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Controlling the assembling/disassembling process of metal-containing superstructures

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Contents

Abstract

Processes in which the self-assembling/disassembling of transition metal containing supramolecular structures can be controlled are reviewed. A distinction is made on the basis of the property which switches on/off the self-assembling or disassembling event: both pH-driven and electrochemically-driven processes are presented, with particular attention to metal helicates. In the case of the electrochemically driven disassembling/self-assembling of copper helicates, the possibility of tuning the potential at which the processes take place is presented, together with the hysteresis-like behaviour of some systems, which discloses their possible use as molecular memories. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Assembling/disassembling process; Metal-containing superstructures; Metal helicates; Cu(II)/Cu(I) redox couple; Electrochemistry

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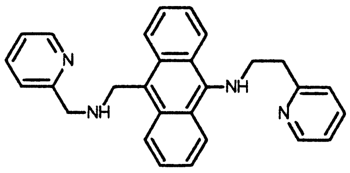
1. Transition metals working for molecular machines

The control of movement at the molecular level is currently one of the focal points of the research for the supramolecular chemist. Translocation of small (usually monoatomic) chemical entities inside or over a molecular system has been described, taking place in solution. In this case, the translocating species could be either an anion [1] or a cation [2], and the movement is controlled through a change of the electrochemical potential applied to the solution or through a drastic variation of the pH. The moving species, in the case of cation translocation, is preferably a transition metal cation, which can itself be the subject of a redox change which induces its movement between two coordinative sites of the molecular system (each one displaying a particular affinity towards one of the two metal oxidation states) [2a,b]; on the other hand, the translocating metal cation may remain in the same oxidation state if it is the ligand that changes the coordinative properties of one of its components, e.g. due to a variation of pH [2c]. However, what is more frequently pursued in this area is the movement of a large molecular fragment with respect to a larger molecular system, to which the fragment belongs and is permanently connected by means of a covalent bond or thanks to topological constraints. Rotaxanes [3], catenanes [4] and scorpionates [5] belong to these kind of systems, which also usually work in solution and are driven again by a change of the applied electrochemical potential or of the pH, and in some cases even by irradiation of light or by changing the solvent polarity. Transition metal cations play a central role in a significant number of systems of this kind: the change of the oxidation state of a coordinate metal cation is known to induce rotation in catenates [4] and ring sliding in rotaxanes [3d,e], while deprotonation of an amine-equipped side arm to attain coordination to a transition metal centre is the driving force for the movements in many scorpionate complexes [5a–c]. It is worth noting that further interest and curiosity on ‘molecular machines’ has been recently extended by considering them from the perspective of building chemical-based ‘wet’ or ‘dry’ computers [6]. A less futuristic use of the ideas behind molecular machines may reside also in the study and control of the rearrangement of large molecular systems between two ordered structures [7], e.g. in connection with the redox-driven processes of folding/unfolding of proteins [8]. The use of transition metal centres appears to be central, in the latter case. Although some work has appeared, in which an overall rearrangement took place in systems featuring several polydentate ligands on changing the oxidation state of coordinated metal centre(s) [9], more work has been done on the control of the self-assembling versus disassembling processes of superstructures like helical (or box-like) complexes of transition metals. In particular, it has been demonstrated that it is possible to have in solution the separate components of an architecturally complex structure, or to have them partially assembled in a simple form, and to make them assemble in the desired superstructure through variation of an applied or bulk parameter of the solution. Moreover, the assembling process is usually reversible, i.e. the reverse disassembling process is allowed on changing back the value of the applied or bulk parameter, so that the system can undergo a huge number of assembling/disassembling cycles without degradation. Finally, compared to the enormous amount of work done on the classical self-assembly processes, the study of the controlled self-assembling/disassembling of metal superstructures has only just begun.



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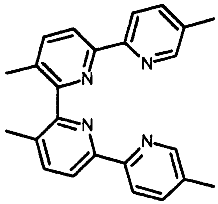

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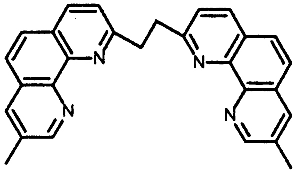

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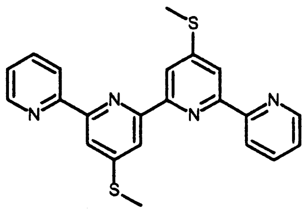

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2. pH-controlled self-assembling/disassembling of transition metal boxes

Transition metal cations display strong preferences towards certain coordination numbers and geometries, and thus are capable of directing the assembly of polydentate polytopic ligands into complicated architectures, including helices [10], boxes [11], squares [12], racks [13] and grids [14]. In the large majority of the published examples, the donor groups involved are nitrogen atoms, usually belonging to heterocycle systems. Due to their behaviour as bases, competition with protons may add complexity to systems made of nitrogen-containing ligands and metals, and this has kept almost all researchers interested in the synthesis of helicates or other superstructures away from protic (and in particular aqueous) solutions. Moreover, it must be stressed that metal cations may undergo hydrolytic processes in aqueous solution, which include the formation of mono- or poly-hydroxide complexes, in which, in the case of multimetal systems, the hydroxide anions may also play a bridging role. However, the experience of water-solution chemists may be useful to transform an apparently complicated situation to a very ordered one: once a metal/ligand stoichiometry is chosen, potentiometric titration experiments allow one to determine which species form in solution, what their stability constants are and, consequently, in which amount each species exists at a chosen pH value. From another viewpoint, this may allow the pH-control of the formation of a chosen species among many others or, alternatively, to have one species self-assemble upon variation of pH. Ligand **1** [15], made of two amino-pyridine bidentate halves separated by a rigid and flat spacer, anthracene, is soluble in aqueous solutions. Due to the enhanced lipophilicity of the anthracene group, **1** cannot be dissolved in pure water, and a two-component solution (1:4 v/v, water:dioxane) has to be used. However, also in this environment it is of course possible to measure pH and to perform classical potentiometric titration experiments. The geometry of **1** is such that it cannot fold and coordinate a single cation with its four nitrogens. Thus, if a 1:1 metal/ligand stoichiometry is chosen, with a metal cation like Cu^{2+}, which prefers coordination number 5, complex species of 2:2 stoichiometry are obtained, in which one copper cation is coordinated by two bidentate halves of two different ligands. Remarkably, these species exist only in restricted pH ranges, as potentiometric titrations have demonstrated. This is illustrated in the distribution diagram (% of species versus pH) for the system ligand **1**/Cu^{2+} (2:2 stoichiometry) (Fig. 1).

Significantly, before pH 2.5 no metal/ligand species exist, while at pH values lower than 4 some single-metal, partially protonated species begin to form: $[Cu(\mathbf{1})_2H]^{3+}$ and $[Cu(\mathbf{1})_2H_2]^{4+}$; on the other hand, dimeric, metal containing species $[Cu_2(\mathbf{1})_2]^{4+}$ and $[Cu_2(\mathbf{1})_2(OH)]^{3+}$ are the prevalent species at pH 7.1 and ≥ 10, respectively. Although an X-ray determined molecular structure is not available, molecular modelling calculations suggest that the two-ligand/two-metal structures are not of *helical* but of '*box-like*' nature, as sketched in Fig. 2 (form b; water molecules complete the coordination polyhedron at the copper centres; a very low log *K* for the formation of the OH^- containing complex from coordinated H_2O

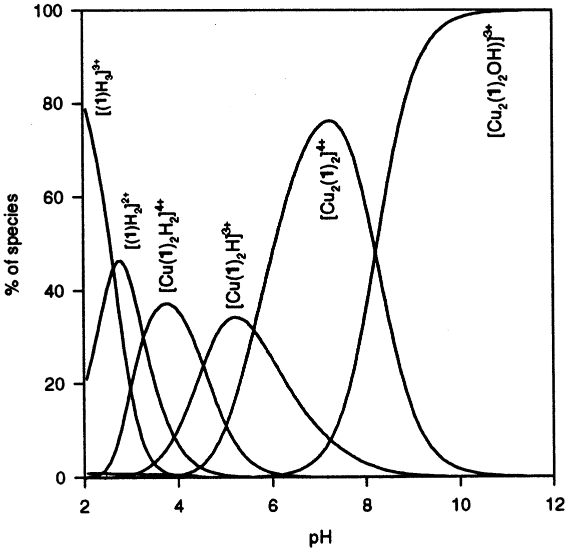


Fig. 1. Distribution diagram (% of species vs. pH) for the system **1**/Cu^{II} (ligand/metal ratio = 1:1) in 1:4 dioxane/water. The species pertinent to each curve are indicated in the figure.

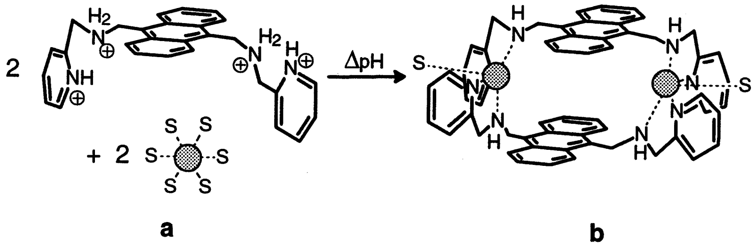


Fig. 2. Sketch of the pH-driven self-assembling process of the 'molecular box' $[Cu_2(\mathbf{1})_2]^{4+}$, on changing pH from 2 (form a) to 7.1 (form b). S represents solvent (water) molecules.

and geometrical considerations suggest that the hydroxide anion is not bridging the two metal centres in $[Cu_2(I)_2(OH)]^{3+}$).

In the perspective put forward by this review, changing the pH, e.g. from 2 to 7.1 induces the self-assembling of a box-like species from components which coexist in solution without interacting (Fig. 2, form a). A reverse change in pH will reversibly disassemble the structure.

3. Redox driven self-assembling/disassembling of transition metal helicates

In order to design systems capable of reversibly assembling (possibly into helicates) and disassembling under an electrochemical impulse, it seems convenient to use a metal centre which has two different oxidation states of comparable stability (when coordinated to some chosen ligands), with the two oxidation states displaying remarkably different geometric or coordination number preferences. Then, a polydentate ligand should be chosen fulfilling the following requirements: (i) the ligand is capable of fully satisfying the coordinative requirements of the metal in one of its oxidation states, thus forming monomeric complexes; (ii) two (or more) molecules of the ligand share only a part of their donor atoms to satisfy the coordinative requirements of the metal in its other oxidation state; (iii) the coordinative requirements of the metal in this second oxidation state should match the number and partition of the donor atoms in such a way that definite ligand/metal stoichiometry is obtained, with a closed structure. The metal of choice is copper, as its oxidation states I and II are known to form stable complexes with the same ligand in a number of cases, especially if it features sp^2 N or sp^3 S donors [16]. Moreover, while the d^{10} Cu^+ cation prefers coordination number 4, with a tetrahedral geometry, the d^9 Cu^{2+} cation chooses either coordination number 6, with strongly elongated tetragonal geometry, or coordination number 5, with square pyramidal or trigonal bipyramidal geometry. A methyl functionalized tetrapyridine ligand, **2**, has been demonstrated to have the correct features: it is able to coordinate a Cu^{2+} cation, arranging around it in a pseudo-square planar fashion [17], giving the molecular cation $[Cu^{II}(\mathbf{2})]^{2+}$ (see sketch a in Fig. 3; in the solid state an apical water molecule brings the coordination number to 5 and the geometry to

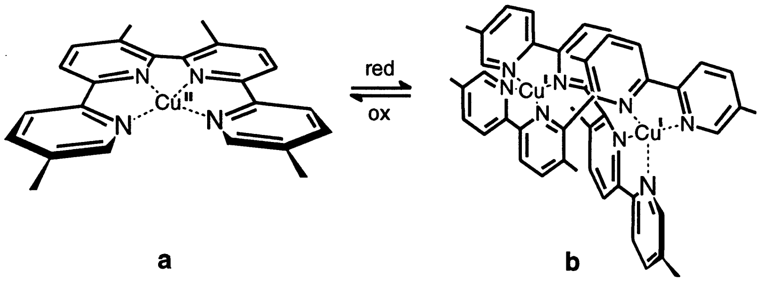
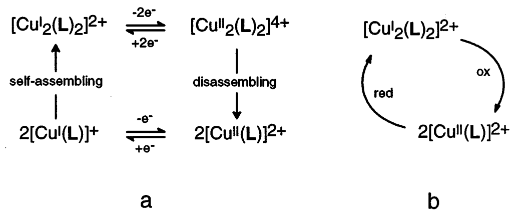


Fig. 3. Pictorial sketch of the electrochemically driven self-assembling/disassembling process involving ligand **2** and copper (1:1 ligand/metal ratio).

square pyramidal), whereas, for simple geometric reasons, it is not able to fold and coordinate a single Cu^+ cation in a tetrahedral fashion. Thus, two bipyridine halves of two different ligands coordinate one Cu^+ cation, while the remaining bipyridine halves coordinate a second cuprous cation. What is obtained is a closed $[Cu^I_2(\mathbf{2})_2]^{2+}$ molecular cation, which is of helical nature [18] (see sketch b in Fig. 3).

Spectroelectrochemical studies in acetonitrile solution indicate that the reduction of the monomeric Cu(II) molecular cation $[Cu^{II}(\mathbf{2})]^{2+}$ is irreversible, because it is followed by a fast dimerization to give $[Cu^I_2(\mathbf{2})_2]^{2+}$. On the time scale of a cyclic voltammetry experiment (run at 10–1000 mV s^{-1}) the reduction peak thus appear as irreversible, i.e. with no return wave. On the other hand, at potentials 500–600 mV higher than that at which reduction takes place, oxidation of $[Cu^I_2(\mathbf{2})_2]^{2+}$ is observed. Interestingly, oxidation is reversible and takes place in two steps, i.e. the mixed valence $[Cu^ICu^{II}(\mathbf{2})_2]^{3+}$ and the fully oxidized $[Cu^{II}_2(\mathbf{2})_2]^{4+}$ species are formed, which are stable and give rise to sharp return waves in the cyclic voltammetry experiment. However, in the $[Cu^{II}_2(\mathbf{2})_2]^{4+}$ species the Cu^{2+} cations are tetracoordinated with a pseudo-tetrahedral geometry and $[Cu^{II}_2(\mathbf{2})_2]^{4+}$ is not stable with respect to $[Cu^{II}(\mathbf{2})]^{2+}$, where Cu^{2+} is expected to reach a more favourable tetragonal coordination. According to this, a very slow $[Cu^{II}_2(\mathbf{2})_2]^{4+} \rightarrow 2[Cu^{II}(\mathbf{2})]^{2+}$ rearrangement takes place. An even slower interconversion between a dimeric, helical Cu(I) structure and a monomeric, pseudo-square planar Cu(II) form is found for the copper complexes of the bis-phenanthroline ligand **3** [19]. While the authors were able to isolate and structurally characterize the compounds containing both the $[Cu^I_2(\mathbf{3})_2]^{2+}$ and copper $[Cu^{II}(\mathbf{3})]^{2+}$ molecular cations, the CV experiments (in a number of solvents) disclosed quasi-reversible redox couples for complexes in both oxidation states, with $E_{1/2}$ values differing by ca. 500 mV: e.g. in acetonitrile, the $[Cu^I_2(\mathbf{3})_2]^{2+}$ complex undergoes a two-electron reversible oxidation, with $E_{1/2} =$ 640 mV versus SCE, while in the same solvent the $[Cu^{II}(\mathbf{3})]^{2+}$ complex undergoes a reversible one-electron reduction with $E_{1/2} = 190$ mV versus SCE. Thus, $[Cu^{II}(\mathbf{3})]^{2+}$ is reduced to $[Cu^I(\mathbf{3})]^+$, while $[Cu^I_2(\mathbf{3})_2]^{2+}$ is oxidized to $[Cu^{II}_2(\mathbf{3})_2]^{4+}$. The appearance in the voltammogram of $[Cu^I_2(\mathbf{3})_2]^{2+}$ of only a trace of the waves expected for $[Cu^{II}(\mathbf{3})]^{2+}$, and vice versa, indicates that the interconversions $2[Cu^I(\mathbf{3})]^+ \rightarrow [Cu^I_2(\mathbf{3})_2]^{2+}$ and $[Cu^{II}_2(\mathbf{3})_2]^{4+} \rightarrow 2[Cu^{II}(\mathbf{3})]^{2+}$ are slow, at least on the



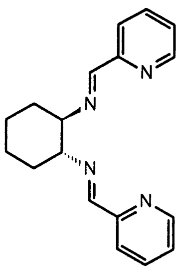
Scheme 1.

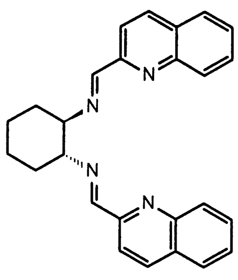
time scale of the sweep rate used (500 mV s^{-1}). Fast Cu(I) helical dimer-Cu(II) monomer interconversion has been found instead for complexes of ligand **4**: [Cu$^I_2$(**4**)$_2$]$^{2+}$ and [Cu$^{II}_2$(**4**)]$^{2+}$ display almost the same CV profile, with separated, irreversible two-electron oxidation and one-electron reduction waves ($\Delta E \cong 350$ mV) [20].

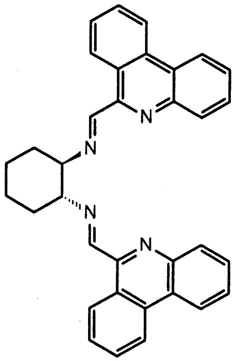
Interestingly, the authors report also a high speed voltammogram (4 kV s^{-1}) in which the return wave for the oxidation peak appears, while that for reduction one is lacking, and is still lacking at 20 kV s^{-1}. Scheme 1a describes the coupled electrochemical/chemical processes which holds for the assembling/disassembling motions of the Cu complexes of ligand **4**. However, due to the very fast nature of the chemical processes following the electrochemical ones, Scheme 1b better describes what happens during a CV experiment.

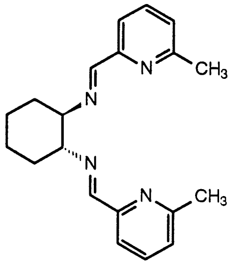
4. Modulating the assembling/disassembling potential

trans-1,2-Cyclohexanediamine appears as a particularly useful fragment to build ligands capable of behaviour similar to that of **1**–**4** when binding copper cations in oxidation state I or II. By a straightforward one-step Schiff reaction with nitrogen heterocycles bearing an aldehyde group in α position, ligands **5a**–**d** are obtained, which feature two imino-heterocycle bidentate halves, separated by the rigid *trans*-1,2-cyclohexanediyl spacer. The sp^2 nitrogen atoms are particularly indicated


5a


5b


5c



5d

to bind advantageously both Cu(II) and Cu(I), while the preorganized, rigid structure of the ligands allows the four donors to arrange around a single cation according to an almost square planar geometry, but not to fold and bind one cation in a tetrahedral fashion. This type of coordination requires that two ligands couple on two metal cations, forming dimeric (usually helical) structures.

Moreover, if a racemic mixture (*R*,*R* + *S*,*S*) of the starting 1,2-cyclohexane diamine is used for synthesis, a racemic mixture (*R*,*R* + *S*,*S*) of ligands **5a**–**d** is obtained, but the use of enantiomerically pure *R*,*R*- or *S*,*S*-1,2-cyclohexane diamine allows the synthesis of enantiomerically pure ligands, which, interestingly, even when uncomplexed follow a helical path (see Fig. 4 for ligand **5b**). The *R*,*R* ligands have an helical pattern of M handedness, while the *S*,*S* ligands are of P handedness [21].

The copper complexes of ligand **5b** have been thoroughly studied both in solution and in the solid state [22]. In this latter case, while the Cu(II) complex is monomeric and displays the expected square planar arrangement of the ligand (see Fig. 5; two $CF_3SO_3^-$ anions occupy the apical sites of a very elongated octahedron), surprisingly, three isomerical molecular cations have been found for the $[Cu^I_2(\mathbf{5b})_2]^{2+}$ complex, depending on the counter anion and on the crystallization solvent. In particular, a homochiral helical symmetric dimer has been found with $CF_3SO_3^-$ counter anions (Fig. 6a), while both a homochiral unsymmetrical helical and a heterochiral (i.e. with one *R*,*R* and one *S*,*S* ligand) box-like dimer co-exist in the same cell when the counter anion is ClO_4^- (Fig. 6b and c, respectively). However,

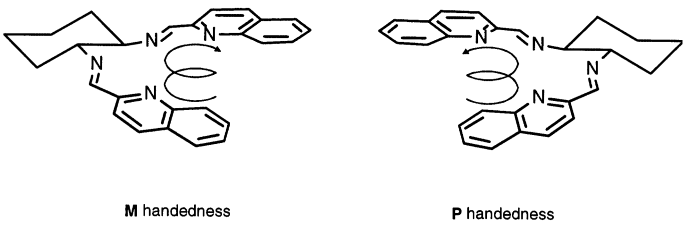


Fig. 4. Pictorial sketch of the 'natural preorientation' of the enantiomers of ligand **5b** along an helical path.

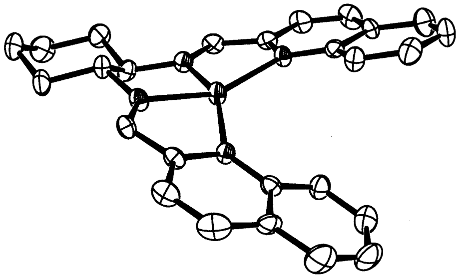


Fig. 5. ORTEP view of $[Cu^{II}(\mathbf{5b})](CF_3SO_3)_2$ with 30% probability displacement ellipsoids. The triflate anions have been omitted for clarity.

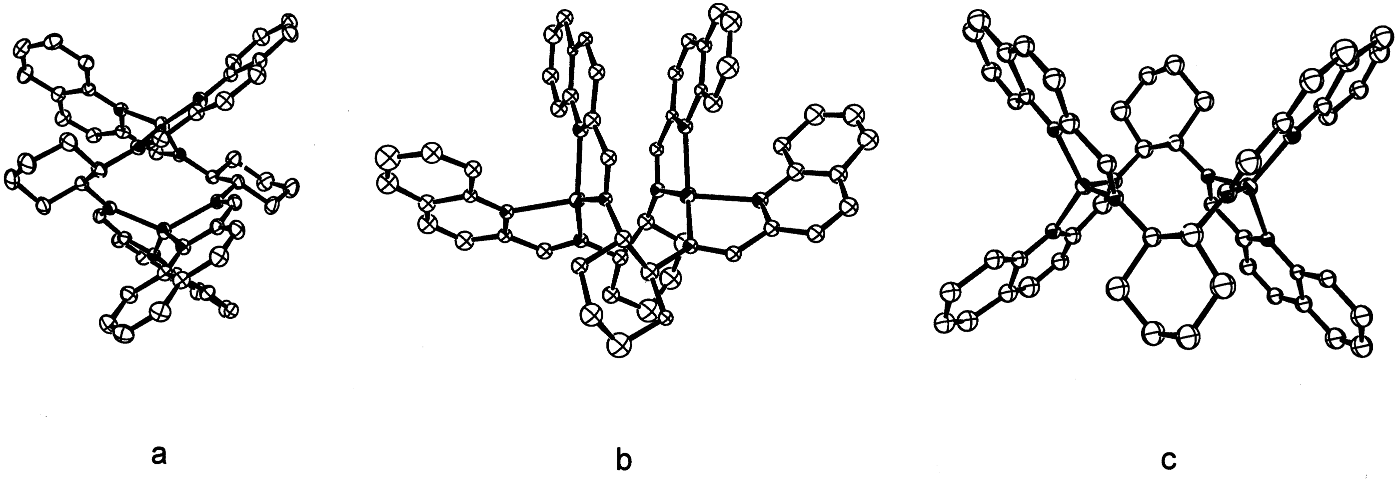


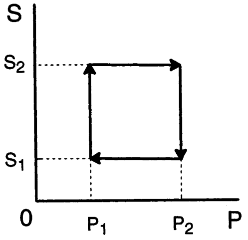
Fig. 6. ORTEP view of $[Cu^{I}_{2}(\mathbf{5b})_{2}](CF_{3}SO_{3})_{2}$ (a), $[Cu^{I}_{2}\mathbf{L}_{2}](ClO_{4})_{2}$ in the unsymmetric helical disposition (b), $[Cu^{I}_{2}\mathbf{L}_{2}](ClO_{4})_{2}$ in the non helical 'box-like' disposition (c). Displacement parameters are drawn at 20% probability level. Anions and solvent molecules have been omitted for clarity.

^{1}H-NMR studies demonstrate that these species easily interconvert, as in solution (CH_3CN), independently of the preparation procedure, the helical, symmetrical, form depicted in Fig. 6a is obtained as the prevailing species (reaching ca. 90% at room temperature). Interestingly, this species is homochiral, i.e. made of $R,R + R,R$ or $S,S + S,S$ ligand couples, due to the self-recognition capability of ligand **5b**, when binding Cu^+ cations.

The CV profiles of the Cu(II) and Cu(I) complexes of ligand **5b**, in acetonitrile solution, are identical. Fig. 7 shows the CV for the Cu(I) complex. Irreversible oxidation and reduction waves are observed, which have no return wave even at the fastest scan rate allowed by the instrumentation employed (20 V s^{-1}), indicating that the molecular disassembling and self-assembling processes are very fast ($\tau <$ 20ms), once the oxidation of $[Cu^I_2(\mathbf{5b})_2]^{2+}$ to $[Cu^{II}_2(\mathbf{5b})_2]^{4+}$ or the reduction of $[Cu^{II}(\mathbf{5b})]^{2+}$ to $[Cu^I(\mathbf{5b})]^+$processes, respectively, have taken place.

Thus, also in this case, Scheme 1b holds. The same behaviour is also displayed by the copper/ligand systems for **5a** and **5c–d** [23], and it is interesting to compare the potential at which irreversible oxidation and reduction (E_{red} and E_{ox}, respectively) take place. E_{red} is 50, 400, 425 and 319 mV versus SCE and E_{ox} 461, 1040, 955 and 810 mV versus SCE for **5a**, **5b**, **5c** and **5d**, respectively. This indicates that keeping the main framework fixed (*trans*-1,2-cyclohexanediyl spacer, imino-nitrogen heterocycle donors) on simply playing on the nature, substituent and dimensions of the two ligand's heterocycles it is possible to prepare a set of systems for which the potentials at which the assembling/disassembling processes take place can be tuned over a substantial range. Although bulkiness and shape play an important role, as a rule of thumb the more the heterocycle displays delocalization, the easier is the reduction and the more difficult is the oxidation, in connection with the increased stabilization that an extended π-system brings by back donation to the soft, d^{10}, Cu^+ cation. However, ΔE, the $E_{ox} - E_{red}$ difference, undergoes less pronounced variations, with a value of 411, 640, 530 and 491 mV along the **5a–d** series. A remarkable ΔE increase is obtained by changing the *trans*-1,2-cyclohexanediyl spacer with *cis*-1,2-cyclohexanediyl in ligand **5c**, which features the bulky phenantridine heterocycle: the different shape in which the ligand is preorganized brings both oxidation to a higher value ($E_{ox} = 1148$ mV versus SCE) and reduction to a lower one ($E_{red} = 184$ mV versus SCE), with respect to the *trans* isomers, so that a ΔE of 964 mV can be measured.

Regarding the reversibility of the assembling disassembling processes, even if the single electrochemical event is irreversible — as can be seen clearly by the missing return waves — that does not mean that the overall process is not reversible. As a matter of fact, as already noticed, electrochemical irreversibility of oxidation and reduction processes for **5a–d** comes from a fast chemical reaction following the electrochemical event. This is fully described by Scheme 1a, which belongs to the category of the electrochemical 'square schemes' [24], in which two EC (electrochemical followed by chemical) reactions combine. Since the system is authentically bistable, the assembling and disassembling chemical reactions do not decompose to any extent any of the components of the supramolecular system, i.e. metal and ligand.



Scheme 2.

As a consequence, the electrochemically driven reduction + self-assembling or oxidation + disassembling processes can be repeated at will: controlled potential coulometry (CPC) experiments, carried out in a cell jacketed to a quartz fiber optic probe connected to a spectrophotometer, allowed one to register the nice series of spectra diplayed in Fig. 8, which gives account of the transformation of a Cu(II) monomeric complex into the Cu(I) helical dimer for ligand **5b**, a transformation which is also optically perceivable, thanks to the change in colour of the solution from pale green (Cu(II) complex) to deep purple (Cu(I) complex). When 1 mol of electrons per mol of Cu(II) complex has passed through the cell, superimposable spectra are obtained: all the $[Cu^{II}(\mathbf{5b})]^{2+}$ complex has been reduced and it has self-assembled into the helical dimer $[Cu^{I}_2(\mathbf{5b})_2]^{2+}$, whose authentic spectrum is indeed obtained at this stage of the experiment. On changing the potential up to values higher than E_{ox} for $[Cu^{I}_2(\mathbf{5b})_2]^{2+}$, the spectra change in the reverse sequence: when another mol of electrons per mol of Cu(I) has passed through the cell, the oxidation + disassembling process is complete, and the spectrum of authentic $[Cu^{II}(\mathbf{5b})]^{2+}$ is obtained again. The cycle can be repeated ad libitum.

5. Storing information in solution

As a general requirement, a substance capable of storing information must be bistable and display hysteresis under the application of an external field of variable intensity. In other words, the chosen substance must be able to exist in two different states (S_1 and S_2), changing one into the other on variation of the value of an external parameter, P, and there must exist a range of values of P in which the substance can be found either in state S_1 or S_2, depending on the 'history' of the system. This is shown schematically in Scheme 2.

However this is not sufficient, as some property of the substance must assume dramatically different values in the S_1 and S_2 states, let's say 0 and 1: this property represents the information and, moreover, it must also be someway *readable*. Quite interestingly, the systems made of ligands **5a–d** (or by their analogues featuring the *cis*-cyclohexanediyl spacer) and the Cu(I)/Cu(II) couple (i) are bistable; (ii) display electrochemical profiles with hysteresis; (iii) have remarkably different absorption spectra in the visible zone. Both solid compounds and acetonitrile solutions of Cu(I) *and* Cu(II) complexes of the same ligand are easily handable and are air and moisture stable. The electrochemical CV profiles measured on the Cu(I) or Cu(II) complexes of the same ligand are superimposable and have the features of an hysteresis cycle: as an example the electrochemical profile reported in Fig. 7 shows that the system made of ligand **5b** and of Cu(I)/Cu(II) may exist, in the 400–1050 mV versus SCE range, either as $[Cu^{I}_{2}(\mathbf{5b})_2]^{2+}$ or $[Cu^{II}(\mathbf{5b})]^{2+}$, depending on the

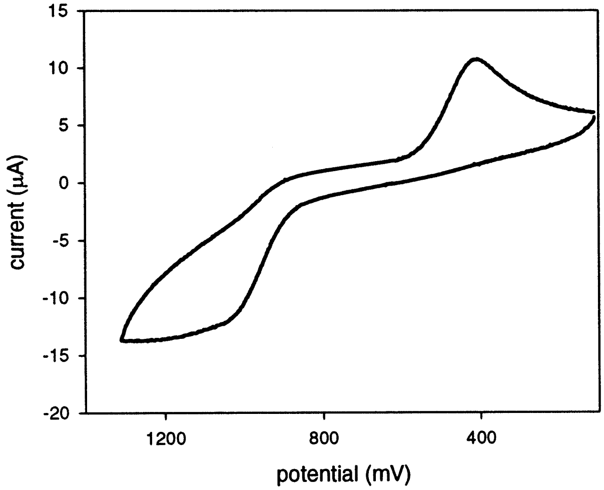


Fig. 7. CV profile for $[Cu^{I}_{2}(\mathbf{5b})_2](CF_3SO_3)_2$, in acetonitrile, 10^{-3} M, scan rate 200 mV s^{-1}. Potentials are referred to the saturated calomel electrode.

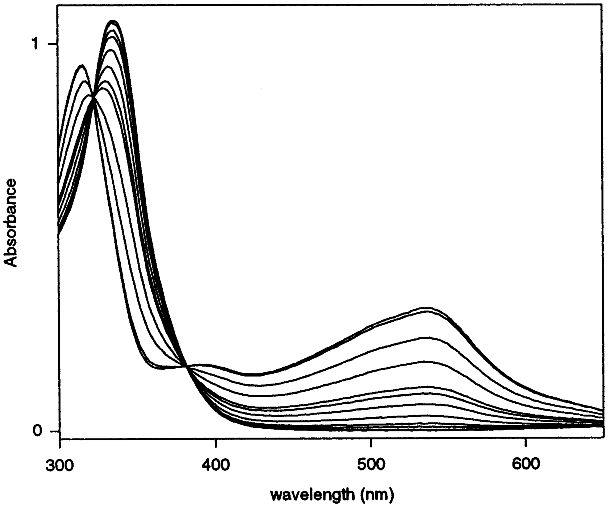


Fig. 8. Series of spectra obtained in the course of the electrochemical reduction + self-assembling of $2[Cu^{II}(\mathbf{5b})]^{2+}$ into $[Cu^{I}_{2}(\mathbf{5b})_2)]^{2+}$. Bands at 536 and 320 nm increase their intensities, while the band at 370 nm decreases it.

electrochemical history of the system. Moreover, this electrochemical hysteresis profile features a 'sense of rotation': the Cu(I) dimer can be transformed into the Cu(II) monomer only on increasing the potential over 1050 mV versus SCE and no effect is obviously obtained on lowering the potential below 400 mV, while a Cu(II) monomer can be transformed into the Cu(I) dimer only upon lowering the potential below 400 mV versus SCE, and nothing obviously happens if the potential is raised over 1050 mV (the electrochemical hysteresis cycle thus works clockwise). Finally, in the visible range, Cu(I) helical dimeric complexes display intense MLCT bands ($\varepsilon = 5000-12000$ m^{-1} cm^{-1}), centred at 468, 536, 558 and 476 nm along the **5a–d** series (with a predictable energy lowering on increasing the dimension of the π-delocalized system), while the Cu(II) complexes have no bands in the 400–600 nm range and display only modest d–d absorptions ($\varepsilon < 200$ m^{-1} cm^{-1}) at wavelengths > 650 nm. According to this, in a solution containing e.g. $[\mathrm{Cu^{II}}(\mathbf{5b})]^{2+}$, information can be written by lowering the applied potential below 400 mV versus SCE: $[\mathrm{Cu_2^{I}}(\mathbf{5b})_2]^{2+}$ is obtained, which displays an intense colour and represents a bit value 1 that can be read, as an example, through a spectrophotometer (which reads an intense absorption at 536 nm). This bit value is maintained if no potential is applied to the solution or if any potential is applied lower than 1050 mV versus SCE. When a potential higher than 1050 mV versus SCE is instead applied, the information is erased, as the $[\mathrm{Cu_2^{I}}(\mathbf{5b})_2]^{2+}$ helical dimer is transformed into the $[\mathrm{Cu^{II}}(\mathbf{5b})]^{2+}$ monomer, which is not coloured, thus representing a bit value of 0, that can be read by a spectrophotometer (which finds now no absorption at 536 nm). Quite interestingly, the portion of the solution capable of working in the described way could be scaled down, at least in principle, to a volume containing only a single $[\mathrm{Cu_2^{I}}(\mathbf{5b})_2]^{2+}$ molecule, thus offering a further interesting example of molecular hysteresis [25]. Although in a quite fanciful and optimistic view, the copper complexes of ligands **5a–d** can thus represent a possible way for storing information for the chemical 'wet computers', and, in this perspective, they offer the advantage of fast information storage, stability and the possibility of tuning both the write/erase potential and the wavelength at which the information can be read.

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