Micro-Raman Imaging of Isomeric Segregation in Small-Molecule Organic Semiconductors

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Micro-Raman imaging of isomeric segregation in small-molecule organic semiconductors

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Charge transport in organic semiconductors is highly sensitive to film heterogeneity and intermolecular interactions, but probing these properties on the length scales of disorder is often difficult. Here we use micro-Raman spectroscopy to assign vibrational modes of isomerically pure syn and anti 2,8-difluoro-5,11-bis(triethylsilyl)ethynyl)anthradithiophene (diF-TES ADT) by comparing to density functional theory calculations. With polarization-dependent measurements, we determine the orientation of crystallites in pure isomers. In mixed-isomer samples, we observe narrow linewidths and superposition spectra, indicating coexistence of isomerically pure sub-domains on length scales smaller than the probe area. Using the ring breathing modes close to 1300 cm\(^{-1}\) as indicators of the pure isomer crystalline sub-domains, we image their spatial distribution with 200-nm resolution. These results demonstrate the power of micro-Raman spectroscopy for investigating spatial heterogeneities and clarifying the origin of the reduced charge carrier mobility displayed in mixed-isomer diF-TES ADT.
Organic \(\pi\)-conjugated systems are appealing for ultrathin, flexible, and low-cost electronic devices applications. Organic thin-film transistors (OTFTs), for example, can be incorporated in flat-panel displays, radio-frequency identification tags, conformable sensor arrays, memory devices, and health monitoring systems when their performance reaches the levels required by such applications\(^{1-4}\). The charge carrier mobility, and thereby device performance in OTFTs, is very sensitive to the molecular structure of the organic semiconductor, as well as its solid state packing and microstructure, which are highly dependent on processing conditions\(^{5-12}\). Control of microstructure and determination of its spatial variation is difficult, especially in the presence of multiple isomers or structures, complicating optimization of performance.

Anthradithiophene (ADT) is a small-molecule organic semiconductor that showed good electronic performance but limited solubility, which precludes its compatibility with flexible and bendable substrates\(^{13,14}\). Solution processability was achieved by adding side groups to the molecular backbone, as for example in 5,11-triethylylthethyl anthradithiophene (TES-ADT). Unfortunately, in the absence of complicated post-processing treatments, TES ADT typically forms amorphous films with insufficient order to support high-performance OTFTs, or polymorphs that vary greatly in electrical properties\(^{15,16}\). Fluorinated analogs, in contrast, benefit from F–H and F–S interactions between adjacent molecules and demonstrate improved crystallinity\(^{17}\). The fluorinated ADT 2,8-difluoro-5,11-bis(triethylsilyl)lthylianthradithiophene (dif-TES ADT) is among the most promising molecules for incorporation in OTFTs (Fig. 1a) with a charge carrier mobility as high as 6 cm\(^2\) V\(^{-1}\) s\(^{-1}\) reported in vapor grown single crystals of this material\(^{18}\). In solution-deposited OTFTs, the mobility varies from 10\(^{-2}\) to 5.4 cm\(^2\) V\(^{-1}\) s\(^{-1}\) depending on the deposition method, chemical modifications of the surface prior to film deposition, and the dielectric\(^{19-23}\). dif-TES ADT films deposited on Au substrates modified with fluorinated self-assembled monolayers (SAMs) such as pentafluorobenzenethiol (PFBT), 4-(trifluoromethyl)-benzenethiol (TFBT), or 2,3,5,6-tetrafluoro-4-(trifluoromethyl)-benzenethiol (TFFP) exhibit a high degree of crystallinity, with the conjugated backbone of the molecules perpendicular to the surface substrate, as illustrated in Fig. 1b\(^{20,22}\). The vertical orientation was induced by selective F–H and F–S interactions between the molecule and the fluorine in the SAM surface\(^{24}\), an orientation that is favorable for in-plane \(\pi\)-orbital overlap and that can improve charge mobility by a factor of ten\(^{19}\).

With a few exceptions\(^{25-27}\), most studies on dif-TES ADT have looked at isomeric mixtures, due to the fact that under standard synthesis procedures, dif-TES ADT is prepared as an inseparable mixture of syn and anti isomers\(^{17}\). The process of separating the isomers is intensive and expensive\(^{26}\). Performance in as-deposited mixed-isomer molecules is lower than devices fabricated from isomerically pure molecules\(^{26,27}\), with the decreased mobility attributed to molecular disorder from the mixed isomers\(^{19}\).

Here we use micro-Raman spectroscopy to investigate the degree of crystalline order and isomeric segregation in dif-TES ADT films. We report on thin films prepared by solvent-assisted crystallization (SAC) on PFBT-treated Au electrodes, yielding improved film quality with highly ordered microstructure in the dif-TES ADT films\(^{30,28,29}\). Raman spectroscopy is sensitive to conjugated molecular systems, with a large scattering cross-section coupled to the \(\pi\)-\(\pi^*\) modes. We utilize this high sensitivity to distinguish the syn and anti isomers, in combination with density functional theory (DFT) calculations. The sub-micron focus possible in Raman spectroscopy minimizes averaging in the molecular signatures, allowing us to resolve the coexistence of pure isomer domains within mixed-isomer thin films with spatial resolution down to 200 nm. Our results suggest that the reduced mobility in mixed-isomer devices can be attributed to the grain boundaries arising from isomeric phase segregation, rather than changes in order, orientation, or intermolecular interactions.

**Results**

**Vibrational modes of pure isomers.** The experimental Raman spectra of syn and anti dif-TES ADT films on PFBT-treated Au electrodes are shown in Fig. 2, with the associated DFT calculations (gray). The calculated spectra were convolved with a Lorentzian with full-width at half-maximum bandwidth of 2 cm\(^{-1}\). The PFBT-modified Au substrate shows a vibrational mode at 1555 cm\(^{-1}\) (Supplementary Figure 1), but the dif-TES ADT thin films were sufficiently thick that this mode was not typically observed. By comparing the experimentally obtained spectra with calculations and previous reports in five-ring small-molecule analogous, pentacene and 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), Raman modes of dif-TES ADT are assigned and shown in Table 1. The calculated displacement vectors for selected vibrational modes are included in Supplementary Figure 2.

In both the syn and the anti isomers, the C–C stretch modes along the long axis of the molecular core appear at 1597 cm\(^{-1}\), consistent with a previously assigned mode in pentacene (1596 cm\(^{-1}\))\(^{30,31}\). Figure 1c shows the atomic displacements, with blue arrows indicating stretching along the long axis of the conjugated backbone. A lower frequency long-axis stretching band appears as a doublet at 1543/1529 cm\(^{-1}\) for both isomers. A similar doublet appears in pentacene, where the splitting arises due to stretch motions predominantly at the central or end rings of the conjugated backbone\(^{32}\). In spite of the similarity in the spectral
positions, the calculations indicate that these frequencies correspond to different atomic motion, with the heteroatom modification suppressing terminal ring stretching and altering the distribution of atomic motion along the long axis (Supplementary Figure 2).

Vibrations of the C-C ring stretch along the short axis are significantly shifted in syn and anti isomers relative to pentacene. In the anti isomer, these vibrational modes occur at 1434 and 1421 cm\(^{-1}\), compared to 1436 and 1407 cm\(^{-1}\) in the syn isomer. The band splitting is in line with previous studies on pentacene, where it is attributed to different displacements of the H atoms located at the terminal rings (1370 cm\(^{-1}\)) from the central rings (1346 cm\(^{-1}\))\(^{32}\). Figure 1c illustrates the atomic displacements of central rings stretching along the short axis of the conjugated backbone with orange arrows.

While pentacene exhibits no signature bands in the range 1200–1300 cm\(^{-1}\), diF-TES ADT molecules possess multiple vibrational modes, assigned as aromatic ring breathing modes. These vibrations result in uniform C-C bond length elongation. The ring-breathing mode in the anti isomer is found at 1300 cm\(^{-1}\), and is red-shifted to 1286 cm\(^{-1}\) in the syn isomer. The C-H bending modes from the sides of the molecular core are also significantly blue-shifted from pentacene (1178 cm\(^{-1}\)) due to the fluorination, appearing at 1200 and 1207 cm\(^{-1}\) for anti and syn isomers, respectively.

While our DFT calculations are performed for an isolated molecule, we find good agreement with the experimental measurements. We also experimentally investigated the possibility of delocalized crystalline vibrational modes. At low Raman shifts, from approximately 300 to 800 cm\(^{-1}\), we observe weak vibrational modes, with no differences detected for the syn, anti, or mixed-isomer structures (Supplementary Figure 3). Previous X-ray diffraction (XRD) measurement confirmed that both isomers possess triclinic structures, resulting in P\(^{-1}\) symmetry\(^{25}\). Therefore, it is reasonable that there is no differentiation in the Raman spectra for different isomers. Furthermore, the low-frequency Raman responses were much reduced in comparison to the molecular vibration modes. We therefore focus on the higher frequency, localized vibrational modes for our studies of crystalline orientation and isomeric phase coexistence.

**Molecular orientation.** The diF-TES ADT films grown on PFBT-treated Au are highly crystalline, as confirmed by XRD studies\(^{20,24,33}\). The narrow linewidths observed in the micro-Raman spectra also indicate high crystallinity, and optical microscope images suggest crystallite sizes on the order of 100 \(\mu m\).
The measured micro-Raman spectra do not vary within a crystallite (Supplementary Figure 4b and c). However, while the positions of vibrational modes do not change, the relative intensities of specific modes do vary on adjacent crystallites (Fig. 3a, b). In particular, the long-axis and short-axis vibrational modes are anticorrelated in intensity. Grazing-incidence X-ray diffraction (GIXD) showed that diF-TES ADT adopts an optimal “edge-on” orientation with either one of the silylethynyl side groups adsorbed on the substrate, resulting in the long axis of the conjugated core oriented perpendicular to the plane of the film, as illustrated in Fig. 1b,34. We therefore attribute the variable intensities of the vibrational modes to changes in the local molecular orientation within the crystallites with respect to the laser polarization. To confirm this hypothesis, we performed angle-dependent polarized Raman spectroscopy, shown for the anti isomer in Fig. 3c. When the incident laser polarization aligns parallel to the long axis (θ = 0°, blue), a maximum Raman scattering intensity is observed for the 1597/1529 cm\(^{-1}\) modes. The in-phase correlation between the two long-axis vibrational modes was also observed in pentacene characterized by polarization-dependent Raman35. The 1421 cm\(^{-1}\) band is in contrast enhanced when the laser polarization is aligned along the short axis (θ = 90°, orange). The polarization dependence of the C-C long axis and C-C short axis are therefore 90° out of phase, and both follow the expected \(\cos^2(\theta)\) dependence (Fig. 3c). These results support the anisotropic structure of diF-TES ADT observed in mixed samples using transient absorption microscopy36.

**Spatial heterogeneity in mixed sample.** With the ability to spectrally distinguish the syn and anti isomers, and determine crystallite orientation, we extend our studies to the Raman spectra of mixed diF-TES ADT films. These mixtures of the two isomer structures showed reduced mobility and increased subthreshold slope, resulting in slower turn-on performance in comparison to pure isomer samples26,27,37. GIXD revealed a similar structure to that of single crystals, indicating extended crystalline domains in the thin-film phase, but the spatial extent of these domains has not been determined18-20,34. Raman spectra of mixed diF-TES ADT are shown in Fig. 4a. The modes observed appear to be a superposition of the pure isomer spectra, shown in black and red, suggesting there is no intermolecular coupling between the two isomers. The linewidths of the vibrational modes are comparable to those for pure spectra, indicating that long-range order is maintained. This result is in agreement with calculations which found that the two isomers segregate into separate domains where they maintain the local crystalline structure of the pure isomers27. We conclude that under the sample preparation conditions for highly ordered films, the mixed sample segregates into pure syn and pure anti crystallites on length scales shorter than the few hundred nanometer focus region in our experiments.

While the Raman spectra for pure isomers indicated spatial homogeneity within tens to hundreds of micron-sized crystallites, the mixed sample displays significant variations over length scales as short as 200 nm. This can be observed in changes in the relative intensity of the two modes at 1300 cm\(^{-1}\) (Fig. 4b), the three modes close to 1420 cm\(^{-1}\) (Fig. 4c), and the doublet vibrational mode close to 1540 cm\(^{-1}\) (Fig. 4d). Since the long-axis and short-axis vibrational modes (1540 cm\(^{-1}\), 1420 cm\(^{-1}\) respectively) vary significantly in intensity with molecular orientation, as discussed above, we focus on the breathing modes at 1300 cm\(^{-1}\) (anti) and 1286 cm\(^{-1}\) (syn) as proxies for the pure isomer crystallites.

To resolve the details of the spatial distribution, we performed spectroscopy and imaging of the mixed sample across a 2 \(\times\) 1 \(\mu\)m\(^2\) region at 200-nm intervals. Figure 5a shows a contour plot of the spectral region 1270–1310 cm\(^{-1}\). Both vibrational modes are consistently resolved in the mixed spectrum, but with variable peak intensity. We are able to resolve correlated changes in the relative intensity of the two vibrational modes. We further extend our analysis to map the integrated intensity ratio \(I_{1300}/I_{1286}\) extracted from these spectra (Fig. 5b). This map demonstrates the
variation of the breathing modes associated with anti and syn isomers, respectively, with yellow regions indicating a higher proportion of anti isomer, and blue regions with more syn isomer. Additional intensity maps showing the raw intensities for the 1300 and 1286 cm\(^{-1}\) modes are shown in Supplementary Figure 5a and 5b.

The variation in the spatially distributed spectra and integrated intensity of both vibrational modes indicate that the mixed-isomer films form into homogeneous anti and syn crystallite sub-domains on length scales below 200 nm. These sub-domains have variable size and local distribution, resulting in superposition spectra with different contributions of anti and syn spectral signatures, as resolved in Figs. 4 and 5. As we observe no regions with only one of the 1286 or 1300 cm\(^{-1}\) vibrational modes, we conclude that the pure isomer sub-domains have spatial extent significantly below the 200-nm step size measured here, possibly on the order of tens of nanometers. Higher spatial resolution techniques are therefore necessary to directly resolve the pure isomer domains.

It is important to note that our observations of isomeric segregation based on Raman spectroscopy apply to the highly ordered structures arising from SAC deposition. This deposition method is known to produce high crystallinity and therefore favorable mobilities, in particular in pure isomer systems. Other thin-film preparations, for example, rapid spin casting, would lead to lower molecular order and therefore reduced phase separation\(^{39}\). Raman spectroscopy can provide valuable information about the degree of order in organic semiconductors, but is additionally helpful in characterizing isomer distribution in highly crystalline systems to optimize mobilities for high-performance applications.

**Discussion**

Micro-Raman spectroscopy is a powerful technique to investigate crystalline order in molecular systems. Here, we demonstrate its use for characterizing the spatial properties of a mixed-isomer organic small-molecule semiconductor, dif-TES ADT, through the spectroscopic signatures of the pure isomers. Our results indicate that crystallites of isomeric purity coexist intimately, while maintaining their high crystallinity and orientational order, even across sub-domains. This phase segregated behavior explains the reduction in mobility and slower turn-on response observed in mixed dif-TES ADT TFTs, with grain boundaries between crystallites potentially introducing defects and reducing the efficiency of charge transfer in spite of their high crystallinity. The ability to spectrally discriminate isomer crystallites and their heterogeneous distribution and packing is important to optimize thin-film preparation in this small-molecule semiconductor, and can also provide information about isomer microstructure in other small molecules. These results highlight the importance of thin-film preparation for control of isomer distribution and domain engineering, and provide a means to characterize and optimize device performance.

**Methods**

**Sample preparation.** The pure form syn and anti dif-TES ADT and 50–50 mixtures of isomers were synthesized by a previously reported method\(^{39}\). n++-doped Si with 200 nm of thermally oxidized SiO\(_2\) was used as the underlying substrate. Contacts patterned by photolithography were deposited by electron
beam evaporation of 5 nm of Ti followed by 45 nm of Au. The substrates were cleaned by soaking in hot acetone, then hot isopropyl alcohol for 10 min each, followed by a 10-min exposure to ultraviolet/ozone and a rinse with deionized water. Upon drying, the substrates were soaked in 30 mM solutions of PFBT in room-temperature ethanol for 30 min, followed by a 5-min sonication in fresh ethanol to remove any excess PFBT. Substrates with Au features were necessary in order to obtain a highly ordered film with molecular orientation out of plane (Fig. 1b), as we have explained in detail elsewhere.35 Solutions of 0.3% w/w DiT-TEE ADT in chlorobenzene were drop cast on these substrates and placed in a closed Petri dish with an additional 250 μL of chlorobenzene, creating a solvent-rich environment. The thin films were formed after the solvents were allowed to evaporate over 1–2 days.

Raman spectroscopy. Micro-Raman spectra were acquired using a Renishaw inVia Raman microscope with 488-nm laser excitation (objective 0.75 NA Olympus, ×50). The corresponding lateral resolution of the beam spot was around 0.32 μm2, defined by λ/2(NA). All samples were measured in air. Spectra were averaged for 20 accumulations each with 2–s duration. In polarized Raman spectra, a half-wave plate was placed between the laser and the sample to control the incident polarization (Fig. 1b). Two-dimensional mapping of the mixed sample was performed using a Horiba LabRAM HR Evolution Raman microscope with 473-nm incident polarization (Fig. 1b). A two-dimensional mapping of the mixed sample was performed using a Horiba LabRAM HR Evolution Raman microscope with 473-nm laser excitation (objective 0.9 NA Olympus, ×100). The corresponding lateral resolution was around 0.26 μm2. The spectra were collected 200 nm apart, with each point averaged for two accumulations with 5-s duration.

DFT calculation. DFT calculations were performed with the GAUSSIAN09 software. The geometry of a symmetric segment was first optimized, then frequency analysis was performed using the B3LYP hybrid functional, and the 6-31G(d) basis set. The frequencies were scaled by a factor of 0.96 for comparison. The molecular core is defined as the conjugated fused acene rings. The dir isomer has a core with C2v symmetry, with the two sulfurs in thiophene rings in inversion correlation. The core of the syn isomer has C2v symmetry.

Data availability. The authors declare that the data within the article and Supplementary Information, as well as additional data supporting the findings of this study, are available upon reasonable request.

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Author contributions
The experiments were conceived by J.M.A. and O.D.J. C.-W.H. performed the experiments, implemented the calculations, and analyzed the data, with help from X.Y. P.J.D. prepared the crystalline films. A.J.P. and J.E.A. synthesized the pure isomers and the mixed molecules. C.-W.H. and J.M.A. wrote the manuscript, with input from all authors, J.M.A. supervised the project.

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