## 1. Title of the project

Crystalline organic-inorganic hybrid semiconductors with tunable spin polarization.

## 2. Applicant

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G14

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## 5. Abstract

There is an increasing interest to develop organic semiconductors that will provide cheaper field effect transistors. The organic materials, however, cannot compete yet with the classical inorganic semiconductors in terms of mobilities. The proposed research combines the processability of organics with the high mobility and versatility of inorganics by designing π-hybrid materials. These materials are expected to be semiconductors with good field effect properties into which magnetic components can be introduced. In this way an easy processable *ferromagnetic semiconductor* could be made. Such a material would be very interesting for the fundamental study of the magnetic properties of isolated spin chains as well as for spin polarized transport. Moreover, they can be utilized in the design of *spinvalves,* which are of major importance in spintronics. This project explores a totally new field of magnetism in hybrids based on inorganic and π-conjugated organic materials.

## 6. Duration of the project.

4 years, starting from august 2006

## 7. Personnel

### 7.1 Senior scientist

| Name | Main task | Time |
|---|---|---|
| Prof. dr. T.T.M. Palstra | Supervision | 10% |

### 7.2 Junior scientist and technician

| Name | Main task | Time |
|---|---|---|
| MSc A.H. Arkenbout (PhD) | Experiments | 90% |
| Technician | Technical support | 10% |

## 8. Cost estimates

### 8.1 Personnel positions
One PhD position for four years

### 8.2 Running budget
15k€  per year

### 8.3 Equipment
Janis micro manipulated cryogenic probe system, model CCR10-4LF-0-CX (~110 k€). Low temperature (15-325K) probe station that recycles its helium. It has 4 independent probe stations  and is very useful to measure FET properties at low temperatures. The Rijksuniversiteit Groningen will pay 25%  (~27 k€) of this investment.

### 8.4 Other support
The project will be supported by the Material Science Center and Rijksuniversiteit Groningen. They will contribute in the positions of the technician, the senior scientist and the purchase of the Janis micro manipulated cryogenic probe system.

**8.5 Budget summary (In k€)**

| | 2006 | 2007 | 2008 | 2009 | 2010 | **TOTAL** |
|---|---|---|---|---|---|---|
| Personnel (positions) | | | | | | |
| PhD students | .4 | 1 | 1 | 1 | .6 | **4** |
| Postdocs | - | - | - | - | - | **-** |
| Technicians | - | - | - | - | - | **-** |
| Visitors | - | - | - | - | - | **-** |
| Personnel costs | 18 | 43 | 43 | 43 | 25 | **172** |
| Running budget | 6 | 15 | 15 | 15 | 9 | **60** |
| Equipment FOM-part | 83 | - | - | - | - | **83** |
| **TOTAL (requested from FOM)** | **107** | **58** | **58** | **58** | **34** | **315** |

## 9. Research programme

**A.** Introduction
**B.** Motivation
**C.** Goals
**D.** Description of the research
**E.** Plan of work

### A. Introduction

Semiconductors are materials that have a small band gap between the conduction and the valence band due to which the conductivity is very low, in the range of $10^{-4}$ to $10^{3}$ Ωcm. In such materials charge carriers, either holes or electrons, can be introduced in the conduction band by means of heat, light and chemical or electrostatic doping. Semiconductors are widely used in field effect transistors (FET), the set up of which is shown in figure 1. In this device, the gate insulator acts like a capacitor and the electric field applied at the gate electrode determines the charge that accumulates at the interface. The charge carrier density at the interface between the semiconductor and the insulator is increased such that a current can flow through this layer from the source to the drain. In this way, the current from the source to the drain can be tuned by the applied gate voltage. Most of the semiconductors that are used in the industry are based on silicon. Very pure silicon crystals are cut in plates (wafers) that are patterned by lithography. Crystalline silicon has a mobility of 450 $cm^2/Vs$ for holes and 1400 $cm^2/Vs$ for electrons and the on/off ratio [(current in the “on” state)/(current in the “off” state)] of the silicon FETs is in the order of $10^6$ [1]. The high mobility is crucial for data processing as it determines the calculation speed.
Currently most logic is performed with these types of field effect transistors. However, in the future a completely different logic may be used that is based op both the spin direction and the charge of electrons. The idea is that not only charge but also the direction of the spin can be used to produce signals. This technology is called *spintronics* and is very promising because it can combine quantum computing and data storage on one chip, reducing the total area of the computer and increasing the speed.

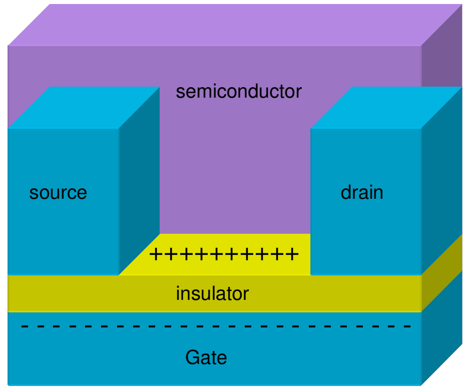


**Figure 1:** In a field effect transistor the source-drain current can be tuned by a gate voltage. For p-type semiconductors, the applied negative gate voltage induces a layer of positive charges in the semiconductor which allow a current to flow from the source to the drain.

## B. Motivation

The recently developed organic semiconductors have some advantages over the conventional inorganic semiconductors. The electric properties of organic materials can easily be tuned by changing the composition. Moreover, the devices can be made by much cheaper processes as spin coating and inkjet printing. And besides, these techniques allow them to be processed on much larger areas than what is possible with the Si-based devices. Examples of good organic semiconductors are pentacene[2] and rubrene[3]. The key factor in organic semiconductors is the dislocation of π electrons over the system, which reduces the band gap. The mobility at room temperature of organic single crystals can be as high as 35 $cm^2/Vs$ in single crystals of pentacene [2]. The first pentacene semiconductors that are implemented in devices are spin coated pentacene FETs that have a mobility of 0.02 $cm^2/Vs$ and an on/off ratio of $10^4$ [4]. The main drawback of these organic semiconductors is that the weak van der Waals interaction between organic molecules imposes an upper limit to the mobility[5]. In combination with the relative poor crystallinity and purity of organic crystals, the charges become localized and the mobility reduced. Thus the switching speed of this kind of materials is too low for high frequency applications like personal computers but high enough for the use in, for example, displays[4].

Hybrid materials consist of layers of organic and inorganic materials and they can be synthesized in the same easy way as organic materials. The electronic properties are expected to be a combination of the bulk properties of the organic material and the inorganic material. Inorganic materials have a higher mobility than organic materials because of the strong electronic overlap between the atoms. Therefore the hybrids are expected to show an increased mobility with respect to the organic crystals, while the synthesis of the crystal is still very easy.

As already mentioned in the introduction, the field of spintronics is very promising for future computation devices. Spintronics is a technology in which both the charge and the orientation of the spin of an electron are used to transport information. In this field it is very important to create conduction electrons with a defined spin orientation and transport, them without this information being lost. To study this spin polarized transport experiments were done in devices (spinfets) in which a semiconductor was placed between two metallic ferromagnets from which the spin polarized charge carries were injected. The barrier for spin injection appeared to be very high in this device and thus it did not function well. It was proposed[6] that the problem could be solved if semiconducting ferromagnets were used instead. As not many semiconducting ferromagnets are known, the magnetic π- hybrids, which are described in this proposal, are of a high interest.

After the polarized spin is created it should be transported without the loss of the polarization direction. One of the means by which the spin polarization can be lost are the scattering processes that are caused by the spin orbit coupling of the atoms in the material through which the electrons are traveling. A rule of thumb is that the spin orbit coupling becomes higher as the atom becomes heavier[7]. Therefore the organic materials show a much smaller spin orbit coupling than the inorganic materials, and it is expected that the spin orientation is much longer preserved. Thus it would be nice to have an organic semiconductor, in which polarized spins can be transported without the polarization loss. The π-hybrids are expected to show the same preservation of the spin orientation as they consist of organic semiconductors and magnetic inorganic chains.

**C. Goals**

The Goals of this project are:

- make an easily processable *ferromagnetic semiconductor* with good field effect properties and a tunable spin polarization.
- fabrication and characterization of a *spinvalve* based on the π-hybrid.

**D. Description of the project**

In this proposed project the properties of inorganics and organics are combined by making hybrid structures, which contain successive layers of organic and inorganic semiconductors. The inorganic layers consist of $MX_2$ (M=metal and X=halide) and forms a backbone to which the organic groups are attached[8]. The organic layers consist of an organic molecule attached to an $NH_3^+$, which connects the organic to the inorganic backbone via a hydrogen like bond with the halide atoms. Hybrid single crystals and thin films can easily be grown from solution [8] [9] [10]. Kagan et al.[9] performed experiments on a field effect transistor with the hybrid $(C_6H_5C_2H_4NH_3)_2SnI_2$ as the semiconductor material. They found a mobility of 0.55 $cm^2/V{\cdot}s$ and an on/off ratio of $10^4$.

The mobility of the hybrid is expected to increase significantly when the organic layers have electronic overlap, which can be realized by using two π-stacked conjugated organic molecules. In the materials made by Kagan et al.[9], no π-stacking was present between the organic molecules and thus the organic material formed an electronic barrier between the one-dimensional inorganic chains. When π-stacked organic layers are used instead, they will form crystalline organic semiconductor channels, which contribute to the mobility as they remove the restricted dimensionality in the material. In this way the hybrid material can become a three dimensional semiconductor with a much higher mobility. The hybrids in which π-stacked semiconducting organic layers are present will be referred to as *π-hybrids*. The synthesis of those π-hybrid materials is based on solution chemistry which needs no expensive equipment.

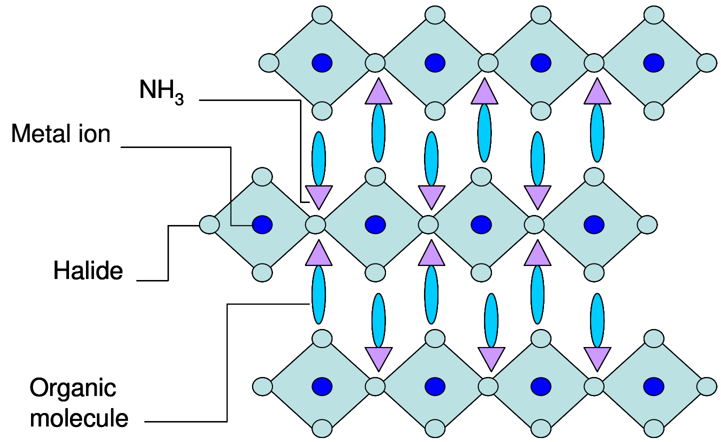


**Figure 2:** A hybrid structure consists of an inorganic backbone to which the organic molecules (denoted by the ovals) are connected via the $NH_3$ group (triangles) .

In comparison with the organic materials a much higher mobility is expected in the π-hybrids caused by improvements in the crystalline and the presence of the inorganic layers, which raise the upper limit in the mobility. The electronic properties can be tuned by changing the ratio of the amount of organic and inorganic as well as the choice of inorganic and organic components. The electronic properties in the broad range of possible π-hybrid materials have a great potential.

The second part of the project is to take advantage of the versatility of inorganic layers and introduce magnetic ions into the π-hybrid structure. In the reported hybrids mostly nonmagnetic metal ions were used like $Sn^{2+}$ and $Pb^{2+}$ [8]. However, the same kind of structures can be expected when a magnetic transition metal is used instead. The magnetic properties of these (magnetically) isolated spin chains have never been studied before. And moreover the interplay between the magnetism in the inorganic layers and the conductivity in the organic cannels could be very promising for the use in spintronic devices.
When these organic materials are combined with magnetically ordered inorganic layers one can make field effect transistor that can generate a spin polarized current (see figure 3). An applied gate voltage will allow a current to flow from source to drain, in the same way as was described by figure 1. The difference in this case is that a very strong magnetic field will be present at the interface of the insulator and the semiconductor as the distance to the ferromagnetic layer is very small (less than 20 Å). Therefore the spin of the carriers in the generated conduction channel will be strongly polarized to lie parallel with the spin direction in the ferromagnetic layers. By changing the gate voltage this polarized current can be turned off and on. And moreover the polarization direction can be switched by changing the direction of the magnetic moments in the magnetically ordered layers by applying an external magnetic field.
When a transistor is made form two π-hybrid materials with different values for the coercive field ($H_{c1}$ and $H_{c2}$) one can create a spin valve (figure 3). In one part the spin polarized current is generated just as is described above.

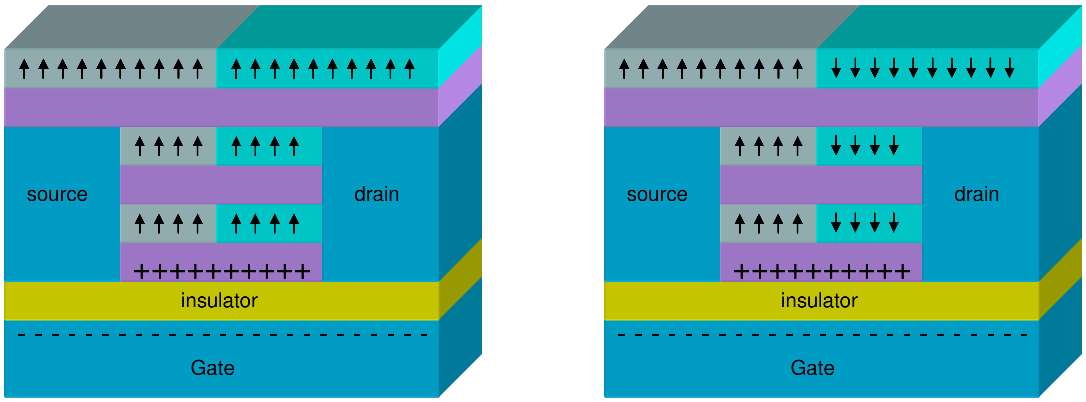


**Figure 3:** A transistor based on two π-hybrids which have different coercive fields can function as a spin valve. The carriers in the conduction channel will be polarized by the magnetic layers. When the two materials have the same orientation (left) the source drain current will be high. However when they are opposite (right) the current will be reduced.

When the polarization in both parts is the same the polarized electrons can easily travel through the channel and generate a current. When a magnetic field (H) is applied for which $H_{c1} < H < H_{c2}$ (just high enough to switch the direction of the magnetic moment in one of the π-hybrids), a situation is created in which the current will be reduced. Namely, the polarized spins that are generated on one site of the device will be repelled by the other part of the FET in which the magnetic moments point in the opposite direction. In this situation the source drain current will be reduced, see figure 4. At higher magnetic fields, $H > H_{c2}$, the magnetic moments in both π-hybrids again point in the same direction and the current is no longer reduced. Thus, the spin polarized current can be tuned by a magnetic field. This spin polarized field effect transistor is very interesting for the study of spin polarized current in organic materials and besides it is a versatile tool in for spintronics in general[11].

**Field effect measurements**

The field effect properties of the π-hybrid will be measured on single crystals to obtain the intrinsic properties of the materials that are less pronounced in thin films because of the presence of grain boundaries. First standard gold electrodes will be used for the hole injection as they work well for other organic materials[2]. Probably, when band structure is known the injection can be optimized by choosing other contact materials in a later stage. The bottom gate set up will be used, in which the π-hybrid will be placed on an Si-wafer that functions as the gate electrode. A thin $SiO_2$ layer will be used as the gate insulator. The field effect properties will be obtained by measuring the I/V characteristics of the FET. In the saturation regime the mobility (μ) of the charge carriers can be extracted from the I/V behavior by the equation:

$$\mu = \frac{L}{W}\frac{1}{C_i}\frac{1}{V_D}\left(\frac{\partial I_D}{\partial V_G}\right)_{V_D \to 0}$$

here w is the gate width and L is the length of the channel. $C_i$ is the capacitance of the gate insulator and $V_D$ and $V_G$ are the drain and gate bias. $I_D$ is the current measured in the trap free region of the space charge limited current.

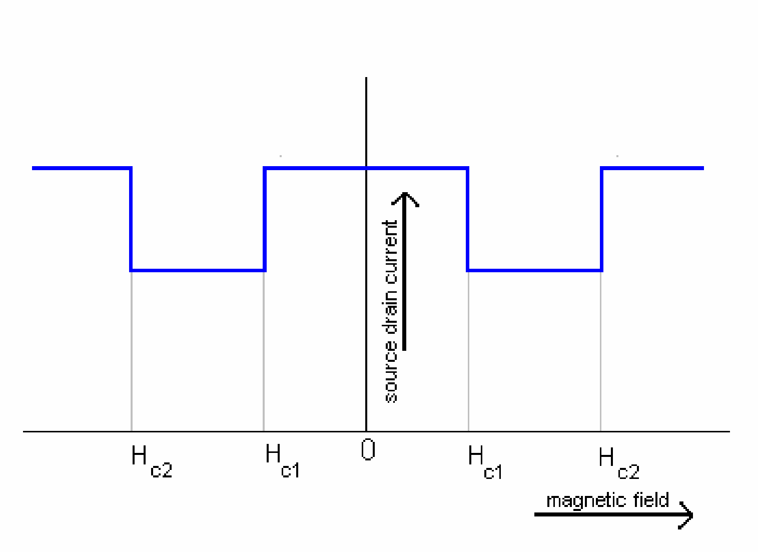


**Figure 4:** The magnetic field dependence in the spin polarized semiconductor as proposed in figure 3. The $H_{c1}$ and $H_{c2}$ refer to the coercive fields of the two different hybrids in the device.

We are aware that the proposed project presents a lot of challenges. The magnetic π-hybrid materials are completely new and it is hard to predict how the magnetization will behave. Therefore it might be hard to realize the ferromagnetic structure at reasonable temperatures even though the bulk properties of the transition metal halides look promising. Another challenge in the synthesis is to achieve the electronic overlap between the organic molecules. This overlap will depend on which organic crystals are chosen but also the lattice parameters of the inorganic chain may influence the electronic overlap. An intrinsic problem with the proposed spin valve is that the inorganic chains in the π-hybrid have a 1 dimensional character that is favorable for the spin polarized transport. However, this reduced dimensionality decreases the mobility, which is not favorable for the field effect properties. Thus, a compromise should be found between this two possibilities. For all the devices that are proposed in this project also some adjustments might be needed with respect to the insulator and contact materials that are used. These adjustments can only be performed when the electronic properties of the material are known, because they strongly depend on the work function and the type of carrier in the material. Another issue with the proposed devices might be the interface effects and the spin injection efficiencies. We believe that the present research will help to solve some of these issues.

## E. Plan of work

The project will take 48 months in total. Below a time schedule is given (in months) for the different stages of the project.

- **1-4:** The first three months of the project will be focused on the design of the π-hybrid material. The criteria for the organic material are that it should be conjugated and show π-stacking with its neighboring molecules. Besides it should be soluble and contain a $NH_2$ group for the connection with the inorganic layer. Examples of good candidates are naphthalene and benzene derivatives. The inorganic material should consist of halogen atoms and magnetic ions. The magnetic interactions in the inorganic layers can be predicted by looking at the bulk properties. The different halides can be used to tune the size of the band gap[8]. Good candidates for the inorganic material are the transition metal halides like $NiI_2$ and $FeI_2$ .

- **5-11:** Subsequently, high quality single crystals will be prepared from these new materials via the established method that is based on wet chemistry, as is described in the literature [8][9][10]. In this part of the research we will collaborate with the organic chemistry groups in our department. Because, although the synthesis is straight forward, not all π-conjugated materials with the required $NH_2$ groups are available. It is expected that the synthesis will cover another six months.

- **12-21:** After the synthesis, the grown crystals will be characterized by single crystal and powder x-ray diffraction to determine the structure of these new materials. Besides the experiments with our lab x-ray sources, synchrotron characterization of the materials will be done to obtain insight in the precise structure of this new material. From these experiments we can also see whether the required π-stacking of the organic molecules is achieved. The same crystals will be used to determine the magnetic properties of the π-hybrid using the Magnetic Properties Measurement System (MPMS).

- **22-29:** The next step is to implement the material in a field effect device so that the mobility and the on/off ratio of the π-hybrid materials can be measured. The methods that are needed for this part of the project can be derived from the methods that were used for the pentacene field effect transistors measurements [2], which were done in our group. In this part of the project the new probe station will be used to determine the I-V curves at various temperatures.

- **30-42:** The last part of the research consists of the characterization of the spin polarized transport in this field effect transistor. The fabrication of the device shown in figure 3 is based on established lithography and spin coat processes. The magnetic field dependence of the source drain current in the device will be determined in the PPMS. As this magnetic field dependence is related to the spin polarized current, this simple current measurements will be very interesting. Other detection methods that can be used to characterize the spin polarized current are photoelectron spectroscopy[12] and the anomalous hall effect[13]. Also in this part of the project we will collaborate with other research groups in the MSC, which are the group of Bart van Wees and Paul Blom, that have ample experience in the field of spintronics and device fabrication.

The remaining 6 months will be used to visit conferences, to write publications and to write the PhD thesis.

## 10. Infrastructure

Most of the facilities that are needed for the proposed project are present in our group. We have the following equipment at our disposal:

- Glove box
- Gold deposition setup
- Huber imaging plate Guinier powder x-ray diffraction setup
- Bruker d8 powder diffractometer
- Bruker Apex single crystal diffractometer
- Quantum Design Magnetic Properties Measurement System (MPMS)
- Physical Properties Measurement System (PPMS)
- Home build FET probe

Other device making tools like spin coat setup and lithography equipment are available via other groups within the Material Science Center.

## 11. Application perspective in industry, other disciplines or society

In spintronics it is attempted to utilize both the spin and the charge of electrons and holes to make efficient computers. An important spintronics goal is to create multifunctional materials that are both semiconducting and ferromagnetic. These materials would allow the possibility of combining logic and data storage on one chip, reducing the total area of the computer and increasing the speed. The proposed project has the aim of producing a ferromagnetic semiconductor by incorporating magnetic ions in a hybrid of organic and inorganic materials. If successful, the project would contribute significantly to the field of spintronics as it provides a versatile tool to manipulate the spin polarized current. Therefore, this research is a valuable attempt to make spintronic materials that might be implemented in the industry.

## 12. References

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