# STUDY OF MAGNETO-OPTICAL BEHAVIORS AT A FERROMAGNETIC/ORGANIC SEMICONDUCTOR INTERFACE

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

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# ABSTRACT

Organic materials have been widely studied for the last 20 years to use for photovoltaic applications. Organic photovoltaic materials have shown promising properties for solar cells, such as very low cost, flexibility, easy fabrication methods, etc. Although power conversion efficiencies for organic-based solar cells have exponentially grown in the last decade, up to about 13% in early 2016, it is still optimal to increase these efficiencies. In order to raise efficiencies, it is important to study the fundamental mechanisms inside organic materials that lead to photovoltaic properties. This thesis reports the magneto-optical effects on the p-type organic semiconductor, tetracene, from a ferromagnetic/semiconductor interface between thin films of cobalt and tetracene. Magnetic field effect measurements were used to study singlet fission inside tetracene and effects from cobalt on singlet fission in tetracene. When a thin layer of cobalt was added, two main effects were determined. Magneto-photoluminescence results gave evidence of spin interactions at the interface causing spin polarization at the surface of tetracene, reducing hyperfine interactions and increasing the density of inter-triplet states, resulting in net increases in singlet fission. Photoluminescence and absorption results gave evidence of electrical interactions at the interface causing electrical polarization at the surface of tetracene, increasing the electron phonon coupling of tetracene as well as quenching photoluminescence. It is proposed that these changes from the ferromagnetic/organic semiconducting interface can be furthered utilized in

photovoltaic and transistor applications based on singlet fission materials and possibly other similar types of organic material-based devices.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Brief History of Inorganic and Organic Photovoltaics

A solar cell is defined as a photovoltaic cell that absorbs solar radiation and converts the photons to electricity. The first solar cell capable of converting enough of the sun's energy into power to run everyday machinery was produced at Bell Telephone Laboratories in 1954, an inorganic silicon solar cell with 4% power conversion efficiency (PCE). The efficiency of these cells reached up to 24% in 1998 (an increase of 20% over a span of more than 40 years).[1,2] Not only are the costs of silicon solar cells high, but the theoretical limit is only 30% efficiency.[3,4] Therefore, new ideas for solar cell systems began to be explored. Organic systems have gained a lot of attention for photovoltaics as the efficiency of such systems have rapidly grown from 4.4% in 2004 up to 11% in 2014 (an increase of 10% over a span of only 10 years).[5,6] Organic photovoltaics (OPVs) have many promising properties for use in solar cells including, but not limited to: flexibility, ultra-thin active layers, low cost and easy fabrication. In order to further improve the efficiencies and abilities for commercial application of OPVs, it is required to study and understand the basic fundamentals behind the mechanisms in organic semiconducting materials that allows for photon conversion to electricity. Tetracene has been heavily studied as a prospect

material for OPVs because of its mechanism of singlet fission.[7-13] In this thesis, tetracene was chosen as the specific organic semiconductor to study singlet fission towards understanding the basic fundamentals of the mechanism for photon conversion in photovoltaic applications. Singlet fission and the advantages of tetracene will be discussed in detail in Chapter 2. In Figure 1-1, a schematic has been provided to show an example of a solar cell based on tetracene.[14] In this example, indium tin oxide (ITO) is used as the anode for hole collection, PEDOT:PSS is used as a hole transport layer, tetracene is the donor material, $C_{60}$ is the acceptor material, bathocuproine (BCP) is used as an exciton blocking layer for electron transport, and finally, aluminum is used as the cathode for electron collection. The working principles of this type of OPV device are explained in detail later in the chapter.

## 1.2 Impact of Interfacial Interactions in Organic Photovoltaic Devices

Interfacial processes and interactions are heavily studied for device processing for many different applications including photovoltaic devices. A p-n heterojunction is one of the well-known interfaces used in organic photovoltaic devices. A tetracene(p-type)/$C_{60}$(n-type), donor/acceptor interface is widely used in tetracene-based organic photovoltaics.[11-14]

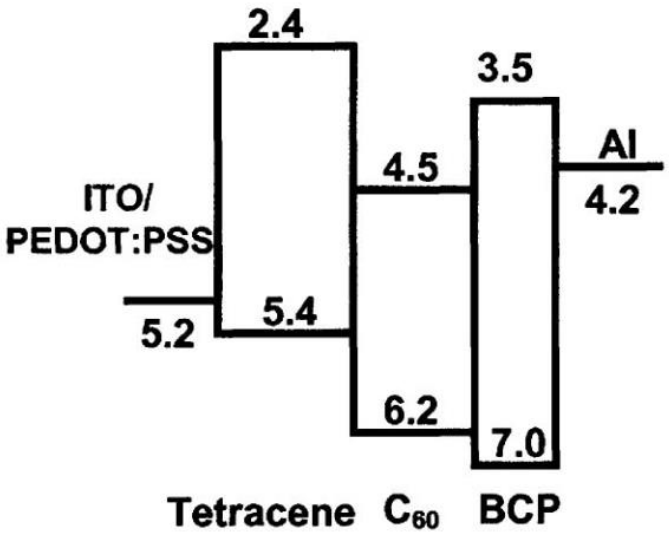


Figure 1-1: Schematic of a Tetracene/$C_{60}$ Based Solar Cell Device Showing the Band Diagram.

Figure 1-2 shows the working principle for an OPV device. Photons are absorbed by the donor layer and are used to form excitons, through singlet fission in tetracene. Then the excitons diffuse through the donor layer, and diffuse through the heterojunction interface by photoinduced electron transfer. Once they diffuse through the acceptor layer, electrons can be collected at the cathode, which forms the electricity through the device.[15] Understanding how excitons diffuse across the interface of a p-n heterojunction inside an OPV is needed to understand the importance of how excitons form in the p-type organic semiconducting active layer. Looking at Figure 1-2, it is clear that if more excitons are formed in the donor layer, it is possible for more electrons to be collected in the cathode to generate more power from the OPV. This process is driven by electrons from the donor layer and holes from the acceptor layer diffusing towards the cathode and anode, respectively. Therefore, there is motivation to study singlet fission and possible ways to increase the rate and amount of singlet fission to generate more excitons for electron collection at the cathode, which will lead to an increase in the power conversion energy (PCE) of the device. Many other types of interfaces have been used in photovoltaic applications to improve desired properties of devices. The main interface this thesis focuses on is an interface between a ferromagnetic layer and an organic semiconducting layer. Many studies have been done on the beneficial effects from a ferromagnetic/organic semiconducting interface.[16-28] Because singlet fission is based on the singlets and triplets of electron states in an organic

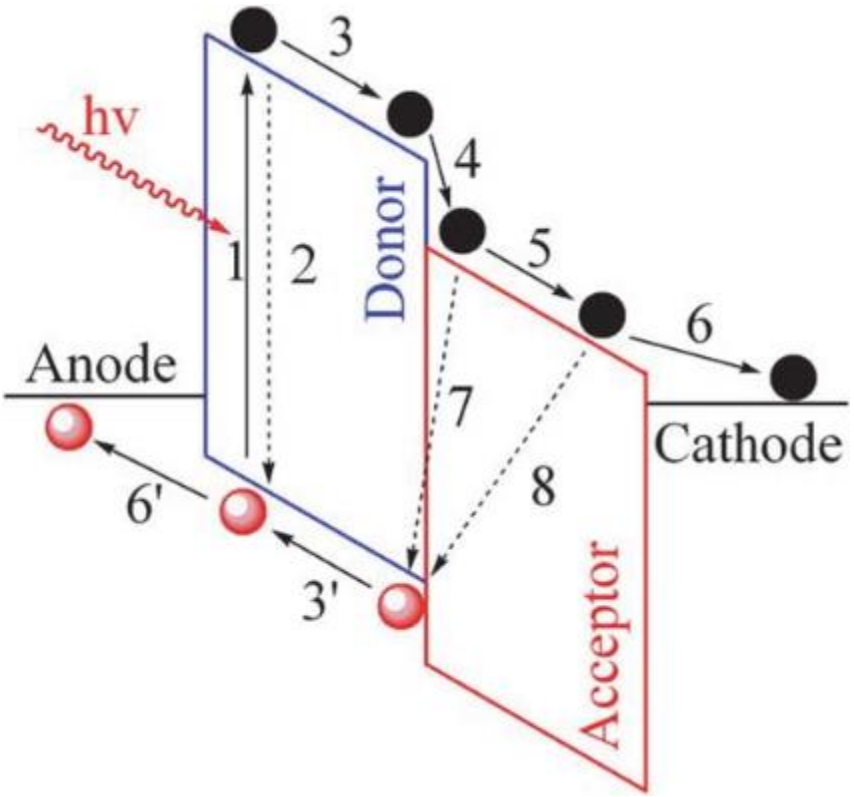


Figure 1-2: Schematic of Working Principle in Organic Bulk-Heterojunction Solar Cells. 1. Photon Absorption; 2. Intra-molecular recombination; 3. Exciton Diffusion through Donor Layer; 3'. Hole Diffusion through Donor Layer; 4. Photoinduced Electron Transfer at Donor-Acceptor Interface; 5. Exciton Diffusion through Acceptor Layer; 6. Electron Collection at the Cathode; 6' Hole Collection at the Anode; 7. Germinated Recombination; 8. Biomolecular Recombination.[15]

semiconducting layer, it is clear that it is a spin-dependent process. Therefore, it is proposed that a ferromagnetic layer in junction with an organic singlet fission layer can create spin polarization at the interface in order to enhance singlet fission in the organic semiconducting layer.

# CHAPTER 2

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Singlet Fission in Organic Semiconductors

Singlet exciton fission, or singlet fission, is a spin-allowed process in which one singlet excited state converts to two triplet excited states. A schematic showing how singlet fission occurs is shown in Figure 2-1. In an organic material, such as tetracene, unexcited neighboring molecules exist as ground state singlets, as shown in Figure 2-1(a). When one photon is absorbed, one molecule is excited from the singlet ground state ($S_0$) to an excited singlet state ($S_1$), as shown by molecule A in Figure 2-1(b). Next, the excited singlet state relaxes to a lower energy excited triplet state ($T_1$) by a process known as intersystem crossing, where the spin of the excited electron is reversed by a radiationless process. This process is allowed by hyperfine interactions, which will be discussed in section 2.3. The energy created from this process by molecule A can be shared with the neighboring molecule B through fluorescence resonance energy transfer. The transferred energy from molecule A is then used by molecule B to excite it from a singlet ground state to an excited triplet state. By this process, it is shown that tetracene is able to absorb one photon, consequently generating two excited triplet states.[7-13,29] The process of singlet fission was first introduced

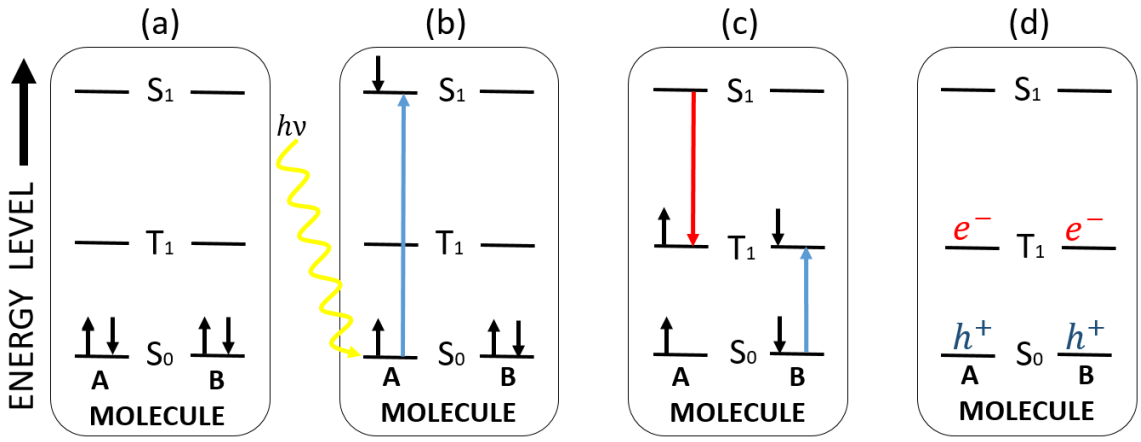


Figure 2-1: Schematic for the Working Principle of Singlet Exciton Fission. (a) Two Neighboring Molecules in their Singlet Ground States in an Organic Semiconducting Material, such as Tetracene (Each molecules represents one electron). (b) A photon is absorbed, which excites one molecule from the ground singlet state to the excited singlet state. (Excited electron is paired with left behind hole) (c) Molecule A relaxes from the excited singlet state to the excited triplet state. Through intersystem crossing Molecule B is excited to the triplet excited state. (d) Each Triplet generates a free electron-hole pair.

in 1965 to describe the photophysics of tetracene. Early studies of magnetic field effects on fluorescence of tetracene helped gain understanding of singlet fission.[30]

Singlet fission is a very important mechanism that has gained great attention for its promising propertiess in OPV devices. When singlet fission is paired with a solar cell with suitable low energy gap materials, it is able to increase power conversion efficiency by enhancing photocurrent in the visible spectrum.[31,32] Tetracene has been shown to be one of the best candidates for singlet fission, which is why it has been chosen as the studied system for this thesis. The triplet yield of tetracene has been shown to reach 153%±5%, generating internal quantum efficiencies (IQE) of 127%±18%. Here, IQE is defined as how many excited triplet states are generated per one photon absorbed. Losses in IQE are caused by singlet exciton dissociation, fluorescence, and triplet exciton diffusion.[11] Also, tetracene specifically absorbs blue and green photons. Singlet fission then generates two triplet excitons with energies of about 1.25 eV. The energy of the triplet excitons generated by tetracene closely match the bandgap of silicon (1.1 eV), which provides special motivation for tetracene-based solar cells to be combined with preexisting silicon solar cells to enhance their PCEs.[14,33-37]

## 2.2 Important Properties of Organic Semiconductors Studied in this Thesis

There are many important properties studied in this work that will be briefly explained in this section. Two of the main properties measured include absorption and photoluminescence. Absorption spectra are measured by first using a blank substrate to calibrate the measurements, by scanning the substrate with UV-Vis light ranging from 330-1000 nm in wavelength to create a baseline of absorption of light. Then, the samples are placed inside the instrument to measure the absorption spectra. The absorption spectrum is important to measure to know what wavelength of light should be used in order to excite the material. After this is done, photoluminescence can be measured by using the proper wavelength of light for photoexcitation (in these experiments a continuous wavelength laser) and collecting the emission from the sample using a spectrometer. An example measurement schematic is shown in Figure 2-2. Photoluminescence is started by the absorption of photons from a photoexcitation source. The energy from the photons excites states inside a material, as shown previously in Figure 2-1(b). The photoluminescence is then generated by the relaxation of excitons to the ground state, which emit photons in the form of emission. The next important property in organic semiconductors to be introduced is hyperfine interactions (HFI). This property is very important for Intersystem crossing, which was previously discussed in Section 2.1 when singlet fission was introduced. Intersystem crossing is the transition of singlet to

triplet states. This process is typically forbidden, because it involves reversing the spin of an orbital electron. However, in organic semiconductors HFI allow this transition to occur. Figure 2.3 shows a simple schematic representation of hyperfine interactions. These interactions occur between the magnetic field generated by the spin momentum of electrons and the inherent magnetic field from the nucleus. HFI is able to induce spin mixing in molecules of tetracene to enable the process of singlet fission. MFE measurements are able to determine relevant information about HFI at low fields (below 150 mT).[38] Electron-phonon coupling is the final important property to be introduced to fully understand the results of the experiments. Electrons move throughout a rigid crystal lattice in a periodic manner. The crystal lattice of all materials is not perfect, which means that it is deformable. Displacements of atoms from equilibrium positions are known as phonons. Electrons interact with these phonons, which is known as electron-phonon coupling. These interactions have many implications in organic semiconductors including a decrease in the electron mobility. This is a relevant issue, since organic solar cells need to transport charge.

## 2.3 Magnetic Field Effect Measurements

Magnetic field effect (MFE) measurements are a unique type of measurements used to study the organic semiconductor, tetracene, and the interface between cobalt and tetracene in this thesis. In these measurements, multiple properties can be measured as a function of the strength of an externally applied magnetic

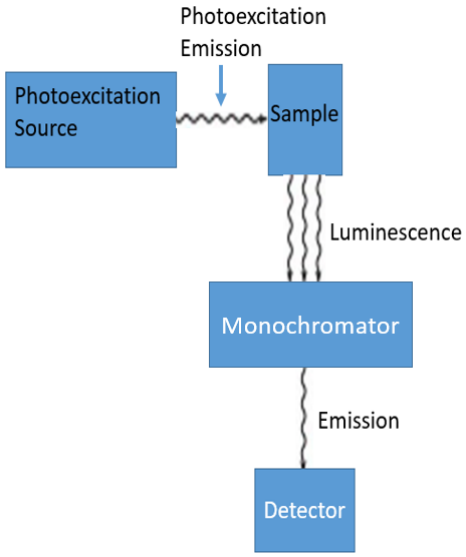


Figure 2-2: Schematic for Measurement Setup of Photoluminescence.

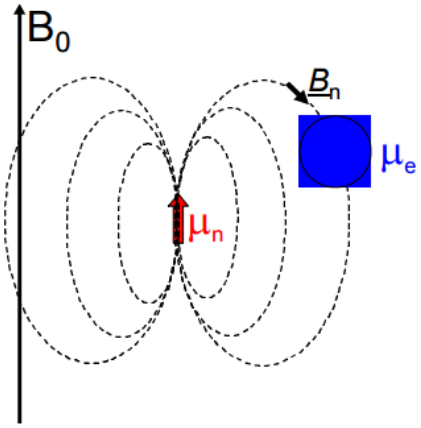


Figure 2-3: Schematic Representation of Hyperfine Interactions.

field. These range from low-field measurements (below 150 mT), to high field measurements (between 150 mT and 900 mT) for the studies in this thesis. There has been a long history of using MFE measurements to study the kinetics of chemical reactions.[39,40] More recently, MFE measurements have been applied to study properties of organic semiconductors such as, magneto-photoluminescence ($MFE_{PL}$)[10,41], magneto-electroluminescence[42,43], magneto-resistance[44,45], magneto-photocurrent[46,47], etc. The fundamental mechanism of MFE measurements on organic semiconductors results from interactions between the external magnetic field and internal magnetic field of paramagnetic excited states including triplet excitons (S=1), free electrons and holes (S=0.5). Because of these interactions, it is well-known that $MFE_{PL}$ measurements can be used to study singlet fission in organic semiconductors.[48] Magneto-photoluminescence is the main experimental tool used in this work. Magneto-photoluminescence is a tool that is commonly used to elucidate the rate of singlet fission inside a material. When an external magnetic field is applied during $MFE_{PL}$ measurements, the percent change of photoluminescence is determined. Using this data, we can analyze the relative density of triplet states inside the material by the amplitude of $MFE_{PL}$. A higher amplitude (positive or negative) of $MFE_{PL}$ means that the density of triplet states increases, which means that the rate singlet fission increases.[10] In this thesis, $MFE_{PL}$ measurements are used to study relative rates of singlet fission in tetracene and the effects of the

cobalt/tetracene interface. The set-up used for the $MFE_{PL}$ measurements is discussed in detail in Chapter 3.

# CHAPTER 3

# EXPERIMENTAL DESIGN

## 3.1 Materials and Sample Design

Tetracene and cobalt wire were purchased from Sigma Aldrich and used as received for sample preparation. The pre-cleaned glass substrates were treated with UV-zone before sample preparation. For thin films without cobalt, tetracene films were deposited on the glass substrates by thermal evaporation with thicknesses of 10, 15, 50, 100, and 150 nm. For thin films with cobalt, cobalt was first deposited on the glass substrates by thermal evaporation with a thickness of 10 nm, then the same tetracene thicknesses from above were deposited onto the cobalt layer. All thermal evaporation was done in a high-vacuum chamber at a pressure of $2x10^{-6}$ torr.

## 3.2 Measurement Designs

All measurements in these experiments were completed at room temperature. Absorption measurements were completed using a Lambda 35 UV/VIS spectrometer from PerkinElmer instruments. Absorption measurements were always completed first on the samples to make sure that exposure to the

photoexcitation source during photoluminescence measurements did not affect the samples. After absorption measurements, photoluminescence was measured for each sample using a 405 nm continuous wavelength (CW) laser as the photoexciation source. The PL spectra were recorded using a Flurolog spectrofluorometer from Horiba. Lastly, magnetic field effect photoluminescence ($MFE_{PL}$) was measured for each sample. For $MFE_{PL}$ measurements the samples were placed between poles of a large electromagnet. The samples were aligned parallel to the applied magnetic field from the electromagnet. The applied magnetic field was slowly increased from 0 to 900 mT. The same 405 nm CW laser was used as the photoexcitation source and was placed at a 60º angle to the sample. The photoluminescence from the sample was then transferred by an optical fiber to be recorded by the same Fluorolog spectrofluorometer used for the PL measurements. $MFE_{PL}$ was defined as

$$MFE_{PL} = \frac{PL_B - PL}{PL} \qquad \text{(Equation 1)}$$

where $PL_B$ is the photoluminescence under the applied magnetic field and PL is the photoluminescence with no applied magnetic field. The schematic shown in Figure 3-1 shows how the $MFE_{PL}$ measurements were setup.

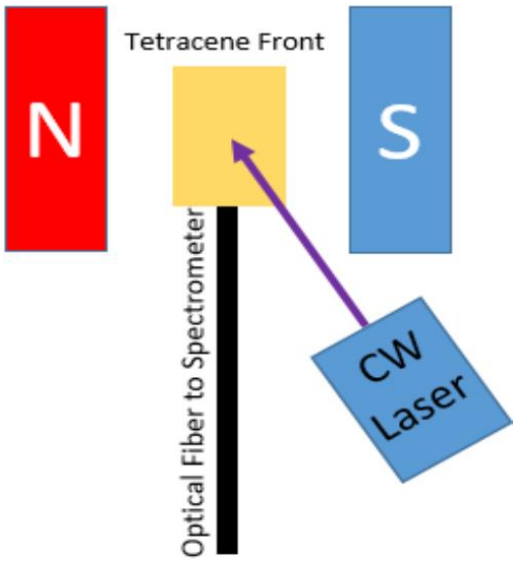


Figure 3-1: Schematic of $MFE_{PL}$ Measurement Setup.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Magnetic Field Effect Results

As discussed in Chapter 2, magnetic field effect measurements have been widely used to study single fission in organic materials. Figure 4-1 shows the percent change of magneto-photoluminescence ($MFE_{PL}$) for tetracene thin films ranging from 10 nm to 150 nm. The curve shape of each sample agrees with previous $MFE_{PL}$ studies in previous literature on thin film tetracene.[10] Figure 4-1(a) shows $MFE_{PL}$ data for tetracene samples without a cobalt layer, and Figure 4-1(b) shows $MFE_{PL}$ data for tetracene samples with a 10 nm cobalt layer between the tetracene and glass substrates. All of the films from 50 nm to 150 nm film thickness in Figure 4-1 have an initial negative $MFE_{PL}$ component at low field (< 50 nm) and then a positive $MFE_{PL}$ signal at high field (> 50 nm). The 10 nm film shows higher negative to positive critical field values from the thicker films, and also changes value when cobalt is added, unlike the thicker films. These low-field effects will be discussed later in this section. In Figure 4-1(a), there is a clear trend in thickness dependence for $MFE_{PL}$, where increasing the thickness of the tetracene thin film increases the maximum percent change in photoluminescence. At an applied magnetic field of 900 mT, the 150 nm film of

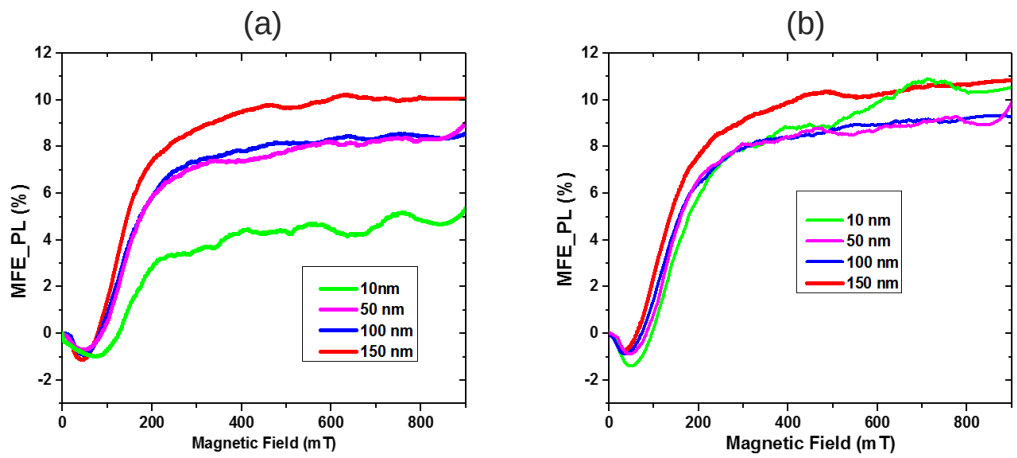


Figure 4-1: Magneto-photoluminescence for Tetracene Sample with Thicknesses of 10, 50, 100 and 150 nm (a) without a Cobalt Layer and (b) with a 10 nm Layer of Cobalt between the Tetracene and Glass.

tetracene reaches a maximum change of 10%, the 100 nm and 50 nm films reach a maximum change of about 8.5% and 9%, respectively, and the 10 nm film reaches a maximum change of ~5%. As discussed in chapter 2, these maximum values of $MFE_{PL}$ can be analyzed to determine the relative density of inter-triplet states formed in the films of tetracene (higher $MFE_{PL}$ maximum means increased inter-triplet density). Therefore, it shows that when the thickness of tetracene is increased, more molecules allow for more generation of inter-triplet states. Consequently, increasing the thickness of tetracene thin films increases the rate of singlet fission. Figure 4-1(b) shows the same measurements as Figure 4-1(a) with the addition of a 10 nm cobalt layer between the tetracene thin films and glass substrates. In Figure 4-1(b), at an applied magnetic field of 900 mT, the 150 nm film of tetracene reaches a maximum change of ~11%, and the 100 nm and 50 nm films reach a maximum change of about 9% and 10%, respectively. Comparing Figures 4-1(a) to 4-1(b), there is only a small change of about 1% in $MFE_{PL}$ maximums for thicker tetracene films of tetracene (50 nm to 150 nm) when cobalt is added. Also, the same thickness dependence from the 50 nm to 150 nm tetracene films is shown with and without cobalt. This shows that interfacial interactions between tetracene and cobalt do not have much of an impact on thicker films of the organic semiconductor. This shows that bulk interactions between molecules inside thicker films of tetracene are dominant over interfacial interactions, forbidding the interfacial interactions to have large impacts of the material properties. To discuss the results from the 10

nm thin film of tetracene, and to analyze the low field phenomena of the system, it is best to refer to Figure 4-2.

Figure 4-2 shows the same $MFE_{PL}$ data from Figure 4-1 for tetracene films of (a) 10 nm and (b) 100 nm thickness with and without cobalt for a more clear view on the effects of the cobalt layer on the organic semiconducting layer. The data in Figures 4-2(c) and 4-2(d) is zoomed-in on the data from 4-2(a) and 4-2(b), respectively, for a clearer view of the low field data. In Figure 4-2(b) and 4-2(d), it is shown that there is very little to no change in the $MFE_{PL}$ when a cobalt layer is added to the thicker tetracene film of 100 nm. As discussed before, this is due to the bulk interactions being the dominant forces in thicker films between molecules. Therefore, the interfacial interactions have little effects on the material properties. However, in Figure 4-2(a) and 4-2(c), there are major changes in the $MFE_{PL}$ in the large-field spin exchange regime and low-field hyperfine regime for the 10 nm tetracene film when the 10 nm cobalt layer is added. Under a larger magnetic field, the maximum $MFE_{PL}$ change increases by about 5.5%. This trend shows that adding the 10 nm cobalt layer to the system is able to greatly increase the density of inter-triplet states. Here, the data clearly shows evidence that the inherent magnetic field of cobalt causes spin interactions, which increases the density of inter-triplet states. Also, Figure 4-2(a) shows a curve shape change in the low-field range from 0 to 200 mT. Here the negative to positive percentage change in $MFE_{PL}$ can be used to determined relative strength of the hyperfine interactions in tetracene. At a low field, each electron

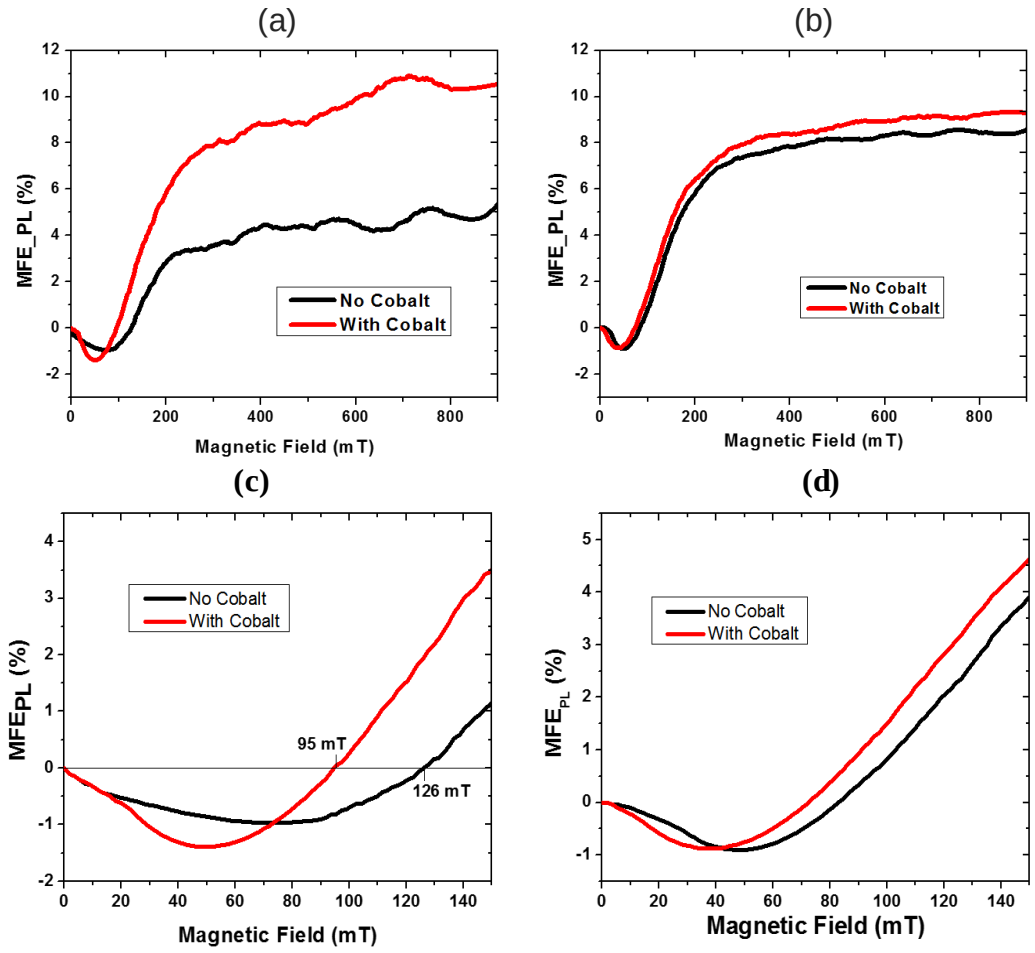


Figure 4-2: Magneto-photoluminescence spectra for tetracene thin films on glass substrates with and without 10 nm cobalt layers with thicknesses of (a) 10 nm tetracene thin films (b) 100 nm tetracene thin films (c) 10 nm tetracene thin films zoomed-in on hyperfine regime (d) 100 nm tetracene thin films zoomed-in on hyperfine regime.

experiences a slightly different field strength because of hyperfine interactions (HFI). As discussed in Chapter 2, HFI are the interactions between an electron and its atomic nucleus. These interactions are seen by the negative component of the $MFE_{PL}$, whereby spin mixing generated by HFI causes an increase in the density of inter-triplet states. The zero crossing point in $MFE_{PL}$ shows the critical magnetic field strength to reduce the hyperfine interactions towards aligning the spins of electrons with the applied magnetic field. When the cobalt layer is added to the system the critical applied magnetic field for the zero crossing point of the $MFE_{PL}$ decreases from 126 mT to 95 mT. This data confirms that adding a thin ferromagnetic layer between the glass and tetracene reduces the effects of HFI at low external magnetic fields. This phenomenon is further evidence that the cobalt/tetracene interface causes spin interactions at the interface, resulting in greater spin polarization in tetracene films.

## 4.2 Non-Magnetic Field Effect Results

Photoluminescence and absorption measurements were also used to study other effects (aside from singlet fission) on tetracene from the ferromagnetic/organic semiconductor interface. Figure 4-3 shows the photoluminescence spectra of tetracene thin films with varying thicknesses ranging from 10 nm to 150 nm. Figure 4-3(a) shows data for samples without a cobalt layer, while Figure 4-3(b) shows data for samples with a 10 nm layer of cobalt between the glass substrate and tetracene thin film. In both cases, it is shown that photoluminescence

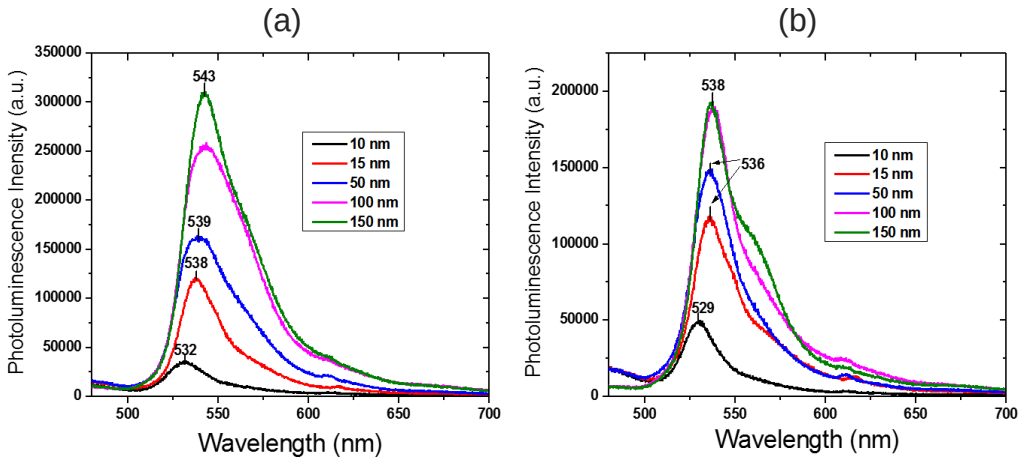


Figure 4-3: Photoluminescence Spectra for Tetracene Samples with Thicknesses of 10, 15, 50, 100 and 150 nm (a) without a Cobalt Layer and (b) with a 10 nm Cobalt Layer Between the Tetracene and Glass.

intensity decreases conversely with decreasing the thickness of the tetracene layer. The thinner films of tetracene are not able to absorb as much photoexcitation and have less molecules to be excited than thicker films, which is characterized here by the decreasing PL intensity with decreasing thickness. It can also be seen in both cases that decreasing the size of the tetracene layer causes a blue shift in the photoluminescence peak. It is known that decreasing the thickness of a thin film semiconductor will decrease its energy bandwidth, increasing its energy band gap explained by molecular orbital theory.[49,50] This is shown by the blue shifts in PL with decreasing film thicknesses. Comparing Figure 4-3(a) to 4-3(b), it can be seen that adding the thin layer of cobalt between the glass and tetracene also causes a blue shift (~3-5 nm depending on thickness of tetracene layer) in the photoluminescence peak. The effect of band bending when semiconducting materials are in contact with other materials has been greatly studied.[51,52] This blue shift occurs from band bending at the interface, where the bands of the tetracene bend upward when it is in contact with cobalt. From this data, evidence is shown that electrical interactions occur between the free electrons on the cobalt surface and the electrons on the tetracene surface, resulting in electrical polarization on the surface of tetracene. Also, adding a cobalt layer shows quenching in the PL for thicker films of tetracene. This further confirms that electrical interactions occur at the interface between cobalt and tetracene causing electrical polarization at the tetracene surface, as quenching of PL is caused by the following two effects from the

interface.

One effect leading to quenching of PL is energy transfer, whereby excitons in tetracene recombine and the released energy from recombination is absorbed by cobalt instead of being released as fluorescence. The other effect leading to quenching is charge transfer, whereby cobalt is able to donate electrons to the tetracene layer. The donated electrons are able to pair with the holes of excitons leading to dissociation of excitons. The dissociation of excitons results in quenching of PL as the dissociated excitons will no longer recombine to give off fluorescence. The charge transfer from cobalt to tetracene will then cause a dipole to be formed at the interface, where cobalt becomes positively charged after donating electrons.

Figure 4-4 shows the absorption spectra of tetracene thin films with and without a 10 nm layer of cobalt. Figure 4-4(a) shows the data for a 10 nm thin film of tetracene, while Figure 4-4(b) shows the data for a 100 nm thin film of tetracene. The absorption data for the tetracene thin films without cobalt are in agreement with previous results.[8] By comparing Figures 4-4(a) and 4-4(b), it is shown that the 525 nm peak from the 10 nm tetracene sample shifts from the 540 nm peak from the 100 nm tetracene sample. This shift in absorption data is caused by a change in band gap due to thin film thickness, as previously discussed. This blue shift in absorption also agrees with the blue shift in photoluminescence. In Figure 4-4(b), there is little to no change in the absorption of the tetracene sample when a thin layer of cobalt is added. This is because of the bulk interactions in

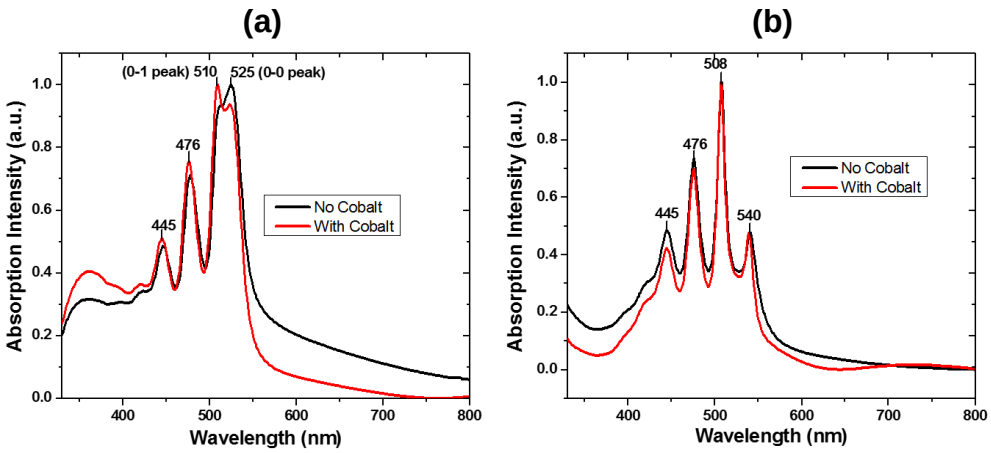


Figure 4-4: Absorption Spectra for Tetracene Samples with and without a 10 nm Cobalt Layer between the Glass and Tetracene for (a) a 10 nm Layer of Tetracene and (b) a 100 nm Layer of Tetracene.

tetracene, as discussed previously. However, in Figure 4-4(a) there is a clear change in relative peak intensity in the 510 and 525 nm peaks. The relative peak intensity change is due to electrical interface interactions between the cobalt and tetracene thin films, which cause electrical polarization inside the tetracene film. The relative peak intensity change can be studied to understand changes in electron-phonon coupling inside the tetracene thin film. Because the electron-phonon coupling trend is shown in the absorption data in Figure 4-4(a), the 510 nm peak is labeled as the 0-1 peak and the 525 nm peak is labeled as the 0-0 peak. It is shown that the 0-1 peak is weaker than the 0-0 peak in tetracene without cobalt. When cobalt is added to the system, the 0-1 peak becomes much stronger than the 0-0 absorption peak in tetracene. This analysis shows that the electrical polarization in tetracene caused by the electrical interfacial interactions with cobalt increases the electron-phonon coupling in the sample. Increases in the electronic phonon coupling is bad for photovoltaic applications, as it make charge transfer more difficult. Therefore, for photovoltaic application it is best to find a way to limit energy loss by making exciton dissociation a quicker process than energy loss to electron phonon coupling.

# CHAPTER 5

# CONCLUSIONS

In summary, this thesis explored the magneto-optical effects of the organic semiconductor tetracene. It mainly explored the effects from interfacial interactions between tetracene and the ferromagnetic layer cobalt towards further understanding of singlet fission for photovoltaic applications. It was shown that the interface can act upon the system in two ways: spin interactions and electrical interactions. Spin interactions at the interface caused spin polarization at the tetracene surface. This resulted in two main property changes. First, the high-field maximum $MFE_{PL}$ greatly increased at the interface showing a large increase in the density of inter-triplet states, thereby increasing singlet fission in the films. Also, the spin interactions at the interface reduced hyperfine interactions at low magnetic fields and increased the inter-triplet density at low fields as well. Electrical interactions at the interface caused electrical polarization at the tetracene surface. This was shown by the photoluminescence and absorption data. In the photoluminescence data the interface caused quenching and a blue shift, giving evidence for electrical interactions causing electrical polarization and band bending at the interface. Finally, electron phonon coupling was analyzed from the absorption data. The addition of cobalt caused an increase in the electron phonon coupling from electrical interactions at the

interface. Overall, the addition of the ferromagnetic layer is able to increase the density of inter-triplet states, thereby increasing the rate of singlet fission from the interfacial interactions.

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# VITA

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