# Origin of the Excited-State Absorption Spectrum of Polythiophene

Ras Baizureen Roseli, Patrick C. Tapping, and Tak W. Kee\*

Department of Chemistry, The University of Adelaide, South Australia 5005, Australia

E-mail: tak.kee@adelaide.edu.au Phone: +61-8-8313-5039

#### Abstract

The excited states of conjugated polymers play a central role in their applications in organic solar photovoltaics. The delocalized excited states of conjugated polymers are short-lived  $(\tau < 40 \text{ fs})$  but are imperative in the photoyoltaic properties of these materials. Photo excitation of poly(3-hexylthiophene) (P3HT) induces an excited-state absorption band but the transitions that are involved are not well understood. In this work, calculations have been performed on P3HT analogues using nonlinear response time-dependent density functional theory to show that an increase in the oligomer length correlates with the dominance of the  $S_1 \rightarrow S_3$  transition. Furthermore, the predicted transition energy shows an excellent agreement with experiment. The calculations also yielded results on intramolecular charge transfer in P3HT due to the  $S_1 \rightarrow S_3$  transition, providing insight into the mechanism of exciton dissociation to form charge carriers.

### Graphical TOC Entry



### Keywords

P3HT, density functional theory, CAM-B3LYP, intramolecular charge transfer, exciton dissociation

Organic solar cells are photovoltaic devices consisting of electron donor and acceptor semiconducting materials with domain sizes of several nanometers.<sup>1,2</sup> Photoexcitation of either the donor or acceptor materials leads to the generation of molecular excitons, which subsequently migrate to the donor-acceptor heterojunction to undergo dissociation to form the hole and electron on the donor and acceptor, respectively.<sup>3,4</sup> Owing to strong Coulombic forces between the hole and electron, these species can still interact across the heterojunction. For organic solar cells that exhibit a significant efficiency, including those composed of a conjugated polymer (donor) and fullerene (acceptor), however, an effective charge separation at the heterojunction has been attributed to rapid diffusion of charges.<sup>5,6</sup> In 2012, a study by Bakulin et al. suggested that delocalized states of the exciton play a role in the effective formation of separated charges.<sup>7</sup> More recently, Gélinas et al. used a combination of ultrafast transient absorption spectroscopy and modeling to show that long-range charge separation requires rapid motion of the hole and electron away from the heterojunction through delocalized states of the exciton.<sup>8</sup> Using the excited-state absorption (ESA) band of blends of a number of conjugated polymers and fullerene, it was shown that electron-hole separation occurs with a time constant of <40 fs.<sup>8</sup> Although the ESA band of conjugated polymers is often used to reveal insight into the dynamics of excitons and separated charges, the physical nature of the absorption band, particularly the transitions that are involved, is insufficiently understood.

Polythiophenes are some of the most widely studied conjugated polymers in organic solar cells.<sup>9</sup> Poly(3-hexylthiophene) (P3HT), as shown in Figure 1, is one of the most studied conjugated polymers.<sup>10,11</sup> Phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) is typically used alongside P3HT as an electron acceptor in a bulk-heterojunction organic photovoltaic device.<sup>12</sup> Regioregular P3HT can aggregate due to face-to-face  $\pi$ - $\pi$  stacking, resulting in crystallization and formation of nanofibers, which have long-range order.<sup>13,14</sup> The use of P3HT nanostructures in organic photovoltaics has led to an improved power conversion efficiency because of efficient exciton and hole transport.  $^{15-19}$ 



Figure 1: (Top) Chemical structure of regioregular P3HT. (Bottom) Two views of the optimized structure of the 3MT heptamer in the  $S_1$  state, showing a C-C-C-S dihedral angle (red asterisks on P3HT structure) of 0°.

The photophysical and photochemical properties of P3HT have been studied with femtosecond laser spectroscopy to reveal exciton lifetime,<sup>20</sup> torsional relaxation,<sup>21</sup> exciton hopping,  $^{22,23}$  self localization,  $^{24,25}$  charge transfer,<sup>26,27</sup> charge generation,<sup>3,28,29</sup> and exciton dissociation of P3HT.<sup>30,31</sup> Excited-state polythiophenes in solution exhibit a nearinfrared (NIR) absorption band centered at 1100 nm.<sup>20,32</sup> This induced absorption band, or an ESA band, <sup>30,33</sup> has been used to understand the relaxation dynamics of P3HT and charge transfer reaction with PCBM.<sup>27,28</sup> The NIR ESA band of P3HT films or aggregates has two components, that is, an exciton band at 1200 nm, which is a major component at early time, and a hole-polaron band at 1000 nm which is present several nanoseconds after charge separation.<sup>20,27,34</sup> Although there is vast literature on the ESA band of P3HT, a detailed understanding of the physical nature of this induced absorption band is still unavailable.

Recently, Ling et al. reported a computational study on the ESA of a different set of oligomers, namely, oligofluorenes, offering insight into the transitions that are involved.<sup>35</sup> These authors performed nonlinear-response time-dependent density functional theory (TD-DFT) calculations using the Coulombattenuated Becke 3-Parameter (Exchange), Lee, Yang, and Parr (CAM-B3LYP) functional on oligofluorenes ranging from the dimer to heptamer, showing that the NIR ESA band is due to a dominant  $S_1 \rightarrow S_5$  transition. The CAM-B3LYP functional has been employed in other recent computational studies of conjugated oligomers, showing high-level performance in predicting the physical and chemical properties of these systems.<sup>36-42</sup> In this study, the electronic properties of the  $S_1$  excited state of oligothiophenes are investigated using nonlinear-response TD-DFT. The computational methods used are shown in the Supporting Information (SI). The 3-hexylthiophene (3HT) oligometric are approximated using 3methylthiophenes (3MT), as shown in Figure 1. We have performed calculations to show that substitution of the hexyl side-chains of oligothiophenes with methyl groups has negligible influences on its electronic structure, as shown in Figure S1 in SI. In addition, we have also shown that the use of the CAM-B3LYP functional is crucial in obtaining the ESA spectrum that agrees with experiment, as shown in Figure S2.

The optimized structure of the heptamer in the  $S_1$  state is shown in Figure 1, highlighting the planar arrangement with a C-C-C-S (red asterisks) dihedral angle of  $0^{\circ}$ . The optimized structure in the  $S_0$  state is given in Figure S3 of SI, showing that the ground-state geometry is nonplanar with an average dihedral angle of  $\sim 30^{\circ}$ . The structures of other oligometrs are also shown in Figure S3, which agree with those by Bhatta et al. on 3HT oligomers.<sup>43</sup> In addition, Figure S4 shows that the length of the alkyl side-chains plays a negligible role in the optimized structure in the  $S_1$  state. In a vertical excitation, an electronic transition occurs from the  $\mathbf{S}_{0}$  to the  $\mathbf{S}_{1}^{*}$  state, which exhibits the greatest Franck-Condon overlap with  $S_0$ .

The subsequent relaxation from  $S_1^*$  to  $S_1$  induces planarization of the oligomers, which has been observed spectroscopically as a spectral shift in both ultrafast transient absorption and photoluminescence studies.<sup>21,25</sup> The torsional motions occur rapidly ( $\sim 100 \, \text{fs}$ ), lowering the excited-state energy and increasing the effective conjugation length of the oligomers, which is evident in the changes of the C-C and C=Cbond lengths in the  $S_0$  and  $S_1$  states. In the excited state, the shortening of the C-C and corresponding lengthening of the C=C bonds are characteristics of the aromatic-to-quinoid like transitions, indicating the presence of the exciton.<sup>44</sup> Interestingly, while the trimer displays a complete inversion to the quinoidal type geometry in the  $S_1$  state, this distortion remains limited to the central region for larger oligomers, with a spatial extent of about three thiophene units. For the heptamer, however, the terminal thiophene rings in the  $S_1$  state exhibit similar bond lengths to those in the  $S_0$  state, suggesting that it can support localization of the exciton. 45,46

Figure 2 shows the oscillator strengths of the ESA peaks of 3MT oligomers as a function of excitation energy. The ESA spectrum of the trimer has two contributions, that is, the  $S_1 \rightarrow$  $S_2$  and  $S_1 \rightarrow S_3$  transitions with similar oscillator strengths. In contrast, the ESA spectra of the tetramer and pentamer have three different contributions, arising from the former transitions and  $S_1 \rightarrow S_5$  transition. For the hexamer and heptamer, only the  $S_1 \rightarrow S_2$  and  $S_1 \rightarrow S_3$  transitions are the contributing transitions. The  $S_1 \rightarrow S_3$  transition, however, has a substantially higher oscillator strength than the  $S_1 \rightarrow S_2$  transition. Figure 2 also shows the significant increase in the oscillator strength of the  $S_1 \rightarrow S_3$  transition as the oligomer lengthens, with it being the dominant transition for the heptamer. The effect of solvent on the ESA spectrum was also investigated and Figure S5 in SI shows the insignificant difference between the calculated ESA spectrum in tetrahydrofuran and vacuum.

The  $S_1 \rightarrow S_3$  ESA peak position of the heptamer is close to the experimental value of P3HT, which is indicated by the dashed line



Figure 2: Calculated ESA peaks for 3MT oligomers. The excitation energies correspond to the transitions from the  $S_1$  state to a higher-lying  $S_n$  excited state, where *n* ranges from 2 to 5. The vertical dashed line indicates the experimental ESA peak position of P3HT.<sup>30</sup>

in Figure 2. Furthermore, the  $S_1 \rightarrow S_3$  energy gap of 3MT oligomers shows a red shift with oligomer length, as shown in SI (Figure S6), exhibiting a 1/n dependence, where n is the number of repeating units. This dependence has been observed for oligothiophenes<sup>47–49</sup> and suggests that only a minor decrease in the  $S_1 \rightarrow S_3$ energy gap is expected for any oligomers longer than the heptamer. Therefore, the heptamer system is sufficiently large to yield quantitative results for comparison with experiment. In this case, the experimental ESA peak position of P3HT chains is 1.17 eV and the predicted value for the heptamer  $(1.22 \,\mathrm{eV})$  differs by only  $<0.1\,\mathrm{eV}$ , showing a good agreement.<sup>30,32</sup> This result is similar to a previous study by Ling et al., in which the predicted and experimental ESA peaks of polyfluorenes differ by  $< 0.2 \,\mathrm{eV}$ .<sup>35</sup> In order to demonstrate the agreement, Figure 3 shows the experimentally measured ESA spectrum of P3HT<sup>30</sup> and the calculated spectrum of the heptamer. The calculated spectrum was broadened using a Gaussian function with a best-fit full width at half maximum of  $0.36 \,\mathrm{eV}$ . The difference between the two spectral peaks in Figure 3 is 0.07 eV. In the inset of Figure 3, the calculated spectrum is shifted by this minor energy difference, showing an excellent agreement to the experimental spectrum.<sup>30</sup>



Figure 3: ESA spectra of P3HT from experiment (red),<sup>30</sup> and as calculated for the 3MT heptamer (black). The inset shows an excellent agreement between the spectra when the calculated spectrum is shifted by  $-0.07 \,\text{eV}$ .

The reproduction the ESA spectrum of P3HT using such a simplified system and relatively

nonresource intensive computational method is initially surprising, given that the accurate calculation of the ground-state absorption spectrum of conjugated polymers can be challenging.<sup>39,50</sup> In solution, thermal and solvent effects cause the polymer to adopt a randomcoil geometry with a wide distribution of intermonomer angles and dihedrals. Consequently, the ground-state chromophores are highly disordered, and thus defining a chromophore precisely is a complex task.<sup>51–53</sup> Furthermore, the absorption spectrum is not solely due to any single chromophore but is composed of an ensemble of chromophores with a variety of environments and geometries. Choosing a representative selection of chromophores is a challenge, even before considering a suitable method and the associated computational costs. To address these obstacles, simulation of the optical properties of conjugated polymers is often performed using classical methods to obtain the polymer geometry and simplified quantum mechanical methods with the ability to scale to systems with hundreds or thousands of chromophores.<sup>49,54,55</sup> In contrast with the groundstate  $S_0$  geometry, the excited  $S_1$  state of P3HT is more ordered and well defined. As shown in Figure S3 and S4 in SI, the  $S_1$  state adopts a planar geometry, regardless of the side-chain substituents. While the vertical  $S_0 \rightarrow S_1^*$  excitation involves  $\sim 20$  thiophene units of a highly disordered chain, the exciton localizes to 5–10 monomeric units, driving the planarization of the chromophore site. Similar to the groundstate absorption, the ESA is also due to an ensemble of chromophores but in this case each individual chromophore can be sufficiently described as a planar oligothiophene of 5 to 10 monomeric units.

The excellent agreement between the measured ESA spectrum of P3HT and that of the 3MT heptamer calculated using TD-DFT with the CAM-B3LYP functional is consistent with a previous study.<sup>35</sup> Ling et al. showed that TD-DFT calculations using CAM-B3LYP produce ESA spectra that exhibit agreement with experiment,<sup>35</sup> demonstrating the importance of accounting for the long-range contributions to the electronic exchange interactions. In addition to excited-state properties, CAM-B3LYP includes charge-transfer contributions to electronic excitations. The application of CAM-B3LYP on predicting the charge-transfer properties of the excited states of a 3MT oligomer is discussed below. Additional results and further discussion on the choice of functional may be found in SI.

To reveal insight into the charge transfer character of the  $S_1 \rightarrow S_3$  transition, we turn to the electron density change involved in this transition. The electron density difference,  $\Delta \rho(r)$ , between the excited state and ground state can be evaluated as

$$\Delta \rho(r) = \rho_{\text{excited}}(r) - \rho_{\text{ground}}(r) \qquad (1)$$

where  $\rho_{\text{excited}}(r)$  and  $\rho_{\text{ground}}(r)$  are the electron densities of the excited and ground states at position r. There is, however, no direct method to calculate the electron density changes of the  $S_1 \rightarrow S_3$  transition. Therefore, eq 2 is used to relate the electron density changes of the  $S_1 \rightarrow$  $S_3$  transition to those of the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow$  $S_3$  transitions.

$$\Delta \rho_{\mathrm{S}_1 \to \mathrm{S}_3}(r) = \Delta \rho_{\mathrm{S}_0 \to \mathrm{S}_3}(r) - \Delta \rho_{\mathrm{S}_0 \to \mathrm{S}_1}(r) \quad (2)$$

This approach provides an indirect route to obtaining the electron density change between the  $S_1$  and  $S_3$  states. On the basis of eq 1, an increase in electron density corresponds to more "electron" character, while a decrease in electron density corresponds to more "hole" character.

Figure 4 shows the electron density difference calculated for the  $S_1 \rightarrow S_3$  transition of the heptamer. The increase in electron density is concentrated in the middle region of the oligomer, with the corresponding decrease occurring along the oligomer's ends, as indicated by the black arrows in Figure 4. The middle region of the 3MT heptamer undergoes a "switch" in the electron and hole positions in comparison with both the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_3$  transitions (SI, Figure S7). An increase in electron density occurs at the central sulfur atom for both the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_3$  transitions. For the  $S_1 \rightarrow S_3$  transition, however, the same sulfur atom shows an electron density decrease, indicating charge movement, or intramolecular charge transfer, along the backbone of the oligomer. This "switch" has also been observed by Denis et al. for the  $S_1 \rightarrow S_n$  transition compared with the  $S_0 \rightarrow S_1$  transition for fluorene homopolymers and fluorene-based copolymers.<sup>56</sup> The electron density difference for the  $S_1 \rightarrow S_3$  transition of other oligomers exhibits a similar behavior and is shown in Figure S8 in SI. The intramolecular charge transfer characters were also investigated using a natural transition orbital analysis and the results are shown in SI (Figure S9).



Figure 4: Electron density difference of the 3MT heptamer for the  $S_1 \rightarrow S_3$  transition, where the violet and turquoise regions represent the increase and decrease, respectively, in electron density. The arrows serve to highlight the movement of charge. The isosurface value used to visualize the electron density difference is 0.0005 Å<sup>-3</sup>

The intramolecular charge transfer process is a primary indicator of the capacity for an exciton to dissociate into free charge carriers. Experimentally, we have used transient absorption spectroscopy to demonstrate charge carrier generation in P3HT chains through targeted photo excitation of the ESA band.<sup>30</sup> We have used a femtosecond pump-push-probe technique to isolate the relaxation processes and products of the higher-lying  $S_n$  state. The computational work presented here offers new insight, confirming that charge carrier generation occurs on isolated polymer chains through an intramolecular charge-transfer intermediate. In the experiment, the visible pump-pulse vertically excites P3HT from the ground-state to form the  $S_1^*$ singlet exciton. The high-energy exciton then undergoes relaxation within  $\sim 100 \,\mathrm{fs}$  to the S<sub>1</sub> state. The NIR push-pulse is tuned to match

the ESA band, further exciting the  $S_1$  exciton to a high-energy state,  $S_n$ . From the results in this study (Figure 2), we can now assign the previously unknown  $S_n$  state to  $S_3$ . From the  $S_3$  state the exciton rapidly relaxes back to  $S_1$ , but in the experiment  $\sim 11\%$  of the S<sub>3</sub> exciton population directly returns to the ground-state rather than back through  $S_1$ . This phenomenon was attributed to dissociation of the exciton into electron and hole-polaron charge carriers. We have now shown that such dissociation on isolated chains is possible due to the charge transfer nature of the  $S_3$  state, where the movement of electrons occurs predominantly from the outer regions to the center of the chromophore. Because the separated electrons and holes are still spatially restricted to a single P3HT chain, geminate recombination occurs rapidly, resulting in a direct return to the  $S_0$  ground-state.

In short, we have used nonlinear response TD-DFT to gain insight into the ESA band of P3HT in the NIR region. Computational studies using the CAM-B3LYP functional have been conducted on the 3MT oligomers ranging from the trimer to heptamer to show that the ESA band corresponds to the  $S_1 \rightarrow S_3$  transition. The oscillator strength of this transition increases as a function of oligomer length and it becomes the dominant transition of the 3MT heptamer. The predicted energy of the  $S_1 \rightarrow S_3$  transition exhibits an excellent agreement with experiment. The results also reveal the charge transfer character of the  $S_1 \rightarrow S_3$  transition, which is consistent with experimental results on exciton dissociation because of optical pumping of the singlet exciton.

Acknowledgement This research was undertaken with the assistance of resources provided at the Phoenix High Performance Computing service at the University of Adelaide. We acknowledge the assistance of Mr. Rohan J. Hudson in the DFT calculations and Dr. David M. Huang for his comments and suggestions for this manuscript.

## Supporting Information Available

(1) Computational methods, (2) influence of side-chain substituents, functional, and solvation on computed excited state transitions, (3) geometry of 3HT and 3MT trimers, 3MT tetramer to heptamer optimized in  $S_0$  and  $S_1$  states, (4) calculated  $S_1 \rightarrow S_3$  transition energies with 3MT oligomer length, (5) electron density difference of 3MT heptamer for  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_3$  transitions, and  $S_1 \rightarrow S_3$  transitions for 3MT trimer to hexamer, (6) natural transition orbitals of the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_3$  transitions of the 3MT heptamer, (7) input commands to compute excited state absorptions using Dalton2016 software, (8) Cartesian coordinates for all molecular structures.

#### References

- Halls, J. J. M.; Walsh, C. A.; Greenham, N.; Marseglia, E. A.; Friend, R.; Moratti, S. C.; Holmes, A. Efficient Photodiodes from Interpenetrating Polymer Networks. *Nature* **1995**, *376*, 498–500.
- (2) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, *270*, 1789– 1791.
- (3) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* 2010, 110, 6736–6767.
- (4) Brédas, J.-L.; Norton, J. E.; Cornil, J.; Coropceanu, V. Molecular Understanding of Organic Solar Cells: The Challenges. Acc. Chem. Res. 2009, 42, 1691–1699.
- (5) Blom, P.; Mihailetchi, V.; Koster, L.; Markov, D. Device Physics of Polymer:fullerene Bulk Heterojunction Solar Cells. Adv. Mater. 2007, 19, 1551–1566.
- (6) Caruso, D.; Troisi, A. Long-range Exciton Dissociation in Organic Solar Cells. *Proc.*

Natl. Acad. Sci. U.S.A. **2012**, 109, 13498–13502.

- (7) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors. *Science* **2012**, *335*, 1340–1344.
- (8) Gélinas, S.; Rao, A.; Kumar, A.; Smith, S. L.; Chin, A. W.; Clark, J.; van der Poll, T. S.; Bazan, G. C.; Friend, R. H. Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes. *Science* **2014**, *343*, 512.
- (9) Hotta, S.; Soga, M.; Sonoda, N. Novel Organosynthetic Routes to Polythiophene and its Derivatives. *Synth. Met.* **1988**, *26*, 267–279.
- (10) Dang, M. T.; Hirsch, L.; Wantz, G.; Wuest, J. D. Controlling the Morphology and Performance of Bulk Heterojunctions in Solar Cells. Lessons Learned from the Benchmark Poly(3-hexylthiophene):[6,6]-Phenyl-C61-butyric Acid Methyl Ester System. Chem. Rev. 2013, 113, 3734– 3765.
- (11) Mehmood, U.; Al-Ahmed, A.; Hussein, I. A. Review on Recent Advances in Polythiophene Based Photovoltaic Devices. *Renewable Sustainable Energy Rev.* 2016, 57, 550–561.
- (12) Dang, M. T.; Hirsch, L.; Wantz, G. P3HT:PCBM, Best Seller in Polymer Photovoltaic Research. Adv. Mater. 2011, 23, 3597–3602.
- (13) Samitsu, S.; Shimomura, T.; Heike, S.; Hashizume, T.; Ito, K. Effective Production of Poly(3-alkylthiophene) Nanofibers by means of Whisker Method using Anisole Solvent: Structural, Optical, and Electrical Properties. *Macromolecules* 2008, 41, 8000–8010.

- (14) Sun, S.; Salim, T.; Wong, L. H.; Foo, Y. L.; Boey, F.; Lam, Y. M. A New Insight into Controlling Poly(3hexylthiophene) Nanofiber Growth Through a Mixed-solvent Approach for Organic Photovoltaics Applications. J. Mater. Chem. 2011, 21, 377–386.
- (15) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.
- (16) Vanlaeke, P.; Swinnen, A.; Haeldermans, I.; Vanhoyland, G.; Aernouts, T.; Cheyns, D.; Deibel, C.; DaHaen, J.; Heremans, P.; Poortmans, J. et al. P3HT/PCBM Bulk Heterojunction Solar Cells: Relation between Morphology and Electro-optical Characteristics. Sol. Energy Mater. Sol. Cells 2006, 90, 2150–2158.
- (17) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.-S. et al. A Strong Regioregularity Effect in Self-organizing Conjugated Polymer Films and High-efficiency Polythiophene:Fullerene Solar Cells. *Nat. Mater.* 2006, *5*, 197–203.
- (18) Marsh, R. A.; Hodgkiss, J. M.; Albert-Seifried, S.; Friend, R. H. Effect of Annealing on P3HT:PCBM Charge Transfer and Nanoscale Morphology Probed by Ultrafast Spectroscopy. *Nano Lett.* **2010**, *10*, 923–930.
- (19) Laquai, F.; Andrienko, D.; Mauer, R.; Blom, P. W. M. Charge Carrier Transport and Photogeneration in P3HT:PCBM Photovoltaic Blends. *Macromol. Rapid Commun.* **2015**, *36*, 1001–1025.
- (20) Cook, S.; Furube, A.; Katoh, R. Analysis of the Excited States of Regioregular Polythiophene P3HT. *Energy Environ. Sci.* 2008, 1, 294–299.

- (21) Parkinson, P.; Muller, C.; Stingelin, N.; Johnston, M. B.; Herz, L. M. Role of Ultrafast Torsional Relaxation in the Emission from Polythiophene Aggregates. J. Phys. Chem. Lett. 2010, 1, 2788–2792.
- (22) Wells, N. P.; Boudouris, B. W.; Hillmyer, M. A.; Blank, D. A. Intramolecular Exciton Relaxation and Migration Dynamics in Poly(3-hexylthiophene). J. Phys. Chem. C 2007, 111, 15404–15414.
- Wells, N. P.; Blank, D. A. Correlated Exciton Relaxation in Poly(3-hexylthiophene). *Phys. Rev. Lett.* 2008, 100, 086403.
- (24) Banerji, N.; Cowan, S.; Vauthey, E.; Heeger, A. J. Ultrafast Relaxation of the Poly(3-hexylthiophene) Emission Spectrum. J. Phys. Chem. C 2011, 115, 9726– 9739.
- (25) Busby, E.; Carroll, E. C.; Chinn, E. M.; Chang, L.; Moulé, A. J., A. J.e; Larsen, D. S. Excited-State Self-trapping and Ground-state Relaxation Dynamics in Poly(3-hexylthiophene) Resolved with Broadband Pump-dump-probe Spectroscopy. J. Phys. Chem. Lett. 2011, 2, 2764–2769.
- (26) Song, Y.; Clafton, S. N.; Pensack, R. D.; Kee, T. W.; Scholes, G. D. Vibrational Coherence Probes the Mechanism of Ultrafast Electron Transfer in Polymer– fullerene Blends. *Nat. Commun.* **2014**, *5*, 4933.
- (27) Clafton, S. N.; Huang, D. M.; Massey, W. R.; Kee, T. W. Femtosecond Dynamics of Excitons and Hole-polarons in Composite P3HT/PCBM Nanoparticles. J. Phys. Chem. B 2013, 117, 4626–4633.
- (28) Guo, J.; Ohkita, H.; Benten, H.; Ito, S. Charge Generation and Recombination **D**vnamics Polv(3inhexylthiophene)/fullerene Blend Films with Different Regioregularities and Morphologies. J. Am. Chem. Soc. 2010, 132, 6154-6164.

- (29) Chen, K.; Barker, A. J.; Reish, M. E.; Gordon, K. C.; Hodgkiss, J. M. Broadband Ultrafast Photoluminescence Spectroscopy Resolves Charge Photogeneration via Delocalized Hot Excitons in Polymer:Fullerene Photovoltaic Blends. J. Am. Chem. Soc. 2013, 135, 18502–18512.
- (30) Tapping, P. C.; Kee, T. W. Optical Pumping of Poly(3-hexylthiophene) Singlet Excitons Induces Charge Carrier Generation. *J. Phys. Chem. Lett.* **2014**, *5*, 1040–1047.
- (31) Kee, T. W. Femtosecond Pump-Push-Probe and Pump-Dump-Probe Spectroscopy of Conjugated Polymers: New Insight and Opportunities. J. Phys. Chem. Lett. 2014, 5, 3231–3240.
- (32) Kraabel, B.; Moses, D.; Heeger, A. J. Direct Observation of the Intersystem Crossing in Poly(3-octylthiophene). J. Chem. Phys. 1995, 103, 5102–5108.
- (33) Yu, W.; Magnanelli, T. J.; Zhou, J.; Bragg, A. E. Structural Heterogeneity in the Localized Excited States of Poly(3hexylthiophene). J. Phys. Chem. B 2016, 120, 5093–5102.
- (34) Guo, J.; Ohkita, H.; Benten, H.; Ito, S. Near-IR Femtosecond Transient Absorption Spectroscopy of Ultrafast Polaron and Triplet Exciton Formation in Polythiophene Films with Different Regioregularities. J. Am. Chem. Soc. 2009, 131, 16869–16880.
- (35) Ling, S.; Schumacher, S.; Galbraith, I.; Paterson, M. J. Excited-State Absorption of Conjugated Polymers in the Near-Infrared and Visible: A Computational Study of Oligofluorenes. J. Phys. Chem. C 2013, 117, 6889–6895.
- (36) Borges, I.; Uhl, E.; Modesto-Costa, L.; Aquino, A. J. A.; Lischka, H. Insight into the Excited State Electronic and Structural Properties of the Organic Photovoltaic Donor Polymer Poly(thieno[3,4b]thiophene benzodithiophene) by Means

of ab Initio and Density Functional Theory. J. Phys. Chem. C **2016**, 120, 21818– 21826.

- (37) Oliveira, E. F.; Roldao, J. C.; Milián-Medina, B.; Lavarda, F. C.; Gierschner, J. Calculation of Low Bandgap Homopolymers: Comparison of TD-DFT Methods with Experimental Oligomer Series. *Chem. Phys. Lett.* **2016**, *645*, 169–173.
- (38) Van den Brande, N.; Van Lier, G.; Da Pieve, F.; Van Assche, G.; Van Mele, B.; De Proft, F.; Geerlings, P. A Time Dependent DFT Study of the Efficiency of Polymers for Organic Photovoltaics at the Interface with PCBM. RSC Adv. 2014, 4, 52658–52667.
- (39) McCormick, T. M.; Bridges, C. R.; Carrera, E. I.; DiCarmine, P. M.; Gibson, G. L.; Hollinger, J.; Kozycz, L. M.; Seferos, D. S. Conjugated Polymers: Evaluating DFT Methods for More Accurate Orbital Energy Modeling. *Macromolecules* **2013**, *46*, 3879–3886.
- (40) Reish, M. E.; Nam, S.; Lee, W.; Woo, H. Y.; Gordon, K. C. A Spectroscopic and DFT Study of the Electronic Properties of Carbazole-Based D–A Type Copolymers. J. Phys. Chem. C 2012, 116, 21255–21266.
- (41) Limacher, P. A.; Mikkelsen, K. V.; Lüthi, H. P. On the Accurate Calculation of Polarizabilities and Second Hyperpolarizabilities of Polyacetylene Oligomer Chains using the CAM-B3LYP Density Functional. J. Chem. Phys. 2009, 130, 194114.
- (42) Zhang, S.; Qu, Z.; Tao, P.; Brooks, B.; Shao, Y.; Chen, X.; Liu, C. Quantum Chemical Study of the Ground and Excited State Electronic Structures of Carbazole Oligomers with and without Triarylborane Substitutes. J. Phys. Chem. C 2012, 116, 12434–12442.
- (43) Bhatta, R. S.; Yimer, Y. Y.; Tsige, M.; Perry, D. S. Conformations and Torsional

Potentials of Poly(3-hexylthiophene) Oligomers: Density Functional Calculations Up to the Dodecamer. *Comput. Theor. Chem.* **2012**, *995*, 36–42.

- (44) Tsoi, W. C.; James, D. T.; Kim, J. S.; Nicholson, P. G.; Murphy, C. E.; Bradley, D. D. C.; Nelson, J.; Kim, J.-S. The Nature of In-Plane Skeleton Raman Modes of P3HT and Their Correlation to the Degree of Molecular Order in P3HT:PCBM Blend Thin Films. J. Am. Chem. Soc. 2011, 133, 9834–9843.
- (45) Gierschner, J.; Cornil, J.; Egelhaaf, H.-J. Optical Bandgaps of π-Conjugated Organic Materials at the Polymer Limit: Experiment and Theory. Adv. Mater. 2007, 19, 173–191.
- (46) Barford, W.; Lidzey, D. G.; Makhov, D. V.; Meijer, A. J. H. Exciton Localization in Disordered Poly(3hexylthiophene). J. Chem. Phys. 2010, 133, 044504.
- (47) Bidan, G.; De Nicola, A.; Enée, V.; Guillerez, S. Synthesis and UV–visible Properties of Soluble Regioregular Oligo(3-octylthiophenes), Monomer to Hexamer. *Chem. Mater.* **1998**, *10*, 1052–1058.
- (48) Zhao, M.; Singh, B. P.; Prasad, P. N. A Systematic Study of Polarizability and Microscopic Third-order Optical Nonlinearity in Thiophene Oligomers. J. Chem. Phys. 1988, 89, 5535–5541.
- (49) Tapping, P. C.; Clafton, S. N.; Schwarz, K. N.; Kee, T. W.; Huang, D. M. Molecular-Level Details of Morphology-Dependent Exciton Migration in Poly(3hexylthiophene) Nanostructures. J. Phys. Chem. C 2015, 119, 7047–7059.
- (50) Böckmann, M.; Doltsinis, N. L. Can Excited Electronic States of Macromolecules with Extended Pi-systems be Reliably Predicted? A Case Study on P3HT. Front. Mater. 2015, 2, 25.

- (51) Beenken, W. J. D.; Pullerits, T. Spectroscopic Units in Conjugated Polymers: A Quantum Chemically Founded Concept? J. Phys. Chem. B 2004, 108, 6164–6169.
- (52) Barford, W.; Marcus, M. Theory of Optical Transitions in Conjugated Polymers. I. Ideal Systems. J. Chem. Phys. 2014, 141, 164101.
- (53) Marcus, M.; Tozer, O. R.; Barford, W. Theory of Optical Transitions in Conjugated Polymers. II. Real Systems. J. Chem. Phys. 2014, 141, 164102.
- (54) Ma, H.; Qin, T.; Troisi, A. Electronic Excited States in Amorphous MEH-PPV Polymers from Large-Scale First Principles Calculations. J. Chem. Theory Comput. 2014, 10, 1272–1282.
- (55) Wang, L.; Beljonne, D. Optical Properties of Regioregular Poly(3-hexylthiophene) Aggregates from Fully Atomistic Investigations. *CrystEngComm* **2016**, *18*, 7297– 7304.
- (56) Denis, J.-C.; Ruseckas, A.; Hedley, G. J.; Matheson, A. B.; Paterson, M. J.; Turnbull, G. A.; Samuel, I. D. W.; Galbraith, I. Self-trapping and Excited State Absorption in Fluorene Homo-polymer and Copolymers with Benzothiadiazole and Tri-phenylamine. *Phys. Chem. Chem. Phys.* **2016**, *18*, 21937–21948.