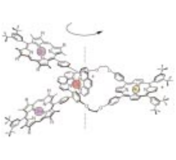
Rotaxanes as new architectures for photoinduced electron transfer and molecular motions



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Rotaxanes are molecular architectures ideally suited for building integrated, multicomponent modular systems, displaying novel chemical and physical properties. In this new field of functional rotaxanes, those incorporating transition metals, which are incidentally used as synthetic templates, are particularly attractive for their photophysical and electronic properties as well as their dynamic behaviour. It is believed that they will provide, in the future, the basic elements for constructing nanoscale machines and motors.

1 Introduction

Chemists usually pursue the imitation of nature, which constructs large and complex systems with high degrees of efficiency. One of the vehicles used for this research are the rotaxanes which are composed of one (or more) macrocycle(s) encircling a single dumbbell component that bears two large blocking groups or stoppers at both ends of the linear thread (Fig. 1).[1,2] These stoppers serve to prevent the macrocycle from slipping off the end. One of the most striking features of

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From left to right: María Jesús Blanco, Valérie Heitz (behind), M. Consuelo Jiménez, Jean-Claude Chambron, Myriam Linke and Jean-Pierre Sauvage

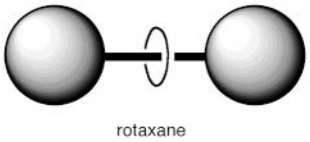

Fig. 1 Schematic representation of the simplest among rotaxanes, a [2]rotaxane, made of a ring threaded onto a dumbbell whose stoppers prevent breaking up.

rotaxane architectures is that their mechanically interlocked components can, in principle, move relative to one another without breaking covalent bonds. Such dynamic processes are currently attracting considerable attention from chemists, physicists and materials scientists because they combine the possibility of precisely positioning the individual components of a molecule with that of changing their relative separation and orientation to order, possibly through the influence of external stimuli.

The photosynthetic reaction center (RC) represents an evolutionary optimized organized assembly where vectorial photoinduced electron transfer leads to effective charge separation.[3] Many of the most debated issues in the biological electron-transfer systems involve questions of how electron transfer events proceed through *non-covalently linked* protein pathways.[4] Substantial efforts were directed to prepare non-covalently linked photosynthetic model systems that might allow for the study of electron transfer processes in formally unlinked but still well-associated donor–acceptor aggregates. With regard to the design of model systems for the photosynthetic RC, many transition-metal complexes including rotaxanes have been investigated during the past few years.[5] In addition, the high resolution X-ray diffraction data from crystals

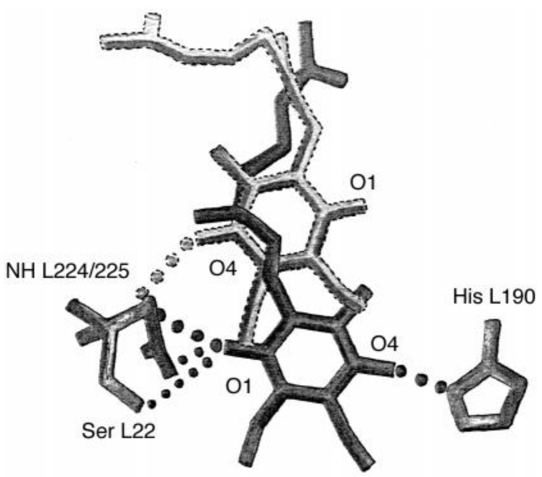

Fig. 2 Superimposition of the partial views of the X-ray crystal structure of the Reaction Center of *Rh. sphaeroides* at 77 K in the dark (dotted lines) or under illumination (full lines), showing that the ubiquinone species (QB) undergoes some motion within its receptor site following light excitation of the system.[6]

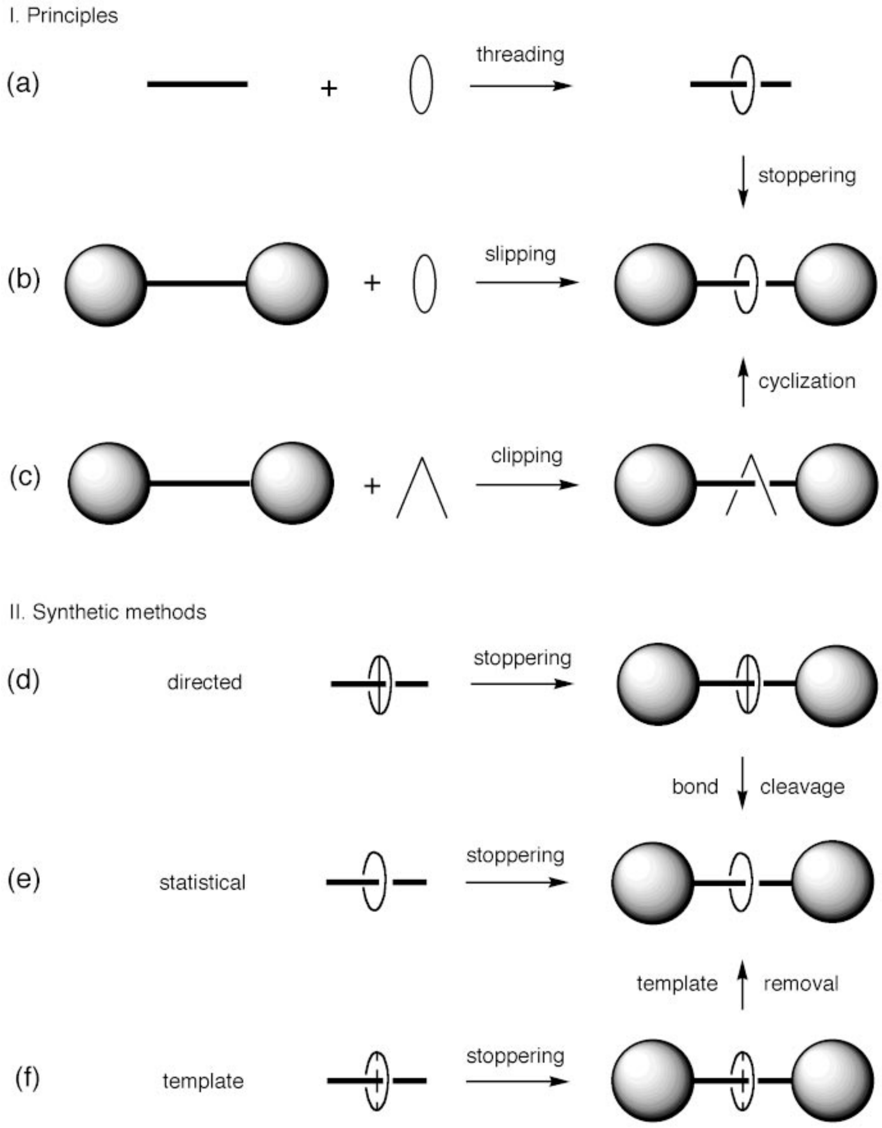

Fig. 3 (a–c) The three principles of rotaxane assembly, and (d–f) the three synthetic methods corresponding to the threading/stoppering principle.

of the *Rhodobacter sphaeroides* photosynthetic RC have pointed towards a structural change accompanying charge separation.[6] A particularly dramatic effect was observed when the rate of electron transfer in RCs that were frozen under illumination was compared with that of those frozen in the dark. The rate of the electron transfer from the primary ubiquinone Q_A to the secondary ubiquinone Q_B was increased by several orders of magnitude when RCs were frozen under illumination, that is, in the charge separation state, as compared to RCs frozen in the dark. The discovery that in the light RC structure, the ubiquinone was moved ~ 4.5 Å and underwent a 180° propeller twist (Fig. 2) highlights the importance of motion between the components of a model system. This fact converts the rotaxanes in suitable architectures to study photoinduced electron transfer processes, possibly coupled to appropriate molecular motions.

In this paper we present an overview of the most recent designs of sophisticated rotaxanes as well as the new development in template synthetic methodology as a powerful tool to prepare successfully threaded molecular systems.

2 General methods

The synthetic challenge associated with the intriguing structure of rotaxanes has prompted numerous efforts to develop efficient

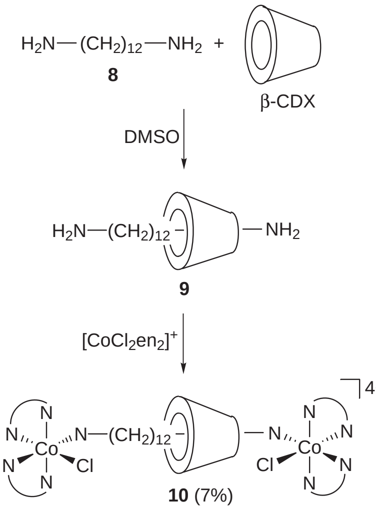

Fig. 5 Ogino's template preparation of a cyclodextrin-based rotaxane (**10**).[10] Hydrophobic interactions control the threading of β-CDX onto 1,12-diaminododecane (**8**) in DMSO, to form prerotaxane **9**. The protruding amino groups of **9** are used to coordinate Co(III) centres bearing ethylenediamine chelates as ancillary ligands, to afford rotaxane **10** in 7% yield.

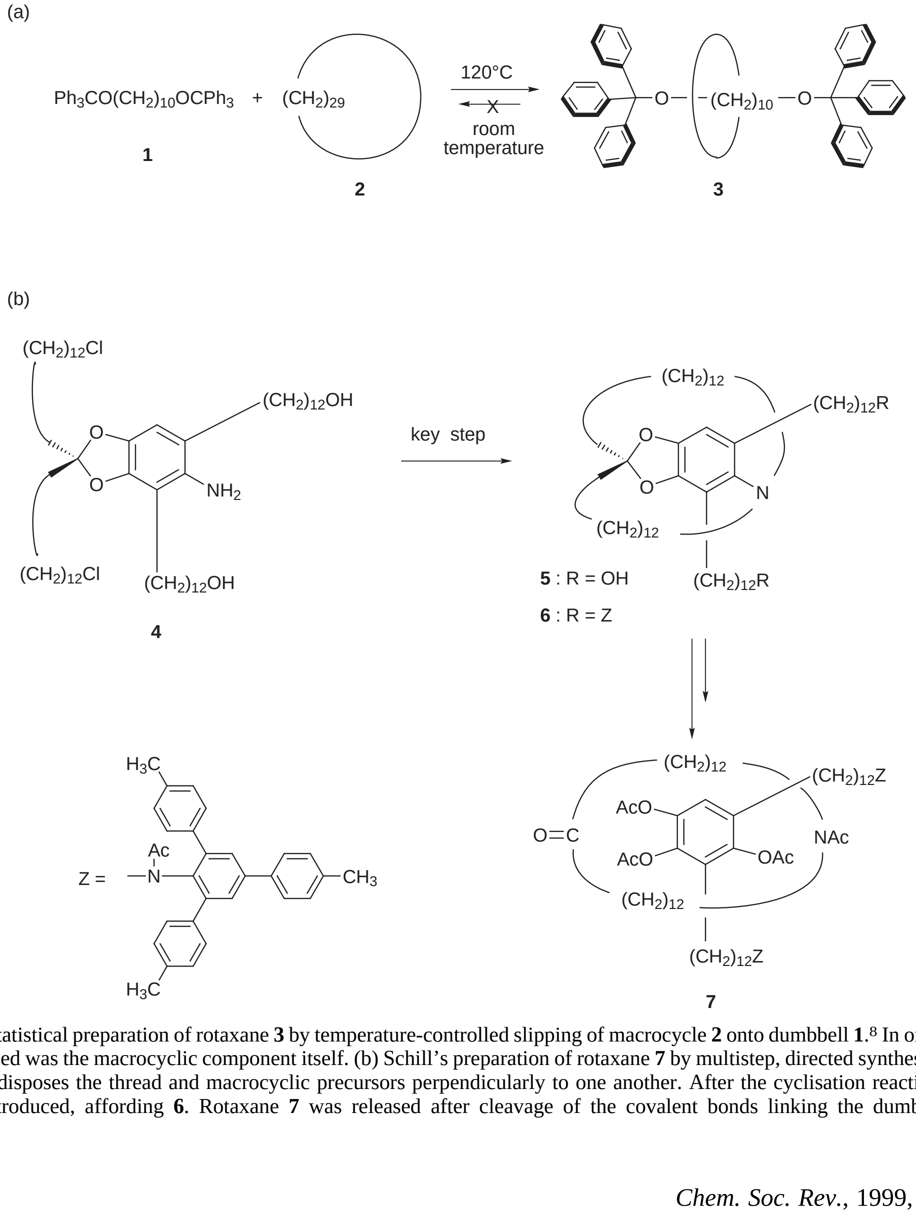

Fig. 4 (a) Harrison's statistical preparation of rotaxane **3** by temperature-controlled slipping of macrocycle **2** onto dumbbell **1**.[8] In order to force the threading process, the solvent used was the macrocyclic component itself. (b) Schill's preparation of rotaxane **7** by multistep, directed synthesis.[9] The key intermediate is acetal **4**, which predisposes the thread and macrocyclic precursors perpendicularly to one another. After the cyclisation reaction of **4** to provide **5**, the stoppers (Z) were introduced, affording **6**. Rotaxane **7** was released after cleavage of the covalent bonds linking the dumbbell component and the macrocycle.

synthetic methodologies to afford them. Three different principles known as *threading*, *slipping* and *clipping* were envisioned (Fig. 3a–c). In the case of *slipping*, a presynthesized size-complementary ring and a dumbbell are assembled under the influence of an appropriate amount of thermal energy. In the *threading* principle, a preformed macrocycle is threaded onto the molecular axle at first, followed by the covalent attachment of the stoppers to the ends of the thread.[7] Finally, in the *clipping* principle the macrocyclization of the ring-component is performed in the presence of the preformed dumbbell-component.

Three synthetic methods: *statistical*, *directed* and *template*, were developed to construct rotaxanes according to the previous principles (Fig. 3d–f). In the *statistical* synthesis, a certain portion of the linear species is inserted through the ring-component as a result of statistical threading. This portion is very minor under normal conditions but it can be more significant if the ring itself is used as solvent. The pioneering work of Harrison[8] on statistical slipping is shown in Fig. 4a. The *directed* method relies on the synthesis of a prerotaxane in which linear and cyclic subunits are linked covalently to each other. Once the rotaxane backbone is built, the covalent bonds are cleaved. This alternative method to the construction of rotaxanes was developed by Schill and coworkers[8] (Fig. 4b). The *template* method requires that the components interact through non-covalent bonds (*e.g.* van der Waals, hydrogen-bonding, π–π stacking or metal–ligand interactions) leading to the assembled prerotaxane.

The different strategies and methods can be combined according to their particular features. Thus, the statistical synthesis relies on the threading or slipping principle, while the directed method only on the clipping one. The template method is more general, since it can make use of *all* the strategies.

The early syntheses of rotaxanes were mainly based upon the statistical or directed methods, whose drawbacks are very particular reaction conditions for the former, numerous chemical steps for the latter. The high degree of control imposed by the use of templates upon these synthetic methodologies has raised the possibility of assembling efficiently and precisely rotaxanes incorporating a wide diversity of chemical modifications. Due to the importance of this technique, we shall discuss it further below.

3 Template synthesis of rotaxanes

The synthetic methodology of rotaxanes based on coordination chemistry, in a broad sense, involves the existence of non-covalent interactions between the components of the rotaxane to be assembled. This approach was found to be highly efficient with regard to the previously developed directed and statistical approaches.

Two main groups of synthetic template methods can be envisioned depending on the type of interactions: the first one comprises all the *organic* template methods and the second one includes the *transition metal* template methods.

3.1 Organic template synthesis of rotaxanes

The kind of assemblies included in this category are those in which the stabilizing force between the components of the rotaxane is a non-covalent interaction, such as the so-called hydrophobic interaction, hydrogen bonding, donor–acceptor stacking, ionic and van der Waals forces. We will discuss below some examples of different families of rotaxanes obtained in this way.

A nice example of threading by hydrophobic interactions is provided by the rotaxanes based on cyclodextrins, which were first obtained in 1981 by Ogino.[10] They consist of a cyclodextrin ring threaded onto an alkyl chain ended by amino groups. The stoppers are inert cobalt(III) complex fragments. One of the

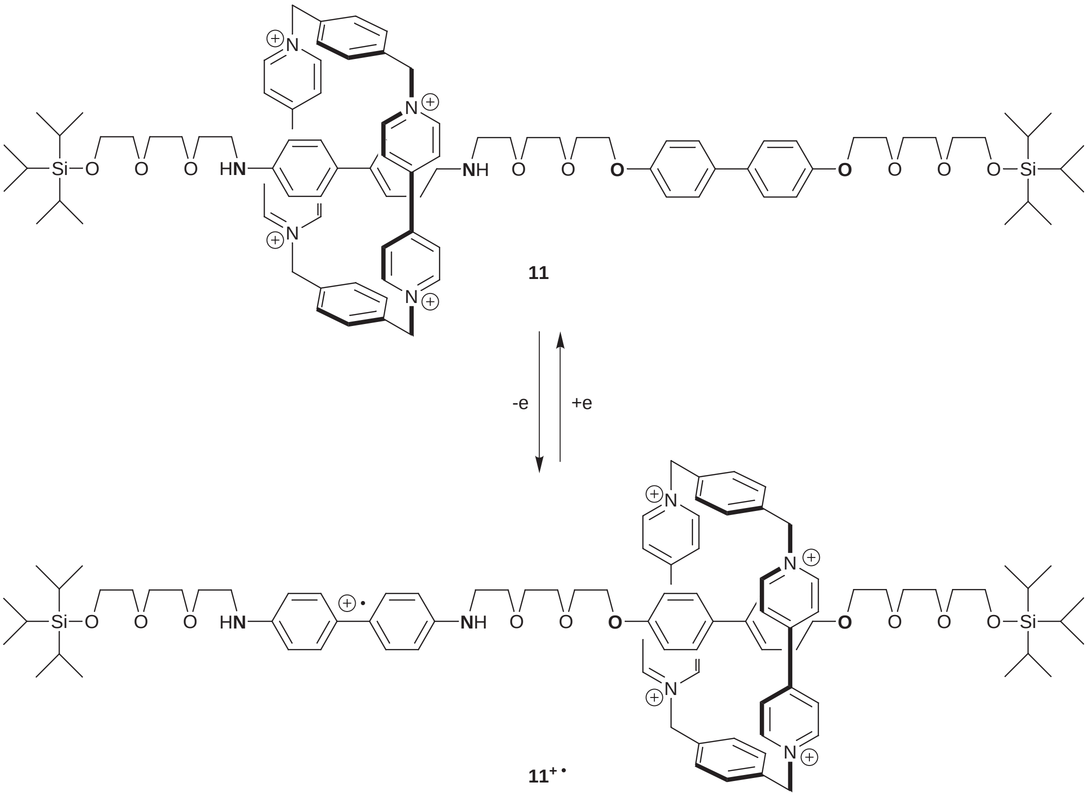

Fig. 6 An electrochemically-driven molecular shuttle (**11**).[14] An electron-deficient tetracationic cyclophane was threaded onto a dumbbell component incorporating two stations with differing electron-donor properties. In the resting state, *ca.* 84% of the macrocycle was bound to the more powerful electron-donor, the benzidine moiety. Electrochemical oxidation of the latter triggers the reversible translation of the macrocycle to the biphenol moiety.

synthetic pathways developed is shown in Fig. 5. 1,12-Diamino-dodecane was allowed to equilibrate with β-cyclodextrin, affording the threaded species, which was treated with [Co-Cl_2en] (en = 1,2-diaminoethane). The corresponding [2]rotaxane **10** was obtained in 7% yield. A further modification of the strategy employing α-cyclodextrin allowed the yield to increase up to 19%.[11]

In a related approach, Kim *et al*. prepared prerotaxanes efficiently by threading a cucurbituril 'bead' (a macrocycle cavitand with D_{6h} symmetry having a hollow core and two identical portals surrounded by carbonyl groups)[12] with phenanthroline derivatives ended by pyridyl groups as precursors of several rotaxanes and polyrotaxanes.

Another kind of rotaxanes, where the components are assembled through aromatic donor–acceptor and hydrogen bonding interactions, are those synthesized by Stoddart and coworkers.[13] This vast family of compounds is highly interesting not only from the synthetic point of view, but also because they are able to respond to an external stimulus, giving rise to molecular motions. In the case of Fig. 6,[14] the rotaxane **11** consists of a tetracationic electron-deficient cyclophane as the macrocycle and a dumbbell component with two stations which are able to interact with the ring, but which differ in their electron-donating properties: a benzidine group, which is the strongest electron donor, and a biphenol-based moiety. In the initial state, the majority of the macrocycle is bound to the benzidine moiety. By means of an external electrochemical stimulus, the macrocycle shifts towards the biphenol station, affording in that way a molecular controllable 'shuttle'.

A different type of organic template strategy developed independently by Hunter[15] and Vögtle *et al*.,[16] initially for making catenanes, is based on van der Waals, π–π and NH···O=C hydrogen bond interactions between the macrocycle and the thread. Many amide-type rotaxanes with various

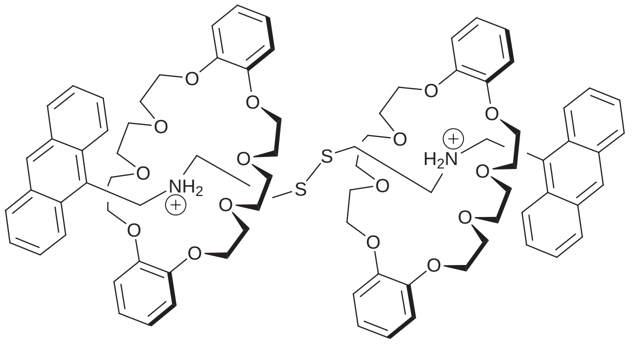

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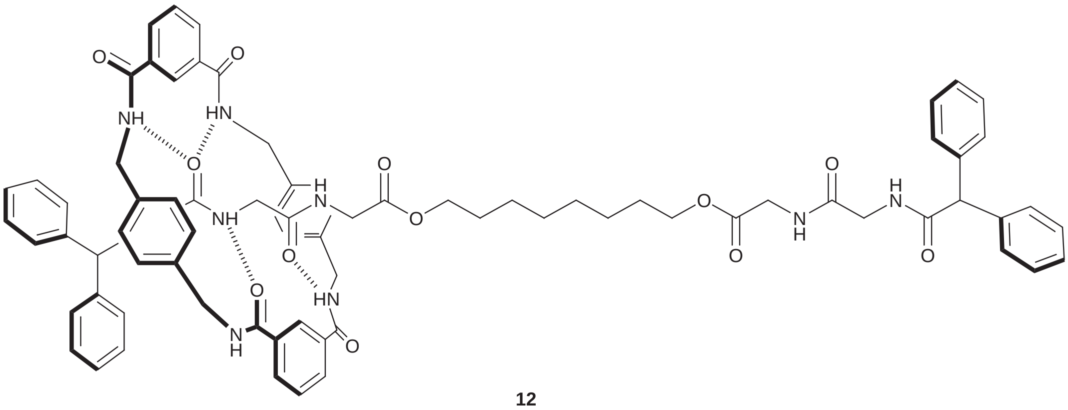
Fig. 8 A [3]rotaxane (**13**) made up with two 24-crown-8 macrocycles threaded onto a bisulfide-bridged, anthracenyl-stoppered dumbbell.[20] Threading was directed by hydrogen bonding between ammonium hydrogen atoms of the dumbbell and oxygen atoms of the macrocycles.



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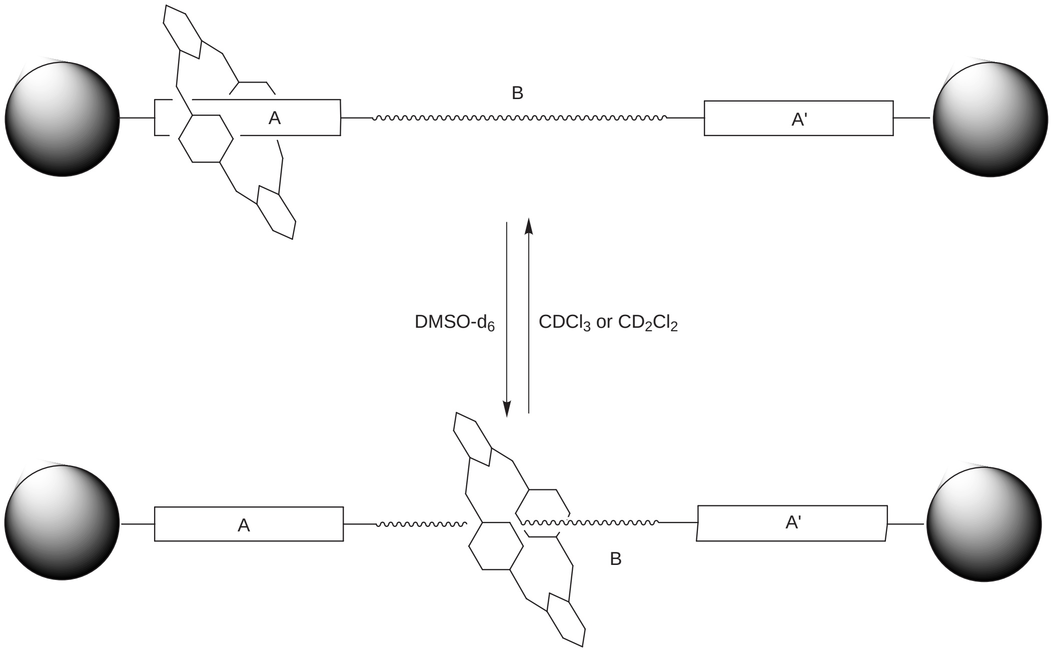

Fig. 7 A molecular shuttle (**12**) piloted by interactions with the solvent.[19] An amide cyclophane was threaded onto a dumbbell component incorporating two stations with differing hydrogen-bonding abilities. In apolar solvents such as chloroform, the macrocycle is bound to the degenerate glycylglycine stations (A and A′), while in hydrogen bonding solvents such as DMSO, the macrocycle is translated to the aliphatic station (B) linking A and A′.

blocking groups could be prepared successfully,[17] often in one-step, one-pot reactions, with yields up to 95%.[18]

As an example, rotaxane **12** (Fig. 7) was synthesized by Leigh and coworkers in two steps from glycylglycine ethyl ester salt to give threads containing two identical peptide stations A and A′ separated by a third, lipophilic station B.[19] Treatment of the thread with isophthaloyl dichloride and *p*-xyxylenediamine gave [2]rotaxane **12** in 30% yield. The property of such a molecule is that the position of the macrocycle on the multistation rod can be controlled: in $CHCl_3$ or CH_2Cl_2, the macrocycle shuttles between the two degenerate hydrogen-bonding stations A and A′, but in DMSO the macrocycle is located at the polarphobic station B.

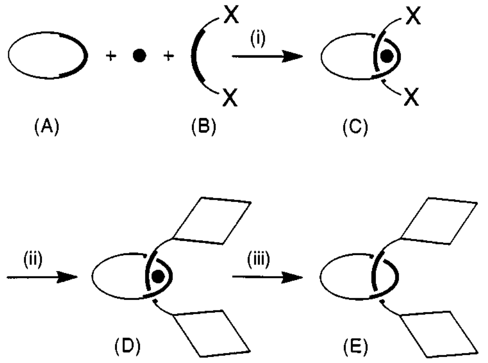

Fig. 9 Schematic representation of the principle of transition-metal templated synthesis of rotaxanes from macrocyclic chelate (A), metal cation (black disk) and open chelate (B). The latter bears functions X at its extremities, which will be used for anchoring or constructing the stoppers (represented as diamonds). (i) Threading step affording prerotaxane (C); (ii) stoppering step affording metal-complexed rotaxane (D); (iii) removal of the metal template to release free rotaxane (E).

Recently, the group of Busch[20] reported a remarkably efficient synthesis of a [3]rotaxane consisting of two 24-crown-8 ether macrocycles threaded onto a disulfide-based bridge dumbbell (Fig. 8). In this example, the *axle–torus* interactions are due to hydrogen bonds between the amine hydrogen and the oxygen atoms of the crown ether as well as [N^+–C–H···O] interactions between the methylene group adjacent to the anthryl unit and the crown ether oxygens. The synthetic strategy relies on the coupling of two prerotaxane moieties, containing an aminothiol axle molecule threaded onto a macrocycle. In that way, complexation of 9-anthrylmethyl(2-mercaptoethyl)ammonium bromide and dibenzo-24-crown-8 ether in the presence of iodine as oxidizing agent afforded the [3]rotaxane **13** in 84% yield by *riveting* two rings together.

3.2 Transition-metal template synthesis of rotaxanes

The prerotaxane components could also be assembled around a transition-metal, which therefore would play the role of a template. A unique feature of this approach is that the template can easily be removed at the end of the synthesis whereas, using strategies based on organic fragments, the interactions between the template and the components of the final rotaxane structure will be maintained. The first successful application of such an approach to the field of catenate chemistry came through previous work from our laboratories.[21] It was based on the fact that Cu(I) forms extremely stable complexes with bidentate 2,9-diphenyl-1,10-phenanthroline (dpp) ligands.[22] Two such

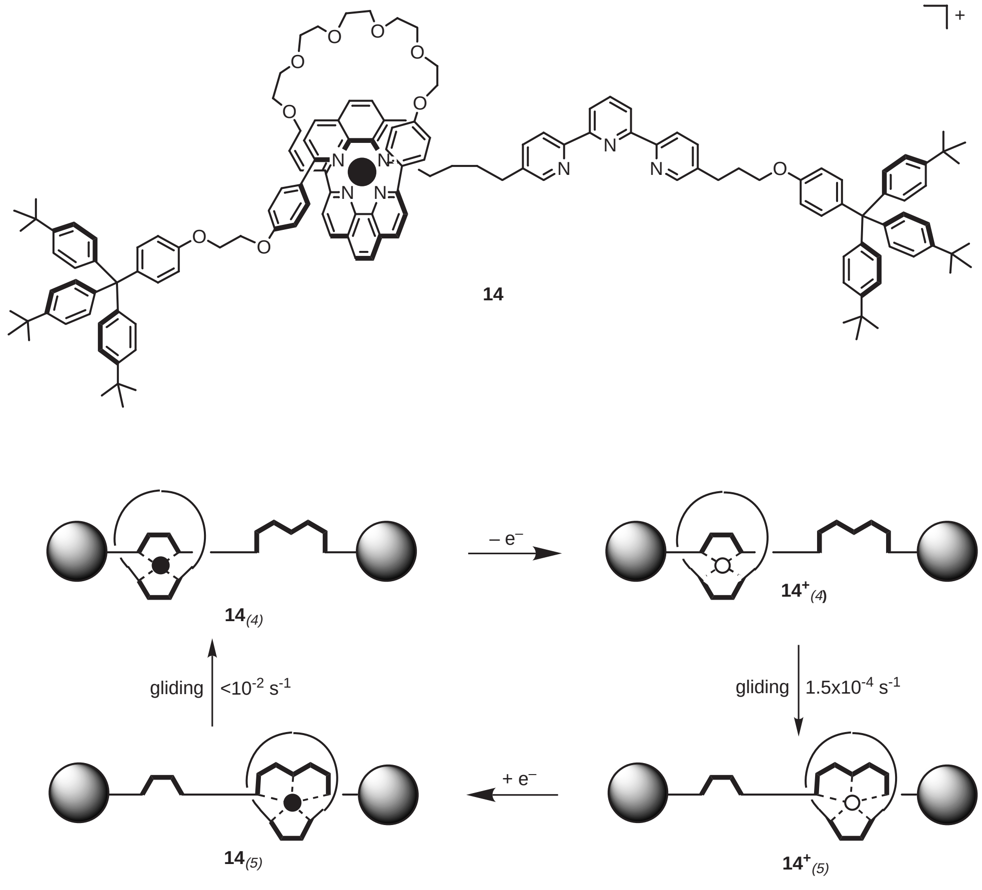

Fig. 10 A rotaxane in motion (**14**) based on the redox state dependence of the stereo-electronic requirements of a transition metal (Cu).[25] Cu(I) and Cu(II) are represented by black and white circles respectively. The linear component incorporates a bidentate (dpp) and a separated terdentate (terpy) chelating site. Initially, the macrocycle coordinates Cu(I) together with the bidentate site of the linear component in a tetrahedral fashion, affording the state **14**$_{(4)}$. Electrochemical oxidation of Cu(I) to Cu(II) produces the state **14**$^+_{(4)}$, which slowly (in *ca.* 1–2 h) converts to the state **14**$^+_{(5)}$, after transfer of the Cu(II)-complexed ring to the terdentate chelate of the thread. Remarkably, the back motion from **14**$^+_{(5)}$ to regenerate **14**$_{(4)}$ *via* **14**$_{(5)}$ is faster: it takes place in minutes.

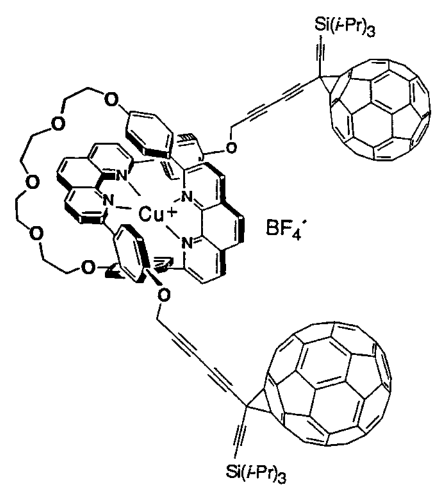

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Fig. 11 A C_{60}-stoppered rotaxane (**15**), based on a copper(I) bis-2,9-diphenyl-1,10-phenanthroline (dpp) complex.[26]

ligands are entwined around the Cu(I) cation forming a tetrahedral complex.

By using the preferential tetrahedral coordinating properties of Cu(I), a transition-metal templated synthesis of rotaxanes was devised. The synthetic strategy is shown in Fig. 9.[23]

The threading step is a complexation reaction which involves a dpp chelate-based macrocycle (A), and a linear fragment incorporating the same dpp chelate (B) end-functionalized by the appropriate reacting groups. The Cu(I) cation templates the assembly of the threaded complex or prerotaxane (C). After stoppering, a Cu(I)-complexed [2]rotaxane (D) is produced. Release of Cu(I) leaves the template-free [2]rotaxane (E). Note that this last step is particular to the transition metal-controlled methodology: neither hydrophobic, nor hydrogen-bonding interactions can be cancelled so easily, except by changing the solvent.[19]

3.2.1 Rotaxanes with innocent stoppers.

In 1991 Gibson and coworkers described the synthesis of a [2]rotaxane in 42% overall yield following the above described strategy.[24]

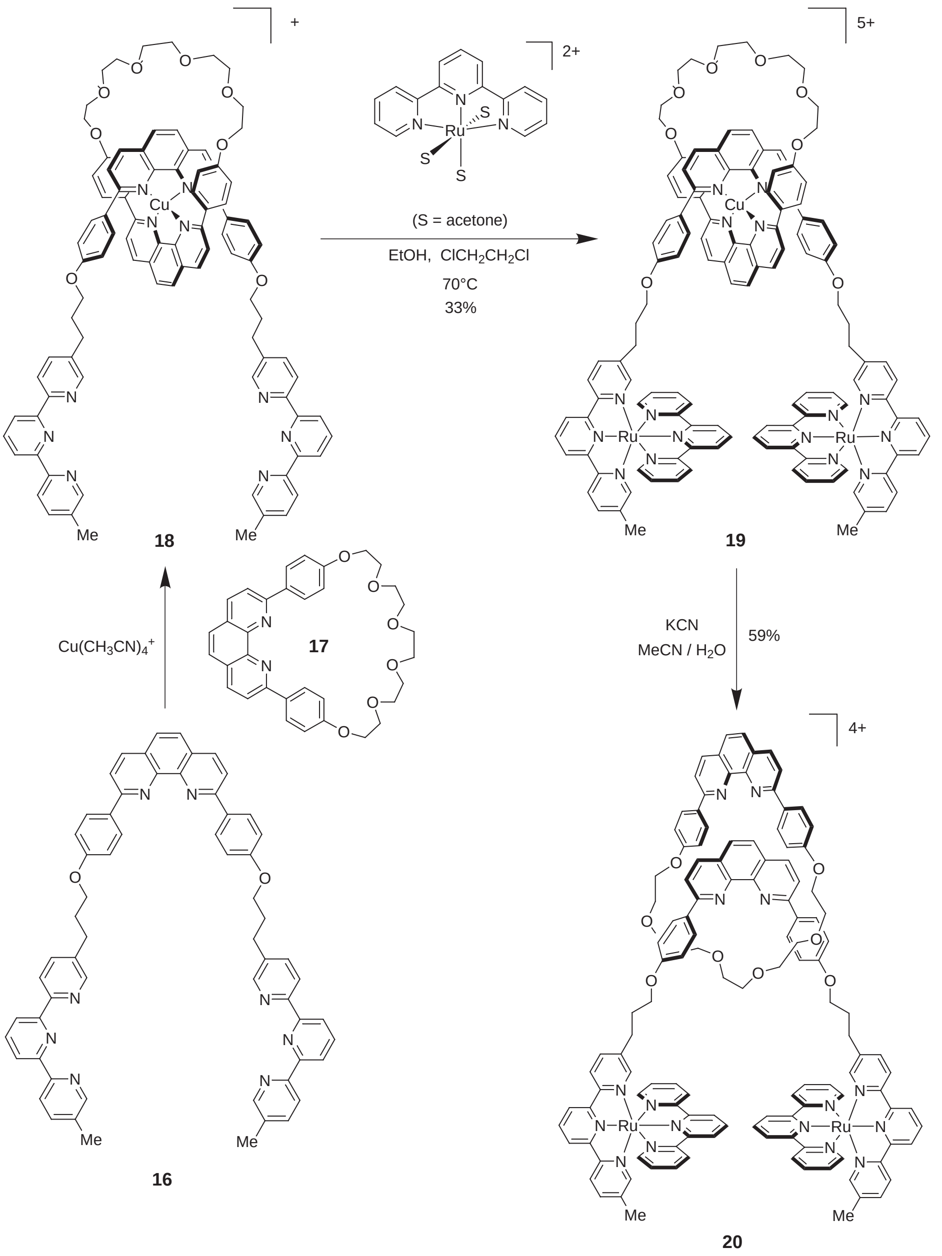

Fig. 12 Preparation of another [2]rotaxane (**20**), whose stoppers are transition metal complex moieties.[27] Copper(I)-templated threading of macrocycle **17** onto molecular thread **16** affords prerotaxane **18**, with pendent terpyridine moieties, which are used to anchor Ru(terpy)$^{2+}$ metal complex fragments. The kinetic inertness of these stoppers allows for selective removal of the Cu(I) template to afford the free rotaxane **20** from its copper(I) complex **19**.

The metallorotaxane **14** of Fig. 10, bearing blocking groups similar to those of the rotaxane of Gibson and coworkers, is of particular interest due to the fact that the dumbbell component entails two *different* sites, such as *bi*dentate and *ter*dentate coordinating units.[25] This structural property in combination with the markedly different stereoelectronic requirements of Cu(I) (tetrahedral) and Cu(II) (square pyramid), were used to study the electrochemically controlled translational motion of the threaded macrocycle between the two chelating sites, as schematically shown in Fig. 10. Compound **14** was synthesized as a Cu(I) complex. In the initial state, the macrocycle stays in the phenanthroline site, due to the preferential coordination number of 4 for Cu(I). Since Cu(II) requires higher coordination numbers than Cu(I), controlled oxidation of Cu(I) to Cu(II) triggers a modification of the coordination sphere of the copper atom, which results in the transfer of the Cu(II)-complexed ring to the terpyridine (terpy) site of the string. Upon reduction, a five-coordinate Cu(I) species is formed as a transient, which finally reorganizes to regenerate the starting complex. In this case, from the synthetic point of view, the threading process was very selective, providing a prerotaxane where the ring was exclusively associated to the bidentate chelate fragment, again because of the very strong preference of Cu(I) for 4-coordinate complexes.

3.2.2 Rotaxanes with chromophores as stoppers.

3.2.2.1 Non-porphyrinic stoppers. Diederich *et al.*[26] envisioned the spherical shape of the C_{60} moiety as an ideal endgroup for a dumbbell component. In Fig. 11 is represented a C_{60}-stoppered rotaxane based on a Cu(I) dpp complex **15**. Thanks to the electron-donor character of the metal-to-ligand-charge-transfer (MLCT) excited state of the complex fragment, electron transfer under light irradiation is thus likely to take place between the Cu(I) central complex and one of the C_{60} stoppers acting as electron acceptor.

[2]Rotaxane **20** prepared in our group, involves metal-complex fragments as stoppers (Fig. 12).[27] Its synthesis represents a new methodology for the preparation of metal-containing rotaxanes. A bifunctional ligand and two different metals participate in the construction of the rotaxane using *pure coordination chemistry*, by taking advantage of the different stereoelectronic requirements of both metals. An ambidentate ligand containing one dpp and two terpy units, was treated with a preformed Cu(I)(dpp) macrocyclic complex to give *regio-selectively* the $Cu(dpp)_2^+$ species. This fact is in accordance with the preferred tetrahedral coordination for Cu(I) complexes. This threaded Cu(I)-complex presenting two free terpy moieties was used for the preparation of a Cu-complexed rotaxane (a catenane was also synthesized from the same precursor). Ru(II) was suitable for the stoppering reaction since it allows the formation of appropriate stoppers from mono(terpy) complexes containing ancillary labile ligands which can be replaced by the free terpy units of the prerotaxane. The Cu-complexed rotaxane was selectively demetallated to give a rotaxane containing two Ru complexes as stoppers in their structure. The high stability of these fragments made them compatible with the template approach as well as with the Cu(I) decomplexation procedure.

3.2.2.2 [2]Rotaxanes with porphyrinic stoppers. Porphyrins as rotaxane stoppers are attractive components, since they are not only bulky groups (*i.e.* good stoppers), but also electro- and photoactive moieties, which can simulate the properties of natural cofactors like hemes or chlorophylls. Several years ago, in our group, the bis-porphyrin conjugate **21** of Fig. 13a was designed and synthesised with the purpose of mimicking the Special Pair (SP)/Bacteriopheophytin (BPh) arrangement and electron transfer properties of the bacterial photosynthetic RC (Fig. 13b).

In the natural system, electron transfer from the excited state of SP to BPh[28] occurs at a rate of $(3\ \mathrm{ps})^{-1}$. In the synthetic model,[29] the electron donor is a zinc porphyrin in its excited state, and the electron acceptor is a Au(III) porphyrin, both being linked by a dpp chelate spacer, and providing a $\Delta G° = -0.75$ eV for the photoinduced electron transfer. Light irradiation of the zinc porphyrin chromophore is followed by fast $[(55\ \mathrm{ps})^{-1}]$ electron transfer to the gold porphyrin acceptor. This process is significantly accelerated when two such bis-porphyrin chelates

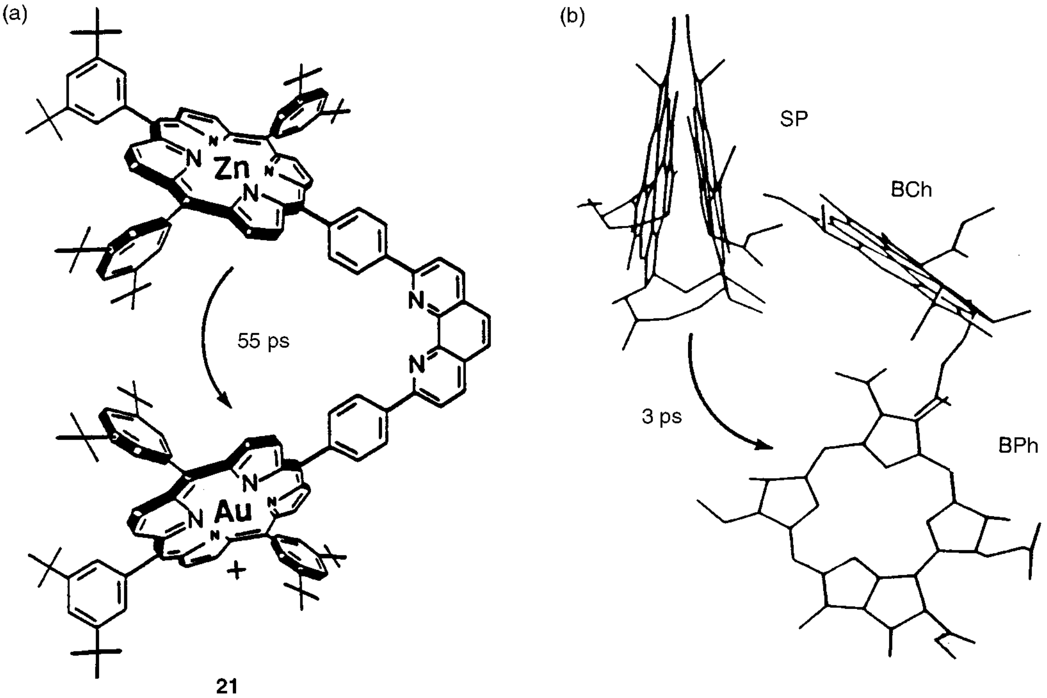

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Fig. 13 (a) A synthetic model **21**[29] of (b) a fragment of the Reaction Center of *Rh. viridis*.[3] The Special Pair (SP) of the RC is mimicked by the Zn porphyrin component of **21**, while the bacteriopheophytin (BPh) of the RC is mimicked by the Au(III) porphyrin component of **21**. BCh is the so-called accessory bacteriochlorophyll, which plays the role of an electronic bridge between SP and BPh. Electron transfer[28] from the excited SP to the BPh takes place at a rate of $(3\ \mathrm{ps})^{-1}$, while in the corresponding model the rate is $(55\ \mathrm{ps})^{-1}$.

21 are entwined around a Cu(I) centre: the rate of photoinduced electron transfer from the donor to the acceptor is very close to what is observed in the natural system.[30] In order to discriminate between the two possible pathways (intra- or interligand electron transfer), the bis-porphyrin ligand was integrated in the [2]rotaxane structure **22** of Fig. 14a, in which the threaded macrocycle contained a complementary dpp chelate.[23]

Photoinduced electron transfer between the zinc and the gold porphyrin occurred, indeed, at a rate close to (2 ps)$^{-1}$, for a slightly larger ΔG (-0.98 eV), due to the different chemical nature of the zinc porphyrin.[31] The kinetics of charge recombination were complicated by the involvement of the Cu(I)/Cu(II) redox couple. They are summarized in Fig. 15. Direct back charge recombination takes place at a rate of (530 ps)$^{-1}$, as in the *bis*-porphyrin dumbbell **21**, but is a minor process (*ca.* 5%). Actually, 95% of the back electron transfer occurs *via* oxidation/reduction of the Cu centre. At first, the Zn porphyrin cation radical oxidizes Cu(I) to Cu(II) at a rate of (20 ps)$^{-1}$. Then Cu(II) is reduced back to Cu(I) by the neutral radical left on the Au(III) porphyrin, at the limiting rate of (2.5 ns)$^{-1}$, restoring the ground state of the rotaxane. The Cu(I)-complexed [2]rotaxane was demetallated with KCN, affording the free [2]rotaxane **23** of Fig. 14, which showed electron transfer properties [(36 ps)$^{-1}$ for the photoinduced electron transfer] very similar to those of the bis-porphyrin dumbbell **21**.[32] To explain the increase of the photoinduced electron transfer rate when **21** was complexed by Cu(I) in Cu(**21**)$_2^+$ or when [2]rotaxane **23** is a Cu(I) complex, as in **22**, a superexchange

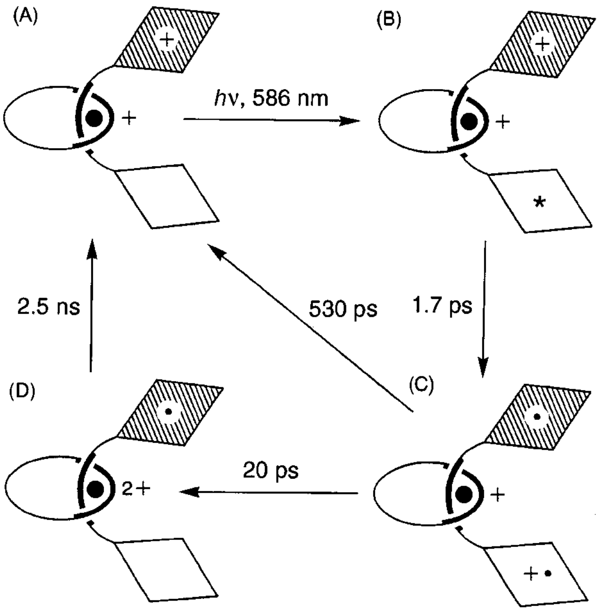
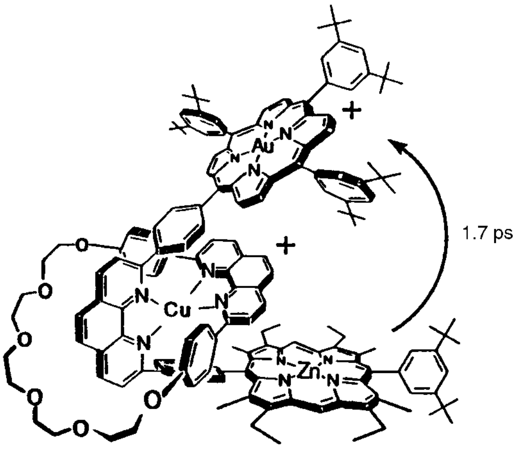


Fig. 15 Kinetics of electron transfer in copper(I)-complexed [2]rotaxane **22**, following light excitation at 586 nm of the Zn(II) porphyrin chromophore.[31] (A) Ground state, (B) Zn(II)-porphyrin-localised excited state, (C) charge separated state, and (D) intermediate charge recombination state of the complex. The Zn(II) porphyrin is represented by a white diamond, and the Au(III) porphyrin is represented by a hatched diamond.



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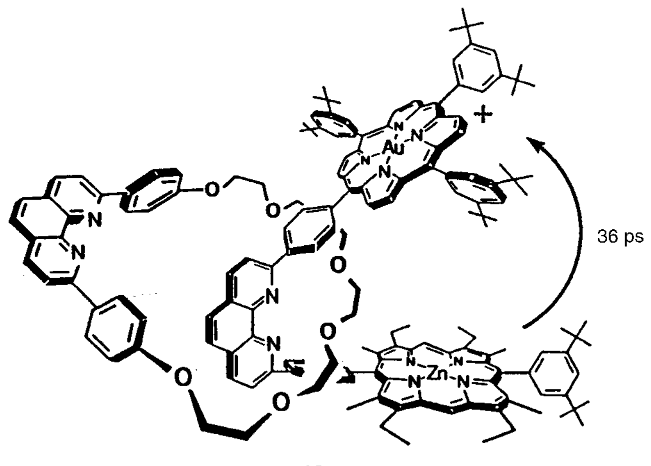


23

Fig. 14 A Cu(I)-complexed [2]rotaxane (**22**) stoppered by zinc(II) and gold(III) porphyrins, and the corresponding free rotaxane (**23**), obtained by removal of the metal template.[23] As in **21**, photoinduced electron transfer takes place between the Zn porphyrin component in its singlet excited state and the Au(III) porphyrin component in its ground state. The rate of electron transfer in the Cu(I) complex **22** was found to be increased by a factor of 20 by comparison with the free rotaxane **23**.[31,32]

mechanism may be invoked. There are at least two distinct ways for this to happen. Firstly, the Cu(I) complex might modulate the energy of the relevant HOMO or LUMO orbitals on the bridging unit. This would be significant if electron transfer occurred through the spacer moiety. Secondly, the accessory 1,10-phenanthroline residue contained in the 30-membered macrocycle ring of the rotaxane **2** could participate in electron transfer since it is most probably interspersed between the two porphyrin rings which undergo forward and reverse electron transfer. This latter situation, which is reminiscent of the bacterial photosynthetic RC complex, would be significant if electron transfer proceeded through space.

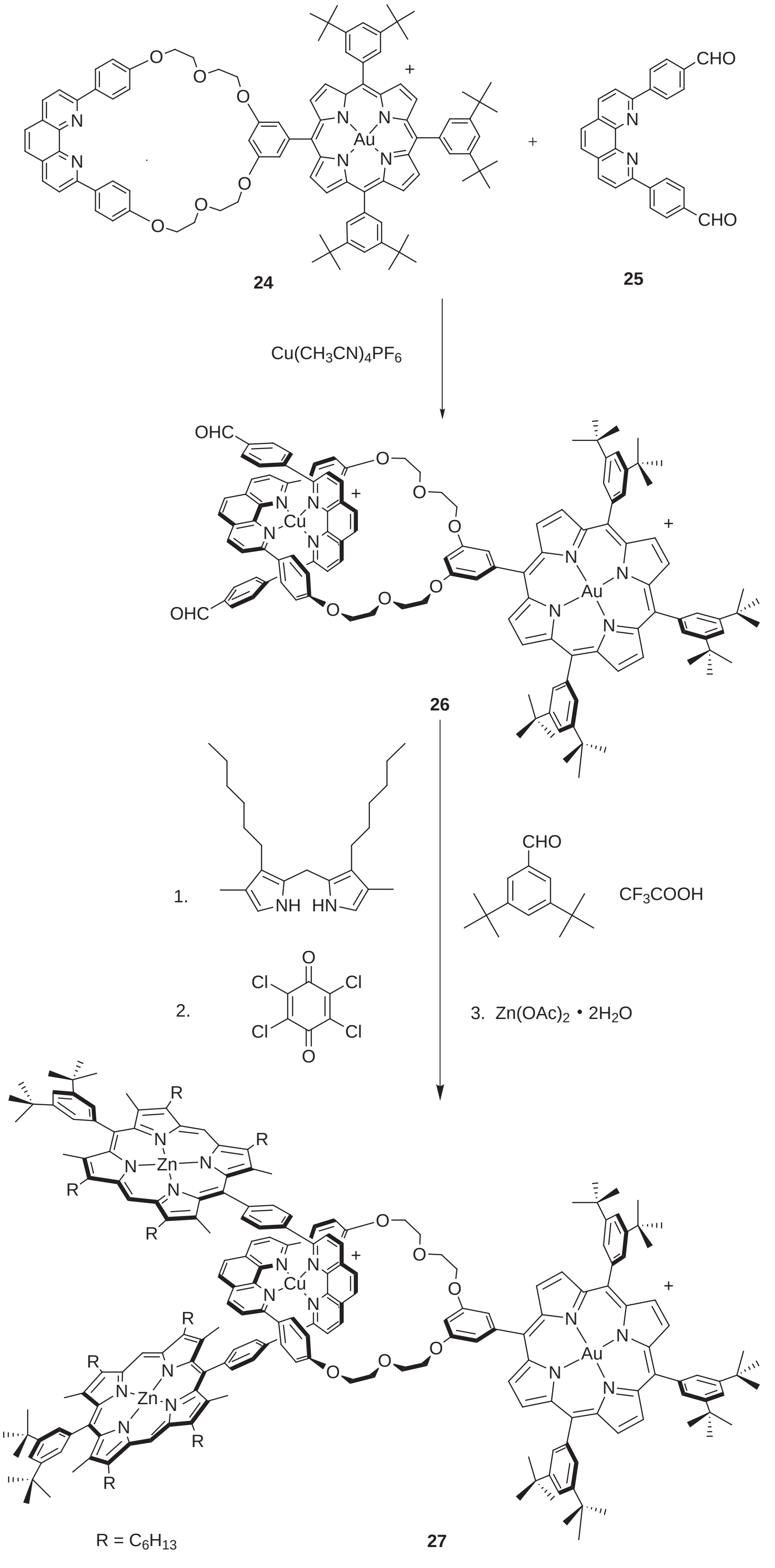


Fig. 16 Copper(I)-templated threading of macrocycle **24** onto dpp-based dialdehyde **25** to afford prerotaxane **26**.[33] One-pot construction of the two porphyrinic stoppers of copper(I)-complexed [2]rotaxane **27**, by reaction of prerotaxane **26** with 4,4′-dimethyl-3,3′-dihexyl-2,2′-dipyrrylmethane and 3,5-di-*tert*-butylbenzaldehyde, followed by treatment with chloranil. The free-base porphyrin rotaxane isolated was complexed with zinc(II) to afford the Cu(I)-complexed [2]rotaxane represented (**27**).

In order to supress any classical bond and, in particular, to make impossible the recognition of an electron transfer pathway involving a bond sequence, a rotaxane system in which the donor and acceptor components are maintained in the same molecule by *mechanical bonds only* would be an ideal target. With this purpose, the Cu(I)-complexed [2]rotaxane **27** (Fig. 16) was synthesized and its photophysical properties studied.[33]

This compound consists of a macrocycle **24** incorporating a dpp chelate and bearing a pendant Au(III) porphyrin, and two Zn(II) porphyrins as stoppering groups. The precursors and the synthetic route (based on the metal-templated effect) leading to the Cu(I) complexed [2]rotaxane **27** are shown in Fig. 16. Threading of the macrocycle **24** onto **25** afforded the prerotaxane **26** quantitatively. The two porphyrin stoppers were constructed in a one-pot procedure by reacting the above prerotaxane, and 3,5-di-*tert*-butylbenzaldehyde, and 4,4′-dimethyl-3,3′-dihexyl-2,2′-dipyrrylmethane. After oxidation of the porphyrinogen with chloranil, and metallation with Zn(II), Cu(I)-complexed [2]rotaxane **27** was obtained in 17% yield.

Removal of Cu(I) was achieved quantitatively by treatment with KCN, giving **28** (Fig. 17). In this case, demetallation is not followed by a pirouetting motion of the macrocycle, but by a *translation motion* of the dumbbell component towards the Au(III) porphyrin of the macrocycle, showing that in both compounds (**27** and **28**) the two porphyrinic stoppers of the dumbbell sandwich the phenanthroline subunit of the macrocycle. A rich coordination chemistry starting from **28** was developed at the bis-dpp tetrahedral site left by the metal template. Thus, rotaxane **28** was metallated with monocations Ag^+ (**29**) and Li^+ (**30**) by treatment with $AgBF_4$ or $LiBF_4$ respectively. In the metallated rotaxanes **27**, **29** and **30** the components incorporating the chromophores and electrophores are connected by metal–ligand bonds, being thus appropriate models for the study of electron transfer through metal–ligand bonds. In the demetallated rotaxane **28**, there is no chemical connection between the electroactive moieties, so this molecule is a suitable model for studying through-space electron transfer processes. The preliminary measurements of steady state luminescence showed the existence of a strong quenching of luminescence of the Zn–porphyrin in the four compounds. In the lithium derivative, the quenching mechanism occurs *via* electron transfer, whereas for the Cu^+ and Ag^+ analogues, the mechanism is less straightforward, since the central complex fragments could participate in quenching processes. For the free rotaxane **28**, which involves only Zn(II) and Au(III) porphyrins as electron transfer partners, the fluorescence of the Zn–

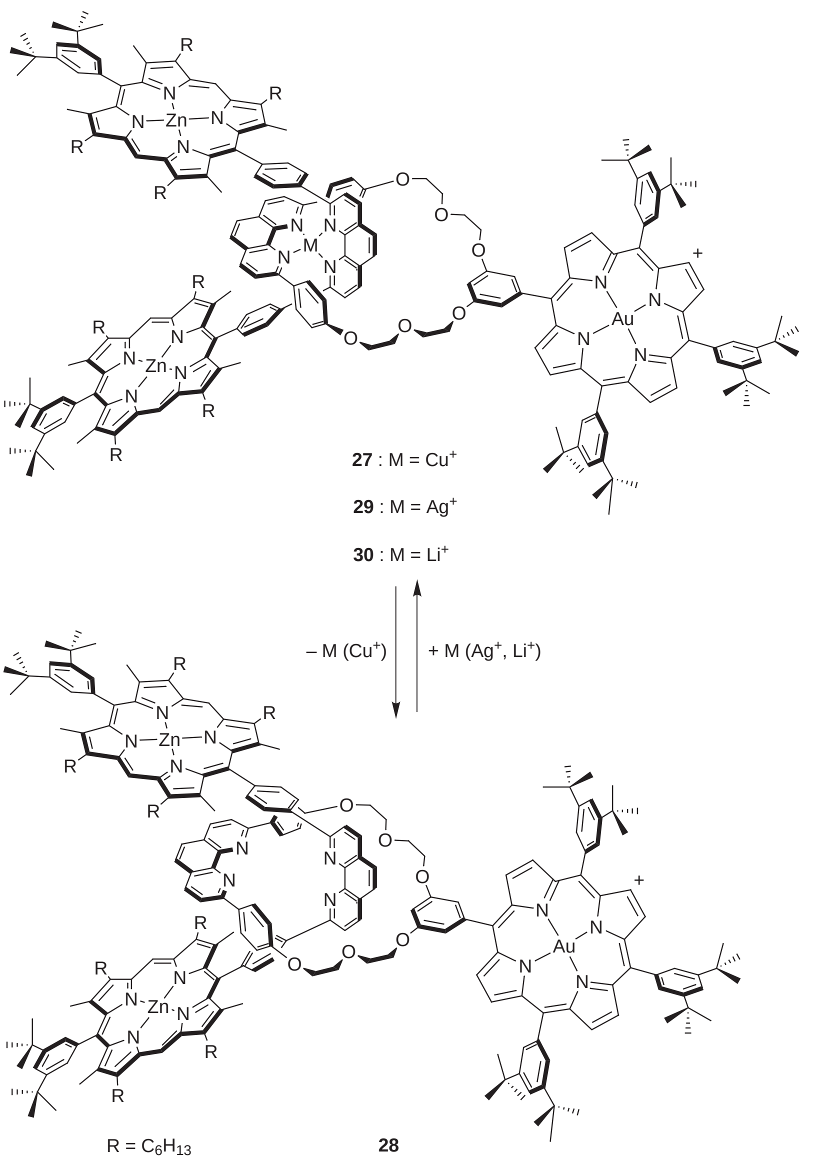
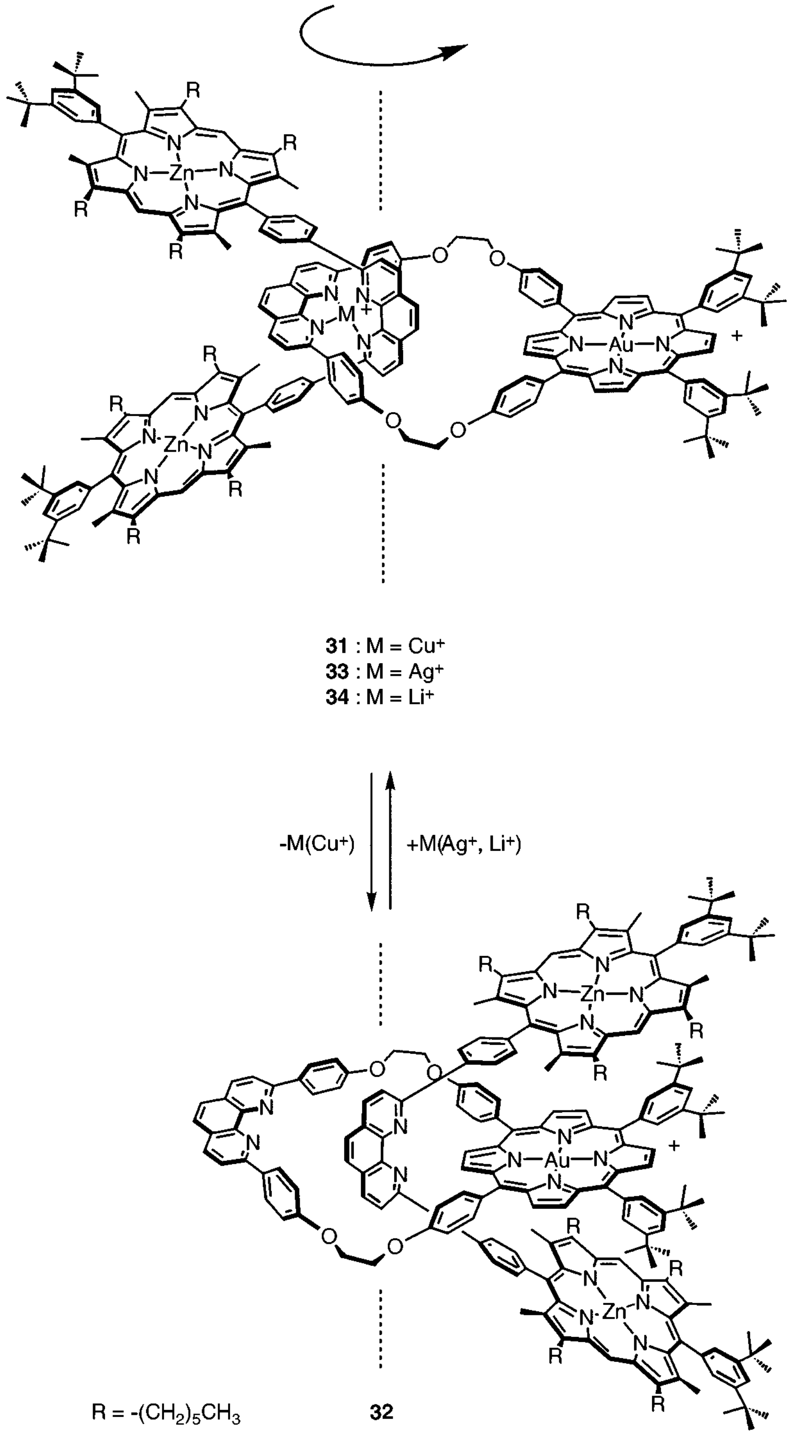


Fig. 17 Removal of the metal template by reaction of copper(I)-complexed [2]rotaxane **27** with KCN to afford [2]rotaxane **28**.[33] The free rotaxane can be complexed again with metals such as Ag^+ or Li^+ to afford rotaxane complexes **29** and **30**.

porphyrin subunits is decreased by 87%. This is due to electron transfer from a Zn–porphyrin stopper in its singlet excited state to the Au–porphyrin cation attached to the ring.

Another system of interest is the multiporphyrinic [2]rotaxane **31** (Fig. 18) in which the Au(III) porphyrin is now part of the ring, the Zn(II) porphyrins still being the blocking groups.[34] It constitutes a nice example showing that complexing or decomplexing the appropriate metal in a coordination site can bring to close proximity, or spread a long distance apart, the porphyrinic components of the system. The principle is depicted in Fig. 19.

Control of the mutual arrangement between the Au–porphyrin (incorporated in the ring, hatched diamond) and the Zn–porphyrins (end-function of the dumbbell, white diamond) is obtained by complexation/decomplexation of a metal centre within/from the coordination site. In the complex, the Au–porphyrin is remote from the two Zn–porphyrins. After removal of the central metal, weak forces may favour an attractive interaction between the Au(III) porphyrin and the Zn(II) nuclei leading to a situation in which the Au(III) porphyrin is pinched between the two Zn(II) porphyrin units. The interconversion between both situations implies a half-turn rotation of the threaded fragment within the ring. This motion is reminiscent of the process taking place in the rotary motor of ATP-synthase.[35] It also leads to dramatic electron transfer property differences between both situations.



31 : M = Cu^+
33 : M = Ag^+
34 : M = Li^+

R = $-(CH_2)_5CH_3$

32

Fig. 18 Metallation–demetallation of rotaxane **32** induces a complete changeover of the molecule.[34] In complexes **31** (M = Cu^+), **33** (M = Ag^+), and **34** (M = Li^+), the Au(III)–porphyrin is remote from the Zn(II)–porphyrinic stoppers, whereas in the free rotaxane **32**, the same Au(III)–porphyrin occupies the cleft formed by the Zn(II) bis-porphyrin dumbbell.

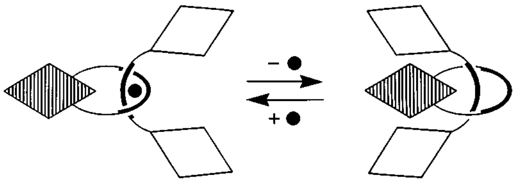


Fig. 19 Control of the mutual arrangement between the gold porphyrin (hatched diamond) and the zinc porphyrins (white diamond) by complexation/decomplexation of a metal centre (black circle) within/from the central coordination site.[35]

The complete changeover of the rotaxane **31** (induced by demetallation) gives **32** (Fig. 18). Space-filling models suggest that within the demetallated rotaxane **31** free rotation of the 'axle' within the ring can take place. The driving force for bringing the gold porphyrin between the two zinc porphyrins is related to their extremely different and complementary electronic properties. Of particular interest are the centre-to-centre (Au–Zn) and the edge-to-edge distances between the Au and the Zn porphyrins. The estimated centre-to-centre separation is *ca.* 19 Å and *ca.* 7 Å for **31** and **32** respectively. The edge-to-edge distance, which is more relevant to electron transfer, is *ca.* 12 Å for **31** and 5 Å in the case of **32**. The interconversion between **31** and **32**, although leading to dramatic geometrical changes, is quantitative and reversible and it can be triggered by other metals, such as Ag^+ (**33**) and Li^+ (**34**).

4 Conclusion

For several decades, rotaxanes have been regarded as exotic species, more related to laboratory curiosities than to compounds of real interest. This was particularly true at the time of Harrison or Schill, when both groups reported their rotaxanes syntheses, the latter one in particular, representing a real synthetic 'tour de force'. Since the beginning of the 80s, rotaxanes have become more and more accessible, which has completely changed our view of these molecules. Functionality of increasing complexity has gradually been introduced, leading to multicomponent systems displaying novel chemical and physical properties in relation with coordination chemistry, photo- and electrochemistry and molecular materials. Transition-metal incorporating rotaxanes are especially promising for their electron transfer properties and for their dynamic behaviour. Efficient models of the photosynthetic RC have been proposed, demonstrating in some examples that fast electron transfer can take place between mechanically linked chromophores. This particular type of linkage (a ring threaded onto a molecular string) is also well adapted to molecular motions, be it the translation of the ring on its thread or the rotation of a wheel on its axle. Such structural elements will be used in the future as key elements for building synthetic molecular machines and motors, the motions within these multicomponent assemblies being driven by electron transfer processes and photonic events.

5 Acknowledgements

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