Self-Assembled Monolayers

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Isophthalic Acid: A Basis for Highly Ordered Monolayers**

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The functionalization and patterning of surfaces frequently relies on molecular self-assembly.[1–4] For classification of this phenomenon molecular orientation, that is, adsorption of molecules parallel to the surface or with a perpendicular orientation, might serve as criterion. An example of the first category, porous two-dimensional supramolecular networks rely on noncovalent intermolecular interactions, with hydrogen bonding, metal–ligand bonding, and van der Waals interactions involved in the structure-determining synthons. Systems of the second category are characterized by dense molecular packing in which enthalpically favored chemisorption of molecules is the major driving force for the maximization of coverage. Self-assembled monolayers (SAMs) of thiols, the most prominent type of compounds for the modification of metal surfaces, belong to this category.

Which orientation is adopted is determined by the balance of molecule–substrate and intermolecular interactions. This is highlighted by aromatic carboxylic acids on graphite or metallic substrates which exhibit a variable behavior depending on the state of the carboxy groups. The neutral COOH moiety with its propensity to dimerize through hydrogen bonds always gives rise to in-plane structures like the honeycomb network of trimesic acid,[5] zig-zag chains of isophthalic acid,[6–8] and Kagomé structures of tetracarboxylic acids.[9–12] Whereas in-plane structures are also commonly formed by deprotonated carboxylic acid groups through formation of metal–organic coordination structures and networks,[2,13–17] an upright orientation can also be realized on metal surfaces as a consequence of the strong interactions between the substrate and the carboxylate anion. Benzoic acid,[18–21] terephthalic acid,[22] trimesic acid,[13,15] and trimellitic acid[23] were investigated on a variety of Cu crystal faces in ultrahigh vacuum (UHV). While a strongly interacting substrate such as copper is required in UHV to realize an upright configuration, this can also be achieved on less strongly interacting surfaces such as gold at an electrified solid–liquid interface.[8,24–26]

The use of the carboxylic acid moiety as an anchoring head group to generate ordered monolayers of upright standing molecules on metal surfaces is an appealing alternative to the intensively exploited thiol SAMs for the functionalization of surfaces. Compatibility of carboxylic acid compounds with chemical synthesis routes, easier introduction of functional groups, and easier handling are reasons why carboxylic acid based molecules are of interest for the design of SAMs. For the preparation of carboxylic acid based SAMs there is, on the one hand, the option of a UHV-based preparation which, however, imposes limitations on the choice of molecules and equipment required. Solution-based preparation, on the other hand, offers simplicity and flexibility, but presents another dilemma. Strongly interacting substrates like copper are prone to oxidation and contamination which impedes SAM formation, whereas gold, a substrate easy to handle, does not interact strongly enough with carboxylic acids. In terms of Pearson's concept there is a mismatch between gold as a soft acid and the carboxylate as a hard acid base. An elegant solution has been reported:[27,28] A monolayer of Cu or Ag formed on gold by underpotential deposition (UPD) has a significantly higher resistance against oxidation. SAMs with ionic head groups, for exampls films of *n*-alkanoic acids[28] and alkane phosphonic acids,[27] could thus be formed; however, their structure is not clear on a molecular scale. Building on these studies we demonstrate herein the potential of the isophthalic acid moiety for the formation of highly crystalline SAMs and as a tecton for the design of functionalized SAMs.

The preparation of an isophthalic acid based SAM is outlined in Figure 1a. Starting from a Au(111)/mica substrate, copper is deposited positive of the Nernst potential in the UPD range (step 1). Rather than depositing a full monolayer at a potential close to 0 V (referenced against Cu/Cu^{2+}) we chose the more positive value of 150 mV, at which a highly ordered structure is obtained in sulfate-containing electrolytes.[29] Easily imaged in air by STM (Figure 1b), a $(\sqrt{3} \times \sqrt{3})$ structure is seen which reflects the arrangement of the sulfate anions. They are centered above the pores of a Cu honeycomb structure; in other words, the Cu coverage corresponds to 2/3 of a monolayer. In step 2 the UPD-modified Cu/Au substrate is then immersed in a solution of either **1** (isophthalic acid, IPA) or **2** (trimesic acid, TMA), and the structure of the sample changes upon treatment. This is apparent on a large scale in Figure 1c, which shows clear domains with an average size of 600 to 800 nm^2. High-magnification images (Figure 1d,e) reveal structures very different from the $(\sqrt{3} \times \sqrt{3})$ arrangement of the sulfate ions, thus indicating that the sulfate has been displaced by the aromatic carboxylic acids. This is also evidenced by X-ray photoelectron spectroscopy (XPS) where the sulfate peak around 168 eV in the S 2p spectrum of the Cu UPD layer is absent after exposure to IPA or TMA (not shown). Importantly, the two carboxylic acids yield the same surface structure with domain orientations reflecting the symmetry

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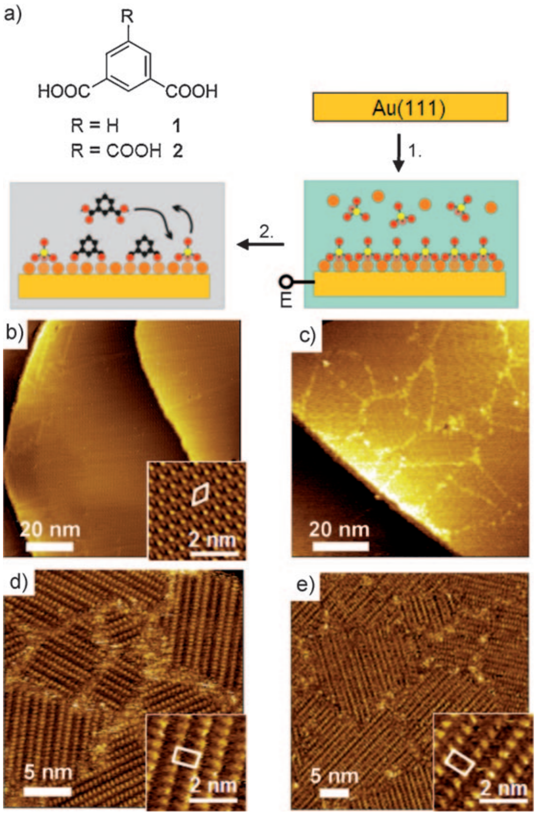

Figure 1. a) Preparation of an isophthalic acid based SAM by Cu UPD from $CuSO_4/H_2SO_4$ (1) followed by adsorption of the carboxylic acid from an aqueous solution (2). STM images of the sulfate-terminated Cu UPD layer (b) and of SAMs of **1** (c,d) and **2** (e). Unit cells of the $(\sqrt{3}\times\sqrt{3})$ Cu UPD sulfate structure (c) and of the $(3\times\sqrt{3})$ structure of the SAMs of **1** and **2** are indicated in the insets of (d) and (e).

of the substrate. With rows running parallel at a distance of approximately 9 Å and protrusions along the rows separated by 5 Å, the structure is described by a $(3\times\sqrt{3})$ unit cell. The most obvious model to explain the common structure for IPA and TMA is to assume that the molecules stand upright with two carboxylic acid groups binding to the substrate as indicated in Figure 1a. TMA would, therefore, constitute a COOH-terminated SAM, whereas IPA would render the surface passive.

This model is corroborated by XPS data shown in Figure 2. The spectra for TMA and IPA display obvious differences: TMA exhibits peaks characteristic of carboxylic acid (≈ 288.9 eV) and carboxylate (≈ 287.5 eV),[15,30] whereas IPA has only the carboxylate signature. The ratio between the carboxylate signal and the C 1s signal from the benzene ring is the same for both molecules, which provides further support that their bonding to the substrate is identical. It is noted that the ratio of carboxylate to ring carbon signals is lower than the 1:3 stoichiometry; this is also in agreement with the model that the carboxylate moieties are beneath the ring and, thus, the respective C 1s signal is attenuated. For the same reason, the signal from the SAM-terminating COOH groups in the TMA SAM is more than half of the carboxylate signal.

The structural identity of TMA and IPA SAMs inferred from XPS and STM data is fully confirmed by mixed layers prepared by substitution of IPA by TMA. As seen from the STM image shown in Figure 3a, a TMA molecule can replace IPA without affecting the molecular packing; in other words, the rows of molecules and the discrete intermolecular distance along the rows are not affected.

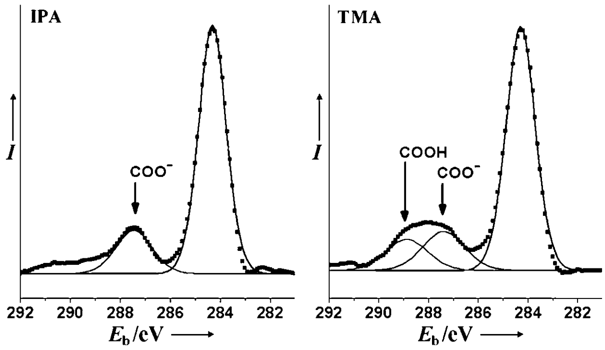

Figure 2. C 1s XP spectra (squares) of SAMs of **1** (IPA, left) and **2** (TMA, right) on UPD Cu modified Au(111)/mica substrate. The solid lines indicate the spectral components obtained from fitting.

The model summarizing all the experimental results is shown in Figure 3b. A crucial feature of this SAM structure is the seamless fit of TMA into the IPA matrix, which consists of rows of molecules running along the $\langle 11\bar{2}\rangle$ directions at a distance of roughly 9 Å and an intrarow separation of the molecules of 5 Å. Another important point is the bipodal anchoring of the IPA/TMA molecules to the substrate which affords a highly rigid structure. Both features suggest that the IPA moiety might serve as a more general basis for a new type of SAM whose structure is much less affected by functionalization compared to monopodal SAMs such as thiols.

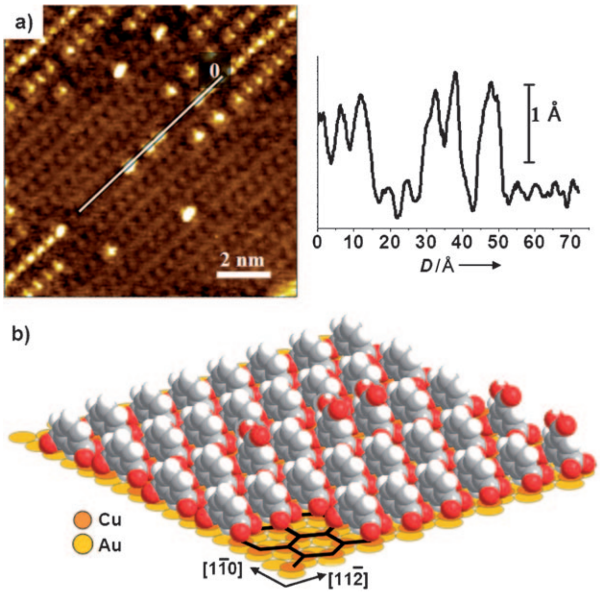

Figure 3. a) STM image (left) of a mixed SAM prepared by substitution of **1** by **2**. Dark and bright protrusions reflect **1** and **2**, respectively. The height profile (right) is along the line indicated in the STM image. b) Structural model of the mixed SAM. Black hexagons indicate the honeycomb structure of the $(\sqrt{3}\times\sqrt{3})$ Cu UPD.

While this model explains all our experimental observations, we would like to stress its tentative character as far as some structural details are concerned. Firstly, it is assumed that the honeycomb structure remains unchanged upon exchange of the sulfate by IPA/TMA. Since we have no direct information on the structure of the Cu UPD layer, this is concluded from the fact that a massive restructuring of the Cu UPD layer to a more compact structure would create areas of bare gold with IPA/TMA molecules adsorbing in a flat lying geometry. Nevertheless, the observed slight increase of the width of the Cu 2p line at 932 eV from 1.13 eV FWHM for the sulfate structure to 1.23 eV for the IPA layer might indicate some relaxation of the Cu structure. Secondly, the exact orientation of the molecules remains to be elucidated. While the presence of the free COOH group in the case of TMA clearly demonstrates an upright orientation, the intrarow separation of the molecules allows for a tilt of the molecules. Furthermore, an alignment of the plane of the aromatic ring parallel to the $\langle 1\bar{1}0 \rangle$ directions is just one possibility of polar orientation. Thirdly, the orientation of the plane of the carboxylate units nearly parallel to the surface is proposed in our model, which is in accordance with other structural models[13] and the fact that carboxylic acids bind to copper in a bidentate fashion.[28,31] However, in contrast to Cu(100) where two mixed adsorption geometries involving one and two carboxyl groups of TMA were suggested to explain striped features,[13] the present structure is based on one adsorption geometry. The monopodal adsorption geometry reported for trimellitic acid on Cu(100) also differs from the present structure although it has the same structural motiv as IPA.[23] Similarly, in the case of a positively charged Au(111) electrode in an electrochemical environment, IPA and TMA form monolayers with a monopodal adsorption geometry of the upright standing molecules.[26] Furthermore, their packing densities are different.[8,24]

The well-defined structure and upright molecular orientation of the IPA moieties make this type of SAM interesting for surface functionalization since substituents can be introduced at positions 4–6 of the aromatic ring. As a first demonstration we exploited TMA in which the COOH group in 5-position can be used to coordinate metal ions and, therefore, to grow metal–organic coordination polymers. By using a layer-by-layer growth technique which has been employed to grow metal–organic coordination layers[32] and, more recently, layers of oriented metal–organic frameworks (MOFs),[33] thin films can be generated in a stepwise fashion by alternating steps of metal coordination and complexation of the metal ions by organic ligands. In this way, a thin film pattern consisting of a Cu/TMA metal–organic coordination polymer (MOCP) was grown on a TMA SAM as documented by Figure 4. As described in the Experimental Section, two different types of SAMs are combined in a pattern generated by microcontact printing.[4] Lines of a TMA SAM alternating with lines of an alkanethiol SAM serve as template for the selective growth of the coordination layer. As demonstrated by the atomic force microscope (AFM) image and the corresponding line profile, the film grows selectively on the COOH-terminated TMA SAM but not in areas of the CH_3-terminated alkanethiol. It is noted that the film growth requires the TMA SAM; that is, no coordination polymer grows on clean gold surfaces.

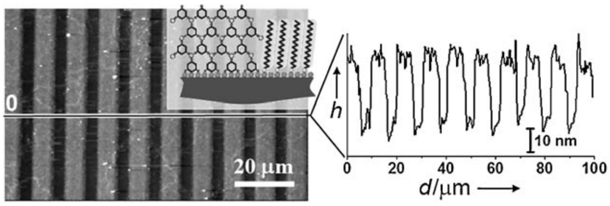

Figure 4. AFM image (left) and height profile (right) of a thin-film pattern of a metal–organic coordination polymer grown from TMA and $Cu(OAc)_2$ by application of 25 cycles of a layer-by-layer growth technique. A SAM pattern consisting of alternating lines of octadecanethiol and TMA acts as a template; the coordination polymer grows only on the TMA SAM. The inset shows a molecular model of the patterned film.

While the growth of a coordination polymer is just one example demonstrating that IPA-based SAMs can be used to functionalize surfaces, we believe that this type of SAM has a significantly wider scope for the design of functionalized organic surfaces and studies of chemical and physical phenomena at the nanoscale as it features a modular design and well-defined dimensions. IPA represents the basic unit, and its bipodal anchoring on the Cu-modified Au substrate yields a highly crystalline row-type arrangement of the molecules, that is, precisely defined intermolecular distances of upright standing molecules. Notably, the area of 45 Å^2 per molecule is significantly larger than in SAMs with a single anchoring group such as thiols where values are in the range of 21–35 Å^2 per molecular depending on the thiol.[34] This, in combination with the identical structure of TMA and IPA SAMs, suggests that the carboxylate moieties determine the packing and, therefore, ensure that the film structure, similar to the case of triazatriangulenium ions[35] is independent of the substituent as long as its cross section does not exceed the footprint of the anchor moieties. For mixed SAMs, in which derivatized IPA molecules are incorporated into an IPA matrix, the substituent sticks out of the IPA layer and sterically more demanding moieties could, thus, maintain their functionality. A rotational degree of freedom could be introduced by the attachment of a phenylenethynylene moiety in the 5-position of IPA which would represent an interesting step towards control of molecular mechanical systems. While it is not yet known how to arrange the functional molecules in an inert IPA matrix in an exactly controllable way, the precisely defined dimensions of the IPA matrix offer, on a statistical basis, the opportunity to study phenomena such as the influence of steric factors on reactivity or coupling between molecules.

Experimental Section

Isophthalic acid (99%, Sigma–Aldrich), trimesic acid (98%, Alfa Aesar), $CuSO_4$ (99.999%, Sigma–Aldrich), $Cu(OAc)_2$ (99.999%, Sigma–Aldrich), octadecanethiol (>95%, Fluka), and ethanol (AnalaR Normapur) were used as received. Au substrates (mica slides with an 300 nm epitaxial Au(111) layer, Georg Albert PVD, Heidelberg, Germany) were flame-annealed prior to immersion into 10 mm $CuSO_4$/50 mm H_2SO_4 solutions for Cu UPD, which was performed by holding the substrate at +150 mV (vs. Cu/Cu^{2+} reference) for 60 s. The UPD Cu/Au(111)/mica sample was then immersed for 10 min at room temperature in aqueous 1 mm solutions of IPA or TMA. Mixed layers as shown in Figure 3 were prepared by immersion of an IPA SAM into a 5 mm aqueous solution of TMA at room temperature for 30–40 min.

For the preparation of the patterned SAM, a uniform TMA SAM was patterned with octadecanethiol by microcontact printing. Using a poly(dimethylsiloxane) stamp (soaked in 1 mm MC18 solution and dried with nitrogen before printing) the TMA was displaced by the thiol in areas of contact between stamp and sample. A contact time of 60 s was sufficient to render the surface passive. Thin films were prepared by the layer-by-layer technique.[33] The sample with the patterned SAM was exposed to 25 cycles of immersion into a 1 mm copper acetate $Cu(OAc)_2$ solution in EtOH for 30 min followed by immersion into a 1 mm solution of TMA in EtOH for another 30 min. The sample was carefully rinsed with ethanol and dried in a nitrogen stream when it was transferred between $Cu(OAc)_2$ and TMA solutions.

STM and AFM measurements were performed with either a Pico SPM or a PicoPlus SPM system (Molecular Imaging, USA). Typical STM parameters were 500 mV (tip positive) and 10–50 pA. AFM images were acquired in contact mode using silicon nitride probes (Veeco Probes, USA).

XPS analysis was performed with a Thermo Scientific Sigma Probe system using monochromatized $Al_{K\alpha}$ radiation. The photoelectrons were detected at an angle of 37° with respect to the surface plane.

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