

A copper-complexed rotaxane in motion: pirouetting of the ring on the millisecond timescale†

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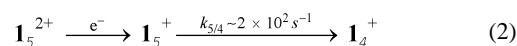
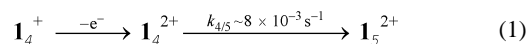
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A new bistable rotaxane, consisting of a 2,2'-bipyridine-containing thread and a ring incorporating both a bidentate chelate and a tridentate fragment, has been prepared; this complex undergoes an electrochemically driven pirouetting motion of the ring around the axis which takes place on the millisecond timescale, *i.e.* several orders of magnitude faster than the other copper-based machines previously described.

Triggering and controlling large amplitude molecular motions is particularly challenging, in relation to electro-, chemo- or photochemical mechanical devices and molecular switches at the nanometre level.¹ Many artificial molecular machines and motors involve catenanes and rotaxanes² but several other systems have also been proposed, either consisting of purely organic compounds³ or based on transition metal complexes.⁴ The rate of the motion is an important factor which has been determined in a limited number of examples. 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,⁵ to seconds or even minutes in other systems involving threading–dethreading reactions⁶ or transition metal-centred redox processes.⁷ Metal hopping between two distinct sites can be relatively fast (hundreds of milliseconds) when the motion is triggered by a pH-change⁸ but it seems to be much slower when it involves ligand exchange following a redox process.⁹ The main weak point of our molecular machines based on the Cu(II)/Cu(I) couple is certainly the long response time of the system.⁷ Till now, the fastest system we had proposed was a

rotaxane whose ring can pirouette between two positions around an axle.¹⁰ It is represented in Fig. 1 (compound **1**ⁿ⁺).

The rotaxane **1**ⁿ⁺ has two stable configurations: the 4-coordinate copper(I) complex (**1**₄⁺) and the 5-coordinate copper(II) species (**1**₅²⁺) – the subscripts refer to the coordination number of the metal centre. The interconversion between these two states is performed electrochemically. Each interconversion process involves two steps: (i) an electron transfer step (oxidation of Cu(I) or reduction of Cu(II) either chemically or, better, electrochemically) and (ii) a rearrangement reaction corresponding to the pirouetting of the ring around the axle from a position to the other. The rate of the motion depends strongly on the oxidation state of the copper centre:



The 5-coordinate copper (I) complex rearranges relatively fast (~50 ms) but it takes minutes for the 4-coordinate divalent copper complex to find its stable form. These rates are obviously far too low if one wants to elaborate practical systems (switches or mechanical devices) based on rotaxanes containing the same fragments as **1**.

In order to improve the rate of the motions, we reasoned that lowering steric hindrance and thus making the metal centre as accessible as possible should certainly be very favourable since ligand exchange within the coordination sphere of the copper centre must be facilitated as much as possible. It is very likely that the rate limiting step of each motion (**1**₄²⁺ → **1**₅²⁺ and **1**₅⁺ → **1**₄⁺) involves decoordination of the metal centre. To verify this hypothesis, the

† Dedicated to the memory of Jean-Marc Kern. He passed away in the tragic airplane accident over Sharm el-Sheikh on the 3rd of January 2004.

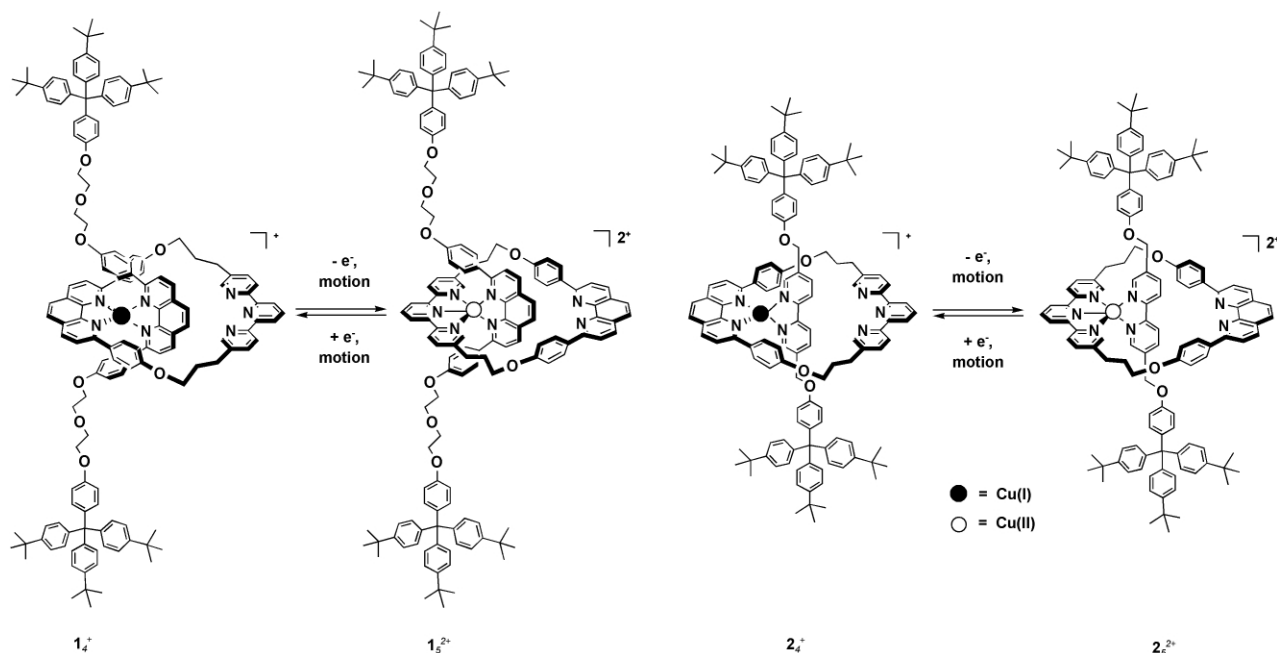


Fig. 1 Copper(I)-complexed rotaxanes in motion. The subscripts 4 and 5 indicate the coordination number of the copper centre; **1**ⁿ⁺ was described a few years ago.¹⁰

new bistable rotaxane 2^{2+} was prepared. Its two forms, 2_4^+ and 2_5^{2+} , are depicted in Fig. 1. The molecular axis contains a 2,2'-bipyridine motif, which is less bulky than a 1,10-phenanthroline (phen) fragment and thus is expected to spin more readily within the cavity of the ring. In addition, and probably more importantly, the bipy chelate does not bear substituents in the α -position to the nitrogen atoms in contrast with the corresponding phen fragment of 1^{2+} .

The new rotaxane has been prepared as the 4-coordinate monovalent copper species, applying the threading approach previously used in our group to make numerous copper(I)-complexed rotaxanes and catenanes.¹¹ Since the stoppering reaction of the threaded copper(I) complex intermediates is generally a relatively low yielding step, especially when both stoppers are introduced at the same time, we selected a two-step procedure, as indicated in Fig. 2.

Compound **3**¹² was first reacted with an excess of **4**¹³ (NaH, THF, 45 °C, 48 h) to afford the asymmetric bipy **5** in 73% yield, with one of its ends already attached to a stopper. **5** was subsequently reacted with the copper(I) complex of **6**, this complex being generated quantitatively *in situ* from the macrocyclic compound and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$. The threading reaction monitored by $^1\text{H-NMR}$ spectroscopy leading to **7**⁺ was also quantitative. **7**⁺ is a moderately stable reddish complex which was subjected to the stoppering reaction (**4**, K_2CO_3 , dibenzo-18-crown-6, CH_2Cl_2 , 35 °C, 48 h) leading to 2_4^+ in a yield of 21%. The copper(I)-complexed rotaxane 2_4^+ was characterized by $^1\text{H-NMR}$ and mass spectroscopy.¹⁴ Its UV-Vis spectrum ($\lambda_{\text{max}} = 418 \text{ nm}$, $\epsilon = 3420$) is characteristic of copper(I) complexes of aromatic diimine ligands,¹⁵ with a relatively intense Metal-to-Ligand Charge

Transfer (MLCT) band in the visible, providing an orange-red colour to solutions of 2_4^+ .

As shown in Fig. 1, it is expected that 2_4^+ rearranges to the 5-coordinate species 2_5^{2+} after oxidation and *vice versa*. The electrochemically driven motions were studied by cyclic voltammetry (CV), which turned out to be the technique of choice to set the molecule in motion, to monitor the movements and to measure their rates. Representative CV data are collected in Fig. 3.

The cyclic voltammograms of 2_4^+ , recorded at two different scan rates, *e.g.* at 100 mV s^{-1} and at 3000 mV s^{-1} are given in Fig. 3. By starting the CV at a potential value of -0.4 V (vs. a silver quasi-reference electrode), no current is observed since 2_4^+ is electrochemically inactive below the oxidation potential at which Cu(I) starts to be oxidized. On increasing the potential towards anodic values, an oxidation peak at $+0.45 \text{ V}$ (at 100 mV s^{-1}) is observed, as expected for the $2_4^+ \rightarrow 2_4^{2+}$ redox process. By comparison with the potential values found for related Cu(II)/Cu(I) couples with analogous ligands,^{15,16} a significant cathodic shift for the $2_4^+ \rightarrow 2_4^{2+}$ process is observed. After the peak potential, Cu(II) is obtained and the current intensity decreases. By investigating the scan potential in the reverse direction, starting from 0.9 V to the cathodic region, it is expected that the Cu(II) species be reduced to Cu(I). If the Cu(II) complex is still 4-coordinate, the return wave should be observed around 0.4 V, corresponding to the $2_4^{2+} \rightarrow 2_4^+$ process. By contrast, if the pirouetting motion is faster than the potential sweep, the return wave corresponding to the reduction of the 4-coordinate Cu(II) complex 2_4^{2+} is not observed any more. Instead, as shown in Fig. 3a, it is replaced by another wave corresponding to the reduction of the rearranged complex 2_5^{2+} at a slightly

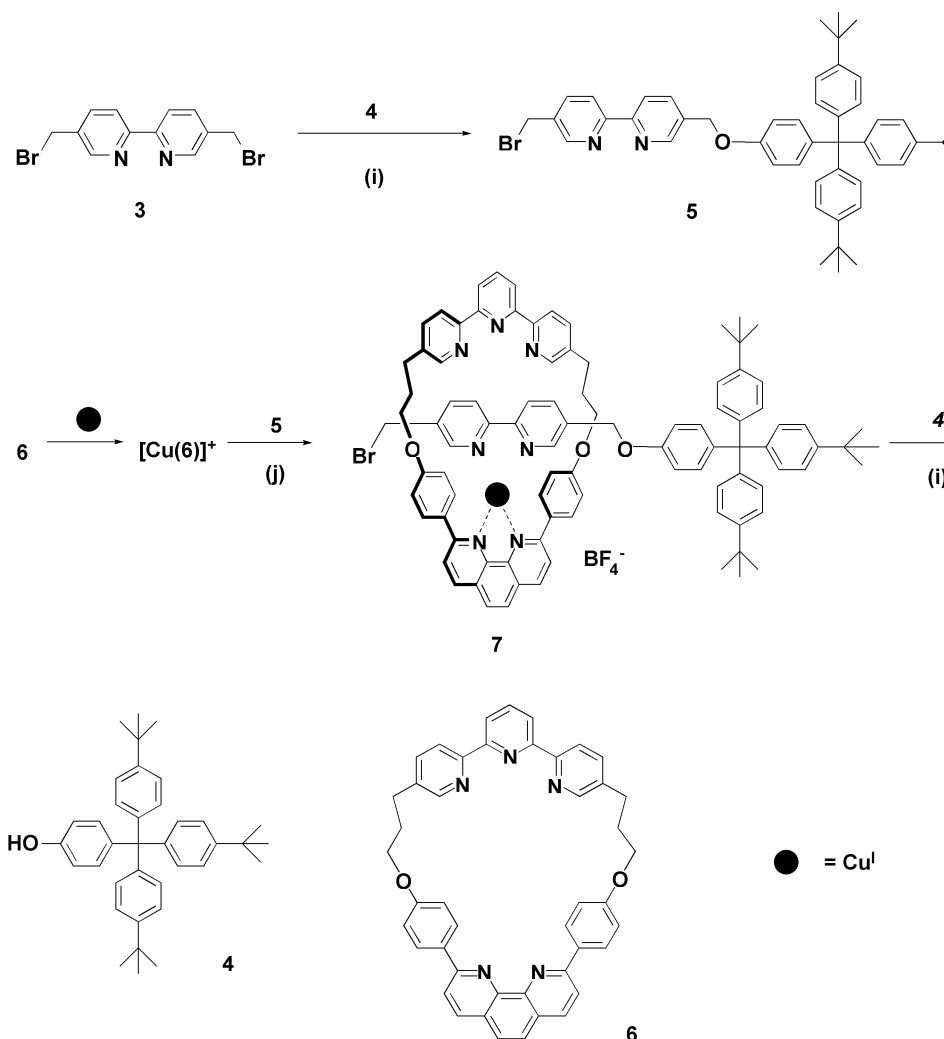
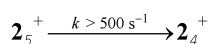
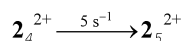


Fig. 2 Synthesis of the 4-coordinate copper(I) complexed-rotaxane 2_4^+ . i: **4**, NaH, THF, 45 °C, 48 h; j: **4**, K_2CO_3 , dibenzo-18-crown-6, CH_2Cl_2 , 35 °C, 48 h.

negative potential ($E_p = -0.04$ V).^{7,16} A second scan between -0.4 V and $+0.9$ V (not shown on Fig. 3b) will allow estimation of the rate of the 5-coordinate copper(i) complex rearrangement: the reoxidation wave expected after reduction of 2_5^{2+} should be observed around 0 V⁷ if the pirouetting process is slow but at a substantially higher potential, corresponding to $2_4^+ \rightarrow 2_4^{2+}$, if this process is fast. Fig. 3a corresponds to a series of 20 scans. In this case as well as in other studies at higher scan rates, 2_5^+ is never observed. This is a clear demonstration that the 5-coordinate copper(i) complex rearranges rapidly. A lower limit for the rate constant of the process can be estimated using the procedure reported by Shain and Nicholson:¹⁷



Using this k -value it can be calculated that $\tau < 2$ ms ($\tau = k^{-1}$). By applying the same treatment on the wave observed around 0.5 V, an estimate of the rearrangement rate for the slower 4-coordinate Cu(ii) complex is obtained:



The measured k -value of 5 s^{-1} (corresponding to $\tau = 200$ ms for 2_4^{2+}) for the $2_4^{2+} \rightarrow 2_5^{2+}$ process shows that 2^{n+} is nearly three orders of magnitude faster to rearrange than its sterically hindered parent compound 1^{n+} . These results also confirm that Cu(i) complexes are substitutionally much more labile than Cu(ii) species.

In conclusion, the use of a non sterically hindering chelate in the rotaxane axis allows fast motion. Clearly, subtle structural factors can have a very significant influence on the general behaviour (rate and reversibility, in particular) of artificial molecular machines. It is expected that further modifications will lead to new systems with even shorter response times.

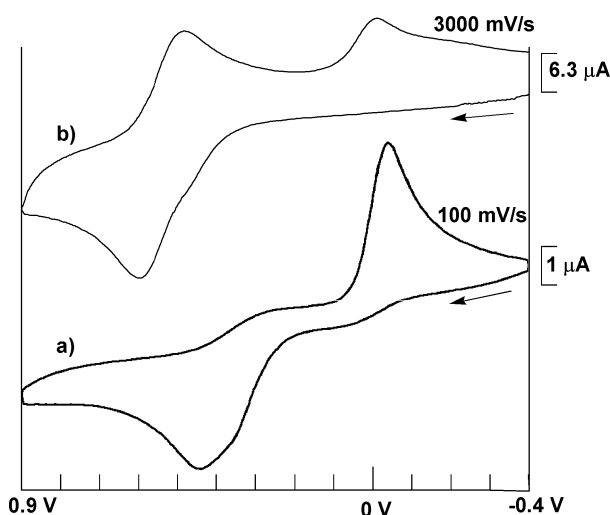


Fig. 3 Cyclic voltammograms of 2^{n+} in MeCN with $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NBF}_4$ at two different scan rates. a) represents 20 cycles and shows that the various CV curves obtained are superimposable. The potentials are referenced versus a silver quasi-reference electrode.

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Notes and references

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- Note: The potentials are referenced in the article against a silver quasi-reference electrode. The $E_{1/2}$ values of $2_4^{2+/+}$ and $2_5^{2+/+}$ vs. SCE in MeCN are $+0.3$ V and -0.1 V respectively.
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