Chapter 1

Introduction to organic spintronics

1.1 Spintronics

The electron spin, an intrinsic magnetic moment derived from quantum mechanics, has been a fascinating subject of interest; playing an important role in our everyday life. Utilizing these spin states in electronics has lead to the field of spintronics that has revolutionized the realm of data storage, sensing and power applications, providing major technological impacts to the life of people [1]. One of the major technological breakthroughs of spintronics is in data storage industry [2]. The discovery of giant magnetoresistance (GMR) effect [3], used in a read-head sensors in hard drives has allowed to increase the storage density to ~1 Tbyte/inch² and more. This field received a special recognition with a Nobel prize for Physics in 2007 [4]. Currently, there is an increased activity from materials research perspective to understand and develop spintronics devices using new interesting materials like, carbon nanotubes, graphene, topological insulators and also organic semiconductors (OSs) for technological applications.

This chapter begins with the investigation of fundamental aspects of electron spin in materials and, next, describes some of the essentials of the spin transport mechanisms in devices, such as the tunneling magnetoresistance (TMR) effect in magnetic tunnel junctions (MTJs) and the GMR effect in spin valves (SVs).
1.1.1 Electronic band structure of Ferromagnets

The notion of a band structure arises from the overlap of the electron wavefunctions, having a spatial and a spin component, forming a solid. Ferromagnetism in such solids arises due to the long range ordering of the electron spins and their angular momentums [5] resulting in an uncompensated total magnetic moment. The electrons total magnetization has two contributions, orbital and spin angular momentum, \( \mu = -\mu_B (g_L \hat{L} + g_S \hat{S}) \); \( \mu_B = 57.9 \mu eV/T \) is the Bohr magneton, the free electron magnetic moment and \( g \sim 2 \) is the g-factor. \( g_L = 1 \) for free electrons but scales inversely with the electron effective mass. In most FM solids, the orbital moment is observed to be almost completely quenched with the spin moment contributing nearly 90% or more of the total moment.

In 3d-transition metal ferromagnets (FMs), like Fe, Co and Ni, the d-bands lie close to the Fermi level and have small bandwidths in the order of 5 eV, which are much smaller than the bandwidths of spherically symmetric delocalized s-bands. Due to their narrow bandwidth, the density of states (DOSs) of d-electrons at the Fermi level \( N(E_F) \) increases and they satisfy the Stoner criterion for ferromagnetism \( N(E_F) \times I > 1 \) [6], where I is the Stoner parameter and represents the intra-atomic exchange and correlation effects. As a result, there is a parallel coupling of the d-electrons that leads to ferromagnetism and exchange splitting on the two d-spin bands by \( \sim 1 \) eV. The calculated DOSs for the transition metals, Copper (Cu), Cobalt (Co) and Iron (Fe) are shown in Figure 1-1 [7]. Special to the case of Co, the DOSs of the minority d-band \( N^-(E_F) \) is larger than the DOS of the majority d-band \( N^+(E_F) \) at the Fermi level. In certain cases, this property has been shown to give rise to negative TMR effect in MTJs [8]. For the case of Ni, Fe and LSMO (oxide ferromagnet), the opposite holds true i.e. \( N^-(E_F) < N^+(E_F) \).

However in FMs, electrical transport occurs via the delocalized s-band electrons at the Fermi energy. However, due to a significant s-d coupling at the Fermi energy, the conduction s-electrons become aligned and this process leads to the generation of spin-polarized carriers.
1.1.2 Magnetoresistance effect

A discussion in the area of spintronics is always incomplete without describing the phenomenon of MR effect. MR is the change the resistance of the device on application of a magnetic field. In the literature, different kinds of MR effect have been reported, such as the anisotropy magnetoresistance (AMR), GMR, TMR, colossal magnetoresistance, extraordinary magnetoresistance, and organic magnetoresistance (OMAR) effect. In this section, we shall describe the GMR and the TMR effect, limiting the contents within the realms of this thesis work.

Figure 1-2 shows a sketch of a typical GMR device, also referred to as a spin-valve (SV) device. Here, the two FM layers are separated by a non-magnetic spacer layer to form a tri-layer device. The two FMs are chosen to have different switching fields (coercivity), such that parallel and anti-parallel alignment of the layers could be achieved by changing the strength of an external magnetic field. When current flows through the tri-layer, the electrons which have spins aligned parallel to the magnetization of the FM layer experience less scattering. On the contrary, when the
Figure 1-2: GMR effect (top): In a GMR device, the two FM layers are separated by a non-magnetic spacer layer. When the magnetization direction of the two FMs are aligned parallel (up-direction), the spin-down electrons sees a low resistance path (shown by the resistor model) compared to the spin-up electron. This gives a low resistance state to the devices. In the anti-parallel state, both the spin-up and spin-down electrons scatter equally and the device is in a higher resistance state. TMR effect (bottom): In a TMR device, two FMs are separated by a thin insulating layer. The different tunneling probability of the two spin channels, due to spin-dependent DOSs of the FMs, in the parallel and anti-parallel alignment of the FMs lead to TMR.
electron spins are aligned antiparallel to the FM layer, they experience a stronger scattering. Thus, when the two FM are aligned parallel, scattering is weak and this leads to a lower resistance state ($R_P$). And when the two FMs are aligned antiparallel, strong scattering leads to a high resistance state ($R_{AP}$). One can reproducibly switch between these two states by simply sweeping an external magnetic field. This gives rise to the GMR effect. The MR in these cases depends on the relative alignment of the magnetization of the two FMs and can be defined as

$$MR = \frac{(R_{AP} - R_P)}{R_P} \times 100$$  \hspace{1cm} (1.1)

If one replaces the non-magnetic spacer layer by a thin insulating layer, a new kind of device called the MTJs is formed (see Fig. 1-2). The MR in these devices arises due to the process of spin-conserved tunneling across the thin insulator barrier. In 1995, Moodera et al. [9] and Miyazaki et al. [10] reported MR signal in such a device, which is appropriately called the tunneling magnetoresistance (TMR). Currently, TMR signals much above 200% are possible at room temperature and hence have found immediate application in the hard drive industry as read-head sensors.

Spin-conserved tunneling is an extremely interface sensitive phenomenon, in which the spin transport properties depends primarily on the DOS of the spins at the interface between the FM and the barrier. The bulk of FM does not play any role in the TMR effect. The tunneling current is in the first order proportional to the product of the electrode’s DOS at the Fermi level. In the FM electrodes, the DOS of the majority and the minority bands at the Fermi level are different (see section 1.1.1) and this difference leads to an asymmetry in the tunneling current for the two separate spin channels. Assuming spin conservation during tunneling, Julliere formalized a simple model to relate TMR with the properties of the FM at the interface, given by [11]:

$$TMR = \frac{2P_1P_2}{1 - P_1P_2}$$  \hspace{1cm} (1.2)
with

\[ P_{1,2} = \frac{(N_{1,2}^{maj} - N_{1,2}^{min})}{(N_{1,2}^{maj} + N_{1,2}^{min})} \]

where \( P_{1,2} \) is the spin polarization of the two FMs (denoted by 1 and 2) determined by the difference in the DOS \((N)\) of the majority \((maj)\) and minority \((min)\) spins at the Fermi level and additionally at the top and bottom interface with the barrier. However, it is important to realize that not all the electrons present at the Fermi level can effectively tunnel through the barrier. As mentioned before in section 1.1.1, it is the spherically symmetric s-like electrons which are delocalized, non-spin split and having a much lower DOS that dominate the tunneling process. Nonetheless, the above expression captures the basic physics of the presence of the MR effect and the relevance of magnetic character of the interface between the FM electrode and the barrier.

### 1.2 Organic semiconductors

OSs are \(\pi\)-conjugated molecular systems which are composed of light elements like C, H, O and N. In some OSs, the molecules also contain heavy atoms that provides additional functionality to OSs, e.g. introducing Ir in the molecule Ir(PPy) induces spin-orbit coupling that affects its optical properties [12]. The \(\pi\)-conjugated molecular structure consists of sp\(^2\)-hybridized C atoms that forms the backbone of the molecule. The lone p\(_z\) electrons in these C atoms couple with each other, both above and below the backbone plane, to form a delocalized electron system. These delocalized electrons give rise to molecular energy levels responsible for the electrical and optical properties of the OSs. The two important energy levels in the study of OS are the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level, similar to the valence band and the conduction band in inorganic solids. The HOMO-LUMO gap of the molecule determines its optical properties. Interestingly, it is these individual molecular levels, rather than the energy bands, which are responsible for the interesting opti-
Figure 1-3: Molecular structure and the HOMO and LUMO energy levels, with respect to the vacuum level, is shown for the non-planar OSs: Alq$_3$ & Rubrene and planar OS: CuPc.

cal properties of OSs. Figure 1-3 shows the HOMO-LUMO energy levels in the three mostly commonly studied OSs, tris(8-hydroxyquinolinato)aluminium (Alq$_3$ - C$_{27}$H$_{18}$AlN$_3$O$_3$), 5,6,11,12-tetraphenylnaphthacene (rubrene - C$_{42}$H$_{28}$) and copper Phthalocyanin (CuPc - C$_{32}$H$_{18}$N$_8$).

In the bulk and thin films of OSs, molecules bond together by the weak van der Waals’ intermolecular forces. Such an interaction weakens the electronic coupling between the molecules that considerably reduces the bandwidth (~0.1 eV) of the HOMO and the LUMO levels in OSs (compared to 10 eV in Si) [13]. As a result, OSs show very low mobility. Further, when the charges reside in a molecule, they locally distort the potential by polarizing the molecules around them, leading to the formation of polarons. Such effects increase the effective mass of the charge carriers and also contribute to the reduced mobility. The presence of defects and impurities also affects the conduction. All these processes make transport studies challenging,
OSs have some unique characteristics that have contributed to the advancement of organic electronics. OSs can be grown using cheap processes like thermal evaporation, vapor phase deposition, roll-to-roll contact printing, solution-based ink jet printing, and imprint lithography [13]. Due to their insensitivity to variations in large-scale structure, and amenability to low-temperature processing, amorphous organic thin films are well-suited for flexible substrates. Also, their optical properties are governed by single molecules which is one of the virtues in this field. Their excellent optical properties have also lead to their use in OLEDs and OPVs. However, on the negative side OSs are prone to degradation. They are readily oxidized or reduced to form different chemical species, most commonly with atmospheric oxygen and moisture. A good encapsulation is hence a must to prevent any degradation effects. Furthermore, weak intramolecular bonding can cause significant structural changes over time, often activated by the presence of charge or simply by Joule heating. Amorphous layers may polymerize or crystallize. Also, thermal evaporation of metal contacts onto soft OS layers can damage them.

1.3 Organic spintronics

Organic spintronics is an emerging field of research that deals with the study of spin injection, transport and manipulation in OSs [14–16]. The last couple of decades have seen considerable activity in the use of OSs in the development of organic electronic devices, such as organic thin-film transistors (OTFTs), organic light emitting diodes (OLEDs) [17] and organic photovoltaics (OPVs) [7, 18]. These developments were possible due to the ability to chemically tune the OS properties at the molecular level, from a bottom-up approach, and to develop cheaper and flexible devices. Only recently, in the last eight years, has there been a major drive to integrate them in spintronics. The spin-orbit (S-O) interaction and the hyperfine interaction, are generally the two mechanisms that are responsible for spin decoherence in a material. These interactions are found to be weak in OSs. The S-O interaction scales with the
Figure 1-4: Hyperfine interaction in OSs arises due to a collective response of the hyperfine fields ($B_{hf}$) created by the hydrogen nuclei in the molecule. In disordered OSs, carriers hop from one molecule to the other ($i \rightarrow j \rightarrow k$). A large residency time of the carriers within the molecule leads to stronger hyperfine interactions causing spin decoherence.

atomic number ($Z$) as $Z^4$, and since the OS molecule is composed of light elements, like C, H, O and N, these interactions are very weak. The S-O interaction, however, is also responsible for the ability to externally manipulate the spin states in the material using electrical (gate voltage in spin-FETs) [19] or optical (circularly polarized light in spin-LEDs) [20, 21] methods. As a result of the weak S-O interaction, these methods do not provide a control on the spin states. Thus, although these traits bring in challenges, they are combined with the vast opportunities to discover newer fundamental phenomena, with the possibility to achieve technological breakthroughs in the future.

While the S-O interactions are weak, interestingly, the hyperfine interactions are observed to play a very dominant role in spin decoherence in OSs [22] (see Fig. 1-4). In the earlier studies, the influence of hyperfine interaction on the spin-dependent properties in OSs was assumed to be negligible. Such an assumption was based on the study that the charge carriers reside in the $p_z$ orbitals of the C atoms, which have a nearly zero-overlap with the hyperfine fields of the C nucleus. However, over the years, it has been widely accepted that each hydrogen nuclei in the molecule generates its own hyperfine fields, and they collectively lead to a significant spatial
overlap with the p$_z$ electron cloud in the OS. Such a collective response makes the hyperfine-field interactions stronger and give rise to many interesting effects, such as the magnetoluminescence effect [23, 24] and also recently, the OMAR effect [25].

One of the important microscopic parameter that determines the spin-dephasing of the carriers residing within the molecule is the spin lifetime ($\tau_s$). Typical spin lifetimes in OSs are relatively long, over 10 $\mu$s [26, 27], which are much longer compared to few tens of ns observed in inorganic counterparts, like Si, GaAs and other III-V semiconductors [1, 28]. In polycrystalline and amorphous films, these molecules are weakly held together by van der Waals’ forces that leads to a hopping transport with mobilities much less than 0.1 cm$^2$/V-s (compared to mobilities higher than 100 cm$^2$/V-s in inorganic counterparts). As a result, the carriers spend sufficiently long time within the molecule, and their interaction with the hyperfine fields scatter the spins. Other factors, like the impurities, defects and phonons also contribute to spin scattering. All these processes put a limit on the distance upto which the spin information can be transported in these materials. This length-scale is referred to as the spin diffusion length ($\lambda_s$). In various OSs, a $\lambda_s$ of only few tens of nm are reported in the literature [15]. However, in most of these studies, the determination of $\lambda_s$ is made on amorphous films of OS that have very low mobility. Studies on polycrystalline or ordered films of OS are expected to improve the spin transport length.

In the last couple of years, with many relevant reports in the literature, interest has developed to study the complex interface-magnetism mechanisms that strongly affect the spin injection process [30–32]. The inherently complicated 3D structure of the OS molecules brings bigger challenges, to achieve sharp interfaces with the ferromagnets (FMs), and also in some cases, to control the interface chemistry that is influenced by the different bonding sites within the molecule structure (changing its molecular orientation at the interface). The latter issue in its entire resplendency can inevitably affect the interface magnetism - crucial for organic spintronics. Recently, a novel approach, using a spin-polarized scanning tunneling microscope, to explore the spin-dependent injection processes at the interface has gained interest [29] (see Fig. 1-
5). By using such novel approaches, spin injection studies on single molecular layers adsorbed, physically or chemically, on an FM film has given very interesting insights. Effects like the spin-injection amplification and the spin-injection inversion at the interface between the FM and the OS have been observed [33, 34]. Such a response is explained by the formation of new hybridized states, that strongly affects the band structure at the interface and, therefore, its electronic and magnetic properties. Thus, the above bottom-up approach can be foreseen to contribute majorly to control and to tailor such interface-magnetism mechanisms.

Over the coming years, the field of organic spintronics is only likely to grow and evolve towards new horizons, requiring a multidisciplinary approach to encompass the knowledge of physics, chemistry, and materials sciences. Some of the areas that have huge potential in the future includes - using chemistry to tailor interface properties for sensor applications, synthesizing novel functional OSs with tunable magnetic proper-
ties (e.g. organic FMs), organic spin-filters and the integration of organic spintronics with spin-excitonics and biophysics. Certainly, the above are only a small subset of the different areas where organic spintronics can make a huge impact in future science and engineering.

1.4 Thesis work

Chapter 1 gives an overview of the field of spintronics and presents the fundamental mechanism of the GMR and TMR effect. Subsequently, the relevance of OSs in spintronics is discussed.

Chapter 2 presents an overview of the developments in the field of organic spintronics. Major findings and discussion since its birth in 2002 up till the recent developments is discussed.

Chapter 3 provides a description of the growth, fabrication, measurement and interface characterization tools that were used in the study of organic devices. For interface studies, a wide number of tools, such as inelastic tunneling spectroscopy, SQUID, x-ray absorption spectroscopy and polarized neutron reflectometry, were used.

In Chapter 4, spin tunneling transport measurements in rubrene based organic magnetic tunnel junctions (OMTJs) is shown. Depending on the morphology of the rubrene molecule at the bottom interface, different response in the MR signals was observed. This was found to happen due to the different interface electronic coupling caused by the different molecule morphologies affecting spin injection.

Chapter 5 focuses on the properties of the top interface. The growth of FM on organic molecules is expected to be complex and give rise to varied interface magnetic response. In this regard, SQUID, x-ray absorption spectroscopy and polarized neutron reflectometry were used to study the interface-magnetism properties on rubrene-based devices.

Following the study on OMTJs using conventional FM sources, Chapter 6 shows a novel technique to inject spin-polarized electrons into rubrene using the spin-filter material EuS. Spin transport studies in these devices showed an unconventional bias
dependence of MR and suggested the possibility of realizing spin-filter effect in organic systems.

The work in Chapter 4 and Chapter 5 showed that the morphology of the molecule strongly influences the nature of interaction at the interface. Chapter 7 presents spin-transport measurement studies performed on a planar molecule with phenalenyl-based radicals that consist of an unpaired spin. These planar molecules show interesting properties giving rise to a spin-filter effect at the interface leading to a new form of magnetoresistance, interface magnetoresistance.

Chapter 8 is reserved for conclusion and to discuss the future of this field and present ideas that may foster new directions and potentials in organic spintronics.

Appendix A discusses the growth and fabrication of single crystal rubrene based spin-OFET devices.

Apart from the thesis work, Appendix B discusses a novel technique called the shadow evaporation technique that was developed to fabricate (inorganic based) nano-junction spintronic devices in the group.