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Synthesis of Copper(I) Catenanes Incorporating a Disulfide Bridge and Their Deposition on a Gold Surface

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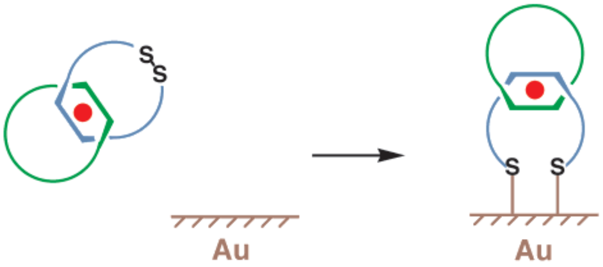
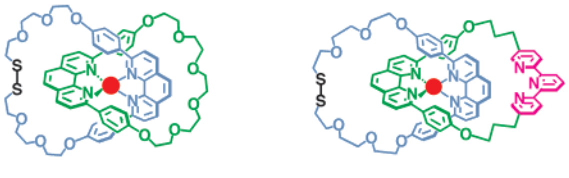
ABSTRACT



The synthesis of two coordinating catenates with the ability to undergo surface-confined chemistry is described. For each catenate, one of the rings includes a 2,9-diphenyl-1,10-phenanthroline unit as a coordinating moiety and a disulfide bridge, which allows adsorption of the catenate onto a gold surface, thus going from a molecular catenate to a [gold-adsorbed] species in which gold atoms are elements of one of the rings.

Interlocking ring systems and rotaxanes are important and promising multicomponent functional assemblies and potential elements of future molecular devices.[1−3] Different routes can be followed to attach catenane or rotaxane assemblies onto a metal surface. In the field of self-assembled monolayers, numerous authors have taken advantage of the strong interaction between gold and sulfur atoms.[4] A remarkable example has recently been reported which involves surface-incorporated catenanes.[5,6] Sulfur atoms are mainly present in the organic substrates as thiol, thioether, or disulfur functionalities. Recently[7] we described the coverage of a gold surface with a pre-rotaxane structure in which the constituent elements are held together via a transition metal, Cu(I). The metal is coordinated to two 2,9-diphenyl-1,10-phenanthroline (dpp) moieties. One of the dpp fragments is included in the wheel of the rotaxane, the other one in the axle. Adsorption onto a gold surface was achieved



Cu.1$^+$ **Cu.2$^+$**

Figure 1. Homo- and heteroleptic copper(I) [2]-catenanes **Cu.1**$^+$ and **Cu.2**$^+$. Each catenate contains a coordinating ring which includes a disulfide bridge.

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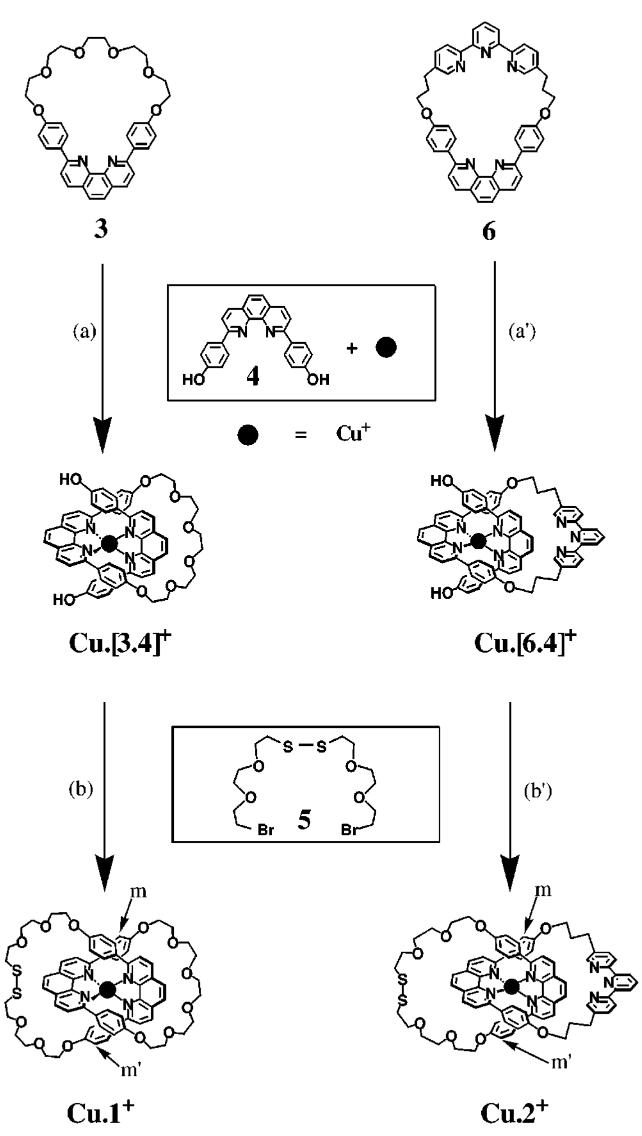

Figure 2. Representation of the threading (a and a′) and ring closing (b and b′) steps which are the key steps of the synthesis of catenates **Cu.1**$^+$ and **Cu.2**$^+$.

via a thiol group attached at each end of the linear thread. As a consequence of the adsorption of the thiol functions linked to the thread of the Cu(I) rotaxane, a catenate structure was expected for the [gold-adsorbed] entity. However, due to the pronounced reducing character of the thiol functionality, only the copper(I)-rotaxane can be prepared and adsorbed. The corresponding copper(II)-rotaxane is too strong an oxidant to be compatible with the presence of thiol functionalities in the molecular structure. The reducing power of the thiol functionalities also explains the low stability of the metallo-rotaxane precursor and of the noncomplexed molecular thread in the presence of air, which leads progressively to the formation of insoluble polydisulfide material.

We now report a new way to anchor metallo-catenanes onto a metallic surface. In this procedure, molecular catenates, already present in solution, are adsorbed onto the metal. One of the constituent rings incorporates a disulfide bridge, which is chemically inert toward oxidation and which will act as an alternative to the thiol functionality in the adsorption process. Moreover, mechanical linkage of the rings in the catenates excludes the possibility of ligand exchange around the metal in the course of the adsorption process.

Two representative examples of such [2]-copper-catenanes are depicted in Figure 1.

Catenate **Cu.1**$^+$ is similar to the prototypical catenate from our group which was published many years ago,[8] the difference being the presence in one ring of the cleavable disulfide fragment. Catenate **Cu.2**$^+$ is related to molecular machines and motors, i.e., molecular assemblies in which some parts can be set into motion by an external signal, such as proton, electron, or photon transfer, while other parts remain motionless.[2,3,9−11] As for catenate **Cu.1**$^+$, a disulfide fragment and a chelating moiety are inserted in one of the rings. The other ring is a hetero bis-chelating macrocycle, including a bidentate (dpp) and a terdentate (terpyridine) moiety.[12] The synthetic routes leading to copper-catenanes **Cu.1**$^+$ and **Cu.2**$^+$ are similar. For each one, the two key steps are represented in Figure 2.

The threading steps (a and a′, Figure 2) take advantage of the powerful template effect of copper(I), which forms with dpp derivatives tetrahedral $Cu(dpp)_2^{2+}$ complexes of particularly high stability.[13,14] Thus, precatenates **Cu[3.4]**$^+$ and **Cu[6.4]**$^+$ are formed quantitatively by reacting Cu(I) ions—such as $Cu(CH_3CN)_4BF_4$ or $Cu(CH_3CN)_4PF_6$—with macrocycles **3** and **6**, respectively, in the presence of stoichiometric amounts of 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline **4**. The ring closing reactions lead from the threaded structures **Cu[3.4]**$^+$ and **Cu[6.4]**$^+$ to the copper [2]-catenanes **Cu.1**$^+$ (15% yield) and **Cu.2**$^+$ (12% yield), respectively. These reactions occur by formation of 34-membered macrocycle **7** (Figure 3) interlocked with **3** or **6** in **Cu.1**$^+$ and **Cu.2**$^+$, respectively. They were achieved by reacting the nucleophilic diphenolate derivative of **Cu[3.4]**$^+$ and **Cu[6.4]**$^+$ with disulfide bridge-incorporating chain **5**, bearing an electrophilic carbon atom at each end. Small amounts of the free macrocycle **7** were isolated.

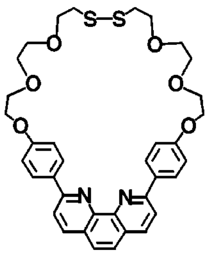

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Figure 3. The dpp-based coordinating subunit of **Cu.1**$^+$ and **Cu.2**$^+$, which includes a disulfide fragment. **7** is a 34-membered ring.

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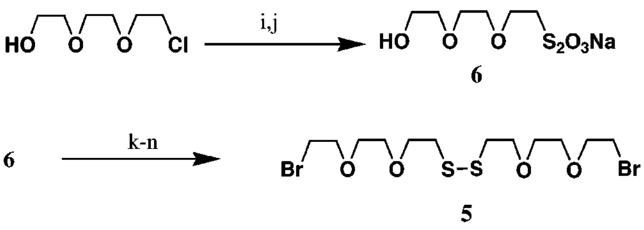
Each sulfur atom of **5** is linked to a 2-(2-bromoethoxy)ethoxyethyl fragment. The sequential reaction steps leading from 2-[2-(2-chloroethoxy)ethoxy]ethanol to **5** are represented in Figure 4. The sulfur−sulfur coupling reaction was done by oxidation with air of the crude hydrolysis product of Bunte salt **6**.[15]



i) NaI, acetone, THF, 60°C, 74% j) Sodium thiosulfate, EtOH, reflux, 50%
k) HCl, H_2O, reflux, quantitative l) O_2, quantitative
m) MsCl, NEt_3, CH_2Cl_2, -5°C, 78% n) LiBr, acetone, reflux, quantitative

Figure 4. Synthetic route leading from commercial 2-[2-(2-chloroethoxy)ethoxy]ethanol to the dielectrophilic reagent **5**. Step 1 is achieved by stirring the hydrolysis crude product of **6** vigorously in the presence of air.

Clear evidence for the catenate structures of **Cu.1**$^+$ and **Cu.2**$^+$ was obtained by ^{1}H NMR and FAB-MS spectroscopies. For **Cu.1**$^+$, ^{1}H NMR shows a strong upfield shift of the doublets corresponding to the protons m and m′ of subunits **3** and **7**, respectively (Figure 2). This shielding is characteristic of entwined 2,9-diaryl-1,10-phenanthroline complexes and is due to the spatial proximity of the phenyl group of one coordinating subunit to the phenanthroline core of the other.[16] For instance, a shielding effect of $\Delta\delta = -1.28$ ppm is observed for the meta protons (H_m) of **Cu.1**$^+$ compared to the corresponding protons in the free ring **3**. A similar shift ($\Delta\delta = -1.09$ ppm) is observed for the meta protons ($H_{m'}$) in **Cu.1**$^+$ and the corresponding protons in **7**. For **Cu.2**$^+$, in which one ring, **6**, incorporates two different coordinating sites, ^{1}H NMR confirms both the catenate structure and the entwining of two dpp subunits (one from each macrocycle) around the metal. The upfield shifts of protons H_m and $H_{m'}$ (Figure 2) ($\Delta\delta = -1.10$ ppm for H_m and $\Delta\delta = -1.17$ ppm for $H_{m'}$) are close to those observed for analogous protons in **Cu.1**$^+$, whereas protons of the terpyridine subunit in **Cu.2**$^+$ resonate at a field similar to those in free macrocycle **6**.

The positive FAB mass spectra of **Cu.1**$^+$ and **Cu.2**$^+$ show a pattern that has already been observed for other metallocatenanes. A characteristic feature of the mass spectroscopy of catenanes is the almost complete absence of ions between the molecular peak and the peak corresponding to one individual macrocycle.[17] Thus, for **Cu.1**$^+$, the spectrum shows the molecular peak **[Cu.1]**$^+$, and the next lowest peaks are those of each of the constituent macrocycles complexed by a copper(I) ion, i.e., **[Cu.3]**$^+$ and **[Cu.7]**$^+$, respectively: $m/z = 1287.3$ for **[Cu.1]**$^+$, calcd 1289.04, $m/z = 721.2$ for **[Cu.7]**$^+$, calcd 722.38, $m/z = 629.2$ for **[Cu.3]**$^+$, calcd 630.21. For **Cu.2**$^+$, the main peaks correspond to **[Cu.2]**$^+$ ($m/z = 1400.1$, calcd 1401.2), **[Cu.6]**$^+$ ($m/z = 740.1$, calcd 742.37), and **[Cu.7]**$^+$ ($m/z = 721.1$, calcd 722.38).

Adsorption experiments were carried out by dipping gold beads into dichloromethane solutions of **Cu.1**$^+$ and **Cu.2**$^+$ ($C = 10^{-3}$ mol·L^{-1}). We observed that maximum coverage was achieved after 15 min of dipping. Since the complexes are electroactive, coverage of the metal could easily be monitored. The reversible redox processes of **Cu.1**$^+$ and **Cu.2**$^+$ in conducting dichloromethane occur in the expected potential range (0.69 V for of **Cu.1**$^+$ and 0.73 V for **Cu.2**$^+$ vs a silver quasi-reference electrode). Indeed, dpp-based copper complexes are all characterized by redox potentials (Cu^{II}/Cu^{I} couple) whose high values are attributed to electronic and geometrical factors.[18] The redox potential of **Cu.2**$^+$ is in agreement with the ^{1}H NMR structural assignment, i.e., the metal is surrounded by two dpp units, one from each macrocycle. Indeed, for pentacoordinated copper—which would correspond here to the situation where the metal is coordinated by one dpp unit and one terpyridine unit—the redox potential is located in a cathodic range (−0.3 V vs SCE).[12]

After the adsorption time, the gold beads were thoroughly rinsed with dichloromethane and dipped into dichloromethane containing only Bu_4NBF_4 as supporting electrolyte. Figure 5 shows the characteristic CV curves, recorded at different potential sweep rates, after dipping a gold bead electrode in a solution of **Cu.1**$^+$.

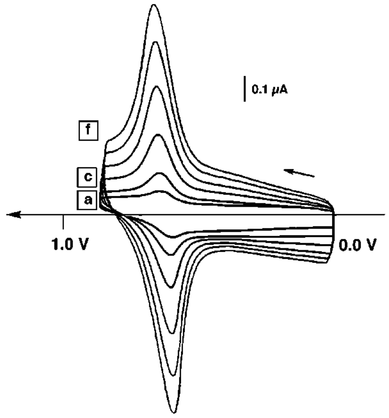


Figure 5. Cyclic voltammetric response of a gold bead electrode after being dipped for 15 min in a CH_2Cl_2 solution of **Cu.1**$^+$ and rinsing. Medium: CH_2Cl_2 with 10^{-1} M nBu_4NBF_4. Potential sweep rates: (a) 20 mV × s^{-1}; (b) 50 mV × s^{-1}; (c) 100 mV × s^{-1}; (d) 200 mV × s^{-1}; (e) 300 mV × s^{-1}; (f) 400 mV × s^{-1}

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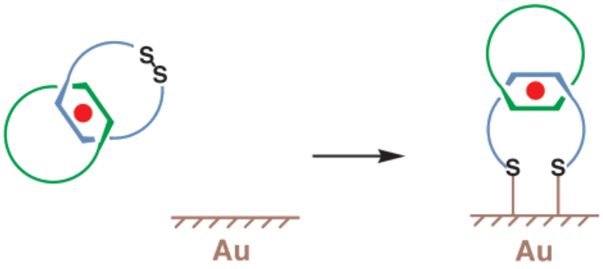
The presence of a reversible electron transfer at 0.58 V vs silver quasi-reference is obvious. Here again, the redox signal is attributed to the $Cu^{II}(dpp)_2/Cu^{I}(dpp)_2$ transition. The difference in potential between oxidation and reduction peaks is less than 60 mV ($\Delta E_p = 20$ mV) and remains unchanged when the potential sweep rate is varied from 50 to 400 mV $\times$ s^{-1}. The intensity of the signals increases linearly with the potential sweep rate, as expected for immobilized electroactive species. The strong adsorption of the molecular catenate onto gold surfaces is a consequence of the Au−S bond formation. The process is represented schematically in Scheme 1.

Scheme 1. Schematic Representation of the Adsorption Process onto a Gold Electrode Which Leads from a Molecular Catenate to an Adsorbed Catenate in which Gold Atoms are Constituent Elements of One Ring



During this process, the disulfide bridge is cleaved, leading subsequently to two Au−S bonds. Thus, macrocycle **7**, which includes the disulfide bridge, is transformed into a new species, which is considered to be a well-defined macrocycle in which gold atoms are constituent elements of the ring. For **Cu.1**$^+$ a value of 40% was obtained for the coverage rate, a value which is compatible with coverage of the surface with a monolayer.[5] Surface analysis studies such as AFM, STM, and PMIRAS are currently in progress to determine the characteristics of the adsorbed layers. The adsorption of **Cu.2**$^+$ leads to an analoguous situation, but in this case, the nonadsorbed ring is a hetero bis-chelating macrocycle. Investigations are currently underway to determine whether, by changing the redox state of the metal, the bis-chelating macrocycle can be induced to undergo a gliding motion through the macrocycle which is adsorbed.

In conclusion, the synthesis of two metallo-catenanes able to undergo surface-confined coordination chemistry is described in this Letter. Their adsorption onto a gold surface leads to immobilized catenates in which closing of one macrocycle is achieved by incorporating the gold atoms of the metal surface.

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