An investigation of the excited state properties of (E)-1,2-bis(2,2’-bithiophene-5-yl) ethylene using femtosecond time resolved spectroscopy

THESIS

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Abstract

The conductive oligomer (E)-1,2-bis(2,2’-bithiophene-5-yl)ethylene (abbreviated T_{2}VT_{2}) was studied in its excited state using transient absorption spectroscopy and femtosecond infrared spectroscopy. The resulting spectra were interpreted and compared to previous experimental data taken using diphenyl stilbene. A single broad transient electronic absorption band was observed to decay according to a biexponential equation with time components on the order of 30-80 ps and 800-1500 ps. Femtosecond stimulated IR spectroscopy reveals no excited state vibrational data, but does have a broad background signal which decays according to a biexponential equation as well, with time constants on the order of 5-20 ps and 700-1500 ps. Early time oscillations were observed but remain unexplored. These results indicate that T_{2}VT_{2} has a long lived excited state with a conformationally constrained structure. The origin of the transient absorption bands was unclear, and could be attributed to between one and three singlet energy levels, or the generation of a free electron by the photoexcitation of the compound.
Dedicated to my fellow lab mates, past and present, who remain constant sources of support during the research process.
Acknowledgments

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Major Field: Chemistry
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Chapter 1: Introduction

Background

Since the 1977 discovery of conductance in halogen doped polyacetylene by Shirakawa, MacDiarmid and Heeger, research in conductive polymers has expanded to cover a wide variety of conjugated molecules such as phenylenes, pyrroles, anilines, and thiophenes. The structural and electronic properties of these polymers have been well described through years of scientific research. The knowledge produced by these studies has led to many practical applications. In the field of electrochemistry, conducting polymers are used in catalysis research, the construction of anticorrosive coatings, field-effect transistors and fuel cell design. Biochemically they have been found to be very useful in the construction of long lasting, environmentally sturdy sensors that are resistant to corrosion, fouling, or unwanted reactions with the molecules of interest. The electro- and photoluminescent properties of the compounds have also seen use in the design of nonlinear optical devices and light emitting diodes. In light of these past successes, further research on different types of conjugated polymers is an area of considerable interest.

Although interest in conducting polymers is great, obtaining useful structure-function relationship data can be very difficult as they are difficult to crystallize and tend to be insoluble, complicating attempts to analyze their structure spectroscopically. In
addition to this, the exact chemical structure of a polymer is not uniform, but will have chemical and structural imperfections such as twisted chain lengths and isolated sp3 hybridized atoms that are difficult to systematically detect and describe. Polymers are also not truly infinite lines of molecules, but have structures such as crosslinks and ring fusions, the exact placement and frequency of which will vary depending on the method used to create them.

To avoid these difficulties, oligomers with structures representative to a polymer of interest may be analyzed instead. As small molecules, oligomers are more easily crystallized and dissolved resulting in less complicated structural analysis. Their chemical structures can be precisely synthesized and verified, allowing for systematic structure-function comparisons to be made. As the chain length of an oligomer increases, its properties begin to resemble those of a true polymer with an infinite chain length. By analyzing a series of oligomers with increasing chain lengths, the properties of small oligomers can be extrapolated to help describe the properties of the full polymer.\textsuperscript{5,6} This process is known as the oligomeric approach to studying polymers. This research has been used to describe the properties of several types of organic polymers both electrochemically and photochemically.\textsuperscript{5–10}

One such oligomer is the compound of interest, (E)-1,2-bis(2,2'-bithiophene-5-yl)ethylene, referred to hereafter as T\textsubscript{2}VT\textsubscript{2}. This oligomer consists of a pair of bithiophene molecules (T\textsubscript{2}) situated trans across a vinyl group (V) [Figure 1]. T\textsubscript{2}VT\textsubscript{2} has been the subject of research primarily as an aid in the study of conjugated organic polymers. Being composed of two of the most common species used to construct conductive polymers,
thiophene and acetylene (vinylene), $T_2VT_2$ is a prime candidate for further oligomeric analysis. First described in the literature by Nakayama et al. in 1986\textsuperscript{11}, solid $T_2VT_2$ takes the form of scaly, yellow-orange crystals. It is only slightly soluble in organic solvents, but even in very dilute solutions the intense fluorescence of the molecule is obvious, emitting bright ~500 nm light under laser radiation. Structurally, $T_2VT_2$ can be described as a well-barrier-well type molecule. These molecules consist of two components: ‘well’ components with low excitation band-gaps where excited state electrons are localized and which are the source of light emission in the molecule, and a connecting ‘barrier’ component with a higher energy band-gap.\textsuperscript{10} In $T_2VT_2$ the thiophene groups serve as the wells, and the vinylene is the barrier.

![Figure 1: $T_2VT_2$ chemical structure](image)

The UV/Vis absorption spectrum of the $T_nVT_n$ ($n =$ integer values between 1-3) series of oligomers was described by Nakayama and Frere, who noted an absorbance band that became red shifted as more thiophenes were added to the ends of the molecule,
indicating increasing conjugation as the chain length lengthened.\textsuperscript{11,12} \(T_2VT_2\) specifically exhibits a broad absorbance peak stretching from 350 – 450 nm with a peak maximum at about 420 nm. The ground state IR and Raman spectra of \(T_2VT_2\) have been analyzed both experimentally and computationally by Casado who examined the vibrational Raman and IR spectra of the compound in both its ground state as well as its oxidized +1 state. The oxidized state was created by doping the oligomer by adsorption of iodine vapor, a procedure commonly used to induce conductance in conjugated polymers.\textsuperscript{5,13,14} These analyses have thoroughly described the structural and electrochemical properties of the molecule in both its ground [Table 1] and oxidized state. The calculations suggested that the thiophene rings are aligned in an anti-coplanar arrangement in the ground state, and determined that the difference in energy band gaps between the thiophene and vinylene groups did not significantly impact the conjugation of the molecule, as it had an effective conjugation length of five thiophene molecules.\textsuperscript{5}

Photoluminescent studies of thiophene oligomers as well as well-barrier-well molecules including \(T_2VT_2\) reported by Kanemitsu et al. determined that the photoluminescent lifetime of pure thiophene oligomers is independent of chain length, but can be highly influenced by the choice of barrier molecule separating the wells.\textsuperscript{10} \(T_2VT_2\) was found to have a radiative lifetime of about 50 ns, a significant increase from a pure thiophene oligomer or comparable thiophene oligomers with methyl or phenylene barrier structures, which had reported radiative lifetimes on the order of 1-5 ns. The radiative lifetimes correlated to the energy required by a thiophene ring to rotate about their barrier structure. Kanemitsu attributed the dependence of the photoluminescent lifetime on the
barrier structure by linking the molecular conformational relaxation to the rotation of the outer thiophene rings, a movement which would be hindered by the rigid vinyl spacer more effectively than the methylene or phenylene barriers used in the other studied oligomers. While these analyses have provided insight into the properties of T₂VT₂ in its ground state, there is currently no evidence in the literature of an ultrafast analysis of the molecule.

Understanding the ultrafast spectra of T₂VT₂ is important both from a fundamental desire to clarify further a novel molecule’s structure, but also on a practical level as knowledge of the excited form of a molecule is important for potential future practical applications. Although T₂VT₂ itself has not been studied in the ultrafast time domain, studies have been performed on the ultrafast electronic activity of thiophene oligomers.¹⁵ ¹⁶ Other well-barrier-well molecules have been studied in the ultrafast domain as well, and may be looked to for guidance when interpreting future findings.

Figure 2: Diphenyl stilbene chemical structure
One well studied well-barrier-well molecule is diphenyl stilbene (DPS), a molecule also known for its luminescent properties and interesting ultrafast dynamics. DPS is structurally similar to T₂VT₂, consisting of two diphenyl groups serving as the well components separated by a vinylene barrier structure [Figure 2]. Gustafson et al. studied the ultrafast spectral properties of DPS using both transient absorption (TA) and picosecond Raman spectroscopy.¹⁷,¹⁸ These studies describe two excited state features which both decayed according to a biexponential function consisting of a short time constant (~10-20 ps) attributed to vibrational cooling and conformational relaxation and a longer time constant (~1 ns) corresponding to excited state decay. Spectral changes observed in the absorption band during the shorter time delays were associated with the diphenyl ‘well’ structures and attributed to vibrational cooling as well as the conformation motion of the phenyl groups as they moved from a non-planar (ground state) to a planar (excited state) structure.¹⁷,¹⁸ This description of a non-planar to planar motion in the well structures matches the relaxation dynamics proposed by Kanemitsu et al. in their analysis of the radiative lifetimes of T₂VT₂ and similar well-barrier-well oligomers.¹⁰

The goal of the research described here is to further characterize T₂VT₂ by providing a description of the electronic and vibrational structure of its excited states on an ultrafast timescale through the use of femtosecond time resolved transient IR (TRIR) and transient absorption UV/Vis (TA) spectroscopy. These data, along with the guidance provided by the previous work of Gustafson on DPS and Kanemitsu on thiophene oligomers, will be used to discuss the relationship between the structure of T₂VT₂ and its physical properties.
Chapter 2: Experimental

Sample preparation

Solid T$_2$VT$_2$ was synthesized by Amneh Young of the Hadad group. The identity and purity of the compound were confirmed using NMR analysis. For TA measurements saturated solutions of T$_2$VT$_2$ in both THF and DCM were diluted with the appropriate solvent until their observed maximum absorbance values were between 0.5-0.8 OD at maximum absorption within a 1-mm path length quartz Starna cell. The solutions were flowed through a 1-mm path length Herrick flow cell during TA analysis. For time resolved IR (TRIR) measurements the compound was saturated in a solution of THF and placed in a 0.1-mm IR cell consisting of two NaCl salt plates. No IR spectra were taken in DCM due to the difficulty of achieving a sufficiently concentrated solution for TRIR analysis. All solvents used in the experiments were obtained and used directly from the manufacturer.

Ground state spectra

Ground state UV/Vis absorption spectra were taken using a Perkin Elmer Lambda 20 spectrometer. Spectra were taken for both the THF and DCM solutions within a 1-mm quartz Starna cell. Both samples used concentrations appropriate for TA analysis. Ground state IR spectra were taken with an Agilent Cary 630 ATR-FTIR spectrometer from 650-4000 cm$^{-1}$. Ground state Raman spectra were taken using a home built stimulated Raman
spectroscopy (SRS) setup using a Raman excitation wavelength of 570 nm at about 1 μJ per pulse. Excitation and emission spectra of the compound were taken in DCM in a 1 cm path length Starna fluorescence cell using a Horiba Fluoromax-4 fluorimeter. The excitation spectra were taken at 500 nm, the emission was measured using 400 nm excitation.

**Time-resolved fluorescence measurements**

The fluorescence lifetime of T₂VT₂ was measured using the time correlated single photon counting (TCSPC) method using a set up consisting of a 445 nm diode laser (Edenborough Instruments) a m300 monochromator, and a photomultiplier tube (Edenborough Instruments). The sample was dissolved in DCM until its absorption was at a level appropriate for UV/Vis analysis, and degassed using nitrogen and placed in a 1 cm path length Starna fluorescence cell. The resulting luminescence decay curve was fit to an exponential function in Igor.

**Calculations**

Density functional theory (DFT) calculations were employed to calculate the molecular orbitals and predict the ground and excited state vibrations of T₂VT₂. The calculations were run using Gaussview 5.0.8 on the Ohio State University supercomputer. The calculations assumed an isolated system and used the B3LYP functional assumption and the 6-31G** basis set. The excited state structure was approximated by making T₂VT₂ an anion.

**Ultrafast spectroscopy method and setup**
Ultrafast spectra were taken using previously detailed transient absorption (TA) [Figure 3] and time resolved IR (TRIR) [Figure 4] experimental setups.\textsuperscript{19} Both experiments have the same general outline. In short, femtosecond laser pulses are generated by a Ti:Sapphire laser (Coherent Mantis-5E) pumped by a diode laser (Coherent Verdi-V5). These pulses seed an ultrafast regenerative amplifier (Coherent Legend) pumped with an Nd:YLF 527 nm laser (Coherent Evolution) which provides the fundamental power for the experiment (800 nm, 1 kHz, 40 fs). After exiting from the Legend, the laser beam is divided by a beam splitter.

In both experimental setups, one portion of the beam is used to generate the probe signal. The TA setup requires very little laser energy, and employs a calcium fluoride crystal to generate a broad band of wavelengths. This crystal is mounted on a rotating stage to prevent burning from long term exposure to the laser. The TRIR probe is generated within an optical parametric amplifier (OPA) with a difference frequency generation (DFG) attachment (Coherent Opera) which adjusts the probe’s wavelength to the desired experimental region, usually within 2-10 μm. In both set ups, the probe beams are then split to form two beams: a probe and a reference, which are focused into the sample. The ratio of the probe and reference samples are used to eliminate the effects of stray light or other background sources of radiation from the final spectra.

The remaining portion of the Legend output beam is used to form the pump, the light responsible for initiating the desired photochemistry in the sample. This beam is directed into an OPA which can be used to tune it to any desired wavelength between 280 to 1600 nm. This light is then directed to the sample cell, where it is adjusted temporally.
and spatially to overlap with the probe. Temporal overlap is achieved using a delay stage which controls the timing between the pump and probe pulses. In the TA setup the delay stage is in the path of the probe, while for the TRIR it is in the path of the pump. The pump power at the sample can be adjusted via neutral density filter and iris in order to keep the beam at an appropriate power. Typical pump powers are about 1 μJ per pulse (1 mW). A half-wave plate in the path of the pump ensures that its light is polarized to the magic angle (54.7°) relative to the probe. Both probe and pump beams travel through choppers which allow the sample to be measured in consecutive pump on/pump off conditions. The TA setup has the choppers aligned in a 2:1 frequency ratio (25 Hz for the probe, 12.5 Hz for the pump) while the TRIR setup simply chops the probe beam at 500 Hz. This allows a ground state (pump off) absorbance spectrum to be subtracted from every excited state (pump on) spectrum measured.

In the IR setup the final signal is detected by a mercury cadmium telluride IR detector (Kolmar Technology) connected to a monochromator/spectrograph (Jobin Yvon Triax 320). The TA setup collects its data using a Triax 550 monochromator/spectrograph (Jobin Yvon) connected to a CCD detector (Jobin Yvon Symphony). The data is collected and processed by a custom Labview program.
Figure 3: Femtosecond UV/Vis transient absorption spectrometer.
Figure 4: Femtosecond time resolved Infrared spectrometer.
Procedure

Ultrafast IR data were taken using T₂VT₂ saturated in THF. The sample was excited at 400 nm generated by feeding the fundamental laser beam into a second harmonic generating (SHG) crystal (1-mm, BBO). Proper spatial overlap was determined by adjusting the pump beam to maximize visually a transient signal from a solid germanium sheet. Temporal overlap was determined by adjusting the delay stage until this transient signal was reduced to 50% of its maximum value. This point was set as time zero for the duration of the experiment. Data were collected at six regions with the spectrometer centered at 1650 cm⁻¹, 1580 cm⁻¹, 1520 cm⁻¹, 1420 cm⁻¹, 1360 cm⁻¹, and 1300 cm⁻¹. Three data cycles were collected and averaged for each region. Ground state UV/Vis measurements were taken between each experimental region to ensure no degradation of the analyte had occurred.

TA data was taken using samples of T₂VT₂ dissolved in THF and DCM, both of which could dissolve in T₂VT₂ to a degree optimal for TA analysis (between 0.5-0.8 OD). The chosen wavelength of excitation was 400 nm generated using an SHG crystal as with the TRIR experiment (1-mm, BBO). Spatial and temporal overlap was determined by a similar method to the IR setup using diphenyl octatetraene (DPO) as a reference compound and monitoring the growth of its ~650 -700 nm transient absorption band. The spectrometer was centered at about 670 nm in an attempt to avoid the emission spectra of the compound that dominates the signal between 400 to 600 nm. In order to observe as broad a range as possible, each sample was collected both with a high pump power (~2 μJ per pulse) and a low pump power (>1 μJ per pulse) as the shorter wavelength regions were
saturated by remaining fundamental signal at high pump powers. Three cycles for each sample were collected and averaged by the Labview program.

Data Processing

Data were processed using home built Labview programs. Representative spectra were visually selected at times which best characterized the decay of the excited state. A spectrum taken at a negative time delay was subtracted from all selected spectra to remove any remaining background features. GVD correction occurred in the program as well. Data were then exported to Igor for further analysis. As the observed signal was broad, with no sharp features, representative frequency values were selected for kinetic trace analysis fairly evenly across each signal region. Kinetic traces were fit to an exponential equation using Igor curve fitting calculations. Several different exponential functions were fitted to the kinetic data, but the biexponential (of the form \( f(x) = A \exp(-x/t_1) + B \exp(-x/t_2) + C \)) was determined to best fit the data as it provided the smallest standard deviation in the time constants, and featured best correlation to the data points. After the best fit was determined, a global fit analysis was performed combining the data points of each of the kinetic traces in order to estimate a final predicted decay constant.
Chapter 3: Results and Discussion

Ground state spectra

The ground state of T2VT2 was compared to previous characterizations using UV/Vis absorption, emission/excitation, Fourier-transform infrared absorption, and stimulated Raman spectroscopy [Figures 5, 6 7 and 8 respectively]. The collected UV/Vis spectra in DCM and THF agrees with previously collected spectra showing an intense absorption band from 350-450 nm with the maximum absorption occurring at about 425 nm, corresponding to the π-π* excitation.11, 12 An additional, smaller absorption band was also seen at ~265 nm. The excitation spectrum largely agrees with the observed absorption spectrum, with maximum excitation occurring at about 420 nm, and a smaller band seen at ~265 nm. The emission spectrum shows a broad signal stretching from 450-600 nm, a result consistent with the observed green light witnessed upon excitation with a laser source at ~400 nm. The emission peak displayed a distinct vibrational fine structure, supporting the prediction of a structurally confined, planar ground state structure.5

Calculated molecular orbital diagrams of T2VT2 in its highest occupied molecular orbital (HOMO) and the predicted lowest unoccupied molecular orbital (LUMO) states are shown in Figure 9. The predicted energy gap between the HOMO and LUMO is 2.77 eV corresponding to a transition of 447 nm. The calculated electronic absorption spectrum shows that this transition corresponds to the intense absorbance band observed in the
ground state UV/Vis spectrum. The predicted molecular structure for T2VT2 agrees with the anti-coplanar structure described by Casado.5 The HOMO displays high pi-bonding character, with electron density primarily centered on the C=C bonds in the ring structure and the bridging vinyl group. The predicted LUMO structures maintain pi-bonding character and the planar structure, with the electron density moved to the bridging C-C bonds as well as the sulfur molecules in the thiophene moieties, breaking up some of the conjugation present on the end thiophenes but maintaining it through the rest of the structure. The calculated spectrum also predicts the smaller ~265 nm band, attributing it to multiple higher energy transitions of mixed pi and non-bonding electron character.

The results of FTIR and DFT vibrational analysis are presented in Table 1. The experimental results are in good agreement with IR values previously reported by Nakayama and Casado.11,13 Results of the DFT calculations result in fair to poor matches to experimental spectra but are used where appropriate to assign an identity to the vibrational motions of each observed mode. Above 1500 cm⁻¹ the only significant mode is a peak at ~3050 cm⁻¹. This peak was reported by Nakayama, but not by Casado who limited his discussion to bands below 1500 cm⁻¹. The closest comparable bands in the DFT are above 3100 cm⁻¹ and suggest these modes are due to CH stretches on the aromatic thiophene groups as well as the trans-vinyl group. Bands below 650 cm⁻¹ are not presented as they were below the range of the instrument.

Below 1550 cm⁻¹ the experimental FTIR spectra align very closely with the peaks reported by Casado and Nakayama. Nakayama’s spectra are missing several of the weaker peaks reported by Casado, but those reported all have analogs in the experimental spectra.
The exceptions to this trend are three peaks at 887, 878, and 849 cm\(^{-1}\). The first two bands are predicted to arise due to CH bending and folding on the outer and inner rings respectively based on the DFT calculations, while the peak at 849 cm\(^{-1}\) is predicted to represent the symmetric C-S stretch of the outer thiophene rings.

Several weaker peaks observed experimentally are not present in the DFT predicted spectrum. In these instances the vibrational assignments given by Casado are reported. For the other vibrational bands the movements predicted by DFT calculations are listed.
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<td>-</td>
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</tr>
<tr>
<td>1045</td>
<td>1048</td>
<td>1044</td>
<td>-</td>
<td>s C-H bend*</td>
</tr>
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<td>944</td>
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<td>945</td>
<td>974</td>
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<td>926</td>
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<td>887</td>
<td>895</td>
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<td>-</td>
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<td>844</td>
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<td>740</td>
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<td>as C-S ring stretching</td>
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<td>704</td>
<td></td>
<td>Ring bending*</td>
</tr>
<tr>
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<td>688</td>
<td>684</td>
<td>697</td>
<td>s C-H outer rings out-of-plane fold</td>
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</tbody>
</table>

Table 1: Comparison of observed ground state IR peaks to those reported in literature. *as* = antisymmetric, *s* = symmetric. All measurements are in wavenumbers (cm$^{-1}$). Asterisks mark assignments given in the literature [2]. Otherwise assignments are based on original DFT calculations.
The Raman bands observed using stimulated Raman spectroscopy match well with those reported in the literature [Figure 7]. The results are summarized in Table 2. Two peaks are attributed to the trans-vinylene group separating the thiophenes, and can be assigned to the symmetrical C=C stretching (1605 cm\(^{-1}\)) and the C-H symmetrical in plane bending (1296 cm\(^{-1}\)) mode. The remaining four peaks have been determined to belong to the thiophene groups by previous studies. The peak at 1541 cm\(^{-1}\) is attributed to the antisymmetric C=C stretch located on the outer thiophene rings, the strong peak at 1439 cm\(^{-1}\) is assigned to a mode stretching across the entire molecule made up of coupled a symmetric C=C stretch and in-plane C-H bending. The peak at 1047 cm\(^{-1}\) is assigned to the symmetric C-H bending modes of the carbons in the beta-positions on the molecule. The weak peak at 1232 cm\(^{-1}\) is assigned to the symmetrical C-C stretching of the alpha carbons in the thiophene rings.

<table>
<thead>
<tr>
<th>Casado (^5)</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1601</td>
<td>1606</td>
<td>C=C vinyl stretch</td>
</tr>
<tr>
<td>1539</td>
<td>1541</td>
<td>(as) C=C ring stretch</td>
</tr>
<tr>
<td>1433</td>
<td>1439</td>
<td>(s) C=C whole chain stretch, C-H bend</td>
</tr>
<tr>
<td>1296</td>
<td>1296</td>
<td>(s) C-H vinyl bend</td>
</tr>
<tr>
<td>1230</td>
<td>1233</td>
<td>(s) C-C alpha stretch</td>
</tr>
<tr>
<td>1047</td>
<td>1048</td>
<td>(s) C-H ring bend</td>
</tr>
</tbody>
</table>

**Table 2:** Comparison of observed ground state Raman peaks to literature values. \(as = antisymmetric\), \(s = symmetric\). All measurements are in wavenumbers (cm\(^{-1}\)).
TCSPC data analysis

The results of the time correlated single photon counting analysis are presented in Figure 10. A single exponential decay equation was found to best fit the data, with an associated time constant of 1.723 +/- 0.003 ns. This value is larger than the photoluminescent lifetimes reported by Gustafson et al. in their analysis of DPS.\textsuperscript{20} In all the probed solvents and temperatures, DPS was found to have a fluorescence decay time constant between 700-920 ps, never more than 1 ns. It is also significantly longer than the photoluminescent lifetime of the polythiophenes reported by Kanemitsu et al. as well, none of which exceeded 800 ps.\textsuperscript{10}

TA data analysis

The TA data for the high power spectra can be seen in Figures 11-16. The spectra taken at lower laser power did not reveal any new peaks and displayed considerable loss of signal at the shorter wavelengths and so are not shown here. Intense emission of the compound dominated the central region of the spectra, from 450 to 600 nm, preventing any potential signals from being observed. Two main features were noted in the remaining spectra: the ground state bleach from 450 nm to 350 nm, and a broad transient absorption band stretching from 620 to 750 nm and beyond into longer wavelengths not observable by the detector. The spectra exhibit no clear solvent difference between the THF and DCM samples.

The shape of the bleach corresponds to that of the ground state UV/Vis absorption band. The kinetic traces of the bleach decay were found to be best described by a biexponential equation, with a short and long time constant of ~60 ps and ~1300-1600 ps
respectively. It is notable that a significant bleach signal remained at the end of the last time point observed (~3000 ps) suggesting the molecule had not entirely returned to its ground state within the time window of this experiment.

The transient absorption band observed from 620 nm onward was broad, with signal still growing at the edge of the region detected. Two features were observed across the band, the first a signal that might correspond to vibrational fine structure at the short wavelength end of the band. The second was the broad background of the band, with signal increasing steadily at the longer wavelength region of the spectra. The entire transient signal almost completely decays by ~3 ns, the longest time delay observed during the experiment, with the structure observed at shorter wavelengths decaying into the broader absorption band, almost completely disappearing after about 1 ns. The decay of the short and long wavelength regions were both fit to separate global kinetic trace equations. The resulting exponential equations provided a best fit line with a biexponential decay function for both regions. Both consist of short time constants of about 30-80 ps, and longer time constants of about 800 - 1500 ps. The calculated time constant for the broad, lower energy band was calculated to be consistently longer (~1300-1500 ps) in duration than the time constant for the narrower, higher energy feature (~800-1000 ps). This dual decay is clearly seen in the kinetic traces taken from the data [Figures 12 and 14]. Unfortunately, the emission spectrum of the compound, at 450 to 600nm, prevents further observation of any features that might appear in the remainder of the TA region.
Table 3: Biexponential decay time constant comparisons of T₂VT₂ in DCM and THF, as well as DPS in acetonitrile, methylene chloride and dioxane as recorded by Gustafson et al.\textsuperscript{18} Lower wavelength refers to the peak seen at 620–650 nm for the T²VT₂ data, and the peak observed at 630 for DPS. Higher wavelength refers to the area of the TA band above the lower wavelength region (designated as 650–720 nm) for T²VT₂ and the band at 725 nm for DPS.

Another feature worth noting is an oscillation in the kinetic trace data, which is especially noticeable at shorter time delays [Figure 15]. Oscillations of this type are typically associated with coherent nuclear motion, and can be used to obtain vibrational information of the molecule. These data still need to be investigated further, but it seems likely these oscillation are due to some conformational motion, such as the twisting of the thiophene rings.

Several differences were noted between the observed transient absorption spectra of T₂VT₂, and those measured by Gustafson et al. for DPS.\textsuperscript{18} Although the transient spectra of both consists of a broad band between 620-750 nm, the TA spectra of DPS had a pair of peaks located at 630 nm and 725 nm, attributed to two distinct higher energy states. Comparatively, T₂VT₂ has what might be a single peak centered at 625 nm on top of an even broader absorption band that increases in intensity at lower wavelengths, but does not form a distinct peak. Given the difference in time constants between the short and

<table>
<thead>
<tr>
<th>Solvent (Sample)</th>
<th>Short wavelength ( \tau_1 ) (ps)</th>
<th>Short wavelength ( \tau_2 ) (ps)</th>
<th>Long wavelength ( \tau_1 ) (ps)</th>
<th>Long wavelength ( \tau_2 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM (T₂VT₂)</td>
<td>40 +/- 20</td>
<td>1000 +/- 200</td>
<td>40 +/- 20</td>
<td>1300 +/- 300</td>
</tr>
<tr>
<td>THF (T₂VT₂)</td>
<td>80 +/- 40</td>
<td>800 +/- 100</td>
<td>31 +/- 7</td>
<td>1500 +/- 200</td>
</tr>
<tr>
<td>Acetonitrile (DPS)\textsuperscript{18}</td>
<td>11 +/- 1</td>
<td>1200 +/- 200</td>
<td>13 +/- 5</td>
<td>1200 +/- 200</td>
</tr>
<tr>
<td>DCM (DPS)\textsuperscript{18}</td>
<td>15 +/- 1</td>
<td>860 +/- 80</td>
<td>22 +/- 4</td>
<td>900 +/- 100</td>
</tr>
<tr>
<td>Dioxane (DPS)\textsuperscript{18}</td>
<td>14 +/- 3</td>
<td>910 +/- 90</td>
<td>20 +/- 5</td>
<td>1100 +/- 200</td>
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</tbody>
</table>
long wavelength regions, these features could be tentatively attributed to a pair of excited state transitions as well. Both DPS and T$_2$VT$_2$ peaks decay with a biexponential function, with a shorter time constant attributed to vibrational cooling processes, and a longer constant attributed to decay of the excited states. The time constants calculated for T$_2$VT$_2$ tend to be longer than those for DPS. The short time constants for both T$_2$VT$_2$ features are between of 30-80 picoseconds compared to 10-20 ps for the DPS features. The absorption bands of DPS had long time components between 0.8 – 1.2 ns, with the lower wavelength band at 650 nm having somewhat shorter values than the band at 725 nm. These values are comparable to the lifetimes measured for the narrower, lower wavelength T$_2$VT$_2$ peak (0.8 – 1.0 ns) but are shorter than the time constant of the broader absorption band stretching to the longer wavelengths ( 1.3 – 1.5 ns). It is also notable that the peak shifts observed in DPS were not present in any of the observed TA spectra for T$_2$VT$_2$. As Gustafson et al. attributed these shifts to conformational motion of the molecule, specifically the rotation of the phenyl rings from a non-planar to planar configuration, it would seem that such motions are either not present, or significantly less pronounced in T$_2$VT$_2$.

**TRIR data analysis**

The results of the TRIR analysis can be seen in Figure 18. A broad continuous signal was seen in all observed spectral regions, with no discernible peaks or bleaches indicative of vibrational motion. The decay of the band was fairly uniform among all observed regions with no additional peaks forming during the decay, which was complete after about two nanoseconds. A blank region centered at about 1450 cm$^{-1}$ is due to the intense THF background peak. As no specific features were seen the kinetics were analyzed by fitting a
An analysis of the kinetic traces suggests the decay process to be made up of two time components, one on the order of 5-10 ps, the other on the order of 1000 ps. Significant variation of these observations were seen between the spectral regions [Table 4]. Although no discernable vibrational information can be seen in these spectra, the broad signal shape is consistent with a potential low energy electronic state. If this is the case, the biexponential kinetic decay can be reasonably attributed to vibrational cooling processes occurring at the shorter time constant, and excited state decay occurring at the longer time component.

<table>
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<tr>
<th>Spectral Range (cm⁻¹)</th>
<th>Short wavelength τ₁ (ps)</th>
<th>Short wavelength τ₂ (ps)</th>
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<tr>
<td>1680-1600</td>
<td>6 +/- 1</td>
<td>1000 +/- 100</td>
</tr>
<tr>
<td>1600-1550</td>
<td>8 +/- 1</td>
<td>880 +/- 80</td>
</tr>
<tr>
<td>1550-1480</td>
<td>21 +/- 3</td>
<td>1500 +/- 300</td>
</tr>
<tr>
<td>1430-1380</td>
<td>5 +/- 2</td>
<td>1100 +/- 400</td>
</tr>
<tr>
<td>1380-1300</td>
<td>9 +/- 1</td>
<td>700 +/- 100</td>
</tr>
<tr>
<td>1300-1260</td>
<td>6 +/- 3</td>
<td>1000 +/- 200</td>
</tr>
</tbody>
</table>

**Table 4:** Biexponential decay constant comparisons of T₂VT₂ in THF.
Figure 5: UV/Vis spectrum of saturated T$_2$VT$_2$ in DCM and THF. Data taken in a 1-mm Starna quartz cell. The blue line shows the absorption of the solute in DCM, the green line in THF.
Figure 6: Emission (black) and Excitation (red) spectra of T$_2$VT$_2$. 
Figure 7: Ground state IR spectrum of solid $\text{T}_2\text{VT}_2$. 
Figure 8: Raman spectra of T₂VT₂ in THF. Spectra collected using a 570 nm Raman pump in a 2-mm quartz cuvette.
Figure 9: Frontier molecular orbital energy diagram of T₂VT₂ with the GaussView 5.0.8 isosurface (isovalue = 0.02) contour plots of selected orbitals. Energy calculated vs. vacuum.
Figure 10: Time correlated single photon counting fluorescence decay of $T_2VT_2$. 

$\tau_f = 1.723 \pm 0.003$ ns
Figure 11: Transient absorption spectra of $T_2V T_2$ in THF with delay times (ps).
**Figure 12 (a):** Global kinetic trace of 620-650 peak region of excited state $T_2VT_2$ in THF. Selected kinetic trace wavelengths are 625 nm (black), 635 nm (red), 645 nm (green), and 655 nm (cyan). (b): Global kinetic trace of 650-750 peak region. Selected kinetic trace wavelengths include 675 nm (blue), and 700 nm (pink).
Figure 13: (a): Bleach region transient absorption spectra of T2VT2 in THF with delay times (ps). Blank region is due to interference by the 400 nm pump. (b): Global kinetic trace of bleach region of excited state T2VT2 in THF. Selected kinetic trace wavelengths are 420 nm (red), 430 nm (green), and 440 nm (cyan).
Figure 14: Transient absorption spectra of T$_2$VT$_2$ in DCM with delay times (ps).
Figure 15 (a): Global kinetic trace of 620-650 peak region of excited state T₂VT₂ in DCM. Selected kinetic trace wavelengths are 625 nm (black), 635 nm (red), 645 nm (green), and 655 nm (cyan). (b): Global kinetic trace of 650-750 peak region. Selected kinetic trace wavelengths are 675 nm (blue), and 700 nm (pink).
Figure 16: (a): Bleach region transient absorption spectra of T$_2$VT$_2$ in DCM with delay times (ps). Blank region is due to interference by the 400 nm pump. (b): Global kinetic trace of bleach region of excited state T$_2$VT$_2$ in DCM. Selected kinetic trace wavelengths are 420 nm (red), 430 nm (green), and 440 nm (blue).
Figure 17: Global kinetic trace fitted for TA spectra of T$_2$VT$_2$ in DCM from 0-50 ps. Selected kinetic trace wavelengths include 675 nm (black), 685 nm (red), 700 nm (orange), 750 nm (green), and 760 nm (blue).
Figure 18: Transient IR spectra of saturated $T_2V_{T_2}$ in THF at different delay times (ps). Left axis shows optical density of transient spectra. Right axis shows transmission of the ground state for comparison. Lack of signal at ~1450 cm$^{-1}$ due to intense THF ground state peak.
Figure 19: Global kinetic trace analysis of TRIR spectra of T$_2$VT$_2$ centered at 1650 cm$^{-1}$.

Figure 20: Global kinetic trace analysis of TRIR spectra of T$_2$VT$_2$ centered at 1580 cm$^{-1}$.
Figure 21: Global kinetic trace analysis of TRIR spectra of T₂VT₂ centered at 1520 cm⁻¹.

Figure 22: Global kinetic trace analysis of TRIR spectra of T₂VT₂ centered at 1420 cm⁻¹.
Figure 23: Global kinetic trace analysis of TRIR spectra of T₂VT₂ centered at 1360 cm⁻¹.

Figure 24: Global kinetic trace analysis of TRIR spectra of T₂VT₂ centered at 1300 cm⁻¹.
Chapter 4: Conclusions

The data collected here have provided insight into the ultrafast properties of an important conjugated oligomer, $T_2VT_2$. After photoexcitation a single broad electronic absorption feature was observed, with three distinct regions studied: a narrow band between 620-650 nm potentially containing some vibrational fine structure, along with a broader band occurring between 620–750 nm and finally a low energy band observed across the entire TRIR spectra. All observed features decay in a biexponential fashion consisting of two steps: a fast component, attributed to vibrational cooling, ruled by a time constant of on the order of tens of picoseconds, and a slower component with a time constant on the order of hundreds of picoseconds. The short time constants observed during the TA experiment were significantly longer than those observed during the TRIR experiment (30-80 ps vs. 5-20 ps). Different solvent environments did not have a significant effect on the observed decay kinetics. This decay pattern is mirrored by the ground state bleach, which recovers in a biexponential fashion with similar long time constants, but does not completely decay even after 3 ns, the longest time point observed during the experiment.

The results of a TCSPC experiment revealed a photoluminescent lifetime for $T2VT2$ significantly longer than any observed for a comparable thiophene oligomer, or the structurally analogous diphenyl stilbene (1.7 ns vs. 0.9 or 0.8 respectively).\textsuperscript{18,21}
Although the state decay lifetimes observed with TA and TRIR were all shorter than those predicted by TCSPC (1.5 ns at the longest vs. 1.7 ns) this difference can be accounted for by the fact that the sample was degassed before the TCSPC experiment, but was not before the TA and TRIR experiment, thus some excited state molecules were likely lost to quenching.

The origin of the transient absorption bands is unclear. It is possible that they represent several distinct excited singlet states. However the peak shapes do not clearly distinguish one region from another, and the differences in the calculated time constants do not clearly differentiate each region. Another possibility is that instead of several discrete states, the electronic structure of T$_2$VT$_2$ in its excited state is better described as a band of electronic energy levels, and that a free electron is excited into this band upon photoexcitation. This explanation is supported by the broad nature of the transient band, as free electrons are known to have absorption spectra that stretch from the near-IR to mid-IR regions, and is supported by the roughly similar decay kinetics observed in each of the excited state regions as well as the recovery of the ground state bleach.

No vibrational detail was discerned from the TRIR data, suggesting weak oscillator strength in IR active vibrational modes of the excited state. This absence of IR bands, along with the absence of peak shifts in the TA data, suggests that the structure of T$_2$VT$_2$ is more resistant to conformational motion than the previously studied DPS, and maintains its ground state planar structure in its excited state.

Although the research collected here has provided some important information on the excited state properties of T$_2$VT$_2$, many important questions remain to be answered.
TRIR analysis did not provide satisfactory observation of ultrafast vibrational motions. In order to help further explore the excited state vibrational properties of T$_2$VT$_2$, it would be informative to collect ultrafast Raman data using femtosecond stimulated Raman spectroscopy (FSRS) to complement the TRIR data collected here, as well as help determine if the transient electronic absorption peaks are indeed due to several discrete singlet states, or are rather due to a single phenomenon, such as the generation of a free electron. A more thorough examination of the oscillations observed in the kinetic trace data might reveal more vibrational information about the molecules as well. In addition, further time resolved experiments in longer time domains could be performed to observe the bleach signal that remains after 3 ns. Once these questions are answered, further experiments on related oligomers which varying thiophene chain lengths, such as T$_1$VT$_1$ or T$_3$VT$_3$, or oligomers with varying well and barrier structures would be of interest in order to further explore trends between oligomeric structure and ultrafast dynamics.
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   doi:10.1039/B210718J

   (American Chemical Society, 2002).


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