Final Report

Unraveling Intermolecular Interactions in Non-Fullerene Acceptor Based Polymer Solar Cells for Manufacturing

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1. TECHNICAL OBJECTIVES

At the beginning of this project (2016), device efficiencies for OPVs made using conjugated donor polymers and non-fullerene acceptors (NFAs) were near 11%. Now, reported efficiencies for new systems exceed 18%, since both polymer donor and molecular acceptor can be tuned to a wide variety of properties and successively iterated on. Over the last few years with this project, we have explored a number of structure-property relationships that stemmed from PCBM-based systems and have evolved into NFA-based systems. In general, we have looked to answer fundamental questions that will help understand the requirements for high-performing and easily processable non-fullerene acceptor systems: 1) What is the nature of charge transfer and charge separation in comparison with fullerenes? 2) What are the morphological differences between polymer:fullerene and polymer:NFA blend films, and how are those differences reflected in the device performance? 3) What polymer properties, such as aggregation and crystallinity, affect the blending process with PCBM vs. NFAs? 4) What is the underlying reason for different active layer thickness tolerances in polymer:NFA blends? 5) How does the donor:acceptor HOMO level offset effect solar cell performance? Understanding these fundamental issues has shed light on the NFA chemistry and has guided the design of polymer donors and NFA molecules for organic solar cells. Further, we have carried this work out using ambient atmosphere roll-to-roll compatible blade coating methods we have developed such that the results obtained in this program will be directly applicable to manufacturing pertaining to this new class of materials. We have leveraged the long-established collaboration of the SoRey group to carry out the chemistry/physics/ materials/device research, supplemented by synthetic consultation with members of the Marder group at University of Colorado (previously Georgia Tech).

2. TECHNICAL APPROACH

In this program, our group is interested in the syntheses and processing of high-performing donor-acceptor polymers for organic photovoltaics. This has led us to synthesize a number of conjugated donor polymers for the purpose of understanding how changes to the polymer material leads to changes in active layer processing, bulk-heterojunction (BHJ) morphology, kinetics of charge and electron transfer, energetic disorder in the blend, solubility, and donor:acceptor miscibility. It was the intent of this proposal to address the underlying mechanism of the photovoltaic effect in these systems by carrying out minor structural modifications to the NFA and conjugated polymer component, carefully processing the materials as blend films in a repeatable and reproducible manner, and subsequently thoroughly probe the morphological, photophysical, and photovolatic properties. A major focus of this program was processing the organic solar cell (OSC) active layer via blade-coating as this is a more industrially compatible technique. We found that controlling polymer aggregation in solution is a facile method to improve BHJ reproducibility and performance while also providing a handle on polymer solubility. We have had the opportunity to study our materials using a number of techniques including GIWAXS, R-SoXS, solid-state 2D-NMR, transient absorption, photoluminescence, and DFT calculations.

Through this program funding, we have had the opportunity to combine our research efforts at Georgia Tech with those of Lee Richter at the National Institute of Standards and Technology, Changduk Yang at Ulsan National Institute of Science and Technology, Seth Marder and Michael Toney at University of Colorado Boulder, Franky So and Kenan Gundogdu at North Carolina State University, Jean-Luc Bredas at the University of Arizona, and Manjunatha Reddy at the University of Lille.

3.1 PROGRESS SUMMARY

3.1 Processing and controlling polymer aggregation for improved photovoltaic performance.

At the beginning of this program, we looked to move from spin coating polymer:PCBM solutions to blade coating while minimizing the effect on BHJ morphology and solar cell performance. We found that no re-optimization of solution composition is necessary when transferring P(T3-TPD):$PC_{71}BM$ inks from spin coating to blade coating. We attribute this to processing from an aggregated solution that predetermines the solid-state morphology regardless of the processing method which is advantageous for the scaling of OPV technology (Fig. 1). Figure 1 shows the temperature dependent UV-vis absorbance of P(T3-TPD) in chloroform indicating that it displays thermochromism in dilute solution (~0.1 mg mL^{-1}). At elevated temperature, the polymer is in a non-aggregated state and the solution appears orange, while at room temperature the polymer is aggregated and the solution appears purple.

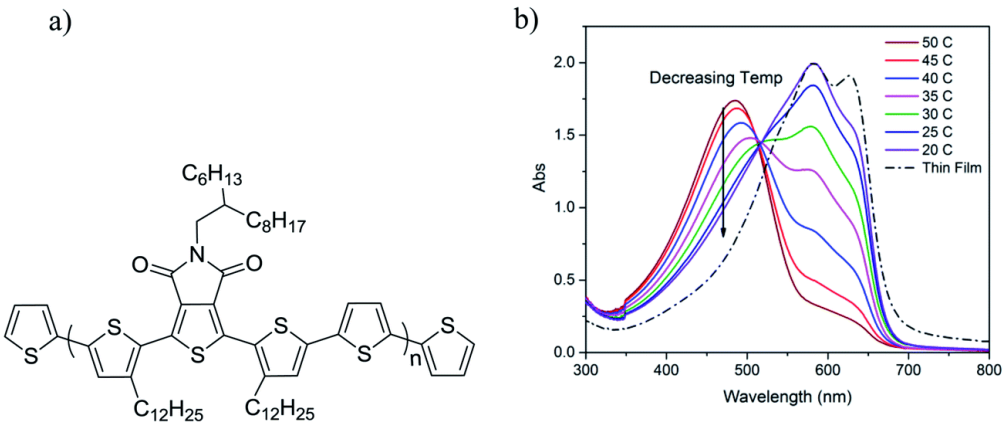

Figure 1. (a) Repeat unit structure of P(T3-TPD), (b) temperature dependent solution UV-vis absorbance spectra of neat P(T3-TPD) in chloroform and thin film UV-vis of neat P(T3-TPD). Adapted from Hernandez et al. *J. Mater. Chem. A* 2017, 5, 39, 20687.

When blade coating is compared to spin coating, the photovoltaic characteristics are similar with comparable reproducibility (5.3% PCE). While spin coated samples were processed in an argon filled glovebox, blade coated samples were processed in ambient air, indicating that this system is not sensitive to processing type or atmosphere, which is advantageous for large scale ambient processing. It was determined that a 1% 1,8-diiodooctane (DIO) additive was necessary in the active layer solution for an optimal BHJ morphology. To gain further insight into how phase separated morphology is developed with the solvent additive DIO, and without DIO (w/o DIO), we perform *in situ* UV-vis absorbance and reflectance on blade coated films. *In situ* thin film measurements, coupled with *ex situ* film measurements, reveal that DIO increases the nucleation density during solidification, leading to reduced domain size and enhanced polymer crystallinity in the BHJ film. This work was published in the *Journal of Material Chemistry A*.

The previous work led to further exploration into processing strongly aggregated polymer solutions using blade coating. In a follow-up study, diketopyrrolopyrrole (DPP) thiophene-based polymer DT-PDPP2T-TT (2-decyltetradecyl diketopyrrolopyrrole 2,5-di-2-thienylthieno[3,2-b]thiophene (Fig. 2a) was used which shows stronger solution aggregation properties (Fig. 2b). Temperature-dependent UV–vis spectroscopy from 25 to 95 °C was performed in dichlorobenzene (DCB) and is shown in Figure 2b, with results that show a decrease in intensity of the lowest energy peak and blue-shift of the peak maximum with increasing temperature as well as a slight decrease in intensity of the higher energy shoulder. These small changes seen over a wide range of temperatures demonstrate the high rigidity of the polymer backbone, which indicates aggregation. The DT-PDPP2T-TT polymer is much more aggregated as compared to P(T3-TPD) where in dilute solution, UV–vis spectroscopy temperatures of around 60 °C was sufficient to molecularly dissolve the polymer and remove all evidence of aggregated species.

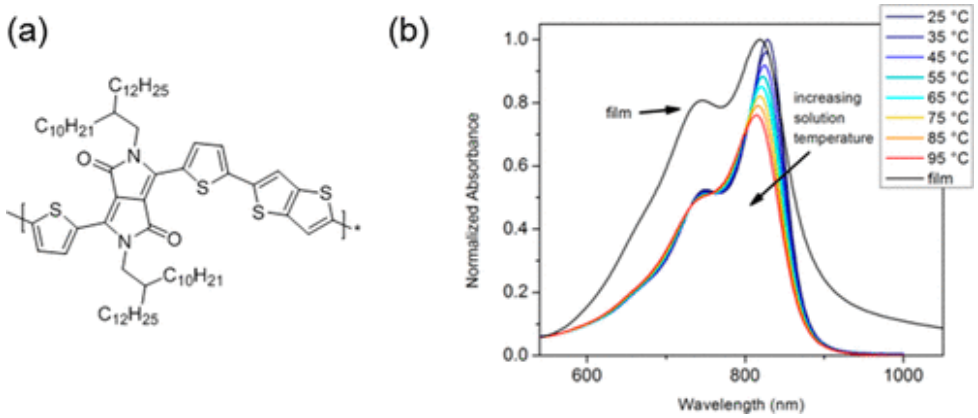

Figure 2. (a) Chemical repeat unit structure of DT-PDPP2T-TT. (b) Temperature-dependent UV–vis spectra of 0.02 mg mL^{-1} DT-PDPP2T-TT in DCB solution, along with the spectrum of a film cast from $CHCl_3$. Adapted from Pelse et al. *ACS App. Mater. & Inter*. 2020, 12, 24, 27416.

Device performance using $PC_{71}BM$ was strongly dependent on the introduction of either o-dichlorobenzene, 1,8-diiodooctane, or diphenyl ether cosolvent into the chloroform solution, which were all shown to drastically improve the morphology. With any of the cosolvents used in this study, domain size decreases with the cosolvent, and nanofibers emerge both on the surface (AFM) and within the bulk (STEM) of the film. This is consistent with a decrease in solvent quality for the polymer as the host solvent chloroform evaporates, leading to eventual polymer aggregation and crystallization. $PC_{71}BM$ tends to aggregate during this drying phenomenon for many polymer/$PC_{71}BM$ blends, but because this particular polymer also tends to aggregate because of low solubility, a variety of additives are capable of achieving optimal morphologies and improved photovoltaic performance over the $CHCl_3$-only cast film. When the polymer/fullerene blend is processed from a mixture of $CHCl_3$ and DCB, polymer crystallization and phase separation are delayed until the end of the drying process. We observed both the formation of small domains and an increase in crystallinity during the evaporation of DCB due to a high nucleation rate from supersaturation. This resulted in percolated bulk heterojunction networks that performed similarly well with a wide range of film thicknesses from 180 to 440 nm, making this system amenable to continuous roll-to-roll processing methods. This work was published in *ACS Applied Materials and Interfaces*.

Although polymers with strong solution aggregation can enhance BHJ morphology and reproducibility, these polymers often come with low solubility and require high-temperature processing. This motivated us to synthesize a set of random terpolymer derivatives of PffBT4T-2OD (PCE 11) by replacing a fraction of the bithiophene linkers with single thiophenes, which led to a family of polymers with (1) a reduced tendency to aggregate and increased solubility of up to 50 mg/mL at room temperature, (2) facile

monomer access similar to PffBT4T-2OD itself, (3) average PCEs approaching 10% in devices, exceeding those based on PffBT4T-2OD, and (4) less demanding processing requirements in device fabrication (Fig. 3).

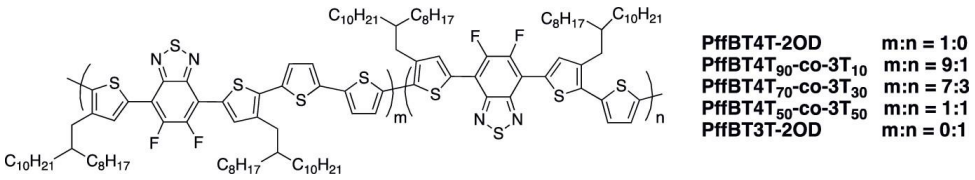

Figure 3. Structures of the alternating and random PCE11-based copolymers. Adapted from Xu et al. *ACS App. Mater. & Inter.* 2018, 10, 51, 44583-44588.

The strong temperature dependence of PffBT4T-2OD to aggregate is manifested by its remarkable thermochromic behavior in dilute solution illustrated in Figures 4a, where the maximum absorption wavelength (λ_{max}) shifts from ~700 nm at 25 °C associated with the aggregated polymers to ~550 nm at 85 °C, as aggregates break up to molecularly dissolved species. In general, the thermochromic behavior becomes less pronounced as the monothiophene content is increased at the expense of the bithiophene content in the polymers. This phenomenon can be easily visualized by the comparison of normalized UV–vis absorption profiles of the five polymer solutions at 25 °C, as shown in Figure 4b. As the thiophene content in the polymer increases, the absorption intensity at around 700 nm reduces; the peak at 700 nm disappears completely for PffBT4T$_{50}$-co-3T$_{50}$ and PffBT3T-2OD, with their λmax found below 600 nm. Solar cells based on random terpolymer-PC$_{71}$BM blends exhibited average power conversion efficiencies of over 9.5% when processed with preheated substrates, with fill factors above 70%, exceeding those from PffBT4T-2OD. Thanks to increased solubility, random terpolymer devices were able to be fabricated on room-temperature substrates, reaching virtually identical performance among all three polymers despite remarkable thicknesses of ~400 nm. Thus, we show that the random terpolymer approach is successful in improving processability while maintaining device performance. This work was published in *ACS Applied Materials and Interfaces.*

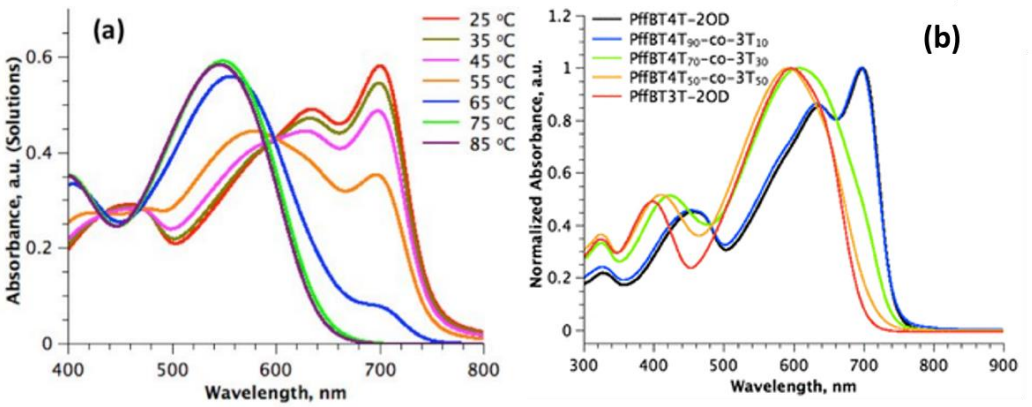

Figure 4. (a) UV-Vis absorption profile of PffBT4T-2OD at 0.02 mg/mL in a o-DCB solution at variant temperatures. (b) Normalized UV–vis absorption profiles of the polymers in dilute o-dichlorobenzene solution (0.02 mg/mL) at 25 °C. Adapted from Xu et al. *ACS App. Mater. & Inter*. 2018, 10, 51, 44583-44588.

Understanding the correlation between polymer aggregation, miscibility, and device performance is important to establish a set of chemistry design rules for donor polymers with NFAs. Employing a donor polymer with strong temperature-dependent aggregation, namely PCE-11 as a base polymer, five copolymer derivatives having a different thiophene linker composition are blended with the common NFA O-IDTBR to investigate their photovoltaic performance. While the donor polymers have similar optoelectronic properties, it is found that the device power conversion efficiency changes drastically from 1.8% to 8.7% as a function of thiophene content in the donor polymer (Fig. 5). Results of structural characterization show that polymer aggregation and miscibility with O-IDTBR are a strong function of the chemical composition, leading to different donor–acceptor blend morphology. Polymers having a strong tendency to aggregate are found to undergo fast aggregation prior to liquid–liquid phase separation and have a higher miscibility with NFA. These properties result in smaller mixed donor–acceptor domains, stronger PL quenching, and more efficient exciton dissociation in the resulting cells. This work was published in *Advanced Energy Materials*.

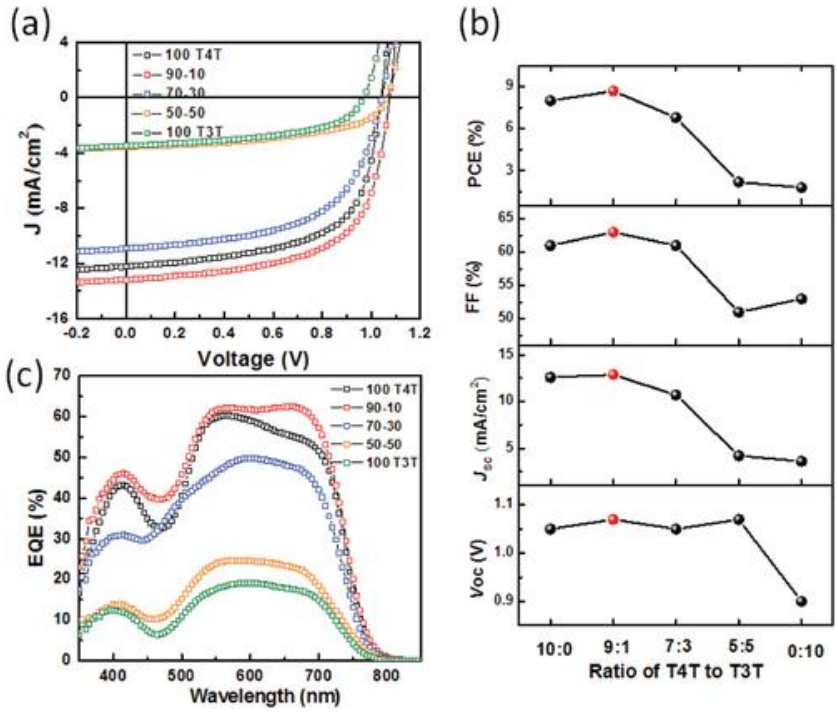

Figure 5. a) Current–voltage (J–V) curves of solar cells with different photoactive layers. b) Evolution of device performance as a function of the content of bithiophene linkers in the polymer backbone. c) External quantum efficiency (EQE) characteristics of solar cells. Adapted from Yi et al. *Adv. Energy Mater.* 2020, 10, 8, DOI: 1902430.

In order to elucidate the optimal levels of aggregation during processing as a function of solution and substrate temperatures, we expanded our original random terpolymer family with the synthesis of PffBT4T$_{80}$-co-3T$_{20}$-2OD (80–20), and it is found to have the optimal balance between processability and performance when combined with IDTBR. In this study, we examine in depth the spin and blade coating of 80–20 with both PC$_{71}$BM and EH-IDTBR to understand the effect of processing temperature on solution and solid-state properties. We highlight the relationship between solution-state polymer aggregation, solid-state microstructure, and device performance with an emphasis on the changes among blends with either the amorphous PC$_{71}$BM or the more ordered IDTBR. Through both spin coating and blade coating device characterization, and a combination of solid-state and real-time processing characterization, we attempt to clarify the role of the acceptor in determining the polymer order in 80–20 BHJs with both PC$_{71}$BM and IDTBR.

The 80–20 composition hit the very edge of room temperature aggregation (Fig. 6a), which may influence reduced temperature processing with respect to the adjacent compositions of 90–10 and 70–30. The thermal properties of the two polymer 80-20 batches are quite similar, with the second heating and cooling scans, as measured by DSC shown in Figure 6b. The curves have the same general shape, with peak melt transition temperatures of 257 and 259 °C for the 51 and 62 kg mol^{-1} polymers, respectively, and peak crystallization temperatures of 239 and 240 °C. The average of the melt and

crystallization temperatures are shown as a function of 3T composition, in Figure 6c, again indicating that the 80–20 polymer has expected properties lying between 90–10 and 70–30. Enthalpies of melting (heat of fusion, ΔHf) for the 51 and 62 kg mol^{-1} polymers are 21.3 and 16.7 J g^{-1}, respectively.

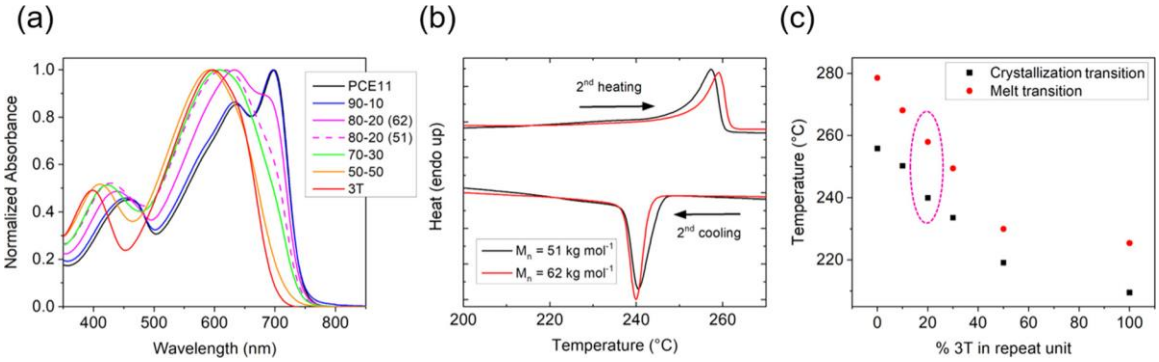

Figure 6. (a) Solution UV/vis spectra of the original family of PffBT4T-2OD (PCE11) random terpolymers as well as two different samples of 80–20 designed for this study (labeled with their respective molecular masses in kg mol^{-1}). Solutions are made at 0.02 mg mL^{-1} in o-DCB and are measured at 25 °C. (b) Second DSC scans of two different batches of pristine 80–20 polymer. (c) DSC melt and crystallization temperatures from the peak of the transition for the second scan, with results from the 80–20 polymers circled. Note that both molecular mass samples have the same transition temperatures within 2 °C. Adapted from Pelse et al. *Chem. Mater.* 2021, 33, 2, 657-667.

We determine that the new terpolymer composition, PffBT4T$_{80}$-co-3T$_{20}$-2OD (80–20), is well behaved with respect to its processability and solid-state performance and is the best candidate for processing IDTBR blend films without using an excessively hot stage and/or processing solution during blade coating, achieving power conversion efficiencies (PCEs) approaching 9%. However, the PCEs of IDTBR devices are lower than those of PC$_{71}$BM devices because of the reduced fill factor, which we attribute to IDTBR's tendency to disrupt polymer crystallization during processing. Using real-time characterization methods (Fig. 7), we discover that both acceptors affect the kinetics and extent of polymer crystallization during processing. Although the fullerene blends have increased polymer crystallinity, IDTBR delays the onset of polymer solidification, and the overall crystallinity in the blend of those otherwise ordered materials is compromised. Delayed polymer solidification with IDTBR suggests that the latter partially solubilizes the polymer, which does not form a favorable morphology for optimum photovoltaic performance when processing via spin or blade coating. This work was published in *Chemistry of Materials*.

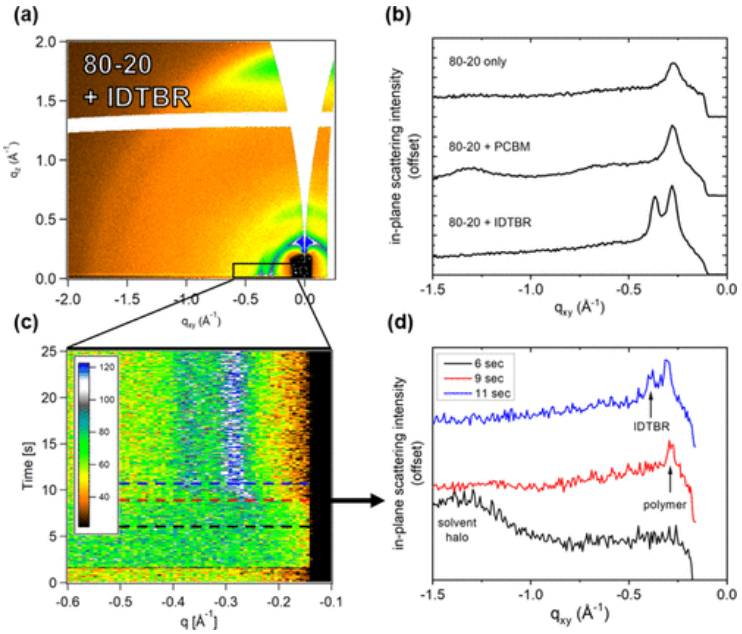

Figure 7. (a) 2D GIWAXS scattering pattern of the 80–20:IDTBR blend. (b) In-plane line cuts of dry films, featuring pristine 80–20, the $PC_{71}BM$ blend, and the IDTBR blend. (a, c, d) In situ workflow and data analysis: the in-plane region from -0.6 Å^{-1} < q < -0.1 Å^{-1} highlighted in (a) and expanded into (c) false color plots of the in-plane scattering over time. (d) Select line cuts from the false color contour plots highlighting three stages of the drying process: black at 6 s, early time dominated by the solvent halo; red at 9 s, emergence of the polymer peak; and blue at 11 s, IDTBR peak and dried film. Adapted from Pelse et al. *Chem. Mater.* 2021, 33, 2, 657.

3.2 Investigating minimal structural changes to conjugated polymers for organic photovoltaics

We employed a family of photoactive conjugated polymers with only a minimal "one-atom" change where each alternating copolymer has a repeat unit containing a TPD acceptor and a bithiophene donor bridged by a Group 14 center atom. Previous studies have shown that DTC-TPD, DTS-TPD, and DTG-TPD (Fig. 8) polymers in fullerene-blend BHJ devices lead to PCE as high as 6.4%, 8.1%, and 8.5%, respectively, showing the substantial impact of a minimal change in repeat unit structure on OPV device performance. However, it is important to recognize that a direct comparison of photovoltaic performance from different studies is not sufficient to isolate and elucidate the structural impact on material and device properties because these materials have different synthetic approaches, molecular weights, and purities, and the devices are constructed using different processing methods and architectures. In this study, we used parallel polymer syntheses and purifications carried out as identically as possible to obtain polymers with similar molecular weights and dispersities, along with chemical and structural purities, allowing us to isolate the effect of changing a single atom on photovoltaic properties. Solution-state properties are examined with proton nuclear magnetic resonance (NMR) and UV–vis-NIR

spectroscopy. The solid-state organization was probed via solid-state NMR and grazing incidence wide-angle X-ray scattering (GIWAXS), redox and electronic properties using steady-state and transient absorption spectroscopies, along with electrochemistry, and electronic structures studied using density functional theory (DFT) calculations to reveal the effect of intermolecular packing between polymer chains on OPV device performance. Transient absorption spectroscopy results indicate a higher bimolecular recombination rate between separated charges in the DTC polymer due to a more stable triplet energy level, which was confirmed by theoretical calculations. Finally, we combine these results to demonstrate how the optoelectronic properties and photovoltaic performance is linked to morphological features in the active films. We demonstrate how they are induced from aggregates that form in the processing solution, which can be correlated with the minimal one-atom differences in polymer repeat unit structure.

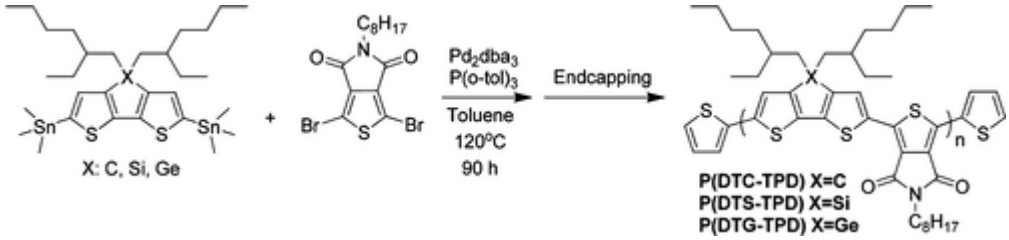

Figure 8. Stille Cross-Coupling Polymerization and Structures of the Fused-Dithiophene-co-thienopyrrolodione Polymers, P(DTC-TPD), P(DTS-TPD), and P(DTG-TPD). Adapted from Lo et al. *Chem. Mater.* 2018, 30, 9, 2995.

Overall, this investigation demonstrated that changing just a single atom within a polymer repeat unit, the ultimate OPV device performance can be drastically altered. Employing a thorough set of experiments, we were able to conclude that this difference originated from the variation in backbone conformation present within the polymer solutions, which then affected the overall morphology and intermolecular packing structures. This observation should encourage researchers to design materials that will allow for further theoretical and experimental studies focusing on the fundamental understanding of structure–property relationship in OPV polymers. This work was published in *Chemistry of Materials*.

We also reported on a family of donor-acceptor polymers with minimal steric bulk on the acceptor moiety to gauge the impact of steric interactions on OPV device performance and serve as a starting point for further studies on the effect of side chain steric effects on donor-acceptor polymer/molecular acceptor intermolecular interactions. Shown in Figure 9, this family of polymers contain acceptor moieties with methyl side chains and a quaterthiophene donor with branched side chains directed away from the acceptor (P(T4-TPD-M), P(T4-DPP-M), and P(T4-iI-M)). The rationale for this D-A polymer design is based around the observation that PCE11 achieves PCEs > 10% in

$PC_{71}BM$ BHJ devices which fits the structural mold of minimal steric bulk on the acceptor moiety alongside a donor with bulky substituents. We sought to modify this structure by replacing the 5,6-difluoro-2,1,3-benzothiadiazole acceptor unit with other minimally substituted acceptors that could ultimately be synthesized with bulkier side chains to isolate the effects of steric modifications on the donor-acceptor blend.

Optimal device efficiencies with $PC_{71}BM$ (7.5%) and ITIC (4.0%) were both obtained using P(T4-TPD-M), while P(T4-DPP-M) and P(T4-iI-M) obtained lower efficiencies with $PC_{71}BM$ (5.4% and 5.3% respectively) and ITIC (2.1% and 2.2% respectively). The differences in OPV device efficiency primarily stem from higher V_{OC} and FF values in the P(T4-TPD-M) devices. Due to the higher device performance with both molecular acceptors, P(T4-TPD-M) will be utilized for a follow up study aimed at replacing the methyl side chain with a longer alkyl chain (n-octyl) and a bulkier alkyl chain (2-ethylhexyl) to assess the impact of sterics on D-A polymer:acceptor interactions and ultimately OPV device performance. This work was published in *Organic Electronics*.

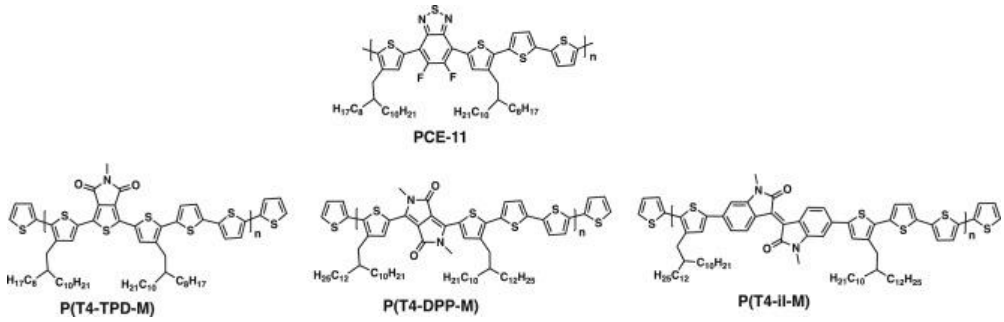

Figure 9. Repeat unit structures of minimally substituted acceptor D-A polymers compared to PCE-11. Adapted from Schmatz et al. *Organic Electronics* 2019, 68, 280.

We developed a follow-up fundamental study in which the side chain of the champion P(T4-TPD-M) polymer was systematically altered to increase the bulk from a minimally sized substituent (methyl) to a bulky substituent (cyclohexylmethyl) (Fig. 10); we predicted that differences in device performance would arise due to variant fullerene docking abilities, as determined by the relative bulk of the DA polymer acceptor unit side chain moiety. While alteration of the side chain bulk of the TPD-based polymers results in different aggregation properties of the neat polymers and the microstructure of the polymer–fullerene blends, these differences do not translate to changes in PCE. In contrast to the starker differences observed in previous PBDTTPD systems the OSC devices with the TPD-based polymers show similar PCEs of ~6% for all four polymers, indicating a notable device tolerance to TPD acceptor unit side chain moiety. While it is possible that side chain modification in our TPD system [R = methyl (M), isopropyl (IP), isobutyl (IB), and cyclohexylmethyl (CM)] merely does not invoke the fullerene docking phenomenon quite as strongly as the side chain modification in the PBDTTPD studies (e.g. n-octyl, ethyl-hexyl, etc.), our TPD system may alternately demonstrate a gap in the field's

knowledge regarding these side chain engineering principles and how they apply to different systems. The findings of this work challenge commonly accepted notions of side chain engineering in OSCs by presenting an avenue for polymer structure and BHJ morphology manipulation sans any commonly observed variations in photovoltaic performance. This work was published in the *Journal of Materials Chemistry C*.

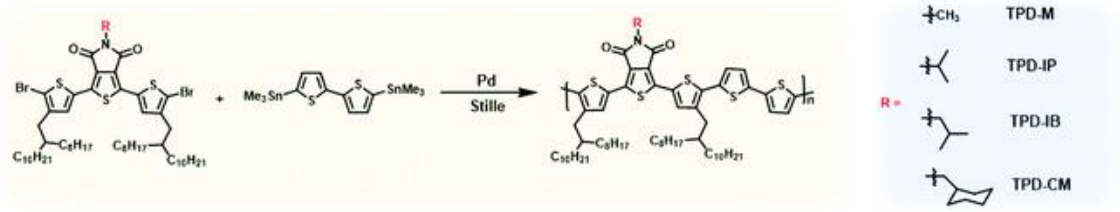

Figure 10. Synthesis of TPD-based DA polymers with variable side chain bulk. Adapted from Advincula et al. *J. Mater. Chem. C* 2020, 8, 46, 16452.

3.3 Unraveling the role of donor-acceptor exciton delocalization, lifetime, frontier molecular orbital offsets, and energetic disorder on solar cell performance

Interfaces between donor and acceptor in a polymer solar cell play a crucial role in exciton dissociation and charge photogeneration. While the importance of charge transfer (CT) excitons for free carrier generation is intensively studied, the effect of blending on the nature of the polymer excitons in relation to the blend nanomorphology remains largely unexplored. In this work, we use several polymer–fullerene blend systems to study the effect of morphology on polarizability using EA spectroscopy. Poly(dithienogermole-alt-thienopyrrolodione) (DTG-TPD) blended with PCBM is the first model system we use for this study. In this system, the morphology and the interfacial area can be controlled via the solvent additive diiodooctane (Fig. 11), which is removed from the film by overnight vacuum drying. Thus, by varying the additive concentration in the blend, we can tune the extent of interaction between the polymer and fullerene. Electroabsorption (EA) spectroscopy was used to study the excited-state polarizability of polymer excitons, and it was found that excited-state polarizability of polymer excitons in the blends is a strong function of blend nanomorphology. The increase in excited-state polarizability with decreased domain size indicates that intermixing of states at the interface between the donor polymers and fullerene increases the exciton delocalization, resulting in an increase in exciton dissociation efficiency. This conclusion is further supported by transient absorption spectroscopy and time-resolved photoluminescence measurements, along with the results from time-dependent density functional theory calculations. These findings indicate that polymer excited-state polarizability is a key parameter for efficient free carrier generation and should be considered in the design and development of high-performance polymer solar cells.

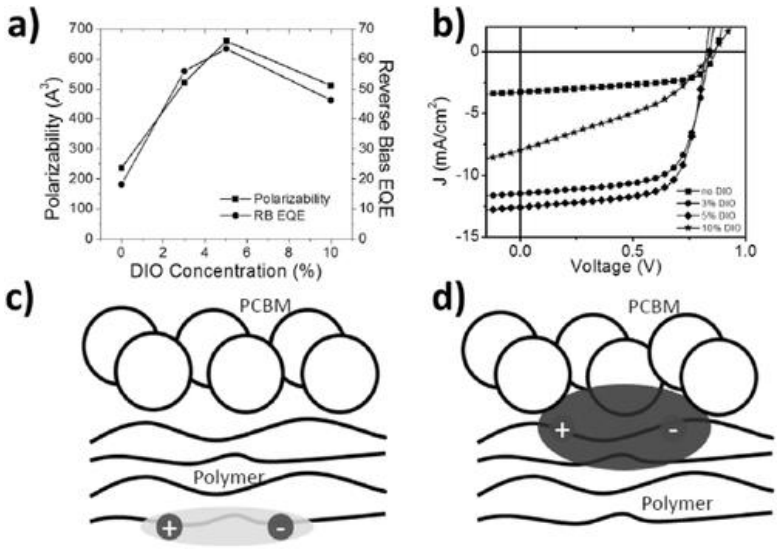

Figure 11. Polarizability and device data for DTG-TPD films with different DIO concentrations. a) Polarizability and reverse bias EQE. b) J–V characteristics. c) Schematic representation of excitons far from the interface. d) Schematic of excitons at the interface. Adapted from Gautam et al. *Adv. Mater.* 2018, 30, 30, DOI: 1801392.

Our results show that blending with fullerene significantly increases the excited-state polarizability, and the exciton dissociation efficiency is correlated with the increased excited-state polarizability due to blending. This dissociation efficiency trend was also supported using transient photoluminescence and transient absorption spectroscopy measurements. In addition to the DTG-TPD:PCBM system, we found a similar increase of excited polarizability due to blending in PTB7 and P3HT blends with fullerene. Our study suggests that the increase in the excited-state polarizability upon blending can change the charge transfer and separation efficiencies and hence the performance of the OPV devices. We show that the nature of the excitons in a donor–acceptor polymer upon blending with fullerene controls the charge transfer, separation, and recombination efficiency and hence the performance of OPV devices. By fitting EA spectra at the band edge of polymer systems using optical absorption data from PDS, we were able to quantitatively determine the trend in excited-state polarizability due to the change in the blend morphology, which is further supported by the results of time-dependent DFT calculations. We propose a physical picture wherein the intermixing of states at the interface between the donor polymers and fullerene increases the exciton delocalization, resulting in an increase in exciton dissociation efficiency. Further, we demonstrate that the excited-state polarizability is a strong indicator of exciton dissociation efficiency. Importantly, we find the donor–acceptor interaction significantly affects the electronic structure of the polymer itself, facilitating the dissociation of polymer excitons prior to the formation of the CT states. This work was published in *Advanced Materials*.

In other work, using PTB7-Th as a donor polymer blended with two NFAs having different molecular configurations: a 3D molecular NFA (SF-PDI4) and a linear A–D–A NFA (ITIC), we correlate the photovoltaic properties of the two blends with the device performance (Fig. 12). The results are also compared with the blend using $PC_{71}BM$. In addition to the fact that the absorption profile and electron mobility of the acceptor play an important role in determining the PCE in OPVs, our results indicate that the NFAs' interaction with the donor polymer and the corresponding nanoscale morphology strongly affect the device performance. Using femtosecond transient absorption spectroscopy, we find that the PTB7-Th:ITIC films exhibit faster singlet exciton decay dynamics, and more obvious triplet exciton formation, compared to the PTB7-Th:SF-PDI4 films, suggesting highly efficient exciton dissociation and charge generation processes in the PTB7-Th:ITIC film. Furthermore, to study the effect of composition on charge transport, we performed temperature dependent space-charge-limited current measurements. We find that the ITIC-based devices exhibit more efficient charge transport, with a higher electron mobility and lower energetic disorder compared to the SF-PDI4-based devices. Results from grazing incidence wide-angle X-ray scattering and resonant soft X-ray scattering show that the ITIC molecules form purer domains with smaller domain spacing, leading to efficient charge extraction. We propose that the linear A–D–A ITIC has a strong electronic coupling with the PTB7-Th donor polymer for efficient exciton splitting and at the same time forms relatively pure domains resulting in efficient charge extraction and hence a better device performance. This work was published in *Advanced Functional Materials*.

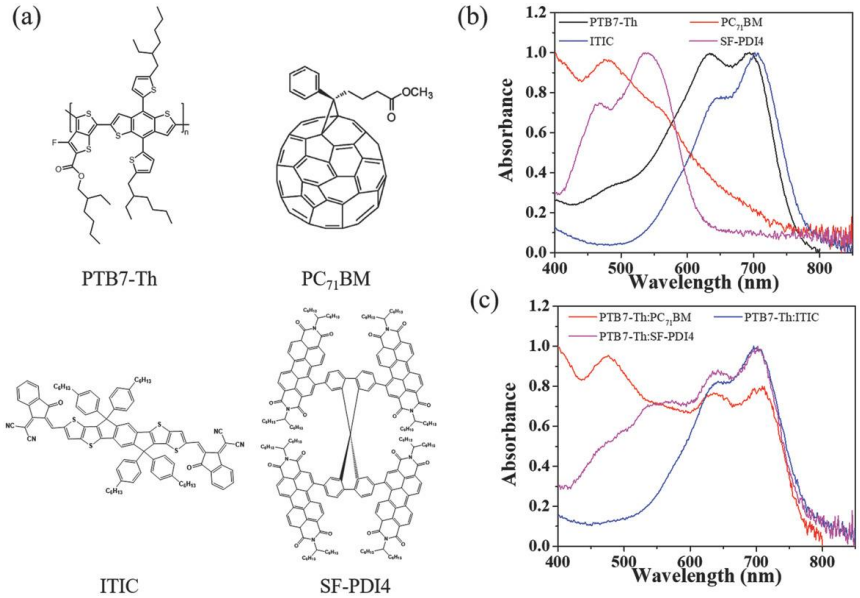

Figure 12. a) Chemical and repeat unit structures of acceptors and the donor polymer used in this study. b) Normalized absorbance spectra of pristine PTB7-Th polymer and PC71BM, ITIC and SF-PDI4 molecules. c) Normalized absorbance spectra of PTB7-Th:$PC_{71}BM$, PTB7-Th:ITIC, and PTB7-Th:SF-PDI4 blend films. Adapted from Yi et al. *Adv. Funct. Mater.* 2018, 28, 32, DOI: 1802702.

To better understand the correlation of the dielectric properties with the photovoltaic response in conjugated polymer:fullerene bulk heterojunction materials, the concept of introducing minimal structural change is employed to increase the polymer dielectric constant via polar cyano groups added to the end of butyl or octyl side chains in the poly(dithienosilole-thienopyrrolodione) system (Fig. 13). This design allows for a systematic investigation into the effect of a specific structural change, namely the addition of polar groups on the conjugated polymer side chains, on the dielectric, optoelectronic, charge transport, and molecular packing properties, and ultimately OPV device performance. Density functional theory calculations confirm that the polar groups do not affect the polymer electronic structure but can lead to an increase in overall dipole moment depending on the polymer chain conformation. Despite the increased dielectric constant (from 2.7 to 4.3 for cyano-octyl side chains and from 2.7 to 3.2 for the cyano-butyl analogues), the device characteristics employing the cyano-containing polymers are inferior to those of the devices made with unfunctionalized alkyl chains. The parent donor polymers DTS-TPD-C8 and DTS-TPD-C4 lead to similar PCEs of ≈ 8%. The high efficiencies benefit from V_{OC} approaching 0.9 V, decent J_{SC} around 14.0 mA cm^{-2}, and FF around 65%. Such results are comparable to the best devices previously reported for DTS-TPD-C8 and exceed the PCE values reported for DTS-TPD-C4. However, both cyano-group containing polymers DTS-TPD-C8-CN and DTS-TPD-C4-CN exhibit a drastic decrease in device performance with J_{SC} between 9 and 10 mA cm^{-2} and FF around 45%. The GIWAX data indicated that the introduction of cyano groups reduced the overall film crystallinity. However, the molecular packing within the semicrystalline domains was not significantly affected, leaving preferred face-on orientation on substrate and a certain degree of isotropic packing retained for all samples, except that the lamellar d-spacing increased slightly for the cyano-containing polymers. It is found that the hole mobilities for the cyano-containing polymers are two orders of magnitude lower compared to those for the parent polymers and suggest this is due to an increase in energetic disorder caused by the strong local permanent dipoles associated with the cyano groups. The study highlights the complexity in the relationship between the dielectric constant of organic materials, the morphologies that are induced, and their photovoltaic performance. This work was published in *Advanced Functional Materials*.

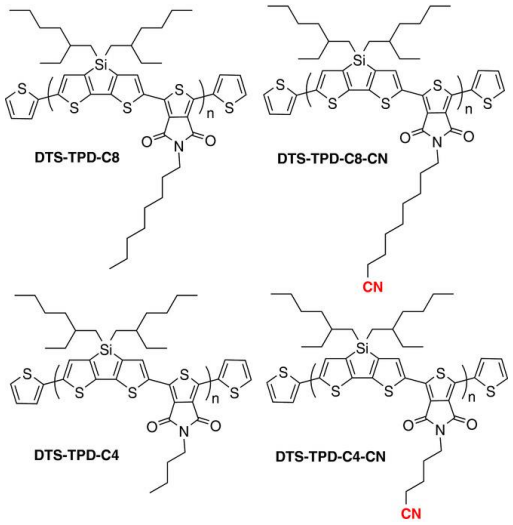

Figure 13. Structures of the four polymers studied in this work. Adapted from Xu et al. *Adv. Funct. Mater.* 2018, 28, 46, DOI: 1803418.

In organic solar cells, maximizing the open-circuit voltage (V_{OC}) via minimization of the ionization energy or electron affinity offsets of the blended donor and acceptor often comes at the expense of achieving a considerable amount of short-circuit current (J_{SC}). To explore a hypothesis for the design of materials that may circumvent this tradeoff, eight structurally similar polymers were synthesized consisting of a fluorinated/non-fluorinated benzothiadiazole (BTDF/BTD) strong acceptor moiety, a thiophene ester (TE) weak acceptor, and various donor units composed of bithiophene (T2), biEDOT, and benzodithiophene (BDT) to form six acceptor gradient and two nongradient polymers (Fig. 14). The acceptor gradient motif was designed and theorized to induce more facile exciton dissociation in low driving force solar cells by creating a further separated intramolecular charge-transfer state between the strong BTD acceptor and various donor units through a bridging TE component. Solar cells were fabricated using the eight polymers blended with $PC_{71}BM$ to reveal two top performing isomeric polymers, T2-BTDF-(TE2) and TE2-BTDF-(T2), which were further tested with several NFAs: EH-IDTBR, ITIC, and ITIC-4F. In order to fabricate optimally performing solar cells, a 0.2 eV ionization energy offset was found to be essential or the short-circuit current of the NFA cells diminished dramatically. Ultimately, optimized NFA solar cells were fabricated using ITIC-4F paired with each of the top performing polymers to produce an average PCE of 7.3% for TE2-BTDF-(T2) (nongradient) and 3.6% for T2-BTDF-(TE2) (gradient). The acceptor gradient effect was not shown to reduce the amount of charge recombination in NFA solar cells mainly due to the inability to fabricate solar cells, with minimal ionization energy or electron affinity offsets along with morphological complications. This work stresses the importance of acquiring accurate ionization energies and electron affinities when characterizing solar cell energetics, as differences as small as 0.1 eV in the offsets can

make a significant impact on overall charge collection. This work was published in *Chemistry of Materials*.

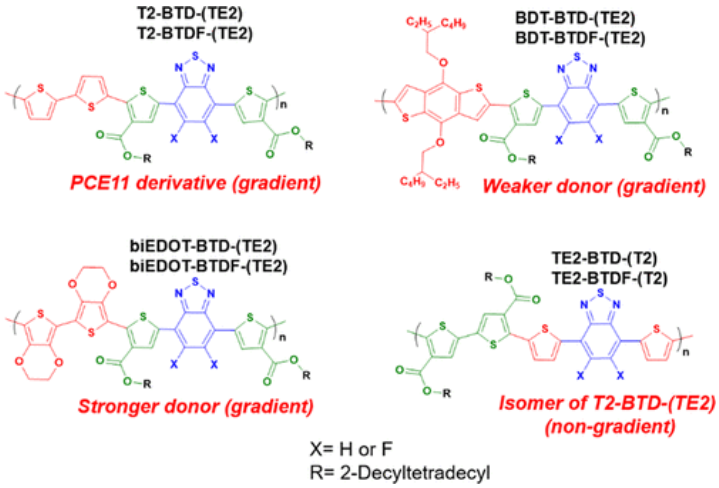

Figure 14. Eight polymers studied in this work. Adapted from Jones et al. *Chem. Mater.* 2019, 31, 23, 9729.

A key factor for these materials implementation into industrial relevant devices is their active layer thickness tolerance as solar cell performances are typically reported with thicknesses on the order of 100–150 nm, but thicker films (ca. 300 nm) are needed for printing and roll-to-roll processing. In this report, two PM7 isomeric derivatives were synthesized featuring a chlorinated benzodithiophene and ester functionalized terthiophene moieties for the incorporation into non-fullerene OSCs (Fig. 15). The fundamental difference between the two isomeric polymers is the location of the ester side chains where the PM7 D1 esters are located on the outer thiophene units, whereas the esters on PM7 D2 are located on the central thiophene unit. This simple modification produced polymers with similar absorption profiles, electrochemical onsets, charge carrier mobilities when blended with ITIC-4F, and grazing-incidence wide-angle X-ray scattering patterns. Thin-film (100 nm) OSCs were fabricated resulting in average PCEs of 11.6% for PM7, 12.1% for PM7 D1, and 9.9% for PM7 D2 when blended with ITIC-4F. In contrast, large differences are observed in PCE when the active layer thickness is increased to 180 nm resulting in a decrease in average PCE for PM7 D2 (5.3%), whereas PM7 D1 was able to retain a 11.9% average PCE (Figure 15). The difference in active layer thickness tolerance between PM7 D1 and PM7 D2 is rationalized by extracting the energetic disorder (σ) for hole transport using temperature dependent space-charge limited current studies. In the end, this study conveys how small changes to polymer structure, such as side chain placement, may have a small effect on thin-film polymer properties and device performance, but significant differences are realized when charges are transported over longer distances (thicker films, >150 nm). This work was published in the *Journal of Materials Chemistry C*.

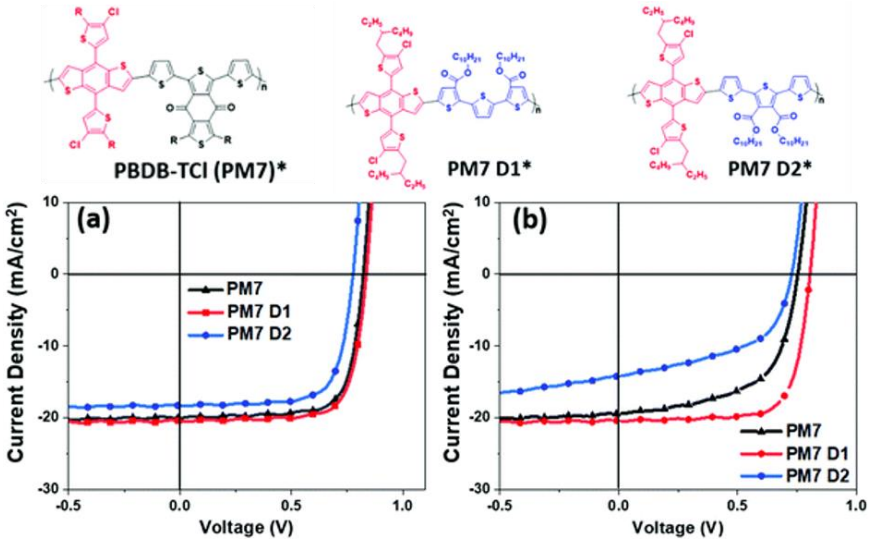

Figure 15. Structures of the polymers used in this study. Current density–voltage characteristics of OPV devices with a (a) 100 nm thick and (b) 180 nm thick active layer. Adapted from Jones et al. *J. Mater. Chem. C* 2020, 8, 43, 15459.

3.4. Discrete molecule ordering and solar cell performance

Our first discrete molecule study aimed to synthesize and characterize two donor–acceptor type conjugated molecules, 2EH-CPDT(FBTTh$_2$)$_2$ and 5EN-CPDT(FBTTh$_2$)$_2$, with different branching points from the backbone (Fig. 16). It was found that the branching point variation strategy slightly tunes the optical and electrochemical properties of the resulting conjugated molecule films owing to the difference between their intermolecular packing. When used as a donor material in PC$_{71}$BM-based OSCs, the power conversion efficiency of 2EH-CPDT(FBTTh$_2$)$_2$ is twice that of the ones processed using 5EN-CPDT(FBTTh$_2$)$_2$. Interestingly, with no post treatments, OSCs were optimized with especially low-donor content within the active layer (donor : acceptor weight ratio = 1 : 9), which allows construction of a highly transparent film with a visible transmittance over 50%, showing potential for application in integrated photovoltaics. We believe that this study contributes to a better understanding of the structure–property relationships in conjugated molecule-based OSCs and facilitates the design of new compounds for advanced high-performance transparent and semi-transparent photovoltaic devices. This work was published in the *Journal of Materials Chemistry C*.

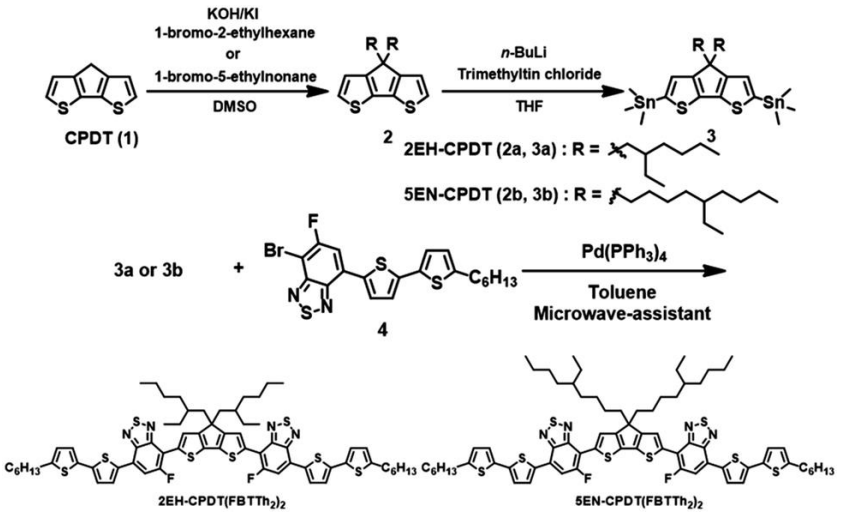

Figure 16. Synthetic route for 2EH-CPDT(FBTTh$_2$)$_2$ and 5EN-CPDT(FBTTh$_2$)$_2$. Adapted from Lee et al. *J. Mater. Chem. C* 2018, 6, 39, 10532.

We also report on two π-conjugated donor–acceptor–donor (D–A–D) molecules of amphiphilic nature, aiming to promote intermolecular ordering and carrier mobility in organic electronic devices (Figure 17). Diketopyrrolopyrrole was selected as the acceptor moiety that was disubstituted with nonpolar and polar functional groups, thereby providing the amphiphilic structures. This structural design resulted in materials with a strong intermolecular order in the solid state, which was confirmed by differential scanning calorimetry and polarized optical microscopy. Langmuir–Blodgett (LB) films of ordered mono- and multilayers were transferred onto glass and silicon substrates, with layer quality, coverage, and intermolecular order controlled by layer compression pressure on the LB trough. Organic field-effect transistors and organic photovoltaics devices with active layers consisting of the amphiphilic conjugated D–A–D-type molecules were constructed to demonstrate that the LB technique is an effective layer-by-layer deposition approach to fabricate self-assembled, ordered thin films. This work was published in *ACS Applied Materials and Interfaces*.

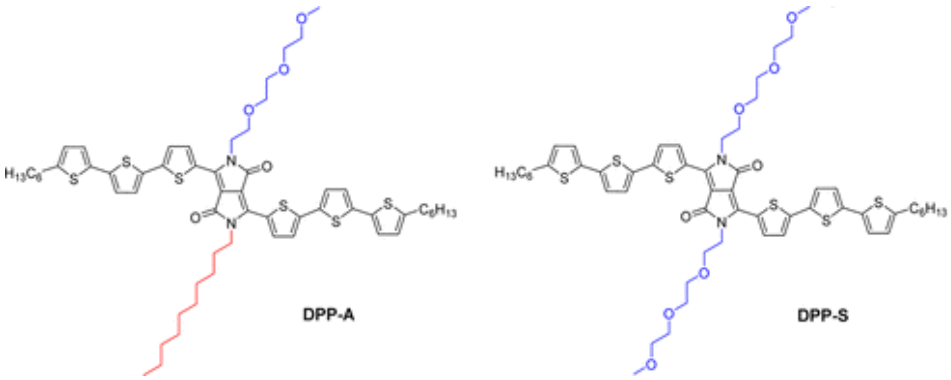

Figure 17. Chemical Structures of DPP-A and DPP-S. Adapted from Lo et al. *ACS Appl. Mater. Interfaces 2018*, 10, 14, 11995.

4. Concluding remarks

It has been an exciting, enlightening, and satisfying time to be involved in organic photovoltaics research throughout the period of this grant. The fact that overall power conversion efficiencies (PCEs) in the field advanced from the exploratory 11%, to values worth considering for commercialization at 18%, indicates that the ONR OPV research has contributed strongly in the field where ultimately lightweight and silent power may be made available across various DOD platforms. While our specific research program was not designed to provide the highest PCEs in champion cells, many of our systems have performed in the 10–15% range indicating the high performance of our materials.

In this specific program we have approached our work through a combination of molecular and macromolecular structures where, most importantly, we understand the chemistry of our systems so we can relate molecule, repeat unit, and higher-level order structure to properties being measured. Evident in our studies investigating the molecular order in donor acceptor compounds, early on we investigated amphiphilicity and how changing from nonpolar to polar side chains affected molecular packing. A major portion of our work has involved polymer synthesis where a number of polymer families have been designed, prepared, tested and shared with collaborators. It was our intent, which we believe successful, to synthesize polymers of the highest quality, and allow others in the field to know that they knew what they were working with. In those syntheses, by providing minimal structural changes in any one system, we have been able to elucidate small molecular effects on a variety of properties that control their ability to provide a photovoltaic response. Much of the work in this grant has been fundamental in nature as we investigated the impact of structure on open circuit voltage, exciton delocalization, lifetime of excited states, how energy offset impacts performance, and the role of energetic disorder on solar cell performance. Through this grant, we learned the importance of aggregation in the polymer solution that will be used as the ink for forming the active layers during printing. By knowing and setting the structure in the processing solution through aggregation, we demonstrated how blade coating could be used as a roll-to-roll mimic as desired for these materials to ultimately be used in commercial solar cells. We look forward to delving into this further in our ONR funded research in collaboration with such groups as Ying Diao, Seth Marder, Michael Toney, Jean-Luc Bredas, and Lee Richter, along with our continued interactions with Franky So.

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Training opportunities

The results generated in this project have resulted in several presentations. This project has allowed our graduate students to learn and practice GIWAXS measurements and data analysis by traveling to Stanford Synchrotron Radiation Lightsource and working with the assistance of Prof. Michael Toney's group at Stanford. Abigail Advincula travelled to the Naval Research Laboratory (NRL) to learn solid state NMR (ssNMR) techniques with Dr. Chris Klug. Ian Pelse traveled to Brookhaven National Laboratory (BNL) to conduct real time GIWAXS measurements on blade coated active layers with Dr. Lee J. Richter from the National Institute of Standards and Technology (NIST).

Honors and awards

Graduate student Ian Pelse completed a National Defense Science and Engineering (NDSEG) Graduate Fellowship, awarded from the Department of Defense with his work on this grant.

Graduate student Rylan Wolfe completed a National Defense Science and Engineering (NDSEG) Graduate Fellowship, awarded from the Department of Defense with his work on this grant.

Graduate student Abigail Advincula is currently in the third year of her National Defense Science and Engineering (NDSEG) Graduate Fellowship, awarded from the Department of Defense.

John Reynolds received an American Chemical Society Cope Scholar Award in 2020.

John Reynolds received the Florida Award from the Florida Section of the American Chemical Society, 2019.

Graduate student Ian Pelse won the Johnson travel award from the Georgia Tech Department of Chemistry and Biochemistry in Spring 2019.