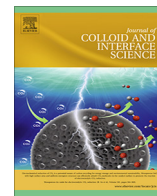




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# The role of the central metal ion of ethane-bridged bis-porphyrins in histidine sensing

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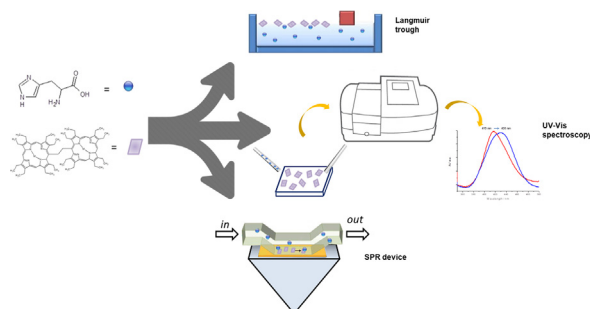
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Ethane-bridged bis-porphyrin derivatives are reported for the selective detection of various analytes in sensing applications. The central metal ion is able to rule specific molecular arrangements upon analyte binding. Three bis-porphyrin compounds: a free base (metal free), Ni complex, and Cu complex, have been tested for histidine detection in aqueous media. Histidine is involved in various biological processes, including such deadly disease as lung cancer. The conformational changes of bis-porphyrins, induced by histidine binding, can be detected by monitoring the Soret band position. The spectroscopic characterization, at the air-water subphase interface, indicates that, in the presence of histidine, the Ni and Cu metallated derivatives undergo conformational changes. This behaviour was confirmed when these two derivatives were deposited onto the solid support by Langmuir-Schaefer (LS) technique. A prototypal Surface Plasmon Resonance (SPR) detection system for histidine based on these two porphyrin LS films was developed. The Cu substituted compound based SPR system allows the histidine sensing down to nanomolar concentration. Furthermore, a SPR response of the Ni bis-porphyrin shows a semilogarithmic dependence on the histidine concentration up to  $10^{-6}$  M proposing the use of these two porphyrins in a sensor array for the monitoring of histidine levels in plasma.

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## 1. Introduction

A very fascinating class of naturally ubiquitous chemical compounds is represented by porphyrinoids. Physico-chemical features of these molecules are strongly influenced by the functional groups

attached to the aromatic ring and by the central metal ion coordinated to the macrocycle [1,2]. In fact, it is well-known that the heme complex, consisting of an iron ion coordinated to protoporphyrin, is used as a prosthetic group in myoglobin and hemoglobin to deliver oxygen to the tissues [3]. If a magnesium ion is coordinated to the porphyrinoid rings (chlorins and bacteriochlorins), these tetrapyrrolic molecules are used to absorb photons in the light harvesting systems during the natural photosynthetic processes [4]. Learning from Nature, porphyrins have been effectively used as active species for numerous applications, such as electronic devices [5,6], sensitizers for medical applications or sensitive molecules able to detect bio-medical and environmentally important compounds [7–9]. Furthermore, by changing the substituent groups and central metal ions, it is possible to obtain active layers highly sensible and selective towards specific classes of compounds [10–12]. Besides, structurally sophisticated systems containing two or more porphyrin units have been successfully designed in order to enhance specific chemical and physical properties [12–15]. In particular, free base, homo- and hetero metallic bis-porphyrins are essentially interesting since they are able to change their molecular arrangement as a function of the chemical environment. Hence, the ethane-bridged bis-porphyrins have been efficiently used for several applications, such as mimicking di-heme proteins [16], generating chiral supramolecular adducts [17], and sensing analytes in vapour and liquid phases [18,19]. The use of these bis-porphyrins highlighted a crucial role of metal central ions in the interaction with analytes that results in the modification of bis-porphyrin spatial arrangement. In general, the ethane-bridged porphyrins can assume three different geometries; *syn*-, *anti*- and tweezer forms (Scheme 1).

These conformers and their interconversion can be easily monitored by means of UV–Visible spectroscopy since the relevant shifts of the Soret band (as the main porphyrin electronic transition) are specific and well-established for all these three forms as in solution [20] and in thin films [21,22]. In particular, according to the exciton coupling theory [23] the *syn*- form is characterized

by the high energy (blue) shift of porphyrin Soret band, and the *anti*-form yields the low energy (red) shift, whilst the tweezer holds an intermediate position [24]. This marked spectroscopic distinction is a facile and convenient indicator, which can be effectively applied for the sensory purposes.

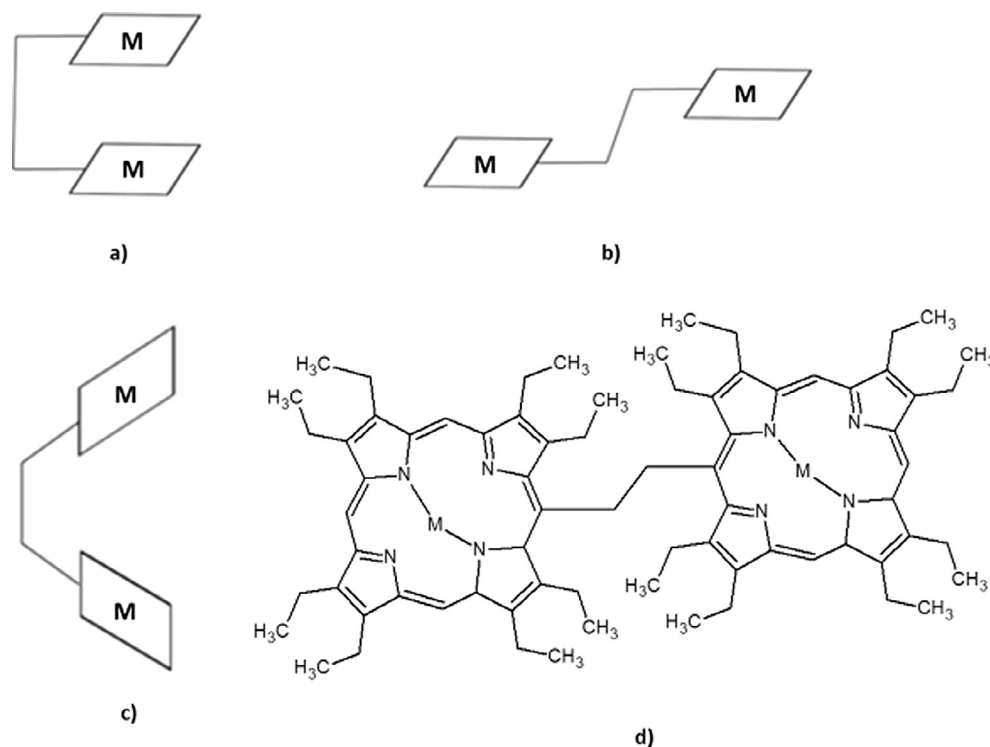
Specifically, in this work, the spectroscopic variations of three different ethane-bridged bis-porphyrins have been proposed as an effective tool for monitoring the interaction between histidine and the active molecules. As reported in Table 1, Ni, Cu complexes and free-base (metal free) bis-porphyrins have been used to evaluate the role of metal central ions in the interaction with histidine molecules dissolved in aqueous solution.

Histidine is an essentially important amino acid owing to a key role in many enzymatic processes [25] and it is reported that its concentration decreases in patients affected by lung cancer [26–30]. Therefore, the level of histidine can be used as a biomarker for a precocious diagnosis of this disease. The presence of histidine as a free-amino acid in human plasma, in fact, was demonstrated to be strongly connected to the lung cancer pathology. In particular, the decrease of histidine concentration under 0.03 mM can be associated to the progression of this disease [26–30]. In this context, the design and assembly of a device, able to selectively detect histidine from human plasma is crucial. Here, we report the sensing abilities of three bis-porphyrins and propose CuCuPo<sub>2</sub> and NiNiPo<sub>2</sub> porphyrins as the most suitable candidates for the active layer to detect histidine in aqueous environment. In particular, Surface Plasmon Resonance (SPR) has been used to design a prototypal sensor and its sensibility toward histidine allows the facile detection of this amino acid in nanomolar concentration.

## 2. Materials and methods

All the chemicals were purchased by Sigma Aldrich and used without any further purification.

Bis-porphyrins were synthesized according with the procedure reported previously in [31] and in [32].



**Scheme 1.** (a) *syn*- (b) *anti*- and (c) tweezer conformers (d) chemical structure of bis-porphyrins. M represent the metal central ions or two protons in the porphyrin unit.

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