

Spin-coated thin films of metal porphyrin–phthalocyanine blend for an optochemical sensor of alcohol vapours

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Available online 3 March 2004

Abstract

Organic thin films based on a blend of two types of metal-co-ordinated macromolecules, i.e. Zn(II) tetra-4-(2,4-di-*tert*-amylphenoxy)-phthalocyanine (ZnPc) and Cu(II) tetrakis(*p-tert*-butylphenyl)porphyrin (CuP) have been deposited by spin-coating and used as optical chemically interacting materials for the detection of methanol, ethanol and isopropanol vapours. This paper reports the use of a specific optical technique consisting of the selection of four specific spectral regions taken in the UV-Vis spectral range corresponding to the typical Q and Soret bands of the phthalocyanine and porphyrin macromolecules and their corresponding blends. The variations in the absorption peaks obtained by the exposure of the single ZnPc and CuP sensing layers to the considered vapours in controlled atmosphere have been analysed and compared with those derived from a thin film obtained by mixing the two metal complexes in an appropriate ratio. The performance of the heterogeneous sensing layer (i.e. ZnPc/CuP blend)-based sensor evaluated in term of response and selectivity is different from that of single homogeneous films.

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Keywords: Metallo-phthalocyanines; Metallo-porphyrin; Thin films; Optical sensors

1. Introduction

Phthalocyanines and porphyrins represent a large family of functional molecular materials with high chemical and thermal stability. These compounds are objects of great interest for chemists, physicists and industrial scientists because of their potential role in emerging technologies including photoconductors, solar cells and chemical sensors [1,2]. These compounds, when deposited as thin films, interact with some oxidising and reducing gases and volatile organic compounds by absorption processes of the gas or vapour molecules onto the sensing layer [3,4]. The gas–surface interaction leads to reversible changes in some physical properties organic macromolecule of a thin film which can be monitored by different technological methodologies like quartz microbalances, surface acoustic wave devices, surface plasmon resonance excitation, optical absorption change and electrical conductivity measurements of the sensing layer [5].

Metallo-phthalocyanines and metallo-porphyrins are a natural choices for the optical detection of volatile organic

compounds because of their open co-ordination sites for axial ligation and their intense coloration. Using metal centres that span a range of chemical “hardness” and ligand-binding affinity, a wide range of volatile analytes might be differentiable. It has been found that porphyrins show significant solvatochromic effects, even with weakly interacting vapours (for example, arenes, halocarbon or ketones) showing distinguishable colorimetric effects [6].

The optical detection of gases and vapours could represent an appealing alternative and the adoption of organic compounds spin-coated films as sensing layers permits to explore the sensitivity and selectivity dependence on the molecular structure through structural modulation. The large panorama of the organic dyes offers various possibilities but there are some advantages in using phthalocyanines and porphyrins as sensing compounds due to their spectral features.

The UV-Vis spectra of phthalocyanines are typically described by two main absorption bands: the Q bands centred, respectively at about 680 and 620 nm and the B band centred at about 350 nm. Porphyrins have an intense absorption band centred at about 450 nm.

In a previous work [7], we reported on the spin-coated thin films of two differently substituted metallo-phthalocyanines suitable to develop reversible optical sensor devices in the UV-Vis spectral range. The monitoring of the variations

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in their absorption spectra induced by the exposure to the headspace of different VOCs allowed us to observe the linearity of the response at different VOC concentrations. The advances of our work involved the enhancement of the selectivity towards specific classes of volatile organic compounds such as the alcohols. At this end, we found that the fabrication of a sensing layer realised by using a ZnPc–CuP mixture played a determinant role in the selectivity improvement. Moreover, since the UV-Vis absorption spectrum of the CuP results fully integrated with ZnPc absorption bands because of the absence of bands overlapping, the selection of this specific phthalocyanine–porphyrin blend makes it possible to discriminate also between specific absorption peaks centred in the spectral region of commercial light emitting diodes (LEDs).

2. Experimental

Zn(II) tetra-4-(2,4-di-*tert*-amylphenoxy)phthalocyanine (ZnPc) and Cu(II) tetrakis(*p*-*tert*-butylphenyl)porphyrin (CuP) (Fig. 3) were synthesised as previously reported. In Fig. 1, the structures of the two employed macromolecules are reported. All the sensing layers were prepared in thin film form by spin-coating on suitable cleaned quartz substrates. In particular, ZnPc spin-coated thin films were prepared by using chloroform as solvent (12 mg ml^{-1} , $8.0 \times 10^{-3} \text{ M}$) and by spinning the solution onto quartz substrates at 2000 rpm for 30 s. Under the same conditions a 5 mg ml^{-1} ($5.6 \times 10^{-2} \text{ M}$) chloroform solution of CuP gave the second coating film. The thin layers exhibited blue–green and red colours, respectively and comparable absorption intensities. Moreover, a mixed layer (ZnPc–CuP) was obtained by spinning at 2000 rpm for 30 s 2 ml of a chloroform solution containing 12 mg of ZnPc and 1 mg of CuP.

UV-Vis solution spectra of the thin films thus realised were recorded by using a Varian Cary 100 scan UV-Vis spectrophotometer. Although all the optical sensing tests were performed by using a filtered light source from AVANTES

tungsten–halogen lamp, guided into an optical fibre, the absorption spectra (in 300–700 nm range) were collected and analysed using a commercial spectrophotometer AVANTES mod. MC 2000. The vapour concentration was varied by using a mass flow controller system MKS Instruments Model 647B equipped with two flowcontrollers. All the chemicals tested as VOCs were purchased from Aldrich Chemical Co. and used as received without further purification. All the solvents were of HPLC grade.

All the optical measurements were performed at room temperature and at normal incidence of the light beam. The vapour effect on the absorption properties of the active layer was measured in a dynamic pressure system implemented in our laboratory, where dry air at ambient pressure was used as carrier and reference gas. The samples were put in four independent stainless steel test chambers, all placed in the principal tube of the test bench in series using swagelock connections suitably modified for this task. First, the samples were exposed to a flow of dry air in order to acquire the baseline to analyse the optical response to the considered VOCs, the corresponding liquid analytes (10 ml each) were introduced into vials (20 ml each) kept at room temperature by a thermostatic tank. The sensor interrogation test was obtained by a means of deviating the flow of dry air in the vial for collecting the saturated vapours at room temperature; these were then diluted into the reference dry air flow in order to obtain a given VOCs concentration that was transferred in this way in the test chamber. The total flow was kept constant at 20 sccm. The integral of absorbance under exposure to each VOC was recorded during a period of time necessary to obtain a saturation signal and to calculate the response of the sensor. The dry air fluxes were set in order to send inside the test chamber the same concentration of each analyte vapours. The mentioned experimental set-up allows to choose independently the spectral range for each of the four channels and simultaneously monitor the UV-Vis spectrum variations in four defined spectral ranges. The selected intervals were chosen in such a way as to cover the whole spectrum of the sensing layer, taking into account the

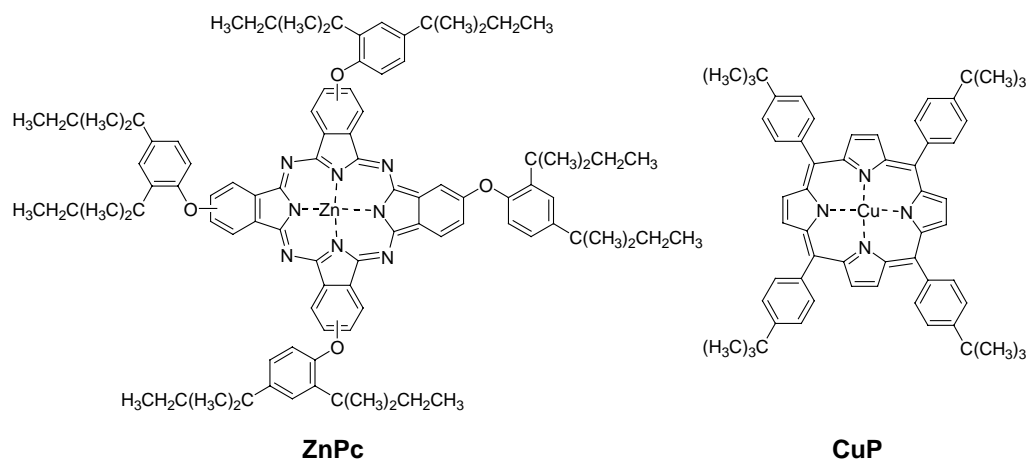


Fig. 1. Macromolecule structures of the ZnPc and CuP used as active layers.

spectral features observed in the mixed sensing layer. The study aimed to obtain detectable variations of the integrals, a reasonable signal-to-noise ratio and the future potential implementation of commercial light sources such as LEDs. Hence, the 300–700 nm spectrum was divided into four spectral intervals: 300–400, 400–450, 500–550 and 550–700 nm and the related integrals of the absorbance were called I_1 , I_2 , I_3 and I_4 , respectively. The first interval is of interest because of the presence of the ZnPc B band, centred at about 350 nm, the second interval is related to the CuP Soret band (421 nm), the remaining intervals monitor the variations occurring in the porphyrinic 540 nm band and in the broad Q absorption band centred on 636 nm with a shoulder located at about 680 nm.

3. Results and discussion

3.1. Spectrophotometric measurements

The CuP spectrum in chloroform is characterised by an intense Soret band at 417 nm and a smaller Q band at 540 nm (Fig. 2), whereas the ZnPc spectrum shows a B band at 344 nm related to the energy of the $n-\pi^*$ bands associated with the lone nitrogen pair orbital of the phthalocyanine ring and two main bands Q_I ($\lambda_{\max} = 683$ nm) and Q_{II} ($\lambda_{\max} = 616$ nm). In order to obtain similar absorption intensities, a 7.2:1.0 ZnPc–CuP molar ratio chloroform solution ($[\text{ZnPc}] = 4.0 \times 10^{-3}$ M) was prepared. The resulting UV-Vis absorption spectrum (Fig. 3) shows small ZnPc red-shifts with respect to the solutions of the single compound. The spin-coated film gave the spectrum shown in Fig. 4, where it is possible to observe the variation of the ZnPc Q bands: a

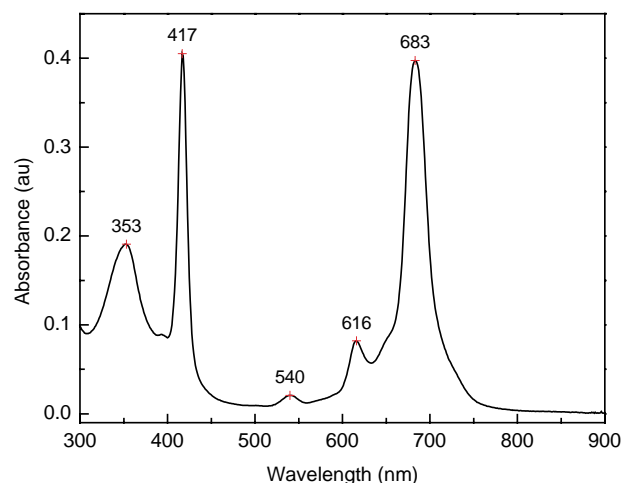


Fig. 3. UV-Vis absorption spectrum of the ZnPc/CuP blend in CHCl_3 solution.

broad band centred at 642 nm is typically due to the phthalocyanine dimers or higher aggregates, whereas the 680 nm shoulder is related to the monomer and corresponds to the Q_I band found in the solution spectrum. The Soret band of the porphyrin results also broaden and slightly red-shifted to 421 nm. A variation of the absorbance in the spin-coated UV-Vis spectrum with respect to the solution spectrum in chloroform was also found. By comparing the absorbances taken at their maximum wavelength, it is possible to observe a constant ratio $A(\text{CuP Soret band})/A(\text{ZnPc B band}) = 2.1$ both in the chloroform and in the spin-coated film spectra, whereas the absorbance related to the Q band decreases dramatically. This is probably due to a strong alteration of the optical behaviour of the CuP/ZnPc blend in the thin film

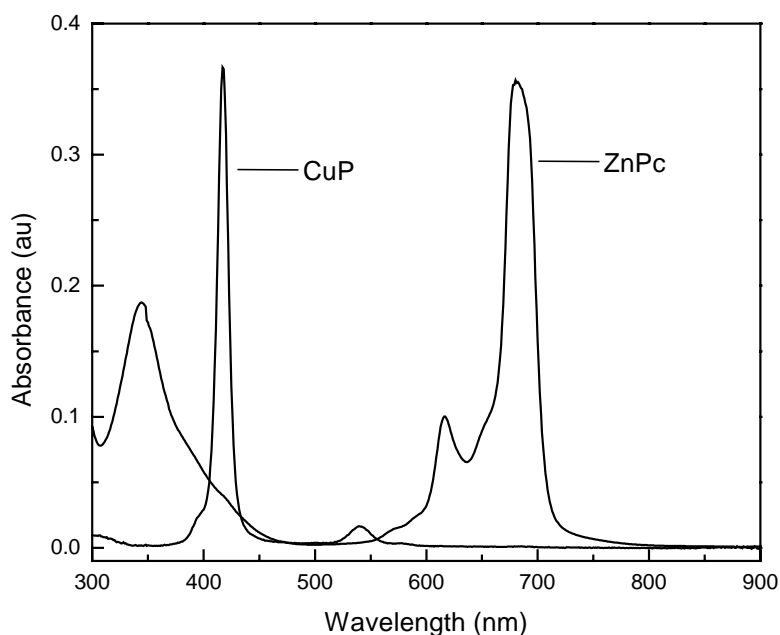


Fig. 2. UV-Vis absorption spectrum of the ZnPc and CuP in CHCl_3 solution overlapping.

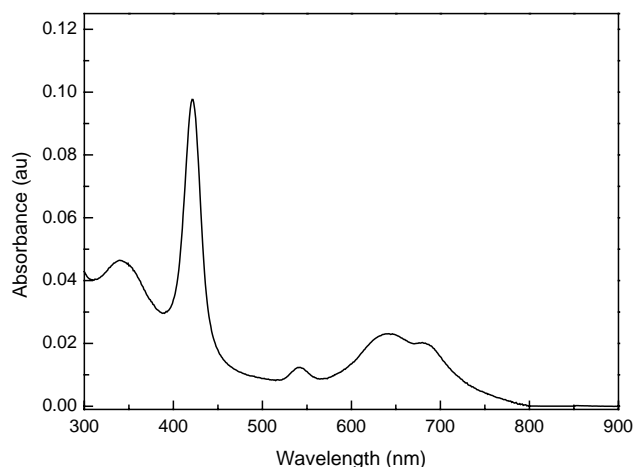


Fig. 4. UV-Vis absorption spectrum of the ZnPc/CuP spin-coated thin film.

form and in particular to a different behaviour of the optical absorption coefficient of the porphyrin with respect to the phthalocyanine macromolecules. The formation of dimers and complexes in thin film phase leads to a decrease in the intensity of the Q bands with respect to the Soret bands of the porphyrins. This behaviour could be due, more probably, to a decrease in the molecular electronic levels disposable for $\pi-\pi^*$ transitions. Nevertheless, further study should be performed in order to obtain a mixed sensing layer containing the same level of absorption peak in the investigated spectral range.

3.2. Optical sensing characteristics

The union between phthalocyanines and porphyrins in a mixed layer for sensory application represented an appealing object of investigation because of the possibility of obtaining certain unique variations of the hybrid material itself by variations of the ZnPc/CuP molar ratio with respect to covalently-linked heterodimers or double-decker hetero-complex of defined stoichiometry. The interactions between the two macrocycles may induce some variation of the co-ordination ability in the central metal ions towards the tested analytes and different molecular packing in the solid state can also be presumed. As a consequence, a different selectivity property, of the ZnPc/CuP film to the considered VOCs were observed by comparing it with the selectivity property of ZnPc and CuP homolayers. The evidence of these variations is confirmed by the comparison of the responses R_n calculated as the difference $I_n - I_n^0$, where I is the integral measured in the presence of the VOC vapours and I_n^0 is the integral measured in dry air flux. The choice to calculate the responses in terms of the difference in the dynamic integrals is due to the consideration that each absorption peak is proportional to the number of active macromolecules in the sensing process. The sensing mechanism involves a portion of these complexes

Table 1

Responses $\Delta I = I_{\text{gas}} - I_{\text{air}}$ calculated in terms of difference of the area integrals (MeOH: methanol, EtOH: ethanol, IPA: isopropyl alcohol)

	MeOH		EtOH		IPA		Acetone	
	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2
R_1	–	–	–	–	–	0.3	–	–0.2
R_2	–	–	–	0.1	0.2	0.3	–	–
R_3	0.2	–	0.4	–	0.5	–	0.2	–
R_4	0.4	0.5	0.8	0.5	1.5	1.0	0.3	–0.2

by an increase or decrease of the peak area. Consequently, we stress that the difference in the integral gives a better evaluation of the sensing phenomenon. The optical response of the thin film versus different analytes (i.e. isopropanol, ethanol, methanol and acetone) was measured by allowing the flow of the vapours into the pipeline of the experimental apparatus for the optical characterisation in controlled atmosphere described above. CuP, ZnPc and ZnPc/CuP-based samples placed in the four separated cells were thus exposed in sequence to the each VOC. The dynamic response was measured by recording the absorbance intensity on four independent channels fixing in 5 min, the time interval of exposure to the vapours and recovering. As an example, in Fig. 5 typical dynamic responses I_1 , I_2 , I_3 and I_4 corresponding to the variation in the absorption curves in the presence of dry air and ethanol vapours, respectively, are reported.

Table 1 represents the average responses calculated from the dynamic curves of the single porphyrin and phthalocyanine active layers. R_2 is the response of the porphyrin-based sensing elements, R_1 , R_3 and R_4 are the responses related to the phthalocyanine-based sensing element. The S_1 data set can be considered as the first sensing system and S_2 is the second, based on the porphyrin-doped Pc layer. The responses are also shown in Fig. 6 as the histograms of R_n versus the analytes. As can be seen, both positive and negative variations of R_n are possible depending on the variation of the absorption bands and their related integrals when exposed to the analyte vapours.

The S_1 system reacts similarly to the different alcohols exposure with a similar behaviour (Fig. 6a), only isopropanol can be discriminated from methanol and ethanol by the porphyrin sensing element (R_2). No significant variation in the R_n pattern was found by comparing methanol and ethanol responses because ZnPc-based sensing elements react with the increasing of I_3 and I_4 . The R_3/R_4 ratio does not change from methanol to ethanol being approximately equal to 1:2 and only a more pronounced sensitivity is observed towards the ethanol vapours. Moreover, acetone can be easily confused with methanol and ethanol because of a great similarity in the responses. The porphyrin-doped S_2 sensing element (see Fig. 6b) shows a different behaviour: isopropanol exposure causes the rise of the porphyrin R_2 and of the phthalocyanine R_4 and R_1 which is absent in the ethanol recog-

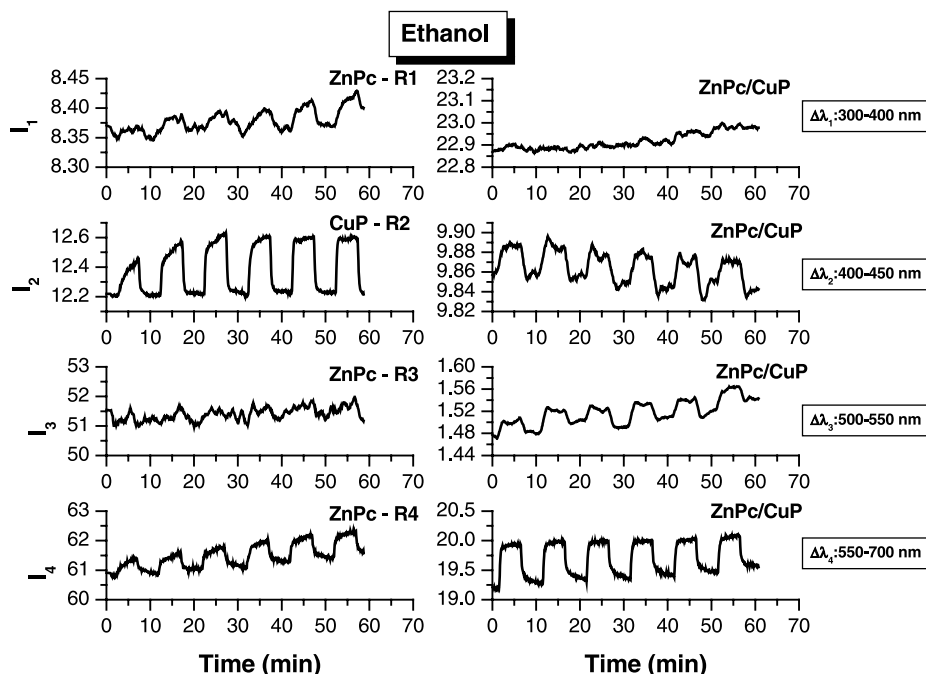
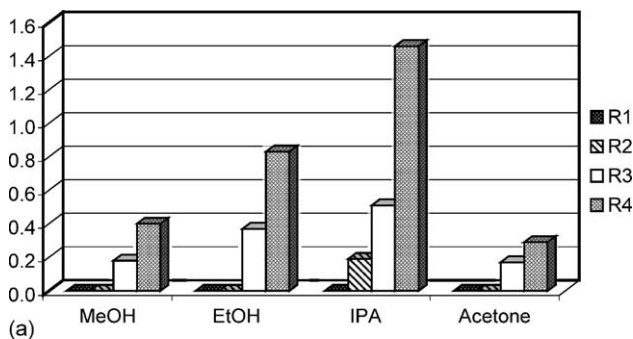
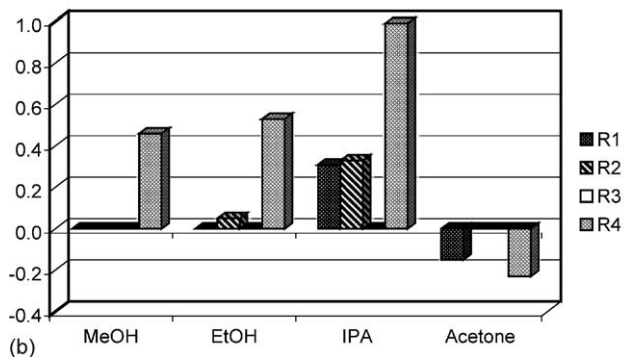


Fig. 5. Typical dynamic responses referred to the four channels for the S_2 system in the presence of ethanol vapours.

nitration R_n pattern, where only a slight but however detectable R_2 is observed together with R_4 . Finally, methanol exposure involves only R_4 response. It is noteworthy that acetone, which is a product of the oxidation of isopropanol, showed a different response pattern having negative values of R_1 and R_4 .



(a)



(b)

Fig. 6. Histogram of the responses calculated on: (a) S_1 sensing elements and (b) S_2 sensing elements.

4. Conclusions

In this work, we reported the optochemical sensing properties of a porphyrin-doped phthalocyanine spin-coated layer (S_2) compared with those related to two single-specie thin film (S_1). The UV-Vis spectra of each system were divided into four intervals in order to monitor the spectral variations in absorbance in the presence of some volatile organic compounds by means of the related integrals of the absorbance. This particular arrangement has been considered as an array of independent sensors located on a single sensing element. The S_2 sensing system showed a different behaviour with respect to the S_1 system with an enhancement of the selectivity. Further study concerning the optimisation of the thin layers in terms of thickness and composition, will also be reported in the near future together with the elaboration of the responses related to a mixture of volatile organic vapours. Principal component analysis will also be performed in order to analyse the responses of the system in terms of selectivity.

Acknowledgements

Many thanks to Mr. F. Casino and Mrs. C. Martucci for skilful technical assistance in the experimental set-up arrangement. This work was partially supported by "SAIA—sensori ottici ed elettroottici per applicazioni industriali ed ambientali" a FIRS project.

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Biographies

Jolanda Spadavecchia obtained her degree in Pharmaceutical Chemistry and Technology from the University of Bari, Italy in 2000 following postgraduate studies at the University of Lecce on the synthesis of phthalocyanines from natural products. Since 2001 she is a Ph.D. student in Material Engineering in the Engineering Faculty of the University of Lecce. His research interests concern the synthesis of organic compounds, sensor applications and characterisation, DNA-based sensors.

Giuseppe Ciccarella obtained his degree in Chemistry from the University of Bari, Italy in 1994. He received his Ph.D. in Chemistry in 1997 from the University of Bari, working on the development of chiral auxiliaries and their application in enantioselective synthesis. After his Ph.D. he worked on organic optoelectronic devices. From 1999 to 2000 he worked as Chemist in the Italian Workers' Compensation Authority (INAIL) working on chemical risk assessment and occupational hygiene. Since 2001 he is Researcher in Chemistry in the Engineering Faculty of the University of Lecce. His research interests concern the synthesis of organic compounds for sensor applications, volatile organic compounds detection, chemical surface functionalizations and biosensors.

Simonetta Capone was born in 1970 and graduated cum laude in Physics at the University of Lecce in 1996 with a thesis on semiconductor gas

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Pietro Siciliano physicist, senior researcher, received his degree in physics in 1985 from the University of Lecce. He took his Ph.D. in Physics in 1989 at the University of Bari. During the first years of activities he was involved in research in the field of electrical characterisation of semiconductors devices. He is currently a senior member of the National Council of Research in Lecce, where he has been working for many years in the field of preparation and characterisation of thin film for gas sensor, being in charge of the Sensors Group. He is the author of about 180 scientific papers, on national and international journals, and a lot of communication, some invited for International Conferences. He is responsible for several national and international projects at IMM-CNR in field of Sensors and Microsystems, mainly for environmental, automotive and agro-food applications. He has been the organiser and Chairman of International Conferences and Director of International Schools on Sensors and Microsystems. He is member of the Steering Committee of AISEM, the Italian Association on Sensors and Microsystems. At the moment he is Director of IMM-CNR in the Department of Lecce.

Roberto Rella physicist, senior researcher, received his degree in Physics in 1985 from the University of Lecce. His initial research activity, developed at the Department of Materials Science of Lecce University, was focused on the growth of semiconductor materials, both in the form of bulk and thin film and their optical and electrical characterisation for application in optoelectronic devices. Actually, he works as a senior researcher at the Institute for Microelectronic and Microsystems of the Council National of Research in Lecce and his research interests include molecular electronics, self assembly and structure of self assembled systems, chemical and biochemical sensors, conducting polymers, etc. He is involved in different national and international projects regarding the development of opto- and bio-chemical sensors based on organic, inorganic and opportunely designed hybrid sensing layers for the analysis of liquids and gases. He is the author of more than 180 publications on these subjects in international journals in the area of the organic and inorganic chemical gas sensors. Actually, he is responsible for the sensor laboratory at the IMM-CNR Institute. He has been organiser and Chairman of International Conferences and he is member of the International Advisory Committee of the European Conference on Organized thin Films.