

Fast Singlet Exciton Decay in Push–Pull Molecules Containing Oxidized Thiophenes

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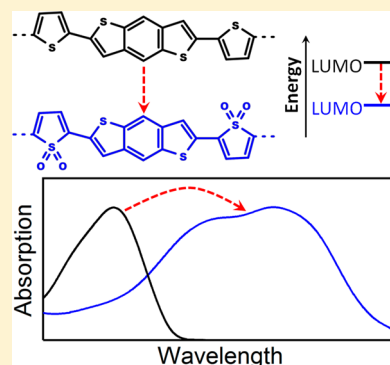
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Supporting Information

ABSTRACT: A common synthetic strategy used to design low-bandgap organic semiconductors employs the use of “push–pull” building blocks, where electron-rich and electron-deficient monomers are alternated along the π -conjugated backbone of a molecule or polymer. Incorporating strong “pull” units with high electron affinity is a means to further decrease the optical gap for infrared optoelectronics or to develop n-type semiconducting materials. Here we show that the use of thiophene-1,1-dioxide as a strong acceptor in “push–pull” oligomers affects the electronic structure and carrier dynamics in unexpected ways. Critically, the overall excited-state lifetime is reduced by several orders of magnitude relative to unoxidized analogs due to the introduction of low-energy optically dark states and low-energy triplet states that allow for fast internal conversion and intramolecular singlet fission. We found that the electronic structure and excited-state lifetime are strongly dependent on the number of sequential thiophene-1,1-dioxide units. These results suggest that both the static and dynamical optical properties are highly tunable via small changes in chemical structure that have drastic effects on the optoelectronic properties, which can impact the types of applications that involve these materials.



INTRODUCTION

A common strategy used to synthesize low-bandgap organic semiconductors is based on conjugating “push–pull” monomers, in which an electron-rich unit (“push”) and an electron-deficient unit (“pull”) are covalently linked to form the backbone of an oligomer or polymer.^{1,2} As a result, the primary optical transition within this class of materials can have significant charge-transfer character and is lower in energy than the corresponding analog of repeating push or pull units alone. The resulting low-bandgap polymers have been widely employed in organic photovoltaic devices,³ leading to single junction cells demonstrating >8% power conversion efficiency.⁴ Using modular building blocks allows for fine-tuning of the hybrid orbitals, where the highest occupied molecular orbital (HOMO) is mainly affected by the “push” units and the lowest unoccupied molecular orbital (LUMO) is affected by the “pull” units.^{5,6} This control of electronic structure is key to maximizing light absorption and photocurrent generation to increase the efficiency of organic photovoltaic devices. This is particularly important because voltage losses are incurred if there is suboptimal alignment between the energy levels of the organic semiconductor and acceptor molecules (e.g., fullerenes).⁷

Interest in near-infrared and n-type organic optoelectronic devices has led to the exploration of various polymer and small molecule materials with increased electron affinity (lower

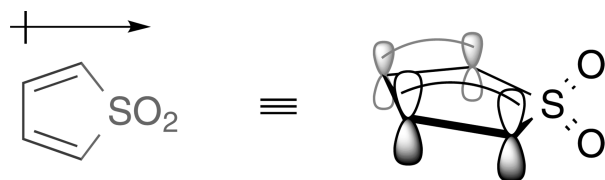
LUMO levels).^{8–11} While this has resulted in the development of stable electron transporting materials and narrow optical gap semiconductors, the effect of using strong acceptor units on the photophysics of conjugated materials has not been thoroughly explored. Because many strong acceptors impart oligoene character (in the ground state) or quinoidal character (in the excited state), the electronic structure of the resulting push–pull materials and the corresponding relaxation dynamics may be significantly altered relative to the aromatic electronic structure of materials bearing weak acceptor units.¹² An interesting building block for organic electronics is thiophene-1,1-dioxide (TDO, Scheme 1).^{13,14} This moiety has particular utility because materials containing thiophene groups, a common unit in organic semiconductors with well-understood chemistry, can be controllably oxidized to yield the TDO analogs.^{15,16} Furthermore, TDO-containing polymers have been recently shown to exhibit high-efficiency intramolecular singlet fission, rendering them interesting candidates for third-generation solar devices employing multiexciton generation schemes to increase efficiency beyond the Shockley–Queisser limit.¹²

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Scheme 1. Chemical Structure of Thiophene-1,1-dioxide, Emphasizing the Diene Electronic Structure and Polar Character



Thiophene-1,1-dioxide (TDO)

Here we examine the carrier dynamics of push–pull oligomers containing TDO strong acceptor units and show how the electronic structure is dramatically altered as compared with the unoxidized control units. In particular, the reduction of the optical gap is accompanied by the development of oligoene-like electronic structure that leads to fast carrier relaxation. This occurs via internal conversion through a low-energy dark state and an intramolecular singlet fission process, which produces short-lived triplet pairs. This drastically impacts the overall excited-state lifetime, which is reduced by several orders of magnitude relative to unoxidized analogs. In this manuscript, we examine the relationship between the oligoene-like electronic structure and the emergence of charge-transfer character in the optically excited singlet state, the formation of low-energy triplet states, and internal conversion through a dark excitonic state. On the basis of these findings, we suggest strategies for utilizing TDO and related acceptor units in light-harvesting applications, consistent with recent reports of

tunable electronic properties of TDO-containing compounds.^{12,17}

EXPERIMENTAL SECTION

We synthesized “push–pull”-type small molecules containing benzodithiophene (B) as the electron-rich unit in a series of molecules coupled to one to three TDO units flanking both sides (BTDO1, BTDO2, BTDO3, respectively) as strong electron acceptors and a thiophene on each end as the terminal subunit (Figure 1). An unoxidized parent compound with three thiophene units (BT3) is also examined here for comparison. Commercially available chemicals were purchased from Sigma-Aldrich and used as received. The synthesis of BT3, BTDO1, and BTDO2 has been described previously,¹² and details of the synthesis of BTDO3 are given in the Supporting Information (SI). In brief, the oligomer materials were synthesized using the palladium-catalyzed Stille coupling reaction, and thiophene-1,1-dioxide (TDO)-based acceptor units were prepared using Rozen’s reagent according to published procedures.¹⁵

Optical attenuation spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Electrochemical measurements were performed using a Princeton Applied Research Parastat 2273-SYS in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) and dichloromethane solution with glassy carbon, platinum wire, and Fc/Fc⁺ as the working, counter, and reference electrodes, respectively. Square-wave mode was used to reduce hysteresis due to background charging. Oxidation and reduction scans were performed separately and compared against a background scan recorded under identical conditions but containing only electrolyte solution (SI).

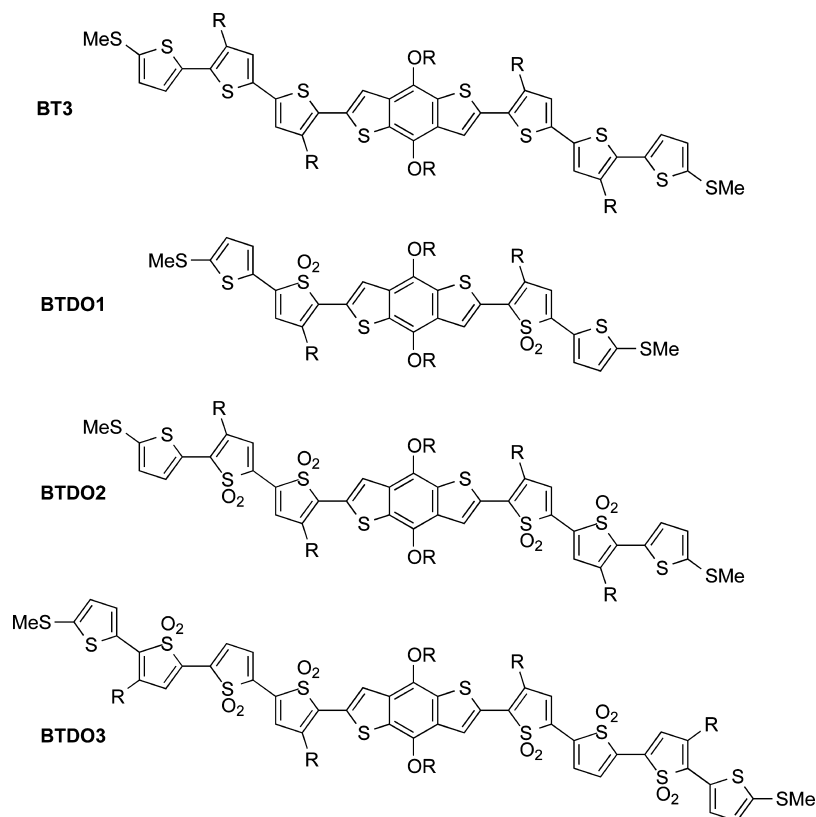


Figure 1. Molecular structures of control (BT3) and thiophene dioxide containing “push–pull” molecules. The number of consecutive thiophene dioxide units is systematically varied from one to three, which primarily affects the excited-state energy level alignment.

Transient absorption measurements were performed using a regeneratively amplified Ti:sapphire laser system (Spectra-Physics, Spitfire Pro) operating at 1 kHz. Ultrafast (~ 100 fs) excitation pulses were generated via a commercial optical parametric amplifier (TOPAS, Light Conversion) and were tuned to resonantly excite the material under study. A portion of the laser fundamental (800 nm) was focused onto a sapphire substrate to generate a broadband supercontinuum probe pulse. Fast multichannel array detectors were used for shot-by-shot detection of the signal and reference beams. The temporal overlap of the pump and probe beams was controlled using a mechanical delay stage. All data shown in this manuscript are from dilute solutions under ambient conditions using chloroform as a solvent. We note that the TDO-containing materials studied here are stable under ambient conditions in solution or solid state, at least for several months.

To separately determine the contributions in the transient signal from different quasiparticles (e.g., singlet and triplet excitons), we used global target analysis (GTA), a differential equations approach to multidimensional data set modeling and deconvolution.^{18,19} In brief, we constructed a finite number of populations and used a set of rate constant to describe the connectivity between these populations. These parameters were used to solve a system of first-order differential equations to generate time-dependent populations, which could then be used as a basis set to fit the complete experimental transient absorption data set. This process was iteratively optimized until satisfactory convergence is achieved. Crucially, this allowed us to separate spectrally overlapping signals based on their different kinetic behavior and describe the dynamical evolution of the different quasiparticle populations. In the TDO-containing materials, the optically excited $1B_u$ state decayed within the instrument response by either internal conversion or singlet fission, and as such, we built a model in which two subpopulations ($2A_g$ and triplet pair) were impulsively generated. These states were populated with a parameter describing the branching ratio and were allowed to decay independently to repopulate the ground electronic state. We note that the resulting deconvoluted spectra of the $2A_g$ and triplet pair were independent of the derived branching ratio.

Computational chemistry studies were performed with molecular geometries optimized with density functional theory (DFT) using the B3LYP functional for the ground state and with its linear-response time-dependent (TDDFT) formalism for the bright state. To compare the doubly excited dark state with the singly excited bright state, we used the restricted active space configuration interaction (RASCI) method, whose RAS(4,4)-2SF variation has been shown to be sufficient for studying these states.²⁰ All calculations were carried out with the 6-31G* basis set using the Q-Chem package.²¹

RESULTS AND DISCUSSION

Electronic and Optical Properties of TDO Containing Molecules. When conjugated with an appropriate “push” unit, the larger electron affinity of TDO relative to thiophene causes significant changes to the overall electronic structure and optical properties. These changes can be readily observed in the optical attenuation spectra of the materials in solution (Figure 2a). The BT3 oligomer contains the push unit conjugated to two sets of three flanking thiophenes. As a result, its optical attenuation spectrum shows a relatively large optical gap, with an onset energy of 2.3 eV and a peak energy of ~ 2.85 eV. Notably, the absorption spectrum is very similar to

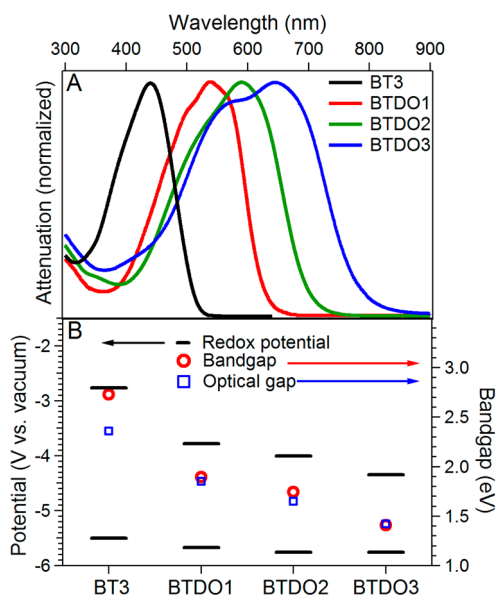


Figure 2. (A) Normalized optical attenuation spectra of thiophene and thiophene dioxide containing small molecules. The absorption spectra of these systems systematically red shift as the number of consecutive thiophene dioxide units increases. (B) Summary of cyclic voltammetry measurements showing the bandgap and redox potentials, which show that the change in the bandgap primarily results from stabilization of the LUMO. The optical gap is also plotted for comparison.

sexithiophene oligomers,^{22,23} indicating that the amount of charge-transfer character that develops due to electronic interaction with the benzodithiophene unit is small. However, upon thiophene oxidation, a dramatic reduction in the optical gap is observed, with the difference between the peak absorption of BT3 and BTDO3 approaching 1 eV. The peak in the optical absorption occurs at considerably lower energy than terthiophene-1,1-dioxide by itself,¹⁵ establishing that the low-energy absorption feature arises due to increased charge transfer character. Furthermore, the absorption energy is strongly dependent on the number of flanking TDO units, such that the trend in the optical gap decreases in the order BT3 > BTDO1 > BTDO2 > BTDO3. We also note that we do not observe photoluminescence in the TDO-containing materials studied here.

The LUMO energy level of the push–pull oligomers shifts to lower energies, resulting in a decreased optical gap. We have used cyclic voltammetry (CV) measurements to quantify the oxidation and reduction potentials of these materials (details in SI). The results are summarized in Figure 2b and compared with the trend in the optical spectra. From these data, we can clearly see that the LUMO level decreases (relative to vacuum) with an increasing number of TDO units and furthermore that the change in the optical absorption is solely derived from changes in the LUMO level of the different materials. In other words, the LUMO level is primarily defined by the TDO electron withdrawing substituent; the HOMO energy is not significantly affected by the thiophene oxidation. Similarly, the effect of thiophene oxidation has also been shown to increase LUMO conductivity and, with the incorporation of several sequential TDO subunits, to result in n-type conductivity.¹⁴ As in the optical spectra, an ~ 1 eV change in the electron affinity is observed between BT3 and BTDO3.

Carrier Dynamics and Transient Optical Properties. Using femtosecond transient absorption spectroscopy (TA) we

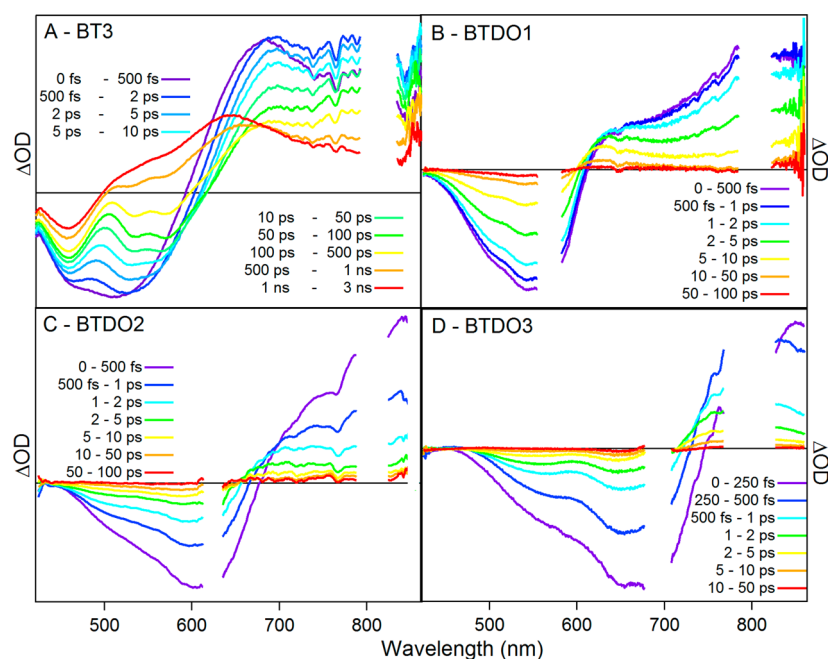


Figure 3. Raw transient absorption spectra of (A) BT3, (B) BTDO1, (C) BTDO2, and (D) BTDO3 showing in the visible and near-infrared regions. The data have been chirp-corrected and binned into discrete time intervals to illustrate the fast spectral evolution in the different molecules. Because of the presence of pump wavelength scatter and detector saturation near the laser fundamental (800 nm), small regions of the data have been excluded for clarity.

observe that the reduction in the optical gap and increase in electron affinity are accompanied by dramatic changes in the excited-state relaxation dynamics. In the unoxidized BT3 molecules, we observe dynamics that are typical of aromatic semiconducting oligomers and polymers, such as polythiophene (Figure 3A). A singlet exciton is formed upon light absorption, as evidenced by the presence of a stimulated emission band ($500 < \lambda < 600$ nm) in the TA spectrum. Over the first tens of picoseconds, the singlet exciton undergoes structural/torsional relaxation on the excited-state potential energy surface and displays a resulting stimulated emission red shift, as is commonly observed for solution-phase polymers.²⁴ Similar to previous observations in polythiophene,²⁴ some singlet excitons undergo intersystem crossing on a time scale of several hundreds of picoseconds. These triplet excitons and their associated photoinduced absorption (PIA) band ($500 < \lambda < 800$ nm) then persist for longer than the 3 ns duration of the TA experiment.

The excited-state dynamics of the systems containing oxidized thiophene are markedly different than their unoxidized counterpart (Figure 3B–D). The most striking difference is the excited-state lifetime, which is several orders of magnitude shorter in TDO-containing systems compared with BT3. The oxidized systems show two PIA features. The first (PIA1) is a broadband nIR absorption peaking at 800, 850, and >850 nm for BTDO1, BTDO2, and BTDO3, respectively. The second feature (PIA2) is a broad feature peaking at 630, 700, and 750 nm for BTDO1, BTDO2, and BTDO3, respectively.

To properly assign the spectral features in the TDO-containing systems, we first discuss the electronic modification caused by the thiophene oxidation. As previously noted,^{12,25} oxidation of the thiophene sulfur results in oligoene-like behavior due to reduced sulfur lone-pair participation in the π -bonding network. This electronic modification changes the thiophene unit from an aromatic 6π -electron system to an

oligoene-like 4π -electron system, which stabilizes a dark electronic state to a level below the bright excitonic state. In orbital symmetry nomenclature (C_{2h} point group), oxidation results in a stabilization of the $2A_g$ singlet dark state such that it lies between the $1A_g$ ground state and the optically coupled $1B_u$ bright state. We assign PIA1 to a transition from the $2A_g$ dark state to a higher-lying singlet state. (PIA from the photoexcited $1B_u$ state is not observed because it decays within the 100 fs instrument response.)¹² The second PIA feature in the TDO-containing systems is absorption from a triplet excitonic state (T_1). In addition to the stabilization of the $2A_g$ dark state, thiophene oxidation also significantly stabilizes triplet electronic states in these materials, such that the triplet energy is equal to or less than half of the singlet energy. As a result, a pair of triplets can be rapidly formed by intramolecular singlet fission. This assignment has been rigorously confirmed in our previous work using a combination of pulse radiolysis triplet transfer and TA experiments.¹²

In all TDO-containing systems studied here, both $2A_g$ and T_1 PIA bands are formed within the ~ 100 fs instrument response. The $2A_g$ state is populated by sub-100 fs internal conversion (IC) from the initially populated $1B_u$ state, as observed in other $4n \pi$ -electron systems.²⁶ The formation of this state, followed by a second internal conversion process to repopulate ground state ($1A_g$), serves as the primary deactivation pathway for singlet excitons. Ground-state repopulation from the singlet manifold occurs within the first few ps, with a lifetime that dramatically decreases with increasing TDO content, from 4.2 ps in BTDO1 to only 0.2 ps in BTDO3. In competition with (unobserved) relaxation from the optically pumped $1B_u$ state to the lowest energy $2A_g$ singlet state, the triplet T_1 state is populated via singlet fission due to the emergence of a low-energy triplet in the TDO containing molecules. The fission rate is not resolved because the formation of triplets ceases once the $2A_g$ dark state is fully populated (<100 fs). After

formation, the triplet T_1 decays back to the ground state with a rate distinctly slower than of internal conversion. Because fission results in triplet pairs ($2\times T_1$), the triplet decay observed here is much faster than typical triplet decay via intersystem crossing or phosphorescence. The difference arises from the spin-allowed, intramolecular triplet–triplet annihilation, which can act as an ultrafast decay mechanism. Interestingly, we find that the $2\times T_1$ decay rate is strongly dependent on the number of TDO units. The singlet fission yield can be estimated by comparing the relative magnitude of the fast and slow components in the ground-state bleach recovery, which correspond to the decay of singlet and triplet populations, respectively. The triplet yields range from 20 to 40% for excitation at the optical gap and are weakly dependent on the number of TDO units. We can understand the variation in yields as resulting from kinetic competition between internal conversion out of the $1B_u$ state and singlet fission; these rates will depend critically on the electronic structure of the oligomer. The evolution of the electronic structure with the number of TDO units is discussed in more detail later.

To deconvolute the $2A_g$ and T_1 PIA spectra and ensure that the proposed kinetic model (Figure 4, inset) appropriately describes the TA data sets, global target analysis (GTA) was conducted. GTA is detailed elsewhere^{18,19} but briefly described

in the methods section. To model the excited-state dynamics we construct a scheme (Figure 4, inset) describing the dynamics wherein the initial excitation populates a bright excitonic state that is deactivated by competing internal conversion to a dark excitonic state and singlet fission to form a pair of triplets within the 100 fs instrument response. The resultant dark-state excitons and triplet pairs then decay independently to replenish the ground electronic state. This model provides a sufficient description of the observed dynamics in the BTDO_n systems and separates the contributions of the otherwise temporally overlapped $T_1 \rightarrow T_n$ and $2A_g \rightarrow nB_u$ difference spectra (Figure 4). We note that red shifts in the linear absorption maxima (and the corresponding negative ground-state bleach signals in the transient data) are accompanied by similar red shifts in the positive photoinduced absorption features of the $2A_g$ and T_1 states. These methods allow us to unambiguously establish the transient optical signature and dynamics of triplet pair states formed via singlet fission and allow for clear comparison with single triplet states formed via sensitization experiments.¹²

Scaling of Energy Levels in TDO Containing Molecules. While all of the BTDO_n compounds behave in qualitatively similar ways, the dynamics show a clear quantitative dependence on the number of sequential TDO moieties in the molecule. To provide the context in which to discuss these trends, we first turn to quantum chemistry calculations using the RAS(4,4)-2SF method. We identify the first bright state, a singly excited state, as the $1B_u$ state, and the first dark state, a doubly excited state, as the $2A_g$ state. Although this method overestimates the absolute excitation energies, it reliably calculates the energy levels of these two states relative to one another and calculates the trend in the energy of each state across the BTDO_n series (Figure 5B).

The calculated energy difference between the $1A_g$ to $1B_u$ energy levels reproduces the experimental trend in which the optical gap decreases with increasing TDO units (Figure 2A). Experimentally, the normalized optical transition energies decrease by $\sim 10\%$ from BTDO1 to BTDO2 and 20% in BTDO3. Our calculations agree quantitatively for BTDO2 but predict a less dramatic shift for BTDO3 ($\sim 13\%$). Additionally, in all materials the $2A_g$ dark state lays below the optically coupled $1B_u$ state at the relaxed TDDFT geometry, which agrees with the above observation of fast internal conversion through an optically dark state. Importantly, the RASCI calculation shows that both relevant electronic states are stabilized by the incorporation of additional TDO moieties but that the $2A_g$ dark state is more sensitive to the number of sequential TDO subunits (Figure 5B). Energetically, this results in a reduction of the $1A_g$ -to- $2A_g$ energy gap as the number of TDO units increases (with normalized energies of 1, 0.8, and 0.7 for BTDO1–3, respectively). This trend provides context in which to interpret the above transient absorption results. The observed $2A_g$ -to- $1A_g$ internal conversion rate increases as the number of sequential TDO moieties increase (Figure 5A, fast component in BTDO_n traces). This increase in rate is correlated with the decrease in the amount of energy dissipated by the internal conversion process (Figure 5B, ΔE_{IC2}). This trend can be interpreted as a result of the energy gap law that has been previously observed in radiation-less transitions in organic molecules.²⁷

The observed decrease in the $2A_g$ dark-state energy level is a function of TDO-induced stabilization of oligoene-like excited-state electronic structure and the associated quinoidal

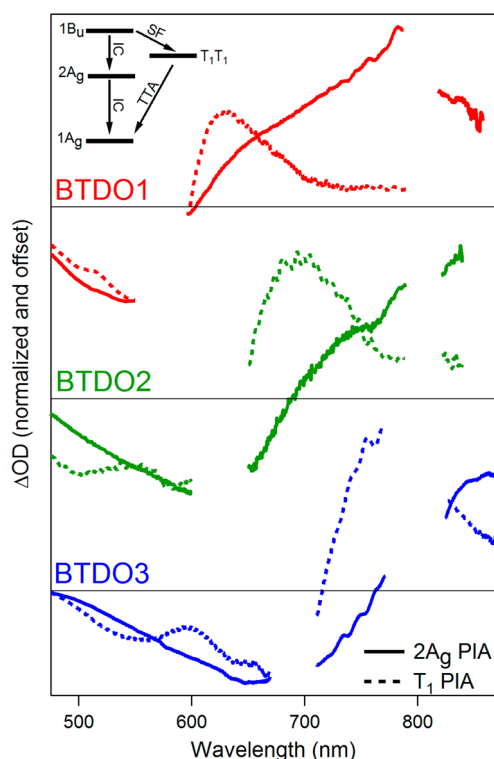


Figure 4. Deconvoluted singlet and triplet transient spectra for BTDO1–3 obtained using global target analysis. Data have been excised from regions obscured by excitation or fundamental (800 nm) scatter. The singlet photoinduced absorption signal in the NIR is dominated by the $2A_g \rightarrow nB_u$ transitions, and the triplet photoinduced absorption signal is dominated by $T_1 \rightarrow T_n$ transitions. (Inset) The model used for global analysis: Photoexcited $1B_u$ states quickly relax (<100 fs) to the $2A_g$ state via internal conversion process or into the triplet manifold via intramolecular singlet fission processes. No fission is observed from the $2A_g$ state. The ground state is rapidly repopulated via a second internal conversion process from the $2A_g$ state or via triplet–triplet annihilation.

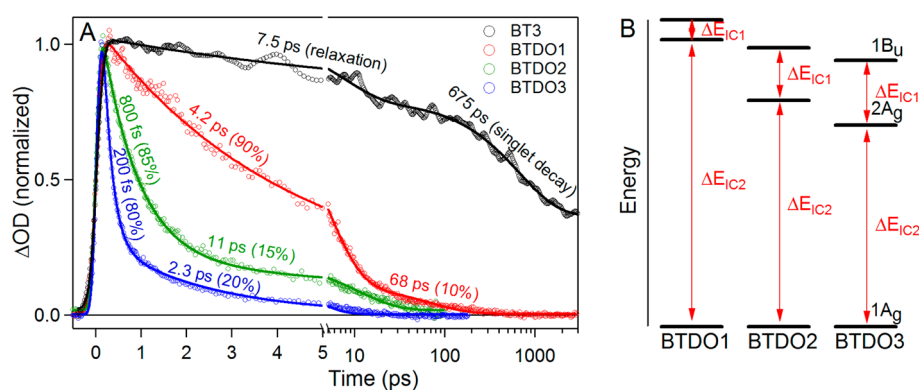


Figure 5. (A) Kinetic traces of ground-state repopulation for BT3 and BTDO1–3 are shown. The traces are generated by averaging over a broad region of the high-energy side of the ground state bleach. This region is chosen to minimize contributions from overlapping photoinduced absorption bands on the low-energy side of the bleach. The data show that the overall excited-state lifetime is reduced as the number of thiophene dioxide units increases. This trend can be explained by quantum chemistry calculations (B), which show additional TDO subunits stabilize the $2A_g$ state more dramatically than the bright $1B_u$ state.

rearrangement of the attached aromatic groups, in this case BDT and the flanking thiophenes. With each additional TDO unit, the thermodynamic driving force for internal conversion becomes more significant. However, within the family of materials studied here, the energy of the $2A_g$ state is more sensitive to molecular structure than the $1A_g$ and $1B_u$ states. As a result, it is plausible that singlet deactivation by internal conversion may be avoided with careful molecular design in future donor–acceptor materials. Incorporating chemical groups that destabilize the excited state quinoidal rearrangement of the aromatic moieties attached to TDO may provide a means of selectively destabilizing the $2A_g$ state, such that it lays above the bright excitonic state. Indeed, recent experiments using photoluminescence¹⁷ and transient optical spectroscopy¹² have shown that TDO containing materials can have an optically bright state as the lowest energy electronic state. Taken all together, these results suggest that the incorporation of strong acceptors, such as TDO, can have dramatic effects on the electronic structure of a molecule and also that subtle changes in the functional groups surrounding the molecular backbone may have similarly large consequences for the carrier dynamics and the ultimate utility of these materials in applications.

SUMMARY AND CONCLUSIONS

We have investigated the effects of oxidation of thiophene on steady-state properties and excited-state dynamics of donor–acceptor molecules. Oxidation results in stabilization of the LUMO, a decrease in optical gap, and the introduction of fast singlet deactivation pathways. Among these pathways are singlet fission and internal conversion through a dark singlet exciton state, the latter being the most prominent singlet deactivation mechanism. We also observe that the internal conversion rate from the dark state to the ground state qualitatively obeys an energy gap law, whereby a large gap leads to a smaller internal conversion rate.

ASSOCIATED CONTENT

Supporting Information

Details of molecular synthesis and optical characterization techniques. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. A New Class of Small Band Gap Organic Polymer Conductors. *Polym. Bull.* **1992**, *29*, 119–126.
- (2) Son, H. J.; He, F.; Carsten, B.; Yu, L. Are We There Yet? Design of Better Conjugated Polymers for Polymer Solar Cells. *J. Mater. Chem.* **2011**, *21*, 18934–18945.
- (3) Kularatne, R. S.; Magurudeniya, H. D.; Sista, P.; Biewer, M. C.; Stefan, M. C. Donor–Acceptor Semiconducting Polymers for Organic Solar Cells. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 743–768.
- (4) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 591–595.
- (5) Pandey, L.; Risko, C.; Norton, J. E.; Brédas, J.-L. Donor–Acceptor Copolymers of Relevance for Organic Photovoltaics: A Theoretical Investigation of the Impact of Chemical Structure

Modifications on the Electronic and Optical Properties. *Macromolecules* **2012**, *45*, 6405–6414.

(6) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. Developments in the Chemistry and Band Gap Engineering of Donor–Acceptor Substituted Conjugated Polymers. *Mater. Sci. Eng., R* **2001**, *32*, 1–40.

(7) Rodovsky, D. B.; Peet, J.; Shao, N.; Azoulay, J. D.; Bazan, G. C.; Drolet, N.; Wu, Q.; Sfeir, M. Y. Quantifying the Relationship between the Maximum Achievable Voltage and Current Levels in Low-Bandgap Polymer Photovoltaics. *J. Phys. Chem. C* **2013**, *117*, 25955–25960.

(8) Dell, E. J.; Campos, L. M. The Preparation of Thiophene-S,S-Dioxides and Their Role in Organic Electronics. *J. Mater. Chem.* **2012**, *22*, 12945–12952.

(9) Duan, C.; Huang, F.; Cao, Y. Recent Development of Push-Pull Conjugated Polymers for Bulk-Heterojunction Photovoltaics: Rational Design and Fine Tailoring of Molecular Structures. *J. Mater. Chem.* **2012**, *22*, 10416–10434.

(10) Foster, M. E.; Zhang, B. A.; Murtagh, D.; Liu, Y.; Sfeir, M. Y.; Wong, B. M.; Azoulay, J. D. Solution-Processable Donor-Acceptor Polymers with Modular Electronic Properties and Very Narrow Bandgaps. *Macromol. Rapid Commun.* **2014**, *35*, 1516–1521.

(11) Guo, X.; Facchetti, A.; Marks, T. J. Imide- and Amide-Functionalized Polymer Semiconductors. *Chem. Rev.* **2014**, *114*, 8943–9021.

(12) Busby, E.; Xia, J.; Wu, Q.; Low, J. Z.; Song, R.; Miller, J. R.; Zhu, X. Y.; Campos, L. M.; Sfeir, M. Y. A Design Strategy for Intramolecular Singlet Fission Mediated by Charge-Transfer States in Donor–Acceptor Organic Materials. *Nat. Mater.* **2015**, DOI: 10.1038/NMAT4175.

(13) Camaioni, N.; Ridolfi, G.; Fattori, V.; Favaretto, L.; Barbarella, G. Oligothiophene-S,S-Dioxides as a Class of Electron-Acceptor Materials for Organic Photovoltaics. *Appl. Phys. Lett.* **2004**, *84*, 1901–1903.

(14) Dell, E. J.; Capozzi, B.; Xia, J.; Venkataraman, L.; Campos, L. M. Molecular Length Dictates the Nature of Charge Carriers in Single-Molecule Junctions of Oxidized Oligothiophenes. *Nat. Chem.* **2015**, DOI: 10.1038/NCHEM.2160.

(15) Amir, E.; Sivanandan, K.; Cochran, J. E.; Cowart, J. J.; Ku, S. Y.; Seo, J. H.; Chabinyc, M. L.; Hawker, C. J. Synthesis and Characterization of Soluble Low-Bandgap Oligothiophene-[All]-S, S-Dioxides-Based Conjugated Oligomers and Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1933–1941.

(16) Wei, S.; Xia, J.; Dell, E. J.; Jiang, Y.; Song, R.; Lee, H.; Rodenbough, P.; Briseno, A. L.; Campos, L. M. Bandgap Engineering through Controlled Oxidation of Polythiophenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 1832–1836.

(17) Tsai, C.-H.; Chirdon, D. N.; Maurer, A. B.; Bernhard, S.; Noonan, K. J. T. Synthesis of Thiophene 1,1-Dioxides and Tuning Their Optoelectronic Properties. *Org. Lett.* **2013**, *15*, 5230–5233.

(18) Mullen, K. M.; Vengris, M.; van Stokkum, I. H. Algorithms for Separable Nonlinear Least Squares with Application to Modelling Time-Resolved Spectra. *J. Global Optim.* **2007**, *38*, 201–213.

(19) van Stokkum, I. H.; Larsen, D. S.; van Grondelle, R. Global and Target Analysis of Time-Resolved Spectra. *Biochim. Biophys. Acta, Bioenerg.* **2004**, *1657*, 82–104.

(20) Casanova, D. Electronic Structure Study of Singlet Fission in Tetracene Derivatives. *J. Chem. Theory Comput.* **2013**, *10*, 324–334.

(21) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; et al. Advances in Molecular Quantum Chemistry Contained in the Q-Chem 4 Program Package. *Mol. Phys.* **2014**, 1–32.

(22) Capozzi, B.; Dell, E. J.; Berkelbach, T. C.; Reichman, D. R.; Venkataraman, L.; Campos, L. M. Length-Dependent Conductance of Oligothiophenes. *J. Am. Chem. Soc.* **2014**, *136*, 10486–10492.

(23) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. Stoichiometric Control of the Successive Generation of the Radical Cation and Dication of Extended A-Conjugated Oligothiophenes: A Quantitative Model for Doped Polythiophene. *Synth. Met.* **1990**, *39*, 243–259.

(24) Busby, E.; Carroll, E. C.; Chinn, E. M.; Chang, L.; Moulé, A. J.; 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.

(25) Oliva, M. a. M.; Casado, J.; Navarrete, J. T. L.; Patchkovskii, S.; Goodson, T., III; Harpham, M. R.; Seixas de Melo, J. S.; Amir, E.; Rozen, S. Do [All]-S,S'-Dioxide Oligothiophenes Show Electronic and Optical Properties of Oligoenes and/or of Oligothiophenes? *J. Am. Chem. Soc.* **2010**, *132*, 6231–6242.

(26) Musser, A. J.; Al-Hashimi, M.; Maiuri, M.; Brida, D.; Heeney, M.; Cerullo, G.; Friend, R. H.; Clark, J. Activated Singlet Exciton Fission in a Semiconducting Polymer. *J. Am. Chem. Soc.* **2013**, *135*, 12747–12754.

(27) Englman, R.; Jortner, J. The Energy Gap Law for Radiationless Transitions in Large Molecules. *Mol. Phys.* **1970**, *18*, 145–164.