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Self-assembly of a nickel(II) pseudorotaxane nanostructure on a gold surface*

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Abstract: Tetraazamacrocyclic complexes of Ni^{II} and Cu^{II} can be used as components of catenanes or rotaxanes showing electrochemically switched intramolecular motion in solution. In our present studies, we modify these compounds with organothiol chains to attach them to the surface of the electrode using the self-assembly method and employ them next as molecular switches, which change conductivity upon applying appropriate potential. The electrochemical properties of these compounds are studied in the solution and, in the case of thiol derivative, immobilized on the electrode surface. The macrocyclic complex of Ni^{II}, immobilized on the Au surface, forms the axis of the rotaxane. This compound can be anchored to the surface by one or two thiol groups. The data obtained from scanning tunneling microscopy (STM) experiments using colloidal Au confirm that the orientation normal to the surface dominates. The electrochemical experiments reveal reversible one-electron oxidation of metal center from +2 to +3. The behavior of the electrode modified with the macrocyclic complex of Ni^{II} upon immersion in a solution containing bismacrocyclic complex of Ni^{II} points to the formation of a new rotaxane-like nanostructure on the surface of the electrode.

Keywords: pseudorotaxane; macrocyclic ligands; nickel complexes; voltammetry; self-as-sembly; monolayers.

INTRODUCTION

The well-known ability of macrocyclic ligands to stabilize unusual oxidation states of coordinated transition-metal ions makes them a promising tool for the construction of molecular devices [1–5]. Recently, we have reported self-assembly of a [2]catenane consisting of an electron-rich component (dibenzo-24-crown-8) and an electron-deficient unsaturated bismacrocyclic [14]cyclidene complex coordinating two metal ions (the same [6] or different: Cu and Ni [7]). In these compounds, the electronrich benzene rings of the interlocked crown ether adopt such a conformation as to maximize the donor–acceptor interactions with the bismacrocyclic subunit. By applying appropriate potentials, the coordinated metal ions can selectively be oxidized to the higher oxidation state (+3), which favors an

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interaction of these centers with the π -electron-rich aromatic rings of the crown ether unit. In consequence, the relocation of benzene rings of the crown toward the oxidized metal center takes place. Integration of such molecules with electronic elements to form functional devices attracts substantial effort, and exciting advances are observed [8,9]. In the bottom-up construction of molecular machines, the tethered molecules assembled into well-organized monolayers or solid substrates are a new and important direction and several exciting examples have been already demonstated [10]. The aim of this work is to synthesize neutral macrocyclic complexes of transition-metal ions which could be useful as π -electron-rich building blocks in the self-assembly of intertwined molecules on solid supports. In this paper, we describe the synthesis of neutral azamacrocyclic complex of Ni (5) and characterize its redox properties both in the solution and immobilized on the surface of the Au electrode. We also demonstrate its ability to form a pseudorotaxane structure with a bismacrocyclic complex of Ni (7) [6,11,12].

EXPERIMENTAL

Voltammetry experiments were done using the Autolab potentiostat (ECO Chemie, Netherlands) in three-electrode arrangement with a silver/silver chloride (Ag/AgCl) as the reference and platinum foil as the counter electrode. Glassy carbon electrode (GCE, BAS, 3 mm diameter) or 200–300-nm Au films evaporated onto borosilicate glass slides precoated with 1–4-nm underlayer of Cr (Arrandee) were used as the working electrodes. Unless stated, the acetonitrile (AN) containing 0.1 M tetrabutylammonium hexafluorphosphate (TBAHFP) was used as the supporting electrolyte solution. The reference electrode was separated from the working solution by electrolytic bridge filled with 0.1 M TBAHFP/AN solution. The reference electrode potential was calibrated using ferrocene oxidation process in the same TBAHFP/AN solution. Argon was used to deaerate the solution, and argon blanket was maintained over the solution during the experiments.

RESULTS AND DISCUSSION

Synthesis

The synthesis of dithiol **5** is outlined in Scheme 1. Transesterification of previously described dimethyl ester (1) [13] with propane-1,3-diol in the presence of catalytic amount of triflic acid gave diol **2**. Reaction of diol (**2**) with mesyl chloride in the presence of triethylamine resulted in formation of dimesyl ester **3**, which in reaction with thiourea followed by hydrolysis was transformed into dithiol **5**.

Compounds 1–5 are composed of tetraazamacrocylic 14-membered rings and Ni²⁺ as central ion. The ligand has charge –2, so it can neutralize the charge of the coordinated metal ion. The compounds differ from each other by substituents on the ester group, therefore, all chemical transformations could be followed by ¹H NMR measurements. Structures of studied complexes were confirmed by electrospray ionization mass spectrometry (ESIMS) (e.g., for $5 + H^+ m/z = 485.1$) and NMR spectra. The 200 MHz ¹H NMR spectrum of dithiol 5 in CDCl₃ solution is very simple and consists of two singlets of macrocycle protons (7.87 ppm, 4 H–C=N– protons; 4.32 ppm, 8 ethylene bridges protons) and three multiplets of propylene protons (4.32 ppm, triplet of 4 –O–CH₂–, J = 7 Hz; 2.86 ppm, triplet of 4 –S–CH₂–, J = 7 Hz; 2.15 ppm, quintet of 4 C–CH₂–C, J = 7 Hz).





Despite the fact that ESIMS might not reflect accurately the solution binding affinities, it provides important information on host–guest complexes and the nature of their interactions [13]. ESIMS of the equimolar mixture (10^{-3} M) of neutral complex 1 and bismacrocyclic receptor 7 in dichloromethane AN (1:3) solution confirmed formation of the host–guest complexes (Fig. 1). A new, +4 charged peak of m/z = 437.2 corresponding to the formation of 1:1 adduct: **7** + 1 was observed in the spectrum of their mixture [15]. These observed interactions between complex 1 and bismacrocycle 7 in the solution led us to tailor a similar system immobilized on the electrode surface.



Fig. 1 ESIMS spectrum of the equimolar mixture of complexes 1 and 7.

Voltammetry in the solution

Linear scan cyclic voltammograms of neutral Ni^{2+} complexes **1**, **2**, and **6** indicate differences in their formal potentials without major deviations from reversibility and no involvement of chemical reactions (Fig. 2). For these complexes, the peaks corresponding to the Ni^{2+}/Ni^{3+} electrode processes are well developed, while further reduction to the Ni^+ form is not observed. This indicates that substituents do not deform the planar coordination environment around Ni^{2+} , which allows the formation of a stable Ni^{1+} complex. The deviation from reversibility observed in the case of dithiol derivative **5** may be ascribed



Fig. 2 Cyclic voltammograms for 5×10^{-4} mol/l Ni complexes: (a) **1**; (b) **2**; (c) **6** in 0.1 M TBAHFP AN/dichloromethane (DCM) and for the dithiol derivative; (d) **5** in 0.1 M TBAHFP/chloroform. Scan rate 0.05 V/s.

to some adsorption of this compound on the electrode surface. The peak potentials are collected in Table 1. The diffusion coefficients of the complexes, D, were calculated from the slope of the peak current-concentration plots using the Randles–Ševcik equation [16]:

$$i_{\rm p} = 0.446 (n^{3/2} {\rm F}^{3/2} / {\rm R}^{1/2} {\rm T}^{1/2}) A D^{1/2} v^{1/2} C_{\rm ox}^0$$
⁽¹⁾

where i_p is the peak current, *n* is the number of electrons, *A* is the electrode area, *v* is scan rate, and C_{ox}^0 is the concentration of the complex.

Table 1 Redox properties and diffusion coefficients of compounds **1**, **2**, **6** in 0.1 M TBAHFP AN/DCM and compound **5** in 0.1 M TBAHFP/chloroform.

Compound	Epa [V]	Epc [V]	E' [V]	Epa-Epc [V]	$D [\mathrm{cm}^2/\mathrm{s}]$
Ni-ester 1	0.850	0.767	0.809	0.083	1.856×10^{-5}
Ni-diol 2	0.876	0.730	0.803	0.146	3.759×10^{-5}
Ni-aldehyde 6	1.011	0.923	0.977	0.088	1.137×10^{-5}
Ni-dithiol 5	1.074	0.776	0.925	0.298	-

Potentials of the Ni²⁺/Ni³⁺ processes depend on the type of the substituent in the macrocyclic ring. The substituents have different electron-donating or -withdrawing properties. For the complex with aldehyde group, the formal potential is the most positive among all examined compounds pointing to the weakest donor properties of this system.

Self-assembly of dithiol complex (5) on the electrode surface

The macrocyclic complex of Ni^{II} **5**, possessing thiol-terminated side chains, was selected as the axis of the rotaxane molecule to be assembled on the Au surface. As shown on the scheme (Fig. 3), this compound can be attached to the surface by one or two thiol groups. Scanning tunneling microscopy (STM) experiments using colloidal Au were performed to show orientation of complex **5** on the Au surface. The colloidal Au can be bound only by the free thiol group, because the second thiol group of the molecule is involved in binding with the surface of the Au electrode (Fig. 4). The data obtained indicate the presence of Au nanoparticles on the surface, hence, they confirm that the orientation normal to the surface dominates. The calculations based on the surface coverage obtained from the charge of the thiol reductive desorption peak also indicate that the monolayer is densely packed and the molecules adopt mainly perpendicular orientation (>90 % of the molecules). It should be, however, kept in mind that the packing densities obtained from electrochemical desorption experiments may be overestimated owing to the contribution of double-layer charging current to the desorption charge [17].

To confirm this orientation, we also performed the voltammetric experiments. Splitting of the surface peaks sometimes observed can be interpreted as due to electrochemical responses of two differently oriented populations of molecules. The differences in peak potentials may result, for example, from different distance of the metal center from the surface of the electrode.

A common solvent for the self-assembly procedure is ethanol, however, the dithiol derivative shows low solubility in ethanol, hence a mixture of solvents–ethanol:chloroform (1:1) had to be used. From STM and voltammetric experiments, it is known that monolayers prepared from this mixture have few defects and are stable during the experiments [16,17].



Fig. 3 Two ways of binding dithiol derivative 5 to the Au surface.



Fig. 4 STM image obtained for dithiol derivative complex-modified Au slide after immersion in an aqueous suspension of Au nanoparticles with a diameter of 5 nm. Bias voltage = 1 V, tunneling current = 1 pA.

Broadening of the voltammetric peaks for the dithiol derivative **5** compared with the theoretical width of the peaks (90.6 V for a 1 e process at room temperature) may be due either to nonidentical orientation of all molecules or to some repulsion between the metal centers in the monolayer. The area per molecule in such a monolayer calculated from the charge of the oxidation peak according to equation Q = nFA is about 43 ± 1.5 Å² (see Fig. 5).

The process of Ni²⁺ center oxidation takes place at rather positive potentials (1 V vs. Ag/AgCl) close to the onset of Au oxidation, which may lead to destroying of the Ni²⁺ complex monolayer. To overcome this difficulty, octane-1-thiol (C₈–SH) was used to "seal" the monolayer. In practice, following self-assembly of the Ni²⁺ complex the electrode was placed in 10⁻² M solution of C₈–SH for 1 h (Fig. 5). Shorter-chain thiols did not block the final Au oxidation current.

The height of the peaks decrease as expected, however, the half-widths of the peaks are smaller and the peak-to-peak separation is smaller by 100 mV.



Fig. 5 Cyclic voltammograms recorded using the Au electrode modified by dithiol derivative 5 in 0.1 M TBAHFP/AN. Scan rate 0.5 V/s. Solid line: following immersion to solution of C_8 -SH for 1 h.

Host-guest interactions: Creating a pseudorotaxane

Anchoring Ni^{2+} complex to the surface of the electrode is the first step in the self-assembly of pseudorotaxane on the electrode. The Ni^{2+} complex constitutes the axis of the rotaxane. The second component of the intertwined structure can be bismacrocyclic complex of Ni 7, which is an acceptor (Fig. 6). Both of these complexes are electroactive.



Fig. 6 Formation of the rotaxane molecule by "thread" complex 5 and threading molecule: bismacrocycle 7.

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Electrode modified by mixed monolayer of Ni²⁺ complex 5 and octane-1-thiol as the sealing component was placed in the solution containing 0.1 mM bismacrocyclic complex 7 in 0.1 M TBAHFP/AN (Fig. 7). The redox process of the bismacrocylic ring occurs at 1.5 V vs. Ag/AgCl on the GCE hence is too positive to be resolved using the Au electrode. The formation of the rotaxane was, therefore, revealed by the gradual shift of the potential of the oxidation of complex 5 with time of immersion of the electrode in the solution of bismacrocyclic compound 7. The potential was shifted toward more positive potentials upon mixing with the excess of bismacrocycle, indicating weaker donor properties of the Ni^{2+} complex 5 in the presence of bismacrocycle 7. This behavior may be interpreted as indicative of associative properties of the bismacrocyclic compound toward Ni²⁺ complex anchored to the electrode surface leading to the formation of the rotaxane structure. The reason why oxidation of the metal center of the axis molecule 5 is more difficult in the environment of highly oxidized ring molecule 7 is probably the π - π interactions between the components of the pseudorotaxane. The molecule of axis is neutral, thus, its interaction with the highly positive bismacrocyclic complex is possible. However, upon oxidation of the Ni^{2+} to Ni^{3+} , the axis becomes positively charged and repulses the ring molecule from its vicinity (dethreads it). This explains why the oxidation peak in the presence of bismacrocyle is more positive than in its absence while the potential of the reduction peak remains unchanged (Fig. 7).

Forming pseudorotaxane is thus a process that takes some time, but also can be switched off by applying potential more positive than Ni^{2+} oxidation. Upon application of 0.4 V for 3 min to the electrode (Fig. 7), the metal center of the axis remains in its +2 oxidation state, interacts with the compound 7, and the pseudorotaxane structure is formed on the surface.



Fig. 7 Cyclic voltammograms recorded using the Au electrode modified by Ni²⁺ complex **5** in 0.1 mM solution of bismacrocyclic complex **7** in 0.1 M TBAHFP/AN. Scan rate 0.5 V/s. Inset: applied potential changes with time.

CONCLUSIONS

By appropriate tuning of the properties of macrocyclic complexes, the formation of host–guest complexes anchored to the electrode can be achieved. The planar dithiol derivative of azamacrocyclic Ni²⁺ complex acts as the axis of a new pseudorotaxane nanostructure assembled on the electrode. It has to be kept in mind that not only the π – π interaction but also electrostatic interactions are important for the stability of the nanostructure. The pseudorotaxane presented in this work undergoes dissociation when the Ni²⁺ center of the axis is oxidized to Ni³⁺ since repulsion between the charged components leads to dethreading of the bismacrocylic unit. The interactions between macrocyclic complexes

demonstrated in the present paper are extremely interesting and promising from the viewpoint of new meccano-molecular devices [18], and work in this direction is carried out in our laboratories.

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REFERENCES

- 1. J.-P. Sauvage (Ed.). *Molecular Machines and Motors, Structure Bonding*, Vol. 99, Springer, Berlin (2001).
- V. Balzani, M. Venturi, A. Credi. *Molecular Devices and Machines*, Wiley-VCH, Weinheim (2003).
- 3. S. Bonnet, J.-P. Collin, M. Koizumi, P. Mobian, J.-P. Sauvage. Adv. Mater. 18, 1239 (2006).
- 4. E. R. Kay, D. A. Leigh, F. Zerbetto. Angew. Chem., Int. Ed. 46, 72 (2007).
- 5. B. Champin, P. Mobian, J.-P. Sauvage. Chem. Soc. Rev. 36, 358 (2007).
- B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak. J. Am. Chem. Soc. 123, 9356 (2001).
- (a) B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak. Angew. Chem., Int. Ed. 43, 1700 (2004); (b) B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak. Angew. Chem. 116, 1700 (2004).
- 8. J. W. Steed, J. L. Atwood. Supramolecular Chemistry, Chap. 8, John Wiley, New York (2000).
- 9. A. E. Kaifer, M. Gomez-Kaifer. *Supramolecular Electrochemistry*, pp. 142–161, Wiley-VCH, Weinheim (1999).
- B. C. Bunker, D. L. Huber, J. G. Kushmerick, T. Dunbar, M. Kelly, C. Matzke, J. Cao, J. O. Jeppesen, J. Perkins, A. H. Flood, J. F. Stoddart. *Langmuir* 23, 31 (2007).
- 11. S. Domagała, A. Więckowska, J. Kowalski, A. Rogowska, J. Szydłowska, B. Korybut-Daszkiewicz, R. Bilewicz, K. Woźniak. *Chem. Eur. J.* **12**, 2967 (2006).
- A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak, B. Korybut-Daszkiewicz, A. Tomkiewicz, J. Mroziński. *Inorg. Chem.* 42, 5513 (2003).
- A. Rybka, R. Koliński, J. Kowalski, R. Szmigielski, S. Domagała, K. Woźniak, A. Więckowska, R. Bilewicz, B. Korybut-Daszkiewicz. *Eur. J. Inorg. Chem.* 172 (2007).
- 14. M. Vincenti. J. Mass Spectrom. 30, 925 (1995).
- W. Grochala, A. Jagielska, K. Woźniak, A. Więckowska, R. Bilewicz, B. Korybut-Daszkiewicz, J. Bukowska, L. Piela. J. Phys. Org. Chem. 14, 63 (2001).
- 16. Z. Galus. *Fundamentals of Electrochemical Analysis*, 2nd ed., Polish Scientific Publishers, Warsaw (1994).
- 17. S. Sęk, A. Misicka, K. Świątek, E. Maicka. J. Phys. Chem. B 110, 19671 (2006).
- 18. R. A. Bissel, E. Cordova, A. E. Kaifer, J. F. Stoddart. Nature 363, 133 (1994).