Molecular Devices

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Fast Electrochemically Induced Translation of the Ring in a Copper-Complexed [2]Rotaxane: The Biisoquinoline Effect**

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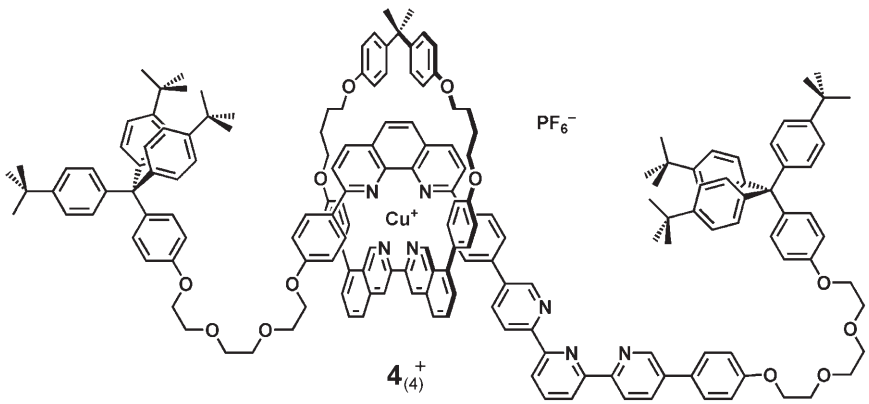
The field of molecular machines has attracted much attention[1] in more recent years, particularly in relation to devices at the nanometer level.[2] Catenanes and rotaxanes[3] occupy a central place in this field, because of the ability of these compounds to undergo large amplitude motions, such as gliding of a ring along an axis on which it is threaded or rotation of a ring within another ring or around an axle, in a reversible fashion[4].

Molecular shuttles are important dynamic systems themselves,[5] but they also constitute essential elements of various complex molecular machines such as muscles[6] and other systems.[7] It is thus important to generate more elaborate fast-moving and efficient compounds. Several years ago, our research group investigated the behavior of a copper-complexed [2]rotaxane as a molecular shuttle.[8] Unfortunately, although the system was set in motion quantitatively by a redox signal (Cu^{II}/Cu^{I}), the back-and-forth motion of the ring and its complexed copper center was slow (minutes).

As shown in Figure 1, the mobile ring contained a highly shielding and hindering 2,9-diphenyl-1,10-phenanthroline (dpp) moiety as the complexing unit, which makes any ligand substitution within the coordination sphere of the metal center very difficult. We assumed that steric reasons were the determining factors for this, and so we designed and synthesized a new ring, in which a sterically nonhindering but endotopic ligand was incorporated, with the hope that shuttles containing such a macrocycle would be set in motion faster than its dpp-containing analogue. The new ring, which contains a 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) unit, and its corresponding rotaxane are illustrated in Figure 1.

Interestingly, copper-complexed rotaxanes undergoing pirouetting of the ring around the axle have been shown to undergo fast motions (micro- to milliseconds) provided the ligand set around the metal center generates little steric hindrance.[9] The new dpbiiq chelating unit and its derivatives have recently been shown to form octahedral three-chelate complexes readily with iron(II) centers, thus demonstrating its sterically nonhindering nature despite its clear endotopic character.[10,11] The synthesis of compound **3** and a homologous 41-membered ring has also been recently reported.[11]

Rotaxane $\mathbf{4}_{(4)}^{+}$ (Scheme 1) was obtained as its PF_6^- salt in 17 steps from **3**, an appropriately substituted stopper fragment, and commercially available compounds. Its synthesis will be described in due course.



Scheme 1. Chemical structure of rotaxane $\mathbf{4}_{(4)}^{+}$.

The electrochemically triggered translation of the copper-complexed ring between the dpp "station" and the 2,2′,6′,2″-terpyridine (terpy) unit was investigated by cyclic voltammetry, as previously described for copper-containing catenanes and rotaxanes.[12,13] By modifying the potential scan rate, the rate of the gliding motion undergone by the copper-complexed ring between the dpp and terpy units can be estimated. A few representative cyclic voltammograms (CV) are represented in Figure 2.

In a similar way to previous studies,[13] the rearrangement rate was estimated from the shape of the cyclic voluammograms. In agreement with the other copper-based molecular machines made and investigated previously by our research group, the unstable five-coordinate copper(I) complex $\mathbf{4}_{(5)}^{+}$ moves much faster than the other unstable species, namely the four-coordinate copper(II) complex $\mathbf{4}_{(4)}^{2+}$. This result can easily be explained by considering that ligand substitution reactions are likely to be more facile around the singly

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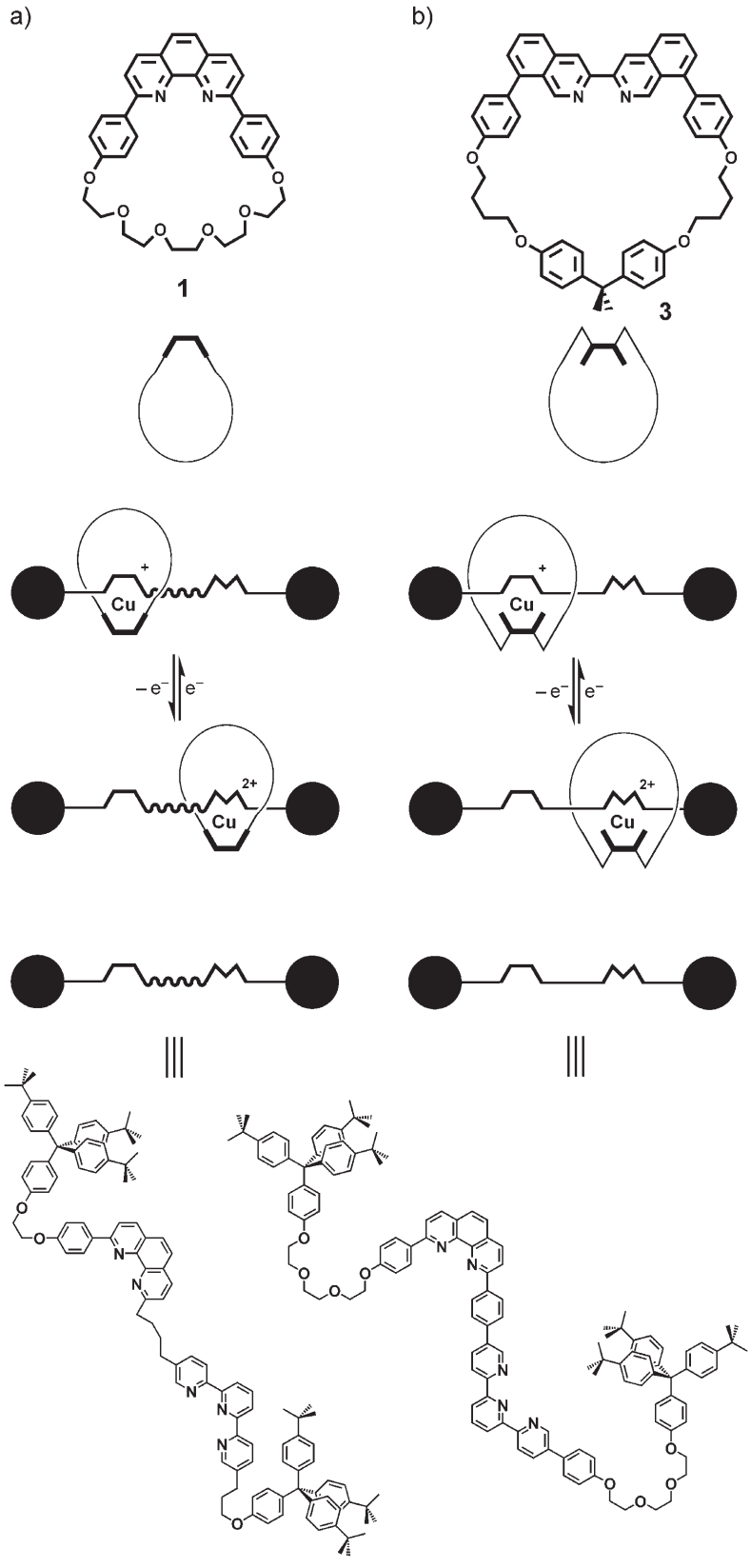

Figure 1. a) The previous system: **1** is a dpp-incorporating 30-membered ring. b) The present molecular shuttle contains a dpbiiq-incorporating 39-membered ring. The two-chelate threads are slightly different for (a) and (b), but they contain similar bidentate or tridentate chelating units. The subscripts (4) and (5) refer to the copper coordination number: 4 for the most stable form of copper(I) and 5 for copper(II).

charged metal center (Cu^{I}) than around a Cu^{II} center. Whereas rearrangement of the Cu^{II}-complexed rotaxane is sufficiently slow to allow the gliding rate constant to be determined by the present technique, the opposite gliding motion experienced by the five-coordinate Cu^{I} rotaxane is too fast to permit estimation of its rate constant. In this case, more sophisticated techniques would be required to afford a relatively precise value. We thus indicate the upper value of this rate constant only. The back-and-forth motion can be described by Equation (1):

$$\begin{aligned}
&\mathbf{4}_{(4)}{}^{+} \xrightarrow{-e^-} \mathbf{4}_{(4)}{}^{2+}\\
&\mathbf{4}_{(4)}{}^{2+} \xrightarrow[\text{gliding}]{k=2\,s^{-1}} \mathbf{4}_{(5)}{}^{2+}\\
&\mathbf{4}_{(5)}{}^{2+} \xrightarrow{-e^-} \mathbf{4}_{(5)}{}^{+}\\
&\mathbf{4}_{(5)}{}^{+} \xrightarrow[\text{gliding}]{k>50\,s^{-1}} \mathbf{4}_{(4)}{}^{+}
\end{aligned} \qquad (1)$$

By comparing the electrochemical behavior of $\mathbf{4}^{n+}$ and that of $\mathbf{2}^{n+}$ ($n=1$ or 2), it is apparent that a pronounced kinetic biisoquinoline effect exists. This ligand leads to a markedly more mobile electrochemically driven machine than the previous copper-based shuttle. The endocyclic but nonsterically protecting or hindering nature of dpbiiq is without doubt responsible for this spectacular improvement.

To compare the dynamic properties of $\mathbf{4}^{n+}$ ($n=1$ or 2) to those of a molecule displaying as much similarity to $\mathbf{4}^{n+}$ as possible in terms of chemical function, we also prepared and studied the rotaxane $[\mathbf{5}_{(4)}{}^{+}][PF_6{}^{-}]$ (Scheme 2). Rotaxane $\mathbf{5}_{(4)}{}^{+}$ contains exactly the same axis and stoppers as $\mathbf{4}_{(4)}{}^{+}$, but the mobile ring is now the strongly shielding macrocycle **1**. This rotaxane allows the effect of replacing the dpp-containing ring **1**, a classical building block of our research group,[14] by the recently prepared dpbiiq-comprising macrocycle to be assessed. The difference is remarkable. As discussed above, the unstable four-coordinate copper(II) complex rearranges within less than one second. By contrast, after oxidation of $\mathbf{5}_{(4)}{}^{+}$ to $\mathbf{5}_{(4)}{}^{2+}$, the thermodynamically unstable form of the complex seems to be stable for several hours, thus also showing that the axis of $\mathbf{4}^{n+}$ and $\mathbf{5}^{n+}$, with its rigid purely aromatic connector between the phen and terpy fragments, is much less favorable to fast gliding than the flexible axis used to prepare $\mathbf{2}_{(4)}{}^{+}$.

To confirm the value of the copper(II) coordination number of both states, $Cu_{(4)}{}^{II}$ (unstable) and $Cu_5{}^{II}$ (stable), electronic

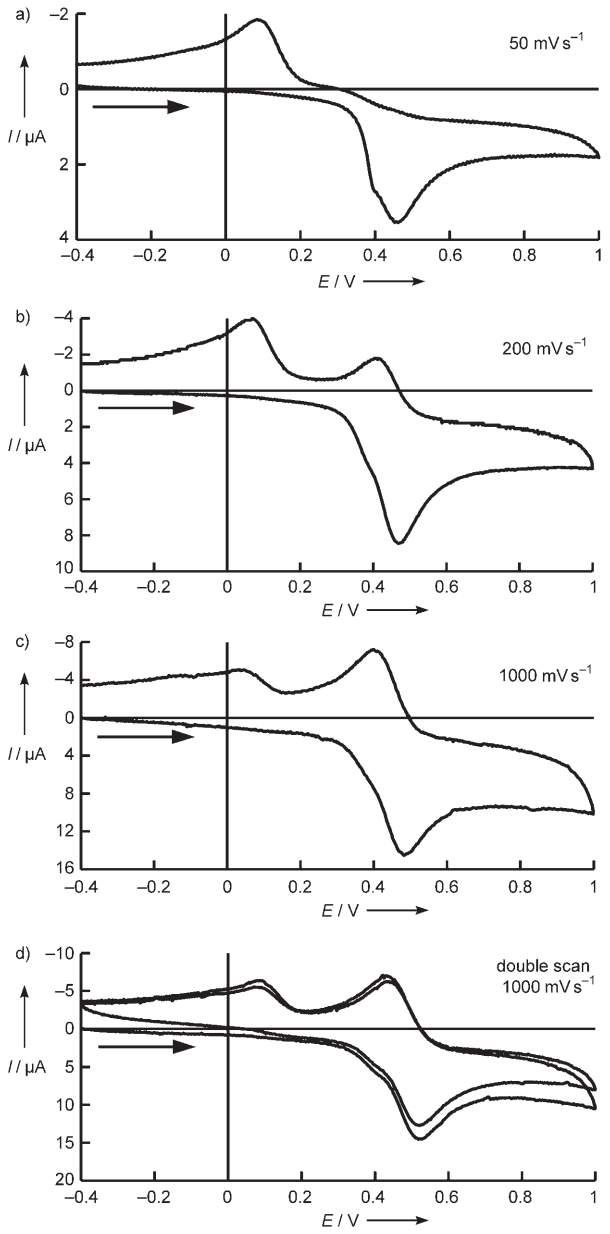

Figure 2. Cyclic voltammetry study of rotaxane $\mathbf{4}_{(4)}^{+}$. a)–c): potential range: −0.4 V to 1.0 V, followed by 1.0 V to −0.4 V; d) two consecutive scans. The electrochemical experiments were performed at room temperature in a 0.1 M solution of Bu_4NBF_4 in $MeCN/CH_2Cl_2$ (9:1), with a Pt working electrode, Ag wire as a pseudoreference electrode, and Pt wire as a counterelectrode.

spectroscopy measurements were performed on $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$. The dark red solution of $[\mathbf{4}_{(4)}^{+}][PF_6^-]$ (2×10^{-4} M) in CH_3CN/CH_2Cl_2 (9:1) was first oxidized with $NO^+BF_4^-$, by analogy with previous work from our research group,[15] which resulted in an instantaneous color change to afford a very pale yellow solution. The electronic spectrum shows a band maximum at $\lambda_{max}\approx640$ nm ($\varepsilon\approx150$), which is a clear indication that the copper(II) complex is five-coordinate.[16] This form of the complex was obtained rapidly (mixing time), as expected from the electrochemical study. By contrast, a similar experiment starting from $[\mathbf{5}_{(4)}^{+}][PF_6^-]$ under the same conditions led to a green solution ($\lambda_{max}\approx670$ nm, $\varepsilon\approx750$), characteristic of a four-coordinate copper(II) complex, as expected for the kinetically inert complex $\mathbf{5}_{(4)}^{2+}$.[12,15]

Another important structural difference between **3** and **1**, besides its nonhindering character, is the less rigid nature of its chelating moiety. Whereas dpp contains a rigid 1,10-phenanthroline nucleus, the dpbiiq part of ring **3** is able to form a complex with a metal center or dissociate from it in a stepwise manner. Indeed, facile rotation between the C–C bond connecting the two isoquinoline fragments (C_3–$C_{3'}$) can take place, which is likely to lower the activation barrier for both the complexation and decomplexation reactions compared to the identical processes with a highly rigid unit such as dpp. Finally, although probably not substantial, the ring-size effect should also be considered: **3** is a larger ring than **1**, which could be favorable.

In conclusion, two different copper-complexed [2]rotaxanes have been prepared and their electrochemically triggered motions have been investigated. Both compounds contain the same thread, which consists of a 2,9-diphenyl-1,10-phenanthroline (dpp) chelating unit and a 2,2′,6′,2″-terpyridine (terpy) unit, whereas the threaded rings are different. In the first case, it is a 30-membered ring derived from dpp. In the second compound, the ring incorporates a 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) chelating moiety, which is at the same time nonsterically hindering but endocyclic. By utilizing the stereoelectronic preferences of copper(I) and copper(II) ions, the ring with its complexed copper atom can be translocated from one station to the other reversibly. For the dpp-containing ring, the electrochemically driven motion is extremely slow (hours to days). By contrast, the dpbiiq-based system is set in motion very readily, with the translation process occurring on the milliseconds to seconds timescale, that is, at least four orders of magnitude faster than for its dpp-based homologue. This characteristic will now be exploited to construct more complex dynamic systems able to fulfil various functions.

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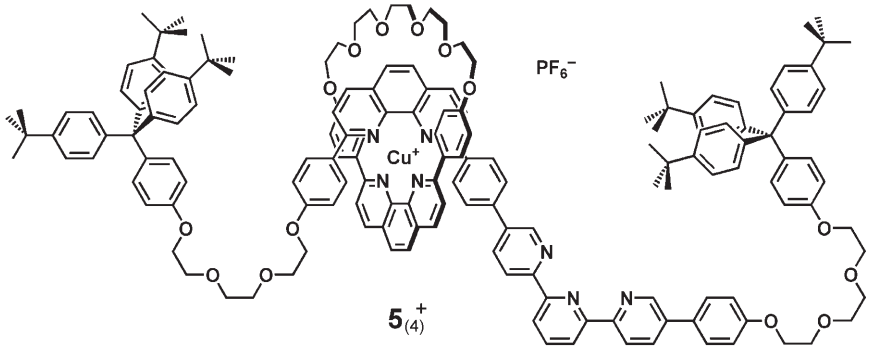

Scheme 2. Chemical structure of rotaxane $\mathbf{5}_{(4)}^{+}$.

Keywords: chelates · coordination modes · copper · molecular devices · rotaxanes

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