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Copper(I) Pseudorotaxane Monolayers Assembled on Gold Electrodes

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Two new copper (I) pseudorotaxanes bearing a thioctic acid appended unit have been prepared and deposited onto a gold electrode surface, leading to surface-attached electroactive pseudorotaxanes.

Catenanes and rotaxanes, multicomponent molecules consisting of interlocked and threaded rings, are promising components of future molecular devices, since their mechanically bound units are able to undergo reversible motions without damaging the chemical structure of the molecule.[1] However, before such molecular systems can be employed in a practical way, they have to be interfaced with the macroscopic world, for example by ordering them in two- or three-dimensional arrays. An attractive approach for such two-dimensional ordering involves the formation of self-assembled monolayers (SAMs) over metal surfaces. These SAMs can be easily prepared by adsorbing organosulfur compounds on gold, taking advantage of the strong sulfur−gold interaction.[2] Recently, some interesting gold electrode-attached catenanes have been reported. These systems have been prepared either by attaching a threaded precursor with sulfur atoms at both ends of the linear thread[3] or by anchoring catenanes incorporating a disulfide bridge in their structures.[4] On the other hand, some examples of surface-confined threaded systems have been described, involving deposition over electrodes by chemisorption[5] or electropolymerization[6] or formation of Langmuir films at air/water interfaces.[7] Pseudorotaxanes mechanically trapped in a rigid matrix or tethered onto the surface of a silica film have also been reported.[8] We would like to report herein the preparation and electrochemical studies of the first gold-attached metal-ion-containing pseudorotaxanes.

The target copper(I) pseudorotaxanes $\mathbf{1}^+$ and $\mathbf{2}^+$ are shown in Chart 1. Both threaded systems consist of a coordinating ring, containing a 1,10-phenanthroline moiety (phen) and a linear fragment (axle) incorporating a phen chelating unit in the middle and a thioctic acid derivative, to be used as anchoring fragment,[9] attached at one end. The main difference between both systems relies on the geometry of the acyclic fragment, being U-shaped in pseudorotaxane $\mathbf{1}^+$ and quasilinear in $\mathbf{2}^+$. The synthetic strategy for the key threading step is based on the three-dimensional template effect of copper(I), introduced by Sauvage in his synthesis of catenanes almost two decades ago.[10] Copper (I) is used as gathering and templating metal center, forcing the axle to thread through the ring while generating a highly stable bischelate complex between the metal ion and the two phen moieties.

The syntheses of the different pseudorotaxanes are sketched in Scheme 1. The axle components are based on previously reported diphenol-1,10-phenanthroline units (**3** and **6**).[11−13]

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(1) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405. Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611. Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. Special issue on molecular machines: *Acc. Chem. Res.* **2001**, *34* (6).

(2) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437. Ulman, A. *Chem. Rev.* **1996**, *96*, 1533. Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421.

(3) Lu, T.; Zhang, L.; Gokel, G. W.; Kaifer, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2542. Kern, J.-M.; Raehm, L.; Sauvage, J.-P. *C. R. Acad. Sci., Ser. IIc: Chim.* **1999**, 41.

(4) Raehm, L.; Hamann, C.; Kern, J.-M.; Sauvage, J.-P. *Org. Lett.* **2000**, *2*, 1991. Raehm, L.; Kern, J.-M.; Sauvage, J.-P.; Hamann, C.; Palacin, S.; Bourgoin, J.-P. *Chem. Eur. J.* **2002**, *8*, 2153.

(5) Vance, A. L.; Willey, T. M.; van Buuren, T.; Nelson, A. J.; Bostedt, C.; Fox, G. A.; Terminello, L. J. *Nano Lett.* **2003**, *3*, 81. Sheeney-Haj-Ichia, L.; Willner, I. *J. Phys. Chem. B* **2002**, *106*, 13094. Kim, K.; Jeon, W. S.; Kang, J.-K., Lee, J. W.; Jon, S. Y.; Kim, T.; Kim, K. *Angew. Chem., Int. Ed.* **2003,** *42*, 2293. Bryce, M. R.; Cooke, G.; Duclairoir, F. M. A.; John, P.; Perepichka, D. F.; Polwart, N.; Rotello, V. M.; Stoddart, J. F.; Tseng, H.-R. *J. Mater. Chem.* **2003**, *13*, 2111.

(6) Zhu, S. S.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 8713. Vidal, P.-L.; Divisia-Blohorn, B.; Bidan, G.; Kern, J.-M.; Sauvage, J.-P.; Hazemann, J.-L. *Inorg. Chem.* **1999**, *38*, 4203. Sauvage, J.-P.; Kern, J.-M.; Bidan, G.; Divisia-Blohorn, B.; Vidal, P.-L. *New J. Chem.* **2002**, *26*, 1287.

(7) Ahuja, R. C.; Caruso, P.-L.; Möbius, D.; Philp, D.; Perece, J. A.; Ringsdorf, H.; Stoddart, J. F.; Wildburg, G. *Thin Solid Films* **1996**, 671. Asakawa, M.; Higuchi, M.; Mattersteig, G.; Nakamura, T.; Pease, A. R.; Raymo, F. M.; Shimizu, T.; Stoddart, J. F. *Adv. Mater.* **2000**, *12*, 1099. Brown, C. L.; Jonas, U.; Preece, J. A.; Ringsdorf, H.; Seitz, M.; Stoddart, J. F. *Langmuir* **2000**, *16*, 1924.

(8) Chia, S.; Cao, J.; Stoddart, J. F.; Zink, J. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 2447.

(9) Liu, H.; Liu, S.; Echegoyen, L. *Chem. Commun.* **1999**, 1493. Fibbioli, M.; Bandyopadhyah, K.; Liu, S.-G.; Echegoyen, L.; Enger, O.; Diederich, F.; Bühlmann, P.; Pretsch, E. *Chem. Commun.* **2000**, 339.

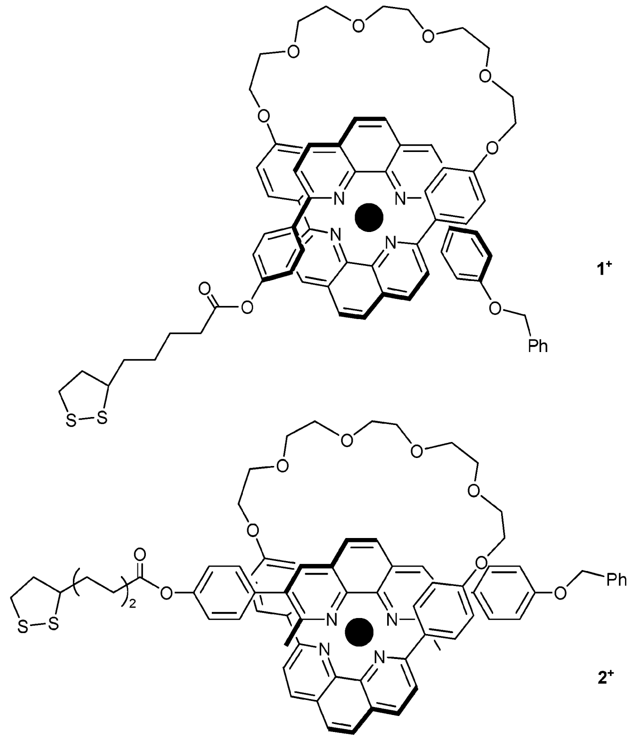
(10) Dietrich-Buchecker, C.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

(11) Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503.

(12) Saitoh, Y.; Koizumi, T.; Osakada, K.; Yamamoto, T. *Can. J. Chem.* **1997**, *75*, 1336.

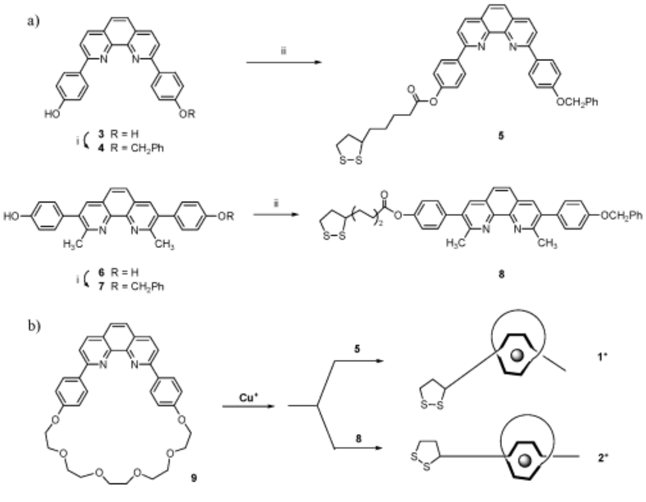
10.1021/ic034797h CCC: $25.00

Chart 1. Pseudorotaxanes $\mathbf{1}^+$ and $\mathbf{2}^{+a}$



^{a} Black circle represents Cu(I).

Scheme 1. (a) Synthetic Route for the Preparation of the Acyclic Fragments **5** and **8** and (b) Schematic Representation of the Threading Steps, Using Cu(I) as Template^a



^{a} (i) $PhCH_2Br$, K_2CO_3, DMF, 60 °C; (ii) thioctic acid, DCC, DMAP, CH_2Cl_2, rt.

Reaction of these precursors with benzyl bromide and K_2CO_3 in DMF yielded phenols **4** and **7**. Subsequent condensation with thioctic acid in the presence of DCC and DMAP afforded the desired ligands **5** and **8** in 78% and 60% yields, respectively. The ring component is in both cases a well-known coordinating macrocycle (**9**).[11] Finally, the threaded compounds [$\mathbf{1}^+$][PF_6^-] and [$\mathbf{2}^+$][PF_6^-] were obtained almost quantitatively by allowing a CH_2Cl_2 solution of the corresponding axle (**5** or **8**) to react with Cu(**9**)$(CH_3CN)_2^+$, prepared in situ from **9** and $Cu(CH_3CN)_4PF_6$, under argon at room temperature. Both pseudorotaxanes were unambiguously characterized by ^{1}H NMR, UV−vis spectroscopy, and FAB-MS.[14,15]

Self-assembled monolayers[16] were obtained by dipping clean gold bead electrodes into acetonitrile solutions of [$\mathbf{1}^+$][PF_6^-] or [$\mathbf{2}^+$][PF_6^-]. Since the complexes are electroactive, due to the presence of the copper center, the adsorption process could be monitored by cyclic voltammetry (CV).[17] Figure 1 shows typical CV curves for SAMs of [$\mathbf{1}^+$][PF_6^-] and [$\mathbf{2}^+$][PF_6^-].

Cyclic voltammograms of $\mathbf{1}^+$ and $\mathbf{2}^+$ have also been performed in solution using platinum as working electrode. Under these conditions, where no deposition occurs, a reversible redox wave at around 0.60 V (vs SCE) is observed, characteristic of the oxidation/reduction process of a copper (I) ion coordinated to two 2,9-disubstituted-1,10-phenanthroline moieties.[18] Thus, the electrochemical response of the gold bead electrodes evidences the adsorption of complexes $\mathbf{1}^+$ or $\mathbf{2}^+$ onto the gold surface. The voltammograms clearly show the cathodic and anodic waves corresponding to the Cu^{II}/Cu^{I} couple. As shown in Figure 1, there is a slight anodic shift of the $E_{1/2}$ values as well as an increase in the

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(13) Jimenez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Eur. J.* **2002**, *8*, 1456.

(14) [$\mathbf{1}^+$][PF_6^-]. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.72 (d, J = 8.5 Hz, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.46 (d, J = 8.3 Hz, 2H), 8.29 (d, J = 8.9 Hz, 1H), 8.23 (d, J = 8.9 Hz, 1H), 7.99 (s, 2H), 7.95 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.46−7.34 (m, 7H), 7.27 (d, J = 8.8 Hz, 4H), 6.36 (d, J = 8.6 Hz, 2H), 6.12 (d, J = 8.7 Hz, 2H), 5.98 (d, J = 8.8 Hz, 4H), 4.70 (s, 2H), 3.84 (s, 4H), 3.75−3.70 (m, 4H), 3.70−3.48 (m, 13H), 3.25−3.12 (m, 2H), 2.55−2.45 (m, 3H), 2.00−1.89 (m, 1H), and 1.81−1.50 (m, 6H). HRMS (FAB) *m/z* (% rel intensity): calcd for $C_{73}H_{68}N_4O_9S_2Cu$ ([M − PF_6]$^+$) 1271.372 (peak maximum mass, 100) and 1273.371 (peak ^{65}Cu, 91); found 1271.376 (100) and 1273.377 (86). UV−vis (CH_3CN) λ_{max} = 437 nm (ϵ = 2050).

(15) [$\mathbf{2}^+$][PF_6^-]. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.67 (d, J = 8.6 Hz, 2H), 8.41 (s, 1H), 8.38 (s, 1H), 8.15 (d, J = 8.6 Hz, 2H), 8.16−8.13 (m, 4H), 7.52−7.37 (m, 11H), 7.34 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.00 (d, J = 8.8 Hz, 4H), 5.16 (s, 2H), 3.69 (s, 4H), 3.65−3.52 (m, 9H), 3.43−3.35 (m, 8H), 3.18−3.07 (m, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.51−2.42 (m, 1H), 2.15 (s, 6H), 1.97−1.88 (m, 1H), and 1.83−1.52 (m, 6H). HRMS (FAB) *m/z* (% rel intensity): calcd for $C_{75}H_{72}N_4O_9S_2Cu$ ([M − PF_6]$^+$) 1299.404 (peak maximum mass, 100) and 1301.405 (peak ^{65}Cu, 93); found: 1299.398 (100) and 1301.402 (91). UV−vis (CH_3CN) λ_{max} = 444 nm (ϵ = 2970).

(16) The gold bead working electrodes were made by annealing the tip of a gold wire (99.999%, 0.5 mm diameter, Aldrich) in a gas−oxygen flame. Subsequently, the hot gold bead was cooled by dipping it in deionized water, and the wire was sealed with glass. The geometric areas of the gold electrodes were calculated from the slopes of the linear plots of anodic peak current versus the square root of the scan rate obtained for the reversible oxidation of ferrocene in acetonitrile (1 mM), taking 2.3×10^{-5} cm^2/s as the diffusion coefficient and knowing the exact concentration from the mass. Typical values for the geometric area of the electrodes varied from 0.04 to 0.06 cm^2.

(17) In a typical experiment, a monolayer was grown by dipping a freshly prepared gold bead electrode into a 1 mM MeCN solution of the corresponding compound for at least 24 h, followed by rinsing with large amounts of MeCN and drying under argon. Cyclic voltammetry experiments were performed on an Autolab PGSTAT12 potentiostat/galvanostat instrument at room temperature, under argon, in a single-compartment electrochemical cell. A three-electrode configuration was used containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, (electrochemical grade) and MeCN as solvent. As reference, a nonaqueous Ag/Ag$^+$ electrode was used; the counter electrode was a platinum wire, and as working electrode, a platinum Ø 2 mm electrode or a SAM-modified spherical gold electrode was used.

(18) Armaroli, N.; Balzani, V.; Collin, J.-P.; Gaviña, P.; Sauvage, J.-P.; Ventura B. *J. Am. Chem. Soc.* **1999**, *121,* 4397.

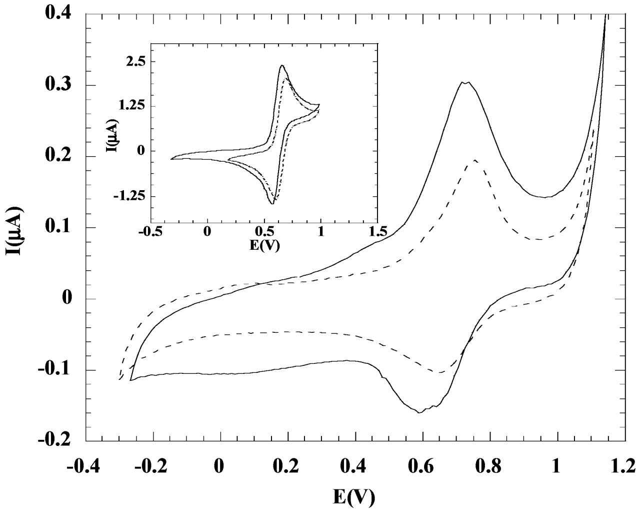

Figure 1. Cyclic voltammograms of **1**$^+$ (—) and **2**$^+$ (- - -) deposited on gold beads.[16] Scan rate: 100 mV·s^{-1}. The inset shows the CV measurements of the same compounds in solution using a platinum Ø 2 mm electrode as the working electrode.

difference in potential (ΔE_p) between the anodic and cathodic peaks with respect to the values in solution.

The intensity of the oxidative peak current increases linearly with the scan rate for both SAMs (Figure 2), indicative of a surface-confined behavior of the redox species.[19] Integration of the anodic peak current yielded a surface coverage of 6.7×10^{-11} mol/cm^2 and 4.9×10^{-11} mol/cm^2 for **1**$^+$ and **2**$^+$, respectively. This coverage is 1 order of magnitude lower than for other SAMs of thioctic ester substituted complexes described before.[8] Among other factors, this could be attributed to (i) the large volume of the pseudorotaxane and (ii) the presence of positive charges on the complexes, leading to electrostatic repulsions which would separate the molecules. PF_6^- anions could also be incorporated between the cationic complexes. A small decrease in the current response after several potential scan cycles is observed (20−25% after 25 cycles of SAMs of **1**$^+$ and 15% after 25 cycles of SAMs of **2**$^+$). These results indicate a good stability of the adsorbed monolayers, taking into account that we are dealing with open species (pseudorotaxanes), which have the possibility of dethreading of the ring during the experiments. An obvious improvement would be the attachment of a bulky blocking group at the end of the strings.

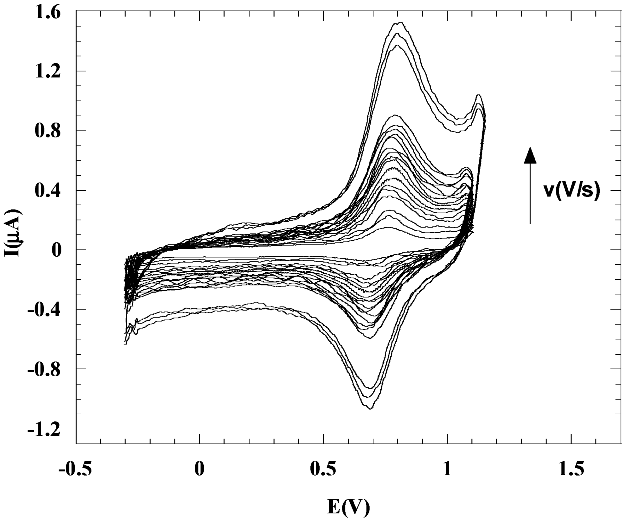

Figure 2. Scan rate dependence of the CV response of **2**$^+$. The scan rate was varied from 100 to 950 mV·s^{-1} in 50 mV·s^{-1} steps. The three more intense curves correspond to scan rates of 1500, 1600, and 1700 mV·s^{-1}. Electrode surface area: 0.04 cm^2.

To summarize, two new copper(I) pseudorotaxanes incorporating a thioctic ester derivative attached at one end of the string have been synthesized. These threaded molecules have successfully been attached onto a gold surface, through the disulfide bridge. The electrochemical response in the solid state, which has been studied by CV, evidences the surface-confined nature of both pseudorotaxane monolayers.

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[19] Bard, A. J.; Faulkner, R. L. *Electrochemical Methods*; Wiley: New York, 1980.