Chemical sensitivity of supramolecular porphyrins assemblies

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Abstract

Metalloporphyrins are used as sensitive materials for many different kinds of chemical sensors. The sensitivity of these molecules is usually correlated with their structure and in particular with the kind of metal ion, aromatic system, and peripheral substituents. Metalloporphyrins can easily self-assemble, via weak forces, to form ordered supramolecular aggregations endowed with defined geometries (e.g. tubes or rods). In addition to the single molecule sensitivity, supramolecular assemblies can be endowed with additional properties that can increase the sensitivity towards selected species. As a result, assemblies may show sensing properties different, and in some case exceeding, those of their molecular constituents.

Keywords: metalloporphyrins, supramolecular structures, nanotubes, molecular films

1. Main text

Porphyrins are an important molecular family mostly known for their role in fundamental life processes, such as the oxygen transport in blood and the photosynthesis in plants. For this reason their chemical properties have been extensively studied. The basic porphyrin structure is an extended aromatic system formed by four pyrrols linked by methynic bridges. This structure is endowed by a central pocket that can be functionalized hosting a metal ion forming the metalloporphyrin complex. The molecule can be further modified with functional groups in the lateral positions outside the aromatic system. Figure 1 shows the structure of a TetraPhenylPorphyrin (TPP) a porphyrin widely used for sensing purposes. This structure forms a complex molecule where different kinds of interactions can contemporaneously take place. Among them the coordination with the metal ion is in considered as the most important, and actually it is exploited for instance in oxygen transport in blood to selectively bind oxygen and carbon dioxide molecules. Nonetheless, also other interactions such as hydrogen bond, π-cation forces, and van der Waals forces may cooperated in binding guest molecules to the metalloporphyrin systems. This richness of interactions is actually utilized for chemical sensing purposes matching molecular layers of metalloporphyrins with basic transducers such as quartz microbalances, field effect transistors, or color detection devices [1]. In all these developments the sensing properties of the sensor reflected the properties of the single molecular unit and scarce importance was devoted to the geometrical arrangement of the molecules on the transducer surface. In the past decades a great attention was devoted to the fabrication of order molecular structures that could emphasize some physical property such as the conductivity in the case of Langmuir-Blodgett films. To this regard,
porphyrins chemical versatility offers also the possibility to drive self-assembled molecular aggregations to ordered geometrical structures such as rods, rings, wires, nanofibers, nanospheres, and three-dimensional lattices [2]. The development of these structures suggested a nanotechnological use of metalloporphyrins even if the most remarkable physical properties of these molecules is their remarkable optical activity and one of the foreseen applications is their use in artificial photosynthesis for solar energy conversion [3]. In this paper examples of sensitive properties of some supramolecular arrangement are illustrated.

![Fig. 1. Structure of a TetraPhenylPorphyrin (TPP). The molecule is formed by the four pyrrolic rings (the porphyrin), the central metal atom, and the four phenyl groups in the peripheral positions.](image1)

![Fig. 2. Structure of the amphiphilic TPP (left). The aggregation mechanism is illustrated on the center: porphyrin fastly aggregate in ribbon-like structures that then interact one each other to form ordered large-scale structures. At the right side the emission spectra observed in presence of different metal ions are shown. Concentration of Hg^{2+} was about one thousand smaller with respect to the other ions (Cu, Cd, and Pb).](image2)

2. Self-assembled structures of amphiphilic porphyrins

Figure 2 shows a modified TPP, the functional group indicated with R in the scheme provides a polar head contrasting the hydrophobic character of the aromatic system. These molecules are dissolved in ethanol and they spontaneously aggregate increasing the water content of the hydro-alcoholic solvent mixture. Spontaneous deposition of the porphyrin J-aggregates as ordered thin films onto a silanized glass surface resulted from a H$_2$O/EtOH (9:1 v:v) solution. Figure 3 illustrate the probable mechanism of aggregation characterized by an initial head-to-tail ribbon like morphology that evolves with time to give very large assemblies of supramolecular structures [4].

These films preserve an appreciable fluorescence emission. That can be conveniently utilized for instance to detect transition metal that are known to quench the luminescence of host molecules. In particular the effect was
found particularly sensitive and selective with respect to Hg\(^{2+}\) [5]. In Figure 2 the emission spectra in aqueous solutions of different metal ions are shown.

3. Porphyrins nanotubes

An intriguing architecture obtained by aggregation of oppositely charged porphyrin units has been recently reported by Shellnut and co-workers [6]. The ionic self-assembly of two porphyrins bearing opposite ionic charge leads to the formation of nanotubular structures, reaching free floating structures having lengths of tens of nanometers. The presence of the inner cavity can give raise to selective endohedral inclusion of different guests, or the interaction with analytes can alter the supramolecular arrangement with dramatic changes of the optical properties of the molecular nanostructure. Figure 3 provides a clear demonstration of nanotubes properties showing the practical absence of sensitivity of the optical spectra of individual constituents and the large changes occurring in the nanotubes spectra [7].

![Absorption spectra of solution of precursors (SnTPyP and H\(_2\)TPPS) and nanotubes in water and after the addition of 10\(^{-3}\) M of triethylamine.](image)

![AFM image of nanotubes layer. Centre: Camera view of the nanotubes layers spotted in four replicas. Right: Differential CSPT absorbance defined as the difference between absorbance in gas and in pure nitrogen. CSPT absorbance is defined as the logarithm of the ratio of the total signal (R+G+B) of camera through the background and through the nanotube layers.](image)

In order to exploit this property also for gas phase detection, nanotubes were deposited by solvent casting on a plastic substrate. Atomic Force Microscopy and absorbance spectra showed that tubular arrangement was preserved, also if a probable flattening of the structures took place. The optical properties of the layer were measured with a Computer Screen Photo-Assisted Technology (CSPT) arrangement. CSPT is an experimental technique based on the
use of a computer screen as a programmable light source and a computer camera as detector, CSPT measure of color
to changes in chemical indicators was demonstrated [8]. Fig. 4 shows the AFM image of the nanotubes layer and the
differential absorbance fingerprints recorded in presence of different gases.

4. Sensitivity of large scale ordered molecular films

Adsorption of airborne molecules in ordered films, such as those obtained by Langmuir-Blodgett, can modulate the
geometrical arrangement of the film.

Among the possibility to monitor the molecular order on a solid substrate, Reflectance Anisotropy Spectroscopy
(RAS) is one of the most efficient. RAS measures the change of intensity of light reflected by a surface rotating of
90° the polarization vector of the incident light. This method, originally applied to clean semiconductor and metal
surfaces, was demonstrated to be extremely sensitive to sub-monolayer coverage of organic films [9] and to ordered
supramolecular structures resulting after porphyrin deposition [4]. The application of RAS in gas sensing has been
not yet explicitly realized; however, preliminary results make very interesting the investigation of analytes by RAS,
in terms of its sensitivity, response time and origin of the measured effect [10]. Recent results about a layer of
porphyrins ordered by Langmuir-Schäfer technique show that RAS spectra are sensitive to gas adsorption and more
importantly, different interaction produce distinct optical feature that can allow for a recognition of the adsorbed
molecule.

5. Conclusions

This paper illustrated with some example that supramolecular self-assembled structures of porphyrins may be
endowed with peculiar sensitivity properties exceeding those of single precursors. The effect appears to be mainly
due to a modulation of the interaction between porphyrins keeping the supramolecular structure in shape. These
results provide a hint for a methodology, to be properly explored, for chemical sensor design considering not only
the molecular functionalization aimed at direct molecular recognition but also those molecular modifications that,
promoting the formation of self-assemblage of ordered structures, may also prompt an increase of sensitivity.

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