Oligopyridine Liquid Crystals—Novel Building Blocks for Supermolecular Architectures Based on Metal Coordination and Hydrogen Bonding

Carsten Tschierske*

2,2′-Bipyridines, 2,2′:6′,2″-terpyridines, phenanthrolines, and other oligopyridines are particularly attractive building blocks for the preparation of supramolecular structures.[1] This is because they easily form well-defined chelate complexes with many metals. Hence, rather complicated and exotic structures, such as catenanes, molecular knots,[2] well-defined helicates,[3] molecular grids,[4] and nanocyclic architectures[5] have been built up in recent years. Additionally, many of their transition metal complexes give rise to interesting paramagnetic, nonlinear optical, photophysical, and redox properties which can be controlled by the rational design of the ligands.

Furthermore, oligopyridines may act as efficient proton acceptors in hydrogen bonding and they can also interact through π-stacking interactions with other aromatic systems. Thus, they provide many different intermolecular interactions useful for designing well-ordered arrays of functional supramolecules. Though the stepwise construction of exotic supramolecular architectures using 2,2′-bipyridines and related oligopyridines has significantly advanced during the recent years, less progress has been achieved in obtaining macroscopic ordered structures built up by these systems. Examples are ordered arrays of molecular grids at the air–water interface[6] and self-assembled helical fibers.[7]

Liquid crystalline phases are especially challenging because they combine order and mobility on a supermolecular level. These well-defined macroscopic structures are the result of a thermodynamically controlled, dynamic self-assembly process. The molecular order provides anisotropic physical (dielectric, magnetic, optic, etc.) properties, whereas the mobility allows the switching between different well-organized states, and this combination leads to a lot of interesting applications.[8]

Many attempts have therefore been made to obtain liquid crystalline oligopyridines and to use them as ligands for the formation of metallomesogens.[9] Thus, Hanabusa et al. described linear polymers **1** comprising 2,2′-bipyridine units whose mesomorphism was however lost when significant quantities of sixfold coordinating cations were introduced.[10] Reports have also appeared of metal complexes of acylated derivatives of 6,6′-diamino-2,2′-bipyridine (**2**)[11] and lyotropic systems based on 4-alkylated 2,2′-bipyridine and 4′-alkylated 2,2′:6′,2″-terpyridine complexes of Ru^{II} and Rh^{II}, such as **3**.[12] Other examples are shown in Figure 1.

However, all these compounds have, if any, only small mesomorphic ranges and rather high melting points.[13–15]

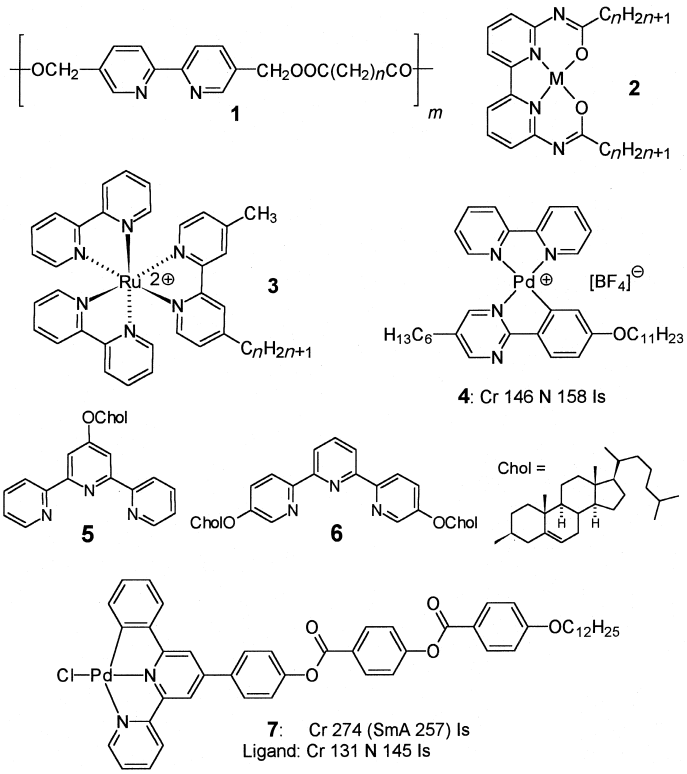
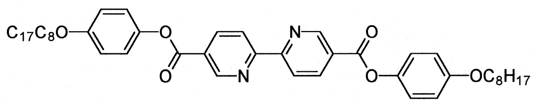


Figure 1. Representative examples of 2,2′-bipyridine mesogens;[10–15] Cr = crystalline phase; N = nematic phase; SmA = smectic A phase; Is = isotropic phase.

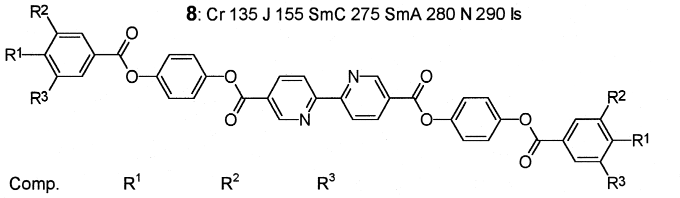
Bruce et al.,[16] Ziessel et al.,[17] and Attias et al.[18] have synthesized molecules incorporating linear 5,5′-disubstituted 2,2′-bipyridine units. These building blocks allow the construction of extended rodlike molecules, for which—according to classic concepts—liquid crystalline phases are likely to occur. Some examples are shown in Figure 2. Indeed broad regions of smectic (SmC, SmA) and nematic (N) phases were obtained for the free ligands **8**. However, the liquid crystalline properties of the parent bipyridines were lost when they were complexed to metal centers.[16b] Clearly, the metal atoms and the additional ligands disturb the parallel alignment of the molecules. In order to reduce this unfavorable steric disturbance it was necessary to enlarge the rigid segment to a minimum of six aromatic rings, which led to the first metallomesogens of this type (for example, **10**).[19] However, such large rodlike molecules with only two terminal alkyl chains have high melting points which inhibit more detailed investigations. Additionally, only nematic phases and layer structures (smectic phases) could be expected for such molecules. To decrease the melting points and to get other mesophases, calamitic bipyridine derivatives with up to six aliphatic chains have been synthesized.[20] Indeed, these polycatenar molecules, such as **9b** and **9c**, have lower melting points and can

---

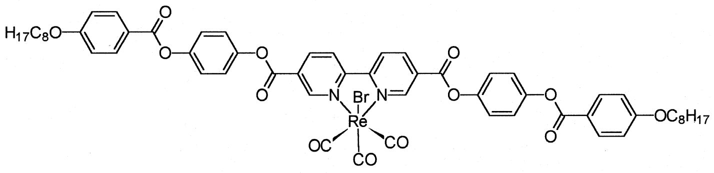
[*] Prof. Dr. C. Tschierske
Institut für Organische Chemie
Martin-Luther-Universität Halle-Wittenberg
Kurt-Mothes-Strasse 2, 06120 Halle (Germany)
Fax: (+49) 345-552-7030
E-mail: Tschierske@chemie.uni-halle.de



8: Cr 135 J 155 SmC 275 SmA 280 N 290 Is

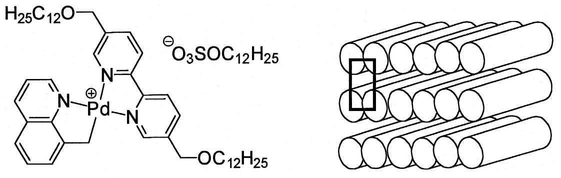


Comp.	R^1	R^2	R^3	
9a	OC_8H_{17}	H	H	Cr 231 SmC 328 N Dec
9b	OC_8H_{17}	OC_8H_{17}	H	Cr 173 SmC 188 Cub 229 Col_h 237 Is
9c	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	Cr 85 Col_1 157 Col_2 165 Is



10: Cr 224 N 315 Is

Figure 2. Representative examples of rodlike 2,2′-bipyridine mesogens[16, 17, 20] and the Re complex derived from **9a**;[19] J = crystalline J phase; SmC = smectic C phase; Cub = cubic mesophase; Col_h = hexagonal columnar phase; Col_1, Col_2 = columnar phases of unknown structure; Dec = decomposition.



11: Cr 131 Col_r 168 SmA 216 Is

Col_r

Figure 3. Structure and transition temperatures (T [°C]) of **11** and a model of the organization of the supermolecular columns in the special Col_r phase (the alkyl chains which fill the space between the layers are not shown).

form not only smectic, but also cubic (Cub) and different types of columnar (Col) mesophases.[20] The investigation of their metal coordination complexes is in progress,[20] but two promising novel types of bipyridine metallomesogens with interesting mesophase structures have been reported by Ziessel et al.

The first one is the Pd^{II} complex **11**, which consists of a positively charged central core unit connected to three flexible and lipophilic alkyl chains, two provided by the bipyridine core and one by the dodecylsulfate ion.[21, 22] Thus, a strongly amphiphilic ionic metallomesogen was obtained with a strong tendency to segregate the polar and rigid central cores from the lipophilic and rather flexible alkyl chains. This material shows a broad liquid crystalline region, whereas the parent uncharged calamitic 2,2′-bipyridine ligand is not mesogenic at all. This means that in contrast to all other earlier attempts with bipyridines, the liquid crystallinity was successfully induced in this case by metal complexation.

Two different liquid crystalline phases have been found: At lower temperatures a columnar phase occurs, in which the nearly flat aromatic central cores stack on top of each other[23] to form columns arranged in a rectangular 2D lattice (Col_r, see Figure 3). However, the structure of this Col_r phase is different from conventional columnar phases, because the columns are not completely surrounded by the alkyl chains. Instead, the polar centers of the columns are in lateral contact with each other, thereby forming layers which are separated from one another by layers of the liquidlike alkyl chains (see Figure 3).

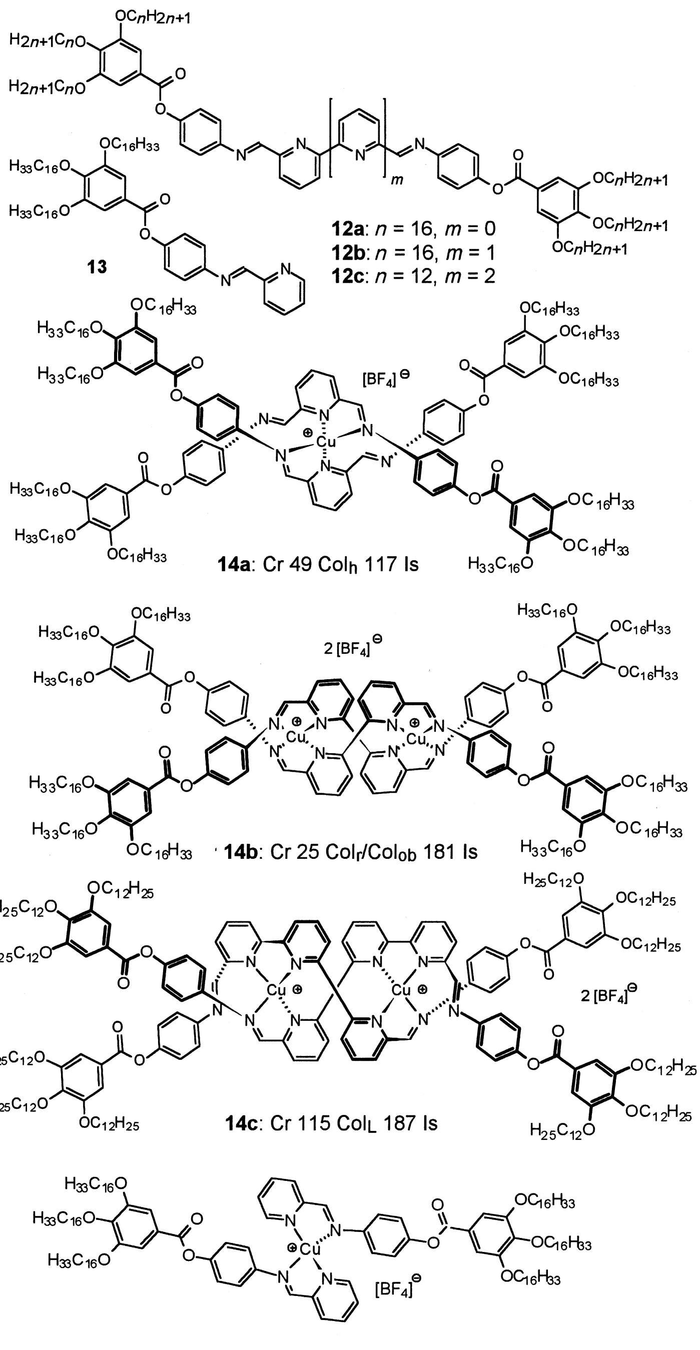
A transition to another mesophase was observed on raising the temperature. Optical investigations indicate a smectic A phase (SmA), whereas X-ray data suggest that a local order of columns is remaining, that is, it could probably be a more disordered variant of the Col_r phase described above.[24]

A second useful approach is based on imino-substituted oligopyridines (Figure 4). These molecules are nonmesomorphic themselves, but they can act as ligands for transition metals. Bisiminobipyridines such as **12**, for example, can form stable Cu^I double helicates incorporating two tetragonal coordinated Cu^I ions. Interestingly, here the bipyridine unit is not the chelate forming unit; only one of the pyridine nitrogen atoms of each bipyridine unit and the neighboring imine group act as chelating ligands, which is in contrast to most other bipyridine complexes.[25]

Such complexes with a sufficiently large number of long alkyl chains can organize into columnar mesophases (Figure 4).[26] In these liquid crystalline phases the nonplanar, polar, and rigid helicates (carrying a positive charge at each of the Cu^I ions and also incorporating the BF_4^- counterions) organize in the centers of the columns which are surrounded by the liquidlike continuum of the nonpolar alkyl chains. This designing principle is not restricted to the bipyridine complexes **14b**, also the Cu^I complexes of the bisiminoterpyridines (for example, **14c**),[27] of the bisiminopyridines (for example, **14a**),[28] and even those of the 2-iminopyridine (**15**)[28] show liquid crystalline properties.

Only one Cu^I ion is coordinated by the two bisiminopyridine ligands in **14a** and by the two iminopyridine ligands in **15**. Hexagonal columnar phases, in which the columns are packed laterally into a two-dimensional hexagonal unit cell, were found for both mononuclear complexes (Col_h, Figure 5). However the diameters of the columns of both compounds are quite different: 60 Å for **15** and only 47 Å for **14a** with the larger ligands. The larger value found for **15** suggests that more than one molecule is located in the diameter of the columns. Since the number of alkyl chains in the complex **15** amounts to only half the number in **14a** this arrangement enables an efficient filling of the peripheral space around the columns. In this respect the organization of **15** is similar to that of the columnar phases of polycatenar liquid crystals[29] and linear stilbazole-Ag^I complexes (for example, **16**).[30] In contrast, the individual molecules of **14a** only stack one on top of the other to form the columns as known for conventional discotic liquid crystals.

However it should be pointed out that, as a result of the pseudotetrahedral coordination geometry provided by the Cu^I ions, these molecules are not flat as are conventional discotic materials. The parallel alignment of rigid discs is



15: Cr 48 Col$_h$ 75 Is

Figure 4. Structures of the nonmesogenic ligands **12** and **13** and their liquid crystalline Cu^I complexes **14** and **15** (T [°C]);[26–28] Col$_r$ = rectangular columnar phase; Col$_{ob}$ = oblique columnar phase; Col$_L$ = lamellar phase built up by the parallel alignment of columnar aggregates.

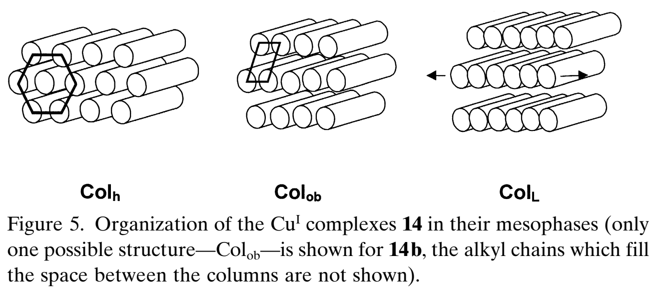
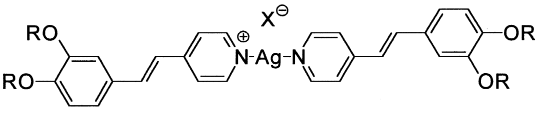
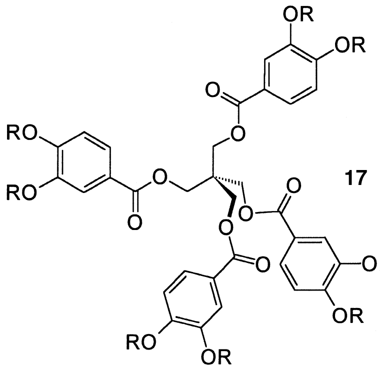


Figure 5. Organization of the Cu^I complexes **14** in their mesophases (only one possible structure—Col$_{ob}$—is shown for **14b**, the alkyl chains which fill the space between the columns are not shown).



16

therefore no driving force for their mesogenity.[31] In this respect the organization of the metallomesogens into columnar phases is strongly related to the organization seen in liquid crystals formed by some purely organic molecules comprising a central tetrahedral carbon atom bearing four semi-rigid subunits with peripheral alkyl chains, such as **17**[32, 33] and its



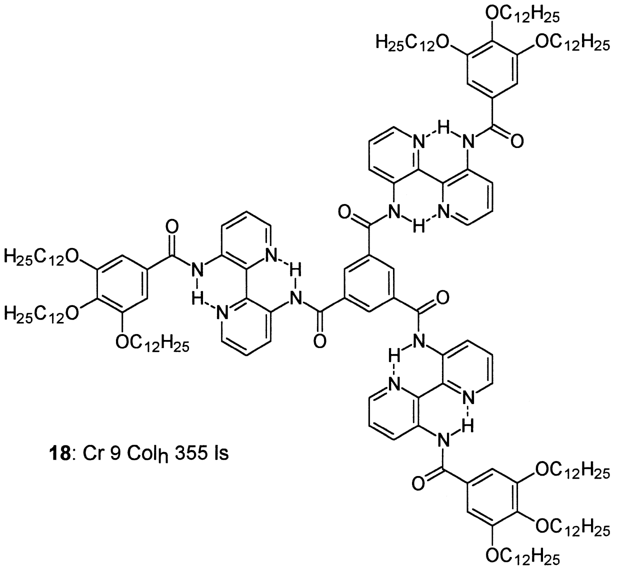
17

semi-fluorinated analogues.[34] For these molecules a micro-segregation of incompatible structural units into different regions, separated by interfaces, was proposed to be the main driving force for mesophase formation.[32, 35] This should be even more important for the organization of **14** and **15**, because the contrast in the intramolecular polarity between the polar cores and the lipophilic chains is much larger in these molecules. Additionally, attractive ionic interactions significantly contribute to their mesophase stability, a feature that is well known for the liquid crystalline phases of anhydrous soaps and other ionic amphiphiles.[36]

Furthermore, geometric and space-filling effects have a large influence on the mesophase structure. This is clear from the comparison of the complexes **14a–c**. In the case of the mononuclear pyridine derivative **14a** the polar rigid centers are rather small and compact. Hence, the long alkyl chains can perfectly surround the columns formed by the polar centers. This allows for the arrangement of the columns in the hexagonal lattice. A lamellar organization was found for terpyridine complex **14c** with the largest central core. In the case of the bipyridine complex **14b** a rectangular or oblique arrangement of the columns (Col$_r$ or Col$_{ob}$, see Figure 5) was detected, which can be regarded as an intermediate phase between columnar and lamellar organization.

The smectic phase of **14c** is again quite unusual as the layers comprise parallel aligned columnar aggregates of the metallohelicates.[24] Hence, this smectic phase is related to the Col$_r$ phase of the Pd complex **11**, as in both cases the layers are formed by the parallel alignment of columns. However, in the smectic phase of **14a** the correlation between the layers is lost and therefore no 2D lattice can be found. Thus, quite different organizations of columns are possible with the bipyridine-derived metallomesogens, and the type of supermolecular self-organization can be fine-tuned by careful molecular design. It is remarkable that the unusual structure of the mesophase of **14c** resembles that of linear DNA stretched across lipid bilayers.[37]

However, coordination of metal ions is not the only feature of oligopyridines that can be used to design novel liquid crystalline materials. The ability of the nitrogen atoms to participate in hydrogen bonding has also been used to design mesomorphic materials incorporating 2,2′-bipyridine units.[38] In the 3,3′-diacylamino substituted 2,2′-bipyridine derivative **18** a high degree of planarity of the molecules is achieved by the large number of intramolecular hydrogen-bonding interactions. This particular shape, the polarity of the central core, and the presence of a sufficiently large number of peripheral lipophilic chains induces hexagonal columnar liquid crystalline behavior. It should be pointed out that these 2,2′-bipyridine derivatives have low melting points, extremely broad regions of liquid crystalline phases, and, additionally, the molecules retain their strong tendency to aggregate also in solutions of apolar solvents.



18: Cr 9 Col$_h$ 355 Is

Thus, significant progress has been achieved in designing oligopyridine derivatives that can self-organize under ambient conditions into well-ordered supermolecular assemblies of macroscopic dimensions. Hopefully, this will allow the construction of novel and more-complex functional supermolecular systems, which are useful for future applications.

---

[1] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; E. C. Constable, *Metals and Ligand Reactivity: An Introduction to Organic Chemistry of Metal Complexes*, VCH, Weinheim, **1995**; F. M. Raymo, J. F. Stoddart, *Curr. Opin. Colloid Interf. Sci.* **1998**, *3*, 150.

[2] J. C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage in *Comprehensive Supramolecular Chemistry*, *Vol. 9* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, K. S. Suslick), Pergamon, Oxford, **1996**, p. 43; D. B. Amabilino, F. M. Raymo, J. F. Stoddart in *Comprehensive Supramolecular Chemistry*, *Vol. 9* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, K. S. Suslick), Pergamon, Oxford, **1996**, p. 85.

[3] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; B. Hasenknopf, J. M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956.

[4] A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1803.

[5] D. P. Funeriu, J. M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1997**, *3*, 99; S. Leininger, B. Olenyuk, P. Stang, *Chem. Rev.* **2000**, *100*, 853.

[6] I. Weissbuch, P. N. W. Baxter, S. Cohen, H. Cohen, K. Kjaer, P. B. Howes, J. Als-Nielsen, G. S. Hanan, U. S. Schubert, J.-M. Lehn, L. Leiserowitz, M. Lahav, *J. Am. Chem. Soc.* **1998**, *120*, 4850.

[7] L. A. Cuccia, J.-M. Lehn, J.-C. Homo, M. Schmutz, *Angew. Chem.* **2000**, *112*, 239; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 233.

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

[9] *Metallomesogens* (Ed.: J. L. Serrano), VCH, Weinheim, **1996**; B. Donnio, D. W. Bruce in *Structure and Bonding 95: Liquid Crystals II* (Ed.: D. M. P. Mingos), Springer, Berlin, **1999**, p. 193.

[10] K. Hanabusa, J.-I. Higashi, T. Koyama, H. Shira, N. Hojo, A. Kurose, *Makromol. Chem.* **1989**, *190*, 1.

[11] T. Kuboki, K. Araki, M. Yamada, S. Shiraishi, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 984.

[12] D. W. Bruce, J. D. Holbrey, A. R. Tajbakhsh, G. J. T. Tiddy, *J. Mater. Chem.* **1993**, *67*, 984; J. D. Holbrey, G. J. T. Tiddy, D. W. Bruce, *J. Chem. Soc. Dalton Trans.* **1995**, 1769.

[13] F. Neve, M. Ghedini, A. Crispini, *Chem. Commun.* **1996**, 2463; F. Neve, M. Ghedini, O. Francescangeli, S. Campagna, *Liq. Cryst.* **1998**, *24*, 673.

[14] E. C. Constable, C. E. Housecroft, *Chimia* **1998**, *52*, 533.

[15] M. Ghedini, D. Pucci, *J. Organomet. Chem.* **1990**, *395*, 105.

[16] D. W. Bruce, K. E. Rowe, *Liq. Cryst.* **1995**, *18*, 161; D. W. Bruce, K. E. Rowe, *Liq. Cryst.* **1996**, *20*, 183.

[17] L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, E. Campillos, R. Deschenaux, *Liq. Cryst.* **1995**, *18*, 157; L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, E. Campillos, R. Deschenaux, *Liq. Cryst.* **1996**, *20*, 235; A. El-ghayoury, L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, *Liq. Cryst.* **1996**, *21*, 143.

[18] A. J. Attias, C. Cavalli, B. Bloch, *J. Chim. Phys.* **1998**, *95*, 1319; A. J. Attias, C. Cavalli, B. Bloch, N. Guillou, C. Noel, *Chem. Mater.* **1999**, *11*, 2057.

[19] K. E. Rowe, D. W. Bruce, *J. Chem. Soc. Dalton Trans.* **1996**, 3913.

[20] K. E. Rowe, D. W. Bruce, *J. Mater. Chem.* **1998**, *8*, 331.

[21] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110*, 1303; *Angew. Chem. Int. Ed.* **1998**, *37*, 1255.

[22] This molecule is in some respect related to compound **4** (Figure 1), which has a nonamphiphilic anion and was reported to show a nematic mesophase.[15]

[23] The polar groups of the amphiphilic anions should be located close to the central cores.

[24] Related lamellocolumnar structures have been found in other classes of compounds: P. Davidson, A. M. Levelut, H. Strzelecka, V. Gionis, *J. Phys. Fr.* **1983**, *44*, L823; G. Lattermann, S. Schmidt, R. Kleppinger, J.-H. Wendorff, *Adv. Mater.* **1992**, *4*, 30; J. Malthête, A.-M. Levelut, L. Liebert, *Adv. Mater.* **1992**, *4*, 37; D. Haristoy, S. Mery, B. Heinrich, L. Mager, J. P. Nicoud, D. Guillon, *Liq. Cryst.* **2000**, *27*, 321.

[25] R. Ziessel, A. Harriman, J. Suffert, M.-T. Youinou, A. De Cian, J. Fischer, *Angew. Chem.* **1997**, *109*, 2621; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2509.

[26] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110*, 2327; *Angew. Chem. Int. Ed.* **1998**, *37*, 2205.

[27] R. Ziessel, L. Douce, A. El-ghayoury, A. Harriman, A. Skoulios, *Angew. Chem.* **2000**, *112*, 1549; *Angew. Chem. Int. Ed.* **2000**, *39*, 1489.

[28] L. Douce, A. El-ghayoury, A. Skoulios, R. Ziessel, *Chem. Commun.* **1999**, 2033.

[29] H. T. Nguyen, C. Destrade, J. Malthete, *Adv. Mater.* **1997**, *9*, 375.

[30] D. W. Bruce, B. Donnio, D. Guillon, B. Heinrich, M. Ibn-Elhaj, *Liq. Cryst.* **1995**, *19*, 537; B. Donnio, D. W. Bruce, *New J. Chem.* **1999**, 275.

[31] Metallomesogens with an octahedral central core have also been reported: A.-M. Giroud-Godquin, A. Rassat, *C. R. Acad. Sci. Ser. 2* **1982**, *294*, 241; H. Zheng, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *111*,

761; S. T. Trzaska, H.-F. Hsu, T. M. Swager, *J. Am. Chem. Soc.* **1999**, *121*, 4518.

[32] A. Pegenau, P. Göring, C. Tschierske, *Chem. Commun.* **1996**, 2563; A. Pegenau, P. Göring, S. Diele, C. Tschierske, *Chem. Eur. J.* **1999**, *5*, 1643.

[33] J. Malthête, *New. J. Chem.* **1996**, *20*, 925.

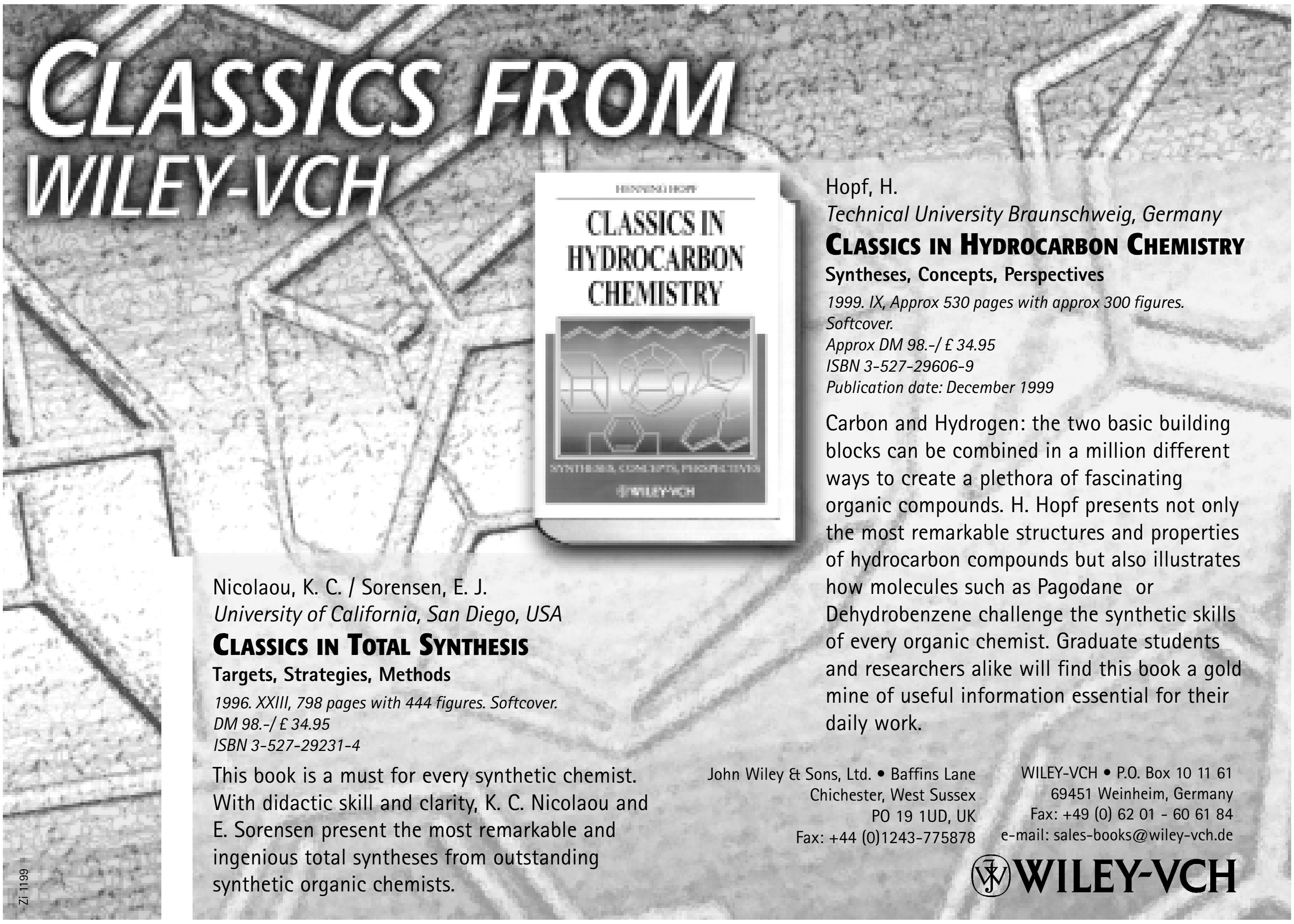
[34] A. Pegenau, X. H. Cheng, C. Tschierske, S. Diele, *New J. Chem.* **1999**, *23*, 465; X. H. Cheng, S. Diele, C. Tschierske, *Angew. Chem.* **2000**, *112*, 605; *Angew. Chem. Int. Ed.* **2000**, *39*, 592.

[35] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485.

[36] C. M. Paleos, *Mol. Cryst. Liq. Cryst.* **1994**, *243*, 159; J. Charvolin, *J. Chim. Phys.* **1983**, *80*, 15.

[37] T. Salditt, I. Koltover, J. O. Rädler, C. R. Safinya, *Phys. Rev. Lett.* **1997**, *79*, 2582; C. R. Safinya, I. Koltover, J. Raedler, *Curr. Opin. Colloid Interf. Sci.* **1998**, *3*, 69; C. S. O'Hern, T. C. Lubensky, *Phys. Rev. Lett.* **1998**, *80*, 4354.

[38] A. R. A. Palmans, J. A. J. M. Vekemans, H. Fischer, R. A. Hikmet, E. W. Meijer, *Chem. Eur. J.* **1997**, *3*, 300; A. R. A. Palmans, J. A. J. M. Vekemans, R. A. Hikmet, H. Fischer, E. W. Meijer, *Adv. Mater.* **1998**, *10*, 873.



CLASSICS FROM WILEY-VCH

Hopf, H.
Technical University Braunschweig, Germany
CLASSICS IN HYDROCARBON CHEMISTRY
Syntheses, Concepts, Perspectives
1999. IX, Approx 530 pages with approx 300 figures. Softcover.
Approx DM 98.-/ £ 34.95
ISBN 3-527-29606-9
Publication date: December 1999

Carbon and Hydrogen: the two basic building blocks can be combined in a million different ways to create a plethora of fascinating organic compounds. H. Hopf presents not only the most remarkable structures and properties of hydrocarbon compounds but also illustrates how molecules such as Pagodane or Dehydrobenzene challenge the synthetic skills of every organic chemist. Graduate students and researchers alike will find this book a gold mine of useful information essential for their daily work.

Nicolaou, K. C. / Sorensen, E. J.
University of California, San Diego, USA
CLASSICS IN TOTAL SYNTHESIS
Targets, Strategies, Methods
1996. XXIII, 798 pages with 444 figures. Softcover.
DM 98.-/ £ 34.95
ISBN 3-527-29231-4

This book is a must for every synthetic chemist. With didactic skill and clarity, K. C. Nicolaou and E. Sorensen present the most remarkable and ingenious total syntheses from outstanding synthetic organic chemists.

John Wiley & Sons, Ltd. • Baffins Lane
Chichester, West Sussex
PO 19 1UD, UK
Fax: +44 (0)1243-775878

WILEY-VCH • P.O. Box 10 11 61
69451 Weinheim, Germany
Fax: +49 (0) 62 01 - 60 61 84
e-mail: sales-books@wiley-vch.de

WILEY-VCH

Zi 1199