Magneto-optical Behaviors at a 2-D Ferromagnetic/Organic Semiconductor Interface for Singlet Fission

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ABSTRACT: This article reports the magneto-optical effects on the singlet fission of the p-type organic semiconductor, tetracene, from a ferromagnetic/semiconductor interface between thin films of cobalt and tetracene. We experimentally show that this interface has two effects on the thin films of tetracene: spin interactions and electrical polarization. The experimental tools used to study the interface include magnetic field effect photoluminescence (MFE_{PL}), photoluminescence and absorption. Spin interaction effects are shown by MFE_{PL} data, where we observe a large increase in the maximum MFE_{PL} when cobalt is introduced, as well as changes in the hyperfine interactions at low magnetic fields. Electrical polarization is analyzed with photoluminescence and absorption measurements, showing small changes in the energy difference between the HOMO and LUMO levels of tetracene, as well as an increase in the electron-phonon coupling in tetracene. Also, electrical polarization is shown to increase electrical interactions between tetracene molecules. Therefore, we conclude that using spin interactions and electrical polarization from the ferromagnetic/organic semiconductor interface can tune the properties of tetracene, ultimately enhancing singlet fission. This work gives new insight to understand the singlet fission process using a ferromagnetic interface. These changes can be further utilized in photovoltaic applications based on this singlet fission material and be applied to other similar types of singlet fission organic semiconductors.

GRAPHICAL ABSTRACT

Electrical polarization and spin interactions due to the interface between cobalt and tetracene cause a change in the conversion rate between triplet pairs. This leads to an increase in triplet state densities, which causes an increase in singlet fission of tetracene.

1. INTRODUCTION

Organic systems have gained high 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).^{1,2} Organic photovoltaics (OPVs) have many promising properties for use in solar cells including, but not limited to: flexibility, transparency, thin active layers, low cost and easy fabrication. On the other hand, the theoretical power conversion efficiency (PCE) of bulk heterojunction solar cells has been determined to be about 23%.³ 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. Singlet fission is a process in certain organic semiconductors that has been a breakthrough towards higher PCEs of organic solar cells. Singlet exciton fission, or singlet fission, is a spin-dependent process in which one singlet excited state converts to two triplet excited states. By this process, it has been shown that organic semiconductors are able to absorb one photon, consequently generating two excited triplet states.⁴⁻¹⁰ During singlet fission, a photon is absorbed from the UV-VIS light spectrum. This photon excites one molecule of the organic semiconductor from the ground singlet state (S_0) to an excited singlet state (S_1). The excited singlet state then relaxes to a preferred excited triplet state (T_1) via intersystem crossing. Electronic coupling between neighboring molecules then allows for the energy from the relaxation of the first molecule to be shared by resonance energy transfer. The energy transfer excites the neighboring molecule from the S_0 state to the T_1 state. Each excited triplet state results in a free electron-hole pair. Tetracene has been heavily studied as a prospect material for OPVs because of its singlet fission process. When singlet fission is paired with a solar cell with suitable low energy gap materials, it has been shown to increase power conversion efficiency by enhancing photocurrent in the visible spectrum.¹¹ Tetracene has been shown to be one of the best candidates for singlet fission due to strong triplet-triplet interactions, which is why it has been chosen as the studied system for this work. The triplet yield of tetracene has been shown to reach $153\% \pm 5\%$, generating internal quantum efficiencies (IQE) of $127\% \pm 18\%$. Here, IQE is defined as how many excited triplet states are generated per one photon absorbed. Interfacial 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. For example, a tetracene(p-type)/ C_{60} (n-type), donor/acceptor interface is widely used in tetracene-based organic photovoltaics.⁸⁻¹¹ Many other types of interfaces have been used in photovoltaic applications to improve desired properties of devices. The main interface this work focuses on is the 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.¹²⁻¹⁸ It is apparent from the

process that singlet fission is a spin-dependent process. Therefore, the most important properties that need to be studied to understand singlet fission in tetracene and at the interface are spin interactions, which directly affect conversion rates between triplet states, and electrical polarization at the interface. These properties are studied to control singlet fission using magnetic field effects.

2. EXPERIMENTAL SECTION

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. All thermal evaporation was done in a high-vacuum chamber at a pressure of 2×10^{-6} torr. All measurements in these experiments were done at room temperature. Absorption data was collected after sample preparation before any other measurements to avoid interference from photoexcitation. Photoluminescence (PL) and magneto-photoluminescence (MFE_{PL}) were measured using a Fluorolog spectrofluorometer from Horiba and a 405 nm CW laser for the photoexcitation source. During MFE_{PL} measurements, samples were placed between poles of a large electromagnet parallel to the applied magnetic field of 0-900 mT, while the photoexcitation source was aligned at around a 60° angle to the sample. MFE_{PL} is defined in Equation 1 as

$$MFE_{PL} = \frac{PL_B - PL}{PL} \quad (1)$$

where PL_B is the photoluminescence under the applied magnetic field and PL is the base photoluminescence with no applied magnetic field. During MFE_{PL} , results were reproducible for multiple samples and reported from the first time the external magnetic field was applied. This was done to ensure that the magnetization memory of the cobalt thin film did not influence the results. Measurements were also repeated on same samples to ensure magnetization memory had no effects on the MFE_{PL} results.

3. RESULTS & DISCUSSION

MFE_{PL} has been shown to be an important experimental tool to elucidate information regarding the singlet fission rate of a material by studying magnetic field effects on the inter-conversion rate between $^5(TT)$ and $^1(TT)$, triplets with quintet characteristics and singlet characteristics, respectively. It is well known that MFE_{PL} can be used to elucidate information about singlet fission.⁷ In this work, we have demonstrated the use of MFE_{PL} to characterize singlet fission in thin films of tetracene and investigate how spin and electrical interactions affect singlet fission. First, we show that electrical interactions between triplet states is thickness dependent in thin films (between 10 and 150 nm), whereby increasing the thickness of the film increases the amount of molecules in the film. Because of this, the probability that electrical interactions occur between excited molecules and unexcited molecules increases, increasing the amount of possible triplet states and enhancing singlet fission. We then show that singlet fission can be enhanced further using a thin semi-transparent layer of cobalt as a ferromagnetic substrate. We demonstrate this by showing a large MFE_{PL} increase when the cobalt/tetracene interface is introduced to the system. Because, the large increases are only shown by thin tetracene films, (10 nm) we verify that the spin-interactions between cobalt and tetracene occur at the interface. Singlet fission rate is determined by the density of $^1(TT)$ states. At low fields, hyperfine interactions can enhance inter-conversion between triplet pair states. Therefore, we see a decrease in MFE_{PL} , which means there is an increase in $^1(TT)$ states and an increase in singlet fission. At high fields, spin-exchange interactions are high, disallowing inter-conversion between triplet states. Therefore, we see an increase in the positive MFE_{PL} am-

plitude, which shows that the density of $^5(\text{TT})$ is high meaning that singlet fission rate is low. However, this decrease in singlet fission rate is caused by disallowing conversion from the external magnetic field. When the high external magnetic field is not applied, the inter-conversion will return to normal allowing for singlet fission. Adding the cobalt layer is shown to increase the amplitude of both the hyperfine and spin-exchange regime. These phenomena are caused by spin interactions at the interface, which cause an increase in the conversion of triplet states, resulting in an increase in singlet fission. Figure 1(a) shows the percent change of magneto-photoluminescence (MFE_{PL}) for tetracene thin films ranging from 10 nm to 150 nm with and without cobalt. The line shape of each sample shows Lorentzian characteristics in the negative components, agreeing with previous studies.⁷

Figure 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. (Inset of Figure 1(b) shows same measurement for 10 nm film of tetracene with and without a 10 nm gold film in place of the cobalt layer.)

All of the films from 50 nm to 150 nm film thickness in Figure 1 have an initial negative MFE_{PL} component at a low field (< 50 mT) and then a positive MFE_{PL} signal at a higher field (> 50 mT). The 10 nm film shows higher zero-crossing point critical field values as compared to the thicker films. In Figure 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 tetracene reaches a maximum change of 10.0%, the 100 nm and 50 nm films reach a maximum change of 8.6% and 9.0%, respectively, and the 10 nm film reaches a maximum change of 5.0%. These maximum values of MFE_{PL} can be analyzed to determine the relative density of triplet pair states formed in the films of tetracene (higher MFE_{PL} maximum means increased density in triplet states). Therefore, it is shown that when the thickness of tetracene is increased, the density of triplet states increases. Once the magnetic field is no longer applied and inter-conversion between triplet states can occur at a normal rate. Therefore, it is shown that the thicker films will have more triplet states available for inter-conversion resulting in increased singlet fission rate. Figure 1(b) shows the same measurements as Figure 1(a) with the addition of a 10 nm cobalt layer. It is shown at an applied magnetic field of 900 mT, the 150 nm film of tetracene reaches a maximum change of 10.8%, and the 100 nm and 50 nm films reach a maximum change of 9.3% and 9.5%, respectively. Comparing Figure 1(b) to Figure 1(a), there are only small changes in MFE_{PL} maximums (0.5-0.8%) 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 inter-

facial interactions between tetracene and cobalt do not have much of an impact on thicker films of the organic semiconductor. This shows that 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. However, for the 10 nm tetracene film, there are major changes in the MFE_{PL} in the large-field spin exchange regime and low-field hyperfine when the 10 nm cobalt layer is added. Under a high magnetic field, the maximum MFE_{PL} change increases by 5.5% to a maximum value of 10.5% MFE_{PL} change. This phenomenon shows that adding the 10 nm cobalt layer to the system is able to greatly increase the density of triplet pair states. Here, the data shows direct evidence that the inherent magnetic field of cobalt causes spin interactions at the interface, which increases the conversion between triplet pair states. There is also a line shape change in the low-field range from 0 to 200 mT for the 10 nm tetracene film. Here the negative component and the zero-crossing point change in MFE_{PL} can be used to gain understanding of the relative strength of the hyperfine interactions in tetracene compared to the strength of interfacial interactions. At a low field, each electron experiences a slightly different field strength because of hyperfine interactions. These interactions are seen by the negative component of the MFE_{PL} , whereby spin mixing generated by hyperfine interactions causes an increase in the inter-conversion of triplet pair states. From the negative MFE_{PL} component at low field, we can see that the critical magnetic field strength required to disturb the hyperfine interactions-based spin mixing becomes lower. This means that the spin interactions at the interface between cobalt and tetracene facilitate aligning the spins of electrons with the applied magnetic field. Therefore, a smaller external magnetic field is required to eliminate spin mixing due to hyperfine interactions. 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 hyperfine interactions at low external magnetic fields. Also, at low fields, it is shown that adding a cobalt film increases the negative amplitude of MFE_{PL} from 1% to 1.5% showing an increase in singlet fission. The inlet of Figure 1(b) shows the same photoluminescence measurements with and without a 10 nm film of gold for a 10 nm film of tetracene. This shows that there are no significant changes in the low field or high field regime when the 10 nm gold layer is added. This data shows that the changes caused by cobalt are true phenomena of the cobalt/tetracene interface as explained above.

Figure 2: 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. (Inset of Figure 2(b) shows same measurement for 10 nm film of tetracene with and without a 10 nm gold film in place of the cobalt layer.)

Photoluminescence and absorption measurements were also used to study the interactions related to electrical polarization at the ferromagnetic/organic semiconductor interface. From photoluminescence measurements it was determined that the energy difference between the HOMO and LUMO levels in the tetracene thin films increased as the thickness of the thin films decreased. It is shown that the cobalt/tetracene substrate caused a blue shift in the photoluminescence spectra. From this phenomenon, it is clear to see that the blue shifts are caused by electrical polarization at the interface. From the evidence that electrical polarization occurs at the interface, we can conclude that the electrical polarization enhances electrical interactions between molecules in tetracene further enhancing singlet fission. Figure 2 shows the photoluminescence spectra of tetracene thin films with varying thicknesses ranging from 10 nm to 150 nm. Figure 2(a) shows data for samples without a cobalt layer, while Figure 2(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 intensity decreases with decreasing thickness of the tetracene layer. This is because the thinner films of tetracene are not able to absorb as much photoexcitation and have less molecules to be excited than thicker films. It can also be seen in both cases that decreasing the thickness of the tetracene layer causes a blue shift in the photoluminescence peak. This is shown by the blue shifts in PL with decreasing film thicknesses. It is known that decreasing the thickness of a thin film semiconductor will increase the energy difference between the HOMO and LUMO levels in organic semiconductors.^{19,20} Comparing Figure 2(a) to 2(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 electrical polarization when semiconducting materials are in contact with metallic materials has been greatly studied.^{21,22} From this data, it is evident that the ferromagnetic/semiconducting interface causes electrical polarization on the thin tetracene thin film. We also note that adding a cobalt layer shows quenching in the PL. This further confirms that electrical polarization occurs at the interface between cobalt and tetracene, 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. In order to understand the charge transfer direction, the energy levels of tetracene and cobalt are important. The HOMO and LUMO levels of tetracene are 5.4 eV and 2.7 eV, respectively. The work function of cobalt is 5.0 eV. From this information, it can be noted that charge transfer occurs from tetracene to cobalt at the interface. 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. The inset of Figure 2(b) shows the same photoluminescence measurements with and without a 10 nm film of gold for a 10 nm film of tetracene. The difference in PL intensity for when gold substrate is added, is explained by photoluminescence quenching due to the organic/metallic interface charge transfer. However, this data shows that there is no blue shift in photoluminescence when the 10 nm gold layer is added, shows that the changes caused by cobalt are true phenomena as explained above, rather than simple causes such as morphological changes due to changing the substrate.

By analyzing the absorption data, it is clear that the electrical polarization at the interface causes an increase in electron-phonon coupling in thin tetracene thin films. Figure 3 shows the absorption spectra of tetracene thin films with and without a 10 nm layer of cobalt. Figure 3(a) shows the data for a 10 nm thin film of tetracene, while Figure 3(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.⁵

Figure 3: 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.

By comparing Figures 3(a) and 3(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 3(b), there are small, negligible changes in the absorption spectrum when cobalt is added. This is due to the fact that interfacial interactions do not have a large impact on thicker films of tetracene. However, in Figure 3(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 polarization at the interface. 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 3(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 makes 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.

4. CONCLUSIONS

In summary, this work explored the magneto-optical effects on the organic semiconductor tetracene from the interfacial interactions between itself and the ferromagnetic layer, cobalt. We used magneto-photoluminescence, photoluminescence and absorption to study the interfacial interactions and found that the interface can act upon the system in two ways: spin interactions and electrical polarization. Spin interactions at the interface caused an increase in the conversion rate of triplet pairs, enhancing the singlet fission of tetracene. Electrical polarization at the interface is able to increase the electrical interactions between molecules, also enhancing singlet fission. Electrical polarization also caused an increase in the HOMO/LUMO energy difference in tetracene. Also, due to electrical polarization at the interface, we observed quenching of photoluminescence and an increase in electron-phonon coupling. Therefore, we see that using the ferromagnetic layer can cause interfacial interactions between cobalt and tetracene enhancing singlet fission towards enhancing its photovoltaic capabilities. Further studies can be done to

ensure that the cobalt layer inside a solar cell device will enhance power conversion efficiencies due to the enhanced singlet fission of tetracene.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

MFE_{PL}, Magnetic field effect photoluminescence; OPV, Organic photovoltaic; PCE, Power conversion energy; IQE, Internal quantum efficiency

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GRAPHICAL ABSTRACT

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