Electrochemically induced molecular motions in a copper(I) complex pseudorotaxane

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A pseudorotaxane consisting of a coordinating ring, a molecular thread bearing two different coordination sites and a copper(I) ion displays electrochemically induced motions of the ring from one site to the other.

Molecular systems whose shape and general physical properties can be modified at will by using an external signal (light pulse, electron or proton transfer, *etc.*) are fascinating.[1,2] They are of special interest in relation with molecular switches and information storage, but also as mimics of proteins undergoing a folding or an unfolding motion triggered by an electrochemical event.[3,4] Transition-metal complexes are particularly well suited to this aim since their coordination sphere geometrical requirement can simply be changed by modifying their oxidation state.[5–7] This has recently been applied in a copper catenane[8] to induce gliding of one ring within the other or in a two-coordination site iron complex to trigger metal hopping between two sites.[9]

Here, we describe a new molecular assembly also undergoing molecular motions, by reducing or oxidizing the complexed copper centre. The principle of the process is shown in Fig. 1, and is based on the difference of preferred coordination number (CN) for the two different redox states of the metal: CN = 4 for $\mathrm{Cu^I}$ and 5 (or 6) for $\mathrm{Cu^{II}}$.

Pseudorotaxane 9^+ consists of a molecular string containing two different coordination sites: a 2-alkyl-9-phenyl-1,10-phenanthroline bidentate chelate and a terdentate ligand, 2,2′,6′,2″-terpyridine (terpy), which is threaded into a coordinating ring containing a 2,9-diphenyl-1,10-phenanthroline moiety *via* coordination to $\mathrm{Cu^I}$. The driving force of this threading process is the great stability of the pseudo-tetrahedral bis-chelate complex formed between $\mathrm{Cu^I}$ and two disubstituted 1,10-phenanthrolines.[10] The motion of the ring and the metal ion from the bidentate to the terdentate chelate can be electrochemically induced by taking advantage of the different geometrical requirements of the two redox states of the $\mathrm{Cu^I}$–$\mathrm{Cu^{II}}$ couple. Thus, 'oxidation of the stable tetrahedral copper(I) complex would lead to a four-coordinate $\mathrm{Cu^{II}}$ state which should rearrange to the more stable five-coordinate species involving both a phenanthroline and a terpy moiety.

The structures of the relevent precursor compounds are shown in Fig. 2.

5,5′-Dimethyl-2,2′,6′,2″-terpyridine **1** was prepared from 2-acetyl-5-methylpyridine by Jameson's method[11] or alternatively from 2-bromo-5-methylpyridine and 2,6-dibromopyridine following Stille's methodology.[12] **1** was deprotonated with LDA in thf giving a deep red compound which was reacted with 1 equiv. of THP-protected bromoethanol (THP = tetrahydropyran-2-yl) to afford **2** in 40% yield. Deprotection with conc. HCl in refluxing ethanol led to a 85% yield of **3**† which was converted first to the mesylate **4** in 86% yield by reaction

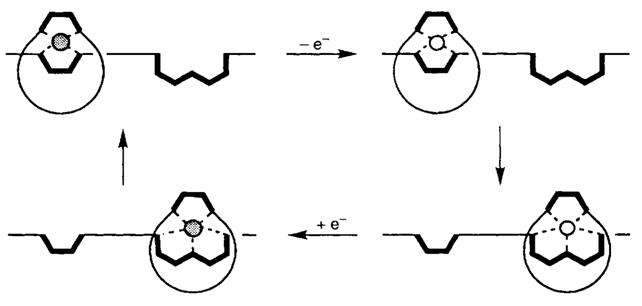


Fig. 1 Principle of the electrochemically induced molecular motions in a copper(I) complex pseudorotaxane. The stable four-coordinate monovalent complex is oxidized to an intermediate tetrahedral divalent species. This compound undergoes a rearrangement to afford the stable five-coordinate copper(II) complex. Upon reduction, the five-coordinate monovalent state is formed as a transient. Finally, the latter undergoes the reorganization process which regenerates the starting complex (the shaded circle represents $\mathrm{Cu^I}$ and the white circle represents $\mathrm{Cu^{II}}$).

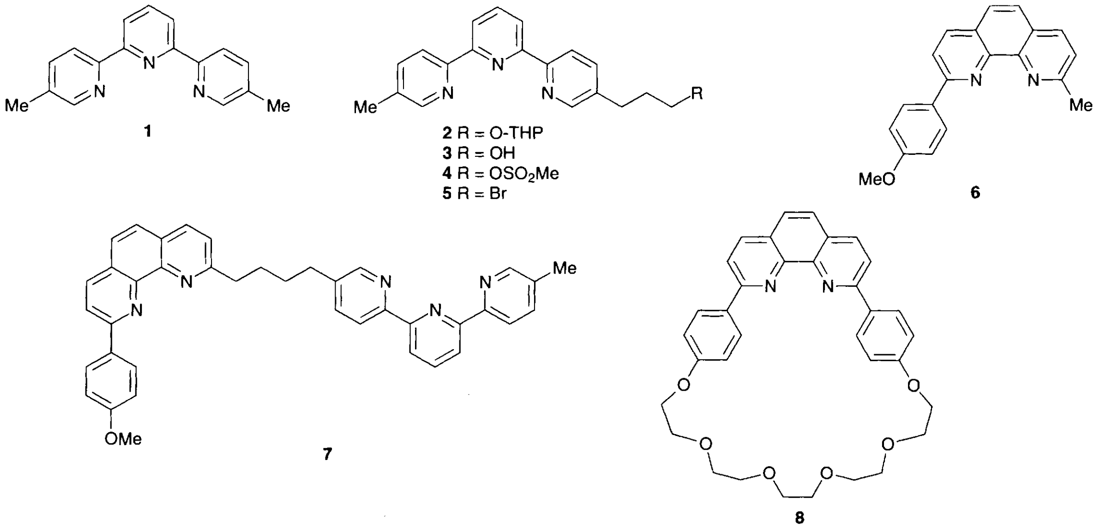
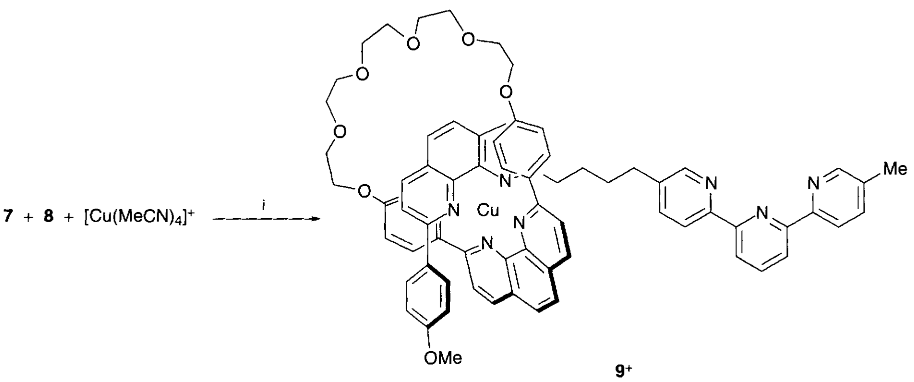


Fig. 2



9^+

Scheme 1 *Reagents and conditions*: i, MeCN–CH_2Cl_2, room temp.

with mesyl chloride and NEt_3 in CH_2Cl_2 and then to the bromo derivative **5** (97%) by reaction with anhydrous LiBr in refluxing acetone. 2-Methyl-9-(*p*-anisyl)-1,10-phenanthroline **6** was prepared from 1,10-phenanthroline following a previously published procedure.[13] Deprotonation of **6** with LDA in thf led to a deep red compound which was reacted with **5** in thf at room temperature to afford the desired ligand **7** in 56% yield after work-up and column chromatography (alumina, CH_2Cl_2–hexane as eluent), as a yellow solid.‡

The synthesis of macrocycle **8** has previously been reported.[14] [9^+][BF_4^-] was obtained by mixing stoichiometric amounts of **7**, **8** and $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2–MeCN under argon at room temperature (Scheme 1). Evaporation of the solvent and column chromatography (alumina, CH_2Cl_2–0.5% MeOH as eluent) afforded the desired pseudorotaxane as a brown–red solid in 75% yield.§ $\mathbf{9}^+$ was unambiguously characterised by FAB mass spectroscopy and ^1H NMR and UV–VIS spectroscopies. The ^1H NMR spectrum showed the typical chemical shifts to higher field of the hydrogens of the phenoxy moieties due to the ring current effects of the 1,10-phenanthroline nuclei, consistent with two phenanthroline units entwined around a copper(I) centre.[15] FABMS confirmed the structure showing an intense peak at *m/z* 1216.4 corresponding to the loss of the counter ion. The main peak, at *m/z* 650.2 corresponds to the loss of the counter ion and the macrocycle.

The cycle described in Fig. 1 has been demonstrated by cyclic voltammetry and linear sweep voltammetry at a rotating disk electrode in conjunction with electronic spectroscopy. The starting red solution of copper(I) complex $\mathbf{9}^+$ in CH_2Cl_2 (λ_{max} = 442 nm, ε = 3350 dm^3 mol^{-1} cm^{-1}) displays a reversible wave centred at +0.84 V (*vs.* SCE) characteristic of a tetrahedral copper(I) species.[8] Upon controlled potential electrolysis (E_{app} = +1.1 V) the solution becomes light green (λ_{max} = 658 nm) and displays a reversible couple at +0.1 V. As already observed in similar complexes,[8] this new redox couple can be attributed to a copper(II) species in a five-coordinate environment. Another weak signal at −0.2 V, corresponding to a six-coordinated copper(II) is also observed and could be due to a minor unthreading process during the electrolysis. A second electrolysis at −0.6 V restores the initial colour and redox couple of $\mathbf{9}^+$. Clearly, a square scheme of *electron transfer-induced reaction* type[16] takes place assuming that the chemical steps (motions of the ring from the phenanthroline to the terpyridine and *vice versa*) are slow in comparison with the timescale of cyclic voltammetry. In MeCN, we observe the same type of phenomena but with a more pronounced unthreading process, probably resulting from faster motions. The introduction of one or two stoppers at the ends of the string threaded into **8** is underway. It should of course prevent any undesirable dethreading process regardless of the medium used.

This work has been supported by the CNRS (France). P. G. thanks the Ministerio de Educación y Ciencia (Spain) for a postdoctoral fellowship.

Footnotes

† **3**: ^1H NMR (200 MHz, $CDCl_3$), δ 8.53–8.47 (m, 4 H), 8.37 (d, *J* 7.8 Hz, 2 H), 7.92 (t, *J* 7.8 Hz, 1 H), 7.70–7.62 (m, 2 H), 3.70 (t, *J* 6.3 Hz, 2 H), 2.79 (t, *J* 7.7 Hz, 2 H), 2.40 (s, 3 H), 2.10 (br s, 1 H), 1.99–1.85 (m, 2 H). Anal. Calc. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.63; H, 6.19; N, 13.61%.

‡ **7**: ^1H NMR (400 MHz, $CDCl_3$), δ 8.57 (d, *J* 2 Hz, 1 H), 8.52 (d, *J* 2 Hz, 1 H), 8.50 (d, *J* 8.0 Hz, 1 H), 8.48 (d, *J* 8.0 Hz, 1 H), 8.39–8.35 (m, 4 H), 8.24 (d, *J* 8.5 Hz, 1 H), 8.14 (d, *J* 8.2 Hz, 1 H), 8.05 (d, *J* 8.5 Hz, 1 H), 7.91 (t, *J* 7.8 Hz, 1 H), 7.75–7.70 (m, 3 H), 7.64 (dd, *J* 8.0, 2 Hz, 1 H), 7.50 (d, *J* 8.2 Hz, 1 H), 7.07 (d, *J* 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.28 (t, *J* 7.8 Hz, 2 H), 2.85 (t, *J* 7.6 Hz, 2 H), 2.41 (s, 3 H), 2.10 (q, *J* 7.8 Hz, 2 H), 1.92 (q, *J* 7.6 Hz, 2 H). FABMS, *m/z* (rel. intensity) 588.2 (MH^+, 100), 313.1 (M − $C_{18}H_{16}N_3$, 10), 300.1 (M − $C_{19}H_{17}N_3$, 16), 287.1 ($C_{19}H_{17}N_3$, 15), 274.1 ($C_{18}H_{16}N_3$, 12).

§ $\mathbf{9}^+$: ^1H NMR (200 MHz, CD_2Cl_2), δ 8.67 (d, *J* 8.3 Hz, 1 H), 8.55–7.65 (m, 19 H), 7.57 (d, *J* 8.3 Hz, 1 H), 7.31 (d, *J* 8.6 Hz, 4 H), 7.14 (d, *J* 8.7 Hz, 2 H), 5.95 (d, *J* 8.6 Hz, 4 H), 5.88 (d, *J* 8.7 Hz, 2 H), 3.80 (s, 4 H), 3.70–3.38 (m, 16 H), 3.46 (s, 3 H), 2.50 (t, *J* 7.8 Hz, 2 H), 2.43 (s, 3 H), 2.29 (t, *J* 7.8 Hz, 2 H), 1.55–1.45 (m, 2 H), 1.30–1.20 (m, 2 H). FABMS *m/z* (rel. intensity) 1216.4 [M − BF_4 (calc. 1216.4), 39], 650.2 [M − BF_4 − **8** (calc. 650.2), 100], 629.1 [M − BF_4 − **7** (calc. 629.2), 28], 588.2 [**7** + H^+ (calc. 588.3), 12], 567.2 [**8** + H^+ (calc. 567.2), 17].

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Received, 6th June 1996; Com. 6/03967G