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Porphyrins Nanosensors

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ABSTRACT

The porphyrin macrocycle, an attractive building block, has been functionalized with nanomaterials such as graphene, graphene oxide, fullerene, quantum carbon dots, Single Walled Carbon Nanotubes (SWCNTs), Multiple Walled Carbon Nanotubes (MWCNTs), Metal Organic Framework to produce enhanced porphyrin nanomaterials, some of which have found application as porphyrin nanosensors in a wide range or realm. These include porphyrin nano biosensors, porphyrin catalytic nanosensors, porphyrin electrochemical anion sensors amongst others.

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Introduction

A chemical sensor is a device that converts chemical data such as the concentration of a single sample component to complete composition analysis, into an analytically usuable signal [1]. It consists basicallty of two components: a receptor which receive the signals and a physicochemical transducer. The receptors can take various form and range from activated or doped surfaces to complex macromolecules that are engaged with specific interactions with the analyte. Figure 1.0 shows a schematic representation of a chemical sensor.

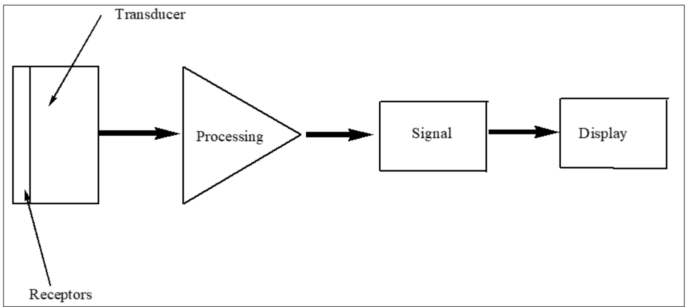

Figure 1.0: Schematic Representation of a Chemical Sensor

Requirements of Sensors

A chemical sensor must maintain a high degree of specificity for the intended analyte in the presence of potentially interfering chemical species to avoid false positive outcomes. A chemical sensor must also have a transducer, responsible for converting the signal created by the receptor-analyte interactions in a readable and recognizable one. Another aspect is that sampling is often overlooked. An analyte cannot accurately be detected if its not delivered to the transducer in a functional form. Fouling of a sensor by other macromolecular or reactive species can be an issue. An advantage of chemical sensing is that the sensor interface can be frequently refreshed or replaced. Monitoring of the recognition events can be performed via several methods, depending on the type of transducer utilized. These include optical, gravimetric or electrochemical [2].

Classification of Chemical Sensors

Chemical sensors can be classified into various types. These include:

- Bio-sensors
- Catalytic sensors
- Electrochemical sensors
- Nanosensors

Nanosensors are nanoscale devices that are constructed to identify a particular molecule, biological, medicinal or environmental component and operate within the nanoscale dimensions. Nanosensors convert chemical data such as the concentration of a single sample component to complete composition analysis into an analytically usuable signal.

Porphyrins Ubiquitous Properties

Porphyrins are a unique class of naturally, intensely colored pigments, naturally found as biologically active compounds in living organisms where they play important roles as the red blood cell pigment responsible for oxygen transport) and chlorophyll (the green plant pigment responsible for light-harvesting and photosynthesis). Porphyrin-based compounds have found applications in Photodynamic Therapy (PDT) as dyes or catalysts, to molecular electronic devices for the conversion of solar energy, biosensors in modern bioanalytical systems.

Porphyrins are a class of terapyrrolic heterocyclic macrocyclic compounds, Fig. 1.0. The four pyrrole rings are joined by four methine bridges at the a-carbon of the pyrrole molecule. They have a total of 26 π electrons of which 18 are in a planar, continuous conjugated macrocycle. Evidences for aromaticity are confirmed by measurements of their heats of combustion and the planarity of the nucleus. Both free base and metalloporhyrins are planar in nature. They can be functionalized to form extended superstructures, "picket fence" porphyrins. Free base porphyrins are those without a metal in the centre. Fig. 1.0. shows the structure of a tetraphenyl porphyrin, a useful synthetic building block in supramolecular and nanotechnology. The four nitrogens in the centre can complex a range of transition metals to form a wide range of metalloporhyins, each of which has its unique metalloporphyrin characteristics. Coupling of the free base porphyrin with a metal, increases the movement capacity of the electrons. Both "free base and metalloporhyrins" have rich photo fluorescence electronic properties. They have also found increasing application in catalysis and photocatalysis. Porphyrins because of their rich photosensing activities have been used in Photodynamic Therapy (PDT) to kill cancer cells. Porphyrins are usually synthesized via the traditional method involving the condensation reaction of pyrrole and benzaldehyde or the reaction of the reaction of dipyrromethene with an aromatic aldehyde followed by oxidation with p-chloranil [3]. In recent years, porphyrins have been finding increasing application in nanotechnology. Porphyrins continue to attract much theoretical interest, and have been called the "pigments of life". Thus, this paper reviews the recent advances in porphyrins-based nanomaterials.

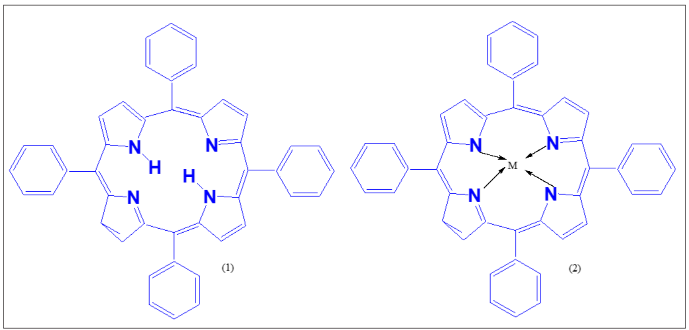

Figure 1.0: (a) Tetraphenyl Porphyrin (b) Metalloporphyrin

Porphyrins as Nanosensors

Porphyrin-based nanoarchitectures have been extensively explored for sensing applications, showcasing distinctive advantages over other nanomaterials. These nanostructures exhibited strong and tunable spectral properties, allowing for efficient detection of analytes through absorbance or fluorescence signals. Their high sensitivity to environmental changes, such as variations in pH or metal ion concentrations, enabled selective detection with superior specificity compared to alternative.

The first novel 5,10,15,20-tetrakis(R-substituted) porphyrin receptor molecule (R = C6H4NHC(O)C5H4CoC5H5+ PF6–)3 was prepared and was shown to spectrally and electrochemically sense halide, nitrate, hydrogen sulfate and dihydrogen phosphate guest anions [5,6].

Following this, a series of novel 5,10,15,20-tetrakis (o-ferrocenyl) carbonylaminophenyl-substituted) zinc metalloporphyrin receptors were synthesized. The free base porphyrins weakly complex anion. However, the zinc metallophyrin atropisomeric receptors strongly complex halide, nitrate and hydrogensulfate and stability constants indicated selectivity trend that is dependent on the atropisomer [7].

Porphyrins have been recognized for their exceptional electronic, optical, and catalytic properties, making them suitable for various nanosensor applications. Their rich 18π electron conjugated nature allows for use as optical electrochemical sensors, and they have been innovatively integrated into nanoarchitectures such as nanoparticles, nanocomposites, nanotubes, and nanosheets. These nanoarchitectures offer unique advantages for specific sensing scenarios, such as colorimetric sensor arrays, photo-electrochemical biosensing, and nanocomposites as peroxidase mimetics for glucose detection. The integration of porphyrins into these nanostructures has led to the development of advanced nanosensors that are superior to conventional sensors in terms of adsorptive capacity, modulation of electrical properties, and compatibility with biological system.

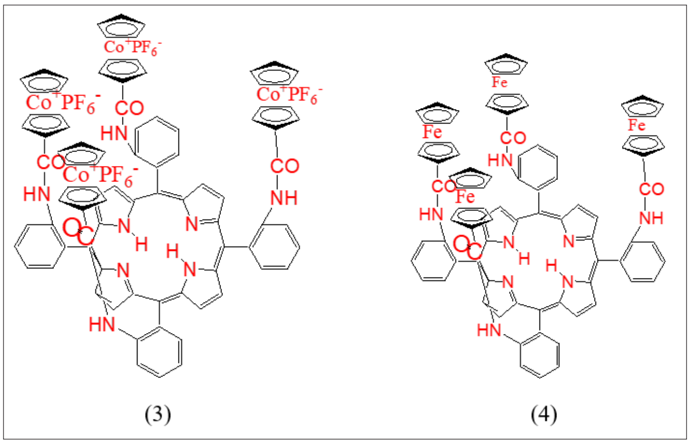

Figure 2.0: First set of Porphyrin Anion Sensors

Nanosensors using porphyrins are a significant advancement in the field of chemical sensing. Porphyrins, known for their remarkable electronic, optical, and catalytic properties, have been innovatively integrated into various nanoarchitectures such as nanoparticles, nanocomposites, nanotubes, and nanosheets. These nanoarchitectures offer unique advantages for specific sensing scenarios, such as colorimetric sensor arrays, photo-electrochemical biosensing, and nanocomposites as peroxidase mimetics for glucose detection. The integration of porphyrins into these nanostructures enhances their sensing capabilities, making them suitable for a wide range of applications, including bioanalysis, clinical, food, and environmental analysis.

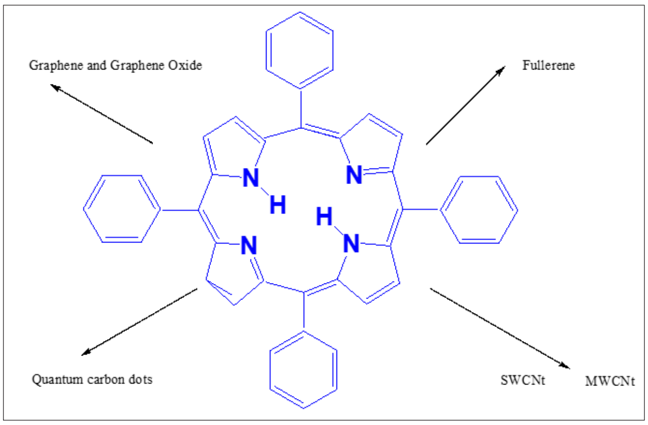

Figure 3.0: Functionalisation of Porphyrins with Different Nanomaterials

In optical chemical sensing, the target analyte is detected by monitoring the changes of one of the optical properties of the sensitive material such as absorbance or luminescence. Porphyrins have intense and distinctive absorption and emission bands, enabling the straightforward use even with consumer electronics set-up such as combination of LED, photodiode and optical filter. The use of nanocomposites, obtained by assembling a set of positively charged porphyrins (Figure 2a) onto graphene oxide, to construct a NIR fluorescent sensor array for discrimination of Hep(heparine) from its Glycosaminoglycan (GAG) analogues [8].

Hematoporphyrin (HP) functionalized graphene oxide nanosheets, a highly fluorescent sensor for copper ions has been synthesized and utilized. These nanosheets have vital roles in several biological processes. It takes full advantage of the high affinity of the pyrrolic macrocycle for Cu2+. The copper ion induces the quenching of the fluorescence of the hybrid material, synthesized by esterification reaction in presence of sulfuric acid, at different concentrations in water. The sensor has been found to have a detection limit of 54 nM, thus could be used in real time water sensing [9].

Porphyrins have been combined with fullerene to produce novel sensors. An electrochemical device was developed for the measurement of DA (dopamine) by immobilizing on GC electrode a system consisting of C60/porphyrin-diazocine-porphyrin dyad held together by non-covalent π–π interactions [10].

An Fe porphyrin derived carbon nanofibers ((Fe-P/CNFs) as a nanozyme have been reported7. These nanofibers exhibit a uniform one-dimensional morphology and demonstrate excellent catalytic performance in the oxidation of peroxidase substrates. Subsequently, a highly sensitive colorimetric sensor for glucose detection, achieving a detection limit of 2.55 μM within a linear range of 0–200 μM has been developed. In addition, Fe-P/CNFs exhibit robust performance as an ascorbic acid sensor, with a detection limit of 0.17 μM. Thus, Fe-P/CNFs is a versatile and efficient nanozymes, making it a strong candidate for applications in biosensing and clinical diagnostics11.

Electrochemical sensors are typically used for the detection of targeted compounds in liquid phase. This is due to the direct measurement of an electrical signal related to the analyte concentration, which results from an electrochemical process occurring at the electrode solution surface. Electrochemical sensors can be divided in two categories, namely, potentiometric and volt-amperometric techniques, where the electrode potential at zero current flow and the current flowing in the cell resulting from redox electrodic reactions are measured, respectively. Several examples belonging to this category have been recently reported in the literature [11].

Metal-Organic Frameworks (MOFs) are a novel class of porous crystalline materials with an exceptionally high surface area and adjustable pore structure. They possess a designable composition and can be easily functionalized with different units. Porphyrins can absorb light from ultraviolet to visible light regions, and their structures and properties can be regulated by altering their peripheral groups or central metal ions. Porphyrin-based MOFs constructed from porphyrin ligands and metal nodes, combine the unique features of porphyrins and MOFs as well as overcoming their respective limitations. In this article, the design, construction, light absorption charge transfer pathways, and strategy for improving the photocatalytic performance of porphyrin-based MOFs, and their applications in the field of CO_2 reduction, hydrogen evolution, organic synthesis, organic pollutant removal, and nitrogen fixation are reported [12].

Conclusion

The design, synthesis, testing and utilization of porphyrin nanosensors is a rapid evolving field in nanotechnology. Amongst porphyrin nanosensors synthesized and tested are: porphyrin nanocomposites, porphyrin graphene oxide nanosheets, C60-porphyrin diode oxide, porphyrin dyad, Fe-porphyrin derived carbon nano-fibres, porphyrin MOF compounds. Each porphyrin nanosensor have shown selectivity for a particular substrate.

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