The Role of Incident Light Intensity, Wavelength, and Exposure Time in the Modification of Conjugated Polymer Structure in Solution

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Abstract

Our recent investigations indicate that simple white light exposure holds intriguing potential to alter the structure of conjugated polymer chains. To provide further insight into how to rationally control this process, we have employed small angle neutron scattering to investigate structural changes occurring in solutions of poly(3-hexylthiophene-2,5-diyl) upon exposure to white light. Our previous results indicate significant change in the structure of the polymer upon illumination, an effect we attribute to an alteration in the thermodynamic interactions of the polymer with the surrounding solvent. This work provides additional information to further refine our understanding of this phenomenon by studying the relationship between the magnitude of exciton creation and subsequent structural changes through a series of exposure time, light intensity, and wavelength sensitive experiments. The results demonstrate a clear and consistent relationship between the number of absorbable photons available to the conjugated polymer chain and more powerful alterations in polymer structural parameters, indicating that net exciton generation provides the fundamental driving force for this phenomenon. This points towards the feasibility of employing light exposure protocols as a powerful unobtrusive in-situ method for

precise tailoring of optoelectronic active layers over a wide range of organic electronic device fabrication procedures.

Introduction

Conjugated polymers have presented the field of material science with exciting possibilities for advanced electronic devices possessing similar functionality as their more traditional counterparts while significantly reducing weight and cost. In order to make the organic electronic devices composed of these materials competitive on a mass market scale, work has largely focused on improving device efficiency through alterations to active layer architectures and morphologies.^{1,2,3,4} Through modifications to solution casting techniques and annealing processes, varying degrees of control of active layer domain patterns and sizes can be realized, which ultimately manifest themselves in the form of changes to such crucial device characteristics as exciton dissociation lengths and heterojunction surface areas, morphological facets which have repeatedly proven to be closely tied to effective device efficiencies.^{5,6,7,8,9} Given the clear importance of comprehensive control of these organic device functional layer morphologies, exploring and properly developing economically feasible and non-intrusive methods for directing organic layer assembly has become key.

Towards this end, recent work has studied the previously overlooked concept of light-induced changes to polymeric physical characteristics through simple white light exposure. Molecular dynamics simulations of simple PPV oligomers have demonstrated a rigidification of the polymer backbone upon the creation of common excited states from illumination.¹⁰ Exploratory experiments by Reiter et al demonstrated that exposing a polymer blend film containing a benchmark conjugated polymer to white light significantly slowed its dewetting rate

and therefore increased the films viscosity, providing definitive indications that simple light-based in-situ methodologies powerfully affect conjugated polymer physical characteristics.¹¹ A limited collection of additional experiments has provided further instances of light exposure altering polymeric materials.^{12,13,14} Our group has sought to further expand the understanding of the interaction between light and conjugated polymers by focusing on the structural differences observed in solution-based samples between light and dark environments, as the solution state has repeatedly proven to be a key stage within most common fabrication techniques, where modifications that exist in solution are consistently carried through to the final solid state device.^{15,16} Our initial work examined the benchmark conjugated material P3HT in a single chain solution system, revealing that light exposure triggers a sharp decrease in Kuhn length and R_g along with a marked decrease in the second virial coefficient, indicating a pseudo-chain collapse upon light exposure.¹⁷ Further experiments conducted in a much higher concentration environment during the thermally driven polymer gelation process provides further evidence of light exposure influencing conjugated polymer solution behavior, as polymer chain aggregation was substantially hindered by the presence of white illumination throughout the temperature ramp.¹⁸ Continued studies have further clarified the nature of these light-induced physical effects and elucidate the thermodynamic mechanism behind it.¹⁹

Specifically, this paper seeks to study the methods by which this light-based effect can be more finely controlled and tuned by way of exposure time and wavelength sensitivity, essentially studying the relationship between total net P3HT absorbable photons, the levels of structural alteration initiated by their absorbance and the subsequent generation of excitons on the polymer backbone. Together our previous work has shown that structural shifts of the conjugated polymer with illumination are not instantaneous, but rather require a given period of exposure time before

full transition is achieved. By varying the amount, type, and total time of light exposure applied to a range of conjugated polymer samples, a more complete understanding of these light driven conformational effects can be attained. Moreover, this information is required to enable its future use in manipulating active layer morphologies, with the goal of developing a non-intrusive in-situ methodology for controlling device structure and ultimately boosting device performance.

Instrumental

Poly(3-hexylthiophene-2,5-diyl) was purchased from Osilla Chemicals with a regioregularity of ~95% and a weight average molecular weight of ~35,000 and a PDI of 1.8, per the manufacturer. This material was used as received, and was dissolved in either deuterated (d8) styrene purchased from Polymer Source, or 1,2-ortho-dichlorobenzene (d4) (ODCB) purchased from Sigma-Aldrich. The samples were kept at 60°C throughout the scattering experiments by a thermally controlled sample holder in order to prevent localized aggregation or gelation.

Samples for use in the small angle neutron scattering experiments were assembled within 2mm quartz solution cells. These sample cells were then either wrapped in 0.1 mm thick aluminum foil to create the dark environment or exposed to illumination provided by an optical illuminator consisting of a 125-watt halogen bulb, generating 50,000 lux at a 5 cm distance at maximum intensity. Aluminum was chosen as a barrier for light exposure due to its near total transparency to neutrons. Regardless, special care was taken during the analysis to be certain that the presence of the aluminum was accounted for in the reduction of the raw data to absolute units. These methods involved, amongst others, separate determination of sample transmittance and empty cell scattering for the light and dark samples.

The small angle neutron scattering experiments (SANS) were conducted on instruments located at both Oak Ridge National Laboratories (ORNL) and the National Institute of Standards and Technology (NIST). ORNL experiments took place at the High Flux Isotope Reactor (HFIR) using the General Purpose SANS (CG-2) beamline. Employing three separate detector distances of 0.3, 2, and 12.5 meters with a wavelength of 6 Å allowed a Q range of 0.0034 to 0.3363 Å⁻¹, where $Q = 4\pi/\lambda\sin(\theta/2)$, λ is the neutron wavelength, and θ is the scattering angle. NIST scattering data was collected at the Center for Neutron Research (NCNR) using the NGB 30 beamline using detector distances of 0.3, 4, and 13 meters with a wavelength of 6 Å.²⁰ The raw data was reduced using NCNR macros and corrected for empty cell (with and without aluminum) scattering, dark current, and detector sensitivity.²¹ Elimination of contributions from background incoherent scattering and thermal fluctuations allowed acquisition of absolute coherent scattering.

Results

In order to study the effects of light on the structure of conjugated polymer samples in solution, we have developed a procedure to conduct mirrored scattering experiments for each prepared solution: once under direct illumination and then again while completely isolated from ambient light via aluminum foil. We will refer to samples analyzed under these conditions as "light" and "dark" respectively throughout the text. In order to establish a control baseline we have applied this methodology to a non-conductive polymer sample in order to confirm that the effects we observe are not conflated with environmental, experimental, or methodological contributions, with the pertinent SANS data plots available in our previous publications.¹⁷ As the data curves overlap completely, this eliminates concerns that thermal effects or the presence of aluminum foil influence our results.

Impact of Light Exposure Time on Structural Changes

Our past experiments have described in detail the structural changes which occur in a conjugated polymer before and after it has been exposed to a light source, however the rate of these changes and the permanence of their nature have yet to be fully investigated. Towards this end, the following experiments are designed to expand our understanding of this phenomenon by examining the structure of the P3HT polymer chain over a wider range of light exposure time sequences and intensities. Firstly, SANS experiments were designed to study the permanence and reversibility of the illumination-induced structural effects by monitoring the change in structure of the P3HT chain after an illuminated sample is returned to a completely dark environment. Figure 1 displays an example of this experiment in the favorable P3HT solvent d-ODCB at 1 wt% polymer loading, where data is collected first after the sample had been kept in the dark for over 8 hours, then while exposed to illumination for 1 hour at 9,000 lux, and then measured again after resting in the dark for 4 hours.

Figure 1: Small angle neutron scattering curves of 1 wt% P3HT in d-ODCB at 60°C in dark (blue triangles), illuminated (red circles) and an additional dark (green squares) environments

The scattering data show that there is a significant shift in scattering intensity at high Q as the sample cycles between dark (blue trace) and light (red trace), a transition indicative of a change in local polymer chain structure brought on by the exposure to illumination. The overlap between the scattering patterns of the two dark samples indicates that these light-induced changes to structure of the P3HT chain quickly subsides upon removal of the light source and returns to an environment free of photons. This effect persists through all studied concentrations of P3HT in this solvent.

Fitting the raw data with the polymer excluded volume model allows quantitative analysis of the structural changes occurring at the local length scales where the most obvious structural changes occur.²² This analysis provides the radius of gyration (R_g) of the conjugated polymer chain throughout the illumination sequence, where Table 1 presents the results for these fits. This analysis confirms the decrease in polymer size that occurs with illumination, as well as the chain's reflex back to its original size once illumination is removed.

Table 1: Results for polymer excluded volume model fits to 1 wt% P3HT in d-ODCB

Sample	$R_g(\text{\AA})$
1 wt% P3HT in d-ODCB "Dark"	58.9 ± 1.2
1 wt% P3HT in d-ODCB "Light"	55.3 ± 1.2
1 wt% P3HT in d-ODCB "Dark 2"	58.7 ± 1.2

To determine the time dependent nature of the change in chain structure with illumination, the exact timescale over which the transitions occur must be more closely observed. In order to quantify the exact time period required for these illumination driven effects to drive polymer structure to an equilibrium state, we have conducted a series of SANS experiments for several select samples. Beginning with a standard "dark" scattering experiment, illumination at 9,000 lux is applied and consecutive scattering curves are obtained over sequential time intervals, resulting in a representation of time evolution of the structural changes that occur with illumination. An example of the data obtained from this experiment is presented in Figure 2, which provides the raw data set for a 1 wt% solution of P3HT in d-ODCB. This data focuses on

the high Q region where the local structural changes of P3HT are consistently observed in this solvent.

Figure 2: Time evolution of the scattering curve at high Q of a 1 wt% solution of P3HT in d-ODCB at 60°C for 0 min (blue circles), 10 min (red triangles), 30 min (green squares), and 50 min (yellow inverted triangles) white light illumination times.

As in the earlier experiments, a characteristic increase in scattering at high Q data is observed with increasing illumination time. Moreover, the timescale of these changes and its equilibration is consistent with the results presented in Figure 1. Analysis of this data using the excluded volume model yields the change in the R_g of the polymer chain with illumination time as shown in Figure 3.

Figure 3: Analysis of 1 wt% P3HT in d-ODCB using the flexible cylinder model over the course of 60 minutes light exposure time with multiple scattering runs of 5 minute duration each.

These results show a gradual decrease in the Rg of P3HT, evolving to a polymer chain size that is consistent with our previous studies of the change in the structure of P3HT in d-ODCB with illumination. These results show that the size of the polymer chain stabilizes after about half an hour of total light exposure. This data indicates that the light-driven P3HT structural changes are not instantaneous and instead require prolonged exposure time in order to allow for proper absorption and creation of the required number of excitons to realize maximum structural effects.

To understand the impact of solvent quality on the time evolution of these structural changes, Figure 4 shows the SANS curves for the change in the structure of a 1 wt% solution of

P3HT in d-styrene, a much less favorable solvent for P3HT. This sample is illuminated under a moderate intensity of roughly 9,000 lux over the course of several hours.

Figure 4: Time sensitivity of 1 wt% P3HT in d-styrene at 60°C after 0 hrs (black circles), 1hr (blue triangles), 2hr (red squares), 3hr (green inverted triangles), and 4hr (yellow diamonds) of total white light exposure.

From the raw data, it is readily apparent that the timescale for P3HT structural transformations in this solvent occur on a much longer timescale than the structural changes of P3HT in d-ODCB. After illumination is applied, a gradual increase in intensity is observed for the low Q data, while the high Q data instead decreases moderately. This may be indicative of complex structural shifts occurring at different length scales, or may actually be a result of structural differences emerging during the finite timescale of the experiment. Regardless, this data indicates that the structure of the P3HT chain continues to evolve in this less favorable

solvent over a substantially longer time period than the previously observed d-ODCB solvent system. Clearly, the timescale of the structural changes are a function of the solvent quality and vary substantially from one environment to another. This may indicate that different polymer-solvent systems require different levels of generated exciton density to create the required thermodynamic environment to observe structural changes to the polymer chain.

Additionally, our understanding of the time dependence of the illumination induced structural changes can be further refined by running a similar experiment over a narrower Q range and altering the illumination intensity to the maximum available with our illuminator, 50,000 lux. Figure 5 contains the time resolved scattering data for a 1 wt% P3HT in d-styrene sample measured in 10 separate runs over the course of 300 minutes of total light exposure time.

Figure 5: SANS data curves for 1 wt% P3HT in d-styrene in the dark and under total light exposure times ranging from 20 to 300 minutes at 60°C

For this moderate-Q region of the scattering range the effect of increasing illumination intensity is quite pronounced, as the raw data plots for the samples evolve much more quickly and substantially with illumination than the sample that was illuminated at the lower intensity of 9,000 lux. Figure 6 presents the Kuhn length of the P3HT as a function of illumination time as determined from fitting the data in Figure 5 to a flexible cylinder model, quantifying the changes in polymer structure with illumination time.

Figure 6: Values for Kuhn length as a function of illumination time (50,000 lux) extracted via the flexible cylinder model for 1 wt% P3HT in d-styrene at 60 °C

Clearly, the decrease in structural size of P3HT in d-styrene, though ultimately more pronounced, takes a substantially longer illumination time to reach equilibrium compared to the P3HT in d-ODCB samples. Whereas the size changes in d-ODCB equilibrate in 60 minutes, the d-styrene sample has yet to begin its most substantial decrease in Kuhn length by this time, instead requiring roughly two hours to reach a steady state. However, though they clearly require a more extended light exposure window in order to materialize, the overall magnitude of the changes observed is substantially larger, equating to a 70% decrease in Kuhn length as opposed to the roughly 10% drop in R_g for d-ODCB. Additionally, this d-styrene data equilibrates after about two hours under high intensity illumination, in sharp contrast to the d-styrene sample which received much lower intensity illumination that had not yet ceased its evolution after four hours of continuous illumination. Both of these examples illustrate the key role which solvent

quality and illumination intensity play in determining the magnitude and timescale of structural changes of conjugated polymer chains elicited by light exposure.

Impact of light wavelength on structural changes

Investigating the structural changes in P3HT upon exposure to wavelength controlled incident light, rather than full spectrum white light exposure employed above, provides additional insight into the mechanisms behind the light-driven effects. In a typical solution state, P3HT absorbs across a wide spectrum from roughly 300-600 nm, with a maximum absorbance around ~450 nm.^{23,24} Given this information, and taking into account the close relationship between photon absorption and the subsequent exciton generation, utilizing filters to limit the wavelength of the light that illuminates the P3HT sample provides a mechanism to more precisely link observed structural effects in the light-absorbing polymers directly to generated exciton density.

To accomplish this goal experimentally, the change in the structure of the P3HT polymer chain is studied when it is illuminated by wavelengths that are within the strongly absorbing range and comparing that an identical sample that is illuminated by light with wavelengths outside the primary absorbing region. If the observed structural effects are indeed predicated on photon absorption and exciton generation, then the sample exposed to illumination from the highly absorbing portion of the P3HT absorption spectrum should exhibit a significantly stronger and/or quicker change in chain structure than changes observed in the sample that is exposed to wavelengths that P3HT does not absorb as strongly.

A series of optical bandgap filters provide a means of controlling the wavelengths of light incident to the sample provided all background light is properly blocked as well. By passing the

generated white light of the optical illuminator through selected filters onto the conjugated polymer sample, experiments that document the impact of the wavelength of light on the observed structural changes can be completed. Figure 7 shows the raw data from an experiment conducted in this fashion with 1 wt% P3HT in d-styrene, where the sample was exposed to light with wavelengths within the strongest absorbing region for P3HT using a 415-590 nm bandgap filter, a sample that exposed to light with wavelengths 610-1200 nm, where P3HT absorbs poorly. The scattering curves of the P3HT solution in the dark and under white light illumination are also plotted in this Figure.

Figure 7: SANS scattering curve of 1 wt% P3HT in d-styrene at 60°C. Red open diamonds indicate sample illuminated with white light at 50,000 lux, pink open triangles indicate sample illuminated with 415-590nm light at 6500 lux, blue closed squares indicate sample illuminated with 610-1200nm light at 2000 lux, and black closed circles indicate sample under no illumination. All illuminated samples received approximately 90 minutes of the appropriate light exposure time each.

The curves representing the entirely dark sample (black traces) and the fully illuminated sample (red traces) appear very similar to those found in previously conducted experiments, while the scattering curves representing the sample exposed to the light that is strongly absorbed by P3HT (415-590 nm; pink traces) and the sample exposed to light in the poorly absorbing region of the P3HT absorption spectrum (610-1200 nm; blue traces) fall in between. Interestingly, the sample exposed to the more strongly absorbing portion of the spectrum exhibits a scattering curve that is higher intensity than the scattering of the sample that is exposed to the wavelengths that P3HT does not absorb as strongly, indicating that the larger amount of absorbable photons elicits a more substantial shift in structure. Analysis and curve fitting of these data curves with the flexible cylinder model quantitatively confirms this relationship, where Figure 8 plots the radius of gyration of the P3HT chain under the various illumination conditions.

Figure 8: R_g values obtained from the flexible cylinder fit for 1 wt% P3HT at 60°C in d-Styrene under (left to right) no illumination, 610-1200 nm light, 415-590 nm light, and white light illumination.

The samples exposed to the un-attenuated illumination source predictably give the largest changes in polymer chain R_g , while the sample that is illuminated by the 415-590 nm wavelength light experiences a less substantial though still pronounced shift in R_g . Finally the sample that is exposed to light with 610-1200 nm wavelengths retains an R_g that is closer to that of the polymer in the dark, decreasing only slightly. These results indicate that by limiting the number of absorbable photons available to the photoactive polymer chains, the extent of the structural changes induced by light exposure can be modulated.

The sensitivity of the structural changes to exposure of light with different wavelengths has also been performed for the more favorable solvent systems as well. Similar to the time sensitive experiments, the scattering curves of P3HT in d-ODCB have been obtained for samples exposed to unfiltered white light, to 610-1200 nm light outside the prime P3HT absorbance band, to 415-590 nm light inside the strong P3HT absorbance region, and in complete darkness. These scattering curves have been analyzed with the excluded volume model at high Q to quantify local changes in chain structure. Figure 9 displays the R_g data for this analysis for the P3HT in ODCB sample for the various illumination conditions.

Figure 9: R_g values obtained for polymer excluded volume model fit for 1 wt% P3HT at 60°C in d-ODCB under (left to right) no illumination, 610-1200 nm light at 2000 lux, 415-590 nm light at 6,500 lux, and white light illumination at 50,000 lux. All illuminated samples received approximately 90 minutes of the appropriate light exposure time each.

As with the samples in d-styrene, increasing photon absorption by P3HT causes a decrease in polymer R_g . Clearly, the data from several solvent environments indicates that controlling the intensity and wavelength of incident light allows for the manipulation of the size of the polymer in solution, where maximizing the absolute intensity of P3HT absorbable light provides a straightforward method to significantly control the structural transformation.

Discussion

The results of these neutron scattering experiments provide further insight into the alteration of the structure of conjugated polymers in solution by illumination. In these studies, the impact of illumination intensity, exposure time, and wavelength of light on the alteration of conjugated polymer structure in solution is monitored. This work builds off of our initial investigations that tied the significant changes observed in conjugated polymer structure upon light exposure to a thermodynamically driven chain collapse induced by alteration of the polymer-solvent interaction parameter due to the presence of excited species on the conjugated polymer backbone.¹⁷ The data shown here provides additional insight into the relationship between total absorbable photons available to the photoresponsive polymer and the magnitude of the subsequent alterations to polymer chain structure.

Our previous work indicates that the number of excitons on a given polymer chain number in the single digits under full white light illumination.¹⁷ Given that these P3HT chains have a molecular weight of ~35,000 g/mol, a of couple excitons may seem intuitively insufficient to elicit the large scale conformational shifts which we consistently observe. However, the time sensitive studies reported here further our understanding of the nature of the relationship between light exposure, exciton density, and subsequent conformation effects.

Inspection of the results of time evolution of structure in P3HT in d-styrene and d-ODCB reveals that a certain amount of exposure time for a given illumination intensity is necessary to elicit the full extent of structural change, showing illumination times of close to an hour for P3HT in d-ODCB, and from 2-5 hours for P3HT in d-styrene. This suggests that the structural change is a cumulative, but reversible, effect. Analyses of Figures 3 and 6 underline this point, where both samples exhibit a very gradual decrease in P3HT chain size which begins immediately upon illumination but which continues steadily until a final structure is attained. This is consistent with an underlying process which hinges not just on the number of excitons per chain, but is also sensitive to the total net number of excited species generated over a given time interval. Essentially each exciton generated contributes its own small "push" towards changing the solvent quality of the system, requiring a significant amount of total exposure time before the requisite amount of total species are generated to accomplish observable structural change. Further evidence of this relationship can be observed by comparing the two scattering curves of the d-styrene samples in Figures 4 and 5 studied under considerable differences in illumination intensity (50,000 lux vs. 9,000 lux), as the clear dependence on total generated excitons again becomes clear. By sharply increasing the amount of incident light and therefore similarly increasing the number of generated excitons, a notable acceleration in the rate of structure change is observed, further demonstrating the strong link between the total amount of exciton generation and the magnitude of change in polymer conformational changes.

The reproducibility experiments further demonstrate the time sensitive yet entirely non-destructive nature of this phenomenon. In the absence of any attempt to thermodynamically freeze the polymer-solvent system, removal of the illumination source will inevitably result in a withdrawal of the previously observed conformational shifts, evidenced by the complete reflex

of observed scattering patterns seen in Figure 1. Once the light exposure ceases and exciton populations return to zero, the thermodynamic pressure is removed and the system is allowed to return to its previous equilibrium state. Additionally, this experiment identifies the non-destructive nature of the light/dark effects. Repeated applications of the light sources over the appropriate timeframe consistently result in identical effects, all of which return to the original ground state upon loss of illumination, indicating no permanent damage or irreversible disruption of the polymer system, a response which is consistent with the non-destructive nature of exciton generation.

Investigating the incident light wavelength dependence of these polymer chain conformational transformations further emphasizes the importance of exciton formation. By separating the spectrum into distinct continuums inside and outside the prime P3HT absorbing region, it becomes clear that only absorbable light significantly influences the P3HT chains. Figures 7 and 8 emphasize that the samples that are measured in the dark and those that are illuminated with 610-1200 nm light are very similar, as are the samples that are measured in full illumination and those exposed to 410-590 nm light. Given that P3HT exhibits strong absorption across the 410-590 nm range, and very poor absorption above 600 nm, these results strongly suggest that the consistently observed changes in polymer structure are directly related to the total number of absorbed photons and subsequently generated excitons, and not the result of thermal effects or photo-degradation arising from persistent light exposure.^{23,25} In the case of the samples exposed to 610-1200 nm light, by selectively limiting the wavelength range of light available to the P3HT chains, the generation of excitons can be effectively suppressed and consequently the fluctuations in polymer chain size are greatly diminished. This remains consistent with the behaviors observed in the accompanying experiments, where any alterations

to experimental procedures that decrease the amount of excitons generated directly and predictably result in clear moderation of the observed light-induced structural changes.

This consistent and sensitive response of the change in conjugated polymer structure in solution by illumination by careful tuning of the illumination methodology presents expansive possibilities for application to device fabrication procedures. Given the proven relationship between polymer conformation in solution and final solid-state device architecture, applying light-driven techniques directly from the onset of common fabrication methods will result in a powerful, tunable, and non-intrusive control of final device morphology. Knowledge of the precise levels of illumination necessary to achieve a targeted structure could allow measured dosages of light via a combination of light exposure time, illumination intensity, wavelength controls, and careful solvent choice to enable control of conjugated polymer conformation throughout the fabrication of a given optoelectronic device. Opportunities exist for expanded control over device patterning via illumination of select areas of a surface with a customizable range of light intensities, wavelengths, and exposure times. By carefully limiting the wavelength of incident light exposure, specific functional conjugated polymers could be targeted for precise structural alteration within a dispersion containing co-component materials, which would remain entirely unaffected. Clearly the availability of in-situ light exposure as a non-destructive control over conjugated polymer conformation and the resultant optoelectronic active layer morphology emphatically expands the versatility of conjugated polymeric materials and offers exciting new possibilities for further application.

Conclusion

Small angle neutron scattering has been utilized to study the effects of varying incident light intensity, exposure time, and wavelength on the changes to conjugated polymer conformation in solution. These results further refine initial findings which demonstrate a consistent and powerful light-induced alteration of polymer structure of solvated conjugated polymers marked by a large and consistent decrease in polymer structural size upon exposure to white light, an effect believed to be driven by light induced deterioration of polymer-solvent interactions. By designing specific experiments to probe precise individual qualities of the relevant light exposure, the relationship between exciton density and the magnitude of subsequent conformational changes becomes clear. These studies reveal that the conformational effects occur gradually over a time period ranging on the order of hours, with their precise time sensitivity varying strongly as a function of initial solvent quality and total absorbable incident light intensity. The data suggests that increasing the number of excited species within the given conjugated polymer sample through prolonged light exposure times, increased light intensities, and targeted use of the ideal polymer absorption band consistently results in quicker realization and greater absolute magnitude of polymer structural changes. Thus by carefully managing the requisite light exposure methodology, conjugated polymer conformation in solution can be manipulated in-situ in a completely non-destructive manner, forming the basis for fabrication techniques permitting precisely controlled formation of device active layers. Further work exploring and refining these exciting new approaches to in-situ active layer manipulation opens the door to an array of possibilities centered around novel device fabrication and patterning methodologies.

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