Surface-Induced Phase of Tyrian Purple (6,6′-Dibromoindigo): Thin Film Formation and Stability

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ABSTRACT: The appearance of surface-induced phases of molecular crystals is a frequently observed phenomenon in organic electronics. However, despite their fundamental importance, the origin of such phases is not yet fully resolved. The organic molecule 6,6′-dibromoindigo (Tyrian purple) forms two polymorphs within thin films. At growth temperatures of 150 °C, the well-known bulk structure forms, while at a substrate temperature of 50 °C, a surface-induced phase is observed instead. In the present work, the crystal structure of the surface-induced polymorph is solved by a combined experimental and theoretical approach using grazing incidence X-ray diffraction and molecular dynamics simulations. A comparison of both phases reveals that π–π stacking and hydrogen bonds are common motifs for the intermolecular packing. In situ temperature studies reveal a phase transition from the surface-induced phase to the bulk phase at a temperature of 210 °C; the irreversibility of the transition indicates that the surface-induced phase is metastable. The crystallization behavior is investigated ex-situ starting from the sub-monolayer regime up to a nominal thickness of 9 nm using two different silicon oxide surfaces; island formation is observed together with a slight variation of the crystal structure. This work shows that surface-induced phases not only appear for compounds with weak, isotropic van der Waals bonds, but also for molecules exhibiting strong and highly directional hydrogen bonds.

INTRODUCTION

During the last few years, the use of hydrogen-bonded pigments has attracted significant interest in organic electronics, due to their promising charge transport mobilities.¹⁻³ Apart from being biodegradable and nontoxic, an important characteristic of this material class is the typically high environmental stability⁴,⁵ and their ability to form hydrogen bonds, which are strong intermolecular interactions compared to van der Waals interactions. In addition, hydrogen bonds are directional interactions. As a consequence, the molecular arrangement within the crystalline structure deviates significantly from the known molecular packing motifs of aromatic hydrocarbons.⁶ For example, the common organic pigment quinacridone is known to form (at least) three significantly different types of crystal structures, which are characterized by different hydrogen-bonded networks.⁷ However, for hydrogen-bonded pigments, the occurrence of surface-induced phases (specific polymorphs within thin films mediated by the presence of a substrate surface during the crystallization) is not reported. Such surface-induced phases are frequently
observed for rod-like conjugated molecules, where a strong influence to application relevant physical properties is observed.\(^8\)

In the field of organic electronics, the structural characteristics of aromatic molecules such as pentacene in thin films have been intensively investigated as organic electronic devices are typically based on such architectures.\(^9\)–\(^12\) Likewise, scientific interest has recently increased for thin films of hydrogen-bonded pigments. The film formation and crystallization at surfaces was studied for indigo\(^13\),\(^14\) and quinacridone, where, in addition, the electronic structure was investigated.\(^15\)–\(^20\) For these systems, stronger intermolecular interactions due to hydrogen bond formation and the presence of stronger bonds toward the substrate result in lower dissociation rates and smaller crystallites.\(^14\) Nevertheless, the preferred molecular orientation can be influenced by substrate surface engineering.\(^2\)

In this work, the structural properties of thin films of 6,6′-dibromoindigo, commonly known as Tyrian purple, are studied. The crystal bulk cell is well-known,\(^21\)–\(^24\) and in addition, a new crystalline phase of Tyrian purple within thin films has been reported,\(^25\) but not yet characterized. Its crystallographic properties are investigated as a function of temperature and film thickness, from the sub-monolayer regime up to thick (multilayer) films. Our study confirms the existence of this yet uncharacterized polymorph of Tyrian purple and provides a crystal structure solution; its thermodynamic stability is also explored.

### EXPERIMENTAL SECTION

Tyrian purple powder was synthesized following the previously reported procedure\(^27\) and purified by temperature gradient sublimation. A first set of thin films was deposited by hot wall epitaxy (HWE) using a base reactor pressure of $1 \times 10^{-6}$ mbar.\(^25\) Pristine, polyethylene-coated glass,\(^26\) as well as thermally oxidized silicon wafers with an oxide thickness of 150 nm served as substrates and were preheated to the desired growth temperature for 30 min, in order to ensure a stable substrate temperature during the deposition process. The material was deposited for 60 min using a source/wall temperature of 240 °C/260 °C.

A second set of samples was prepared by physical vapor deposition (PVD), in order to have better control over the film thickness, especially in the monolayer regime. Tyrian purple powder was purchased from ENDOTHERM Ltd. and used without any further purification. A steel Knudsen cell and a base pressure of $3 \times 10^{-5}$ mbar were used. Plasma-etched and chemically cleaned silicon substrates (150 nm thermal oxide) were used. The chemical cleaning procedure involved sonication in acetone for 10 min and subsequent rinsing with isopropanol. The plasma cleaned substrates were prepared using a Femto plasma cleaner by Diener electronic after the chemical cleaning procedure. The oxygen plasma was ignited for 42 s. The plasma etching changes the surface energy of the substrate from 61 mN/m after the chemical cleaning to 73 mN/m after plasma etching, where the difference could be assigned solely to changes in the polar part of the surface energy. Films were deposited with a deposition rate of 0.18 nm/min with final nominal thicknesses between 0.6 and 9 nm, as determined with a quartz crystal microbalance; the substrates were kept at room temperature.

Atomic force microscopy (AFM) studies were performed using a Digital Instruments Dimension 3100 in tapping mode. The images were acquired at a scan speed of 5 μm/s using SiC tips exhibiting a cone angle of 40°. Nominal values for the resonance frequency and the tip radius were 325 kHz and 10 nm, respectively.

Specular X-ray scattering studies were performed with a PANalytical Empyrean system using $K_{\alpha}$ radiation from a sealed Cu-tube. At the primary side, a multilayer X-ray mirror was used to generate a monochromatic ($\lambda = 1.54 \text{ Å}$) and parallel beam with a height of 100 μm; at the secondary side, a 100 μm receiving slit and a 0.02 rad Soller slit were used in combination with a PANalytical PIXcel 3D detector acting as a point detector. The X-ray diffraction (XRD) as well as the X-ray reflectivity (XRR) data are plotted as a function of the scattering angle $\theta$ via $q = 4\pi/\lambda \sin \theta$, $\lambda$ being the wavelength and $\theta$ half of the scattering angle 2$\theta$. The X-ray reflectivity data were fitted using the software Stoechfit\(^27\) to determine an electron density profile across the thin film. The error of the peak position is determined from the experimental shifts of the critical angles to $\Delta q = \pm 0.002 \text{ Å}^{-1}$. The size of the crystallites was determined by the Scherrer equation using the full width at half-maximum of the Bragg peaks. In-situ temperature studies were performed by means of a DHS900 heating stage (Anton Paar Ltd.). The experiments were performed under inert conditions using a dynamic flow of helium. Typical measurement times were 15 min per temperature step. Between the measurements, the samples were heated to the next temperature with a heating rate of 50 °C/min.

Grazing incidence X-ray diffraction (GIXD) was performed at the beamline ID10 (ESRF Grenoble, France) using a pseudo z-axis geometry.\(^28\)–\(^29\) A wavelength of 0.564 Å was used with a beam size of 20 μm × 20 μm. The incidence angle was chosen between 0.075° and 0.09°, which is slightly below the critical angle of the substrate, in...
order to minimize the signal from the substrate and to enhance the diffracted intensity due to the evanescent wave. The diffracted signal was recorded by a PILATUS 1 M detector mounted on a goniometer. The typical illumination time was 30 s. The diffraction pattern was transformed into reciprocal space using the software library xrayutilities. The calculation of the peak positions and structure factors was performed using the custom-made software PyGID.

The molecular packing within the experimentally determined unit cell has been calculated by theoretical modeling, where a combination of molecular dynamics (MD) and density functional theory (DFT) was applied. MD simulations were carried out using the LAMMPS code in combination with the CHARMM General Force Field v. 20f. In a first step, several hundred trial structures were created by placing one molecule randomly into a slightly expanded unit cell. During the subsequent MD run, the system was allowed to relax while the unit-cell was shrunk continuously to its experimental size. The most promising structures were further refined using DFT geometry optimizations as implemented in the CASTEP program. Ultrasoft pseudopotentials were used in combination with a plane wave cutoff energy of 280 eV. A Monkhorst—Pack grid with a density of 0.05 Å−1 was used for choosing the k-points.

### RESULTS

Figure 1 depicts AFM micrographs of Tyrian purple thin films grown on polyethylene surfaces, which were prepared at substrate temperatures of 50, 100, and 150 °C. The formation of elongated islands together with elevated hillocks is observed. The latter exhibit heights of up to 400 nm, whereas the elongated islands have a maximum height of 80 nm. The lateral size of the islands increases with growth temperature: at low temperatures the length of the islands is below 1 μm, the size of the islands then increases to several micrometers in length while remaining less than 1 μm in width for a growth temperature of 100 °C; at 150 °C the overall size of the islands is further increased. Interestingly, ridge-like structures with a typical height of several nanometers are found within the islands. Partly, the heights of the ridges are irregular (cf. Figure 1D) and in some cases terrace-like structures with step heights of 1.2 nm (about the length of a single molecule), but also of about 4 nm are found (cf. Figure 1E).

Specular X-ray diffraction was performed on these three films grown at different temperatures; the results are depicted in Figure 2. In the case of the films prepared at 150 °C, Bragg peaks from two different interplanar distances and their higher-order reflections are observed. One peak series (labeled as 00L in Figure 2) is observed up to sixth order, with the first order peak corresponding to an interplanar distance of 12.1 Å. This value is in good agreement with the interplanar distance of the 001 peak (d_{001} = 12.2 Å) taken from the known bulk crystal structure with a unit cell of a = 11.611(12) Å, b = 4.842(2) Å, c = 12.609(16) Å, and β = 104.42(6)°. The observed intensities of the 00L peak series agree well with the respective calculated intensities for the known bulk phase. Therefore, we conclude that the known bulk structure of Tyrian purple is present within the sample with a preferred orientation of the crystallites; i.e., their (001) planes are parallel to the substrate surface (001 fiber texture). The preferred orientation reveals that the molecules are standing at the substrate surface, however, with a tilt angle of ∼40° with respect to the surface normal (the van der Waals length of the molecule is 17.8 Å). Note that epitaxial growth of Tyrian purple on polyethylene single crystals results in a different orientation with the (010) plane of Tyrian purple parallel to (110) of polyethylene.

The first peak in the other series of peaks corresponds to an interplanar distance of 15.2 Å, where higher-order reflections are also observed (labeled as surface induced phase (SIP) in Figure 2; arrows indicate the peak positions) and cannot be explained by any known polymorph. This peak series is also indexed by 00L; since the observed interplanar distance of the Bragg peaks is comparable to the bulk structure. The distance of 15.2 Å suggests that the molecules are similarly oriented in this unknown polymorph, however, with a smaller tilt angle to the surface normal of about 25°. Similar features of polymorphism are found in thin films of other rod-like conjugated molecules where the polymorph with the smaller tilt angle is found to be a SIP. In the following discussion we will use the term SIP for the unknown phase and give further evidence justifying the presence of a surface-induced phase in Tyrian purple films.

The films prepared at a lower substrate temperature of 50 °C show both crystallographic phases, however, with strongly reduced intensity of the bulk crystal structure relative to the SIP. In contrast, at a substrate temperature of 50 °C only Bragg peaks assigned to the surface-induced polymorph are present. As an aside we note that this temperature dependent polymorphism of Tyrian purple is also observed in thin films prepared on thermally oxidized silicon as well as on glass surfaces (not shown).

In-situ temperature studies were performed to investigate the thermodynamic stability of crystalline Tyrian purple. In Figure 3, such a temperature study of a film grown on a polyethylene surface at a substrate temperature of 100 °C is shown. Starting from room temperature, the dominant diffraction peak arises due to the SIP, and only weak traces of the bulk phase are present. With increasing temperature, a slight reduction of the SIP peak intensity is observed. At a temperature of 210 °C, a sudden change in the diffraction pattern takes place: the 001 bulk phase peak increases considerably in intensity, which is accompanied by a sudden drop in intensity of the 001 SIP peak. This phase transition is also accompanied by a drastic change of the peak width. Subsequent cooling to room temperature did not result in a reversible behavior of the phase transition, and the bulk phase remains the only one present. The irreversible nature of the phase transition reveals that the temperature dependent phase behavior of Tyrian purple is not enantiotropic. Additionally, the irreversibility of the phase transition shows that the SIP is a metastable phase.
Heating samples beyond 210 °C reveals a rather constant peak intensity of the bulk phase up to a temperature of 250 °C; at higher temperatures the Bragg peak of the bulk phase disappears. Cooling back to room temperature is not accompanied by the reappearance of any Bragg peaks as the molecular material has sublimated from the substrate surface.

The next step of the experimental investigations was performed on Tyrian purple films prepared at room temperature by PVD. Figure 4 shows X-ray reflectivity (XRR) measurements of samples prepared with different thicknesses. The nominal film thickness of the films varies from a submonolayer coverage of 0.6 nm to a monolayer coverage of 1.5 nm up to multilayer coverages of up to 9 nm. The X-ray reflectivity curves show critical angles between 0.193° (qz = 0.027 Å−1) and 0.203° (qz = 0.029 Å−1), which is close to the expected critical angle of amorphous silicon dioxide (αC = 0.216°, qz = 0.031 Å−1) and that of crystalline Tyrian purple (αC = 0.204°, qz = 0.029 Å−1). In the case of films grown on chemically cleaned surfaces (Figure 4A), two characteristic features are observed with increasing film thickness. First, a distinct minimum is formed at qz ≈ 0.45 Å−1 and second, a Bragg peak at qz ≈ 0.45 Å−1 develops. The peak position of the Bragg peak shifts with the nominal film thickness from 0.456 Å−1 (nominal thickness 0.6 nm) to 0.422 Å−1 (9.0 nm); detailed values are given in Table 1. Thin films prepared on plasma-etched silicon oxide surfaces show a comparable tendency of peak shift as a function of nominal film thickness (Figure 4B). In general, the position of the Bragg peak clearly confirms that the SIP is present within the thin films. Nevertheless, the interplanar distance varies between 14.9 and 13.8 Å for crystallites grown on chemically cleaned silicon oxide and 15.1 Å to 14.7 Å on the plasma-etched silicon oxide surface. This might suggest that in the very low thickness regime, a slight variation of the molecular packing occurs. Another possible explanation for this peak shift could be a coherent superposition of X-ray reflectivity from a molecular underlayer with X-ray diffraction due to three-dimensional crystallites, as has already been observed for the initial growth of pentacene in thin films. The presence of Bragg peaks for nominally submonolayer thick films reveals that island formation dominates the film growth. Estimated crystallite sizes, calculated on the basis of the peak width, are given in Table 1. The formation of a continuous monolayer across the substrate surface is not observed.

Table 1. Peak Positions qz, Interplanar Distance d001, and Crystallite Size Λ, of Films with Different Nominal Thicknesses Prepared on Two Different Substrates, as Deduced from the 001 Bragg Peak

| film thickness [nm] | qz [Å−1] | d001 [Å] | Λ [Å] |
|---------------------|---------|----------|------|
| chemically cleaned SiO2 | plasma-etched SiO2 |
| 0.6                 | 0.456   | 13.8     | n/a  |
| 0.9                 | 0.455   | 13.8     | 83   | 0.417 | 15.1 | n/a  |
| 1.5                 | 0.460   | 13.7     | 79   | 0.426 | 14.8 | 80   |
| 3.0                 | 0.448   | 14.0     | 115  | 0.439 | 14.3 | 93   |
| 4.5                 | 0.438   | 14.4     | 114  | 0.438 | 14.4 | 106  |
| 6.0                 | 0.431   | 14.6     | 137  | 0.433 | 14.5 | 127  |
| 9.0                 | 0.422   | 14.9     | 171  | 0.428 | 14.7 | 159  |

For ultrathin films no reliable values could be extracted from the measurements.
Fits of the X-ray reflectivity curves were performed to obtain total electron density profiles across the thin film. Figure 5A shows the fitted curves superimposed on the experimental data, the electron density profiles obtained from the fits are depicted in Figure 5B. Oscillations of the electron density are due to the regular crystalline packing across the layers. A slight reduction of the electron density is observed at the substrate/organic interface around \( z \approx 1 \) nm. It seems that the order at the interface is better developed for the chemically cleaned surface, since the oscillations are sustained down to the silicon oxide interface. The continuous reduction of the electron density at \( z > 7 \) nm appears due to surface roughness.

After the detailed investigations of the out-of-plane order by X-ray reflectivity and specular X-ray diffraction, the in-plane order of the films is studied by grazing incidence X-ray diffraction (GIXD). Characteristic GIXD patterns are given in Figure 6 for films of 9 nm nominal thickness prepared on chemically cleaned (Figure 6A) and plasma-etched silicon oxide surfaces (Figure 6B).

Strong Bragg peaks reveal crystallographic in-plane order within the thin films. Rods with distinct Bragg peaks along \( q_z \) are found at \( q_{xy} \) values of 1.08, 1.63, and 1.91 Å\(^{-1}\). The indexation of Bragg peaks corresponding to the surface-induced structure is performed on the basis of assigning the peaks observed in the specular scan (\( q_{xy} = 0 \)) as 00L as described above (i.e., the 001 plane is parallel to the substrate surface); as a consequence, the crystallographic axes \( a \) and \( b \) are parallel to the substrate surface. In a subsequent step, the Bragg peaks along \( q_{xy} = 1.08 \) Å\(^{-1}\) are assigned to the 0 \( \pm 1 \)L peak series, peaks along \( q_{xy} = 1.63 \) Å\(^{-1}\) to \( \pm 10L \) and peaks along \( q_{xy} = 1.91 \) Å\(^{-1}\) to \( \pm 11L \). The lattice constants of a triclinic unit cell can be
determined by using three clearly defined $q_{fi}$ values and three $q_{z}$ values together with their corresponding Miller indices. Analytical expressions are derived to calculate the lattice constants for a triclinic unit cell with the $ab$-plane parallel to the substrate surface (see eqs 1 and 2).

\[
\begin{pmatrix}
q_{xy1}^2 \\
q_{xy2}^2 \\
q_{xy3}^2
\end{pmatrix} = \begin{pmatrix}
h_1^2 k_1^2 - 2h_1 k_1 \\
h_2^2 k_2^2 - 2h_2 k_2 \\
h_3^2 k_3^2 - 2h_3 k_3
\end{pmatrix} \begin{pmatrix}
\frac{2\pi}{a \sin \gamma} \\
\frac{2\pi}{b \sin \gamma} \\
\frac{2\pi}{c \sin \epsilon}
\end{pmatrix}
\]

(1)

\[
\begin{pmatrix}
q_{z1} \\
q_{z2} \\
q_{z3}
\end{pmatrix} = \begin{pmatrix}
-h_1 - k_1 l_1 \\
-h_2 - k_2 l_2 \\
-h_3 - k_3 l_3
\end{pmatrix} \begin{pmatrix}
\frac{2\pi}{a \sin \delta} \\
\frac{2\pi}{b \sin \mu} \\
\frac{2\pi}{c \sin \epsilon}
\end{pmatrix}
\]

(2)

where

\[
\mu = \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \gamma \sin \epsilon}, \quad \delta = \frac{\cos \beta - \cos \alpha \cos \gamma}{\sin \gamma \sin \epsilon}
\]

and

\[
\sin \epsilon = \frac{\sqrt{1 - \cos \alpha^2 - \cos \beta^2 - \cos \gamma^2 + 2 \cos \alpha \cos \beta \cos \gamma}}{\sin \gamma}
\]

By solving the first set of eq 1 the unit cell parameters which lie in-plane, namely $a$, $b$, and $\gamma$, can be determined. $q_{xy}$ values from three independent Bragg peak series (here 01L, 10L, and 11L) are required. Solving the second set of eqs 2 leads to parameters $\alpha$ and $\beta$, using the relations

\[
\cos \alpha = \frac{\mu + \delta \cos \gamma}{\sqrt{\sin^2 \gamma + \delta^2 + \mu^2 + 2\delta \mu \cos \gamma}},
\]

\[
\cos \beta = \frac{\delta + \mu \cos \gamma}{\sqrt{\sin^2 \gamma + \delta^2 + \mu^2 + 2\delta \mu \cos \gamma}}
\]

and the lattice constant $c$ can be calculated from $\frac{2\pi}{c \sin \epsilon}$ using

\[
\sin \epsilon = \frac{\sin \gamma}{\sqrt{\sin^2 \gamma + \delta^2 + \mu^2 + 2\delta \mu \cos \gamma}}
\]

The most convenient method to solve eqs 1 and 2 is by calculating the inverse matrices.

In the case of the film prepared on the chemically cleaned silicon oxide (Figure 6A), the following values were used for the calculation of $a$, $b$, and $\gamma$: $q_{xy} = 1.08 \AA^{-1}$, $q_{z} = 1.63 \AA^{-1}$, and $q_{fi} = 1.91 \AA^{-1}$ with Miller indices 01L, −10L, and 11L, respectively. To determine $\alpha$, $\beta$, and $c$, three peaks with different $q_z$ values are taken: $q_z = 0.32 \AA^{-1}$ (101), $q_z = 0.75 \AA^{-1}$ (−102), and $q_z = 1.01 \AA^{-1}$ (012); the resulting lattice constants are given in Table 2. The volume of the crystallographic unit cell is 328.9 Å³, which is slightly smaller than the volume of one Tyrian purple molecule in the bulk crystal structure (340.9 Å³). This shows that the unit cell contains only one molecule.

Table 2. Calculated Unit Cell Parameters for the Surface-Induced Phase of Tyrian Purple on Chemically Cleaned and Plasma-Etched Silicon Oxide

|                  | chemically cleaned SiO₂ | plasma-etched SiO₂ |
|------------------|--------------------------|-------------------|
| $a$ [Å]          | 3.86                     | 3.84              |
| $b$ [Å]          | 5.83                     | 6.00              |
| $c$ [Å]          | 14.86                    | 14.67             |
| $\alpha$ [deg]   | 98.2                     | 94.0              |
| $\beta$ [deg]    | 94.2                     | 93.0              |
| $\gamma$ [deg]   | 87.1                     | 87.0              |
| $V$ [Å³]         | 328.87                   | 336.31            |

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In the case of the film prepared on the plasma-etched surface (Figure 6B), the following peaks and $q$ values were used to calculate the unit cell: 011 ($q_{xy} = 1.05 \AA^{-1}/q_{z} = 0.50 \AA^{-1}$), −102 ($q_{xy} = 1.64 \AA^{-1}/q_{z} = 0.78 \AA^{-1}$), 110 ($q_{xy} = 1.90 \AA^{-1}/q_{z} = 0.15 \AA^{-1}$), which results in slightly different lattice constants and a slightly enlarged volume of the unit cell compared with the structure found on chemically cleaned substrates (cf. Table 2).

On the basis of the experimentally determined crystallographic unit cell of the surface-induced phase of Tyrian purple on a plasma-etched silicon oxide surface, molecular dynamics (MD) simulations were performed to determine the molecular packing and give a complete crystal structure solution. Initial starting structures were generated by expansion of the unit cell volume by 30% and the random alignment of a single molecule. A short MD run of 10 ps was performed at 150 K, during which the unit cell was shrunk back to its experimental dimensions. The resulting structures were sorted in groups based on the simulated powder diffraction pattern and the total energy. The molecule was allowed to bend during the simulation, but due to the structure of the chemical bonds within the molecule the best solutions were straight again. The best structures were used as a starting point for further MD simulations in which the initial volume of the unit cell was expanded only by 5% and the alignment of the single Tyrian purple molecule rocked randomly by 0.3 degrees along Cartesian directions. The structures with the lowest energies were selected and optimized with density functional theory. All selected solutions pack in an identical way as could be expected from basic packing consideration of a single molecule with the given size of the crystallographic unit cell. The molecules form stacks with their aromatic planes along the $a$-axis, hydrogen bonding along the $b$-axis and a slight tilt of the long molecular axis relative to the pole of the $ab$-plane. The final structure was selected on the basis of the experimental intensities by calculating structure factors and comparing them to the experimental peak intensities. Please note that due to experimental limitations this comparison is not fully correct since experimental geometry factors, e.g. Lorentz and polarization factors, sample absorption, area factor, etc., are not taken into account.41,42

In the case of the 9 nm film prepared on plasma-etched silicon oxide, the crystal structure with the best agreement is compared to the experimental diffraction data in Figure 6B. Bragg peaks are represented by circles where the exact position is given by their centers and the structure factors by their areas. Overall, we find an excellent agreement for the Bragg peaks along $q_{xy} = 1.05 \AA^{-1}$ and $q_{z} = 1.64 \AA^{-1}$ where the intensity variation of the peaks matches the calculated structure factors.
The solution of the surface-induced phase of Tyrian purple is provided as CCDC 1449758.

The molecular arrangement in relation to the crystallographic unit cell is depicted in Figure 7A. Tyrian purple forms molecular π-stacks with the aromatic planes closely packed parallel to each other. Within one stack the average distance between the aromatic planes of neighboring molecules is 3.27 Å. Hydrogen bonds connect two stacks along the b-axis, where a single molecule of one stack is connected laterally to a single molecule in the neighboring stack. In total, four hydrogen bonds are formed by a single molecule, they all have an equal distance of 2.80 Å between the nitrogen and oxygen atoms. Along the c-axis, the stacks are separated by layers of bromine atoms with an intermolecular distance of 3.90 Å. Since the shortest distance between neighboring bromine atoms is larger than the sum of the van der Waals radii (3.7 Å), it can be concluded that halogen interactions are not decisive for the molecular packing.

The present molecular packing is similar to that of the bulk structure of Tyrian purple, as depicted in Figure 7B. There, likewise, molecular stacks are formed with an average distance between the aromatic planes of 3.45 Å. However, molecules in neighboring stacks are tilted in opposite directions so that a single molecule of one stack is connected to two molecules of a neighboring stack. Even in that case, one molecule forms four hydrogen bonds with a hydrogen bond distance of 2.95 Å. The closest distance between two bromine atoms is 3.53 Å.

DISCUSSION

The crystallization of the molecule Tyrian purple was investigated in thin films on the weakly interacting surfaces polyethylene and silicon oxide. The variation of thin film preparation conditions such as substrate temperature and film thickness, combined with X-ray diffraction studies, reveals two key results. First, a surface-induced polymorph with a previously unknown crystal structure is found when the thin film preparation is performed at a substrate temperature of 50 °C, while at elevated substrate temperatures of 150 °C the known bulk phase of Tyrian purple forms (cf. Figure 2). Second, we observe a non-negligible dependence of the crystal structure on the type of silicon oxide surface employed (cf. Figure 4 and Figure 6).

The formation of the new polymorph of Tyrian purple in thin films is in analogy to other aromatic molecules, where surface-induced phases are clearly assigned. Rod-like, rigid molecules like pentacene and its derivatives, α-sexithiophene, diindenoperylene, but also rod-like molecules with flexible (alkyl-) side chains like diocetyl-terthiophene (DOTT) or diocetylxy-benzothienobenzothiophene (C₈-O-BTBT-OC₈), crystallize with their long molecular axes approximately perpendicular to the substrate surface with an overlap of the aromatic units parallel to the substrate surface. Moreover, a strong interplay between growth kinetics and SIP formation has been clearly demonstrated. We observe that the formation of the Tyrian purple SIP is favored at low temperatures, analogously to pentacene, but in contrast to the SIPs of p-sexiphenyl and α-sexithiophene, which appear at elevated temperatures. In-line with our observations, surface-induced phases often show a metastable character as observed by solvent treatment, thermal annealing, and aging experiments.

Our growth studies reveal that Tyrian purple shows island growth (Volmer–Weber type), since already at sub-monolayer coverage, the 001 Bragg peak is observed in specular X-ray diffraction, which reveals three-dimensional growth. This is in clear contrast to the film growth of other organic electronic molecules on silicon dioxide surfaces. There, the formation of an initial closed first monolayer is often observed where the molecular packing may deviate slightly from the molecular packing of the subsequently formed three-dimensional crystallites.

The GIXD patterns of the surface-induced phase prepared on the chemically cleaned and the plasma-etched surfaces are slightly shifted with respect to each other (cf. Figure 6). Determination of the crystallographic unit cells by indexing the reciprocal space maps gives slightly different values for the lattice constants (cf. Table 2). Surprisingly, no differences are observed for the lattice constant a, some variations are observed for the lattice constants b and c. Comparing this result to the molecular packing within the surface-induced polymorph (Figure 7A) reveals that the π-π stacking of the Tyrian purple molecules forms along the a-axis and therefore does not vary. This means that the formation of stacks of parallel-arranged Tyrian purple molecules is only weakly influenced by different substrates. However, since the lattice parameter b varies considerably and the hydrogen bonds are directed along this axis, this suggests that the different hydrogen bonding geometries of neighboring molecular stacks might be

Figure 7. (A) Molecular packing of Tyrian purple molecules in the surface-induced crystal phase, as viewed along the b-axis. (B) The bulk structure of Tyrian purple viewed along the b-axis with the depiction of two consecutively arranged molecular stacks, the stack behind is displayed with light gray atoms.
responsible for the observed variation in the molecular packing. Note that the main difference between the bulk and the surface-induced structure of Tyrian purple is, indeed, the hydrogen bonding geometry between neighboring stacks. In the surface-induced phase two neighboring stacks are oriented parallel to one another, while in the bulk phase one stack is tilted with respect to its neighboring stack (cf. Figure 7B). Comparably small variations of the molecular packing have also been reported recently for TIPS-pentacene, where, additionally, a marked influence on the performance of organic electronic devices was found.36

■ CONCLUSION

To summarize, a surface-induced polymorph of Tyrian purple was found via physical vapor deposition on weakly interacting surfaces, namely, silicon oxide and polyethylene. This phase forms at substrate temperatures below 50 °C, while at a substrate temperature of 100 °C the well-known bulk structure of Tyrian purple forms. Heating experiments show that the surface-induced phase undergoes a solid-state phase transition to the bulk phase at 210 °C. The irreversibility of this transition reveals the metastable character of the surface-induced phase.

The formation of the surface-induced phase is studied at two different silicon oxide surfaces: the first is a plasma-etched surface with a higher polar part of the surface energy than the second, chemically cleaned, surface. In both cases, a closed monolayer of up-right standing molecules does not form and instead the formation of three-dimensional islands is already observed in the nominal sub-monolayer regime. Volmer–Weber type growth behavior is identified by the appearance of Bragg peaks at nominal coverages in the sub-monolayer regime. Calculated electron densities from XRR investigations reveal reduced electron densities close to the substrate/organic interface and also a highly rough thin film surface due to the presence of islands. Slight variations of the Bragg peak positions are observed as a function of the crystallite size and the substrate type.

The crystal structure of the surface-induced phase is solved for a thin film with a nominal thickness of 9 nm grown on a plasma-etched silicon oxide surface. Grazing incidence X-ray diffraction patterns were successfully indexed, and the lattice constants of a triclinic unit cell were deduced using analytical expressions. These unit cell dimensions were used as input for molecular dynamics simulations with density functional theory calculations. It is found that the packing motif of this novel polymorph is comparable to the bulk phase; Tyrian purple molecules stack with their aromatic planes parallel to each other while the molecular stacks are interconnected by hydrogen bonds. The main difference between the two polymorphs is the nature of the hydrogen bond network between the neighboring stacks. For the surface-induced phase grown on two different surfaces, we observed small packing differences which are also due to slightly varying hydrogen bond geometries, as variations of the unit cell parameter along the direction of the hydrogen bonds are experimentally observed.

■ ASSOCIATED CONTENT

Accession Codes

CCDC 1449758 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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