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STUDIES ON MAGNETORESISTANCE OF ORGANIC SEMICONDUCTORS UTILIZING FIELD-EFFECT TRANSISTOR STRUCTURES

PHAM SONG TOAN

SEPTEMBER 2014
STUDIES ON MAGNETORESISTANCE OF ORGANIC SEMICONDUCTORS UTILIZING FIELD-EFFECT TRANSISTOR STRUCTURES

A dissertation submitted to

THE GRADUATE SCHOOL OF ENGINEERING SCIENCE OSAKA UNIVERSITY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY IN SCIENCE

BY

PHAM SONG TOAN

SEPTEMBER 2014
ABSTRACT

Organic semiconductors have been considered in the past few decades as promising candidates for future electronic devices. The organic materials research has been driven by their potential advantages such as low production cost with relative ease of processing, high electrical and electroluminescent efficiency, and structural flexibility of the devices.

An intrinsic magnetic field dependent current observed in organic semiconductors, so-called, organic magnetoresistance (OMAR) is of great scientific interest because of its unique properties compared to other magnetoresistive effects. The OMAR effect can have a relatively large magnetoresistance value (up to 10–20%) at room temperature and small magnetic fields of 10 mT without using ferromagnetic contacts. Many models are suggested to explain this effect, but debate still exists about its nature.

In this thesis, I have studied the OMAR utilizing field effect transistor structures, which delivers many advantages compared with transitional sandwich devices. The type of charge carrier, mobility, current density can be controlled and determined by the voltage applied to the gate electrode, which is very potent to elucidate the mechanism of OMAR.

Firstly, the magnetoresistance effect of photocurrent on single-crystalline pentacene (PEN) and perfluoropentacene (PFP) field-effect-transistors have been demonstrated. General observation of MR can be obtained from highly disordered materials. Now, we can observe the OMAR on high order materials, pentacene and PFP single crystals. Our results indicate that it is required double carrier to cause the OMAR effect, hence, the bipolaron model is not suitable for explanation of OMAR. This statement has been confirmed by the gate voltage dependence of MR value in thin film of bilayer PEN/PFP FETs. Moreover, by analyzing the dependency of MR on gate voltage, drain source voltage, traps density and temperature, I suggested the possible mechanism based on the combination of electron-hole pair and exciton-charge interaction models.

Secondly, the formation of electron-hole pair is essential to cause OMAR as shown in the study of bilayer thin film PEN/PFP FETs. The external magnetic field tents to increase triplet state density due to less mixing between singlet and triplet electron-hole states. The triplet electron-hole pairs can recombine into triplet excitons, which then interact with charges or traps causing different influences on current. The sign change showed in multilayer PEN/PFP comes from the switch in mechanism between triplet exciton detrapping and triplet
exciton charge interaction process. The exciton-charge interaction becomes dominant when there is a large current density in device.

Finally, I demonstrated a magneto-electroluminescence (MEL) effect of 1.3% for alpha sexithiophene (α-6T) light emitting FET (LEFET) under 100 mT at room temperature. The study confirms that the origin of magneto-conductance (MC) and MEL is different, MEL is independent with MC. The magnetic-field-induced increase in the singlet exciton formation probability derives from intermolecular quantum correlated effect and the enhancement in irradiated recombination efficiency at the α-6T/Al interface. Therefore, by optimizing the magnetic field effect and device structures, the luminous efficiency of the LEFETs can be improved.
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<table>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HF</td>
<td>Hyperfine Field</td>
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<tr>
<td>ISC</td>
<td>Intersystem Crossing</td>
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<tr>
<td>LEFET</td>
<td>Light Emitting Field Effect Transistor</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<td>MC</td>
<td>Magnetococonductance</td>
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<td>MEL</td>
<td>Magnetoelectroluminescence</td>
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<tr>
<td>MFE</td>
<td>Magnetic-Field Effect</td>
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<td>MR</td>
<td>Magnetoresistance</td>
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<tr>
<td>OFET</td>
<td>Organic Field Effect Transistor</td>
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<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
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<tr>
<td>OMAR</td>
<td>Organic Magnetoresistance</td>
</tr>
<tr>
<td>PEN</td>
<td>Pentacene (C$<em>{22}$H$</em>{14}$)</td>
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<tr>
<td>PFP</td>
<td>Perfluoropentacene (C$<em>{22}$F$</em>{14}$)</td>
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<tr>
<td>SOC</td>
<td>Spin-Orbit Coupling</td>
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<td>SC</td>
<td>Single Crystal</td>
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CHAPTER 1: INTRODUCTION

Research in organic material has progressed remarkably over the past few decades. The greatest success has been realized in the field of organic photovoltaic and optoelectronics devices initiated by the commercialization of organic light emitting diodes (OLEDs). The organic materials research has been driven by their potential advantages over inorganic ones, such as low cost, easy processing of the substrates, high electroluminescent efficiency, and especially the wide variety of compounds and structural flexibility of the devices.

In 1963, the first conducting polymer was reported in iodine-doped oxidized polypyrrole [1]. Ten years later, Mc Ginness, Corry and Proctor reported in Science that melanins can be made to ‘switch’ from a poorly conducting to a highly conducting state at low electric fields (from 10 kΩ.cm to 100 Ω.cm at a field of 300 V/cm) [2]. In 1977, doped polyacetylene was shown to be conducting polymers first discovered by Shirakawa [3]. Subsequently, Heeger and MacDiarmid showed that the polymer would undergo an increase in conductivity of 10 orders of magnitude by oxidative doping, which helped raise the world’s interest in such materials [4]. This contribution brought the Nobel Prize in Chemistry in 2000 to Alan Heeger, Alan G. MacDiarmid and Hideki Shirakawa. Since then, research in organic materials has progressed immensely from conducting, semiconducting to superconducting organic materials for electron (n-type), hole transport (p-type) and ambipolar transport (both hole and electron) materials. The understanding and controlling both the charge and spin transport in organic materials is a fundamental part of this technological research.

The evolution of organic material opens the creation of novel architectures for electronic devices. Organic compounds have more potential than inorganic counterpart does to be employed in the fabrication of electronic devices because their properties can also be tuned by chemical synthesis. Another important motivation for the interest in organic (semi)conductors is the expected low cost of the products. The flexibility of the organic material allows low-cost manufacturing techniques of bendable display screens, radio-frequency identification (RFID) tags, large solar cell panel… The organic electronics application will be much more attractive because the organic industry may not demand to construct complex and costly manufacturing plants, which require cleanrooms, lithography, implantation… comparing with silicon industry.

The studies of organic material can be divided into two primary fields: organic electronic and organic spintronic.
Organic Electronic

Organic materials are fascinating in that they own unique electronic properties not found in other materials. Simple organic molecules are planar, with three of the four carbon valence electrons forming $sp_2$ hybrid orbitals, while the fourth valence electron is in a $p_z$-orbital perpendicular to the molecular plain. The $sp_2$ hybridization in organic materials is important because there is one electron per atom to form its own band. Two of the $sp_2$ orbitals on each carbon atom form covalent bonds with neighboring carbons; the third generally forms a covalent bond with a hydrogen or side group. This is called a $\sigma$-bond, which is any bond with cylindrical symmetry around the internuclear axis. The $\sigma$-bonds are the building blocks of the molecular skeleton and are therefore responsible for the molecule’s integrity. The unhybridized $p_z$ orbital can overlap with the unhybridized $p_z$ orbital of neighboring carbon, forming a $\pi$-bond, which is any bond that arises from electrons approaching side by side, off the internuclear axis. Since the $\pi$-bonds are weakly bound, the electrons are delocalized across all the contiguous $\pi$ bonds in the molecule. These electrons become conducting electrons in organic materials. Figure 1 summarizes all above explanation.

![Image](a) The creation of a $\pi$-bond between two C atoms and (b) energy level diagram showing the formation of $\pi$ and $\sigma$ bonds in carbon (adapted from andromeda.rutgers.edu website).

Figure 1: (a) The creation of a $\pi$-bond between two C atoms and (b) energy level diagram showing the formation of $\pi$ and $\sigma$ bonds in carbon (adapted from andromeda.rutgers.edu website).
According to Bloch theory (assuming equidistant bond-lengths), solids with half-filled shells have partially filled bands giving metallic behavior [5]. However, a \( \pi \)-conjugated molecule with equidistant bond lengths is unstable. The electrons want to localize between the carbon nuclei in order to screen their nuclear charges, thus the chain of carbon atoms forms alternating single (long) and double bonds (short), which causes formation of the Peierls distortion. As a result, the simple metallic band splits into two sub-bands separated by an energy gap of 2-3 eV, a completely filled valence band (highest occupied molecular orbital or HOMO level) and an empty conduction band (lowest unoccupied molecular orbital or LUMO level) [6]. Hence, the material is a semiconductor.

The electrical transport of organic materials is very different in many aspects from inorganic materials, like silicon or gallium arsenide. The disorder, the polaronic nature of the carriers and the dielectric constant create large exciton binding energy and the hopping transport in almost organic materials. Hence, their mobility/conductivity is low comparing with band transport in inorganic. The typical mobility of organic thin films is around \( 10^{-5} \) to \( 10^{-1} \) cm\(^2\)/Vs (in amorphous silicon \( \mu \sim 5 \times 10^{-1} \) cm\(^2\)/Vs). In recent times, the mobility of solution-processed organic semiconductors has improved significantly to room-temperature values greater than 1cm\(^2\)/Vs. [7]

Organic Light Emitting Diode (OLED) is one of the best examples of the potential of organic electronics. OLED screen is now commercially available such as in displays for mobile phones, car radios, digital cameras and portable digital media players, OLED TV… In the near future, new types of OLED will be presented with amazing properties such as the rollable display as in Figure 2.

Figure 2: Rollable organic light emitting diode display presented by Sony.
Organic Spintronic

Organic material are also interesting materials for spintronics applications because of their long spin lifetimes [8,9], resulting from small spin–orbit coupling (SOC) due to the low-weight atoms organic materials are composed of (SOC scales with $Z^4$, where $Z$ is the atomic number). One has to remark though that the long spin lifetime is accompanied by relatively small mobility [10]. In addition, organic spintronics offers the opportunity to integrate magnetic functions to existing organic electronics. Two main topics of organic spintronics are organic spin valve and organic magnetoresistance (OMAR).

The organic spin valve effect is a very interesting field because of the fundamental physics nature and the important applications. In organic spin valves, spin transport occurs through an organic spacer layer, which is just a replacement of the inorganic spacer layer in inorganic spin valve, and studies electron-spin transport through this nonmagnetic layer of organic materials sandwiched between ferromagnetic electrodes. If the spin diffusion length is comparable to the distance between the electrodes, the current through such device can depend strongly on the mutual direction of the magnetization of electrodes. This mutual direction can be switched between parallel and anti-parallel by an external magnetic field. It can cause a strong dependence of the current on applied magnetic field. This effect can be used in magnetic sensors, in reading magnetic information in hard disks, memory... Main reason of spin relaxation is the interactions of the spins with random local hyperfine fields of surrounding hydrogen nuclei [11]. Numerous works have been done in the field of organic spin valves to address conductivity mismatch and to elucidate the question that observed magnetoresistance comes from spin injection or tunneling.
In about last ten years, organic magnetoresistance (OMAR) is a great scientific interest since it has numerous fascinating properties that make it distinctive compared to other magnetoresistive effects. The OMAR can have relatively large magnetoresistance (MR) value (up to 10–20%) at room temperature and small magnetic fields of 10 mT without using any ferromagnetic contacts. OMAR is among the largest magnetoresistive effects of any bulk material, and is therefore an interesting spintronics effect in its own right. These properties may make OMAR devices desirable for magnetic field sensors that could become an important component for future application of organic industry [13].

Figure 3: Schematic representation of a typical device that consists of two ferromagnetic electrodes and an organic semiconductor spacer, (b) scanning electron micrograph of a functional organic spin-valve and (c) GMR loop of a spin-valve device measured at 11 K as reported by Xiong [12]. The anti-parallel (AP) and parallel (P) configurations of the magnetization orientations are shown in the insets.

Figure 4: (a) Common devices structure and (b) typical MC curves of various organic materials as reported by Francis [14].
The OMAR in various organic materials has been studied and shows promising potential for adding magnetic features to organic electronic devices [13]. The suppression of the hyperfine-field induced mixing by a magnetic field is responsible for the observed changes in current/resistance and electroluminescence of organic materials. This role of the hyperfine fields was confirmed by Nguyen et al. via experiments with a deuterated polymer [11]. They observed an increased spin-diffusion length on replacing the hydrogen with deuterium and much narrower magneto-electroluminescence curves were obtained that were claimed to be due to the much smaller hyperfine coupling constant for deuterium. This study confirms that the competition between the hyperfine fields and the external field is actually responsible for OMAR. However, the detail mechanism is still under investigation.
**Brief History of OMAR**

In the 1960s and 1970s, a low magnetic field effect (<500 mT) was observed in various properties of numerous organic semiconducting materials [15–19]. The phenomenon of organic magnetoresistance usually abbreviated to OMAR, refers to the change in electrical resistivity in sandwich structures of nonmagnetic metals and organic materials under a magnetic field of up to 500 mT.

In 2003, Kalinowski and coworkers found an increase of up to 5% in the electroluminescence intensity and current of aluminum tris(8-hydroxyquinolate) (Alq₃) based OLED at quite high magnetic field of 300 mT (Figure 5) [20]. They explained this magnetic field effect on the electroluminescence by suggesting a hyperfine scale magnetic-field-dependent mixing of singlet and triplet electron-hole pair states. According to them, an applied magnetic field would decrease this intersystem crossing rate, leading to an increase of singlet exciton density and electroluminescence intensity. The magnetic field effect on the device current was explained that the singlet excitons diffuse to the cathode, leading to an efficient injection of electrons.

![Figure 5: OLED structure reported by Kalinowski and coworkers and Alq₃ molecule](image)

While studying polyfluorene OLEDs structure, Francis et al. found a large (up to 10%) magnetoresistance effect occurring in small magnetic fields (10 mT) and at room temperature [14]. They studied its dependence on external magnetic field direction, voltage, temperature, film thickness, electrode materials, and impurity concentration. Their key conclusions were that the effect is independent of the direction of the applied magnetic field, and shows weak temperature dependence. The MR sign can be positive or negative, depending on the operating voltage. Therefore, they concluded that OMAR is a bulk effect, related to the hole current. Although no theoretical explanation of the effect was given, they eliminated well-
known mechanisms for magnetoresistance such as Lorentz forces, hopping magnetoresistance, electron-electron interactions and weak localization. They suggested that magnetic-field mediated spin-dependent reactions between electrons and/or holes might be the key to the mechanism for OMAR. Similar results were also reported by the same group for Alq3-based devices [21].

In 2005, Reufer et al. [22] showed that the external magnetic field increases both fluorescence (singlet exciton emission) and phosphorescence (triplet exciton emission). They concluded that there is no conversions between singlet and triplet electron-hole pair states and the singlet/triplet exciton recombination ratio is still 1:3. This discovery disputes the mechanisms based on the conversion from triplet to singlet exciton, as proposed by J. Kalinowski et al. [20] and later also by others.

Later, Mermer et al. [23] performed a comprehensive study on OMAR of various polymers and small organic molecules. A standing conclusion is that all the MR(B) curve seem to fit one of two types of empirical line shapes. One is a Lorentzian line shape given by

\[ MR \sim MR_{\infty} \frac{B^2}{(|B| + B_0)^2} \]

or non-Lorentzian line shape as shown in Figure 6:

\[ MR \sim MR_{\infty} \frac{B^2}{B^2 + B_0^2} \]

![Figure 6: Lorentzian and non-Lorentzian curve.](image-url)
Gärditz et al. [24] investigated the influence of the magnetic field on the singlet and triplet emission in Alq$_3$-based devices. They observed an increase with magnetic field in both the singlet and triplet emission intensity (which is agreed with Reufer’s work [22]), and they attributed the effect to triplet-triplet annihilation. However, Hu et al. concluded the triplet-triplet annihilation could not be the mechanism of OMAR [25].

Prigodin et al. [26] reported a large change in the magnetoresistance of thin films of Alq$_3$, when doped with PtOEP and Ir(ppy)$_3$ complexes. They proposed a model based on a magnetic-field effect on the spin-interconversion of electron-hole pairs in the presence of hyperfine interaction, similar to the mechanism suggested by Kalinowski [20].

In 2007, Desai et al. [27–29] explained that OMAR may derive from trapping of charge carriers at triplet excitons, proposed earlier by Ern and Merrifield [30]. Mostly triplet excitons are present due to their long lifetime (in few tens of millisecond). A triplet exciton can transfer its energy to a charge carrier on recombing to the ground state, called an exciton–charge interaction. Meruvia et al. [31] reported a magnetic field induced release of trapped charges in poly(fluorenylenevinylene) devices in the absence of an applied voltage, but after stressing the device at high voltage. They suggest that field induced detrapping of charges might be the origin of OMAR.

Desai et al. also proposed a possibility that the magnetic field converts triplet excitons into singlet excitons (intersystem crossing process), leading to a reduction in the triplet population. Subsequently, the charge carriers-triplet exciton scattering is related to the triplet density, hence the external magnetic field increases the charges mobility. However, the intersystem crossing between singlet and triplet excitons is greatly questionable as the energy splitting is very large (0.7eV in Alq$_3$) compared to the Zeeman splitting by a typical hyperfine field (0.5 meV at 5 mT).

Hu and Wu [32] observed a sign change of the magnetoresistance. By changing film thicknesses of poly(methyl methacrylate) (PMMA), an insulating material, they adjusted the electron or hole injection to devices. Their results was explained by the several exciton-based proposed mechanisms.

The bipolaron mechanism for organic magnetoresistance was proposed in 2007 by Wohlgenannt and Bobbert [33]. An electron/hole in a material may cause a distortion of neighboring lattice (Figure 7). The combination of electron/hole and distortion is known as a polaron because their interaction is polarization. When two polarons are close together, they
share the same distortions, which cause an attractive force between them, which form a bipolaron. The bipolaron mechanism is based on a competition between magnetic-field dependent (singlet) bipolaron formation and magnetic field independent hopping of charge carriers. It is noted that bipolaron model a single-carrier mechanism, while the exciton-based mechanisms is double-carrier models.

![Figure 7: Artist view of (a) a polaron and (b) a bipolaron. A conduction electron in organic semiconductor repels the negative ions and attracts the positive ions.](image)

In 2008, Wang et al. [34] showed an evidence that MFE is composed of several components that depend on concentrations of π-conjugated polymers blending with fullerenes. A dominant positive low-field component dramatically decreases and broadens in the blends, thus separating positive high-field and negative low-field components. The positive high-field components are produced by e-h pairs in unblended devices and charge transfer pairs in the blends, which are dominated by two different field-induced spin mixing mechanisms. While the negative low-field one is due to e-e and h-h pairs; this is confirmed by studying in unipolar devices (only hole and only electron), which lack of positive MC component.

Later, Bloom et al. [35,36] found a correlation between the temperature and voltage dependent sign changes of OMAR and the onset of minority carrier injection. Moreover, they explained the temperature dependence of OMAR by a shift of the threshold voltage for minority carrier injection to lower values with increasing temperature. They concluded that the magnetoresistance has two different effects, which are in agreement with the bipolaron model.

The assumption of multiple components OMAR was also proposed by Xiong et al. [37]. Magneto-electroluminescence results and energy-level diagram indicate that long lifetime triplet excitons and excessive holes are in these devices. Their observations suggest that triplet
exciton-hole interaction is responsible for the negative MC while positive MC is derived from hyperfine mixing of e-h pairs.

In 2013, Janssen et al. [38] revealed that OMAR can be tuned in a blend of organic materials, and mechanisms can be distinguished using MR line shapes and voltage dependencies. They found that different mechanisms can dominate, depending on the exact material choice, morphology and operating conditions.

Mahato et al. [39] reported on an exceptionally large (>2000%), room temperature, small-field (~14 mT) MR effect in one-dimensional systems formed by molecular wires embedded in a zeolite host crystal. This ultra-high MR effect is attributed to spin blockade in one-dimensional electron transport. The bipolaron model can elucidate the effect.

Besides that, there have been few reports on OMAR in field effect transistors (FETs). Reichert and Saragi have reported negative and positive MR in the photo induced current of thin-film pentacene (PEN)-based [40,41] and tetracene-based FETs [42], respectively, in which the irradiation of light is essential to observe OMAR. The exciton-related models were used to explain the mechanism of these experiments.
Three Models of OMAR

Three groups of models have been introduced based on the pairs of particles that they consider for spin-dependent interactions: bipolaron model [33,34,43], electron-hole pair model [20,26,44–47], and exciton-charge interaction model [25,27,29].

First is the bipolaron model. Due to the energetic and positional disorder, charge transport occurs via a limited number of percolation paths. The Pauli principle precludes that two electron with the same spin can occupy the same state. On such paths, one carrier may be blocking the passage of another carrier. This spin blockade for two electrons starting from a spin-triplet configuration was first observed in quantum dots at low temperatures [48]. In organic molecules, spin blockade can happen at room temperature due to stronger wave function confinement. Besides, the triplet bipolaron has a much higher energy than the singlet bipolaron due to strong on-site exchange interaction, the formation of triplet bipolaron from the triplet polaron pair is energetically unfavorable.

![Figure 8: Illustration of spin-blocking in bipolaron formation. Two particles with parallel spins cannot form an intermediate bipolaron [49].](image)

The bipolaron model now treats the situation depicted in Figure 8. Suppose a charge carrier is quasi-stationary trapped at an energetically relatively low-lying state, and a nearby carrier relies on the occupied position to form an intermediate bipolaron state and then follows its route through the organic semiconductor. Depending on the spins of the two particles, a bipolaron can be formed, subsequently allowing the carrier to pass. This is only possible if the spins of the two carriers are in a singlet configuration, as illustrated in Figure 8. Then, if the two carriers happen to be in a triplet-configuration, the current is effectively blocked. Even without an external magnetic field, the carriers still experience magnetic fields from the nearby hydrogen nuclei, the hyperfine fields $B_{hf}$ (~5 mT). The local hyperfine field is the sum of many random hyperfine fields of neighboring hydrogen nuclei. Therefore, two carriers at different
state will experience a different local hyperfine field. In a local hyperfine field, spins will perform a precession, which can change the spin configuration of a carrier pair (Figure 9a). It has been shown that hyperfine interaction can lift the spin blockade in QDs [50]. At high external fields, the spins will precess around the sum of this field and the local hyperfine field, see Figure 9b. When the external field is much larger the hyperfine field (≈5 mT), the spins experience approximately the same total field. As a result, two spins will remain parallel, blocking is regained and spin character becomes well-preserved. Thus, the bipolaron mechanism gives rise to a magnetic field dependence of the (e and/or h) mobility.

![Figure 9: Illustration of spin precession of two neighboring spins in (a) only the local hyperfine fields \( \overrightarrow{B}_{hf} \) and (b) the sum field \( \overrightarrow{B}_{sum} \) of the local hyperfine field and the external field \( \overrightarrow{B}_{ext} \) [49].](image)

In the electron–hole pair model, the loss of free carriers by recombination is considered. Figure 10 shows the possible paths from free electron and hole to recombination to the ground state. At first, free electron and hole are Coulombically attractive to become singlet and triplet e–h pairs with a ratio 1:3. Singlet and triplet e–h pairs can be mixed by the hyperfine fields as show in Figure 11, which have probability of intersystem crossing with a rate \( m_{ISC} \). These e-h pairs can recombine into excitons (with rates \( k_S \) and \( k_T \)) or dissociate back to free polarons (with rates \( q_S \) and \( q_T \)). There is a large energy gap between singlet and triplet excitons energy level due to the exchange interaction. The recombination to the ground state of singlet exciton happens in very short timescale and can emit the light (fluorescence), while triplet excitons last for longer time.
Figure 10: Diagram of possible routes for recombination of free electrons and holes to the ground state, by first forming an e–h pair which turns into an exciton.

Figure 11: Without an external field, the hyperfine field mixes the singlet S and all three triplet states, T-, T0, and T+. An external field splits three triplet states due to Zeeman effect, hence mixing occurs only between S and T0.

The recombination and dissociation of e–h pairs are believed to be different for singlet and triplets. Hence, a change in their ratio by a magnetic field can change the current/resistance.

Figure 11 shows the energy diagram of the spin state of two carriers. At zero external field, singlet state and all three triplet states are degenerate and are all mixing by the random local hyperfine fields. However, an applied magnetic field splits three triplet states in energy due to Zeeman effect. As a result, there is only mixing of singlet state S and T0 state. In the work of Prigodin et al., it is assumed that singlets have a larger recombination rate than triplets (ks > kT) [26,46]. The triplets then mostly contribute to dissociation, hence the less mixing due to B, the less recombination. This reduction leads to more current and thus a positive MC. In addition, an attempt was made by the authors to explain a negative MC by introducing a regime
where the current responds oppositely to a change in recombination. The formation of secondary charges from e–h pair dissociation was studied by Bagnich et al. [45], who introduced one essential requirement: the lifetime of the e–h pair should be larger than the time of spin evolution to allow for mixing. This lifetime is expected to be shortened in a large electric field.

The exciton-charge model is proposed by Desai based on the long lifetime of triplet excitons (~25ms in Alq3) and the spin-dependence of exciton-charge interaction. The authors then suggested that an external magnetic field affects the intersystem crossing rate of singlet and triplet excitons, reducing the number of triplet excitons [27,29]. This would then give a reduced scattering of free charges on the triplet excitons, thus a positive MC. Desai et al. also considered the dissociation of the excitons into free carriers through interactions with free charge carriers, causing negative MC. Controversially, this suggested magnetic-field dependence of the intersystem crossing between excitons does not seem possible as the energy splitting between singlet and triplet exciton is very large (0.7 eV in Alq3) [51] while the Zeeman splitting by a hyperfine field of around 5mT is just 5 meV.

In brief, three groups of models have been used to explain the mechanism of OMAR. First, in the bipolaron model, spin blockage can be lift off when polarons can form a bipolaron if their spin is in a singlet configuration. A magnetic field suppresses hyperfine field mixing of spin states, regaining the spin blocking. Second, the e–h model requires the crucial condition is that either the recombination rate or the dissociation rate of an e–h pair is different for singlets and triplets. The singlet e–h pairs are believed to have higher dissociate and recombine rate than the triplet ones. These differences lead to increase in the current or positive MC when a magnetic field suppresses mixing and increases the singlet/triplet e-h pair ratio. Finally, in the exciton–charge interaction model, the effect of the magnetic field on this spin-dependent interaction is responsible for the OMAR. Positive MC results from releasing of trapped charges which then contribute to current. While negative MC derives from a recombination of excitons after the interaction.
Methodology and Motivation

Thermal Evaporation

Thermal evaporation is one of the most widely practiced techniques of physical vapor deposition. This thin film deposition is a vacuum process wherein pure materials are coated over the surface of many different substrates. This technique can deposit thin films with thickness in the range of single layer (few angstroms) to microns and can compose of a single or multiple layer materials. The depositing materials can be either organic molecules or metals.

Thermal evaporation is a process wherein a solid material is heated inside a high vacuum chamber to a temperature which generates some vapor pressure. Inside the vacuum, even a very low vapor pressure is adequate to create a vapor cloud within the chamber. This evaporated material now becomes vapor stream and attaches onto the substrate as a film. Since, in a majority of cases, the material becomes liquid by heating it to its melting temperature, it is normally placed in the bottom of the chamber, often in some form of upright crucible. The vapor then rises above from this bottom source and reaches the substrates that are held at the top of the chamber, with surfaces to be coated facing down toward the rising vapor to acquire their coating.

![Diagram](image-url)

Figure 12: An electron beam deposition scheme where there is no direct line of sight deposited filament to the deposition material (adapted from wikipedia.com website).

In our group setup, the thermal evaporation PVD systems feature quartz crystal deposition control to provide real time deposition rate monitoring and control in order to...
achieve the desired thickness. Two heat sources are predominantly used for heating the source material, namely the filament source and the electron beam (e-beam) source. The method that uses the filament source is called as filament evaporation, wherein the heat source is a simple electrical resistive heat element or filament. The filament source provides the safety of low voltage, but requires very high current, typically in the range of several amps. In my works, all the organic deposition and Al was used the filament evaporation. The Cr/Au electrode used the e-beam as a heat source. The source itself is an e-beam ‘gun’ (Figure 12), where electrons are boiled off by a tiny and very hot filament, followed by subsequent acceleration by the high voltage to create an electron beam (normally 10,000 volts) with substantial energy. This beam is magnetically directed into the chamber and heats the material contained in a hearth that is cooled down by water to avoid its own destruction.

**Measurements**

Field effect transistor (FET) structure opens a new approach to study the MFE on photo-induced current because it can control the infected current by applied gate voltage [52,53]. The thin film FET structure of n⁺-Si/SiO₂ substrate with patterned-gold electrodes. Based on this structure, the OMAR effect can be detected with or without the light radiation.

However, one of the drawbacks is that a time dependent change in the current, also called drift, is observed when measuring at constant voltage. This may come from the strong bias stress effect in these devices when a gate voltage is applied. Bias stress causes an increase in the threshold voltage and source-drain resistance with time when the gate voltage is applied continuously due to an increase in the number of carriers immobilized by deep traps. Another reason can derive from the degradation or conditioning, especially with the radiation of light [54]. However, as the drift is not linear in time and this change is larger than the small variation of the resistance with the magnetic field, the line shape can be erroneously modified.

Nevertheless, these problems can be overcome by alternatively switching the applied magnetic field on and off in a series. Then, the resistances with and without magnetic field are defined and the MR is determined [40].
The MR values are not directly estimated from the output or transfer characteristic but from time dependence of $I_{DS}(t)$ with constant $V_{DS}$. When magnetic field was switched on and off alternatively in a series with increasing magnitude as shown in Figure 13a, the source current was measured during time (open-red circle in Figure 13b). The baseline $I_{BASE}(t)$ was then created by linear interpolation based on the photocurrent at B=0 (blue line in Figure 13b). After baseline correction, I can obtain the curve in Figure 13c, which shows the change of photocurrent depending upon the magnetic field on the light irradiated devices and MR was calculated by the equation:

$$MR(t) = \frac{R_B - R_0}{R_0} = \frac{U}{I_{DS} - I_{BASE}} = \frac{I_{BASE}(t) - I_{DS}(t)}{I_{BASE}(t)}$$
Finally, MR versus Magnetic Field curve can be extracted by averaging and collecting MR values at different B (Figure 13d). It is noted that in literature, the magneto-conductance (MC) is also used frequently. The MR and MC have nearly equal absolute value, but the sign is opposite.

\[
MR = \frac{l_0 - l_B}{l_B} \approx -\frac{l_B - l_0}{l_0} = -MC
\]

All the measurements were performed by using a Keithley 487 (apply gate voltage) and a Keithley 6517A (applying \(V_{DS}\) and measuring \(I_{DS}\)) characterization system. All measurements were performed under vacuum of \(10^{-4}\) Pa. The measurements under light irradiation used a tungsten-halogen lamp (Megalight 100, Hoya-Schott) with intensity approximately 10 mW/cm\(^2\).
**Difficulties and Motivation**

OMAR study is still in its infancy, but attention given to it is continuously growing. Before realistic applications can be achieved, more experimental and theoretical work is needed to understand its mechanism. The observed OMAR effect seems to have different performances from small molecules, oligomers to polymers, and from weak to strong magnetic field. All these investigations show that the MR is diverse and is dependent on extrinsic parameters such as film thickness, applied voltage, temperature, charge-transfer integral, and the concentration of carriers… Besides, many effects can happen in organic material are reported to be magnetic-field dependence such as triplet-triplet annihilation, singlet to triplet fission, intersystem crossing effect… Thus, understanding these effects on OMAR would give important factors in the explanation of OMAR.

There are many open questions about the MFE on organic semiconductor, but the organic material itself is not an easy object to study due to the electrical instability and ambiguous performance. In organic devices, changing only one parameter is very difficult because many processes are linked, which make it becomes more challenging. Up to now, only one commonly agreement in OMAR field is that this effect derives from the hyperfine interaction between electron and nuclear spins. There are many works should be done to elucidate this effect.

In doctoral works, I focus on the MFEs on the current, and electroluminescence, photocurrent by developing a new approach based on field effect transistor structure. The common device structure used for studying OMAR is described in Figure 4(a). Comparing with two-terminal devices, three-terminal devices such as field-effect transistors (FET) have advantages that the sign of charge carriers in this device is defined by the gate voltage, and the mobility and density of charge carriers can be determined independently. Therefore, the FET structure is very potential to discovery more hints to elucidate the OMAR’s mechanism. Furthermore, since FET is fundamental component in electronic devices, understanding its operation under magnetic field may provide useful information for application such as the increase in performances due to small magnetic field.

Particularly, single crystal devices are more convenient for the study of more intrinsic material properties of organic semiconductors than polycrystalline thin film devices, due to the absence of grain boundaries. Single crystals of organic materials show high mobility and band-like transport, which is an important object for determination of OMAR mechanism. Thus, I
study the MFE on photo-induced current of organic single-crystals using FET structures. In this works, I plan to clarify whether single carriers or double carriers play the main role in OMAR by studying the MFE on photocurrent of pentacene and PFP single crystals in the form of FETs, which are both single-carrier devices.

Furthermore, the most obvious test to discriminate between the bipolaron model and the other models is the measurement of OMAR in ambipolar FET. For this purpose, the bilayer FET of pentacene (C_{22}H_{14}, PEN) and perfluoro-pentacene (C_{22}F_{14}, PFP) was fabricated on n^+-Si/300nm-SiO2 by thermal evaporation in high vacuum. In this device, the type of injected carrier and the density of electron and hole at the PFP/PEN interface can be controlled by the gate voltage. Hence, the conditions at which shows the MR will give the confirmed answer whether single carrier model (bipolaron model) or double carrier model (electron-hole pair model and exciton-related model) causes OMAR.

Finally, I have studied the MFE onto luminescence intensity of light-emitting FET (LEFET) based on alpha-sexithiophene (α-6T). The MFE on the luminescence will give the information about the magnetic field dependence on the singlet exciton formation. The MC also can be measured simultaneously with magneto-electroluminescence (MEL), so the mutual relation between MC and MEL can be clarified.
Thesis Structure

The remainder of this thesis is organized as follows:

Chapter 2 demonstrates the OMAR effect on photo-induced current of the single crystalline FET based on pentacene and perfluoro-pentacene. In these high mobility devices, the OMAR showed that charge carrier mobility and the exciton diffusion length were not important factors to determine the MR ratios. The interaction between triplet excitons and traps was thought to govern the OMAR behaviors.

Chapter 3 reports the OMAR effect on the organic thin film FET made of bilayer of pentacene and perfluoro-pentacene. The holes and electrons were injected into the device and their distance can be controlled by the voltage applied to gate electrode. Results showed that the closer the distance is, the larger the MR value obtain, which points at the presence of both electron and hole is required to cause OMAR. Thus, the bipolaron model can be ruled out as the mechanism of OMAR on FET. In addition, I have succeeded in tuning the amplitude and the sign of the MR ratio by the gate and drain-source voltages in organic FET based on multilayer of pentacene and perfluoropentacene. By increasing drain-source voltage, the positive MR ratio up to 0.37 % decreased and turned into negative values. This phenomenon can be qualitatively explained by the proposed triplet exciton-charge interaction model.

Chapter 4 shows the study of the improvement in emitting efficiency of LEFET based on α-6T by magnetic field. The external magnetic field can enhance the emitting of α-6T LEFET intensity of 1.3%. The probability of singlet exciton formation is thought to increase due to spin scattering caused by magnetic field. It is proven that understanding MFE can improve the performance of organic electronic devices.

Chapter 5 summarizes the works on OMAR of FET and explains the experimental results. The future plans are also proposed to expand the study of OMAR based on FET structure.
CHAPTER 2: OMAR IN SINGLE CRYSTAL PEN AND PFP FET

Organic magnetoresistance (OMAR) of single-crystalline (SC) pentacene (C\textsubscript{22}H\textsubscript{14}) and perfluoropentacene (C\textsubscript{22}F\textsubscript{14}) was studied using field-effect transistor structures. The gate voltage effect showed that the OMAR originates from photo-induced current and requires both electrons and holes in the transport channel. The temperature dependence showed the maximum magnetoresistance (MR) ratio up to -6% under light irradiation at approximately 200 K and magnetic field of 80 mT. The charge carrier mobility and the exciton diffusion length were not important factors to determine the MR ratios. The interaction between triplet excitons and traps was thought to govern the OMAR behaviors.

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Introduction

**Pentacene and Perfluoropentacene**

Pentacene (from penta = five, and acene= polycyclic aromatic hydrocarbons with fused benzene rings) is a planar aromatic hydrocarbon and has been widely studied as a p-type semiconductor as it has demonstrated the highest hole mobility for organic molecular crystals (~40 cm²/Vs at room temperature [55]).

Fluorine is used to create perfluoropentacene (C$_{22}$F$_{14}$), which attempts to tune the frontier energy levels of pentacene by substituting in electron-withdrawing groups. Previously, it is demonstrated that aromatic perfluorocarbons were efficient n-type semiconductors for the electron-transport layer of organic light-emitting diodes [56]. Because fluorine is the most electronegative among all the elements and relatively small, perfluorination is an effective way to convert a p-type organic semiconductor to a n-type one without changing the molecular size greatly.

To fabricate the organic p-n junction, the n-type organic semiconductor should have similar physical and electrical properties except for the type of carriers. Pentacene and perfluoropentacene have similar molecular shapes and sizes, and their thin-film d-spacings are almost identical (1.54 and 1.58 nm, respectively). The C-C bond distances range from 0.135-0.145 nm and are quite similar to those of pentacene (0.134-0.146 nm). As shown in Figure 14, pentacene and perfluoropentacene adopt herringbone structures with the angles of 51.9° and 91.2°, respectively. The X-ray diffraction of perfluoropentacene at room temperature showed the d-spacing calculated from the first reflection peak is 1.58 nm, which is close to the d-spacing observed in the single crystal (1.55 nm). In the case of pentacene, the d-spacing of the thin-film phase (1.54 nm) is much larger than that of the single crystal (1.41 nm) [57].

For all above, PFP is the n-type organic semiconductor of choice for constructing high-performance p-n junction with pentacene. However, very smooth surface is required in order to obtain the good heterojunction.
Figure 14: Molecular packing diagrams of (a) pentacene and (b) perfluoropentacene [57].

**Organic Single Crystals**

Single-crystals (SC) of organic semiconductors like rubrene and pentacene are similar to the single-crystal structures of inorganic electronics. Ultra-pure organic single-crystals can be grown and their electronic properties are well-reproducible [52]. In organic SC, grain boundaries are eliminated and the concentration of charge traps is minimized, making them ideal system for studying the intrinsic electronic properties of organic materials.

Charge transport in organic molecular semiconductors strongly depends on the degree of molecular order. The reported benchmark values of carrier mobility (20–40 cm²/Vs) are one order of magnitude larger in single crystalline organic FETs than those typically reported for conventional thin-film transistors of polycrystalline semiconductors [55,58–61]. It also shows that the triplet excitons have long diffusion length of few micrometers in single crystals of rubrene as a result of disorder-free materials [62].

Hence, organic single crystals play an important role to study intrinsic properties in molecular semiconductor systems, because of the nearly perfect periodicity of the molecular stacking and absence of grain boundaries.
**Experiments**

Pentacene (PEN) and perfluoropentacene (PFP) were purchased from Aldrich and Kanto Denka Kogyo, respectively. Single crystals of pentacene and PF-pentacene were fabricated by horizontal physical vapor growth method in a high temperature glass tube under the flow of nitrogen as carrier inert gas [63]. The equipment is set up as in the scheme below:

![Scheme of horizontal physical vapor transport method](image)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Source temperature</th>
<th>Growth tube temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentacene</td>
<td>265°C</td>
<td>220-240°C</td>
</tr>
<tr>
<td>PF-Pentacene</td>
<td>285°C</td>
<td>240-260°C</td>
</tr>
</tbody>
</table>

Figure 15: Schematic illustration and real image of horizontal physical vapor transport method.

The system includes an outer tube containing a train of 3 smaller tubes. This arrangement makes it easy to take out the crystals and also convenient for purification procedure. Commercial pentacene (99.9%) and PFP powder, purchased from Aldrich, were put in the source tube and heated up to the evaporated temperature. Then, the molecules were transported by nitrogen gas and crystallized at the top of growth tube. In materials purification procedure, the source tube is replaced by the growth tube in regrowth process; typically, the single crystals are obtained after 3 regrowth processes. Based on this method, we have succeeded in the fabrication of single crystalline pentacene and PFP with the conditions shown in Figure 15. Single crystals of pentacene are disk-like shape with typical diameters of 5-10 mm. In case of PFP, the crystals have lath-like shape with the size of 2x10 mm. Then, only
single crystals with the thickness less than 500 nm were used for lamination on 300-nm-thick SiO$_2$/n$^+$-Si substrate with patterned-gold electrodes to make the bottom contact FET.

![AFM topography and height profile of single crystalline Pentacene and PFP on SiO$_2$ substrate](image)

Figure 16: (a) Real picture of largest Pentacene crystal has been grown, (b) AFM topography and height profile of single crystalline Pentacene and (c) PFP on SiO$_2$ substrate show crystal thickness of ~ 200-300nm and surface roughness of ~3nm.

The device was placed between the poles of an electromagnet. The magnetic field was applied perpendicular with respect to the direction of the current flow in FETs. The magnetic field was varied in the range from -100 to +100 mT. The FETs characteristics were measured under light irradiation using a tungsten-halogen lamp (Hoya-Schott) with intensity approximately 10 mW/cm$^2$. The MR ratio (%) was calculated for the resistance at 100 mT with respect to that at zero magnetic field.
Results and Discussions

The OMAR effect was observed only when the device was irradiated by light. The MR curves observed both for PEN and PFP SCs were fitted well with non-Lorentzian line shape as shown in Figure 18. Since gate voltage \( V_G \) determines the number of injected charge carriers in the conducting channel, control the gate voltage leads to the change of injected current to photocurrent ratio. As shown in Figure 19, the MR was enhanced when the gate was biased positively and negatively with respect to the grounded drain electrode for PEN (p-type) and PFP (n-type) FETs, respectively. At high \( V_G \), depletion is formed at the interface of organic SCs and SiO\(_2\) substrate. There is mainly photocurrent in transport channel and the contribution of injected current is negligible, which means the MR mainly derives from the photocurrent. The MR of photocurrent in FETs is a strong evidence that both electrons and holes are required for OMAR. Thus, the bipolaron model is not suitable for explanation of the OMAR mechanism in the present work. The MR curve is well fitted by non-Lorentzian line shape with \( B_0 \) is around 9 mT, which well agrees with the Reichert’s work [40].
Figure 18: MR curves of (a) SC PEN and (b) SC PFP FETs at low temperature and 80 mT.

Figure 19: Dependence of MR on $V_G$ of (a) SC PEN at $V_{DS} = -0.5$ V and (b) SC PFP at $V_{DS} = -10$ V at 80 mT.

Figure 20a shows the plots of drain current $I_{DS}$ versus drain voltage $V_{DS}$ at different gate voltages $V_G$ measured in the dark, which displays clear linear and saturation regimes. Figure 20b depicts transfer characteristics measured in the dark and under light irradiation by a tungsten-halogen lamp. Only the p-channel operation is observed, indicating that holes are the majority charge carriers. The charge carrier mobilities were calculated in the linear regime ($V_{DS} = -0.5$ V) by using the equation:

$$I_{DS} = \frac{\mu WC}{L}(V_G - V_T)V_{DS}$$

where $L$ is the channel length, $W$ is the channel width, $C$ is the capacitance per unit area of the insulator (~ 11.5 nF/cm² for 300 nm-thick SiO₂), $V_T$ is the fitted threshold voltage, and $\mu$ is the
charge carrier mobility. The typical mobility of pentacene single crystals is around 1 cm$^2$/Vs and increase to 1.5 cm$^2$/Vs under light radiation. Together with the shifted toward positive values of threshold voltage, they indicate the optical depletion of traps by illuminating the sample [54].

As a result, the current increases during light exposure, with the decrease of MR when increasing of radiated duration (Figure 21). It means that the OMAR strongly depends on the effect of traps, mainly from the interaction of triplet excitons with traps due to their longer lifetime comparing with singlet ones.

Figure 20: FET characteristic of pentacene single crystal.

Figure 21: (a) The current depends on exposed time and (b) the MR ratio after different light radiated duration at $V_{DS} = -0.5$ V, $V_G = 50$ V and light radiation.
The role of triplet excitons is further investigated by the measurements of MR at different temperature. The lifetime of triplet excitons becomes longer at low temperature due to reduction of phonon scattering [64]. Our data demonstrated that at low temperature, the OMAR effect increase and the MR ratio at 173 K was about 10 times larger than this value at 250 K (Figure 22). It is noted that, in common observations, only a weak temperature dependence of OMAR is reported [23]. Only a literature presents the sign change in Alq3-based device from positive to negative at the temperature of 183 K, which have not reported in other material [36]. Thus, our result of strong temperature dependence may derive from the long diffusion length of the exciton in single crystals [62]. However, at lower temperature, the resistance of the system increases, so the MR also decreases.

Figure 22: Temperature dependence of MR of FET based on (a) SC PEN at $V_{DS} = -0.1$ V, $V_{G} = 30$ V and (b) SC PFP at $V_{DS} = 10$ V, $V_{G} = -50$ V.

Significant differences in the temperature dependence of OMAR were not observed between thin film based and SC-based FETs, although the exciton diffusion length and mobility of carriers in SC devices are expected to be larger by a few orders of magnitudes [62]. Therefore, neither the mobility of charge transport nor the diffusion length of excitons is thought to be important factors to govern the OMAR characteristics. The OMAR effect reaches its maximum at approximately 175-200 K, which is about 10 times larger than the value at room temperature (300 K) (Figure 24). Previous works using two terminal devices showed weak temperature dependence [23].

The dependence of MR on the drain-source voltage is investigated at different temperature. The results indicate that MR depends weakly on $V_{DS}$ as shown in Figure 23. At
$V_G = -50 \text{ V}$, there is negligible injected current in the transport channel of PFP device, thus the $V_{DS}$ may affect the lifetime of the excitons and electron-hole pairs. As a result, increasing the dissociated rate and MR is reduced.

Figure 23: Dependency of MR on $V_{DS}$ of SC PFP device at $V_G = -50 \text{ V}$, 80mT and different temperature.

Figure 24. Temperature dependence of (a) SC and thin film PEN FETs, and (b) SC PEN and SC PFP FETs at magnetic field of 80 mT.
The ratio of singlet and triplet states can be adjusted by intersystem crossing (m\textsubscript{ISC}) in the form of electron-hole pair (Figure 25). Thus, OMAR mechanism can be explained on the basis of electron-hole pair model.

![Illustration diagram of our proposed mechanism of OMAR.](image)

The major product of light absorption is the generation of intra-molecular singlet excited states (Frenkel excitons) based on the spin-selection rule. Then, singlet excitons can partly convert to triplet excitons through intersystem crossing due to internal interaction of hyperfine field or SOC. However, the energy splitting of singlet and triplet exciton (~0.5 eV) is much larger than the Zeeman splitting energy by a typical hyperfine field (0.5 meV at 5 mT). Hence the ISC is believed to occur in electron-hole pair states. The singlet excitons then soon dissociate toward the generation of photocurrent in the sub picosecond process [65] via intermediate states of singlet electron-hole pairs while the triplet excitons last for so much longer time. The difference between the dissociation rate between singlet and triplet e-h pair comes from the difference in their lifetime. The singlet polaron pairs can be partially converted into triplet polaron pairs through ISC. In turn, they can reform triplet excitons from their recombination [66] or dissociation to free electrons and hole. However, triplet pairs have smaller contributions to photocurrent than singlet ones because there are some possibilities that they are unavailable for contributing to the current resulted from a loss of excitons by the interaction with traps.

Without the external magnetic field, the S\textsubscript{0} state is mixed with three triplet states T\textsubscript{+}, T\textsubscript{0}, T\textsubscript{-} (Figure 9c). When an external magnetic field applied comparable to the internal magnetic interaction in strength, an external magnetic field can further increase the triplet splitting
(external Zeeman effect), reduce the singlet and triplet states mixing (now is just between $S_0$ and $T_0$ in Figure 9d) and consequently increase the triplet electron-hole pairs density. Consequently, it leads to a decrease of photocurrent and the observation of negative MR effect.

The dependence on temperature also can be explained based on the longer diffusion length [62] and lifetime [64] of excitons in single crystals at low temperature, which can raise the rate of triplet excitons-traps interaction and increase the numbers of lost excitons. In contrast, the drain-source voltage plays an opposite role that enhances the dissociation process in triplet states by applied electrical field. Hence, the MR decreases when large $V_{DS}$ is applied.

**Conclusion**

We showed the negative MR in SC PEN and PFP FETs under light irradiation. The charge carrier mobility and the diffusion length of excitons were not important factors in OMAR. A possible explanation for this phenomenon is the intersystem crossing in e-h pair states and interaction of triplet excited states with traps. Besides, the MR depends on temperature, which may come from the triplet excitons interaction.
CHAPTER 3: OMAR IN BILAYER PEN/PFP FET

Magnetoresistance (MR) in ambipolar field-effect transistors (FETs) consisting of bilayers of pentacene (C$_{22}$H$_{14}$, PEN) and perfluoropentacene (C$_{22}$F$_{14}$, PFP) were studied. The ambipolar FET exhibits positive MR of approximately 1% at 100 mT and room temperature. This effect is considered to originate from the accumulated carriers at the interface between PEN and PFP. The gate voltage dependence showed that MR was enhanced with increasing number of electrons and holes accumulated at the PFP-PEN interface. The observed results support the proposed double-carrier models as the mechanism of organic magnetoresistance.

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Introduction

The most obvious test to distinguish between the bipolaron model and the other models relying on the presence of e–h pairs or excitons is the measurement of OMAR in single-carrier devices. The bipolaron model, on the other hand, predicts an effect even in single-carrier devices. However, it is generally a question if there are really no opposite charges present. Some minority carriers might still be injected in the tails of the HOMO or LUMO, and there might be adjustments of the energy levels at the interface, changing the expected injection barriers.

The FET structure is useful for studying this phenomenon since the carrier injection and transport properties can be controlled via the bias voltage applied to the gate electrode. There have been few reports on OMAR in FETs. Reichert and Saragi have reported negative MR [R(B)<R(0)] and positive MR [R(B)>R(0)] in the photo-induced current of thin-film pentacene (PEN)-based [40] and tetracene-based FETs [42], respectively, in which the irradiation of light is essential to observe OMAR.

In the present work, I report OMAR without the presence of light in ambipolar FETs consisting of PEN and perfluoropentacene (PFP) bilayers. The MR ratio was modified via the gate voltage (V_G), and it was shown that OMAR was enhanced when the distance between electrons and holes decreased.
**Experiments**

Thin films of PEN (Aldrich Co.) and PFP (Kanto Denka Kogyo Co.) were thermally evaporated on octadecyltrichlorosilane (OTS)-treated 300-nm-thick SiO₂/n⁺-Si substrates with golden source-drain electrodes to fabricate bottom-contact FETs with a channel length of 5 μm.

![Figure 26: (a) Effect of magnetic field on current of SiO₂\(\text{PFP}(20 \text{ nm})\text{PEN}(100 \text{ nm})\) device. (b) The MR curve of SiO₂\(\text{PFP}(20 \text{ nm})\text{PEN}(100 \text{ nm})\) FET, fitted with Lorentzian and non-Lorentzian curves.](image)

In the MR measurements, the specimen was placed between the poles of an electromagnet. A magnetic field was applied perpendicularly (in-plane with the organic film) to the current flow in the FETs. The drain current was measured using a Keithley 6517A electrometer while the magnetic field was switched on and off at 3s intervals with increasing strength in the range from -100 to +100 mT, as shown in Figure 26(a). All measurements were performed at room temperature.

**Results and Discussions**

Figure 27 shows the ambipolar FET characteristics for SiO₂\(\text{PFP}\text{PEN}\) and SiO₂\(\text{PEN}\text{PFP}\) devices. Although both double-layer devices exhibited ambipolar behavior, the SiO₂\(\text{PFP}\text{PEN}\) device showed more symmetric electron and hole mobility of approximately \(5\times10^5 \text{ cm}^2/\text{Vs}\).
The FET based on SiO\textsubscript{2}\textbackslash PFP\textbackslash PEN\textbackslash PEN(100 nm) showed the largest positive MR ratio at $V_G = -30$ V, $V_{DS} = 30$ V, as displayed in Figure 26(b). This MR curve was more closely fitted with a Lorentzian line shape $MR \sim B^2/(B^2 + B_0^2)$ than with a non-Lorentzian line shape $MR \sim B^2/(|B| + B_0)^2$. On the other hand, it was reported that the photoinduced MR observed in PEN-based FETs is negative and can be well fitted with a non-Lorentzian line shape. [40] We also prepared a PEN FET device and observed that the MR curves obtained under light irradiation at different value of B were very well fitted using a non-Lorentzian line shape. The differences in the sign and curve of the photoinduced and injected MR may originate from different mechanisms in which singlet excitons and triplet excitons are dominant, respectively.
Figure 28: (a) Energy alignment of PEN and PFP, (b) in situ conductivity measurement of SiO\_2\(\text{PFP(20 nm)}\)\(\text{PEN(100 nm)}\) and SiO\_2\(\text{PEN(20 nm)}\)\(\text{PFP(100 nm)}\) devices, (c) accumulated interface of SiO\_2\(\text{PFP}\) device.

On the basis of the energy alignment shown in Figure 28(a), differences in the ionization potential and electron affinity of PEN and PFP are initially compensated by interfacial charge accumulation upon junction formation within a few molecular layers of the PEN-PFP interface, as in the case of copper phthalocyanine (CuPc) and fluorinated copper phthalocyanine (F\(_{16}\)CuPc) [67,68]. Figure 28(b) shows the result of an in-situ drain current measurement during film growth at a drain-source voltage of 10 V, which was performed to confirm this effect. While the first 20 nm-thick layer of PEN (PFP) was being deposited, the drain current remained nearly zero. When the second layer of PFP (PEN) started to be deposited, the drain current sharply increased by three orders of magnitude. We also studied SiO\_2\(\text{PEN}\)\(\text{PFP}\) devices to confirm that the high conductivity indeed originated from the PFP-PEN interface, and was due to the accumulation of charges. The FET had an open channel at zero gate voltage and operated in the “normally on” mode. At the interface, mobile electrons accumulated in the n-type sites (PFP) whereas mobile holes accumulated in the p-type site.
(PEN). When the distance between the electrons and holes decreased, the injected electrons and holes can form excitation states.

![Figure 29: V_G dependence of MR ratio in (a) SiO_2\PEN\PFP and (b) SiO_2\PFP\PEN devices.](image)

An advantage of the FET structure is that the gate voltage (V_G) can be used to adjust the density of charge carriers at the PFP-PEN interface. In the SiO_2\PEN\PFP device, when a negative bias voltage is applied to the gate, holes accumulate near the SiO_2\PEN interface while electrons tend to move away from the interface. In other words, fewer electrons and holes accumulate at the PEN\PFP interface region reducing the exciton formation. On the other hand, a positive V_G enhanced the OMAR effect, probably because of the adjacency of the p- and n-channels when more electrons and holes are concentrated near the interface region, as shown in Figure 29(a). The opposite tendency was observed in the SiO_2\PFP\PEN device, as shown in Figure 29(b), in which the p- and n-layers were interchanged. The V_G dependence shows that the smaller the average distances between the electrons and holes, the larger the MR ratio that is obtained. Thus, the MR observed at the interface at which electron and holes had accumulated also indicating that OMAR requires both electrons and holes.
When electrons and holes are injected into the conducting channel at a PEN-PFP interface, the formation ratio of singlet to triplet electron-hole pairs has been theoretically predicted to be approximately 1/3. These can recombine into excitons or dissociate back to free secondary charge carriers. Triplet electron-hole pairs can transform into singlet pairs through intersystem crossing. Singlet states have relatively larger dissociate rates owing to their more effectively interact with the local electrical field and shorter lifetime comparing with triplet states. An triplet exciton can transfer its energy to a charge carrier on recombining to the ground state, called an exciton–charge interaction [17]. There should have the probability of scattering and trapping of free carriers at these triplets [27,29]. In other words, the more triplet states in the channel, the higher the resistance is. When an external magnetic field is applied, the triplet exciton density is believed to increase, leading to an increase in the channel resistance, resulting in positive MR. The external magnetic field reduces (i) the probability of the intersystem crossing of triplet to singlet electron-hole pairs by the Zeeman effect and/or (ii) the decrease in the spin flip rate.
**OMAR of Multilayer PEN/PFP FET**

In order to increase the interface between PEN and PFP, multilayer layer devices was fabricated for further investigation. It is noteworthy that the co-evaporation sample showed large resistance and no FET behavior, probably because of the discontinuous of the channel. The device structure is illustrated in Figure 30(a) and it shows both hole and electron transport FET.

![Device Structure](image)

Figure 30: (a) The illustration of pentacene/perfluoropentacene FET device structure. Each layer is approximately 10nm (5 layers). The PEN top layer was deposited around 100 nm as a cap layer. (b) The gate voltage dependence of the drain-source current.

![Gate Voltage Dependence](image)

Figure 31: The MR ratio in the multi-layer pentacene/perfluoropentacene FET.
Figure 31 shows the MR measured at different $V_G$ and $V_{DS}$. At given $V_{DS}$, the MR value reaches a maximum when the $V_G$ is around -10 V to 0 V, which points at the optimizing condition of OMAR can be achieved when the density of electron and hole is balance. Besides, while increasing the $V_{DS}$, the sign change was observed.

The sign of OMAR could give an important clue in validating the models. Hu et al. considered the total MFE to be a balance of e–h mixing (positive) and exciton–charge interaction (negative). The ratio can be changed by changing the charge balance or the electric field [25]. When the electrons and holes are unbalanced, the exciton–charge interactions dominate, resulting in a negative effect [32]. At high electric fields, the e–h pairs can dissociate more easily, resulting in a positive effect [25].

However, in my work, the sign of MFE can only be changed due to the electrical field. The gate voltage can adjust the balance of injected charge carrier. Positive (negative) voltage applied to gate electrode will allow more electron (hole) injection. The MR sign change from positive to negative just happened when the drain source current become larger or the higher current density.

![Diagram](image)

**Figure 32: Proposed multi-change mechanism on multi-layer PEN/PFP FET.**

When the electron-hole pairs are formed, approximately 75% are triplet state, 25% are singlet state. The electron-hole pair can recombine to singlet or triplet exciton or dissociation to free charges due to electrical field. The triplet exciton has a longer lifetime than the singlet one and it can diffuse and interact with other species more efficiently. Triplet excitons can detrap the trapped charges according to $T + q^* \rightarrow S_0 + q$. The outcome of this process will
decrease the current or +MR. However, with increasing current density, triplet excitons can interact with free charge, then dissociate into secondary charge carriers as $T + q \rightarrow e + h + q$, whereas $q^*$, $q$, $e$, and $h$ are trapped charges, free charges, electrons, and holes, respectively [32,69,70]. The exciton-charge interactions increase the $I_{DS}$ causing negative MR. Therefore, by adjusting the current density, the dominant process can be switched between triplet exciton detrapping and triplet exciton charge interaction, causing positive and negative MR, respectively.

**Conclusions**

We demonstrated positive MR in ambipolar FETs based on bilayers of PEN and PFP. Although the electrical conduction occurred at both the organic/organic and organic/SiO₂ interfaces, the accumulation of carriers at the organic/organic interfaces determined the MR behavior. We could tune the MR ratio by changing the number of carriers at the organic/organic interface via the gate voltage. This implies that the bipolaron model of OMAR is not applicable to our devices. The positive MR in ambipolar FETs originates from a decrease in the singlet to triplet state ratio, since a magnetic field decreases the intersystem crossing rate of triplet to singlet electron-hole pairs and/or the spin flip rate.

The sign change showed in multilayer PEN/PFP comes from the switch in mechanism between triplet exciton detrapping and triplet exciton charge interaction process. The exciton-charge interaction becomes dominant when there is a large current density in device. The electron-hole balance does not contribute to the mechanism change (between electron-hole pair and triplet exciton-charge interaction) as the previous report.
CHAPTER 4: MAGNETIC FIELD EFFECT IN LUMINESCENCE OF ALPHA SEXITHIOPHENE

We demonstrated the effect of a magnetic field on the luminous intensity and electric current of light-emitting field-effect transistors (LEFETs) based on alpha sexithiophene (α-6T). Sublimate-grade α-6T was thermally deposited on an n+-Si/300nm-SiO₂ substrate with patterned asymmetric gold-aluminum electrodes to fabricate a bottom-contact LEFET. We observed an increase in luminous intensity of approximately 1.3% under a magnetic field of 100 mT. A possible explanation for this is that the magnetic field increased the probability of singlet formation at the α-6T/Al interface. While the magneto-electroluminescence (MEL) was reported to be derived from the magneto-conductance (MC) in ordinary light emitting diodes, the MEL in LEFET was independent with MC. This indicates that the luminous efficiency can be improved by optimizing the MFE.

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**Introduction**

The effects of external magnetic field on the electrical conductance and electroluminescence (EL) of organic materials have been observed in various organic semiconductors since the 1960s [15–19], demonstrating the potential application of magnetic features to organic electronic devices without using ferromagnetic compounds [13,71]. In 2003, Kalinowski *et al.* showed an increase in EL of up to 5% in tris-(8-hydroxyquinolinato) aluminum (III) (Alq3)-based organic light-emitting diodes (OLEDs) with an external magnetic field of 300 mT at room temperature [20]. There are two distinct possible types of MFE on EL: (i) $EL(B) \sim \eta I(B)$ and (ii) $EL(B) \sim \eta(B)I$ where $\eta$ and $I$ are the EL quantum efficiency and current, respectively. In type (i), the current through the device is affected by the magnetic field and the EL quantum efficiency itself did not change. In type (ii), the quantum efficiency is dominantly affected by the magnetic field. It has been reported that the magneto-EL (MEL) of OLEDs examined so far is proportional to the magneto-conductance (MC) [type (i)] [23,72,73].

MC and MEL are defined as:

$$MC = \frac{I(B) - I(0)}{I(0)} = \frac{\Delta I}{I(0)}$$

$$MEL = \frac{EL(B) - EL(0)}{EL(0)} = \frac{\Delta EL}{EL(0)}$$

In this work, we study the MFE in alpha-sexithiophene [$\alpha$-6T, Figure 34(a)]-based light-emitting field-effect transistors (LEFETs). The FET structure is useful for studying this phenomenon since the carrier injection and transport properties can be controlled via the bias voltage applied to the gate electrode ($V_G$) [74]. The $\alpha$-6T-based LEFETs showed an increase in EL of approximately 1.3% under a magnetic field of 100 mT at room temperature; however, there was no significant change in the drain-source current. This indicates that MEL is independent of MC. The mechanism of MEL can be explained on the basis of the increase in the electroluminescence quantum efficiency owing to the external magnetic field [type (ii)].
Experiments

Interdigital electrodes of Cr (10 nm)/Au (20 nm) and Al (20 nm) were formed on the SiO$_2$ layer using conventional photolithography and lift-off techniques (Figure 33). The α-6T powder was purchased from Aldrich and purified twice by train sublimation prior to use. Thin films of α-6T were thermally evaporated on 300-nm-thick SiO$_2$/n$^+$-Si substrates with Cr/Au-Al electrodes to fabricate a bottom-contact FET with a channel length of 5 μm. The typical thickness of α-6T was approximately 100 nm.

![Figure 33: Fabrication of interdigital electrodes of Cr (10 nm)/Au (20 nm) and Al (20 nm) on the SiO$_2$ layer using conventional photolithography and lift-off techniques.](image)

![Figure 34: (a) Molecular structure of α-6T and (b) a schematic view of LEFET. The orange light emission was observed near the Al electrode. (c) The illustration of experiment setup to measure MEL and MC.](image)

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Figure 34(b) shows a schematic view of the fabricated device. In the MEL measurements, the specimen was placed between the poles of an electromagnet as shown in Figure 34(c). A magnetic field was applied perpendicularly (in plane with the organic film) to the current flow in the FETs. The light intensity was determined using a Si photodiode (Hamamatsu, S1226-8BK) placed 20 mm above the device. The drain current and photo intensity were measured simultaneously using electrometers (Keithley 6517A and Keithley 487) while the magnetic field was switched on and off at 3 s intervals while increasing the strength in the range from -100 to +100 mT. The magnetic effect on the silicon photodiode is negligible. All measurements were carried out in vacuum of $5 \times 10^{-4}$ Pa at room temperature.

**Results and Discussions**

Figure 35(a) and Figure 35(b) show the EL and drain-source current as a function of the gate voltage and output characteristics of $\alpha$-6T-based FETs with Cr\Au-Al electrodes, respectively. These results indicate that the $\alpha$-6T film exhibits p-type semiconducting behavior with hole mobility $\mu \sim 3 \times 10^{-3}$ cm$^2$/Vs. Orange light was emitted at the $\alpha$-6T/Al interface when $|V_G|$ exceeded 60 V, which is visible to naked eyes. The device with asymmetric Cr\Au-Al electrodes exhibited stronger luminescence than that with symmetric Cr\Au-Cr\Au electrodes, since the injection of electrons is improved by using an Al electrode instead of a Cr\Au electrode [75].

![Figure 35: (a) Gate voltage dependence of drain current and emitting photo intensity detected by using a Si photodiode and (b) output characteristics of $\alpha$-6T FETs with Cr\Au-Al electrodes.](image)

Figure 36 shows the MEL and MC responses of the $\alpha$-6T-based LEFET as a function of the magnetic field. The MEL was approximately 1.3% at $V_G = -70$ V and a magnetic field of
100 mT. With increasing $|V_G|$, the $EL(0)$ intensity increased while the change in EL, $\Delta EL$, remained constant, leading to a decrease in MEL value (as shown in Figure 36). MC was detected simultaneously during the measurement of MEL, but no significant change in conductance was observed. This indicates that MEL and MC have different origins. This was also pointed out by Buchschuster et al., who observed a significant reduction in the magnetoresistance magnitude of an Alq3-based OLED when the injection of holes into the electron transport layer was prevented while the corresponding MEL was not affected [76].

![Figure 36: MEL and MC of the α-6T LEFET at different gate voltages and magnetic field of 100 mT.](image)

In the e–h model, the recombination probability of singlet e–h pairs is assumed to be higher than that of triplet pairs, and thus the triplet states mostly contribute to dissociation [26,44]. Therefore, with less mixing of singlet and triplet electron-hole pairs due to the magnetic field, there is less recombination, resulting in a higher current or positive MC. However, in the present experiment, MC changed slightly under the magnetic field while a positive MEL was still detected. Thus, we concluded that MC was hardly observed because of the lack of electron-hole pair interaction because only holes were injected into the conducting channel and passed through the organic layer in the LEFET device with a negative bias voltage applied to the gate electrode. When the holes reached the Al electrode, they were collected at the electrode or recombined instantly with electrons in a limited area near the Al electrode where the light came out. Besides, Reufer et at. and Nguyen et al. showed that both luminescence and phosphorescence signal increased with applied magnetic field [22,77]. Hence, the MEL of α-6T-based LEFETs may be derived from the magnetic-field-induced increase in the singlet exciton formation probability due to intermolecular quantum correlated
effect and/or the irradiated recombination efficiency at the α-6T/Al interface [78]. If no external magnetic field exists, the intensity value of hyperfine field is identical for each molecule and uniform in space. On the other hand, for a given external magnetic field, the sum of external fields and hyperfine field becomes non-uniform distribution (Figure 37). This non-uniform field may act like disorder in an energy distribution which strengthens spin scattering and enhances hole-electron pairs formation probability [78,79]. Besides, the external magnetic field can reduce spin mixing, that inhibits the transition from singlet hole-electron pair to a triplet exciton, hence effectively increases the number of singlet excitons [25].

Conclusions

In summary, we demonstrated a MEL effect of 1.3% for α-6T LEFETs under 100 mT at room temperature and its independence of MC. There have been several reports on MEL of diode structures, in which both the current and luminous intensity increased with magnetic field. The quantum efficiency itself was not improved [23,72,73]. The magnetic-field-induced increase in the singlet exciton formation probability due to intermolecular quantum correlated effect and/or the irradiated recombination efficiency at the α-6T/Al interface. The luminous efficiency of the LEFETs can be enhanced by optimizing the MFE and device structures.
CHAPTER 5: THESIS CONCLUSIONS

Magnetic effects on organic material open new applications for organic devices where low costs, light weight, and biocompatibility are more important than durability and high performance. For instance, room temperature magnetic field sensor [71], pen input OLED [13] or room temperature organic transduction between magnetic and optic information [80]… This thesis focuses on elucidate the mechanism behind these application by utilizing the FET structures.

General observation of MR can be obtained from highly disordered materials on sandwich structures. Chapter 2 showed the OMAR on high order materials, pentacene and PFP single crystals under light irradiation. Firstly, the photo-induced OMAR results show that it is required double carrier to cause the OMAR effect. Furthermore, the charge carrier mobility and the diffusion length of excitons, which have a large effect on the bipolaron model, were not important factors in OMAR on FET devices. Therefore, the bipolaron model is not suitable for the mechanism for explanation of OMAR effect. This statement has been confirmed by the gate voltage dependence of MR value in thin film PEN/PFP FETs (in chapter 3). Secondly, I suggested the possible mechanism based on the combination of electron-hole pair and excitons-charge interaction models. The difference in lifetime of singlet and triplet e-h pair causing the difference in their dissociation rates. With less mixing due to magnetic field, less singlet state will be converted to triplet state. The singlet states contribute mainly to the current, hence the magnetic field increase the current and cause negative MR. By analyzing the dependency of traps density and temperature, there may have the triplet exciton-charge interaction in the devices.

Chapter 3 demonstrated that the formation of electron-hole pair is essential to cause OMAR as shown in the study of thin film PEN/PFP FET. In contrast with photo-induced OMAR, the current in thin film PEN/PFP derives from the charge injection from electrode at the interface between PEN and PFP. Therefore, the singlet/triplet exciton ratio in the device is approximately 1/3. The external magnetic field tents to increase triplet state density due to less mixing between singlet and triplet e-h states. The triplet electron-hole pairs can recombine into triplet excitons, which then interact with charges or traps causing different influences on current. The sign change showed in multilayer PEN/PFP comes from the switch in mechanism between triplet exciton detrapping and triplet exciton charge interaction process. The exciton-
charge interaction becomes dominant when there is a large current density in device. It opens a new door to adjust the MR value and also the sign of OMAR.

Finally, in chapter 4, I demonstrated a MEL effect of 1.3% for α-6T LEFETs under 100 mT at room temperature. This work points out that the origin of MC and MEL is different, MEL is independent with MC, contrasting many studies on sandwich structures. Besides, the magnetic-field-induced increase in the singlet exciton formation probability may derive from the intermolecular quantum correlated effect and/or the improvement in irradiated recombination efficiency at the α-6T/Al interface. Thus, by optimizing the MFE and device structures, the luminous efficiency of the LEFETs can be raised.
FUTURE PLAN

The MFE in different bilayer FET structures shows the diverse characteristic that is nevertheless difficult to fully interpret. In my work, I suffer some initial results which indicate potential for expanding study based on pentacene, α-6T, (2E,2’E)-3,3’-(2,5-bis(hexyloxy)-1,4-phenylene)bis(2-(5-(4-(trifluoromethyl)phenyl)thiophen-2-yl)acrylonitrile (Hex-4-TFPTA), C₆₀. These molecules have many unique magnetic properties when combine with each other to form a bilayer structure due to the difference in charge transfer energy (as depicted in Figure 38).

Figure 38: Energy alignment and molecular structure of Pentacene, α-6T, PFP, Hex-4-TFPTA and C₆₀.

Magnetic Field Effect on Singlet Fission

It is well known that the pentacene/C₆₀ have a high rate of singlet fission that is also magnetic field dependent. The absorbed photon at pentacene layer creates a singlet exciton that then fission into two triplet excitons in a short time (1/80 fs) [81,82].

Figure 40 shows a schematic diagram showing the relevant excitonic energy levels. It should be noted that the triplet energy of pentacene (0.86 eV) is less than half the energy of the lowest-lying singlet (1.83 eV) [83], hence, the singlet exciton fission process is expected to
occur without thermal activation. The present of C_{60} layer enhances the charge separation due to the difference (~0.45 eV) between the acceptor’s LUMO and the donor’s HOMO smaller than the triplet excitons binding energy in pentacene (0.86 eV). This separation at the pentacene-C_{60} interface contributes to the photo current.

![Figure 39: Output characteristic of SiO_{2}/pentacene/C_{60} FET with light irradiation and in dark.](image)

In the SiO_{2}/pentacene/C_{60} device, it shows negative MR curves with a maximum peak [Figure 41(a)]. The amplitude increasing of external magnetic field first increases then decrease the singlet fission rate [84], the value of MR also increases and then decreases as shown in Figure 41. In the dark, the C_{60}/pentacene FET device still shows the OMAR effect which may
derive from the magnetic field dependence of intersystem crossing as shown in the pentacene\perfluoro-pentacene FET devices [74].

![Figure 41](image1.png)

Figure 41: The OMAR of SiO$_2$\C$_{60}$\pentacene FET (a) with light and (b) without light irradiation.

![Figure 42](image2.png)

Figure 42: OMAR of SiO$_2$\PEN\C$_{60}$ FET.

However, OMAR of the SiO$_2$\PEN\C$_{60}$ did not display the same behavior (Figure 42). That raises the concern about the accuracy of mechanism. The negative MR becomes dominant while the positive MR just shows at small magnetic field.
Magnetic Field Effect on Charge-Transfer System

Recently, Kim et al. showed remarkable improvement in operation of pentacene FET by a discontinuous layer of Hex-4-TFPTA [85]. The mobility increase significantly due to the charge-transfer formation at pentacene/Hex-4-TFPTA interface.

Thin films of pentacene (Aldrich Co.) and Hex-4-TFPTA (synthesized by group of Prof. Park, Seoul National University) were thermally evaporated on octadecyltrichlorosilane (OTS)-treated 300-nm-thick SiO₂/n⁺-Si substrates with golden source-drain electrodes to fabricate bottom-contact FETs with a channel length of 25 μm. Figure 43 contains the plots of drain current \( I_{DS} \) versus drain voltage \( V_{DS} \) at different gate voltages \( V_{G} \) (output characteristic) measured in darkness of the FET characteristics of pentacene/Hex-4-TFPTA device. In output characteristics, we exclusively detected p-channel activity. Therefore, holes are the majority charge carriers in the conducting channel.

Figure 43: Output characteristic of pentacene/Hex-4-TFPTA FET with light irradiation and in dark.

Figure 44: Energy diagram of PEN and Hex-4-TFPTA.
In pentacene/Hex-4-TFPTA FET devices, besides the singlet fission process, there is the fast diffusion of a singlet exciton to the radical ion pair generated by the ground-state charge-transfer interaction in the Hex-4-TFPTA film, resulting the dissociation to free electron and hole later. The triplet exciton formed via singlet fission may interact with charge carriers and recombination due to its long lifetime. Instead of dissociation like in case of PEN/C₆₀, the triplet excitons in this device will decrease the current, because the triplet energy is comparable to the charge-transfer energy as shown in Figure 44. Hence, the small external MF increases the triplet exciton density, causing decrease in photocurrent and positive MR. Then MR value decrease due to decrease in the singlet fission rate when MF continuing increase as observed in Figure 45.

Besides, with the overlaying Hex-4-TFPTA layer, the photo induced MR sign of pentacene single layer FET turn from negative non-Lorentzian line shape as reported in ref. 24 into positive MR value. The observed MR curves do not follow the Lorentzian or non-Lorentzian line shape but they show as the sum of positive low field effect and negative high field effect or as the magnetic field dependence of singlet fission effect (Figure 45) [84,86]. Besides, the larger the applied gate voltage is, the higher charge is accumulated at the interface, which reduces the inject current and improves the photo induced MR signal. Thus, this positive MR is related to the charge-transfer of the formation excitons at interface between pentacene and Hex-4-TFPTA.

![Figure 45: OMAR of (a) Hex-4-TFPTA/pentacene FET and (b) pentacene\Hex-4-TFPTA FET.](image)

By comparing the pentacene/Hex-4-TFPTA and pentacene/C₆₀ bilayer FET under light irradiation, I demonstrate the opposite of photo induced MR sign between these devices. Multi-mechanism is thought to happen and contribute to the overall MFE, which can be explained
based on the singlet fission effect on the pentacene layer in PEN/C₆₀ device or charge separation at the interface and triplet-charge interaction in pentacene/Hex-4-TFPTA device. However, further study is required to elucidate the mechanism.

**Magnetic Field on Alpha Sexithiophene FET**

The α-6T is complicated molecule, which show many extraordinary behaviors such as the sign change by changing the film thickness, temperature or current density [44]. In the α-6T FET device therefore also demonstrate the strange photo-induced MR curve. It seems that there are two components with opposite MR sign (Figure 46). Both two effect increase at larger positive voltage applied to gate electrode, in which the photo-induced current is dominant. Besides, the positive MR effect can be enhanced when Hex-4-TFPTA or C₆₀ is deposited on top of the α-6T film (Figure 47). Therefore, the positive MR may derive from the charge transfer at the interface. The negative value is under investigation and the dependence on applied gate voltage is also unclear.

![Graph showing MR vs Magnetic Field for different gate voltages](image)

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