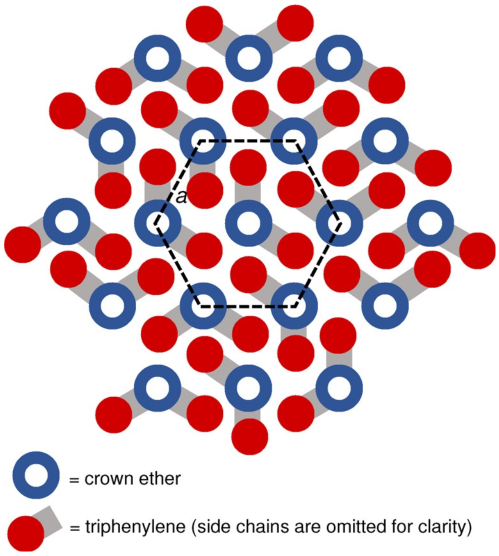


Figure 7. Proposed stacking model in the columnar hexagonal mesophase (Col_h) for triphenylene crown ethers **4**.

Each crown unit is surrounded by six triphenylene units to form a smaller mixed hexagonal lattice with a lattice parameter of approximately *a*/2. The alkyl side chains fill the free space in between. This packing leads to a partial mixing of crown-ether units and side chains in agreement with the relative broadness of the fundamental reflection, whereas triphenylenes remain segregated in columns as well as the chains in the interstices.[27] Such a packing pattern is in good agreement with previous studies by Tschierske, Ungar, and co-workers on tetraphilic liquid crystals.[28]

The observation that for each chain length the lattice parameter *a* of the triphenylenes **4** is smaller than that of the corresponding *o*-terphenyls **2** (Figure 5) might be rationalized as follows. Presumably, intracolumnar π–π interactions are more pronounced in the case of triphenylenes **4**, resulting in smaller thermal out of column fluctuations, and thus, a smaller lattice parameter. In contrast, the twisting of the *o*-terphenyl units requires at least a twisting of two neighboring molecules **2** within the crown column so that the smaller mixed hexagonal lattice and the larger hexagonal lattice expand leading to increased lattice parameters.

3. Conclusions

We synthesized a series of [15]crown-5 ether-based columnar liquid crystals (**2** and **4**) and studied the influence of δ-methyl-branched side chains and the flatness of the mesogenic core on the formation of room-temperature mesophases and the phase stability. The mesophase widths of selected derivatives **2** and **4** with branched side chains were compared with those of the corresponding *o*-terphenyls **1** and triphenylenes **3** bearing linear alkoxy side chains[18b] (Figure 8). The presence of the δ-methyl-branched side chains caused a larger depression of the melting points than of the clearing points, leading to room-temperature mesophases. The mesophase ranges already increased for the twisted *o*-terphenyls **2b**,**c** in comparison with those of **1b**,**c**. In contrast, for dihydrocitronellyl-bearing **4a**, a temperature depression was not observed. As previously reported, the increased flatness of triphenylenes **3b**,**c** led to broader mesophase ranges than for *o*-terphenyls **1b**,**c**.[18b] This effect was also observed for triphenylenes **4b**,**c** with δ-methyl-branched chains, as well as derivative **4a** with dihydrocitronellyl side chains.

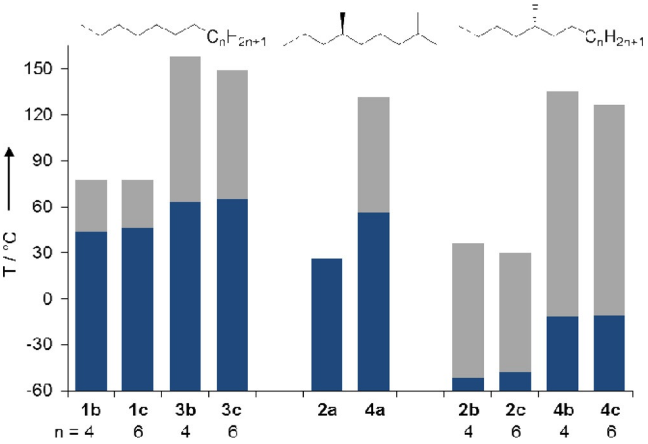


Figure 8. Mesophase widths of terphenyl and triphenylene crown ethers **2a** and **4a** with dihydrocitronellyl side chains as well as **2b**,**c** and **4b**,**c** with δ-methyl-branched side chains and their counterparts bearing linear side chains of the same lengths[18b] upon first cooling. Phases: blue = crystalline, gray = columnar hexagonal (Col_h). Compounds **2g** and **4g** did not show any peaks upon subsequent heating/cooling cycles in the DSC.

We conclude that it is the δ-methyl branching that shifted the mesophase to room temperature. Moreover, it is not just a simple shift when going from compounds **2** to **4**. The temperature range became even broader. We therefore assume that the presence of a stable mesophase is not only due to an additive effect of π–π interactions and δ-branching, but that both parameters cooperatively influence the mesophase properties. In the case of **4a**, the additional terminal branching in the dihydrocitronellyl side chain obviously counteracts the γ-branching, resulting in a phase behavior similar to that of the linear derivatives **3**.

This design concept should not only be amenable for crown ethers as model systems for ion transporters, due to their supramolecular channel architecture[29] and luminescent hybrid materials,[30] but also for other columnar systems. Although chirality was not within the scope of this study, the simultaneous introduction of side-chain branching, chirality, and flatness might be useful for the design of polar columnar liquid crystals in general.[31]

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Keywords: crown compounds · crown ether · discotic · liquid crystals · mesophases

[1] S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana* **1977**, *9*, 471–480.

[2] a) S. Kumar in *Handbook of Liquid Crystals, Vol. 4*, 2nd ed., (Eds.: J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. F. Gleeson, P. Raynes), Wiley-VCH, Weinheim, **2014**, pp. 467–520; b) B. Roy, N. De, K. C. Majumdar, *Chem. Eur. J.* **2012**, *18*, 14560–14588; c) R. J. Bushby, K. Kawata, *Liq. Cryst.* **2011**, *38*, 1415–1426; d) B. R. Kaafarani, *Chem. Mater.* **2011**, *23*, 378–396; e) S. Kumar, *Liq. Cryst.* **2009**, *36*, 607–638; f) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902–1929; g) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887; *Angew. Chem.* **2007**, *119*, 4916–4973.

[3] a) V. Bhalla, A. Gupta, M. Kumar, D. S. S. Rao, S. K. Prasad, *ACS Appl. Mater. Interfaces* **2013**, *5*, 672–679; b) A. Bayn, X. Feng, K. Müllen, H. Haick, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3431–3440; c) V. Bhalla, H. Singh, M. Kumar, S. K. Prasad, *Langmuir* **2011**, *27*, 15275–15281; d) Y. Zilberman, U. Tisch, W. Pisula, X. Feng, K. Müllen, H. Haick, *Langmuir* **2009**, *25*, 5411–5416; e) N. Boden, R. J. Bushby, J. Clements, B. Movaghar, *J. Mater. Chem.* **1999**, *9*, 2081–2086.

[4] a) S. J. Kang, S. Ahn, J. B. Kim, C. Schenck, A. M. Hiszpanski, S. Oh, T. Schiros, Y.-L. Loo, C. Nuckolls, *J. Am. Chem. Soc.* **2013**, *135*, 2207–2212; b) T. Hori, Y. Miyake, N. Yamasaki, H. Yoshida, A. Fujii, Y. Shimizu, M. Ozaki, *Appl. Phys. Express* **2010**, *3*, 101602-1–101602-3; c) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122.

[5] a) S. Diring, F. Camerel, B. Donnio, T. Dintzer, S. Toffanin, R. Capelli, M. Muccini, R. Ziessel, *J. Am. Chem. Soc.* **2009**, *131*, 18177–18185; b) T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, H. Bock, *Angew. Chem. Int. Ed.* **2001**, *40*, 2060–2063; *Angew. Chem.* **2001**, *113*, 2119–2122.

[6] a) M. Funahashi, *Polym. J.* **2009**, *41*, 459–469; b) Y. Shimizu, K. Oikawa, K. Nakayama, G. Guillon, *J. Mater. Chem.* **2007**, *17*, 4223–4229.

[7] a) C. Tschierske, *Angew. Chem. Int. Ed.* **2013**, *52*, 8828–8878; *Angew. Chem.* **2013**, *125*, 8992–9047; b) C. Tschierske, *Isr. J. Chem.* **2012**, *52*, 935–959.

[8] Recent examples: a) K. M. Psutka, J. Williams, J. A. Paquette, O. Calderon, K. J. A. Bozek, V. E. Williams, K. E. Maly, *Eur. J. Org. Chem.* **2015**, 1456–1463; b) K. J. A. Bozek, V. E. Williams, *Soft Matter* **2014**, *10*, 5749–5754; c) B. Wu, K. Chen, Y. Deng, J. Chen, C. Liu, R. Cheng, D. Chen, *Chem. Eur. J.* **2015**, *21*, 3671–3681; d) S. Chen, F. S. Raad, M. Ahmida, B. R. Kaafarani, S. H. Eichhorn, *Org. Lett.* **2013**, *15*, 558–561; e) X. Li, A. Liu, S. Xun, W. Qiao, X. Wan, Z. Y. Wang, *Org. Lett.* **2008**, *10*, 3785–3787; f) O. B. Akopo-

va, N. M. Logacheva, V. E. Baulin, A. Yu, Tsivadze, *Russ. J. Gen. Chem.* **2008**, *78*, 2118–2124.

[9] a) Y. Okada, S. Matsumoto, Y. Takanishi, K. Ishikawa, S. Nakahara, K. Kishikawa, H. Takezoe, *Phys. Rev. E* **2005**, *72*, 020701-1–4; b) H. Takezoe, K. Kishikawa, E. Gorecka, *J. Mater. Chem.* **2006**, *16*, 2412–2416; c) D. Miyajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2010**, *132*, 8530–8531; d) D. Miyajima, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, T. Aida, *Science* **2012**, *336*, 209–213.

[10] S. K. Varshney, H. Nagayama, V. Prasad, H. Takezoe, *Liq. Cryst.* **2011**, *38*, 1321–1329.

[11] D. M. Collard, C. P. Lillya, *J. Am. Chem. Soc.* **1991**, *113*, 8577–8583.

[12] M. J. Hollamby, T. Nakanishi, *J. Mater. Chem. C* **2013**, *1*, 6178–6183.

[13] a) W. Pisula, M. Kastler, D. Wasserfallen, M. Mondeshki, J. Piris, I. Schnell, K. Müllen, *Chem. Mater.* **2006**, *18*, 3634–3640; b) W. Pisula, Z. Tomović, B. El Hamaoui, M. D. Watson, T. Pakula, K. Müllen, *Adv. Funct. Mater.* **2005**, *15*, 893–904; c) W. Pisula, D. Wasserfallen, T. Pakula, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 8074–8075.

[14] a) T. Yang, J. Pu, J. Zhang, W. Wang, *J. Org. Chem.* **2013**, *78*, 4857–4866; b) W. Pisula, Z. Tomović, U. Kolb, K. Müllen, *Langmuir* **2011**, *27*, 1524–1529; c) X. Feng, M. Liu, W. Pisula, M. Takase, J. Li, K. Müllen, *Adv. Mater.* **2008**, *20*, 2684–2689; d) S. Sergeyev, E. Pouzet, O. Debever, J. Levin, J. Gierschner, J. Cornil, R. Gómez Aspe, Y. H. Geerts, *J. Mater. Chem.* **2007**, *17*, 1777–1784.

[15] a) A. Jankowiak, D. Pociecha, J. Szczytko, P. Kaszyński, *Liq. Cryst.* **2014**, *41*, 1653–1660; b) S. K. Varshney, V. Prasad, H. Takezoe, *Liq. Cryst.* **2011**, *38*, 53–60; c) F. Camerel, R. Zeissel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita, J.-P. Bucher, *Angew. Chem. Int. Ed.* **2007**, *46*, 2659–2662; *Angew. Chem.* **2007**, *119*, 2713–2716; d) H. Lee, D. Kim, H.-K. Lee, W. Qiu, N.-K. Oh, W.-C. Zin, K. Kim, *Tetrahedron Lett.* **2004**, *45*, 1019–1022; e) J. Wu, M. D. Watson, L. Zhang, Z. Wang, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 177–186; f) M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky, R. H. Grubbs, *Angew. Chem. Int. Ed.* **1999**, *38*, 2741–2745; *Angew. Chem.* **1999**, *111*, 2909–2912; g) P. G. Schouten, J. F. Van Der Pol, J. W. Zwikker, W. Drenth, S. J. Picken, *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 291–305.

[16] A. G. Gürek, V. Ahsen, F. Heinemann, P. Zugenmaier, *Mol. Cryst. Liq. Cryst.* **2000**, *338*, 75–97.

[17] a) O. Fernández, G. de La Torre, F. Fernández-Lázaro, J. Barberá, T. Torres, *Chem. Mater.* **1997**, *9*, 3017–3022; b) J. A. Duro, G. de La Torre, J. Barberá, J. L. Serrano, T. Torres, *Chem. Mater.* **1996**, *8*, 1061–1066.

[18] a) P. Staffeld, M. Kaller, S. J. Beardsworth, K. Tremel, S. Ludwigs, S. Laschat, F. Giesselmann, *J. Mater. Chem. C* **2013**, *1*, 892–901; b) M. Kaller, S. J. Beardsworth, P. Staffeld, S. Tussetschläger, F. Giesselmann, S. Laschat, *Liq. Cryst.* **2012**, *39*, 607–618; c) M. Kaller, P. Staffeld, R. Haug, W. Frey, F. Giesselmann, S. Laschat, *Liq. Cryst.* **2011**, *38*, 531–553.

[19] a) M. Kaller, C. Deck, A. Meister, G. Hause, A. Baro, S. Laschat, *Chem. Eur. J.* **2010**, *16*, 6326–6337; b) M. Kaller, S. Tussetschläger, P. Fischer, C. Deck, A. Baro, F. Giesselmann, S. Laschat, *Chem. Eur. J.* **2009**, *15*, 9530–9542.

[20] Review: S. Kumar in *Handbook of Liquid Crystals*, 2nd ed. (Eds.: J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. F. Gleeson, P. Raynes), Wiley-VCH, Weinheim, **2014**, pp. 467–520.

[21] a) L. Kloppenburg, D. Song, U. H. F. Bunz, *J. Am. Chem. Soc.* **1998**, *120*, 7973–7974; b) E. Gomar-Nadal, C. Rovira, D. B. Amabilino, *Tetrahedron* **2006**, *62*, 3370–3379.

[22] M.-C. Yeh, Y.-L. Su, M.-C. Tzeng, C. W. Ong, T. Kajitani, H. Enozawa, M. Takata, Y. Koizumi, A. Saeki, S. Seki, T. Fukushima, *Angew. Chem. Int. Ed.* **2013**, *52*, 1031–1034; *Angew. Chem.* **2013**, *125*, 1065–1068.

[23] For similar procedures see a) T. Wöhrle, J. Kirres, M. Kaller, M. Mansueto, S. Tussetschläger, S. Laschat, *J. Org. Chem.* **2014**, *79*, 10143–10152; b) A.-J. Attias, C. Cavalli, B. Donnio, D. Guillon, P. Hapiot, J. Malthête, *Chem. Mater.* **2002**, *14*, 375–384.

[24] a) G. Kohnen, M. Tosoni, S. Tussetschläger, A. Baro, S. Laschat, *Eur. J. Org. Chem.* **2009**, 5601–5609; b) Y. Shirai, M. Seki, M. Mori, *Eur. J. Org. Chem.* **1999**, 3139–3145; c) S. Kuwahara, K. Mori, *Agric. Biol. Chem.* **1983**, *47*, 2599–2606; d) K. Mori, S. Tamada, *Tetrahedron* **1979**, *35*, 1279–1284; e) K. Mori, T. Ohtaki, H. Ohrui, D. R. Berkebile, D. A. Carlson, *Eur. J. Org. Chem.* **2004**, 1089–1096.

[25] a) K. Mori, S. Masuda, T. Suguro, *Tetrahedron* **1981**, *37*, 1329–1340; b) A. Yajima, H. Takikawa, K. Mori, *Liebigs Ann.* **1996**, 1083–1089.

[26] H. Chang, T. Shiozaki, A. Kamata, K. Kishida, T. Ohmori, D. Kiriya, T. Yamauchi, H. Furukawa, S. Kitagawa, *J. Mater. Chem.* **2007**, *17*, 4136–4138.

[27] We would like to thank one of the referees for suggesting this packing model.

[28] X. Zeng, R. Kieffer, B. Glettner, C. Nürnberger, F. Liu, K. Pelz, M. Prehm, U. Baumeister, H. Hahn, H. Lang, G. A. Gehring, C. H. M. Weber, J. K. Hobbs, C. Tschierske, G. Ungar, *Science* **2011**, *331*, 1302–1306.

[29] C. D. Assouma, A. Crochet, Y. Chérémond, B. Giese, K. M. Fromm, *Angew. Chem. Int. Ed.* **2013**, *52*, 4682–4685; *Angew. Chem.* **2013**, *125*, 4780–4783.

[30] S. K. Nayak, M. Amela-Cortes, C. Roiland, S. Cordier, Y. Molard, *Chem. Commun.* **2015**, *51*, 3774–3777.

[31] a) H. Takezoe, F. Araoka, *Liq. Cryst.* **2014**, *41*, 393–401; b) H. Takezoe, *Ferroelectrics* **2014**, *468*, 1–17; c) F. Araoka, H. Takezoe, *Jpn. J. Appl. Phys.* **2014**, *53*, 01AA01–1–6; d) F. Araoka, S. Masuko, A. Kogure, D. Miyajima, T. Aida, H. Takezoe, *Adv. Mater.* **2013**, *25*, 4014–4017.

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