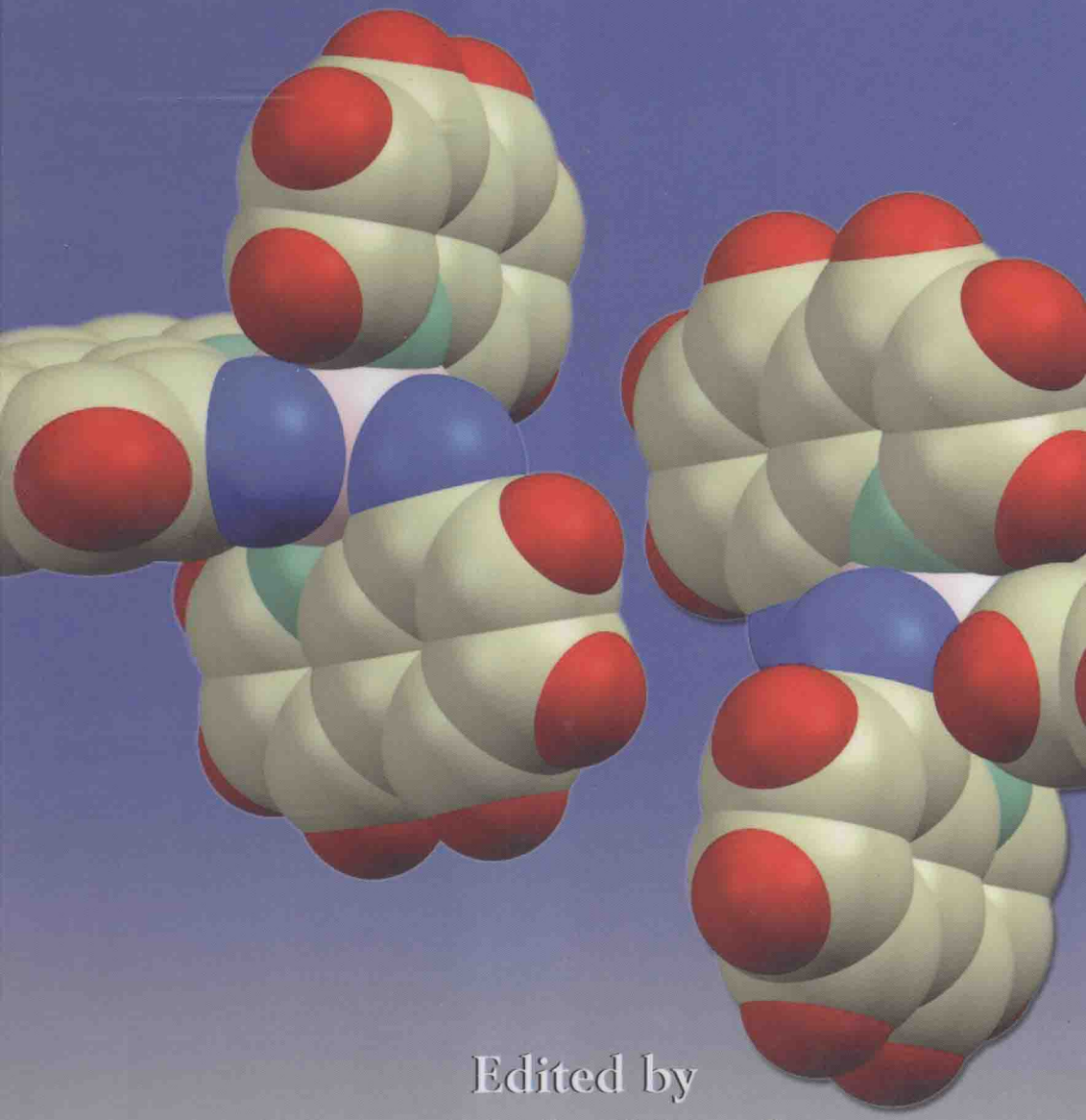
ORGANIC SPINTRONICS



Edited by

Zeev Valy Vardeny

CRC Press
Taylor & Francis Group

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number: 978-1-4398-0656-2 (Hardback)

Library of Congress Cataloging-in-Publication Data

Organic spintronics / editor, Zeev Valy Vardeny.
p. cm.
"A CRC title."
Includes bibliographical references and index.
ISBN 978-1-4398-0656-2 (hard back : alk. paper)
1. Spintronics. 2. Organic electronics. I. Vardeny, Z. V.

TK7874.887.O74 2010
621.381--dc22 2009049450

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ORGANIC SPINTRONICS

Preface

The field of organic electronics has progressed enormously in recent years as a result of worldwide activity in many research groups around the world. Advances have been made in the fields of both device science and fabrication, as well as in the underlying chemistry, physics, and materials science. The impact of this field continues to influence many adjacent disciplines, such as nanotechnology, sensors, and photonics. The advances in organic electronics have generated a vital and growing interest in organic materials basic research, and could potentially revolutionize future electronic applications. It is expected that the present worldwide funding in this field would stimulate a major research and development effort in organic materials research for lighting, photovoltaic, and other optoelectronic applications.

The growth of organic electronics has indeed been impressive. The first commercial products, started two decades ago, were based on conducting polymer films, a business now with annual sales in the billion-dollar range. Organic light-emitting diodes (OLEDs) and displays based on OLEDs were introduced to the scientific community about two decades ago, and to the market about ten years; a large expansion in market penetration has been forecasted for the next decade. A bright future awaits organic white light-emitting diodes, which are viable to replace the Edison-type bulb. In addition, thin-film transistor-based circuits, and electronic circuits incorporating several hundred devices on flexible substrates have been recently demonstrated. Organic photodiodes have been fabricated with quantum efficiencies in excess of 50%, and organic solar cells with certified power conversion efficiencies above 6% have been reported. Also, laser action in organics was introduced in 1996. The initial enthusiasm has given way to more realistic expectations on the fabrication of current-injected organic laser action. There continue to be advances made in the synthesis of new compounds and in improved synthetic procedures of important materials.

Until a few years ago, the *electron spin* was ignored in the field of organic electronics. However, in 2002, as substantive magnetoresistance in a two-terminal organic device was obtained at room temperature, a new field was born: *organic spintronics*. The technology of spintronics (or spin-based electronics), where the electron spin is used as the information carrier in addition to the charge, offers opportunities for a new generation of electronic devices that combines standard microelectronics with spin-dependent effects that arise from the interaction between the carrier spin and externally applied magnetic fields. Adding the spin degree of freedom to the more conventional charge-based electronics substantially increases the functionality and performance of electronic devices. The advantages of these new devices may be increased data processing speed, decreased electric power consumption, and increased integration densities. In addition, spintronic devices may also serve as the writing/reading active element in magnetic memory systems.

The discovery of the giant magnetoresistance in 1988 is considered to be the beginning of the new generation of spin-based electronics; this discovery has led to

the 2007 Nobel Prize in Physics. As a result, the role of electron spin in solid-state devices and possible technology that specifically exploits spin in addition to charge properties have been studied extensively. The transition from discovery to commercialization has happened very fast for spintronics. For example, the application of giant magnetoresistance and tunneling magnetoresistance to magnetic information storage occurred within a period of six years following their discovery, and a "read-head" device for magnetic hard disk drives based on spintronics was announced in 1997 by IBM.

Until the 2002 discovery of magnetoresistance in organic devices, only slight attention was paid to the use of organic semiconductors, such as small molecules and π-conjugated polymers, as spin transporting materials. The conductive properties of the π-conjugated polymers were discovered in the late seventies, and this gave birth to organic, or plastic, electronics. Organic semiconductors are mainly composed of light atom elements such as carbon and hydrogen, which leads to large spin diffusion length due to very weak spin orbit coupling, and moderate hyperfine interaction. These properties hold promise for the field of organic spintronics, and thus there is no wonder that this field has flourished during the last few years. A series of international meetings on organic spintronics, dubbed "Spins in Organic Semiconductors (SPINOS)," has been established, with ~100 delegates from all over; the third meeting in the series is planned to be held in September 2010 in Amsterdam.

This book is an updated summary of the experimental and theoretical aspects of organic spintronics. A substantial advance has recently occurred in the field of organic magnetotransport, mainly in three directions: spintronic devices, such as *organic spin valves*, where spin injection, transport, and manipulation have been demonstrated; *magnetic field effects* in OLEDs, where both conductivity and electroluminescence have been shown to strongly depend on magnetic field; and optically and *electrically detected magnetic resonance* effects, where coherent spin control has been obtained in organic electronic devices. Therefore, the book is organized to reflect these three avenues. Chapters 1 to 2 are mainly focused on spin injection and manipulation in organic spin valves. Chapter 3 introduces the magnetic field effect in OLEDs, and Chapters 4 and 5 further discuss this spin transport effect in relation with spin manipulation, which is the focus of the first two chapters. Chapter 6 is devoted to the coherent control of spins in organic devices using the technique of electrically detected magnetic resonance, and Chapter 7 summarizes the possibility of using organic spin valves as sensors. In addition, organic magnets as spin injection electrodes in organic spintronics devices are thoroughly discussed in Chapter 4. Both experiment and theory are well represented in this book. Whereas Chapter 2 and some parts of Chapter 3 are devoted to the theoretical aspects of spin injection, transport, and detection in organic spin valves, Chapters 3 to 5 discuss in detail the underlying mechanism of the magnetoresistance and magnetoelecroluminescence in OLEDs.

Upon the completion of this book, I would like thank the various contributors for their diligent and thorough efforts that made it possible to complete this project on time. I am also grateful to my wife, Nira Vardeny, for the support she gave me during the time period that I was busy planning and preparing the book, as well as writing the chapter that I am involved with (Chapter 5)—the relief time that I needed

when not working on the book. I am also grateful to the authorities of the Physics Department at the University of Utah for the partial relief they gave me in teaching during the spring 2008–2009 semester—a time period that was crucial for the writing endeavor and advance in the subject matter. I am also grateful to my friend and collaborator over the years, Prof. Eitan Ehrenfreund, for his contribution to our collaborative efforts in the field of organic spintronics, and especially for his friendly hospitality during my sabbatical at the Technion.

Finally, I also thank the DOE and NSF funding agencies for providing the financial support needed to complete this book during the 2009 spring and summer semesters, and the Lady Davis Foundation for the stipend in support of my stay at the Technion in spring 2009, during which a major part of my contribution to this book was formulated.

Salt Lake City, Utah

The Author

Z. Valy Vardeny is distinguished professor of physics at the University of Utah. He received his BS (1969) and PhD (1979) in physics from the Technion, Haifa, Israel. He received the Alon Price in 1982, the University of Utah Research award in 1996, the Willard Award of Art and Science in 1997, the Lady Davis Professorship at the Technion in 2000 and again in 2005 and 2009, the Utah Governor's Medal of Science and Technology in 2005, the 2008 Frank Isakson APS Prize for Optical Effects in Solids, and the University of Utah Rosenblatt Award for Excellence in 2009. He is a fellow of the American Physical Society (1996). He is regional editor of the *Journal of Synthethic Metals* and consultant with two major corporations: Cambridge Display Technologies, and Plextronics. Vardeny has published more than 480 peer-reviewed research articles, is the editor of 4 books, and holds 12 patents and provisional patents.

His research interests include optical, electrical, and magnetic properties of organic semiconductors; fabrication of organic optoelectronic organic light emitting diodes (OLEDs) and solar cells and spintronics (spin valve) devices; optically detected magnetic resonance, laser action, nonlinear optical spectroscopy, and ultrafast transient spectroscopy from the THz to UV of organic semiconductors, amorphous semiconductors, nanotubes, fullerenes, and graphite; fabrication and properties of 3D dielectric photonic crystals; metallodielectric and metallic photonic crystals; 2D plasmonic lattices, quasicrystals, fractals, and other nonperiodic structures of hole arrays in metallic films; magnetoconductivity and magnetoelectroluminescence in OLEDs; and other two-terminal devices.

The Contributors

F. L. Bloom
Department of Applied Physics
Technische Universiteit Eindhoven
Eindhoven, The Netherlands

P. A. Bobbert
Department of Applied Physics
Technische Universiteit Eindhoven
Eindhoven, The Netherlands

Christoph Boehme
Department of Physics and Astronomy
University of Utah
Salt Lake City, Utah

Valentin Dediu
Institute for the Study of Nanostructured Materials
National Research Council
Bologna, Italy

E. Ehrenfreund
Physics Department
Technion–Israel Institute of Technology
Haifa, Israel

A. J. Epstein
Departments of Physics and Chemistry
Ohio State University
Columbus, Ohio

B. Koopmans
Department of Applied Physics
Technische Universiteit Eindhoven
Eindhoven, The Netherlands

Dane R. McCamey
Department of Physics and Astronomy
University of Utah
Salt Lake City, Utah

Jagadeesh S. Moodera
Francis Bitter Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

Mirko Prezioso
Institute for the Study of Nanostructured Materials
National Research Council
Bologna, Italy

V. N. Prigodin
Department of Physics
Ohio State University
Columbus, Ohio
and
Ioffe Institute
St. Petersburg, Russia

Karthik V. Raman
Francis Bitter Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

Alberto Riminucci
Institute for the Study of Nanostructured Materials
National Research Council
Bologna, Italy

P. P. Ruden
University of Minnesota
Minneapolis, Minnesota

Tiffany S. Santos
Center for Nanoscale Materials
Argonne National Laboratory
Argonne, Illinois

D. L. Smith
Los Alamos National Laboratory
Los Alamos, New Mexico

Z. V. Vardeny
Physics Department
University of Utah
Salt Lake City, Utah

M. Wohlgenannt
Department of Physics and Astronomy
Optical Science and Technology Center
University of Iowa
Iowa City, Iowa

Jung-Woo Yoo
Departments of Physics and Chemistry
Ohio State University
Columbus, Ohio

interview

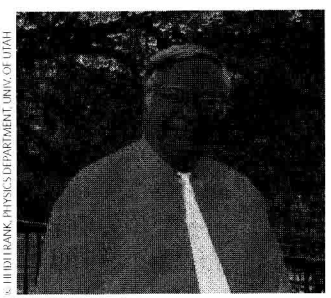
A new face for organics

In 2004, after two decades' worth of experience investigating the photophysical properties of conducting polymers, Z. Valy Vardeny demonstrated a spin valve with an organic active layer. *Nature Materials* asked him about his views on the achievements in organic spintronics and the future of the field.

What inspired you to study physics?
At the time I had to go to university, the Technion in Haifa was possibly the most famous engineering school in Israel, and nuclear physics was very fashionable. So initially that's what I wanted to do. However, once I began to study, I realized that condensed matter was much more complex and intriguing. I had to join the military service temporarily, and when I came back to the Technion I had made up my mind that I would become a condensed-matter physicist, rather than a nuclear one.

Were you already interested in organic compounds?
Not really. My general training was in photophysical phenomena, but at the beginning of my career my research was focused on amorphous silicon. In particular, after my PhD on Raman scattering spectroscopy of copper halide crystals, I took a postdoctoral position at Brown University, in Providence, Rhode Island, in the group of Jan Tauc, where I developed a set-up for ultrafast and continuous-wave spectroscopy on hydrogenated amorphous silicon. Incidentally, there are plenty of similarities between this material and organic semiconductors. But my interest in the organics arose later, after attending a seminar by Alan Heeger in 1981. He was talking about transport in conducting polymers, namely *trans*-polyacetylene (on which he was awarded the Nobel Prize in Chemistry in 2000, together with Alan McDiarmid and Hideki Shirakawa), and I suddenly realized that there was an opportunity for me to study photophysics with these materials. I proposed that to Heeger who then gave me some samples, and we started a fruitful collaboration that lasted for several years afterwards.

So that became your main interest?
Indeed, especially because my supervisor went on sabbatical in 1982, and not only did he ask me to take care of his research group at Brown University, but also gave me the freedom to choose my own future research direction. Later, when I took my position at the University of Utah, there was no research programme on organic semiconductors, so I started one. And I have kept on working on these materials for so long because they have not allowed me to become bored. Through the years, the organic semiconductors have changed face several times, and I had to learn new aspects of their properties. Initially they were studied mainly for batteries and electromagnetic shielding on doping. In the 1980s the focus moved to nonlinear optics. Then in the early 1990s, when Richard Friend demonstrated organic light-emitting diodes (OLEDs) with a π-conjugated polymer as the active material, I could see that this was my natural field. After all, once you inject an electron and a hole in the polymer, they form a polaron pair and subsequently an exciton, and the rest is photophysics.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And now even spintronics. How did the idea of an organic spin valve come about?
Well, in 2002 I saw the paper from the group in Bologna claiming spin injection from a ferromagnetic (FM) electrode into an organic semiconductor[1]. At that time, Jing Shi had just joined our department at the University of Utah. Coming from a company such as Motorola meant he had vast experience in inorganic spintronics. So we combined our different expertises, and we realized a vertical spin valve with an organic active layer[2].

Do you think our understanding of spin-related phenomena in organic semiconductors has increased considerably since these first results?
Definitely. For example, when magneto-resistance was observed in organic spin-valve devices a few years ago, no one could be sure whether this was due to the fact that spin-polarized carriers were injected in the organic semiconductor or that they were tunnelling through it. The problem is that there is no easy way to check. Let's compare organic semiconductors with inorganic III–V semiconductors, such as GaAs, which is a classical direct-gap semiconductor. By looking at the circular polarization of the emitted light in a two-terminal device, it is possible to infer the spin polarization of carriers injected in the material from the FM electrodes. By contrast, in organic semiconductors the spin–orbit interaction is so weak that the polarization of the emitted light is lost when excitons recombine. So we need other, more complex techniques. And recently, low-energy muon spin rotation and two-photon photoemission have confirmed that spin-polarized carriers are actually injected in the organic semiconductors from FM electrodes[3,4].

What about fundamental issues that need solving and are currently under intense investigation?
One important question is the role of the hyperfine interaction (HFI) in the spin-polarized carrier transport in organic spin devices. We know that the spin–orbit interaction is weak in organic semiconductors, leading to a spin-lattice relaxation rate in these materials that is much smaller than in inorganic semiconductors. However, the role of the HFI in determining the spin-lattice relaxation rate at the magnetic field strength used in spintronics devices is not clear. This is an unanswered question that is the focus of intense theoretical[5] and experimental endeavours (T. D. Tho *et al.* manuscript in preparation) at the present time. Another unanswered question is the understanding of the relatively large magnetic field effect (MFE) in electroluminescence and conductivity that has been obtained in regular OLEDs with no FM electrodes[6]. The physics of the MFE seems to be coupled with the interaction of same-charge and opposite-charge polaron pairs; and this is an opportunity to thoroughly investigate these species in the organic semiconductors, which was not available to us before. And we should

keep in mind that HFI could also affect the organic spin-valve response[5], which would lead to a fascinating connection between these seemingly unrelated effects, that is, magnetotransport and MFE.

■ But what is the advantage of working with organic spintronics when one could study more stable and reliable inorganic materials?

This is an old question, which precedes organic spintronics and relates to organic electronics in general. First of all, organic structures are much cheaper to fabricate, which has obvious advantages for both research and applications. Scientists can enter the field even without huge amounts of funding, and we can foresee devices that can be replaced after a short period of time as the cost is low. In addition, the active material in spintronics devices is very versatile. Chemists can really adapt a compound quite easily to the functionality that they have in mind.

■ Apart from spin valves, are there other types of devices for which organic compounds are suitable?

Surely. We need to remember, first of all, that when we talk about organic spintronics we do not necessarily refer to spin-transport phenomena, but more generally to magnetic field effects. We can imagine devices of different types, with two FM electrodes — such as spin valves or spin transistors — but also with one FM electrode. For example, an organic diode with one ferromagnet can actually act as a detector of the polarization of the ferromagnet electrode itself[7]. And finally, OLEDs without any FM electrodes can take advantage of the huge electroluminescence and conductance response to a magnetic field. For example, a magnetic field of only about 100 gauss can change the electroluminescence intensity by 20 or 30% (ref. 8). All these aspects were well-represented in the latest SPINOS conference that took place in Salt Lake City, in February 2009.

■ Are there spintronics applications that are unique to organic semiconductors?

Yes, and they stem from the fact that organic semiconductors can emit both fluorescence (from the recombination of singlet excitons) and phosphorescence (from triplet excitons), which have different colours. So you can imagine having an OLED with two FM electrodes, and by applying even a small magnetic field you could change both the intensity and colour of the emitted light. That would be amazing, and unique for organics.

■ What about using organic magnets, similar to the case of dilute magnetic semiconductors in inorganic spintronics?

The problem, as far as I can tell, is that the spin polarization in organic magnets has not been measured as yet; thus it may not be really high enough to inject substantial spin-polarized carriers into an organic interlayer. The other issue is that in inorganic spintronics there is a well-known hurdle concerning the conductivity mismatch between metallic FM electrodes and the active semiconductor, which is a problem for spin injection[9–11]. In organics this is not really an important problem because carrier injection is mainly due to tunnelling; and the tunnel barrier may be strongly magnetic-field dependent for an injecting FM electrode. Consequently, it may act as a spin-dependent filter for carrier injection[12].

■ Do you think the interest in organic spintronics from both academia and industry has risen since the Bologna paper and yours?

I would say it has. Of course I — like anyone else in the field — might be biased, but just take a look at the numbers. In 2007, Carlo Taliani organized the first SPINOS 2007 conference in Bologna, and there were about 50 participants. At the SPINOS 2009, there were already about 100 delegates. In addition, I know that there are international collaborations sponsored by the European Union on the topic. So at least from an academic perspective, the interest has certainly risen. For industry the situation is different. The field is still in its infancy, and particularly in the current economic situation it is understandable that there would not be investments in such a young field. We need to wait until considerable magnetoresistance is observed at room temperature, and then I am sure things will change.

■ Do you think that the different languages of scientists with different backgrounds is a serious obstacle to the development of the field?

Not more than in other fields. Taking my experience as an example; when I started working on conducting polymers I came from a background of physics of amorphous materials. Others, like Heeger and McDiarmid, were chemists. It took us some time to simply understand each other's language, namely definitions and concepts. The chemists used radicals, the physicists used spin-½ excitations. We physicists talked about valence and conduction bands, the chemists said highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The same happened with OLEDs. Richard Friend came from a semiconductor-physics background, but it took some time to understand what electron injection into organics meant. There are always language barriers initially, but they shrink with time and eventually we contribute together to the development of a field using different points of view. I am sure that scientists with backgrounds in spintronics think organic-semiconductor researchers often do not know what they are talking about, and vice versa. But eventually we will understand each other. Collaboration is probably the best solution. For example, I believe that the research group at THALES has started collaborating with that in Bologna; and I think this can produce important results.

■ What are the advances in the field that you foresee in the near future?

I think they will be mainly in two areas. First, on the spin-injector front. At present, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is the most widely used material because it is a half-metal (namely, at the Fermi level the carriers are almost fully spin polarized), but I do not think this is necessarily the best possibility, because its spin-aligned carrier-injection capability drastically decreases at room temperature. The magnetic properties of the interface between the FM electrode and the organic semiconductor need better understanding. Also, chemists will be able to synthesize compounds with much higher fluorescence and phosphorescence emission efficiencies, which will be fundamental in realizing the devices I mentioned before. What I think could revolutionize the field is if theorists achieve better understanding of spin injection into organics, in order to actually predict the spin-injection capability of given electrode–semiconductor pairs, which experimentalists could then verify, for example, by measuring spin-dependent photoemission[4].

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INTERVIEW BY FABIO PULIZZI

Contents

1 Spin-Polarized Transport in Organic Semiconductors

Jagadeesh S. Moodera, Tiffany S. Santos, and Karthik V. Raman

CONTENTS

ABSTRACT

Organic spintronics is a hybrid of two hot fields: organic electronics and spintronics. The excitement in this field of spin transport in organics, mainly organic semiconductors, has evolved rapidly in the last five years. Combined with the novelty and the expectation of a large travel length in organic compounds for spins without being perturbed, the field is marching on. With the possibility of creating unique molecular systems from a bottom-up approach, the field has opened up vast opportunities for discovering newer, fundamental phenomena. This is bound to lead toward technological breakthroughs. In this chapter we give the reader an overview of the activities so far in this very young

field, mainly from the perspective of spin transport in spin valve structure and tunnel junctions. It is clear that this highly interdisciplinary topic holds much promise, encompassing areas of physics, chemistry, and materials science. We have attempted to highlight the challenges that need to be overcome as well as where activity is needed, hoping to create intense activity in this field to arrive at the anticipated properties.

1.1 INTRODUCTION

The vast area of organic semiconductors (OSs), among literally millions of organic compounds, has seen considerable activity in the past couple of decades aimed toward exploring organic electronics from the fundamental physics point of view as well as with the promise of developing cheaper and flexible devices, such as organic light-emitting diodes (OLEDs) and organic field effect transistors (OFETs).[1–5] One of the great incentives in this field is the ability to chemically tune the properties at the molecular level for a bottom-up approach, which could be expected to lead the future science and technology, as is happening today in biological fields. Commensurate with the vastness of the field, although the parameter space to search and discover is undoubtedly daunting, the prospectus is exciting.

Organic electronics has been emerging in the last few decades as a new field with many unexplored phenomena,[5–7] whereas the even more complicated phenomenon of organic spintronics is already on the horizon. This nascent field of organic spintronics is a hybrid of the two hot fields organic electronics and spintronics.[8,9] From this viewpoint, of growing interest is the potential to transport and manipulate spin information in OS. Spin-orbit and hyperfine interactions are two of the main causes for spins to lose their orientation. Given that OSs are composed mostly of light elements (i.e., C, H, N, O), they have a weaker spin-orbit interaction than inorganic semiconductors. Thus, a relatively longer spin lifetime expected in OS promises a technological breakthrough in organic spintronics. In fact, the weak hyperfine interactions are found to dominate the spin scattering processes in some cases.[10] Certainly, these weak mechanisms suggest longer timescales for spins to relax or lose their phase coherence.[11] However, currently most OSs show a substantially lower mobility in the range of 10^{-8} to 10^{-2} cm^2/Vs, compared to standard, inorganic semiconductors Si and GaAs (hole mobility $\geq$ 400 cm^2/Vs and electron mobility $\geq$ 1,500 cm^2/Vs), limiting coherent transport lengths. Despite this fact, relatively longer spin lifetimes are reported experimentally.[12–14]

While many OS materials are exploited for their tunability of charge carrier transport properties, their spin transport study is the least explored area. This can be attributed to various factors. Even the simplest OSs, oligomers such as pentacene ($C_{22}H_{14}$) and rubrene ($C_{42}H_{28}$), are very large molecules consisting of many atoms (Figure 1.1) compared to Si, Ge, or GaAs. Their inherently complicated structure poses bigger challenges to obtaining "atomically" sharp interfaces, for example, with a metal, not to mention the all-important interfacial chemistry and charge transfer.[15,16] The latter issue in its entire resplendency should inevitably affect the interfacial magnetism—crucial for organic spintronics. As shown schematically in Figure 1.2, this would be

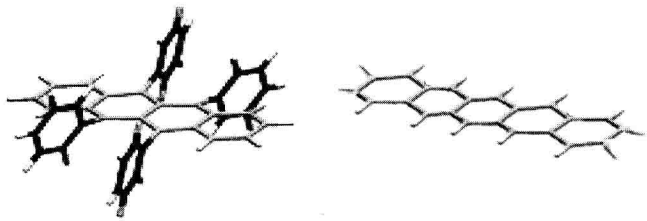

FIGURE 1.1 Molecular structure of organic semiconductors (a) rubrene ($C_{42}H_{28}$) and (b) pentacene ($C_{22}H_{14}$). (Taken from D. Käfer, G. Witte, *Phys. Chem. Chem. Phys.* 7, 2850 [2005].)

strongly dictated by the actual physical structure of the interface, which in itself is becoming a huge branch of research. Along these lines, what may eventually evolve is the ability to create an OS that is also magnetic at higher temperatures (such as $V[TCNE]_x$ discovered by Epstein's group[17,18]) and may seamlessly be grown over some high-mobility OS layer with reduced interfacial defect formation for efficient spin injection in an all-organic structure.

Despite the simplicity of creating the layers of OS, say by either physical vapor deposition or spin coating, handling them becomes nontrivial because of their soft and fragile nature. Standard semiconductor processing to make nanoscale devices is incompatible, as most of the organic solvents dramatically attack the OS layers. Novel techniques such as soft lithography have been developed with some degree of success for nanoscale device fabrication.[19] Maintaining a clean surface thus becomes challenging and complicates the investigation of the intrinsic behavior, especially when using bulk single crystals and *ex situ* processing is involved. Uncontrolled and unknown interfacial conditions can lead to huge contact resistance, irreproducibility, and artifacts in the measurements. These limitations magnify when dealing with spin injection and transport, due to the fact length scales below a nanometer become important. In some cases, what is called the flip method is adopted, wherein the OS crystal is placed on pre-prepared thin-film electrodes, such as Au, for four terminal

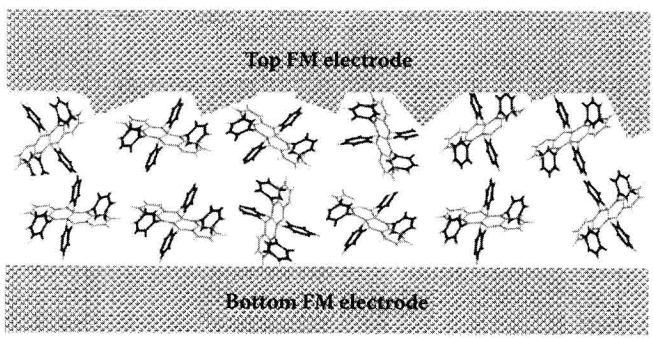

FIGURE 1.2 Growth of a ferromagnetic electrode on top of the organic layer leads to rougher interfaces compared to the bottom one. The interfacial magnetic properties are hence expected to be different in the two cases.

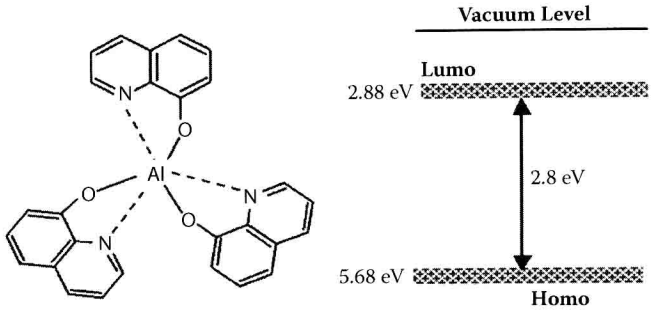

FIGURE 1.3 Energy-level diagram of organic semiconductor Alq_3. The HOMO-LUMO gap is ~2.8 eV.

charge transport measurement. The flip method minimizes the processing of single crystals, thereby reducing the risk of damaging the surface.

Not all is lost. With all of the above limitations in exploring the OS, very interestingly, the field of organic spintronics has taken off in the last few years. Many groups worldwide have begun serious spin transport studies in OS showing considerable success and promise. This is bound to open up hitherto unforeseen phenomena in this open and high-potential field. Among myriad possible OSs, some of the popular ones for spin transport studies are Alq_3, pentacene, rubrene, CuPc, and so on, because they are already being explored for their charge transport potential as well as electroluminescent capability[1,20–22] in organic electronics such as OFETs and OLEDs. For example, the organic π-conjugated molecular semiconductor Alq_3 ($C_{27}H_{18}N_3O_3Al$) is the most widely used electron-transporting and light-emitting material in OLEDs. Alq_3 has been extensively studied for this application since it displayed high electroluminescence (EL) efficiency nearly two decades ago.[1] A band gap of ~2.8 eV separates the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), shown in Figure 1.3. Typically, the film thickness of the Alq_3 layers in OLED structures is hundreds of nanometers, whereas for spin transport studies it is in the range of tens to a few hundreds of nanometers.

1.2 SPIN TRANSPORT IN OS USING SANDWICH STRUCTURES AND MATRICES

This section presents an overview of work on organic spin valves and magnetic tunnel junctions. Both types of organic spintronic devices comprise an organic spacer layer between two ferromagnetic electrodes, with the main distinction being the *effective* thickness of the organic spacer, which determines the carrier transport mechanism through the OS: by hopping conduction or by tunneling, which can be very different. In general, the probability of electron tunneling from one electrode to the other scales exponentially with thickness and is most effective for spacer layers that are very thin, less than ~5 nm. The organic layer acts as a tunnel barrier, and the tunneling electrons are not injected into the LUMO level. We apply the