

Full Research Paper

A Novel Gas Sensor Transducer Based on Phthalocyanine Heterojunction Devices

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Abstract: Experimental data concerning the changes in the current-voltage (I-V) performances of a molecular material-based heterojunction consisting of hexadecafluorinated nickel phthalocyanine (Ni(F₁₆Pc)) and nickel phthalocyanine (NiPc), (Au|Ni(F₁₆Pc)|NiPc|Al) are introduced as an unprecedented principle of transduction for gas sensing performances. The respective *n*- and *p*-type doped-insulator behaviors of the respective materials are supported, owing to the observed changes in surface potential (using the Kelvin probe method) after submission to electron donor (ammonia) and electron acceptor gases (ozone). On the other hand, the bilayer device exhibits strong variations in the built-in potential of the junction and in its rectification ratio. Moreover, large increases occur in forward and reverse currents in presence of ammonia vapors. These make possible a multimodal principle of detection controlled by a combined effect between the heterojunction and the NiPc|Al contact. Indeed, this metal/organic junction plays a critical role regarding the steady asymmetry of the I-V profiles during the device's doping even using high ammonia concentrations. This approach offers a more sophisticated alternative to the classically studied, but at times rather operation-limited, resistive gas sensors.

Keywords: molecular materials, phthalocyanine, organic heterojunction, gas sensor, transduction.

1. Introduction

Nowadays, thin films of organic materials having semiconducting properties are being extensively studied due to the very promising applications of Organic Electronics [1]. Among organic semiconductors (OS), the metallophthalocyanines (MPc), thanks to skills such as great processability, stability and rich substitution chemistry are one of the best candidates for novel molecular electronic devices. In addition, their electrical properties are extremely sensitive to the effect of electron-accepting and donating gases, so their gas sensing properties have been widely explored since about twenty years [2, 3]. In this regard, ozone (O_3) sensors based on thin films of nickel phthalocyanine (NiPc) for pollution control have been proposed [4, 5], as other phthalocyanine-based sensors for reducing gases as ammonia (NH_3) [6].

The literature shows that most of gas sensors based on semiconducting molecular materials are based on resistors, which principle of detection are merely based on the changes of resistance depending on the electronic nature of the gas analytes under study. One of the authors of this manuscript have reported some few examples of phthalocyanines as sensitive element in molecular field effect transistors-based gas sensors [3, 7]. Schottky diode sensors based on inorganic materials as Si or III-V compounds as InP have been also proposed [8-10], as well as inorganic *p-n* junctions [11]. The chemical sensitivity of such devices, but based on conducting polymers, has been discussed in terms of work function modulation [12].

Concerning molecular materials, metal/OS junctions have been extensively studied since early eighties [13]. The realization of organic heterojunctions has been made possible thanks to the confirmation of *n*-type semiconducting behavior in molecular materials [14]. Originally, these materials were used as *n*-channels organic field-effect transistors (OFETs) [15, 16] and in organic photovoltaic cells [17, 18]. Very recently, heterojunctions [19, 20] between copper phthalocyanine (CuPc) and perfluoro-copper phthalocyanine ($Cu(F_{16}Pc)$) have been used to control the electrical characteristics of an OFET [21]. On the other hand, fluorinated phthalocyanines as $Zn(F_{16}Pc)$ had been shown to be sensitive to reducing gases due to the withdrawing effect of fluorine atoms [6, 22]. This causes fluorinated phthalocyanines to be easier reduced than non-substituted phthalocyanines, then more inert to oxidization.

In this work, we propose a structure made from both *p*- and *n*-type semiconducting materials, namely non-substituted nickel phthalocyanine (NiPc) and nickel hexadecafluorophthalocyanine ($Ni(F_{16}Pc)$), in a combined organic heterojunction-Schottky diode configuration, ($Au|Ni(F_{16}Pc)|NiPc|Al$), as a novel device based on organic materials able to be used in gas sensing applications. For comparison purposes, single layer samples having the same electrode configuration are also discussed. The diode-like performance of the device is presented and discussed, besides its sensitivity and reversibility to an electron donor agent as ammonia (NH_3). The use of the electrical features of organic junctions based on OSs presented in this paper constitutes a new principle of transduction for gas sensing applications.

Before presenting the heterojunction-based device, we report on the semiconducting behavior of both *p*- and *n*-type molecular materials. For this purpose, the changes of surface potential of single layer films (by the Kelvin-Zisman vibrating capacitor probe (KP)) after being submitted to different atmospheres were taken as the base of the discussion, correlating them to the nature of majority charge carriers.

2. Experimental Section

2.1. Samples preparation

For the construction of the single-layer and heterojunction sandwich devices, high purity NiPc, purchased from Fluka, and Ni(F₁₆Pc) powders, synthesized following reported processes [23], were vacuum sublimed at 10⁻⁶ torr and 400 °C and 450 °C over a polycrystalline gold (Au) electrode covering a glass substrate (average thickness: 0.8-1.0 μm). To ensure the contact Au/glass, a chromium (Cr) thin film was deposited between both materials. Aluminum (Al) forms the top electrode in the devices. Overall, for the heterojunction-based device, up to five masks were used for the preparation, without breaking the vacuum between each stage.

2.2. Electrical measurements

The electrical features (current-voltage characteristics and activation energy) of single layer devices (Au|NiPc|Al and Au|Ni(F₁₆Pc)|Al) were measured in a vacuum cryostat at a temperature range from 100 to 300K. Current-voltage (I-V) measurements were performed in vacuum, in argon (Ar) and in active atmospheres using an electrometer KEITHLEY 6517 with an incorporated DC voltage supply. The electrometer is controlled by self-made software *via* the GP-IB board. The DC voltage can be applied continuously, following several sweep cycles, or during pulsed periods at different values. The polarity of voltages is provided for the bottom Au electrode. Prior to and during each test the devices were stored under light tight conditions to avoid any photoelectric effect.

For the Kelvin probe (KP) measurements, a thin round gold sheet (2 mm diameter) was used as reference electrode. The frequency of vibration was 175 Hz. As a driving mechanism of the KP, a piezoelectric design is applied. The setup is capable of measuring the surface potential in a range of -9.6 V — +9.6 V with the accuracy ±1 mV [24]. The experiments were performed in real ambient conditions and at room temperature.

2.3. Gas sensing experiments

The KP was used as transduction technique of the surface dipole changes detected by the films after being submitted to different gas atmospheres (N₂, as cleaning or purging gas, and NH₃ and O₃ as active atmospheres). All sensing experiments were also performed in air at room temperature. O₃ was created with a portable ozone generator (ECO SENSORS, Ozone source calibrator model OG-3) that supplied 0.1 ppm concentration, diluted in air. Concerning NH₃, the headspace coming from an aqueous solution, using N₂ as gas carrier, was used as ammonia source.

In the case of the gas sensing properties of the organic heterojunction-based device, the headspace coming from an NH₃ aqueous solution was used, using Ar as gas carrier. The sensor was placed in a 250 ml glass chamber covered by a metallic top protected by a varnish. Tightening between the top and two glass tubes ensuring the gas flow, and with BNC electrical contacts, is obtained using seals and Teflon ribbon. Electric gates allow diversion of the gas streams out of the chamber during the non-exposure periods.

3. Results and Discussion

3.1. Surface potential measurements

The KP is a well established technique for measuring work function changes in a molecular material and it is sensitive to the band bending of energy levels at the surface of organic films [24-26]. Thus, we have analyzed the changes in surface potential as a function of time for NiPc and Ni(F₁₆Pc) thin films deposited on Au electrodes, under streams of O₃ and NH₃, using N₂ as purging gas between cycles. These experiments are expected to inform about the nature of the majority charge carriers in the molecular materials, since the selected gases are well-defined electron acceptor (oxidizing) and donor (reducing) species, respectively. Actually, this approach entails a novel way of characterization of the *p*-type and *n*-type doped insulator properties of un-substituted and fluorinated phthalocyanines, such a property already elucidated by pure electrical measurements (chemiresistors) and recently by photoelectronic spectroscopy methods [27].

In general, the mechanism of electrical sensors based on phthalocyanine thin films is founded on the analyte adsorption/binding at the surface, followed by the formation of charge transfer complexes between both species that dissociate and diffuse into the film [3], which lead to a variation in the majority charge carriers, and then in the conductivity. This mechanism can involve either weak or chemical interactions (hydrogen bondings, metal-gas adducts, etc.) depending on the chemical nature of both the gas and the phthalocyanine material [28]. In case of NiPc, in comparison with, for instance, CoPc, the effect of oxidizing gases as O₃ was ascribed to the chemistry of the tetrapyrrolic macrocycle, rather than an oxidization of the metal, as previously demonstrated by electrochemical studies [29] and X-ray Photoelectron Spectroscopy (XPS) [5].

So, Figure 1 shows the evolution of the surface potential of single phthalocyanine layers when passing from a N₂ environment to the above-mentioned active atmospheres. When NiPc is submitted to a 0.1 ppm O₃ stream (Figure 1a), one can perceive a noticeable increase in surface potential of ca. 60 mV. Concerning the Ni(F₁₆Pc) film (Figure 1b), under the same conditions, no changes in its surface properties are observed. On the other hand, Figure 1c illustrates how NH₃ vapors provoke a clear boost in the surface potential of the fluorinated phthalocyanine film, which is ca. 70 mV. It is also of note how the desorption kinetics upon switching to N₂ is not as fast as that observed in the adsorption phenomenon, besides as that of the O₃ interaction with NiPc. This behavior is ascribed to the slow desorption of wet NH₃. The understanding of the differential electrical trends should be explained in terms of variation of majority charge carriers, namely, positive in case of NiPc and negative in Ni(F₁₆Pc). Therefore, an acceptor molecule as O₃ augments the density of positive charges in NiPc – i. e. the ratio between the number of free holes and the number of NiPc molecules forming the molecular material at the surface increases – thus increasing its surface potential. Regarding the fluorinated phthalocyanine, because of the powerful electron withdrawing effect of the sixteen fluorine atoms per molecular unit, the orbital frontier energy levels are strongly stabilized [22, 27], leading to the experimental inertia in surface potential vs. O₃. Conversely, an electron donor species as NH₃ causes a significant increasing of surface potential due to the enhancement of the density of negative charge carriers at the surface (probably due to some adduct formation between Ni and NH₃). As a result, using a technique as the KP, one can support that the majority charge carriers of NiPc are mostly *p*-type and in case of Ni(F₁₆Pc), essentially *n*-type. This result agrees well with recent studies

performed by other novel approaches based on Ultraviolet and Inverse Photoemission Spectroscopies (UPS and IEPS, respectively) [27]. Actually, the energy levels (HOMO and LUMO) are shifted to lower energies by more than 1 eV when going from non-substituted phthalocyanines to their perfluorinated derivatives. Therefore, the occurrence of an energy barrier between both molecular materials forming a heterojunction is expected.

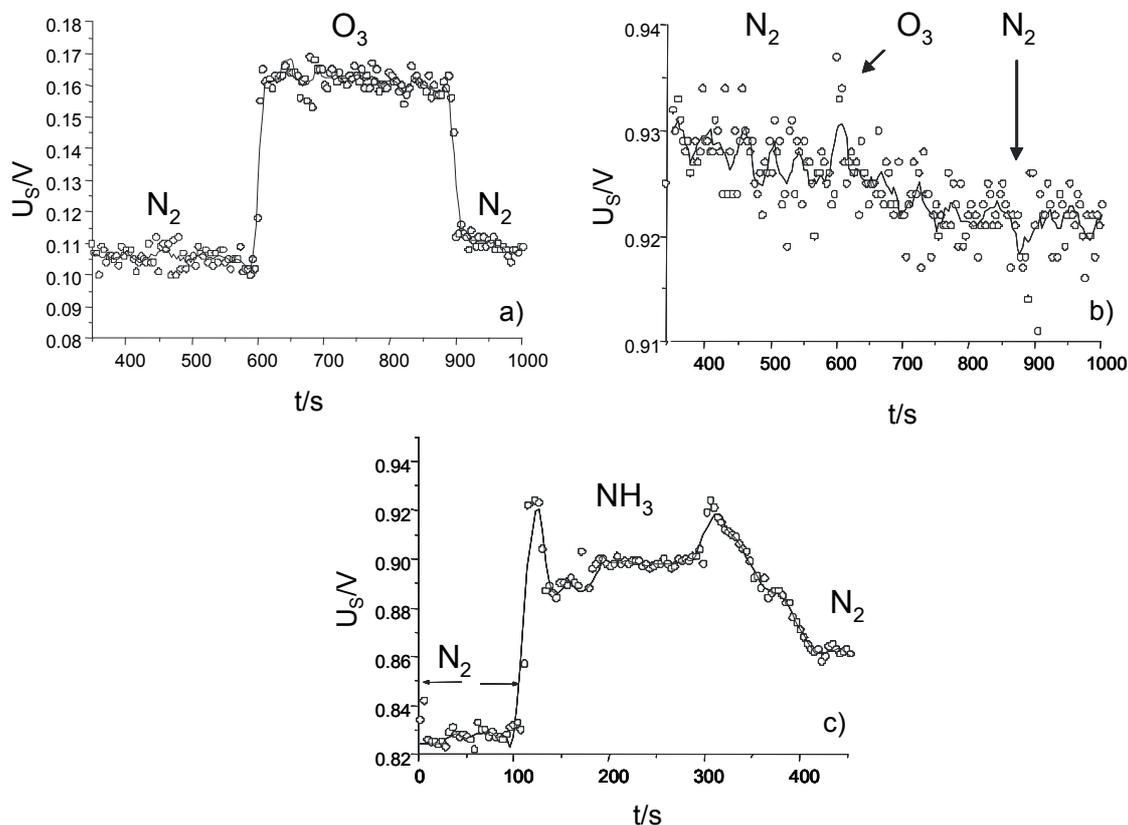


Figure 1. KP measurements showing the changes in surface potential under different atmospheres; a) An evaporated NiPc film under N_2 and O_3 (0.1 ppm) atmospheres; b) The same experiment for Ni($F_{16}Pc$); c) A Ni($F_{16}Pc$) film in N_2 and NH_3 (from a 0.5 % aqueous solution) atmospheres.

3.2. Electrical characterization of the samples.

Prior to the study of the effect exerted by different atmospheres on the electrical behavior of samples, we focused on the characterization of their conducting features. This would allow a supported knowledge regarding the principles of operation when being submitted to active atmospheres.

Concerning I-V experiments under high vacuum Au|NiPc|Al and Au|Ni($F_{16}Pc$)|Al sandwich devices, interestingly, no rectification effects were displayed, as illustrated in Figure 2. In case of the Au|NiPc|Al device, its behavior is in accordance with that observed in ZnPc-based samples, also under high vacuum. In other words, there is no forward rectification without air's oxygen at the metal/OS interface [13]. Furthermore, a thorough analysis reveals that there is some degree of asymmetry between forward and direct regimes (Figure 3), ascribed to the different work functions of the metal contacts, in particular at low bias voltages, when the thermal injection of charges acts. In forward bias, Ohmic conduction is found up to 1 V, whereas SCLC conduction is suggested at higher potentials [30],

according to an exponential distribution of traps in the material [31]. The density of these trapping states is determined by structural defects, dipoles and impurities [32, 33]. In SCLC regime, the bulk properties of material are dominating the contact effects. In relation to the perfluorinated phthalocyanine, and considering that Al forms Ohmic contacts with Ni(F₁₆Pc), the lack of rectification currents suggests that Au also forms an Ohmic contact with Ni(F₁₆Pc), in non-oxygenated atmospheres, as previously stated by different authors [21, 22, 34]. Thus, the dependence of activation energy does not follow terms of SCLC regime, as a possible result of the interaction of the molecule with Al atoms, as demonstrated in the case of Cu(F₁₆Pc) [35].

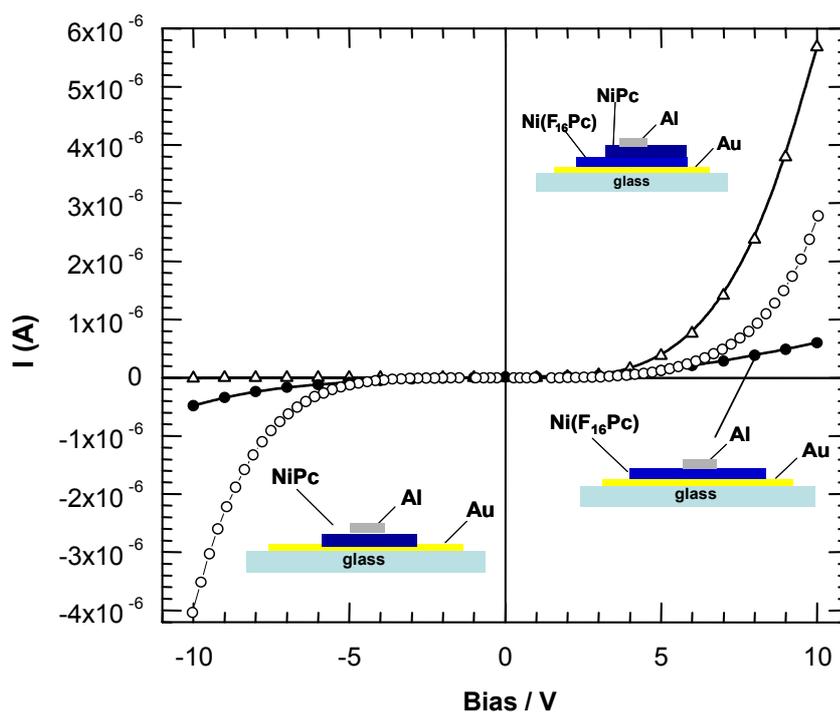


Figure 2. Current-voltage characteristics of Au|NiPc|Al (o), Au|Ni(F₁₆Pc)|Al (•) and Au|NiPc|Ni(F₁₆Pc)|Al (Δ) devices. Inset: schematic views of the samples' structures.

With respect to the I-V characteristics of the organic heterojunction Au|Ni(F₁₆Pc)|NiPc|Al, in an Ar atmosphere, it is worth noting the completely different performance in comparison with single layer structures (Figure 3). In the bilayer sample, a new electrical feature is now introduced, a self-bias (known as built-in potential) motivated by the contact between *p*-type NiPc and *n*-type Ni(F₁₆Pc), which accumulates holes and electrons in each respective side. This entails the formation of a space-charge layer between the semiconducting materials. Thus, forward bias applied on the device reduces the space-charge region, and then the transport of charges through this region is allowed.

In particular, a high rectification ratio (RR) and a strong asymmetry in the curve (Figures 2, 3) are obtained. The RR at ± 10 V bias, in an Ar atmosphere, is higher than 500, value much larger than that reported by Pietro et al. [36, 37] for a non-Schottky type rectification junction as Au|Cu(F₈Pc)|NiPc|Au. In our case, the marked rectification effect found is assumed to be controlled by a combined effect due to the charge carrier transfer across the organic heterojunction and the presence

of the NiPc|Al blocking junction, eventually favored by the oxygen doping at the metal/OS interface, estimated to be larger than 1.0 eV [38]. From the sharpest portion of the log I-V curves, at low voltages up to ± 1 V, one can observe good linear fittings, as illustrated in figure 3 for both forward and reverse bias. This correlates well with the classical Shockley equation for *p-n* and for thermionic emission and diffusion theories for Schottky diodes, indicating diode-type behavior [39]. Such an unsymmetrical I-V trend can thus be attributed to the occurrence of the mixed heterojunction-Schottky diode behavior. Forward conduction is rather controlled by the organic heterojunction, whereas the blocking Al contact would govern the reverse conduction, as a result of the limited current raising when increasing the applied bias.

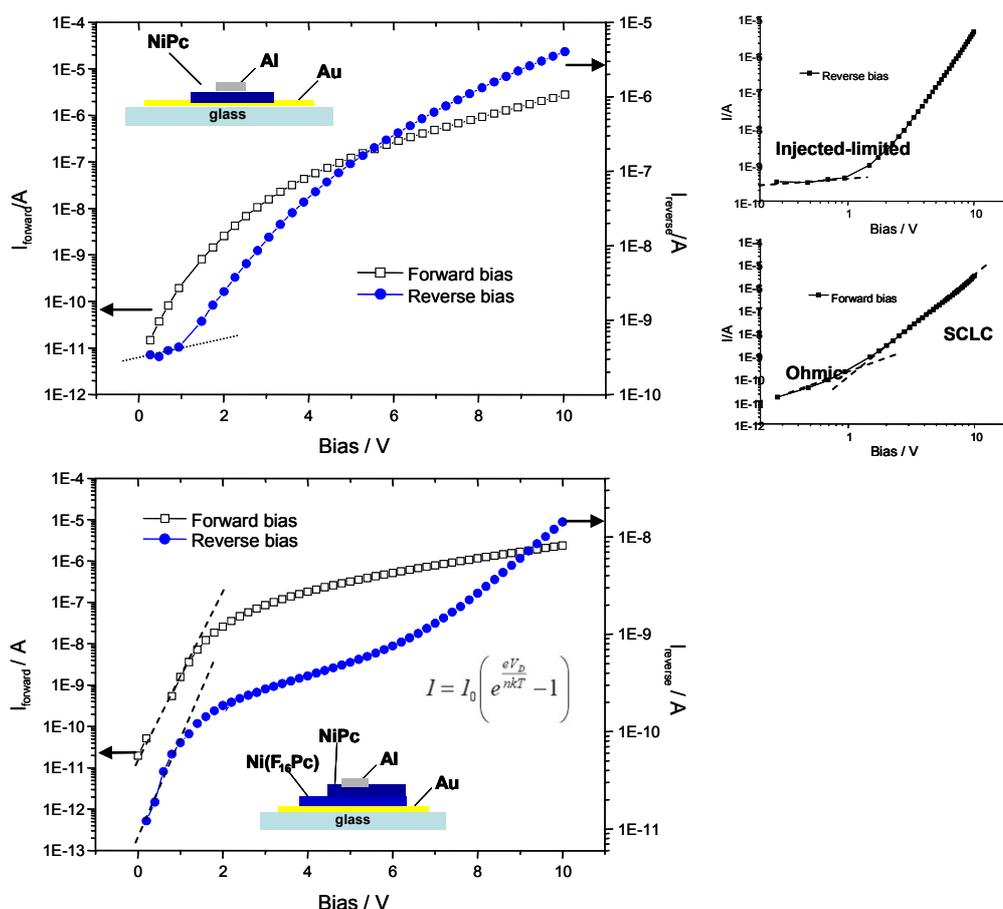


Figure 3. Current-voltage behavior of Au|NiPc|Ni(F₁₆Pc)|Al bilayer device in semi-logarithmic scale (bottom) compared to that of Au|NiPc|Al sample (top), the log-log curves are shown. Straight lines correspond to Schottky, Ohmic and SCLC equation fittings, depending on the case.

Moreover, to extract practical information regarding the charge injection properties, a useful tool to control the interface between metals and molecular materials is to study the dependence of electrical activation energies on the bias voltage (E_a (V)), in terms of space charge limited current (SCLC) method [30, 40]. Herein, the shape of the E_a (V) trend would be influenced by the presence of charge carrier local trapping states in the energy gap [32].

In Figure 4a, the experimental results for Au|NiPc|Al using Au as hole injecting metal is illustrated. Two different levels of energy traps are observed, with exponentially fitted values of ca. 0.85 and 0.50

eV. On the other hand, E_a (V) trends for the bilayer sample were markedly different. One can observe a gradual decreasing dependence, with fitted values much lower than those obtained in single layers, in both senses of polarization. Therefore, the organic heterojunction plays a critical role in the electrical properties of the device, which becomes less metal injection-dependant (the SCLC regime would predominate).

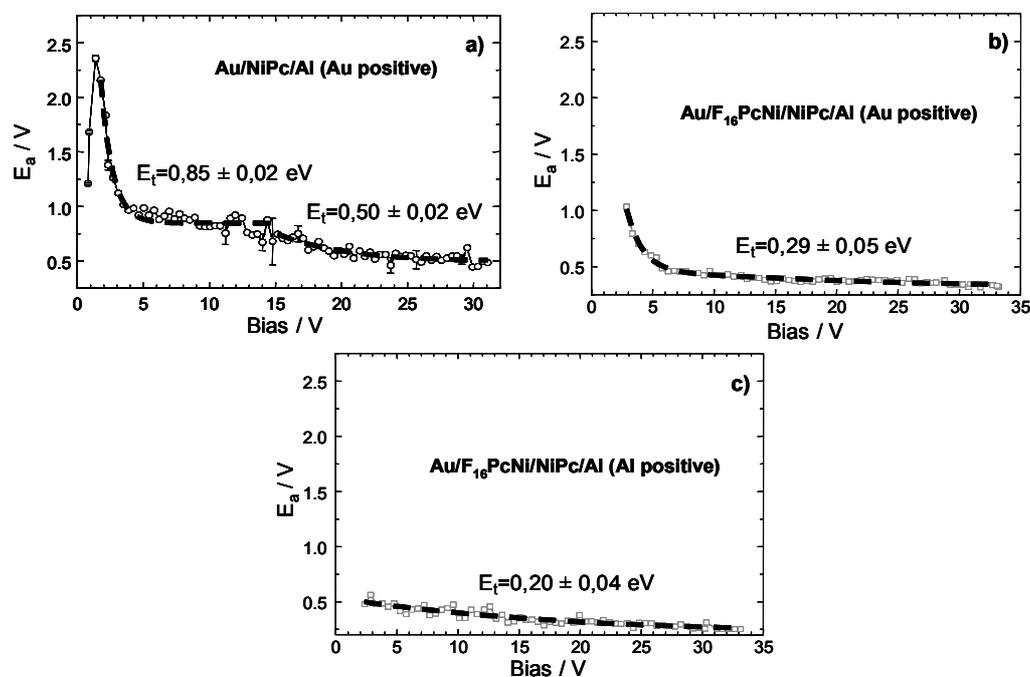


Figure 4. Dependence of activation energy (E_a) on the applied voltage for the Au|NiPc|Al sample, with Au as positive electrode (a) and for Au|NiPc|Ni(F₁₆Pc)|Al structure, with Au (b) and Al (c) as positive electrodes, respectively.

3.3 Gas sensing properties

The study of the gas interactions between doping vapors and the heterojunction-based device can be profited as a useful tool to support its particular conduction features.

In agreement with its *p*-type semiconducting behavior, NiPc undergoes a decrease in current transport after being doped with electron donor atmospheres as NH₃, the contrary effect that electron acceptor agents as O₃ provoke [4, 5]. Figure 5a shows the evolution of the *I-V* characteristics of the device after switching the environmental atmospheres from Ar to NH₃ for a short period (3 min). At first glance, it is worth noting two relevant experimental evidences: i) a noticeable increasing of both forward and reverse currents, and ii) strong variations in the device's performance, namely built-in potential of the junction, owing to the shift of the onset voltage at forward bias ($V_{\text{switch-on}}$), and RR all along the applied bias. Furthermore, from Figures 5b and 5c, both represented in semi-logarithmic scale, one can extract quantitative parameters dealing with the different sources of detection accessible by this heterojunction-Schottky device. Table 1 collects some of the values related to changes in the conductive properties from the initial state in Ar to the last exposure to NH₃ vapors. These results indicate that doping the fluorinated phthalocyanine layer realizes a definitive task in the conduction

mechanism, according to its *n*-type behavior. Moreover, the larger the NH₃ exposure, the shorter the RR of the device is. Finally, an interesting phenomenon comes from the observed constant current asymmetry, as a result of the concurrent contribution of the blocking NiPc|Al junction in the conduction mechanism. This further enlarges the possibilities of the device, since it helps to avoid the accomplishment of chemiresistor behavior even though the *n*-type material is strongly doped, as in the present case. The modifications of the built-in potential are likely to be explained according to a Fermi levels bending at the organic-organic interface, mainly due to the *n*-doping of Ni(F₁₆Pc). Regarding the reverse current increase, and considering the manifest *n*-doping that is exerted on the system, the occurrence of an E_F alignment promoting the charge transport through the device is expectable. Actually, it is known that *p*-type phthalocyanines (in air) can be changed to *n*-type by gas doping [41], forming an *n-n* isotype heterojunction. In this regard, underway experiments with analogous device's structure but with NiPc covering completely the *n*-type layer has shown a markedly different trend in presence of NH₃, even using much lower concentrations. Essentially, the forward current weakly diminish, according to the majority of charge carriers on NiPc, whereas the RR ratios reveal much slighter changes. Therefore, it is concluded that the presence of free surfaces of Ni(F₁₆Pc) in contact with the atmosphere is critical. This moves towards the use of diode-like structures in the accomplishment of gas sensing selectivity vs. electron acceptor species, only by modifying the device's configuration.

Table 1. List of quantitative values reporting the sensitivity of the bilayer sample when passing from an Ar atmosphere to a NH₃-based one during three minutes.

Gas sample	RR ₁₀	Forward V _{switch-on} / V	I _{max rev} / A	I _{max fwd} / A	%[ΔI/I ₀] ₋₁₀	%[ΔI/I ₀] ₁₀
Ar	520	6.6	1.1x10 ⁻⁸	5.9x10 ⁻⁶		
NH ₃ vapor	17	5.0	1.8x10 ⁻⁵	3.2x10 ⁻⁴	350	45

RR₁₀: rectification ratio at ± 10 V; V_{switch-on}: onset voltage extrapolated to forward current zero from the sharpest portion of the I-V curves, corresponding to the initial and final sample's state; I_{max}: maximum currents attained under Ar and NH₃ from zero to 10 V bias for both reverse (rev) and forward (fwd) regimes; %[ΔI/I₀]_V: average values (n = 7) of sensitivity at different bias.

Finally, one of the most critical features of a sensing device is its reversibility in applications that required fast responses and low recovery times after the gas samples action. To check this property, voltage pulses at +10 V_{dc} and -10 V_{dc} all along the time of the experiment were applied. After several alternating exposure/rest cycles (NH₃ 3 min / Ar 8 min), one can observe how the asymmetry of the curve and the overall current were modified in both positive and negative bias values (Figure 6). In any case, a steady state is rapidly and reproducibly fulfilled, indicating a good reversibility in successive sensing responses. The RR value at ± 10 V decreases from Ar to NH₃, and the sensitivity (%[ΔI/I_{Ar}] = 100(I_{NH3}-I_{Ar})/ I_{Ar}) is higher at negative bias, as collected in Table 1. Both quantitative changes can be used as further device responses in gas sensing applications, according to the above-mentioned multimodal principle of detection.

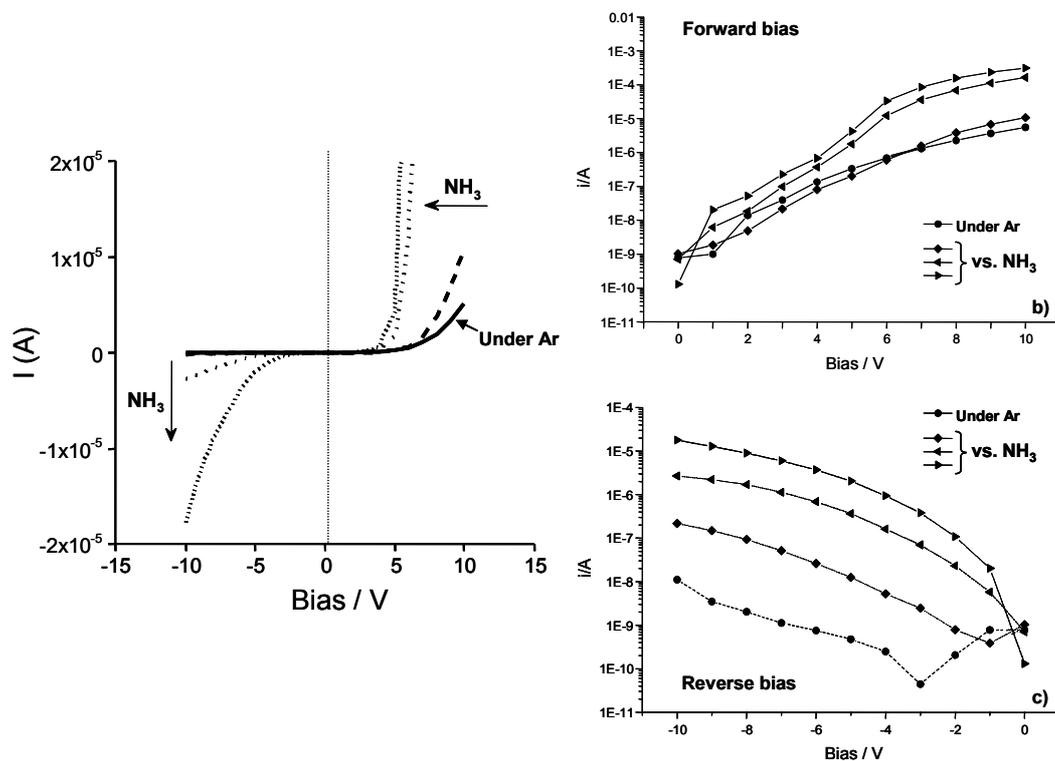


Figure 5. Effect of NH_3 (from a 10% aqueous solution) on the I-V behavior of $\text{Au}|\text{NiPc}|\text{Ni}(\text{F}_{16}\text{Pc})|\text{Al}$, in linear scale (a), and in semi-logarithmic scale for forward (b) and reverse (c) bias, respectively.

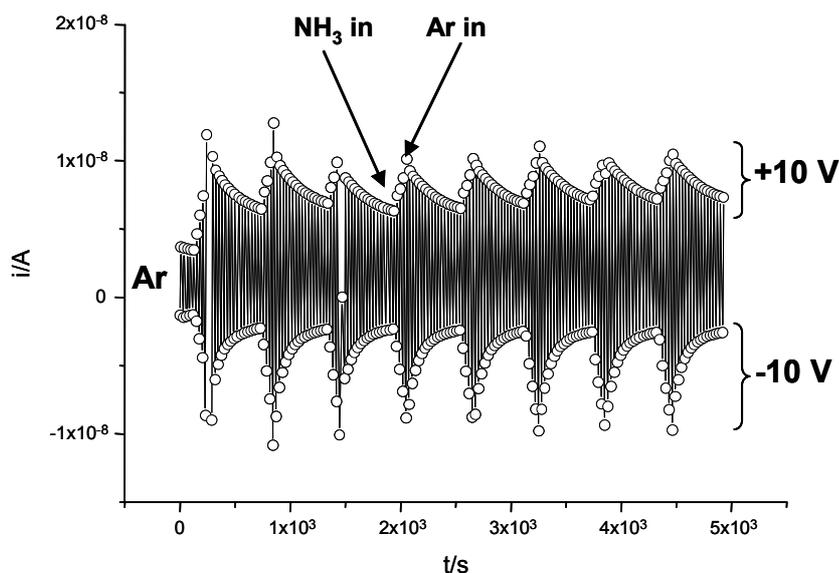


Figure 6. Steady current and reversibility of $\text{Au}|\text{NiPc}|\text{Ni}(\text{F}_{16}\text{Pc})|\text{Al}$ heterojunction sample after being submitted to cycles NH_3/Ar in dynamic rest (2 min/8 min).

4. Conclusions

In conclusion, the organic heterojunction formed by a *n*-type phthalocyanine as Ni(F₁₆Pc) and a *p*-type one as NiPc, at room temperature, is very sensitive to a donor gas as NH₃, as supported by the changes in RR, current and heterojunction potential. The blocking metal/OS junction assists the performance of the device by keeping the asymmetry of the current at forward and reverse regimes (i. e. avoids the attainment of a chemiresistor behavior). Selectivity vs. electron acceptor gases (oxidant) would be accessible by covering the *n*-type material completely using the *p*-type layer. This novel principle of transduction offers a profitable multimodal detection for gas sensors and enlarges the field of applications of molecular material-based junctions.

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