DOI: 10.1002/ejic.200700215

Pirouetting Copper(I)-Assembled Pseudo-Rotaxanes: Strong Influence of the Axle Structure on the Motion Rate

Jean-Paul Collin,^[a] Fabien Durola,^[a] Pierre Mobian,^[a] and Jean-Pierre Sauvage*^[a]

Keywords: Pseudo-rotaxanes / Diimine ligands / Copper complexes / Coordination modes / Pirouetting motion

Based on the gathering and threading effect of copper(I), three different pseudo-rotaxanes have been prepared and characterised in solution. They consist of the same two-chelate ring and various coordinating fragments threaded through the ring. The ring-incorporated chelates are a 2,2',6',6''-terpyridine (terpy) unit and a 2,9-diphenyl-1,10-phenanthroline (dpp) motif. The threaded chelates are a 2,9-bis(*p*-anisyl)-1,10-phenanthroline (dap), a 6,6'-bis(*p*-anisyl)-2,2'-bipyridine (dabipy) or a 8,8'-diphenyl-3,3'-biisoquinoline (dpbiiq) derivative. Using electrochemical techniques, the pirouetting motions of the axle within the ring through which it is threaded have been investigated. In dichloromethane/acetonitrile, a strong dependence of the motion rate on the structure of the threaded chelate has been observed, evidencing that rigidity of the thread-contained chelate and steric hindrance lead to slow moving molecular machines. Pirouetting is the main dynamic process observed but unthreading of the string-like organic component represents another minor electrochemically induced reaction.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The field of synthetic molecular machines and motors is receiving much attention,^[1] either in relation to catenanes and rotaxanes^[2] or based on non-interlocking molecules.^[3] In this former family of compounds, transition metal-containing systems have been much investigated.^[4] As far as interlocking molecular assemblies are concerned, transition metals play an equally important role. Our group has proposed several types of dynamic systems, the mobile components of the machine being set in motion either by an electrochemical signal,^[5] a photochemical stimulus^[6] or a chemical reaction.^[7] Copper-containing pirouetting rotaxanes represent an interesting subclass of such dynamic systems. They can be regarded as simple models of future rotary motors, whose elaboration seems today to be highly complex when interlocking compounds are used.^[8] They can also be of interest by themselves as bistable species whose states display very different geometrical properties.

In this article we would like to report on the synthesis and the dynamic properties of three copper-complexed pseudo-rotaxanes whose motions are triggered by a redox process (Cu^{II}/Cu^I). By comparing the electrochemical behaviour of these three compounds, important information on the influence of the structural parameters on the motion rate could be obtained. As far as we are aware, limited studies have been carried out on the controlled dynamic proper-

 [a] Laboratoire de Chimie Organo-Minerale, UMR 7177 du CNRS Institut de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal, 67000 Strasbourg Cedex, France Fax: +33-390-241-368 E-mail: sauvage@chimie.u-strasbg.fr

InterScience[®]

ties of pseudo-rotaxanes. The first one is particularly significant since it triggered the interest of the scientific community for interlocking compounds-based molecular machines.^[9] Later on, our group has made and investigated a shuttle-like pseudo-rotaxane^[10] and its corresponding rotaxane.^[11] Although shuttling of the pseudo-rotaxane was clearly evidenced, we could also identify another process, the unthreading reaction, which interfered with the ring translation motion. Obviously, the rates of both processes must be related since some of the rearrangement steps for these distinct reactions are identical.

Results and Discussions

The pirouetting rearrangement described herein is sketched in Scheme 1. The three threaded species have been prepared according to the classical procedure from our group, based on coordination of two bidentate chelates on a copper(I) centre.^[12] Obviously, the cyclic nature of **4** prevents formation of tetrahedral copper(I) complexes consisting of two such dpp-containing ligands. This simple principle has important consequences since the coordination reaction will necessarily lead to the formation of a threaded species provided the correct copper(I)-two-bidentate ligand stoichiometry is respected.^[13] The copper(I)-induced gathering and threading reaction is represented in Figure 1 along with the chemical formulae of the various precursors and the products.

Compound **4** is a 33-membered ring that has been used in several studies carried out in our group on controlled dynamic catenanes and rotaxanes. The presence of the terpy





Scheme 1. Pirouetting principle of copper complexed pseudo-rotaxanes. The U-shaped symbols represent bidentate chelates (dpp for the ring-comprised chelate and dap, dabipy or dpbiiq for the chelates belonging to the thread). The M-shaped symbol designates the tridentate terpy coordinating motif.

site in its structure does not interfere with the threading reaction since copper(I) interacts preferably with bidentate chelates such as dpp. This behaviour has been unambiguously demonstrated by ¹H-NMR analysis of the concerned pseudo-rotaxanes. The three string-like fragments contain

FULL PAPER

markedly different chelates. 5 incorporates a dpp unit. It is thus a highly rigid block due to the presence of the 1,10phenanthroline core. At the same time it is rather bulky due to the two phenyl groups close to the coordination site of the ligand. 6 is equally sterically hindering but the pyridine nuclei of the 2,2'-bipy fragment can easily rotate with respect to one another about the $C^2-C^{2'}$ bond. Finally, the dpbiiq fragment of 7 is such that steric hindrance around the complexing site of the ligand is limited, due to the large separation between the two lateral phenyl rings borne by the 3,3'-biisoquinoline nucleus. In addition, free rotation about the $C^3-C^{3'}$ bond allows this ligand to rearrange easily. Ligand 7 could be obtained in high yield via a two-step procedure as depicted in Figure 2. The first step concerns the formation of diphenol compound 9 from 8,8'-dianisyl-3,3'-biisoquinoline (8) using a classical ether deprotection method. The resulting diphenol 9 was then converted into the target ligand 7 following a classical Williamson methodology (Cs₂CO₃, DMF, 55 °C) by reaction with 2 equiv. of commercially available 2-(6-bromohexyloxy)-tetrahydro-2*H*-pyran.

Three complexes 1_4^+ , 2_4^+ and 3_4^+ were synthesized as shown in Figure 1. The synthesis of these copper complexes were performed using a methodology usually employed in our group. In a typical procedure, the macrocycle 4 was dissolved in a degassed solution of dichloromethane and



Figure 1. Copper(I)-directed synthesis of the three pseudo-rotaxanes $\mathbf{1}_{4^+}$, $\mathbf{2}_{4^+}$ and $\mathbf{3}_{4^+}$ described in this article. The subscript 4 refers to the coordination number of the copper centre. In the copper(I) complexes of the graphic, the coordination number is equal to 4 since the metal is coordinated to a dpp fragment and another bidentate chelate belonging to the thread.

FULL PAPER



Figure 2. Preparation of ligand 7 from 8,8'-bis(*p*-anisyl)-3,3'-bisoquinoline (8). The demethylation reaction is quantitative. Compound 7 can be obtained in good yield from 9 after chromatographic separation.

acetonitrile (1:1). Upon addition of the copper salt (1 equiv.), the solution turned immediately to dark orange. The reaction mixture was stirred for 20 min and the diimine ligand (respectively 5, 6 and 7) was then added. A dark red solution was instantaneously obtained. This color, which is

characteristic of copper(I) complexes of aromatic diimine ligands, indicates that the complexation process occurred efficiently. After, the solution was stirred for two hours under argon at room temperature, and the solvents were evaporated. The complexation process occurred quasi-quantitavely as evidence by ¹H-NMR spectroscopy. Due to their instability on chromatographic supports, complexes 1_4^+ , 2_4^+ or 3_4^+ were not further purified and were directly submitted to the electrochemical measurements.

Electrochemically-Driven Molecular Motions

The cyclic voltammograms of Scheme 2 have been obtained by scanning first from -0.4 V to +1.0 V, with a silver wire as a pseudo-reference electrode, the return scan being carried out immediately after the potential of +1.0 V was reached. The oxidation potential for the reaction

4-coordinate Cu^{I} complex $-e^{-} \rightarrow$ 4-coordinate Cu^{II} complex

is thus easily read from the cyclic voltammograms. Their values at a scan rate of 800 mV/s are indicated on the Scheme 2.



Scheme 2. Cyclic voltammograms of complexes 1_4^+ , 2_4^+ and 3_4^+ recorded with a Pt working electrode in CH₂Cl₂/CH₃CN (1:9) with 0.1 M Bu₄NBF₄ at four different scan rates (20, 100, 400 and 800 mV/s). The electrochemical responses of the four-coordinate copper(II) complexes are found around +0.7 V (for 1^{2+} and 2^{2+}) or around +0.5 V (for 3^{2+}), whereas reduction of five-coordinate copper(II) complexes 1_5^{2+} , 2_5^{2+} and 3_5^{2+} occurs around -0.1 V.

At a high scan rate, the return wave corresponding to the following process

4-coordinate Cu^{II} complex + $e^- \rightarrow$ 4-coordinate Cu^I complex

is easily observed, which allows to determine $E_{1/2}$ and ΔEp for the three studied complexes:

$$\mathbf{1}_4^{2+}/\mathbf{1}_4^{+}$$
: $E_{1/2} = +0.76$ V

 $2_4^{2+}/2_4^+$: $E_{1/2} = +0.77 \text{ V}$

 $3_4^{2+}/3_4^+$: $E_{1/2} = +0.49$ V

 ΔEp varies between 80 mV and 120 mV within the series of three complexes. At a lower scan rate, rearrangement of the thermodynamically unstable four-coordinate copper(II) takes place, at least in part, before this complex is reduced back to its monovalent corresponding state. This is clearly seen by the presence of a peak between -0.2 V and 0 V.

From the $E_{1/2}$ values of the four-coordinate complexes, it is clear that the four-coordinate copper(I) state is more stabilised in $\mathbf{1}_4^+$ and $\mathbf{2}_4^+$ than in complex $\mathbf{3}_4^+$. This can easily be understood by considering the steric arrangements of the compounds. Whereas $\mathbf{1}_4^+$ and $\mathbf{2}_4^+$ contain a highly shielding set of ligands (both chelates of each complex bear phenyl rings attached on the *ortho* positions to the N atoms), the thread of $\mathbf{3}_4^+$ is less encumbering.

As far as the five-coordinate copper(I) or copper(II) states are concerned, important information can be obtained at low scan rate. By analogy with the oxidation potentials of the four-coordinate copper(I) complexe, the reduction potentials of the corresponding five-coordinate copper(II) complexes can easily be estimated from the cyclic voltammograms. They are also indicated on Scheme 2, for a scan rate of 20 mV/s. It is noteworthy that the reduction potentials (Cu^{II}/Cu^I) for the three studied complexes are almost identical ($E_{red} \approx -0.07$ V). This observation tends to indicate that, as expected, the five-coordinate state is less sensitive to steric hindrance than the tetrahedral or pseudotetrahedral geometry.

The chemical reversibility of the redox processes depends much on the nature of the complex and on the scan rate. As already observed with pirouetting rotaxanes,^[5] as the scan rate is increased, the reversibility of the four-coordinate copper(I) complex oxidation reaction increases. By scanning at a lower and lower rate, rearrangement of the system becomes more and more noticeable, as evidenced by the increase of the wave corresponding to the reduction of the five-coordinate copper(II) complex. In parallel, the reduction wave for the four-coordinate complex decreases. Generally speaking, if this latter one is intense, this implies that the compound has no time to rearrange substantially. By contrast, if the reduction wave around +0.42 V (for 3_4^{2+}) is small, the complex undergoes a complete rearrangement to a large proportion.

If the scan rate is sufficiently slow (< 20 mV/s), the three complexes have time to rearrange as shown by the absence of any reduction wave at +0.4 V to +0.8 V. On the other hand, the presence of a reduction wave at a slightly negative potential may indicate that a certain proportion of the four-coordinate copper(II) complex underwent a pirouetting

motion, which does not exclude that a certain amount led to unthreading and dissociation.

By comparing 1^{n+} and 2^{n+} , especially at 100 mV/s, it is obvious that 1_4^{2+} is much less mobile than 2_4^{2+} . This is confirmed at 400 mV/s since at this scan rate, 1_4^{2+} does not seem to rearrange significantly whereas the major part of 2_4^{2+} is converted into the rearranged complex 2_5^{2+} . The difference between 1^{n+} and 2^{n+} holds to the presence of a 1,10phenanthroline (phen) unit in the thread of the former complex and 2,2'-bipyridine (bipy) chelate for the latter complex. The comparison between their electrochemical properties allows to estimate the effect of having a rigid block (phen) vs. a potentially flexible chelate (bipy) with rotation around the C–C bond connecting the two pyridine nuclei. It should be noticed that both threads (in 1^{n+} and 2^{n+}) are equally sterically hindering since they contain the same number of phenyl rings at identical positions.

Very spectacular is the effect of the biisoquinoline ligand, as demonstrated by the electrochemical behaviour of 3^{n+} . Even at 800 mV/s reversibility is almost completely lost, with the appearance of a relatively intense wave at ≈ -0.1 V corresponding to the reduction process of the rearranged complex 3_5^{2+} . This observation is directly related to the non sterically hindering nature of 7 which facilitates ligand exchange in the coordination sphere of the metal. The presence of two elongating groups attached on the phenolic oxygen atoms of 7 may also increase the chemical reversibility of the pirouetting process, inhibiting at least in part the unthreading reaction.

A rough estimation of the rate constant for the rearrangement of the four-coordinate copper(II) complex can be obtained from electrochemical measurements and, in particular, from Scheme 2:

$$\begin{split} \mathbf{1}_{4}^{2+} &\to \mathbf{1}_{5}^{2+}, \, k \approx 0.1 \, \mathrm{s}^{-} \\ \mathbf{2}_{4}^{2+} &\to \mathbf{2}_{5}^{2+}, \, k \approx 1 \, \mathrm{s}^{-1} \\ \mathbf{3}_{4}^{2+} &\to \mathbf{3}_{5}^{2+}, \, k \approx 5 \, \mathrm{s}^{-1} \end{split}$$

Concerning the pirouetting motion, pseudo-rotaxane 3^{n+} , incorporating a dpbiiq fragment in its thread, is about 50 times more efficient than pseudo-rotaxane 1^{n+} , which threaded ligand (dap) is more rigid and more sterically hindering.

As far as the rearrangement of the five-coordinate copper(I) complexes is concerned, the reaction was shown to be too fast for the presently used electrochemical techniques. This is in good agreement with previous studies.^[5]

Conclusion

Three copper(I)-assembled pseudo-rotaxanes were synthesized. These molecular machine precursors contain the same two-chelate ring and three different diimine ligands threaded through the macrocycle. The rearrangement of these complexes from the four-coordinate Cu^{II} to the fivecoordinate Cu^{II} species has been investigated by cyclic voltammetry. The electrochemical responses clearly show a great difference of dynamic behaviour between these three

FULL PAPER

prepared pseudo-rotaxanes. An estimation of the rate of ligand exchange was possible. These results highlight that the flexibility of the threaded chelate and low steric hindrance of its coordination site give rise to fast-moving molecular machines.

Experimental Section

The following chemicals were obtained commercially and were used without further purification: 2-(6-bromohexyloxy)-tetrahydro-2*H*-pyran (Aldrich), cesium carbonate (Aldrich).

Dry solvents were obtained with suitable dessicants: *N*,*N*-dimethylformamide was distilled from anhydrous aluminum oxide, dichloromethane from calcium hydride. Fluka aluminum oxide (no. 17994) was used for alumina columns and filtrations.

¹H NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz, ¹H) spectrometer using deuterated solvents. The spectra were collected at 25 °C and the chemical shifts were referenced to residual solvent protons as internal standards. ¹H: [D₆]DMSO δ = 2.50 ppm, CD₂Cl₂ δ = 5.32 ppm, CD₃CN δ = 1.93 ppm. Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in positive or negative mode (ES-MS).

Electrochemical measurements were performed with a three-electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and a silver wire as a pseudo-reference electrode. All measurements were carried out at room temperature under Ar, in degassed spectroscopic grade solvents, using 0.1 M nBu_4NBF_4 solutions in CH₂Cl₂/CH₃CN (1:9) as supporting electrolyte. An EG&G Princeton Applied Research model 273A potentiostat connected to a computer was used (software from Electrochemistry Research).

8,8'-Dihydroxyphenyl-3,3'-biisoquinoline (9): 8,8'-Dianisyl-3,3'-biisoquinoline **(8)** (1.00 g, 2.13 mmol) and pyridinium chloride (about 10 equiv., 2.5 g) are mixed into a little flask and heated to reflux in an adapted microwave oven for 10 min. Twice, the same quantity of pyridinium chloride is added and the mixture heated to reflux again for 10 min. The mixture is dissolved in distilled water (1 L) and then neutralised with sodium hydroxide to give a suspension of a pale yellow precipitate. After filtration, the given compound is quantitatively obtained without further purification (pale yellow solid, 94 mg, 100%). M.p. > 300 °C. ¹H NMR ([D₆]-DMSO, 300 MHz): δ = 9.35 (s, 2 H), 9.09 (s, 2 H), 8.15 (d, *J* = 8.2 Hz, 2 H), 7.94 (t, *J* = 7.7 Hz, 2 H), 7.65 (d, *J* = 7.0 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 4 H), 7.00 (d, *J* = 8.4 Hz, 4 H) ppm. ES-MS: *m*/*z* = 441.1559 (calculated 441.1598 for C₃₀H₂₀N₂O₂ + H⁺).

Ligand 7: 2-(6-Bromohexyloxy)-tetrahydro-2*H*-pyran (180 mg, 0.68 mmol), cesium carbonate (150 mg, 0.45 mmol) and 8,8'-dihydroxyphenyl-3,3'-biisoquinoline **9** (50 mg, 0.11 mmol) were mixed in dry DMF (10 mL) and stirred under Ar at 55 °C overnight. The solvent was removed and the residue was taken up with CH₂Cl₂/H₂O. The organic phase was separated and the aqueous phase extracted twice with dichloromethane. The combined organic phases were washed first with brine, then with distilled water. The solvent was removed and the residue purified by chromatography over aluminium oxide by using dichloromethane/pentane (1:4) as the eluent to give the title compound (white solid, 60 mg, 65%). ¹H NMR (CD₂Cl₂, 300 MHz): δ = 9.47 (s, 2 H), 8.98 (s, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.78 (dd, *J* = 8.1, 8.4 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 8.7 Hz, 4 H), 7.12 (d, *J* = 8.7 Hz, 4 H), 4.60 (t, *J* = 3.7 Hz, 2 H), 4.12 (t, *J* = 6.6 Hz, 4 H), 3.92–3.74 (m, 4 H), 3.54–

3.40 (m, 4 H), 1.93–1.42 (m, 28 H) ppm. ES-MS: m/z = 809.4720 (calculated 809.4530 for $C_{52}H_{60}N_2O_6 + H^+$).

Cu^I Complexes 1_4^+ , 2_4^+ and 3_4^+ : In a typical procedure, Cu(CH₃CN)₄PF₆ was added to a stirred and degassed solution of macrocycle 4 dissolved in CH₂Cl₂/CH₃CN (50:50). A deep orange coloration appeared instantly. After 30 min at room temperature, the diimine ligand (respectively 5, 6 or 7) was added as a solid to the solution, which immediately turned dark red. After the solution was stirred for two hours under argon at room temperature, the solvents were removed under high vacuum. A dark red solid was obtained quasi-quantitavely (NMR control). Due to its instability on alumina and on silica gel, complexes were not further purified and were directly submitted to the electrochemical measurements.

1₄⁺: ¹H NMR (CD₂Cl₂, 300 MHz): δ = 8.76 (d, *J* = 7.2 Hz, 2 H), 8.68 (br., 2 H), 8.49 (d, *J* = 8.4 Hz, 2 H), 8.45 (d, *J* = 8.7 Hz, 2 H), 8.41 (br., 2 H), 8.10 (t, *J* = 7.2 Hz, 1 H), 8.04 (s, 2 H), 7.99 (s, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.7 Hz, 2 H), 7.75 (br., 2 H), 7.48 (d, *J* = 8.7 Hz, 4 H), 7.40–7.34 (m, 4 H), 6.11–6.00 (m, 8 H), 3.49 (s, 6 H), 3.25 (br., 4 H), 2.95 (br., 4 H), 2.14 (br., 4 H) ppm. ES-MS: *m*/*z* = 1132.3584 (calculated 1132.3606 for C₇₁H₅₅CuN₇O₄⁺).

2₄⁺: ¹H NMR (CD₂Cl₂, 300 MHz): δ = 8.84 (d, *J* = 7.8 Hz, 2 H), 8.75 (br. s, 2 H), 8.51 (d, *J* = 7.8 Hz, 2 H), 8.40 (d, *J* = 8.4 Hz, 2 H), 8.05 (t, *J* = 7.5 Hz, 1 H), 7.92 (s, 2 H), 7.84 (d, *J* = 8.4 Hz, 4 H), 7.74–7.67 (m, 4 H), 7.57 (d, *J* = 8.7 Hz, 4 H), 7.35 (d, *J* = 6.9 Hz, 2 H), 7.21 (d, *J* = 8.7 Hz, 4 H), 6.36 (d, *J* = 8.7 Hz, 4 H), 5.95 (d, *J* = 8.7 Hz, 4 H), 3.69 (br., 4 H), 3.35 (s, 6 H), 3.06 (br., 4 H), 2.29 (br., 4 H) ppm. ES-MS: *m*/*z* = 1108.3585 (calculated 1108.3606 for C₆₉H₅₅CuN₇O₄⁺).

3₄⁺: ¹H NMR (CD₃CN, 300 MHz): δ = 9.03 (s, 2 H), 8.71 (br. s, 2 H), 8.59 (d, *J* = 8.4 Hz, 2 H), 8.55 (s, 2 H), 8.50 (d, *J* = 7.8 Hz, 2 H), 8.32 (s, 2 H), 8.12 (t, *J* = 7.8 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 2 H), 8.01 (s, 2 H), 7.80–7.74 (m, 6 H), 7.56–7.53 (m, 6 H), 7.15 (d, *J* = 8.7 Hz, 4 H), 6.86 (d, *J* = 8.4 Hz, 4 H), 6.14 (d, *J* = 8.7 Hz, 4 H), 4.48 (t, *J* = 4.5 Hz, 2 H), 3.94–3.90 (m, 4 H), 3.74–3.60 (m, 4 H), 3.35 (br., 8 H), 2.90 (br., 4 H), 2.03 (br., 4 H), 1.70–1.38 (m, 28 H) ppm. ES-MS: *m*/*z* = 1548.6520 (calculated 1548.6533 for C₉₇H₉₅CuN₇O₈⁺).

Acknowledgments

Funding from the following institutions is gratefully acknowledged: the Centre National de la Recherche Scientifique (CNRS) and the Région Alsace (fellowship to F. D.), the European Commission (MOLDYNLOGIC) and the European Communities (BIOMACH NMP-2002-3.4.1.1-3, contract 505487-1; financial support and fellowship to P. M.).

Special Issue: Acc. Chem. Res. 2001, 34, 341; J.-P. Sauvage, Structure and Bonding: Molecular Machines and Motors, Springer: Berlin, Heidelberg, 2001, 99; V. Balzani, M. Venturi, A. Credi, Molecular Devices and Machines, Wiley-VCH, Weinhein, 2003; E. R. Kay, D. A. Leigh, F. Zerbetto, Angew. Chem. Int. Ed. 2007, 46, 72.

^[2] R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* 1994, 369, 133; J.-P. Sauvage and C. O. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, 1999; C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* 2000, 289, 1172; A. N. Shipway, I. Willner, *Acc. Chem. Res.* 2001, 34, 421; A. Harada, *Acc. Chem. Res.* 2001, 34, 456; D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Na*-

ture 2003, 424, 174; B. Korybut-Daszkiewicz, A. Wieckowska, R. Bilewicz, S. Domagata, K. Wozniak, *Angew. Chem. Int. Ed.* 2004, 43, 1668; J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* 2004, 303, 1845; K. Kinbara, T. Aida, *Chem. Rev.* 2005, 105, 1377; J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* 2005, 4, 704; V. Balzani, M. Clemente-Leon, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *PNAS* 2006, 103, 1178.

- [3] L. Zeeikovich, J. Libman, A. Shanzer, *Nature* 1995, 374, 790;
 T. R. Kelly, H. de Silva, R. A. Silva, *Nature* 1999, 401, 150; L. Fabbrizzi, F. Foti, S. Patroni, P. Pallavicini, A. Taglietti, *Angew. Chem. Int. Ed.* 2004, 43, 5073; A. Koçer, M. Walko, W. Meijberg, B. L. Feringa, *Science* 2005, 309, 755; J. Vicario, N. Katsonis, B. Serrano Ramon, C. W. M. Bastiaansen, D. J. Broer, B. L. Feringa, *Nature* 2006, 440, 163.
- [4] S. Bonnet, J.-P. Collin, M. Koizumi, P. Mobian, J.-P. Sauvage, Adv. Mater. 2006, 18, 1239; B. Champin, P. Mobian, J.-P. Sauvage, Chem. Soc. Rev. 2007, 36, 358.
- [5] A. Livoreil, C. O. Dietrich-Buchecker, J.-P. Sauvage, J. Am. Chem. Soc. 1994, 116, 9399; L. Raehm, J.-M. Kern, J.-P. Sauvage, Chem. Eur. J. 1999, 5, 3310; M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, Angew. Chem. Int. Ed. 2000, 39, 3284;
 I. Poleschak, J.-M. Kern, J.-P. Sauvage, Chem. Commun. 2004, 474; U. Létinois-Halbes, D. Hanss, J. M. Beierle, J.-P. Collin, J.-P. Sauvage, Org. Lett. 2005, 7, 5753.
- [6] N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, J. Am. Chem. Soc. 1999, 121, 4397; J.-P. Collin, A.-

C. Laemmel, J.-P. Sauvage, *New J. Chem.* **2001**, *25*, 22; P. Mobian, J.-M. Kern, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2004**, *43*, 2392; S. Bonnet, J.-P. Collin, J.-P. Sauvage, *Inorg. Chem.* **2006**, *45*, 4024.

- [7] M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, Angew. Chem. Int. Ed. 2000, 39, 3284–3287; J.-P. Collin, C. O. Dietrich-Buchecker, P. Gaviña, M. C. Jiménez-Molero, J.-P. Sauvage, Acc. Chem. Res. 2001, 34, 477.
- [8] D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* 2003, 424, 177; J. V. Hernandez, E. R. Kay, D. A. Leigh, *Science* 2004, 306, 1532.
- [9] R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301.
- [10] J.-P. Collin, P. Gaviña, J.-P. Sauvage, Chem. Commun. 1996, 2005.
- [11] J.-P. Collin, P. Gaviña, J.-P. Sauvage, New J. Chem. 1997, 21, 525; N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, J. Am. Chem. Soc. 1999, 121, 4397.
- [12] C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, *Tetra-hedron Lett.* 1983, 24, 5098; C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* 1987, 87, 795.
- [13] J.-C. Chambron, C. O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, J. Chem. Soc., Chem. Commun. 1993, 801; J.-C. Chambron, C. O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, Pure Appl. Chem. 1994, 66, 1543.

Received: February 16, 2007 Published Online: April 26, 2007