

Chapter 2

Why Bring Organic and Molecular Electronics to Spintronics

In the previous chapter we introduced few spintronic concepts that will allow to understand the effects observed in this work. Before starting the discussion on the organic spintronics field, a brief introduction on organic and molecular electronics and the specificities of molecules is also necessary to understand the advantages that these systems can bring to spintronics.

2.1 Introduction to Organic and Molecular Electronics

Since the '70s the electronic properties of organic materials have raised an increasing interest in the scientific community. While organics were traditionally considered insulating, in 1977 A.J. Heeger, A. MacDiarmid and H. Shirakawa [1] discovered the possibility to dope a polymer and make it semiconductor. This discovery opened a new conception of organic materials and the idea to replace classical silicon with organic semiconductors to fabricate low cost electronic components arose. The important discovery of conductive polymers was rewarded in 2000 with the Nobel prize in Chemistry and nowadays this research field is called **organic electronics**. Products based on active thin-film organic devices are already in the market place and other devices are being developed. Some examples are the very bright and colourful thin displays based on organic light emitting diodes (OLEDs), the organic photovoltaic cells (OPVs) for low-cost solar energy generation and the organic field effect transistors (OFETs). This technology sets great promise for the near future with an entirely new generation of *ultralow-cost, lightweight and flexible* electronic devices. An example is shown in Fig. 2.1a.

Another highly promising branch of organic systems is **molecular electronics**: looking at the ultimate downscaling for behind CMOS and relating to the study of devices formed by single or few molecules. This field was born in 1971 when B. Mann and H. Kuhn measured the tunnel current through an insulating molecule with the objective to study its electronic properties [3]. In 1974 M. Ratner and A. Aviram proposed a method to make a rectifier based on a single organic molecule

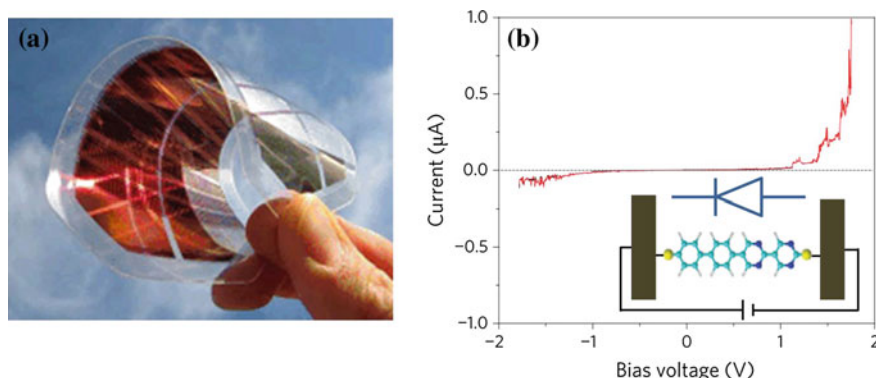


Fig. 2.1 **a** Example of flexible organic photovoltaic cell. **b** Example of a molecular rectifier formed by a non-symmetric dipyrimidinyl-diphenyl molecule bound to two electrodes. In the graph is represented the typical I–V characteristic. A schematic of the device and its electrical equivalent are represented in the inset. Adapted by permission from Macmillan Publishers Ltd: Nature Chemistry [2], copyright 2009

[4]. Their work sets the basis to the idea that, if it is possible to link the chemical structure of a molecule to its electrical behaviour, it must be potentially possible to replace every electric component with the appropriate molecule. One example of molecular rectifier device is shown in Fig. 2.1b. The possibility to replace an electrical component with one single molecule could represent a final *miniaturization* for devices. For these reasons molecular electronics is often proposed as a candidate to overcome the possible downscaling limitations in silicon. Very interestingly, since the electrical properties of organic molecules can be altered by molecular design and synthesis, this offers in theory unlimited possibilities for technological development of functional devices based on the properties of a single molecule.

The *versatility* of chemistry is thus one strong advantage since it is relatively simple from a chemical point of view to change properties from one molecule to the other with just very small variations.

2.2 Main Difference Between Organic and Inorganic Materials

To understand the key advantages brought by molecules to organic spintronics, it is important to remark the substantial difference that exists between an organic and inorganic material, as represented in Fig. 2.2.

While inorganic materials are formed by a continuum of states and electrons are delocalized within the bands (Fig. 2.2a), organics are composed by discrete levels (Fig. 2.2b). Every level is associated to a molecular orbital that can be strongly localized on a group or bond of the molecule, or delocalized on the whole (or large part)

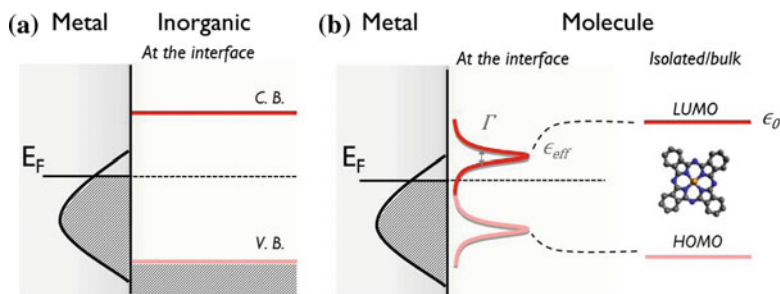


Fig. 2.2 Schematic representation of **a** the interface between a metal and an inorganic material such as a semiconductor or insulator versus **b** what happens when an isolated molecule is brought in proximity with a metallic surface. For simplicity, a flat band configuration is used for the semiconductor in the first few nanometers from the interface. As opposed to the inorganic materials, molecules present discrete levels. When interacting with the metal, the initial discrete levels of the isolated molecule broaden and shift relative to the density of states of the metal. Reference [5], reproduced with permission

of it. The two orbitals that are involved in the charge transport are the “Highest Occupied Molecular Orbital” (HOMO) and the “Lowest Unoccupied Molecular Orbital” (LUMO) that are separated by a “gap”. These orbitals can be compared to the valence and conduction bands of inorganic semiconductors. In the case of inorganic materials electrons are delocalized on the crystal and give rise to bands, while this is mainly not the case in a molecule.

2.2.1 Behaviour at the Interface

Let see now what happens when a molecule, from isolated, is brought in proximity to a metal. First we consider a discrete and isolated molecular level, for example the LUMO of Fig. 2.2b. Being isolated, the lifetime of this state is infinite, and its energy ϵ_0 is precisely known (the time-energy equivalent to the Heisenberg uncertainty principle). But, what happens to this at an interface in a device? When brought in proximity to a metallic electrode, the initially isolated molecular level gets progressively hybridized by coupling with the many states of the metal. This leads to two main effects:

- the lifetime (τ) of the molecular level becomes finite since the charge has a certain probability to escape to the metal. As a consequence, the energy δE is no more completely defined, resulting in the level **energy broadening** with a finite width $\Gamma \approx \hbar/\tau$ which, in the first approximation, is proportional to the density of states (DOS) of the metal. Depending on the strength of the interaction this broadening can range from below the meV up to the eV range [6].

- an **energy shift** of the molecular level from the initial position of the isolated molecule ε_0 to the final ε_{eff} one also results from the interaction with the metal. This shift is dependent on the metal DOS and includes, among other contributions, the combined effects of interfacial dipoles or image forces [7].

2.2.2 Electronic Properties of Molecules

We will briefly review here some ideas about the main features of transport properties through isolated molecules and molecules organized in a thin layer.

Isolated Molecule

We start by considering the simple case of an isolated molecule. The properties of a molecule depend on its chemical structure and on the energy position of its orbitals. For example, in the case of an alkane and alkene chain, the different electronic properties of the two molecules depend on the orbital hybridization of carbon atoms.

In Fig. 2.3a is shown the structure of an alkane chain which is insulating. Carbon atoms present an hybridization sp^3 and their σ orbitals are bonded to two neighbour carbons and to two hydrogen atoms. As shown in Fig. 2.3b, the σ orbitals of two carbons are frontally overlapped and they form a node on each carbon atom which prevents the electron delocalization on the whole chain. The molecule is thus insulating and the HOMO-LUMO gap has been calculated and experimentally measured [8] to be around 8–9 eV. Since the orbital overlap is too weak, gap value is not expected to change a lot with the chain length of the molecule.

On the contrary, one example of semiconductor molecule is an alkene chain (Fig. 2.4a) where carbon atoms present an hybridization sp^2 . Here the three σ orbitals are bonded to two neighbour carbons and one hydrogen atom, while the p_z orbital out of plane overlaps with the neighbouring p_z orbitals (Fig. 2.4b). This overlap results in the formation of π -bonds that allow a delocalization of the π -electrons along the molecule. This leads to the formation of two thin energy bands. The delocalized electrons occupy the bonding π -orbitals, while the anti-bonding π -orbitals remain

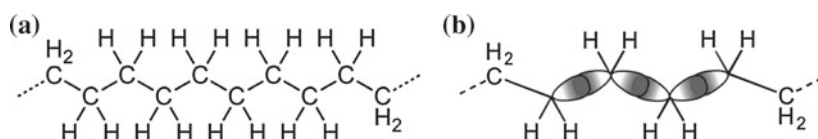


Fig. 2.3 **a** Structure of an alkane chain. Carbon atoms present an hybridization sp^3 and they are bonded one to each other through σ orbitals. **b** This forms a node on each carbon and prevents electron delocalization, making the molecule insulating

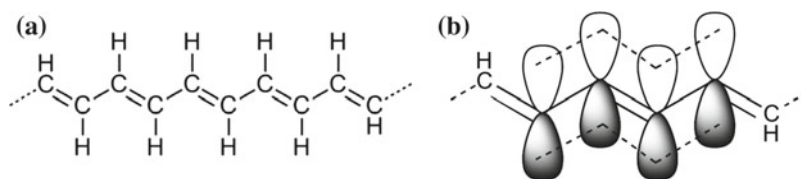


Fig. 2.4 **a** Structure of an alkene chain. Carbon atoms present an hybridization sp^2 . They form σ -bonds with the adjacent carbons and the p_z orbital out of plane overlaps with the neighbouring p_z orbitals **b** allowing the delocalization of electrons on the molecule. This makes the molecule to be semiconductor

empty. The gap for these molecules is smaller than the saturated chain and its value is about 1–3 eV. Moreover, since the orbitals are overlapped, in this case the value of the gap is expected to change with the length of the molecule.

Molecular Layer

We will see now what happens if molecules are grouped to form a thin molecular layer. Molecules can be organized in an amorphous, polycrystalline or crystalline phase depending on the deposition conditions. They interact each other through Van der Waals interactions and this assures the layer cohesion. Van der Waals forces that exist between molecules are weaker than covalent or ionic bondings, that are typical of inorganic crystals, and this is the cause of the lower rigidity of molecules in comparison to inorganic materials.

Moreover, the orbital overlap between adjacent molecules is often weak and it prevents (or almost prevents) the electrons delocalization on more molecules. Depending on the orbital overlapping there can be two conduction regimes: (i) *band transport* when the overlap between π -orbitals is strong enough to allow the delocalization of charges in an energy band formed by a quasi-continuum of states (Fig. 2.5a). (ii) *Hopping transport* where charges jump from one localized state of a molecule to another (Fig. 2.5b).

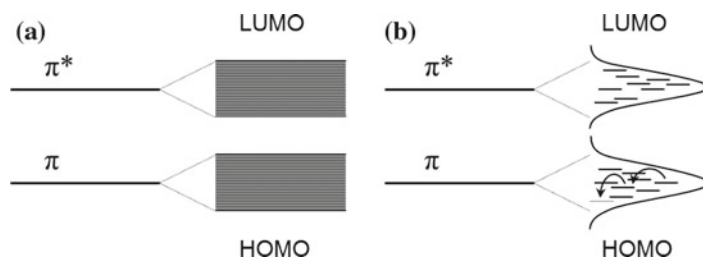


Fig. 2.5 **a** Representation of the structure for band transport. If the overlap between molecules is strong enough, the overlap of bonding and anti-bonding π orbitals leads to the formation of energy bands formed by a quasi-continuum of states. **b** Representation of the structure for hopping transport. In an amorphous material disorder leads to a dispersion of localized states. Transport occurs by hopping and it is assisted by phonons

Depending on the molecule itself, its interactions and defects (as dopants...), it is possible to find molecules with every characteristic: insulators, semiconductors, metallic and even superconductors.

However, in reality no many molecules behave as a metallic or semiconducting inorganic crystal with band transport such as TTF-TCNQ [9] but the majority of molecules presents a hopping transport. This is often due to an amorphous organisation of the molecules and the weak interaction between them. The charge hopping between localized sites can be described by phonon assisted tunneling. One example of semiconductor molecule behaving like this is the largely used Alq₃.

The weak orbital overlap is also at the origin of the low charge mobility that is usually found in organic materials. Normal values are between $10^{-6} - 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$ (for example charge mobility in Alq₃ is $\mu_e = 1.4 \times 10^{-6} \text{ cm}^2/\text{V} \cdot \text{s}$ [10]). The limit value between hopping transport and band transport is normally fixed around $1 \text{ cm}^2/\text{V} \cdot \text{s}$ [11]. Examples of high mobility molecules are rubrene ($10 \text{ cm}^2/\text{V} \cdot \text{s}$) [12] or C8-BTBT [13] with a record mobility around $43 \text{ cm}^2/\text{V} \cdot \text{s}$. To compare, mobility values usually found in inorganic semiconductors as Si are $\mu_e \approx 1500 \text{ cm}^2/\text{V} \cdot \text{s}$ and $\mu_h \approx 500 \text{ cm}^2/\text{V} \cdot \text{s}$.

In conclusion, we have seen in this section that the different structure between an organic material, formed by discrete levels instead of a continuum of states, and an inorganic one, leads to fundamental differences. These can be summarized with:

(i) an energy shift and broadening of the molecular states at the interface with a metal.

(ii) weak Van der Waals interactions resulting in a transport in the bulk material mainly governed by charges hopping, leading to a lower mobility of molecules in comparison to inorganics. But, as a counterpart, the weak Van der Waals interactions are also at the base of molecules flexibility properties.

We will see in the next section how some of these characteristics give rise to specific advantages for organic spintronics that are not achievable with inorganic materials.

2.3 Advantages of Organic and Molecular Materials for Spintronics

Organic spintronics is a very recent and promising field that combines the potential of chemistry to the non-volatility and the spin degree of freedom of spintronics towards electronics for beyond CMOS applications.

From the merging of these two domains the main advantages of organic spintronics can be resumed in three baselines:

- The first advantages are the ones of organic electronics vs. classical electronics. They can be resumed in the potentiality to implement *flexible, low production cost and large area easy-processing* electronics.

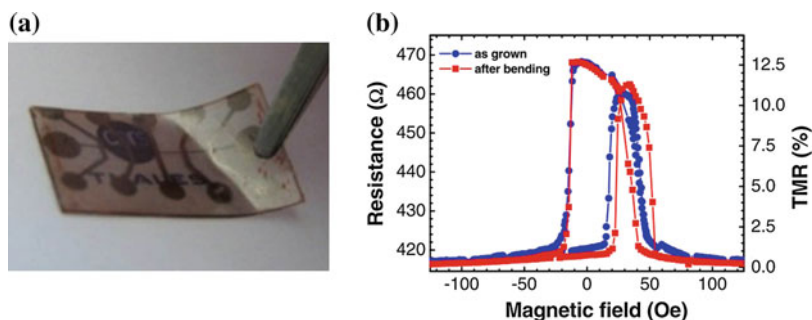


Fig. 2.6 **a** Picture of a flexible Co/Al₂O₃/Co MTJ grown on a polyester organic substrate. **b** TMR curves recorded before and after the device bending. No difference could be recorded in the signal demonstrating that bending is not damaging the device. Reprinted with permission from [14]. Copyright 2010, AIP Publishing LLC

The possibility to combine spintronic devices with flexible substrates was first proposed in 1992 [15] and has been already demonstrated with prototype devices [16–19].

For example, in Fig. 2.6 is shown a Co/Al₂O₃/Co magnetic tunnel junction grown on a polyester organic substrate [14]. After twisting and bending the MTJs, the TMR signal is maintained unchanged. This indicates that spin dependent tunneling properties are preserved and demonstrates that MTJs based spintronic devices are compatible with embodied flexible organic electronics.

- One of the main advantages that initially attracted much of the attention to organic materials is their expected *longer spin lifetime* [20, 21]. At the origin of this effect is the low spin-orbit coupling due to the low-weight atoms from which organic materials are composed of (spin-orbit coupling scales with Z^4 , where Z is the atomic number). Moreover, hyperfine interactions are also weak in organic materials since transport mainly occurs through π -orbitals and the spin of mobile carriers is weakly sensible to spins of the nuclear atoms of the molecule. As a consequence, the spin of a carrier weakly interacts in the organic environment and the spin information can be potentially maintained for a long time. For these materials, spin lifetimes in the μ s range and higher have been predicted [22] and deduced by experiments [23]. To compare, the typical spin lifetime in an inorganic metal or semiconductor is in the *ps* range or maximum *ns* range.

This property of organic materials could be exploited for spin manipulation into molecules and for the spin transport. However, spin transport has to face with the drawback of low carrier mobility presented by most of the organic materials (normally $\mu \simeq 10^{-5} - 10^{-2} \text{ cm}^2/\text{V} \cdot \text{s}$) that limits the spin diffusion length to some tens of nanometers. Very interesting materials in this regard are carbon nanotubes and graphene that present a high mobility around $10^4 \text{ cm}^2/\text{V} \cdot \text{s}$ and where long spin diffusion lengths $>100 \mu\text{m}$ could be measured [24].

- Finally, it has been recently unveiled that new spintronics tailoring opportunities, unachievable or unthinkable with inorganic materials could arise from the chemical versatility brought by molecules and molecular engineering. It has been

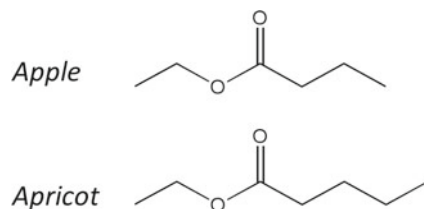


Fig. 2.7 Chemical structure of the molecule responsible for **a** apple flavour and **b** apricot flavour. The difference of just a carbon atom in the molecule leads to completely different properties

shown that spin-polarized hybridization at the ferromagnetic metal/molecule interface can drastically influence the spin transport properties of molecular spintronic devices and provide new functionalities beyond that of conventional inorganic ones. Indeed, the interface hybridization can be used to tune the spin polarization and thus the spintronic device properties [25].

As already remarked before, chemistry is extremely *versatile* and it is possible to find molecules with all the functionalities of inorganic materials. The choice of molecules is unlimited and molecules present very reach functionalities as optical switchers or molecular magnets. It is also relatively simple from a chemical point of view to change properties from one molecule to the other. One example is reported in Fig. 2.7 where adding just one C atom, the molecule changes from the flavour of apple to the one of apricot. Hence, thanks to chemistry versatility it is possible to envisage the possibility to *engineer at the molecular level* the spintronic properties of the devices.

All these advantages motivated an increasing interest in the field of organic spintronics. However, this field not only combines the advantages of the two domains that it fusions but also, unfortunately, their technological problems. For example from spintronics it gets the high sensitivity to interfaces, while from molecular electronics it gets the difficulty to fabricate contacts on molecules. All these points will be described more in details later in the manuscript. In the next section we will start by briefly presenting the state of the art in organic spintronics.

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Monolayers

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