RESEARCH FRONT

CSIRO PUBLISHING

Full Paper

www.publish.csiro.au/journals/ajc

Aust. J. Chem. **2009**, *62*, 1231–1237

Copper-Complexed Pirouetting [2]pseudorotaxanes with Sulfur-Containing End-Groups Attached to the Thread: Synthesis, Electrochemical Studies, and Deposition on Gold Electrodes

Jean-Paul Collin,[A] *Pierre Mobian,*[A] *Jean-Pierre Sauvage,*[A,C] *Angélique Sour,*[A]
Yi-Ming Yan,[B] *and Itamar Willner*[B]

[A]Laboratoire de Chimie Ogano-Minérale, LC3 UMR 7177 du CNRS, Université de Strasbourg,
Institut de Chimie, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France.
[B]Institute of Chemistry, The Hebrew University of Jerusalem, 91904, Jerusalem, Israel.
[C]Corresponding author. Email: sauvage@chimie.u-strasbg.fr

Two copper [2]pseudorotaxanes incorporating a macrocycle with two chelating sites (2,9-diphenyl-1,10-phenanthroline and 2,2′,6′,2″-terpyridine) and a thread based on crescent-shaped 2,2′-bipyridine derivatives have been synthesized and characterized. One of the threads was a hindering 2,2′-bipyridine functionalized by two thioctic-ended arms. The second thread was an 8,8′-diphenyl-3,3′-biisoquinoline functionalized by two thioether-ended arms. The electrochemical studies of the two copper [2]pseudorotaxanes, both in solution and anchored on a gold surface, showed only fast-moving systems in solution. The reasons of the inertness of the deposited complexes on gold electrode have been explored.

Manuscript received: 15 June 2009.
Manuscript accepted: 11 August 2009.

Introduction

Molecular machines are particularly promising in relation to future applications in various fields such as information storage and processing, nano-scale electro- or photo-chemically driven mechanical devices and imaging. This is illustrated by recent spectacular results.[1–12] Catenanes and rotaxanes[13–19] constitute an important family of such systems. The Strasbourg team has been particularly interested in transition metal complexed interlocking compounds.[20–33] When used in solution, such dynamic systems could be important to catalyze given chemical reactions or to facilitate various chemical processes related to conformational changes. However, most of the devices which could derive from these species are related to information storage, nanometric mechanical tools or imaging, which implies that the compounds are used in condensed phase (components of liquid crystals or crystalline networks, vesicles and micelles, or surface grafted species). Several examples of surface-deposited catenanes and rotaxanes have been reported.[34–41] More important in the context of molecular machines, a few recent examples showed that machine-like species could be grafted on a given surface and still retain their ability to undergo large amplitude motions.[42–47]

Transition metal-based systems have been shown to move only very slowly or even not to undergo motions at all once attached onto an electrode surface.[48–51] This disappointing observation has prompted us to modify some of the species prepared in our group whose motions are particularly fast in solution and to attach them onto a gold electrode, with the hope that electrochemically driven motions would be observed. The fastest-moving systems in solution are 'pirouetting' [2]rotaxanes, which consist of rings incorporating a dpp fragment (dpp: 2,9-diphenyl-1,10-phenanthroline), a terpy chelate (terpy: 2,2′,6′,2″-terpyridine) and a sterically undemanding axis threaded through the ring. The most efficient systems in terms of fast movements contain either a bipy (bipy: 2,2′-bipyridine) or a dpbiiq (dpbiiq: 8,8′-diphenyl-3,3′-biisoquinoline) unit in the thread.[31,52,53]

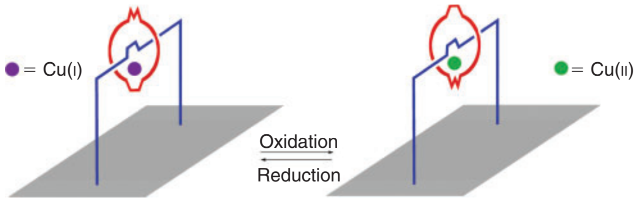

Fig. 1. Pirouetting principle of a [2]rotaxane on a surface. The U- and W-shaped symbol represent bi- and tridentate chelates respectively.

Results and Discussion

The pirouetting principle of a [2]rotaxane grafted on a surface is represented in Fig. 1.

Since the threaded components should preferably be crescent-shaped in order to facilitate a two-point attachment on the surface, the 2,2′-bipy derivative substituted at the 5,5′ positions was excluded because of its linear geometry. The two selected chelates are thus a functionalized bipy bearing two aromatic groups at the 6 and 6′ positions (dpbipy: 6,6′-diphenyl-2,2′-bipyridine) and a dpbiiq fragment. The ring is the classical two-chelate ring used by us for building several pirouetting rotaxanes and catenanes.[24,31,52]

© CSIRO 2009 10.1071/CH09334 0004-9425/09/101231

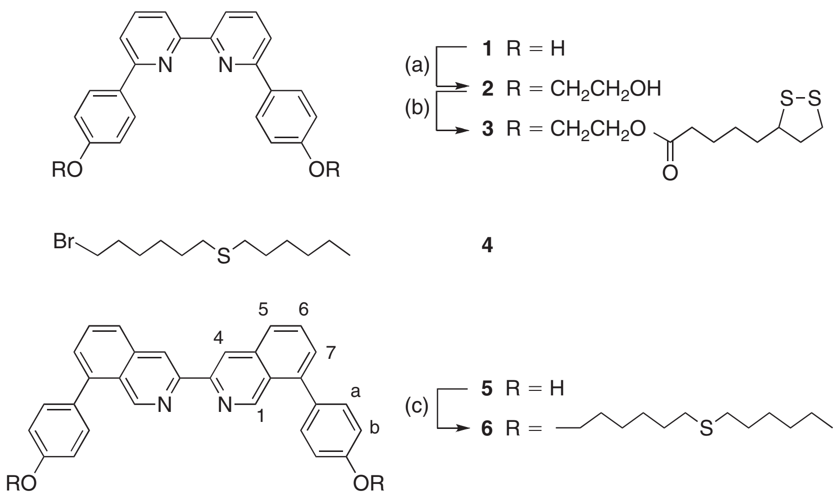

Fig. 2. Reagents and conditions for the synthesis of the threads. (a) 2-(2-bromoethoxy)tetrahydro-2*H*-pyran, Cs_2CO_3, DMF, 60°C, 84%; (b) thioctic acid, DCC, DMAP, DMF, 53%; (c) 1-bromo-6-(hexylthio)hexane, Cs_2CO_3, DMF, 45°C, 55%.

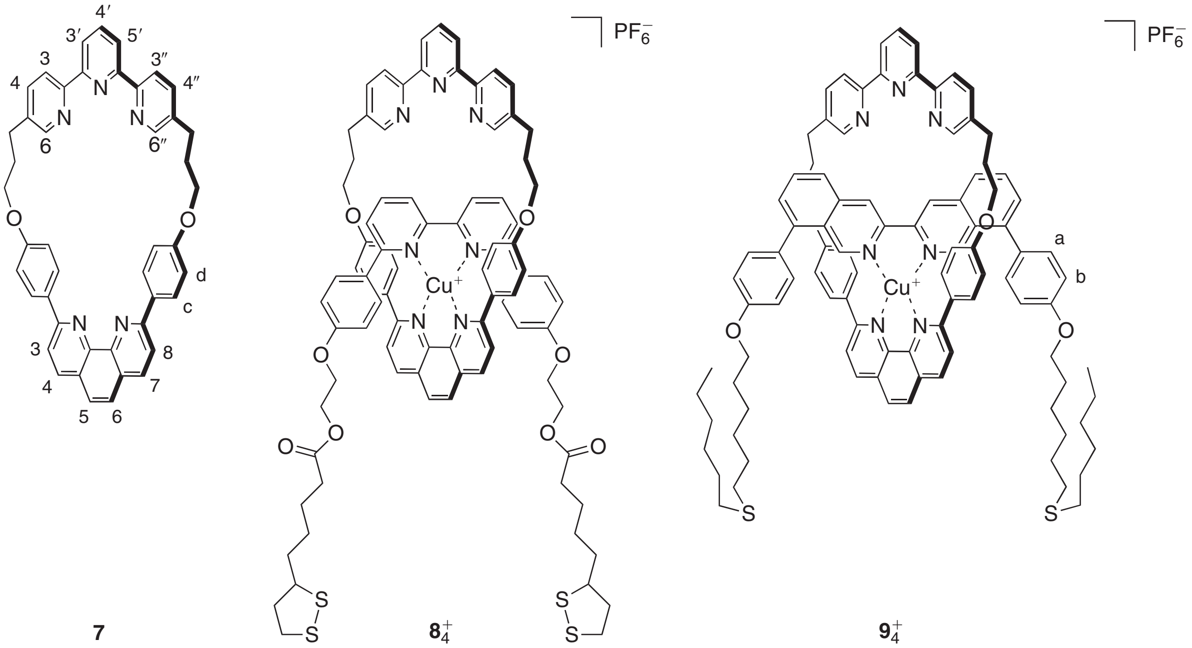

Fig. 3. Macrocycle **7** and [2]pseudorotaxanes $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$.

Synthesis and Characterization of the Compounds

The preparation of the end-functionalized bidentate chelates **3** and **6** is illustrated in Fig. 2. Thread **3** was prepared in two steps starting from 6,6′-di-*p*-hydroxyphenyl-2,2′-bipyridine (**1**), which was synthesized according to the literature procedure.[54] Reaction of **1** with protected 2-bromoethanol in the presence of Cs_2CO_3 in N,N-dimethylformamide (DMF) at 60°C, followed by removal of the protecting groups with a catalytic amount of HCl in ethanol afforded diol **2** (84% yield). An esterification reaction performed with thioctic acid in the presence of N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in DMF at room temperature gave the desired thread **3** in 53% yield. Thread **6** was synthesized from 8,8′-di-*p*-hydroxyphenyl-3,3′-biisoquinoline (**5**), whose synthesis has already been described in the literature.[31] Treatment of **5** with the sulfur-containing arms **4** (obtained by reaction of 1,6-dibromohexane with thiohexane[55]) in the presence of Cs_2CO_3 in DMF at 45°C afforded thread **6** in 55% yield.

The gathering and threading steps leading to the [2]pseudorotaxanes $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$ have been performed in a classical manner (Fig. 3).[20] Reaction of the macrocycle **7** with a stoichiometric amount of $[Cu(CH_3CN)]PF_6$ in CH_3CN/CH_2Cl_2 and, subsequently, the thread (**3** and **6**) at room temperature led quantitatively to the deep red [2]pseudorotaxanes ($\mathbf{8}_4^+$ and $\mathbf{9}_4^+$, respectively) as their PF_6^- salt.

^1H NMR and electronspray mass spectrometry (ES-MS) spectra are in full accordance with the expected structures. Fig. 4 presents the ^1H NMR spectra of compounds **6**, **7**, and $\mathbf{9}_4^+$ and illustrates the chemical shift changes characteristic of the copper complexation. In particular, protons 1 and 4 of thread **6** undergo

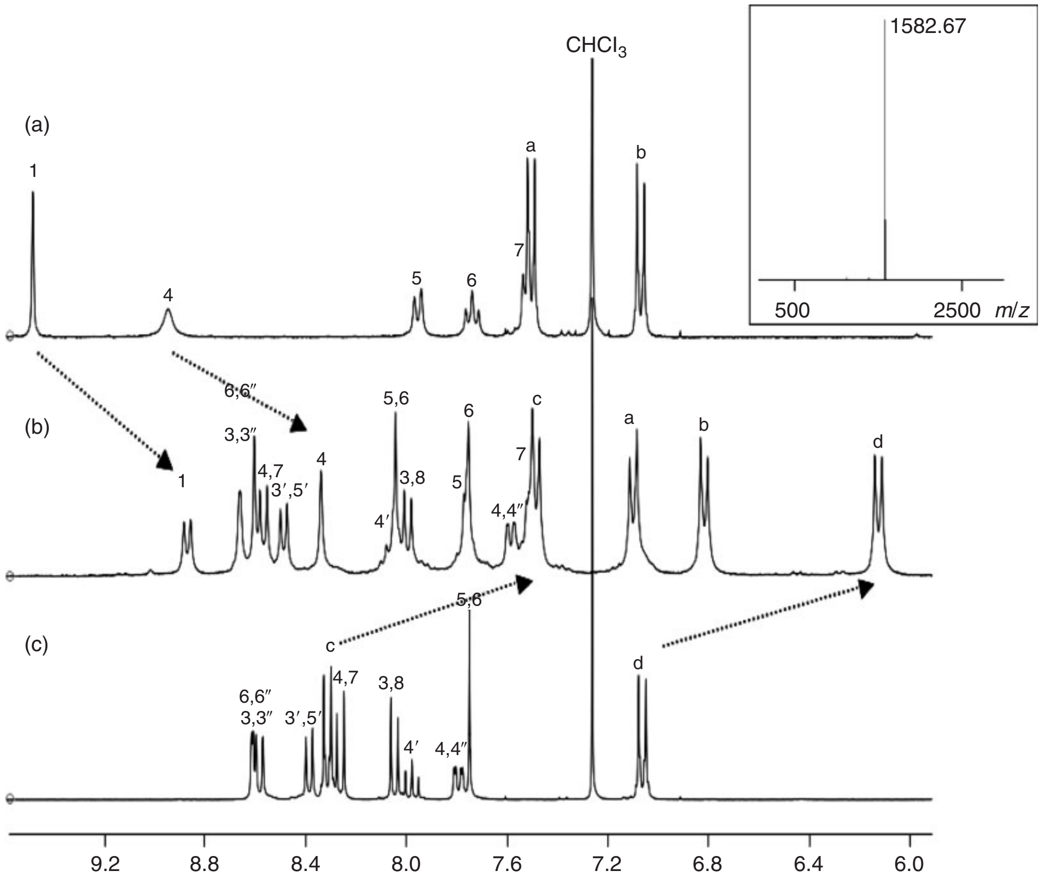

Fig. 4. ^{1}H NMR spectra (300 MHz, aromatic part) of (a) thread **6** (in $CDCl_3$), (b) [2]pseudorotaxane $\mathbf{9}_4^+$ (in CD_2Cl_2), and (c) macrocycle **7** (in $CDCl_3$). Inset: ES-MS of $\mathbf{9}_4^+$.

a strong upfield shift. The *a*, *b*, *c*, and *d* protons on the phenyl rings of both constituents of the pseudorotaxane $\mathbf{9}_4^+$ also present an upfield shift, which is more pronounced for macrocycle **7**. The green Cu(II)-[2]pseudorotaxane $\mathbf{8}_5^{2+}$ has been obtained in a similar manner from thread **3**, macrocycle **7** and $Cu(BF_4)_2$ salt. High resolution ES-MS spectra shows an intense peak observed at *m/z* 1544.44 (calculated for $[M]^+$ 1544.45).

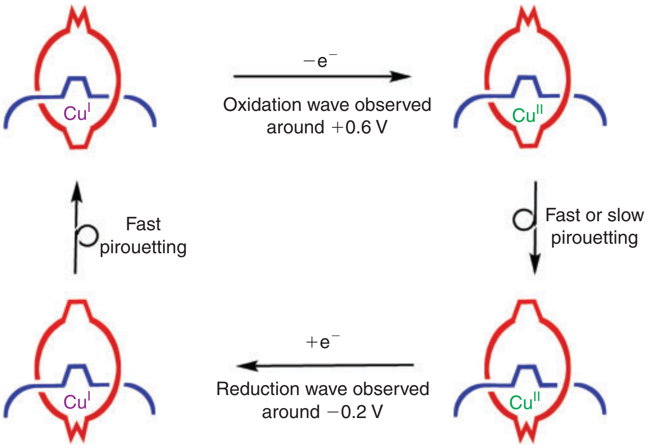

Fig. 5. Pirouetting principle of the copper complexed [2]pseudorotaxanes $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$.

Electrochemical Studies

As previously demonstrated with related systems,[24,31,56] cyclic voltammetry is very well adapted to study systems displaying coupled electron transfer and chemical reactions. A square scheme as shown on Fig. 5 has been evidenced in the case of copper complex rotaxanes and catenanes.[24,31,56] It is based on the markedly different stereoelectronic requirements of copper(I) and copper(II) complexes. This characteristic will provide the driving force of the chemical pirouetting reactions. Whereas a coordination number of 4 implicates a stable monovalent cation, copper(II) requires a coordination number of 5 or 6. Thus, by switching alternatively between copper(I) and copper(II), the whole molecule, by a pirouetting motion, will change its geometry to afford a coordination favourable to the corresponding oxidation state.

The two complexes $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$ have been studied both in solution and anchored on gold electrode surfaces. The cyclic voltammograms of $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$ in CH_2Cl_2/CH_3CN mixture (9:1) recorded at a scan rate of 200 mV s^{-1} are given in Fig. 6. By starting the cyclic voltammograms (CV) at a potential value of −0.5 V, no current is observed since $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$ are electrochemically inactive below the oxidation potential at which Cu(I) starts to be oxidized. On increasing the potential towards anodic values, oxidation peaks around 0.6 V are observed, as expected for the oxidation process of copper(I) to copper(II). After the peak potential, Cu(II) is obtained and the current intensity decreases. By investigating the scan potential in the reverse direction, starting from 1.1 V towards the cathodic region, it is expected that the Cu(II) species can be reduced to Cu(I). If the Cu(II) complex is still four-coordinate, the return wave should be

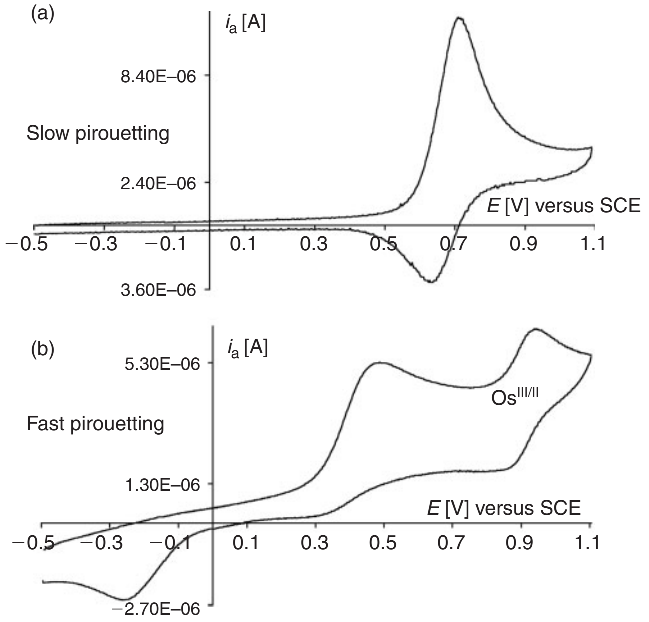

Fig. 6. Cyclic voltammograms of complexes $\mathbf{8}_4^+$ (a) and $\mathbf{9}_4^+$ (b) recorded on a Pt working electrode in CH_2Cl_2/CH_3CN (1:9) with 0.1 M Bu_4NPF_6 at 200 mV s^{-1}. The redox couple Os$^{III/II}$ corresponds to the complex Os(tterpy)$_2$(PF$_6$)$_2$ (tterpy = 4′-*p*-tolyl-2,2′,6′,2′-terpyridine) used as internal reference (E Os$^{III/II}$ = 0.9 V versus SCE in this electrolyte).

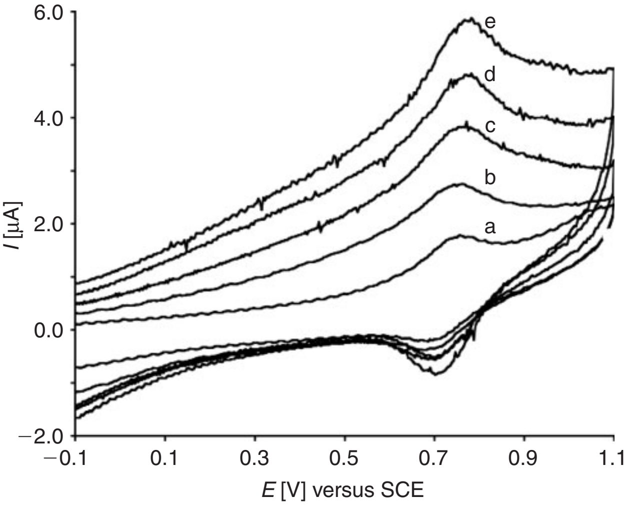

Fig. 7. Cyclic voltammograms response of a gold bead electrode (CH_2Cl_2/CH_3CN (9:1) with 0.1 M Bu_4NPF_6) after dipping (30 min) in a solution of $\mathbf{8}_4^+$ (10^{-3} M). The scan rates are a: 100, b: 200, c: 400, d: 600, e: 800 mV s^{-1} respectively.

observed, corresponding to a reversible redox process. By contrast, if the pirouetting motion is faster than the potential sweep rate, the return wave corresponding to the reduction of the four-coordinate Cu(II) complex is not observed anymore. Instead, it is replaced by another wave corresponding to the reduction of the rearranged complex at a much lower potential (around −0.2 V).

Complexes $\mathbf{8}_4^+$ and $\mathbf{9}_4^+$ showed a noticeable difference of electrochemical behaviour especially at potential scan rate higher than 200 mV s^{-1} (Fig. 6). Complex $\mathbf{8}_4^+$ shows an oxidation peak at 0.72 V as expected for oxidation processes and corresponds to the formation of the four-coordinate Cu(II) complex $\mathbf{8}_4^{2+}$. This redox couple obtained at 200 mV s^{-1} is probably due both to $\mathbf{8}_4^+$ in solution and of the same species already fixed on the platinum surface (*vide infra*). We essentially observe the reduction of complex $\mathbf{8}_4^{2+}$ to $\mathbf{8}_4^+$. Complex $\mathbf{9}_4^+$ also shows an oxidation peak (at 0.50 V), but the corresponding return wave is only weakly detected signifying that the pirouetting motion is faster than the potential sweep rate. Instead, a peak located at −0.26 V (corresponding to the reduction of the rearranged 5-coordinate complex $\mathbf{9}_5^{2+}$) is observed. At slow potential sweep rate (50 mV s^{-1}), the pirouetting motion is faster than the potential sweep rate for both complexes, and the reduction of the rearranged complexes $\mathbf{8}_5^{2+}$ or $\mathbf{9}_5^{2+}$ at negative potential is observed (not shown).

As expected, the rate of the pirouetting motion for the sterically hindered $\mathbf{8}_4^+$ is nearly 10 times slower than for its less encumbered parent $\mathbf{9}_4^+$ as shown by CV experiments at various scan rates. However, the electrochemical behaviour of $\mathbf{8}_4^+$ seems also to indicate a slower motion than an analogous copper complex rotaxane based on a 6,6′-dianisyl-2,2′-bipyridine.[31] This latter copper rotaxane[31] and $\mathbf{8}_4^+$ differ in particular by the nature of the end-groups attached to the threads. The thioctic end-groups are known to have a very strong affinity for gold surfaces, but they are also able to bind to platinum surfaces.[57] One part of the redox signal can be assigned to the species in solution and the other part to a species confined at the surface of the platinum electrode. This hypothesis is corroborated by CV experiments with a carefully rinsed platinum electrode soaked in pure electrolyte, which still displays the characteristic redox couple $\mathbf{8}_4^{2+/+}$.

The surface attachment of complex $\mathbf{8}_4^+$ is also readily obtained by dipping a gold bead electrode into a CH_2Cl_2 solution of $\mathbf{8}_4^+$ for a period of a few minutes to hours. The electrode is then rinsed carefully with CH_2Cl_2. The CV voltammograms obtained with this electrode in a pure electrolyte at various scan rates are represented on Fig. 7. For the $\mathbf{8}_4^{2+/+}$ redox couple, the intensity of the anodic peak current increases linearly with the sweep rate as expected for a surface-anchored redox species. However, the various conditions (scan rates, potential ranges, continuous polarization before scanning) used with this type of electrode do not permit to observe any new redox wave and therefore any molecular rearrangement inside the adsorbed copper rotaxane species. This behaviour can be related to the structure of the adsorbed layer. A high compactness can slow down or freeze all large molecular motions. This should be especially true in an amorphous and thick layer of copper pseudorotaxane. In fact, it seems to be the case because an approximate calculation by integration of current-voltage curves corresponds to four layers deposited on the gold electrode surface. We tried to circumvent this feature by adsorbing compound $\mathbf{9}_4^+$ in which the thioether functions should lead to the deposition of a monolayer. Furthermore, the presence of a biisoquinoline ligand in the thread is expected to allow fast rearrangement in solution.

Fig. 8 shows the characteristic CV curves, recorded at various potential sweep rates, after deposition of $\mathbf{9}_4^+$ on a gold electrode. In the phosphate buffer solution (pH 7.4) a reversible electron transfer at 0.15 V versus saturated calomel reference electrode (SCE) can be assigned to the redox couple $\mathbf{9}_4^{2+/+}$. As displayed on the inset of Fig. 8, the linear correlation between the anodic potential peak and the scan rate demonstrates the grafting of $\mathbf{9}_4^+$ on the gold surface. Unfortunately, as already observed in the case of $\mathbf{8}_4^+$ no other redox couples can be

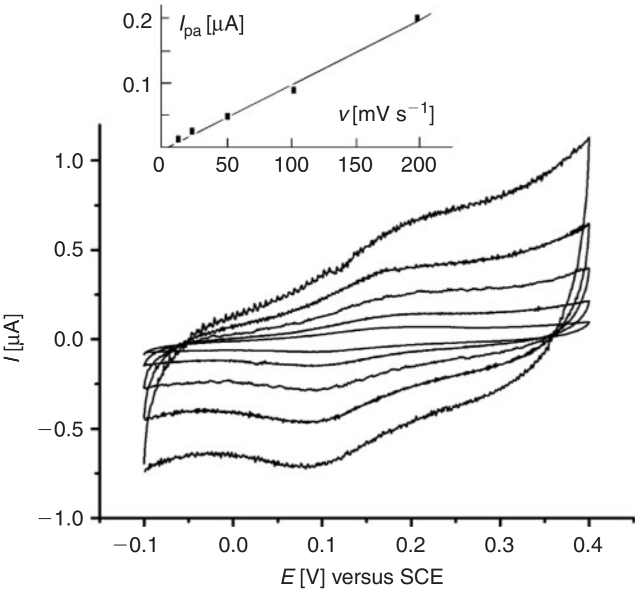

Fig. 8. Cyclic voltammograms (CV) of the gold-deposited $\mathbf{9}_4^+$ electrode in the pH 7.4 phosphate buffer solution (0.1 M) at different scan rate: 10, 20, 50, 100, 200 mV s^{-1} (from inside to outside). Inset: the linear relationship between the anodic peak current (I_{pa}) and the scan rate [mV s^{-1}] recorded from the CV of gold-deposited $\mathbf{9}_4^+$ electrode.

detected at negative potential. It seems that in the conditions used in this type of experiments no rearrangement, implying large amplitude motions, can be possible inside the layer of deposited copper[2]pseudorotaxanes.

In conclusion, although several examples of surface-confined molecular systems have been shown by other research groups to behave as molecular machines, because they could be set in motion by electrochemical signals, the copper-based catenanes and rotaxanes elaborated and investigated in our team do not seem to undergo large amplitude molecular motions once attached onto an electrode surface. In contrast, these catenanes and rotaxanes, as well as the two new rotaxanes presented in this study can easily be set in motion in solution by using redox signals. Once again, we could confirm that steric hindrance plays a determining role and that, in order for the systems to undergo fast movements, the central copper atom has to be as accessible as possible so as to facilitate ligand substitution reactions. As far as the surface-confined species are concerned, the steric shielding ensured by the gold surface itself and by the deposited layer is likely to have a similar detrimental effect on the rate of the hypothetical rearrangement reactions as bulky substituents around the copper atom for solution species. In the future, it will be important to graft the compounds on the electrode surface while making sure that the central metal can still be easily accessed by potential ligands, thus facilitating ring motions.

Experimental

General Methods

Dry solvents were distilled from suitable drying agents (CH_3CN from CaH_2, CH_2Cl_2 from P_2O_5). TLC was carried out using pre-coated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV$_{254}$). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063–0.200 μm). Flash column chromatography was carried out using silica gel (Merck Geduran, silica gel 60, 40–63 μm). Nuclear Magnetic Resonance (NMR) spectra were acquired on Bruker AVANCE 300 spectrometer. The ^{13}C NMR spectra were proton-decoupled. The spectra were referenced to residual proton-solvent signals (^{1}H: CD_2Cl_2 at 5.32 ppm, $CDCl_3$ at 7.25 ppm, d$_6$-DMSO at 2.54 ppm; ^{13}C: CD_2Cl_2 at 54.0 ppm, $CDCl_3$ at 77.23 ppm). Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS). Matrix-assisted laser desorpton–ionization analyses were performed on an Autoflex II TOF/TOF Bruker Daltronics spectrometer. Electrochemical measurements were performed with a three-electrode system consisting of 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 argon, in degassed spectroscopic grade solvents, using 0.1 M n-Bu_4NBF_4 solutions in CH_2Cl_2/CH_3CN (1:9) as supporting electrolyte. A platinum disk electrode (2 mm diameter) was used for CV experiments of the [2]rotaxanes in solution. The gold bead working electrodes were made by annealing the tip of a gold wire (99.999%, 0.5 mm diameter) in a gas oxygen flame. After being cooled, the gold bead was immersed in a 10^{-3} mol L^{-1} solution of the [2]rotaxanes $\mathbf{8}_4^+$ or $\mathbf{8}_5^{2+}$ in CH_2Cl_2/CH_3CN for times varying from 10 min to 18 h. The electrode was then washed with pure CH_2Cl_2. An EG&G Princeton Applied Research model 273A potentiostat connected to a computer was used. For compound $\mathbf{9}_4^+$, the experimental conditions were as follows: the Au/$\mathbf{9}_4^+$ modified electrode was prepared by assembling the clean Au-electrode (0.5 mm diameter Au wire, geometrical area ~0.29 cm^2) in the solutions of $\mathbf{9}_4^+$ (1.6 mg in 200 μL of DMF) for 24 h. Then, the modified electrode was cleaned by washing with ethanol three times. A conventional three-electrode cell, consisting of the modified Au working electrode, a glassy carbon auxiliary electrode isolated by a glass frit, and a SCE connected to the working volume with a Luggin capillary, were used for the electrochemical measurements. The pH 7.4 phosphate buffer (0.1 M) solution was used as the electrolyte. All potentials are reported with respect to the SCE. Argon bubbling was used to remove oxygen from the solutions in the electrochemical cell. Cyclic voltammetry was performed using an Autolab electrochemical analyzer (ECO Chemie, Netherlands).

Starting Materials

All chemicals were of the best commercially available grade and used without further purification (except when mentioned). Compounds **1**,[54] **4**,[55] **5**,[31] and **7**[24] were prepared according to the literature procedures.

Compound **2**

6,6′-Diphenol-2,2′-bipyridine **1** (150 mg, 0.44 mmol) was dissolved in degassed DMF (20 mL), Cs_2CO_3 (500 mg, 2.6 mmol) was added and the resulting mixture was stirred at 60°C for 30 min. 2-(2-Bromoethoxy)tetrahydro-2H-pyran (500 mg, 2.4 mmol) was then added and the reaction was stirred overnight. After evaporation of the solvent, the crude product was dissolved in dichloromethane and the organic phase was washed with water, dried over Na_2SO_4, filtered, and evaporated. The crude material was then washed with pentane, and then dissolved in ethanol (30 mL). This solution was heated under reflux overnight in presence of a catalytic amount of HCl (3 drops). After cooling, the solvent was removed under reduced pressure to afford a yellow solid, which was then taken with a mixture of $EtOH/CH_2Cl_2$ (1:10) and washed with aqueous $NaHCO_3$ (10%, 10 mL) and water. It was then concentrated under vacuum leading to the precipitation of **2** which was filtered off (159 mg, 84%) Found: C 68.88, H 5.49, N 6.00; $C_{26}H_{24}N_2O_4{\cdot}H_2O$ requires C 69.94, H 5.87, N 6.27%. ^{1}H NMR (300 MHz, d$_6$-DMSO) δ 8.46 (2H, d, *J* 7.0), 8.21 (4H, d, *J* 8.8), 8.01 (4H, m), 7.09 (4H, d, *J* 8.8), 4.92 (2H, m), 4.08 (4H, t, *J* 4.8). ^{13}C NMR (75 MHz, d$_6$-DMSO) δ 160.2, 155.6, 155.4, 155.1, 138.7, 137.6, 131.3, 128.4, 120.0, 115.1, 70.1, 60.0.

Compound **3**

To a suspension of compound **2** (100 mg, 0.23 mmol) in dry and degassed DMF (20 mL) was added thioctic acid (272 mg, 1.32 mmol). After 30 min of stirring, DMAP (32 mg, 0.26 mmol) and DCC (364 mg, 3.1 mmol) were added. The mixture was stirred for 24 h at room temperature and the solution became limpid. DMF was removed under vacuum, and the crude mixture was taken with dichloromethane (10 mL). The organic layer was washed with water and dried over Na_2SO_4. The crude product was purified over silica gel chromatography (CH_2Cl_2/MeOH 4%) affording **3** as a white solid in 53% yield (100 mg) Found: C 58.76, H 5.92, N 3.12; $C_{42}H_{48}N_2O_4{\cdot}2H_2O$ requires C 59.97, H 6.23, N 3.33%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (2H, dd, *J* 0.8, 7.8), 8.12 (4H, d, *J* 11.7), 7.88 (2H, t, *J* 7.8), 7.72 (2H, d, *J* 7.8), 7.05 (2H, d, *J* 11.7), 4.48 (4H, t, *J* 4.3), 3.53 (2H, m), 3.11 (4H, m), 2.44–2.37 (6H, m), 1.70 (2H, m), 1.65–1.46 (16H, m). ^{13}C NMR (75 MHz, d$_6$-DMSO) δ 173.2, 159.5, 155.7, 155.7, 137.5, 132.3, 128.1, 119.4, 118.7, 114.6, 66.1, 62.5, 56.4, 54.1, 40.2, 38.5, 34.5, 33.9, 28.6, 24.6.

Compound **6**

To a solution of compound **5** (120 mg, 0.272 mmol) in dry DMF (20 mL) was added Cs_2CO_3 (266 mg, 0.816 mmol) under argon. The resulting suspension was stirred at 50°C for 1 h. A solution of 1-bromo-6-(hexylthio)hexane **4** (230 mg, 0.816 mol) in CH_2Cl_2 (4 mL) was added and the mixture allowed to stir at 45°C for 24 h. The solvents were then removed and the crude compound was redissolved in CH_2Cl_2 (30 mL) and washed with water (50 mL). The aqueous phase was further washed with in CH_2Cl_2 (3×20 mL). The combined organic phases were dried with Na_2SO_4, filtered and evaporated to dryness. The crude product was subjected to a silica gel chromatography using CH_2Cl_2/MeOH (0 to 4%) as the eluent to afford compound **6** (126 mg) in 55% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (2H, s), 8.95 (2H, s), 7.95 (2H, d, *J* 8.4), 7.74 (2H, dd, *J* 7.7), 7.50 (6H, m), 7.07 (4H, d, *J* 8.8), 4.07 (4H, t, *J* 6.5), 2.54 (8H, m), 1.87 (8H, m), 1.68–1.30 (32H, m), 0.89 (6H, t, *J* 7.0). *m/z* (ES) calc. for $C_{54}H_{68}N_2O_2S_2$ $[M+H]^+$ 841.48; found 841.47.

Compound $\mathbf{8}_4^+$

Macrocycle **7** (20 mg, 0.029 mmol) was dissolved in a mixture of degassed dichloromethane and acetonitrile (4.5 mL, 8:1). $Cu(CH_3CN)_4{\cdot}PF_6$ (11 mg, 0.029 mmol) was then added and the mixture turned brown-orange immediately. After 30 min of stirring under argon, bipyridine ligand **3** (23.75 mg, 0.029 mmol) was added. The colour of the reaction mixture turned instantaneously deep red. Stirring was continued for 3 h, and the solvents were evaporated to dryness giving 49 mg of a red powder in a quantitative yield. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.79 (2H, d, *J* 7.5), 8.69 (2H, s, 8.47) (2H, d, *J* 7.8), 7.86 (2H, s), 7.81 (4H, d, *J* 8.4), 7.68 (4H, s), 7.52 (4H, d, *J* 8.5), 7.31 (2H, s), 7.16 (4H, d, *J* 8.5), 6.31 (4H, d, *J* 8.5), 5.92 (4H, d, *J* 8.6), 4.18 (4H, t, *J* 4.6), 6.70–3.50 (8H, m), 3.3–3.0 (8H, m), 2.40–2.20 (8H, m), 1.87 (2H, m), 1.70–1.40 (20H, m). *m/z* (HR-MS) calc. for $C_{87}H_{83}N_7O_8CuS_4$ $[M]^+$ 1544.45; found 1544.43.

Compound $\mathbf{8}_5^{2+}$

To a degassed solution of ligand **3** (11.9 mg, 0.014 mmol) and macrocycle **7** (10 mg, 0.014 mmol) in a mixture of dichloromethane and acetonitrile was added a stoichiometric quantity of $Cu(BF_4)_2$. Upon addition of the copper salt, a green colour appeared progressively. The resulting solution was stirred overnight at room temperature and concentrated under vacuum to afford 25 mg (95% yield) of a green solid. *m/z* (ES) calc. for $C_{87}H_{83}N_7O_8CuS_4$ $[M]^+$ 1544.45; found 1544.44.

Compound $\mathbf{9}_4^+$

A degassed solution of macrocycle **7** (20 mg, 0.0295 mmol) in CH_2Cl_2 was added to a degassed solution of $Cu(CH_3CN)_4{\cdot}PF_6$ (11 mg, 0.0295 mmol) in CH_3CN. The mixture was stirred at room temperature for 15 min. A degassed solution of compound **6** (24.8 mg, 0.0295 mmol) in CH_2Cl_2 was added. The resulting deep red solution was stirred at room temperature for 4 h, and the solvents are evaporated to dryness, giving 51 mg of a red powder in a quantitative yield. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.88 (2H, d, *J* 8.0), 8.67 (2H, br. s), 8.61 (2H, s), 8.57 (2H, d, *J* 8.4), 8.49 (2H, d, *J* 7.9), 8.35 (2H, s), 8.09 (1H, t, *J* 7.9), 8.05 (2H, s), 8.00 (2H, d, *J* 8.4), 7.76 (4H, m), 7.59 (2H, dd, *J* 7.9, 1.9), 7.53–7.47 (6H, m), 7.10 (4H, d, *J* 8.6), 6.81 (4H, d, *J* 8.8), 6.12 (4H, d, *J* 8.8), 3.90 (4H, t, *J* 6.4), 3.34 (4H, t, *J* 6.2), 2.89 (4H, m), 2.49 (8H, m), 2.04 (4H, m), 1.72 (4H, m), 1.58–1.28 (28H, m), 0.88 (6H, m). *m/z* (ES) calc. for $C_{99}H_{103}N_7O_4S_2Cu^+$ $[M]^+$ 1580.68; found 1580.67.

Acknowledgement

We thank the CNRS and the EC STREP FET-open MOLDYNLOGIC for financial support.

References

[1] 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. doi:10.1126/SCIENCE.289.5482.1172

[2] A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456. doi:10.1021/AR000174L

[3] D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, *424*, 174. doi:10.1038/NATURE01758

[4] M. Cavallini, F. Biscarini, S. León, F. Zerbetto, G. Bottari, D. A. Leigh, *Science* **2003**, *299*, 531. doi:10.1126/SCIENCE.1078012

[5] A. Kocer, M. Walko, W. Meijberg, B. L. Feringa, *Science* **2005**, *309*, 755. doi:10.1126/SCIENCE.1114760

[6] J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Pérez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* **2005**, *4*, 704. doi:10.1038/NMAT1455

[7] K. Kinbara, T. Aida, *Chem. Rev.* **2005**, *105*, 1377. doi:10.1021/CR030071R

[8] Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C.-M. Ho, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 9745. doi:10.1021/JA051088P

[9] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. Serrano Ramon, C. W. M. Bastiaansen, D. J. Broer, B. L. Feringa, *Nature* **2006**, *440*, 163. doi:10.1038/440163A

[10] T. D. Nguyen, Y. Liu, S. Saha, K. C.-F. Leung, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2007**, *129*, 626. doi:10.1021/JA065485R

[11] J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Delonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414. doi:10.1038/NATURE05462

[12] V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines – Concepts and perspectives for the Nanoworld* **2008** (Wiley-VCH: Weinheim).

[13] G. Schill, *Catenanes, Rotaxanes and Knots* **1971** (Academic Press: New York, NY).

[14] C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795. doi:10.1021/CR00080A007

[15] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725. doi:10.1021/CR00040A005

[16] J.-P. Sauvage, C. O. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots* **1999** (Wiley-VCH: Weinheim).

[17] G. Fioravanti, N. Haraszkiewicz, E. R. Kay, S. M. Mendoza, C. Bruno, M. Marcaccio, P. G. Wiering, F. Paolucci, P. Rudolf, A. M. Brouwer, D. A. Leigh, *J. Am. Chem. Soc.* **2008**, *130*, 2593. doi:10.1021/JA077223A

[18] K. M. Mullen, J. M. Gunter, *J. Org. Chem.* **2008**, *73*, 3336. doi:10.1021/JO800276W

[19] C.-J. Chuang, W.-S. Li, C.-C. Lai, Y.-H. Liu, S.-M. Peng, I. Chao, S.-H. Chiu, *Org. Lett.* **2009**, *11*, 385. doi:10.1021/OL802648H

[20] C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, *Tetrahedron Letters* **1983**, *24*, 5095. doi:10.1016/S0040-4039(00)94050-4

[21] C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-M. Kern, *J. Am. Chem. Soc.* **1984**, *106*, 3043. doi:10.1021/JA00322A055

[22] C. O. Dietrich-Buchecker, A. Khemiss, J.-P. Sauvage, *Chem. Commun.* **1986**, *17*, 1376.

[23] J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319. doi:10.1021/AR00178A001

[24] (a) A. Livoreil, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399. doi:10.1021/JA00099A095
(b) D. J. Cárdenas, A. Livoreil, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 11980. doi:10.1021/JA962774E

[25] N. Solladié, J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 906. doi:10.1002/ANIE.199609061

[26] B. Mohr, M. Weck, J.-P. Sauvage, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1308. doi:10.1002/ANIE.199713081

[27] D. Pomeranc, D. Jouvenot, J.-C. Chambron, J.-P. Collin, V. Heitz, J.-P. Sauvage, *Chem. Eur. J.* **2003**, *9*, 4247. doi:10.1002/CHEM.200304716

[28] C. Hamann, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2003**, *42*, 1877. doi:10.1021/IC020381C

[29] J.-C. Chambron, J.-P. Collin, V. Heitz, D. Jouvenot, J.-M. Kern, P. Mobian, D. Pomeranc, J.-P. Sauvage, *Eur. J. Org. Chem.* **2004**, 1627. doi:10.1002/EJOC.200300341

[30] F. Durola, L. Russo, J.-P. Sauvage, K. Rissanen, O. S. Wenger, *Chem. Eur. J.* **2007**, *13*, 8749. doi:10.1002/CHEM.200700684

[31] J.-P. Collin, F. Durola, P. Mobian, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **2007**, 2420. doi:10.1002/EJIC.200700215

[32] A. I. Prikhod'ko, F. Durola, J.-P. Sauvage, *J. Am. Chem. Soc.* **2008**, *130*, 448. doi:10.1021/JA078216P

[33] J. A. Faiz, V. Heitz, J.-P. Sauvage, *Chem. Soc. Rev.* **2009**, *38*, 422. doi:10.1039/B710908N

[34] S. S. Zhu, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1996**, *118*, 8713. doi:10.1021/JA9619667

[35] Y. L. Zhao, Y. Cheng, M. Wang, Y. Liu, *Org. Lett.* **2006**, *8*, 1267. doi:10.1021/OL052978C

[36] K. Nikitin, E. Lestini, M. Lazzari, S. Altobello, D. Fitzmaurice, *Langmuir* **2007**, *23*, 12147. doi:10.1021/LA701657R

[37] Y. H. Jang, S. S. Jang, W. Goddard, *J. Am. Chem. Soc.* **2005**, *127*, 4959. doi:10.1021/JA044762W

[38] S. R. Bayly, T. M. Gray, M. J. Chmielewski, J. J. Davis, P. D. Beer, *Chem. Commun.* **2007**, 2234. doi:10.1039/B701796K

[39] E. Coronado, A. Forment-Aliaga, P. Gaviña, F. M. Romero, *Inorg. Chem.* **2003**, *42*, 6959. doi:10.1021/IC034797H

[40] C. M. Whelan, F. Gatti, D. A. Leigh, S. Rapino, F. Zerbetto, P. Rudolf, *J. Phys. Chem. B* **2006**, *110*, 17076. doi:10.1021/JP061836C

[41] K. M. Mullen, P. D. Beer, *Chem. Soc. Rev.* **2009**, *38*, 1701. doi:10.1039/B806041J

[42] C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172. doi:10.1126/SCIENCE.289.5482.1172

[43] E. Katz, O. Lioubashevsky, I. Willner, *J. Am. Chem. Soc.* **2004**, *126*, 15520. doi:10.1021/JA045465U

[44] K. Nørgaard, B. W. Laursen, S. Nygaard, K. Kjaer, H.-R. Tseng, A. H. Flood, J. F. Stoddart, T. Bjørnholm, *Angew. Chem. Int. Ed.* **2005**, *44*, 7035. doi:10.1002/ANIE.200501538

[45] D. Payer, S. Rauschenbach, N. Malinowski, M. Konuma, C. Virojanadara, U. Starke, C. Dietrich-Buchecker, J.-P. Collin, J.-P. Sauvage, N. Lin, K. Kern, *J. Am. Chem. Soc.* **2007**, *129*, 15662. doi:10.1021/JA075886M

[46] Y. B. Zheng, Y.-W. Yang, L. Jensen, L. Fang, B. K. Juluri, A. H. Flood, P. S. Weiss, J. F. Stoddart, T. J. Huang, *Nano Lett.* **2009**, *9*, 819. doi:10.1021/NL803539G

[47] S. Angelos, Y.-W. Yang, K. Patel, J. F. Stoddart, J. I. Zink, *Angew. Chem. Int. Ed.* **2008**, *47*, 2222. doi:10.1002/ANIE.200705211

[48] J.-M. Kern, J.-P. Sauvage, G. Bidan, M. Billon, B. Divisia-Blohohorn, *Adv. Mater.* **1996**, *8*, 580. doi:10.1002/ADMA.19960080710

[49] L. Raehm, C. Hamann, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2000**, *2*, 1991.

[50] L. Raehm, J.-M. Kern, J.-P. Sauvage, C. Hamann, S. Palacin, J.-P. Bourgoin, *Chem. Eur. J.* **2002**, *8*, 2153. doi:10.1002/1521-3765(20020503)8:9<2153::AID-CHEM2153>3.0.CO;2-E

[51] N. Weber, C. Hamann, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2003**, *42*, 6780. doi:10.1021/IC0347034

[52] I. Poleschak, J.-M. Kern, J.-P. Sauvage, *Chem. Comm.* **2004**, 474.

[53] U. Létinois-Halbes, D. Hanss, J. M. Beierle, J.-P. Collin, J.-P. Sauvage, *Org. Lett.* **2005**, *7*, 5753. doi:10.1021/OL052051C

[54] J.-P. Collin, D. Jouvenot, M. Koizumi, J.-P. Sauvage, *Inorg. Chem.* **2005**, *44*, 4693. doi:10.1021/IC050246A

[55] F. M. Menger, L. Shi, *J. Am. Chem. Soc.* **2006**, *128*, 9338. doi:10.1021/JA062807I

[56] J.-P. Collin, P. Gaviña, J.-P. Sauvage, *New J. Chem.* **1997**, *21*, 525.

[57] R. Klajn, L. Fang, A. Coskun, M. A. Olson, P. J. Wesson, J. F. Stoddart, B. A. Grzybowski, *J. Am. Chem. Soc.* **2009**, *131*, 4233. doi:10.1021/JA9001585