Supramolecular Chemistry

DOI: 10.1002/ange.200700308

A Liquid-Crystalline [2]Catenane and Its Copper(I) Complex**

Etienne D. Baranoff, Julie Voignier, Takuma Yasuda, Valérie Heitz, Jean-Pierre Sauvage,* and Takashi Kato**

Catenanes and rotaxanes attract much attention, particularly because of their dynamic properties.[1–3] Many molecular machines and motors have been proposed over the last 15 years which incorporate such interlocking or threaded molecular systems[4] as well as non-interlocking species.[5] The combination of molecular machines[1–5] and liquid crystals,[6–8] which are mobile and ordered condensed states, is a new promising approach towards practical devices, although the study of such compounds in solutions is interesting in itself. The liquid-crystalline (LC) molecular order will provide the molecular machinery part with an organized dynamic environment. Moreover, molecular machines can control the self-assembled behavior of LC molecules. However, as far as we know, very few examples of LC catenanes or rotaxanes have been described to date.[9] In a recent review article[9] Godt suggested that [2]catenanes consisting of two interlocking 87-membered rings, as well as the constitutive rings themselves, lead to the formation of thermotropic liquid crystals. The introduction of [2]catenanes into nanosegregated LC structures is particularly promising in relation to LC molecular machines.

Here we report on a LC free [2]catenane (**1**) and its copper(I) complex (**2**) which form organized structures in their bulk states over a wide range of temperatures. The design and synthesis of the target compounds **1** and **2** are outlined in Scheme 1. Our design focuses on the attachment of mesogenic forklike dendrons to functionalized [2]catenanes. The mesogenic core of the dendron is a fluoro-substituted cyclohexylbiphenyl unit which tends to show relatively wide smectic LC phases with lower melting points than a normal three-ring mesogenic core.[10] The cross-sectional area of the central [2]catenane part is larger than those of normal mesogenic molecules. We expected that the incorporation of the forklike dendrons into the [2]catenanes would induce layered self-assembled structures with smectic LC phases.

Free [2]catenane **1** was obtained in 75 % yield by double esterification of **3** with **4** mediated by EDC (Scheme 1). Subsequent reaction of **1** with a stoichiometric amount of $[Cu(CH_3CN)_4]PF_6$ in CH_3CN/CH_2Cl_2 at room temperature led quantitatively to **2** as its PF_6 salt. The compounds were characterized by mass spectrometry (MALDI-TOF) as well as one- and two-dimensional NMR spectroscopy. Their spectroscopic properties are in accordance with previous results on related molecules.[10,11]

The visible region in the absorption spectrum of **1** in $CHCl_3$ is mostly free of absorption bands, while **2** exhibits the usual broad band attributed to the metal-to-ligand charge-transfer (MLCT) transitions of the copper(I) complex (see the Supporting Information). The complexation can be further evidenced by comparing the chemical shifts of the aromatic protons of **1** and **2** in the ^1H NMR spectra (Figure 1). In particular, the *ortho* and *meta* protons of the phenyl groups (H_o and H_m) of the 1,10-phenanthroline nucleus are used to probe the environment of the 1,10-phenanthroline fragments. In free [2]catenane **1**, the signals corresponding to the phenyl groups attached at the 2- and 9-positions of the 1,10-phenanthroline moiety are observed in the expected range ($\delta = 8.3$ and 7.1 ppm, respectively). On the other hand, once coordinated to a metal center as in **2**, the signals for H_o and H_m undergo a strong upfield shift (to $\delta = 7.2$ and 6.0 ppm, respectively) characteristic of "entwined" compounds. These NMR data, as well as the visible absorption spectrum, clearly demonstrate the possibility of modifying the relative position of the two macrocycles constituting the [2]catenane by the presence or absence of copper(I) ions.[11] The results also demonstrate that the introduction of the mesogenic forklike dendrons does not noticeably alter the physical properties of the [2]catenane in solution.

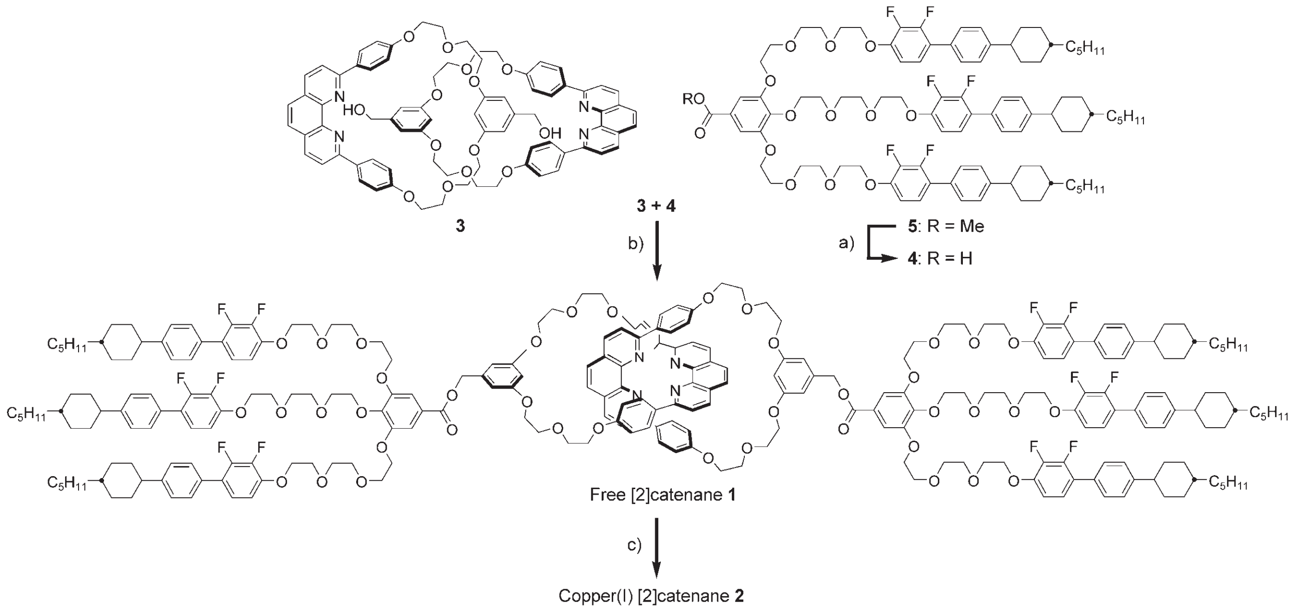
The mesomorphic and thermal properties of **1**, **2**, **4**, and **5** were examined by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS) measurements (Table 1). All these compounds show smectic LC phases. It is of interest that free

---

[*] J. Voignier, Dr. V. Heitz, Prof. Dr. J.-P. Sauvage
Laboratoire de Chimie Organo-Minérale
Institut de Chimie
Université Louis Pasteur, UMR CNRS no. 7177
4, rue Blaise Pascal, 67070 Strasbourg Cedex (France)
Fax: (+33) 390-241-368
E-mail: heitz@chimie.u-strasbg.fr
sauvage@chimie.u-strasbg.fr
Homepage: http://wwwchimie.u-strasbg.fr/~lcom/
Dr. E. D. Baranoff, Dr. T. Yasuda, Prof. Dr. T. Kato
Department of Chemistry and Biotechnology
School of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-8661
E-mail: kato@chiral.t.u-tokyo.ac.jp
Homepage: http://chem-web.chem.t.u-tokyo.ac.jp/chembio/labs/kato/index-e.html

[**] This work was partially supported by a Grant-in-Aid for Creative Scientific Research of "Invention of Conjugated Electronic Structures and Novel Functions" (no. 16GS0209; T.K.) from the Japan Society for the Promotion of Science (JSPS) and by the 21st Century COE Program of "The Frontiers of Fundamental Chemistry Focusing on Molecular Dynamism" (T.K., E.D.B., and T.Y.) from the Ministry of Education, Culture, Sports, Science, and Technology. E.D.B. is thankful for financial support from the JSPS Postdoctoral Fellowship for Foreign Researchers.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis and structures of LC free [2]catenane **1** and its copper(I) complex **2**. Reagents and conditions: a) NaOH, THF/MeOH/H_2O, reflux; b) EDC, DMAP, CH_2Cl_2, RT; c) $[Cu(CH_3CN)_4]PF_6$, CH_3CN/CH_2Cl_2, RT. EDC = 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride, DMAP = 4-dimethylaminopyridine.

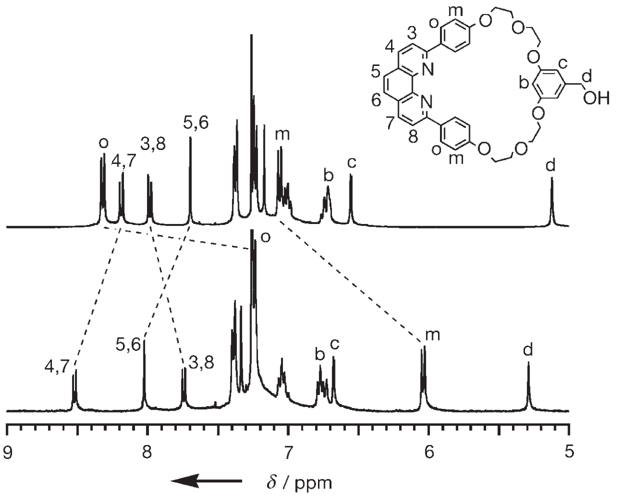


Figure 1. Partial ^1H NMR spectra (400 MHz) of free [2]catenane **1** (top) and the corresponding copper(I) [2]catenane **2** (bottom) in $CDCl_3$. The inserted structure shows the assignment of the aromatic protons of the macrocycle constituent of **1** and **2**.

Table 1: Thermal properties of **1**, **2**, **4**, and **5**.

Compound	Phase transition behavior[a]										
1	G	69	S_X	83	S_A	117	Iso				
2	G	68	S_A	147	Iso						
4	G	2	S_{A2}	176	Iso						
5	G	−5	S_C	40	S_{A2}	129	S_{Ad}	136	N	141	Iso

[a] Transition temperatures (°C) determined by DSC (second cooling; 5 °C min^{-1}). G: glassy, S_{A2}: bilayered smectic A, S_{Ad}: interdigitated smectic A, S_C: smectic C, S_X: unidentified smectic phase, N: nematic, Iso: isotropic.

[2]catenane **1** exhibits almost the same glass transition temperature as that of its copper(I) complex **2**. In contrast, the isotropization temperature of **2** is higher by 30 °C than that of **1**. This finding shows that the formation of the copper(I) complex leads to thermal stabilization of the LC phase. The complexation increases the rigidity of the central part of the molecule and stabilizes the assembled structure through interionic interactions. In contrast, the ethylene oxide chains and the mesogenic moieties can maintain the low glass transition temperature despite the change in the central part of the molecule.

The polarized optical microscopy images (Figure 2) and the SAXS patterns (Figure 3) for **1** and **2** suggest that these compounds exhibit smectic A (S_A) phases. Figure 2a,c indicate that, for compounds **1** and **2**, the molecules align perpendicularly (homeotropic alignment) to a glass substrate on slow cooling (1 °C min^{-1}) from the isotropic phases. Figure 2b shows one of the representative textures of the S_A phase observed for **2** on faster cooling (10 °C min^{-1}). Peaks at 78.7, 39.3, and 26.3 Å corresponding to the (100), (200), and (300) reflections are observed in the SAXS pattern of **1** at 85 °C (Figure 3). The interlayer spacing of 78.7 Å can be ascribed to an extended form of the molecule, and a possible organized structure of **1** in the LC phase, is represented schematically in Figure 4. It is noteworthy that the interlayer spacing of **1** is also the same as that of **2** (see the Supporting Information). The interlayer spacings of these compounds are independent of temperature. These results show that both compounds, **1** and **2**, present a similar linearly extended conformation in the layered LC states. Therefore, the possible organization of **1** in the LC phase presented in Figure 4 may also be applied to **2**. This organization leads to alternate layers of mesogenic cores, closely packed parallel to one another, and of [2]catenane linkages, embedded into the flexible ethylene oxide chains.

Molecules related to **3** have been studied in solution and in the solid state.[11] The geometry of copper(I) [2]catenanes is known relatively well both in solution and in the solid

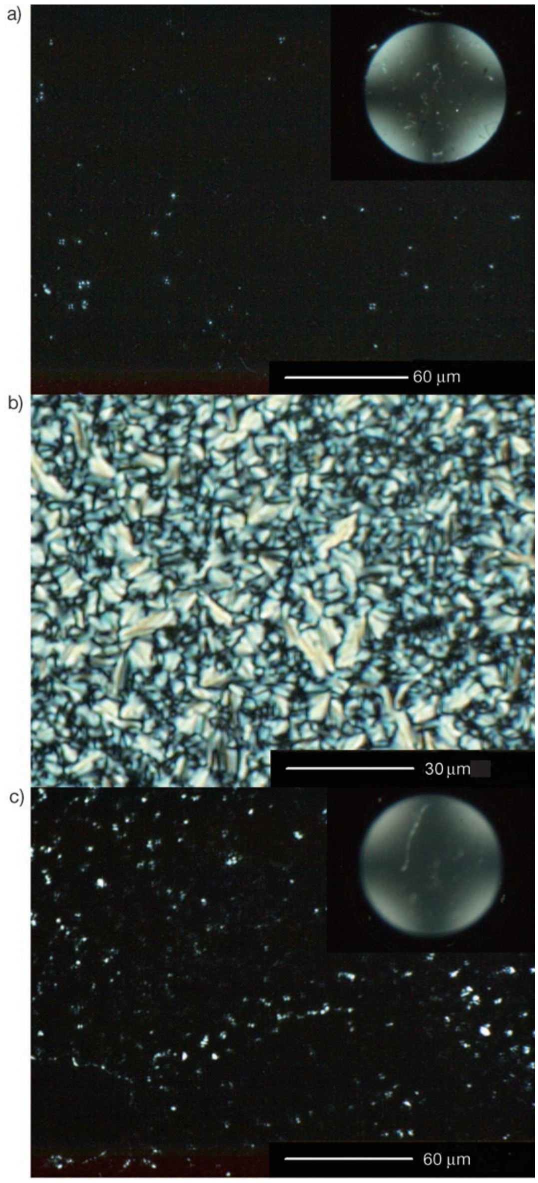


Figure 2. Polarized optical photomicrographs of **1** and **2** at 100 °C on cooling: a) homeotropic alignment of **1** after slow cooling; b) fan-shaped texture of non-aligned **2**; c) homeotropic alignment of **2** after slow cooling. Insets: conoscopic images.

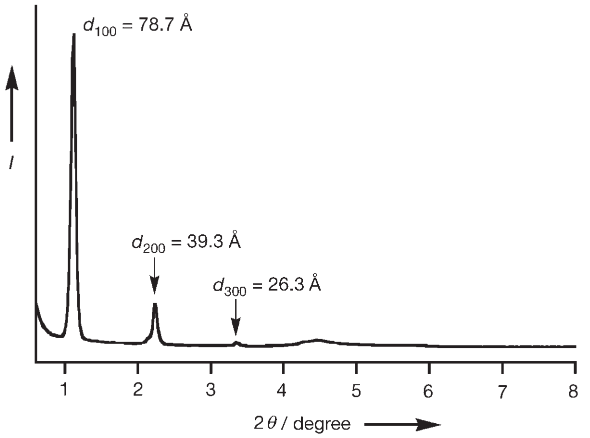


Figure 3. Small-angle X-ray scattering pattern of **1** at 85 °C on cooling.

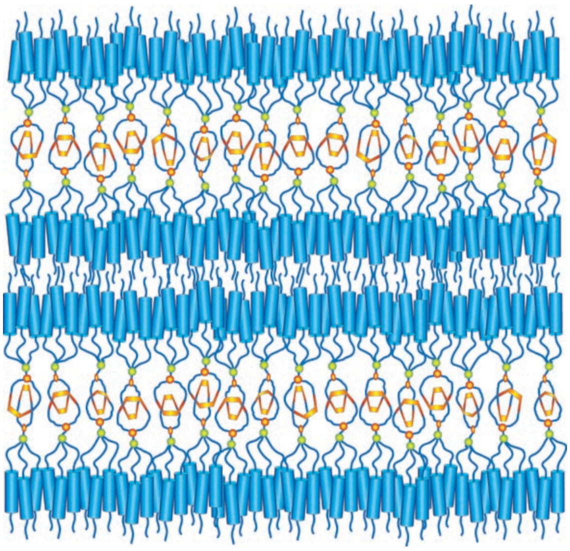


Figure 4. Possible organization of **1** in the LC phase.

state,[2d,11] while the conformation of the corresponding free [2]catenane in the solid state is different from that of the copper(I) [2]catenane. In the solution state, the rings of the free [2]catenane can rotate rapidly on the ^{1}H NMR timescale, and the compounds show a broad distribution of conformers with very different geometrical situations. Therefore, for the free [2]catenane whose rings are totally disconnected, we have generally very poor control over the geometry of the system and, in particular, over the mutual arrangement of both rings in solution. In contrast, acceptor–donor[2a,3n] and hydrogen-bonding interactions[2g,3o,p] are still present after the catenane-forming reaction has been performed.

The arrangement of free [2]catenane **1** in the LC phase exerts a significant effect on the conformation of the two macrocycles. The layered LC structures of **1** and **2** revealed in the present study suggest that the large difference in the conformational preference of the free [2]catenane and its copper(I) complex in solution has no influence on the organization of the molecules in the layered LC structures. It is of interest that the smectic LC organization induced by the forklike dendrons stabilized the conformation of free [2]catenane **1**, which is not stable in dilute solution. In other words, the packing in the LC phase forces the two macrocycles to be in similar mutual positions, regardless of the presence of a copper(I) ion.

The copper(I) ion can be seen as a chemical stimulus to control the relative conformation of the two 1,10-phenanthroline fragments in solution.[2d,4c] The LC phase provides a new mechanical stimulus to achieve control over the relative conformation of the two 1,10-phenanthroline fragments in the free [2]catenane. In addition, as the two 1,10-phenanthroline fragments are entwined without using any charge-transfer, hydrogen-bonding, or other related interactions, the conformation obtained is usually unfavorable, which is likely to give new properties and unforeseen possibilities to this family of catenanes.

In conclusion, we have succeeded in the organization of topological compounds on the nanometer scale by using the organizing properties of liquid crystals. The mesogenic core chosen in this study induces an LC smectic A organization, with alternating layers of free [2]catenane or the copper(I) complex and of the mesogenic moieties. Self-assembled structures of such topological molecules in ordered condensed states can be used to control their geometrical conformation. We are now working on expanding the specific properties of the catenanes in solution to those in the LC states. This approach may lead to the positional ordering of molecular machines as well as using molecular machines to control the LC behavior.

Received: January 23, 2007

Keywords: catenanes · liquid crystals · nanomaterials · self-assembly · supramolecular chemistry

---

[1] For early work, see: G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**.

[2] a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; b) F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451–460; c) *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**; d) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795–810; e) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53–61; f) K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96–107; g) E. R. Kay, D. A. Leigh, F. Zerbett, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191.

[3] a) T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2000**, *122*, 9876–9877; b) D. L. Simone, T. M. Swager, *J. Am. Chem. Soc.* **2000**, *122*, 9300–9301; c) B. Korybut-Daszkiewicz, A. Wieckowska, R. Bilewicz, S. Domagala, K. Wozniak, *J. Am. Chem. Soc.* **2001**, *123*, 9356–9366; d) M. J. Gunter, N. Bampos, K. D. Johnstone, J. K. M. Sanders, *New J. Chem.* **2001**, *25*, 166–173; e) C. A. Stanier, M. J. O'Connell, W. Clegg, H. L. Anderson, *Chem. Commun.* **2001**, 493–494; f) I. Willner, V. Pardo-Yissar, E. Katz, K. T. Ranjit, *J. Electroanal. Chem.* **2001**, *497*, 172–177; g) P. Samorí, F. Jäckel, Ö. Ünsal, A. Godt, J. P. Rabe, *ChemPhysChem* **2001**, *2*, 461–464; h) J. A. Wisner, P. D. Beer, M. G. B. Drew, M. R. Sambrook, *J. Am. Chem. Soc.* **2002**, *124*, 12469–12476; i) P. Ghosh, O. Mermagen, C. A. Schalley, *Chem. Commun.* **2002**, 2628–2629; j) H. W. Gibson, N. Yamaguchi, L. Hamilton, J. W. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 4653–4665; k) N. Watanabe, N. Kihara, Y. Furusho, T. Takata, Y. Araki, O. Ito, *Angew. Chem.* **2003**, *115*, 705–707; *Angew. Chem. Int. Ed.* **2003**, *42*, 681–683; l) A. Bogdan, M. O. Vysotsky, T. Ikai, Y. Okamoto, V. Böhmer, *Chem. Eur. J.* **2004**, *10*, 3324–3330; m) P. D. Beer, M. R. Sambrook, D. Curiel, *Chem. Commun.* **2006**, 2105–2117; n) P. R. Ashton, T. T. Goodnow, A. E. Kaifer, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *Angew. Chem.* **1989**, *101*, 1404–1408; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1396–1399; o) F. Vögtle, S. Meier, R. Hoss, *Angew. Chem.* **1992**, *104*, 1628–1631; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1619–1622; p) A. G. Johnston, D. A. Leigh, R. J. Pritchard, M. D. Deegan, *Angew. Chem.* **1995**, *107*, 1324–1327; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1209–1212.

[4] a) A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, B. Ventura, *J. Am. Chem. Soc.* **1997**, *119*, 12114–12124; b) "Structure and Bonding": *Molecular Machines and Motors, Vol. 99* (Ed.: J.-P. Sauvage), Springer, New York, **2001**; c) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem.* **2000**, *112*, 3422–3425; *Angew. Chem. Int. Ed.* **2000**, *39*, 3284–3287; d) P. Mobian, J.-M. Kern, J.-P. Sauvage, *Angew. Chem.* **2004**, *116*, 2446–2449; *Angew. Chem. Int. Ed.* **2004**, *43*, 2392–2395; e) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175; f) V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178–1183; g) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines: A Journey into Nano World*, Wiley-VCH, Weinheim, **2003**; h) B. Korybut-Daszkiewicz, A. Wieckowska, R. Bilewicz, S. Domagata, K. Wozniak, *Angew. Chem.* **2004**, *116*, 1700–1704; *Angew. Chem. Int. Ed.* **2004**, *43*, 1668–1672; i) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456–464; j) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* **1997**, *119*, 7605–7606.

[5] a) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, O. Manabe, *J. Am. Chem. Soc.* **1981**, *103*, 111–115; b) L. Zelikovich, J. Libman, A. Shanzer, *Nature* **1995**, *374*, 790–792; c) T. R. Kelly, H. de Silva, R. A. Silva, *Nature* **1999**, *401*, 150–152; d) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, *401*, 152–155; e) L. Fabbrizzi, F. Foti, S. Patroni, P. Pallavicini, A. Taglietti, *Angew. Chem.* **2004**, *116*, 5183–5187; *Angew. Chem. Int. Ed.* **2004**, *43*, 5073.

[6] a) *Handbook of Liquid Crystals* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, **1998**; b) *Thermotropic Liquid Crystals* (Ed.: G. W. Gray), Wiley, Chichester, **1987**; c) *Metallomesogens: Synthesis, Properties and Applications* (Ed.: J. L. Serrano), Wiley-VCH, Weinheim, **1996**; d) D. W. Bruce in *Inorganic Materials* (Eds: D. W. Bruce, D. O'Hare), Wiley, Chichester, **1996**, pp. 429–522; e) A.-M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem.* **1991**, *103*, 370–398; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375–402; f) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44–74; *Angew. Chem. Int. Ed.* **2006**, *45*, 38–68; g) M. Muthukumar, C. K. Ober, E. L. Thomas, *Science* **1997**, *277*, 1225–1232; h) M. L. Bushey, T.-Q. Nguyen, W. Zhang, D. Horoszewski, C. Nuckolls, *Angew. Chem.* **2004**, *116*, 5562–5570; *Angew. Chem. Int. Ed.* **2004**, *43*, 5446–5453; i) C. D. Simpson, J. Wu, M. D. Watson, K. Müllen, *J. Mater. Chem.* **2004**, *14*, 494–504; j) G. H. Mehl, *Angew. Chem.* **2005**, *117*, 678–679; *Angew. Chem. Int. Ed.* **2005**, *44*, 672–673; k) T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem.* **2007**, *119*, 512–535; *Angew. Chem. Int. Ed.* **2007**, *46*, 506–528; l) R. Eelkema, B. L. Feringa, *Org. Biomol. Chem.* **2006**, *4*, 3729–3745; m) T. Kato, *Science* **2002**, *295*, 2414–2418.

[7] a) T. Chuard, R. Deschenaux, *J. Mater. Chem.* **2002**, *12*, 1944–1951; b) D. Guillon, R. Deschenaux, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 515–525; c) S. Campidelli, T. Brandmüller, A. Hirsch, I. M. Saez, J. W. Goodby, R. Deschenaux, *Chem. Commun.* **2006**, 4282–4284; d) N. Tirelli, F. Cardullo, T. Habicher, U. W. Suter, F. Diederich, *J. Chem. Soc. Perkin Trans. 2* **2000**, 193–198; e) T. Chuard, R. Deschenaux, *Helv. Chim. Acta* **1996**, *79*, 736–741.

[8] a) I. M. Saez, J. W. Goodby, *J. Mater. Chem.* **2005**, *15*, 26–40; b) I. M. Saez, J. W. Goodby, R. M. Richardson, *Chem. Eur. J.* **2001**, *7*, 2758–2764; c) L. Cseh, G. H. Mehl, *J. Am. Chem. Soc.* **2006**, *128*, 13376–13377; d) C. Keith, G. Dantlgraber, R. A. Reddy, U. Baumeister, C. Tschierske, *Chem. Mater.* **2007**, *19*, 694–710.

[9] A. Godt, *Eur. J. Org. Chem.* **2004**, 1639–1654.

[10] a) K. Kishimoto, M. Yoshio, T. Mukai, M. Yoshizawa, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2003**, *125*, 3196–3197; b) M. Yoshio, T. Mukai, K. Kanie, M. Yoshizawa, H. Ohno, T. Kato, *Adv. Mater.* **2002**, *14*, 351–354; c) M. Kimura, T. Yasuda, K. Kishimoto, G. Götz, P. Bäuerle, T. Kato, *Chem. Lett.* **2006**, *35*, 1150–1151.

[11] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* **1983**, *24*, 5095–5098; b) C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-M. Kern, *J. Am. Chem. Soc.* **1984**, *106*, 3043–3045; c) M. Cesario, C. O. Dietrich-Buchecker, J. Guilhem, C. Pascard, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1985**, 244–247.