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Supramolecular sensing mechanism of corrole thin films

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ABSTRACT

Porphyrins and related macrocycles have been widely exploited as sensing layers of different kind of chemical sensors. Among the different porphyrin analogs, corrole has been object of an increasing attention in the last few years; because of its peculiar coordination chemistry, corrole can be a useful system to study the influence of analytes coordination in an overall sensing mechanism. We have synthesized different corrole derivatives in order to use them as sensing layers of nanogravimetric chemical sensors. The resulting sensors have been exposed to volatile organic compounds and gases chosen as model analytes. Sensors performances have been compared with those of similar devices functionalized with analogous porphyrin derivatives. The results show that in the case of corrole the supramolecular binding mechanism is more efficient than coordination for CO and NO detection, and that the two binding mechanisms can actually cooperate to increase the sensitivity.

1. Introduction

Chemical sensors is generally formed by two distinct compartments: the sensing material and the transducer [1]. The typical sensing material is a solid layer of an inorganic or organic compound where the interaction with the target analytes takes place. These binding interactions should change one or more physico–chemical properties, which can be transformed into a readable signal by the second component, the transducer. Although the perfect match of both subunits is necessary to optimize the performances of the resulting sensor, most of the research attention has been focused in the preparation and chemical modification of the sensing materials. This because the designed preparation of these components is essential for the realization of a reliable and efficient chemical sensor.

Among the manifold of compounds suitable to be used as a sensing materials, porphyrins are a class of organic compounds particularly interesting. The richness of properties allows the use of a wide range of transducers, ranging from nanogravimetric to optical devices [2]. Since several years, we have been interested in the exploitation of porphyrins and related macrocycles as sensing materials devoted to the detection of both liquid or gaseous analytes [3]. In order to optimize the devices it is important to elucidate the sensing mechanisms [4].

From this point of view, sensing materials based on porphyrins are expected to mimic most of the porphyrins biological functions [5], with a reversible binding of gaseous analytes. To this scope, the coordinated metal has a fundamental importance and the sensitivity and selectivity properties can be tuned by changing the metal ion coordinated to the porphyrin core. Considering that such a macrocycle is probably the most versatile ligand, able to chelate with different geometries the majority of the elements present in the periodic table [6], it is possible to create a wide library of different sensing materials using the same porphyrin framework. This opportunity can be further expanded by modification of the peripheral substituents or by the molecular skeleton, which can further modify the coordination chemistry of the resulting macrocycle [7].

All these interactions are focused on the properties of the single molecular unit, but for the exploitation in chemical sensors, porphyrins should be deposited as a solid layer, and the aggregation in the solid state can of course influence the sensing mechanism.

In the past the thin film deposition has been simply considered in terms of the preservation of the binding mechanisms usually observed in solution. More recently it has became evident that the aggregation in the solid state should not be considered from a negative point of view, but the porphyrin aggregates can offer additional opportunities for the analyte binding not possible to the single porphyrin species [8]. We have first demonstrated this opportunity with the exploitation of porphyrin nanotubes [9]; in this case the operating sensing mechanism was based on the changes of the visible spectrum of the porphyrin aggregates, induced by the interaction with the different analytes. Because of their peculiar optical spectrum, porphyrin nanotubes were able to detect analytes not

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able to coordinate and then undetectable by single porphyrin subunits.

More recently, we have also reported the sensitivity to CO showed by thin films of the tetra(3,5-dihydroxyphenyl)porphyrin derivatives [10]. CO is a typical analyte for which the coordination to the metalloporphyrin is expected to be the driving interaction. Anyway, in this case a free base porphyrin was used and then this binding mechanism must be ruled out but nonetheless even free base porphyrins have been able to detect CO. In this case the sensing mechanism is likely due to the entrapment of CO inside the porous porphyrin network generated by hydrogen bonds of the hydroxy peripheral substituents.

Of course in general all the different sensing mechanisms can cooperate to the analyte binding and it is important to evaluate the importance of each of them to rationally develop the sensing material. For this aim, it is necessary to compare different sensing materials, where the different interaction mechanisms can be selectively operating, but also to couple them with a transducer where all these interaction can be detected. From this point of view nanogravimetric transducers, such as Thickness Shear Mode Resonators (TSMRs), are the best suited, because these devices are not selective since any kind of interactions leading to receptor-analyte binding result in an increase of mass [11].

In this work, we report the development of TSMRs functionalized with different tetrapyrrole complexes (Fig. 1), together the characterization of their sensing behavior towards different volatile organic compounds (VOC) and gases.

2. Experimental

Reagents and solvents (Sigma–Aldrich, Fluka and Carlo Erba Reagenti) were of synthetic grade and used without further purification. Silica gel 60 (70–230 mesh) was used for chromatography.

^{1}H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). UV–vis spectra were measured on a Cary 50 spectrophotometer.

Compounds **1**–**4** were prepared as previously described [12,13].

Synthesis of corrole. 5,10,15-tris-(3,5-Dimethoxyphenyl)corrole was synthesized starting from pyrrole and 3,5-dimethoxybenzaldehyde, following literature method [14].

5,10,15-tris-(3,5-Dihydroxyphenyl)corrole 5. This compound was prepared by demethylation of 5,10,15-tris-(3,5-dimethoxyphenyl)corrole with pyridinium hydrochloride following method reported in literature [15]; 200 mg of corrole (0.28 mmol) and 8.27 g of pyridinium hydrochloride (71.6 mmol) were heated at 200 °C under nitrogen for 1 h:30′. After this period the mixture was left to cool at room temperature, poured into 300 mL of aqueous $NaHCO_3$ and extracted with ethyl acetate. Organic phase was washed twice with water and dried over Na_2SO_4. Solvent was removed under reduced pressure and chromatographed over silica gel column using THF/ethyl acetate 1:4 as eluent. The green faction was collected and crystallized by ethyl acetate/hexane. Yield: 100 mg (57%). ^{1}H NMR (300 MHz, acetone d_6, J [Hz]): δ = 9.02 (d, 4H, J = 3.42 Hz, β-pyrrole), 8.64 (br s, 4H, β-pyrrole), 7.36 (s, 6H, phenyl), 7.18 (s, 3H, phenyl), 6.75 (s, 6H, OH). UV/vis: λ_{max} (acetone), nm (log ε): 416 (5.07), 574 (4.33), 615 (4.31), 647 (4.28). Anal. Calcd for $C_{37}H_{26}N_4O_6$: C, 71.37; H, 4.21; N, 9.00. Found: C, 71.26; H, 4.15; N, 8.89.

[*5,10,15-tris-(3,5-dihydroxyphenyl)corrolato*]*Cu 6*. Corrole free base (31 mg, 0.05 mmol) and $Cu(AcO)_2$ (0.15 mmol) were dissolved in methanol, and mixture stirred to reflux, monitoring the course of the reaction by UV–vis spectroscopy. After 1 h solvent was removed under vacuum and residue purified by a silica gel plug eluted with acetone. Fraction corresponding to corrole complex was collected and crystallized by acetone/hexane. Yield: 29 mg (93%). UV/vis: λ_{max} (methanol), nm (log ε): 416 (4.69), 546 (3.93), 613 (3.69). Anal. Calcd for $C_{37}H_{23}CuN_4O_6$: C, 65.05; H, 3.39; N, 8.20. Found: C, 64.92; H, 3.42; N, 8.24.

[*5,10,15-tris-(3,5-dihydroxyphenyl)corrolato*]*FeCl 7*. Corrole free base (50 mg, 0.08 mmol) and $FeBr_2$ (0.32 mmol) were dissolved in THF, and mixture stirred at 50 °C overnight, then solvent is removed under reduced pressure and residue purified with a silica gel plug eluted with ethyl acetate/hexane 1:1 to remove traces of unreacted corrole, then, with pure ethyl acetate. Fraction containing iron corrole was collected, washed with HCl 1 M, dried over Na_2SO_4 and solvent removed. Residue was finally crystallized by THF/hexane. Yield: 30 mg (55%). UV/vis: λ_{max} (methanol), nm (log ε): 359 (4.57), 421 (4.66), 503 (4.08), 631 (3.71). Anal. Calcd for $C_{37}H_{26}ClFeN_4O_6$: C, 62.51; H, 3.26; N, 7.88. Found: C, 62.44; H, 3.19; N, 7.77.

[*5,10,15-tris-(3,5-dihydroxyphenyl)corrolato*]*Co 8*. Corrole free base (31 mg, 0.05 mmol) and $Co(AcO)_2$ (0.15 mmol) were dissolved in methanol, and mixture stirred to reflux, monitoring the course of the reaction by UV–vis spectroscopy. After 1 h solvent was removed under vacuum and residue purified by a silica gel plug eluted with ethyl acetate. Red fraction was collected and crystallized by ethyl acetate/hexane. Yield: 26 mg (77%). UV/vis: λ_{max} (methanol), nm (log ε): 393 (4.46), 547 (3.89). Anal. Calcd for $C_{37}H_{26}CoN_4O_6$: C, 65.49; H, 3.42; N, 8.26. Found: C, 65.37; H, 3.34; N, 8.19.

2.1. Sensors preparation

The nanogravimetric transducers were AT-cut quartzes (Electroquartz) oscillating in the thickness shear mode, with a fundamental frequency of 20 MHz; the quartz crystal diameter is 7.0 mm, the gold electrodes diameter is 5.0 mm. Thin films of sensing materials were deposited by spray-coating technique on both sides of TSMR quartz disks from 10^{-3} mol/L $CHCl_3/CH_3OH$ (1:1) solutions. TSMR sensors are mass transducers [11], where the resonance frequency shift is linearly correlated to mass loading according to the Sauerbrey equation [15]:

$$\Delta f = -k_q \cdot \Delta m \quad (1)$$

in which the quartz constant was experimentally estimated to be k_q = 4.8 Hz/ng, with a mass resolution of 0.2 ng, considering a minimum reliable frequency measurement of 1 Hz. TSMRs were connected to an oscillator circuit during the deposition process and the frequency decrease was measured via a frequency counter. A frequency change of about 12 kHz was obtained for all deposited layers.

Coated TSMRs were housed in a stainless steel measurement chamber having a volume of 10 mL and maintained at the constant temperature of 298 K. Each sensor was connected to an electronic oscillator circuit and frequency variations were measured by means of an integrated frequency counter.

2.2. Measurement protocols

Vapors of the volatile organic compounds (VOCs) were generated by bubbling a N_2 stream into a liquid sample of the compounds. The concentration of the (VOC) in these saturated vapors was calculated by the Antoine's law [16]. These saturated vapors were diluted with nitrogen (or synthetic air) and fluxed into the sensor chamber by a computer-driven 4 channel mass-flow controller (MKS). The flow rate was kept at the constant value of 200 cm^3/min. The sensors were exposed to the following VOC: ethanol, triethylamine and hexane. Carbon monoxide diluted in nitrogen certified tank (500 ppm, Rivoira) and nitrogen monoxide diluted in nitrogen certified tank (525 ppm, Rivoira) were used; the different concentrations of gases were obtained by dilution of the gas mixture with nitrogen and then fluxed by the same mass-flow controller into the