

A pH-Sensitive Supramolecular Switch Based on Mixed Carboxylic Acid Terminated Self-Assembled Monolayers on Au(111)

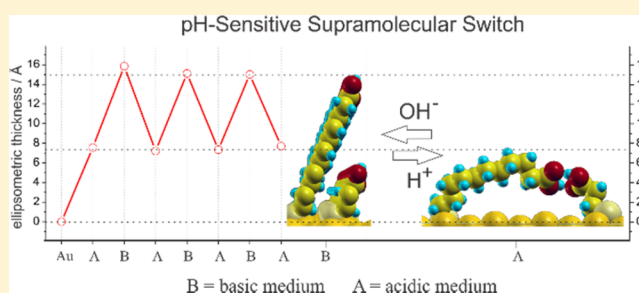
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Supporting Information

ABSTRACT: We show that homogeneously mixed self-assembled monolayers (SAMs) of mercaptoalkanoic acids of different chain lengths can be used to build up a pH-sensitive supramolecular switch. The acids with short and long alkyl chains interact via the strong hydrogen bond between carboxylic acid groups. The pH acts as a trigger by breaking or restoring the hydrogen bond interaction in basic or acidic solutions, respectively. The corresponding changes in the monolayer structure were determined by ellipsometry, surface-enhanced Raman spectroscopy, and contact angle measurements. Density functional theory (DFT) calculations were performed to elucidate the structures of interacting molecules compatible with the surface coverage obtained from electrochemical reductive desorption experiments. The simplicity of the preparation procedure assures a high reproducibility whereas the stability of the homogeneous mixed SAM guarantees the reversibility of the switching process.



INTRODUCTION

Smart surfaces are capable of reversibly altering their properties depending on external conditions.^{1,2} Many stimuli can be used to switch surfaces between different states, including light, pH, redox, and ion triggers.^{3,4} The stimuli-responsive surface relies on switching molecules between different configurations by the external stimuli. The basis of many switchable molecules relies on isomerization processes such as the *cis*–*trans* photoisomerization of the azo group^{5,6} or the open-closed ring isomerization of dithienylethene.^{7,8}

Molecular switches based on the reversible noncovalent interactions between two or more molecules are referred to as supramolecular switches. A typical example is the electrostatic interaction between a secondary ammonium ion and a crown ether. In these supramolecular structures, the switching is achieved by pH stimulation. Upon protonation of the amine group, a strong hydrogen bonding interaction is established between $-\text{NH}_2^+$ and the oxygen atoms of the ethyleneoxy units of the crown ether, whereas upon the addition of base, the decomplexation of the amine molecule and the crown ether occurs.¹ The use of pH to trigger reversible conformational changes has been reported in different systems such as polymeric brushes grafted on silicon surfaces,⁹ the switching transport through nanopores,¹⁰ and in pH clock-operated mechanized nanoparticles.¹¹

When anchored to a surface, the availability of free volume around the molecule is essential for the performance of a switch. Therefore, the surface functionalization process is often

more complex than the formation of a compact organic monolayer. In the case of gold surfaces, low-density SAMs of mercaptoalkanoic acids¹² have been exploited to build switching surfaces using different methodologies. Low-density 16-mercaptohexadecanoic acid films on gold can be obtained by performing ion exchange on monolayers made from tetralkylammonium–mercaptohexadecanoate ion pairs.¹³ A different strategy is to use a precursor molecule in which the carboxylic group is capped by a bulky (2-chlorophenyl)diphenylmethyl ester group, which prevents a dense packing of the alkyl chains during the self-assembly process. When the ester group is cleaved, a low-density SAM of 16-mercaptohexadecanoic acid is obtained on Au(111).¹⁴

On a conducting surface, voltage-induced conformational changes can be exploited in the development of smart surfaces. Molecular switches have been built using flexible alkyl chains terminated by a carboxylic group. The terminal $-\text{COOH}$ group is attracted to the positively biased surface exposing the hydrophobic backbone, whereas for the unbiased surface the hydrophilic $-\text{COOH}$ group is exposed.^{13,14} The switching behavior of $-\text{COOH}$ terminated monolayers is not restricted to the gold surface.^{13,14} It has also been predicted theoretically on the hydrogenated silicon surface functionalized with a mixed ω -carboxyalkyl/alkyl monolayer.¹⁵

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Mixed SAMs of 3-mercaptopropionic (MPA) and 11-mercaptoundecanoic acids (MUA) form homogeneous mixtures on Au(111) despite the large chain length difference.¹⁶ The driving force leading to the formation of the homogeneous mixture was proposed to be the strong hydrogen bond interaction between the adjacent carboxylic groups of MPA and MUA molecules.¹⁶ The observation of homogeneous SAM mixing inspired the present work to develop a pH-sensitive supramolecular switch. The switch is easily and reproducibly built on the Au(111) surface using homogeneously mixed SAMs of mercaptoalkanoic acids of different chain lengths. The straightforward formation of the mixed SAM using the immersion method avoids the complexities related to the formation of low-density SAMs. The switching properties arise from the formation (acidic pHs) and breakage (alkaline pHs) of the hydrogen bond interaction between the terminal carboxylic groups of adjacent MUA–MPA molecules. Besides the simplicity of the formation procedure to build the switch, we also show it is highly reversible with respect to the pH trigger.

EXPERIMENTAL SECTION

Gold Substrates. A gold monocrystal of 4 mm in diameter and oriented better than 1° toward the (111) face (MaTeck, Jülich, Germany) was used as a working electrode for cyclic voltammetry. The surface was cleaned by repeated cycles of annealing on a H₂ flame and cooling in a N₂ atmosphere. Ellipsometric measurements were performed with Au films (500 nm thick) evaporated on heat resistive glasses. These substrates were annealed in a butane flame for 2 min and cooled down to room temperature in a stream of nitrogen. Surface-enhanced Raman spectroscopy (SERS) measurements were performed with roughened gold surfaces prepared electrochemically using the following procedure:¹⁷ voltage step of 2.4 V during 10 min in 0.5 M H₂SO₄ solution and then a linear potential sweep at 0.02 V s⁻¹ from 2.4 to -0.6 V was applied.

Preparation of SAMs. 3-Mercaptopropionic and 11-mercaptoundecanoic acids were purchased from Sigma-Aldrich. The monolayers were prepared by immersing the previously annealed gold substrates in millimolar ethanolic solutions of the thiols for 12 h. All chemicals were used as received without further purification. The mixed MPA–MUA monolayers were prepared by 12 h immersion in an ethanolic solution with 80% of MPA and 20% of MUA (homogeneous SAM). A phase segregated SAM was prepared from an alkaline ethanolic solution with 45% of MPA and 55% MUA. A concentrated ethanolic NaOH solution was added to the ethanolic forming solution until pH 9 was reached.

Electrolytic solutions were prepared with Milli-Q water (Millipore Corp., Billerica, MA). Merck suprapure chemicals were employed to prepare 0.1 M KOH and 0.1 M HCl.

Electrochemical Measurements. Cyclic voltammograms (CV) for the reductive desorption experiments were performed with a Solartron 1260 electrochemical interface and a conventional electrochemical three-electrode cell with separate compartments for reference (Ag/AgCl (NaCl, 3 M)) and counter electrode (Pt wire). The working electrode is positioned above the solution so that a meniscus is formed. This assures a reproducible electrode area in contact with the solution. The 0.1 M KOH electrolyte was thoroughly deoxygenated by bubbling with nitrogen prior to each experiment.

Ellipsometric Measurements and Modeling. A Rudolph Research rotating-analyzer automatic ellipsometer with a 75 W tungsten halogen light source was used. All measurements were made at an angle of incidence of 70.00° and at a wavelength of 405.0 nm. The calculation of the film thickness was based on the three-phase ambient/SAM/gold model.¹⁸ For each measurement of the ellipsometric Δ and Ψ angles, this model has five parameters: the refractive index and adsorption coefficient of the substrate, the refractive index and adsorption coefficient of the monolayer, and the monolayer

thickness. The optical constants of the substrate were determined immediately after the annealing of the gold surface. The corresponding monolayer was then formed, and the ellipsometric Δ and Ψ angles were measured (Figure S1). As the SAMs are nonabsorbing, the absorption coefficient is zero. Therefore, the monolayer thickness and the monolayer refractive index were calculated from each measurement of Δ and Ψ based on the three-phase model of the complex Fresnel reflection coefficient of the interphase.¹⁸ Figure S2 shows that the refractive index has small variations upon insertion of the mixed MUA/MPA monolayer in the acid and basic solutions. The average refractive index was 1.46 (Figure S2).

A compact and homogeneous monolayer structure is adequately described by the single layer model, and its thickness and refractive index are obtained from the fitting procedure. In the case of segregated phases (an heterogeneous monolayer) or a structure with the MUA molecules extending beyond the short MPA molecules (a double-layer structure with an inner compact layer and an outer less dense layer), more complex optical models have to be considered. However, if the ellipsometric angles for such structures are fitted to the single-layer model, effective refractive indexes and thicknesses are obtained. It is our experience that the deficiencies of the single-layer model are mainly “absorbed” by the effective refractive index whereas the thickness is less affected. The results below show that the single layer modeling gives quite reasonable thicknesses, which are within the range of thicknesses for the pure MPA and pure MUA monolayers.

Surface-Enhanced Raman Spectroscopy. A Horiba LabRAM HR spectrometer was used. A long-working distance objective (8 mm) with a numerical aperture of 0.7 and a magnification of 100 were used. A 632.8 nm He–Ne laser was used for excitation with a power of about 5 mW on the sample.

Contact Angle. The wettability of the monolayers was tested with static contact angle measurements using a custom-built goniometer. A 2.0 μ L drop of Milli-Q water was used. The monolayers were rinsed with ethanol and dried under a N₂ flow for 3 min before measuring the contact angle.

Theoretical Methods and Surface Modeling. Periodic density functional theory (DFT) calculations were performed with the Quantum Espresso code,¹⁹ which uses plane waves to expand the one-electron wave functions and norm-conserving ultrasoft pseudopotentials²⁰ to describe the core electrons. The Perdew–Burke–Ernzerhof exchange–correlation functional was used.²¹ van der Waals interactions were considered in the calculations by using a van der Waals density functional.²² The plane wave expansion was done up to a kinetic energy cutoff of 30 Ry (180 Ry for the density). Brillouin zone integration was performed using a (4 × 4 × 1) Monkhorst–Pack mesh.²³ A vacuum thickness of 10 Å was introduced between the slabs. The periodic supercell approach was employed to describe a 3 × 4√3 unit cell of the Au(111) surface containing the adsorbate molecules. The surface was modeled using a slab with three gold layers. The positions of all the adsorbate atoms as well as those of the two topmost Au layers were fully optimized.

RESULTS AND DISCUSSION

Figure 1 shows CV profiles for monolayers of MPA and MUA as well as for mixed MPA/MUA monolayers prepared from ethanolic solutions. The pure monolayers show sharp reductive desorption peaks at -0.74 V (MPA, curve a) and -0.91 V (MUA, curve d). The mixed SAM prepared from an ethanolic solution with a 20:80 MUA:MPA ratio has a reductive desorption peak (curve b) at an intermediate potential (-0.82 V) between those of the pure monolayers, which indicates it is homogeneous. Whereas the full width at half-maximum (fwhm) of the reductive desorption peak of MUA is 24 mV, the fwhm of the mixed monolayer is 84 mV. The broadening of the peak is an indication of increasing disorder. The mixed monolayer also has a lower surface coverage than the MUA monolayer. The MUA monolayer has a reductive desorption charge of 80 μ C/cm², which corresponds to a full

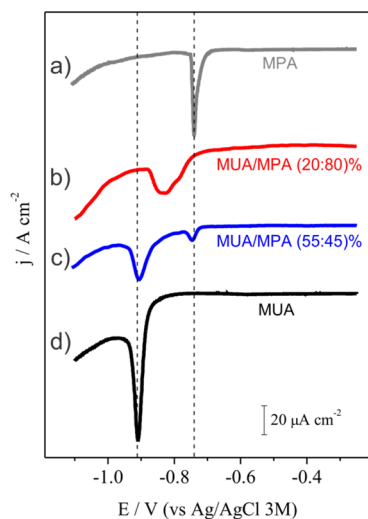


Figure 1. CV profiles for the reductive desorption of (a) pure MPA monolayer, (b) mixed MUA/MPA monolayer formed in an ethanolic solution with a 20:80% composition, (c) mixed MPA/MUA monolayer formed in an ethanolic solution of pH = 9.0 with a 55:45% composition, and (d) pure MUA monolayer. Scan rate: 20 mV/s. Electrolyte: 0.1 M KOH.

coverage of 0.33 (one thiolate for every three gold atoms). However, the mixed monolayer has reductive desorption charge of $63.3 \mu\text{C}/\text{cm}^2$ from which a surface coverage of 0.26 can be obtained. The CV profiles for mixed monolayers prepared with different MUA:MPA ratios are shown in Figure S3, and in all cases a homogeneous mixture is obtained.

A heterogeneous mixture of MPA–MUA can only be obtained after immersion of the gold substrate in an alkaline (pH = 9.0) ethanolic solution with 55% of MPA and 45% of MUA. Under these conditions, in which the carboxylic groups are deprotonated, the large chain length difference between MPA and MUA produces the phase separation. This is clearly observed in the CV profile of Figure 1c which shows two separate reductive desorption peaks at the potentials corresponding to each of the pure components. This shows that electrochemistry is very sensitive to the degree of homogeneity of mixed SAMs.

After the formation of the mixed homogeneous SAM, it was successively immersed for 1 min in 0.1 M solutions of NaOH and HCl in order to deprotonate and to protonate back the terminal –COOH groups, respectively. After the immersion in each solution, the surface was rinsed with ethanol and dried with nitrogen and the ellipsometric Δ and Ψ angles were measured from which the monolayer thickness and refractive index were calculated. Every point in Figures 2 and 3 corresponds to a single measurement.

Figure 2 shows the switching properties of the mixed layer. Two well-defined and very reproducible monolayer thicknesses are observed after immersion in acidic and basic solutions. This indicates that the transformations of the mixed monolayer are reversible. The formation of the switching surface is also very reproducible. To illustrate this, Figure 2 shows the results of five different experiments. In all cases, the same switching behavior is observed.

The lowest thickness is observed after immersion in HCl, and the highest thickness is observed after immersion in NaOH. This is interpreted as the folding and unfolding of the alkyl chain of MUA to form hydrogen bond interactions with

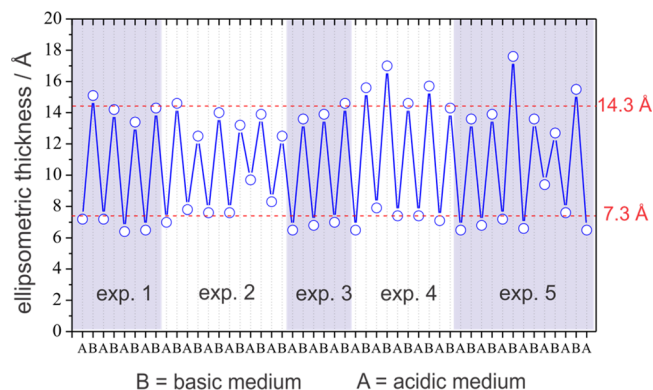


Figure 2. Ellipsometric thicknesses of homogeneous MPA/MUA monolayer measured after successive immersions in acidic (A) and basic (B) media. Five different experiments are shown. Measurements performed in air.

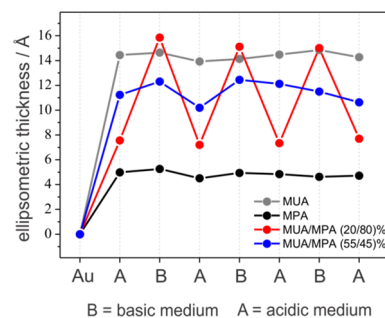


Figure 3. Monolayer thicknesses measured after successive immersions in acidic (A) and basic (B) media for pure MUA monolayer, pure MPA monolayer, mixed homogeneous MUA/MPA monolayer prepared from 20:80% forming solution, and mixed heterogeneous MUA/MPA monolayer prepared from 55:45% ethanolic solution of pH 9.0.

the surrounding MPA molecules (acidic pH) or to avoid repulsive interactions between carboxylate anions (basic pH). The hydrogen-bond interaction between carboxylic groups is very strong only when they lie on the same plane, with an energy of 16.8 kcal/mol.¹⁶ Lahann et al.¹⁴ found using ellipsometry that a low coverage monolayer of 16-mercaptohexadecanoic acid with laterally spaced molecules collapses on the Au surface upon exposure to air when the carboxylic terminal groups are deprotonated. In our case the deprotonated carboxylic groups of MUA cannot bind to Au due to the repulsion with the deprotonated carboxylic groups of MPA. This prevents the collapse of deprotonated MUA molecules within the MPA matrix.

The fact that the switching behavior originates from the homogeneous mixture of MPA and MUA in the monolayer was proved by two different experiments: (a) the pure monolayers have no switching behavior, and (b) the heterogeneous mixture has no switching properties either.

Figure 3 shows the ellipsometer thicknesses of pure MPA and MUA monolayers measured after successive immersions in the acidic and basic solutions. The monolayer thickness remains constant in both cases (4.9 Å for MPA and 14.4 Å for MUA), indicating that the compact single-component monolayers have no switching properties. These thicknesses are compatible with the molecular dimensions.¹⁶ As discussed above, this behavior is expected as the switchable molecules

require free volume around, which is not available in the compact monolayer.

Figure 3 also shows that the phase-separated MPA–MUA monolayer prepared in the alkaline ethanolic solution has no switching behavior. Its average thickness remains approximately constant after the immersions in the acidic and basic solutions.

Monolayer thicknesses measured by ellipsometry provide additional evidence about the homogeneous/heterogeneous nature of the mixed monolayers. In the case of a heterogeneous mixture containing phases of MPA and MUA with different thicknesses, the ellipsometric measurement yields an effective layer thickness that is intermediate between those of both phases. This is effectively observed in Figure 3. On the other hand, the maximum thickness of a layer formed by a homogeneous mixture of thiols with different chain lengths will be that of the longest thiol. Figure 3 shows that after immersion in the alkaline solution the thickness of the homogeneous mixed layer is virtually the same as the pure MPA monolayer, thus confirming its homogeneous structure.

Water contact angles for a pure MUA and for mixed MUA/MPA monolayers are shown in Figure 4 after immersion in the

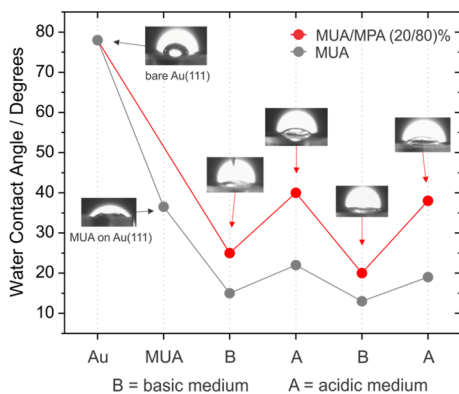


Figure 4. Contact angles of MUA monolayer and mixed MUA/MPA monolayer after immersion in basic (B) and acidic (A) solutions. The contact angles of the bare Au(111) surface (Au) and the freshly prepared MUA monolayer (MUA) are also included.

acidic and basic solutions. The value for a pure MUA was measured after rinsing the freshly prepared monolayer in ethanol during 1 min. For both the MUA and the mixed monolayer, the contact angles change reversibly. However, the changes are more pronounced for the mixed monolayer (around 20°) than for the MUA monolayer (around 5°), thus showing the switching properties of the former. After immersion in the acidic solution, the MUA monolayer is slightly less hydrophilic than in the deprotonated form with a contact angle of around 20°, whereas the mixed monolayer is more hydrophobic with an average contact angle of 40°. For the sake of comparison, Figure 4 also shows the static contact angle of a bare Au surface and a freshly prepared MUA monolayer. There is a large discrepancy in contact angles for carboxylic-terminated thiol adlayers in the literature.^{24–27} This dispersion has been attributed to the formation of a bilayer as a consequence of interlayer hydrogen bonding between COOH groups.²⁷ Although this effect may affect the value of the contact angle of the freshly prepared layer, it is eliminated after the successive immersion cycles in NaOH and HCl solutions. Figure 4 shows that for both the MUA and the MUA/MPA

layers reproducible contact angles are observed after immersion in the alkaline and acid solutions.

The conformational changes of the mixed monolayer after immersion in acidic and basic solutions were monitored by SERS. The vibrational contributions of the gauche (G) and trans (T) intensities in the $\nu(\text{C-S})$ region are indicative of the extent of order and crystallinity in the SAMs. In the case of an ordered monolayer with a predominantly trans conformation, the intensity of the T contribution is higher than that of the G contribution.^{20,28} Figure 5a shows that both in the acidic and

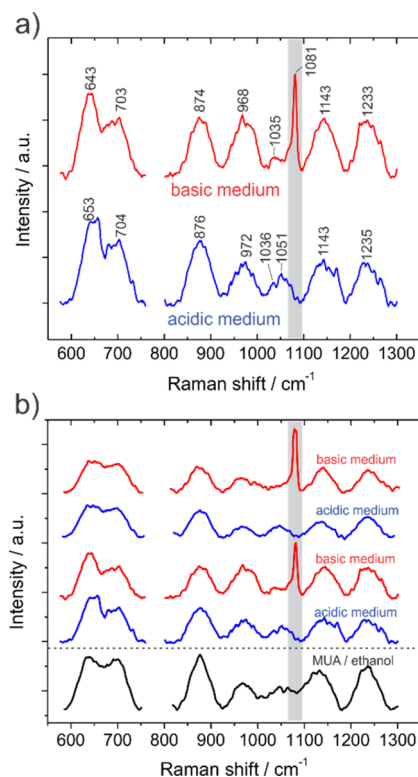


Figure 5. (a) SERS spectra of mixed MUA–MPA monolayer after immersion in acidic (blue) and basic media (red). Both spectra correspond to the same monolayer. (b) SERS spectra of a newly prepared mixed MUA–MPA monolayer taken after successive immersions in acidic and basic media. As a reference we show the spectrum of a pure MUA monolayer prepared in an ethanolic solution.

basic media the $\nu(\text{C-S})_G$ band at 653 and 643 cm^{-1} , respectively, has a higher intensity than the $\nu(\text{C-S})_T$ band at 704 and 703 cm^{-1} , respectively.

The predominance of the G band therefore indicates the structure of alkyl chains near the Au surface is disordered. This is consistent with the broad reductive desorption peak observed in the electrochemical measurements (Figure 1, curve c). The intensities of the $\nu(\text{C-S})_G$ and $\nu(\text{C-S})_T$ bands do not show major changes in the acidic and basic electrolytes, indicating that the structure of the alkyl chains closer to the metal surface is equally disordered.

The bands at 876 (874) cm^{-1} and 972 (968) cm^{-1} after immersion of the mixed monolayer in acidic (basic) solutions can be assigned to $\nu(\text{C-COOH})$ and $\nu(\text{C-COO}^-)$ vibrational modes.^{30,31} However, the CH_2 rocking mode is observed at 869 cm^{-1} .³² Figure 5a shows that only the band assigned to $\nu(\text{C-COO}^-)$ is sensitive to the pH changes, and its intensity increases upon immersion in the basic solution.

The structure of the alkyl chains further away from the metal surface can be monitored by the $\nu(\text{C}-\text{C})_{\text{G}}$ and $\nu(\text{C}-\text{C})_{\text{T}}$ bands. In the case of a MUA monolayer on silver these bands have been observed at 1029 and 1099 cm^{-1} , respectively,³⁰ and in the case of a propanethiol monolayer on silver, the bands at 1033 and 1088 have been assigned to $\nu(\text{C}-\text{C})_{\text{G}}$ and $\nu(\text{C}-\text{C})_{\text{T}}$ modes, respectively.³¹ Figure 5a shows that after immersion in the acidic solution low-intensity bands are observed at 1036 and 1051 cm^{-1} . When the same sample is immersed in the alkaline solution, a lower intensity band is observed at 1035 cm^{-1} , no band is observed at around 1050 cm^{-1} , and a sharp and well-defined band appears at 1081 cm^{-1} . On the basis of previous assignments, we therefore identify the bands at 1036 cm^{-1} (acidic solution) and 1035 cm^{-1} (basic solution) with the gauche $\nu(\text{C}-\text{C})$ mode, whereas the appearance of the band at 1081 cm^{-1} in the alkaline solution is attributed to the trans $\nu(\text{C}-\text{C})$ mode. These results imply there is an ordering of the alkyl chains upon immersion of the mixed monolayer in the alkaline solution. Such an ordering is expected as the alkaline media breaks intralayer hydrogen-bond interactions between $-\text{COOH}$ groups as a consequence of the deprotonation of the carboxyl group. The SERS results are thus in agreement with the ellipsometric measurements consistent with the unfolding of MUA molecules after immersion in the alkaline electrolyte.

Figure 5b shows the degree of reproducibility of the Raman measurements. The mixed monolayer in Figure 5b is different from that in Figure 5a, and the spectra were taken after immersion in the acidic and basic solutions. The spectra are very reproducible, and the peak at 1081 cm^{-1} is consistently observed after immersion in the alkaline electrolyte. We point out that this feature was only observed for the mixed monolayers. Figure 5b also shows the spectrum for a freshly prepared MUA monolayer. We obtained the same spectrum after immersing the MUA monolayer in the alkaline or acid solution, and the sharp peak at 1081 was never observed. This observation is consistent with a previous Raman study of MUA on silver in which the intensity of the band corresponding to $\nu_{\text{s}}(\text{COO})$ was found to be independent of pH.³⁰

DFT calculations were performed to gain a deeper insight into the structure of the mixed monolayer. As electrochemistry shows that the surface coverage of the mixed layer is 0.26, we built a $3 \times 4\sqrt{3}$ unit cell (24 Au atoms per layer) with five MPA molecules and one MUA molecule having a surface coverage of $6/24 = 0.25$. Figure 6 shows side and top views of the most stable structure found. The MUA molecule is folded and lies down on the surface with its carboxylic group matching that of an MPA molecule (Figure 6a). The $-\text{COOH}$ groups are on the same plane with a short hydrogen-bond distance of 1.6 Å (Figure 6b). The arrow in Figure 6a shows the average ellipsometric thickness of 7.3 Å measured after immersion of the monolayer in the acidic solution (Figure 2). Therefore, the geometry of the most stable structure found is in very good agreement with the ellipsometric thickness. If one performs a calculation with four MPA molecules and two MUA molecules (thus keeping the surface coverage of 0.25), the lack of free space on the surface avoids the alkyl chains of MUA to lie flat on the surface, and thus the alkyl chains adopt other configurations to form MUA–MPA hydrogen bonds, which result in a higher thickness. Therefore, only the surface MUA:MPA ratio of 1:5 is compatible with the ellipsometric thickness and the surface coverage obtained from electrochemistry.

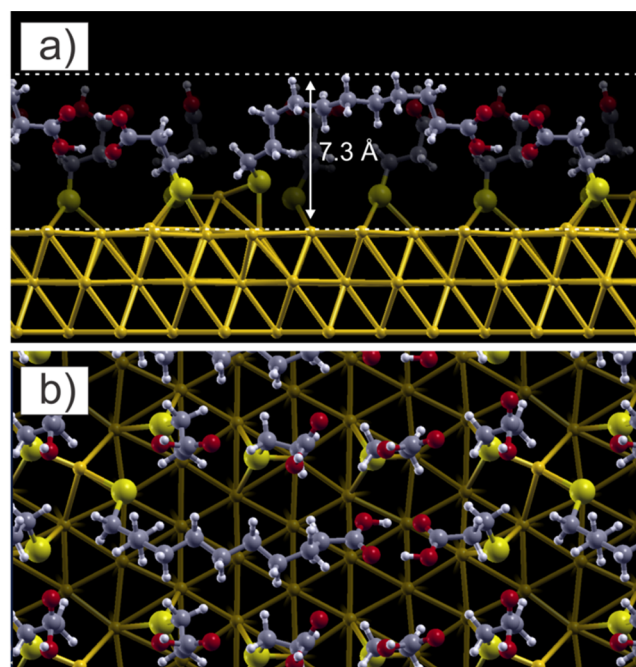


Figure 6. Equilibrium geometries of side (a) and top (b) views of interacting MUA–MPA molecules on Au(111). The arrow in (a) indicates the thickness of 7.3 Å obtained from ellipsometry after immersion in acidic medium. Calculations performed in a $3 \times 4\sqrt{3}$ unit cell.

CONCLUSIONS

Homogeneous mixed self-assembled monolayers of MPA and MUA allow a reproducible and simple procedure for building a reversible pH-sensitive supramolecular switch on the Au(111) surface. The conformational changes upon protonation and deprotonation of the $-\text{COOH}$ terminal groups were accurately measured by ellipsometry. The conformational changes of the alkyl chains were also confirmed by contact angle and SERS measurements. DFT calculations showed that the ellipsometric thickness obtained in acidic pHs corresponds to a structure in which the alkyl chain of MUA is bent toward that of MPA in order to favor the formation of the strong hydrogen bonds between the adjacent carboxylic groups.

The basic principle behind the supramolecular switch described in this work is the hydrogen bonding between the terminal groups. Therefore, the building of the switch has two requirements: (a) the formation of a homogeneous mixed monolayer with flexible molecules of different chain lengths and (b) terminal groups capable of forming strong hydrogen-bond interactions. These general requirements can be applied for building many other pH-sensitive switches on surfaces. In this work we have used carboxylic end groups, but sulfonic and phosphonic end groups, as well as mixtures of amine and acidic terminal groups, should also work equally well.

In the case of metals where the thiol anchor group diffuses along the surface during the self-assembly process, the phase separation between molecules of very different chain lengths may hinder the formation of the switch. This could be in principle avoided by decreasing the immersion time in the forming solution in order to obtain a homogeneous mixture. However, this will not be a problem for other substrates such as silicon on which the organic molecules are fixed to the surface by strong covalent Si–C bonds. In the case of the hydrogenated silicon surface, for example, the hydrosilylation reaction³³ of

mixtures of 1-alkenes with alkyl chains of different lengths and terminated by the $-COOH$ group should also lead to the formation of a pH-sensitive switch.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b03807.

Ellipsometric modeling and experimental Δ and Ψ angles; electrochemical measurements of samples prepared with ethanolic solutions of different MUA:MPA ratios (PDF)

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Notes

The authors declare no competing financial interest.

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