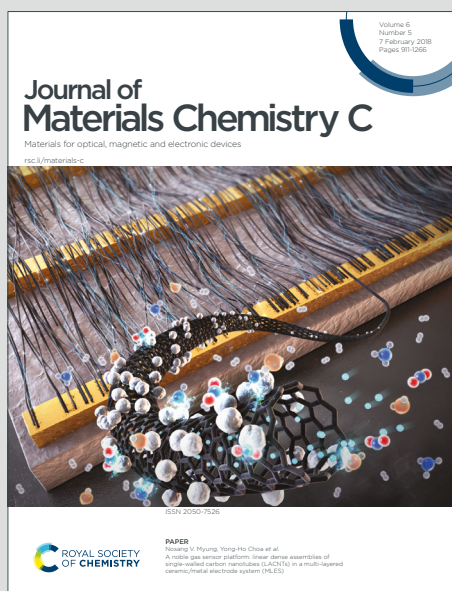


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Self-Healing of Defects in Uniaxially Aligned Semiconducting Polymer Crystals via Molecular Doping: Insights into Crystallization from Transient vs. Settled Amorphous Phases

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Abstract:

We present the self-healing of defects and enhanced crystallinity in uniaxially aligned poly(3-hexylthiophene) (P3HT) crystal via molecular doping with F4TCNQ. Using eutectic friction transfer (EFT), highly aligned P3HT films ($P3HT_{EFT}$) were fabricated, exhibiting superior alignment and planarity compared to spin-cast P3HT ($P3HT_{SC}$). Upon doping, the self-healing of defects in $P3HT_{EFT}$ films led to a significant increase in the charged-ordered phase from 5.4% to 80.3%, transforming transient amorphous phases into well-ordered crystalline domains. In contrast, the conventional $P3HT_{SC}$ films formed settled amorphous phases, and exhibited no self-healing behavior. Structural analysis using polarized UV-VIS, FT-IR, Raman spectroscopy, and GIWAXS confirmed significant improvements in crystalline order and charge carrier mobility. This led to a dramatic increase in electrical conductivity, with doped $P3HT_{EFT}$ (d- $P3HT_{EFT}$) films exhibiting four orders of magnitude higher conductivity compared to their spin-cast counterparts (d- $P3HT_{SC}$). These findings highlight the distinct crystallization behaviors of transient versus settled amorphous phases, emphasizing the critical role of uniaxial alignment in realizing highly crystalline semiconducting polymers for organic electronic applications.



Introduction:

With the rapid advancement of wearable and implantable electronics, semiconducting polymers have become a focal point in research as active materials for organic devices, including organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic thermoelectric generators (OTEGs).¹⁻⁶ This interest largely stems from their cost-effectiveness, processability, and mechanical flexibility.⁷⁻⁹ Additionally, the electrical and optical properties of semiconducting polymers can be extensively tuned through various methods, such as chemical structure modification, crystallization, molecular arrangement, and doping. Optimizing electrical conductivity in semiconducting polymers, in particular, often relies on strategies like chain alignment and charge-transfer (CT) doping. Unlike their inorganic counterparts, semiconducting polymers do not typically follow the Wiedemann-Franz law, and the correlation between σ and κ is weak.¹⁰⁻¹² This weak correlation allows semiconducting polymers to avoid the usual trade-offs between electrical and thermal performance when employing CT doping. Studies have shown that the conductivity of *n*- or *p*-type semiconducting polymers can be significantly enhanced by several orders of magnitude through the introduction of a specific quantity of electron- or hole-donating CT dopants.¹³⁻¹⁶ However, despite these improvements in conductivity, it is important to note that incorporating dopants into long semiconducting polymer chains can lead to structural distortions. These distortions disrupt the ordered microstructure, complicating the understanding of the CT mechanism in these materials.^{17,18} Moreover, the effect of pre-formed polymer microstructures on doping efficiency and conductivity remains unclear.¹⁹ The anisotropic microstructure of semiconducting polymers across various length scales



can significantly influence doping efficiency and charge transport. This underscores the need for further investigation into the impact of doping on the structure-function relationship in these materials, particularly considering the structural challenges posed by CT doping.

The electronic coupling in conducting polymers is highly sensitive to the conformation and packing characteristics of individual chains. Depending on their intrachain order, the optical spectra can exhibit either H-type or J-type behavior. In H-type aggregates, the 0–0 transition is forbidden, whereas in J-type aggregates, the 0–0 transition is allowed.^{20–29} Due to defects such as bends or kinks in the conjugation that hinder intrachain transport, J-type packing rarely occurs because it requires a high degree of intrachain order. To address this challenge, uniaxial alignment in conjugated polymers has been employed to enhance their conjugation length and planarity—characteristics associated with J-type packing. These structural improvements contribute to enhanced electrical properties by facilitating charge transport along extended π orbitals in the planar polymer backbone. This configuration minimizes the reliance on slow and energetically demanding interchain hopping events.

In this study, we present the spontaneous removal of defects in uniaxially aligned poly(3-hexylthiophene) (P3HT) films prepared via the eutectic friction transfer (EFT) method during *p*-doping with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) (Figures 1a-b). To achieve uniaxial alignment in semiconducting polymer films, our group previously demonstrated that the EFT method can be effectively employed.³⁰ Highly crystalline films were obtained by simply rubbing pellets composed of semiconducting polymers and small-molecule matrix materials that form eutectic mixtures.



We intentionally chose matrix materials that can be easily removed through sublimation. P3HT films prepared either by EFT method (P3HT_{EFT}) or by conventional spin casting method (P3HT_{SC}) were analyzed using polarized UV-VIS, FT-IR, and Raman spectroscopy. Compared to P3HT_{SC}, P3HT_{EFT} exhibited highly anisotropic characteristics in polarized spectra. Deconvolution of the Raman spectra provided insights into the fraction of neutral-disordered, charged-disordered, neutral-ordered, and charged-ordered domains within the films. Before doping with F4TCNQ, both P3HT_{SC} and P3HT_{EFT} exhibited similar fractions of neutral-disordered (24.7% vs. 24.0%), charged-disordered (1.0% vs. 0.9%), neutral-ordered (66.6% vs. 69.5%), and charged-ordered (7.7% vs. 5.4%) phases. After doping, the total disordered fraction (charged and neutral) in P3HT_{EFT} significantly decreased from 24.9% to 2.7%, accompanied by a dramatic increase in the charged-ordered fraction from 5.4% to 80.3%. In contrast, P3HT_{SC} showed minimal change in the total disordered fraction, remaining relatively constant at 24.7% compared to its initial value of 25.7%. These results suggest that F4TCNQ molecules effectively and uniformly interact with P3HT in the uniaxially aligned films, reorganizing torsional defects in the polymer chains.²⁴⁻²⁶

Results and Discussions

Uniaxially aligned P3HT films were prepared using the EFT method (P3HT_{EFT}), with slight modifications as described in a previous report.³⁰ Briefly, P3HT and the matrix material, 1,3,5-trichlorobenzene (1,3,5-TCB), were mixed in a 1:1 weight ratio and completely dissolved in chloroform. The solution was filtered through a syringe filter (PTFE, 0.2 μm pore) and then dried at room temperature for 4 hr. After drying, the



resulting powder was ground again and compressed under a pressure of ~600 MPa to form a pellet, which was subsequently cut and inserted into a pencil as the lead for EFT writing. The P3HT_{EFT} films were prepared by simply rubbing the pellets in one direction onto silicon substrates heated to 55 °C (Figure 1c). Frictional heat generated during the rubbing process caused eutectic melting of P3HT and 1,3,5-TCB, facilitating easy transfer under mild pressure conditions (< 0.1 MPa). Although 1,3,5-TCB was spontaneously removed by sublimation during the rubbing process due to its high vapor pressure, additional sublimation was performed by placing the samples in a vacuum oven at 50 °C for 24 hr. The prepared P3HT_{EFT} films were then doped with F4TCNQ by applying F4TCNQ solutions dissolved in acetonitrile ($c = 0.1\sim 3.0$ mg/mL) for 10 s, followed by removing excess solution by spinning at 3000 rpm (Figure 1c). The resulting F4TCNQ-doped P3HT_{EFT} (d-P3HT_{EFT}) showed a slightly dark color.

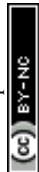
Figures 1d-i display the polarized optical microscopy (POM) micrographs of the P3HT_{EFT} and the d-P3HT_{EFT} films. Both P3HT_{EFT} and d-P3HT_{EFT} exhibited strong birefringence responses under cross-polarizers when the drawing direction was aligned at 45° to the polarizer, while no response was observed when it was parallel to the polarizer (Figures 1d and 1g). In contrast, the P3HT films prepared by spin casting (P3HT_{SC}) show no birefringence response at any angle on POM (Figure S1). When a retarder was inserted, P3HT_{EFT} and d-P3HT_{EFT} films presented two different colors depending on their orientation: a yellow color when the drawing direction was perpendicular to the retarder (Figures 1e and 1h) and a blue color when the drawing direction was parallel to the retarder (Figures 1f and 1i). Considering that P3HT crystals exhibit negative birefringence and that their optical axis corresponds to the direction of π -



π stacking between the thiophene rings, these results suggest that the polymer backbone of P3HT is uniaxially aligned along the drawing direction in the P3HT_{EFT} films.

Figures 2a-b display the UV-VIS absorption spectra of the d-P3HT_{SC} and d-P3HT_{EFT} with varying doping concentrations from 0 to 3.0 mg/mL. The P3HT_{EFT} film exhibited a broad absorption peak at $\lambda_{\text{peak}} = 558$ nm with a small shoulder at $\lambda_{\text{peak}} = 605$ nm, which are assigned as 0–1 and 0–0 electronic transitions, respectively. In contrast, no such vibronic features were observed in the P3HT_{SC} film. Depending on their intrachain order, the optical spectra can exhibit either H-type or J-type behavior.²⁰⁻²⁹ The ratio of $I_A^{0-0} / I_A^{0-1} = 0.83$, which is less than unity, indicates that the P3HT_{EFT} film mainly exhibits H-type packing with some contribution from the allowed 0–0 transition.^{20,31} Upon doping with F4TCNQ, several new peaks appeared in both d-P3HT_{SC} and d-P3HT_{EFT}, with intensities increasing alongside the concentration of F4TCNQ ($c = 0-3.0$ mg/mL). The peaks observed at $\lambda_{\text{peak}} = 450 \sim 530$ nm and $\lambda_{\text{peak}} = 758$ nm correspond to the polaron absorption bands assigned to neutral peak (N) and P2, respectively.^{32,33} Noticeably, the d-P3HT_{EFT} showed two distinct features upon doping with F4TCNQ: first, the position of the 0–1 absorption peak shifted toward a lower wavelength region; second, the intensity of the 0–0 absorption peak nearly disappeared. In contrast, the d-P3HT_{SC} showed no significant changes in these peaks. These observations suggest that H-packing was further enhanced in the d-P3HT_{EFT} film through F4TCNQ doping. Especially, the disappearance of the 0–0 transition indicates that F4TCNQ doping induces almost purely H-type packing while suppressing any J-type characteristics.

The generation of new vibronic states by polarons and a weakening of interchain interactions, potentially due to the intercalation of F4TCNQ molecules within the



thiophene units. As the concentration of F4TCNQ increased, the intensity of the P2 polaron peak ($\lambda_{P2} = 758$ nm), and the F4TCNQ anion peaks ($\lambda_{F4TCNQ^-} = 416$ nm and 770, 873 nm) gradually increased and eventually saturated in both d-P3HT_{EFT} and d-P3HT_{SC} (Figures 2a-b). The P2 polaron and the F4TCNQ anion peaks overlap at 700~1000 nm.³⁴ The charge orientation of the d-P3HT_{EFT} film was analyzed using polarized UV-VIS spectroscopy. When the incident polarized light was aligned parallel to the polymer chain direction, the P2 ($\lambda_{P2} = 758$ nm) polaron peak was prominently observed with minimal contribution from the F4TCNQ anion peaks. Additionally, a P2 polaron around 900 nm overlapped with the F4TCNQ anion peak at 873 nm. In contrast, when the incident polarized light was perpendicular to the polymer chain direction, distinct F4TCNQ anion peaks appeared at $\lambda_{F4TCNQ^-} = 413$ nm, 660 nm, 770 nm, and 873 nm (Figure 2d) This suggests that the orientation of the charged species in the d-P3HT_{EFT} film is highly anisotropic, with the P2 polaron transitions aligning along the polymer backbone and the F4TCNQ anion transitions oriented perpendicular to it. The full UV-VIS absorption spectra are represented in Figure S2 . In contrast, no anisotropy in UV-VIS spectra was observed in d-P3HT_{SC} (Figure 2c). The anisotropic properties of d-P3HT_{EFT} film originate from its highly aligned charge orientation. The P3HT polarons formed along the uniaxially aligned backbone, while the F4TCNQ anions are situated between the polymer side chains, oriented perpendicular to the backbone direction. The measurement of neutral F4TCNQ, shown as the dotted line in Figure 2d, displays a neutral peak at 385 nm and minor charged peaks at 770 nm, and 873 nm due to exposure to air. Notably, the d-P3HT_{EFT} film does not exhibit the neutral F4TCNQ peaks, indicating that all F4TCNQ molecules were completely doped without the neutral residue.



Characterization via polarized FT-IR spectroscopy provided detailed insights into charge orientation by investigating the C \equiv N stretching of F4TCNQ anions ($\tilde{\nu} = 2188 \sim 2180 \text{ cm}^{-1}$) and doping-induced modes of P3HT ($\tilde{\nu} = 1350 \sim 1000 \text{ cm}^{-1}$).^{16,33,35,36} The scan area for the polarized FT-IR mapping (highlighted with a red dotted square) is depicted in Figure 3a, with the corresponding spectra of the d-P3HT_{EFT} film presented in Figure 3b. Figures 3c-d represent polarized FT-IR mapping images calibrated to the doping-induced mode of P3HT ($\tilde{\nu} = 1350 \sim 1000 \text{ cm}^{-1}$), revealing a uniform distribution with high intensity when the polarized light was parallel to the backbone direction (Figure 3c). In contrast, lower intensity was observed when the polarized light was perpendicular to the backbone direction (Figure 3d). These results impart that the doping-induced modes of P3HT were notably activated when the polarized light was aligned parallel to the backbone direction. In contrast, the C \equiv N stretching peak of F4TCNQ anions was prominently activated when the polarized light was perpendicular to the backbone direction. Figures 3e-f present polarized FT-IR mapping images calibrated to the C \equiv N stretching of F4TCNQ anions ($\tilde{\nu} = 2188 \sim 2180 \text{ cm}^{-1}$). These images revealed high intensity with perpendicular light and low intensity with parallel light, indicating the perpendicular arrangement of F4TCNQ anions relative to the backbone direction. Consistent with the polarized UV-VIS data, these results indicate that P3HT polarons are uniaxially aligned along the polymer backbone, while the F4TCNQ anions are oriented perpendicularly to the polymer chains. However, the d-P3HT_{SC} film did not show anisotropic properties (Figure S3).

Subsequently, P3HT films were characterized using polarized Raman spectroscopy (Figure 4). A 785 nm laser was employed for excitation due to its effective



interaction with polarons. We note that our chosen laser wavelength biases to the the ordered fraction in the films.²⁷ Under polarized laser irradiation parallel to the backbone direction, the P3HT_{EFT} film exhibited strong C – C (1380 cm⁻¹) and C = C (1452 cm⁻¹) peaks. Conversely, these peaks were significantly diminished when the polarized laser was oriented perpendicular to the backbone direction (Figure 4c-d). The d-P3HT_{EFT} film also exhibited highly anisotropic Raman spectra, depending on the laser irradiation direction. Under the parallel laser excitation, the d-P3HT_{EFT} film revealed distinct polaron peaks corresponding to the charged-ordered (1421 cm⁻¹) and charged-disordered (1397 cm⁻¹) components. Additionally, the C = C peak showed a redshift of 35 cm⁻¹, with a high $I_{C-C} / I_{C=C}$ ratio, indicating a high degree of planarity in the polymer backbone (Figure 4c).^{37,38} Peaks corresponding to F4TCNQ anions at 1452 cm⁻¹ and 1700~1600 cm⁻¹ range were observed under perpendicular laser orientation relative to the backbone. The neutral F4TCNQ peak, indicated by the dotted line, displayed a 2 cm⁻¹ shift upon charge formation (Figure 4d). On the other hand, both P3HT_{SC} and d-P3HT_{SC} films showed isotropic properties without the peak shift (Figures 4a-b).

During the process of F4TCNQ doping, the presence of positively charged polarons impacts the distribution of delocalized electron charges along the polymer backbone. In the crystalline regions of the polymer, characterized by a stiff, planar backbone, the Coulomb force exerted by the delocalized charge is relatively weak. Consequently, the formation of polarons does not significantly alter bond lengths in these regions. However, in the amorphous regions, where the Coulomb force is stronger and interacts with localized charges, the creation of polarons results in noticeable changes in bond lengths. By extracting only the peaks corresponding to P3HT and its



polaron□excluding the F4TCNQ anion peak□it becomes possible to differentiate between polarons formed on an ordered (crystalline) backbone, termed ordered-polarons, and those on a disordered (amorphous) backbone, referred to as disordered-polarons.^{37,38} The polarized Raman spectra of the uniaxially oriented d-P3HT_{EFT} film satisfy this criterion, allowing for such a distinction. To ascertain the specific phase composition of the films, the C = C double bond region (1500 ~ 1300 cm⁻¹) was subjected to deconvolution (Figures 5a-d). The C - C vibration modes shown in Figure 5 (noted as green dotted lines) were excluded for the composition calculations, since only the the C=C intra-ring vibration modes contribute to the charging of the conjugated thiophene backbone.³⁷⁻³⁹ From the deconvolution data, the P3HT_{EFT} film was composed of 24.0% neutral-disordered phase (1467 cm⁻¹), 69.5% neutral-ordered phase (1444 cm⁻¹), 5.4% charged-ordered phase (1421 cm⁻¹), and 0.9% charged-disordered phase (1397 cm⁻¹) (Figure 5e). In the P3HT_{SC} film, the phase distribution was 24.7% neutral-disordered phase, 66.6% neutral-ordered phase, 7.7% charged-ordered phase, and 1.0% charged-disordered phase, which is comparable to that of the P3HT_{EFT} film. A trace amount of polaron was formed by oxidation from atmospheric oxygen prior to doping. After F4TCNQ doping, the composition of the d-P3HT_{EFT} film altered to 1.9% neutral-disordered (1477 cm⁻¹), 17% neutral-ordered (1443 cm⁻¹), 80.3% charged-ordered (1412 cm⁻¹), and 0.8% charged-disordered phase (1376 cm⁻¹) (Figure 5e). For the d-P3HT_{SC}, the composition changed to 18.8% neutral-disordered, 55.1% neutral-ordered, 20.2% charged-ordered, and 5.9% of charged-disordered.

The analysis indicates that the P3HT_{EFT} film underwent a significant transformation from the disordered phase to the ordered phase after F4TCNQ doping.



The disordered phase, which originally comprised 25.1% of the total content in the P3HT_{EFT}, was reduced to only 2.7% in the d-P3HT_{EFT} (Figure 5e). This substantial decrease highlights the pronounced ordering effect induced by the doping process. In contrast, such an ordering effect was not observed in the P3HT_{SC} film. The disordered phase, which originally comprised 25.7% of the total in the P3HT_{SC}, remained virtually unchanged at 24.7% in the d-P3HT_{SC} (Figure 5e). This disparity suggests that the disordered amorphous phase can be categorized into two types, referred to as the *transient-amorphous* and *settled-amorphous* phases.

As previously discussed, the P3HT_{EFT} forms a highly aligned structure while maintaining planarity of both thiophene and alkyl-side groups. However, there may be points where planarity is disrupted due to slightly rotated moieties or dislocation of polymer chains, contributing to the formation of the amorphous phase. These chains, however, can be readily ordered through the formation of polaron-anion pairs, which induce electrostatic interactions. In contrast, the polymer chains in the P3HT_{SC} are randomly distributed and entangled, making it difficult to induce phase transition. Hence, the P3HT_{EFT} predominantly forms the transient-amorphous phase, which can transform into the ordered crystalline phase through the doping process, while the P3HT_{SC} mainly creates the settled-amorphous phase. This difference in the nature of the amorphous domains also leads to a significant difference in doping efficiency. As shown in Figure 5e, the charged-ordered phase in the d-P3HT_{EFT} dramatically increased from 5.4% to 80.3%, derived both directly from the neutral-ordered domain and from transformation of the disordered phase. In contrast, the d-P3HT_{SC} only exhibited 20.2% of the charged-ordered phase, which is 4 times less than that of the d-P3HT_{EFT}.



To better understand the P3HT_{EFT} film, grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted (Figure 6). When the incident X-ray was parallel to the polymer backbone, high-order peaks, specifically the (100), (200), and (300) peaks, emerged in the in-plane region, while the (010) peak became prominent in the out-of-plane region (Figures 6a-d). The d-spacing corresponding to the (100) and (010) peaks were 1.64 nm and 0.38 nm, respectively, which is consistent with the lamellar stacking distance and π - π stacking distance of P3HT.^{40,41} When the incident X-ray was perpendicular to the backbone, the diffraction pattern revealed the presence of the (010), (001), and (011) peaks (Figures 6b and 6d). These observations suggest that the P3HT_{EFT} film is uniaxially well-aligned with a face-on arrangement (Figures 7a-b). Upon doping, the d-P3HT_{EFT} film exhibited slight changes in the d-spacing: the lamellar stacking distance, represented by the (100) peak, expanded from 1.64 nm to 1.84 nm, while the π - π stacking distance, represented the (010) peak, contracted from 0.38 nm to 0.36 nm, all while preserving the crystal structure (Figures 6a-d, 7c-d). In contrast, the P3HT_{SC} film displayed isotropic characteristics with a broad amorphous band (Figure S4). Similar to the d-P3HT_{EFT} film, the d-spacing of the (100) plane also increased from 1.6 nm to 1.8 nm, and the (010) plane decreased from 0.38 nm to 0.36 nm for the d-P3HT_{SC} film. The crystallite correlation lengths for the lamellar and the π - π stacking distance were calculated using the Scherrer equation based on the (100) and (010) peaks, respectively (Figures 6f and S5). After doping, the correlation length for the lamellar stacking increased from 16.9 nm to 17.9 nm for the P3HT_{EFT} film, while the correlation length for the π - π stacking remained unchanged. This suggests that the lateral ordering of the P3HT_{EFT} was improved by doping. In contrast, the doping process hampered both the lateral and



vertical ordering of the P3HT_{SC}, as indicated by a decrease in the correlation length from 12.95 nm to 7.95 nm for lamellar stacking and from 4.48 nm to 2.95 nm for π - π stacking (Figures 6f and S5). Previous UV-VIS data revealed that the P3HT_{EFT} film primarily consists of H-type packing but with a minor contribution from J-type packing. As depicted in Figure 7a-b, this minor contribution of J-type packing may be attributed to torsional defects in the P3HT_{EFT} structure. Upon F4TCNQ doping, these torsional defects were corrected, leading to the conversion of J-type packing into H-type packing in the d-P3HT_{EFT} film. These results indicate that defects in uniaxially aligned P3HT_{EFT} polymer chains can be spontaneously removed during the doping process, leading to a significant increase in the crystallinity of d-P3HT_{EFT}. Due to this improvement, the electrical conductivity of d-P3HT_{EFT} was four orders of magnitude higher than that of d-P3HT_{SC} (Figure S6).

Conclusion

In summary, we demonstrated the significant impact of eutectic friction transfer (EFT) and subsequent F4TCNQ doping on the structural ordering and electrical performance of uniaxially aligned P3HT films. The EFT method allowed for the creation of highly aligned P3HT films (P3HT_{EFT}) with superior planarity compared to conventional spin-cast P3HT (P3HT_{SC}). Upon p-doping with F4TCNQ, the P3HT_{EFT} films exhibited a dramatic increase in the charged-ordered domain from 5.4% to 80.3%, facilitated by the spontaneous removal of defects. Characterization through polarized UV-VIS, FT-IR, Raman spectroscopy, and GIWAXS showed that the uniaxially aligned structure of P3HT_{EFT} contributed to enhanced charge carrier mobility and crystallinity. The d-P3HT_{EFT}



films exhibited four orders of magnitude higher electrical conductivity compared to d-P3HT_{SC} films, underscoring the benefits of anisotropic alignment for charge transport. In contrast, P3HT_{SC} films retained a largely disordered phase after doping, highlighting the limitations of spin-cast films. Overall, the combination of uniaxial alignment via EFT and effective molecular p-doping proves to be a promising approach for enhancing the crystallinity and electrical performance of semiconducting polymer films, providing a valuable pathway for the development of organic electronic devices.



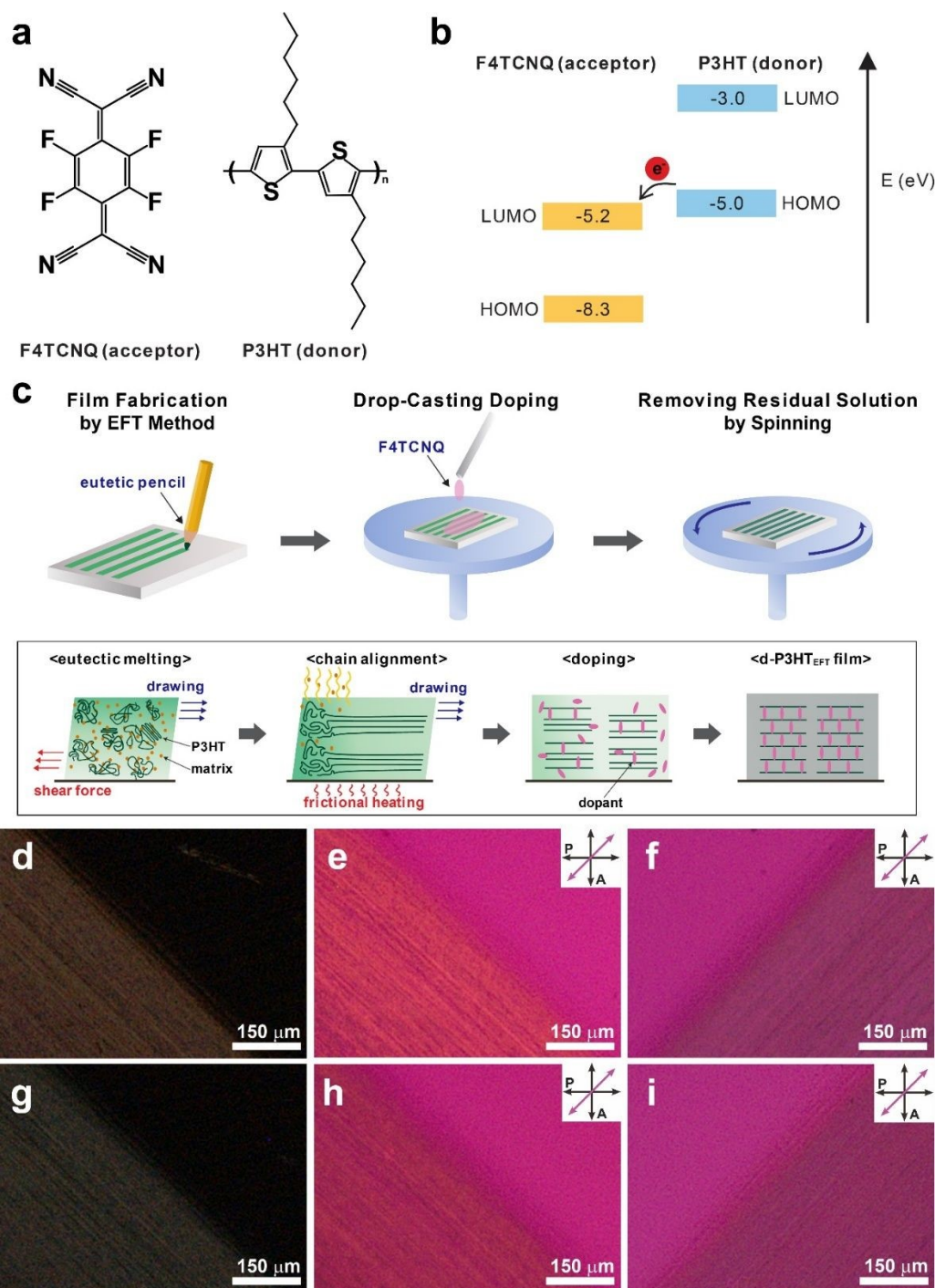


Figure 1. (a) Molecular structure of F4TCNQ and P3HT. (b) Schematic illustrations of the electron transfer process between their respective energy levels. (c) Fabrication process of the d-P3HT_{EFT} using the eutectic friction transfer (EFT) method. (d-f) Polarized optical microscopy images of the P3HT_{EFT} film under crossed polarizers. (g-i) Polarized optical microscopy images of d-P3HT_{EFT} film under crossed polarizers. A retarder is inserted (e, h) perpendicular and (f, i) parallel to the drawing direction, which is aligned at 45° to the polarization direction of the light.



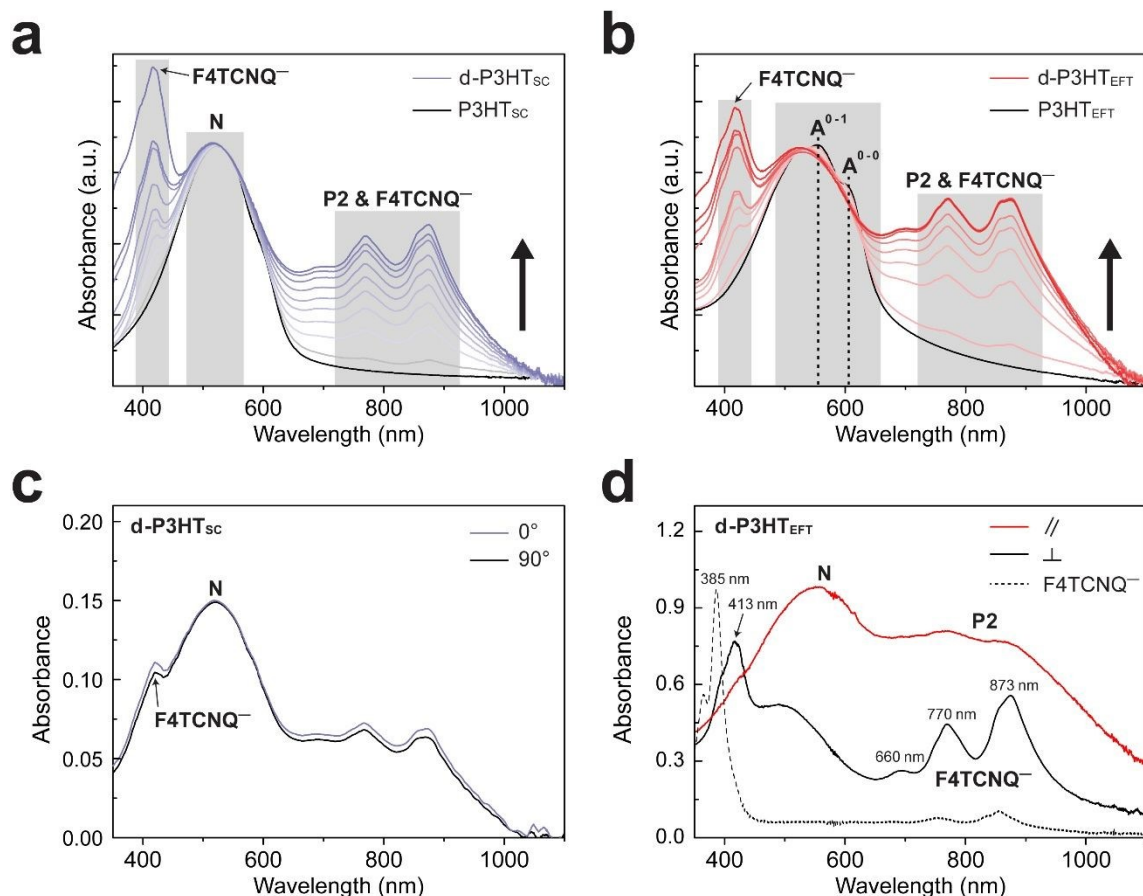


Figure 2. UV-VIS spectra of (a) d-P3HT_{sc} and (b) d-P3HT_{EFT} films taken at varying F4TCNQ concentrations from 0 to 3.0 mg/mL. The characteristic bands including F4TCNQ⁻, N, P2 & F4TCNQ⁻, A⁰⁻¹, and A⁰⁻⁰ are highlighted in grey. (c) Polarized UV-VIS spectra of the d-P3HT_{sc} film, with the polarizer rotated 0° and 90° from the original position. (d) Polarized UV-VIS spectra of the d-P3HT_{EFT} film, with the polarizer aligned parallel (red solid line) and perpendicular (black solid line) to the drawing direction. The polarized UV-VIS spectrum of neutral F4TCNQ is shown as a dashed line.



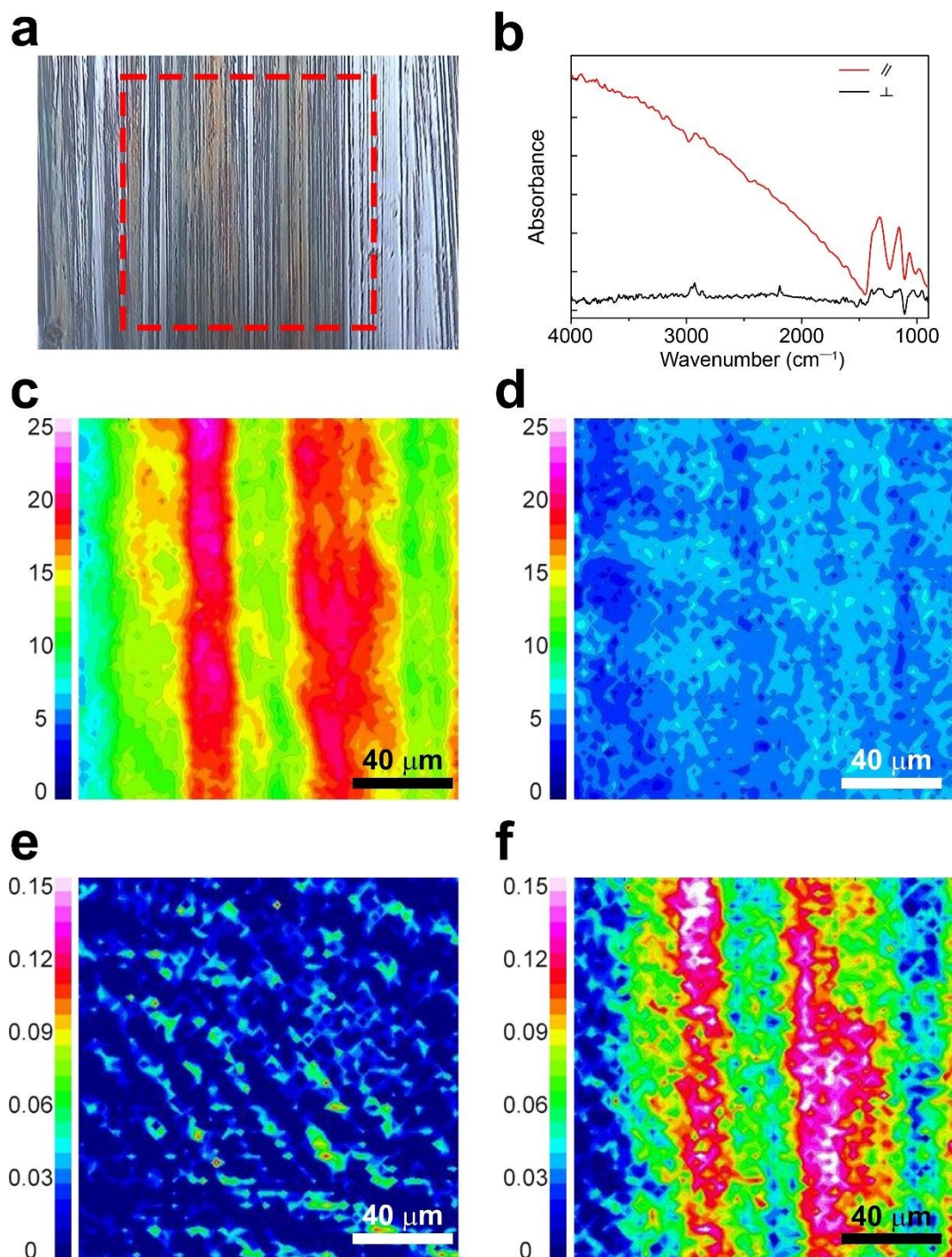


Figure 3. (a) Optical microscopy image of the d-P3HT_{EFT} film, showing the polarized FT-IR mapping area. (b) Polarized FT-IR spectra of the d-P3HT_{SC} film under polarized conditions. The red and solid lines correspond to the polarizer aligned parallel and perpendicular to the drawing direction, respectively. FT-IR mapping micrographs of d-P3HT_{EFT} using (c, d) the doping-induced mode of P3HT ($\tilde{\nu} = 1350 \sim 1000 \text{ cm}^{-1}$) and (e, f) the F4TCNQ anion vibronic band ($\tilde{\nu} = 2188 \sim 2180 \text{ cm}^{-1}$) obtained with the polarizer (c, e) parallel and (d, f) perpendicular to the drawing direction.



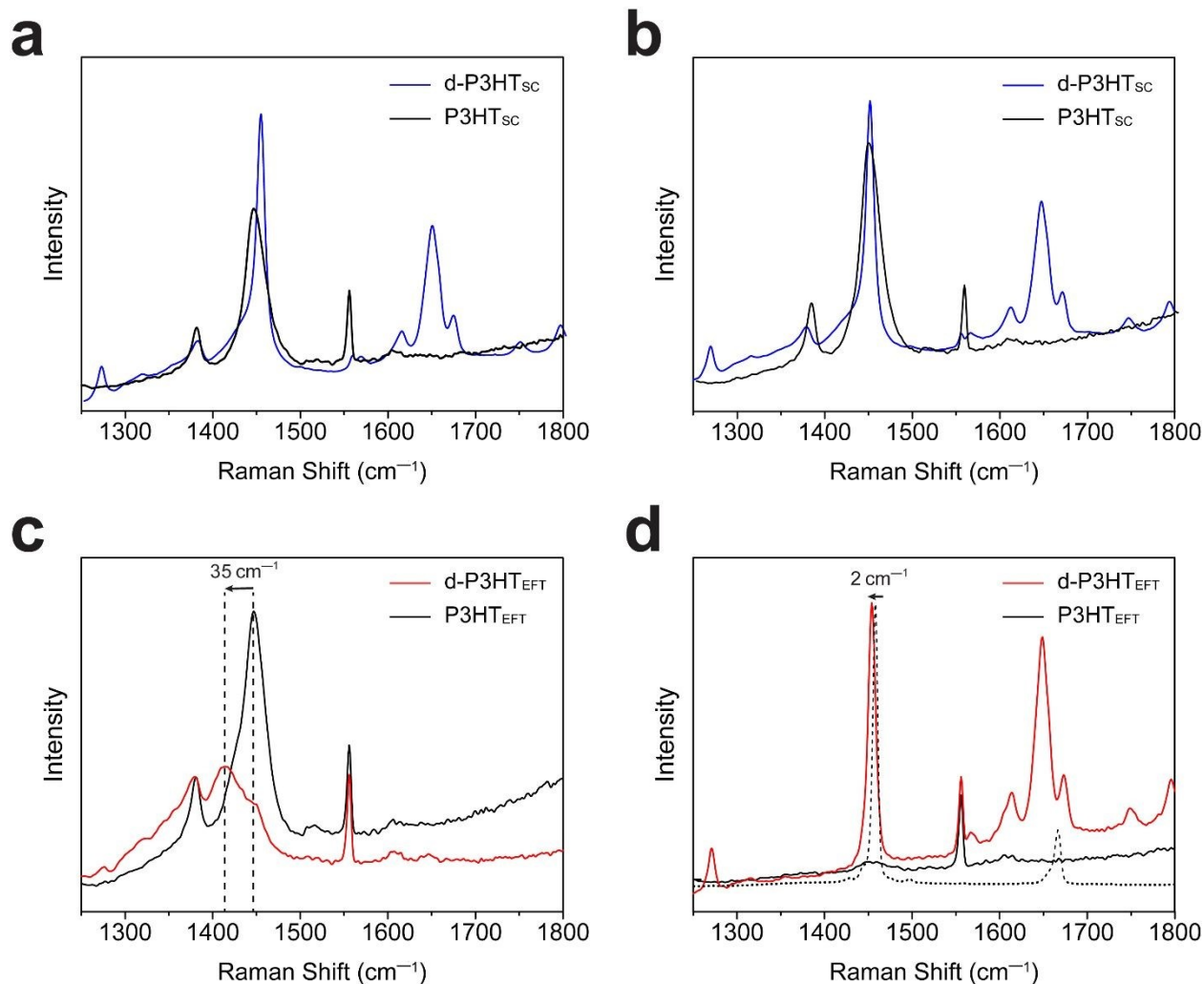


Figure 4. Polarized Raman spectra of P3HT_{SC} and d-P3HT_{SC} films with the polarizer rotated (a) 0° and (b) 90° from the original position. Polarized Raman spectra of P3HT_{EFT} and d-P3HT_{EFT} films with the polarizer aligned (c) parallel and (d) perpendicular to the drawing direction.



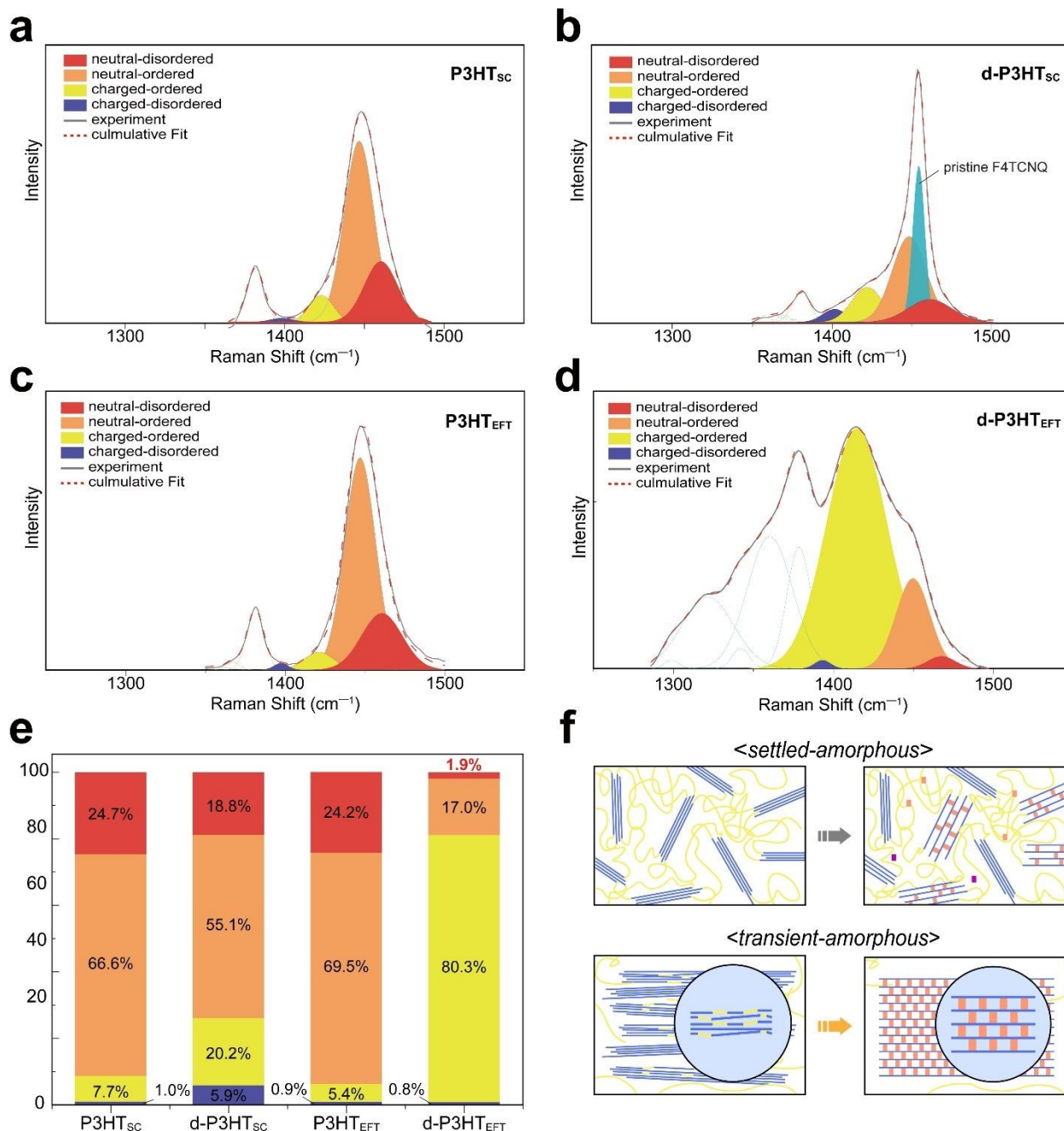


Figure 5. Deconvoluted Raman spectra of (a) P3HT_{SC}, (b) d-P3HT_{SC}, (c) P3HT_{EFT}, and (d) d-P3HT_{EFT} films, respectively. (e) Compositional changes of phases in P3HT_{SC} and P3HT_{EFT} films upon doping. (f) Schematic illustration of settled- and transient-amorphous phases.



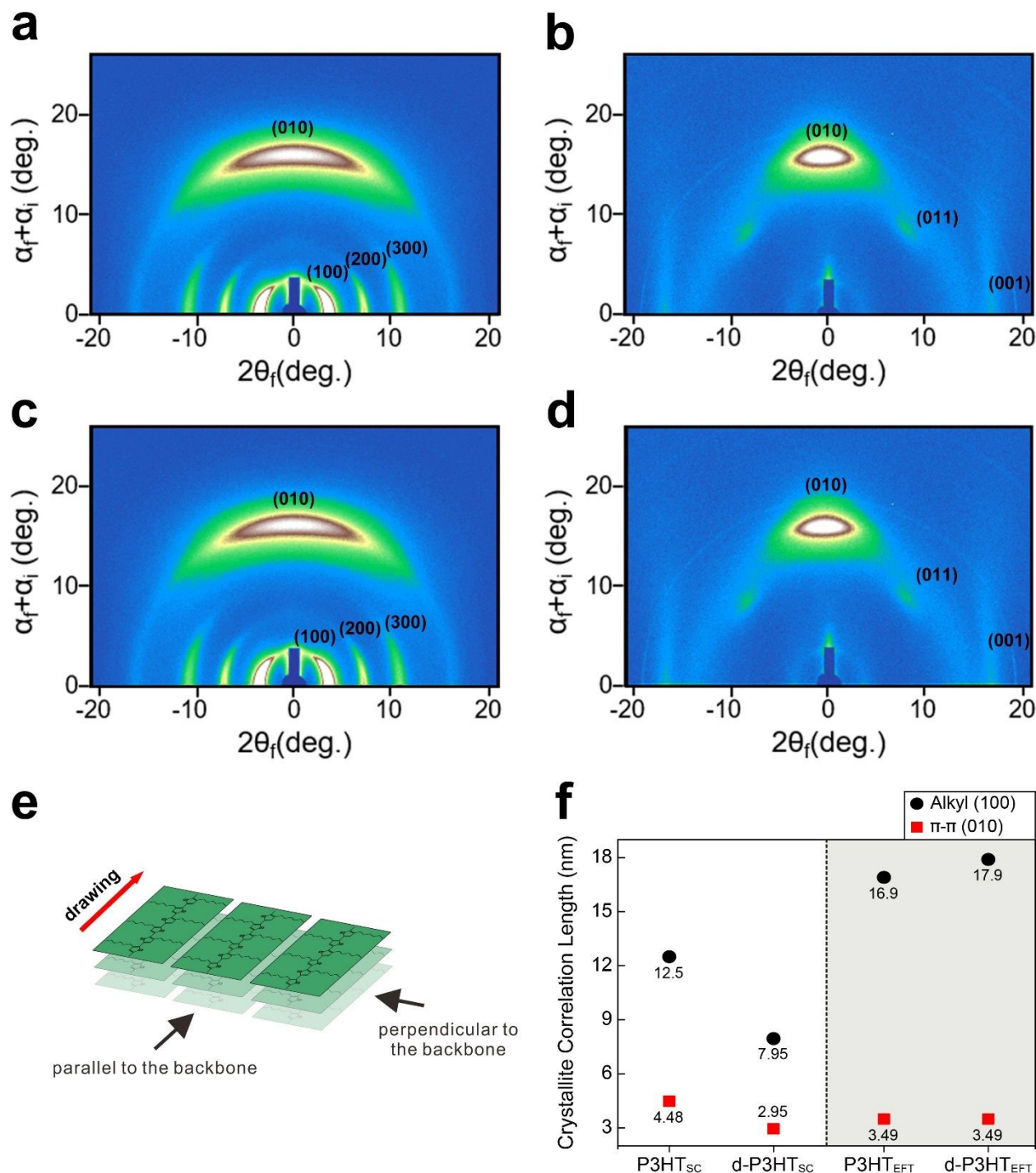


Figure 6. The GIXD patterns of (a, b) P3HT_{EFT} and (c, d) d-P3HT_{EFT} films, taken with the X-ray illumination (a, c) parallel and (b, d) perpendicular to the drawing direction. (e) Illustration showing the direction of X-ray illumination parallel and perpendicular to the drawing direction. (f) Crystallite correlation length of the alkyl and π - π packing distances.



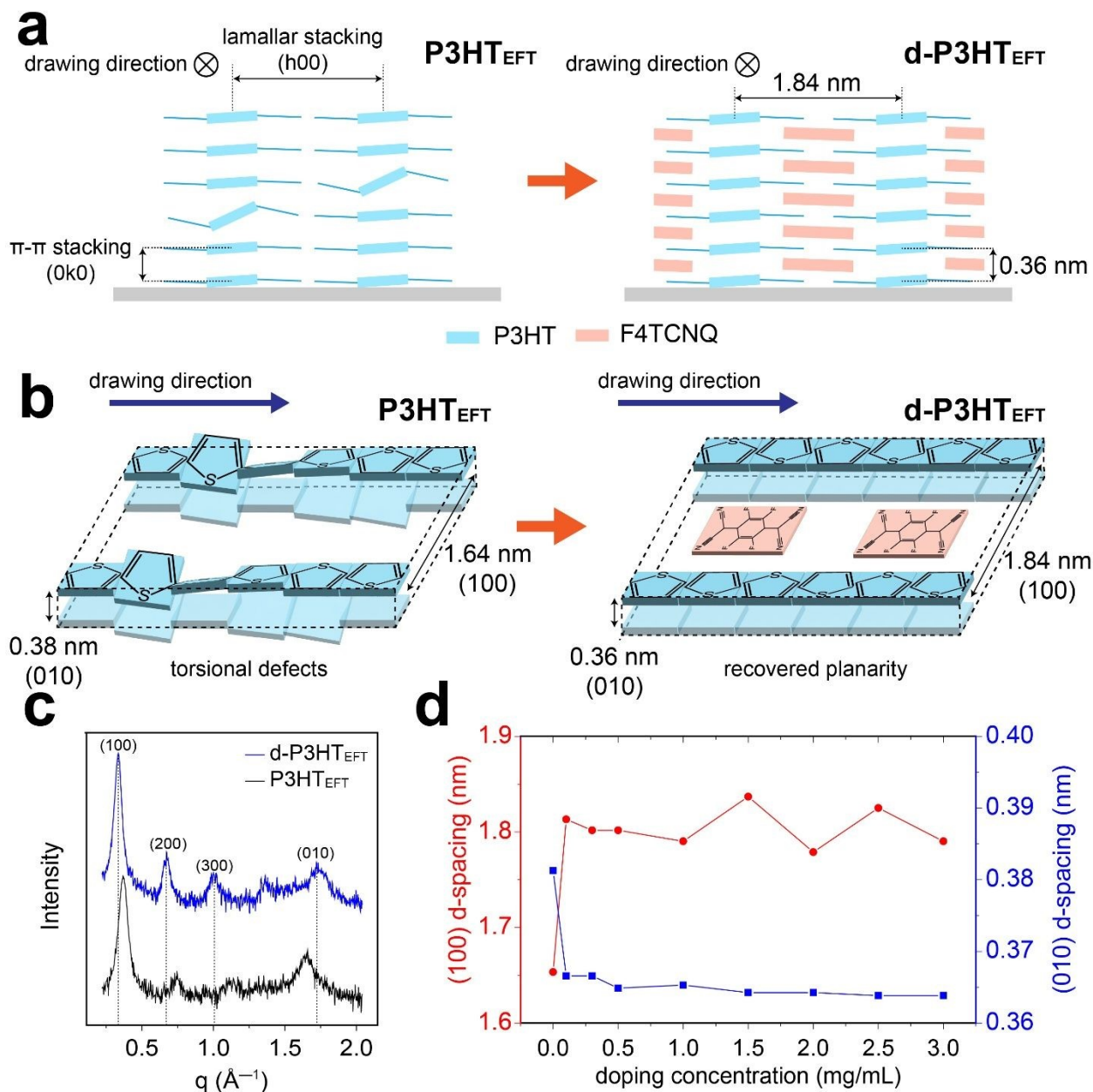


Figure 7. (a-b) Structural illustrations of P3HT_{EFT} and d-P3HT_{EFT} films viewed from different perspectives. (c) GIWAXS profiles of P3HT_{EFT} and d-P3HT_{EFT} films. (d) Changes of the d-spacings of (100) and (010) planes with a variation of the F4TCNQ concentration.



Data availability

Further experimental details and supplementary figures are described in the ESI.

Author contributions

H.J. and S.E. designed and conducted experiments including sample preparation and most of measurements. S.C. assisted for the Raman measurements. T.V.V, J.H.S., J.C., S.P., S.K., S.B., and H.L. assisted with X-ray, FT-IR, POM, UV-VIS measurements. H.C. helped to analyze the data and revise the manuscript. Y.K. conceived and supervised the project.

Conflicts of interest

There authors declare no competing financial interest.

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Further experimental details and supplementary figures are described in the ESI.

