

Transition metal-complexed catenanes and rotaxanes as molecular machine prototypes†

Jean-Pierre Sauvage

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Transition metal-containing catenanes and rotaxanes are ideally suited to build molecular machines and motors; in the present review article, three examples from our group are discussed which consist of (i) a fast-moving electrochemically-driven pirouetting machine, (ii) a linear rotaxane dimer whose behaviour is reminiscent of muscles, in the sense that it can be stretched or contracted and (iii) a light-driven machine consisting of a catenane constructed around a ruthenium(II) centre.

Molecular chemists are used to looking at their compounds as dynamic species. Processes such as the chair/boat equilibrium of cyclohexane or nitrogen inversion in amines have been studied for decades and are now in all the organic chemistry textbooks. Very different and much more recent is the elaboration and the study of molecular systems in which motion can be triggered and controlled at will by the intervention of an external signal. The molecules then behave like “molecular machines” or, at least, their prototypes. This field has experienced spectacular development in the course of the last decade and books have even been published on this new area of research.¹

The field of catenanes and rotaxanes² is particularly important in relation to molecular machines. Promising systems have been proposed which are based on redox reactions involving, in particular, formation or dissociation of organic acceptor–donor complexes³ or of transition metal complexes,⁴ photochemical reactions (isomerisation of $N=N^5$), photoinduced electron transfer^{6–8} or protonation/deprotonation, leading to dissociation and/or formation of given subcomplexes within a multicomponent structure.⁹ Our group has been particularly interested in copper and, more recently, ruthenium(II)-containing interlocking or threaded ring systems.¹⁰ The compounds can be set in motion using either an electrochemical signal, a chemical reaction or a photochemical process.

1. An electrochemically driven machine based on a copper-complexed rotaxane: pirouetting of the ring on the millisecond time scale¹¹

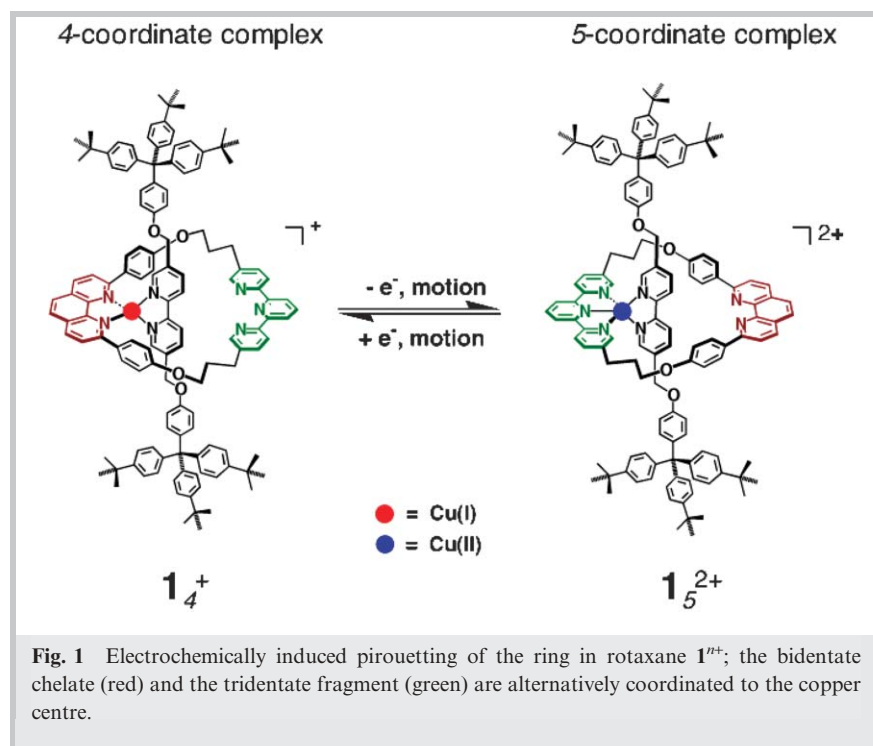
The rate of the motion in artificial molecular machines and motors is an important factor. Depending on the nature of the movement, it can range from microseconds, as in the case of organic rotaxanes acting as light-driven molecular shuttles,⁸ to seconds or even minutes in other systems involving threading–unthreading reactions¹² or metal-centred redox processes based on the Cu(II)/Cu(I) couple.⁴

In order to obtain increased rates of the motion, a new rotaxane in which the metal centre is as accessible as possible was prepared. The 2,9-disubstituted 1,10-phenanthroline ligand of the axis, in the previous systems,⁴ was replaced by a bipy chelate, which is at the same time thinner and less sterically hindering than the phenanthroline, since it does not bear substituents close to the metal centre. Ligand exchange within the coordination sphere of the metal is thus facilitated as much as possible. The two forms of the new bistable rotaxane, 1_4^+ and 1_5^{2+} , are depicted in Fig. 1 (the subscripts 4 and 5 indicate the coordination number of the copper centre). The molecular axis contains a “thin” 2,2′-bipyridine motif, which is less bulky than a 1,10-phenanthroline fragment and thus is expected to spin more readily within the cavity of the

† This article is dedicated to the memory of a good friend, Bernard Dietrich.

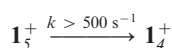


Jean-Pierre Sauvage is a CNRS director of research. His current interests span from models of the photosynthetic reaction centre, using transition metal complexes and porphyrins, to topology (catenanes and knots) and molecular machines and motors. He is a member of the French Academy of Sciences

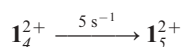


ring. In addition, the bipy chelate does not bear substituents in the α -position to the nitrogen atoms.

1_4^+ rearranges to the 5-coordinate species 1_5^{2+} after oxidation and *vice versa*. The electrochemically driven motions were studied by cyclic voltammetry (CV). A lower limit for the rate constant k of the process can be estimated as $>500 \text{ s}^{-1}$ or ($\tau < 2 \text{ ms}$, with $\tau = k^{-1}$).



The rearrangement rate for the 4-coordinate Cu(II) complex is smaller than for the monovalent complex. It is nevertheless several orders of magnitude larger than in related catenanes or rotaxanes with more encumbering ligands:

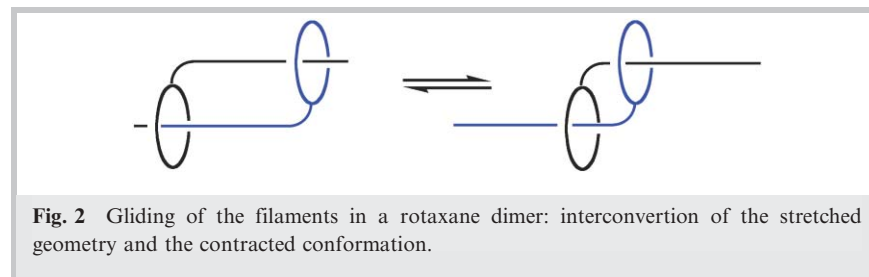


This first example shows that subtle structural factors can have a very significant influence on the general behaviour (rate of the movement, in particular) of copper(II/I)-based molecular machines. Further modifications will certainly lead to new systems with even shorter response times.

2. Use of a chemical reaction to induce the contraction/stretching process of a muscle-like rotaxane dimer¹³

Linear machines and motors are essential in many biological processes such as, in particular, contraction and stretching of the skeletal muscles. In relation to “artificial muscles”, one-dimensional molecular assemblies able to undergo stretching and contraction motions represent thus an exciting target.

A multicomponent system able to contract or stretch under the action of an external chemical signal was designed and made in our group a few years ago. The system is based on a symmetrical doubly threaded topology as represented in Fig. 2. The motion is easy to visualize: both “strings” (mimicking the myosin-containing thick filament and the actin thin filament of the striated muscle)

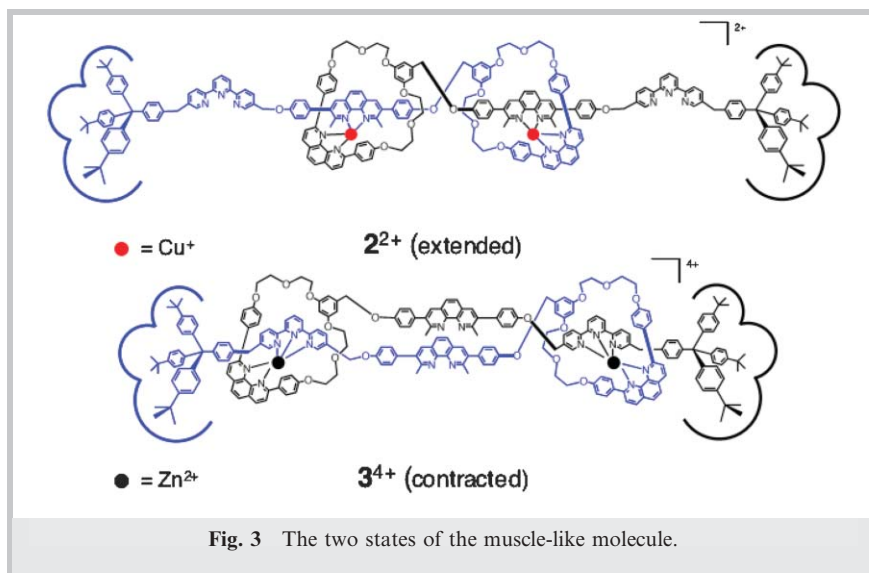


move along one another but stay together thanks to the rotaxane nature of the system.

The copper-complexed rotaxane dimer 2^{2+} was synthesized (more than 20 steps from commercially available compounds). As shown in Fig. 3, each “filament” contains both a bidentate chelate (coordinated to copper(I) in compound 2^{2+}) and a tridentate chelate of the terpy type, which is free in the copper(I) complex 2^{2+} . The rotaxane dimer was set in motion by exchanging the complexed metal centres. The free ligand, obtained in quantitative yield by reacting the 4-coordinate copper(I) complex 2^{2+} (stretched geometry) with an excess of KCN, was subsequently remetalated with $\text{Zn}(\text{NO}_3)_2$ affording quantitatively the 5-coordinate Zn^{2+} complex 3^{4+} in the contracted situation (Fig. 3). The reverse motion, leading back to the extended situation 2^{2+} , could be easily induced upon addition of excess $\text{Cu}(\text{CH}_3\text{CN})_4^+$. From CPK model estimations, the length of the organic backbone changes from 85 to 65 Å between both situations.

3. Photoinduced decoordination and thermal recoordination of a ring in a ruthenium(II)-containing [2]catenane

Photonic stimuli are particularly promising.^{1,5-8} Our group has recently described multicomponent ruthenium(II) complexes in which one part of the molecule can be set in motion photochemically.^{14,15} In these systems, the light-driven motions are based on the formation of dissociative excited states. Complexes of the $[\text{Ru}(\text{diimine})_3]^{2+}$ family are particularly well adapted to this approach. If distortion of the coordination octahedron is sufficient to significantly decrease the ligand field, which



can be realized by using one or several sterically hindering ligands, the strongly dissociative ligand-field state ($^3d-d^*$ state) can be efficiently populated from the metal-to-ligand charge transfer (3MLCT) state to result in expulsion of a given ligand. The principle of the whole process is represented in Fig. 4.

The [2]catenanes **4** and **5** of Fig. 5 were synthesized¹⁶ by using an octahedral ruthenium(II) centre as template. Compound **4** consists of a 50-membered ring which incorporates two 1,10-phenanthroline (phen) units and a 42-membered ring which contains the

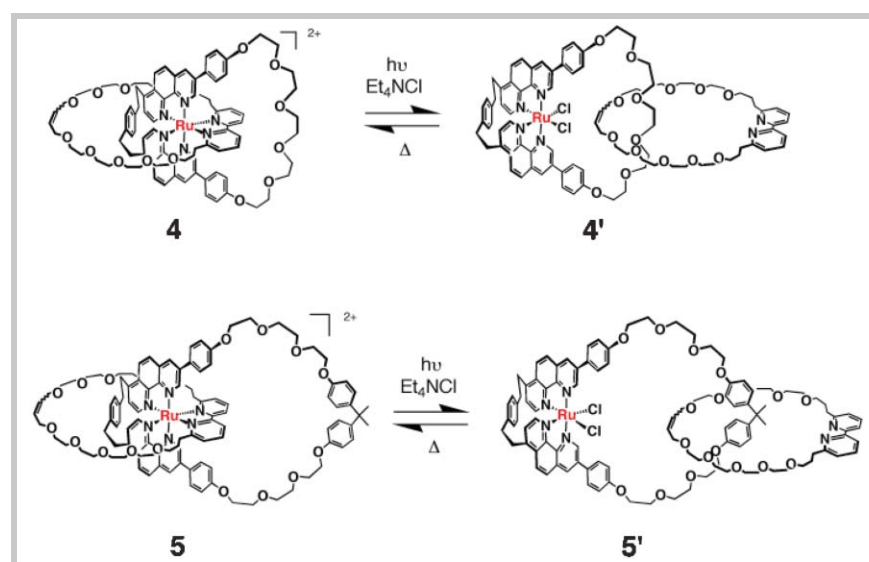
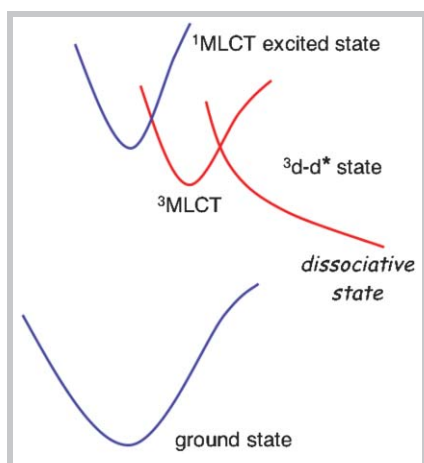
2,2'-bipyridine (bipy) chelate. Compound **5** contains the same bipy-incorporating ring as **4**, but the other ring is a 63-membered ring. The light-induced motion and the thermal back reaction carried out with **4** or **5** are represented in Fig. 5. They are both quantitative, as shown by UV/Vis measurements and by 1H NMR spectroscopy.

Catenanes **4'** and **5'** contain two disconnected rings since the photochemical reaction leads to decomplexation of the bipy chelate from the ruthenium(II) centre. In a typical reaction, a degassed CH_2Cl_2 solution of **5** and $NEt_4^+.Cl^-$ was irradiated with visible light, at room

temperature. The colour of the solution rapidly changed from red (**5**: $\lambda_{max} = 458$ nm) to purple (**5'**: $\lambda_{max} = 561$ nm) and after a few minutes the reaction was complete. The recoordination reaction $5' \rightarrow 5$ was carried out by heating a solution of **5'**. The quantum yield for the photochemical reaction $5 \rightarrow 5'$ at 25 °C and $\lambda = 470$ nm (± 50 nm) can be very roughly estimated as 0.014 ± 0.005 . One of the weak points of the present system is certainly the limited control over the shape of the photoproduct since the decomplexed ring can occupy several positions. It is hoped that, in the future, an additional tuneable interaction between the two rings of the present catenanes will allow better control over the geometry of the whole system. In parallel, two-colour machines will be elaborated, for which both motions will be driven by photonic signal operating at different wavelengths.

Prospective view

What are the motivations of the researchers involved in the field of artificial molecular machines and motors? The most important one to many groups, including ours, is certainly the synthetic challenge that the elaboration of such systems represents. It is indeed very challenging to reproduce some of the simplest functions of the natural biological



motors (motor proteins, DNA polymerase, bacterial flagella, *etc.*) using synthetic molecular systems. It must nevertheless be kept in mind that the presently accessible molecular machines and motors are **extremely primitive** compared to the beautiful and exceedingly complex molecular machines of Nature.

As far as practical applications are concerned, several possibilities can be explored, although technological applications are probably not for tomorrow. Information storage and processing at the molecular level is for the moment the most popular field of application since the spectacular reports of Heath, Stoddart and their coworkers.¹⁷ Other ambitious and futuristic practical outcomes could be considered such as the fabrication of useful nanoscale molecular devices able to perform various functions: transport molecules or ions through a membrane, sort different molecules, store energy, *etc.* There are many functions that nano-mechanical devices should be able to fulfil in the future. In medicinal chemistry it is conceivable that such devices could carry a given drug to a specific target where it is needed, open or close a gate or a valve which controls delivery of a drug from a micro-device, and act as a nano-syringe able to inject a given molecule inside a cell.

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Jean-Pierre Sauvage

Laboratoire de Chimie Organo-Minérale,
UMR 7513 du CNRS, Institut Le Bel,
Université Louis Pasteur, 4 rue Blaise Pascal,
67000, Strasbourg Cedex, France

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