XX Ambipolar materials for gas sensing

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"It is in exchanges and hybridizations that new things are created", translated from "C'est dans les échanges et les hybridations que l'on crée des choses nouvelles", Thierry Marx, a famous starred French chef, on the France Info radio, June 22nd, 2019.

ABSTRACT

Ambipolar sensors appeared in the present decade, i.e. very late compared to the first ambipolar electronic devices. They were obtained with resistors, organic field-effect transistors and heterojunctions. It is not sufficient to own ambipolar materials to observe ambipolar sensors. A key point is to be able to stabilize the p and n states, by changing one external parameter. For further developments, it will be necessary to master a trigger capable to go from p-type to n-type behavior and *vice versa*. This can be an external bias, as in transistors, or any light.

X.1 Introduction

Whereas organic electronic devices, including field-effect transistors (FET), diodes and photovoltaic cells, were developed far after their inorganic counterparts and whereas molecular material – based sensors are far less developed than inorganic material – based sensors, the reality is different for ambipolar chemical sensors. Indeed, among less than fifteen papers, only three include inorganic semiconductors, among which one is a hybrid device that combines both organic and inorganic semiconductors. The transducers are mainly FETs and resistors, even though one paper uses a photovoltaic cell as a transducer and another one a particular heterojunction called molecular semiconductor – doped insulator heterojunction (MSDI).

X.1.1 Generalities on gas sensors

For chemical sensors, the first criteria to fulfill are contained in the 3S rule, namely sensitivity, selectivity and stability¹.

Sensitivity is mainly related to the transducer characteristics, since the absolute sensitivity is limited by the signal over noise ratio (S/N ratio). The limit of detection (LOD) is often defined as three times the noise, whereas the limit of quantification is defined as ten times the noise. The S/N ratio is imposed by the transducer's electronics. However, the signal can be generally improved by increasing the interaction between the material and the target analyte. It is the reason why sensitivity depends on morphological parameters of the sensing materials, namely the specific surface, rugosity, porosity and the size of crystallites, which define the density of adsorption sites^{2,3}. The adsorption phenomena can be described by the Langmuir's theory^{4,5}. This theory allows to explain why a saturation phenomenon can

occur for the response of a chemical sensor when exposed to an increasing concentration of a target gas, in relation with the saturation of the adsorption sites⁶. Selectivity depends directly on the choice of sensing materials that have to be adapted to the target species. Of course, it cannot be defined independently of the transduction mode, which is chosen as a function of the physical parameter that is modified by the analyte-sensing material interaction^{7,8}. Selectivity to a target species has to be considered for each particular application. Indeed, a sensor will be considered as selective in a given environment, but may be unselective in another one where an interfering species is present.

Stability is the third main property required for sensors. At first, it supposed that the gas-sensing material interactions are reversible. Reversibility can be improved with sensing materials in the form of very thin and amorphous films. Indeed, in crystalline materials and in thick films, long exposure periods to a gas will induce an occupation of rather unaccessible sites, from which the adsorbed species may have difficulty getting out. It occurs when the adsorbed species diffuse deeply inside thick and/or crystalline films³. Reversibility can also be limited by the presence of poisoning species, such as sulfur containing compounds for tin oxide resistor used for gas detection¹.

For all these reasons, it is of the utmost importance to design adapted molecules and to master the materials processing to get efficient sensors and optimize their performances for given applications.

X.1.2 Ambipolar materials

Before going through ambipolar chemical sensors, let us resume the response of unipolar transducers to gaseous species. As long as conductometric transducers are concerned, an analyte can affect not only their density of charge carriers, by doping

the material, i.e. an increase in majority charge carriers, or by neutralization of charge carriers, a decrease in majority charge carriers, but also their mobility. Redox active species like ozone or nitrogen dioxide, strong oxidizing agents, increase the density of majority charge carriers in p-type materials and decrease this density in n-type materials. An inverted effect is observed with electron-donating species like ammonia, NH_3 , that increases the majority charge carriers in n-type materials, and decreases it in p-type materials. On the contrary, volatile organic compounds (VOC) that are not known as redox active species can affect the current going through a conductometric transducer by modifying the mobility of electrons or holes by changing the dielectric constant of the material. This is particularly true in molecular materials where charge transport occurs by a hopping process from molecule to molecule. The localized charges polarize their molecular surrounding, and the degree of localization increases with the dielectric constant, leading to a lower mobility⁹. This is generally what happens when water molecules interact with a semiconductor.

The first ambipolar behavior ever observed in an OFET was with the lutetium bisphthalocyanine, LuPc_2 , as molecular semiconductor¹⁰. Although the term ambipolar was not mentioned 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 LuPc_2 , depending on the experimental conditions. This is a consequence of its particularly narrow energy gap, ca. 0.4 eV^{11,12}, resulting from its radical nature. Moreover, in this case, the SiO_2 dielectric material was modified by long alkyl chains¹⁰, well-known now for avoiding electron trapping at the semiconductor – dielectric material interface¹².

Ambipolar devices result from the combination of two materials, as bilayer structures or under the form of blends. Several examples were reported in the literature, including poly-phenylene vinylene or polyhexylthiophene as hole-transporting material with a fullerene derivative (PCBM) as electron-transporting semiconductor¹³, a pentacene derivative associated with a perylenediimide¹⁴ or a perfluoro-phthalocyanine¹⁵ as n-type materials, blends of benzimidazolebenzophenanthroline ladder polymer (BBL) and copper phthalocyanine¹⁶, and mixtures of two phthalocyanines, one bearing octyloxycarbonyl substituents, Cu((CO₂C₈H₁₇)₈Pc), and the other one alkoxy chains, Cu((OC₈H₁₇)₈Pc)¹⁷. Organic heterostructures, including p-n heterojunctions and ambipolar transistors, have been reported¹⁸. Finally, we can also cite interesting reviews on ambipolar OFETs¹⁹⁻²¹.

Likewise a balance that owns only one equilibrium state but an infinity of unbalanced positions, the ambipolarity can be achieved only if the positive and negative mobile charges participate equally to the electrical current. Obviously, theoretically this condition is attained with intrinsic semiconductors, but its observation can be prevented by trapping effects and specific interactions with environment.

X.2 Inorganic ambipolar devices

Surprisingly, to our knowledge, only two papers report on the use of inorganic materials in gas sensors, with molybdenum telluride (MoTe₂)²² and a bromide perovskite (CsPbBr₃)²³. MoTe₂, known as a two-dimensional transition metal chalcogenide semiconducting material, exhibits an ambipolar behavior, as demonstrated in field-effect transistors used to determine the channel mobility of positive and negative charge carriers, depending on the sign of the gate voltage. However, in the particular case of MoTe₂, under illumination, only the n-type channel

is kept. The disappearance of the p-type behavior was attributed to the removal of dioxygen molecules from the surface. When exposed to NH_3 , the current increases, whatever measurements are carried out in the dark or under illumination. Thus, this device cannot be considered as an ambipolar gas sensor, even though the device is ambipolar by nature. It means that, even in the dark, the n-type behavior outweighs this of p-type. Interestingly, the sensitivity to NH_3 highly increases under UV light, by a factor of 25. Surprisingly, the response of the device to NH_3 was reported only at positive gate voltage.

Among perovskites, CsPbBr_3 was chosen for its high stability in ambient air. The devices consist of porous network of CsPbBr_3 that generate a photocurrent under visible-light irradiation, which was used to detect various concentrations of dioxygen, in the range 1%-100%, and acetone and ethanol in the ppm range, with very quick response and recovery time²³. The important point is that both dioxygen and the slightly reducing volatile organic compounds (VOC) give positive responses, indicating the ambipolar behavior of the device. Even though the photocurrent was very small (a few nA), it is worth noting that the sensor is a self-powered device. The relative response, RR, defined as $100 \times (I_{\text{gas}} - I_0) / I_0$, was about 90 % for pure O_2 , operating the device in 200 s/200 s exposure/recovery cycles (see Figure X.1). The response to 1 ppm acetone is 3%, and about the same to 1 ppm ethanol, without selectivity between the two analytes.

[Insert Figure X.1 here]

X.3 Field-effect transistors

A. Dodabalapur reported the first example of chemical sensor based on an ambipolar thin film transistor, consisting of two superposed semiconducting layers, namely zinc oxide (ZnO) covered by pentacene, which are of n-type and p-type, respectively (see Scheme X.1)²⁴. In p-channel accumulation mode ($V_{GS} < V_{DS} < 0$), a decrease of current observed under ethanol vapors, as a result of positive charges trapping in the pentacene layer. On the contrary, in the n-channel linear regime ($V_{DS} < V_{GS} < 0$), a current increase was observed. It is believed that, under ethanol, the polar molecules trap the positive charges and get stabilized. This effect is analogous to a decrease in the magnitude of the gate bias, which results in an increase of the drain-source current. It is worth noting that in the n-channel accumulation regime ($V_{GS} > V_{DS} > 0$), the device revealed to be insensitive to ethanol. This sensor combines the sensitivity of organic materials to polar analytes, as a result of dipolar chemical interactions, with the stability of metal oxide semiconductors, which is protected from air. Clearly, the response of the chemical sensor can be triggered by applied voltages.

[Insert Scheme X.1 here]

Besides this example using two materials, the use of a diketopyrrole-based ambipolar transistor was also reported to detect xylene vapors and discriminate between the three xylene isomers at 40 ppm²⁵. In terms of applications, it is quite interesting because this value is below the NIOSH long-term exposure limit. Even though these results are obtained in dry nitrogen, but not in real atmospheric conditions, this remains a very good example of the potentiality of ambipolar

transistors. Indeed, the rationale behind this approach is that such an ambipolar OFET can operate alternatively in n-channel and p-channel modes, and, as consequence, it generates double-sensing parameters. Thus, changes in hole voltage threshold, ΔV_{th-h} , normalized changes in hole mobility, $\Delta \mu_h / \mu_{hb}$, and hole subthreshold swing, ΔSS_h , were used as sensing parameters, and the same parameters dealing with electrons, ΔV_{th-e} , $\Delta \mu_e / \mu_{eb}$ and ΔSS_e , were used in a combined pattern recognition method to discriminate between the three xylene isomers. Among other parameters, ΔV_{th-e} does not depend on the isomer, while clearly ΔV_{th-h} increases in the order m-xylene < p-xylene < o-xylene (see Figure X.2). In the same time, the ΔSS_h variation remains very small for o-xylene but important for m and p-xylenes and ΔSS_e is more important for o-xylene than for m- and p-xylenes (see Figure X.2). The geometry of this OFET is different from the previous one, with a bottom contact configuration (see Scheme X.1). A classical transistor is already a multimodal sensor, but the multimodality is enriched by the ambipolarity. So, from two measurements of the source to drain current, one at a negative gate voltage and the other one at a positive gate voltage, a principal component analysis allowed for a good discrimination (see Figure X.2). This is made possible because one operating parameter can act as a trigger, which is here the sign of the gate voltage. A further improvement should be to reproduce such a discrimination by measurements in air, which requires to keep both p- and n-channels.

[Insert Figure X.2 here]

X.4 Phthalocyanine - based resistors

X. 4. 1. Electrochemical properties of multidecker phthalocyanine complexes

A series of double decker (LnPc_2) and triple decker (Ln_2Pc_3) lanthanide phthalocyanine complexes were synthesized and used as ambipolar materials by the teams of Y. Chen and J. Jiang (see Scheme X.2). As described in the first section of this chapter, LnPc_2 complexes are radical species, easily oxidized and reduced. Their energy gap, $E_{\text{HOMO}}-E_{\text{LUMO}}$, as deduced from their redox potentials determined by cyclic voltammetry (CV) in solution, is about 0.4 eV, which make them intrinsic semiconductors¹². It is worth noting that it is generally admitted that the energy of frontier orbitals has to be determined from the onset potentials, defined as the potentials at which the initial electron transfer from the HOMO, or towards the LUMO, becomes visible on the CV as a rise in anodic or cathodic currents, respectively^{26,27}. This determination results in values slightly smaller, ca. 0.25 eV, for the energy gap of radical double decker complexes (see Table X.1).

On the contrary, Ln_2Pc_3 complexes do not own unpaired electron. However, they exhibit a small energy gap, in the range 0.8-1.0 eV, because of their extended conjugated electronic structure. Exceptionally, unsymmetrical triple decker complexes have smaller energy gap, such as $\text{PcEu}_2[\text{Pc}(\text{POE})_8]_2$ (0.6 eV) and $\text{TPyPEu}_2[\text{Pc}(\text{O-butyl})_8]_2$ (0.43 eV). In all cases, the orbitals are stabilized and the molecules harder to be oxidized and easier to be reduced, in the presence of electron-withdrawing substituents, e.g. naphthoxy moieties, and the reverse in the presence of electron-donating substituents, e.g. alkoxy groups. In all cases, multidecker phthalocyanine complexes are more conductive than monophthalocyanines that own an energy gap higher than 1.2 eV (see Figure X.3).

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[Insert Scheme X.2 here]

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[Insert Figure X.3 here]

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[Insert Table X.1 here]

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N°	Molecules	Ref.	Electroch. Method	E ^{Ox} _{Onset} (V vs SCE)	E ^{Red} _{Onset} (V vs SCE)	HOMO (<i>litt.</i>) (eV)	LUMO (<i>litt.</i>) (eV)	Gap (eV)	OFET	Sensor
1	CuPcF ₈	28				(-6.06 ^a)	(-3.91 ^a)			p/n
2	ZnPcCl ₈	29								p/n
3	CuPc(CO ₂ -octyl) ₈	17	DPV			(-5.58)	(-3.95)		n	
4	CuPc(O-octyl) ₈	17	DPV	1.03	-0.25	-5.43 (-5.18)	-4.15 (-3.65)	-1.28	p	
5	LuPc ₂	30	CV	0.42	0.18	-4.82	-4.58	-0.24	p/n	p ^b
6	Eu[Pc(SPh) ₈] ₂	31	CV			(-4.74)	(-3.6)		p/n	n ^b
7	Ho[Pc(SPh) ₈] ₂	31	CV	0.59	0.35	-4.99 (-4.72)	-4.75 (-3.59)	-0.24	p/n	n ^b
8	PcEuPc(SPh) ₈	31	CV			(-4.66)	(-3.54)		p	p ^b
9	PcHoPc(SPh) ₈	31	CV	0.48	0.23	-4.88 (-4.61)	-4.63 (-3.52)	-0.25	p	p
10	PcEuPc(ONh) ₈	32	DPV	0.66	0.46	-5.06 (-4.85)	-4.86 (-3.61)	-0.2	p/n	p/n
11	Eu[Pc(ONh) ₈] ₂	32	DPV	0.74	0.56	-5.14 (-4.95)	-4.96 (-3.73)	-0.18	p/n	n ^c
12	Eu ₂ [Pc(S-hexyl) ₈] ₃	33	DPV	0.36	-0.46	-4.76 (-4.96)	-3.94 (-3.92)	-0.82	p/n	n ^c
13	PcEu ₂ [Pc(POE) ₈] ₂	34	DPV	0.33	-0.27	-4.73 (-4.85)	-4.13 (-4.08)	-0.6	p/n	p/n
14	Pc(OCH ₂ CF ₃) ₈ Eu ₂ [Pc(POE) ₈] ₂	35	DPV	0.24	-0.75	-4.64 (-4.74)	-3.65 (-3.61)	-0.99	p/n	p/n
15	Pc(OCH ₂ CF ₃) ₈ Eu ₂ [Pc(O-octyl) ₈] ₂	35	DPV	0.3	-0.62	-4.70 (-4.82)	-3.78 (-3.75)	-0.92	p/n	p/n
16	Gd ₂ [Pc(OPh) ₈] ₃	36	DPV	0.74	-0.15	-5.14 (-5.28)	-4.25 (-4.19)	-0.89	p/n	p/n
17	Tb ₂ [Pc(OPh) ₈] ₃	36	DPV	0.78	-0.15	-5.18 (-5.23)	-4.25 (-4.22)	-0.93	p/n	p/n
18	TPyPEu ₂ Pc ₂	37	DPV	0.35	-0.56	-4.75 (-4.9)	-3.84 (-3.71)	-0.91	p/n	p/n
19	TPyPEu ₂ [Pc(O-butyl) ₈] ₂	39	DPV	-0.07	-0.5	-4.33 (-4.36)	-3.9 (-3.74)	-0.43	p/n	p/n
20	[Pc(O-butyl) ₈] ₂ Y[BiPc(O-butyl) ₁₂] ₂ Y[Pc(O-butyl) ₈]	38	DPV	-0.225	-1.02	-4.175 (-4.32)	-3.38 (-3.31)	-0.8	p/n	n ^c
21	[Pc(S-hexyl) ₈] ₂ Eu ₂ [BiPc(S-hexyl) ₁₂] ₂ Eu ₂ [Pc(S-hexyl) ₈] ₂	33	DPV	0.52	-0.25	-4.92	-4.15	-0.77	p/n	n ^c

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a: determined by photoelectron spectroscopy; b: determined only towards NH_3 ; c:
the sensors give a negative response to NO_2 and no response to NH_3

X. 4. 2. Double decker phthalocyanine complexes

As demonstrated early for LuPc_2 ¹⁰, these molecules lead to p-type and n-type channels in OFETs^{31,33,35}. However, the chemical sensors prepared with this series of compounds are chemoresistors. The first example is that of $\text{PcEu}[\text{Pc}(\text{ONh})_8]$ that exhibits a current decrease under NO_2 , as for any n-type material³². However, under NH_3 , the current decreases too, indicating a p-type behavior. This is the first example of ambipolar gas sensor using a single component. On the contrary, the symmetrical $\text{Eu}[\text{Pc}(\text{ONh})_8]_2$ complex exhibits a n-type behavior under NO_2 , but with a lower sensitivity than the unsymmetrical complex, and no response to NH_3 . In the case of thiophenoxy substituents, the symmetrical complex $\text{Ln}[\text{Pc}(\text{SPh})_8]_2$ ($\text{Ln} = \text{Eu}, \text{Ho}$) lead to ambipolar OFETs whereas the unsymmetrical complexes $\text{PcLn}[\text{Pc}(\text{SPh})_8]$ ($\text{Ln} = \text{Eu}, \text{Ho}$) show only n-type channels³¹. Under NH_3 , the symmetrical complexes behave as n-type materials, with a current increase whereas the unsymmetrical complexes show a p-type behavior, with a current decrease. So, these symmetrical thiophenoxy-substituted complexes do not behave as ambipolar sensor, at least in the experimental conditions, even though p- and n-channel can be evidenced in OFETs.

X. 4. 3. Triple decker phthalocyanine complexes

Triple decker complexes bearing p-fluorophenoxy moieties, $\text{Ln}_2[\text{Pc}(\text{OPhF})_8]_3$, ($\text{Ln} = \text{Gd}, \text{Tb}$), exhibit a current decrease under NO_2 and under NH_3 , which is an unexpected feature if we consider a unique type of charge carriers³⁶. Clearly, this is the signature of the ambipolar behavior of these sensors. A limit of detection as good

as 0.14 ppm was calculated when 1 min/4 min exposure/recovery cycles are used, which is a remarkable value for molecular materials-based sensors operating at room temperature. In addition, these chemoresistors are unsensitive to H₂S, the selectivity coming from a larger binding energy between fluorine atoms and NH₃ molecules compared to F - H₂S interactions.

The triple decker complex bearing thiohexyl groups, Eu₂[Pc(S-hexyl)₈]₃, that exhibits both p- and n-channels in OFETS, behaves as a n-type material in chemoresistor configuration, with a current decrease under NO₂³³. However, they are unsensitive to NH₃ and H₂S, up to a concentration of 10 ppm, resulting from a low intermolecular interaction between these electron-donating analytes and the sensing materials, as depicted from the electronic static potential calculated by density functional theory.

Heteroleptic amphiphilic triple decker complexes, bearing polyoxyethylene or n-butoxy moieties, were also synthesized to allow the formation of self-assembled films by a simple quasi-Langmuir-Shäfer (QLS) method. PcEu₂[Pc(POE)₈]₂³⁴, (POE = (OC₂H₄)₃-OCH₃), Pc(OCH₂CF₃)₈Eu₂[Pc(POE)₈]₂ and Pc(OCH₂CF₃)₈Eu₂[Pc(O-octyl)₈]₂³⁵ exhibit a negative response to NO₂, as n-type materials, but they behave differently towards electrodonating analytes. Thus, PcEu₂[Pc(POE)₈]₂ exhibits a positive response to NH₃, as seen previously for double decker complexes whereas Pc(OCH₂CF₃)₈Eu₂[Pc(POE)₈]₂ is unsensitive to NH₃ and H₂S in the 2-10 ppm range. On the contrary, Pc(OCH₂CF₃)₈Eu₂[Pc(O-octyl)₈]₂ exhibits a positive response towards H₂S but a negative under NH₃. This apparent incoherence is due to the ambipolar nature of the material. In some cases, the increase or decrease of majority charge carriers has to be considered, but in other cases the increase of minority charge carriers reveals to be predominant as discussed by Y. Chen et al.³¹. Actually, not only the density of charge carriers and their mobility have to be considered, but

also the trapping of charges. Thus, a polar molecule can trap charges whereas a true electro-donating species will neutralize one type of charges and will increase the density of charges of opposite sign. Additionally, these processes will depend on the concentration of analyte. At this point, the sensor users could consider ambipolar materials to have erratic and unpredictable behaviors. This is true as long as the operator is passive, looking on the response of a given sensor to different analytes. This is why ambipolar sensors require an operation mode of their own. We must be able to control the p or n character of the device before its use. For this, we need a trigger capable of passing the device from a n-type behavior to a p-type behavior and vice versa.

Mixed (phthalocyaninato)(porphyrinato) europium triple-decker complexes, TPyPEu₂Pc₂³⁷ and TPyPEu₂ [Pc(O-butyl)₈]₂³⁹, in which the electron-withdrawing pyridyl substituents onto the meso position of the porphyrin ring ensure the sufficient hydrophilicity and suitable HOMO and LUMO energy levels to get amphiphilic ambipolar semiconductor. These molecules lead to ambipolar chemoresistors, with negative response towards NO₂ and NH₃, showing their n-type and p-type typical behavior, respectively (see Figure X.4).

[Insert Figure X.4 here]

X. 4. 4. Extended multi-decker phthalocyanine complexes

Finally, another type of phthalocyanine complexes were synthesized that include a binuclear phthalocyanine allowing to associate in one molecule two triple-decker moieties, as in the dimeric phthalocyanine-containing quintuple-decker [Pc(S-hexyl)₈]₂Eu₂[BiPc(S-hexyl)₁₂]Eu₂[Pc(S-hexyl)₈]₂³³, or two double-decker moieties, as in the

binuclear phthalocyanine dimer-containing yttrium double-decker complex $[\{\text{Pc}(\text{O-butyl})_8\}\text{Y}\{\text{BiPc}(\text{O-butyl})_{12}\}\text{Y}\{\text{Pc}(\text{O-butyl})_8\}]^{38}$. These two materials reveal to be ambipolar semiconductors, with high charge carriers mobilities, as measured in organic OFETs, with 0.07 and $0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons and holes, respectively, for the first material, and up to 2.3 and $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the later. These values are higher than those encountered for classical double- and triple-decker complexes, as a result of the extension of the π -conjugated system and an intensification of intermolecular interactions in the solid state. As chemoresistors, the quintuple-decker complex shows a sensitivity towards NO_2 doubled compared to this of the triple-decker analogue, namely $47\% \text{ ppm}^{-1}$, in the $100\text{-}500 \text{ ppb}$.

X. 5. Phthalocyanine-based heterojunctions

Beside resistors and transistors, heterojunctions have been used as conductometric transducers in chemosensors. They can be based on inorganic, organic or hybrid organic/inorganic materials. However, to our knowledge, only two examples of heterojunction - based ambipolar sensors have been reported so far^{17,26}. Obviously, these heterojunctions involved two materials, but of different natures and with totally different origins for their ambipolarity. The first one, is made from the superposition of two monophthalocyanines deposited on interdigitated gold electrodes, namely $\text{CuPc}(\text{CO}_2\text{-octyl})_8$ and $\text{CuPc}(\text{O-octyl})_8$, each layer bearing their own majority charge carriers, n-type and p-type, respectively, in relation with the electron-withdrawing and electron-donating character of their substituents¹⁷. The two-component OFETs prepared by successive solution processing steps of both materials exhibit an ambipolar behavior. The p/n bilayer structure is more conductive than the n/p bilayer structure, with slightly higher mobilities, in particular for holes, $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

against 0.03, and about the same electron mobility, around $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, such high electron mobility was obtained under nitrogen and in a dry environment for the n/p structure, due to the high sensitivity of such a device to negative charge neutralization and trapping. In the p/n structure, the positive top layer acts as a protective layer for the negative charges present in the sublayer. The both bilayer OFET devices, prepared onto treated SiO_2/Si substrates and gold electrodes, exhibit positive response to ethanol vapors, in the 100-800 ppm, with a higher sensitivity for the p/n structure. However, devices prepared on ITO interdigitated electrodes, which are not transistors, exhibit higher responses and relative responses, namely 350% at 700 ppm against about 120% for the OFET, both in the p/n structure. A sensitivity of $0.49\% \text{ ppm}^{-1}$ was determined for the p/n structure in the range 200-700 ppm, the LOD being estimated to be 100 ppm.

The other one, named historically molecular semiconductor – doped insulator heterojunction (MSDI), combines a low conductive material, e.g. a monophthalocyanine, as a sublayer, with a semiconductor, the bisphthalocyanine, LuPc_2 , as a top layer⁴⁰. This makes a high difference compared to the previous case. Indeed, due to the high resistance of the sublayer, under polarization, charges go across the thin sublayer, typically 50 nm in thickness, move in the top layer, or at the interface between the two materials, and cross again the sublayer (see in Scheme X.3)⁴¹. This is the reason why the interface between the two molecular materials plays a key role in the transport properties of this heterojunction.

[Insert Scheme X.3 here]

The response of MSDI to a gas depends on the nature of majority charge carriers in the sublayer. Thus, the LuPc₂/CuPc MSDI responds positively to ozone, while the perfluoro-copper phthalocyanine containing LuPc₂/CuPcF₁₆ MSDI responds negatively to ozone, and the reverse is observed under NH₃. The unique feature of MSDIs is that the only material in contact with the analyte remains the same in both cases, this is the LuPc₂ top layer⁴⁰. This behavior was demonstrated with other n-type materials, like the perylene tetracarboxylic dianhydride, the N,N'-di(2,2,3,3,4,4,4-heptafluorobutyl)-3,4,9,10-perylenetetracarboxylic-diimide⁴², the N,N'-dineopentyl 3,4,9,10-perylenetetracarboxylic-diimide⁴³ and a tetracyanotriphenyldioxazine bearing two triisopropylsilylethynyl moieties⁴⁴. As p-type sublayers, additionally to CuPc, the 5,5'-dihexyl- α,ω -sexithiophene (6T)⁴³ and the zinc 2,9,16,23-tetra-{2-(2-thienyl)ethoxy}-1,3,4,8,10,11,15,17,18,22,24,25-dodecafluorophthalocyanine, ZnPc(OR₄)F₁₂⁴⁵ and the cobalt 2,3,9,10,16,17,23,24-octa(hexyloxycarbonyl) phthalocyanine, CoPc(CO₂C₆H₁₃)₈²⁶, were also reported. The two later examples were designed to observe an ambipolar behavior, but it was not, the octaester phthalocyanine leading to a p-type behavior and ZnPc(OR₄)F₁₂ too, the balance between electron-donating and electron-withdrawing effects was not sufficient. On the contrary, the octafluoro-copper phthalocyanine, CuPcF₈ exhibits a unique feature, since the LuPc₂/CuPcF₈ MSDI presents a positive or a negative response to NH₃ depending of the operating conditions²⁶. This means that this is an ambipolar device. In dry air, the current decreases under NH₃, showing a p-type behavior, but in humid atmospheres the response is more complex. At first, without ammonia, during exposure to 70% of relative humidity (rh), the current sharply decreases, by 5% in 5 s, down to a minimum value, then increases to go back to the initial value into 20 s, this behavior being observed at each new exposure to humidity

after a long period in dry air. This transient behavior is unusual with conductometric transducers that usually show a monotonous response when exposed to an analyte. It means that water molecules are not only trapping or neutralizing majority charge carriers as expected for p-type materials, but are capable to commute the majority charge carriers in the device.

But, let us see the response of this device to NH_3 . The current increases under NH_3 at 70 % and 50 % rh, whereas it decreases at 30 % and 10 % rh (see Fig. X.5). Quantitatively, the relative response to 30 ppm NH_3 is +3.7 % at 70 % rh and +1.5 % at 50 % rh, but turns to negative values at 30 % rh (-1.4%) and at 10 % rh (-1.6%). In air, the MSDI exhibits a p-type behavior, but water molecules trap majority (positive) charge carriers in the top layer when the humidity increases. It is believed that the current is governed by minority (negative) mobile charges and the device behaves as a typical n-type MSDI, with an increase of the current under NH_3 . These results confirm the ambipolar behavior of the MSDI. Indeed, due to its very low energy gap, LuPc_2 is an intrinsic semiconductor with a high density of positive and negative charges. In air, LuPc_2 is a p-type material, because of a partial neutralization of negative charge carriers by dioxygen, but, compared to the sublayer, it has to be considered rather as a charge reservoir, whatever the nature of charges. At a first glance, the response of this sensor to NH_3 seems quite bad, since it is positive or negative depending on the rh value. However, if the rh is stable, or known, e.g. by combining the MSDI device with a humidity sensor, it can be used as a NH_3 sensor.

[Insert Figure X.5 here]

Enhanced chemosensing properties using phthalocyanine-based MSDI were recently reported⁴⁶. A modulation of the energy barrier at the electrode-sublayer interfaces was achieved by electrografting of organic layers, as demonstrated by impedance spectroscopy. For the LuPc₂/CuPcF₁₆ MSDI, the best results were obtained by electrografting dimethoxybenzene, which doubles the relative response towards NH₃, as well as the sensitivity in the 1-9 ppm range. This electrografting allowed attaining a LOD as good as 140 ppb in air. However, this method remains to apply to ambipolar sensors.

Finally, the authors studied octachloro-metallophthalocyanines, MPcCl₈, with M = Co(II), Cu(II) and Zn(II)²⁹. They exhibit dramatically different electrical properties when engaged in MSDI. Thus, Co(Cl₈Pc) is a n-type material, Cu(Cl₈Pc) a p-type material and Zn(Cl₈Pc) is an ambipolar material, as deduced from the response of the heterojunctions towards NH₃.

Conclusion and perspectives

Whereas ambipolar materials have been studied since a few decades in organic electronics, they remain rarely used in chemical sensors. The key point for this application is the capability of the operator to control the change of electronic behavior, from p-type to n-type and vice versa (see Scheme X. 4). If it occurs by the change in a gas concentration, it means that this is an interfering species and it is without any interest in applications, except in sensor arrays combining them with unipolar sensors. The unique behavior of ambipolar sensors would enrich the set of data coming from the sensor array. Thus, multivariate analyses, such as the principal component analysis, would take advantage of the differences in their responses to give access to both the concentration of NH₃ and the rh value. So, the ambipolar

behavior of the conductometric sensor enables a multimodal detection, as above mentioned in section X.3, with polymer-based ambipolar transistors.

[Insert Scheme X.4 here]

Contrarily, if the change is induced by an applied voltage or a particular light, then, we may talk about the control of the electronic state of the material by a trigger. If this aim is attained, then, the use of ambipolar materials in gas sensors offers additional possibilities for the multimodal detection, the sensor owing different operating states. This clearly indicates that OFETs are good candidates for ambipolar gas sensors, since the nature of the channel can be controlled by the gate. However, to go further towards applications, sensor responses need to be stable in air, in the presence of variable rh contents. For this reason, MSDI-type heterojunctions, or other bilayer structures where one layer can act as a protecting layer towards humidity, appear as good candidates to push ambipolar gas sensors to applications. The use of light for such an application is also worthy of investigation, but everything remains to be explore.

References

- 1 C. Pijolat, in *Chemical Sensors and Biosensors*, ed. R. Lalauze, John Wiley & Sons, Inc., Saint-Etienne, 2013, pp. 93–125.
- 2 J. D. Wright, *Prog. Surf. Sci.*, 1989, **31**, 1.
- 3 J. D. Wright, *Molecular Crystals*, Cambridge University Press, 1995.
- 4 D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, Butterworths and Co., London, 2nd edn. 1964.
- 5 S. Ross and J. P. Oliver, *On Physical Adsorption*, John Wiley, New York, 1964.
- 6 M. Bouvet and A. Pauly, in *The Encyclopedia of Sensors*, eds. C. A. Grimes, E. C. Dickey and V. Pishko, American Scientific Publishers, American Scientific Publishers. 2006, vol. 6, pp. 227–270.
- 7 F. I. Bohrer, C. N. Colesniuc, J. Park, M. E. Ruidiaz, I. K. Schuller, A. C. Kummel and W. C. Trogler, *J. Am. Chem. Soc.*, 2009, **131**, 478.

- 8 C. Di Natale, A. Macagnano, G. Repole, G. Saggio, A. D'Amico, R. Paolesse and T. Boschi, *Mater. Sci. Eng. C*, 1998, **5**, 209.
- 9 E. A. Silinsh, *Organic Molecular Crystals, Thier Electronic States*, Springer-Verlag, Berlin, Heidelberg, 1980.
- 10 G. Guillaud, M. Al Sadoun, M. Maitrot, J. Simon and M. Bouvet, *Chem. Phys. Lett.*, 1990, **167**, 503.
- 11 J.-J. André, K. Holczer, P. Petit, M.-T. Riou, C. Clarisse, R. Even, M. Fourmigué and J. Simon, *Chem. Phys. Lett.*, 1985, **115**, 463.
- 12 M. Bouvet and J. Simon, *Chem. Phys. Lett.*, 1990, **172**, 299.
- 13 E. J. Meijer, D. M. de Leeuw, S. Setayesh, E. van Veenendaal, B. H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf and T. M. Klapwijk, *Nat. Mater.*, 2003, **2**, 678.
- 14 H. Shim, A. Kumar, H. Cho, D. Yang, A. K. Palai and S. Pyo, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17804.
- 15 M. Jea, A. Kumar, H. Cho, D. Yang, H. Shim, A. K. Palai and S. Pyo, *J. Mater. Chem. C*, 2014, **2**, 3980.
- 16 A. Babel, J. D. Wind and S. A. Jenekhe, *Adv. Funct. Mater.*, 2004, **14**, 891–898.
- 17 Y. Wu, P. Ma, N. Wu, X. Kong, M. Bouvet, X. Li, Y. Chen and J. Jiang, *Adv. Mater. Interfaces*, 2016, **3**, 1600253.
- 18 H. Wang and D. Yan, *NPG Asia Mater.*, 2010, **2**, 69.
- 19 H. Sirringhaus, *Adv. Mater.*, 2005, **17**, 2411.
- 20 J. Zaumseil and H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296.
- 21 Y. Zhao, Y. Guo and Y. Liu, *Adv. Mater.*, 2013, **25**, 5372.
- 22 Z. Feng, Y. Xie, E. Wu, Y. Yu, S. Zheng, R. Zhang, X. Chen, C. Sun, H. Zhang, W. Pang, J. Liu and D. Zhang, *Micromachines*, 2017, **8**, 155.
- 23 H. Chen, M. Zhang, R. Bo, C. Barugkin, J. Zheng, Q. Ma, S. Huang, A. W. Y. Ho-Baillie, K. R. Catchpole and A. Tricoli, *Small*, 2018, **14**, 1702571.
- 24 S. Dutta, S. D. Lewis and A. Dodabalapur, *Appl. Phys. Lett.*, 2011, **98**, 213504.
- 25 B. Wang, T.-P. Huynh, W. Wu, N. Hayek, T. T. Do, J. C. Cancilla, J. S. Torrecilla, M. M. Nahid, J. M. Colwell, O. M. Gazit, S. R. Puniredd, C. R. McNeill, P. Sonar and H. Haick, *Adv. Mater.*, 2016, **28**, 4012.
- 26 A. Wannebroucq, S. Ouedraogo, R. Meunier-Prest, J.-M. Suisse, M. Bayo and M. Bouvet, *Sens. Actuators: B. Chem.*, 2018, **258**, 657.
- 27 L. Leonat, G. Sbârcea and I. V. Brânzoi, *U. P. B. Sci. Bull., Series B*, 2013, **75**, 111.
- 28 R. Murdey, N. Sato and M. Bouvet, *Mol. Cryst. Liq. Cryst.*, 2006, **455**, 211.
- 29 S. Ouedraogo, R. Meunier-Prest and M. Bouvet, to be published.
- 30 M. L'Her, Y. Cozien and J. Courtot-Coupez, *C. R. Acad. Sc. Paris*, 1986, **302**, 9.
- 31 Y. Chen, X. Kong, G. Lu, D. Qi, Y. Wu, X. Li, M. Bouvet, D. Sun and J. Jiang, *Mater. Chem. Front.*, 2018, **2**, 1009.
- 32 X. Kong, Z. Dong, Y. Wu, X. Li, Y. Chen and J. Jiang, *Chin. J. Chem.*, 2016, **34**, 975.
- 33 G. Lu, X. Kong, C. Wang, L. Zhao, D. Qi, Y. Jiang, S. Zhao, Y. Chen and J. Jiang, *Dyes Pigments*, 2019, **161**, 240.
- 34 H. Wang, X. Kong, S. Zhao, J. Wu, X. Li and Y. Chen, *New J. Chem.*, 2017, **41**, 11955.
- 35 S. Liu, H. Wang, X. Wang, S. Li, H. Liu, Y. Chen and X. Li, *J. Mater. Chem. C*, 2019, **7**, 424.
- 36 S. Zhao, X. Kong, X. Wang, X. Li, G. Yang and Y. Chen, *IEEE Trans. Electron Dev.*, **66**, 1930.

- 37 K. Abdullah, Y. Wu, S. Zhao, X. Kong, X. Li and Y. Chen, *Inorg. Chem. Comm.*, 2017, **86**, 1.
- 38 G. Lu, K. Wang, X. Kong, H. Pan, J. Zhang, Y. Chen and J. Jiang, *ChemElectroChem*, 2018, **5**, 605.
- 39 K. Abdullah, Y. Chen and J. Jiang, *J. Porphyrins Phthalocyanines*, 2017, **21**, 893.
- 40 V. Parra, J. Brunet, A. Pauly and M. Bouvet, *Analyst*, 2009, **134**, 1776.
- 41 M. Bouvet, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze and J.-M. Suisse, *Org. Electron.*, 2015, **26**, 345.
- 42 P. Gaudillat, A. Wannebroucq, J.-M. Suisse and M. Bouvet, *Sens. Actuators: B. Chem.*, 2016, **222**, 910.
- 43 M. Bouvet, H. Xiong and V. Parra, *Sens. Actuators: B. Chem.*, 2010, **145**, 501.
- 44 A. Wannebroucq, G. Gruntz, J.-M. Suisse, Y. Nicolas, R. Meunier-Prest, M. Mateos, T. Toupance and M. Bouvet, *Sens. Actuators: B. Chem.*, 2018, **255**, 1694.
- 45 A. Wannebroucq, R. Meunier-Prest, J.-C. Chambron, C.-H. Brachais, J.-M. Suisse and M. Bouvet, *RSC Advances*, 2017, **7**, 41272.
- 46 M. Mateos, R. Meunier-Prest, J.-M. Suisse and M. Bouvet, *Sens. Actuators: B. Chem.*, 2019, **299**, 126968.

FIGURE AND TABLE CAPTIONS

Scheme X.1 Architecture of OFETs including two semiconductors, of p- and n-type (left) and one ambipolar semiconductor (right) (adapted from ²⁴ and ²⁵).

Scheme X.2 Top: Top views of an octasubstituted phthalocyanine, a tetra(4-terpyridyl) porphyrin and a benzene-linked binuclear phthalocyanine, from left to right; the anions are represented. Bottom: Schematic view of mono, bis, triple decker and two types of binuclear phthalocyanine – containing complexes.

Scheme X.3 Scheme of a MSDI (right) compared to this of a resistor (left).

Scheme X.4 Schematic view of triggers (voltage, light and humidity) capable to change from n-type to p-type an ambipolar sensor.

Figure X.1 Response of the CsPbPr₃ - based device towards pure oxygen (left) and 1 ppm acetone (right) under visible light activation (modified from ²³).

Figure X.2. a) electron subthreshold swing, b) hole voltage threshold, c) hole subthreshold swing and d) PCA score plot for the three xylene isomers at 40 ppm (modified from ref ²⁵).

Figure X.3 Energy gap of a series of double (▲) and triple (●) decker complexes compared to this of one monophthalocyanine (■). Compound numbers refer to those used in Table X.1.

Figure X.4 Current variation as a function of time during exposure-recovery cycles, a) exposure to NO₂ and b) to NH₃ (modified from ³⁹).

Figure X.5. Response of a LuPc₂/CuPcF₈ MSDI (solid line) to 30 ppm NH₃ (dotted line) at a relative humidity value of 30 % (upper curve) and 70 % (lower curve), during twenty exposure/recovery cycles (1 min/4 min) ²⁶.

Table X.1 Redox properties of a series of phthalocyanine complexes, as depicted from cyclic voltammetry (CV) or differential pulse voltammetry (DPV), their HOMO and LUMO energies, calculated from the onset potentials and their deduced energy gap. The energies of frontier orbitals reported in literature are indicated in brackets. The nature of charge carriers observed in OFETs and in gas sensors are given.