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Review

Optical Sensing Volatile Organic Compounds Using Porphyrins

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Abstract: Detection of volatile organic compounds (VOCs) is a rapidly growing research area due to importance of VOCs in environmental pollution, human health assessment, food quality control, and homeland security. Optical sensing materials based on porphyrins are particularly appealing for VOCs detection, owing to availability of porphyrins, their exceptional optical and binding properties, as well as their photo- and chemical stability. As research and technology continue to advance, optical sensors involving these materials are expected to play an increasing role in various applications. This article presents a comprehensive overview of porphyrin-based sensing materials developed for use as optical sensors for VOCs. First, sensing films composed exclusively of porphyrin molecules are discussed followed by materials obtained by grafting or incorporation of porphyrins into organic and inorganic polymer matrices. Considering growing interest to multianalyte analysis with porphyrin-based sensor arrays, special section is devoted to this area.

Keywords: optical sensors; porphyrins; volatile organic compounds

1. Introduction

Volatile organic compounds (VOCs) are a group of diverse organic chemicals (including alcohols, amines, carboxylic acids, halogenated compounds, and nitroaromatics) that exhibit low boiling points and readily evaporate at room temperature. They are commonly found in indoor air as pollutants, as by-products of waste management and agriculture, as fuel vapors formed during its storage and transport, in industrial emissions or released by bacteria and other living organisms including humans. Many of these compounds pose significant risks to the environment and human health. [1,2] Monitoring VOCs is also crucial in many everyday social tasks, such as human health assessment or food control, as many products and living organisms emit specific odors. [3,4] Thus, there is a growing interest in developing efficient sensors for VOCs. [5–7]

Detection of various chemical compounds has developed within a vast and interdisciplinary field of knowledge, playing a crucial role in daily human life and applied to different types of analyses, ranging from qualitative recognition of target analytes to quantification and real-time monitoring. Many analytical laboratory instruments, such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Spectrometry (ICP), and Gas Chromatography-Mass Spectrometry (GC-MS), enable complex analyses to be performed within a reasonable timeframe. While these instruments are indispensable and irreplaceable for our daily comfort, they are also expensive, require experienced operators, and cannot be used in the field. In many cases, the target analysis does not necessitate all the capabilities these methods offer but instead requires a precise assessment of the presence or quantity of a target analyte in a routine manner. This has prompted numerous studies on simplified sensing devices based on various signal transduction schemes, such as chemiresistors, mass transducers, electrochemical, photoelectrochemical and optical sensors.

Modern sensors are generally electronic devices that generate signals in response to the presence of an analyte. Such devices logically consist of two main components: a sensing compound or material (the receptor) and a transducer which can involve complicated signal-processing software.

Optical sensors utilize light to gather information about the analyte.[8] The most of these devices deliver these data due to the change of light absorption or luminescence, but sensors employing other spectroscopies as well as other optical parameters such as refractive index and reflectivity, have also been developed.[9] Optimized non-invasive optical sensors can achieve high sensitivity and selectivity, providing rapid response and enabling remote sensing using portable devices. This allows for real-time monitoring and on-site measurements in various conditions.

Sensing materials for these devices vary widely and can include metal oxides, polymers, or organic-inorganic hybrid materials. Molecular chemistry contributes to this field by developing efficient receptors and sensitive transducers, which can sometimes be part of a single molecule. Although molecular compounds can be dissolved and used for detection as chemosensors in solution, the solid-state sensors are more convenient due to their high robustness and reliability, and ease of integration into electronic devices.

Among organic compounds suitable for fabrication of optical sensors, porphyrins are of great value due to their specific structural and optical properties providing highly sensitive detection, albite porphyrin-based chemosensors exhibits in general rather low selectivity. Porphyrins absorb light in different regions of the visible spectrum, primarily due to electronic transitions within their conjugated π-electron systems. Two distinct types of bands are typically observed: the Soret band (400–450 nm), corresponding to $S_0 \rightarrow S_2$ transitions, and the Q-bands (500–700 nm), corresponding to $S_0 \rightarrow S_1$ transitions. Additionally, charge-transfer bands are permitted in complexes where electronic interactions occur between the d-orbitals of metal atoms (such as Fe and Mn) and the conjugated π-electron system of the porphyrin ring. This spectral diversity enables multichannel transduction schemes. High sensitivity of these chemosensors results from their exceptional molar absorptivity in particular in Soret region and their moderate fluorescence. This enable to increase the detection limits that is particular important for optic sensors which are typically less sensitive compared to electrochemical devices. Moreover, many free-base porphyrins and their metal complexes (such as Pd, Sn, and In) produce long-lived triplet states through an excited-state process known as intersystem crossing (ISC) being irradiated by visible light. The triplet state of porphyrins is prone to react with reagents (such as oxygen), which can be utilized in the sensing of these compounds.

There are also numerous ways in which free base porphyrins in the ground state can interact with an analyte primary due to the presence of a large aromatic macrocycle in these molecules. These macrocycles often engage in π-π stacking interactions, as well as other weak interactions such as hydrogen bonding, van der Waals forces, and dipole interactions with the analyte. The periphery of the macrocycle can be easily modified with functional groups or more complex binding residues, allowing for specific responses to target analytes.[10] Unfortunately, the common synthetic strategy for developing chemosensors based on the covalent binding of a receptor and signaling units is relatively inefficient for porphyrin derivatives. Porphyrin conjugates are typically prepared by functionalizing *meso*-positions of the macrocycle using 1,4-phenylene linkers,[11] which are tilted with respect to the macrocycle's main plane. As a result, the degree of conjugation in such molecules is relatively low, leading to a reduced optical response to analyte binding compared to other chromogenic chemosensors. For this reason, many researches in sensing focuses on metalloporphyrins, which can bind analytes *via* axial coordination to metal centers located in the macrocycle cavity. The binding of a ligand or ligand exchange results in a change in symmetry of molecules that induces the spectral changes observed. This approach is effective for the development of VOC sensors, as many VOCs are Lewis bases that readily bind to metal ions.

Another interesting feature of bulky porphyrins is that when organized into supramolecular aggregates in solution or on solid supports, they do not lose their high absorptivity and often remain emissive. While non-structured aggregates generally absorb and emit less light compared to their molecular counterparts and partially lose their ability to bind an analyte, structurally ordered porphyrin aggregates obtained under specific conditions can display intriguing sensing properties not observed in their molecular precursors. [12–14]

The use of porphyrins and related compounds for chemical sensor applications has been reviewed in the past. [15–17] The aim of this review is to draw attention to the use of porphyrin molecules in VOCs detection in gaseous phase. We describe optical chemical sensors that use these derivatives as sensing materials emphasizing various strategies for their immobilization. This is a key step in the fabrication of optical sensors. First, sensing films composed exclusively of porphyrin molecules are discussed followed by materials obtained by their incorporation into organic and inorganic polymer matrices. Considering growing interest to multianalyte analysis with array-based porphyrin sensors, special section is devoted to this area. The detection of other gaseous compounds, such as oxygen, nitrogen oxides, and ammonia, in which porphyrins also play a significant role, is beyond the scope of this review. Readers interested in these topics are encouraged to consult numerous other reviews for a comprehensive understanding. [15,18–25]

2. Sensing Materials Based on Single Porphyrin Derivatives

Porphyrins have gathering significant interest in the detection of VOCs partly because they are highly sensitive transductors and partly because many metalloporphyrins can axially coordinate Lewis bases yielding stable complexes. Among VOCs, Lewis bases are frequent and metalloporphyrins are excellent host for these compounds.

In sensing applications, thin films of porphyrin are often fabricated to increase the number of binding sites available for interaction with analytes. These films exhibit varying degrees of structural order, depending on the preparation method. Supramolecular aggregation of porphyrin molecules is commonly observed in these materials, regardless of the synthesis strategy employed. The optical and coordination properties of these supramolecular aggregates are influenced by their structure. Consequently, the selectivity and sensitivity of optical sensors are highly dependent on the method used to prepare the sensing material. Unfortunately, comparative studies where the same host molecules are immobilized according different synthetic methods are scarce. Most research focuses on sensor sensitivity to one or a few VOCs; however, some studies do report multi-analyte analyses, offering varying levels of insight into the selectivity of these sensors.

Most commonly employed transduction schemes in porphyrin-based sensors involve absorption and fluorescence spectroscopy, although altering other physical properties have also been explored. Surface plasmon resonance (SPR), which assesses changes in thickness and swelling of the thin film upon exposure to the analyte, has garnered increasing attention. Additionally, change of the refractive index at a metal-dielectric interface and within waveguide configurations have also been utilized for analyte detection. [26,27] Crystalline porous materials based on porphyrins enable the use of specific optical methods for signal transduction, which will be discussed below.

2.1. Thin Film Formed From Only Porphyrin Molecules

Porphyrins can be deposited as thin films on solid supports using various experimental techniques, which significantly influence their structural organization and sensing efficiency. Many of these methods do not require specific functionalization of the porphyrin molecules, and commercially available derivatives are typically investigated.

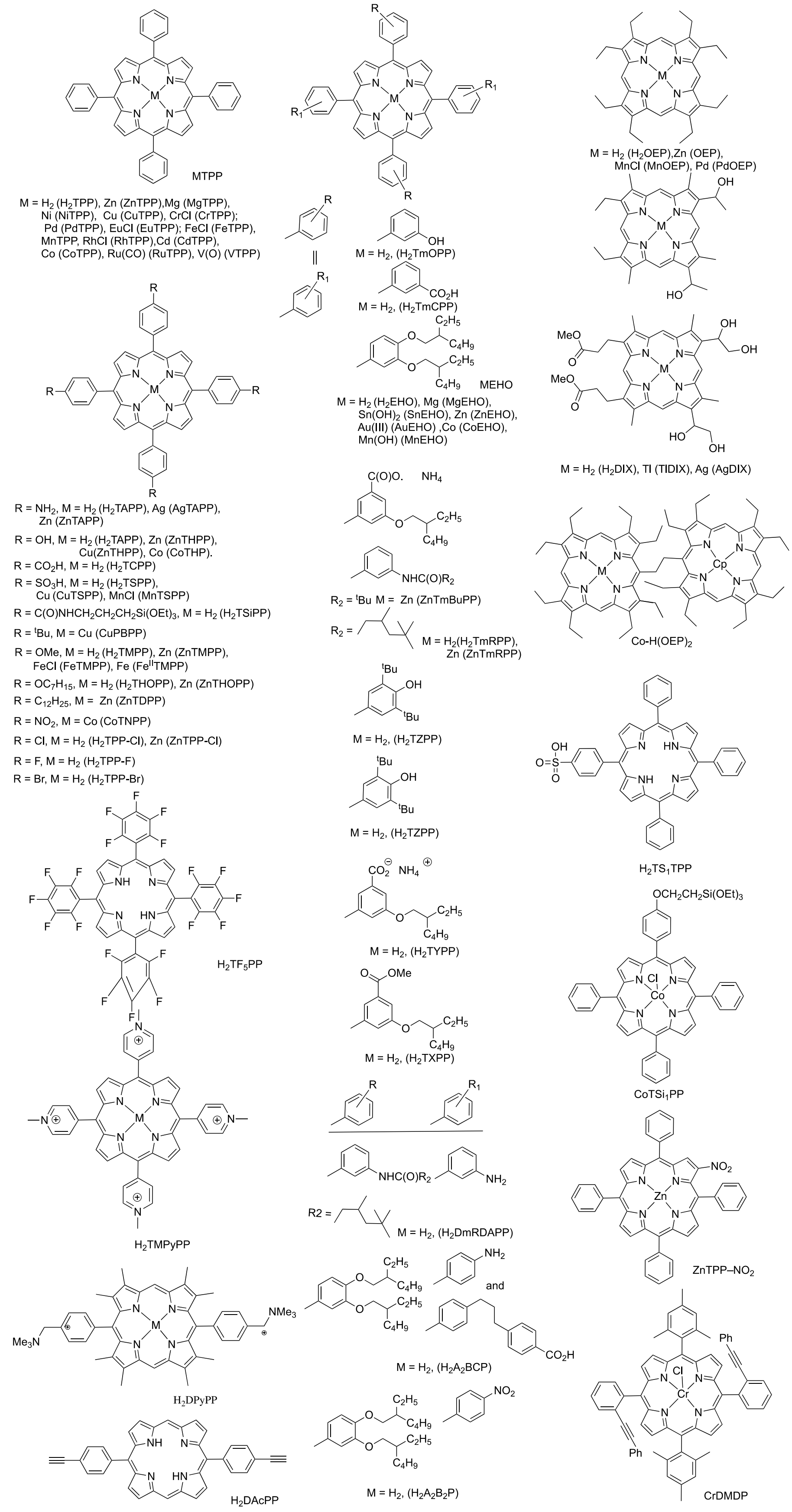

Figure 1. Illustration of porphyrins discussed in this review.

2.1.1. Dip-coating and drop-casting

Dip-coating is a well-established technique for fabricating thin films, offering some control over the deposition of porphyrin onto solid substrates to produce films with relatively uniform thickness. The process involves immersing a solid support into a porphyrin solution and then withdrawing it at a controlled speed. The thickness of the resulting film depends on factors such as solution concentration, withdrawal speed, solution viscosity, and temperature. The self-assembly of porphyrin molecules on the solid surface can occur due to electrostatic or other specific weak interactions, enhancing the uniformity and overall morphology of the film. In this context, highly charged *meso*-tetraaryl or *meso*-tetramethylpyridylporphyrins (anionic and cationic species, respectively) are of particular interest for this deposition method.

Salleh and co-corkers obtained a dense self-assembled monolayer (SAM) by immersing a quartz substrate in an aqueous solution of Cu(II) *meso*-tetra(4-sulfonatophenyl)porphyrin (CuTSPP) for 30 min, followed by lifting the slide at a constant speed of 15 mm min^{-1}.[28] The deposition process was controlled by electrostatic interactions between the negatively charged sulfonate groups and the crystalline support. Due to the repulsion among the negatively charged porphyrin molecules, the formation of multilayers was prevented and a monolayer film was obtained (Figure 2). The sensing properties of this film were studied in a closed chamber equipped with a gas inlet, a two-arm fiber reflectance probe, and a green LED light source (514 nm). This sensor demonstrated sensitivity to ethanol (EtOH), 2-propanol (^{i}PrOH), and cyclohexane vapors, yielding a fast optical response with good reproducibility, despite only small optical changes being observed upon exposure to the analytes.

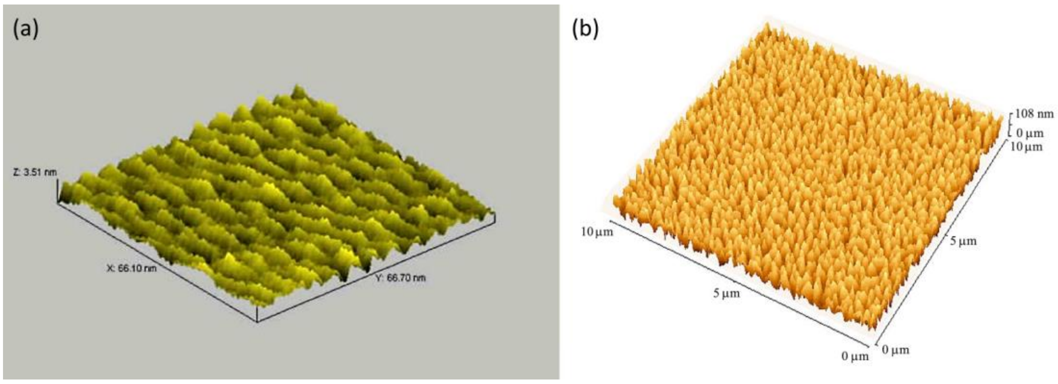

Figure 2. AFM images of (a) CuTSPP film obtained by dip coating. Ref. 28. Reproduced with permission of Elsevier; (b) ZnTPP thin film prepared by spin-coating. Ref. 29. Reproduced with permission of Elsevier.

Dip-coating can also be used for the deposition of nanoparticles and the preparation of sol-gel films. For instance, a thin film composed of TiO_2 nanoparticles covered by iron(III) *meso*-tetraphenylporphyrin chloride (FeTPP) was obtained using a glass slide coated with Poly-L-Lysine as the solid substrate.[30] In comparison to sensing films prepared using a similar procedure from nanoparticles formed by only porphyrin molecules, the composite material showed higher sensitivity to EtOH, ^{i}PrOH, and acetone, as investigated by fluorescence spectroscopy.

Dip coating also useful for deposition of porphyrin H_2TSPP onto optical fibers when combined with UV irradiation of the porphyrin solution in dichloromethane (CH_2Cl_2).[31] Such fibers have potential applications in the remote detection of VOCs.[32]

A drop of a porphyrin solution is sometimes deposited onto a solid support and allowed to evaporate in the air, resulting in a thin film material.[33] Ding, Peng, and their co-workers used this deposition technique, commonly known as drop casting, to prepare a fluorescent "ON-OFF" sensor for the detection of diethylchlorophosphate (DCP), a simulant of the nerve agent Sarin. They deposited a dichloromethane solution of 5,10-(4-ethynylphenyl)porphyrin (H_2DAcPP) onto silica plates using a syringe, followed by air-drying for 5 h. The sensor based on this composite material demonstrated excellent sensitivity, with a detection limit as low as 10 ppt, while also being reversible and photostable.[34]

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2.1.2. Spin-Coating

Spin coating is the most widely used method for depositing porphyrins onto solid supports, thanks to its low-cost equipment and the ability to control film thickness by adjusting spin speed, duration of the process, and solution concentration. Moreover, spin coating can be applied to a wide range of solid substrates enabling optimization of sensing properties and the adaptation of sensing material to various signal transduction methods. Typically, for preparation of optical sensors, diluted solutions (10^{-4} – 10^{-5} M) of porphyrins in chlorinated solvents are deposited onto transparent supports such as glass, quartz, or Au-covered glass substrates. The resulting films can be dried at elevated temperatures to remove solvent traces, that may improve molecular packing in the films and optimize the sensors performance and robustness.[35] This technique can be used for the deposition of molecular compounds, nanoparticles or in preparation of doped polymer matrices and array-based sensor systems. The sensing materials prepared according this strategy are listed in Table 1 and most important results are discussed in the corresponding sections.

The thickness of films obtained by spin-coating commonly exceeded 100 nm (Figure 2) and undesirable porphyrin aggregates often observed in such materials. [29] Their sensing properties can be improved by tailoring the molecular structure of porphyrins to minimize aggregation within the films. This can be achieved by using metalloporphyrins with axial ligands (Fe(III), Mn(III), In(III), Rh(III)), in which π-π stacking is less pronounced. [36,37] Introducing bulky functional groups or alkyl chains at the macrocycle periphery also diminishes the aggregation of chromophores, providing improved sensor characteristics. [38,39] Such functionalization of porphyrins can also create specific binding sites for target VOCs and enhance the solubility of these aromatic compounds in organic solvents, thereby facilitating material preparation. [40,41]

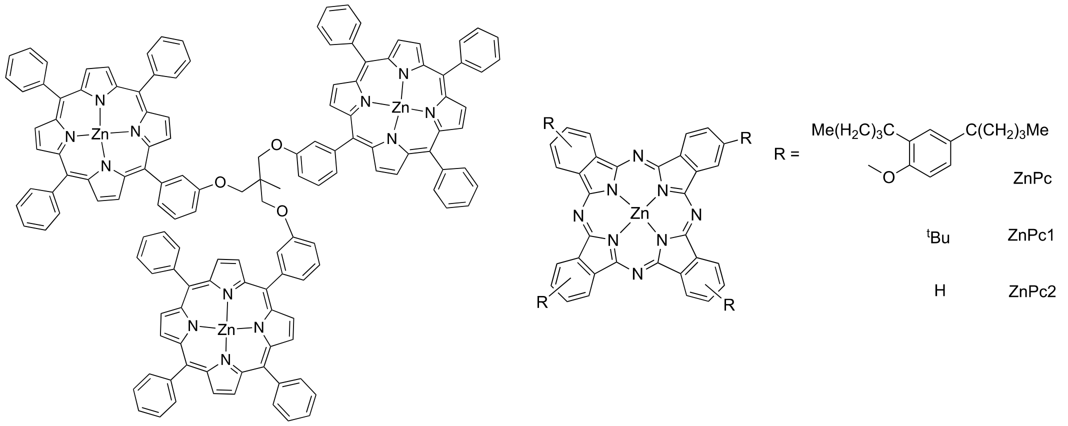
Another approach was investigated by Roales and co-workers, who synthesized a triphenylmethane analogue featuring three porphyrinyl residues (ZnTriad, Figure 3).[42] In this bulky molecule, π-π stacking is reduced, leading to better accessibility of Zn centers for guest molecules. The sensing properties of thin films composed of ZnTPP and ZnTriad were compared studying volatile amines as analytes. A total of five primary amines were examined: three linear primary amines of increasing length, one bulky primary amine (*tert*-butylamine), and one aromatic compound (Table 1). The exposure of ZnTriad films to these analytes resulted in specific responses toward each of amine studied, allowing discrimination of analytes due to the difference on their size and basicity.

As it was discussed above, the axial coordination of analytes to the metal centers within the macrocyclic cavity typically enhances sensor sensitivity, as the resulting complexes are stable and exhibit specific spectral properties. However, a contrasting situation arises for analytes that are not strong Lewis bases. Sensors that utilize metalloporphyrins may exhibit lower selectivity for certain of these analytes compared to those that use free-base porphyrins, as such VOCs can be more easily bound through weak interactions with the large aromatic tetrapyrrolic macrocycles. This was observed when acetone and chloroform ($CHCl_3$) were detected using spin-coated films fabricated from octaethyl-substituted porphyrins H_2OEP and ZnOEP.[43] This data explains why both free-base porphyrins and their metal complexes are employed in sensing materials and in particular array sensors based on porphyrins.

As shown in Table 1, most reported sensors register changes in light absorbance in the UV-vis region upon exposure of sensing materials to VOCs. The changes in both the positions and intensities of the bands are relatively small, and less pronounced compared to studies conducted in solution. This was attributed to the strong tendency of porphyrin molecules to aggregate within these materials and the low diffusion rate of gaseous analytes in non-porous films. Consequently, considerable attention has been directed toward developing efficient methods of signal treatment. The simplest approach involves the comparative integration of the Soret band before and after exposure of the sensor to analyte vapors.[36] To perform dynamic analyses of alcohols using a spectrophotometer with spin-coating film of MgTPP, Kerdcharoen's group developed in-house software based on Principal Component Analysis (PCA), one of the most widely used pattern recognition methods for analyzing gas sensors.[35] The acquired data were analyzed in real time for the identification of methanol (MeOH), EtOH, and ^{i}PrOH. This sensor exhibited varying sensitivities for these analytes, with the highest response observed for MeOH.

Spadavecchia and coworkers quantified analytes by comparing the relative variations of the absorbance integral within specific wavelength intervals. [29,39] When the spectral data were treated in this manner, a linear dependence of the ZnTPP-based sensor response on 4-aminophenol concentrations was observed in the 5–40 ppb concentration range of the analyte.[29] The remarkable sensitivity, reversibility, and reproducibility of this sensor highlight the advantages of spin-coating for the immobilization of porphyrins.

To increase sensitivity using this signal treatment method, two chromophores (porphyrin CuPBPP and phthalocyanine ZnPc (Figure 3)) that absorb light at different wavelengths were mixed into the same film.[38] Dynamic responses to the presence of VOCs were recorded using four channels in the 300–700 nm range, each covering 50–100 nm. This method enabled the identification of organic compounds within complex matrices of VOCs (Table 1).



(**a**) (**b**)

Figure 3. The structure of (A) ZnTriad (B) phthalocyanines used for preparation of drop-casting films and LB films.

Further development of this approach was reported by Seesaard and coworkers, who developed optical sensors capable of discriminating among the odors of three pathogenic bacteria.[44] This was achieved by preparing a sensing film composed of two porphyrins (ZnTPP and MgTPP) and phthalocyanine ZnPC1 (Figure 3). An in-house optical artificial nose system based on light-emitting diodes and a photodetector was fabricated using commercially available components. It consisted of a hybrid optical sensor and a data acquisition algorithm involving multichannel signal registration.

Development of optical waveguide sensing is of great importance for performing remote measurements.[45] In a sensor operating according to this principle, a MnTPP film was used, which was obtained by spin-coating a porphyrin solution onto the surface of a K^+ exchange glass optical waveguide with a thickness of 1–2 mm. [46] Linear response to the presence of triethylamine (NEt_3) was observed in the concentration range of 0.1–1000 ppm of the analyte. The response time was only 1.5 s, while the recovery time was 50 s.

The same strategy was employed in the development of sensors for ethylenediamine (EDA) vapors. [47–49] The optical waveguide was prepared using a spin-coated film of H_2TCPP. This sensor was studied for the detection of eighteen VOCs and exhibited a high response only in the presence of EDA vapors, with a detection limit of 0.1 ppm.[47] When H_2TSPP was immobilized using spin-coating, the resulting H_2TSPP-magnetite film exhibited higher selectivity compared to the film containing only porphyrin.[50] Recently, H_2THPP-based films were prepared by the same method for further optimization of EDA sensing.[49]

Surface plasmon resonance (SPR), which has garnered significant attention in the development of optical sensors due to its high sensitivity,[51] is still rarely employed in the development porphyrin-based sensors.[43]Tonezzer and co-workers developed planar metal-cladding leaky waveguides, where a thin porphyrin film serves as the guiding layer.[52] Detection of analytes was achieved by monitoring changes in the refractive index of the guiding layer upon interaction with the analyte. Using a film composed of H_2TPP molecules, a very fast (t_{90} < 30 s) linear optical response was observed as a function of ethanol vapor concentration in air, within the range of 375–3000 ppm concentration range of the analyte.

Table 1. Spin-coated film for VOCs sensing.

Porphyrin precursor[a]	Solid Support	Matrix	Optical response	VOCs	Ref
H_2TPP or CoTPP or FeTPP	P-doped (100) silicon wafer	-	UV–vis spectroscopy	MeOH, EtOH, ^{i}PrOH	37
FeTPP or MnTPP	Glass	-	UV–vis spectroscopy	Py, NEt_3, Me_2NH	36
CoTPP	silica	-	UV–vis spectroscopy	EtOH	53
ZnTPP	Quartz	-	UV–vis spectroscopy	Py, MeOH, ethyl acetate	40
MgTPP	Glass	-	UV–vis spectroscopy	MeOH, PrOH, ^{i}PrOH	35
ZnTPP–NO_2	Quartz	-	UV–vis spectroscopy	Py, NEt_3, MeOH, ethyl acetate	40,41
ZnTriad	Glass	-	UV–vis spectroscopy	$PrNH_2$, $BuNH_2$, $HexNH_2$, $PhNH_2$, $^{t}BuNH_2$	42
MnTPP	K^+-exchanged glass optical waveguide	-	UV–vis spectroscopy	NEt_3	46
H_2TCPP	K^+-exchanged glass optical waveguide	-	UV–vis spectroscopy	ethylenediamine	47
H_2TMPP	K^+-exchanged glass optical waveguide	-	UV–vis spectroscopy	ethylenediamine	48
H_2TSPP	glass optical waveguides		UV–vis spectroscopy	ethylenediamine	50
H_2TSPP	maghemite-covered glass optical waveguides	-	UV–vis spectroscopy	ethylenediamine	50
H_2THPP	TiO_2-covered glass optical waveguides	-	UV–vis spectroscopy	ethylenediamine	49
H_2OEP or ZnOEP	Au- covered glass	-	SPR	$CHCl_3$, acetone	43
H_2TPP	Au-covered glass	-	Reflectance spectroscopy	EtOH,	52

H_2TPP or ZnTPP or CdTPP	Glass	SiO_2	Fluorescence spetroscopy	2,4,6-trinitrotoluene, 2,4-dinitrotoluene, nitrobenzene	54
H_2TMPyPP or H_2DPyPP	Glass substrate	PMMA PVP	Fluorescence spetroscopy	2,4,6-trinitrotoluene, 2,4-dinitrotoluene, nitrobenzene	55
CuTBPP +ZnPC[b]	Quartz	-	UV–vis spectroscopy	MeOH, EtOH, ^{i}PrOH, acetone	39
CuTBPP +ZnPC[b]	Quartz	-	UV–vis spectroscopy	MeOH, EtOH, ^{i}PrOH, $PhNEt_2$, Py, 2-bromopyridine, Hex, acetone, ^{t}BuNH$_2$	38
ZnTPPP+MnTPP +ZnPC1[b]	Glass	-	UV–vis spectroscopy	EtOH, acetone, MeCO$_2$H, acetone, ethyl acetate, formaldehyde	44
array of M-PCN- 222[c] M=Ag, Zn, Fe, Cu, Co	Glass	PDMS	UV–vis spectroscopy	acetone, $CHCl_3$, CH_2Cl_2, EtOH, hexanal, $BuNH_2$, tetrahydrofuran, toluene, 2,4-dinitrotoluene	56
array of MTPP M=Mg, Zn	Glass	-	UV–vis spectroscopy	MeOH, EtOH, ^{i}PrOH, acetone, MeCO$_2$H, methyl benzoate	57

[a] Porphyrin and phthalocyanine structures are shown in Figure 1. [b] Structures of phthalocyanines are illustrated in Figure 3. [c] PCN-222 is Zr-based MOF with 5,10,15,20-tetrakis(4-carboxy- phenyl)porphyrin linkers.

2.1.3. Vacuum Evaporation

In vacuum evaporation technique, solid porphyrin evaporated at high temperature (300 °C) in a high vacuum (10^{-4} Pa) and the vapors are deposited on solid substrate enabling the formation of thin films on various substrates. This ensures that the deposited film maintains high purity and uniformity. Depending on the application, post-deposition treatments such as annealing may be performed to improve film quality, crystallinity, or adhesion. This method has rarely been used for the preparation of VOC sensing materials because it requires expensive equipment and the film preparation process is time-consuming. Thin films of H_2TPP, FeTPP, and CoTPP porphyrins were deposited on P-doped (100) silicon wafers.[37] These three sensors were compared to the corresponding films obtained by spin coating in the detection of alcohols (MeOH, EtOH, and ^{i}PrOH). The vacuum-evaporated films were significantly more sensitive and exhibited much faster responses for all alcohols compared to the spin-coated films. This increased sensitivity was attributed to the high purity of the vacuum-evaporated films, which did not contain traces of solvent ($CHCl_3$), resulting in greater reactivity toward analyte molecules.

2.1.4. Glow-Discharge-Induced Sublimation

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Glow-discharge-induced sublimation (GDS) is an alternative to vacuum evaporation, particularly useful for depositing compounds that are difficult to evaporate using traditional thermal methods. In this process, sublimation is triggered by a glow discharge within a vacuum chamber evacuated to approximately 10^{-4} Pa. The glow discharge occurs when a gas, typically an inert gas like argon or helium, at a pressure of about 20 Pa, is ionized by applying a high voltage, creating a plasma that can be sustained at low pressure. As the sublimated material interacts with the substrate in the presence of the glow discharge, a thin film forms on the solid surface. The energy from the plasma also enhances the adhesion and orientation of molecules in the deposited films. Materials obtained through GDS are typically very pure and possess a small thickness – two features that are highly desirable in sensing applications.

Tonezzer and co-workers use this method to deposit CoTPP onto a silica substrate.[53] CoTPP was also immobilized on the silica substrates using spin-coating (CoTPP-SC) and vacuum evaporation (CoTPP-VE). The three films exhibited very different morphologies, as shown in Figure 4. Specifically, CoTPP-VE displayed a flat surface, while CoTPP-SC contained shallow holes formed due to solvent evaporation. In contrast, the CoTPP-GD film was composed of microsized particles and exhibited a rough surface. Different supramolecular organization of the films was also observed using UV–vis spectroscopy. Unfortunately, the sensing properties of these materials were investigated only briefly. The CoTPP-GD film demonstrated significantly higher sensitivity to EtOH vapor compared to CoTPP-SC and CoTPP-VE, exhibiting an optical response that was both rapid and reversible.

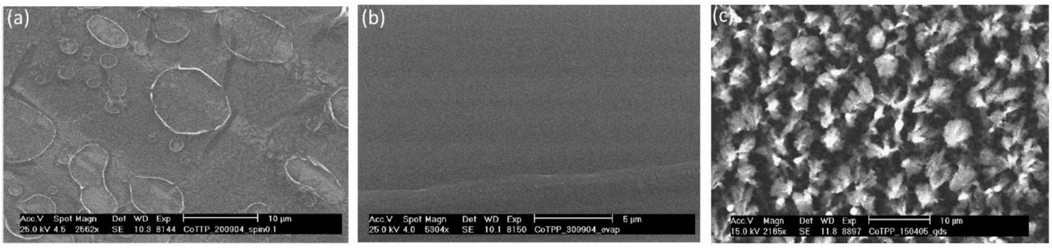


Figure 4. SEM images of CoTPP thin films formed by spin-coating (a), vacuum evaporation (b) and GDS (c). Ref. 53. Reproduced with permission of Elsevier.

2.1.5. Langmuir-Blodgett/Langmuir-Schäfer films

Langmuir-Blodgett (LB) and Langmuir-Schäfer (LS) techniques, [58,59] rely on the supramolecular organization of molecules at gas–liquid (generally air–water) interfaces applying surface pressure and subsequent transfer of the monolayers thus formed onto solid supports oriented perpendicularly (LB) or parallel (LS) to the liquid surface.[60] Both hydrophilic and lipophilic solid supports can be covered by molecular monolayers, and the thickness of the film thus obtained can be precisely controlled by changing the number of transferred layers. Recent studies have demonstrated that these techniques are not only valuable for producing thin films from traditional amphiphilic molecules with long alkyl chains but also yield excellent results in the deposition of complex functional molecules and nanoparticles. [61–65] When the LB technique is employed to fabricate thin films from porphyrins, the π–π stacking of the tetrapyrrolic macrocycles often serves as a key driving force for the supramolecular organization of the films. This organization is further influenced by various weak interactions between the peripheral substituents and the macrocycle. The structure of porphyrin molecules should be tailored because not all of these compounds form stable Langmuir monolayers on the water surface. Moreover, even when compression isotherm at air–water interface can be obtained three-dimensional aggregates with ill-defined shapes are usually formed both at water and on solid surfaces. [66–68] However, LB/LS techniques offer greater control over the structural and optical characteristics of molecular films compared to spin-coating, leading to improved sensitivity, selectivity, and functionality of sensors. While complete control over the monolayer structures is not yet possible, practical guidelines are available, and monitoring their structure using compression isotherms and fiber-optic spectroscopy (UV–vis and fluorescence) simplifies the investigation and structural optimization of the films thus obtained. [59,64,69]

LB/LS porphyrin-based films are widely explored as gas sensors [70] and researches related to VOC analysis summarized in Table 2. As shown in the table, most sensors were prepared using vertical deposition (LB film), while the LS method was employed much less frequently. UV–Vis absorption and reflectance spectroscopy are commonly used in signal transduction schemes due to the exceptional absorption properties of porphyrin molecules. These methods are compatible with a fiber setup. [3,71] Reflectance anisotropy spectroscopy, which has recently gained significant interest, [72–74] allows not only the detection of analytes but also provides valuable insights into the structural organization of the films before and after analyte binding.

Recent research has also focused on the use of SPR in signal transduction. [75,76] SPR-readout has been shown to be effective for detecting aromatic compounds.[76] Comparative studies on the binding of acetic acid ($MeCO_2H$) and methyl amine ($MeNH_2$) with LS films composed of H_2OPP molecules, utilizing UV–Vis spectroscopy and SPR, have demonstrated that sensor sensitivity is largely independent of the signal transduction method in these setups.[75]

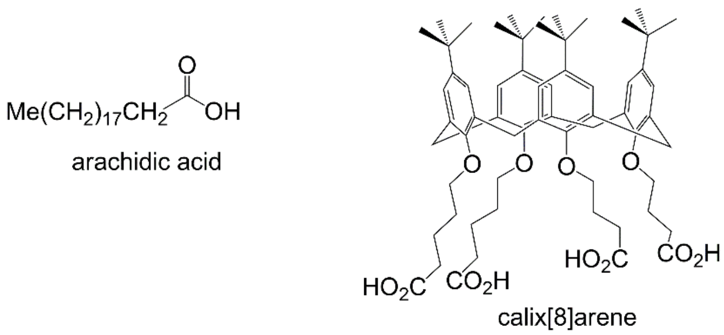
Magneto-optical SPR combines the principles of magneto-optical effects with surface plasmon resonance, allowing for analyte detection by analyzing changes in the refractive index of films as well as the magneto-optical properties of materials near the surface. This signal transduction technique was employed to prepare a sensor using LS films of porphyrin dimer $Co\text{-}H(OEP)_2$ (Figure 1). This sensor demonstrated remarkable sensitivity to all three investigated alcohols (MeOH, EtOH, and ^{i}PrOH), providing a linear response within the range of $1–14 \times 10^{-4}$ ppm of the analytes despite its sensing performance varied depending on the structure of the alcohol.

Porphyrin-based LB/LS films allowing naked-eye detection of VOCs were reported only recently.[77] In this study, a 15-layer LS film of ZnTPP on a glass substrate enables detection of Py visually, despite a relatively small red-shift of only 5 nm being observed after exposing the film to the analyte vapors for 1 min. The sensitivity of the film to vapors of other amines was not investigated.

Preparation of highly ordered LB/LS films is essential for developing optical sensors and remains a primary focus in this field. Despite understanding that the structure of these films is influenced by the nature of substituents on the periphery of the tetrapyrrolic macrocycle and the metal centers within it, preparation of well-structured monolayer films is still challenging. [68,77–80] Several guidelines have been reported to reduce the aggregation of porphyrin molecules in the monolayers.

The oldest and simplest method involves preparing mixed porphyrin–fatty acid monolayers. [3,71,81,82] Fatty acids such as arachidic acid (Figure 5) also facilitate the transfer of the monolayer onto solid substrates, as fatty acids are well-known for their ability to form stable films on solid substrates.

Another strategy is based on the preparation of LB films using mixtures of porphyrins with an amphiphilic calix [8]arene derivative (Figure 5). [78,83,84] Comparative studies of LB films prepared from MEHO (M = Zn, Mn) with and without calixarene have shown that the separation of porphyrin molecules by this macrocyclic molecules decreases the size of nanoaggregates in the LB films, which induces an increase in both the magnitude and rate of the optical sensor response. The binding of amines by these two sensors is reversible and produced spectral changes which are depended on the amine structure and temperature.



arachidic acid

calix[8]arene

Figure 5. The structure of compounds used for preparation mixed LB films.

In the case of free-base porphyrins, the formation of dense aggregates in the Langmuir monolayer can be decreased by adding carboxylic acids to the water subphase. Partial protonation of the tetrapyrrolic macrocycle significantly changes the supramolecular organization of the monolayer, yielding rarified layers in which analytes diffuse easily to.[85]

Metal centers play a crucial role in sensor design, as clearly demonstrated by Dunbar and co-workers, who compared the optical response of LB films formed by the free-base porphyrin H_2EHO and six metal complexes with this ligand in the presence of ten VOCs (Table 2). [83,86] Metalloporphyrins with axial ligands form rarified films due to steric hindrance imposed by the ligand, which enhances diffusion and improves analyte binding.[36] However, films composed of complexes with very strong axial ligands, such as the two hydroxyl ligands in SnEHO, did not show any response to the analytes. [83,86] The highest optical responses were observed for the Co(II) complex, which can alter its oxidation state in the presence of certain analytes, resulting in Co(III) complexes with different light absorption properties.[86] The Mg complex produced the largest optical response in the presence of $MeCO_2H$ among the ten studied VOCs, likely due to its transformation into the free-base porphyrin H_2EHO under acidic conditions, followed by chemisorption of this analyte.[83]

Aggregation of porphyrin molecules in LB/LS films can also be decreased by introducing alkyl chains at the periphery of this macrocyclic molecule. This approach has been widely investigated and applied to VOC detection. [72,76,87] For instance, Richardson and co-workers compared the sensitivity properties of LB films obtained from two *N*-alkyl substituted derivatives of [5,10,15,20-tetrakis(3-amidophenyl)porphinato]zinc(II) ZnTmBuPP and ZnTmRPP (Figure 1). The porous film formed from the bulky compound ZnTmRPP exhibited a faster and higher response compared to its analogue ZnTmBuPP in the detection of a series of primary, secondary, and tertiary amines.[87]

Interestingly, the rate of porphyrin deposition on solid substrates influences the morphologies of films and their sensing properties, due to the increased porosity of non-homogeneous films obtained at ultra-fast deposition rates (1000 mm min^{-1}).[88] This was found application in the development of portable sensors for 2-methylbutan-2-ol, which is shown in Figure 6 and represents a prototype of a useful portable toxic gas sensors.[89] The device consists of a commercial blue LED that emits light detected by a phototransistor. The phototransistor is coated with an LS film of MEHO obtained by the ultra-fact deposition. Upon exposure to 2-methylbutan-2-ol, the film undergoes a subtle shift in its absorbance characteristics, which varies the light intensity received by the phototransistor. This results in a change in the voltage across the phototransistor when sensor is exposed to the analyte. Under dynamic conditions, the optical response of this device stabilizes after approximately 300 sec. Absorbance changes are initially rapid, reaching about half of the maximum output in under 30 sec. The highly reproducible response increases linearly with the concentration of the analyte below 41 ppt concentration of the analyte.

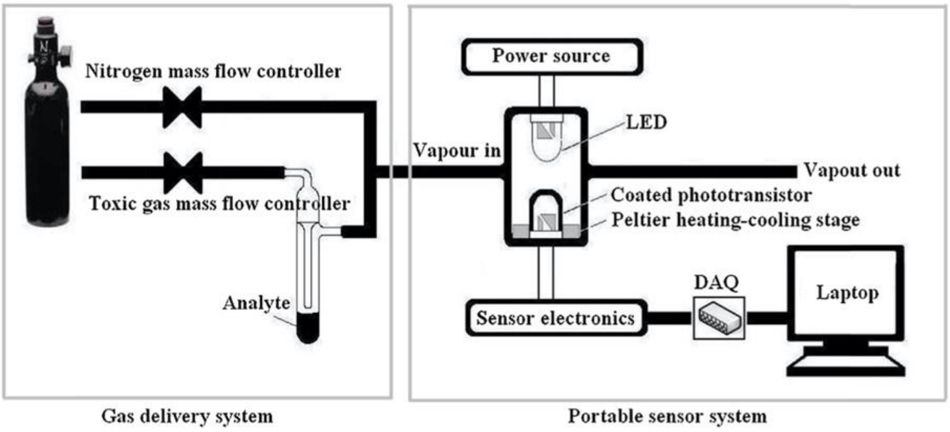


Figure 6. Schematic representation of portable sensing device using LS film of MgEHO as sensing material. Ref. 89. Reproduced with permission of Elsevier.

It has been reported that the selectivity of sensing by LB/LS films can be increased by covering these films with protective thin layers containing specific molecules capable of providing size-selective diffusion. Evyapan and Dunbar have shown that such a layer can be obtained by performing the deposition of PMMA and carboxylic acid-substituted calix [8]arene (Figure 5) on top of the H_2EHO LS film.[85] This protective LS film served as a barrier to the diffusion of bulky carboxylic acids, enabling an increase of $MeCO_2H$ selectivity.

Sometimes sensing properties of LB/LS films can be improved by their annelation at 50–100 °C. [81,90] The surface of the film obtained after annealing was found to be smoother, indicating a significant structural reorganization of the aggregated species transferred onto the glass surface during the heating process.

Thus, despite some degree of structural organization in LB/LS films, selective detection of VOCs has not been yet achieved, although the optical signals of different analytes were distinguishable and useful for their identification. [78,84]

Table 2. Optical sensors based on porphyrins LB/LS films for VOCs determination.

Porphyrin precursor [a]	Method of deposition/Substrate	Optical response	VOCs	Ref
ZnTPP	LS/ glass	UV–vis spectroscopy	Py	77
MnTPPCl	LB/ glass	Reflectance spectroscopy	EtOH	90
RuTPP+ arachidic acid[b]	LB/ glass substrate	Reflectance spectroscopy	MeOH, EtOH, ^{i}PrOH	81
H_2THOPP	LB/ oxidized Si(001)	Reflectance anisotropy spectroscopy	EtOH	72
ZnTHOPP	LS/ quartz	Reflectance anisotropy spectroscopy	EtOH, Hex, NMe_3	73
ZnTHOPP	LB/ quartz	Reflectance anisotropy spectroscopy	EtOH, Hex	74
ZnEHO or ZnEHO	LB/ HMDS-covered glass	UV–vis spectroscopy	$MeCO_2H$, butanone, ethyl acetate, HexSH,	78

+calix [8]-arene[b]			HexNH$_2$, HepCHO, OctOH, OctNH$_2$, NEt$_3$, P(OMe)$_3$	
ZnEHO	LB/ HMDS-covered glass	UV–vis spectroscopy	PrNH$_2$, BuNH$_2$, PeNH$_2$, HexNH$_2$, HepNH$_2$, OctNH$_2$	78
H$_2$EHO	LS[d]/ HMDS-covered glass	UV–vis spectroscopy	MeCO$_2$H, PrCO$_2$H, PeCO$_2$H	85
H$_2$EHO, or MgEHO or SnEHO or ZnEHO or ZnEHO+calix [8]-arene[b]	LB/ HMDS-covered glass	UV–vis spectroscopy	MeCO$_2$H, butanone, ethyl acetate, HexSH, HexNH$_2$, HepCHO, OctOH, OctNH$_2$, NEt$_3$, P(OMe)$_3$	83
MEHO M=Mg, Sn, Zn,Au,Co, Mn	LB/ HMDS-covered glass	UV–vis spectroscopy	MeCO$_2$H, butanone, ethyl acetate, HexSH, HexNH$_2$, HepCHO, OctOH, OctNH$_2$, NEt3, P(OMe)$_3$	86
MnEHO+calix [8]-arene[b] ZnEHO+calix [8]-arene[b]	LB/ hydrophobic glass	UV–vis spectroscopy	PrNH$_2$, BuNH$_2$, PeNH$_2$, HexNH$_2$, HepNH$_2$, OctNH$_2$, NonNH$_2$, NHEt$_2$, NHPr$_2$, NHBu$_2$, NHHex$_2$, NEt$_3$, NPr$_3$	84
ZnTmBuPP ZnTmRPP	LB/ hydrophobic glass	UV–vis spectroscopy	MeCO$_2$H, butanone, ethyl acetate, HexSH, HepCHO, OctOH, P(OMe)$_3$, PrNH$_2$, BuNH$_2$, NHPr$_2$, NHBu$_2$, NPr$_3$, NBu$_3$	87
MgEHO	LS/ HMDS-covered glass	Phototransistor	2-methyl-butan-2-ol	89
H$_2$EHO	LS/ glass or Au (Au-coated glass SPR chip)	SPR and UV–vis spectroscopy	MeCO$_2$H, MeNH$_2$	75
Co-H(OEP)$_2$	LS/ Au (Au/Co/Au coated SPR chip)	Magneto-optical SPR	MeOH, EtOH, ^{i}PrOH, NMe$_3$	91
ZnTDPP	LB/ gold coated SPR chip	SPR	benzene, toluene, ethyl benzene, xylene	76

array of ZnTPP, ZnPc2^c	LB/ quartz	UV–vis spectroscopy	pyridine, methanol	92
array of FeTPP, FeOEP, each mixed with arachidic acid	LB/ glass	UV–vis spectroscopy	2-propanol, acetone, cyclohexane, ethanol.	71
array of MnOEP FeOEP CoOEP RuOEP, each mixed with arachidic acid	LB/ glass	UV–vis spectroscopy	EtOH, ^{i}PrOH, acetone, cyclohexane	82
array of FeTPP, MnTPP, CoTMPP, CoOEP, each mixed with arachidic acid	LB/ glass	UV–vis spectroscopy	fresh capsicum annum, dried capsicum annum, fresh capsicum minimum	3
array of H_2DmRDAPP, H_2TmOPP, H_2EHO, H_2EHO, H_2TmRPP, H_2A_2BCP, H_2TZPP	LB/ HMDS-covered glass	UV–vis spectroscopy	$MeCO_2H$, butanone, ethyl acetate, HexSH, $HexNH_2$, HepCHO, OctOH, $OctNH_2$, NEt_3, $P(OMe)_3$	93
array of H_2TXPP, H_2TYPP H_2TPPP-Br, $H_2A_2B_2$P	LB/ HMDS-covered glass	UV–vis spectroscopy	$MeCO_2H$, butanone, ethyl acetate, HexSH, $HexNH_2$, HepCHO, OctOH, $OctNH_2$, NEt_3, $P(OMe)_3$	93
ZnTPP	LS/ glass	UV–vis spectroscopy	Py	77
MnTPPCl	LB/ glass	Reflectance spectroscopy	EtOH	90
RuTPP+ arachidic acid^b	LB/ glass substrate	Reflectance spectroscopy	MeOH, EtOH, ^{i}PrOH	81

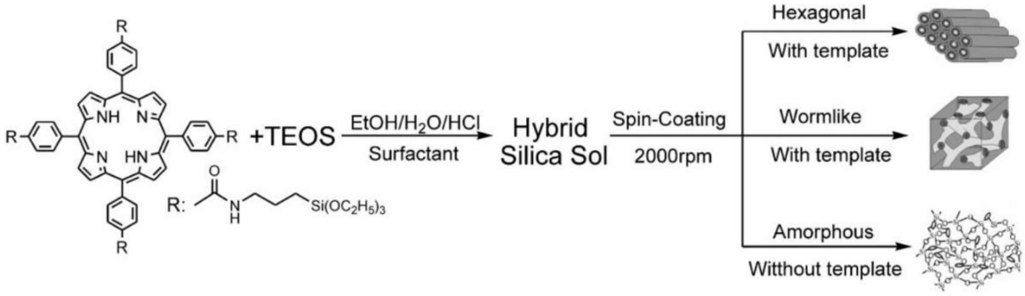
[a] The structure of porphyrins are illustrated in Figure 1. [b] The structures of calix [8]arene and arachidic acid are present in Figure 5. [c] The structure of this compound is shown in Figure 3. [d] Langmuir layers were formed after adding $MeCO_2H$ in the water subphase to reduce the aggregation of H_2EHO in the monolayer.

2.2. Materials Based on Oxide Matrices

Immobilization of chemosensors into transparent silica matrices is a promising strategy for preparing sensing materials, owing to the versatility of the sol-gel process. When organosils are prepared, this process involves the hydrolysis and polycondensation of a siloxane solution in the presence of chemosensors, which may or may not be functionalized with anchoring siloxane groups. A more or less porous 3D or 2D materials are formed under these conditions, within which chemosensor molecules are either encapsulated or covalently bonded to a micro- or mesoporous silica matrix, allowing analyte molecules to diffuse easily through the film. The accessible range of chemosensor loading and the porosity of the matrix are highly dependent on experimental conditions, which should be optimized to achieve the best sensing performance of the material thus prepared. Functionalized optical fibers for remote spectroscopic detection can also be obtained using this technique. Immobilization of porphyrins through the sol-gel process is quite challenging due to their low solubility in the polar protic solvents (such as alcohols and water) generally required for this process.

Silica monolite containing Co(III) porphyrin Co(MSiTPP) have shown low efficiency in the detection of pyridine (Py) due to low diffusion of the vapors in this monolithic material. [94] This work highlights particular importance of 2D materials in detection of gaseous analytes.

To prepare transparent mesoporous silica films on glass slides, spin-coating is a convenient method because this technique allows fine-tuning of structural parameters of sol-gel films. This can be achieved by adding surfactants to the solution of porphyrin and siloxane, which is then deposited on the solid surface. Li and coworkers synthesized sensing films from the porphyrin H_2TSiPP functionalized with siloxane anchoring groups (Scheme 1) and tetraethoxysilane (TEOS) in the absence and presence of small molecular (cetyltrimethylammonium bromide (CTAB)) and polymeric (Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$)) surfactants.[54] The films exhibited different mesostructures, being respectively non-porous, hexagonal, and worm-like (Scheme 1).



Scheme 1. Synthesis and schematic representation of sensing materials based on porphyrin H_2TSiPP. Ref.54. Reproduced with permission Royal Chemical Society.

The insertion of zinc and cadmium ions into the incorporated tetrapyrrolic macrocycles occurs rapidly, yielding the corresponding complexes. Only the mesoporous films revealed a fast fluorescence response to trace amounts of nitro-containing aromatics (2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT)). The best results (quenching efficiency close to 60% after 10 s of exposure) were achieved in the detection of TNT with the CdTPPP-based worm-like film, which enables rapid diffusion of TNT molecules to the metalloporphyrin residues that can bind them due to coordinative binding of nitro groups to metal atoms and/or π-stacking between the aromatic macrocycle and this electron-deficient analyte. Finally, the energy-level matching between the porphyrin molecules and TNT allows for fluorescence quenching in the presence of the analyte.

To overcome the solubility problems associated with the traditional sol-gel process, the incorporation of porphyrin into a silica matrix using atmospheric pressure dielectric barrier discharge (AP-DBD) was investigated by Boscher's group.[95] In this method, plasma is generated and maintained at atmospheric pressure using high voltage, eliminating the need for expensive high vacuum systems. However, controlling film thickness may be more complex compared to the preparation of films under vacuum. AP-DBD, which generates low-temperature plasmas, offers the opportunity to work with heat-sensitive compounds and can be easily adapted for industrial production. Using this technique, a solution of the porphyrin CrTPP and hexamethyldisiloxane (HMDS) in CH_2Cl_2 was sprayed through an ultrasonic atomizing nozzle onto transparent polyethylene terephthalate foils placed on the moving stage of an AP-DBD reactor. This setup allows for the prompt exposure of the deposited liquid layer to the plasma discharge, facilitating the polymerization of the siloxane precursor. SEM images of the resulting material have shown that the film was porous and composed of agglomerated nano-spheres. Unfortunately, the sensing ability of the film was explored only briefly despite their promising morphology. A UV–vis response (a 5 nm hypsochromic shift of the Soret band) was observed in the presence of triethylamine (NEt_3), but it was too small to be visible by the naked eye. The reported experimental data do not allow for a conclusion regarding whether all metal centers in the film were accessible to the analyte molecules.

This porphyrin was also incorporated into polyvinylsiloxane matrix, replacing HMDS with vinyltrimethoxysilane.[4] The resulting films were tested as sensors for trimethylamine (NMe_3), NEt_3, and dimethylamine ($NHMe_2$) under both static and dynamic flow conditions. Notably, the sensor was able to detect concentrations as low as 10 ppm of NEt_3 under dynamic conditions and was successful in monitoring fish spoilage. However, once again, the color changes were too subtle for detection by the naked eye.

To optimize the film porosity, a mixture of isomers of sterically bulky CrDMDP porphyrins was embedded onto HMDS matrix using AP-DBD technique.[96] Porous films based on CrDMDP was sensitive to NEt_3; however, the ultimate objective of naked-eye detection has not yet been achieved.

Carboxylate-substituted porphyrins can also be adsorbed on TiO_2 support. Although carboxylate anchoring groups yield less stable materials compared to phosphonate anchors,[97] their stability is adequate for sensing gaseous analytes. Zn(II) 5,10,15,20-tetra(3-carboxyphenyl)porphyrin (ZnTmCPP) and Zn(II) 5,10,15,20-tetra(4-carboxyphenyl)porphyrin (ZnTCPP) were anchored onto porous microcolumnar TiO_2 thin films (with a thickness of 150–400 nm), yielding structurally different materials. [98,99] FTIR analysis revealed that ZnTmCPP molecules are bound to the support by all carboxylic groups, in contrast to those of ZnTCPP, where only one or two of these groups participate in material formation. As a result, the optical properties of the two materials differ. The Soret band of the *para*-substituted derivative in the film is hypsochromically shifted compared to the solution spectrum, indicating formation of H-aggregates in the film thus obtained. In contrast, grafted ZnTmCPP remained monomeric due to its planar orientation on the TiO_2 surface. Both thin films exhibited colorimetric responses in the presence of acetone, acetonitrile (MeCN), butylamine ($BuNH_2$), $CHCl_3$, EtOH, and tetrahydrofuran. The optical response of the ZnTmCPP/TiO_2 was found to be more pronounced and faster than that of the ZnTCPP/TiO_2 film. The ZnTmCPP/TiO_2 film was also more sensitive to the nature of the studied analytes.

2.3. Hybrid Materials Based on Organic Polymers

Polymer matrices are widely used to immobilize chemosensors. They offer many advantages and compare well with sol-gel materials the detection of gaseous analytes. The most commonly used polymer supports are polyvinyl chloride (PVC), polystyrene, polymethyl methacrylates (PMMA), and cellulose derivatives. Dyes can be chemisorbed on polymer surfaces, encapsulated within the polymer matrix, or co-polymerized with inert monomers.

Sensing materials prepared by impregnating WypAll X60 or 100% woven cotton with various metalloporphyrins were used for the development of portable sensors for EtOH.[100] No significant differences in color were observed between the two supports; however, the nature of the porphyrin ligand played a key role. Chemisorbed complexes of Deuteroporphyrin IX bis ethyleneglycol (H_2DIX) showed a stronger response compared to those of *meso*-tetra(4-aminophenyl)porphyrin (H_2TAP).

Encapsulation of H_2TPP in PVC matrices is performed by dissolving PVC, a plasticizer, the dye, and sometimes specific additives in THF, then casting this solution onto glass plates. Electrostatic interactions between H_2TPP and EtOH induce a significant decrease in fluorescence. This process yields films with a thickness that exceeded 5 μm. H_2TPP encapsulated in a PVC matrix is sensitive to this guest molecule over a wide range of concentrations.[101] After optimizing the plasticizer, the doped polymer enabled a linear response in the range of 1 to 75% of saturated vapor pressure and was

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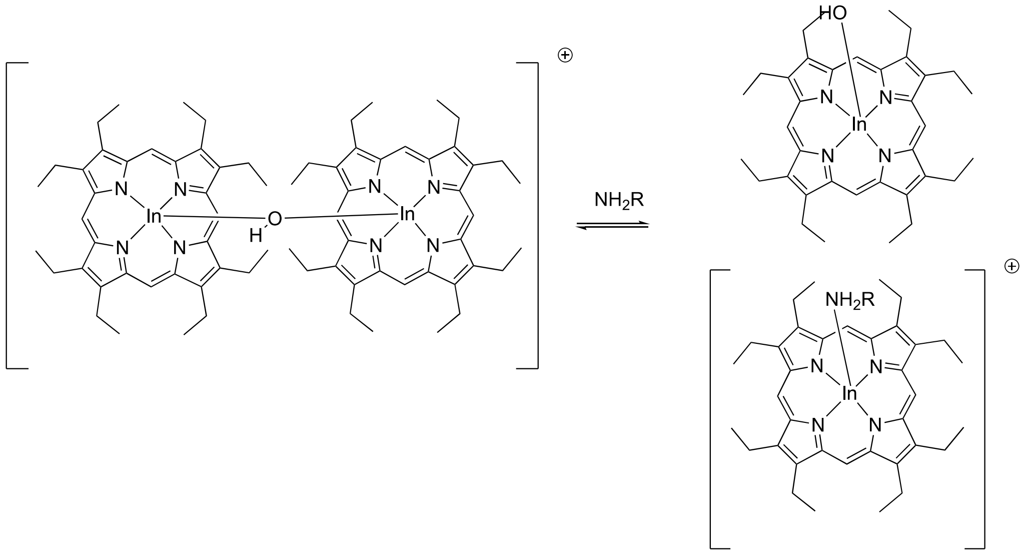
applied to the determination of EtOH in various types of wines and whisky. The detection limit was as low as 0.05 vol%, which is rarely achieved with other previously reported optical sensors.

Films of tetramethylpyridinium porphyrin tetrachloride ($H_2TMPyPP$) and 2,3,7,8,12,13,17,18-octamethyl-5,15-bis- [4-trimethylammoniumylphenyl)porphyrin dichloride (H_2DPyPP) in PMMA and polyvinyl pyrrolidone (PVP) were prepared by spin-coating. The sensing properties of these films with thickness of ca. 1 mm were investigated with respect to benzene. Membranes containing encapsulated H_2DPyPP were more sensitive but cannot be used for monitoring of benzene in air where this toxic compound is acceptable in the level of ppb.[55]

To increase the optical response of sensor, Meyerhoff and co-workers used the monomer – dimer equilibrium of In(III) complexes of hydroxo(2,3,7,8,12,13,17,18-octaethylporphyrinato)indium(III) encapsulated in PVC membrane in the presence of sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate.[102]



Scheme 2. Detection of NEt_3 by the dimeric In(III) complex.

This salt with a lipophilic anion enables dimerization of porphyrins within polymers (Scheme 2). The sensing mechanism involves axial coordination of amines to metal centers in the polymeric matrix, accompanied by the formation of two monomer species. This process induces a red shift of the Soret band of up to 16 nm due to the significant structural difference between the bridged dimer and the two monomeric complexes formed after amine binding. The best sensitivity was obtained using *o*-nitrophenyl octyl ether as a plasticizer. Depending on the relative partition coefficient into the polymer film and the ligating properties, different degrees of monomer formation were observed for eight primary alkylamines and Py studied in this work. With optimized film composition, $BuNH_2$ was detected at a level of 0.1 ppm, while the detection limit for less lipophilic primary amines did not exceed 10 ppm.

Porphyrin nanotubes prepared by Wang’s method[103] were embedded in polydimethylsiloxane to prepare a thin film containing spatially separated nanotubes suitable for sensing.[13] This film was investigated as a sensing material for NEt_3, EtOH, toluene, and acetic acid. The polymeric matrix demonstrated good permeability to the studied analytes, and the response of the sensing layer was measured using the differential absorbance method. The analytes were successfully identified; however, they interacted with the porphyrin molecules through a variety of ways rather than being incorporated into the inner cavity of the nanotubes.

A serious drawback of the functionalized polymers discussed above is their low porosity. To increase the surface area of the sensing material, O’Donnell and co-workers prepared crosslinked polymer membranes by performing the polymerization of free base 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (H_2THPP) and succinyl chloride at THF–CH_2Cl_2 interfaces, modifying previously reported methods [104,105] for the preparation of microporous membranes.[106]

Unfortunately, the porosity and morphology of the films thus obtained were not characterized, but their investigation by UV–vis spectroscopy showed a high degree of dye aggregation in this polymeric matrix. The membranes were then deposited onto glass supports and transformed into materials containing metalloporphyrin residues by treating them with Zn(II), Cu(II), and Co(II) salts. These metalloporphyrin membranes were exposed to alcohols (MeOH, EtOH, and ^{i}PrOH), ketones (acetone, butanone, and 2-pentanone), and toxic chlorinated compounds (CH_2Cl_2, $CHCl_3$, and 1,2-dichloroethane) vapors to test their efficiency as vapochromic materials using colorimetry. The spectral changes were rather small, and the absorbance of the films was monitored at two wavelength (425 nm and 550 nm) before and after exposure to analytes. The percentage difference in absorbance at each wavelength was calculated and averaged to draw final conclusions. The CuTHPP-based membrane showed the best discrimination among the three alcohol vapors, while the thin film containing ZnTHPP enabled efficient detection of MeOH vapors. Sensors based on H_2THPP, CuTHPP, and ZnTHPP exhibited reversible responses toward ketones and membranes containing H_2THPP and ZnTHPP could distinguish between different ketones. In contrast, the CoTHPP-based membrane was efficient only in the discrimination of chlorinated compounds.

Wang and co-workers prepared a nanoporous membrane by copolymerizing Zn(II) 5,10-bis(4-aminophenyl)-15,20-diphenylporphyrin (ZnDADPP) with pyromellitic dianhydride (PMDA) and oxydianiline (ODA) using an electrospinning technique, followed by heating the nanofibers up to 250 °C.[107] The structure of the resulting polymer is shown in Figure 7.

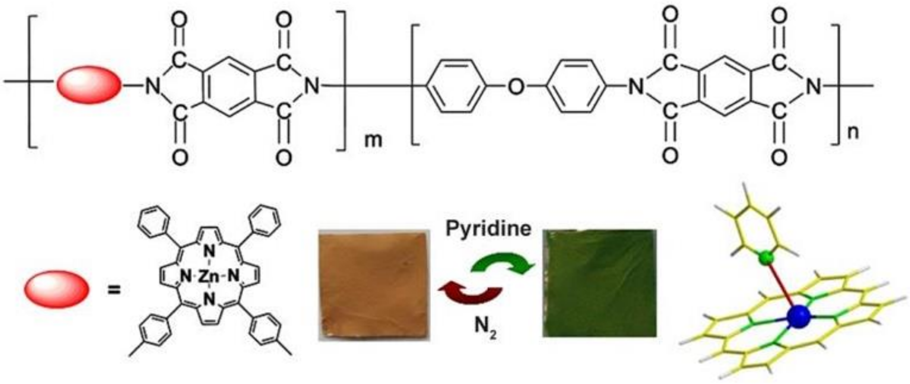


Figure 7. Naked-eye sensing of Py using a membrane based on ZnDADPP. Reproduced with permission from Ref. [107], which is open access article distributed under the Creative Commons Attribution License (CC BY), MDPI.

The membrane, consisting of these fibers, enables rapid and reversible detection of pyridine vapor, with a detection limit of 0.041 ppm, achieved due to a color change visible to the naked eye. Notably, this membrane demonstrated excellent selectivity for Py over common amines ($NHEt_2$, NEt_3, pyrrole, and cyclohexylamine) and other potential gaseous compounds (CO_2 and H_2O). The selectivity of the membrane for Py was attributed to differences in the basicity of the analytes. However, it is also important to consider the high stability of the zinc porphyrin complexes with Py, as well as the low accessibility of the metal centers within this polymeric matrix.

2.4. Supramolecular Assemblies and Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are porous crystalline materials composed of metal ions or clusters coordinated with organic ligands. These frameworks offer exceptional tunability in their structural, physical and chemical properties, making them highly promising for various applications, including gas storage, separation, and catalysis. Their high surface area, abundance of binding sites, and adjustable pore sizes are particularly advantageous for sensing applications and the removal of VOCs. MOFs have already found their specific role as optical sensors for gaseous analytes, [108–110] but their use in the detection of VOCs remains relatively rare. [111–113] Reported studies demonstrate that these materials hold significant potential for developing optical sensors for VOCs

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with various signal transduction mechanisms, including light absorption, emission, and refractive index changes. MOFs also show selectivity towards certain VOCs, often based on size exclusion or a correspondence of hydrophilic-lipophilic balance between MOF and an analyte. However, the main challenge in this field lies in fabrication of sensing materials that are compatible with the conditions of target signal transduction schemes, as these materials are often difficult to integrate with existing devices due to their 3D character, and the technology for growing MOFs on solid supports is still underdeveloped.

MOFs based on porphyrin ligands not only exhibit high porosity but also demonstrate strong light absorption in the visible spectrum. Additionally, they efficiently generate singlet oxygen, which can be utilized for the removal of VOCs through performing photocatalytic oxidation reactions.[114] However, porphyrin-based MOFs have been scarcely investigated as VOCs sensors. They have been reported as sensing elements in optical sensing arrays, which are discussed in the following sections.

Coordination-based supramolecular chemistry offers also a pathway to create a wide variety of rigid, discrete multi-metal complexes featuring well-defined nanoscale cavities. These compounds hold significant promise for small-molecule sensing. In optimized structures, analyte retention can be achieved by adapting the size of the cavity to match the dimensions of the analyte. In such materials, optical sensing transduction is typically achieved by changes in color or luminescence upon analyte binding. However, they also enable more sophisticated signal transduction schemes. Hupp and co-workers reported a proof-of-concept study showing that light diffraction could be used in sensing of gaseous analytes (the photonic lattice method).[114] The self-assembly of the porphyrin ZnDPyMBP (Figure 8) and [ReCl(CO)$_5$] resulted in the formation of tetra-metallic complex defining an open-ended nanoscale box with a cavity of approximate dimensions of 18 × 18 × 18 Å. In crystal form, these cavities align to create one-dimensional channels and this structural organization can be easily achieved evaporating solutions of this complex. To prepare a sensing material, a micropatterned elastomeric stamp was covered with this porphyrin-based tetramer. This resulted in a square-perforated grid covering a few square millimeters and containing several thousand perforations. The presence of benzene, dioxane, and Py within the pores of this material was detected and the analytes were distinguished using photonic lattice diffraction measurements.

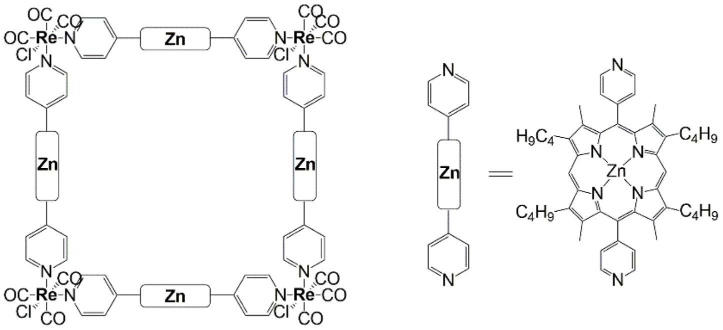

Figure 8. Schematic representation of molecular squares based on ZnDPyMBP.

3. VOCs Sensing Based on Porphyrin Arrays

The challenge of detecting VOCs arises from the limited number of binding sites in their molecules, which generally results in their weak interactions with host molecules. These interactions are predominantly governed by Brønsted or Lewis acid/base forces, making the development of selective sensors a difficult task. In nature, mammals use around four hundred different receptors to distinguish among thousands of odorants.[115] Inspired by these biological olfactory systems, artificial array-based sensing strategy has been developed. This strategy employs multiple sensing elements, each providing a specific yet non-selective response, which work in unison to produce a unique, combined response for each analyte in a complex mixture. Artificial noses that modulate optical signals have emerged in this century as promising, low-cost, environmentally friendly, and portable sensors. Optical arrays based on color changes in dyes, photonic crystals and fluorescence have been developed. Recently, sensor arrays utilizing near-infrared reflectance have also gained increasing interest.[116]

Colorimetric sensing arrays (CSAs) operate by relying on color changes produced by each component of the array in response to specific analytes. Commonly sensing arrays include different classes of dyes, such as Brønsted acidic or basic dyes, Lewis acidic or basic dyes, and chromophores with large permanent dipoles, which are among the most studied options for colorimetric sensing. [22,117] This structural diversity of components enhances the differentiation of VOCs. CSAs often require specific equipment to analyze the color changes, such as flatbed scanners, digital cameras (including photo cameras), or specialized optical detectors. These devices capture images of the colorimetric array, allowing for the analysis of color and its intensity, often with the aid of sophisticated software.

One of the earliest and simplest opto-electronic noses developed by Di Natale and co-workers is illustrated in Figure 9.[118]

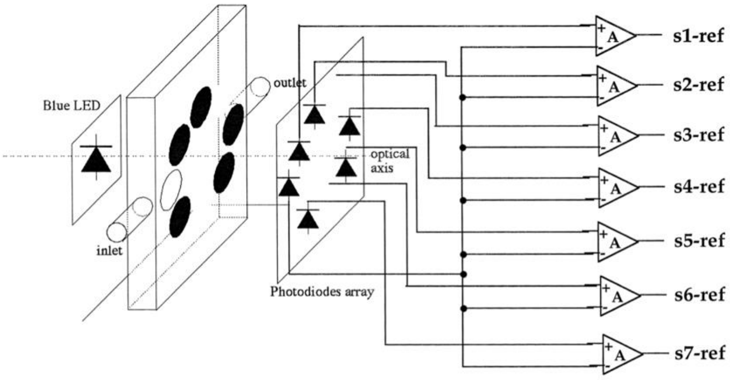

Figure 9. Schematic representation of opto-electronic noses. Ref. 33. Reproduced with permission of Elsevier.

This home-made device consisted of a low-cost blue LED and an array of photodiodes. Sensing films were deposited on one of the internal surfaces of a Plexiglass chamber equipped with gas inlets and outlets, with each porphyrin film positioned along a specific light path. Four sensing films were prepared by drop-casting Co(II) and Rh(III) porphyrin complexes (CoTNPP and RhTPP), as well as two other porphyrinoids: Mn(III) 2,3,7,8,12,13,17,18-octamethylcorrole and 3,17-diethyl-2,3,7,8,12,18,22,23-octamethylsapphyrin.

In preliminary studies, light absorption changes of sensor components to the presence of various VOCs such as hexane (Hex), propanal, MeOH, EtOH, acetone, $MeCO_2H$, and NEt_3 were evaluated. The highest optical responses were recorded in the presence of carboxylic acids and amines, although most of the analytes were detectable with these films. Consequently, these complexes were selected as working components for the development of an opto-electronic nose, with the output signals analyzed using the Self-Organizing Map (SOM). Notably, this CSA was composed solely of porphyrinoids, whereas recent practical colorimetric arrays typically include other organic dyes.

This and other early works, particularly from Suslick's group, [119–122] highlighted both the interest and complexity of developing opto-electronic noses, prompting further extensive research to optimize each component of detection systems and analysis methods. These researches have been recently discussed in excellent reviews. [15,22] Readers interested in these devices are encouraged to consult these and other reviews, [22,123–125] which detail all the steps involved in developing opto-electronic noses. In our review, we focus specifically on various strategies for preparing sensing materials for these devices, as well as highlighting selected remarkable results obtained using sensor arrays with principally porphyrins as dyes. Porphyrin-based CASs reported recently are summarized in Table 3.

Table 3. Recently reported (2018-2024) porphyrin-based CSAs for VOCs sensing.

Porphyrin precursor	Solid support	VOCs	Ref
ZnTPP, MnOEP BMG[a]	reverse-phase silica gel plate	ethanol, ethyl acetate and acetic acid	116
H_2TPP, ZnTPP, EuTPP, H_2TTPS$_1$, H_2TF$_5$PP Sodium fluorescein[a]	PMMA plate	p-xylene, isoprene, styrene, and hexanal	126
H_2TPP, CuTPP, ZnTPP, MnTPP, PdTPP, H_2TPP-Cl, ZnTPP-Cl, ZnTPP-F, ZnTMPP BCG[a]	reverse-phase silica gel plate	2,4,5-Trimethyloxazole	127
FeTPP, NiTPP, CoTPP, PdTPP, MnOEP, FeTMPP, Fe^{II}TMPP, MnTSPP, H_2TSPP Doil[a], pCarDPM[a], NO_2Br_2BDP[a], NaiOCH$_3$BDP[a], and 4 other dyes	silica gel plate	VOCs formed in the storage process of oysters	128
H_2TPP, FeTPP, MnTPP, CuTPP, VTPP, H_2TMPP FeTMPP, H_2OEP,MnOEP, PdOEP, Phenol red[a] Bromocresol purple[a]	reverse-phase silica gel plate	VOCs formed in the storage process of beef	129
PCN-222[b], PCN-222(Ag), PCN-222(Zn), PCN-222(Fe), PCN-222(Cu) PCN-222(Co)	PDMS[c] membrane	acetone, $CHCl_3$, CH_2Cl_2, EtOH, PenCHO, $BuNH_2$, THF, toluene, DNT	56

[a] The structure of this compounds is illustrated in Figure 10. [b] PCN-222 – Zr-based MOF with H_2TCPP ligands. PCN-222(M) – Zr-based MOF with MTCPP ligands M = (Ag, Zn, FeCl, Cu, CoCl). [c] PDMS – poly(dimethylsiloxane).

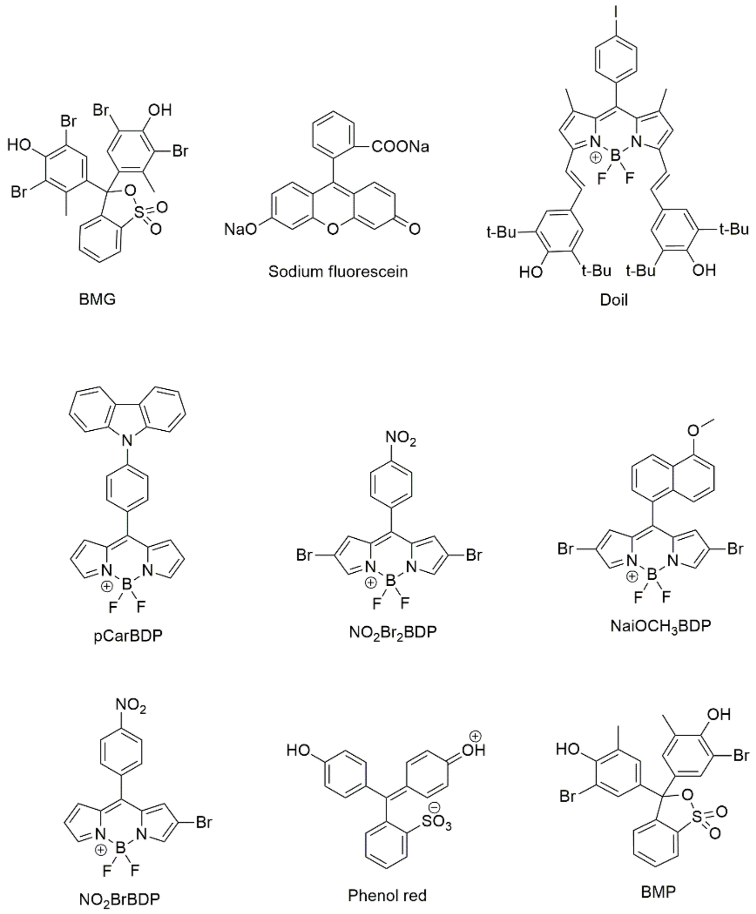

Figure 10. The structures of dyes which was used in CASs. For references see Table 3.

Given that free-base porphyrins and their metal complexes offer specific responses to target analytes as discussed above, sensor arrays frequently include different metal complexes of the same tetrapyrrolic ligand, with H_2TPP often being a commonly used choice.

The importance of the substitution pattern of the tetrapyrrolic macrocycle for developing CSAs was clearly demonstrated by Brittle and co-workers.[93] They explored sensing properties of two arrays based on free-base porphyrins, which were prepared deposited on glass substrates using LB technique. The analytes they employed for discrimination included octanol (OctOH), hexylamine ($HexNH_2$), octylamine ($OctNH_2$), NEt_3, octanal, $MeCO_2H$, 1-hexanethiol, 2-butanone, ethyl acetate, and $P(OMe)_3$. Two arrays, comprising six and four sensing elements respectively, exhibited distinct sensing behaviors influenced by both the molecular structure of dyes and their packing within the films. Notably, LB films of porphyrins containing only electron-donating substituents on the macrocycle periphery produced a significantly stronger response compared to those with both electron-donating and electron-withdrawing groups, contrasting their performance in solution detection. This finding underscores the key role of molecular packing in LB films, suggesting that a porphyrin exhibiting a robust chemosensory response in solution might not perform similarly when incorporated into a thin film. This study also indicated that fabrication of CSAs based on porphyrins with electron-donating substituents could be a crucial strategy for developing highly sensitive optical sensors for VOCs. Nevertheless, this conclusion requires further experimental validation, as the complexity of these sensor systems and the limited number of examples reported previously may not completely represent the behavior of all porphyrins in LB/LS sensing films.

Methods of porphyrin immobilization used in the preparation of colorimetric arrays are generally similar to those discussed in the previous section, with drop-casting being a commonly utilized technique. Porphyrins were immobilized onto solid supports using diverse substrates such as reverse-phase silica gel plates, [40,41,118–121,129–132] silica gel plates, [128] polyethylene terephthalate (PET) foils,[133] polyvinylidene fluoride (PVDF) membrane, [134–136] poly(methyl methacrylate) (PMMA) plate,[126] and filter paper.[137] Efficient CAS were also prepared according LB/LS technique (Table 2) and spin coating (Table 1).

Dyes can also be embedded in polymeric matrices to serve as sensing materials in CAS. Huo and co-workers incorporated a mixture of chemosensors and 2,4-dinitrophenylhydrazine into a PEG-100 matrix. The 16-channel CSA thus prepared demonstrated excellent discrimination of nine aldehydes in a low concentration range (40 ppb to 10 ppm).[138]

The importance of porosity of sensing materials was highlighted long ago. Suslick and co-workers utilized the incorporation of dyes into various silica matrices to obtain porous organosil materials.[133] By combining this sol-gel tecknique with rational molecular design of sensing components and improving data analysis methods, this group developed numerous advanced CSAs. For example, they achieved sensitivities below 1 ppm for detecting seven different amines ($NHPr_2$, $HexNH_2$, cyclohexylamine, $OctNH_2$, pyridine, pyrrolidine, homopiperidine) and DMF, using a CSA with 24 components, of which eighteen were involved porphyrin derivatives.[121] In another study, they developed a 36 channel system capable of differentiating among 19 toxic industrial chemicals, including four VOCs ($NHEt_2$, $EtNH_2$, NH_2NHMe, NMe_3), after just 2 min of exposure to analytes at concentrations considered hazardous to health.[133]

Functionalized nanomaterials have recently emerged as promising candidates to improve sensor arrays. Coating nanoparticles with dyes enhances the surface area of materials, which in turn improves the accessibility of the receptor sites. Gu and co-workers use colloidal crystalline beads (CCB) (Figure 11) as a solid support for chromophores in developing fluorescent sensor. [139,140] Colloidal crystals composed of three-dimensional ordered arrays of submicrometer particles, often formed by self-assembly. In this work, these species were prepared from nanosized silica synthesized according to a modified Stöber method in a microfluidic device. The CCBs, with diameters of about 300 μm, were initially hydrophobized using trimethoxy(octadecyl)silane and then functionalized with a series of porphyrins (ZnTPP, SnTPP, ZnTAP, H_2TPP, H_2TCPP, and H_2TAP) using a dip-coating process.[140] This sensor generated fluorescent responses which was displayed for calculation the absolute difference between the RGB colors of the porphyrins during exposure to gaseous analytes. Carboxylic acids, ketones, and amines (cyclohexane, ethyl acetate, $MeCO_2H$, acetone, MeOH, EtOH) were distinguished by this sensor array. Notably, the fluorescent response differed for MeOH and EtOH, allowing semi-quantitative analysis of EtOH in the concentration range of 10–60 ppm.

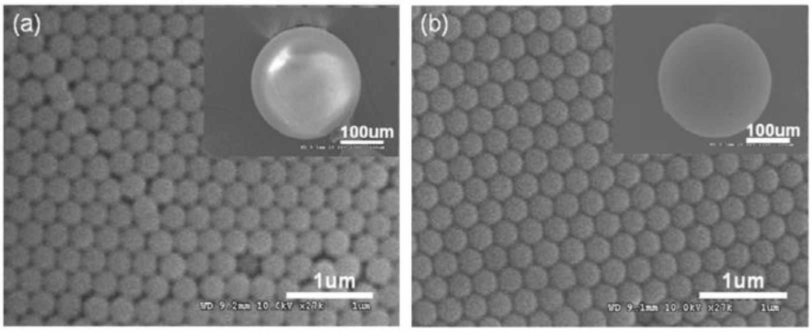

Figure 11. HR SEM images of CCB before (a) and after (b) covering with ZnTPP. SEM images is shown in the inlets. Ref. 140. Reproduced with permission of American Chemical Society.

Pedrose and co-workers utilized TiO_2 thin film prepared by glancing angle physical vapor deposition (GAPVD), as host material for carboxylate-substituted porphyrins.[98] This solid support is transparent in the visible spectrum, non-dispersive, and porous, making it suitable for gas sensing *via* UV–visible and IR spectroscopies. Metalloporphyrins were deposited from ethanol solutions using impregnation, a technique that did not prevent dye aggregation. Porphyrin/TiO_2 films, each containing one of 11 different porphyrins, were exposed to 12 VOCs. Spectral changes observed in the Soret band region were explored using imaging spectroscopy, generating a recognition pattern that enables the easy identification of each VOC. This sensor exhibited a rapid (within a few seconds), reversible, and reproducible response, that was attributed to significant porosity of the TiO_2 film with a columnar structure and open pores.

Recently, Pedrose and co-workers developed a rapid and straightforward microwave-assisted method to synthesize nano-sized Zr-based MOFs incorporating *meso*-tetra(4-carboxyphenyl)porphyrin residues (PCN-222).[56] The insertion of various metal ions (M = Fe, Co, Cu, Zn, Ag) into the tetrapyrrolic macrocycles within this matrix proceeded smoothly, resulting in materials labeled as PCN-222(M) (Figure 12).

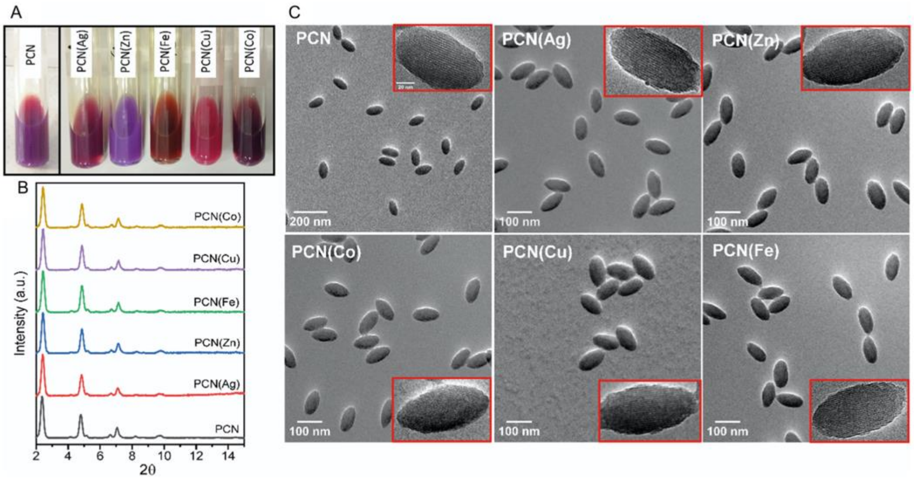

Figure 12. A) Photographs of suspensions of PCN-222(M) in methanol. B) PXRD patterns of PCN-222 and PCN-222(M). C) SEM images of PCN-222(M). Reproduced with permission from Ref. 56, which is open access article distributed under the Creative Commons Attribution License (CC BY), Wiley.

These modified MOFs were then used to prepare a CSA. The nano-sized MOFs were dispersed into poly(dimethylsiloxane) (PDMS) to prepare transparent and flexible membranes. The sensing properties of these materials were tested against nine different VOCs, including DNT, acetone, $CHCl_3$, CH_2Cl_2, THF, $BuNH_2$, hexanal, toluene, and EtOH, as well as gases like hydrogen sulfide, hydrogen chloride, and ammonia, using UV–vis spectroscopy. The analytes produced distinct barcode-like identification patterns following 30 minutes of exposure, enabling easy differentiation between them. The membranes also demonstrated good stability, maintaining their functional properties for at least three months after fabrication.

Opto-electronic noses hold significant societal importance across various fields. As discussed earlier, they can be effectively utilized for the quantification of toxic industrial compounds, playing a critical role in environmental safety and pollution control. They are also crucial for monitoring human health. [126] For instance, Huo and co-workers developed a CSA specifically designed to detect lung cancer-related VOCs. [126,134,138] For instance, reported CSA based on a combination of free-base porphyrins (H_2TPP, H_2TF5PP, H_2MS5PP), two metalloporphyrins (ZnTPP, EuTPP), and sodium fluorescein. This CSA successfully discriminated among key VOCs such as *p*-xylene, styrene, isoprene, and hexanal, which are associated with lung cancer, when their concentrations were varied within the 50–500 ppb range. [126] This level of sensitivity is essential for early diagnosis and continuous monitoring of health conditions.

In the recent years, CSA are becoming increasingly popular for control of food freshness during storage. [127–129,132,136,137,141] The porphyrin dyes are particularly appealing here because being incorporated in sensing materials they can detect a wide range of specific VOCs released during food spoilage, including amines, aldehydes, 2,4,5-trimethyloxazole, and other degradation products, even at very low concentrations. Since VOCs emitted by food products often exhibit complex compositions, detecting target analytes in these mixtures is essential. Porphyrin-based CSA facilitate the analyses of complex gaseous mixtures and are suitable for creating portable devices that are compatible with smartphone cameras.

4. Conclusions

Detection of volatile organic compounds (VOCs) is a rapidly expanding research field due to their significance in environmental monitoring, human health assessment, food quality control, and homeland security. Expanding our knowledge of biosystems and progress of industry are significantly broadening the scope and applications of VOC analysis.

Porphyrins and related compounds hold considerable promise for the optical sensing small-molecules. Porphyrins, known for their exceptional light absorption properties, are widely used as sensing materials in UV–visible and reflectance spectroscopy-based signal transduction, and these materials hold great promise for the development of portable devices using photodiodes and smartphone cameras. Although porphyrins have moderate emission, their high light absorption afforded finally relatively high brightness, making them valuable for sensor development. However, most fluorescent porphyrin-based sensors currently operate in an ON-OFF mode, which presents serious limitations for practical applications.

Porphyrins are also excellent building blocks for preparation of porous nanomaterials that can be employed in design of devices utilizing diverse optical signal transduction mechanisms, including methods based on changes in refractive index. Furthermore, many free-base porphyrins and their metal complexes exhibit outstanding thermal, photochemical, and chemical stability, which surpasses that of most other organic dyes. This stability provides a solid background for developing robust devices that deliver reliable and reproducible responses over extended periods of use.

The use of porphyrins in VOC detection has advanced significantly in this century, with key contributions coming primarily from physicists and physical chemists. Modern miniature sensors can now feature up to 36 channels, enabling the discrimination and quantification of target VOCs in complex mixtures. However, many of these sensors still rely on readily available porphyrin derivatives that are not specifically designed to interact with the target analytes. Enhancing the sensing materials, both at the molecular level and through improved synthetic techniques, is anticipated to make significant strides in progress of this field.

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