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Crystallization of Tyrian Purple (6,6'-Dibromoindigo) Thin Films: The Impact of Substrate Surface Modifications

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Abstract

The pigment 6,6'-dibromoindigo (Tyrian purple) shows strong intermolecular hydrogen bonds and the film formation is, therefore, expected to be influenced by the polar character of the substrate surface. Thin films of Tyrian purple were prepared by physical vapor deposition on a variety of substrates with different surface energies: from highly polar silicon dioxide surfaces to hydrophobic polymer surfaces. The crystallographic properties were investigated by X-ray diffraction techniques such as X-ray reflectivity and grazing incidence X-ray diffraction. In all cases, crystallites with “standing” molecules relative to the substrate surface were observed independently of the substrate surface energy. In the case of polymer surfaces, additional crystallites are formed containing “lying” molecules with their aromatic planes parallel to the substrate surface. Small differences in the crystallographic lattice constants were observed as a function of substrate surface energy, the corresponding small changes in the molecular packing are explained by a variation of the hydrogen bond geometries. This work reveals that despite the limited influence of the surface energy on the molecular orientation, the crystalline packing of Tyrian purple within thin films is altered and slightly different structures form.

Keywords

A1. polymorphism; A3. organic thin films; A1. X-ray diffraction; B1. hydrogen-bonded pigments

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1 Introduction

Hydrogen-bonded pigments have attracted significant interest over the last few years due to their high environmental stability and their potential applications as the active material in organic electronic devices [1,2]. Tyrian purple, a natural dye known for more than three thousand years, is one prominent representative of this materials class, which has been successfully employed in organic thin film transistors [3]. Such devices can be fabricated on a large variety of dielectric surfaces ranging from natural polymers like, e.g., cellulose, to synthetic polymer surfaces such as polyethylene, as well as inorganic dielectrics like silicon oxide [4]. The crystallographic properties of Tyrian purple adsorbed on such surfaces in the form of thin films are of fundamental importance, because charge transport between the transistor source and drain electrodes is typically confined to the first few molecular layers of the organic adsorbate. As charge transport in organic semiconductors is typically highly anisotropic [5], molecular orientation and order as well as polymorphism [6] in the vicinity of the dielectric interface is crucial for device performance [7].

Extensive studies have been carried out during the last two decades on the crystallographic order of van der Waals bonded organic electronic molecules on dielectric surfaces [8,9,10,11]. In these studies it was found that, within thin films on silicon oxide surfaces, prototypical rod-like conjugated molecules like, e.g., pentacene [12] or its derivatives [13,14], tend to grow with their long molecular axis in an up-right standing orientation, that is, with a strong preferred orientation with respect to the substrate (fiber texture). The systematic variation of the surface energy of thermally oxidized silicon wafers has been shown to have an influence on the film morphology and nucleation density, e.g. in thin films of pentacene [15] or α -sexithiophene [16]. Similar observations were reported for the preferred orientation of pentacene on polymeric surfaces; a clear change of the thin film morphology and nucleation density was observed as a function of the surface energy [17,18,19]. On polar surfaces, the growth mode was observed to be essentially two-dimensional in nature, while, in contrast, more three-dimensional growth in the form of molecular islands occurs on non-polar surfaces; this behavior can be related to the diffusivity of the molecules across the substrate surface upon deposition [20,21]. However, in contrast to the film morphology, the preferred orientation of the molecules (and, therefore, that of the crystallites) appears to be unaffected by the surface energy [17,18,22].

Pigments like quinacridone and indigo, which form hydrogen bonds (in addition to van der Waals-interactions) that augment their interaction, show strong islanding on silicon oxide surfaces already in the monolayer regime. For thicker films, a strong preferred orientation of the crystallites formed by molecules in a “standing” orientation is observed [23,24]. Tyrian purple was shown to form a surface-induced crystal structure upon physical vapor deposition of thin films at room temperature, where the type of substrate did not significantly impact phase formation [25]. This surface-induced phase has been crystallographically well characterized for thin films prepared on thermally oxidized silicon wafers, providing a full structure solution for this polymorph [25]. The surface-induced phase shows a significantly different type of molecular packing compared to the bulk structure of Tyrian purple [26,27], since elongated distances between bromine atoms - beyond the sum of the van der Waals radii - reveal that enhanced intermolecular interactions between bromine atoms are not

decisive for the molecular packing. Rather hydrogen bonds and π - π interactions are responsible for the crystalline structure of the surface-induced phase. Although detailed knowledge has been gained for Tyrian purple films grown on thermally oxidized silicon, the crystallographic properties of such films on different dielectric surfaces remain, unknown to date, despite their high potential for further applications like, e.g., flexible electronics employing dielectric polymer substrates.

Here, we aim to close this gap by exploring the crystallographic properties of Tyrian purple prepared on isotropic surfaces with systematically varied surface energies. To that end, we employ a multitude of different substrates ranging from reactive polar (plasma-etched silicon oxide) to weakly interacting non-polar surfaces (a perfluorinated polymer) in order to study the influence of surface polarity on the thin film morphology and the crystallization behavior of Tyrian purple.

2 Experimental

6,6'-Dibromoindigo (Tyrian purple) powder was purchased from ENDOTHERM Ltd. and used without any further purification; the chemical structure of the molecule is depicted in Fig. 1A. Thin films were prepared by physical vapor deposition from a steel Knudsen cell at a base pressure of 3×10^{-5} mbar. Films were deposited at a rate of 0.18 nm/min with final nominal thicknesses between 1.5 nm and 47.5 nm, as determined with a quartz crystal microbalance. The substrates were kept at room temperature during evaporation to prepare the surface-induced phase of Tyrian purple [25]. Thermally oxidized silicon wafers (150 nm oxide) and various polymer surfaces were used as substrates. The chemical cleaning procedure of silicon oxide surfaces (CC-SiO₂) involved sonication in acetone and subsequent rinsing with isopropanol. Following the chemical cleaning procedure, plasma-etched silicon oxide substrates (PE-SiO₂) were prepared using a Femto plasma cleaner (Diener electronic) where oxygen plasma was ignited for 42 s.

Polymer surfaces were prepared on native oxide silicon wafers by chemical vapor deposition. Polymers of ethylene-glycol-dimethacrylate (EGDMA, Sigma Aldrich, 98%) and 1H,1H,2H,2H,-perfluorodecylacrylate (PFDA, Sigma Aldrich, 97%) were obtained by initiated chemical vapor deposition using a custom built reactor chamber [28]. The monomers, EGDMA and PFDA, and the initiator, tert-butylperoxide (TBPO, Sigma Aldrich, 98%) were used without further purification. The polymer of EGDMA (p-EGDMA) was deposited using a 1:1 ratio between monomer and initiator flow rates at a working pressure of 800 mTorr. The polymer of PFDA (p-PFDA) was deposited at a 1:2 ratio of monomer:initiator flow rates at a working pressure of 160 mTorr. The filament and the substrate temperatures were kept at 300 °C and 30 °C, respectively, for both depositions. Polymer films of hexamethyldisiloxane (HMDSO, Sigma Aldrich, 98%) were prepared by plasma-enhanced chemical vapor deposition, a description of the chamber is given elsewhere [29]. The monomer flow rate was 2 sccm in 10 sccm of Argon. The working pressure was kept at 500 mTorr and the plasma power at 25 W. The chemical structures of all polymers are depicted in Fig. 1B-D.

The surface energies were determined using the Drop Shape Analyser DSA100 (Krüss Ltd.). Drops with a volume of 2 μl were deposited on the substrate surface and the contact angles were measured; diiodomethane, benzylalcohol, glycerine and water were used as test liquids. The surface energies were determined by the method of Owens and Wendt [30], separating the total surface energies into dispersive and polar parts.

Atomic force microscopy (AFM) studies were performed using a Nanosurf easyScan 2 AFM in tapping mode. The images were acquired at a scan speed of 3 $\mu\text{m/s}$ using doped silicon tips exhibiting a cone angle of 30° . Nominal values for the resonance frequency and the tip radius were 190 kHz and 8 nm, respectively.

Specular X-ray scattering studies were performed using a PANalytical Empyrean system using K_α radiation from a sealed Cu-tube ($\lambda = 1.5418 \text{ \AA}$). At the primary side, a multilayer X-ray mirror was used to generate a monochromatic and parallel beam with a height of 100 μm ; at the secondary side, a receiving slit and a 0.02 rad Soller slit were used in combination with a PANalytical PIXcel 3D detector. The setup for specular X-ray diffraction (XRD) used a 7.5 mm antiscatter slit and the detector was operating in 1D scanning line mode, whereas for X-ray reflectivity (XRR) measurements a 100 μm antiscatter slit was used and the detector was acting as a point detector. The X-ray diffraction and X-ray reflectivity data are plotted as a function of the out-of-plane component of the scattering vector q_z ($q_z = 4\pi/\lambda \sin \theta$), λ being the wavelength and θ half of the scattering angle 2θ . The instrumental error is determined from the experimental shifts of the critical angles of the thermally oxidized silicon and of Tyrian purple, a value of $\pm 0.002 \text{ \AA}^{-1}$ is obtained. The X-ray reflectivity data were fitted using Parratt's formalism [31] taking surface and interface roughness into account by the method of Névot and Croce [32]. The *X'Pert Reflectivity* software package was used to perform the fits.

Grazing incidence X-ray diffraction (GIXD) measurements were performed at the beamline ID10 (ESRF, Grenoble, France) using a pseudo z-axis geometry. A wavelength of 0.564 $\text{\AA}$ was used with a beam size of 20 $\mu\text{m} \times 20 \mu\text{m}$. The incidence angle was chosen between 0.06° and 0.075° , which is slightly below the critical angle of the silicon oxide, in order to minimize the signal from the substrate. The diffracted signal was recorded by a PILATUS 300K detector mounted on a goniometer. The typical illumination time was 30 s. The diffraction patterns were transformed into reciprocal space maps using the *xrayutilities* software package [33] and evaluated using the custom-made software package *PyGID* [34]. The indexation error is $\pm 0.03 \text{ \AA}$ for the lattice constants a , b and c and $\pm 0.2^\circ$ for α , β and γ and is due to the full width at half maximum of the diffraction peaks. The reciprocal space maps are plotted on a linear scale.

3 Results

3.1 Substrate Characterization

A detailed investigation of the substrate surfaces used for the thin film growth of Tyrian purple was performed; the respective surface energies are listed in Table 1 with the substrates sorted by their total surface energy (γ) in descending order. The highest value of the total surface energy is obtained for PE-SiO₂, where the dispersive part (γ^d) as well as the

polar part (γ^h) are the highest of all substrates. The other substrate surfaces show a decreasing total surface energy, with the polar part falling towards zero for p-PFDA, which renders this substrate the most hydrophobic of the present study.

The morphologies of the polymer substrate surfaces were investigated by AFM, characteristic height images are depicted in Fig. 2. The polymer surfaces show a hillock-like structure with lateral extensions of about 100 nm for p-EGDMA, 50 nm for p-HMDSO and 200 nm for p-PFDA. The characteristic height variations between the hillocks are 4 nm for p-EGDMA, 8 nm for p-HMDSO and 12 nm for p-PFDA. The resulting root mean square roughness of the polymer surfaces is given in Table 1.

The substrates were further characterized by X-ray reflectivity (XRR); the experimental curves are depicted in Fig. 3A-E and labeled as “substrate”. Fitting the experimental data allowed for the determination of thickness and surface roughness. Both silicon oxide surfaces (PE-SiO₂ and CC-SiO₂) show an identical oxide layer thickness of 150 nm and a low surface roughness of 0.3 nm [35]. The polymer layers exhibit thicknesses between 16.6 nm and 70 nm with roughnesses between 0.7 nm and 3 nm (*cf.* Table 1). Apparent deviations between the roughness values determined by AFM and XRR are likely due to methodical reasons, such as, the convolution of the microscopy tip (of finite and unknown radius) with the surface topography (AFM) and the assumption of Gaussian roughness for data modelling (XRR). However, in agreement with each other both methods show equal trends for the roughness of the different types of substrates.

3.2 Characterization of Tyrian purple thin films

X-ray reflectivity curves of thin Tyrian purple films with different thicknesses grown on PE-SiO₂ are shown in Fig. 3A. Weakly pronounced Kiessig fringes [36] are observed for $q_z < 0.35 \text{ \AA}^{-1}$, but a dominant Bragg peak appears at $q_z \sim 0.43 \text{ \AA}^{-1}$. The slight shift of the peak position from $q_z = 0.438 \text{ \AA}^{-1}$ for the film with a nominal thickness of 4.5 nm to $0.428 \text{ \AA}^{-1}$ for a 9 nm thick film either results from a change of the lattice constants at small crystallite sizes or from a coherent overlap of the scattering amplitudes from X-ray reflectivity and X-ray diffraction [37], which cannot be decided on the basis of the present data. Clearly, however, the 001 Bragg peak of the surface-induced phase of Tyrian purple [25] can be assigned to these peaks, thus allowing the determination of the orientation of Tyrian purple molecules relative to the substrate: the molecules adopt an up-right standing orientation with their long molecular axes slightly tilted by an angle of $\sim 25^\circ$ with respect to the surface normal. In the case of Tyrian purple grown on CC-SiO₂ substrates, similar diffraction features are observed (Fig. 3B): Kiessig fringes together with a dominant Bragg peak and a small shift of the Bragg peak position with increasing film thickness. However, the final value for the peak position at $q_z = 0.422 \text{ \AA}^{-1}$ is now slightly lower than that observed for the film grown on PE-SiO₂. On both silicon oxide surfaces, the Tyrian purple thin films show a clear Bragg peak already for nominal film thicknesses as low as 1.5 nm, which corresponds to the thickness of a closed monolayer of up-right standing molecules. The presence of a Bragg peak for nominal monolayer coverage indicates the formation of three dimensional molecular islands, as it was recently reported for indigo [23].

The X-ray reflectivity data of Tyrian purple grown on p-EGDMA show clear Kiessig fringes for $q_z < 0.3 \text{ \AA}^{-1}$, which are due to the 16.6 nm thick polymer layer of the substrate (Fig. 3C). In this case, the 001 Bragg peak is hardly observable in films as thick as 6.4 nm and 9.7 nm (nominal thickness); for a film thickness of 47.5 nm, the 001 Bragg peak becomes more clearly visible at $q_z = 0.419 \text{ \AA}^{-1}$. In the case of the p-HMDSO substrate (Fig. 3D), Kiessig fringes of the 70.0 nm thick polymer layer are observed for $q_z < 0.25 \text{ \AA}^{-1}$ and the 001 Bragg peak is observed at $q_z = 0.417 \text{ \AA}^{-1}$ in a Tyrian purple film with a nominal thickness of 18.4 nm. The X-ray reflectivity curve of the 18 nm Tyrian purple film grown on the p-PFDA substrate (Fig. 3E) shows only strong features from the p-PFDA layer, but no diffraction features of Tyrian purple crystallites can be observed. Kiessig fringes at $q_z < 0.1 \text{ \AA}^{-1}$ translate into a film thickness of 61.7 nm and a surface roughness of 3.1 nm is deduced for the p-PFDA layer. Additional strong Bragg peaks appear at $0.198 \text{ \AA}^{-1}$, $0.390 \text{ \AA}^{-1}$, and $0.585 \text{ \AA}^{-1}$ which can be assigned to the bilayer structure of the smectic B phase of p-PFDA [38]. The Laue fringes on either side of the Bragg peaks reveal the uniform thickness of the p-PFDA crystallites [28].

Grazing incidence X-ray diffraction studies were performed on films with highest nominal thicknesses. Three selected reciprocal space maps are depicted in Fig. 4. The out-of-plane part of the scattering vector (q_z) is given on the y -axis and on the x -axis the in-plane part of the scattering vector (q_{xy}) is given.

Two different characteristic diffraction features are observed in the maps: a series of peaks which are arranged along vertical rods of constant q_{xy} values ($1.1 \text{ \AA}^{-1}$, $1.6 \text{ \AA}^{-1}$ and $1.9 \text{ \AA}^{-1}$) and strong peaks which are smeared along Debye-Scherrer rings of constant values of the scattering vector q . In the first step of data evaluation, the peak series along constant q_{xy} are analyzed for the thin film grown on PE-SiO₂ (Fig. 4A). The Bragg peaks are indexed on the basis of the known surface-induced crystal structure with a 001 texture (as known from specular diffraction). The peak series along the three rods belong to $\pm(10L)$, $\pm(01L)$ and $\pm(11L)$ of the surface-induced phase. The dominant appearance of the 012 and -102 peaks can be explained by the crystal structure solution of the surface-induced phase, as both peaks are due to crystallographic planes densely populated by molecules [25].

The reciprocal space maps of the crystallites grown on surfaces other than silicon oxide show Bragg peaks at slightly different positions (see, e.g., the intensity distribution around $q_{xy} = 1.9 \text{ \AA}^{-1}$ and $q_z = 0.2 \text{ \AA}^{-1}$ in Fig. 4). In order to refine the unit cell parameters, an indexation of the reciprocal space maps was performed starting from the known surface-induced crystal structure. The lattice constants were then optimized until a good agreement between the experimentally observed peaks and the calculated peak positions was obtained. As a result, Tyrian purple crystallites grown on different types of substrates show deviating sets of lattice constants, as listed in Table 2, that is, surface-induced polymorphism is observed. It is worth noting that in all cases the value of the lattice constant a stays essentially unchanged. The lattice constants b and c , however, show variations of almost 4% from the crystal structure grown on PE-SiO₂.

The second apparent characteristic feature in the reciprocal space maps is the smearing of Bragg peaks along circles of constant q -values. In most cases, only segments of such circles

are observed. The peak smearing is low for crystallites grown on silicon oxide surfaces (PE-SiO₂ and CC-SiO₂) while it is significantly more pronounced for crystallites grown on the polymer surfaces. Such a smearing is caused by the mosaicity of the crystallites, i.e., by a deviation of crystallite orientation from the (001) fiber texture. The large mosaicity of the Tyrian purple crystallites grown on the polymer surfaces is likely due to the soft nature and the higher roughnesses of these surfaces compared to silicon oxide. Note that a similar preferred orientation of large mosaicity was also reported for the growth of pentacene on polymer surfaces [18].

Most interestingly, however, for Tyrian purple grown on the p-PFDA and p-EGDMA polymer surfaces, the specular diffraction patterns show an additional distinct Bragg peak at $q_z = 1.94 \text{ \AA}^{-1}$ ($d = 3.24 \text{ \AA}$) marked by an arrow in Fig. 5 (only weakly present for p-HMDSO). This peak cannot be assigned to the 001 texture of crystallites formed by upright-standing molecules, as described above.

An interpretation of this diffraction peak is possible in combination with a weak diffraction feature observed in GIXD measurements at low values of q_{xy} . Fig. 6 shows a zoomed portion of the reciprocal space map of the film on p-EGDMA (Fig. 4B). The ring-like structure at $q = 0.41 \text{ \AA}^{-1}$ can be assigned to the 001 peak of Tyrian purple, which now appears dominant in the in-plane direction. Together with the specular diffraction peak ($d = 3.24 \text{ \AA}$) it can be assigned to a second type of preferred orientation of Tyrian purple crystallites. The crystallites are formed by molecules with their aromatic planes π - π stacked parallel to the substrate surface, i.e., the molecules are oriented with their long molecular axes as well as their aromatic planes essentially parallel to the substrate surface (i.e. lying molecules). The observation of more than one type of preferred orientation of crystallites within organic thin films occurs quite frequently; there are several examples in literature where crystallites formed by standing and by lying molecules are simultaneously present [39,10,40,23,41,42]. In these cases, however, the lying orientation was not due to a surface-induced phase, but assigned to crystalline bulk polymorphs instead. This is in clear contrast to the present case of Tyrian purple grown on polymer substrates, where it forms its surface-induced phase in both orientations.

4 Discussion

Our crystallographic investigations on Tyrian purple thin films on silicon oxide and polymer substrates reveal the presence of the surface-induced crystal structure in all cases. However, changing the substrate from a plasma-etched thermally oxidized silicon wafer to another surface induces changes in the crystal structure observed by the (slightly) different lattice constants of the respective crystallographic unit cells. In all cases, the preferred orientation of the crystallites with their 001 plane parallel to the substrate surface – formed by standing molecules – does not change. In case of polymer surfaces, however, a second preferred orientation of crystallites, formed by molecules oriented with their aromatic planes parallel to the substrate surface, appears. Importantly, both orientations are found to grow in a surface-induced phase, i.e., the presence of the substrate induces crystallographic phases which are different to the bulk crystal structure. These two types of molecular orientations are depicted in Fig. 7.

We attribute the appearance of this second type of preferred orientation with molecules arranged in a “flat-on” configuration to the soft nature of the polymeric substrate rather than to the influence of its surface energy. The polymers have high structural flexibility to adapt to single Tyrian purple molecules or crystallites. In particular, even the highest substrate surface energy of 73 mN/m (PE-SiO₂) appears to be insufficient to force the molecules to arrange exclusively with their long molecular axes parallel to the substrate surface, thereby forming hydrogen bonds between the molecule and the substrate. Obviously, the molecules gain more energy if they pack in a π - π stacked motif and saturate their hydrogen bond donors and acceptors with neighboring molecules (*cf.* Fig. 7A).

Another interesting aspect of the present study is the variation of the crystal structure upon changing the nature of the substrate, as observed by the variation of the geometry of crystallographic unit cells. Interestingly, the lattice constant a remains essentially constant at $a = 3.85 \text{ \AA}$ for all the crystal structures observed within thin films (*cf.* Tab.2). This distance is associated with the π - π stacking direction of the surface-induced polymorph and is a constant parameter during the crystallization process. The largest variation is observed for the lattice constants b and c , where the b -axis extends along the direction of the hydrogen bonds and the c -axis represents the distance along the long molecular axis of the upright-standing molecules. Comparing the two crystal structures solved for Tyrian purple – the bulk and the surface-induced phases – reveals that their main difference is in the hydrogen bonding between neighboring molecules [25]. It seems that the development of the hydrogen bonds occurs relatively late during the crystallization process of Tyrian purple only *after* clusters of π - π stacked molecules have already formed. Hence, the hydrogen bonding differs between the different polymorphs and arrangements since the molecules must adopt a highly defined geometry with respect to each other in order to form hydrogen bonds. The influence of the surface energy on the crystallization process relates to these clusters of π - π stacked molecules and to their ability to migrate across the substrate surface, change their orientation relative to neighboring clusters, and to their capability to finally find a fixed position relative to a neighboring cluster. Both the intermolecular interactions and the interaction with the substrate surface influence the nucleation of the first crystallites at the substrate surface, which is decisive for the subsequent crystallization process and, finally, for the overall structure formed.

5 Conclusion

Thin films of the molecule Tyrian purple were prepared on different dielectric surfaces assessing the preferred orientation of the crystallites as well as their polymorphism. The surface energies and polarities of the substrate surfaces were systematically varied to determine the influence of hydrogen bonds on the crystallization behavior. In the case of silicon oxide surfaces with high surface energy and surface polarity, the formation of islands was observed at a nominal coverage of just one monolayer. This reveals that the intermolecular interactions dominate over the substrate-molecule interaction inducing three-dimensional growth. These crystallites consist of “standing” molecules with a 001 fiber texture and grow in the surface-induced structure of Tyrian purple. Depending on the substrate nature, however, variations in the molecular packing occur, as deduced from variations of the respective lattice constants. On all polymer surfaces two types of preferred

crystal orientations were found, that is, crystallites comprising “standing” as well as “lying” molecules. We suggest the higher surface roughness together with the softness of the polymer surfaces to be responsible for the occurrence of this second type of preferred orientation rather than the lower surface energy of the substrate. Therefore, changes in the surface energy of the substrate is, perhaps surprisingly, not found to alter the structure of Tyrian purple thin films significantly.

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Fig. 1.
Chemical structures of the used organic materials: (A) Tyrian purple, (B) polyethylene glycol dimethacrylate (p-EGDMA), (C) poly-hexamethyldisiloxane (p-HMDSO) and (D) poly-1H,1H,2H,2H-perfluorodecyl acrylate (p-PFDA)

Fig. 2. Height images obtained by AFM of the polymer substrates: (A) p-EGDMA, (B) p-HMDSO, (C) p-PFDA. The scale of the colorbars is given in nm.

Fig. 3. Specular X-ray reflectivity of Tyrian purple films of varying thicknesses on different substrates shown along side X-ray reflectivity curves of the clean substrates: (A) on PE-SiO₂, (B) on CC-SiO₂, (C) on p-EGDMA, (D) on p-HMDSO, (E) on p-PFDA.

Fig. 4. Grazing incidence X-ray diffraction reciprocal space maps for Tyrian purple films on different substrates. (A) 9 nm thick film on PE-SiO₂, (B) 47.5 nm thick film on p-EGDMA, (C) 18 nm thick film on p-PFDA. The calculated positions of the Bragg peaks are given together with their Miller indices. The encircled area of B is shown in Fig. 6 in more detail.

Fig. 5. Specular X-ray diffraction of Tyrian purple films of varying thicknesses on different substrates: 9 nm thick on PE-SiO₂ and on CC-SiO₂, 47.5 nm thick on p-EGDMA, 18.4 nm thick on p-HMDSO and 18 nm thick on p-PFDA. 00L indices indicate diffraction peaks from crystals formed by “standing” molecules. The arrow points towards an additional diffraction peak of Tyrian purple crystallites formed by lying molecules.

Fig. 6. Detail of the grazing incidence X-ray diffraction map from Fig.4B for a Tyrian purple film grown on a p-EGDMA surface. The arrow indicates the 001 Bragg peak of the surface-induced phase with a preferred orientation of the crystallites formed by lying molecules.

Fig. 7.

Two different orientations of the surface-induced phases of Tyrian purple. (A) Standing molecules viewed along the b-axis (found on all surfaces); (B) Lying molecules viewed along the molecular plane (found only on polymer surfaces). Part (A) is based on the crystal structure solution from thin films while Part (B) is a schematic sketch of the molecular packing.

Table 1

Surface energies γ (total γ , dispersive γ^d and polar part γ^h) of the substrate surfaces employed. Morphology of the substrates with top layer thickness (d) and roughness of the surface layers, as obtained by fitting of the X-ray reflectivity curves (σ_{XRR}), or determined by atomic force microscopy (σ_{AFM}).

substrate	γ [mN/m]	γ^d [mN/m]	γ^h [mN/m]	d [nm]	σ_{XRR} [nm]	σ_{AFM} [nm]
PE-SiO ₂	73.4	38.5	34.9	150	0.3	0.2
CC-SiO ₂	61.3	37.4	23.9	150	0.3	0.3
p-EGDMA	43.2	31.2	12.1	16.6	1.2	0.98
p-HMDSO	25.0	19.1	5.9	70.0	0.7	0.38
p-PFDA	12.4	12.3	0.1	61.7	3.1	3.02

Table 2

Lattice constants of Tyrian purple crystallites grown on different surfaces. The error margins are $\pm 0.03 \text{ \AA}^{-1}$ for the lattice constants a , b and c and $\pm 0.2^\circ$ for α , β and γ .

substrate	PE-SiO ₂	CC-SiO ₂	p-EGDMA	p-HMDSO	p-PFDA
a [Å]	3.84	3.86	3.85	3.84	3.84
b [Å]	6.00	5.83	6.20	5.78	5.78
c [Å]	14.60	14.86	14.92	15.16	14.92
α [°]	94.0	98.2	94.0	95.3	95.3
β [°]	93.0	94.2	91.5	93.6	93.8
γ [°]	87.0	87.1	88.9	86.5	86.5