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Magnetism: A Supramolecular Function

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PREFACE

This book arises from the NATO Advanced Research Workshop which took place in Carcans Maubuisson (France) on September 16 - 20, 1995.

The basic idea which gave rise to this workshop is that supramolecular chemistry on the one hand, and molecular magnetism on the other hand have developed in the last few years as disjoint disciplines which essentially ignore each other. Such a situation is surprising, and actually not satisfying. The heart of molecular magnetism concerns the design and the synthesis of new molecular assemblies exhibiting bulk properties such as long-range magnetic ordering or bistability. In this context, molecular magnetism may be considered as the facet of supramolecular chemistry dealing with open-shell units. In other respects, most of supramolecular chemists work with closed-shell units. When they exceptionally handle chemical groups carrying unpaired electrons, they usually do not care about the physics associated with these electrons. There is, therefore, an obvious complementarity between those two disciplines. The main goal of this workshop was to explore this complementary further, to allow the two communities to know each other, and eventually to interact.

We are convinced that much may be expected from the cross-fertilization of the two disciplines. The laws discovered by supramolecular chemists to assemble molecular units in a perfectly controlled manner may be of the utmost importance to the colleagues focusing on the design of molecular assemblies exhibiting bulk magnetic properties. In a similar way, the incorporation of open-shell units in supramolecular assemblies should lead to appealing systems, with possibly quite new physical properties. To investigate this physics at the molecular or mesoscopic scale, the collaboration with physicists is essential. We are pleased that quite a few colleagues belonging to the physics community also participated to the workshop.

This book contains thirty contributions which are gathered as follows : The first eight contributions present the state-of-the-art in organic supramolecular chemistry. The main emphasis concerns the interlocked systems, such as catenanes and rotaxanes, as well as the molecular trees or dendrimers. The following six contributions are devoted to molecular materials

constructed from organic radicals or from both organic radicals and transition-metal containing units. Several brand new molecular-based magnets entering in this category are described. Then, six contributions focus on the various facets of molecular bistability. The most extensively investigated example of molecular bistability is probably the phenomenon of spin transition. Other very interesting kinds of molecular bistability are also introduced. Afterwards, six contributions are essentially devoted to metal-organic and coordination magnetic materials. Several new trends in inorganic supramolecular chemistry are introduced here, and a series of new molecular-based compounds exhibiting a spontaneous magnetization are reported. The last contribution deals with a new approach of nano-sized metal particles.

Molecular magnetism is essentially an interdisciplinary area of research, meeting together organic, organometallic and inorganic chemists, as well as theoreticians, physicists, and material science and life science people. The content of this book reflects both this diversity and this complementarity. It also allows to understand why molecular magnetism has developed so tremendously in the last decade. Indeed, it shows that this field of research combines the eastitic appeal of supramolecular chemistry and the excitement of a new physics.

Olivier Kahn

ROTAXANES AND CATENANES IN ACTION

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ABSTRACT. Not only are rotaxanes and catenanes aesthetically and topologically attractive molecules, but they can also be used as functional systems, able to undergo electronic and molecular motions under the action of an external stimulus. Porphyrin-stoppered rotaxanes are functional models of the photosynthetic Reaction Centre, leading to ultrafast interporphyrin electron transfer under light irradiation. Interestingly, the efficiency of the process strongly relies on the rotaxane nature of the compound, being mostly determined by the properties of the central transition metal complex. Different is the function of a non-symmetrical copper catenate, consisting of a two-coordination site ring interlocked to a one-chelate incorporating cycle. The oxidation state of the copper centre (I or II) entirely determines the set of ligands coordinated to the metal. Oxidizing or reducing the central copper atom thus induces a complete gliding motion of one cycle within the other. This process can be regarded as electrochemically triggered swinging of the copper catenate.

1. Introduction

Until now, topologically fascinating molecules like rotaxanes, catenanes and knots [1,2] have mostly been regarded as static species, although interesting examples of molecular systems undergoing motions have recently been reported [3-5]. We will now discuss two types of compounds undergoing controlled electron transfer (ET) or real molecular motions under the action of an external perturbation such as light excitation or electrochemical signal.

2. Ultrafast Electron Transfer Within a Bis-Porphyrin Stoppered Rotaxane

In order to mimic some of the essential features of the photosynthetic Reaction Centre [6] (RC) and, with the purpose of studying long-range ET processes within large molecular systems of controlled geometry, *rotaxanes* bearing porphyrinic stoppers have been prepared [7] and studied [8]. We have in particular concentrated on modelling the primary ET step between tetrapyrrolic units (bacteriochlorophyll of the special pair, acting as an electron donor in its singlet excited state, to bacteriopheophytin) which occurs within 3 ps

in the RC complex [9], despite the 17 Å centre-to-centre separation. The two bis-porphyrin compounds first investigated are represented in Figure 1.

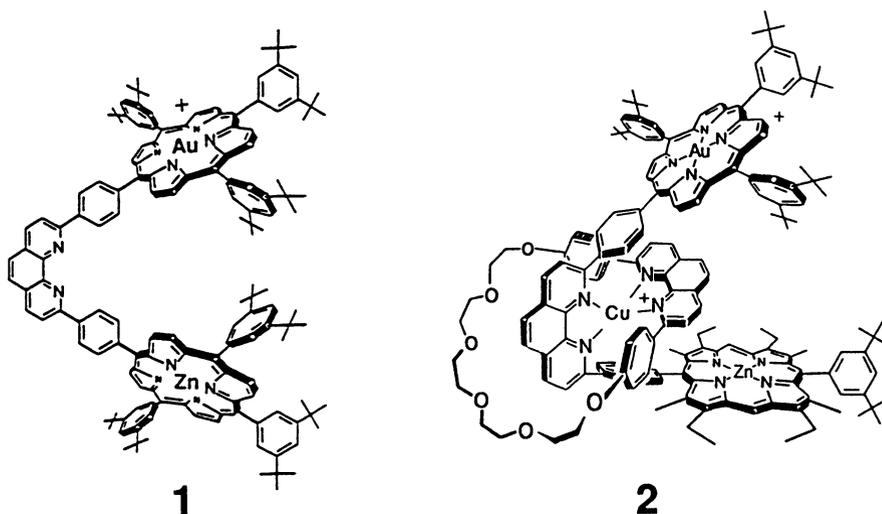


Figure 1.

Zinc(II) and gold(III) porphyrins have been selected as electron donor and acceptor, respectively, and represent acceptable models for the bacteriochlorophyll special pair (primary donor) and bacteriopheophytin (primary acceptor) of the bacterial photosynthetic RC. Compound **1** (Figure 1) is obtained in multistep procedure, by applying relatively conventional porphyrin synthesis methodology to 1,10-phenanthroline (phen) derivatives, followed by controlled metalation of the corresponding free-base bis-porphyrin precursor [10]. The rotaxane **2** (Figure 1) is also prepared in a multistep procedure [7]. Threading of an open-chain fragment bearing one porphyrin at one end into a coordinating ring is first accomplished, followed by the construction of the second porphyrin [7]. The synthesis of the rotaxane with, in particular, the crucial gathering and threading step, relies on the templating rôle of copper(I), able to collect and orient two bidentate chelates in its coordination sphere. The centre-to-centre distance for both compounds **1** and **2** is close to 13.5 Å. (17 Å for the RC).

Laser flash photolysis studies carried out with **1** in CH₃CN solution at 25°C show that ET from the singlet excited state of the zinc porphyrin to the gold(III) porphyrin takes place in ca. 55 ps, compared to ca. 3 ps for the corresponding process in the RC. The electron transfer rate in **1** is thus surprisingly slow if the process involves superexchange with the aromatic spacer (phen=1,10-phenanthroline). It was anticipated that, by constructing rotaxanes such as **2**, the presence of a central metal (Cu(I)) coordinated to the spacer (phen) would strongly influence the energy level of the LUMO and the HOMO orbitals of the bridge. It would thus allow to modulate the superexchange properties of the spacer and consequently provide control over ET rate. This is indeed what was observed. Following selective excitation into the zinc(II) porphyrin subunit of **2**, the radical pair was formed in ca. 1 ps. The 55-fold increase in the rate of ET for **2** relative to the corresponding bis-porphyrin **1** is entirely consistent with a superexchange mechanism. The molecular orbitals localized on the bridge (phen for **1** or copper(I) complex for **2**) are energetically much more favorably disposed in **2** than in **1** to accelerate ET via superexchange between the donor (zinc porphyrin) and the acceptor (gold(III) porphyrin).

The drastic effect of the central copper(I) complex on ET rate between the donor and the acceptor in **2** is reminiscent of the probable rôle played by the accessory bacteriochlorophyll in the RC and also assumed to facilitate electron transfer between the primary donor and the primary acceptor [12].

In order to confirm the importance of the electronic properties of the spacer onto ET rate, compounds derived from **2** were prepared and their ET properties were investigated and compared to those of **1** and **2**. The copper(I) rotaxane **2** was first demetalated, leading to the free rotaxane **3**. This compound was subsequently recomplexed with zinc(II), to afford the zinc(II) rotaxane **4**. The series of reactions is shown in Figure 2.

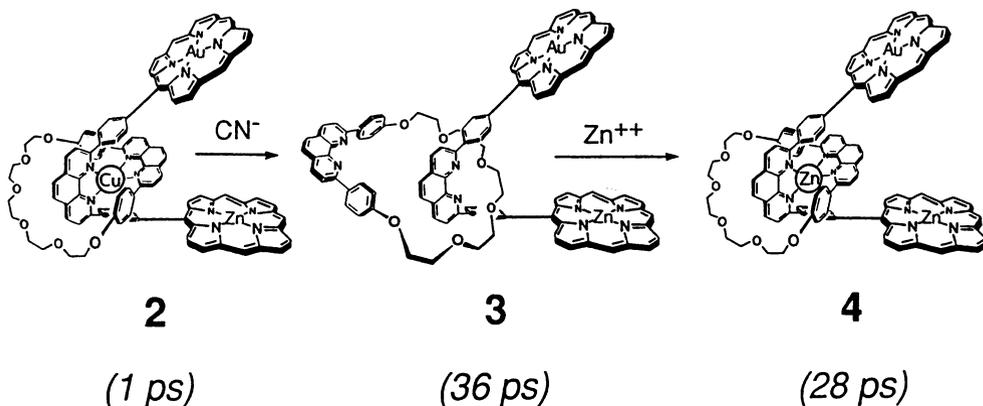


Figure 2. The copper(I) centre can be quantitatively demetalated by CN^- . The free rotaxane thus obtained is readily recomplexed by Zn(II) . The ET rates between the donor and the acceptor are indicated below each molecule. If the free rotaxane **3** undergoes much slower ET than **2**, zinc(II) coordination to afford **4** does not significantly affect ET rate.

$^1\text{H-NMR}$ spectroscopy measurements provide precious information about the geometry of **2**, **3** and **4**. The free rotaxane **3** has indeed undergone a complete rearrangement by decomplexation, the phen moiety incorporated in the ring now lying at the outside of the molecule whereas remetalation with zinc to afford **4** regenerates the characteristic intertwined geometry of **2**. As expected, these changes have profound effects on electron transfer rates, as indicated in the bottom line of Figure 2. Either in the free rotaxane **3** or in the zinc(II) rotaxane **4**, ET is much slower than in the copper(I) rotaxane **2**. Noteworthy, the geometry of **4** is identical to that of **2** but, nevertheless, it undergoes comparatively slow electron transfer. These observations point to the importance of the electronic properties of the chemical group interspersed between the donor and the acceptor in determining ET rate.

3. Electrochemically Triggerred Molecular Motions : Swinging of a [2]-Catenate

Bistability is an essential property for imaging and information storage. An inorganic example has recently been reported which demonstrates electrochemical hysteresis [13]. Some other related systems of linkage isomerism induced by a redox process have also been described [14-16]. The principle of the present system, recently reported as a

preliminary communication [17], is based on a linkage isomerism reaction utilizing a [2]-catenate, i.e., a transition metal complex whose organic backbone consists of two interlocked coordinating rings [2]. The interconversion between both forms of the complex is electrochemically triggered and corresponds to the sliding motion of one ring within the other. It leads to a profound rearrangement of the compound and can thus be regarded as a complete metamorphosis of the molecule.

The principle of the process is explained in Figure 3. Essential is the difference of preferred coordination number (CN) for the two different redox states of the metal : CN=4 for copper(I) and CN=5 (or 6) for copper(II).

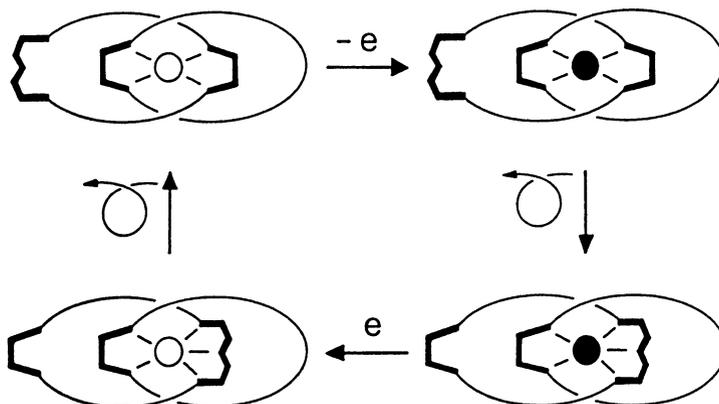


Figure 3. Principle of the electrochemically triggered rearrangement of non-symmetrical [2]-catenate. The stable 4-coordinate monovalent complex [top left, the white circle represents Cu(I)] is oxidized to an intermediate tetrahedral divalent species [top right, the black circle represents Cu(II)]. This compound undergoes a complete reorganization process to afford the stable 5-coordinate Cu(II) complex (bottom right). Upon reduction, the 5-coordinate monovalent state is formed as a transient (bottom left). Finally, the latter undergoes the conformational change which regenerates the starting complex.

The organic backbone of the non-symmetrical catenate consists of a 2,9-diphenyl-1,10-phenanthroline (dpp) bidentate chelate included in one cycle and, interlocked to it, a ring containing two different subunits : a dpp moiety and a terdentate ligand, 2,2',6',2''-terpyridine(terpy). Depending upon the mutual arrangement of both interlocked rings, the central metal atom (copper, for instance) can be tetrahedrally complexed (two dpp's) or 5-coordinate (dpp + terpy). Interconversion between these two complexing modes results from a complete pirouetting of the two-site ring. It can, of course, be electrochemically induced by taking advantage of the different geometrical requirements of the two redox states of the copper(II)/copper(I) couple. From the stable tetrahedral monovalent complex, oxidation leads to a 4-coordinate Cu(II) state which rearranges to the more stable 5-coordinate compound. The process can be reversed by reducing the divalent state to the 5-coordinate Cu(I) complex obtained as a transient species before a changeover process takes place to afford back the starting tetrahedral monovalent state.

The non-symmetrical copper(I) catenate $5_{(4)}^+$ (the subscript 4 indicates the coordination number) of Figure 4 was prepared in a multistep procedure, following a synthetic strategy derived from the previously reported methodology developed for making various interlocking ring systems [2].

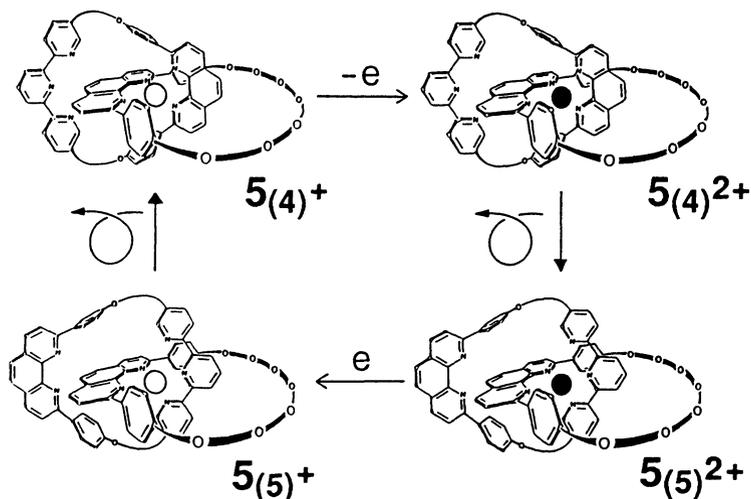
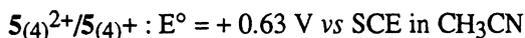


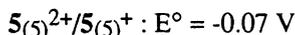
Figure 4. The square scheme starting from of 4-coordinate copper(I) catenate $5_{(4)}^+$. Each electrochemical step is followed by a changeover reaction corresponding to the gliding motion of one ring within the other. The white circle represents Cu(I) whereas the black disk corresponds to Cu(II). The hexaethylene glycol fragment of the ring containing a dpp chelate only is represented in a schematic way (a CH_2CH_2 motif is represented by an arc of a circle).

By applying the principle of Figure 3 to $5_{(4)}^+$, it is clear that for the same oxidation state (either Cu(I) or Cu(II)), the two forms should display significantly different physical properties. In particular, it is expected that the spectroscopic and electrochemical properties of the divalent copper catenates depend strongly on the coordination number of the metal [18]. This could be demonstrated by oxidizing the copper(I) catenate $5_{(4)}^+$ and subsequently monitoring the absorption spectrum and the redox properties of the divalent complex obtained as a function of time. $5_{(4)}^{2+}$, the tetrahedral Cu(II) species obtained immediately after oxidation, either by Br_2 or via electrolysis, is a deep green complex in solution ($\lambda_{\text{max}} = 670 \text{ nm}$; $\epsilon = 830 \text{ M}^{-1} \text{ cm}^{-1}$ in CH_3CN). The electronic spectrum of the oxidized solution changes with time. A drastic intensity decrease around 670 nm is observed within a few days to give a pale yellow-green complex. This slow process is in agreement with the changeover reaction represented in Figure 4 and leading to the 5-coordinate copper(II) complex $5_{(5)}^{2+}$, in which a coordinated dpp chelate has been replaced by the incoming terpy unit belonging to the same cycle. The spectral properties of the starting species $5_{(4)}^{2+}$ and its isomeric product $5_{(5)}^{2+}$ are in accordance with the coordination number and the geometry assumed around each copper centre [18,19].

Interestingly, the transformation of Figure 4 is accompanied by a change in the electrochemical properties of the complex, paralleling the spectroscopic changes. As expected, the tetrahedral copper complex has a relatively high redox potential,

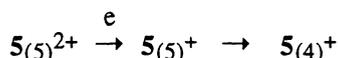


whereas the 5-coordinate species has a slightly negative potential, pointing to the greater stabilization of the divalent copper than in the 4-coordinate species,



The electrochemical processes are reversible ($\Delta E_p \sim 60 \text{ mV}$) for both complexes. Both methods (electrochemical and spectroscopic) afford similar kinetics. The conversion $5_{(4)}^{2+} \rightarrow 5_{(5)}^{2+}$ is first-order, with a rate constant of $2 \times 10^{-5} \text{ s}^{-1}$ at 20°C in CH_3CN .

Finally, as indicated in Figure 4, reduction of $5_{(5)}^{2+}$ can quantitatively be carried out by electrolysis to regenerate the starting copper(I) complex :



Electrochemical studies indicate that the rearrangement $5_{(5)}^+ \rightarrow 5_{(4)}^+$, which restores the initial species, is relatively fast in CH_3CN (seconds). The changeover process of the monovalent complex, $5_{(5)}^+ \rightarrow 5_{(4)}^+$, is much faster than the reverse rearrangement on the divalent copper complex. The sliding process has to involve decoordination of the metal at some stage, and, clearly, this step is expected to be much slower for Cu(II) than for Cu(I) due to the greater charge of the former cation. Previous kinetic studies on the metalation reaction of a catenand and involving related sliding motions pointed to the importance of the nature of the metal center and the oxidation state [20] in accordance with the present observation. The reaction cycle of Figures 3 and 4 could thus be completed.

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4. References

- [1] Schill G. In *Catenanes, Rotaxanes and Knots* ; Academic Press : New-York, **1971**.
- [2] Dietrich-Buchecker C.O.; Sauvage J.P. *Bioorg. Chem. Frontiers* **1991**, 2, 195.
Dietrich-Buchecker C.O.; Sauvage J.P. *Chem. Rev.* **1987**, 87, 798.
- [3] Philp D.; Stoddart J.F. *Synlett* **1991**, 445 and references therein.
Ashton P.R.; Brown C.L.; Chrystal E.J.T.; Parry K.P.; Pietraszkiewicz M.;
Spencer N.; Stoddart J.F. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 1042.

- Ballardini R.; Balzani V.; Gandolfi, M.T.; Prodi L.; Venturi M.; Philp D.; Ricketts H.G.; Stoddart J.F. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301.
- [4] Bissell R.A.; Cordova E.; Kaifer A.E.; Stoddart J.F. *Nature* **1994**, *369*, 133.
- [5] Ashton P.R.; Philp D.; Spencer N.; Stoddart J.F. *J. Chem. Soc., Chem. Commun.* **1992**, 1124.
- [6] Deisenhofer J.; Michel, H. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 829.
Huber R. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 848.
- [7] Chambron J.-C.; Heitz V.; Sauvage J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 12378.
- [8] Chambron J.-C.; Harriman A.; Heitz V.; Sauvage J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109.
Chambron J.-C.; Harriman A.; Heitz V.; Sauvage J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 7419.
- [9] Breton J.; Martin M. *Proc. Natl. Acad. Sci.* **1991**, *88*, 8880 and references.
- [10] Heitz V.; Chardon-Noblat S.; Sauvage J.-P. *Tetrahedron Lett.* **1991**, *32*, 197.
- [11] Brun A.M.; Harriman A.; Heitz V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657.
- [12] Bixon M.; Jortner J.; Michel-Beyerle M.E.; Ogrodnik A.; Lersch. W. *Chem. Phys. Lett.* **1987**, *140*, 626.
Creighton S.; Hwang J.K.; Warshel A.; Parson W.W.; Norris J.R. *Biochemistry* **1988**, *27*, 774 (1988).
Plato M.; Möbius K.; Michel-Beyerle M.E.; Bixon M.; Jortner J.; *J. Am. Chem. Soc.* **1988**, *110*, 7279.
Bixon M.; Jortner J.; Michel-Beyerle M.E.; Ogrodnik. A. *Biochim. Biophys. Acta* **1989**, *977*, 273 (1989).
- [13] Sano M.; Taube H. *J. Am. Chem. Soc.* **1991**, *113*, 2327.
Sano M.; Taube H. *Inorg. Chem.* **1994**, *33*, 705.
- [14] Many examples of linkage isomerization processes involving $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{3+/2+}$ are known, with L being an ambidentate ligand ; see, for example : Katz N.E.; Fagalde F. *Inorg. Chem.* **1993**, *32*, 5391 and references cited therein.
- [15] Geiger W.E.; Salzer A.; Edwin J.; Von Philipsborn W.; Piantini V.; Rheingold A.L. *J. Am. Chem. Soc.* **1990**, *112*, 7113.
Richards T.C.; Geiger. W.E. *J. Am. Chem. Soc.* **1994**, *116*, 2028.
- [16] Roth T.; Kaim. W. *Inorg. Chem.* **1992**, *31*, 1930.

- [17] Livoreil A.; Dietrich-Buchecker C.O.; Sauvage. J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 9399
- [18] For recent studies on 5-coordinate Cu(I) and Cu(II) complexes with imine-type ligands, see : Goodwin J.A.; Stanbury D.M.; Wilson L.J.; Eigenbrot C.N.; Scheidt. W.R. *J. Am. Chem. Soc.* **1987**, *109*, 2979.
Goodwin J.A.; Bodager G.A.; Wilson L.J.; Stanbury D.M.; Scheidt. W.R. *Inorg. Chem.* **1989**, *28*, 35.
Goodwin J.A.; Wilson L.J.; Stanbury D.M.; Scott R.A. *Inorg. Chem.* **1989**, *28*, 42
- [19] Dietrich-Buchecker C.O.; Sauvage J.-P.; Kern J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791
- [20] Albrecht-Gary A.-M.; Dietrich-Buchecker C.O.; Saad Z.; Sauvage J.-P. *J. Am. Chem. Soc.* **1988**, *110*, 1467.

AMIDE-BASED CATENANES AND ROTAXANES BY NON-IONIC TEMPLATE SYNTHESIS

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1. Introduction

Unlike other organic molecules catenanes and rotaxanes are not only defined and held together by common chemical bonds, they also bear mechanical bonds in their structure. Catenanes (lat. catena = chain) consist of two or more macrocycles that are intertwined as the links of a chain [1]. The term rotaxane is a combination of the two Latin words *rota* (= wheel) and *axis* (= axle). Indeed, these compounds possess (at least) one wheel and one axle running through it. The latter is equipped with large stopper units that prevent the wheel from slipping off [1] (fig. 1).



Figure 1. Schematic depiction of a catenane and a rotaxane.

The existence of catenanes has already been discussed in 1912 by *R. Willstätter* [2]. This is particularly remarkable because larger macrocycles were still unknown at that time until in 1926 polymembered-ring ketones with 15 and 17 carbon atoms were described by *L. Ruzicka* in the case of the fragrances Civetone and Muscone [3]. Many years later, in 1960, *E. Wasserman* eventually reported the first successful catenane synthesis [4]. It

took seven more years until *Schill* and *Zollenkopf* [5] and also *Harrison* and *Harrison* [6] published the first preparations of rotaxanes almost simultaneously.

While in the early days of catenane and rotaxane syntheses mechanical bonds were either formed statistically (see section 2.1.) or *via* multistep “directed” syntheses (see section 2.3.), present-day methods base on so-called template effects [7] (see section 3.) that are caused by non-covalent (supramolecular) interactions creating molecular recognition processes. Understanding these processes is crucial since the function of most enzymes is based on these fundamental principles. As certain reactions are often catalyzed by template effects [8] applications seem to be likely an issue in future technology.

2. Classical catenane and rotaxane syntheses

2.1. STATISTICAL CATENANE AND ROTAXANE SYNTHESSES

Lüttringhaus was the first to report a feasible (statistical) synthetic method to prepare catenanes [9]. The principle of this synthetic pathway is shown in the following illustration:

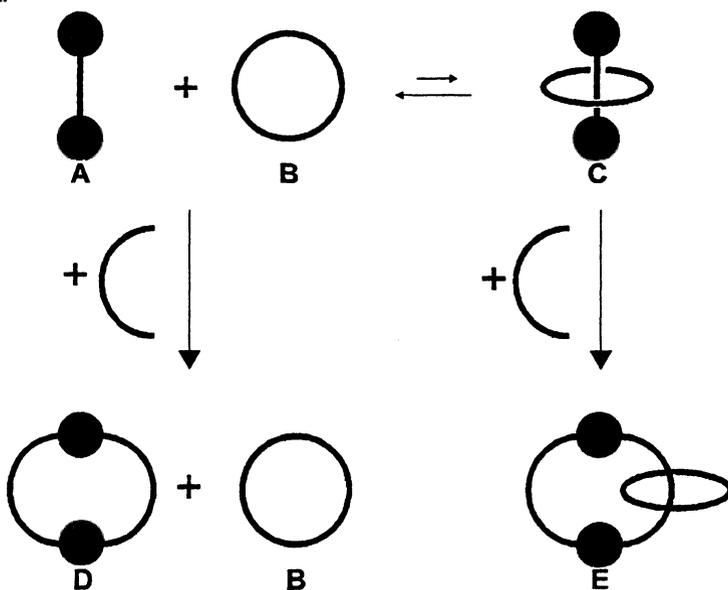


Figure 2. Scheme of the statistical catenane synthesis.