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Schiff-based bipyridine ligands. Unusual coordination features and mesomorphic behaviour

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Dedicated to the memory of Professor John Osborn

Contents

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Abstract

Recent investigations from our laboratory have described compelling experimental evidence that Schiff-based pyridine, bipyridine (bipy), terpyridine (terpy), phenanthroline (phen), naphthyridine (naphthy) and pyridine–pyridazine (pyridaz) ligands exhibit a rich coordination chemistry towards transition metal complexes providing unusual coordination modes. This is well illustrated with bipy and phen frameworks which exhibit a bridging type of coordination compared to the classical chelating behaviour. In such a way metallo-helicates are produced in a straightforward manner. A similar helicoïdal complex is prepared with the naphthy ligand while a tetranuclear tissue-like complex is obtained with the pyridaz frame. The stability constants for these copper(I) complexes were determined by spectrophotometric titrations and global analytical techniques. Each step of the assembly process could be deciphered and the association constants of the final complexes are high. An important caveat of these studies is that positive cooperativity is not mandatory to obtain a helicate template as the final product. Judicious grafting of flexible and paraffinic tails to these multichelating ligands insure the formation of mesomorphic material after a selective metal-induced wrapping of the non-mesomorphic strands around the copper(I) cations. By careful design of the system either columnar or columnaro-smectic mesophases are observed at room-temperature. This simple approach of using Schiff-based scaffoldings which are easy to obtain in a pure form, also facilitates the extension of the size of the supramolecular assembly and the alteration of the molecular shape. Other metals such Ni(II), Fe(II), Cd(II) could be complexed easily which testify to the remarkable properties of this family of compounds. Finally, some consideration is given to the preparation of larger systems and their possible use in molecular based-devices.

Keywords: Oligopyridines; Schiff-based ligands; Copper(I) complexes; X-ray structures; Stability constants; Liquid crystalline properties; Packing

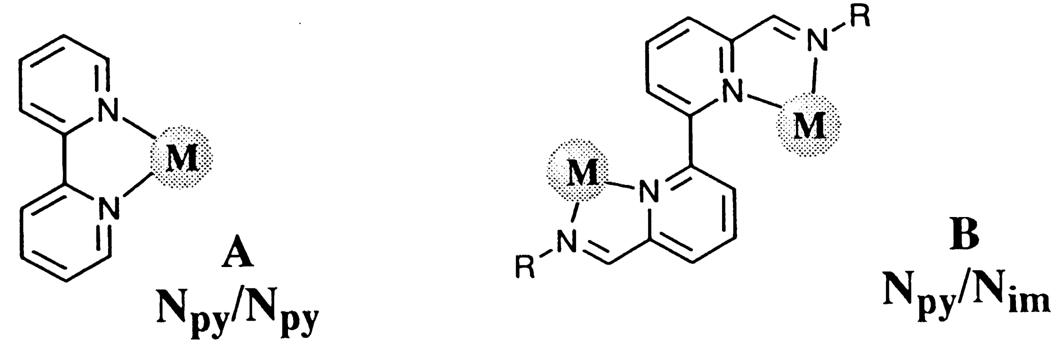
1. Introduction

One of the most challenging research areas in modern chemistry is the design and synthesis of multifunctional compounds and materials with desirable or predictable properties such as luminescence, transport of information, catalytic activity and macroscopic ordering in mesophases [1–4]. In recent years there has been a tremendous growth in these scientific areas loosely described as material science and supramolecular chemistry. A plethora of fascinating molecular structures, often involving interlocking of complementary molecular components has arisen for possible use in the future development of innovative miniaturized devices [5]. Numerous examples of supramolecular assemblies based on selective metal to ligand interactions have been engineered with the view point of forming symmetrical and esthetic structures. Elegant strategies have been elaborated in order to build these assemblies and to provide examples of discrete and infinite helical frameworks [6], hydrogen-bonded [7] or π–π interacting networks [8], three-dimensional supramolecular complexes displaying defined channels [9], cucurbituril assemblies [10], highly symmetric coordination clusters [11] and organometallic polymers [12].

Many of the new inorganic supermolecules generated over the last few years rely on the coordination of transition metal cations to polypyridine fragments incorporated into oligomeric ribbons or macroscopic loops [13–15]. This work has combined ingenious synthetic strategies with state-of-the-art of characterization, in some cases relying on novel analytical methodologies [16]. By virtue of forming relatively stable and well-defined complexes with metal cations, polypyridine ligands have facilitated assembly of molecular double or triple stranded helicates-[6,17,18], catenates [19], ladders and related exotic frameworks [20,21]. Such elaborate molecular architectures are made possible by incorporating several polypyridine units into oligomeric or macrocyclic multitopic ligands. Subsequent coordination with cationic metal centers provides the impetus for self-organization into ordered structures, some of them exhibit useful catalytic activity [22], mesomorphic [23] or electronic [24] properties. Some attempts have been made to identify the driving forces for the formation of one structure versus another by systematic variation of the metal and ligand component, but very little is known about the mechanism of formation of these metal-induced self-organized structures [25–30]. The thermodynamic stability of the organized scaffoldings is rarely available and is definite if we required to use them in organized mesophases with potential applications such as in photoconduction, in catalysis, as chemiosensors or as molecular-based logic gates.

Most of the classical systems require time-consuming multi-step syntheses from expensive starting materials, and tedious chromatographic separations which affords the targeted ligands in low yields. We recently adopted a different strategy based on the addition of coordination sites (imino-functions) around a single and central bipyridine coordination shell. The ready availability of these Schiff-based ligands, the simplicity of the purification procedures, the mildness of the reaction conditions, and the high yields allow the preparation of multigramm scale materials. Furthermore, it is anticipated that the addition of targeted functions to the ligand is a very attractive feature. It is supposed that the presence of two additional donor atoms nearby the central bipyridine frame will by-pass the conventional chelating coordination mode (A) of the bipyridine to a non-conventional mode of coordination (B) where the ligand bridges two metal centers (Scheme 1) [30].

It is the aim of the present account to give a cursory examination of recent developments in the construction of supramolecular frameworks which combine the covalent bond-forming capability of metallic centers with imino-derivated oligopyridine ligands. Different mechanistic aspects will be clarified concerning: (i) the mechanism of assembly and subsequent dissociation in the presence of a competing ligand; (ii) the stabilization of the metallo-helicate against oxidative dissociation and the implication for redox catalysis; (iii) the internal flexibility of the emerging metallo-helicate; (iv) the integration of the helicoidal structures into organized assemblies notably liquid crystals; (v) analytical tools by which to best resolve the molecular structures; (vi) and finally the structure requirements for metallo-helicate assembly and their possible applications.



Scheme 1.

2. Imino–bipyridine and imino–phenanthroline helicates

2.1. Arene–chromium–tricarbonyl complexes

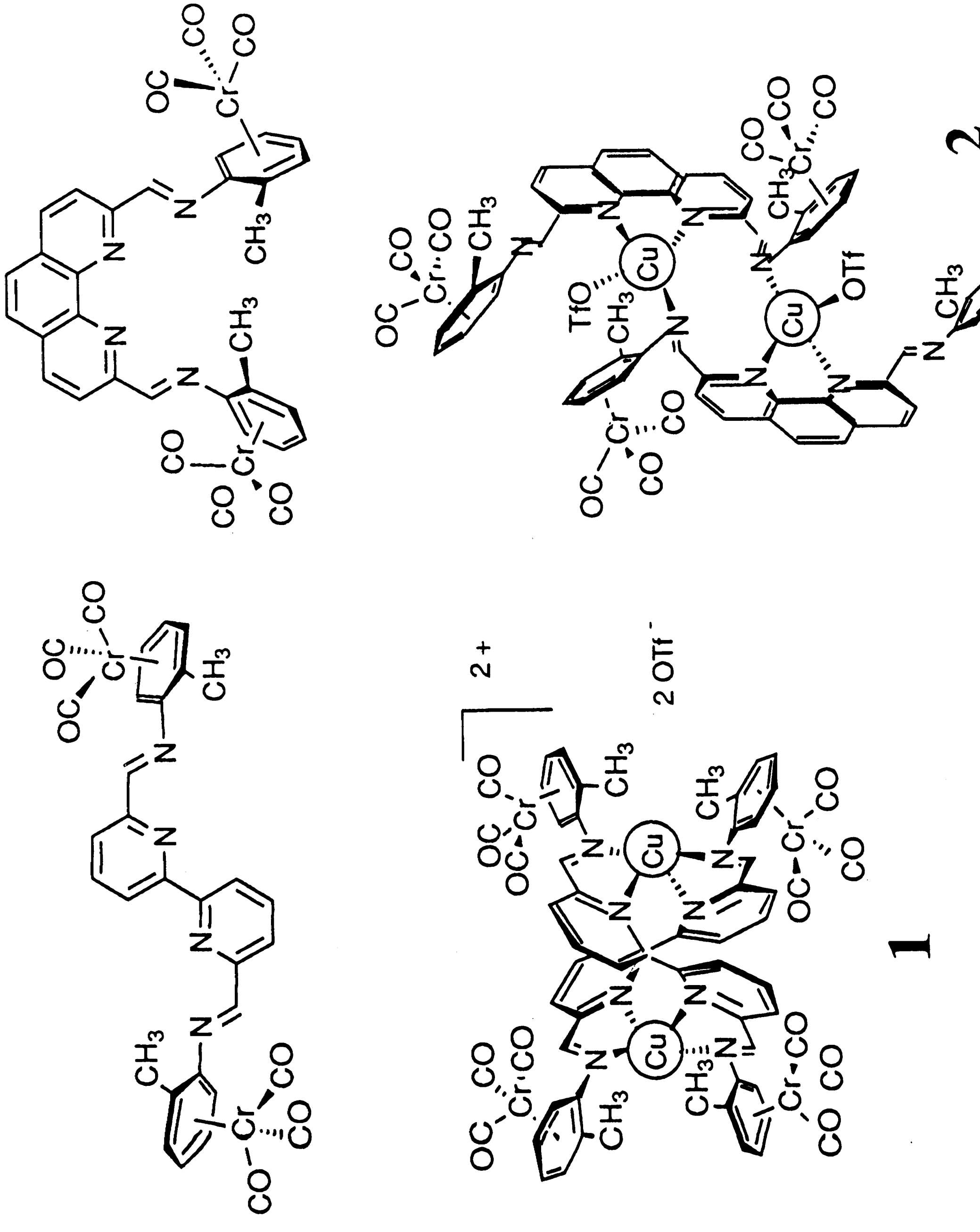
We entered in this field when we discovered that imino-substituted 2,2′-bipyridine and 1,10-phenanthroline units grafted in close proximity to the central N_{py},N_{py} core with two arene–chromium *ortho*-toluidine subunits, formed non-conventional polynuclear complexes **1** and **2** (Scheme 2) with an unexpected two ligands/two copper(I) stoichiometry [31].

The deep-violet bipy complex **1** is best described as a helicate where two ligands are wrapped around the two copper(I) centres in a helical arrangement. The chelating centres are provided by the imino–pyridine units and each metal is coordinated by two of these fragments. For the more rigid phen ligand a hybrid situation is found where the deep-red ladder complex **2** is isolated and in which each copper centre chelates to the central *N*,*N*-phen core, in a classical fashion, and to the imino function of a second ligand. A triflate anion completes the first coordination shell of the metal. In **2**, two uncomplexed imino functions are clearly evidenced by FT-IR and NMR spectroscopies [31]. It is worth pointing out that both complexes were converted quantitatively, in acetonitrile, to the more conventional deep-orange complexes **3** and **4** displaying a classical two ligand/one copper stoichiometry (Scheme 3).

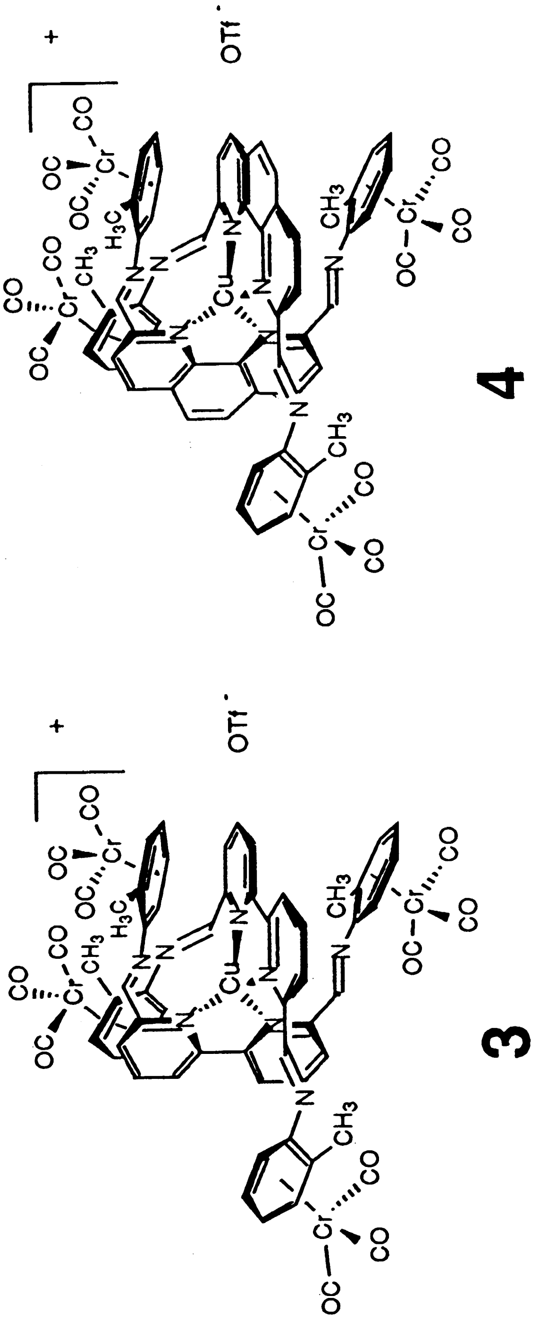
It was surmised at that time that the dicopper(I) complexes were the kinetic products of complexation — formed rapidly under non-equilibrating conditions in a non-polar solvent such as dichloromethane — whereas the mononuclear complexes are the thermodynamic product of complexation when prepared under equilibrating conditions in a coordination solvent such as acetonitrile. It was unfortunately not possible at that time to decipher the mechanism of formation of these unexpected dicopper complexes [31]. These studies raised interesting questions concerning the possible involvement of an electronic effect inherent to the strong withdrawing character of an arene–chromium tricarbonyl moiety and of a possible steric crowding around the potential N_{py},N_{py} chelating center versus the N_{py},N_{im} fragment. This motivated a research program aimed at the construction of analogous imino–oligopyridine frameworks constructed with fluoroaniline, anisidine and anilines substituted with flexible chains.

2.2. Schiff-based complexes

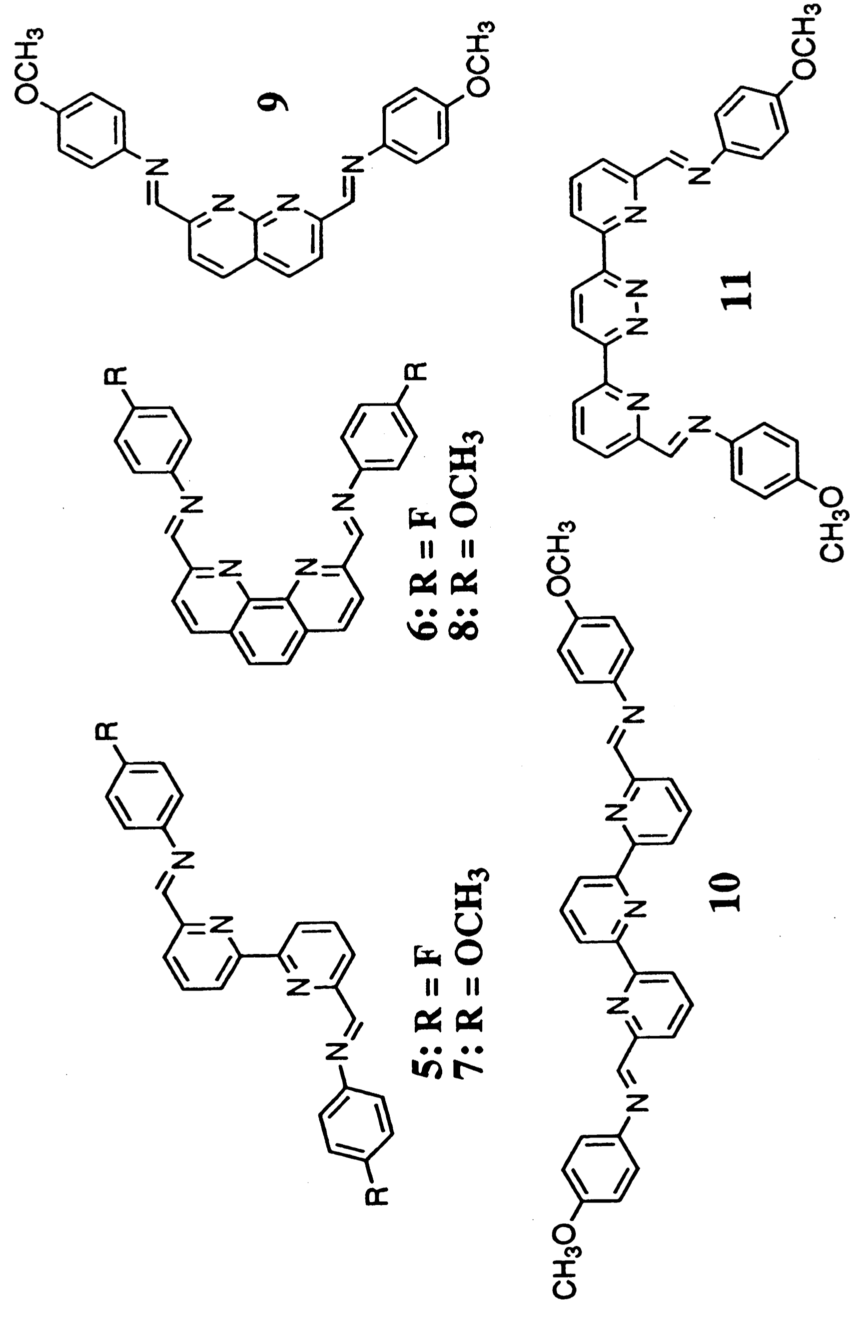
Some relevant examples are given in Scheme 4 and synthetic details, purification procedures and characterization may be found in the cited literature. These ligands were synthesized by a classical protocol inspired from Schiff-based synthesis of podands, macrocycles and macrobicycles, and utilizing a condensation reaction of the formyl substituted molecules with the targeted aniline derivatives in the presence of trace amounts of acids.



Scheme 2.



Scheme 3.



5: R = F
7: R = OCH$_3$

6: R = F
8: R = OCH$_3$

9

10

11

Scheme 4.

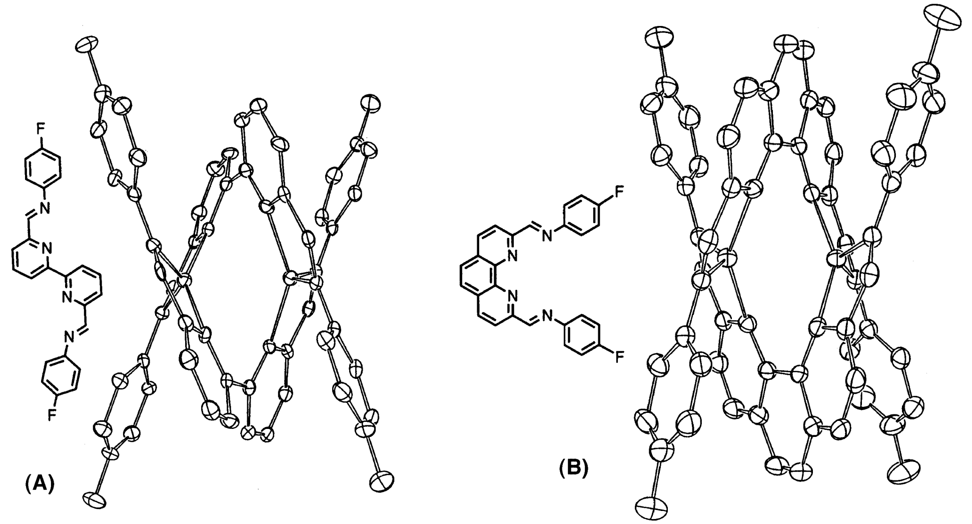


Fig. 1. ORTEP drawings of the $[Cu_2(L)_2](ClO_4)_2$ complexes, showing 50% probability thermal ellipsoids, (A) L = **5** and (B) L = **6**. The hydrogen atoms are omitted for clarity.

In the first step, ligands **5** and **6** were studied and allowed to react with copper(I) cations affording deep-green dinuclear complexes in near quantitative yields. Here, the Cu(I) cations bind preferentially at the N_{py},N_{im} part of the ligand rather than at the central N_{py},N_{py} fragment as found previously with arene–chromium substituted ligands under thermodynamic conditions (acetonitrile). This novel coordination mode was deduced from NMR and FT-IR spectroscopies and later confirmed by an X-ray molecular structure for each type of complex (Fig. 1).

Indeed, the solid-state structures are best described as double-stranded helicates with the two copper(I) cations lying at center-to-center separations of 2.885 and 2.748 Å, respectively, for $[Cu_2(\mathbf{5})_2]^{2+}$ and $[Cu_2(\mathbf{6})_2]^{2+}$. These separations are among the shortest metal–metal distances yet found in inorganic helicates [32], being of the same order as found in many copper-containing enzymes [33], but there is no clear indication of a copper–copper bond. Each ligand wraps around the two copper(I) cations with the bipyridine units being twisted by 33° about the exocyclic central C–C bond. Interestingly, the copper(I) center is significantly closer to the imino N atom than to the adjacent pyridine unit. In the phen case this twist is also indicated clearly in the solid state but significantly less pronounced (ca. 6°, see Fig. 1B). The severe internal distortion apparent in the X-ray structures of these helicates is strong testimony to the coordinative ability of the imino-function.

These crystallographic structures clearly indicate that, at least in the solid state, individual pyridine groups within a given ligand are complexed to separate cations. Each copper(I) ion is coordinated to four nitrogen atoms, provided by the imine and pyridine groups of two distinct ligands, to give a distorted tetrahedron with a bite angle of 80°. It appears, therefore, that incorporation of imine groups at the α,α′ positions of a bipy or phen ligand causes the central unit to become non-chelating and, instead, to adopt a bridging role. Whereas, is not too surprising for **5**, where individual pyridines can rotate freely, it is unparalleled in the case of the phen-based ligand **6** where the pyridino N atoms are well sited to form a chelate.

These two unique complexes were the first examples which unveiled the ability of bipyridine and phenanthroline frameworks to act selectively as bridging ligands rather than bidentates.

Clearly this unprecedented coordination mode of the bpy and phen units leading to metallo-helicates opens the possibility to construct novel molecular architectures which are relatively easy to prepare from inexpensive starting materials and conveniently characterized by classical spectroscopic tools.

Furthermore, the phen-based ligand has permitted isolation under specific experimental conditions [30], of a key intermediate [formulated as $Cu(Imphen)_2$] prior to helicate formation. This mononuclear complex also lacks the characteristic MLCT absorption band (at ca. 450 nm) characteristic of copper(I) bis chelating phenanthroline complexes [34]. Ligand **6** has a high tendency to coordinate to a copper(I) center via the imino–pyridine fragment. Isolation of this pivotal intermediate allowed us to infer the overall reaction mechanism without undue speculation.

3. Mechanism of formation and stability

3.1. Association and dissociation constants

We have used extensive spectrophotometric titrations with global analytical techniques to elicit stability constants for each step in helicate formation (Fig. 2).

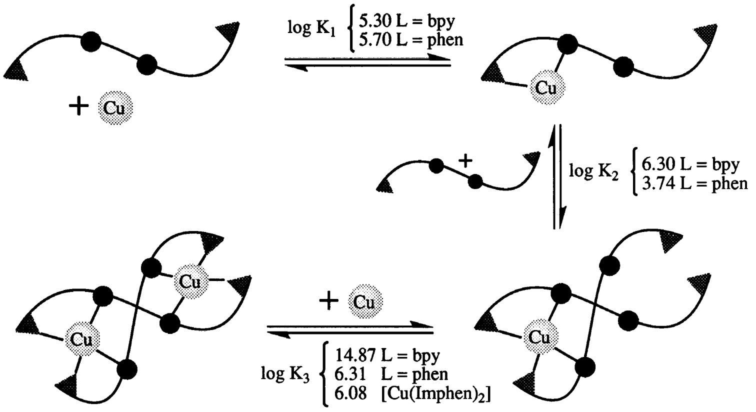


Fig. 2. Schematic representation of the helicate formation with ligands L = **5** (bpy) and L = **6** (phen), with the stability constants determined for each steps. For K_3 the stability constant has also been determined starting from the isolated $[Cu(Imphen)_2]$ complex. The triangle and the circle correspond to the N_{im} and N_{py}, respectively.

As expected, it was possible in the case of the phen ligand **6** to confirm the stability constant for the final step of helicate formation by titration from the isolated [Cu(Imphen)$_2$] complex.

$$Cu^+ + L \rightleftharpoons [Cu(L)]^+ \quad K_1 \tag{1}$$

$$[Cu(L)]^+ + L \rightleftharpoons [Cu(L)_2]^+ \quad K_2 \tag{2}$$

$$Cu^+ + [Cu(L)_2]^+ \rightleftharpoons [Cu_2(L)_2]^{2+} \quad K_3 \tag{3}$$

Additionally, the overall stability constant (β_L) for each imino-derived complex could be obtained by way of dissociative titration with 2,9-dimethyl-1,10-phenanthroline (neocuproine, N). These reactions (Eqs. (4) and (5)) could be followed due to the development of the intense MLCT absorption band of $[Cu(N)_2]^+$.

$$[Cu_2(L)_2]^{2+} + 4N \rightleftharpoons 2[Cu(N)_2]^+ + 2L \quad \beta_4 \tag{4}$$

$$[Cu(L_2)_2]^+ + 2N \rightleftharpoons [Cu(N)_2]^+ + 2L_2 \quad \beta_5 \tag{5}$$

We can express these β values in terms of the overall stability constant for formation of copper(I) bis-neocuproine ($\log \beta_N = 14.2$) since $\beta_4 = \beta_N^2/\beta_L$ where $\beta_L = K_1 \cdot K_2 \cdot K_3$, while $\beta_5 = \beta_N/K_1 \cdot K_2$. A detailed mechanism for the dismantlement of the metallo-helicate is given in Fig. 3.

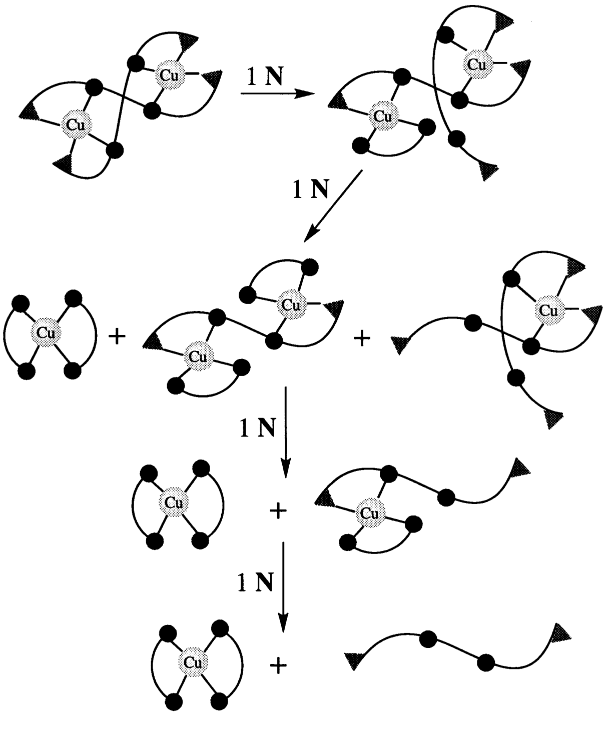


Fig. 3. Schematic representation of the dismantle of the helicate with the bidentate neocuproine competitor (**N**). The triangle and the circle correspond to the N_{im} and N_{py}, respectively.

These data together with molecular mechanics simulations are in keeping with the first step involving attachment of a copper(I) fragment to a single N donor atom belonging to the imino function. However, this step could not be resolved during the titration. Subsequent attachment to an adjacent pyridino N donor requires internal torsional motion driven by the chelate effect. In the second step, coordination of a second ligand to the mononuclear fragment (K_2) should be in competition with dimerization to form $[Cu_2(L)_2]^{2+}$ due to the titration conditions used (addition of Cu(I) to excess ligand). For the phen ligand the coordination of the second ligand is not favourable due to steric crowding and we observe a serious drop in stability constant.

Finally, the metallo-helicate assembly following coordination of a second copper(I) center (K_3) is considerably easier with the more flexible bpy-based ligand than with its phen analogue. This difference is attributed to the relative capacity for internal rearrangement to provide a suitable binding pocket. It is during this third step that major differences emerge between the two multitopic ligands. It appears that the bpy-ligand **5** exhibits positive cooperativity towards Cu(I) in that $K_1 < K_2 < K_3$ and the overall stability constant for the metallo-helicate is $\log \beta_L = 26$ and compares quite well with the only available literature datum for a somewhat comparable process [35]. In case of the phen-ligand **6** the helicate formation is not driven by positive cooperativity since $K_2 < K_1 < K_3$ and the overall stability constant ($\log \beta_L = 16$) reflects the relative difficulty in attaining a suitable geometry. As a matter of fact even for the phen ligand, the mononuclear complex is rather difficult to isolate and the final helicate is the sole compound which is easily isolated in near quantitative yield. The conventional copper(I) bis chelating N_{py},N_{py} complex has never been observed nor isolated. This is a rather surprising example comparing with the plethora of phenanthroline complexes described in the literature [36]. The systems described with imino–bpy and imino–phen are significantly more rigid than those traditionally used to prepare metallo-helicates [13] and an important caveat of this study is that positive cooperativity is not a prerequisite for helicate formation. A remarkable aspect of this hybrid ligand is that they do not operate as single chelators towards Cu(I) cations but that individual N atoms act independently as secondary coordination sites. Metal-induced self-organisation of these ligands into helicoïdal structures is a multistep process but with **6** we were fortunate to isolate a crucial intermediary complex which is on the road to form the helicate. With phenanthroline ligands however helicate formation is restricted by thermodynamic considerations rather than by kinetic factors as in the certain pentanuclear helicates [37]. These metallo-helicates displaying copper(I) centers in close proximity can be dismantled under mild conditions by (i) chemical or electronic oxidation (ii) competitive complexation or (iii) addition of excess ligand in the case of the phen ligand **6**.

3.2. Redox properties

The redox behaviour of these unusual helicoïdal complexes is also very interesting and helicate-scaffoldings have rarely been studied in detail up to date. Here the dinuclear copper(I) helicates exhibit four quasi-reversible reduction peaks corresponding to stepwise reduction of each coordinated imino group while in the related free ligands only irreversible reductions were observed. This is interesting because complexation of the imino ligand strongly stabilizes the imine function and favours its reversible reduction. Nonetheless, the oxidation of the copper(I) cations is irreversible on the cyclic voltammetry time-scale and resulted in the decoordination of one copper center. Poor thermodynamic stability of the resultant copper(II) complex reflect that a distorted tetragonal coordination site is unsuitable for binding of Cu(II). Indeed, chemical oxidation of the helicate with Ce(IV) results in formation of a stable, lime-green colored complex typical of a five-coordinate mononuclear copper(II) assembled via complexation to two bpy subunits and a single imino-group (Fig. 4). Reformation of the dinuclear metallo-helicate is quantitative when hydrazine or ascorbic acid are used as reducing agent.

Such structural reorganization due to preferential binding of cationic species to secondary complexation sites [translocation process] has also been observed in related complexes built with ligands possessing additional coordination sites such as terpyridine ligands (Scheme 5). The segmented pentadentate imino–terpy ligand **10** offers many of these facets. Indeed, the X-ray crystal structure shows that the

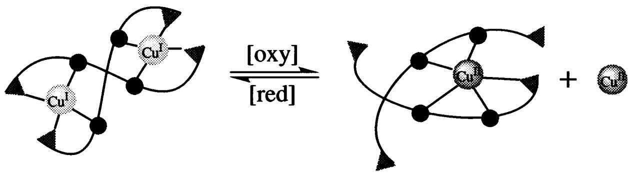
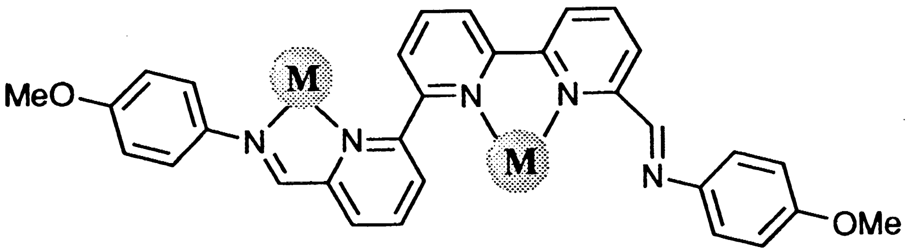


Fig. 4. Schematic representation of the dismantle of the helicate under oxidative conditions and helicate reformation under reductive conditions. The triangle and the circle correspond to the N_{im} and N_{py}, respectively.



C

$N_{im},N_{py}/N_{py},N_{py}$

Scheme 5.

helicate formed between the imino–terpy **10** and copper(I) cations possess similar environment for the metal centers lying at 3.278 Å. Each segmented imino–terpy ligand is coordinated to two copper(I) centers in a non-symmetric fashion. One metal being chelated to a pyridine/imine fragment while the remaining two pyridines are chelated to a second cation (Scheme 5). The coordination sphere of each copper centre is completed by the coordination of an additional segmented ligand but in a reverse way versus the first ligand.

It is noteworthy that the additional imine function is not coordinated (2.629 Å from the copper centre), but the fact that a quasi *cis*-conformation is observed is auspicious for some electronic interactions as well for coordination to a metal in a higher oxidation state [38].

Indeed, redox cycling in these segmented copper helicates is effective and the helicate is stable in different oxidation states of the metal and also for successive reduction of the ligands. Such stability is derived from the ability of the ligand to provide both four- and five-coordinate geometries around the metal centers. These requirements are essential if the metallo-helicate is to be used as a redox catalyst or artificial enzyme. There appear to be a limited number of examples of copper helicates or other such related structures that do not undergo large-scale structural reorganization following oxido-reduction reactions.

It is worth pointing out here that redox cycling in appropriate topological scaffoldings is a concept which has led to the discovery of molecular hysteresis [39,40], molecular memory [41], molecular machines [42] and precursors of molecular electromechanical motors [43]. In particular redox-induced movement occurring in multifunctional systems incorporating multi-strand arms bearing distinct coordination sites has been found by changing the oxidation state of an iron cation [44,45]. Furthermore, electrochemically induced molecular and ring-gliding motions in pseudo-rotaxane and catenate derivatives have been observed in copper(I) complexes containing different interlocked rings [46].

One clear advantage of these imino-based systems is that very stable complexes could be formed and that the terminal imino group is readily functionalized without disruption of the helicate structure. This provides the key element by which to include the local molecular architecture into an organized macroscopic ensemble, such as calamitic mesophases.

4. Liquid-crystals from imino–polypyridine based helicates

4.1. General trends

Metallo-mesogens (liquid-crystals containing metal ions) have also concurrently become a topic of increasing interest and it has been anticipated that the introduction of transition metal centres into liquid-crystalline materials may result in significant modification of their physical properties such as colour, conduction, magnetic or redox behaviour [47,48]. The ability of transition metal ions to adopt different coordination geometries, and also to organize elemental synthons around a central core, as shown in the previous section, could in principle permit preparation of a wide variety of novel metallo-mesogens. Nowadays, many different metallic centres and coordination geometries have been incorporated into mesogenic materials and *ortho*-palladated complexes which afforded ferroelectric and cholesteric metallo-mesogens form a major cornerstone of the subject [49].

Furthermore, 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 the area of supramolecular chemistry concerns the identification of viable applications (macroscopic function), other than analytical chemistry and the integration of individual superstructures into an organized network that can be addressed macroscopically [50]. The challenge here is to obtain more functional systems, by selective coordination processes around metallic centres, in order to build aesthetic molecular scaffolds (such as helices, grids, ladders, cyclic helicates, tissues...) and to provide access to more sophisticated systems mimicking, after macroscopic ordering, basic biological functions. Additionally, the conjunction of such molecular processes and self-assembly of the discrete units at the macroscopic level to form liquid-crystalline materials offers many interesting features, where unexpected properties could emerge.

Indeed, major goals for the emerging field of supramolecular chemistry are: (i) to relate local molecular architecture to macroscopic ordering of the system, (ii) to identify useful applications other than analytical chemistry, and (iii) to integrate individual supramolecular species into organized networks. Such large-scale organization is probably essential for the construction of practical devices from intricate molecular units [51]. Despite this realization little genuine progress has been made with regard to the integration of local order into large-scale multidimensional arrays. In marked contrast, tremendous advances have been made with respect to the construction of exotic supermolecules by stepwise acretion of simple building blocks.

A simple strategy is to assemble non-mesomorphic but lipid-like organic strands around d-block transition metals to promote formation of a liquid-crystalline state. Our recent discovery widely described in the previous section (vide supra), that a stable copper(I) helicate containing bridging bis-imino–bipyridine subunits is formed selectively and quantitatively by a cooperative process has prompted exploration of paraffin substituted imino–bipyridine ligands as building blocks. These non-discoidal units represent the key element by which to include the local molecular architecture [double-helix] into an organized macroscopic ensemble [mesophase].

4.2. Bipyridine based frameworks

Many kind of Schiff-based bipy ligands bearing an increasing number of flexible chains as well as aromatic cycles have been prepared and studied (Fig. 5). All these

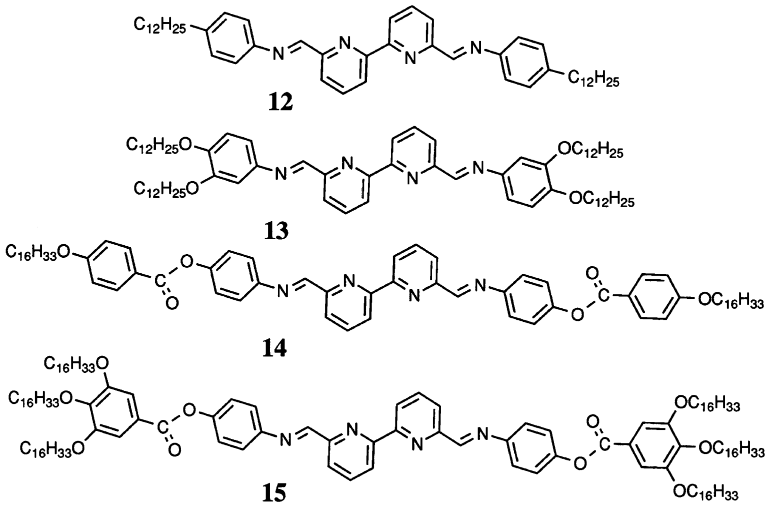


Fig. 5. Schematic representation of Schiff-based bpy ligands bearing flexible appendages.

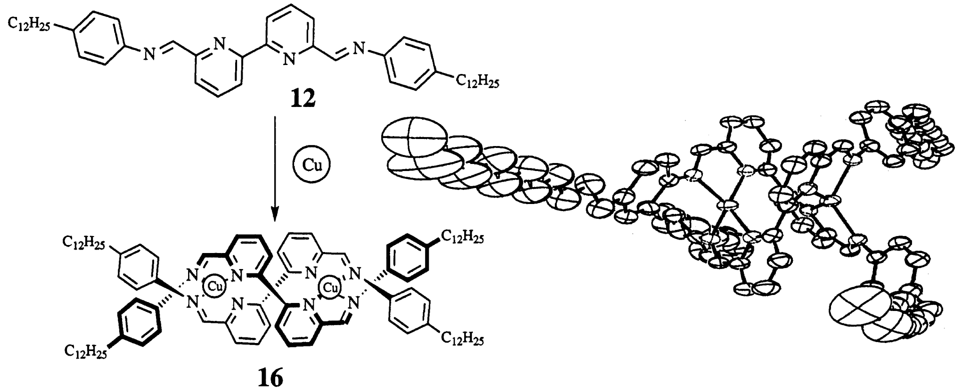


Fig. 6. Molecular structure of complex **16** and a schematic representation exhibiting the wrapping of the non-mesomorphic ligands around the cations.

new frameworks display well defined melting points and formed selectively deep-green dinuclear complexes with copper(I) precursors. The helicoidal arrangement was deduced from NMR spectroscopy and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and in the case of complex **16** by a X-ray molecular structure determination (Fig. 6).

In the case of complexe **17**, formed from ligand **15** and copper(I) salts (Fig. 7), a well defined columnar mesophase was formed and observed at room-temperature under a polarizing optical microscope and studied by X-ray diffraction. The phase transition was analyzed by differential scanning calorimetry (DSC). This system, being the first liquid-crystalline metallo-helicate, is a rare example of a room temperature metallo-mesogen and illustrates the tremendous organizational ability of copper(I) cations. It is, in fact, remarkable that the cation is able to organize these flexible ligands, as well illustrated by comparing molar volumes calculated for the ligand ($V_m = 1356$ cm^3 mol^{-1}) and the cation ($V_m = 2.2$ cm^3 mol^{-1}).

The key element of this approach lies with the helix providing rigidity and polarizability to counterbalance the flexibility and non-polarizability imposed by the paraffinic chains. It is this subtle balance between organized and chaotic domains that controls the fate of the mesomorphic material. This system illustrates the tremendous organizational ability of copper(I) cations which are able to induce order at both molecular and supramolecular levels considering the large volume and structural disorder inherent to the non-disklike ligands. The tremendous complexation ability of imino-bipyridine ligands to form selectively and quantitatively by a cooperative process copper(I)-helicates is the key element by which to include the local molecular architecture into an organized macroscopic ensemble. The morphology of the liquid-crystalline phase appears to consist of columns of rigid cores surrounded by molten alkyl chains and laterally packed according to a two-dimensional lattice of rectangular or oblique symmetry (Fig. 8).

While numerous examples of copper(I) helicates are known it has proved extremely difficult to assemble them into organized assemblies. Special attention has to be given to the number, length and nature of the lipid-like chains and it appears clear that there is a high barrier to arrange self-organized structures into liquid crystalline material. In this respect, the onset of liquid-crystalline behaviour

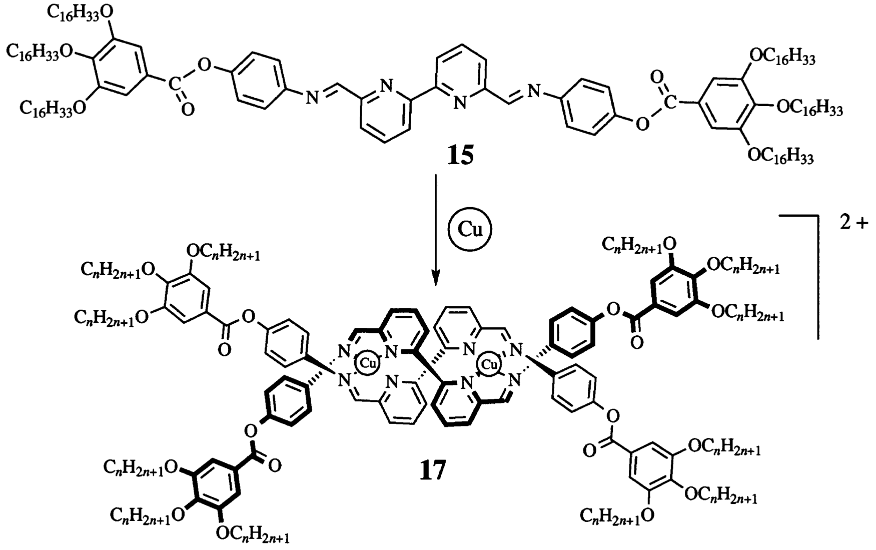


Fig. 7. Schematic representation of the mesomorphic metallo/bipyridine-helicate (**17**) formed by a copper(I) induced self-organization process of ligand **15**.

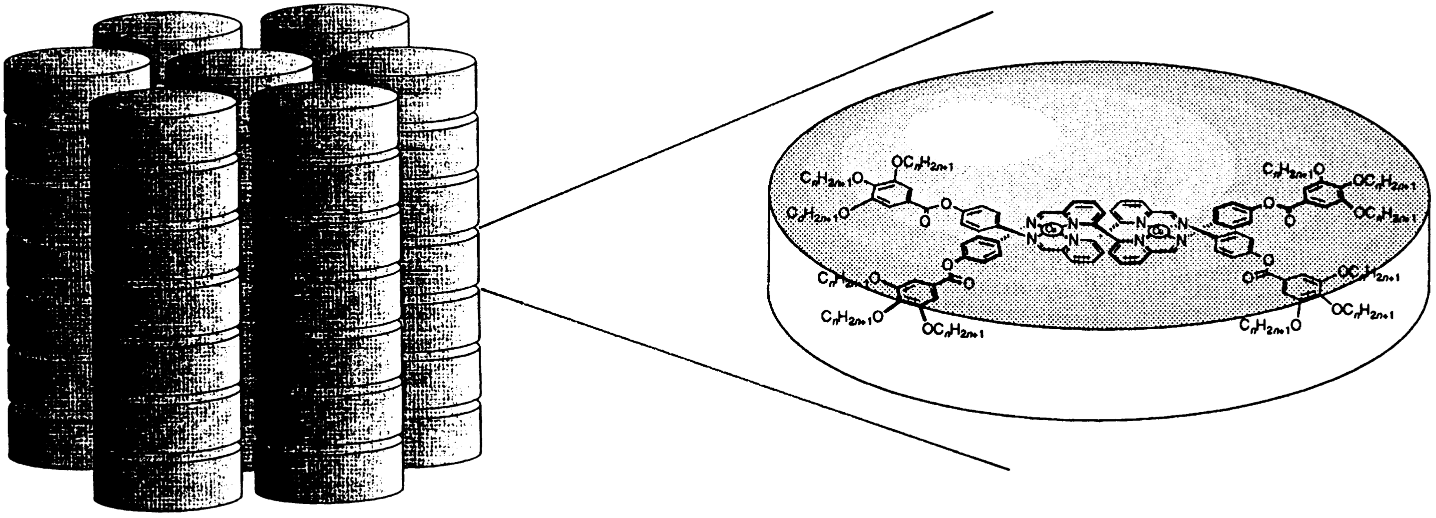


Fig. 8. Idealized packing of the metallo-helicate **17** within the columnar mesophase.

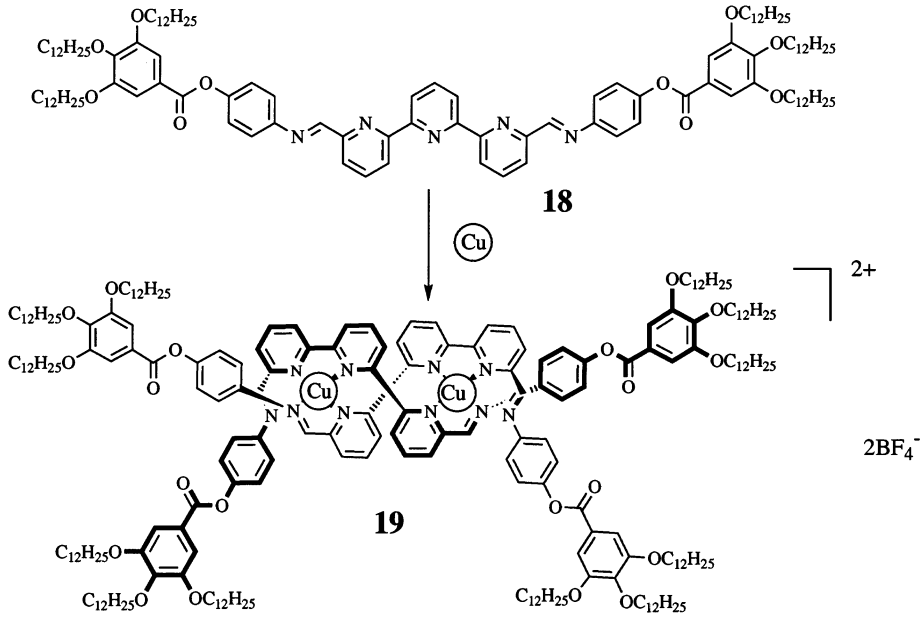


Fig. 9. Schematic representation of the mesomorphic helicate **19** formed by a copper(I) induced self-organization process of the segmented terpyridine ligand (**18**).

can be seen as a fine balance between ordering (helix) and chaos (alkyl chains). The net result of optimizing this balance is to produce low-temperature metallo-mesogens [23]. The initial step in the overall process involves formation of a stable metallo-helicate and is itself a challenging proposition in view of the bulky alkyl chains that complicate the gathering of the ligands around the cations. The helix provides essential rigidity that favors subsequent stacking of the aromatic cores.

4.3. Terpyridine and analogues

Another significant point noticed during this research programme is that the introduction of more flexibility into the supermolecular structure do not detract from its ability to assemble into organized networks. It turns out that this delicate operation can be achieved by using a central core constructed from a segmented terpyridine ligand bearing two imino appendages equipped with paraffinic tails (Fig. 9) [52].

Complexation to copper(I) cations gives unlocked complexes and the first thermotropic terpy-based metallo-mesogens. Moreover the liquid-crystalline material displays an unusual type of molecular ordering in the mesophase wherein individual molecules align to form columnar liquid crystals with a lamellar morphology,

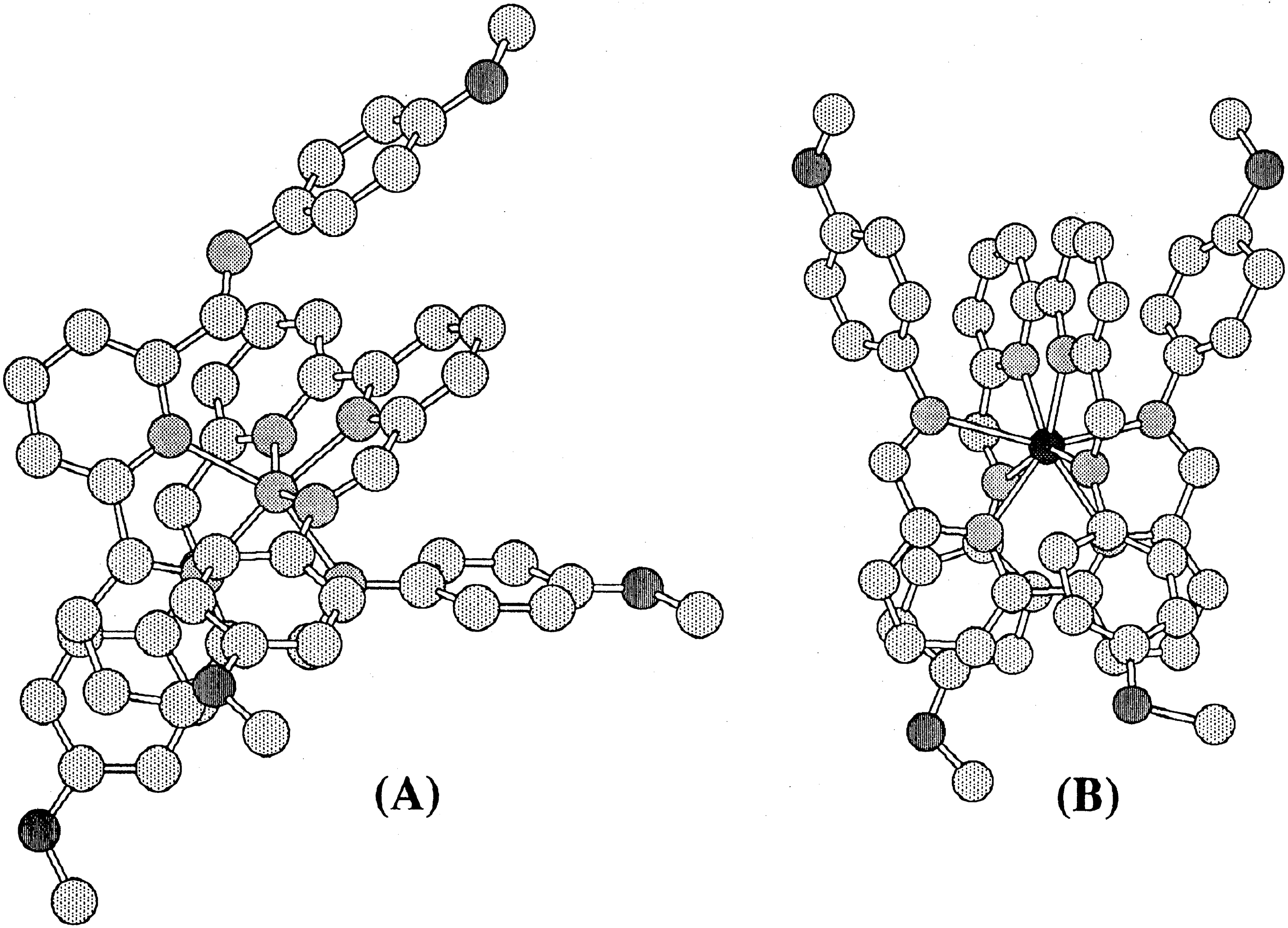


Fig. 10. (A) MolView drawings of the [Ni(**7**)$_2$](ClO$_4$)$_2$ complexes, (B) MolView drawings of the [Fe(**7**)$_2$](ClO$_4$)$_2$ complexes. The hydrogen atoms are omitted for clarity (data from solid-phase crystal structure determination).

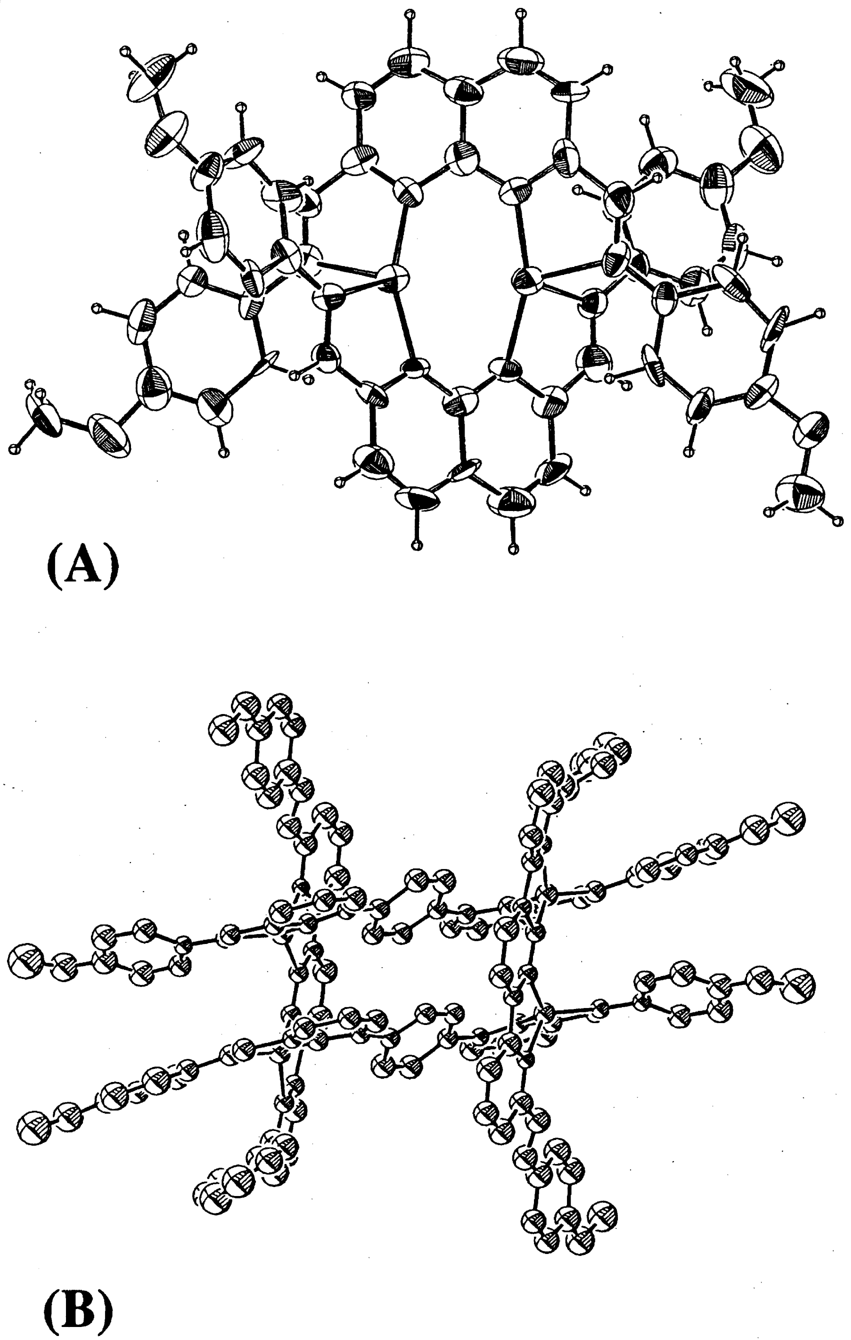


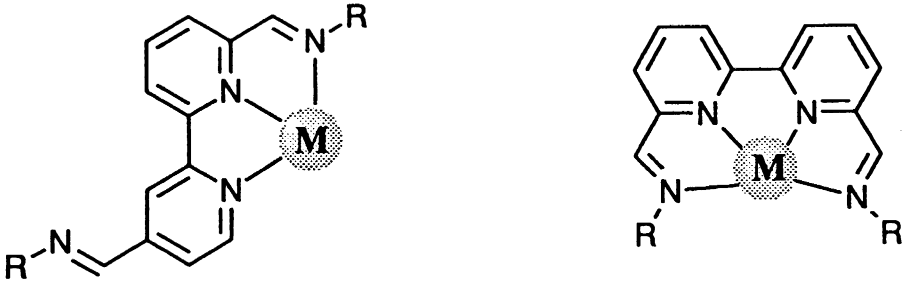
Fig. 11. (A) ORTEP drawings of the $[Cu(\mathbf{9})_2](ClO_4)_2$ complexes, (B) ORTEP drawings of the $[Cu(\mathbf{11})]_4(ClO_4)_4$ complexes. The hydrogen atoms are omitted for clarity and 50% probability for the thermal ellipsoids has been used for the drawings.

somewhat similar to that found earlier for charge transfer assemblies [53], macrocyclic–aza complexes [54] and orthometallated compounds [55]. This liquid-crystalline phase has a genuine smectic structure and resembles that of linear DNA stretched across a lipid bilayer [56]. Similarities between the smectic liquid-crystalline phase found with this pentadentate ligand and the oriented DNA molecule is striking and of some interest. It is considered that local segregation of the polar helicate from the paraffinic chains creates an interface that facilitates adoption of a non-discoidal liquid-crystalline phase. This seems to be a viable method by which to obtain new types of self-organized assemblies of nanoscopic dimensions.

Further developments will include the use of these ligands to complex metals in an octahedral environment. As a first step towards this goal we prepared Fe(II) and Ni(II) complexes and their molecular structures have been determined by a X-ray diffraction on single crystals (Fig. 10) [57]. Indeed with Ni(II) coordinated to two ligands **7**, the metal atom is surrounded by 4 N atoms belonging to the bipy subunits and 2 N atoms of the imino functions of two different bipy-ligands. Two of the imino-functions lie at 4.4 and 3.4 Å in a *trans* conformation for the former and in a *cis* conformation for the latter pointing to some electronic interaction. Here the mode of coordination of the ligand is of type D as shown in Scheme 6. In the Fe(II) complex of ligand **7**, the metal is surrounded by two imino–bipy ligands in a chelating fashion. The 8 N donor atoms define a distorted triangulated dodecahedron which is composed of two sets of trapezoidal arrangements in a perpendicular orientation (Fig. 10B).

The structure of this complex exhibit some striking similarities with the [Fe(1,8-naphthyridine)$_4$]$^{2+}$ species, which also shows a dodecahedral arrangement of the ligands and the coordination mode of the ligand is of type E as depicted in Scheme 6.

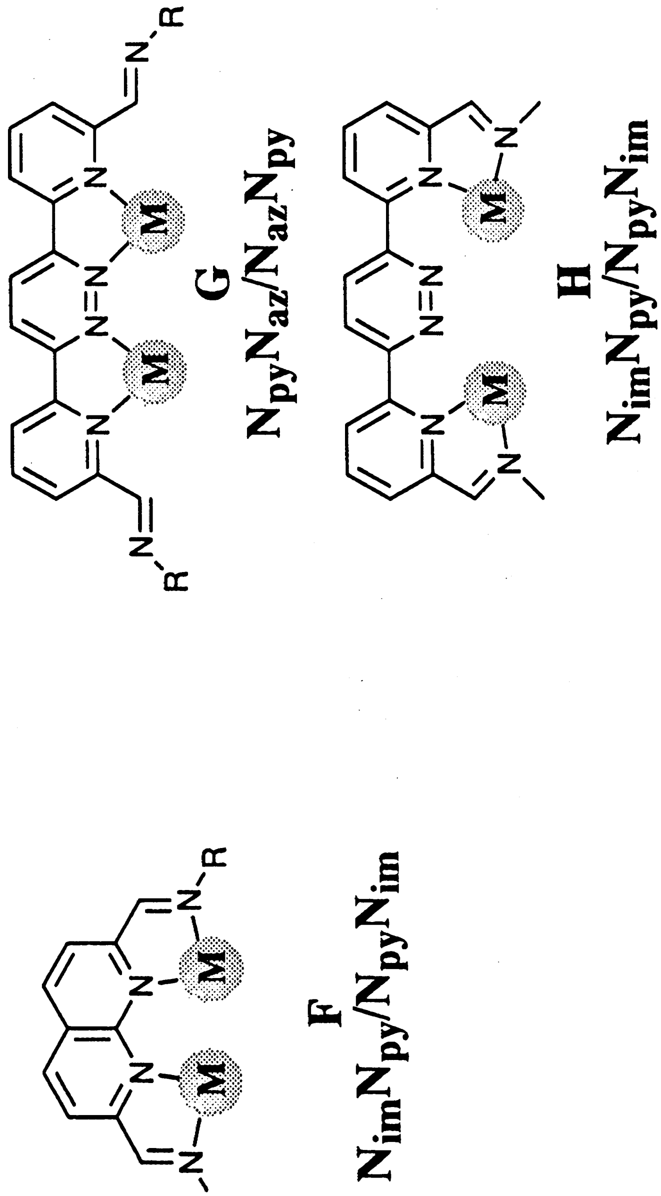
Furthermore, the success achieved with the previous complexation reactions with copper(I) salts prompted us to investigate the possible construction of heli-



D
$N_{py}N_{py}N_{im}$

E
$N_{im}N_{py}N_{py}N_{im}$

Scheme 6.



F

$N_{im}N_{py}/N_{py}N_{im}$

G

$N_{py}N_{az}/N_{az}N_{py}$

H

$N_{im}N_{py}/N_{py}N_{im}$

Scheme 7.

cates with the naphthyridine ligand **9** and larger supramolecular systems with the diazine based building block **11**. Indeed, the first helicate formed with a naphthyridine based ligand was obtained and characterized by an X-ray structure [58] (Fig. 11A) with a F-type coordination mode. With ligand **11** a tetranuclear complex assigned by a X-ray molecular structure (Fig. 11B) was obtained selectively. Further illustration of the versatility and ambivalent coordination mode of these kinds of Schiff-based ligand is shown here where the same ligand within a single complex adopts two different coordination modes labelled **G** and **H** in Scheme 7 [59].

5. Conclusion

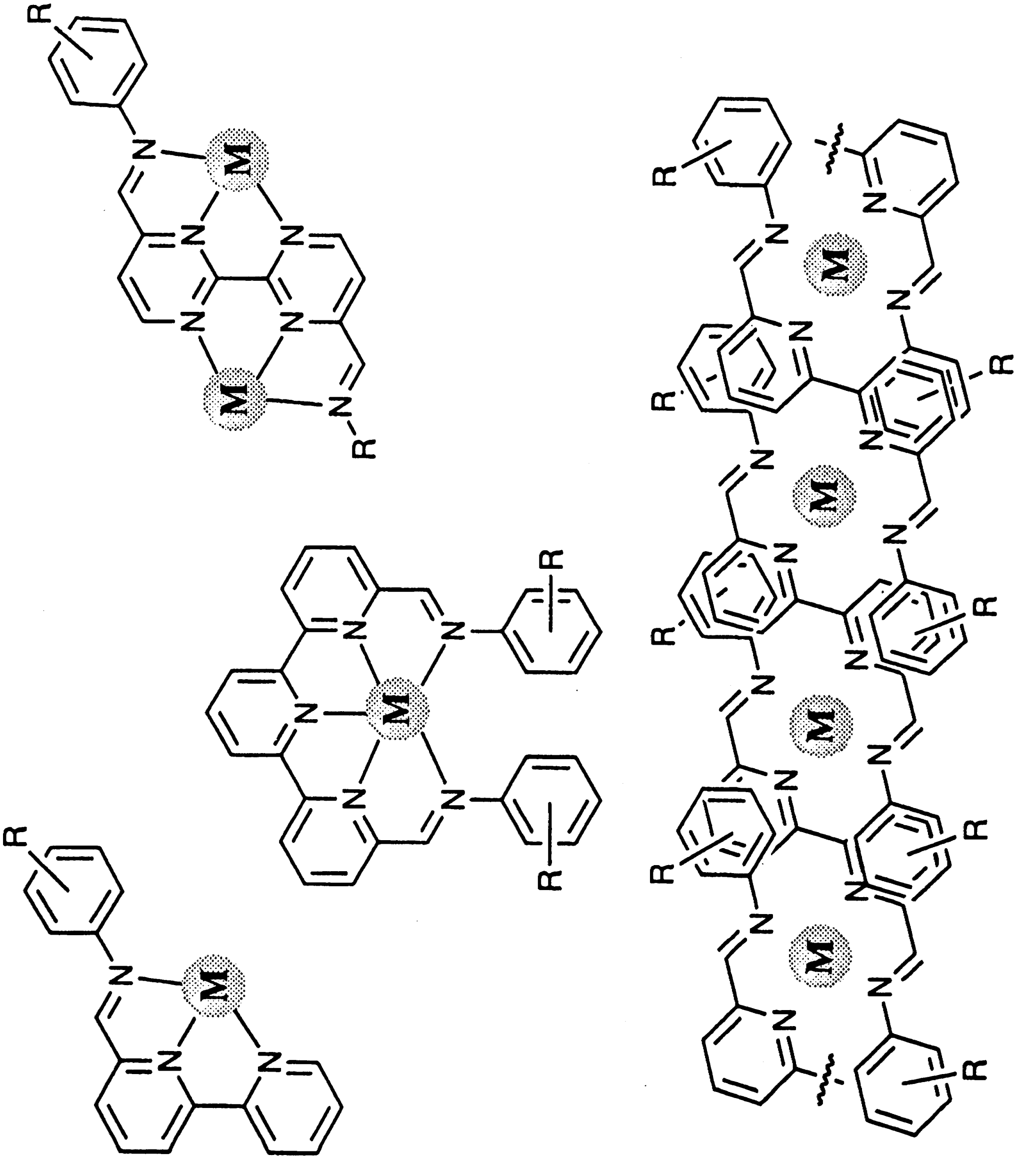
Research to synthesize self-assembled structures has blossomed during the past several years. There is every reason to believe that it will remain an area of intense investigation in the future. It is also likely that a great deal of the work devoted to the unfruitful attempts to produce liquid-crystalline materials with supermolecules has not yet appeared in the open literature. Consequently, in the light of the present results, general trends could be exposed concerning the series of metallomesogens constructed from imino–oligopyridinic scaffolding. While the mesophase obtained with the Cu–terpy helicate is smectic that of the corresponding bpy complex is columnar and that obtained with a mononuclear copper(I) imino–pyridine complex is columnar with hexagonal symmetry [60]. There are two main structural differences between these polypyridine complexes that might account for this variation in mesogenic morphology. Firstly, the extended length of the central aromatic core is expected to stretch the molecule into a calamitic shape that favors a smectogenic arrangement. Secondly, the fluxional motion inherent to the terpy-based metallohelicate increases the entropy of the system which favours the formation of the mesophase. It is this local fluctuation that establishes microdomains sustaining liquid-crystalline behavior 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 3D correlation of the layers. Such structures are made possible by combining (i) internal flexibility of the coordinated polytopic ligands, (ii) ancillary coordination sites to stabilize emerging redox centers, and (iii) multiple flexible sidechains.

The realization that such cationic complexes are liquid-crystals at room temperature opens the door to several broad and fruitful areas of supramolecular chemistry. With this information in hand, it might be expected that the design and construction of nanometre-scale molecular assemblies and supramolecular arrays intended to store, transfer or display information could be reached in the near future. 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 supramolecular structure. This point was further substantiated by the qualitative comparision of the pyridine, bipyridine and terpyridine Schiff-based ligands bearing paraffinic tails.

A key element of this work 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. It becomes clear from the few examples of liquid-crystalline materials obtained from these artificial molecular architectures, that the list of novel assemblies will grow rapidly in the near future despite the difficulty to find the targeted properties and to properly characterize the emerging mesophases. The self-assembling process is very versatile and allows the preparation of a great number of discrete supramolecular species with well-defined, predesigned shapes and geometries. The most important advantages of this approach are its wide applicability and the large and different number of potentially suitable transition metal complexes and multidentate nitrogen or oxygen containing ligands available as building blocks. The excellent product yields and the high thermodynamic stability constants of the complexes formed that are inherent to such self-assembled processes has been observed in many cases. These results demonstrate two key points with respect to the design of self-assembling systems. First, it is possible to combine imino functions with bipyridine and terpyridine fragments to create in a productive fashion, stable supramolecular complexes. Second, judicious tailoring of the ligand with flexible alkyl chains can produce macroscopicaly organized phases which texture strongly depend on the architecture of the rigid frame. Other scaffolding constructed from additional building blocks providing isolated or polymeric structures (Scheme 8), is currently being tested in order to have more insight into the balance required to produce liquid crystalline material.

6. Outlook and perspectives

Nowadays there has been a steady and progressive interest in the synthesis of oligopyridines and an impressive number of such substances are now known. These compounds are not especially appealing in their own right, although there are some interesting synthetic facets and certain compounds show important antibiotic and fungicidal character, but they form stable complexes with many cations. It is this interest for the synthesis of metal complexes that has driven research into finding new and improved oligopyridines and such complexes figure prominently in historical accounts of both coordination chemistry and analysis. More recently, metal oligopyridines have been used to construct exotic molecular architectures, to sensitize photoelectrochemical cells, to label biomaterials, as the basis for selective sensors, and as magnetic materials. In the future oligopyridines will find even more applications especially as materials scientists seek to develop miniaturized devices. We have argued the case that Schiff-based templates endow certain metal complexes with special properties and this claim is the result of a determined and sustained effort to produce a comprehensive catalogue of suitably derivatized



Scheme 8.

compounds. In the present survey, we have outlined a synthetic strategy for grafting imino-groups to a variety of different oligopyridines. The synthetic route have been adapted to ensure that various terminal groups (from one to three paraffinic chains) can be attached and to provide means by which to tune the flexibility and microseggregation behaviour of the emerging material. Throughout this work, we have become evermore convinced that these hybrid ligands should not be considered as classical bipy, phen or terpy frameworks but should be regarded as new type of ligands. We are only just beginning to explore the multiple opportunities provided by these ligands and, while they might not be a cure-all for every problem, their versatility and scope are such that they will become fundamental building blocks in emerging molecular machinery. The greatest challenge facing this field is how far it would be possible to correlate the microscopic architecture with the morphology of the emerging mesomorphic material. Accordingly, this molecular-structure/mesomorphic relationship is not easily quantified and remains essentially empiric.

The next phase of this work is to construct larger molecules bearing targeted functions that facilitate formation of mesomorphic materials or molecules able to undergo self-segregation. Here, we foresee that this kind of Schiff-based oligopyridine will control the local geometry and electronic properties at the molecular level while ancillary functions favor self-association into organized arrays. An elegant avenue would be to nanostructure these mesophases into polymeric matrixes where the memory of the initial supramolecular arrangement is preserved and to use them in targeted catalytic processes.

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