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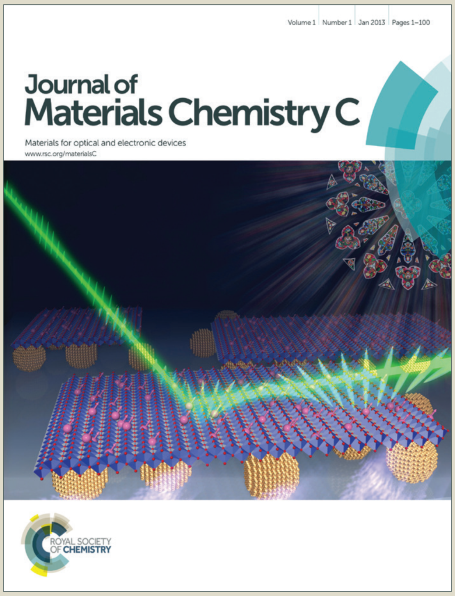

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Probing interfacial molecular packing in TIPS-pentacene organic semiconductors by Surface enhanced Raman Scattering

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In organic thin film transistors (OTFTs), the molecular structure of the first few monolayers at the semiconductor-dielectric interface is crucial to device performance. The assumption of homogeneous molecular packing throughout the thickness of the film is not always valid considering interfacial effects. However, it remains challenging to unambiguously determine molecular packing at both the top surface and the buried bottom interface, due to lack of nanoscopic tool. Here we show that a combination of Raman spectroscopy and surface enhanced Raman scattering (SERS) provides a means for effective characterization of interfacial packing in 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS-pentacene) films. We observed that the TIPS-pentacene crystal lattices assume a non-equilibrium packing state near the substrate interface, which gradually relaxes towards the equilibrium packing near the top interface. Our further investigation suggests the existence of non-equilibrium molecular packing for TIPS-pentacene.

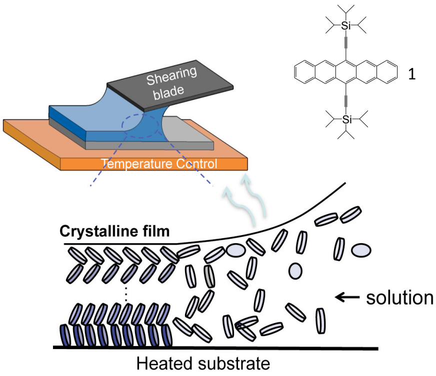
Introduction

Organic molecular semiconductors (OTFTs) are receiving considerable attention because of their promise for flexible, low-cost large-area electronics.[1-3] Much effort has been directed toward improving the charge carrier mobility in organic semiconductors. Since the charge transport in organic thin film transistor predominantly occurs in the first few monolayers above the dielectric layer, molecular structure of organic semiconductors at the dielectric interface is critical to the discussion of the OTFT performance.[4]

X-ray and electron diffraction techniques are the primary tools for characterizing the molecular packing structure in thin film samples, which usually gives a thickness-averaged molecular packing. However, the molecular packing in the buried interfacial layer may be significantly different from that in the top surface layer of the film, as inferred from indirect thick-ness-dependent measurements reported previously.[5,6] Several techniques have been utilized for probing buried interfaces, such as near-edge X-ray absorption fine structure spectroscopy (NEXAFS) combined with delamination techniques[7,8] and vibrational sum frequency generation (SFG) spectroscopy.[9,10] Nonetheless, a more readily accessible method is needed for direct structural characterization of such interfacial layers in semiconductor thin films.

Raman scattering techniques, in particular Surface enhanced Raman scattering (SERS) have been shown to provide information of the interfacial layer in thin films.[6,11,12] The vibration modes of a molecule are mapped out through the inelastic scattering of light, making Raman spectroscopy sensitive to subtle structural changes between different crystalline poly-morphs in organic semiconductors, such as shown with copper (II) phthalocyanine (CuPc)[13] and pentacene.[14] SERS is a unique characterization technique that provides greatly enhanced Raman scattering from molecules that have been adsorbed onto certain specially prepared metal surfaces.[15] The enhancement factor has been regularly observed on the orders of magnitude, and can be as much as 10^{10} to 10^{11} for some system.[16,17] Due to this surface enhancement, which is a combination of local enhancement of the electromagnetic field and contributions from chemical interactions between molecules and metal surface, the surface signal overwhelms the bulk signal, making SERS particularly useful for characterization of molecular features near the surface.[18] Combining their ad-vantages, the use of both Raman spectroscopy and SERS can provide a means for rapid characterization of the interfacial molecular packing in organic semiconductors.

6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) (1 in Schematic 1) is a well-known high-performance solution-processable organic semi-conductor. It was recently discovered that lattice strained non-equilibrium TIPS-pentacene films prepared by the solution-shearing method exhibits close to an order of magnitude higher hole mobility.[19,20] Furthermore, the molecular packing of TIPS-pentacene can be controlled by simply varying the solution shearing speed. Although the average molecular packing has been characterized by grazing incidence X-ray diffraction (GIXD), the vertical variation of molecular packing in solution-sheared films, especially at the interfaces remain unexplored. Such information is important for understanding the origin of non-equilibrium packing, and for correlating structural information with device performances.



Scheme 1. Presentation of solution shearing process. The discs represent TIPS-pentacene (1) molecules.

In this paper, we report the application of Raman/SERS to the characterization of interfacial molecular packing in TIPS-pentacene thin films deposited using the solution shearing method. We first investigate the use of Raman spectroscopy to characterize the change in molecular packing in TIPS-pentacene films. Secondly, we investigate the molecular packing at both the top and the buried bottom interfaces by SERS method. Furthermore, top surface SERS experiments were carried out using TIPS-pentacene films with sequentially reduced film thickness to trace the molecular packing evolution throughout the film in the vertical direction. Finally, the existence of non-equilibrium molecular packing in TIPS-pentacene films is inferred from the thickness-dependent molecular packing. We show that the combined Raman and SERS is a powerful and readily accessible tool for direct structural characterization of interfacial layers in organic semiconductor thin films.

Experimental

Materials and sample preparation

The TIPS-pentacene (received from 3M) was used without further purification. Highly doped n-type silicon wafers with a 300 nm thermally grown silicon oxide gate dielectric film were used as the substrates. The silicon wafer (1.5×3cm^2) treated with a monolayer of phenyltrichlorosilane (PTS) was used as the bottom substrate. The top shearing plate, a silicon wafer with 300-nm thermally grown oxide was treated with a monolayer of octadecyltrichlorosilane (OTS). Detailed description of the OTS and PTS treatment was published previously.[19] The gold layers that deposited on the bottom substrate and the surface of TIPS-pentacene were about 9 nm grown at a rate of 1 Å/s.

Solution shearing of TIPS-pentacene films

The TIPS-pentacene solution was prepared at a concentration of 8 mg ml^{-1} in toluene. Both the device substrate and the shearing plate were held in place by vacuum while the device substrate was mounted on a resistively heated stage (a thermoelectric module from Custom Thermoelectric) held at 90℃. After placing about 20 μl/cm^2 of TIPS-pentacene solution on the device substrate, the shearing plate was lowered with a micromanipulator to make contact with the solution. The device substrate was horizontal while the shearing plate was placed at a tilt angle of 8° from the horizontal. The gap distance between the device substrate and the shearing plate was fixed at 100 μm. The shearing plate was translated at different velocities by a stepper motor. The resulting sheared film was left on the heating stage for 2–3 min at 90℃ to remove residual solvent. Film thickness was measured with tapping mode atomic force microscopy (AFM) using a Multimode Nano-scope Ⅲ and a Dektak profilometer for films thicker than 20 nm.

Solution-sheared film characterizations

All SERS spectra and Raman spectra of TIPS-pentacene films were collected on an Aramis confocal microscope Raman spectrometer (Horiba Johib Yvon, Edison, NJ). A 633 nm He-Ne laser served as the excitation light source and was kept below 0.5 mW to prevent thermal damage of the TIPS-pentacene thin film. The spatial resolution of the beam spot was around 1 μm^2, attained using a 100× objective microscope lenses. For avoiding artifacts, 10× objective microscope lens was also used to get an averaged value. Every Raman spectrum was taken an average of ten spectrums and at least 5 spectra at different areas were measured for each sample. Grazing incidence X-ray diffraction (GIXD) was conducted at Stanford Synchrotron Radiation Light source (SSRL), beam line 11-3 with an area detector (MAR345 image plate). The incidence angle is 0.12°. The incident energy is 12.7keV. The qxy and qz are the components of the scattering vector parallel and perpendicular to the substrate respectively. The image analysis is performed with software WxDiff.[21] The peak positions and the crystal structure of TIPS-pentacene with the highest degree of lattice strain were published previously.[19]

Results and Discussion

Raman spectra of solution-sheared TIPS-pentacene films.

TIPS-pentacene films were fabricated with the solution-shearing method. The observed Raman modes were assigned based on the quantum calculation of James[22] and ourselves (Figure S1a). In our experiment, we select two vibration modes to monitor (Figure S1b). The peak at 1157 cm^{-1} is assigned to be C-H bending modes from the end of the pentacene back-bone, while the peak at 1374 cm^{-1} corresponds to the C-C ring stretching vibrations in the conjugated pentacene backbone, primarily oriented along the short-axis of pentacene. Figure 1 shows the Raman spectra of bulk TIPS-pentacene films solution sheared at different speeds (the optical images is shown Figure 1a). The shearing speed was varied to tune the molecular packing as reported previously and confirmed by GIXD.[19] It is worth mentioning that in addition to shearing speed, variation in the film thickness can also affect molecular packing as discussed later in the manuscript. For reference, the strongest C-C stretching vibration at 1374 cm^{-1} was used as an internal intensity standard. With an increasing shearing speed, the C-H vibration band shifts slightly to a lower frequency. (The enlarged region of 1140 -1170 cm^{-1} is shown in Figure S2(a)) Similar subtle frequency shift of C-H bending modes was also reported in ultra-thin pentacene films by Brillante et al.[23] Nonetheless, considering the environmental interference to the positions of Raman bands,[24] the small shift of the C-H stretching vibration is not a suitable parameter for monitoring the evolution of molecular packing in TIPS-pentacene films (we have put all frequency shift data in Figure S2 as a reference). We have not observed clear lattice phonons in the low-energy region for the ultra-thin TIPS-pentacene films, indicating no long-range order in such a polycrystalline film.

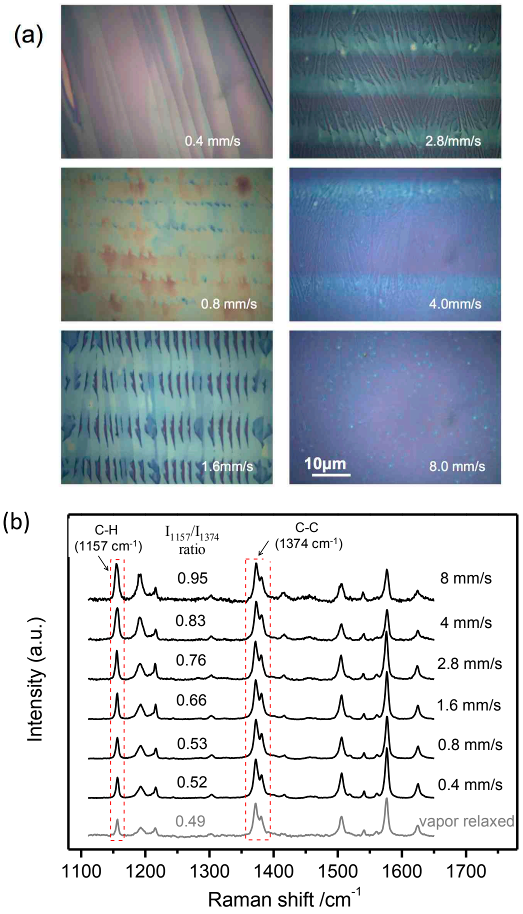


Figure 1. (a). Optical image of TIPS-pentacene films solution-sheared at different speeds. These optical images show that the films are homogeneous at the µm to mm length scales. (b). Raman spectra of TIPS-pentacene film solution sheared at different speeds with 8 mg/ml solution concentration. The spectrum in gray color at the bottom corresponds to the Raman spectra of toluene vapor-annealed TIPS-pentacene film. Theses spectra were normalized to the intensity of the strongest C-C band at 1374 cm^{-1}. Spectra are offset for clarity.

On the other hand, with an increasing shearing speed, an obviously monotonic increase in the intensity of C-H in plane bending modes (1157 cm^{-1}) was observed. According to previous Raman studies on pentacene,[6,14] this increased intensity implied increased motions (or degrees of freedom) of the H-atoms at the end of the conjugated core for a non-equilibrium film. The slight red shift of the C-H in-plane bending band and the increased vibration frequency of the H-atoms reflect a weakened intermolecular interaction between molecules that are arranged in the non-equilibrium TIPS-pentacene film. Based on our previous GIXD results,[14,25] we infer an increased average (010) d-spacing with the increase of shearing speed[19] (Figure S5, Table S1). We observed that the trend of I_{1157}/I_{1374} in Raman spectra was correlated with the extent of lattice deviation from the equilibrium packing characterized by the (101) and (010) d-spacing changes from GIXD.[19] Therefore, the I_{1157}/I_{1374} ratio can be used to characterize the lattice packing variation in TIPS-pentacene films, which is a quick and convenient alternative to GIXD. To further verify this point, we relaxed the non-equilibrium packing using toluene vapor annealing treatment[19] and compared the Raman spectrum before and after toluene vapor annealing shown in Figure 1. A de-ceased I_{1157}/I_{1374} ratio was observed in the vapor-relaxed film (equilibrium state), again consistent with the GIXD observa-tions.[19]

The films in this work are prepared by solution-shearing method, which allows fabrication of uniform, aligned thin films. In the thickness dependence experiment, the film alignment is the same across all samples, parallel to the shearing direction (Figure S3). In this case, the change of the relative ratios across different samples is not caused by the alignment effect. Furthermore, we did Raman measurements on five different areas of a drop-casted TIPS-pentacene film (equilibrium packing).[19] Although the alignment direction is quite different at each location because of the variation in film morphology (images of different location are shown in Figure S4). However, the relative ratios of the two modes that we used in our work are nearly the same at these five locations. It confirms that the film alignment direction contributes little to the ratio change in our work.

Molecular Packing on Top and Buried Interfaces of TIPS-pentacene film

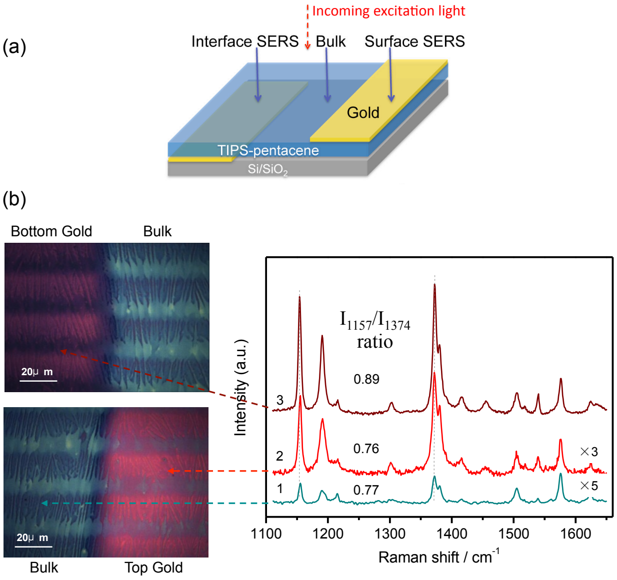


Figure 2. (a) A schematic diagram of the SERS/Raman measurement arrangement and the incident beam is normal to the film plane. (b) Left: An optical image of TIPS-pentacene film solution-sheared at 2.8 mm/sec on gold (top left), SiO$_2$/Si substrate (top right / bottom left) and beneath gold (bottom right). Right: Spectra 1, 2 and 3 correspond to the Raman, surface SERS spectra and interface SERS spectra of TIPS-pentacene film, respectively. The signals for the spectra 1 and 2 are multiplied by 5 and 3 times. Spectra are offset for clarity.

Taking advantage of Raman and SERS, we employed sample configurations shown in Figure 2a to carry out interfacial SERS and bulk characterizations of solution-sheared TIPS-pentacene films. An ultra-thin (~9 nm) evaporated gold layer, either atop or beneath the film, did not seem to alter the overall molecular packing as discussed later in the manuscript. When measuring SERS spectra of the TIPS-pentacene film, a strongly enhanced Raman signal is detected (spectrum 2, 3 of Figure 2b). The vibration modes, which are associated with a component of the polarizability tensor along the short molecular axis such as 1157 cm^{-1} and 1374 cm^{-1}, are maximally enhanced.

Based on surface selection rules[26] (the intensities of the SERS modes involving vibrations associated with a component of the polarizability tensor that is normal to the surface are found to be selectively enhanced), we confirm that TIPS-pentacene takes an “edge-on” orientation with respect to the substrate by combing with GIXD established evidence,[19] which is consistent with what was derived from electron diffraction results.[27] As the enhancement effect is the greatest for those molecules at the surface, the surface signal overwhelms the bulk signal in SERS spectra. (In surface SERS spectra, the signals are weaker because of laser scattering from Au.) Thus we could use SERS to characterize the molecular packing at bottom and top interfaces of TIPS-pentacene film. In Figure 2b, we observed that the relative ratio I_{1157}/I_{1374} in the surface spectrum is essentially the same as that in the bulk spectrum, while the interface SERS spectrum features noticeably greater I_{1157}/I_{1374}. As the SERS effect alone contributes little to the changing of relative ratio of I_{1157}/I_{1374} (as shown in Figure S8), we infer that the crystal lattice near the film-substrate interface exhibits a larger extent of deviation from the equilibrium packing than that in the bulk and at the surface.

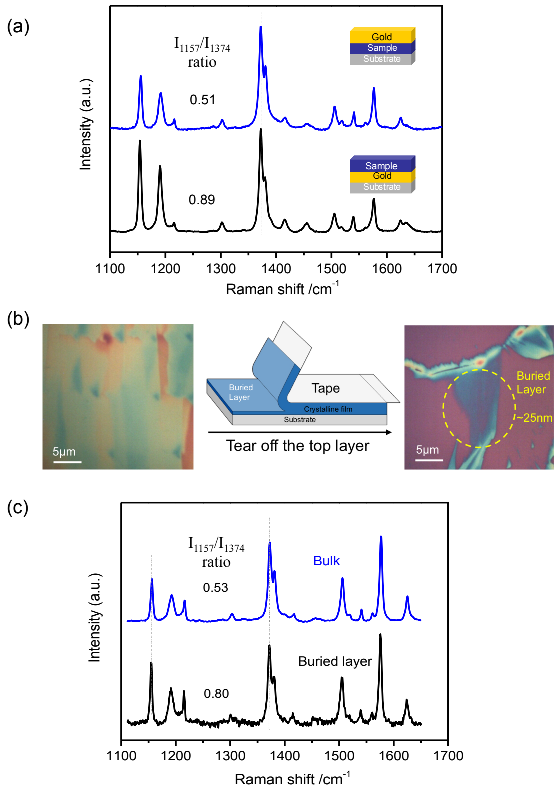


Figure 3. (a): SERS spectra of TIPS-pentacene film with gold layer on the film sample surface (gray) and beneath the film (navy). (b). The process of the cleavage method. (c): Raman spectra of bulk (black) and the buried layer of TIPS-pentacene film (blue). This film is solution sheared at 0.8 mm/sec with 8mg/ml solution concentration. Theses spectra were normalized to the intensity of the strongest C-C band at 1374 cm^{-1}. Spectra are offset for clarity. The dashed lines serve as guide to the eye.

For a film prepared with a lower shearing speed, an appreciably greater I_{1157}/I_{1374} difference between the interface SERS spectrum and the corresponding surface SERS/bulk spectrum was observed (Figure 3). This observation indicates that the molecules in the first few monolayers near the substrate pack in a different structure from the equilibrium bulk structure, even when the film is prepared at a very low shearing speed while the molecular packing at the top surface showed the equilibrium packing. To confirm our observation, we tore off the upper layers of the film by a mechanical cleavage method (the process is shown in Figure 3c),[8,28] exposing the buried interface layer of the film. Since the spot size of the incident laser beam is around 1 μm^2, the exposed buried region is large enough for Raman measurement. In Figure 3b, we observed that the ratio of I_{1157}/I_{1374} was greater in the buried interface layer and almost the same as the interface SERS value, suggesting SERS is indeed a useful tool for characterizing molecular packing at the buried interface. In addition, when the film thickness is ultra thin (~10nm, ~5MLs), the ratios of averaged Raman signal and interface SERS are high and nearly the same, both consistent with the GIXD results.(Figure S8, S6b) This again demonstrates that the ratio here is useful for characterizing the extent of lattice deviation from the equilibrium packing for TIPS-pentacene films.

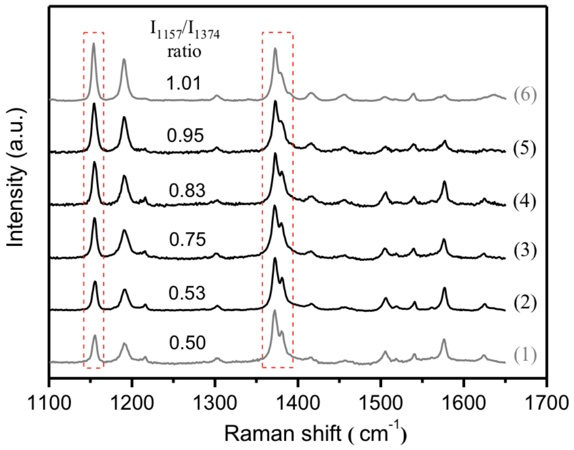


Figure 4. (1) Top SERS spectra of vapor relaxed TIPS-pentacene film. 2)-4) Surface SERS spectra of TIPS-pentacene film solution sheared at 0.8mm/s, 2.8 mm/s, 4 mm/s and 8.0 mm/s, respectively. (5) Interface SERS spectra of TIPS-pentacene film solution sheared at 8.0mm/s. All the spectra were normalized to the intensity of the C-C band at 1374 cm^{-1}. Spectra are offset for clarity.

Figure 4 (2)-(4) show the normalized surface SERS spectra of TIPS-pentacene film prepared at different shearing speeds. With low shearing speeds, the molecular packing on the top interface is close to the equilibrium packing based on I_{1157}/I_{1374} ratio (Figure 4 (1), (2)). At very high shearing speeds, the molecular packing on the top interface becomes comparable to that on the bottom interface, indicated by the high I_{1157}/I_{1374} ratio (Figure 4 (4)-(6)). Considering that the film thickness decreases with increasing shearing speed (the film thickness as a function of the shearing speed is shown in Figure 5a), our observations suggest the possible existence of non-equilibrium molecular packing of TIPS-pentacene near the substrate surface, which exhibit incremental changes in crystal packing from that of the bulk crystal. With a continuous decrease in the film thickness, we hypothesize that the non-equilibrium molecular packing may become dominant throughout the entire film.

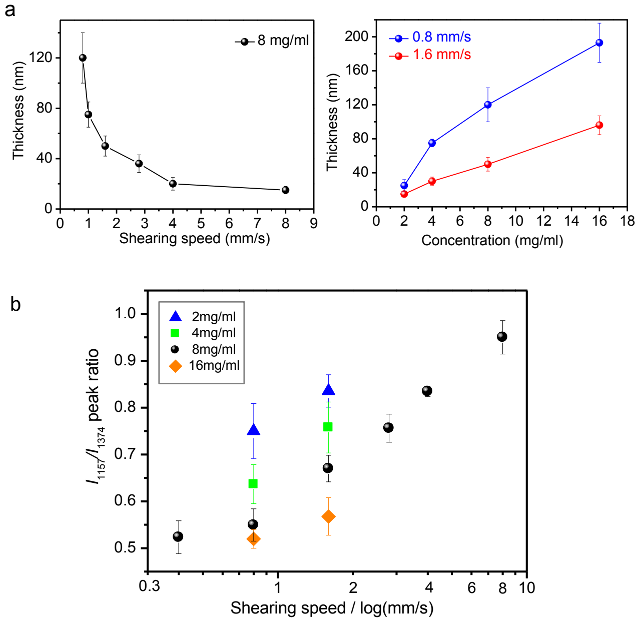


Figure 5. (a) Film thickness as a function of shearing speed (left) and solution concentration (right). (b) Ratio of I_{1157}/I_{1374} in surface SERS spectra vs. shearing speed for TIPS-pentacene films sheared with different solution concentration. The error bars show the standard error of the mean, calculated by dividing the standard deviation of the ratio by the square root of 5 spectra measured. (The range of shearing speed investigated corresponds to shearing rate by the formula: Shearing rate =shearing speed/gap distance.

In this regard, we would like to make it clear that this ultra-thin (~9 nm) evaporated gold layer, either atop or beneath the film, did not alter the overall molecular packing in this work. Firstly, we have performed GIXD on thin films from 40nm down to 10nm (Figure S6, S7) but did not observe change in packing comparing with or without Au. Secondly, figure 3 shows the Raman signal ratio of the buried interface (used to correlate with interfacial packing) was almost the same as the interfacial SERS results, confirming that the molecular packing on gold substrate interface indeed reflect the interfacial packing on silicon oxide. Thirdly, we performed GIXD for an ultra thin film (~10nm, ~6MLs) before and after gold deposition. It shows that there is no structure change in such thin film (Figure S7), suggesting Au deposition post film formation has no effect on the molecular packing of the film. In the end, the insensitivity of molecular packing to the substrate can be understood from the perspective of crystal growth dynamics. Using in-situ synchrotron X-ray diffraction techniques at Cornell High Energy Synchrotron Source (CHESS) and Stanford Linear Accelerator Center (SLAC), we found that the crystallization starts from the top interface, and grow downward (manuscript in preparation). This growth mode leads to independence of the molecular packing to the substrate chemistry, as long as the contact angle between the ink solution and the substrate is comparable. We have measured the dynamic contact angle during drying of the ink solution on Au as compared to on PTS treated silicon oxide. It showed that neither the dynamic contact angle nor the film morphology is affected by the presence of Au (Figure S6). All these additional experiments convincingly prove that the gold layer did not perturb the interfacial layer structure.

Thickness-dependent molecular packing in TIPS-pentacene films

To test the above hypothesis, we reduced the film thickness by decreasing the solution concentration while keeping the same shearing speed at 0.8 mm/s and 1.6 mm/s (the film thickness as a function of the shearing speed is shown in Figure 5a). Figure 5b shows the I_{1157}/I_{1374} ratio of surface SERS spectra as a function of shearing speed. As expected, we observed that I_{1157}/I_{1374} increased by decreasing the solution concentration (at a fixed shearing speed), following the same trend as when increasing the shearing speed (at a fixed solution concentration as discussed earlier).

We also used GIXD to characterize the overall molecular packing in these films. The shifts of (010) and (011) peak positions indicate that the crystal lattice deviates further from the equilibrium packing in films prepared from solutions with lower concentration (lower thickness), consistent with the SERS experiment (Figure 6).

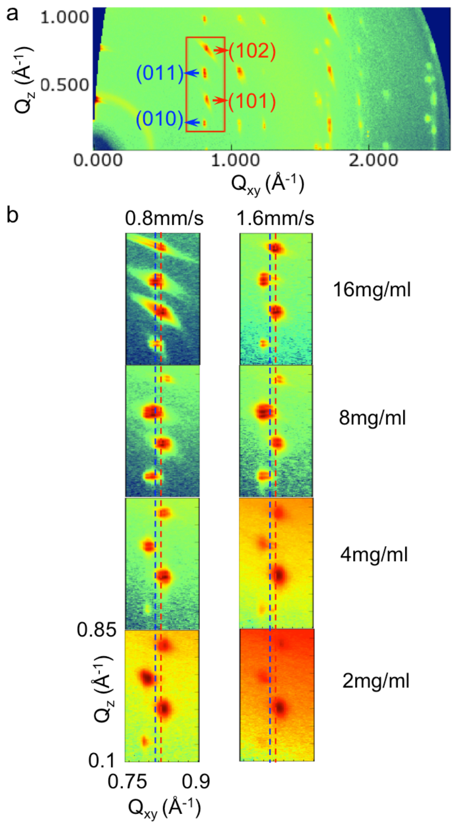


Figure 6. GIXD images of TIPS-pentacene showing dependence of molecular packing on solution concentration at two shearing speed 0.8 mm/s and 1.6 mm/s. a, GIXD images of a solution sheared thin film. Phi-scan was performed on this aligned film so that all the diffraction peaks were captured on the image plate. b, (101) and (011) peaks for indicating deviation from the equilibrium packing obtained with films prepared from various solution concentration. The red and blue dotted

lines indicate the equilibrium peak positions of (101) and (011) respectively. These peak positions are listed in Table S1.

From the I_{1157}/I_{1374} ratio plotted as a function of the film thickness (Figure 7), we observed that for the most part, the I_{1157}/I_{1374} ratio from the Raman spectra mainly depended on the film thickness, regardless of the shearing speeds or solution concentrations. This observation indicates the existence of non-equilibrium molecular packing of TIPS-pentacene. This phenomenon may arise from the restricted degrees of freedom that TIPS-pentacene molecules experience near the solution substrate interface, which increases the kinetic barrier to re-laxation to the equilibrium packing. In thicker films, the top layers (and bulk) molecules are more prone to relaxation back to the equilibrium packing as they are less restricted by the substrate. Non-equilibrium molecular packing have been observed before for other organic semiconductors,[6] however, it has not been reported previously for TIPS-pentacene. Nonetheless, we would like to point out that reducing the film thickness alone seems insufficient for achieving the molecular packing observed at 8mm/s from 8mg/ml solution (Figure 6), which has the largest deviation from the equilibrium packing structure. This indicates that kinetic trapping may also play an important role in accessing metastable states of TIPS-pentacene at certain conditions. Finally, from the perspective of enhancing charge carrier mobility by tuning molecular packing, it is advantageous to achieve non-equilibrium packing by lowering the solution concentration as opposed to increasing the shearing speed, so as to preserve the aligned film morphology at low shearing speed (Figure S9).

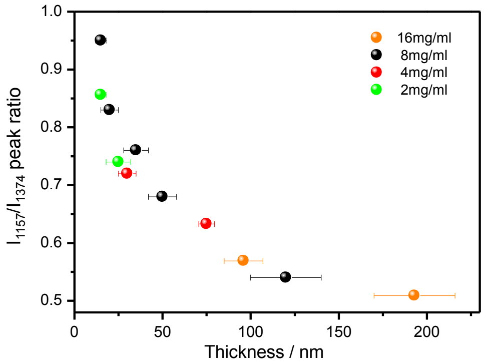


Figure 7. Ratio of I_{1157}/I_{1374} in bulk Raman spectra vs. film thick-ness for TIPS-pentacene films. The film thickness was altered either by changing the shearing speed or the solution concentration. The error bars were derived from the thickness measurement error. Each point was obtained by averaging over 5 spectra.

Overall, we show that Raman spectroscopy is very sensitive for detecting subtle structural changes between different crystalline polymorphs in TIPS-pentacene. The consistency be-tween the SERS/Raman data with GIXD results over a wide range of film thickness (esp. for thin films of a few molecular layers in thickness) provides a convincing proof that SERS can be used for probing buried interface.

Conclusions

In conclusion, we demonstrated that combined Raman and SERS is a useful tool for investigating interfacial molecular packing in organic semiconductor thin films. This method complements the commonly used X-ray based techniques for probing molecular structures and presents advantages as a surface-specific and readily accessible technique. By this method, we elucidated the vertical distribution of TIPS-pentacene molecular packing, particularly at interfaces. We observed that the TIPS-pentacene crystal lattices assume a non-equilibrium packing state near the substrate interface, which gradually relaxes towards the equilibrium packing near the top interface. Our further investigation suggests the existence of non-equilibrium molecular packing for TIPS-pentacene and shed light on the effect of interfaces on the formation of thin film molecular packing.

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Notes and references

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