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A new molecular switch: redox-driven translocation mechanism of the copper cation†

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Received (in Cambridge, UK) 29th April 2002, Accepted 21st May 2002

First published as an Advance Article on the web 5th June 2002

We report the synthesis of a novel molecular switch based on a double-stranded ditopic ligand which operates through the Cu^{II}/Cu^{I} couple; the mononuclear cuprous and cupric complexes were characterised by absorption spectrophotometry; reversible motion of the copper ion between the two binding sites is driven by an auxiliary oxidation and reduction reaction; the rate-limiting steps of this translocation process were determined as well as the corresponding kinetic parameters.

The development of molecular switches and logic gates is an exciting prospect in supramolecular chemistry.[1] A better understanding of the signal propagation processes in functional molecules constitutes a challenge for physico-chemists. In recent years, we have gained expertise in the synthesis and physico-chemical studies of homoditopic ligands and their helical diferric complexes.[2,3] We have reported the first example of a redox-driven switch based on a triple-stranded heteroditopic ligand and Fe^{III}/Fe^{II} redox pair.[4] Recently, a number of molecular switches, which could be triggered by chemical or electrochemical means, were reported in the literature.[5–8] We present here the synthesis of a new heteroditopic ligand **L** (Scheme 1). The corresponding double-stranded mononuclear cupric $Cu^{II}\mathbf{L}_{N_2O_2}$ and cuprous $Cu^{I}\mathbf{L}_{N_4}$ species (Fig. 1) were prepared and characterised by absorption spectrophotometry. The kinetics of the translocation process, which was chemically triggered in solution, was examined using a fast mixing technique.

Ligand **L** was built in a stepwise procedure (Scheme 1). The linking of two equivalents of 2,2′-bipyridyl-5,5′-dicarboxylate **2** with one equivalent of 3,3-bis(aminomethyl)dithiolane **1** was followed by hydrolysis of the diester groups and led to compound **3**. The coupling of **3** with two equivalents of 2-aminomethyl-8-hydroxyquinoline **4** yielded **L**. The structure of **L** was fully characterised by ^1H NMR, UV-visible spectrophotometry and FAB-MS.[9] A 'medium' binding site, constituted of two 8-hydroxyquinoline groups (N_2O_2) preferentially coordinates the cupric cation. A 'soft' receptor with two 2,2′-bipyridyl units (N_4) selectively prefers the cuprous cation (Fig. 1). The disulfide ring maintains the relative orientation of the binding sites once 'anchored' to a gold electrode or a semiconductor surface.[10] The two coordination sites were chosen for the large difference in their respective affinities for Cu^{II} and Cu^{I}.[11] Moreover, the electron-withdrawing effect of the amide linkers enhances the Cu^{I} selectivity of the bipyridyl moieties.[12] According to our previous results,[4] we have used a short spacer (–C(O)NHCH$_2$–) in order to accelerate the translocation process.

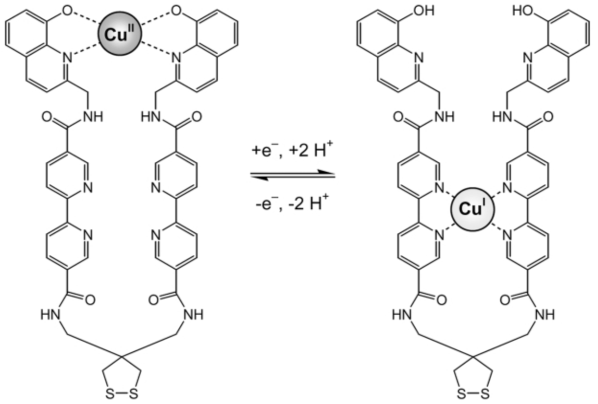
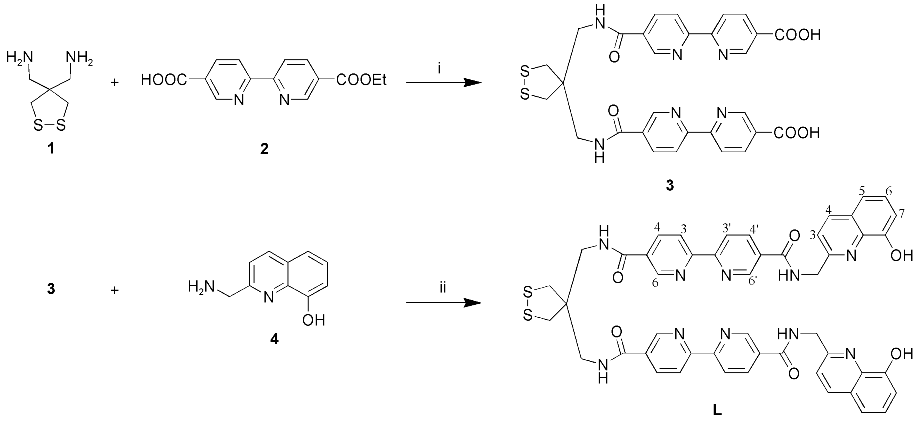


Fig. 1 Chemical structures of the Cu^{II} and Cu^{I} complexes of ligand **L**.



Scheme 1 Synthetic route to the molecular switch **L**. *Reagents and conditions*: (i) 1. HOBt, DIC, DMF, 2. NaOH; (ii) HOBt, DIC, DMF.

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† Electronic supplementary information (ESI) available: Fig. S1: cyclic voltammetry of $Cu^{II}\mathbf{L}_{N_2O_2}$ in DMSO. See http://www.rsc.org/suppdata/cc/b2/b204145f/

DOI: 10.1039/b204145f

A stoichiometric mixture of cupric acetate with **L** led to the brown–yellow cupric complex $Cu^{II}\mathbf{L}_{N_2O_2}$ in DMF–water (80:20 v/v). The brown–red cuprous $Cu^{I}\mathbf{L}_{N4}$ species was obtained by the stoichiometric reaction of $Cu(CH_3CN)_4PF_6$ with **L** in the same solvent. 2-Morpholinoethanesulfonic acid was used as a buffer (MES, 20 mM) at pH = 6.0.

The absorption spectrum of $Cu^{II}\mathbf{L}_{N_2O_2}$ (Fig. 2) displays a shoulder at 398 nm (ε_{398} = 3700 ± 400 M^{-1} cm^{-1}) on the absorption band of the ligand centred at 302 nm. A similar large red shift was observed in $CHCl_3$ for the binding of Cu^{II} with 8-hydroxyquinoline.[13] The electronic spectrum of $Cu^{I}\mathbf{L}_{N_4}$ (Fig. 2) displays an absorption band with a shoulder at 480 nm (ε_{480} = 2400 ± 200 M^{-1} cm^{-1}), which corresponds to the MLCT band of bis(2,2′-bipyridyl)copper(I) systems.[14]

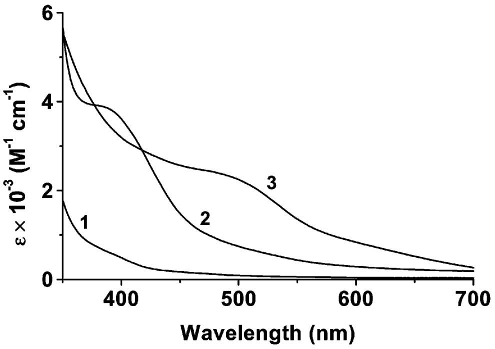
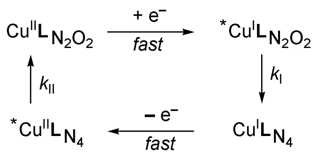


Fig. 2 Electronic spectra of ligand **L** and of its cupric and cuprous complexes. Spectrum 1: **L**; 2: $Cu^{II}\mathbf{L}_{N_2O_2}$; 3: $Cu^{I}\mathbf{L}_{N_4}$. Solvent: 20 mM MES in DMF–water (80:20 v/v), pH = 6.0, T = 25.0(2) °C. Solutions were thoroughly deaerated with argon.

Cyclic voltammetry of $Cu^{II}\mathbf{L}_{N_2O_2}$ in DMSO was carried out and showed a very large hysteresis for the Cu^{II}/Cu^{I} redox system, suggesting the metal ion translocation between the two binding sites upon reduction and reoxidation. A large potential span of ~0.5 V, where both $Cu^{II}\mathbf{L}_{N_2O_2}$ and $Cu^{I}\mathbf{L}_{N_4}$ are stable, was observed.

We examined various oxidising and reducing agents and chose ascorbic acid to reduce $Cu^{II}\mathbf{L}_{N_2O_2}$ and *tert*-butyl hydroperoxide to oxidise $Cu^{I}\mathbf{L}_{N_4}$. These oxidation and reduction reactions were faster than the translocation process of Cu^{I} or Cu^{II} and allowed us to separately follow the intramolecular movement of the copper cation. Our experiments with stopped-flow spectrophotometer confirmed the already published reduction mechanism of cupric complexes by ascorbic acid[15] and the well known oxidation mechanism of cuprous species by *tert*-butyl hydroperoxide.[16] The first-order rate constants, relative to the intramolecular motion of the copper cation, were determined. The chemically triggered redox switch reversibly interconverts with the respective first-order rate constants k_I = (2.3 ± 0.2) × 10^{-2} s^{-1} for the translocation of the cuprous cation and k_{II} = (9 ± 2) × 10^{-4} s^{-1} for that of the cupric cation (Scheme 2).



Scheme 2 Functioning principle of the redox-driven molecular switch presently discussed. $^{*}Cu^{I}\mathbf{L}_{N_2O_2}$ and $^{*}Cu^{II}\mathbf{L}_{N_4}$: kinetic intermediates; $Cu^{II}\mathbf{L}_{N_2O_2}$ and $Cu^{I}\mathbf{L}_{N_4}$: thermodynamic complexes. Solvent: 20 mM MES in DMF–water (80:20 v/v), pH = 6.0, T = 25.0(2) °C.

This work constitutes the first kinetic study of a chemically triggered motion of cations in a supramolecular edifice. We were able to determine the translocation rates of the copper cation between the two compartments of a molecular switch. Our physico-chemical approach pointed out a significant difference between the translocation rates of Cu^{II} and Cu^{I}, which could be explained by a larger lability of the cuprous intermediate $^{*}Cu^{I}\mathbf{L}_{N_2O_2}$ than that of the cupric kinetic species $^{*}Cu^{II}\mathbf{L}_{N_4}$. This result motivates further synthesis of ligands able to decrease the inertness of the intermediates and hence to accelerate the translocation of the cations. Thermodynamic and kinetic studies are clearly of great relevance in the development of fast and reversible molecular switches with possible applications as chemical memory elements.

This work has been supported by the Centre National de la Recherche Scientifique (CNRS) and in part by the G. M. J. Schmidt Minerva Center on Supramolecular Architectures and the Center for Molecular Design. C. Dietrich-Bucheker is gratefully acknowledged for the gift of $Cu(CH_3CN)_4PF_6$. This paper is dedicated in memory of Dr Jacqueline Libman. D.K. thanks the Ministère de la Recherche et de la Technologie for a post-doctoral grant.

Notes and references

1 (*a*) C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath and J. F. Stoddart, *J. Am. Chem. Soc.*, 2001, **123**, 12632–12641; (*b*) G. Y. Tseng and J. C. Ellenbogen, *Science*, 2001, **294**, 1293–1294; (*c*) A. Batchold, P. Hadly, T. Nakanishi and C. Dekker, *Science*, 2001, **294**, 1317–1320.

2 J. Libman, Y. Tor and A. Shanzer, *J. Am. Chem. Soc.*, 1987, **109**, 5880–5881.

3 S. Blanc, P. Yakirevitch, E. Leize, M. Meyer, J. Libman, A. Van Dorsselaer, A. M. Albrecht-Gary and A. Shanzer, *J. Am. Chem. Soc.*, 1997, **119**, 4934–4944.

4 L. Zelikovich, J. Libman and A. Shanzer, *Nature*, 1995, **374**, 790–792.

5 C. Canevet, J. Libman and A. Shanzer, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2657–2660.

6 (*a*) J. P. Collin, P. Gaviña and J. P. Sauvage, *New J. Chem.*, 1997, **21**, 525–528; (*b*) A. Livoreil, J. P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni and B. Ventura, *J. Am. Chem. Soc.*, 1997, **119**, 12114–12124.

7 (*a*) C. Belle, J. L. Pierre and E. Saint-Aman, *New J. Chem.*, 1998, 1399–1402; (*b*) T. R. Ward, A. Lutz, S. P. Parel, J. Ensling, P. Gütlich, P. Buglyó and C. Orvig, *Inorg. Chem.*, 1999, **38**, 5007–5017.

8 (*a*) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–1175; (*b*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 3348–3391; (*c*) V. Balzani, A. Credi, S. J. Langford, F. M. Raymo, J. F. Stoddart and M. Venturi, *J. Am. Chem. Soc.*, 2000, **122**, 3542–3543.

9 ^{1}H NMR (400 MHz, DMSO-d_6), δ 9.70 (s, 2H, HQ-OH), 9.50 (s, 2H, HQ-CH_2N*H*), 9.22 (d, $^{4}J_{HH}$ = 6.0 Hz, 4H, bipy-H6, bipy-H6’), 9.08 (t, 2H, $^{3}J_{HH}$ = 6.3 Hz, CCH_2N*H*), 8.60 (dd, 4H, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 6.0 Hz, bipy-H3, bipy-H3’), 8.46 (m, 4H, bipy-H4 , bipy-H4’), 8.30 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, HQ-H5), 7.58 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, HQ-H4), 7.38 (m, 4H, HQ-H3, HQ-H6), 7.11 (d, 2H, $^{3}J_{HH}$ = 7.1 Hz, HQ-H7), 4.88 (s, 4H, HQ-CH_2NH), 3.60 (d, 4H, $^{3}J_{HH}$ = 5.6 Hz, CCH_2NH), 3.20 (s, 4H, SCH_2). Assignments were made by 2D COSY experiments. FAB-MS m/z 931.5 [M + H]$^{+}$. UV-visible (20 mM MES in DMF–water (80:20 v/v), pH = 6.0) λ_{max}/nm (ε/ M^{-1} cm^{-1}) 302 (50000).

10 (*a*) T. Moav, A. Hatzor, H. Cohen, J. Libman, I. Rubinstein and A. Shanzer, *Chem. Eur. J.*, 1998, **4**, 502–507; (*b*) G. Ashkenasy, D. Cahen, R. Cohen, A. Shanzer and A. Vilan, *Acc. Chem. Res.*, 2002, **35**, 121–128.

11 (*a*) R. Nagar, *J. Inorg. Biochem.*, 1990, **40**, 349–352; (*b*) A. Odani, H. Masuda, K. Inukai and O. Yamauchi, *J. Am. Chem. Soc.*, 1992, **114**, 6294–6300; (*c*) B. James and R. Williams, *J. Chem. Soc.*, 1961, 2007–2019; (*d*) E. Onstott and H. Laitinen, *J. Am. Chem. Soc.*, 1950, **72**, 4724–4728.

12 N. Fatin-Rouge, S. Blanc, A. Pfeil, A. Rigault, A. M. Albrecht-Gary and J. M. Lehn, *Helv. Chim. Acta*, 2001, **84**, 1694–1711.

13 K. Sone, *J. Am. Chem. Soc.*, 1953, **75**, 5207–5211.

14 M. T. Youinou, R. Ziessel and J. M. Lehn, *Inorg. Chem.*, 1991, **30**, 2144–2148.

15 K. P. Balakrishnan, H. Gampp and A. D. Zuberbühler, *Helv. Chim. Acta*, 1984, **67**, 2155–2160.

16 M. Masarwa, H. Cohen, D. Meyerstein, D. L. Hickman, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1988, **110**, 4293–4297.