Polarization Dependent Spectral Analysis Reveals Dipole Alignment and Intermolecular Coupling in Anthradithiophene Organic Semiconducting Crystals

Andrew Lam
Department of Physics, Oregon State University
Advisor: Matthew Graham

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Abstract

Organic photovoltaics are being explored as the next generation material for semiconducting and optoelectronic devices but are limited by their stability and efficiency. One new candidate is crystallized Anthradithiophene (ADT), which is a promising photo-voltaic material due to its high quantum yield and adjustable side groups. The side derivatives TES-F, TDMS-F, and TSBS-F, change the distribution of excited state electrons, affecting charge transfer in the crystal system without changing of the molecule’s optoelectronic properties. Previous experiments have observed the absorption, reflection, and transmission spectra of these derivatives in solution with respect to the polarization of incident light but the electronic transitions at specific emission bands have not been explored. Additionally, we discover in ADT variants different H-aggregate and J-aggregate dipole orientations.

An analysis of these side groups is done by measuring a photoluminescence excitation spectrum of ADT and the spectra is compared against the absorption as a function of wavelength. By varying the wavelength of incident light on the sample using a monochromator system, an EMMCD camera images the sample as it is being excited. The response is recorded as a function of the wavelength of incident light and single domain regions are analyzed. By analyzing multiple emission peaks and isolating these bands, we compare the excitation spectra across different bands to the absorption spectra. This confirms non-unique transition behavior across each derivative and determine that each PLE spectra fits to the absorption spectrum through a scalar constant.

From the polarization of light on the sample, we find a tunable response that determines an H-like and J-like response from the system, isolating a specific angle that maximizes the coupling from the H or J-aggregate dipole orientation. TES-F appears maximally J-like at 45° and maximally H-like at 117°. TDMS-F has a maximum J-like response at 90° and a maximal H-like response at 45°. TSBS-F exhibits J like behavior across all polarization measurements, with 90° being the strongest.
Contents

1 Introduction 5
  1.1 Motivation and Objective ............................................. 5
  1.2 Background ................................................................. 6
  1.3 Theory .............................................................. 7
    1.3.1 Emission and Excitation ........................................... 7
    1.3.2 H and J Aggregates ................................................. 8
    1.3.3 Crystal Structure and Coupling ................................... 10

2 Experimental Process 11
  2.1 Crystal Growth .............................................................. 11
  2.2 Measurement Process ....................................................... 11
    2.2.1 Emission ................................................................. 12
    2.2.2 Excitation ............................................................... 13
  2.3 Manipulating the Data ..................................................... 14

3 Results and Discussion 15
  3.1 ADT-TES-F Spectra ........................................................ 16
  3.2 ADT-TDMS-F Spectra ....................................................... 18
  3.3 ADT-TSBS-F Spectra ....................................................... 20
  3.4 Data Analysis .............................................................. 22
    3.4.1 Excitation to Absorption Comparison ............................... 22
    3.4.2 H and J aggregate appearance as a function of polarization ........ 24

4 Summary 28
List of Figures

1.1 Molecular Structure of ADT and side groups ........................................ 5
1.2 $\triangle R/R$ Spectrum of ADT-TES-F as a function of polarization .............. 6
1.3 Nuclear Potential Wells ........................................................................ 7
1.4 Excitation Spectrum plot of ADT-TES ................................................... 8
1.5 2-D System of Molecules ...................................................................... 9
1.6 H and J aggregate stacking structure ..................................................... 10
2.1 Experimental Set-up ........................................................................... 11
2.2 ADT-TESF Crystal ........................................................................... 12
2.3 Dipole Moment Orientation Diagram ................................................... 12
2.4 Polarization of TES and TDMS ............................................................ 13
3.1 Emission and Absorption of ADT .......................................................... 15
3.2 Absorption of ADT-TES-F .................................................................. 16
3.3 PLE of ADT-TES-F at 575 nm band ..................................................... 17
3.4 PLE of ADT-TES-F at 640 nm band ..................................................... 17
3.5 Absorption of ADT-TDMS-F ............................................................... 18
3.6 PLE of ADT-TDMSF at 570 nm band ................................................... 19
3.7 PLE of ADT-TDMS-F at 620 nm band ................................................... 19
3.8 Absorption of ADT-TSBS-F ................................................................. 20
3.9 PLE of ADT-TSBS-F at 550 nm band ................................................... 21
3.10 PLE of ADT-TSBS-F at 570 nm band ................................................... 21
3.11 PLE and Absorption of ADT-TSBS-F at $0^\circ$ ..................................... 22
3.12 PLE and Absorption of ADT-TDMS-F at $90^\circ$ ................................... 23
3.13 PLE and Absorption of ADT-TSBS-F at $90^\circ$ ................................... 24
3.14 Adjusted Excitation of ADT-TES-F at 640 nm band ............................. 25
3.15 Adjusted Excitation of ADT-TDMS-F at 640 nm band ......................... 26
3.16 Adjusted Absorption of ADT-TSBS-F ............................................... 27
1 Introduction

1.1 Motivation and Objective

Present silicon-based photovoltaic devices have reached their efficiency limit, slowing further optimization for the next-generation devices. Organic semiconductors have a diverse molecular make-up, which renders them to be flexible, customizable, and lightweight, while also being inexpensive [1]. This classification encourages further research and funding to fully optimize organic photovoltaics (OPVs) to compete in the silicon-dominated market. However, these organic cells have current limitations in efficiency and stability which downplays their practicality in current electronics. Crystallized anthradithiophene (ADT) is an amorphous semiconductor that exhibits these detrimental behaviors but has a high quantum yield, making it a favored material in OPV research. The key attribute of ADT is the tunable side groups which exhibit different functional features. These side groups impact the strength of the intermolecular interaction, shown by the differences in the emission spectrum, while also keeping the structural integrity of the device. The different molecular structures are seen below in Figure 1.1.

We examine the side group derivatives Triethylsilyl (TES-F), Tri-sec-butylsilyl (TSBS-F), and TDMS-F through light-matter interaction, utilizing different polarizations of light to analyze the emission, absorption, and excitation spectra of each derivative and how they respond to the changing polarizations. This work reports the emission behavior of ADT by conducting a photoluminescence excitation measurement and compares it against the corresponding absorption spectra. Additionally, we examine the relative shift in peak heights as a function of the polarization angle, determining the molecule-to-molecule arrangement within the sample and the preferred charge transfer. By exploring these photo-luminescent properties of these optoelectronic materials, we aim to further understand the light-based behaviors of ADT.

![Figure 1.1](image.png)

Figure 1.1: The molecular structure of anthradithiophene (ADT) along with its adjacent side groups. The R side groups represent limbs on the molecule where the subsequent derivatives can be attached. Each connection between the main molecule and a side group unique orientations that present different optical characteristics but keep structural stability intact [2].
1.2 Background

The Graham µE (Micro-Femto Energetics) Laboratory uses optoelectronic devices and methods to study spectroscopy and electronic transport, including the examination of new semiconducting materials as potential replacements for silicon. With recent discoveries showing OPVs having exceptional characteristics compared to silicon, continued research on these materials is likely to show promising results about its viability, as currently its low efficiency is a major consequence holding OPVs back [2]. Previously, both Grimm and Brandt reported on this class of ADT derivatives within the Graham µE lab group. They examined the polarization dependence of the absorption, transmission, and reflection intensities of these materials [2], [3]. Grimm was able to determine variance in the intensity of the absorption spectrum through polarization on single domain crystals of ADT, and by observing the various stacking structures and morphology of these derivatives, Brandt found that the ADT crystals showed anisotropy within their electronic properties, presenting unique values of reflection based on polarization as shown in Figure 1.2. This extends the work of Brandt & Grimm through PLE measurements.

![Figure 1.2: ΔR/R spectrum of ADT-TES-F as a function of polarization angle of the incident light. Distinct reflection peaks are noted at approximately 400, 425, 525, and 575 nm over incremented polarization angles [4]. Conducting excitation analysis on this derivative is expected to show similar peak results.](image-url)
1.3 Theory

1.3.1 Emission and Excitation

Through photoluminescence (PL), an excited molecule can release the energy it absorbed from incident light as photons. The spectral details of this emission can be used to characterize the material. This is widely shown in systems such as the harmonic oscillator in quantum mechanics, nebula gas characterization in astrophysics, and examination of chemical materials. The emission spectrum created through the PL process is the emitted intensity from the sample as a function of the wavelength, holding the excitation light constant. The peak height indicates the number of photons being emitted at that particular energy, where each energy value corresponds to a particular wavelength value.

The excited electrons will decay from their excited state and would normally transition back to their original energy state, but in some OPVs like ADT, the decay is a non-radiative transition. These different decays are partially dependent on the coupling between the molecules within the crystal. [5]. Due to the different types of coupling present in ADT, there are phonon-assisted transitions that change the energy required for particular transitions. We see this in Figure 1.3 where there is overlap between the $S_0$ state and the $S_1$ state. Once excited to a higher state, the electrons can non-radiatively relax by the emission of a phonon to a lower vibrational state before emitting a photon at a lower energy. The phonon energy is dissipated as heat. Emission is particularly useful in optoelectronics as it describes charge transfer between energy states.

From an emission spectrum, we locate regions with high photon activity, indicated by the peak locations. From an excitation measurement, we can observe the type of decay of the electrons from their excited state. As mentioned earlier, an excited state electron will decay to its original energy

![Figure 1.3: The nuclear potential wells representing the ground ($S_0$) and excited states ($S_1$) of an OPV like ADT. $\lambda$ is the Huang-Rhys factor and is the interband energy between vibrational energy states. We see the contribution of these two factors above. indicates the transition from the 0th vibrational state to the 0th vibrational state. Figure from Spano [5].](image)
state (the ground state), but through molecule interactions from the side groups, the electrons may vibronically decay into lower vibrational states before transitioning back to the ground state. The added benefit of an excitation measurement is to remove Rayleigh scattering effects that are present in the absorption spectrum. Figure 1.4 shows the excitation of a TES sample at the 600nm band, noting peaks at 422, 480, 520, and 549nm. Analyzing the excitation spectrum shows preferred charge transport of our TES sample.

![Figure 1.4](image)

**Figure 1.4:** The plot above is a photoluminescence spectrum, which is a full PL spectrum for each excitation wavelength. We see variance in the scale of the curve as we change the polarization angle. The S1b and S1a peaks denotes wavelengths of incident light that lead to the emission of photons with wavelength energy at the 600 band. A third peak is noted at approximately 480 nm is unidentified but is significant enough to identify as a peak. The peak at 425nm is the S2 peak. Figure is reproduced from [6].

As we saw from Figure 1.4, by applying linearly polarized light at different angles, the excitation peak corresponding to the 425 nm wavelength changes drastically. Using the emission spectrum, we can organize an excitation measurement to observe the decay of excited electrons. By comparing the excitation behavior to the absorption of the sample, we can see how these electrons decay over their lifetime and whether they directly decay to the ground state, or whether they present uncharacteristic transitions to different states that are activated by changing the energy of incident light.

### 1.3.2 H and J Aggregates

H and J aggregate systems have two distinct types of intermolecular coupling, both relating the dipole orientation of a sample to the charge transfer of electrons to different excited states. By exciting the wave function that corresponds to either an H-like or J-like system, we can demonstrate light harvesting behavior and increase solar-cell efficiency. To understand H and J aggregate
behavior, we observe the case for a linear aggregate of N periodically arranged molecules. We can describe the wave function of this system as a collection electrons occupying either an excited state or the ground state, as shown in equation 1.1.

\[ |\Psi\rangle = |g, g, g, ..., e, ..., g\rangle \quad (1.1) \]

By assuming coupling with its nearest neighbors, we introduce a new matrix element for our Hamiltonian. This matrix element, \( V_{nn'} \), denotes the dipole-dipole interaction between neighboring molecules and has magnitude J. The sign of J in a 1-D system is determined by the angle of the dipole moment with respect to the chain of molecules as shown in Figure 1.5 However, since we have a more complex system that cannot be described as a 1-D chain of molecules, we observe different parameters to determine if our organic crystal is H-like or J-like.

![Figure 1.5: A depiction of N molecules arranged in a 2 dimensional system. The α term refers to the spacing between molecules and β refers to the angle of the dipole moment with respect to the chain. The β term determines if the system is H-like (β > 54.7°) or J-like (β < 54.7°). Figure reproduced from [7].](image)

For a polymeric semiconductor like ADT, the H-like and J-like characteristics are based on the stacking structure between molecules. This in turn affects the energy gap between the ground state and excited state of our system. We see this depicted in Figure 1.6. For a head-to-head stacking arrangement, the system is J-like and there is an energy dip between the ground state of the electron to the excited state. For an H-like system, the stacking structure is side-to-side, creating an energy hill. The excited electrons will move to the lowest point on this energy hill and in turn, affecting the coupling in the system. We see that the decay to the ground state at this point is not favorable, and so the transition becomes heavily suppressed, making phonon-assisted transitions more favored over radiative transitions.
Figure 1.6: The stacking structure for H and J aggregate systems. A J-like system exhibits a head-to-tail stacking structure and allows radiative emission to the ground state. In an H-like system, the stacking structure is from side to side. We see that in H-like systems, the transition to the ground state is prohibited and only accessible through phonon-assisted transitions. Figure reproduced from Spano [8].

1.3.3 Crystal Structure and Coupling

The diFluorinated ADT for TES, TDMS, and TSBS derivatives each have a silicon center that does not affect the central orbitals from the core molecule. TES and TSBS have 2D $\pi$-stacking and 1D sandwich-herringbone molecular stacking, respectively [3]. Both TES and TDMS resemble a triclinic crystal structure, in which the angle between each axis vector is different [9]. TES exhibits a miller index of (001), indicating its molecular plane intercepts only the c axis of the molecule. TDMS and TSBS represent (010) and (011) miller indices respectively.

The nature of the coupled system shows that every state that is excited is also vibronically connected. This allows for electrons located in the bottom of their local potential well to move down to the bottom of the global potential well when some energy is applied to their system.
2 Experimental Process

2.1 Crystal Growth

The ADT crystals were provided by the Ostroverkhova Lab. The ADT solution is made in Chlorobenzene because of its high vaporization point, allowing the crystals to settle. TES and TSBS crystals were grown on a glass microslip rinsed with acetone, isopropyl alcohol, and deionized water and are cooled for 3-5 hours in order for the Chlorobenzene to evaporate.

TDMS was more difficult to grow due to rapid evaporation of the solution. An indent on the glass slide was created to settle the solution within the crevice of the glass. This allows the solution to initiate nucleation and crystallization on a time scale quicker than evaporation.

2.2 Measurement Process

The 500W Xenon arc lamp, iHR monochromator, and the Princeton Electron-Multiplying Charge Coupling Device (EMCCD) camera are set to the functioning specifications for PL emission and excitation measurements. A comprehensive diagram of the experimental set-up is provided below in Figure 2.1.

![Experimental set-up for spectroscopy measurements, excluding emission.](image)

**Figure 2.1:** Experimental set-up for spectroscopy measurements, excluding emission. The Xenon arc lamp coupled with the monochromator applies light through the fiber optic cable from below the sample. A tunable knob allows adjustment of the angle of polarization onto the sample. The translator circuit, TC, and connects from the internal circuitry of the light source to the EMCCD camera, allowing for proper triggering software after incrementing to a new wavelength. Image from G. M. Brandt [4].

The crystals are laid onto a glass substrate on the stage below the camera objective. The FluorEssence software prepares the iHR monochromator for an emission spectrum measurement. The Lightfield software allows for enhanced imaging of the sample and is prepared to take pictures of the sample at each wavelength. The Xenon arc lamp is set to 467 nm (the brightest wavelength) and the microscope objective is manually adjusted until the ADT sample is in focus. Regions of interest from the sample are qualitatively determined such that there are a minimum number of domains layered on top of each other and a region of just the substrate can also be seen. Figure 2.2 shows a focused image of the ADT-TES-F sample used in this report and Figure 2.3 shows the dipole moment orientations within an arbitrary sample.
Figure 2.2: Analyzed region of ADT-TES-F under a 40x objective. The left and right crystals are analyzed for their intensities as a function of wavelength. The darker region likely indicates a minimum in intensity with respect to the polarization angle at that wavelength. The left crystal shows multiple domains, indicated by the difference in contrast throughout. Image taken by G. M. Brandt and G. M. Mayonado [6]

2.2.1 Emission

The sample is placed under the microscope which is illuminated with monochromatic light using the Fluorlog double monochromator system. The sample is scanned by having the monochromator adjust the angle of the diffraction grating, changing the wavelength of light.

Figure 2.3: An example of the different dipole orientations within a single region. Each arrow indicates the direction of the dipole moment, while each section indicates a different domain. Individual regions are selected to properly measure the polarization with respect to these domains. [6]
2.2.2 Excitation

Based on the spectra generated from the emission spectrum, a bandpass filter is placed between the EMCCD camera and magnifying objective. A bandpass filter is selected such that only photons with energy matching that of the emission peaks are allowed through. These photons are recorded by the EMCCD camera. FluorEssence is then adjusted to measure an excitation spectrum, here the wavelength region begins from the visible range of light (390 nm) and ends before the cutoff wavelength of the filter. Lightfield is adjusted to record the image of the sample for every increment in the wavelength through the scanning process. After the scan is complete, the collection of images is saved onto the local database for the research group, and the bandpass filter is removed. A transmission scan is done immediately after, differing in that it allows all wavelengths transmitted by the sample and the lamp to be recorded by the camera. The process is once again repeated for a different value of the polarization for both excitation and transmission. Figure 2.4 shows the effect on the crystals as a scan is done at a different polarization angle for both ADT-TES-F and ADT-TDMS-F. A spectrum of the lamp is also obtained to normalize the intensity spectra.

![Figure 2.4: The crystal samples of ADT-TES-F (a) and ADT-TDMS-F (b). The ADT-TES-F crystal was set to 225° polarization. (a) We can distinctly see at least two domains on the right crystal labeled D1 and D2 indicated by the difference in the shading. (b) The ADT-TDMS-F sample also show very faint signs of multiple dipole moment orientations at 350 degree polarization. An attempt is made to distinguish particular domains, noted as D3 and D4. Images taken by Brandt and Mayonado.](image-url)
2.3 Manipulating the Data

The collection of images from each file (denoted as a 'movie') is examined and a single domain of the sample is selected. The average intensity within that region is taken using the snipping tool and used as one of the variables to determine the total PLE value. An algorithm calculates the total PLE value after extracting each variable. The algorithm takes the raw lamp data, background data, excitation data, and the scaling factor of the quantum efficiency to calculate a ratio between the contribution of the lamp and the energy of the sample and plots this ratio as a function of wavelength. We find the proper relationship between the intensity of the sample versus the lamp by subtracting the background (dark) contribution to the PLE spectrum and dividing it by the raw lamp spectrum. We then multiply by the quantum efficiency (QE) of the EMCCD camera. We mathematically display the calculated data via equation 2.1.

\[
PLE = \left( \frac{PLE_{\text{sample}} - Dark}{Lamp} \right) QE \tag{2.1}
\]

The data are compared alongside a curve representative of the absorption (A) which is calculated as a function of the transmissive light through the sample. The transmissive intensity is composed of two parts due to the contribution from the glass substrate \( T_{\text{sub}} \) and from the sample itself \( T_{\text{sample}} \).

\[
A = \frac{T_{\text{sub}} - T_{\text{sample}}}{T_{\text{sub}}} = \frac{\Delta T}{T} = 1 - \frac{T_{\text{sample}}}{T_{\text{sub}}} \tag{2.2}
\]

For each polarization plot, we use a comparison of \( \Delta T/T \) (absorption) and PLE (excitation) to observe the energy (in wavelengths) required to excite an electron such that it will emit a particular energy. In typical materials, the absorption of the material can be composed by a scalar fit from any of its PLE spectra, regardless of the observed wavelength. The absorption can also be composed of the linear combinations of each PLE spectrum and we can demonstrate this in equation (2.3) below where \( \alpha \) and \( \beta \) are arbitrary constants. We apply the same logic to ADT and its side groups to determine whether the excitation of the sample behaves similar to any other organic aggregate or if there is unique behavior is being exhibited regarding the emission energy of the photons.

\[
A = \alpha PLE_{\lambda_1} + \beta PLE_{\lambda_2} + \ldots \tag{2.3}
\]

Each derivative has two definite emission peaks and so each plot corresponds to a band that aligns with that peak. However, if the sample behaves like that of a typical OPV, than a single PLE spectrum will match the absorption by a scaler factor, as described in equation (2.4)

\[
A = \gamma PLE \tag{2.4}
\]

Figures 3.3 through 3.10 show the PLE of each ADT derivative at multiple bands along with the absorption.
3 Results and Discussion

The plot shown in Figure 3.1 details the absorption and emission of different ADT compositions. We use this plot to determine the different bands of light that emit a particular value energy from the sample. With this information, we conduct an excitation measurement of each derivative by having the EMCCD camera focus on those bands.

Images of the samples are saved on the local group drive, where they are organized based on sample used, crystal observed, band of wavelength, and polarization of light. The data is also separated based on the measurement done (PLE and absorption). Each data set is then plotted and each transition peak is labeled and marked on the graphs.

Figure 3.1: The emission and absorption spectrum of the side group derivatives of ADT, the left line curve corresponds to the absorption of the material while the right line curve displays the emission spectrum. Each derivative has been offset along the vertical axis to avoid layering. Image given to us by the Ostroverkhova Lab [9].
3.1 ADT-TES-F Spectra

The PLE and absorption spectra for ADT-TES-F are shown from figures 3.2 to 3.4 below. Polarization angles were done with 36° increments. The ADT-TES-F crystal was of much higher quality compared to the other samples and so more polarizations were taken here. Each transition peak is labeled and a marker is placed around their approximate location.

![Absorption of ADT-TES-F](image)

**Figure 3.2:** The absorption spectrum for ADT-TES-F. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, the S1c transition is located at the 485 nm peak, and the S2 transition is located at the 420 nm peak.
Figure 3.3: The PLE spectrum for ADT-TES-F, focused on the 575 nm band. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, the S1c transition is located at the 485 nm peak, and the S2 transition is located at the 420 nm peak.

Figure 3.4: The PLE and absorption spectrum for ADT-TES-F, focused on the 640 nm band. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, the S1c transition is located at the 485 nm peak, and the S2 transition is located at the 420 nm peak.
3.2 ADT-TDMS-F Spectra

The PLE and absorption spectra for ADT-TDMS-F are shown from figures 3.5 to 3.7 below. Only three polarization angles were done for this sample. Few polarization angles were done because enough information could be drawn from each current measurement. The wavelength range for these samples were limited to a maximum of 540 nm for both the absorption and 570 band. This results in the S1a transition being omitted. The S1a transition still does occur in both these plots and can be seen in the 620 nm band.

![Absorption of ADT-TDMS-F](image)

**Figure 3.5:** The absorption spectrum for ADT-TDMS-F. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 516 nm peak, the S1c transition is located at the 485 nm peak, and the S2 transition is located at the 420 nm peak.
**Figure 3.6:** The PLE spectrum for ADT-TDMS-F, focused on the 570 nm band. The S1b transition is located at the 515 nm peak, the S1c transition is located at the 485 nm peak and the S2 transition is located at the 420 nm peak.

**Figure 3.7:** The PLE spectrum for ADT-TDMS-F at the 485, focused on the 620 nm band. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, the S1c transition is located at the 485 nm and the S2 transition is located at the 420 nm peak.
3.3 ADT-TSBS-F Spectra

The PLE and absorption spectra for ADT-TSBS-F are shown from figures 3.8 to 3.10 below. The emission spectra between ADT-TSBS-F is largely different than that of the other 2 ADT derivatives. From the emission plot in figure 3.1 for ADT-TSBS-F, there is a very prominent absorption peak that is not seen on the other derivatives. This peak is theorized to not show up in the emission due to the increased number of paths available after the crystallization of ADT-TSBS-F, giving a higher photon count spread through the sample and a smaller stokes shift [6].

![Absorption of ADT-TSBS-F](image)

**Figure 3.8:** The absorption spectrum for ADT-TSBS-F. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, the S1c transition is located at the 484 peak, and the S2 transition is located at the 420 nm peak.
Figure 3.9: The PLE spectrum for ADT-TSBS-F, focused on the 550 nm band. The S1a transition is located at the 550 nm peak, the S1b transition is located at the 515 nm peak, and the S2 transition is located at the 420 nm peak.

Figure 3.10: The PLE spectrum for ADT-TSBS-F, focused on the 570 nm band. The S1a transition is located at the 530 nm peak, the S1b transition is located at the 495 nm peak, and the S2 transition is located at the 420 nm peak.
3.4 Data Analysis

We provide an analysis of both a comparison between bands and their emission peaks to the absorption spectra as well as a look at the dependence of the samples across the polarization of light for H and J-like occurrence within each derivative.

3.4.1 Excitation to Absorption Comparison

By plotting both the absorption and PLE together, we can compare the shape of each band spectra to the absorption spectrum. We provide comparisons of each sample under specific polarizations. Figures 3.11 to 3.13 show plots of ADT-TES-F, ADT-TDMS-F, and ADT-TSBS-F at 9 degrees, 90 degrees, and again 90 degrees polarization respectively.

Figure 3.11: A plot of the PLE and absorption of ADT-TES-F at 9 degrees polarization. The 575 band cuts short because as the wavelength of light begins to approach the bandpass filter, the light being recorded would match that of being emitted which would obstruct the data. The S1a and S1b peaks still line up at the same wavelength in both band spectra as well as the absorption spectra. The vertical axis measures the PL and absorption, both of which are given in arbitrary units (normalized).

The ADT-TES-F plot above displays near exact spectra shape, with both the S1a and S1b emission peaks being located at the same wavelength. Relative peak heights and areas qualitatively look identical. From these plots, we confirm non-unique transitions based on the wavelength of incident light, determining that the sample behaves normally.
Figure 3.12: A plot of the PLE and absorption of ADT-TDMS-F at 90 degrees polarization. The S1a peak is not included because the measurement was stopped for both the absorption and 570 band at 540 nm. The data for both the PL and absorption measurements is not as precise, likely due to the lower quality of the crystal. The vertical axis is once again unitless and is a measure of the normalized PL or absorption of the sample.

Once again we see excitation peaks that are equivalent, by a scalar factor, across the bands when compared to the absorption. The S1b and S1c transitions are located at the same wavelength for all measurements (515 nm and 485 nm). We expect the S1a transition to also be at the same wavelength but cannot measure it for the 570 band because of the incident light being recorded as emitted light. For the 0 and 45 degree polarization measurements, the transition peaks are fairly low, but the relative spectra shapes still match. Additional measurements should be taken on a new sample to confirm spectra matching across bands. We take the 90 degree polarization comparison to still be valid and confirm non-unique transitions for ADT-TDMS-F as well.
Figure 3.13: A plot of the PLE and absorption of ADT-TSBS-F at 90 degrees polarization. The S1a peak is not seen in the 550 band as it occurs too close to the band pass filter, and so measurement halted there. All transition peaks are displayed at very clear wavelengths, and are all relatively close in height.

We again see a matching curve with respect to peak location and height. The S1a, S1b, and S1c transition peaks converge at the same wavelength. General curve form also matches that across all polarizations and bands. We do see a difference in peak height in the 570 band versus the absorption spectrum. We suspect this to be an error in the measurement, as the peak dips considerably for this polarization measurement. With this plot, we confirm that all three ADT samples present non-unique transitions with respect to the wavelength of incident light.

3.4.2 H and J aggregate appearance as a function of polarization.

We now look at the effect of the polarization angle to the peak heights in the S1 transitions. We describe H-aggregate systems that have higher phonon-assisted transition peaks (S1b and S1c) with respect to the non-assisted transition peak (S1a). We adjust each PLE plot to observe only polarization effects, so the vertical axis is no longer numerically correct, which allows for qualitative judgment of each polarization. Figures 3.14 to 3.16.
Figure 3.14: The plot above shows the adjusted spectra of ADT-TES-F at different polarizations, focused on the 640 nm band. The polarization measurements were equalized at 450 nm. The peak response from the sample is the largest at 45 degrees, and decreases at each angle increment until 153° and 9°.

The figure above shows the change in the relative peak heights at each polarization measurement. The 45° polarization gives the strongest response, indicated that the sample is the most J-like at that polarization, incrementing in polarizations from then result in the sample becoming more and more H-like. The PL begins to become more J-like once again at the 153° and 9° polarizations. These both occur at least 90 degrees after the highest J-like response at 45°. We can infer then that a J-aggregate dipole orientation is perpendicular to an H-aggregate dipole orientation, and is found between 45° and 9° degrees. We then find that we can tune the H and J response from ADT-TES-F by adjusting the polarization of light from the sample.
Figure 3.15: The plot above shows the adjusted spectra of ADT-TDMS-F at different polarizations, focused on the 620 nm band. The polarization measurements were equalized at 435 nm. The highest peak response is at 90° while the lowest is located at 45°. The J-aggregate dipole orientation is then located around the 90° polarization angle while the H-aggregate dipole orientation is around the 45° polarization.

From the figure above, we see a minimum peak response at 45°, opposite to that of ADT-TES-F. Additionally, the most J-like response occurs at 90°, which is not perpendicular to the H-like response. This implies that either the system has a more complex H and J-aggregate dipole orientation or the most J-like response is some angle past 90° and the most H-like is below 45°. We still are able to conclude the availability of tuning the H and J response from the sample based on the polarization of light.
Figure 3.16: The plot above shows the adjusted spectra of ADT-TSBS-F at different polarizations for absorption. The $90^\circ$ polarization for this sample shows the strongest J-like response, while $0^\circ$ shows the weakest, with $45^\circ$ being in between but is closer aligned to the $90^\circ$ polarization.

For analyzing the H and J-like response for ADT-TSBS-F, we use the absorption because it has the least irregularities in the data and captures all transition peaks. Additionally, from our conclusion earlier, we have enough similarity between the PLE and absorption that the resulting interpretation applies for both.

For ADT-TSBS-F, we see shifts in the peak height that correspond to an adjustable J-like system. However, through all the three measurements, the sample appeared as J-like. Due to TSBS-F unique molecular stacking structure (herringbone), we assume that the sample is generally J-like in nature, but additional polarization measurements would be able to confirm this.

With the addition of this plot, we are able to confirm that the H and J aggregate coupling can be isolated through the angle of polarization of incident light on the sample. This is shown consistently through all bands and measurements.
4 Summary

We have observed the side group structures of ADT, TES-F, TDMS-F, and TSBS-F, in order to report the excited state transitions in both PL and absorption. Using a transmissive experimental set-up, we are able to isolate specific bands with high photon emission. By isolating these bands, the contribution to a specific emission peak can be seen through a PLE measurement. We then compare these contributions to that of the absorption of the samples. By comparing the spectra that correspond to the same polarization, we see that regardless of band, the samples do not show unique or preferred transitions. Instead the samples exhibited behavior that is more consistent within OPVs, as seen in the scaled fit between the absorption and PLE.

We then continue our analysis to observe the H and J-aggregate coupling within the sample. By adjusting the polarization of the sample, we find that we can tune the H and J response to a noticeable degree. ADT-TES-F exhibited both H and J-like behavior, with it being the most J-like at 45°. ADT-TDMS-F showed strange results with the most H-like response not being perpendicular to the most J-like response. However ADT-TSBS-F showed maximal H-like and J-like responses at orthogonal angles, which is expected based on H and J-aggregate dipole orientations. The results for these three samples demonstrate our capacity to tune the optical response from the sample by engineering the wave function through stacking morphology. This allows us to increase our solar cell’s efficiency by applying different polarizations of light to single out the response for particular optoelectronic techniques.

Future work could look into increase measurements of ADT-TDMS-F and ADT-TSBS-F to finalize a definite conclusion to the H and J-like response (whether it is mostly J-like in TSBS-F and whether the maximal responses are less than 45° from each other). Additionally, more optoelectronic analysis techniques could explore the effect of the stacking structure within ADT-TSBS-F.
References


[9] Private communications with the Ostroverkhova Lab.