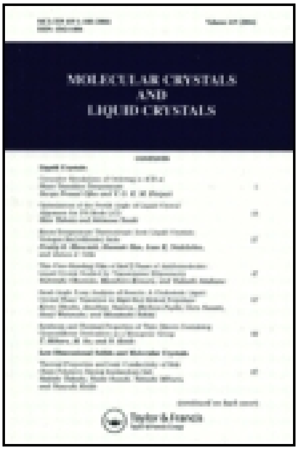


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid-Crystalline Metallo-Helicates: New Pathways for Cooperative Properties

Laurent Douce [a] & Raymond Ziessel [a]

[a] Université Louis Pasteur (ULP), Ecole de Chimie, Polymères, Matériaux (ECPM), Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires associé au CNRS, 25 Rue Becquerel, F-67087, Strasbourg, Cedex 02, France

Version of record first published: 24 Sep 2006

To cite this article: Laurent Douce & Raymond Ziessel (2001): Liquid-Crystalline Metallo-Helicates: New Pathways for Cooperative Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 362:1, 133-145

To link to this article: http://dx.doi.org/10.1080/10587250108025765

Mol. Cryst. Liq. Cryst., Vol. 362, pp. 133-145
Reprints available directly from the publisher
Photocopying permitted by license only

Liquid-Crystalline Metallo-Helicates: New Pathways for Cooperative Properties

LAURENT DOUCE and RAYMOND ZIESSEL*

Université Louis Pasteur (ULP), Ecole de Chimie, Polymères, Matériaux (ECPM), Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires associé au CNRS, 25 Rue Becquerel, F-67087 Strasbourg Cedex 02, France

Recent advances in the fields of liquid crystals and supramolecular chemistry have led to the discovery of mesomorphic *metallo-helicates* formed by selective complexation of non-mesomorphic oligopyridinic ligands built from flexible imino-appendages. Different types of mesophases, ranging from columnar to ordered smectic biaxial, have been generated. In cases where the segmented ligand is adequately engineered, gliding of the coordinated ligands across the metal centers present in the emergent dinuclear complex is made possible by the provision of ancillary imino binding sites and this behavior facilitates liquid-crystalline properties at room-temperature, after supercooling. Furthermore, formation of a mesogenic mixed-valence complex following selective oxidation has been realized. An attempt is made to provide insight on how the strategy of using imino-based oligopyridinic scaffolds permits generation of liquid-crystalline materials with morphologies determined by their molecular components.

Keywords: metallo-mesogens; metallo-helicate; copper; imino-oligopyridines; hybrid-N-ligands

INTRODUCTION

Over the past two decades the area of metallo-mesogens (liquid-crystals containing metal ions) has become a topic of increasing interest. It has been anticipated that the introduction of transition metal centres into liquid-crystalline materials may result in significant modification of certain physical properties, e.g. colour, conduction, magnetism or redox behaviour.[1,2] The ability of transition metal ions to adopt different coordination geometries, and also to organize elemental synthons around a central core, could in principle permit preparation of a wide variety of novel metallo-mesogens. Nowadays, many different metallic centres

---

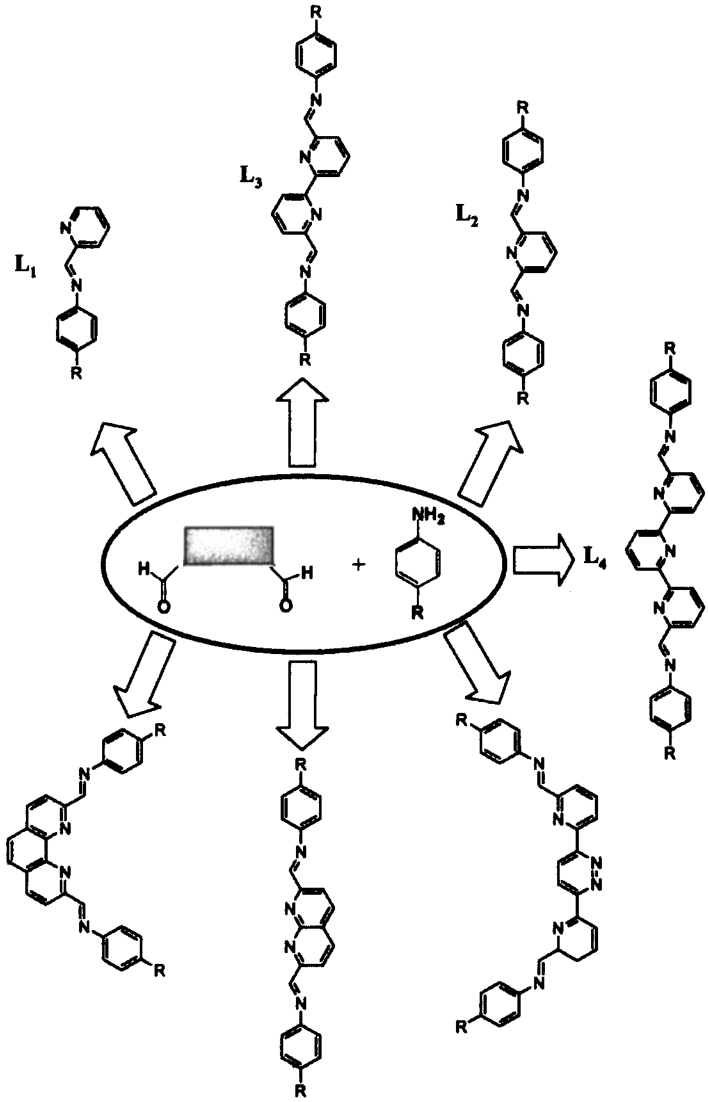
* Corresponding author.

and coordination geometries have been incorporated into the morphology of metallo-mesogens.[3]

In addition, one of the most active research subjects being pursued worldwide concerns the design and construction of nanometre-scale molecular assemblies and supramolecular arrays intended to store, transfer or display information.[4] Chemical information, as expressed through molecular recognition, allows for directing the spontaneous formation of supramolecular species from complementary components. Although control of the supramolecular structure is still a demanding challenge, careful choice of the molecular building blocks makes it possible to predict the nature of the emergent assembly. One of the major challenges remaining in this area concerns the indentification of viable applications (macroscopic function), other than analytical chemistry, for the superstructures and integrating individual supramolecular species into an organized network that can be adressed macroscopically.[5]

The challenge here is to obtain more functional systems, by selective coordination processes around metallic cores, in order to build aesthetic molecular scaffolds (such as helices, grids, ladders, cyclic helicates, tissues…)[6] and to provide access to more sophisticated systems mimicking basic biological functions. Furthermore, these systems are required to operate as molecular-scale electronic devices, such as advanced switches, wires, shuttles, sensors and molecular machines. Moreover, the conjunction of molecular processes (e.g. metal-induced organization of ligands around metallic cations to produce selectively targetted assemblies) and self-assembly of these units at the macroscopic level to form liquid-crystalline materials offers many interesting features, where unexpected properties could emerge. Our research is aimed primarily at these two target areas and here we summarize our strategies for building liquid-crystalline materials from *metallo-helicate* cores.[7]

To date this area has been largely ignored but materials scientists have taken great inspiration from the observation that certain liquid-crystalline materials can self-assemble, at the molecular level, by way of directed hydrogen-bonds.[8] In some cases, these hydrogen-bonds are able to stabilize the molecular edifice in the liquid-crystalline state and/or favour formation of aggregates of non-mesomorpic but complementary modules. Over the past few years, we have explored the possibility of promoting liquid-crystalline behaviour in transition metal complexes formed by controlled coordination of suitably-designed ligands around one or several metal cations. Some of these compounds possess a tetrahedral metallic core,[9] a geometry rarely explored in the field of metallo-mesogens. Our introduction into this fascinating world of metal-induced generation of discrete aggregates, which themselves self-associate at the macroscopic level to form liquid-crystalline materials, has relied heavily on the availability of polyimino-based ligands (pyridine-, phenanthroline-, naphtyridine-, bipyridine-, terpyridine- and pyridazine/pyridine-imines).[10] Because of the readily availability of suitable starting materials, this family of multitopic ligands is highly attractive for the preparation of well-defined organometallic architectures (Scheme 1).



SCHEME 1 Patchwork of selected ligands prepared during this research programme

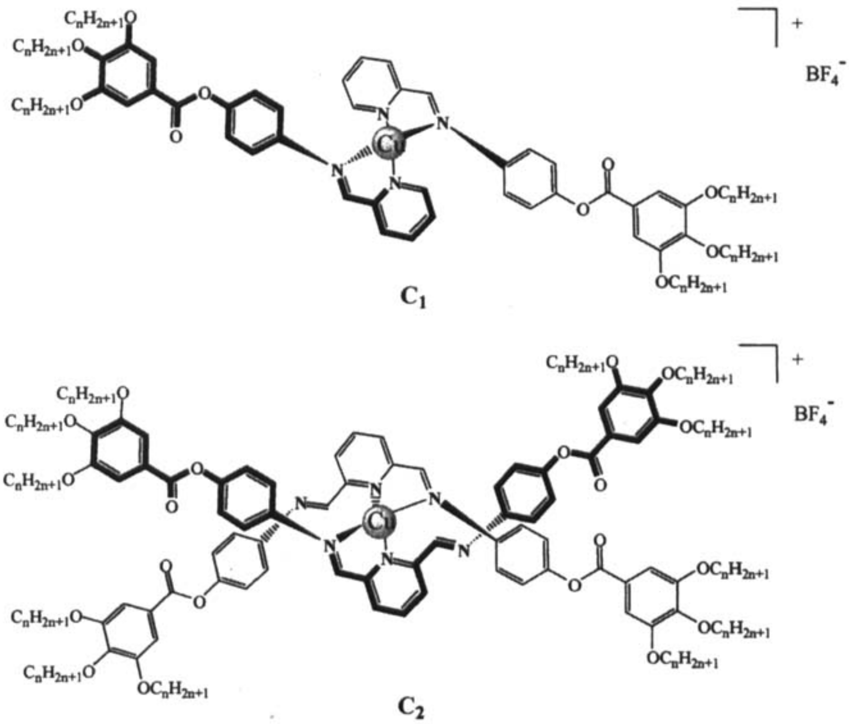
Certain oligopyridines have been used previously for the construction of thermotropic liquid-crystalline polymers based on the homopolyester of 5,5′-substituted-2,2′-bipyridine[11,12] and alkanoyl derivatives of 6,6′-diamino-2,2′-bipyridine.[13] Some of these materials have been complexed with transition metals.[14] Furthermore, it is known that some symmetrical 4,4′- or 5,5′-diester-2,2′-bipyridine ligands,[12] ethynylene substituted frameworks[15] and dissymmetrical stilbene substituted-2,2′-bipyridine moities[11] exhibit a variety of liquid-crystal mesophases. Recently, we reported the synthesis of a family of ligands derived from 5-methyl-5′-[2-(4-alkyloxyphenyl)-2-hydroxyethyl]-2,2′-bipyridine where stabilization of nematic and SmA mesophases is promoted by the presence of directed hydrogen-bonds.[16]

In addition, an unusual type of molecular ordering has been reported for a family of liquid-crystalline cyclopalladated/bipyridine complexes where palladium plays the pivotal role of inducing macroscopic ordering of non-mesomorphic bipyridine modules bearing a reduced number of phenyl groups.[17] In this survey, we explore the opportunity to generate liquid-crystalline materials from selective coordination processes and we highlight particular aspects of our recent discoveries.

RESULT AND DISCUSSION

The synthesis of polyimines is based on the condensation of primary amines with aldehydes grafted onto oligopyridino frameworks. The advantages of this method are: i) the ability to access a wide variety of amino appendages (of differing nature and bearing variable numbers of paraffinic chains); and ii) the isolation of imino derivatives in excellent yield and high purity. Some examples studied involve the formation of metallomesogens by coordination of several non-mesomorphic ligands around a single metallic cation, such as copper(I).[18] In order to highlight this important finding, we shall focus on the synthesis of pyridino compounds bearing imine functions at the 2 or 2,6-positions. The required anilino derivatives were already known in the literature.[19] These ligands were prepared in excellent yields by refluxing 2-formyl pyridine or 2,6-diformyl pyridine with the corresponding amines in ethanol in the presence of a trace amount of acetic acid. Each product has a well defined melting point and, consequently, does not exhibit mesomorphic behaviour.

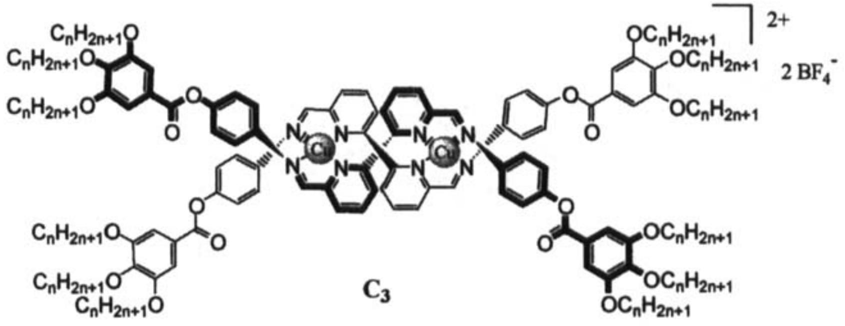
These ligands react with $[Cu(MeCN)_4]BF_4$ to afford deep-red complexes. This coloration is testimony to the presence of four nitrogen atoms coordinated to the metallic centre. Indeed, as confirmed by X-ray structural determinations made on single crystals for related compounds bearing a methoxy substituent, two ligands



SCHEME 2 Chemical drawings of complexes C_1 and C_2

are interlocked around a single copper cation. It is especially notable that for complex C_2, NMR and IR spectroscopic studies indicate fast exchange between coordinated and free imino N atoms.[18] This hemi-lability of the ligands induces increased entropy in the system and certainly plays a major role in the emergence of the mesophase (vide infra). Moreover, this unlocked system should be highly favourable for the preparation of copper complexes in different oxidation states. In turn, this realization provides a rare opportunity to investigate the influence of oxidation states on the morphology of the liquid-crystalline phase, bearing in mind that, by increasing the oxidation state, an increasing number of counter-anions are present in the system. The electronic and magnetic properties of the resulting material might also present some fascinating facets.

Although non-mesomorphic themselves, ligands L_1 and L_2 produce thermotropic liquid-crystalline complexes when coordinated to copper(I) centres. Complexes C_1 and C_2 have been characterized by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. All results obtained with



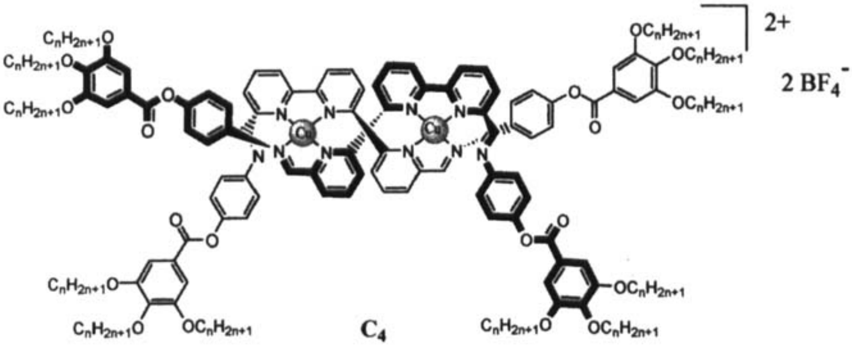
C_3

SCHEME 3 Chemical structure of complex C_3

these techniques remain entirely consistent with a columnar mesophase where the columns are packed laterally into a two-dimensional hexagonal unit cell having parameters of 60 Å and 47 Å for C_1 and C_2 respectively. The larger value found for C_1 suggests that a *"phasmidic type"* of columnar mesophase is present where several individual molecules aggregate to form disk-like entities capable of stacking one on top of the other to generate the columnar mesophase.[18,20]

It is worth pointing out that complex C_1 is able to self-organize at different levels from a trivial coordination process: (i) at the *supramolecular level* with the formation of an aggregate estimated at 60 Å, and (ii) at the *macroscopic level* by formation of a mesophase with a correlation length of more than a hundred ångströms. This system shows a sequential and hierarchic self-organization process. These complexes are uncommon examples of thermotropic liquid crystals containing a tetrahedral centre and are auspicious for the formation of mesomorphic helicoidal assemblies. The key point here is to control the local molecular architecture by a selective coordination process induced by the metal in order to obtain a coherent arrangement at the macroscopic level (liquid-crystalline state). In this perspective, we have prepared the bipyridine ligand L_3 bearing two imino appendages at the 6,6′-substitution positions.[7]

This compound is a segmented multitopic ligand where the metal could be complexed either by a pyridine and an imino fragment or by the two N atoms of the central bipyridine subunit. With the former type of coordination mode, dinuclear complexes should be formed whereas in the latter case only classical interlocked mononuclear complexes should result. When ligand L_3 was allowed to react with $[Cu(MeCN)_4]BF_4$ a deep-green air-stable complex assigned as C_3 was formed in quantitative yield. Based on NMR spectroscopy, we concluded that the two pyridine units of a single ligand are twisted about the central exocyclic C-C

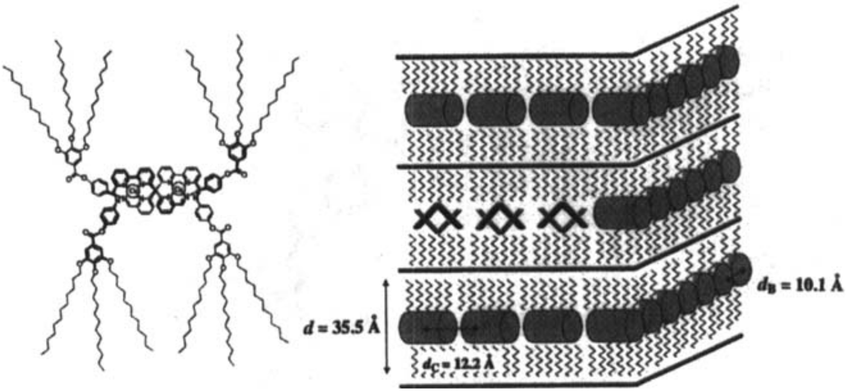


SCHEME 4 Chemical structure of complex C_4

bond and that the two ligands are wrapped around two copper(I) cations to form a helicoidal complex – so-called a *metallo-helicate*. This unexpected, but very interesting, coordination mode has now been confirmed by an X-ray structure on a single crystal for related fluoroanilino derivatives.[21]

The *metallo-helicate* C_3 have been characterized by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. All the techniques are in agreement with a single liquid-crystalline phase over a wide range of temperature (room-temperature to 180°C). The structure consists of columns of rigid cores surrounded by molten alkyl chains and laterally packed in a two-dimensional lattice of rectangular or oblique symmetry.[7] This system, being the first known liquid-crystalline *metallo-helicate*, illustrates the tremendous organizational ability of copper(I) cations. It is, in fact, remarkable that the tiny cation is able to induce order at both molecular and supramolecular levels, considering the large volume and structural disorder inherent to the non-discoïdal ligands. This point is well illustrated by comparison of the molar volumes calculated for the ligand ($V_M = 1356$ cm^3 mol^{-1}) and for the cation ($V_M = 2.2$ cm^3 mol^{-1}).

In order to further illustrate these findings and to increase the coordination versatility of the ligand it was tempting to prepared segmented terpyridine ligands, such as L_4, bearing two imino appendages.[22] Here, the coordination mode of the ligands is more difficult to predict in advance but it seems likely that the presence of multiple donor atoms will favour the formation of very interesting coordination compounds. In fact, the non-mesomorphic ligand L_4 was synthesized in excellent yield by an acid-catalyzed reaction of the pivotal 6,6″-diformyl-2,2′:6′,2″-terpyridine with the appropriate polyfunctionalized anilines.[23] As expected, this versatile ligand self-associates in the presence of a

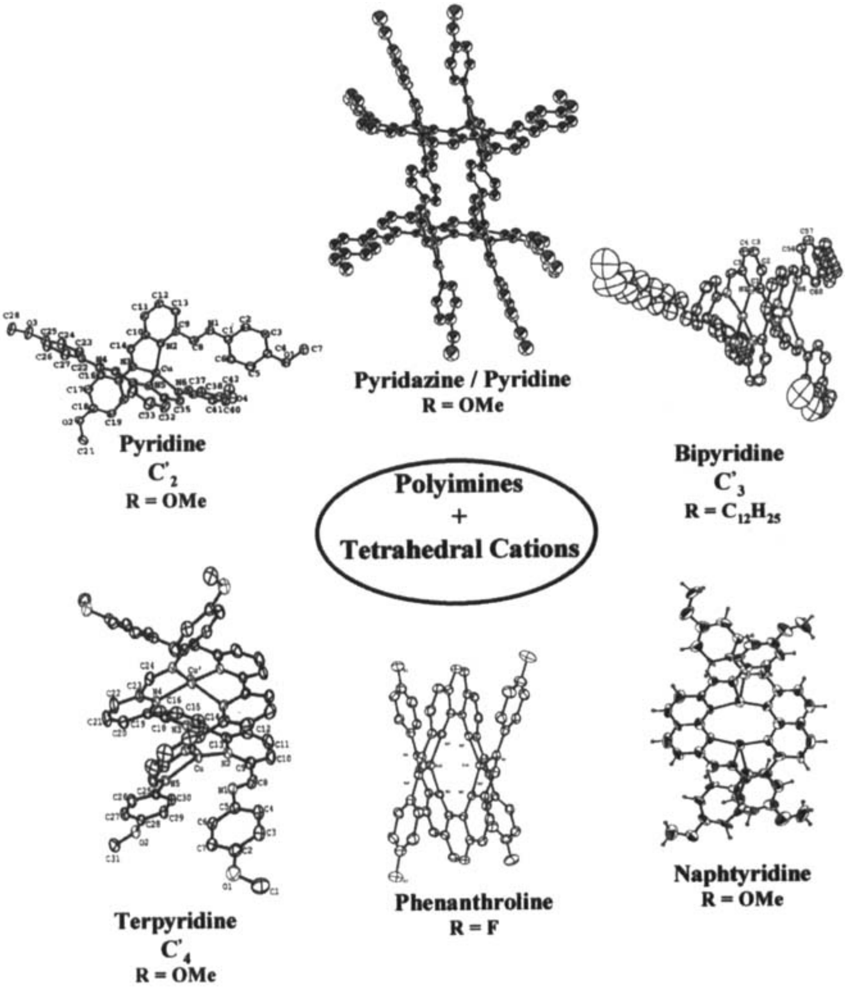


SCHEME 5 (Right) idealized schematic front and lateral view of the smectic layering. The rigid helicate cores (also represented as cyclinders) are arranged in single layers separated by the molten alkyl chains (wavy lines); (Left) schematic representation of the metallo-helicate used in the package

copper(I) precursor to afford a deep-brown, air-stable binuclear metallo-helicate in quantitative yield assigned as complex C_4 (Scheme 4). The two heteroditopic ligands are wrapped around two copper(I) and each metal centre is coordinated to three pyridino N atoms and one imino N atom, leaving a vacant imine fragment on each ligand. The coordination behaviour of this hybrid terpy ligand was determined unambigously by X-ray crystallography on the corresponding methoxy-substituted species (see Scheme 6).

As for complex C_2, NMR and IR spectroscopic studies show that these complexes must be in a state of dynamic fluctuation whereby the two coordinated terpy ligands glide across the metal centers. Despite the fact that this internal flexibility observed in solution might also exist in the liquid-crystalline state it is surmized that this process could be of extreme importance in controlling the morphology of the emerging mesophase. Copper(I) is particularly useful in this regard since many of its diimine complexes are labile, allowing ligand interchange to occur until the most thermodynamically stable assembly has been attained. Furthermore, we note that recent studies on octahedral complexes, have established that certain conformationally unlocked complexes form chiral microdomains within columnar mesophases.[24]

The mesomorphic behaviour of complex C_4 has been studied by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction. All the techniques show an original structure of the liquid-crystalline phase which consists of a smectic biaxial mesophase where the molecules are arranged in regularly spaced layers with the size of a layer corresponding almost exactly to the



SCHEME 6 Patchwork of selected X-ray structures of Cu(I) complexes prepared during this research programme

length of one stretched *metallo-helicate*. Within the aromatic sublayers, about 22 molecules [interaction through the rigid shells] are stacked one on the top of the other to form a column while relatively loose packing inside the row is restricted to about 3.5 repeat units.[23] It is of some interest to note that while the mesophase obtained with the Cu-terpy helicate is smectic that of the corresponding bpy complex is columnar (Scheme 5).

There are two main structural differences between these polypyridine complexes that might account for this variation in mesogen structure: (i) firstly, the extended length of the central aromatic core is expected to stretch the molecule into a calamitic shape that favors a smectic arrangement; (ii) secondly, the fluctional motion inherent to the terpy-based *metallo-helicate* increases the entropy of the system and favours formation of the mesophase. It is this local fluctuation that establishes microdomains sustaining liquid-crystalline behaviour at room temperature. Furthermore, the Cu-terpy helicate forms a highly unusual smectic mesophase comprising layers of *metallo-helicates* arranged in equidistant columns but without 3-D correlation of the layers. Such structures are made possible by combining internal flexibility of the coordinated polytopic ligands, ancillary coordination sites to stabilize emerging redox centers, and multiple flexible sidechains. The unique properties of these liquid-crystalline complexes arise from the combination of order and mobility at the molecular level and to an adequate mismatch between the central helicoidal shell and the flexible swallowed-shaped paraffinic tails. The principles elucidated by these studies may certainly be applicable to other classes of molecules as well and suggest that the introduction of flexible coils in self-assembled supramolecular structures might provide access to a novel strategy to construct multidimensional nanostructures. Hence, it is striking to see a remarkable similarity with the mesophase observed for linear DNA stretched across phospholipid bilayers.[25]

Future developments of this research programme will be devoted to the study of naphtyridine dinuclear copper(I) and of tetranuclear copper(I) complexes arranged as an inverse grid (Scheme 6). The molecular structures of these complexes have readily been determined by X-ray diffraction on single crystals, with the bipyridine ligand bearing the methoxy substituents. The polycatenar ligand discussed within this review also favours preparation of nickel (II), cadmium (II) and iron (II) complexes with octahedral coordination geometries. We are now beginning to witness such octahedral liquid-crystalline complexes and we expect to extend this science to include other useful physical properties such as photoconduction and cooperative magnetism.

CONCLUSION AND OUTLOOK

The key elements of our approach involve: (i) the use of copper(I) cations to self-assemble a functionalized *metallo-helicate* and (ii) the subsequent self-organization of the helicate into a network displaying liquid-crystalline properties. The structural demands that allow optimization of each step are contrary such that spontaneous formation of the liquid-crystal requires delicate balancing between organized and chaotic subunits. The fact that a *metallo-helicate* can be so readily formed from ligands described in this account is remarkable. The self-assembly of these helicates into a low-temperature liquid crystal is astonishing and certainly deserves further development. The pioneering results described herein open the way to a new class of metallo-mesogens. The standard practice of employing discoid components for the assembly of a metallo-mesogen around a pseudo-tetrahedral center is shown to be outdated.

The design and preparation of organized molecular networks wherein individual molecules act cooperatively to fulfill a useful function is certainly an avenue which has some future. Such arrays are commonplace in biology, where protein scaffolds hold the various cofactors in place, but are very difficult to realize in artificial systems. In principle, valuable networks could be assembled around metallo-mesogens where the redox-active metal center would perform the task and the outer paraffinic chains would ensure proper alignment of individual molecules. For this reason, attention has focussed on the design of liquid-crystalline materials from *metallo-helicates* but, in general, results have been far from satisfactory. Many bidentate ligands are known to form metallo-mesogens, but these require relatively high temperatures and lack redox capability. In trying to overcome these difficulties, we have explored the use of pentadentate ligands as the basic building blocks; a field largely ignored to date.

A key element of the terpyridine case involves the use of segmented polytopic ligands bearing a vacant coordination site. This facilitates formation of symmetrical *metallo-helicates* that remain in unlocked conformations. Fluctional motion of the ligands gliding across the metal centers provides for the low-temperature mesogenic phase and for stabilization of higher-valence states. Recognition of this simple realization could lead to the generation of new metallo-mesogens displaying highly desirable properties.

As discussed in this survey, the molecular architecture paradigm allows the creation of a remarkable variety of artificial self-assembling systems of different shapes, sizes and structures. Such molecular processes are highly versatile and allow the ready formation of a great number of discrete supramolecular species with well-defined and predesigned shapes. Some of these supramolecular assemblies are generated by cooperative processes but positive cooperativity is not mandatory for the selective formation of a single structure. Furthermore, the structural and functional features of self-assembled supramolecular entities result from the information encoded in their components and the intrinsic properties are dictated by the presence of additional functional groups (such as the terpy case). The most striking advantages of this molecular approach are its wide applicability and the large and different number of potentially suitable transition metal complexes and multidentate nitrogen-containing scaffolds that are available as building blocks. The excellent product yields and tidiness inherent to such processes make them highly suitable for the generation of metal containing mesophases. The applicability of these new materials, employing coordination as the motif, clearly allows the manipulation of the macroscopic properties. The creation of future supramolecular species and nanoscale devices with specific and precisely-tuned properties, functions and microenvironments will be achieved rapidly. This new generation of attractive synthetic targets deserve more attention and could provide answers to the following questions: (i) how large can the self-assembled molecular system become; (ii) what will be the effect of transition metals of varying coordination geometries, electronic structures and charges; and finally (iii) what will be the physical properties of the emerging mesophases with respect of stability, resistivity or photoconductivity. These answers will be essential if we are to continue the discovery of new materials beyond the next decade.

Acknowledgements

We express our sincere appreciation to Dr. Abdelkrim El-ghayoury who defended his doctoral thesis in 1999, and to our colleages from IPCMS, named in the cited literature, for their helpful and stimulating discussions. Our special thanks goes to Dr. Antoine Skoulios for his enthusiasm and outstanding expertise. Without his specialist skills this review and the related publications could not have been undertaken. We thank the ECPM, ULP and CNRS for continuous financial support. We are also indebted to Professor Anthony Harriman for his encouragement of this research programme.

References

[1] A. P. Polishchuk, T. V. Timofeeva, *Russ. Chem. Rev.* **62**, 291 (1993); R. Deschenaux and J. W. Goodby, in *"Ferrocenes"*, edited by A. Togni and T. Hayashi, VCH, Weinheim, Ch. 9, pp 471–495 (1995); D. W. Bruce, in *"Inorganic Materials 2nd Edition"*, edited by D. W. Bruce, D. O'Hare, Wiley & Sons, pp 429- 522 (1996); J. L. Serrano, *Metallomesogens*, VCH, Weinheim, (1996); A. M. Giroud-Godquin, Coord. Chem. Rev., **178–180**, 1486 (1998).

[2] C. Tschierske, *Prog. Polym. Sci.*, **21**, 775 (1996); J. L. Serrano, *Prog. Polym. Sci.*, **21**, 873 (1997); U. Stebani, G. Lattermann, M. Wittenberg, J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.*, **35**, 1858 (1996); C. Tschierske, *J. Mater. Chem,*. **8**, 1485 (1998).

[3] B. Donnio, D. W. Bruce, *Structure and Bonding (Berlin)*, **95**, 193 (1999).

[4] J.-M. Lehn, *Supramolecular Chemistry*, VCH Weinheim, (1995); M. Munakata, L. P. Wu, T Kuroda-Sowa, *Adv. Inorg. Chem.*, **46**, 173 (1999); C. Piguet, *J. Incl. Phen. Macro. Chem.*, **34**, 361 (1999).

[5] K.E. Drexler in *Nanosystems, Molecular Machinery, Manufacturing and Computation*, Wiley, New York, (1992).

[6] J.S. Lindsey, *New J. Chem.*, **15**, 153 (1991); D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.*, **95**, 2229 (1995); D. Phip, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl. 35*, 1154 (1996); C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.*, **97**, 2005 (1997); B. Olenyuk, A. Fechtenkötter, P.J. Stang, *J. Chem. Soc., Dalton Trans.*, 1707 (1998); J.-P. Sauvage, *Acc. Chem. Res.*, **31**, 611 (1998).

[7] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem. Int. Ed*, **37**, 2205 (1998).

[8] R. Klepppinger, C. P. Lillya, C. Yang, *J. Am. Chem. Soc.*, **119**, 4097 (1997) and references therein; M. Suarez, J.-L. Lehn, S.C. Zimmerman, A. Skoulios, B. Heinrich, *J. Am. Chem. Soc.*, **120**, 4097 (1998).

[9] F. Neve, M. Ghedini, A. Crispini, *Chem. Commun*, 2463 (1996).

[10] Abdelkrim El-ghayoury, Université Louis Pasteur doctoral thesis (1999).

[11] D. W. Bruce, K. E. Rowe, *Liq. Cryst.*, **18**, 161 (1995), *ibid*, **20**, 183 (1996).

[12] L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, E. Campillos, R. Deschenaux, *Liq. Cryst.*, **18**, 157 (1995); *ibid*, **20**, 235 (1996).

[13] K. Hanabusa, J.-I. Higashi, T. Koyama, H. Shirai, N. Hojo, A. Kurose, *Makromol. Chem.*, **190**, 1 (1989).

[14] T. Kuboki, K. Araki, M. Yamada, S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **67**, 948 (1994).

[15] A. El-ghayoury, L. Douce, R. Ziessel, R. Seghrouchni, A. Skoulios, *Liq. Cryst.*, **21**, 143 (1996).

[16] L. Douce, R. Ziessel, H.-H. Lai, H-C. Lin, *Liq. Cryst.*, **26**, 1797 (1999).

[17] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem. Int. Ed.* **37**, 1255 (1998).

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

[19] H.-T. Nguyen, C. Destrade, J. Malthête, Adv. Mater., **9**, 375 (1997) and references therein.

[20] D. Guillon, *Structure and Bonding (Berlin)*, **95**, 41 (1999) and reference therein.

[21] R. Ziessel, A. Harriman, J. Suffert, M.-T. Youinou, A. De Cian, J. Fischer, *Angew. Chem. Int. Ed. Engl.*, **36**, 2509 (1997).

[22] A. El-ghayoury, A. Harriman, A. De Cian, J. Fischer, R. Ziessel, *J. Am. Chem. Soc.*, **120**, 9973 (1998).

[23] R. Ziessel, L. Douce, A. El-ghayoury, A. Harriman, A. Skoulios, *Angew. Chem. Int. Ed.*, **39**, 1489 (2000).

[24] S. T. Trzaska, H.-F. Hsu, T. M. Swager, *J. Am. Chem. Soc.*, **121**, 4518 (1999).

[25] T. Salditt, I. Koltover, J. O. Rädler, C. R. Safinya, *Phys. Rev. Letters*, **79**, 2582 (1997).