CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200802249

Electrochemically Driven Sequential Machines: An Implementation of Copper Rotaxanes

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We propose to use the redox states and ligand reorganization characteristics of a copper rotaxane mechanical machine[2] to realize a finite-state machine, that is, a logic machine that possesses an integral memory unit.[3–7] These compounds provide two definite advantages for the implementation of finite-state set–reset machines: 1) A large ligand reorganization when the redox state of the Cu ion changes, which leads to a clear and reliably observable molecular hysteresis[8] and 2) a rate of reorganization comparable to the voltage sweep rate in cyclic voltammetry. We provide concrete experimental results and a simulation as proof of the principle of the operation of an all-electrochemical-cyclable finite-state machine.

Catenanes and rotaxanes constitute an important class of artificial motors[9–11] based on transition-metal complexes.[2] In view of their proposed applications as logic machines, the rate of mechanical motion is an important factor and depends on the nature of the movement.[1,12,13]

We have recently reported fast motors[14,15] based on single-copper dynamic rotaxanes, which can pirouette between two positions around the axle on a millisecond timescale. The rotaxane is made of an axle that consists of a bidentate (2,2′-bipyridine) chelate ligand with two bulky stopper groups and a ring or wheel containing a bidentate 1,10-phenantroline and a tridendate (terpyridine) binding site to which the copper ion can bind (see Figure 1). The electrochemical conversion of Cu^+ into Cu^{2+} results in the reorganization of the four-coordinate complex ($Cu^+(4)$) into a five-coordinate one ($Cu^{2+}(5)$; Eqs. (1) and (2)), a reorganization that can proceed by pirouetting of the ring around the axle. The rate of rotation was characterized by cyclic voltammetry experiments, which show that this reorganization process is a reversible reaction.[14]

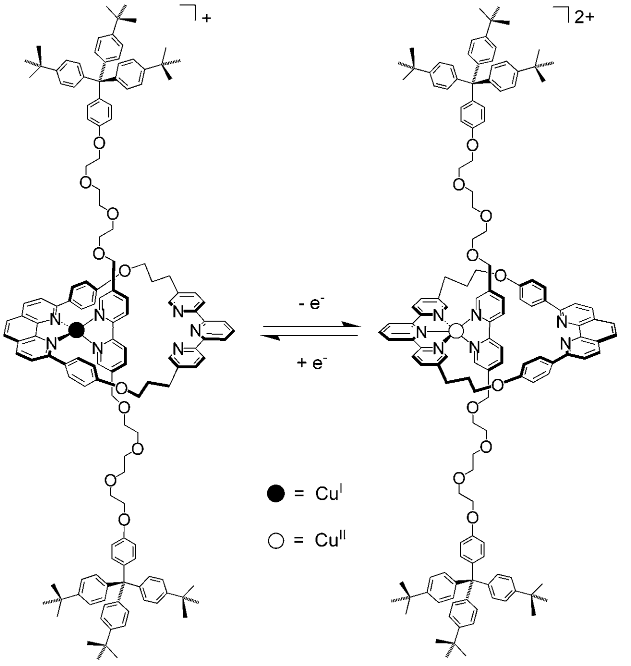

Figure 1. The structure of the synthesized fast-moving copper rotaxane[14] that is the basis for this study. The reduced $Cu^+(4)$ complex is four-coordinated whereas the oxidized one, $Cu^{2+}(5)$, is five-coordinated.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802249.

$$\mathrm{Cu^{+}(4)} \xrightleftharpoons[+e]{-e} \mathrm{Cu^{2+}(4)} \xrightarrow{5\,\mathrm{s^{-1}}} \mathrm{Cu^{2+}(5)} \quad \text{oxidation} \qquad (1)$$

$$\mathrm{Cu^{2+}(5)} \xrightleftharpoons[-e]{+e} \mathrm{Cu^{+}(5)} \xrightarrow{500\,\mathrm{s^{-1}}} \mathrm{Cu^{+}(4)} \quad \text{reduction} \qquad (2)$$

The ability of Cu rotaxanes to undergo reversible geometrical reorganization between the two different metal oxidation states makes them attractive candidates for implementing memory units. We propose here to go beyond that to the implementation of a set–reset machine,[3,4] which in addition to acting as a memory unit can also respond to inputs that switch its state.

A finite-state logic machine starts in an initial state and processes inputs one at a time; given the current state and input, the new state and output are determined by a transition table. This is shown in Table 1 and is represented in Figure 2. The notation (*n*,*m*) shows the values of the two inputs (*n*,*m*=0 (off) or 1 (on)). The stable states are represented by the two circled structures in Figure 2. The input (1,1) is not allowed because the two inputs are meant to set (1,0) or to reset (0,1) the state of the machine, so (1,1) makes no physical sense.

Table 1. Transition table for the operation of the set–reset machine.

Entry	Current state (*Q(t)*)	Set (*S*)	Reset (*R*)	Action	Next state (*Q*-(*t*+1))
1	0 ($\mathrm{Cu^{+}}$(4))	0	0	Do nothing	0 ($\mathrm{Cu^{+}}$(4))
2	0 ($\mathrm{Cu^{+}}$(4))	1	0	Set	1 ($\mathrm{Cu^{2+}}$(5))
3	0 ($\mathrm{Cu^{+}}$(4))	0	1	Reset	0 ($\mathrm{Cu^{+}}$(4))
4	1 ($\mathrm{Cu^{2+}}$(5))	0	0	Do nothing	1 ($\mathrm{Cu^{2+}}$(5))
5	1 ($\mathrm{Cu^{2+}}$(5))	1	0	Set	1 ($\mathrm{Cu^{2+}}$(5))
6	1 ($\mathrm{Cu^{2+}}$(5))	0	1	Reset	0 ($\mathrm{Cu^{+}}$(4))

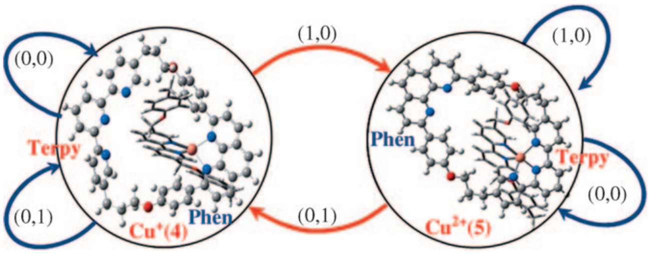

Figure 2. Operation of a set–reset logic machine based on electrochemical switching of the redox states in a Cu rotaxane followed by ligand reorganization ($\mathrm{Cu^{+}}$(4) to $\mathrm{Cu^{2+}}$(5)). The geometries of $\mathrm{Cu^{+}}$(4) and $\mathrm{Cu^{2+}}$(5) are also shown. For clarity, the 2,2′-bipyridine axle ligand is shown as sticks and the wheel ligand as balls. (Terpy: 2,2′,6′,2“-terpyridine and Phen: 1,10-phenanthroline).

While the implementations of molecular logic gates is a flourishing field (for recent reviews and examples, see refs. [16–18] and references therein), very few designs for molecular sequential machines have been reported up to now. They are driven completely[19] by light or by a combination of light and other inputs[20–22] (chemical, electrochemical) or can be addressed electrically.[6] Bistable catenanes and rotaxanes have been used by Heath, Stoddart and coworkers to implement reconfigurable logic gates by electrical addressing,[23,24] and more recently to implement highly dense memory.[25] The implementation of a set–reset machine entirely driven by an electrochemical process, proposed herein, opens the way to completely cyclable finite-state devices.

An essential characteristic of the operation of our machine is the hysteresis[8] that distinguishes between the set and reset transitions. This is due to the nature of the reorganization of the coordination about the Cu ion. During the set transition, which is initiated by an electrochemical oxidation of the $\mathrm{Cu^{+}}$ ion, a four-coordinated $\mathrm{Cu^{2+}}$ configuration is rearranging to a five-coordinated one. During the reset the five-coordinated $\mathrm{Cu^{+}}$ ion returns to its stable four-coordinated structure (Figure 2).

The molecular hysteresis is the basis of the reported implementation and leads to two well-separated oxidation and reduction peaks as can be seen in Figure 3 below. However, the reported implementation goes far beyond a mere reading of the experimental cyclic voltammogram (CV) because the time-dependent voltage profiles necessary to implement the logic operations are different from those used in cyclic voltammetry.

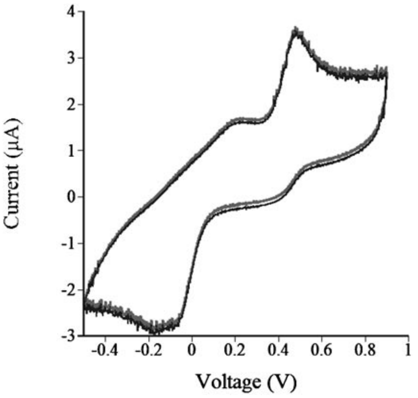

Figure 3. Experimental (——) and simulated (——) CVs based on the experimental rate constants (forward reaction rate constant $k_f = 5\ \mathrm{s^{-1}}$; backward rate constant $k_b = 500\ \mathrm{s^{-1}}$) for the copper rotaxane, determined by using the cyclic voltammetry method. See the Supporting Information for details. The following parameters were used for simulations: Platinum working electrode; number of cycles $N = 2000$; $\beta = 0.25$; potential range −0.4–1.0 V; concentrations: $C_{ox} = C_{red} = 0.001\ \mathrm{M}$; the values of the diffusion coefficients are $D_{ox}(\mathrm{Cu^{+}}(4)) = 2.642\times10^{-6}\ \mathrm{cm^2\,s^{-1}}$ and $D_{red}(\mathrm{Cu^{2+}}(5)) = 1.01\times10^{-6}\ \mathrm{cm^2\,s^{-1}}$; reaction time = 1 ms for one cycle; scan rate = 3000 mV s^{-1}; number of electrons $n = 1$; transfer coefficients $\alpha cn = \alpha an = 0.5$; electrode area $A = 3.1\ \mathrm{mm^2}$; uncompensated solution resistance $Ru = 800\ \Omega$.[14,15] In a forthcoming publication, rate constants derived theoretically from electronic structure computations (see the Supporting Information) will be compared with the experimental values.

To simulate the operation of the set–reset machine, we have implemented an explicit finite difference numerical method[26–28] and extended it to a non-monotonic variation of the applied voltage and to the computation of the concentrations of all the species ($\mathrm{Cu^{+}}$(4), $\mathrm{Cu^{2+}}$(4), $\mathrm{Cu^{+}}$(5) and

Cu^{2+}(5)) involved in the electrochemical processes. The simulated voltammogram is shown in Figure 3 (——). It is in very good agreement with the experimental one,[14] which validates our extension of the numerical method for simulating the reversible copper-rotaxane electrochemical process. More details about the method can be found in the Supporting Information.

The operation of the set–reset machine is shown in Table 1. In the implementation that we discuss herein, the set and reset inputs are provided as an applied potential difference and the state of the machine is encoded in the two stable redox species Cu^+(4) and Cu^{2+}(5). Logic state 0 corresponds to the four-coordinated Cu^+ ion and logic state 1 corresponds to the five-coordinated Cu^{2+} ion. Because of the hysteretic nature of the process, the Cu^+(4) and Cu^{2+}(5) species are reached by applying different potentials and this is what allows the set–reset machine to be realised.

The set–reset implementation requires three values of potential to be defined: set, reset and do-nothing values.[3] The value of the set potential was taken to be +1.0 V, which as one can see from Figure 3 is the potential at which Cu^{2+}(5) (logic state 1) is the stable species, whereas that of the reset potential was fixed at −0.4 V, which is the region in which Cu^+(4) is stable (logic state 0). We take the value of the do-nothing potential to be at +0.2 V. Because of the hysteresis in the redox cycle (see Figure 3), at the do-nothing potential, the machine is in state 0 (Cu^+(4)) for the oxidation process and in state 1 (Cu^{2+}(5)) in the reduction stage.

While the values of the potential for the set, reset and do-nothing actions can be inferred from the CV, it does not give precise enough information on the relative amounts of the different species that coexist at a given value of the applied potential. It is however essential for the operation of the machine, and in particular for its cyclability, that for each line of Table 1, the dominant species is the one indicated in the last column. To ensure that this is indeed the case, we used our numerical simulation method to find the optimal values for the switching rate and duration of the voltage steps. The results are shown in Figure 4.

In Figure 4 top, we show the profile of voltage that realizes a do-nothing action followed by a set, a reset and then a do-nothing step. The resulting time evolution of the concentrations of Cu^+(4) (state 0), Cu^{2+}(4), Cu^{2+}(5) (state 1) and Cu^+(5) species is shown in Figure 4 bottom, and was computed as a function of the applied voltage by using the kinetic model described in the Supporting Information.

During the forward scan, −0.4 to +1.0 V, the computed concentration profiles shown in Figure 4, bottom, clearly show the depletion of Cu^+(4) species, the formation of the transient Cu^{2+}(4) species and then rearrangement to stable Cu^{2+}(5). This is accompanied by anodic peak current at +0.46 V as shown in Figure 3. When the direction of the potential scan is reversed at +1.0 V to a negative scan rate, Cu^{2+}(5) remains the dominant species until the applied potential becomes sufficiently negative, at around −0.1 V, to cause the reduction of Cu^{2+}(5) to the transient Cu^+(5) species, which then rearranges into Cu^+(4). The corresponding cathodic peak can be seen at −0.14 V in Figure 3. The steps at which the set and the reset potential are kept constant for the operation of the machine ensure that the conversion to the stable Cu^{2+}(5) species (oxidation) or to the Cu^+(4) species (reduction) is complete.

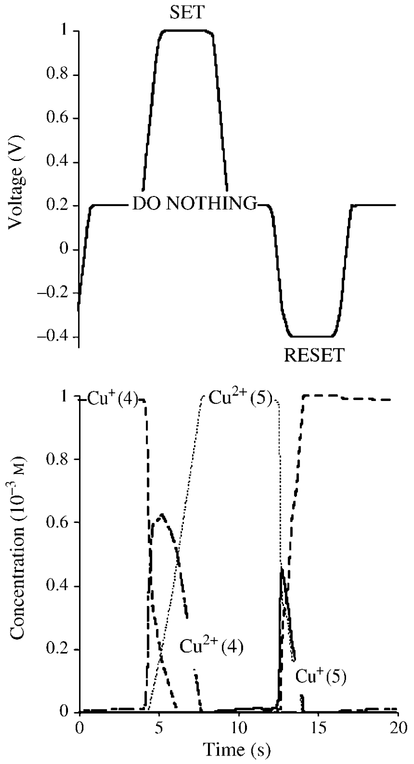

Figure 4. Operation of the set–reset machine. Top: Applied time-dependent voltage profile. The set potential value is +1.0 V, the reset potential is −0.4 V and the base line or do-nothing value is 0.2 V. The value of the scan rate is 3 V s $^{-1}$ as in Figure 3. The length of the step for constant value was chosen such that there is complete conversion for the slowest process (reorganization of Cu^{2+}(4) to Cu^{2+}(5)). Bottom: computed concentrations of the four species Cu^+(4), Cu^{2+}(4), Cu^+(5) and Cu^{2+}(5) as a function of the applied voltage potential, see the Supporting Information for details.

One can see from Figure 4 that the set operation from logic state 0 to 1 (Table 1, entry 2) and the reset operation from state 1 to 0 (Table 1, entry 6) are readily obtained as expected from the CV shown in Figure 3. Because the reset potential that we applied (−0.4 V) is higher than the one expects for the reduction of Cu^+(4),[29] applying the reset potential does not change the logic state of the machine when it is in state 0 (Table 1, entry 3). Similarly, applying the set potential to Cu^{2+}(5) does not lead to its oxidation, which is expected to occur at a higher potential[30] and, therefore, does not alter the state of the system (Table 1, entry 5).

The steps that pose a challenge for the correct operation of a set–reset machine are the do-nothing actions applied to logic states 0 and 1 (Table 1, entries 1 and 4). The response to "do nothing" is not easy to realise experimentally because the same range of do-nothing potential must leave the system in logic state 0 if it was initially in this state (Table 1, entry 1) and similarly, logic state 1 must remain unchanged when the do-nothing potential is applied (Table 1, entry 4). It is possible to realise these two lines in Table 1 because of the hysteresis in the redox process. If the system is in state 0 (physically in the Cu^+(4) state) and one applies a potential of +0.2 V, one can see from Figure 4 that the machine remains in state 0. The same reasoning applies for the do-nothing action on logic state 1. If the system is in the Cu^{2+} (5) state and the potential is brought to +0.2 V, the machine remains in state 1 (Cu^{2+}(5)).

To summarize, we propose a physical implementation of a set–reset machine that is entirely electrochemically driven. The redox process and the geometrical reorganization that follows the oxidation change are used in an essential way to realise all the actions of a set–reset machine. The state of the machine is encoded in the two stable forms of the two redox states of a Cu ion, Cu^+(4) and Cu^{2+}(5), which differ in their coordination number. While it is not required to read the state of the machine when it operates as a set–reset (because it is a Moore machine[3]), the state could be detected by using cathodic and anodic currents, as shown in Figure 3. When the machine is in state 0 and a set potential is applied, an anodic peak (oxidation) is observed, whereas if the machine is in state 1 and the reset potential is applied, one observes a cathodic peak (reduction).

An important practical feature of the machine is that it can be cycled a large number of times. Another appealing prospect would be to demonstrate the operation of the machine when the copper rotaxane is anchored on a surface.[31]

Acknowledgements

This work is partially supported by the EC STREP FET-open MOLDYNLOGIC. The work of G.P. is supported by an Inter-University Attraction Pole (AIP) project “Clusters and Nanowires” of the Belgian federal government. F.R. is also at FNRS, Belgium.

Keywords: copper • molecular devices • molecular hysteresis • rotaxanes • set–reset machines

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Received: October 29, 2008