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Fluorescence Microscopy of Materials with Energy Applications

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Fluorescence Microscopy of Materials with Energy Applications

by

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Dedication

To my family

To all of my friends

This wouldn't have been possible without you

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Abstract

Fluorescence Microscopy of Materials with Energy Applications

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One of the largest drivers of modern materials research is the advancement of renewable energy, particularly solar power. This objective has seen the rise of several different materials systems, each with their own advantages and disadvantages. Before any of these alternatives to traditional inorganic semiconductors can be effectively utilized at a commercial scale, they must first be understood at the fundamental level such that they can be tuned through utilization of the structure-property relationship. This dissertation describes the use of fluorescence-based microscopy techniques to explore material systems relevant to energy production at the smallest possible levels, ranging from single molecules and aggregates to small scale surface structures in order to unravel the microscopic heterogeneities that influence photophysical performance. First, two different conjugated polymers were studied. Poly(3-(2'-methoxy-5'-octylphenyl)thiophene) (POMeOPT) aggregates were studied in bulk solution in order to probe charge transfer character in the excited state. Nonpolar solution environments led to more than hundredfold increases in the fluorescence intensity of this material, demonstrating the importance of the environment in manipulating the photophysics of conjugated polymers and illustrating the role the charge transfer state plays in the excited state. Next, a polyphenylenevinylene (PPV) based block copolymer designed for controlled folding was examined at the single molecule level with excitation polarization spectroscopy, revealing not only the robustness of the folding functionality, but also that the resulting folds spaced the chromophores far enough apart to severely limit interactions between them. Shifting to a different class of energy materials, single perylene diimide (PDI) aggregates were then formed with solvent vapor annealing (SVA) and studied with fluorescence microscopy. These experiments revealed a vast heterogeneity amongst small aggregates as well as provided strong evidence for emissive excited states with triplet character occurring even in small aggregates. The final class of material studied was a Ruddlesden-Popper phase quasi-2D organolead halide perovskite. Confocal fluorescence microscopy was utilized to image film degradation in the presence of moisture, and provided insights into the mechanism behind moisture-driven surface crystallite growth. Taken together these experiments demonstrate the power of fluorescence microscopy to advance the understanding of energy materials systems by examining small scale heterogeneity.

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Chapter 1: Introduction

In recent years, optoelectronic devices, particularly those pertaining to solar energy have risen in prominence in both the commercial and academic realms. The desire for more efficient and stable devices has driven an increase in related research. With this increase has come the rise of new materials that go beyond traditional inorganic semiconductors that exhibit properties suited for special applications, such as enhanced flexibility or multiple exciton generation. One of the major limitations in optoelectronic devices is that they must be operable at maximum possible effectiveness at a large scale. Single ultra-pure crystals are not commercially viable for many of these applications, particularly solar energy. Unfortunately, large scale processing and production methods produce microscopic heterogeneities of different types within material systems that may seem homogenous to the naked eye. These heterogeneities alter the local photophysics and can impact multiple processes necessary for effective device functionality. In order to better understand these heterogeneities and work towards minimizing them, we must understand the interactions behind them. Fluorescence and fluorescence microscopy have proven to be valuable tools for studying these heterogeneities when these materials are emissive and how different fundamental interactions change their spectral behavior. This dissertation explores unraveling the interactions that occur in three promising optoelectronic materials, conjugated polymers (CPs), perylene diimides (PDIs), and 2D Ruddlesden-Popper (RP) perovskites, using fluorescence and fluorescence microscopy-based techniques.

1.1 HETEROGENEITY OF MATERIALS

To the casual observer, films made of one or a few components may seem quite homogeneous. Even the bulk emission spectra of films tend to be fairly uniform when taken at different locations in a film. This is a result of the limitations of the technique, which averages the signal both temporally and spatially. The latter average is particularly problematic, given the approximate dimensions of a single basic PDI emitter are approximately 1.15 nm x .49 nm,¹ far

smaller than even the diffraction limit of light, which is given by equation 1, where λ is the wavelength of light and *NA* is the numerical aperture of an objective lens²:

$$Diffraction \ limit = \frac{.61\lambda}{NA} \tag{1}$$

When observed under microscopy techniques, however, these films are extremely heterogeneous, possessing many disruptions to the uniformity ranging in scale from single molecule and aggregates up to larger scale defects in the hundreds of nm. Whether due to different crystalline domains, degradation processes, changes in material conformation, formation of surface structures, physical defects, or any number of processes, these heterogeneities change the fundamental photophysics at play within the materials. Despite being so small, the interactions caused by these heterogeneities can have significant consequences. Figure 1.1 shows an example of this in the form of near-field scanning optical microscopy measurements of a 'homogeneous' film of the CP poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) performed by Nguyen and Schwartz.³ Emission spectra taken within 1 µm of one another exhibit dramatically different emission spectra due to the differences in local environments caused by interactions within the material. Heterogeneity is not unique to just polymer systems. It exists at different length scales in almost any class of material that can be used for optoelectronic systems.^{4–} ⁶ Despite these limitations, however, fluorescence emission is still a powerful tool in unraveling the nature of the heterogeneities, as emission spectra are extremely sensitive to changes in interactions and material composition, as is detailed further in section 1.2.

One method to better understand the interactions that lead to these heterogeneities is to turn to smaller scale systems and observe how these interactions build up with increasing size. Aggregate and single molecule fluorescence studies serve as the main avenues to achieve this. Instead of looking at films with random heterogeneities and interactions, aggregates can be formed that control the interactions in a more uniform way. This allows for both studies of individual aggregates as well as ensemble solution-state experiments that still have applications to films. The theory behind the photophysics of molecular aggregates has been widely explored, particularly in the H- and J-aggregate model,⁷ which defines aggregates based on whether the inter- or intramolecular interactions between chromophores dominate the system. These theories are derived for idealized systems and many questions remain for both polymeric and disordered molecular systems. In order to properly understand the difference that aggregation of molecules makes they must be compared to isolated molecules. This can be achieved in several different ways. First, in a solution-based experiment, the system can be measured prior to forced aggregation. Under these circumstances, interactions are taken to be minimal, and in systems such as CPs the chains are assumed to be in the unfolded, extended chain configuration.^{8,9} Another means that complements this solution foundation is to synthetically tune a version of the desired chromophore in order to inhibit interactions through protecting groups¹⁰ or forced spacing, which is used in the work described in **Chapter 2**. An alternative means of achieving this is through extreme dilution to the single molecule level, thus forcing complete isolation of the system. Single molecule and single aggregate techniques allow for observations of these systems at the smallest and most isolated scales so the impacts of specific interactions¹¹ or structural designs^{12,13} can be probed. Microscopy provides a means of unraveling these heterogeneities at the scale at which they occur, particularly when coupled with the environmental sensitivity and composition of fluorescence emission.



Figure 1.1: Topographic profiles (right) and normalized spatially resolved photoluminescence (SRPL) spectra (left) of MEH-PPV films in different environments cast from 1% w/v solutions. A) Topography over a 5 x 5 µm area of an MEH-PPV film cast from chlorobenzene (left) and SRPL (right) collected on one of the bumps (dashed curve) and from a flat region of the film (solid curve). B) Topography over a 10 x 10 µm area of an MEH-PPV cast from tetrahydrofuran (right) and SRPL (left) collected on one of the bumps (dashed curve) and from a flat region of the film (solid curve). The inset shows the chemical structure of MEH-PPV. (Taken from the work of Nguyen, et al.³)

1.2 FLUORESCENCE EMISSION

In reference to cover slips that were not properly cleaned, Dr. David Vanden Bout once said, "you think to yourself that nothing fluoresces... then you look in the microscope and realize that EVERYTHING fluoresces." While this is a slight hyperbole used to make a point, there is still a degree of truth to it. Fluorescence lurks all around in unexpected places, ranging from the LEDs that cover every day electronics both as indicators and for show to the fabric, or scrim, that lies beneath the adhesive in duct tape, which fluoresces in different patterns depending on the manufacturer and aids in forensics.¹⁴ One key area where fluorescent materials have dramatically risen in prominence as components is in the realm of solar energy and other optoelectronic devices.^{15–23}

By definition, fluorescence is the radiative transition from the electronically excited state, S_1 , to the electronic ground state, S_0 .²⁴ After the initial excitation, however, there are a number of processes that can occur prior to and instead of fluorescence emission that all change the information that is collected by a spectrometer. Some of these processes are illustrated in the Jablonski diagram shown in **Figure 1.2**. Because of these processes, collecting information about emission can provide a great deal of information about the excited states of fluorescent systems. Many techniques are tailored to different types of systems at different scales, some of which will be detailed further in **section 1.3**.^{25–30}

There are many factors that influence fluorescence spectra, but they typically boil down to some form of interaction being responsible for the changes, which is what makes it such a powerful tool for probing system heterogeneities. In the simplest case with no external interactions, an isolated emitter with a well-aligned excited state will typically have an emission spectrum that is a mirror-image of the absorption spectrum shifted to the red, each with a well-defined vibronic progression.³¹ With respect to conjugated polymers, the first main deviation typically observed is a loss of the vibronic progression in the absorption spectrum, which is attributed to the varying conjugation lengths along the chain resulting in chromophores of different sizes absorbing and broadening the spectrum.^{31–34} Upon excitation, however, the exciton travels to the lowest energy

sites to emit, resulting in the defined vibronic progression for the emission spectrum as it is primarily coming from units with a single conjugation length (**Figure 1.3**).³¹

The vibronic progression can be broadly understood by reviewing the Franck-Condon principle. The Franck-Condon principle states that both absorption and emission are represented by vertical lines on a plot of energy versus internuclear distance showing multiple excited states.²⁴ This can be combined with Kasha's rule, which states that emission from the excited state occurs after relaxation to the vibrational ground state of the excited electronic state (v'' = 0) to any vibrational state in the electronic ground state (v'). This combination is illustrated in **Figure 1.4**. While some systems exhibit broad spectra without visible vibronic progressions, at the single molecule level many systems do exhibit them, and thanks to the Franck-Condon principle and Kasha's rule, valuable information can be gleaned from this progression. The particular shape of the vibronic progression can be characterized by the ratios of vibronic peaks, which depend on the nature of the excited state. These ratios serve as a means of estimating different aspects of the excited state, including degrees of interchain electronic coupling strength in the excitons in aggregates.^{7,35–37} **Chapter 2**, in particular, takes advantage of the ratio of the second vibronic peak to the first in absorption spectra, $\frac{A_0-0}{A_{0-1}}$, which serves as an estimation of the interchain excitonic coupling, where an increased ratio is indicative of reduced interchain coupling.^{7,37}



Figure 1.2: Jablonski diagram illustrating photophysical transitions. Straight arrows represent radiative processes and wavy arrows represent nonradiative transitions (Taken from the work of Valeur et al.³⁸)



Figure 1.3: Steady-state absorption and fluorescence spectra of MEH-PPV solution in toluene and thin MEH-PPV film (cast from 2 g/L solution) at 77 K and room temperature. (Taken from the work of Mirzov and Scheblykin.¹⁹)



Figure 1.4: Illustration of Franck-Condon Principle. The simplified potential energy curves with vibrational functions show how the overlap of vibrational wavefunctions determines the shape of the absorption (dotted line) and emission (solid line) spectra. (Taken from the work of Burnet.³⁹)

1.3 TECHNIQUES IN MICROSCOPY

While standard film and solution based fluorescence techniques can provide a wealth of valuable information, one aspect remains constant throughout them: they average over the entire sample set, which can lead to loss of information and can wash out effects that could have a significant impact on the photophysics. A prime example of this comes from near-field scanning optical microscopy (NSOM) measurements performed by Nguyen and Schwartz on 'homogeneous' conjugated polymer films. Despite the films being spun from a single batch of polymer, the NSOM experiments showed different domains that exhibited dramatically different fluorescence spectra at points even 1 µm apart from one another.³ Heterogeneity to this degree at the smallest scales can then lead to decreased device performance. It is for this reason that there have been large pushes both in materials design to control conformation and morphology and in developing techniques to probe systems at the smallest possible scales to build up to larger systems that can be viably used in devices. Variations on high powered fluorescence microscopy have answered the call in analyzing many different systems at the small scale, be it by isolating analytes to single molecule concentrations or by separating out different spectral components. Small scale probing of the emissive behavior of energy material systems has blossomed into a very diverse field. Scanning probe microscopies, for example, have found some utility in this regard, despite lacking the ability to achieve atomic resolution in some of these systems.^{30,40} Scanning probe techniques have even been coupled directly with fluorescence microscopes to create hybrid instruments with very specific capabilities.³⁰ Even within the realm of pure fluorescence, there are many options beyond just pure microscopy, including hyperspectral imaging of surfaces for composition determination,41 detection of delayed emission and fluorescence lifetime measurements to probe processes in the excited state,^{4,42,43} fluorescence correlation spectroscopy to elucidate the number of emitting species,²⁶ and even linear dichroism to examine molecular structure.⁴⁴ This is by no means a comprehensive list, and many techniques can be applied to microscopy, all of which present different opportunities for studying samples at the smallest scale.

The microscope utilized in the experiments described throughout this dissertation operates
with an argon ion laser in both a wide field arrangement and a confocal path, both arriving at a 100x objective. **Figure 1.5** depicts a simplified widefield configuration, utilized for bulk excitation and high throughput analysis. The wide field pathway utilizes an electro-optical modulator in conjunction with two wave plates ($\lambda/2$ and $\lambda/4$ placed before and after respectively) to produce linearly polarized light that rotates with respect to an applied bias. It achieves this with a crystal that exhibits the electro-optic effect, where the refractive index changes with respect to an applied bias. By cycling the voltage with a function generator, this rotation can be tuned and controlled in order to perform excitation polarization spectroscopy, a technique that has been extensively utilized on both single molecules and aggregates.^{11,12,25,45–48} This utilizes the rotating excitation polarization to create a trace of emission intensity with respect to the angle of polarization (θ). This trace is then fit with equation 2:

$$I(\theta) \propto 1 + M \cos 2(\theta - \phi) \tag{2}$$

where ϕ is the polarization angle of maximum absorption.^{13,25,45,46,49} The modulation depth, *M*, is the projection of the absorption tensor onto the *x*-*y* plane, and serves as a measure of the anisotropy of the system represented by equation 3:

$$M = \frac{I_{Max} - I_{Min}}{I_{Max} + I_{Min}} \tag{3}$$

where $M \rightarrow 1$ signifies an ordered, anisotropic system while $M \rightarrow 0$ is the isotropic, disordered case (Figure 1.6). In this equation I_{Max} and I_{Min} represent the maximum and minimum fluorescence intensities respectively. These experiments provide insights into the order and disorder of the system, and can also be used in conjunction with other processes to see how changes in system order relate to changes in excited state behavior. It is important to note that the modulation depth only serves as an approximation of the relative packing of the chromophores and system order due to the fact that information about the z-direction tilt and position, are lost in the projection. Despite this, the shape and mean of a histogram of M values can be very illuminating. After excitation, the light is then sent to a cooled charge coupled device (CCD) camera that records movies of the modulation process that can then be analyzed with Matlab code. These movies allow for counting the number of fluorescent emitters for concentration control. They also prove quite useful in confirming sample quality, as any contaminants and defects in the sample are immediately visible. These movies also enable the viewing of annealing processes, as described below.

The confocal pathway provides options for different types of experiments that are localized in a single spatial location. After excitation, the emitted light passes on to one of two detectors, as shown in the simplified schematic shown in Figure 1.7. The first step of confocal experiments is to focus the excitation beam into a tight spot and direct the light collected back from the sample to an avalanche photodiode (APD). In all of these experiments the resolution is determined by the size of the excitation beam, as the only part of the sample that is being excited is within this tight focus. The emission can then be collected on an APD to create higher resolution images that are zoomed in more than the wide field is capable of, as well as to direct placement of the beam onto specific locations within the sample for data collection. The APD is also capable of taking fluorescence transients that plot the number of photons collected with respect to time at small timescales with no differentiation by wavelength. These transients are used to monitor blinking behavior in emitters, which allows for monitoring of quenching behavior, as well as approximation of the number of active chromophores and if they are behaving independently with one another. Alternatively, the emitted light can be directed to a liquid nitrogen cooled CCD-based spectrometer. While spectra are typically taken at longer time scales (10-30 seconds for single molecule experiments) to achieve an acceptable signal to noise ratio, this system allows for spectroscopy of isolated species, free of interactions and systemwide averaging that would be present in film or solution studies in a standalone spectrometer. Spectra are taken in series of 3-4 on the same spot to monitor for intensity, shape, and position changes. This allows for monitoring of bleaches, blinks, shifts, and other phenomena that may occur during extended periods of laser excitation. The spectra are then processed with a Matlab program, which allows for ensemble averaging, fitting, and determination of the Huang-Rhys parameter. As described in previously in section 1.2, changes in spectral characteristics indicate changes in the interactions between the chromophores and can thus be linked to the variable changed between samples.

In addition to the detectors, the microscope system is equipped with auxiliary equipment that allows for special experimental variants. The most prominent of these pieces is a home-built gas/solvent vapor flow chamber specially equipped for performing solvent vapor annealing (SVA). This technique utilizes either a single poor solvent that is sufficient to swell the matrix or a blend of good and poor solvents for the analyte.⁵⁰ The solvent vapors swell the optically inert matrix allowing for either rearrangement of conformation⁵¹ or the formation of aggregates⁵⁰ depending on the annealing conditions. It is an extremely tunable process, with differing results based on analyte concentration, solvent selection, flow rate, annealing time, and, most significantly, solvent selection, which is the main means of altering aggregate size (**Figure 1.8**).⁵⁰ In order to facilitate the SVA process, the custom made sample holder allows samples to be placed under controlled atmospheres. Most recently, this system was modified to allow in situ switching between nitrogen, which is what was traditionally used, to air at the same pressure. This system was installed to explore triplet formation, given that triplet states quench in the presence of oxygen.^{52–55}



Figure 1.5: A basic wide-field fluorescence microscope setup used in this dissertation



Figure 1.6: A schematic representation of polarization excitation experiments. E_{ex} is the direction of linearly polarized excitation at an angle θ (left). A representative fluorescence intensity trace as a function of excitation polarization angle. The black line is the experimental data and the red line is the fitted curve (right). (This figure was taken from the works of Bolinger et al.⁵⁶ and Hu et al.²⁵)



Figure 1.7: A basic confocal microscopy setup used in this dissertation



Figure 1.8: Wide-field fluorescence images of highly diluted MEH-PPV/PMMA thin films before and after undergoing different processing conditions. The chloroform/acetone ratio for 30 min SVA is denoted in the parentheses above the images. The same MEH-PPV/PMMA concentrations were used for each sample. An excitation wavelength of 488 nm with an intensity of approximately 1.5 W/cm² was used, and the same z-scale was applied to all images. (Taken from the work of Vogelsang, et al.⁵⁰)

1.4 MATERIAL SYSTEMS

This dissertation covers a variety of different energy materials, each of which serves a different role in the field. Each section below provides a brief background into key questions surrounding each material system, while each of the primary chapters provides a more in-depth introduction into the specific properties under study.

1.4.1 Conjugated Polymers

Conjugated polymers (CPs) possess a wide range of desirable properties, including accessible energetic bandgaps, synthetic versatility, and mechanical flexibility, which make them attractive for flexible and wearable optoelectronic devices. An accurate and comprehensive understanding about the morphology-photophysics relations in CPs lays the groundwork for their development in these applications. However, due to the complex roles of chemical structure, side-chains, backbone, and intramolecular interactions, CPs can exhibit heterogeneity in both their morphology and optoelectronic properties as previously discussed. This heterogeneity can even manifest at the single chain level. This molecular level heterogeneity together with complicated intermolecular interactions found in bulk CP materials severely obscures the deterministic information about the morphology and photophysics at different hierarchy levels. To counter this complexity and offer a clearer picture for the properties of CP materials, material systems with specific structural features are often probed via single molecule/aggregate spectroscopy.

By definition, conjugated polymers possess backbones consisting of alternating double bonds and as the chain length extends, the electrons become increasingly delocalized along the chain. As monomers are added to the chain, the p_z orbitals begin to overlap on adjacent carbon atoms, forming a low energy π -bonding orbital (HOMO) and a high-energy π^* -antibonding orbital (LUMO). With further monomer addition, more and more π and π^* energy levels are added to the system, increasing the density of states. As the density of states increases, eventually electronic bands are formed, as is illustrated in **Figure 1.9**, resulting in semiconducting properties in a polymeric material.⁵⁷ While devices made from conjugated polymers do not match the efficiencies of many inorganic semiconductors, they possess the same general functionality while having the capability to be printable and foldable, opening up new possibilities for devices.

Despite the promise of CP-based optoelectronics, they are still very complex systems that exhibit massive degrees of heterogeneity at every possible size scale, particularly in films, as was shown in Figure 1.1. Given that films are the primary form needed for devices, unraveling these heterogeneities becomes crucial to improving device performance. There are two primary components of CPs that have been targeted at the single molecule level to control morphology and photophysics: the backbone and the side chains. In the CP unit, the backbone is not only the primary determinant of mechanical properties via molecular class and molecular weight, but also the primary photoactive unit, as it is the segment that actively absorbs and emits light. While a long chain of repeating double bonds could, in principle, yield an infinitely long conjugation length resulting in total electron delocalization, defects, kinks, and folds disrupt this system.⁵⁸ A more accurate model of a CP is then a series of chromophores of certain lengths of repeating units that are connected to one another. Previous studies have used techniques such as incorporating designed kinks,⁴⁸ altering backbone stiffness with reinforcing functionality,⁵⁹ and even incorporating flexible linkers between small oligomeric chromophores^{12,26,27,60} to control the photophysics and folding of CP backbones at the single molecule level. The work described in **Chapter 3** takes advantage of backbone design and flexible linkers between chromophores to influence single molecule folding in a conjugated polymer system.



Figure 1.9: Band formation from molecular repeat unit to π -conjugated polymer. (Taken from the work of Gutzler et al.⁵⁷)

The side chains, while not the fundamentally emitting unit, still have important functions beyond just serving as solubilizing groups. The relative position (or regularity) of these side chains has shown a pronounced effect on packing order and distance of chromophores.^{46,49} The latter of these effects can dramatically impact the interactions both at the single chain and single aggregate levels by either allowing or inhibiting interchain interactions and changing the nature of the excited state.^{10,61,62} The work described in **Chapter 2** takes advantage of bulky side chains to explore the nature of the excited state in molecular aggregates. The phenomena described here are only a subset of the different outcomes from altering the backbone and side chains in conjugated polymers. For further details on how molecular architecture influences morphology and photophysics, **Appendix A** serves as a fairly comprehensive review on the topic.

1.4.2 Perylene Diimides

In the quest to enhance solar cells, perylene diimides (PDIs), the general structure of which is shown in **Scheme 1.1**, have recently become a popular option. PDIs possess excellent photostability and molar extinction ($\sim 5 - 10 \times 10^4 M^{-1} cm^{-1}$), high thermal stability, and decent chemical resistance which is why they have traditionally been used as industrial pigments and, in particular, automotive paints.^{63–67} In addition to these properties, PDIs fit the very distinct energetic requirements to undergo singlet exciton fission (SF).^{68–71} Singlet fission is a special case of internal conversion in which a singlet exciton converts into two triplet excitons, each of approximately half of the energy of the initial singlet

$$E(S_1) \approx 2E(T_1) \tag{4}$$

where S_I and T_I refer to the excited singlet and triplet states respectively.^{71–73} A simplified diagram of this process is shown in **Figure 1.10**. One of the main hindrances to increasing the efficiency of modern photovoltaic cells is energy loss through charge carrier thermalization. This pathway, which represents approximately 50% of the energy loss in silicon photovoltaics,⁷⁴ occurs when a cell absorbs a photon of a higher energy than the bandgap. These excited charges rapidly relax down to the band edge, releasing the excess energy as heat.⁷⁵ In order to mitigate this process and reclaim this lost energy, materials that utilize high energy photons to excite multiple charge carriers have been integrated into devices through processes such as singlet fission.^{68–71} While intersystem crossing (conversion of a singlet to a triplet) is a spin-forbidden process in two electron systems, which dramatically reduces the probability of occurrence, singlet to triplet conversion can be spin allowed in a four electron system, as a superposition of two triplets produces a net singlet, conserving the spin angular momentum.⁷⁵ Singlet fission is described further in **Chapter 4.1**.

Because PDIs possess the previously detailed qualities regarding stability and a low lying triplet state that satisfies equation 4,^{63,65,76} they are popular candidates for singlet fission experiments aimed at further enhancing triplet exciton yields. Previous studies have shown the pronounced effect that packing geometry has on the SF rate in these systems,^{6,72,77} yet there is no way to achieve uniform assembly of these materials in the films that would be required in commercially viable devices, which have been shown to exhibit singlet fission.^{63,78} The research described in **Chapter 4** focuses on exploring the smallest possible unit of PDIs that can exhibit singlet fission: molecular dimers. Here small single aggregates isolated in an inert polymer film were studied to examine heterogeneity in the aggregates and differences in the emission spectra as compared to single molecules. This work looked at initial differences in how the single molecules and aggregates interacted with atmospheric oxygen as a means of probing triplet formation.



Scheme 1.1: The general form of a perylene diimide (PDI) dye molecule



Figure 1.10: Diabatic states that can facilitate SF between two identical molecules A and B.
Electron transfer from A to B followed by back electron transfer can prepare a triplet pair state. An analogous path can be drawn where hole transfer from A to B precedes electron transfer. (Taken from the work of Le, et al.⁷⁸)

1.4.3 Ruddlesden-Popper Phase Perovskites

One very active field of research is currently solar energy devices based on metal halide perovskite semiconductors. These materials, based on the ABX₃ crystal structure where A is usually an organic 1+ cation, B is a metallic 2+ cation, and X is a halide, have set records for photovoltaic device efficiencies, even breaking 23%.^{79,80} Unfortunately, 3D metal halide perovskites possess many qualities that make them unsuitable materials for commercial solar devices, the most significant of which involve stability. Specifically, most organolead halide perovskite materials, such as the prototypical methylammonium lead triiodide (MAPI), are extremely vulnerable to, amongst other things, both moisture and, most importantly for solar applications, light.^{81–83}

There has been significant effort in recent years to develop systems that utilize this high device efficiency while lacking this rampant instability. One material class that has grown in popularity is the 2D Ruddlesden-Popper (RP) phase organolead halide perovskites. These materials follow the chemical formula $A'_2A_{n-1}B_nX_{3n+1}$, where A' is an amphiphilic alkylammonium species, such as *n*-butylammonium (nBA), which serves as a spacer forcing the perovskite crystal lattice to separate into quasi-2D sheets.⁸⁴ As shown in Figure 1.11 these sheets can be tuned to consist of different amounts of corner-sharing metal halide octahedra.^{85,86} This count of adjacent octahedra is referred to as the *n*-phase of the material. Photophysically, these domains behave similar to quantum wells, where n controls the well thickness, bandgap, and the exciton binding energy.^{79,86} While the perovskite phase governs the optical properties, the organic spacers between the sheets have a pronounced impact on the mechanical properties, such as elasticity and thermal transition temperature,⁸⁶ as well as the barrier thickness, the barrier height, and the out-of-plane mobility in the quantum well.⁷⁹ It has been shown by multiple groups that these Ruddlesden-Popper phase perovskites are significantly more stable in humidity than the 3D materials.^{81,87–90} This enhanced water stability is believed to be due to the degradation producing a passivating layer on the surface that isolates the bulk of the material from the hydration layer.⁸¹ Unlike 3D perovskites, which form remarkably homogeneous films,⁹¹⁻⁹³ RP perovskite films are naturally heterogeneous, phase separating by n value in the z direction of a film, with low n values preferentially forming closer to the substrate.⁵ This heterogeneity only increases as these samples are exposed to moisture and degradation sets in. The research in **Chapter 5** focuses on understanding the root of this degradation process by studying 2D RP phase perovskites at various stages of degradation with fluorescence microscopy.



Figure 1.11: Fundamental crystal structures of Ruddlesden-Popper phase perovskites sharing the chemical formula $A'_2A_{n-1}B_nX_{3n+1}$, where n = 2, 3, and 4. Here A' is *n*-butylammonium, A is methylammonium, B is Pb, and X is iodide. (Assets for this figure were provided by Bryan Wygant of the Mullins group at the University of Texas at Austin)

1.5 DISSERTATION OVERVIEW

Given the consistency throughout energy materials that heterogeneity influences device photophysics at microscopic scales, this dissertation is dedicated to unraveling the nature of these heterogeneities through fluorescence and microscopy techniques. The ultimate goal is to eventually improve optoelectronic performance through understanding and eliminating heterogeneity.

Chapter 2 examines the effect of environmental dielectric on the emission of aggregates of a polythiophene derivative with a bulky side chain as an exploration of material design principles intent on destabilizing a charge transfer state in aggregates. The synthetic route for creating the polymer as well as solution state fluorescence measurements are presented for poly(3-(2'-methoxy-5'-octylphenyl)thiophene) (POMeOPT). These fluorescence experiments serve to probe how environment influences microstructure in CP aggregates and, consequently, the photophysics.

Chapter 3 further builds upon utilizing materials design to tailor materials at the smallest scale by studying a specially designed block copolymer with functionality incorporated to fold single chains into β -sheets. This series of experiments was undertaken in collaboration with the Weck group at New York University with wide field single molecule fluorescence microscopy coupled with modulation depth studies and single molecule fluorescence spectroscopy to expand on molecular design and force structural organization at the smallest possible scale in conjugated polymers.

Chapter 4 presents preliminary data collected from single perylene diimide aggregates isolated in a polymer matrix with confocal single molecule fluorescence microscopy of N,N'-bis(2-phenylethyl)-3,4,9,10-perylenedicarboximide in collaboration with the Roberts group at the University of Texas at Austin. This particular PDI has shown a good propensity for singlet fission in films. Single aggregates were formed with solvent

vapor annealing and studied with the aim of elucidating a relationship between aggregate structure and singlet fission rate to assist in eventual upscaling to film structure optimization.

Chapter 5 presents a study in collaboration with the Mullins group at the University of Texas at Austin on the degradation of 2D Ruddlesden-Popper phase perovskites. When exposed to moisture for extended periods of time, crystallites form on the surface of the films. Confocal microscopy and spectroscopy were utilized to study the formation of these crystallites and provide insights into the processes leading to their formation so that future work can lead to improving film stability and maintaining homogeneity throughout moisture exposure.

Chapter 2: Characterizing the Excited States of POMeOPT

2.1 INTRODUCTION

A critical aspect of modern materials design is using theory in order to predict the properties of a novel material. As is discussed in further detail in Chapter 3 and Appendix A and was briefly discussed in Chapter 1, conjugated polymers have become very popular systems for materials design due to the wide degree of tunability. This tunability is complimented by the ease of polymeric processing, relative flexibility compared to inorganic semiconductors, and capacity to make optoelectronic devices. Unfortunately, modern computational methods cannot accurately predict excited state behavior of conjugated polymer systems because the molecules are too complex to model the interactions of extended chains.⁹⁴ In order to alleviate this, researchers have turned to making modifications on benchmark systems that can be compared to the unmodified system and compared against computational efforts. Poly-3-hexylthiophene (P3HT) and other polythiophene derivatives have become a very popular material for this sort of experimentation due to small, easily tunable band gaps and strong networks of delocalized π -electrons along the molecular backbone.⁹⁵ Previously, several groups have used molecular aggregates to study the excited states of conjugated polymers, particularly regioregular P3HT (rr-P3HT).^{10,96} Although this system has been widely studied, many groups have reported a decrease of the fluorescence quantum yield of P3HT in the presence of interchain interactions.^{10,26,55,97-100} This observation and the development of the weaklyinteracting H-aggregate model by Spano et al. in which the 0-0 transition from the first excited state to the ground state is symmetry forbidden,^{7,97} have led to the revelations of different contributing factors of this effect. These contributions to the dimming stem from singlet-triplet exciton annihilation,⁵⁵ polarons, and polaron pairs.^{98–100} More prominently however, Scheblykin et al. and Silva et al. have reported the presence of interchain chargetransfer character in the excited states of these materials as a contributing factor to the reduced emission.^{10,42} Given all of these contributions, the full nature of the excited state in the presence of interchain interactions is still not completely understood.

Despite extensive studies on solution state aggregates of the P3HT homopolymer, molecular solutions do not accurately represent the inherently heterogeneous films that are utilized in devices. In previous studies within our group a model rod-coil-rod triblock copolymer, poly(3-hexylthiophene)-block-poly(tert-butyl acrylate)-block-poly(3hexylthiophene) (P3HT-b-PtBA-b-P3HT) (Scheme 2.1A) has been used to simulate film spectra in solutions. When dissolved in a good solvent, this polymer accurately replicates the electronic spectra of P3HT solutions. Upon addition of a poor solvent, however, the triblock copolymer collapses, forcing the P3HT segments into a more confined confirmation. When collapsed, the electronic spectra mimic those of P3HT films.²⁷ In order to better understand the interchain character of the excited state, aggregates of this material were formed in solutions of varying dielectric, ε .²⁶ In polar solvents ($\varepsilon > 3$), the aggregates exhibit a low fluorescence quantum yield, just as in bulk films, and demonstrate H-aggregate behavior where a non-emissive charge-transfer state dominates, as determined by fluorescence lifetime measurements. By contrast, when the solution dielectric is low (ε < 3), the fluorescence quantum yield increases nearly tenfold with an accompanying spectral shift more typical of exciton character.²⁶ This is due to the preferential stabilization of charge transfer-type states in polar environments allowing this state to compete with the emissive exciton. Simulation predicts that in the triblock system, when $\varepsilon > -2.2$, the charge transfer state becomes a rival alternative to the standard excitation.²⁶ As $\varepsilon \approx 3-7$ in P3HT films, they lie beyond this threshold, suggesting a stabilized charge transfer-type state as a primary cause of the decreased emission.

In order to more fully develop the theory upon which simulation and material design are based, experiments were performed on the thiophene derivative poly(3-(2'-methoxy-5'-octylphenyl)thiophene) (POMeOPT) (Scheme 2.1B). These experiments were an evolution of those performed on the triblock copolymer, once again using a variety of good/poor solvent mixes to create aggregates in different dielectric environments. The polymer was selected because of its large substituent groups that should limit the proximity of the chains to one another. It is hypothesized that this would reduce interchain interactions and the subsequent formation of the charge transfer state. It was predicted that the forced chain separation would create a plot of fluorescence quantum yield vs. solution dielectric that adopts a sigmoidal pattern contrasting the exponential decay exhibited by the triblock copolymer. The material was not expected to show any major decrease in emission intensity until a more significant increase in solution polarity to overcome the handicap of the chain spacing and populate the charge transfer state in any meaningful amount.



Scheme 2.1: A) Structure of P3HT-b-PtBA-b-P3HT triblock copolymer. B) Structure of the conjugated polymer POMeOPT

2.2 EXPERIMENTAL

All chemicals were purchased from Sigma Aldrich (now Millipore-Sigma) without further purification. The triblock copolymer was obtained from stocks used for previous reports.^{26,27} Gel permeation chromatography (GPC) was performed with a Viscotek GPCmax VE-2001 with a Tetrahydrofuran mobile phase. Absorption and emission measurements were performed with Agilent 8453 UV-visible spectrophotometer (Agilent Technologies Inc.) and Fluorolog-3 spectrofluorometer (Jobin-Yvon), respectively.

2.3 SYNTHESIS OF POMEOPT

Due to a dwindling supply of the material and the lack of any suitable collaborators to synthesize it, a multi-stage synthesis of POMeOPT was undertaken. There is no direct publication of the synthetic route to the substituent and neither the monomer nor direct precursors are commercially available, with only limited recounting of the last few steps in the literature.¹⁰¹ The full synthetic route utilized is detailed in **Scheme 2.2**.

In order to create the monomer, the substituent precursor that could then be attached to the appropriate thiophene ring prior to polymerization was first synthesized. Following a previously published procedure for bromination of para-substituted phenols, 4-octylphenol was functionalized with a bromine via electrophilic aromatic substitution (**Scheme 2.3**).¹⁰² 2 g of the alkylphenol were dissolved in 10 mL CHCl₃ in a 100 mL round bottom flask and chilled in an ice bath with a stir bar to chill the reaction flask to 0° C. 1 g of sodium bicarbonate was then added to neutralize HBr that forms as a byproduct of the reaction. In an additional beaker, .6 mL of chilled Br₂ was dissolved in 4 mL CHCl₃. The bromine solution was then added dropwise using a Pasteur pipette, taking care to keep the bromine solution off the walls of the reaction vessel to reduce residual bromine at the end. Reaction progress was measured via thin layer chromatography (TLC) with a 90% petroleum ether and 10% ethyl acetate mix (all TLC and column chromatography utilize

this ratio unless otherwise noted). Comparison of the reaction vessel contents against the 4-octylphenol revealed that most of the starting material had reacted after approximately 20 minutes. The TLC plate revealed two distinct spots of products, one of which was the desired compound. The additional spot was attributed to a doubly brominated compound. The residual solid was removed via vacuum filtration and washed with chloroform before being dried in a rotary evaporator. The desired product was then isolated via column chromatography. The identity of the product was then confirmed with both mass spectrometry and ¹H-NMR (**Figure B.1**). The final yield of the reaction was 63.75%. All mass spectra and NMR spectra for the material synthesis are found in **Appendix B**.

The next step in the synthesis is the methylation of the hydroxyl group on the phenol to produce the ether. Initially, a methylation reaction that was also from Müller, et al. was used.¹⁰² The phase transfer catalysis mechanism utilizes a quaternary ammonium catalyst to remove the proton and splice on the desired alkyl group from an alkyl halide in a 2-phase system. An equal volume mix of dichloromethane (DCM) and water served as the dual solvents and foundations of the organic and aqueous phases respectively. After solvating the brominated phenol to this mixture, NaOH (15:1 molar ratio with respect to the phenol), MeI (30:1 molar ratio with respect to the phenol), and the benzyl tri-n-butylammonium bromide catalyst (1:1 molar ratio with respect to the phenol) were added to the solution. The solution was then stirred vigorously for 12 hours. After the reaction, the organic layer was separated and the aqueous layer was extracted twice with DCM. The organic extractions were then combined with the organic layer and evaporated in a rotary evaporator. TLC revealed multiple components, so the product was purified using column chromatography, and confirmed using ¹H-NMR and mass spectrometry. Unfortunately, the yield was low (47.9%) so an alternative technique was sought to create the methoxy group.

In order to improve the yield of the substitution on the hydroxyl group, a different and simpler reaction based on the electrophilic *O*-methylation mechanism was utilized (**Scheme 2.4**).¹⁰³ This single phase reaction utilizes six molar equivalents of methyl iodide (MeI) and two molar equivalents of potassium carbonate per one molar equivalent of the phenol, and the reaction runs for an extended time scale (~24 hours) at room temperature in dimethylformamide (DMF). Reaction progress was monitored with TLC. After 24 hours, TLC revealed nearly total conversion. The contents of the reaction flask were then vacuum filtered with DCM, yielding a solution that was milky in color due to excess MeI. The resulting solution was then placed in a rotary evaporator before being purified via column chromatography. It was then concentrated in the rotary evaporator once more and dried overnight with nitrogen gas. Product purity was then confirmed with both ¹H-NMR and mass spectrometry (**Figure B.2**). This reaction showed 83% conversion to the desired substituent molecule, a vast improvement to the originally utilized phase transfer catalysis reaction.

The next step in producing POMeOPT was to produce the full monomer and was suggested in the literature.¹⁰¹ In order to achieve this, the newly synthesized substituent molecule was grafted onto 3-thienylboronic acid using a Pd(0)-based catalyst in a modified Suzuki coupling reaction based on the work of Gronowitz and Peters that connects a boronic acid with a halide.¹⁰⁴ The substituent and the boronic acid were dissolved in 10 mL 1,2-dimethoxyethane in a round bottom flask. During this phase, 20% more boronic acid (by moles) than substituent was added in order to reduce the incidence of undesirable byproducts, as reported by Gronowitz and Peters.¹⁰⁴ 5 mL of 1 M sodium bicarbonate solution in water were then added to the reaction vessel, and the system was sparged with nitrogen for 15 minutes. The Pd(0) catalyst (tetrakis(triphenylphosphine) Pd(0)) was then added in excess. The system was then refluxed at 70°C under a condenser with vigorous

stirring overnight. During this period, the solution took on a black hue due to the Pd. After cooling, the solution was vacuum filtered and condensed on a rotary evaporator. 40 mL deionized water were then added, and the system was extracted three times with ethyl ether. The ether phase, which had taken on the black hue, was then washed with a saturated saltwater solution then dried with magnesium sulfate, vacuum filtered, and once again, condensed in a rotary evaporator. In order to obtain pure monomer, two columns were run with 98% petroleum ether to 2% ethyl acetate, which yielded complete separation from impurities. After NMR and mass spectrometry (**Figure B.3**), the product and its purity were confirmed at a yield of 66.7%.



Scheme 2.2: Synthetic pathway of POMeOPT



Scheme 2.3: Mechanism for electrophilic aromatic substitution



Scheme 2.4: Mechanism of the O-methylation reaction

Unlike the synthesis of the substituent, the polymerization reaction is detailed in the literature, and proceeds via an oxidative polymerization with FeCl₃.^{101,105} The direct mechanism for this polymerization is not currently known, but the generally accepted route is that it proceeds via a radical cation. This reaction took place in a glovebox in order to protect the catalyst. The monomer was dissolved in chloroform to a .05 M concentration and was set on a stir plate. A secondary beaker was used to create a .2 M slurry of the FeCl₃. Because the literature states that the key to regioregularity is very slow addition of the FeCl₃,¹⁰⁵ small additions to the reaction flask were made every 30 minutes over a 6 hour period. The mixture was then allowed to stir for an additional 1 hour before being removed from the glovebox and poured into a beaker of MeOH, thus precipitating the This precipitate was vacuum filtered, rinsed with MeOH, and crimson polymer. redissolved in chloroform. In order to completely dedope the polymer, an excess of 5 M ammonium hydroxide was added and heated to boiling with stirring for 30 minutes. The organic phase was then separated and washed four times with 5 M ammonium hydroxide solution and twice with a .053 M EDTA solution in water. After phase separation, the chloroform solution was then washed with water and filtered. It was then placed on a hot plate to reduce the total volume before being poured into another beaker of MeOH to reprecipitate. After vacuum filtration revealed that the polymer had only partially precipitated, as was evident from the deep red solution, the chloroform was evaporated off with a rotary evaporator. The remaining MeOH suspension was then filtered and evaporated several more times until the wash was a pale orange, at which point filtration was considered complete. The bright red polymer was then purified with a soxhlet extraction in diethyl ether to remove low molecular weight and non-regioregular material until the extraction washes were clear. The desired polymer was then dissolved in chloroform and dried, resulting in a purple powder. The identity and regioregularity of the material were confirmed by ¹H- and ¹³C-NMR respectively, and the molecular weight distribution was assessed by gel permeation chromatography (GPC) (**Figure B.4 and A2.5**). Fractions of desired molecular weights were then prepared with GPC, dried, and kept in a nitrogen glovebox.

2.4 RESULTS AND DISCUSSION

Prior to experimentation on POMeOPT, the experiments on the triblock copolymer were reproduced to validate the findings. These results were successfully reproduced when the solvent mixture was changed from a 50:50 toluene : methanol mix to a 15 : 85 toluene : hexanes mix. The fluorescence quantum yield increased dramatically in the nonpolar hexanes solution, evidencing the dominance of an emissive exciton type state, as was previously reported.²⁷

POMeOPT with a number average molecular weight $M_n = 45,234$ g/mol with a narrow polydispersity index (PDI = 1.465) was used. These values were determined using GPC. Absorption and emission spectra (540 nm excitation, 3 nm slitwidth) were taken of solutions of equal concentration in pure chloroform as a control molecular solution and eight different chloroform/poor solvent mixes of varying solution dielectrics, as shown in **Table 2.1**. The solution dielectric was approximated as the weighted average of the dielectric of the poor solvent and the chloroform, as has been previously utilized.²⁶ Absorption spectra showed a significant red shift from the molecular spectrum, which is shown in **Figure 2.1**, (~40 nm between the maxima), as well as the evolution of a pronounced vibronic structure (**Figure 2.2A**). The lack of shoulders in the wavelength range of the molecular spectrum is evidence of majority aggregation. Upon normalization, the absorption spectra all showed local maxima in the 0-1 transition with only slight variations in spectral positioning. There were, however, changes in the relative intensities

of the vibronic peaks. Within the framework of weak interchain coupling in the H-aggregate model, the ratio of the absorbance peaks $(\frac{A_{0-0}}{A_{0-1}})$ serves as an estimation of the interchain excitonic coupling, where an increased ratio is indicative of reduced interchain coupling, as was mentioned in **Chapter 1.2**.^{7,37} For these aggregates, as the solution decreased in polarity through *tert*-butanol, the ratio increased, indicating a reduction in interchain coupling (**Figure 2.2B**). The ratio then decreased to a minimum before spiking to its max with hexanes, indicating the two least polar systems have both the most and least interchain coupling.

Poor Solvent	ε (pure solvent)	Volume ratio (Chloroform/poor)	ε (mixture of Chloroform/poor)
Acetonitrile	37.5	50/50	21.15
Methanol	32.7	50/50	18.8
Ethanol	24.5	50/50	14.7
2-propanol	20.2	50/50	12.5
tert-butanol	12.5	40/60	9.4
Ethoxyethanol	5.3	50/50	5.1
1,4-dioxane	2.2	10/90	2.5
Hexanes	1.9	15/85	2.3

Table 2.1: Solvent conditions used in the POMeOPT aggregation experiments



Figure 2.1: Absorbance (black) and emission (blue) spectra of POMeOPT in chloroform solution.



Figure 2.2: A) Absorbance spectra of POMeOPT taken in poor solvent/chloroform mixes normalized to the 0-1 transition. Solution dielectric (ε) decreases from Acetonitrile to hexanes. B) Plot of the ratio of the 0-0 and 0-1 absorption peaks $\left(\frac{A_{0-0}}{A_{0-1}}\right)$, which is inversely proportional to interchain excitonic coupling.
Due to the strongest absorption peak existing at \sim 540 nm for all species, 540 nm was chosen for the excitation wavelength for the fluorescence experiments. As can be seen in the raw emission spectra and the plot of the emission integral with respect to solution dielectric shown in Figure 2.3, the non-polar hexanes solution showed a much more dramatic increase in fluorescence quantum yield than the triblock copolymer. The hexanes aggregates showed emission an average of 138 times brighter than the polar acetonitrile solution. The predicted trend where the emission would remain high until ε ~13 was not, however, observed. The fluorescence integrals seemed to show a decay pattern except for the points at $\varepsilon = 2.2$ for 1,4-dioxane and $\varepsilon = 5.3$ for ethoxyethanol. Despite the initial belief that the data point representing *tert*-butanol ($\varepsilon = 9.4$) was anomalous, testing proved otherwise, as this point was reproducible with multiple bottles of fresh solvent. The aggregates made with 1,4-dioxane were only $\sim 1/3$ as bright as those made in hexanes, marking a tremendous drop in emission intensity despite an estimated difference in solution dielectric of only 0.3 between the two solutions. Upon further investigation, it was found that commercial 1,4-dioxane contains BHT as a stabilizer to inhibit degradation into hazardous products. It is possible that this skewed the solution dielectric into a more polar regime, resulting in the inaccurate data point, although the stabilizer is not present in large concentrations. Another alternative is that there is some sort of interaction between the BHT stabilizer and the polymer chains that is causing a drop in the quantum yield. By contrast, ethoxyethanol does not contain a stabilizer to explain its deviation from the trend, and after testing with multiple fresh bottles reproduced the trend, it was hypothesized that there is an interaction that takes place between the ether portion of the solvent and the methoxy group in the substituent of POMeOPT that leads to a change in the local interactions, although this hypothesis was never tested. Treating 1,4-dioxane and ethoxyethanol as anomalous, however, would explain the deviations in the $\frac{A_{0-0}}{A_{0-1}}$ ratio, and

create a more reasonable trend with a nearly sigmoidal increase. Additional solvents that do not contain stabilizers or ether groups in this low dielectric regime, such as cyclohexane, triethylamine, and γ -terpinene, were proposed for testing in order to more thoroughly flesh out the emission integral data set and to verify the anomalous nature of the 1,4-dioxane and ethoxyethanol points, however these tests were never performed due to equipment relocation. Even with these data points taken as potential anomalies, the correlation between fluorescence quantum yield and environmental dielectric still provides evidence for a non-emissive charge transfer state playing a significant role in the excited state while lending credence to the theory that the bulky substituent on POMeOPT chains assist in the destabilization of this state. In striking contrast to the triblock copolymer, which showed fairly constant low emission intensity with $\varepsilon > -3$, POMeOPT does not reach this minimized plateau until $\varepsilon > \sim 14$ with the ethanol sample. It required much more extreme polar conditions to reach dominance of the non-emissive state, which represents a much more energetically favorable charge transfer state. On the other hand, the non-polar end showed far greater enhancement over the polar aggregates than the triblock copolymer, which could be due both to more dramatic destabilization of the charge transfer state due to the substituents and to more chromophores emitting within the aggregate, both of which could be tested with further experimentation.

After assessing the changing fluorescence emission intensities, the spectra were normalized to the 0-1 transition to assess changes in vibronic progression as well as any evolution in the position of the 0-0 transition (**Figure 2.4A**). Unfortunately, there was no clear trend observed with the relative intensities of the 0-0 and 0-1 transitions, so no distinct claims could be made regarding changes in the H- or J- character of the aggregates. The position of the 0-0 peak, however, was slightly more telling. **Figure 2.4B** shows the position of the 0-0 emission peak plotted against the estimated solution dielectric. Even

when factoring in the potentially anomalous nature of the 1,4-dioxane and ethoxyethanol points, the spectra exhibit a general red shift as the solution gets progressively more polar. This trend only deviates with the most polar solvent mix, the acetonitrile sample, which shifted back towards the blue. The hexanes sample was consistently bluer than the other samples. This suggests that the aggregates tend to adopt more stable conformations in more polar solvent mixes, even if only slightly (7 nm range).



Figure 2.3: Raw emission spectra of POMeOPT aggregates in mixes of poor solvents and chloroform. Solution dielectric decreases from acetonitrile to hexanes.



Figure 2.4: A) Emission spectra of POMeOPT aggregates taken in poor solvent/chloroform solutions normalized to the 0-1 transition. There was not a consistent trend observed for 0-0 enhancement or suppression, and only minor changes were observed to this ratio. B) Position of the 0-0 transition with respect to solution dielectric (ε), showing the general red shift as the environment increased in polarity.

Comparison of the shape of the absorption spectra to the emission spectra does reveal an interesting trend. In a molecular solution or a system where there is no charge mobility along a chain, the emission spectrum should be a mirror image of the absorption spectrum. POMeOPT, on the other hand, is different. The normalized absorption spectra show a dominance of the 0-1 peak compared to the other transitions. The normalized emission spectra (**Figure 2.4A**), however, show a dominance of the 0-0 transition in the emission, implying that the exciton is funneling to low energy sites with different excited state behavior before emitting.

While other factors have been shown to contribute to the low fluorescence quantum yields of conjugated polymer systems, these experiments provide evidence that environmental stabilization of a non-emissive charge transfer state plays a significant role. Despite the fact that the predicted sigmoidal trend in fluorescence intensity was not observed, the sheer magnitude of the increase in fluorescence intensity when making aggregates with nonpolar hexanes compared to more polar solvents such as acetonitrile with minimal changes in the shape of the emission spectra shows that solvent polarity has a drastic influence on the photophysics of conjugated polymers. Unfortunately, due to polymer supply and facility complications, further experimentation was terminated so conclusions must be limited to the qualitative, but there is great potential for future work. First, more solvents could be used in order to flesh out the observed trends and determine the validity of the 1,4-dioxane and ethoxyethanol data sets. An introduction of delayed fluorescence and fluorescence lifetime experiments would speak more to the specific nature and processes of what takes place in the excited states in these aggregates and how these processes change with respect to environmental dielectric. The experiments could then be translated to other materials, both PPV and thiophene based to determine if this is a universal phenomenon or if it is limited to materials that meet very specific parameters.

The natural culminations for this work would be to then extend it to the single molecule level, utilizing a variety of different solvents and matrices to produce aggregates while monitoring their photophysics and sizes at the smallest possible level, and films, which are more representative of real world applications. Single aggregate fluorescence anisotropy measurements would be particularly powerful in these experiments, as they could provide insights into how aggregate microstructure is changing as a function of aggregate environment.

2.5 CONCLUSIONS

Thanks to their ease of processing and relatively high degree of flexibility, conjugated polymers exist as an interesting class of semiconducting materials. Due to the high degree of complexity within even the smallest CP systems, the true nature of the excited states in these materials remains elusive. In order to more properly design materials for optoelectronic devices, experiments on small scale systems must unravel the nature of the interactions and states that occur at this level. To this effect, aggregates of the conjugated polymer POMeOPT were created in solution in a series of solvent mixes that produce different dielectric environments ranging from polar to nonpolar. These aggregates exhibited a dramatic increase in fluorescence quantum yield as the solution dielectric decreased in polarity. This suggests the existence of a charge-transfer type state offering competition to emissive pathways at low dielectric that is destabilized as the system changes to a nonpolar medium. The presence of the bulky side chain in POMeOPT seems to have assisted in this destabilization by forcing space between the polymers in order to hinder CT state formation, providing a foundation for a materials design technique in order to access previously inaccessible emission yields in conjugated polymers. Further experimentation in this area are necessary in order to gain a more fundamental

understanding of how the nature of the excited states of CP aggregates are influenced by environmental conditions and forced chain spacing in order to scale these effects to bulk films and, eventually, optoelectronic devices.

Chapter 3: Poly(*p*-phenylene vinylene)-based β-sheet Polychromophores¹

3.1 INTRODUCTION

Understanding the relationship between structure and molecular order has led to significant improvements in polymer-based optoelectronic materials in recent years by optimizing conformation and eliminating heterogeneity.^{106,107} One emergent means of combatting the microscale heterogeneity in conjugated polymers is controlling folding behavior at the single molecule scale by designing materials that fold in particular ways, going so far as to incorporate linkers in the backbone and forcing chromophore π -stacking in some cases, as is touched upon throughout **Appendix A**.^{10,12,27,48,61,62,108–113} Many of these studies have centered around highly controlled, small oligomers that only serve as model systems.^{12,27,108–110} This motivation has extended beyond just optoelectronics into the realm of biopolymers that achieve 3D folded architectures such as α -helices^{114–119} and, to a lesser extent, β -sheets.^{120,121} These 'foldamers' are typically constructed around the inclusion of peptidic and/or proteinic residues^{122,123} that drive self-assembly through complementary hydrogen bonding elements in conjunction with hydrophobic interactions and charges.^{114,124,125}

While materials designed to adopt specific conformations at the single molecule level can be probed with bulk techniques as films, none of these techniques can ensure that the designed conformation is what is actually being adopted. Even techniques such as

¹ Parts of this chapter were previously published as 'Synthesis and folding behavior of poly (*p*-phenylene vinylene)-based β -sheet polychromophores.' (Elacqua, E., Geberth, G. T., Vanden Bout, D. A. & Weck, M. Synthesis and folding behaviour of poly(*p* - phenylene vinylene)-based β -sheet polychromophores. *Chemical Science* (2019) doi:10.1039/C8SC05111A.). The author of the dissertation was responsible for the solution absorption and emission spectra as well as the collection and analysis of the single molecule data.

atomic force microscopy (AFM) and scanning tunneling microscopy (STM) cannot achieve the resolution necessary to distinguish the conformation of polymer chains, particularly in films.³⁰ While device performance can be measured, this, too, fails to confirm that the intended conformation is what the majority of chains have adopted. Wide angle x-ray scattering (WAXS) can be a useful tool for understanding interactions that are taking place as an average within a film, but to gain strong evidence for the validity of a single molecule chain conformation, the system must be taken down to the single molecule level. By examining designed folding systems with single molecule excitation polarization spectroscopy to measure the modulation depth compared to a homopolymer that does not contain the folding components, a strong case can be made for the validity of the design. When combined with single molecule fluorescence spectroscopy approximations can be made regarding the interactions between the chromophores at the smallest possible scale, the scale at which the material was actually designed.

Unlike many of the previous cases where oligomers were studied, the tetra-block copolymer studied with these experiments, designed and synthesized by the Weck group at New York University, is based on a true living polymerization. There was no purification between steps to get chromophores or linkers of exact lengths, only naturally occurring ranges. While this results in a more commercially realistic material, it opens the door for heterogeneities within the very mechanisms that allow the design to function. This polymer is based around PPV chromophores spliced together with a flexible polymer that favors intrachain collapse.¹²⁶ The linker unit, based on poly(norbornene)(PNB), capitalizes on quadrupolar interactions within the phenyl/perfluorophenyl π -stacking (**Figure 3.1**) that ultimately creates a 'zipper' effect, forcing the linker to adopt β -hairpin turns. Five examples of the copolymer were synthesized, each with one additional β -turn added in order to test the validity of the folding mechanism at high molecular weights and determine

if the intrinsic heterogeneity from polymerization forces a breakdown in the fold as more turns are added. These studies serve to enhance the field of molecular design to control folding, particularly in the vein of using conjugation-interrupting linkers.^{127–129}



Figure 3.1: Schematic depicting the supramolecular design strategy to engineer synthetic β-sheet polymers using iterative ROMP and targeted model tetra block copolymers.

3.2 EXPERIMENTAL

All chemicals for synthesis were purchased from Sigma Aldrich, Alfa Aesar, or TCI America, and used as received unless otherwise indicated. NMR spectroscopic characterization was conducted on a Bruker Avance 500 or 600 MHz spectrometer using CDCl₃ unless otherwise indicated. Chemical shifts are reported in ppm, and referenced to residual CHCl₃. Polymer molecular weights and dispersities were measured using an Agilent 1200 gel-permeation chromatograph (GPC, Agilent Technologies) and operated using a ChemStation program equipped with ASTRA V program. An Agilent 1200 series isocratic pump coupled with a UV detector and the Optilab rEX differential refractive index detector (Wyatt Technology Corporation; Santa Barbara, CA) were calibrated with poly(styrene) standards. The column and guard column utilized were pre-packed (AM GPC Gel, CHCl₃; American Polymer Standards) and the column temperature was maintained at 40 °C. All samples were measured with a mobile phase consisting of chloroform. The injection volume was 100 µL and the flow rate was 1 mL min⁻¹. The concentrations utilized for GPC measurements are ca. 1-3 mg mL⁻¹, owing to aggregation of the PPV systems in more concentrated solutions through the duration of the measurements. Data obtained from the UV and RI detectors were in agreement. X-ray diffraction data was collected on a Bruker D8 DISCOVER GADDS microdiffractometer equipped with a VÅNTEC-2000 area detector. X-rays were generated with a sealed Cu tube, monochromated by a graphite crystal, and collimated by a 0.5 mm MONOCAP ($\lambda =$ 1.54178 Å). Samples for WAXS were measured as thin films in bulk, and compared to the parent polymers. Measurements were collected at room temperature via mounting of the polymer films onto a silicon wafer.

3.2.1 Polymerizations

3.2.1.1 ROMP – PPV homopolymer

ROMP wass conducted at 50 °C, and monitored via ¹H-NMR spectroscopy for conversion. After the reaction is completed, the polymerization mixture was added to a dichloromethane solution with the desired CT (4.0 eq., relative to initiator used), and allowed to stir at room temperature over a period of 16 hours. The polymer solution after quenching was purified using reprecipitation into methanol and acetone. The polymer Dp was confirmed through ¹H-NMR spectroscopic end group analysis.

3.2.1.2 ROMP – PPV-PNB_{Ph}-PNB_{PFP}-PPVs

The above procedure was utilized except that upon completion of ROMP, the polymer solution is transferred back to the glove box, and 5-exo-norbornene carboxylic acid, phenyl ester (NB-Ph) was added and polymerized at room temperature for 15 minutes, followed by 5-exo-norbornene carboxylic acid, perfluorophenyl ester (NB-PFP), which was also polymerized for 15 minutes at room temperature. After incorporation of the interior PNB blocks, a fresh equivalent of pCpd was added. After completion, an aliquot of the polymer is subsequently quenched while further equivalents of the PNB blocks (and pCpd) were added. As the series of polymers was sequentially polymerized and quenched from a single pot, the general procedure was as follows:

1T) 50 mg (0.0001085 mol) of pCpd was dissolved in 0.5 mL of CDCl3, with Hoveyda-Grubbs II initiator (6.2 mg, CDCl3 solution) then introduced. Polymerization was conducted at 50 °C. Upon complete consumption, the desired amount of NB-Ph was added and polymerized, followed by NBS-3 PFP. An equal equivalent of pCpd ((0.0001085 mol) was then added and polymerized. Upon completion, ¹/₅ of the overall solution was drawn and quenched with ethyl vinyl ether (EVE) overnight, affording 1T. 2T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000868 mol). Upon completion, ¹/₄ of the overall solution was drawn and quenched with EVE overnight, affording 2T.

3T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000651 mol). Upon completion, $\frac{1}{3}$ of the overall solution was drawn and quenched with EVE overnight, affording 3T.

4T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000434 mol). Upon completion, $\frac{1}{2}$ of the overall solution was drawn and quenched with EVE overnight, affording 4T.

5T) The remaining solution was utilized for subsequent polymerizations, wherein the desired amount of NB-Ph and NB-PFP were polymerized in sequence, followed by pCpd (0.0000217 mol). Upon completion, the solution was drawn and quenched with EVE overnight, affording 5T.

3.2.2 Spectroscopy

Polymer solutions for bulk spectroscopy were prepared in chloroform (Fisher). Absorption and emission measurements were performed with Agilent 8453 UV-visible spectrophotometer (Agilent Technologies Inc.) and Fluorolog-3 spectrofluorometer (Jobin-Yvon), respectively. All polymer solutions were excited at 488 nm, and fluorescence emission was measured from 500-700 nm. Single molecule samples were prepared by creating ultra-dilute polymer solutions in 2 wt% PMMA/chloroform and spin-casting onto piranha cleaned coverslips with resulting PMMA/polymer films ~200 nm thick. During all single molecule experiments, samples were protected with a flow of N_2 gas and held at ambient temperature. An electro-optical modulator (Fastpulse Technology, model 3079-4) was used to generate a linearly rotating 488 nm excitation beam (Melles Griot, model 35-IMA-040-208). A high numeric aperture objective (Zeiss, Achrostigmat, x100, oil immersion, N.A. 1.25) was used in a wide-field optical microscope (Zeiss, Axiovert 200) in order to expose the sample plane to a collimated laser beam during fluorescence excitation polarization measurements. Methods are described in further detail elsewhere.⁴⁵ Fluorescence signals were captured with an EMCCD detector (Andor, model iXon+ DU-897E). Fluorescence emission spectra were collected under a confocal scheme in which the laser beam was focused to a diffraction limited spot on the sample with an intensity of ~30 W cm⁻². A home-written LabView program (National Instruments) was used to control the piezo stage. Emitted light was filtered through a 496 nm long pass edge filter (Semrock) and directed onto the spectrograph (Princeton Instrument, Acton SP-150) that was coupled to a liquid N₂ CCD detector. Three consecutive spectra, each taken with an integration time of 15 s, were averaged to increase the signal-to-noise ratio.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis

The final structure of the ABCA tetrablock copolymer, was achieved using a modified, iterative ring opening metathesis polymerization (ROMP) reaction. The strategy for this reaction is detailed in **Scheme 3.1** and was fully elaborated on in the experimental section (**section 3.2.1**). ROMP is a reaction that utilizes a cyclic olefin that results in a backbone containing double bonds. For more information about the specifics of ROMP, consult chapter 7-8 of George Odian's *Principles of Polymerization*.¹³⁰ Throughout the reaction, monomer consumption and block lengths were monitored via ¹H-NMR. PPV

block lengths were approximately 10 repeat units while the PNB block lengths were approximately 20-25 units. Six distinct samples were prepared, each with increasing numbers of PNB turns. These samples were designated HP for the PPV homopolymer control and 1T-5T for the block copolymers where the number designates the number of turns. **Table 3.1** contains molecular weight and dispersity data, which was calculated using GPC and ¹H-NMR as noted in the table. Wide angle x-ray scattering (WAXS) of films was utilized to gain some insight into the contributions of different components into the material folding. As more β -turns were installed in the backbone, the WAXS data showed an increase in the inter-backbone alkyl-alkyl signal relative to the π - π stacking. This suggests that the side-chains play a prominent role in the folding mechanism. The breadth of the side-chain-related signals is also indicative of interdigitation with the phenyl/perfluorophenyl groups as opposed to face-to-face π - π stacking that PPV chromophores are well-known to engage in,¹³¹ indicating a significant distance between the PPV chromophores.



Scheme 3.1: Iterative ROMP strategy to achieve folded PPV-(PNB-PNB-PPV)_n architectures. The final active carbene illustrated is either quenched to afford the 1T sample, or subsequent iterations of steps (b)-(d) are performed to achieve higher folded structures. All PPV block lengths are 10 repeat units, while PNB block lengths of 20-25 units were targeted.

Polymer	M _n ª	M _w	Ð	М _п ь
PPV Homopolymer	7600	11,000	1.41	4,800
PPV-(PNB-PNB)-PPV (1T)	20,900	24,600	1.17	15,000
PPV-(PNB-PNB-PPV) ₂ (2T)	48,700	56,600	1.16	28,000
PPV-(PNB-PNB-PPV) ₃ (3T)	56,000	80,300	1.43	44,000
PPV-(PNB-PNB-PPV) ₄ (4T)	65,200	90,500	1.39	56,000
PPV-(PNB-PNB-PPV)₅ (5T)	75,600	96,000	1.27	70,000

Table 3.1: Polymer characterization for the PPV homopolymer and PPV-(PNB-PNB-PPV)_n samples. Molecular weights were measured both (a) by GPC with a chloroform mobile phase against poly(styrene) standards for both number (M_n) and weight average (M_W), and (b) by ¹H-NMR spectroscopic end-group analysis for number average. Polydispersity (Đ) closer to 1 indicates a narrow distribution of molecular weights. For more information on polymer molecular weight measures and polydispersity, see George Odian's *Principles of Polymerization*.¹³⁰

3.3.2 Effect of Self-Assembled β-Turns and Chromophore Count on Single-Chain Folding Order

To investigate the role of the β -turn in these polymers, the electronic spectra of the PPV homopolymer (HP) and the series of PPV-(PNB-PNB-PPV)_n (1T-5T) copolymers were measured in bulk solutions. The absorption of the PPV homopolymer exhibited little structure and peaked at a wavelength of 465 nm (Figure 3.2). The folded PPV-(PNB-PNB-PPV)_n polymers demonstrated similar behavior. A slight shift to lower energies was evidenced by a shoulder at 532 nm in the three highest molecular weight samples (3T-5T), likely resulting from some aggregation. In contrast to the absorption, the emission spectra were virtually identical, exhibiting an emission wavelength of 524 nm. They also demonstrated a clear vibronic progression with spacing of ~280,000 cm⁻¹. The ratio of the first two peaks (I₀₋₀/I₀₋₁) produced a value of 1.6. The aggregation observed in the folded 3T-5T polymers did not play a significant role in the emission given that all of the spectra exhibited identical λ_{max} and vibronic progressions. The parent PPV exhibited a slightly broader emission spectrum compared to the folded materials and shows a slightly increased emission from the first vibronic peak. These changes are small and likely the result of the homopolymer having longer stretches of PPV repeat units (more than 25) compared to the heteropolymers (10-15). Based on aggregation models, it would be expected that electronic interactions between the chromophores would lead to both spectral shifts and changes in the ratio of the 0-1 peak to the 0-0 peak.⁷ Since neither of these effects was observed, it was concluded that the active chromophores are maintained despite the presence of the flexible non-conjugated PNB blocks and that there is limited, if any, electronic coupling between the chromophore strands.

To examine the folded functionality on the structure of the polymers, single molecule excitation polarization spectroscopy was performed, as described in **section 1.3**.⁴⁵ Histograms were constructed using the M values of approximately 1,000 molecules

for each of the different polymer samples (Figure 3.3). The modulation depths were binned by rounding to the nearest 0.1 for the M value. This histogram served as a visualization to ascertain both the average folding order and approximate how many different conformations a material adopted, and how prevalent the conformations were based on the broadness or narrowness of the histograms, or if any skews were present in the typically Gaussian curves. The PPV homopolymer displayed an average M value of 0.67, which is comparable to other conjugated polymer systems, such as high molecular weight MEH-PPV^{45,56} or regionegular poly(3-hexylthiophene).¹³² Even with the relatively high average in the modulation depth value, the distribution for the homopolymer was relatively broad. Moreover, the peak in the distribution was actually at the lower value of 0.5 - 0.6. The homopolymer histogram appeared somewhat broader than the folded polymer histograms and is shifted slightly to lower M values, indicating a wider variety of possible conformations, particularly less ordered ones. The introduction of the interior PNB block led to a slight increase in the modulation depth distribution. All of the folded polymers exhibited a slightly higher mean M values of ~ 0.7 , with the exception of the largest sample, 5T, which exhibited a mean M value of 0.68. As the number of β -turns increased in the 1T-4T materials, the distribution started to narrow and shift slightly to higher M values. While there is a small shift in the mean, it is more relevant to look at the shape of the overall distribution. As the number of β -turns increases up to 4, the distribution skews to higher M values and narrows. In the polymer sample comprising the most folds, 5T, however, the distribution appeared to broaden again and resemble the homopolymer distribution. This resulted in a shift in the mean M value down to 0.68. The slight lowering observed in the 5T polymer suggested that the heterogeneities inherent in both the chromophores and the internal PNB functionalities started to disrupt the clean folding of the polymer at higher molecular weights. For the 1T-4T polymers, the tighter M values skewed to the more ordered end of the distribution, implying that the polymers displayed a less heterogeneous distribution of conformations that is more anisotropic in nature. The distributions of the modulation depths were reproducible, indicating that the folding is extremely robust.



Figure 3.2: Solution absorption and fluorescence emission spectra of the homopolymer (HP, teal) and the folded PPV-(PNB-PNB-PPV)_n polymer samples (1T-5T) in chloroform.



Figure 3.3: Histograms of the ensemble of fluorescence intensity modulation depth, **M**, of the homopolymer (top) and the folded PPV-(PNB-PNB-PPV)_n polymer samples.

3.3.3 Effect of Folding on Electronic Properties

To determine the effect of the folded perfluoro-phenyl/phenyl poly(norbornene) (PNB) functionality on the polymer photophysical behavior, the spectra of single polymer molecules were examined. These spectra were then compared both to each other, and the bulk solution spectra. In solution, when the chains are assumed to adopt unfolded, noninteracting conformations, the fluorescence spectra of all of the polymers followed the same vibronic progression with a 0-0 transition maximum at 524 nm (Figure 3.2). The bulk spectra from solution can be compared to ensemble spectra of the single molecules taken in the solid state (Figure 3.4). Each of the folded materials demonstrated a 0-0 transition energy fairly close to the bulk solution maximum with a nearly identical lineshape. The 4T polymer displayed a slight deviation from this pattern, having shifted slightly to the red compared to both the solution and the other materials. The largest variation is observed for the homopolymer, which exhibited an ensemble spectrum very different from both the other materials and the bulk solution. The homopolymer single molecule ensemble spectrum is red shifted by approximately 20 nm. In addition, it has a broader fluorescence envelope with less distinct vibronic features. This suggests that the homopolymer single molecules have a broader distribution of contributing chromophores compared to the folded PPV-(PNB-PNB-PPV)_n materials.

To comprehend the underlying distribution of spectra, histograms (**Figure 3.5**) of the peak 0-0 emission energies for each individual single molecule spectrum were examined. These were taken as the center wavelength of the most prominent higher energy transition, which was presumed to be the 0-0 peak for each sample. This data indicates that each folded material is dominated by single molecules with a peak at 521 nm which is similar to the bulk maximum at 524 nm. The folded samples also show sub-ensembles of molecules that emit ~514 nm and ~532 nm. This abundance of dominant 521 nm emitting molecules suggests that in the majority of the polymers there are little to no electronic interactions and that the chromophores behave much as they do in the solution state. The slight difference in the wavelength could be due to the different instruments used for the two experiments or subtle changes in environment in going from chloroform to a PMMA matrix.

Given that the interior PNB functionality should hold the chromophores in a folded ordered conformation sustained by phenyl/perfluorophenyl interactions, the lack of strong changes in the emission spectra suggests that they position the PPV chains at distances far enough away from one another that they are not electronically coupled. In contrast, the homopolymer is distinctly different. The individual molecules display a wide variety of fluorescence maxima ranging from 505 nm to nearly 550 nm with no emerging dominant species. This is representative of a wide array of conformations and conjugation lengths of the chromophores. This distribution of spectral positions is consistent with the broadening and shoulders exhibited in the generated ensemble spectrum of the homopolymer as well as the solution spectrum (**Figure 3.5**).

To further examine the predominate form of the polymer that emits at 521 nm, subensemble spectra were created by combining all the spectra that exhibited 521 nm peak emission (**Figure 3.6**). Between the five folded samples, all sub-ensemble spectra are effectively identical to one another, demonstrating identical breadth and vibronic progressions. Additionally, the vibronic progression is the same as that observed in the bulk solution, where the chains are assumed to be unfolded, yielding the same I_{0-0}/I_{0-1} ratio of ~1.6 for all copolymer samples. Given that even weak electronic coupling should result in changes in the vibronic progressions upon aggregation,⁷ it appears that the polymer folds into structures in which the chromophores are sufficiently far apart to avoid electronic interactions. This is true even as the number of chromophores increases up to 6.



Figure 3.4: Ensemble spectra generated by summing all of the individual single molecule spectra acquired for the homopolymer (HP) and the folded PPV-(PNB-PNB-PPV)_n polymer samples.



Figure 3.5: Histograms of the 0-0 vibronic transition in the single molecule spectra for both the homopolymer (HP) and each of the folded PPV-(PNB-PNB-PPV)_n polymer samples.



Figure 3.6: Sub-ensemble spectra generated by summing all of the individual single molecule spectra that exhibited the 0-0 transition at 521 nm acquired for the folded PPV-(PNB-PNB-PPV)_n polymer samples.

3.4 CONCLUSION

Tetrablock copolymers based on the PPV chromophore that were designed to utilize phenyl/perfluorophenyl interactions in a flexible linker to fold into β -hairpin turns were successfully synthesized using an iterative ROMP strategy. This synthetic route was used to produce foldamers containing up to five β -turns. These materials behave very similar photophysically to the PPV homopolymer in solution, however films suggest that the foldamers engage in side-chain interdigitation, as the pendants in the PNB linker are predominantly responsible for the folding. At the single molecule level, this designed linker proved extremely robust, with the block copolymers showing a higher anisotropy than the homopolymer, with very little change as the number of β -turns increased. Additionally, the block copolymers showed much less spectral variation at the single molecule level than the homopolymer, indicating a much narrower set of possible interactions in the system. Given that this was a polymerized system, not an oligomer, the inherent heterogeneities in monomer count did not have a pronounced effect as chain length increased. These tests show the validity of this linker and synthetic route as a promising tool for future materials design that reduces heterogeneity in molecular behavior at the single molecule level, and would be expected to do so at the single aggregate and bulk film levels as well.

Chapter 4: Fluorescence Microscopy of Single Perylene Diimide Aggregates

4.1 INTRODUCTION

As was mentioned in **Chapter 1**, Perylene diimides have grown in interest in recent years because of their photostability and capacity to undergo singlet fission. This process of multiple exciton generation represents a sizeable increase in the maximum possible efficiency of photovoltaics. Without multiple exciton generation, the maximum energy conversion efficiency of a single-junction photovoltaic, referred to as the Shockley-Queisser limit, is limited to 33%.⁷⁵ This is the limit with the assumption of one electronhole pair per photon, but still serves as a good measure for possible device efficiency. Part of the reason this limit is so low is because high energy photons are not directly converted. The excess energy over the bandgap is released as heat.⁷⁵ When multiple exciton generation is taken into account, the Shockley-Queisser limit can be surpassed and the maximum possible device efficiency expands to approximately 50%.⁷² Any means of increasing the occurrence of multiple exciton generation drives photovoltaic efficiency closer to this limit.

Given the significant impact that efficient singlet fission could have on renewable energy, a great deal of research has gone into understanding the process behind it. At the simplest level, singlet fission is the process by which a singlet exciton splits into two triplet excitons with long lifetimes.^{73,75} These two triplets lying on adjacent molecules produce a net singlet state known as a correlated triplet pair, denoted as ¹(TT).^{73,75} It is believed that this process proceeds through a charge transfer exciton state,^{73,77,78} but it is still unclear how the correlated triplet pair transforms into separated triplet excitons.⁷³ The energy level matching between the excited singlet and the triplet state mentioned in **Chapter 1** is only one requirement for this process. For singlet fission to occur, the degree of vibronic coupling between the two chromophores must exist in a specific regime, because if coupling is too weak the fission pathway is not available, but if coupling is too strong new relaxation pathways become available reducing the probability of SF.⁷³ This requirement in particular has led to work regarding the structure-function relationships as they relate to singlet fission.

From a molecular structure perspective, there are multiple ways to influence the photophysics in perylene-based materials, particularly through the use of substituents. Firstly, the initial change from a perylene to a perylene diimide, the inclusion of the imide functionality, has little impact on the photophysics, instead influencing the aggregation and solubility of the dye. This is because the nitrogen atoms lie in the HOMO and LUMO nodal planes, as can be seen in **Figure 4.1**, so they do not factor into the primary excitations and emissions.^{6,133} Along the basic PDI structure, there are two key positions for substituent tuning also shown in Figure 4.1: the bay position, and on the nitrogen in the imide position. Substitutions into the bay position primarily impact the optical and electronic properties, but also have the potential to disrupt π -stacking during aggregation through alterations to the HOMO and LUMO as well as forced backbone distortion.¹³³ These substituents can lead to both red and blue shifts, depending on what substituents are applied. Instead of altering the spectroscopic properties of individual emitters, substituents in the imide position primarily adjust π -stacking in aggregates, ^{6,134–136} which alters the spectroscopic properties of these aggregates.^{6,137} These substituents are what is typically tuned in singlet fission studies in order to alter the relative positions of two molecules within dimers. This is because sub-angstrom displacements within a dimer have an enormous impact on the strength of the coupling between the two molecules in a dimer, particularly when shifting along the longitudinal dipole.^{72,136–138} These shifts result in net sign changes in the coupling, as the orbital overlap between the two molecules changes.¹³⁸ Most crucially, they prevent orbitals from cancelling one another out. Orbital cancellation inhibits singlet fission, and these slip stacks have shown enhanced singlet fission over non-shifted π -stacks.⁷² Understanding how the packing structure of these small clusters influences the photophysics at the small scale is crucial for tuning the properties and eventual film order as the initial structure of small aggregates has been shown to influence large scale crystallization.^{137,139}

An advantage of using triplets in optoelectronics is that the long-lived state provides more time for charge separation to occur. Unfortunately, this timescale also provides more opportunity for quenching.⁷² The typical processes associated with triplets are emissive and non-emissive relaxation to the ground state, but other routes are available. One example is quenching from external sources. For example, triplets are vulnerable to quenching from spin ½ particles, such has the hole or excess electron left on a chromophore as a result of charge separation that would occur in a photovoltaic.⁷² Oxygen is another entity that has been well documented for quenching triplets through multiple processes.^{52–54,140,141} While quenching triplets can improve photostability and quantum yield in some materials by forcing triplets to reset and reform into radiative states, it has been shown to accelerate photobleaching in rylene derivatives.⁵⁴ This is believed to occur either due to photooxidation of the dyes or due to the formation of a non-fluorescing oxygen complex with the emitter leading to photobleaching.^{54,140} Even while irreversibly bleaching a chromophore, oxygen still serves as a valuable probe into the roles that triplet states play in the excited states of emitters.⁵⁴



Figure 4.1: Frontier orbitals of N,N'-dimethyl PDI, according to DFT calculations. (Modified from the work of Huang et al.¹³³)

While PDI aggregates have been studied in the past due to rylene-derivatives' natural proclivity to aggregate into dimers at concentrations greater than 3×10^{-3} M.¹⁴² little work has been done on isolated small PDI aggregates.⁷² Most of the experiments have been performed in the last fifteen years and focus on the more easily produced solutions of aggregates and larger aggregates and nanostructures consisting of hundreds of dye molecules.^{6,134–137,143} Part of the reason for this vacancy is the difficulty in forming isolated dimers, as the dimers must form at concentrations well below the natural aggregation concentration. To address this, the experiments below utilize a technique that has previously been reliably used to form isolated aggregates in polymer matrices that is highly tunable: solvent vapor annealing (SVA).^{50,144} This technique, described in Chapter 1.4, has also been used in PDI studies of films to create nanobelts on the scale of tens of nm,^{6,136} but it has not been reported to have been used to create small isolated aggregates at the time of writing. The experiments below utilize SVA to create isolated small aggregates (likely dimers and trimers) of a PDI that is known to undergo singlet fission in films at a high rate. The specific PDI is N,N'-bis(2-phenylethyl)-3,4,9,10perylenedicarboximide, shown in Scheme 4.1. This particular material was chosen because it has a maximum predicted triplet yield of 189%, so is a good candidate to undergo singlet fission. In this study, single aggregates of the PDI were prepared in a PMMA matrix via solvent vapor annealing and studied with fluorescence microscopy under both nitrogen and air. The aim is to both explore the link between aggregate morphology and triplet formation at the smallest possible scale for singlet fission and to understand how PDIs evolve from the well defined spectra of isolated emitters to the broad featureless film spectra that result from internal heterogeneity.

4.2 EXPERIMENTAL

N,N'-bis(2-phenylethyl)-3,4,9,10-perylenedicarboximide (CAS 67075-37-0) was purchased at 98% purity from Sigma Aldrich/Millipore Sigma and was not purified further. Chloroform (99.9% extra dry over molecular sieve, stabilized) was purchased from ACROS Organics and was used for all processes involving chloroform besides the bulk CHCl₃ solution emission spectra, which were provided by Sean Roberts lab at the University of Texas at Austin. The film absorption and emission spectra were also provided by the Roberts group. Microscopy samples were prepared by diluting solutions in CHCl₃ to absorbances of 0.1 at 488 nm. These vials were then dried and stored in a nitrogen glovebox. They were then resolvated and diluted to single molecule concentrations with a 2% by weight PMMA in CHCl₃ solution. Films were spin cast in the glovebox on piranha cleaned coverslips before being transferred to the sample holder and connected to a nitrogen gas line. Nitrogen and air pressures were matched prior to any scans by setting the focus spot, switching gases, and matching the focus spot again by adjusting the pressure. For all microscopy experiments the excitation wavelength was 488 nm. For wide field experiments the laser power was between 30 and 60 µW. Wide field movies were taken at 3 seconds per frame for 201 frames including a minimum 10 frame background scan without illumination before analysis in a custom MatLab program. For confocal experiments the laser power was 100 nW. Single molecule and aggregate spectra were taken in sets of four spectra with 30 second integration times and were processed in a custom MatLab program. Fluorescence transients were taken for 120 seconds with .025 s/data point. Confocal images were taken at 7 ms dwell times. Transients and spectra were both performed by beginning the scan with the beam focused near, but not on, the molecule or aggregate, then moving onto the target. While this leads to a brief rise time in the transients and slightly reduced counts in the first of the four spectra, it was necessary to
capture any processes that happen rapidly shortly after excitation. The microscope optics are the same as those described in **Chapter 1**. Solvent vapor annealing was primarily performed with 99.8 % extra dry acetone purchased from ACROS Organics unless otherwise noted.



Scheme 4.1: Structure of N,N'-bis(2-phenylethyl)-3,4,9,10-perylenedicarboximide used in these experiments.

4.3 RESULTS AND DISCUSSION

4.3.1 Imaging and Spectroscopy

Before single molecule and single aggregate samples were prepared, bulk absorption and emission spectra were collected both from films and in solution. These spectra are shown in **Figures 4.2A and B** respectively. The vapor deposited film spectra are both extremely broad and featureless ($\lambda_{Ex} = 402$ nm for emission). This is due to the wide array of emitting microstructures present that are all contributing to the emission spectra. By contrast, in dilute solution, where the PDI molecules can separate from one another, both the absorption and emission spectra are much narrower and take on welldefined vibronic progressions, characteristic of isolated emitters, as discussed in **Chapter 1**. This stark difference between film and solution has been previously shown in the literature.⁷⁸

In order to estimate concentrations, provide a high throughput means of counting molecules before and after annealing, and record the annealing process, PDI single molecule samples were initially examined under wide field excitation, both with and without excitation polarization. PDI nanobelts have been shown to have polarized emission¹³⁶ and would likely show response to excitation polarization experiments. These experiments could also potentially have yielded some insight into molecular order in isolated aggregates. Unfortunately, the molecules were just too small and too dim to show up reliably. There was not an adequate signal to noise ratio, even when multiple filters were placed in the optical path to reduce background noise. The MatLab code could not distinguish single molecules, and as a result, the wide field experiments were abandoned.

Single PDI molecules were reliably imaged on an APD with confocal scans. These scans do not distinguish based on wavelength, and only document the presence of molecules based on fluorescence counts with respect to spatial positioning. **Figure 4.3A**

shows an example of a single molecule sample imaged with the confocal setup under nitrogen. The identities of the sample spots were confirmed with spectroscopy. The red points are artifacts of the software and should be ignored. Spectroscopically, the single molecule emission (Figure 4.4) is very similar to the bulk CHCl₃ solution spectra seen in Figure 4.2B. The single molecules exhibit a very well pronounced vibronic progression and do not exhibit much deviation, with the emission of the I_{0-0} transition only existing in the narrow range of 526-536 nm, with 531 nm occurring most frequently. The solution spectrum maximum is at 534 nm, by comparison. The difference between the single molecule mode and the bulk maximum can be attributed to slight differences in the detectors and their calibrations. Over the time period of 2 minutes, during which four 30 second spectra were taken per molecule, there was little to no evolution of the single molecule spectra. Under nitrogen, the spectra are extremely consistent, showing minimal changes throughout. Under air, the spectra were identical to those in nitrogen, however some of the molecules bleached within the 2 minute sampling window, but this was not accompanied by an evolution in terms of their progression or wavelength in most cases. For all spectra shown in this chapter, the suffixes A, B, C, and D refer to subsequent 30 second spectra of the same molecule or aggregate. They act as extremely robust single chromophores, particularly under nitrogen which was expected for these control tests. Single molecule transients were also characteristic of single emitters. Under nitrogen they were constant for the duration of the scan in almost every experiment, showing constant intensity with respect to time, and in the few cases when bleaches occurred, they were late in the scan and exhibited single step photobleaches. In air, the emission was once again constant in terms of intensity, however bleaches occurred much more frequently and much more quickly than in the nitrogen case. Figure 4.5A and B show single molecule transients under both nitrogen and air. Both of these transients are consistent with the single molecule

transients taken by Renn, Seelig, and Sandoghdar on terrylene dyes,⁵⁴ with the longer duration of the PDIs likely being due to the improved stability of the system over terrylene.

Samples were annealed for different time scales, but it was optimized at 1 hr 15 minutes of acetone exposure with nitrogen gas followed by 10 minutes of sparging with nitrogen. Acetone was chosen over a solvent blend because it had previously been utilized in conjugated polymer experiments to reproducibly create the smallest aggregates compared to blends⁵⁰ while still being a very poor solvent for PDIs. Samples were not exposed to air until nitrogen spectra and transients had been collected. Figure 4.3B shows a confocal image under a nitrogen atmosphere after successful solvent vapor annealing. In order to approximate the size of aggregates the number of spots was counted by hand and averaged for three regions prior to annealing and three regions following annealing. The former was then divided by the latter to give an approximation of aggregate size. There is undoubtedly error in this approximation due to the human based method for counting and the potential for non-emissive aggregates, but there was no efficient means available to digitize the method to at least slightly reduce error. Given this error, in most successful annealing experiments, the average aggregate size was approximated to be 2-3 molecules per aggregate, which was the targeted range. Moreover, the counting yields an upper bound unless some of the spots in the image are still single molecules.



Figure 4.2: A) Film absorbance (solid) and emission (dashed) spectra of the PDI. B) Chloroform solution absorbance (black) and emission (red) spectra of the PDI.



Figure 4.3: Confocal fluorescence microscopy images of the PDI of interest under nitrogen A) before solvent vapor annealing and B) after successful solvent vapor annealing in extra dry acetone.



Figure 4.4: Representative spectra taken from a single PDI molecule under nitrogen. A, B, C, and D refer to subsequent 30 second spectra of the same molecule.



Figure 4.5: Fluorescence transients of single molecules in A) nitrogen and B) air. The rise at the beginning is the rise time for the piezo stage to move the excitation beam onto the molecule.

Unlike the single molecules, the aggregates tended to irreversibly bleach in under 120 seconds, regardless of atmosphere. As a result, spectra and transients could not both be taken from the same aggregate. Photophysically, the aggregates formed via solvent vapor annealing proved to be extremely heterogeneous. There was no uniform pattern displayed by the spectra in either gas. Aggregates exhibited both red and blue shifts as well as both suppression and enhancement of the 0-0 transition with respect to the 0-1 transition. In most cases the spectra also showed intensity fluctuations throughout the scans before irreversibly bleaching. Due to the nature of the spectroscopic experiments it is unclear what the nature of the intensity fluctuations was other than the final bleach. Figure 4.6 shows histograms of the 0-0 transition position of both single molecule spectra and aggregate spectra regardless of gas, as gas did not seem to have any impact on the transition position. As this histogram shows, extreme shifts were not uncommon in the aggregates, even pushing into the 496 nm long pass filter that is in place to protect the detectors from residual laser light. Figure 4.7 shows examples of spectra in both nitrogen and air of red shifts, blue shifts, 0-0 enhancement, and 0-0 suppression. In the case of the blue shift the clipping due to the presence of the long pass filter is extremely apparent, suggesting that in some cases the spectra are not accurate representations of the photophysical behavior in that particular aggregate as well as evidence that there were potentially aggregates that could not be seen due to shifting beyond the filter. Because there are no changes in substituents on the PDIs, these shifts must be due to changes in the stacking within the aggregates due to different shifts between the molecules, as was discussed in Section 4.1.^{6,137} Beyond just the molecule counts in the images, the broad array of spectral changes served as further evidence that aggregates had formed. There was no apparent link between the emission energies and the corresponding fluorescence intensity in either of the gases.

Fluorescence transients were also taken in both nitrogen and air. These transients also displayed a high degree of heterogeneity. After collection, transients were qualitatively placed into one of three main categories: one-step photobleach, "spike", which was classified as one sharp spike of intensity prior to a bleach with less than 3 seconds of emission, or "other". Transients classified as "other" exhibited behavior such as blinking or multi-step photobleaches. None of these phenomena occurred at a high enough rate to merit their own particular category. Figure 4.8A and B show a comparison of a one-step bleach transient compared to a "spike" transient while Figure 4.8C and D show examples of spectra taken from the "other" category. These transients were also sorted by what gas they occurred in, and the results are presented in Table 4.1 as percentages of the total number of transients. While both atmospheres yielded a similar amount of one step bleaches, those aggregates that were measured in air exhibited "spike" transients much more frequently than in nitrogen, such that 86% of the air transients fit into either the one step bleach or spike categories. The abundance of "spike" behavior is likely due to the sensitivity of triplet states to oxygen, as was discussed in the introduction of this chapter, and was taken as additional evidence that these small PDI aggregates can undergo singlet fission, or have excited states with some triplet character.¹⁴⁰ Most of the aggregates, regardless of atmosphere and classification exhibited one step blinking or bleaching, despite being made of more than one potential emitter. This behavior is characteristic of single emitter species, as multi-chromophore species usually exhibit multiple steps if there are multiple chromophores acting independently, as has been shown in conjugated polymer studies.⁴⁶ The rapid permanent bleaching in the air samples is most likely due to an oxidation reaction occurring when oxygen reacts with the excited triplets.

Of the transients placed in the "other" category, many of them could be classified into one of the two sub-classes shown in **Figure 4.8C and D**, where there was no irreversible bleach. In one case the aggregate spent the bulk of the experiment emitting but would briefly blink off. In the other, the aggregate spent the bulk of the experiment in a non-emissive state but would briefly blink on. Off states in transients are usually attributed to triplet states or other non-emissive intermediate states such as radical ion states or even potentially charge transfer states.¹⁴⁰ Given that there is evidence that charge transfer states play a crucial role in the singlet fission process as an intermediate,^{72,73,78} it is plausible that these off states could be due to long lived charge transfer and triplet states within the system. Previous work on single PDI molecules by Cordes et al., however, has observed similar blinking behavior in an anaerobic environment and attributed the short-lived off-states to radical anion formation on the PDI molecules.¹⁴⁵ This particular pathway could be contributing to some of the behavior exhibited by the aggregates in the "other" classification. Additional tests such as time resolved resonance raman would be required to determine the nature of these states to determine any triplet character. No quantitative analysis was performed on the fluorescence transients to explore differences in intensity between samples.



Figure 4.6: Histograms of the position of the 0-0 transition in single molecules (red) and single aggregates (blue).



Figure 4.7: Example single aggregate spectra in (A-C) nitrogen and (D-F) air. The spectra exhibit the following deviations from the typical single molecule emission spectrum: A) Suppression of the 0-0 transition relative to 0-1 and a red shift; B) Enhancement of the 0-0 transition and a blue shift; C) Blue shift to the point of clipping on the filter; D) Suppression of the 0-0 transition and a red shift; F) Blue shift to the point of clipping on the filter. *The spectrum labeled "E" is an ensemble of multiple 30 second spectra of the same aggregate that were averaged together to reduce noise. All spectra involved exhibited the same photophysical behavior.



Figure 4.8: Example fluorescence transients of single aggregates of each classification: A) One-step photobleach; B) "Spike" photobleach; C-D) Other, where C blinks on and D blinks off.

Transient Classification	N ₂	Air
One-Step photobleach	41%	45%
"Spike" photobleach	26%	41%
Other behavior	33%	14%

 Table 4.1: Percentage of total transients that fit into each classification based on the atmosphere during the experiment.

4.3.2 Experimental Termination and Future Directions

These results should serve as preliminary data for future work and were largely never taken beyond qualitative analyses. Part of the reason for this is experimental failures. After an extended period of reliable and reproducible aggregate formation via SVA, the process lost its effectiveness and aggregates could no longer be formed. The failures were thoroughly investigated both on the chemical and mechanical sides. Additional solvent blends of acetone and chloroform that had reliably produced very large aggregates in conjugated polymers were tested,⁵⁰ but resulted in little to know aggregate formation. The present theory is that, despite the fact that a dehumidifier was introduced to the room to provide some degree of humidity control, water vapor, either in the atmosphere or the nitrogen supply, somehow impedes aggregate formation in PDIs, but this has not been confirmed.

The original plans for these experiments were to acquire a larger sample population then begin a more thorough quantitative analysis with the aim of linking the spectral and transient behavior to understand what systems lead to the highest triplet yields. One parameter that would prove particularly useful to acquire from the transients is bleaching number, which is defined as the average number of photons emitted prior to bleaching.⁵⁴ Comparison of this parameter between nitrogen and air systems provides valuable insights into the roles of triplets in the excited states. This data could be related to aggregate structure through simulation as the excitation polarization experiments proved unsuccessful. Subsequent studies would introduce solvent blends to the annealing process in order to systematically create gradually larger aggregates so as to understand at what point the heterogeneous behavior of assorted small aggregates transitioned to homogeneous bulk film photophysics and if at any point the small aggregates achieve any degree of homogeneity prior to film behavior. If they do not, material design techniques could be introduced to dictate packing behavior. The preliminary data provided in this chapter shows a great deal of potential for single PDI aggregate experiments.

4.4 CONCLUSIONS

PDIs represent a very interesting class of chromophores for solar devices due to their stability and capacity for singlet fission. Unraveling the relationship between structure and singlet fission efficiency at the smallest achievable scale and building up to film photophysics would be a valuable step towards improving device efficiency. Fluorescence microscopy shows great potential for aiding in this undertaking, particularly when combined with solvent vapor annealing. The annealing process has the capacity to serve as a reliable means of producing aggregates, not only of dimers and trimers, but of tunable size, but there are still factors related to that process that are not fully understood and that are beyond the control of the current setup in the Vanden Bout lab. When small aggregates are formed by the SVA method, they form extremely heterogeneously, exhibiting both red and blue shifts as well as different degrees of electronic coupling between the molecules. Fluorescence transients of single PDI aggregates taken under both nitrogen and air atmospheres provided evidence that singlet fission was occurring at this smallest scale through blinking and bleaching behavior. Additional experimentation is necessary to complement and expand upon these studies, before evolving them to the level of optimizing film structure for maximum triplet production.

Chapter 5: Examination of Moisture-Driven Formation and Growth of Quasi-2D Organolead Halide Perovskite Crystals²

5.1 INTRODUCTION

In recent years, Ruddlesden-Popper (RP) phase quasi-2D organolead halide perovskites have been shown to exhibit enhanced stability over traditional 3D perovskite materials,^{81,87–90} making them an appealing research avenue towards improved photovoltaic devices. As was discussed in **Chapter 1**, these materials are made up of sheets of metal halide octahedra of a tunable width spaced out by an alkylammonium species with a tunable alkyl chain.^{84–86} This layered structure of alternating inorganic and organic layers results in an electronic structure where the perovskites behave as quantum wells while the alkylammonium components serve as barriers.^{23,79,85} Because of this behavior, adjusting the thickness of the perovskite layer (the *n* phase) changes the photophysical properties of the material. As a result, each of the different *n* phases of RP perovskites produces its own characteristic emission spectrum where higher *n* phases are shifted further to the red as the bandgap is reduced.^{23,146}

RP perovskite films tend to be naturally heterogeneous to the point where the emission spectra collected from the frontside and backside of the film are drastically different because of the phases that exist on each side.^{5,81} The films naturally phase separate with low-*n* phases preferentially forming closer to the substrate and high-*n* material favoring the surface.^{5,147,148} This *n*-phase gradient forms due to an increase in thermodynamic stability as *n*-decreases.¹⁴⁸ Despite improved moisture stability over their 3D counterparts, RP phase perovskites are not immune to its effects, as can be seen in the

² Portions of this chapter have been submitted for review at ACS Applied Energy Materials as 'Moisture-Driven Formation and Growth of Quasi-2D Organolead Halide Perovskite Crystallites.' (Wygant, B. R. *et al.* Moisture-Driven Formation and Growth of Quasi-2D Organolead Halide Perovskite Crystallites. *ACS Appl. Energy Mater.* Submitted (2020). The author of the dissertation was responsible for the confocal fluorescence imaging and spectroscopy experiments.

data taken by the Mullins group at the University of Texas at Austin (**Figure 5.1**).⁸¹ They have been shown to undergo a disproportionation based degradation mechanism that disrupts this layering by forming a passivating layer of low-*n* material at the surface, hindering further degradation.^{81,87} This seemingly self-protecting mechanism was recently shown to have a downside, however, as small crystallites were observed to form at or near the surface of *n*-butylammonium methylammonium lead iodide (nBA-MAPI) films that were exposed to moisture.⁸¹ Despite X-ray scattering experiments suggesting their composition is low-*n*, just as in the passivating layer, they present large, thick disruptions perpendicular to the otherwise smooth and fairly homogeneous surface of the film. This unresolved heterogeneity may induce damage to the film itself during formation, and ultimately could disrupt device performance both through film damage and contact disruption between device layers. In order to combat this, it is imperative to determine the nature of these crystallites and the mechanism behind their formation so that their formation can be stunted.

In this study, a wide array of characterization techniques are utilized to unravel the nature of these crystallites. X-ray diffraction spectroscopy (XRD) and wide angle X-ray scattering (WAXS) was used to verify that fresh films exhibit high crystallinity and the proper orientation on the substrate as well as to show the presence of low-*n* material after extended humidity exposure. Atomic force microscopy (AFM) was used to image the surface of a film periodically over a 72 hour period of humidity exposure to monitor the growth of crystallites on the surface. Confocal fluorescence microscopy and spectroscopy enabled spatially resolved measurements of phase composition of the crystallites as well as measurements of the spatial heterogeneity within the crystallites. A combination of time of flight secondary ion mass spectrometry (ToF-SIMS) and AFM was then used to study the topography of the interiors of both films and model photovoltaic devices that had been

exposed to moisture to uncover the beginnings of crystallite formation within the perovskite layer. The results of these experiments were then taken together to formulate a proposed mechanism linking the disproportionation degradation to crystal growth to provide a foundation for preventing the rise of surface heterogeneity, thus improving performance and stability in future devices. All work was performed in collaboration with the Mullins group in Chemical Engineering at the University of Texas at Austin. Contributions from Geoffrey Geberth were primarily regarding the confocal characterization. The larger findings of these studies are included to provide context for the confocal microscopy work.



Figure 5.1: Normalized power conversion efficiency (PCE) of MAPI, nBA-MAPI, and 2D/3D MAPI devices following exposure to 78% relative humidity over the course of 48 hours, showing the decrease in PCE for all devices as they degrade. (Taken from the work of Wygant et al.⁸¹)

5.2 EXPERIMENTAL

5.2.1 Film and Device Fabrication

Film fabrication and controlled moisture exposure was performed by the Mullins group. The nBA-MAPI films were fabricated using a hot casting method described in detail elsewhere.⁸¹ Briefly, solutions of *n*-butylammonium iodide (nBAI, GreatCell Solar), methylammonium iodide (MAI, GreatCell Solar), and PbI₂ (99.99%, AlfaAesar) in *N*,*N*-dimethylformamide (DMF, 99% ultra-dry, Acros Organics) were prepared in a N₂-filled glovebox (VAC Atmospheres, H₂O, O₂ < 5 ppm) by stirring for at least 24 hours prior to film fabrication. The solutions were 0.5 M with respect to Pb²⁺ in solution, with a solution stoichiometry of (nBA)₂(MA)₃Pb₄I₁₃. Clean 2x2 cm² F:SnO₂ (FTO) coated glass substrates (TEC15, Harford Glass) were washed in 1% (m/m) Contrex AP solution through sonication for 15 minutes, and then lightly scrubbed and rinsed to remove any grease or debris. This was followed by 5 minutes of sonication in acetone and then 5 minutes more in isopropanol, before being dried with compressed air. After drying, the substrates were brought into the glovebox.

Prior to film deposition, an aliquot (typically 300-800 μ L) was filtered through a 0.2 μ m PTFE filter into a 2 mL glass vial and heated on a 75°C hotplate for at least 20 minutes. Likewise, FTO substrates were allowed to heat on a 110°C hotplate for at least 20 minutes to ensure thorough heating as part of the hot casting procedure. Following heating, the substrate was rapidly moved to the chuck of a spin coater, where 80 μ L of the preheated solution was pipetted onto the center of the film. The substrate was then immediately ramped to 5000 rpm and held for 20 seconds. Within 5 seconds, the substrate turned a dark brown color as the perovskite film crystallized. After spin coating, the film was removed from the chuck and allowed to continue cooling. Films were typically prepared as close to the time of experimentation as possible, and stored out of direct light to inhibit

photodegradation. To controllably degrade the films under humid conditions, they were placed in a sealed container containing a saturated solution of KCl in water, which kept the atmosphere inside the container at a relative humidity of 78%, for a pre-determined period of time. After degradation, the films were removed from the container and analyzed as quickly as possible.

Model PV devices for ToF-SIMS/AFM analysis were prepared similarly, with some modifications. After drying, the FTO substrates were treated with UV/O₃ (BioForce Nanosciences) for 25 minutes to create a hydrophilic surface, then a PEDOT:PSS (Heraeus) film was applied to the surface. A 1:2 dilution of the polymer in methanol (Fisher Scientific, ACS Grade) was used for spin coating. Two drops of the PEDOT:PSS solution were filtered through a 0.2 micrometer PTFE filter onto the center of the substrate, which was then spun at 4000 rpm for 40 s, using a 3 second ramp and deceleration. Following coating, the substrates were annealed at 150 °C for 10 minutes before being immediately brought into the glovebox. Perovskite film deposition onto these substrates was accomplished in a manner identical to the procedure listed above. To complete the model devices, 40 nm of C₆₀ (MER Corp., 99.9%) and 7 nm of bathocuproine (BCP, Sigma-Aldrich, 99.9%) were thermally evaporated using an AMOD thermal evaporator at a base pressure of approximately 8×10^{-7} torr. The first 10 nm of C₆₀ were deposited at a rate of 0.2 Å/s, while the remaining 30 nm were deposited at 1 Å/s; the 7 nm BCP film was deposited 0.2 Å/s. Following deposition, of at thin strips the BCP/C₆₀/Perovskite/PEDOT:PSS stack was scratched away with a razor blade from two sides of the device to expose the FTO beneath. 125 nm of gold were then deposited through a shadow mask via electron beam evaporation using a Cooke Evaporation System to create the top contacts (0.2 cm^2) , as well as gold contacts for the FTO bottom contact to reduce unnecessary series resistance. Similar to C₆₀, the first 10 nm of Au were deposited at 0.2

Å/s and the remaining 115 nm were deposited at 1 Å/s. The finished devices were then stored in an Ar-filled MBraun glovebox ($O_2/H_2O < 0.1$ ppm) until testing. This process was also performed by the Mullins group.

5.2.2 Instrumental Characterization

X-ray diffraction (XRD) was performed by the Mullins group on a Rigaku Ultima IV diffractometer in a thin film configuration using a Cu Ka X-ray source. Atomic force microscopy (AFM) was conducted by the Mullins group on a Park NX10 atomic force microscope in noncontact mode. This microscope is enclosed in a climate-controlled box allowing a constant RH to be maintained during analysis. The box was purged with ultrahigh purity N_2 gas for 1 hour prior to sample loading to reduce the humidity to <15% before the fresh films were analyzed, then the humidity was increased to 78% for film exposure. For the ToF-SIMS/AFM measurements the AFM box was purged continuously with ultrahigh purity N₂ gas, which kept the RH level very low in order to minimize the reaction between residual water and the Cs-sputtered spots. Photoluminescence spectroscopy (PL) was performed by the Mullins group on a Horiba Jobin Yvon Fluorolog3 spectrophotometer, using an excitation wavelength of 450 nm and a typical 90° detector geometry, with the film held at 45°. Excitation was performed on both the front (shining directly on the perovskite film) and the back (shining through the glass) of the films. Wide angle x-ray scattering (WAXS) was performed by the Roberts group on a Xenocs Ganesha small angle scattering instrument fitted with a moveable Dectris 300k detector to record wide angle scattering data. The instrument is fitted with a microfocus Cu Ka source operated at 50kV and 0.6mA. A manufacturer supplied utility, SAXSGUI, was used to reduce 2D scattering intensity images into intensity vs. scattering angle plots. Data was collected from a 0.7 x 12 mm area, using a 1° tilt of the substrate. Scanning electron microscopy (SEM) was performed by the Mullins group with an FEI Quanta 650 ESEM, using an accelerating voltage of 15 kV at a vacuum of approximately 5×10^{-6} torr.

5.2.3 Fluorescence Microscopy

In preparation for confocal fluorescence microscopy (CFM) studies, the perovskite films were placed face-up on fresh piranha cleaned coverslips in a custom-machined sample holder that held them together with a secure contact. Due to the highly emissive nature of the samples and the sensitivity of the detectors, the excitation power was too low to be measured. The emitted light was filtered through a 496 nm long pass filter and a 721 nm short pass filter prior to detection Each crystallite had spectra taken at three positions, once on each end and once in the middle. Each location on a given crystal had three consecutive spectra taken with 25 s integration times. These three spectra were then averaged to increase the signal-to-noise ratio. Due to how the samples were assembled in the sample holder, atmospheric controls were not usable.

5.2.4 ToF-SIMS

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling in negative polarity was performed using a Bi_{3}^{+} (30 keV ion energy, 0.8 pA measured sample current) analysis beam to raster scan a 100x100 μ m² area located within the boundaries of a larger crater (300x300 μ m²) created using a Cs⁺ sputtering beam (500 eV ion energy, ~40 nA measured sample current). The pressure inside the analysis chamber was typically below 1.5x10⁻⁹ torr during analysis. Both films and devices analyzed using ToF-SIMS were split in half inside the glovebox prior to analysis, with one half left inside the glovebox as a control and the other half exposed to humidity. After exposure, the device or film was brought back into the glovebox and loaded with the control into an inert atmosphere transfer vessel to limit exposure to the environment while transferring the devices to and

from the ToF-SIMS instrument. Following sputtering, the samples were loaded back into the vessel and transferred back to a glovebox to prepare them for AFM analysis. The samples were transferred under inert atmosphere into the AFM box (<15% RH) and analyzed quickly to prevent any physical and chemical interactions of water or oxygen with residual Cs in the sputtered areas.

5.3 RESULTS AND DISCUSSION

5.3.1 X-ray Analysis

nBA-MAPI that was nominally n = 4 stoichiometrically was utilized for these experiments, similar to what has been done in previous studies.^{81,89} As was stated in the introduction, crystallographic orientation in quasi-2D perovskite materials has been shown to impact device efficiency,¹⁴⁹ so the films were fabricated via a hot casting technique that has previously produced well-oriented films.⁸⁹ XRD and WAXS experiments were performed to verify crystallographic uniformity in the samples as well as to monitor changes after 6, 12, 24, 48, and 72 hours of exposure to 78% relative humidity. The XRD results are shown in **Figure 5.2**. The spectrum for the fresh film exhibits two distinct peaks near $2\theta = 14.2^{\circ}$ and 28.5° while lacking any activity below $2\theta = 10^{\circ}$, which would have been characteristic of un-oriented films.¹⁴⁶ WAXS spectra of the unexposed film (Figure 5.3) corroborate this, showing distinct Bragg diffraction spots characteristic of planes nBA-MAPI perpendicular to the substrate.^{89,90} The XRD spectra exhibited only slight shifts in the two primary peaks, which could be attributed to expansion of the perovskite unit cell as a result of hydration or an increase in the quantity of lower-*n* perovskites.¹⁴⁶ After 48 hours the XRD spectra showed peaks evolving at $2\theta = 8.2^{\circ}$ and 9.7° which are indexed to the n = 4 phase. After 72 hours of moisture exposure, these peaks evolved further and were complemented by an additional peak at $2\theta = 8.65^{\circ}$ that can be attributed to $n = 2.146^{\circ}$ WAXS spectra of these two films showed the formation of Debye-Scherrer diffraction rings, and subsequent radial integration showed that these corresponded to the $2\theta = 8.65^{\circ}$ and 9.7° peaks visible in the XRD spectra.¹⁴⁶ These rings typically represent unoriented crystals in films,¹⁵⁰ suggesting low-*n* crystals are forming as part of the film undergoing disproportionation.⁸¹

5.3.2 Atomic Force Microscopy

To study topographic changes in the nBA-MAPI films during moisture exposure, a sample was scanned with an AFM in a sealed container over 72 hours, with images collected at t = 6, 12, 24, 48, and 72 hours. These scans are shown in **Figure 5.4**. The t = 0 scan showed a smooth homogeneous film, but as time went on, cracks and pits began to form in the surface. The cracks in particular seem to form along grain boundaries. Further scans of the same area of the film showed increases in the amount of cracks in the surface as time went on and crystallites began to form within these cracks. These crystallites averaged 2-3 µm in length and approximately 100 nm wide that seem to be protruding from the surface as opposed to lying on top of it. After 72 hours, the surface was very heterogeneous with crystals and cracks that grew wider as the crystallites thickened. Given that these crystallites correspond to the new features in the XRD and WAXS experiments, it corroborates the idea that the crystallites form from low-*n* material, but none of these techniques can locally differentiate between the different materials to identify the phase of the crystallites.

5.3.3 Bulk Film Fluorescence

In order to gain insights into the phase makeup of these crystallites, fluorescence emission spectroscopy was utilized. This is possible because each phase has a characteristic emission spectrum, as was discussed in **section 5.1**.^{23,86,146} Bulk film

emission spectra were taken both on the front and backsides of the films (Figure 5.5A and **B**). The unexposed sample spectra showed peak distributions that were in agreement with the literature.^{5,81} where the front-side spectrum was broad and centered at approximately 715 nm with a shoulder towards the blue while the backside spectrum is broad with a distribution of peaks corresponding to n = 2-5.¹⁴⁶ The reason for the differences between front and back of the fresh sample is because these films inherently form gradients in the *n*-phase with respect to depth, as was discussed earlier. 5,147,148 As has been previously reported.⁸¹ the exposed samples revealed the growth of low-n emission in the frontside spectra in as early as 6 hours of exposure, with them growing in strength as exposure time increased. The backside spectra showed only slight changes with respect to exposure time. Both front and backside spectra exhibited slight red shifts in the n = 3 peak indicative of crystallographic change in response to moisture exposure and, in the case of the frontside, the formation of higher *n* species through disproportionation. Difference spectra (Figure 5.5C and D), where the spectrum from the unexposed sample is subtracted from the exposed spectra, of the front sides of the samples show the clear growth of both low-n (n = 2-5) as well as a very distinct peak near 740 nm that is attributed to high-n/3D-like perovskite based on the literature.⁵ This high-n peak is visible in spectra from both sides and increases correspond to decreases in the n > 5 peak. This combination of a decrease in one particular phase accompanied by increases in both higher and lower order phases is evidence for a disproportionation reaction and supports the observations from the x-ray experiments. While the experiments up to this point taken collectively support the idea that these crystallites form from low-*n* phases via disproportionation, they do not provide direct confirmation.



Figure 5.2: A) Selected regions of the XRD spectrum of an nBA-MAPI film over 72 hours of exposure to 78% relative humidity, showing a shift in the (111) and (202) peaks. B) Low two theta region of the nBA-MAPI film XRD spectrum over 72 hours of humidity exposure, showing formation of n = 2 and 4 phases in the film.



Figure 5.3: WAXS spectra of nBA-MAPI films at A) 0 hours, B) 6 hours, C) 12 hours, D) 24 hours, E) 48 hours, and F) 72 hours of exposure to 78% relative humidity. All samples show well-oriented crystal structures, as indicated by the clear spots for the (0 0 -2), (-1 5 -2), and (-1 1 -1) reflections. Spectra after 48 hours of exposure (E and F) show the formation of rings at low-q (indicated by white arrows), indicating the formation of un-oriented low-n perovskite phases after sufficient exposure.



Figure 5.4: AFM images of a single area of an nBA-MAPI film in non-contact mode after A) 0, B), 6, C) 12, D) 24, E) 48, and F) 72 hours of exposure to 78% relative humidity. Upon extended exposure to humidity, cracks (location I) and holes (location II) begin to form, with elongated crystals forming later. Some grain boundaries also experience subsidence (location III) prior to crystal growth. Other areas exhibit crystal growth without apparent damage to the film previously (location IV).



Figure 5.5: PL spectra taken from the front (A) and back (B) of an nBA-MAPI film over the course of 72 hours of exposure to 78% relative humidity. New peaks in the 575 to 650 nm range, corresponding to n = 2-5 phases, appear on the front side (A) after exposure, and the primary peak at 715 nm shifts to 725 nm. Similar spectral changes are observed in B). Normalized PL difference plots from the front (C) and back (D) of the same film, showing the formation of low-*n* species and a 3D-like species accompanied by the loss of the n > 5 species with exposure.

5.3.4 Fluorescence Microscopy

Confocal fluorescence microscopy and spectroscopy provide an avenue to achieve this direct confirmation thanks to the spatial and spectral resolution. While variants of fluorescence microscopy have been used on RP perovskite systems in recent years, to date no groups have utilized it to probe individual crystallites formed in a thin film.^{5,23,41,151,152} By making slight adjustments to the single molecule-capable microscope utilized in Chapters 3 and 4, imaging and analyzing these crystallites becomes possible. Due to the highly fluorescent nature of the system and the sensitivity of the APDs, the laser power was significantly reduced to below levels where it could be accurately measured. Initial scans of a degraded perovskite film showed no signs of crystallites and point spectra of the surface showed a single emission peak near 740 nm (Figure 5.6). This is significantly shifted from the primary peak observed in the bulk emission spectra, but it agrees more closely with features observed in the line-scanning experiments performed by Liu et al., and was interpreted as a thin surface layer of a 3D-like perovskite.⁵ A commercially available 721 nm short pass filter was inserted prior to the detectors in order to favor data collection in the low-n spectral regime and prevent this peak from overwhelming the other signals at the cost of some spectral information in the red, high-*n* region.

Confocal fluorescence images of samples that had not been exposed to moisture showed no signs of crystal growth on the surface, as can be seen in **Figure 5.7A**. After 12 hours of moisture exposure, crystallites were observed on the sample surface, appearing as linear streaks across the surface. Higher resolution images, such as the 24 hour exposure example shown in **Figure 5.8** allowed for approximate measurements of the crystallites, which approximately agreed with the AFM-collected dimensions of 1 μ m in length and 100 nm wide. These images also showed regions accompanying the linear structures that are distinctly non-emissive. These appear to be cracks in the surface from which the

crystallites are protruding, which is reinforces that the emissive structures are the same crystallite structures observed with the AFM. **Figure 5.7B-E** shows example images from 12, 24, 48, and 72 hours of moisture exposure. As the moisture exposure time increased, the crystallites increased in quantity and size until the surface was nearly completely covered after 72 hours. This finding also agrees with what was observed in the AFM experiments.

In order to discern the phase makeup of the crystals, localized spectra were taken. Spectra of the unexposed films with the filter in place showed no peaks that correspond to low-*n* material, instead rising into one broad peak that hits the spectral wall imposed by the short pass filter, as seen in Figure 5.9A. In samples that had been exposed to moisture, spectra were collected in areas not occupied by crystallites to serve as controls as well as three distinct spots upon the crystallites: the middle and each end. Off-crystallite background spectra were averaged at each time point, producing spectra identical to the unexposed sample surface (Figure 5.9A). All of the on-crystal spectra for each given time point were combined to produce an average crystallite spectrum for that exposure time, as is shown in Figure 5.9B. These spectra were then normalized to the large, red, clipped peak. Unlike the unexposed and background spectra, crystallite spectra show a very distinct growth of low-*n* peaks, specifically n = 3-5, before blending into the large peak that terminates at the filter. These peaks each correspond to a different phase in the material, as was previously mentioned. By using both the average crystallite spectra and the average background spectra, average background-subtraction spectra for the crystallites to more clearly see the changes in peak intensity with respect to exposure time (Figure **5.10**). As moisture exposure time increased, the relative signals for each low-*n* peak also increased, indicating that these phases increase within the crystallites as moisture exposure increases. When compared to the low-*n* phases in the bulk spectra, these peaks are all

shifted approximately 10 nm to the red of the bulk. This sort of shift has previously been observed as a result of pressure effects, 153 and was taken as evidence of crystal compression due to the surrounding film. Overall, the changes in phase intensity and overall spectral shape agree with what was shown in the bulk spectra, indicating that these crystallites are responsible for the low-*n* material seen to have grown in in those spectra.


Figure 5.6: Point fluorescence spectrum from an nBA-MAPI film without a short pass filter showing a strong peak near 750 nm



Figure 5.7: CFM images of a nBA-MAPI films at A) 0 hours, B) 12 hours, C) 24 hours, D) 48 hours, and E) 72 hours of exposure to 78% relative humidity with a 721 nm short-pass filter. The red crosshairs and numbers are artifacts from the imaging software.



Figure 5.8: CFM image of an nBA-MAPI film exposed to 78% relative humidity for 24 hours, showing localized fluorescence below 721 nm from crystal-like structures.



Figure 5.9: Average normalized point fluorescence spectra from CFM of areas off- (A) and on-crystal (B) taken from nBA-MAPI films exposed to 78% relative humidity over 72 hours. In A) only the shoulder of the large peak at 750 nm can be observed for all samples. In B), there is a clear increase in peaks at 620, 660, and 680 nm with exposure time, corresponding to formation of n= 3, 4, and 5 peaks, respectively.



Figure 5.10: Average background-corrected point fluorescence spectra from low-n nBA-MAPI crystals after moisture exposure for 72 hours, showing an increase in the intensity of n = 3-5 peaks with increasing exposure to humidity.

Upon completion of the averaging studies, the spectra were then broken down by crystal position and exposure time to further elucidate crystallite composition as a function of position. Unfortunately, these fluorescence techniques sacrifice information regarding z-positioning, so it is impossible to determine if one of the sides of the crystallites is embedded as the AFM images and spectral shifts suggest. Still, the spectra were compared for each crystallite based on the three sampled positions of the visible portion. Each crystal was then classified into one of four categories based on the spectra: homogeneous, where all three spectra are indistinguishable, 1 side inhomogeneous, where one of the two ends differed from the middle and the other end, middle inhomogeneous, where the ends were indistinguishable but the middle differed, and heterogeneous, where each of the three positions showed different spectral behavior. Figure 5.11A-B shows examples of the 1 side inhomogeneous and heterogeneous classifications. Each of these occurrences for each time point was then counted and plotted as a percentage of the total spectra for each time with respect to exposure time (Figure 5.11C). As exposure time increased, there was a distinct decline in 1 side inhomogeneous crystallites which was accompanied by a corresponding increase in heterogeneous crystals, which reached approximately 80% of the occurrences by the 72 hour decomposition mark. Overall, very few crystallites fit into the middle inhomogeneous category. These findings suggest that as moisture exposure persists, the crystals do not change uniformly along their length. Unfortunately, experimental limitations prevent more quantitative assessments or even more refined spatial information. Despite this, confocal fluorescence microscopy proved to be an effective technique for both imaging the crystals and confirming their phase makeups as primarily n = 3-5, a capability that eluded the other imaging techniques.

5.3.5 ToF-SIMS/AFM

Each of the techniques presented in this chapter thus far have been surface based techniques, and several of them have provided evidence that the crystallites begin forming within the surface cracks that form during degradation. In order to understand the degradation process, the interior of the film must be probed both before and after degradation. In order to achieve this, a combination time-of-flight secondary ion mass spectrometry (ToF-SIMS) and AFM was used to sputter into the film then probe the newly exposed surface respectively. ToF-SIMS has been used in the past to controllably sputter into both 2D materials¹⁵⁴ and solar devices¹⁵⁵ prior to AFM imaging of the interior. **Figure 5.12 A-C** show the ToF-SIMS depth profile of an nBA-MAPI film and AFM images of films sputtered to the midpoint of the film, one prior to moisture exposure and one that had been exposed for 8 hours. The small nodules visible in the images are likely a result of the sputtering process. These AFM images show 1-2 µm cracks forming in the film as well as some small structures that appear to be the beginnings of crystallite formations, lending credence to the theory that these crystallites originate deep within the films.

In order to bring the model of thin films closer to real world applications, model devices were then fabricated and run through the same ToF-SIMS and AFM experiments. It was hypothesized that the additional layers of a device should provide the nBA-MAPI some protection from moisture thus hindering crystallite formation to a certain extent. The resulting ToF-SIMS profile and AFM images are shown in **Figure 5.12 D-F**, where the AFM images were taken after sputtering halfway into the nBA-MAPI layer of the unexposed and exposed devices. The devices that were exposed were subjected to 24 hours of humidity in order to replicate what previous reports have shown to be a moderate degree of damage.^{81,89} The AFM image of the exposed device reveals two linear structures nearly 1 μ m in length and 100 nm in width. This suggests the presence of crystal formation even

within the protected device, although the density is much lower than in unprotected films. This suggests that while the layers do, in fact, provide some degree of protection from the moisture, it does not completely inhibit exposure, instead delaying crystallite growth. Fluorescence microscopy experiments were not performed as compliments to these postsputtering experiments as it would not be possible to reliably locate the sputtered region with the microscope.



Figure 5.11: Point fluorescence spectra taken from three different locations of the same nBA-MAPI crystal using CFM at A) 12 hours and B) 72 hours of exposure to 78% relative humidity. The inset image in each provides an example of the locations sampled for each spectrum. Scale bar equal to 1 μm. C) Plot showing the prevalence of different levels of crystal homogeneity in nBA-MAPI crystals over 72 hours of exposure. Over time, different locations of the crystals begin to show varying quantities of different *n*-phases.



Figure 5.12: Negative ion polarity ToF-SIMS depth profiles for A) a bare nBA-MAPI film and D) a model PV device. PbI₂⁻ represents the inorganic portion of the perovskite, CN⁻ represents the organic portion of the perovskite, SnO⁻ represents FTO, Au₄⁻ represents the Au contact, C₂N⁻ represents BCP, C₉⁻ represents the C₆₀ layer, and ³⁴S⁻ represents the PEDOT:PSS layer. A fresh film (B) and one exposed to 78% relative humidity for 8 hours (C) were sputtered to the dashed line in A) and the surface was imaged by AFM, showing the presence of new crystals (I) and cracks (II) only in interior of the exposed sample. A fresh device (E) and one exposed to humidity for 24 hours (F), likewise showing the formation of crystals (III) inside the film.

5.3.6 Proposed Crystal Growth Mechanism

In response to the results discussed in this chapter and other reports in the field, Bryan Wygant of the Mullins group developed a proposed mechanism for the crystallite formation in the presence of moisture. This mechanism, shown in Figure 5.13, begins with water diffusion into the film through vulnerabilities such as grain boundaries. Given the inherent phase gradient, the water makes its way through the high-n surface into a mixed phase region containing segregated areas of n = 3-5 material, solvating material as it progresses. Related systems have shown evidence of mixed regions of this nature, providing a basis for this proposal.¹⁵⁶ These segregated zones of low-n material act as nucleation sites where the solvated material collects and recrystallizes into additional more thermodynamically stable low-n material.¹⁵⁷ The more favorable solubility of the alkylammonium portions over the Pb-I components encourages the disproportionation mechanism previously reported by the Mullins group,⁸¹ resulting in higher-*n* species and recrystallized material at the surface, leading to the passivation layer that has been hypothesized to form.^{81,87} As more material diffuses down to the nucleation sites, the crystallites grow perpendicular to the substrate, eventually leading to the observed opening of the grain boundaries. These broader openings result in further moisture openings, accelerating crystallite growth and opening additional vulnerabilities in the surface. The forced compression of the crystallites within the cracks would result in the red-shifted spectra observed in the microscopy experiments. Extended exposure to humidity would continue the crystallite growth process under this model, resulting in an extremely heterogeneous terrain forming on the once smooth film surface. Based on the ToF-SIMS and AFM data, it follows that this process is at least somewhat responsible for the gradual decay in power conversion efficiency observed in nBA-MAPI devices that have been exposed to moisture.⁸¹ Because this process hinges upon the inherent heterogeneity of the

perovskite films, combatting the heterogeneity should lead to improvements in device stability. Recent strides have been made regarding improving homogeneity by adjusting the temperature of film fabrication⁵ and by adding an additional linker species,¹⁵⁸ and further experiments are currently underway throughout the field to this effect. This proposed degradation pathway is detailed further in the manuscript 'Moisture-Driven Formation and Growth of Quasi-2D Organolead Halide Perovskite Crystallites', which, at the time of writing, has been submitted to ACS Applied Energy Materials for review.



Figure 5.13: Proposed growth mechanism for low-*n* nBA-MAPI crystallites. A) water diffuses through grain boundaries in the *n* > 5 surface, carrying solvated perovskite components to low-*n* nuclei buried in the film. The nuclei begin to grow, causing the film to split (B) and allowing more water to diffuse into the film. (C)The crystals increase in girth, as well as disproportionation. (D)Crystals eventually cease vertical growth near the film surface but continue to lengthen and widen as exposure continues.

5.4 CONCLUSION

Ruddlesden-Popper phase quasi-2D organolead halide perovskites represent an interesting evolution over traditional 3D perovskite materials due to their enhanced stability. Despite this enhanced stability, the 2D systems are still vulnerable to degradation, particularly via crystallite formation in the presence of moisture. In order to better understand the degradation process, nBA-MAPI films were studied both prior to moisture exposure and after set periods of exposure in a controlled environment. Initial bulk and surface scans showed the presence of both low-*n* and 3D-like species growing in while AFM images revealed the presence of cracks and eventually crystallites on the surface after extended exposure to moisture. Unfortunately, these techniques could not verify the crystallites as the source of this low-n signal. Confocal fluorescence microscopy and spectroscopy of the degraded films, however, was able to determine the phase makeup of the crystallites as this low-n material, and monitored the changes in crystallite composition with respect to time, showing an increase in phase heterogeneity along the length of the crystallite as exposure time increased. These results prompted AFM experiments performed midway through the film depth after ToF-SIMS was used to bore into both films and devices, which revealed that the crystallites form deep within the films before protruding through the surface of the nBA-MAPI. Taken as a whole, all these experiments led to the formation of a new proposed mechanism for crystallite formation in the presence of water, wherein water infiltrates through phase boundaries, carrying material deep into the film where it recrystallizes on nucleation sites and progressively expands. This mechanism is based on the inherent heterogeneity of nBA-MAPI films, and efforts to reduce that heterogeneity present and encouraging way forward towards improving 2D perovskite stability and, as a result, photovoltaic performance.

Chapter 6: Outlooks

This objective of this dissertation was to show how techniques focused on probing samples at small scales, particularly fluorescence microscopy, provide the insights necessary to eventually improve materials at the large scale. A method to understand the processes and interactions involved in bulk system formation and function is to examine the materials broken down to the most fundamental levels. Materials design has played a crucial role in achieving this end, whether by altering the substituents or backbones of conjugated polymers to achieve desired morphological results, as was seen in **Chapters 2** and **3**, tuning the substituents on perylene diimides to control packing and maximize singlet exciton fission yields, as was seen in **Chapter 4**, or altering the fundamental structure of perovskites into a quasi-2D system in order to improve stability, as was seen in **Chapter 5**. Each of these systems shows great potential for optoelectronic applications through further investigation to reduce the small scale heterogeneity and create uniform bulk materials that have been designed to maximize performance.

A great deal of work has already been done regarding material design in conjugated polymers, as can be seen in **Appendix A**,²⁵ but due to the complex nature of even single polymer chains, these systems have nearly limitless possibilities. Even so, the conjugated polymer experiments discussed in this dissertation have their own next steps to further build upon what has been laid out here. The POMeOPT experiments have two main directions. The first is to transition to the solid state and observe single aggregates of POMeOPT both in matrices of varying dielectric and formed via solvent vapor annealing with solvent mixes of varying composition. These experiments would provide further insights into the nature of this dramatic difference in fluorescence quantum yield with respect to environmental polarity. One of the most telling pieces of information would be obtained from fluorescence excitation polarization experiments, as information pertaining

to how these aggregates pack in different environments complimenting quantum yield data would be a powerful means of determining what design philosophies can be taken to access this emissive behavior in less dramatic environmental conditions. The second potential avenue of research would be system modification, both by adding a larger substituent to the thiophene backbone to observe whether or not this effect can be driven further, and by changing to the other prominent CP backbone, PPV, and noting how this environmental control over quantum yield changes with a slightly differently behaving backbone.

The conjugated polymers with the designed folding backbone from **Chapter 3** present a completely different path forward in terms of material design. While the zipper functionality was shown to be extremely reliable and robust at the single molecule level, single molecules are a long way away from bulk films useful in devices. Single aggregate studies facilitated by solvent vapor annealing to produce aggregates of varying sizes would show the larger scale potential of this functionality for making morphologically homogeneous films. Fluorescence excitation polarization studies on aggregates of different sizes would determine what modifications need to be made in the molecular design in order to maintain order as the system scales up, until eventually films are produced. Just as it was used to show the heterogeneity of MEH-PPV films,³ NSOM, in combination with other surface-based techniques, could provide insights into the large scale homogeneity of designed polymer films.

Eventual scaling up to larger systems is also the main route for advancement beyond the PDI experiments presented in **Chapter 4**. As was discussed, film spectra exhibit dramatically different spectra from single molecules. Filling in the gap between these two scales would provide a great deal of insight into the interactions and photophysical processes that occur in these fascinating materials, similar to how Marques et al. scaled up a terrylene derivative from monomers to single extended crystals.¹³⁷ The first step in this journey, however, is to understand small aggregate formation and the factors that influence it. It is unfortunate that the experiments presented in this dissertation were unable to continue, but despite the obstacle, solvent vapor annealing was shown to be a viable means of making isolated PDI aggregates, and the tunability of the technique when it works has a great deal of potential regarding scaling up PDI systems. Expansion to larger aggregates and nanoparticles presents a logical route for building up to film behavior. Beyond size expansion, however, there is still much that can be learned from the small aggregates. Experiments that correlate the alignment of the PDI molecules of the aggregate with the spectra and the transients would, once again, turn the spotlight to material design, as the immense heterogeneity in the small aggregates could be reduced through synthetic means, producing more aggregates that favor singlet fission. Ultimately, reduction in the aggregate heterogeneity is an appetizing path towards moving beyond the Shockley-Queisser limit via multiple exciton generation.

Ruddlesden-Popper phase perovskites present different routes forward that do not involve building up from the small scale. The mechanism for crystallite growth proposed in **Chapter 5** hinges on the heterogeneity of the films to provide low-*n* phase nuclei for crystallite growth. Reducing the heterogeneity of these inherently heterogeneous films may provide a means of maintaining the initial power conversion efficiencies exhibited by devices instead of succumbing to steady decay in the presence of moisture. Synthetic routes to tune the composition of the perovskite octahedra and modifications in material processing present the most promising means of reducing systematic heterogeneity, but there is still more that fluorescence microscopy techniques can unveil. While fluorescence microscopy was able to identify the source of the spectral changes seen on the frontside of the films when exposed to moisture, the backside was not examined, despite undergoing bulk spectral changes of its own. Beyond just crystallite growth experiments, however, fluorescence microscopy demonstrated its value for localized phase identification in small scale features in RP perovskite systems. As these systems continue to evolve and develop, that capacity will likely find a great deal of use in examining surface features and phase layouts with the aim of producing stable perovskite-based materials. The methods demonstrate the ability of fluorescence microscopy to untangle thin film materials when the heterogeneities can be optically resolved.

The different material systems presented in this dissertation are all dramatically different from one another, yet research into each of these systems all shares a common goal of improved optoelectronic performance. Although the specifics of how each system must go towards this goal are as varied as the systems themselves, methods used in these quests are not necessarily so diverse. Fluorescence based techniques, specifically those involved in high power microscopy, while not the only useful techniques, have yielded invaluable insights into each of these systems and have the potential to continue to do so. It is through understanding systems at the small scale that the systems can be altered and designed to remedy whatever deficiencies might exist and these systems can reach their true potentials and usher in a new wave of optoelectronics.

Appendix A: Effects of Molecular Architecture on Morphology and Photophysics in Conjugated Polymers from Single Molecules to the Bulk³

A.1 INTRODUCTION

Flexible and wearable optoelectronic devices, being light, bendable, low-cost, and even stretchable, represent exciting future technologies in displays, light sources, solar cells, and wearable sensors, to name a few.¹⁵⁹⁻¹⁶⁵ The advent of the rapidly blossoming field of flexible optoelectroincs has been mostly triggered by the advancements in exploring solution-processable, low-cost, and mechanically flexible semiconducting materials, especially organic semiconductors.^{161,162} The excellent plasticity and tunable optical and electrical properties of conjugated polymers (CPs) make them an important class within the realm of organic semiconductors. In most of the CP-based optoelectronic devices, CPs as an active layer are employed in the form of thin films with thicknesses of tens to hundreds of nanometers. Governed jointly by external processing methods (solvents, coating conditions, etc.) and internal molecular structures (backbone, sidechains, etc.), bulk films in most cases are morphologically heterogeneous, possessing domains with varying degrees of order and non-uniform grain boundaries. Such morphological heterogeneity largely originates from the molecular and nanometer scale and propagates to bulk films. Given these facts, optical and electronic information from bulk films are then an average of this large heterogeneity thus limiting the usefulness of conventional analytical tools on bulk films for making connections between structure and function.

³ Parts of this chapter were previously published as 'Effects of molecular acrchitechture on morphology and photophysics in conjugated polymers: from single molecules to bulk' (Hu, Z., Shao, B., Geberth, G. T. & Vanden Bout, D. A. Effects of molecular architecture on morphology and photophysics in conjugated polymers: from single molecules to bulk. *Chemical Science* (2018) doi:10.1039/C7SC03465B.). The author of the dissertation was primarily responsible for the sections on system heterogeneity and sidechains.

In order to effectively leverage CP materials in an array of applications, a fundamental understanding and a precise engineering regarding the morphological, optical, and electronic properties at different hierarchy levels from the bottom up are essential. To counter the heterogeneity in bulk CP films, there have been many research efforts dedicated to studying nanoscale and molecular systems such as nano-aggregates and single CP chains in the past decade. Since the pioneering work from Paul F. Barbara's laboratory in the late 1990s on poly(2-methoxy-5-(2'-ethlyhexyloxy)-p-phenylene vinylene) (MEH-PPV) (Scheme A.1), single molecule/aggregate spectroscopy (SMS) has expanded greatly to elucidate the hidden morphological, optical and electronic properties at the nanoscale and single-molecule levels.^{166–168}

By zooming in on individual CP chains from highly heterogeneous bulk states, single molecules represent the smallest possible scale for studying CPs. Yet, it does not necessarily exclude possible heterogeneities at the single chain level such as different single chain conformations. Recent research endeavors have revealed that CPs can even be morphologically and optoelectronically heterogeneous at the single chain level given the complex roles of side-chains, backbone, and possible intramolecular interchain interactions.^{132,169–174} Single chain folding of materials with high molecular weight, for example, can lead to the formation of molecular aggregates based on intramolecular interchain interactions between different sections of the same backbone, which behaves profoundly different from an isolated, non-interacting chain. As a result, even working at the molecular level, one still cannot completely break out of molecular heterogeneity.



Scheme A.1: Structure of poly(2-methoxy-5-(2'-ethlyhexyloxy)-p-phenylene vinylene) (MEH-PPV).

To uncover deterministic relations between morphology and photophysics in CPs, one needs not only the analysis at the single molecule or nano-aggregate level but, more importantly, structurally well-defined and designed systems. with the molecular weight, backbone, side-chains, assembly, etc., under strict control. Meanwhile, a bottom-up approach is also crucial so as to circumvent the complex interactions within a larger scale. By starting with well-defined molecular systems and understanding how factors such as molecular weight, side-chains, and backbone influence the morphological and photophysical behavior at the molecular level, higher order nanoscale systems – the building blocks of films – can be achieved by controlled assembly from single CP chains. This then facilitates new evolutions in the bulk film photophysics.

A.2 FROM SINGLE MOLECULES TO AGGREGATES

A.2.1 Backbone

The backbone, the core structure of a polymer chain, plays a dominant role in determining the single chain conformation and the optoelectronic properties. Recent studies have demonstrated the usage of specifically designed CP systems to probe the effects of backbone structural variation on single chain conformation and corresponding photophysical properties. These structural changes include manipulating defects, conjugation length, rigidity, and chromophore and main chain shape.

The impact of different types of defects along the backbone on the conformation and electronic properties has been investigated by the Barbara group using random copolymers of MEH-PPV that intentionally incorporated different chemical defect sites (**Figure A.1A**).⁴⁸ As shown by the modulation depth, *M*, distribution histograms in **Figure A.1B**, together with molecular dynamics (MD) simulations, the rigid *para*-terphenyl defects appear to preserve the linear conformation of the backbone, while *ortho*-terphenyl defects twist the backbone and lead to disordered chain conformations. Saturated defects allow for torsional freedom and lead to a wide range of conformations with high defect inclusion in the polymer chain. The structural variations result in blue-shifted absorption of the polymers with more defects, as conjugation along the polymer chain is interrupted by the defect sites. On the other hand, there is no substantial difference in the emission spectra due to efficient energy transfer to the lowest energy emitting sites, which exist even in highly defected polymers.

Hildner et al studied the impact of conjugation length on fluorescence spectral properties for a ladder-type (p-phenylene) dimer and its corresponding polymer methyl-substituted ladder-type poly(p-phenylene), MeLPPP.¹⁷⁵ It was revealed that when going from the dimer to the polymer there is a significant change in the electron-phonon coupling to intramolecular vibration mode. As shown in **Figure A.2A**, the low-energy skeletal stretch mode at ~150 cm⁻¹ observed for the single dimer molecule (solid, top) disappears in the spectra of single MeLPPP chains (solid, bottom),^{175,176} which is attributed to a reduced electron-phonon coupling strength and/or a reduced vibrational energy of the skeletal stretch mode with increasing pi-electron delocalization. Compared to the dimer, the MeLPPP molecules exhibit a broader distribution in zero phonon lines (ZPLs) as a result of an increasing conformational disorder. On the other hand, the linewidths of ZPLs of the dimer and the polymer do not show differences as they are typically determined by interactions with the local environment.

The backbone rigidity strongly affects the morphology of single chains and nanostructures as well as the corresponding photophysics. Basché et al studied a ladder-type CP poly(ladder-type pentaphenylene) (LPPentP) (**Figure A.2B**), which is based on poly(para-phenylene) and constituted of stiff chromophores that cannot bend. Purely electronic ZPL have been observed in 66% of single LPPentP chains at low temperature.⁵⁹

On the contrary, for MEH-PPV, a material with relatively more flexibility, only about 10% of the molecules showed ZPL.¹⁷⁷ This lack of ZPL was assigned to linear electron-phonon coupling, which originated in the less rigid backbone of MEH-PPV giving rise to geometrical relaxation following electronic excitation.⁵⁹ Single molecule excitation and emission spectroscopy showed multiple absorption sites with a single emitting site.

This result unmasked the nonemitting donor chromophores, which transfer their excitation energy to a low-energy emitting chromophore, leading to emission from a single emitting site. Gesquiere et al. investigated the effect of backbone rigidity on single chain conformation and crystallinity of nanofibers of polythiophenes.¹⁷¹ By examining PL spectra and emission polarization anisotropy, the authors found that the single polymer chain conformations do not necessarily translate into their respective self-assembled nanofibers,¹⁷⁸ as factors such as side-chain interactions, solvent environment, and intermolecular interactions all might contribute to the overall morphology in aggregates. Therefore, care should be taken when correlating the isolated single CP chains' conformation with their morphology in self-assembled nanostructures.

Besides backbone rigidity, the shape of CP backbone also has a profound influence. It has been reported that electron delocalization or conjugation is persistent even with bending and twisting of the individual chromophore segment.¹⁷⁹ Bending of the chromophores, however, would make them less stable and more prone to environmental effects such as oxidation, which ultimately reduces the effective conjugation. Such change in chromophore shape (at least for phenylene-vinylenes), rather than the overall conformation of a single chain, greatly influences the spectroscopic properties. A comparison of low-temperature single molecule emission spectral data between PPV oligomers (7-mer and 17-mer) and polymers showed that spectral broadening is intrinsic to single chromophores.¹⁸⁰ Bending of the chromophore has a substantial effect on ultrafast

electronic dephasing and spectral diffusion, which are two additional potential physical origins (except aggregation) for spectral broadening. The effect of backbone shape on ultrafast structural relaxation and exciton trapping has been studied by Lupton et al in model systems of linear oligomers and cyclic structures based on carbazole-bridged phenylene-ethynylene-butadiynylene units (**Figure A.3A**).⁴⁴ **Figure A.3B** shows that the dimer exhibits the largest red-shift in energy during the first 200 ps, indicating a strong structural relaxation. In contrast, the torsional relaxation is largely inhibited in the structurally rigid macrocycle. Furthermore, the emission linear dichroism data shown in **Figure A.3C** reveals that exciton delocalization processes are also different: while the exciton acts as a linear transition dipole in linear oligomers, it localizes randomly on different segments on the cyclic structure and results in linear dichroism values around zero.¹⁸¹ Collectively, these above studies surrounding backbone structure engineering underline the potential for synthetic strategies by manipulating backbone features to tune the chain conformation and the optoelectronic properties.



Figure A.1: A) Structures of *para*-terphenyl-MEH-PPV (i), *ortho*-terphenyl-MEH-PPV (ii), and saturated MEH-PPV (iii), respectively. B) Modulation depth, M, distribution histograms of polymers shown in (A). (Adapted from the work of Buonos et al.)⁴⁸



Figure A.2: A) Low-temperature emission spectrum (solid) of a single dimer (top) and a single MeLPPP molecule (bottom) imbedded in polystyrene. The dashed curves show corresponding ensemble emission spectra. Corresponding structure of the dimer and the MeLPPP polymer are exhibited on the right. (Adapted from the work of Baderschneider et al.¹⁷⁵) B) Structure of LPPentP (left); fluorescence excitation (black) and emission spectra (grey) of a single LPPentP chain exhibiting single emitting site with multiple absorption sites (right). (Adapted from the work of Zickler et al.⁵⁹)



Figure A.3: A) Structure of the repeat unit for the linear oligomers and the ring's rim of the macrocycle. Panel B) shows the temporal shift of the emission peak plotted as the relative energy change relative to detection time 0. Panel C) displays the distribution histograms of the linear dichroism (LD) of single molecules of the macrocyle and the dimer. The LD data were estimated from two orthogonal emission polarizations via LD=(I_x-I_y)/(I_x+I_y). (Adapted from the work of Thiessen et al.⁴⁴)

A.2.2 Side-Chains

While the backbone of a CP provides the basis for the chain conformation and photophysics, side-chains function far more than just as solubilising groups. Significant experimental evidence has shown that side-chains can drastically alter not only the morphology, but also the photophysics, introducing an extra means of 'tuning' the materials' properties. Factors such as the arrangement, size, side-chain density, and interactions between side-chains or with the surrounding matrix can alter the morphology and photophysics from the single molecule level.

The impact of regioregularity of side-chains on the morphology and physics of single chains has been interrogated in the prototypical poly(3-hexylthiophenes) (P3HTs) by our group and the Chen group (Figure A.4A). SMS studies on P3HTs with high molecular weight (M_n above 30 kDa) revealed higher values of the modulation depth (mean M value of 0.65) in regioregular-P3HT (rr-P3HT), indicating more ordered single chain conformation than the *rra*-P3HT case (mean M value of 0.43) (Figure A.4B).^{132,169,182} It should be noted that with these high M_n , intramolecular chain folding occurs. Therefore, the disordered single chain conformation in regiorandom-P3HT (rra-P3HT) could be due to disordered intramolecular interchain packing and/or disordered unpacked chain segments. SMS data reported later on for P3HTs with M_n of 10 kDa, at which no chain folding would be expected, ^{171,178} showed that the mean M values of rr-P3HT and rra-P3HT are close, with M values of 0.70 and 0.62, respectively.¹⁶⁹ This observation suggests that the conformation of the short rra-P3HT chains is not severely disrupted by the random side-chain arrangement. It also indicates that the random side-chain arrangement in the rra-P3HT has a more dramatic influence on the interchain packing, which is intramolecular in the case of high M_n rra-P3HT. Theoretical calculations of the dihedral angle between adjacent thiophene rings from MD simulated structures of rra-P3HT revealed that the

head-to-head (H-H) side-chain coupling twists the single chain conformation characterized by a dihedral angle of ~55 degrees (**Figure A.4C**), and therefore leads to unfavorable packing between chains and a shorter conjugation length along the chains.⁴⁶ Furthermore, to check if a longer distance of H-H coupling (i.e., reduced side-chain density) could mediate the twisted backbone conformation observed in *rra*-P3HT, we studied the regiorandom poly(3-hexyl-2,5-thienylene vinylene) (*rra*-P3HTV), which has an increased H-H coupling distance due to the presence of C=C bonds between thiophene rings.⁴⁶ SMS study revealed that *rra*-P3HTV single chains exhibit highly ordered single chain conformation. This result, in turn, substantiates that the twisted conformation in *rra*-P3HT is induced by close H-H arrangement, which can be largely eliminated by the longer distance of H-H coupling in *rra*-P3HTV (**Figure A.4C**).

Experimental evidence has also shown that bulky side-chains usually prevent single polymer chains from forming a closely packed or an ordered conformation.^{10,61,62} Vacha et al have reported that the grafting of long polystyrene (PS) side-chains on polythiophene significantly suppresses photoblinking and high anisotropy as observed for polythiophene with short side-chains. This was attributed to inhibited exciton localization to one or a few segments in polythiophenes with PS branch side-chains as a result of hampering the collapse into ordered chain conformations.^{61,62} Side-chain structural modifications can also be utilized to inhibit interactions at the single molecule and aggregate level through means such as backbone protection with self-threading side-chains as reported by Scheblykin et al.¹⁰ At the single chain level, these bulky substituents increase the effective conjugation length by preventing defect or kink formation, but much more distinctly they inhibit aggregation and packing. This prevents interchain energy transfer while allowing intrachain transfer along the backbone.

Recent experiments, both at the bulk and single molecule level have utilized hydrogen-bonding (H-bonding) and other dynamic bonding interactions for device and materials design applications. In bulk films dynamic H-bonding has been used as a form of non-covalent cross-linking in order to enhance material elasticity for flexible devices and facilitate a means of 'healing' cracks in the devices due to mechanical strain.^{160,183} At the single molecule level, we have taken advantage of H-bonding in order to selectively fold polymeric systems into desired configurations.¹² Figure A.5A shows structures of a polymer with no H-bonding (control polymer) and two H-bonding capable polymers containing carboxylic acid and urea groups, respectively. Compared to the control polymer, the two H-bonding capable polymer chains exhibited relatively higher average M values, indicative of more ordered folded conformations (Figure A.5B). The urea-containing polymer in particular (Figure A.5A-3), which was designed to display 'face-on' stacking of chromophores, has the largest mean M value (0.8) of the three polymers. In addition, this polymer also exhibits ~ 0.06 eV red shift in the emission relative to the other two polymers. While these data do not definitively prove that these polymers fold as designed, it is strong evidence to support the idea that side-chains alone can be used to force polymers to fold in certain ways.

Furthermore, the modification of side-chains in CPs can also affect interactions with matrices, thus altering phase separation. Vacha et al recently utilized this approach to isolate side-chain engineered polyfluorene molecules in vertical cylinders of a phase-separated block copolymer film. With the successes in this material's engineering, the authors have demonstrated single-molecule electroluminescence and accessed specific photophysics in polyfluorene.¹⁸⁴ This work offers a unique approach to engineering single CP chains in surrounding media and device configurations.



Figure A.4: A) Structures of *rr*-P3HT, *rra*-P3HT, and *rra*-P3HTV. B) *M* distribution histograms of *rr*-P3HT (top) and *rra*-P3HT (bottom) with different M_n (grey for 10kDa, red for 146 kDa). (Adapted from the work of Vacha and Habuchi.¹⁶⁹) C) Probability density distribution of the dihedral angle between neighbouring thiophene rings for the H-H (red) and T-T (blue) couplings in *rra*-P3HT (top) and *rra*-P3HTV (bottom). (Adapted from the work of Hu et al.⁴⁶)



Figure A.5: A) Structures of polymers with no H-bonding (1) and H-bonding capable polymers containing carboxylic acids (2) and urea (3) groups. A corresponding schematic drawing of proposed folding is given next to each structure. B) *M* distribution histograms of polymers. (Adapted from the work of Shao et al.¹²)

A.2.3 OLIGOMERS

To interrogate the morphological and photophysical interactions between conjugated segments (i.e., chromophores) in CPs, CPs themselves, even at single chain level in some cases, are not necessarily excellent models due to the possible and random existence of bends, kinks, twists or chemical defects along single chains. In comparison, shorter conjugated oligomers (COs) have specific advantages in structural control, synthetic repeativity, and purification.¹⁸⁵ By eliminating the inherent heterogeneity in long CP chains, COs have been used as excellent model systems for accurately probing the morphological and physical behaviour between chromophores in CPs.

For the prototypical MEH-PPV, the bimodal distribution of fluorescence emission (i.e., red and blue emission) has been observed in both single molecule and bulk studies. The origin of the red emission, originally ascribed to low energy sites due to intramolecular interchain aggregation,¹⁸⁶ has been questioned and elucidated by intrachain chromophores with a longer conjugation length.^{187,188} By studying PPV oligomers with SMS and theoretical calculations, Vacha et al revealed that distinct spectral forms can be due to variation in conjugation length caused by torsional defects.¹⁸⁹ In addition, spectral jumps were also observed between different spectral forms possibly due to torsional flips of a single phenylene ring, suggesting the dynamic nature of exciton delocalization even in short PPV oligomers. Kim et al studied the effect of chain length on conformation and exciton dynamics in oligothiophenes.¹⁹⁰ The authors observed that with the increase in chain length, from 4-mer to 6-mer to 10-mer, the conformational order and the exciton delocalization reduces due to the bending of chains. COs have also been used to fabricate aggregates to probe morphology and spectroscopic information at nanoscale by the Peteanu group.^{191,192}

Linked conjugated oligomers (LCOs), in which COs are joined through covalent linkers, not only inherit the aforementioned specific advantages of COs but also offer possible controllable interactions between conjugated segments. The latter offers a unique route in studying interactions between chromophores either along a single chain or spatially between different chains. The H-bonding capable polymers demonstrated in Fig. 4 also serve as a good example here. The dynamic nature of energy transfer between chromophores was elegantly examined by Lupton et al using LCOs with two oligomers in either an oblique-angle or parallel geometry (Figure A.6A).¹⁹³ The Förster resonance energy transfer (FRET) dynamics was examined by probing the emission polarization and the intensity as a function of time. Figure 6A shows the data obtained for the open dimer. Interestingly, strong fluctuations of emission polarization were detected when the two oligomer chromophores were active as shown in the fluctuation of linear dichroism in Figure A.6A. This suggests that the FRET pathways switch reversibly between the two oligomers, that is, each oligomer temporarily takes the role of FRET donor or acceptor prior to photodegradation occurring in one, possibly due to temporal stabilization of a certain chromophore. This study clearly demonstrates that the excitation energy in CPs should be pictured as a dynamic process where a random three-dimensional FRET pathway is present. The morphology dependent energy transfer process in MEH-PPV was explored by Ghiggino et al using a pendant LCO of PPV which has a saturated backbone spacer between the pendant PPV oligomers.¹⁹⁴ Despite the nominally same lengths of the pendant PPV oligomers, energy transfer to single emitting sites was detected for most LCO molecules using defocused wide-field microscopy. This result indicates that the specific morphology of each individual chromophore, as well as its interaction with the surrounding matrix, play significant roles in determining their electronic landscape and the energy transfer processes.



Figure A.6: A) Left: two oligomer chromophores (orange) were organized using one clamping unit (gray) to give an open dimer. Right top: fluorescence intensity transient of an open dimer. Right bottom: the linear dichroism (LD) transient estimated from two orthogonal emission polarizations. Both chromophore units were active within the first 10 s (light-gray shaded area) with strong fluctuations of the LD, as indicated schematically in the cartoon. A bleaching event took place after 10 s, leaving only one chromophore active (dark-gray shaded area), with correspondingly reduced LD fluctuations. (Adapted from the work of Stangl et al.¹⁹³) B) MD simulated conformations for PPV based LCOs with different length of oligomers (from left to right: trimer, pentamer, and septamer). (Adapted from the work of Traub et al.¹⁰⁹)
In order to study how to control the folding properties of polymeric systems, our group designed LCOs in which conjugated bis(2-ethylhexyl)-p-phenylene vinylene (BEH-PPV) oligomers are joined by different morphological directing groups, i.e., flexible, bent, and rigid linkers.¹⁰⁸ The LCOs with rigid linkers produce ordered single chain conformation wherein the oligomers are aligned, while by contrast, the LCOs with bent linkers exhibit distorted conformations. Interestingly, the LCOs with flexible linkers exhibit a dependence of single chain conformation on the length of the conjugated oligomer segments (Figure A.6B).¹⁰⁹ By increasing the length of oligomers, more ordered conformations of the LCO single chains are observed due to the stronger interactions between longer conjugated units as demonstrated by the structures from MD simulations shown in Figure A.6B. The mean M value increases from 0.39 for the LCO of trimer to 0.75 for the heptamer. Furthermore, recently our group demonstrated that by modifying the side-chain interaction via hydrogen-bonding, the LCO of trimers with flexible linkers can be tuned from disordered to ordered conformations (Figure A.5).¹² Recently, Barnes et al has designed LCOs with different linker lengths and examined how the length affects the folding of LCOs.¹²⁷ In this study, the relatively short flexible linkers could act more like a simple pivot or defect in CPs. The authors discovered that the longer flexible linker leads to chromophore interaction as long as the chromophore movement is allowed. In contrast, the use of short linkers can constrain the chain folding. These systematic studies have provided not only a clear picture of the factors affecting the folding properties in polymeric systems but also a new route for synthetic consideration to achieve desired morphologies and functionalities in a more controllable way.

A.2.4 Nano-aggregates

For CP films applied in various optoelectronic applications, the morphology is usually dominated by nanoscale domains which are connected with relatively amorphous domain boundaries. Therefore, the nanoscale domains not only are building blocks for bulk films but act as a bridge between the gap of single CP chains and bulk states. Isolated and easily handled nano-aggregates can be viewed as model systems of the domains in bulk films. The knowledge about the morphology and physics in the nano-aggregates is important to understand, predict, and control the film phenomena.¹⁹⁵⁻²⁰² Barbara et al studied the size-dependence of spectroscopic properties of MEH-PPV nanoparticles and found that bulk-like properties can be achieved with MEH-PPV nanoparticles larger than 10 nm.²⁰³ Frechet et al found that with enhanced regioregularity of side-chains the crystallinity of P3HT nanoparticles increases and the PL spectrum red shifts correspondingly. Barnes et al revealed that the crystallinity of P3HT nanoparticles increases with the size, which could be responsible for a fast PL depolarization in large crystalline nanoparticles.²⁰⁴ In a recent study, our group fabricated P3HT aggregates with a triblock polymer (P3HT-PtBA-P3HT, here PtBA represents a flexible linker of poly(tertbutyl acrylate)) in a series of solvents of which the dielectric constant are tuned ranging from 2 to 20. These experiments produced compelling evidence of the charge-transfer state as a major reason for the drop of P3HT emission quantum yield in aggregated state. It should be noted that the CP nano-aggregates reported in these initial works were usually prepared with a simple reprecipitation method. Typically, in this method CPs in a good solvent are quickly mixed with a poor solvent, leading to a rapid agglomeration of CP chains. Hence, the morphology of nano-aggregates formed in this way is not precisely defined.

To get a clearer picture about the relations between nanoscale morphology and photophysics, control in the morphology of nano-aggregate was exerted via fabrication techniques. Grey et al assembled P3HT nanofibers slowly from a hot toluene solution and discovered photophysical behaviour of J-aggregates (i.e., stronger 0-0 transition relative to 0-1 side-band) (Figure A.7A-B).²⁰⁵ The formation of J-type nanofibers can be ascribed to enhanced intrachain order over the interchain counterpart. In comparison, mixed H-type nanofibers (i.e., with dampened 0-0 emission) can be formed via rapid growth in anisole. Meanwhile, Barnes et al demonstrated a molecular weight dependence of the H- and J-type character in P3HT nanofibers, where small chains tend to pack to H-type aggregates while high molecular weight chains tend to have J-type character due to enhanced chain extension as a result of folding.²⁰⁶ Grey et al further studied the influence of J- and H-type character in the nanofibers on the exciton interconversion and interactions between triplet and singlet using excitation intensity modulation spectroscopy.²⁰⁷ This method involves fluorescence intensity modulation by repetitive cycles of a sequence of variable-intensity excitation pulses on single nanostructures.²⁰⁸ The fluorescence intensity drop (modulation depth) at the beginning of each pulse is ascribed to singlets quenching by triplets. It was found that for the assembled nanofibers with J-type character, the modulation depth is much higher than the H-type nanofibers (Figure A.7C). This interesting observation has been elucidated by the formation of triplets from delocalized and long-lived polarons in the J-type nanofibers, evidenced by the fluorescence modulation depth and its sensitivity to oxygen. Furthermore, the discoveries referenced above demonstrate the control of self-assembled nanostructures in understanding and manipulating the exciton coupling and spin state photophysics.

A more precise control in the morphology and size of the nano-aggregates was realized using a so-called solvent vapour annealing (SVA) technique developed by Vogelsang et al,^{50,144,209} which is schematically illustrated in **Figure A.8**. In this method a concentrated single-molecule sample is treated with a solvent vapor of a mixture of good and poor solvents, where the good solvent can dissolve both the single CP chains and the poly(methyl methacrylate) (PMMA) matrix while the poor solvent can only dissolve the matrix. By tuning the ratio of the good and poor solvent and the concentration of the initial single molecule sample, the size of the formed aggregates can be controlled. During SVA, the diffusion of CP molecules inside the swollen PMMA matrix triggers the formation of CP aggregates. These authors assembled highly ordered MEH-PPV aggregates consisting of 25-45 chains and observed ultralong distances of energy transfer from 20-30 nm up to 60 nm.⁵⁰

The deterministic effect of side-chain arrangement and size on the interchain interaction was systematically investigated by our group using SVA assembled aggregates of rr-P3HT, rra-P3HT and a polythiophene derivative with bulky side-chains poly(3-(2'methoxy-5'-octylphenyl)thiophene) (POMeOPT) (Figure A.9A).¹⁶⁹ It was found that the ordered side-chains in rr-P3HT strongly favour the ordered interchain morphology, as indicated by an average M value of 0.80 for aggregates with ~ 100 chains (Figure A.9B). With this size, the aggregates exhibit emission intensity blinking as a single molecule, indicating an efficient exciton migration in these ordered *rr*-P3HT aggregates (Figure A.9C). Exciton diffusion up to a length scale of 30-40 nm was approximately estimated from the blinking data in bigger sized aggregates. In stark contrast, the random distribution of side-chains in rra-P3HT drastically disrupts the interchain morphology even between only a few chains as demonstrated in Figure A.9B, which correspondingly inhibits efficient exciton coupling and migration between the chains (Figure A.9C). With POMeOPT aggregates, we discovered that the interchain exciton coupling is strongly prohibited (except for relatively short chain aggregates) evidenced by a chain-by-chain photo-degradation behaviour displayed in Figure A.9C. The long interchain packing distance (~7 Å) and the slightly disordered packing

account for a part, but definitely not all, of the reduction in the interchain excitonic coupling in POMeOPT. The competition between intrachain and interchain coupling mechanisms has further been revealed by comparing the POMeOPT aggregates with different polymer chain size in terms of their blinking behaviour and spectral characteristics. Very recently, Vogelsang et al also demonstrated successful control over interchain coupling (i.e., H-type, J-type, and suppressed electronic coupling) in isolated CP aggregates by tuning the side-chain structure of CPs and the SVA process.²¹⁰

Backbone fluorination has proven to be an important strategy in developing highperformance conjugated polymers for photovoltaic applications. The fluorination effect of the polythiophene backbone on the electronic and optical properties was recently interrogated by our group using two polymers, i.e., regioregular poly(3-ethylhexylthiophene) (rr-P3EHT) and poly(3-ethylhexyl-4-fluorothiophene) (*rr*-F-P3EHT) (Figure A.9A).¹¹ Despite the high regioregularity, the rr-P3EHT single chains exhibit a broad distribution of conformations due to the large size of the side-chains. This, in turn, results in relatively disordered interchain morphology in SVA assembled aggregates with several polymer chains (Figure A.9D). On the other hand, for rr-F-P3EHT, a more extended and ordered single chain conformation was confirmed with both M measurement and MD simulation. Thus, ordered single F-P3EHT chains generated highly ordered interchain packing in F-P3EHT aggregates as seen in the M distribution histogram in Figure A.9D. Surprisingly, for the typical 4-chain F-P3EHT aggregates, about 4-step photodegradation behaviour was observed (Figure A.9E) and ~3.5 emitters were calculated in the photon correlation measurement (Figure A.9F). Therefore, despite the ordered interchain morphology and the close interchain packing (~3.8 Å), the exciton coupling in F-P3EHT aggregates is hampered. This is attributed to the dominant and competitive coupling along F-P3EHT chains due to the fluorine-induced extended backbone. Meanwhile, it was also found that the highly ordered packing in F-P3EHT surprisingly leads to a reduction in the energetic heterogeneity of the individual chains as the intrachain coupling is increased, based on the aggregate spectral data. This provides an unusual result that the ensemble of chains in the aggregate has a narrower distribution of energies than the corresponding distribution of individual polymer chains. This study highlights the intricate and subtle interplay between interchain and intrachain exciton coupling as a function of interchain ordering and single chain conformation.



Figure A.7: A) TEM images of H- (top) and J-type (bottom) P3HT nanofibers. B)
Corresponding absorption and PL spectra for the H- and J-type NFs. C) top: a cycle containing four excitation windows, each with a different excitation intensity, is repeatedly applied to a selected single NF; middle and bottom: time-averaged fluorescence transient (synchronously time-averaged over many cycles) of a single H-type and J-type NFs, respectively, acquired while modulating the excitation laser intensity as shown in the top panel. (Adapted from the work of Thomas et al.²⁰⁷)



Figure A.8: Solvent-vapor-annealing method to assemble single polymer chains into nano-aggregates in a controllable way. Adapted from the work of Stangl et al.²⁰⁹



Figure A.9: A) Structures of POMeOPT, P3EHT, and F-P3EHT. B) *M* distribution histograms of 100-chain *rr*-P3HT aggregates, 6-chain *rra*-P3HT aggregates, and 4-chain POMeOPT aggregates. The fluorescence time traces at high excitation power are shown in panel C) correspondingly. Panel D) displays the M distribution histograms of 5-chain P3EHT aggregates and 4-chain F-P3EHT aggregates. Panel E) and F) show the fluorescence time trace and photon correlation result of a typical 4-chain F-P3EHT aggregate. (Adapted from the works of Vacha and Habuchi,¹⁶⁹ and Hu et al.¹¹

A.3 CONCLUSIONS AND OUTLOOK

Morphology and photophysics play significant roles in determining the functionality and performance of CP materials in a broad range of optoelectronic applications. The combination of the SMS technique and structurally well-defined model systems offers the ability to explore the information washed out by heterogeneities in ensemble measurements. With manipulations in side-chains, backbone, oligomer model systems, and controlled assembly of CP aggregates, recent research efforts have revealed new insights into the morphological dependence of exciton coupling, exciton trapping, energy transfer, charge transfer, excitation interactions, etc, at different hierarchy levels. Taken together, these results create a clearer picture of how the morphology and photophysics of CPs evolve from individual chains up to bulk states. Meanwhile, these investigations serve to motivate researchers to develop material systems with the desired morphology and functions that are appropriate for specific applications. We believe that the continuous efforts in SMS on CPs will keep contributing to revealing complicated phenomena in CPs and pushing forward the materials and device engineering for advancements in organic semiconductor electronics.

The majority of SMS works so far have been focused on prototypical CP systems such as PPV and P3HT. Investigations on material systems with better performance and/or new functionality, such as low bandgap CPs, n-type CPs, and conjugated metallopolymers, are still lacking although these CP systems have been in the field for years. Many fundamental questions regarding in-depth molecular morphology and photophysics in these complex systems are still open. For these complicated CP systems, simplified model systems such as oligomers and copolymers could play more important roles to sort out research targets from the heterogeneous pool.

From the technique point of view, the vast majority of the current SMS approaches are dominantly based on fluorescence. Momentum is needed to push forward the advancement of the technique, for instance, by developing new characterization techniques in single molecule spectroscopy and by integrating SMS with other characterization or manipulating techniques. The Orrit group recently demonstrated exciting simultaneous measurement of both absorption and PL emission of single MEH-PPV molecules using using near-critical xenon in photothermal microscopy.²¹¹ Such a demonstration has enriched the tool kit of SMS. Further revelation of single molecule absorption will certainly benefit our understanding of photophysical behavior of single molecules. Additionally, the coupling of SMS with other characterization techniques is expected to be very useful in the study of morphology, optical and electronic properties of CPs. For instance, scanning tunneling spectroscopy, with a capability of probing local single chain or aggregate morphology and electronic properties, can be combined with the SMS to explore more direct property relationships. Atomic force microscopy can also work together with SMS, as demonstrated by the Vacha group,^{212,213} to investigate the optical and electronic properties as a function of mechanical stimuli of single chain or aggregate, which will offer useful information for developing flexible optoelectronics of CPs.



Appendix B: Structural Conformation Data for POMeOPT Synthesis

Figure B.1: A) ¹H-NMR and B) mass spectrum of the brominated octylphenol POMeOPT precursor. B) Primary masses are 283 and 285 Da are due to isotopes of bromine.



Figure B.2: A)1H-NMR spectrum and B) mass spectrum of the full substituent precursor after O-methylation. The added methyl group is responsible for the peak at 3.87 ppm in A. The exact mass of the substituent for mass spectroscopy is 298.09 Da. The additional peaks in this region are due to isotopes. (R = C_8H_{17})



Figure B.3: A) ¹H-NMR and B) mass spectrum of the fully synthesized monomer. A) The additional peaks in the 6.8-7.6 ppm range are attributed to the thiophene ring hydrogens. B) The mass of the monomer is 302 Da.



Figure B.4: A) ¹³C- and B) ¹H-NMR spectra of the synthesized POMeOPT polymer. A) The peaks in the 125-155 ppm range correspond to the carbons in the rings while the peak at 111.20 ppm corresponds to the methoxy group. The alkyl chain carbons are not shown, but exist at low ppm (10-35 ppm range). B) The loss of peaks in the 6.8-7.6 ppm range is indicative of the loss of hydrogens on the thiophene rings.



Figure B.5: Plot of the GPC results used to confirm high M product of POMeOPT, where WF refers to the weight fraction. These results yielded $M_n = 35,148$ Da, $M_w = 78,650$ Da, $M_z = 134,222$ Da, and a polydispersity index (PDI) $\left(\frac{M_w}{M_n}\right) = 2.238$. While this is a broad dispersity, samples were then fractionated to low PDI fractions of the desired M_n prior to spectroscopic experiments.

References

- 1. Xu, Z. *et al.* Molecular Size, Shape, and Electric Charges: Essential for Perylene Bisimide-Based DNA Intercalator to Localize in Cell Nuclei and Inhibit Cancer Cell Growth. *ACS Applied Materials & Interfaces* **7**, 9784–9791 (2015).
- 2. Jradi, F. M. & Lavis, L. D. Chemistry of Photosensitive Fluorophores for Single-Molecule Localization Microscopy. *ACS Chemical Biology* **14**, 1077–1090 (2019).
- 3. Nguyen, T.-Q. *et al.* Near-Field Scanning Optical Microscopy (NSOM) Studies of the Relationship between Interchain Interactions, Morphology, Photodamage, and Energy Transport in Conjugated Polymer Films. *The Journal of Physical Chemistry B* **105**, 5153–5160 (2001).
- 4. Hao, X.-T., McKimmie, L. J. & Smith, T. A. Spatial Fluorescence Inhomogeneities in Light-Emitting Conjugated Polymer Films. *The Journal of Physical Chemistry Letters* **2**, 1520–1525 (2011).
- 5. Liu, N. *et al.* Probing Phase Distribution in 2D Perovskites for Efficient Device Design. *ACS Applied Materials & Interfaces* (2020) doi:10.1021/acsami.9b17047.
- 6. Balakrishnan, K. *et al.* Effect of Side-Chain Substituents on Self-Assembly of Perylene Diimide Molecules: Morphology Control. *Journal of the American Chemical Society* **128**, 7390–7398 (2006).
- 7. Spano, F. C. & Silva, C. H- and J-Aggregate Behavior in Polymeric Semiconductors. *Annu. Rev. Phys. Chem.* 65, 477–500 (2014).
- 8. Lin, H. *et al.* Fate of Excitations in Conjugated Polymers: Single-Molecule Spectroscopy Reveals Nonemissive "Dark" Regions in MEH-PPV Individual Chains. *Nano Letters* **9**, 4456–4461 (2009).
- 9. Collison, C. J., Rothberg, L. J., Treemaneekarn, V. & Li, Y. Conformational effects on the photophysics of conjugated polymers: A two species model for MEH-PPV spectroscopy and dynamics. *Macromolecules* **34**, 2346–2352 (2001).
- Sahoo, D., Sugiyasu, K., Tian, Y., Takeuchi, M. & Scheblykin, I. G. Effect of Conjugated Backbone Protection on Intrinsic and Light-Induced Fluorescence Quenching in Polythiophenes. *Chem. Mater.* 26, 4867–4875 (2014).
- 11. Hu, Z. *et al.* Impact of backbone fluorination on nanoscale morphology and excitonic coupling in polythiophenes. *P Natl Acad Sci* **114**, 5113–5118 (2017).
- Shao, B., Zhu, X., Plunkett, K. N. & Vanden Bout, D. A. Controlling the folding of conjugated polymers at the single molecule level via hydrogen bonding. *Polym. Chem.* 8, 1188–1195 (2017).
- 13. Elacqua, E., Geberth, G. T., Vanden Bout, D. A. & Weck, M. Synthesis and folding behaviour of poly(p -phenylene vinylene)-based β -sheet polychromophores. *Chemical Science* (2019) doi:10.1039/C8SC05111A.
- 14. Mehltretter, A. H. Forensic Analysis and Discrimination of Duct Tapes. **3**, 19.

- 15. Lewis, N. S. Research opportunities to advance solar energy utilization. *Science* **351**, aad1920–aad1920 (2016).
- 16. Xu, X., Austin, A., Mylon, S. E., Plenge, J. & Szarko, J. M. Improving the Quantum Yields of Perylene Diimide Aggregates by Increasing Molecular Hydrophobicity in Polar Media. *ChemPhysChem* **18**, 2430–2441 (2017).
- 17. Würthner, F. *et al.* Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. *Chemical Reviews* **116**, 962–1052 (2016).
- 18. Schenning, A. P. H. J. *et al.* Towards supramolecular electronics. *Synthetic Metals* **147**, 43–48 (2004).
- 19. Mirzov, O. & Scheblykin, I. G. Photoluminescence spectra of a conjugated polymer: from films and solutions to single molecules. *Physical Chemistry Chemical Physics* 8, 5569 (2006).
- 20. Sirringhaus, H., Tessler, N. & Friend, R. H. Integrated optoelectronic devices based on conjugated polymers. *Science* **280**, 1741–1744 (1998).
- 21. Huynh, W. U., Dittmer, J. J. & Alivisatos, A. P. Hybrid nanorod-polymer solar cells. *Science* **295**, 2425–2427 (2002).
- 22. Friend, R. H. *et al.* Electroluminescence in conjugated polymers. *Nature* **397**, 121–128 (1999).
- 23. Feng, J. *et al.* Single-crystalline layered metal-halide perovskite nanowires for ultrasensitive photodetectors. *Nature Electronics* **1**, 404–410 (2018).
- 24. Engel, T. & Reid, T. *Physical Chemistry*. (Pearson Education, Inc., Glenview, IL).
- 25. Hu, Z., Shao, B., Geberth, G. T. & Vanden Bout, D. A. Effects of molecular architecture on morphology and photophysics in conjugated polymers: from single molecules to bulk. *Chemical Science* (2018) doi:10.1039/C7SC03465B.
- 26. Hu, Z. *et al.* An insight into non-emissive excited states in conjugated polymers. *Nat Commun* **6**, (2015).
- 27. Brazard, J., Ono, R. J., Bielawski, C. W., Barbara, P. F. & Vanden Bout, D. A. Mimicking Conjugated Polymer Thin-Film Photophysics with a Well-Defined Triblock Copolymer in Solution. *J. Phys. Chem. B* **117**, 4170–4176 (2013).
- 28. Chen, J. et al. Single-Molecule FRET Studies of HIV TAR–DNA Hairpin Unfolding Dynamics. The Journal of Physical Chemistry B 118, 12130–12139 (2014).
- 29. Farooq, S. & Hohlbein, J. Camera-based single-molecule FRET detection with improved time resolution. *Phys. Chem. Chem. Phys.* **17**, 27862–27872 (2015).
- 30. Groves, C., Reid, O. G. & Ginger, D. S. Heterogeneity in Polymer Solar Cells: Local Morphology and Performance in Organic Photovoltaics Studied with Scanning Probe Microscopy. *Accounts of Chemical Research* **43**, 612–620 (2010).

- 31. Heimel, G. *et al.* Breakdown of the mirror image symmetry in the optical absorption/emission spectra of oligo(*para* -phenylene)s. *The Journal of Chemical Physics* **122**, 054501 (2005).
- 32. Rauscher, U., Bässler, H., Bradley, D. D. C. & Hennecke, M. Exciton versus band description of the absorption and luminescence spectra in poly(*p* phenylenevinylene). *Physical Review B* **42**, 9830–9836 (1990).
- 33. Yu, J. *et al.* Experimental and theoretical studies of absorption and photoluminescence excitation spectra of poly(p-phenylene vinylene). *Synthetic Metals* **74**, 7–13 (1995).
- 34. Mulazzi, E., Ripamonti, A., Athouël, L., Wery, J. & Lefrant, S. Theoretical and experimental investigation of the optical properties of poly(paraphenylene): Evidence of chain-length distribution. *Physical Review B* **65**, (2002).
- 35. Yu, Z. H. & Barbara, P. F. Low-temperature single-molecule spectroscopy of MEH-PPV conjugated polymer molecules. *J Phys Chem B* **108**, 11321–11326 (2004).
- 36. Bässler, H. & Schweitzer, B. Site-Selective Fluorescence Spectroscopy of Conjugated Polymers and Oligomers. *Accounts of Chemical Research* **32**, 173–182 (1999).
- Spano, F. C. Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films. *The Journal of Chemical Physics* 122, 234701 (2005).
- 38. Valeur, B. Molecular fluorescence principles and applications, second edition. (2013).
- 39. Burnett, G. M. *Transfer and Storage of Energy by Molecules, Vol. 1: Electronic Energy.* (Wiley-Interscience).
- 40. Jang, Y. J. *et al.* Upconversion-Triggered Charge Separation in Polymer Semiconductors. *The Journal of Physical Chemistry Letters* **8**, 364–369 (2017).
- 41. Ruggeri, E. *et al.* Controlling the Growth Kinetics and Optoelectronic Properties of 2D/3D Lead–Tin Perovskite Heterojunctions. *Advanced Materials* **31**, 1905247 (2019).
- 42. Paquin, F. *et al.* Charge Separation in Semicrystalline Polymeric Semiconductors by Photoexcitation: Is the Mechanism Intrinsic or Extrinsic? *Physical Review Letters* **106**, (2011).
- 43. Lee, S., Müller, A. M., Al-Kaysi, R. & Bardeen, C. J. Using Perylene-Doped Polymer Nanotubes as Fluorescence Sensors. *Nano Letters* 6, 1420–1424 (2006).
- 44. Thiessen, A. *et al.* Exciton Localization in Extended π -Electron Systems: Comparison of Linear and Cyclic Structures. *The Journal of Physical Chemistry B* **119**, 9949–9958 (2015).

- 45. Adachi, T. *et al.* Highly Ordered Single Conjugated Polymer Chain Rod Morphologies [†]. *The Journal of Physical Chemistry C* **114**, 20896–20902 (2010).
- 46. Hu, Z. *et al.* Excitonic Energy Migration in Conjugated Polymers: The Critical Role of Interchain Morphology. *J. Am. Chem. Soc.* **136**, 16023–16031 (2014).
- 47. Hu, D. H. *et al.* Collapse of stiff conjugated polymers with chemical defects into ordered, cylindrical conformations. *Nature* **405**, 1030–1033 (2000).
- 48. Bounos, G. *et al.* Controlling Chain Conformation in Conjugated Polymers Using Defect Inclusion Strategies. *Journal of the American Chemical Society* **133**, 10155–10160 (2011).
- 49. Hu, Z. *et al.* Effect of the Side-Chain-Distribution Density on the Single-Conjugated-Polymer-Chain Conformation. *ChemPhysChem* **14**, 4143–4148 (2013).
- 50. Vogelsang, J., Adachi, T., Brazard, J., Vanden Bout, D. A. & Barbara, P. F. Selfassembly of highly ordered conjugated polymer aggregates with long-range energy transfer. *Nature Materials* **10**, 942–946 (2011).
- 51. Vogelsang, J., Brazard, J., Adachi, T., Bolinger, J. C. & Barbara, P. F. Watching the Annealing Process One Polymer Chain at a Time. *Angewandte Chemie International Edition* **50**, 2257–2261 (2011).
- Steiner, F., Lupton, J. M. & Vogelsang, J. Role of Triplet-State Shelving in Organic Photovoltaics: Single-Chain Aggregates of Poly(3-hexylthiophene) versus Mesoscopic Multichain Aggregates. *Journal of the American Chemical Society* 139, 9787–9790 (2017).
- 53. Schweitzer, C. & Schmidt, R. Physical Mechanisms of Generation and Deactivation of Singlet Oxygen. *Chemical Reviews* **103**, 1685–1758 (2003).
- 54. Renn, A., Seelig, J. & Sandoghdar, V. Oxygen-dependent photochemistry of fluorescent dyes studied at the single molecule level. *Molecular Physics* **104**, 409–414 (2006).
- 55. Steiner, F., Vogelsang, J. & Lupton, J. M. Singlet-Triplet Annihilation Limits Exciton Yield in Poly(3-Hexylthiophene). *Physical Review Letters* **112**, (2014).
- 56. Bolinger, J. C. *et al.* Conformation and Energy Transfer in Single Conjugated Polymers. *Accounts of Chemical Research* **45**, 1992–2001 (2012).
- 57. Gutzler, R. Band-structure engineering in conjugated 2D polymers. *Physical Chemistry Chemical Physics* 18, 29092–29100 (2016).
- 58. Schwartz, B. J. Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morpholgy Influence Energy Transfer and Interchain Interactions. *Annual Review of Physical Chemistry* **54**, 141–172 (2003).

- 59. Zickler, M. F., Feist, F. A., Jacob, J., Müllen, K. & Basché, T. Single Molecule Studies of a Ladder Type Conjugated Polymer: Vibronic Spectra, Line Widths, and Energy Transfer. *Macromol Rapid Comm* **36**, 1096–1102 (2015).
- 60. Zhu, X., Traub, M. C., Vanden Bout, D. A. & Plunkett, K. N. Well-Defined Alternating Copolymers of Oligo(phenylenevinylene)s and Flexible Chains. *Macromolecules* **45**, 5051–5057 (2012).
- 61. Sugimoto, T., Ebihara, Y., Ogino, K. & Vacha, M. Structure-Dependent Photophysics Studied in Single Molecules of Polythiophene Derivatives. *ChemPhysChem* **8**, 1623–1628 (2007).
- 62. Sugimoto, T., Habuchi, S., Ogino, K. & Vacha, M. Conformation-Related Exciton Localization and Charge-Pair Formation in Polythiophenes: Ensemble and Single-Molecule Study. *The Journal of Physical Chemistry B* **113**, 12220–12226 (2009).
- 63. Eaton, S. W. *et al.* Singlet Exciton Fission in Polycrystalline Thin Films of a Slip-Stacked Perylenediimide. *Journal of the American Chemical Society* **135**, 14701– 14712 (2013).
- 64. *High performance pigments edited by Edwin B. Faulkner and Russell J. Schwartz. High performance pigments* (Wiley-VCH).
- 65. Ford, W. E. & Kamat, P. V. Photochemistry of 3,4,9,10-perylenetetracarboxylic dianhydride dyes. 3. Singlet and triplet excited-state properties of the bis(2,5-ditert-butylphenyl)imide derivative. *The Journal of Physical Chemistry* **91**, 6373–6380 (1987).
- 66. Löhmannsröben, H. G. & Langhals, H. Laser performance of perylenebis (dicarboximide) dyes with long secondary alkyl chains. *Applied Physics B Photophysics and Laser Chemistry* **48**, 449–452 (1989).
- 67. The chemistry and physics of coatings edited by Alastair Marrion. The chemistry and physics of coatings (Royal Society of Chemistry).
- 68. Hanna, M. C. & Nozik, A. J. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *Journal of Applied Physics* **100**, 074510 (2006).
- Tayebjee, M. J. Y., Gray-Weale, A. A. & Schmidt, T. W. Thermodynamic Limit of Exciton Fission Solar Cell Efficiency. *The Journal of Physical Chemistry Letters* 3, 2749–2754 (2012).
- Tayebjee, M. J. Y., McCamey, D. R. & Schmidt, T. W. Beyond Shockley–Queisser: Molecular Approaches to High-Efficiency Photovoltaics. *The Journal of Physical Chemistry Letters* 6, 2367–2378 (2015).
- 71. Le, A. K., Bender, J. A. & Roberts, S. T. Slow Singlet Fission Observed in a Polycrystalline Perylenediimide Thin Film. *The Journal of Physical Chemistry Letters* **7**, 4922–4928 (2016).

- 72. Smith, M. B. & Michl, J. Singlet Fission. *Chemical Reviews* **110**, 6891–6936 (2010).
- 73. Ito, S., Nagami, T. & Nakano, M. Molecular design for efficient singlet fission. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **34**, 85–120 (2018).
- 74. Shockley, W. & Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. 11.
- 75. Piland, G. B., Burdett, J. J., Dillon, R. J. & Bardeen, C. J. Singlet Fission: From Coherences to Kinetics. *The Journal of Physical Chemistry Letters* **5**, 2312–2319 (2014).
- 76. Fukuzumi, S. *et al.* Control of Photoinduced Electron Transfer in Zinc Phthalocyanine–Perylenediimide Dyad and Triad by the Magnesium Ion. *The Journal of Physical Chemistry A* **112**, 10744–10752 (2008).
- 77. Nakano, M. *et al.* Quantum Master Equation Approach to Singlet Fission Dynamics in Pentacene Linear Aggregate Models: Size Dependences of Excitonic Coupling Effects: Quantum Master Equation Approach to Singlet Fission Dynamics in Pentacene Linear Aggregate Models: Size Dependences of Excitonic Coupling Effects. *Journal of Computational Chemistry* (2018) doi:10.1002/jcc.25539.
- 78. Le, A. K. *et al.* Singlet Fission Involves an Interplay between Energetic Driving Force and Electronic Coupling in Perylenediimide Films. *Journal of the American Chemical Society* **140**, 814–826 (2018).
- 79. Silver, S., Dai, Q., Li, H., Brédas, J. & Kahn, A. Quantum Well Energetics of an n = 2 Ruddlesden–Popper Phase Perovskite. Advanced Energy Materials 9, 1901005 (2019).
- 80. Jeon, N. J. *et al.* A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells. *Nature Energy* **3**, 682–689 (2018).
- 81. Wygant, B. R. *et al.* Probing the Degradation Chemistry and Enhanced Stability of 2D Organolead Halide Perovskites. *Journal of the American Chemical Society* **141**, 18170–18181 (2019).
- 82. Bryant, D. *et al.* Light and oxygen induced degradation limits the operational stability of methylammonium lead triiodide perovskite solar cells. *Energy & Environmental Science* 9, 1655–1660 (2016).
- 83. Leguy, A. M. A. *et al.* Reversible Hydration of CH₃ NH₃ PbI₃ in Films, Single Crystals, and Solar Cells. *Chemistry of Materials* **27**, 3397–3407 (2015).
- 84. Cao, D. H., Stoumpos, C. C., Farha, O. K., Hupp, J. T. & Kanatzidis, M. G. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *Journal of the American Chemical Society* **137**, 7843–7850 (2015).

- 85. Soe, C. M. M. *et al.* Structural and thermodynamic limits of layer thickness in 2D halide perovskites. *Proceedings of the National Academy of Sciences* **116**, 58–66 (2019).
- 86. Spanopoulos, I. *et al.* Uniaxial Expansion of the 2D Ruddlesden–Popper Perovskite Family for Improved Environmental Stability. *Journal of the American Chemical Society* **141**, 5518–5534 (2019).
- 87. Stoumpos, C. C. *et al.* High Members of the 2D Ruddlesden-Popper Halide Perovskites: Synthesis, Optical Properties, and Solar Cells of (CH 3 (CH 2) 3 NH 3) 2 (CH 3 NH 3) 4 Pb 5 I 16. *Chem* 2, 427–440 (2017).
- 88. Grancini, G. *et al.* One-Year stable perovskite solar cells by 2D/3D interface engineering. *Nature Communications* **8**, (2017).
- 89. Tsai, H. *et al.* High-efficiency two-dimensional Ruddlesden–Popper perovskite solar cells. *Nature* **536**, 312–316 (2016).
- Wang, Z. *et al.* Efficient ambient-air-stable solar cells with 2D–3D heterostructured butylammonium-caesium-formamidinium lead halide perovskites. *Nature Energy* 2, (2017).
- 91. Baranowski, M. & Plochocka, P. Excitons in Metal-Halide Perovskites. *Advanced Energy Materials* 1903659 (2020) doi:10.1002/aenm.201903659.
- 92. Ceratti, D. R. *et al.* Self-Healing Inside APbBr ₃ Halide Perovskite Crystals. *Advanced Materials* **30**, 1706273 (2018).
- 93. Zhao, Y. *et al.* A polymer scaffold for self-healing perovskite solar cells. *Nature Communications* 7, (2016).
- 94. Shi, T., Li, H., Tretiak, S. & Chernyak, V. Y. How Geometric Distortions Scatter Electronic Excitations in Conjugated Macromolecules. J. Phys. Chem. Lett. 5, 3946–3952 (2014).
- 95. Dou, L., Liu, Y., Hong, Z., Li, G. & Yang, Y. Low-Bandgap Near-IR Conjugated Polymers/Molecules for Organic Electronics. *Chem. Rev.* (2015) doi:10.1021/acs.chemrev.5b00165.
- 96. Clark, J., Silva, C., Friend, R. H. & Spano, F. C. Role of Intermolecular Coupling in the Photophysics of Disordered Organic Semiconductors: Aggregate Emission in Regioregular Polythiophene. *Phys. Rev. Lett.* **98**, 206406 (2007).
- 97. Spano, F. C. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Accounts of Chemical Research* **43**, 429–439 (2010).
- 98. Cook, S., Furube, A. & Katoh, R. Analysis of the excited states of regioregular polythiophene P3HT. *Energy Environ. Sci.* **1**, 294–299 (2008).
- 99. Piris, J. *et al.* Photogeneration and Ultrafast Dynamics of Excitons and Charges in P3HT/PCBM Blends. *The Journal of Physical Chemistry C* **113**, 14500–14506 (2009).

- 100. Sheng, C.-X., Tong, M., Singh, S. & Vardeny, Z. V. Experimental determination of the charge/neutral branching ratio η in the photoexcitation of π -conjugated polymers by broadband ultrafast spectroscopy. *Physical Review B* **75**, (2007).
- 101. Anderson, M. R. *et al.* Synthesis of regioregular phenyl substituted polythiophenes with FeCl3. *Synthetic Metals* **101**, 11–12 (1999).
- 102. Fuchs, A., Rempel, V. & MÃ¹/₄ller, C. E. The Natural Product Magnolol as a Lead Structure for the Development of Potent Cannabinoid Receptor Agonists. *PLoS ONE* 8, e77739 (2013).
- 103. Lygo, B. Enantioselective synthesis of dityrosine and isodityrosine via asymmetric phase-transfer catalysis. *Tetrahedron Letters* **40**, 1389–1392 (1999).
- Gronowitz, S. & Peters, D. Convenient Synthesis of Various Terheterocyclic Compounds by Pd(0)-Catalyzed Coupling Reactions. *Heterocycles* 30, 645–658 (1990).
- 105. Andersson, M. R. *et al.* Regioselective polymerization of 3-(4-octylphenyl) thiophene with FeCl3. *Macromolecules* **27**, 6503–6506 (1994).
- 106. Ostroverkhova, O. Organic Optoelectronic Materials: Mechanisms and Applications. *Chemical Reviews* **116**, 13279–13412 (2016).
- 107. Hide, F., Díaz-García, M. A., Schwartz, B. J. & Heeger, A. J. New Developments in the Photonic Applications of Conjugated Polymers. *Accounts of Chemical Research* **30**, 430–436 (1997).
- 108. Zhu, X., Shao, B., Vanden Bout, D. A. & Plunkett, K. N. Directing the Conformation of Oligo(phenylenevinylene) Polychromophores with Rigid, Nonconjugatable Morphons. *Macromolecules* **49**, 3838–3844 (2016).
- 109. Traub, M. C. *et al.* Chromophore-Controlled Self-Assembly of Highly Ordered Polymer Nanostructures. *The Journal of Physical Chemistry Letters* **4**, 2520–2524 (2013).
- 110. Allolio, C. *et al.* H-Aggregation Effects between π -Conjugated Chromophores in Cofacial Dimers and Trimers: Comparison of Theory and Single-Molecule Experiment. *The Journal of Physical Chemistry B* **122**, 6431–6441 (2018).
- 111. Willenbacher, J., Altintas, O., Roesky, P. W. & Barner-Kowollik, C. Single-Chain Self-Folding of Synthetic Polymers Induced by Metal-Ligand Complexation. *Macromolecular Rapid Communications* 35, 45–51 (2014).
- 112. Willenbacher, J. *et al.* Reversible single-chain selective point folding via cyclodextrin driven host–guest chemistry in water. *Chemical Communications* **50**, 7056 (2014).
- 113. Gonzalez-Burgos, M., Latorre-Sanchez, A. & Pomposo, J. A. Advances in single chain technology. *Chemical Society Reviews* 44, 6122–6142 (2015).

- Haldar, D., Jiang, H., Léger, J.-M. & Huc, I. Interstrand Interactions between Side Chains in a Double-Helical Foldamer. *Angewandte Chemie International Edition* 45, 5483–5486 (2006).
- 115. Reuther, J. F. *et al.* Facile Synthesis of Rod–Coil Block Copolymers with Chiral, Helical Polycarbodiimide Segments via Postpolymerization CuAAC "Click" Coupling of Functional End Groups. *Macromolecules* **48**, 3207–3216 (2015).
- 116. Lu, Y.-X., Shi, Z.-M., Li, Z.-T. & Guan, Z. Helical polymers based on intramolecularly hydrogen-bonded aromatic polyamides. *Chemical Communications* **46**, 9019 (2010).
- 117. Yashima, E., Maeda, K., Iida, H., Furusho, Y. & Nagai, K. Helical Polymers: Synthesis, Structures, and Functions. *Chemical Reviews* **109**, 6102–6211 (2009).
- Yashima, E., Maeda, K. & Furusho, Y. Single- and Double-Stranded Helical Polymers: Synthesis, Structures, and Functions. *Accounts of Chemical Research* 41, 1166–1180 (2008).
- 119. Gillies, E. R., Deiss, F., Staedel, C., Schmitter, J.-M. & Huc, I. Development and Biological Assessment of Fully Water-Soluble Helical Aromatic Amide Foldamers. *Angewandte Chemie International Edition* **46**, 4081–4084 (2007).
- 120. Elacqua, E. *et al.* Supramolecular Multiblock Copolymers Featuring Complex Secondary Structures. *Journal of the American Chemical Society* **139**, 12240– 12250 (2017).
- 121. Sebaoun, L., Maurizot, V., Granier, T., Kauffmann, B. & Huc, I. Aromatic Oligoamide β-Sheet Foldamers. *Journal of the American Chemical Society* 136, 2168–2174 (2014).
- 122. Gellman, S. H. Foldamers: A Manifesto. *Accounts of Chemical Research* **31**, 173–180 (1998).
- 123. Cheng, R. P., Gellman, S. H. & DeGrado, W. F. β-Peptides: From Structure to Function. *Chemical Reviews* 101, 3219–3232 (2001).
- 124. Guo, L. *et al.* Stereospecific Synthesis of Conformationally Constrained γ-Amino Acids: New Foldamer Building Blocks That Support Helical Secondary Structure. *Journal of the American Chemical Society* 131, 16018–16020 (2009).
- 125. De, S., Koley, D. & Ramakrishnan, S. Folding a Polymer via Two-Point Interaction with an External Folding Agent: Use of H-Bonding and Charge-Transfer Interactions. *Macromolecules* **43**, 3183–3192 (2010).
- 126. Lu, J., ten Brummelhuis, N. & Weck, M. Intramolecular folding of triblock copolymers via quadrupole interactions between poly(styrene) and poly(pentafluorostyrene) blocks. *Chemical Communications* **50**, 6225 (2014).

- 127. Lucas, J. M. *et al.* Carpenter's Rule Folding in Rigid-Flexible Block Copolymers with Conjugation-Interrupting, Flexible Tethers Between Oligophenylenevinylenes. *J Phys Chem A* **119**, 8010–20 (2015).
- 128. Zhao, X. *et al.* Complementary Semiconducting Polymer Blends: The Influence of Conjugation-Break Spacer Length in Matrix Polymers. *Macromolecules* **49**, 2601–2608 (2016).
- 129. Zhao, Y. *et al.* Conjugation-Break Spacers in Semiconducting Polymers: Impact on Polymer Processability and Charge Transport Properties. *Macromolecules* **48**, 2048–2053 (2015).
- 130. Odian, G. Principles of Polymerization. (John Wiley & Sons, Inc., 2004).
- 131. Chen, S. H., Su, A. C., Han, S. R., Chen, S. A. & Lee, Y. Z. Molecular Aggregation and Luminescence Properties of Bulk Poly(2,5-di- *n* -octyloxy-1,4phenylenevinylene). *Macromolecules* **37**, 181–186 (2004).
- 132. Adachi, T. *et al.* Regioregularity and Single Polythiophene Chain Conformation. *The Journal of Physical Chemistry Letters* **2**, 1400–1404 (2011).
- 133. Huang, C., Barlow, S. & Marder, S. R. Perylene-3,4,9,10-tetracarboxylic Acid Diimides: Synthesis, Physical Properties, and Use in Organic Electronics. *The Journal of Organic Chemistry* **76**, 2386–2407 (2011).
- 134. Sapagovas, V., Gaidelis, V., Kovalevskij, V. & Undzenas, A. 3,4,9,10-Perylenetetracarboxylic acid derivatives and their photophysical properties. *Dyes and Pigments* **71**, 178–187 (2006).
- 135. Ghosh, S., Li, X.-Q., Stepanenko, V. & Würthner, F. Control of H- and J-Type π Stacking by Peripheral Alkyl Chains and Self-Sorting Phenomena in Perylene Bisimide Homo- and Heteroaggregates. *Chemistry - A European Journal* 14, 11343–11357 (2008).
- 136. Datar, A., Oitker, R. & Zang, L. Surface-assisted one-dimensional self-assembly of a perylene based semiconductor molecule. *Chemical Communications* 1649 (2006) doi:10.1039/b518060k.
- 137. Marques, S. R., Labastide, J. A. & Barnes, M. D. Evolution of HJ Coupling in Nanoscale Molecular Self-Assemblies. *The Journal of Physical Chemistry C* **122**, 15723–15728 (2018).
- 138. Hestand, N. J. & Spano, F. C. Molecular Aggregate Photophysics beyond the Kasha Model: Novel Design Principles for Organic Materials. *Accounts of Chemical Research* **50**, 341–350 (2017).
- 139. Shahar, C. *et al.* Precrystalline Aggregates Enable Control over Organic Crystallization in Solution. *Angewandte Chemie International Edition* **55**, 179–182 (2016).

- 140. Gust, A. *et al.* A Starting Point for Fluorescence-Based Single-Molecule Measurements in Biomolecular Research. *Molecules* **19**, 15824–15865 (2014).
- 141. Hübner, C. G., Renn, A., Renge, I. & Wild, U. P. Direct observation of the triplet lifetime quenching of single dye molecules by molecular oxygen. *The Journal of Chemical Physics* **115**, 9619–9622 (2001).
- 142. Salamon, Z. & Bässler, H. fluorescence properties of perylene aggregates in a polymer matrix. *Chemical Physics* **100**, 393–400 (1985).
- 143. Hestand, N. J. & Spano, F. C. Interference between Coulombic and CT-mediated couplings in molecular aggregates: H- to J-aggregate transformation in perylene-based π -stacks. *The Journal of Chemical Physics* **143**, 244707 (2015).
- 144. Vogelsang, J. & Lupton, J. M. Solvent Vapor Annealing of Single Conjugated Polymer Chains: Building Organic Optoelectronic Materials from the Bottom Up. *The Journal of Physical Chemistry Letters* **3**, 1503–1513 (2012).
- 145. Cordes, T. *et al.* Single-Molecule Redox Blinking of Perylene Diimide Derivatives in Water. *Journal of the American Chemical Society* **132**, 2404–2409 (2010).
- 146. Stoumpos, C. C. *et al.* Ruddlesden–Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chemistry of Materials* **28**, 2852–2867 (2016).
- 147. Liu, J., Leng, J., Wu, K., Zhang, J. & Jin, S. Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimentional Perovskite Films. *Journal of the American Chemical Society* **139**, 1432–1435 (2017).
- 148. Quintero-Bermudez, R. *et al.* Compositional and orientational control in metal halide perovskites of reduced dimensionality. *Nature Materials* **17**, 900–907 (2018).
- 149. Chen, A. Z. *et al.* Origin of vertical orientation in two-dimensional metal halide perovskites and its effect on photovoltaic performance. *Nature Communications* **9**, (2018).
- 150. Soe, C. M. M. *et al.* Understanding Film Formation Morphology and Orientation in High Member 2D Ruddlesden-Popper Perovskites for High-Efficiency Solar Cells. *Advanced Energy Materials* **8**, 1700979 (2018).
- 151. Li, L. *et al.* Unraveling the Growth of Hierarchical Quasi-2D/3D Perovskite and Carrier Dynamics. *The Journal of Physical Chemistry Letters* **9**, 1124–1132 (2018).
- 152. Zhang, Y. *et al.* Quantitative imaging of anion exchange kinetics in halide perovskites. *Proceedings of the National Academy of Sciences* **116**, 12648–12653 (2019).
- 153. Postorino, P. & Malavasi, L. Pressure-Induced Effects in Organic–Inorganic Hybrid Perovskites. *The Journal of Physical Chemistry Letters* **8**, 2613–2622 (2017).

- 154. Chou, H., Ismach, A., Ghosh, R., Ruoff, R. S. & Dolocan, A. Revealing the planar chemistry of two-dimensional heterostructures at the atomic level. *Nature Communications* **6**, (2015).
- 155. Griffin, M. P., Gearba, R., Stevenson, K. J., Vanden Bout, D. A. & Dolocan, A. Revealing the Chemistry and Morphology of Buried Donor/Acceptor Interfaces in Organic Photovoltaics. *The Journal of Physical Chemistry Letters* 8, 2764–2773 (2017).
- 156. Lin, Y. *et al.* Unveiling the operation mechanism of layered perovskite solar cells. *Nature Communications* **10**, (2019).
- 157. Quan, L. N. *et al.* Ligand-Stabilized Reduced-Dimensionality Perovskites. *Journal* of the American Chemical Society **138**, 2649–2655 (2016).
- 158. Qiu, J. *et al.* 2D Intermediate Suppression for Efficient Ruddlesden–Popper (RP) Phase Lead-Free Perovskite Solar Cells. *ACS Energy Letters* **4**, 1513–1520 (2019).
- 159. Xu, J. *et al.* Highly stretchable polymer semiconductor films through the nanoconfinement effect.pdf. *Science* **355**, 59–64 (2017).
- 160. Oh, J. Y. *et al.* Intrinsically stretchable and healable semiconducting polymer for organic transistors. *Nature* **539**, 411–415 (2016).
- 161. Logothetidis, S. Handbook of flexible organic electronics: Materials, manufacturing and applications. (Elsevier, 2014).
- Someya, T., Kaltenbrunner, M. & Yokota, T. Ultraflexible organic electronics. MRS Bull 40, 1130–1137 (2015).
- 163. Liao, C. *et al.* Flexible organic electronics in biology: materials and devices. *Adv Mater* **27**, 7493–7527 (2015).
- 164. Casalini, S., Bortolotti, C. A., Leonardi, F. & Biscarini, F. Self-assembled monolayers in organic electronics. *Chem Soc Rev* **46**, 40–71 (2017).
- 165. Xu, R.-P., Li, Y.-Q. & Tang, J.-X. Recent advances in flexible organic lightemitting diodes. *J Mater Chem C* **4**, 9116–9142 (2016).
- 166. Barbara, P. F., Gesquiere, A. J., Park, S.-J. & Lee, Y. J. Single-Molecule Spectroscopy of Conjugated Polymers. *Accounts of Chemical Research* **38**, 602– 610 (2005).
- 167. Orrit, M., Ha, T. & Sandoghdar, V. Single-molecule optical spectroscopy. *Chem Soc Rev* **43**, 973–976 (2014).
- 168. Lupton, J. M. Single-Molecule Spectroscopy for Plastic Electronics: Materials Analysis from the Bottom-Up. *Adv Mater* **22**, 1689–1721 (2010).
- 169. Vacha, M. & Habuchi, S. Conformation and physics of polymer chains: a singlemolecule perspective. *NPG Asia Mater* **2**, 134–1142 (2010).

- 170. Thiessen, A. *et al.* Unraveling the chromophoric disorder of poly(3-hexylthiophene). *P Natl Acad Sci* **110**, E3550–E3556 (2013).
- 171. Hu, Z., Liu, J., Simón-Bower, L., Zhai, L. & Gesquiere, A. J. Influence of Backbone Rigidness on Single Chain Conformation of Thiophene-Based Conjugated Polymers. *J Phys Chem B* **117**, 4461–4467 (2013).
- 172. Simine, L. & Rossky, P. J. Relating Chromophoric and Structural Disorder in Conjugated Polymers. *J Phys Chem Lett* **8**, 1752–1756 (2017).
- 173. Raithel, D. *et al.* Emitting Species of Poly(3-hexylthiophene): From Single, Isolated Chains to Bulk. *Macromolecules* **49**, 9553–9560 (2016).
- 174. Paquin, F. *et al.* Two-dimensional spatial coherence of excitons in semicrystalline polymeric semiconductors: Effect of molecular weight. *Phys Rev B* **88**, (2013).
- 175. Baderschneider, S., Scherf, U., Köhler, J. & Hildner, R. Influence of the Conjugation Length on the Optical Spectra of Single Ladder-Type (*p* -Phenylene) Dimers and Polymers. *The Journal of Physical Chemistry A* **120**, 233–240 (2016).
- 176. Hildner, R., Lemmer, U., Scherf, U., van Heel, M. & Köhler, J. Revealing the Electron–Phonon Coupling in a Conjugated Polymer by Single-Molecule Spectroscopy. *Advanced Materials* **19**, 1978–1982 (2007).
- Feist, F. A., Zickler, M. F. & Basché, T. Origin of the Red Sites and Energy Transfer Rates in Single MEH-PPV Chains at Low Temperature. *ChemPhysChem* 12, 1499–1508 (2011).
- 178. Liu, J. *et al.* Insight into How Molecular Structures of Thiophene-based Conjugated Polymers Affect Crystallization Behaviors. *Polymer* **52**, 2302–2309 (2011).
- 179. Lupton, J. M. Chromophores in Conjugated Polymers-All Straight? *ChemPhysChem* **13**, 901–907 (2012).
- 180. Becker, K. *et al.* How Chromophore Shape Determines the Spectroscopy of Phenylene–Vinylenes: Origin of Spectral Broadening in the Absence of Aggregation. *The Journal of Physical Chemistry B* **112**, 4859–4864 (2008).
- 181. Aggarwal, A. V. *et al.* Fluctuating exciton localization in giant π -conjugated spoked-wheel macrocycles. *Nat Chem* **5**, 964–970 (2013).
- 182. Chen, P.-Y., Rassamesard, A., Chen, H.-L. & Chen, S.-A. Conformation and Fluorescence Property of Poly(3-hexylthiophene) Isolated Chains Studied by Single Molecule Spectroscopy: Effects of Solvent Quality and Regioregularity. *Macromolecules* **46**, 5657–5663 (2013).
- 183. Kahle, F.-J., Saller, C., Köhler, A. & Strohriegl, P. Crosslinked Semiconductor Polymers for Photovoltaic Applications. *Adv Energy Mater* 7, 1700306-n/a (2017).
- 184. Honmou, Y. *et al.* Single-molecule electroluminescence and photoluminescence of polyfluorene unveils the photophysics behind the green emission band. *Nature Communications* **5**, (2014).

- Zade, S. S., Zamoshchik, N. & Bendikov, M. From Short Conjugated Oligomers to Conjugated Polymers. Lessons from Studies on Long Conjugated Oligomers. *Acc Chem Res* 44, 14–24 (2011).
- Yu, J., Hu, D. H. & Barbara, P. F. Unmasking electronic energy transfer of conjugated polymers by suppression of O-2 quenching. *Science* 289, 1327–1330 (2000).
- 187. Köhler, A., Hoffmann, S. T. & Bässler, H. An Order–Disorder Transition in the Conjugated Polymer MEH-PPV. *J Am Chem Soc* **134**, 11594–11601 (2012).
- 188. Feist, F. A., Tommaseo, G. & Basche, T. Single-Molecule Spectroscopy of MEH-PPV Polymer Molecules in Different Host Matrices. *J Phys Chem C* **113**, 11484– 11490 (2009).
- 189. Kobayashi, H., Tsuchiya, K., Ogino, K. & Vacha, M. Spectral multitude and spectral dynamics reflect changing conjugation length in single molecules of oligophenylenevinylenes. *Phys Chem Chem Phys* 14, 10114–8 (2012).
- 190. Kim, T. W. *et al.* Chain-Length-Dependent Exciton Dynamics in Linear Oligothiophenes Probed Using Ensemble and Single-Molecule Spectroscopy. *J Phys Chem Lett* 7, 452–8 (2016).
- 191. Hong, J. et al. The Effects of Side-Chain-Induced Disorder on the Emission Spectra and Quantum Yields of Oligothiophene Nanoaggregates: A Combined Experimental and MD-TDDFT Study. *The Journal of Physical Chemistry A* 118, 10464–10473 (2014).
- 192. So, W. Y. *et al.* Effects of Solvent Properties on the Spectroscopy and Dynamics of Alkoxy-Substituted PPV Oligomer Aggregates. *J Phys Chem B* **116**, 10504–10513 (2012).
- 193. Stangl, T. *et al.* Temporal switching of homo-FRET pathways in singlechromophore dimer models of pi-conjugated polymers. *J Am Chem Soc* 135, 78– 81 (2013).
- 194. Hooley, E. N., Tilley, A. J., White, J. M., Ghiggino, K. P. & Bell, T. D. Energy transfer in PPV-based conjugated polymers: a defocused widefield fluorescence microscopy study. *Phys Chem Chem Phys* **16**, 7108–14 (2014).
- 195. Jiang, Y. & McNeill, J. Light-Harvesting and Amplified Energy Transfer in Conjugated Polymer Nanoparticles. *Chem Rev* **117**, 838–859 (2017).
- 196. Panzer, F., Sommer, M., Bässler, H., Thelakkat, M. & Köhler, A. Spectroscopic Signature of Two Distinct H-Aggregate Species in Poly(3-hexylthiophene). *Macromolecules* 48, 1543–1553 (2015).
- 197. Panzer, F., Bässler, H., Lohwasser, R., Thelakkat, M. & Köhler, A. The Impact of Polydispersity and Molecular Weight on the Order–Disorder Transition in Poly(3hexylthiophene). J Phys Chem Lett 5, 2742–2747 (2014).

- 198. Tuncel, D. & Demir, H. V. Conjugated polymer nanoparticles. *Nanoscale* **2**, 484–494 (2010).
- 199. Pecher, J. & Mecking, S. Nanoparticles of Conjugated Polymers. *Chemical Reviews* **110**, 6260–6279 (2010).
- 200. Tenery, D. & Gesquiere, A. J. Effect of PCBM Concentration on Photoluminescence Properties of Composite MEH-PPV/PCBM Nanoparticles Investigated by a Franck-Condon Analysis of Single-Particle Emission Spectra. *ChemPhysChem* 10, 2449–2457 (2009).
- 201. Wu, C. F., Peng, H. S., Jiang, Y. F. & McNeill, J. Energy transfer mediated fluorescence from blended conjugated polymer nanoparticles. *J Phys Chem B* **110**, 14148–14154 (2006).
- 202. Hu, Z. & Gesquiere, A. J. PCBM concentration dependent morphology of P3HT in composite P3HT/PCBM nanoparticles. *Chem Phys Lett* **476**, 51–55 (2009).
- 203. Grey, J. K. *et al.* Effect of temperature and chain length on the bimodal emission properties of single polyfluorene copolymer molecules. *J Phys Chem B* **110**, 18898–18903 (2006).
- 204. Labastide, J. A. *et al.* Time- and Polarization-Resolved Photoluminescence of Individual Semicrystalline Polythiophene (P3HT) Nanoparticles. *The Journal of Physical Chemistry Letters* **2**, 2089–2093 (2011).
- 205. Niles, E. T. *et al.* J-aggregate behavior in poly-3-hexylthiophene nanofibers. *J Phys Chem Lett* **3**, 259–263 (2012).
- 206. Baghgar, M., Labastide, J. A., Bokel, F., Hayward, R. C. & Barnes, M. D. Effect of polymer chain folding on the transition from H- to J-aggregate behavior in P3HT nanofibers. *J Phys Chem C* **118**, 2229–2235 (2014).
- 207. Thomas, A. K., Garcia, J. A., Ulibarri-Sanchez, J., Gao, J. & Grey, J. K. High Intrachain Order Promotes Triplet Formation from Recombination of Long-Lived Polarons in Poly(3-hexylthiophene) J-Aggregate Nanofibers. ACS Nano 8, 10559– 10568 (2014).
- 208. Gesquiere, A. J., Lee, Y. J., Yu, J. & Barbara, P. F. Single molecule modulation spectroscopy of conjugated polymers. *J Phys Chem B* **109**, 12366–12371 (2005).
- 209. Stangl, T. *et al.* Mesoscopic quantum emitters from deterministic aggregates of conjugated polymers. *P Natl Acad Sci* **112**, E5560–E5566 (2015).
- 210. Eder, T. *et al.* Switching between H- and J-type electronic coupling in single conjugated polymer aggregates. *Nat Commun* **8**, 1641 (2017).
- 211. Hou, L., Adhikari, S., Tian, Y., Scheblykin, I. G. & Orrit, M. Absorption and Quantum Yield of Single Conjugated Polymer Poly[2-methoxy-5-(2ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) Molecules. *Nano Lett* 17, 1575–1581 (2017).

- 212. Kobayashi, H., Hirata, S. & Vacha, M. Mechanical Manipulation of Photophysical Properties of Single Conjugated Polymer Nanoparticles. *The Journal of Physical Chemistry Letters* 4, 2591–2596 (2013).
- 213. Vacha, M., Sharma, D. K. & Hirata, S. Single-molecule studies beyond optical imaging: Multi-parameter single-molecule spectroscopy. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* (2017) doi:10.1016/j.jphotochemrev.2017.11.003.