The Skeleton Counts! A Study of the Porphyrinoid Structure Influence on the Sensing Properties

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Received date (to be automatically inserted after your manuscript is submitted)
Accepted date (to be automatically inserted after your manuscript is accepted)

ABSTRACT: A series of porphyrinoids has been tested as sensing layers for the development of nanogravimetric chemical sensors using quartz crystal microbalances (QMB) as transducers. The macrocycles have been studied as Ni complexes, Cu in the case of corrole, to elucidate the influence of the molecular skeleton on the sensing properties of the related sensors. For the first time subphthalocyanines have been tested in sensor applications. The study has been carried out by testing different volatile organic compounds chosen as model analytes. The results obtained demonstrate that the exploitation of different porphyrinoids offers useful insights for the development of cross-sensitive sensor arrays and can open novel perspectives for their applications in the sensor field.

KEYWORDS: porphyrinoids, chemical sensors, sensor arrays,

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INTRODUCTION

Chemical sensors are devices that can be schematized as constituted by two main components: the sensing material and the transducer [1]. The sensor performances depend on the perfect match among these elements, although the most important properties of the device, such as sensitivity and selectivity, mainly depend on the characteristics of the sensing material. Also, the choice of the transducer is of course related to the characteristics of the material chosen as the receptor layer. For this reason, the synthetic optimization of the sensing material is a crucial step for the realization of a functional device, especially when a molecular material is chosen as the sensing layer. This is the case when porphyrins are used for the development of chemical sensors [2]. Our group has been involved in this research topic and we have reported how the performances of quartz crystal microbalances (QMB) functionalized with porphyrin layers can be optimized by changing the coordinated metal, the peripheral substituents, or the molecular framework of the pyrrolic macrocycles [3]. From this last point of view, porphyrinoids are a large family of macrocycles showing skeletal variations to respect the parent porphyrin macrocycle, offering a wide choice for possible modifications of the tetrapyrrolic skeleton [4]. While the influence of coordinated metals and the peripheral substituents have been studied in detail, the impact of the changes in the molecular skeleton was mainly restricted to the comparison among porphyrins and corroles [5].

The aim of this work is to perform a detailed investigation of the influence of the structure of the pyrrolic macrocycle on the sensing properties of the related chemical sensors.

Considering our previous studies, we decided to use quartz crystal microbalances (QMB) as transducers, because they are not selective and may report all the possible interactions among analytes and the sensing layer [6].

Among the different porphyrin analogs, phthalocyanines have been widely studied for sensor applications, including also their exploitation to functionalize QMB [7-12]. In this work, we have chosen a phthalocyanine (Pc) symmetrically substituted with butyloxy groups (Chart 1). The choice of butyloxy group has been made to allow the solubility of the phthalocyanine, which necessary for the spray coating technique used for the deposition and because these substituents have been successfully used to produce porous thin films in the case of tetraphenylporphyrin (TPP) complexes. We have included in the array also a naphthalocyanine (NPc), peripherally substituted with *tert*-butyl groups, because it offers the possibility to evidence the importance of the extended π-aromatic system on the sensing behavior.

We have also included three different subphthalocyanines (SubPc), with the aim to investigate the influence of peripheral substituents on their sensing behavior. These contracted phthalocyanines have been of particular interest as molecular materials [13-15], but, to the best of our knowledge, they have not been studied for sensing applications yet. For the sake of comparison, we have added one TPP and a triphenylcorrole (TPC), macrocycles already tested in QMB sensors (Chart 1) [5].

EXPERIMENTAL

NiNPc and NiPc were purchased from Sigma-Aldrich. SubPc-H, SubPc-F and SubPc-Cl were prepared according literature methods [16], such as CuTPC [17] and NiTPP [18]. Volatile Organic Compounds (VOC) were reagent grade from Sigma Aldrich and used as received.

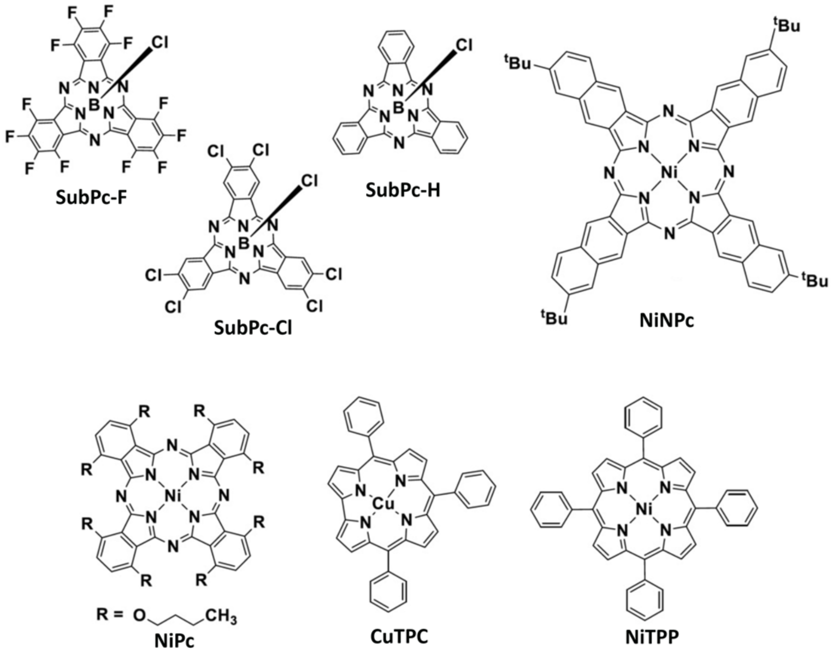

Chart 1

Sensors preparation and characterization

Quartz microbalance (QMBs) were AT-cut quartzes oscillating in the thickness shear mode, with a fundamental frequency of 20 MHz; the crystal diameter was 7.0 mm and the gold electrodes diameter was 5.0 mm (KVG GmbH). QMBs sensors are mass transducers, where the shift of the resonance frequency is, in the small perturbations regime, linearly correlated to the mass loading. The used quartz has a nominal mass sensitivity of about 4.8 Hz/ng, considering a minimum reliable frequency measurement of 1 Hz, which corresponds to a mass resolution of approximately 0.2 ng. The gold electrode of the QMB is the sensitive portion of the device. Thin films of the sensing layers have been deposited by spray coating technique on both sides of quartz disks, from 10^{-3} M porphyrinoid solutions in $CHCl_3$. Deposition of the sensitive layer was controlled, resulting in a total frequency shift of approximately 30 KHz. Each sensor was connected to an electronic oscillator circuit and the signal frequencies were sequentially measured by an integrated frequency counter. The sensor system used was the last version of a series of instruments being designed at the University of Rome Tor Vergata. It may accommodate up to twelve QMBs in a measurement cell of approximately 8 cm^3 volume. The gas sensors are completed by temperature and relative humidity sensors. The instrument is connected and powered via a single USB connection. Functions and data acquisition are controlled with in-house software running in MatLab®. Sensors were tested with vapors of compound members of different chemical families: hexane, toluene, methanol, ethanol, acetic acid, water, and triethylamine. The liquids were kept at the constant temperature of 303 K, and the saturated vapors of each VOC were diluted with molecular Nitrogen at dilution percentage from 1% to 8% by mass-flow controllers (from MKS) always maintaining the total flux at 200 sccm. The VOC concentration was calculated with the Antoine law using the parameters of the volatile compound available at the NIST database (available at www.nist.gov/webbook).

Principal Component Analysis (PCA) was used for exploration and classification purposes. All data analysis was performed in MatLab®.

RESULTS AND DISCUSSION

To investigate the influence of the molecular structure on the sensing properties of the resulting porphyrinoids, the macrocycles reported in Chart 1 have been exploited. They belong to different families of pyrrolic macrocycles, starting from the parent porphyrin, represented by tetraphenylporphyrin as Ni complex (NiTPP). Phthalocyanines are represented by NiPc, which is symmetrically substituted to allow its solubility; NiNPc is representative of a π-enlarged macrocycle, while corrole (as CuTPC) and subphthalocyanines (SubPc-H, -F and -Cl) are examples of contracted porphyrinoids. For all macrocycles, the coordinated metal has been chosen to minimize the possible coordination interactions with model analytes, allowing for better evidence of the influence of the molecular structure on the sensing properties. Ni was the metal ion chosen for TPP and Pc, while in the case of corrole Cu was the choice because Ni corroles are not stable complexes [19]. SubPcs are known only as Boron complexes; in this case, the peripheral substituents have been modified because it is known that β-substituents strongly influence the electronic properties of these macrocycles [15].

For these studies, we used model VOCs to represent the influence of polarity, acid or base character on the binding interaction of these receptors.

To carry out the measurement, we used the electronic nose developed in Rome Tor Vergata, which can host up to 12 QMB, so allowing us to do the measurements of the different macrocycles in the same conditions.

QMB were functionalized by spray coating technique, which can allow control of the amount of the macrocycle deposited onto the quartz surfaces by following the decrease of the oscillating frequency of the QMB. We fixed this amount to a frequency shift of approximately 30 kHz, equally distributed between the two electrodes. Spray coating technique does not allow obtaining a controlled layer morphology, but in the case of QMB this control is not mandatory since it is more important to have porous layers [20].

The behavior of the sensor responses, reported in Figure 1 for the functionalized QMB towards methanol (A) and triethylamine (B), further evidences the importance of porous layers. For NiNPc the responses are always slower than the other porphyrinoids, confirming that π-π stacking favors the aggregation of such a species, reducing the film porosity. On the other hand, for the other receptors the kinetic of the responses depends on the particular VOC; in all these other cases, we can reasonably assume that the spray coating technique allows the deposition of porous layers and that the changes in time responses depend on the diffusion of an analyte due to the interactions with the particular receptor and not from its packed aggregation.

These results also indicate that the kinetic of the responses contains several information that can be used for VOC discrimination in addition to the total frequency decrease usually taken as the sensor response. Remarkably, the recovery portion of responses offers very peculiar patterns that may indicate the chemical identity of compounds. The extraction and evaluation of features during the desorption phase will be deeper studied in a dedicated work.

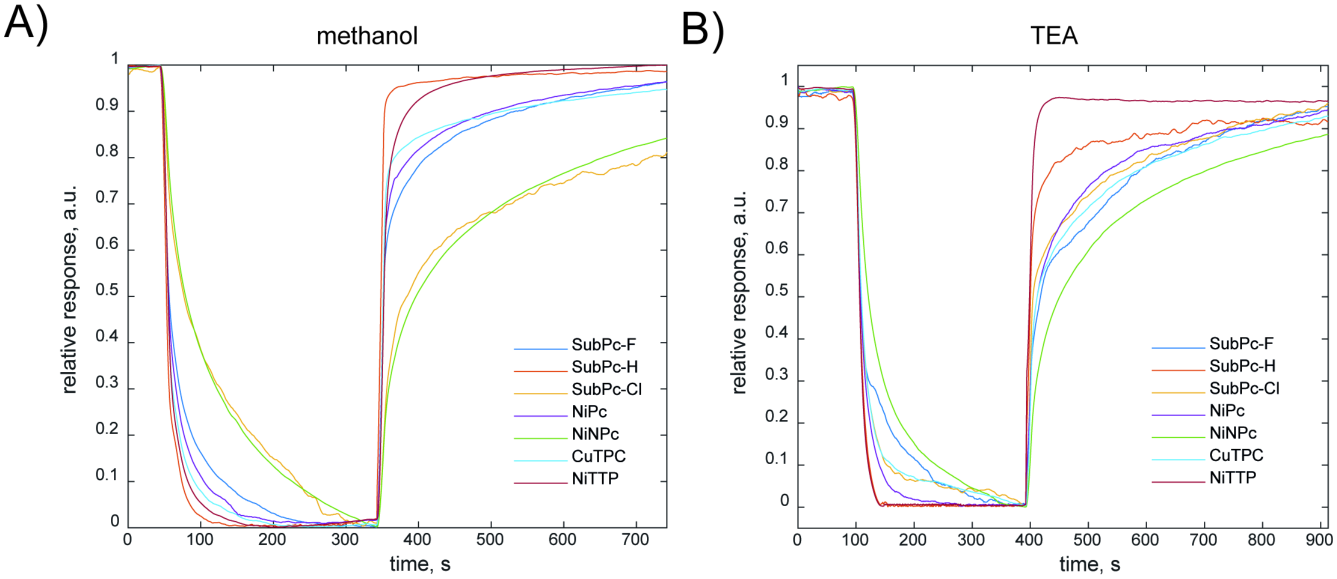

Figure 1.

In Figure 2 we report the responses of the functionalized QMB toward the model analytes tested. The mass amount of the receptors deposited onto the quartz surfaces was similar, so we can consider almost constant the number of receptors deposited onto the QMB surfaces, fixing the frequency shift variation upon deposition to 30 kHz, because the molecular masses of the macrocycles are more or less in the same range; for this reason the variations observed can be ascribed to the different interaction of porphyrinoids with VOCs. First of all, higher responses were observed in the case of NiNPc, confirming that when coordination interaction cannot be possible, dispersion and π-π interactions rule the VOC-porphyrinoid binding, which is stronger with the expanded aromatic system of NiNPc. For all porphyrinoids, the highest responses are observed with toluene, hexane and TEA, confirming again that dispersion and π-π interactions are the driving binding modes among VOC and sensing layers. It is interesting to note the significant difference observed in the case of NiTPP, where the interactions with these compounds are significantly higher than those with polar analytes.

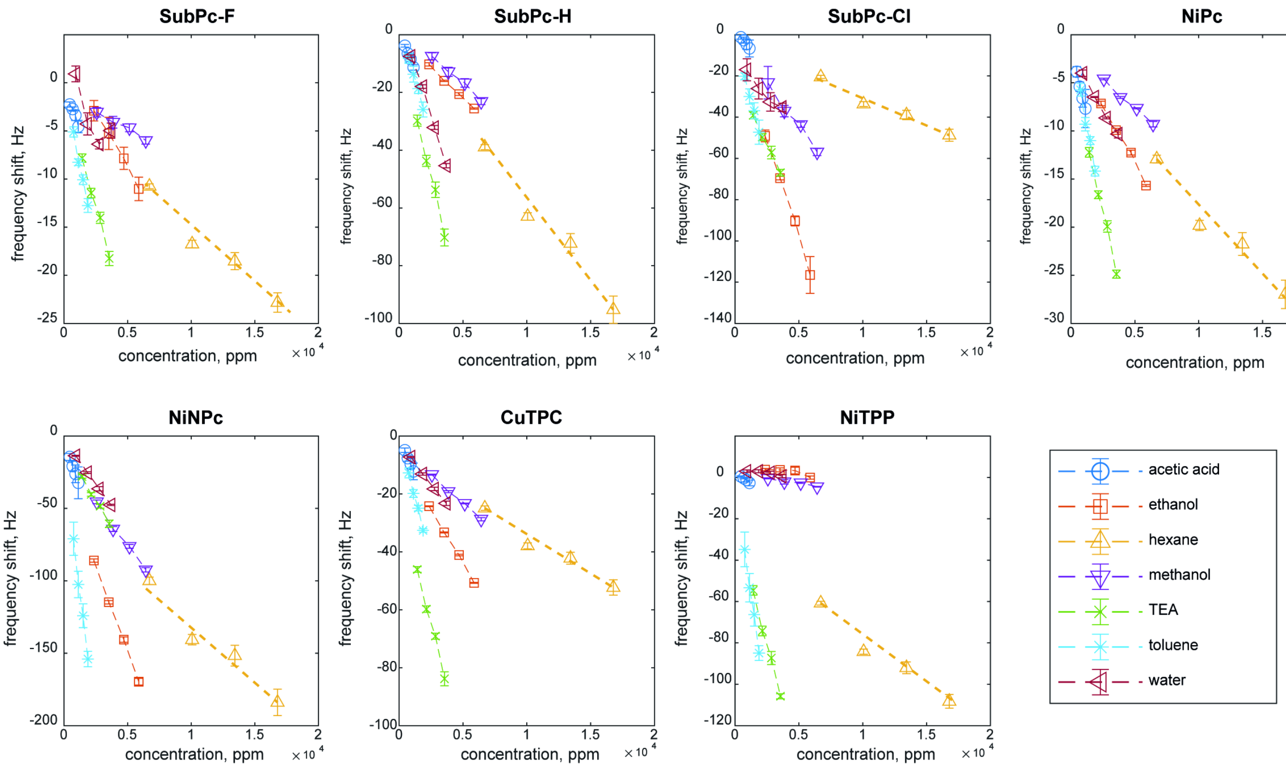

Figure 2.

In Figure 3 the sensitivities of the porphyrinoid functionalized QMB towards the different VOCs are illustrated. The sensitivity is calculated as the derivative of the sensor response with respect to the concentration. Thus, sensitivities are constant in the range considered when a linear fitting equation is supposed to model the relationship between sensor responses and VOC concentrations. Sensitivities are here reported in logarithmic scale since the range of concentrations is different due to the different saturated vapor pressures of samples.

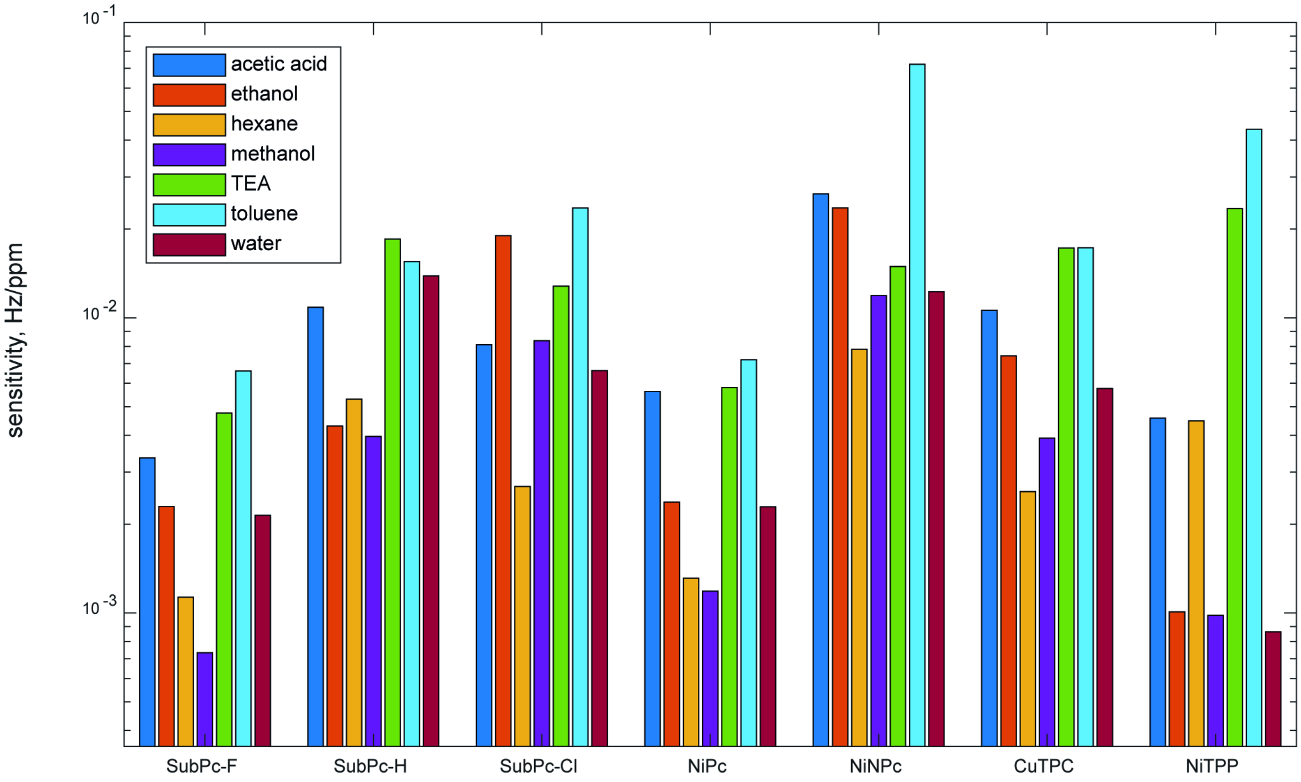

Figure 3. chloranil.

It is possible to note that the sensitivity pattern presents differences among the porphyrinoids, suggesting their useful integration in a sensor array. Some affinities can be reasonably explained, confirming the highest sensitivity showed by NiNPc toward toluene, which can be again related to enhanced p-p interaction among the aromatic VOC with the macrocycle having the extended p-system. It is interesting to note the behavior of the three SubPcs: the pattern of SubPc-F and SubPc-Cl is similar, while the unsubstituted SubPc-H shows a different scheme, with an increased sensitivity towards polar compounds such as water and acetic acid, as expected for the higher dipole moment of this SubPc [15].

Finally, the Principal Components Analysis (PCA) treatment of the data allows for comparing in better detail the sensor behavior (Figure 4). In order to remove the concentration contribution, data has been linearly normalized before being processed by PCA algorithm. Usually concentration introduces a linear correlation among all the sensor responses resulting in a strong influence among the main principal component. In the case of linear normalization, data are divided by the overall magnitude of responses, compensating for concentration effects [21].

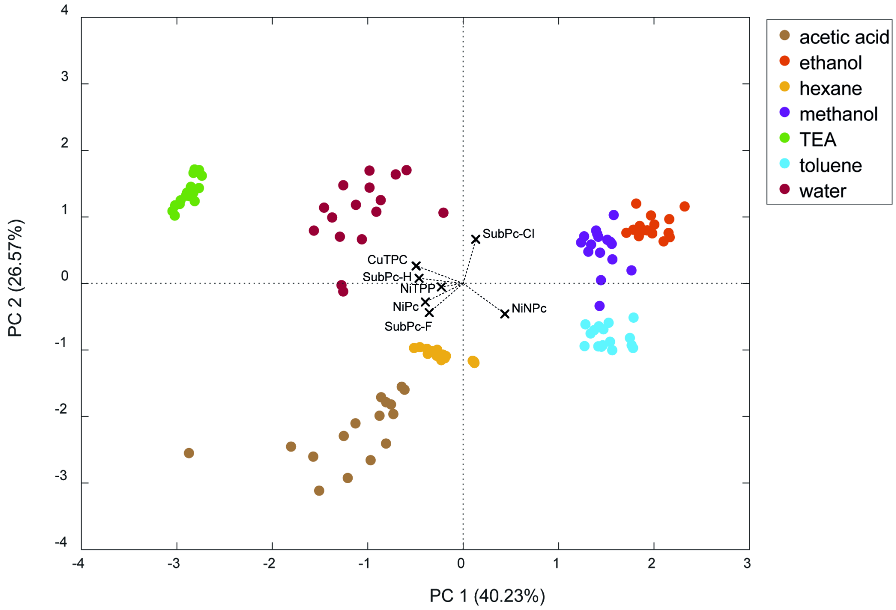

Figure 4. .

When PC2 and PC3 are considered, a nice discrimination of the VOCs according to their chemical nature can be observed (Figure 5). The bi-plot allows the identification of the sensor contributions to the sample separation. Indeed sensor loadings (x markers) point toward the compounds to which they respond the most. The highest affinity of NiNPc to the aromatic VOC toluene is confirmed, while again CuTPC is oriented towards TEA, as expected for the radical character of this complex, which can interact with an electron donor, such as the amine. It is also interesting to note that the three SubPcs are oriented orthogonally to each other, and their behavior seems to be connected to their dipolar character, with the less polar SubPc-F oriented toward hexane and SubPc-H oriented toward water and TEA. This feature is particularly appealing for their integration into a sensor array because their responses are not correlated.

CONCLUSIONS

The results obtained in this work further support a further tool to develop cross-sensitive sensor arrays by synthetic manipulation of porphyrinoids. In the past we have demonstrated the possibility to tune the sensing properties of porphyrin-based QMB sensors by variation of the metal ion coordinated to the macrocyclic ring. In this case, the coordination interaction between VOC and the porphyrin inner core metal center allowed to orient the sensor sensitivity to the different families of VOC according to the Pearson law. Macrocycle peripheral substituents from one side can introduce selective interaction with VOC and on the other side can offer aggregation motifs in the solid that can allow VOC binding modes not possible to the single porphyrin units. A further possibility to orient porphyrin sensor selectivity is their grafting onto inorganic nanostructures, such as ZnO nanoparticles.

In this work, we demonstrate that skeletal modification of the pyrrolic macrocycle can allow for the fine-tuning of the sensing properties of the resulting device. This opportunity can allow to greatly expand the receptor layers that can be prepared from porphyrinoid macrocycles, opening the way for the preparation of efficient and reliable sensor arrays.

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