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Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies

Marcel Bouvet [a,*], Pierre Gaudillat [a], Abhishek Kumar [a,c], Tilman Sauerwald [b], Marco Schüler [b], Andreas Schütze [b], Jean-Moïse Suisse [a]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), CNRS UMR 6302, Université de Bourgogne Franche-Comté, 21078 Dijon, France
[b] Laboratory for Measurement Technology, Department of Mechatronics, Saarland University, 66123 Saarbruecken, Germany
[c] Institut Pascal, LASMEA, Université Blaise Pascal Clermont II, 63177 Aubière Cedex, France

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ABSTRACT

The core activity of this work was to give a new interpretation of the electronic behavior of Molecular Semiconductor – Doped Insulator heterojunctions (MSDI), a new organic device combining two molecular materials with very different electronic properties. We focused on understanding the phenomenon occurring at the interface of fluorinated and non-fluorinated phthalocyanines that appears to be a determining factor for the electronic charge transport in the two-component thin film and ultimately deciding the nature of gas sensing, as illustrated with ozone and ammonia chosen as examples of accepting and donating gases. The impedance measurements showed that the Schottky contact between the sublayer and the electrodes also plays a key role. They, furthermore, provide complementary data for the selective detection of ammonia and relative humidity in air.

1. Introduction

Historically, organic devices were developed on the basis of their inorganic counterparts. Thus, organic diodes made from p–n junctions were reported after their inorganic p–n counterparts [1] and molecular materials-based Schottky junctions as well, with phthalocyanines or merocyanines [2–4]. Other examples are organic heterojunctions used as light emitting diodes [5,6] and photovoltaic cells [7] developed after inorganic p–n junction-based devices. And the same goes for conductometric sensors, molecular materials-based resistors were reported after inorganic metal oxide resistors and Organic Field-Effect Transistors (OFETs) used as chemosensors after inorganic FETs. Whereas most of the molecular materials-based electronic devices have been developed after their inorganic counterparts, as p–n junctions and FETs [8], we recently designed and patented a new organic device, called MSDI, for Molecular Semiconductor – Doped Insulator heterojunction [9], which has no equivalent among inorganic devices and that revealed to exhibit a particularly original sensing behavior [10].

The class of compounds called molecular materials has grown enormously in the last few decades, extending into the areas that were previously a monopoly of inorganic materials. In terms of intermolecular forces, molecular materials can be defined as the materials having intermolecular forces between two adjacent molecules often less than 10 kcal mol^{-1} [11]. This energy is very small compared to covalent bonds responsible for the atomic cohesion inside molecules (50–200 kcal mol^{-1}). Molecular materials for electronics are a term used to refer to conducting polymers and organic semiconductors, with examples being P3HT (poly-3-hexyl-thiophene), pentacene, perylene derivatives, fullerenes and phthalocyanines. At present, these materials are being widely used in the research domain of electronics and sensors with potential applications anticipated in the realms of microelectronics and new energy technology like Organic Light Emitting Diode (OLED) [7,12,13], Organic Field-Effect Transistor (OFET) [14–20], Organic Photovoltaic Cells (OPV) [21–24], displays [25,26] and sensors using OFET architecture [27–32] or other conductometric devices [33–37]. One of the advantages of molecular materials is that, besides conventional thin film techniques like evaporation [38], they offer the possibility to use low-cost solution processing

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* Corresponding author.

E-mail addresses: marcel.bouvet@u-bourgogne.fr (M. Bouvet), schuetze@LMT.uni-saarland.de (A. Schütze).

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techniques like spin-coating, but mainly inkjet printing and roll-to-roll processing for device fabrication on large substrates and at low temperature [39,40].

For research and development on these materials, it is important to know the fundamental physical properties of the materials and how they are related to molecular parameters. Equally important is the knowledge of the influence of each part of a molecule on the properties of the materials in order to choose the most suitable compound to synthesize. Usually, the arrangement of molecules in the solid state [23] and the extent of intermolecular interactions are the chief determining factors of the physical properties of the materials.

The family of phthalocyanines (Pc) (Fig. 1) is one of the most promising candidates in the prime research area of organic electronics due to their tunable electronic properties achieved by applying slight chemical modification. For instance, copper phthalocyanine, CuPc, is known as a p-type material in air, whereas its perfluorinated analog, $Cu(F_{16}Pc)$, is one of the few organic semiconductors that have demonstrated high performance and stability in air for n-channel operation [41–43]. Besides metal(II) monophthalocyanines, $M^{II}Pc$, lanthanide (III) bisphthalocyanines, $LnPc_2$, exhibit very particular properties. Especially lutetium bisphthalocyanine, $LuPc_2$, is the first intrinsic molecular semiconductor reported with an uncommonly high density of free charge carriers ($5{\cdot}10^{16}\ cm^{-3}$), related to an unusually small energy gap (0.5 eV), giving rise to quite high electronic conductivity at room temperature ($5{\cdot}10^{-5}\ \Omega^{-1}\ cm^{-1}$) [44,45]. As a result, depending on the conditions, $LuPc_2$ can exhibit intrinsic p-type or n-type behavior. The size of the lutetium(III) cation is not small enough to be accommodated into the square planar cavity of one phthalocyanine ring, so Lu^{3+} is placed between two phthalocyanine rings in a sandwich structure. In the solid state, out of two phthalocyanine rings in $LuPc_2$, one ring is the dianion Pc^{2-} while the other is the radical anion $Pc^{\cdot -}$, which is responsible for its capability to donate or accept an electron easily to or from a neighboring molecule [11].

Due to their radical and semiconducting nature, lanthanide bisphthalocyanine derivatives have already been used in the field of organic electronics, e.g., in OFETs [18], molecular magnets [46–48] and gas sensing [49–53]. OFETs made with $LuPc_2$ exhibit n-channel under vacuum but p-channel in air [18]. This clearly indicates that the density of charge carriers of both p- and n-type can be high, depending on the experimental conditions, so its ambipolar character.

Among phthalocyanine-based heterojunctions, the so-called MSDI, for Molecular Semiconductor – Doped Insulator heterojunction, combines an organic semiconductor to another organic material with a relatively low conductivity. The first MSDIs reported were based on the exceptional electronic properties of $LuPc_2$ as abovementioned [9,10]. When it is combined with the non-substituted copper phthalocyanine (CuPc) [10] or the 5,5′-dihexyl-α, ω-sexithiophene [54], both p-type materials, the device is called p-MSDI. In these two materials, the energy gap is near 2 eV and the density of charge carriers is less than $10^8\ cm^{-3}$, i.e., very low compared to that of $LuPc_2$. In MSDIs, the semiconducting layer completely covers the doped insulator and is not in contact with the electrodes (Fig. 2). In the case of n-MSDIs, bilayer heterojunctions were realized with $LuPc_2$ and the perfluorinated copper phthalocyanine, $Cu(F_{16}Pc)$ [10], or a perylene diimide derivative, namely the N,N′-dineopentyl-3,4,9,10-perylenetetracarboxylic-diimide [54], respectively.

The behavior of MSDIs is different from the one of other devices based on organic materials. Traditional ChemFETs, as reviewed by Janata, are silicon-based transistors in which the gate is used as a sensing material, which can be an organic material [35,55]. In this case, the current path through the silicon, as in suspended gate FETs [56]. In the contrary, in OFETs used as chemosensors, the current, modulated by the gate voltage, path through the organic material that is also the sensing material. Basically, since MSDIs are two-electrode devices, they are not transistors.

The configuration of MSDI resembles a heterojunction between two organic semiconductors of widely altered band gap and charge carrier concentration. The charge transport behavior of an n-MSDI can be understood in a simplified manner, considering the system as an n–p–n system, since, in air, majority charge carriers are positive in $LuPc_2$. It implies that a charge carrier is first injected from one electrode into the n-type region, then crosses over the n–p junction and enters the p-type region before it re-enters into the n-type region to reach the other electrode. Since the $Cu(F_{16}Pc)$ region is highly resistive due to its large band gap, charges prefer to cross the n–p junction and go into highly conducting $LuPc_2$ region, as depicted in Fig. 2. This is the reason why this conduction model can be described as an n–p–n model. In the case of p-MSDI, there is obviously no p–n junction at the interface, since the nature of the majority carriers is the same in both layers, however there still is some potential at the interface developed due to the difference of work function between the two materials.

As already reported [10,57,58], the response of conductometric devices towards gases can give information on their transport properties. Gas sensing is a two-step process in which gaseous molecules first interact with the surface by a physisorption process, followed by their diffusion into the bulk and, depending on their chemical nature, a charge transfer with the sensing material. The latter is of utmost importance for conductometric sensors since it induces a variation of the free charge carrier density. The behavior of MSDIs in interacting with oxidizing and reducing gases is determined mainly by the electrical nature of the insulating sublayer. On exposure to a reducing gas like ammonia, which acts as an electron donor, the density of majority charge carriers in the upper layer, $LuPc_2$, is reduced. When the sublayer is of p-type, i.e., in the case of p-MSDIs, the current through the device decreases as well. However, with a n-type sublayer, the current increases, indicating that the response towards gases is governed

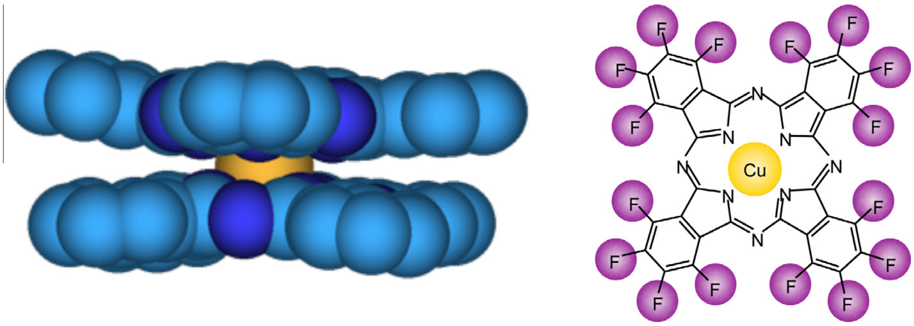

Fig. 1. Side view of lutetium bisphthalocyanine $LuPc_2$, without the H atoms (left) and a schematic view of copper perfluorophthalocyanine $Cu(F_{16}Pc)$ (right).