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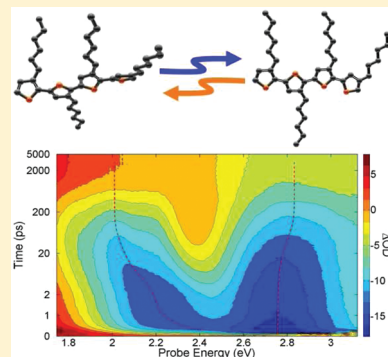
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 Supporting Information

ABSTRACT: Broadband femtosecond transient absorption spectroscopy is used to explore the mechanisms underlying excited-state and ground-state exciton relaxation in poly(3-hexylthiophene) (P3HT) solution. We focus on the picosecond spectral shifts in the ground and excited states of P3HT, using pump–probe (PP) and pump–dump–probe (PDP) techniques to investigate exciton relaxation mechanisms. Excited-state PP signals resolved a dynamic stimulated emission Stokes shift and ground-state reorganization; PDP signals resolved a blue-shifting nonequilibrium ground-state bleach. Initial structural reorganization is shown to be faster in the excited state. Ground-state reorganization is shown to be dependent on dump time, with later times resulting in relatively more population undergoing slow (~ 20 ps) reorganization. These observations are discussed in the context of structural relaxation involving small-scale (< 1 ps) and large-scale (> 1 ps) planarization of thiophene groups following photoexcitation. Excited-state and ground-state dynamics are contrasted in terms of electronic structure defining the torsional potential energy surfaces. It is shown that the primary excitonic relaxation mechanism is excited-state self-trapping via the torsional relaxation rather than exciton energy transfer.

SECTION: Kinetics, Spectroscopy



Polymer–fullerene mixtures have been intensely studied for use in organic solar cells and have, to date, demonstrated photoconversion efficiencies up to 8.3%¹ for organic cells and up to 5.4%² for devices using poly(3-hexylthiophene) (P3HT) as the donor polymer. The final efficiencies of such solar cells have been shown to be particularly sensitive to polymer morphology, including domain size, domain composition, polymer crystallinity, and fullerene aggregation.^{3,4} Photodynamics in these materials is complex, and understanding the dependence of primary excited-state processes on morphology is a critical step toward designing efficient devices. Excitonic transport and localization dynamics define both the time scales and mechanisms that lead to efficient charge transfer and device efficiency.^{5–7} Resolving the processes that manipulate exciton migration and localization has implications for charge transport in photovoltaic cells because they account for carrier migration across domain discontinuities, exciton quenching, and efficiency-reducing trapping.^{7–14} In order to optimize polaron mobility, charge collection, and therefore device efficiency, conjugation-extending dynamics associated with structural rearrangement following optical excitation must be well understood.^{15,16}

Time-resolved optical spectroscopy studies have yielded important information about the dynamic mechanisms controlling the photoelectrical efficiency of polymer devices,^{17–20} including

exciton and free-charge carrier dynamics.^{21–23} Recently, the following picture of primary photodynamics has emerged for P3HT films and aggregated solutions with comparable morphologies: (1) the primary photoexcitation generated on a polymer chain is considered a singlet Frenkel exciton that is initially delocalized over ~ 15 monomers. (2) This exciton quickly (≤ 100 fs) self-localizes to ≤ 10 monomers via structural distortion (self-trapping) processes.²⁴ (3) Through C=C vibrational relaxation, larger torsional relaxation, and excitonic energy transfer (EET), the exciton further relaxes.^{9,16,24} Steps 2 and 3 are accompanied by a large Stokes shift (~ 570 meV) in the emission spectrum.²⁴ These three steps constitute exciton self-trapping, which is well studied in solid-state P3HT systems.^{10,16,24} Amorphous P3HT systems, where significant aggregation and interchain π -stacking are not present, are not as clearly addressed in the literature. These amorphous polymer conditions play an important part in film microstructures²⁵ but are more easily studied in solution phase.

Theoretical and transient absorption/emission studies have presented arguments both for and against exciton localization by

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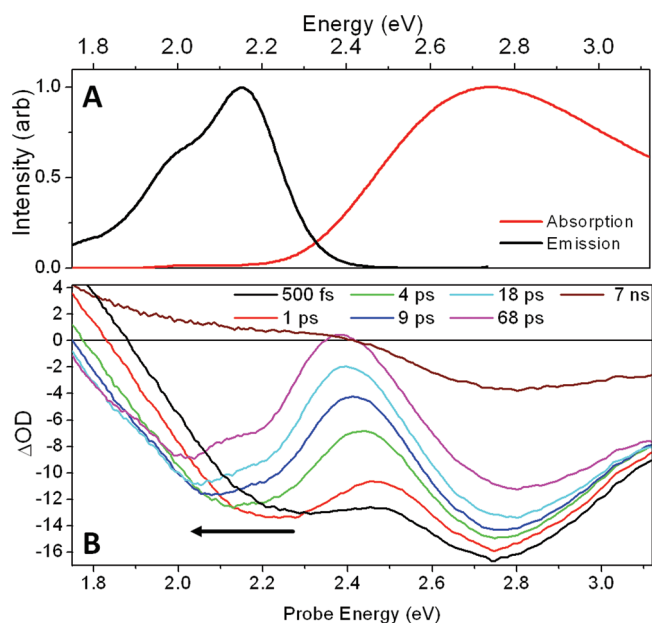


Figure 1. (A) Steady-state absorption and emission of RR-P3HT in chloroform are displayed. (B) Pump–probe data of P3HT in chloroform at varied probe delay times. The GSB (2.5–3.1 eV), SE (1.8–2.5 eV), and triplet exciton (1.7–2.3 eV at $t > 1$ ns) states are resolved. The arrow highlights the stimulated emission red shifting. The excitation energy is 3.1 eV.

conformational disorder in amorphous, solution-phase thiophene systems.^{24,26–28} The observed large dynamic Stokes shifts are generally attributed to either (1) EET between disordered conjugated segments and/or (2) self-trapping dynamics resulting in planarization and conjugation extension.^{11,24,28} Self-trapping, as discussed here, is defined as a monomolecular structural and/or vibrational relaxation resulting in the energetic stabilization of an exciton. Exciton localization was previously considered to result from stochastic excited-state self-trapping, as has been observed in other polymers like MEH-PPV.^{29,30} However, two-color three-photon echo peak shift (2C-3PEPS) experiments, performed by Blank and co-workers, found that the initial (<200 fs) exciton relaxation in low-concentration P3HT in chloroform is highly correlated⁹ and not the result of random dynamics. Instead, the initial Stokes shift is driven by coherent low-frequency torsional excited-state self-trapping, which reorganizes the polymer to lower the free energy of the exciton and creates a local minimum, or trap, on the excited-state potential energy surface. Bardeen and co-workers have characterized exciton dynamics in pristine MEH-PPV thin films using pump–dump–probe anisotropy spectroscopy and observed dump anisotropy decay caused by EET with a rate of exciton diffusion that decreases with time following excitation. Their results confirm that EET is a disorder-driven hopping process in aggregated films.³⁰ For P3HT in chloroform, femtosecond transient absorption anisotropy experiments show that depolarization kinetics could only be reproduced when a model utilizing both EET and torsional excited-state self-trapping was invoked.^{9,11} Currently, the extent and mechanism for excited-state self-trapping and/or EET in isolated P3HT have not been conclusively resolved.

To better understand these structural dynamics, femtosecond broadband pump–probe (PP) and pump–dump–probe (PDP) spectroscopies were used to resolve the excited-state and ground-state dynamics of regioregular (RR) P3HT in chloroform. The polymer is studied at low concentrations under single-strand

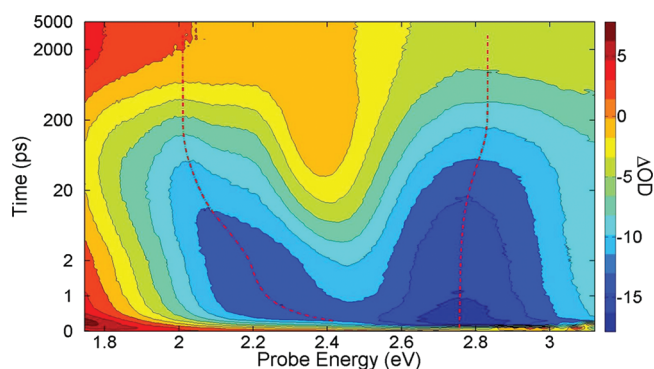


Figure 2. Time- and frequency-resolved transient absorption PP data in P3HT following excitation with 3.1 eV laser pulses. Blue shading indicates negative ΔOD signals (GSB or SE). Red shading indicates positive ΔOD signals (ESA). The peaks of the GSB and SE bands are highlighted. The excitation energy is 3.1 eV. Stimulated emission peak fits and parameters are displayed in Figure 4.

conditions without contributions from interchain interactions.^{10,31} While PP signals follow the exciton evolution along the excited-state potential energy surface, PDP signals follow the nonequilibrium ground-state (NGS) evolution along the ground-state potential energy surface as it relaxes to equilibrium. The PP technique probes excited-state processes like triplet formation, excited-state self-trapping, and EET, and the PDP technique probes ground-state processes like structural relaxation after excited-state distortion to the equilibrium ground-state geometry on the ground-state potential energy surface or, as applied by Bardeen and co-workers, excited-state energy transfer resulting in anisotropy decay.^{30,32,33}

The PP signals of P3HT (Figure 1) are characterized by a ground-state bleach (GSB) and a stimulated emission (SE) band, which red shifts by 200 meV over approximately 100 ps before evolving to a triplet exciton with a broad positive peak (Figure 1; 7 ns curve). The GSB also exhibits a small blue shift that is probably due to overlapping triplet absorption on the red side of the bleach. The spectral shifting dynamics of both the SE and GSB bands is best seen on a contour plot (Figure 2), which is shown with overlapping fits through the minima of the GSB and SE peaks at each time point (red curves)

A red-shifting stimulated emission is a signature of exciton relaxation to a lower-energy state, which may include excitonic energy transfer or relaxation. The observed SE shift is consistent with both excited-state self-trapping and EET hopping mechanisms (Figure 2). Because the P3HT sample is at a low concentration and the static spectra (Figure 1A) compare closely with known nonaggregated P3HT spectra,³¹ interchain contacts do not exist to facilitate significant interchain EET, which is commonly observed under aggregated solution or film sample conditions,¹⁰ and do not affect the photodynamics discussed here. Intrachain EET may exist, whereby nascent excitons can migrate to lower-energy regions of the polymer, which has been proposed by Pullerits and co-workers and Heeger and co-workers to explain red-shifting dynamics in amorphous P3HT in chlorobenzene with PP transient absorption and transient luminescence; however, the PDP data presented here provide new insight on the relaxation mechanism.^{24,34}

Both intrachain EET and excited-state self-trapping mechanisms exhibit red-shifting SE kinetics (Figure 2). To distinguish between the two, the spectral evolution of the GSB is considered, which provides some insight about the nature of the exciton

relaxation. When EET occurs, the excitation and, therefore, the bleach are effectively moving to lower-energy, more red-absorbing regions of the polymer chain. This induces a red-shifting SE band and a red shifting of the bleach and is commonly observed in the dynamics of multichromophore photosynthetic complexes.³⁵ Bleach shifting in P3HT would be unique to EET in amorphous systems. EET must result in a spectral shift under the studied conditions because the excitation is moving to a portion of the polymer that would be more red absorbing than the initially excited region. This does not apply to films because the *interchain* exciton formed in films will not necessarily result in a bleach shift. The lack of bleach shift in films is due to the *interchain* exciton signal being one that forms a new species rather than moving the excitation to a previously existing, red-absorbing segment of the polymer. Because this newly formed species is not optically accessible from the ground state, the bleach remains unchanged. If it were just transferring to another chain or to another segment in the same chain, bleach shift would be observed. It is however a delocalization across multiple chains, which would form a new state and thereby not result in a shifting GSB. For the excited-state self-trapping mechanism, the bleach would not display a time-dependent spectral red shift, and the GSB would be unaffected. Because there is no observed red shifting of the bleach for the P3HT PP signals (Figure 2), the data argue that excited-state self-trapping is mostly responsible for the red shift of the SE band rather than EET. EET cannot be completely ruled out, but there is no evidence for significant EET contribution.

To further investigate the excited-state exciton relaxation mechanism, regiorandom (RRa) P3HT, a form of P3HT differing from RR-P3HT by only the random arrangement of side-chain direction, was studied. The PP signals from RRa-P3HT demonstrate peak shift kinetics (Figure S11, inset, Supporting Information) comparable to RR-P3HT, however with a decreased peak shift amplitude (Figure S11, Supporting Information). The near-identical kinetics for RR- and RRa-P3HT indicate that identical relaxation mechanisms exist in both polymers. Given that the polymers are in amorphous, solvated conditions, the differences in dynamic Stokes shift amplitude must be attributed to differences in the extent to which an *intrachain* relaxation mechanism is able to proceed.³⁶ The excited-state planarization in RRa-P3HT proceeds, similarly to RR-P3HT, until the side-chain steric hindrance halts the torsional motion. Both the similar Stokes shift kinetics (Figure S11, inset, Supporting Information) and the differing Stokes amplitude (Figure S11, Supporting Information) are consistent with the torsional relaxation mechanism presented above.

PP measurements can be subject to overlapping signals from growth of excited-state absorption (e.g., triplet exciton or charge-separated states); to ensure that the lack of red shifting in the GSB in PP measurements was correctly interpreted, the ground-state evolution was investigated using PDP spectroscopy. In the dispersed PDP experiment, the first laser pulse (3.1 eV) generates an exciton population that evolves unhindered until dumped by a second laser pulse (2.07 eV) that is resonant with the stimulated emission and transfers exciton population to the ground electronic state. This ground-state population is then probed by a third pulse^{37,38} and the dynamics of this NGS population is best revealed in the $\Delta\Delta\text{OD}$ difference signals

$$\Delta\Delta\text{OD}(\lambda, t, \Delta) = \text{PDP}(\lambda, t, \Delta) - \text{PP}(\lambda, t) - \text{DP}(\lambda, \Delta, t) \quad (1)$$

Table 1. Fit Parameters for SE and NGS Peak Shifts (Figure 4)^a

	A_1	τ_1 (fs)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
SE	0.63	60	0.16	2	0.21	14
500 fs dump	0.62	200	0.23	0.7	0.15	20
1 ps dump	0.59	200	0.22	0.95	0.19	20
2 ps dump	0.48	200	0.27	1.2	0.35	20

^a Fits are a sum of three exponentials with pre-exponential factor A_n and time constant τ_n .

The PP, DP, and PDP signals in eq 1 are representative of the difference spectra of the pump–probe, dump–probe, and pump–dump–probe pulse sequences. The $\Delta\Delta\text{OD}$ signals show the change in optical density change due to the dump pulse as a function of wavelength (λ), the pump–probe time delay (t), and the dump time (Δ). This $\Delta\Delta\text{OD}$ signal tracks the ground-state evolution in a similar fashion to how the excited-state evolution is tracked in PP signals,^{30,32,39} with positive signals representing dump-pulse-induced depletions of both SE and GSB bands. The tracking of the ground-state evolution is the key advantage of the PDP technique over previously applied techniques; the evolution along the ground state can be directly observed to give important details on the structural and electronic configurations of P3HT. The PDP SE band dynamics tracks the SE dynamics in the PP signal and represents only the loss of the PP SE signal; hence, this contains no new information, and the peak maxima for both the PP SE and PDP SE signals overlap when plotted in the postdump (>2 ps) regime (not shown). The observed NGS signal demonstrates that the initially formed ground-state population is red shifted (~ 2.4 eV) from the thermally equilibrated ground-state population (2.74 eV) and subsequently blue shifts to form the equilibrated ground state. NGS and SE peak shifts are compared using a normalized peak shift function

$$S(t) = \frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)} \quad (2)$$

The kinetics of the NGS blue shift is sensitive to the dump time (Figure 4 and Table 1) in the time range over which half of the dynamic Stokes shift and primary exciton localization occur (<2 ps).²⁴ The initial and final NGS time scale (τ_1 and τ_3) are independent of dump time; however, the intermediate NGS shift component (τ_2) slows with later dump times. The ratio of fast (~ 200 fs) and slow (~ 20 ps) pre-exponential factors (Table 1) shows that later dump times results in relatively more population in the slower shift component, as would be expected with recovery from larger-scale excited-state planarization.

Kim et al. argued from Raman and resonant Raman signals that the ground-state structure of P3HT in chloroform is torsionally disordered with respect to inter-ring rotation.⁴⁰ Similarly to previous computational and transient absorption studies by Bishop and co-workers showing quinoidal rearrangement in PPV,⁴¹ upon excitation, the double bonds on the P3HT chain undergo rearrangement to form a quinoidal structure (Figure 5-1), thereby steepening the excited-state torsional potential energy surface.⁴² The newly relocated double bonds induce planarization to reduce π -bond angular strain (Figure 5-2). After the population is dumped to the ground electronic state, the inter-ring bonds are more single bond in character and are no longer constrained to be planar (Figure 5-3). The polymer will then relax back into the nonplanar equilibrated geometry (Figure 5-4).

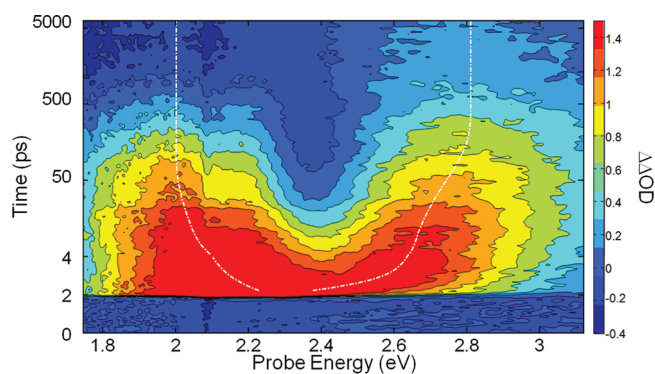


Figure 3. Time- and frequency-resolved $\Delta\Delta\text{OD}$ data in RR-P3HT. The dump time is 2 ps. The time is in picoseconds after the dump pulse. Depletion of GSB (2.5–3 eV) and SE (1.8–2.4 eV) is resolved. The blue shifting of the NGS and the red shifting of the stimulated emission bands are highlighted. The excitation energy is 3.1 eV. NGS peak fits and parameters are displayed in the caption of Figure 4.

Previous transient fluorescence studies by Heeger and co-workers have attributed structural relaxation to two time scales, including fast (small-scale, <1 ps) and slow (large-scale, >1 ps) torsional relaxation.²⁴ Substantial small-scale self-trapping (~ 100 meV) occurs in the first 500 fs,²⁴ and at later times, further excited-state relaxation (~ 100 meV) occurs on larger, presumably macromolecular scales.²⁴ In a recent molecular modeling study, Meijer and co-workers demonstrate that the ground-state inter-ring torsional angle of well-solvated P3HT in solution is a bimodal distribution centered at approximately 60 and 110° (with 0° being in-plane)²⁶ and that less than 5% of torsion angles satisfy conditions necessary for extended electronic conjugation. Unlike P3HT films,⁴³ the extent of ring-to-ring conjugation in the equilibrium ground state is minimal in well-solvated systems like chloroform, as presented in this study,²⁶ and may extend over only single monomers or dimers. The exciton quickly undergoes reorganization due to the steep excited-state potential energy surface introduced by the quinoidal rearrangement. The reorganization on the excited-state potential energy surface that occurs in the first 500 fs has a dramatic effect on the ground electronic state, as demonstrated by the dramatic NGS red shift (Figure 3). In agreement with results published on *p*-phenyleneethynylene by Yaron, Berg, and co-workers, the initial low extent of conjugation can cause even minor extension of conjugation through localized inter-ring torsional relaxation to result in a dramatic change on the ground-state potential energy surface.²⁷ The slower expansion of conjugation by large-scale planarization dynamics that occurs after the first few hundred femtoseconds has a less pronounced effect on the ground state than the excited state, which continues to exhibit significant red shifting. The slower, larger-scale rearrangement has little effect on the fast NGS reorganization (Figure 4 and Table 1) but does have an effect on slower NGS reorganization. At later dump times, there is slower NGS relaxation, which is consistent with more large-scale excited-state reorganization that occurs between 500 fs and 2 ps. This reorganization is likely from stochastic relaxation out of the nonequilibrium planarized structure and into a thermally occupied distribution of conformations on the ground-state potential energy surface.

To conclude, we have presented a novel, multi-pulse study of ultrafast photodynamics of P3HT in amorphous solution to dissect the primary spectral evolution of excitons in both the excited and ground electronic states. By applying PP and PDP

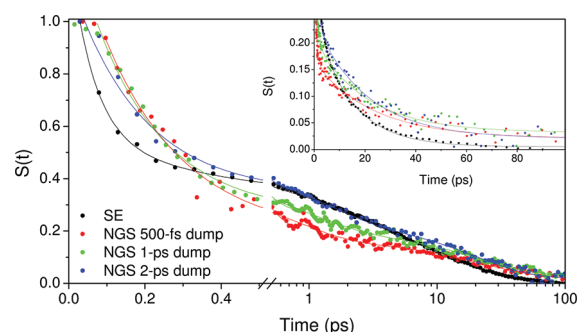


Figure 4. Comparison of spectral peak evolution (S) dynamics in RR-P3HT. Red shifting of the SE band and blue shifting of the NGS are compared. Exponential fits are displayed for traces (Table 1). The inset emphasizes the slower shifting kinetics of the NGS versus the SE at later times.

spectroscopy, the primary mechanism for excitonic relaxation is ascribed to excited-state self-trapping by torsional relaxation. In these conditions, we argue that both *interchain* and *intrachain* EET contributions are negligible. PDP spectroscopy is uniquely suited for analysis of structural relaxation and has been applied to examine the mechanism for relaxation on both the excited- and ground-state potential energy surfaces. Initial excited-state self-trapping is found to be substantially faster than the equivalent ground-state reorganization, which is ascribed to the excited-state quinoidal electronic structure imposing a steepened excited-state torsional potential energy surface. Primary photodynamics in these materials is complex, and understanding the dependence of primary excited-state processes on polymer morphology is an important step toward designing efficient devices. This study contributes to the basic understanding of exciton dynamics in P3HT, with particular impact on P3HT in amorphous conditions.

EXPERIMENTAL SECTION

Regioregular P3HT (92% regioregularity, Aldrich) and regiorandom P3HT (Aldrich) were dissolved in spectroscopic-grade chloroform (Aldrich) to form ~ 0.16 mg/mL solutions. Steady-state absorption spectra were measured with a Shimadzu UV-1700 UV/vis spectrophotometer, and emission spectra were collected using an Ocean Optics DH2000 light source and HR2000 CG-UV-NIR spectrometer. Dispersed transient absorption measurements were performed with the setup described in detail elsewhere,⁴⁴ but it is briefly described below. Pump pulses were made by frequency-doubling the Ti:Sapphire laser fundamental in a 0.1 mm β -barium borate crystal, producing 50 fs, 400 nm pulses ($42 \mu\text{J}/\text{cm}^2$). Dump pulses ($5 \mu\text{J}/\text{cm}^2$) were generated with a noncollinear optical parametric amplifier. Photoinduced absorption difference signals were monitored with an ultrafast white light continuum (340–800 nm) generated in a slowly translating 2 mm thick CaF_2 disk.

For the PDP measurements, the visible pulses were sent onto a computer-controlled translation stage (Newport) before being focused into the sample with the pump and probe beams. The transmitted probe light was spectrally dispersed and imaged onto a 256 pixel diode array and read on a shot-by-shot basis. Two optical choppers were used to modulate the pump pulses at 500 Hz and the dump pulses at 250 Hz to alternately obtain spectra under the four exposure combinations. From these spectra, PP, DP, and PDP difference spectra are calculated as

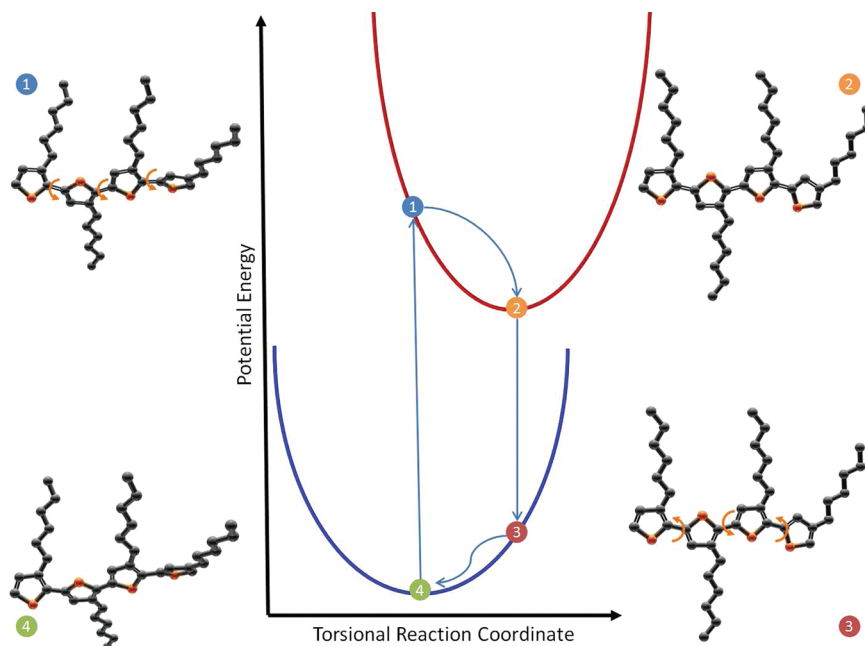


Figure 5. Excited-state self-trapping ($1 \rightarrow 2$) and ground-state torsional relaxation ($3 \rightarrow 4$) are depicted for a tetramer segment of P3HT. The steady-state structure (4) is excited, thereby causing double bond rearrangement to form the excited electronic state (1). The excited state undergoes excited-state self-trapping by planarization (2). The excited electronic state is depleted via stimulated emission to yield a planar NGS (3), which can then stochastically relax back to the equilibrium ground state (4). Torsional motion is highlighted with orange curved arrows.

$\Delta A = -\log(I(\lambda)_{\text{pumped}}/I(\lambda)_{\text{unpumped}})$. Pump and dump pulses were set to parallel polarization, and the white light was linearly polarized at a magic angle (54.7°) with respect to the pump and dump pulses.

■ ASSOCIATED CONTENT

S Supporting Information. Additional figures and captions, as referenced in the text of this Letter, are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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