CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901923

Tuning the Functional Properties of Metal Complexes Containing Polytopic Heteroaromatic Nitrogen Ligands

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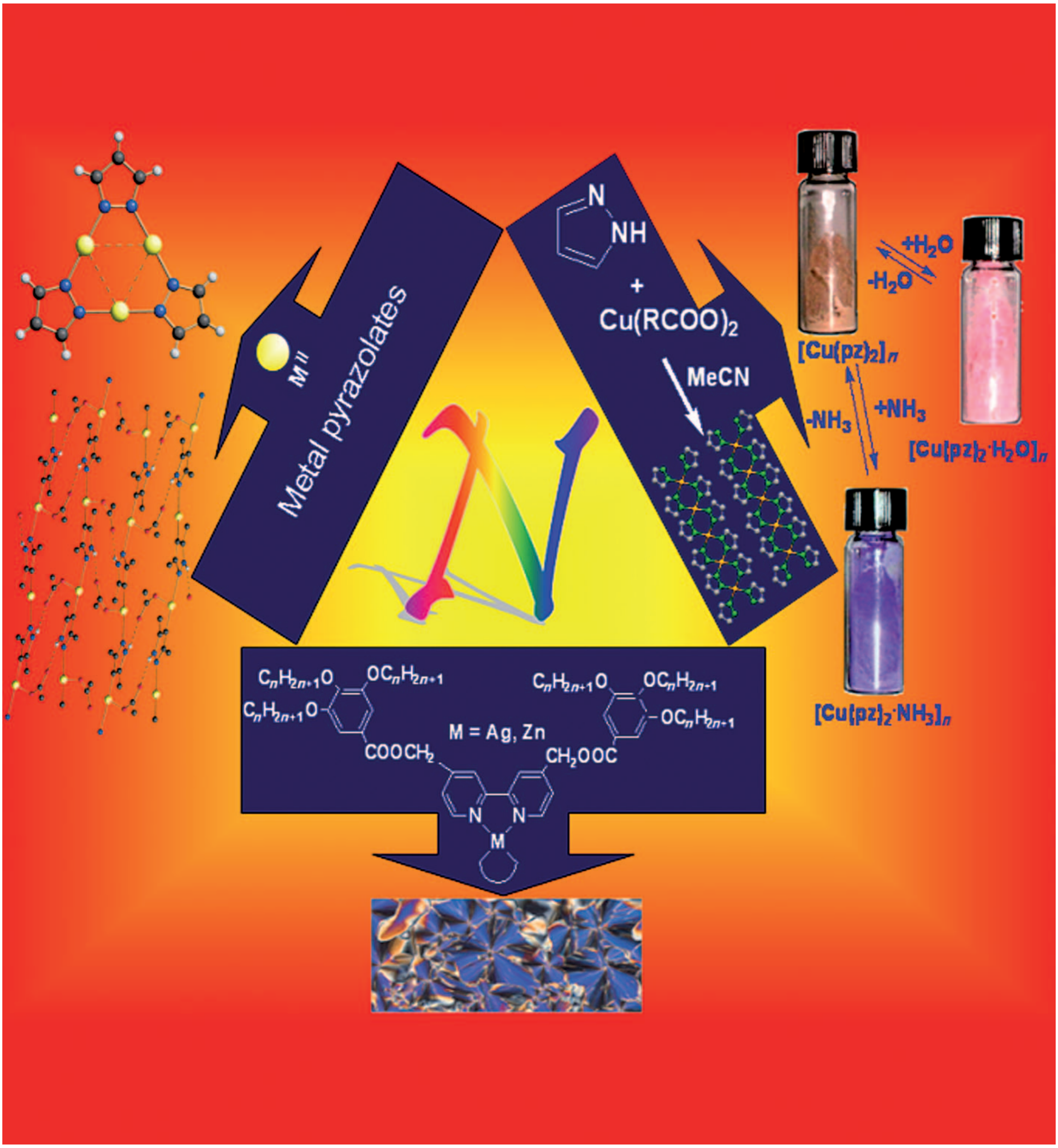

Abstract: The preparation, characterization, and optimization of the functional properties of mono- and polynuclear coordination complexes containing heteroaromatic nitrogen ligands are discussed here, taking the advantage of numerous studies performed in our laboratories on exploring a variety of different metal ions and polytopic ligands. We highlight how very minor changes in connectivity, composition, and polarity of the molecular entities employed in the self-assembly steps may significantly affect the structural, thermal, sorptive, magnetic, and mesomorphic behavior of the resulting materials. Examples from three different classes are included: 1) pyrazolate-based polynuclear coordination compounds, 2) homoleptic and heteroleptic coordination polymers, and 3) 2,2′-bipyridine metal-based liquid crystals.

Keywords: coordination polymers • liquid crystals • N ligands • transition metals

Introduction

The synthesis and manufacture of functional materials represent one of the great challenges in the current academic and industrial research.

Different classes of such materials are currently under study and particularly interesting functional materials are the so-called coordination polymers (CPs), which are normally obtained thanks to the (self)-assembling of metal centers with polytopic ligands. The functionalities of these systems often have a cooperative character, linked either to the local geometry of the "active" centers and to their three-dimensional arrangement within the crystal lattice. In these systems, ions and molecules spontaneously self-assemble into ordered aggregates, as a result of covalent and non-covalent interactions (coordinative bonds, hydrogen bonds, and van der Waals and π–π interactions) between the building units of the supramolecular assembly.[1] CPs develop in one, two, or three dimensions and in some cases a more or less relevant porosity may be present in the crystal lattice. Porous coordination polymers (PCPs) have recently displayed a wide range of appealing properties for advanced technological applications, such as molecular separation and pollution prevention, not only in air, but also in water and in other liquids, in which they can be employed as ion-exchangers and/or molecular sieves. The advantage of these hybrid materials, over classical (natural and synthetic) porous species (zeolites, active carbons, silica, etc.), resides in the possibility of easy optimization and fine tuning of their functional properties by using modification or substitution strategies of the organic ligands, and through the choice of the suitable metallic ions.[2] Moreover, the simultaneous presence of channels (or cavities) and metal ions capable of catalytic activity makes these materials particularly interesting as heterogeneous catalysts for the transformation of small molecules (e.g., in the Fischer–Tropsch synthesis, in epoxydation or polymerization reactions); these heterogeneous catalysts are easily synthesizable (and recoverable), and, if the pores are suitably "decorated", can display significant size-, regio-, and enantioselectivity.[3]

Another challenge in a neighboring field is the synthesis of soft functional materials based on different molecular motifs, for high-tech applications, such as liquid-crystalline systems, in which the peculiar combination of order and mobility allows both a significant responsiveness to external excitation and a ready tuning of physical and morphological properties.[4] This goal has been recently attained through different strategies,[5] among which is the incorporation of a metal center in selected chemical structures of organic ligands. Indeed, tailoring "unconventional" liquid crystals around a metal ion could offer an effective way of coalescing intermolecular interactions, nano-segregation, and novel shapes in a single soft species, the metallomesogens,[6] the structures of which are able to expand the traditional range of technological applications of liquid crystals,[7] as they are unapproachable for organic mesomorphic systems, are able to expand the traditional range of technological applications of liquid crystals.

Accordingly, here we briefly review the results obtained in the last years in our laboratories, subdividing the discussion into three main chapters, each one referring to specific classes of compounds: CPs based on pyrazolate and pyrazole trinuclear complexes, homoleptic and heteroleptic mononuclear based CPs, and 2,2′-bipyridine metal-based liquid crystals. Comparison of their performances in a number of fields will also be addressed, highlighting the large structural and functional changes observed upon minor modifications, and tuning of the building blocks and, where pertinent, of the reaction conditions.

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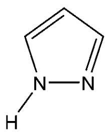
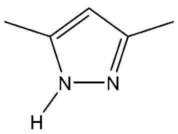
Trinuclear Pyrazolate-Based Coordination Polymers

In the last decade, heterocyclic N-donor ligands were widely employed in the formation of polynuclear, often polymeric, metal complexes as perspective functional materials for their adsorption capacity,[8] and their electrical,[9] catalytic,[10] magnetic,[11,12] and luminescent properties.[13] In the mainstream of this research, we have specifically focused our attention to the study of the interaction of very simple ligands such as pyrazole (hereafter Hpz) and 3,5-dimethylpyrazole (Hpz*), with metal(II) carboxylates that, depending on reaction conditions, (solvent, temperature, strength of carboxylate anions, and metal and azole employed) generated different polycatenated polynuclear species, through the self-assembling of either trinuclear (triangular)[14–17] or mononuclear secondary building units (SBUs).[14a,18,19] In the following paragraphs, the specific features of trinuclear-based systems will be highlighted, while those based on mononuclear SBU will be discussed in a later section.



Hpz



Hpz*

$[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$-based structures: The reactions of copper(II) carboxylates with Hpz in protic solvents (water or moist alcohols) easily yielded, for a wide set of organic residues (collectively listed in Scheme 1), trinuclear Cu^{II} clusters; within these species, the metal atoms lie in nearly equilateral triangular geometry, bridged by a μ_3-hydroxyl, bearing the other ligands in the periphery of the molecule.

Structurally similar trinuclear triangular Cu^{II} complexes capped by OH^-, O^{2-}, or halogenide ions have been known for some time, but they were obtained through the deprotonation of suitable ligands promoted by hexogenous bases, such as potassium hydroxide, sodium carbonate, amines, and so on.[20] The nature of the bases and methods employed are also relevant: Sakai et al.[20c] reported that the reaction between $Cu(NO_3)_2{\cdot}3H_2O$ and $[Cu(Hpz)_4(NO_3)_2]$ in the presence of NaOH yields an hexacopper complex with bridging hydroxides, pyrazolates, and nitrate, which is different from the trinuclear compound $[\{Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Hpz)_2\text{-}(NO_3)_2\}{\cdot}H_2O]$ reported by Reedjik[20a] formed upon oxidation of $[Cu(Hpz)_2(NO_3)]$ in moist air, even though in both compounds are present the same $[\{Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3]^{2+}$ moieties. Closely related $[Cu_3(\mu_3\text{-}X)_2(pz^{NO_2})_3]$ systems, containing halides and not hydroxide bridging groups have been reported in the reaction of nitropyrazole (Hpz^{NO_2}) with CuX_2, but always in the presence of bases.[20g]

Abstract in Italian: *La preparazione, caratterizzazione e ottimizzazione delle proprietà funzionali di complessi di coordinazione mono e polinucleari contenenti leganti eteroaromatici poliazotati, vengono di seguito discusse, sfruttando le conoscenze sviluppate nei nostri laboratori nel corso di studi su differenti ioni metallici e leganti politopici. Si evidenzia come piccole variazioni nella connettività, composizione e polarità delle entità molecolari utilizzate in vari stadi dell'auto-assemblaggio possano profondamente influire sulle caratteristiche strutturali, termiche, di adsorbimento, magnetiche e mesomorfiche dei materiali sintetizzati. In particolare, si riportano esempi riguardanti tre diverse classi di materiali: 1) polimeri di coordinazione basati su leganti pirazolato, 2) polimeri di coordinazione omolettici ed eterolettici, e 3) cristalli liquidi basati su complessi metallici 2,2′-bipiridinici.*

Even though the mechanism of the reaction depicted in Scheme 1 has not been exhaustively clarified, it is evident that in our case are the basic carboxylate ions which deprotonate Hpz and water and generate anions (pyrazolate and OH^-) capable to cluster, in the presence of Cu^{II} ions, into a very stable triangular core, containing a nine-membered [-

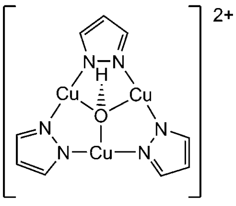
Claudio Pettinari was born in 1964 in Camerino (Italy). He studied Chemistry at the Università degli Studi di Camerino where he received his degree in Chemistry in 1989. He became University Researcher in 1992 at Camerino University and then associate professor, in 2000, at the same University. His research activity has been mainly carried out in the field of coordination chemistry of N-, O and S-donor heterocycles, of scorpionates and/or of ancillary ligands as phosphines and diphosphines toward main groups, transition and rare earth metals and in the field of organometallic chemistry of Sn, Rh, Ir, Pd, and Ru. His current research interest is in the synthesis and characterization of new metal organic frameworks (MOFs) or coordination polymers (CPs), based on transition metals and O- or N-donor ligands.

Norberto Masciocchi was born in 1959 in Como (Italy). He studied Chemistry at the Università degli Studi di Milano and received his Ph.D. in 1989 working on structural aspects of high-nuclearity carbonyl clusters. After postdoctoral studies at IBM Almaden Research Center, San José, CA, under the supervision of the late William Parrish, and at Kernforschungsanlage Jülich, he returned to Milan in 1991, as a University Researcher. In 1999 he moved to the University of Insubria as associate professor, and, in 2004, became Professor of Inorganic Chemistry at the same University. His current research interests are structural methods, mostly from polycrystalline samples, applied to functional molecules and materials: porous coordination polymers, polymorphs of active pharmaceutical agents, nanocrystalline species of technological or biochemical relevance and development of methodological aspects for powder diffraction structural analysis.

$$3Cu(RCOO)_2 + nHpz + mH_2O \xrightarrow{H_2O,\ MeOH\ or\ EtOH} [Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(RCOO)_2L_xL'_y]\ mH_2O + 4\ RCOOH$$

1–**10**

1 R = H, $n = 5$, L = L' = Hpz, $x = y = m = 1$
2 R = CH_3, $n = 4$, L = Hpz, $x = 1$, $y = m = 0$
3a R = CH_3CH_2, $n = 3$, L = EtOH, $x = 1$, $y = m = 0$
3b R = CH_3CH_2, $n = 3$, L = H_2O, $x = 1$, $y = m = 0$
3c R = CH_3CH_2, $n = 3$, L = H_2O, $x = 1$, $y = 0$, $m = 1$
4 R = $CH_3(CH_2)_2$, $n = 3$, L = MeOH, L' = H_2O, $x = y = 1$, $m = 0$
5 R = $CH_3(CH_2)_3$, $n = 3$, L = H_2O, $x = 1$, $y = m = 0$
6 R = $CH_3CH_2CH(CH_3)$, $n = 3$, L = L' = EtOH, $x = y = 1$, $m = 0$
7 R = $CH_3(CH_2)_4$, $n = 3$, L = EtOH, $x = 1$, $y = m = 0$
8 R = $CH_3(CH_2)_5$, $n = 3$, L = EtOH, $x = 1$, $y = m = 0$
9a R = $CH_2{=}CH$, $n = 4$, L = Hpz, L' = H_2O, $x = 1$, $y = 2$, $m = 0$
9b R = $CH_2{=}CH$, $n = 3$, L = MeOH, $x = 1$, $y = m = 0$
10 R = $CH_2{=}C(CH_3)$, $n = 3$, $x = y = m = 0$

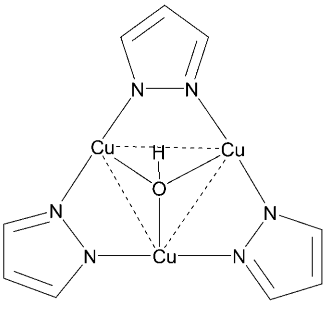


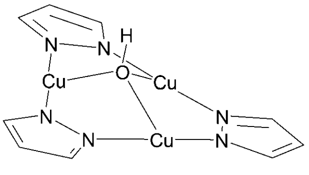
Scheme 1.

Cu-*N*-N-]$_3$ ring. Moreover, two carboxylates (granting electroneutrality) and other neutral ligands (water, Hpz, and/or alcohols) typically complete the coordination sphere of the three copper(II) ions, which are often involved, in the solid state, in supramolecular interactions with carboxylate oxygen atoms of other trinuclear units, thus generating one and two-dimensional CPs, discussed hereafter.

The reaction is extremely significant if we consider that copper complexes with varying nuclearity are the active sites of a number of proteins and enzymes and that in the last decade a number of researchers, in an attempt to activate O_2 to mimic the oxygenase activity of the enzymes,[21] encapsulated transition-metal complexes, including copper(II) acetate, in the cavities of zeolites and exhaustively investigated the peculiar properties of such "zeo-zymes".[22]

The reactions proceed smoothly, in the air at room temperature and the products have been normally obtained in short times, with rather good yields, as crystalline material or solids which were recrystallized from water or alcohols. As anticipated, conventional single-crystal X-ray diffraction analyses, carried out on compounds **1**–**4** and **9** and **10**, showed that in all cases the three Cu^{II} ions occupy the vertices of slightly distorted equilateral triangles (with Cu···Cu non-bonding distances in the 3.08–3.40 Å range). Cu–OH distances are very similar, spanning the limited 1.95–2.02 Å range, with the μ_3-oxygen placed about 0.3–0.5 Å away from the plane defined by the three metal ions.



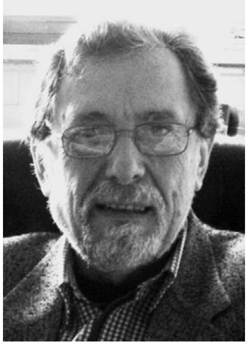


In spite of their similar trinuclear structures, the molecular clusters present in species **1**, **2**, **3a** and **4** self-assemble, in the solid state, with distinct topological features.

Particularly, while in compound **1** the trinuclear moieties mutually interact through different carboxylato bridges generating a two-dimensional CP[14b] (Figure 1), in compounds **2**, **3a** and **4** two trinuclear units are joined together by two μ_2-η^1 carboxylato bridges, forming hexanuclear clusters (Figure 2).[14a,b]

In addition, while the hexanuclear clusters of compound **4** do not further interact each other through coordinative bonds,[23] those of compound **2** generate fused 28-membered loops that are arranged in a complex, layered, two-dimensional CP (Figure 3).[14b]

Finally, the propionato-based hexanuclear units in **3a**[14b] self-assemble through two *syn–syn* carboxylato bridges forming 12-membered loops and yielding the one-dimensional CP shown in Figure 4 (top), in which 12-membered and 4-membered cycles are clearly seen. In the strictly relat-



Luciano Pandolfo was born in 1947 in Padova (Italy). He received his Laurea in Chimica at the Università degli Studi di Padova in 1971, working on the structure and solution equilibria of Ni^{II} and Co^{II} complexes of secondary phosphines. After a long period of teaching in the secondary school, he became University Researcher in 1990 at the University of Padova. In 1998 he moved to the University of Basilicata as Associate Professor, and, in 2002, came back to Padova, where he is now Associate Professor at the Department of Chemical Sciences. His current research interest is in the synthesis, characterization and study of the functional properties of metal organic frameworks (MOFs) or coordination polymers (CPs), mainly based on late-transition metals interacting with polyoxygen and/or polynitrogen ligands.

Daniela Pucci was born in 1965: she graduated in chemistry in 1989 and obtained her Ph.D. at the University of Calabria, Italy, under the guidance of Professor Mauro Ghedini, in 1993. She worked as a postdoctoral fellow in the field of supramolecular chemistry with Jacques Malthete at the Paris Sud University (Laboratoire de Physique des Solides, Orsay). She is currently Associate Professor at the University of Calabria since 2001 and her research field interests are design, synthesis, and characterization of functional materials based on coordination complexes with liquid cristalline and/or antitumour properties.

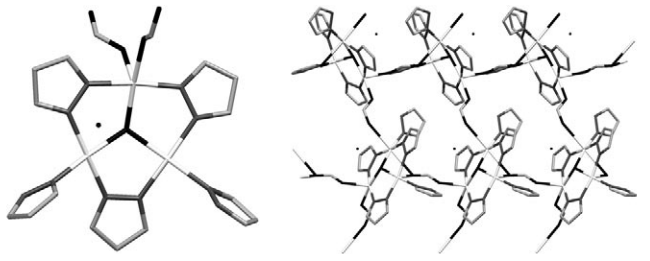


Figure 1. Trinuclear triangular core of **1** (left) generating a two-dimensional CP through multiple formate bridges (right). Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

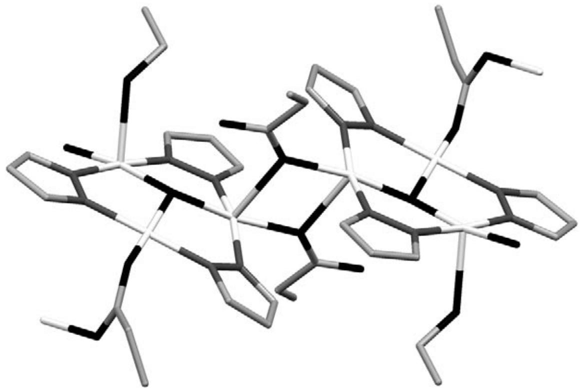


Figure 2. The hexanuclear structure of compound **3a**. Similar structural motifs are present also in **2** and **4**. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

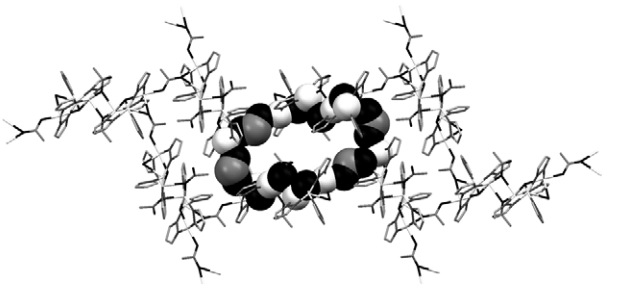


Figure 3. Drawing of the two-dimensional CP of **2** formed through the connection of three 28-membered macrocycles, one of which is evidenced through a space-filling representation. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

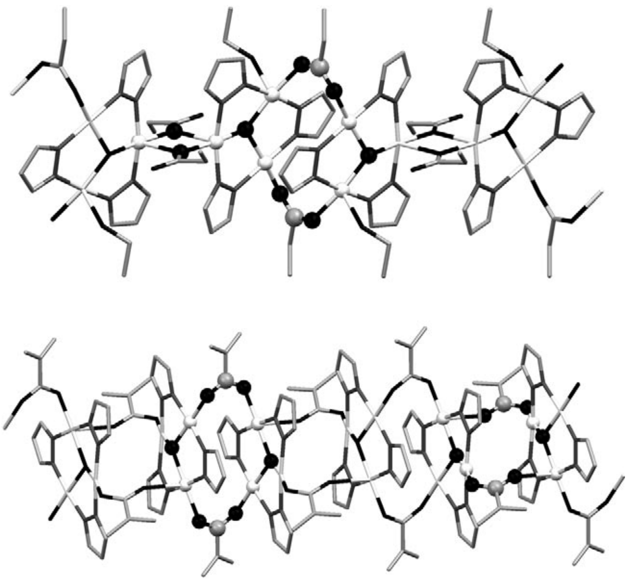


Figure 4. Schematic drawing of the one-dimensional CPs formed by connecting the hexanuclear moieties of **3a** through 4-membered and 12-membered loops (top), and by connecting trinuclear clusters of **10** alternating *syn-syn* and *syn-anti* carboxylato bridges (bottom). The 12- and 4-membered loops are evidenced through ball-and-stick representations. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

ed methacrylato derivative **10**, a different one-dimensional CP is generated, where two kinds (*syn–syn* and *syn–anti*) of 12-membered loops alternate (Figure 4, bottom).[16]

Also the reaction of copper(II) valerate, 2-methyl-butyrate, hexanoate and heptanoate with Hpz yielded species containing trinuclear triangular cores (compounds **5**–**8**, respectively). In these cases we were unable to isolate material suitable for single-crystal XRD determinations, nevertheless their IR, UV/Vis, ^{1}H NMR spectra, ESI MS and magnetic susceptibilities, as well as catalytic properties and electrochemical behavior, were found similar to those of compounds **1**–**4**[14c] and **9** and **10**.[16] These data suggest that the size of the carboxylates does not influence the (local) structure and the properties of these compounds for which the trinuclear metallacycle structure has been proposed.[15]

At variance, we found that the steric and electronic properties of the azoles employed in our studies strongly affect the nature of the reaction products. As a matter of fact, trinuclear derivatives were obtained only with Hpz, while by reacting copper(II) acetate with a series of substituted pyrazoles (namely 3,5-dimethylpyrazole, 4-methylpyrazole, 3,4,5-trimethylpyrazole, 3-methyl-4-phenylpyrazole or 3-methyl-5-phenylpyrazole, collectively labeled by Hpz$^{\#}$), deprotonation of water and azoles was never observed and only mononuclear $[Cu(CH_3COO)_2(Hpz^{\#})_2]$ or dinuclear $[\{Cu(CH_3COO)_2(Hpz^{\#})\}_2]$ complexes were obtained, depending on the reaction conditions and stoichiometric ratios.[14a] Moreover, it has been found that the reaction of copper(II) acetate with 3-methylpyrazole (Hpz^{Me}) gives $[Cu(CH_3COO)_2(Hpz^{Me})_2]$[24] and $[\{Cu(CH_3COO)_2(Hpz^{Me})\}_2]$,[25] Also the basicity of the carboxylate employed determines the product obtained, as indicated by the reaction of $Cu(CF_3COO)_2$ with Hpz, which yielded a one-dimensional CP based on the mononuclear $[Cu(CF_3COO)_2(Hpz)_2]$ SBUs bridged by the trifluoroacetate anions (see below).[14a]

The structures and supramolecular assemblies are determined not only by the reagents, but also by the reaction conditions, solvent, and temperature. As an example, when the reaction of copper(II) propionate with Hpz was performed using water as solvent (instead of ethanol), the trinuclear clusters $[\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3(\mathrm{EtCOO})_2(\mathrm{H_2O})]$ formed that do not couple into hexanuclear assemblies.[14c] More specifically, when the crystallization was carried out at about 20 °C, relatively weak hydrogen bonds form, connecting the trinuclear metal complexes, **3b**, in a supramolecular two-dimensional network (Figure 5, top). At variance, at a slightly lower temperature (ca. 12 °C), an additional water molecule of crystallization for each trinuclear moiety resulted trapped in the crystal lattice of **3c** and participate to a series of hydrogen-bond interactions, generating helices of opposite handness coupled in a centrosymmetric supramolecular network (Figure 5, bottom).

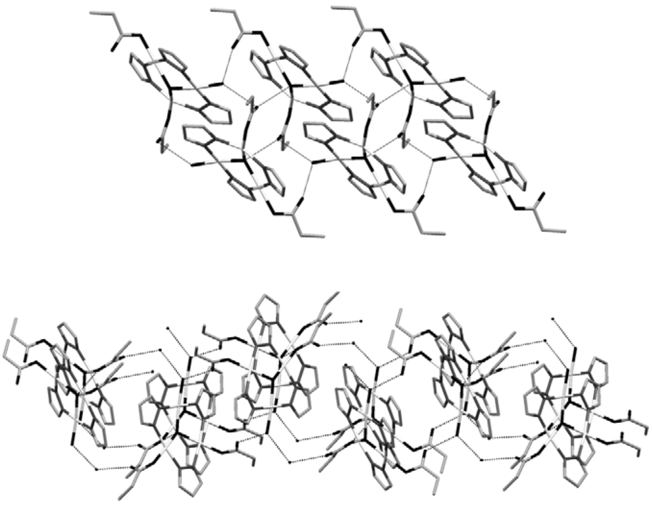


Figure 5. Top: Two-dimensional network developed in **3b** through hydrogen bonds. Bottom: Parallel helices of opposite handness present in the crystal packing of **3c**. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

Also the reaction of copper(II) acrylate with Hpz yielded different products: **9a** in water, and **9b** in methanol. In both cases, slightly different hexanuclear clusters formed: in **9a**, just as in **4**, they behave as isolated islands with no further coordinative interactions, while in **9b** they self-assemble in a one-dimensional CP analogue of **3a**, alternating 12-membered loops formed by carboxylate bridges in a *syn-syn* geometry with 4-membered rings.[16]

In all the above reported cases the $[\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ core formed, thus suggesting a particular stability of this assembly. Thus we tested this feature in the reaction with aqueous HCl: by using as a probe $[\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3(\mathrm{MeCOO})_2(\mathrm{Hpz})]$ (**2**), three different derivatives, in which the trinuclear core was maintained, and the mononuclear complex $[\mathrm{CuCl_2}(\mathrm{HPz})_4]$ were isolated.[26] Specifically, HCl displaces one acetate ion for each trinuclear moiety, destroying the two-dimensional network shown in Figure 3, but maintaining the hexanuclear core. In this way the cationic hexanuclear derivative $[\{\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3(\mathrm{Hpz})_2\}_2(\mu\text{-MeCOO})_2]\mathrm{Cl_2}\cdot 2\,\mathrm{H_2O}$ (**11**) was obtained, in which the double carboxylato bridge joining the two trinuclear units is still present (Figure 6, top). A further HCl attack yields $[\{\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3(\mathrm{Cl})(\mathrm{Hpz})_3\}_2(\mu\text{-Cl})_2]\cdot\mathrm{H_2O}$ (**12**), which is a neutral hexanuclear species in which the bridging carboxylates are also removed and substituted by chloride bridges (Figure 6, bottom). The crystal structure evidences the presence of a crystallization water molecule that strongly interacts, through hydrogen bonds, with OHs capping two of the trinuclear fragments (as H acceptor) and with one chloride of the double bridge (as H donor).[26]

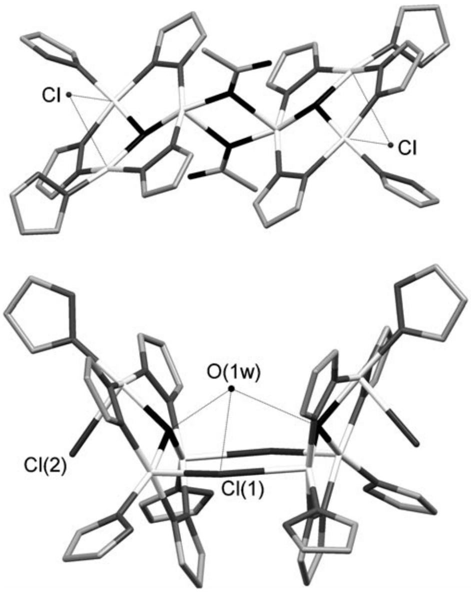


Figure 6. Molecular drawing of **11** (top) and **12** (bottom). Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

Nevertheless, the presence, in compounds **11** and **12**, of coordinated neutral Hpz, as well as the isolation of the above-mentioned $[\mathrm{CuCl_2}(\mathrm{HPz})_4]$ complex, indicate that HCl protonates pz$^-$ ligands of **2**, partly disrupting the trinuclear core. This decomposition is further evidenced by the isolation of $[\{\mathrm{Cu_3}(\mu_3\text{-OH})(\mu\text{-pz})_3(\mathrm{Cl})_2(\mathrm{Hpz})_2(\mathrm{H_2O})\}_2\{\mathrm{CuCl_2}(\mathrm{Hpz})_2\}]$, (**13**; Figure 7). In this heptanuclear species, a coordinatively unsaturated $[\mathrm{CuCl_2}(\mathrm{Hpz})_2]$ fragment acts, through two bridging chlorides, as a sort of joint between two trinuclear moieties.

Actually, Cu(4) interacts with Cl(1) of the two trinuclear fragments, while Cl(3) weakly coordinates to Cu(1). Another relevant supramolecular interaction is evident in compound **13**, since each Cl(1) ion coordinates also to the Cu(1) ion of another trinuclear fragment and, by this way, the macrocycles shown in Figure 8 (left) are obtained. The latter further self-assemble generating an extended two-dimensional network in which hexagonal cavities with an effective free diameter of about 4.5 Å are evident (Figure 8 right). These two-dimensional networks stack in a parallel manner and generate a PCP having empty channels of nearly hexagonal section.[26] The PCP generation trough a chloride ion tem-

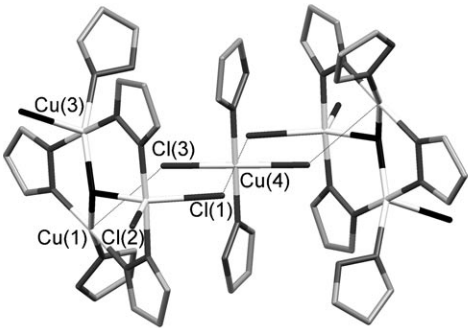


Figure 7. Chloride bridges connecting the mononuclear $[CuCl_2(Hpz)_2]$ fragment to two trinuclear triangular units, $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(Cl)_2(Hpz)_2(H_2O)]$, forming species **13**. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

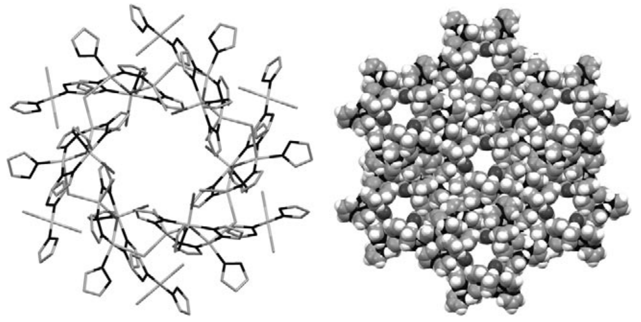


Figure 8. Schematic representation of the connectivity of supramolecular assembly of **13** generating one macrocycle (left) and the space-filling representation of the extended CP evidencing solvent-free hexagonal channels running down the crystallographic *c* axis (right). Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

plate self-assembly seems to parallel the reaction reported by Kamiyama et al. who describes a new cage-type hexacopper complex in which the chloride is at the center of the cage.[27]

$[Hg_3(pz)_3]^{3+}$-based structures: Trinuclear mercury derivatives have recently received increasing attention due to their reactivity[28] and supramolecular structures,[29] which often generate peculiar features such as luminescence[29] and catalytic properties.[30] It is possible that trinuclear mercury pyrazolate systems were synthesized in the late 1976 (the authors considered the species obtained simply as mononuclear or polynuclear complexes),[31] but no crystal structure was reported confirming the presence of the $[\{Hg(pz)\}_3]$ moiety until to 2006.[17] In particular, a trinuclear triangular species, $[Hg_3(CH_3COO)_3(pz)_3]$ (**14**) was obtained in the reaction between $[Hg(CH_3COO)_2]$ and Hpz, carried out in a diethyl ether/methanol mixture.[17] More precisely, XRD determination evidenced that two trinuclear triangular clusters $[Hg_3(pz)_3]^{3+}$ are doubly bridged by two acetate anions according to a *syn–anti* geometry, forming the hexanuclear assembly shown in Figure 9.

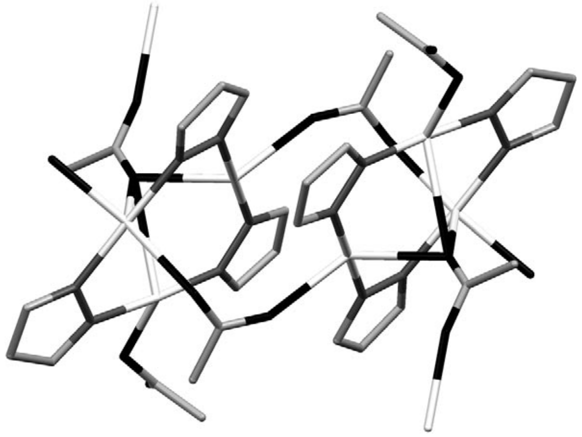


Figure 9. The hexanuclear assembly of **14** determined by two acetate ions bridging two trinuclear moieties with a *syn–anti* geometry. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), mercury (white).

A further acetate ion (for each trinuclear unit) is involved in other more or less strong interactions. First of all, the three Hg ions are capped by one oxygen of this carboxylate, while the other one generates a rather complicated three-dimensional CP by bridging differently oriented hexanuclear assemblies. In Figure 10 a view down the crystallographic *c* axis of this CP is depicted, showing a rather complicated rhombohedral structure in which each unit cell contains 18 “isolated” trinuclear triangular $[Hg_3(pz)_3]^{3+}$ fragments, with essentially linearly coordinated Hg^{II} ions.

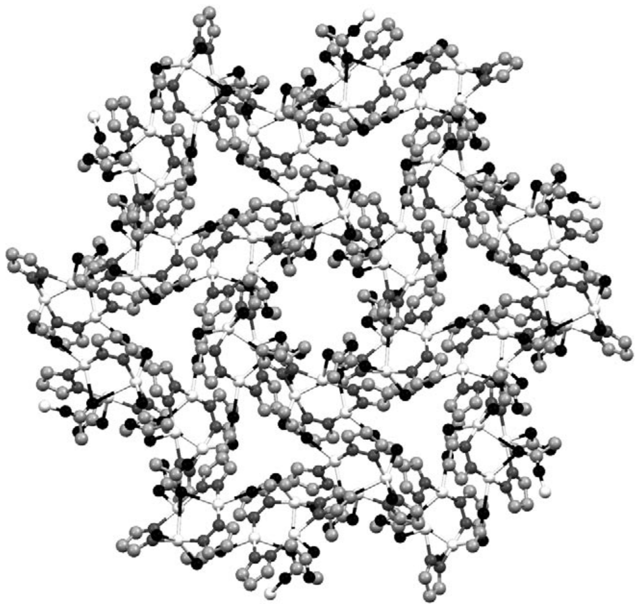


Figure 10. View down the crystallographic *c* axis of the crystal packing of **14**. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), mercury (white).

Homoleptic and Heteroleptic Mononuclear-Based CPs

Pyrazole- and pyrazolate-based CPs: Among the most interesting materials, coordination polymers with simple formulation, easy chemical synthesis, well-defined periodicity, and, possibly, predictable structures, have appeared in the literature.[2,32] While poly-dimensional networks have been found to favor extremely relevant functional properties, one-dimensional chains are also fascinating systems, particularly for the anisotropy of their optical, magnetic, and structural properties, which, in some cases, generate very appealing materials for technological applications.[33]

In this regard, during our studies on trinuclear triangular Cu^{II} clusters (discussed above), we found that the reaction of copper(II) carboxylates with Hpz yielded also CPs based on mononuclear SBUs.

Apparently, the basicity of the CF_3COO^- ion is insufficient to deprotonate water and Hpz. Thus, analogously to what is found in the reaction of Hpz with several Cu^{II} salts of strong inorganic acids,[34] the reaction of $Cu(CF_3COO)_2$ with Hpz produces the $[Cu(CF_3COO)_2(Hpz)_2]$ derivative (**15**) upon coordination of neutral Hpz to the copper center. This complex acts as a mononuclear SBU forming a one-dimensional CP through trifluoroacetate ions bridging Cu^{II} ions in a *syn–anti* conformation, as shown in Figure 11.[14a]

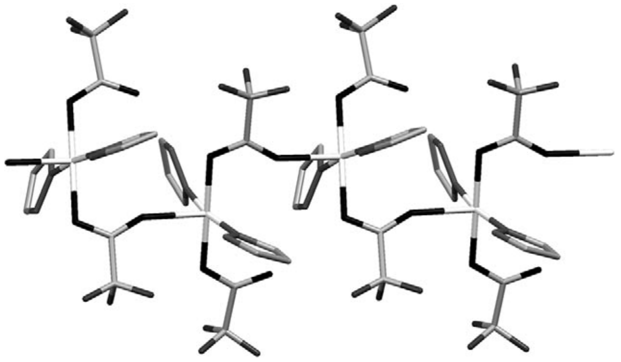


Figure 11. One-dimensional CP in which develops compound **15** formed through *syn–anti* trifluoroacetato bridges. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

Although not being a homoleptic species, this material proved that, depending on the used synthons, the nearly ubiquitous trinuclear clusters can be avoided, and one-dimensional chains systems can be isolated. Incidentally, our compound is quite different from that reported by Kogane et al.,[35] prepared by reaction of $[Cu(hfac)_2]$ with pyrazole in petroleum ether and in which the copper coordination environment consists of four pyrazoles and two carboxylato groups.

Similarly, we saw that the influence of the solvent, evidenced above in the formation of the different trinuclear species **3a–c** and **9a**,**b**, is of paramount relevance when copper(II) carboxylates were reacted with Hpz in CH_3CN. Quite unexpectedly, a light-beige one-dimensional CP, β-$[Cu(\mu\text{-}pz)_2]_n$ (**16**), was quantitatively obtained according to Scheme 2;[18a] here the symbol β is used to distinguish **16** from the green $[Cu(\mu\text{-}pz)_2]_n$ phase (hereafter, α), previously synthesized through a completely different procedure.[36]

$$n\,\mathrm{Cu(RCOO)_2} + 2n\,\mathrm{Hpz} \xrightarrow[\text{i)}]{\text{MeCN}} \underset{\textbf{16}}{\beta\text{-}[\mathrm{Cu}(\mu\text{-pz})_2]_n} + 2n\,\mathrm{RCOOH}$$

Scheme 2. i) Filtration of a light pink solid followed by heating the solid at about 60 °C and 0.1 Torr.

While in the α phase the coordination of nitrogen atoms around the Cu^{II} centers is tetrahedral, in **16** the copper ions adopt a square-planar coordination and the one-dimensional CP shown in Figure 12 is formed. The difference in their local structure is also nicely reflected by the different colors of these species.

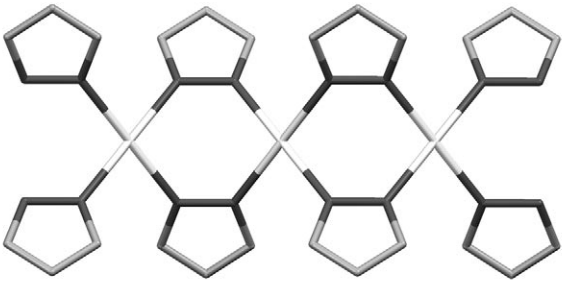


Figure 12. Portion of the one-dimensional chain found in species **16**. Color codes: nitrogen (dark grey), carbon (light grey), copper (white).

Even though in compound **16** there are no evident pores, channels, or cavities, nevertheless this species was found to easily transform into the pale-pink one-dimensional CP $[Cu(\mu\text{-}pz)_2{\cdot}H_2O]_n$ (**17**) by adsorbing water vapor, which is hosted between adjacent, and parallel, one-dimensional chains (see Figure 13). It is worth noting that the square-planar nitrogen environment around Cu^{II} is practically unperturbed and H_2O cannot really be considered to be coordinated to Cu (Cu···O ca. 2.91 Å);[18a] nevertheless, the overall crystal structure is instead strongly modified, demonstrating the flexibility of this crystal phase.

This unexpected behavior can be evidenced by using space-filling representations of **16** and **17** (Figure 14): their comparison reveals that water molecules are placed in voids, previously absent, that are formed through some kind of cooperative process driven by host–guest interactions,[18b,c] in a typical case of “porosity without pores”.[37]

The relevant modification of the crystal lattice, which can be easily followed by in-situ X-ray powder diffraction experiments, is accompanied by a color change of the solid, which acquires a pale-pink hue. The adsorption of water is reversible—compound **16** can easily regenerated by heating

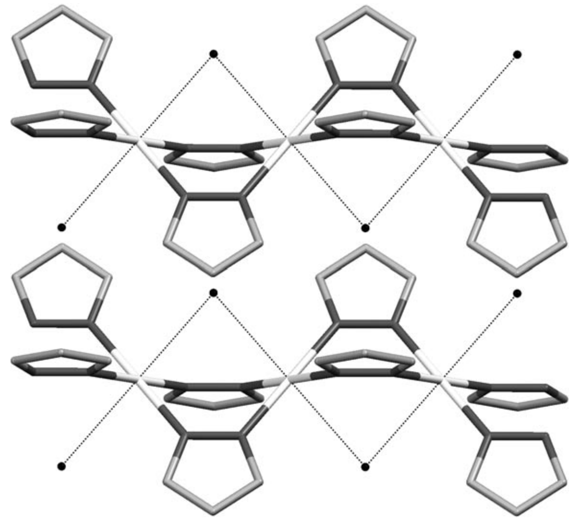


Figure 13. Crystal structure of **17** evidencing the weak contacts between guest water molecules and Cu^{II} ions. Black points indicate the oxygen atoms of adsorbed water. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

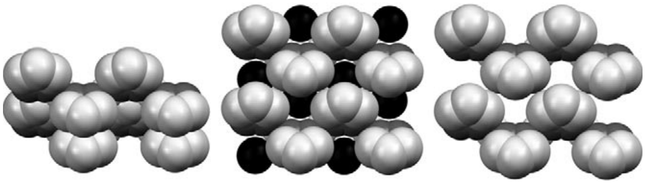
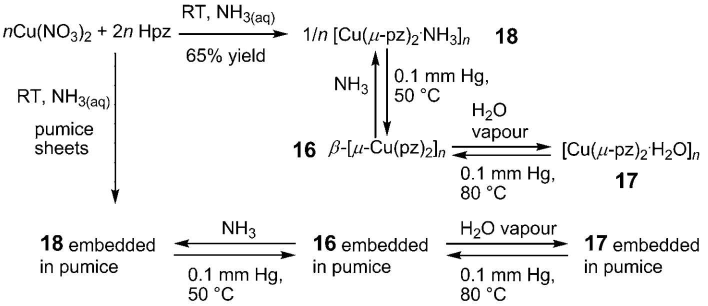


Figure 14. Space-filling comparison between the crystal packing of **16** (left) and **17** (middle), evidencing the modification produced by the adsorption of water. The oxygen atoms of the water molecules are indicated by black spheres. The figure on the right, obtained by fictionally removing water molecules from **17**, evidences the "pores" formed to host water molecules, which are absent in **16**. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), copper (white).

17 at about 80 °C and 0.1 torr. This process can be repeated indefinitely without any evident decomposition. In parallel experiments, we found that compound **16** adsorbs also gaseous NH_3 giving the dark-blue, microcrystalline one-dimensional CP $[Cu(\mu\text{-pz})_2{\cdot}NH_3]_n$ (**18**). Also in this case **16** is completely restored by gently heating **18** under vacuum.[18a]

Compound **18** was synthesized also through a different procedure, that is, by mixing ammoniated solutions of copper(II) salts and Hpz (Scheme 3).[18b,c] Incidentally, by using this method, it was possible to generate solid **18** embedded in a porous inert material (pumice sheets), in which it fully maintains the chemical, crystal, and spectral features of the pure material. For example, NH_3 can be easily eliminated as indicated in Scheme 3, giving pumice-embedded **16** and allowing the preparation of a hybrid ceramic-based material, that possibly can act as a gas sensor.

Beside water and ammonia, **16** quickly adsorbs also methylamine, while CH_3CN, pyridine and methanol vapors require longer adsorption times; finally, dimethyl- and trimethylamine are not adsorbed, thus suggesting that steric factors are important in determining the adsorption.



Scheme 3.

The rich host–guest chemistry of the β-$[Cu(pz)_2]_n$ polymer, capable of sorbing a number of gases with O or N donor sites, is therefore different from that of cyclic neutral species of general $[\{cis\text{-}Cu(\mu\text{-}OH)(\mu\text{-pz})\}_n]$ formula ($n=6$, 8, 9, 12, 14), serendipitously prepared in an attempt to remove Cl atoms from $[Cu_3(\mu_3\text{-}O)(\mu\text{-pz})_3Cl_3]^{2-}$;[38] indeed, these metallacycles self-assemble as discrete molecules with the lipophilic side of the pz^- ligands oriented toward the outer surface and the hydrophilic OH groups pointing toward an encapsulated anion at the inner cavity of the whole assembly.

CPs based on mononuclear SBUs have been obtained also in the reactions carried out in alcohols or water between $Zn(CH_3COO)_2{\cdot}2H_2O$ and Hpz in ratios ranging from 1:2.5 to 1:1.[19] Specifically, the reaction in EtOH (Zn : Hpz = 1:2.5) generated, upon partial zinc salt hydrolysis and Hpz deprotonation, the dinuclear complex, $[\{Zn(CH_3COO)(\mu\text{-pz})(Hpz)\}_2]$, while, when the reaction was performed with a Zn/Hpz 1:1 molar ratio, the insoluble $[\{Zn(\mu\text{-}CH_3COO)(\mu\text{-pz})\}_n]$ species is formed. The latter compound contains polymeric two-dimensional layers stacked in their normal direction through weak van der Waals H···H interactions. Each metal ion is tetrahedrally coordinated by four distinct moieties, that is, two pyrazolate and two acetate ligands, all of the bridging type: the pyrazolates act in the common *N,N'*-exobidentate mode, keeping two Zn^{II} ions at a non-bonding distance of approximately 3.59 Å, while the acetate ligands span a much longer Zn···Zn vector (4.80 Å), thanks to the less common *syn–anti* conformation of the μ-RCO_2 fragment. The $\{Zn(\mu\text{-pz})\}_2$ core present in this compound resembles that found in $[\{Zn(CH_3COO)(\mu\text{-pz})(Hpz)\}_2]$ and in $[Zn(\mu\text{-pz})_2]_n$, described below, but is linked through the acetate ligands to symmetry equivalent fragments, in an ordered layer of $p2_1/b$ symmetry.

By using a Zn/Hpz ratio of 1:2 and a water/MeOH mixture as solvent, the acetate ions completely deprotonate Hpz to pz^-, giving rise to the one-dimensional CP, $[Zn(\mu\text{-pz})_2]_n$, previously obtained by using zinc chloride and ammonia as deprotonating agent;[39] in this species, the Zn^{II} ions show a tetrahedral coordination and supramolecular features analogous to those found in the α-$[Cu(\mu\text{-pz})_2]_n$ phase cited above.[36] Interestingly, from the mother liquors of the reaction leading to [{$Zn(CH_3COO)$(μ-pz)(Hpz)}$_2$] it was possible to obtain well-formed crystals of [{$Zn(CH_3COO)_2$-$(Hpz)_2$}·CH_3COOH], in which the acetic acid was generated through the deprotonation of Hpz by the acetate ions.

One-dimensional CPs have also been obtained by reacting cadmium and mercury acetates with Hpz or Hpz*. Specifically, the reaction between $Cd(CH_3COO)_2$ and Hpz gave two polymorphs of the one-dimensional CPs [{Cd(μ-$CH_3COO)_2(Hpz)_2$}$_n$], containing hexacoordinated cadmium ions with local CdN_2O_4 geometry.[17] In both cases, each metal center bears two monodentate pyrazole ligands in a *trans* position and is connected, through bridging acetato groups, to two other Cd^{II} ions, according to a *syn–anti* geometry; the most relevant differences between the two polymorphs are in the packing of the chains. The two-dimensional CPs [{Cd_3(μ$_3$-$CH_3COO)_4$(μ-pz)$_2(Hpz)_2$}$_n$] and [{Cd(μ-CH_3COO)(pz)}$_n$] can also be prepared by controlled thermal treatment of one of the [{Cd(μ-$CH_3COO)_2(Hpz)_2$}$_n$] forms.[17]

Finally, by reacting [$Hg(CH_3COO)_2$] with Hpz*, the one-dimensional CP [{$Hg(CH_3COO)$(μ-Hpz*)}$_n$] (**19**) was obtained. It contains chains of Hg^{II} ions bridged by rare C-mercuriated Hpz* ligands, which arrange parallel to the crystallographic *b* axis (Figure 15).[17]

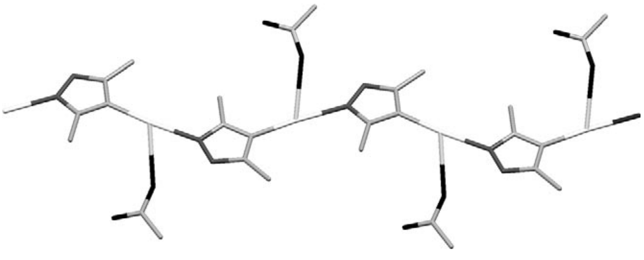
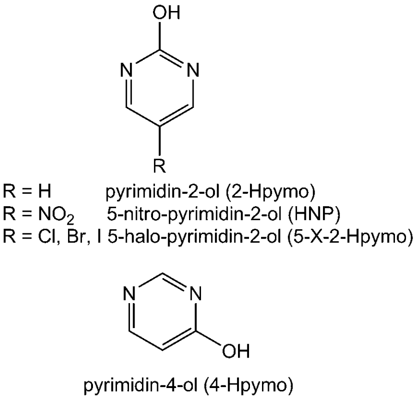


Figure 15. Supramolecular assembly of mononuclear [$Hg(CH_3COO)$(μ-Hpz*)] moieties generating the one-dimensional CP **19**. Note the rare C-mercuriation of the heteroaromatic rings. Color codes: oxygen (black), nitrogen (dark grey), carbon (light grey), mercury (white).

Ring mercuration in the case of 3,5-dimethyl substituted pyrazoles[40] has been previously reported and the reaction seems to proceed spontaneously and rapidly when mercury(II) acetate was employed as starting material.[41]

It is worth noting that when the reaction between [Hg-$(CH_3COO)_2$] and Hpz was carried out in hydroalcoholic solvents, a nearly amorphous [{$Hg(CH_3COO)$(μ-pz)}$_n$] derivative was obtained. This compound has Hg/CH_3COO/pz = 1:1:1 ratios that are identical to those of the above reported trinuclear [{$Hg_3(CH_3COO)_3$(μ-pz)$_3$}$_n$] (**14**) obtained in ethyl ether/methanol mixture. Nevertheless, on the basis of ^{13}C-CPMAS solid-state NMR, showing strong analogies with [{$Hg(CH_3COO)$(μ-Hpz*)}$_n$], the presence of a C-mercuriated pyrazolic ring has been hypothesized also in this case.[17]

Pyrimidinolate-based CPs: In recent years we have been interested also in the coordination chemistry of simple heterocycles based on the 2- and 4-hydroxy-pyrimidine molecules. While some of the materials were originally prepared by us,



most of this work has been later performed in strict collaboration with the coordination chemistry group lead by Prof. Navarro at the University of Granada, to whom the authors are profoundly indebted. Accordingly, only a small portion of the pertinent results is here presented, the reader being invited to directly address his/her curiosity to other review papers[42] or to the original literature.[43–51]

Thanks to the acidity of the (tautomeric) proton and to the resonance-assisted stabilization of the anionic form (hereafter, 2-pymo), this ligand was coupled to a number of transition-metal ions in the formation of oligomeric and polymeric materials showing very interesting chemical, structural, and functional properties, summarized in the following. This large zoo of polymeric complexes, after gathering experimental evidence on the different species, allows the rationalization of their structure and activity in a coherent manner.

Polycrystalline materials of general [{M(2-pymo)}$_x$] formulation can be easily prepared by reacting the heterocyclic ligand in its protonated form with the pertinent metal salts and, when necessary, a deprotonating, but not coordinating, agent, such as a trialkylamine. In particular, 2-pymo, coupled to monovalent coinage metal ions, allowed the preparation of:

1) The hexanuclear [{Ag(2-pymo)}$_6$] complex,[52] obtained by controlled thermal treatment or by ethyl orthoformate-promoted water elimination of the long-known crystalline [Ag(2-pymo)]$_n$·2$n$$H_2O$ polymer;[53] such a reaction proved to be fully reversible, in that ring-opening polymerization was easily promoted by stirring [{Ag-(pymo)}$_6$] in wet acetone.
2) The unexpected [{Cu(2-pymo)}$_6$]·12/n[Cu(2-pymo)]$_n$ crystal phase,[54] the first species ever characterized containing, at the same time in the same crystal lattice, cyclic oligomers and polymeric (here, helical) strands of the same monomeric entity. Figure 16 shows a molecular sketch of the hexamer and of the helical polymer.

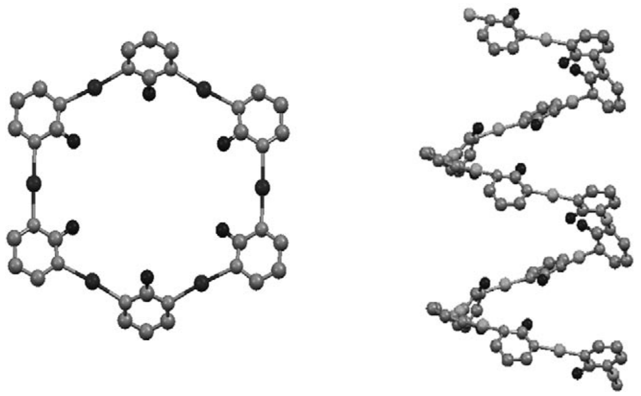


Figure 16. Molecular drawing of the $[\{Cu(2\text{-pymo})\}_6]$ hexamer (left) and of a portion of the infinite helix of $[Cu(2\text{-pymo})]_n$ (right). The hexamer is also representative of the Ag^I analogue, in its anhydrous form. Color codes: oxygen and copper (black), other atoms (grey).

If divalent cations were employed instead, three-dimensional frameworks were isolated:

1) $[Cu(2\text{-pymo})_2]_n{\cdot}2n\,H_2O$[55] and $[Pd(2\text{-pymo})_2]_n{\cdot}2n\,H_2O$,[56] containing sodalitic cages prone to strong host–guest interactions within cavities about 1 nm wide and pore openings large enough to allow easy diffusion of gaseous molecules, (see Figure 17). These species, upon removal of the guest water molecules, showed remarkable sorption properties for a number of environmentally relevant gases, including hydrogen at cryogenic temperatures. Moreover, both these zeomimetic frameworks have been recently employed by Corma et al. in a number of catalytic experiments,[57] with significant activity and remarkable size-shape selectivity, easily attributed to the confinement of molecules within the crystal lattice. In addition, the copper species was found to crystallize in the presence of a number of simple inorganic salts, as a porous phase hosting a variety of ionic pairs in its cavity.[58] However, if exposed for longer periods to large alkali cations, or to rare earth nitrates,[59] the quantitative conversion into layered phases was observed, which requires reorientation of the 1,3-alternate disposition of 2-pymo ligands into a pinched-cone conformation, favoring coordination to the guest metal ions. This effect, that is, the mineralomimetic conversion from sodalitic to muscovitic structures, coupled to the organization of the rare-earth sublattice, generated 3d–4f magnetic interactions responsible for remarkably different couplings at low temperatures.

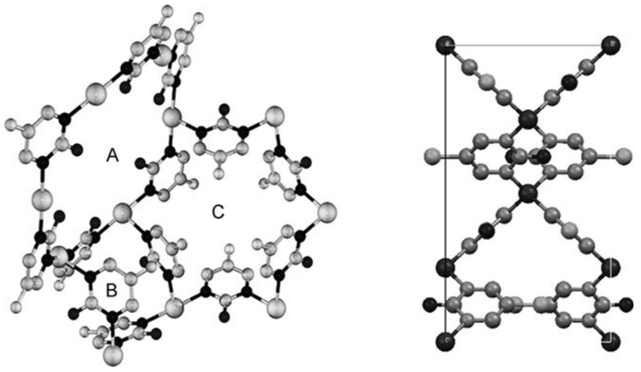


Figure 17. Left: Structural motifs found in the pseudosodalitic $[M(2\text{-pymo})_2]_n$ polymers (M = Cu, Pd): metallacalix[6]arene (A), metallacalix[4]arene (B) and planar hexagon (C). Color codes: oxygen and nitrogen (black), other atoms (grey). Right: The dense crystal packing of the $[M(2\text{-pymo})_2]_n$ species (M = Co, Zn, and, to some extent, Ni), viewed down [001]. Color codes: oxygen and metal atoms (black), other atoms (grey).

2) At variance, $[M(2\text{-pymo})_2]_n$ species[60] (M = Ni, Co and Zn) crystallize as diamondoid structures (see Figure 17), without cavities nor sorptive properties (for gases, liquids, or dissolved salts). Their rather dense structures, and the chemical inertness of the unsubstituted 2-pymo ligand are, however, at the basis of the very high thermal stability, which, in the case of $[Zn(2\text{-pymo})_2]_n$, reaches an exceptionally high decomposition temperature at 570 °C.

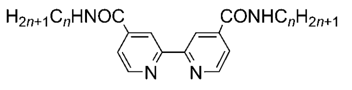
More recently, 5X-substituted pymo ligands (with X = halides or $\text{-}NO_2$) were prepared, and several interesting two-dimensional and, more often, three-dimensional polymers were isolated, which, along with the 2H-pymo and 4H-pymo derivatives, showed relevant non-linear-optical, magnetic or sorptive properties. The discussion of the very rich crystal chemistry of these extended networks, which includes reversible dehydration processes, phase transformations induced by heating, polymorphism, intercalation of 4f ions, and molecular alloy formation, is not reported here, and will be the subject of an upcoming review.

2,2′-Bipyridine–Metal-Based Liquid Crystals

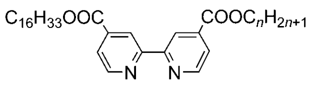
To design new functional inorganic liquid crystals of versatile optical, electronic and thermal properties, we have recently employed a multi-motif approach based on the spontaneous associations of single tectons into anisotropic aggregates. Thus, we have selected 4,4′-substituted-2,2′-bipyridines together with silver(I) and zinc(II) ions,[61–63] as potential synthons in the formation of self-assembled supramolecular arrays, driven by: 1) the presence and/or nature of the substituents on the N,N-donor ligand, 2) the coordinating ability of the main and the ancillary ligands, 3) the metal-coordination number typology, and 4) the possible counterions.

We have initially developed and optimized a method for the synthesis of symmetrically substituted 2,2′-bipyridines, introducing functionalities able to impart a rod (L^1–L^6)[64–66] or a hemi-disklike molecular shape (L^7, L^8)[67] to the bipyridine unit.

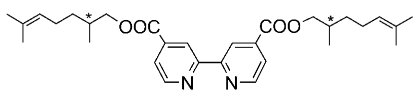
The L^1–L^6 series is based on a 2,2′-bipyridine central core bearing two aliphatic tails of variable lengths in 4,4′-positions, connected to the core through amidic or ester links, while L^7 and L^8 ligands are based on a hexacatenar framework with a rigid core inflated by the presence of two fur-



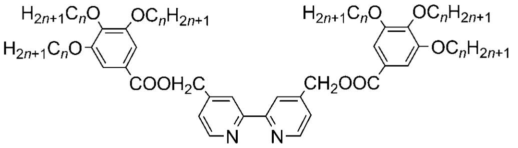
n = 10 2,2'-bipyridine-4,4'-bis-(*n*-decylamide), L1
n = 18 2,2'-bipyridine-4,4'-bis-(*n*-octadecylamide), L2



n = 8 dioctyl 2,2'-bipyridine- 4,4'-dicarboxylate, L3
n = 16 dihexadecyl 2,2'-bipyridine- 4,4'-dicarboxylate, L4
n = 22 didocosyl 2,2'-bipyridine- 4,4'-dicarboxylate, L5



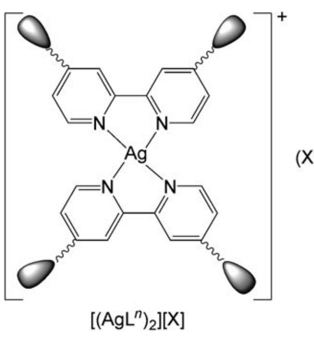
dicitronellyl 2,2'-bipyridyl-4,4'-dicarboxylate, L6



n = 12 4,4'-bis(3,4,5-tridodecyloxybenzoyloxymethyl) 2,2'-bipyridine, L7
n = 16 4,4'-bis(3,4,5-trihexadecyloxybenzoyloxymethyl) 2,2'-bipyridine, L8

ther aromatic rings, surrounded in turn by three aliphatic chains of variable lengths.

Silver complexes from 2:1 ligand-to-metal ratio: Silver(I) coordination architectures are widely influenced by several factors such as the reaction conditions,[68] the type of counter anions present in the ionic derivatives, the metal-to-ligand ratio,[69] and the nature of the ligand used,[64] making these systems appealing candidates for the production of interesting structural motifs with intriguing electronic properties.[71] The first synthetic strategy used to induce mesomorphism upon metal complexation has been based on the reaction of AgX salts containing anions of different coordinating ability [BF_4^-, PF_6^-, OTf (triflate), DOS (dodecylsulphate)] with two equivalents of the selected L^n bipyridine ligand. This approach allowed the isolation of a number of ionic silver(I) complexes of general formula $[Ag(L^n)_2][X]$ with two bipyridine units joined around a tetracoordinated Ag^I ion.[65,66,72]



$[(AgL^n)_2][X]$

For these homoleptic bis-chelated complexes, the mesomorphism arises only in the presence of appropriately long terminal chains on the bipyridine ligands, depending on the molecular anisometric ratio (length-to-breath ratio) of the overall molecule, and in the presence of anions of moderate coordination strength, the role of which is crucial in driving the organization of both the single molecular units and the overall supramolecular motifs. In particular, the mesogenic triflate and dodecylsulphate homologues show hexagonal or rectangular columnar phases as summarized in Table 1.

Table 1. Thermal behavior of $[Ag(L^n)_2][X]$ complexes

Complexes	Mesomorphism[a]
$[Ag(L^1)_2][OTf]$	Cr 138.9 Col_r 178.6 Iso 175.3 Col_r 135.0 Cr
$[Ag(L^2)_2][OTf]$	Cr 73.3 Cr′ 108.5 Cr″ 117.5 Col_h 299.0 Iso_{dec}
$[Ag(L^4)_2][OTf]$	Cr 33 Cr′ 59 Col_h 71 Iso 48 Col_h/Cr[b]
$[Ag(L^4)_2][DOS]$	Cr 77 Cr′ 81 Col_r 85 Iso 64 Col_r 48 Cr
$[Ag(L^6)_2][OTf]$	Col_h 91.0 Iso
$[Ag(L^6)_2][DOS]$	Col_h 56.8 Iso
$[Ag(L^8)_2][OTf]$	Cr 49 Cr′ 69 Col_h 97 Iso 96 Col_h 44 Cr
$[Ag(L^8)_2][DOS]$	Cr 58Cr′ 77 Col_r 90 Iso 55 Col_r/Cr

[a] Cr: crystal; Col: columnar; Iso: isotropic liquid. [b] Only a broad peak for the two transitions.

The role of the substituents on the N,N-ligand was found to be fundamental in modulating the properties of the corresponding $[Ag(L^n)_2][X]$ complexes. As regards the thermal behavior, the presence of the amidic functionality in the L^1 and L^2 derivatives induces an extremely ordered structural organization, due to their ability to give rise to H-bonding interactions, leading to high transition temperatures.[65] Instead, when the amidic groups were replaced by ester residues (keeping the overall rodlike molecular shape of the bipyridine) or with alkylene units connecting a further aromatic ring bearing three terminal chains (thus giving a global hemi-disc shape to the corresponding ligands), a lowering of the clearing temperatures of 100–200 °C has been observed.[66–72]

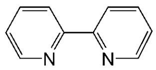
The presence of stereogenic centers in the terminal alkoxy in L^6 induces helical twisting about the columnar axis in the corresponding room-temperature zinc(II) mesogen. CD experiments in solution and on the liquid crystalline films confirmed that, in these systems, chirality is induced from the single molecule level to a supramolecular columnar liquid-crystalline organization. Therefore, the supramolecular arrangement achieved gives rise to a helical structure formed by the entire molecular columns in the mesophase.[66]

Moreover, the photophysical studies conducted on all the silver(I) derivatives allowed to define these complexes as multifunctional materials very promising for their application as light-emitting diodes, owing to the successful combination of mesomorphism and luminescence simultaneously occurring, in several cases, even at room temperature. In fact, very few metallomesogens that are luminescent in the mesophase have been reported up to now, but none of them show mesomorphism and luminescence at room temperature.[73]

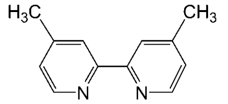
In conclusion, for this class of complexes the nature of substituents on the N,N-ligands are the key elements for driving the onset of the desired functionalities in the resulting silver(I) species.

Silver complexes from 1:1 ligand-to-metal ratio: We have extended the work keeping the same building blocks used for the homoleptic bis-chelated $[Ag(L^n)_2][X]$ complexes, but changing the ligand-to-metal ratio in order to further investigate the influence of the coordination capability of the nitrogen ligands and of the nature of the counterions on the molecular structures, supramolecular architectures, and functional properties of the resulting silver(I) derivatives.

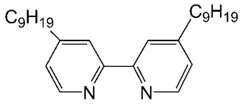
Thus we have selected as nitrogen donor ligands, apart from the promesogenic dihexadecyl 2,2′-bipyridine-4,4′-dicarboxylate (L^4), also a number of 2,2′-bipyridines (shown here) able to confer to the resulting Ag^I complexes a higher chance for crystallization. We combined them in a one by one reaction with a series of Ag^I salts of anions with decreasing coordinating capability ($X = C_7H_4NO_3S^-$ (sac), NO_3^-, OTf, ClO_4^-).



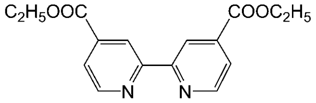
L^9



L^{10}



L^{11}



L^{12}

The peculiar versatility in the coordination capability of the 2,2′-bipyridines allows us to tune, in dependence of the coordination strength of the counterion used, the electroneutrality, the topology, and the liquid crystalline properties of the silver(I) derivatives. Indeed, as regards the coordinating saccharinate and nitrate anions, they compete with the chelating bipyridine ligand in the coordination of the Ag^I ion, giving rise only to neutral 1:1 products $[Ag(L^n)(X)]$, (Figure 18) preventing the appearance of any mesomorphic behavior even in the highest homologues.

In contrast, the presence of the non-coordinating perchlorate anion forces a 3:2 stoichiometry in the ionic $[Ag_2(L^n)_3](ClO_4)_2$ derivatives, with two Ag^I ions chelated by a bipyridine ligand and held together through a third bipyridine as bridging ligand, acting as a pincer and pulling the silver ions into such a proximity to form significant metal–metal interactions (Figure 19).

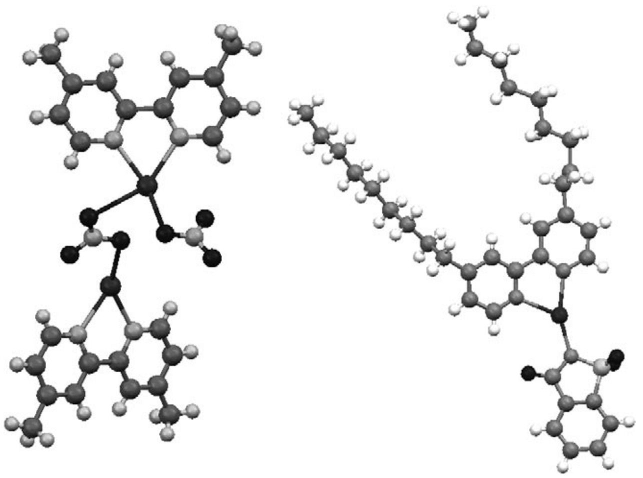


Figure 18. Perspective view of complexes $[Ag(L^{10})(NO_3)]$ (left) and $[Ag(L^{11})(sac)]$ (right). Color codes: oxygen and silver atoms (black), other atoms (grey).

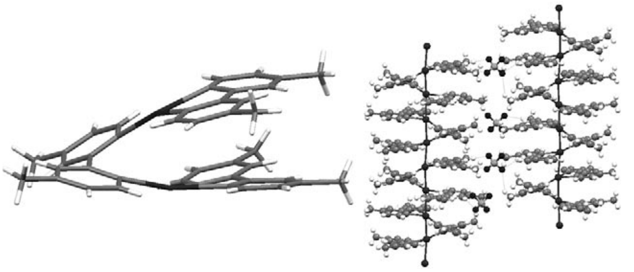


Figure 19. A perspective view (left) and crystal packing (right) of the cation $[(L^{10})_3Ag_2]^{2+}$in the ionic $[(L^{10})_3Ag_2](ClO_4)_2$ complex.[74] Color codes: oxygen and silver atoms (black), other atoms (grey).

This self-assembled supramolecular arrangement is the tool for inducing the successful combination of argentophilic interactions and nano segregation, which allows the onset of liquid crystalline properties with lamello-columnar mesomorphism in the highest homologues.[75]

The presence and the nature of the substituents on the 2,2′-bipyridine ligands deeply influence the coordination sphere of the silver(I) center and the subsequent coordination networks in presence of the moderately coordinating triflate anion. In particular, in the presence of electron-donor groups on the 4,4′-positions of the 2,2′-bipyridine, the coordination capability of the bipyridine ligand is larger than that of the triflate anion, giving rise to ionic species with a 3:2 ligand-to-metal formula $[Ag_2(L^n)_3](OTf)_2$ ($n = 9$–11) in which the silver coordination sphere is completely filled by the bipyridine ligand. On the other hand, when the bipyridine ligand is naked or substituted with electron-withdrawing groups, its basicity drops off and the triflate anion participates in the coordination of the silver ion, giving rise to neutral species $[Ag(L^n)OTf]$ ($n = 9$–11) with a 1:1 ligand-to-metal stoichiometry. In this case a homochiral polymeric arrangement with a unique screw sense of helical organization has been found in the solid state (Figure 20) and a CD experiment performed in the solid state proved the spontaneous resolution of the homochiral coordination polymer in the crystalline solid state, confirming that, even in the ab-

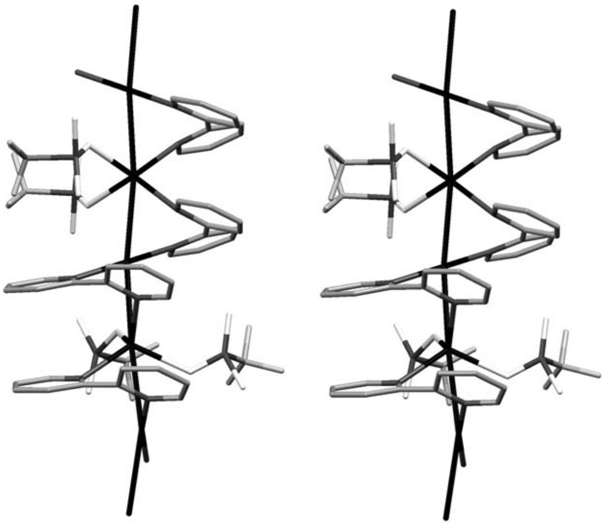


Figure 20. Helices showing the full coordination sphere of the Ag^I ions along the b axis of the $[Ag(L^9)(OTf)]$ complex.[75]

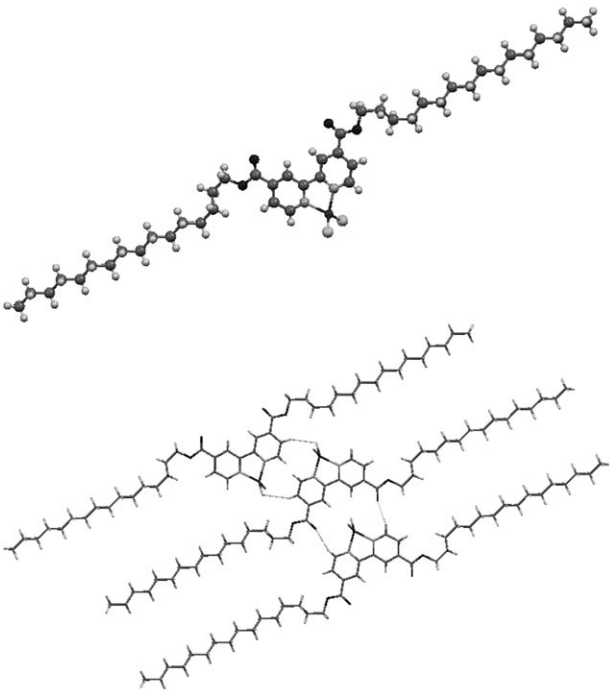


Figure 21. Ball and stick representation of the crystal packing of complex $[Zn(L^4)Cl_2]$ viewed along the b axis (top) and separate view (bottom) showing the C−H···X (X = Cl, O) intermolecular contacts. Color codes: oxygen and zinc atoms (black), other atoms (grey).

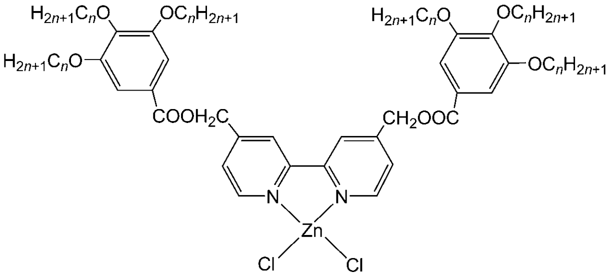
sence of chiral sources, these silver(I) compounds provide homochirality based on their same metallosupramolecular architecture.

This is true also for the L^4 derivative that, despite the differences in the coordination sphere and in the single molecular structure with respect to the perchlorato derivative, shows a self-assembled supramolecular arrangement responsible for the liquid-crystalline properties with lamello-columnar phase organization.[75]

Zinc(II) complexes: Zinc(II) complexes are widely applied in OLED technology[76] for their electron-transporting ability, light-emitting efficiency, high thermal and redox stability, and tunable electronic properties, but only very few examples of mesomorphic zinc(II) derivatives were reported up to 2004,[77] the tetrahedral geometry being thought to prevent mesophase formation.[78]

However, the design of zinc(II) derivatives showing at the same time order and mobility able to help the molecular organization to change in reply to any external stimuli, proper of liquid-crystalline systems, could further develop their applications. In this light, starting from the rodlike L^3–L^5 ligands, we prepared the corresponding tetra-branched $[Zn(L^n)Cl_2]$ ($n = 3$–5) derivatives with tetrahedral geometry (Figure 21), the intermolecular interactions of which (such as hydrogen bonds and π–π contacts) are too strong to induce mesomorphic behavior.[79]

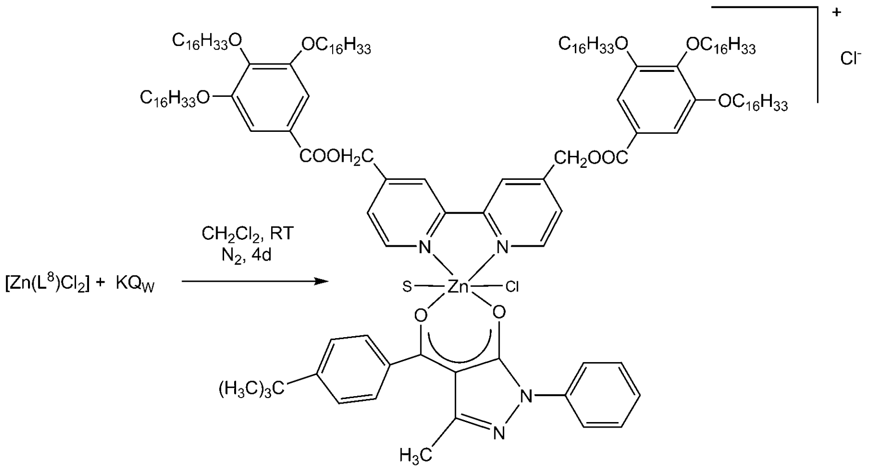
The change of the nature of the substituents of the N,N-ligands was fundamental for inducing the appearance of mesomorphism in these systems. Indeed by using the hemidisk ligands L^7 and L^8, the presence of two further aromatic rings, fully surrounded by long terminal tails, enables the formation of the liquid-crystalline state, driven by the segregation of the incompatible molecular segments into distinct regions, in the corresponding complexes. Therefore, for $[Zn(L^n)Cl_2]$ ($n = 7$, 8) complexes, a hexagonal columnar mesomorphism is induced through the self-organization of the single molecules, regardless their rigid central core and the tetrahedral geometry around the metal ion.[67]



$[L^7ZnCl_2]$ Cr 46.2 Col$_{h1}$ 122.6 Col$_{h2}$ 132.1 Iso
$[L^8ZnCl_2]$ Cr 58.5 Cr' 90.6 Col$_h$ 111.4 Iso

The mesomorphism is retained also after introduction of an efficient and versatile chelating β-diketonate such as a 4-acyl-5-pyrazolone (HQw), which replaces two chlorine groups (Scheme 4). The optical, thermal, and structural studies performed on the $[Zn(L^8)(Qw)Cl]$ revealed that the hexagonal mesomorphism showed by the Zn^{II} precursor not only is retained, but with a significant decrease in the transition temperatures.

Several attempts for adding a further unit of diketonate ligand around the Zn(II) ion gave rise to the recovery of only the $[Zn(Qw)_2]$ homoleptic complex, suggesting a labile



Scheme 4.

coordination of the main bipyridine ligand around the zinc(II) center with respect to the O,O-chelating ancillary ligand Qw. However, from preliminary synthetic works currently underway, the introduction of a more basic N,N-ligand such as a 4,7-disubstituted-1,10-phenantroline appears to be beneficial for the stability of the resulting system, and confirms the “ligand-dependence” of such systems in order to easily reach selected mesomorphic properties suitable for new applications.

Conclusion

In this work we have reviewed the very recent activities of the inorganic chemistry groups at the Universities of Camerino, Insubria, Padova, and Calabria, in the field of coordination complexes containing polytopic nitrogen ligands. Particular emphasis was given to the subtle variations in the structural and functional properties induced by small changes in reaction conditions or in the periphery of the organic portions and, in some cases, by exchanging, or mixing, the metal ions. This work has been performed under the umbrella of a wide National Project, with the aim of preparing, characterizing, and optimizing, hybrid metal–organic species of different functionality, such as molecular recognition, gas sorption and storage capability, mesomorphic behavior, luminescence, and so forth. The variety and abundance of the ligands employed, ranging from simple heterocyclic anions (e.g., pyrazolates), to resonance-assisted oxo-bearing pyrimidines (pyrimidinolates) and to 4,4-disubstituted-2,2′-bipyridines, together with the large set of transition-metal ions used as coordination centers, concur to the extreme versatility of these systems, as also witnessed by the (crystalline, polymeric or mesogenic) supramolecular arrangements.

Whether any of these materials can be successfully used in direct technological applications is not known, or unlikely, even if the remarkable gas sorption and selectivity of some of them have been recognized in an internationally granted patent, jointly deposited by the Universities of Granada, Milan, Insubria and CSIC Oviedo (PCT/ES 2006/000349). Nevertheless, the amount of chemical and structural information accumulated during these years has allowed the deep comprehension of the structure-directing properties of these systems; this has permitted us to prepare flexible polymers with larger cavities, based on bis-pyrazolyl spacers, which demonstrated specific surfaces exceeding 2000 $m^2 g^{-1}$, CO_2/CH_4, selectivity ratios well above 10:1 and, above all, easy and cheap synthetic methods.[80] Finally, it is worth noting that the cooperation among the different groups (in conjunction with external support when specific expertise was not locally available) has allowed the dissemination of less conventional analytical and structural characterization techniques (^{13}C CP-MAS NMR, ab-initio X-ray powder diffraction, in-situ X-ray thermodiffractometry, optical polarized microscopy, etc.) within the national chemistry community, as an inevitable fall-out of the research activities presented above. Not surprisingly, these techniques are now becoming part of modern chemical research laboratories, and are progressively introduced in the curricula of (under)-graduate chemistry and material science students.[81]

Acknowledgements

The results presented have benefited from significant financial support by MIUR (Project PRIN2006: Polimeri di Coordinazione con Proprietà Funzionali per l’Ottica Non-Lineare, il Magnetismo, la Catalisi Eterogenea ed il Riconoscimento Molecolare) and of other funding Agencies: Fondazione CARIPLO (Project 2007-5117), Valle Esina SPA. The authors are heartily indebted to many scientists and young collaborators who, through the years, have participated in the development of this ongoing project; their names and affiliations can be found in the cited references. Indeed, without their continuous support and specific skills, the scientific results discussed above would not have been possible to attain.

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[1] In recent literature CPs are often distinguished from the so-called metal organic frameworks (MOFs), the latter compounds being characterized by stronger coordination bonds than the former ones. In particular, MOFs, not possessing metal-unbound counterions, are normally neutral species in which di- or polytopic anionic linkers connect relatively distant metal ions or polynuclear assemblies (such as oxo- or hydroxo metal clusters). A very recent series of review papers on CPs and MOFs has appeared in the 2009 metal–organic frameworks special issue of the *Chem. Soc. Rev.* **2009**, *6*; classifications and definitions are detailed in: D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. -O’Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257–1283; see also K. Biradha, A. Ramanan, J. J. Vittal, *Cryst. Growth Des.* **2009**, *9*, 2969–2970; in this context, we decided to indicate the polymers here reported as CPs rather than MOFs, even

though, in most cases, it is possible to detect specific neutral triatomic secondary building units (SBUs) connected one to each-other through monocarboxylato linkers.

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Received: July 10, 2009