Molecular Devices

DOI: 10.1002/anie.200903311

A Rapidly Shuttling Copper-Complexed [2]Rotaxane with Three Different Chelating Groups in Its Axis**

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Molecular machines are particularly promising in relation to potential applications in the fields of information storage and processing, imaging, and nanoscale electro- or photochemically driven mechanical devices, as illustrated by recent spectacular results.[1–10] Catenanes and rotaxanes[11–14] constitute an important subclass of such systems, and our research group has been particularly interested in transition-metal-complexed interlocking compounds.[15–22] Most of these previously reported systems were two-geometry compounds, which were able to switch between a stable five-coordinate copper(II) complex where the copper(II) center is coordinated to a bidentate and a tridentate chelate and a second form, which is a four-coordinate copper(I) complex. In the latter form, the copper(I) center is coordinated to two bidentate ligands. A rare example of a three-geometry system was reported in 1996, and was based on a [2]catenane that consisted of two identical rings, each ring incorporating two different chelating units (a bi- and a tridentate ligand). The copper center could thus be four-, five-, or six-coordinate.[17b] Molecular "shuttles"[23–30] represent the archetype of molecular machines and, equally importantly, they are often used in the fabrication of real devices.[9] The shuttle-like [2]rotaxanes reported to date are two-station systems. These rotaxanes consist of a mobile ring threaded by an axis that incorporates two distinct functional groups, which are able to interact with the ring. To the best of our knowledge, no molecular shuttles with three distinct stations have been reported to date. However, catenanes have been described in which one or two rings (considered as mobile) are threaded through a larger ring that incorporates three different functional groups, which are able to interact with the mobile ring(s).[31] A particularly elegant compound that belongs to this family of catenane-based molecular machines was reported in 2003.[3] This molecule was the first example of a catenane-based rotary motor, that is, a machine that displays controlled directionality during the dynamic process.[3] Incidentally, non-interlocking rotary machines had already been reported by other research groups,[32,33] and continue to attract much attention.[34,35]

Herein, we describe the synthesis and electrochemical behavior of a rotaxane that acts as an electrochemically driven molecular shuttle over a long distance. The rotaxane consists of a coordinating ring threaded by an axis that incorporates three different chelates. It was expected that by introducing an intermediate "station" between the two terminal chelating groups, the gliding motion of the metal-complexed ring would be much faster than the analogous motion without the intermediate chelating group, as the distance between the terminal stations is the same for the two systems.

In the present system, the distance between the two terminal coordination sites is approximately 23 Å. Without a relay between the two end-chelates of the axis, the shuttling motion between these two stations would be expected to be very slow. It has already been shown that the presence of an aromatic spacer between the end-stations slows the shuttling motion significantly.[36–37] The two forms of the rotaxane are shown in Scheme 1.

As discussed below, the introduction of a 2,2′-bipyridine (bipy) between the two end-chelates of the thread facilitates the gliding process. The translational motion over 23 Å is as fast as the related motion in a two-station rotaxane that incorporates a 2,9-diphenyl-1,10-phenanthroline (dpp) unit and a 2,2′,6′,2″-terpyridine (terpy) chelate, that is, the same groups as the terminal chelates of the present system, but over a distance of less than 10 Å. The coordinating units on the axis are 1) a dpp chelate, 2) a bipy chelate and 3) terpy, which is a tridentate ligand. The ring incorporates an 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) bidentate ligand. This endocyclic but nonsterically hindering chelate is a key component, which favors fast translational or rotational motions within shuttle-like rotaxanes or pirouetting systems, respectively.[20b,30] The principle of the electrochemically driven motion relies on the relative stabilities of the various copper(I) and copper(II) complexes formed with the various ligands. Within the following sequence, the thermodynamic stability of the copper(I) complexes increases from $[Cu(terpy)(dpbiiq)]^+$ to $[Cu(dpp)(dpbiiq)]^+$: $[Cu(terpy)(dpbiiq)]^+ < [Cu(bipy)(dpbiiq)]^+ < [Cu(dpp)(dpbiiq)]^+$. The stability sequence is reversed for Cu^{II} complexes: $[Cu(dpp)(dpbiiq)]^{2+} < [Cu(bipy)(dpbiiq)]^{2+} < [Cu(terpy)(dpbiiq)]^{2+}$.
These relative stabilities of the complexes within these two sequences reflect the electrochemical properties of the models listed above and, in particular, their redox potentials.

The Cu^{II}/Cu^{I} redox potentials of the threaded model complexes (see the Supporting Information) and those of the two-station shuttle $\mathbf{5}_{(4)}^{+}$ as well as their chemical structures,

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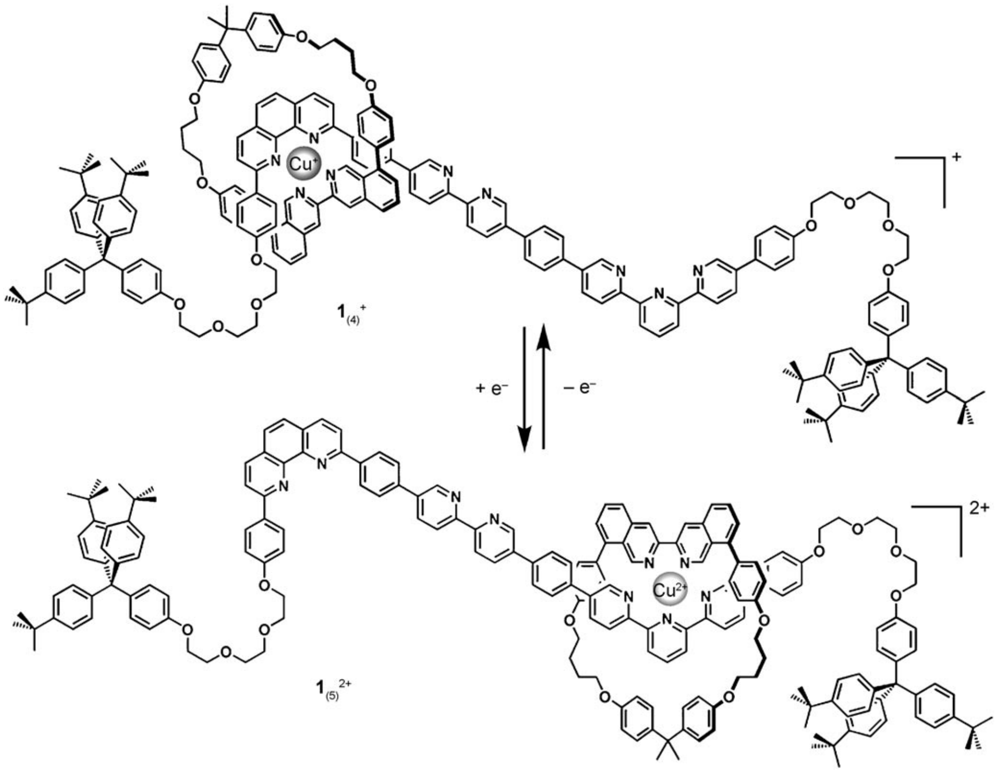
[**] Funding from the CNRS and Région Alsace is acknowledged (fellowships to F.D. and J.L.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200903311.

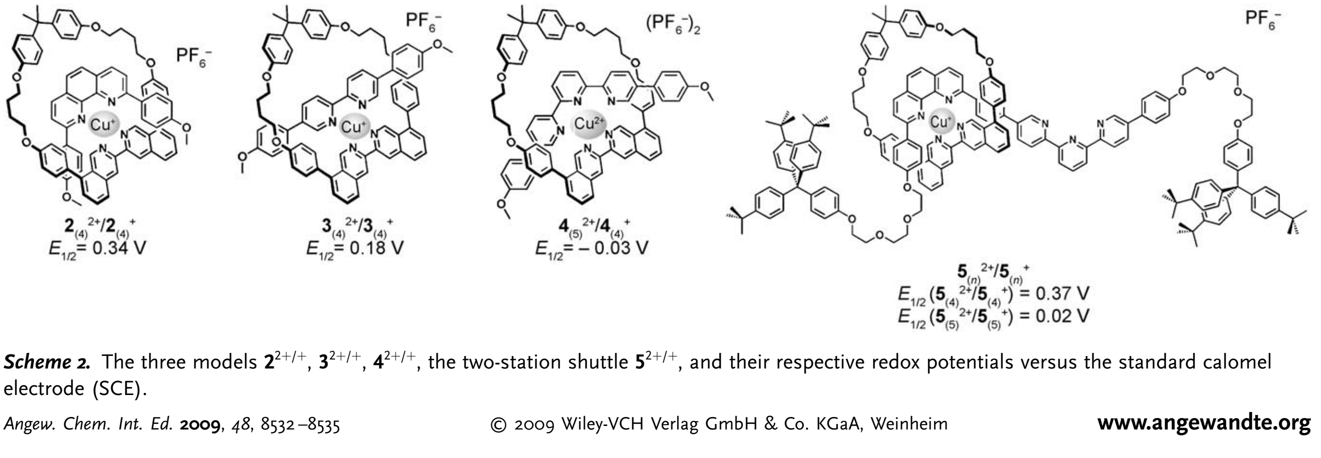


Scheme 1. Structures of the four-coordinate Cu^{I} ($\mathbf{1}_{(4)}^{+}$) and five-coordinate Cu^{II} ($\mathbf{1}_{(5)}^{2+}$) molecular shuttles in their thermodynamically stable forms. The subscripts 4 and 5 indicate the coordination number of the copper center, excluding possible solvent molecules or counterions.

are given in Scheme 2. Each complex is almost identical to the corresponding form of the three-station [2]rotaxane (four-, five-, or six-coordinate). The redox potential values are thus expected to be very close for the models and for the shuttling [2]rotaxane $\mathbf{1}_{(n)}^{+}$.

By oxidizing or reducing a given thermodynamically stable state, the complex switches from one form to another so as to afford the most stable form of the compound—either $[Cu(dpp)(dpbiiq)]^{+}$ for the reduced state (four-coordinate) or $[Cu(terpy)(dpbiiq)]^{2+}$ (five-coordinate) for the oxidized state. The general principle of the shuttling rotaxane is represented in Figure 1.

As previously described for related systems,[17,30] cyclic voltammetry is well-adapted to the study of systems that display coupled electron transfer and chemical reactions such as those shown in Figure 1. The cyclic voltammograms (CVs) of $\mathbf{1}_{(4)}^{+}$, of models $\mathbf{2}_{(4)}^{+}$, $\mathbf{3}_{(4)}^{+}$, $\mathbf{4}_{(5)}^{2+}$, and of $\mathbf{5}_{(4)}^{+}$ are shown in Figure 2. The synthesis of $\mathbf{1}_{(4)}^{+}$ and the reference compounds is described in the Supporting Information. The CV of $\mathbf{2}_{(4)}^{+}$ shows a quasi-reversible redox couple at 0.34 V ($\Delta E_{p} = 160$ mV). An additional reversible redox couple at 0.63 V ($\Delta E_{p} = 100$ mV) is unambiguously assigned[17a] to $[Cu(dap)_2]^{+}$ (dap = 2,9-dianisyl-1,10-phenanthroline). The CV of the reference complex $\mathbf{3}_{(4)}^{+}$ displays a quasi-reversible redox couple at 0.18 V ($\Delta E_{p} = 170$ mV). This low redox potential reflects the high stabilization of the Cu^{II} oxidation state by two 2,2′-bipyridine-type ligands. The CV of $\mathbf{4}_{(5)}^{2+}$ and of the two-station shuttle $\mathbf{5}_{(4)}^{+}$[30b–c] also indicate a high stabilization of the copper(II) ion in a five-coordinate environment, with redox couples at −0.03 ($\mathbf{4}_{(5)}^{2+}/\mathbf{4}_{(5)}^{+}$) and 0.02 V ($\mathbf{5}_{(5)}^{2+}/\mathbf{5}_{(5)}^{+}$) respectively. For complex $\mathbf{5}_{(4)}^{+}$, the partially reversible redox couple at 0.37 V is assigned to the couple $\mathbf{5}_{(4)}^{2+}/\mathbf{5}_{(4)}^{+}$. Interestingly, the CV of the molecular shuttle $\mathbf{1}_{(4)}^{+}$ displays only two redox signals, which are located at 0.38 and −0.02 V and can be easily assigned by comparison with the model complexes to the redox couples $\mathbf{1}_{(4)}^{2+}/\mathbf{1}_{(4)}^{+}$ and $\mathbf{1}_{(5)}^{2+}/\mathbf{1}_{(5)}^{+}$, respectively. This pattern suggests that the two motion steps of the copper(II)-complexed ring from the dpp site to the bipy site and from the bipy site to the terpy site are fast on the CV timescale. This hypothesis is supported by the observation that the concentration of the species involving the intermediate bipy ligand is negligible. By varying the potential scan rate, the rate constant for the rearrangement of the four-coordinate $\mathbf{1}_{(4)}^{2+}$ to the five-coordinate $\mathbf{1}_{(5)}^{2+}$ can be



Scheme 2. The three models $\mathbf{2}^{2+/+}$, $\mathbf{3}^{2+/+}$, $\mathbf{4}^{2+/+}$, the two-station shuttle $\mathbf{5}^{2+/+}$, and their respective redox potentials versus the standard calomel electrode (SCE).

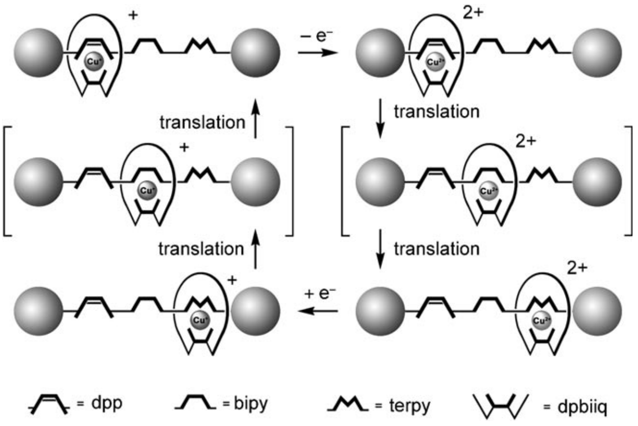


Figure 1. Principle of the electrochemically driven molecular shuttle based on copper(I) and copper(II) coordination.

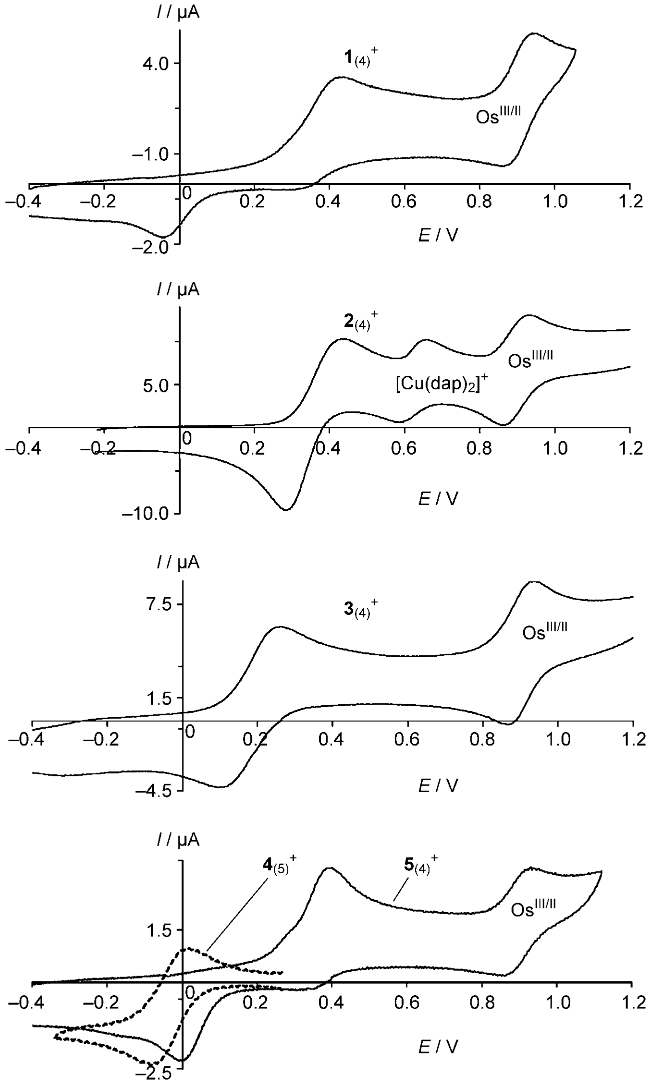


Figure 2. Cyclic voltammograms of complexes $\mathbf{1}_{(4)}^{+}$, $\mathbf{2}_{(4)}^{+}$, $\mathbf{3}_{(4)}^{+}$, $\mathbf{4}_{(5)}^{2+}$ and $\mathbf{5}_{(4)}^{+}$, recorded on a Pt working electrode in CH_2Cl_2/CH_3CN (1:9) with 0.1 M Bu_4NPF_6 at 100 $mV\,s^{-1}$. The reversible redox couple at 0.9 V versus SCE arises from $[Os(tterpy)_2](PF_6)_2$, which is used as an internal reference (see the Supporting Information).

estimated to be $0.4\,s^{-1}$.[38,39] An upper value of $50\,s^{-1}$ is estimated for the conversion of five-coordinate $\mathbf{1}_{(5)}^{+}$ to four-coordinate $\mathbf{1}_{(4)}^{+}$. The rates of these translational motion over a distance of 23 Å compare favorably with those of other related shuttles that involve shorter distances.[30b–c] This observation illustrates the importance of intermediate energy states provided by properly chosen ligands.

In conclusion, a long-distance but rapidly moving copper-based molecular shuttle, as well as threaded model compounds have been prepared and studied by electrochemical techniques. The presence of an intermediate 2,2′-bipyridine group interspersed between the two terminal chelating groups apparently has a dramatic influence on the shuttling process rate. Although it is still not certain whether the bipy group behaves as a real "station", with a certain residence time of the mobile part on this station, or if its function is simply to modify the nature of the axis and stabilize a coordinatively unsaturated copper centre during the motion, the present observations pave the way to long-distance copper-based shuttles and related molecular machines that are able to undergo linear motion.

Received: June 18, 2009

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

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