OPTIMIZATION OF MOLECULAR RECOGNITION IN THICKNESS SHEAR MODE RESONATOR CHEMICAL SENSORS

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Since several years, the advances in supramolecular chemistry concepts offer many opportunities to develop molecules endowed with molecular recognition properties.

A general approach to achieve molecular recognition feature is to design compounds containing a binding site where more interactions can cooperate to selectively one molecular species or molecular classes. Typical examples of molecular recognition are given by cavitands where geometric shape cooperate with some, for instance, hydrogen bonding site, to incorporate selected molecules inside the cavity [1]. Molecular recognition properties are generally studied in solution but they are very attractive to develop chemical sensors for analytes detection in gaseous phase. Indeed the specificity, observed in solution, and the characteristics of low-energy interactions may lead to specific, reversible, and stable chemical sensors.

On the other hands, chemical sensors are devices that convert the chemical interaction into an electric signal, so that it is necessary to find out a proper transducer able to convert the adsorption of molecules into something electronically readable.

From this point of view, the most traveled way to develop a chemical sensor from a molecule endowed with molecular recognition is that of mass transducers. Indeed, mass transduction disregards the electronic properties of the absorbing layer, being the transduction operating by piezoelectric elements sensitive to mass variations due to the molecular absorption.

In order to work properly, the mass transducer, such as thickness shear mode resonator (TSMR), need to be mechanically connected to the absorbing film.

Furthermore, a rough calculation of the TSMR sensitivity and resolution suggests that in order to obtain a large dynamics and an effective exploitation of the molecular recognition effects the film has to be deposited with a certain thickness. Namely, the adsorption between analytes and sensing material is not only a surface process but it also takes place in the volume of the film, and then is necessary to take in account the diffusion processes of adsorbed molecules into the sensitive film.

As a consequence, the molecule originally designed to maximize the molecular recognition interaction has to be optimized at synthesis level in order to make possible the deposition of films mechanically connected with the TSMR surface and with a sufficiently large diffusion coefficient in order to exploit the whole film volume.

A final variable is given by the TSMR. Mass transduction indeed is absolutely unspecific, disregarding if the interaction takes place in the molecular recognition site or elsewhere in the film. Then the synthetic modifications of the original molecule introduce novel unspecific interaction sites that tend to hide the specific molecular recognition effect.

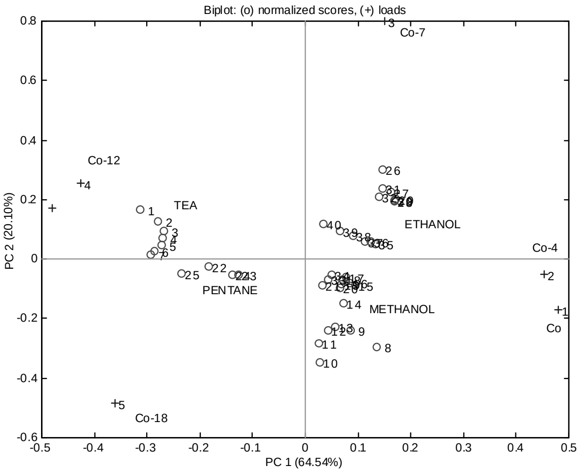
In this paper the optimization of metalloporphyrin molecules for TSMR sensors is investigated. In particular, the case of Cobalt TetraPhenylPorphyrin (Co-TPP) is presented. Such molecule indeed exhibits coordination interaction at the metal site that can be broadly rationalized through the HSAB Pearson principle, which makes this molecule quite selective for alcohols [2]. Being the porphyrin an aromatic planar molecule, when it is filmed (e.g. with spray casting technique) $\pi-\pi$ interactions result in a very compact film with low diffusion coefficients. When used as a sensitive layer of a TSMR sensor the consequence is a slow responding sensor with a limited sensitivity.

In order to enhance the response time (increasing the diffusivity) and the sensitivity (increasing the amount of film effective absorbing volume) it is necessary to insert some spacer in the lateral positions of the porphyrin. The simplest solution is to use an alkyl chain that does not exhibit any interaction properties with the exception of the dispersion interaction.

As the length of the spacer increase the relative amount of dispersion interactions hides the specific coordination. A compromise for the optimization of the molecule has to be found considering the sensitivity and the specificity.

As an example of the obtained results, an experiment considering five Co-TPP each with four alkyl chains with variable lengths (0, 4, 7 ,12, 18) is here considered. Sensors were exposed to alcohols, amine, and pentane. The effect of length can be made visible for instance printing the bi-plot (scores and loadings) of the Principal Component Analysis of the data set; where the position of the sensor loadings drifts from the alcohol direction (coordination interaction) to the pentane direction (dispersion interaction).

On the other hand, the alkyl chain can be functionalized in order to provide further specific interaction site that can enrich the sensitivity of the sensors. Details will be given in the conference presentation.



PCA bi-plot of the data-set of five CoTPP with alkyl chains of different lengths exposed to four volatile compoounds. The increase of the length moves the loadings from the alcohol direction (right-ward) to the pentane direction (left-ward) canceling the specific character of the interaction.

References

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