ELECTRICAL BISTABILITY IN ORGANIC SEMICONDUCTORS AND SPIN INJECTION USING ORGANIC MAGNETIC SEMICONDUCTOR

DISSERTATION

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By

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Abstract

Organic semiconductors have attracted much attention for their electronic and magnetic properties. They have served as a electronic functional part in light-emitting diodes and photovoltaic cells, as well as the bistable memory devices. In addition, the emergent organic-based magnetic semiconductor makes itself an alternative candidate for spintronic applications.

This thesis is composed of two parts: organic bistable device and organic spin valve. In the first part, I will discuss a pentacene-based bistable memory device using Fe as the top electrode and compare it to the Al/pentacene/Al devices. The device displays stable switching from the low-current OFF state to the high-current ON state and long retention time. Our results suggest that Fe has the advantage over Al as the top electrode because it lowers the switching threshold voltage. The device is promising as a Write-Once Read-Many (WORM) memory. I will also discuss a study of the electrical bistability and bias-controlled spin valve effect in an organic device using rubrene (5,6,11,12-tetraphenylnaphacene) as an organic semiconductor channel. The half-metallic La_{0.7}Sr_{0.3}MnO_3 (LSMO) and Fe are used as the two ferromagnetic electrodes. The device displays reproducible switching between a low-impedance (ON) state and a high-impedance (OFF) state by applying different polarities of high biases. In the ON state, the device shows a spin valve effect with magneto-resistance values up to 3.75%. The observed spin valve effect disappears when the device recovers to the initial OFF state.

In the second part, I will focus on the spin injection using organic-based magnetic semiconductor V[TCNE]_x (x~ 2, TCNE: tetracyanoethylene). I will show the demonstration spin injection/detection in an all-organic-based magnetic tunnel junction using two organic-
based $V[TCNE]_x$ magnets as the magnetic contacts and organic semiconductor rubrene ($C_{42}H_{28}$) as the spacer. For the $V[TCNE]_x$ film growth, we exploited two different growth techniques, chemical vapor deposition and molecular layer deposition, which result in different coercivities of $V[TCNE]_x$ films. The spin valve devices show negative magnetoresistance (MR), the sign of which does not change with temperature and bias. We propose that the unusual negative MR originates from the different spin polarizations of the molecular energy levels of $V[TCNE]_x$. Our results show the significance of bias induced energy level shift in organic spintronic devices due to relatively narrow spin polarized bandwidths. I will also discuss the experimental results of room-temperature spin injection using $V[TCNE]_x$ as well as the effect of the organic spacer on the device performance.
To my parents.
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5.1 Advancement of the solar cell efficiency. 

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Chapter 1
INTRODUCTION

1.1 Organic Semiconductor

1.1.1 History Background

The research of organic semiconductors can be traced back to the first studies of the photoconductivity of anthracene in the early 20th century,\textsuperscript{27,28} followed by the electroluminescence research in the 1960s.\textsuperscript{29,30} The successful synthesis and doping of conjugated polymer in the 1970s which won the Nobel Prize in Chemistry in 2000\textsuperscript{31–33} attracted a lot of attentions. However, organic semiconductor devices did not catch researchers’ eyes until the report of an two-layer organic photovoltaic cell,\textsuperscript{34} organic thin film transistor using conjugated polymers,\textsuperscript{35} high-performance electroluminescence from diodes from organic small molecular films as well as conjugated polymers.\textsuperscript{36–39} Afterwards, huge efforts have been put into this field from both the academia and the industry. Particularly, organic light-emitting diodes (OLEDs) have made great advancement and is the most successful commercial device. Organic photovoltaic (OPV) is also developing rapidly in response to the high energy demand.

1.1.2 Materials

Organic semiconductors can be divided into two classes: small molecular materials and polymers. The bonds between neighboring carbon atoms are covalent bonds. Carbon atoms can form three hybrid orbitals $sp$, $sp^2$, and $sp^3$ by the superposition of $s$ and $p$ orbitals.\textsuperscript{1}
Figure 1.1: The geometry of the $sp^2$ and $sp^3$ orbital structure.¹

Figure 1.2: Representations of ethylene: (a) ball and stick model; (b) chemical structure; (c) orbital diagram.¹

Figure 1.1 shows the schematic illustration of the $sp^2$ and $sp^3$ orbital structure.

There are two important types of carbon-carbon bonds: $\sigma$ bond and $\pi$ bond. The $\sigma$ bond is formed by the hybridized $sp^2$ orbitals. The $\pi$ bond is formed by sharing of the remaining unhybridized $p_z$ orbitals. Single bond among $sp^2$ hybridized molecules are formed using $\sigma$ orbitals, double bonds are typically a product of one $\sigma$ and one $\pi$ bond.¹ Take ethylene as an example (Figure 1.2). It has two $sp^2$ bonded carbon atoms.

The alternating single and double bonds lead to the delocalization of $\pi$ electrons. The energy levels associated with the delocalization are molecular orbitals. Similar with the valence and conduction bands in the inorganic semiconductors, organic semiconductors
have the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

1.1.3 Charge Carrier Transport

There are two charge carrier transport mechanisms in organic semiconductors: band or hopping transport. Band transport is typically observed in highly purified molecular crystals at not too high temperatures and the bandwidth is small as compared to inorganic semiconductors due to weak electronic delocalization. At room temperature the mobilities of molecular crystals reach the range 1 to 10 cm$^2$/Vs. The temperature dependence follows a power law behavior upon going to lower temperature as

\[ \mu = A T^{-n} \]

where $A$ and $n$ are constants.
\[ \mu \propto T^{-n}(n = 1\ldots3). \quad (1.1) \]

Hopping transport dominates in the amorphous organic solid with much lower mobility values. The mobility follows as an activated behavior as \(^2\)

\[ \mu(E, T) \propto \exp\left(-\frac{E_a}{kT}\right) \cdot \exp\left(\frac{\beta \sqrt{E}}{kT}\right). \quad (1.2) \]

1.1.4 Charge Injection into Organic Semiconductor

Charge injection into inorganic semiconductors has been studied extensively, which is the foundation of the information technology industry. Recently, organic semiconductors have attracted much attention due to their potential of low cost and easy fabrication. Especially organic light emitting diodes (OLEDs) have been applied in commercialized flat screen displays. the contact between metal and organic semiconductor has been a hot research area within the organic electronics community.

There are five basic transport process for metal-semiconductor contact. They are (1) emission of electrons from the semiconductor over the potential barrier into the metal, (2) quantum-mechanical tunnelling of electrons through the barrier, (3) recombination in the space-charge region, (4) diffusion of electrons in the depletion region, and (5) holes injected from the metal that diffuse into the semiconductor.41

The organic semiconductor community has been using theory models developed for conventional semiconductors to explain the charge transport in metal-organic contact. However, there is one difficulty in extending from crystalline to amorphous molecular semiconductors because the charge transport in organic semiconductor is no longer by free propagation in extended states, but rather by hopping in a manifold of localized states.3

Figure 1.5 shows a simplified energy level diagram of a single layer organic device. The energy barriers that determine hole and electron injection are \( \varphi_h = I - \Phi_{anode} \) and \( \varphi_e = \Phi_{cathode} - A \), where \( \Phi \) is the work function of the anode/cathode, I is the ionization energy and A is the electron affinity.
Depending on the magnitude of the barrier height $\Delta$ a measured current can either be injection limited or transport limited, i.e., space charge limited. One requirement for space charge limited current is that one of the electrodes has to be Ohmic and it must be able to supply more charge carriers per unit time than the sample can transport.\textsuperscript{42} This requires the injection barrier to be small enough to guarantee efficient injection without the assistance of an external electric field. The space charge limited (SCL) current is the maximum current a sample can sustain at a given electric field unless the exit contact is able to inject an amount of opposite charge carriers sufficient to compensate for the internal space charge.\textsuperscript{42} For a trap-free case, the SCL current is given by the Mott-Gurney law:\textsuperscript{3}

\[ J_{\text{SCL}} = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{E^2}{L} \]

where $L$ is the sample thickness. Generally, the SCL current follows the form $J_{\text{SCL}} \propto E^{l+1}/L^l$, while $l > 1$ in the presence of an exponential distribution of traps. However, in practice the field dependence of the current is often insufficient to distinguish trap-limited SCL conduction from injection-limited conduction. In that case the dependence on the sample thickness differentiates them. Injection-limited current should not depend on sample thickness while SCL currents do.\textsuperscript{42}
Thermionic-Emission

Thermionic emission describes the charge injection by electrons with energy sufficient to overcome the potential barrier between the metal and the semiconductor. The theory is developed by Bethe under the assumption that (1) the barrier height $q\phi_B$ is much larger than $kT$, (2) thermal equilibrium is established at the plane that determines emission, and (3) the existence of a net current flow does not affect this equilibrium so that one can superimpose two current fluxes — one form metal to semiconductor, the other from semiconductor to metal, each with a different quasi Fermi level. The thermionic-emission current follows:

$$J_{s\rightarrow m} = \frac{4\pi qm^*k^2}{\hbar^3} T^2 \exp\left(-\frac{e\phi_B}{kT}\right) \exp\left(\frac{eV}{kT}\right).$$

Considering Schottky effect (image force lowering) and the condition that the current should be zero in the absence of an applied voltage, this can be rewritten as:

$$J = \frac{4\pi qm^*k^2}{\hbar^3} T^2 \exp\left(-\frac{e\phi_B}{kt}\right) \exp\left(\frac{e^3E}{4\pi\epsilon\epsilon_0k^2T^2}\right)^{1/2} \left[\exp\left(\frac{eV}{kT}\right) - 1\right]$$

Obviously, the thermionic emission current is strongly temperature dependent.

Field-Emission

Field Emission is usually referred to tunneling. One of the mostly cited model is the FN model proposed by R. H. Fowler and L. Nordheim. The FN model considered tunneling of electrons from the metal through a triangular barrier into unbound continuum states and the current follows:

$$J(E) = BE^2 \exp\left[-\frac{4(2m^*)^{1/2}\Delta^{3/2}}{3\hbar eE}\right]$$

where $\Delta$ is the barrier height. The signature of tunneling is its independence of temperature.

Real Devices Transport

Charge injection has been widely studied in organic light emitting diodes (OLEDs). As Davids et al. pointed, charge injection into the organic material can occur by thermionic emission and by tunneling. For Shottky energy barriers less than about 0.3-0.4 eV, the
current low is space charge limited and the electric field in the structure is highly nonuniform. For larger energy barriers the current is injection limited. In the injection limited regime, the net injected charge density is relatively small, the electric field in the structure is nearly uniform, and space charge effects are not important. At smaller bias in the injected limited regime, thermionic emission is the dominant injection mechanism and at higher bias the injection is dominated by tunneling.\textsuperscript{36}

1.1.5 Devices

Figure 1.6 shows three organic semiconductor devices: organic light-emitting diode (OLED), organic photovoltaic (OPV) cell and organic field-effect transistor (OFET). For the OLED, HTL stands for hole transport layer and ETL for electron transport layer. EML is the emission layer. Here, Alq\textsubscript{3} and TPD [N,N’-diphenyl-N,N’- bis(3-methylphenyl)-1,1’-diphenyl-4,4’-diamine] act as the ETL/EML and HTL, respectively. For the case of polymer light-emitting diodes (PLED), conductive polymer (PEDOT:PSS) and luminescent polymers PPV are used.\textsuperscript{2}

In order to increase the interface area between the electron transport material and the hole transport material, the so-called bulk-heterojunction structure is employed in the organic photovoltaic cell. The heterojunction consists of a mixture of soluble PPV (or P3AT) and fullerene derivatives. Small molecules like CuPc and C\textsubscript{60} can also be used.\textsuperscript{2}

Organic field-effect transistors use organic semiconductors as the channel materials. Here in the figure, small molecule pentacene is used as a p-channel while P3AT can also be used. Fullerene C\textsubscript{60} can be employed in n-channel transistors.\textsuperscript{2}

1.2 Organic-based Magnet

Experimental evidence of bulk ferromagnetic behavior in molecular-species-based compounds has been limited to the electron-transfer salts comprised of decamethylmetalallocenes and tetracyanoethylene (TCNE) and/or 7,7,8,8-tetracyano-p-quinodimethane (TCNQ), and \(\beta\)-p-NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}NIT\textsuperscript{5}. Bulk ferromagnetic behavior was first observed below the critical tem-
Figure 1.6: Typical organic semiconductor devices: (a) Organic light-emitting diodes (OLED). (b) Organic photovoltaic (OPV) cell. (c) Organic field-effect transistor (OFET).
temperature $T_c$ of 4.8 K for [Fe-(C$_5$Me$_5$)$_2$]$^{•+}$[TCNE]$^{•−}$ (Me = methyl)$^5$. The first reported organic magnet is [Mn(C$_5$Me$_5$)$_2$]$^{•+}$[TCNE]$^{•−}$ with a magnetic ordering temperature $T_c$ of 8.8 K.$^4$

V[TCNE]$_x$ is the first reported room-temperature molecule-based magnet with magnetic ordering temperature $T_C \sim 400$ K.$^6$ Originally, this material was synthesized by adding V(C$_6$H$_6$)$_2$ to an excess of TCNE in dichloromethane at room temperature, which results in the precipitation of a black amorphous solid. The empirical composition of this extremely air-sensitive material is V(TCNE)$_x$·yCH$_2$Cl$_2$.$^6$ The magnetic hysteresis loop is shown in Figure 1.10. The magnetic order originates from the antiferromagnetic coupling between the V$^{2+}$ ion’s three unpaired electrons in 3$d(t_{2g})$ orbitals with a total spin $S = 3/2$ and the [TCNE]$^{−}$ anion’s unpaired electrons in $\pi^*$ orbital with $s = 1/2$.$^{47}$ Stoichiometry shows that there is approximately one V$^{2+}$ ion on average for two [TCNE]$^{−}$ anions, leading to a net spin of 1/2 for the repeat unit (see Figure 4.19). This high-$T_c$ magnetic materials can be prepared as powder in dichloromethane (see Figure 1.8),$^6$ or grown as a thin film (see Figure 1.9) by low-temperature ($\sim 40$ °C) chemical vapor deposition (CVD).$^7$ Extended x-ray absorption fine structure (EXAFS) analysis showed that each vanadium ion is coordinated by 6 nitrogen atoms at a room-temperature average distance of 2.084(5) Å, suggesting strong binding between V and TCNE.$^{48}$ Recently, a molecular layer deposition (MLD) method has been developed for V[TCNE]$_x$ films.$^{49}$ MLD is able to precisely control the thickness of the film within a mono-layer by exposing the substrate alternatively and sequentially
to different precursors.\textsuperscript{49} V[TCNE]\textsubscript{x} has a unique half-semiconductor electronic structure with fully spin-polarized valence and conduction bands.\textsuperscript{8,47} Because of the on-site Coulomb repulsion $U_c$, the $\pi^*$ level of $[\text{TCNE}]^-$ is split into two sublevels, occupied $\pi^*$ and unoccupied $\pi^* + U_c$ with opposite spin polarizations. It was shown that the energy split between the $\pi^*$ and the $\pi^* + U_c$ levels is approximately 2 eV.\textsuperscript{50} Results of photoelectron spectroscopy (PES) and resonant photoemission (RPE) studies suggested that the occupied $\pi^*$ level lies about 1.5 eV below the V(3d) state, while the unoccupied $\pi^* + U_c$ level is 0.5 eV higher than V(3d) state (see Figure 1.12).\textsuperscript{51} An activation energy of 0.5 eV is determined from the temperature dependence of the conductivity for CVD-prepared thin film, coinciding with the energy difference between the 3d($t_{2g}$) and $\pi^* + U_c$ levels.\textsuperscript{47} The activation energy of MLD films is approximately 0.4 eV, slightly lower than that of CVD film.\textsuperscript{49}
Figure 1.9: Photograph of a thin coating of the V[TCNE]$_x$ magnet (black) on Teflon tape (white), being attracted to a Co$_5$Sm magnet at room temperature.$^4$

Figure 1.10: Hysteresis M(H) of V(TCNE)$_x$$^y$(CH$_2$Cl$_2$) at room temperature.$^6$
Figure 1.11: a) The saturation magnetization. b) Remanent magnetization of V[TCNE]$_x$ film scratched from the glass substrate [cooled to 2 K in a 500 Oe applied field, then the applied magnetic field was reduced to zero and $M(T)$ was monitored on warming up to 400 K]. c) Zero field cooled magnetization of another V[TCNE]$_x$ sample measured on warming from 4 to 400 K at 3 Oe applied magnetic field. d) Magnetization of measured at 3 Oe field on cooling after 20 min and annealing at 400 K.

Figure 1.12: Energy levels of V[TCNE]$_x$. 

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Figure 1.12: Energy levels of V[TCNE]$_x$. 

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12
1.3 Spintronics

1.3.1 Spin-based Electronics

Conventional electronics makes use of the electron charges to process and transfer information. A new paradigm of electronics called spintronics or spin-based electronics manipulates the spin degree of freedom of the electron, using the spin to carry information. Each electron has a spin state, either ‘spin up’ or ‘spin down’, which could correspond to the ‘1’ and ‘0’ bits in the binary system. The principle spintronics device is the spin valve which has a three-layer sandwich structure: a non-magnetic layer embedded between two ferromagnetic layers (see Figure 1.13). Depending on the alignment of the magnetic moments of the two ferromagnetic layers, the structure shows high resistance or low resistance.

The most successful application of spintronics device is the read head of the hard disk drive. Figure 1.14 shows the schematic view of the structure of a read head. Usually the magnetic moment of one of the ferromagnet layer is pinned through antiferromagnetic coupling, leaving the magnetic moment of the other layer free. As the read head move over the surface of the hard disk, the moment of the free layer will change depending on the local field, leading to the variation of the current through the read head. Another promising application is the Magnetic Random Access Memory (MRAM). Figure 1.15 shows the element array of the MRAM. Every element bit consists of a spin valve structure.
Compared to conventional memory, MRAM has the advantage that the information will not be lost after the power is off. This property will substantially reduce the boot up time of the computer. Other techniques including spin logic circuits and spin quantum computing are also under development.

### 1.3.2 Tunneling Magnetoresistance and Giant Magnetoresistance

Magnetoresistance was first discovered in 1857 by W. Thomson. He found that the effect of longitudinal and transverse magnetic field on the resistance of magnetic metal (iron and nickel) were different. This phenomenon is lately known as the anisotropic magnetoresistance (AMR). Grnberg and Fert discovered the giant magnetoresistance (GMR) in Fe/Cr/Fe structure and Fe/Cr superlattice respectively, for which they both won the 2007 Nobel Prize for Physics.

Besides AMR and GMR, there is another magnetoresistance effect named tunneling magnetoresistance (TMR). Because of the commercial applications in the data storage industry, TMR has been an interesting field for researchers.

The typical magnetic tunnel junction structure contains two ferromagnetic electrodes.
Between the two electrodes is a thin layer of insulator. The resistance when the magnetizations of the two ferromagnetic electrodes align in parallel usually will be smaller than the resistance corresponding to the anti-parallel case.

In 1970, Meservey and Tedrow found the quasiparticle energy states in superconducting aluminum films were split by magnetic field by measuring the tunneling conductance of Al/Al₂O₃/Ag junctions. The magnitude of the splitting was 2µH. After that, they did tunneling measurement on junctions between very thin superconducting aluminum films and ferromagnetic nickel films in a high magnetic field. The results showed that the tunneling current was spin-dependent.

The discovery of spin-polarized tunneling is the foundation of the TMR research. Julliere reported the first magnetoresistance measurement on a Fe-Ge-Co junction. The maximum conductance variation ΔG/G is about 14%.

Julliere’s model is widely used to explain the mechanism of tunneling magnetoresistance. This model is based upon the assumption that the tunneling current is proportional to the number of tunneling electrons. More general, people use the densities of states (DOS) instead of the number of tunneling electrons. Hence, the current is proportional to the product of the DOS in the two electrodes.

If one uses ↑ and ↓ to denote the parallel and antiparallel case of electrons’ spin direction
Figure 1.16: Experimental plots for several values of magnetic field of superconducting conductance divided by the normal-state conductance\textsuperscript{10}.

Figure 1.17: The experimental curve 8 (above) has been resolved into two identical trial curves (dashed lines) of the DOS for spin-up spin-down particles\textsuperscript{10}.
Figure 1.18: (a) Schematic representation of a TMR device, consisting of two FM materials (dark grey) separated by a tunnel barrier (light grey). The magnetization can be parallel (P) or antiparallel (AP), denoted by the arrows. Spin subbands of the FM materials are given for the P magnetization (b) and AP magnetization (c). The dashed (solid) arrow represents low (high) spin current.\textsuperscript{11}
with respect to the magnetization direction of the two electrodes, the densities of states of electrons can be expressed as \( n_{1,2}^\uparrow \) and \( n_{1,2}^\downarrow \), in which subscripts 1 and 2 represent the two electrodes. Since the two spin-polarized tunneling channels are independent with each other, one can regard them as parallel. The relation between the current and the DOS is given as:

\[
I^P = I^{\uparrow\uparrow} + I^{\downarrow\downarrow} \propto n_{1,2}^\uparrow n_{1,2}^\uparrow + n_{1,2}^\downarrow n_{1,2}^\downarrow
\]

\[
I^{AP} = I^{\uparrow\downarrow} + I^{\downarrow\uparrow} \propto n_{1,2}^\uparrow n_{1,2}^\downarrow + n_{1,2}^\downarrow n_{1,2}^\uparrow
\]

where \( I^{\uparrow\uparrow} \) is the majority electron current tunneling from the first to second electrode and \( I^{\downarrow\downarrow} \) is the minority electron current tunneling from the first to second electrode. \( I^{\uparrow\downarrow} \) is the current produced by majority electrons from the first electrode tunneling into the second electrode as minority electrons and vice versa for \( I^{\downarrow\uparrow} \). The polarization is defined as:

\[
P_{1,2} = \frac{n_{1,2}^\uparrow - n_{1,2}^\downarrow}{n_{1,2}^\uparrow + n_{1,2}^\downarrow}.
\]

Tunneling magnetoresistance (TMR) is often expressed as

\[
TMR = \frac{R_{AP} - R_P}{R_P} = \frac{2P_1P_2}{1 - P_1P_2}.
\]

Some paper also use another definition named tunnel junction magnetoresistance (JMR):

\[
JMR = \frac{R_{AP} - R_P}{R_{AP}} = \frac{2P_1P_2}{1 + P_1P_2}.
\]

Giant magnetoresistance effect was first discovered in 1988 by Grünberg and Fert. Grünberg et al. investigated Fe-Cr-Fe structure and found that the resistance of the structure when the magnetization of the two Fe layer was antiparallel was higher than that when the two Fe layer had parallel magnetization. Fert et al. studied the Fe/Cr superlattice and found that the resistance of the superlattice at zero magnetic field was higher than that in a magnetic field. Grünberg and Fert also won the 2007 Nobel Prized for the discovery of the giant magnetoresistance.

Mott’s model can be used to understand GMR. First, the electrical conductivity of
metal can be described as two independent conducting channels, corresponding to the spin-up and spin-down electrons. The probability of spin-flip scattering processes in metal is normally small as compared to the probability of the scattering processes in which the spin is conserved. As a result, the two spin channel can be regarded as parallel with respect to the conduction. Second, in ferromagnetic metals the scattering rate of the spin-up and spin-down electrons are quite different. According to Mott, the electric current is primarily carried by electrons from the valence $sp$ bands due to their low effective mass and high mobility. The $d$ band plays an important role in providing final states for the scattering of the $sp$ electrons. In ferromagnets the $d$ bands are exchange-split, so that the density of states is not the same for the spin-up and spin-down electrons at the Fermi energy. The probability of scattering into these states is proportional to their density, so that the scattering rates are spin-dependent.

The simple magnetic structure can be modeled by a resistor network (Figure 1.19) in which the independent spin-up and spin-down electron current channels are represented by two parallel circuits and the resistance of the different layers represented by resistors:

$$R_P = \frac{R^\uparrow R^\downarrow}{R^\uparrow + R^\downarrow}$$

$$R_{AP} = \frac{R^\uparrow + R^\downarrow}{2}$$
The structure difference is the layer between the two ferromagnetic electrodes. Magnetic tunnel junction contains a thin insulator layer while GMR device applies a non-ferromagnetic metal layer. The essential difference between TMR and GMR effect is that the former is based on spin-polarized tunneling while the latter is based on spin-dependent scattering. Therefore, TMR is pure interface effect and does not require spin transport in the non-magnetic layer\textsuperscript{11,61}.

1.3.3 Conductivity Mismatch

One fundamental problem for spin injection from a metal into semiconductor is the conductivity mismatch. Usually the conductivity of the semiconductor is much lower than that
of the metal. If the resistance of the whole device is dominated by the resistance of the semiconductor spacer, the overall resistance change is negligible\textsuperscript{11}.

Two possible methods are able to solve this problem. One is to use a fully spin-polarized ferromagnetic material such as a half-metal. In the classical ferromagnetic materials such as Fe and Co, the conduction electrons mainly have 4s character, whereas the polarized electrons are in the more localized 3d-band. This electronic structure leads to a spin polarization at the Fermi level far below 100%. In a half-metal, only one spin subband is occupied at the Fermi level and the spin polarization P therefore approaches 100% at low temperatures\textsuperscript{11}.

Another way is the introduction of a large spin-dependent resistance, such as a tunnel barrier in between the FM metal contact and the semiconductor spacer. This spin-dependent resistance gives a larger change in resistance between the parallel and anti-parallel configuration\textsuperscript{11}.

1.3.4 Spin Relaxation

The spin relaxation time $\tau_s$ is given by\textsuperscript{11}:

$$\frac{1}{\tau_s} = \frac{1}{\tau_{\uparrow\downarrow}} + \frac{1}{\tau_{\downarrow\uparrow}},$$

where $\tau_{\uparrow\downarrow}$ indicates the average time for an up-spin to flip to a down-spin, the $\tau_{\downarrow\uparrow}$ for the reverse process.

Two classes of spin relaxation can be distinguished\textsuperscript{11}. One is the decay of a net spin component along the axis of spin quantization, which is usually as the z-axis. The z-component of the total spin, $S_z$, decays exponentially to the equilibrium due to individual spin flips on a timescale $T_1$. This $T_1$ is equal to spin relaxation time $\tau_s$. As this process requires energy exchange with the environment, it is a rather slow process. The second process does not require energy exchange and affects the spin component perpendicular to the quantization axis $S_\perp$. This process affects the quantum-mechanical phase of individual spins and leads to loss of coherence on a timescale $T_2$. For different spins within an ensemble the phase are in general affected unequally, which results in the spins getting out of phase,
with a timescale related to this process of ensemble dephasing is often denoted as $T_2^*$. In inorganic materials, the dominant spin relaxation mechanisms are spin-orbit coupling and hyperfine interaction, which both turn out to be weak in organic materials\textsuperscript{11}.

**Spin-orbit coupling**

Spin-orbit coupling is a relativistic effect, describing the interaction between the electron’s spin and its orbital motion around an atomic nucleus\textsuperscript{11}. Generally, spin-orbit coupling occurs whenever a particle with non-zero spin moves in a region with a finite electric field. In the rest frame of a particle moving at a relativistic velocity, a static electric field Lorentz transforms in a field with a finite magnetic component\textsuperscript{11}. Thus, the spin degree of freedom interacts with an electric field via spin-orbit coupling. Spin-orbit coupling increases as the atomic number $Z$ gets larger. Since organic materials are mostly consist of low-$Z$ elements such as carbon and hydrogen, spin-orbit coupling is usually small in organic materials. The spin-orbit-coupling-related relaxation mechanisms directly affect $T_1$, and indirectly $T_2$\textsuperscript{11}.

**Hyperfine interaction**

The hyperfine interaction originates from the interaction of the electron spin with nuclear spins of the host material. The coupling Hamiltonian is given by\textsuperscript{11}:

$$H_{hyp} = \sum_i N A_i \vec{I}_i \cdot \vec{S},$$

where $\vec{I}_i$ and $\vec{S}$ are the spin operator for nucleus $i$ and the electron spin, respectively, and $A_i$ the coupling strength between them. The nuclear spins affect the spin relaxation time $T_1$ by so-called electron-nuclear flip-flops and fluctuating nuclear spins also result in dephasing, thus affecting $T_2$\textsuperscript{11}.

The nuclear spins in organic materials are mainly originating from the isotopes $^1H(I = 1/2)$, $^{13}C(I = 1/2)$, and $^{14}N(I = 2)$\textsuperscript{11}. Despite the presence of nuclear spins, the hyperfine interaction in organic materials is usually weak. The reason is that for organic conductors often use is made of $\pi$-conjugated molecules with delocalized states that have practically no overlap with the C or H atoms, since the wavefunctions of the $\pi$-electrons mainly consist of
$p_Z$ orbitals, whose nodal plane coincides with the molecular plane\cite{11}.

1.3.5 Why Organic Spintronics?

Recently organic semiconductors have attracted a lot of attentions. The molecular structure can be tuned by chemical synthesis to have different properties. With modern chemistry techniques, millions of organic materials can be synthesized with various properties to meet different demands. Organic materials are also able to be deposited upon flexible substrates to make flexible devices. What’s more, organic-based devices can be fabricated by roll-to-roll process at a fraction of the cost of traditional semiconductor manufacturing cost.

Research efforts in the field of spintronics are being evolved from metal-based materials and the semiconductor to the organic materials. In order to process information carried by electron spins, long spin lifetime is preferred. Due to low spin-orbit coupling and weak hyperfine interaction, spin lifetime in organic semiconductor is long, which makes organic semiconductors the potential next-generation materials for spintronics research. With the use of organic-based magnet as the spin injector/detector and organic semiconductor as the spin transport layer, the conductivity mismatch between ferromagnetic metals and semiconductors can be avoided, leading to better spin injection/detection. Combined with the advantages such low cost and flexibility, organic spintronics devices have huge potentials to play an important role.
2.1 Thin Film Deposition

The fabrication of organic semiconductor devices requires the deposition of thin films. There are several techniques involved in the thin film deposition process.

2.1.1 Thermal Evaporation

Thermal evaporation is widely used in thin film deposition. The source material is evaporated in vacuum and the vapor particles travel directly to the substrate and condense.\(^{62}\)

Quartz-crystal microbalance using resonant crystalline quartz wafers is used to monitor the thickness of the deposited thin film. The resonant frequency of the quartz wafer \(\nu_r\) depends on the mass of the wafer, and can be crudely modeled as a mass-spring oscillator: \(^{13}\)

\[
\nu_r = \frac{1}{2\pi} \sqrt{\frac{k}{m}}
\]

where \(k\) is the spring constant and \(m\) is the mass. By comparing the loaded \(\nu_r\) with the \(\nu_r\) of a reference crystal located in the instrument’s control unit, the mass of the deposited thin film can be calculated.

The commonly used evaporation source is shown as below:\(^{13}\):

The mean free path characterized the mean distance that a particle travels in a gas before encountering a collision. It can estimated by the following formula:

\[
l = \frac{1}{\sqrt{2\pi a^2 n}}
\]
Figure 2.1: Evaporation sources: (a) twisted-wire coil, (b) dimpled boat, and (c) heat-shielded crucible\textsuperscript{13}. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.1}
\end{figure}
where \( a \) is the diameter of gas molecules and \( n \) is the molecular concentration\(^{13}\). The mean free path at 1 Pa and room temperature is about 1 cm for small molecules. In order to determine whether the deposition process is operating in the high-vacuum regime or the fluid-flow regime, Knedsen number is introduced as: \( Kn = \frac{l}{L} \), where \( L \) is a characteristic dimension in the process, such as the distance between the source and the substrate\(^{13}\). For \( Kn > 1 \), the process is in high vacuum, which is also known as the molecular flow regime, since the molecules flow independently of each other and collide only with the walls\(^{13}\). For \( Kn < 0.01 \), the process is in fluid flow.

### 2.1.2 Chemical Vapor Deposition

In a chemical vapor deposition process, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit\(^{63}\). In terms of operating pressure, the CVD can be divided into low-pressure CVD (LP-CVD) and atmospheric pressure CVD (AP-CVD).

Organic-based magnet \( V[TCNE]_x \) (TCNE: tetracyanoethylene, \( x \sim 2 \)) can be prepared as thin films by CVD process. The chemical reaction is:

\[
V(CO)_6 + 2TCNE \rightarrow V(TCNE)_2 + 6CO \uparrow.
\]

The experimental set up for the CVD deposition is shown in Fig.2.2.

### 2.1.3 Atomic Layer Deposition

Atomic layer deposition (ALD) is a process that a thin film is deposited by exposing the precursors to the growth surface one-at-a-time sequentially and repeatedly. ALD is similar in chemistry to CVD, except that the ALD reaction breaks the CVD reaction into two half-reactions\(^{64}\). The schematic view of this process is shown in Fig.2.3.
Figure 2.2: CVD apparatus for thin-film deposition of $V[TCNE]_x$. The TCNE side of the reactor is heated to 60°C and the $V(CO)_6$ side is cooled to 10°C in a silicon oil bath. The Ar carrier gas is pulled from the controlled atmosphere glove box$^{7,14}$.

Figure 2.3: Schematic representation of ALD process$^{15}$. 
2.2 Electric and Magnetic Transport Measurements

The electric and magnetic transport measurements are performed in the physical property measurement system from Quantum Design which is able to control the temperature and magnetic field in the sample chamber. After the thin film deposition, the device is mounted on the sample puck of PPMS, electrically connected to the pins and the sample puck is then inserted into the sample chamber. While the PPMS controls the temperature and magnetic field, the electric measurements are conducted using Keithley 2400 sourcemeter and Keithley 617 electrometer. The typical wired device on a sample puck is shown in Fig.2.4. The PPMS system is shown in Fig.2.5.
Figure 2.5: Physical property measurement system (PPMS).
Chapter 3

Organic Bistable Devices

3.1 Bistable Devices

Presently, the three leading technologies in memory devices are Dynamic Random Access Memory (DRAM), flash memory, hard disk drive (HDD). Enormous efforts have been put into the research and development of new memory technology which can combine the speed of the DRAM, the nonvolatility of flash memory, and the low cost, data density, and cycling endurance of HDD\textsuperscript{65}.

Bistable devices have two or more conductive states, usually including low-conductance states (OFF states) and high-conductance states (ON states). The transition between these two states are realized by applying different voltages. This property allows the bistable devices to be used in nonvolatile memory device applications, such as flash memory and random access memory\textsuperscript{17}. The switching between different conductive states is either reversible or irreversible, while the former can be used as rewritable memory device and the latter can be utilized as the write-once read-many-times (WORM) device\textsuperscript{21}.

3.2 Device Structures and Theory Models

3.2.1 Triple-Layer Devices

Organic bistable device with triple-layer structure was first reported by Prof. Yang’s group at UCLA\textsuperscript{16,66}. Triple-layer devices usually involve a thin metal nanoparticles layer inside the organic layer. Figure 3.1 shows the typical device structure and current-voltage ($I$-$V$)
In the first voltage scan from 0 V to 5 V, the device shows a very low current in the low-voltage range, indicating the device is in the high-impedance state. At some critical voltage, the current has a sharp increase, showing the transition from the high-impedance state to the low-impedance state. The second scan from 5 V to 0 V is totally different from the first scan in terms of $I-V$ curves and the device shows high current even in the low-voltage range. By simply applying a reverse bias pulse, the device can recover to high impedance state from low impedance state. The transition from the OFF state to the ON state is equivalent to the “writing” process in a digital memory cell, and the reverse bias pulse acts as the “erase” bias.

A theory model has been proposed by Prof. Yang’s group to explain the bistability. Due to slow deposition, the metal nano-clusters are consist of metallic cores and Aluminum oxide coatings. Free electrons can easily tunnel through the thin oxidized layer between nano-clusters. On the energy diagram (Figure 3.2), the nano-clusters are showed as a distribution of many energy wells sandwiched between two organic layers. When the applied bias is high enough, the free electrons tunnel through the barriers, leading to the polarization...
of the Al-nanocluster layer and stored charges on both sides of the middle layer. The stored charges induce changes of the conductance of the adjacent organic layers. As a result, the device undergoes a dramatic change of conductance. If the applied bias is removed, the polarized charges cannot recombine, thus the device remains in the high-conductance state. Only a reverse bias can recover the device.

Another theory model has been proposed by L.D. Bozano and J. C. Scott\textsuperscript{67,68} using the theory developed by Simmons and Verderber for the metal-insulator-metal diodes\textsuperscript{69}. Originally, this theory was used to describe the electroforming process in a gold-SiO interface. The gold atoms were moved from the electrode into the SiO layer and they form an impurity band of charge transport levels, as well as deeper charge-trapping levels\textsuperscript{67}. As charges tunnel into the trapping sites, the built space-charge field opposes the applied field and inhibit the carriers injection and thus the current is reduced. However, there are some difficulties in explaining the organic bistable device. One of the problems is that the pristine state of the formed device in SV model is the ON state, while the transport level and the trapping sites are uncharged. But for organic bistable devices, the initial state right after the device fabrication is the OFF state.
3.2.2 Single-Layer Devices

Single layer devices has a simple device structure of metal-organic-metal. It is first reported by D. Tondelier et al. in 2004\textsuperscript{19}. A single pentacene layer was deposited onto aluminum electrode and covered by another aluminum electrode. Figure 3.3 shows the $I$-$V$ curves for a single layer device as well as a triple layer device\textsuperscript{19}. Both devices showed clear transition from the low-conductance OFF state to the high-conductance ON state. Figure 3.4 and Figure 3.5 show the morphology dependence and the pentacene thickness dependence. The results suggest that the morphology of the pentacene film did not affect the critical voltages while that voltage increases as the pentacene film get thicker.

While no bistable effect was observed for the single layer device without the top electrode mechanically contacted with a thin wire, Tondelier claimed that the the inclusion of metal nanoparticles in the organic layer is the physical mechanism responsible for both the triple-layer and single-layer devices. The bistable effect in the 1L device is attributed to the inclusion of Al nanoparticles in the pentacene during the evaporation of the top electrode and the switching to the ON state is due to field-induced percolation of the nanoparticles, thus forming nano-filamentary metallic pathways through the organic film\textsuperscript{19}.

The filamentary conduction mechanism is supported by the results reported by Cölle et al.\textsuperscript{20} They used IR detection system to study the transition between different states. As Figure 3.6 shows, in the high-conductance state, we can clearly see several hot spots, while in the low-conductance state, some of the spots disappear.

3.3 Experimental

My research project is to study the impact of the electrode metals on the performance of the single layer organic bistable device.

Figure 3.7 shows the schematic view of our device and the chemical structure of pentacene molecule. Both Al and Fe have been used as the electrodes. To fabricate devices, glass substrates were cleaned ultrasonically with the detergent, acetone, and isopropanol for 10 minutes, respectively. Then a UV-Ozone cleaner was used to remove the organic
Figure 3.3: Typical current-voltage curves for the 3L-OBD (solid square); for the 1L-OBD (solid triangle). The data represented by solid circle is for a 1L-OBD without top electrode and mechanically contacted with a thin wire\textsuperscript{19}. Reprinted with permission from Ref.\textsuperscript{19}. Copyright 2004, American Institute of Physics.

Figure 3.4: Current-voltage curves for 1L-OBD with two different deposition rate: 0.07Å·s\textsuperscript{−1} (solid square) and 2.5Å·s\textsuperscript{−1}\textsuperscript{19}. Reprinted with permission from Ref.\textsuperscript{19}. Copyright 2004, American Institute of Physics.
Figure 3.5: Current-voltage curves for 1L-OBD with different pentacene film thickness$^{19}$. Reprinted with permission from Ref. $^{19}$. Copyright 2004, American Institute of Physics.

Figure 3.6: Photographs made by IR detection system when the device is switched from the highest state (a) to a lower state (b), then to a pristine state (c) and subsequently back to the highest state (d) again$^{20}$. Reprinted with permission from Ref. $^{20}$. Copyright 2006, Elsevier.
residues on the substrate. After the cleaning procedure, the glass substrates were transferred to a high vacuum chamber with the pressure under $2 \times 10^6$ Torr. Aluminum was used as the bottom electrode and deposited thermally at a rate of 0.4 Å/s for 80 nm. The cross junction area of 0.2 mm by 0.2 mm was enclosed by 300 nm SiO$_2$ deposited by e-beam. 80 nm of pentacene served as the organic spacer and was thermally deposited with a controlled source temperature (115°C). The thickness of the pentacene film was measured by a quartz crystal monitor and verified by an AFM. Fe was used as the top electrode and deposited by e-beam at a rate of 0.2 Å/s. For the Al/pentacene/Al devices, Al was deposited on top of pentacene at a rate of 0.4Å/s. The electrical measurements were conducted in a Quantum Design PPMS with a programmed Keithley 2400 sourcemeter. The morphology of the pentacene films was measured with a Veeco scanning probe microscope using tapping mode. The AFM images were processed with WSxM software from Nanotec Electronica. The x-ray diffraction experiment was done using a Bruker D8 x-ray diffractometer.

3.4 Result and Discussion

We first carried out the I-V characterization for the Fe electrode devices. Figure 3.8.(a) shows the typical I-V curve of the Al/pentacene/Fe memory devices. The voltage was
scanned from 0 V to 5 V and back to 0 V. Initially, as the scan starts from 0 V, the device stays in the low-current state which is referred to as the OFF state. At a threshold voltage $V_T = 1.4$ V, the current increases abruptly, indicating the device is undergoing a transition to the high-current state which is referred to as the ON state. This process can be regarded as the “write” operation in the digital memories. In the second scan from 5 V to 0 V, the current remains high all the time until the vicinity of 0 V. This hysteresis loop clearly shows the bistable behavior of this memory device. The switching of this pentacene device is irreversible. The device cannot return to the initial OFF state by applying a negative voltage pulse. This property makes it potentially suitable for applications as the write-once ready-many (WORM) memory. A voltage higher than $V_T$ can be used to conduct the “write” operation and a voltage smaller than $V_T$ can be used to read out the information. The device shows robust performance during the 50,000 s retention time test as shown in Figure 3.8.(b).

We also fabricated devices with Al as both of the electrodes with the structure of Al (80 nm)/pentacene (80 nm)/Al (50 nm), of which the I-V characterization is also shown in Figure 3.8.(a). The threshold voltage $V_T$ is about 2.0 V, 0.6 V higher than the device
with Fe top electrode. Lower operational voltage is always preferable in microelectronics industry for less power consumption. Thus, Fe has the advantage over Al in this bistable memory device.

We checked the morphology of two pentacene films deposited upon glass substrate at two different deposition rates, 1.6 nm/min and 6.4 nm/min, as shown in Figure 3.9. The AFM images suggest that the film deposited at 1.6 nm/min is rougher and has larger grain size. In addition, the film deposited slower has one more peak in the XRD, indicating it is better-order than the other film. In order to investigate the impact of morphology on the bistable threshold voltage, two kinds of devices were fabricated using these two growth parameters and I-V characterizations were carried out after the deposition. As shown in Figure 3.9, at about 1.4 V, both of the two devices undergo the transition from the OFF state to the ON state. It is suggested that the morphology does not play an essential role in our experiments.

The temperature dependence behaviors were checked in both of the ON and OFF states, as shown in Figure 3.10. This temperature dependent resistance reflects carrier injection at the metal/organic interface, which introduces strong increase of device resistance as the temperature is lowered\textsuperscript{22}. This effect of carrier injection typically saturates below 100 K\textsuperscript{71}. Further increase of device resistance below 100 K can be contributed to hopping transport in the bulk of pentacene layer. This temperature dependent resistance indicates the device in the initial OFF state is controlled by carrier transport through the bulk of the organic semiconductor layer and free of pinhole channels and/or filamentary conduction channels of metallic inclusions. On the other hand, the device demonstrates a metallic behavior in the ON state, which is possibly attributed to the filamentary conduction. Tondelier et al. reported similar temperature behavior in Al/pentacene/Al devices\textsuperscript{19}.

It has been reported by Yang’s group that a device with the structure of Cu/buffer-layer/organic/Cu could show the nonvolatile memory effect by controlling the copper ion concentration within the organic layer\textsuperscript{72}. Copper get ionized at the anode under positive bias and drift into the organic layer, leading to the formation of a continuous Cu+ distribution and the ON state of the device\textsuperscript{72}.
Figure 3.9: (a) X-ray diffraction patterns of the pentacene films at two different deposition rates. (b) AFM image (10 µm·10 µm) of the pentacene film deposited on glass substrate at 1.6 nm/min. (c) AFM image (10 µm·10 µm) of the pentacene film deposited on glass substrate at 6.4 nm/min. (d) I-V characterization of the bistable memory device with pentacene deposited at 1.6 nm/min. (e) I-V characterization of the bistable memory device with pentacene deposited at 6.4 nm/min. Reprinted with permission from Ref. 21. Copyright 2010, Elsevier.
We suggest that the similar mechanism plays an essential role here in the pentacene device. In the initial OFF state, the conductive channels have not been formed and the device resistance is dominated by the bulk resistance of the pentacene film. As a result, the device shows a thermally activated behavior. When we apply high voltage across the device, Fe atoms migrate into the pentacene layer. The Fe distribution forms conductive channels, leading to the high-current ON state. The metallic temperature dependence in the ON state supports the existence of the Fe conductive channels.

One possible explanation to the difference in the threshold voltages could be the difference in the interface energy barriers. However, we extracted the same value of the activation energy from the temperature dependence behavior for both device configurations. This suggests that the interface does not play a crucial role in determining the threshold voltages. Another possible explanation to our result that Fe devices have lower threshold voltages is the penetration of the Fe atoms. It has been reported that metal atoms can diffuse into organic semiconductors during the deposition. It is possible that in our devices Fe atoms penetrate deeper into the pentacene layer than Al does during the deposition of the top electrode, since Fe atoms are much more massive than Al. As Fe atoms are already
closer to the bottom electrode, it required lower voltage to make Fe atoms to migrate and form conductive channels\textsuperscript{21}. 
4.1 Spin Valve Devices

The present information industry is based on microelectronics technology, which uses the electrical charge property of the electrons to process information. The electrons also have another intrinsic quantum property - 'spin'. Spintronics is the new paradigm of electronics which use electron spin to carry information. Adding the spin degree of freedom to conventional semiconductor charge-based electronics or using the spin degree of freedom alone will lead to the development of new devices with substantially more capability and performance such as increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices.

The principle spintronics device, the spin valve, has a three-layer structure: a non-magnetic

![Figure 4.1: Schematic view of spin valve devices](image)
layer sandwiched between two ferromagnetic layers. The device resistance depends on the magnetization alignment of the two ferromagnetic layers, as shown in Figure 4.1. One of the most widely used applications of spin valves is the read heads for hard drives on every single modern computer. Another application which is called magnetic random access memory (MRAM) is promising to replace the current Dynamic Random Access Memory (DRAM) used in all the computers. The information stored in MRAM will not lose even the power is off, so the MRAM will significantly reduce the computer’s boot up time. Other techniques including spin logic circuits and spin quantum computing are also under development.

4.2 Why Organic Spintronics

Recently organic semiconductors have attracted a lot of attentions. The molecular structure can be tuned by chemical synthesis to have different properties. With modern chemistry techniques, millions of organic materials can be synthesized with various properties to meet different demands. Organic materials are also able to be deposited upon flexible substrates to make flexible devices. What’s more, organic-based devices can be fabricated by roll-to-roll process at a fraction of the cost of traditional semiconductor manufacturing cost.

Research efforts in the field of spintronics are being evolved from metal-based materials and the semiconductor to the organic materials. In order to process information carried by electron spins, long spin lifetime is preferred. Due to low spin-orbit coupling and weak hyperfine interaction, spin lifetime in organic semiconductor is long, which makes organic semiconductors the potential next-generation materials for spintronics research. With the use of organic-based magnet as the spin injector/detector and organic semiconductor as the spin transport layer, the conductivity mismatch between ferromagnetic metals and semiconductors can be avoided, leading to better spin injection/detection. Combined with the advantages such low cost and flexibility, organic spintronics devices have huge potentials to play an important role.
4.3 Organic-based hybrid spin valve

4.3.1 Experimental

Here, we name the device with organic spacer and inorganic (metal or oxides) magnetic contacts as “hybrid spin valve”. Figure 4.2 shows the schematic view of our device structure. We used La_{0.7}Sr_{0.3}MnO_3 (LSMO) and Fe as the ferromagnetic electrodes and rubrene (5,6,11,12-tetraphenylnaphthacene) as the organic semiconductor spacer. The epitaxial 50 nm of LSMO was grown on lattice-matching (001) (LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7} (LSAT) substrate by pulsed laser deposition in Prof. Eom’s lab at University of Wisconsin-Madison. Three unit cells of LaAlO_3 (LAO) were deposited on top of LSMO to provide efficient spin injection into organic semiconductor spacer, by protecting the surface polarization of the LSMO as well as acting as a tunnel barrier. The cross junction area of 0.2 mm by 0.2 mm was enclosed by 300 nm SiO_2 deposited by e-beam evaporation (Figure 4.3). 50 nm of sublimed rubrene (Aldrich) was used as an organic semiconductor channel and thermally deposited with controlled source temperature (105 °C). The thickness of the rubrene layer was measured by a quartz crystal monitor and verified with a profilometer. A rigorous inspection of the surface morphology over wide range of area via AFM showed the typical rms roughness of our thermally deposited rubrene layer was 1 nm ± 0.3 nm and maximum peak to peak distances were 7 nm ± 3 nm. On top of the rubrene layer, 30 nm of Fe was
used as a second ferromagnetic layer which was deposited by e-beam evaporation. The magnetotransport measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with an external Keithley 2400 sourcemeter running home-made LabView programs. Figure 4.5 displays the magnetic hysteresis loops of a 50 nm LSMO film on LSAT (001) substrate and a 30 nm Fe film, respectively.\textsuperscript{22} It is clearly showed that Fe has a larger coercive field than LSMO.

### 4.3.2 Results and Discussions

The relationship between the temperature and the device resistance is a good indicator revealing the charge-transport properties of the device. The temperature dependence of the resistance of the device LSMO/LAO/rubrene (50 nm)/Fe in the initial OFF state is
Figure 4.5: Magnetic hysteresis loops of LSMO (50 nm) on LSAT (001) substrate and Fe (30 nm) on glass substrate\textsuperscript{22}. Reprinted with permission from Ref.\textsuperscript{22}. Copyright 2010, Elsevier.

Figure 4.6: Temperature dependent resistance (OFF state) of the LSMO (50 nm)/ LAO/rubrene (50 nm)/Fe (30 nm) junction\textsuperscript{22}. Reprinted with permission from Ref.\textsuperscript{22}. Copyright 2010, Elsevier.
presented in Figure 4.6. This temperature dependent resistance reflects carrier injection at the metal/organic interface, which introduces strong increase of device resistance as the temperature is lowered. This effect of carrier injection typically saturates below 100 K\(^{71}\). Further increase of device resistance below 100 K can be attributed to hopping transport in the bulk of rubrene layer. This temperature dependent resistance indicates the device in the initial OFF state is controlled by carrier transport through the bulk of the organic semiconductor layer and free of pinhole channels and/or filamentary conduction channels of metallic inclusions.

An interesting result from this device is the electrical bistability. The current versus voltage curves were recorded in a series of bias scans at 10 K, using a two-probe configuration. Figure 4.7 displays typical I-V curves of our device, which show the electrical bistability effect. In the first sweep, the device shows very low current in the high negative bias to low positive bias range, indicating it stays in the OFF state. However, at a threshold bias, about 4.5 V, the current increases sharply, showing the device has undergone a transition from the OFF state to the ON state. This transition can be regarded as the “write” operation in the digital memory. Furthermore, the device is able to remain in the ON state without any supplied power, which is an essential characteristic of the non-volatile memory. In the second bias sweep, started at +5 V, the current remains at high level. The I-V curve is completely different from the first scan, indicating the device remains in the ON state. The device will not recover to the initial OFF state unless a high negative bias (-5 V) is applied, and this process is analogous to the “erase” operation in the digital memory. The third bias scan is identical with the fist one, and the I-V curve overlaps the first sweep curve. The comparison of the I-V curves in the two states at different temperatures is displayed in Figure 4.8 The current goes up as the temperature increases, and the two states are distinct at both low temperature and room temperature.

In addition to the electrical bistability, the device also shows spin valve effect. The magnetic field dependence of the device resistance was measured while an in-plane magnetic field was swept from +3000 Oe to -3000 Oe and then back to +3000 Oe. The spin valve magnetoresistance (MR) value is defined as:
Figure 4.7: $I$-$V$ curves of the hybrid organic bistable device of structure LSMO (50 nm)/LAO/rubrene (50 nm)/Fe (30 nm) at 10 K. Initially, the device is in the OFF state. At about 4.5 V, the current increases sharply, indicating the transition of the device from the OFF to the ON state. The device is able to return to the OFF state by applying a high negative voltage. The inset shows the enlarged curves near zero bias$^{22}$. Reprinted with permission from Ref.$^{22}$. Copyright 2010, Elsevier.
Figure 4.8: Temperature dependence of the I-V curves. Red circles represent data points in the ON state, and black squares represent data points in the OFF state. (a) $T = 10$ K. (b) $T = 100$ K. (c) $T = 200$ K. (d) $T = 300$ K$^{22}$. Reprinted with permission from Ref.$^{22}$. Copyright 2010, Elsevier.
where $R_{AP}$ and $R_P$ refer to the device resistance when the magnetization directions of the two ferromagnetic layers are anti-parallel and parallel, respectively. We obtained a spin valve MR value of up to 3.75% in the ON state, while no spin valve effect was observed in the OFF state. Fig.4(c), (d) and (e) show the magnetoresistance curves of a 50 nm rubrene device in the ON state with a bias of 2.0 V, 2.5 V and 3.0 V, respectively. The bias voltage dependence of the spin valve MR value is presented in Fig.4(f), and the maximum spin valve MR 3.75% was obtained when 3.0 V was applied. We emphasize here that the spin valve effect of our device was controllable via applied bias, and it was observed only when the device was in the ON state. We did not observe this spin valve effect in room temperature, because the polarization of the LSMO decreases as the temperature increases. Another difference of the magnetoresistance curves between the two states is the shape. As shown in Figure 4.9 (a) and (b), the high field magnetoresistance curve in the OFF state is almost flat, while the high field magnetoresistance curves in the ON state show a “wing” shape that the device resistance decreases as the external magnetic field increases. We define a high field magnetoresistance (HFMR) as:

\[
HFMR(\%) = 100 \times \frac{R(0)_{\text{max}} - R(\pm 3000\text{Oe})_{\text{min}}}{R(0)_{\text{max}}}
\]

Here, we propose an explanation for this combination of the electrical bistability and the bias-controlled spin valve effect. The magnetoresistance curves we obtained from the ON state show additional “wing” shape magnetoresistance. Note this shape of MR effects is similar to the reported results of Sakai et al. in a Co-C$_{60}$ hybrid nanocomposite channel and Kusai et al. in a Co-rubrene hybrid nanocomposite channel between nonmagnetic electrodes. The MR effects in those previous results were attributed to the spin dependent tunneling between the Co nanoparticles through the organic molecules. Another similar MR behavior can be found in the phenomenon that was termed organic magnetoresistance (OMAR). In our devices, this MR feature appeared only when the device was switched
Figure 4.9: Magnetoresistance curves of the 50 nm rubrene device at 10 K. (a) Magnetoresistance curve in the OFF state under 1.5 V (+ 3000 Oe to -3000 Oe). (b) Magnetoresistance curves in the ON state under 2.5 V (+ 3000 Oe to -3000 Oe). (c) In the ON state under 2.0 V bias. (d) In the ON state under 2.5 V bias. (e) In the ON state under 3.0 V bias. (f) Bias dependence of the spin valve MR value and high field MR value. Reprinted with permission from Ref. Copyright 2010, Elsevier.
to “ON” states. This indicates that this additional high field MR feature in our devices is not intrinsic as the case in OMAR. We suggest that some Fe atoms migrate into the rubrene layer under high bias, forming conductive channels, although the microscopic mechanism still needs to be investigated. Starting from the OFF state in which the channels were closed, the device showed low current. At a threshold voltage, the conductive channels were turned on and the current jumped to a high level. After the power supply was removed, the channels were still open and the device remained in the ON state. Only if a high negative bias was applied, those channels were disrupted and the device recovered to the OFF state. In the ON state the conductive channels also provided efficient transport paths for the spin polarized carriers. This high-voltage induced conduction channel introduces high field MR effects similar to the reports of Co-rubrene nanocomposite channel with nonmagnetic electrodes. In addition, the ferromagnetic electrodes in our devices introduce spin valve effects at the same time.

In the OFF state, the bulk resistance of the rubrene layer dominated and it was much larger than the interface resistance. In principle, the spin valve effects rely on the spin dependent scattering at the interface. The device resistance in the OFF state was almost one order of magnitude larger than that in the ON state. Given the fact that even the maximum MR value we obtained in the ON state was relatively small — 3.75 %, any resistance change at the interface in the OFF state is likely overshadowed by the bulk resistance of rubrene layer. Additionally in the OFF state, the travel distance through the rubrene layer for the spin-polarized carriers could be longer than the spin-diffusion length \( \lambda_s \). The carriers would lose their spin information before they reach the other ferromagnetic electrode. Though the spins in carbon based materials are typically perceived to have long lifetime, the transport in small molecule film heavily rely on the hopping between neighboring molecules leading to long transit time between two ferromagnetic electrodes. However, in the ON state, the presence of the conductive channels made the effective spin travel distance much shorter. The carriers could effectively maintain their initial spin state during the transport, leading to the spin valve effect.
4.3.3 Thickness dependence

This multi-functionality also appears in devices with thicker rubrene layers. Figure 4.10 shows the $I-V$ curves for a device with 70 nm rubrene layer. The $I-V$ curves show clear bistability with distinct high-current and low-current states. Only in the high-current state, we saw clear MR signals (see Figure 4.11 and Figure 4.12). As temperature increases, the MR value decreases.

4.4 All-organic-based spin valve

$V[TCNE]_x$ is the first reported room-temperature molecule-based magnet with magnetic ordering temperature $T_C \sim 400$ K. The magnetic order originates from the antiferromagnetic coupling between the $V^{2+}$ ion’s three unpaired electrons in $3d(t_{2g})$ orbitals with a total spin $S = 3/2$ and the $[TCNE]^-$ anion’s unpaired electrons in $\pi^*$ orbital with $s = 1/2$. Stoichiometry shows that there is approximately one $V^{2+}$ ion on average for two $[TCNE]^-$ anions, leading to a net spin of 1/2 for the repeat unit (see Figure 4.19). This high-$T_c$
Figure 4.11: The magnetoresistance measurements in the low-current state for the 70 nm rubrene device at 10 K with a bias of 1000 mV.

Figure 4.12: MR measurement in the high-current state for the 70 nm rubrene device at 10 K with a bias of 1000 mV.
Figure 4.13: Temperature dependence of the MR for the 70 nm rubrene device.

Figure 4.14: $I$-$V$ curves for a device with 60 nm rubrene layer at 10 K.
Figure 4.15: MR in the low-current state for the 60 nm rubrene device with a bias of 500 mV.

Figure 4.16: MR in the high-current state for the 60 nm rubrene device with a bias of 500 mV.
Figure 4.17: MR in the low-current state for the 60 nm rubrene device with a bias of 1000 mV.

Figure 4.18: MR in the high-current state for the 60 nm rubrene device with a bias of 1000 mV.
magnetic materials can be prepared as powder in dichloromethane, or grown as a thin film by low-temperature (\(\sim 40^\circ\text{C}\)) chemical vapor deposition (CVD). Extended x-ray absorption fine structure (EXAFS) analysis showed that each vanadium ion is coordinated by 6 nitrogen atoms at a room-temperature average distance of 2.084(5) Å, suggesting strong binding between V and TCNE. Recently, a molecular layer deposition (MLD) method has been developed for V[TCNE] \(_x\) films. MLD is able to precisely control the thickness of the film within a mono-layer by exposing the substrate alternatively and sequentially to different precursors. V[TCNE] \(_x\) has a unique half-semiconductor electronic structure with fully spin-polarized valence and conduction bands. Because of the on-site Coulomb repulsion \(U_c\), the \(\pi^*\) level of [TCNE]\(^-\) is split into two sublevels, occupied \(\pi^*\) and unoccupied \(\pi^* + U_c\) with opposite spin polarizations. It was shown that the energy split between the \(\pi^*\) and the \(\pi^* + U_c\) levels is approximately 2 eV. Results of photoelectron spectroscopy (PES) and resonant photoemission (RPE) studies suggested that the occupied \(\pi^*\) level lies about 1.5 eV below the V(3d) state, while the unoccupied \(\pi^* + U_c\) level is 0.5 eV higher than V(3d) state. An activation energy of 0.5 eV is determined from the temperature dependence of the conductivity for CVD-prepared thin film, coinciding with the energy difference between the 3d\((t_{2g})\) and \(\pi^* + U_c\) levels. The activation energy of MLD films is approximately 0.4 eV, slightly lower than that of CVD film.

As shown in Figure 4.19, the overall structure of the device is, starting from the bottom: Al/V[TCNE] \(_x\)/rubrene/ V[TCNE] \(_x\)/Al. The V[TCNE] \(_x\) films serve as two ferromagnetic (FM) contacts with different coercive fields while the organic semiconductor rubrene \((C_{42}H_{28})\) is used as the spacer. Al (50 nm) is deposited on clean glass substrates as electrodes. V[TCNE] \(_x\) film grown by MLD (40 layers, \(\sim 50\) nm) serves as the bottom FM layer. Rubrene is well known for its high charge mobility and has been demonstrated as an efficient tunnel barrier. 10 nm of rubrene is thermally evaporated on top of MLD-grown V[TCNE] \(_x\) using an effusion cell. The thickness of the rubrene layer is within the tunneling regime \((< 15\) nm) previously reported. Another V[TCNE] \(_x\) (300 nm) film grown by CVD is used as the top FM layer. Al (30 nm) is then deposited as the top electrode. The injected carriers are polarized by the first V[TCNE] \(_x\) layer encountered and then tunnel through.
Figure 4.19: (a) Device structure and (b) schematic view of the energy level of V[TCNE]$_x$ (x~2, TCNE: tetracyanoethylene)\textsuperscript{23}. Reprinted with permission from Ref.\textsuperscript{23}. Copyright 2011, John Wiley & Sons, Inc.

the barrier, reaching the second V[TCNE]$_x$ which acts as the analyzer. The magnetization hysteresis curves of the two V[TCNE]$_x$ films are recorded separately by a superconducting quantum interference device (SQUID). In a spin valve, the device resistance depends on the relative magnetization direction (parallel or antiparallel) of the two FM layers. The magnetoresistance (MR) is defined as $MR = (R_{AP} - R_P)/R_P$, where $R_{AP}$ and $R_P$ are the device resistances corresponding to antiparallel and parallel configuration, respectively.

The measurements were performed between 10 K and 300 K. Figure 4.20 shows the $I$-$V$ characteristics for the spin valve device with the structure of Al(50 nm)/V[TCNE]$_x$(50 nm)/rubrene(10 nm)/V[TCNE]$_x$(300 nm)/Al(30 nm). The $I$-$V$ curves are nonlinear and strongly temperature dependent, similar with the reported LSMO/rubrene/V[TCNE]$_x$ tunnel junction.\textsuperscript{8} Figure 4.20 also presents the temperature dependence of the normalized device resistance with comparison to the bulk resistances of the CVD-grown and MLD-grown V[TCNE]$_x$ films. At high temperatures, the current of the device is controlled by
Figure 4.20: $I-V$ curves of the spin valve device at different temperatures. The upper inset shows enlarged figure near $V_b=0$ V. The lower inset shows the temperature dependent resistances for the spin valve device (black) as well as the bulk resistance of V[TCNE]$_x$ films. The two V[TCNE]$_x$ films are deposited by CVD (red) and MLD (blue) respectively$^{23}$. Reprinted with permission from Ref. $^{23}$. Copyright 2011, John Wiley & Sons, Inc.
Figure 4.21: Magnetization hysteresis curves of V[TCNE]$_x$ films recorded by SQUID at $T=100$ K. Red data sets denote the MLD-grown film and black curves represents the CVD-grown film. The lower inset shows enlarged hysteresis loop of CVD-grown film at different scales. The upper inset shows the $dI/dV$ curves for the tunnel junction at different temperatures$^{23}$. Reprinted with permission from Ref.$^{23}$. Copyright 2011, John Wiley & Sons, Inc.

the injection of charge carriers between the organic magnets and the organic semiconductor. Below 100 K, the bulk resistances of V[TCNE]$_x$ films which increase exponentially with decreasing temperature start to dominate the total device resistance. The crossover between injection-limited regime and V[TCNE]$_x$ bulk-limited regime was also reported in V[TCNE]$_x$-based hybrid device.$^8$ As shown in Figure 4.21, the $dI/dV$ curves have similar shapes at different temperatures. As discussed in previous literature, The absence of zero bias anomaly indicates that rubrene forms a good tunneling barrier.$^{86}$

The magnetization hysteresis curves of the CVD-grown and MLD-grown V[TCNE]$_x$ films are presented in Figure 4.21. Note that the coercive field of the MLD-grown film is much larger than that of the CVD-grown sample. The MLD film was prepared at much slower deposition rate ($\sim 0.98$ nm per cycle) and the MLD film has larger density, which
suggest that this increased coercive field is possibly due to more complete metal-ligand coordination as well as stronger coupling between V$^{2+}$ and [TCNE]$^\text{-}$. The variation of the device resistance as a function of the applied in-plane magnetic field recorded at 120 K and 4 V is shown in Figure 4.22. Clean and reproducible negative MR curves are obtained which correspond well to the coercive fields of the FM layers. The higher coercive field is ascribed to MLD-grown V[TCNE]$_x$ and the lower field to the CVD-grown V[TCNE]$_x$. The device resistance depends on the relative alignment of the magnetization of the magnetic layers, as the parallel configuration resistance $R_P$ differs from the antiparallel resistance $R_{AP}$. At high magnetic field larger than 100 Oe, the magnetic moments of the two FM layers align in parallel. As we sweep the external field, the CVD-grown V[TCNE]$_x$ film switches its magnetic moment first, resulting an antiparallel configuration with a change of device resistance. After the switch of the other FM layer, the device returns to parallel alignment. The maximum MR value 0.04% is obtained at 100 K. Below 100 K, the device resistance is dominated by the bulk resistance of V[TCNE]$_x$ films and becomes too large, thus it is difficult to detect any field-dependent interface resistance changes. The MR value decreases as temperature goes up, which was common in reported magnetic tunnel junctions and explained by temperature dependence of the defect density. MR value varies slightly with bias, while vanishing above 6 V. This negative MR is found to be independent of the bias polarity.

We observed the spin valve effect in 14 devices out of the total 16 devices we fabricated, all of which showed inverted spin valve effect, with the low-resistance state corresponding to the antiparallel configuration. We note that both positive and negative MR effects have been reported in organic spin valves. The inverted spin valve effect has been suggested to be due to ballistic channels from pinholes which occur during the metal deposition on top of the organic semiconductor. However, the fabrication process of our devices rules out this possibility, because the rubrene is covered by V[TCNE]$_x$ film prepared by CVD at low temperature ($\sim 40 \, \text{°C}$) rather than a thermally deposited ferromagnetic metal and the charge transport through V[TCNE]$_x$ will also preclude the metal migration and the formation of ballistic channels due to pinholes. Barraud et al. pointed out that for organic
Figure 4.22: Magnetoresistance curve measured at 120 K with $V_b=4$ V. The left inset shows the temperature dependence of the MR value with $V_b=4$ V. The right inset shows the bias voltage dependence of the MR value at $T=100$ K. Reprinted with permission from Ref. 23. Copyright 2011, John Wiley & Sons, Inc.
Figure 4.23: Simplified energy diagram for a V[TCNE]ₙ/rubrene/V[TCNE]ₙ tunnel junction. a) The left shows the energy levels without external bias, and the right presents the bias-induced level shifts (Δ is the energy shift due to applied bias). b) In the parallel configuration, the electron on the left π⁺ level cannot tunnel into the right π⁺ + U_c level. This tunneling process can take place in the antiparallel alignment ²³. Reprinted with permission from Ref. ²³. Copyright 2011, John Wiley & Sons, Inc.
spin valves, the first molecule layer at the electrode interface plays a crucial role, even could change the sign of the spin polarization of the FM electrode.\(^{94}\) They proposed a spin-hybridization-induced polarized state (SHIPS) model with an ‘effective’ spin polarization \((P^*)\) due to the specific bonding of different band states of the FM electrodes at the organic interface.

The possibility that the rubrene layer contributes to the MR is also ruled out, because the organic magnetoresistance (OMAR)\(^{80–83,98–100}\) originates from the bulk transport in organic semiconductors and our devices are dominated by tunneling through the 10 nm rubrene thin layer. In addition, the reported magnetoresistance of V[TCNE]\(_x\) films are one order of magnitude smaller than the MR value obtained in our spin valve devices.\(^{47,101}\) The negative sign of MR observed in our devices is independent of temperature and bias voltage, which is different from the previously reported MR results that negative sign could be changed to positive with the variation of temperature and bias voltages.\(^{90}\) We suggest that the negative MR in our devices is an intrinsic feature of V[TCNE]\(_x\) related spin polarized energy levels, as shown in Figure 4.23. Here we propose a simple phenomenological bias-enhanced selective tunneling (BEST) model to explain the negative MR. As an external bias is applied to the device, the energy levels of the V[TCNE]\(_x\)/rubrene/V[TCNE]\(_x\) junction are shifted. The effect of external bias on the alignment of energy levels is shown schematically in Figure 4.23.a, indicating the energy of one V[TCNE]\(_x\) film is raised up and the other is lowered due to applied external bias. At certain voltage, the \(\pi^*\) level of one V[TCNE]\(_x\) contact is leveled with the energy of \(\pi^* + U_c\) of the other V[TCNE]\(_x\) contact. Note that the 3d\(t_{2g}\) orbital is highly localized upon V\(^{2+}\) ion, while the \(\pi^*\) and \(\pi^* + U_c\) orbitals are delocalized over the relatively large [TCNE]\(^-\) anion due to \(\pi\)-conjugation.\(^{102}\) We suggest that most of the tunneling is happening between the \(\pi^*\) and the initially unoccupied \(\pi^* + U_c\) levels. According to the Pauli exclusion principle, the allowable spin direction of the \(\pi^*\) and \(\pi^* + U_c\) level are opposite to each other (i.e., spin \(\uparrow\) (\(\downarrow\)) in \(\pi^*\) level while spin \(\downarrow\) (\(\uparrow\)) in \(\pi^* + U_c\) level). When the magnetization of the two V[TCNE]\(_x\) layers align parallel, the spins of the electrons on both of the \(\pi^*\) levels on each side are in same direction. As in Figure 4.23, the spin \(\downarrow\) electron from the left \(\pi^*\) level tunnels through the barrier into the \(\pi^* + U_c\) level on the
other side. However, the allowable spin state on that $\pi^* + U_c$ level is spin $\uparrow$. As a result, this spin $\downarrow$ electron cannot enter that $\pi^* + U_c$ level and the device shows a high resistance. Under the antiparallel configuration, the spin $\downarrow$ electron from the left $\pi^*$ level can tunnel into the $\pi^* + U_c$ level on the right, since the allowable state on that level is spin $\downarrow$. Thus, the device shows a low resistance. The bias dependence in the $I-V$ curves related with the alignment of contact energy levels (see Fig.4.20) is obscured with the field dependent and phonon assisted tunneling.\textsuperscript{71} It is noted that the MR is independent of bias polarity, which is due to the same electronic structure of V[TCNE]$_x$ prepared by different deposition methods. We need to emphasize here that this energy-level diagram is simplified. The details of the band structure still remain unclear. The energy level alignment of V[TCNE]$_x$ and other organic semiconductors still needs to be understood. It is noted that the possibility of the involvement of traps or impurity states is not ruled out. Additional careful studies should be conducted to uncover the details of the spin tunneling process.

### 4.5 Room temperature spin injection/detection using organic based magnet

A spin valve is a sandwich device which consists of two ferromagnetic (FM) layers with different coercivities separated by a nonmagnetic spacer. The device can switch between parallel and antiparallel magnetization configurations by sweeping an external magnetic field. In our experiments, V[TCNE]$_x$ and Fe were chosen as the two magnetic contacts of the spin valve, while rubrene acted as the tunnel barrier. Figure 4.24 illustrates the device structure. We fabricate the spin valve by thermal evaporation using \textit{in situ} shadow masks. To begin the device fabrication, glass substrates were cleaned ultrasonically and dried with nitrogen. Then organic solvent residue was removed by a UV-ozone cleaner. All the cleaning procedures were performed in a Class 1000 cleanroom. Right after the cleaning, the substrates were transferred into a vacuum deposition system integrated in an argon glovebox for film depositions. The base pressure of the vacuum chamber was $5 \times 10^{-7}$ Torr. 50 nm of Fe was deposited by e-beam evaporation at a rate of 0.2 Å/s. 10 nm of rubrene
was deposited thermally using a Knudsen cell at a controlled temperature ($\sim 105^\circ$C). We have reported that a single 5 nm rubrene layer was too thin to provide a uniform coverage or to form a good barrier. Lin et al. also reported that maximum tunneling thickness for rubrene is about 15 nm. Thus 10 nm of rubrene should form a proper tunnel barrier. The $\text{V[TCNE]}_x$ layer was grown by low temperature ($\sim 40^\circ$C) CVD with a thickness of about 300 nm. Another 30 nm of Al was deposited as the top contact. The effective junction area was 1 mm $\times$ 1 mm. The electric and magnetic measurements were performed in a physical property measurement system (PPMS) from Quantum Design with Keithley 2400 sourcemeter. The magnetic hysteresis loops are measured with a superconducting quantum interference device (SQUID).

Figure 4.25 shows the typical current-voltage ($I-V$) characteristics of the device at different temperatures, which are similar with the reported LSMO/LAO/rubrene/Fe magnetic tunnel junction. The absence of zero bias anomalies in the conductance vs bias plot ($dI/dV$
Figure 4.25: (a) $I$-$V$ characteristics of the spin valve with the structure of Fe (50 nm)/rubrene (10 nm)/V[TCNE]$_x$ (300 nm) at different temperatures: 100 K, 150 K, 200 K and 250 K. (b) $dI$-$dV$ as a function of bias voltage at different temperatures: 100 K, 150 K, and 200 K. Reprinted with permission from Ref. 24. Copyright 2011, American Institute of Physics.

Figure 4.26: Coercive fields of Fe (50 nm) film and V[TCNE]$_x$ (300 nm) film measured separately by SQUID at 100 K. The inset figure shows enlarged detail of the hysteresis loop for V[TCNE]$_x$ film. Reprinted with permission from Ref. 24. Copyright 2011, American Institute of Physics.
vs $V$, see Figure 4.25) suggests that the rubrene formed a good tunnel barrier, as discussed in literatures.\textsuperscript{84,86} Figure 4.26 shows the hysteresis loops of the two FM layers measured by SQUID separately. At 100 K, 50 nm Fe film has a coercive field of 160 Oe and $\text{V[TCNE]}_x$’s coercive field is about 5 Oe. The resistance of a spin valve varies depending on the relative alignment of the magnetization of the two FM layers. The magnetoresistance (MR) value is defined as $\text{MR} = (R_{AP} - R_P)/R_P$, where $R_{AP}$ and $R_P$ are the device resistance corresponding to antiparallel (AP) and parallel (P) configurations, respectively. Figure 4.27 shows the typical MR curves obtained from our devices. At high applied magnetic field, the two FM layers align parallel with the external field. When the field reaches the coercive field of one of the FM layer, the device resistance has a sharp change as the two FM align antiparallel. Out of a total 16 devices we measured, 12 devices showed spin valve effect and all of the MR values are negative, which corresponds to lower device resistance for antiparallel alignment. The sign of the MR is independent of bias polarity. The temperature dependence of MR is presented in Figure 4.28, obtained by measuring MR under 500 mV at different temperatures, showing the maximum MR 0.06 \% occurs at 100 K. The device resistance increased rapidly as the temperature was decreased (see Figure 4.28). Below 100 K, the device resistance became too high for us to detect any MR. The decrease of MR with increasing temperature is a common behavior for magnetic tunnel junction and can be explained by the increase of defect density and inelastic transport at high temperature.\textsuperscript{84} Our device kept showing spin valve effect up to 300 K, with a MR value of 0.01 \%. Although the absolute MR value at room temperature is small, it remains 16.7 \% of its peak value obtained at 100 K. The bias dependence of the MR values at 100 K are presented in Figure 4.28. At 100 K, the maximum MR obtained is 0.18 \% under 100 mV. The rapid decrease of MR value with increasing bias is observed in various magnetic tunnel junctions.\textsuperscript{59,84}

As a control experiment, we measured the resistance of the 50 nm Fe film as a function of applied magnetic field separately using the exact same measurement set-up as the spin valve. We did not observe any MR from the Fe film. It has been reported that the MR of CVD-grown $\text{V[TCNE]}_x$ film increases linearly with increasing external magnetic field with no shift.\textsuperscript{47,101} The estimated MR of $\text{V[TCNE]}_x$ film at 100 Oe would be two order of
Figure 4.27: Magnetoresistance (MR) measurements of the spin valve with the structure of Fe (50 nm)/rubrene (10 nm)/V[TCNE]x (300 nm) at 100K under a bias of 2500 mV$^{24}$. Reprinted with permission from Ref. $^{24}$. Copyright 2011, American Institute of Physics.

Figure 4.28: (Black square) Bias dependence of MR values at 100 K. (Red triangle) Temperature dependence of MR values under 500 mV. The inset shows temperature dependent resistance of the spin valve device and V[TCNE]x film measured separately$^{24}$. Reprinted with permission from Ref.$^{24}$. Copyright 2011, American Institute of Physics.
magnitude smaller than the MR we observed. Thus we believe the MR is from the spin-
dependent tunneling. We observed negative MR with lower device resistance corresponding
to antiparallel magnetization configuration. This is consistent with our previous reported
results on the all-organic-based spin valve which were explained by a proposed bias-enhanced
selective tunneling (BEST) model. We want to emphasize here that the interface plays a
 crucial role in the tunneling, as pointed by Barraud et al. and their SHIPS model. In our
previous reported LSMO/rubrene/V[TCNE]x tunnel junction, we have shown that a single
5 nm rubrene could not provide a good tunnel barrier while hybrid barrier LAO/rubrene
give rise to a clear MR signal. Here we believe that the reason accounting for the relatively
small MR values is the imperfect interface.

4.6 Effect of organic spacer in organic spin valve

Organic spacer is an important part in organic spin valve. Here we report our studies of
the effect of organic spacer on the performance of an organic spin valve based on organic
magnetic semiconductor vanadium tetracyanoethylene (V[TCNE]x, x~2). We observed
spin valve effect in devices without non-magnetic spacer and show that the introduction of
organic spacer greatly improved the MR value of the devices.

V[TCNE]x is the first reported room temperature organic-based magnet with magnetic
ordering temperature \( T_c \sim 400 \text{ K} \). The \( V^{2+} \) ion’s three unpaired electrons in
3\( d(t_{2g}) \) orbitals are antiferromagnetically coupled to the [TCNE]– anion’s unpaired electron in \( \pi^* \)
orbital, leading to a net spin \( S = 1/2 \) for the repeat unit. V[TCNE]x can be grown as
a thin film by low-temperature (\( \sim 40^\circ \text{C} \)) chemical vapor deposition (CVD) or molecular
layer deposition (MLD). Extended X-ray absorption fine structure (EXAFS) analysis
showed that each vanadium ion is coordinated by six nitrogen atoms at an average distance
of 2.084(5) Å. V[TCNE]x has a unique half-semiconductor electronic structure with fully
spin-polarized valence and conduction bands. We have reported hybrid spin valve as well
as all-organic-based spin valve, successfully demonstrated spin injection/detection using
organic-based magnet. Optical detection of spin injection from organic-based magnet
Detail description of the device fabrication procedure is discussed in earlier publication\textsuperscript{24}. The bottom Fe contact and the organic spacers were thermally evaporated in two high-vacuum deposition chambers separately (base pressure: $10^{-7}$ Torr) inside of an argon-filled glovebox, onto pre-cleaned glass substrates using shadow masks. 300 nm of V[TCNE]$_x$ films grown by CVD were used for the second ferromagnetic layers. Finally, the devices were capped by 30 nm of Al top electrode. The device area is around 1 mm $\times$ 1 mm, defined by a cross-bar structure. We fabricated and compared two types of devices with the device structures of Fe (30 nm)/V[TCNE]$_x$ (300 nm)/Al (30 nm), Fe (30 nm)/Alq$_3$ (10 nm)/V[TCNE]$_x$ (300 nm)/Al (30 nm). We also compared the results from previous report on Fe (30 nm)/rubrene (10 nm)V[TCNE]$_x$ (300 nm)/Al (30 nm)\textsuperscript{24}. All the electrical and magneto transport measurements were performed in a physical property measurement system (PPMS) from Quantum Design. After the device fabrication in the argon glovebox, the samples were immediately transferred to PPMS using an argon-filled protective package, to minimize the air exposure.

Figure 4.29 shows the current-voltage ($I$-$V$) characteristics of the device with the structure of Fe (30 nm)/V[TCNE]$_x$ (300 nm)/Al (30 nm) at different temperatures. The $I$-$V$ curves are non-linear and strongly temperature-dependent. As discussed in previous literature\textsuperscript{84,86}, the appearance of zero bias anomalies in the conductance vs bias plot is mostly due to the metallic interdiffusion through the barrier and the absence of zero bias dips usually indicates the quality of the tunnel barrier. Here we prevent this metallic interdiffusion problem by employing organic-based magnet grown by low temperature CVD. Figure 4.30 displays the magnetoresistance (MR) measurements results of the Fe/V[TCNE]$_x$/Al device. Figure 4.30(a) shows three MR curves recorded at a bias voltage of 1000 mV at different temperatures: 80 K, 100 K and 150 K. The higher coercive field is attributed to Fe and V[TCNE]$_x$ film has a smaller coercivity of 4.5 Oe at 100 K. The MR value is defined as: $MR = (R_{AP}-R_P)/R_P \times 100\%$, where $R_{AP}$ and $R_P$ are the device resistances corresponding to antiparallel and parallel configurations respectively. At 80 K, the value of MR is 0.11\% and continuously decreases as $T$ increases (Fig 4.30(b)). MR disappeared as $T$ was increased.
Figure 4.29: (a) $I-V$ characteristics of the device with the structure of Fe/V[TCNE]$_x$/Al) at different temperatures: 80 K, 100 K, 150 K and 200 K. (b) $dI/dV$ at different temperatures: 80 K, 100 K and 150 K$^{25}$. Reprinted with permission from Ref. $^{25}$. Copyright 2012, Elsevier.
Figure 4.30: (a) Magnetoresistance (MR) curves of the device with the structure of Fe/V[TCNE]_x/Al) at different temperatures: 80 K, 100 K, and 150 K at a bias voltage of 1000 mV. (b) Bias dependence (black) of MR values at 100 K and temperature dependence (red) of MR values at 1000 mV. Reprinted with permission from Ref. 25. Copyright 2012, Elsevier.

over 200 K. The plot of MR vs applied bias is displayed in Fig. 4.30(b). The MR value increases as the bias voltage is raised, and reached to a value of 0.11% at a bias voltage of 3000 mV. We did not apply bias voltages higher than 3000 mV to avoid device breakdown.

Figure 4.31 shows the I-V curves of the device with 10 nm Alq3 spacer at different temperatures. The I-V curves are also non-linear and strongly temperature dependent. The absence of zero bias anomalies in the $dI/dV$ vs bias plots implies the Alq3 forms a good tunnel barrier. Figure 4.32 presents MR curves of the Fe/Alq3/V[TCNE]_x/Al device.
Figure 4.31: (a) $I-V$ characteristics of the device with the structure of Fe/Alq$_3$/V[TCNE]$_x$/Al at different temperatures: 80 K, 100 K, 150 K and 200 K. (b) $dI/dV$ at different temperatures: 80 K, 100 K, 150 K and 200 K$^{25}$. Reprinted with permission from Ref.$^{25}$. Copyright 2012, Elsevier.
at different temperatures range from 100 K to 300 K. The MR of the devices decreases as the temperature increases, which is typical behavior of magnetic tunnel junction\textsuperscript{84,86}. At a bias voltage of 500 mV, the MR decreases from 0.32\% at 100 K to 0.05\% at 300 K. Note that we also realized room-temperature spin injection/detection in this system, as we reported before using rubrene as the spacer\textsuperscript{24}. Compared to the Fe/V[TCNE]\textsubscript{x}/Al device, the device with Alq\textsubscript{3} spacer shows a different bias dependence of MR values (see Figure 4.33(a)). As applied bias voltage increases, the MR value decreases, which is typical behavior of magnetic tunnel junction. The opposite bias dependence of the previous device might be due to the fact that voltage drop in that device occurs mostly through the bulk of V[TCNE]\textsubscript{x} rather than the tunnel barrier. At 150 K, we obtained a MR of 0.7\% at 10 mV and the MR decreased to 0.09\% at 2000 mV. Figure 4.33(b) displays the recorded MR curves at 150 K at different bias voltages. Compared to the MR curves of the device without spacer, the Fe/Alq\textsubscript{3}/V[TCNE]\textsubscript{x}/Al device shows more sharp and distinct switch at the coercive fields of the ferromagnetic layers. We also measured the device resistance as a function of temperature. As shown in Figure 4.34, the resistances of both devices increased by several orders of magnitude as we lowered the temperature from 300 K to around 60 K. In the device without barrier, the activation is mostly due to the bulk of V[TCNE]\textsubscript{x}. The device with Alq\textsubscript{3} spacer displays stronger temperature dependence reflecting the presence of activation barrier between two ferromagnetic layers.

Previously, one of the difficulties in device fabrication is to eliminate pinholes. When ferromagnetic metals are deposited onto soft organic spacer layer, hot metal atoms would penetrate into the organic layer and form filamentary pinholes\textsuperscript{104}. One of the advantages of using organic-based magnet is the low temperature deposition process which avoid the penetration of metal atoms. The temperature-dependent non-linear I-V curves as well as the semiconductor-like temperature-dependent device resistance imply that our devices are free of pinholes. Particularly, as Åkerman et al. suggested\textsuperscript{105}, examining temperature dependence of the resistance is a reliable way to rule out pinholes through the barrier. As shown in Figure 4.34, the slope of the Fe/Alq\textsubscript{3}/V[TCNE]\textsubscript{x}/Al device is larger than that of the device without Alq\textsubscript{3} spacer, indicating the resistance of the former increases more
rapidly as the temperature decreases. This could be attributed to the presence of activation barrier between the two ferromagnetic layers.

By making two ferromagnetic layers directly contacting each other, one may expect the exchange interaction between them would hinder free rotation of the magnetization vectors in the absence of a spacer to decouple the two contacts. However, in our experiments, the device without Alq3 spacer shows distinct MR up to 200 K. One possible reason accounting for this discrepancy is the existence of a thin Fe oxide layer on top of deposited Fe film. Even though the Fe deposition and following CVD process were performed in an argon-filled glovebox without the sample’s exposure to air, the metallic film cannot be guaranteed to be free of oxidation. Another possibility is the formed ‘dead layer’ due to chemical reaction between the V[TCNE]x and Fe, similar with the ‘ill-defined layer’ proposed by Xiong et al. in the report of the first vertical organic spin valve. Careful probe and analysis of the interface between the V[TCNE]x and Fe would be helpful to confirm this possibility.

Both the two types of devices show smaller MR value at higher temperature. This
Figure 4.33: (a) Temperature dependence (red) of MR values of the device with the structure of Fe/Alq₃/\text{V[TCNE]}ₓ/Al at a bias voltage of 500 mV. Bias voltage dependence (black) of MR values at 150 K. (b) MR curves recorded at 150 K at different bias voltages range from 100 mV to 1500 mV. Reprinted with permission from Ref.²⁵. Copyright 2012, Elsevier.
Figure 4.34: (a) Device resistances as a function of temperature for Fe/V[TCNE]$_x$/Al (black) and Fe/Alq$_3$/V[TCNE]$_x$/Al (red). (b) Comparison of MR values at 100 K at different bias voltages$^{25}$. Reprinted with permission from Ref. $^{25}$. Copyright 2012, Elsevier.
temperature dependence is common in reported magnetic tunnel junctions and explained by the temperature dependence of the defect density in the barrier\textsuperscript{34}. Interestingly, the two types of devices have different bias dependence of MR values. The device with Alq\textsubscript{3} spacer has decreasing MR with increasing bias voltages, while the device without Alq\textsubscript{3} spacer shows opposite behaviour. The reason for this discrepancy is unclear.

Most importantly, the introduction of Alq\textsubscript{3} spacer greatly enhanced the MR value. The MR value of the Fe/Alq\textsubscript{3}/V[TCNE]\textsubscript{x}/Al device is one order of magnitude larger than that of the Fe/V[TCNE]\textsubscript{x}/Al device. For example, at 100 K and 500 mV, the former has a MR value of 0.34\% while the latter only has 0.07\%. The Alq\textsubscript{3} device also outperforms the rubrene device we reported before\textsuperscript{24} which employed 10 nm rubrene as the spacer while other layers remained the same. The rubrene device had a maximum MR of 0.18\% at 100 K, much smaller than that of 0.6\% obtained at 100 K from the Alq\textsubscript{3} device. We also noticed that the rubrene device showed higher current in the $I$-$V$ plots, in part due to the high mobility of the rubrene film. However, the relation between the mobility of the spacer material and the MR is unclear.
Organic electronics and spintronics is a very rich field for research. Due to the complexity of the organic materials, the research is also complicated, requiring proper materials handling, device characterization and theoretical modeling. Although some of the existing theories in the inorganic counterpart could be borrowed to model the organic system, one should always be careful with the appropriateness. For example, magnetoresistance can occur in a homogeneous ferromagnetic film due to domain wall scattering\textsuperscript{106–109}. However, this concept is not applicable to organic magnet film such as V[TCNE]\textsubscript{x}. Because the magnetic ordering is relatively weak in V[TCNE]\textsubscript{x}, it might be inappropriate to describe the system using domain wall-related concepts. Rather, the magnetoresistance in V[TCNE]\textsubscript{x} is explained by the change of activation gap in the magnetic field\textsuperscript{47}.

Another important aspect is surface/interface analysis in organic devices. The metal-organic interface plays a crucial role in device performances, involving with interface dipole formation, charge transfer, chemical reaction, energy level alignment, in-diffusion\textsuperscript{110}. The organic-organic interface usually involves with energy level alignment, band bending, charge separation, Debye screening\textsuperscript{110}. The techniques for surface/interface analysis include photoemission spectroscopy, inverse photoemission spectroscopy, scanning probe microscopy, near edge X-ray absorption find structure (NEXAFS), and secondary ion mass spectroscopy, etc. However, it is difficult to apply these tools to V[TCNE]\textsubscript{x} studies, mainly due to the air sensitivity of the film. Future development of film deposition technique and property-controlling methods might enhance our ability to study the interfaces.
Figure 5.1: Advancement of the solar cell efficiency.26
The most successful practical applications of the organic electronic devices are organic photo-voltaic cell (OPV) and organic light-emitting diode (OLED). Figure 5.1 shows the advancement of the efficiency of the solar cells over the years. The OPV has passed the 10% benchmark. In the forseen future, it would be a vital part of our energy solution. In addition, Samsung has applied active-matrix organic light-emitting diode (AMOLED) technique to their mobile phone displays. As the production cost goes down, OLED would be the replacement for the current LED displays.

Compared with OLED and OPV, organic spintronics research is still in its infancy. It is an emergent field and lots of efforts are needed to make advancements.

Let us remember the famous scene from the 1967 film “The Graduate”.

Mr. McGuire: I want to say one word to you. Just one word.

Benjamin: Yes, sir.

Mr. McGuire: Are you listening?

Benjamin: Yes, I am.

Mr. McGuire: Plastics.


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