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Ordered Growth of Substituted Phthalocyanine Thin Films: Hexadecafluorophthalocyaninatozinc on Alkali Halide (100) and Microstructured Si Surfaces

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Physical vapor deposition of hexadecafluorophthalocyaninatozinc ($F_{16}PcZn$) is performed under UHV conditions from monolayer coverages to an average thickness of about 20 nm on the (100) surfaces of NaCl, KCl, and KBr and on quartz glass as well as on microstructured interdigitated electrode arrays on amorphous SiO_2. UV−vis absorption spectroscopy indicates stacks of cofacial parallel molecules for thin films on SiO_2 and NaCl, whereas a component typical for a head-to-tail arrangement of molecules is detected on KCl and KBr. Atomic force microscopy shows well-defined crystals oriented in a defined azimuth angle relative to the substrate lattice on KCl and KBr, indicating a growth in molecular square lattices parallel to the substrate surface which is confirmed by molecular mechanics and periodic surface potential calculations. Plateaus of molecules predominantly standing upright on the surface are seen for the films on NaCl and SiO_2 which is confirmed by the relative intensity of optical absorptions and by the electrical conductivity changes observed during growth on SiO_2. The temperature dependence of the electrical conductivity of films on SiO_2 yields an increase of the thermal activation energy around 200 °C corresponding to a loss in spectral fine structure as reported earlier [*J. Phys. Chem. B* **1999**, *103*, 3078]. A clear correlation is seen between film structure and electrical as well as optical properties of molecular semiconductor thin films.

1. Introduction

Thin films of phthalocyanines (Pc) and related molecular semiconductors are of considerable interest in fundamental as well as applied research due to their electrical and optical properties. Chemical modification of the core system provides a high versatility in molecule structure and hence intermolecular interactions. The film structure as well as electrical and optical characteristics can be adjusted in a rather wide range. Perfluorinated phthalocyanines ($F_{16}Pc$) turned out to be an interesting example to study such influence on the position of molecular energy levels as well as solid-state structure. A cofacial parallel orientation of molecules and layered growth, e.g., could be obtained for $F_{16}Pc$ in thin films on SiO_2.[1−4] Structural variations in $F_{16}Pc$ thin films can be expected to lead to significant changes in electrical properties as already observed for films of unsubstituted phthalocyanines in a series of time-of-flight measurements which revealed changes in defect and excess electron mobilities dependent on temperature-induced structural reorganizations in the films detected by changes in optical absorption spectra.[5−7] The high electronegativity of the F atoms leads to a stabilization of the frontier orbitals as seen by shifts in the redox potentials in solution and in thin films[8] and by ultraviolet photoelectron spectroscopy (UPS).[9,10] This ease of reduction leads to n-type doping of films during film preparation by physical vapor deposition even under UHV conditions.[11,12] The decrease in conductivity following exposure to air is explained by compensation of this n-doping by oxygen[4,11−13] while the mobility of

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charge carriers was found to be constant during this change.[2]

Single-crystalline substrates offer a regular structure which was found to influence the growth of molecular materials considerably.[14] Commensurate or coincident lattices of crystalline molecular thin films can be formed and were found in many examples of Pc and related materials.[15] Alkali halide surfaces are most suitable to provide a well-ordered optically transparent substrate. Epitaxial relationships could be established in the past for Pc and related molecules. Especially the optical absorption properties are changed considerably by the intermolecular orientation and hence chromophore coupling.[16−19]

In the present study, thin films of $F_{16}PcZn$ are prepared on amorphous SiO_2 (quartz glass) and on well-ordered NaCl, KCl, and KBr (100) surfaces and studied by optical absorption and atomic force microscopy. Chromophore coupling is analyzed in a dipole model and intermolecular orientations as well as morphology of films are discussed as dependent on substrate, deposition conditions, and film thickness. The electrical conductivity during film growth on amorphous SiO_2 is monitored in situ as dependent on film thickness and sample temperature by use of a microstructured interdigitated metal electrode array (IDE) prepared on a Si substrate. The growth mode of films, and the temperature dependence of intermolecular interactions are discussed in detail.

2. Experimental Section

$F_{16}PcZn$ was synthesized by heating a 4:1 mixture of sublimed 3,4,5,6-tetrafluorophthalo-1,2-dinitrile (Aldrich) and zinc acetate (Aldrich) in a vacuum-sealed glass tube to 180 °C. The dark blue reaction products were treated in a Soxhlet apparatus with water and light petroleum (bp 140 °C) to remove remaining reactants and possible side products. The products were then dried before the materials were sublimed in high vacuum and characterized by DCI-MS.

Alkali halide crystals (Horiba Seisakusho) were freshly cleaved prior to each experiment and stored under vacuum for the minimum time required to establish UHV conditions (10^{-8} Pa) in the deposition and analyzing chamber. $F_{16}PcZn$ was then evaporated from cryo-shielded (liquid N_2) quartz Knudsen cells at 30-cm distance from the substrate which was kept at about 30 °C. The deposition was monitored by the frequency change of a quartz resonator calibrated by ellipsometry performed at PcVO films. The composition of the gas phase during heat treatment of films is monitored by use of a Balzers quadrupole mass spectrometer Prisma QMS 200 M3. UV−vis absorption spectra were measured in transmission of each film in the single-beam mode of a Hitachi U-4000 high precision spectrometer after the films were taken out of vacuum. AFM analysis was carried out in tapping mode with a Nanoscope III (Digital Instruments) using silicon tips on a standard TM cantilever. Coincident or commensurate orientations of the $F_{16}PcZn$ layer with respect to the KBr substrate were calculated by use of the EpiCalc routine provided by the group of M. Ward, University of Minnesota. It calculates the relative periodicity of lattices at different relative parallel rotations, allowing a discussion of epitaxial relationships based on commensurability or "point-on-line coincidence".[20,21] Molecular mechanics calculations were performed using the mm^+ force field[13] as implemented in Hyperchem (Hypercube Inc.).

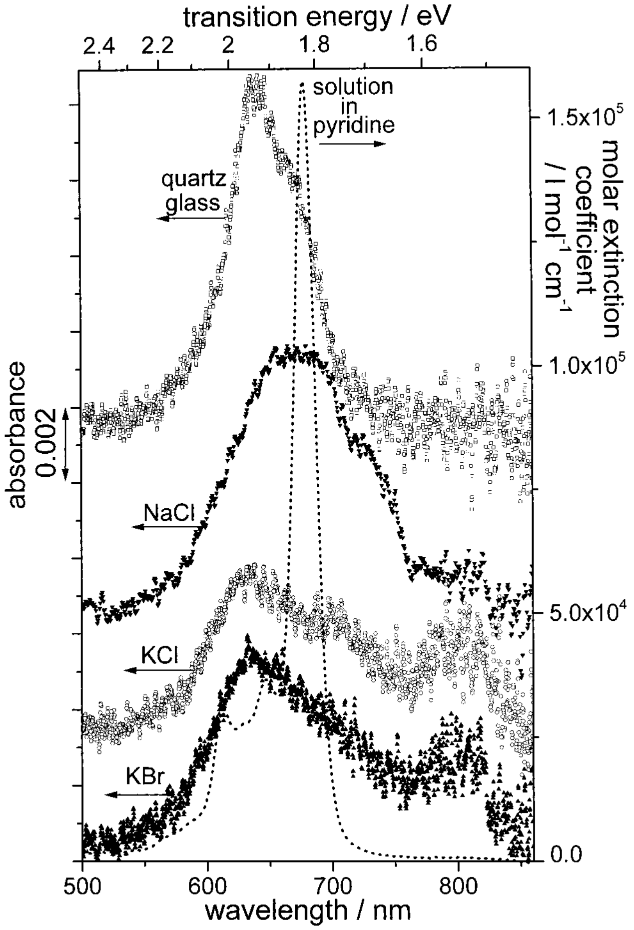

Figure 1. UV−vis absorption spectra observed in transmission of 0.7-nm thin films of $F_{16}PcZn$ on the substrates as indicated. A solution spectrum as obtained in pyridine is added (dashed line) to indicate absorption without any chromophore coupling.

As a substrate for the conductivity measurements microelectrode arrays of gold electrodes at a spacing of 2 μm on a Si substrate with an amorphous SiO_2 insulating layer were used. A polycrystalline silicon resistive heating layer and a gold resistant sheet for temperature measurements (calibrated by IR emission of test structures or attached thermocouples) are integrated into the structure. A schematic representation is included in Figure 5, details of the substrates and their preparation are described elsewhere.[22]

3. Results

3.1. UV−Vis Absorption. Analysis of ultrathin films of an average film thickness corresponding to about a monolayer (0.7 nm) of $F_{16}PcZn$ on quartz glass and the surfaces (100) of the alkali halides NaCl, KCl and KBr are shown in Figure 1 as compared to a solution

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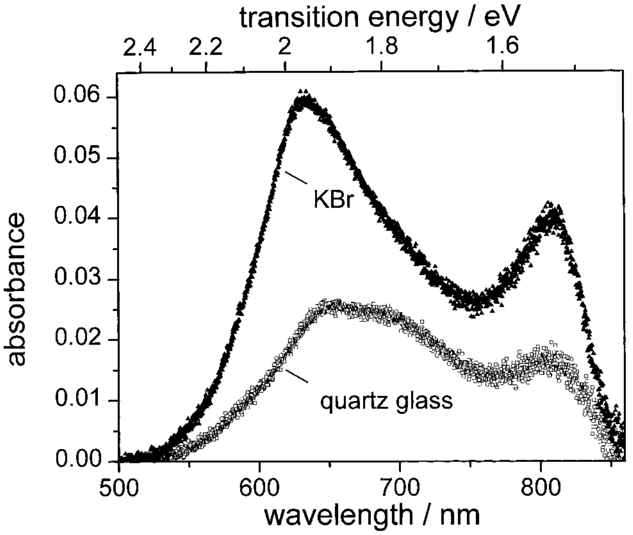

Figure 2. UV−vis absorption spectra of 18-nm films of F_{16}PcZn on the KBr (100) and quartz glass as indicated.

spectrum in pyridine. The films were prepared during the same deposition which defines exactly the same film thickness on all substrates. Clear differences are observed on the different substrates in the position of the absorptions in the Q-band region, indicating different intermolecular orientation, chromophore coupling, and hence band splitting when compared to a spectrum in solution.[15,16,18,19] The rather narrow absorption band of the film on quartz glass shifted to higher energy (640 nm) points toward a cofacial parallel arrangement of chromophores.[3] On NaCl, this absorption is present also, but another band is observed at 690 nm close to the absorption in solution (678 nm) speaking for a high extent of rather weak and ill-defined interactions and hence an amorphous growth. On KCl and KBr, on the other hand, already in this initial stage of film growth a band at lower energy (around 800 nm) is seen which is typical for crystalline samples of F_{16}PcZn with the molecules in a still parallel but close to a head-to-tail arrangement of chromophores.[3,19] However, the bands of highest intensity are found at 632 nm, even stronger blue-shifted than for the spectrum on quartz glass.

This spectral characteristic generally becomes dominant for thicker films as shown in Figure 2 for films of 18-nm average film thickness on quartz glass and KBr. Again the films stem from an identical deposition. On quartz glass, the band at 800 nm shows a smaller relative intensity than observed before during growth on heated substrates[3] and the bands at 632 nm and at 680 nm which dominated the spectrum in Figure 1 are still the most intense bands. On KBr, the band assigned to amorphous growth of F_{16}PcZn around 690 nm is of considerably lower intensity and the bands at 632 and 808 nm are clearly dominating the spectrum. The absorbance of the film on KBr when integrated over all energies is more than double that of the film on quartz glass. By assuming a constant sticking coefficient of F_{16}PcZn during deposition on the different substrates at 30 °C, the amount of chromophores present on the substrate is identical and the preferential orientation of molecules relative to the propagation direction of light (perpendicular to the substrate surface) can be discussed. The transition moments of the degenerate transitions in the phthalocyanine Q-band (predominantly $\pi-\pi^*$) both are positioned in the molecular plane.[23] The smaller absorbance for the films on quartz compared to those on KBr speaks for a smaller overlap of the electromagnetic vector of the light and hence a preferential arrangement of molecules parallel to the beam direction and perpendicular to the quartz substrate surface (“standing”), as concluded also earlier from the X-ray diffraction of films[2] and electrical conductivity measurements.[3]

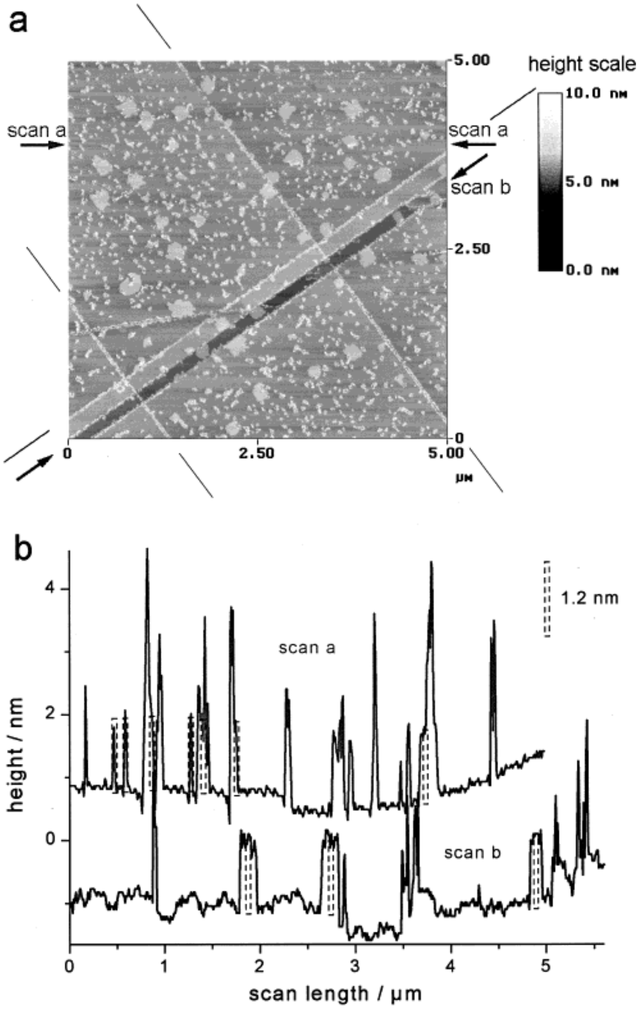

Figure 3. (a) Height image of 0.7-nm F_{16}PcZn on NaCl as obtained by AFM in tapping mode with the substrate [010] and [001] azimuth directions indicated as straight lines and (b) single height scans as marked by the arrows.

3.2. Atomic Force Microscopy. Atomic force microscopy at these films of different film thickness prepared on different substrates can be used to obtain direct insight into the morphology and growth mode of films and some evidence for film structure can be obtained. Figure 3 shows the results of a 0.7-nm thin film of F_{16}PcZn on NaCl (100) with the [010] and [001] azimuth directions of the substrate indicated in the figure and two height profiles of single scans. Two different classes of F_{16}PcZn particles are observed. A rather high concentration of small but high (3 nm) particles is seen in areas of high densities of NaCl steps, especially found in the directions [010] and [001]. Such

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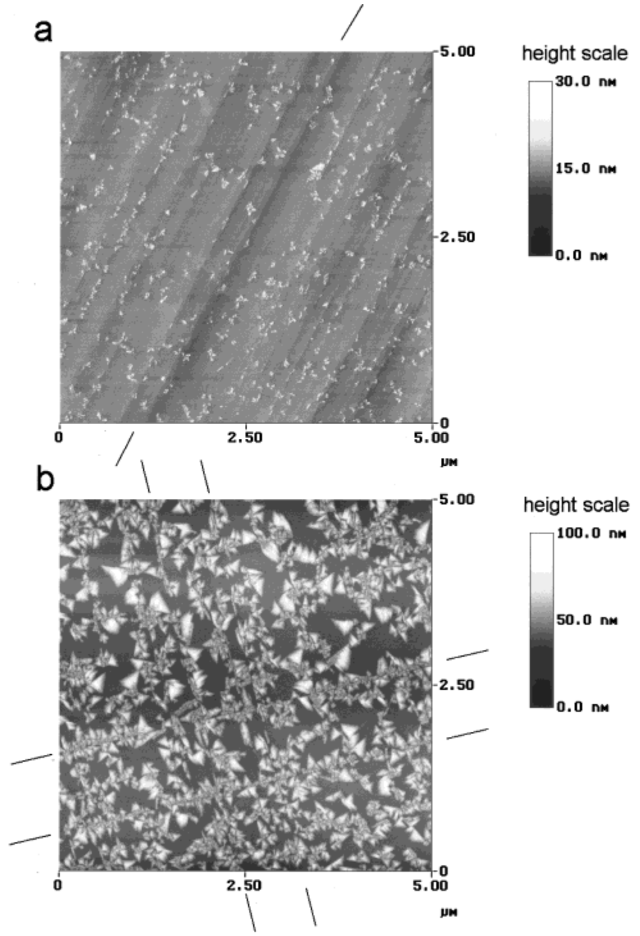

Figure 4. AFM-height image of (a) 0.7-nm and (b) 18-nm (b) F_{16}PcZn on KBr with the substrate [010] and [001] as straight lines.

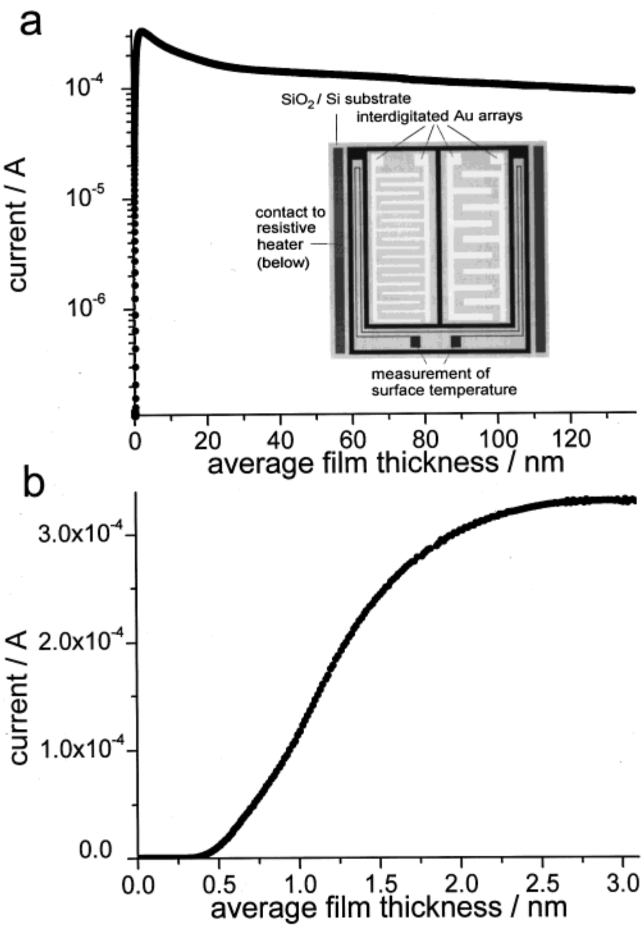

Figure 5. Electrical conductivity measured at 5 kV cm^{-1} during the growth of F_{16}PcZn on a microstructured Si substrate as shown in the inset: (a) over the whole range investigated and (b) focused on the initial growth.

a behavior was also observed earlier under comparable conditions for the growth of tetrapyridotetraazaporphyrins (TPyTAP) on alkali halide surfaces.[19] Also found, however, are rather extended flat areas (up to about 200 nm in length or width) with a uniform thickness of about 1.2 nm. In Figure 4 two films (0.7 and 18 nm average thickness) of F_{16}PcZn on KBr are compared. For the thin film, rather small particles, again growing at step edges of the substrate are observed of approximately spherical geometry as seen in individual line scans (not shown). Some larger ensembles of particles are detected with an orientation of 27° relative to the KBr [010]. The thicker film mainly consists of well-defined particles of triangular shape with edges about 100−300 nm long, rather flat when compared to the spherical particles of the thinner film. One angle within the triangles almost always equals 90°, the two others often are found between 45° and 50°. The triangular objects as a whole have a preferential orientation of 15°−25° of one of their edges relative to KBr [010], with angles around 18° and 22° most frequently found.

3.3. Electrical Characterization. Figure 5 shows the current as measured during deposition of F_{16}PcZn on an interdigitated Au microelectrode array on Si isolated by a thermal oxide layer. Starting from the beginning of the deposition the current increases quickly, then saturates, even decreases and does not show any further increase even at an average thickness of up to 140 nm. In part b of the figure, the initial phase of film growth in the monolayer regime is shown and it is seen that first conductive paths are formed already at about 0.35 nm. The following sigmoidal increase saturates at about 2.5−3.0 nm.

In Figure 6 a is shown the temperature dependence (Arrhenius plot) of the observed current under mass spectrometric control in the range from 298 to 670 K. In a wide range, a thermally activated behavior of the current is observed as typical for semiconductors. The slope corresponds to an activation energy of 0.27 eV. At about 400 K, the slope increases leading to a second linear range between 500 and 550 K with a slope corresponding to an activation energy of 0.56 eV. This change in activation energy is reversible as it is also observed in subsequent scans if the film is allowed to cool intermittently. It is not observed, however, during the cooling step. It is thereby indicated that a slowly reversible change in intermolecular interaction is the reason for this increase in activation energy. Above this temperature the current saturates and then decreases from 570 K but decreases at a considerably higher rate beyond 650 K. At 658 K, the current drops below the initial value at 298 K and then slightly increases again at higher temperatures due to irreversible changes in the substrate as also seen in separate experiments at a bare substrate. The mass spectrometer was set to monitor the signal at $m/e = 200$ corresponding to $C_8N_2F_4^+$, a prominent fragment of F_{16}PcZn in the

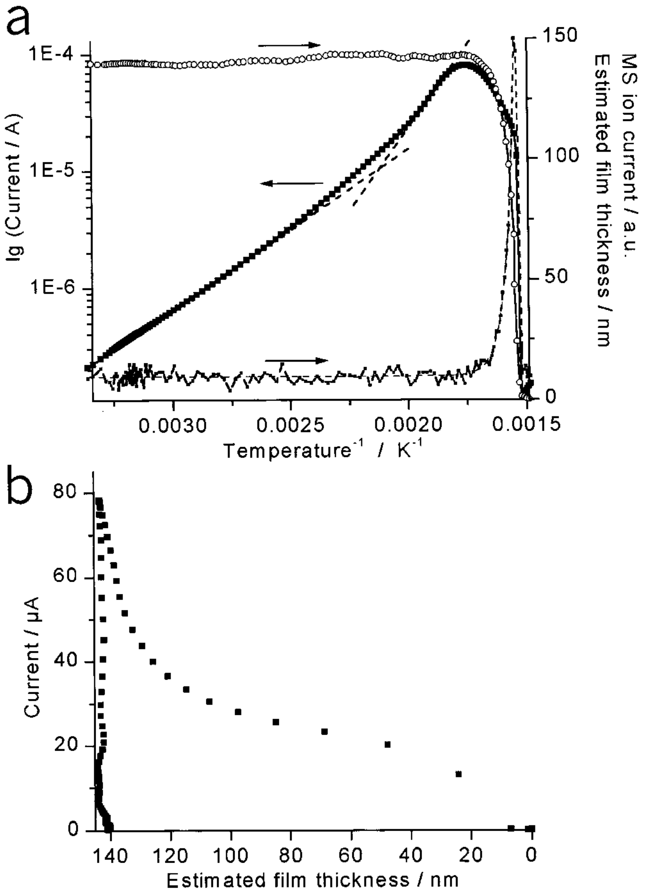

Figure 6. (a) Electrical conductivity (■) and mass signal of $m/e = 200$ (∗) as measured during heat treatment of a 140-nm film on Si/SiO_2 (see Figure 5) and decreasing film thickness during desorption as estimated from the mass signal as well as (b) the dependence of the observed current on the decreasing film thickness (see text).

accessible mass range. Beginning at about 580 K, the signal increases above the background signal and reaches its peak at 650 K. At 658 K, the end of the peak is reached and the intensity drops back to the background value. The mass signal is typical for the evaporation of F_{16}PcZn and a sublimation temperature of 580 K is determined from the present experiments.

The change of the mass signal is used to estimate the remaining average film thickness of F_{16}PcZn at the higher temperatures based on the assumption that the integral mass signal corresponds to complete desorption of F_{16}PcZn and the so calculated film thickness is also plotted in Figure 6a. It is clearly seen that the decay of the current coincides with the beginning of desorption but the saturation may occur before desorption starts. In Figure 6b, the observed current is plotted as dependent on the estimated remaining film thickness and in a way corresponds to the reversal of Figure 5b, although the very different conditions should be kept in mind. The increase of current at 140 nm summarizes the observed thermal activation which is followed by a nonlinear decrease with decreasing average film thickness. After a rapid initial decrease a plateau is reached between 100 and 40 nm average thickness which collapses in a rather narrow range at around 10 nm. This range lies at higher film thickness than the saturation during film growth (Figure 5a) but still falls rather close to it when the considerably higher temperature is considered.

4. Discussion

The orientation of F_{16}PcZn molecules deposited on the different substrates can be derived from the position of the observed absorption maximum as well as from the integral absorption as indicated above. A predominantly parallel cofacial arrangement of chromophores (blue shift) vertical to the quartz glass surface (small integral absorbance) as opposed to growth in lattices with a considerably larger contribution of molecules in a head-to-tail orientation of chromophores (red shift) parallel to the surfaces of KCl and KBr (high integral absorbance) is derived from the optical measurements. The quantitative comparison of intensities (factor 2.2), however, according to the cosine rule also shows that none of the two arrangements is reached perfectly as an ideal film of molecules parallel to the surface should show an integral absorbance of 3 times that of a film without any preferential molecular alignment and an ideal film of molecules vertical to the surface should show almost no absorbance.[23]

Atomic force microscopy performed at the films grown on the alkali halide surfaces allows further conclusions to be drawn. On NaCl for which UV–vis analysis did not allow a detailed assignment large plateaus of about 1.2-nm height are seen (Figure 3) aside from a high number of smaller grains of rather unspecific orientation relative to the substrate. The height of 1.2 nm would be explained by arrays of molecules stacked vertical to the surface with two of the benzene moieties in contact to the surface when the size of a F_{16}PcZn molecule is calculated from the distance of 1.32–1.46 nm as detected earlier in crystal lattices.[2,3,24] Nevertheless only a rather small contribution from a band split to higher energy from the transition in solution is detected by band broadening in the optical absorption of films on NaCl (Figure 1) which would be expected to be the dominant absorption for such an arrangement. A rather high degree of lateral disorder in these arrays despite the rather large domain size is thereby indicated.

On KBr, a crystallization of F_{16}PcZn along step edges of the substrate is seen (Figure 4a) as also observed for the growth of TPyTAP on alkali halides.[19] In thicker films, however, well-shaped domains are formed (Figure 4b) which show a preferential orientation relative to the substrate lattice. Growth of F_{16}PcZn in crystalline domains is hereby indicated. To discuss the characteristic angles of 90° and 45–50° within the F_{16}PcZn crystals as well as the preferential alignment of crystal edges along 18° and 22° relative to the [010] of the KBr substrate, calculations were made by considering the relative alignment of crystal lattices. In the range of lattice constants (1.32–1.46 nm) as already reported for F_{16}PcZn, two commensurate square lattices were found relative to the KBr surface mesh, namely $2\sqrt{2} \times 2\sqrt{2}$, $R = 45°$ (A) and $\sqrt{10} \times \sqrt{10}$, $R = 18.4°$ (B). Both square lattices would explain the angle of 90° often observed within the crystals as arising from the [100] and [010] axes of the F_{16}PcZn lattice. Angles around 45°

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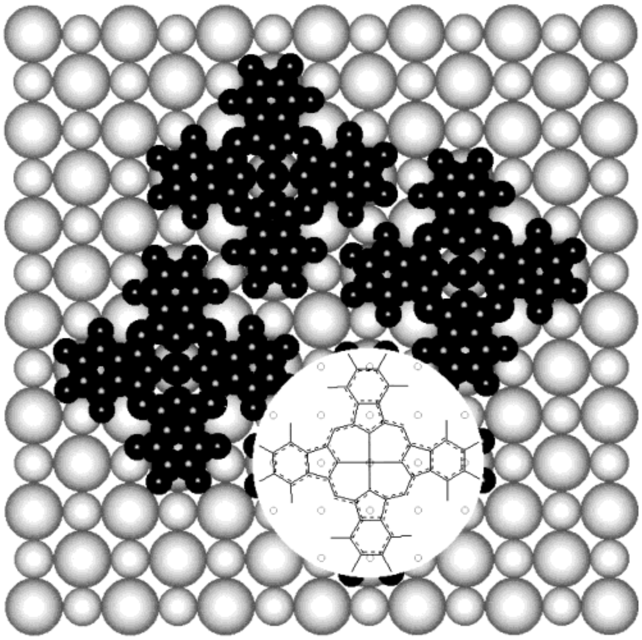

Figure 7. Square lattice of molecules in an ideal crystal of $F_{16}PcZn$ on KBr (100) as concluded from optical absorption, orientation of crystals, periodic surface potential, and molecular mechanics calculations.

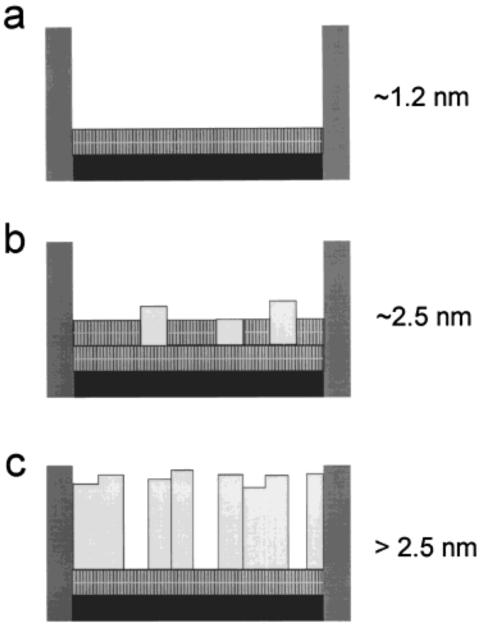

Figure 8. Growth of $F_{16}PcZn$ on amorphous SiO_2 dependent on film thickness as observed in optical absorption on quartz glass and the electrical conductivity measured on a microstructured electrode array.

would then correspond to the angle between [100] and [110] of the $F_{16}PcZn$ lattice. Two $F_{16}PcZn$ molecules would be spaced at 1.32 nm in A and at 1.47 nm in B. A distance of 1.32 nm in A is not consistent with the splitting as observed in the UV vis absorption spectra. A lattice constant that small was only detected for films having a considerably larger splitting of the band, red shifting it to 820 nm, a significantly longer wavelength as measured in the present experiments. Further, a preferred orientation of $F_{16}PcZn$ [100] at 26.6° relative to KBr [010] in B is more compatible with the angles of the $F_{16}PcZn$ crystals relative to the substrate as detected in the AFM images (see above; Figure 4a,b).

Molecular mechanics calculations were performed for both commensurate lattices to further discuss their feasibility according to molecular interactions. Structure A with an intermolecular distance of 1.32 nm could not be realized in a stable way by any rotation of the molecules on different lattice sites. It was already mentioned earlier that such a distance of molecules can barely be realized in a square lattice.[3] In Figure 7 a representation of structure B is shown with the molecules geometrically optimized in their intramolecular structure, in the relative intermolecular positions and on the positions relative to the KBr surface ions. It is seen that structure B, especially with the molecules centered on top of K^+ or Br^-, leads to a stable arrangement of molecules on the surface and hence is proposed as the structure of ideal crystalline films of $F_{16}PcZn$ on KBr. It is in very good agreement with the structure found for a fluorinated phthalocyaninatooxovanadium (F_xPcVO) on KCl and KBr as concluded earlier from high-resolution electron microscopy and diffraction[1] and confirmed recently by reflection high-energy electron diffraction at films of $F_{16}PcVO$ on these substrates.[25] As in the present study, crystalline domains of triangular rather than quadratic shape were detected also in those studies. This, at first sight, surprising observation could point to rather stable or to least slowly growing (110) faces of $F_{16}Pc$ or, considering that one such plane is detected in most crystals, to a crystallization predominantly proceeding from substrate step edges oriented along this direction.

Of special interest is the growth on SiO_2 surfaces due to the control of electrical properties. On substrates such as NaCl, quartz glass, or microstructured Si which do not offer epitaxial growth conditions, $F_{16}PcZn$ grows according to a rather different mechanism compared to that described above for KCl and KBr. The optical absorption of thin films on quartz glass (Figure 1) clearly shows the band split to higher energy from the transition in solution which is expected to occur for stacks of cofacially parallel chromophores and hence molecules of $F_{16}PcZn$. In this thickness range the electrical conductivity rapidly increases showing close contact within such thin films. The maximum current during film growth is observed at a film thickness of 2.5−3.0 nm. This thickness corresponds to about two monolayers if the domain height of $F_{16}PcZn$ on NaCl of 1.2 nm (Figure 3) is taken as a measure of a monolayer thickness. At higher film thickness, the current decreases and an increased portion of a head-to-tail arrangement of chromophores is detected in UV−vis absorption (Figure 2), indicating that at the expense of the initial structure, a different modification of $F_{16}PcZn$ grows which leads to less conducting films. From the similarity of the optical absorption spectra of thicker films on KBr and quartz glass and of films on KBr at different film thickness, it is concluded that this modification consists of the same structure based on the square lattice as discussed above (Figure 7). From the smaller integral

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absorption for the film on quartz glass, it is seen that the crystals are not, however, aligned relative to the quartz surface. The growth of F_{16}PcZn as concluded from the present experiments is summarized in Figure 8.

When a thick film of F_{16}PcZn on SiO_2 is studied at increasing temperature, a change in activation energy is observed that points toward a reversible change in molecular interactions. Such change has also been concluded from earlier experiments of temperature-dependent optical absorption on glass where a clear decrease of spectral fine structure was observed close to the desorption temperature of F_{16}PcZn.[3] A decrease in the coupling of chromophores and hence less interaction of molecular π-systems was thereby seen, especially in the head-to-tail coupling component. This decrease in interaction leads to an increased barrier of charge transport in the film and hence to the observed increase in activation energy (Figure 6a). Both changes, the decreased chromophore coupling and the increased barrier of charge transport, occur reversibly, and the original spectrum as well as activation energy is obtained after relaxation of the film into the original structure at room temperature. The observed correlation of structural change and activation energy of electrical conductivity is reminiscent of reversible increases in charge carrier mobilities as observed during the cooling of unsubstituted Pc samples which also were accompanied by changes in the optical absorption spectra.[6,7] Unlike a reversible transition between two crystalline phases observed below ~200 K in the latter example the present results at F_{16}PcZn rather point to a loss of molecular interactions above ~400 K, leading to a rather amorphous solid.[3]

Heating the substrate beyond the range of reversible change leads to desorption of F_{16}PcZn and hence the observed decrease of conductivity. This decrease, however, is not linear with respect to the decreasing film thickness as is clearly seen in Figure 6b. The initial rather fast decrease would be caused by decreasing contact of bulk particles and/or by a further decrease of conduction within these particles. The following range of rather constant conduction which collapses in the narrow range around 10 nm points to the presence of a rather stable conducting layer. Only when the molecules within this layer desorb does the conductivity drop to the background level, confirming the model giving inFigure 8 to be valid even under conditions of proceeding desorption.

5. Conclusions

Films of well-defined structure and morphology are obtained on ordered alkali halide surfaces as well as on amorphous SiO_2. Rather different growth modes are observed on KCl and KBr which provide conditions for growth of F_{16}PcZn in a square lattice of molecules parallel to the surface as opposed to NaCl and quartz glass where these conditions are not given and growth occurs in cofacial stacks of molecules predominantly with the molecular plane vertical to the surface. The unique electrical properties of F_{16}PcZn thin films are explained by this growth mode on amorphous SiO_2 as are the observed changes in electrical conduction as dependent on film thickness and temperature. The high conductivity parallel to the surface at ultrathin films opens interesting aspects of chemical sensing of these materials because of rather short time constants that can be expected for conductivity changes following exposure of such films to reactive gas atmospheres due to spatially very limited diffusion. Rather high levels of electrical conductivity vertical to the substrate surface as desired in layered devices of organic heterojunctions such as rectifiers, photovoltaic cells, and light-emitting diodes can be expected for those films of F_{16}PcZn in the square-lattice structure. Further work is currently in progress to study the three-dimensional growth of F_{16}Pc in such square lattices and their electrical properties.

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