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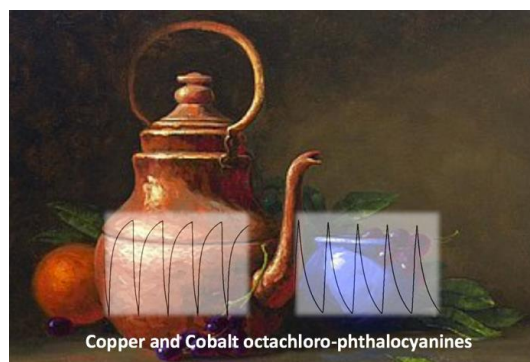
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p-Type and n-type conductometric behaviors of octachloro-metallophthalocyanine-based heterojunctions, the key role of the metal

Seydou Ouedraogo*, Tahirou Coulibaly, Rita Meunier-Prest, Mabinty Bayo-Bangoura, Marcel Bouvet*

The electrical properties of octachloro-phthalocyanines are determined. In combination with LuPc_2 , they are engaged in heterojunctions used as ammonia sensors. Cobalt, copper and zinc complexes exhibit dramatically different electrical behaviors. $\text{Co}(\text{Cl}_8\text{Pc})$ is a n-type material, $\text{Cu}(\text{Cl}_8\text{Pc})$ a p-type material and $\text{Zn}(\text{Cl}_8\text{Pc})$ is an ambipolar material.



p-Type and n-type conductometric behaviors of octachloro-metallophthalocyanine-based heterojunctions, the key role of the metal

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ABSTRACT: In the present work, we determined the electrical properties of octachlorinated metallophthalocyanines, with Co(II) and Cu(II) ions as metal centers. We engaged them in heterojunctions, with the lutetium bisphthalocyanine as a partner. Surprisingly, cobalt and copper complexes show opposite behaviors, the first one being a n-type material whereas the latter is a p-type material, as deduced from the response of the heterojunctions towards ammonia; the zinc complex showing an intermediate behavior. While the LuPc₂/Cu(Cl₈Pc) complex exhibits a negative response to ammonia, the LuPc₂/Co(Cl₈Pc) complex exhibits a positive response to ammonia, with a sensitivity of 1.47%.ppm⁻¹ at concentrations lower than 10 ppm and a limit of detection of 250 ppb. All the devices operate at room temperature and in real atmosphere.

KEYWORDS: molecular semiconductor, conductometric transducer, gas sensor, ammonia, devices.

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INTRODUCTION

Among porphyrinoid complexes, highly used as sensing materials in chemical sensors [1-5], with acoustic, conductometric and optical transducers, phthalocyanine complexes are mainly associated with conductometric transducers. In metallophthalocyanine complexes, the metal center plays a key role in their magnetic properties and catalytic activities [6]. On the contrary, the electrical properties do not depend on the nature of the metal center, but rather on the electronic density in the macrocycle. Indeed, the frontier molecular orbitals, HOMO and LUMO, involved in the creation of charge carriers are of π -type and localized on the phthalocyanine ring. Thus, in molecular materials, it is well known that the energy gap is directly related to the difference between the first reduction and first oxidation potentials determined for the molecule in solution when they deal with the macrocycle [7]. In addition, even the nature of majority charge carriers depends on the electron-donating, or electron-withdrawing character of the substituents. Thus, perfluorinated phthalocyanines are n-type materials whereas the non substituted phthalocyanines are p-type, as a result of the stabilization of the occupied and empty energy levels, as determined by photoelectron spectroscopy [8]. As a consequence, perfluorinated phthalocyanines lead to organic field-effect transistors with a n-type channel [9] and were used as n-type materials in heterojunctions [10-13]. On the contrary, chlorinated phthalocyanines were rarely reported, certainly because of their higher sublimation temperature, in relation with their higher molecular weight and stronger van der Waals interactions compared to fluorinated compounds. However, we can cite the work of Pakhomov showing the decrease in conductivity of perchloro-copper phthalocyanine under nitrogen dioxide, which indicates the n-type nature of majority charge carriers in this materials, contrarily to tetrachloro- and unsubstituted analogues [14]. Very thin films of octachloro-zinc phthalocyanine were studied by scanning tunneling microscopy under ultra-high vacuum, showing the molecular packing was driven by C-Cl...H-C hydrogen bonds between adjacent molecules, but their electrical properties were not determined [15]. The electrical properties of tetra, octa and hexadeca-chloro-cobalt phthalocyanines were also reported, but on pressed pellets and without determination of the nature of charge carriers [16].

The metal center plays generally a minor role on the electrical properties of phthalocyanines. Only one study of the sensitivity of metallophthalocyanine-based chemiresistors (MPc, M = Co, Ni, Cu, Zn and 2H) towards a series of vapor phase electron-donating gases was reported [17]. Their responses and recovery times were exponentially correlated with the binding enthalpy of analytes with the sensing materials. Even though their responses to one gas were not very different from each other, the analysis of the relative sensitivities of all studied MPcs allowed to distinguish among the series of analytes, regardless of their concentrations. It is a remarkable example of the metal effect on the sensing properties of phthalocyanines.

In the present paper, we report on the electrical properties of 2,3,9,10,16,17,23,24-octachloro-cobalt phthalocyanine (**1**) and 2,3,9,10,16,17,23,24-octachloro-copper phthalocyanine (**2**). Films were deposited by evaporation under secondary vacuum and characterized by Raman spectroscopy and current-voltage (I(V)) responses. Heterojunctions were prepared from these two molecules as sublayers, in association with the lutetium bisphthalocyanine, LuPc₂, and used to detect ammonia in the ppm range. This type of conductometric transducer was designed and patented by one of the authors [13,18,19].

EXPERIMENTAL

Chemicals

2,3,9,10,16,17,23,24-octachloro-cobalt phthalocyanine (1). A mixture of 4,5-dichlorophthalic anhydride (0.5 g, 2.72 mmol), cobalt (II) acetate tetrahydrate (0.169 g, 0.8 mmol), of urea (1.4 g, 3 mmol) and ammonium heptamolybdate (0.015 g) was refluxed in nitrobenzene for 5 hours. The solid obtained was filtered off, washed successively with ethanol and distilled water, then treated by hot 10% aqueous HCl solution, followed by successive washings with toluene, ethanol, methanol and acetone in a soxhlet. 0.288 g (0.4 mmol) of an intense blue color powder was obtained. Yield = 60%. Anal. calcd. for $C_{32}H_8Cl_8N_8Co$: C, 45.38; H, 0.95; N, 13.23; found: C, 44.1; H, 1.01; N, 13.18. MALDI-TOF-MS (matrix DIT) m/z : 846.6399 (M^+); calculated for $C_{32}H_8Cl_8N_8Co$: 846.7658. FT-IR, (ν , cm^{-1}): 1603, 1523, 1416, 1388, 1339, 1292, 1201, 1138, 1086, 1073, 965, 886, 850, 783, 749, 708, 661, 551, 503, 439, 430.

2,3,9,10,16,17,23,24-octachloro-copper phthalocyanine (2). A mixture of 4,5-dichlorophthalic anhydride (0.5 g, 2.72 mmol), copper (II) acetate tetrahydrate (0.169 g, 0.8 mmol), urea (1.4 g, 3 mmol) and ammonium heptamolybdate (0.015 g) was refluxed in nitrobenzene for 5 hours. The solid obtained was filtered off, washed successively with ethanol and distilled water, then treated by hot 10% aqueous HCl solution, followed by successive washings with toluene, ethanol, methanol and acetone in a soxhlet. 0.288 g (0.4 mmol) of an intense blue color powder was obtained. Yield = 60%. Anal. calcd. for $C_{32}H_8Cl_8N_8Cu$: C, 45.13; H, 0.95; N, 13.16; found: C, 44.1; H, 0.87; N, 13.21. MALDI-TOF-MS (matrix DIT) m/z : 850.6697 (M^+); calculated for $C_{32}H_8Cl_8N_8Cu$: 850.7545. FT-IR, (ν , cm^{-1}): 1604, 1512, 1410, 1387, 1341, 1297, 1201, 1140, 1086, 1071, 965, 889, 851, 785, 749, 705, 660, 548, 501, 432.

UV-visible, Infra-red and Raman spectroscopies, and mass spectrometry

UV-visible electronic absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer in transmission mode, using KBr pellets. Raman spectroscopy was conducted employing a Renishaw inVia Raman microscope with a 473 nm laser. Mass spectra were recorded on a MALDI (matrix assisted laser desorption ionization) BRUKER Proflex III spectrometer, using 1,8,9-anthracenetriol as a matrix.

Devices and electrical measurements

Electrical measurements were carried out with Indium Tin Oxide (ITO) interdigitated electrodes (IDE), separated by 75 μm , lithographed on a 1 x 1 cm^2 glass substrate. Thin films of phthalocyanines were prepared by sublimation under secondary vacuum (ca. 10^{-6} mbar) in a UNIVEX 250 thermal evaporator (Oerlikon, Germany), by heating in a temperature range of 400-450°C for $LuPc_2$, and in the range 500-550°C for the chlorinated phthalocyanines. The deposited thicknesses were 30 nm for each chlorinated phthalocyanine complex and 50 nm for $LuPc_2$, as determined by a quartz crystal microbalance during the deposition process. The workbench used for NH_3 exposure, at different relative humidity (rh) values, was described previously [20]. Synthetic air, ammonia gas, 1000 ppm and 100 ppm in synthetic air were used from standard cylinders, purchased from Air Liquide, France. The total flow was in the range 0.5-0.55 $NL \cdot min^{-1}$ depending on ammonia concentration and the volume of the test chamber was 8 cm^3 . Gas sensing experiments were carried out in a

dynamic fashion, with rest periods alternating with exposure periods, the length of which are precised in the text. In the present study, all the electrical measurements were carried out at the lab temperature (18–22 °C) unless otherwise specified.

RESULTS AND DISCUSSION

Synthesis and characterization of octachloro-metallophthalocyanine complexes

The cobalt and copper octachloro-phthalocyanines **1** and **2** were synthesized from the 4,5-dichlorophthalic anhydride, by reaction with metal acetate, in the presence of urea and ammonium heptamolybdate, by reflux in a solvent, as previously reported for unsubstituted phthalocyanines (Scheme 1) [21]. Even though the 4,5-dichlorophthalonitrile was obtained from the 4,5-dichloroanhydride [22,23], octachloro-metallophthalocyanines were mainly synthesized from the corresponding phthalimide, based on a method firstly reported by Linstead [24,25]. MALDI-TOF high resolution mass spectra of compounds **1** and **2** show a parent ion at that corresponds to $[M]^+$. Thus, for compound **1**, the most intense peak lies at $m/z = 846.6399$, for a calculated value of 846.7658. The isotopic profiles of obtained and calculated peaks are given in Supplementary Materials (Fig. S1). For compound **2**, the most intense peak lies at $m/z = 850.6697$, for a calculated value of 850.7545.

Films characterizations

The electronic absorption spectra of bilayers were the superimposition of the spectra of each material, as shown in Figure 1 for the LuPc₂/**2** bilayer, indicative of no significant charge transfer between the two layers. The maximum wavelength, at 668 nm, belongs to LuPc₂ and the shoulders at 635 and 701 nm belong to **2**. The weak band at 470 nm corresponds to a transition of a filled orbital towards the semi-occupied orbital of LuPc₂ [26,27]. The same type of spectrum was observed for LuPc₂/**1** (Fig. S2).

Raman spectroscopy analysis was conducted on powders of **1**, **2** and LuPc₂ and on the devices made from films of **1** and **2** covered by LuPc₂. The results are compiled in Table 1. The Raman spectra show peaks that can be directly attributed to the two layers, as shown by the superimposition of the spectra of sublayers, LuPc₂ and heterojunctions (Fig. S3 and S4), and exemplified in the range 1350-1650 cm⁻¹ for **2** (Fig. 2 right). Thus, for the LuPc₂/**2** device, peaks can be directly attributed to the LuPc₂ layer [28], in particular the peaks at 578 cm⁻¹ corresponding to Pc breathing, at 781 cm⁻¹ to C=N aza breathing and at 1158 cm⁻¹ to pyrrole breathing (Table 1). The one at 1335 cm⁻¹ is attributed to C=C pyrrole and benzene stretching and this at 1408 cm⁻¹ to isoindole stretching. The peak at 1513 cm⁻¹ corresponds to C=C pyrrole stretching and coupling of pyrrole and aza stretching. Other peaks can be assigned to the sublayer, at 659, 812, 864, 1051, 1531 and 1581 cm⁻¹. Additionally, peaks are common to both materials, such as the peaks at 547 cm⁻¹ (Pc breathing), 1121 cm⁻¹, 1175 cm⁻¹ (C-H bending), 1206 and 1302 cm⁻¹ (C-H bending) and 1600 cm⁻¹ (benzene stretching). These results confirm that the vacuum evaporation of **1** and **2** has been achieved correctly.

Electrical properties

Resistors made from **1** and from **2** exhibited a very high resistivity, estimated to be ca. 10⁹-10¹⁰ Ω.cm. However, they were engaged as sublayers in heterojunctions, by vacuum evaporation of lutetium bisphthalocyanine, LuPc₂, 50 nm in thickness, on films of **1** and **2**. The I(V) characteristics of heterojunctions are non linear, but symmetrical, with a current

value at +10 V of ca. 6.3 μA for LuPc₂/1 and 3 μA for LuPc₂/2 (Fig. 3). The conductivity value remained in the same decade for both devices. The observed difference could come from a slight different in morphology. The non linearity clearly shows that an energy barrier exists between the two materials or/and between the electrodes and the sublayers. A plateau exists at low voltages, but above a given potential the I(V) curve is linear. The non linearity of these curves can be characterized by a threshold voltage obtained by the intercept of the linear part of curves with the x-axis. Thus, for LuPc₂/1 and LuPc₂/2 devices, values of 1.86 V and 2.75 V were obtained, respectively, showing that the energy barrier is slightly higher with 2.

Chemical sensors

We first studied the devices at 90 ppm NH₃, with long exposure/recovery cycles, namely 10 min/40 min cycles (Fig. 4). The two devices behave differently; the current increases under NH₃ for LuPc₂/1 whereas it decreases for LuPc₂/2. LuPc₂/1 exhibits a n-type behavior whereas LuPc₂/2 exhibits a p-type behavior. The relative response, RR, defined as $RR (\%) = \frac{I_f - I_0}{I_0} \times 100$, is ca. +50% for LuPc₂/1 against -55% for LuPc₂/2. For the first time, it appears that the nature of charge carriers changed with the metal in the phthalocyanine complex. It is worth noting that LuPc₂, an intrinsic semiconductor, owns positive majority charge carriers in air, with a decrease of the current under NH₃ for LuPc₂ resistors. However, they are poor ammonia sensors due to a low RR value and an important drift of the baseline [29]. For understanding the particular electrical behavior of octachloro-phthalocyanines, we need to remind us of this of the octafluoro-copper phthalocyanine, Cu(F₈Pc), which was reported as an ambipolar material [30]. Depending on the experimental conditions, the Cu(F₈Pc) – based conductometric device exhibits a positive or a negative response towards ammonia. 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. In the present case, the change of the metal center can bring the small variation necessary to move the system from a p-type to a n-type behavior.

The effect of the NH₃ concentration was studied during short exposure/recovery cycles (1 min/4 min), in the range 10-90 ppm (Fig. 5). For LuPc₂/1, except at the first exposure period, the response was stable cycle after cycle and dependent of the NH₃ concentration, with a RR value of 84% at 90 ppm and 13% at 10 ppm. The LuPc₂/2 heterojunction exhibits also a very stable response, with a lower RR, of -27% and -7% at 90 and 10 ppm, respectively. However, the difference between the RR values at 90 and 60 ppm is very small, showing that a saturation occurs in this concentration range. To evidence this phenomenon, we studied also the devices at lower NH₃ concentrations, in the 1-9 ppm range (Fig. 6). For LuPc₂/2, at 1 ppm, the limit of detection (LOD) seems attained. Taking into account the baseline current I_0 and the noise N at 1 ppm, on the I(t) curve, LOD can be calculated (Eq. 1):

$$LOD = \frac{3N}{S \cdot I_0} \quad (1)$$

By plotting the RR value as a function of the NH₃ concentration (Fig. 6 right), two domains can be defined with different sensitivity values. Sensitivity is defined as $S = \Delta RR / \Delta [\text{NH}_3]$. For LuPc₂/2, S is -0.14 % ppm⁻¹ above 10 ppm and -0.39

%.ppm⁻¹ below 10 ppm NH₃, with a LOD of 1.18 ppm. For LuPc₂/1, S is 0.90 %.ppm⁻¹ above 10 ppm and 1.47 %.ppm⁻¹ below 10 ppm NH₃, with a LOD of 250 ppb. Such a value is of the same order of magnitude as the best ammonia sensors operating at room temperature. Thus, conducting polymer – carbone nanotube based resistors exhibit a LOD of 200 ppb [31,32]. However, other reported heterojunctions, based on the combination of a conducting polymer with LuPc₂, exhibited a LOD of 314 ppb [33] and 450 ppb [34], in the same ammonia concentration range, depending on the nature of the polymer and on the geometry of the heterojunction.

CONCLUSION

We showed that the octachloro-phthalocyanines can behave as p-type or n-type materials, depending on the metal center. The cobalt complex exhibits a n-type behavior whereas the copper complex exhibits a p-type behavior. As expected for monophthalocyanines, their conductivity is low, but their combination with LuPc₂ allowed forming a heterojunction capable to detect ammonia in the ppm range. We have to keep in mind that, in the same experimental conditions, LuPc₂ resistors exhibit a very bad response to ammonia, in particular with an important drift of the baseline [29]. The sensitivity of the devices comes from the radical nature of lutetium bisphthalocyanine, which makes it easily oxidized and reduced. However, the key role of the octachlorinated phthalocyanine as a sublayer in the heterojunction is clearly established, since the response is totally inverted when going from a p-type to a n-type sublayer. The highest sensitivity, 1.47 %.ppm⁻¹ below 10 ppm NH₃, was obtained with the cobalt complex as a sublayer, with a LOD of 250 ppb, which makes it among the best ammonia sensors operating in ambient air and at room temperature. The copper complex is less sensitive with a LOD of ca. 1 ppm in the same conditions.

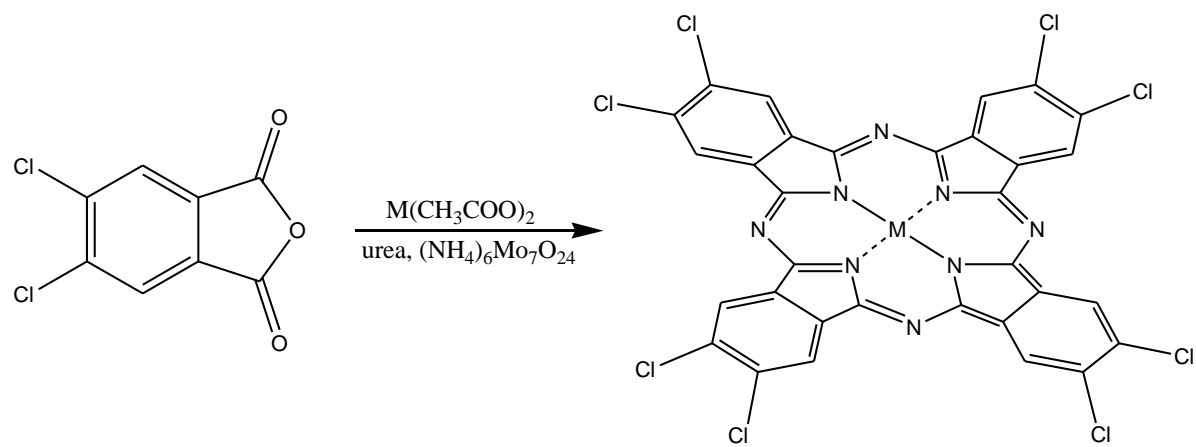
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Scheme 1. Synthetic route to obtain octachloro-phthalocyanines **1** ($M = \text{Co}$), **2** ($M = \text{Cu}$) and **3** ($M = \text{Zn}$).

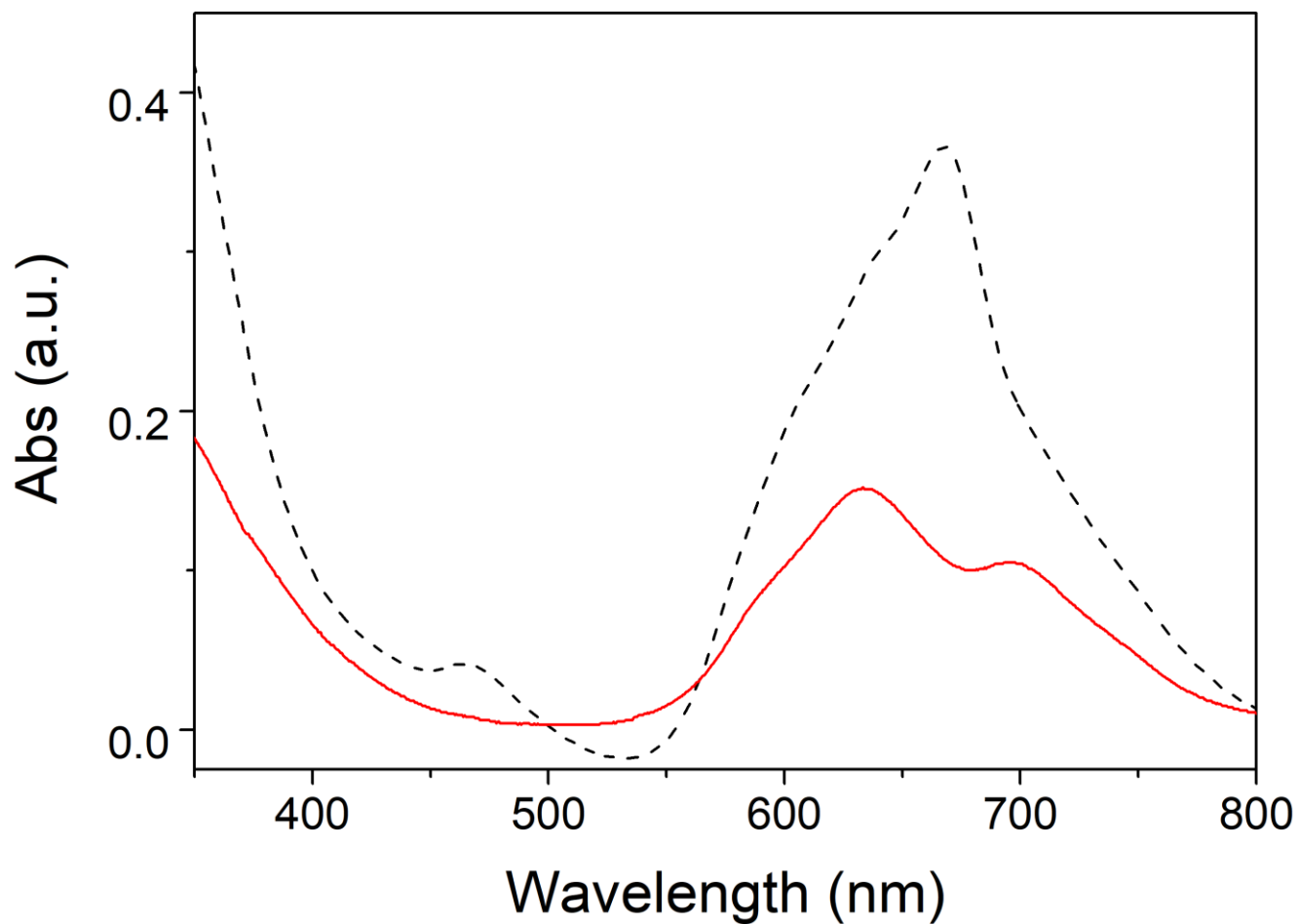


Figure 1. UV-vis electronic absorption spectra of a film of LuPc₂/2 on glass (black dashed line), compared to this of a film of **2** (red solid line).

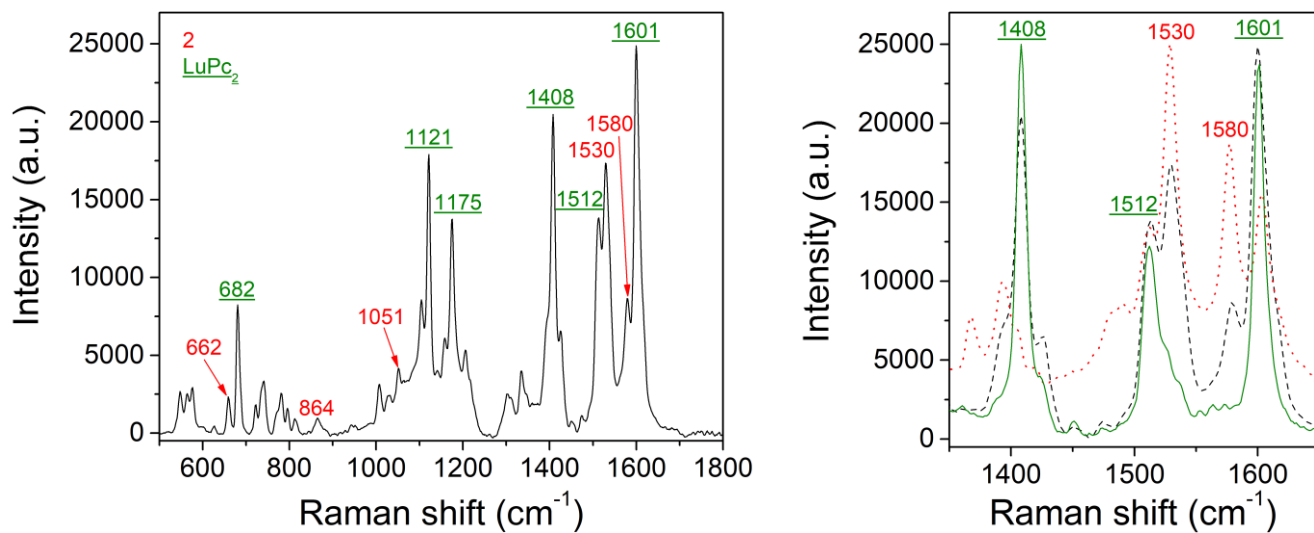


Figure 2. (left) Raman spectrum of a LuPc₂/2 heterojunction. The assignment of peaks characteristic of both materials is given; (right) superimposition of spectra of **2** (dotted line), LuPc₂ (solid line) and LuPc₂/2 (dashed line) in the range 1350-1650 cm⁻¹; the Raman shift value of the most intense peaks of the two components is given.

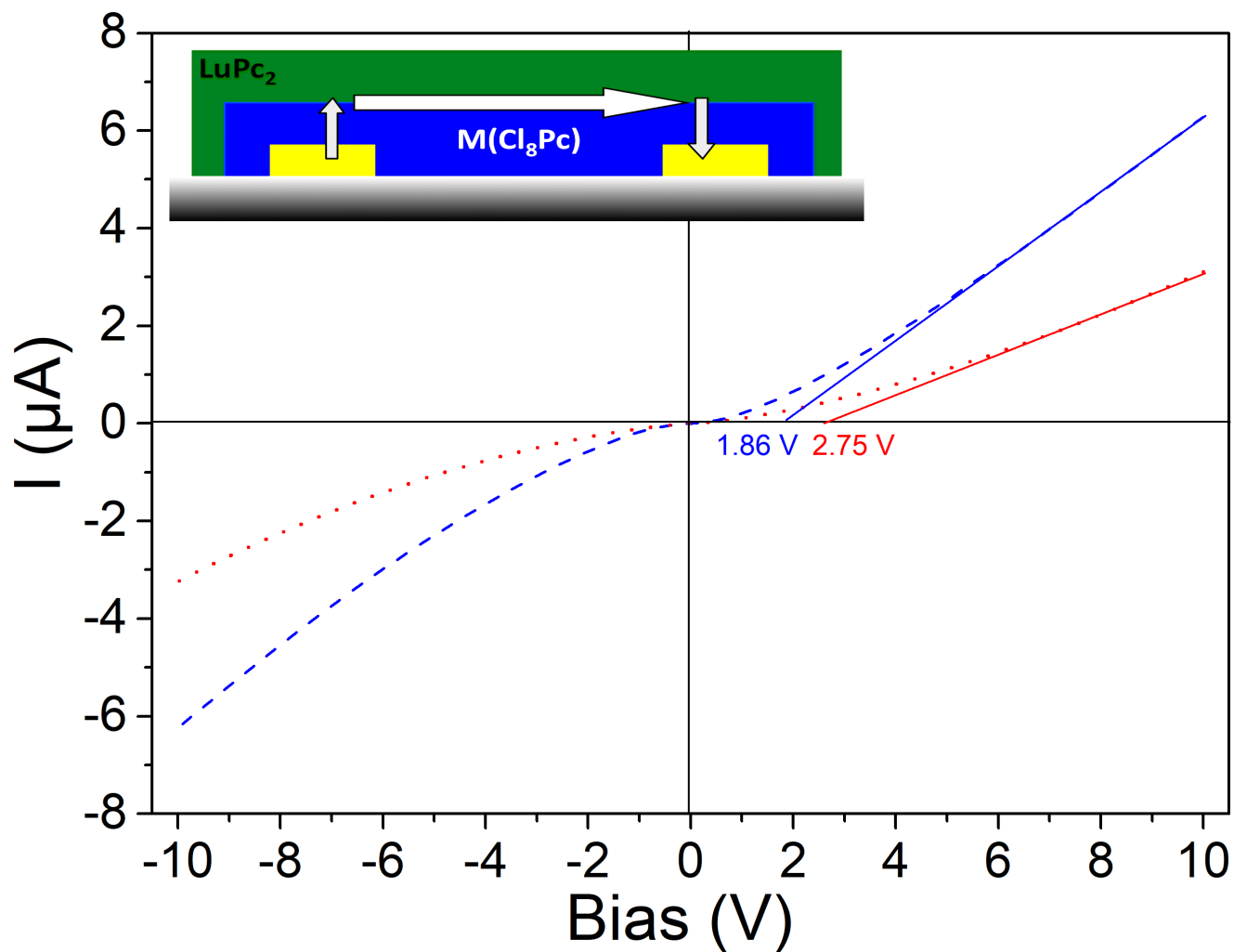


Figure 3. Typical $I(V)$ characteristics of LuPc₂/1 (dashed line) and LuPc₂/2 (dotted line) heterojunctions; the value of the threshold voltage is given for the two devices. A schematic view of the heterojunctions is given; the arrows indicate the main path for charges.

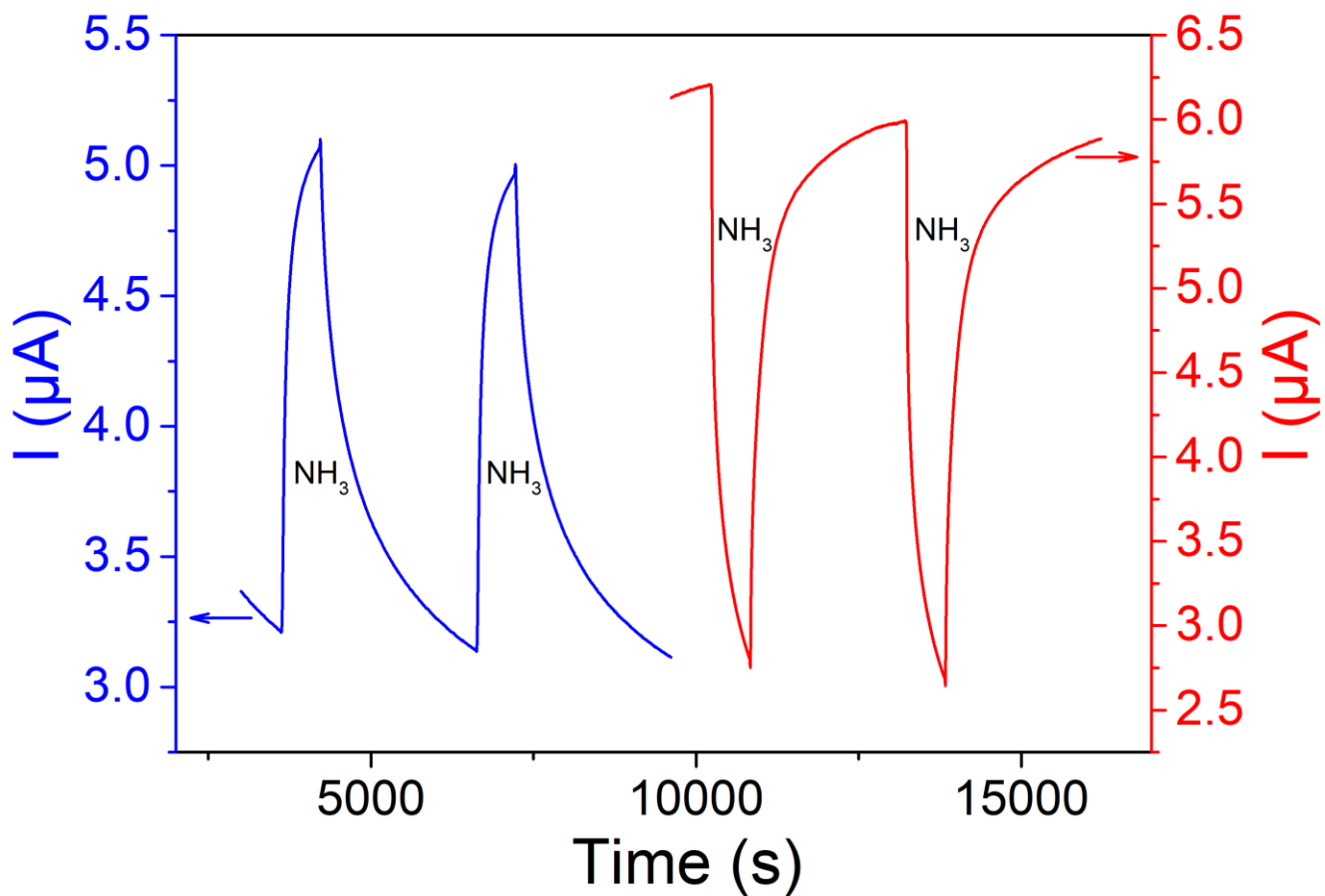


Figure 4. Response of LuPc₂/1 (left) and LuPc₂/2 (right) heterojunctions to 90 ppm ammonia, at 30% relative humidity, both during exposure/recovery cycles (10 min/40 min), at RT, with a bias of 1 V. The x-axis of the right curve has been arbitrary shifted for clarity.

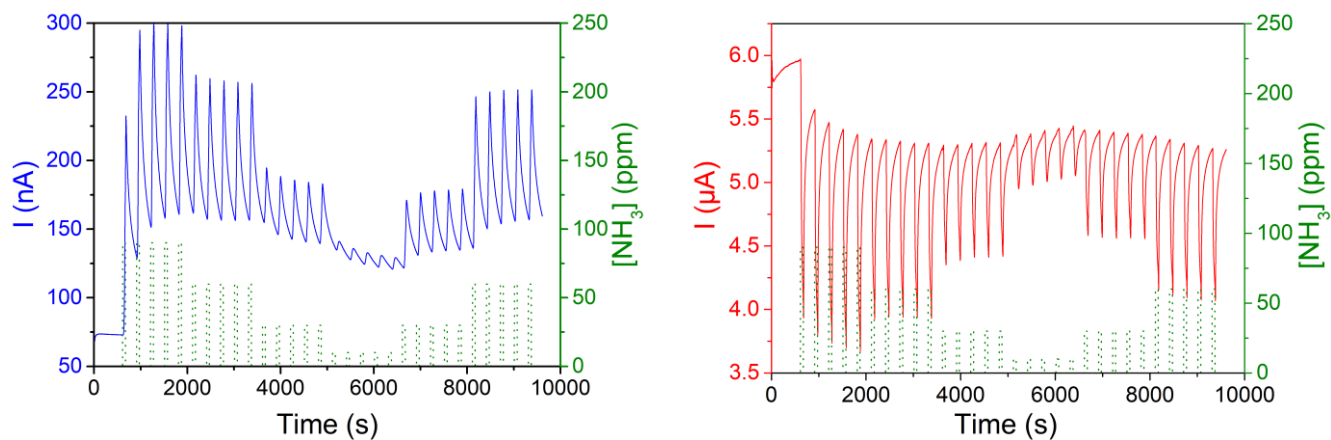


Figure 5. Response of LuPc₂/1 (left) and LuPc₂/2 (right) heterojunctions to NH₃, in the 10-90 ppm range, at 30% relative humidity, during exposure/recovery cycles (1 min/4 min), at 20 °C, with a bias of 1 V.

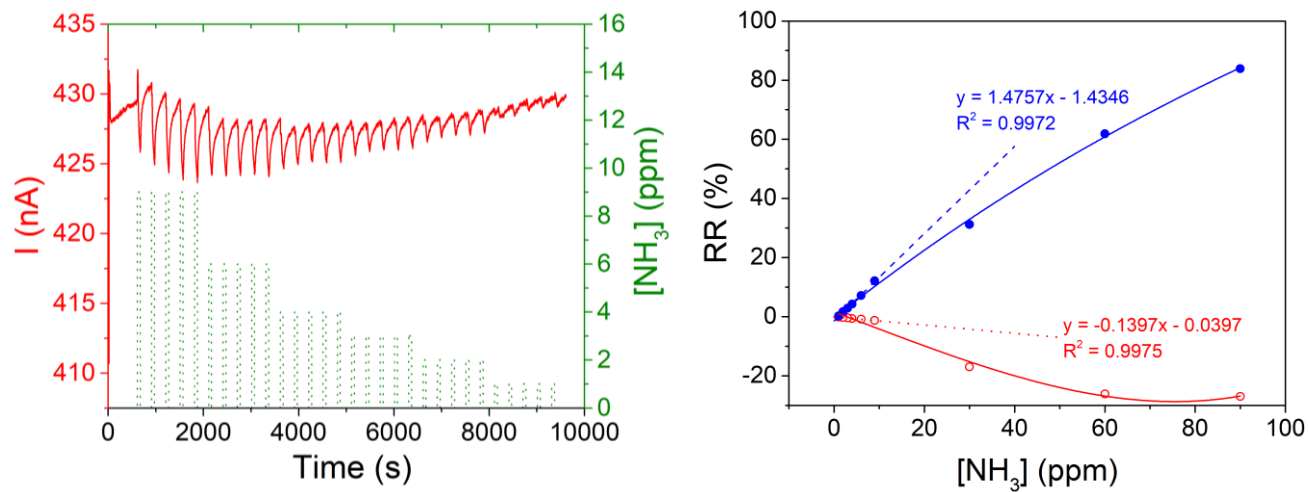


Figure 6. Response of LuPc₂/2 to NH₃, in the 1-9 ppm range, at 30% relative humidity, during exposure/recovery cycles (1 min/4 min), at 20 °C, with a bias of 1 V (left) and relative response as a function of the NH₃ concentration for LuPc₂/1 (●) and LuPc₂/2 (○) heterojunctions (right).

Table 1. Raman data (in cm^{-1}) of LuPc₂/1, LuPc₂/2, and LuPc₂/3 devices compared to these of each product as powder, and their attribution (s: strong, m: medium and w: weak).

1 powder	LuPc ₂ /1 MSDI	2 powder	LuPc ₂ /2 MSDI	3 powder	LuPc ₂ /3 MSDI	LuPc ₂ powder	Assignment
549 w	556, 565 w	547 w	547 w	547 w	550, 565 w	548 w	Pc breathing
-	579 w	-	576 w	-	578 w	578 w	Pc breathing
-	-	-	-	-	-	-	Pc breathing
663 s	663 w	661 s	659 w	660 s	659 w	-	Pc breathing
690 m	682 m	689 w	680 m	685 w	682 s	682 s	Pc breathing
751 w	742 w	748 w	741 w	749 w	743 m	735 m	C-H wagging
-	783 w	-	781 w	-	783 m	781 m	C=N aza stretching
817 w	819 w	812 w	812 w	812 w	815 w	-	Pc breathing
-	-	-	-	-	-	-	
868 m	867 w	864 w	864 w	861 w	861 w		
-	1008 w	-	1007 w	-	1007 w	1012 w	C-H bending
-	-	-	-	-	-	1033 w	C-H bending
1056 m	1055 w	1051 m	1051 w	1046 m	1048 w		C-H bending
1091 w	1105 w	1093 w	1104 w	1092 w	1104 w	1104 w	C-H bending
-	1122 s	-	1121 s	-	1122 s	1122 s	
-	1159 w	-	1158 s	-	1158 w	1147 w	pyrrole breathing
1174 m	1175 m	1169 m	1175 s	1167 m	1176 s	1177 m	C-H bending
1188 m	-	1182m	-	1191 m	-	-	C-H bending
1209 s	1211 w	1207 m	1206 w	1210 m	1210 w	1217 w	C-H bending
1304 m	1304 w	1303 w	1302 w	1319 w	1301 w	1303 w	C-H bending
-	1336 w	-	1335 w	-	1333 w	1333 w	C=C pyrrole and benzene stretching
1386 s	1387 m	1367 m, 1392 s		1394 s	1394 m		
-	1409 s	-	1408 s	1410 w	1409 s	1408 s	isoindole stretching
-	1429 w	-	1426 w	-	-	-	isoindole stretching
-	-	1490 w	-	-	-	-	C=C pyrrole stretching
-	1513 m	-	1513 s	1510 s	1512 s	1512 s	Coupling of pyrrole and aza stretching
1547 s	1546 m	1529 s	1531 s		-	-	benzene stretching
1584 s	-	1577 s	1581 m	1571 s	1574 w	-	benzene stretching
1607 s	1601 s	1603 s	1600 s	1604 m	1599 s	1601 s	benzene stretching