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Infrared Vibrational Nano-Crystallography and -Imaging

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Short Title: Infrared Nano-Crystallography and -Imaging

Teaser (125 characters): Nanoscale spectroscopy and imaging of organic materials reveal heterogeneity in molecular orientation within and between crystalline domains.

Molecular solids and polymers can form low symmetry crystal structures exhibiting anisotropic electron and ion mobility in engineered devices or biological systems. The distribution of molecular orientation and disorder then controls the macroscopic material response, yet is difficult to image with conventional techniques on the nanoscale. Here we demonstrate a new form of optical nano-crystallography combining scattering-type scanning near-field optical microscopy (s-SNOM) with both optical antenna and tip selective infrared vibrational spectroscopy. From the symmetry selective probing of molecular bond orientation with nanometer spatial resolution, we determine crystalline

phases and orientation in aggregates and films of the organic electronic material perylenetetracarboxylic dianhydride (PTCDA). Mapping disorder within and between individual nanoscale domains, the correlative hybrid imaging of nanoscale heterogeneity provides insight into defect formation and propagation during growth in functional molecular solids.

Introduction

Heterogenous molecular spatial distribution, morphology, and structure define coupling and photophysical properties of organic electronic materials and biological systems. Directional bonding and intermolecular interactions lead to anisotropic ion, electron, and hole mobilities. In molecular devices, charge mobility is typically confined to one or two dimensions and has a high sensitivity to crystallinity, defects, and nanoscale orientation. Mobility enhancements of over two orders of magnitude have been demonstrated by, *e.g.*, improving long-range orientational ordering in spin-cast conductive polymers (1, 2) and engineering oriented growth of crystals within field-effect transistors and organic light-emitting diodes (3, 4).

Optical crystallography measures crystal axis orientation through the anisotropic response of electronic or vibrational modes, based on the projection of transition dipoles along the electric field vectors of incident radiation (5). Complex soft matter has significant heterogeneity on the nanometer length scale, however, and conventional techniques typically measure only a diffraction-limited response that is spatially averaged over a large sample area. Superresolution methods can determine molecular orientation in materials but require suitable optical response or exogenous fluorescent probes (6–8). High spatial resolution crystallography is in principle possible using electron or X-ray methods but restrictions abound due to the low scattering cross section of organic materials, requirements for sufficient crystallinity, special sample preparation requirements, and sample damage (9–12).

Vibrational spectroscopy can be used for non-destructive optical crystallography across a wide range of inorganic, organic, and biological systems, additionally providing information on crystalline phase, chemical identity, and local chemical environment (13–16). Selective probing of characteristic vibrational modes can directly measure molecular orientation and crystallinity. Infrared optical crystallography utilizes an anisotropic material response proportional to the projection of vibrational transition dipole, symmetry selected by polarization and k -vector of incident and emitted radiation, albeit limited in momentum space compared to X-ray techniques and optical spatial resolution.

Here, we use scattering-type scanning near-field optical microscopy (s -SNOM) with combined tip- and vibrational-mode polarization and spectral selectivity for optical nano-crystallography as shown in Figure 1a. In s -SNOM, the metallized tip of an atomic force microscope (AFM) localizes and enhances the optical field linearly polarized parallel with respect to the tip axis. The resulting anisotropic linear and nonlinear optical response of the coupled tip and sample has already been applied to phonon selection rules in solids and broken symmetries in ferroelectrics (17–19). We extend this approach to IR nano-crystallography of molecular and soft matter using **linearly polarized near-field excitation with selection rules for** vibrational modes, simultaneously providing chemical and polymorph identification and mapping heterogeneity in the local environment. We measure crystalline orientation with sub-domain spatial resolution in films and aggregates of the molecular semiconductor perylenetetracarboxylic dianhydride (PTCDA). We perform hybrid correlative imaging by combining optical and topographic information in order to determine the characteristic length scales of order. We observe orientational defects with implications towards understanding growth mechanisms and enabling directed design of molecular devices.

PTCDA has attracted interest in organic electronics due to its high charge carrier mobility, crystallinity, and chemical stability (20). Good device performance can be obtained in

high purity thin films with well-ordered morphology and large crystalline domains, typically forming in one of two polymorphs, α or β , with both monoclinic structures containing stacked sheets of PTCDA arranged in a herringbone pattern, as shown in Figure 1b. However, the charge carrier mobility of PTCDA is anisotropic and is significantly higher along the direction of π -stacking (21). Even in devices with high crystallinity and μm grain size, misorientation of crystalline domains with respect to the larger device architecture can decrease performance (3, 22). In vacuum deposited films, PTCDA crystals can be grown with the a -axis oriented along surface normal, favoring π -stacking (Figure 1c). However, the morphology is sensitive to growth conditions (23–25), substrate interactions (26), surface polymorphs distinct from the bulk phase (27, 28), minority phases (29), and defects. Although the structure in PTCDA and related molecular materials has been investigated at length scales ranging from molecular adsorption conformation to ensemble-averaged crystallinity, a unified understanding of defects and domain structure remains elusive.

Experiment

We use the combination of both narrowband IR s -SNOM based on tunable quantum cascade lasers (QCLs) and broadband synchrotron infrared nano-spectroscopy (SINS) (30–32). Figure 1a shows the IR s -SNOM setup. Polarized IR light from a tunable laser or synchrotron is focused onto a metalized AFM tip operated in intermittent contact mode (see Methods). Tip-scattered near-field signal is combined with light from a reference arm and interferometrically amplified and detected, measuring the complete IR optical response through the frequency dependent optical amplitude $A_{NF}(\bar{\nu})$ and phase $\Phi_{NF}(\bar{\nu})$ (32–34).

The frequency dependent **optical response for linearly polarized near-field excitation of characteristic modes with known transition dipoles** is a general measure of molecular orientation relative to the s -SNOM tip and substrate. We implement tip-enhanced IR optical nano-

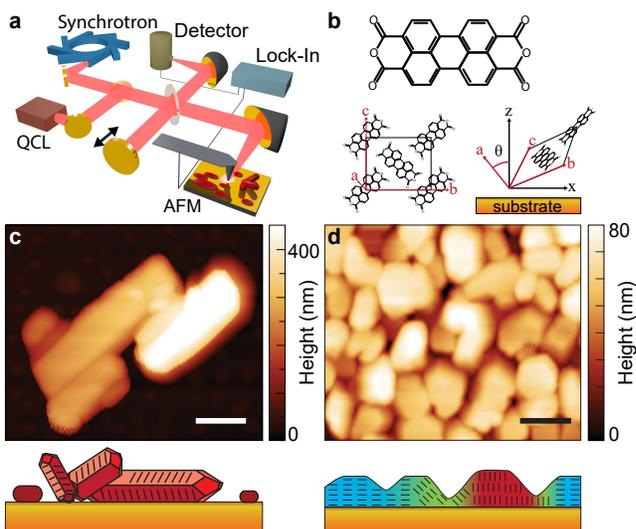


Figure 1: (a) Schematic of IR *s*-SNOM using both synchrotron and quantum cascade laser (QCL) radiation. (b) (top) Lewis structure and (bottom) crystal structure of PTCDA in the β phase. (bottom right) Crystal axes (red) oriented relative to the substrate, with θ indicating the angle between the *a*-axis of the crystal and *z*-axis of surface normal. (c) AFM height of aggregates, depicted schematically (bottom). Scale bar 200 nm. (d) AFM height of vacuum-deposited film, with (bottom) schematic showing growth of molecules with the *a*-axis parallel to the *z*-axis (blue) and (red and green) defects with the *a*-axis perpendicular to the *z*-axis. Scale bar 500 nm.

crystallography by selectively detecting only the material response along the tip axis, combining vertically polarized incident light, anisotropic field enhancement by the tip, and surface optical selection rules in order to measure the projection of vibrational dipoles along the tip axis. The selected orthogonal vibrational normal modes we probe have transition dipoles parallel to the primary molecular axes, thus reflecting the crystal axes for monoclinic PTCDA crystals (for details see Supplementary Materials).

Figure 1c-d show AFM topography of drop-cast PTCDA aggregates and vacuum-deposited films, respectively. AFM topography across the surface shows well-separated regions containing clusters of PTCDA with a typical grain size in the range of 0.5 μm to 2 μm . The AFM height image of vacuum-deposited films in Figure 1d shows islands with an average height of

~ 80 nm relative to the Au substrate. Island growth is observed by AFM tapping phase images, which identify islands and the spacing between them via differences in the tapping phase (Supplementary Materials) (35, 36). The topography is consistent with previous observations of PTCDA films grown under similar conditions, producing modified Stranski-Krastanov growth and appearing as 3D islands for films greater than a few nm thick.

Results

Figure 2a shows far-field FTIR spectra of PTCDA crystallites over two spectral regions of interest, 700 to 900 cm^{-1} and 1600 to 1900 cm^{-1} , with the full spectra shown in the Supplementary Materials. The low wavenumber region contains three prominent peaks assigned to C–H out-of-plane bending modes, while the carbonyl stretching region contains four overlapping peaks assigned to the anhydride groups. The anhydride modes are split into four peaks in the carbonyl region due to dipole-dipole coupling (37). Although broad line shapes prevent distinguishing between α and β phases, the splitting is consistent with the typical herringbone crystal structure and indicates high crystallinity of the powdered sample (38).

We fit the far-field transmission spectrum in order to quantify peak position and oscillator strength (Supplementary Materials). The measured transmission of each peak is proportional to the vibrational oscillator strength for an ensemble measurement of isotropically dispersed particles. We find good agreement between measured and previously reported oscillator strengths (38).

Figure 2b shows synchrotron IR nanospectroscopy (SINS) point spectra of $\Phi_{NF}(\bar{\nu})$ collected from different drop-cast PTCDA crystallites. As in the far-field spectrum (Figure 2a), three C–H bending modes are observed in the low frequency region and four C=O stretching modes appear in the high frequency region. In *s*-SNOM spectra from different spatial regions containing sub-ensembles with distinct orientations, the C–H and C=O modes alternate in peak

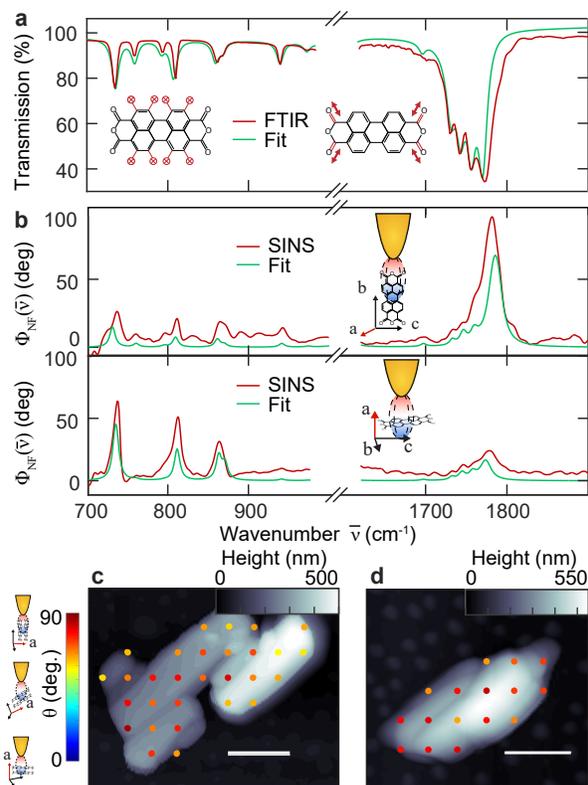


Figure 2: (a) Far-field transmission spectrum of dispersed PTCDA particles, fit to calculated reflectance using Lorentz model. Inset, schematic of C–H out-of-plane vibrations and C=O stretch of the anhydride. (b) SINS spectra (red) collected at two different nanoscale locations with (green) fit to spherical dipole model with Lorentz oscillators. (c-d) Molecular orientation is measured from SINS spectra in a spatial map across large crystals of PTCDA. Point spectra (circles) show fits of point spectra for θ , represented on a false color scale. Scale bars are 200 nm.

height. While the far-field spectra represent an isotropic ensemble-averaged sample response, near-field $\Phi_{NF}(\text{C-H})$ and $\Phi_{NF}(\text{C=O})$ measure anisotropic linear dichroism of an oriented nanoscale sub-ensemble.

In order to determine local crystallographic orientation, we calculate the near-field optical response of the coupled tip and sample system. The frequency-dependent IR dielectric constant $\epsilon(\bar{\nu})$ of PTCDA can be expressed as the sum of individual molecular vibrations using a Lorentz model for vibrational oscillators. The transition dipole of the C–H modes is parallel to the a -axis, while the transition dipole of the C=O modes is along the $b - c$ plane of monoclinic PTCDA crystals and nearly isotropic in two dimensions. We include the Lorentz oscillator model in the well-known spherical-dipole model for near-field scattering (see Supplementary Materials), which approximates the AFM tip as a polarizable sphere (39–42). **The optical near-field maintains the polarization of incident light oriented parallel to or perpendicular to the tip axis (43) particularly in the strongly localized and enhanced region at the tip apex that dominates the signal.** We then use the combined Lorentz oscillator and spherical dipole model to quantitatively calculate the IR s -SNOM signal as a function of molecular and crystalline orientation.

Figure 2b also shows the resulting fits of the model to the s -SNOM scattered signal from two representative PTCDA crystallites. The measured **spectra** quantifies the projection of each mode along the tip axis and is insensitive to molecular rotation about the tip axis. We fit each spectrum to determine the projection angle θ of the crystalline a -axis along the surface normal z , as shown in Figure 1b. The angle θ is the only free fit parameter, while the oscillator strength and line widths of each normal mode are left as constants. The resulting values for θ in Figure 2b are $70 \pm 10^\circ$ and $20 \pm 10^\circ$ respectively.

From repeated measurements on a spatial grid, and analysis from above, Figure 2c-d show molecular orientation measured across two PTCDA crystallites. Color scale indicates orienta-

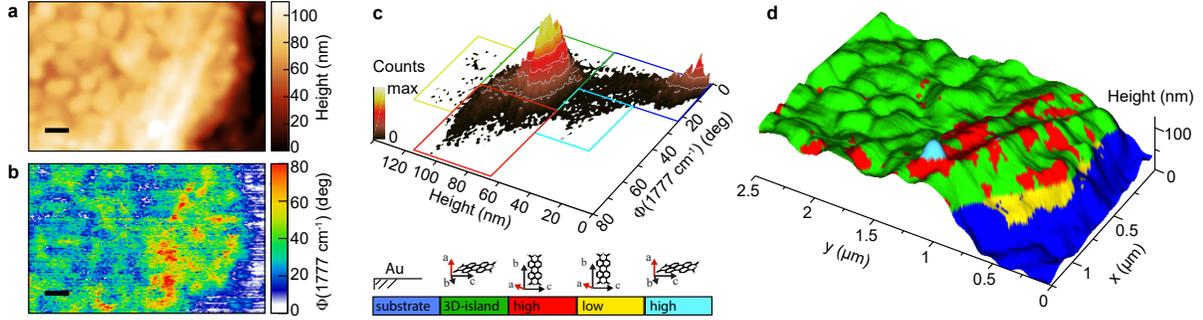


Figure 3: (a) AFM topography of vacuum-deposited PTCDA near the film edge and (b) corresponding near-field $\Phi_{NF}(1777\text{cm}^{-1})$ measured on resonance with the carbonyl mode. (c) Histogram constructed from the images (a-b) showing correlation between AFM height and $\Phi_{NF}(1777\text{cm}^{-1})$. Distinct sub-populations are identified by their statistical correlation and labeled by the colored borders. (d) Spatial map reconstructed from the correlated populations identified in (c) overlaid on AFM height image. The majority population (green) has the a -axis of PTCDA parallel to surface normal, with smaller populations (light-blue) uplifted with the a -axis parallel to surface normal, (red) uplifted regions with the a -axis oriented away from surface normal, and (yellow) regions with less coverage and a -axis oriented away from surface normal. Substrate shaded dark blue. Scale bar (a,b) 500 nm.

tion at each location in the image, with blue corresponding to $\theta = 0^\circ$ and a red corresponding to $\theta = 90^\circ$ with the a -axis parallel to the substrate. These spectrally resolved maps identify large oriented regions with the a -axis nearly parallel to the substrate across μm size crystallites as well as preferential ordering in stacked aggregates. **The spectral features and orientation-dependent enhancement are also consistent across all vibrational modes in the spectral range of SINS measurements (700 to 900 cm^{-1}) and are relatively insensitive to topographic variations or eigenmodes appearing due to sample geometry.** Measured angles of $\theta = 60 - 90^\circ$ across most of the crystallite demonstrate quantitative and robust measurement of orientation.

We extend IR optical nano-crystallography to high resolution single wavelength imaging of orientational ordering in device-relevant thin films. Near-field $\Phi_{NF}(\bar{\nu})$ quantitatively measures the orientation θ by the relative contribution of C–H versus C=O peaks. Close agreement between calculated fits and broadband SINS spectra across all modes in PTCDA aggregates

with different orientation establishes that Φ_{NF} at a selected frequency resonant with only one mode can be used to determine θ in the case of polycrystalline molecular semiconductors with uniform density. Further, the near-field $\Phi_{NF}(\bar{\nu})$ is also independent of laser intensity, enabling quantitative comparison between measurements using different IR sources.

Figure 3a shows AFM topography at the edge of a vacuum deposited ~ 80 nm thick film with the expected morphology of 3D islands across most of the continuous film. Figure 3b shows corresponding *s*-SNOM imaging resonant with the carbonyl mode at 1777cm^{-1} , $\Phi_{NF}(\text{C=O})$. $\Phi_{NF}(\text{C=O})$ measures the projection of the C=O transition dipole along the tip axis. The resonant $\Phi_{NF}(\text{C=O})$ image shows significant spatial variation and several distinct regions across the image, as opposed to Φ_{NF} at non-resonant frequencies which shows no optical contrast across the sample (Supplementary Materials).

Several distinct regions are seen in the $\Phi_{NF}(\text{C=O})$ image. The Au substrate is non-resonant and serves as a reference region, with $\Phi_{NF}(\text{C=O})$ near 0° , whereas $\Phi_{NF}(\text{C=O}) = 10 - 30^\circ$ is observed across most of the PTCDA. Near the film edge, regions with $\Phi_{NF}(\text{C=O}) \geq 70^\circ$ are observed. Comparing the resonant $\Phi_{NF}(\bar{\nu})$ across the PTCDA to the calculated *s*-SNOM signal with the spherical dipole model, we can assign the orientation distribution across most of the sample area. Away from the edge, $\theta = \leq 20^\circ$, while the region of higher $\Phi_{NF}(\bar{\nu})$ corresponds to a larger $\theta = 50 \pm 10^\circ$, with uncertainties calculated from the 95% confidence limit of Φ_{NF} .

Correlation analysis (Figure 3c) of topography and $\Phi_{NF}(\text{C=O})$ provides for assignment of spatial regions with distinct crystal orientation. Regions of lowest height also have $\Phi_{NF}(\text{C=O}) \sim 0^\circ$ indicating non-resonant response, which can be assigned to the exposed Au substrate. Higher topography corresponds to the thin film with 3D-islands. The majority population of PTCDA regions has a low measure $\Phi_{NF}(\text{C=O})$ and θ , while smaller populations are observed to exhibit a larger $\Phi_{NF}(\text{C=O})$ and θ .

Figure 3d shows the resulting orientational map. The majority of the image (green) has a

height near the average film thickness and $\theta = 10 - 20^\circ$ measured by $\Phi_{NF}(C=O)$. Near the edge, however, a region is perturbed with both higher topography and greater θ (red). Although much of the uplifted region near the edge has greater θ , one of the tallest island features (light-blue) exhibits low θ , similar to the response of the unperturbed region (green). At the edge of the PTCDA region, a small region (yellow) of low height yet with large θ is also observed as a spatially distinct sub-ensemble, unobservable from either height or θ alone.

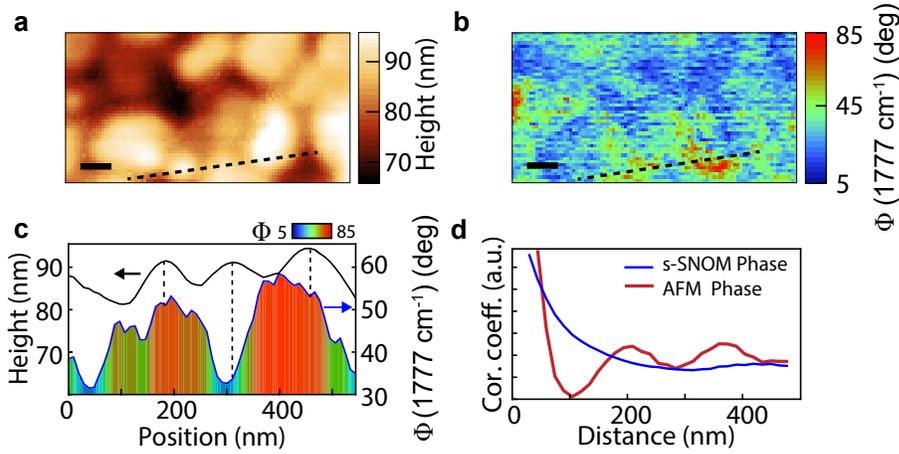


Figure 4: (a) Topography and (b) $\Phi_{NF}(C=O)$ images of PTCDA. Scale bars 100 nm. (c) Line cut of AFM height and $\Phi(\nu)$ along the dashed transect indicated in (a-b) showing that molecular orientation is uncorrelated with topographic features. (d) Radial correlation function (red) of the AFM tapping phase, indicating the presence of 3D-islands with characteristic size and spacing and $\Phi(\nu)$ (blue), which shows an extended correlation length of crystallite orientation.

We next analyze a small region of PTCDA in a central region of the overall film in order to study intrinsic heterogeneity in the vacuum deposited film. Figure 4a-b shows a high resolution AFM and *s*-SNOM image of a small region containing orientational defects. The AFM height shows morphological features associated with the 3D island growth of PTCDA. The $\Phi_{NF}(C=O)$ image resonant with the carbonyl mode shows that across most of the image, the molecular orientation is relatively flat, as expected for vacuum deposited growth on Au. Across most of the image, a weak correlation is observed between features observed in AFM height

and in $\Phi_{NF}(C=O)$, whereas in two distinct regions with higher $\Phi_{NF}(C=O)$ (Figure 4b), the a -axis is oriented significantly away from the surface normal. In particular, the defect in the lower right portion of the image has a maximum $\Phi_{NF}(C=O)$ of 85° localized to a region of ~ 100 nm as well as an extended region with $\Phi_{NF}(C=O)$ near 45° . From the corresponding line scan (Figure 4c) of the location indicated by the dotted lines in Figure 4a-b, we observe regions of high $\Phi_{NF}(C=O)$ in regions with both low and high topography. Spatial variations in $\Phi_{NF}(C=O)$ appear uncorrelated with height and extend across and beyond the edge of the 3D-islands.

Figure 4d shows the radial correlation functions from AFM and $\Phi_{NF}(C=O)$ signals. We analyze the AFM tapping phase, which is found to be a sensitive measure of islands and the regions between islands, which may be due to differences in sample viscoelasticity, adsorbed water, or geometrical effects (35, 36). Periodicity in the AFM tapping phase signals indicate well-separated island features with 200 nm spacing as measured by the location of the first maximum in the radial correlation function. However, the radial correlation function of the optical phase decays monotonically with no periodic recurrence of correlation, supporting the finding that the observed θ is uncorrelated with morphological features or edge effects. Further, the correlation length $\Phi_{NF}(C=O)$ is comparable to or greater than the spacing of morphological features. The long radial correlation of the $\Phi_{NF}(C=O)$ agrees with the conclusions from the line scan in Figure 4c and supports the idea that orientational defects are not confined to within a single morphological feature and may in fact extend across multiple island features.

Discussion

Our IR s -SNOM optical nano-crystallography and -imaging shows the presence of well-oriented PTCDA in macroscopically disordered drop-cast crystallites. Conversely, vacuum-deposited PTCDA is macroscopically ordered in the crystalline thin film with molecules primarily ori-

ented with $\theta \simeq 10 - 20^\circ$, in close agreement with previous ensemble-averaged measurements (26). However, we find nanoscale spatial variation of molecular orientation in otherwise morphologically well-ordered regions of the vacuum-deposited thin film. Line scans and correlation analysis of $\Phi_{NF}(\text{C}=\text{O})$ suggest that defects and crystalline domains may not be confined to individual morphological features.

The observed orientational radial correlation length across the PTCDA sample can be expected to occur during growth by vacuum deposition. Thin film growth of different morphologies with varying crystallinity, polymorphs, and even amorphous growth can occur as a function of growth rate and temperature. Roughness of the substrate may also play a role, which for our template-stripped Au has a measured root-mean squared roughness of 0.5 nm, yet with many features as high as 5 nm and rare pit defects. Defect propagation during vacuum-deposition is expected to be influenced by both the density of seed crystals as well as the molecular surface diffusion rate across morphological features.

Infrared vibrational nano-crystallography extends related tip-enhanced nanoscale crystallography efforts to molecular materials. Imaging orientation of inorganic crystals has been demonstrated via IR *s*-SNOM using crystallographic anisotropy of the phonon response (17), although quantitative determination of orientation angle and structural information were inaccessible. Symmetry selectivity of nonlinear response has also been used to image domain order in ferroelectrics (18). The polarizability tensor has also been used in tip-enhanced Raman spectroscopy to measure orientation of inorganic micro-crystals (19).

With the combination of selected wavelength imaging and broadband IR spectroscopy the approach of *s*-SNOM based optical crystallography can be generalized and extended to a much wider range of materials. The low photon energy of IR light and lower field enhancement in IR *s*-SNOM provide minimally invasive imaging, suitable for organic materials even under ambient and device-relevant conditions. Individual-wavelength IR *s*-SNOM enables rapid imaging

of $\Phi_{NF}(\bar{\nu})$ simultaneously with AFM information under the conditions of spatially invariant chemical identity and density. These methods can be expanded to image more complex and multi-component materials. **IR *s*-SNOM nanocrystallography measured using both horizontal and vertical polarized optical fields can measure molecular orientation through linear dichroism of a single vibrational mode even with varying molecular concentration and oscillator density.** Hyper-spectral imaging of several vibrational modes with different point group symmetry can uniquely reflect molecular orientation, while also measuring chemical identity.

Broadband IR-nano-crystallography based on hyper-spectral imaging can be improved with faster spectral acquisition times using sources of adequate average power and a carefully selected frequency bandwidth. By overcoming these technical limitations, our methods and analysis are generalizable to imaging orientational heterogeneity in virtually any soft matter, multi-component, or partially ordered system.

Summary

In summary, we have implemented IR *s*-SNOM for optical nano-crystallography, using tip-enhanced **spectroscopy of molecular vibrations with infrared selection** to quantify molecular and crystalline orientation, while providing simultaneous spectral sensitivity for chemical identification and measurement of crystalline phases and variation in the local chemical environment. We measure heterogeneity of polycrystalline PTCDA on the natural length scales of disorder, including orientation distribution and correlation across domain boundaries and morphological features. We observe both correlation between nanoscale crystallinity and associated morphological features as well as local variation in molecular orientation that is uncorrelated with morphological features. We directly measure molecular level structure and interactions that govern macroscopic properties, adding unique insight into crystalline growth and defect propagation in device relevant films.

1 Materials and Methods

In the IR *s*-SNOM apparatus, light from a tunable laser or synchrotron radiation is focused onto a metalized atomic force microscope (AFM) tip operated in intermittent contact mode $\nu_0 \sim 250 \text{ kHz}$. Near-field signal is detected at a higher harmonic of the tapping frequency using lock-in demodulation. In both CW and broadband implementations, the tip-scattered near-field signal is combined with light from a reference arm and interferometrically detected with a HgCdTe photovoltaic detector.

SINS is performed using a Bruker Innova AFM modified for *s*-SNOM. Point spectra are measured interferometrically with a modified FTIR (Nicolet 6700), collected as asymmetric interferograms. Interferograms are Fourier transformed to produce near-field amplitude $A_{NF}(\bar{\nu})$ and phase $\Phi_{NF}(\bar{\nu})$ spectra. A single interferogram at 8 cm^{-1} is collected within 2 seconds, and spectra are averaged over typically 60-1000 repeated scans and referenced to a non-resonant bare Au substrate. For spatially resolved spectroscopic imaging, faster resolution imaging is performed at a lower resolution of 16 cm^{-1} .

Selected, fixed wavelength imaging is performed using a tunable quantum cascade laser (QCL Daylight Solutions Inc.) with an Anasys Nano-IR2s AFM. Fixed wavelength imaging within the range ($1650\text{-}1850 \text{ cm}^{-1}$) measures $A_{NF}(\bar{\nu})$ and $\Phi_{NF}(\bar{\nu})$ simultaneously with AFM topographic information.

PTCDA films and aggregates are prepared from sublimation purified $\geq 99\%$ pure powder (Sigma-Aldrich). Transition dipole strength of vibrational modes is determined from FTIR of crystallites dispersed in KBr powder, with similar results observed for dropcast crystallites. Aggregated crystallite samples are prepared drop-cast from a low-solubility suspension in dichloromethane solvent on substrates of freshly prepared template-stripped Au substrates with a root-mean-squared roughness of 0.5 nm. Vacuum-deposited films are prepared by or-

ganic molecular beam deposition from a Knudsen cell held at 630 K at a rate of ~ 2 nm/min, producing films with a thickness of nominal thickness 80 nm.

Film morphology is characterized with tapping mode AFM, and far-field FTIR spectra are collected in transmission mode (Nicolet 6700 2 cm^{-1} resolution) as well as a far-field transmission and reflectance FTIR microscope (Continuum) with N.A. = 0.65 with a $50 \times 50\ \mu\text{m}^2$ aperture.

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