

IMPACT OF POLYMER SOLUTION AGGREGATION AND ASSEMBLY ON ORGANIC
SOLAR CELL MORPHOLOGY AND DEVICE PROPERTIES

BY

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DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemical Engineering
in the Graduate College of the
University of Illinois Urbana-Champaign, 2024

Urbana, Illinois

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ABSTRACT

Owing to various forms of intermolecular interactions, conjugated polymers self-assemble to form distinct types of aggregates in their solution-state, which play an important role on the film morphology and optoelectronic properties of organic electronic devices. Upon increasing the solution concentration, they can further assemble into more complex multistep secondary phases, which can be directly translated to the solid-state during evaporative solution processing of thin films. Numerous studies have shown that solution-state aggregation of conjugated polymers influence the film morphology of organic solar cells (OSCs); however, their detailed aggregate structures in the solution-state and their assembly pathways during solution processing remain unresolved. Therefore, the objective of my thesis is to elucidate the exact structure of solution-state aggregates and their assembly pathways and to further investigate how they influence the blend film morphology and device properties of organic solar cells.

In my first study (Chapter 2), we investigated the impact of polymer backbone conformation on the solution aggregate structures of conjugated polymers. A combination of X-ray scattering and microscopic imaging techniques allowed us to observe the formation of semi-crystalline fiber aggregates and amorphous network aggregates depending on the polymer backbone conformation. We further reveal that amorphous, network-like aggregates are conducive to superior device performance in blade-coated OSCs owing to the formation of blend films with short π - π stacking distance, small domain spacing, and face-on preferred molecular orientation, whereas the fiber-like aggregates lead to large π - π stacking distance, large domain spacing, and isotropic molecular orientation in the blend film which deteriorate the device performance. It was also revealed that the fiber aggregates are highly temperature-sensitive compared to the polymer network aggregates, leading to more processing temperature sensitive performance.

Next in Chapter 3, we demonstrated how polymer aggregate structures can be tuned by the solvent environment to give distinct aggregate structures that determine the blend film morphology and device performance of organic solar cells. We found that solvent affinity towards the polymer backbone and the alkyl side chains drastically tunes the polymer solution aggregate structures and the resultant blend film morphologies. Our findings reveal that a poor side chain solvent leads to semiflexible amorphous networks with strong side chain associations, whereas a poor backbone solvent gives a rise to semicrystalline fiber aggregates. Mutual solvents, on the other hand, balance the polymer backbone and side chain solubility, resulting in rigid amorphous networks with weak/no side chain interactions. Upon film deposition via blade coating, both semicrystalline fibers and flexible amorphous network aggregates yield highly crystalline films with large domains, whereas the rigid amorphous aggregates with weak or no side chain associations prevented excessive crystallization, yielding the most favorable blend film morphologies.

Finally in Chapter 4, we explored the concentration-dependent lyotropic liquid crystalline phase mediated assembly of conjugated donor polymers and its influence on the blend morphology and device properties of organic solar cells. Using solution X-ray scattering and microscopic imaging tools, we discovered that D18 polymer assembles into both achiral and chiral lyotropic liquid crystalline phase upon increasing the solution concentration. We further show that the nature and extent of assembly during film deposition can be controlled by the coating regime and the processing solvent, which collectively determine the drying dynamics and kinetics of the meniscus-guided coating process. We demonstrate that coating in the evaporation regime drives the assembly towards the liquid crystalline phase formation, which not only enhances the film alignment and crystallinity but reduces unfavorable phase separation, resulting in improved OSC performance and stability for D18:Y6 blend system.

ACKNOWLEDGMENTS

First and foremost, I would like to express my deepest gratitude to my advisor, Prof. Ying Diao, for her exceptional mentorship and guidance throughout my time in her lab. I have been continually inspired by her enthusiasm for research, her fearlessness in tackling new and challenging problems, and her dedication and optimism in driving continuous progress. Prof. Diao's ability to identify the most critical questions and provide insightful suggestions for improvement challenged me from the start to think more critically and to strive to be more scientifically rigorous, a mindset I will continue to apply throughout my research career and beyond.

I would also like to thank my thesis committee members, Prof. Charles M. Schroeder, Prof. Charles E. Sing, and Prof. Nicholas E. Jackson for devoting time to be on my committee and providing valuable feedback on my research. I thank Prof. Nick Jackson, in particular, for being a crucial collaborator on my first project.

I want to sincerely thank my collaborators, Prof. John R. Reynolds and Dr. Austin L. Jones from Georgia Tech, for providing guidance during the first years of my PhD. I am especially thankful to Prof. Reynolds for his time giving valuable career advice for me and sharing his experiences, which meant a great deal to me. I would also like to thank my collaborator Dr. Dean M. DeLongchamp from NIST, whose expertise and willingness to share his extensive knowledge have greatly inspired me as a young researcher. I was fortunate to collaborate with numerous experts and scientists at several national synchrotron facilities including Advanced Photon Source at Argonne National Laboratory, Advance Light Source at Lawrence Berkeley National Laboratory, and National Synchrotron Light Source at Brookhaven National Laboratory. I am thankful for Dr. Eliot Gann for his immense support on resonant soft X-ray scattering measurements; Dr. Chenhui Zhu and Dr. Joseph Strzalka for providing support on grazing incident

X-ray diffraction measurements, and Dr. Lin Yang for his support on solution X-ray scattering measurements. I also thank Dr. Kathy Walsh from the Materials Research Laboratory at UIUC for training me on several instruments at the shared facility.

I would like to thank all the current and past Diao group members who have helped me throughout the past several years. I am thankful to the post-docs in our lab, especially Dr. Jong-Hoon Lee, Dr. Kyung Sun Park, Dr. SangKyu Park, and Dr. Pravini S. Fernando, whose support and advice were invaluable during my PhD. I am deeply grateful to our group alumni Dr. Justin Kwok, Dr. Bijal Patel, Dr. Prapti Kafle, and Dr. Daniel Davies for their kindness and willingness to help not only in research problems but also in navigating PhD, future career, and beyond. I am also grateful to have had the pleasure working with some talented undergraduate students (Jasmine Williams, Andrew Cheng, Jessica Komar, and Raymond Susilo) and all the other Diao group members from whom I learned a great deal. My time here at UIUC would have been incomplete without the friends from my cohort and MCO. Their companionship has made my PhD an experience I will cherish.

I want to thank my mentors from my undergraduate program, Prof. Nina Lin and Dr. Tatyana Saleski from the University of Michigan, for introducing me to research and encouraging me to pursue graduate school. I also extend my gratitude to everyone from the MCO at Michigan, whose support made adjusting to life in a new country much smoother. My heartfelt thanks go to my high school chemistry teacher, Batbileg Jargalsaikhan, who has first instilled in me the joy of learning science. I am also grateful to my friend Orgil-Erdene amongst many for being there for me during times in need and to all my friends and relatives both back home and around different parts of the world. Despite being thousands of miles away and almost a decade of being apart, they continue to hold a special place in my heart.

Lastly, I want to express my sincerest gratitude to my parents, Khasbaatar and Ariunaa. I would not have had the privilege of pursuing my dreams without the challenges my parents overcame for me and my siblings. I am forever indebted to my father, who always believed in me and celebrated every success, no matter how small, and to my mother, whose wisdom and unconditional care have been a constant source of support. I am thankful for my grandmother, whose liveliness even in her 90s reminds me of what is truly important. I am grateful to have my two younger siblings whose presence gives me the strength to face any adversity. I am also thankful to Frank, whose unwavering support, friendship, and belief in me make everything possible, and to my two cats who bring immense joy into my life.

To my family

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Chapter 1

Introduction

1.1 Organic solar cells¹

The discovery of conjugated organic molecules as electronic materials in the 1950s sparked extensive research into their applications in cutting-edge technologies such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic solar cells (OSCs).¹ These materials possess unique properties that make them highly desirable for their application in flexible and transparent electronic devices. One of the key advantages that sets organic electronic devices apart from their inorganic counterparts is their compatibility with solution-processing methods. These cost-effective fabrication techniques enable the production of electronic materials on a large scale, opening exciting possibilities for their widespread implementation. In particular, organic photovoltaics is an emerging renewable energy technology that can reduce the cost of solar cell production using solution processing techniques as compared to the energy intensive manufacturing of silicon based solar cells. In addition to their cost-effective production, OSCs possess numerous features that make them truly remarkable. They are not only lightweight, transparent, and flexible, but they also possess the ability to harness the power of indoor lighting,² which drives OSCs far beyond the limitations of traditional silicon based solar cells.

First introduced in 1986 by Tang and co-workers, OSCs have rapidly progressed from exhibiting less than 1% efficiency to over 19% efficiency for a single junction cell today.^{3,4} This drastic progress can be associated with several pioneering works, starting from the invention of

¹ Partially adapted from the following publication: **Khasbaatar, A.**; Xu, Z.; Lee, J-H.; Alvarado, G. C.; Hwang, C.; Onusaitis, B. N.; Diao, Y.; From Solution to Thin Film: Molecular Assembly of π -Conjugated Systems and Impact on (Opto)electronic Properties. *Chemical Reviews* 2023, 123, 13, 8395-8487

bulk heterojunction (BHJ) structures exhibiting interpenetrating network-like morphology from a phase-segregated mixture of two semiconducting polymers.^{5,6} This structure has been adopted to overcome the short exciton diffusion length (typically, ≈ 10 nm) and low charge carrier mobility of organic semiconductors.⁷ The BHJ structure and the development of fullerene-based electron acceptor⁸ have since driven the field, steadily increasing the efficiency of OSCs to $\approx 12\%$ by 2016.⁹ Since 2017, polymer donor and non-fullerene acceptor (NFA) based OSCs have begun to outperform fullerene based OSCs,¹⁰ shifting the focus of the research community toward molecular design of NFA based OSCs. The rapid development of NFAs has boosted the efficiency of OSCs to over 19% only within the past few years.^{4,11}

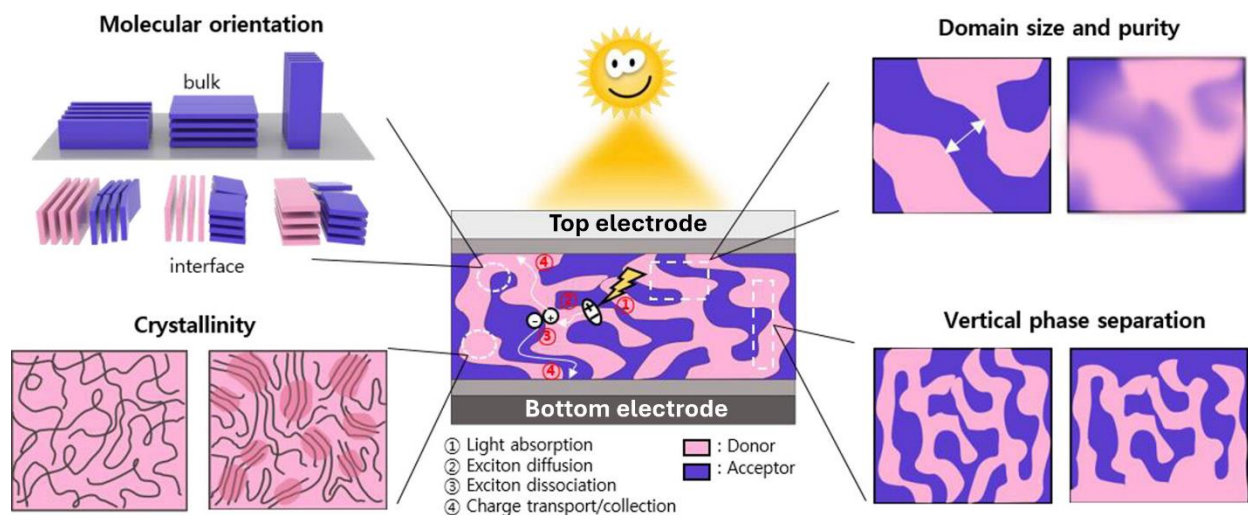


Figure 1.1. Schematic illustration of an OSC device and the working mechanism.

Shown in **Figure 1.1** is a schematic illustration of a typical OSC device, comprised of a photoactive layer that is sandwiched between top and bottom electrodes, alongside the hole and electron transporting layers. Upon light illumination or photon absorption, electrons within the donor material are excited to form bound electron-hole pairs or excitons. These excitons diffuse through the material until they reach the donor-acceptor interface, where they undergo charge separation. During charge separation, the excitons dissociate into free electrons and holes at the

interface due to the lowest unoccupied molecular orbital (LUMO) energy level offset between the donor and acceptor materials. In particular, this energy level offset needs to be greater than the Coulomb binding energy of the exciton, enabling the electron transfer to be energetically downhill.¹² The separated charges then migrate through their respective transport layers – typically made of materials that block the undesired holes and electrons – to the top and bottom electrodes, creating an electric current.

This charge generation and transport process depend strongly on blend film morphology of the photoactive layer including the crystallinity, domain size and purity, molecular orientation, and vertical phase separation as illustrated in **Figure 1.1**. Crystallinity refers to the extent to which polymer chains are aligned in an ordered manner, forming closely packed regions called crystalline regions. Conjugated polymers typically form semicrystalline films with small ordered/crystalline domains intermixed within large amorphous domains. A higher degree of crystallinity in polymer films is generally desirable since crystalline films has a longer diffusion length compared to amorphous films and has lower density of trap sites, resulting in enhanced exciton dissociation yields and charge trapping during charge transport.¹³ In BHJ based OSCs, however, there is often a tradeoff between crystallinity and domain sizes, which refers to the size of the regions where the donor and acceptor materials phase separate within the active layer. While higher crystallinity typically enhances charge transport, excessively large crystalline domains can impede the formation of an interpenetrating network of nanoscale donor and acceptor domains, limiting the interfacial area available for exciton dissociation. Since the lifetime of excitons is limited and its diffusion length is only ≈ 10 nm, the domain sizes need to be confined to several tens of nanometers in length scale to ensure efficient charge separation.¹⁴ The donor and acceptor phases can also undergo vertical phase separation, which refers to the non-uniform distribution of the donor and

acceptor components in the vertical direction. Vertical phase separation can depend on numerous factors including the thermodynamics, kinetics, and the difference in surface free energy and solubility of the donor and acceptor materials, resulting in one component to be enriched at the top or the bottom surface.¹⁵ In general, the donor-rich and the acceptor-rich phases need to be located at the appropriate electrodes for efficient charge extraction. Besides these mesoscale properties, molecular properties such as the orientation of the donor and acceptor materials in the bulk as well as at the interface can also play an important role in the electronic properties of OSCs.^{16–18} In OSCs, face-on molecular orientation where the polymers are π - π stacked along the vertical direction facilitates vertical charge transport, whereas edge-on oriented molecules with in-plane π - π stacking direction is favored for field-effect transistor devices. It has also been recently reported that the molecular orientation can influence the energetic levels of the molecule, resulting in changes in the open-circuit voltage of OSC devices.¹⁹

1.2 Solution-state aggregation of conjugated polymers

Recent studies suggest that the BHJ morphology of OSCs strongly depends on the solution-state properties of conjugated polymers, particularly the nature and extent of solution-state aggregates.^{20–23} Conjugated polymers can readily aggregate into mesoscale aggregate structures even in their initial solution-state prior to film deposition owing to various forms of intermolecular interactions, particularly π - π stacking and Van der Waals forces. From the thermodynamics point of view, the extent of solution-state aggregation is governed by the Gibbs free energy of mixing (ΔG_{mix}), where $\Delta G_{\text{mix}} > 0$ or < 0 indicates the presence and the absence of polymer aggregation, respectively. The Gibbs free energy of mixing can also be related to the Flory-Huggins interaction parameter (χ), which is proportional to polymer – polymer, polymer – solvent, and solvent – solvent interaction energies. Thus, the extent of solution-state aggregation is governed by these

intermolecular interactions, particularly the polymer – polymer and polymer - solvent interactions, which largely depend on the molecular structure and conformation of the polymers and the solvent environment.

The polymer – polymer interaction is mainly influenced by the polymer backbone conformation and rigidity, which depend on molecular attributes such as the dihedral angles, bond angles, and noncovalent interactions between different moieties.²² The conformation of conjugated polymers is quantified by the persistence length (l_p), which is defined as the characteristic length scale over which the polymer chain maintains a relatively fixed orientation before undergoing significant bending or twisting. Depending on the relative magnitude of the l_p to the contour length of the polymer chain (l_c), the chain can adopt flexible coil ($l_c \gg l_p$), rigid rod ($l_c \gg l_p$), and semiflexible or worm-like ($l_c \approx l_p$) chain conformation.²⁴ It is suggested that rigid polymer conformations of conjugated polymers lead to higher degree of aggregation due to the strong π - π interactions between polymer chains.²² The alkyl sidechains also play an important role on the solution-state aggregation as bulky sidechains often increase the solubility of conjugated polymers by introducing steric hindrance and disrupting the π - π interactions.²⁵ In particular, branched alkyl chains generally increase the solubility of conjugated polymers compared to linear alkyl chains as their bulkiness hinders interchain interactions.²⁶ Molecular dynamic (MD) simulations, however, suggest that branched alkyl chains could still exhibit strong polymer – polymer interactions through backbone – side chain interactions, suggesting that the role of alkyl side chains on solution-state aggregation cannot be overlooked.²⁵ The length and branching alkyl side chains also impact the persistence length of polymer chains by affecting the dihedral potential or introducing steric constraints.^{27,28} For example, poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) exhibits a relatively high degree of stiffness with a measured persistence length around 6 nm,

which increases to over 40 nm by the addition of large bulky side groups due to the sterically favored planar trans conformation.²⁹

Besides polymer – polymer interactions, poor solvent – polymer interactions also influence polymer conformation and the extent and nature of aggregation of conjugated polymers in the solution-state.³⁰ In a good solvent, an isolated single polymer chain adopts an extended conformation forming a swollen coil, whereas in poor solvents, they collapse into a globule or a collapsed coil to minimize the unfavorable solvent – polymer interaction.³¹ This transition is commonly referred to as the coil – globule transition. However, conjugated polymers rarely undergo this coil – globule transition due to their stiff conjugated backbone. Instead, they lead to chain planarization in poor solvents, leading to more elongated or extended conformation as the polymer starts to freeze out rotational degrees of freedom.³² Kolinsku and Yari et al. suggested that in contrast to stiff polymers, flexible polymer chains have stronger attractive interactions, which lead to polymer chains to collapse on itself before their rotational degrees of freedom freezes out, leading to the disordered globule state. Further increasing the solvent quality, an isolated stiff polymer chain forms highly ordered collapsed aggregates. In semi-dilute solutions in which polymer chains start to overlap, rather than forming collapsed aggregates, they typically form extended interchain aggregates involving different polymer chains. Although the solubility of conjugated polymers is largely dictated by the conjugated backbone, it is reported that the side chain solubility can influence the polymer solubility as the side chains become larger and bulkier.³³

Studies suggest that solution-state aggregation plays an important role in the phase separation process during film deposition.^{23,34} During solution processing, the donor and acceptor materials undergo either solid-liquid or liquid-liquid phase separation depending on the miscibility of the components. When the molecules are poorly miscible, liquid-liquid demixing occurs, leading

to large scale phase segregated domains that are unfavorable for charge generation. However, inducing solution-state aggregation of conjugated polymers via solution aging and adding poor solvents has proven effective in delaying large scale liquid-liquid phase separation. Solution-state aggregation of conjugated polymers also improve the film crystallinity and in-plane alignment.^{35,36} For instance, a notable work done by Reichmanis et al. showed that inducing solution-state aggregation of P3HT using UV-aging increases the (100) lamellar peak intensity, attributed to the increasing size and/or number of crystallites in the film.³⁷ Besides the extent of solution-state aggregation, some studies suggest that the exact nature or structure of solution-state aggregates also influences the morphology.^{38,39} However, the detailed nature of polymer aggregated structures and their influence on the film morphology for blend systems relevant for OSCs remains largely unexplored.

1.3 Assembly of conjugated polymers

In addition to forming primary solution-state aggregates, conjugated polymers may undergo complex multistep concentration-dependent assembly pathways, which can influence the thin film morphology and electronic properties of organic electronic devices. Of particular significance is the lyotropic liquid crystalline-mediated assembly pathway of conjugated polymers, which has been shown to affect film alignment, crystallinity, and molecular orientation in the solid-state.^{40–42} Lyotropic mesophases are often formed from geometrically anisotropic particles upon reaching a critical concentration. The formation of the LC phase was theoretically described for the first time by Onsager, who showed that thin hard rods must form a nematic liquid crystal at sufficiently high densities to minimize the overlapping excluded volume effects.⁴³ Although most conjugated polymers satisfy the Onsager rule of anisotropic shape of the mesogens, extensive entanglement of polymer aggregates due to strong intermolecular interactions can make it difficult

to form the LC phase.⁴⁴ The LC phase is also proposed to occur when enhancing the amphiphilic nature of the conjugated polymer through dissolution of its side chains.³³ Bridges and Segalman *et al.* reported that introducing bulky side chains to the PCDTPT polymer allowed selective dissolution of its side chains to nonpolar solvents, resulting in the formation of an LC phase. Xu and Diao *et al.* also highlighted the importance of solvent selectivity on the assembly of PII-2T polymers, in which either poor side chain or backbone solvents suppressed the formation of LC mediated assembly pathways.⁴⁵

Recent findings reveal that some achiral conjugated polymers can further organize into chiral liquid crystalline phases, forming helical fiber aggregates as the solution concentration increases. The formation of chiral LC phase typically occurs when molecules with chiral centers form a liquid crystalline phase where they twist with respect to each other to form a helix.⁴⁶ However, it has recently been suggested that the chiral LC formation is not only limited to molecules that exhibit chiral centers but also happens to bent-shaped achiral molecules, resulting in the twist-bent nematic phase.⁴⁷ The formation of chiral LC phase has also been observed in achiral systems under curved spatial confinement due to twist deformation of the mesogens.⁴⁸ In conjugated polymers, we found that PII-2T and DPP-BTz films exhibit chiral LC phase at solution concentrations above 100 mg/mL, which was attributed to their torsional backbone conformations. Interestingly, this chiral LC mediated assembly was translated into the solid-state, forming chiral twinned domains upon printing in the evaporation regime. When printed in the transition regime, this intermediate phase was eliminated to form highly aligned films upon planarizing the backbone, suggesting that the impact of processing conditions on the assembly pathway of conjugated polymers should not be neglected.

In OSCs, the concentration-dependent multistep assembly of conjugated polymers and how it influences the blend film morphology of OSCs is not well-investigated. Although it has been demonstrated that thermotropic liquid crystalline molecules can improve the crystallinity and thickness tolerance of OSCs,^{49,50} the LC phase transition occurs at temperatures (160 – 230 °C) that are much higher than the thermal annealing temperatures of OSCs (typically around 100 °C), which could result in excessive phase separation and poor device performance. On the other hand, lyotropic LC phase is concentration-dependent and can be formed under evaporative processing conditions without the need for high temperature annealing, suggesting its potential for use controlling the thin film morphology of OSCs.

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Chapter 2

Solution aggregate structures of donor polymers determine the morphology and processing resiliency of organic solar cells²

2.1 Introduction

Organic photovoltaics have emerged as a promising renewable energy technology that can reduce the cost of solar cell production using solution-based processing methods as compared to silicon-based solar cells which require energy intensive manufacturing.¹ Owing to their lightweight, flexibility and transparency, OSCs can also be used in a variety of novel applications including smart windows² and powering portable devices or internet of things (IoTs).³ Although the device performance of OSCs have now reached a promising 19 % efficiency with a single junction cell on a laboratory scale,⁴ the processing method for most high performance materials has been limited to spin coating, which is incompatible with large area production of OSCs.⁵ On the other hand, meniscus-guided coating or solution printing techniques are not only compatible with large-scale roll to roll manufacturing, but can minimize solution waste to as low as 5 %.⁶ However, transferring from spin coating to large-scale compatible processes is often challenging as the BHJ OSC morphology is sensitive to changes in the film drying dynamics and transport processes.⁷⁻⁹ Furthermore, the BHJ morphology of OSCs is not only sensitive to the processing techniques, but also dependent on processing parameters¹⁰⁻¹² and environmental conditions,¹³ further complicating the device optimization of OSCs. Currently, controlling the morphology of OSCs for optimal device performance remains a bottleneck, typically requiring time-consuming trial-and-error based approaches to adjust numerous processing parameters for device

² The contents of this section appear in **Khasbaatar, A.**, Cheng, A., Jones, A. L., Komar, J., Kwok, J., Lin O., Jackson, N., Chen, Q., DeLongchamp, D. M.; Reynolds, J. R.; Diao, Y., “Donor Polymer Aggregate Structure in the Solution-state Determines the Morphology and Processing Resiliency of Organic Solar Cells”, *Chemistry of Materials* 2023, 35, 7, 2713–2729.

optimization. Therefore, achieving high-performing OSCs that can maintain their morphology regardless of the processing parameters and environmental conditions is crucial for the successful commercialization of organic photovoltaics.

Recent studies have emphasized that solution-state aggregation of polymers is central to controlling the blend film morphology of OSCs, thereby potentially helping to overcome the aforementioned morphology control challenges.¹⁴⁻¹⁶ For instance, a prominent work done by Qian and Hou *et al.* has shown that using a strongly aggregated solution of PBDTBDD for fabrication of OSCs yielded a superior device performance owing to the formation of nanoscale phase-separated domains, whereas using a thermally treated solution with reduced aggregation led to larger domains limiting charge generation and worsening the device performance.¹⁶ From the processing aspect, Hernandez and Reynolds *et al.* has shown that using an aggregated polymer solution leads to the same film morphology and device performance for both spin coated and blade coated OSCs as the morphology could be predetermined by the solution-state aggregation.¹⁴ In contrast, studies have also demonstrated that excessive aggregation of polymers in solution causes difficulty in processing¹⁷ and leads to large crystalline domains which are detrimental to charge generation.¹⁵ Recently, using polymers that exhibit temperature-dependent aggregation in solution partially resolved this issue as the strong solution-state aggregation of these polymers can be reduced by simply increasing the solution temperature before film deposition.¹⁷ However, these temperature-dependent polymer aggregates have been reported to make the final morphology and device performance sensitive to processing parameters such as the spin coating rate,¹⁷ thermal history of the solution,¹⁶ solution temperature,¹⁷ processing temperature,^{10,11,18} and solution aging time.¹⁹ On the other hand, more recently, Seo and Kim *et al.* reported that using a donor polymer with temperature-tolerant aggregation behavior improves processing temperature-resiliency of

OSCs.²⁰ Although these studies emphasize the importance of solution-state aggregation in controlling the morphology and processing resiliency of OSCs, detailed understanding of solution-state aggregates and their impact on the morphology and processing resiliency remain unclear. Therefore, the purpose of this study is to fill this knowledge gap by conducting a thorough investigation of polymer solution-state aggregation and its impact on the solid-state properties.

In this work, we investigate the solution-state aggregate structures of donor polymer PM7 and its ester-functionalized derivatives PM7 D1 and D2 as shown in **Figure 1.1a**. Using small angle X-ray scattering (SAXS), freeze-dried solution imaging and optical spectroscopy, we find that PM7 generates a combination of fiber aggregates and amorphous network of polymer chains, whereas PM7 D1 and D2 solutions are primarily composed of amorphous network-like aggregates. Interestingly, we find that the fiber aggregates of PM7 is highly sensitive to the solution temperature, whereas the amorphous network-like aggregates remain stable. Furthermore, we report that these two types of aggregates lead to substantially different film morphologies and processing temperature resiliency in blade-coated non-fullerene based OSCs. Specifically, temperature-tolerant network-like aggregates lead to superior device performance by forming favorable BHJ morphology with strong processing resiliency, whereas temperature-sensitive large fibrillar aggregates lead to inferior device performance and film morphologies which are highly sensitive to the processing temperature.

2.2 Results and discussion

The repeat unit structures of the three donor polymers (PM7, PM7 D1, and PM7 D2) and the molecular acceptor (ITIC-4F) are presented in **Figure 2.1a**. The donor phase polymers have similar repeat unit structures with the only difference being the structure of the acceptor moiety in the main chain. In PM7, the highly fused benzodithiophenedione (BDD) based acceptor moiety is

incorporated, while for PM7 D1 and D2 polymers, this BDD based moiety is replaced with an ester functionalized terthiophene moiety which leads to a wider optical bandgap.^{21,22} The difference between the molecular structures of PM7 D1 and D2 is the location of ester group substitution, *i.e.*, in PM7 D1 the two ester groups are located on the first and third thiophene units while in PM7 D2 they are both located on the central thiophene. Recently, Jones *et al.* showed that this structural modification reduced the required synthetic steps while still maintaining the device performance. Those authors have achieved the optimal device performance of 11.6 %, 12.1 %, and 9.9 % respectively for spin coated PM7, PM7 D1, and PM7 D2 when using ITIC-4F as the small molecule acceptor.²³ Interestingly, the authors reported that this structural modification led to a more blue-shifted featureless UV-Vis absorption in both PM7 D1 and D2 solutions as compared to PM7 solution suggesting that the solution-state aggregation could be different. In this work, we will study the solution-state aggregation of these polymers in detail and investigate how different polymer aggregates impact the solid-state morphology and device properties of OSCs.

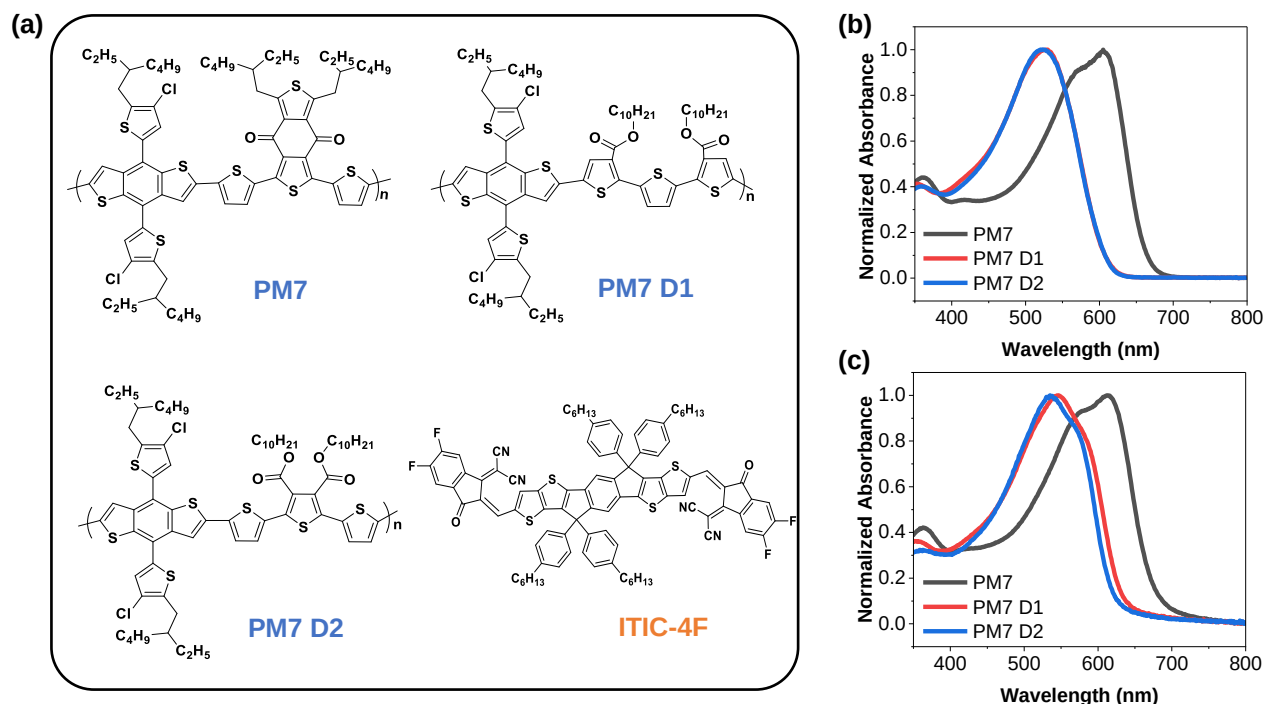


Figure 2.1. (a) PM7, PM7 D1, and PM7 D2 donor polymers (blue) and ITIC-4F acceptor molecule (orange) structures; (b) Normalized UV-Vis absorption spectroscopy of donor polymers in chlorobenzene (CB) solution at 20 mg/mL concentration; (c) Normalized UV-Vis absorption spectroscopy of neat polymer films blade coated from 20 mg/mL concentration of CB solutions.

Determining the polymer solution-state aggregate structures

The neat polymer solutions (20 mg/mL concentration in chlorobenzene) were first investigated using UV-Vis spectroscopy as shown in **Figure 2.1b**. The UV-Vis spectra of PM7 solution contains 0-0 and 0-1 vibronic peaks at 609 nm and 572 nm respectively indicating that the PM7 polymer backbone is highly ordered.^{24,25} On the other hand, PM7 D1 and D2 solutions both show blue-shifted absorption spectra without vibronic peaks suggesting increased backbone disorder with a shorter effective conjugation length.²⁴ Furthermore, the similarity of the solution and film UV-Vis spectra of PM7 (**Figure 2.1b and 2.1c**) implies that PM7 may be strongly aggregated in solution. However, for highly rigid polymers, UV-Vis cannot distinguish strongly aggregated solutions from highly rigid isolated polymers.²⁶ Therefore, we cannot rule out the possibility that PM7 solution is composed of highly rigid isolated polymers based on its UV-Vis

spectra. On the other hand, the film UV-Vis spectra of PM7 D1 and D2 becomes more red-shifted than their solution-state UV-Vis, and the 0-0 and 0-1 vibronic peaks start to emerge, indicating that the polymers become more planarized due to further aggregation from solution to the solid-state. This indicates that PM7 D1 and D2 polymer backbones are more disordered in the solution-state. Nevertheless, UV-Vis spectroscopy measurements can only describe polymer backbone conformation and ordering and thus do not provide direct information regarding the solution-state aggregation of these polymers, let alone their detailed aggregate structures.

Therefore, we studied their solution-state aggregated structures using small angle X-ray scattering (SAXS) as well as directly imaging the aggregates by freeze-drying the solutions to complement SAXS results. Freeze-drying is an effective technique to transfer the solution-state properties to the solid-state by freezing the solution-state aggregates in place. This method is extensively used to preserve protein drugs and vaccines as well as for preservation of biomaterials and cells in a dry form.²⁷ In the field of organic electronics, freeze-drying has also been previously utilized successfully to preserve the solution-state aggregation of polymers.²⁸⁻³¹ To preserve the solution-state aggregation, we use a liquid mixture of 63% propane and 37% ethane which has a large heat capacity to rapidly freeze the sample and prevent crystallization during the cooling process.³² Shown in **Figure 2.2a-c** is the SAXS scattering profiles of each polymer solution along with their total model fitting which will be discussed later. As presented in **Figure 2.2a**, the scattering profile for PM7 solution exhibits two Guinier knee regions around $0.01 \text{ \AA}^{-1}$ and $0.3 \text{ \AA}^{-1}$ which correspond to the cross sections of large fiber-like aggregates and single polymer chains in solution respectively as we previously demonstrated in other conjugated polymer systems.³⁰ Atomic Force Microscopy (AFM) phase and Transmission Electron Microscopy (TEM) images of the freeze-dried solution of PM7 confirm the existence of the fiber aggregates as shown in **Figure**

2.2d and 2.2g (AFM height images are provided in **Supplementary Figure 2.1**). Based on the AFM phase imaging, an average fiber radius of 9.5 ± 2.5 nm was determined which is consistent with the radius of 11.5 ± 0.1 nm obtained from model fitting as we discuss later. This consistency between the freeze-dried samples and SAXS measurements indicates that the solution-state aggregate structures are maintained during freeze-drying. Furthermore, at high Q region ($\approx 0.3 \text{ \AA}^{-1}$), we observe a crystalline lamellar peak ($d_{\text{lamellar}} = 2.2$ nm) indicated by an arrow in the inset plot of **Figure 2.2a**, suggesting that these fiber aggregates are semi-crystalline. We also find that the fibers exhibit π - π stacking ($d_{\pi-\pi} = 3.65 \text{ \AA}$) using solution wide-angle X-ray scattering (WAXS) measurement (**Supplementary Figure 2.2**). In addition to the fiber aggregates, the scattering profile of PM7 solution suggests that there are polymer chains which adopt rigid-rod like conformation as evidenced by the intermediate Q region ($0.03 - 0.3 \text{ \AA}^{-1}$) with a Porod slope of -1 (**Figure 2.2a**).

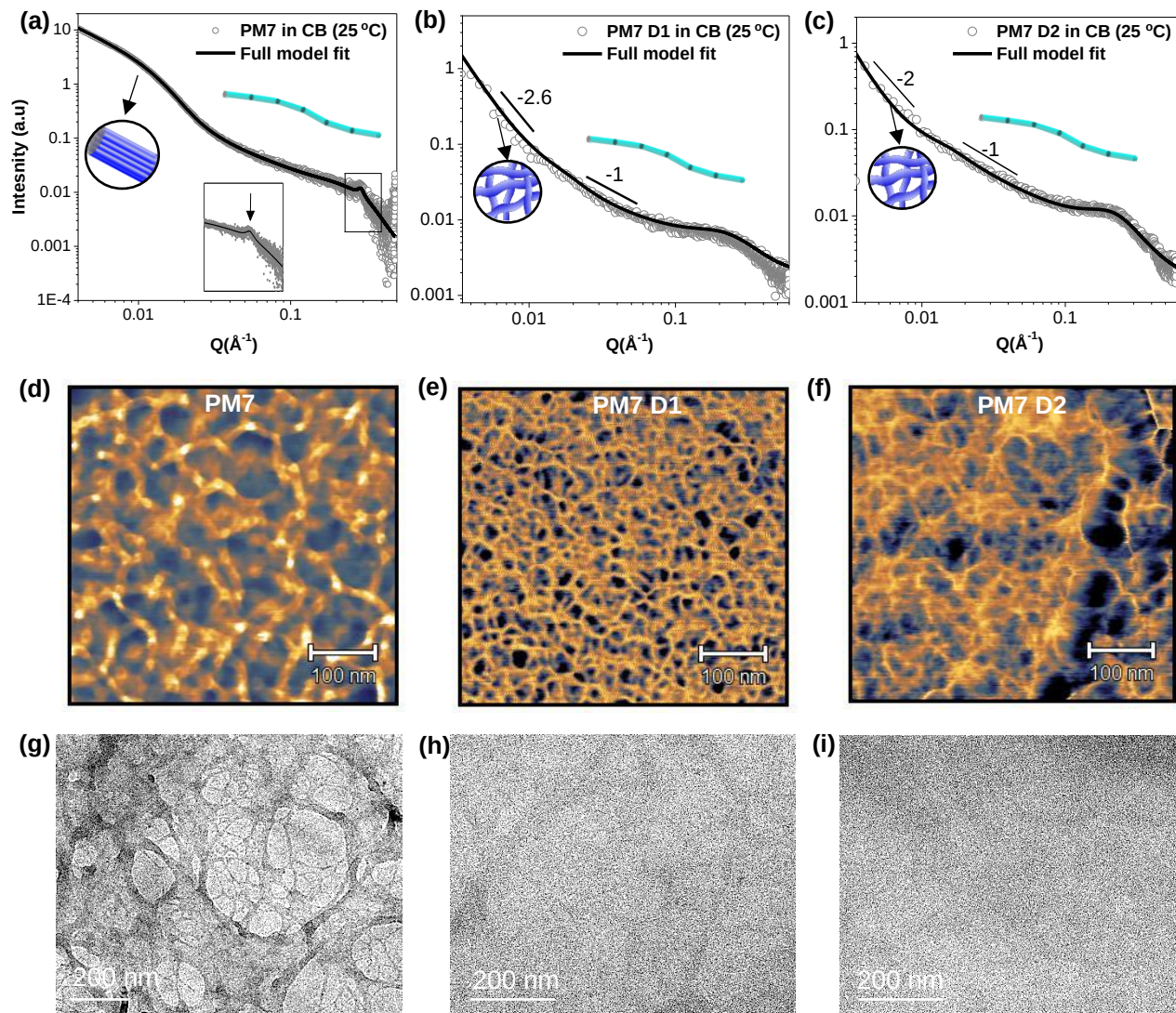


Figure 2.2. Neat polymer solution-state characterization results in CB solvent: 20 mg/mL neat polymer solution SAXS plots of (a) PM7, (b) PM7 D1, (c) PM7 D2 conducted at 25 °C; AFM phase imaging of 20 mg/mL freeze-dried neat polymer solutions of (d) PM7, (e) PM7 D1, (f) PM7 D2; TEM images for the 20 mg/mL freeze-dried neat polymer solutions of (g) PM7, (h) PM7 D1, (i) PM7 D2.

In stark contrast to PM7, the scattering profiles for PM7 D1 and D2 solutions (**Figure 2.2b and 2.2c**) do not possess a Guinier knee corresponding to large fiber aggregates in the Q region accessible for SAXS. Instead, we observe two Porod regions with a slope between -2 and -3 at low Q , a slope of -1 at the intermediate Q , and a broad structure factor peak attributed to lamellar stacking^{33,34} at high Q for both PM7 D1 and D2 solutions. The Porod slope of -1, as previously

mentioned for PM7 solution, corresponds to rigid-rod like polymer chains or chain segments, whereas power law slopes between -2 and -3 at low Q region indicate that there might be large-scale aggregates in these solutions beyond the Q region accessible for SAXS ($Q > \approx 0.004 \text{ \AA}^{-1}$ or length scale $> \approx 150 \text{ nm}$). However, we find that TEM imaging of the freeze-dried solutions for PM7 D1 and D2 are mainly featureless, suggesting that no large-scale aggregates exist beyond $\approx 150 \text{ nm}$ (**Figure 2.2h** and **2.2i**). Interestingly, based on AFM phase imaging (**Figure 2.2e** and **2.2f**), we notice network-like aggregates in PM7 D1 and D2 freeze-dried samples composed of single polymer chains as the width of these features are less than $\approx 5 \text{ nm}$ (the exact width cannot be determined precisely since AFM resolution is limited by the AFM tip radius of 2-5 nm). It has been previously demonstrated that network or fractal-like structures exhibit power law slopes between -2 and -3, corresponding to the mass fractal of these aggregates,^{35,36} which appears to be consistent with our results. Alternatively, such power law slopes at low Q can also be caused by excess scattering due to concentration fluctuations known as Picot and Benoit scattering.³⁷ However, we excluded this possibility as excess scattering due to concentration fluctuations is highly sensitive to the solution preparation method and temperature of the solution.³⁷, while the low Q scattering features we observe are not sensitive these factors. For instance, we re-measured PM7 D2 solution using SAXS after preparing the solution by thermally annealing the solution at 100 °C and then stirring the solution at 25 °C overnight and observed that power law region at low Q is still maintained (**Supplementary Figure 2.3**). Furthermore, the structure factor peaks at high Q region indicates that the polymer chains are associated, rather than existing as dispersed polymer chains in the solution.

To further explain the origin of network-like aggregates, we compare the SAXS profile of PM7 D2 solution in CB with the scattering of PM7 D2 solution prepared in chloronaphthalene

(CN) since CN solution exhibits a more pronounced power law region at low Q as shown in **Supplementary Figure 2.4a**. We find that CN is a better solvent for PM7 D2 than CB, evident from its more blue-shifted UV-Vis spectra (**Supplementary Figure 2.4b**). Due to this improved solvent quality, the intensity of the intermediate Q region corresponding to rigid polymer chains in CN is substantially reduced than in CB. Although polymer backbone becomes well-dissolved in CN, the power law region at low Q corresponding to the network-like structure is maintained and the broad structure factor peak at high Q in CN solution becomes more pronounced. We believe that in CN solution, the network aggregates are formed by well-solubilized polymer chains, forming an amorphous network-like structure likely through sidechain interactions, leading to the broad structure factor peak observed at high Q .²⁸ Similarly for CB solution, we attribute the power law region at low Q to the scattering from the network-like aggregates. However, different from CN, CB solution has a more intense intermediate Porod region corresponding to larger number of rigid polymer chain segments, which is consistent with its decreased solvent quality.²⁴ From WAXS measurements, we did not observe π - π stacking as the intensity is quite low to overcome background scattering. However, using TEM electron diffraction measurements on the freeze-dried samples, we observe a coherence feature at 4.8 Å and 5 Å in PM7 D1 and D2 freeze-dried samples (**Supplementary Figure 2.5**), corresponding to amorphous alkyl sidechain stacking distance.³⁸ This implies that PM7 D1 and D2 polymers form amorphous network-like aggregates via alkyl sidechain association, resulting in the broad lamellar stacking peak in their scattering profiles. We also note that the freeze-dried sample of PM7 exhibits alkyl sidechain stacking at 4.5 Å (**Supplementary Figure 2.5**), slightly closer than those of PM7 D1 and D2, likely due to the crystalline lamellar stacking of the fiber aggregates, forming closer sidechain interactions.

Based on the scattering features from SAXS plots and freeze-dried imaging of the neat polymer solutions, we have established that PM7 solution consists of two distinct populations which are fiber aggregates and rigid-rod like polymer chains (which we will later show as part of a network-like aggregate), whereas PM7 D1 and D2 solutions are comprised of network-like aggregates with rigid polymer segments. With this knowledge, we can proceed with fitting the scattering profiles to obtain quantitative information such as the size of aggregates and polymer chains. When fitting the SAXS profiles, using an appropriate model that accurately describes the system is critical since multiple models can produce equally good fits, leading to the lack of model uniqueness.³⁹ Obtaining some knowledge about the system by using complementary measurements thus ensures selecting a model that can capture the actual macromolecular structures in the solution-state. For a multi-particulate system such as a polymer solution comprised of fibers and single polymer chains, we have recently published a model fitting approach which has successfully described similar donor-acceptor (D-A) conjugated polymer solutions at various concentrations and solvents.³⁰ In this model, we describe the fiber aggregates and the polymer chains by using the flexible cylinder model^{40,41} which is commonly used for fitting the scattering profiles from semiflexible donor-acceptor conjugated polymer systems. If there are network-like aggregates and lamellar stacking present in the solution, this model can be modified to include power law and pseudo-Voigt function to fit the scattering at low Q and the lamellar structure factor peak at high Q region, respectively.

For PM7 solution, we firstly fit the scattering plot to a combination of two flexible cylinder models (or 2FC model) to capture two different populations in the solution (fibers and polymer chains). When the 2FC model is used to fit the scattering profile of PM7 solution, we find that it does not fully capture the low and high Q regions (**Supplementary Figure 2.6a**) and leads to a

large chi squared value of 5.2 and a large variation in the residuals (**Supplementary Figure 2.6b**). We also find that this model gives an extremely small cylinder radius of 3.5 Å which is not physically possible for polymers with long alkyl sidechains (8 carbon atoms). Considering that network-like aggregates lead to scattering at both low and high Q regions due to the dimensionality of the network and lamellar interactions as previously discussed, we hypothesize that PM7 solution contains polymer network aggregates in addition to fiber-like aggregates. We validated this inference using temperature-dependent SAXS shown later. To include the contribution from the network-like aggregates, we thus add power law and pseudo-Voigt peak functions to describe the dimensionality of the aggregate and the hidden broad lamellar structure factor peak originating from sidechain interactions within the network, respectively. This modified 2FC model shows an improved fit with a reduced chi squared value of 2.2 and smaller variations in the residuals (**Supplementary Figure 2.7**). To capture the lamellar stacking peak arising from the fibrillar aggregates, we added a Lorentz peak function to this modified 2FC model which gives a chi squared value of 1.9 and residuals as shown in **Supplementary Figure 2.8**. For PM7 D1 and D2 solutions, since there is no contribution from fiber aggregates, we removed one of the flexible cylinder contributions from the modified 2FC model. Using this approach, we obtained the final model fitting results provided in **Supplementary Figure 2.9** and **Supplementary Table 2.3** which show the full details of the deconvolution of the model fits and the resulting fitting parameters, respectively.

When fitting the scattering profiles to a model with multiple parameters, parameter correlations need to be considered, especially when there is no adequate signal, and the functions are overlapped. To avoid parameter correlations, we fix the parameters that can be estimated using other methods. For example, since there is no Guinier knee corresponding to the length of fibers

and polymer chains for PM7, we fix the length parameter of the two flexible cylinder contributions (L_1 and L_2) which represent the polymer chain length and the fiber length, respectively, to 100 nm which is close to the contour length of the polymer (**Supplementary Table 2.1**). However, we expect that the polymer chain segments within the network-like aggregates would be smaller than this value. Additionally, since the Guinier knee from the cross section of polymer chains and pseudo-Voigt peak overlaps at high Q , we fix the polymer chain radius ($R_p = 1.5$ nm) based on the radius obtained from model fitting results from PM7 D1 where we were able to see the pseudo-Voigt peak more clearly. Using this fitting procedure, we find that the cross-sectional radius of fiber aggregates of PM7 is $R_f = 11.4 \pm 0.07$ nm (error is the fitting error from the model), consistent with the average radius of 9.5 ± 2.5 nm obtained from AFM imaging of the freeze-dried samples (**Figure 2.2**). Furthermore, all polymer solutions contain broad structure factor peaks corresponding to lamellar stacking distances within the network aggregates as indicated in **Table 2.1**. These values are larger than the lamellar stacking distance of 1.9-2.2 nm observed in the blend films as shown later from grazing incidence wide-angle X-ray scattering (GIWAXS), which could be due to the swelling of the lamella in the solution-state.⁴² We were also able to extract the length of the rigid polymer chain segments of PM7 D1 and D2 polymers and found that it is consistent with the length of polymer segments obtained from AFM phase imaging of the freeze-dried solutions as shown in **Figure 2.2e** and **2.2f** (20-30 nm). The persistence length of these polymer chain segments are 7.9 nm and 10 nm, respectively, whereas for PM7 the persistence length could not be accurately determined due to the overshadowing Guinier knee from the fiber cross section, but it is expected to be significantly higher than the polymer chain radius ($l_p \gg R_p$). Nevertheless, we predict that PM7 is highly rigid due to its planar BDD and conformationally locked acceptor

core which has been shown to induce strong aggregation and backbone planarity in many polymer systems.^{43,44}

Table 2.1. Summary of quantitative details of the solution-state of the polymers.

Parameters	PM7 25 °C	PM7 D1 25 °C	PM7 D2 25 °C
Length of polymer chain segment (nm)	100*	30.3 ± 13.7	28.4 ± 3.9
Persistence length (nm)	$\gg R_p$	7.9 ± 3.0	10.3 ± 3.5
Polymer chain radius, R_p (nm)	1.5 [#]	1.5 ± 0.6	1.4 ± 0.3
Lamellar stacking distance within the network (nm)	3.9 ± 0.7	3.4 ± 0.6	3.4 ± 0.4
FWHM of lamellar stacking of the network ($\text{\AA}^{-1}$)	0.28 ± 0.01	0.31 ± 0.02	0.28 ± 0.01
Fiber length (nm)	100*	-	-
Fiber radius, R_f (nm)	11.5 ± 0.1	-	-
Lamellar stacking distance within fibers (nm)	2.16 ± 0.01	-	-
FWHM of lamellar stacking of the fibers ($\text{\AA}^{-1}$)	0.016 ± 0.001	-	-
π - π stacking distance ($\text{\AA}$)	3.65 ± 0.01	-	-

*Values were fixed during model fitting due to the absence of Guinier knee corresponding to the length at low Q.

[#] Value was fixed based on the radius obtained from PM7 D1 due to function overlap of the Guinier knee of flexible cylinder and the Pseudo-Voigt peak functions at high Q.

To further investigate how BDD and ester substituted thiophene groups affect polymer backbone conformation, we compared the potential energy scans of the dihedral angles corresponding to these groups by using DFT with the wB97xD method at 6-31G (d, p) basis set.⁴⁵⁻

⁴⁸ This dispersion-corrected functional is a more accurate DFT method in estimating the torsional barrier and dihedral angles of conjugated molecules than the commonly used B3LYP functional which overestimates the torsional barrier and overly stabilizes the planar conjugated conformations due to its many-electron self-interaction error.⁴⁸ In **Figure 2.3a**, the potential energy plots corresponding to the dihedral angle between thiophene and BDD groups (thiophene-BDD) of PM7

(red) and the dihedral angle between thiophene and ester substituted thiophene groups (thiophene-ester) of both PM7 D1 and D2 (blue) are presented and show significantly different features. The fragments used for obtaining the potential energy plots are shown in the inset plot of **Figure 2.3a**. We focus our discussion on comparing these dihedral angles since the potential energy scans of dihedral angles between donor and acceptor moieties were found similar for PM7 and its derivatives (**Supplementary Figure 2.10**). In **Figure 2.3a**, 0° on the horizontal axis refers to the anti-conformation in which sulfur atoms on the adjacent thiophene groups are facing the opposite directions while at 180° sulfur atoms are syn or on the same side. Each plot indicates two local minima corresponding to the dihedral angles of anti and syn conformations. Since the energy difference between the local minima is close to 1 kT at room temperature for both plots as indicated by the dashed line in **Figure 2.3a**, there is no energetic preference between anti and syn conformations. Nevertheless, the minimum-energy dihedral angles of thiophene-ester groups of PM7 D1 and D2 are shifted towards the maximum dihedral angle of 90° as compared to the thiophene-BDD dihedrals of PM7 (indicated by arrows) suggesting that PM7 D1 and D2 exhibit larger dihedral angles than PM7 regardless of their conformation. Furthermore, by optimizing the dimers (anti-conformations) of these molecules as shown in **Figure 2.3c** we demonstrate that the large dihedral angles of PM7 D1 and D2 disrupt the backbone planarity of PM7. Specifically, from the side view images of **Figure 2.3a**, we can clearly see that PM7 D1 and D2 dimers exhibit backbone twist angles of 31.4° and 30.6° , respectively, while PM7 has a much lower backbone twist of 18.4° .

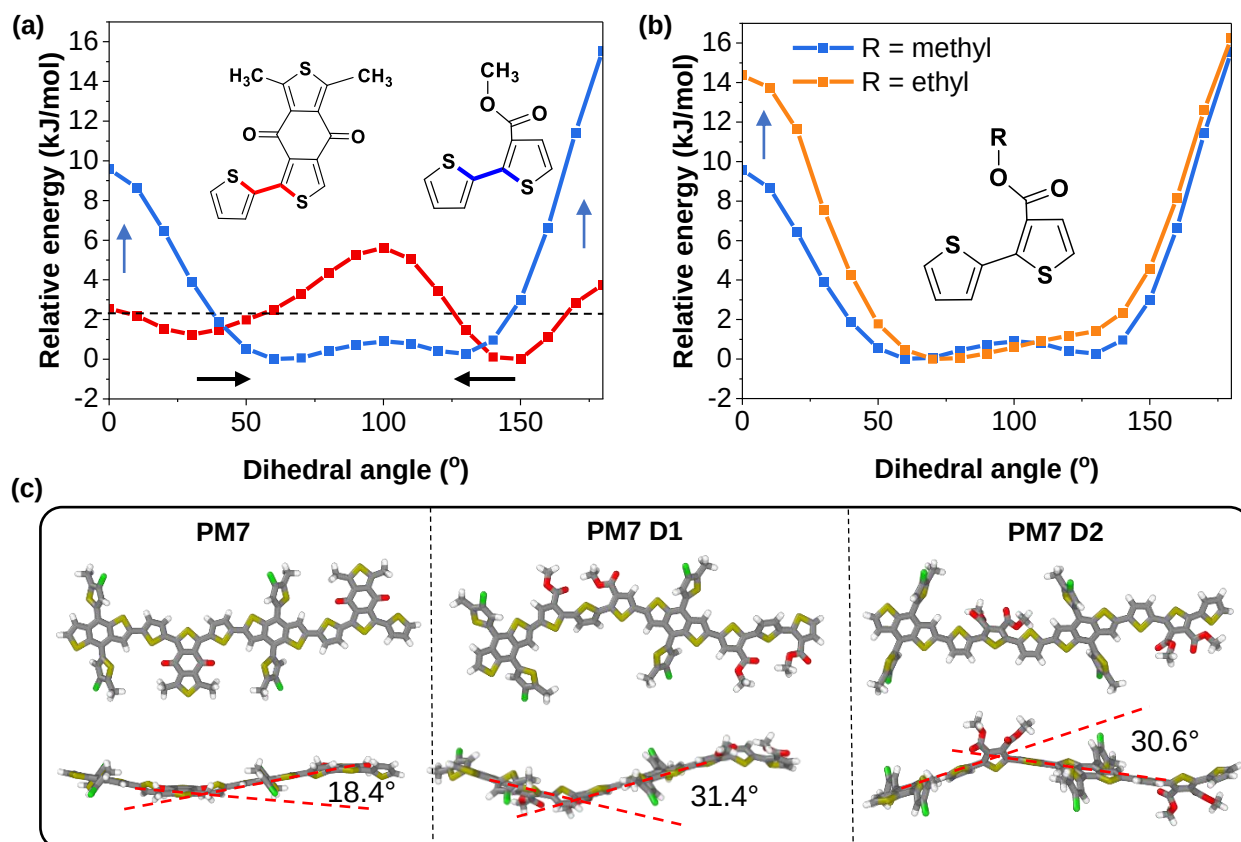


Figure 2.3. DFT calculation results for comparing the backbone conformation: (a) Potential energy scans for the dihedral angle between thiophene and BDD groups (thiophene-BDD) for PM7 (red) and the dihedral angle between thiophene and ester substituted thiophene groups (thiophene-ester) for both PM7 D1 and D2 (blue); (b) comparison of potential energy scans for the thiophene and ester-thiophene dihedral of PM7 D1 and D2 when the sidechain is replaced from methyl to an ethyl group; (c) face (top) and side (bottom) view images of the optimized dimer conformations (anti) of the three polymers.

Another major difference between the potential energy plots is the energy barrier to planarize the dihedral angles which indicates the likelihood of forming planar backbone (indicated by the blue arrows in **Figure 2.3a**). As shown in **Figure 2.3a**, the energy barriers required to planarize the dihedral angle between thiophene and ester-thiophene groups of PM7 D1 and D2 to 0° and 180° reach 9-10 kJ/mol and 13-16 kJ/mol, respectively, while the energy barriers to planarize the thiophene-BDD dihedral angle of PM7 are only around 2.5 kJ/mol and 3.5 kJ/mol (approximately 1 kT and 1.4 kT at room temperature). We attribute these high energy barriers to planarize the ester-thiophene dihedral angle of PM7 D1 and D2 to the steric hindrance originating

from the alkyl sidechain connected to the ester group. Indeed, when the methyl group is replaced with an ethyl group, the energy barriers to planarize this dihedral angle increase further as shown in **Figure 2.3b** suggesting that alkyl sidechains induce strong steric hindrance, making it difficult to planarize the dihedral angle. On the other hand, for PM7, sidechains are substituted further from the adjacent thiophene unit likely causing less steric hindrance as compared to sidechains directly connected to the ester group in the case of PM7 D1 and D2. Moreover, we observe that the energy barrier between anti and syn conformations for the dihedral angle of PM7 D1 and D2 are lower than that for PM7 (**Figure 2.3a**), suggesting that PM7 D1 and D2 are not only more torsionally distorted from planarity and less likely to planarize, but also more flexible than PM7. We note that the ester groups of PM7 D1 and D2 are rotationally flexible so the configuration where carbonyl (C=O) oxygen of ester group faces the thiophene group as shown in **Supplementary Figure 2.11** is also possible. However, regardless of this ester group configuration, we observe the same trend in the potential energy scans where PM7 D1 and D2 have larger minimum-energy dihedral angles, higher energy barriers to planarize, and lower energy barrier to switch from anti to syn conformation than PM7 (**Supplementary Figure 2.11**).

Overall, our DFT results suggest that the planarity disrupting ester functionalized acceptor moieties make PM7 D1 and D2 more torsional and flexible than PM7 which could explain why they do not form fiber aggregates in solution but instead form an amorphous polymer chain network. We also note PM7 D1 and D2 possess long unbranched alkyl sidechains which could contribute to making them more solubilized by disrupting backbone interactions. On the other hand, we believe that the more rigid and planar PM7 polymer forms fiber aggregates via strong polymer chain interactions as evidenced by the lamellar and π - π stacking interactions observed in the solution-state.

Temperature dependence of the polymer solution-state aggregate structures

The effect of solution temperature on the solution-state aggregation behavior was further investigated by using temperature-dependent SAXS and UV-Vis spectroscopy. From the temperature-dependent SAXS solution experiment for PM7 (**Figure 2.4a**), we observe that the Guinier knee region, which corresponds to the cross section of the large fiber-like aggregates, completely disappears when the solution temperature is increased. This led to revelation of the previously hidden Porod region at low Q with a slope close to -2.6, attributed to the contribution from network-like aggregates. This indicates that the fibers are dissolved with increasing temperature, leading to a solution mainly composed of network-like aggregates. By fitting the SAXS profile for PM7 solution at 65 °C, we find that the length of the rigid chain segments is 26 ± 3.8 nm (**Supplementary Table 2.3**) which is shorter than the contour length of the polymer chain (**Supplementary Table 2.1**), indicating that the network aggregates are comprised of the rigid chain segments. In addition to the dissolution of fibers, we observe that the sharp lamellar peak disappears with increasing temperature (inset plot in **Figure 2.4a**). We also found that the intensity of π - π stacking peak for the 105 °C became too low to overcome background scattering from WAXS measurement. These observations indicate that the lamellar and π - π interactions occur within the fiber aggregates in solution and disappear when the fibers are dissolved at high solution temperatures. The temperature-dependent solution UV-Vis of PM7 (**Figure 2.4d**) also demonstrates that the vibronic fine structure decreases with increasing temperature, suggesting an increase in the backbone disorder.^{49,50} On the other hand, the temperature-dependent SAXS profiles of PM7 D1 and D2 solutions (**Figure 2.4b and 4c**) only show a decrease in the intensity of the structure factor peak while the power law scattering at low Q remains, indicating that the amorphous network structure is still maintained. It is, however, notable that the intensity of the broad structure factor peak decreases more substantially in PM7 D1 and D2 than in PM7 and that

the temperature-dependent UV-Vis spectra indicates a more significant blue-shift in PM7 D1 and D2 solutions than in PM7 with increasing temperature (**Figure 2.4d-e**). In addition to the blue-shift, an isosbestic point is observed in both PM7 D1 and D2 solution UV-Vis absorption. The blue-shifted UV-Vis spectra indicate that PM7 D1 and D2 become more flexible due to further backbone twist,⁵¹ and the apparent isosbestic point suggests that polymer chains transition between anti and syn conformations, which is consistent with the low potential energy barrier determined from the DFT calculations (**Figure 2.3a**). We thus attribute the decrease in the intensity of the broad structure factor peak to the increased flexibility of PM7 D1 and D2 polymer chains, leading to fewer chain associations as the solution temperature rises. In PM7 solution, on the other hand, the polymer chains are expected to be highly rigid, thus requiring more thermal energy to make them more flexible and well-solubilized. Despite the rigid polymer chains of PM7, however, the semi-crystalline fiber aggregates are highly sensitive to temperature, leading to a substantial order-to-disorder transition whereas the amorphous network-like aggregates of PM7 D1 and D2 are maintained.

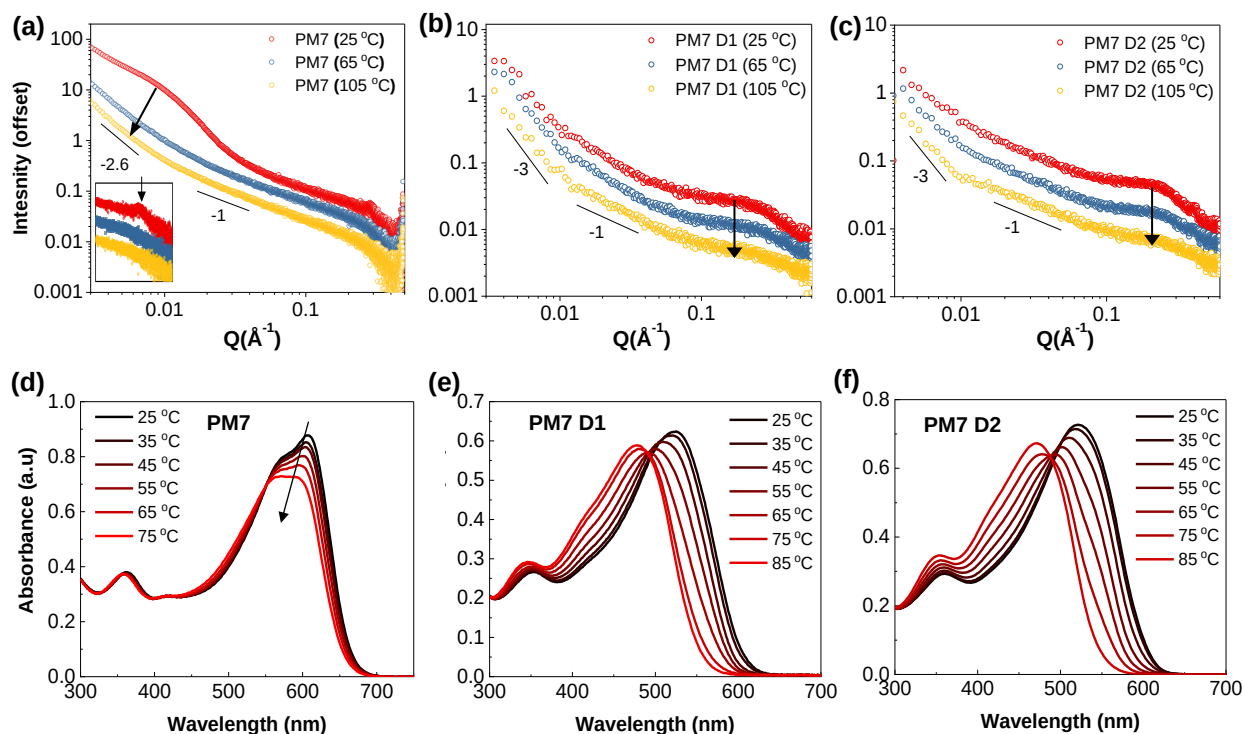


Figure 2.4. Temperature dependence of the neat polymer solutions. Temperature-dependent SAXS results for 20 mg/mL neat polymer solutions of (a) PM7, (b) PM7 D1, (c) PM7 D2 (25 °C and 65 °C curves were shifted up by a multiplication of 4 and 2, respectively); temperature-dependent UV-Vis for 20 mg/mL neat polymer solutions of (d) PM7, (e) PM7 D1, (f) PM7 D2.

Based on the solution-state characterization results, we propose schematics for the polymer aggregate structures and their temperature dependence as shown in **Figure 2.5**. The schematics indicate that PM7 solution contains semicrystalline fiber aggregates composed of lamellar and π - π stacking as well as network-like aggregates of polymer chains formed via alkyl sidechain associations. The fibrillar aggregates of PM7 dissolves at high solution temperatures, resulting in a solution mainly comprised of the network-like aggregates. PM7 D1 and D2, on the other hand, form sidechain associated network-like aggregates that can maintain their structures at high temperatures despite having fewer sidechain associations due to their increased chain flexibility. We hypothesize that this temperature-resiliency of the network-like structures of PM7 D1 and D2 will make them more resilient to processing temperature during fabrication of OSCs.

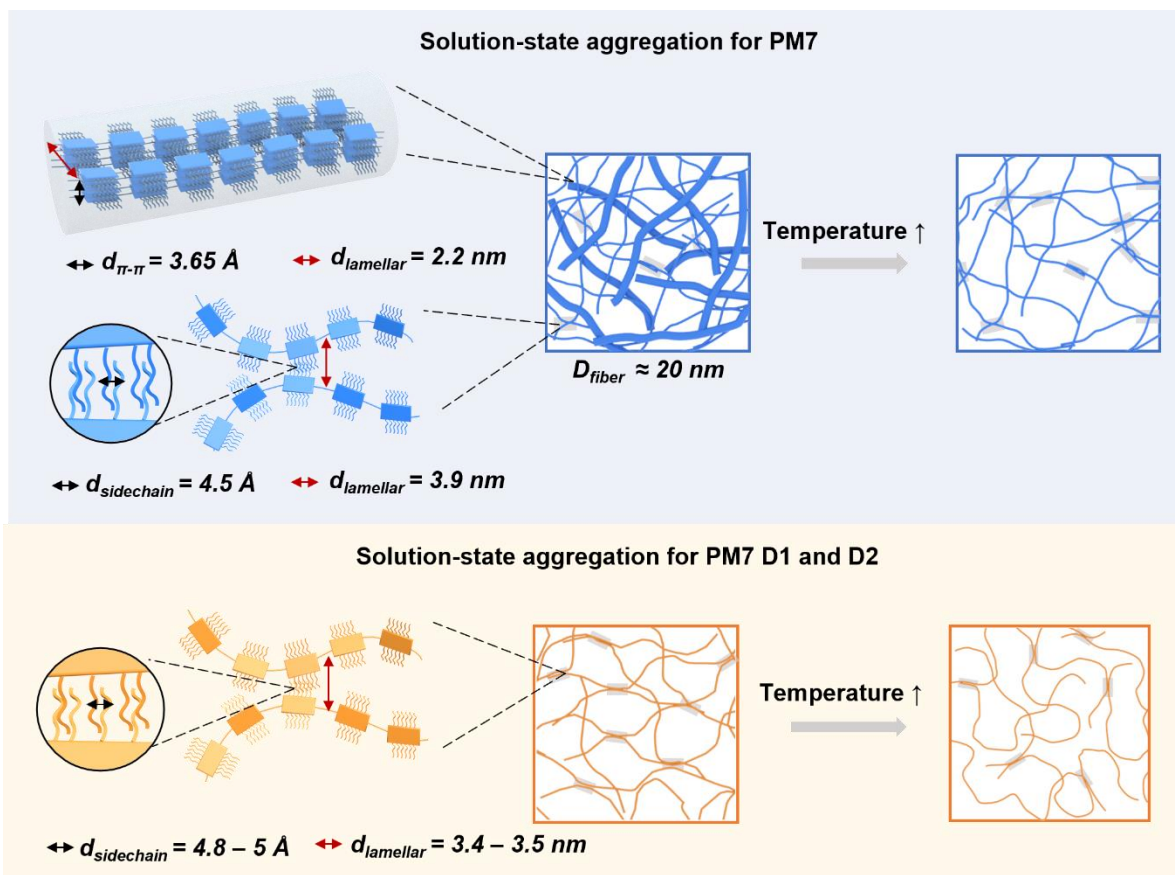


Figure 2.5. Proposed solution-state aggregated structure and temperature-dependence of the three polymers: The top row shows the detailed structure of the fiber and network aggregates in PM7 solution and the temperature dependence of the solution-state aggregation with increasing temperatures. The bottom row represents the detailed structure for PM7 D1 and D2 aggregates in solution and their solution temperature dependence. The grey squares in the figure indicate sidechain associations within the network-like aggregates.

Thus far, we have investigated the neat polymer solution-state aggregate structures and their solution temperature-dependence. However, BHJ based OSCs are typically fabricated from a blend solution of donor and acceptor materials. Therefore, it is critical to determine whether the acceptor material influences the aggregate structures of donor polymers and their temperature dependence. Using SAXS on blend solutions of the donor polymer and the small molecule acceptor, ITIC-4F, we discovered that the presence of ITIC-4F has no effect on the solution-state aggregate structures of the donor polymers. Shown in **Supplementary Figure 2.12** is the scattering profiles of the blend solutions which closely resemble the scattering profiles of the neat

donor polymer solutions (**Figure 2.2a-c**). Furthermore, we also obtained the temperature-dependent UV-Vis spectroscopy of the blend solutions (**Supplementary Figure 2.13a-c**) to investigate whether the temperature-dependent behavior of the donor polymer is altered by the presence of ITIC-4F. When the neat solution spectra of ITIC-4F (**Supplementary Figure 2.14**) is subtracted from the blend solution UV-Vis spectra, we obtain the temperature-dependent UV-Vis spectra of only the donor polymers from the blend solutions (**Supplementary Figure 2.13d-f**) which closely matches temperature-dependent UV-Vis of the neat polymer solution spectra (**Figure 2.4d-f**). Based on these results, we conclude that the solution-state aggregation of donor polymers and their temperature-dependent behavior are not altered by the presence of small molecules.

Determining the processing conditions for blade coating

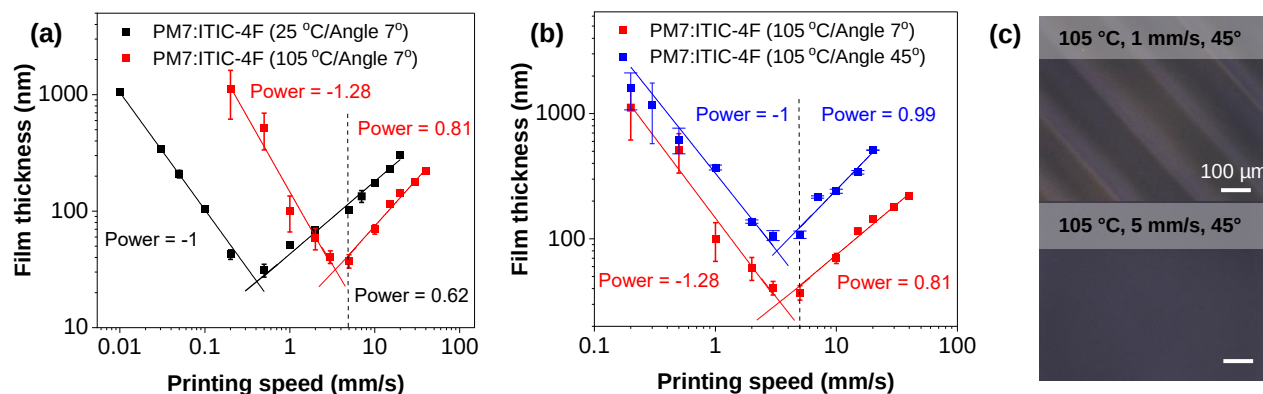


Figure 2.6. Film thickness versus printing (coating) speed relationship of the blend films printed at (a) 25 °C and 105 °C coating temperatures while maintaining the same blade angle of 7°, (b) 7° and 45° at the same coating temperature of 105 °C; (c) uniformity comparison between films printed in the evaporation regime (1 mm/s) and LL regime (5 mm/s) at 105 °C and a blade angle of 45°.

It is well-known that carrying out active film formation by spin-coating under an inert atmosphere using 1, 8-diiodooctane (DIO) as an additive can provide high performance solar cells, and PM7:ITIC-4F pair has been reported to have a PCE up to 14 %.⁵² In this work, we employed meniscus-guided coating in air without additives to demonstrate compatibility with scalable large-

area coating techniques under more practical conditions. Unlike spin coating, in which the spin speed of the substrate is the only processing parameter, the blade coating process involves several processing parameters such as coating speed, substrate temperature, and blade angle which all influence the film thickness, uniformity, and device performance of OSCs. The objective is to obtain uniform films with an optimal film thickness of around 80-100 nm under various substrate temperatures to investigate the effect of substrate temperature on the solid-state morphology and device performance of OSCs. Therefore, we first determined how each of the processing parameters affect the film thickness and uniformity. To demonstrate how the film thickness and uniformity are affected by the processing parameters, we take PM7:ITIC-4F film deposition as an example to show the thickness as a function of coating speed relationship by (1) varying the substrate temperatures while keeping the blade angle constant (**Figure 2.6a**) and (2) varying the blade angles while keeping the substrate temperature constant (**Figure 2.6b**). As seen from **Figure 2.6a**, when the substrate temperature is 25 °C with a blade angle of 7°, the film thickness decreases as the coating speed increases from 0.01 mm/s to ≈ 0.5 mm/s. This inverse relationship between the coating speed and film thickness corresponds to the evaporation regime⁵³ where the solution evaporation rate governs the relationship between the final film thickness and the coating speed. In this regime, we observe poor film uniformity (**Figure 2.6c**) due to stick-and-slip meniscus instability caused by a competition between pinning and depinning forces at the contact line.^{54,55} On the other hand, in the Landau-Levich (LL) regime where the film thickness increases with coating speed, the deposited films are more uniform which is desirable to reduce device-to-device performance variations (**Figure 2.6c**). Although the films are more uniform in the LL regime, the film thickness changes substantially when the substrate temperature is increased from 25 °C to 105 °C at a blade angle of 7° (the red plot in **Figure 2.6a**). In fact, we can see that the entire

thickness versus coating speed relationship (both evaporation and LL regime) shifts to the right due to an increased evaporation rate and the change in the physical properties of the solution at an elevated temperature. Due to this shift, the film thickness is significantly reduced in the LL regime from ≈ 100 to ≈ 50 nm when increasing the substrate temperature from 25 °C to 105 °C while maintaining the same coating speed of 5 mm/s, as indicated by the dashed line in **Figure 2.6a**. To increase the film thickness without changing the concentration of the solution or the coating speed at a substrate temperature of 105 °C, we increased the blade angle from 7° to 45° which shifted the entire curve upwards as shown in **Figure 2.6b** resulting in the final thickness of ≈ 100 nm at 5 mm/s as indicated by the dashed line. We attribute this upward shift to the increase in the back meniscus height with increasing the blade angle, allowing us to vary the film thickness at any substrate temperature without changing the solution concentration or the coating speed.

Blend film morphology and device performance characterization

Using the abovementioned approach to deposit thin uniform films, we firstly investigated the solid-state morphology of the blend films blade coated at low (25 °C) and high (105 °C) substrate temperatures using GIWAXS. In **Figure 2.7a**, we show the 2D GIWAXS images of the blend films printed at 25 °C where all blend films exhibit in and out-of-plane (010) peaks at around $q \approx 1.8 \text{ \AA}^{-1}$ which correspond to edge-on and face-on π - π stacking, respectively, with respect to the substrate. We attribute the π - π stacking peaks to the polymer backbone stacking because all neat polymer films possess (010) peak while the neat acceptor film has an amorphous halo which does not contribute to the observed π - π stacking peak of the blend film (**Supplementary Figure 2.15**). Furthermore, all blend films exhibit lamellar stacking peaks (100) around $q \approx 0.3 \text{ \AA}^{-1}$ as shown in **Supplementary Figure 2.16** which represents the color scales adjusted GIWAXS patterns and the linecut profiles. The peak locations and FWHM of (010) and (100) peaks are summarized in **Supplementary Table 2.4**. Based on the location of (100) and (010) peaks,

lamellar and π - π stacking distances for PM7:ITIC-4F, PM7 D1:ITIC-4F, and PM7 D2:ITIC-4F blend films processed at room temperature were obtained as shown in **Table 2.2**. Although PM7:ITIC-4F has the shortest lamellar stacking distance, its π - π stacking distance is larger (3.53 Å) than those of PM7 D1 and D2 blend films (3.42 Å and 3.45 Å). Interestingly, when a high substrate temperature (105 °C) is used for blade coating (2D GIWAXS patterns and the linecut profiles of these films are shown in **Supplementary Figure 2.17**), the π - π stacking distance for PM7:ITIC-4F decreases from 3.53 Å to 3.44 Å whereas those of PM7 D1:ITIC-4F and PM7 D2:ITIC-4F remain almost unchanged (**Table 2.2**). We note that this result is highly consistent with the temperature-dependent fibrillar aggregates of PM7 and temperature-resilient properties of PM7 D1 and D2 in the solution-state. In particular, since the fibrillar aggregates in the solution-state already exhibits large π - π stacking distance of 3.65 Å, these aggregates may be directly translated to the blend films, thereby resulting in the large π - π stacking distance observed in the room temperature processed films.

We further compare the polymer orientation distribution of the three polymer blend films using the molecular orientation analysis as described in earlier works.⁵⁶⁻⁵⁸ The pole figures shown in **Figure 2.7b** are obtained by plotting the intensity of the (010) peak as a function of the azimuthal angle, χ , with 10° interval starting from 0° to 90° which represents face-on and edge-on crystallites respectively. The (010) peak intensity at each angle is obtained by peak deconvolution due to the overlap of the amorphous and π - π stacking peaks as previously reported.⁵⁶ The obtained peak intensities are then normalized by their exposure time and irradiated volume and multiplied with $\sin\chi$ which corrects the intensity underestimation at high χ due to the scattering geometry. Based on the analysis, we observe that the molecular orientation of the PM7:ITIC-4F blend film leads to a measurable change with respect to the coating temperature as shown in **Figure 2.7b** in which the

polymer orientation switches from more isotropic population to a population with predominantly face-on orientation as illustrated in **Figure 2.7d**. On the other hand, in the PM7 D1 and D2 blend films, we observe only a slight enhancement of the face-on population (**Figure 2.7b**). The extent of molecular orientation change can be more clearly quantified by calculating the Herman's orientation parameter (S)^{59,60} from the (010) π - π stacking peak. The S parameter ranges from a value of -0.5 which corresponds to a complete edge-on population to a value of 1 which is a total face-on population when the director is chosen as the surface normal. The S value of 0 corresponds to a mixture of both face-on and edge-on orientations. Based on **Figure 2.7c**, the PM7 blend film printed at 25 °C shows a value of 0.098 which represents an isotropic population whereas the PM7 D1 and D2 blend films printed at 25 °C are more face-on with S values of 0.173 and 0.145, respectively. At a high coating temperature of 105 °C, there is an increase in the S value for PM7 reaching 0.205 while only a slight improvement is observed for PM7 D1 and D2, indicating that their molecular orientation in the solid-state is less dependent on the substrate temperature as compared to PM7. We attribute this isotropic orientation of the PM7 blend film printed at 25 °C to the fibrillar aggregates observed in solution which may already possess their thermodynamically favorable orientations in the solution-state.

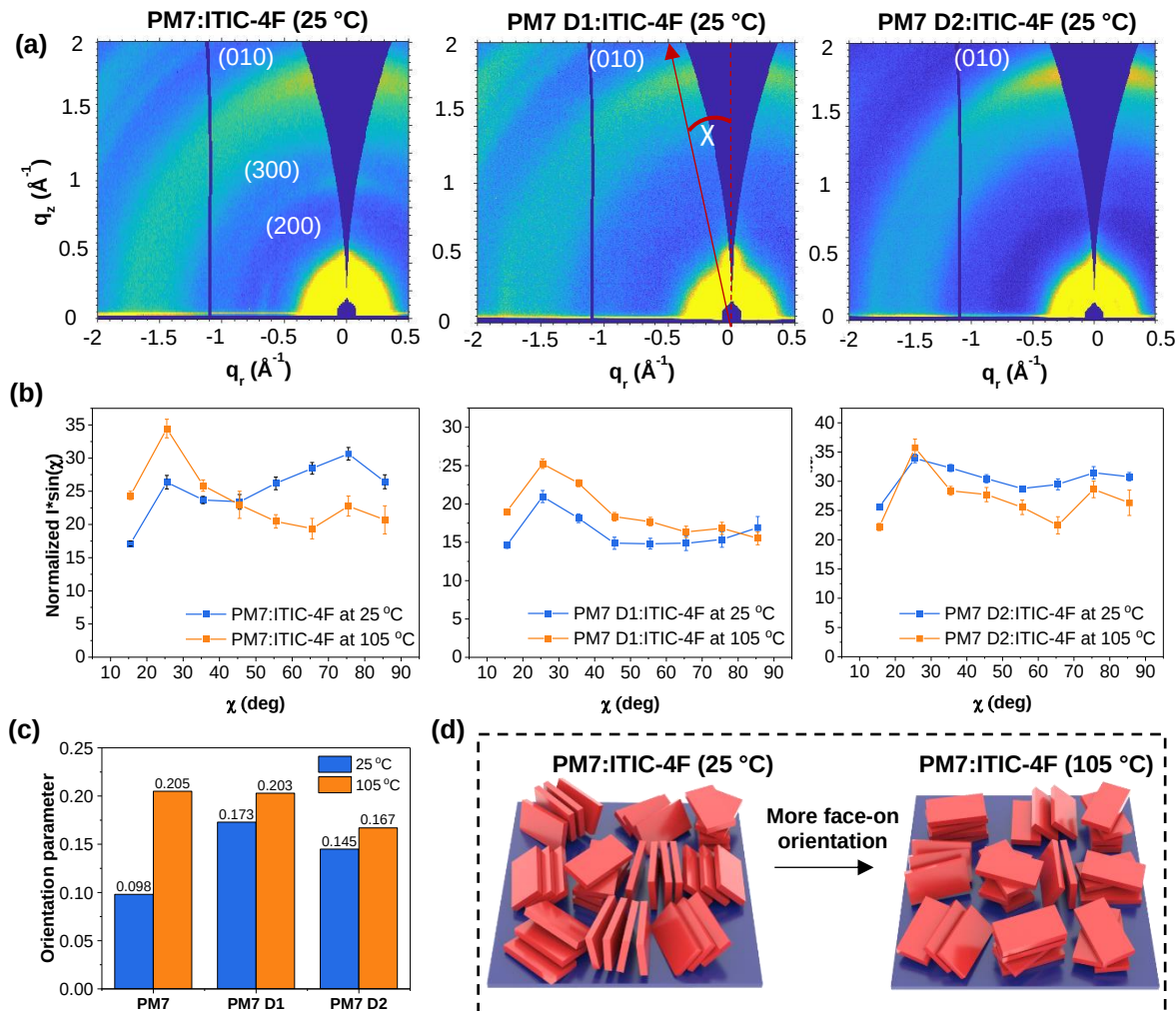


Figure 2.7. Polymer orientation analysis by GIWAXS: (a) Comparison of the diffraction patterns between PM7:ITIC-4F, PM7 D1:ITIC-4F, PM7 D2:ITIC-4F films printed at 25 °C temperature and 5 mm/s coating speed; (b) comparison of geometrically corrected orientation profiles using the π - π stacking peaks of the three blend films printed at 25 °C and 105 °C, respectively. In these plots, $\chi = 0^\circ$ represents face-on orientation, and $\chi = 90^\circ$ represents edge-on orientation; (c) Herman's orientation parameter value comparison for three blend films printed at 25 °C and 105 °C to quantify the orientation change with respect to temperature; (d) illustration of molecular orientation change for PM7:ITIC-4F blend film with respect to the coating substrate temperature.

Table 2.2. Lamellar and π - π stacking distances obtained from GIWAXS.

Samples	Lamellar stacking distance ($\text{\AA}$)	π - π stacking distance ($\text{\AA}$)
PM7:ITIC-4F 25 °C	19.7	3.53
PM7:ITIC-4F 105 °C	19.6	3.44
PM7 D1:ITIC-4F 25 °C	22.4	3.42
PM7 D1:ITIC-4F 105 °C	22.8	3.42
PM7 D2:ITIC-4F 25 °C	21.6	3.45
PM7 D2:ITIC-4F 105 °C	21.9	3.44

To investigate the phase separated structures of the blend films, we use Resonant Soft X-ray Scattering (RSoXS)⁶¹ whereby the X-ray energy can be tuned to the aromatic C1s $\rightarrow\pi^*$ to improve the contrast between the donor and acceptor domains. Although RSoXS of OSC systems is often applied at a single energy that delivers high scattering contrast, the origin of that contrast cannot be determined from a single energy. Possible origins of contrasts include compositional contrast between two or more OSC components and compositional contrast between those components and vacuum (roughness at the top interface) or SiN (roughness at the bottom interface). Orientational contrast is also possible wherein the contrast comes from between differently oriented populations of a single component or between non-isotropic populations of multiple components. Orientational fluctuations in a compositionally homogeneous film can give rise to considerable scattering intensity and features describing the length scales of orientational heterogeneity⁶². The key to unraveling the origins of contrast in an RSoXS measurement is the detailed energy dependence of the total scattering intensity/invariant (TSI), the expectation of which for binary pairs of materials has been shown to be directly calculable from measured spectroscopic dielectric functions by Ferron et al.⁶³ As our data was collected only at 90° incidence, we will compare a quasi-TSI to calculated binary contrast functions under the assumption that the scattering intensity varies along the unmeasured thickness axis the same way as along the lateral axes.

We begin with RSoXS data obtained at 284.8 eV for which the scattering intensity reaches maximum (**Figure 2.8a**), with other energies shown in **Supplementary Figure 2.18**. The PM7:ITIC-4F blend film exhibits a shift in the shoulder peak location to higher Q at the higher processing temperature as indicated by the arrow, indicating a decrease in characteristic length scale, whereas the shoulder peaks from PM7 D1 and PM7 D2 blend films do not shift as

significantly with increasing processing temperatures. For PM7 D1 and D2 blend films, an additional shoulder peak at low Q ($\approx 0.005 \text{ \AA}^{-1}$), also seen in the Kratky plots (**Supplementary Figure 2.19**), was found to be attributable to our SiN substrate as it is observed from RSoXS patterns of the blank substrate (**Supplementary Figure 2.20**). The detailed energy dependence of the scattering intensity provides further confidence that this peak originates from roughness at the SiN – polymer interface; an integrated scattering intensity of this peak near $\approx 0.005 \text{ \AA}^{-1}$ compares well to binary contrast functions between SiN and the hydrocarbons, as calculated by the method described in Ferron et al. (**Supplementary Figure 2.21a, b**), whereas an integrated scattering intensity of the higher- Q peak does not appear to be influenced by SiN roughness (**Supplementary Figure 2.21a, c**). It is also possible to rule out a top interface roughness contribution by examining vacuum contrast functions of all neat materials and their material contrast functions (donor and acceptor) as presented in **Supplementary Figure 2.22a**. Our experimentally obtained TSI versus energy plots (**Supplementary Figure 2.22b**) do not resemble these vacuum contrast functions. This result is consistent with film topology; all blend film samples exhibit rather smooth surfaces with root-mean-square (RMS) value of less than 5 nm as shown in **Supplementary Figure 2.23**, where PM7 D1 and D2 exhibit even less than 1 nm.

We can thus narrow down the possible origins of RSoXS contrast of the principal scattering features to material and/or orientation contrasts. To develop anisotropic dielectric functions, we obtained incident-angle-dependent near edge X-ray absorption fine structure (NEXAFS) spectroscopy of the neat materials (**Supplementary Figure 2.24**). These NEXAFS spectra were converted into real and imaginary index of refraction contributions δ and β using a Kramers-Kronig transform.⁶⁴ Contrast between ordinary and extraordinary orientations of each component, and the combinatorial distributions between the two components were then calculated (**Supplementary**

Figure 2.25). Pure compositional contrast between OSC components would be represented only by the contrast between isotropic, or NEXAFS “magic angle” components. We observe that the TSI vs energy plots do not exactly match the magic angle binary contrast function, suggesting that orientational effects cannot be neglected (**Supplementary Figure 2.25**). This conclusion is consistent with the significant pattern anisotropy that is observed in our raw patterns (**Supplementary Figure 2.26**). No single binary contrast function exactly matches our measured TSI vs. energy, which suggests that a distribution of orientations of one or both components are responsible for the contrast.

Although we find that the scattering features are the result of a mixture of orientational and compositional heterogeneity, the center-to-center distance or spacing of regions with homologous orientation and/or composition is still relevant to the blend morphology and charge transport landscape of OSCs. Therefore, using the Debye-Anderson-Brumberger (DAB) model derived for a randomly distributed two phase system from autocorrelation function,⁶⁵ we obtained the correlation length corresponding to the average distance between two phases as shown in **Figure 2.8b** (values are summarized in **Table 2.3**). We note that scattering anisotropy does not influence the DAB model fitting significantly in the parallel and perpendicular directions with respect to the electric field (**Supplementary Figure 2.27** and **Supplementary Table 2.5**), suggesting that the shape of the domains have minimal influence on the scattering features although it is non-negligible. Nevertheless, since the domain form factor and structure factor cannot be uniquely separated, we obtained a single length scale using the DAB model based on the circularly averaged scattering profiles. Based on **Figure 2.8b** and **Table 2.3**, the PM7:ITIC-4F blend film processed at room temperature exhibits the largest correlation length which substantially decreases when the film is processed at high temperatures. This result is consistent with the order-disorder transition

of fiber aggregates of PM7, leading to the processing temperature-sensitive morphology. In contrast, PM7 D1 and D2 yield smaller correlation length, which is almost unaffected by the processing temperature, suggesting that the temperature-resilient amorphous polymer network aggregates help to maintain the phase separated structures of the blend film.

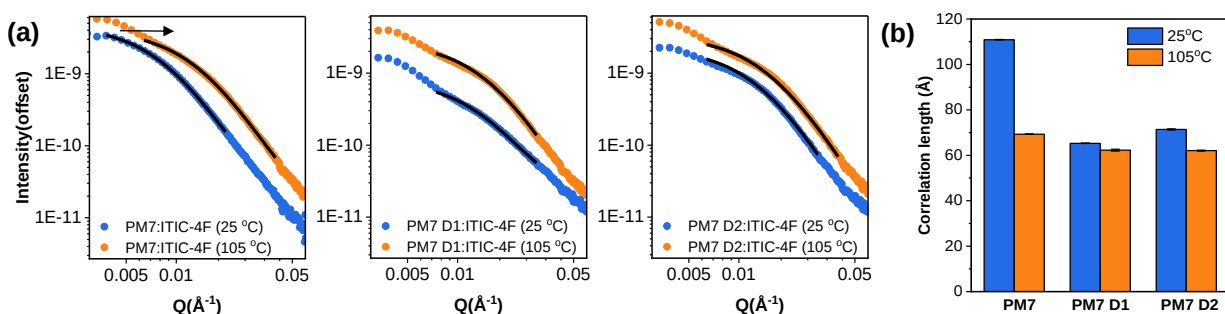


Figure 2.8. Blend film morphology characterization using RSoXS measurements: (a) Intensity versus q plots of all three polymer blend films printed at 25 °C and 105 °C temperatures where the arrows represent scattering due to surface roughness of SiN; (b) The correlation length comparison of the blend films obtained from the DAB model with flat background.

Table 2.3. Correlation length obtained from the DAB model (the uncertainties here represent the model fitting error).

Samples	Correlation length (Å)
PM7:ITIC-4F 25 °C	110.9 ± 0.1
PM7:ITIC-4F 105 °C	69.3 ± 0.1
PM7 D1:ITIC-4F 25 °C	65.3 ± 0.1
PM7 D1:ITIC-4F 105 °C	62.3 ± 0.4
PM7 D2:ITIC-4F 25 °C	71.4 ± 0.3
PM7 D2:ITIC-4F 105 °C	62.1 ± 0.2

To correlate the solution aggregate structures and the blend film morphology to the device performance of OSCs, we carried out device fabrication using substrate temperatures of 25 °C, 65 °C, and 105 °C from a room temperature solution (using both hot solution (105 °C) and room temperature solution (25 °C) lead to similar performances as shown in **Supplementary Figure 2.28** and **Supplementary Table 2.6** due to the small amount of solution (≈ 5 uL) used for blade coating). At each coating temperature, we retained the coating speed at 5 mm/s and varied the blade angle as discussed previously to achieve uniform films with optimal thickness of ≈ 80 nm.

The *J-V* performance of inverted geometry devices with an ITO/ZnO/active layer/MoO₃/Ag architecture in which ITO acts as an electron collecting electrode (cathode) and Ag as the hole collecting electrode (anode) is shown in **Figure 2.9a-c**. In **Figure 2.9d**, we observe that the PM7:ITIC-4F device performance changes substantially with increasing coating temperature, showing $\approx 50\%$ increase in the PCE from 5.8 % to 8.7 % when PM7 converted from fiber aggregates to network aggregates in solution upon heating. In comparison, the PCEs of the PM7 D1 and D2 based devices exhibited less statistical variation with only about $\approx 10\%$ and $\approx 15\%$ increase with increasing temperature respectively. The drastic device performance change in the PM7 based devices with increasing coating temperature is mainly attributed to the short circuit current (J_{SC}) and fill factor (FF) improvement (**Table 2.4**, **Figure 2.9e** and **9f**) which are highly correlated with the morphology of the blend films. On the other hand, we do not observe any trend in V_{OC} values **Figure 2.9g** which could be due to factors unrelated to morphology change such as defects during device fabrication (e.g. thermal evaporation at high temperatures) which are inconsistent from sample to sample. At low coating temperature, the PM7 blend film morphology exhibits large domains where polymers are oriented isotropic while PM7 D1 and D2 form small domains where polymers are oriented predominantly face-on. This morphology difference correlates well with the inferior J_{SC} and FF of the PM7 polymer-based devices fabricated at low coating temperature as the charge generation and transport are reduced due to the large domains and the unfavorable molecular orientation. When the coating temperature is increased, we observe a significant change in the device performance of PM7 which also corresponds to the morphology change observed in the solid-state, more specifically, the domain size reduction, closer π - π stacking and enhancement of the face-on molecular orientation. For PM7 D1 and D2 based

devices, the device performance resiliency is also correlated with their robust solid-state morphology which is less sensitive to the processing temperature.

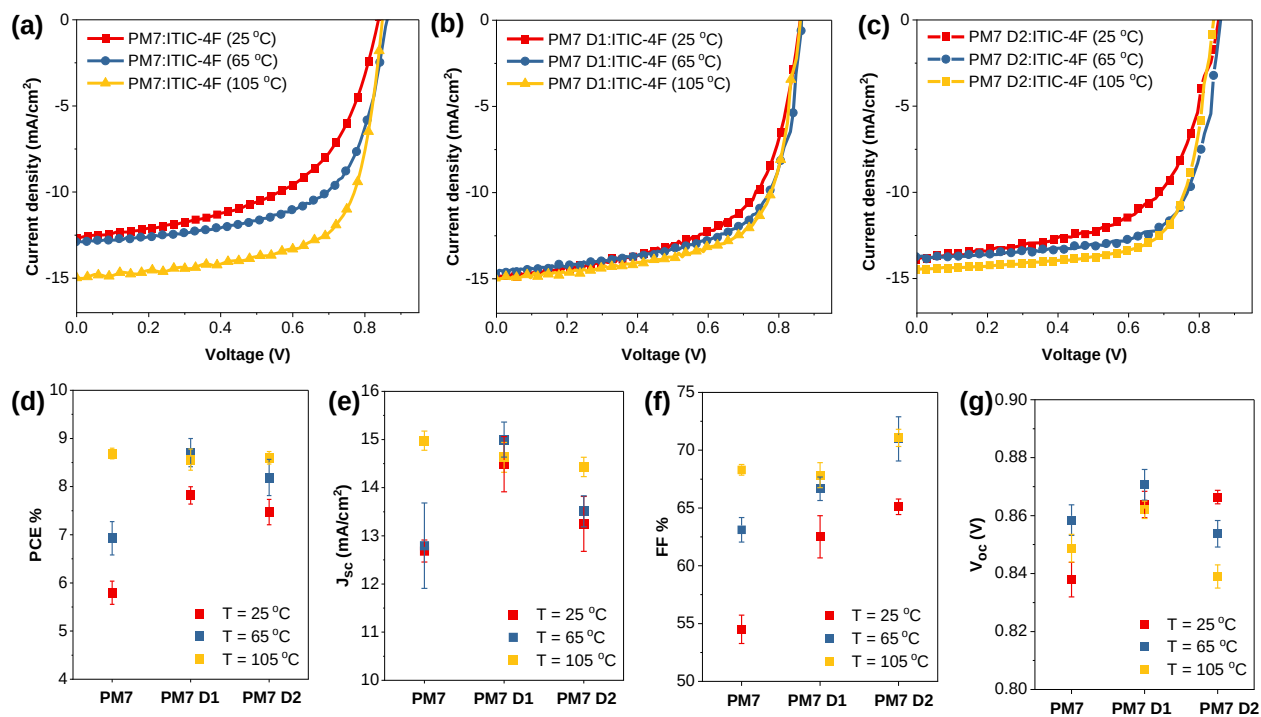


Figure 2.9. Device characterization results: Current-voltage ($J-V$) curves of (a) PM7:ITIC-4F, (b) PM7 D1:ITIC-4F, and (c) PM7 D2:ITIC-4F devices fabricated at three different processing temperatures; the comparison of device performances: (d) PCE, (e) J_{sc} , (f) FF, and (g) V_{oc} in which the average and error (sample standard deviation) are based on ≈ 10 -15 devices. The solution concentration is 20 mg/mL for the polymer and acceptor, and the coating speed is maintained at 5 mm/s at all conditions. The blade angle is varied to optimize the thickness for all films ≈ 80 nm.

Overall, our film morphology and device performance results indicate that the initial solution-state aggregate structures of donor polymers largely determine the final film morphology and device performance of OSCs. We found that the large fiber-like aggregates formed in the solution-state led to large π - π stacking distance and large domain spacing without preferential molecular orientation while network-like aggregates resulted in shorter π - π stacking and smaller domain spacing with predominantly face-on orientation. Since the small molecule acceptor, ITIC-4F, is amorphous based on our GIWAXS results (**Supplementary Figure 2.15**), we predict that

the donor polymer aggregation in solution likely templates the film morphology which has been demonstrated in other studies.^{16,66,67}

Table 2.4. Device performance results of polymer blend films printed at varying temperatures

Samples	PCE (%)	FF (%)	J _{sc} (mA/cm ²)	V _{oc} (V)
PM7:ITIC-4F at 25 °C	5.8 ± 0.2	55 ± 1.3	12.7 ± 0.2	0.84 ± 0.01
PM7:ITIC-4F at 65 °C	6.9 ± 0.4	63 ± 1.0	12.8 ± 0.9	0.86 ± 0.01
PM7:ITIC-4F at 105 °C	8.7 ± 0.1	68 ± 0.5	15.0 ± 0.2	0.85 ± 0.01
PM7 D1:ITIC-4F at 25 °C	7.8 ± 0.2	62 ± 1.8	14.5 ± 0.6	0.86 ± 0.01
PM7 D1:ITIC-4F at 65 °C	8.7 ± 0.3	67 ± 1.0	15.0 ± 0.4	0.87 ± 0.01
PM7 D1:ITIC-4F at 105 °C	8.6 ± 0.2	68 ± 1.1	14.6 ± 0.3	0.86 ± 0.01
PM7 D2:ITIC-4F at 25 °C	7.5 ± 0.3	65 ± 0.7	13.2 ± 0.6	0.87 ± 0.01
PM7 D2:ITIC-4F at 65 °C	8.2 ± 0.4	71 ± 1.9	13.5 ± 0.3	0.85 ± 0.01
PM7 D2:ITIC-4F at 105 °C	8.6 ± 0.1	71 ± 0.7	14.4 ± 0.2	0.84 ± 0.01

2.3 Conclusion

Previous studies have shown the importance of donor polymer solution-state aggregation on the morphology and device performance of OSCs. However, little is known of the exact structure of polymer aggregates in the solution-state and how it determines the BHJ morphology and performance of OSCs. In this article, we have investigated the donor polymer aggregate structures of PM7 polymer and its ester-functionalized derivatives with reduced backbone planarity, PM7 D1 and D2, to highlight the importance of polymer aggregate structures on the morphology, device performance, and processing temperature resiliency of blade coated OSCs. By employing SAXS and microscopy measurements, we revealed that PM7 forms semi-crystalline fiber aggregates, whereas PM7 D1 and D2 lead to amorphous network-like aggregates of single polymer chains at room temperature. Our DFT studies indicated that PM7 D1 and D2 polymers are more non-planar and flexible than PM7 due to their rotationally flexible ester functionalized terthiophene acceptor moieties which reduce the likelihood of forming large fiber-like aggregates

observed in PM7. Furthermore, we demonstrated that these fiber aggregates yield OSCs with inferior device performance by leading to large π - π stacking distance and large domain spacing without preferential molecular orientation in the blend film. We also observed that the fiber aggregates undergo a drastic order-disorder transition with increasing solution temperature, yielding devices that are strongly dependent on the processing temperature. On the other hand, the amorphous network-like aggregates of PM7 D1 and D2 not only showed an improved processing temperature-resiliency but also yielded higher PCEs due to their favorable BHJ morphology consisting of short π - π stacking distance, small domain spacing, and face-on dominant molecular orientation. Consistently, we found that PM7 yields improved performance when it formed amorphous network-like aggregates at high solution temperatures. Overall, our findings suggest that the polymer aggregate structure in the solution-state determines the solid-state morphology, device performance and processing resiliency of non-fullerene OSCs. In particular, we show that as compared to semi-crystalline fiber-like aggregates, forming amorphous network-like aggregates in the solution-state improves the device performance and processing resiliency in blade coated OSCs. Besides the two types of aggregate structures described in this work, polymer solutions can form other types of aggregates which may impact the BHJ morphology and device properties. Therefore, further investigation will be needed to understand the impact of various types of polymer aggregates on the optoelectronic properties of OSCs.

2.4 Experimental methods

Material and solution preparation:

The donor polymers (PM7, PM7 D1 and PM7 D2) used in this study were synthesized according to Jones *et al.*²³ with similar number average molecular weights between 38 kg/mol and 41 kg/mol with dispersity below 2.5 as shown in Supplementary Table 2.1. The molecular

acceptor, ITIC-4F, with > 99% purity was purchased from Brilliant Matters, Inc.* The neat polymer solutions were prepared by dissolving each polymer in chlorobenzene (anhydrous, 99.8%, Sigma-Aldrich, Inc) to obtain a solution of 20 mg/mL concentration and stirred at 40 °C for over 12 hours and cooled down to room temperature for 2-3 hours before each experiment. The blend solutions for device fabrication were prepared by mixing each polymer with the small molecule acceptor at 1:1 weight ratio and dissolving the mixture in chlorobenzene to obtain a solution with a total concentration of 40 mg/mL. These blend solutions were also stirred at 40 °C for over 12 hours and cooled to room temperature for 2-3 hours before device fabrication.

***Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.**

Density Functional Theory Calculations:

DFT calculations were used for molecular geometry optimization and obtaining potential energy scans of the dihedral angles. All calculations were performed with the Gaussian 16 package by using wB97xD method at 6-31G (d, p) basis set. In all calculations, the long alkyl sidechains on both donor and acceptor moieties were replaced with methyl groups for simplification. To obtain the potential energy scans of a dihedral angle, molecular fragments relevant to the dihedral angle of interest were firstly optimized at the wB97xD/6-31G (d, p) level of theory. These molecular fragments are provided in each potential energy scan plots. Afterwards, a rigid scan where the single point energy of the optimized molecule was computed when the dihedral angle was varied from 0° to 180° at 10° interval while fixing other dihedral angles. The resulting single

point energies were then plotted against the respective dihedral angle to obtain potential energy plots.

Solution-state characterization:

UV-Vis spectroscopy: UV-vis (Cary 60 UV-Vis, Agilent) spectroscopy was used to measure the absorbance of 20 mg/mL polymer solutions in a short path-length of 10 μm quartz cell (Starna Cells). Before each solution measurement, a blank solvent measurement was taken for background subtraction. For temperature-dependent UV-Vis measurements, a resistive heater and a thermocouple were incorporated into a metal sample holder to heat the solution to the desired temperature at a rate of 2-3 $^{\circ}\text{C}/\text{min}$. Due to the low amount of solution in a narrow quartz cell, the highest temperature for UV-Vis measurement in chlorobenzene solution was 75-85 $^{\circ}\text{C}$ before solution evaporation.

Small Angle X-ray Scattering (SAXS) experiments: SAXS experiments were performed at 12-ID-B beamline of the Advanced Photon Resource at Argonne National Laboratory using a beamline energy of 13.3 keV at detector distances of 2 m and 4 m to probe different scattering vector, Q , ranges. Before performing the polymer solution scattering measurements, the pure solvent background measurement was taken at each experimental temperature to ensure proper background subtraction. Both background and solution measurements were performed using flow cells which were prepared by using a 1 mm diameter quartz capillary connected to PTFE tubing by PTFE heat shrink tubing. Each polymer solution in the flow cell was cycled back and forth to avoid beam damage. Each solution measurement was taken at 0.1 s exposure time with an interval of 2-3 seconds for a total exposure time of 1 s. The obtained raw 2D scattering pattern was reduced to a 1D profile of intensity as a function of the scattering vector from which the solvent background was subtracted to obtain the scattering profile from the polymer only. The resulting scattering

profiles were then fit to the model from reference³⁰ using SASView program. For modeling fitting in SASView, we selected dI data for weighting, Levenberg-Marquardt with 200 steps for the algorithm where the uncertainties are determined from the covariance matrix, and χ^2 values and the residuals plot were used as the goodness of fit metrics.

Freeze-drying method for imaging the solution-state aggregates: Freeze-drying experiments were conducted to image the structure of aggregates in solution by using microscopic techniques including Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). The freeze-drying process involves rapid freezing of polymer solutions in liquid ethane and propane mixture (63% propane and 37% ethane) followed by liquid nitrogen storage. The purpose of using liquid ethane mixture is to ensure rapid freezing of the solution due to its large heat capacity and prevent polymer aggregation during the cooling process. The resulting frozen polymer solution is then quickly transferred to a Linkam stage at -120 °C under vacuum. The Linkam stage temperature is then slowly increased at a rate of 0.5 °C/min to -80 °C (far below the melting point of chlorobenzene solvent mp = -45 °C) followed by 6-8 hours of constant monitoring with cross polarized microscopy to ensure sublimation of all solvent. The sample is then imaged using AFM (Asylum Research Cypher) with tapping mode, and TEM (Hitachi H9500). TEM based electron diffraction measurements were also conducted to determine π - π stacking in the freeze-dried samples. Electron diffraction was taken by a Gatan US1000 CCD camera equipped on a 300kV Hitachi H9500 environmental TEM with guarded ring LaB₆ cathode. Filament current was set automatically at 3.5 uA to reduce beam damage during operation. Patterns were taken at 3s exposure time each and six images were summed to produce the final image. Beam block and astigmatism were removed and monitored

upon azimuthal integration for the intensity line profile. The length scale was calibrated with an Au nanoparticle sample and 4.08 Å was used as its lattice constant.

OSC device fabrication:

OSCs were fabricated using the inverted architecture (glass/ITO/ZnO/polymer:ITIC:4F/MoO₃/Ag). Before film deposition, 20 x 15 cm ITO-patterned glass substrates (Ossila, Inc,) were cleaned by sonicating sequentially with water, acetone and finally isopropanol for 10 minutes each. The cleaned substrates were then dried with nitrogen and plasma treated (Harrick Plasma PDC-001-HP) for 6 minutes at 300 mTorr of dry air and high power (30 W). To deposit the electron transporting layer, ZnO solution was prepared by dissolving 1 g of zinc acetate dihydrate (Sigma Aldrich) and 0.28 g ethanolamine (Sigma Aldrich) in 10 mL of 2-methoxyethanol (Sigma Aldrich) under vigorous stirring for over 12 hours in air. This solution was then filtered with a 0.45 µm PTFE syringe filter before deposition. The filtered solution was deposited on the cleaned ITO substrates by spin-coating for 30 seconds at 4000 rpm in ambient atmosphere which resulted in an active layer thickness of $\approx$ 20-30 nm measured by Bruker Dektak XT profilometer. After spin-coating, the ZnO layer was annealed in air at 200 °C for 30 min followed by slow cooling to room temperature for active layer deposition. We find that it was important to anneal the substrates immediately after ZnO deposition to prevent device failures. The photoactive layer solution for all devices were prepared by dissolving the polymer and ITIC-4F (Sigma Aldrich) at 1:1 (wt/wt) ratio in chlorobenzene without any additives. The resulting blend solution was stirred at 40 °C overnight and brought to room temperature 1-2 hours before deposition. The photoactive layer was then blade coated on the ZnO coated ITO-glass substrate at coating temperatures of 25 °C, 65 °C, and 105 °C at 5 mm/s coating speed. For blade coating, the substrates were first stabilized at the coating temperatures for about 5 minutes and the blade is kept

at room temperature. To ensure the same film thickness when coating at different temperatures, the blade angle was varied from 10° to 55° with a solution volume of $\approx 5 \mu\text{L}$ (wet width of the blade is around 6 mm). By varying the blade angle, the optimal film thickness for all devices was kept at $\approx 80 \text{ nm}$. All thin films were then annealed in a nitrogen filled glovebox at 100 °C for 10 minutes. Finally, 8 nm hole transporting layer and 120 nm of Ag electrode was deposited by using a Thermal Evaporator (Kurt J. Lesker Nano36) by slowly ramping the rate of deposition to 0.1 Å/s and 1 Å/s respectively.

Device and film morphology characterization:

Device characterization: The current density (J - V) curves were characterized by using an automated Solar Cell I-V test system (Ossila) under AM 1.5G illumination (100 mW/cm) with a class AAA solar simulator (SciSun-150 by ScienceTech). Before each test, the solar simulator was calibrated by reference single-crystal Si cell (ScienceTech). Each sample includes 8 pixels and a total of three samples, or 24 devices were tested under each condition for reliable experimental results. For calculating the device performance, mismatch factor was not applied.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS): GIWAXS measurements were performed at 8-IDE beamline of the Advanced Photon Source at Argonne National Laboratory using an incident beam energy of 10.86 keV on a two-dimensional detector (PILATUS) with an incident angle of 0.14°. For sample preparation, ZnO was firstly deposited on a Si wafer followed by the photoactive layer deposition and thermal annealing the same way that all OSC devices were fabricated. From GIWAXS measurement, 2D scattering images were obtained and converted to 1D scattering profiles by using the beamline GIXSGUI package written for MATLAB. For molecular orientation analysis, the 1D GIWAXS pattern of intensity versus scattering vector was

azimuthally integrated from $-10^\circ < \chi < -80^\circ$ with 5° interval to yield an intensity versus the χ angle.

Resonant Soft X-ray Scattering (RSoXS): RSoXS data were collected at the Advanced Light Source beamline 11.0.1.2 in transmission geometry. For sample preparation, the photoactive layer was blade coated and thermally annealed using the same device fabrication conditions on a polystyrene sulfonate (PSS) film which was spin coated from a 10% PSS solution in water. The PSS solution was stirred overnight at room temperature before depositing on a Si wafer substrate. After photoactive layer deposition, the sample on a Si substrate was immersed in water which dissolved the PSS layer and separated the sample from the substrate. The sample was then picked up with a 1 x 1 mm, 100-nm-thick Si_3N_4 membrane supported on a 5 x 5 mm, 200- μm -thick Si frame (Norcada) and transferred into the vacuum chamber for RSoXS measurement. RSoXS measurements were performed at the beam energy from 270 eV to 290 eV with 5 seconds of exposure time per scan. The collected 2D scattering images were then converted into 1D profiles using the Nika package supported in the Igor Pro environment. The obtained 1D profiles were normalized by the incoming beam intensity, I_0 , provided by a gold mesh and photodiode, and total illuminated volume which is determined by the multiplication of the illumination area and sample thickness. Since the total illuminated area is same for all films, thickness measurements were used to normalize the intensity.

Angular NEXAFS TEY measurements: To determine vacuum and binary contrast functions, we have obtained NEXAFS TEY measurements on the neat films. The samples for NEXAFS TEY were prepared by coating the neat films on a 1 x 1 cm Si wafer using the same conditions used for device fabrication. The samples were then measured at the beam energy from 270 eV to 320 eV using different polarization angles while fixing the incident angle. NEXAFS data were double

normalized by the Au mesh current and photodiode calibration followed by pre-edge normalization using the QANT software package supported in Igor Pro environment.

Film thickness measurements: Film thickness was measured by using the Bruker Dektak XT profilometry with the stylus force of 3 mg with a scan range of 1000-2000 μm . For thickness measurements, a part of the film was removed with a cotton swab with toluene solvent. The thickness measurements were repeated in 3-5 different positions to obtain the average and standard deviation.

2.5 Supporting information

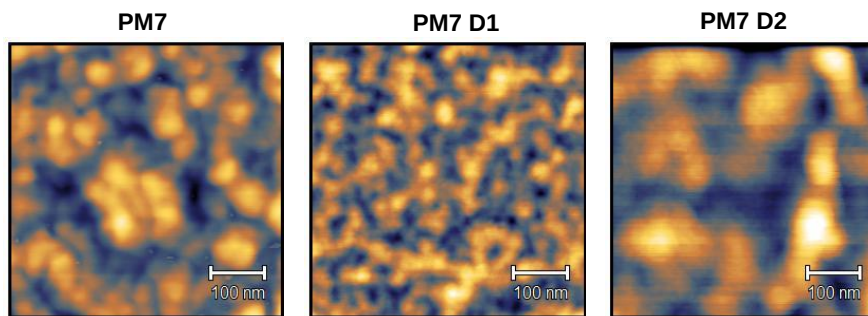
Supplementary Table 2.1. Donor polymer synthesis results.

Materials	M_n	M_w	PDI	Contour length (nm)
PM7	38.5 kg/mol	84.2 kg/mol	2.1	130
PM7 D1	41 kg/mol	98.4 kg/mol	2.4	154
PM7 D2	39 kg/mol	80.3 kg/mol	2.1	124

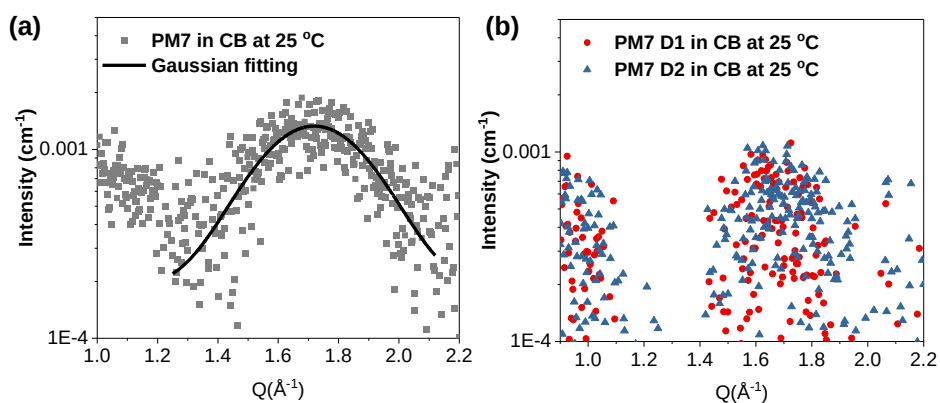
Size exclusive chromatography conditions

Gel permeation chromatography (GPC) was performed using a Tosoh EcoSEC high temperature GPC instrument with RI detector to determine the number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity ($\mathcal{D}$) for all polymers. Experiments were run using 1, 2, 4-trichlorobenzene (TCB) as eluent at 140 $^{\circ}\text{C}$ at a flow rate of 1 mL/min on two 7.8 mm x 30cm, 13 μm TSK-Gel GMHHR-H(S) HT2 columns in series. The instrument was calibrated using polystyrene standards (1,390-1,214,000 g/mol) and the data were analyzed using 8321GPC-WS analysis software. The GPC samples were prepared by dissolving the polymers in TCB at a 1mg/mL concentration and stirred at 110 $^{\circ}\text{C}$ for at least 3 hours before filtering through a 0.45 mm PTFE filter.

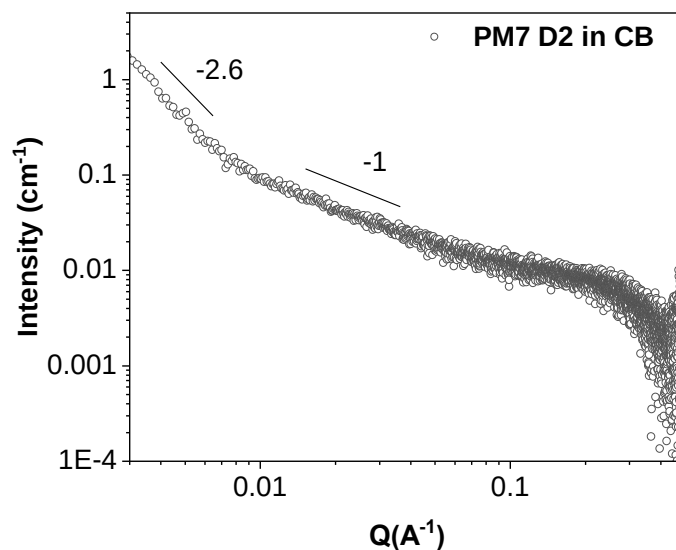
Supporting information for the solution-state characterization



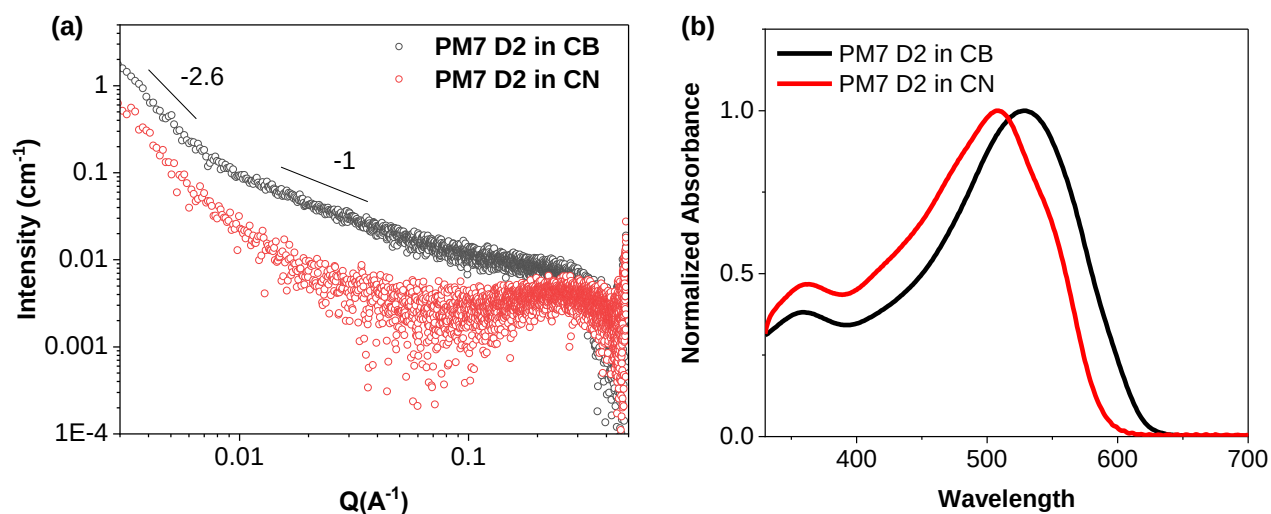
Supplementary Figure 2.1. AFM Height images of the freeze-dried neat polymer solution samples (20 mg/mL concentration solution using CB as the main solvent).



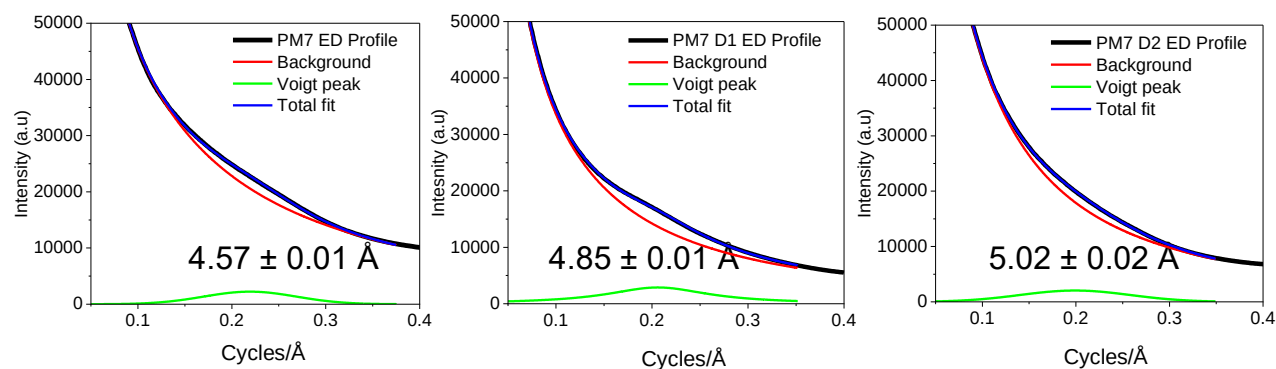
Supplementary Figure 2.2. Solution WAXS profiles for (a) PM7 solution and (b) PM7 D1 and D2 solutions in CB at 25 °C. Gaussian fitting results for PM7 solution: peak center = $1.72 \pm 0.01 \text{ \AA}^{-1}$, peak full width half maximum = $0.35 \pm 0.02 \text{ \AA}^{-1}$.



Supplementary Figure 2.3. SAXS profile for 20 mg/mL PM7 D2 solution in CB after thermally annealing at 100 °C and stirring at 25 °C overnight.



Supplementary Figure 2.4. (a) Comparison of scattering profiles for 20 mg/mL neat PM7 D2 solutions in CB and CN. (b) Comparison of UV-Vis spectra of 20 mg/mL neat PM7 D2 solutions in CB and CN.



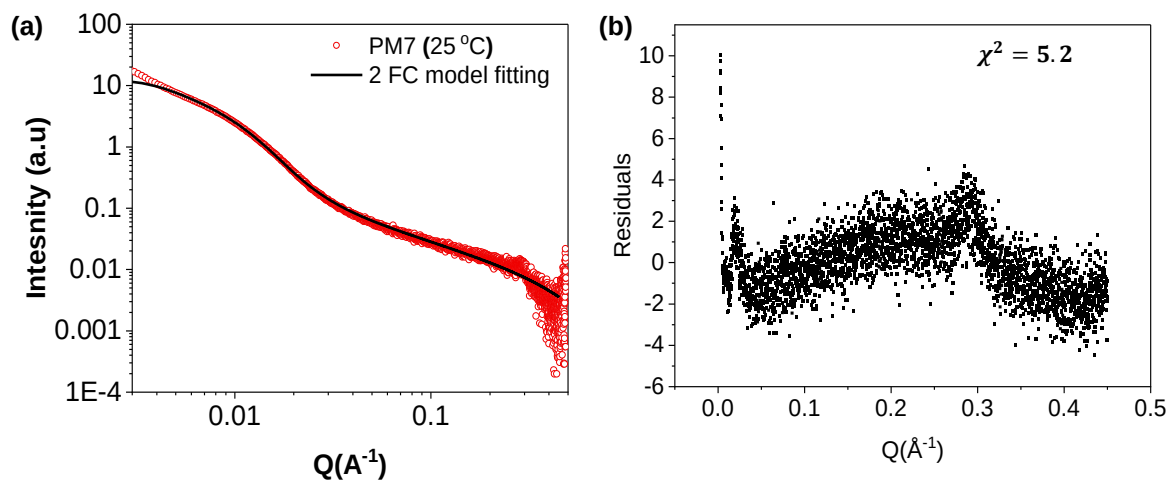
Supplementary Figure 2.5. TEM electron diffraction (ED) measurements on the freeze-dried samples of neat polymer solutions (20 mg/mL). The coherence features were determined by fitting the background scattering to a Voigt profile and then constraining the background to fit the remaining features to another Voigt peak.

Supplementary Table 2.2. Fitting parameters obtained from TEM ED measurements.

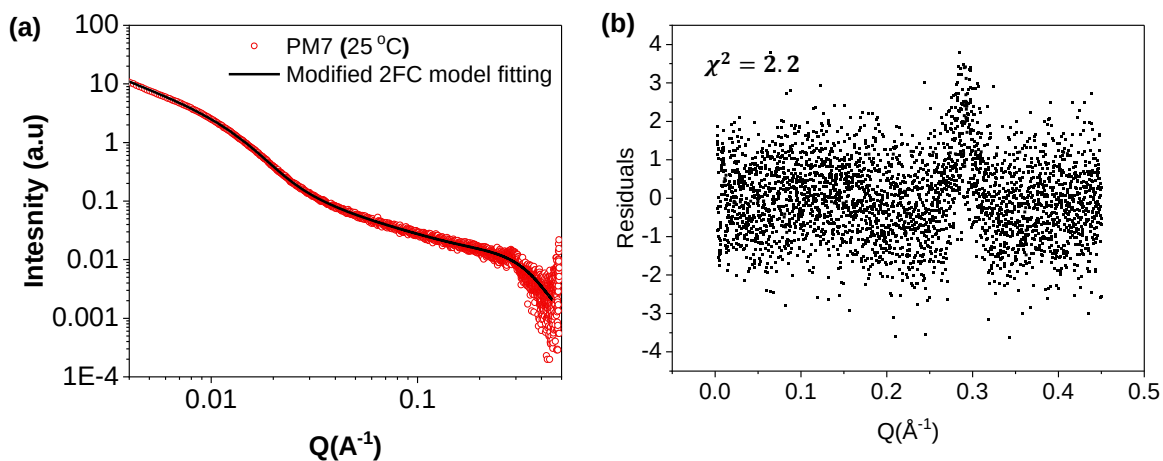
Sample	Background (Voigt function 1)			Coherence feature (Voigt function 2)		
	Peak center (cycles/Å)	Gaussian FWHM (cycles/Å)	Lorentzian FWHM (cycles/Å)	Peak center (cycles/Å)	Gaussian FWHM (cycles/Å)	Lorentzian FWHM (cycles/Å)
PM7	-0.205 ± 0.003	0.163 ± 0.003	0.0079 ± 0.0001	0.218 ± 0.001	0.122 ± 0.001	N/A*
PM7 D1	-0.132 ± 0.001	0.127 ± 0.001	0.016 ± 0.001	0.210 ± 0.001	N/A*	0.13 ± 0.003
PM7 D2	-0.104 ± 0.001	0.098 ± 0.001	0.0169 ± 0.0001	0.200 ± 0.001	0.123 ± 0.001	N/A*

*Fitting values were extremely low, indicating that the coherence feature is entirely Gaussian/Lorentzian.

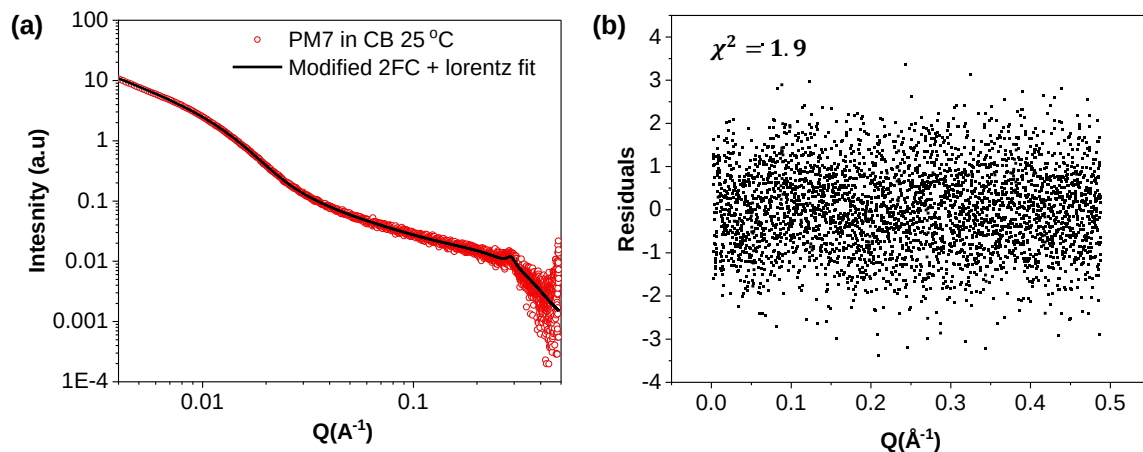
Details of SAXS fitting results



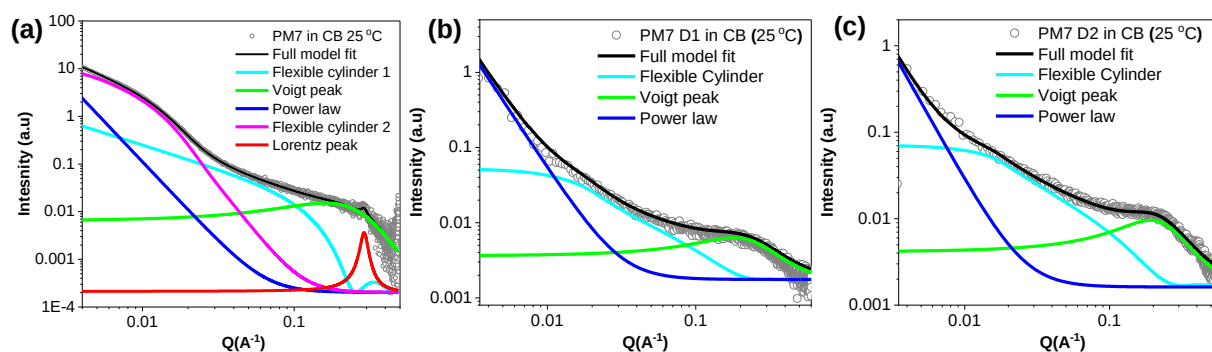
Supplementary Figure 2.6. (a) Model fitting results for PM7 solution using 2 FC model. (b) The residuals and chi squared values demonstrating the goodness of fit when using the 2FC model.



Supplementary Figure 2.7. (a) Model fitting results for PM7 solution using the modified 2FC model. (b) The residuals and chi squared values demonstrating the goodness of fit when using the modified 2FC model.



Supplementary Figure 2.8. (a) Model fitting results for PM7 solution using the modified 2FC model combined with Lorentz peak function. (b) The residuals and chi squared values demonstrating the goodness of fit when using the modified 2FC model with Lorentzian function.



Supplementary Figure 2.9. Deconvolution of the model fits for (a) PM7, (b) PM7 D1, and (c) PM7 D2 neat polymer solutions (CB) with 20 mg/mL concentration.

Supplementary Table 2.3. Full parameter list obtained from model fitting shown in Supplementary Figure 2.9 as well as model fitting results for PM7 solution at 65 °C (description of the parameters is provided below).

Parameters	PM7 25 °C	PM7 D1 25 °C	PM7 D2 25 °C	PM7 65 °C
L_1 (nm)	100*	30.3 ± 13.7	28.4 ± 3.9	26.0 ± 3.8
l_p (nm)	$\gg R_p$	7.9 ± 3.0	10.3 ± 3.5	$\gg R_p$
R_p (nm)	1.5 [#]	1.5 ± 0.6	1.4 ± 0.3	1.5 [#]
q_c (Å ⁻¹)	0.160 ± 0.003	0.18 ± 0.03	0.18 ± 0.02	0.130 ± 0.005
w (Å ⁻¹)	0.28 ± 0.01	0.31 ± 0.02	0.28 ± 0.01	0.270 ± 0.009
μ	0.6 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
k	-3.1 ± 0.2	-3.1 ± 0.4	-2.6 ± 0.5	2.4 ± 0.1
L_2 (nm)	100*	-	-	-
L_p (nm)	$\gg R_f$	-	-	-
R_f (nm)	11.5 ± 0.1	-	-	-
σ	0.40 ± 0.03	-	-	-
q_l (Å ⁻¹)	0.29 ± 0.001	-	-	-
w_l (Å ⁻¹)	0.016 ± 0.001	-	-	-

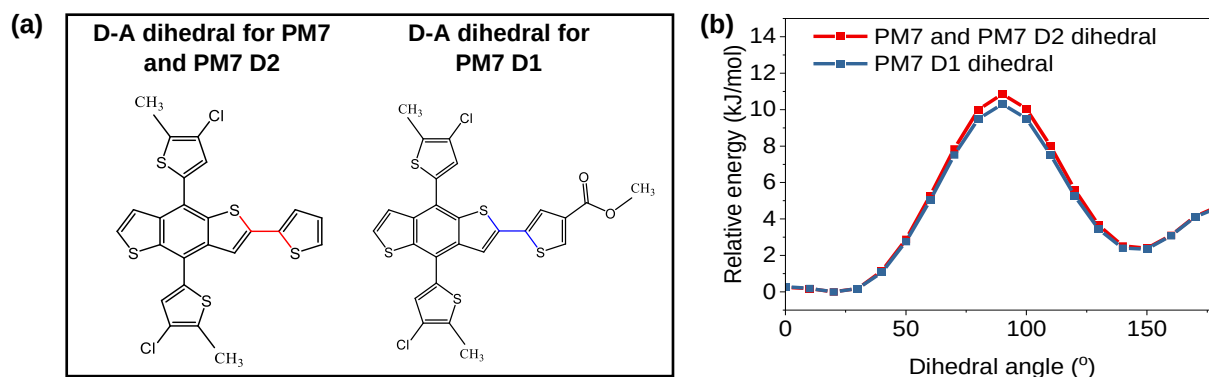
*Values were fixed during fitting due to the absence of Guinier knee.

[#] Value was fixed based on the radius obtained from PM7 D1 due to function overlap from the cross section of flexible cylinder 1 and the Pseudo-Voigt peak.

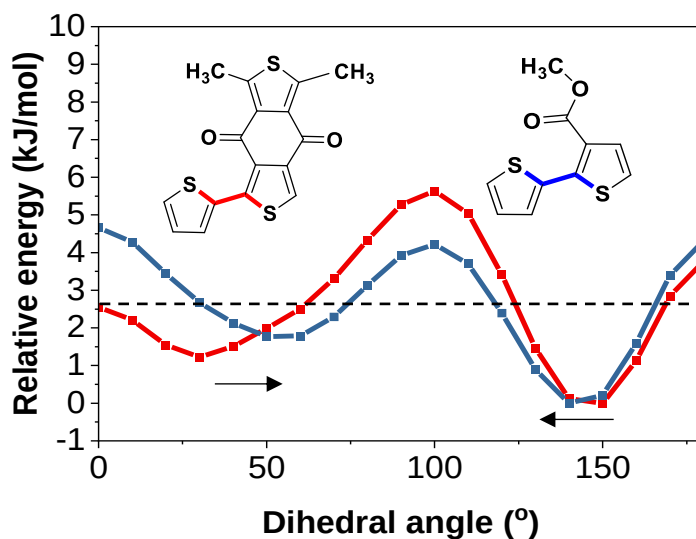
Description of the fitting parameters:

L_1 (nm)	Length of flexible cylinder 1 corresponding to the length of polymer chain segments
l_p (nm)	Persistence length of flexible cylinder 1
R_p (nm)	Radius of flexible cylinder 1 related to polymer chains
q_c (Å ⁻¹)	Pseudo-Voigt peak center
w (Å ⁻¹)	FWHM of the Pseudo-Voigt peak
k	Power law slope
μ	Lorentzian fraction of Pseudo-Voigt peak
L_2 (nm)	Length of flexible cylinder 2 corresponding to fibers
L_p (nm)	Persistence length of flexible cylinder 2
R_f (nm)	Radius of flexible cylinder 2 related to fibers
σ	Polydispersity of the flexible cylinder 2 radius
q_l	Lorentzian peak center
w_l	FWHM of the Lorentzian peak

Supporting information for the DFT calculation results

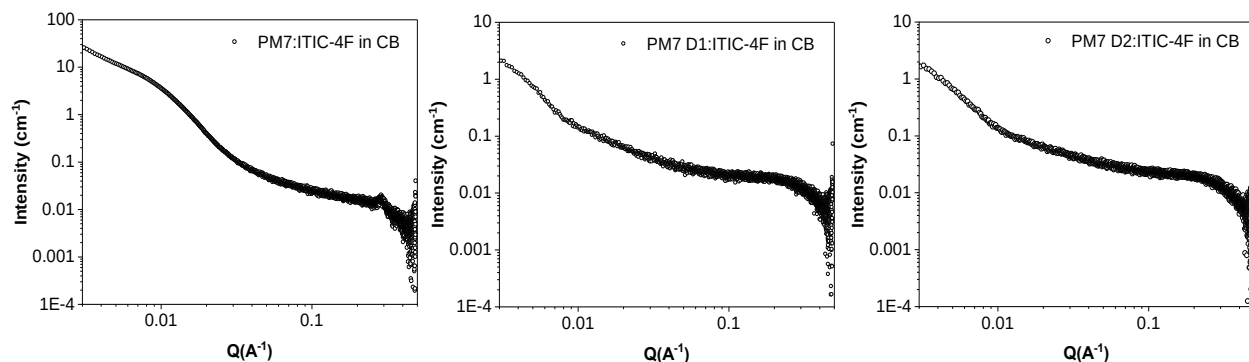


Supplementary Figure 2.10. Potential energy scan of dihedral angles between the donor-acceptor (D-A) moieties. (a) Molecular structures of the fragments used for dihedral energy scan. Note that PM7 and PM7 D2 have the same D-A fragments. Dihedral angles used for the calculation are colored in red and blue. All long alkyl sidechains were replaced with methyl group as shown. (b) Potential energy scan of comparison of the dihedral angle between the D-A moieties shown in (a).

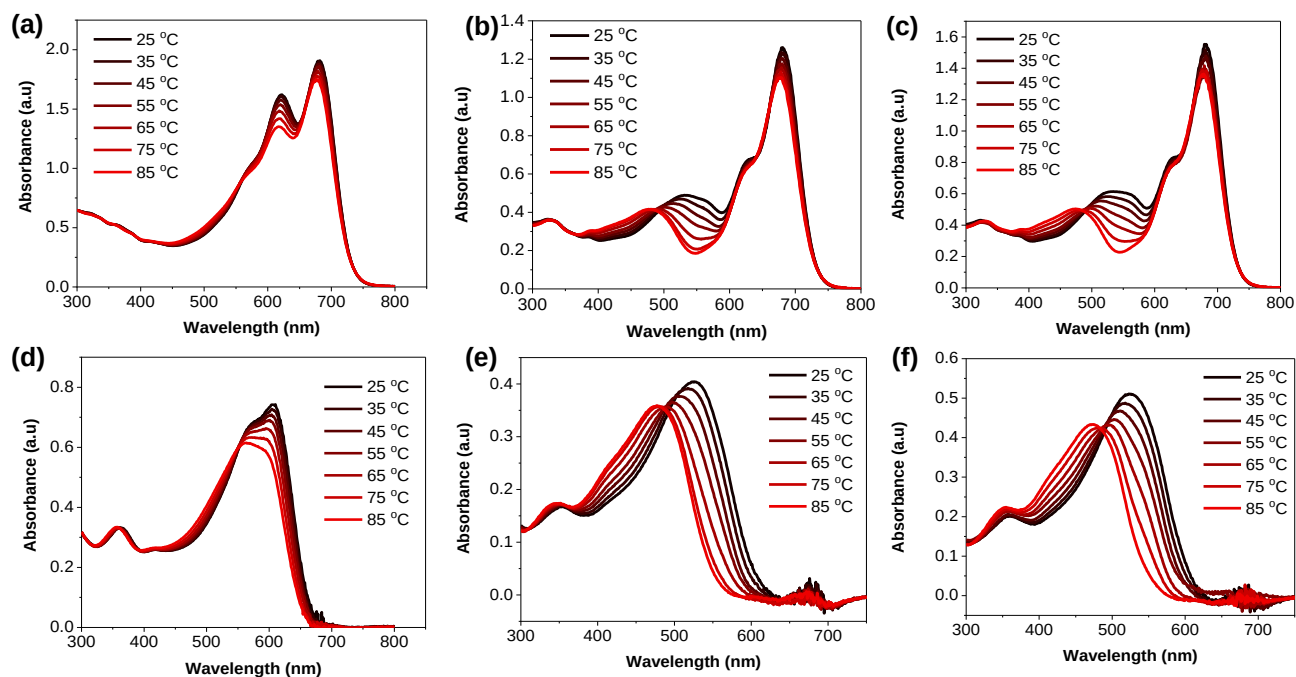


Supplementary Figure 2.11. Potential energy scans of dihedral angle between thiophene and BDD group of PM7 (red) and dihedral angle between thiophene and ester-thiophene group (carbonyl facing the thiophene configuration) of PM7 D1 and D2 (blue). The potential energy scan of the dihedral angle between thiophene and ester-thiophene has larger minimum-energy dihedral angles as indicated by the arrows, higher energy barriers to planarize, and lower energy barrier to switch from anti to syn conformation as compared to the potential energy scan corresponding to PM7.

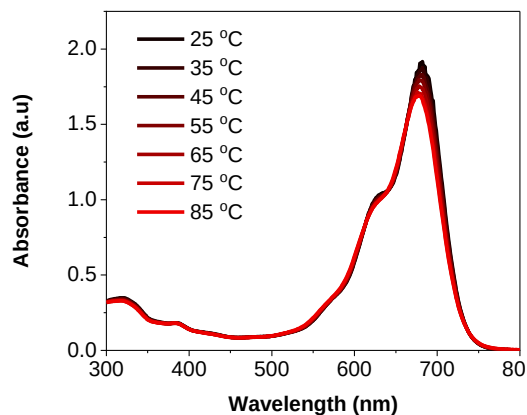
Blend solution-state characterization results



Supplementary Figure 2.12. SAXS profiles of the blend solutions with the same concentration as the coating solution (20 mg/mL of donor and acceptor materials, respectively): (a) PM7:ITIC-4F, (b) PM7 D1:ITIC-4F, and (c) PM7 D2:ITIC-4F in CB solvent.

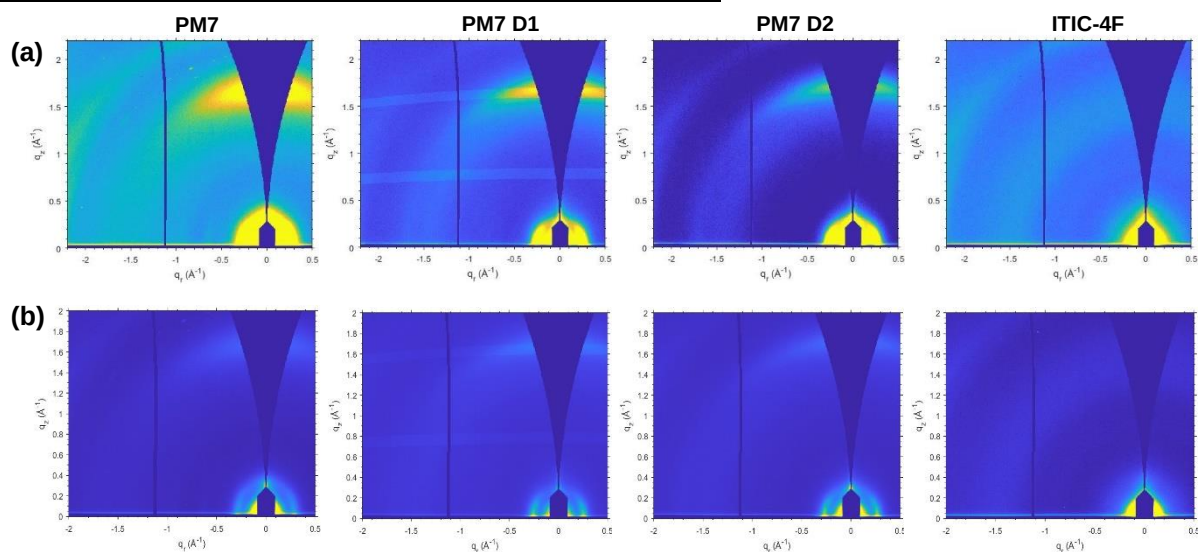


Supplementary Figure 2.13. Temperature-dependent UV-Vis spectra of 20 mg/mL blend solutions of (a) PM7:ITIC-4F, (b) PM7 D1:ITIC-4F, and (c) PM7 D2:ITIC-4F in CB. Temperature dependent UV-Vis spectra of donor polymers in the blend solution (d) PM7, (e) PM7 D1, and (f) PM7 D2 after subtracting the UV-Vis spectra of ITIC-4F.

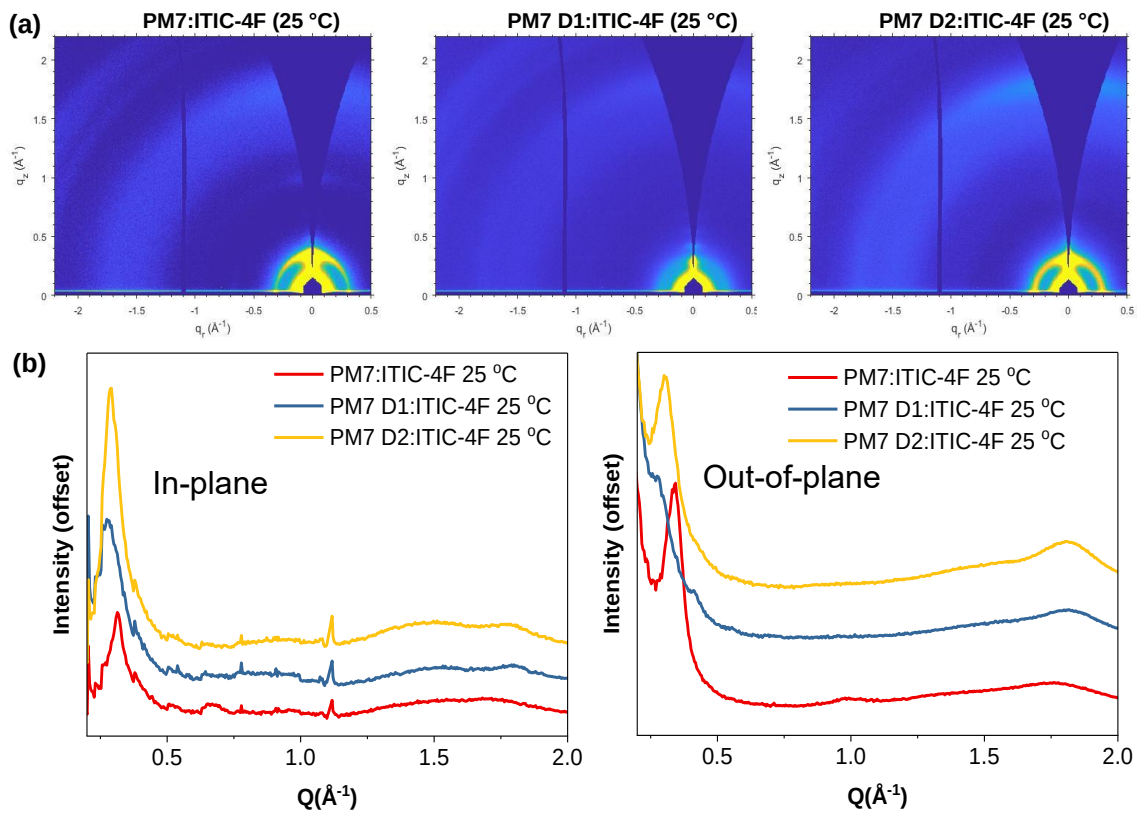


Supplementary Figure 2.14. Temperature-dependent UV-Vis spectra of 20 mg/mL ITIC-4F acceptor solution in chlorobenzene.

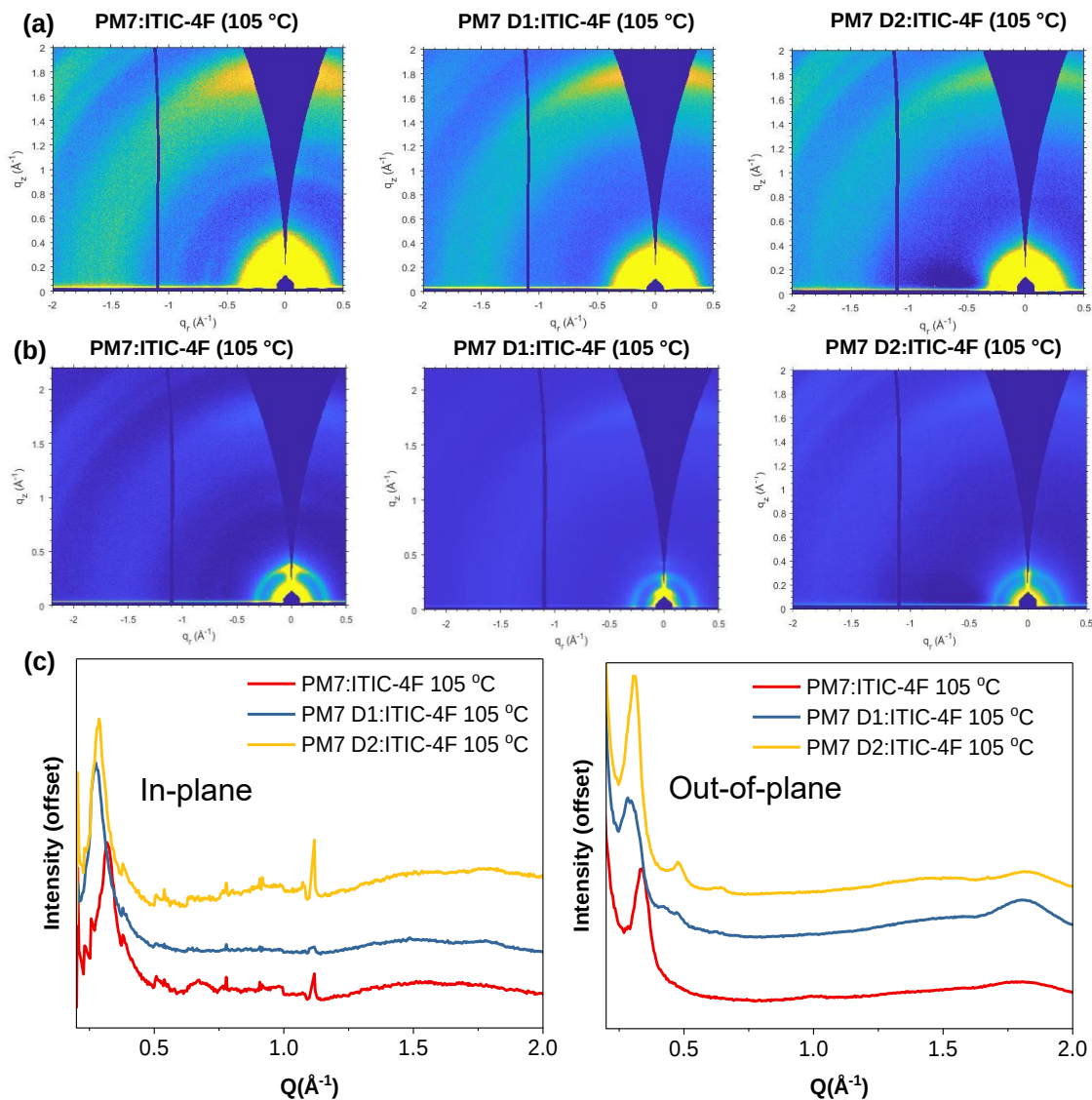
Supporting information for GIWAXS measurements



Supplementary Figure 2.15. (a) GIWAXS profiles of neat polymer and acceptor films printed at 105 °C and 5 mm/s printing conditions. The scattering pattern of ITIC-4F acceptor is mainly featureless with an amorphous ring around 1.5 Å. (b) Color-adjusted GIWAXS patterns of (a) to show the lamellar stacking peaks (100).



Supplementary Figure 2.16. (a) 2D GIWAXS patterns of the blend films printed at 25 °C and 5 mm/s printing speed. The color scales were adjusted to show the lamellar stacking peaks (100) and (010) and (b) their corresponding in-plane and out-of-plane linecut profiles.

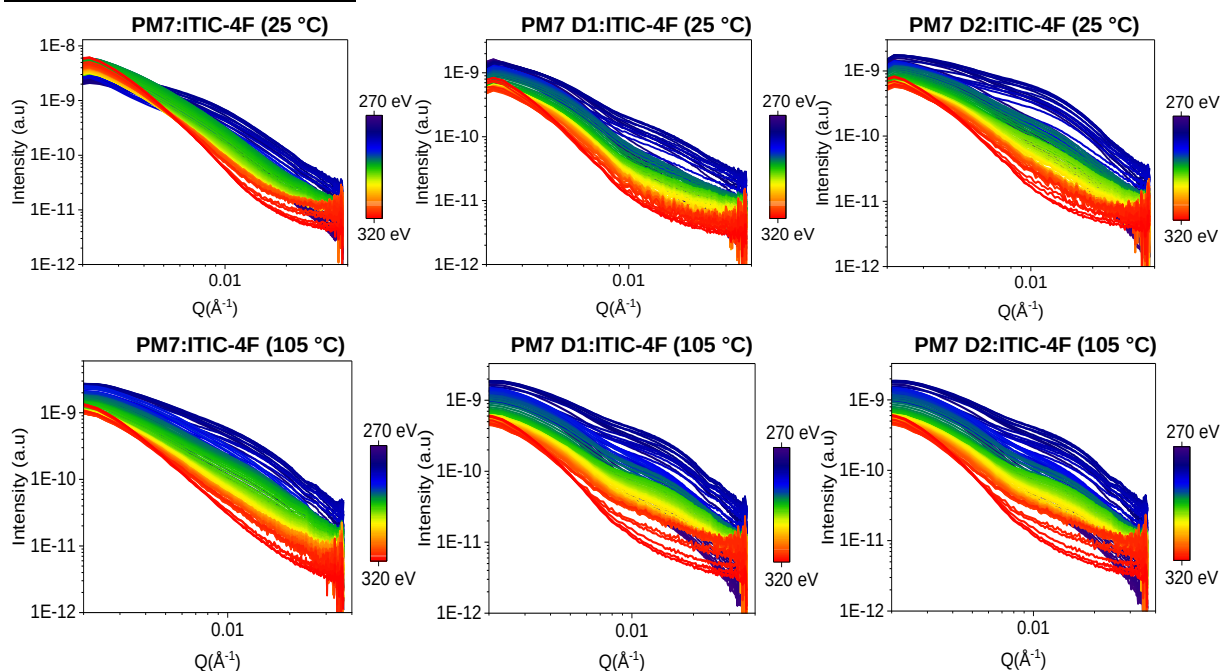


Supplementary Figure 2.17. (a) 2D GIWAXS patterns of blend films processed at the optimized conditions at 105 °C, (b) color scale adjusted 2D GIWAXS patterns of blend films printed at 105 °C to show the lamellar stacking peaks, and (c) their corresponding in-plane and out-of-plane linecut profiles.

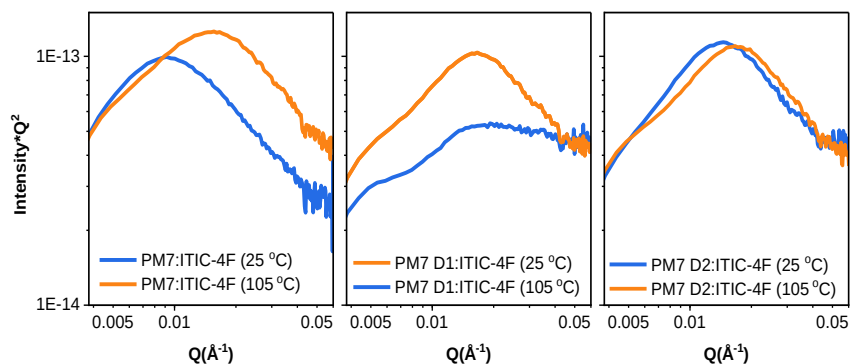
Supplementary Figure 2.4. Peak locations and FWHM of (010) and (100) peaks determined from the linecut profiles.

Samples	(100) location ($\text{\AA}^{-1}$)	(100) FWHM ($\text{\AA}^{-1}$)	(010) location ($\text{\AA}^{-1}$) ₁₎	(010) FWHM ($\text{\AA}^{-1}$)
PM7:ITIC-4F 25 °C	0.319	0.094 ± 0.004	1.78	0.313 ± 0.005
PM7 D1:ITIC-4F 25 °C	0.280	0.118 ± 0.013	1.84	0.235 ± 0.004
PM7 D2:ITIC-4F 25 °C	0.290	0.093 ± 0.005	1.83	0.221 ± 0.003
PM7:ITIC-4F 105 °C	0.320	0.110 ± 0.012	1.83	0.297 ± 0.004
PM7 D1:ITIC-4F 105 °C	0.276	0.088 ± 0.014	1.84	0.216 ± 0.004
PM7 D2:ITIC-4F 105 °C	0.287	0.100 ± 0.004	1.82	0.222 ± 0.004

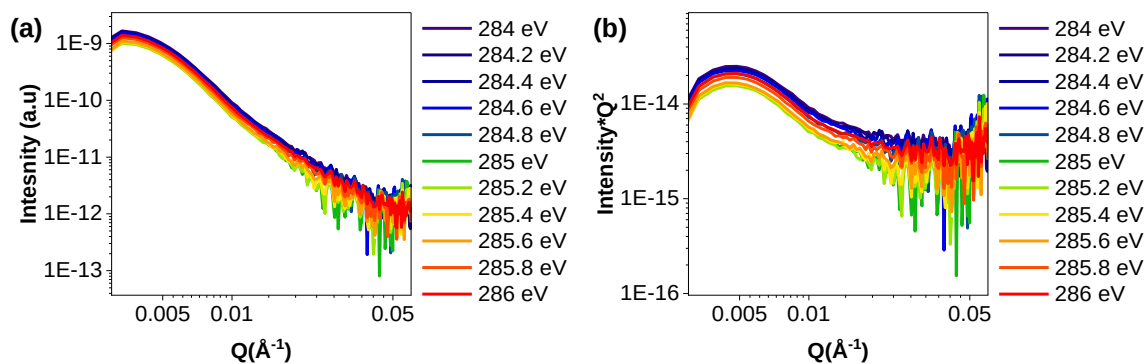
Details of RSoXS analysis



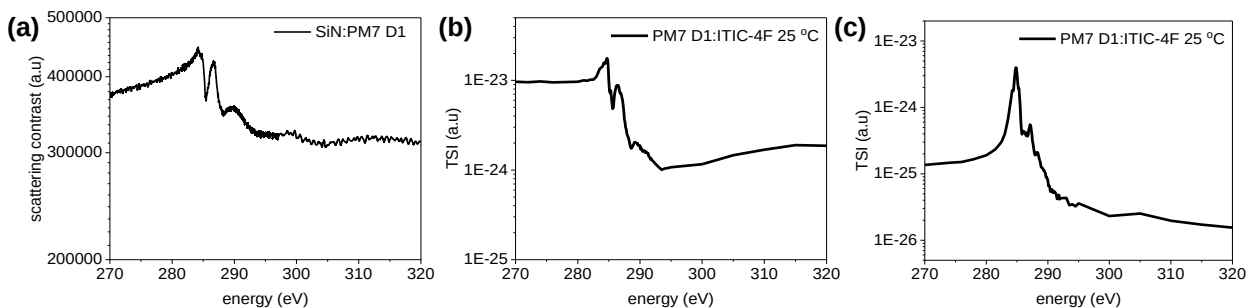
Supplementary Figure 2.18. RSoXS intensity versus Q profiles of polymer blend films at both 25 °C (top) and 105 °C (bottom) conditions at varying X-ray energies. The scattering features are maximized at the X-ray energy of 284.8 eV which was therefore used for further RSoXS analysis.



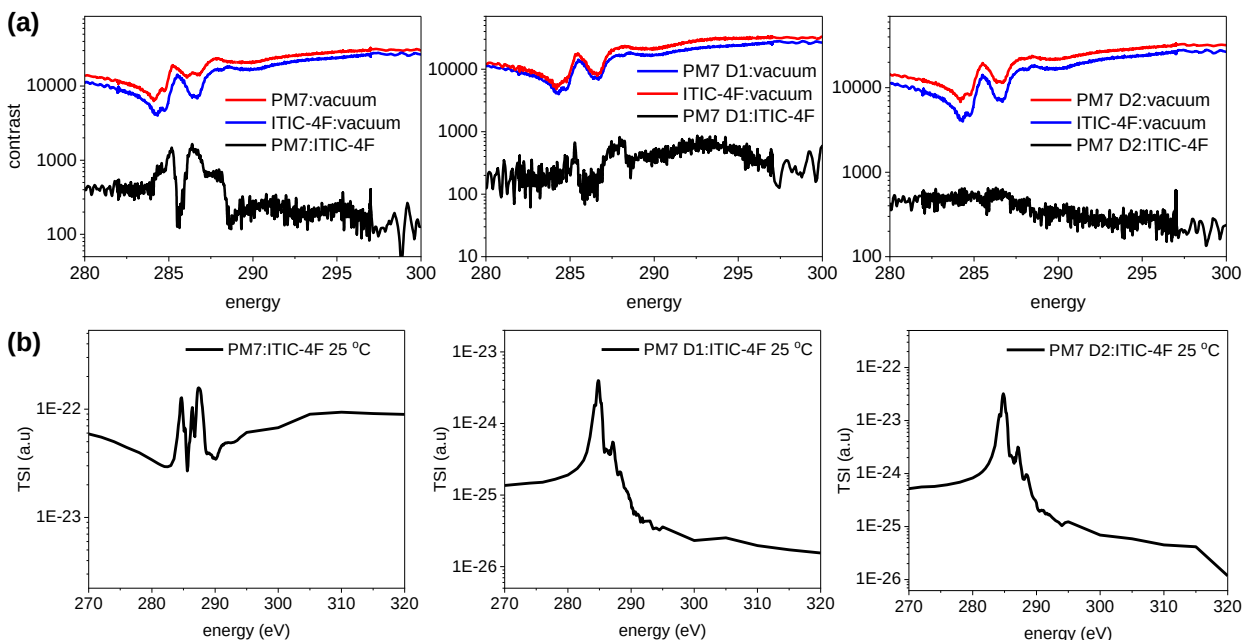
Supplementary Figure 2.19. Kratky plots ($\text{Intensity} \cdot Q^2$ versus Q) of the blend films where PM7 D1 and D2 exhibit a shoulder peak at low Q region ($\approx 0.005 \text{ \AA}^{-1}$).



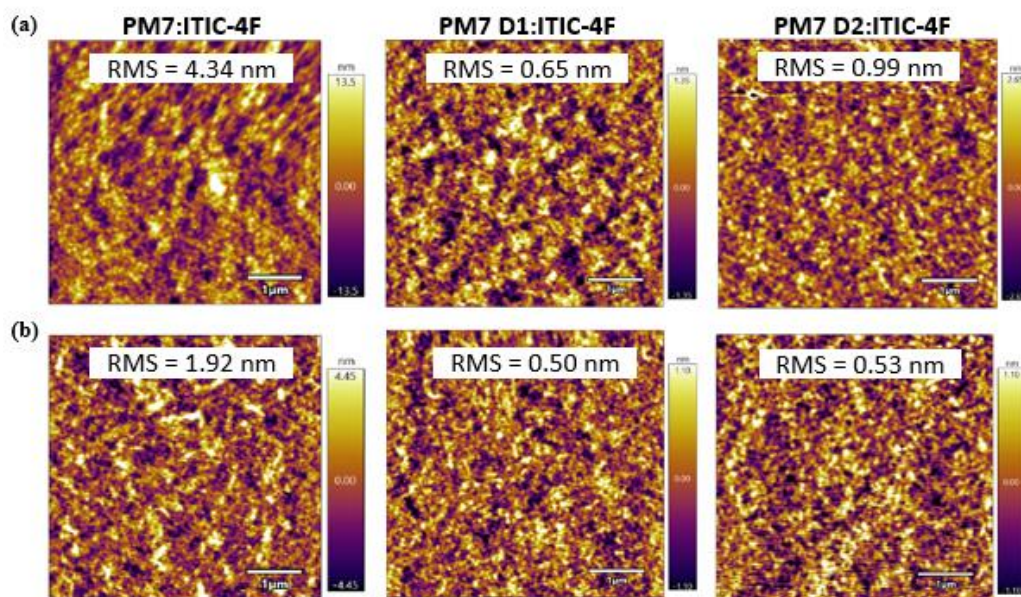
Supplementary Figure 2.20. (a) Blank SiN scattering at various X-ray energies. (b) Kratky plots of the blank SiN scattering at various X-ray energies indicate a peak around $\sim 0.005 \text{ \AA}^{-1}$.



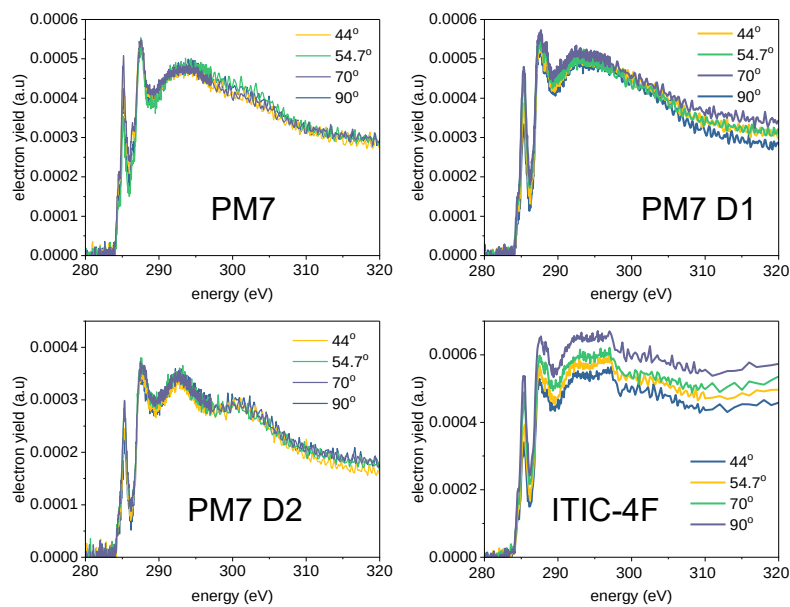
Supplementary Figure 2.21. (a) Binary contrast function of SiN:PM7 D1; (b) TSI versus energy plot of the low Q region (0.002 to $\sim 0.006 \text{ \AA}^{-1}$); (c) TSI versus energy plot of the higher Q region (~ 0.006 to $0.04 \text{ \AA}^{-1}$).



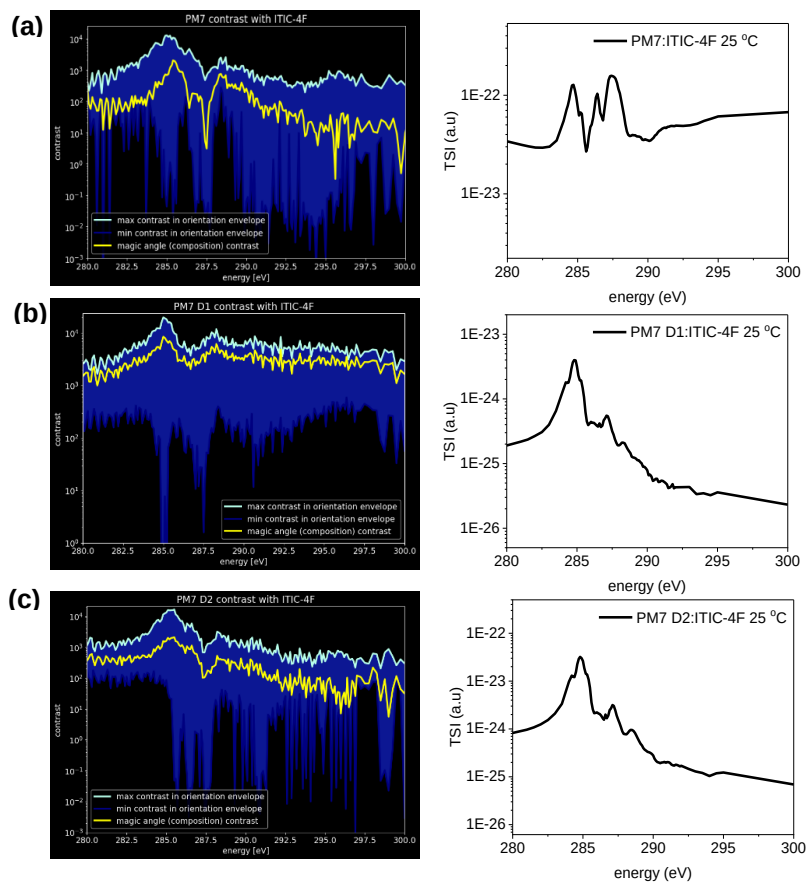
Supplementary Figure 2.22. (a) Comparison of vacuum and material contrasts of the donor and acceptor materials; (b) TSI versus energy plots of the blend films coated at 25 °C (higher Q regions were used for PM7 D1 and D2 to estimate the TSI to avoid contribution from SiN-polymer scattering).



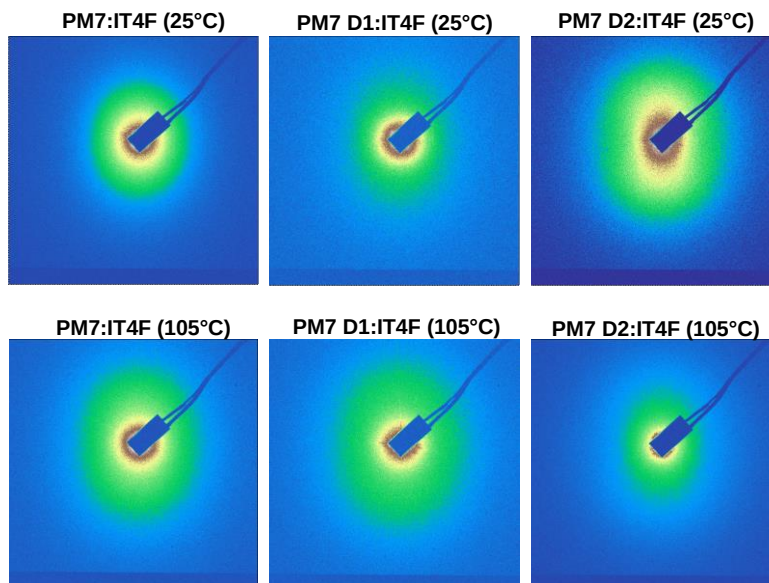
Supplementary Figure 2.23. AFM images and their corresponding root-mean-square (RMS) roughness values for the blend films coated at (a) room temperature and (b) 105 °C temperature.



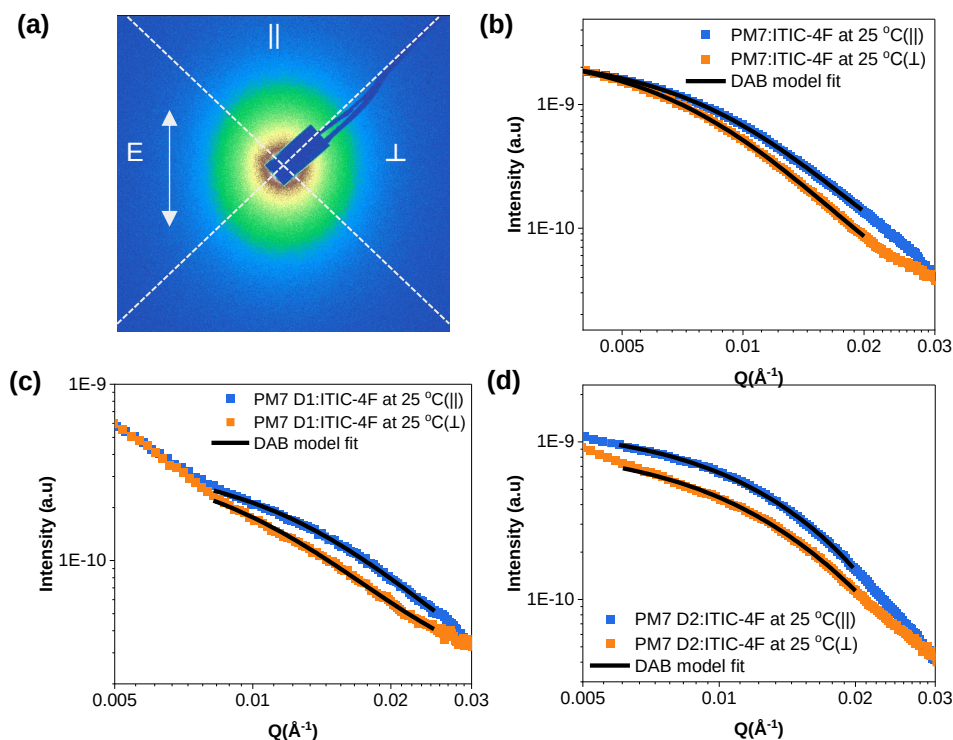
Supplementary Figure 2.24. Angular NEXAFS TEY measurements of neat films obtained by varying the incident angle from 44° to 90° (without post-edge normalization).



Supplementary Figure 2.25. Comparison between the combinatorial contrast function and the TSI versus energy curves for (a) PM7:ITIC-4F, (b) PM7 D1:ITIC-4F, and (c) PM7 D2:ITIC-4F.



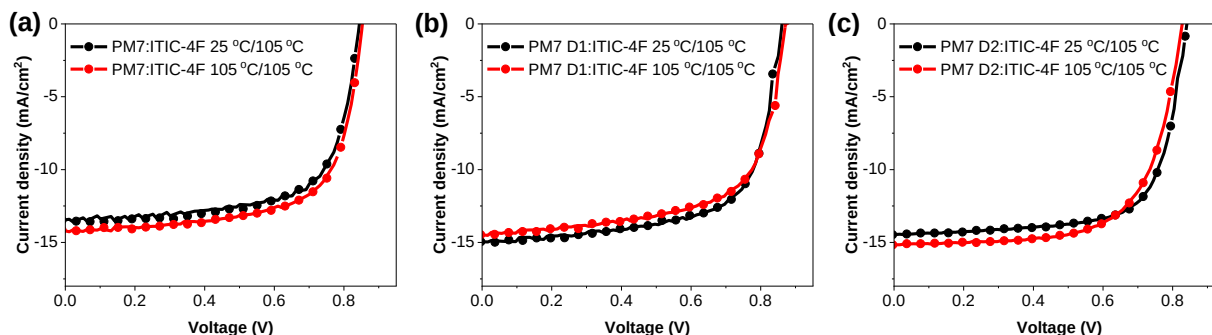
Supplementary Figure 2.26. Raw RSoXS patterns of the blend films processed at 25 °C (top) and 105 °C (bottom), all exhibiting an anisotropic pattern obtained at the X-ray energy of 284.8 eV.



Supplementary Figure 2.27. (a) Representation of the sector cut parallel (||) and perpendicular (⊥) to the electric field direction. Parallel and perpendicular sector cut averaged data and their DAB model fits with flat background for (b) PM7:ITIC-4F at 25 °C, (c) PM7 D1:ITIC-4F at 25 °C, and (d) PM7 D2:ITIC-4F at 25 °C.

Supplementary Table 2.5. DAB model fitting parameters.

Samples	Correlation length
PM7:ITIC-4F at 25 °C ($\perp$)	115.7 ± 0.6
PM7:ITIC-4F at 25 °C ($\parallel$)	97.4 ± 0.7
PM7 D1:ITIC-4F at 25 °C ($\perp$)	74.3 ± 0.5
PM7 D1:ITIC-4F at 25 °C ($\parallel$)	60.6 ± 1.2
PM7 D2:ITIC-4F at 25 °C ($\perp$)	65.6 ± 0.7
PM7 D2:ITIC-4F at 25 °C ($\parallel$)	60.8 ± 0.9

Device performance results for solution temperature variation**Supplementary Figure 2.28.** Device characterization results: Current-voltage (J - V) curves of (a) PM7:ITIC-4F, (b) PM7 D1:ITIC-4F, and (c) PM7 D2:ITIC-4F devices fabricated from two different solution temperatures (25 °C and 105 °C) at the same substrate temperature of 105 °C.**Supplementary Table 2.6.** Device performance comparison of polymer blend films.

	PCE (%)	FF (%)	Jsc (mA/cm ²)	Voc (V)
PM7:ITIC-4F 25 °C/105 °C	7.9 ± 0.5	69 ± 0.3	13.6 ± 0.9	0.85 ± 0.01
PM7:ITIC-4F 105 °C/105 °C	8.1 ± 0.3	67 ± 1.8	14.1 ± 0.2	0.85 ± 0.01
PM7 D1:ITIC-4F 25 °C/105 °C	8.6 ± 0.2	68 ± 1.0	14.6 ± 0.3	0.86 ± 0.01
PM7 D1:ITIC-4F 105 °C/105 °C	8.0 ± 0.3	64 ± 2.0	14.6 ± 0.1	0.87 ± 0.01
PM7 D2:ITIC-4F 25 °C/105 °C	8.6 ± 0.1	71 ± 0.7	14.4 ± 0.2	0.84 ± 0.01
PM7 D2:ITIC-4F 105 °C/105 °C	8.4 ± 0.3	67 ± 2.2	15.1 ± 0.5	0.83 ± 0.01

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Chapter 3

Tuning the solution aggregate structure of PM7 based conjugated polymer to enable green solvent processing of organic solar cells³

3.1 Introduction

Owing to the development of non-fullerene-based molecular acceptors, the efficiency of OSCs has rapidly progressed over the past decade, triggering a renaissance in the field. Remarkably, power conversion efficiencies (PCEs) have now surpassed 19% in single junction cells,^{1–5} enabling opportunities for successful commercialization of organic solar cells (OSCs). Despite these advances, processing of these highly efficient OSCs often involves toxic halogenated solvents, which poses serious health and environmental risks.^{6,7} Therefore, using less toxic non-halogenated, or green solvents, is crucial for eco-friendly processing of OSCs, particularly for large-scale manufacturing. Green solvent processed OSCs, however, often underperform devices processed from halogenated solvents due to the limited solubility of donor-acceptor based conjugated polymers in most non-halogenated solvents, yielding undesirable film morphologies. To overcome this challenge, molecular engineering approaches have been utilized to increase the solubility of conjugated polymers to improve the processability of OSCs in green solvents.⁸ These approaches mainly involve increasing the side chain length of the conjugated polymer to improve solubility, functionalizing the side chains or the backbone to decrease the backbone rigidity to reduce intermolecular interactions.^{6,9} While molecular design approaches have significantly contributed to improving the solubility of conjugated polymers in green solvents, enhancing the

³ The contents of this section appear in **Khasbaatar, A.**; Jones, A. L.; Fernando P. S.; Sai, H.; Zhu, C.; Gann, E.; Reynolds, J. R.; Diao, Y., “Tuning the Solution Aggregate Structure of a PM7-Based Conjugated Polymer to Enable Green Solvent Processing of Organic Solar Cells”, *Chemistry of Materials* 2024, 36, 6, 2819-2834.

solubility via molecular design alone has not been sufficient to close the performance gap, suggesting further morphology improvements needed for green solvent processed OSCs.

Conjugated polymers typically undergo self-assembly processes in solution via π - π stacking and side chain interactions, leading to polymer aggregates that substantially impact the solid state morphology.^{10–13} Numerous studies have shown that solution-state aggregation of conjugated polymers enhance alignment,^{14,15} crystallinity,^{16–18} and out-of-plane molecular orientation.^{19,20} Aggregation of conjugated donor polymers in solution has also been found to be advantageous for OSCs as it prevents large-scale phase segregation caused by liquid-liquid demixing in both fullerene and other molecular acceptor (MA) based systems.^{21–23} Notably, Wang and Bredas *et al.* proposed that the extent of aggregation of conjugated polymers, determined by the Flory-Huggins interaction parameter, has a strong correlation with film morphology, particularly domains sizes and crystal coherence lengths.²⁴ Besides the extent of aggregation of conjugated polymers, the structure of polymer aggregates in solution, plays an important role on the morphology and device performance of OSCs. Our previous work revealed that amorphous network aggregates are beneficial for the morphology of MA based OSCs, leading to small domains with predominantly face-on molecular orientation.²⁵

When transitioning from halogenated to non-halogenated solvents, change in the solution-state aggregation behavior is inevitable as non-halogenated solvents are often poor solvents for conjugated polymers. Therefore, understanding how solvent environment influences the aggregation and assembly behavior of conjugated polymers is crucial for enhancing the active layer morphology of green solvent processed OSCs. Previous studies have shown that the nature and extent of solution-state aggregation of conjugated polymers is highly dependent on the quality of solvents towards conjugated polymers.²⁶ For instance, using small angle X-ray scattering

(SAXS), Nahid and McNeill *et al.* have shown that solution-state aggregation of P(NDI2OD-T2) polymer (repeat unit structure shown in **Supplementary Figure 3.1a**) changes from coil-like polymer chains in good solvents to elongated rigid-like aggregates in poor solvents, which enhanced molecular ordering in thin films and maximized the device performance of organic field effect transistor (OFET) devices.²⁶ Similarly, using SAXS and freeze-dried imaging, Zheng and Pei *et al.* found that BDOPV-based conjugated polymer (repeat unit structure shown in **Supplementary Figure 3.1b**) can form either 1D rod-like structure in a good solvent or 2D lamellar aggregates in a poor solvent, which are then directly inherited to the solid state, improving the charge mobility from 1.8 to 3.2 cm² V⁻¹ s⁻¹ in OFETs.²⁷ Besides influencing the initial solution aggregate structures, solvents can also tune the assembly pathways of conjugated polymers during solution processing.^{28,29} Our group has previously reported that tuning the solvent selectivity towards conjugated backbone versus side chains of PII-2T polymer led to three distinct assembly pathways, which are direct crystallization, liquid crystal (LC) mediated crystallization, and random agglomeration during solution processing.²⁹ When using a backbone selective solvent 1-chloronaphthalene, direct crystallization of the conjugated polymer led to the highest degree of film alignment, and thus a 20-fold increase in the charge mobility compared to LC mediated crystallization and random agglomeration pathways. Although solvents can drastically influence solution-state aggregation and assembly pathways of conjugated polymers from solution to solid state, their implications on BHJ based OSCs are rarely investigated, particularly for green solvent processed OSCs. Therefore, the purpose of this study is to examine the polymer aggregate structure-assembly-morphology relationship in the context of green solvent processing.

Herein, using a benzodithiophene-based donor polymer (PM7 D2)³⁰ as our model system and a range of halogenated and non-halogenated solvents, we demonstrate how solvent properties,

particularly solvent – backbone and solvent – side chain interactions, impact the polymer solution-state aggregate structures and their crystallization behavior. The donor polymer PM7 D2 is chosen in this study due to its good solubility in a wide range of halogenated and non-halogenated solvents compared to its counterpart, PM7, which strongly aggregates even in chlorobenzene because of its highly planar backbone.²⁵ Depending on the solvent properties, three distinct aggregate structures of PM7 D2 were obtained: semiflexible amorphous networks in a poor side chain solvent, rigid amorphous networks in mutual solvents, and semicrystalline fiber aggregates in a poor backbone solvent. Upon film deposition, both semiflexible amorphous network and semicrystalline fiber aggregates led to highly crystalline films with large domains, yielding 7.1 % and 5.8 % PCEs in PM7 D2:ITIC-4F based devices, respectively. In contrast, rigid amorphous network aggregates formed in mutual solvents achieved a more balanced crystallization of PM7 D2, resulting in PCEs of 8-9 %, with devices being fully fabricated under ambient conditions. Importantly, we demonstrate that the semicrystalline fiber aggregates formed in the poor backbone solvent anisole, the green solvent studied in this work, undergo an order-to-disorder transition to form rigid amorphous network aggregates at high temperatures. Consequently, processing PM7 D2:ITIC-4F based devices at elevated temperatures when cast from the green solvent substantially enhanced the device performance from 5.8 % to 9.0 %. Our findings thus highlight that forming rigid amorphous network aggregates, compared to crystalline fiber aggregates or semiflexible amorphous network aggregates, is critical to achieving a favorable blend film morphology, thereby enabling green solvent processing of non-fullerene organic solar cells.

3.2 Results and discussion

Materials Systems and Solvent Properties. Figure 3.1a shows the repeat unit structure of the conjugated donor polymer, PM7 D2, used in this study (the synthesis results are tabulated in

Supplementary Table 3.1). First reported by Jones and Reynolds *et al.*,³⁰ PM7 D2 is a derivative of the benzodithiophenedione (BDD)-based PM7 donor polymer featuring an ester-functionalized terthiophene group, which was found to be more soluble than PM7 in chlorobenzene due to its flexible backbone conformation and reduced tendency to form semicrystalline fiber aggregates.²⁵ As a result, OSCs fabricated from this donor polymer have been found to be more resilient to different coating temperatures.³⁰ Compared to PM7, we also found that PM7 D2 is soluble in toluene even at 20 mg/mL, whereas PM7 does not dissolve in the same solvent (**Supplementary Figure 3.2a**). Due to its poor solubility, PM7 based devices exhibit an extremely poor performance of 3.1 % when blade coated from toluene solution (**Supplementary Figure 3.2b**), making it difficult to use for green solvent processing. Other high performing donor polymers, such as D18, are also poorly soluble in toluene due to their highly conjugated backbone.³¹ In contrast, the improved backbone flexibility of PM7 D2 polymer makes it an excellent model system to study the impact of solvent environment on the polymer aggregate structure and morphology. In this study, we thus investigate how varying the solvent-polymer affinity, particularly when transitioning from halogenated to non-halogenated solvents, impacts the solution aggregate structures of PM7 D2. **Figure 3.1b and c** show the molecular structures of the small molecule acceptor, ITIC-4F, and a series of halogenated (1-chloronaphthalene – CN and chlorobenzene – CB) and non-halogenated (toluene – TL and anisole – AN) solvents used in this study, respectively. The color background of **Figure 3.1c** indicates that solvent becomes greener moving from CN to AN. Larsen and Edman *et al.* have recently published an online tool³² that provides a quantitative sustainability score (G) for common solvents in printed electronics using the GlaxoSmithKline (GSK) green solvent selection guide.^{33–35} Based on this guideline, the G index for CB, TL, and AN are found to be 5.4, 6, and 7.4 respectively, suggesting that AN is the greenest solvent amongst

this series of solvents (G index for CN has not been determined but it is reported to be more lethal to health compared to CB).⁶ It is also worth mentioning that AN is a natural product found in plants, *Peristeria Elata* and *Phallus Impudicus* and is even used as a food additive,³⁶ which is another strong indication of its potential as a useful green solvent to process printed electronic devices.

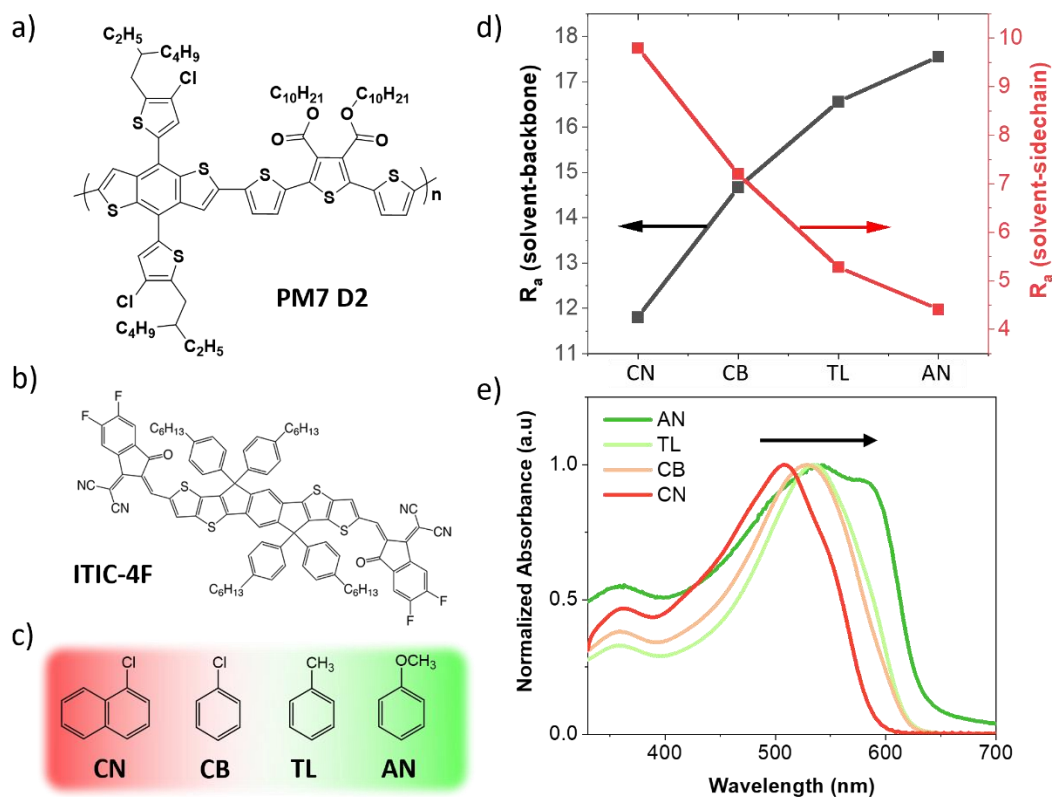


Figure 3.1. Molecular structures of a) PM7 D2, b) ITIC-4F, and c) solvents (CN – 1-chloronaphthalene, CB – chlorobenzene, toluene – TL, anisole – AN) used in this study; d) Hansen solubility distance (R_a) comparison for the conjugated backbone and the side chain of PM7 D2 depending on the solvent; e) UV-Vis spectra of PM7 D2 solutions (20 mg/mL) in these four solvents.

Conjugated polymers are often poorly dissolved in non-chlorinated or green solvents, making it challenging to obtain uniform thin films. Therefore, determining the solvent quality is a crucial step towards morphology control in green solvent processed OSCs. We resort to Hansen solubility parameters for initial estimation of solvent quality, which is based on the “like-dissolves-like” principle and is calculated using a group contribution approach.³⁷ Although it remains in

question whether Hansen solubility theory is applicable to π -conjugated systems featuring extensive electron delocalization, recent work has shown that it correlates well with solubility in common solvents due to the dominating impact of dispersion interactions.³⁸ The Hansen solubility method takes three solubility parameters into consideration: 1) dispersion (δ_D); 2) polar (δ_P); and 3) hydrogen bonding contributions (δ_H). By using these parameters for the polymer (1) and the solvent (2), the solubility distance (R_a), a relative measure of solubility, is then calculated as follows:

$$R_a^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2$$

A low R_a value implies that the polymer has a good solubility, thereby exhibiting strong polymer-solvent interactions. In poor solvents with large R_a value, on the other hand, polymer-polymer interaction is stronger than polymer-solvent interaction, making it easier to form solution-state aggregates.²⁴ Since polymer-polymer interaction involves backbone – backbone, side chain – side chain and side chain – backbone components, it is imperative to compare the quality of solvents for the conjugated backbone and the side chains, respectively. Accordingly, we estimated the solubility distance for the backbone and side chain of PM7 D2 polymer in these halogenated and green solvents using the group contribution method by van Krevelen and Hoftyzer,³⁹ which uses the individual functional groups or structural elements to estimate the solubility parameters. Using the molecular structures of the conjugated backbone and the alkyl side chain (**Supplementary Figure 3.3**), the solubility distance for each solvent was determined as shown in **Figure 3.1d** (details of the solubility parameters are tabulated in **Supplementary Table 3.2**). Due to its fused-ring aromatic core, CN appears to be the best solvent for the conjugated backbone but the poorest solvent for the alkyl-ester side chains. In fact, CN has also been demonstrated to be a poor solvent

for alkyl side chains in other conjugated polymer systems including PII-2T and P(NDI2OD-T2).^{15,29}

Moving towards greener solvents, solvent quality decreases towards the conjugated backbone as evidenced by the increase in the R_a value, which closely aligns with the trend observed in the dispersion contribution (δ_D) among the four solvents (**Supplementary Table 3.2**). The δ_D parameter is strongly correlated with the solvation enthalpy of conjugated polymers based on molecular dynamic simulations.³⁸ The fact that halogenated solvents are generally good solvents for the π -conjugated backbone due to their larger van der Waals coefficient of chlorine atoms compared to carbon atoms³⁸ is also consistent with our findings. This result is further confirmed by the UV-Vis spectroscopy measurements of these polymer solutions as shown in **Figure 3.1e**. The UV-Vis absorption onset of PM7 D2 redshifts from CN to AN, suggesting an increase in the conjugation length or the backbone rigidity due to the decreasing solvent affinity towards the backbone.⁴⁰ We note, however, that red-shift in the UV-Vis spectra can also be related to the solvatochromic effect due to the change in solvent polarity, making it difficult to directly correlate the wavelength shifts to polymer conformation.⁴¹ Besides the red-shift in the absorption onset, a shoulder peak at 585 nm emerges in AN, indicating formation of ordered aggregates.^{42,43} We also observed micron-scale large aggregates in PM7 D2 solution in AN under microscopy (**Supplementary Figure 3.4a**), validating that the shoulder peak in the UV-Vis is due to aggregation. In TL, a weak shoulder peak is also observed in the UV-Vis spectra, implying a small amount of such ordered aggregates. Interestingly, CN solution seems to have a shoulder peak at 545 nm; however, the location of this peak is at a much lower wavelength compared to the aggregate peak, denoting that this peak likely originates from vibronic transitions. The energy

separation between this shoulder peak and the main absorption of CN solution at 510 nm is 0.16 eV, which lies in the range of 0.14 to 0.18 eV for vibronic progressions.^{44,45}

Polymer Solution-State Aggregation. To investigate the solution aggregate structures of PM7 D2 in various solvents, we utilized small angle X-ray scattering (SAXS), which has been widely used to decipher the solution-state aggregate structures of conjugated polymers.^{25,46–48} Shown in **Figure 3.2a** are the 1D scattering profiles as well as their model fits of PM7 D2 in four different solvents. Because of the poor solubility of PM7 D2 in AN, we used a mixture of TL and AN solvent with 25 vol% of TL content (TL+AN), which dissolved the micron-scale aggregates observed in pure AN (**Supplementary Figure 3.4b**). Based on the scattering profiles, it is clearly observed that PM7 D2 in TL+AN contains two Guinier knees around 0.01 and 0.3 Å⁻¹, which can be attributed to the cross sections of fiber aggregates and single polymer chains, respectively.^{25,47} Using the model fitting approach that we previously reported for conjugated polymer solutions containing polymer fibers and single polymer chains,⁴⁷ the diameter of these fiber aggregate is determined to be ≈10 nm (**Supplementary Table 3.3**). Further details of fitting the scattering profiles are provided in **Supplementary Note 1**, which includes deconvolution of the model fits (**Supplementary Figure 3.5**) and the resulting fitting parameters (**Supplementary Table 3.3**). Notably, the scattering profile of PM7 D2 in TL+AN also contains a crystalline lamellar peak at 0.25 Å⁻¹, corresponding to a lamellar stacking distance of $d_{lamellar} = 2.5$ nm. This suggests that the fiber aggregates of PM7 D2 formed in this solvent are semicrystalline.

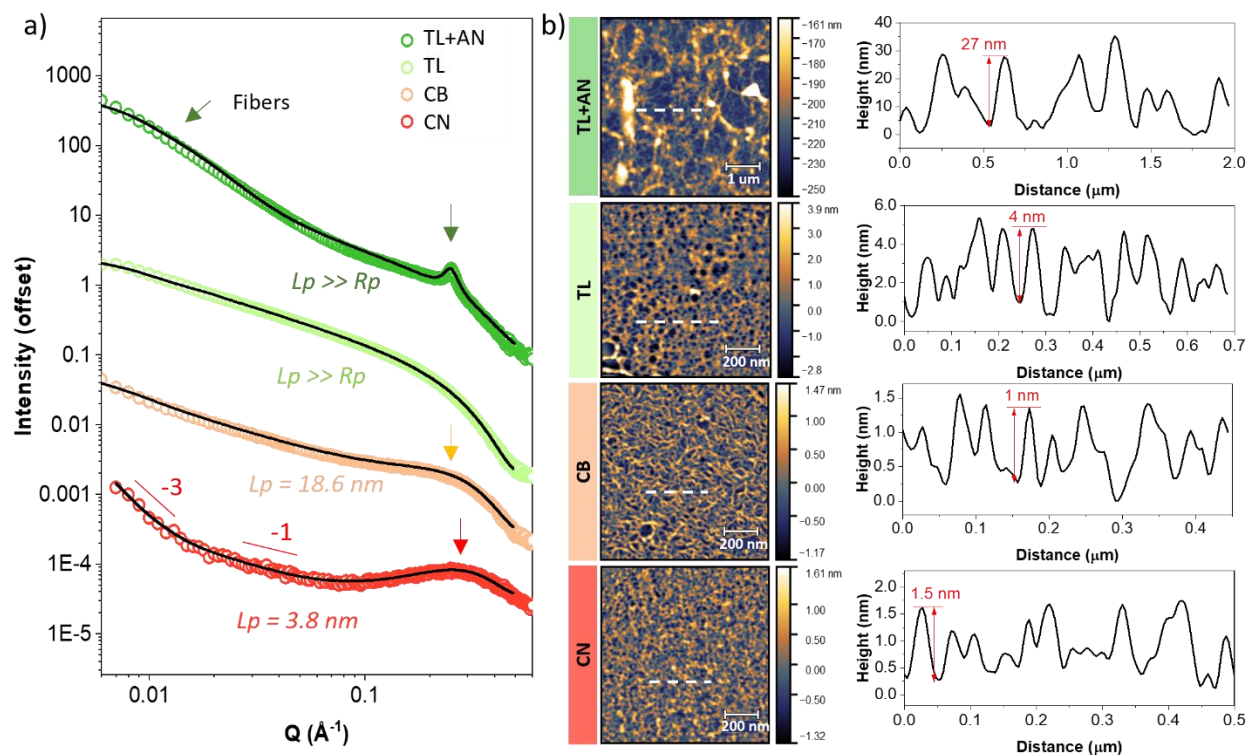


Figure 3.2. a) Solution SAXS profiles for PM7 D2 in CN, CB, TL, and TL+AN solvents at 20 mg/mL concentration; (b) AFM height images of the freeze-dried PM7 D2 solutions in the same four solvents and their corresponding height profiles across the dashed lines. The concentration used for freeze-drying is also 20 mg/mL for all solutions.

In comparison to PM7 D2 in TL+AN, the scattering profiles for PM7 D2 in CN, CB, and TL are rather featureless with no Guinier knee at low Q ($Q < 0.03 \text{ \AA}^{-1}$) or crystalline lamellar peak at high Q range ($Q > 0.1 \text{ \AA}^{-1}$). However, a broad structure factor peak at $0.26 \text{ \AA}^{-1}$ ($d_{\text{lamellar}} = 2.4 \text{ nm}$) is visible in CN but becomes less apparent in CB and disappears entirely in TL. We attribute this broad structure factor peak to disordered or amorphous lamellar interactions based on its proximity to the crystalline lamellar peak observed in TL+AN. The fact that this broad peak is more obvious in CN but less apparent in CB and completely absent in TL is consistent with the fact that CN is a poor side chain solvent and that the solubility towards the side chain progressively increases from CN to CB to TL (**Figure 3.1d**). Besides the broad structure factor peak, the scattering profile for PM7 D2 in CN contains a Porod region with a slope of -3 at low Q , which represents a fractal or

network like structure,^{49,50} confirmed with freeze-dried imaging discussed later. This observation suggests that PM7 D2 forms amorphous network aggregates via side chain associations. At the intermediate region of PM7 D2 in CN, the Porod slope changes from -3 to -1 due to the contribution from rigid polymer chains or chain segments. Compared to PM7 D2 in CN, the scattering profiles of CB and TL are dominated by the Porod region with a slope of -1, indicating that the polymer chains become more rigid. Accordingly, the model fitting results indicate that the persistence length of polymer chains increases from 3.8 nm in CN to 18.7 nm in CB, which is consistent with the decreasing solvent quality towards the conjugated backbone. The persistence lengths of polymer chains in TL and TL+AN cannot be determined accurately due to the slope of -1 being too close to the asymptotic limit for the flexible cylinder model, but they are expected to be highly rigid ($l_p \gg R_p$).⁴⁷

Although polymer chains become rigid when transitioning to non-halogenated solvents, the exact nature of aggregates in CB and TL is difficult to determine from SAXS measurements because the low Q region in our SAXS measurements is limited to $0.006 \text{ \AA}^{-1}$. It is possible that PM7 D2 exists as fully dispersed, non-interacting polymer chains in these solvents. However, we observe a broad scattering feature around $1.5 - 1.7 \text{ \AA}^{-1}$ ($d = 3.8 - 4.2 \text{ \AA}$) from our wide-angle X-ray scattering (WAXS) measurements (**Supplementary Figure 3.6a, b**), indicative of loose packing of alkyl side chains and/or backbone interactions. In a poor side chain solvent CN, this WAXS scattering feature has a d-spacing of $4.2 \text{ \AA}$, consistent with the typical alkyl side chain stacking distance.^{51,52} In contrast, CB and TL solutions have a shorter d-spacing around $3.8 \text{ \AA}$, which is much smaller than the alkyl side chain stacking distance observed even in crystalline octadecyltrichlorosilane (OTS) films ($d = 4.2 \text{ \AA}$).⁵² Furthermore, considering the weak lamellar stacking of PM7 D2 in CB and the absence of lamellar stacking in TL, the broad peak near $1.65 \text{ \AA}$

in the WAXS measurements of CB and TL solutions is attributed to interactions between polymer backbones rather than alkyl side chains. Furthermore, for PM7 D2 in TL+AN, we observe an additional π - π stacking peak at $d_{\pi-\pi} = 3.6 \text{ \AA}$ (**Supplementary Figure 3.6a**), which is close to the crystalline π - π stacking in most conjugated polymer films. Our X-ray scattering measurements thus suggest that PM7 D2 in TL+AN forms semicrystalline fiber aggregates through crystalline lamellar and π - π stacking, whereas CN forms semiflexible amorphous network aggregates via side chain associations. Mutual solvents including CB and TL, on the other hand, lead to rigid amorphous network aggregates via polymer backbone interactions.

To complement our SAXS results, we further conducted atomic force microscopy (AFM) imaging on the freeze-dried solutions as shown in **Figure 3.2b**. Freeze-drying is an effective technique to preserve the solution-state aggregates by rapidly quenching the solutions using cryogenics (i.e. liquid ethane), which has been applied to deciphering the solution aggregate structures of conjugated polymers in previous studies.^{25,47,53,54} Based on AFM imaging on the freeze-dried samples, fibers aggregates with thickness of around 20-30 nm were observed in TL+AN as shown **Figure 3.2b**. This result is larger than the diameter of 10 nm obtained from SAXS fitting, which could be due to the polydispersity of these polymer fibers and the instrument limitation of SAXS. Compared to TL+AN, no large-scale aggregates are observed in all other solutions; instead, small polymer network-like aggregates can be seen in AFM height imaging. These networks are likely comprised of single polymer chains since the height profiles indicate thicknesses less than 5 nm. For CB and CN, the thickness of the network aggregates is only 1-1.5 nm, clearly suggesting that the network aggregates are comprised of single polymer chains. For TL, the thickness of these aggregates is around 4 nm, somewhat larger than those of CB and CN, which could be correlated with more extended/solubilized side chains and/or absence of side chain

associations for holding together a tight network of polymer chains. To the polymer chains being overlapped during the freeze-drying process. In contrast, the network aggregates of CN are more compact likely due to the strong side chain associations, which agrees with the more intense lamellar peak observed in the scattering profile.

We have previously demonstrated that the donor polymer, PM7, forms semicrystalline fiber aggregates that are sensitive to solution temperature.²⁵ Notably, the fiber aggregates of PM7 D2 formed in TL+AN also depend strongly on temperature as evidenced by our temperature-dependent SAXS (**Figure 3.3**). With increasing solution temperature, the Guinier region corresponding to the fiber aggregates and the crystalline lamellar stacking peaks completely disappear, suggesting dissolution of these aggregates. As the fiber aggregates dissolve at high temperatures, the crystalline π - π stacking peak also disappears based on our temperature dependent WAXS measurements (**Supplementary Figure 3.6c**). Nevertheless, the broad scattering feature at $d = 3.8 \text{ \AA}$, corresponding to amorphous backbone interactions between polymer chains remains at high temperatures. This observation suggests that the TL+AN sample at high temperatures is composed of rigid amorphous network aggregates, resembling those found in PM7 D2 in TL and CB. It is interesting to note that compared to previous studies where temperature-dependent aggregation has been correlated to molecular design,^{55,56} our findings reveal that temperature-dependent aggregation is a more general behavior that is dependent on polymer-solvent interactions. Compared to TL+AN, all other solutions are less dependent on the solution temperature, only leading to a decrease in the scattering intensity, which is consistent with the absence of semicrystalline fiber aggregates in these solutions.

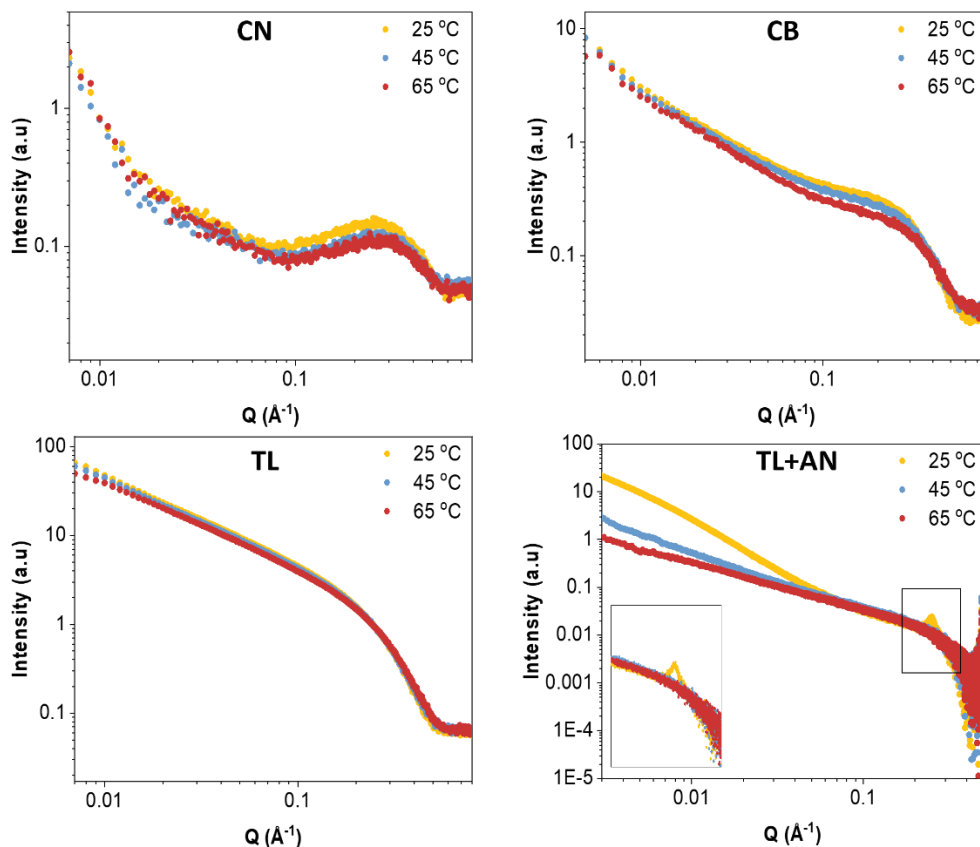


Figure 3.3. The temperature dependent SAXS profiles of PM7 D2 in four different solvents. The scattering profile for PM7 D2 in TL+AN changes most drastically with increasing temperatures as the semicrystalline fiber aggregates dissolve at high temperatures.

Figure 3.4 depicts the schematics of the solution-state aggregates as a function of solvent and solution temperature based on our X-ray scattering and freeze-dried imaging results. In poor side chain solvent CN, PM7 D2 forms semiflexible amorphous network aggregates with strong lamellar and side chain interactions ($d_{\text{lamellar}} = 2.4$ nm and $d_{\text{sidechain}} = 4.2$ Å), whereas in poor backbone solvent (TL+AN), the polymer chains become more rigid, eventually forming semicrystalline fiber aggregates in TL+AN with crystalline lamellar ($d_{\text{lamellar}} = 2.5$ nm) and π - π stacking ($d_{\pi-\pi} = 3.6$ Å). In mutual solvents (CB and TL), PM7 D2 forms rigid amorphous network aggregates mainly through polymer backbone associations ($d_{\text{backbone}} = 3.8$ Å) with weak ($d_{\text{lamellar}} = 3.2$ nm) or no lamellar stacking. Rigid amorphous network aggregates, resembling those in CB

and TL, are also obtained from semicrystalline fiber aggregates when increasing the solution temperature of TL+AN.

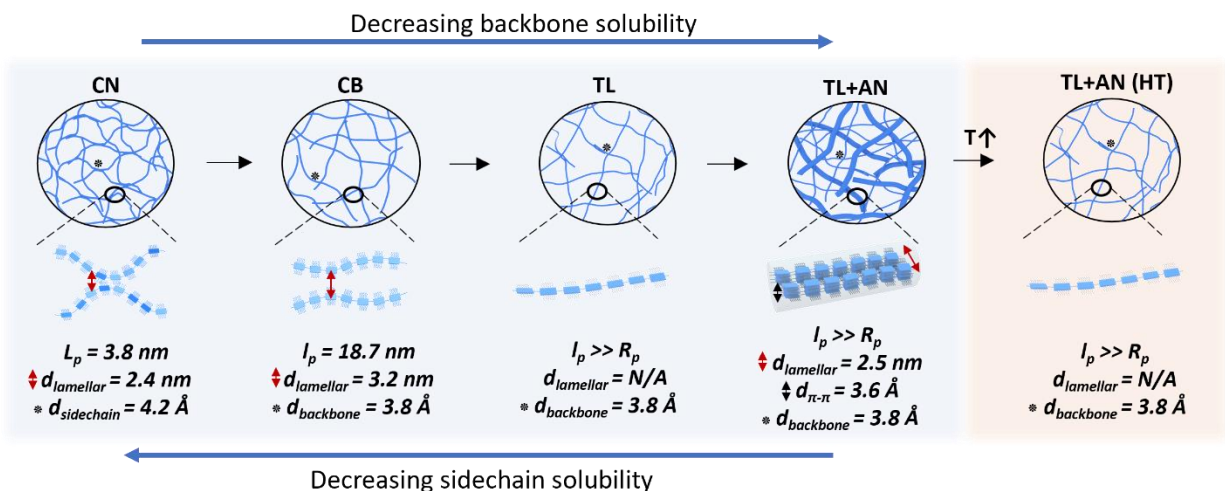


Figure 3.4. Schematic illustration of the solution-state aggregates depending on solvent and solution temperature. Transitioning from halogenated to non-halogenated solvents decreases the backbone solubility, which causes polymer aggregate structure to transition from amorphous networks with strong side chain associations (CN) to semicrystalline fiber aggregates (TL+AN). In solvents where the side chain and backbone solubility are balanced (CB and TL), the polymer also forms amorphous network aggregates but mainly through backbone interactions than side chain associations compared to the CN case. Similar amorphous network aggregates are also obtained by increasing the solution temperature of TL+AN, which leads to an order-to-disorder transition of semicrystalline fiber aggregates. Solution-state aggregate structures at high solution temperatures of CN, CB, and TL are not shown since the structure does not change with increasing solution temperature.

Device performance characterizations. We subsequently investigated how these distinct solution-state aggregates of PM7 D2 impact the device performance of OSCs. Using the inverted (ITO/ZnO/PM7 D2:ITIC-4F/MoO₃/Ag) architecture, we fabricated BHJ based OSCs, in which the photoactive layer was blade coated from a blend solution of PM7 D2:ITIC-4F (1:1) under ambient conditions without additives for relevance to industrial manufacturing of OSCs. All other fabrication steps and device testing were also conducted under glovebox-free or ambient conditions. **Figure 3.5a** shows the comparison of the current density (J_{sc}) as a function of voltage (V) depending on the casting solvent with the device parameters provided in **Table 3.1**, which also includes the coating temperatures used for blade coating. In all cases except for CN, room

temperature (25 °C) was selected as the coating temperature, whereas in CN, a coating temperature of 122 °C was selected due to its high boiling point. At these coating temperatures, the vapor pressures of all solvents are matched to ensure similar drying times, except for TL (**Supplementary Table 3.4**). Due to the high volatility of TL, the coating temperature had to be decreased much lower than room temperature to match the vapor pressures of the other solvents, which was impractical due to considerations such as water condensation at low temperatures. For the TL+AN mixed solvent, we note that the drying kinetics becomes more complicated than a single solvent system due to the different boiling points of TL and AN. Although the vapor pressure of the initial TL+AN mixture matches that of CB at room temperature (**Supplementary Table 3.4**), TL has a lower boiling point than AN, resulting in increased volume fraction of AN later in the drying stage, and thus overall slower drying kinetics. However, we show that devices cast from CB and TL do not depend significantly on the coating temperatures as the film thickness is matched by varying the coating speed (**Supplementary Figure 3.7**). This implies that drying time differences arising from unmatched vapor pressures likely have minimal impact on the performance of devices cast from TL and TL+AN.

When comparing the device parameters as shown in **Figure 3.5a** and **Table 3.1**, it is apparent that the intermediate solvents, CB and TL, yield higher efficiencies compared to the two extreme cases when either backbone selective (CN) or side chain selective (TL+AN) solvents are used. This result implies that forming rigid amorphous network aggregates with weak or no side chain interactions by balancing the solubility of polymer backbone and side chains is critical for optimizing the device performance of OSCs. Besides using mutual solvents, these rigid amorphous aggregates can also be formed from semicrystalline fiber aggregates when the solution temperature is increased (**Figure 4**). Accordingly, when we fabricate devices at high coating temperatures

(HT), devices cast from TL+AN yielded a drastic enhancement on the performance from 5.8 to 9.0 % (**Figure 3.5b, c**). On the other hand, devices cast from CB and TL showed minimal dependence on the coating temperatures, consistent with the relative stability of PM7 D2 aggregates depending on the solution temperature as compared to TL+AN (**Supplementary Figure 3.7** - due to the high boiling point of CN and instrument limitations, CN based devices are not fabricated at temperatures higher than 122 °C). Nevertheless, it is important to highlight that a slight improvement in PCE was observed with an increase in the coating temperature, especially when employing CB (**Supplementary Figure 3.7**). This implies that coating temperature and/or drying kinetics have a minimal but non-negligible effect on the device performance, likely inducing changes in the blend film morphology.⁵⁷ In contrast to CB and TL, TL+AN devices exhibit a strong coating temperature dependence, which can be primarily attributed to the structural transition of semicrystalline fiber aggregates to form rigid amorphous network aggregates at high temperatures. We also note that this result closely aligns with our previous report where semicrystalline fiber aggregates of PM7 polymer formed in CB lead to a substantial enhancement in OSC performance from 5.8 to 8.7 % as these aggregates form amorphous network aggregates during hot solution processing.²⁵

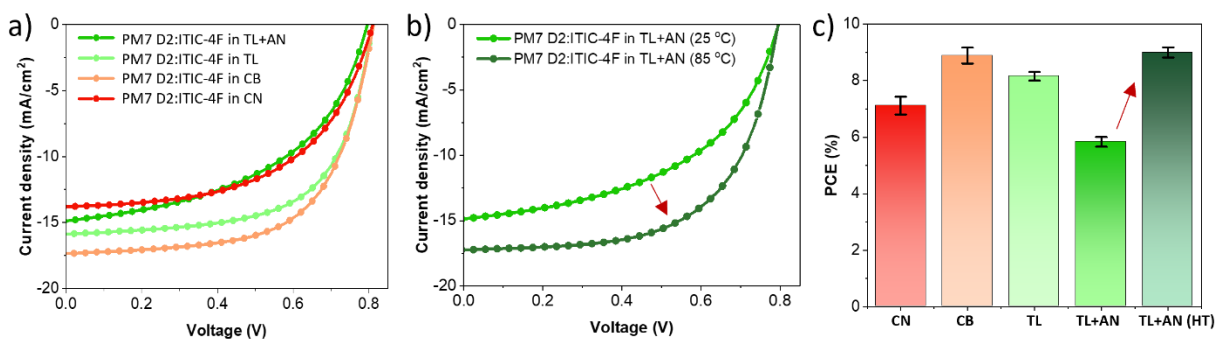


Figure 3.5. a) Current density and voltage (*JV*) characteristic curve for PM7 D2:ITIC-4F based devices blade coated from various solvents; b) those cast from TL+AN mixture solvent at room temperature and 88 °C, which will be referred to as high temperature (HT). c) Comparison of the power conversion efficiencies for the devices in a) and b). All devices are fabricated and tested under ambient or glovebox free conditions.

Table 3.1. Photovoltaic parameters of PM7 D2:ITIC-4F based OSCs blade coated from different solvents under an illumination of air mass 1.5 global (AM1.5G) at 100 mW/cm².

Samples	Coating Temperature (°C)	PCE (%)	FF (%)	J _{sc} (mA/cm ²)	V _{oc} (V)
CN	122	7.1 ± 0.3	56.6 ± 1.6	15.3 ± 0.8	0.82 ± 0.01
CB	25	8.9 ± 0.3	62.7 ± 1.2	17.4 ± 1.2	0.82 ± 0.01
TL	25	8.2 ± 0.2	63.2 ± 0.9	15.9 ± 0.1	0.81 ± 0.01
TL+AN	25	5.8 ± 0.2	49.3 ± 0.9	14.9 ± 0.1	0.80 ± 0.01
TL+AN (HT)	88	9.0 ± 0.2	68.8 ± 0.4	16.4 ± 0.3	0.80 ± 0.01

Film morphology characterizations. As shown in **Table 3.1**, the differences in the device efficiencies are mainly due to the large short circuit current (J_{sc}) and fill factor (FF), which depend on the blend film morphology.⁵⁸ Therefore, to better understand the trend observed in the device performance of OSCs, we studied the morphology of the blend films using various X-ray diffraction methods including grazing-incidence-wide-angle X-ray scattering (GIWAXS), resonant soft X-ray scattering (RSoXS) and complementary imaging techniques including photo-induced force microscopy (PiFM) and conductive AFM (c-AFM). Shown in **Figure 3.6a** are the 2D scattering patterns of the blend films obtained from GIWAXS measurements. The scattering patterns and linecut profiles for the neat donor and acceptor films are provided in **Supplementary Figure 3.8** and **S9**. Both neat donor polymer and blend films exhibit in-plane and out-of-plane (010) peaks, corresponding to π - π stacking distance around $q = 3.6 \text{ \AA}$, determined from the linecut profiles (**Supplementary Figure 3.10**). Notably, this distance is the same as the π - π stacking distance observed in the fiber aggregates in TL+AN solution. However, ITIC-4F acceptor barely shows any (010) peak (**Supplementary Figure 3.9**), suggesting that the π - π stacking peaks observed in the blend films arise largely from crystallization of the donor polymer. When comparing the scattering patterns, it is evident that the blend film cast from CN exhibits a strong in-plane (010) peak, which corresponds to edge-on polymer orientation in the crystalline domains. To better compare the distribution of molecular orientation in these blend films, partial pole figures

were obtained (**Supplementary Figure 3.11a**) using approaches previously reported.^{59–62} These pole figures are constructed by plotting the intensity of (010) peak from 5° sector cut profiles from the scattering patterns within the range of $10^\circ < \chi < 80^\circ$, where $\chi = 0^\circ$ corresponds to the out-of-plane direction. The peak intensities are then normalized to the 0-1 scale for direct comparison of the molecular orientations across different films. Based on these pole figures, a sharp increase in the intensity of (010) peak at higher χ angles is observed for the blend film cast from CN, which is more drastic compared to other films.

We further estimated Herman's orientation parameter (S)^{63,64} based on the distribution of (010) peak using the sample normal as the director as shown in **Figure 3.6b**. The S parameter ranges from -0.5 to 1, corresponding to a complete edge-on to face-on population when the azimuthal angle is selected along the surface normal. **Figure 3.6b** clearly shows that the S parameter is more negative for CN compared to the other films, which is a clear indication of predominantly edge-on molecular orientation in the crystalline domains. Interestingly, we found that the orientation parameter is significantly more negative at the air-liquid interface for the CN case (**Supplementary Figure 3.11b**). Therefore, we attribute the edge-on preferred molecular orientation in CN to the unfavorable side chain and solvent interactions of PM7 D2 and CN, causing the side chains to orient towards air. Compared to the blend film cast from CN, other films yield preferential face-on orientation, which is evident from their positive S parameters. Since edge-on orientation is often unfavorable for charge transport in OSCs, the fact that devices cast from CN yield poorer performance is not surprising. However, molecular orientation does not seem to be the main reason for the poor performance in devices cast from TL+AN at room temperature given that the orientation is mainly face-on, which is expected to favor charge transport in OSCs.

To compare the crystallinity of the blend films, we determined the full width at half-maximum (FWHM) of the (010) and (100) peaks and the relative degree of crystallinity of the blend films using GIWAXS measurements as shown in **Figure 3.6c, d** respectively. Based on **Figure 6c**, FWHM of both (010) and (100) peaks are much smaller in CN and TL+AN films than in CB and TL, suggesting larger crystal sizes and/or lower paracrystalline disorder⁶⁵ compared to the films cast from CB and TL. In CN, high order lamellar peaks are also clearly visible compared to other films, suggesting its long-range crystalline order. We also calculated the relative degree of crystallinity (rDoC) by integrating the geometrically corrected (010) peak intensities over χ following the protocols of previous reports.^{59,66} **Figure 3.6d** shows the comparison of rDoC in these blend films, suggestive of the higher crystallinity of PM7 D2 cast from CN and TL+AN solvents compared to CB and TL.

To understand why CN and TL+AN yield more crystalline films than CB and TL, we first investigated the assembly pathways of PM7 D2 using cross polarized optical microscopy (CPOM). As we increase the solution concentration to 200 mg/mL using the drop and drying method (see Experimental Methods for details), we observe the emergence of lyotropic liquid crystalline (LC) phases in CB, TL, and TL+AN, with TL+AN more readily forming LC phases even at 60 mg/mL (**Supplementary Figure 3.12**). In CN, PM7 D2 shows some birefringence at the edge of the solution at 200 mg/mL although the bulk of the solution is still mainly isotropic. This observation aligns with previous findings suggesting that poor backbone solvents are more likely to induce lyotropic LC phase.⁶⁷ On the other hand, we observe that semiflexible amorphous network aggregates, particularly those formed in CN, delay the formation of LC phases. Given that CN does not readily crystallize or form LC phase even at 200 mg/mL, it is surprising that the blend film is more crystalline than other films based on our GIWAXS results. Investigating the

crystallization mechanism of PM7 D2 in CN using in-situ CPOM measurement reveals direct crystallization of PM7 D2, same as our previous report on the crystallization of PII-2T polymer in CN.²⁹ We thus attribute the pronounced crystallization of PM7 D2 in CN to the strong side chain interactions within these amorphous network aggregates caused by the poor solvent quality of CN towards the side chains. We also note that the top and bottom surface of the dried film of PM7 D2 in CN show different birefringence under CPOM (**Supplementary Figure 3.13**), consistent with the different molecular orientation at the interface (edge-on) versus in the bulk of the film (face-on).

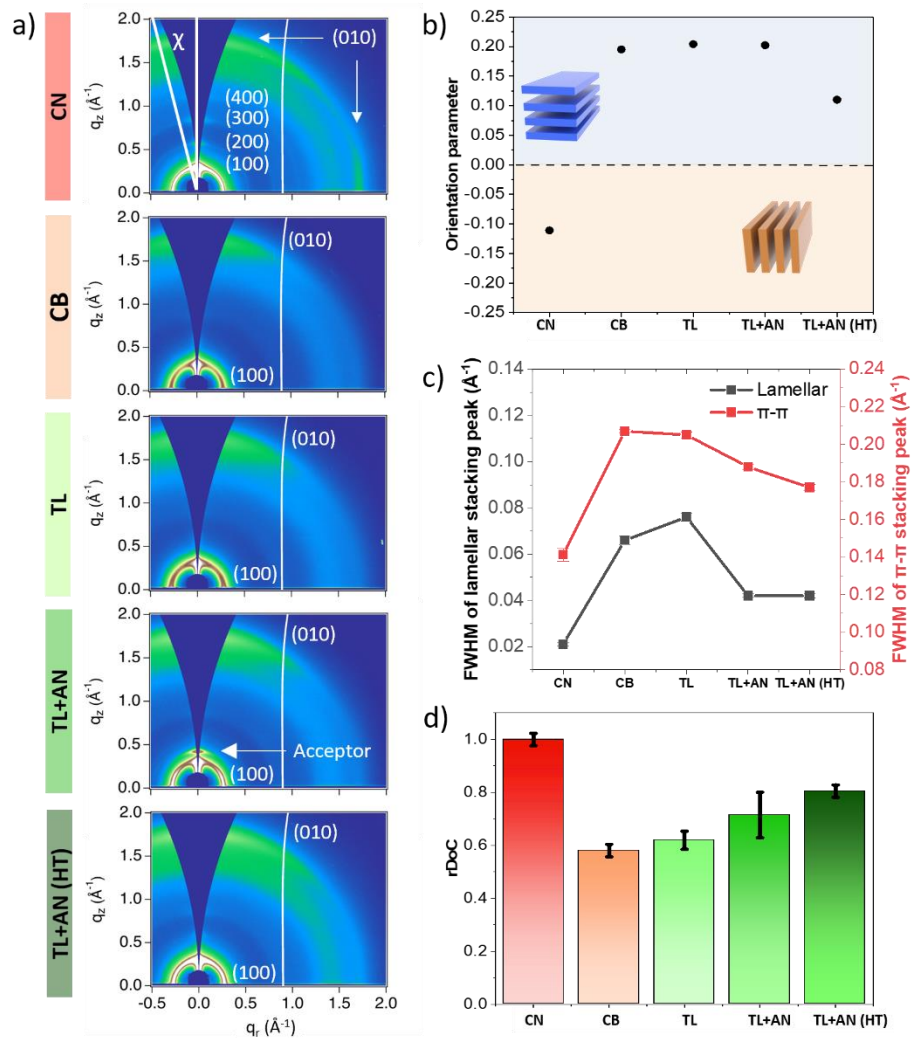


Figure 3.6. a) 2D GIWAXS patterns of PM7 D2:ITIC-4F blend films; b) Comparison of Herman's orientation parameter where more negative value corresponds to edge-on population; c) FWHM of (010) and (100) peaks from the GIWAXS patterns; d) Comparison of relative degree of crystallinity (rDoC) of blend films cast from different solvents.

In contrast to CN, where PM7 D2 undergoes direct crystallization, the higher crystallinity of PM7 D2 in TL+AN could be attributed to its tendency to form an LC phase (**Supplementary Figure 3.12**). However, our findings suggest that LC phase formation is suppressed or bypassed when the film is blade coated in the Landau-Levich (LL) regime, highlighting the importance of coating regimes on the assembly pathway of conjugated polymers as previously reported.⁶⁸ To demonstrate this, we compared the assembly pathways of PM7 D2 under the evaporation regime

vs. the Landau-Levich (LL) regime.⁶⁹ When the films were coated in the evaporation regime at low coating speeds, all films are highly birefringent under CPOM (**Supplementary Figure 3.14**), implying that the crystallization process undergoes LC mediated assembly pathway. However, coating in the evaporation regime led to highly non-uniform films due to the stick and slip effect,⁷⁰ prompting us to choose the LL regime for OSC fabrication. When PM7 D2 solution in TL+AN was printed in the LL regime, however, we did not observe any LC phase formation during the coating process under CPOM imaging. Typically, crystallization mediated by the LC phase shows highly birefringent features at the triple phase contact line before crystallization.^{61,68} **Supplementary Figure 3.14** also shows that all films become less birefringent, and thus more isotropic in the LL regime compared to those coated in the evaporation regime at very low coating speeds, indicating that LC mesophase is suppressed or bypassed to result in the direct crystallization pathway. Therefore, we attribute the improved crystallinity of PM7 D2 cast from TL+AN to the direct crystallization of the pre-existing crystalline fibers rather than the LC mediated crystallization. As shown in **Figure 3.6a**, we also observe an out-of-plane peak near $0.4 \text{ \AA}^{-1}$, which is not observed in any other blend films. Based on the neat acceptor GIWAXS patterns, we attribute this peak to ITIC-4F acceptor (**Supplementary Figure 3.9c**). The fact that this peak is more pronounced in TL+AN solvent seems to suggest that the semicrystalline fiber aggregates also enhance crystallization of ITIC-4F. It is also worth noting that even at an elevated temperature of $88 \text{ }^{\circ}\text{C}$, the film cast from TL+AN (HT) retains its crystallinity (**Figure 3.6c, d**) even though the fiber aggregates dissolve at high temperatures. This suggests that PM7 D2 still maintains its strong tendency to crystallize in TL+AN due to the reduced nucleation barrier in a poor solvent.⁷¹

Since PM7 D2 undergoes direct crystallization in TL+AN when coated in the LL regime, it also implies that CB and TL lead to direct crystallization of PM7 D2 since CB and TL are less

conducive to LC phase (**Supplementary Figure 3.12**). The film crystallinity of PM7 D2 in CB and TL, however, is lower compared to TL+AN, which is attributed to the formation of rigid amorphous network aggregates of PM7 D2 in CB and TL solutions that delay the formation of crystalline fiber aggregates during drying, thereby preventing strong crystallization of PM7 D2. The lower crystallinity of CB and TL films compared to CN is also attributed to the rigid amorphous network aggregates of PM7 D2 in CB and TL. Unlike the flexible amorphous aggregates of PM7 D2 with strong side chain associations in CN, these rigid amorphous network aggregates only possess weak or no side chain associations, which prevent the strong crystallization at the air-liquid interface. Furthermore, the rigid amorphous network aggregates likely undergo crystallization through backbone ordering rather than side chain ordering, which could contribute to increased nucleation density and small crystal sizes in the solid-state.¹⁵

To sum up, although PM7 D2 can form an LC phase in all solvent systems at high solution concentrations, we found that coating films in the LL regime suppresses formation of LC phase, even in TL+AN, which readily forms the LC phase. Ultimately, PM7 D2 undergoes direct crystallization in all solvents, where the structure of solution aggregates tuned the film crystallinity. In CN, semiflexible amorphous network aggregates led to strong crystallization driven by their strong side chain associations at the air-liquid interface. Similarly, semicrystalline fiber aggregates formed in TL+AN also led to high film crystallinity by acting as the seed crystallites (e.g. heterogeneous crystallization). On the other hand, rigid amorphous network aggregates formed in CB and TL led to reduced film crystallinity owing to the more balanced side chain and backbone solubility.

Besides crystallinity and molecular orientation, the phase-separated structure of the photoactive layer is crucial for charge generation in organic solar cells. To quantify the domain

sizes in the blend films, we used resonant soft X-ray scattering (RSoXS), which uses X-ray energies near the aromatic C 1s $\rightarrow$ pi* to enhance contrast between the donor and acceptor materials. As previously reported, the scattering contrast, however, not only originates from material contrast but also includes contributions from molecular orientation and surface roughness.^{72,73} Based on our previous study, the surface roughness contribution is negligible for PM7 D2:ITIC-4F system, but molecular orientation contribution in this case cannot be easily separated from material contrast.²⁵ This suggests that scattering features from RSoXS have origins from both material and orientation contrasts. **Figure 3.7a, b** shows the RSoXS scattering profiles for blend films cast from different solvents and films cast from TL+AN at different temperatures. Based on **Figure 3.7a**, the scattering features for CN and TL+AN are located at the lower Q range, corresponding to larger length scale, which is consistent with their high crystallinity. When coating PM7 D2 in TL+AN at a high coating temperature, on the other hand, the scattering feature shifts towards the higher Q range or smaller length scale (**Figure 3.7b**). Using the Debye-Anderson-Brumberger (DAB) model for randomly distributed two phase systems to fit the scattering profiles,⁷⁴ we estimated the correlation length or spacing between the donor and acceptor materials as shown in **Figure 3.7c**. This figure clearly shows that CN and TL+AN lead to larger correlation lengths compared to CB, TL, or TL+AN (HT).

Since the scattering features from RSoXS involve contributions from molecular orientation, we utilized PiFM as a complementary technique to compare the phase separated structure of the blend films. PiFM is a scanning probe technique, which combines AFM with a tunable infrared (IR) laser to impart chemical contrast, and it has only recently been used to investigate the blend film morphology of OSCs.^{2,75-77} During the PiFM measurement, the IR laser is focused on the region of the sample that interacts with the AFM probe, inducing an electric

dipole from the sample, which then creates a mirror dipole on the AFM tip.⁷⁶ The dipole-dipole attractive forces between the sample and the tip then creates a compositional map of the blend film at 10 nm resolution. **Figure 3.7d, e** shows the IR spectra of PM7 D2 and ITIC-4F films obtained from Fourier Transform Infrared (FTIR) for the bulk and PiFM for the sample surface, respectively. Both FTIR and PiFM spectra match very well; particularly, the major peaks at 1280 cm^{-1} and 1540 cm^{-1} for ITIC-4F and 1180 cm^{-1} and 1720 cm^{-1} for PM7 D2 are clearly observed in both FTIR and PiFM. The IR excitation wavelength was then tuned to 1280 cm^{-1} to image the blend films as shown in **Figure 3.7f**. We note, however, that it was difficult to selectively map the donor rich regions due to the poor absorption of the donor material in the blend films even at peak wavelengths 1180 and 1720 cm^{-1} . Nonetheless, the dark regions in **Figure 3.7f** can be attributed to the donor rich domains, which clearly shows that PM7 D2 forms large domains when cast from CN and TL+AN compared to those in CB, TL, and TL+AN (HT), consistent with our RSoXS results.

Since the donor domains could not be selectively mapped with PiFM, we also employed c-AFM to map the PM7 D2 domains as shown in (**Figure 3.7g**). Using high work function top and bottom electrodes (PEDOT:PSS for hole transporting layer and Au probe), we were able to map the hole-only transport or donor regions in the blend films.^{78,79} The bright regions in **Figure 3.7g** thus shows regions with high current due to hole transport, which correspond to PM7 D2 domains. Although the resolution of the images is lower compared to PiFM, we can clearly see large polymer domains in CN and TL+AN, consistent with PiFM imaging. Overall, it is worth noting that our RSoXS, PiFM, and c-AFM results are strongly correlated with the trend observed in the device performance results (**Figure 3.5c**), suggesting the importance of domain sizes on the OSC performance. It is also generally observed that the more crystalline films tend to form larger

domains in blend films, except for TL+AN (HT), which still retained its crystallinity while forming relatively small domains in the blend film. This result could be attributed to the temperature-dependent aggregation behavior of PM7 D2 in TL+AN. It is consistent with previous reports that conjugated donor polymers with temperature-dependent aggregation enables morphology control by processing at elevated temperatures, leading to highly crystalline films with desirable domain sizes.^{45,55,80}

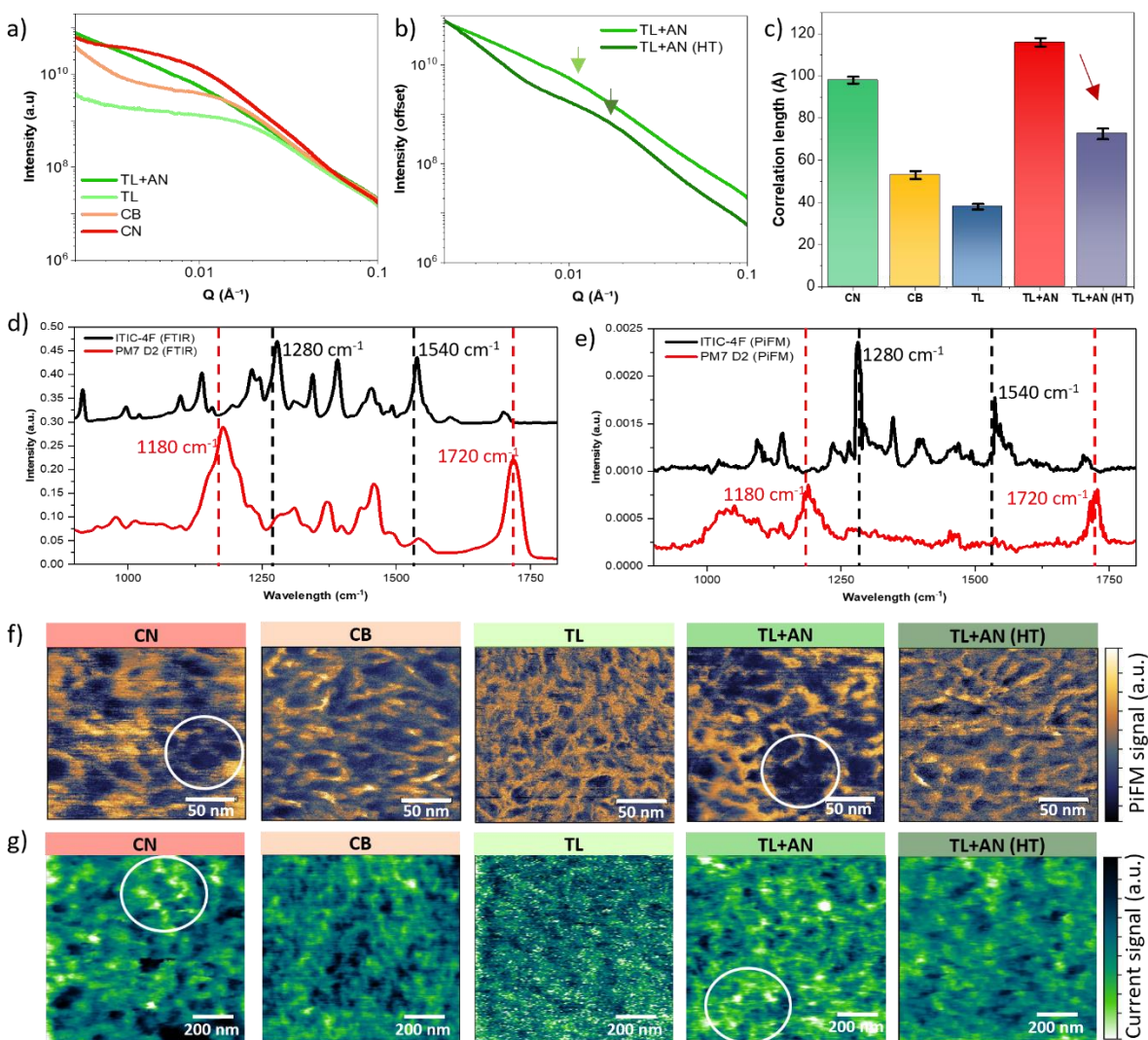


Figure 3.7. Characterization of phase separated morphology. RSoXS profiles of a) PM7 D2:ITIC-4F blend films cast from four different solvents and b) those cast from TL+AN at 25 °C and high coating temperatures (HT) at 88 °C; c) Correlation lengths of blend films based on DAB model fitting; d) Bulk FTIR measurement results for PM7 D2 and ITIC-4F materials; e) Surface PiFM measurements on PM7 D2 and ITIC-4F neat films blade coated from CB; f) PiFM imaging results

(**Figure 3.7. cont.**) for the blend films when using the IR laser tuned at 1280 cm^{-1} , where the circled regions correspond to the donor-rich domains g) c-AFM images of the blend films using a bias voltage of +3 V, where the circled regions correspond to the donor-rich domains.

The assembly pathways of PM7 D2, as inferred from our solution and film characterization results, are illustrated in **Figure 3.8**. The schematics portray the relationship between solvent quality, structure of polymer aggregates, and their crystallization pathways. As solvent affinity decreases towards the conjugated backbone while increases towards the side chains, the structure of polymer aggregates transitions from semiflexible amorphous networks to rigid amorphous networks and semicrystalline fibers. There exhibits a Goldilocks effect, featuring rigid amorphous network aggregates with weak or no side chain association, which is the most conducive to favorable morphology for BHJ organic solar cells. During the coating process, both fiber aggregates and semiflexible amorphous networks with strong side chain interactions showed a greater propensity to crystallize, resulting in blend films with large domains and high crystallinity. When the solvent quality is intermediate for both the backbone and the side chains, rigid amorphous network aggregates with weak or no side chain interactions form to prevent excessive crystallization, reducing the domain sizes in the blend film. These rigid amorphous network aggregates can also be achieved from the semicrystalline fiber aggregates by simply raising the solution temperature, resulting in small phase separated morphology. Notably, even after the dissolution of fiber aggregates at high temperatures, crystallinity can be maintained while yielding small domain sizes, which is attributed to the temperature-dependent aggregation behavior of PM7 D2 in TL+AN.

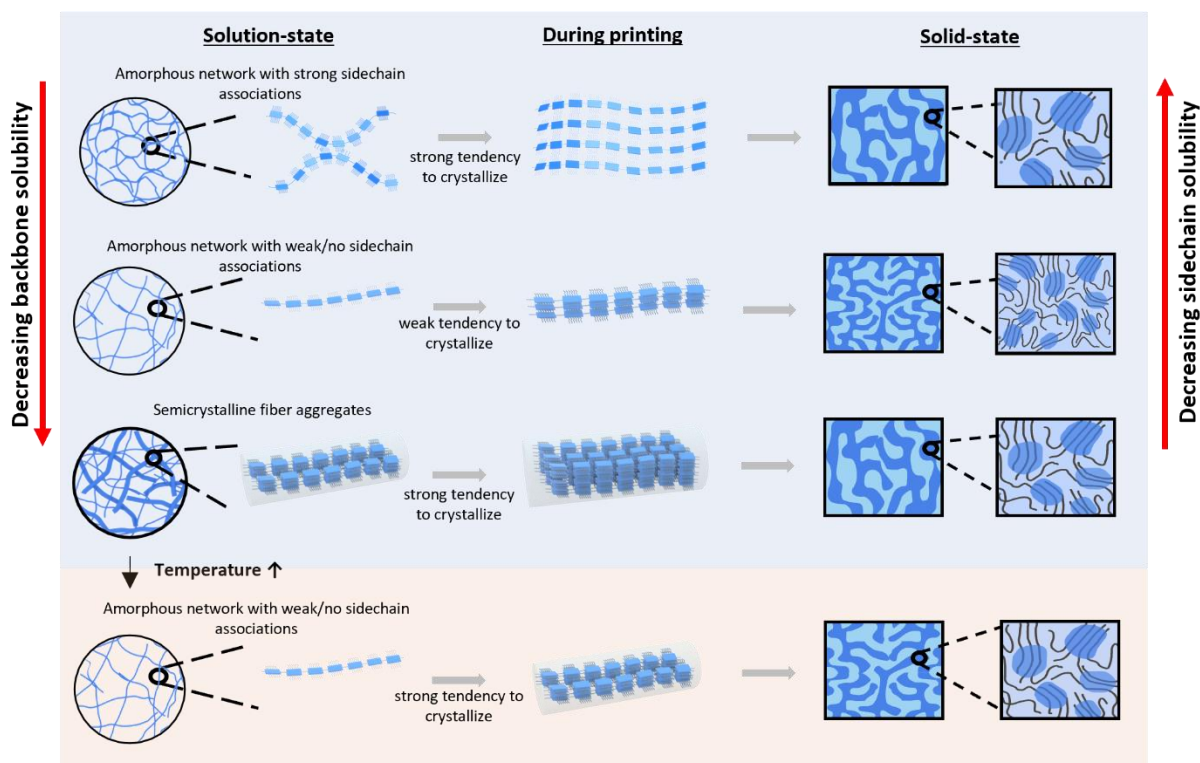


Figure 3.8. Overall schematics of the assembly pathways for PM7 D2 during OSC processing depending on solvent and coating temperature. Poor backbone and side chain solubility lead to semicrystalline fiber aggregates and amorphous networks with strong side chain associations, respectively, both resulting in excessive crystallization and large domain sizes. Balancing the backbone and side chain solubility, on the other hand, forms amorphous network aggregates with weak or no side chain associations, yielding the most favorable blend morphology with small crystalline domains.

3.3 Conclusion

In summary, using PM7 D2 as our model system, along with a series of halogenated and non-halogenated solvents, we demonstrated that the backbone and side chain solubility of conjugated polymers plays the key role in determining the structure of polymer aggregates in solution, their assembly pathways, and the blend film morphology. We found that the solvent affinity towards the conjugated backbone decreased while it increased for the side chains when transitioning from halogenated to non-halogenated solvents. As a result, we obtained three distinct conjugated polymer aggregate structures for PM7 D2 depending on the solvent properties: semiflexible amorphous networks in a poor side chain solvent, rigid amorphous networks in

mutual solvents, and semicrystalline fiber aggregates in a poor backbone solvent. During solution processing, the semicrystalline fiber aggregates acted as the nucleation seeds to promote crystallization, leading to large crystalline domains that are detrimental to OSC performance. Similarly, semiflexible amorphous network aggregates also led to excessive crystallization via crystallization at the air-liquid interface. On the other hand, rigid amorphous network aggregates with weak to no side chain interactions led to the most favorable blend film morphology owing to the balanced crystallization of PM7 D2, yielding small domain sizes. The rigid amorphous network aggregates were also achieved when raising the temperature of a poor backbone solvent. Efficient green solvent processed OSCs were thus enabled by tuning the solution aggregate structures using hot solution processing, which substantially improved the device performance from 5.8 to 9 %. Our findings also revealed that despite PM7 D2's ability to form an LC mesophase at high solution concentrations, coating the films in the LL regime suppressed the LC mesophase formation. Instead, direct crystallization pathways were observed in all cases where crystallization of the conjugated polymer strongly depended on the solution aggregate structures. Through this work, we highlight the importance of balancing the backbone and side chain solubility of conjugated polymers to achieve favorable blend film morphology for fabrication of efficient OSCs.

3.4 Experimental methods

Materials

PM7 D2 was synthesized based on the synthesis procedures outlined in Jones and Reynolds *et al.*³⁰ with the corresponding molecular weight and dispersity results provided in **Supplementary Table**

3.1. The molecular acceptor, ITIC-4F (purity > 99 %), was purchased from Brilliant Matters.

UV–Vis Spectroscopy

UV–vis (Cary 60 UV–Vis, Agilent) spectroscopy was used to measure the absorbance of 20 mg/mL polymer solutions of PM7 D2 in a short path length of 10 μ m quartz cell (Starna Cells).

Before each solution measurement, a blank solvent measurement for each solvent was taken for background subtraction.

SAXS Measurement

SAXS experiments were performed at the 16-ID beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory to probe the Q ranges between $0.006 < Q < 3 \text{ \AA}^{-1}$ using multiple Pilatus detectors.⁸¹ The samples were measured using a 1.5 mm diameter quartz capillary and custom-made flat sample cells made of 100 μm ultrathin glass windows from Schott AG. Before performing solution scattering measurements, both empty cells and blank solvents were measured for proper background subtraction. For each measurement, 10-20 repeated measurements were taken on various parts of the sample using X-ray energy at 13.5 keV with 1 s exposure time to avoid beam damage. The scattering profiles were then obtained by averaging the repeated measurements and subtracting the empty cell and blank solvent contributions using a Python package *py4xs* in Jupyter notebooks.⁸² The model fitting of the scattering profiles was performed using SASView program with dI data for weighting, Levenberg–Marquardt with 200 steps for the algorithm where the uncertainties are determined from the covariance matrix, and χ^2 values and the residuals plot were used as the goodness of fit metrics.

Freeze-Drying Method for Imaging the Solution-State Aggregates

Freeze-drying experiments were conducted to image the structure of aggregates in solution by using AFM. The freeze-drying process involves rapid freezing of polymer solutions in liquid ethane and propane mixture (63 % propane and 37 % ethane) with a melting point followed by liquid nitrogen storage. The purpose of using the liquid ethane mixture is to ensure rapid freezing of the solution due to its large heat capacity and prevent polymer aggregation during the cooling process. The resulting frozen polymer solution is then quickly transferred to a Linkam stage at $-120 \text{ }^\circ\text{C}$ under vacuum. The Linkam stage temperature is then slowly increased at a rate of 0.5

°C/min to -80 °C (far below the melting point of chlorobenzene solvent mp = -45 °C and 1-chloronaphthalene mp = -20 °C) followed by 6–8 h of constant monitoring with cross-polarized microscopy to ensure sublimation of all solvent. For TL and TL+AN solvents, liquid nitrogen (bp = -195.8 °C) was used to freeze the solutions due to the low freezing points of TL and TL+AN (mp = -95 °C). The samples were then transferred to the Linkam stage at -135 °C, which is then slowly increased at a rate of 0.5 °C/min to -100 °C, followed by over 12 h of solvent sublimation. The freeze-dried samples were then imaged by the Cypher AFM from Asylum Research using tapping mode.

Device Fabrication

OSCs were fabricated using the inverted architecture (glass/ITO/ZnO/polymer:ITIC:4F/MoO₃/Ag). Before film deposition, 20 × 15 cm ITO-patterned glass substrates (Ossila, Inc.) were cleaned by sonicating sequentially with water, acetone, and finally isopropanol for 10 min each. The cleaned substrates were then dried with nitrogen and plasma treated (Harrick Plasma PDC-001-HP) for 6 min at 300 mT of dry air and high power (30 W). To deposit the electron transporting layer, ZnO solution was prepared by dissolving 1 g of zinc acetate dihydrate (Sigma-Aldrich) and 0.28 g of ethanolamine (Sigma-Aldrich) in 10 mL of 2-methoxyethanol (Sigma-Aldrich) under vigorous stirring for over 12 h in air. This solution was then filtered with a 0.45 µm PTFE syringe filter before deposition. The filtered solution was deposited on the cleaned ITO substrates by spin-coating for 30 s at 4000 rpm in an ambient atmosphere, which resulted in an active layer thickness of ≈20–30 nm measured by a Bruker Dektak XT profilometer. After spin-coating, the ZnO layer was annealed in air at 150 °C for 30 min followed by slow cooling to room temperature for active layer deposition. The photoactive layer solution for all devices was prepared by dissolving the polymer and ITIC-4F (Sigma-Aldrich) at 1:1 (wt/wt) ratio in CN, CB, TL, and TL+AN without any additives. The resulting blend solution was stirred at 40 °C overnight and

brought to room temperature and stirred for at least 12 h before deposition before blade coating. The blend solutions were then blade coated using a blade angle of 7° and a solution volume of 3 μ L. The conditions used for coating from each solvent are provided in **Supplementary Table 3.4** and **S3.5**. The film thickness corresponding to these optimal coating conditions was ~80 nm. After blade coating, all films were thermally annealed at 100 °C for 10 minutes in air before thermal evaporation of MoO₃ and Ag electrode using Kurt J. Lesker Nano36 Thermal Evaporator System.

Device Characterization

The current density (J – V) curves were characterized by using an automated Solar Cell I-V Test System (Ossila) under AM 1.5G illumination (100 mW/cm) with a class AAA solar simulator from Newport under glovebox-free or ambient environment. Before each test, the solar simulator was calibrated by reference single-crystal Si cells (Sciencetech). Each sample includes eight pixels and a total of three samples, or 24 devices were tested under each condition. The active area of all devices is 0.04 cm². For calculating the device performance, mismatch factor was not applied.

Solution characterization using CPOM

Solution characterization under CPOM was performed by sandwiching the polymer solutions in between two microscope glass coverslips placed on a Si wafer during the CPOM measurements using the reflection mode. High concentration solutions were obtained by the drop and dry method,⁸³ where the concentration of the pristine solution is increased by drying a certain amount of solution and then adding a 1 μ L of solution to the dried droplet and mixing the solution by shearing with the microscope cover glasses to increase the concentration. For instance, 200 mg/mL solution was achieved by drying 9 μ L of 20 mg/mL solution and adding 1 μ L solution to increase the concentration of 20 mg/mL solution by ten-fold. The solution samples then underwent thermal annealing cycles to reach an equilibrium state before imaging under CPOM.

GIWAXS

GIWAXS measurements were performed at 7.3.3 beamline of the Advanced Light Source at Lawrence Berkeley National Laboratory using incident angles of 0.08° , 0.1° , 0.12° , and 0.14° with X-ray energy of 10 keV and a beam size of 30 x 50 μm . All samples were placed in a helium chamber for measurement. For sample preparation, ZnO was firstly deposited on a Si wafer followed by the photoactive layer deposition and thermal annealing the same way that all OSC devices were fabricated. From GIWAXS measurement, 2D scattering images were obtained and converted to 1D linecut profiles by using the beamline NIKA package in Igor Pro.⁸⁴ The Ewald sphere correction (missing wedge correction) for the 2D images were obtained using the WAXSTools plugin⁸⁵ in Igor Pro. For molecular orientation analysis, pole figures are constructed by plotting the geometrically corrected intensity of (010) peak from 5° sector cut profiles from the scattering patterns within the range of $10^\circ < \chi < 80^\circ$. The intensity of (010) peak at each χ angle was determined by gaussian peak deconvolution analysis. For rDoC analysis, the geometrically corrected intensities were integrated over χ and normalized by the total illumination volume (thickness and area of the sample) as previously reported.⁵⁹

RSoXS

RSoXS data were collected at the National Synchrotron Light Source II at the beamline 7-ID-1 in the transmission geometry. For sample preparation, the photoactive layer was blade coated and thermally annealed using the same device fabrication conditions on a polystyrene sulfonate (PSS) film, which was spin coated from a 10% PSS solution in water. The PSS solution was stirred overnight at room temperature before depositing on a Si wafer substrate. After photoactive layer deposition, the sample on a Si substrate was immersed in water, which dissolved the PSS layer and separated the sample from the substrate. The sample was then picked up with a 1×1 mm, 100

nm-thick Si_3N_4 membrane supported on a 5×5 mm, 200 μm -thick Si frame (Norcada) and transferred into the vacuum chamber for RSoXS measurement. RSoXS measurements were performed at the beam energy from 270 to 290 eV with 5 s of exposure time per scan. The collected 2D scattering images were then converted into 1D profiles using the Nika package supported in the Igor Pro environment.

PiFM measurements

The PiFM measurements were conducted using VistaScope from Molecular Vista, Inc., using Pt coated silicon cantilevers from Molecular Vista. Before starting the measurement, the laser power was recorded within the IR range of $733 - 1960 \text{ cm}^{-1}$, followed by the laser alignment using a parabolic mirror to ensure that the laser was focused on the tip of the cantilever. The wavelength of the quantum cascade laser (QCL) used for alignment was tuned to 1850 cm^{-1} at an intensity of 20 % of the recorded maximum power. For PiFM imaging, a scan size of $500 \text{ nm} \times 500 \text{ nm}$ with a pixel size of 256×256 was used at a speed of 1 line/sec. During the measurement, 1280 cm^{-1} laser was tuned to <5% of the maximum power with 20-30 s duration per spectrum. To obtain PiFM spectra of the neat films, QCL laser was first turned off to obtain only AFM topography images using a scan size of $1 \mu\text{m} \times 1 \mu\text{m}$. Afterwards, the point spectra were obtained based on the collected AFM topography images with an IR intensity of <5 % of the maximum power with 20-30 s duration per spectrum. The bulk FTIR spectra of neat materials using solid powder samples were also obtained using Thermo Nicolet iS50 spectrometer as a comparison with the PiFM spectra on neat films.

c-AFM measurements

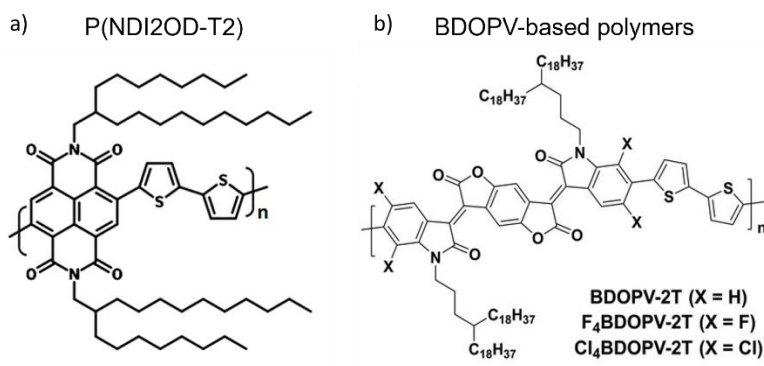
Hole current mapping was conducted using an AIST-NT SmartSPM on the XploRA-Nano system by Horiba, Inc. Budget sensors ContGB-G Au-coated conductive probes with a manufacturer-specified spring constant of 0.2 Nm^{-1} and a probe radius less than 25 nm were employed to record

c-AFM scans. An applied probe-sample force ranged between 3-5 nN, with a substrate bias voltage of +3 V. High work function top and bottom electrodes (PEDOT:PSS for hole transport layer and Au probe) were used to ensure hole-only transport.

Film Thickness Measurements

Film thickness was measured by using the Bruker Dektak XT profilometry with 12.5 μm radius stylus. During thickness measurements, a stylus force of 3 mg and a scan range of 1000–2000 μm were used at a speed of 50 $\mu\text{m/s}$. For thickness measurements, a part of the film was removed with a cotton swab with toluene solvent. The thickness measurements were repeated in three to five different positions to obtain the average and standard deviation.

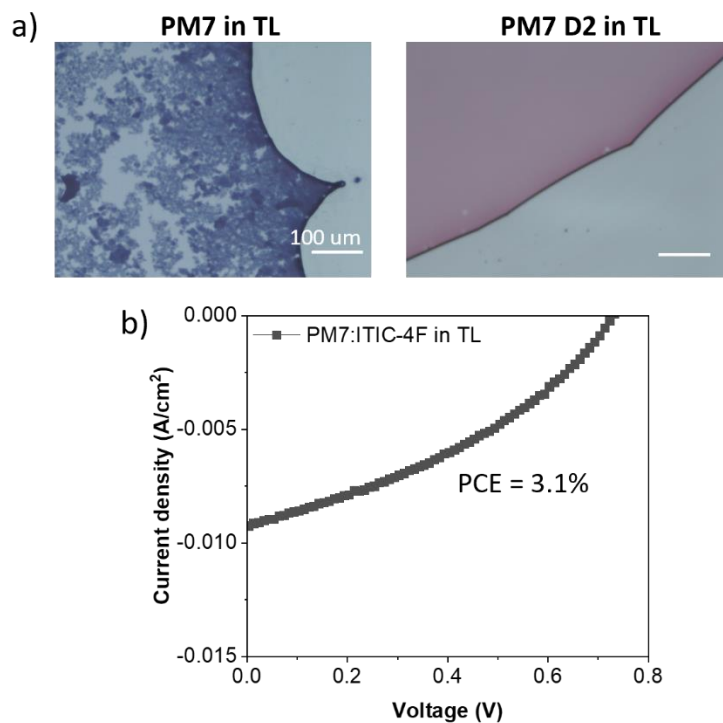
3.5 Supporting information



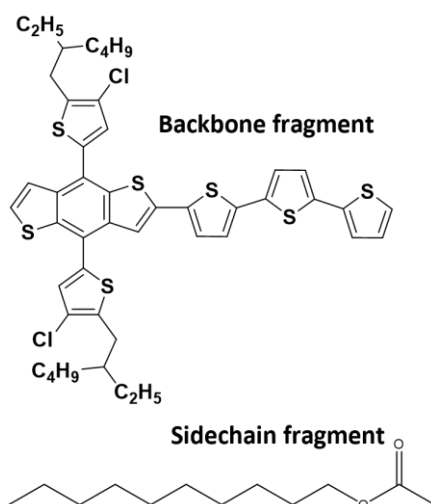
Supplementary Figure 3.1. Repeat unit structures of a) P(NDI2OD-T2) and b) BDOPV-based polymers.

Supplementary Table 3.1. Synthesis results for PM7 D2 polymer.

Materials	M_n	M_w	PDI	Contour length (nm)
PM7 D2	39 kg/mol	80.3 kg/mol	2.1	124



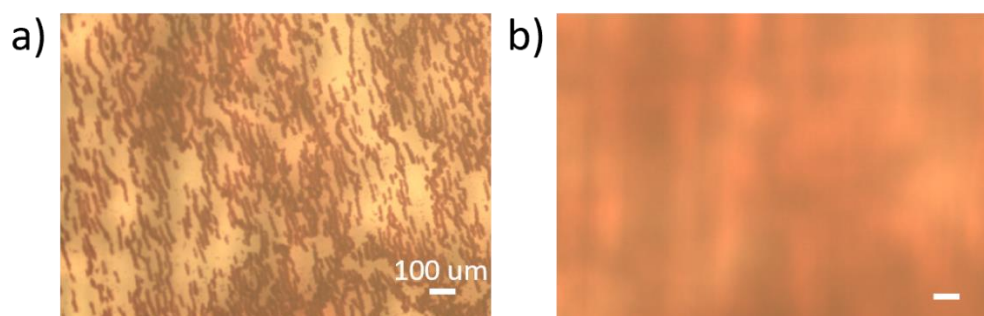
Supplementary Figure 3.2. a) Comparison of microscope images of PM7 and PM7 D2 in TL solvent (20 mg/mL), showing the poor solubility of PM7 polymer as a comparison to PM7 D2. b) Current density and voltage plot for PM7:ITIC-4F devices blade coated at room temperature. Due to the poor solubility of PM7, PM7:ITIC-4F based devices (blade coated at room temperature) show only 3.1% efficiency.



Supplementary Figure 3.3. Molecular structures of the conjugated backbone and sidechains of PM7 D2 that are used to estimate the Hansen solubility distance.

Supplementary Table 3.2. Solubility parameters obtained from the group contribution theory.

Materials	Dispersion	Polarity	Hydrogen	Ra (backbone)	Ra (sidechain)
CN	20.5	4.9	2.5	11.8	9.7
CB	19	4.3	2	14.6	7.1
Tol	18	1.4	2	16.5	5.2
Ani	17.8	4.4	6.9	17.5	4.4
PM7 D2 backbone	26.26	2.32	2.71	-	-
PM7 D2 sidechain	16.05	2.11	5.49	-	-

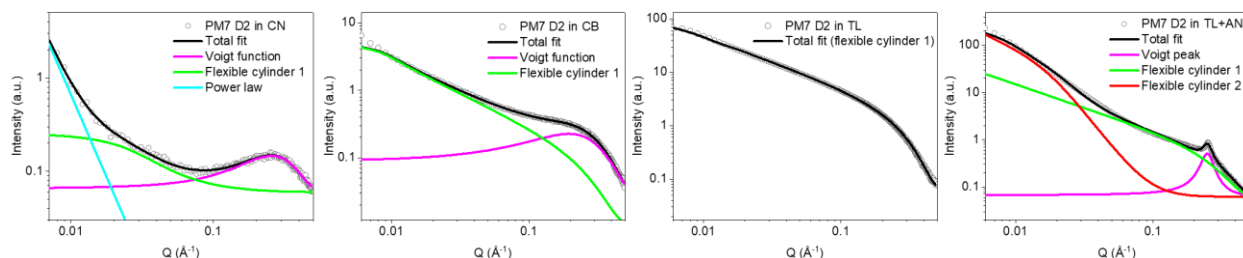


Supplementary Figure 3.4. Microscope image of 20 mg/mL solution of PM7 D2 polymer in a) pure anisole and b) in 20% toluene and 80% anisole mixture.

Supplementary Note 1. Details of fitting the solution SAXS profiles.

The solution scattering profiles of PM7 D2 in various solvents were fit using the combination of flexible cylinder, power law, and pseudo-Voigt peak as previously demonstrated in similar conjugated polymer systems.^{1,2} As shown in Supplementary Figure 3.3, two flexible cylinder models were used to fit the scattering profiles for PM7 D2 in TL+AN, corresponding to polymer fibers and single polymer chains since the scattering profile for PM7 D2 in TL+AN clearly showed contributions from these two populations. The crystalline lamellar stacking peak in PM7 D2 in TL+AN, is also fit using the pseudo-Voigt peak function. For CN, CB, and TL only one flexible cylinder model was sufficient to fit the single polymer chain contributions since there is no Guinier knee corresponding to the cross section of fiber aggregates. In CN, however, power law model was added to include contributions from the power law scattering in the low Q region ($< 0.01 \text{ \AA}^{-1}$) and pseudo-Voigt function to fit the structure factor peak at high Q region ($0.1 < Q < 0.5 \text{ \AA}^{-1}$). For CB and TL, the power law scattering is not clearly observed, so the model only includes contributions from one flexible cylinder model and pseudo-Voigt peak when needed.

To avoid parameter correlations when multiple functions are present, we fixed the length and radius parameters in the flexible cylinder model for CN, CB, and TL+AN cases based on the fitting parameters obtained PM7 D2 in TL, which only uses the flexible cylinder model without contributions from different functions. The length of flexible cylinder 2 for PM7 D2 in TL+AN corresponding to the length of fibers was also fixed to 100 nm since the length scale is beyond Q range visible in SAXS.



Supplementary Figure 3.5. Deconvolution of model fitting for the solution scattering profiles of PM7 D2 in various solvents

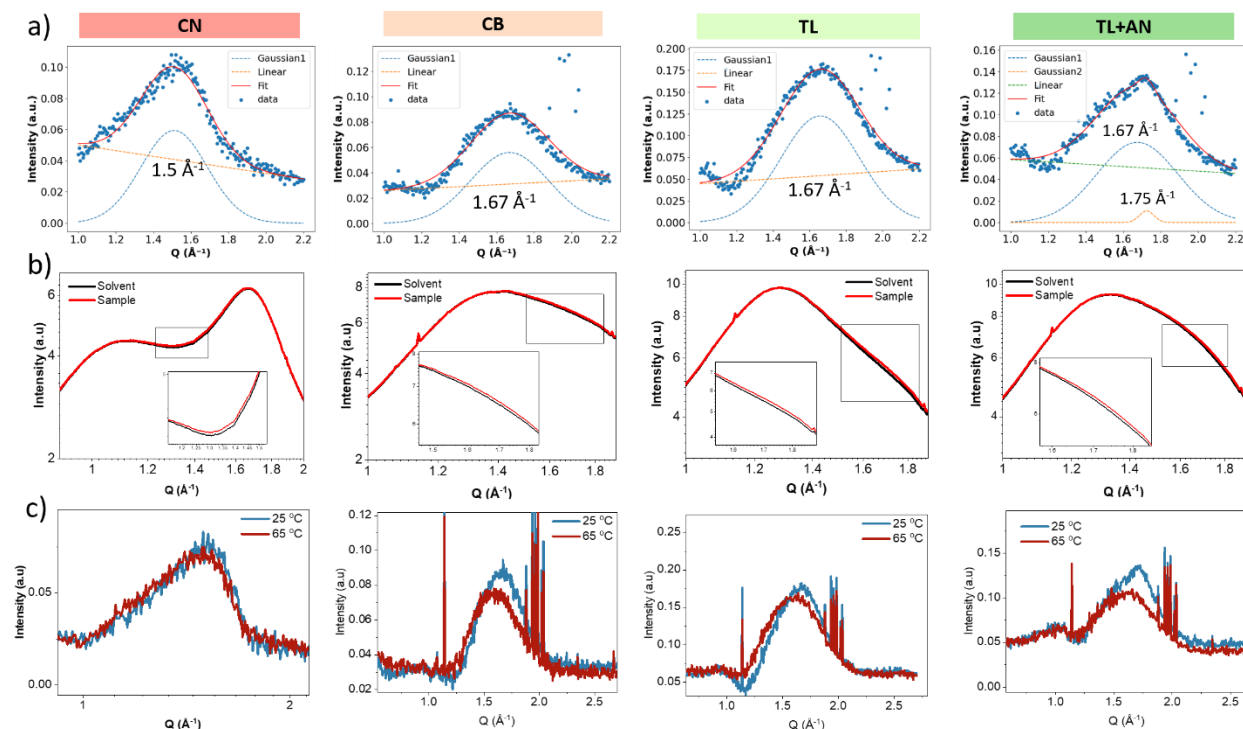
Supplementary Table 3.3. Fitting parameters obtained from SAXS.

Parameters	CN	CB	TL	TL+AN
L_1 (nm)	58.2*	58.2*	58.2 ± 1.0	58.2*
L_{p1} (nm)	3.8 ± 1.6	18.6 ± 5.5	$\gg R_1$	$\gg R_1$
R_1 (Å)	6.78*	6.78*	6.78 ± 0.03	6.78*
Power	3.9 ± 0.5	-	-	-
q (Å ⁻¹)	0.258 ± 0.002	0.195 ± 0.001	-	0.249 ± 0.001
$FWHM$	0.27 ± 0.04	0.31 ± 0.01	-	0.057 ± 0.001
w	0	0.57 ± 0.18	-	1
L_2 (nm)	-	-	-	100*
L_{p2} (nm)	-	-	-	$\gg R_2$
R_2 (nm)	-	-	-	5.3 ± 0.1
Polydispersity	-	-	-	1.00 ± 0.03

*Values were fixed during fitting

Description of the fitting parameters:

Parameters	Description
L_1	Length of flexible cylinder 1, corresponding to the length of polymer chains
L_{p1}	Persistence length of flexible cylinder 1, corresponding to the persistence length of polymer chains
R_1	Radius of flexible cylinder 1, corresponding to the radius of polymer chains
Power	Slope from the power law model
q	Location of the pseudo-Voigt peak
$FWHM$	Full width half maximum of the pseudo-Voigt peak
w	Lorentzian fraction of the pseudo-Voigt peak
L_2	Length of flexible cylinder 2, corresponding to the length of fibers
L_{p2}	Persistence length of flexible cylinder 2, corresponding to the persistence length of fibers
R_2	Radius of flexible cylinder 2, corresponding to the radius of fibers
Polydispersity	Polydispersity in the radius of fibers

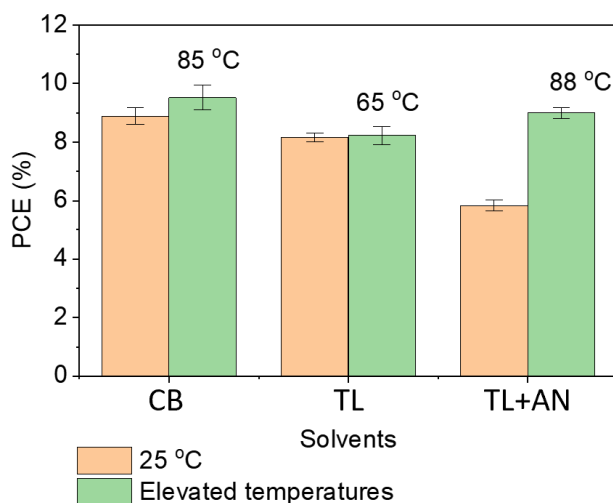


Supplementary Figure 3.6. Wide angle X-ray scattering (WAXS) results for PM7 D2 solutions in a) CN, CB, TL, and TL+AN, with solvent and empty cell contributions subtracted. All solutions contain scattering features between 1.5 – 1.8 $\text{\AA}^{-1}$, corresponding to backbone/side chain interactions due to aggregation. b) Raw solvent and sample WAXS scattering profiles (empty cell contribution is subtracted). c) Comparison of WAXS profiles of PM7 D2 solutions at 25 °C and 65 °C.

Supplementary Table 3.4. Blade coating conditions used for device fabrication.

Solvents	Coating temperature (°C)	Vapor pressure (bar)*	Coating speed (mm/s)
CN	122	0.0147	0.05
CB	25	0.0147	3
TL	25	0.038	1
TL+AN	25	0.0147	7

*Vapor pressures were determined using the data provided by the National Institute of Standards and Technology. For TL+AN mixture, the vapor pressure was obtained from constructing the vapor liquid equilibrium plot using the CHEMCAD software.

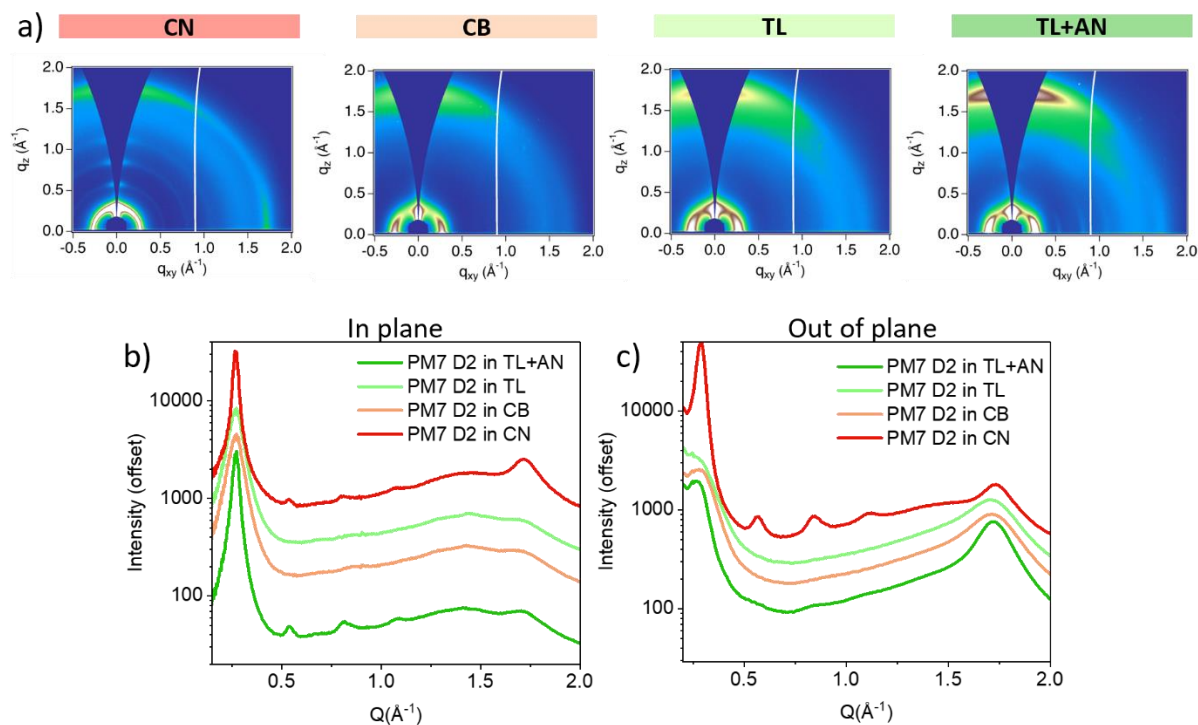


Supplementary Figure 3.7. Power conversion efficiency (PCE) of PM7 D2:ITIC-4F devices fabricated at different coating temperatures cast from CB, TL, and TL+AN, respectively. The elevated coating temperatures are selected to match the vapor pressures of the casting solvent.

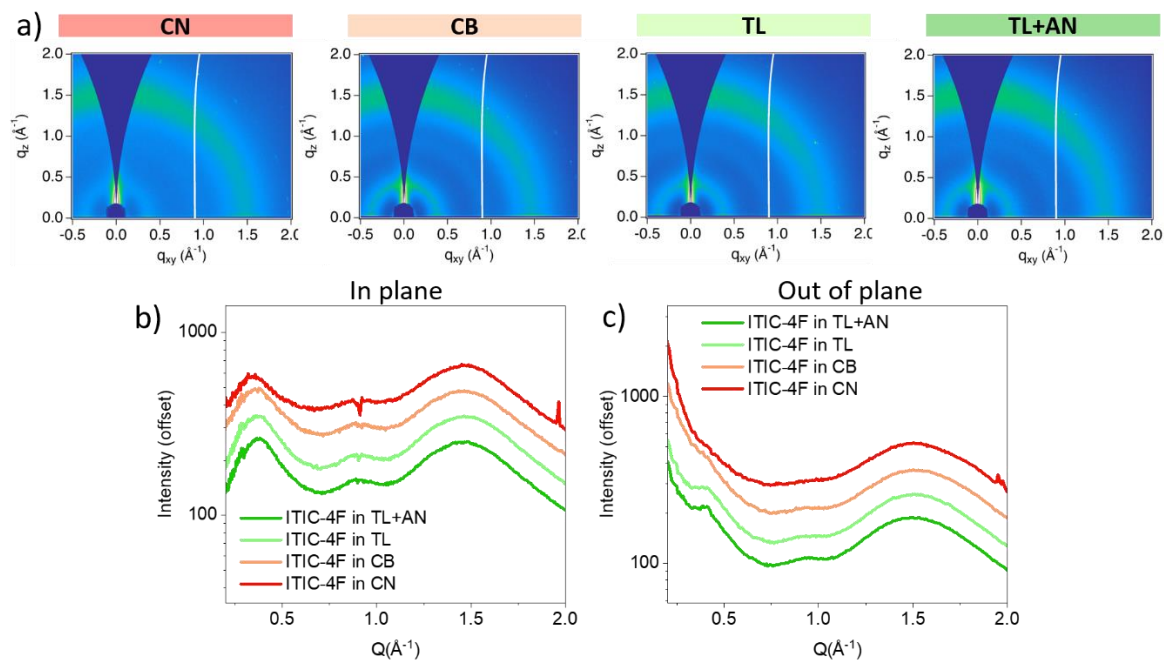
Supplementary Table 3.5. Blade coating conditions used for device fabrication (elevated coating temperatures)

Solvents	Coating temperature (°C)	Vapor pressure (bar)*	Coating speed (mm/s)
CB	85	0.235	15
TL	65	0.235	10
TL+AN	88	0.235	15

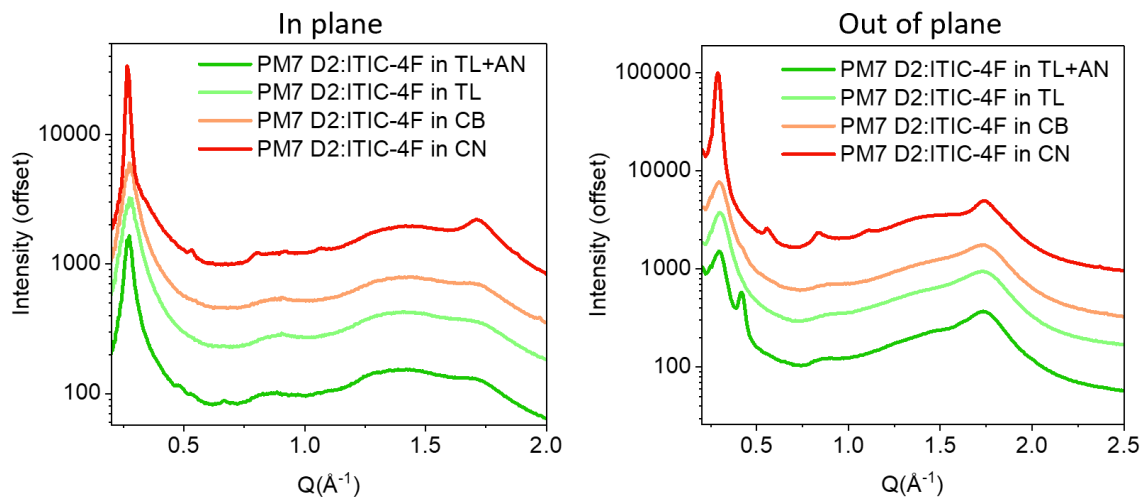
*Vapor pressures were determined using the data provided by the National Institute of Standards and Technology. For TL+AN mixture, the vapor pressure was obtained from constructing the vapor liquid equilibrium plot using the CHEMCAD software.



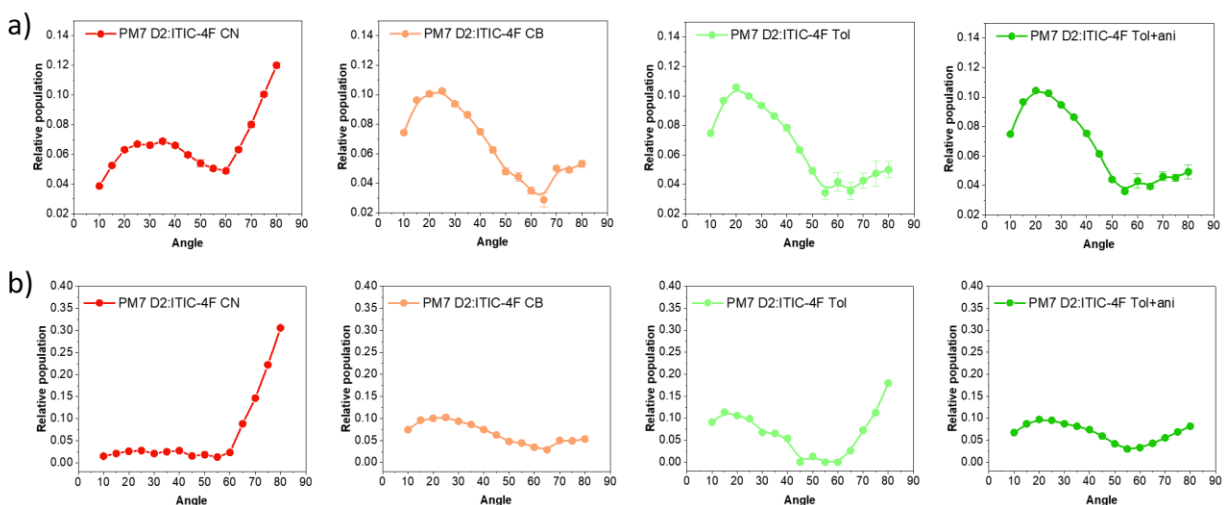
Supplementary Figure 3.8. a) GIWAXS patterns of the PM7 D2 neat films blade coated from CN, CB, TL, and TL+AN solvents, respectively; b) In-plane linecut profile and c) out-of-plane linecut profiles of the GIWAXS patterns.



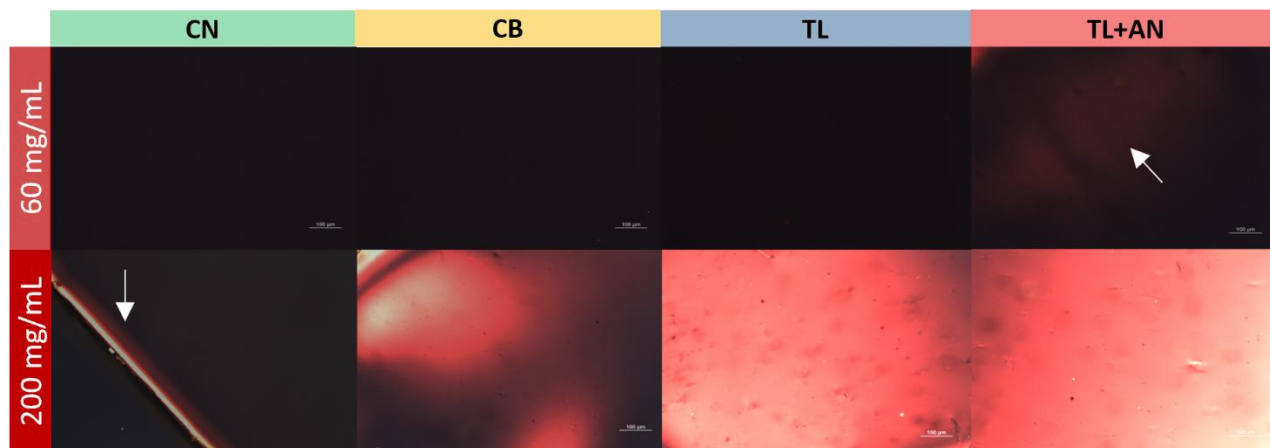
Supplementary Figure 3.9. a) GIWAXS patterns of the ITIC-4F neat films blade coated from CN, CB, TL, and TL+AN solvents, respectively; b) In-plane linecut profile and c) out-of-plane linecut profiles of the GIWAXS patterns.



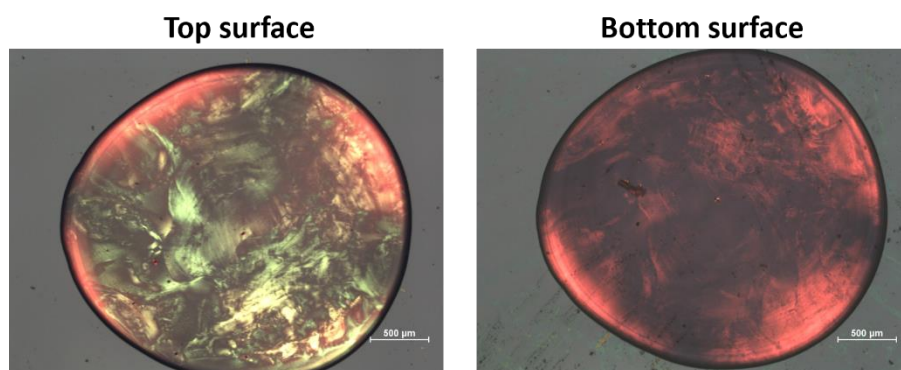
Supplementary Figure 3.10. In plane and out-of-plane linecut profiles for PM7 D2:ITIC-4F blend films cast from various solvents.



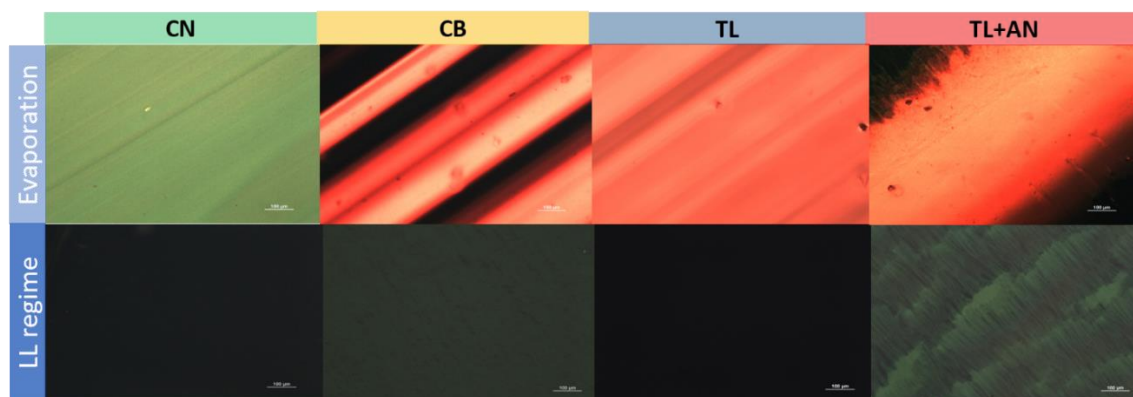
Supplementary Figure 3.11. Pole figures of PM7 D2:ITIC-4F blend film cast from various solvents obtained a) at the bulk of the sample using grazing incidence angle of 0.14° and b) at the air-liquid interface using grazing incidence angle of 0.1° .



Supplementary Figure 3.12. CPOM images of PM7 D2 solutions at concentrations of 60 and 200 mg/mL.



Supplementary Figure 3.13. CPOM images of top and bottom surface of PM D2 film, drop cast from CN at 122 °C.



Supplementary Figure 3.14. CPOM images of neat PM7 D2 printed at low coating speeds around 0.06-0.01 mm/s (evaporation regime) and high speeds around 3-5 mm/s (Landau-Levich regime). The regimes were determined by the film thickness dependence with coating speeds.

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Chapter 4

Lyotropic liquid crystalline phase mediated assembly of donor polymer D18 enhances the device performance and stability of organic solar cells⁴

4.1 Introduction

Organic solar cells (OSCs) are a promising cost-effective alternative to silicon solar cells owing to their ease of fabrication using solution-processing techniques.^{1,2} Their tunable molecular structures, inherent flexibility and transparency also make them desirable for use in many emerging applications.^{3,4} Over the past decade, design of novel photovoltaic materials have rapidly progressed OSCs to yield a commendable power conversion efficiency (PCE) exceeding 19 %.^{5,6} Nonetheless, one of the main bottlenecks remains the difficulty in controlling the bulk heterojunction (BHJ) morphology, particularly when using scalable coating techniques.^{7–9} BHJ based OSCs are comprised of an interpenetrating mixture of donor and acceptor materials, which form nanoscale phase separated morphology with crystalline donor and acceptor phases for efficient charge generation and transport.^{10–12} Other morphological parameters such as vertical phase separation, molecular orientation of the donor and acceptor materials can also influence the device performance.^{13–15} These morphological parameters depend strongly on the coating conditions, often resulting in time-consuming trial-and-error based experiments to optimize the device performance of OSCs.^{16–18} Although high-throughput experimentations coupled with machine learning techniques show promise in alleviating these efforts,^{19–21} a more general understanding of the structure – property relationship remains to be elucidated.

⁴ The contents of this section appear in Khasbaatar, A., Williams, J. S.; Fernando, P. S.; Damron, A.; Zhu, C.; Gann, E.; Lee, J-H., Diao, Y., Lyotropic Liquid Crystalline Mediated Assembly of Donor Polymer D18 Enhances the Device Performance and Stability of Organic Solar Cells. *To be submitted*

Central to understanding the structure – property relationship is the molecular assembly of conjugated systems, particularly conjugated polymers, from solution to solid-state.²² During solution processing, conjugated polymers can undergo complex concentration-dependent hierarchical self-assembly that governs the film morphology and optoelectronic properties of organic electronic devices.^{22–24} Even at low concentrations, conjugated polymers can form various types of primary aggregates in their solution-state depending on their molecular conformation, molecular weight, and solvent environment.^{18,25–27} Besides forming primary solution aggregate structures, they may further assemble into secondary self-assembled structures such as lyotropic liquid crystalline mesophases and gel-like networks.^{23,28,29} Studies suggest that liquid crystalline mediated assembly of conjugated polymers enhances film alignment, crystallinity, and affects molecular orientation, particularly at the air-liquid interface.^{30,31} Recent works on OSCs also indicate that thermotropic liquid crystalline molecules enhance the film crystallinity of OSCs, resulting in devices that are more tolerant to variations in film thickness.^{32,33} Nevertheless, thermotropic liquid crystalline phase transitions occur at temperatures far above the typical annealing temperature of OSCs, posing a challenge for their use in high-performance systems. On the other hand, lyotropic liquid crystalline assembly of conjugated polymers occurs simply upon increasing solution concentration, which is inherent to solution processing. However, studies on the lyotropic liquid crystalline assembly of conjugated polymers are mainly conducted on neat films, making it less relevant for BHJ based OSCs. Therefore, the purpose of this work is to elucidate the impact of polymer assembly pathways on the blend film morphology and device performance of OSCs.

Herein, we investigated the concentration-dependent assembly of conjugated donor polymer D18 and its dependence on the coating conditions by employing meniscus-guided coating,

which is a prototype scalable coating method. We found that D18 forms semicrystalline fiber aggregates upon increasing the solution concentration and further assemble into an achiral lyotropic LC phase before further transitioning into a chiral LC phase. We also demonstrate that the assembly pathway is strongly determined by the coating regime to give two distinct assembly pathways: (1) lyotropic liquid crystalline mediated assembly in the evaporation regime and (2) random fiber aggregation in the Landau-Levich regime. The extent of these assembly pathways is strongly determined by the boiling point of the processing solvent, which can kinetically quench the assembly process. Regardless of the solvent, we report that the lyotropic liquid crystalline mediated pathway enhances the crystallinity of the donor polymer and reduces the phase separated domain sizes to yield improved device performance and stability.

4.2 Results and discussion

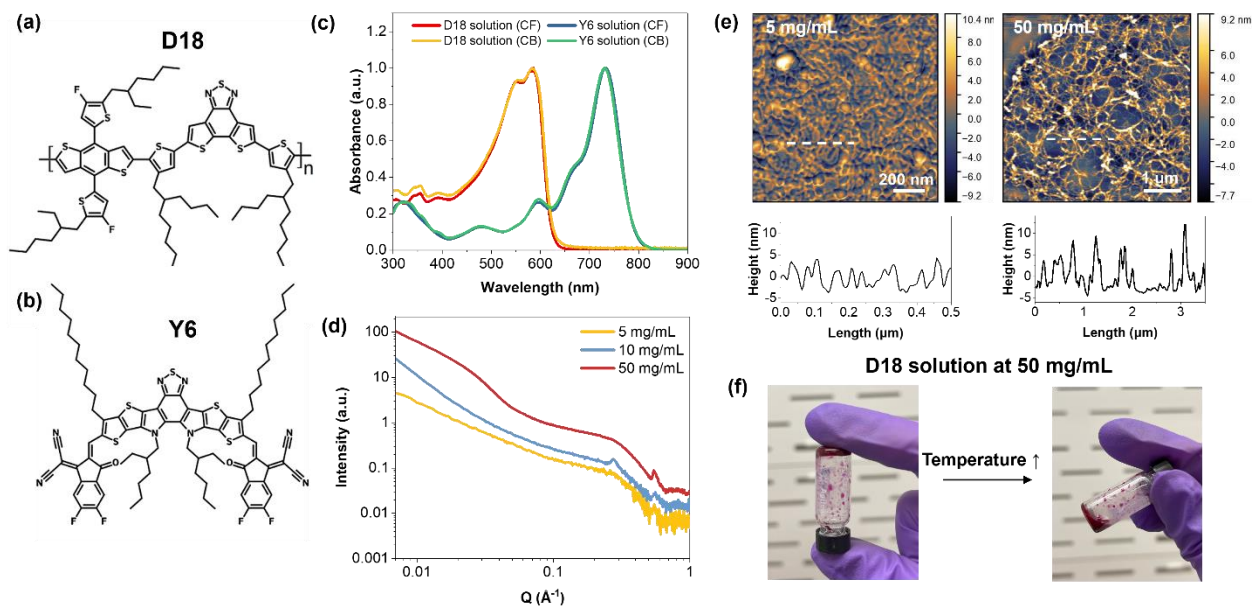


Figure 4.1. (a) Molecular structures of the donor polymer D18 and (b) small molecular acceptor Y6 used in this study. (c) UV-Vis spectra of D18 and Y6 solutions at 5 mg/mL and 8 mg/mL respectively prepared using both chlorobenzene and chloroform. (d) Concentration-dependent SAXS profiles of D18 solution in chlorobenzene. (e) Freeze-dried AFM height images of 5 and 50 mg/mL D18 solution from chlorobenzene. (f) Photo images of 50 mg/mL D18 solution in chlorobenzene at room temperature before and after heating to 85 °C.

Figure 4.1a, b shows the molecular structures of the conjugated donor polymer D18 and the small molecule acceptor Y6 system used in this study. First reported by Liu *et al.*, this system has been extensively investigated in the field to obtain the record efficiency exceeding 19% in single junction solar cells.^{5,6} Recently, D18 polymer was also used to make large area OSC module (15.64 cm²) based on ternary PM6:D18:BTP-eC9 system to give a PCE of 16.70 %, demonstrating its potential for commercial applications.³⁴ Nevertheless, the concentration-dependent assembly pathway of D18 and how it influences the BHJ morphology and device properties of OSCs, particularly when using scalable coating methods, has not been investigated. Thus, we begin our investigation by first studying the solution-state aggregation of D18. **Figure 4.1c** shows the UV-Vis spectroscopic measurements of D18 and Y6 solutions in chlorobenzene and chloroform, in which there is no difference in the spectra observed depending on the solvent (**Figure 4.1c**). In both solvents, D18 adopts J-type aggregation behavior with clear 0-0 and 0-1 vibronic peaks, indicative of its highly ordered polymer conformation in the solution-state.³⁵ To determine the exact nature of the polymer solution aggregates, we employed Small Angle X-ray Scattering (SAXS) measurements on D18 solutions at various concentrations as shown in **Figure 4.1d**. The scattering profile of the initial solution at 5 mg/mL is mainly featureless with a Porod decay of -1 in the Q range of $Q < 0.1 \text{ \AA}^{-1}$, indicating rod like polymer chains, consistent with its strong J-aggregation behavior. At a higher Q range, a weak structure factor contribution corresponding to weak lamellar stacking/sidechain association of the rigid polymer chains is observed. The existence of this structure factor peak indicates that the polymers are aggregated in the solution-state, rather than existing as non-interacting single polymer chains.³⁶ Furthermore, freeze-dried AFM imaging of D18 at 5 mg/mL concentration (**Figure 4.1e**) reveals polymer network-like structure as previously observed in other conjugated polymer systems.^{18,26}

As the solution concentration increases to 10 mg/mL, the Porod slope in the low Q region ($Q < 0.03 \text{ \AA}^{-1}$) first increases to -2.3, indicating that the polymer chains become more aggregated to form a more distinct fractal/network structure.³⁷ Further increasing the solution concentration to 50 mg/mL leads to the formation of fibril aggregates as evidenced by the emergence of a new Guinier knee in the low Q region.¹⁸ Using the fibril aggregate model,³⁶ we found that the diameter of these fiber aggregates are $12.4 \pm 0.6 \text{ nm}$, consistent with the width of these fibers based on the AFM height image of the freeze-dried sample (see **Supplementary Figure 4.1** and **Supplementary Table 4.1** for the deconvolution of the model fits and the resulting parameters). We also observe that the solution becomes highly viscous and immobile at 50 mg/mL (**Figure 4.1f**) likely due to physical cross-linking/overlapping of the fiber aggregates in the solution-state.²⁸ Upon increasing the solution temperature, however, the solution becomes less viscous or more fluidic (**Figure 4.1f**) as the fiber aggregates start to dissolve at high solution temperatures (**Supplementary Figure 4.2**).

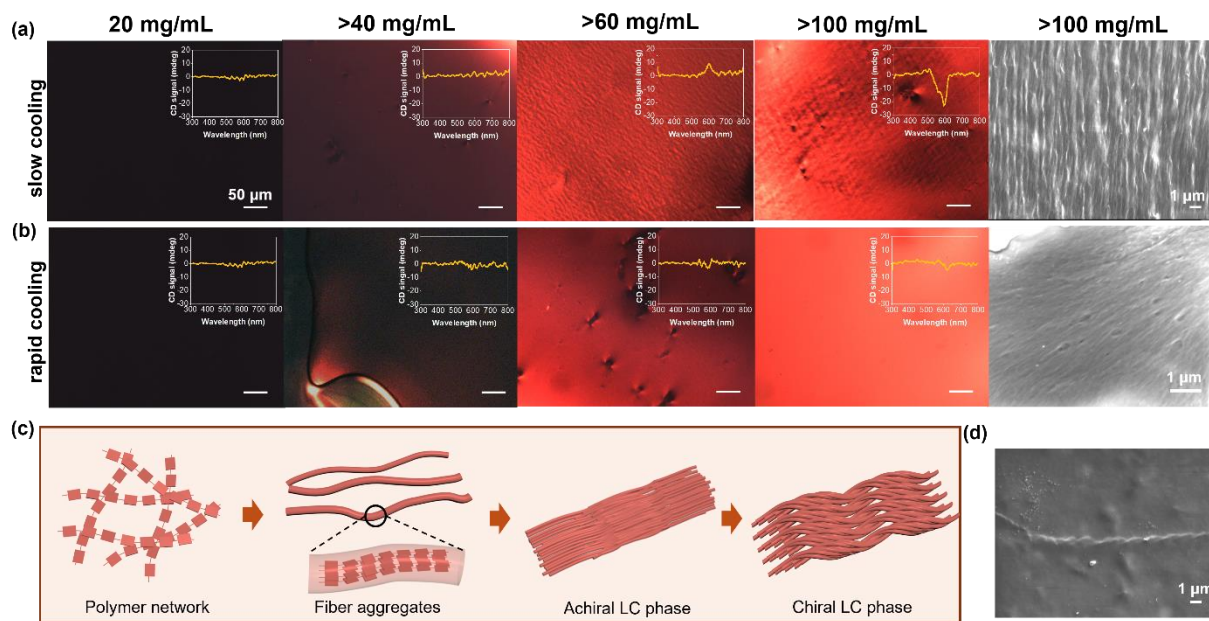


Figure 4.2. (a) CPOM images of D18 solutions in chlorobenzene at various concentrations (images were taken at the edge of the solutions, so the actual concentrations are likely higher than the

(**Figure 4.2. cont.**) concentrations indicated). The solutions were first heated to 100 °C to reach the isotropic phase and then cooled down to room temperature at a rate of 10 °C/min. (b) CPOM imaging of the same D18 solutions prepared by rapidly quenching the solution to room temperature from the isotropic phase. (c) SEM imaging of the freeze-dried 100 mg/mL solutions prepared from the slowly cooled versus the rapidly quenched solutions. (d) SEM imaging of a helical fiber found in a thick region of the slowly cooled solution sample. (e) Schematic representations of concentration-dependent assembly pathway of D18.

We further employed cross-polarized microscopy (CPOM) and circular dichroism (CD) spectroscopy to investigate the concentration-dependent assembly pathway of D18 in chlorobenzene at solution concentrations up to ≈ 100 mg/mL using the drop-and drying-method (chloroform solution studies show similar results as shown in **Supplementary Figure 4.3**). Due to the gelation/physical cross-linking of D18 fibers at high concentrations (**Figure 4.1f**), the solutions were first heated up to 100 °C to reach the isotropic phase and then cooled down to room temperature at a cooling rate of 10 °C/min before taking CPOM and CD measurements as shown in **Figure 4.2a**. Compared to the isotropic solution at 20 mg/mL, the solution at 40 mg/mL begins to display birefringent features, implying polymer alignment attributed to the emergence of a lyotropic liquid crystalline phase. Upon increasing the solution concentration to 60 mg/mL, a striped periodic pattern emerges along with a weak but apparent CD signal (in the inset of **Figure 4.2a**), which further increases to give a g-factor of 4×10^{-4} at 100 mg/mL. We note that this striped pattern resembles the twist-bent chiral LC phases observed in other systems.^{23,24,38,39} SEM imaging of the freeze-dried solution at 100 mg/mL suggests that this chiral LC phase is comprised of micron scale helical fibers (**Figure 4.2b**). A clearer image of the large helical fiber with a pitch length of 1.6 ± 0.2 μm is shown in **Figure 4.2d**, which was taken in the bulk region of the freeze-dried sample.

We demonstrate that these large-scale helical fibers are formed from the nanoscale semicrystalline fibers that first assemble into an achiral LC phase. We observed that the periodic striped phase emerges after the initial isotropic phase at high temperature forms a featureless

birefringent LC phase (without the stripe pattern) upon cooling. By rapidly quenching the solution to room temperature from the isotropic solution at high temperatures, we were able to preserve this featureless birefringent phase, which we found was achiral based on the CD measurements (**Figure 4.2b**). Freeze-dried SEM imaging of this achiral LC phase at 100 mg/mL reveals highly aligned nanoscale fibers (**Figure 4.2c**), which is clearly distinct from the micron-scale helical fibers formed in the chiral solution. Therefore, we believe that chiral liquid crystalline phase succeeds the formation of the achiral LC phase, in which the achiral nanoscale fibers twist and form the micron scale fibers in the chiral LC phase. The formation of the chiral liquid crystalline phase from achiral molecules has been previously reported in several conjugated polymers including PII-2T and DPP-based polymers, which has been attributed to their torsional backbone conformations leading to the twist-bent chiral LC phases.^{23,40} It is interesting to note that highly conjugated and stiff polymer such as D18 can also exhibit similar concentration-dependent chiral LC mediated assembly. We attribute this chiral emergence from an achiral LC phase of D18 to the semiflexible nature of the nanofibers, causing the fibers to undergo twist deformation and assemble into supramolecular helical fibers.

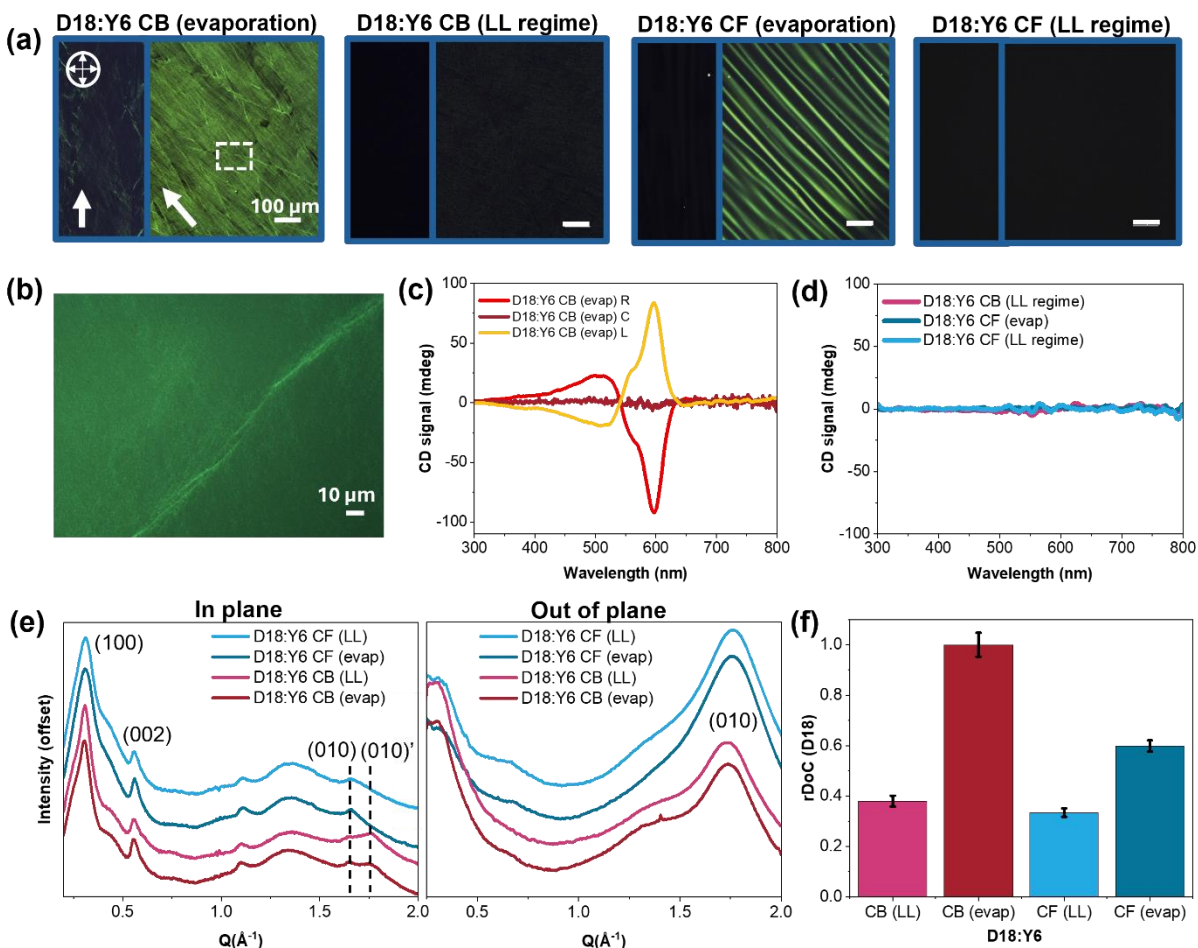


Figure 4.3. (a) D18:Y6 CB and D18:Y6 CF blend films coated in the evaporation and Landau-Levich (LL) regimes. (b) Zoomed in CPOM image of the highlighted region with dashed lines in (a) showing formation of large helical fiber in D18:Y6 CB film coated in the evaporation regime. (c) CD measurements of D18:Y6 CB coated in the evaporation regime taken at the right (R), center (C), and left (L) side of the film. (d) CD measurements of D18:Y6 CB coated in the LL regime and D18:Y6 CF coated in both evaporation and LL regimes. (e) In and out-of-plane sector profiles of the GIWAXS patterns for blend films. (f) relative degree of crystallinity (rDoC) comparison of the blend films based on the (200) peak from D18.

Although conjugated polymers can undergo complex multistep assembly, film deposition conditions can drastically alter the assembly pathways of conjugated polymers.⁴⁰ In particular, the coating regime during meniscus-guided coating plays an important role in dictating the assembly of conjugated polymers, and their resultant film morphology. Depending on the coating speed and film thickness relationship, the coating regimes can be either in the evaporation or in the Landau-Levich (LL) regime.⁴¹ In the evaporation regime, the coating speed is slow enough that the film

deposition is driven by the evaporation rate of the solvent. As a result, film thickness has an inverse relationship with the coating speed. In the LL regime, which occurs at high coating speeds, film deposition is determined by the viscous shear force imparted by the blade. We have previously shown that in between these two regimes occurs the transition regime, which results in the highest strain rate that can planarize the conjugated polymer backbone.⁴⁰ However, coating in the transition regime often results in extremely thin films < 50 nm, inappropriate for optimal performance of OSCs unless the solution concentration or blade angle is dramatically increased. We thus limit our coating regimes to either evaporation and LL regimes using both CB and CF as the main solvents.

Figure 4.3a shows the CPOM images of the D18:Y6 blend films coated in two different regimes using CF and CB, respectively (the coating conditions are the same as the optimal device fabrication conditions). When coated in the evaporation regime at low coating speeds, D18:Y6 films give highly birefringent films in both solvents, implying the formation of LC mediated pathways. However, when coated in the LL regime at high coating speeds, we observe that the blend films become isotropic without clear birefringent features, indicating that the LC assembly is likely suppressed. Furthermore, the zoomed in CPOM image of the blend film deposited from CB solution in the evaporation regime suggests the existence of large helical fibers (**Figure 4.3b**), confirming the LC mediated assembly of D18. Interestingly, **Figure 4.3c** shows that the CD signal at the center of the film is weakly chiral whereas the left- and right-hand side of the films exhibit g-factors of 0.004 and -0.004, representing left and right-handed helical fibers. This handedness inversion can be attributed to the flow direction during mesophase formation (see **Supplementary Figure 4.4** for the CPOM image of the films at the edge), which provides an asymmetric driving force for handedness selection.⁴² Without such asymmetric flow towards the edge of the film (e.g.

center of the film), it is expected that both handedness have an equal probability, thereby resulting in an overall weak CD signal.⁴³ When coated in the LL regime or using CF as the main solvent, no CD signal was observed in any these blend films (**Figure 4.3d**), although the film is highly birefringent when coated in the evaporation regime. We believe that the assembly is kinetically quenched due to the low boiling point of CF, which leads to insufficient time for the chiral LC formation.

Using grazing incident wide angle X-ray scattering measurements (GIWAXS), we further demonstrate that the assembly pathway has a strong correlation with the degree of crystallinity of the blend films. Shown in **Figure 4.3e** is the in and out-of-plane sector profiles of the 2D GIWAXS patterns obtained for the blend films (**Supplementary Figure 4.5a**). Based on these plots, it is apparent that the blend films exhibit strong lamellar (010) and π - π stacking (100) peaks in the in-plane and out-of-plane directions, respectively. The in-plane direction, there are distinct (010) and (010)' peaks from D18 and Y6, respectively, corresponding to the π - π stacking distances of 3.8 and 3.6 Å. In the out-of-plane direction, however, there is only one (010) peak likely due to the convolution of the two peaks. Besides the lamellar and π - π stacking peaks, we also observed a (002) peak corresponding to the backbone ordering of D18 in the in-plane direction.⁴⁴ This peak is also present in the neat D18 films (**Supplementary Figure 4.5b**) as well as in the 50 mg/mL D18 solution based on our SAXS measurements (**Figure 4.1d**). To compare the crystallinity of the blend films, we determined the relative degree of crystallinity (rDoC) using this backbone ordering peak since the π - π stacking peaks are too convoluted to uniquely separate D18 and Y6 contributions. The rDoC of the films were obtained by integrating the geometrically corrected intensities of the (002) peak.⁴⁵ The comparison of the rDoC values reveals correlation with the assembly of D18 (**Figure 4.3f**). Regardless of the solvent, films formed via the LC mediated

assembly in the evaporation regime yield more crystalline films, with those coated from CB exhibiting the highest degree of crystallinity. In contrast, films coated in the LL regime result in low degree of crystallinity, which is consistent with their featureless CPOM images.

From neat film GIWAXS measurements (**Supplementary Figure 4.6** and **Supplementary Figure 4.7**), we also report that the coating regime has a minimal influence on the crystal size/paracrystallinity of the neat films as the full width half maximum of the (010) and (100) peaks remain unchanged regardless of the printing regime. This suggests that the improved degree of crystallinity in blend films formed via the lyotropic LC mediated pathway is mainly due to the formation of the increasing number of crystalline domains. We also note that solvent has a drastic impact on the FWHM of the (010) and (100) peaks and the molecular orientation, which have been reported to make the D18:Y6 based OSCs highly sensitive to the processing solvent.

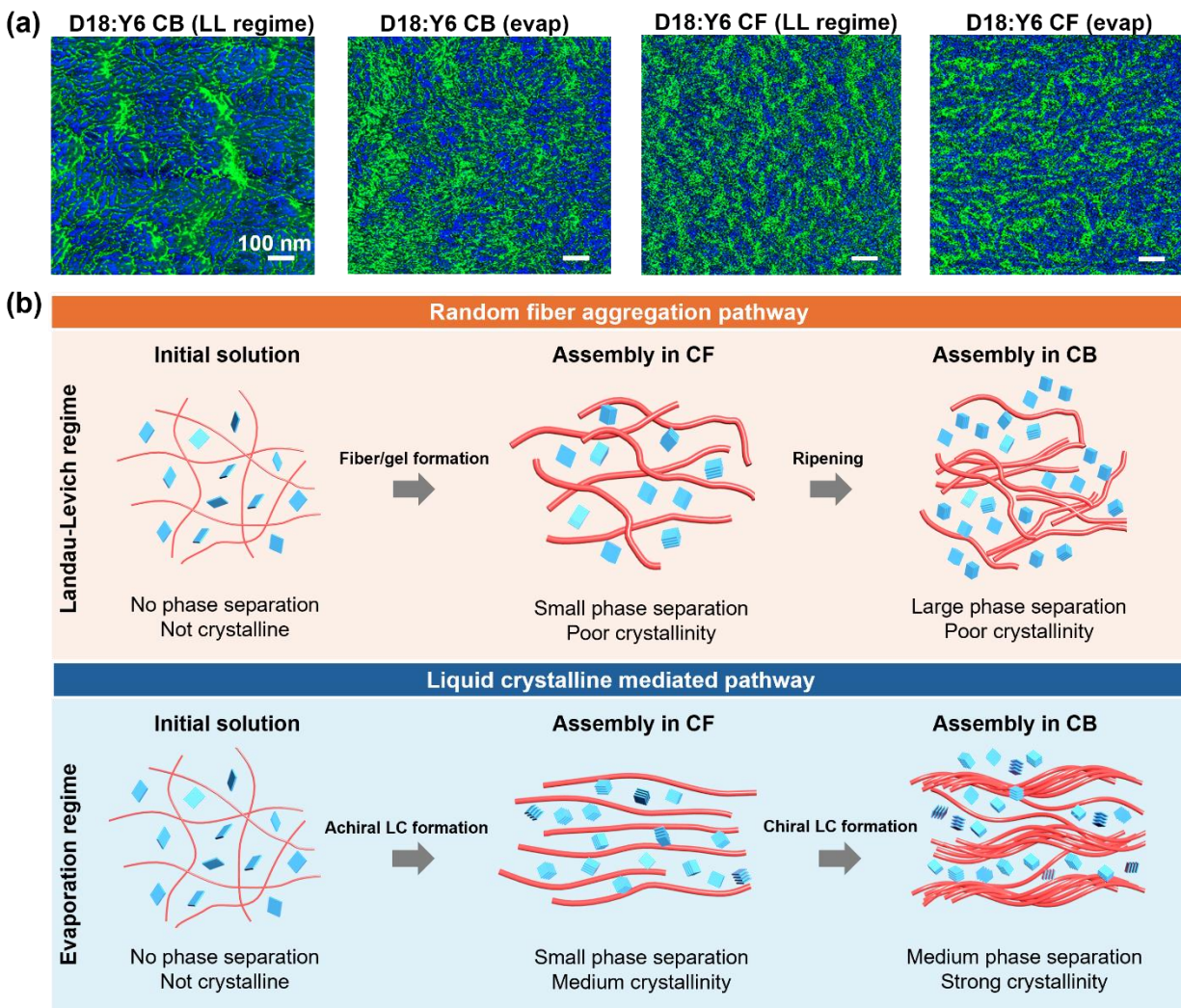


Figure 4.4. (a) Photo-induced Force Microscopy (PiFM) images of the blend films where the green and blue region represents the donor and acceptor domains, respectively. (b) Proposed assembly pathways of D18 in the blend solution depending on the printing regimes. In the LL regime, D18 undergoes random fiber aggregation pathway whereas in the evaporation regime, it undergoes liquid crystalline mediated assembly. Solvent determines the extent of assembly pathways in both cases, in which using CF results in kinetically quenched assembly with small phase separation and poor to medium crystallinity depending on the coating regimes. Using CB extends the film deposition time, leading to large scale phase separation.

Next, we investigated how the phase-separated morphology depends on the coating conditions using Photo-induced Force Microscopy (PiFM). PiFM is a relatively novel scanning probe technique, which combines AFM with a tunable infrared (IR) laser for imaging the blend films of OSCs with chemical specificity.^{46,47} Unlike IR-based AFM, PiFM is conducted in

noncontact mode, producing high-resolution measurements in the sub-10 nm range under ambient conditions.⁴⁶ In recent years, PiFM has been successfully used in imaging the nanoscale phase-separated blend film morphology of OSCs, enabling direct observation of the complex phase segregated BHJ morphology.^{48–50} **Figure 4.4a** shows the false color overlayed PiFM images of the blend films (individual PiFM images representing only donor and acceptor domains before overlaying are provided in **Supplementary Figure 4.8**). The green and blue regions represent the donor and acceptor materials, respectively, each probed at wavelengths of 823 cm⁻¹ and 1437 cm⁻¹ based on the IR spectra on the neat films (**Supplementary Figure 4.8**). We note that the PiFM spectra of the neat films shown in **Supplementary Figure 4.8** resembles the bulk material spectra obtained from the Fourier transform infrared (FTIR) spectroscopy (**Supplementary Figure 4.8**).

These PiFM images suggest that the phase separated morphology depends intimately on the solvent and coating regimes. When coated in the LL regime from CB, D18:Y6 forms a blend morphology mainly dominated by Y6. In contrast, coating in the evaporation regime drives the aggregation of D18 likely facilitated by the lyotropic LC formation, reducing the large Y6 domains. The most drastic change occurs when changing the solvent from CB to CF, which results in significantly reduced donor and acceptor phase separated domain sizes. This drastic change in the phase separated structures is attributed to the kinetically quenched morphology when processing from CF. Interestingly, the coating regime in the case of CF has a minimal effect on the blend film morphology, which is also confirmed with resonant soft X-ray scattering (RSoXS) measurements (**Supplementary Figure 4.9**).

The morphological characterization results allow us to predict the assembly pathways under different coating regimes as depicted in **Figure 4.4b**. In the LL regime, D18 undergoes random fiber aggregation as evidenced by the poor film crystallinity and alignment in the blend

films. If the assembly is allowed to proceed further by using CB, the fibers ripen further to give large D18 and Y6 domains. In contrast, D18 undergoes a lyotropic liquid crystalline mediated pathway, forming either chiral or achiral lyotropic LC phases depending on the extent of assembly also determined by the solvent drying time. Chiral LC formation drives further aggregation of D18, resulting in large phase separated domains. Compared to the random aggregation of D18, however, chiral LC formation reduces large Y6 domains formed in the blend film. If the assembly and aggregation of D18 are kinetically suppressed by CF, this results in smaller-scale phase separation that remains largely independent of the coating regime.

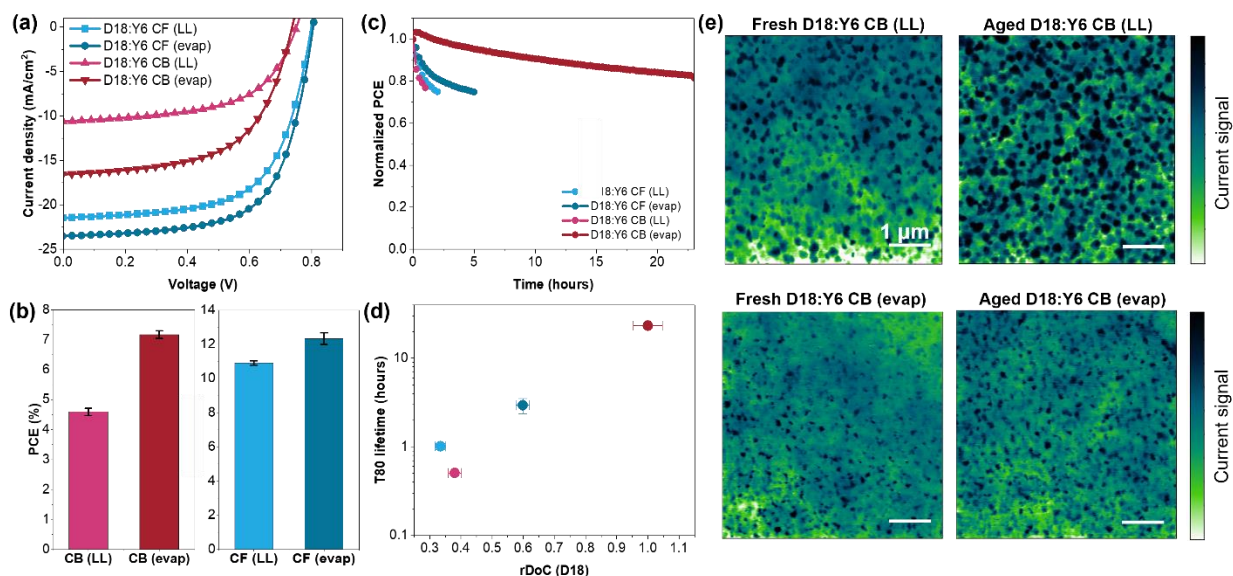


Figure 4.5. (a) Current density – voltage relationship plots and (b) device performance comparison of D18:Y6 system fabricated in the two regimes from two different solvents. (c) Device stability comparison of devices prepared from the four conditions. (d) T80 lifetime as a function of rDoC of D18 in the blend film. (e) c-AFM images of D18:Y6 blend films cast from CB in the evaporation and the LL regimes before and after light aging (1-sun) for 24 hours under N_2 atmosphere.

Finally, we fabricated OSC devices using the conventional architecture (ITO/PEDOT:PSS/D18:Y6/PDINN/Ag) to determine how different assembly pathways and their resultant film morphology impact the device performance and stability of OSCs. **Figure 4.5a** and **b** show the current density – voltage plots as well as the PCE comparison of the devices fabricated

from different solvents and coating regimes. Regardless of the solvent, devices coated in the evaporation regime outperform those coated in the LL regime, which is consistent with the improved film crystallinity owing to the LC mediated pathways. **Supplementary Figure 4.10** shows that this trend holds true for a wide range of film thicknesses. The difference, however, becomes more pronounced in the CB case since the phase separated morphology is strongly impacted by the LC pathway (**Figure 4.4a**). Furthermore, we tested the light stability of the devices fabricated from different conditions (**Figure 4.5c**) to find that the devices fabricated in the evaporation regime, particularly from CB, show enhanced light stability. Importantly, we find that the T80 lifetime, the time it takes the devices to reach 80 % of their initial performance, is correlated with the degree of crystallinity of the D18 in the blend film (**Figure 4.5d**). To understand the improved stability of devices fabricated from D18:Y6 CB in the evaporation regime, we first examined the UV-Vis spectroscopy of the fresh and aged blend films to determine if degradation occurs due to chemical changes. However, the UV-Vis spectra of the blend films before and after light aging remained unchanged (**Supplementary Figure 4.11**), indicating that there is no significant chemical degradation in D18:Y6 under a nitrogen atmosphere. When comparing the fresh and aged blend films using conductive atomic force microscope (c-AFM) imaging, however, we observed the formation of large Y6 domains in the aged D18:Y6 CB blend films coated in the LL regime. In contrast, the film coated in the evaporation remains relatively unchanged. We attribute the more stable blend morphology of the evaporation regime coated films to the enhanced crystallinity due to LC mediated assembly pathway of D18.

4.3 Conclusion

In summary, we reported that the D18 polymer undergoes lyotropic LC mediated assembly upon increasing concentration, resulting in both achiral and chiral LC phases. By employing

extensive film morphology characterization, we further demonstrated that the assembly pathway of D18 during solution processing depends on the coating regimes to give (1) lyotropic LC mediated assembly in the evaporation regime and (2) random fiber aggregation pathway in the LL regime. The crystallinity of the D18 phase in the blend film is greatly enhanced by the LC mediated assembly, yielding improved OSC performance and stability. We also show that using CF as the main solvent kinetically suppressed the assembly pathway of D18, leading to small phase separated domains, which do not depend significantly on the coating regimes. On the other hand, the blend film morphology cast from CB solution depends strongly on the coating regimes, resulting in large Y6 domains when coated in the LL regime, which is reduced by the formation of lyotropic LC phase formation of D18 upon coating the blend films in the evaporation regime.

4.4 Experimental methods

Materials

The materials used in this work D18 (MW = 74,586 kDa, PDI = 2.38), Y6 (purity > 98 %), PDINN (purity > 98 %), and PEDOT:PSS (Al 4083) were purchased from Ossila, Inc. Chlorobenzene (anhydrous, ≥ 99.8 %) and chloroform (≥ 99.8 %) were purchased from Sigma Aldrich.

UV–Vis Spectroscopy

UV–vis (Cary 60 UV–Vis, Agilent) spectroscopy was used to measure the absorbance of 5 mg/mL solutions of D18 and 8 mg/mL solutions of Y6 in chlorobenzene and chloroform solvents in a short path length of 10 μm quartz cell (Starna Cells). Before each solution measurement, a blank solvent measurement for each solvent was taken for background subtraction.

SAXS Measurement

SAXS experiments were performed at the 16-ID beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory to probe the Q ranges between $0.006 < Q < 3 \text{ \AA}^{-1}$ using multiple Pilatus detectors.⁸¹ The samples were measured using a 1.5 mm diameter quartz

capillary. Before performing solution scattering measurements, both empty cells and blank solvents were measured for proper background subtraction. For each measurement, 10-20 repeated measurements were taken on various parts of the sample using X-ray energy at 13.5 keV with 1 s exposure time to avoid beam damage. The scattering profiles were then obtained by averaging the repeated measurements and subtracting the empty cell and blank solvent contributions using a Python package *py4xs* in Jupyter notebooks.⁸² The model fitting of the scattering profiles was performed using SASView program with dI data for weighting, Levenberg–Marquardt with 200 steps for the algorithm where the uncertainties are determined from the covariance matrix, and χ^2 values and the residuals plot were used as the goodness of fit metrics.

Freeze-Drying Method for Imaging the Solution-State Aggregates

Freeze-drying experiments were conducted to image the structure of aggregates in solution using AFM and SEM. The freeze-drying process involves rapid freezing of polymer solutions in liquid ethane and propane mixture (63 % propane and 37 % ethane) with a melting point followed by liquid nitrogen storage. The resulting frozen polymer solution is then quickly transferred to a Linkam stage at $-100\text{ }^{\circ}\text{C}$ under vacuum. The Linkam stage temperature is then slowly increased at a rate of $0.5\text{ }^{\circ}\text{C}/\text{min}$ to $-80\text{ }^{\circ}\text{C}$ (far below the melting points of chlorobenzene at $\text{mp} = -45\text{ }^{\circ}\text{C}$ and chloroform $\text{mp} = -63\text{ }^{\circ}\text{C}$) followed by 6–8 h of constant monitoring with cross-polarized microscopy to ensure sublimation of all solvent. The freeze-dried samples were then imaged by the Cypher AFM from Asylum Research using tapping mode.

Device Fabrication

OSCs were fabricated using the conventional architecture (glass/ITO/PEDOT:PSS/D18:Y6/PDINN/Ag). Before film deposition, $20 \times 15\text{ cm}$ ITO-patterned glass substrates (Ossila, Inc.) were cleaned with toluene, acetone, and isopropyl alcohol. The cleaned substrates were then dried with nitrogen and plasma treated (Harrick Plasma PDC-001-HP) for 6 min at 300 mT of dry air

and high power (30 W). To deposit the hole transporting layer, PEDOT:PSS solution was filtered with a 0.45 μm PTFE syringe filter before deposition. The filtered solution was deposited on the cleaned ITO substrates by spin-coating for 30 s at 4000 rpm in an ambient atmosphere, which resulted in an active layer thickness of $\approx 20\text{--}30$ nm measured by a Bruker Dektak XT profilometer. After spin-coating, the PEDOT:PSS layer was annealed at 150 $^{\circ}\text{C}$ for 20 min followed by slow cooling to room temperature for active layer deposition. The photoactive layer solution for all devices was prepared by dissolving D18 and Y6 at 1:1.6 (wt/wt) ratio in CB and CF without any additives. The resulting blend solution was stirred at 40 $^{\circ}\text{C}$ overnight and brought to room temperature and stirred for 2-3 hours before deposition by blade coating. The blend solutions were then blade coated using a blade angle of 25° and a solution volume of 3 μL for CB and 5 μL for CF. The film thickness corresponding to these optimal coating conditions was ~ 100 nm. After blade coating, 1 mg/mL PDINN solution in methanol was spin coated at 3000 rpm for 30 seconds, followed by Ag electrode deposition using Thermal Evaporator System from Angstrom Engineering.

Device Characterization

The current density (J - V) curves were characterized by using an automated Solar Cell I-V Test System (Ossila) under AM 1.5G illumination (100 mW/cm) with a class AAA solar simulator from Newport under glovebox-free or ambient environment. Before each test, the solar simulator was calibrated by reference single-crystal Si cells (Sciencetech). A total of eight devices were tested under each condition. The active area of all devices is 0.04 cm^2 . For calculating the device performance, mismatch factor was not applied.

Solution characterization using CPOM

Solution characterization under CPOM was performed by sandwiching the polymer solutions in between two microscope glass coverslips placed on a Si wafer during the CPOM measurements

using the reflection mode. High concentration solutions were obtained by the drop and dry method,⁸³ where the concentration of the pristine solution is increased by drying a certain amount of solution and then adding a 1 μL of solution to the dried droplet and mixing the solution by shearing with the microscope cover glasses to increase the concentration. For instance, 200 mg/mL solution was achieved by drying 9 μL of 20 mg/mL solution and adding 1 μL solution to increase the concentration of 20 mg/mL solution by ten-fold. The solution samples then underwent thermal annealing to 100 $^{\circ}\text{C}$ reach the isotropic phase and then cooled down to room temperature at 10 $^{\circ}\text{C}/\text{min}$ (slow cooling) or rapidly quenched to room temperature before imaging under CPOM.

GIWAXS

GIWAXS measurements were performed at 7.3.3 beamline of the Advanced Light Source at Lawrence Berkeley National Laboratory using incident angles of 0.08° , 0.1° , 0.12° , and 0.14° with X-ray energy of 10 keV and a beam size of 30 x 50 μm . All samples were placed in a helium chamber for measurement. For sample preparation, a Si wafer followed by the photoactive layer deposition and thermal annealing the same way that all OSC devices were fabricated. From GIWAXS measurement, 2D scattering images were obtained and converted to 1D linecut profiles by using the beamline NIKA package in Igor Pro.⁸⁴ The Ewald sphere correction (missing wedge correction) for the 2D images were obtained using the WAXSTools plugin⁸⁵ in Igor Pro. The intensity of (010) peak at each χ angle was determined by gaussian peak deconvolution analysis. For rDoC analysis, geometrically corrected intensities of (002) peak from 5° sector cut profiles from the scattering patterns within the range of $10^{\circ} < \chi < 80^{\circ}$ were integrated and normalized by the total illumination volume (thickness and area of the sample).

RSoXS

RSoXS data were collected at the National Synchrotron Light Source II at the beamline 7-ID-1 in the transmission geometry. For sample preparation, the photoactive layer was blade coated and

thermally annealed using the same device fabrication conditions on a polystyrene sulfonate (PSS) film, which was spin coated from a 10% PSS solution in water. The PSS solution was stirred overnight at room temperature before depositing on a Si wafer substrate. After photoactive layer deposition, the sample on a Si substrate was immersed in water, which dissolved the PSS layer and separated the sample from the substrate. The sample was then picked up with a 1×1 mm, 100 nm-thick Si_3N_4 membrane supported on a 5×5 mm, 200 μm -thick Si frame (Norcada) and transferred into the vacuum chamber for RSoXS measurement. RSoXS measurements were performed at the beam energy from 270 to 290 eV with 5 s of exposure time per scan. The collected 2D scattering images were then converted into 1D profiles using the Nika package supported in the Igor Pro environment.

PiFM measurements

The PiFM measurements were conducted using VistaScope from Molecular Vista, Inc., using Pt coated silicon cantilevers from Molecular Vista. Before starting the measurement, the laser power was recorded within the IR range of $733 - 1960 \text{ cm}^{-1}$, followed by the laser alignment using a parabolic mirror to ensure that the laser was focused on the tip of the cantilever. The wavelength of the quantum cascade laser (QCL) used for alignment was tuned to 1750 cm^{-1} at an intensity of 20 % of the recorded maximum power. For PiFM imaging, a scan size of $1 \mu\text{m} \times 1 \mu\text{m}$ with a pixel size of 256×256 was used at a speed of 1 line/sec. During the measurement, 1437 and 823 cm^{-1} laser was tuned to <5% of the maximum power with 30 seconds duration per spectrum. To obtain PiFM spectra of the neat films, QCL laser was first turned off to obtain only AFM topography images using a scan size of $1 \mu\text{m} \times 1 \mu\text{m}$. Afterwards, point spectra were obtained based on the collected AFM topography images with an IR intensity of <5 % of the maximum power with 20-30 s duration per spectrum. The bulk FTIR spectra of neat materials using solid powder samples

were also obtained using Thermo Nicolet iS50 spectrometer as a comparison with the PiFM spectra on neat films.

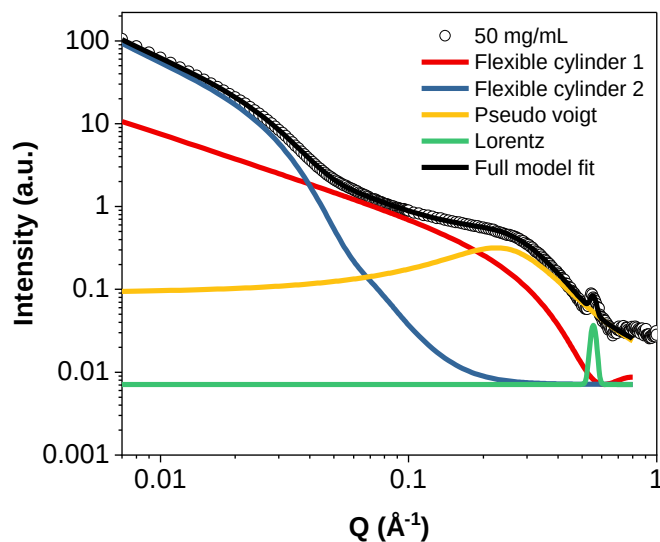
c-AFM measurements

Hole current maps were acquired using the AIST-NT SmartSPM instrument on the XploRA-Nano system by Horiba, Inc. BudgetSensors ContGB-G Au-coated conductive probes were utilized, with a manufacturer-specified spring constant of 0.2 N/m and a probe radius of less than 25 nm. A substrate bias voltage of +3 V was applied, and the probe-sample force ranged from 5-7 nN. To ensure hole-only transport, high work function top (Au probe) and bottom electrodes (PEDOT:PSS coated ITO glass) were used.

Film Thickness Measurements

Film thickness was measured by using the Bruker Dektak XT profilometry with 12.5 μm radius stylus. During thickness measurements, a stylus force of 3 mg and a scan range of 1000–2000 μm were used at a speed of 50 $\mu\text{m/s}$. For thickness measurements, a part of the film was removed with a cotton swab with toluene. The thickness measurements were repeated in three to five different positions to obtain the average and standard deviation.

4.5 Supporting information



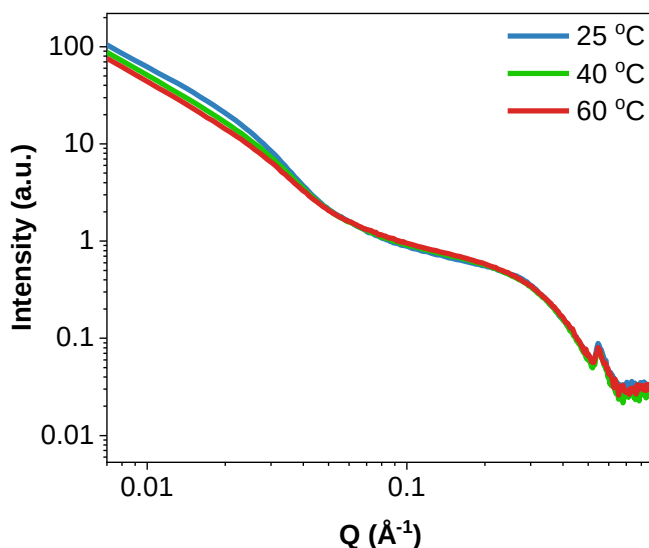
Supplementary Figure 4.1. SAXS deconvolution of the model fit using the double flexible cylinder model.

Supplementary Table 4.1. Model fitting results for 50 mg/mL solution of D18 in CB.

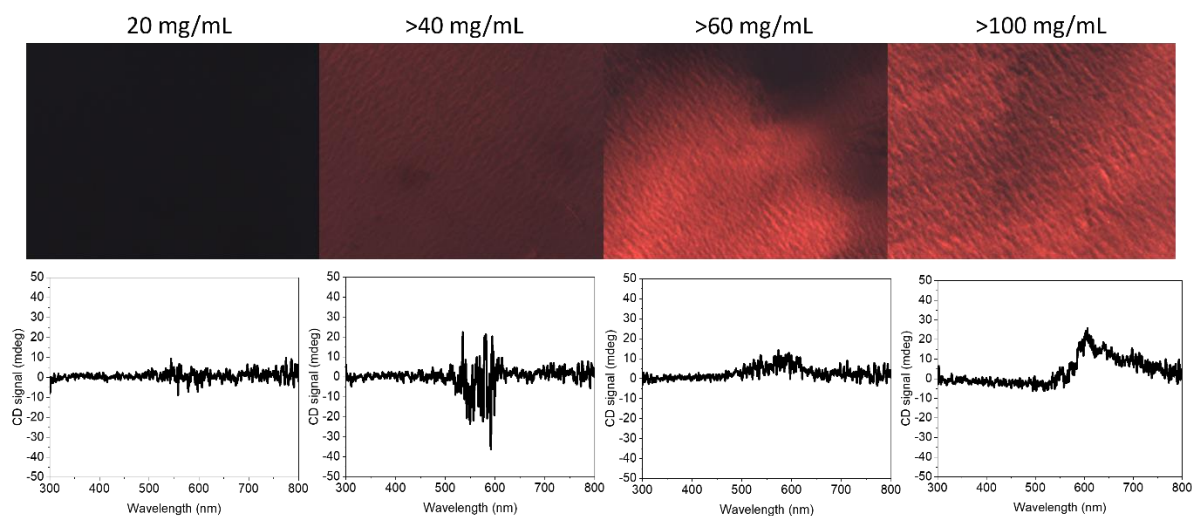
Parameters	Values
L_1 (nm)	100*
L_{p1} (nm)	$\gg R_1$
R_1 (Å)	6.2 ± 0.3
q_1 (Å ⁻¹)	0.218 ± 0.002
$FWHM_1$	0.258 ± 0.008
w_1	0
q_2 (Å ⁻¹)	0.554 ± 0.001
$FWHM_2$	0.019 ± 0.002
L_2 (nm)	100*
L_{p2} (nm)	46.1 ± 10.5
R_2 (nm)	6.3 ± 0.2
<i>Polydispersity</i>	0.28

Description of the fitting parameters:

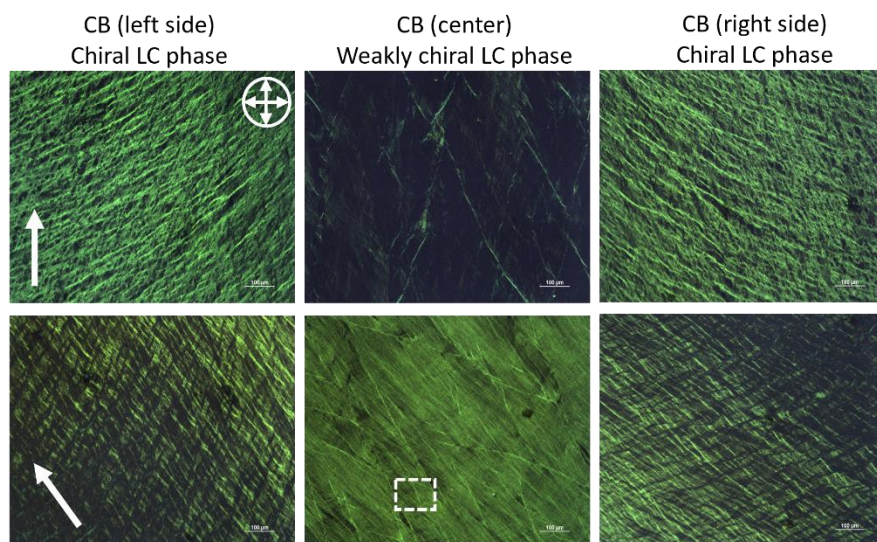
Parameters	Description
L_1	Length of flexible cylinder 1, corresponding to the length of polymer chains
L_{p1}	Persistence length of flexible cylinder 1, corresponding to the persistence length of polymer chains
R_1	Radius of flexible cylinder 1, corresponding to the radius of polymer chains
q_1	Location of the pseudo-Voigt peak
$FWHM_1$	Full width half maximum of the pseudo-Voigt peak
w_1	Lorentzian fraction of the pseudo-Voigt peak
q_2	Location of the Lorentz peak
$FWHM_2$	Full width half maximum of the Lorentz peak
L_2	Length of flexible cylinder 2, corresponding to the length of fibers
L_{p2}	Persistence length of flexible cylinder 2, corresponding to the persistence length of fibers
R_2	Radius of flexible cylinder 2, corresponding to the radius of fibers
<i>Polydispersity</i>	Polydispersity in the radius of fibers



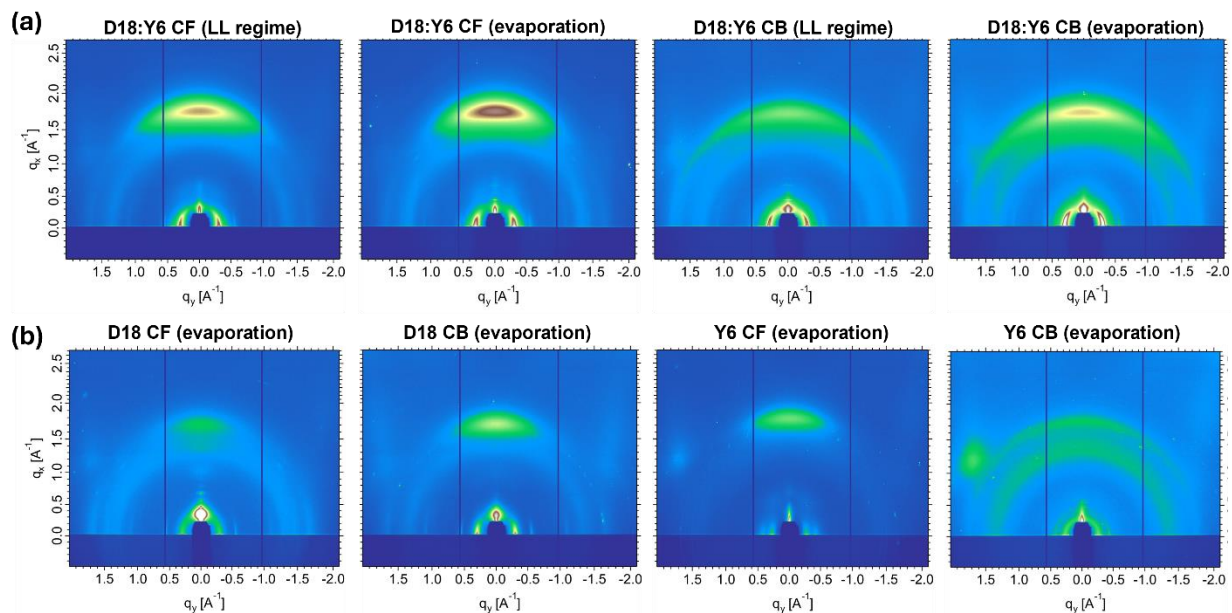
Supplementary Figure 4.2. Temperature dependent SAXS measurements for 50 mg/mL solution of D18 in chlorobenzene, suggesting that the intensity of the fiber aggregates decreases with increasing temperature.



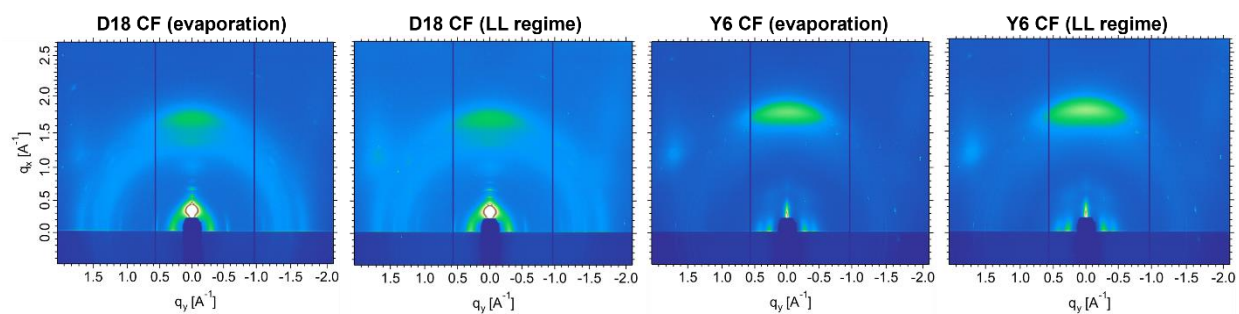
Supplementary Figure 4.3. CPOM images of D18 CF solutions at different concentrations. The solutions were prepared by heating the solution to 55 °C and cooling down to room temperature at a cooling rate of 10 °C/min.



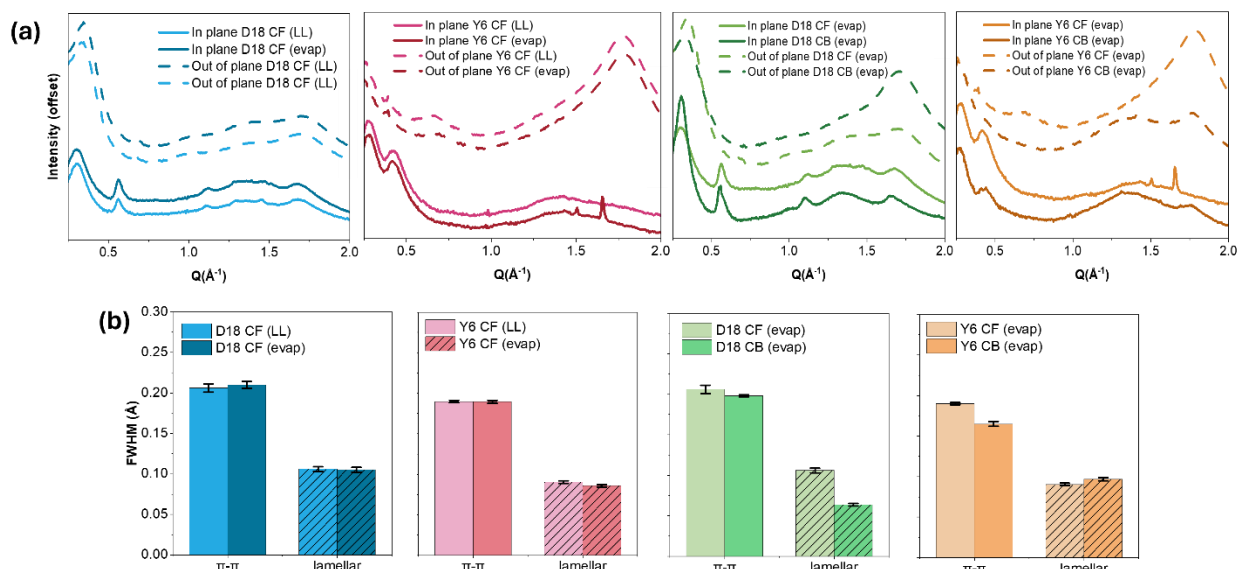
Supplementary Figure 4.4. CPOM images of the left and right edge of the D18:Y6 CB film coated in the evaporation regime. The film coating direction is along the arrows indicated.



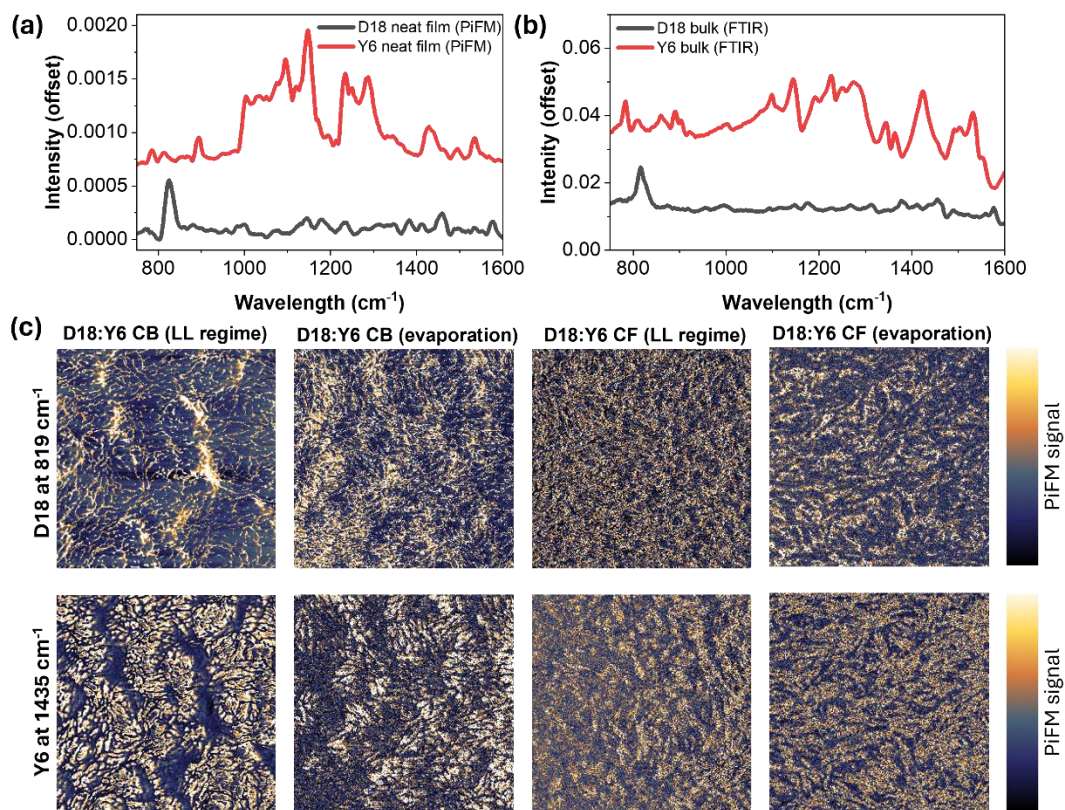
Supplementary Figure 4.5. 2D GIWAXS patterns of (a) D18:Y6 blend films coated from CB and CF in the evaporation and LL regimes and (b) D18 and Y6 neat films coated from CB and CF in the evaporation regime.



Supplementary Figure 4.6. 2D GIWAXS patterns and D18 and Y6 films coated from CF in the evaporation and LL regimes.

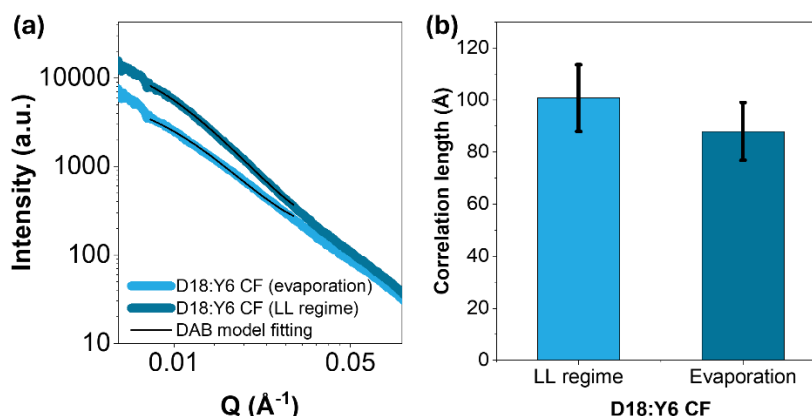


Supplementary Figure 4.7. (a) In-plane and out-of-plane sector profiles of the neat films (D18 and Y6) comparing the effect of regimes and solvent. (b) Comparison of the full width half maximum (FWHM) of the π - π stacking and lamellar stacking peaks based on the 1D profiles in (a).

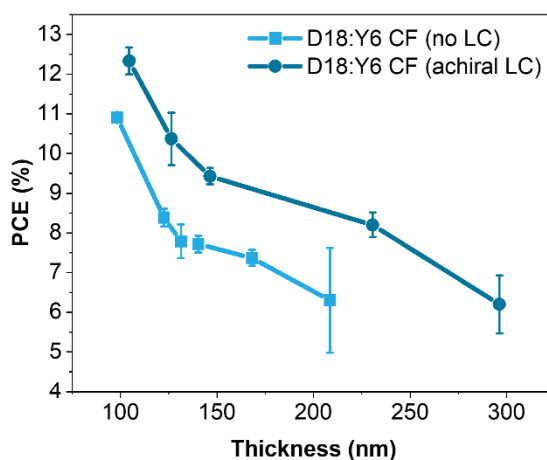


Supplementary Figure 4.8. (a) PiFM spectra of the neat films of D18 and Y6 coated in the evaporation regime. (b) FTIR spectra of D18 and Y6 powders. (c) PiFM measurements of the

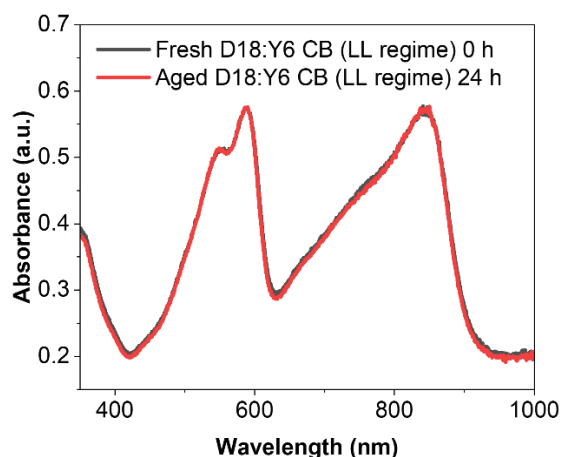
(Supplementary Figure 4.8. cont.) blend films probed at 823 cm^{-1} , showing the D18 domains (top) and at 1437 cm^{-1} , showing the Y6 domains (bottom).



Supplementary Figure 4.9. (a) Resonant soft X-ray scattering (RSoXS) profiles of D18:Y6 CF blend films depending on the coating regimes. (b) Correlation length comparison based on fitting the RSoXS profiles to the Debye-Anderson-Brumberger (DAB) model, showing no differences in the domain spacing.



Supplementary Figure 4.10. Power conversion efficiencies as a function of thickness for D18:Y6 CF devices.



Supplementary Figure 4.11. UV-Vis spectra of D18:Y6 CB blend films coated in the LL regime before and after light aging for 24 hours in the glovebox with N₂ atmosphere.

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Chapter 5

Conclusion

In conclusion, we have investigated the nature of solution-state aggregates of conjugated polymers and their concentration-dependent assembly pathways by utilizing a combination of X-ray scattering and microscopic imaging tools. We reveal that the structure of conjugated polymers strongly depends on their molecular properties such as the polymer backbone conformation and the solvent environment, particularly the solvent affinity towards the conjugated backbone and the alkyl sidechains. A more planar backbone conformation and poor solvent affinity towards the backbone is conducive to forming semicrystalline fiber aggregates, which result in unfavorable large domain sizes in the blend films that result in poor OSC performance. By reducing the backbone planarity via molecular design and/or using solvents that exhibit better affinity to the polymer backbone reduces the strong aggregation property of conjugated polymers, resulting in finer nanoscale phase separated blend film morphologies that lead to optimal OSC performance. We also found that solvents that exhibit poor alkyl side chain affinity can be detrimental to the OSC performance despite being selective to the conjugated backbone because of the strong side chain induced crystallization of the polymer at the air-liquid interface. Therefore, using solvents that balance the backbone and side chain interactions to prevent strong aggregation of conjugated polymers were found effective in achieving favorable phase separated structures in OSCs that optimizes the device performance.

Beyond the initial solution-state aggregate structures, we also investigated the concentration-dependent assembly of conjugated polymers and its impacts on the blend film morphology and device properties of OSCs. Using the ubiquitous conjugated donor polymer D18, we demonstrated that its concentration-dependent assembly pathway involves formation of both

achiral and chiral liquid crystalline phases at high solution concentrations. Importantly, using detailed morphological characterizations, we revealed that the assembly of D18 in the blend solution is drastically tuned by the coating regimes to give (1) lyotropic liquid crystalline mediated assembly in the evaporation regime and (2) random fiber aggregation pathway in the Landau-Levich regime. We demonstrated that the lyotropic liquid crystalline pathway increases the crystallinity of D18 in the blend film, resulting in improved OSC performance and stability. Importantly, we also revealed that when the acceptor forms large crystalline domains in the blend, forming lyotropic liquid crystalline mediated pathway can suppress the formation of large acceptor domains by enhancing the aggregation of the donor polymer.

Overall, my thesis has provided key insights into controlling the blend film morphology of organic solar cells via the design of polymers, solvent environment, and solution processing conditions to tune the aggregation and assembly of conjugated polymers. We believe that this insight can be applied to other conjugated polymer systems to rationally design conjugated polymer materials and control the blend film morphology of organic solar cells for further improving the opto-electronic properties of OSCs.