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ABSTRACT

Mechanically interlocked molecules such as rotaxanes are fascinating for their potential in molecular-scale devices. Rotaxane, stimuli-responsive "molecular shuttles" are molecules where a macrocyclic 'bead' is locked onto a linear "thread" by bulky "stoppers". Large amplitude motion of the macrocycle can be induced by external stimuli (e.g. light, electrons, heat, pH, polarity of the environment etc.). While the solution chemistry of rotaxanes has been explored extensively, the study of the surface chemistry of these species has been limited to a few examples. Here we report detailed direct information on the surface morphology and the packing of rotaxane on self-assembled monolayer on quartz and silicon oxide/Si(110) followed by the photophysical studies.

Keywords: rotaxane, X-ray photoemission spectroscopy, atomic force microscopy, time resolved fluorescence.

1. INTRODUCTION

Biological motors, both singularly [1] and cooperatively [2], are capable of transporting objects many times more massive than themselves and have been used to power prototypical hybrid mechanical devices [3], [4]. However, performing macroscopic mechanical tasks with the wholly synthetic molecular machines [5], [6] has proved more elusive. Considerable interest has been focused on the preparation and characterization of functionalized, switchable, ordered arrays of molecular motors for the development of new promising multifunctional materials. Mechanically interlocked molecules such as rotaxanes are aesthetically fascinating and of interest for their potential in molecular-scale devices. While the physical and chemical properties of rotaxanes in solution have been explored extensively, there are only few studies of these species grafted to surfaces [5], [6], [17]-[20]. Aim of this work was to investigate the structural and the photophysical properties of naphthalimide rotaxane when anchored on a non-conducting surface, namely quartz or p-type Si(100) covered with a controlled oxide layer. We grafted naphthalimide rotaxane *via* hydrogen bonding [17] between the pyridine group of the macrocycle and the carboxylic acid end groups of a silanized self-assembled monolayer. The surface morphology was studied by atomic force microscopy (AFM), the coverage (functionalization yield) of rotaxane on self-assembled monolayer (SAM) was determined by X-ray photoemission spectroscopy (XPS), and the polar character of these surfaces was investigated using contact angle measurements. The photophysical properties of the prepared surfaces were studied by using time-resolved fluorescence. As sketched in Figure 1 our films featured complete and uniform coverage of the SAM with a monolayer of shuttles, with the long axis of the rotaxane thread lying parallel to the surface. The rotaxane bonded to the surface by the macrocycle should have the ability to perform movements of the thread when exposed to external stimuli.
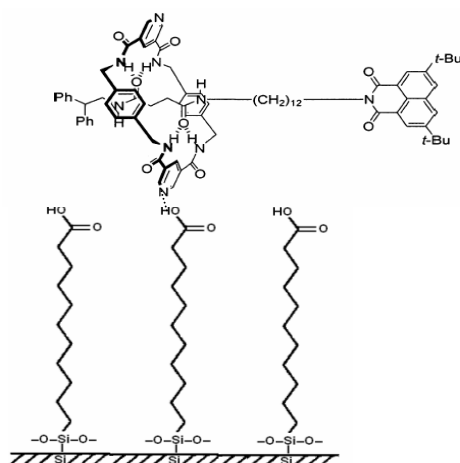
Figure 1. Simplified representation of the functionalization of carboxylic acid terminated self-assembled monolayer with naphthalimide rotaxane.

A similar rotaxane with two phenyl groups in the place of two pyridine groups of the macrocycle already demonstrated the switching properties in a solution either after the excitation by a laser pulse [7] or after electron transfer at the electrode [8]. The investigated systems are viewed as potential elements for molecular machinery and the change in position of the subunits has been used as a nanoscale mechanical switch to vary physical properties such as conductivity [9], induced circular dichroism [10] and fluorescence [11].

2. EXPERIMENTAL

Naphthalimide rotaxane were synthesized as described in [12]. Quartz was selected as the surface for time-resolved fluorescence measurements in transition. Since XPS was data was required for quantitative analysis, surface charging was minimized by performing the analysis on rotaxanes grafted onto an acid-terminated SAM on an Si(100) covered with oxidized layer [13]. The AFM experiments were performed also on an oxidized layer on Si(100) in order to compare with the XPS quantitative data on the same substrate. The self-assembled monolayers (SAMs) were prepared by immersing quartz or the oxidized silicon wafer in 10^{-3} M solution of 2',2',2'-trifluoroethyl-11-(trichlorosilyl)undecanoate in a freshly distilled toluene for 2 hours, at room temperature (21 °C). The samples were than sonicated three times in freshly distilled toluene and dried in an argon flow. The carboxyl modified substrates were obtained by hydrolysis of ester groups into carboxylic acid by immersing into 8 M HCl solution at 90 °C, for 2 hours. The samples were then ultrasonically cleaned in water (Milli-Q, 18.0 MΩ) and dried under an argon flow. The carboxylic acid terminated SAM was immersed into 10^{-3} M naphthalimide rotaxane solution in dichloromethane for six days, at room temperature (21 °C). The X-ray photoelectron spectroscopy (XPS) measurements were performed using an X-PROBE Surface Science Laboratories photoelectron spectrometer with the monochromatic Al Kα X-ray source (hν=1486.6 eV). The energy resolution was set to 1.65 eV to minimize data acquisition time and the photoelectron take off angle was 37°. The binding energies were referenced to the Si 2p core level set to the SiO$_2$ reference value of 103.0 eV.[14] The base pressure in the spectrometer was 2×10^{-10} Torr. Spectral analysis included a Shirley background subtraction and a peak separation using mixed Gaussian-Lorentzian functions in a least squares curve-fitting program (Winspec). The AFM measurements were performed in air, on the NanoLaboratory Ntegra Probe (NT-MDT, Russia) operating in both contact and tapping mode. The Si$_3$N$_4$ tips with spring constants of 0.05 N/m were used for contact mode imaging. Tapping mode images were acquired using "Golden" silicon probes. The time resolved fluorescence measurements were performed using a streak camera system with a synchroscan sweep unit (Hamamatsu). The sample was irradiated by the frequency-tripled output (325 nm) of a tunable 76 MHz Ti:Saphire laser (Mira 900, Coherent), which was pumped by an all-solid-state diode-pumped, frequency doubled Nd:YVO$_4$ laser (Verdi, Coherent).

3. RESULTS AND DISCUSSION

3.1 X-ray photoemission spectroscopy

Figure 2 (top panel) illustrates a survey scan for the carboxylic acid terminated SAM showing O 1s, C 1s, Si 2s and Si 2p core level photoemission lines as expected for the monolayer. The bottom panel of Figure 2 shows naphthalimide rotaxane functionalized SAM. The most convincing evidence that the rotaxanes are present on the surface comes from the analysis of the nitrogen 1s core level region, which is shown in the inset of the bottom panel of Figure 2. The peak centered at 400.0 eV is shifted by 0.5 eV to higher binding energy relative to the

reference compound $C_6H_5CONH_2$ (399.5 eV) [18]. Presumably, this is the consequence of an additional bonding to the CH_2 group [15] and perhaps, to a lesser extent, involvement in intermolecular hydrogen bonding interactions[20]. Since no fluorine and no chloride can be detected in photoemission spectra of these samples we can be sure that the hydrolysis process was complete [16] and no solvent molecules (CH_2Cl_2) were incorporated into the layer [17].
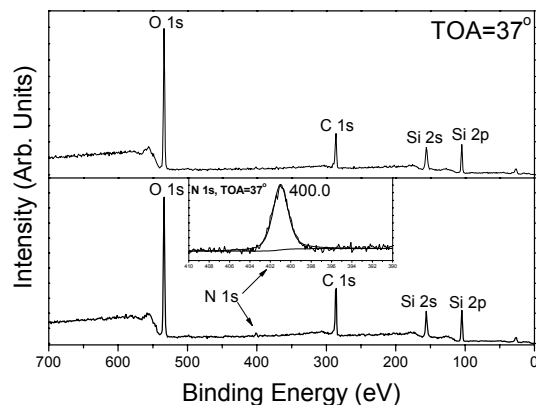

Figure 2. Photoemission survey of the carboxylic acid- terminated SAM (top panel,) and of the carboxylic acid terminated SAM functionalized with naphthalimide rotaxane (bottom panel).

Additional evidence for the successful functionalization of the carboxylic acid terminated SAM comes from Figure 3 where we compare the C 1s photoemission line the bare SAM (panel a) with that obtained after grafting the naphthalimide rotaxanes (panel b). For the bare SAM the first photoemission peak at 285.0 eV is assigned to the aliphatic carbon of the alkyl chains. The signal due to carbons bond to the acid groups is found at 286.6 eV, and the last peak at 289.6 eV corresponds to the carboxylic carbon [18]. While rigorously there are ten chemically distinct carbon environments in the naphthalimide rotaxane shown in Figure 1, in practice XPS may not distinguish between six types of phenyl ring carbon. Hence, the decomposition procedure of the spectrum in Figure 3b consists of fitting a minimum number of peaks consistent of raw data and the molecular structure of the adsorbate with the simplification of assuming equivalent aromatic carbon atoms. Figure 3b illustrates the mathematical reconstruction to the experimental data (constrained by the theoretical intensity ratio) assuming a molecule with three distinct chemically shifted C 1s core level emissions, occurring at 284.7, 285.4, 286.4, 287.7, and 289.4 eV, assigned to the aromatic, aliphatic, carbons bound to the acid groups, amide, and carbonyl components with shake-up structure associated with $\pi-\pi^*$ transitions of the phenyl rings located at 291.4 eV. The 0.9 eV binding energy shift relative to benzene (284.3 eV) is understandable given that 19% of the phenyl ring carbon are bound to CH_2NH or NHCO moieties. We also compared the experimentally determined atomic percentages, obtained from the photoemission peak areas, with those calculated for the functionalization of 2, 4, 5 and 8% of the acid groups of the SAM. In the calculations, we considered a model surface of 100 silanes and computed the atomic percentages for N, C and O. We found that a functionalization of 5% of all acid groups fits best with the experimental data.

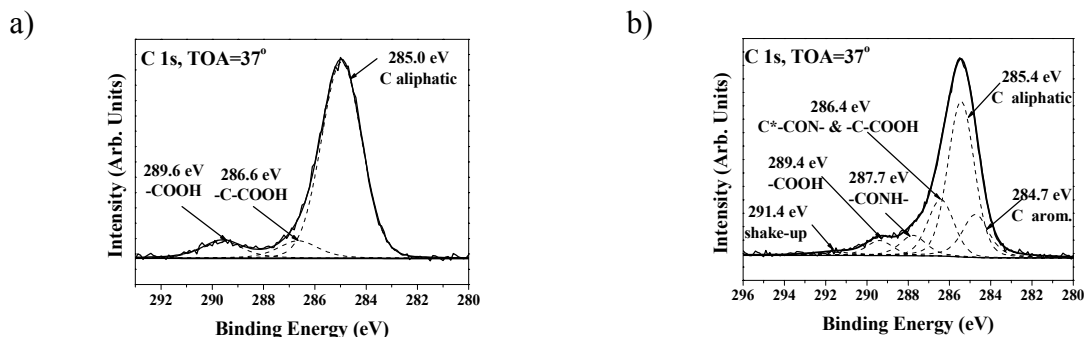a)   b)

Figure 3. Photoemission spectra (—) and mathematical reconstruction (--) of the C 1s core-level region for an acid-terminated self-assembled monolayer (a) and an acid-terminated self-assembled monolayer functionalized with rotaxane (b).

3.2 Atomic force microscopy

The AFM image on a scale of 400 x 400 nm^2 of the SAM on the silicon oxide/Si(100) substrate is presented in Figure 4a and shows a smooth homogeneous surface. Roughness analysis of this topographic image yields a R_{ms} value of 0.07 nm (from 300x300 nm^2 areas in contact mode). For tapping mode the roughness increases (R_{ms} is

a)   b)   c)
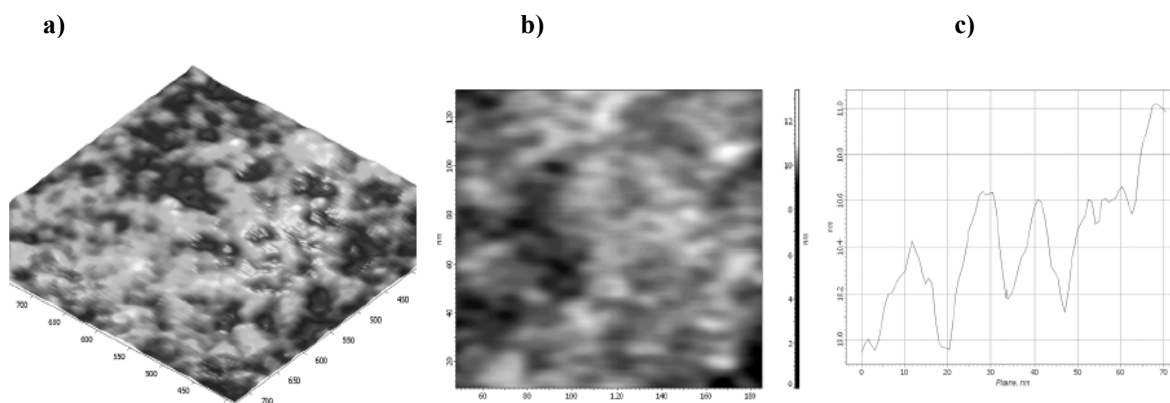

Figure 4. AFM topographical image a) carboxylic acid terminated self-assembled monolayer (SAM); b) naphthalimide rotaxane grafted onto SAM; c) topographical profile.

0.11 nm) due to strong inelastic interaction between oscillating tip and rather long C-C chains of the SAM layer. The naphthalimide rotaxane adsorption clearly changes the morphology of the surface as shown in Figure 4b. The surface roughness of naphthalimide rotaxane grafted onto SAM yields a R_{ms} value of 0.37 nm for area of 300x300 nm^2, which is higher than the one obtained for the SAM alone. This can easily be explained taking into account that the average diameter of naphthalimide rotaxane molecule is relatively large (2 nm). The topographical profile, presented in Figure 4c, gives the size of molecules of 5 nm. The lateral dimensions are larger than expected for the size of a single naphthalimide rotaxane molecule because of the convolution with the tip shape (diameter 20nm). Since the AFM features are affected by the convolution with the tip shape, when the naphthalimide rotaxane molecules are very closely packed on the surface, it is necessary to know the exact tip shape to detect the exact size and distance between molecules.

The values of the contact angle obtained on carboxylic acid terminated SAM 60 s after deposition of the water drop was 10 ± 2°, as expected for such a hydrophilic surface [19]. After functionalization of the SAM with naphthalimide rotaxane contact angle of the water drop increases to 67 ± 2°, which confirms presence of rotaxane whose phenyl, imide and ester groups are responsible for the more hydrophobic character of the surface.

3.3 Time-resolved fluorescence

Figure 5 shows the time-resolved fluorescence measurements of the acid-terminated SAM on quartz, of 1mM naphthalimide rotaxane solution in dichloromethane, and of the naphthalimide rotaxane functionalized acid-terminated SAM on quartz. Although, in our experimental conditions, the acid-terminated self-assembled monolayers on quartz showed a very weak fluorescence (data not shown here) we did not observe any decay of this fluorescence with time. The measurements performed on the naphthalimide rotaxane solution in dichloromethane showed a single fluorescence decay of 1400 ps, and remain in agreement with previous measurements [20]. The time-resolved fluorescence measurements of naphthalimide rotaxane functionalized SAM showed two lifetimes of fluorescence arising from naphthalimide moiety of the rotaxane molecule as illustrated in Figure 5.
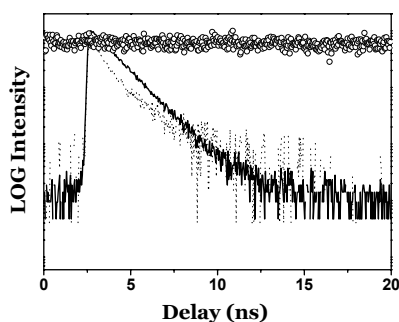

Figure 5. Integrated fluorescence decay of acid-terminated SAM/quartz alone (o), of the naphthalimide rotaxane in a dichloromethane solution (—), and of carboxylic acid-terminated SAM functionalized with naphthalimide rotaxanes/quartz (--) for 325nm excitation wavelength.

The first calculated decay time, 500 ps, was shorter than the one obtained for the solution of naphthalimide rotaxane in dichloromethane, 1400 ps. The difference between the decay times measured in solution and on a solid substrate stems from the difference in interactions between naphthalimide rotaxane molecules and the solvent and between the rotaxanes and the substrate. It was already reported that the decay time of the naphthalimide rotaxane in a solution can vary from 1600 to 3300 ps, depending on the solvent used [20]. In our case the naphthalimide moiety of the rotaxane may interact with the carboxylic moiety of the acid-terminated monolayer, and consequently influence the observed fluorescence lifetime. While the first decay time was always the same for different samples and different points on a particular sample, the second calculated decay time varied from 2000 ps to 4000 ps for different points of the examined samples. Such a scatter of the second decay time can be explained as resulting from the interaction between naphthalimide moieties of the neighbouring rotaxanes molecules in the sub-monolayer on the SAM. Therefore, if we assume two, three or four naphthalimide groups interacting, we can obtain two, three or more decay times. Unfortunately, the signal from the naphthalimide group of the rotaxane was too weak and too noisy to permit a more detailed analysis of the lifetime.

4. CONCLUSIONS

The AFM technique can be used to characterize the self-assembled monolayers and supramolecular species on non-conducting substrates like silicon oxide on Si(100). The XPS and AFM data obtained for naphthalimide rotaxane grafted on acid-terminated SAM shows a tightly packed arrangement of "molecular shuttles". Time-resolved fluorescence spectroscopy measurements of naphthalimide rotaxane adsorbed on the acid-terminated SAM on non-conducting surfaces shows at least two decay times, probably due to interactions between naphthalimide moieties of rotaxane molecules. Moreover, the photophysical analysis indicates that the naphthalimide moiety interacts with the carboxylic groups of the SAM, which validates the orientation of the molecules with the thread parallel to the surface, as previously inferred from electrochemistry measurements [20].

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