

## UV-Vis and QCM analyses of 5,10,15,20-tetraphenylporphyrin and tetraphenylporphyrin cobalt LB films for chemosensing applications

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**Abstract** – The sensitivity of 5,10,15,20-tetraphenylporphyrin (H<sub>2</sub>TPP) and 5,10,15,20-tetraphenylporphyrin cobalt (CoTPP) to the presence of NO<sub>2</sub> gas in Langmuir-Blodgett (LB) films deposited onto a quartz crystal microbalance (QCM) and a quartz slide was investigated by mass quantitative analyses and UV-Visible spectroscopy. The energies involved in the red/blue shift of the Soret band during the experiments were compared with the mass adsorbed or desorbed, respectively. The  $t_{50}$  and  $t_{90}$  response times for the first exposure of H<sub>2</sub>TPP and CoTPP LB films to NO<sub>2</sub> gas were compared and the recovery time of films under a dry N<sub>2</sub> flux was calculated.

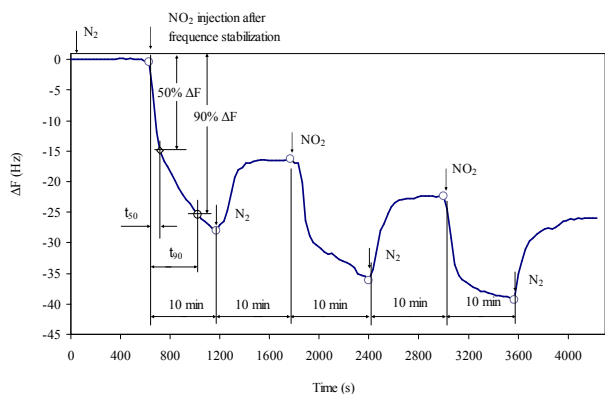
Supramolecular assemblies of porphyrins have been extensively studied for two major applications: mimicking the natural photosynthesis process and forming components in molecular devices. For these applications, it is very important to control the molecular arrangement of porphyrins in films. The porphyrin orientation and the distance between the rings in monolayers and films are two important parameters influencing the interactions between the rings [1].

The exposure of porphyrins to oxidizing or strong reducing gases induces dramatic changes in the ultraviolet-visible (UV-Vis) absorption spectrum (Soret and Q bands) that is associated with  $\pi \rightarrow \pi^*$  transitions and provides the basis for a remarkably interesting gas-sensing capability [2,3].

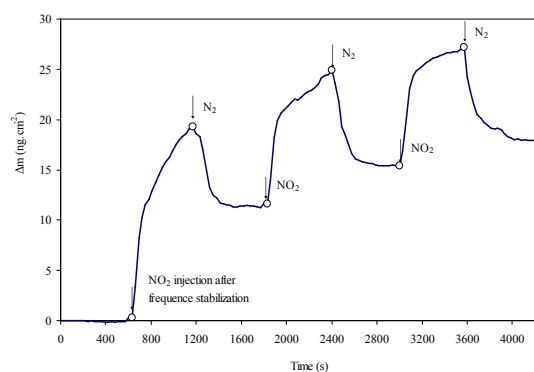
Many parameters of process such as: temperature subphase, pH and concentration were studied to control the organization of supramolecular assemblies of H<sub>2</sub>TPP films [4].

Two sensors of H<sub>2</sub>TPP and CoTPP were exposed at a constant time (10 min) to the NO<sub>2</sub> gas at concentration of 700 ppm and to the N<sub>2</sub> gas for desorption.

The H<sub>2</sub>TPP sensor was obtained at a 15 mN.m<sup>-1</sup> and the area per molecule estimated was 80 Å<sup>2</sup>.molecule<sup>-1</sup>. This sensor showed responses  $t_{50}$  of 60 s and  $t_{90}$  of 390 s. We have made three cycles of adsorption/desorption with equal 10 min for each cycle, consequently the  $t_{50}$  and the  $t_{90}$  referred here are concerned to this time (Figure 1). The average time  $t_{50}$  for the three cycles was 103 s and the  $t_{90}$  was 390 s. The total adsorbed mass after the three cycles were 19.3 ng, 13.3 ng and 11.8 ng, respectively, and the average adsorption of mass for the three cycles was 14,7 ng  $\pm$  0,2 ng of NO<sub>2</sub> gas at constant flux of 0,2 l/min (Figure 2). After each cycle the desorption occurred was inferior to the adsorption. This indicates a general tendency to the saturation of the sensor and a disposibility of sites for adsorption and probably a major thickness.



**Figure 1:** Frequency response of a H<sub>2</sub>TPP sensor exposed to a NO<sub>2</sub> 700 ppm in three cycles.



**Figure 2:** Mass adsorption response of a H<sub>2</sub>TPP sensor exposed to a NO<sub>2</sub> 700 ppm in three cycles.

### References

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