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Nanoimaging of Orientational Defects in Semiconducting Organic Films

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ABSTRACT: The development of defect analysis for inorganic semiconductors in the past century paved the way for the success story of today's electronics. By analogy, defect analysis plays a critical role in developing and improving devices based on organic molecular semiconductors. However, because of weak molecular interactions, absent in inorganic semiconductors, device-relevant thin organic films are susceptible to the formation of defects in the molecular orientation, which in turn have a profound impact on the performance in the optoelectronic applications. To address this problem, we broaden the applicability of scattering-type scanning near-field optical microscopy (s-SNOM) and utilize the light-induced anisotropic response of vibrational modes to reveal the defects in molecular orientation. We show that in the case of molecular islands with steep crystal facets only the scattered s-SNOM optical amplitude can be exploited to describe the molecular



arrangement reliably, while the phase-based analysis leads to artifacts. The presented s-SNOM analysis of molecular defects can be universally applied to diverse topographies, even at the nanoscale.

INTRODUCTION

Defect analysis has played a major role in the development of inorganic semiconductors for more than 50 years.^{1,2} It is equally essential for the organic molecular semiconductors, as only highly ordered films are suitable for stable, efficient, and reproducible performance of novel organic-based devices.³⁻⁵ In contrast to inorganic semiconductors, the weak van der Waals interactions between the molecules and a rotational degree of freedom lead to a new class of local structural defects and polymorphic phases absent in conventional semiconductors.⁶ Furthermore, because of the inherent anisotropic shape in the majority of π -conjugated molecules, additional defects in molecular orientations can occur. These orientation-dependent defects have a strong influence on the optoelectronic properties (e.g., power conversion efficiency) as well as on the mechanical ones.⁷⁻¹¹ Predominantly optical techniques are employed to characterize the orientation of molecules or polymers. Unfortunately, the diffraction limit severely restricts the measurement to relatively large areas, and the optical response is thus averaged over many nanoobjects.^{12,13} A significantly better spatial resolution can, in principle, be achieved by X-ray spectroscopy and scattering techniques, which, on the other hand, are limited by low scattering cross sections and small damage thresholds.^{14,15}

A technique that overcomes the diffraction limit and enables nanoimaging and spectroscopy with unprecedented spatial

resolution compared to optical spectroscopy techniques utilizes photons for localized nanotip-enhanced sensing and leads to a wavelength-independent resolution at the nanoscales even in the far-infrared or terahertz region.^{13,16-19} The most advanced method is the scattering-type scanning near-field optical microscopy (s-SNOM) which allows access to detailed physicochemical properties of a wide range of materials.^{20–24} s-SNOM enables hyperspectral imaging with a high spatial resolution, providing information about the inherent nanocrystalline structure, local polymorphs, heterogeneity, or strain in thin films. It is also known that the molecular orientation is in principle accessible from the s-SNOM response, as the transition dipole moment of the molecular vibrations interacts with the light-induced dipole in the probing tip.^{13,18,25,26} Despite immense progress in recent years, the molecular orientation analysis by s-SNOM is still not well established, and only a few reports were published (see refs 27 and 28). So far, the alignment of the molecules was determined from the scattered near-field phase exclusively, which might be beneficial

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Article

for relatively flat surfaces but might lead to artifacts for discontinuous layers and grains, occurring either as a growthinduced feature or as a defect.

In this paper, we investigate the defects in the molecular orientation, exploiting the frequency-dependent optical amplitude of the scattered IR light. We observe orientational defects uncorrelated to the surface topography that have direct implications for the functionality of organic electronic systems. Furthermore, we show that the near-field phase is not an appropriate metric for mapping the molecular alignment in nanocrystals. For our study, diindenoperylene (DIP, $C_{32}H_{16}$) was used as a representative π -conjugated material that was shown to be promising for organics optoelectronics.^{29,30} However, the technique presented is universal and can be applied to any material with an anisotropic vibrational response.

METHODS

Sample Preparation. DIP molecules were thermally evaporated on a few-layer MoS₂ substrate by organic molecular beam deposition (OMBD). The cell temperature was set to 255 °C, giving the average deposition rate of ~1.5 Å/min (monitored in real time with a quartz microbalance) for the ambient pressure below $\sim 2 \times 10^{-8}$ mbar. The temperature of the MoS₂ underlayer was kept at 50 °C during the molecular deposition. The few-layer MoS₂ substrate was prepared by the magnetron sputtering of 1 nm thick molybdenum layer onto the (0001) Al_2O_3 substrate. Mo film was subsequently annealed in sulfur vapors at 800 °C in a N2 ambient atmosphere.³¹ The so-prepared MoS₂ substrate shows an inplane alignment of MoS_2 atomic layers; that is, the (001) lattice planes are oriented parallel to the substrate surface.³² For the FTIR ATR measurements, we utilized 16 nm thick DIP layers deposited by OMBD on a Si substrate with a native oxide layer.

IR s-SNOM. We employed a commercially available type of the scattering scanning near-field optical microscope (neaS-NOM, Neaspec GmbH), operated in the AFM tapping mode with standard PtIr-coated Si probes of ~20 nm tip radius (NCPt arrow, NanoAndMore GmbH). Sample imagining was performed by using a tunable QCL laser (MIRcat, Daylight Solutions) at a fixed wavelength of 1450 cm⁻¹ and spectral line width of ≤1 cm⁻¹ (FWHM). Detection was performed in a pseudo-heterodyne interferometric setup with HgCdTe and a lock-in amplifier. The detected signal was demodulated at the second harmonic of the tapping frequency (~250 kHz) to eliminate the background interference.

NanoFTIR Mode of s-SNOM. In the broadband spectroscopy mode of s-SNOM, the AFM tip is illuminated by a broadband mid-IR laser source (Toptica Photonics AG), emitting between 650 and 2200 cm⁻¹, with the output power of ~2 mW. The spectral analysis of the backscattered light from the AFM tip is performed by the asymmetric Michelson interferometer. Fourier transformation of the detected signal (being a function of a reference mirror position) simultaneously yields the optical amplitude and phase, which encode the reflectivity and absorption spectra, respectively.

FTIR ATR. We utilized a FTIR spectrometer (Vertex 70v, Bruker) with a microscope (HYPERION 3000, Bruker) coupling. A dedicated ATR objective ($20\times$) with a Ge crystal was used. The obtained ATR data were converted to absorbance spectra by removing the water vapor and CO₂ spectra. **GIWAXS.** We used a custom-made laboratory system equipped by a MetalJet X-ray source (Excillum) with the Xray energy of 9.25 keV ($\lambda = 1.34$ Å). The samples were measured in a vacuum at the angle of incidence of 0.2°. The total X-ray flux was ~10⁸ photons/s, which is far below the damage threshold of the molecular film for a typical counting time of 600 s. The GIWAXS diffraction maps were collected by a hybrid-pixel two-dimensional detector (Pilatus 300 K, Dectris), containing a 320 μ m thick Si sensor.

DFT Calculations. Normal-mode frequencies and the corresponding transition-dipole derivatives were calculated on the optimized structure of DIP by applying DFT with hybrid B3LYP functional and Pople's triple- ζ basis set with additional polarization and diffusion functions (6-311++G-(d,p)). The calculations were performed by the Gaussian 16 software package.³³

RESULTS AND DISCUSSION

Figure 1a shows the topography of thermally evaporated DIP molecules on a few-layer MoS_2 substrate measured by AFM.



Figure 1. Nano-FTIR and s-SNOM signals. (a) AFM topography of DIP islands formed on a few-layer MoS_2 substrate. (b) Average nano-FTIR signal obtained by scanning across DIP crystallites. Near-field optical (c) amplitude and (d) phase of the detected s-SNOM signal at 1450 cm⁻¹. (e) IR-scattered amplitude overlaid on AFM topography (merge of (a) and (c) shown in 3D view). Two distinct molecular orientations—lying-down and standing-up—are indicated by blue and red colors, respectively. The 3D image is rotated in the plane with respect to (a) and (c) for better visibility of individual islands. Scale bar: 2 μ m.

The film exhibits small, spatially separated crystalline molecular islands with an average height of ~ 50 nm. The island-type molecular growth is typical for strongly interacting twodimensional (2D) substrates, with the molecules being commonly arranged in the lying-down orientation.^{8,34-} Simultaneously with the surface topography, we performed nanoscale Fourier transform infrared (nano-FTIR)³⁸ spectroscopy on a few DIP crystallites. The recorded nano-FTIR phase spectra are directly related to the absorption of the sample.^{6,25,39,40} Figure 1b shows the absorption spectrum of DIP crystallites that was obtained as an average of the spectra measured at different locations across several DIP islands. The position of the most prominent absorption peak at ~1450 cm⁻¹ is consistent with the experimental value obtained by Duva et al.41 and the theoretical value calculated by the density-functional theory (DFT) (see Figure S7 in the Supporting Information).

To locally map the DIP orientation in the crystallites, we used s-SNOM (see Figure S1), which is known for its sensitivity to the anisotropic response of molecular vibrational modes relative to the tip-enhanced dipolar field.^{27,28} Besides the standard topography, the scattered light from below the AFM tip enables the reconstruction of the complex dielectric constant of the sample encoded in the near-field amplitude $(A_{\rm NF})$ and phase $(\Phi_{\rm NF})$ of the scattered light.^{25,42} Figures 1c and 1d show a high-resolution imaging of $A_{
m NF}$ and $\Phi_{
m NF}$ using laser illumination at 1450 cm⁻¹, respectively. In the $A_{\rm NF}$ scan (Figure 1c), islands of mainly two distinct magnitudes are clearly visible, represented by blue (smaller $A_{\rm NF}$) and red (larger $A_{\rm NF}$) color. The magnitude of $A_{\rm NF}$ depends on the orientation of the molecular transition dipole with respect to the IR-field-induced dipole along the AFM tip direction.^{13,21} Accordingly, Figure 1c indicates islands with two different (almost orthogonal) molecular orientations within the scanned area. The islands with smaller A_{NF} values (blue) comprise of molecules oriented perpendicular to the tip axis-molecules arranged in the lying-down orientation. This orientation is typical for π -conjugated molecules on 2D substrates, and it significantly prevailed on our sample as well,⁴³ mostly in the areas further from the sample edges (see Figure S2). On the other hand, large $A_{\rm NF}$ values (red) suggest molecules oriented parallel with the tip direction, that is, the standing-up configuration, as schematically indicated in Figure 2a. In the case of the targeted hybrid van der Waals heteroepitaxy, the standing-up molecules represent the defects in molecular



Figure 2. Optical signal dependence on molecular orientation and GIWAXS. (a) Scattered IR amplitude $(A_{\rm NF}$ at 1450 cm⁻¹) dependence on the height of the molecular islands. The tentative orientation of the molecules with respect to the AFM tip is shown for the two dominant $A_{\rm NF}$ magnitudes. (b) GIWAXS pattern of DIP film on a few-layer MoS₂ substrate, showing two distinct molecular orientations and the Yoneda peak.

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orientation that occur due to imperfections of the MoS_2 underlying substrate. The MoS_2 underlayer consists of grains with predominant horizontal orientation of the atomic layers.^{31,32} However, grains with vertical orientation of MoS_2 layers may occur, inducing the standing-up orientation of the DIP molecules.⁴³

At this point, we would like to emphasize that the molecular orientation (relative to s-SNOM tip and substrate surface) has so far been determined from the phase $\Phi_{\rm NF}$ rather than from the amplitude $A_{\rm NF}$.²⁷ We find this approach applicable to relatively smooth surfaces where the optical phase change is caused solely by the dipole moment projection change with respect to tip direction. Most importantly, we found that the change of $\Phi_{\rm NF}$ magnitude can be also induced by steep changes of the morphology (see Figure 1d). Figure 1d shows significant alterations in $\Phi_{
m NF}$ on several molecular islands that are predominantly located on the longer edges of the crystallites (see also Figures S2d and S5b). Similar changes were also observed in the mechanical phase (Φ_{mech}) obtained from the AFM microscope (see Figure S2b). Simultaneous variations in $\Phi_{\rm NF}$ and $\Phi_{\rm mech}$ bound to sharp edges of the crystallites indicate deficiencies in the electronic signal feedback processing rather than abrupt changes of the inherent sample properties. Such phase perturbations are caused by the detection technique, which has a different response for amplitude and phase change. In tapping-mode AFM, the amplitude is linearly proportional to the tip-sample distance during surface scanning. On the other hand, the phase response is highly nonlinear with tip-sample distance, and the changes in phase are greater when compared to the amplitude.^{44,45} The high phase sensitivity is effectively used for material detection with minimal change in the height profile, e.g., for polymer surfaces, cells, or self-assembled monolayers.⁴ However, in the case of abrupt height changes in surface topography, such a nonlinear phase response can lead to erroneous signals. The tapping-mode AFM phase is thus not reliable for determination of the molecular orientation as its magnitude contains artifacts that have no connection with the real dipole reorientation (in the case of $\Phi_{\rm NF}$) or variation of the sample's mechanical properties (in the case of Φ_{mech}). In contrast, $A_{\rm NF}$ is more suitable for direct determination of the molecular arrangement as it is less sensitive to abrupt morphological changes. For this reason, we used $A_{\rm NF}$ solely for the evaluation of the molecular orientation. We note that we observed a topography-related artifact in $A_{\rm NF}$ (see Figure 1c,e) as well. It is described as the edge-darkening artifact causing the $A_{\rm NF}$ reduction at the sharp edges due to the lift of AFM tip.^{24,26,42} However, its contribution was minor compared with the strong artifacts occurring in $\Phi_{\rm NF}$.

Figure 1e shows the surface topography complemented by a tentative molecular orientation in the crystallites. It is evident that the highest islands are formed by the lying-down molecules, where the scattered $A_{\rm NF}$ signal is low. However, the standing-up molecules localized on the substrate's defects form islands with an average height of only ~40 nm. Considering the DIP length of 18.4 Å,⁴⁷ the islands are composed of at least 20 molecular layers. We expect the molecules to fill the whole volume of the molecular island. If only a few molecular layers would cover the bulk defects of the substrate, the magnitude of $A_{\rm NF}$ would be significantly influenced by the number of DIP layers due to the finite s-SNOM penetration depth, which is of the order of tens of nanometers.^{20,27} In the limit of the observed thick molecular

islands, the scattered amplitude is independent of the island height for the standing-up and lying-down molecules, as shown in Figure 2a.

To obtain a more extensive and representative set of $A_{\rm NE}$, we analyzed a larger area of the sample, performing several s-SNOM scans across the surface. The clustering of the $A_{\rm NF}$ values into two sets, as shown in Figure 2a, indicates that only two distinct molecular orientations are present in molecular islands. These orientations are represented by the average $A_{\rm NF}$ value of 1.7 ± 0.4 and 4.0 ± 0.5 , which were provisionally described as lying-down and standing-up molecules, respectively. Here, we would like to emphasize that the position of the long molecular axis with respect to the tip direction, as shown in Figure 2a, was only a rough estimate. To evaluate the molecular orientation more precisely, we employed the grazing-incidence wide-angle X-ray scattering (GIWAXS). A two-dimensional GIWAXS map obtained from the surface area close to the edge of the sample is shown in Figure 2b. The GIWAXS pattern shows the two principal Bragg reflections located at q = 0.38 Å⁻¹, which represent the 001 diffraction peaks of DIP for two different molecular orientations.⁴³ In addition, an intense Yoneda peak is visible at $q_z = 0.02$ Å⁻¹ and a doubling of both 001 diffractions in the vicinity of q = 0.38 $Å^{-1}$ for both molecular alignments. We note that this vertical replication of 001 peaks is caused by the substrate-induced refraction effects, and only the lower peak from the peak doublet corresponds to the direct Bragg diffraction.⁴⁸ The 001 peak position can be utilized to determine the exact molecular orientation with respect to the sample surface, since the unit cell (UC) parameters of thin DIP film and the molecular position within the UC are known (see ref 35 for more details). Employing this knowledge, we calculated the molecular orientations for both 001 diffraction peaks. For the lying-down molecules (where the reciprocal space vector q_{001} is tilted ~13° of the sample surface), the angle between the long molecular axis and the sample surface is $\sim 4^{\circ}$. On the other hand, for the standing-up molecules (where $q_{001}||q_z$), the inclination of the long molecular axis with respect to sample normal (i.e., the direction of the AFM tip) is 19°. For details on the geometrical configurations of the molecules within the unit cell and the sample surface, see Figure S6. The GIWAXS analysis validates independently that the two groups of molecular crystallites detected by s-SNOM with distinct scattering amplitudes can be unambiguously assigned to two, almost perpendicular, molecular orientations that are semantically described as lying-down and standing-up.

In the following, we will explain the $A_{\rm NF}$ ratio obtained by s-SNOM for the two distinct molecular orientations based on the density functional theory (DFT) calculations. From a theoretical point of view, the dependence of spectral-signal magnitude on the molecular orientation is captured by anisotropy of the dielectric tensor at a given frequency. We calculated the dielectric constant ($\varepsilon(\nu)$) of DIP at the highest absorption frequency (i.e., 1450 cm^{-1} ; note that this frequency is slightly shifted in the DFT calculations, see the Methods section), employing the Lorentz model for harmonic oscillators in the local coordinate basis of the molecule (see the Supporting Information). While the oscillator parameters were based on the single-molecular DIP normal modes obtained by DFT, the orientation of the molecules was taken into account by expressing the dielectric constant in the local molecular coordinate frame. In this way, the three diagonal elements of $\varepsilon(\nu)$ are directly related to the optical response of pubs.acs.org/JPCC

the molecule as it is oriented to the incoming field by its long axis (ε_{xx}) , short axis (ε_{yy}) , or the molecular-plane normal (ε_{zz}) .⁴⁹ We further evaluated the ratio of the diagonal components of $\varepsilon(1450 \text{ cm}^{-1})$, i.e., ε_{xx} and ε_{yy} , which corresponds to $A_{\rm NF}$ for two perpendicular orientations of the molecules. We note that only the real part of $\varepsilon(\nu)$ corresponds to $A_{\rm NF}(\nu)$. For the upright-standing molecules with their long axes parallel to the tip axis, the obtained value of $\varepsilon_{xx}/\varepsilon_{yy} \sim 2.3$. Taking into account the tilted orientation of the molecules with respect to the tip axis, being approximately 19° for the standing-up molecules (see Figure S6), the calculated ratio of $\varepsilon_{xx}/\varepsilon_{yy}$ is lowered to ~2.1. This ratio is in good agreement with the experimental value $A_{\rm NF}^{\rm S-U}/A_{\rm NF}^{\rm L-D} \sim 2.4 \pm 0.6$, where $A_{\rm NF}^{\rm S-U}$ and $A_{\rm NF}^{\rm L-D}$ are the scattering optical amplitudes for the standingup and lying-down molecules, respectively. A similar ratio was obtained for $\Phi_{\rm NF}$ when the edge artifacts were ignored, and only the signal from the center of the crystallites was considered (see Figures S3 and S4). The surprisingly small ratio of A_{NF} for two perpendicular molecular orientations can be explained by the existence of an orthogonal vibrational mode in the spectral vicinity of the dominant vibration at 1450 cm⁻¹, as schematically depicted in Figure 3. Figure 3 shows the



Figure 3. Adjacent orthogonal vibrational modes in the IR spectrum of DIP. ATR spectrum of thin DIP film (black curve) together with the Lorentzian fits of three pronounced absorptions in the vicinity of 1450 cm⁻¹ (green, blue, and red peaks). The fits emphasize the coupling of the two orthogonal vibrating modes at the s-SNOM measuring wavelength of 1450 cm⁻¹. Deformation patterns of the two adjacent vibrational modes positioned at 1441 and 1450 cm⁻¹ are illustrated. The arrows indicate the dominant movement of the carbon and hydrogen atoms. The green peak represents a vibrational mode at 1421 cm⁻¹ that does not interfere with the pronounced peak at 1450 cm⁻¹.

IR spectrum of the thin DIP layer in the vicinity of the most intense absorption at 1450 cm⁻¹. The IR spectrum was measured by an FTIR microscope in the attenuated total reflection mode (ATR), and the peaks were fitted by a Lorentzian function. According to DFT calculations, the absorption peak at 1450 cm⁻¹ corresponds to the vibrational mode with B_{1u} symmetry, having the transition dipole along the long molecular axis. However, another vibrational mode is present at 1441 cm⁻¹ with the transition dipole along the short molecular axis (B_{2u} symmetry). Theoretical analysis confirms that because of the finite broadening $\Gamma \sim 3$ cm⁻¹ of the dominant peak, there is a substantial coupling between the two orthogonal modes near 1450 cm⁻¹. Such crosstalk reduces the overall A_{NF} signal measured by s-SNOM for the standing-up molecules and enhances the A_{NF} signal for the lying-down

molecules at 1450 cm⁻¹. The calculated ratio of $\varepsilon_{xx}/\varepsilon_{yy}$ or the experimentally determined value of $A_{\rm NF}^{S-U}/A_{\rm NF}^{L-D}$ is thus considerably reduced. Finally, comparing the scattered optical amplitudes obtained by s-SNOM and calculated by the DFT calculations, one can directly determine the molecular orientation with a rather high accuracy (provided that the crystallites are of the same material). We would like to emphasize that while the results presented here were obtained for DIP, this technique is universal as it can be generally applied to essentially any material with an anisotropic optical response. However, the resolution in molecular orientation is limited by the spectral proximity of the orthogonal vibration modes.

In summary, we employed IR s-SNOM to map defected molecular crystallites on the nanoscale. We found that the defected crystallites have different orientations of π -conjugated molecules induced by the substrate imperfections. We presented a qualitatively new approach that exploits the optical amplitude of the scattered light rather than the optical phase, which has been used so far. We show that the IR field response to molecular vibrations encoded in the optical amplitude shows minimal perturbations for abrupt changes of local surface topography. On the other hand, the optical phase exhibited a highly nonlinear behavior that was strongly correlated to structural variations or topography edges. We observed two distinct groups of molecular islands with almost orthogonal molecular orientations on the low-dimensional underlying substrate. The relatively small ratio of the optical amplitudes for the determined molecular arrangement was explained by the vicinity of two orthogonal normal vibrations. We further showed that the presented s-SNOM technique is based on the relative ratio between the standing-up and lyingdown molecules for a given material and does not require a comparison with a reference. We believe that the extraordinary combination of molecular alignment sensitivity and the resolution at nanoscale offered by the tip-enhanced IR microscopy, as demonstrated in our paper, will contribute to the analysis of the defects in the semiconducting organic films and subsequently extend their application in organic (opto)electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c00059.

Figures S1-S7 and Table S1 (PDF)

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Notes

The authors declare no competing financial interest.

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