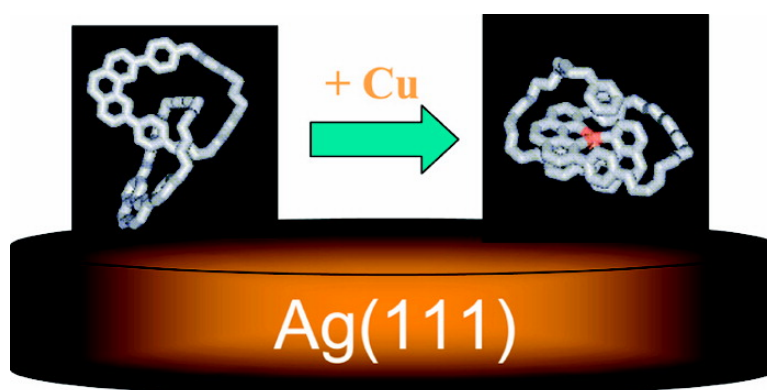


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Toward Mechanical Switching of Surface-Adsorbed [2]Catenane by *in Situ* Copper Complexation

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Abstract: Using scanning tunneling microscopy (STM), electrospray ionization mass spectrometry (ESI-MS), and X-ray photoelectron spectroscopy (XPS), we demonstrate that a free [2]catenane consisting of two interlocking 30-membered rings (cat-30) can be deposited on a Ag(111) surface by vacuum sublimation without decomposition. The deposited cat-30 molecules self-organize as ordered dimer chain structures at the surface, presumably via intermolecular π - π stacking. An *in situ* addition of Cu atoms to the surface-adsorbed catenanes induces a drastic change in the molecular organization, i.e., from the dimer chain structure to isolated species. The nitrogen core level spectra suggest that the cat-30 phenanthroline units coordinate with Cu, indicating that the free catenane has been transformed into a Cu-complexed [2]catenane. Since it is known that the two interlocked macrocyclic rings of the free ligand cat-30 completely rearrange, i.e., circumrotate, upon complexation to copper, our results reveal that when adsorbed on the silver surface, the two macrocyclic rings of the free [2]catenane can glide within one another so as to generate the corresponding copper complex by *in situ* Cu complexation.

Introduction

Catenanes are topologically nontrivial species (i.e., whose molecular graph cannot be represented in a two-dimensional space without crossing points) consisting of interlocked cyclic components.^{1–4} Catenanes and rotaxanes represent promising candidates for the development of nanoscale mechanical and electronic devices since the interlocked parts may undergo relative rotation (or motion) through external stimuli, e.g., chemical potential or light.^{5–8} So far the vast majority of synthesis and characterization of catenanes (and rotaxanes) have

been performed by means of solution-based chemistry. Under such conditions it is very difficult to address individual molecules directly and to make macroscopic contacts with molecules. In recent years there has been increasing interest in grafting catenanes or rotaxanes on solid surfaces. This approach offers a route to “wire” catenanes (and rotaxanes) to the macroscopic world, which is an essential requirement if the field of molecular motors or molecular switches is to be extended toward practical applications in the future.^{9–12} It is of great importance to understand the behavior of catenanes (and rotaxanes) upon adsorption on solid surfaces, e.g., adsorption strength, conformation relaxation, mobility on the surfaces, and, in particular, the ease of mechanical switching. Furthermore, adsorption on a surface may allow for detecting stimulated mechanical processes at a single-molecule level and for controlling intramolecular motions of single molecules by advanced scanning probe techniques.

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- (1) Sauvage, J. P.; Dietrich-Buchecker, C. *Molecular Catenanes, Rotaxanes and Knots*; Wiley-VCH, Weinheim, 1999.
- (2) Nierengarten, J. F.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 375–376.
- (3) Amabilino, D. B.; Ashton, P. R. et al. *J. Am. Chem. Soc.* **1995**, *117*, 1271–1293.
- (4) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed.* **1995**, *34*, 1209–1212.
- (5) (a) Collin, J.-P.; Dietrich-Buchecker, C.; Gavina, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477. (b) Bonnet, S.; Collin, J.-P.; Koizumi, M.; Mobian, P.; Sauvage, J.-P. *Adv. Mater.* **2006**, *18*, 1239.
- (6) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.
- (7) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25–35.
- (8) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391. (b) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines – A Journey into the Nano World*; Wiley-VCH, Weinheim, 2003.

- (9) (a) Flood, A. H.; Wong, E. W.; Stoddart, J. F. *Chem. Phys.* **2006**, *324*, 280–290. (b) Tseng, H. R.; Wu, D.; Fang, N. X.; Zhang, X.; Stoddart, J. F. *ChemPhysChem* **2004**, *5*, 111–116.
- (10) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H. R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759.
- (11) Jang, S. S.; Jang, Y. H.; Kim, Y. H.; Goddard, W. A., III; Flood, A. H.; Laursen, B. W.; Tseng, H. R.; Stoddart, J. F.; Jeppesen, J. O.; Choi, J. W.; Steuerman, D. W.; DeLonno, E.; Heath, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 1563–1575.
- (12) Barth, J. V.; Costantini, G.; Kern, K. *Nature* **2005**, *437*, 671–679.

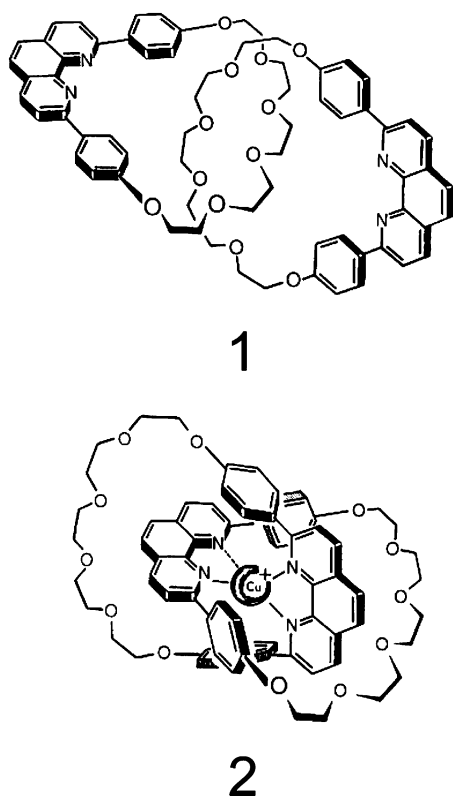


Figure 1. Schematic molecular model of the free-ligand **1** and Cu-complexed **2**.

It was demonstrated that STM can resolve single [2]catenane molecules composed of 87-member rings which were prepared by depositing solution droplets of the [2]catenane at a HOPG substrate.¹³ Under vacuum conditions, rotaxane and catenane films deposited on a Au substrate by sublimation were studied by XPS, UPS, and infrared adsorption spectroscopy, indicating that the molecules were intact.^{14–16} Intra- or inter-ring motions of catenane molecules in a vacuum-evaporated thin film were suggested based on second harmonic generation experiments.¹⁷ However, achieving and detecting a controlled movement of single catenane (or rotaxane) species mounted on surfaces are very demanding. To our knowledge, direct molecular level evidence that surface-adsorbed catenanes (or rotaxanes) can perform controlled intramolecular motions is still missing, although such motions were predicted by theory.^{18,19} Here we report on single-molecular level observations that (i) the free [2]catenanes cat-30 (see Figure 1) can be deposited on a Ag(111) surface by sublimation at relatively high temperature without chemical degradation whereas (ii) the corresponding Cu(I) complex is not stable enough to resist the sublimation conditions; in addition, (iii), once the [2]catenane molecules are adsorbed on the Ag(111) surface, an *in situ* Cu complexation

induces a complete rearrangement of the system, the two macrocyclic subunits of the [2]catenane gliding within each other in a similar way as what was observed in solution.^{20a}

The free [2]catenane cat-30 (**1**) studied here is shown in Figure 1.²⁰ It consists of two identical interlocking 30-membered rings, each ring incorporating a 2,9-diphenyl-1,10-phenanthroline subunit (dpp). The previous crystallographic study revealed that the two dpp fragments are fully disentangled, affording a rather extended molecular conformation in which the two virtual coordination sites are 1.12 nm apart.²⁰ Complexation with Cu(I) forms the copper-complexed [2]catenane (**2**) (cf. Figure 1) which shows an entirely different conformation: The two dpp subunits are now entangled, coordinating the Cu(I) center through four N–Cu bonds in a highly distorted tetrahedral geometry. The long distance between the two diphenyl phenanthroline fragments in the free ligand is dramatically shortened while the pentaethyleneoxy chains, which are in close proximity in the free ligand, are unravelled.²⁰ We chose **1** and **2** as our model systems assuming that the substantial conformation variation between **1** and **2** is detectable by high-resolution STM, which should allow us to unambiguously distinguish **1** and **2**. We first deposited the free ligand **1** on a clean and atomically flat Ag(111) surface in UHV by sublimation. The STM, ESI-MS, and XPS show that **1** stays intact after it has been subjected to sublimation and deposition. These surface-adsorbed molecules assemble as dimer chains due to the intermolecular π – π interaction between the outward extending dpp subunits. Then, we deposited Cu atoms *in situ* on the same surface. The XPS measurements indicated that the 1,10-phenanthroline fragments bind to Cu through N–Cu coordination forming Cu-coordinated metallo[2]catenane (**2**). By controlling the Cu deposition in a stepwise manner we observed a gradual disappearance of the dimer chains and a formation of isolated molecules with a different shape identified by STM. These results corroborate the picture that the two dpp subunits of the free ligand **1** are remote from one another before complexation but, once the copper complex **2** is formed, they are intimately entangled with each other. As a consequence, the dpp units are not available anymore for intermolecular interactions, resulting in the dissolution of the dimer chains and the appearance of individual species. Therefore a circumrotation between the two interlocked macrocyclic rings has been accomplished through Cu complexation for these surface-adsorbed [2]catenanes.

Experimental Section

The syntheses of **1** and **2** were carried out following literature methods, and the bulk crystal structures, obtained by X-ray diffraction measurements.²⁰ To identify single molecules unambiguously by STM it is necessary that the molecules of **1** are adsorbed on a clean and atomic flat substrate. This is done by sublimating a high purity powder sample of **1** and depositing it on a Ag(111) surface with a submonolayer coverage in ultrahigh vacuum (UHV). The XPS and STM measurements were performed under UHV conditions *in situ* to avoid contaminations. The vacuum system for the XPS and STM measurements operate at a base pressure of 2×10^{-10} mbar and 2×10^{-11} mbar, respectively. Both systems are equipped with standard equipments for sample cleaning and preparation. The atomically flat Ag(111) surface was

- (13) Samori, P.; Jäckel, F.; Ünsal, Ö.; Godt, A.; Rabe, J. *ChemPhysChem* **2001**, *2*, 461–464.
 (14) Mendoza, S. M.; Whelan, C. M.; Jalkanen, J. P.; Zerbetto, F.; Gatti, F. G.; Kay, E. R.; Leigh, D.; Lubomska, M.; Rudolf, P. *J. Chem. Phys.* **2003**, *123*, 244708.
 (15) Fustin, C. A.; Haq, S.; Wingen, A.; Gregoire, C.; Raval, R.; Dumas, P.; Hannam, J. S.; Leigh, D.; Rudolf, P. *Surf. Sci.* **2005**, *580*, 57–62.
 (16) Fustin, C. A.; Gouttebaron, R.; De Nadai, C.; Caudano, R.; Zerbetto, F.; Leigh, D.; Rudolf, P. *Surf. Sci.* **2001**, *474*, 37–46.
 (17) Gase, T.; Grando, D.; Chollet, P. A.; Kajzar, F.; Murphy, A.; Leigh, D. A. *Adv. Mater.* **1999**, *11*, 1303–1306.
 (18) Jang, Y. H.; Jang, S. S.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2005**, *127*, 4959–4964.
 (19) Deleuze, M. S. *J. Am. Chem. Soc.* **2000**, *122*, 1130–1143.

- (20) (a) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 3043–3045. (b) Dietrich-Buchecker, C. O.; Sauvage, J. P. *Chem. Rev.* **1987**, *87*, 795–810. (c) Cesario, M.; Dietrich-Buchecker, C. O.; Guilhem, J.; Pascard, C.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 244–247.

prepared by repeated cycles of sputtering with 500 eV Ar⁺ ions and subsequent annealing to 800 K. The cat30 molecules were deposited in UHV onto the Ag(111) surface by means of organic molecular beam epitaxy (OMBE), with the crucible containing the cat-30 molecule powder constantly held at a temperature of 600 K and the Ag(111) substrate kept at 300 K during deposition. Typical deposition rates are 1 monolayer (ML) in 20 min, with an ML being defined as the surface completely covered without second layer growth. Usually a quarter to a half of the Ag(111) surface was covered by molecules. Cu atoms were deposited by means of an Omicron e⁻-beam evaporator out of a crucible, with typical deposition rates of 1 ML in 10 min.

After preparation the samples were transferred to the XPS and STM measurement stages without breaking the vacuum. The XPS measurements were conducted with a high-resolution Electron Spectroscopy for Chemical Analysis (ESCA) system. The XPS data were acquired using a monochromatized laboratory Al K α radiation source and an analyzer with a pass energy of 10 eV. The STM data were acquired using a home-built Besocke type STM operated at a temperature of 5 K, with the STM measurements being performed in the constant-current mode using electrochemically etched W-tips. The denoted bias voltages are referenced to the sample.

Electrospray ionization (ESI) mass spectrometry is a soft ionization technique that can create molecular ion beams from solution. Typically the ionized molecules remain intact. A home-built linear time-of-flight mass spectrometer with a nanospray ion source (Proxeon Biosystems, Odense, Denmark) was employed.²¹ ESI is used to identify **1** and **2** by rinsing Au/mica surfaces that are coated by vacuum deposition of the powder sample of **1** and **2**·BF₄ at 600 K.²² The ion beams for all presented samples were generated from a solution of dichloromethane and ethanol (1:3) acidified with 0.1% formic acid. Pure dichloromethane is used to rinse off the molecules deposited on the gold surfaces by vacuum evaporation. This solution is then diluted with ethanol and acidified for ESI-MS. In addition reference samples were prepared by depositing solution droplets, i.e., dissolving powder samples of **1** and **2** in dichloromethane and further diluting in dichloromethane/ethanol solution and then depositing on Au/mica substrates. Due to the higher concentration of molecules in the reference solution it is not necessary to acidify the reference solutions in order to get a good signal. The mass spectra obtained are compared with those of reference samples.

Results and Discussion

In the first step, we examined the integrity of **1** upon sublimation and deposition. We applied ESI-MS and XPS to identify the molecules of **1** present on the surface that were deposited by vacuum sublimation.

The reference ESI-MS spectrum of **1** is displayed in Figure 2a, top, showing peaks of nearly the same intensity at 567 Th and 1132 Th. These peaks correspond to doubly and singly charged molecules of **1**. No other ions are observed for this compound. The mass spectrum of **1** can be distinguished from the spectrum of a single macrocyclic ring M30, which is detected as M30⁺, 2M30⁺, and 3M30⁺. The peaks for one and two M30 macrocycles are at the same positions as the singly and doubly charged **1**. However, the mass spectra of **1** and M30 differ in the relative intensities and by the peak for 3 M30⁺ (see Supporting Information Figure S1). Furthermore they behave differently upon nozzle-skimmer fragmentation. The spectrum of vacuum sublimated **1** is the same as the spectrum of its reference (Figure 2a, bottom) and does not show any of

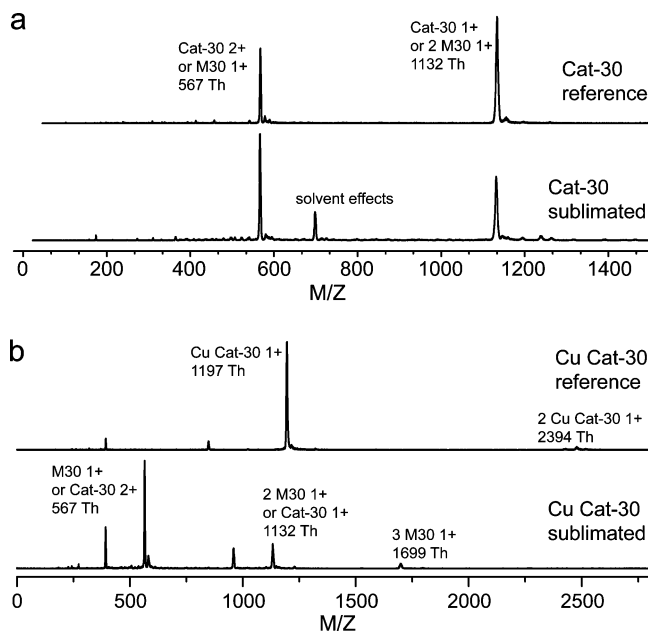


Figure 2. (a) Electrospray mass spectrum of evaporated **1** rinsed off a gold substrate compared (bottom) with the spectrum of a reference sample (top). The peaks at 1132 Th and 567 Th correspond to single and double charged catenane. (b) Electrospray mass spectra of evaporated **2**·BF₄ (bottom) and of a reference solution (top). The reference solution shows a strong peak at 1196.8 Th. The evaporated sample does not show a peak at this position. Instead it shows peaks at 567 Th, 1132 Th, and 1699 Th. The relative abundances of these peaks correspond to single charged M30 molecules and 2M30⁺ and 3M30⁺ clusters.

the features typical for M30. The peak at 689 Th is ascribed to solvent contamination due to the addition of formic acid. The comparable mass spectra of the vacuum-sublimated molecules and the reference samples show that **1** is able to be sublimed in vacuum and is intact after deposition on a metal surface. The reference spectrum of **2**·BF₄ (Figure 2b, top) shows only one strong peak, which corresponds to a singly charged molecule of **2**. However the vacuum-sublimated sample shows an entirely different spectrum (Figure 2b, bottom). The peak of **2** disappears, and instead the typical spectrum of M30⁺, 2M30⁺, and 3M30⁺ is found. This finding indicates the decomposition of **2**·BF₄ at the sublimation temperature and the evaporation of single macrocyclic ring M30 molecules upon heating. The decomposition is presumably due to the ionic nature of **2**·BF₄.

Additionally we acquired XP spectra of the vacuum sublimation prepared sample and the reference sample. We compared the Binding Energies (BEs) of the C 1s, O 1s, and N 1s electrons. Any decomposition will be expressed in modifications of these spectra, especially shifts in the BE or changes in the line shape. As shown in Figure 3, no modification compared to the reference data can be identified. This result further shows that **1** is intact after sublimation and deposition. A detail analysis shows that the relative intensity of the three major chemical components C/N/O agrees well with the chemical composition of a cat-30 molecule (see Table 1). In particular the double peak feature of carbon, which can be decomposed into two peaks with an intensity ratio of 0.45, can be attributed to the two types of carbons (10 in pentaethyleneoxy and 24 in diphenyl phenanthroline) of the cat-30.

STM measurements revealed molecular-level information of the cat-30 catenanes adsorbed on the Ag(111) surface. The as-deposited sample shows irregular clusters consisting of protrusion

(21) Rauschenbach, S.; Stadler, F.; Lunedei, E.; Malinowski, N.; Koltsov, S.; Costantini, G.; Kern, K. *Small* **2006**, *2*, 540–547.
 (22) (a) Ouyang, Z.; Takats, Z.; Blake, T. A.; Gologan, B.; Guymon, A. J.; Wiseman, J. M.; Oliver, J. C.; Davison, V. J.; Cooks, R. G. *Science* **2003**, *301*, 1351–1354. (b) Takats, Z.; Wiseman, J. M.; Gologan, B.; Cooks, R. G. *Science* **2004**, *306*, 471–473.

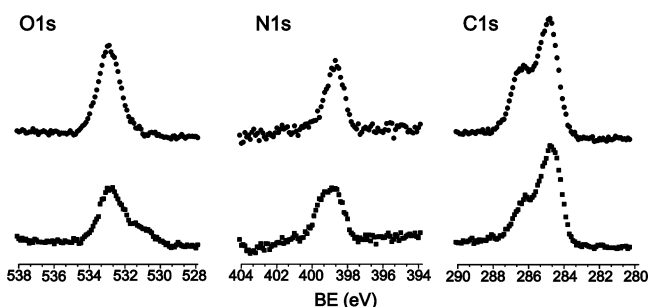


Figure 3. Comparison of XPS data acquired at the vacuum sublimated sample of **1** (bottom) and the reference sample (up). All three elements, carbon, oxygen, and nitrogen (at different scales), show similar spectroscopic features for both samples. The deviation, which is more apparent in the oxygen signal, is presumably attributed to X-ray induced damage due to the longer data acquiring time of the sublimated sample.

Table 1. Chemical Composition Analysis of the Reference Sample and the Vacuum-Sublimated Sample, Compared with the Stoichiometry of the Cat-30 Molecule

element	cat-30 molecule	reference sample	sublimated sample
carbon	81.0%	82.0%	81.1%
oxygen	14.3%	14.8%	15.1%
nitrogen	4.7%	3.2%	3.8%

sions of an identical size. These protrusions have an average height of 1.04 ± 0.1 Å, independent of the tunneling parameters used in our experiments. After annealing the sample to 450 K the formation of ordered structures was observed. As shown in Figure 4a the predominant structures are linear chains consisting of pairs of protrusions (dimers). A high-resolution STM topography (Figure 4b) allows estimating the peak-to-peak distance (d_1) within each dimer to 1.6 ± 0.1 nm and the distance between the neighboring dimers along the chain direction (d_2) to 2.1 ± 0.1 nm. The individual protrusions within the structure have a very uniform, circular or oval shape. Their diameter, defined as the full width at half-maximum (fwhm), is 1.62 ± 0.18 nm and their height is 1.07 ± 0.06 Å, very close to those measured in the disordered clusters before annealing. The dimer chain structures could be imaged with a large variety of tunneling parameters without shifting the molecules. Typical tunneling parameters were $U = 750$ mV and $I = 200$ pA.

A structural model of **1** is drawn in Figure 4b at the same scale as that of the STM image. Comparing the size of **1** with the STM data, we can rule out the possibility that each dimer corresponds to a single cat-30 molecule. Furthermore, the STM data show that many clusters contain an odd number of protrusions and single protrusions bound to step edges or a single protrusion attached to a pair of protrusions. All these observations support the concept that single protrusions within the dimers are individual molecules of **1**. We also observed some bright protrusions, as marked by the arrow in Figure 4a. We propose these objects are molecules that adsorb on top of the dimer chains.

We cannot provide unambiguous proof of the model of the dimer chain structure based on our data since the inner structure of single molecules could not be resolved with our experimental means. The proposed dimer chain structure is, however, very close to the bulk structure of **1** determined by X-ray crystallography,²⁰ which shows a pairwise arrangement of the molecules. It is therefore likely that the intermolecular bonding motif

of **1** on Ag(111) is the same as that encountered in the bulk crystal structure. In the bulk phase, molecular packing is stabilized by π - π stacking between the diphenyl phenanthroline units of the neighboring molecules. Although the molecular conformation might be modified upon surface adsorption, the structural similarity to the bulk phase suggests that the surface-adsorbed molecules also bind through the π - π stacking between the diphenyl phenanthroline units, as illustrated in a tentative model shown in Figure 4c.

In a next step we tested the possibility of complexing the surface-adsorbed molecules of **1** with Cu forming **2**, i.e., to achieve *in situ* metal complexation at the surface. We have recently demonstrated that by depositing Cu atoms on a Ag(111) surface one can fabricate an artificial two-dimensional Cu atom gas with a chemical activity comparable to that for the native Cu atoms.²³ This provides the opportunity to react **1** on the surface by depositing Cu atoms onto the Ag(111) surface carrying the dimer chain structures.

We performed XPS measurements on the Cu-added samples focusing on the Binding Energy (BE) of the N 1s electrons. The nitrogen atoms in the phenanthroline of **1** are uncoordinated, whereas in **2** the N atoms are engaged in coordination toward the Cu(I) center. This difference should be expressed in different BEs of the N 1s electrons. For example it was shown that the N 1s BEs of metal-free porphyrins and metalloporphyrins are separated by about 1 eV.²⁴ Such different BEs of the N 1s can also be observed in other systems with N-atoms involved in coordination bonds.²⁵ Figure 5a is a N 1s spectrum of a reference sample that was prepared by depositing solution droplets of a powder sample of **1**. Figure 5b and c show the N 1s spectra of the vacuum-deposited **1** before and after adding an excessive amount of Cu (2 ML), respectively. Figure 5d is a N 1s spectrum of a reference sample of **2** that was prepared by depositing solution droplets. It is clear that upon Cu addition the BE of the N 1s electrons shifts from 398.7 to 399.6 eV, in good agreement with the reported values.^{24,25} A comparison of the four spectra in Figure 5 shows that upon *in situ* Cu addition the N-atoms of **1** have been changed to the same chemical state as that of the N-atoms of **2**. This result implies that under our experimental conditions **1** reacts with Cu to give **2**. Metal complexation by mixing organic ligands and metal atoms that adsorb on surfaces under UHV conditions has been demonstrated recently.^{24,26} Our results show that the rather complicated ligands of cat-30 can coordinate with Cu through phenanthroline at the surfaces. The oxidation state of the Cu cannot be determined by XPS since the Cu 2p peak of Cu(I) and Cu(0) is not discernible.

- (23) Lin, N.; Payer, D.; Dmitriev, A.; Strunskus, T.; Wöll, C.; Barth, J. V.; Kern, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1488–1491.
- (24) (a) Gottfried, J. M.; Flechtner, K.; Kretschmann, A.; Lukaszczuk, T.; Steinrück, H. P. *J. Am. Chem. Soc.* **2006**, *128*, 5644–5645. (b) Lukaszczuk, T.; Flechtner, K.; Merte, L. R.; Jux, N.; Maier, F.; Gottfried, J. M.; Steinrück, H.-P. *J. Phys. Chem. C* **2007**, *111*, 3090–3098. (c) Kretschmann, A.; Walz, M. M.; Flechtner, K.; Steinrück, H. P.; Gottfried, J. M. *Chem. Commun.* **2007**, 568–570.
- (25) (a) Finn, P.; Jolly, W. L. *Inorg. Chem.* **1972**, *11*, 1434–1435. (b) Sarkar, D. K.; Zhou, X. J.; Tannous, A.; Louie, M.; Leung, K. T. *Solid State Commun.* **2003**, *125*, 365–368. (c) Parmigiani, F.; Depero, L. E. *Struct. Chem.* **1994**, *5*, 117–121.
- (26) (a) Lin, N.; Dmitriev, A.; Weckesser, J.; Barth, J. V.; Kern, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4779–4783. (b) Dmitriev, A.; Spillmann, H.; Lin, N.; Barth, J. V.; Kern, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2670–2673. (c) Clair, S.; Pons, S.; Fabris, S.; Baroni, S.; Brune, H.; Kern, K.; Barth, J. V. *J. Phys. Chem. B* **2006**, *110*, 5627–5632. (d) Stepanow, S.; Lin, N.; Payer, D.; Schlickum, U.; Klappenberger, F.; Zoppelloro, G.; Ruben, M.; Brune, H.; Barth, J. V.; Kern, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 710–713.

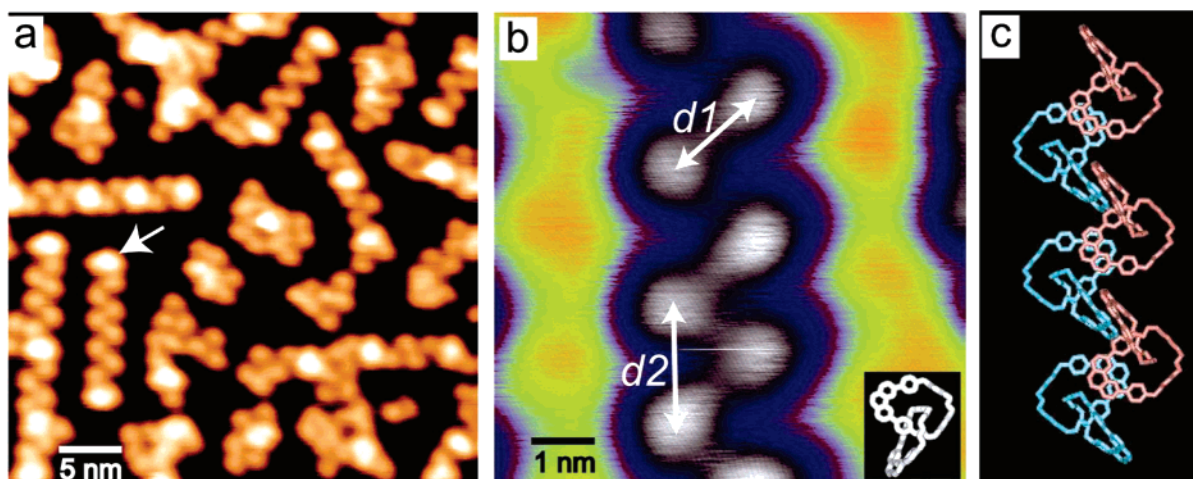


Figure 4. (a) STM topography of dimer chain structures of **1** on a Ag(111) surface. The arrow points to a molecule sitting on top of a chain. (b) High-resolution STM topography showing the uniform circular or oval shape molecules of **1**, where d_1 (1.6 ± 0.1 nm) is the peak-to-peak distance within a dimer and d_2 (2.1 ± 0.1 nm) is the peak-to-peak distance between the neighboring dimers along the chain direction. Inset shows a molecular structure of **1** at the same lateral scale of the STM image. (c) A tentative model of the dimer chain structure derived from the STM data and the solid-phase X-ray crystallography of **1**, where the overlapping phenanthroline units of the neighboring molecules interact via π - π stacking. Different colors are used for clarity. Tunneling parameters: $U = 750$ mV and $I = 200$ pA.

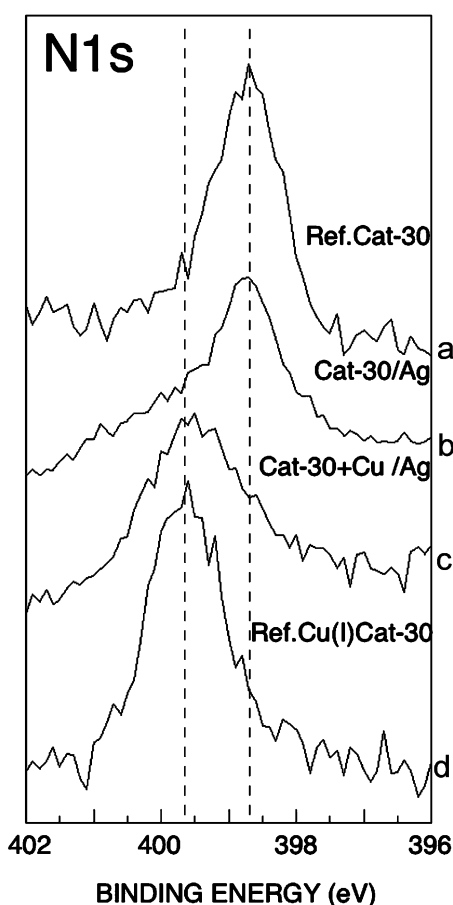


Figure 5. N 1s XPS spectra of the reference sample prepared by depositing of solution droplets of cat-30 (a), vacuum-sublimated cat-30 (b), vacuum-sublimated cat-30 after adding excessive Cu (c), and the reference sample prepared by depositing solution droplets of Cu(I)cat-30 (d). The N 1s peak is shifted by 0.9 eV upon Cu addition, consistent with a chemical change from free cat-30 to Cu coordinated metallo-cat-30.

The structural variations induced by the Cu addition are monitored on the molecular level by STM. We first prepared a sample of the ordered dimer chain structure and then deposited in a stepwise manner small amounts of Cu atoms onto the

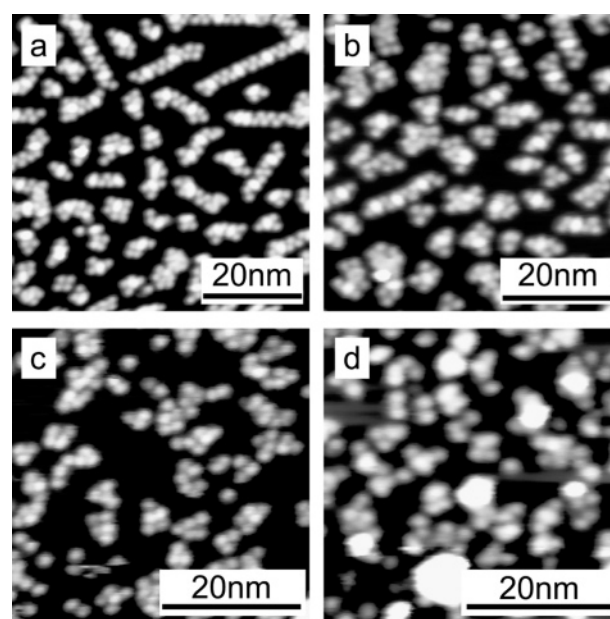


Figure 6. STM data showing the structural change of cat-30 adsorbed at Ag(111) surface upon Cu addition. (a) The pristine dimer chain structures. (b–d) Dissolution of the dimer chain structure with addition of $\sim 1\%$, $\sim 2\%$, and $\sim 5\%$ ML of Cu, respectively. Bright protrusions in (d) correspond to excess Cu forming Cu clusters. Tunneling parameters: $U = 2000$ mV, $I = 200$ pA.

sample. After each deposition step, STM data were acquired. Figure 6a shows the initial ordered dimer chains before adding Cu. Figure 6b shows that after the deposition of $\sim 1\%$ of a monolayer (ML) of Cu atoms, the population of the dimer chains decreased and disordered clusters developed. Figure 6c shows that, after an additional deposition of Cu, giving a total amount of Cu of $\sim 2\%$ ML, no dimer chains can be identified. Instead, one can see isolated protrusions as well as disordered clusters. As the modification of the molecular organization on the surface goes hand in hand with the amount of Cu added on the surface, one can correlate the structural change with the Cu-induced reaction of **1**. Based on the XPS results we know that the added Cu complexes **1** give **2**, and we conclude that the observed

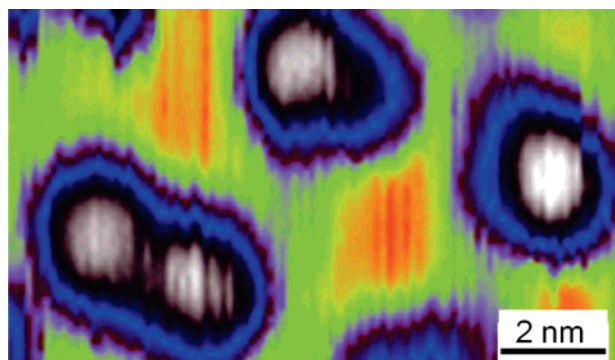


Figure 7. High-resolution STM data showing the isolated Cu-complexed catenane of **2**. Tunneling parameters: $U = 2000$ mV, $I = 200$ pA.

structural change is due to the fact that the newly formed molecules of **2** have a different lateral interaction and therefore different organizational behavior on the surface. Figure 6d shows that, after further Cu deposition, with a total amount of Cu of $\sim 5\%$ ML, isolated protrusions and disordered clusters are present on the surface together with Cu islands, showing that all molecules of **1** adsorbed on the surface already reacted with Cu and the excess Cu aggregated into Cu islands.

The high-resolution STM data shown in Figure 7 reveal that the individual protrusions have a size with a fwhm of 1.78 ± 0.2 nm and a height of 1.41 ± 0.24 Å. These values are consistent with the size of a single molecule of **2**; we thus assign the individual protrusions to single species of **2**. The measured height is significantly larger than that of pristine molecules of **1**. We attribute this to different molecular conformations, electronic effects, or both. The two macrocyclic rings (M30) of the free ligand **1** are more flexible and stretched leading to a more planar adsorption geometry. In contrast **2** has a compact globular conformation, which appears higher in the STM topograph. In addition the molecular orbitals, which determines the STM signal, of **2** must be very different from those of **1** because the presence of the coordinated Cu center in **2** modifies its electronic structures.

These two effects, the different molecular conformation and the different electronic states, can also rationalize the different molecular organization of **1** and **2**. The phenanthroline groups

of **2** are entangled at the core of the molecules as the N-atoms are involved in coordination toward the Cu center. Thus intermolecular π - π stacking through the phenanthrolines is not possible, and consequently the ordered dimer chain structures are destabilized. Furthermore **2** carries a positive charge because of the presence of the Cu(I) center, which applies coulomb repulsion between the molecules and effectively decreases the intermolecular binding.

Conclusions

Using electron spectroscopy, scanning tunneling microscopy, and mass spectroscopy, we demonstrated that the [2]catenane molecules cat-30 can be sublimated in UHV at a temperature of 600 K without fragmentation. Single-molecule resolution imaging acquired by STM allows us to identify the cat-30 molecular organization on the surface, implying that they bind through π - π stacking as in the bulk phase. We further demonstrated that the free ligand catenane can react *in situ* with added Cu atoms to form a Cu-complexed metallocatenane on the surface. This reaction is reflected in a significant chemical shift of the nitrogen 1s core level peak due to the coordination to Cu. We showed that this reaction is accompanied by a remarkable structural change which is caused by the different intermolecular interaction of the free and the complexed molecules due to their distinctive conformations. Our results clearly show that, once [2]catenane cat-30 has been adsorbed on the Ag(111) surface, the two interlocking rings of the compound can glide within one another to afford a completely rearranged species following *in situ* Cu complexation. This study exemplifies a first step toward molecular mechanical machines working at surface supports.

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Supporting Information Available: (S1) The full author list of ref 3; (S2) ESI spectrum of M30. This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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