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Monolayer and aggregate formation of a modified phthalocyanine on mica determined by a delicate balance of surface interactions

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ABSTRACT

An ordered layer of a phthalocyanine modified with ether tails can be formed on muscovite mica if removed from solution and dried. This ordered layer forms on potassium terminated as well as on sodium terminated mica, but not on a hydronium terminated surface. The molecules lie flat on the surface, as shown by AFM and X-ray diffraction, giving a layer thickness of approximately 1 nm. In solution, however, no in-plane ordering exists. The material is attracted to the substrate surface but instead of ordering, it aggregates in a liquid-like mobile fashion. This is likely caused by the fact that the water present in solution has a stronger interaction with the potassium ions on the mica surface than with the ether tails of the phthalocyanine.

1. Introduction

Technology aims for smaller and smaller structures. In this process surfaces and surface structures become increasingly important. This feeds the need for knowledge about surface processes and deposition methods. Different parameters have to be taken into account for nanoscale structures opposed to microscale films. Another trend is the search for organic substitutes for conventional electronics [1,2], in order to reduce costs. The combination of these trends makes it relevant to study the formation of (molecular) monolayers [3–7], not only on electrically conducting surfaces, but also on insulating surfaces. Muscovite mica is a well known example [8–10], commonly used because of its atomically flat surface after cleavage [11]. The ionic nature of this surface can, however, be a drawback, which can be circumvented by modification of the surface [12,13]. The surface ions, on the other hand, can also be used to initiate binding and ordering of large molecules on the surface, creating a smooth and functionalized surface.

Phthalocyanines show interesting organic electronic properties [14,15], having potential in solar cell and sensor applications. Therefore, monolayers of this material on various surfaces received considerable interest [16,17]. Recently, π-conjugated 2D polymeric monolayers of this molecule with promising magnetic properties have been deposited on crystalline substrates [18,19]. In our study we use a zinc (II) phthalocyanine modified with eight triethylene gycol (ether) tails (EPc) to create affinity with the potassium ions on the mica surface. In this case two tails together can mimic a crown ether entangling the potassium ions. The ether tails were chosen instead of actual crown ethers to create flexibility and mobility of the molecules. We have investigated the interaction of this phthalocyanine with the mica surface and the growth of mono and multilayers using (liquid) Atomic Force Microscopy (AFM) and Surface X-ray Diffraction (SXRD).

2. Experimental

2.1. Sample preparation

Muscovite mica has a layered crystal structure, which is easily cleaved along the (001) plane, giving a charged (001) surface with potassium ions on top (Fig. 1a). Muscovite mica (V1 quality from S&J Trading) was cleaved using scotch tape before each experiment. Solutions were prepared using ethanol (Merck, absolute for analysis) and purified water (Millipore) with a resistance of 18.2 MΩ/cm and total organic content lower than 4 ppb. The etherified phthalocyanine (EPc, chemical formula $C_{104}H_{136}N_{32}O_{24}Zn$) was synthesized in house (for details, see Supporting information). Eight ether tails were attached to the Zn phthalocyanine core using a click-chemistry method [20]. The structure of the EPc molecule is shown in Fig. 1b.

Mono and multilayers of EPc were deposited on freshly cleaved muscovite mica substrates from ethanol solutions with an EPc concentration ranging from 10^{-4} M to 10^{-7} M. All experiments were carried out at room temperature. Ethanol/water mixtures used for investigating the influence of water on the deposition process contained comparable

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amounts of EPc. The cleaved mica was incubated in the solution for a period of time ranging from seconds to days. Two methods were used for removing the sample from the solution. In the first method the mica plate was removed slowly, keeping it in contact with the edge of the container, allowing most of the fluid to flow off the substrate and then dried horizontally in nitrogen flow. In the second method the mica plate was placed in a holder in which the mica was kept in a vertical position and removed slowly from the solution (in 5 to 10 s) and then dried vertically for 2 to 3 min using a nitrogen flow. Finally, the sample was dried horizontally for at least an hour using a nitrogen flow. The second method gives more reproducible results. Compared to the horizontal approach, the liquid surface film left after removal of the specimen flows downward in a more controlled, “smooth” way assisted by gravity. This reduces rupture of the liquid layer and thus the development of unwanted dewetting patterns [21]. All samples were investigated the same day as they were prepared.

SXRD was carried out on dry samples and in solution. Dry samples were prepared by placing a large piece of mica, approximately $5 \times 5\ \mathrm{cm}^2$ in size, in a 10^{-5} M EPc solution in ethanol for 5 min. After removing, it was allowed to dry vertically in air keeping one edge in contact with a tissue. Subsequently, it was mounted on a plateau in a closed cell using double sided tape. Nitrogen was continuously flowing through this cell during the experiment in order to maintain a water-free environment. For in situ experiments again a $5 \times 5\ \mathrm{cm}^2$ piece of mica was placed in a 10^{-5} M EPc solution in ethanol for 5 min. Then the mica sample was removed from solution and was directly covered with mylar foil (13 μm thickness from Lebow company). In this way a thin film of ethanol, containing EPc, was created on the mica surface. Some ethanol was put in the closed cell in order to have an equilibrium vapor pressure and thereby to prevent drying in of the film.

Surface ions were exchanged following procedures described by Osman et al. [22] by leaving a cleaved mica sample in a 4×10^{-2} M solution of sodium chloride (Merck, pro analysis) in water to obtain a sodium covered surface. A 10^{-4} M HCl (diluted from concentrated HCl, Baker, analyzed 37%–38%) solution in ethanol was used to obtain a hydronium ion covered surface. The samples were kept in solution for several hours, subsequently washed with ethanol and dried in a nitrogen flow.

2.2. Characterization

Ex situ AFM measurements were performed using a Dimension D3100 AFM in tapping mode at room temperature and approximate humidity of 50% using NSG-10 tips. In situ AFM measurements were done on a Nanoscope 4 multimode instrument using SNL-10 tips in a liquid cell closed with a plastic ring.

Surface X-ray diffraction measurements were performed at the ID3 beamline at the European Synchrotron Radiation Facility (ESRF) using a *z*-axis [23] diffractometer fitted with a Medipix 256×256 pixel 2D detector. X-rays with an energy of 24 keV ($\lambda = 0.517$ Å) were used. Crystal truncation rods (CTR's) and specular reflectivity were measured using the stationary geometry [24], allowing very rapid data collection. The substrates were of such good quality, that no rocking scans were needed to measure a reflection. Integrated intensities were derived using a MATLAB (MathWorks) script, written for this purpose. Structure factors were derived after applying the standard correction factors [24]. Fitting of the data to structure models was done using the ROD software [25]. The diffraction indices h and k denote the in-plane momentum transfer, while l is the diffraction index along the perpendicular direction. For the bulk model of muscovite mica atom positions from the ICDS database were used [26]. Unit cell dimensions of the monoclinic muscovite mica structure were found to be: $a = 5.202$ Å, $b = 9.023$ Å, $c = 20.002$ Å, $\alpha = \gamma = 90°$, $\beta = 95.81°$.

The {001} cleavage plane of mica, which is the surface of interest, can be located at two different heights in the unit cell, corresponding to two different planes with K^+ ions, see Fig. 1a. These two planes are symmetry related by the c-glide plane of the C2/c spacegroup. Although mica surfaces are smooth without steps over very large areas, it is to be expected that in our measurement geometry equal areas of the two different surface terminations are irradiated. To account for this, each structure factor is calculated as the incoherent average of the value for the two domains [27].

3. Results and discussion

3.1. Layer structures

When the substrate is dried horizontally directly after removal from solution, no full monolayers are formed, but a multilayer structure is created showing dewetting patterns (shown in Fig. 2). In this case we find that new layers start to grow before the first layer is fully closed. The results vary significantly depending on the location on the mica surface. The first layer has smooth features, but subsequent layers show more pronounced dewetting patterns and are rougher.

To improve reproducibility the vertical drying method described in the Experimental section was used for all other ex situ experiments. Using this method it is possible to create a smooth monolayer on the surface from a 10^{-5} M solution of EPc. With increasing residence time

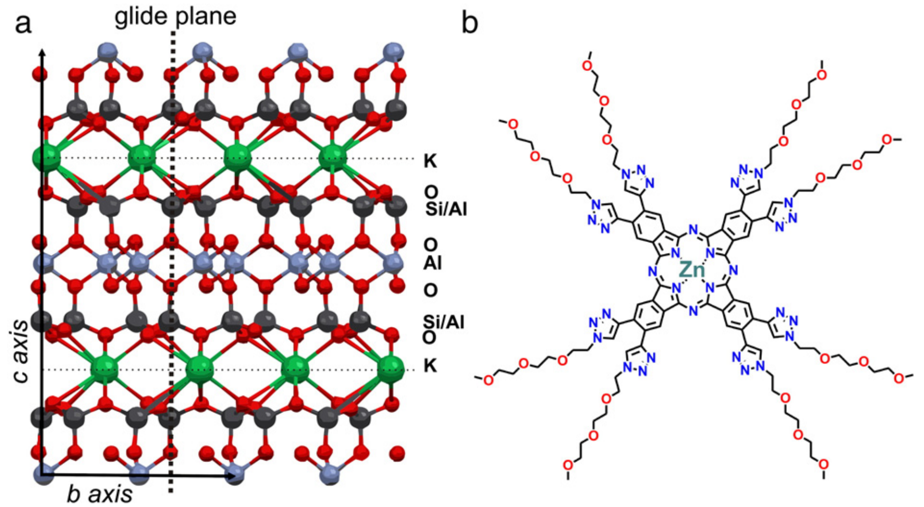

Fig. 1. a) Structure of muscovite mica viewed along the a axis. The c-glide plane is illustrated by the thick dotted line and the two symmetry related cleavage planes are illustrated by the thin dotted lines; b) structure of the Zn phthalocyanine with ether tails (EPc).