



On the interest of ambipolar materials for gas sensing

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ABSTRACT

Based on the electrochemical properties of a series of metallophthalocyanines this article shows that the phthalocyanine bearing four alkoxy groups and twelve fluorine atoms behaves approximately as those with eight fluorine atoms. This indicates that the electron-donating effect of one alkoxy group balances the electro-withdrawing effect of one fluorine atom. We engaged three metallophthalocyanines, namely the octafluoro copper phthalocyanine, Cu(F₈Pc), an octaester metallophthalocyanine and a phthalocyanine bearing four alkoxy groups and twelve fluorine atoms, Zn(T₄F₁₂Pc), in building original conductometric transducers that are Molecular Semiconductor – Doped Insulator heterojunctions (MSDIs) in association with the highly conductive lutetium bisphthalocyanine, LuPc₂. Whereas the octaester derivative and Zn(T₄F₁₂Pc) exhibited a negative response to ammonia, as expected for p-type materials, Cu(F₈Pc) exhibited a particular behavior. At low humidity levels, 30 and 10% rh, the current of the Cu(F₈Pc)/LuPc₂ MSDI decreases, similarly to p-type devices, but at higher relative humidity values, 70% rh, the current increases under ammonia, which is the signature of a n-type behavior. This ambipolar behavior is unique amongst semiconducting sensing materials. This work opens the way to the study of ambipolar materials as sensing materials for the development of a new type of conductometric gas sensors.

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1. Introduction

Most molecular materials used in organic electronics only exhibit an unipolar behavior, with either electrons or holes as majority charge carriers [1,2]. However, devices that can transport both electrons and holes are very important to design complementary integrated circuits without requiring the implementation of two types of field-effect transistors with p- or n-type channels. The first ambipolar behavior ever observed in an OFET was with the lutetium bisphthalocyanine, LuPc₂, as molecular semiconductor [3]. Although the term ambipolar was not used in the published paper, the authors did observe both n and p channels, under vacuum and in air, respectively. This clearly indicates that the density of charge carriers of both p- and n-type can be high in LuPc₂, depending on the experimental conditions. This is a consequence of its particularly low energy gap, ca. 0.5 eV [4,5], resulting from its radical nature. Moreover, in this case, the SiO₂ dielectric mate-

rial was modified by long alkyl chains, known for avoiding charge trapping at the semiconductor – dielectric material interface [5].

Generally, ambipolar devices result from the combination of two materials, including blends of polymers. There are several examples in the literature, including poly-phenylene vinylene or polyhexylthiophene as hole-transporting material with a fullerene derivative (PCBM) as electron-transporting semiconductor [6], a pentacene derivative associated with a perylene diimide [7] or a perfluorophthalocyanine [8] as n-type materials, blends of benzimidazolebenzophenanthroline ladder polymer (BBL) and copper phthalocyanine [9], and blends of two phthalocyanines, one bearing octyloxy carbonyl substituents, Cu((COOC₈H₁₇)₈Pc), and the other one alkoxy chains, Cu((OC₈H₁₇)₈Pc) [10]. Organic heterostructures, including p-n heterojunctions and ambipolar transistors, have been described in detail by H. Wang and D. Yan [13]. We can also cite interesting reviews on ambipolar OFETs, by H. Sirringhaus [1,2,11,12].

The historical LuPc₂ example aside, several families of molecules were reported that exhibit an ambipolar behavior with a single semiconductor layer capable of conducting both electrons and holes. For instance, the [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) – a C60 derivative that is known as a n-type material can

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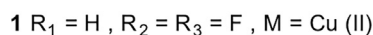
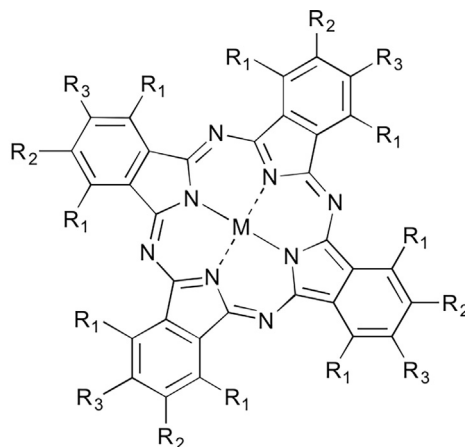
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exhibit a p-type channel with gold electrodes on SiO₂ treated with hexamethyldisilazane as the dielectric material [14]. In the same way, a donor–acceptor conjugated polymer derived from BDOPV (benzodifurandione-based oligo *p*-phenylene vinylene) exhibited a n-type behavior under vacuum and an ambipolar behavior when doped by oxygen [15].

From these examples, it is clear that particular operating conditions of the devices and specific atmospheres are required to observe an ambipolar charge transport. Donor–acceptor copolymers based on naphthalenediimide acceptor and (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene donor [16], or on polyfluorene derivatives [6], which have a band gap energy of 1.55 eV, are also nice examples of single component ambipolar materials. There is also the work of Y. Chen on lanthanide double decker [17] and triple decker complexes [18,19]. These cases are similar to the abovementioned LuPc₂ complex, since the ambipolarity results from the low energy gap, ca. 0.5 and 1.0 eV for lanthanide double and triple decker complexes, respectively. In addition, halogenated tetracene and pentacene and heteroatoms containing acenes [20–22], quinoidal quaterthiophen derivatives and tetracyanothienoquinoids [23,24] can also lead to an ambipolar behavior.

The ambipolar character of a material can be anticipated from the knowledge of the energy of its frontier orbitals, HOMO and LUMO [25], but relatively to the work function of the electrodes, since it determines whether charge injection is likely [2]. However, the emergence of such a behavior and its observation is highly dependent on the morphology of materials [9]. Tuning of electronic properties of materials can be achieved by the introduction of electron-donating or electron-withdrawing substituents on macrocyclic molecules [26–28]. It is well-known that fluorine substituted macrocycles exhibit stabilized frontiers orbitals compared to non substituted counterparts, e.g. by 1.2 eV for hexadecafluorometallophthalocyanines, M(F₁₆Pc), relatively to the non fluorinated phthalocyanines, MPc [29]. Thus, perfluorinated phthalocyanines are n-type materials whereas non substituted phthalocyanines are p-type materials. The introduction of fluorine atoms on the phthalocyanine ring leads to n-type semiconductors useful to get n-type OFETs [30] and *p-n* heterojunctions [31], which can be used as gas sensors [32]. It is worth mentioning that the effect of the central metal of metallophthalocyanines on their chemosensing properties is rather weak compared to the electronic effect of substituents on the macrocycle. However, A. C. Kummel and W. C. Troglér reported the effect of the coordination strength of analytes on the central metal for five metallophthalocyanine resistors studied towards a series of VOCs [33].

Reported examples of ambipolar devices used for chemosensing are very rare. Thus, an ambipolar hybrid organic-inorganic thin film transistor, containing pentacene and zinc oxide as semiconductors, was employed as an ethanol vapor sensor [34]. In p-channel accumulation mode, a decrease of current with the introduction of analyte was observed, while in the n-channel triode mode, an increase in current with analyte delivery was observed. In this case, the ambipolarity allowed for carrying out chemosensing experiments in two different operation modes. Another example is the one combining n and p phthalocyanines. The *p/n* bilayers were much more sensitive to ethanol than the corresponding n/p bilayer, even though in both cases the current increases under ethanol [10]. The same devices exhibit a current decrease under ammonia, but both with a very low sensitivity. However, the response observed is not clearly related to the ambipolar character of the devices, since the morphology of sensing material can be different in both structures. In the case of diketopyrrolopyrrole-based ambipolar transistors, the interest of ambipolar character comes from the number of physical parameters to measure, like both electron and hole mobilities, additionally to conductivity [35]. Thus,



Scheme 1. List of the phthalocyanine complexes studied in this work.

using a combined pattern-recognition method along with these multiple sensing parameters, a detection down to 40 ppm of xylene and a discrimination between xylene isomers were achieved. These few examples stress the need for studying the interest of ambipolar materials for chemosensing.

While the interest in ambipolar materials is obvious in organic electronics, it is completely looked over in conductometric sensors. Generally, in sensors, the increase or decrease of the measured electrical current gives a first indication on the nature of chemical species in the atmosphere in contact with the device. This is the reason why we want to discuss the interest of ambipolar materials for gas sensing.

In the present paper, we report on the electrochemical and chemosensing properties of three differently substituted phthalocyanines, the octafluorophthalocyanine Cu(F₈Pc), **1**, the octacarboxylate hexyl ester cobaltphthalocyanine Co((COOC₆H₁₃)₈Pc), **2**, and a recently synthesized phthalocyanine bearing both electron-donating and electron-withdrawing substituents, the zinc tetra-{2-(2-thienyl)ethoxy}-dodecafluorophthalocyanine, Zn(T₄F₁₂Pc), **3**, (Scheme 1) [36]. The conductometric transducer used in this study is a Molecular Semiconductor – Doped Insulator heterojunction, hereafter called MSDI. MSDIs are devices designed and patented by one of the authors [37,38]. They are formed by a thin film-based heterostructure combining a rather poor conducting sublayer in contact with two interdigitated electrodes and a highly conductive top layer made of LuPc₂.

2. Experimental

2.1. Chemicals

The 2,3,9,10,16,17,23,24-octafluorinated copper phthalocyanine, Cu(F₈Pc), **1**, was obtained by reaction of 4,5-difluoro-1,2-dibromobenzene with copper cyanide as described previously [37]. The cobalt 2,3,9,10,16,17,23,24-octa(hexyloxycarbonyl) phthalocyanine, Co((COOC₆H₁₃)₈Pc), **2**, was obtained in this work (Suppl. Mater.). The 2,9,16,23-tetra-{2-(2-thienyl)ethoxy}-1,3,4,8,10,11, 15,17,18,22,24,25-dodecafluoro- zinc phthalocyanine, Zn(T₄F₁₂Pc), **3**, was synthesized recently in the ICMUB, by heating the 4-{2-(2-thienyl)ethoxy}-3,5,6-trifluoro- phthalonitrile

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