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ScienceDirect
Sensors and Actuators B 121 (2007) 238–246
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Metalloporphyrins based artificial olfactory receptors

Corrado Di Natale [a,*], Roberto Paolesse [b], Arnaldo D'Amico [a]

[a] *Department of Electronic Engineering, University of Rome "Tor Vergata", Via di Tor Vergata 110, 00133 Roma, Italy*
[b] *Department Chemical Science and Technology, University of Rome "Tor Vergata", via della Ricerca Scientifica, 00133 Roma, Italy*

Available online 17 October 2006

Abstract

Metalloporphyrins offer almost unique opportunities to design artificial receptors for chemical sensors. These molecules can be tailored, at the synthetic level, changing in a almost controlled way the sensor selectivity that can be oriented toward desired analyte families. Optical and electrochemical properties of metalloporphyrins are known since several years and they have been adequately exploited as potentiometric sensors for ions in solutions. In gas sensing the optical characteristics were utilized to detect gases like O_2 and NO_2 for which metalloporphyrins have a good selectivity. In gas environment, beside these gases the interactions are very rich but rather unselective, nonetheless this feature is interesting for artificial olfaction where a certain degree of cross-selectivity is required. As a consequence, arrays of gas sensors based on metalloporphyrins and optical and mass transducers have been demonstrated in the last decade. In this paper the properties of such arrays are reviewed evidencing the high flexibility of such sensors and their wide spectrum of applications.

Keywords: Metalloporphyrins; Electronic noses; Artificial receptors

1. Introduction

Physiology of olfaction made considerable advances, and models of receptor mechanisms explaining the sensitivity to volatile compounds are now available, the genetic repertoire expressing the olfactive receptors is known [1]. Recent studies begin also to unveil the signal pathways leading from the generation of olfactory neuron signal to the cognitive identification of the odors [2]. Nonetheless, olfaction still remains a mysterious sense basically because of its strong connection with unconscious perceptions at which corresponds an unusual scarcity of semantic expressions limiting the communication of olfactive experiences. With respect to other senses (vision, hearing, and touch) for which technological correspondent exists since more than one century, the attempts to endow artificial systems with odor recognition features has been thwarted for a long time.

The most important element of an artificial olfaction system is the ensemble of sensors translating the primary stimuli in a accessible signal, usually electric. For vision and hearing, physics provides a sufficient background to develop artificial receptors. In the case of odor only in the last few decades the interaction of solid-state devices with volatile molecules started to be systematically investigated making possible the development of gas sensors. The analysis of odors, namely the investigation of gaseous samples composed by several volatile compounds is a typical subject of analytical chemistry where several methods of separation of mixtures in individual compounds are available (e.g. gas-chromatography). The principle of sample separation looks different from natural olfaction where the odor seems to interact at once with the globality of receptors. In order to analyze without separation a gaseous mixture it is then necessary a set of selective sensors, in the sense that each sensor senses only one of the many molecular species. Actually, many solid-state sensors developed since the seventies are intrinsically non-selective, making them not useful to replace the analytical goal of measuring at once the concentration of many different compounds.

The non-selectivity of chemical sensors were considered as one of the main problems limiting their diffusion for practical applications. Nonetheless, physiological investigations about olfaction receptors shown that Nature strategy for odor recognition is completely different from the analytical approach. Receptors were found to be rather unselective, namely each receptor senses several kinds of molecules and each molecule is sensed by many receptors [3]. After this discovery, it was proposed

* Corresponding author at: Department of Electronic Engineering, University of Rome "Tor Vergata", Via del Politecnico 1, 00133 Roma, Italy.
Tel.: +39 06 7259 7348; fax: +39 06 2020 519.
E-mail address: dinatale@uniroma2.it (C. Di Natale).

0925-4005/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.snb.2006.09.038

that arrays of non-selective chemical sensors may show properties similar to that of natural olfaction [4]. On the basis of this conjecture, the development of artificial olfaction became possible. Such systems were soon dubbed as "electronic noses", and this denomination is currently given to arrays of unselective chemical sensors coupled with some multicomponent classifier. Since the eighties almost all sensor technologies were used to assemble electronic noses. Odor classification properties of artificial systems were tested on several different fields proving that electronic noses could be in principle used to replace human olfaction in practical applications such as food quality and medical diagnosis [5].

The features of electronic noses are fundamentally dependent on the sensing properties of the artificial receptors. The possibility to have some versatile tool to tailor the sensitivity and selectivity of sensors is of primary importance to capture either large or narrow ranges of chemicals allowing for electronic nose application oriented optimizations. To this point of view, organic synthetic receptors offer an unlimited number of possibilities to assemble molecules endowed with differentiated sensing features.

In this paper the development of electronic noses based on a particular family of organic molecules (the metalloporphyrins) is reviewed and commented.

2. Metalloporphyrins properties

Metalloporphyrins are a well-known molecular family investigated since more than one century. They are in particular well-known for their functions in living beings where they play key roles such as oxygen transportation in mammalian blood and photosynthesis in plants.

The basic porphyrin ring is an extended aromatic system formed by four pyrrolic rings linked by methynic bridges. This basic structure is turned into a metalloporphyrin when a transition metal atom replaces the two hydrogen atoms at the central core. Further modifications include compounds at lateral positions. In Fig. 1, an example of a complete receptor is shown.

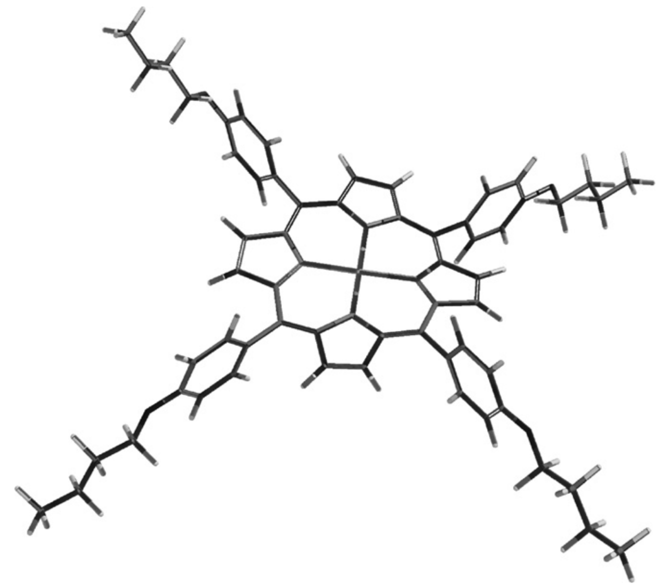

Fig. 1. The structure of a porphyrin used as artificial olfactory receptor. A tetraphenlyporphyrin is modified adding a Zinc metal in the central core and four butyloxy-chains at peripheral positions.

An important argument about the suitability of metalloporphyrins as artificial olfaction receptors can be obtained considering that natural olfaction receptors likely contains metal ions at their active sites [6]. Although only a clue, this is a strong argument in favor of the investigation of metallo-organic molecules as artificial receptors for odorant molecules, and among the metallo-organic molecular families metalloporphyrins are surely the most versatile, rich and flexible. These molecules in fact are rather stable compounds and their properties can be finely tuned by simple modifications of their basic molecular structure. The coordinated metal, the peripheral substituents, the conformations of the macrocyclic skeleton influence the coordination and the related sensing properties of these compounds. Almost all metals present in the Periodic Table have been coordinated to the porphyrins; furthermore the organic chemistry of these compounds is well developed, and a wide range of different substituents can be introduced at their peripheral positions. All together these characteristics increase the versatility of these molecules and different transducers have been proposed for porphyrin-based chemical sensors, all showing outstanding properties in terms of stability, chemical sensitivity and reproducibility.

A metalloporphyrin offers a large variety of interaction mechanisms that can be exploited for chemical sensing. Hydrogen bonds, polarization, and polarity interactions are expected to take place between volatile molecules and the porphyrin. Furthermore, the role of metal is of primary importance to determine the sensitivity and selectivity properties of the molecule since [7] coordination interactions takes place at the metal center in metalloporphyrin complexes. From this point of view, since almost all metals may be combined to form metalloporphyrin complexes, metalloporphyrins ligand properties enjoys a large versatility.

Particular molecular arrangement can also be assembled in order to provide metalloporhyrins with more enhanced selectivity. As an example in Fig. 2 a dyad of porphyrins endowed with enantioselectivity is shown. Sensors based on this molecule were demonstrated to be able to discriminate between the two chiral forms of limonene [8].

3. Metalloporphyrins based sensors

To exploit in an artificial system the sensing properties of a sensing material it is essential to match the molecules with some transducer able to translate the interaction events into readable signals (usually electric). For this scope, it is necessary to consider which physical parameters of the porphyrin changes as a consequence of a binding event [9].

The most simple approach consists in considering the variation of mass. A film of metalloporphyrins indeed after the absorption of volatile compound is expected to change its mass. Devices able to measure the difference of mass of thin molecular films are actually available such as quartz microbalance (QMB) and surface acoustic wave (SAW). Another possibility is offered