Adsorption of Fumaramide [2]Rotaxane and Its Components on a Solid Substrate: A Coverage-Dependent Study

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The coverage-dependent adsorption on Au(111) of a fumaramide [2]rotaxane and its components, a benzylic amide macrocycle and a fumaramide thread, is studied using high-resolution electron energy loss spectroscopy (HREELS). Up to monolayer coverage, the relative intensity of out-of-plane to in-plane phenyl ring vibrational modes indicates that the macrocycle adopts an orientation with the phenyl rings largely parallel to the surface. The formation of a chemisorption bond is evidenced by the presence of a Au−O stretching vibration. In contrast, the thread shows no evidence of chemisorption or a preferential orientation. The introduction of the thread into the macrocycle partly disrupts the film order so that the resulting chemisorbed rotaxane shows intermediate behavior with a preferential orientation up to 0.5 ML coverage. A decrease in film order and the absence of a preferred molecular orientation is observed for all three molecules at multilayer coverages. The spectral differences are addressed by molecular dynamics simulations in terms of the mobility of the phenyls of the three molecules on Au(111).

1. Introduction

Rotaxanes are a class of molecules with mechanically interlocked components in which one or more macrocycles are threaded by a linear molecule terminated at both ends by bulky stoppers.[1] Initially regarded as curiosities, these compounds are now being explored in areas that range from functional polymers[2] to chemically assembled molecular-based electronic switching devices.[3]

Establishing methods for controlling intramolecular movement is a prerequisite for the application of such materials. To this end, the use of chemical,[4] thermal,[5] electrochemical,[6] and photochemical[7] stimuli have been demonstrated. Although most of this work has been carried out in solution, the structural conformation and even the activity of rotaxanes at surfaces have also been studied, both experimentally[8] and theoretically.[9] These findings and related studies on macrocycles[10,11] and catenanes[12,13] provide useful insights for the incorporation of these molecules into the design of smart materials and the possible creation of nanoscale devices.[14]

In our ongoing research into the exploitation of molecular systems that display large-amplitude internal linear and/or rotary motions, we have synthesized a range of fumaramide-based rotaxanes.[15] In an inexpensive and simple preparative procedure, fumaramide threads template the assembly of benzylic amide macrocycles to form rotaxanes in exceptionally high yields. It can be seen from the X-ray crystal structure of fumaramide [2]-rotaxane shown in Figure 1 that the two hydrogen bond-accepting groups of the thread are fixed in an arrangement that is complementary to the hydrogen bond-donating sites of the

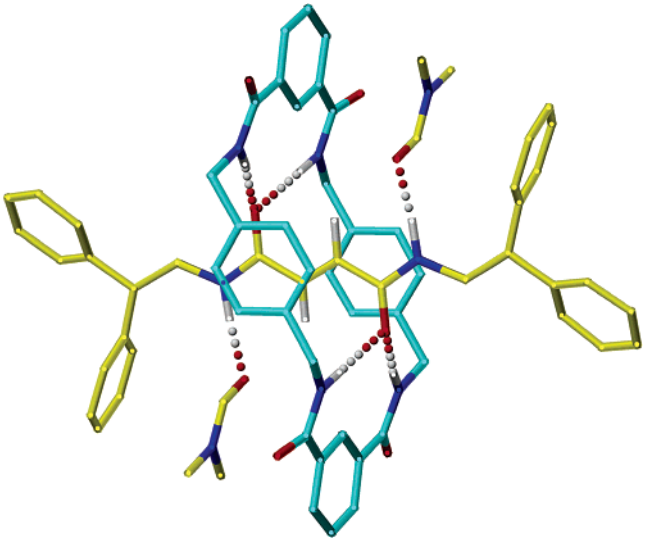

Figure 1. The X-ray crystal structure of fumaramide [2]rotaxane comprising a benzylic amide macrocycle mechanically interlocked with a fumaramide thread. Two solvent molecules are shown bonded to the thread. For clarity, carbon atoms of the thread are shown in yellow while those of the macrocycle are cyan; oxygen atoms are shown in red, nitrogen atoms in dark blue, and *selected* hydrogen atoms in white. Dotted bonds show intramolecular hydrogen bonds.

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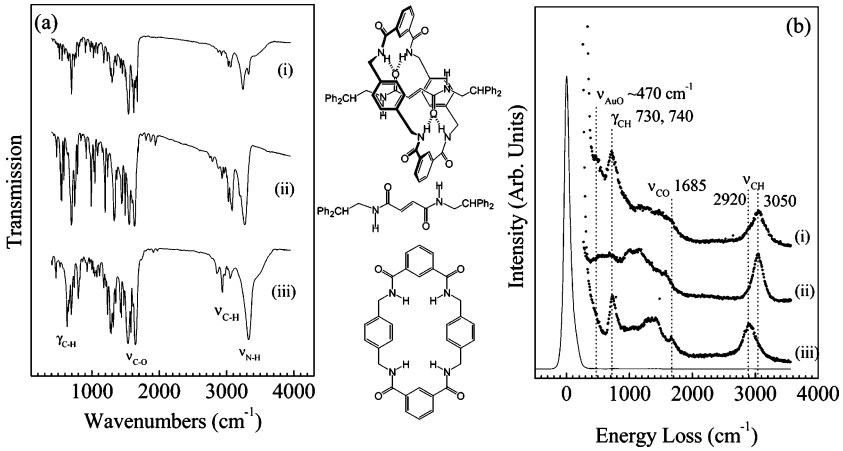

Figure 2. Left (a): Solid-state FTIR spectra corresponding to (i) fumaramide [2]rotaxane, (ii) fumaramide thread, and (iii) benzylic amide macrocycle; Center: the schematic structures of the three molecules (Ph = phenyl ring); Right (b): HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45°$) from 0.1 ML coverages of (i), (ii), and (iii) adsorbed on Au(111) at 300 K. The primary beam energy is 6.0 eV. Vertical lines indicate the primary vibrational bands of interest.

macrocycle. Interestingly, the rate of rotation of the interlocked components of fumaramide [2]rotaxanes can be dampened by 2 to 3 orders of magnitude by applying an external oscillating electric field[16] and accelerated by over 6 orders of magnitude following photoisomerization of the double bond.[17]

To exploit the properties of fumaramide-derived rotaxanes, we need to build a technical foundation for their integration with other materials. In particular, if we consider molecular-scale devices, surface-attached molecules on solid substrates must be considered. Previously, we have reported on the coverage-dependent chemisorption behavior of a benzylic amide macrocycle on Au(111).[10,11] More recently, we extended the investigation to the adsorption of fumaramide [2]rotaxane at monolayer and multilayer coverage on Au and Ag surfaces.[18] In the present report, we detail our findings on the coverage-dependent bonding configuration of fumaramide [2]rotaxane and its component parts, a benzylic amide macrocycle and the fumaramide thread, as determined by high-resolution electron energy loss spectroscopy. The experimental results are complemented by molecular dynamics simulations.

2. Experimental Section

The synthesis of fumaramide [2]rotaxane ([2]-(1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(*E*)-(*N*,*N*′-bis(2′,2′-diphenylethyl)-2′-butendiamide)), benzylic amide macrocycle (1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane), and fumaramide thread ((*E*)-(*N*,*N*′-bis(2′,2′-diphenylethyl)-2-butendiamide) are reported elsewhere.[15] The thin films were prepared by in-situ sublimation of the molecule of interest on Au(111) at 300 K using a well-outgassed custom-built cell consisting of a Pyrex crucible heated resistively to ~500 K with the temperature being measured by a chromel−alumel junction fixed at the tube exit. The exposures were monitored using an uncalibrated Bayard−Alpert ionization gauge. A process consisting of dosing multilayers and then desorbing excess material leaving only the chemisorbed monolayer on the surface was used to define a monolayer coverage (ML) film for each molecule. The monolayer spectra observed following annealing of multilayer samples were then reproduced by controlled sublimation with the corresponding dose in langmuirs (where 1 langmuir = 1×10^{-6} Torr s) being defined as 1 ML exposure. All coverages corresponding to less than or more than a monolayer produced by controlled sublimation were defined as a fraction of a monolayer or several monolayers depending on the dosing time.

The Au single crystal (10 × 7 × 2 mm) oriented to within 0.5° of the (111) plane (Metal Crystals and Oxides Ltd.) was cleaned in-situ by cycles of argon ion bombardment (0.5 kV, 15 mA) and annealing to ~800 K. The surface crystallography and cleanliness were established using LEED and HREELS. After cleaning, LEED revealed a sharp, low background pattern typical of a reconstructed Au(111)-($\sqrt{3} \times 22$) surface.

The HREELS experiments were carried out in an UHV system (SEDRA ISA RIBER) equipped with sample-preparation and main analyzer chambers operated at base pressures in the low 10^{-9} and 10^{-10} Torr range, respectively. The spectrometer consisted of a 180° hemispherical monochromator and analyzer ensemble described in more detail elsewhere.[19] To prevent contamination of the spectrometer vessel, sample annealing and dosing was performed in the preparation chamber. Spectra were recorded at 6.0 eV primary electron beam energy (E_p) in both specular ($\theta_i = \theta_r = 45°$) and off-specular ($\theta_i = 45°$, $\theta_r = 25°$) scattering geometries. The instrumental resolution, defined by the full width at half-maximum (fwhm) of the elastic peak, varied between 12 and 21 meV for this study. The resolution of the data is not a consequence of the instrumentation used (this spectrometer routinely achieves a resolution of 3 meV on well-ordered single-crystal surfaces) but a result of the relatively small domains observed in organic overlayers such as those studied here.

The solid-state Fourier transform infrared (FTIR) study was performed on macrocycle, thread, and rotaxane powders pressed into pellets in a KBr matrix with a pure KBr pellet as a reference. The data were recorded with a resolution of 2 cm^{-1} using a BIO-RAD FT 60A Fourier transform spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector.

3. Results and Discussion

Fumaramide [2]rotaxane, fumaramide thread, and benzylic amide macrocycle are shown schematically at the center of Figure 2. They only contain amide, phenyl, and methylene groups that give rather complicated infrared (IR) spectra as shown in Figure 2a. While the detailed assignment of all the IR peaks is beyond the scope of this paper, identification of the main vibrational bands serves as a reference for the subsequent HREELS characterization, which, in turn, provides

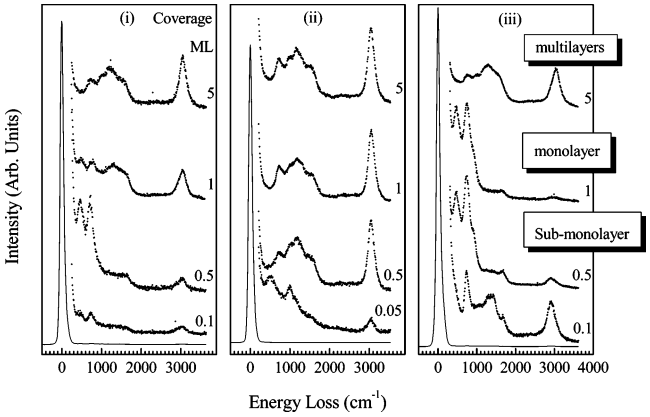

Figure 3. HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45°$) from selected submonolayer, monolayer, and multilayer coverages of (i) fumaramide [2]rotaxane, (ii) fumaramide thread, and (iii) benzylic amide macrocycle adsorbed on Au(111) at 300 K. The primary beam energy is 6.0 eV. Coverages are reported in monolayers (ML).

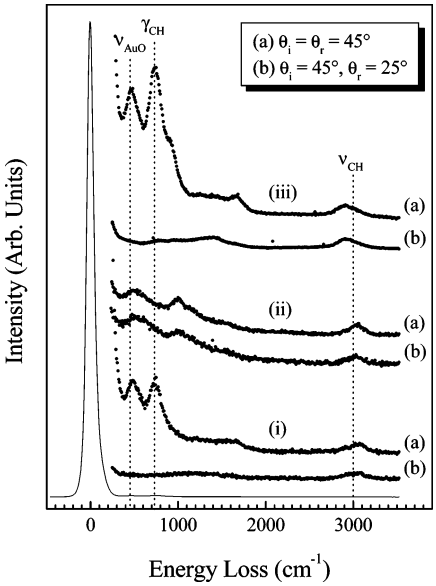

Figure 4. HREELS spectra collected in specular (a) $\theta_i = \theta_r = 45°$ and (b) off-specular $\theta_i = 45°$, $\theta_r = 25°$ scattering geometries from submonolayer coverages of (i) fumaramide [2]rotaxane, (ii) fumaramide thread, and (iii) benzylic amide macrocycle adsorbed on Au(111) at 300 K. The primary beam energy was 6.0 eV.

data on the molecular orientations of these species adsorbed on the Au(111) surface.

Once compared with the IR spectra, the HREELS spectra recorded at 300 K at submonolayer coverage, Figure 2b, allow the identification of the main vibrational bands (see vertical lines), with the exception of the N−H stretching vibrations expected to occur with low intensity beyond the C−H stretching region at ∼3330 cm^{-1}.[20,21] A more detailed analysis is given below.

The Rotaxane. Figure 3(i) shows a series of HREELS spectra collected at 300 K in specular scattering geometry from submonolayer, monolayer, and multilayer film coverages of fumaramide [2]rotaxane adsorbed on Au(111). At all coverages, the existence of aliphatic and aromatic groups is indicated by the presence of C−H in-plane stretching (ν_{CH}) at ∼3050 cm^{-1}. The complex group of unresolved low-intensity bands between 1800 and 900 cm^{-1} is due to many different vibrations (C−H in-plane bendings, ring breathings and stretching, amide group deformations, N−H bendings, and C−N and C−O stretching vibrations). In contrast, the peak at 730 cm^{-1}, particularly intense at low coverages (<1 ML), is characteristic of out-of-plane C−H deformations (γ_{CH}) of the phenyl rings. Since benzene desorbs from Au(111) above 200 K, the presence at 300 K of typical benzene vibrations suggests that the rotaxane adsorbs intact, in agreement with XPS data reported elsewhere.[18] Vibration of the entire molecule against the surface, that is the frustrated *z*-translation, appears at ∼470 cm^{-1},[10,11] together with Au−O stretching (ν_{AuO}).[12,22,23]

Upon increasing the submonolayer coverage (from 0.25 to 0.5 ML), the intensities of the ∼470 cm^{-1} and the phenyl C−H out-of-plane bending (740 cm^{-1}) bands increase with respect to the C−H in-plane modes (3050 cm^{-1}). Since the frustrated *z*-translation usually has much lower intensity than what is observed here,[10,11] this energy-loss band must contain predominantly contributions from Au−O stretching (ν_{AuO}). Indeed, HREELS studies of formic acid on Au(111)[22,23] and [2]catenane adsorption on Au(111)[12] show the occurrence of Au−O stretching vibrations at 480 and 484 cm^{-1}. The presence of Au−O stretching indicates interaction between the substrate and the adsorbate. Similar behavior has been reported by Fustin et al. in the case of the adsorption of the related [2]catenane on Au(111).[12]

As monolayer coverage is approached, the intensity pattern changes again with the attenuation of bands corresponding to C−H out-of-plane deformations and Au−O stretching in favor of in-plane modes.

The Thread. Figure 3(ii) displays a series of HREELS spectra recorded at 300 K for the fumaramide thread adsorbed on Au(111). The presence of aliphatic and aromatic groups is indicated by the bands of C−H in-plane stretching at 3050 cm^{-1}. Out-of-plane C−H deformations of the phenyl rings (γ_{CH}) and Au−O stretching (ν_{AuO}) that appeared as the most dominant bands for the rotaxane are usually not resolved in the case of the thread. Very low coverages (<0.1 ML) are required to resolve the low-energy-loss features in the form of bands at 510 cm^{-1} (assigned to ring out-of-plane bending) and a 1000 cm^{-1} band.

The Macrocycle. Figure 3(iii) complements previous findings relative to the HREELS characterization of a benzylic amide macrocycle adsorbed on Au(111).[10,11] At low macrocycle coverage, the intensity of the Au−O stretching vibrations and of the phenyl ring out-of-plane C−H bendings at 740 cm^{-1} is large relative to the C−H in-plane modes at 2920 cm^{-1}. At coverages in excess of monolayer saturation, in-plane modes are favored.

Comparison of the HREELS Spectra of the Three Molecules. As a function of coverage, the strongest similarities in Figure 3 occur between the HREELS spectra of the macrocycle and the rotaxane. However, in the case of the macrocycle, the phenyl ring out-of-plane C−H vibrations and Au−O stretching dominate from submonolayer to monolayer coverage, whereas, for the rotaxane this behavior only persists up to 0.5 ML coverage.

The rotaxane, the macrocycle, and the thread share the same constituent moieties (amide, phenyl, and methylene groups). It is therefore not surprising that their infrared spectra are similar. The HREELS spectra, however, differ substantially as a function of coverage because of the presence of the metal surface selection rule (MSSR)[24] that depends on the orientation of the molecules with respect to the substrate.[25]

Figure 4 compares HREELS spectra collected at 300 K in specular and off-specular scattering geometries for films of the three molecules adsorbed on Au(111) at submonolayer coverage.

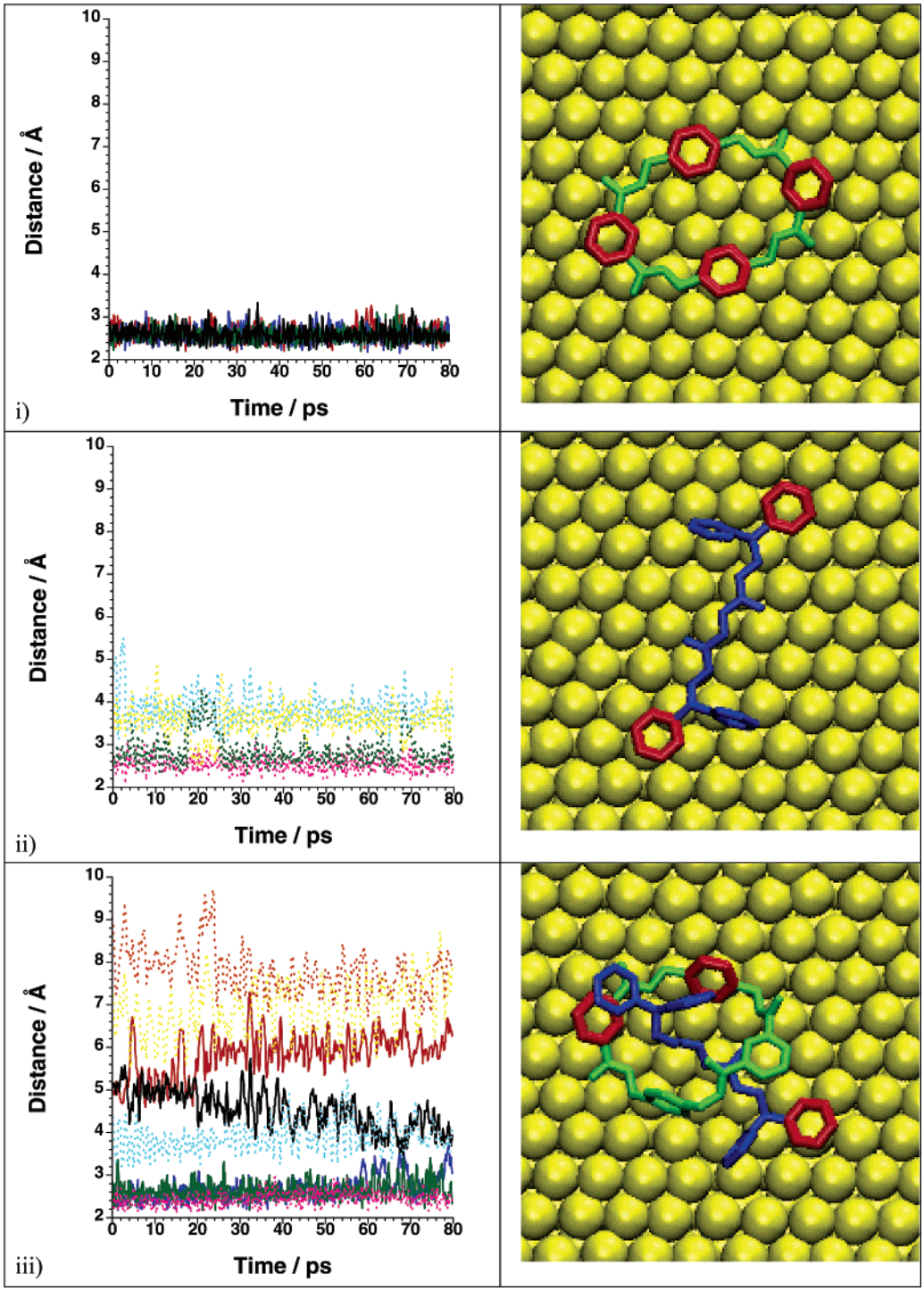

Figure 5. Molecular dynamics at 300 K. Left: Phenyl group distances from the Au(111) surface of (i) benzylic amide macrocycle, (ii) fumaramide thread, and (iii) fumaramide [2]rotaxane. Solid lines are for the phenyls of the macrocycle, dotted lines for the phenyls of the thread. Right: Snapshots of the simulation, the phenyls lying mostly flat on the Au(111) surface are in red.

The sharp decrease in intensity in the spectra of films of the macrocycle and the rotaxane collected in off-specular geometry suggests the existence of preferred orientations for Au−O bonding, the phenyl rings, and amide functionalities. In contrast, the thread shows no evidence of a preferential orientation at any coverage. Multilayer films (not shown) have no preferential orientation.

Further insight into film formation is given by the observation of the fwhm of the elastic peak. In the specular spectrum of the macrocycle monolayer, the fwhm is 12 meV, which can be attributed to the ordered nature of the film and the relatively narrow distribution of dipolar losses. From previous work it is known that the domain size is larger than 80 Å.[11] This value increases to 16 meV for the rotaxane and to 20 meV for the thread. Hence, it appears that the introduction of the thread in the macrocycle, thus forming the rotaxane, disrupts the film order and reduces the range of coverage that possesses a preferential orientation.

Molecular Dynamics of Single Molecules on Au(111). The HREELS spectra at submonolayer coverage show a different behavior for the three molecules. The growth of the first layer is ordered for the macrocycle all the way to full coverage,

ordered only up to 50% for the rotaxane, and disordered for the thread. The ring adopts a planar conformation on Au(111) that readily explains the tendency to order. Less trivial to explain on the basis of common chemical sense is the origin of the partial order observed for the largest system.

We decided to examine the dynamics, at room temperature, of the three molecules on Au(111) with a model that we have found useful to explain Au−organic interactions. Examples of past applications are (1) the adsorption of alkanes and 1-alkenes on Au(111),[26] where the adsorption energies of short chains, up to 10 carbon atoms, were reproduced with an average error of less than 1 kcal mol^{-1}, and the unexpected transition to disorder that occurs for the deposition of alkyl chains between 18 and 26 carbon atoms was explained; (2) the substitution kinetics of thiols on self-assembled monolayers;[27] (3) the existence of two surface reconstructions for C_{60} adsorbed on Au(110);[28] (4) the mobility of DNA bases on Au(111);[29] and (5) the structure of the present macrocycle on the Au(111) surface.[11]

In the model, the gold surface is described by the "glue model",[30] which contains a many-body term (in addition to the usual two-body interactions), which mimics the "gluing" character of the atoms cohesion. In practice, the energy of an atom depends on its effective coordination. The metal−molecule interactions are the sum of Coulomb interactions, with the charges calculated on-the-fly by the charge equilibration (Q_{Eq}) scheme of Rappe and Goddard,[31] and a short-range Born−Mayer potential, which accounts for the dispersion forces and avoids nuclear fusion when charges or dipoles interact attractively. The model is implemented in a modified version of the TINKER program,[32] which has been widely used by us.[33] A total of 896 Au atoms in four layers were used. The cell axes were 40.39 Å, 29.984 Å, and 50.00 Å for *a*, *b*, and *c*, respectively; the long *c*-axis was necessary to isolate the surface from its image. Ewald summation of charges was used both for gold and the adsorbed molecules, which were simulated by the MM3 model.[34] Molecular dynamics simulations were run with 20-ps equilibration and at least 80 ps of production. Although not ab initio, the present model, should account for charge flow and metal−organic interactions in a more thorough way than the Lennard−Jones potentials that are presently in use for this kind of simulation,[35] or even when the metal is described by an Embedded Atom Model,[36] and may be comparable in complexity to treatment with the Universal Force Field[37] where, however, predefined gold−gold or the gold−organic connectivities may be used, a feature absent here so that the adsorption sites are determined entirely by the dynamics of the system.

Figure 5 shows the distance of the center of mass of each phenyl group from the gold surface. The four phenyls of the macrocycle undergo very small oscillations, and the entire molecule is lying flat on the surface. In the case of the thread, only two phenyls interact strongly with the surface. They belong to different stoppers and are in a "trans" arrangement with respect to each other. Notice that one of these two phenyls is not consistently lying flat and temporarily leaves the surface. For the rotaxane, there are three phenyls lying flat on the surface—two of them belong to the macrocycle and are linked to each other, and one of them belongs to the stopper farther away from the adsorbed part of the macrocycle. Figure 5 also shows a snapshot of the simulation with the different geometrical arrangement of the phenyls.

The picture provided by the simulations is consistent with analysis of the HREELS spectra. The out-of-plane phenyl vibrations are more intense for the macrocycle because of its four phenyls lying flat on the surface, followed by the rotaxane with its three flat-lying phenyls adsorbed, and lastly by the thread.

Inspection of the simulations (see movies in the Supporting Information) also shows the origin of the greater degree of disorder observed for the thread. Both macrocycle and rotaxane appear to be firmly anchored on the Au(111) surface and undergo relatively small displacements. The thread, however, shifts along the metal surface. Mobility was estimated as the largest displacement, in angstroms, from the initial position for any phenyl group. The ratios are 4.8:23.0:7.5 for macrocycle/thread/rotaxane. The molecular dynamics simulations therefore imply that the disorder observed up to monolayer coverage for the thread is due to its high mobility on the metal surface, a feature not shared by the rotaxane and the macrocycle.

4. Conclusion

We have presented coverage-dependent HREELS characterization of the adsorption on Au(111) of fumaramide [2]rotaxane and its two components, a benzylic amide macrocycle and the fumaramide thread. Chemisorption of the macrocycle and rotaxane is evidenced by the presence of Au−O stretching vibrations. The relative intensities of out-of-plane and in-plane phenyl ring vibrations for these two molecules indicate that their phenyl rings are oriented predominantly parallel to the Au(111) surface at up to 0.5-ML coverage for the rotaxane and 1-ML coverage for the macrocycle. The thread shows no evidence of chemisorption, and the absence of a preferential orientation, according to molecular dynamics simulations, is due to a substantially larger surface mobility compared with the other two molecules.

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Supporting Information Available: Three movies with the motions of each of the three molecules on the Au(111) surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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